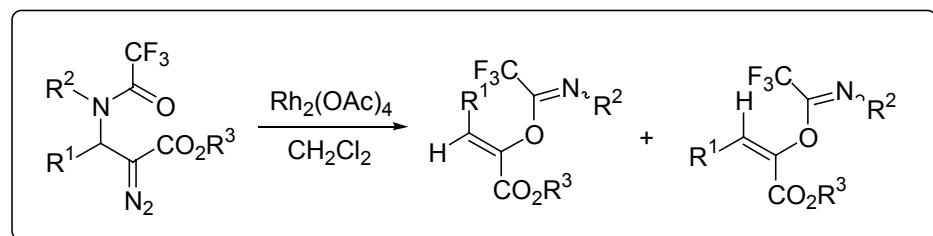


Supporting Information for

**2,3-Migration in Rh(II)-Catalyzed
Reaction of β -Trifluoroacetamido α -Diazocarbonyl Compounds**

Feng Xu, Shiwei Zhang, Xiangnan Wu, Yu Liu, Weifeng Shi and Jianbo Wang^{*}

Beijing National Laboratory of Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China



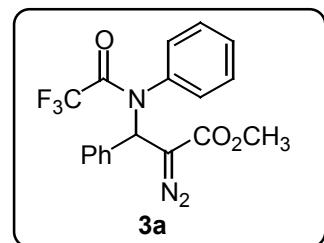
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Caution: Diazo compounds are generally toxic and potentially explosive. They should be handled with care in a well-ventilated fume hood.

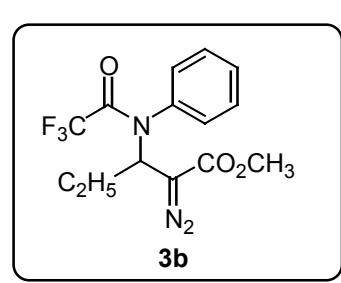
General information. All reactions with air- and moisture-sensitive components were performed under a nitrogen atmosphere in a flame-dried reaction flask. All solvents were distilled prior to use. CH_2Cl_2 was freshly distilled from CaH_2 and THF was freshly distilled from Na before use. The boiling point of petroleum ether is between 30 and 60 °C. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz with a Varian Mercury 200 spectrometer or 300 and 75 MHz with a Varian Mercury 300 spectrometer. Chemical shifts are reported by ppm using tetramethylsilane as internal standard. Mass spectra were obtained on a VG ZAB-HS mass spectrometer. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer.

Methyl 2-Diazo-3-[(N-phenyl)trifluoroacetamido]-3-phenylpropionate (3a)



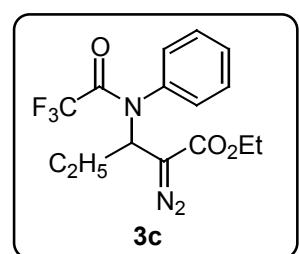
TLC R_f (petroleum ether : acetone 8 : 1) = 0.41; IR (film) 2956, 2109, 1699, 1595, 1493, 1438, 1336, 1209, 1179, 1153, 1113, 1032, 952, 839, 742, 725, 698 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 3.84 (s, 3H), 6.05 (s, 1H), 7.14~7.42 (m, 10H); ^{13}C NMR (75 MHz, CDCl_3) δ 52.2, 64.8, 116.1 (q, $J_{\text{C}-\text{F}} = 287.1$ Hz, CF_3), 126.8, 128.5, 128.8, 129.2, 129.5, 134.0, 138.7, 157.4 (q, $J_{\text{C}-\text{C}-\text{F}} = 35.7$ Hz), 166.0; EI-MS (m/z , relative intensity): 349 [(M-28) $^+$, 23], 290 (13), 189 (11), 172 (100), 115 (25), 102 (15), 91 (23), 77 (74); Anal. calcd for $\text{C}_{18}\text{H}_{14}\text{F}_3\text{N}_3\text{O}_3$: C, 57.30; H, 3.74; N, 11.14. Found: C, 57.52; H, 4.04; N, 11.05.

Methyl 2-Diazo-3-[(N-phenyl)trifluoroacetamido]pentanoate (3b)



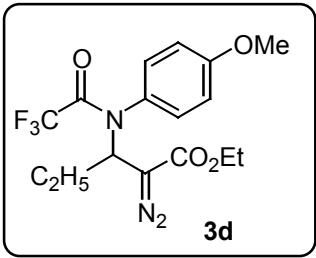
TLC R_f (petroleum ether : acetone 8 : 1) = 0.40; IR (film) 2973, 2106, 1699, 1596, 1495, 1439, 1293, 1207, 1182, 1146, 1088, 962, 881, 705 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.03 (t, $J = 7.2$ Hz, 3H), 1.84~1.97 (m, 2H), 3.82 (s, 3H), 5.13 (s, 1H), 7.16~7.47 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 10.5, 22.9, 52.2, 59.2, 116.1 (q, $J_{\text{C}-\text{F}} = 287.3$ Hz, CF_3), 129.3, 129.4, 129.6, 136.8, 156.6 (q, $J_{\text{C}-\text{C}-\text{F}} = 35.7$ Hz), 166.2; EI-MS (m/z , relative intensity): 301 [(M-28) $^+$, 6], 272 (66), 242 (10), 189 (19), 172 (54), 144 (18), 130 (12), 113 (36), 91 (21), 77 (100); Anal. calcd for $\text{C}_{14}\text{H}_{14}\text{F}_3\text{N}_3\text{O}_3$: C, 51.07; H, 4.29; N, 12.76. Found: C, 51.08; H, 4.33; N, 12.95.

Ethyl 2-Diazo-3-[(N-phenyl)trifluoroacetamido]pentanoate (3c)



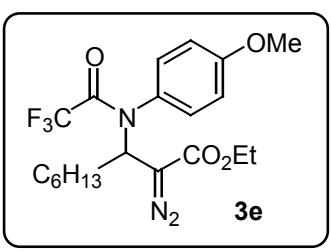
TLC R_f (petroleum ether : acetone 15 : 1) = 0.32; IR (film) 2978, 2908, 1697, 1596, 1495, 1373, 1207, 1182, 1146, 1085, 903, 704 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.03 (t, $J = 7.2$ Hz, 3H), 1.30 (t, $J = 7.2$ Hz, 3H), 1.80~1.96 (m, 2H), 4.22~4.33 (m, 2H), 5.16 (s, 1H), 7.15~7.47 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 10.5, 14.4, 22.9, 59.1, 61.3, 116.1 (q, $J_{\text{C}-\text{F}} = 287.3$ Hz, CF_3), 129.3, 129.6, 129.6, 136.5, 136.5, 156.6 (q, $J_{\text{C}-\text{C}-\text{F}} = 35.6$ Hz), 165.8; EI-MS (m/z , relative intensity): 315 [(M-28) $^+$, 3], 286 (39), 242 (9), 189 (11), 172 (42), 144 (12), 120 (20), 99 (25), 77 (70), 69 (20), 55 (20), 29 (100); Anal. calcd for $\text{C}_{15}\text{H}_{16}\text{F}_3\text{N}_3\text{O}_3$: C, 52.48; H, 4.70; N, 12.24. Found: C, 52.50; H, 4.64; N, 12.32.

Ethyl 2-Diazo-3-[[N-(4-methoxy)phenyl]trifluoroacetamido]pentanoate (3d)



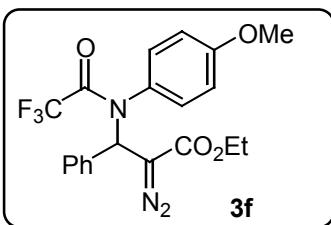
TLC R_f (petroleum ether : acetone 8 : 1) = 0.40; IR (film) 2976, 2097, 1698, 1608, 1511, 1296, 1253, 1182, 1146, 1085, 1033, 843, 739 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.03 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.75~1.92(m, 2H), 3.85 (s, 3H), 4.22~4.33 (m, 2H), 5.20 (s, 1H), 6.92~6.95 (m, 2H), 7.04~7.07 (m, 1H), 7.21~7.23 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 10.5, 14.4, 23.0, 55.4, 58.7, 61.2, 114.3, 116.2 (q, J_{C-F} = 287.1 Hz, CF₃), 128.6, 130.6, 157.0 (q, J_{C-C-F} = 35.1 Hz), 160.1, 165.8; EI-MS (*m/z*, relative intensity): 345 [(M-28)⁺, 10], 272 (11), 219 (100), 202 (43), 174 (8), 149 (21), 122 (25), 107 (15), 99 (53); Anal. calcd for C₁₆H₁₈F₃N₃O₄: C, 51.48; H, 4.86; N, 11.26. Found: C, 51.30; H, 4.89; N, 11.25.

Ethyl 2-Diazo-3-[[N-(4-methoxy)phenyl]trifluoroacetamido]nonanoate (3e)



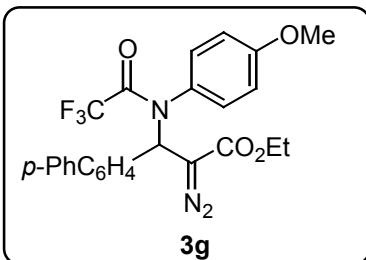
TLC R_f (petroleum ether : acetone 8 : 1) = 0.34; IR (film) 2933, 2098, 1698, 1608, 1512, 1298, 1253, 1205, 1182, 1153, 1097, 1034, 841, 757, 739 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.89 (t, J = 6.6 Hz, 3H), 1.23~1.43 (m, 11H), 1.75~1.82 (m, 2H), 3.84 (s, 3H), 4.22~4.33 (m, 2H), 5.27~5.29 (m, 1H), 6.92~6.95 (m, 2H), 7.03~7.06 (m, 1H), 7.19~7.22 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 13.9, 14.4, 22.4, 25.8, 28.7, 29.7, 31.4, 55.4, 56.9, 61.2, 114.3, 116.2 (q, J_{C-F} = 286.7 Hz, CF₃), 128.6, 130.6, 156.7 (q, J_{C-C-F} = 35.1 Hz), 160.1, 165.8; EI-MS (*m/z*, relative intensity): 401 [(M-28)⁺, 11.2], 328 (14), 219 (100), 202 (58), 149 (19), 109 (35); Anal. calcd for C₂₀H₂₆F₃N₃O₄: C, 55.94; H, 6.10; N, 9.79. Found: C, 56.16; H, 6.13; N, 9.50.

Ethyl 2-Diazo-3-[(N-4-methoxyphenyl)trifluoroacetamido]-3-Phenylpropionate(3f)



TLC R_f (petroleum ether : acetone 8 : 1) = 0.48; IR (film) 2982, 2109, 1698, 1607, 1511, 1300, 1249, 1207, 1179, 1167, 1154, 1109, 1032, 842, 740, 715 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.30 (t, J = 7.2 Hz, 3H), 3.79 (s, 3H), 4.29 (q, J = 7.2 Hz, 2H), 6.09 (s, 1H), 6.84~7.05 (m, 3H), 7.34~7.44 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 14.3, 55.3, 61.3, 64.3, 113.8, 114.6, 116.1 (q, J_{C-F} = 287.3 Hz, CF₃), 126.8, 128.4, 129.1, 130.1, 130.8, 134.2, 157.5 (q, J_{C-C-F} = 35.7 Hz), 160.1, 165.6; EI-MS (*m/z*, relative intensity): 421(M⁺, 0.6), 393 [(M-28)⁺, 46], 347 (16), 320 (51), 219 (51), 203 (77), 175 (59), 147 (100), 122 (23); Anal. calcd for C₂₀H₁₈F₃N₃O₄: C, 57.01; H, 4.31; N, 9.97. Found: C, 57.25; H, 4.35; N, 9.93.

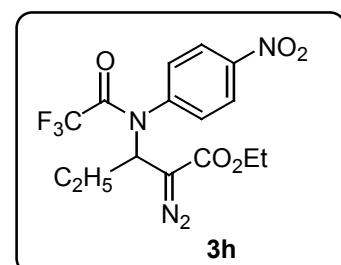
Ethyl 2-Diazo-3-[(N-4-methoxyphenyl)trifluoroacetamido]-3-(4-phenyl)phenylpropionate (3g)



TLC R_f (petroleum ether : acetone 8 : 1) = 0.31; IR (film) 2110, 1698, 1607, 1511, 1299, 1249, 1207, 1180, 1167, 1106, 1033, 839, 752, 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.22 (t, J = 7.2 Hz, 3H), 3.70 (s, 3H), 4.19~4.26 (m, 2H), 6.03 (s, 1H), 6.76~7.16 (m, 3H), 7.27~7.56 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 14.4, 55.4, 61.4, 64.2, 113.9, 114.7, 116.2 (q, J_{C-F} = 287.5 Hz, CF₃), 127.0, 127.3, 127.8, 128.8, 130.1, 130.9, 133.1, 140.0, 141.3, 157.6 (q, J_{C-C-F} = 35.7 Hz), 160.1, 165.7; EI-MS (*m/z*, relative intensity): 469 [(M-28)⁺, 100],

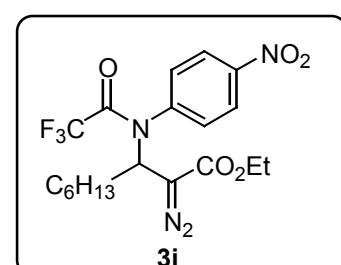
423 (69), 396 (31), 354 (45), 286 (50), 202 (46); Anal. calcd for $C_{26}H_{22}F_3N_3O_4$: C, 62.77; H, 4.46; N, 8.45. Found: C, 62.58; H, 4.74; N, 8.19.

*Ethyl 2-Diazo-3-[(*N*-4-nitrophenyl)trifluoroacetamido]pentanoate (3h)*



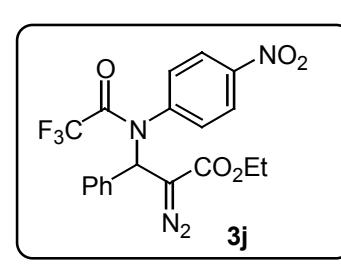
TLC R_f (petroleum ether : acetone 15 : 1) = 0.24; IR (film) 2980, 2105, 1702, 1595, 1529, 1349, 1291, 1210, 1171, 1147, 1086, 855, 704 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.04 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H), 1.95~2.05 (m, 2H), 4.24~4.34 (m, 2H), 4.87 (s, 1H), 7.42~7.66 (m, 2H), 8.32~8.35 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 10.6, 14.3, 22.8, 58.9, 61.4, 115.7 (q, J_{C-F} = 287.1 Hz, CF_3), 124.6, 130.2, 143.4, 147.9, 157.3 (q, J_{C-C-F} = 35.7 Hz), 165.7; EI-MS (m/z , relative intensity): 360 [(M-28) $^+$, 5], 331 (100), 287 (27), 217 (68), 99 (27); Anal. calcd for $C_{15}H_{15}F_3N_4O_5$: C, 46.40; H, 3.89; N, 14.43. Found: C, 46.48; H, 3.90; N, 14.50.

*Ethyl 2-Diazo-3-[(*N*-4-nitrophenyl)trifluoroacetamido]nonanoate (3i)*



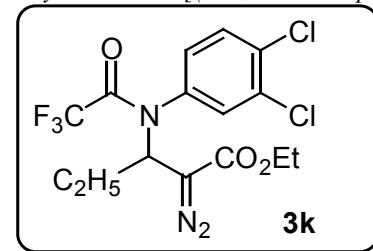
TLC R_f (petroleum ether : acetone 15 : 1) = 0.28; IR (film) 2932, 2861, 2105, 1704, 1595, 1530, 1348, 1288, 1210, 1171, 1153, 1098, 854, 703 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.87 (t, J = 6.6 Hz, 3H), 1.29~1.42 (m, 11H), 1.95 (s, 2H), 4.24~4.34 (m, 2H), 4.95 (s, 1H), 7.42~7.65 (m, 2H), 8.33~8.36 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 14.3, 22.4, 26.0, 28.6, 29.5, 31.4, 59.2, 61.4, 115.6 (q, J_{C-F} = 287.1 Hz, CF_3), 124.7, 130.2, 143.5, 148.0, 156.3 (q, J_{C-C-F} = 36.1 Hz), 165.7; EI-MS (m/z , relative intensity): 416 [(M-28) $^+$, 4], 387 (10), 343 (39), 331 (66), 299 (20), 234 (23), 217 (100), 109 (52); Anal. calcd for $C_{19}H_{23}F_3N_4O_5$: C, 51.35; H, 5.22; N, 12.61. Found: C, 51.60; H, 5.33; N, 12.31.

*Ethyl 2-Diazo-3-[(*N*-4-nitrophenyl)trifluoroacetamido]-3-phenylpropionate (3j)*



TLC R_f (petroleum ether : acetone 8 : 1) = 0.45; IR (film) 2986, 2111, 1705, 1595, 1529, 1348, 1213, 1168, 1108, 1017, 855, 729, 699 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.33 (t, J = 7.2 Hz, 3H), 4.29~4.38 (m, 2H), 5.90 (s, 1H), 7.33~7.48 (m, 7H), 8.27~8.29 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.4, 61.5, 66.0, 115.8 (q, J_{C-F} = 287.3 Hz, CF_3), 124.7, 126.7, 130.0, 129.5, 133.2, 144.6, 148.0, 156.9 (q, J_{C-C-F} = 36.7 Hz), 165.6; EI-MS (m/z , relative intensity): 408 [(M-28) $^+$, 41], 335 (19), 234 (14), 217 (100), 147 (28), 122 (15), 103 (41), 91 (25), 77 (28); Anal. calcd for $C_{19}H_{15}F_3N_4O_5$: C, 52.30; H, 3.46; N, 12.84. Found: C, 52.38; H, 3.59; N, 12.78.

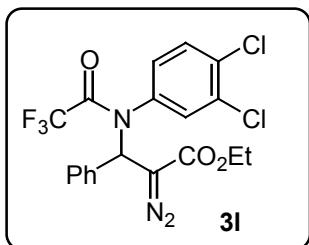
*Ethyl 2-Diazo-3-[(*N*-3,4-dichlorophenyl)trifluoroacetamido]pentanoate (3k)*



TLC R_f (petroleum ether : acetone 30 : 1) = 0.21; IR (film) 2979, 2107, 1702, 1588, 1561, 1473, 1373, 1292, 1211, 1178, 1149, 1086, 910, 806, 738 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.03 (t, J = 7.2 Hz, 3H), 1.31 (t, J = 7.2 Hz, 3H), 1.94 (s, 2H), 4.28 (q, J = 7.2 Hz, 2H), 4.91 (s, 1H), 7.05~7.56 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 10.6, 14.4, 22.8, 58.8, 61.4, 115.8 (q, J_{C-F} =

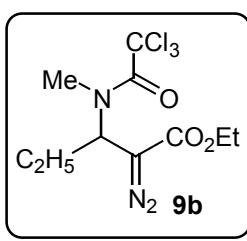
287.1 Hz, CF₃), 128.6, 130.8, 131.2, 134.2, 136.7, 156.9 (q, *J*_{C-C-F} = 35.7 Hz), 165.67; EI-MS (*m/z*, relative intensity): 383 [(M-28)⁺, 3], 354 (23), 257 (9), 240 (27), 145 (18), 127 (15), 99 (61); Anal. calcd for C₁₅H₁₄Cl₂F₃N₃O₃: C, 43.71; H, 3.42; N, 10.19. Found: C, 43.65; H, 3.40; N, 9.98.

Ethyl 2-Diazo-3-[(N-3,4-dichlorophenyl)trifluoroacetamido]-3-phenylpropionate (3l)



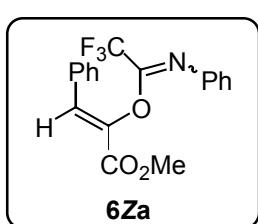
TLC *R_f*(petroleum ether : acetone 15 : 1) = 0.43; IR (film) 2982, 2113, 1705, 1586, 1563, 1472, 1373, 1319, 1213, 1172, 1155, 1107, 1016, 823, 740, 723, 705 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.32 (t, *J* = 7.2 Hz, 3H), 4.28~4.36 (m, 2H), 5.89 (s, 1H), 7.28~7.49 (m, 8H); ¹³C NMR (75 MHz, CDCl₃) δ 14.4, 61.5, 65.7, 115.9 (q, *J*_{C-F} = 287.3 Hz, CF₃), 126.7, 128.3, 128.5, 129.4, 130.8, 133.4, 134.2, 138.2, 157.1 (q, *J*_{C-C-F} = 36.1 Hz), 165.54; EI-MS (*m/z*, relative intensity): 431 [(M-28)⁺, 10], 240 (34), 192 (10), 175 (12), 147 (34), 105 (100), 77 (30); Anal. calcd for C₁₉H₁₄Cl₂F₃N₃O₃: C, 49.58; H, 3.07; N, 9.13. Found: C, 49.40; H, 3.25; N, 8.99.

Ethyl 2-Diazo-3-[(N-methyl)trichloroacetamido]pentanoate (9b)



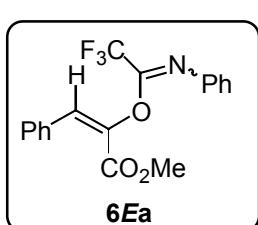
TLC *R_f*(petroleum ether : acetone 15 : 1) = 0.44; IR (film) 2976, 2101, 1689, 1463, 1371, 1319, 1243, 1148, 1075, 951, 913, 843, 811, 746 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.02 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.81~2.08 (m, 2H), 3.05 (s, 3H), 4.18~4.30 (m, 2H), 4.53 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 10.6, 14.3, 21.9, 38.5, 61.0, 93.4, 160.2, 166.3; EI-MS (*m/z*, relative intensity): 301 [(M-28)⁺, 1], 272 (82), 244 (18), 237 (16), 209 (13), 158 (18), 117 (20), 99 (21), 82 (15), 55 (18), 29 (100); Anal. calcd for C₁₀H₁₄Cl₃N₃O₃: C, 36.33; H, 4.27; N, 12.71. Found: C, 36.30; H, 4.28; N, 12.68.

(Z)-Methyl 2-(2,2,2-Trifluoro-N-phenylacetimidoyloxy)3-phenyl-2-propenoate (6Za).



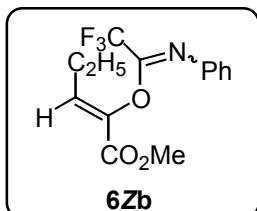
TLC *R_f*(petroleum ether : acetone 30 : 1) = 0.39; IR (film) 2954, 1729, 1651, 1597, 1489, 1450, 1437, 1321, 1269, 1209, 1162, 1128, 1114, 1072, 971, 920, 756, 690 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.83 (s, 3H), 6.70~6.72 (m, 2H), 7.04~7.18 (m, 4H), 7.41~7.63 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 52.7, 119.6, 124.7, 126.2, 128.5, 128.9, 130.16, 131.6, 137.5, 142.6, 162.1; EI-MS (*m/z*, relative intensity): 349 (M⁺, 25), 172 (100), 86 (11), 77 (89); Anal. calcd for C₁₈H₁₄F₃NO₃: C, 61.89; H, 4.04; N, 4.01. Found: C, 62.03; H, 4.13; N, 3.87.

(E)-Methyl 2-(2,2,2-Trifluoro-N-phenylacetimidoyloxy)3-phenyl-2-propenoate (6Ea).



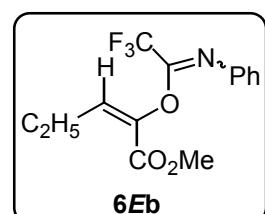
TLC *R_f*(petroleum ether : acetone 30 : 1) = 0.46; IR (film) 2954, 1727, 1597, 1488, 1437, 1328, 1208, 1162, 1130, 1130, 931, 777, 754, 717, 694 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.71 (s, 3H), 6.81~6.84 (m, 2H), 7.00 (s, 1H), 7.09~7.14 (m, 1H), 7.25~7.34 (m, 7H); ¹³C NMR (75 MHz, CDCl₃) δ 52.1, 114.1, 119.6, 124.7, 128.0, 128.7, 129.0, 129.5, 131.6, 138.3, 143.0, 161.5; EI-MS (*m/z*, relative intensity): 349 (M⁺, 16), 172 (95), 118 (10), 86 (21), 77 (100); Anal. calcd for C₁₈H₁₄F₃NO₃: C, 61.89; H, 4.04; N, 4.01. Found: C, 62.05; H, 4.09; N, 3.92.

(Z)-Methyl 2-(2,2,2-Trifluoro-N-phenylacetimidoyloxy)-2-pentenoate (6Zb).



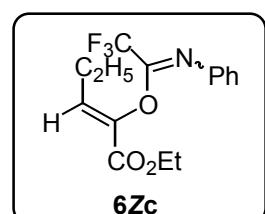
TLC R_f (petroleum ether : acetone 15 : 1) = 0.46; IR (film) 2974, 1729, 1657, 1598, 1489, 1438, 1361, 1332, 1229, 1208, 1133, 1074, 1029, 932, 777, 754, 694 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.04 (s, 3H), 2.54 (s, 2H), 3.80 (s, 3H), 6.05 (s, 1H), 6.77~6.79 (m, 2H), 7.06~7.11 (m, 1H), 7.24~7.30 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.4, 20.3, 52.0, 119.6, 124.4, 128.6, 135.8, 137.8, 143.2, 161.5; EI-MS (*m/z*, relative intensity): 301 (M⁺, 5), 272 (26), 172 (100), 119 (15), 88 (58), 77 (90); Anal. calcd for C₁₄H₁₄F₃NO₃: C, 55.82; H, 4.68; N, 4.65. Found: C, 55.87; H, 4.62; N, 4.75.

(E)-Methyl 2-(2,2,2-Trifluoro-N-phenylacetimidoyloxy)-2-pentenoate (6Eb).



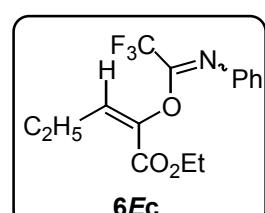
TLC R_f (petroleum ether : acetone 15 : 1) = 0.41; IR (film) 2974, 1736, 1668, 1598, 1489, 1439, 1328, 1304, 1249, 1209, 1132, 1114, 1074, 971, 754, 694 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.07 (t, *J* = 7.2 Hz, 3H), 2.20~2.30 (m, 2H), 3.77 (s, 3H), 6.51 (s, 1H), 6.78~6.81 (m, 2H), 7.07~7.29 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 12.5, 19.3, 52.3, 119.5, 124.5, 128.5, 133.0, 138.4, 143.1, 161.5; EI-MS (*m/z*, relative intensity): 301 (M⁺, 8), 272 (12), 172 (100), 77 (69); Anal. calcd for C₁₄H₁₄F₃NO₃: C, 55.82; H, 4.68; N, 4.65. Found: C, 55.92; H, 4.65; N, 4.56.

(Z)-Ethyl 2-(2,2,2-Trifluoro-N-phenylacetimidoyloxy)-2-pentenoate (6Zc).



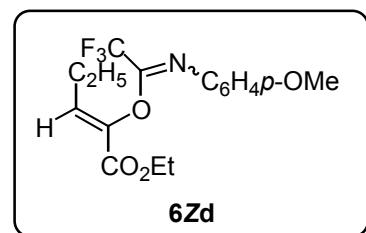
TLC R_f (petroleum ether : acetone 15 : 1) = 0.54; IR (film) 2982, 1724, 1598, 1489, 1374, 1332, 1227, 1207, 1134, 1074, 1033, 923, 777, 694 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.04 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 2.55 (s, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 6.04 (s, 1H), 6.78~6.81 (m, 2H), 7.07~7.12 (m, 1H), 7.25~7.30 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 13.5, 14.0, 20.3, 61.3, 119.7, 124.4, 128.6, 135.7, 138.0, 143.3, 161.0; EI-MS (*m/z*, relative intensity): 315 (M⁺, 6), 286 (48), 172 (100), 77 (96); Anal. calcd for C₁₅H₁₆F₃NO₃: C, 57.14; H, 5.12; N, 4.44. Found: C, 57.13; H, 5.12; N, 4.42.

(E)-Ethyl 2-(2,2,2-Trifluoro-N-phenylacetimidoyloxy)-2-pentenoate (6Ec).



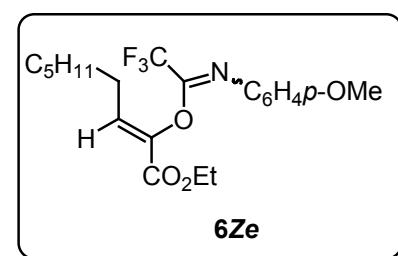
TLC R_f (petroleum ether : acetone 15 : 1) = 0.51; IR (film) 2978, 1730, 1669, 1598, 1489, 1328, 1300, 1277, 1248, 1208, 1161, 1133, 1114, 1073, 1026, 922, 780, 753, 694 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.07 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 2.23~2.27 (m, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 6.52 (s, 1H), 6.79~6.82 (m, 2H), 7.07~7.29 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 12.5, 14.0, 19.3, 61.5, 119.5, 124.5, 128.5, 132.6, 138.7, 143.1, 161.0; EI-MS (*m/z*, relative intensity): 315 (M⁺, 7), 286 (13), 172 (100), 77 (60); Anal. calcd for C₁₅H₁₆F₃NO₃: C, 57.14; H, 5.12; N, 4.44. Found: C, 57.14; H, 5.14; N, 4.41.

(Z)-Ethyl 2-[2,2,2-Trifluoro-N-(4-methoxyphenyl)phenylacetimidoyloxy]-2-pentenoate (**6Zd**).



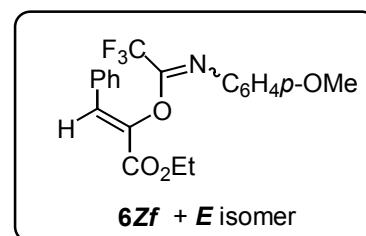
TLC R_f (petroleum ether : acetone 8 : 1) = 0.66; IR (film) 2981, 1726, 1657, 1608, 1506, 1331, 1292, 1228, 1206, 1135, 1034, 924, 835, 755 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.03~1.12 (m, 3H), 1.31 (t, J = 7.2 Hz, 3H), 2.54 (s, 2H), 3.78 (s, 3H), 4.25 (q, J = 7.2 Hz, 2H), 6.01 (t, J = 7.5 Hz, 1H), 6.82 (s, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.5, 14.0, 20.3, 55.3, 61.3, 113.9, 118.2, 121.8, 135.0, 138.2, 157.0, 161.1; EI-MS (m/z , relative intensity): 345 (M^+ , 5), 219 (100), 202 (37), 122 (67), 109 (177), 71 (76); Anal. calcd for $\text{C}_{16}\text{H}_{18}\text{F}_3\text{NO}_4$: C, 55.65; H, 5.25; N, 4.06. Found: C, 55.62; H, 5.19; N, 4.09.

(Z)-Ethyl 2-[2,2,2-Trifluoro-N-(4-methoxylphenyl)acetimidoyloxy]-2-nonenoate (**6Ze**).



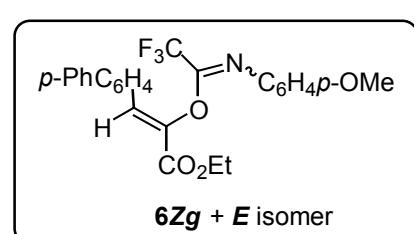
TLC R_f (petroleum ether : acetone 60 : 1) = 0.39; IR (film) 2931, 2859, 1727, 1655, 1608, 1506, 1446, 1330, 1291, 1241, 1206, 1136, 1035, 927, 835, 755 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.88 (t, J = 6.6 Hz, 3H), 1.28~1.40 (m, 11H), 2.53 (s, 2H), 3.78 (s, 3H), 4.24 (q, J = 7.2 Hz, 2H), 6.03 (t, J = 7.8 Hz, 1H), 6.82 (s, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 25.5, 26.7, 28.9, 29.0, 31.5, 55.3, 61.2, 113.9, 121.5, 133.8, 136.1, 138.5, 156.9, 161.1; EI-MS (m/z , relative intensity): 401 (M^+ , 11), 219 (15), 202 (100), 122 (8), 107 (17); Anal. calcd for $\text{C}_{20}\text{H}_{26}\text{F}_3\text{NO}_4$: C, 59.84; H, 6.53; N, 3.49. Found: C, 59.95; H, 6.55; N, 3.39.

(Z/E)-Methyl 2-[2,2,2-trifluoro-N-(4-methoxylphenyl)acetimidoyloxy]-3-phenyl-2-propenoate (**6Zf/6Ef**).



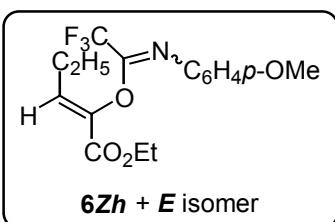
An inseparable mixture; TLC R_f (petroleum ether : acetone 10 : 1) = 0.44; ^1H NMR (200 MHz, CDCl_3) δ 1.23 (t, J = 7.2 Hz, 1.8H, E), 1.31 (t, J = 7.2 Hz, 3H, Z), 3.73~3.75 (m, 4.7H, E and Z), 4.19 (q, J = 7.2 Hz, 1.1H, E), 4.25 (q, J = 7.2 Hz, 2H, Z), 6.62~7.65 (m, 16H, E and Z); ^{13}C NMR (50 MHz, CDCl_3) δ 13.7, 14.1, 55.1, 61.5, 62.0, 113.7, 113.9, 121.6, 127.8, 128.7, 128.7, 128.8, 129.4, 129.9, 130.3, 131.8, 131.8, 157.1.

(Z/E)-Methyl 2-[2,2,2-trifluoro-N-(4-methoxylphenyl)acetimidoyloxy]-3-(4-phenyl)phenyl-2-propenoate (**6Zg/6Eg**).



An inseparable mixture; TLC R_f (petroleum ether : acetone 30 : 1) = 0.24; ^1H NMR (200 MHz, CDCl_3) δ 1.18 (t, J = 7.2 Hz, 1.1H, E), 1.33 (t, J = 7.2 Hz, 1.3H, Z), 3.77 (s, 1.1H, E), 3.79 (s, 0.9H, Z), 4.13~4.32 (m, 2H, E and Z), 6.69~7.74 (m, 14H, E and Z); ^{13}C NMR (50 MHz, CDCl_3) δ 13.8, 14.1, 55.3, 55.4, 61.6, 62.0, 113.7, 114.0, 121.6, 126.6, 127.0, 127.0, 127.4, 127.6, 127.9, 128.8, 128.9, 130.2, 130.7, 130.8, 130.9, 138.0, 139.9, 140.3, 141.6, 142.6, 155.0, 157.1.

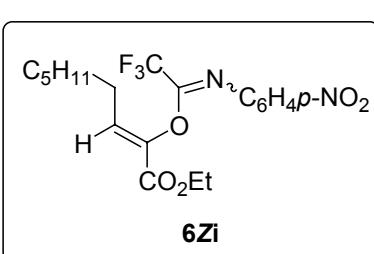
(Z/E)-Ethyl 2-[2,2,2-Trifluoro-N-(4-nitrophenyl)acetimidoyloxy]-2-nonenoate (6Zh/6Eh).



144.4, 149.2, 149.4, 160.7, 160.7.

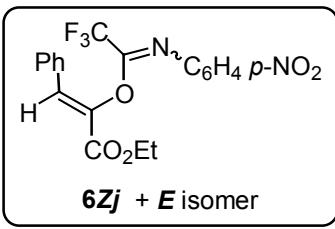
An inseparable mixture; TLC R_f (petroleum ether : acetone 60 : 1) = 0.36; ^1H NMR (200 MHz, CDCl_3) δ 1.08 (t, J = 7.2 Hz, 3H, *E*), 1.35 (t, J = 7.2 Hz, 3H, *Z*), 2.20~2.36 (m, 0.9H, *E*), 2.52~2.67 (m, 1.2H, *Z*), 4.22~4.35 (m, 2H, *E* and *Z*), 6.14 (t, J = 7.8 Hz, 0.5H, *Z*), 6.55 (t, J = 7.8 Hz, 0.3H, *E*), 6.86~6.93 (m, 2H, *E* and *Z*), 8.12~8.20 (m, 2H, *E* and *Z*); ^{13}C NMR (75 MHz, CDCl_3) δ 12.5, 13.3, 14.0, 19.4, 20.3, 61.6, 61.8, 119.9, 120.0, 120.4, 124.6, 125.0, 133.5, 136.6, 138.4, 144.3, 144.4, 149.2, 149.4, 160.7, 160.7.

(Z)-Ethyl 2-[2,2,2-Trifluoro-N-(4-nitrophenyl)acetimidoyloxy]-2-nonenoate (6Zi).



TLC R_f (petroleum ether : EtOAc 60 : 1) = 0.41; IR (film) 2931, 2859, 1728, 1657, 1593, 1519, 1375, 1330, 1211, 1164, 1137, 1110, 1022, 930, 852, 753 695 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.88 (t, J = 6.6 Hz, 3H), 1.29~1.45 (m, 11H), 2.54~2.62 (m, 2H), 4.30 (q, J = 7.2 Hz, 2H), 6.16 (t, J = 7.8 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 8.20 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 14.1, 22.5, 26.8, 28.8, 28.9, 31.5, 61.5, 115.9 (q, $J_{\text{C-F}}=283.1$ Hz, CF_3), 120.0, 124.6, 135.5, 138.1, 144.4, 149.4, 160.8; EI-MS (m/z , relative intensity): 416 (M^+ , 4), 343 (17), 331 (42), 299 (16), 217 (100), 171 (20), 122 (33), 92 (16); Anal. calcd for $\text{C}_{19}\text{H}_{23}\text{F}_3\text{N}_2\text{O}_5$: C, 54.80; H, 5.57; N, 6.73. Found: C, 55.00; H, 5.73; N, 6.46.

(Z/E)-Methyl 2-[2,2,2-Trifluoro-N-(4-nitrophenyl)acetimidoyloxy]-3-phenyl-2-propenoate (6Zj/6Ej)

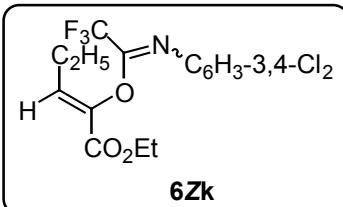


148.9, 149.0, 160.6, 161.2.

An inseparable mixture; TLC R_f (petroleum ether : EtOAc 30 : 1) = 0.22; ^1H NMR (300 MHz, CDCl_3) δ 1.70 (t, J = 7.2 Hz, 1.0H, *E*), 1.37 (t, J = 7.2 Hz, 3H, *Z*), 4.21 (q, J = 7.2 Hz, 0.7H, *E*), 4.33 (q, J = 7.2 Hz, 2H, *Z*), 6.80~8.21 (m, 14H, *E* and *Z*); ^{13}C NMR (75 MHz, CDCl_3) δ 13.6, 14.0, 61.7, 62.2, 115.9 (q, $J_{\text{C-F}}=282.0$ Hz, CF_3), 119.8, 119.9, 124.4, 124.6, 126.7, 127.2, 127.7, 128.0, 128.3, 129.0, 129.2, 129.5, 130.2, 130.5, 130.6, 131.2, 131.3, 137.2, 138.1, 144.5, 148.7,

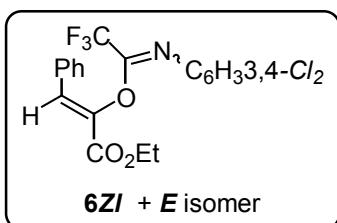
148.9, 149.0, 160.6, 161.2.

(Z)-Ethyl 2-[2,2,2-Trifluoro-N-(3,4-dichlorophenyl)acetimidoyloxy]-2-pentenoate (6Zk).



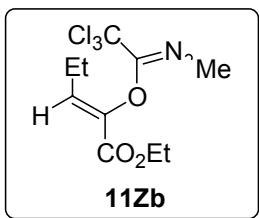
TLC R_f (petroleum ether : EtOAc 30 : 1) = 0.56; IR (film) 2982, 1724, 1656, 1593, 1556, 1466, 1375, 1334, 1227, 1209, 1140, 1124, 1030, 954, 814, 743, 698 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.06 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H), 2.57 (s, 2H), 4.27 (q, J = 7.2 Hz, 2H), 6.07 (t, J = 7.8 Hz, 1H), 6.56~6.80 (m, 1H), 6.94 (s, 1H), 7.33~7.36 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.4, 14.0, 20.4, 61.5, 119.4, 121.8, 128.2, 130.3, 132.5, 136.2, 138.0, 142.8, 160.6; EI-MS (m/z , relative intensity): 383 (M^+ , 6), 354 (27), 240 (100), 145 (45), 109 (11); Anal. calcd for $\text{C}_{15}\text{H}_{14}\text{Cl}_2\text{F}_3\text{NO}_3$: C, 46.90; H, 3.67; N, 3.65. Found: C, 47.19; H, 3.78; N, 3.67.

*(Z/E)-Methyl 2-[2,2,2-Trifluoro-N-(3,4-dicholophenyl)acetimidoyloxy]-3-phenyl-2-propenoate (**6ZI/6El**)*



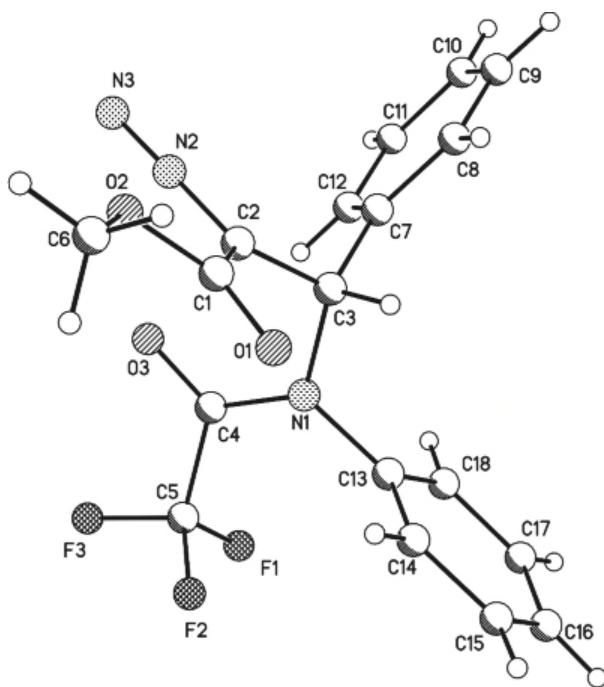
TLC R_f (petroleum ether : EtOAc 30 : 1) = 0.38; ¹H NMR (300 MHz, CDCl₃) δ 1.50 (t, J = 7.2 Hz, 2.0H, *E*), 1.36 (t, J = 7.2 Hz, 3H, *Z*), 4.17 (q, J = 7.2 Hz, 1.3H, *E*), 4.31 (q, J = 7.2 Hz, 2H, *Z*), 6.55~7.62 (m, 15H, *E* and *Z*); ¹³C NMR (75 MHz, CDCl₃) δ 13.6, 14.1, 61.7, 62.2, 119.3, 121.6, 126.7, 127.9, 128.4, 129.0, 129.1, 129.8, 130.1, 130.3, 130.4, 131.4, 131.5, 132.5, 132.7, 137.5, 142.2, 161.3.

*(Z)-Ethyl 2-(2,2,2-trichloro-N-methylacetimidoyloxy)-2-pentenoate (**11Zb**).*

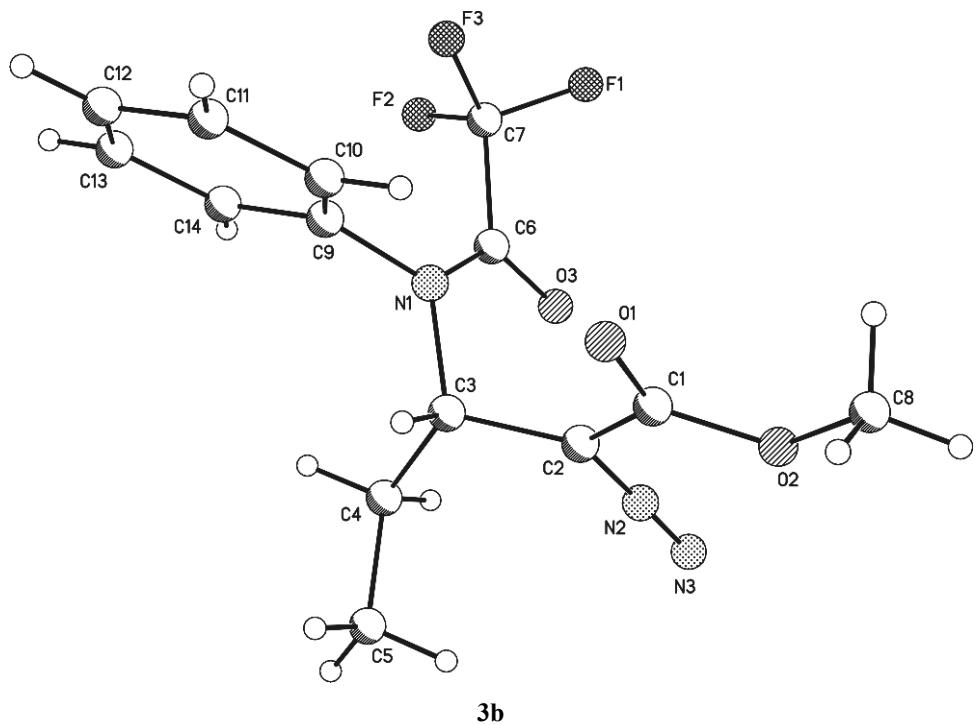


TLC R_f (petroleum ether : acetone 15 : 1) = 0.44; IR (film) 2976, 1728, 1693, 1643, 1463, 1374, 1312, 1231, 1144, 1105, 1062, 1035, 936, 877, 826, 793, 742 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 1.08 (t, J = 7.2 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H), 2.51~2.66 (m, 2H), 3.25 (s, 3H), 4.29 (q, J = 7.2 Hz, 2H), 5.81 (t, J = 7.5 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 13.8, 14.0, 20.1, 36.2, 61.3, 128.3, 140.3, 148.9, 161.6; EI-MS (*m/z*, relative intensity): 302 [(M+1)⁺, 4.98], 272 (8), 256 (3), 158 (100), 117 (59), 99 (4), 82 (18), 55 (27), 39 (24), 29 (91); Anal. calcd for C₁₀H₁₄Cl₃NO₃: C, 39.69; H, 4.66; N, 4.63;. Found: C, 39.85; H, 4.87; N, 4.50.

Figure 1. X-ray structure of **3a** and **3b**

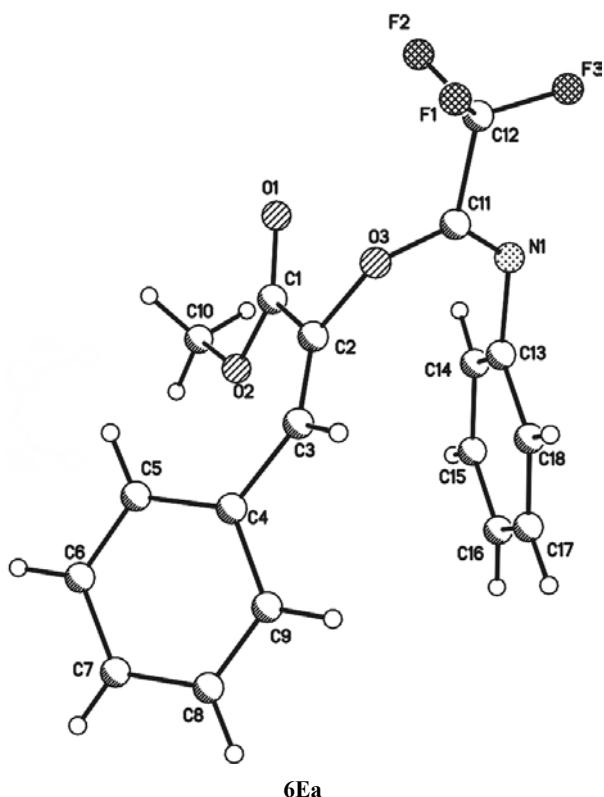


3a

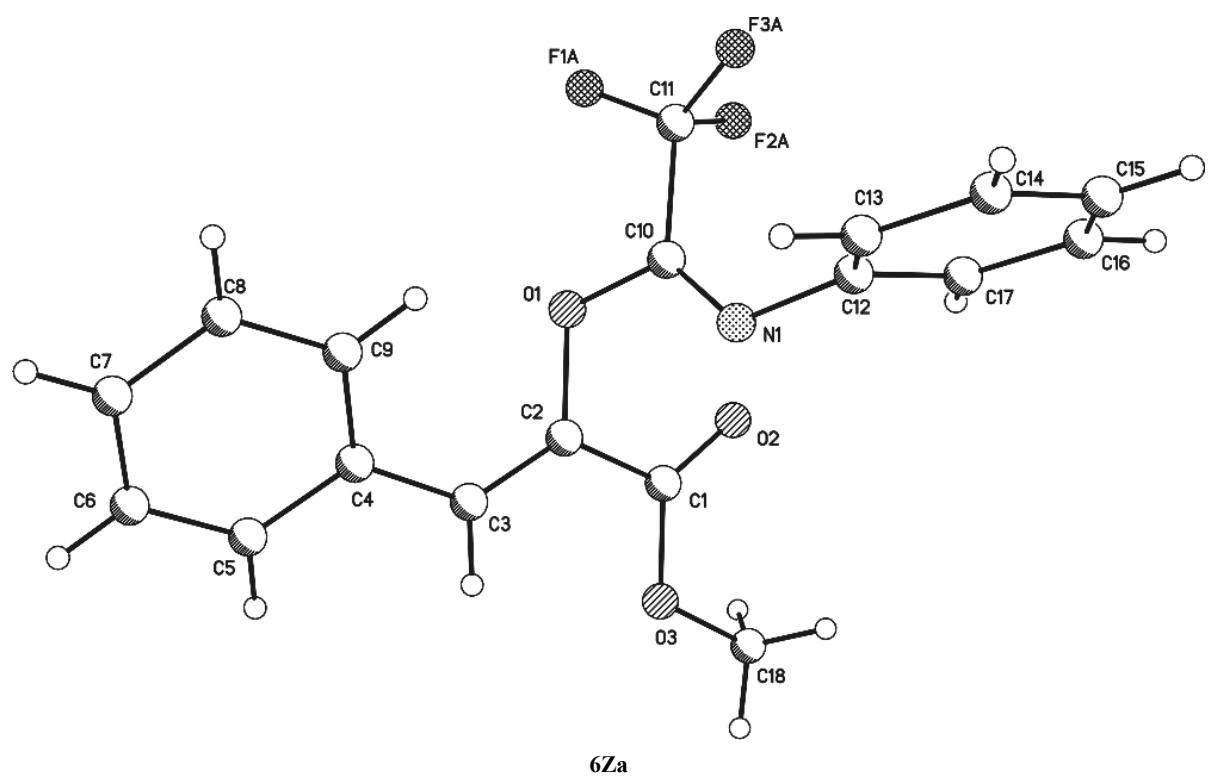


3b

Figure 2. X-ray structure of **6Ea** and **6Za**



6Ea



6Za