SUPPORTING INFORMATION

Facile Approach to Optically Pure α-Alkylidene-β-amino Esters by Thermal Overman Rearrangement

Sung Il Lee[†], Soon Young Moon[†], Geum-Sook Hwang*[,‡] and Do Hyun Ryu*[,†].

† Department of Chemistry, Sungkyunkwan University, Suwon, 440-746, Korea,

‡ Korea Basic Science Institute, 5St, Anam-Dong, Seongbuk-Gu, Seoul, Korea.

Corresponding author dhryu@skku.edu, gshwang@kbsi.re.kr

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General Methods

All reactions were carried out under a dry argon atmosphere in vacuum-flame dried glassware. Dichloromethane were distilled from calcium hydride. MeCN and Cl_3CCN were distilled from P_2O_5 prior to use. Toluene were dried by distillation from sodium wire. Thin layer chromatography was carried out on Merck silica gel 60 F254. Column chromatography was carried out on Merck silica gel 60 (230-400 mesh).

^1H and ^{13}C NMR spectra were recorded on a Varian at 300 and 75 MHz. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($C\mathbf{H}Cl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, qd = quartet of doublet, br = broad, m = multiplet), coupling constants (Hz), integration.

Infrared spectra were recorded on a Bruker Vertex 70. LRMS data were obtained by Varian GC/MS 4000 system or Varian LC/MS 500 system. Optical rotation were collected on PerkinElmer 343 plus and chiral HPLC analysis was performed using FUTECS NS-4000 system.

(*R*)-(*Z*)-β-iodo-MBH esters(**7**) were prepared by reported procedure.

(Senapati, B. K.; Hwang, G.-S.; Lee, S.; Ryu, D. H. *Angew. Chem. Int. Ed.* **2009**, *48*, 4398.)

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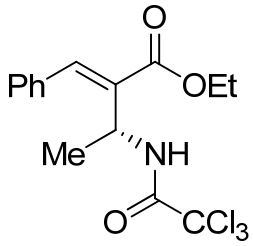
(Lee, S. I.; Hwang, G.-S.; Ryu, D. H. *Synlett* **2007**, 59.)

Typical procedure for the α-alkylidene-β-amino esters (R^1 = Aromatic)

In a 25ml round bottom flask fitted with a septum, nitrogen inlet, and magnetic stirring bar were charged with β-branched MBH ester (1.0mmol) in 5.0ml of freshly distilled MeCN. At ambient temperature, DBU 30µl (0.20mmol) and Cl_3CCN 501µl (5.0mmol) were added. The solution was stirring for 15min. When the reaction was finished all volatile materials were evaporated *in vacuo.* Resulting crude mixture was filtered quickly through silica gel column (I.D x H=1cm x 1.5cm) using EtOAc:Hexane (1:1) solution as eluent. The combined solution was concentrated and dissolved in 30ml of toluene. The reaction vessel fitted on top with a reflux condenser. The solution was heated to reflux. After 1 h, the reaction mixture was cooled to room temperature and the addition funnel and condenser were replaced with a short-path distillation head. The mixture was concentrated by distillation (air-cooling) to a volume of ca. 5 mL. The crude product was purified by flash chromatography (EtOAc:Hexane = 1:10 as eluent) to afford α-alkylidene-β-amino esters.

Typical procedure for the α-alkylidene-β-amino esters (R^1 = Aliphatic)

In a 25ml round bottom flask fitted with a septum, nitrogen inlet, and magnetic stirring bar were charged with β-branched MBH ester (1.0mmol) in 5.0ml of freshly distilled CH_2Cl_2. The solution was cooled to a 0 ^oC, NaH 80mg (60% dispersion in mineral oil, 1.0mmol) and Cl_3CCN 501µl (5.0mmol) were added. The solution was stirring for 30min. When the reaction was finished, 5.0ml of saturated aqueous NH_4Cl solution were added. The reaction mixture was extracted with CH_2Cl_2 (3x5 ml). The organic extracts were combined, dried over Na_2SO_4 then concentrated *in vacuo.* The crude product was dissolved in 30ml of toluene. The reaction vessel fitted on top with a reflux condenser. The solution was heated to reflux. After 2 h, the reaction mixture was cooled to room temperature and the addition funnel and condenser were replaced with a short-path distillation head. The mixture was concentrated by distillation (air-cooling) to a volume of ca. 5 mL. The crude product was purified by flash chromatography (EtOAc:Hexane = 1:10 as eluent) to afford α-alkylidene-β-amino esters.



(*R*,*E*)-ethyl 2-benzylidene-3-(2,2,2-trichloroacetamido)butanoate (Table 1, entry 1), (Table 3, entry 1)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 288 mg (79%) of **8a** and 25mg (7%) of (*Z*)-isomer as a white solid.

^{1}H NMR (300MHz, $CDCl_3$): δ 1.40 (t, *J* = 7.2Hz, 3H), 1.47 (d, *J* = 6.9Hz, 3H), 4.33 (q, *J* = 7.2Hz, 2H), 5.41 (dq, J_{AB} = 8.7Hz, J_{AC} = 6.9Hz, 1H), 7.37-7.48 (m, 5H), 7.79 (s, 1H), 8.25 (d, *J* = 8.7Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.38, 20.78, 45.20, 61.54, 92.95, 129.00, 129.16, 129.37, 130.94, 134.04, 141.83, 160.84, 167.27.

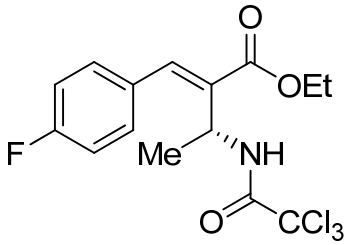
IR υ_{max} 3354, 2962, 2924, 1712, 1689, 1517, 1239, 1021, 824 cm^{-1}.

LRMS (CI) m/z 366 (M+3, 8.8), 329 (78), 287 (100), 159 (23), 131 (60).

HRMS(EI) Exact mass calcd for $C_{15}H_{16}Cl_3NO_3$ [M]+: 363.0196; found: 363.0197.

HPLC condition: Chiralcel OJ-H column, *n*-hexane/2-propanol = 99:1, 1.0 mL/min, 256 nm UV detector, *t*R = 7.81 min (major) and *t*R = 6.85 min (minor).

$[\alpha]^{20}_D$ = -69.50 (*c* 3.23, $CHCl_3$, 89% *ee*). **Mp** 71-73 °C



(*E*)-ethyl 2-(4-fluorobenzylidene)-3-(2,2,2-trichloroacetamido)butanoate (Table 1, entry 2)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 306 mg (80%) of **8b** as a white solid.

^{1}H NMR (300MHz, $CDCl_3$): δ 1.39 (t, *J* = 7.2Hz, 3H), 1.47 (d, *J* = 6.9Hz, 3H), 4.33 (q, *J* = 7.2Hz, 2H), 5.37 (dq, J_{AB} = 9.0Hz, J_{AC} = 6.9Hz, 1H), 7.10-7.18 (m, 2H), 7.40-7.46 (m, 2H), 7.73 (s, 1H), 8.21 (d, *J* = 9.0Hz, 1H).

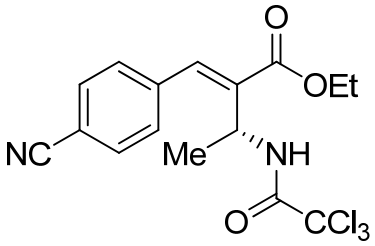
^{13}C NMR (75MHz, $CDCl_3$): δ 14.37, 20.67, 45.10, 61.58, 92.88, 116.17 (d, *J*=21.4Hz), 130.09 (d, *J* = 3.3Hz), 130.99 (d, *J* = 1.1Hz), 131.23 (d, *J* = 8.2Hz), 140.61, 161.24 (d, *J* = 43.4Hz), 164.85, 167.08.

IR υ_{max} 3355, 2978, 1699, 1510, 1240, 1094, 830, 773, 684 cm^{-1}.

LRMS (CI) m/z 384 (M+3, 9.3), 347 (56), 305 (100), 281 (25), 177 (17), 149 (39).

HRMS(EI) Exact mass calcd for $C_{15}H_{15}Cl_3FNO_3$ [M]+: 381.0102; found: 381.0104.

Mp 67-69 °C



(*R*,*E*)-ethyl 2-(4-cyanobenzylidene)-3-(2,2,2-trichloroacetamido)butanoate (Table 1, entry 3), (Table 3, entry 2)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 339 mg (87%) of **8c** as a white solid.

^{1}H NMR (300MHz, $CDCl_3$): δ 1.40 (t, *J* = 7.2Hz, 3H), 1.47 (d, *J* = 6.9Hz, 3H), 4.35 (q, *J* = 7.2Hz, 2H), 5.23 (dq, J_{AB} = 8.7Hz, J_{AC} = 6.9Hz, 1H), 7.56 (d, *J* = 8.1Hz, 2H), 7.75 (d, *J* = 8.1Hz, 2H), 7.75 (s, 1H), 8.07 (d, *J* = 8.7Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.32, 20.56, 45.12, 61.88, 92.66, 112.74, 118.46, 129.61, 132.67, 133.51, 138.68, 139.36, 161.01, 166.32.

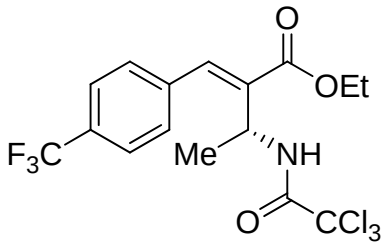
IR υ_{max} 3424, 2984, 2226, 1712, 1506, 1256, 1142, 825, 684 cm^{-1}.

LRMS (CI) m/z 391 (M+3, 17), 355 (90), 312(100), 258 (18), 156 (36), 129 (21).

HRMS(EI) Exact mass calcd for $C_{16}H_{15}Cl_3N_2O_3$ $[M]^+$: 388.0148; found: 388.0148.

HPLC condition: Chiralcel AD-H column, *n*-hexane/2-propanol = 97:3, 1.0 mL/min, 256 nm UV detector, *t*R = 14.07 min (major) and *t*R = 12.32 min (minor).

$[\alpha]^{20}_D$ = -94.43 (*c* 2.15, $CHCl_3$, 79% *ee*). **Mp** 75-77 °C



(*E*)-ethyl 2-(4-trifluoromethylbenzylidene)-3-(2,2,2-trichloroacetamido)butanoate (Table 1, entry 4)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 381 mg (88%) of **8d** and 38mg (9%) of (*Z*)-isomer as a colorless crystal.

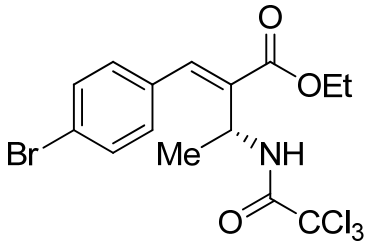
^{1}H NMR (300MHz, $CDCl_3$): δ 1.40 (t, *J* = 7.2Hz, 3H), 1.47 (d, *J* = 6.9Hz, 3H), 4.35 (q, *J* = 7.2Hz, 2H), 5.28 (dq, J_{AB} = 9.0Hz, J_{AC} = 6.9Hz, 1H), 7.54 (d, *J* = 8.1Hz, 2H), 7.71 (d, *J* = 8.1Hz, 2H), 7.78 (s, 1H), 8.12 (d, *J* = 9.0Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.48, 20.79, 45.30, 61.92, 92.90, 126.07 (q, *J* = 3.8Hz), 127.73, 129.40, 133.06, 137.76, 137.78, 140.15, 161.10, 166.76.

IR υ_{max} 3335, 2926, 1709, 1694, 1516, 1323, 1250, 1124, 1068, 834, 825 cm^{-1}.

LRMS (CI) m/z 434 (M+3, 19), 398 (65), 355(100), 282 (36), 203 (36), 180 (39).

Mp 71-73 °C



(*E*)-ethyl 2-(4-bromobenzylidene)-3-(2,2,2-trichloroacetamido)butanoate (Table 1, entry 5)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 408 mg (92%) of **8e** and 35mg (8%) of (*Z*)-isomer as a white solid.

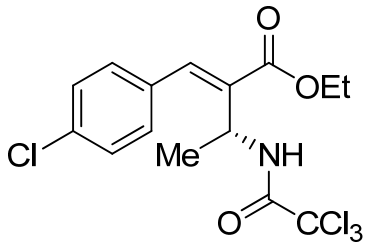
^{1}H NMR (300MHz, $CDCl_3$): δ 1.39 (t, *J* = 7.2Hz, 3H), 1.46 (d, *J* = 7.2Hz, 3H), 4.33 (q, *J* = 7.2Hz, 2H), 5.32 (dq, J_{AB} = 8.4Hz, J_{AC} = 7.2Hz, 1H), 7.30 (d, *J* = 8.4Hz, 2H), 7.69 (d, *J* = 8.4Hz, 2H), 7.69 (s, 1H), 8.15 (d, *J* = 8.4Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.38, 20.65, 45.16, 61.65, 94.72, 123.76, 130.68, 131.74, 132.25, 132.94, 140.46, 160.94, 166.92.

IR υ_{max} 3702, 3332, 2974, 2866, 1709, 1689, 1517, 1247, 1055, 1031, 1012, 824 cm^{-1}.

LRMS (CI) m/z 444 (M+3, 5), 411 (31), 408(100), 364 (99), 130 (26).

Mp 83-85 ^oC



(*E*)-ethyl 2-(4-chlorobenzylidene)-3-(2,2,2-trichloroacetamido)butanoate (Table 1, entry 6)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 286 mg (72%) of **8f** and 25mg (6%) of (*Z*)-isomer as a white solid.

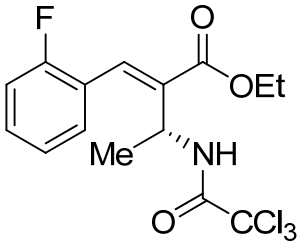
^{1}H NMR (300MHz, $CDCl_3$): δ 1.39 (t, *J* = 7.2Hz, 3H), 1.47 (d, *J* = 6.9Hz, 3H), 4.33 (q, *J* = 7.2Hz, 2H), 5.33 (dq, J_{AB} = 8.7Hz, J_{AC} = 6.9Hz, 1H), 7.39-7.44 (m, 4H), 7.72 (s, 1H), 8.18 (d, *J* = 8.7Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.36, 20.65, 45.12, 61.63, 92.84, 129.28, 130.47, 131.58, 132.44, 135.43, 140.42, 160.93, 166.93.

IR υ_{max} 3707, 3355, 2981, 2864, 1709, 1689, 1517, 1247, 1033, 822, 684 cm^{-1}.

LRMS (CI) m/z 400 (M+3, 7.9), 364 (100), 320(72), 299 (24), 167 (33), 130 (36).

Mp 67-69 ^oC



(*E*)-ethyl 2-(2-fluorobenzylidene)-3-(2,2,2-trichloroacetamido)butanoate (Table 1, entry 7)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 291 mg (76%) of **8g** and 87mg (23%) of (*Z*)-isomer as a white solid.

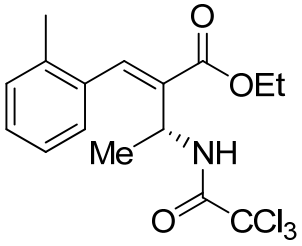
^{1}H NMR (300MHz, $CDCl_3$): δ 1.42 (t, *J* = 7.2Hz, 3H), 1.47 (d, *J* = 6.9Hz, 3H), 4.34 (q, *J* = 7.2Hz, 2H), 5.25 (dq, J_{AB} = 9.0Hz, J_{AC} = 6.9Hz, 1H), 7.10-7.16 (m, 1H), 7.16-7.25 (m, 1H), 7.36-7.40 (m, 1H), 7.48 (td, J_{AB} = 7.5Hz, J_{AC} = 0.9Hz, 1H), 7.78 (s, 1H), 8.20 (d, *J* = 9.0Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.33, 20.55, 29.83, 45.62, 61.71, 92.88, 115.82, 116.11, 121.89, 122.07, 124.67, 124.72, 130.29, 130.32, 131.32, 131.42, 132.91, 134.80, 134.86, 158.70, 160.89, 162.01, 166.78.

IR υ_{max} 3377, 2983, 1701, 1496, 1452, 1307, 1259, 1026, 820, 765, 622 cm^{-1}.

LRMS (CI) m/z 384 (M+3, 28), 348 (35), 306(100), 177 (19), 149 (52), 129 (20).

Mp 41-43 °C



(*E*)-ethyl 2-(2-methylbenzylidene)-3-(2,2,2-trichloroacetamido)butanoate (Table 1, entry 8)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 243 mg (64%) of **8h** and 30mg (8%) of (*Z*)-isomer as a white solid.

^{1}H NMR (300MHz, $CDCl_3$): δ 1.40 (t, *J* = 7.2Hz, 3H), 1.42 (d, *J* = 6.9Hz, 3H), 2.27 (s, 3H), 4.34 (q, *J* = 7.2Hz, 2H), 5.13 (dq, J_{AB} = 8.7Hz, J_{AC} = 6.9Hz, 1H), 7.22-7.30 (m, 4H), 7.83 (s, 1H), 8.14 (d, *J* = 8.7Hz, 1H).

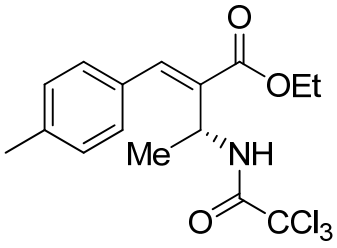
^{13}C NMR (75MHz, $CDCl_3$): δ 14.50, 20.22, 20.95, 45.64, 61.65, 93.09, 126.41, 128.38, 129.32, 130.52, 131.85, 133.65, 136.74, 141.88, 160.83, 167.18.

IR υ_{max} 3384, 2988, 1704, 1513, 1252, 1122, 820, 775, 685 cm^{-1}.

LRMS (CI) m/z 380 (M+3, 11), 344 (60), 302 (100), 175 (29), 147 (56), 117 (39).

HRMS (EI) Exact mass calcd for $C_{16}H_{18}Cl_3NO_3$ $[M]^+$: 377.0352; found: 377.0352.

Mp 39-41 °C



(*E*)-ethyl 2-(4-methylbenzylidene)-3-(2,2,2-trichloroacetamido)butanoate (Table 1, entry 9)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 150 mg (40%) of **8i** and 40mg (10%) of (*Z*)-isomer as a white solid.

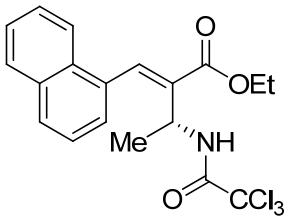
^{1}H NMR (300MHz, $CDCl_3$): δ 1.39 (t, *J* = 7.2Hz, 3H), 1.48 (d, *J* = 6.9Hz, 3H), 2.38 (s, 3H), 4.32 (q, *J* = 7.2Hz, 2H), 5.44 (dq, J_{AB} = 8.4Hz, J_{AC} = 6.9Hz, 1H), 7.25 (d, *J* = 8.1Hz, 2H), 7.32 (d, *J* = 8.1Hz, 2H), 7.76 (s, 1H), 8.28 (d, *J* = 8.4Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.40, 20.75, 21.55, 45.22, 61.47, 92.99, 129.29, 129.74, 130.14, 131.16, 139.72, 141.94, 160.84, 167.46.

IR υ_{max} 3390, 2936, 1702, 1515, 1300, 1250, 1119, 818, 774, 685 cm^{-1}.

LRMS (CI) m/z 380 (M+3, 4), 343 (100), 300 (83), 277 (28), 145 (44), 130 (38).

Mp 57-59 ^oC



(*E*)-ethyl 2-(naphthalen-1-ylmethylene)-3-(2,2,2-trichloroacetamido)butanoate (Table 1, entry 10)

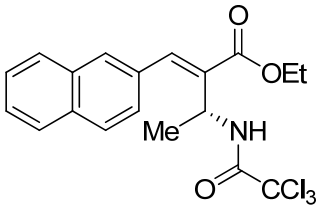
Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 270 mg (65%) of **8j** and 20mg (5%) of (*Z*)-isomer as a colorless liquid.

^{1}H NMR (300MHz, $CDCl_3$): δ 1.39 (d, *J* = 6.9Hz, 3H), 1.44 (t, *J* = 6.9Hz, 3H), 4.40 (q, *J* = 7.2Hz, 2H), 5.24 (dq, J_{AB} = 8.7Hz, J_{AC} = 6.9Hz, 1H), 7.51-7.58 (m, 4H), 7.82-7.91 (m, 3H), 8.17 (d, *J* = 8.7Hz, 1H), 8.27 (s, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.43, 20.99, 45.86, 61.66, 93.02, 124.39, 125.71, 126.50, 126.62, 127.00, 128.85, 129.65, 131.32, 131.42, 133.14, 133.63, 140.68, 160.69, 167.01.

IR υ_{max} 3397, 2984, 1711, 1502, 1256, 819, 732, 632 cm^{-1}.

LRMS (APCI) m/z 414 (M+1, 1,4), 370 (43), 253 (80), 207 (90), 179 (100), 149(22).



(*E*)-ethyl 2-(naphthalen-2-ylmethylene)-3-(2,2,2-trichloroacetamido)butanoate (Table 1, entry 11)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 299 mg (72%) of **8k** as a white solid.

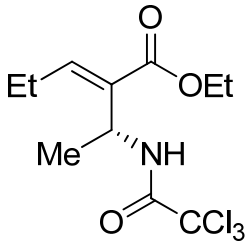
^{1}H NMR (300MHz, $CDCl_3$): δ 1.41 (t, *J* = 7.2Hz, 3H), 1.50 (d, *J* = 6.9Hz, 3H), 4.35 (q, *J* = 7.2Hz, 2H), 5.55 (dq, J_{AB} = 9.0Hz, J_{AC} = 6.9Hz, 1H), 7.50-7.54 (m, 3H), 7.82-7.92 (m, 4H), 7.92 (s, 1H), 8.26 (d, *J* = 9.0Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.39, 20.77, 45.34, 61.52, 93.02, 126.21, 126.77, 127.23, 127.79, 128.72, 129.28, 131.15, 131.46, 133.21, 133.45, 141.78, 160.82, 167.29.

IR υ_{max} 3343, 2987, 1678, 1508, 1246, 1026, 825, 740, 638 cm^{-1}.

LRMS (APCI) m/z 414 (M+1, 1,1), 253 (26), 227 (7), 207(70), 179 (100).

Mp 79-81 ^oC



(*E*)-ethyl 2-(1-(2,2,2-trichloroacetamido)ethyl)pent-2-enoate (Table 1, entry 12)

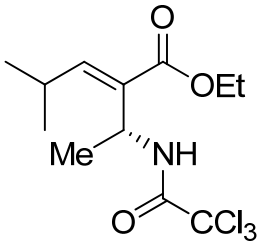
Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 193 mg (61%) of **8l** and 123mg (39%) of (*Z*)-isomer as a colorless liquid.

^{1}H NMR (300MHz, $CDCl_3$): δ 1.11 (t, *J* = 7.5Hz, 3H), 1.34 (t, *J* = 7.2Hz, 3H), 1.41 (d, *J* = 6.9Hz, 3H), 2.26-2.46 (m, 2H), 4.25 (qd, J_{AB} = 7.2Hz, J_{AC} = 0.6Hz, 2H), 5.11 (dq, J_{AB} = 8.1Hz, J_{AC} = 6.9Hz, 1H), 6.85 (t, *J* = 7.8Hz, 1H), 8.22 (d, *J* = 8.1Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 13.36, 14.30, 20.40, 21.77, 44.68, 61.08, 92.94, 130.32, 146.97, 160.96, 166.89.

IR υ_{max} 3404, 2978, 1716, 1695, 1501, 1247, 1154, 820, 746 cm^{-1}.

LRMS (CI) m/z 318 (M+3, 100), 259 (40), 240 (21), 156 (46), 128 (58), 112 (30).



(*E*)-ethyl 4-methyl-2-(1-(2,2,2-trichloroacetamido)ethyl)pent-2-enoate (Table 1, entry 13)

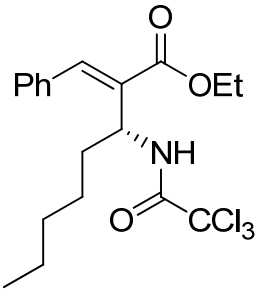
Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 199 mg (60%) of **8m** and 85mg (26%) of (*Z*)-isomer as a colorless liquid.

^{1}H NMR (300MHz, $CDCl_3$): δ 1.07 (d, *J* = 5.7Hz, 3H), 1.09 (d, *J* = 5.7Hz, 3H), 1.32 (t, *J* = 7.2Hz, 3H), 1.42 (d, *J* = 6.9Hz, 3H), 2.84-2.91 (m, 1H), 4.24 (qd, J_{AB} = 7.2Hz, J_{AC} = 0.6Hz, 2H), 5.13 (dq, J_{AB} = 8.1Hz, J_{AC} = 6.9Hz, 1H), 6.65 (d, *J* = 10.5Hz, 1H), 8.20 (d, *J* = 8.1Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.32, 20.72, 22.29, 22.53, 27.88, 44.89, 61.13, 92.94, 128.65, 151.84, 160.90, 167.20.

IR υ_{max} 3407, 2966, 1715, 1696, 1501, 1264, 1031, 821, 736, 684 cm^{-1}.

LRMS (CI) m/z 332 (M+3, 100), 287 (31), 274 (24), 254 (24), 170 (39), 124 (54).



(*E*)-ethyl 2-benzylidene-3-(2,2,2-trichloroacetamido)octanoate (Table 2, entry 1)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 318 mg (76%) of **8n** and 35mg (8%) of (*Z*)-isomer as a colorless liquid.

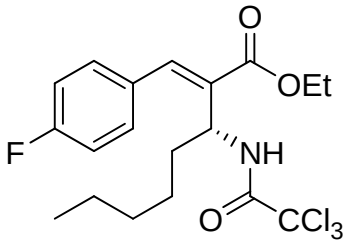
^{1}H NMR (300MHz, $CDCl_3$): δ 0.79 (t, *J* = 6.9Hz, 3H), 1.09-1.25 (m, 6H), 1.38 (t, *J* = 7.2Hz, 3H), 1.64-1.73 (m, 1H), 1.82-1.87 (m, 1H), 4.32 (q, *J* = 7.2Hz, 2H), 5.27-5.35 (m, 1H), 7.35-7.48 (m, 5H), 7.82 (s, 1H), 8.16 (d, *J* = 9.6Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 13.97, 14.32, 22.45, 25.64, 31.17, 34.73, 49.27, 61.44, 93.04, 128.89, 129.04, 129.18, 130.27, 134.10, 142.28, 161.14, 167.33.

IR υ_{max} 3396, 2932, 1715, 1695, 1501, 1252, 1099, 820, 735, 700 cm^{-1}.

LRMS (CI) m/z 420 (M+1, 0.8), 348 (12), 338 (20), 304 (100), 177 (6.6), 143 (12).

HRMS(EI) Exact mass calcd for $C_{19}H_{24}Cl_3NO_3$ $[M]^+$: 419.0822; found: 419.0826.



(*R*,*E*)-ethyl 2-(4-fluorobenzylidene)-3-(2,2,2-trichloroacetamido)octanoate (Table 2, entry 2), (Table 3, entry 3)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 379 mg (87%) of **8o** and 42mg (9%) of (*Z*)-isomer as a colorless liquid.

^{1}H NMR (300MHz, $CDCl_3$): δ 0.80 (t, *J* = 7.2Hz, 3H), 1.09-1.30 (m, 6H), 1.39 (t, *J* = 7.2Hz, 3H), 1.43-1.71 (m, 1H), 1.71-2.05 (m, 1H), 4.32 (q, *J* = 7.2Hz, 2H), 5.26 (dt, J_{AB} = 9.6Hz, J_{AC} = 9.0Hz, 1H), 7.11-7.18 (m, 2H), 7.46-7.52 (m, 2H), 7.77 (s, 1H), 8.12 (d, *J*=9.6Hz, 1H).

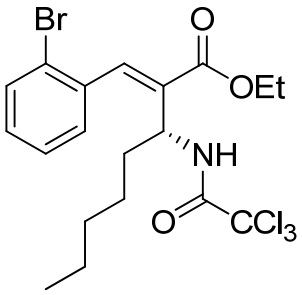
^{13}C NMR (75MHz, $CDCl_3$): δ 13.99, 14.35, 22.47, 25.70, 31.19, 34.64, 49.24, 61.52, 92.98, 116.10 (d, *J*=21.8Hz), 130.18 (d, *J*=3.0Hz), 132.38 (d, *J*=8.2Hz), 131.20 (d, *J*=9.0Hz), 141.12, 161.37 (d, *J*=10.5Hz), 164.76, 167.19.

IR υ_{max} 3403, 2959, 1714, 1696, 1508, 1252, 1234, 912, 821, 735 cm^{-1}.

LRMS (CI) m/z 438 (M+1, 1.2), 402 (6.7), 368 (32), 323 (100), 195 (13), 147 (8).

HPLC condition: Chiralcel AD-H column, *n*-hexane/2-propanol = 99.9:0.1, 1.0 mL/min, 256 nm UV detector, *t*R = 13.28 min (major) and *t*R = 10.63 min (minor).

$[\alpha]^{20}_D$ = -125.9 (*c* 1.23, $CHCl_3$, 97% *ee*). **Mp** 39-41 °C



(*E*)-ethyl 2-(2-bromobenzylidene)-3-(2,2,2-trichloroacetamido)octanoate (Table 2, entry 3)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 397 mg (80%) of **8p** and 87mg (17%) of (*Z*)-isomer as a colorless liquid.

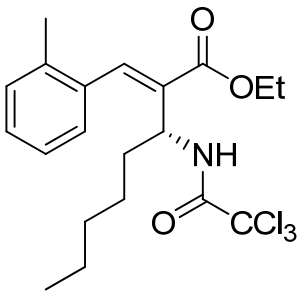
^{1}H NMR (300MHz, $CDCl_3$): δ 0.77 (t, J = 7.2Hz, 3H), 1.04-1.26 (m, 6H), 1.40 (t, J = 7.2Hz, 3H), 1.67-1.76 (m, 2H), 4.34 (q, J = 7.2Hz, 2H), 5.03 (dt, J_{AB} = 9.6Hz, J_{AC} = 8.8Hz, 1H), 7.25 (td, J_{AB} = 7.5Hz, J_{AC} = 1.5Hz, 1H), 7.44 (td, J_{AB} = 7.5Hz, J_{AC} = 1.2Hz, 1H), 7.56 (dd, J_{AB} = 7.5Hz, J_{AC} = 1.2Hz, 1H), 7.63 (dd, J_{AB} = 7.5Hz, J_{AC} = 1.2Hz, 1H), 7.80 (s, 1H), 8.08 (d, J = 9.6Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.01, 14.33, 22.46, 25.55, 31.16, 34.55, 49.55, 61.66, 93.00, 123.74, 127.95, 130.49, 130.54, 131.34, 132.80, 134.77, 141.87, 161.14, 166.84.

IR υ_{max} 3397, 2931, 1716, 1699, 1501, 1249, 1098, 1027, 819, 747 cm^{-1}.

LRMS (CI) m/z 500 (M+3, 17), 418 (67), 384 (100), 349 (42), 230 (98), 159 (43).

HRMS(EI) Exact mass calcd for $C_{19}H_{23}BrCl_3NO_3$ $[M]^+$: 496.9927; found: 496.9929.



(*E*)-ethyl 2-(2-methylbenzylidene)-3-(2,2,2-trichloroacetamido)octanoate (Table 2, entry 4)

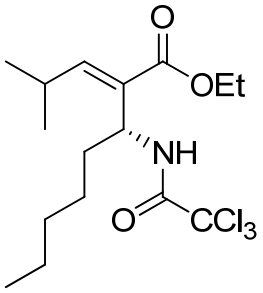
Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 328 mg (75%) of **8q** and 28mg (7%) of (*Z*)-isomer as a colorless liquid.

^{1}H NMR (300MHz, $CDCl_3$): δ 0.78 (t, J = 7.2Hz, 3H), 1.03-1.21 (m, 6H), 1.39 (t, J = 7.2Hz, 3H), 1.63-1.68 (m, 1H), 1.76-1.81 (m, 1H), 2.27 (s, 3H), 4.33 (q, J = 7.2Hz, 2H), 5.04 (dt, J_{AB} = 9.6Hz, J_{AC} = 8.1Hz, 1H), 7.22-7.34 (m, 4H), 7.87 (s, 1H), 8.08 (d, J = 9.6Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 13.99, 14.35, 20.07, 22.48, 25.65, 31.15, 34.69, 49.54, 61.48, 93.09, 126.29, 128.49, 129.12, 130.27, 130.88, 133.51, 136.51, 142.33, 160.99, 167.19.

IR υ_{max} 3394, 2929, 1718, 1696, 1499, 1251, 1098, 820, 747 cm^{-1}.

LRMS (CI) m/z 434 (M+1, 0.8), 352 (18), 318 (100), 157 (22), 129 (16).



(*E*)-ethyl 2-isopropyl-3-(2,2,2-trichloroacetamido)octanoate (Table 2, entry 5)

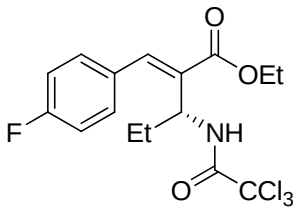
Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 363 mg (94%) of **8r** and (*Z*)-isomer as a colorless liquid.

^{1}H NMR (300MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.3Hz, 3H), 1.05 (d, *J* = 2.4Hz, 3H), 1.08 (d, *J* = 2.4Hz, 3H), 1.25-1.30 (m, 6H), 1.34 (t, *J* = 7.2Hz, 3H), 1.58-1.72 (m, 1H), 1.78-1.89 (m, 1H), 2.79-2.95 (m, 1H), 4.20-4.31 (m, 2H), 4.96 (dt, J_{AB} = 9.3Hz, J_{AC} = 8.4Hz, 1H), 6.67 (d, *J* = 10.5Hz, 1H), 8.05 (d, *J* = 9.3Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.09, 14.34, 22.25, 22.62, 22.65, 26.06, 27.99, 31.49, 34.40, 49.21, 61.11, 93.09, 127.78, 152.45, 161.18, 167.30.

IR υ_{max} 3402, 2962, 2933, 1717, 1697, 1501, 1260, 1157, 820, 734 cm^{-1}.

LRMS (CI) m/z 386 (M+1, 20), 314 (71), 270 (100), 226 (15), 181 (14), 95 (14).



(*R*,*E*)-ethyl 2-(4-fluorobenzylidene)-3-(2,2,2-trichloroacetamido)pentanoate (Table 2, entry 6), (Table 3, entry 4)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 286 mg (65%) of **8s** and 21mg (5%) of (*Z*)-isomer as a white solid.

^{1}H NMR (300MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.2Hz, 3H), 1.38 (t, *J* = 7.2Hz, 3H), 1.68-1.77 (m, 1H), 1.85-1.95 (m, 1H), 4.32 (q, *J* = 7.2Hz, 2H), 5.17 (dt, J_{AB} = 9.3Hz, J_{AC} = 9.0Hz, 1H), 7.10-7.18 (m, 2H), 7.45-7.49 (m, 2H), 7.78 (s, 1H), 8.12 (d, *J* = 9.3Hz, 1H).

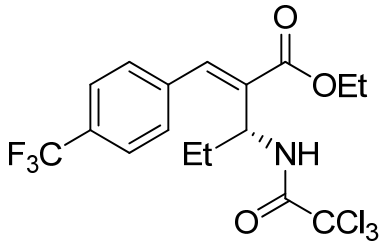
^{13}C NMR (75MHz, $CDCl_3$): δ 10.72, 14.33, 27.98, 50.83, 61.52, 93.03, 116.10 (d, *J*=24.4Hz), 130.13, 130.19 (d, *J* = 3.3Hz), 131.22 (d, *J* = 8.3Hz), 141.34, 161.43 (d, *J* = 2.8Hz), 164.77, 167.16.

IR υ_{max} 828, 1128, 1239, 1504, 1600, 1709, 2975, 3398 cm^{-1}.

LRMS (APCI) m/z 396 (M+3, 32), 350 (83), 322 (18), 235 (100), 189 (57), 161 (54).

HPLC condition: Chiralcel OJ-H column, *n*-hexane/2-propanol = 98:2, 1.0 mL/min, 256 nm UV detector, *t*R = 29.40 min (major) and *t*R = 21.62 min (minor).

$[\alpha]^{20}_D$ = -149.7 (*c* 1.19, $CHCl_3$, 96% *ee*). **Mp** 53-55 °C



(*E*)-ethyl 2-(4-trifluoromethylbenzylidene)-3-(2,2,2-trichloroacetamido)pentanoate (Table 2, entry 7)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 439 mg (90%) of **8t** and 33mg (6%) of (*Z*)-isomer as a white solid.

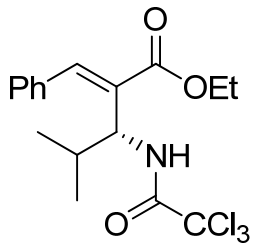
^{1}H NMR (300MHz, $CDCl_3$): δ 0.84 (t, *J* = 7.5Hz, 3H), 1.40 (t, *J* = 7.2Hz, 3H), 1.68-1.80 (m, 1H), 1.83-1.95 (m, 1H), 4.34 (q, *J* = 7.2Hz, 2H), 5.08 (dt, J_{AB} = 9.6Hz, J_{AC} = 8.7Hz, 1H), 7.58 (d, *J* = 8.1Hz, 2H), 7.72 (d, *J* = 8.1Hz, 2H), 7.85 (s, 1H), 8.09 (d, *J* = 9.6Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 10.70, 14.28, 27.88, 50.90, 61.74, 92.88, 125.87 (q, *J*=3.8Hz), 129.33, 130.63, 131.07, 131.97, 137.75, 140.76, 161.42, 166.73.

IR υ_{max} 3397, 2973, 1715, 1502, 1325, 1128, 1068, 821, 737, 646 cm^{-1}.

LRMS (CI) m/z 446 (M+1, 4.5), 416 (31), 372 (100), 307 (10), 245 (14), 211 (20).

Mp 37-39 ^oC



(*E*)-ethyl 2-benzylidene-4-methyl-3-(2,2,2-trichloroacetamido)pentanoate (Table 2, entry 8)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 311 mg (79%) of **8u** and 34mg (9%) of (*Z*)-isomer as a white solid.

^{1}H NMR (300MHz, $CDCl_3$): δ 0.70 (d, *J* = 6.9Hz, 3H), 0.93 (d, *J* = 6.9Hz, 3H), 1.39 (t, *J* = 7.2Hz, 3H), 2.05-2.13 (m, 1H), 4.32 (q, *J* = 7.2Hz, 2H), 4.98 (dd, J_{AB} = 9.6Hz, J_{AC} = 9.9Hz, 1H), 7.34-7.52 (m, 5H), 7.88 (s, 1H), 8.19 (d, *J* = 9.6Hz, 1H).

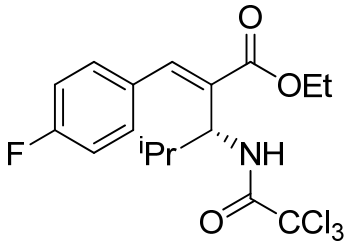
^{13}C NMR (75MHz, $CDCl_3$): δ 14.37, 19.60, 19.82, 32.81, 55.58, 61.52, 93.19, 128.93, 129.11, 129.20, 129.59, 134.26, 143.33, 161.35, 167.59.

IR υ_{max} 3377, 2969, 2862, 1697, 1501, 1252, 1143, 1097, 822, 774, 694 cm^{-1}.

LRMS (CI) m/z 392 (M+1, 34), 348 (19), 304 (100), 232 (21), 185 (13), 143 (20).

HRMS(EI) Exact mass calcd for $C_{17}H_{20}Cl_3NO_3$ $[M]^+$: 391.0509; found: 391.0511.

Mp 63-65 ^oC



(*E*)-ethyl 2-(4-fluorobenzylidene)-4-methyl-3-(2,2,2-trichloroacetamido)pentanoate (Table 2, entry 9)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 333 mg (81%) of **8v** and 41mg (10%) of (*Z*)-isomer as a white solid.

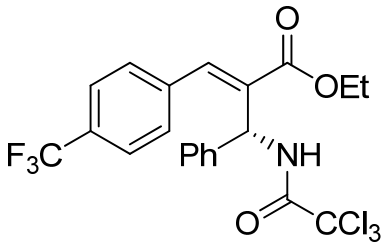
^{1}H NMR (300MHz, $CDCl_3$): δ 0.70 (d, *J* = 6.6Hz, 3H), 0.94 (d, *J* = 6.6Hz, 3H), 1.39 (t, *J* = 7.2Hz, 3H), 2.05-2.14 (m, 1H), 4.32 (q, *J* = 7.2Hz, 2H), 4.91 (dd, J_{AB} = 9.6Hz, J_{AC} = 9.9Hz, 1H), 7.11-7.17 (m, 2H), 7.50-7.55 (m, 2H), 7.82 (s, 1H), 8.16 (d, *J* = 9.6Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.37, 19.64, 19.82, 32.70, 55.58, 61.59, 93.10, 116.12 (d, *J* = 21.4Hz), 129.65, 130.29 (d, *J* = 3.3Hz), 131.29 (d, *J* = 8.2Hz), 142.15, 161.45 (d, *J* = 6.1Hz), 164.72, 167.40.

IR υ_{max} 3383, 2968, 2925, 1697, 1503, 1238, 1144, 1098, 823, 680 cm^{-1}.

LRMS (CI) m/z 410 (M+1, 14), 367 (54), 323 (100), 249 (32), 195 (27), 133 (18).

Mp 82-84 ^oC



(*E*)-ethyl 3-(4-trifluoromethylphenyl)-2-(phenyl(2,2,2-trichloroacetamido)methyl)acrylate (Table 2, entry 10)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 374 mg (76%) of **8w** and 61mg (12%) of (*Z*)-isomer as a white solid.

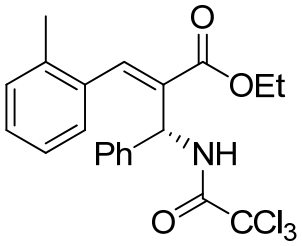
^{1}H NMR (300MHz, $CDCl_3$): δ 1.30 (t, *J* = 7.2Hz, 3H), 4.26 (q, *J* = 7.2Hz, 2H), 6.42 (d, *J* = 9.6Hz, 1H), 7.21-7.38 (m, 5H), 7.57 (d, *J* = 8.4Hz, 2H), 7.70 (d, *J* = 8.4Hz, 2H), 8.05 (s, 1H), 8.53 (d, *J* = 9.6Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.36, 51.65, 62.07, 92.95, 125.81, 126.21 (q, *J*=8.3Hz), 128.20, 129.20, 129.49, 131.16, 131.25, 137.47, 137.49, 138.53, 141.92, 161.66, 166.71.

IR υ_{max} 3707, 3676, 2865, 1718, 1498, 1373, 1247, 1062, 1014, 824, 755 cm^{-1}.

LRMS (CI) m/z 496 (M+3, 0.08), 449 (9.0), 413 (100), 386 (34), 303 (7.3), 260 (10).

Mp 67-69 ^oC



(*E*)-ethyl 2-(phenyl(2,2,2-trichloroacetamido)methyl)-3-o-tolylacrylate (Table 2, entry 11)

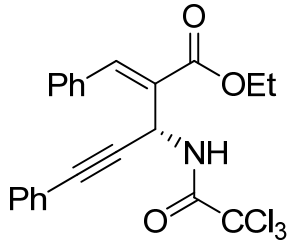
Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 130 mg (29%) of **8x** and 56mg (13%) of (*Z*)-isomer as a pale yellow oil.

^{1}H NMR (300MHz, $CDCl_3$): δ 1.29 (t, *J* = 7.2Hz, 3H), 2.34 (s, 3H), 4.25 (q, *J* = 7.2Hz, 2H), 6.28 (d, *J* = 9.3Hz, 1H), 7.18-7.35 (m, 9H), 8.08 (s, 1H), 8.56 (d, *J* = 9.3Hz, 1H).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.24, 20.18, 51.87, 61.67, 92.17, 125.79, 126.46, 127.74, 128.26, 128.84, 129.55, 130.00, 130.51, 133.21, 136.89, 139.11, 143.33, 161.22, 167.02.

IR υ_{max} 2923, 2853, 1721, 1495, 1462, 1247, 1121, 751, 698 cm^{-1}.

LRMS (CI) m/z 491 (M+2, 0.03), 393 (11), 359 (100), 331 (25), 233 (23), 205 (37).



(*E*)-ethyl 2-benzylidene-5-phenyl-3-(2,2,2-trichloroacetamido)pent-4-ynoate (Table 2, entry 12)

Purification by column chromatography (gradient elution with 10% EA-hexane) afforded 266 mg (59%) of **8y** and 36mg (8%) of (*Z*)-isomer as a pale yellow oil.

^{1}H NMR (300MHz, $CDCl_3$): δ 1.42 (t, *J* = 7.2Hz, 3H), 4.39 (q, *J* = 7.2Hz, 2H), 6.25 (d, *J* = 9.0Hz, 1H), 7.30-7.33 (m, 3H), 7.34-7.54 (m, 7H), 7.89 (s, 1H), 8.42 (d, *J* = 9.0Hz, 1H).

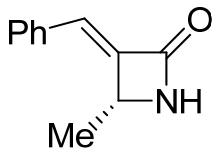
^{13}C NMR (75MHz, $CDCl_3$): δ 14.43, 41.52, 61.81, 84.42, 85.28, 92.50, 122.18, 127.62, 128.40, 128.91, 129.14, 129.46, 129.89, 132.08, 133.62, 142.62, 160.61, 166.36.

IR υ_{max} 2924, 2853, 1718, 1699, 1490, 1261, 1106, 821, 740, 692 cm^{-1}.

LRMS (CI) m/z 420 (M+1, 0.8), 348 (12), 338 (20), 304 (100), 177 (6.6), 143 (12).

HRMS(EI) Exact mass calcd for $C_{15}H_{16}Cl_3NO_3$ $[M]^+$: 449.0352; found: 449.0350.

Procedures for the α-alkylidene-β-lactams



(*R*,*E*)-3-benzylidene-4-methylazetidin-2-one (10a)

To a solution of the corresponding α-alkylidene-β-amino ester **8a** (273mg, 0.75mmol, ee = 89%) in 10.0ml of H_2O/EtOH (1:1) solution, 7.5mmol of KOH was added. The solution was heated to reflux for 30min, cooled to room temperature. To a resulting solution was added 10M $HCl_{(aq)}$ until reached at pH 1. The mixture was concentrated under reduced pressure. Crude solid was completely dried under high vacuum 15.0ml of freshly distilled MeCN was added. At ambient temperature, 2,2'-dipyridyldisulfide (3.0mmol), triphenylphosphine (3.0mmol) and triethylamine (3.75mmol) were added in one-portion. After 30min, the mixture was quenched by water (5ml). The reaction mixture was extracted with CH_2Cl_2 (3x5 ml). The organic extracts were combined, dried over Na_2SO_4 then concentrated *in vacuo*. The crude product was purified by flash chromatography (EtOAc:Hexane=1:1 as eluent) to afforded 110mg (85%) of (*R*,*E*)-3-benzylidene-4-methylazetidin-2-one (**10a**) as white solid.

^{1}H NMR (300MHz, $CDCl_3$): δ 1.47 (d, J = 6.0Hz, 3H), 4.67 (qd, J_{AB} = 6.0Hz, J_{AC} = 1.5Hz, 1H), 6.75 (s, 1H), 6.97 (d, J = 1.5Hz, 1H), 7.34-7.43 (m, 5H).

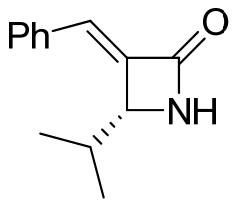
^{13}C NMR (75MHz, $CDCl_3$): δ 18.53, 53.57, 124.96, 128.95, 129.29, 129.42, 133.62, 142.93, 165.02.

IR υ_{max} 3157, 2928, 1730, 1494, 1379, 1275, 1186, 1071, 764, 690 cm^{-1}.

LRMS (CI) m/z 174 (M+1, 83), 144 (87), 130 (100), 115 (55), 102 (33).

HRMS (FAB) Exact mass calcd for $C_{11}H_{12}NO$ $[M+H]^+$: 174.0919; found: 174.0915.

$[\alpha]^{20}_D$ = +2.36 (*c* 1.12, $CHCl_3$, 89% *ee*). **Mp** 113-115 °C



(*R*,*E*)-3-benzylidene-4-isopropylazetidin-2-one (10u)

To a solution of the corresponding α-alkylidene-β-amino ester **8u** (294mg, 0.75mmol, ee = 89%) in 10.0ml of H_2O/EtOH (2:1) solution, 15mmol of KOH was added. The solution was heated to reflux for 7 hours, cooled to room temperature. To a resulting solution was added 10M $HCl_{(aq)}$ until reached at pH 1. The mixture was concentrated under reduced pressure. Crude solid was completely dried under high vacuum 15.0ml of freshly distilled MeCN was added. At ambient temperature, 2,2'-dipyridyldisulfide (3.0mmol), triphenylphosphine (3.0mmol) and triethylamine (3.75mmol) were added in one-portion. After 1h, the mixture was quenched by water (5ml). The reaction mixture was extracted with CH_2Cl_2 (3x5 ml). The organic extracts were combined, dried over Na_2SO_4 then concentrated *in vacuo*. The crude product was purified by flash chromatography (EtOAc:Hexane=1:3 as eluent) to afforded 92mg (61%) of (*R*,*E*)-3-benzylidene-4-isopropylazetidin-2-one (**10u**) as white solid.

^{1}H NMR (300MHz, $CDCl_3$): δ 0.80 (d, *J* = 6.9Hz, 3H), 1.01 (d, *J* = 6.9Hz, 3H), 2.23 (m, 1H), 6.60 (dd, J_{AB} = 3.0Hz, J_{AC} = 1.5Hz, 1H), 6.53 (s, 1H), 7.02 (d, *J* = 1.5Hz, 1H), 7.27-7.40 (m, 5H).

^{13}C NMR (75MHz, $CDCl_3$): δ 13.34, 20.10, 28.34, 63.36, 125.70, 128.93, 129.30, 134.02, 140.40, 165.60.

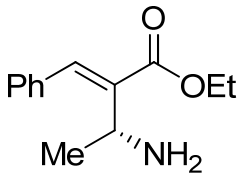
IR υ_{max} 3204, 2959, 1735, 1702, 1455, 1172, 976, 760, 683, 649 cm^{-1}.

LRMS (CI) m/z 202 (M+1, 85), 160 (81), 133 (90), 117 (100), 104 (39).

HRMS(EI) Exact mass calcd for $C_{13}H_{15}NO$ $[M]^+$: 201.1154; found: 201.1155.

$[\alpha]^{20}_D$ = -2.33 (*c* 0.30, $CHCl_3$, 89% *ee*). **Mp** 109-111 ^oC

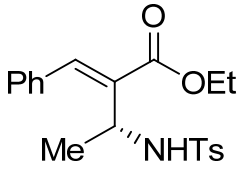
Procedures for selective deprotection of trichloroacetamide



(*R*,*E*)-ethyl 3-amino-2-benzylidenebutanoate (11a)

To a solution of the corresponding α-alkylidene-β-amino ester **8a** (92.8mg, 0.255mmol, ee = 89%) in 1.5ml of DMSO, Cs_2CO_3 (208mg, 0.64mmol) was added. The solution was heated to 100°C for 10 min, cooled to room temperature. The resulting solution was purified by flash chromatography (EtOAc:Hexane=1:3 to CH_2Cl_2:MeOH=1:10 as eluent) to afford (*R*,*E*)-ethyl 3-amino-2-benzylidenebutanoate (**11a**) containing inseparable DMSO.

^{1}H NMR (300MHz, $CDCl_3$): δ 1.38 (t, *J* = 7.2Hz, 3H), 1.46 (d, *J* = 6.3Hz, 3H), 2.76 (br s, 2H), 4.17 (m, 1H), 4.29 (q, *J* = 7.2Hz, 2H), 7.26-7.38 (m, 5H), 7.60 (s, 1H).



(*R*,*E*)-ethyl 2-benzylidene-3-(p-toluenesulfonamido)butanoate (12a)

To a solution of the **11a** and DMSO mixture in 4.0ml of CH_2Cl_2, TsCl (72mg, 0.382mmol) was added. The solution was stirred at room temperature. After 1h 20min, the mixture was quenched by saturated $NaHCO_{3(aq)}$ (2ml). The reaction mixture was extracted with CH_2Cl_2 (3x5 ml). The organic extracts were combined, dried over Na_2SO_4 then concentrated *in vacuo*. The crude product was purified by flash chromatography (EtOAc:Hexane=1:3 as eluent) to afforded 68mg (72%) of (*R*,*E*)-ethyl 2-benzylidene-3-(p-toluenesulfonamido) butanoate(**12a**) from **8a** as white solid.

^{1}H NMR (300MHz, $CDCl_3$): δ 1.29 (t, *J* = 7.2Hz, 3H), 1.44 (d, *J* = 6.9Hz, 3H), 2.40 (s, 3H), 4.16 (q, *J* = 7.2Hz, 2H), 4.74 (dq, J_{AB} = 10.2Hz, J_{AC} = 7.2Hz, 1H), 5.91 (d, *J* = 10.2Hz, 1H), 7.13 (d, *J* = 8.1Hz, 2H), 7.18-7.21 (m, 2H), 7.38-7.48 (m, 5H).

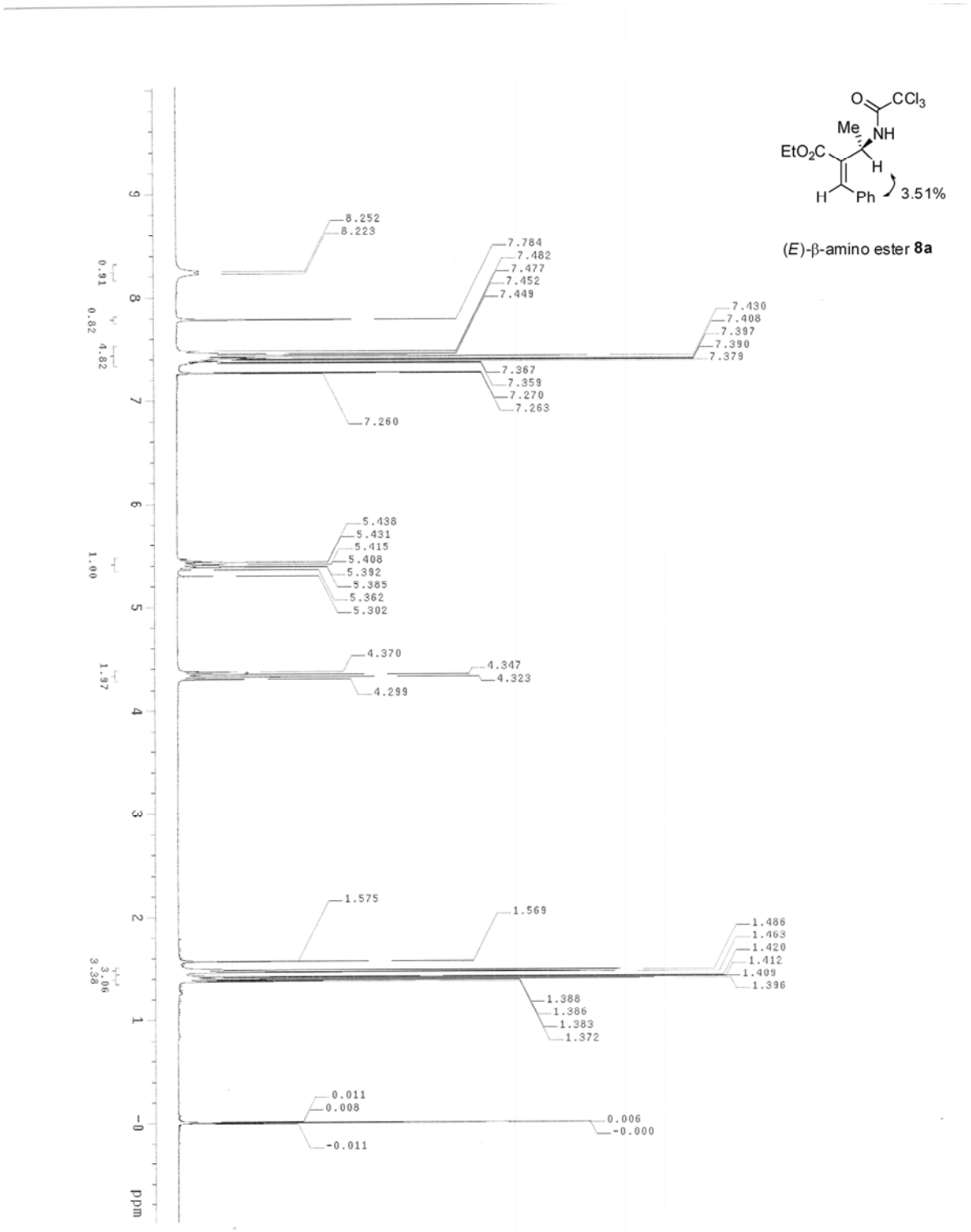
^{13}C NMR (75MHz, $CDCl_3$): δ 14.30, 21.63, 22.17, 47.40, 61.12, 127.22, 128.84, 129.06, 129.20, 129.40, 131.88, 134.20, 138.07, 140.49, 142.96, 166.58.

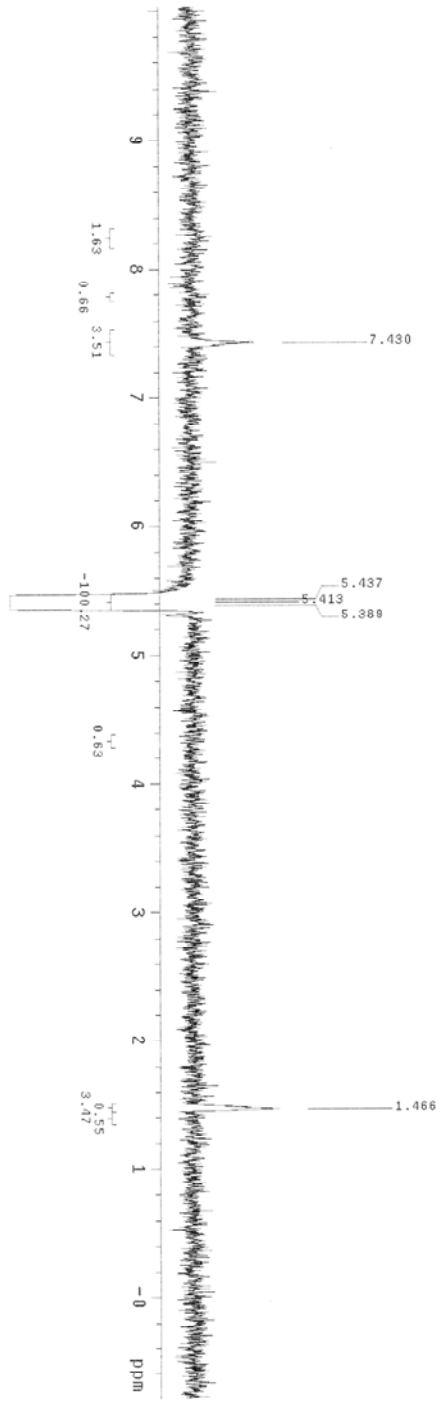
IR υ_{max} 3256, 2932, 2860, 1692, 1437, 1329, 1252, 1166, 816, 678 cm^{-1}.

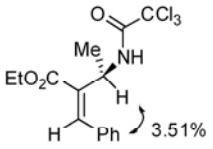
LRMS (APCI) m/z 372 (M-1, 100), 344 (6), 319 (9), 291 (5), 269 (5), 228(4), 196(3).

$[\alpha]^{20}_D$ = -87.96 (*c* 0.46, $CHCl_3$, 89% *ee*). **Mp** 105-107 °C

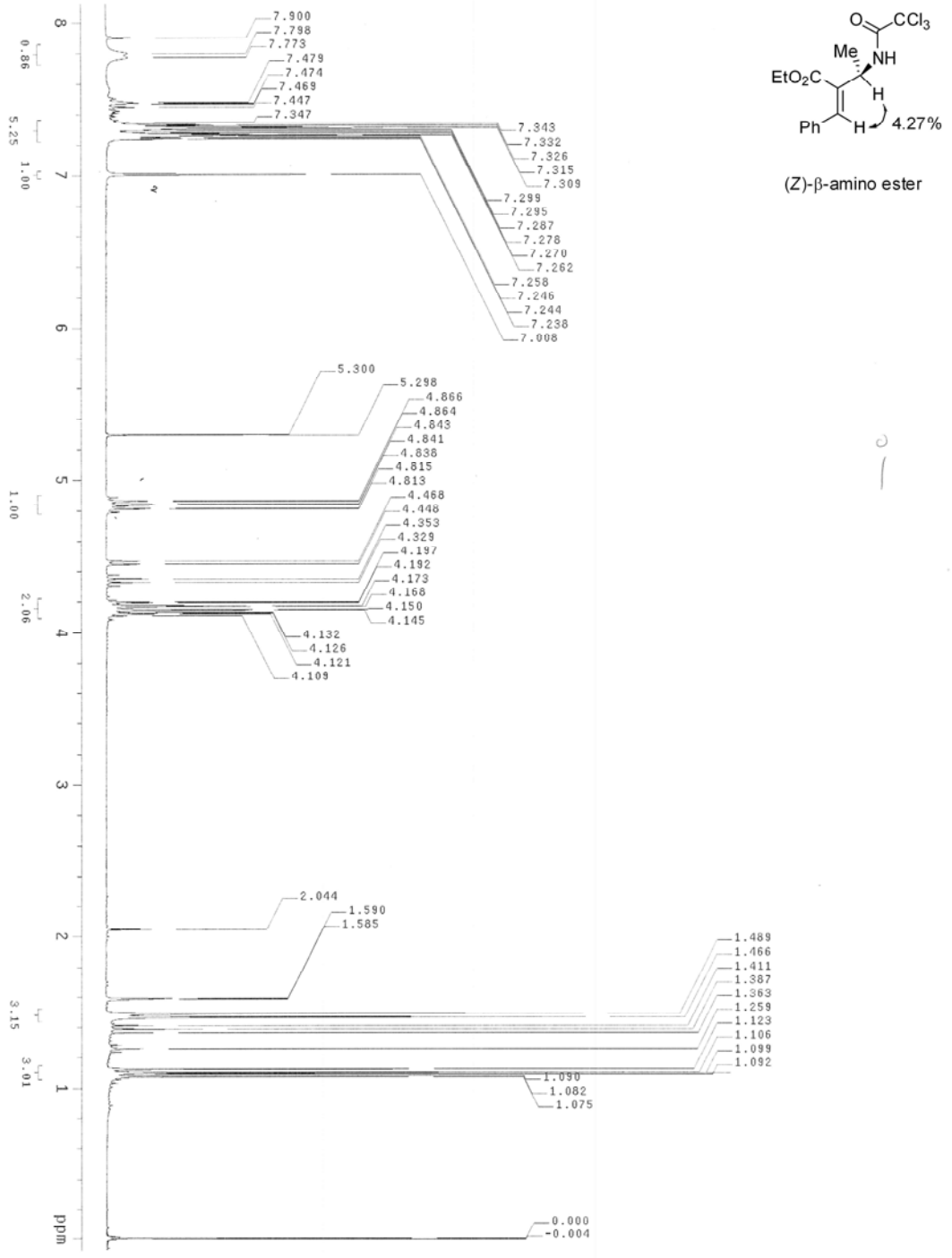
1D NOE spectral analysis of (*E*)-and (*Z*)-α-alkylidene-β-amino esters



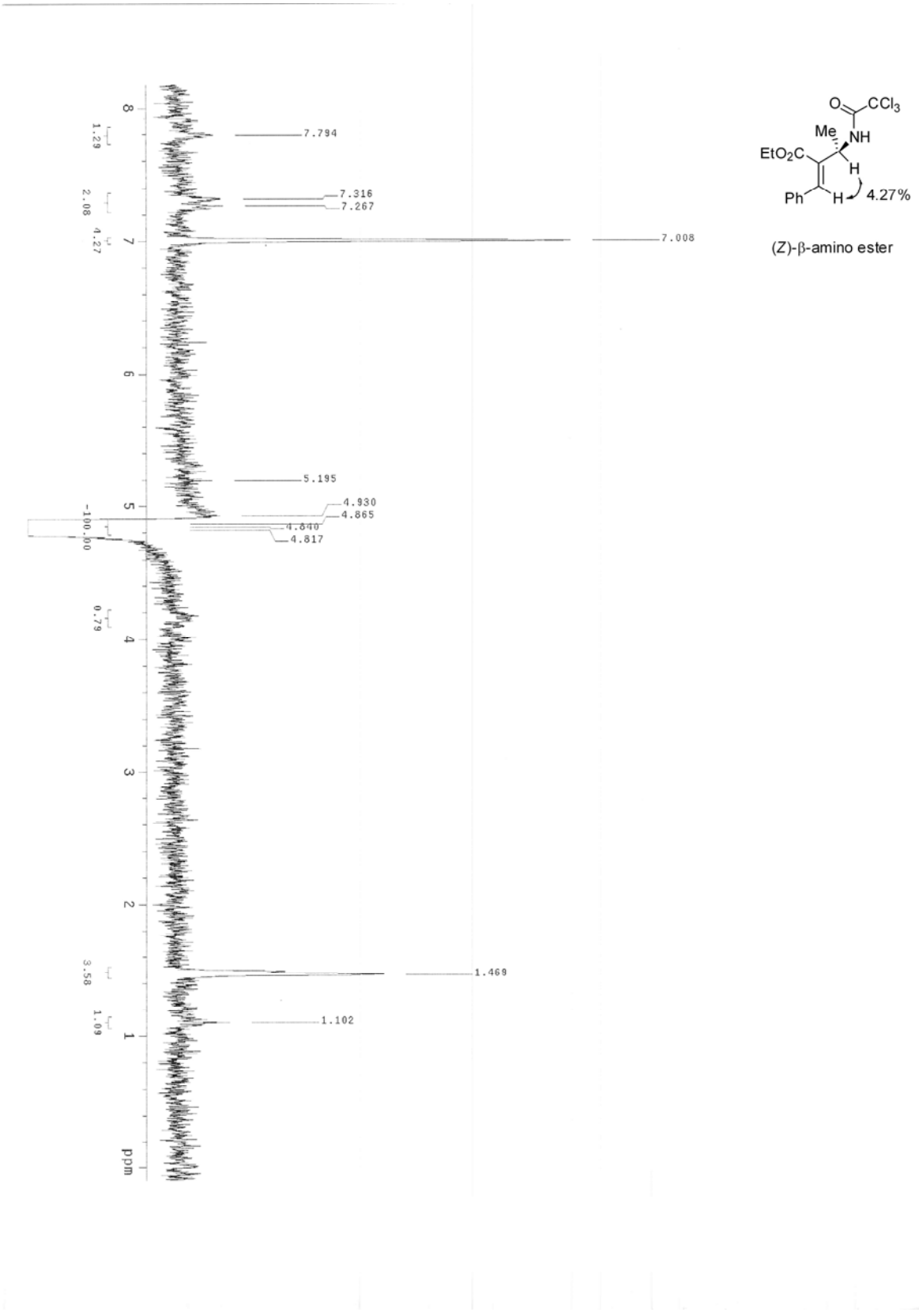




(*E*)-β-amino ester **8a**



(Z)-β-amino ester



(Z)-β-amino ester