Supporting Information

Ru-Catalyzed Highly Chemo- and Enantioselective Hydrogenation of γ-Halo-γ,δ-Unsaturated-β-Keto Esters under Neutral Conditions

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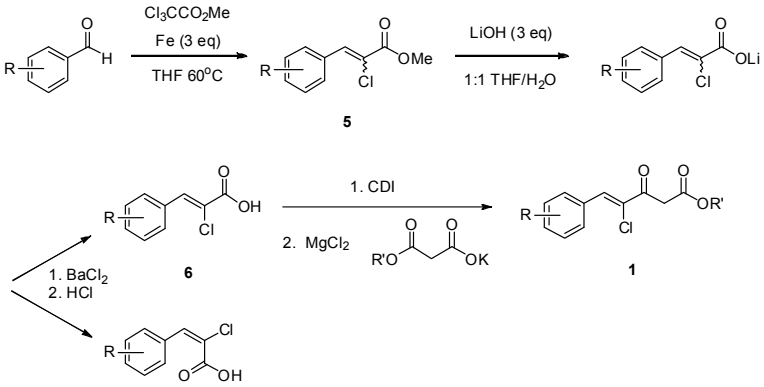
Contents

General and Materials

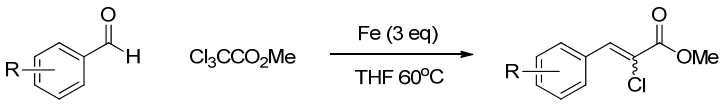
General: All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. ^{1}H NMR, ^{13}C NMR and spectra were obtained on a 400 MHz NMR spectrometer. The chemical shifts for ^{1}H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm using the central peak of $CDCl_3$ (77.16 ppm), DMSO-d_6 (39.52 ppm) or Acetone-d_6 (29.84 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Flash column chromatography was performed on silica gel (300-400 mesh).

Materials: Commercially available reagents were used throughout without further purification other than those detailed below. The solvents used in catalyst preparation and hydrogenation reactions were pretreated by the following procedures: MeOH and EtOH were distilled over magnesium under nitrogen. CH_2Cl_2 were distilled over calcium hydride under nitrogen. *n*-PrOH was distilled over first sodium tetrahydroborate then calcium hydride under nitrogen.

1. Preparations of 1a-n and their spectra data



1.1 Preparations of methyl 2-chloro-3-arylacrylates



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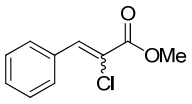
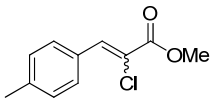


5a **Methyl 2-chloro-3-phenylacrylate**[1,2]

5a was synthesized follow a modified reported procedure.[3] To a pre-heated (oil bath temperature 55-60 °C) suspension of reduced iron power (95.0 g, 1.70 mol, 3.0 eq. commercial, activated by stirring in 3% HCl for 10 min, washed with pure water, EtOH and Et_2O successively, dried under vacuum.) in 1.3 L anhydrous THF, a THF solution (170 mL) of benzaldehyde (60.0 g, 0.57 mol, 1.0 eq.) and methyl trichloroacetate (126.6 g, 0.68 mol, 95% wt, 1.2 eq.) was added dropwise within 6 hours. The reaction was exothermic and the color of reaction mixture darkened gradually. After addition, stirred for another 1-2 h then quenched by water. (The dechlorinated byproduct methyl cinnamate formed when aldehyde was only partial converted, quenched the reaction when the amount of methyl cinnamate was >2%, monitored by GC) Filtered through Celite, the solvent was evaporated off, and the residual was dissolved with EtOAc (500 mL), dried over Na_2SO_4. The solvent was removed under vacuum, the residual was purified by flash chromatography on silica gel (petrol ether/EtOAc = 50/1) to give 66.5 g product, as pale yellow oil (*Z*/*E* = 7/1). Yield: 60%.

Z-**5a**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.86 – 7.83 (m, 2H), 7.45 – 7.41 (m, 3H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 137.3, 132.9, 130.7, 130.3, 128.6, 121.8, 53.4.

E-**5a**[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 5H), 7.22 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 137.4, 133.7, 129.0, 128.4, 128.3, 122.4, 52.8.

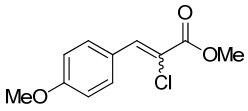


5b **Methyl 2-chloro-3-(p-tolyl)acrylate**[4]

Yield: 59%, pale yellow solid (*Z*/*E* =5/1).

Z-**5b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.79 – 7.74 (m, 2H), 7.26 – 7.22 (m, 2H), 3.90 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 140.9, 137.3, 130.9, 130.2, 129.4, 120.8, 53.4, 21.6.

E-**5b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 5H), 3.77 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 139.2, 137.7, 130.8, 129.1, 128.6, 121.5, 52.8, 21.4.

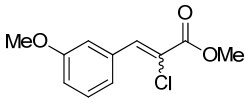


5c **Methyl 2-chloro-3-(4-methoxyphenyl)acrylate**[1]

Yield: 62%, pale yellow solid (*Z*/*E* =5/1).

Z-**5c**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 3H), 6.98 – 6.92 (m, 2H), 3.89 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 161.1, 136.8, 132.7, 125.4, 119.0, 114.0, 55.3, 53.2.

E-**5c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 –7.30 (m, 2H), 7.16 (s, 1H), 6.89 – 6.83 (m, 2H), 3.82 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 160.2, 137.9, 130.6, 125.9, 120.0, 113.7, 55.2, 52.8.

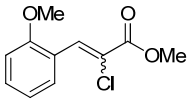


5d **Methyl 2-chloro-3-(3-methoxyphenyl)acrylate**[2]

Yield: 43%, pale yellow oil (*Z*/*E* =5/1).

Z-**5d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.46 – 7.29 (m, 3H), 6.99 – 6.93 (m, 1H), 3.90 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 159.3, 137.0, 133.8, 129.4, 123.3, 121.7, 116.0, 115.4, 55.1, 53.2.

E-**5d**[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.17 (s, 1H), 6.90 – 6.83 (m, 2H), 3.79 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 159.1, 136.7, 134.7, 129.2, 122.4, 120.8, 114.5, 113.6, 55.0, 52.7.

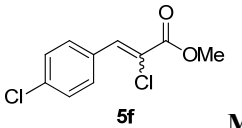


5e **Methyl 2-chloro-3-(2-methoxyphenyl)acrylate**

Yield: 60%, pale yellow oil (*Z*/*E* =6/1).

Z-**5e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.09 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.05 – 6.97 (m, 1H), 6.92 (dd, *J* = 8.4, 0.8 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 158.1, 132.5, 131.7, 130.2, 122.1, 122.0, 120.3, 110.7, 55.7, 53.4. HRMS Calculated for $C_{11}H_{11}ClO_3$ (M+Na) 249.0294, found: 249.0287.

E-**5e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.23 – 7.20 (m, 1H), 6.94 – 6.89 (m, 1H), 6.87 (dd, *J* = 8.4, 0.8 Hz, 1H), 3.83 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 156.7, 134.0, 130.6, 129.9, 123.2, 122.9, 120.4, 110.7, 55.6, 52.8. HRMS Calculated for $C_{11}H_{11}ClO_3$ (M+Na) 249.0294, found: 249.0300.

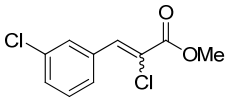


5f **Methyl 2-chloro-3-(4-chlorophenyl)acrylate**[5]

Yield: 56%, white solid (*Z*/*E* =7/1).

Z-**5f**[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.81 – 7.76 (m, 2H), 7.43 – 7.38 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 136.3, 136.0, 132.0, 131.4, 129.0, 122.4, 53.6.

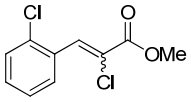
E-**5f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.28 – 7.22 (m, 2H), 7.17 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 136.6, 134.9, 132.1, 129.9, 128.6, 123.1, 52.9.



5g **Methyl 2-chloro-3-(3-chlorophenyl)acrylate**

Yield: 45%, white solid (*Z*/*E* =10/1), *E*-**5g** was not isolated.

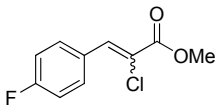
Z-**5g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 2H), 7.68 (dt, *J* = 6.4, 1.8 Hz, 1H), 7.40 – 7.33 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 135.8, 135.6, 134.6, 130.29, 130.26, 129.9, 128.8, 123.3, 53.6. HRMS Calculated for $C_{10}H_8Cl_2O_2$ (M+H) 230.9980, found: 230.9967.



5h **Methyl 2-chloro-3-(2-chlorophenyl)acrylate**[6]

Yield: 44%, yellow oil (*Z*/*E* =20/1), *E*-**5h** was not isolated.

Z-**5h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.99 – 7.93 (m, 1H), 7.48 – 7.42 (m, 1H), 7.36 – 7.30 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 163.4, 134.8, 134.1, 131.4, 130.9, 130.7, 129.7, 126.6, 124.6, 53.5.

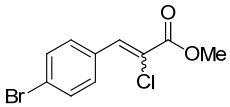


5i **Methyl 2-chloro-3-(4-fluorophenyl)acrylate**[7]

Yield: 56%, white solid (*Z*/*E* =8/1).

Z-**5i**[7]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 3H), 7.16 – 7.08 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 163.6 (d, *J* = 252.8 Hz), 136.0, 132.9 (d, *J* = 8.5 Hz), 129.2 (d, *J* = 2.8 Hz), 121.5, 115.8 (d, *J* = 21.7 Hz), 53.5.

E-**5i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.18 (s, 1H), 7.07 – 6.99 (m, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 163.0 (d, *J* = 250.1 Hz), 136.9, 130.7 (d, *J* = 8.3 Hz), 129.9 (d, *J* = 2.9 Hz), 122.5, 115.5 (d, *J* = 21.8 Hz), 52.9.

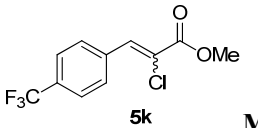


5j **Methyl 3-(4-bromophenyl)-2-chloroacrylate**

Yield: 51%, white solid (*Z*/*E* =8/1).

Z-**5j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.73 – 7.69 (m, 2H), 7.58 – 7.54 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 136.0, 132.1, 131.9, 131.8, 124.7, 122.5, 53.6. HRMS Calculated for $C_{10}H_8BrClO_2$ (M+Na) 296.9294, found: 296.9296.

E-**5j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.20 – 7.16 (m, 2H), 7.15 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 136.7, 132.7, 131.6, 130.2, 123.3, 53.1. ^{13}C NMR (100 MHz, Acetone-d6) δ 164.3, 136.4, 133.8, 132.3, 131.3, 123.6, 123.5, 53.3. HRMS Calculated for $C_{10}H_8BrClO_2$ (M+H) 274.9474, found: 274.9481.

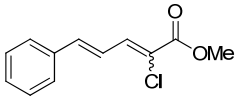


5k **Methyl 2-chloro-3-(4-(trifluoromethyl)phenyl)acrylate**[1]

Yield: 51%, white solid (*Z*/*E* =9/1).

Z-**5k**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 3H), 7.68 (d, *J* = 8.0 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 136.4, 135.6, 131.6 (q, *J* = 32.8 Hz), 130.7, 125.5 (d, *J* = 3.4 Hz), 124.3, 123.8 (q, *J* = 272.4 Hz), 53.7.

E-**5k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.25 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 137.4, 136.2, 130.7 (q, *J* = 32.8 Hz), 128.8, 125.3 (d, *J* = 3.5 Hz), 124.9, 124.0 (q, *J* = 271.8 Hz), 53.0.



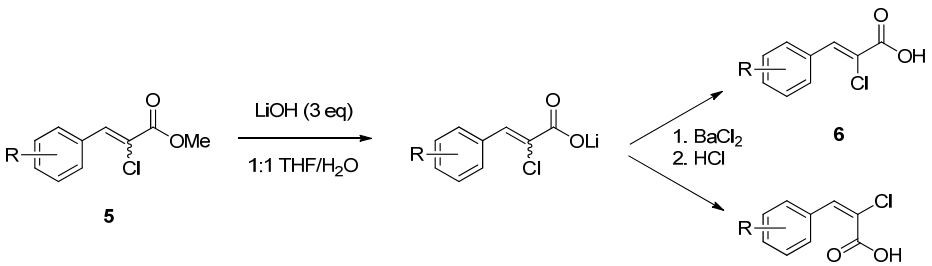
5l **(4*E*)-Methyl 2-chloro-5-phenylpenta-2,4-dienoate**[1,2]

Yield: 41%, *Z*: yellow solid , *E*: pale yellow oil (Z/E =4/1).

(2*Z*,4*E*)-**5l**[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 10.8, 0.6 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.41 – 7.31 (m, 3H), 7.21 (dd, *J* = 15.7, 10.8 Hz, 1H), 7.01 (d, *J* = 15.7 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 142.3, 138.1, 135.9, 129.6, 129.0, 127.6, 122.9, 122.2, 53.2.

(2*E*,4*E*)-**5l**[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 15.7, 11.5 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.39 – 7.29 (m, 3H), 7.06 (dd, *J* = 11.5, 0.9 Hz, 1H), 6.82 (d, *J* = 15.7 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 142.6, 141.6, 136.1, 129.3, 128.8, 127.6, 124.0, 120.7, 52.8.

1.2 Preparations of (*Z*)-2-chloro-3-arylacrylic acids



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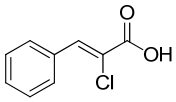
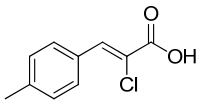


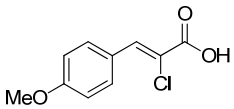
6a **(*Z*)-2-Chloro-3-phenylacrylic acid**[8]

To a solution of **5a** (15.3 g, 78.0 mmol, 1.0 eq.) in THF (100 mL), an aqueous solution (100 mL distilled water) of LiOH•H_2O (9.8 g, 233.2 mmol, 3.0 eq.) was added, and the reaction mixture was stirred for 15 hours at room temperature. Most solvent was rotavapored off, distilled water was added until a clear solution formed. The aqueous solution was washed with DCM (10 mL), then an aqueous solution (80 mL) of $BaCl_2$•$2H_2O$ (22.8 g, 93.0 mmol, 1.2 eq.) was added,[9] white precipitate formed immediately, filtered after 30 min, washed with distilled water in several portions. The white barium salt was suspended in 100 mL distilled water, acidified with concentrated HCl to pH=1. The mixture was extracted with EtOAc (100 mLx2), dried over Na_2SO_4. Solvent was removed under vacuum, the crude acid (12.8 g) was purified by recrystallization, and white long-needle crystal was obtained (7.8 g, 55% yield) from 30:1 Hexanes/EtOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.91 – 7.88 (m, 2H), 7.48 – 7.44 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ169.1, 139.6, 132.7, 131.1, 131.0, 128.8, 121.0.



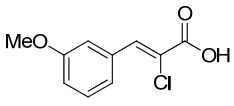
6b **(*Z*)-2-Chloro-3-(p-tolyl)acrylic acid**[10]

Recrystallized from 5.5:1 Hexanes/EtOH, white solid. Yield: 62%.
^{1}H NMR (400 MHz, DMSO) δ 13.59 (s, 1H), 7.91 (s, 1H), 7.81 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 164.1, 140.5, 136.2, 130.6, 130.0, 129.4, 121.5, 21.2.



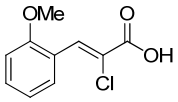
6c **(*Z*)-2-Chloro-3-(4-methoxyphenyl)acrylic acid**[11]

Recrystallized from 5:1 Hexanes/EtOH, white solid. Yield: 66%.
^{1}H NMR (400 MHz, DMSO) δ 13.49 (s, 1H), 7.94 – 7.89 (m, 3H), 7.07 – 7.02 (m, 2H), 3.81 (s, 3H).
^{13}C NMR (100 MHz, DMSO) δ 164.3, 160.9, 136.0, 132.7, 125.2, 119.7, 114.3, 55.4.



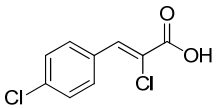
6d **(*Z*)-2-Chloro-3-(3-methoxyphenyl)acrylic acid**

Recrystallized from 30:1 Hexanes/EtOH, white needle crystal. Yield: 70%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.50 – 7.41 (m, 2H), 7.37 (t, J = 8.0 Hz, 1H), 7.01 (ddd, J = 8.0, 2.6, 0.8 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 159.6, 139.5, 133.9, 129.8, 123.9, 121.2, 117.0, 115.8, 55.5. HRMS Calculated for $C_{10}H_9ClO_3$ (M+Na) 235.0138, found: 235.0128.



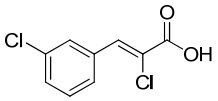
6e **(*Z*)-2-Chloro-3-(2-methoxyphenyl)acrylic acid**[11]

Recrystallized from 20:1 Hexanes/EtOH, pale yellow needle crystal. Yield: 52%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.16 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.07 – 7.00 (m, 1H), 6.94 (dd, *J* = 8.3, 0.7 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 158.4, 134.6, 132.3, 130.4, 121.7, 121.1, 120.4, 110.8, 55.8.



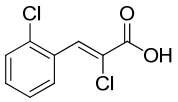
6f **(*Z*)-2-Chloro-3-(4-chlorophenyl)acrylic acid**[11]

Recrystallized from 6:1 Hexanes/EtOH, white needle crystal. Yield: 54%.
^{1}H NMR (400 MHz, DMSO) δ 13.73 (s, 1H), 7.96 (s, 1H), 7.94 – 7.90 (m, 2H), 7.58 – 7.53 (m, 2H).
^{13}C NMR (101 MHz, DMSO) δ 163.7, 135.0, 134.8, 132.1, 131.6, 128.8, 123.2.



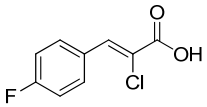
6g **(*Z*)-2-Chloro-3-(3-chlorophenyl)acrylic acid**[12]

Recrystallized from 30:1 Hexanes/EtOH, white needle crystal. Yield: 40%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.90 (t, *J* = 1.6 Hz, 1H), 7.73 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.45 – 7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 138.0, 134.8, 134.4, 130.8, 130.6, 130.0, 129.2, 122.5



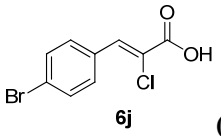
6h **(*Z*)-2-Chloro-3-(2-chlorophenyl)acrylic acid**[12]

Recrystallized from 30:1 Hexanes/EtOH, white crystal. Yield: 64%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.06 – 8.01 (m, 1H), 7.50 – 7.45 (m, 1H), 7.41 – 7.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 136.3, 135.2, 131.4, 131.2, 130.9, 129.9, 126.8, 123.8.



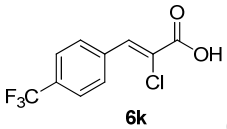
6i **(*Z*)-2-Chloro-3-(4-fluorophenyl)acrylic acid**

Recrystallized from 10:1 Hexanes/EtOH, white crystal. Yield: 51%.
^{1}H NMR (400 MHz, DMSO) δ 13.66 (s, 1H), 8.04 – 7.93 (m, 3H), 7.38 – 7.28 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ 163.9, 162.8 (d, *J* = 249.6 Hz), 135.1, 132.9 (d, *J* = 8.6 Hz), 129.3 (d, *J* = 2.8 Hz), 122.3, 115.8 (d, *J* = 21.7 Hz). HRMS Calculated for $C_9H_6ClFO_2$ (M+Na) 201.0119, found: 201.0128.



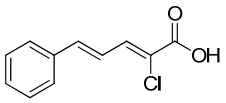
6j **(*Z*)-3-(4-Bromophenyl)-2-chloroacrylic acid**[13]

Recrystallized from 5:1 Hexanes/EtOH, pale yellow crystal. Yield: 62%.
^{1}H NMR (400 MHz, DMSO) δ 13.73 (s, 1H), 7.94 (s, 1H), 7.86 – 7.80 (m, 2H), 7.71 – 7.65 (m, 2H).
^{13}C NMR (100 MHz, DMSO) δ 163.7, 135.0, 132.2, 131.9, 131.7, 123.7, 123.3.



6k **(*Z*)-2-Chloro-3-(4-(trifluoromethyl)phenyl)acrylic acid**

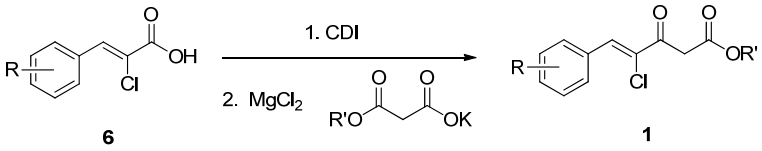
Recrystallized from 10:1 Hexanes/EtOH, white crystal. Yield: 44%.
^{1}H NMR (400 MHz, DMSO) δ 13.87 (s, 1H), 8.06 (d, J = 8.4 Hz, 2H), 8.05 (s, 1H), 7.84 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 163.5, 136.8, 134.8, 130.9, 129.8 (q, J = 32.1 Hz), 125.4 (d, J = 3.2 Hz), 125.1, 123.9 (q, J = 272.2 Hz). HRMS Calculated for $C_{10}H_6ClF_3O_2$ (M+H) 251.0087, found: 251.0079.



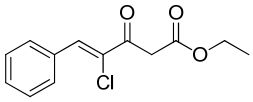
6l **(2*Z*,4*E*)-2-Chloro-5-phenylpenta-2,4-dienoic acid**[11]

Z/*E* Methyl esters could be completely separated by flash chromatography, *Z*-acid was obtained directly after hydrolysis, $BaCl_2$•$2H_2O$ was not added. Yellow solid. Yield: 98%
^{1}H NMR (400 MHz, DMSO) δ 13.42 (s, 1H), 7.68 (d, J = 10.6 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.45 – 7.34 (m, 3H), 7.30 (d, J = 15.6 Hz, 1H), 7.16 (dd, J = 15.6, 10.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 163.5, 142.4, 137.3, 135.7, 129.6, 129.0, 127.6, 122.8, 122.5.

1.3 Preparations of 1a-n



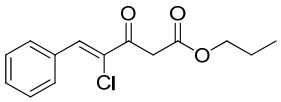
6 **1**



1a **(*Z*)-Ethyl 4-chloro-3-oxo-5-phenylpent-4-enoate**

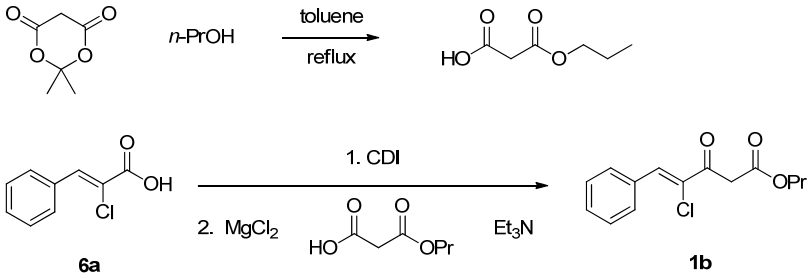
To a solution of **6a** (16.7 g, 91.0 mmol, 1.0 eq.) in anhydrous THF (150 mL), CDI (17.9 g, 106.0 mmol, 1.1 eq.) was added in several portions, after addition, the reaction mixture was stirred at room temperature for 2 h. In another flask, $MgCl_2$ (10.5 g, 110.0 mmol, 1.2 eq.) and potassium 3-ethoxy-3-oxopropanoate (38.9 g, 229.0 mmol, 2.5 eq.) were suspended in anhydrous THF (150 mL) under nitrogen, stirred for 1 hour. To this white suspension, the acid-Im solution was added dropwise. After addition, the reaction mixture was stirred for 10 h then quenched by water, acidified with 2M HCl to pH=2, extracted with EtOAc (100 mLx2). Combined organic layer was washed with saturated

$NaHCO_3$ and brine, dried over Na_2SO_4. Solvent was removed and the crude product was purified by flash chromatography on silica gel (petrol ether/EtOAc = 50/1) to give 16.2 g product, as off-white solid. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 7.88 – 7.84 (m, 2H), 7.82 (s, 1H), 7.47 – 7.43 (m, 3H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). Enol form: δ 12.44 (s, 1H), 7.81 – 7.78 (m, 2H), 7.70 (s, 1H), 7.44 – 7.35 (m, 3H), 5.84 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 173.1, 167.3, 167.0, 136.6, 133.6, 132.6, 131.2, 131.1, 130.8, 130.4, 129.5, 128.7, 128.6, 128.4, 124.0, 90.7, 61.6, 60.7, 45.9, 14.2, 14.1. HRMS Calculated for $C_{13}H_{13}ClO_3$ (M+Na) 275.0451, found: 275.0441.



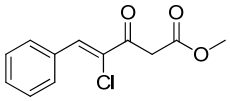
1b

(*Z*)-Propyl 4-chloro-3-oxo-5-phenylpent-4-enoate



6a **1b**

To a solution of **6a** (3.0 g, 16.4 mmol, 1.0 eq.) in anhydrous THF (50 mL), CDI (3.4 g, 90 wt%, 18.1 mmol, 1.1 eq.) was added in several portions, after addition, the reaction mixture was stirred at room temperature for 1 hour. In another flask, to a mixture of $MgCl_2$ (1.9 g, 19.7 mmol, 1.2 eq.) and 3-oxo-3-propoxypropanoic acid (6.7 g, 90 wt%, 41.1 mmol, 2.5 eq. prepared from 1:1 Meldrum's acid and *n*-PrOH in reflux toluene[14]) in anhydrous THF (50 mL) under nitrogen, Et_3N solution (4.2 g, 41.1 mmol, 2.5 eq. in 10 mL THF) was added dropwise at 0 °C, then the reaction mixture was stirred for 1 hour at room temperature. To this white suspension, the acid-Im solution was added dropwise. After addition, the reaction mixture was stirred for 10 h then quenched by water, acidified with 2M HCl to pH=2, extracted with EtOAc (50 mLx2). Combined organic layer was washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4. Solvent was removed and the crude product was purified by flash chromatography on silica gel (petrol ether/EtOAc = 80/1) to give 1.1 g product, as pale yellow solid. Yield: 26%. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 7.89 – 7.83 (m, 2H), 7.82 (s, 1H), 7.47 – 7.42 (m, 3H), 4.14 (t, *J* = 6.8 Hz, 2H), 3.92 (s, 2H), 1.68 (sex, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). Enol form: δ 12.44 (s, 1H), 7.81 – 7.77 (m, 2H), 7.70 (s, 1H), 7.42 – 7.34 (m, 3H), 5.85 (s, 1H), 4.17 (t, *J* = 6.8 Hz, 2H), 1.73 (sex, *J* = 7.2 Hz, 2H), 0.99 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 173.3, 167.4, 167.1, 136.6, 133.7, 132.6, 131.24, 131.15, 130.9, 130.5, 129.5, 128.8, 128.6, 128.5, 124.1, 90.8, 67.3, 66.4, 46.1, 22.1, 22.0, 10.5, 10.4. HRMS Calculated for $C_{14}H_{15}ClO_3$ (M+Na) 289.0607, found: 289.0608.

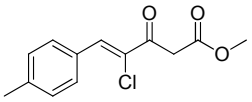


1c

(*Z*)-Methyl 4-chloro-3-oxo-5-phenylpent-4-enoate

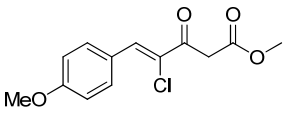
Same procedure with **1a** but potassium 3-methoxy-3-oxopropanoate was used. Yield: 83%, pale yellow

solid. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 7.89 – 7.84 (m, 2H), 7.82 (s, 1H), 7.47 – 7.42 (m, 3H), 3.94 (s, 2H), 3.78 (s, 3H). Enol form: δ 12.34 (s, 1H), 7.81 – 7.77 (m, 2H), 7.71 (s, 1H), 7.42 – 7.35 (m, 3H), 5.85 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 173.5, 167.5, 167.4, 136.7, 133.7, 132.6, 131.4, 131.2, 130.9, 130.6, 129.6, 128.8, 128.5, 124.0, 90.4, 52.7, 51.8, 45.8. HRMS Calculated for $C_{12}H_{11}ClO_3$ (M+Na) 261.0294, found: 261.0287.



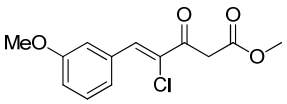
1d **(*Z*)-Methyl 4-chloro-3-oxo-5-(p-tolyl)pent-4-enoate**

Yield: 80%, pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 7.80 (s, 1H), 7.79 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 3.92 (s, 2H), 3.78 (s, 3H), 2.40 (s, 3H). Enol form: δ 12.35 (s, 1H), 7.71 (d, J = 8.2 Hz, 2H), 7.68 (s, 1H), 7.22 (d, J = 8.2 Hz, 2H), 5.83 (s, 1H), 3.81 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 173.6, 167.7, 167.6, 141.7, 140.0, 136.8, 131.41, 131.35, 130.9, 130.6, 129.9, 129.5, 129.3, 127.6, 123.0, 90.1, 52.6, 51.7, 45.8, 21.7, 21.6. HRMS Calculated for $C_{13}H_{13}ClO_3$ (M+Na) 275.0451, found: 275.0437.



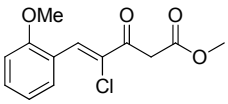
1e **(*Z*)-Methyl 4-chloro-5-(4-methoxyphenyl)-3-oxopent-4-enoate**

Yield: 81%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 7.92 – 7.87 (m, 2H), 7.78 (s, 1H), 6.99 – 6.94 (m, 2H), 3.92 (s, 2H), 3.87 (s, 3H), 3.77 (s, 3H). Enol form: δ 12.36 (s, 1H), 7.83 – 7.79 (m, 2H), 7.66 (s, 1H), 6.96 – 6.91 (m, 2H), 5.81 (s, 1H), 3.85 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 173.6, 167.9, 167.7, 161.8, 160.7, 136.5, 133.5, 132.5, 131.0, 126.33, 126.27, 125.3, 121.6, 114.3, 114.0, 89.6, 55.5, 55.4, 52.6, 51.7, 45.8. HRMS Calculated for $C_{13}H_{13}ClO_4$ (M+Na) 291.0400, found: 291.0398.



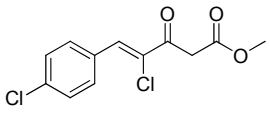
1f **(*Z*)-Methyl 4-chloro-5-(3-methoxyphenyl)-3-oxopent-4-enoate**

Yield: 61%, yellow oil, frozen in freezer. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 7.79 (s, 1H), 7.46 – 7.44 (m, 1H), 7.43 – 7.40 (m, 1H), 7.39 – 7.34 (m, 2H), 3.93 (s, 2H), 3.85 (s, 3H), 3.78 (s, 3H). Enol form: δ 12.35 (s, 1H), 7.68 (s, 1H), 7.34 – 7.30 (m, 1H), 7.00 (ddd, J = 8.0, 2.8, 1.2 Hz, 2H), 6.96 – 6.91 (m, 1H), 5.85 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 173.5, 167.5, 167.3, 159.6, 159.5, 136.6, 134.9, 133.8, 131.3, 129.7, 129.5, 128.6, 124.1, 124.0, 123.3, 116.9, 115.9, 115.5, 90.5, 55.4, 55.3, 52.6, 51.8, 45.7. HRMS Calculated for $C_{13}H_{13}ClO_4$ (M+Na) 291.0400, found: 291.0403.



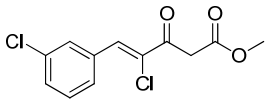
1g **(*Z*)-Methyl 4-chloro-5-(2-methoxyphenyl)-3-oxopent-4-enoate**

Yield: 61%, yellow oil, gradually frozen in freezer. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 8.19 (s, 1H), 8.12 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.05 – 6.99 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 2H), 3.88 (s, 3H), 3.78 (s, 3H). Enol form: δ 12.34 (s, 1H), 8.02 (s, 1H), 8.00 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.03 – 6.97 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.83 (s, 1H), 3.87 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 173.4, 167.6, 167.5, 158.4, 157.9, 132.3, 132.2, 130.9, 130.1, 130.0, 129.0, 126.6, 124.0, 122.4, 121.4, 120.2, 120.1, 110.6, 110.5, 90.0, 55.6, 55.5, 52.4, 51.6, 45.5. HRMS Calculated for $C_{13}H_{13}ClO_4$ (M+Na) 291.0400, found: 291.0410.



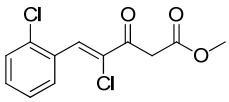
1h **(*Z*)-Methyl 4-chloro-5-(4-chlorophenyl)-3-oxopent-4-enoate**

Yield: 65%, off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 7.82 – 7.78 (m, 2H), 7.77 (s, 1H), 7.44 – 7.40 (m, 2H), 3.92 (s, 2H), 3.78 (s, 3H). Enol form: δ 12.33 (s, 1H), 7.75 – 7.71 (m, 2H), 7.65 (s, 1H), 7.40 – 7.36 (m, 2H), 5.84 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 173.4, 167.4, 167.1, 136.9, 135.4, 135.2, 132.4, 132.1, 131.8, 131.0, 130.0, 129.1, 128.8, 124.5, 90.7, 52.7, 51.9, 45.7. HRMS Calculated for $C_{12}H_{10}Cl_2O_3$ (M+Na) 294.9905, found: 294.9905.



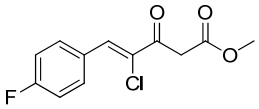
1i **(*Z*)-Methyl 4-chloro-5-(3-chlorophenyl)-3-oxopent-4-enoate**

Yield: 68%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 7.88 – 7.85 (m, 1H), 7.75 (s, 1H), 7.72 – 7.67 (m, 1H), 7.44 – 7.36 (m, 2H), 3.93 (s, 2H), 3.78 (s, 3H). Enol form: δ 12.32 (s, 1H), 7.82 – 7.78 (m, 1H), 7.64 (s, 1H), 7.64 – 7.59 (m, 1H), 7.36 – 7.32 (m, 2H), 5.86 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 173.3, 167.3, 166.8, 135.3, 134.9, 134.7, 134.4, 134.2, 130.7, 130.6, 130.1, 129.9, 129.8, 129.7, 129.4, 129.2, 128.6, 125.3, 90.9, 52.7, 51.9, 45.7. HRMS Calculated for $C_{12}H_{10}Cl_2O_3$ (M+Na) 294.9905, found: 294.9897.



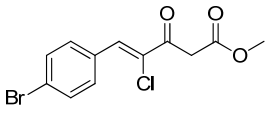
1j **(*Z*)-Methyl 4-chloro-5-(2-chlorophenyl)-3-oxopent-4-enoate**

Yield: 51%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 8.07 (s, 1H), 7.39 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 3.95 (s, 2H), 3.79 (s, 3H). Enol form: δ 12.31 (s, 1H), 8.00 – 7.96 (m, 1H), 7.93 (s, 1H), 7.90 – 7.85 (m, 1H), 7.49 – 7.42 (m, 2H), 5.86 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 173.4, 167.3, 166.8, 135.4, 134.8, 133.8, 132.3, 131.4, 131.24, 131.16, 130.9, 130.8, 130.3, 129.9, 129.7, 128.6, 126.7, 126.6, 126.5, 91.2, 52.8, 51.9, 45.8. HRMS Calculated for $C_{12}H_{10}Cl_2O_3$ (M+Na) 294.9905, found: 294.9900.



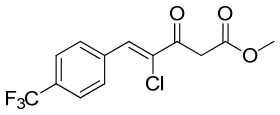
1k **(*Z*)-Methyl 4-chloro-5-(4-fluorophenyl)-3-oxopent-4-enoate**

Yield: 59%, off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 7.92 – 7.86 (m, 2H), 7.79 (s, 1H), 7.17 – 7.11 (m, 2H), 3.92 (s, 2H), 3.78 (s, 3H). Enol form: δ 12.34 (s, 1H), 7.83 – 7.77 (m, 2H), 7.66 (s, 1H), 7.12 – 7.07 (m, 2H), 5.84 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 173.5, 167.5, 167.2, 163.5 (d, *J* = 253.8 Hz), 163.1 (d, *J* = 251.4 Hz), 135.3, 133.4 (d, *J* = 8.6 Hz), 132.6 (d, *J* = 8.3 Hz), 130.1, 129.9 (d, *J* = 2.2 Hz), 128.8 (d, *J* = 2.2 Hz), 128.1, 123.6, 116.0 (d, *J* = 21.8 Hz), 115.7 (d, *J* = 21.7 Hz), 90.4, 52.65, 51.8, 45.7. HRMS Calculated for $C_{12}H_{10}ClFO_3$ (M+Na) 279.0200, found: 279.0194.



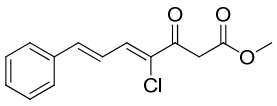
1l **(*Z*)-Methyl 5-(4-bromophenyl)-4-chloro-3-oxopent-4-enoate**

Yield: 64%, off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 7.75 (s, 1H), 7.75 – 7.71 (m, 2H), 7.60 – 7.56 (m, 2H), 3.92 (s, 2H), 3.78 (s, 3H). Enol form: δ 12.33 (s, 1H), 7.68 – 7.64 (m, 2H), 7.63 (s, 1H), 7.56 – 7.52 (m, 2H), 5.85 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 173.4, 167.4, 167.0, 135.2, 132.5, 132.0, 131.9, 131.8, 131.4, 130.1, 128.9, 125.4, 124.6, 123.8, 90.7, 52.7, 51.9, 45.7. HRMS Calculated for $C_{12}H_{10}BrClO_3$ (M+Na) 338.9400, found: 338.9391.



1m **(*Z*)-Methyl 4-chloro-3-oxo-5-(4-(trifluoromethyl)phenyl)pent-4-enoate**

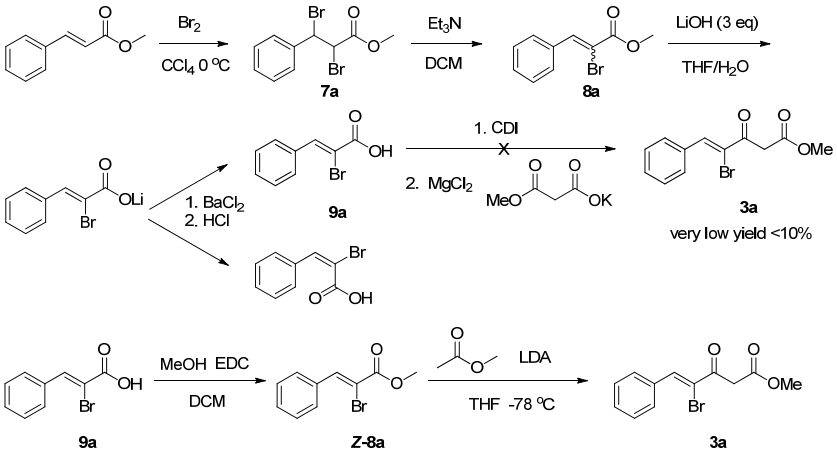
Yield: 48%, off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.84 (s, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 3.95 (s, 2H), 3.79 (s, 3H). Enol form: δ 12.34 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.72 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 5.88 (s, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 173.3, 167.3, 166.6, 137.1, 136.0, 134.6, 132.0 (q, *J* = 32.5 Hz), 131.1, 130.9 (q, *J* = 32.5 Hz), 130.6, 130.4, 129.7, 126.2, 125.6 (d, *J* = 3.2 Hz), 125.4 (d, *J* = 3.2 Hz), 123.9 (q, *J* = 272.3 Hz), 123.8 (q, *J* = 272.7 Hz), 91.3, 52.7, 51.9, 45.7. HRMS Calculated for $C_{13}H_{10}ClF_3O_3$ (M+Na) 329.0168, found: 329.0177.



1n **(4*Z*,6*E*)-Methyl 4-chloro-3-oxo-7-phenylhepta-4,6-dienoate**

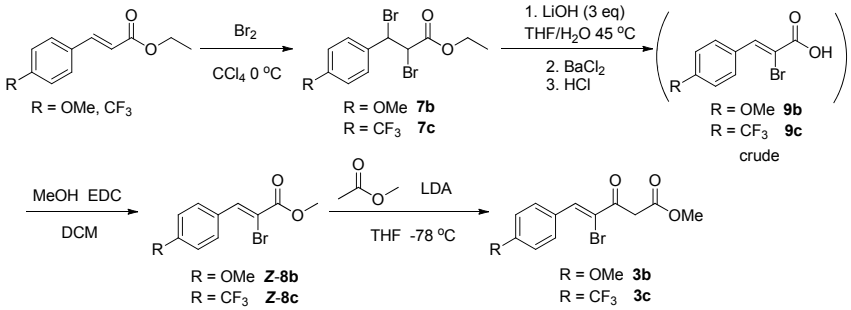
Yield: 89%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 7.57 (d, *J* = 10.4 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.42 – 7.37 (m, 3H), 7.22 (dd, *J* = 15.6, 10.4 Hz, 1H), 7.11 (d, *J* = 15.6 Hz, 1H), 3.86 (s, 2H), 3.77 (s, 3H). Enol form: δ 12.19 (s, 1H), 7.53 – 7.49 (m, 2H), 7.45 (d, *J* = 10.8 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.23 (dd, *J* = 15.6, 10.8 Hz, 1H), 6.96 (d, *J* = 15.6 Hz, 1H), 5.75 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 173.4, 167.5, 166.7, 144.5, 140.6, 137.8, 136.3, 135.8, 132.2, 130.0, 129.4, 129.2, 129.0, 128.9, 127.8, 127.4, 124.8, 123.3, 122.9, 90.2, 52.6, 51.7, 45.7. HRMS Calculated for $C_{14}H_{13}ClO_3$ (M+Na) 287.0451, found: 287.0443.

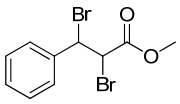
2. Preparations of 3a-c and their spectra data



It was failed while preparing **3** using the same procedure as **1**, the yield of last step was very low (<10%). Condensation with methyl acetate gave **3a** in 66% yield.

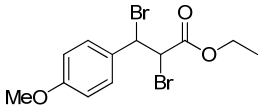
3b and **3c** were prepared in similar route.





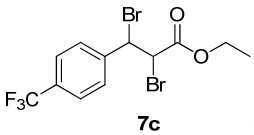
7a **Methyl 2,3-dibromo-3-phenylpropanoate**[15]

To a solution of methyl cinnamate (150.0 g, 925.0 mmol, 1.0 eq.) in CCl_4 (400 mL), bromine (155.0 g, 971.0 mmol, 1.05 eq.) was added dropwise at 0 °C, precipitate formed gradually. After addition, the reaction mixture was stirred for 2 h at room temperature. DCM was added to dissolve the solid, and then washed with saturated $NaHSO_3$ solution and brine, dried over Na_2SO_4. Solvent was rotavapored off, the crude product was recrystallized by Hexanes and DCM to give pure **7** (253.5 g, 85% yield) as white crystal. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 5H), 5.34 (d, J = 11.8 Hz, 1H), 4.85 (d, J = 11.8 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 137.6, 129.5, 129.0, 128.2, 53.6, 50.7, 46.8.



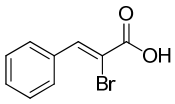
7b **Ethyl 2,3-dibromo-3-(4-methoxyphenyl)propanoate**[16]

Precipitated from CCl_4, filtered and wash with small portions of cold CCl_4, pure enough for next step. Yield: 75%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 6.93 – 6.88 (m, 2H), 5.36 (d, J = 11.8 Hz, 1H), 4.82 (d, J = 11.8 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 160.2, 129.7, 129.4, 114.3, 62.7, 55.4, 51.2, 47.4, 14.0.



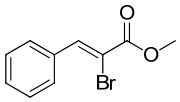
7c **Ethyl 2,3-dibromo-3-(4-(trifluoromethyl)phenyl)propanoate**

No precipitate formed during addition of bromine. Purified by flash chromatography (Hexanes/EtOAc = 50/1). Yield: 70%. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 5.36 (d, J = 11.8 Hz, 1H), 4.79 (d, J = 11.8 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 141.6, 131.4 (q, J = 32.7 Hz), 128.6, 126.0 (d, J = 3.4 Hz), 123.8 (q, J = 272.4 Hz), 62.9, 49.1, 46.5, 14.0.



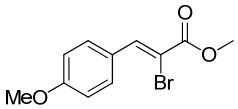
9a **(*Z*)-2-Bromo-3-phenylacrylic acid**[17]

To a solution of **7a** (34.4 g, 107.0 mmol, 1.0 eq.) in DCM (200 mL), Et_3N (17.1 g, 169.0 mmol, 1.6 eq.) was added dropwise. The reaction mixture was stirred for 12 h at room temperature, and then washed with 3 M HCl and brine. DCM was rotavapored off, the crude product (*Z*/*E* = 1/1.8) was dissolved with THF (100 mL), and an aqueous solution (80 mL distilled water) of $LiOH{\bullet}H_2O$ (13.5 g, 321.0 mmol, 3.0 eq.) was added, and the reaction mixture was stirred for 15 hours at room temperature. Most solvent was rotavapored off, distilled water was added until a clear solution formed. The aqueous solution was washed with DCM (10 mL), then an aqueous solution (100 mL) of $BaCl_2{\bullet}2H_2O$ (31.3 g, 128.1 mmol, 1.2 eq.) was added, white precipitate formed immediately, filtered after 30 min, washed with distilled water in several portions. The white barium salt was suspended in 100 mL distilled water, acidified with concentrated HCl to pH=1. The mixture was extracted with EtOAc (100 mLx2), dried over Na_2SO_4. Solvent was removed under vacuum, the crude acid (7.6 g) was purified by recrystallization, and white long-needle crystal was obtained (5.2 g, 69% yield) from 30:1 Hexanes/EtOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.94 – 7.87 (m, 2H), 7.48 – 7.42 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 143.6, 133.4, 131.0, 130.8, 128.7, 111.6.



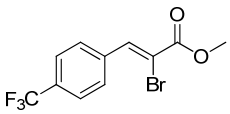
Z-8a **(*Z*)-Methyl 2-bromo-3-phenylacrylate**[18]

Some esterification methods were tired and EDC was chosen because it could minimize the *Z*/*E* isomerization. To a suspension of acid **9a** (2.8 g, 12.3 mmol, 1.0 eq.) in DCM (30 mL), EDC (2.8 g, 14.8 mmol, 1.2 eq.) was added in several portions at 0 °C. The reaction mixture was stirred for 30 min, and then MeOH (15 mL) was added, stirred for 24 h. Solvent was rotavapored off, the residual was dissolved with DCM (30 mL), washed with 5% HCl and brine, dried over Na_2SO_4. The solvent was removed under vacuum, and the crude product was purified by flash chromatography (Hexanes/EtOAc = 30/1), 2.5 g (85% yield) pale yellow oil was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.89 – 7.82 (m, 2H), 7.47 – 7.39 (m, 3H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 141.0, 133.5, 130.24, 130.20, 128.4, 112.4, 53.5.



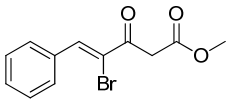
Z-8b **(*Z*)-Methyl 2-bromo-3-(4-methoxyphenyl)acrylate**[19]

Yield: 45% based on crude *Z*-acid **9b**. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.95 – 7.84 (m, 2H), 6.98 – 6.88 (m, 2H), 3.89 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 161.3, 140.7, 132.6, 126.2, 114.0, 109.6, 55.5, 53.6.



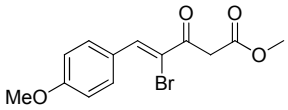
***Z*-8c** **(*Z*)-Methyl 2-bromo-3-(4-(trifluoromethyl)phenyl)acrylate**

Yield: 40% based on crude *Z*-acid **9c**. Off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 139.6, 137.3, 131.6 (q, J = 32.6 Hz), 130.4, 125.5 (d, J = 3.5 Hz), 123.9 (q, J = 272.1 Hz), 115.3, 53.9.



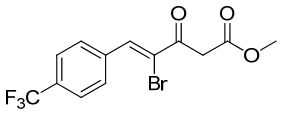
3a **(*Z*)-Methyl 4-bromo-3-oxo-5-phenylpent-4-enoate**

To a solution of diisopropylamine (2.0 g, 20.1 mmol, 2.55 eq.) in anhydrous THF (20 mL) under nitrogen, *n*-BuLi (2.4 M in hexane, 8.2 mL, 19.7 mmol, 2.5 eq.) was added dropwise at -10 °C, after addition, stirred for 30 min at -5~0 °C. Cooled down to -65 °C, methyl acetate (1.5 g, 19.7 mmol, 2.5 eq.) solution (5 mL anhydrous THF) was added dropwise, keeping temperature below -60 °C. After addition, stirred for 20 min at -65~-55 °C. Cooled down again to -78 °C, a solution of **8a** (1.9 g, 7.9 mmol, 1.0 eq.) in anhydrous THF (10 mL) was added dropwise, keeping temperature below -70 °C. After addition, the reaction mixture was stirred for 20 min at -70~-65 °C, then warmed to -60~-55 °C for another 30 min. When the reaction was completed, monitored by TLC, poured into 2 M HCl (50 mL) and ether (50 mL), organic layer was separated, washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4. Solvent was rotavapored off, the residual was purified by flash chromatography (Hexanes/EtOAc = 40/1), 1.5 g (66% yield) yellow oil was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 8.09 (s, 1H), 7.91 – 7.85 (m, 2H), 7.47 – 7.43 (m, 3H), 3.99 (s, 2H), 3.78 (s, 3H). Enol form: δ 12.42 (s, 1H), 8.01 (s, 1H), 7.79 – 7.75 (m, 2H), 7.43 – 7.36 (m, 3H), 5.91 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 173.3, 167.8, 167.4, 141.0, 135.0, 134.4, 133.2, 130.8, 130.6, 130.0, 129.4, 128.5, 128.2, 120.9, 114.9, 92.1, 52.5, 51.7, 45.8. HRMS Calculated for $C_{12}H_{11}BrO_3$ (M+Na) 304.9789, found: 304.9794.



3b **(*Z*)-Methyl 4-bromo-5-(4-methoxyphenyl)-3-oxopent-4-enoate**

Yield: 80%. Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 8.05 (s, 1H), 7.97 – 7.92 (m, 2H), 6.99 – 6.95 (m, 2H), 3.98 (s, 2H), 3.87 (s, 3H), 3.77 (s, 3H). Enol form: δ 12.45 (s, 1H), 7.85 – 7.80 (m, 2H), 6.95 – 6.92 (m, 2H), 5.87 (s, 1H), 3.85 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 173.6, 167.8, 166.6, 161.9, 160.7, 140.8, 134.7, 133.2, 132.3, 130.8, 127.0, 125.8, 118.3, 114.2, 113.9, 91.5, 55.6, 55.4, 52.7, 51.8, 46.1. HRMS Calculated for $C_{13}H_{13}BrO_4$ (M+Na) 334.9895, found: 334.9897.



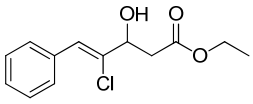
3c **(*Z*)-Methyl 4-bromo-3-oxo-5-(4-(trifluoromethyl)phenyl)pent-4-enoate**

Yield: 54%. Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) Ketone form: δ 8.11 (s, 1H), 7.93 (dd, *J* = 8.2, 0.6 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 4.00 (s, 2H), 3.79 (s, 3H). Enol form: δ 12.42 (s, 1H), 8.02 (s, 1H), 7.83 (dd, *J* = 8.2, 0.6 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 5.93 (s, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 173.2, 167.3, 167.1, 139.0, 138.1, 136.9, 133.5, 131.8 (q, *J* = 32.7 Hz), 130.7 (q, *J* = 32.7 Hz), 130.6, 130.1, 125.4 (d, *J* = 3.3 Hz), 125.2 (d, *J* = 3.3 Hz), 123.9 (q, *J* = 272.3 Hz), 123.7 (q, *J* = 272.2 Hz), 123.0, 117.4, 93.0, 52.6, 51.8, 45.9. HRMS Calculated for $C_{13}H_{10}BrF_3O_3$ (M+Na) 372.9663, found: 372.9667.

3. Typical procedure for the asymmetric hydrogenation

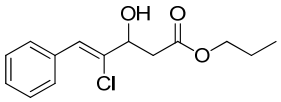
To a 20 mL Schlenk tube were added $[Ru(benzene)Cl_2]_2$ (5.0 mg, 0.01 mmol) and (*S*)-SunPhos (14.8 mg, 0.022 mmol) under nitrogen. The tube was vacuumed and purged with nitrogen again before addition of freshly distilled and freeze-and-thaw degassed EtOH/CH_2Cl_2 (2 mL/2 mL). The resulting mixture was heated at 50 °C for 1 h and then cooled to room temperature. The solvent was then removed under vacuum to give the catalyst as a brownish yellow solid. The catalyst was dissolved in degassed MeOH (8 mL) and then the solution was equally divided into 4 vials which contained 1 mmol substrates (2 mL MeOH each). Then the vials were taken into an autoclave. The autoclave was purged three times with H_2 and the required pressure of H_2 was set. The autoclave was stirred under specified reaction conditions. After being cooled to ambient temperature and careful release of the hydrogen, the autoclave was opened and the solvent was evaporated. The enantiomeric excess was determined by HPLC on Chiralpak IC-3 column after passing the samples through a short pad of silica gel eluted with petroleum ether and ethyl acetate.

4. Spectra and HPLC data of 2a-n and 4a-c



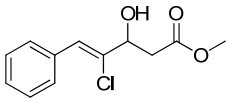
2a **(*Z*)-Ethyl 4-chloro-3-hydroxy-5-phenylpent-4-enoate**

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.40 – 7.27 (m, 3H), 6.91 (s, 1H), 4.79 – 4.74 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.34 (d, *J* = 5.0 Hz, 1H), 2.90 – 2.74 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 134.0, 133.6, 129.3, 128.3, 128.2, 125.1, 72.5, 61.1, 40.0, 14.2. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 1.0 mL min^{-1}, 254 nm): t_1 = 12.7 min, t_2 = 15.3 min or hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm, t_1 = 26.7 min, t_2 = 33.5 min. HRMS Calculated for $C_{13}H_{15}ClO_3$ (M+Na) 277.0607, found: 277.0597.



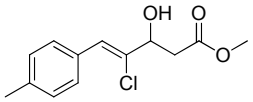
2b **(*Z*)-Propyl 4-chloro-3-hydroxy-5-phenylpent-4-enoate**

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.40 – 7.27 (m, 3H), 6.91 (s, 1H), 4.80 – 4.73 (m, 1H), 4.11 (td, *J* = 6.8 Hz, 1.2 Hz, 2H), 3.36 (d, *J* = 4.8 Hz, 1H), 2.92 – 2.74 (m, 2H), 1.67 (sex, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 134.1, 133.5, 129.4, 128.34, 128.26, 125.3, 72.6, 66.8, 40.0, 22.0, 10.4. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm): t_1 = 22.8 min, t_2 = 28.5 min. HRMS Calculated for $C_{14}H_{17}ClO_3$ (M+Na) 291.0764, found: 291.0767.



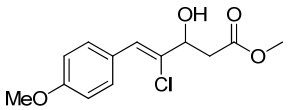
2c **(*Z*)-Methyl 4-chloro-3-hydroxy-5-phenylpent-4-enoate**

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.40 – 7.34 (m, 2H), 7.33 – 7.27 (m, 1H), 6.91 (s, 1H), 4.81 – 4.75 (m, 1H), 3.75 (s, 3H), 3.30 (d, *J* = 5.1 Hz, 1H), 2.92 – 2.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 134.1, 133.5, 129.4, 128.34, 128.28, 125.3, 72.6, 52.2, 39.9. The *Z*-olefin was confirmed by 1D-NOE. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm): t_1 = 29.2 min, t_2 = 35.0 min. HRMS Calculated for $C_{12}H_{13}ClO_3$ (M+Na) 263.0451, found: 263.0444.



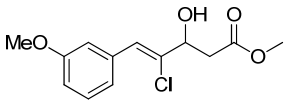
2d **(*Z*)-Methyl 4-chloro-3-hydroxy-5-(p-tolyl)pent-4-enoate**

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.20 – 7.14 (m, 2H), 6.86 (s, 1H), 4.80 – 4.73 (m, 1H), 3.74 (s, 3H), 3.25 (d, *J* = 5.0 Hz, 1H), 2.91 – 2.74 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 138.2, 132.6, 131.2, 129.3, 129.0, 125.2, 72.6, 52.1, 39.9, 21.4. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.7 mL min^{-1}, 254 nm): t_1 = 21.3 min, t_2 = 25.6 min. HRMS Calculated for $C_{13}H_{15}ClO_3$ (M+Na) 277.0607, found: 277.0585.



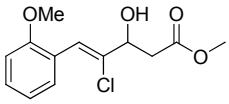
2e **(*Z*)-Methyl 4-chloro-3-hydroxy-5-(4-methoxyphenyl)pent-4-enoate**

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 6.93 – 6.87 (m, 2H), 6.82 (s, 1H), 4.80 – 4.72 (m, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 3.21 (d, *J* = 4.9 Hz, 1H), 2.90 – 2.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 159.5, 131.4, 130.8, 126.6, 124.8, 113.7, 72.7, 55.3, 52.1, 39.9. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.9 mL min^{-1}, 254 nm): t_1 = 28.4 min, t_2 = 34.4 min. HRMS Calculated for $C_{13}H_{15}ClO_4$ (M+Na) 293.0557, found: 293.0566.



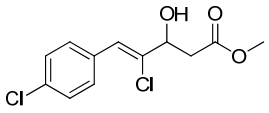
2f **(*Z*)-Methyl 4-chloro-3-hydroxy-5-(3-methoxyphenyl)pent-4-enoate**

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.0 Hz, 1H), 7.23 – 7.21 (m, 1H), 7.20 – 7.16 (m, 1H), 6.88 (s, 1H), 6.86 (ddd, *J* = 8.0, 2.6, 1.0 Hz, 1H), 4.79 – 4.74 (m, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 3.32 (d, *J* = 5.0 Hz, 1H), 2.92 – 2.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 159.3, 135.3, 133.8, 129.2, 125.0, 122.0, 114.6, 114.0, 72.5, 55.2, 52.0, 39.9. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.9 mL min^{-1}, 254 nm): t_1 = 24.1 min, t_2 = 28.8 min. HRMS Calculated for $C_{13}H_{15}ClO_4$ (M+Na) 293.0557, found: 293.0546.



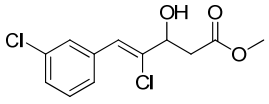
2g **(*Z*)-Methyl 4-chloro-3-hydroxy-5-(2-methoxyphenyl)pent-4-enoate**

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.31 – 7.26 (m, 1H), 6.97 (td, *J* = 7.6, 1.2 Hz, 1H), 6.88 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.85 – 4.79 (m, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.14 (d, *J* = 5.0 Hz, 1H), 2.91 – 2.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 157.2, 134.0, 129.8, 129.5, 122.9, 120.8, 120.1, 110.4, 72.7, 55.5, 52.0, 40.0. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 90/10, 0.7 mL min^{-1}, 254 nm): t_1 = 22.8 min, t_2 = 28.4 min. HRMS Calculated for $C_{13}H_{15}ClO_4$ (M+Na) 293.0557, found: 293.0553.



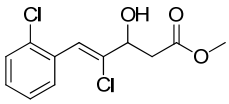
2h **(*Z*)-Methyl 4-chloro-5-(4-chlorophenyl)-3-hydroxypent-4-enoate**

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.35 – 7.31 (m, 2H), 6.87 (s, 1H), 4.78 – 4.72 (m, 1H), 3.75 (s, 3H), 3.31 (d, *J* = 5.0 Hz, 1H), 2.93 – 2.72 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 134.1, 134.0, 132.6, 130.7, 128.6, 124.1, 72.5, 52.2, 39.8. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.7 mL min^{-1}, 254 nm): t_1 = 16.6 min, t_2 = 19.5 min. HRMS Calculated for $C_{12}H_{12}Cl_2O_3$ (M+Na) 297.0061, found: 297.0056.



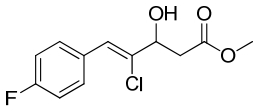
2i **(*Z*)-Methyl 4-chloro-5-(3-chlorophenyl)-3-hydroxypent-4-enoate**

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 1H), 7.50 – 7.44 (m, 1H), 7.32 – 7.25 (m, 2H), 6.87 (d, *J* = 0.5 Hz, 1H), 4.78 – 4.72 (m, 1H), 3.75 (s, 3H), 3.40 (d, *J* = 5.0 Hz, 1H), 2.93 – 2.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 135.8, 135.0, 134.2, 129.5, 129.1, 128.2, 127.5, 123.9, 72.4, 52.2, 39.8. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.5 mL min^{-1}, 254 nm): t_1 = 24.5 min, t_2 = 27.6 min. HRMS Calculated for $C_{12}H_{12}Cl_2O_3$ (M+Na) 297.0061, found: 297.0070.



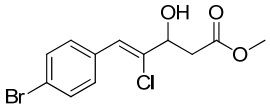
2j **(*Z*)-Methyl 4-chloro-5-(2-chlorophenyl)-3-hydroxypent-4-enoate**

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 1H), 7.41 – 7.38 (m, 1H), 7.30 – 7.21 (m, 3H), 7.09 (s, 1H), 4.85 – 4.79 (m, 1H), 3.76 (s, 3H), 3.33 (d, *J* = 5.2 Hz, 1H), 2.94 – 2.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 136.3, 133.8, 132.6, 130.6, 129.4, 129.2, 126.4, 122.6, 72.2, 52.1, 39.8. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm): t_1 = 28.5 min, t_2 = 31.2 min. HRMS Calculated for $C_{12}H_{12}Cl_2O_3$ (M+Na) 297.0061, found: 297.0045.



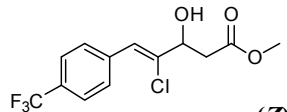
2k **(*Z*)-Methyl 4-chloro-5-(4-fluorophenyl)-3-hydroxypent-4-enoate**

Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 2H), 7.08 – 7.01 (m, 2H), 6.87 (s, 1H), 4.78 – 4.72 (m, 1H), 3.75 (s, 3H), 3.30 (d, *J* = 4.9 Hz, 1H), 2.92 – 2.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 162.3 (d, *J* = 248.7 Hz), 133.3, 131.1 (d, *J* = 8.0 Hz), 130.1 (d, *J* = 2.5 Hz), 124.1, 115.3 (d, *J* = 21.5 Hz), 72.5, 52.1, 39.8. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.7 mL min^{-1}, 254 nm): t_1 = 17.2 min, t_2 = 20.2 min. HRMS Calculated for $C_{12}H_{12}ClFO_3$ (M+Na) 281.0357, found: 281.0359.



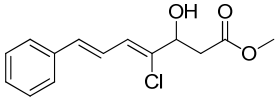
2l **(*Z*)-Methyl 5-(4-bromophenyl)-4-chloro-3-hydroxypent-4-enoate**

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 4H), 6.85 (d, *J* = 0.8 Hz, 1H), 4.77 – 4.72 (m, 1H), 3.75 (s, 3H), 3.35 (d, *J* = 5.0 Hz, 1H), 2.92 – 2.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 134.3, 133.0, 131.5, 130.9, 124.2, 122.2, 72.5, 52.2, 39.7. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm): t_1 = 25.4 min, t_2 = 30.7 min. HRMS Calculated for $C_{12}H_{12}BrClO_3$ (M+Na) 340.9556, found: 340.9554.



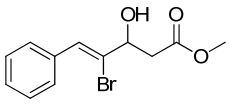
2m **(*Z*)-Methyl 4-chloro-3-hydroxy-5-(4-(trifluoromethyl)phenyl)pent-4-enoate**

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 6.97 (s, 1H), 4.80 – 4.74 (m, 1H), 3.76 (s, 3H), 3.40 (d, *J* = 5.0 Hz, 1H), 2.96 – 2.73 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 137.7, 136.0, 129.9 (q, *J* = 32.5 Hz), 129.7, 125.2 (d, *J* = 3.3 Hz), 124.1 (q, *J* = 272.0 Hz), 123.9, 72.4, 52.1, 39.8. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 97/3, 0.6 mL min^{-1}, 254 nm): t_1 = 19.5 min, t_2 = 23.0 min. HRMS Calculated for $C_{13}H_{12}ClF_3O_3$ (M+Na) 331.0325, found: 331.0331.



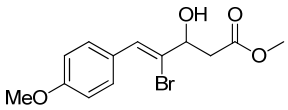
2n **(4*Z*,6*E*)-Methyl 4-chloro-3-hydroxy-7-phenylhepta-4,6-dienoate**

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.37 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 7.09 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.71 (d, *J* = 15.6 Hz, 1H), 6.65 (d, *J* = 10.4 Hz, 1H), 4.76 – 4.70 (m, 1H), 3.74 (s, 3H), 3.22 (br, 1H), 2.86 – 2.72 (m, 2H). The *Z*-geometry of C4-C5 double bond was confirmed by 1D-NOE. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 136.8, 136.2, 134.5, 128.8, 128.4, 126.9, 125.9, 123.0, 71.7, 52.1, 39.7. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.7 mL min^{-1}, 254 nm): t_1 = 23.6 min, t_2 = 27.7 min. HRMS Calculated for $C_{14}H_{15}ClO_3$ (M+Na) 289.0607, found: 289.0617.



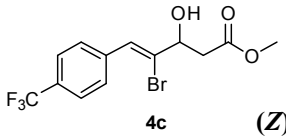
4a **(*Z*)-Methyl 4-bromo-3-hydroxy-5-phenylpent-4-enoate**

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.40 – 7.29 (m, 3H), 7.20 (s, 1H), 4.81 – 4.75 (m, 1H), 3.75 (s, 3H), 3.25 (d, *J* = 5.1 Hz, 1H), 2.92 – 2.77 (m, 2H). The *Z*-olefin was confirmed by 1D-NOE. ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 134.9, 129.2, 128.6, 128.3, 128.2, 127.0, 73.8, 52.2, 40.6. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.6 mL min^{-1}, 254 nm): t_1 = 25.9 min, t_2 = 31.7 min. HRMS Calculated for $C_{12}H_{13}BrO_3$ (M+Na) 306.9946, found: 306.9936.



4b **(*Z*)-Methyl 4-bromo-3-hydroxy-5-(4-methoxyphenyl)pent-4-enoate**

Racemate: white solid. Enantio-rich form: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.11 (s, 1H), 6.92 – 6.87 (m, 2H), 4.78 – 4.72 (m, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 3.19 (d, *J* = 5.0 Hz, 1H), 2.90 – 2.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 159.5, 130.7, 128.0, 127.2, 125.0, 113.6, 73.9, 55.3, 52.1, 40.6. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 90/10, 0.9 mL min^{-1}, 254 nm): t_1 = 18.4 min, t_2 = 22.9 min. HRMS Calculated for $C_{13}H_{15}BrO_4$ (M+Na) 337.0051, found: 337.0075.



4c **(*Z*)-Methyl 4-bromo-3-hydroxy-5-(4-(trifluoromethyl)phenyl)pent-4-enoate**

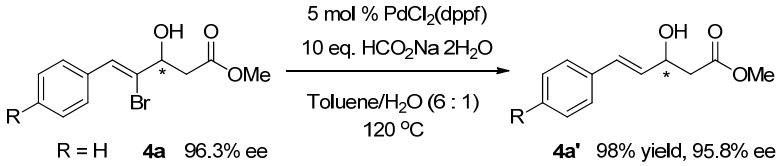
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 4.82 – 4.76 (m, 1H), 3.76 (s, 3H), 3.40 (d, *J* = 5.0 Hz, 1H), 2.97 – 2.75 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 138.6, 130.0 (q, *J* = 32.5 Hz), 129.4, 129.3, 127.2, 125.2 (d, *J* = 3.4 Hz), 124.1 (q, *J* = 272.0 Hz), 73.6, 52.2, 40.3. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.6 mL min^{-1}, 254 nm): t_1 = 15.4 min, t_2 = 18.6 min. HRMS Calculated for $C_{13}H_{12}BrF_3O_3$ (M+Na) 374.9820, found: 374.9815.

5. Typical procedure for the racemates of 2a-n and 4a-c

To a solution of **1c** (200.5 mg, 0.840 mmol, 1.0 eq.) and $CeCl_3$•$7H_2O$ (313.1 mg, 0.840 mmol, 1.0 eq.) in MeOH (3 mL), $NaBH_4$ (35.0 mg, 0.924 mmol, 1.1 eq.) was added in several portions, then the reaction mixture was stirred for 10 min, quenched by saturated NH_4Cl solution. Most solvent was rotavapored off, the residual was extracted with EtOAc (10 mLx2), dried over Na_2SO_4. Concentrated

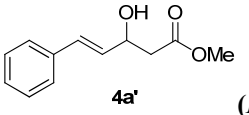
and then purified by flash chromatography (Hexanes/EtOAc = 5/1) to give 182.3 mg pale yellow oil. Yield: 90%.

6. Typical procedure for debromination of 4a-c and spectra data of 4a'-c'



R = H **4a** 96.3% ee
R = OMe **4b** 96.4% ee
R = CF_3 **4c** 95.4% ee

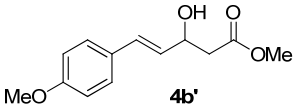
4a' 98% yield, 95.8% ee
4b' 99% yield, 96.3% ee
4c' 92% yield, 95.7% ee



4a'

(*E*)-Methyl 3-hydroxy-5-phenylpent-4-enoate[20]

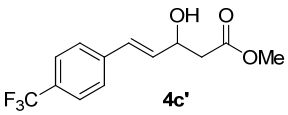
To a 10 mL Schlenk tube were added $PdCl_2(dppf)\cdot CH_2Cl_2$ (5.6 mg, 6.91 μmol, 5 mol %) and **4a** (39.4 mg, 0.14 mmol, 96.3% ee) under nitrogen, toluene (3 mL) was added, and then an aqueous solution (0.5 mL) of $HCO_2Na\bullet 2H_2O$ (144.0 mg, 1.38 mmol, 10 eq.) was added. The mixture was stirred for 5 min at room temperature before it was heated at 120 °C for 2 h. The color changed to dark, TLC showed **4a** was consumed completely. EtOAc (5 mL) and water (2 mL) were added to the cold reaction mixture, after layers separation, the aqueous layer was extracted with EtOAc (5 mL) again. Combined organic layer was rotavapored to dryness, the residual was purified by flash chromatography (Hexanes/EtOAc = 5/1) to give 27.9 mg pale yellow oil. Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.35 – 7.29 (m, 2H), 7.27 – 7.22 (m, 1H), 6.66 (dd, *J* = 15.9, 1.1 Hz, 1H), 6.23 (dd, *J* = 15.9, 6.1 Hz, 1H), 4.77 – 4.70 (m, 1H), 3.74 (s, 3H), 3.00 (brs, 1H), 2.72 – 2.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 136.3, 130.6, 130.0, 128.5, 127.7, 126.5, 68.8, 51.8, 41.4. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 90/10, 0.9 mL min^{-1}, 254 nm): t_1 = 19.1 min, t_2 = 22.0 min. 95.8% ee.



4b'

(*E*)-Methyl 3-hydroxy-5-(4-methoxyphenyl)pent-4-enoate

Yield: 99%. Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 6.88 – 6.83 (m, 2H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.08 (dd, *J* = 15.9, 6.4 Hz, 1H), 4.75 – 4.67 (m, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 2.94 (d, *J* = 4.1 Hz, 1H), 2.71 – 2.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 159.4, 130.5, 129.2, 127.8, 127.7, 114.1, 69.2, 55.4, 52.0, 41.6. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 90/10, 1.0 mL min^{-1}, 254 nm): t_1 = 33.1 min, t_2 = 38.2 min. 96.3% ee. HRMS Calculated for $C_{13}H_{16}O_4$ (M+Na) 259.0946, found: 259.0951.

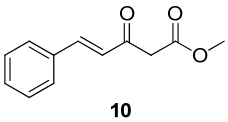


4c'

(*E*)-Methyl 3-hydroxy-5-(4-(trifluoromethyl)phenyl)pent-4-enoate

Yield: 92%. Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 15.9 Hz, 1H), 6.31 (dd, *J* = 15.9, 5.7 Hz, 1H), 4.79 – 4.71 (m, 1H), 3.73 (s, 3H), 3.30 (brs, 1H), 2.73 – 2.57 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 140.0, 132.6, 129.6 (q, *J* = 32.5

Hz), 129.4, 126.8, 125.6 (d, J = 3.5 Hz), 124.2 (q, J = 271.7 Hz), 68.6, 52.1, 41.2. HPLC (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.8 mL min^{-1}, 254 nm): t_1 = 20.7 min, t_2 = 23.4 min. 95.7% ee. HRMS Calculated for $C_{13}H_{13}F_3O_3$ (M+Na) 297.0714, found: 297.0728.



10 **(*E*)-Methyl 3-oxo-5-phenylpent-4-enoate**[21]

Same procedure with **1**, 60% yield from cinnamic acid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (d, J = 1.4 Hz, 0.4H)(enol), 7.63 – 7.54 (m, 2H), 7.52 – 7.46 (m, 1H), 7.43 – 7.30 (m, 3H), 6.81 (d, J = 16.1 Hz, 0.7H)(ketone), 6.45 (dd, J = 15.9, 1.4 Hz, 0.5H)(enol), 5.18 (s, 0.4H)(enol), 3.78 (s, 1.2H)(enol), 3.77 (s, 1.8H)(ketone), 3.72 (s, 1.4H)(ketone). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 173.2, 169.3, 167.5, 144.8, 137.0, 135.3, 134.1, 131.0, 129.4, 129.0, 128.9, 128.6, 127.6, 125.2, 121.8, 91.7, 52.5, 51.4, 47.3.

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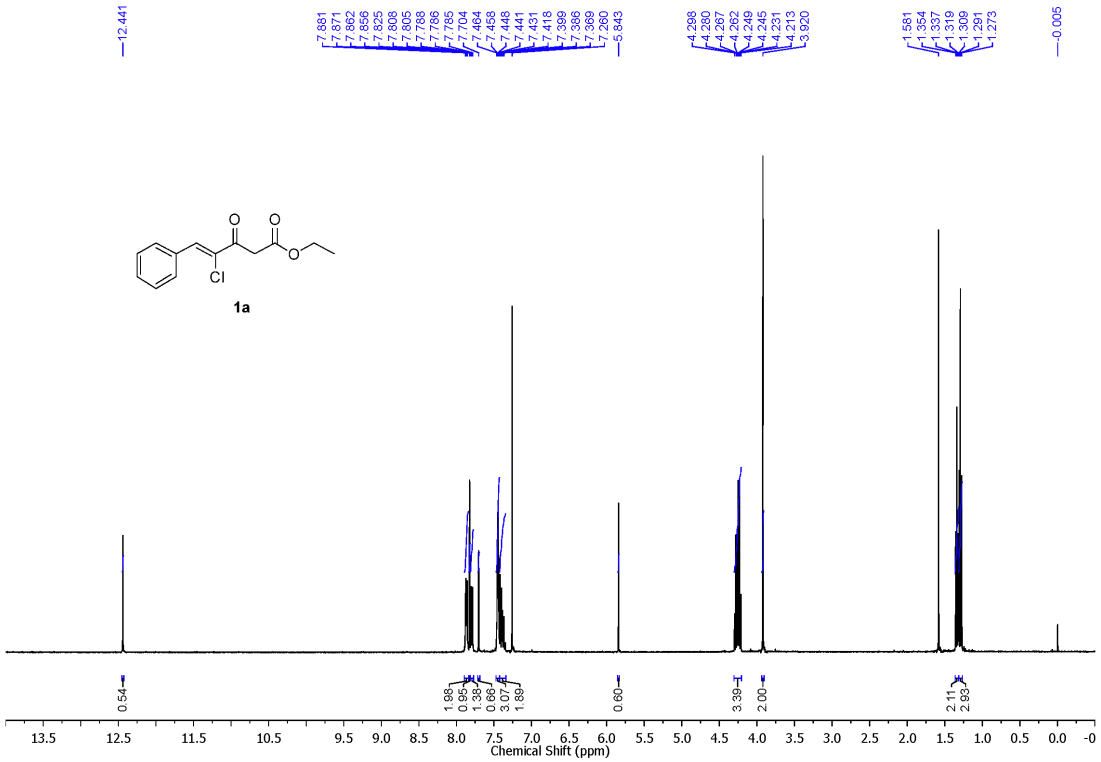
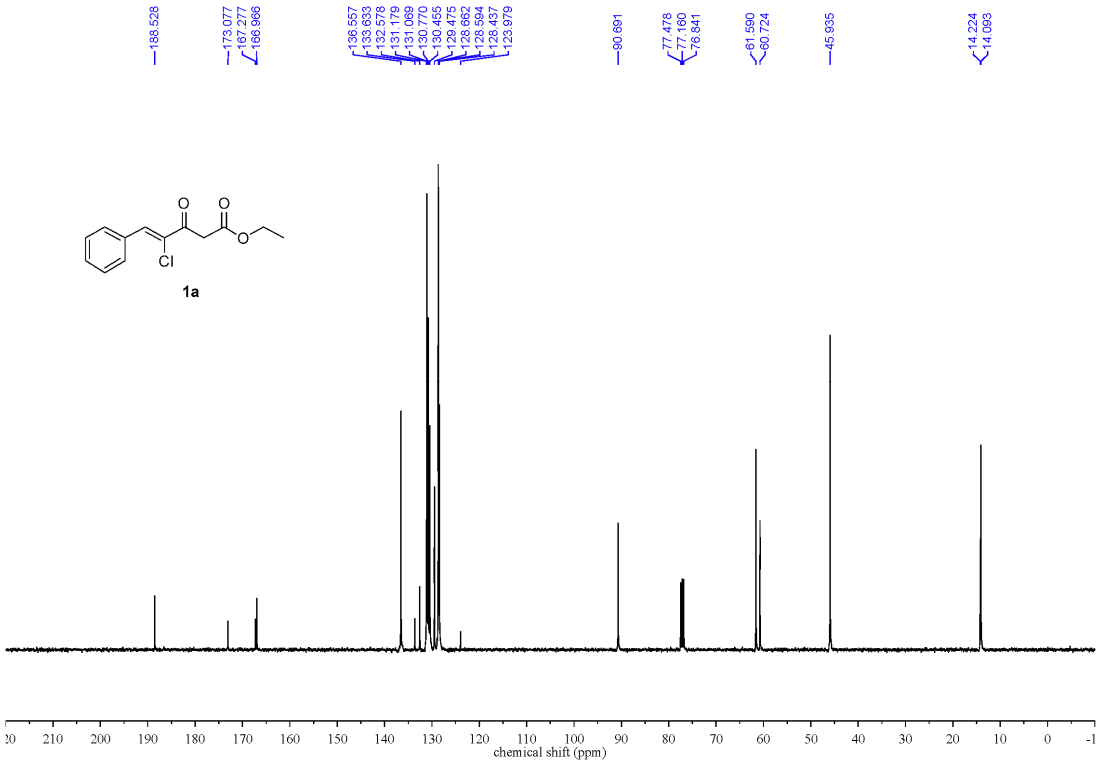
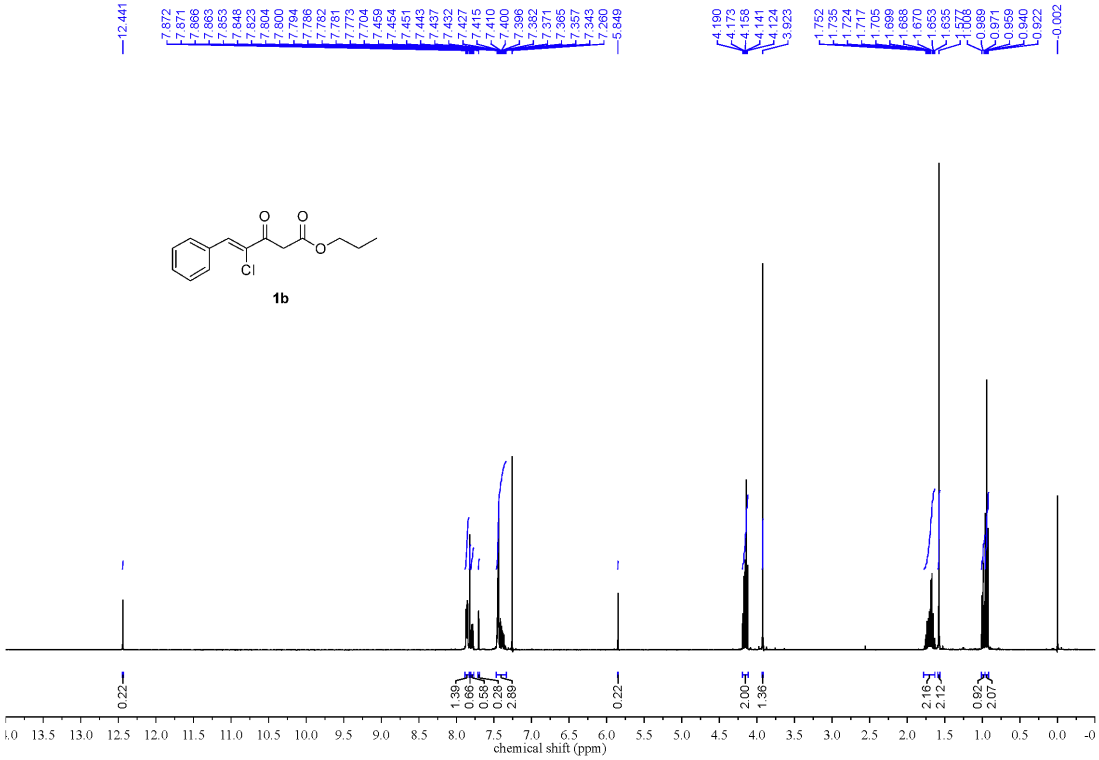
Copy of ^{1}H & ^{13}C NMR of 1-4 and 5e, 5g, 5j, 6d, 6i, 6k, 7c, 8c

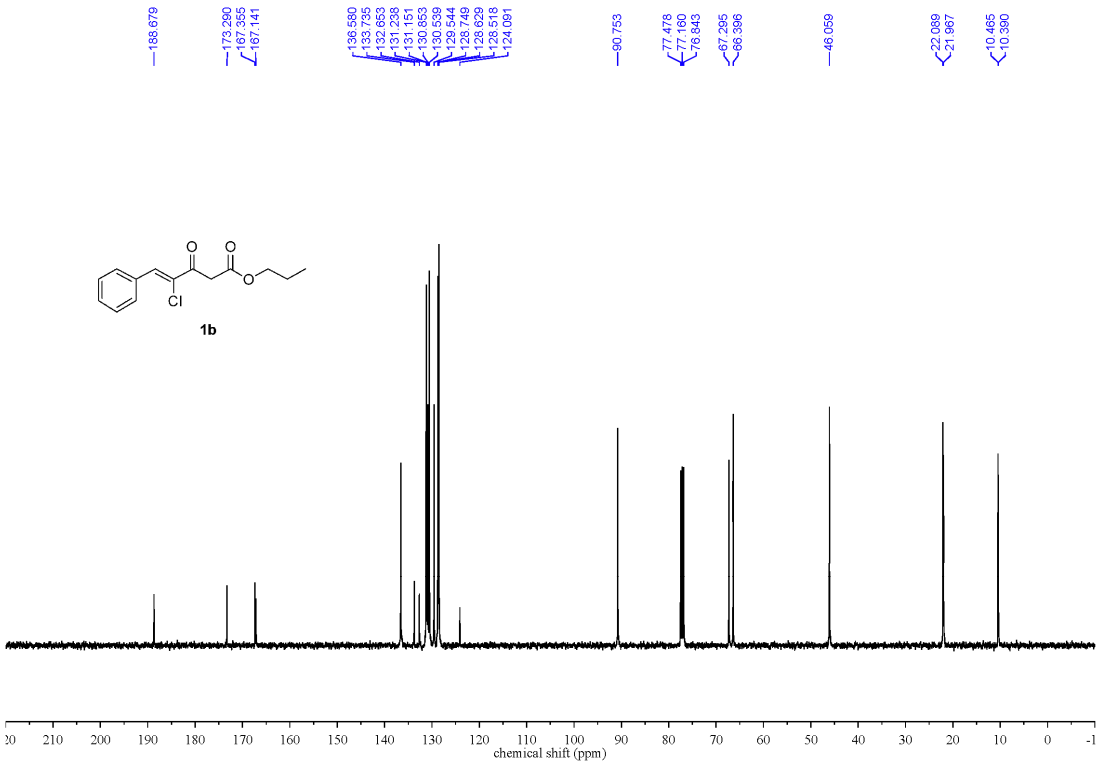
(*Z*)-Ethyl 4-chloro-3-oxo-5-phenylpent-4-enoate (1a)



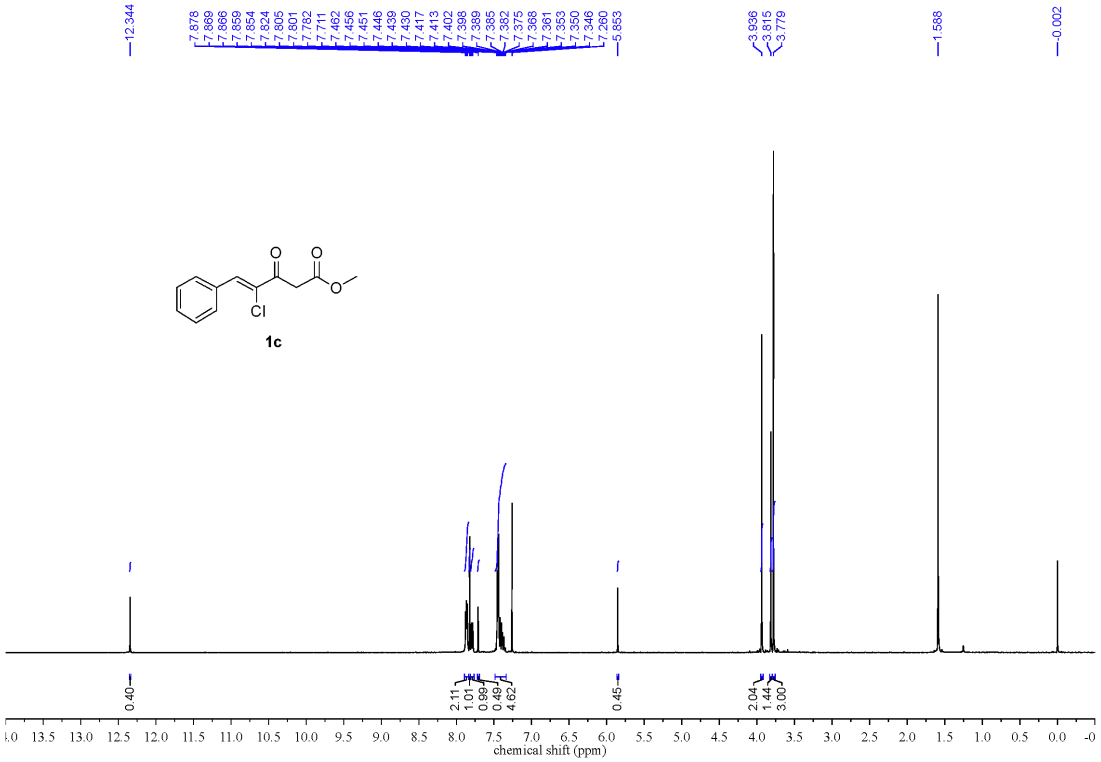


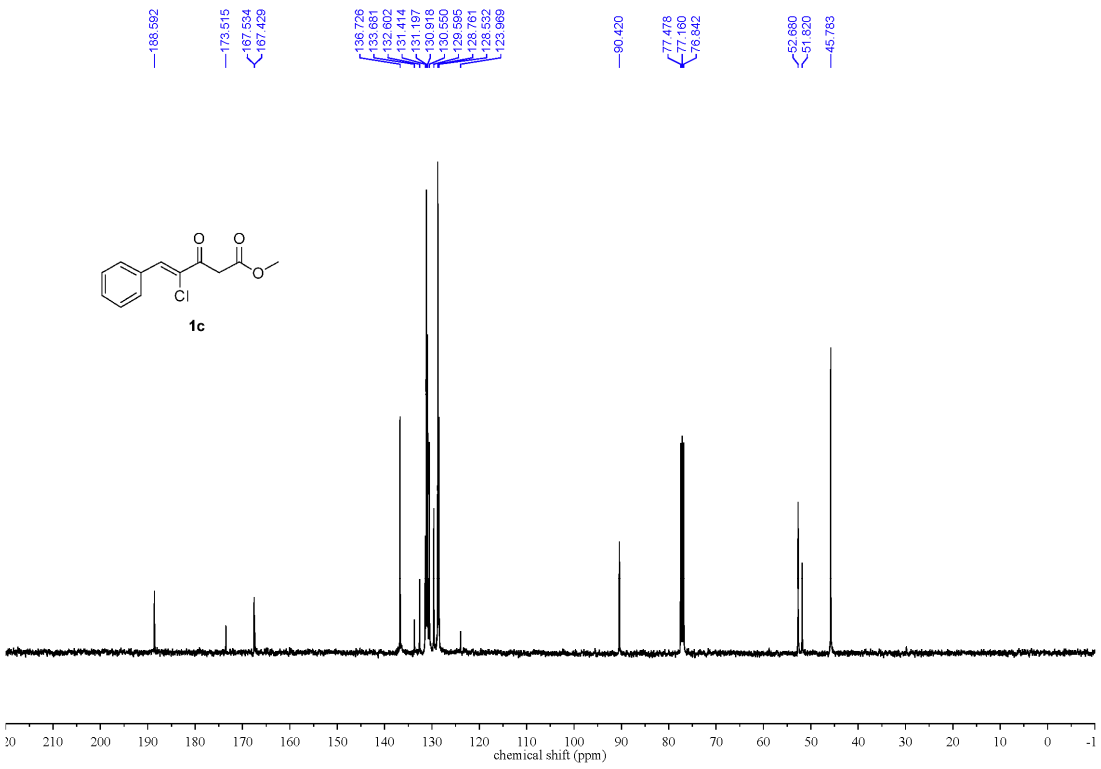
(*Z*)-Propyl 4-chloro-3-oxo-5-phenylpent-4-enoate (1b)



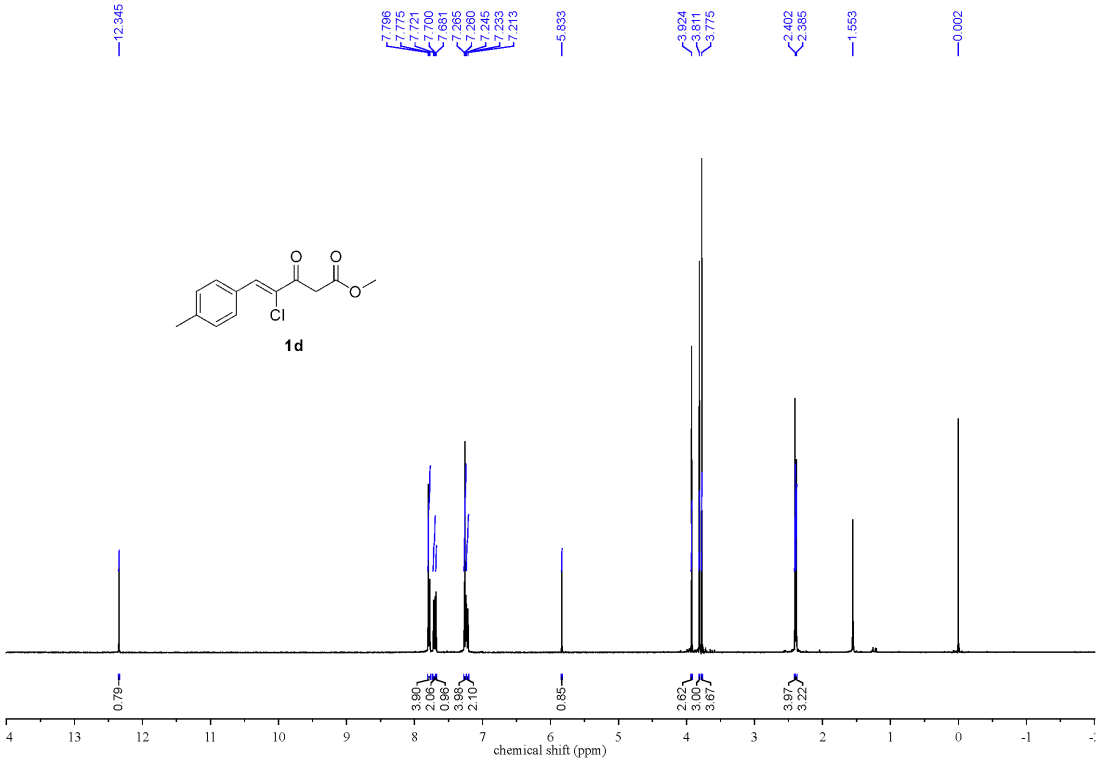


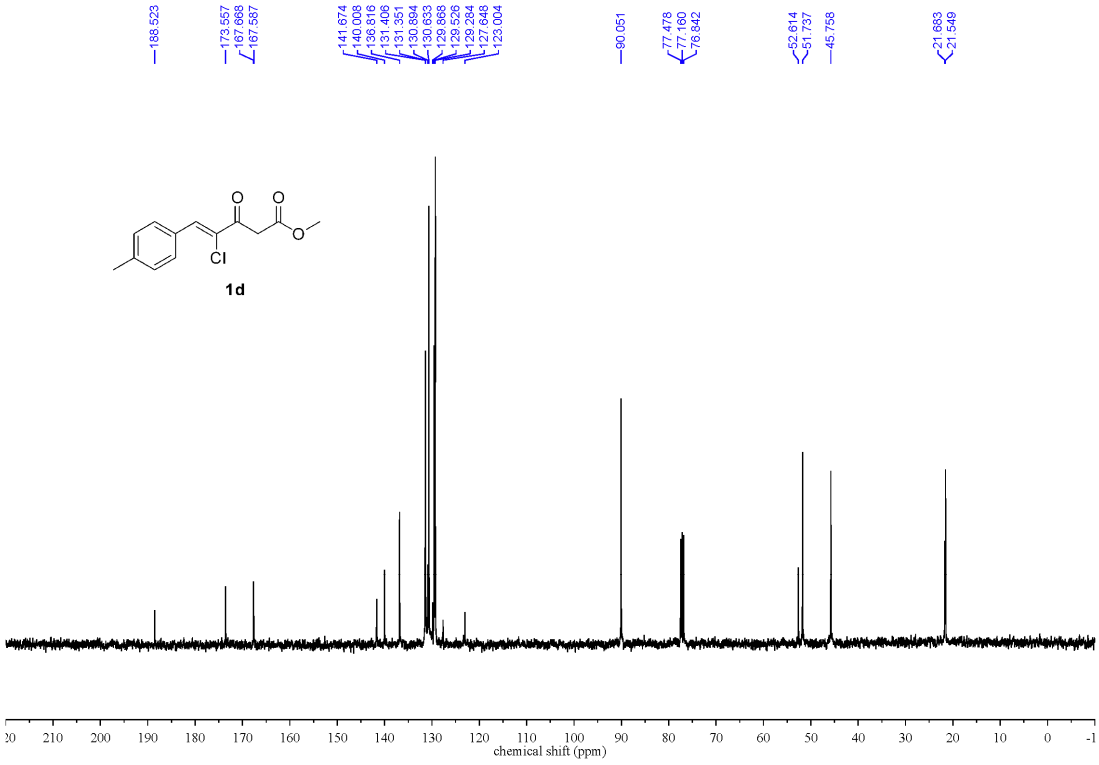
(*Z*)-Methyl 4-chloro-3-oxo-5-phenylpent-4-enoate (1c)



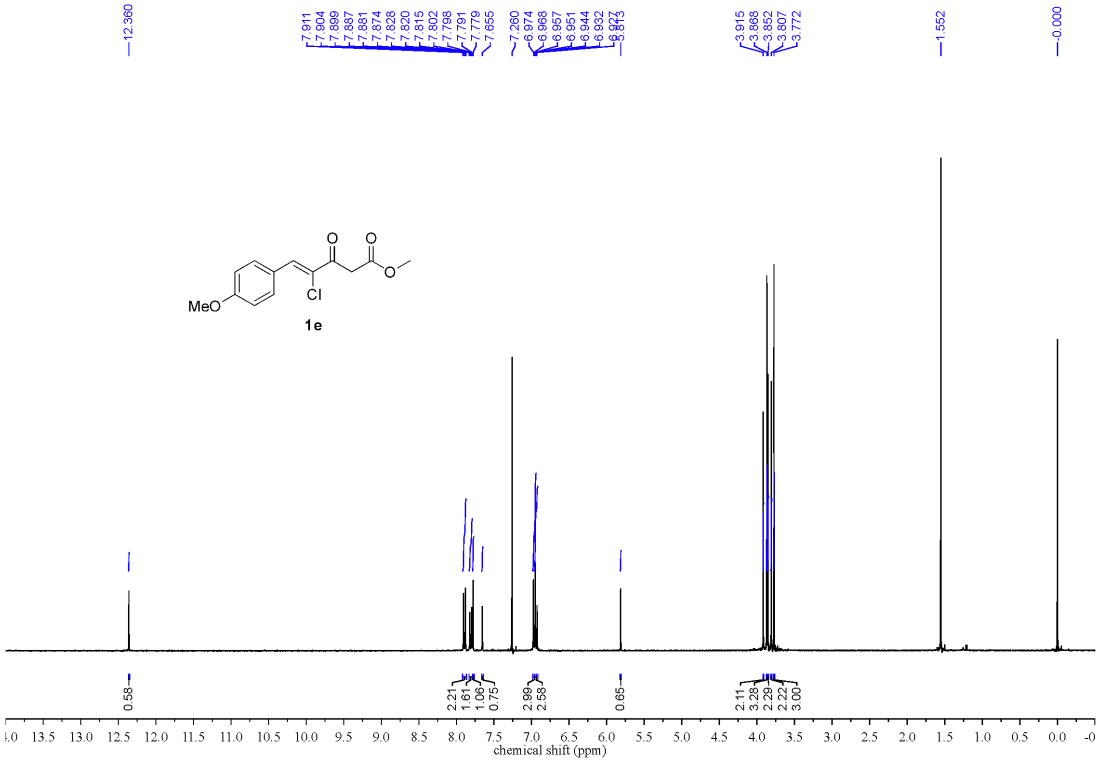


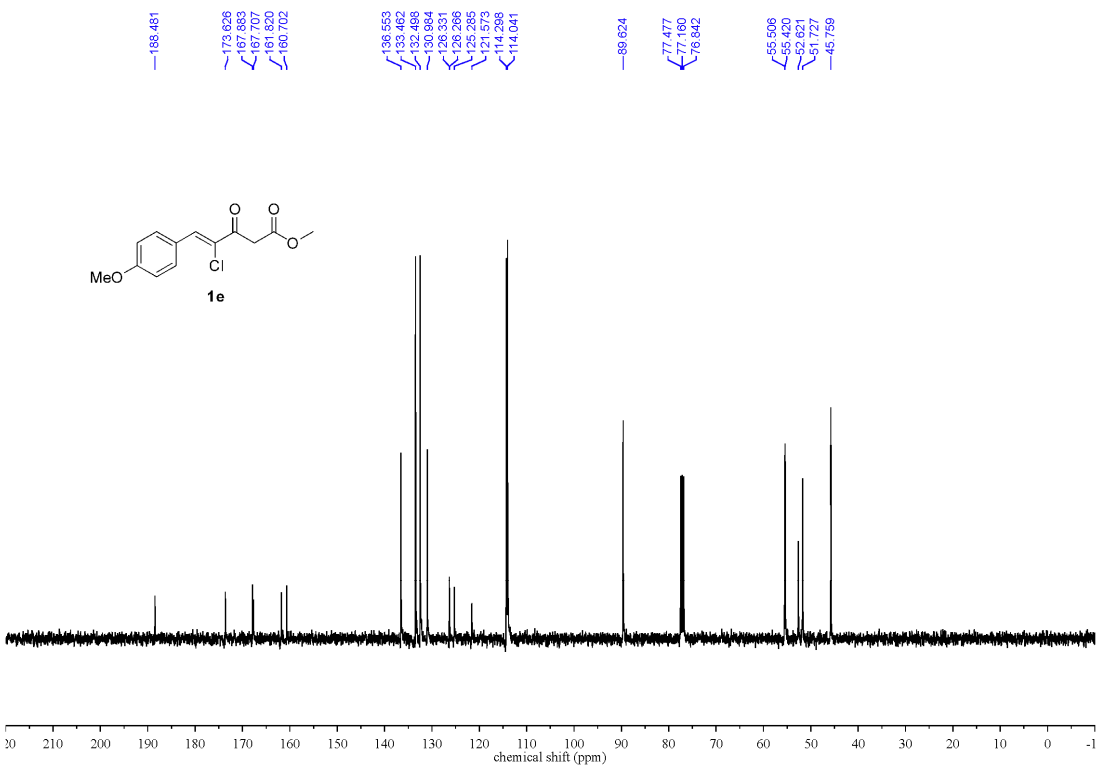
(*Z*)-Methyl 4-chloro-3-oxo-5-(p-tolyl)pent-4-enoate (1d)





(*Z*)-Methyl 4-chloro-5-(4-methoxyphenyl)-3-oxopent-4-enoate (1e)





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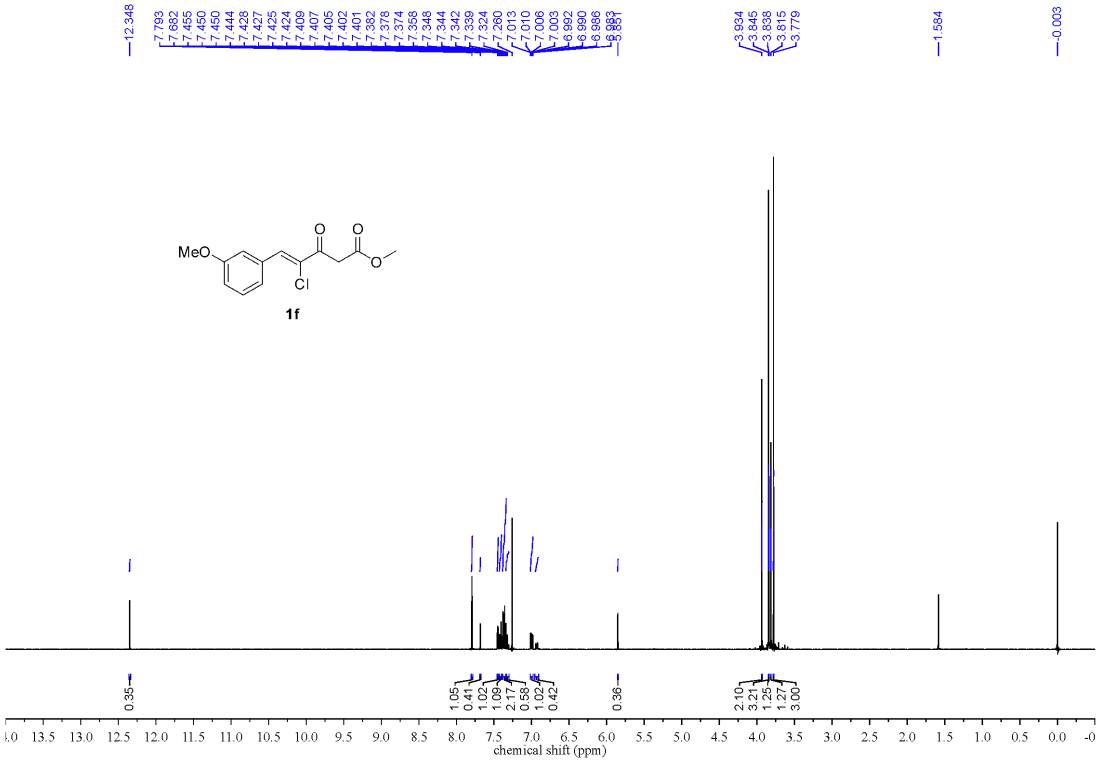

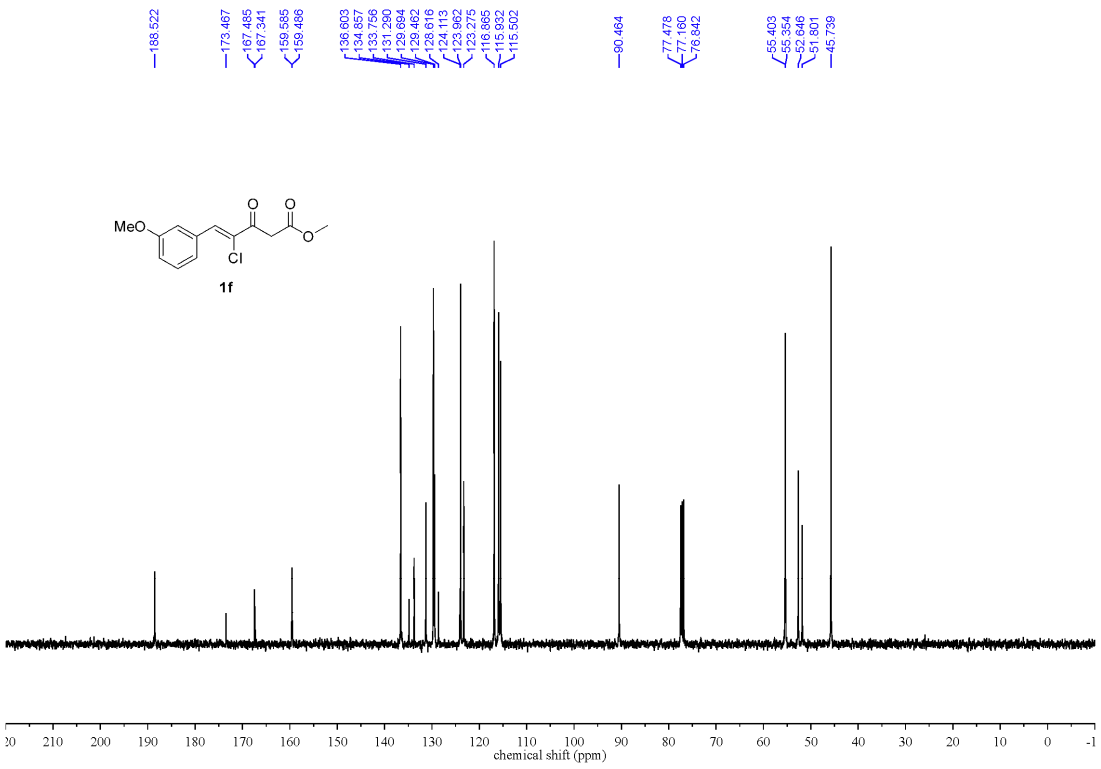

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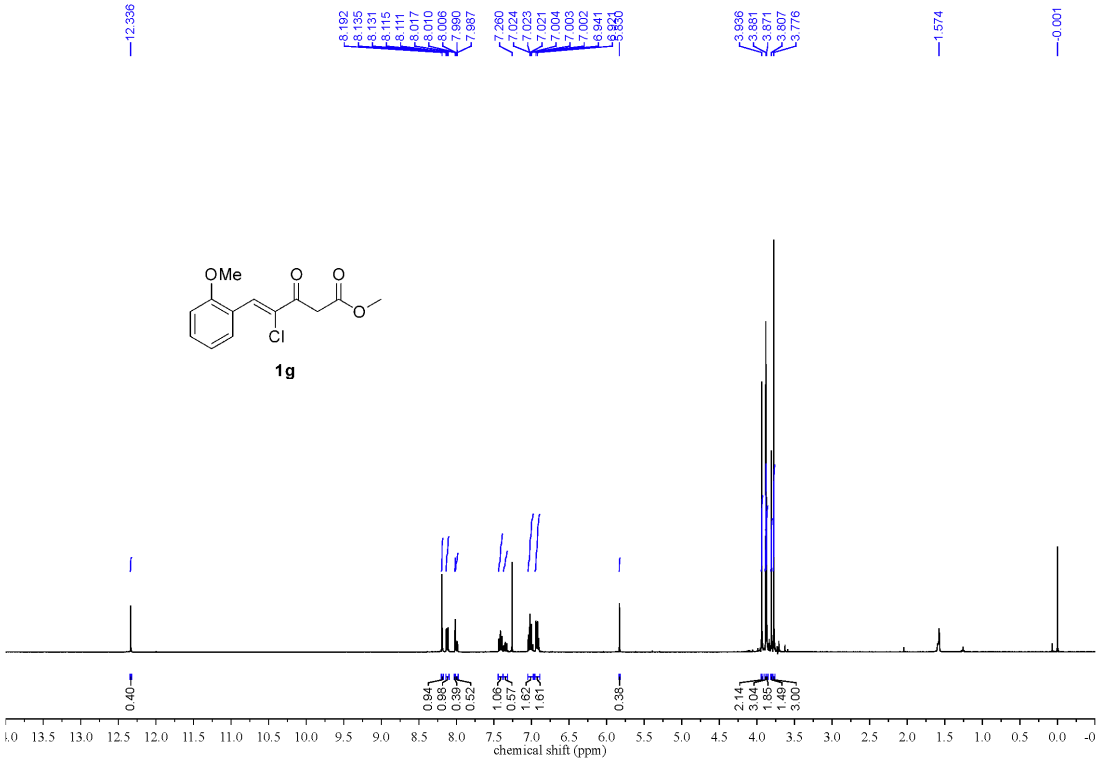
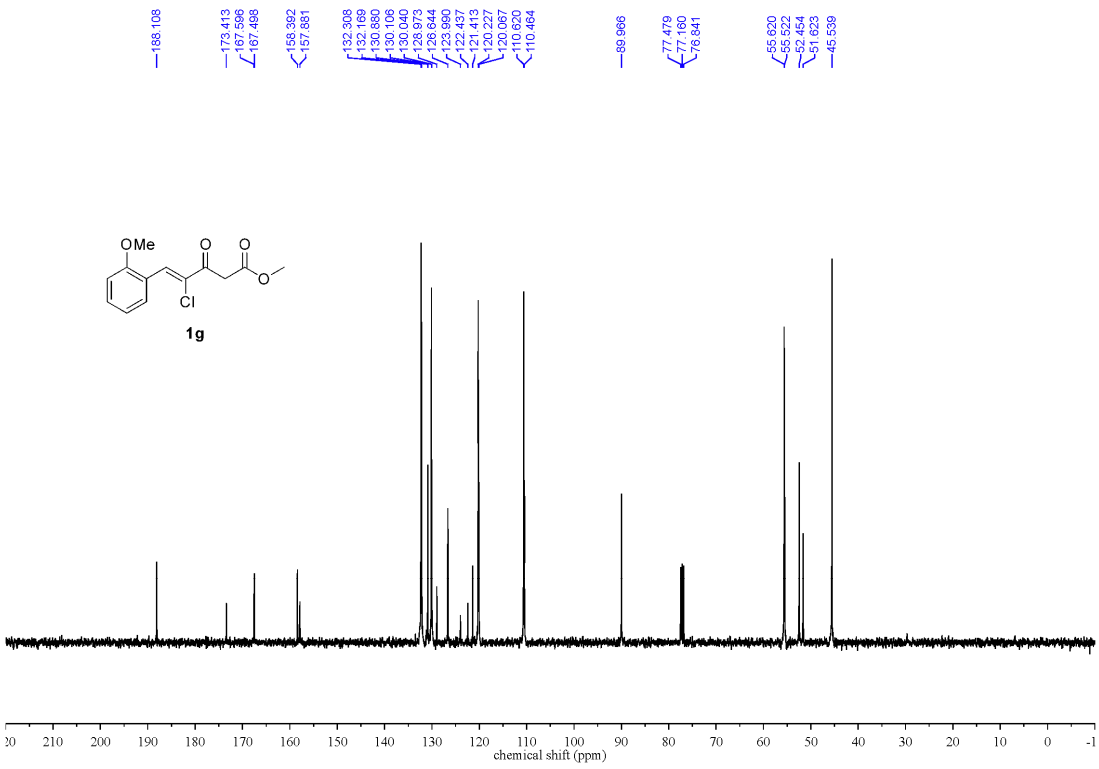
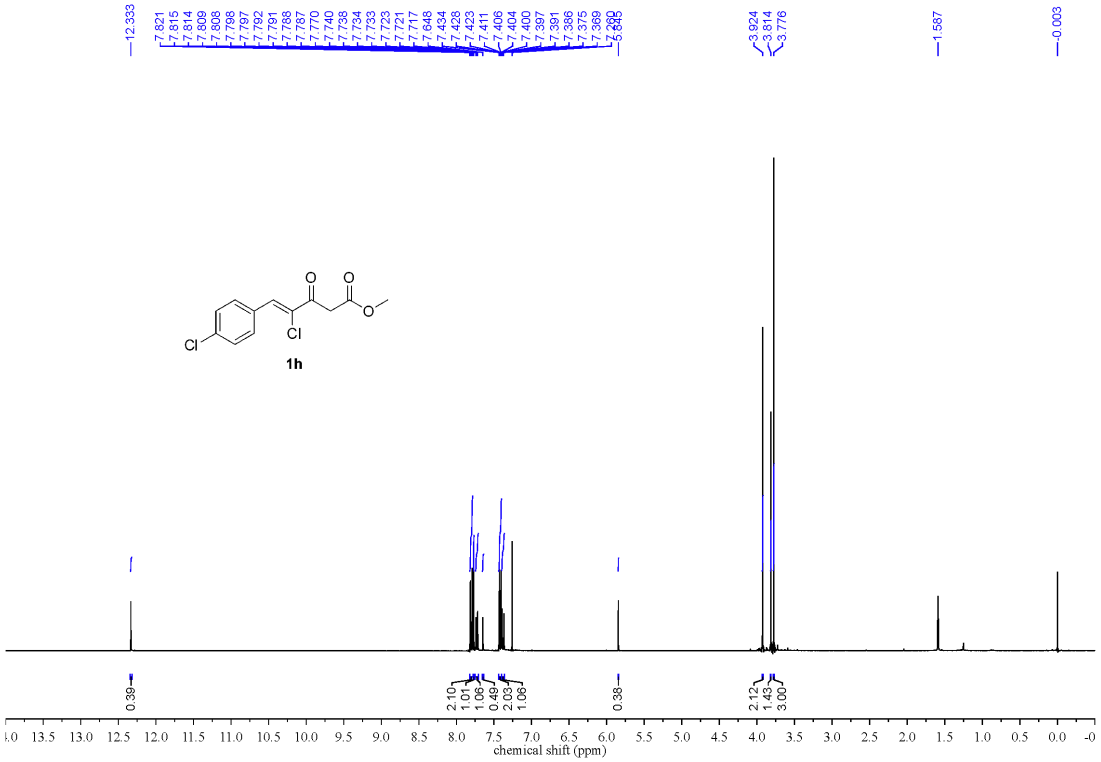
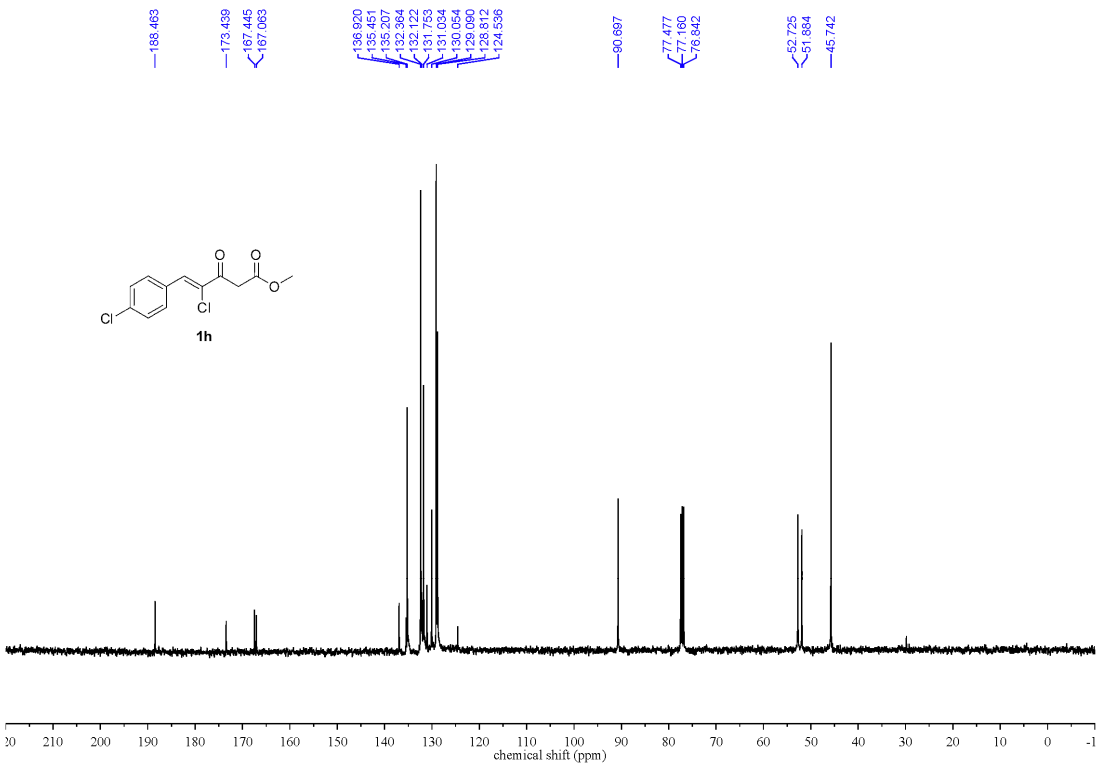




(*Z*)-Methyl 4-chloro-5-(4-chlorophenyl)-3-oxopent-4-enoate (1h)





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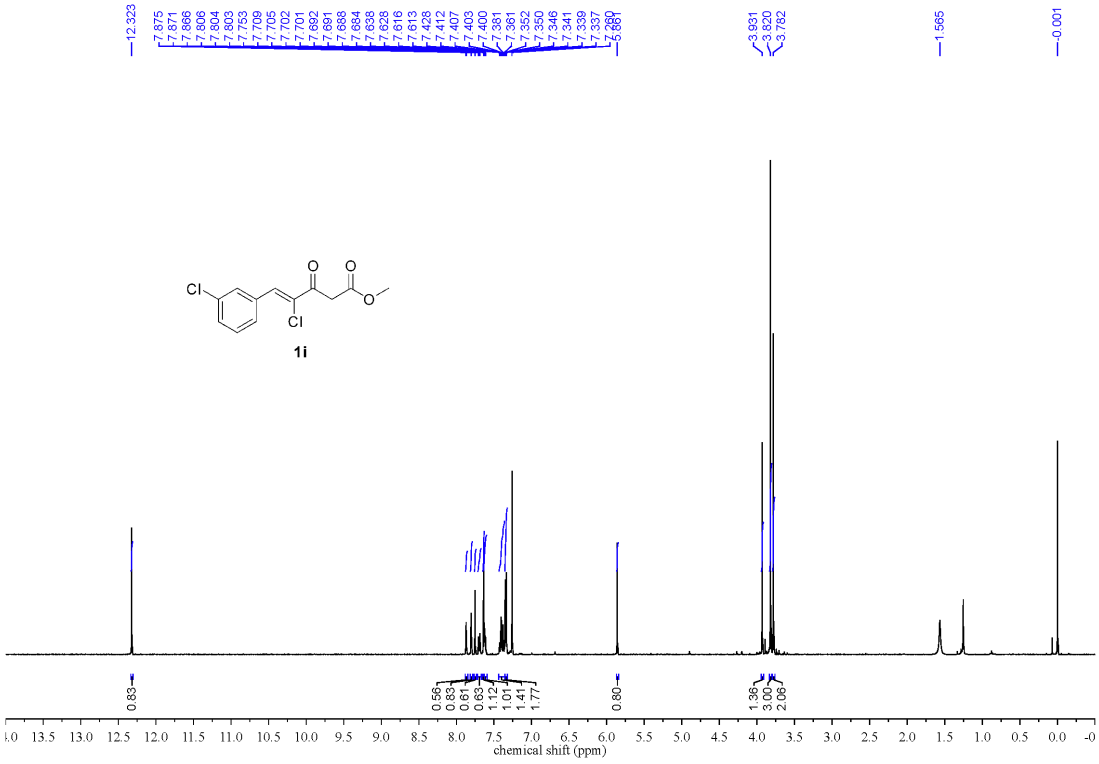
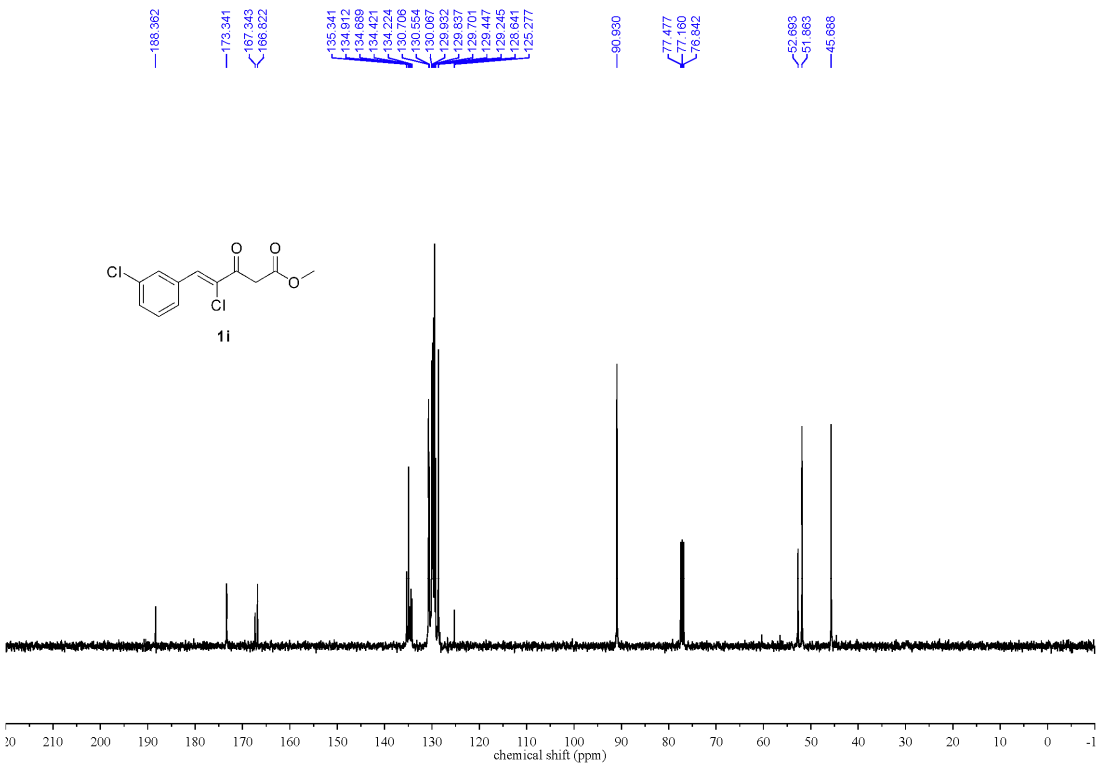
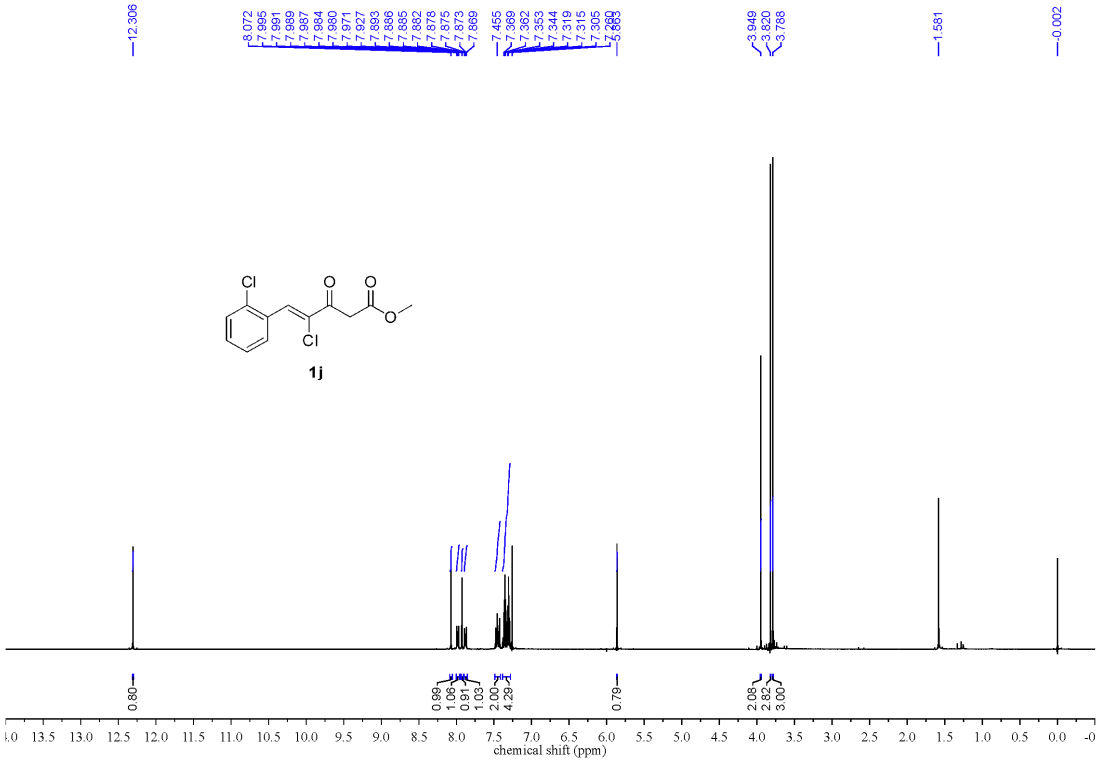
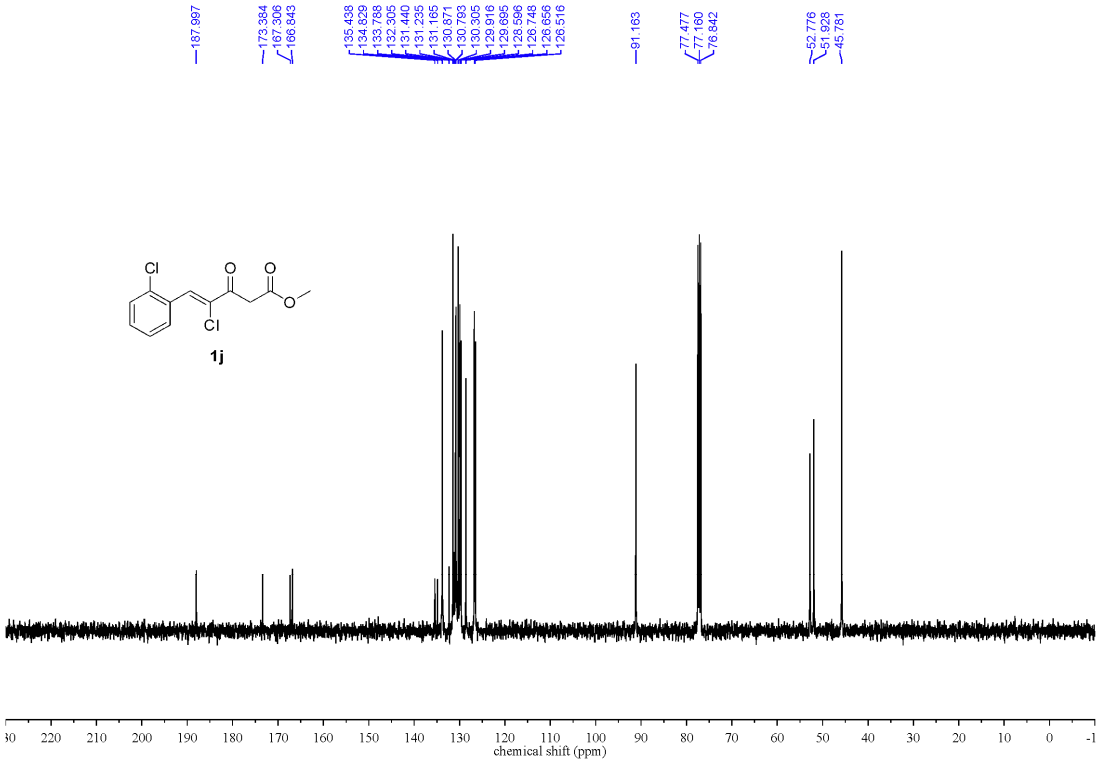




(*Z*)-Methyl 4-chloro-5-(2-chlorophenyl)-3-oxopent-4-enoate (1j)





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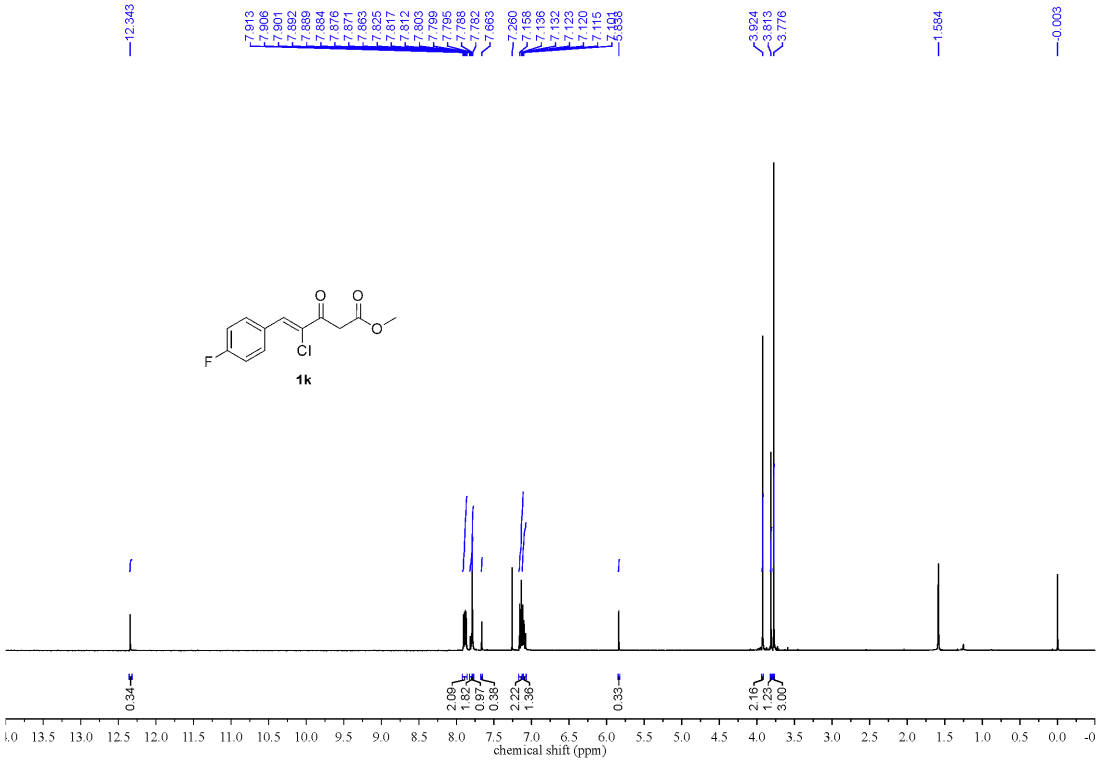
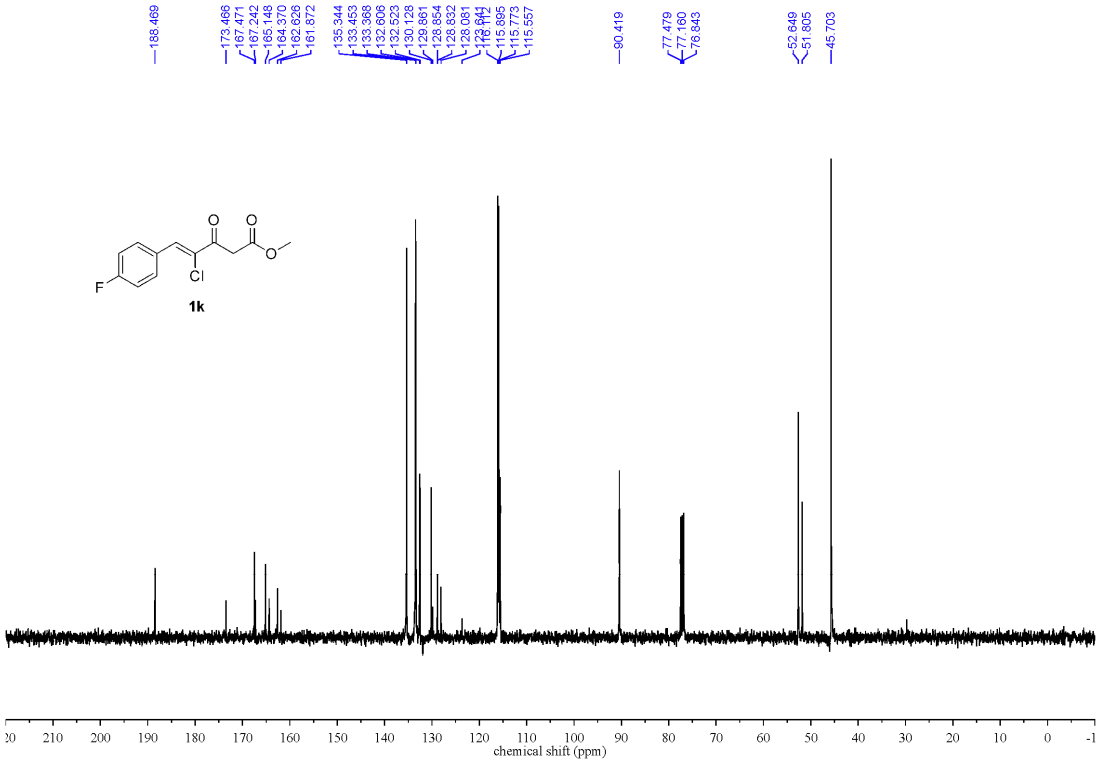
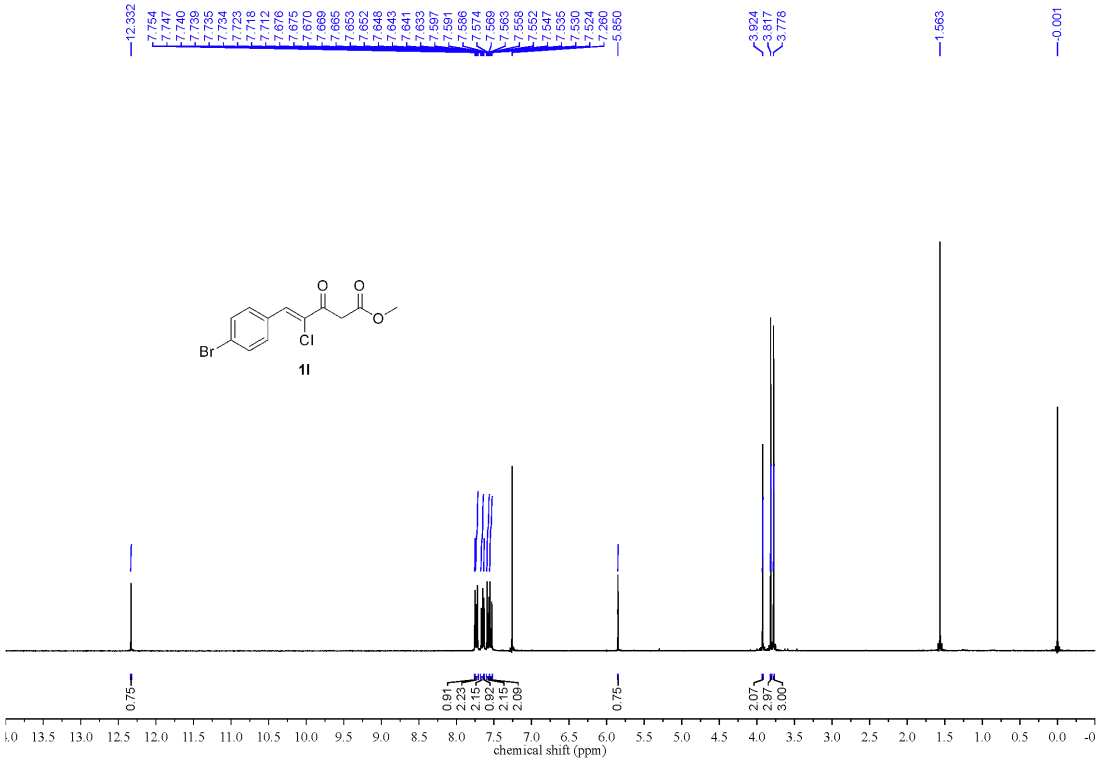
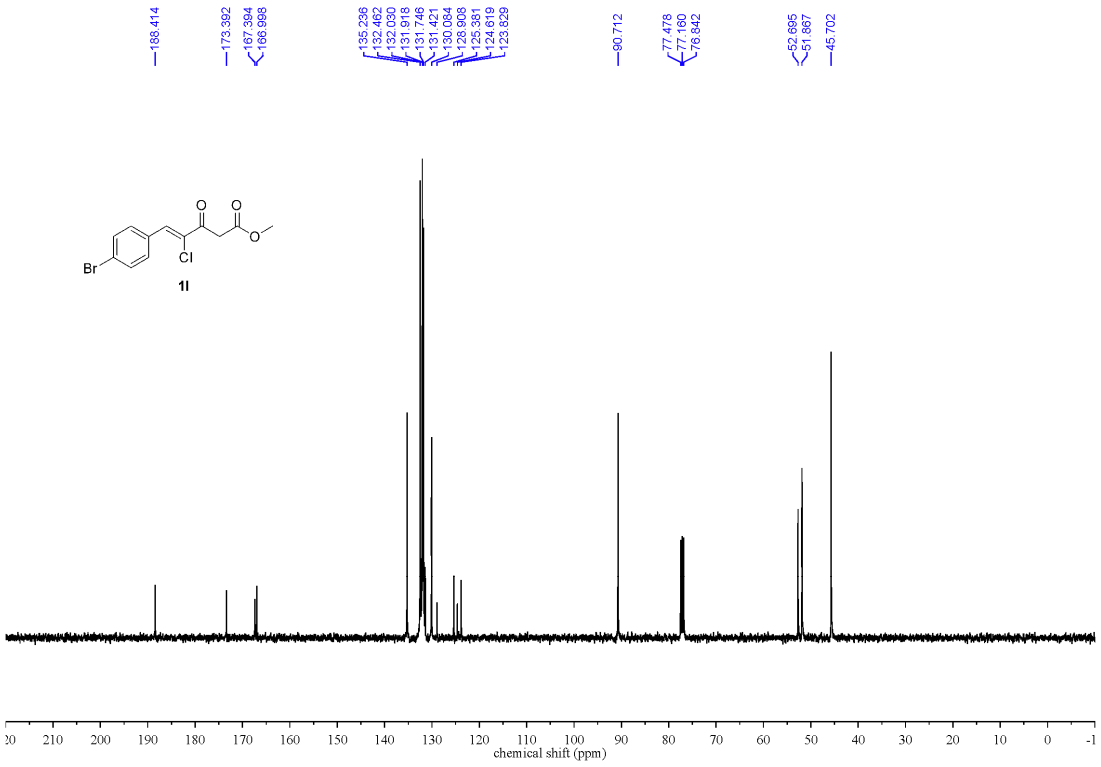


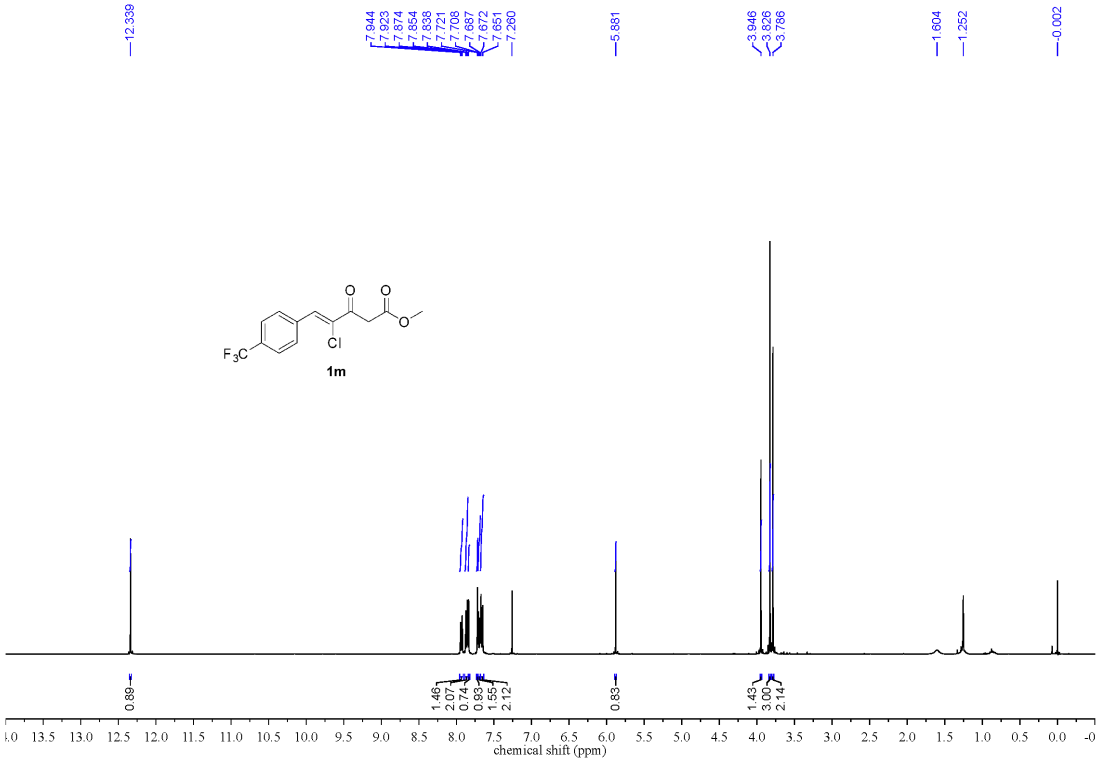


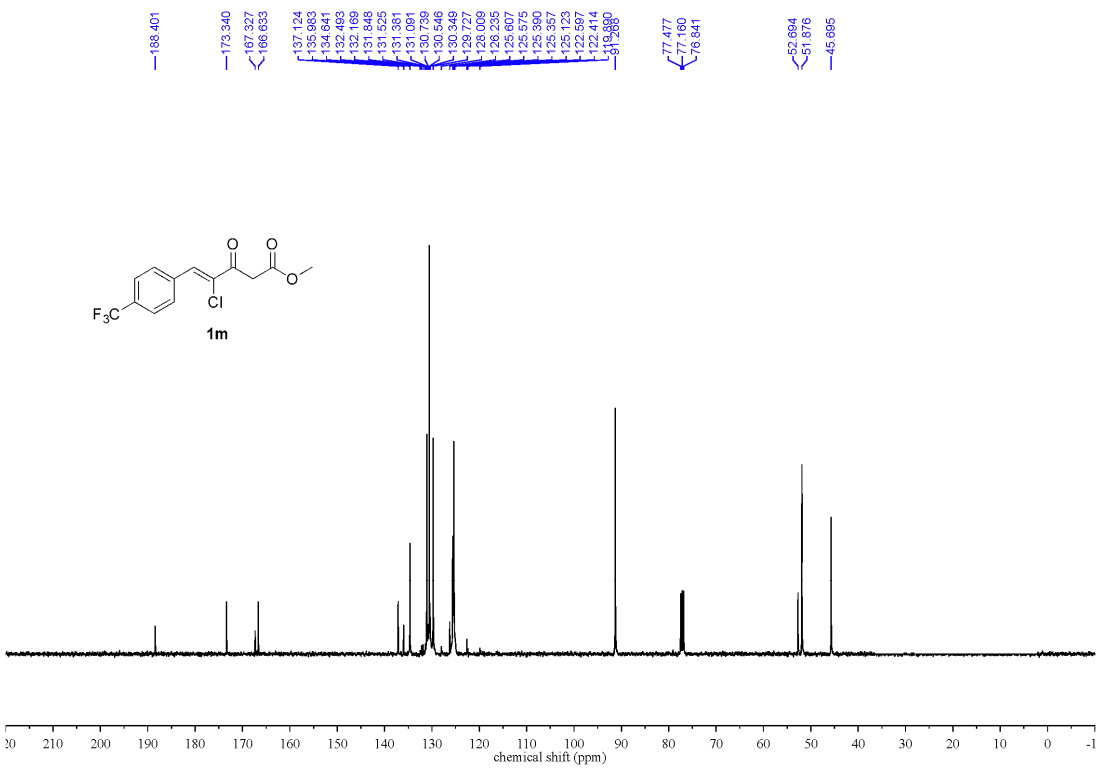
(*Z*)-Methyl 5-(4-bromophenyl)-4-chloro-3-oxopent-4-enoate (1l)



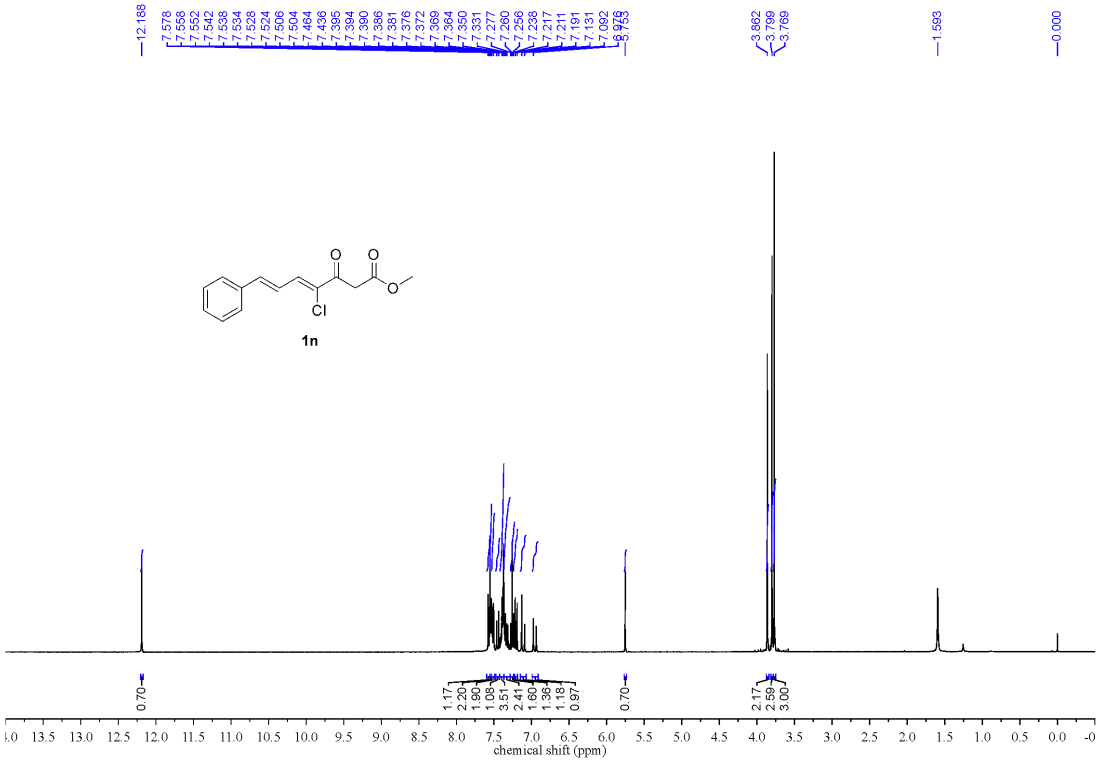


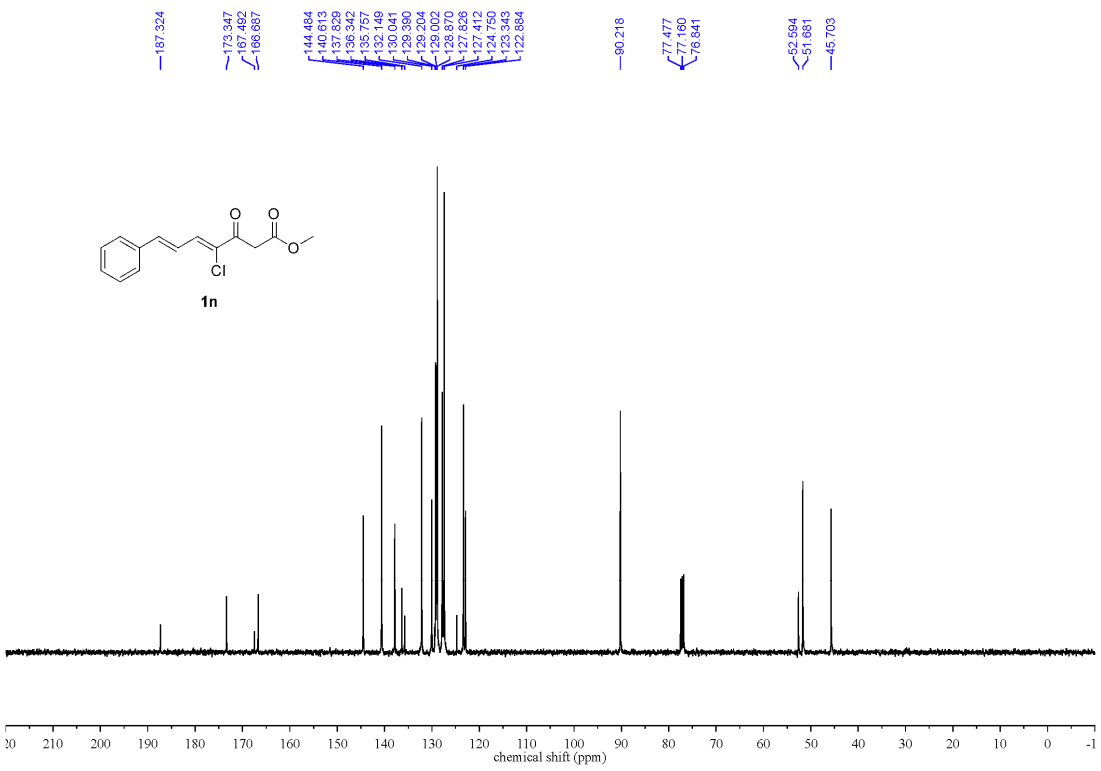
(*Z*)-Methyl 4-chloro-3-oxo-5-(4-(trifluoromethyl)phenyl)pent-4-enoate (1m)



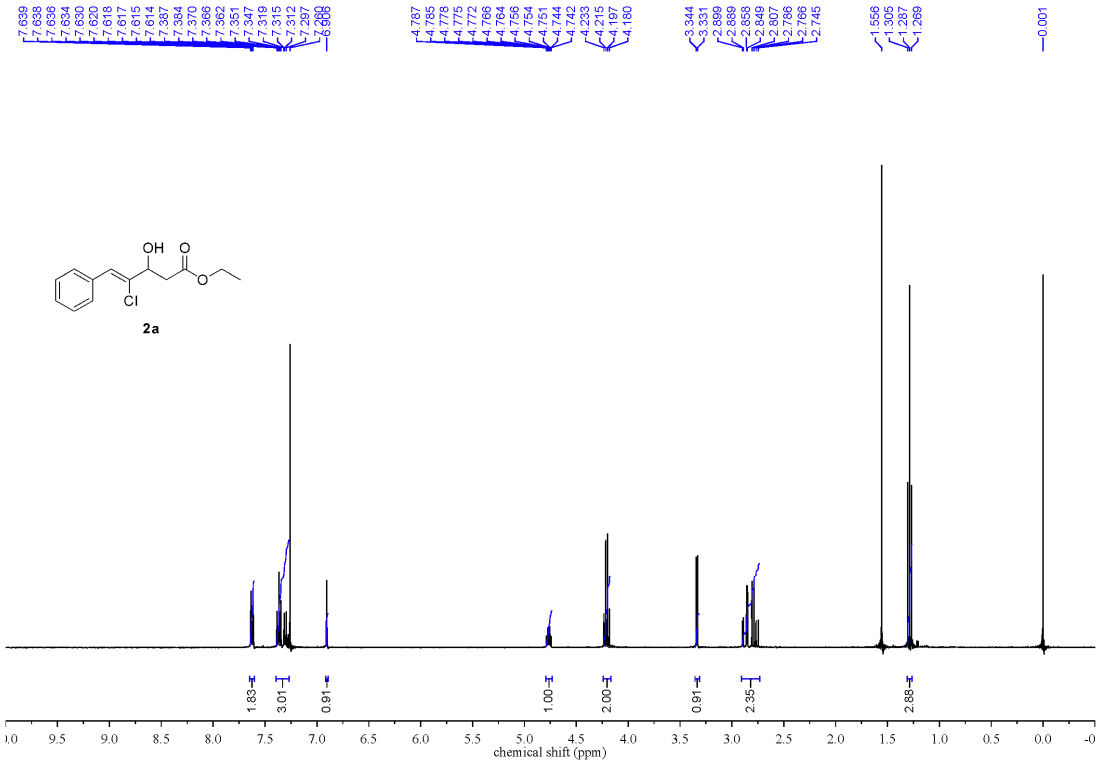


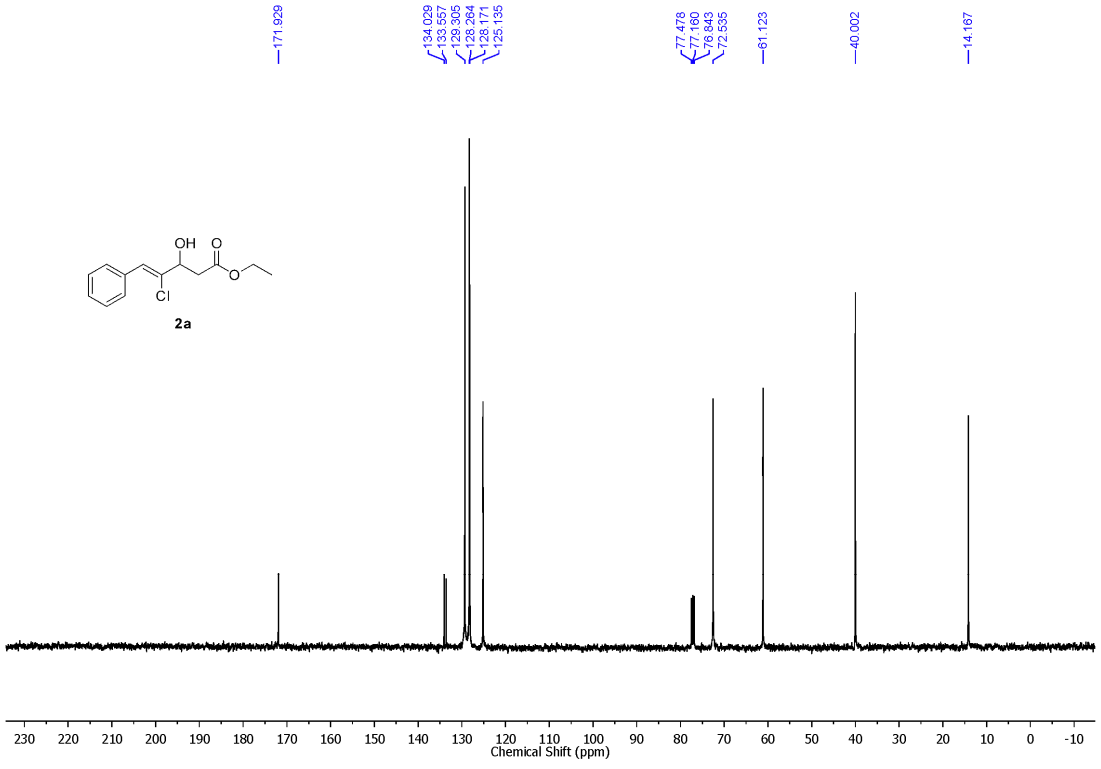
(4*Z*,6*E*)-Methyl 4-chloro-3-oxo-7-phenylhepta-4,6-dienoate (1n)



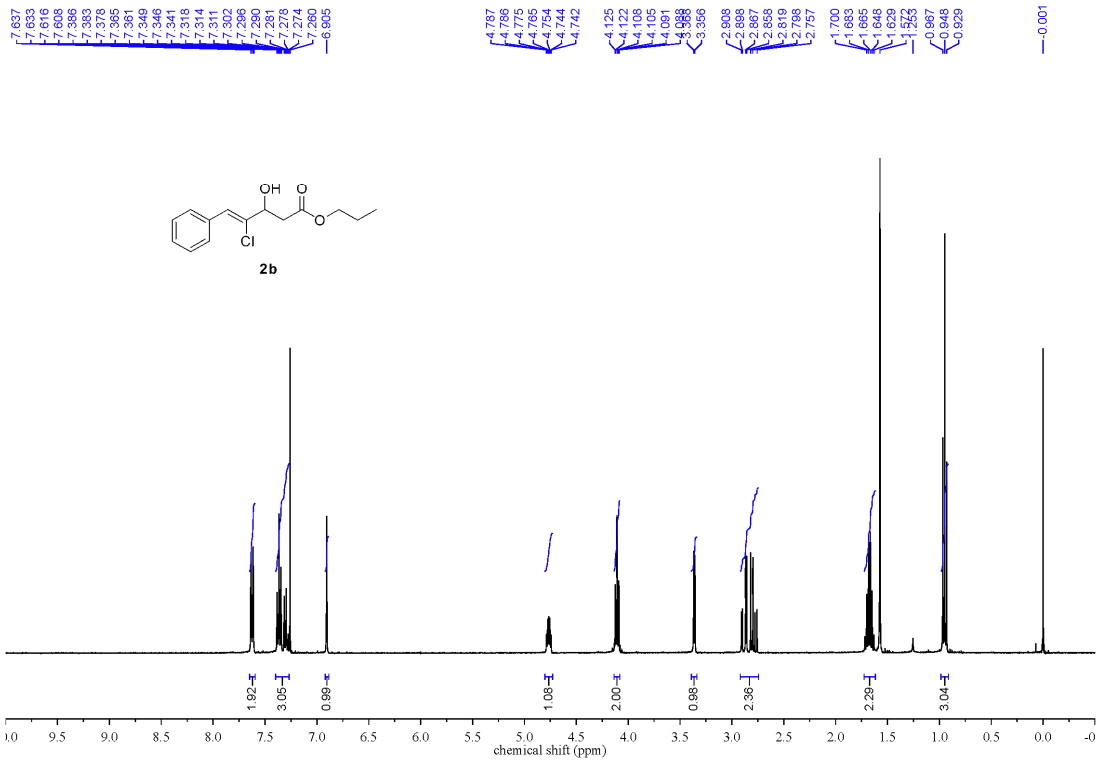


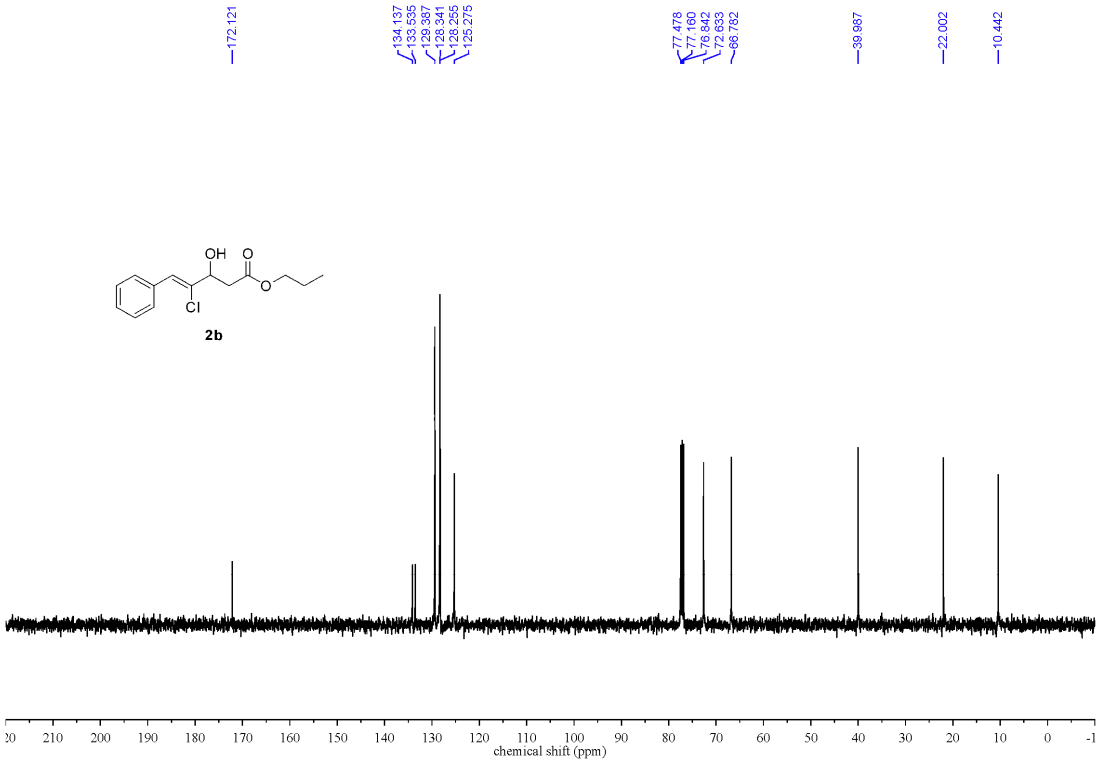
(*Z*)-Ethyl 4-chloro-3-hydroxy-5-phenylpent-4-enoate (2a)



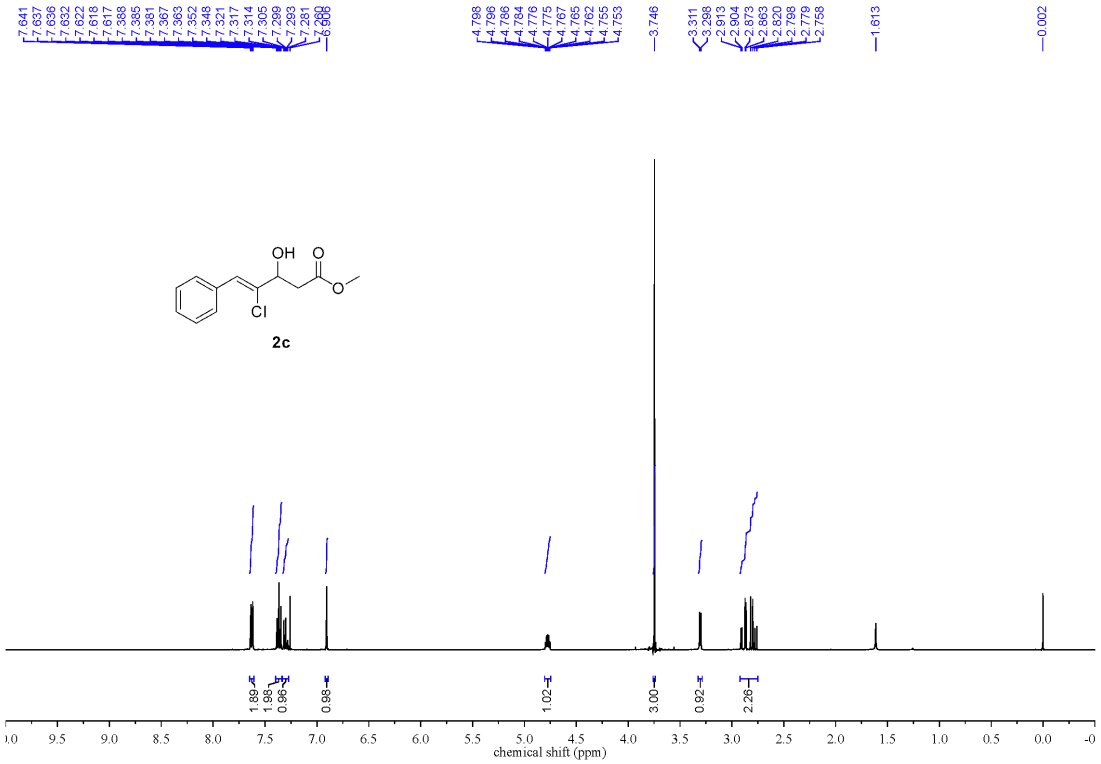


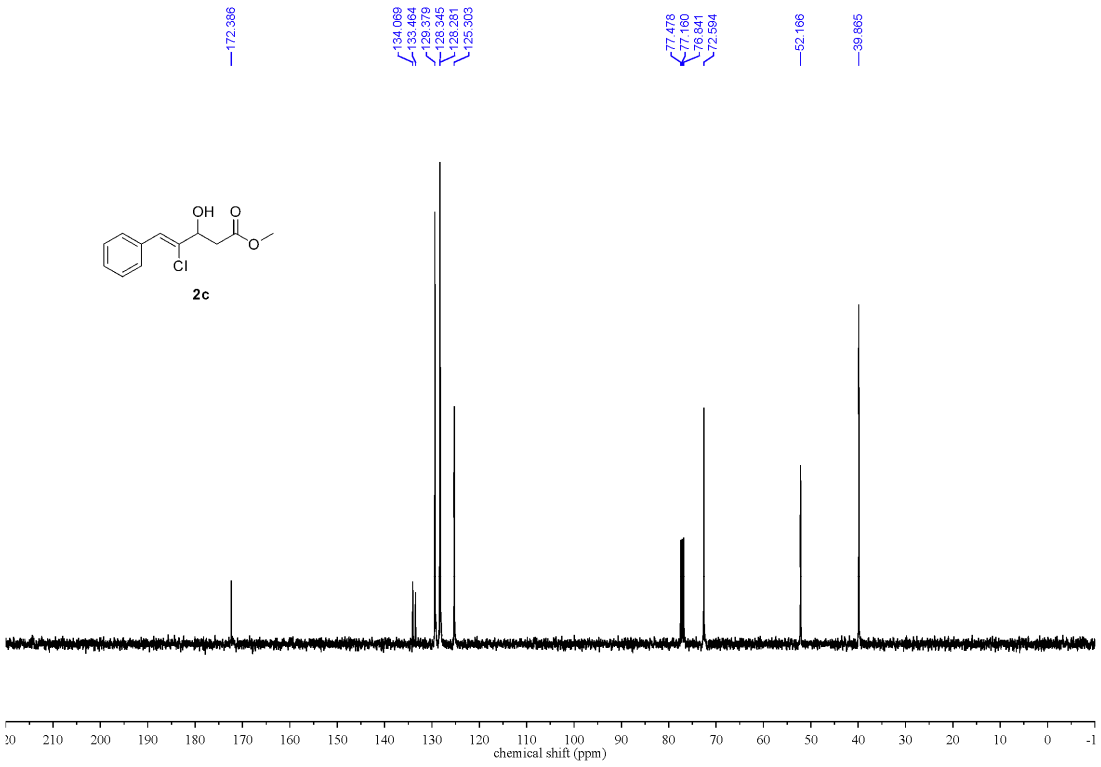
(*Z*)-Propyl 4-chloro-3-hydroxy-5-phenylpent-4-enoate (2b)



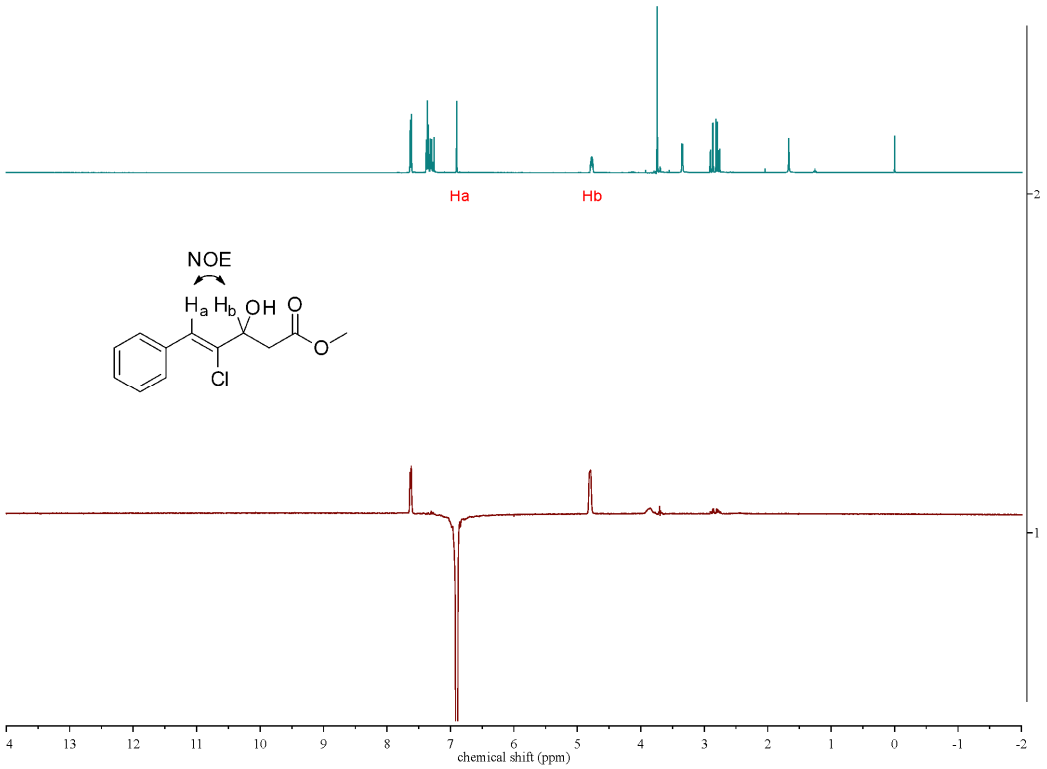


(*Z*)-Methyl 4-chloro-3-hydroxy-5-phenylpent-4-enoate (2c)

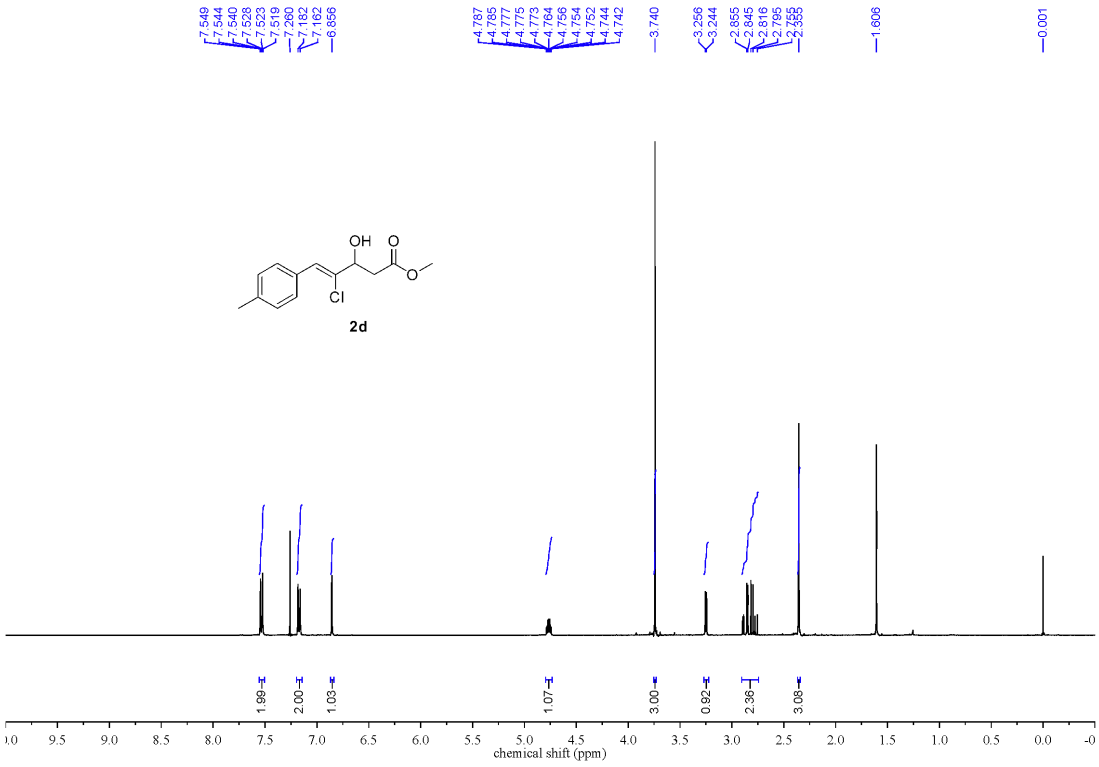


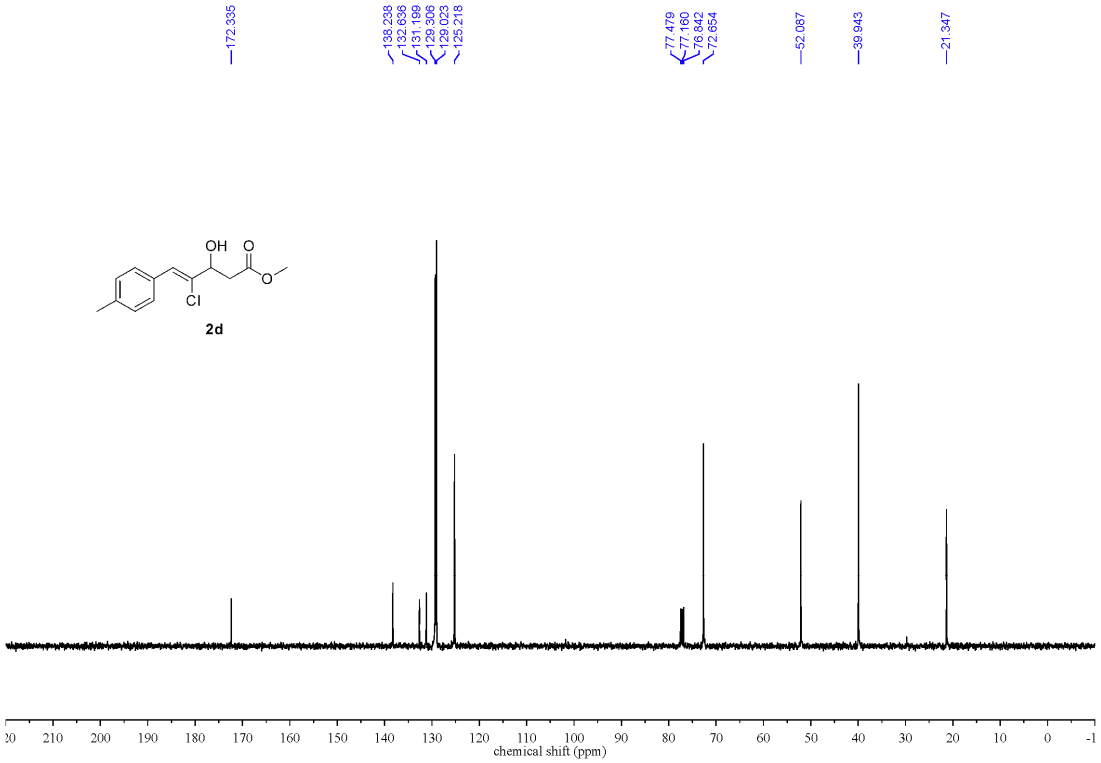


1D-NOE: irradiate on H_a

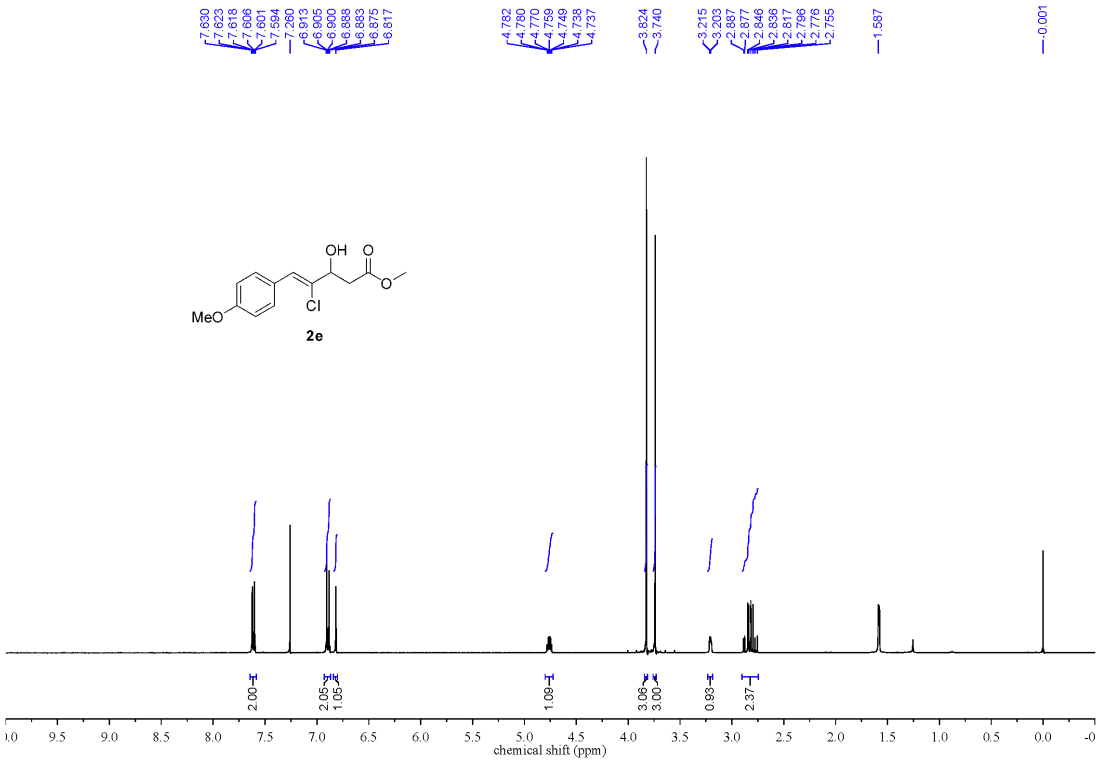


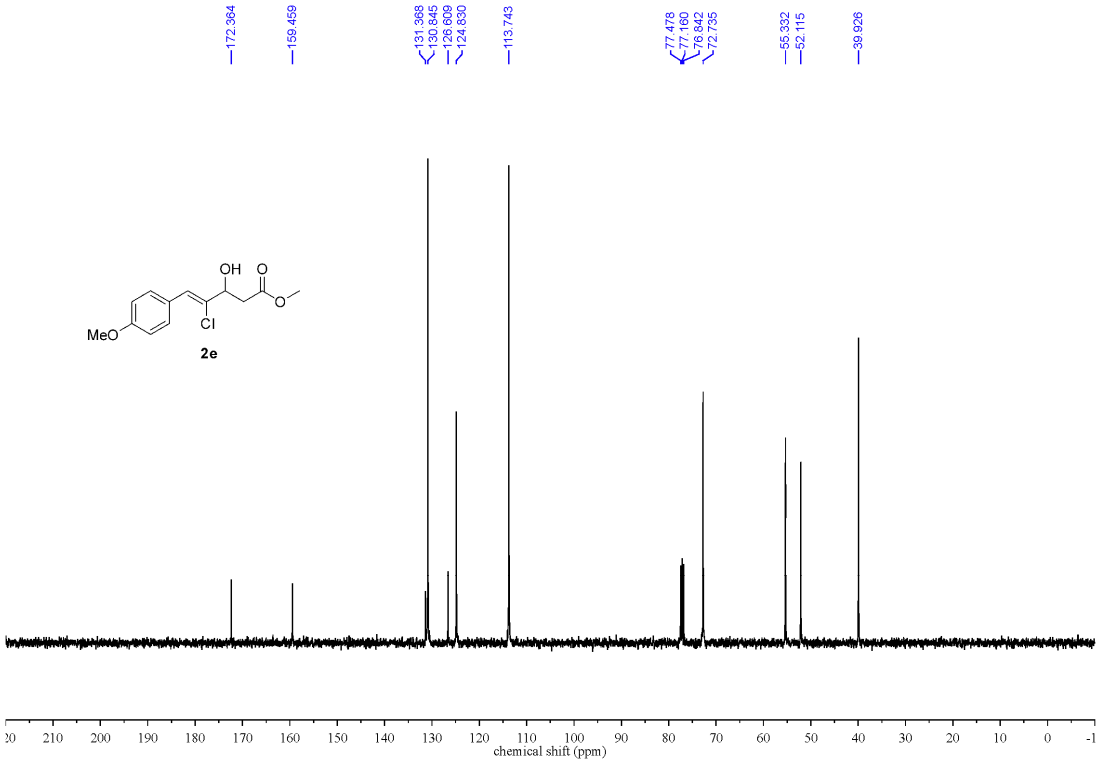
(*Z*)-Methyl 4-chloro-3-hydroxy-5-(p-tolyl)pent-4-enoate (2d)



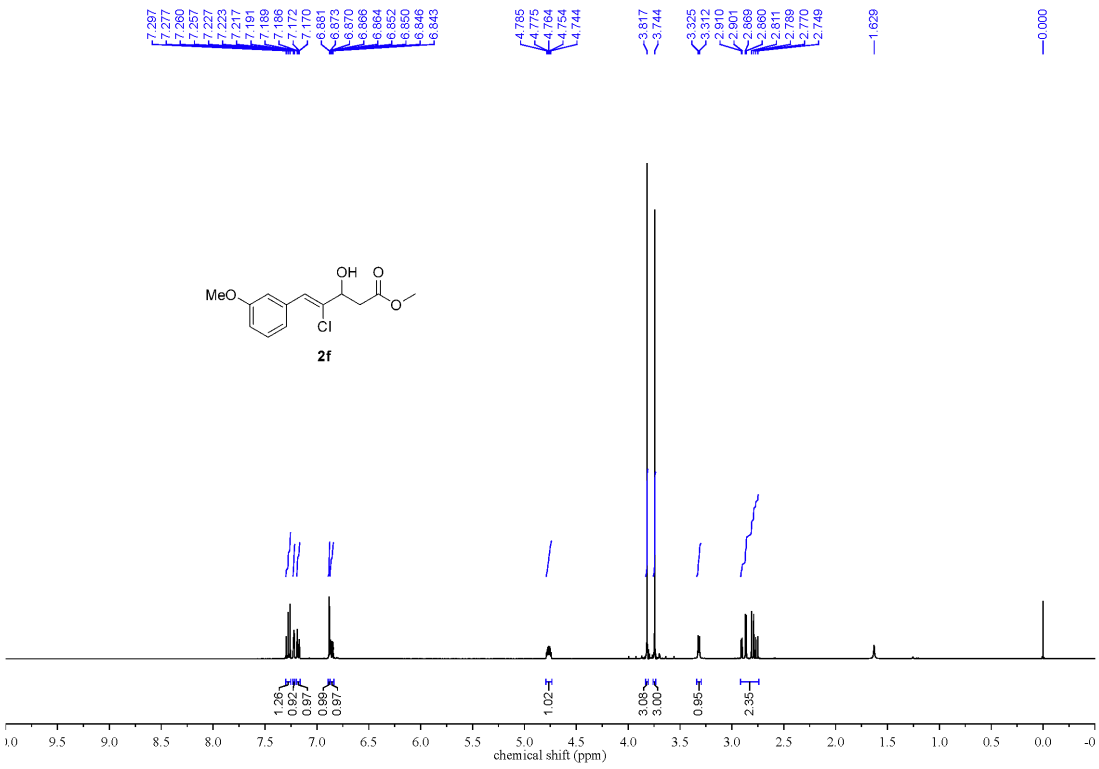


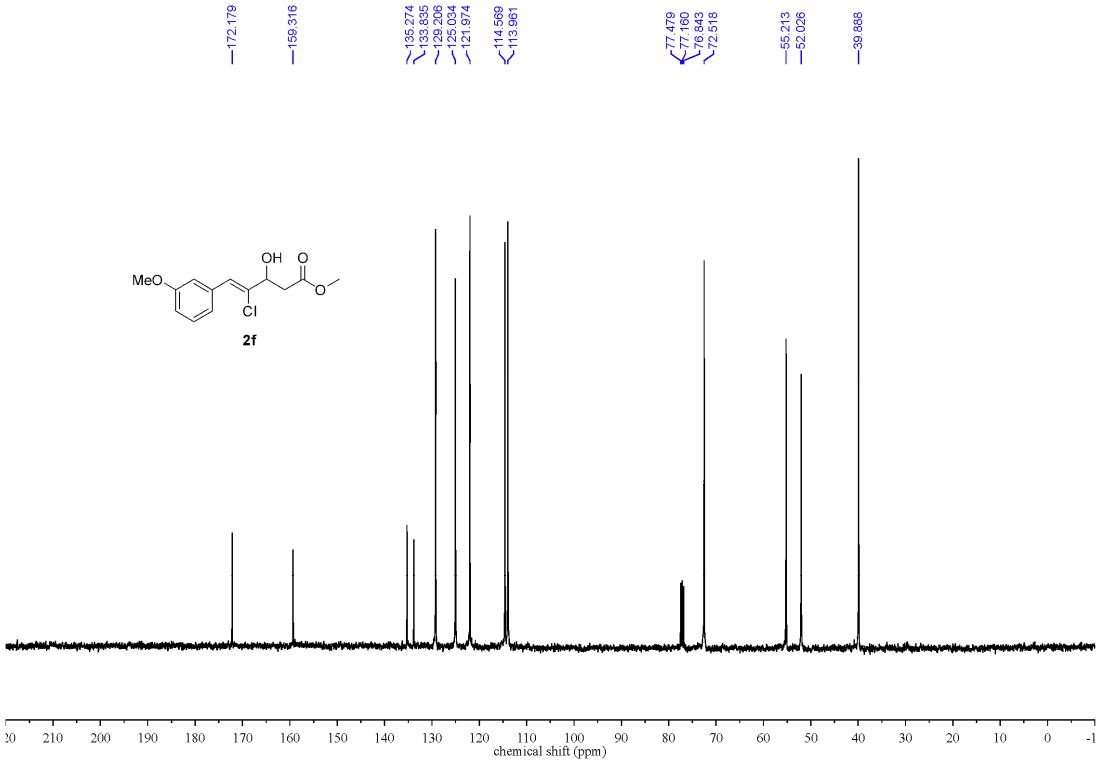
(*Z*)-Methyl 4-chloro-3-hydroxy-5-(4-methoxyphenyl)pent-4-enoate (2e)



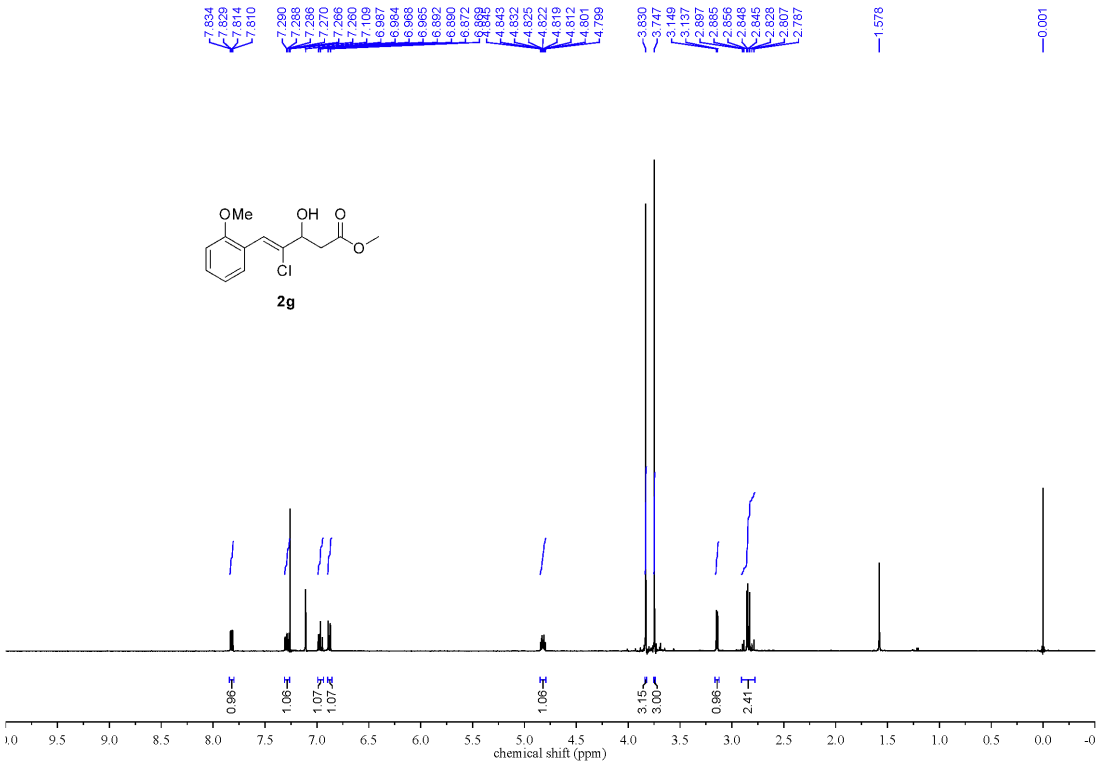


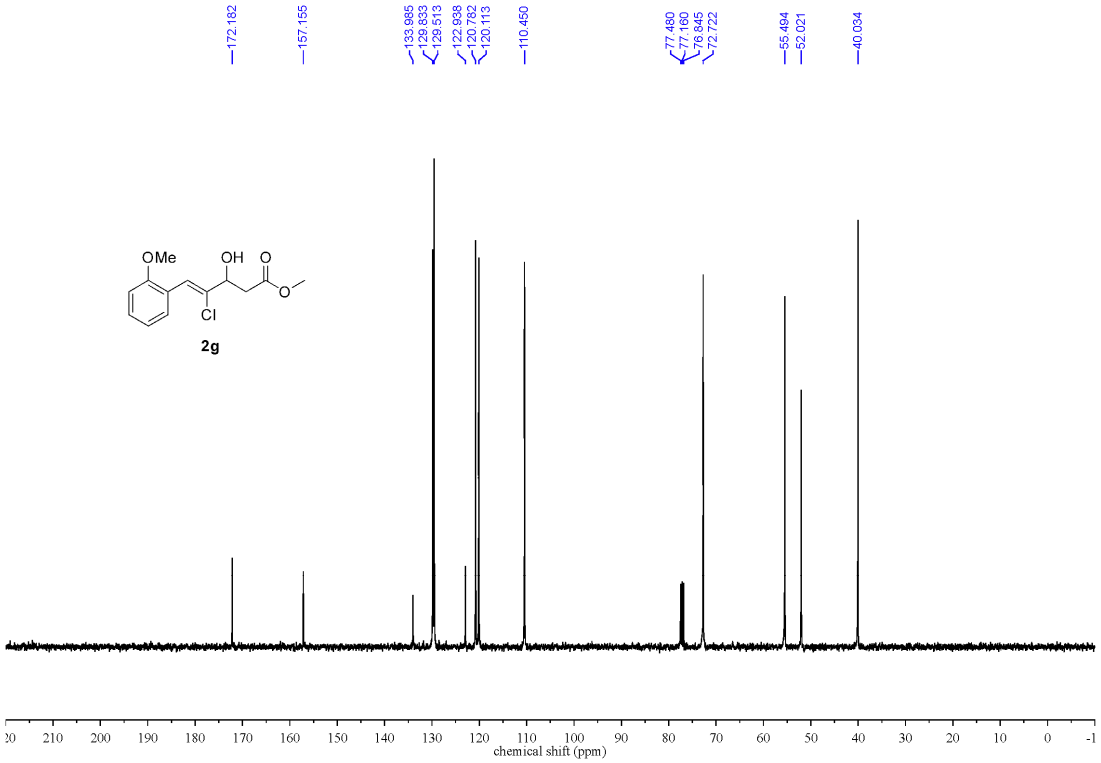
(*Z*)-Methyl 4-chloro-3-hydroxy-5-(3-methoxyphenyl)pent-4-enoate (2f)



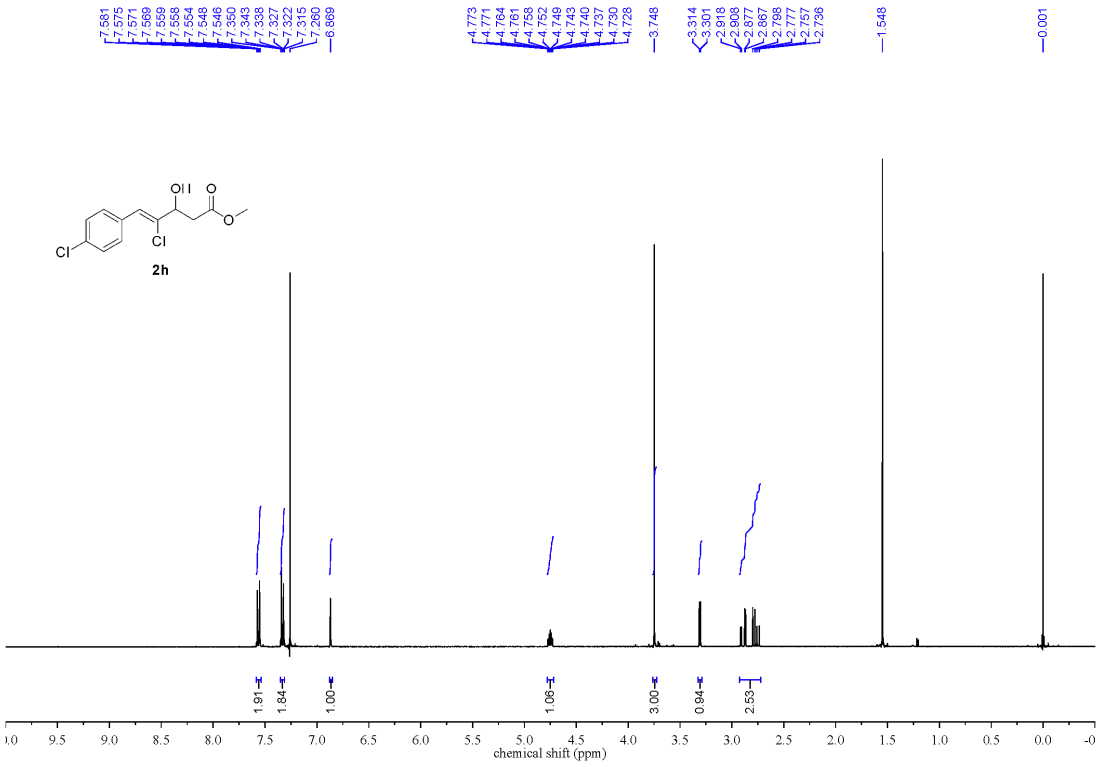


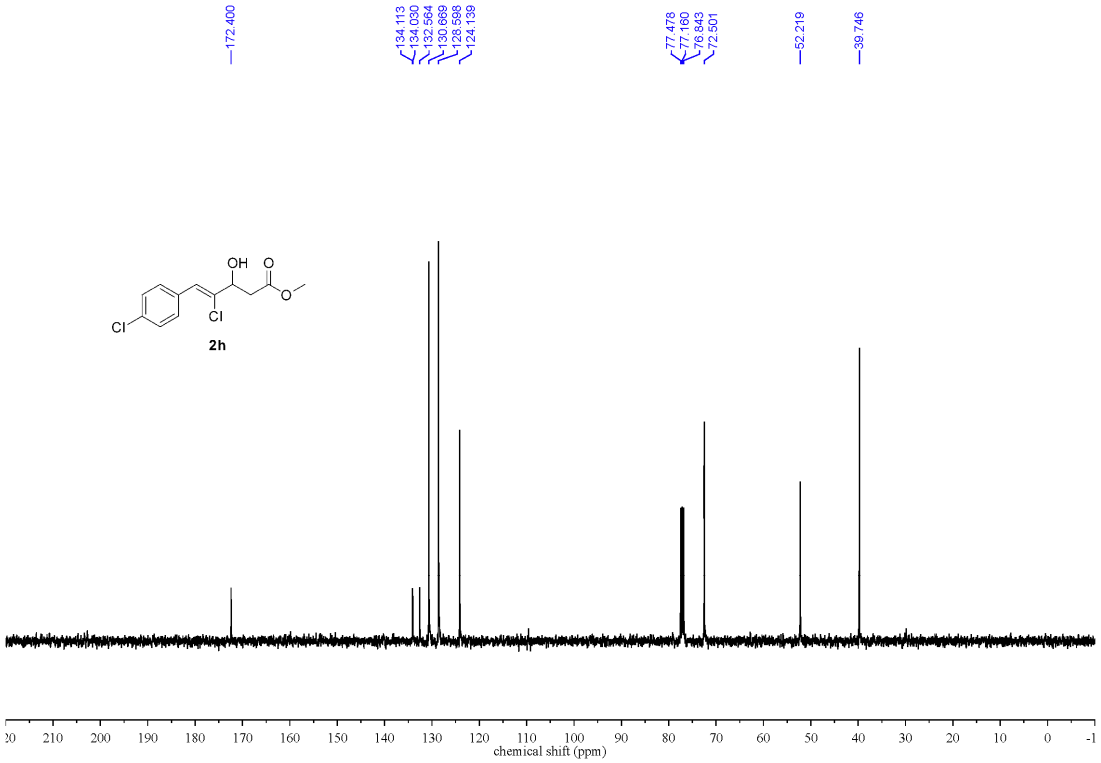
(*Z*)-Methyl 4-chloro-3-hydroxy-5-(2-methoxyphenyl)pent-4-enoate (2g)



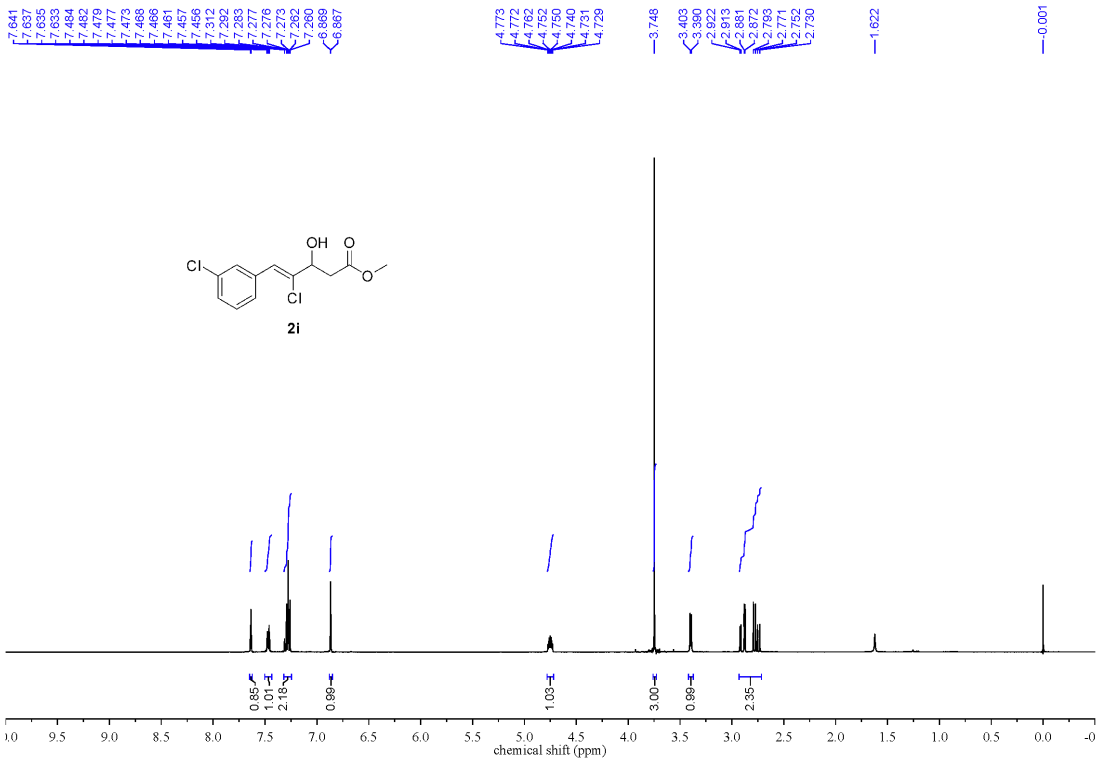


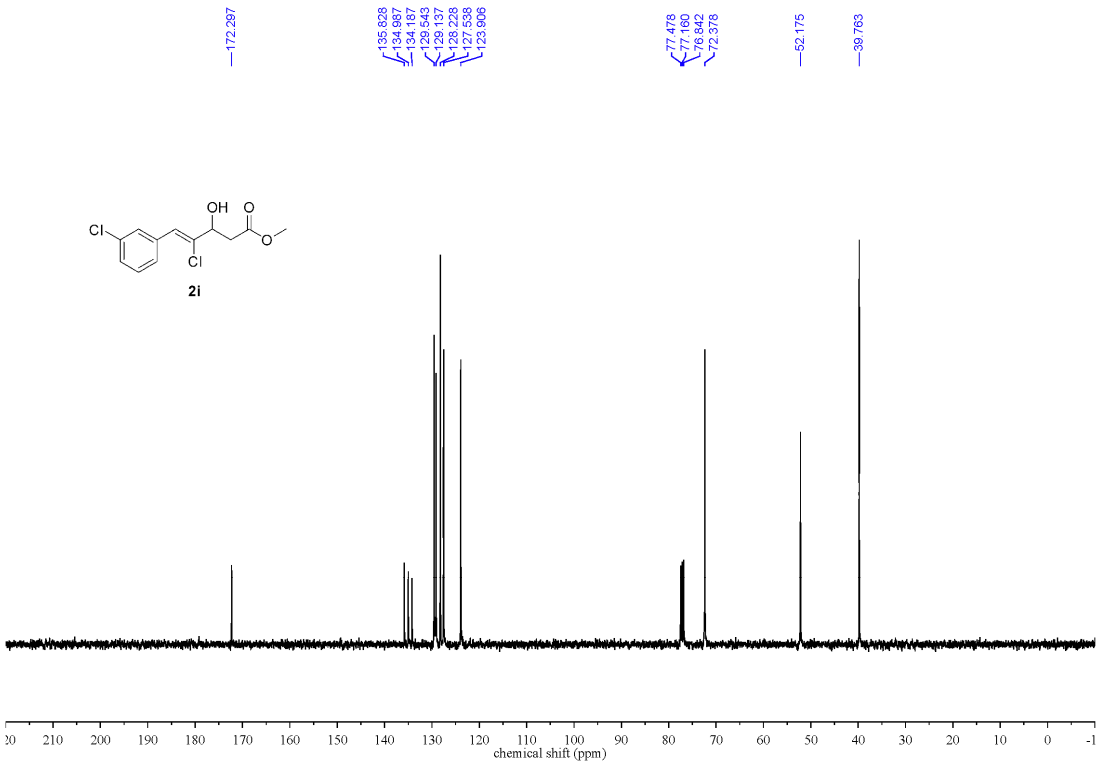
(*Z*)-Methyl 4-chloro-5-(4-chlorophenyl)-3-hydroxypent-4-enoate (2h)



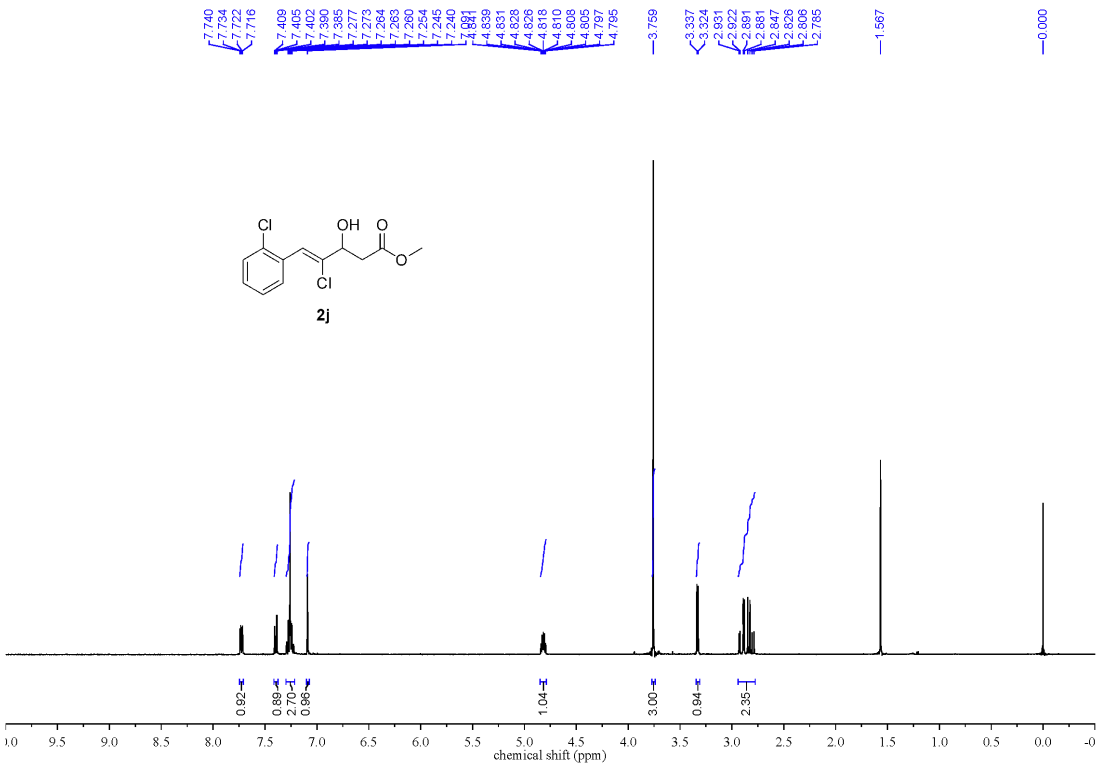


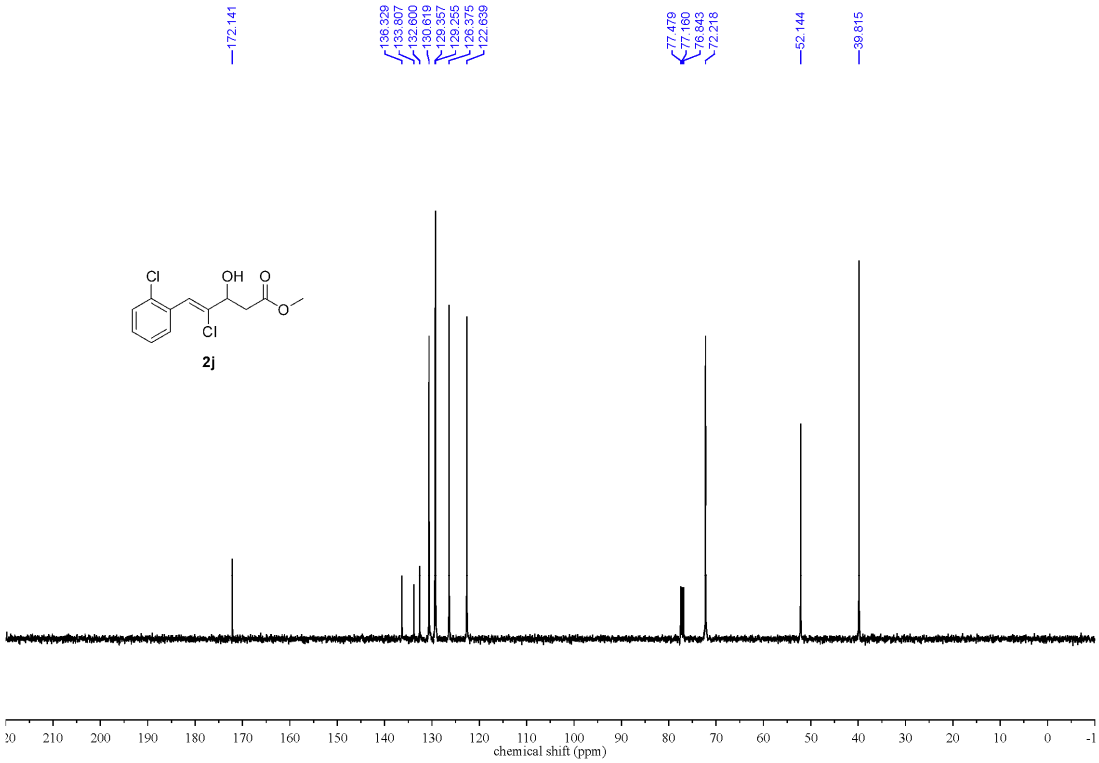
(*Z*)-Methyl 4-chloro-5-(3-chlorophenyl)-3-hydroxypent-4-enoate (2i)



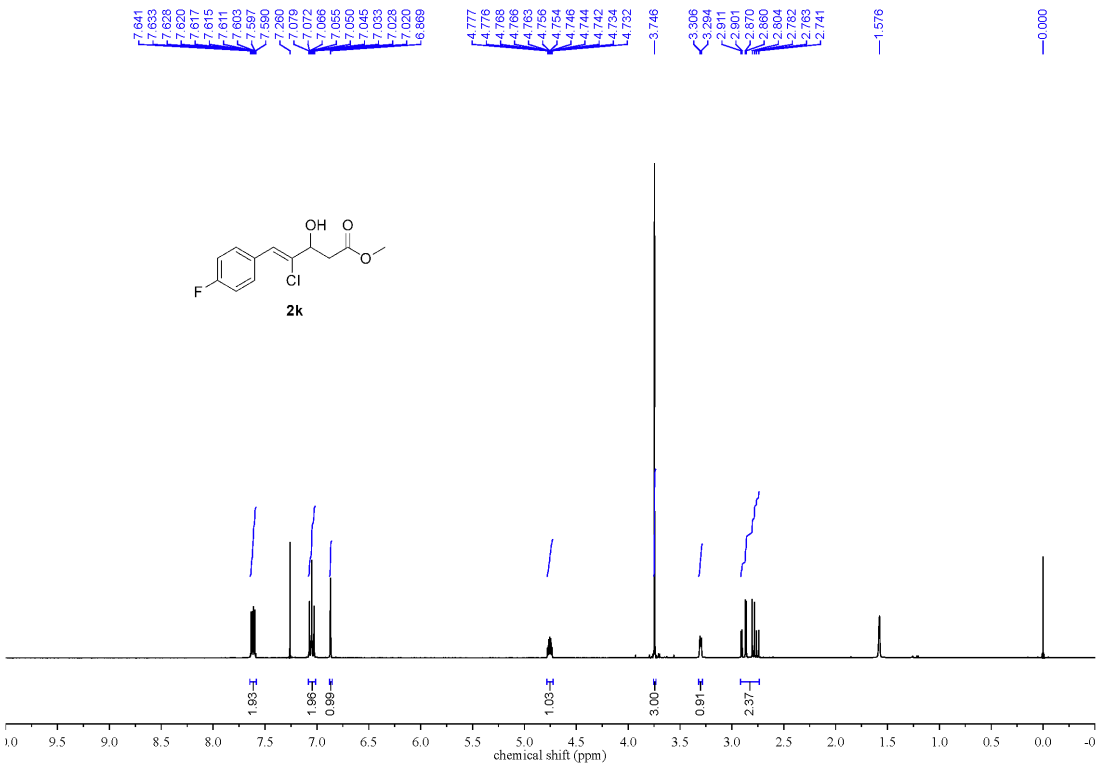


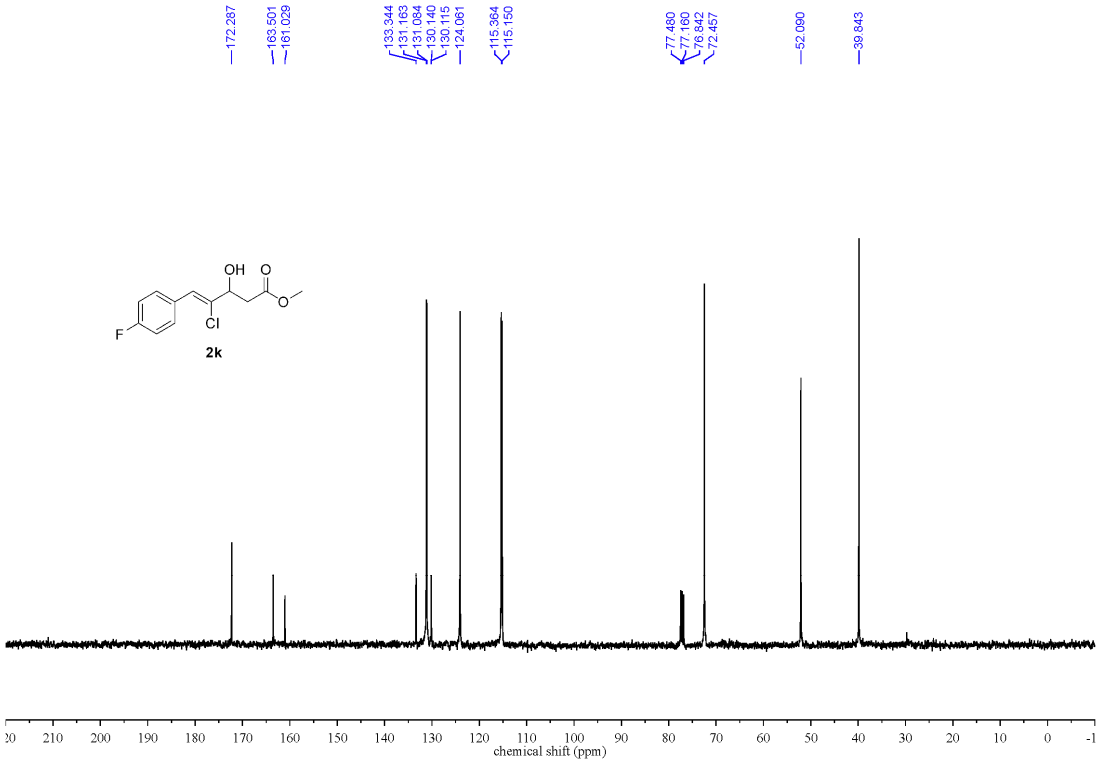
(*Z*)-Methyl 4-chloro-5-(2-chlorophenyl)-3-hydroxypent-4-enoate (2j)



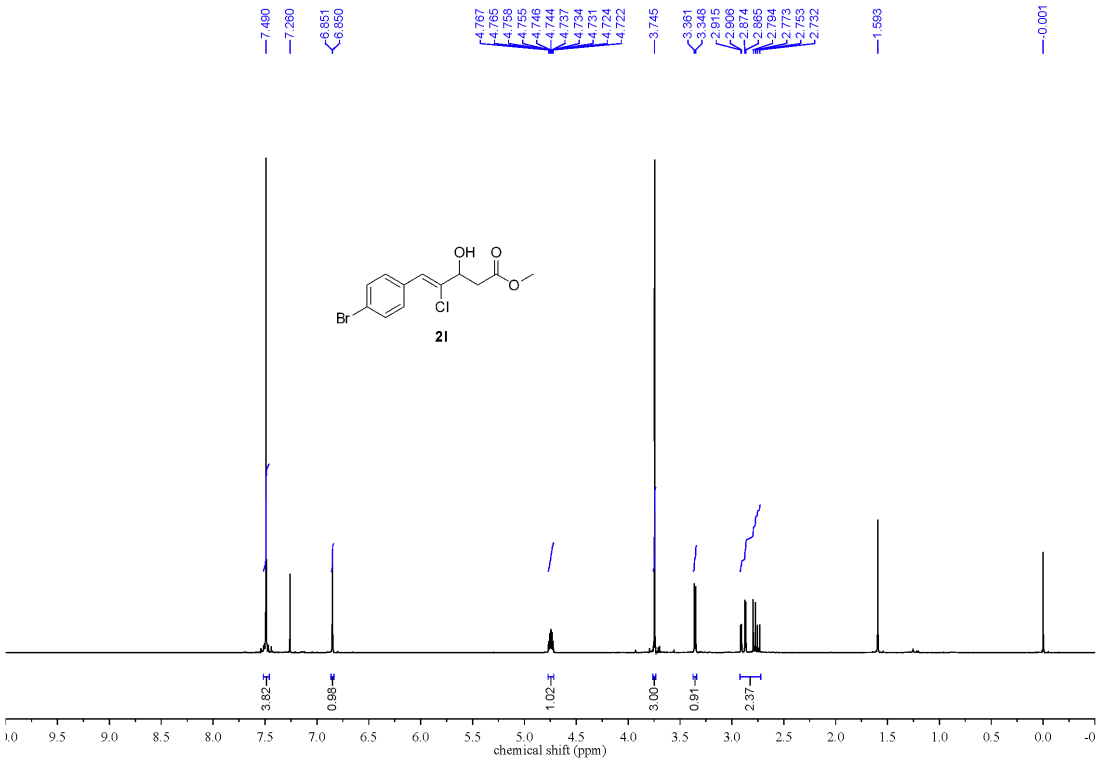


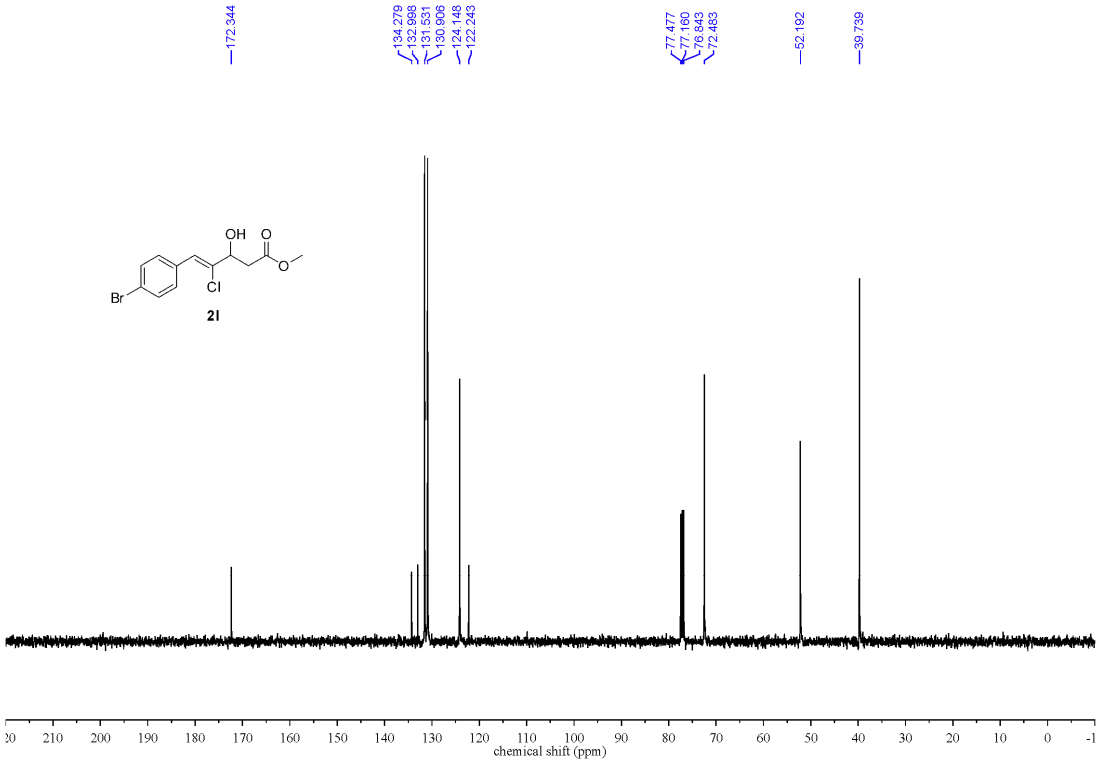
(*Z*)-Methyl 4-chloro-5-(4-fluorophenyl)-3-hydroxypent-4-enoate (2k)



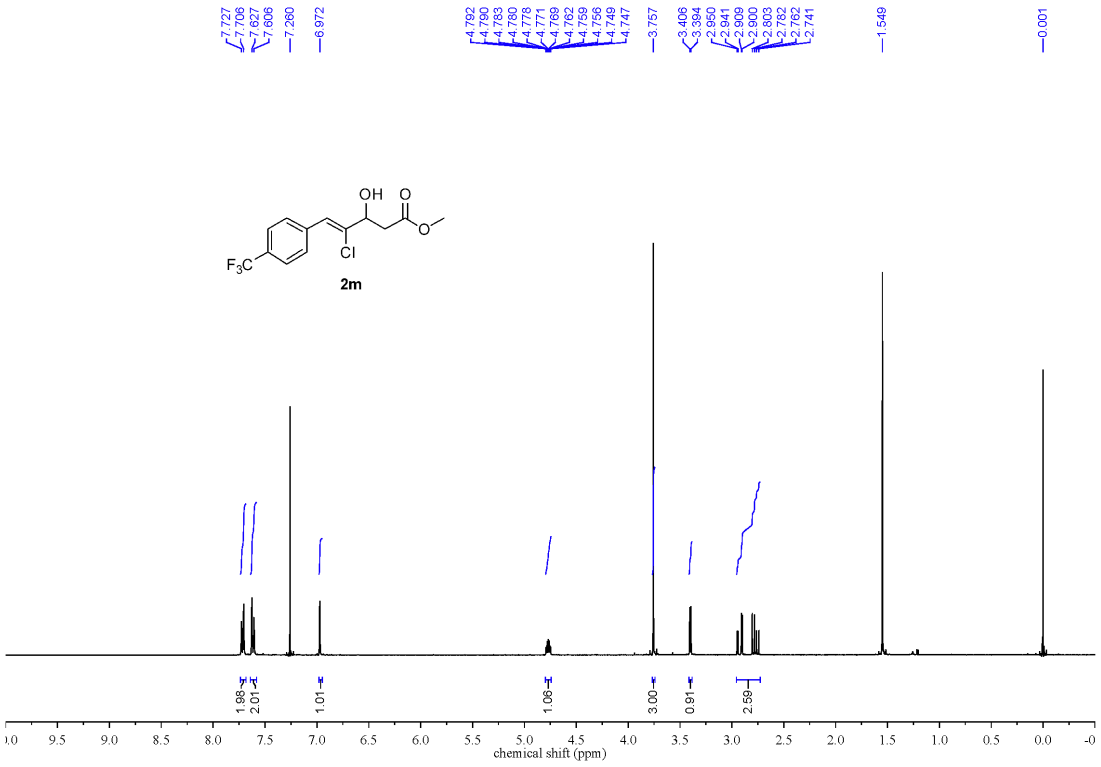


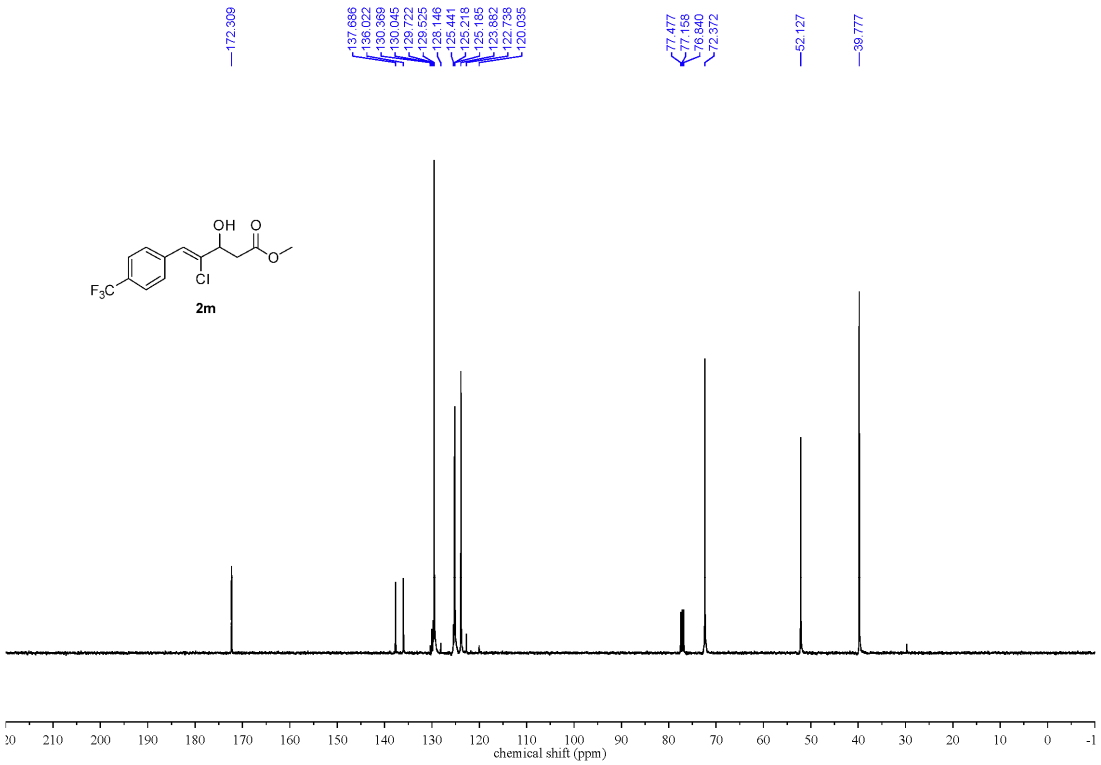
(*Z*)-Methyl 5-(4-bromophenyl)-4-chloro-3-hydroxypent-4-enoate (2l)



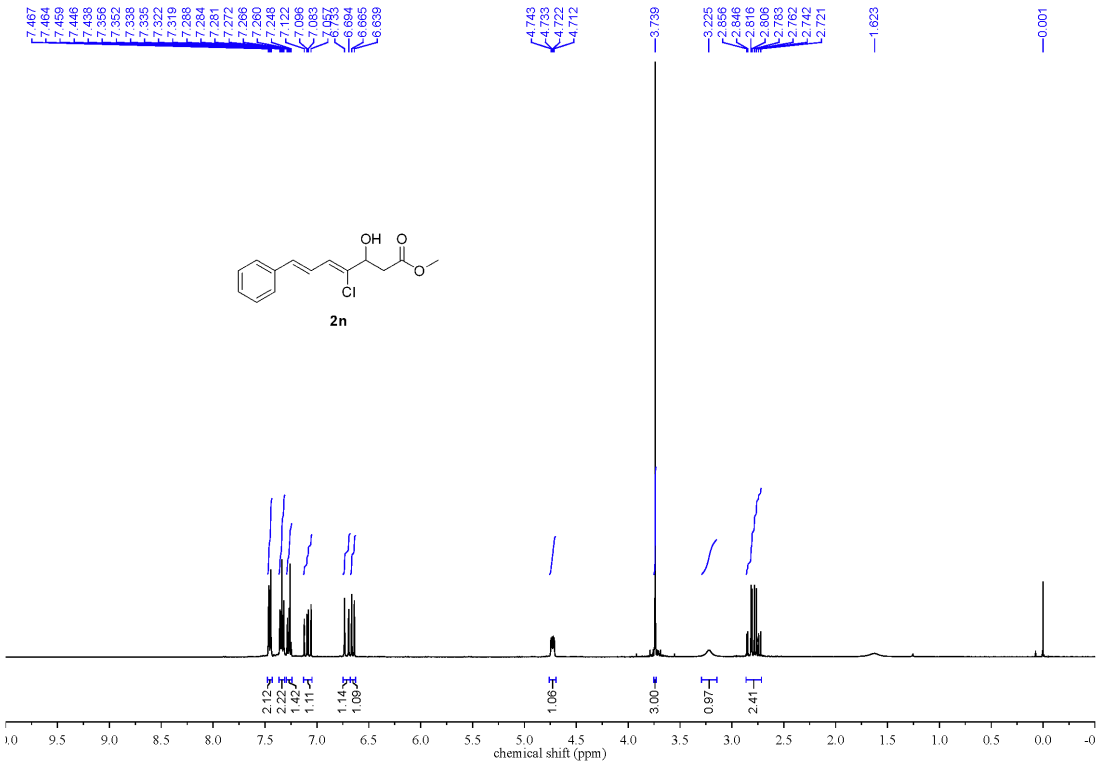


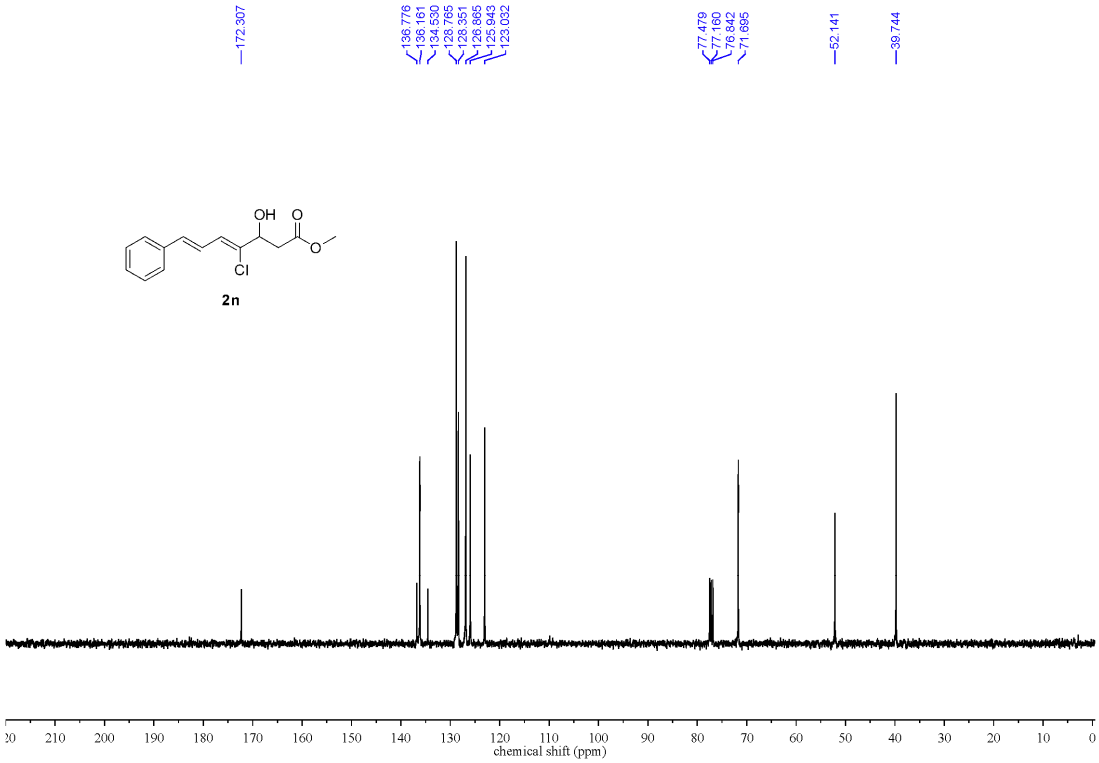
(*Z*)-Methyl 4-chloro-3-hydroxy-5-(4-(trifluoromethyl)phenyl)pent-4-enoate (2m)



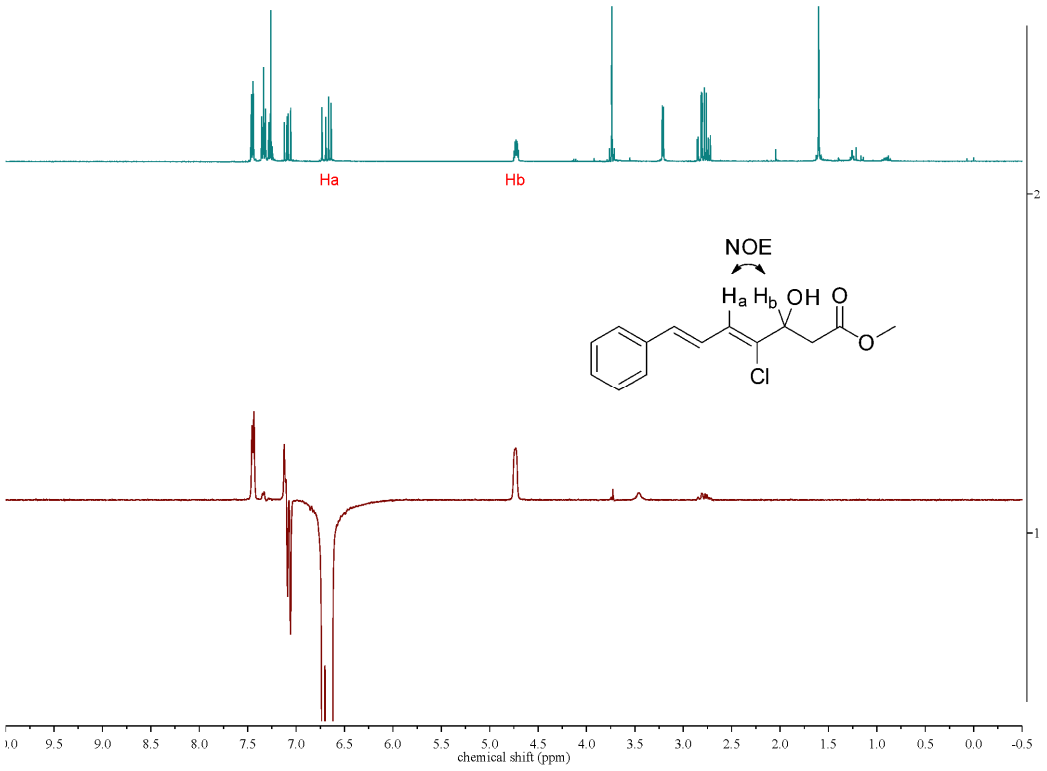


(4*Z*,6*E*)-Methyl 4-chloro-3-hydroxy-7-phenylhepta-4,6-dienoate (2n)

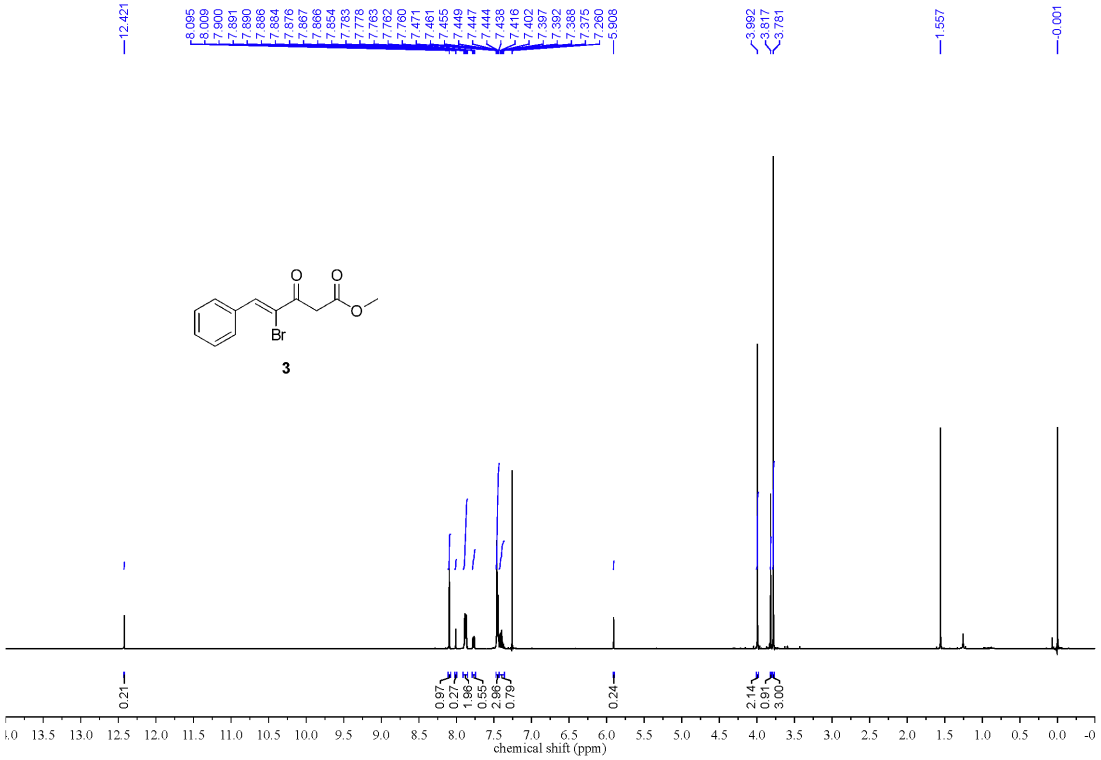


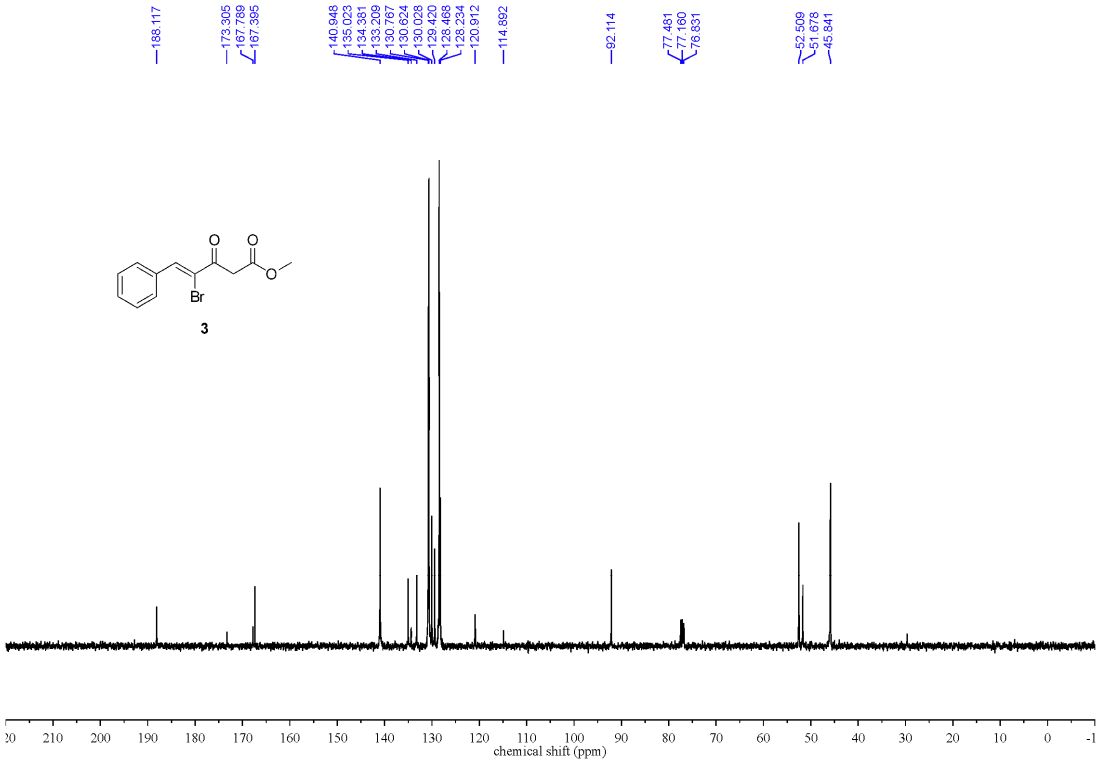


1D-NOE: irradiate on H_a

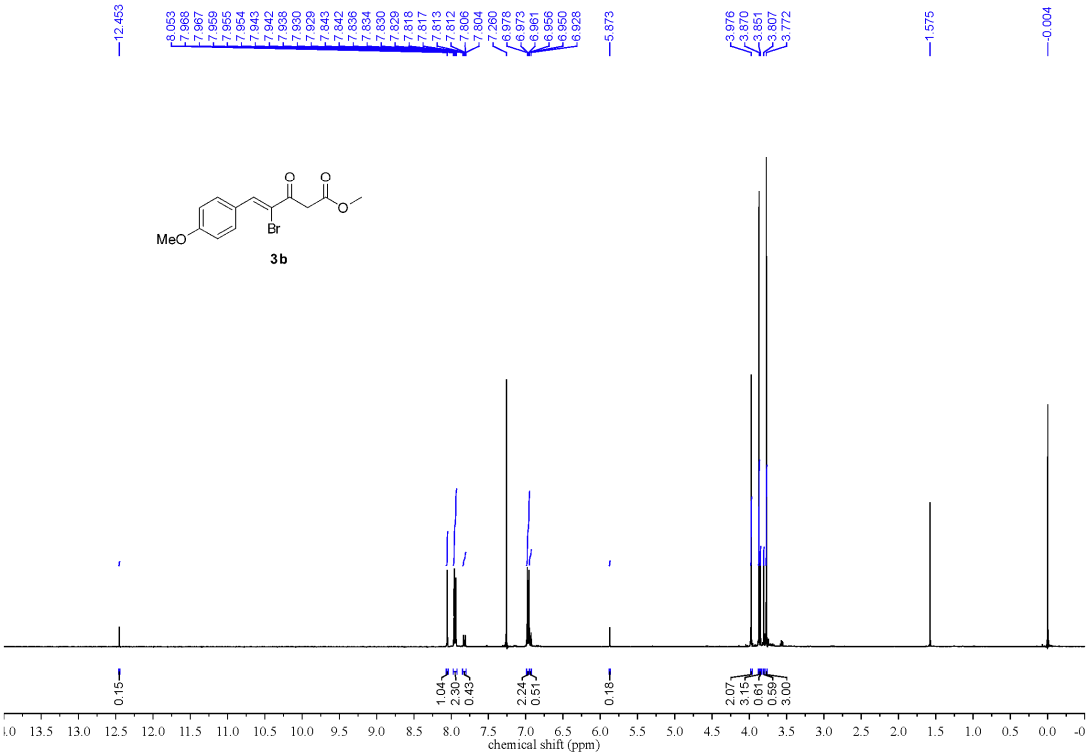


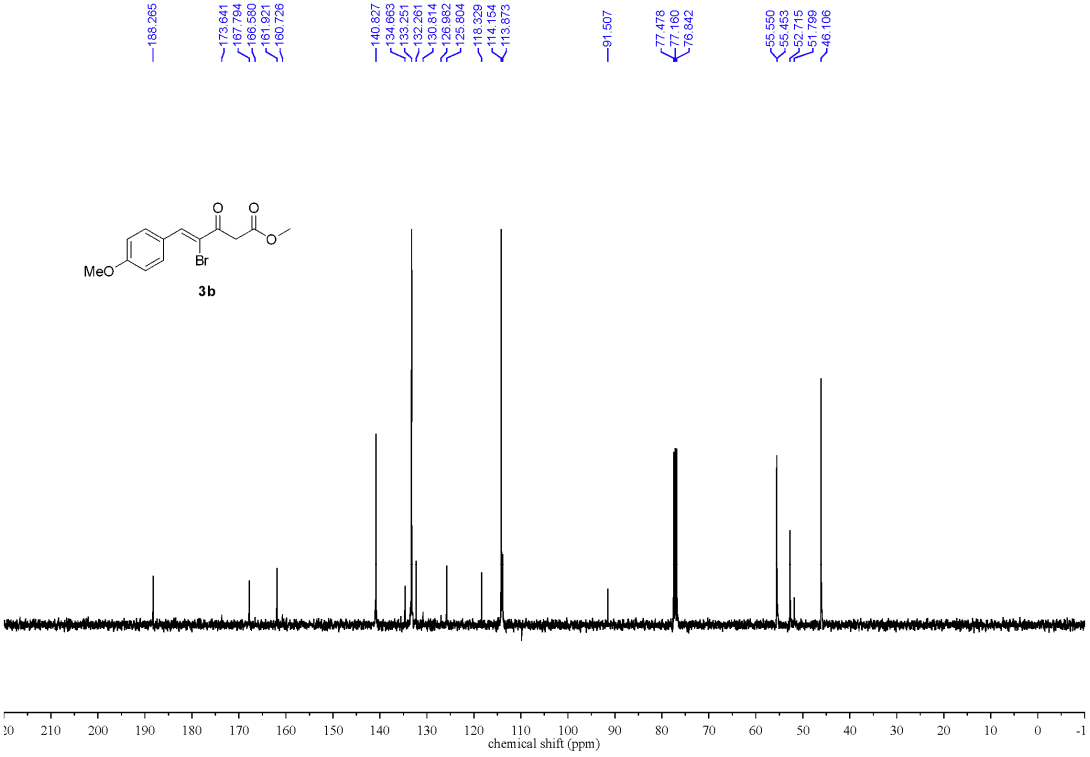
(*Z*)-Methyl 4-bromo-3-oxo-5-phenylpent-4-enoate (3a)



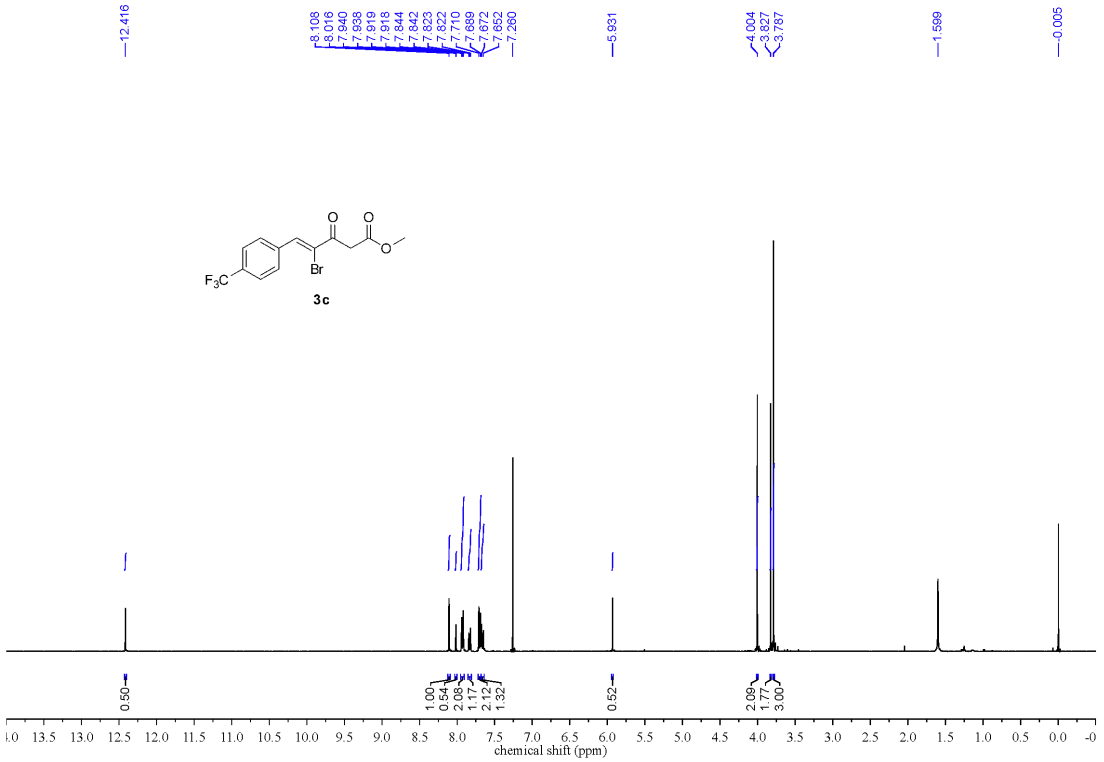


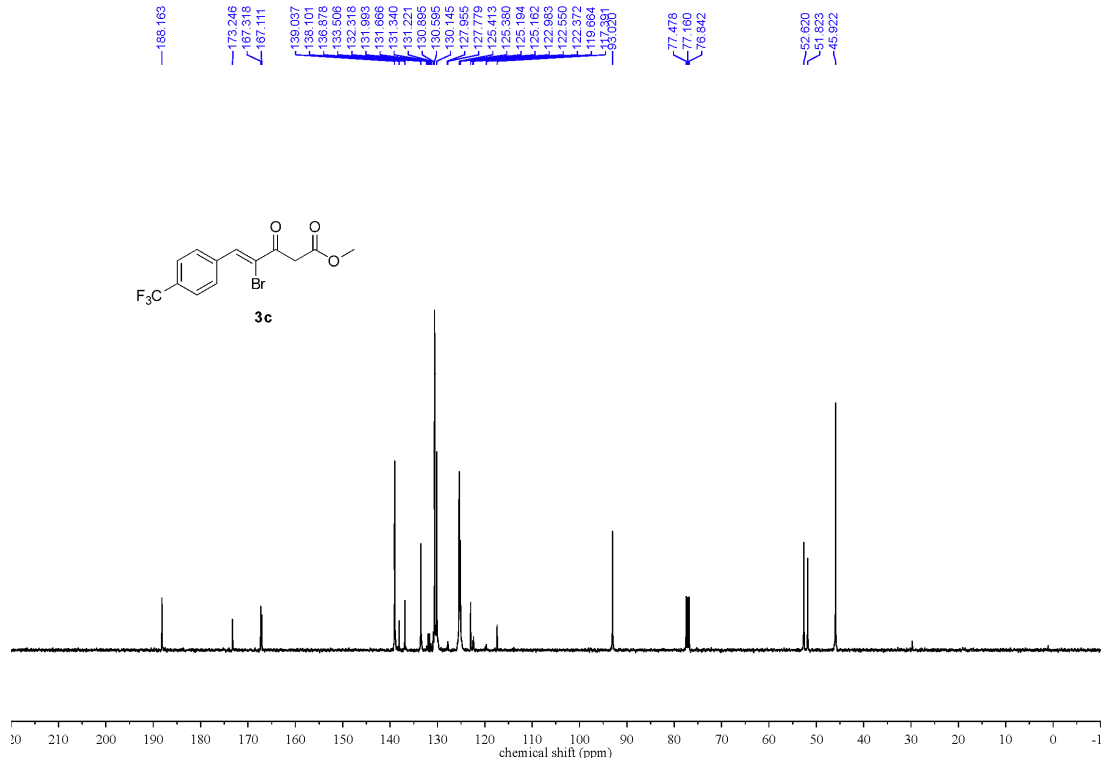
(*Z*)-Methyl 4-bromo-5-(4-methoxyphenyl)-3-oxopent-4-enoate (3b)



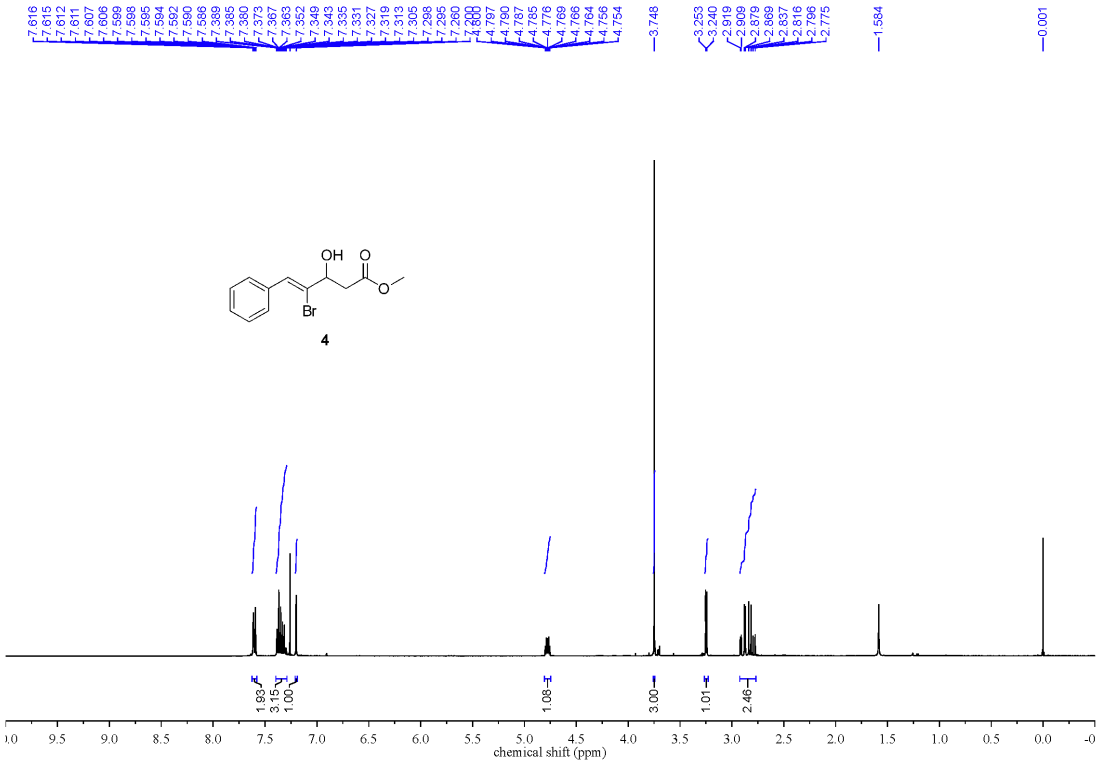


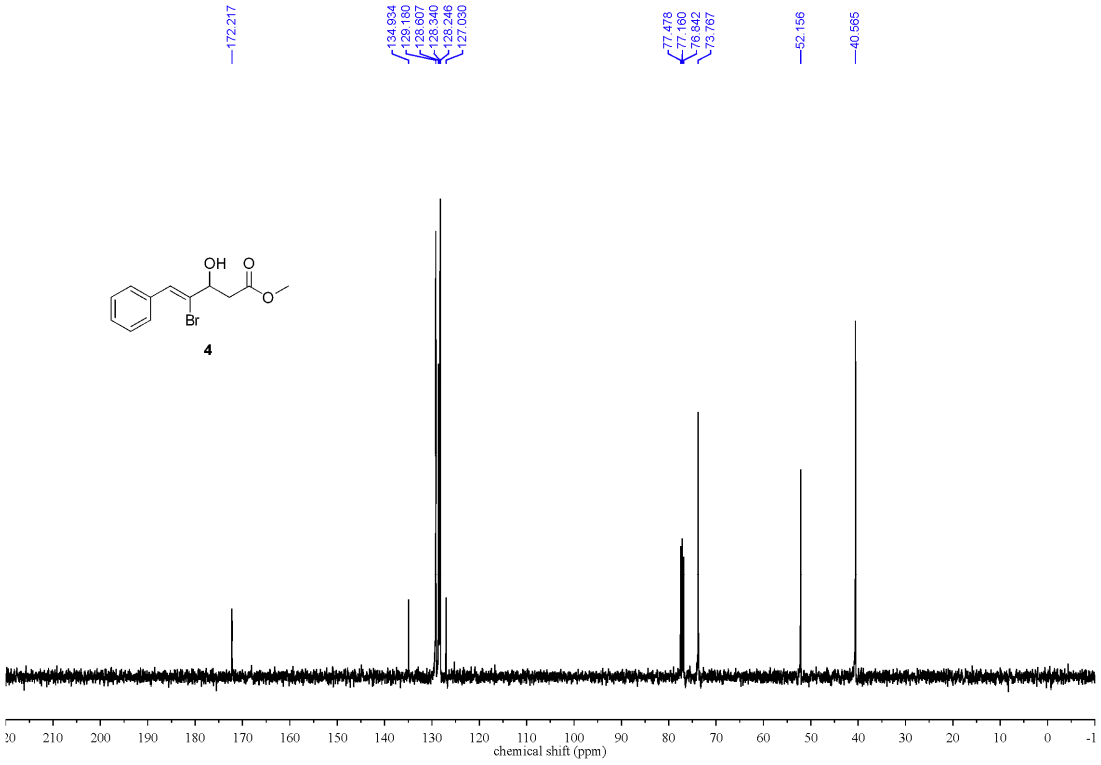
(*Z*)-Methyl 4-bromo-3-oxo-5-(4-(trifluoromethyl)phenyl)pent-4-enoate (3c)



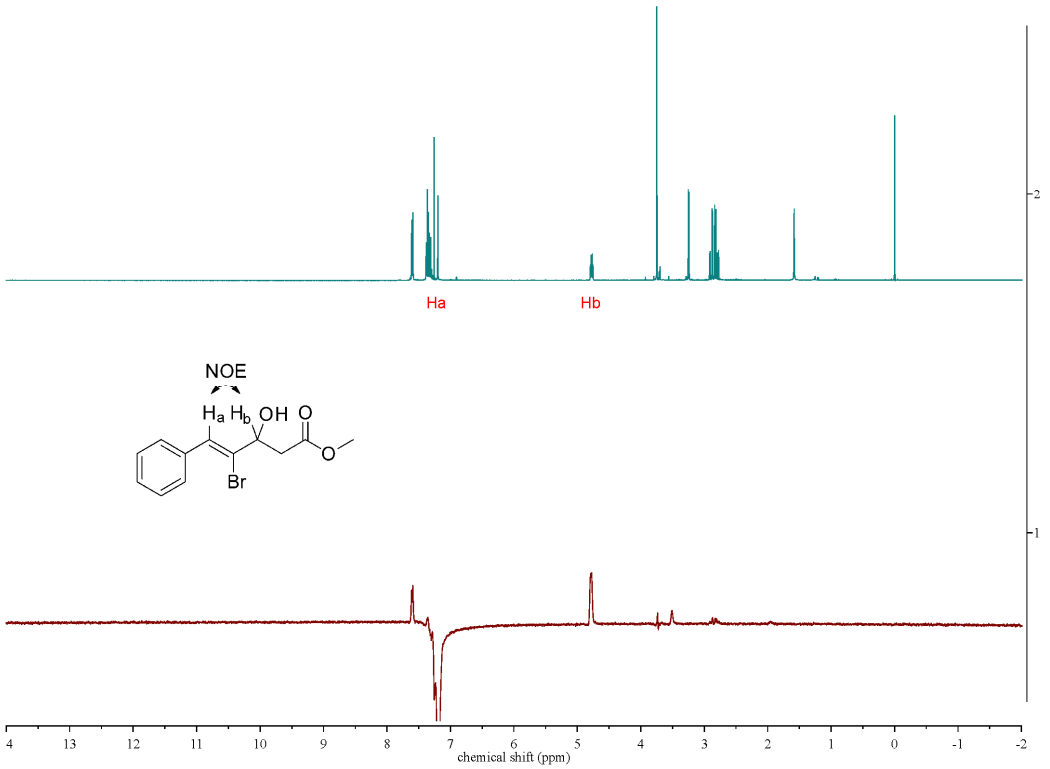


(*Z*)-Methyl 4-bromo-3-hydroxy-5-phenylpent-4-enoate (4a)

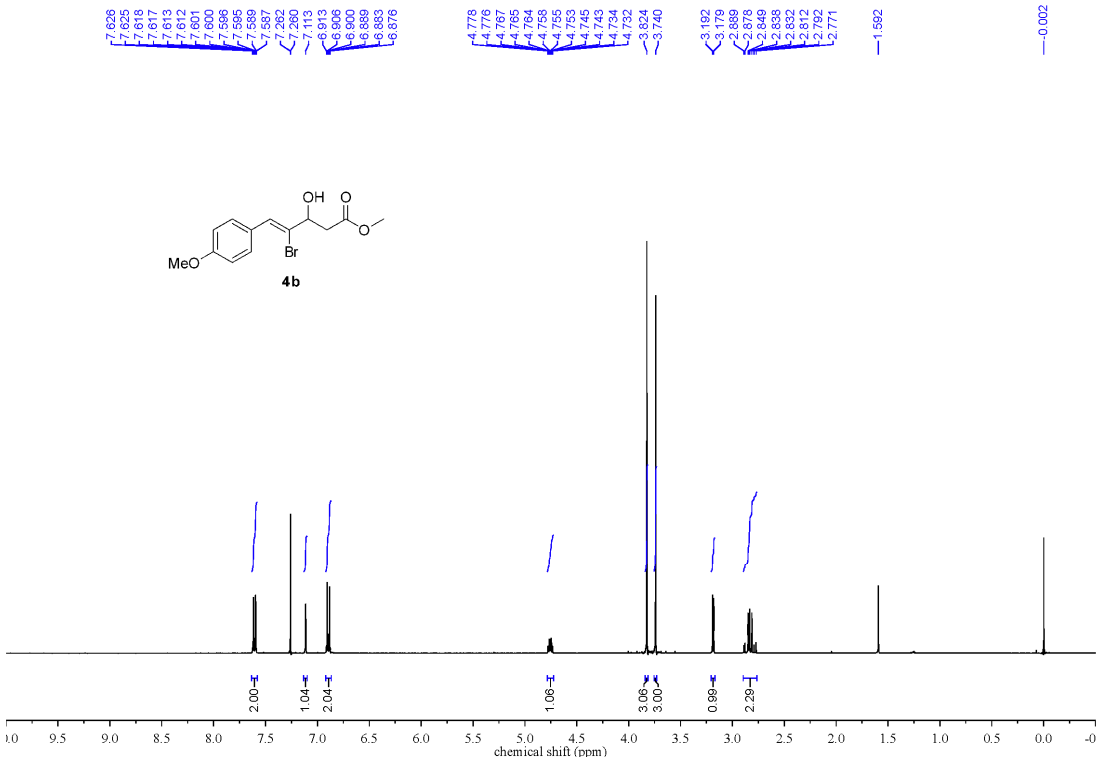


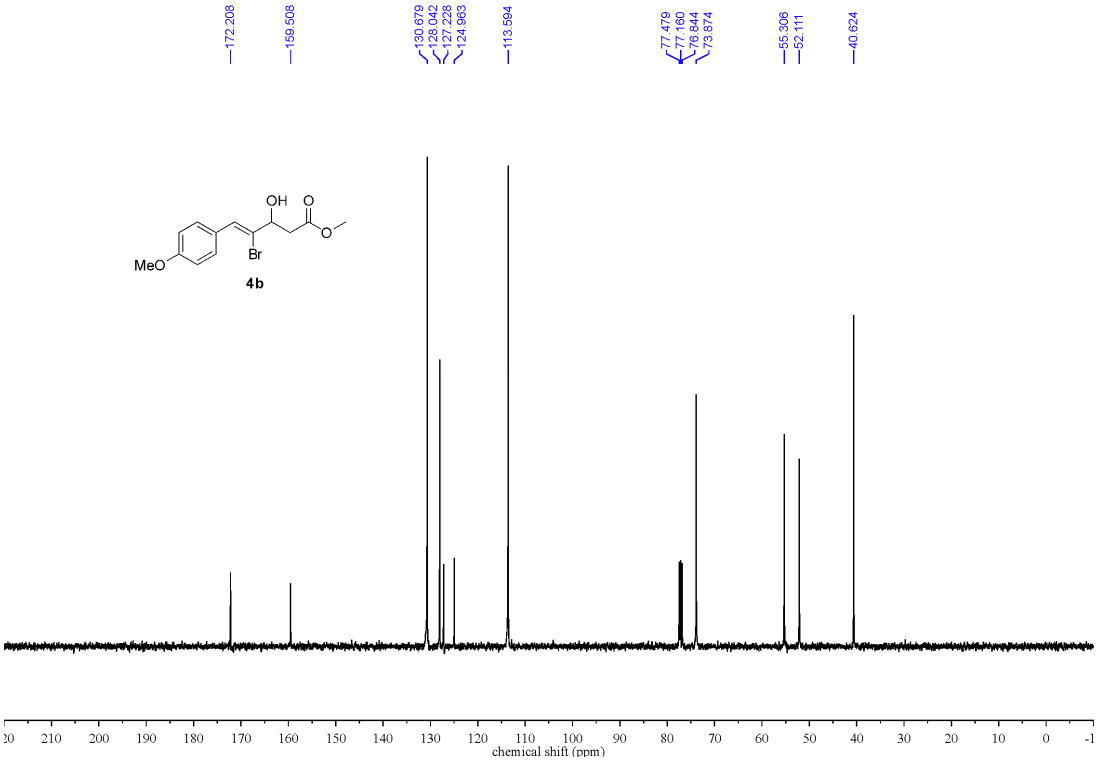


1D-NOE: irradiate on H_a

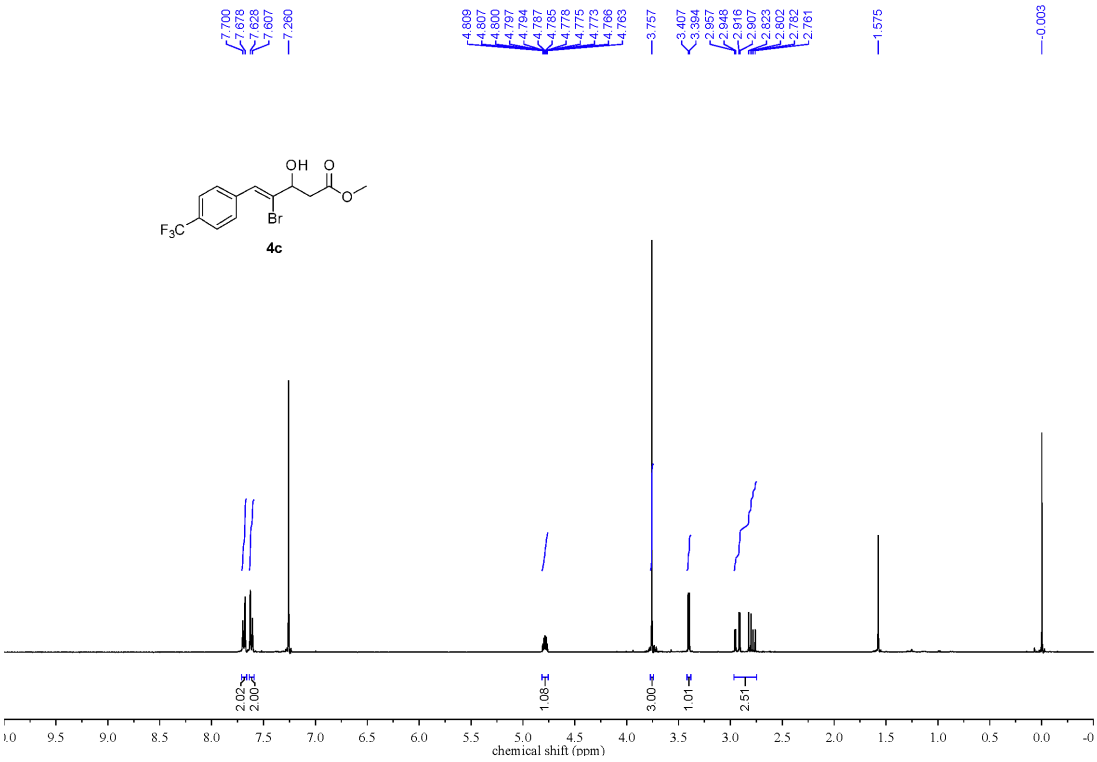


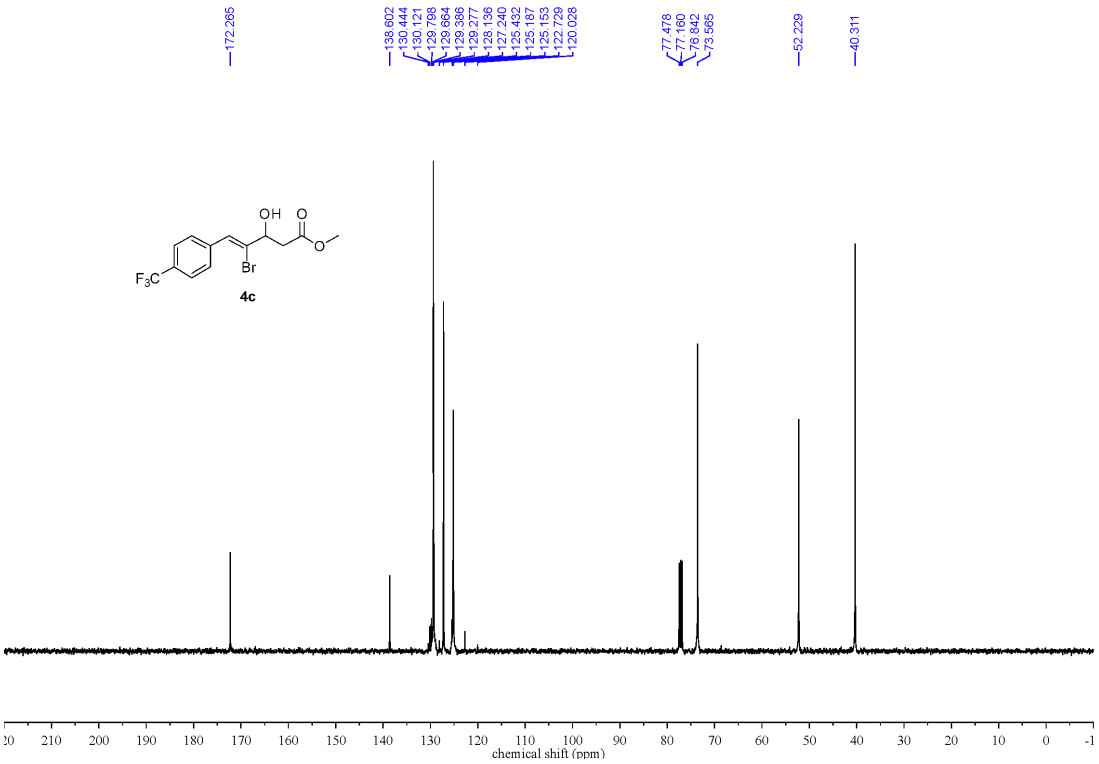
(*Z*)-Methyl 4-bromo-3-hydroxy-5-(4-methoxyphenyl)pent-4-enoate (4b)



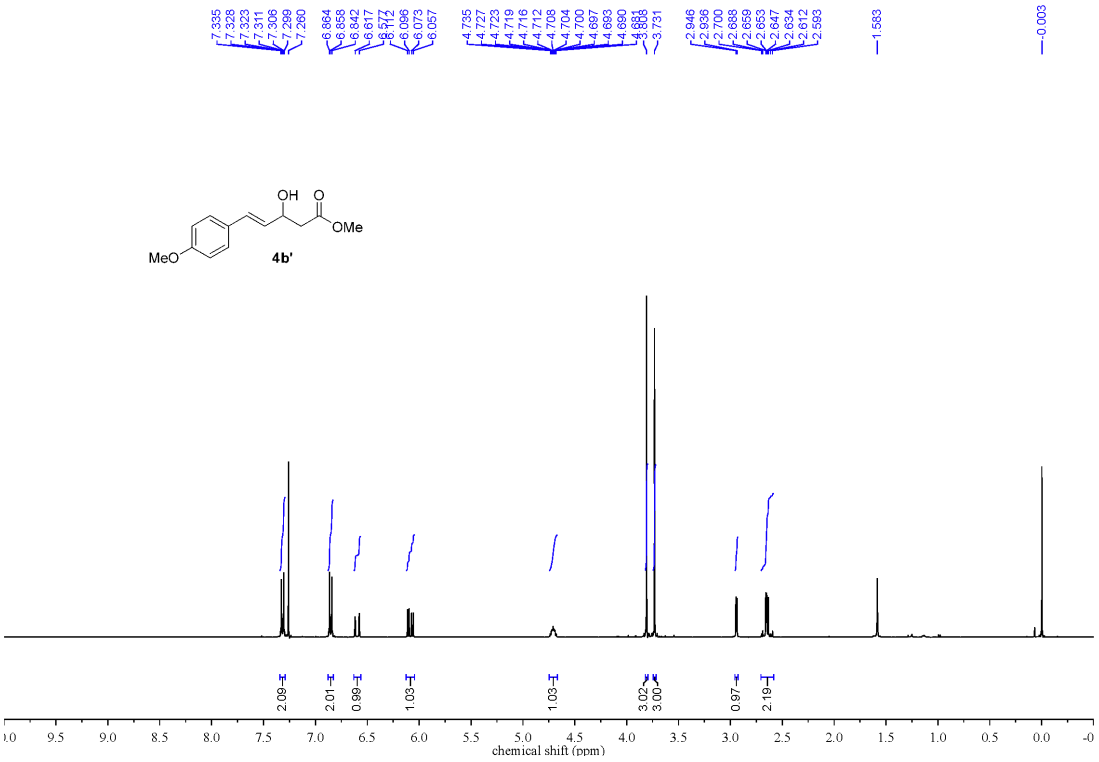


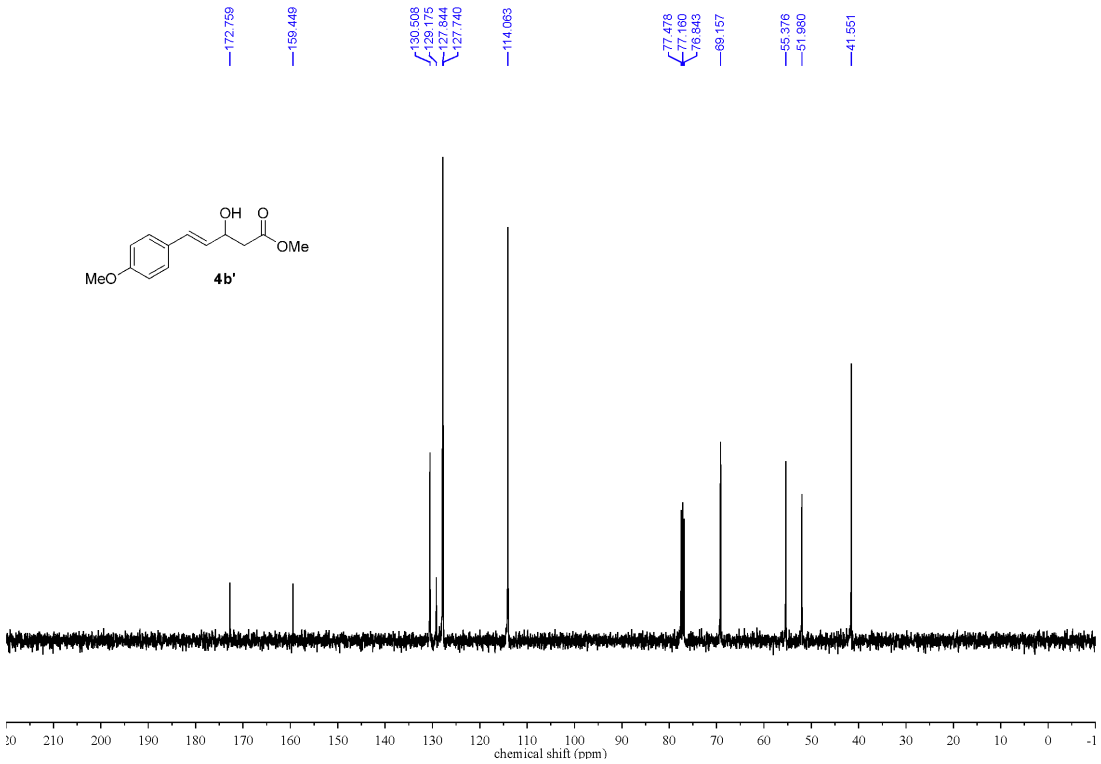
(*Z*)-Methyl 4-bromo-3-hydroxy-5-(4-(trifluoromethyl)phenyl)pent-4-enoate (4c)



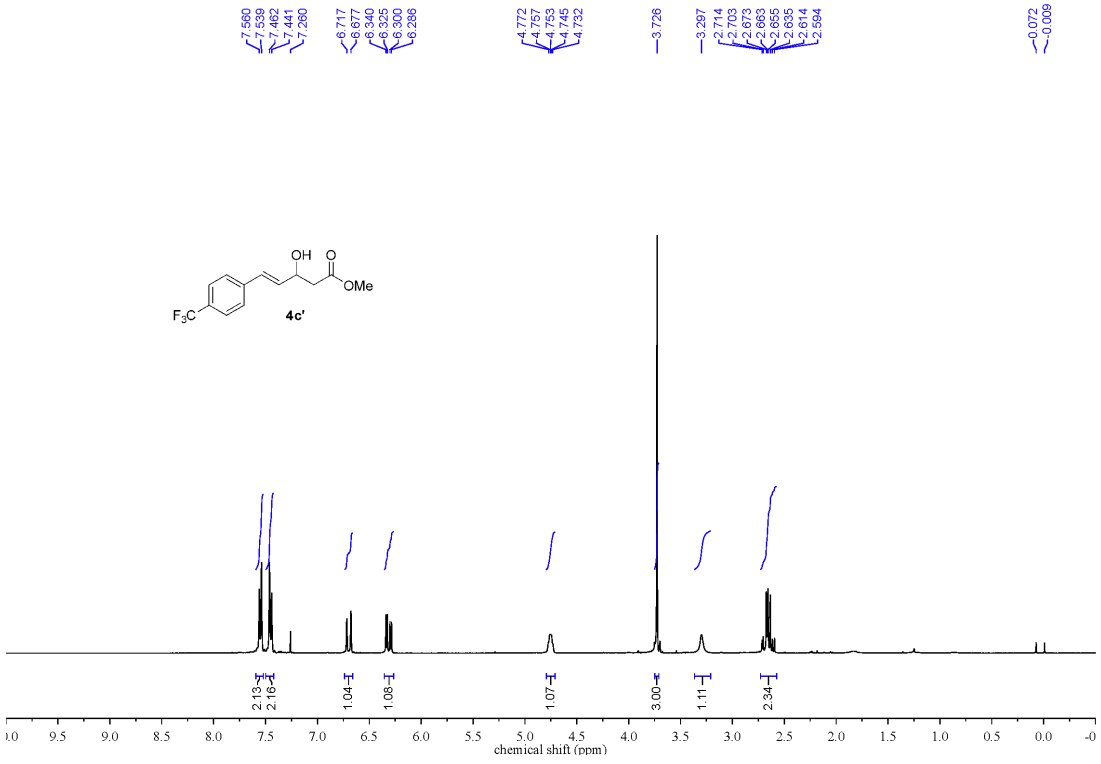


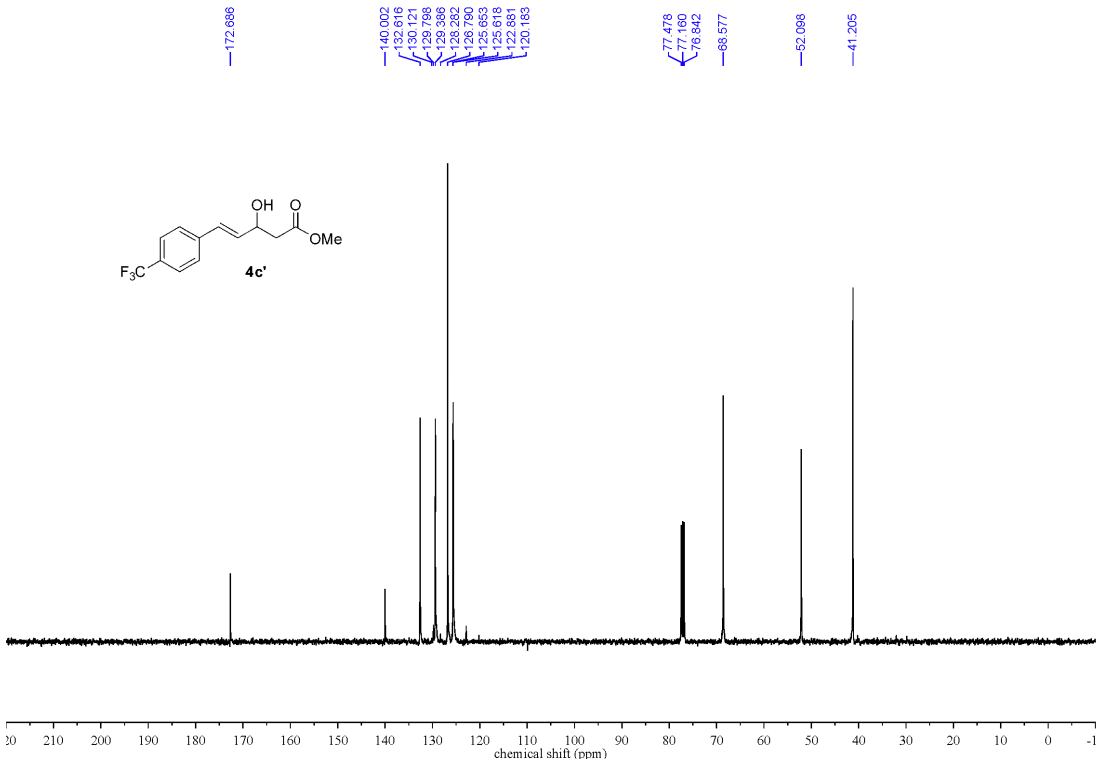
(*E*)-Methyl 3-hydroxy-5-(4-methoxyphenyl)pent-4-enoate (4b')



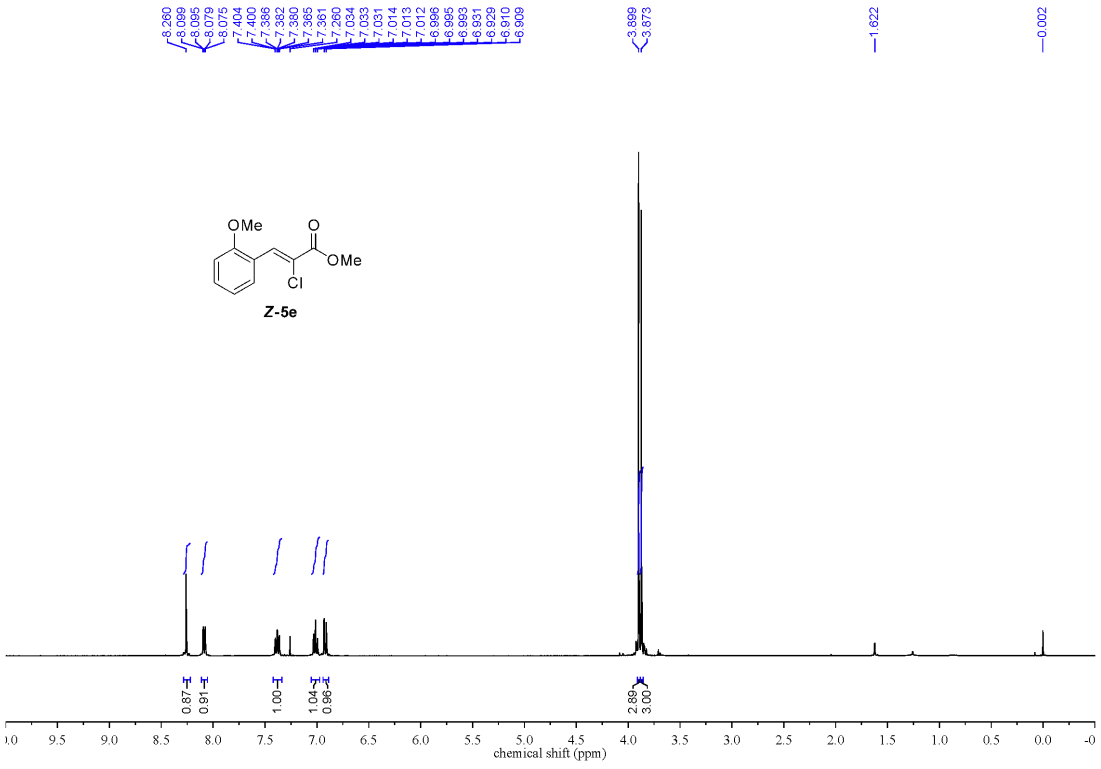


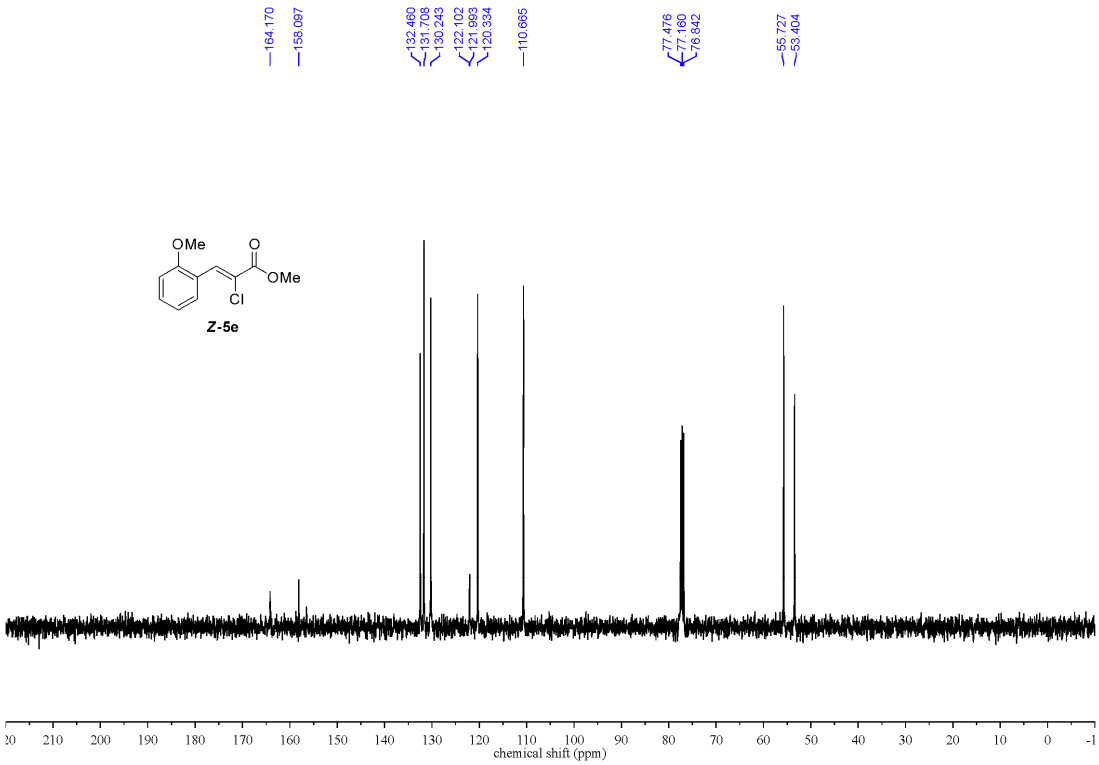
(*E*)-Methyl 3-hydroxy-5-(4-(trifluoromethyl)phenyl)pent-4-enoate (4c')



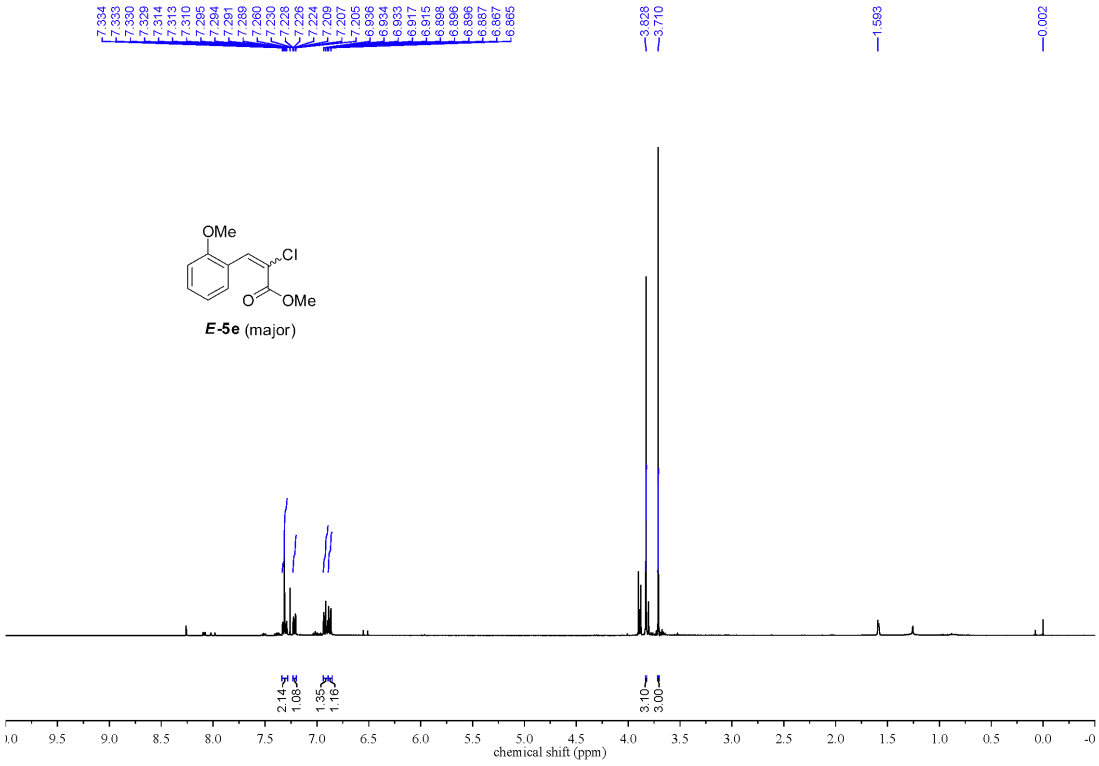


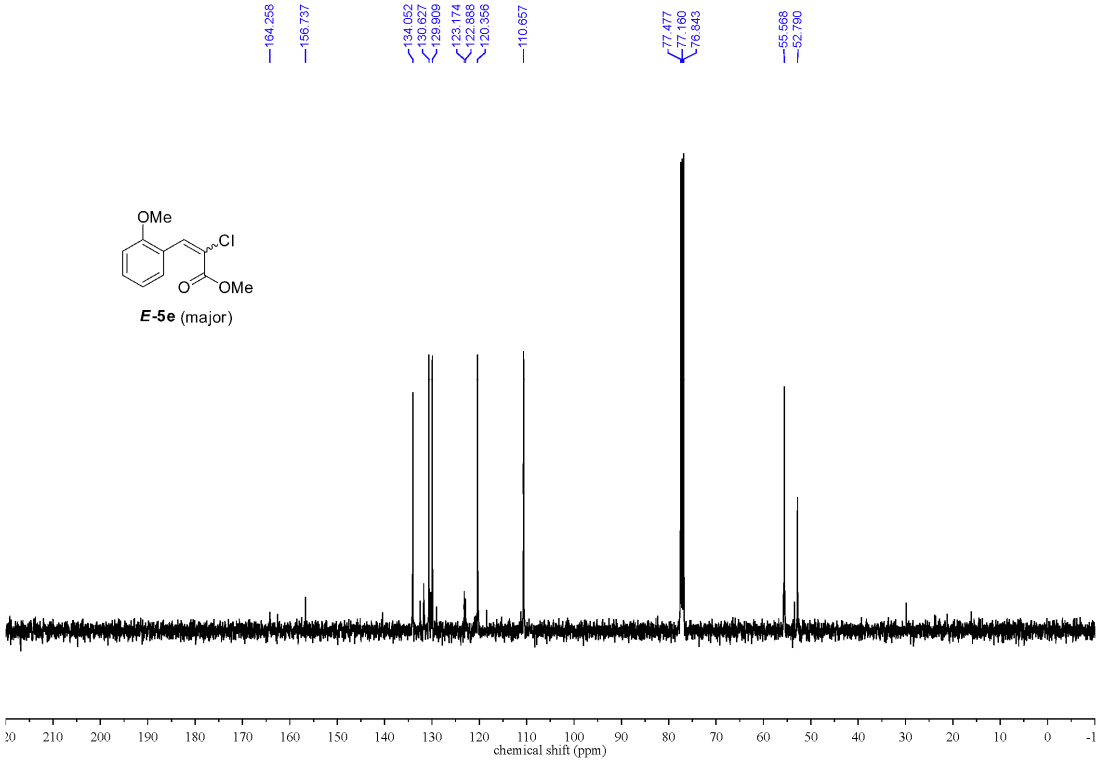
(*Z*)-Methyl 2-chloro-3-(2-methoxyphenyl)acrylate (*Z*-5e)



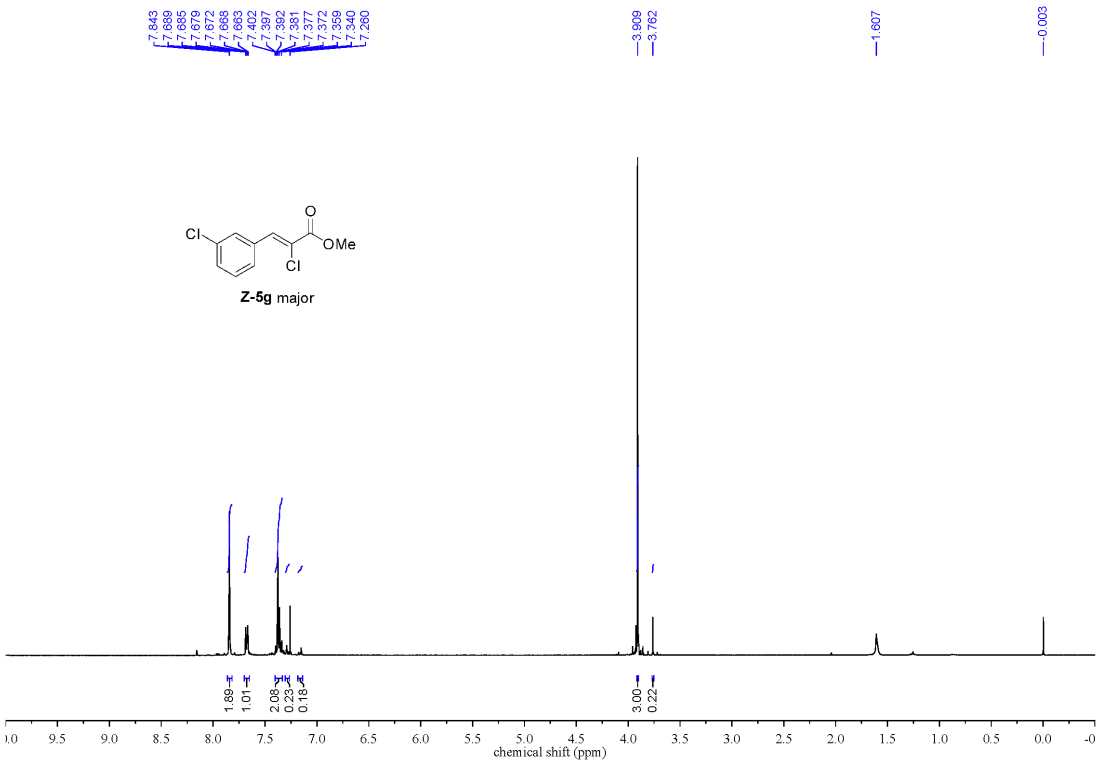


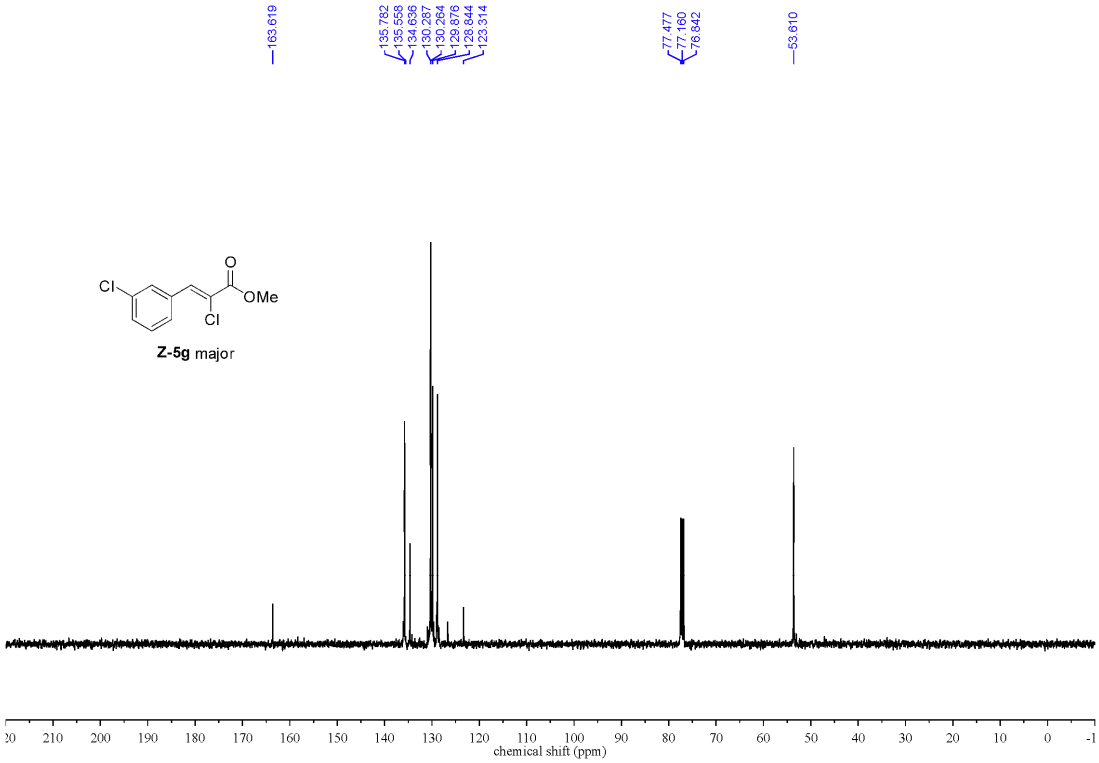
(*E*)-Methyl 2-chloro-3-(2-methoxyphenyl)acrylate (*E*-5e)



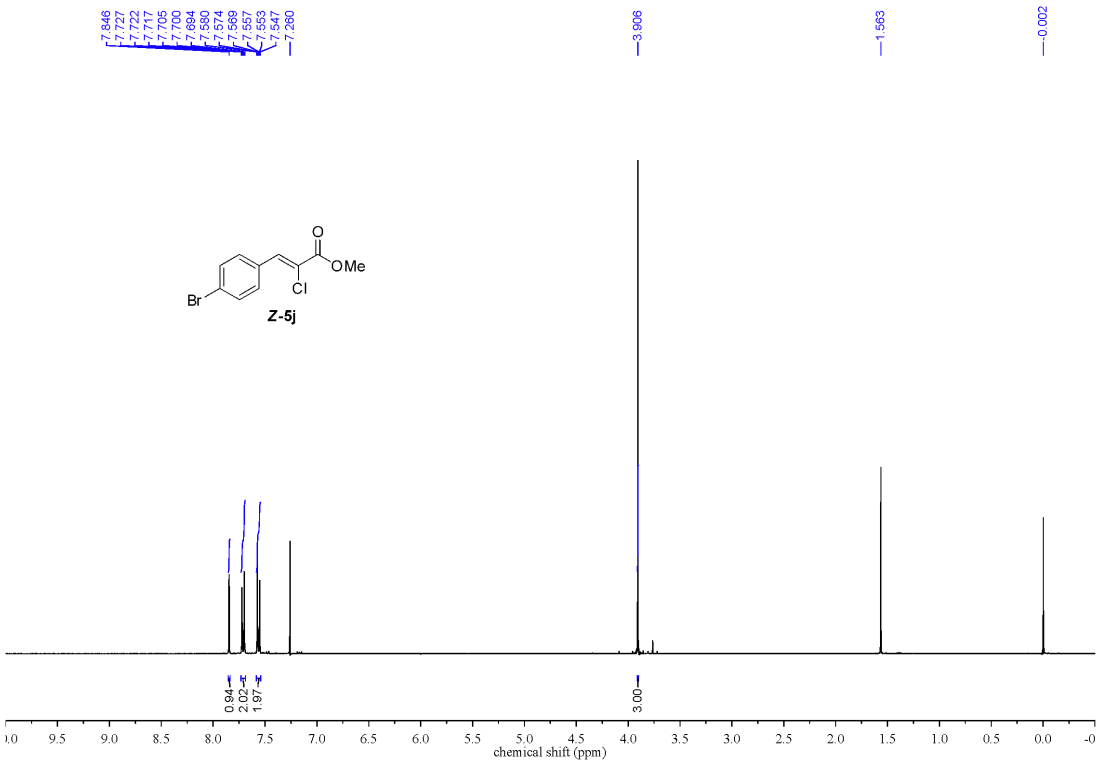


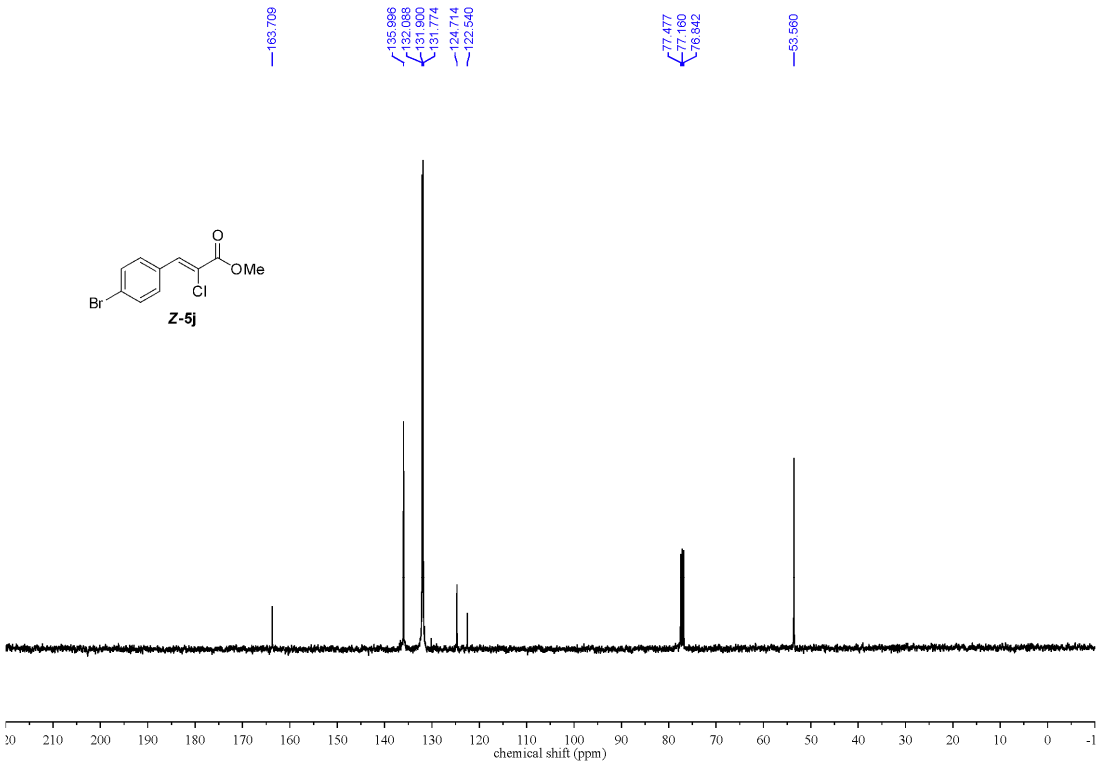
(*Z*)-Methyl 2-chloro-3-(3-chlorophenyl)acrylate (*Z*-5g)



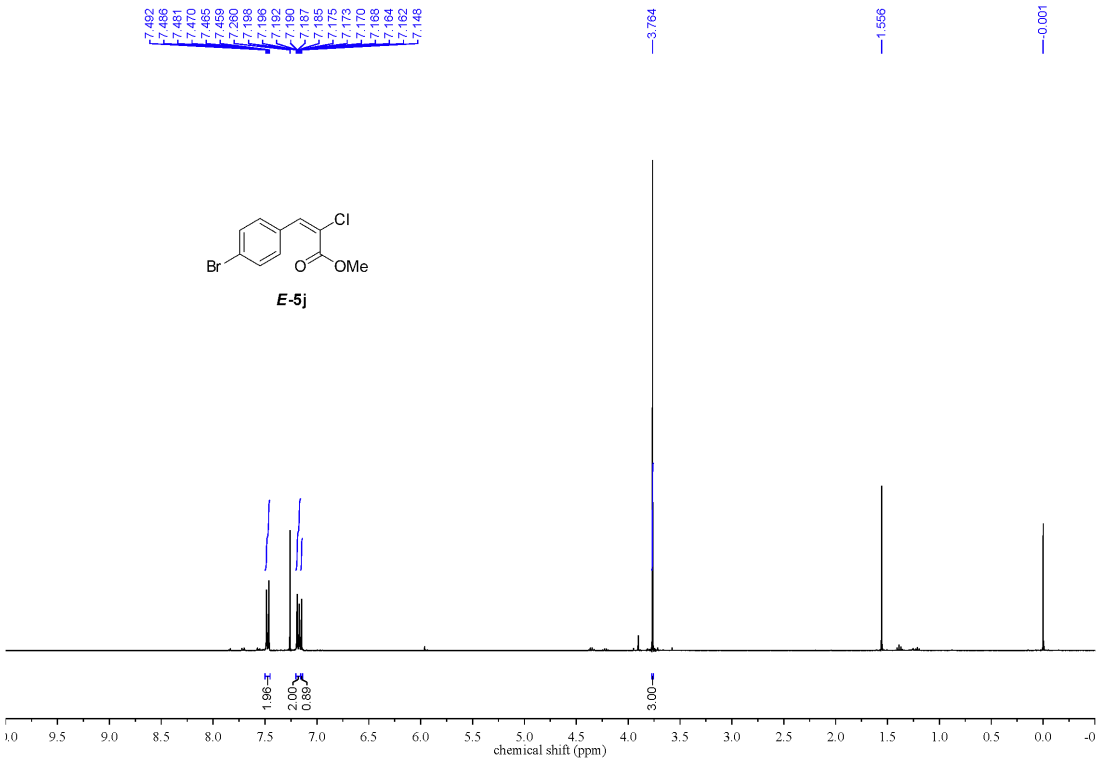


(*Z*)-Methyl 3-(4-bromophenyl)-2-chloroacrylate (*Z*-5j)

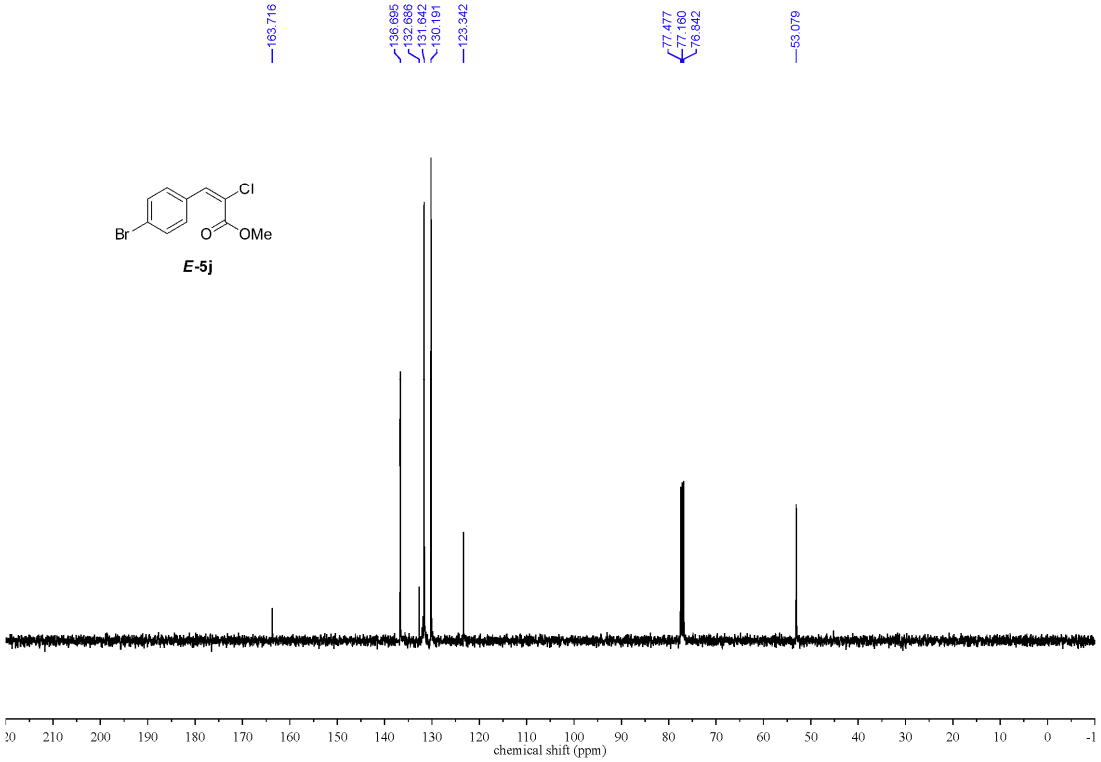




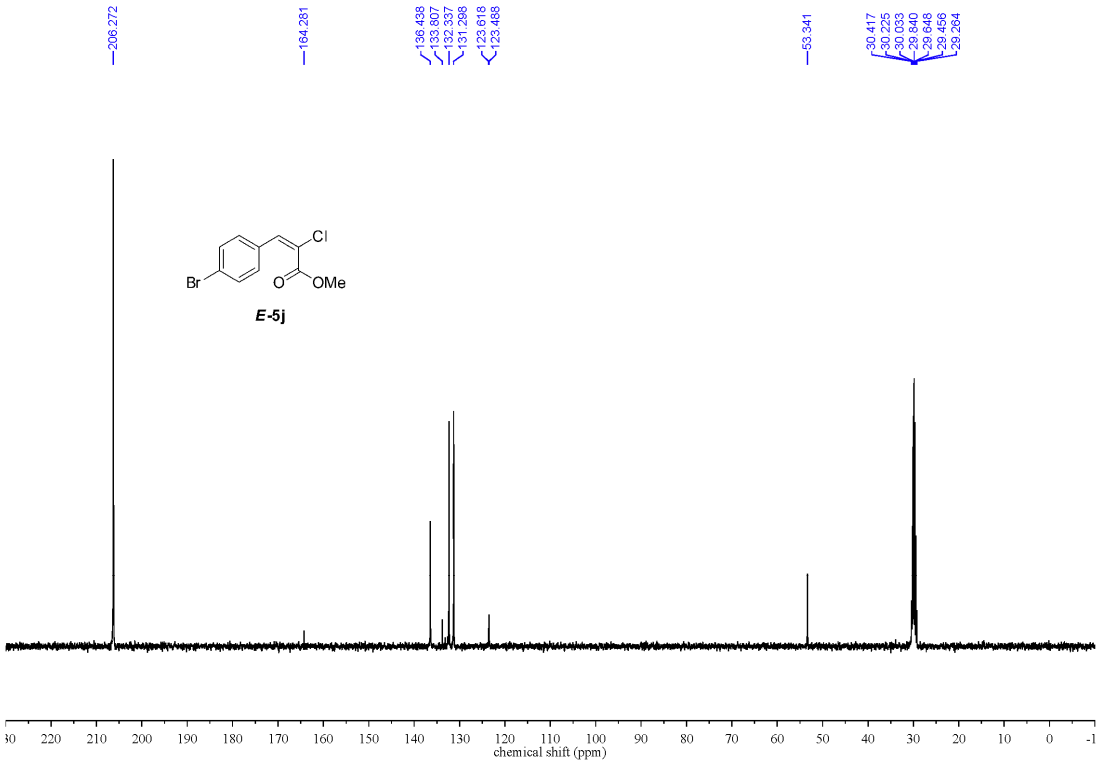
(*E*)-Methyl 3-(4-bromophenyl)-2-chloroacrylate (*E*-5j)



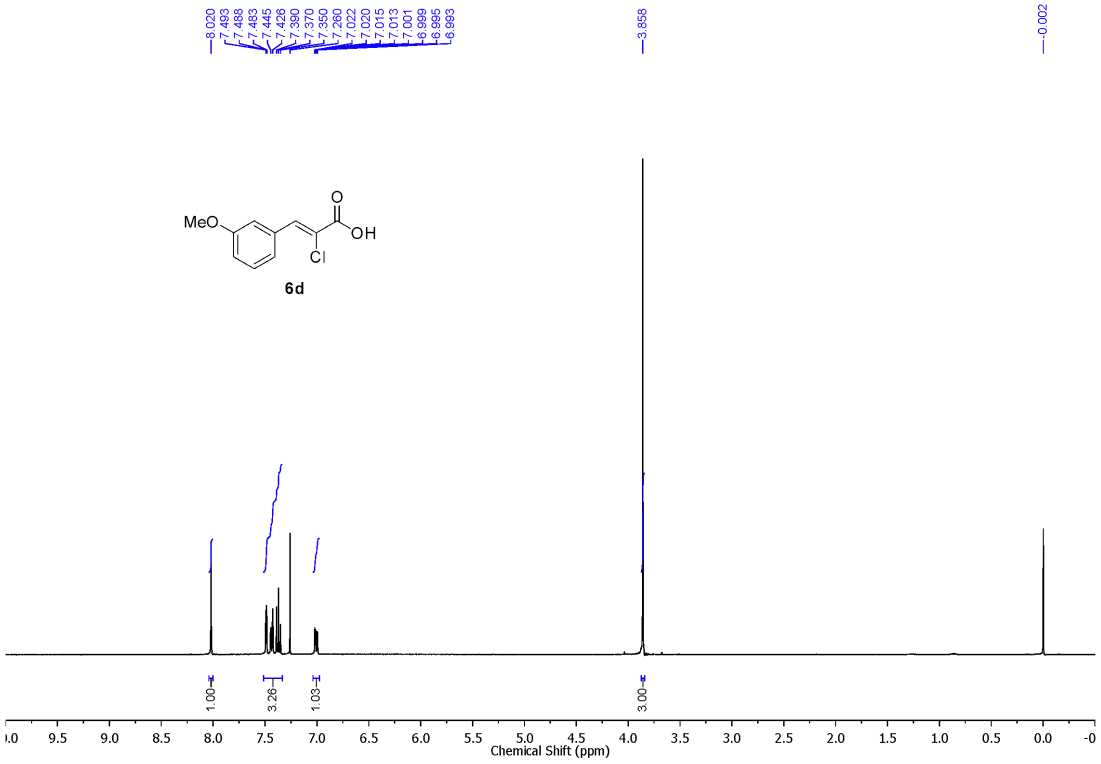
In $CDCl_3$

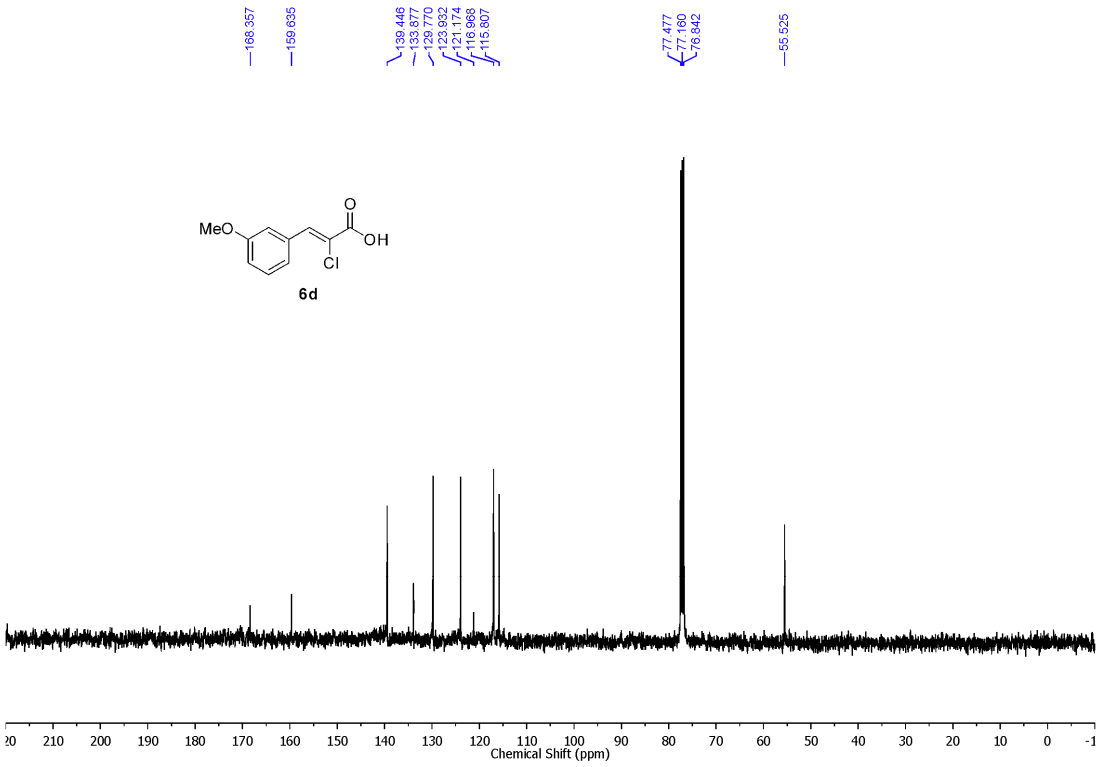


In acetone-d_6

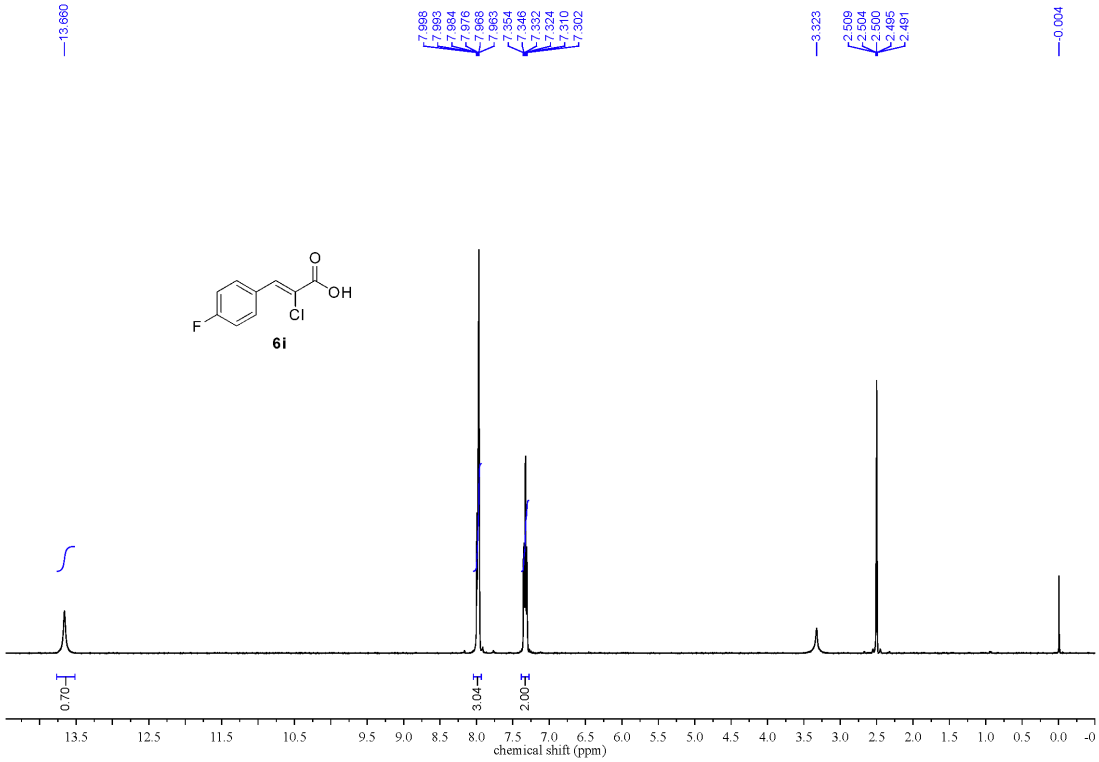


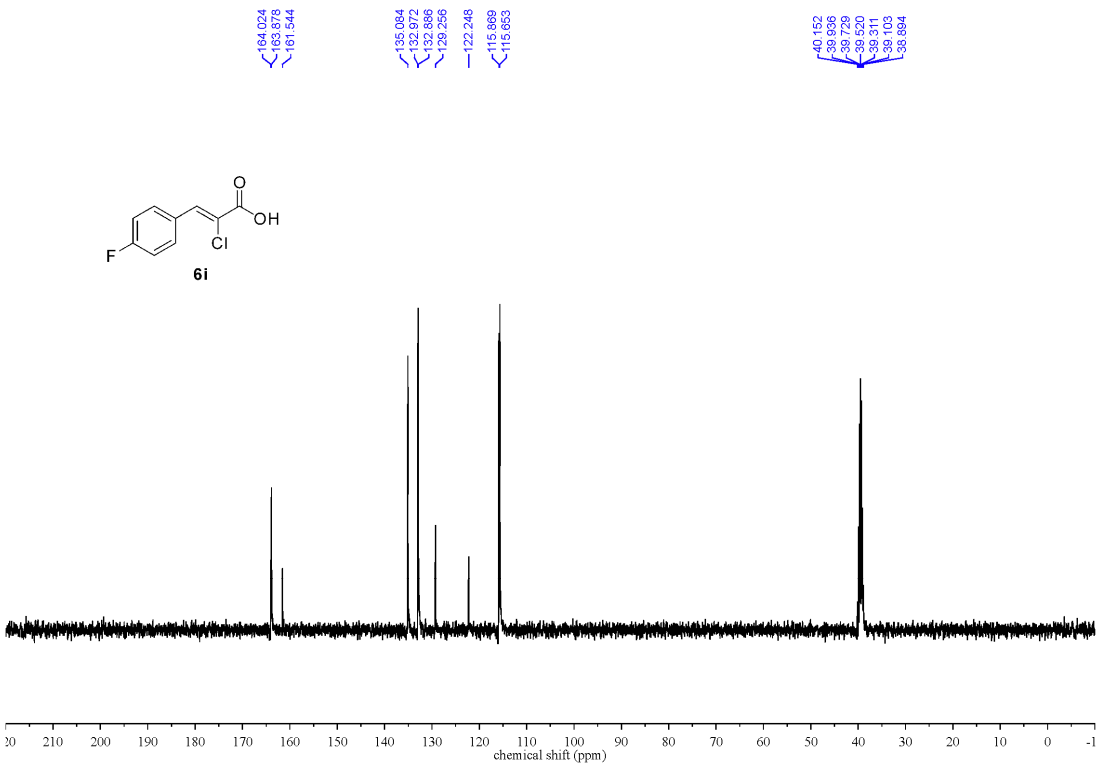
(*Z*)-2-Chloro-3-(3-methoxyphenyl)acrylic acid (6d)



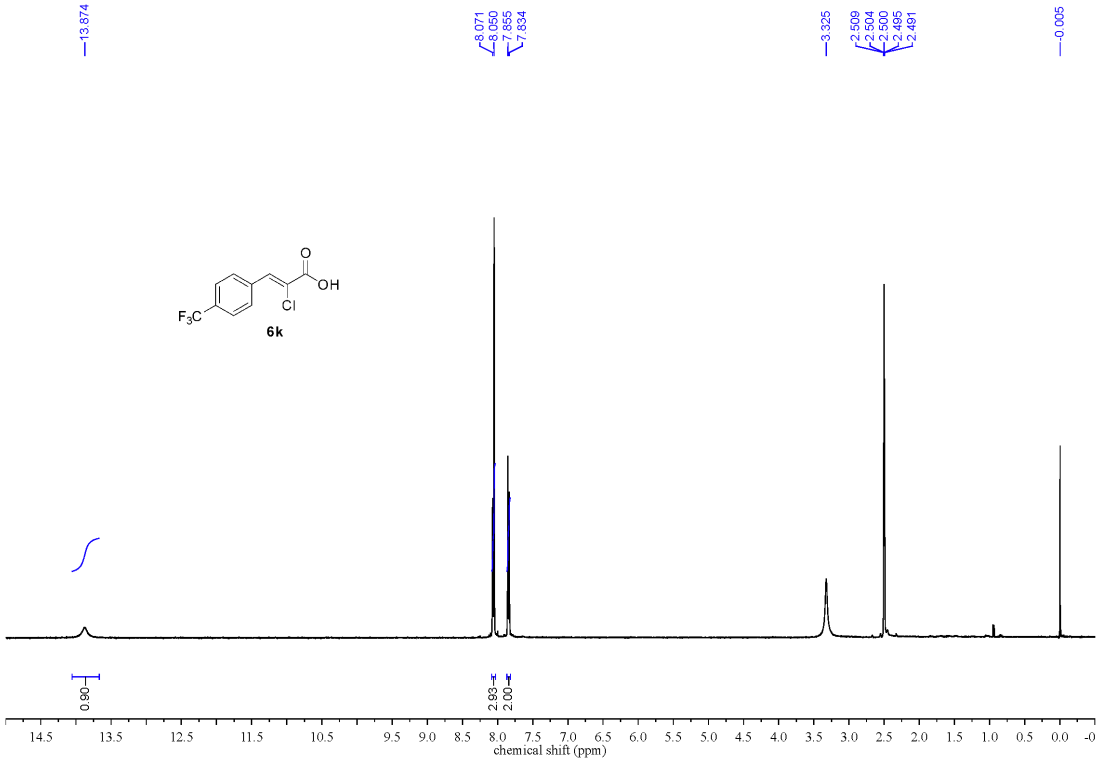


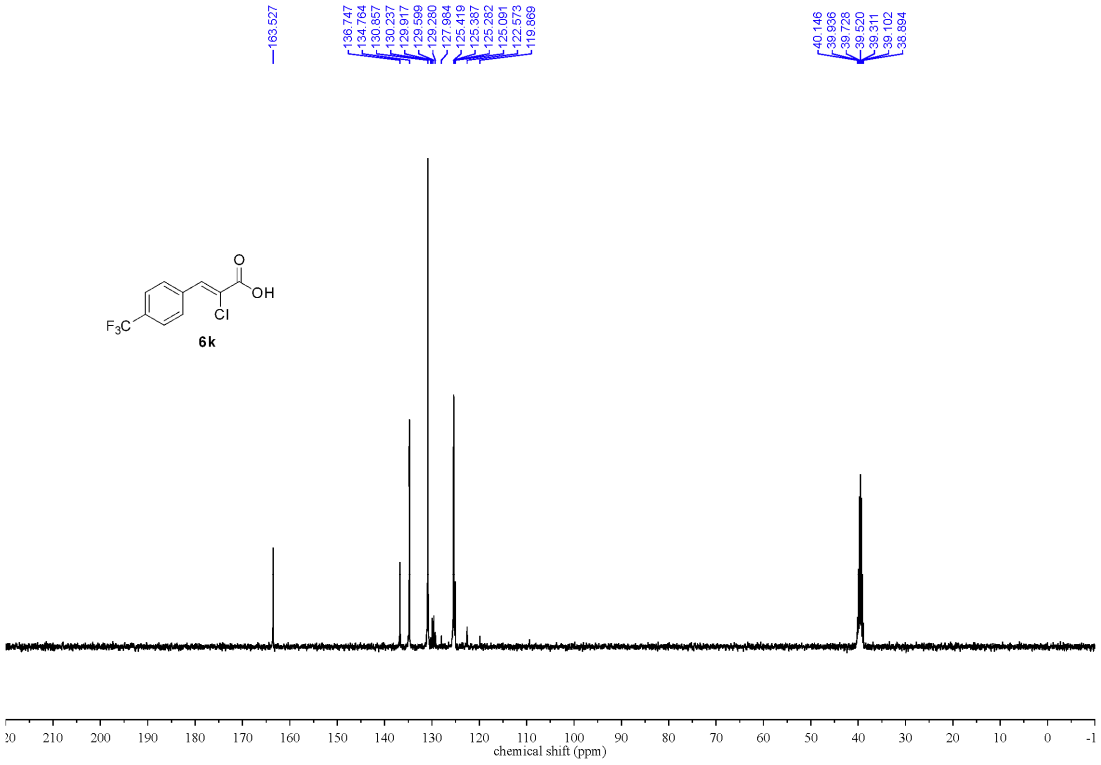
(*Z*)-2-Chloro-3-(4-fluorophenyl)acrylic acid (6i)



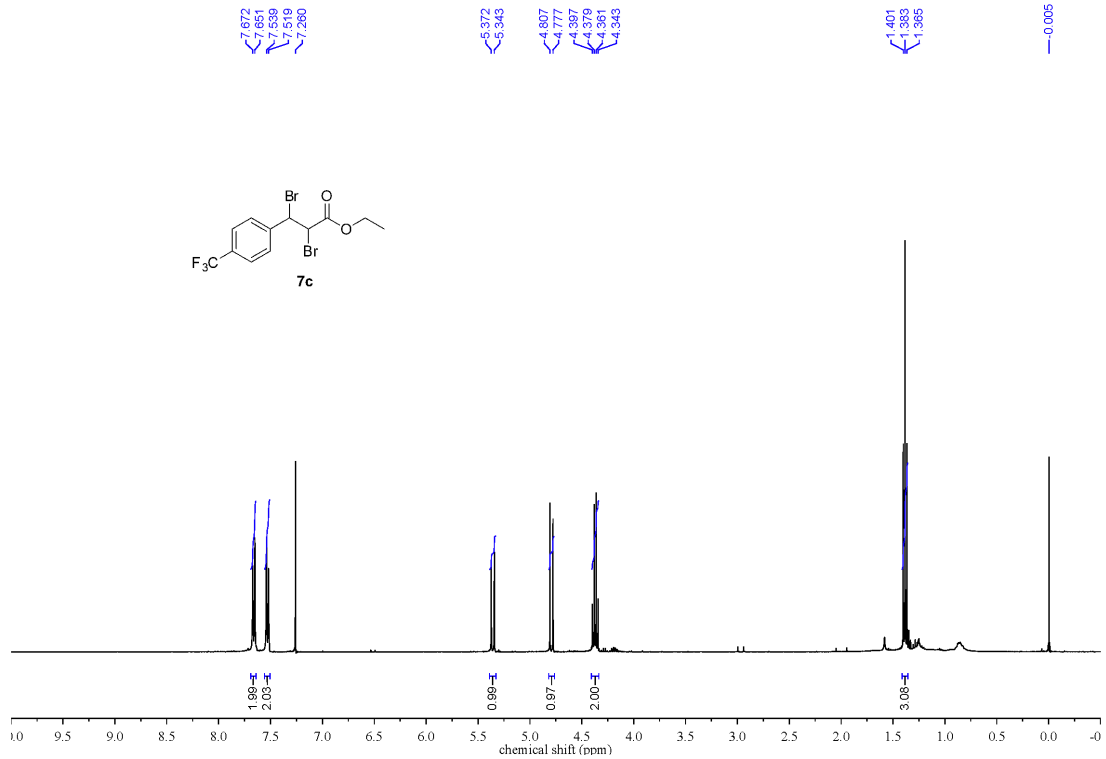


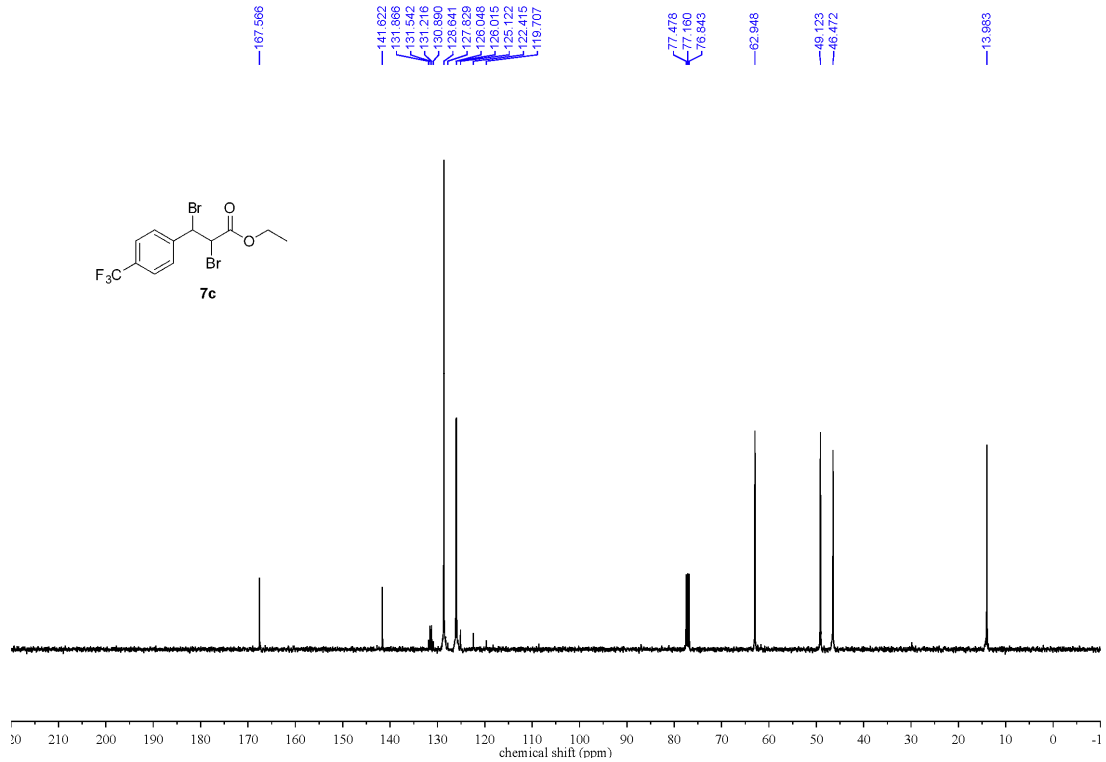
(*Z*)-2-Chloro-3-(4-(trifluoromethyl)phenyl)acrylic acid (6k)



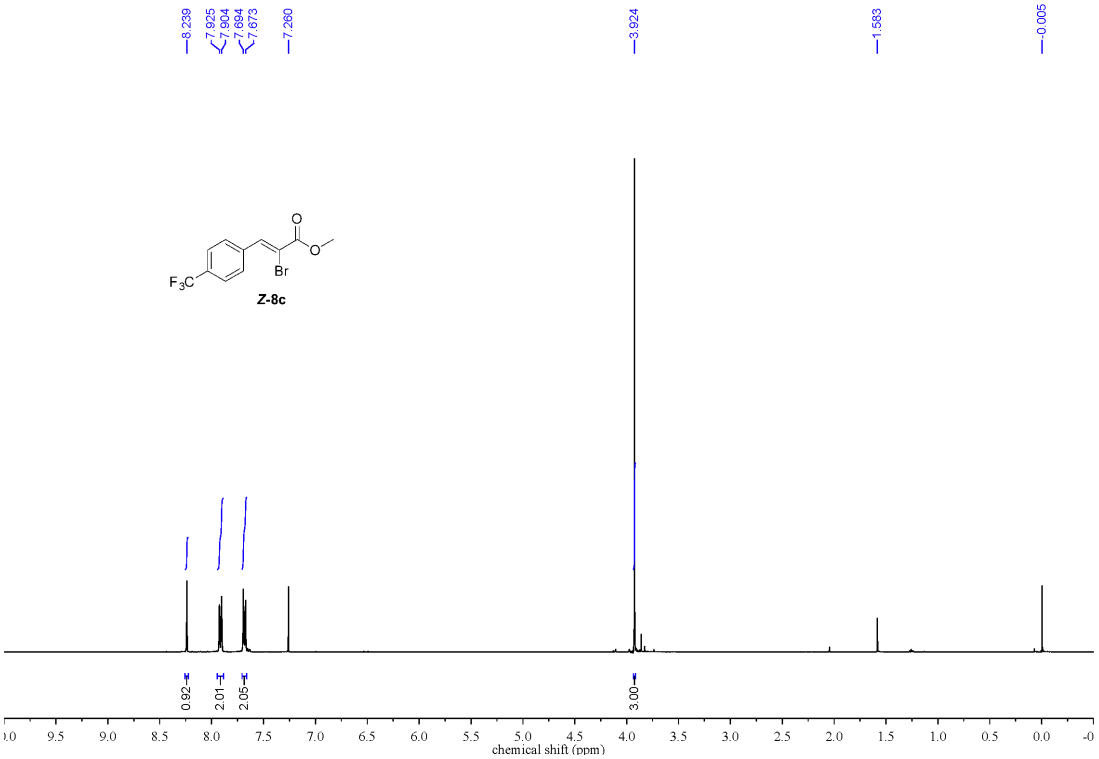


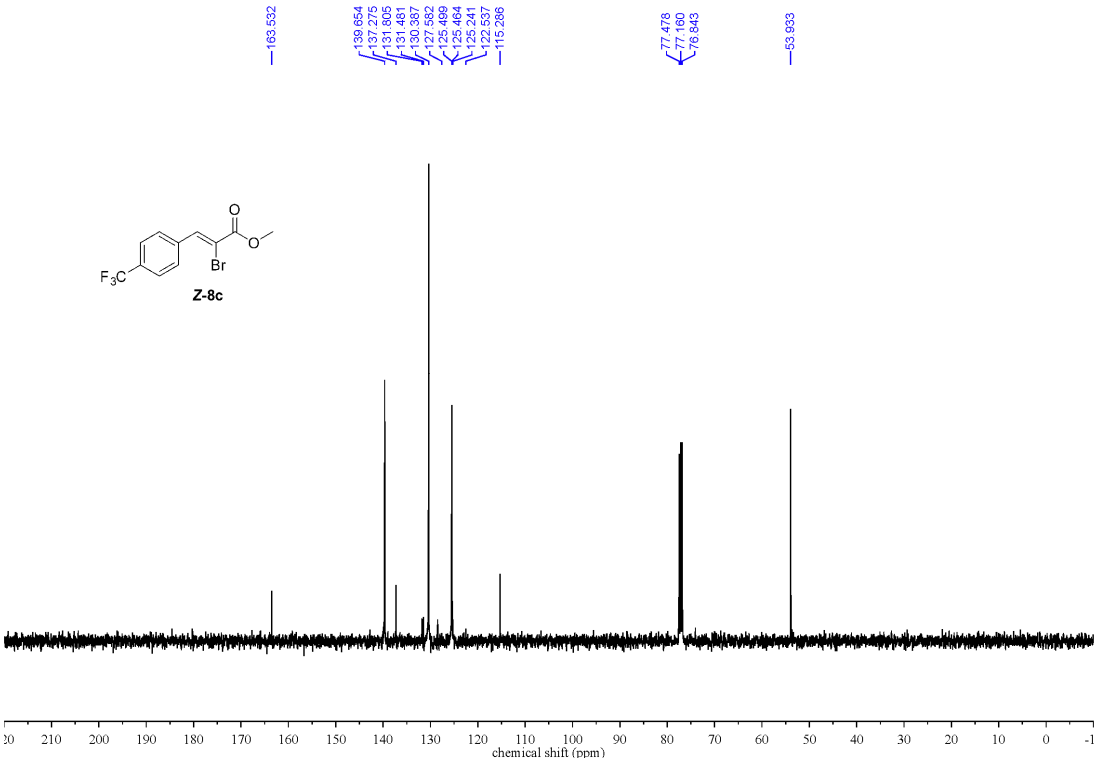
Ethyl 2,3-dibromo-3-(4-(trifluoromethyl)phenyl)propanoate (7c)



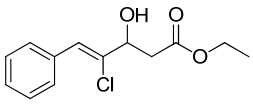


(*Z*)-Methyl 2-bromo-3-(4-(trifluoromethyl)phenyl)acrylate (8c)



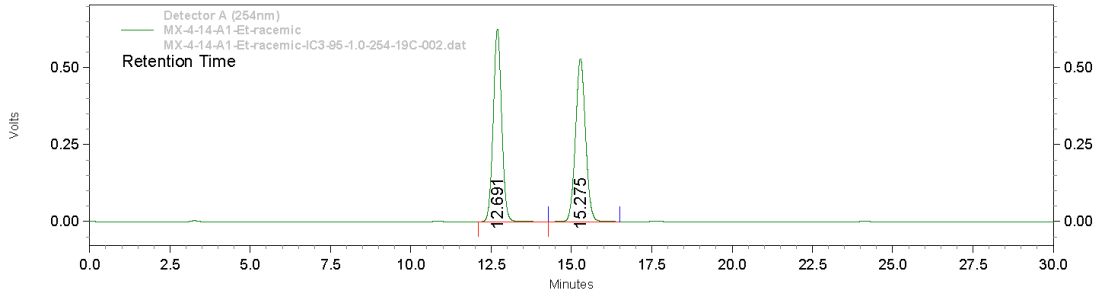


HPLC copies of 2a-n and 4a-c, 4a'-c'



2a

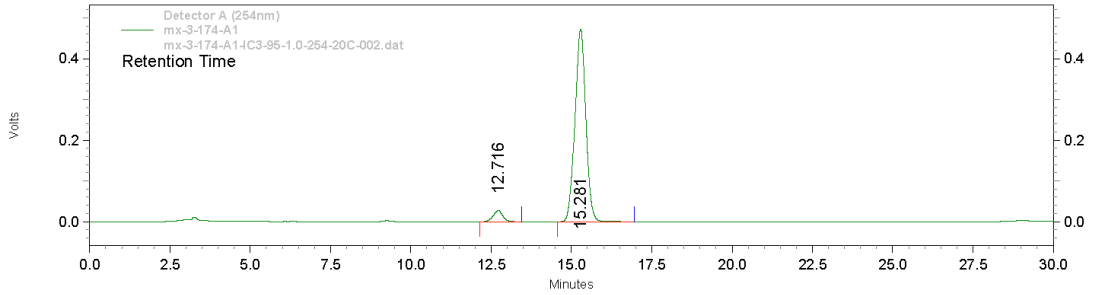
Racemate (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 1.0 mL min^{-1}, 254 nm)



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.691	11433001	49.939	625438	54.146
2	15.275	11460894	50.061	529660	45.854
Totals		22893895	100.000	1155098	100.000

Scheme 1, L = (*S*)-SunPhos

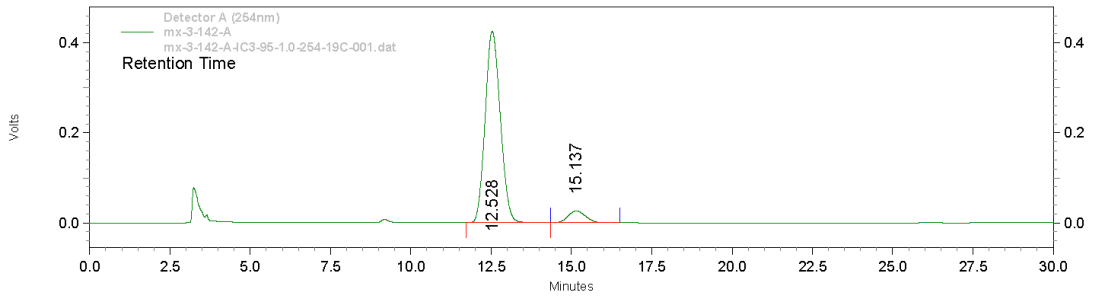


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.716	545301	4.691	27172	5.440
2	15.281	11079221	95.309	472283	94.560
Totals		11624523	100.000	499455	100.000

90.6% ee

Scheme 1, L = (*R*)-Tol-SunPhos

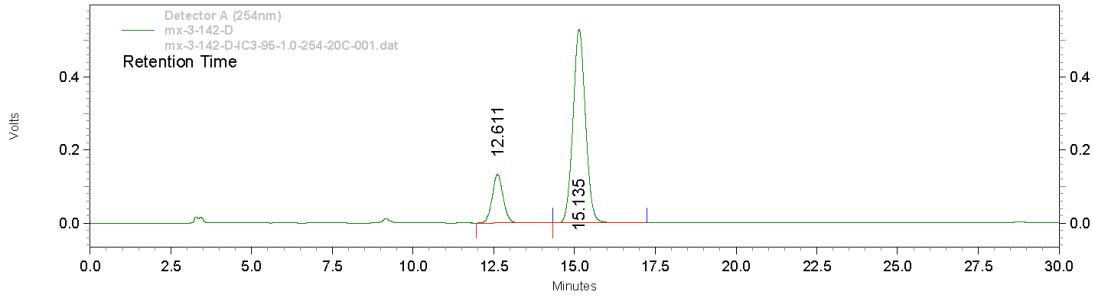


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.528	13998644	93.369	426023	94.201
2	15.137	994096	6.631	26226	5.799
Totals		14992740	100.000	452249	100.000

86.7% ee

Scheme 1, L = (*R*)-DTBM-SunPhos

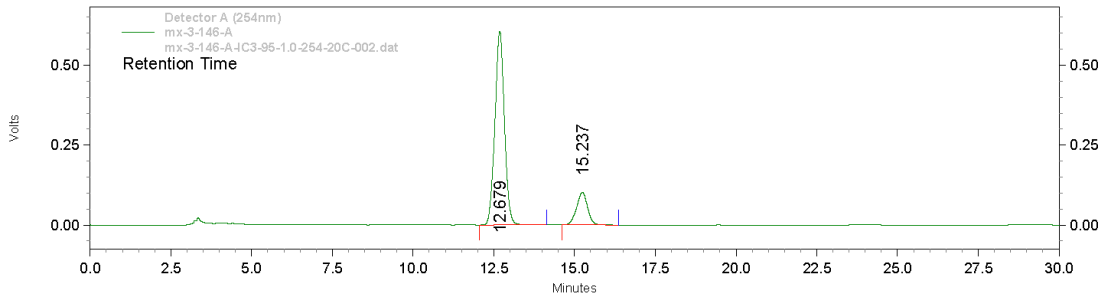


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.611	3126806	17.993	133089	20.075
2	15.135	14251539	82.007	529873	79.925
Totals		17378345	100.000	662962	100.000

64.0% ee

Scheme 1, L = (*R*)-BINAP

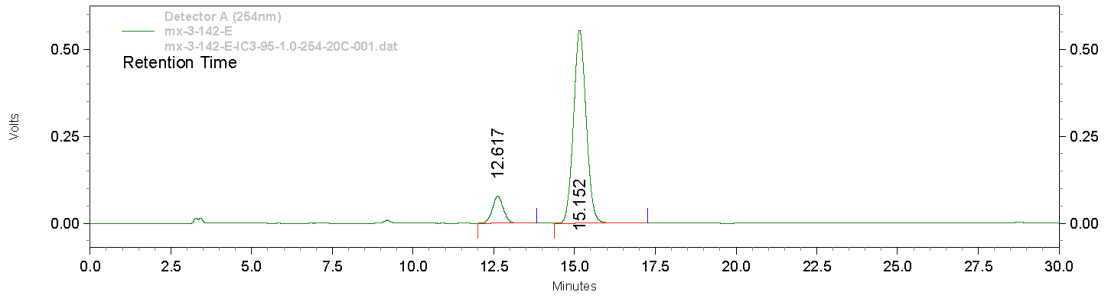


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.679	12389304	83.763	605345	85.572
2	15.237	2401540	16.237	102063	14.428
Totals		14790844	100.000	707408	100.000

67.5% ee

Scheme 1, L = (*S*)-SEGPhos

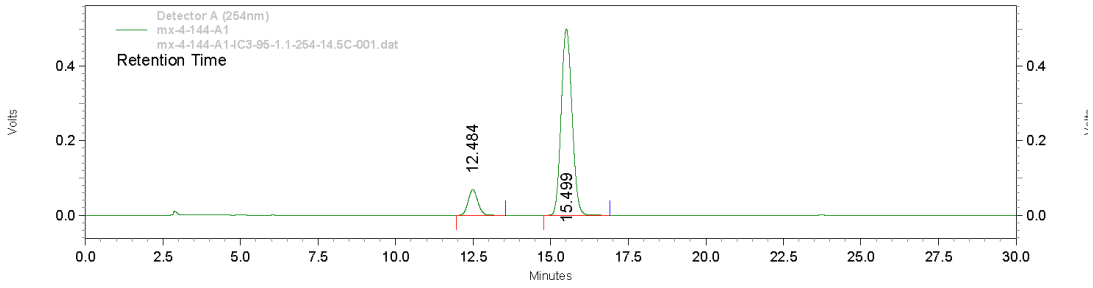


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.617	1828281	10.776	77628	12.288
2	15.152	15137931	89.224	554125	87.712
Totals		16966212	100.000	631754	100.000

78.4% ee

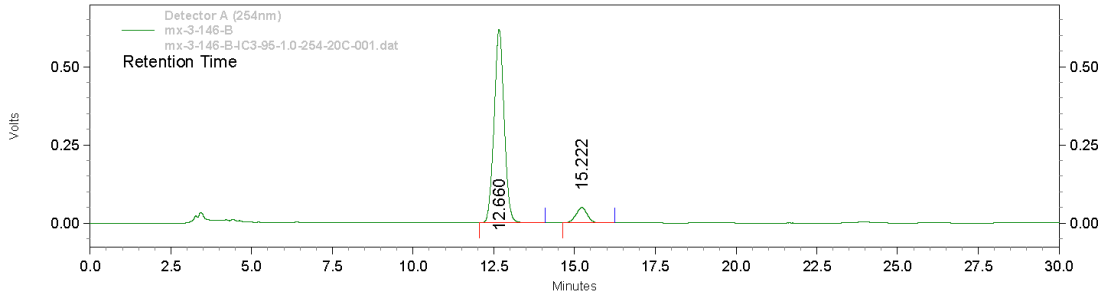
Scheme 1, L = (*S*)-MeO-BIPHEP



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	12.484	1472390	10.841	68233	12.019	78.3% ee
2	15.499	12109823	89.159	499465	87.981	
Totals		13582213	100.000	567698	100.000	

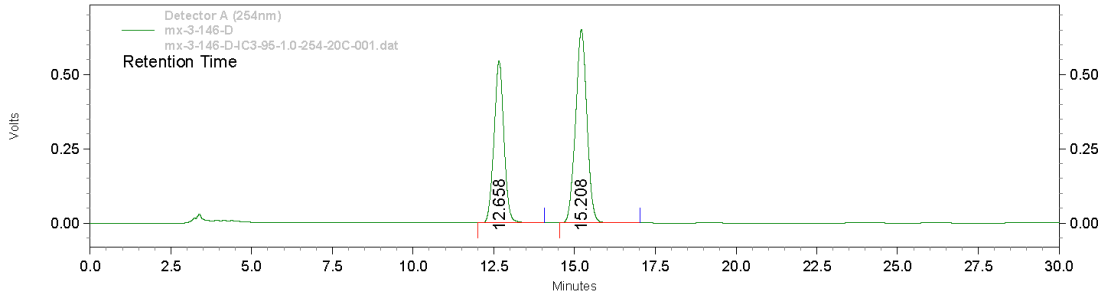
Scheme 1, L = (*R*)-SYNPhos



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	12.660	13434688	91.761	618991	92.558	83.5% ee
2	15.222	1206241	8.239	49768	7.442	
Totals		14640929	100.000	668759	100.000	

Scheme 1, L = (*S*)-*p*-CF_3-SYNPhos

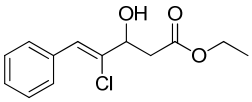


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.658	11636829	42.255	545878	45.580
2	15.208	15902835	57.745	651746	54.420
Totals		27539664	100.000	1197625	100.000

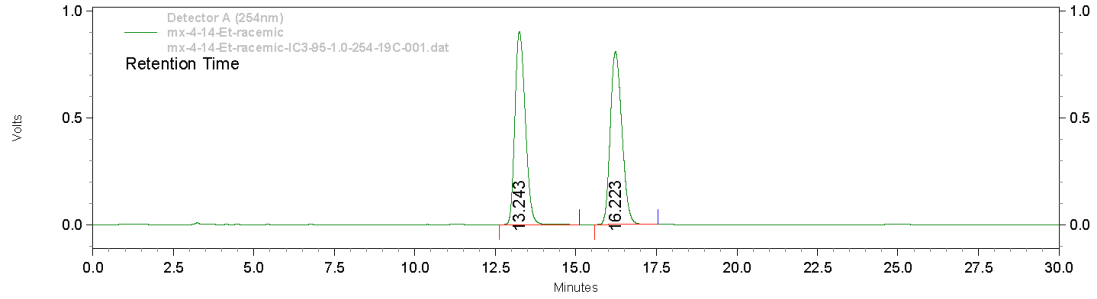
15.5% ee

Table 1



2a

Racemate (Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 1.0 mL min^{-1}, 254 nm)

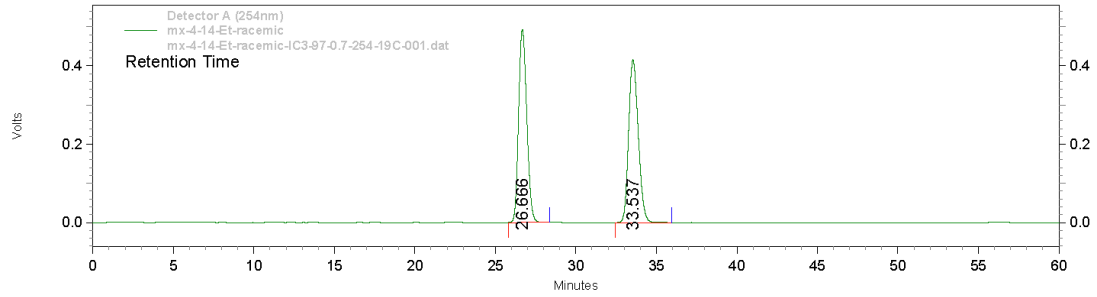


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	13.243	20235609	49.899	903557	52.769
2	16.223	20317143	50.101	808730	47.231
Totals		40552752	100.000	1712287	100.000

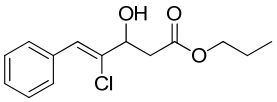
Retention time changed a little due to temperature changed. We don't have thermostatted column compartment.

Racemate (Chiralpak IC-3 column, hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm)



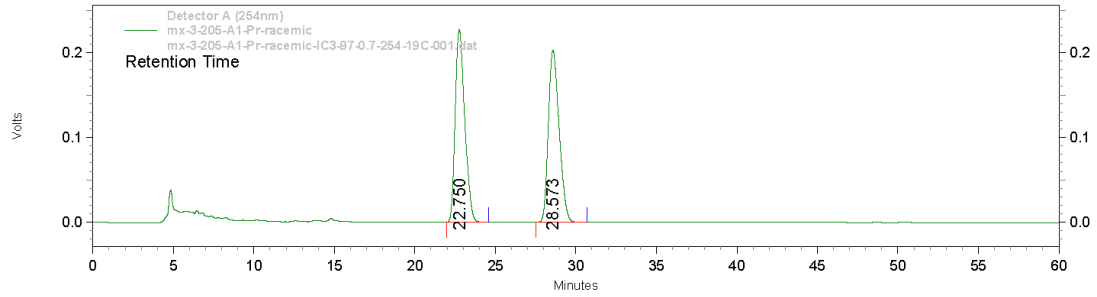
Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	26.666	17432053	50.129	492935	54.236
2	33.537	17342017	49.871	415941	45.764
Totals		34774070	100.000	908876	100.000



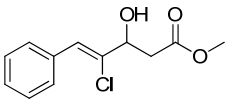
2b

Racemate (Chiralpak IC-3 column, hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm)



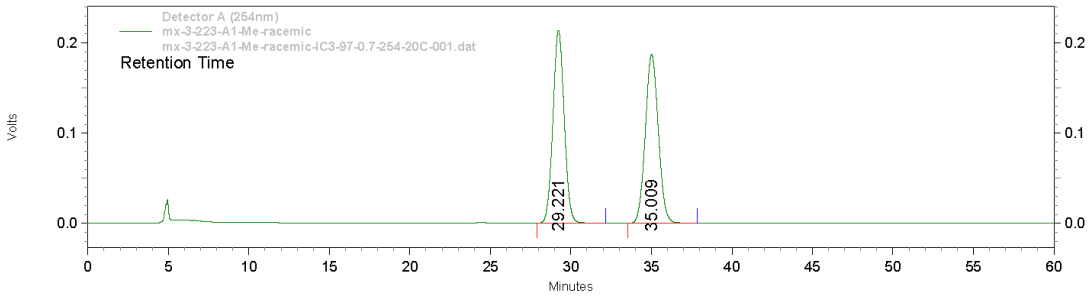
Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	22.750	9361323	49.706	227247	52.856
2	28.573	9472096	50.294	202689	47.144
Totals		18833419	100.000	429936	100.000



2c

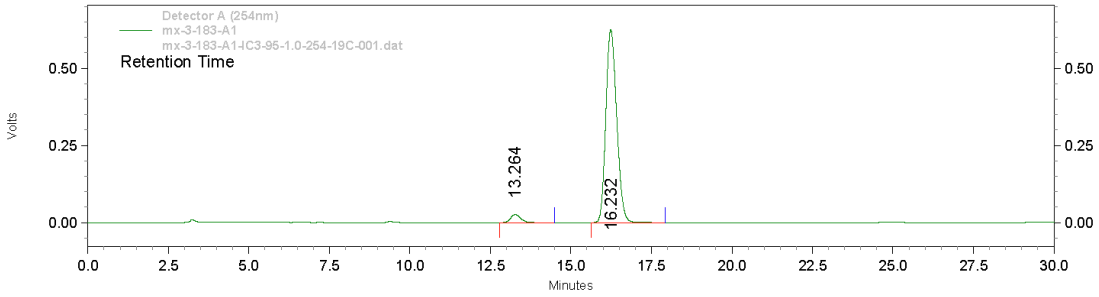
Racemate (Chiralpak IC-3 column, hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm)



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	29.221	10413312	49.798	213513	53.301
2	35.009	10497818	50.202	187065	46.699
Totals		20911130	100.000	400578	100.000

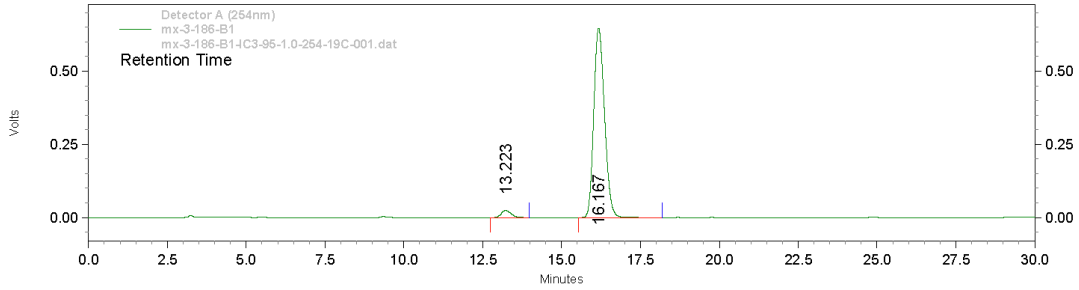
Table 1, entry 1 (**2a**) (hexane/*i*-PrOH 95/5, 1.0 mL min^{-1}, 254 nm)



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	13.264	547659	3.606	25520	3.920	92.8% ee
2	16.232	14638115	96.394	625449	96.080	
Totals		15185774	100.000	650969	100.000	

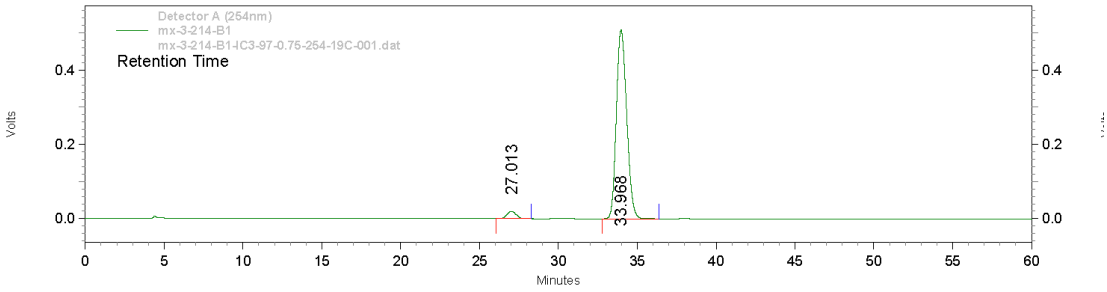
Table 1, entry 2 (**2a**) (hexane/*i*-PrOH 95/5, 1.0 mL min^{-1}, 254 nm)



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	13.223	513383	3.246	23893	3.566	93.5% ee
2	16.167	15304752	96.754	646134	96.434	
Totals		15818135	100.000	670027	100.000	

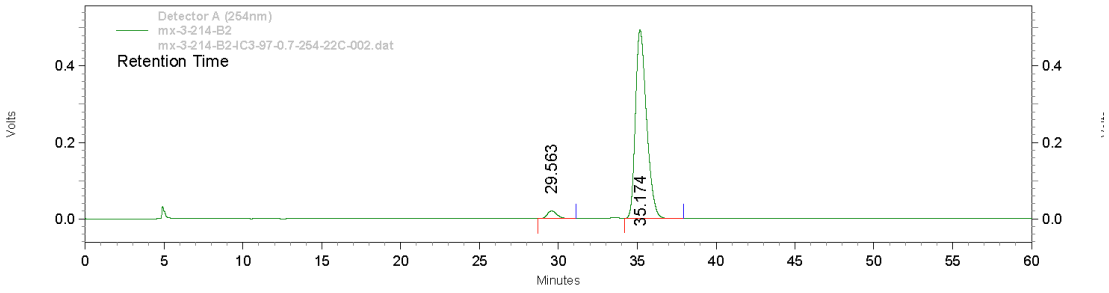
Table 1, entry 3 (**2a**) (hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm)



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	27.013	796148	3.324	19835	3.752	93.4% ee
2	33.968	23158409	96.676	508825	96.248	
Totals		23954557	100.000	528659	100.000	

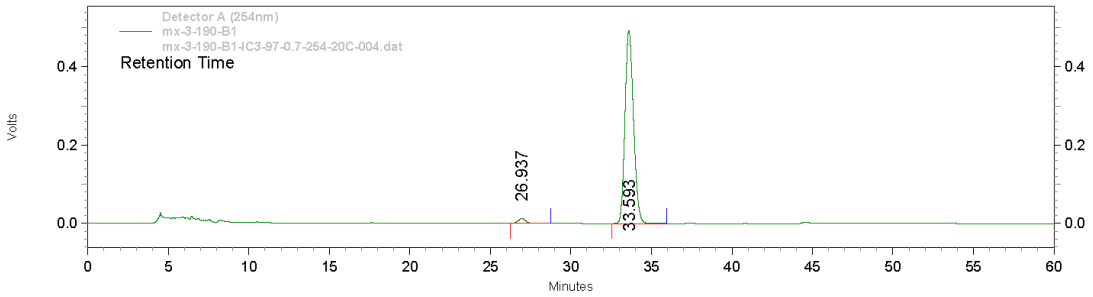
Table 1, entry 3 (**2c**) (hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm)



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	29.563	849963	3.405	20262	3.938	93.2% ee
2	35.174	24110525	96.595	494328	96.062	
Totals		24960488	100.000	514590	100.000	

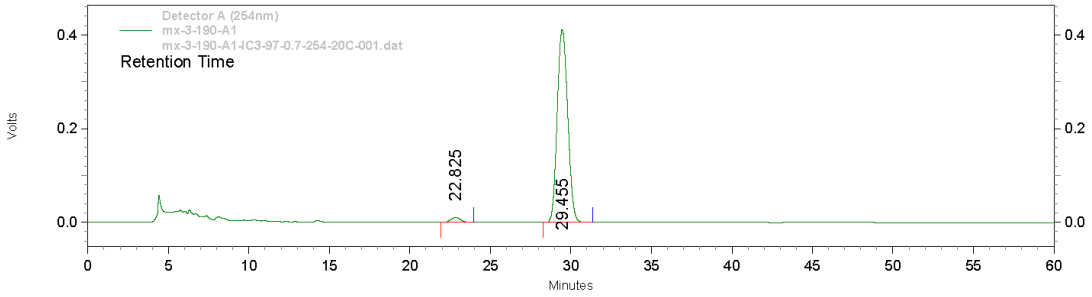
Table 1, entry 4 (**2a**) (hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm)



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	26.937	421518	2.266	12752	2.521	95.5% ee
2	33.593	18184367	97.734	493081	97.479	
Totals		18605885	100.000	505833	100.000	

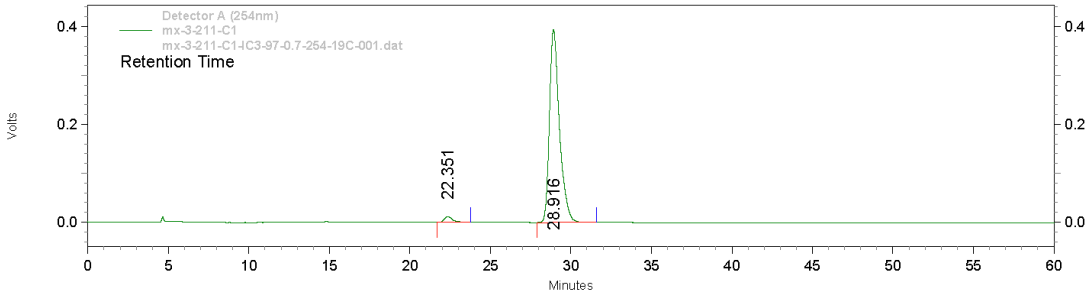
Table 1, entry 4 (**2b**) (hexane/*i*-PrOH 97/3, 0.7 mL min^{-1})



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	22.825	422419	2.208	9910	2.351	95.6% ee
2	29.455	18709242	97.792	411651	97.649	
Totals		19131661	100.000	421561	100.000	

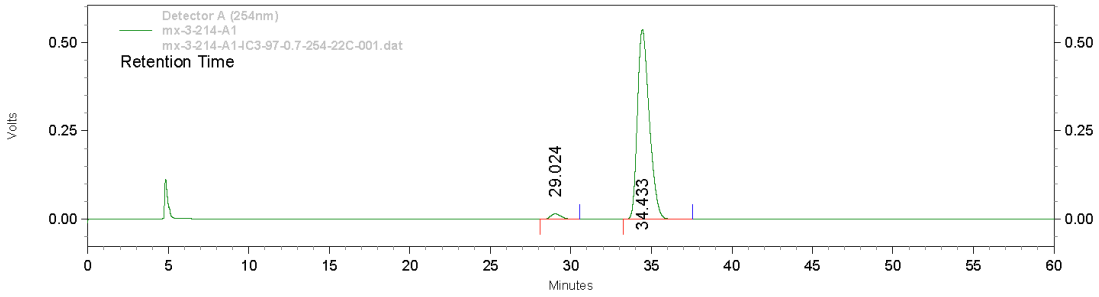
Table 1, entry 5 (**2b**) (hexane/*i*-PrOH 97/3, 0.7 mL min^{-1})



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	22.351	422856	2.425	11947	2.938	95.2% ee
2	28.916	17016561	97.575	394634	97.062	
Totals		17439416	100.000	406582	100.000	

Table 1, entry 6 (**2c**) (hexane/*i*-PrOH 97/3, 0.7 mL min^{-1})

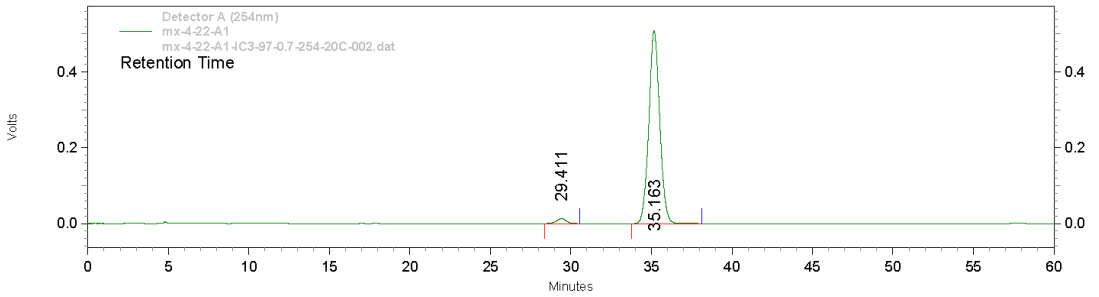


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	29.024	717738	2.536	15254	2.762
2	34.433	27582809	97.464	537116	97.238
Totals		28300547	100.000	552370	100.000

94.9% ee

Table 1, entry 7 & Table 2, entry 1 (**2c**) (hexane/*i*-PrOH 97/3, 0.7 mL min^{-1})

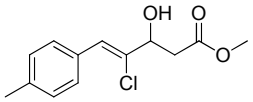


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	29.411	526424	2.160	12916	2.472
2	35.163	23847865	97.840	509454	97.528
Totals		24374289	100.000	522369	100.000

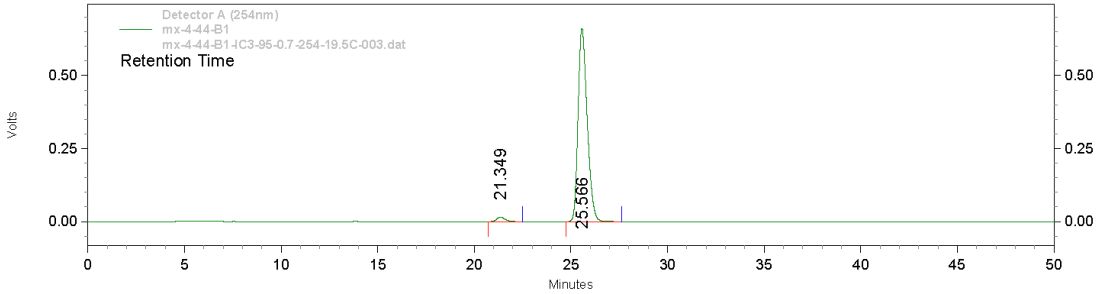
95.7% ee

Table 2, entry 2 (**2d**)



2d

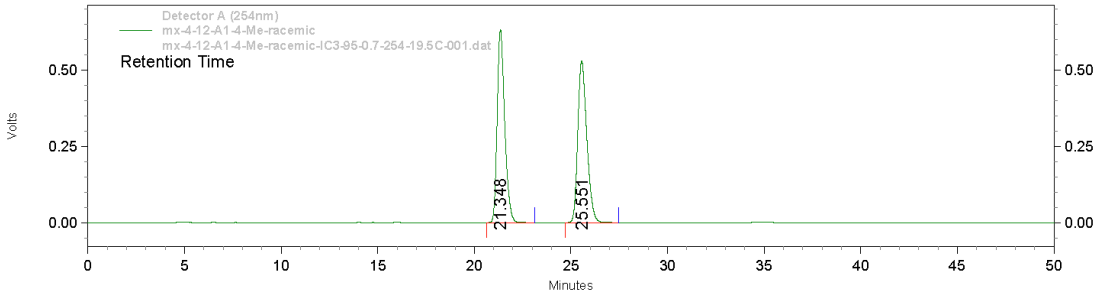
Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.7 mL min^{-1}, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	21.349	439236	1.985	15814	2.336	96.0% ee
2	25.566	21685188	98.015	661291	97.664	
Totals		22124424	100.000	677105	100.000	

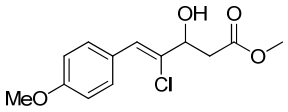
Racemate



Detector A (254nm)

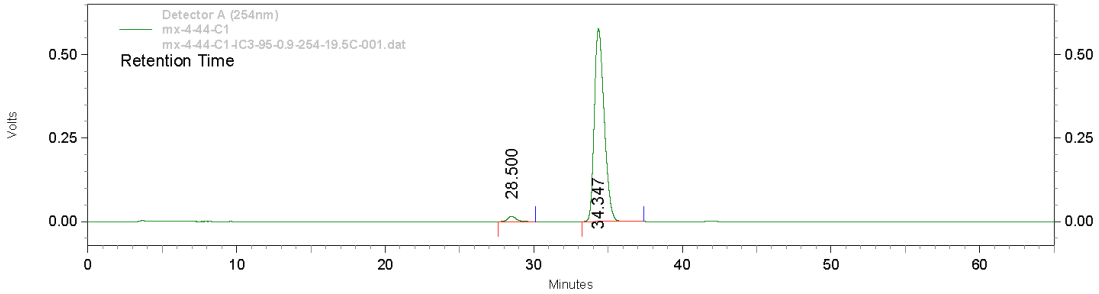
Pk #	Retention Time	Area	Area %	Height	Height %
1	21.348	17109236	49.810	632349	54.468
2	25.551	17239772	50.190	528600	45.532
Totals		34349008	100.000	1160949	100.000

Table 2, entry 3 (**2e**)



2e

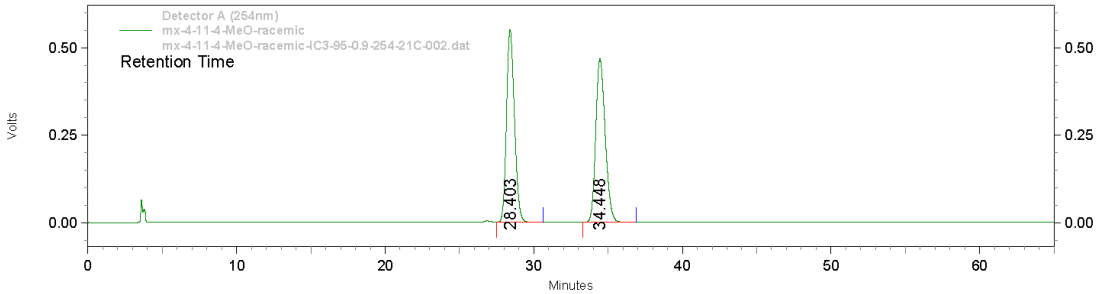
Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.9 mL min^{-1}, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	28.500	599752	2.202	15351	2.585	95.6% ee
2	34.347	26638906	97.798	578573	97.415	
Totals		27238658	100.000	593924	100.000	

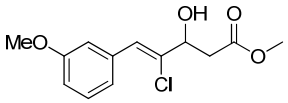
Racemate



Detector A (254nm)

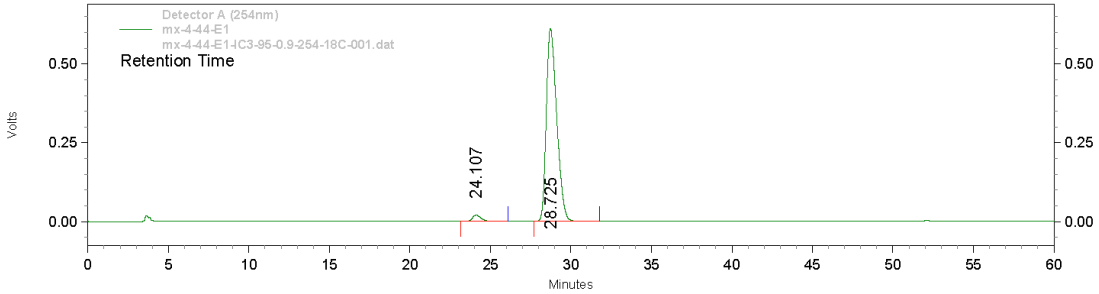
Pk #	Retention Time	Area	Area %	Height	Height %
1	28.403	20524716	49.764	551154	54.118
2	34.448	20719744	50.236	467279	45.882
Totals		41244460	100.000	1018433	100.000

Table 2, entry 4 (**2f**)



2f

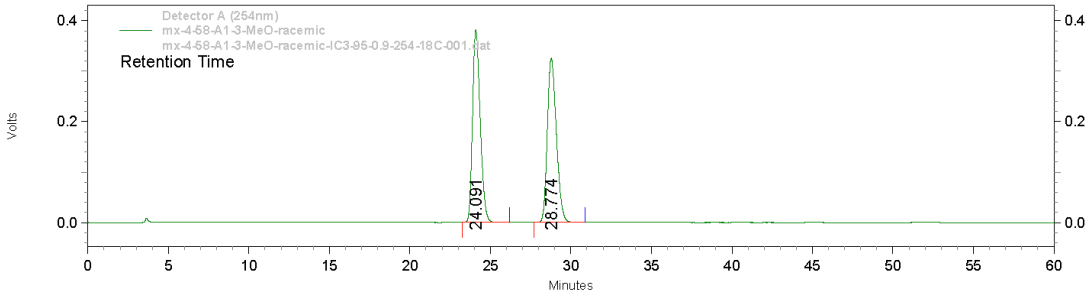
Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.9 mL min^{-1}, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	24.107	744569	2.627	19645	3.111	94.7% ee
2	28.725	27596554	97.373	611912	96.889	
Totals		28341124	100.000	631557	100.000	

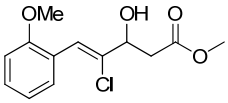
Racemate



Detector A (254nm)

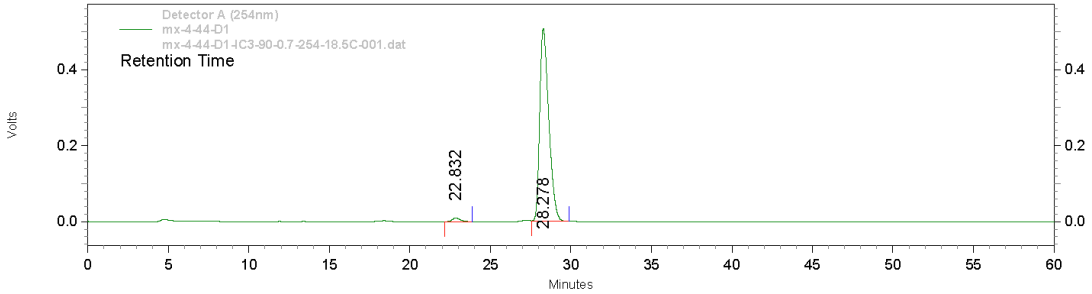
Pk #	Retention Time	Area	Area %	Height	Height %
1	24.091	12667111	49.744	382227	54.032
2	28.774	12797283	50.256	325184	45.968
Totals		25464394	100.000	707411	100.000

Table 2, entry 5 (**2g**)



2g

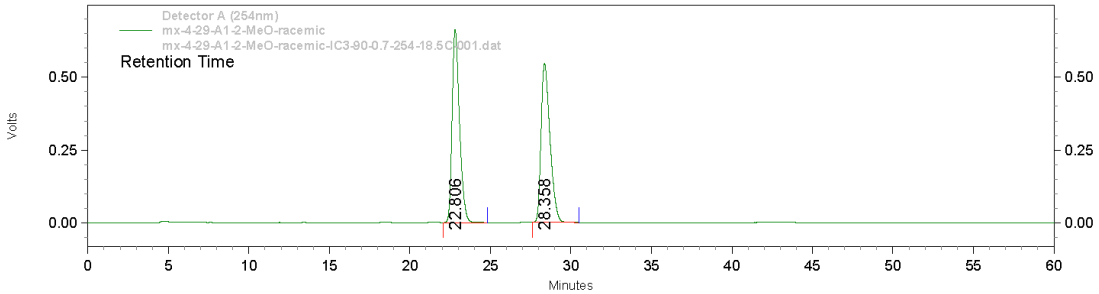
Chiralpak IC-3 column, hexane/*i*-PrOH 90/10, 0.7 mL min^{-1}, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	22.832	303726	1.509	9490	1.839	97.0% ee
2	28.278	19829582	98.491	506622	98.161	
Totals		20133308	100.000	516112	100.000	

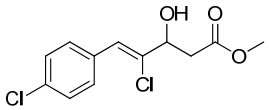
Racemate



Detector A (254nm)

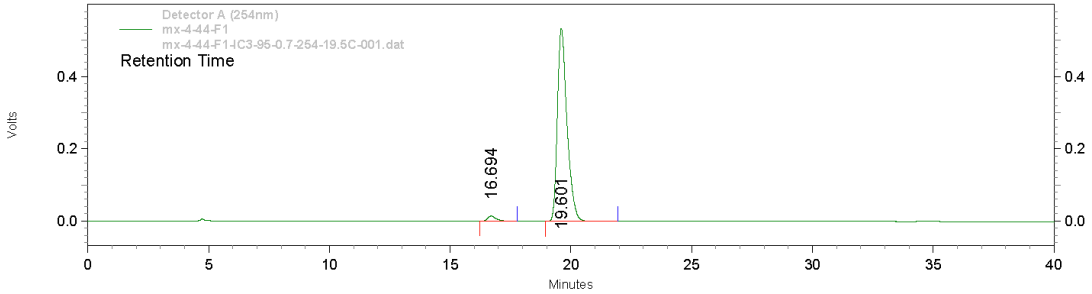
Pk #	Retention Time	Area	Area %	Height	Height %
1	22.806	21185829	50.192	664206	54.843
2	28.358	21023669	49.808	546900	45.157
Totals		42209498	100.000	1211106	100.000

Table 2, entry 6 (**2h**)



2h

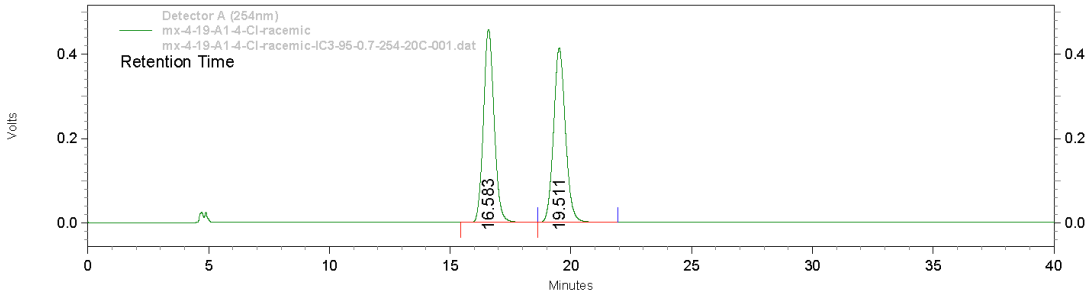
Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.7 mL min^{-1}, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	16.694	353452	2.328	14500	2.645	95.3% ee
2	19.601	14831456	97.672	533733	97.355	
Totals		15184908	100.000	548233	100.000	

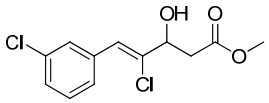
Racemate



Detector A (254nm)

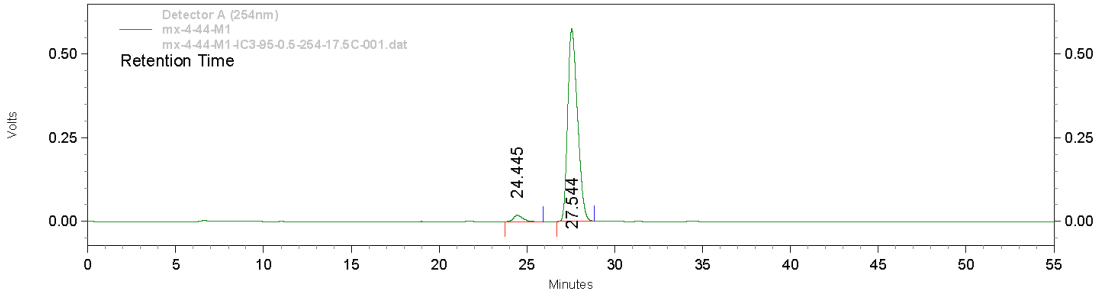
Pk #	Retention Time	Area	Area %	Height	Height %
1	16.583	14112902	49.907	458624	52.549
2	19.511	14165251	50.093	414125	47.451
Totals		28278153	100.000	872749	100.000

Table 2, entry 7 (**2i**)



2i

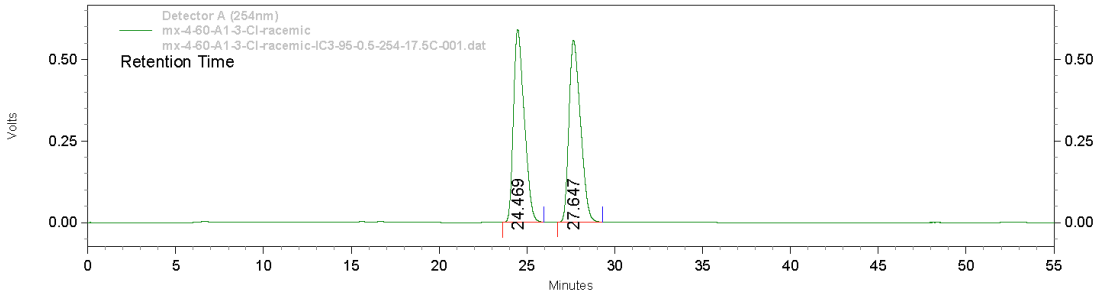
Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.5 mL min^{-1}, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	24.445	670611	2.918	18782	3.157	94.2% ee
2	27.544	22309548	97.082	576143	96.843	
Totals		22980159	100.000	594925	100.000	

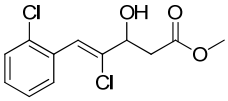
Racemate



Detector A (254nm)

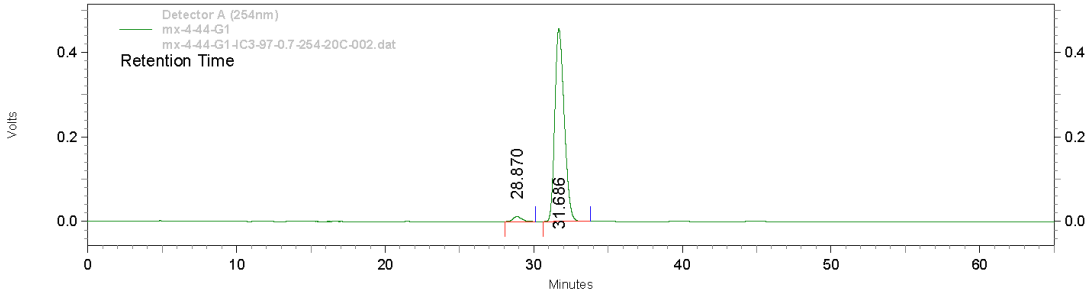
Pk #	Retention Time	Area	Area %	Height	Height %
1	24.469	25193065	49.788	590745	51.466
2	27.647	25407237	50.212	557100	48.534
Totals		50600302	100.000	1147845	100.000

Table 2, entry 8 (**2j**)



2j

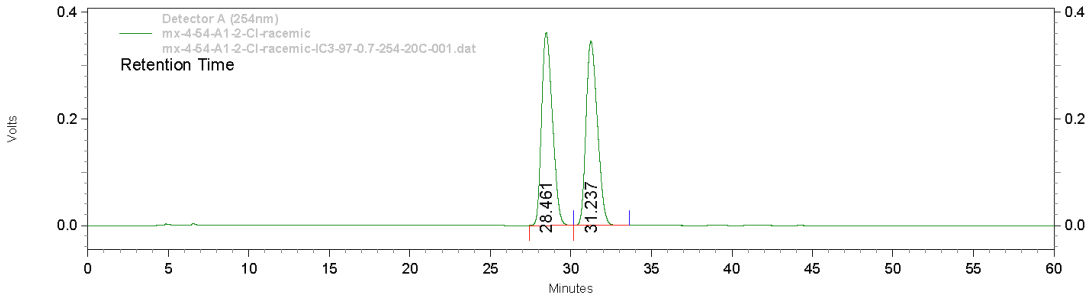
Chiralpak IC-3 column, hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	28.870	456490	2.226	11610	2.479	95.5% ee
2	31.686	20053652	97.774	456715	97.521	
Totals		20510142	100.000	468325	100.000	

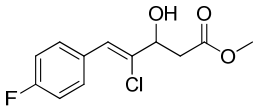
Racemate



Detector A (254nm)

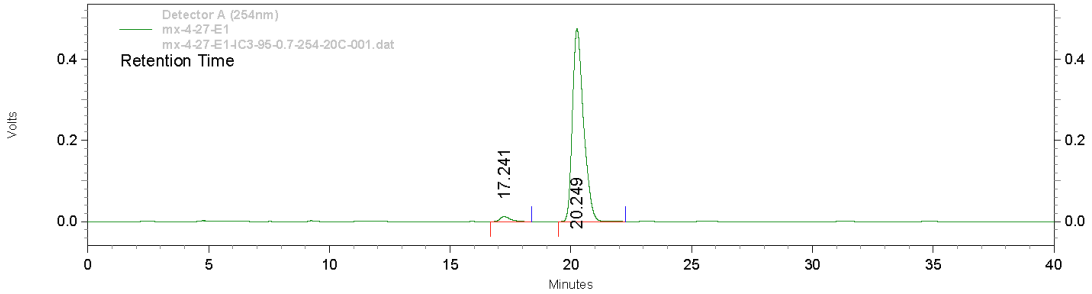
Pk #	Retention Time	Area	Area %	Height	Height %
1	28.461	16945502	50.043	361316	51.121
2	31.237	16916643	49.957	345467	48.879
Totals		33862144	100.000	706782	100.000

Table 2, entry 9 (**2k**)



2k

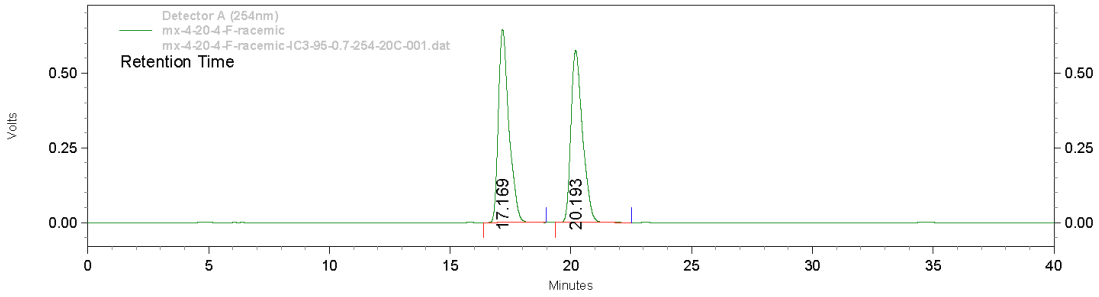
Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.7 mL min^{-1}, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	17.241	353165	2.280	12356	2.537	95.4% ee
2	20.249	15133227	97.720	474651	97.463	
Totals		15486393	100.000	487007	100.000	

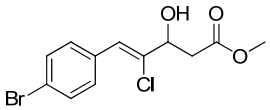
Racemate



Detector A (254nm)

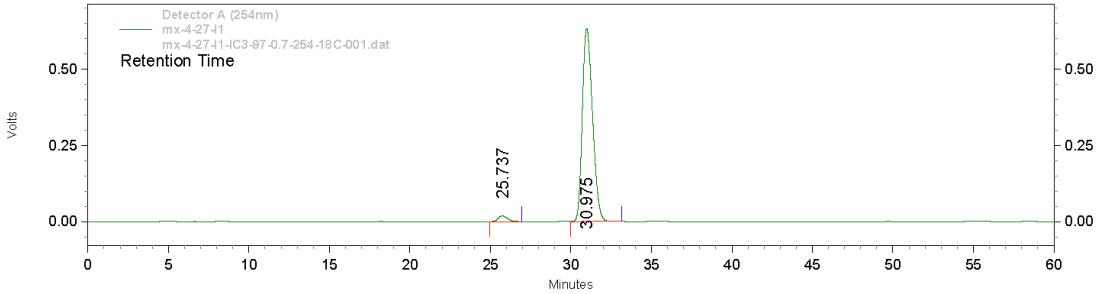
Pk #	Retention Time	Area	Area %	Height	Height %
1	17.169	19589233	50.537	645164	52.855
2	20.193	19173310	49.463	575464	47.145
Totals		38762543	100.000	1220627	100.000

Table 2, entry 10 (**2l**)



2l

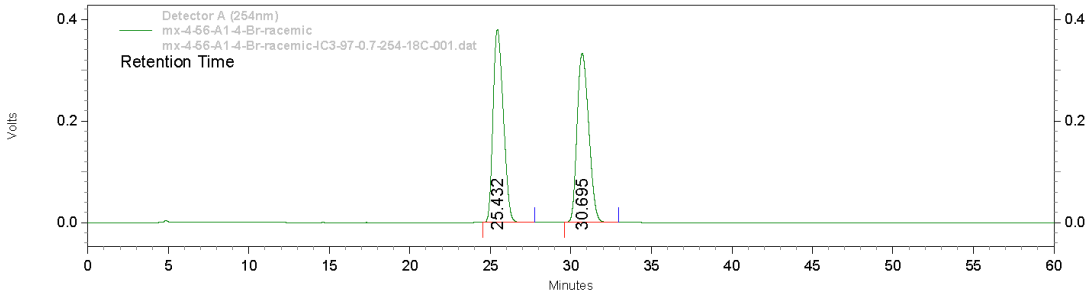
Chiralpak IC-3 column, hexane/*i*-PrOH 97/3, 0.7 mL min^{-1}, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	25.737	697674	2.447	18270	2.809	95.1% ee
2	30.975	27815156	97.553	632074	97.191	
Totals		28512829	100.000	650344	100.000	

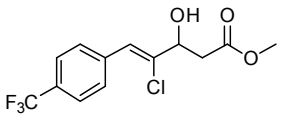
Racemate



Detector A (254nm)

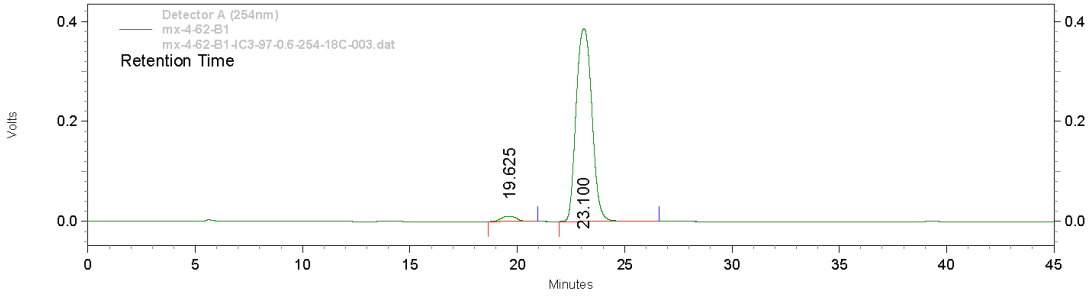
Pk #	Retention Time	Area	Area %	Height	Height %
1	25.432	16839185	50.102	379857	53.259
2	30.695	16770858	49.898	333370	46.741
Totals		33610043	100.000	713227	100.000

Table 2, entry 11 (**2m**)



2m

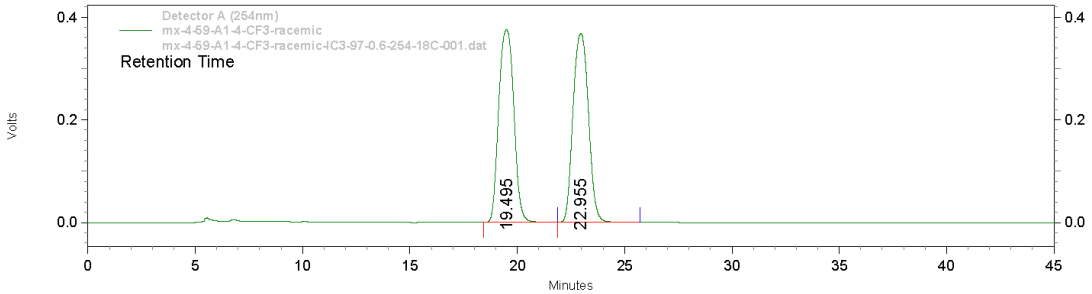
Chiralpak IC-3 column, hexane/*i*-PrOH 97/3, 0.6 mL min^{-1}, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	19.625	519045	2.571	10590	2.671	94.9% ee
2	23.100	19665860	97.429	385923	97.329	
Totals		20184905	100.000	396513	100.000	

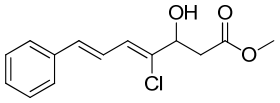
Racemate



Detector A (254nm)

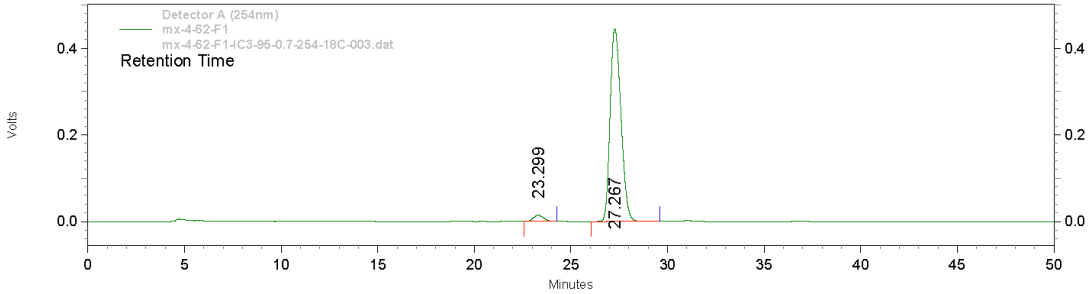
Pk #	Retention Time	Area	Area %	Height	Height %
1	19.495	18403861	50.022	375629	50.534
2	22.955	18387626	49.978	367683	49.466
Totals		36791487	100.000	743312	100.000

Table 2, entry 12 (**2n**)



2n

Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.7 mL min^{-1}, 254 nm

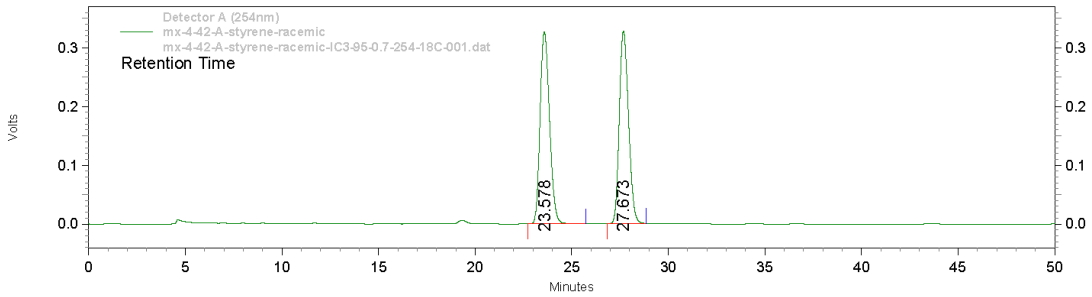


Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	23.299	524440	2.933	14145	3.077
2	27.267	17358130	97.067	445542	96.923
Totals		17882570	100.000	459687	100.000

94.1% ee

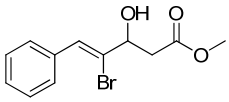
Racemate



Detector A (254nm)

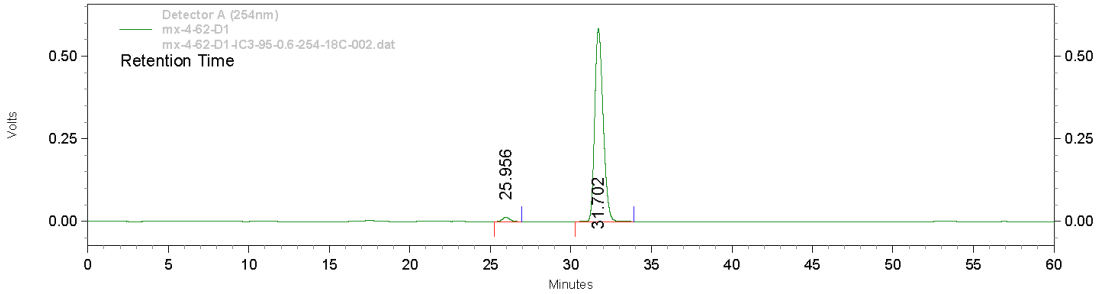
Pk #	Retention Time	Area	Area %	Height	Height %
1	23.578	11107145	50.490	326928	49.921
2	27.673	10891738	49.510	327962	50.079
Totals		21998883	100.000	654891	100.000

Scheme 2 **4a-c**



4a

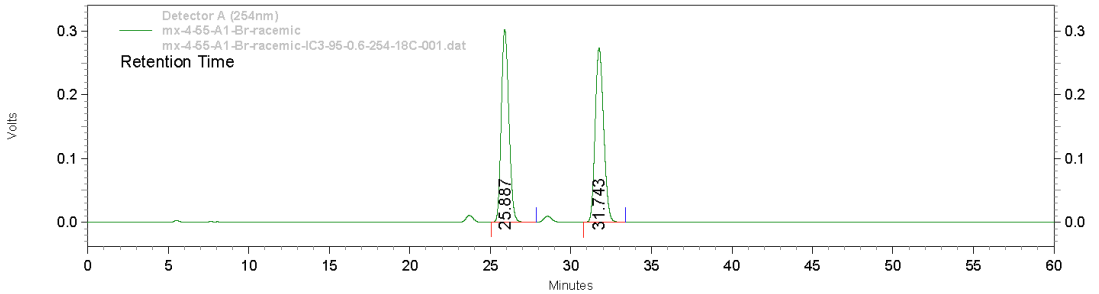
Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.6 mL min^{-1}, 254 nm



Detector A (254nm)

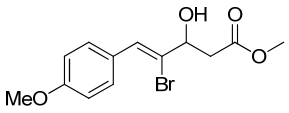
Pk #	Retention Time	Area	Area %	Height	Height %	
1	25.956	398011	1.853	13165	2.204	96.3% ee
2	31.702	21082008	98.147	584157	97.796	
Totals		21480019	100.000	597322	100.000	

Racemate



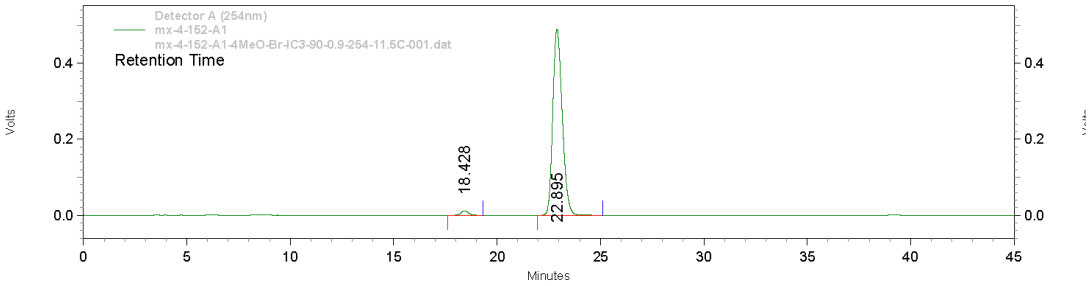
Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	25.887	9922574	49.855	302339	52.535
2	31.743	9980267	50.145	273163	47.465
Totals		19902841	100.000	575502	100.000



4b

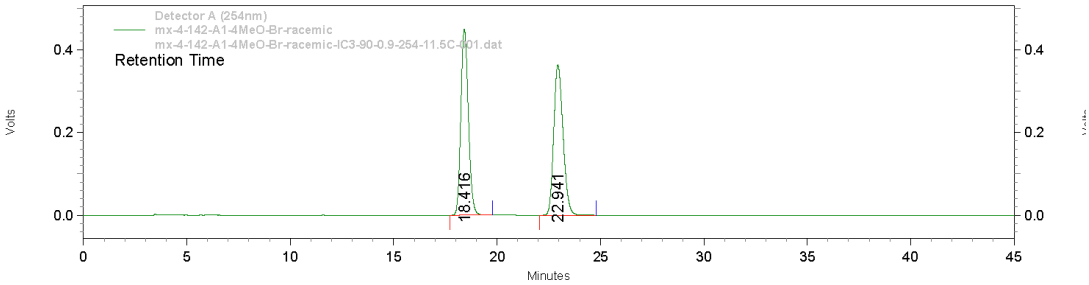
Chiralpak IC-3 column, hexane/*i*-PrOH 90/10, 0.9 mL min^{-1}, 254 nm



Detector A (254nm)

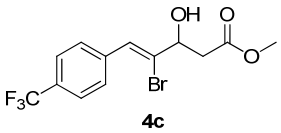
Pk #	Retention Time	Area	Area %	Height	Height %	
1	18.428	282108	1.786	11173	2.230	96.4% ee
2	22.895	15514724	98.214	489931	97.770	
Totals		15796832	100.000	501103	100.000	

Racemate



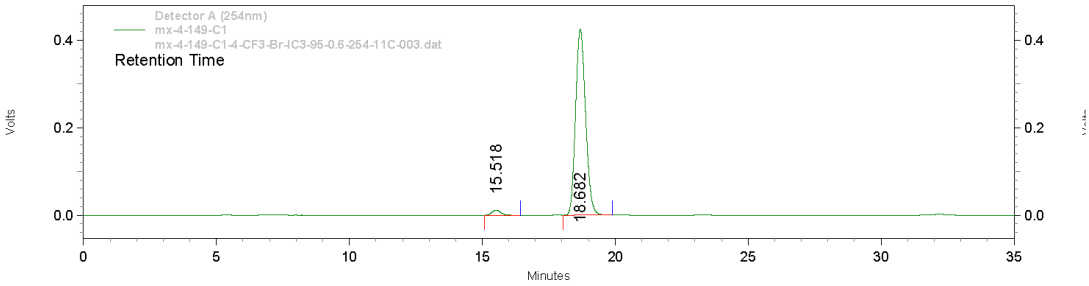
Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	18.416	11361335	50.047	449430	55.319
2	22.941	11340063	49.953	363007	44.681
Totals		22701398	100.000	812437	100.000



4c

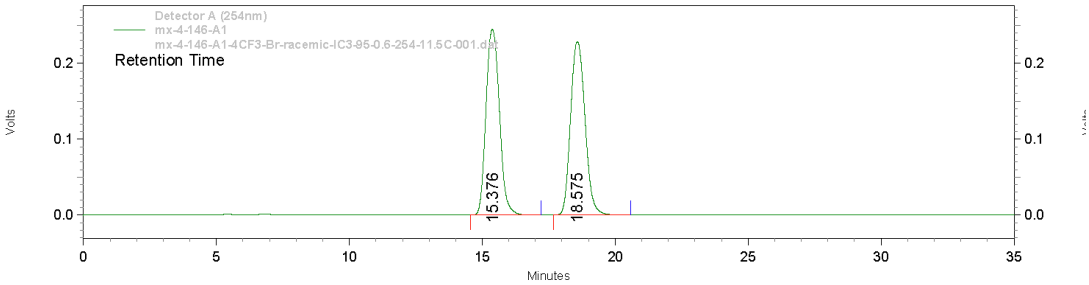
Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.6 mL min^{-1}, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	15.518	264010	2.322	11616	2.660	95.4% ee
2	18.682	11107804	97.678	425076	97.340	
Totals		11371814	100.000	436692	100.000	

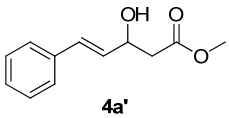
Racemate



Detector A (254nm)

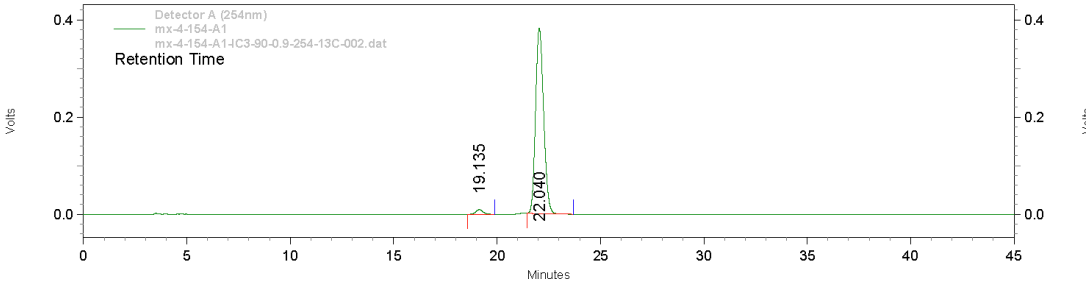
Pk #	Retention Time	Area	Area %	Height	Height %
1	15.376	8612375	50.006	244983	51.730
2	18.575	8610156	49.994	228595	48.270
Totals		17222531	100.000	473578	100.000

Scheme 2 **4a'-c'**



4a'

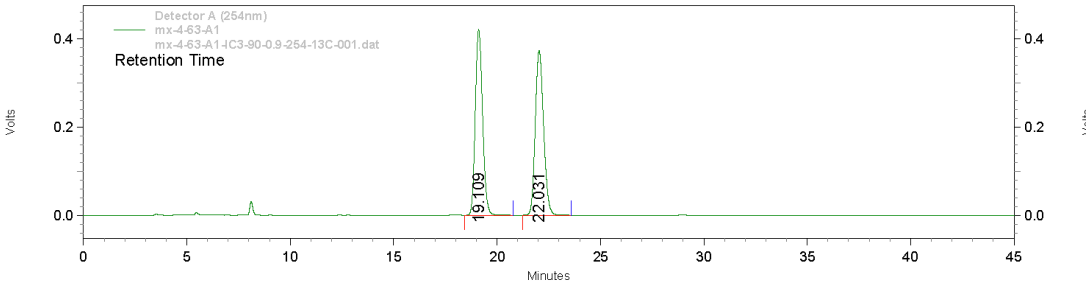
Chiralpak IC-3 column, hexane/*i*-PrOH 90/10, 0.9 mL min^{-1}, 254 nm



Detector A (254nm)

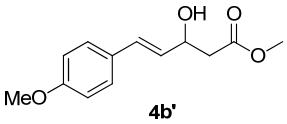
Pk #	Retention Time	Area	Area %	Height	Height %	
1	19.135	218531	2.078	9323	2.385	95.8% ee
2	22.040	10299049	97.922	381556	97.615	
Totals		10517580	100.000	390880	100.000	

Racemate



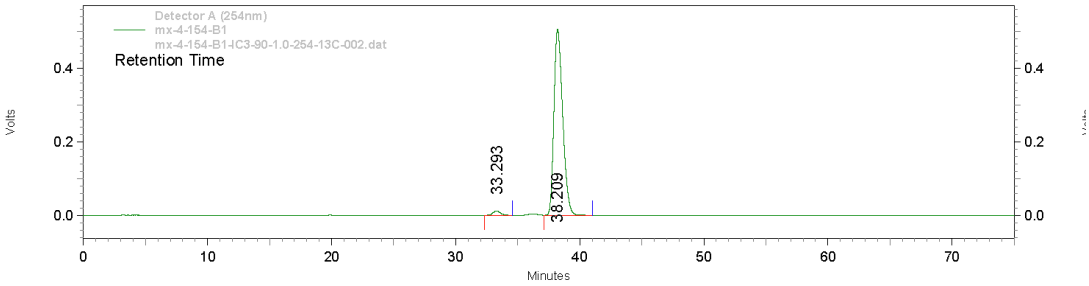
Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	19.109	10278541	49.791	421139	53.094
2	22.031	10364992	50.209	372058	46.906
Totals		20643533	100.000	793197	100.000



4b'

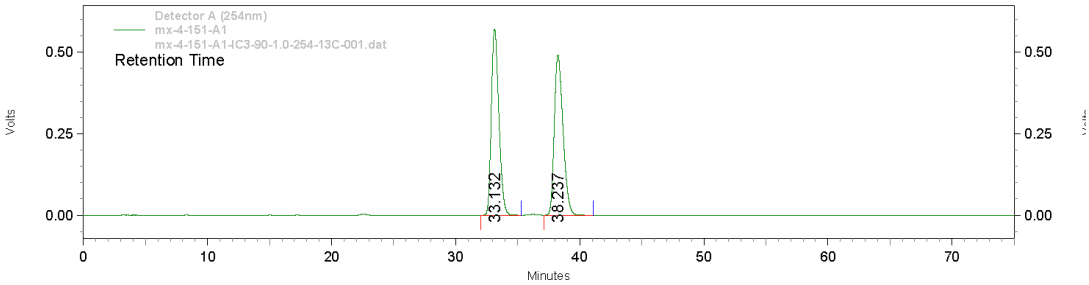
Chiralpak IC-3 column, hexane/*i*-PrOH 90/10, 1.0 mL min^{-1}, 254 nm



Detector A (254nm)

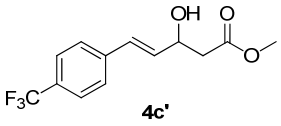
Pk #	Retention Time	Area	Area %	Height	Height %	
1	33.293	468815	1.862	11505	2.226	96.3% ee
2	38.209	24714342	98.138	505319	97.774	
Totals		25183157	100.000	516824	100.000	

Racemate



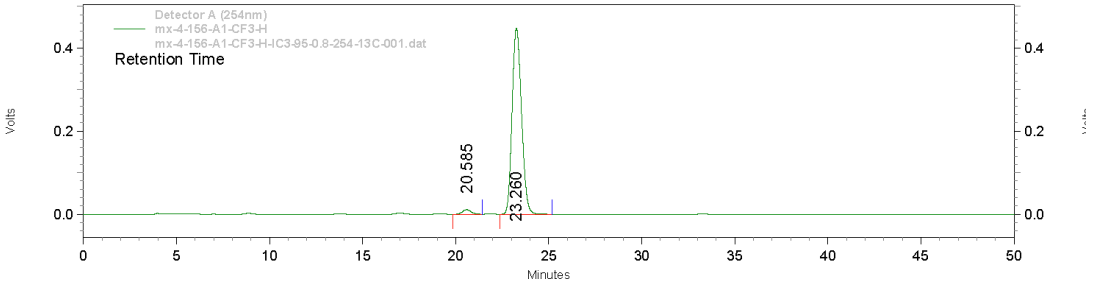
Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	33.132	24096112	50.084	570940	53.750
2	38.237	24015063	49.916	491273	46.250
Totals		48111175	100.000	1062214	100.000



4c'

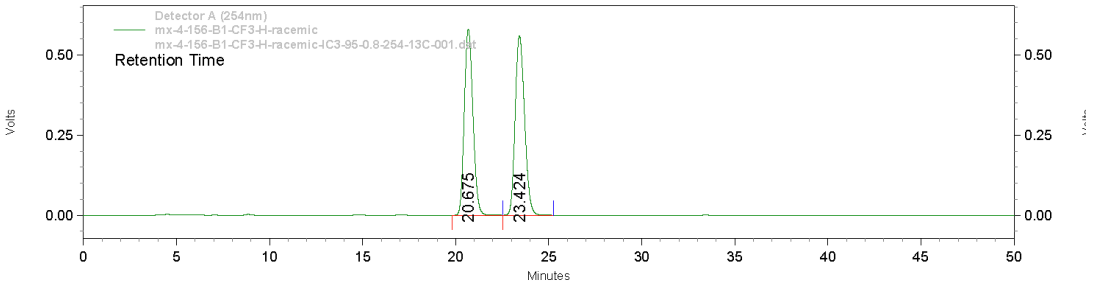
Chiralpak IC-3 column, hexane/*i*-PrOH 95/5, 0.8 mL min^{-1}, 254 nm



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %	
1	20.585	345509	2.150	10878	2.371	95.7% ee
2	23.260	15723280	97.850	447928	97.629	
Totals		16068789	100.000	458806	100.000	

Racemate



Detector A (254nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	20.675	18706436	48.810	580492	50.892
2	23.424	19618890	51.190	560139	49.108
Totals		38325325	100.000	1140631	100.000