Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Hydroxy-Assisted Regio and Stereoselective Synthesis of Functionalized Alkenes via Phosphine-Catalyzed *β′*-Umpolung Addition of *o*-Hydroxy Aromatic Aldimines to Allenoates

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Table of Contents

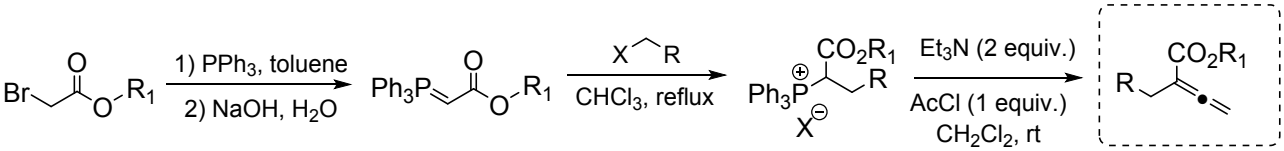
1. General Information

All reactions were performed in dry solvents and anhydrous conditions. DCM, THF, DMSO and MeCN etc. were freshly distilled over CaH_2 prior to use. All other reagents were used as received from commercial sources. Reactions were monitored through thin layer chromatography (TLC) on 0.25-mm SiliCycle silica gel plates and visualized under UV light. NMR spectra of the new product were recorded using Bruker Avance-300 and Bruker Avance-500 instruments, calibrated to $CD(H)Cl_3$ as the internal reference (7.26 and 77.0 ppm for ^1H and ^{13}C NMR spectra respectively), calibrated to DMSO-d_6 as the internal reference (2.50 and 39.5 ppm for ^1H and ^{13}C NMR spectra respectively). ^1H NMR spectral data are reported in terms of chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectral data are reported in terms of chemical shift (δ, ppm) and multiplicity. The following abbreviations indicate the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Enantiomeric excesses (ee) were determined by HPLC analysis on Shimadzu HPLC with Daicel chiral column.

2. Experimental Procedure

2.1 Allenoate Preparation

All of the allenoate were prepared using reported methods.[a]



2.2 Substituted Diethyl hydroxybenzylidene amino malonate Preparation

All of the diethyl hydroxybenzylidene amino malonate were prepared using methods.[b]

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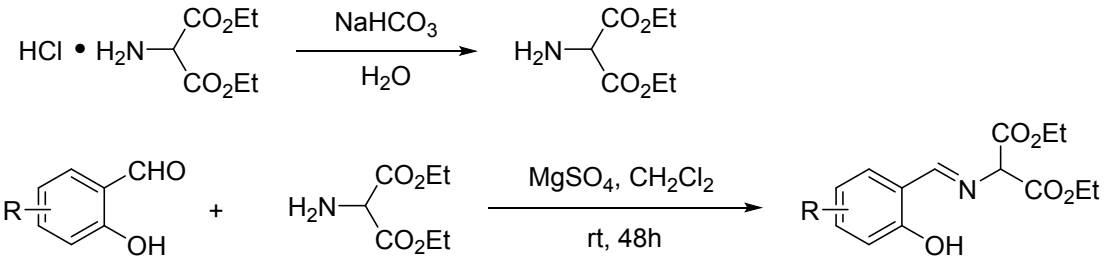
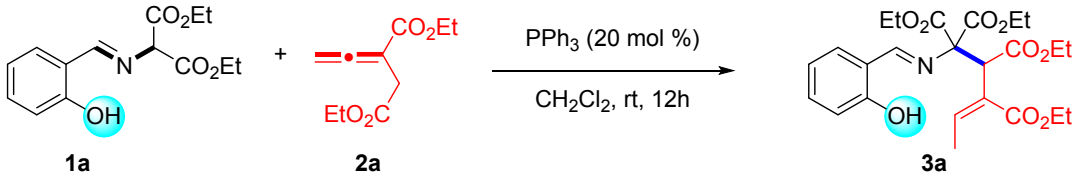


2.3 General Procedure for Phosphine-Catalyzed *β′*-Umpolung Addition



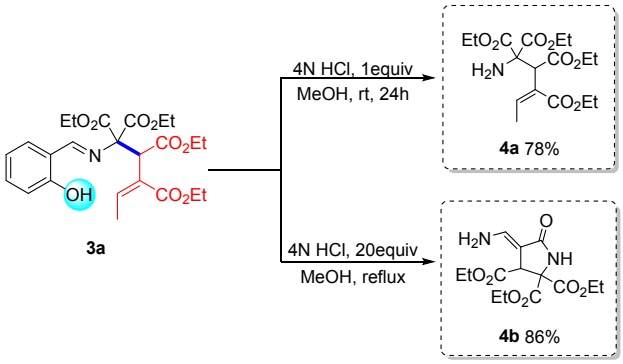
To a mixture of diethyl hydroxybenzylidene amino malonate **1a** (0.1 mmol) and allene **2a** (0.12 mmol) in CH_2Cl_2 (1 mL), PPh_3 (0.02 mol, 5.3 mg) was added. The resulting solution was stirred at room temperature for 12h. After removal of solvent, the product was purified through silica gel to give the desired products **3a**.

Assignments of the geometries of the trisubstituted alkenes were made based on the chemical shift of the *β*-vinyl proton of the enoate, and further confirmed through NOESY-NMR spectroscopic analysis of **3a** for NOESY-NMR spectra.

(a) R. Na, C. Jing, Q. Xu, H. Jiang, X. Wu, J. Shi, J. Zhong, M. Wang, D. Benitez, E. Tkatchouk, W. Goddard III, H. Guo and O. Kwon, *J. Am. Chem. Soc.*, 2011, **133**, 13337-13348.

(b) Z. Huang, Y. Bao, Y. Zhang, F. Yang, T. Lu and Q. Zhou, *J. Org. Chem.*, 2017, **82**, 12726-12734.

2.4 Derivatization of Compound 3a



2.4.1 Transformation to 4a

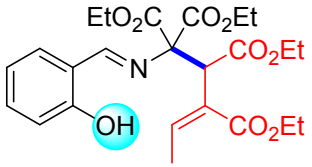
To a solution of **3a** (47.5 mg, 0.1 mmol) in CH_3OH (1 mL) was added 0.025 mL of 4 N HCl. Stirring was then continued at room temperature until the starting material had been consumed. The solvent was removed in vacuo, the mixture was quenched by water, and the aqueous layer was extracted with CH_2Cl_2. The organic layers were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography (petroleum ether: ethyl acetate = 3:1), affording **4a** (29.1 mg) in 78% yield as a colorless oil.

2.4.2 Further transformation to 4b

To a solution of **3a** (47.5 mg, 0.1 mmol) in CH_3OH (1 mL) was added 0.5 mL of 4 N HCl. Stirring was then continued at reflux until the starting material had been consumed. The solvent was removed in vacuo, the mixture was quenched by water, and the aqueous layer was extracted with CH_2Cl_2. The organic layers were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography (petroleum ether: ethyl acetate = 2:1), affording **4b** (28.1 mg) in 86% yield as a yellowish oil.

3. Characterization Data

Tetraethyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3a)



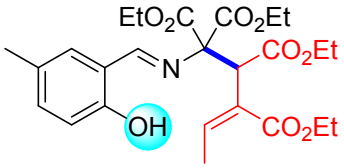
3a, 82%

Prepared according to the general procedure. Compound **3a** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 5:1) to afford a yellow oil in 82% yield (39.1 mg).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 13.01 (s, 1H), 8.59 (s, 1H), 7.34 (d, *J* = 7.29 Hz, 2H), 6.99 (d, *J* = 8.48 Hz, 1H), 6.90 (t, *J* = 7.50 Hz, 1H), 6.30 (q, *J* = 7.09 Hz, 1H), 4.79 (s, 1H), 4.37–4.09 (m, 8H), 2.01 (d, *J* = 7.36 Hz, 3H), 1.32–1.22 (m, 12H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.4, 169.7, 167.2, 167.1, 166.7, 161.2, 143.3, 133.0, 132.6, 126.4, 119.0, 118.6, 117.2, 76.5, 62.6, 62.5, 61.2, 60.8, 52.3, 16.2, 14.0 (2C), 13.9 (2C).

Tetraethyl-(3*E*)-1-((2-hydroxy-5-methylbenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3b)



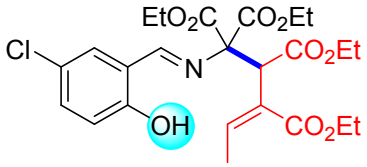
3b, 58%

Prepared according to the general procedure. Compound **3b** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 7:1) to afford a yellow oil in 90% yield (28.5 mg).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 12.75 (s, 1H), 8.54 (s, 1H), 7.16 (d, *J* = 9.13 Hz, 2H), 6.90 (d, *J* = 8.17 Hz, 1H), 6.30 (q, *J* = 7.20 Hz, 1H), 4.78 (s, 1H), 4.31–4.10 (m, 8H), 2.30 (s, 3H), 2.01 (d, *J* = 7.27 Hz, 3H), 1.29–1.21 (m, 12H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.4, 169.7, 167.2, 167.1, 166,7, 159.0, 143.4, 134.1, 132.7, 127.6, 126.3, 118.6, 117.0, 76.5, 62.6, 62.5, 61.2, 60.8, 52.3, 20.2, 16.3, 14.0 (2C), 13.9 (2C).

Tetraethyl-(3*E*)-1-((5-chloro-2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3c)



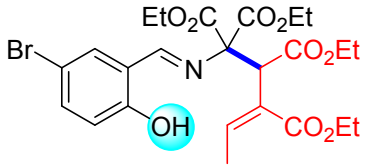
3c, 60%

Prepared according to the general procedure. Compound **3c** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 7:1) to afford a yellow oil in 60% yield (30.7 mg).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 12.98 (s, 1H), 8.57 (s, 1H), 7.35 (d, *J* = 2.59 Hz, 1H), 7.32–7.30 (m, 1H), 6.94 (d, *J* = 8.84 Hz, 1H), 6.29 (q, *J* = 7.26 Hz, 1H), 4.80 (s, 1H), 4.33–4.13 (m, 8H), 2.02 (d, *J* = 7.22 Hz, 3H), 1.34–1.26 (m, 12H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.4, 168.7, 166.9 (2C), 166.6, 159.7, 143.4, 132.8, 131.7, 126.3, 123.2, 119.8, 118.8, 76.5, 62.7(2C), 61.2, 60.9, 52.3, 16.3, 14.0 (2C), 13.9 (2C).

Tetraethyl-(3*E*)-1-((5-bromo-2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3d)



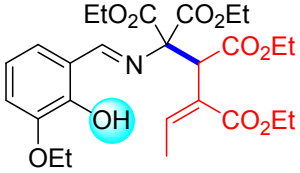
3d, 56%

Prepared according to the general procedure. Compound **3d** was purified by silica gel chromatography (petroleum ether : ethyl acetate = 7:1) to afford a yellow oil in 56% yield (31.1 mg).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 13.05 (s, 1H), 8.54 (s, 1H), 7.51–7.38 (m, 2H), 6.88 (d, *J* = 8.79 Hz, 1H), 6.28 (q, *J* = 7.22 Hz, 1H), 4.77 (s, 1H), 4.31–4.09 (m, 8H), 2.01 (d, *J* = 7.27 Hz, 3H), 1.32–1.23 (m, 12H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.4, 168.6, 166.9, 166.8, 166.6, 160.2, 143.4, 135.6, 134.7, 126.3, 120.4, 119.3, 110.0, 76.5, 62.7, 62.7, 61.3, 60.9, 52.3, 16.3, 14.0 (2C), 13.9 (2C).

Tetraethyl-(3*E*)-1-((3-ethoxy-2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3e)



3e, 90%

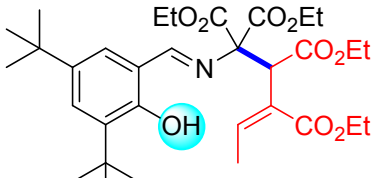
Prepared according to the general procedure. Compound **3e** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 4:1) to afford a yellow oil in 90% yield (46.9 mg).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 13.22 (s, 1H), 8.57 (s, 1H), 7.01–6.95 (m, 2H), 6.82 (t,

J = 7.85 Hz, 1H), 6.32 (q, *J* = 7.21 Hz, 1H), 4.84 (s, 1H), 4.25–4.11 (m, 10H), 2.00 (d, *J* = 7.24 Hz, 3H), 1.48 (t, *J* = 7.01 Hz, 3H), 1.29–1.24 (m, 12H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.4, 169.9, 167.3, 167.1, 166.8, 151.8, 147.6, 143.5, 126.2, 124.6, 119.2, 118.0, 117.0, 76.4, 64.8, 62.6, 62.5, 61.2, 60.8, 52.0, 16.3, 14.9, 14.0 (2C), 13.9 (2C).

Tetraethyl-(3*E*)-1-((3,5-di-tert-butyl-2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3f)



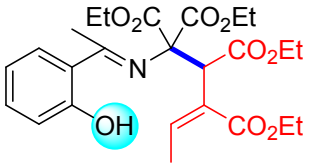
3f, 82%

Prepared according to the general procedure. Compound **3f** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 8:1) to afford a yellow oil in 82% yield (28.5 mg).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 13.34 (s, 1H), 8.56 (s, 1H), 7.42 (d, *J* = 2.40 Hz, 1H), 7.16 (d, *J* = 2.40 Hz, 1H), 6.33 (q, *J* = 7.19 Hz, 1H), 4.80 (s, 1H), 4.34–4.11 (m, 8H), 2.04 (d, *J* = 7.36 Hz, 3H), 1.45 (s, 9H), 1.32 (s, 9H), 1.30–1.22 (m, 12H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.6, 170.5, 167.4 (2C), 166.7, 158.3, 143.9, 140.0, 136.8, 127.8, 127.3, 126.2, 118.0, 76.5, 62.5, 62.4, 61.1, 60.8, 52.2, 35.1, 34.1, 31.5 (3C), 29.4 (3C), 16.3, 14.0 (2C), 13.9 (2C).

Tetraethyl-(3*E*)-1-((1-(2-hydroxyphenyl)ethylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3g)



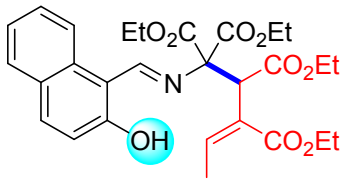
3g, 62%

Prepared according to the general procedure. Compound **3g** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 4:1) to afford a yellow oil in 82% yield (30.4 mg).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 14.38 (s, 1H), 7.58 (dd, *J* = 8.03, 1.63 Hz, 1H), 7.36–7.30 (m, 1H), 6.99 (dd, *J* = 8.32, 1.28 Hz, 1H), 6.83 (td, *J* = 8.25, 1.29 Hz, 1H), 6.47 (q, *J* = 7.24 Hz, 1H), 4.92 (s, 1H), 4.32–4.13 (m, 8H), 2.28 (s, 3H), 2.04 (d, *J* = 7.19 Hz, 3H), 1.34–1.26 (m, 12H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 175.6, 170.8, 168.3, 167.6, 167.1, 161.6, 144.0, 132.7, 128.6, 125.8, 120.9, 118.3, 117.6, 74.1, 62.7 (2C), 61.4, 61.0, 52.4, 21.0, 16.6, 14.1 (2C), 13.9, 13.8.

Tetraethyl-(*Z*)-1-(((*E*)-(2-hydroxynaphthalen-1-yl)methylene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3h)



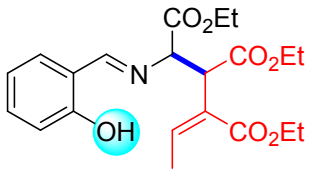
3h, 63%

Prepared according to the general procedure. Compound **3h** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 3:1) to afford a yellow oil in 63% yield (33.2 mg).

^{1}H NMR (300 MHz, DMSO-d_6) δ 14.61 (d, J = 3.70 Hz, 1H), 9.30 (d, J = 3.73 Hz, 1H), 8.05 (d, J = 8.48 Hz, 1H), 7.94 (d, J = 9.22 Hz, 1H), 7.82 (d, J = 7.87 Hz, 1H), 7.58 (td, J = 6.90, 3.28 Hz, 1H), 7.37 (d, J = 7.48 Hz, 1H), 7.06–7.01 (m, 1H), 6.26 (q, J = 7.06 Hz, 1H), 4.72 (s, 1H), 4.32–4.06 (m, 8H), 1.92 (d, J = 7.15 Hz, 3H), 1.28–1.16 (m, 12H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 167.8, 165.8, 164.5, 164.2, 163.8, 161.0, 141.3, 134.3, 131.0, 127.1, 126.3, 124.7, 123.8, 121.4, 119.4, 116.8, 105.7, 72.9, 61.0, 60.7, 59.0, 58.6, 50.6, 13.9, 11.8, 11.7 (3C).

Triethyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,2,3-tricarboxylate (3i)



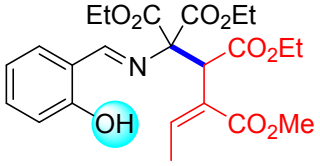
3i, 52%

Prepared according to the general procedure. Compound **3i** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 6:1) to afford a yellow oil in 52% yield (21.1 mg).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 12.48 (s, 1H), 8.36 (s, 1H), 7.36 (td, J = 8.64, 1.74 Hz, 2H), 6.99 (d, J = 7.28 Hz, 1H), 6.90 (d, J = 7.49 Hz, 1H), 6.32 (q, J = 7.22 Hz, 1H), 4.59 (s, 1H), 4.56 (s, 1H), 4.22–4.17 (m, 6H), 2.03 (d, J = 7.21 Hz, 3H), 1.30–1.24 (m, 9H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 168.6, 168.2, 161.0, 144.4, 142.9, 133.0, 132.0 (2C), 118.7 (2C), 117.1, 117.0, 71.8, 61.6, 61.2, 60.5, 53.0, 16.0, 14.1 (2C), 14.0.

1,1,2-triethyl-3-methyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3j)



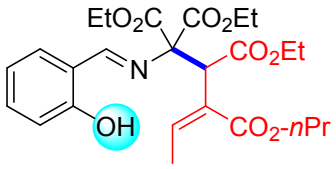
3j, 68%

Prepared according to the general procedure. Compound **3j** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 5:1) to afford a yellow oil in 68% yield (31.5 mg).

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.71 (s, 1H), 8.55 (s, 1H), 7.59 (dd, J = 7.60, 1.71 Hz, 1H), 7.41 (td, J = 7.78, 1.68 Hz, 1H), 7.00–6.89 (m, 2H), 6.21 (q, J = 7.16 Hz, 1H), 4.62 (s, 1H), 4.30–4.07 (m, 6H), 3.60 (s, 3H), 1.91 (d, J = 7.20 Hz, 3H), 1.24–1.14 (m, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.9, 169.7, 167.1, 166.9, 166.7, 160.6, 143.2, 133.8, 133.2, 126.3, 119.3, 119.2, 117.1 , 76.7, 63.0 , 62.8 , 61.2 , 52.3 , 52.0 , 16.4 , 14.2 , 14.1 (2C).

1,1,2-triethyl-3-propyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3k)



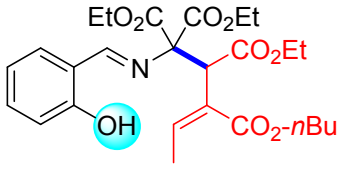
3k, 86%

Prepared according to the general procedure. Compound **3k** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 6:1) to afford a yellow oil in 66% yield (32.4 mg).

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.70 (s, 1H), 8.56 (s, 1H), 7.58 (dd, J = 7.69, 1.71 Hz, 1H), 7.41 (td, J = 7.75, 1.66 Hz, 1H), 6.94 (td, J = 7.89, 1.92 Hz, 2H), 6.22 (q, J = 7.12 Hz, 1H), 4.63 (s, 1H), 4.29–3.95 (m, 8H), 1.92 (d, J = 7.19 Hz, 3H), 1.54 (q, J = 7.06 Hz, 2H), 1.23–1.16 (m, 9H), 0.83 (t, J = 7.39 Hz, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 170.0, 169.7, 167.1, 166.9, 166.4, 160.6, 142.7, 133.8, 133.1, 126.6, 119.2 (2C), 117.1, 76.8, 66.5, 62.9, 62.8, 61.2, 52.4, 21.7, 16.3, 14.2, 14.1, 14.0, 10.7.

3-butyl-1,1,2-triethyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3l)



3l, 44%

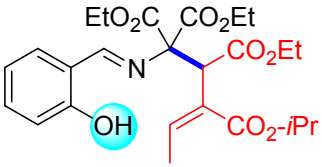
Prepared according to the general procedure. Compound **3l** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 6:1) to afford a yellow oil in 44% yield (22.2 mg).

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.69 (s, 1H), 8.56 (s, 1H), 7.57 (dd, J = 7.63, 1.74 Hz,

1H), 7.41 (td, *J* = 7.76, 1.73 Hz, 1H), 6.98–6.88 (m, 2H), 6.22 (q, *J* = 7.16 Hz, 1H), 4.62 (s, 1H), 4.29–3.95 (m, 8H), 1.91 (d, *J* = 7.20 Hz, 3H), 1.56–1.43 (m, 2H), 1.28–1.14 (m, 11H), 0.84 (t, *J* = 7.33 Hz, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.9, 169.7, 167.1, 166.9, 166.4, 160.6, 142.8, 133.8, 133.1, 126.7, 119.2 (2C), 117.1, 76.8, 64.7, 62.9, 62.8, 61.2, 52.4, 30.3, 19.1, 16.3, 14.2, 14.1, 14.0, 13.9.

1,1,2-triethyl-3-isopropyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3m)



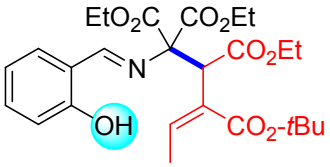
3m, 57%

Prepared according to the general procedure. Compound **3m** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 6:1) to afford a yellow oil in 57% yield (28.0 mg).

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.72 (s, 1H), 8.56 (s, 1H), 7.58 (dd, *J* = 7.65, 1.72 Hz, 1H), 7.45–7.36 (m, 1H), 6.99–6.88 (m, 2H), 6.18 (q, *J* = 7.17 Hz, 1H), 4.86 (p, *J* = 6.24 Hz, 1H), 4.62 (s, 1H), 4.30–4.05 (m, 6H), 1.91 (d, *J* = 7.22 Hz, 3H), 1.24–1.12 (m, 15H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 170.0, 169.7, 167.2, 166.9, 166.0, 160.7, 142.1, 133.8, 133.1, 126.9, 119.2, 119.2, 117.1, 76.7, 68.8, 62.9, 62.8, 61.2, 52.2, 21.9, 21.8, 16.3, 14.2, 14.1 (2C).

3-(tert-butyl)-1,1,2-triethyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3n)



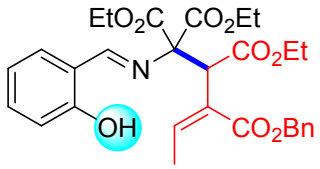
3n, 33%

Prepared according to the general procedure. Compound **3n** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 6:1) to afford a yellow oil in 33% yield (16.7 mg).

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.84 (s, 1H), 8.54 (s, 1H), 7.57 (dd, *J* = 7.69, 1.67 Hz, 1H), 7.40 (td, *J* = 8.05, 1.68 Hz, 1H), 6.98–6.88 (m, 2H), 6.14 (q, *J* = 7.16 Hz, 1H), 4.65 (s,

1H), 4.28–4.07 (m, 6H), 1.90 (d, J = 7.21 Hz, 3H), 1.39 (s, 9H), 1.24–1.14 (m, 9H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 170.2, 169.8, 167.3, 167.0, 165.8, 160.8, 141.7, 133.8, 133.2, 127.6, 119.3 (2C), 117.2, 81.6, 76.6, 62.9, 62.8, 61.2, 51.6, 28.2 (3C), 16.4, 14.3, 14.1 (2C).

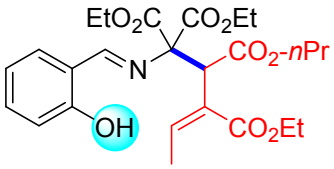
3-benzyl-1,1,2-triethyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3o)



3o, 58%

Prepared according to the general procedure. Compound **3o** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 5:1) to afford a yellow oil in 58% yield (31.3 mg).
^{1}H NMR (300 MHz, DMSO-d_6) δ 12.72 (s, 1H), 8.56 (s, 1H), 7.59 (dd, J = 8.00, 1.74 Hz, 1H), 7.46–7.28 (m, 6H), 6.95 (t, J = 7.49 Hz, 2H), 6.25 (q, J = 7.20 Hz, 1H), 5.11 (d, J = 12.40 Hz, 1H), 5.03 (d, J = 12.40 Hz, 1H), 4.65 (s, 1H), 4.30–4.00 (m, 6H), 1.90 (d, J = 7.07 Hz, 3H), 1.23–1.10 (m, 9H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 169.9, 169.8, 167.1, 166.9, 166.2, 160.6, 143.3, 136.0, 133.9 (2C), 133.2, 128.8, 128.6, 128.5, 126.4, 119.3, 119.2, 117.1 (2C), 76.8, 66.7, 63.0, 62.8, 61.2, 52.4, 16.4, 14.2, 14.1, 14.0.

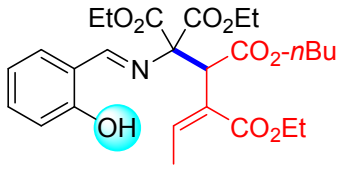
1,1,3-triethyl-2-propyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3p)



3p, 56%

Prepared according to the general procedure. Compound **3p** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 6:1) to afford a yellow oil in 56% yield (27.5 mg).
^{1}H NMR (300 MHz, DMSO-d_6) δ 12.66 (s, 1H), 8.56 (s, 1H), 7.56 (dd, J = 7.53, 1.76 Hz, 1H), 7.40 (td, J = 7.34, 1.74 Hz, 1H), 6.97–6.89 (m, 2H), 6.21 (q, J = 7.18Hz, 1H), 4.64 (s, 1H), 4.29–4.15 (m, 4H), 4.08–3.94 (m, 4H), 1.91 (d, J = 7.20 Hz, 3H), 1.62–1.50 (m, 2H), 1.24–1.13 (m, 9H), 0.85 (t, J = 7.42 Hz, 3H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 170.1, 169.7, 167.2, 167.0, 166.4, 160.7, 142.9, 133.9, 133.2, 126.7, 119.3, 119.2, 117.1, 76.8, 66.7, 63.0, 62.8, 61.0, 52.5, 21.8, 16.3, 14.2, 14.1 (2C), 10.6.

2-butyl-1,1,3-triethyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3q)



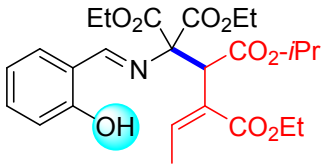
3q, 60%

Prepared according to the general procedure. Compound **3q** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 5:1) to afford a yellow oil in 60% yield (30.3 mg).

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.69 (s, 1H), 8.56 (s, 1H), 7.57 (dd, J = 7.63, 1.74 Hz, 1H), 7.40 (td, J = 7.46, 1.73 Hz, 1H), 6.98–6.89 (m, 2H), 6.21 (q, J = 7.16 Hz, 1H), 4.62 (s, 1H), 4.28–4.14 (m, 4H), 4.08–3.97 (m, 4H), 1.90 (d, J = 7.19 Hz, 3H), 1.58–1.47 (m, 2H), 1.34–1.24 (m, 2H), 1.23–1.10 (m, 9H), 0.85 (t, J = 7.34 Hz, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 170.0, 169.7, 167.1, 166.9, 166.3, 160.6, 142.8, 133.8, 133.1, 126.6, 119.3, 119.2, 117.1, 76.7, 64.9, 62.9, 62.8, 60.9, 52.4, 30.3, 18.9, 16.3, 14.2, 14.1, 14.0, 13.8.

1,1,3-triethyl-2-isopropyl-(3*E*)-1-((2hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3r)



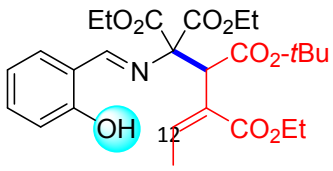
3r, 54%

Prepared according to the general procedure. Compound **3r** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 6:1) to afford a yellow oil in 54% yield (26.5 mg).

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.69 (s, 1H), 8.55 (s, 1H), 7.56 (dd, J = 7.55, 1.75 Hz, 1H), 7.40 (td, J = 7.36, 1.72 Hz, 1H), 6.97–6.90 (m, 2H), 6.19 (q, J = 7.19Hz, 1H), 4.91 (p, J = 6.23 Hz, 1H), 4.60 (s, 1H), 4.29–4.16 (m, 4H), 4.10–4.00 (m, 2H), 1.91 (d, J = 7.24 Hz, 3H), 1.25–1.18 (m, 9H), 1.17–1.12 (m, 6H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.7, 169.5, 167.2, 167.0, 166.4, 160.7, 142.6, 133.8, 133.2, 126.7, 119.3, 119.2, 117.1, 76.7, 68.8, 63.0, 62.8, 61.0, 52.5, 21.8, 21.6, 16.4, 14.3, 14.1 (2C).

2-(tert-butyl)-1,1,3-triethyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3s)



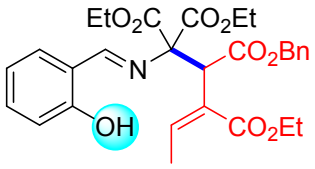
3s, 80%

Prepared according to the general procedure. Compound **3s** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 6:1) to afford a yellow oil in 80% yield (40.4 mg).

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.76 (s, 1H), 8.53 (s, 1H), 7.57 (dd, J = 7.93, 1.59 Hz, 1H), 7.40 (td, J = 7.49, 1.71 Hz, 1H), 6.98–6.90 (m, 2H), 6.16 (q, J = 7.19 Hz, 1H), 4.56 (s, 1H), 4.31–4.14 (m, 4H), 4.06 (q, J = 7.10 Hz, 2H), 1.91 (d, J = 7.23 Hz, 3H), 1.37 (s, 9H), 1.25–1.14 (m, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 169.8, 169.0, 167.3, 167.0, 166.6, 160.7, 142.0, 133.8, 133.2, 127.1, 119.3, 119.2, 117.1, 81.7, 76.6, 62.9, 62.8, 60.9, 52.9, 27.9 (3C), 16.4, 14.3, 14.2, 14.1.

2-benzyl-1,1,3-triethyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,1,2,3-tetracarboxylate (3t)



3t, 56%

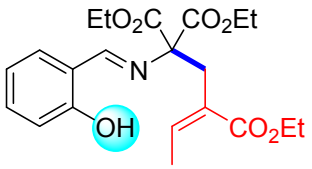
Prepared according to the general procedure. Compound **3t** was purified by silica gel chromatography (petroleum ether: ethyl acetate = 5:1) to afford a yellow oil in 56% yield (30.2 mg).

^{1}H NMR (500 MHz, DMSO-d_6) δ 12.69 (s, 1H), 8.56 (s, 1H), 7.54 (dd, J = 7.67, 1.74 Hz, 1H), 7.43–7.32 (m, 6H), 6.98–6.92 (m, 2H), 6.20 (q, J = 7.17 Hz, 1H), 5.17 (d, J = 12.45 Hz, 1H), 5.11 (d, J = 12.45 Hz, 1H), 4.71 (s, 1H), 4.23–4.14 (m, 4H), 4.06–3.99 (m, 2H), 1.90 (d, J = 7.22 Hz, 3H), 1.22–1.13 (m, 9H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 169.9, 169.7, 167.1, 167.0, 166.3, 160.7, 143.2, 136.1, 133.9 (2C), 133.1, 128.8, 128.6, 128.5, 126.4, 119.3 (2C), 117.1 (2C), 76.7, 66.7, 63.0, 62.9, 61.0, 52.4, 16.3, 14.2, 14.1 (2C).

Triethyl-(3*E*)-1-((2-hydroxybenzylidene)amino)pent-3-ene-1,1,3-tricarboxylate (3v)

Prepared according to the general procedure. Compound **3v** was purified by silica gel



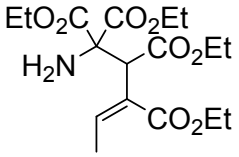
3v, 88%

chromatography (petroleum ether: ethyl acetate = 8:1) to afford a yellow oil in 88% yield (35.6 mg).

^{1}H NMR (500 MHz, DMSO-d_6) δ 12.70 (s, 1H), 8.49 (s, 1H), 7.58 (dd, J = 7.66, 2.15 Hz, 1H), 7.45–7.37 (m, 1H), 6.98–6.89 (m, 2H), 6.85 (q, J = 7.14 Hz, 1H), 4.30–4.20 (m, 4H), 3.91 (q, J = 7.04 Hz, 2H), 1.68 (d, J = 7.20 Hz, 3H), 1.25–1.22 (m, 6H), 1.10 (t, J = 7.12 Hz,

3H).
^{13}C NMR (125 MHz, DMSO-d_6) δ 168.4, 168.1, 167.4, 167.3, 167.1, 160.6, 141.3, 133.8, 132.9, 127.5, 119.3, 117.1, 75.0, 62.4 (2C), 60.7, 33.2, 16.0, 15.0, 14.2 (2C).

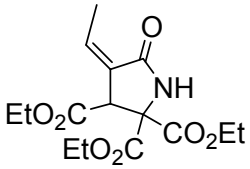
Tetraethyl (*Z*)-1-aminopent-3-ene-1,1,2,3-tetracarboxylate (4a)



4a, 78%

Afford 29.1 mg in 78% yield as a colorless oil
^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.35 (q, *J* = 7.19 Hz, 1H), 4.50 (s, 1H), 4.28–4.12 (m, 8H), 2.48 (s, 2H), 2.00 (d, *J* = 7.22 Hz, 3H), 1.30–1.22 (m, 12H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.5, 170.9, 168.2, 166.9, 142.0, 127.6, 68.7, 62.3, 62.2, 61.2, 60.5, 53.6, 16.0, 14.0(2C), 13.9(2C).

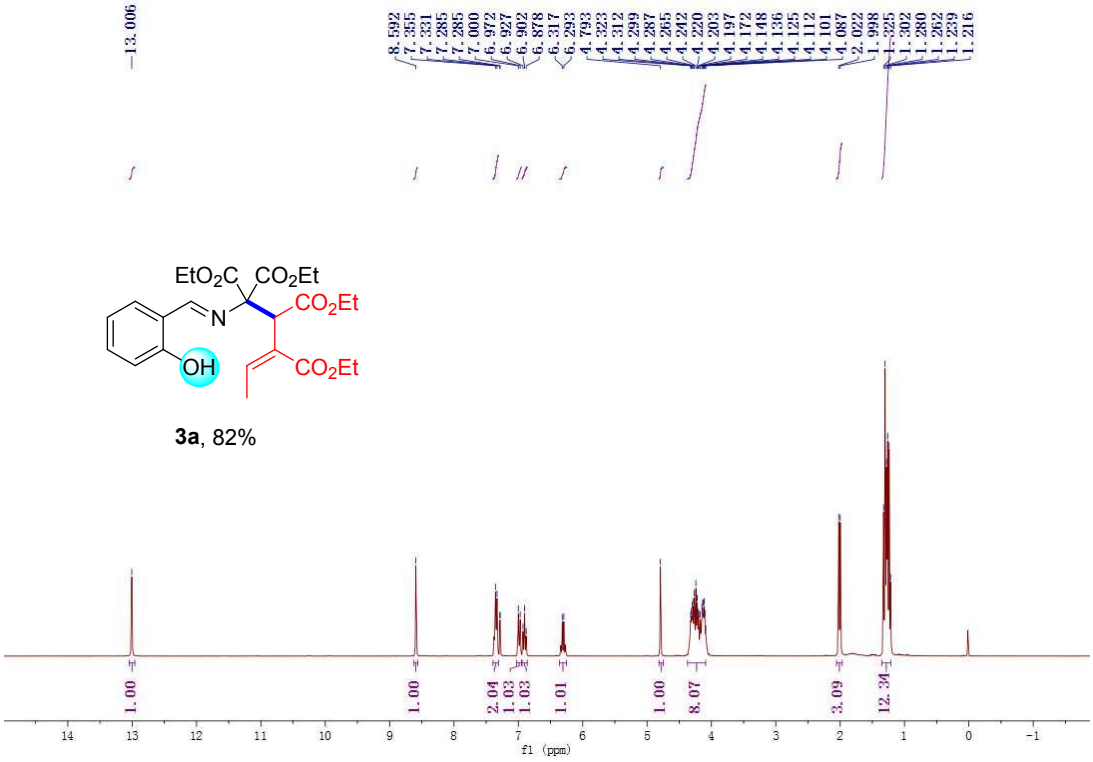
Triethyl (*Z*)-4-ethylidene-5-oxopyrrolidine-2,2,3-tricarboxylate (4b)



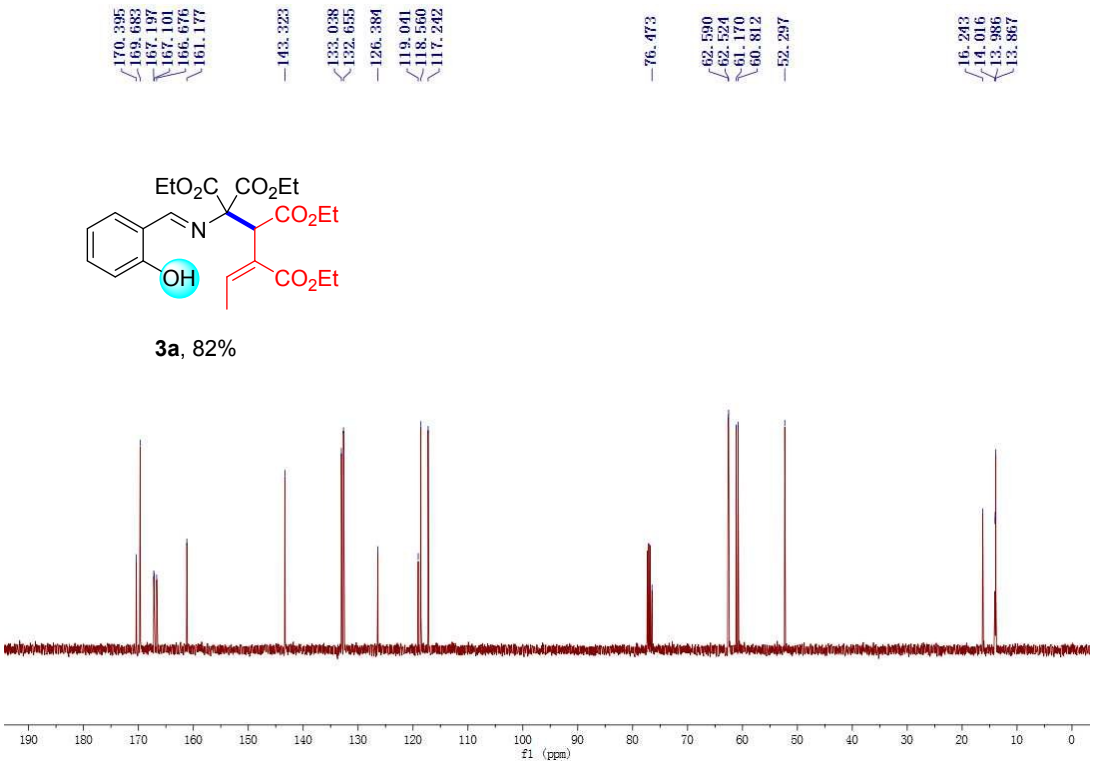
4b, 86%

Afford 28.1 mg in 86% yield as a yellowish oil.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.57 (s, 1H), 6.32 (q, J = 7.19 Hz, 1H), 4.47 (s, 1H), 4.31–4.20 (m, 4H), 4.15 (q, *J* = 7.09 Hz, 2H), 2.21 (dd, *J* = 7.37, 1.59 Hz, 3H), 1.30–1.23 (m, 9H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 169.1, 167.4, 167.2, 166.7, 137.7, 126.8, 67.2, 63.1, 62.6, 61.7, 51.4, 13.9, 13.8, 13.8, 13.6.

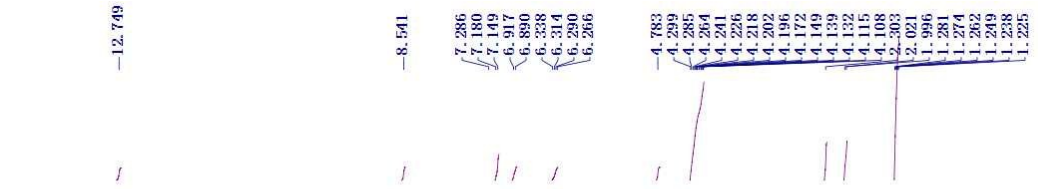
4. Copies of ^{1}H NMR, ^{13}C NMR spectra



3a, 82%



3a, 82%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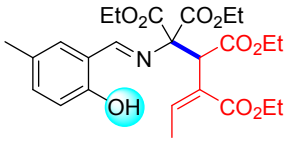
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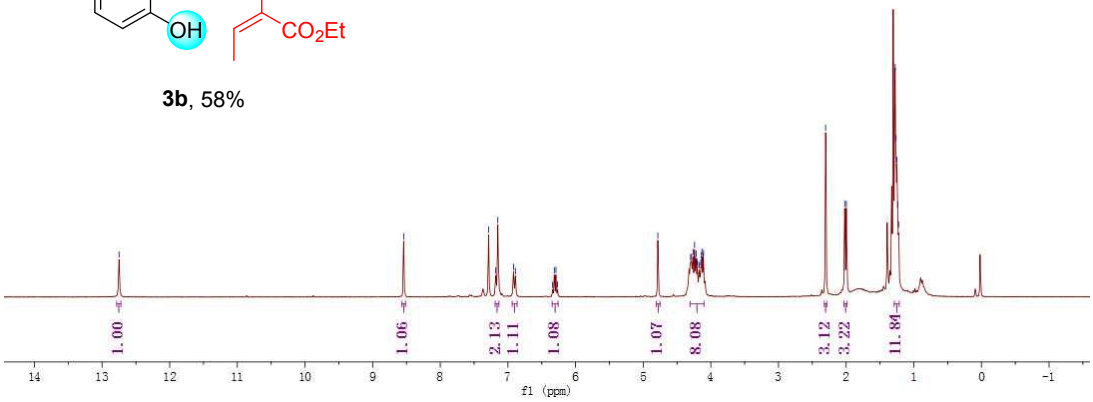
N
CO2Et
OH
CO2Et

3b, 58%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1.08
1.07
8.08
3.12
3.22
11.84
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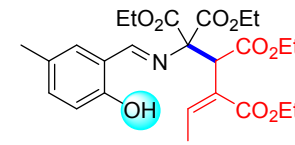
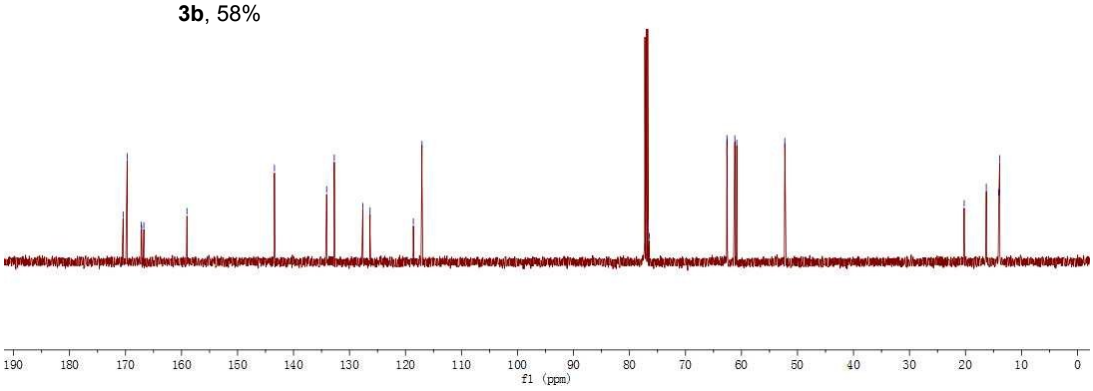
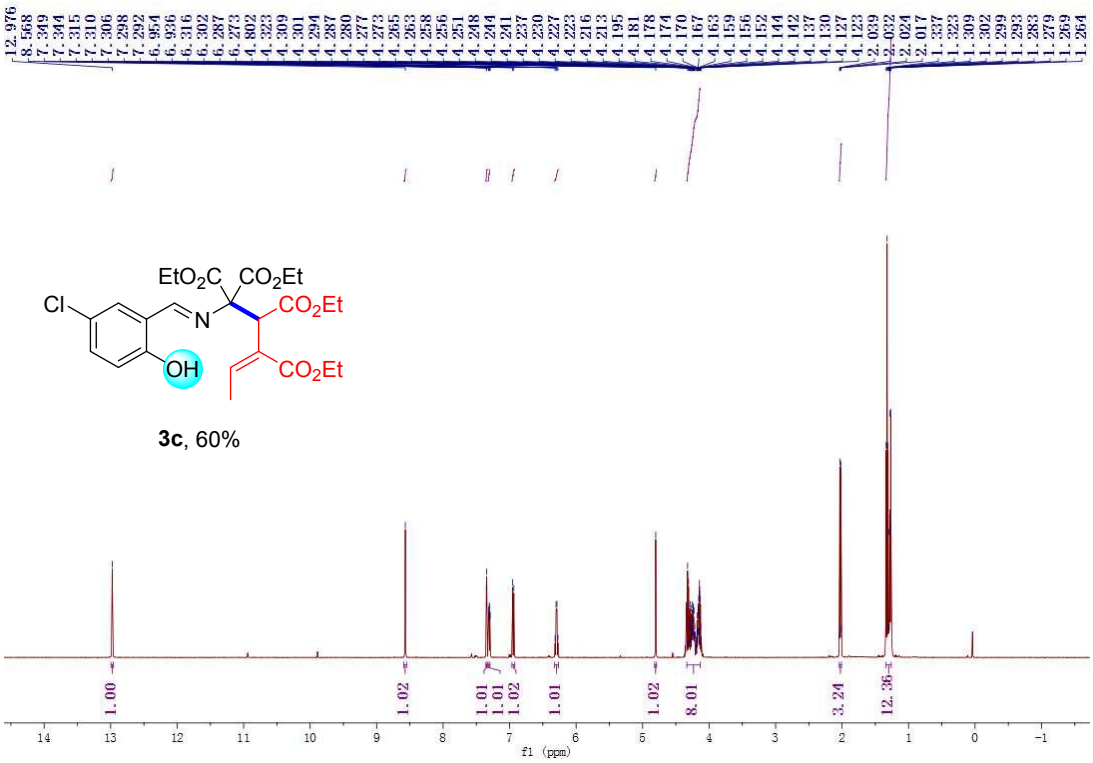
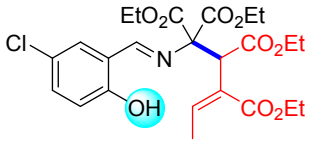

EtO2C
CO2Et
N
CO2Et
OH
CO2Et

3b, 58%

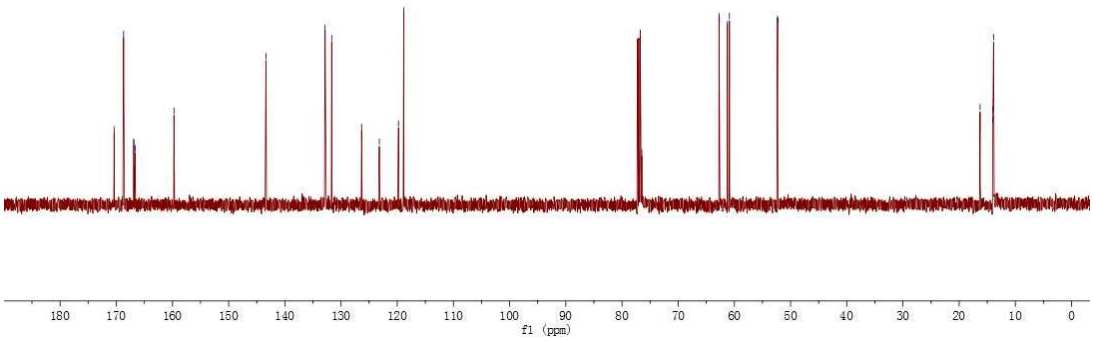

f1 (ppm)

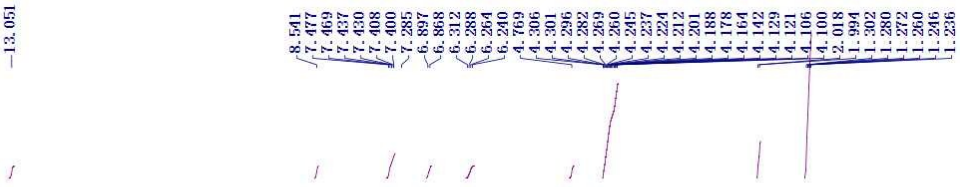


3c, 60%



3c, 60%

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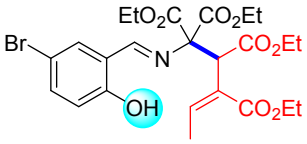
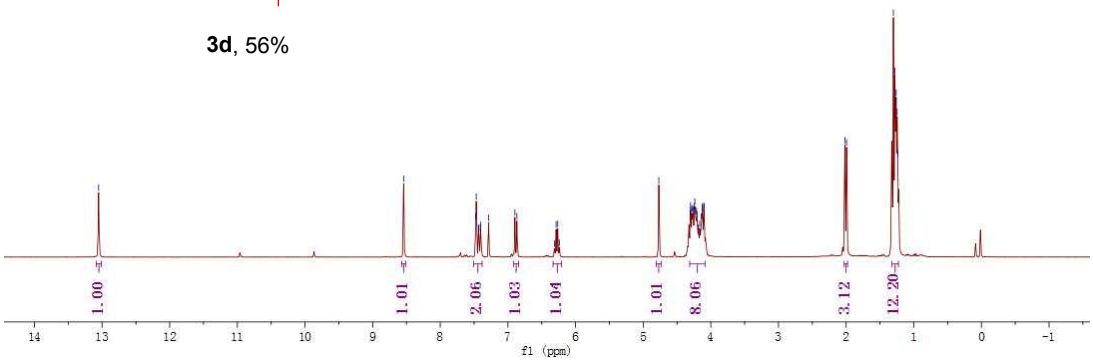
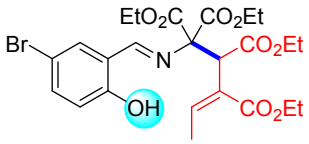

EtO2C
CO2Et
Br
N
CO2Et
OH
CO2Et

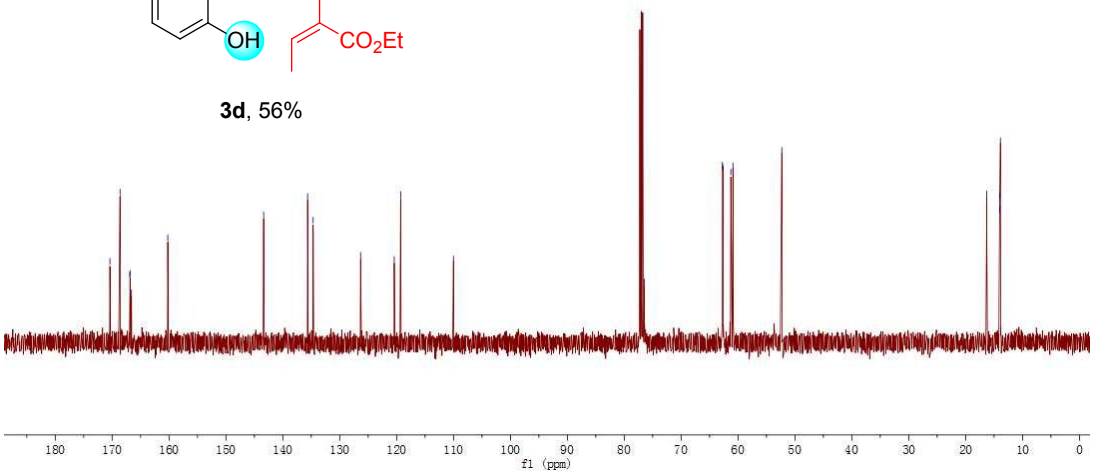
3d, 56%

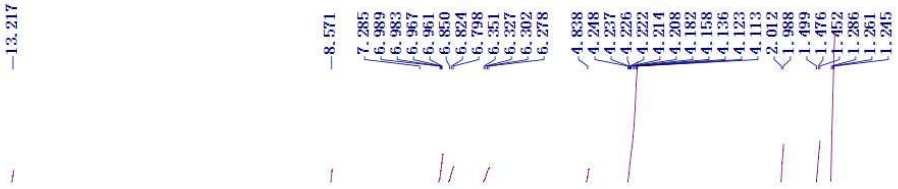

1.00
1.01
2.06
1.03
1.04
1.01
8.06
3.12
12.20
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

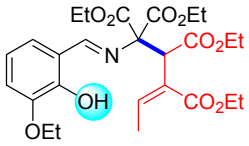

170.391
168.607
166.894
166.852
166.604
160.213
143.368
135.644
134.675
126.329
120.418
119.290
110.012
76.462
62.746
62.682
61.263
60.892
52.300
16.281
14.038
13.995
13.882


EtO2C
CO2Et
Br
N
CO2Et
OH
CO2Et

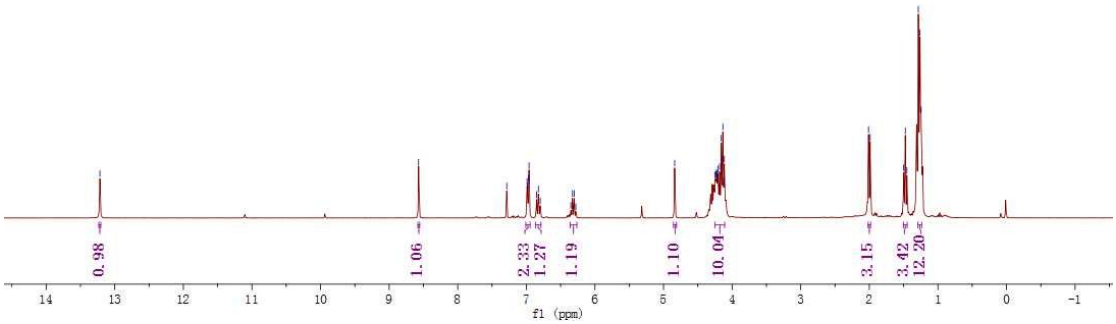
3d, 56%


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

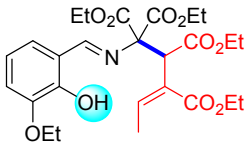

13.217
8.571
7.285
6.989
6.983
6.967
6.961
6.850
6.824
6.798
6.351
6.327
6.302
6.278
4.838
4.248
4.237
4.226
4.222
4.214
4.208
4.182
4.158
4.136
4.123
4.113
2.012
1.988
1.499
1.476
1.452
1.286
1.261
1.245


EtO2C
CO2Et
N
CO2Et
OH
CO2Et
OEt

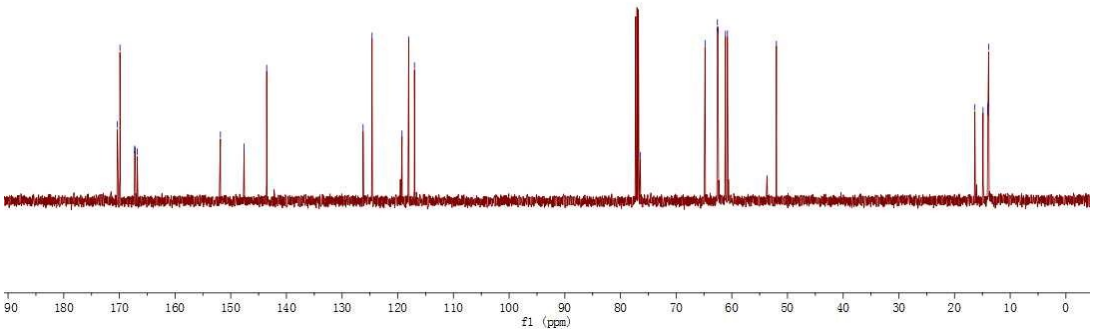
3e, 90%

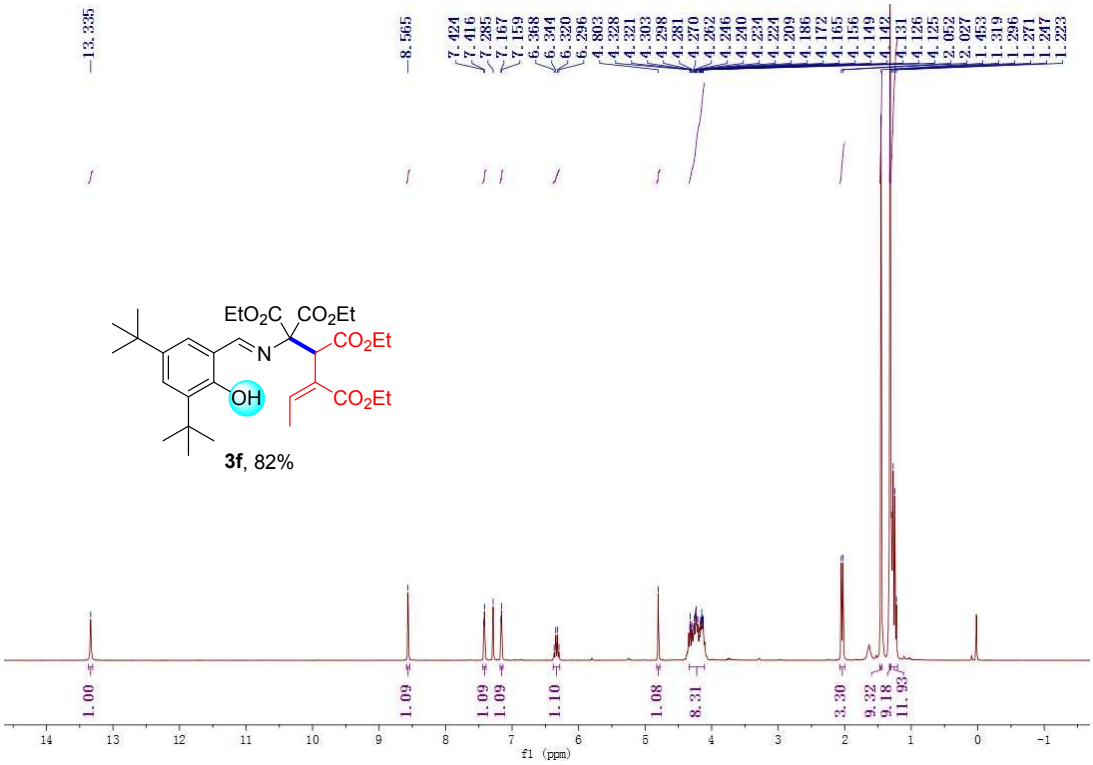

0.98
1.06
2.33
1.27
1.19
1.10
10.04
3.15
3.42
12.20
f1 (ppm)


170.364
169.904
167.277
167.147
166.793
151.856
147.607
143.546
126.228
124.624
119.237
118.028
117.003
76.434
64.813
62.582
62.497
61.154
60.788
51.994
16.347
14.875
14.054
13.996
13.873

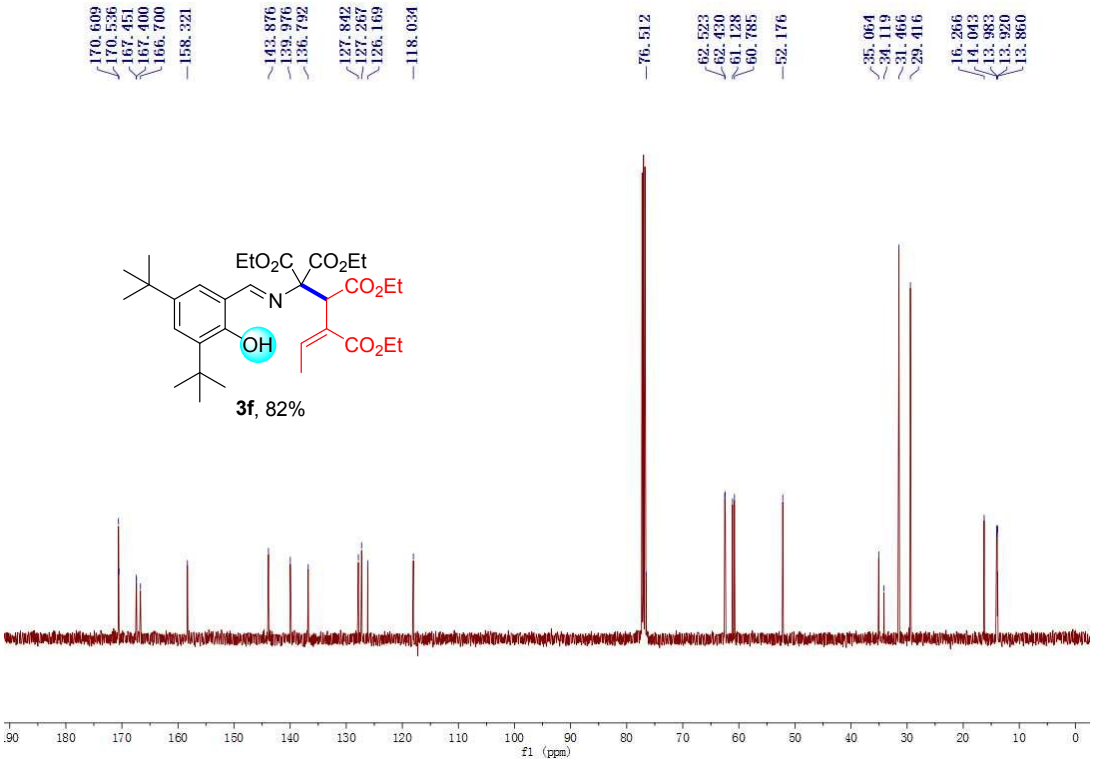

EtO2C
CO2Et
N
CO2Et
OH
CO2Et
OEt

3e, 90%

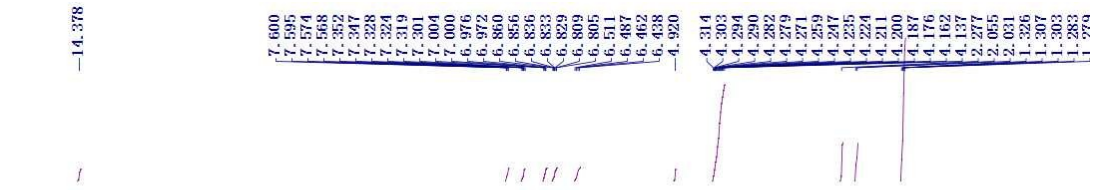

f1 (ppm)

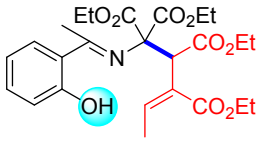

13.335
8.565
7.424
7.416
7.285
7.167
7.159
6.368
6.344
6.320
6.296
4.803
4.328
4.321
4.303
4.298
4.281
4.270
4.262
4.246
4.240
4.234
4.224
4.209
4.186
4.172
4.165
4.156
4.149
4.142
4.131
4.126
4.125
2.052
2.027
1.453
1.319
1.296
1.271
1.247
1.223
EtO2C
CO2Et
CO2Et
N
OH
CO2Et
1.00
1.09
1.09
1.09
1.10
1.08
8.31
3.30
9.32
9.18
11.93
f1 (ppm)

3f, 82%


170.609
170.536
167.451
167.400
166.700
158.321
143.876
139.976
136.792
127.842
127.267
126.169
118.034
76.512
62.523
62.430
61.128
60.785
52.176
35.064
34.119
31.466
29.416
16.266
14.043
13.983
13.920
13.860
EtO2C
CO2Et
CO2Et
N
OH
CO2Et
f1 (ppm)

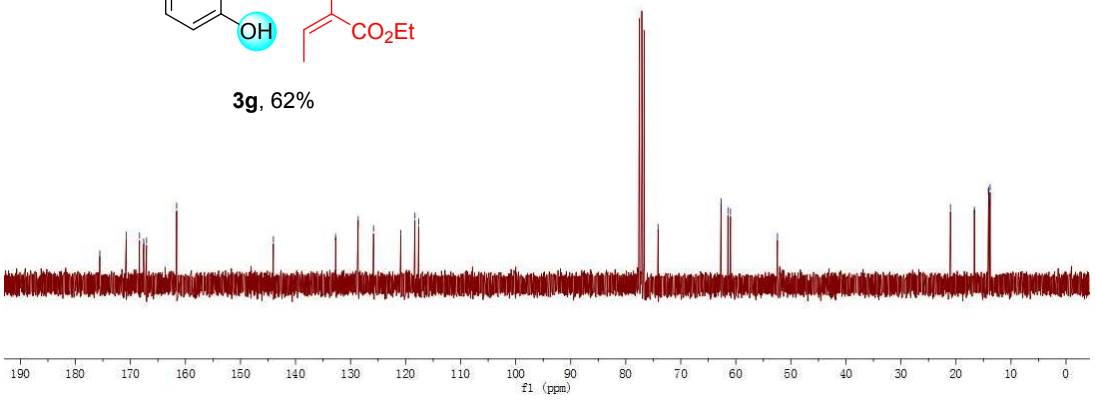
3f, 82%

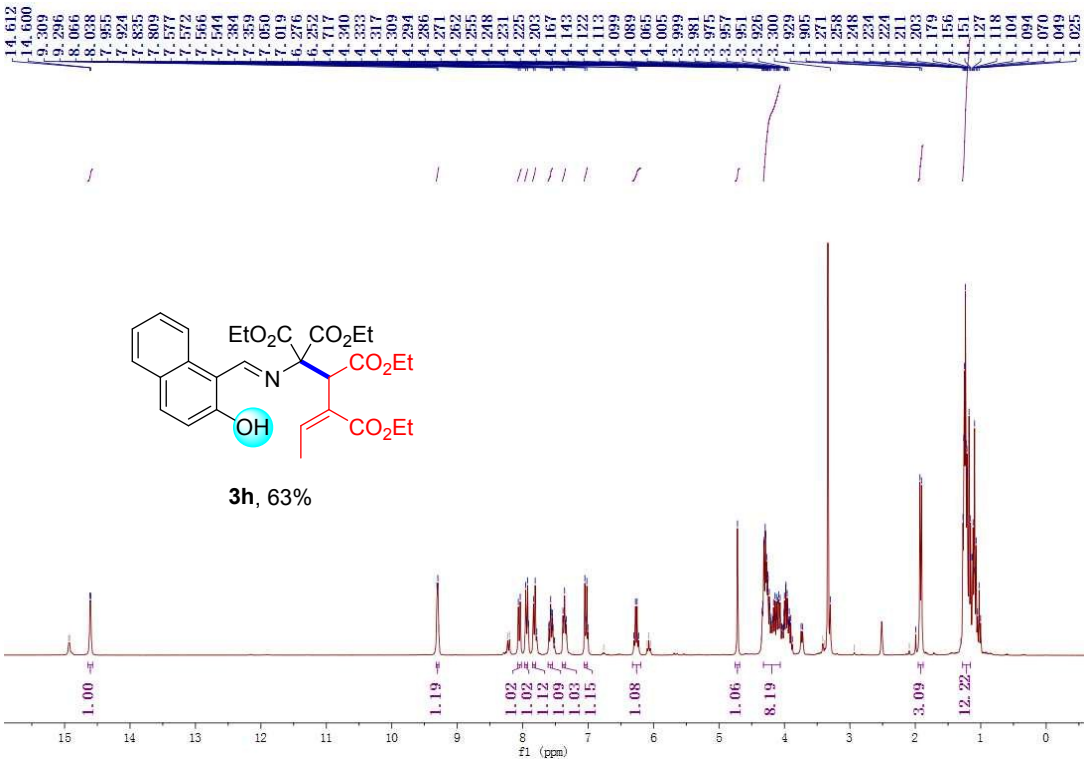




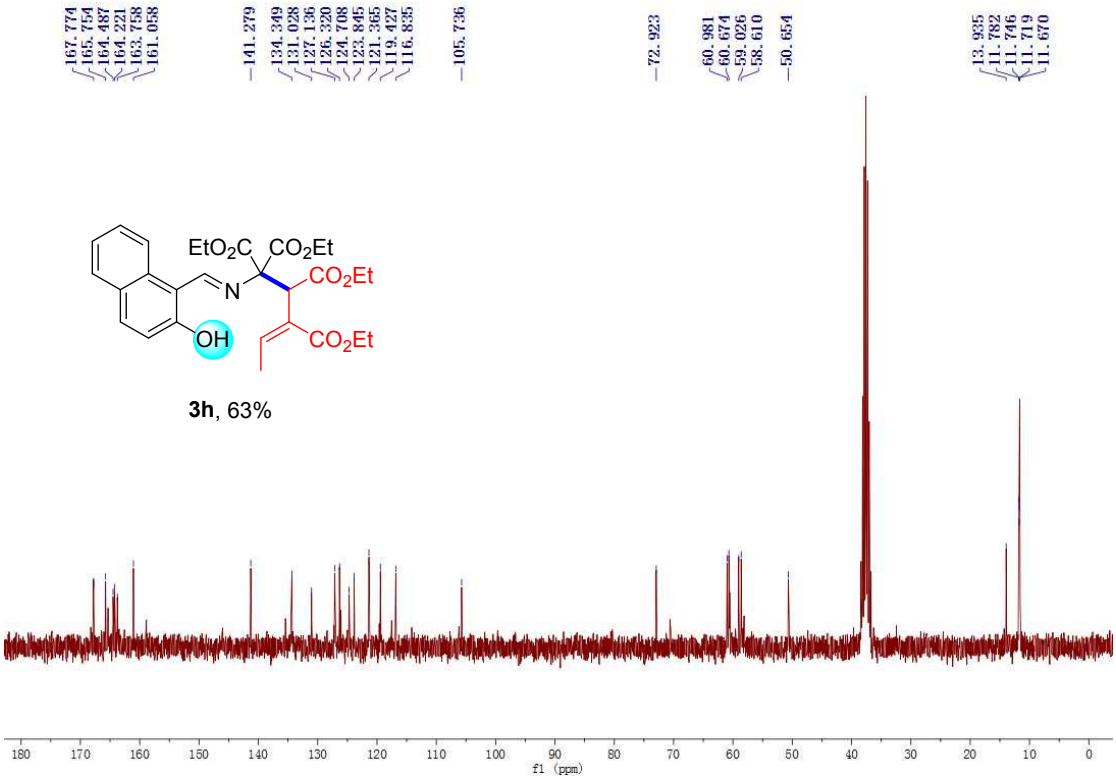
3g, 62%

3g, 62%

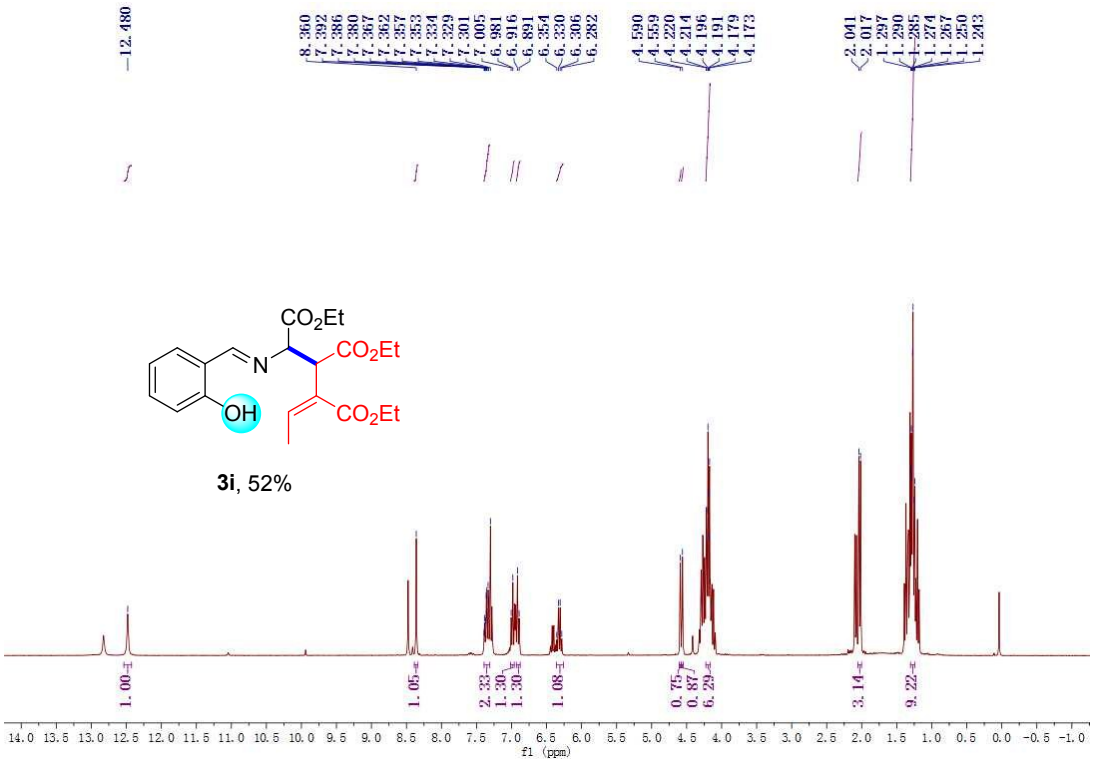


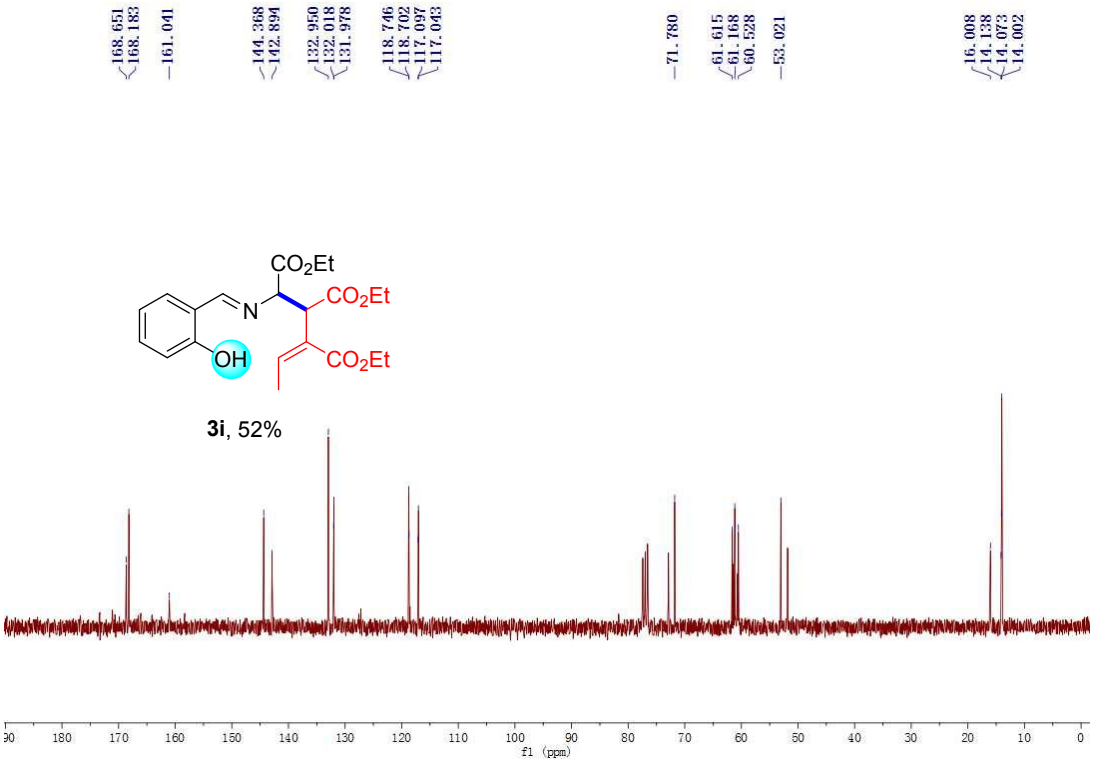

EtO2C
CO2Et
CO2Et
N
OH
CO2Et
f1 (ppm)

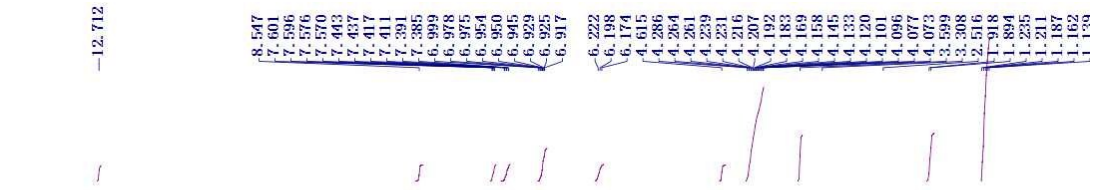
3h, 63%

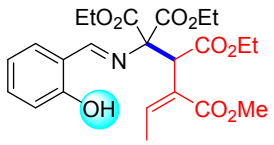

EtO2C
CO2Et
CO2Et
N
OH
CO2Et
f1 (ppm)

3h, 63%

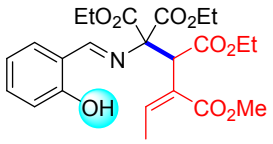

12.480
8.360
7.392
7.386
7.380
7.367
7.362
7.357
7.353
7.334
7.329
7.301
7.005
6.981
6.916
6.891
6.354
6.330
6.306
6.282
4.590
4.559
4.220
4.214
4.196
4.191
4.179
4.173
2.041
2.017
1.297
1.290
1.285
1.274
1.267
1.250
1.243
CO2Et
CO2Et
N
OH
CO2Et
3i, 52%
1.00
1.05
2.33
1.36
1.30
1.08
0.75
0.87
6.29
3.14
9.22
f1 (ppm)


168.651
168.183
161.041
144.368
142.894
132.950
132.018
131.978
118.746
118.702
117.097
117.043
71.780
61.615
61.168
60.528
53.021
16.008
14.138
14.073
14.002
CO2Et
CO2Et
N
OH
CO2Et
3i, 52%
f1 (ppm)

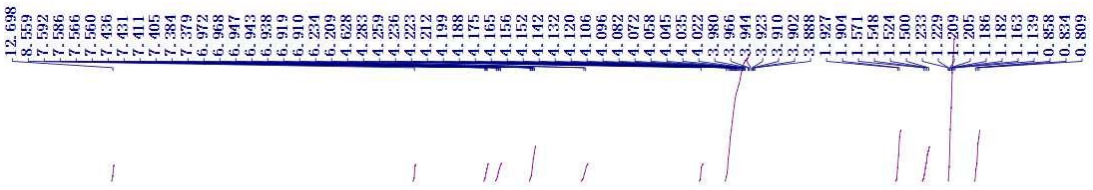


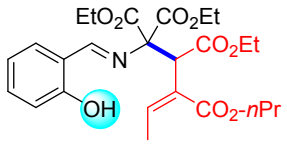


3j, 68%

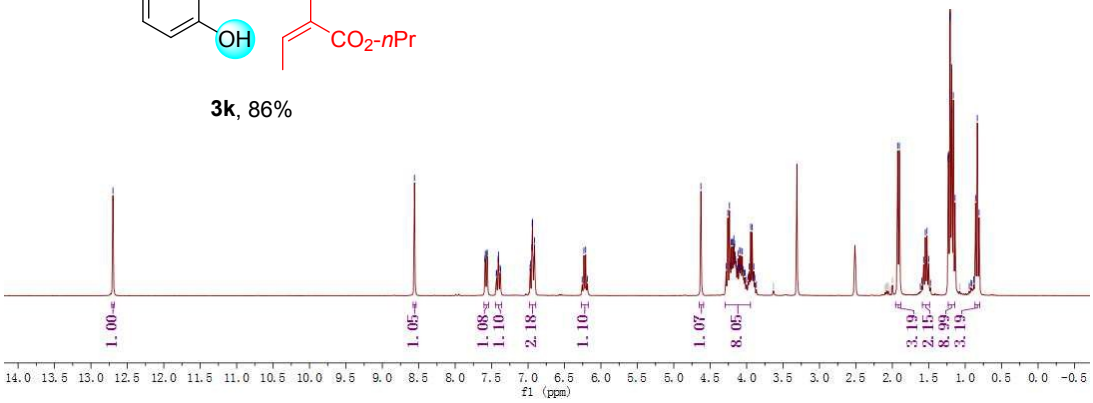


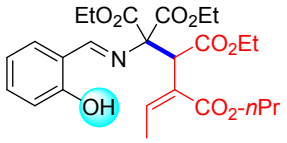
3j, 68%



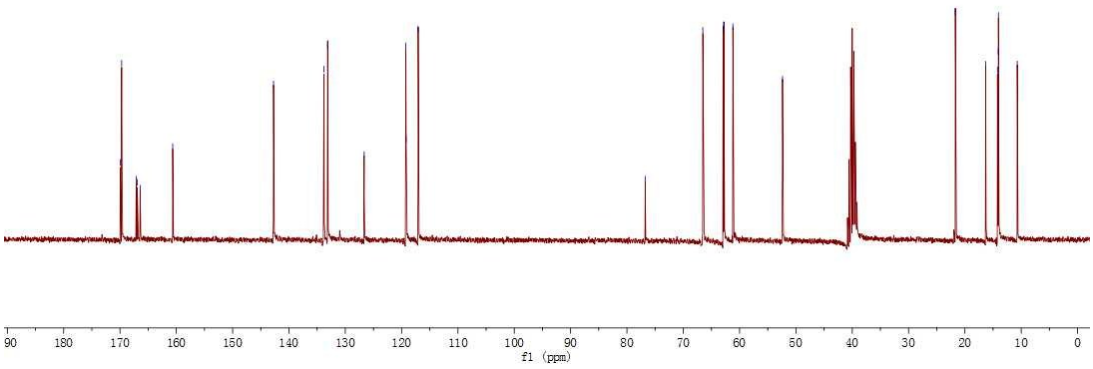


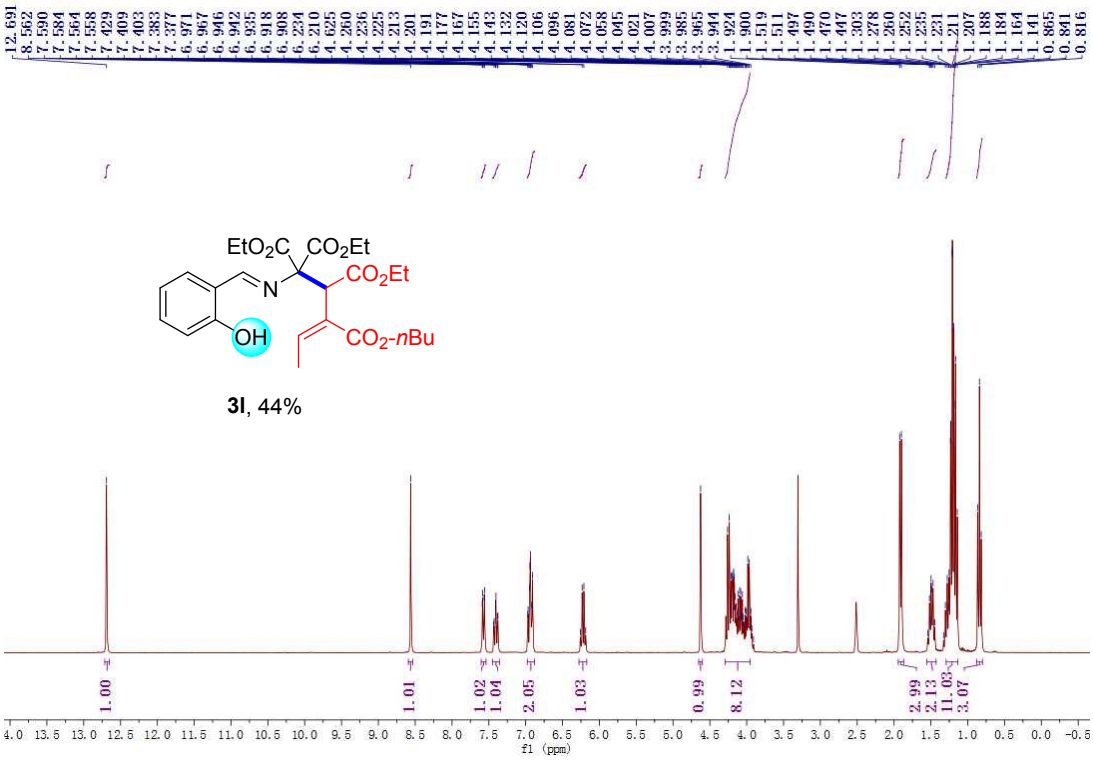
3k, 86%



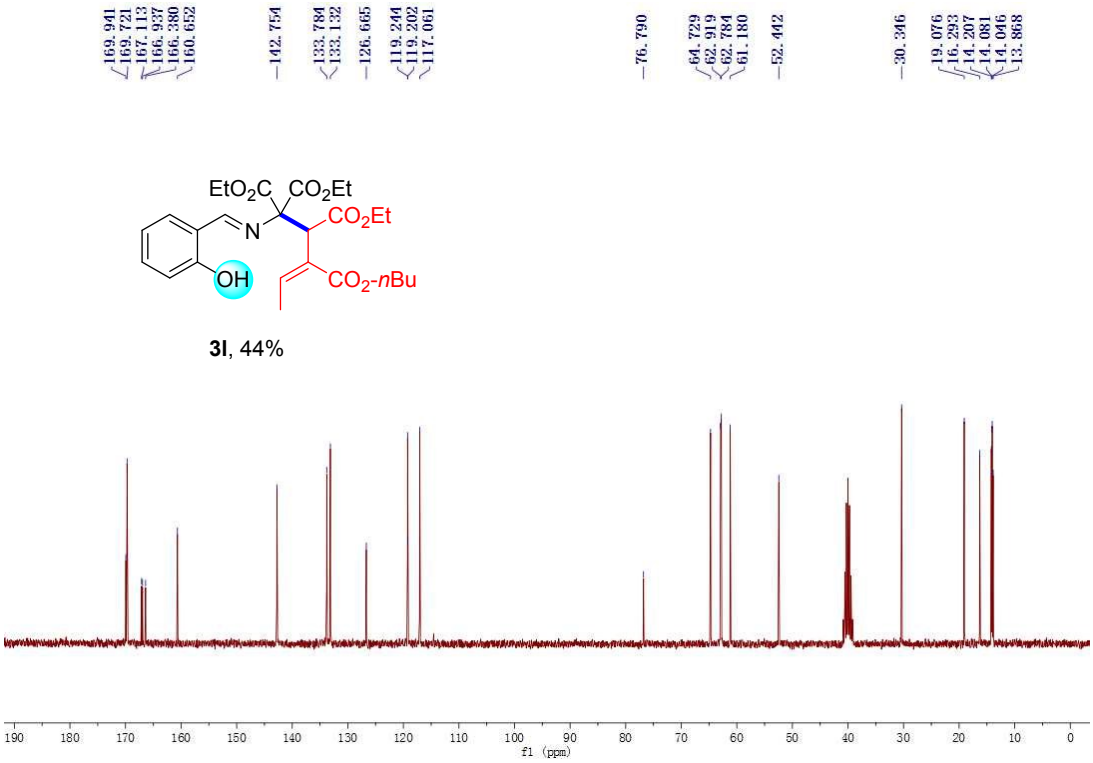


3k, 86%

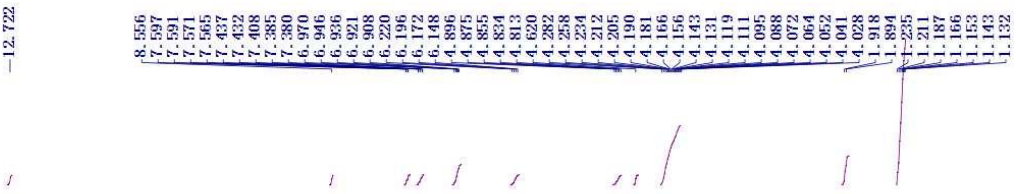


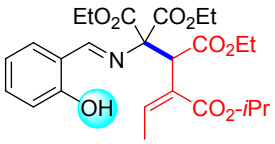

12.691
8.562
7.590
7.584
7.564
7.558
7.429
7.409
7.403
7.383
7.377
6.971
6.967
6.946
6.942
6.935
6.918
6.908
6.234
6.210
4.625
4.260
4.226
4.225
4.213
4.201
4.191
4.177
4.167
4.155
4.143
4.132
4.120
4.106
4.096
4.081
4.072
4.058
4.045
4.021
4.007
3.999
3.985
3.965
3.944
1.924
1.900
1.519
1.511
1.497
1.490
1.470
1.447
1.303
1.278
1.260
1.252
1.235
1.231
1.211
1.207
1.188
1.184
1.164
1.141
0.865
0.841
0.816
EtO2C
CO2Et
CO2Et
N
OH
CO2-nBu
1.00
1.01
1.02
1.04
2.05
1.03
0.99
8.12
2.99
2.13
11.03
3.07
f1 (ppm)

3l, 44%

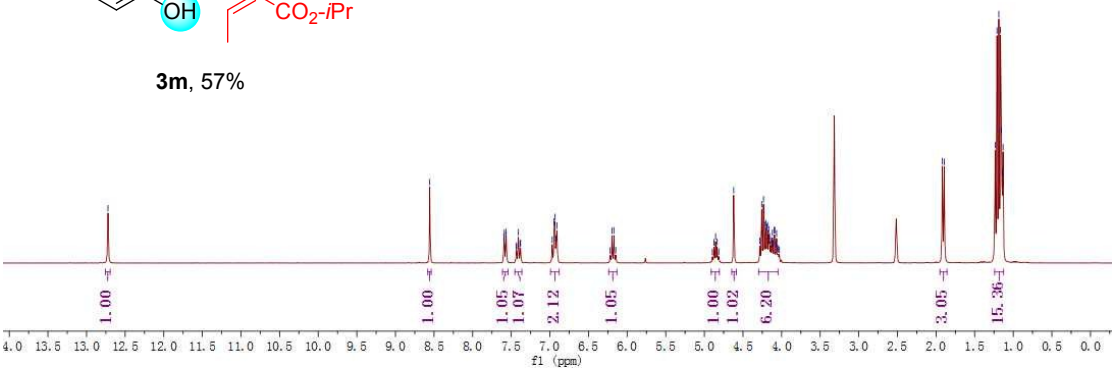

169.941
169.721
167.113
166.937
166.380
160.652
142.754
133.784
133.132
126.665
119.244
119.202
117.061
76.790
64.729
62.919
62.784
61.180
52.442
30.396
19.076
16.293
14.207
14.081
14.046
13.868
EtO2C
CO2Et
CO2Et
N
OH
CO2-nBu
f1 (ppm)

3l, 44%

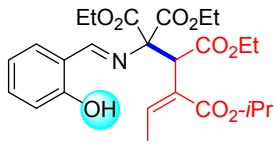

12.722
8.556
7.597
7.591
7.571
7.565
7.437
7.432
7.408
7.385
7.380
6.970
6.946
6.936
6.921
6.908
6.220
6.196
6.172
6.148
4.896
4.875
4.855
4.834
4.813
4.620
4.282
4.258
4.234
4.212
4.205
4.190
4.181
4.166
4.156
4.143
4.131
4.119
4.111
4.095
4.088
4.072
4.064
4.052
4.041
4.028
1.918
1.894
1.235
1.211
1.187
1.166
1.153
1.143
1.132


EtO2C
CO2Et
N
CO2Et
OH
CO2-iPr

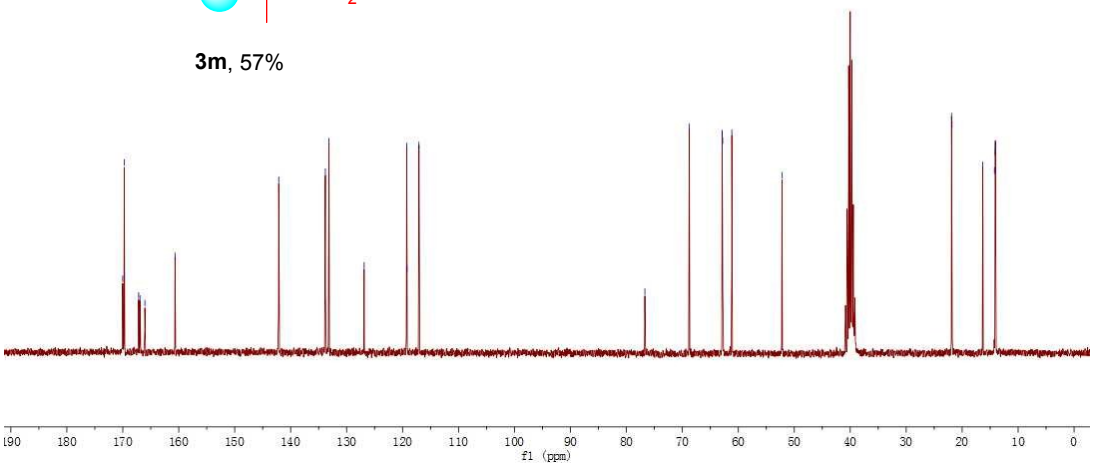
3m, 57%

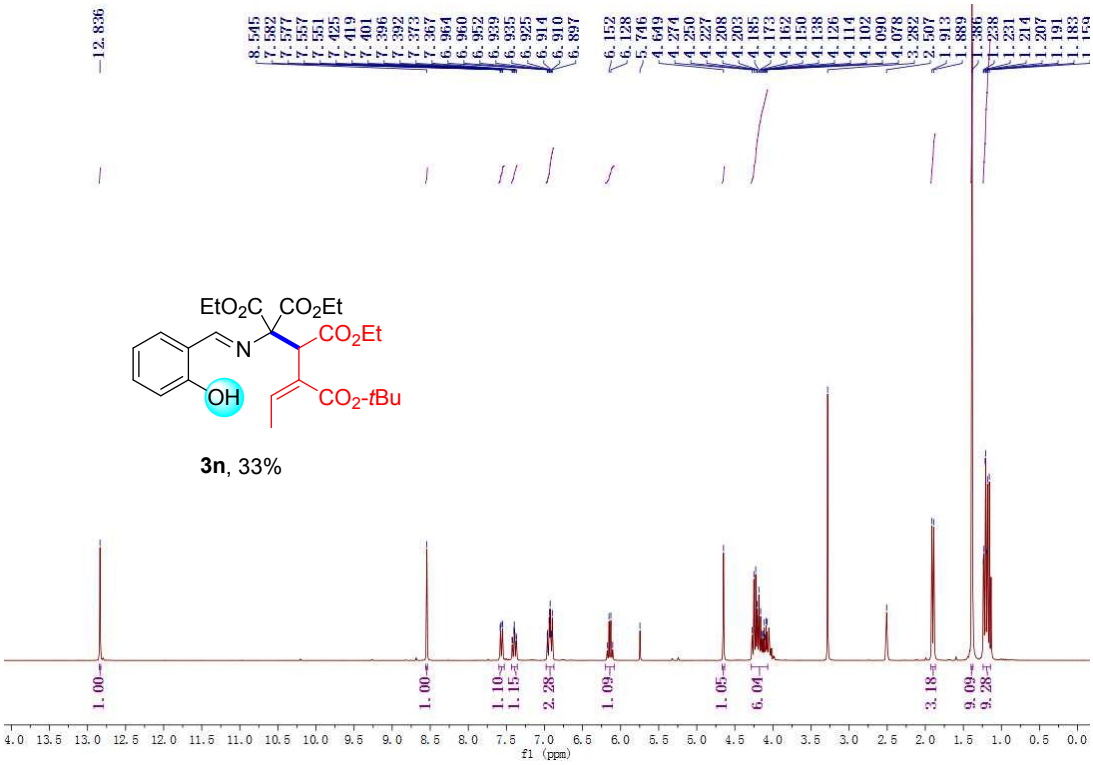

1.00
1.00
1.05
1.07
2.12
1.05
1.00
1.02
6.20
3.05
15.36
f1 (ppm)


170.020
169.735
167.164
166.932
166.056
160.670
142.134
133.800
133.148
126.869
119.256
119.196
117.072
76.701
68.769
62.896
62.805
61.166
52.200
21.896
21.815
16.308
14.234
14.095
14.064

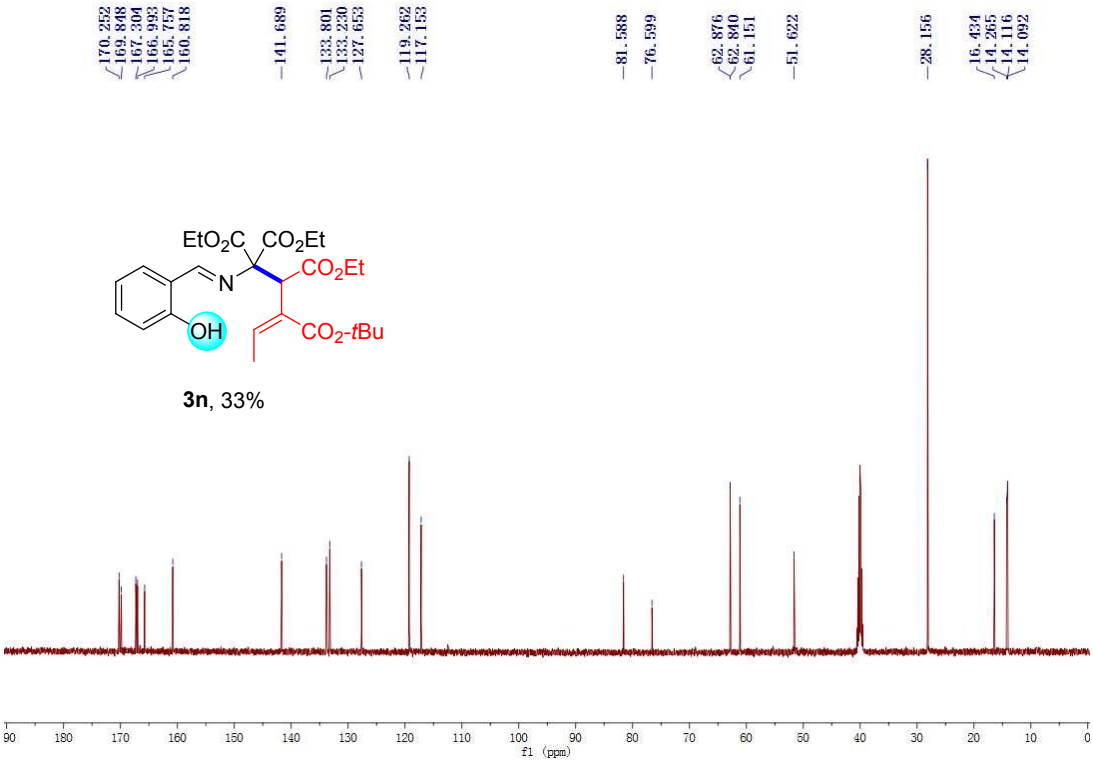

EtO2C
CO2Et
N
CO2Et
OH
CO2-iPr

3m, 57%

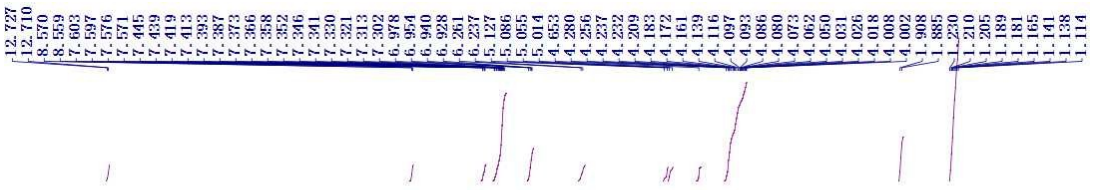

f1 (ppm)

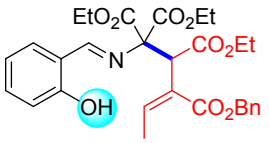


3n, 33%

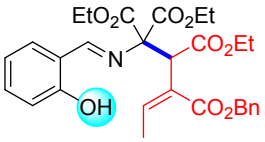


3n, 33%

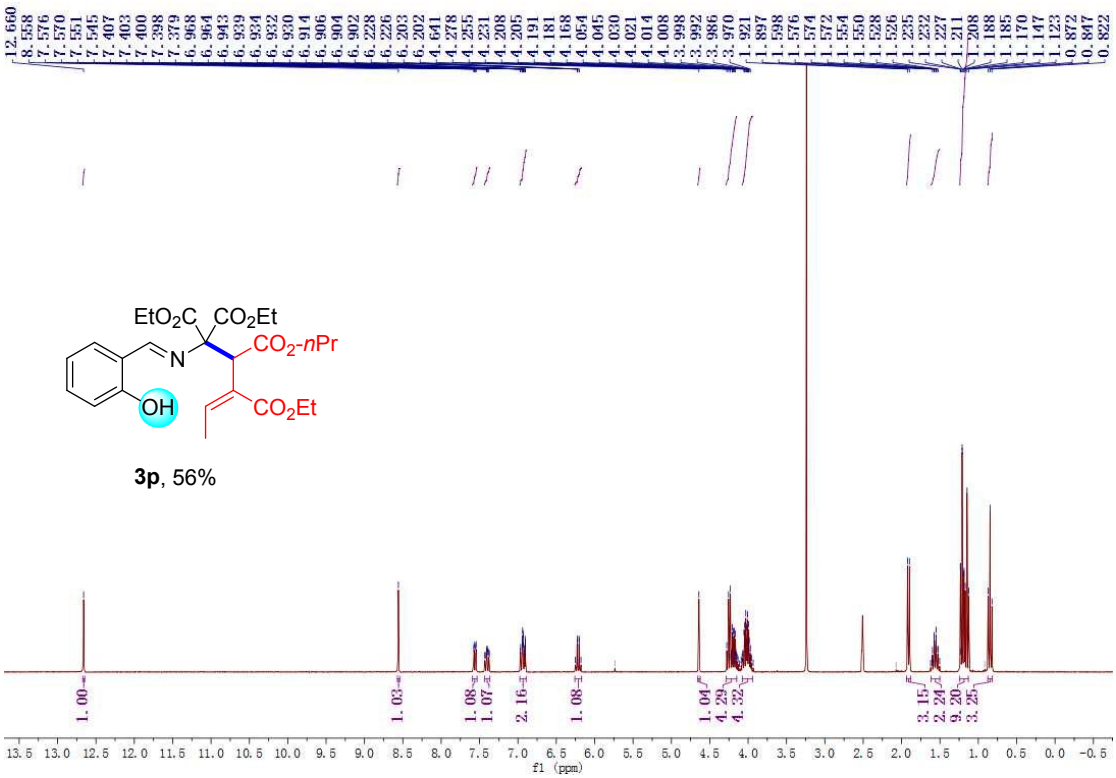


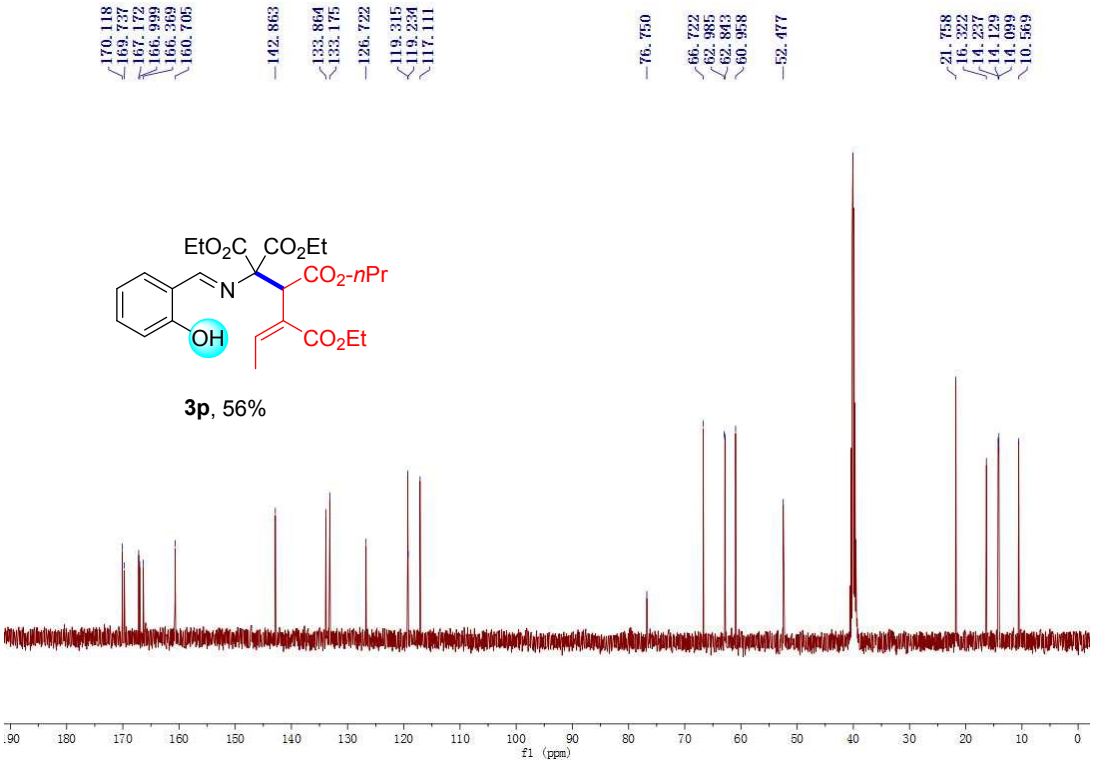


3o, 58%



3o, 58%


12.660
8.558
7.576
7.570
7.551
7.545
7.407
7.403
7.400
7.398
7.379
6.968
6.964
6.943
6.939
6.934
6.932
6.930
6.914
6.906
6.904
6.902
6.228
6.226
6.203
6.202
4.641
4.278
4.255
4.231
4.208
4.205
4.191
4.181
4.168
4.054
4.045
4.030
4.021
4.014
4.008
3.998
3.992
3.986
3.970
3.921
1.897
1.598
1.576
1.574
1.572
1.554
1.550
1.528
1.526
1.235
1.232
1.227
1.211
1.208
1.188
1.185
1.170
1.147
1.123
0.872
0.847
0.822
EtO2C
CO2Et
CO2-nPr
N
OH
CO2Et
3p, 56%
1.00
1.03
1.08
1.07
2.16
1.08
1.04
4.29
4.32
3.15
2.24
9.20
3.25
f1 (ppm)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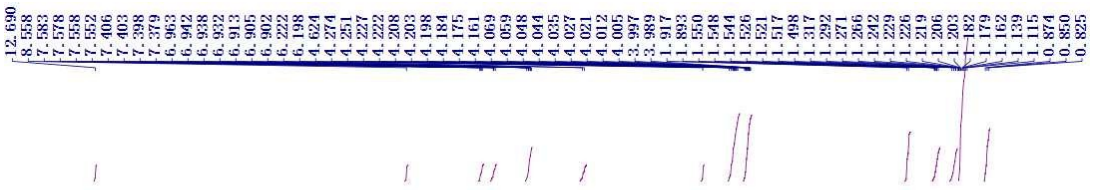
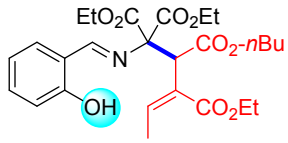
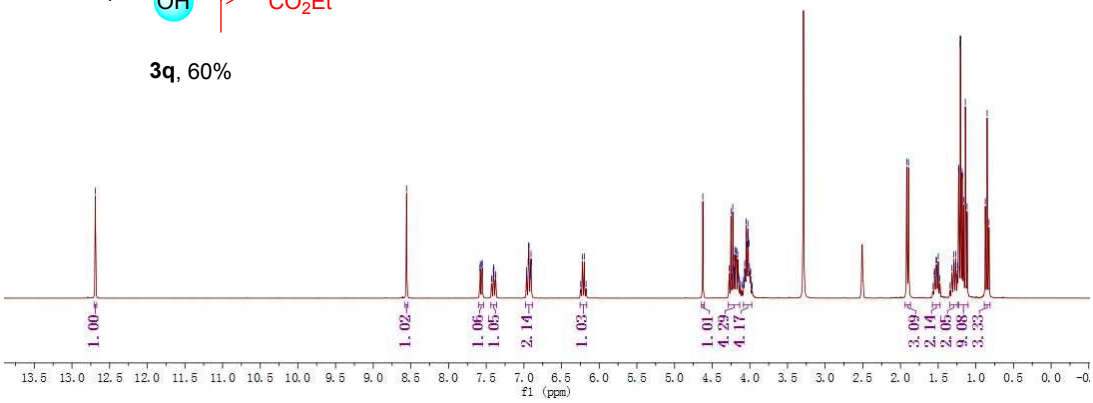
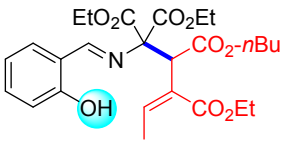
169.737
167.172
166.999
166.369
160.705
142.863
133.864
133.175
126.722
119.315
119.234
117.111
76.750
66.722
62.985
62.843
60.958
52.477
21.758
16.322
14.237
14.129
14.099
10.569
EtO2C
CO2Et
CO2-nPr
N
OH
CO2Et
3p, 56%
f1 (ppm)



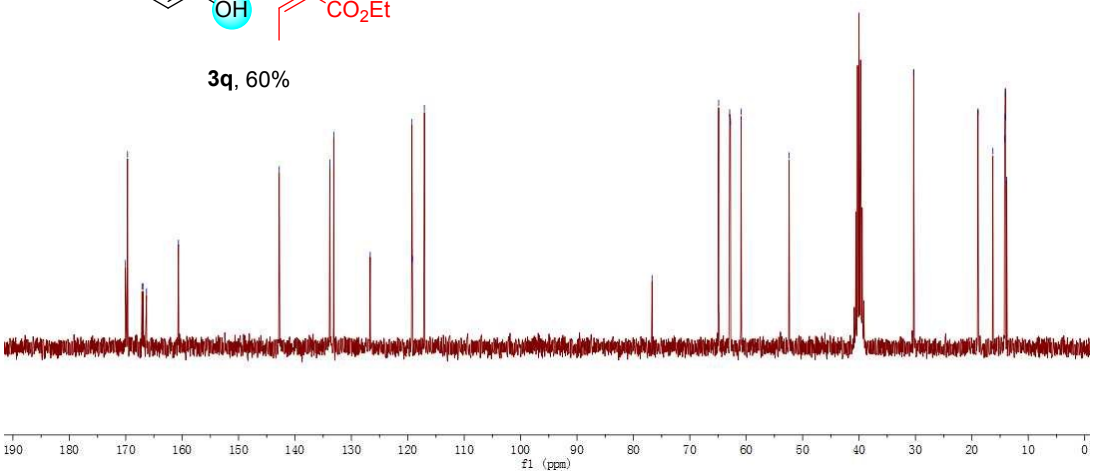


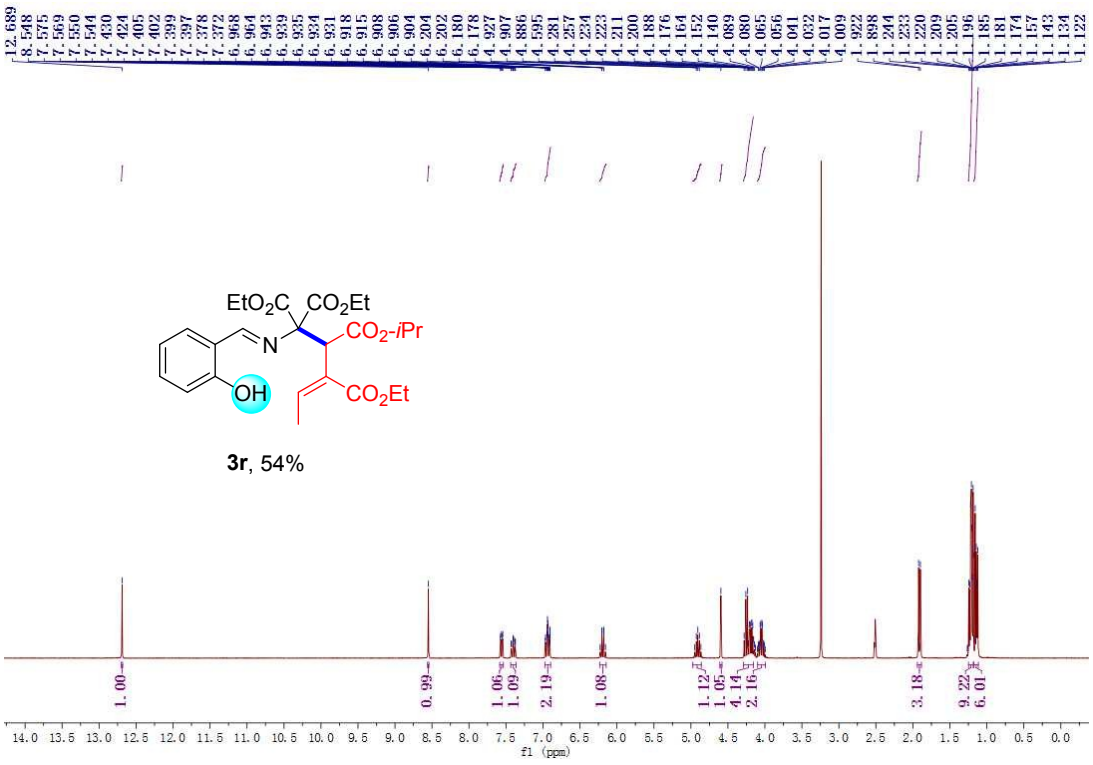
3q, 60%



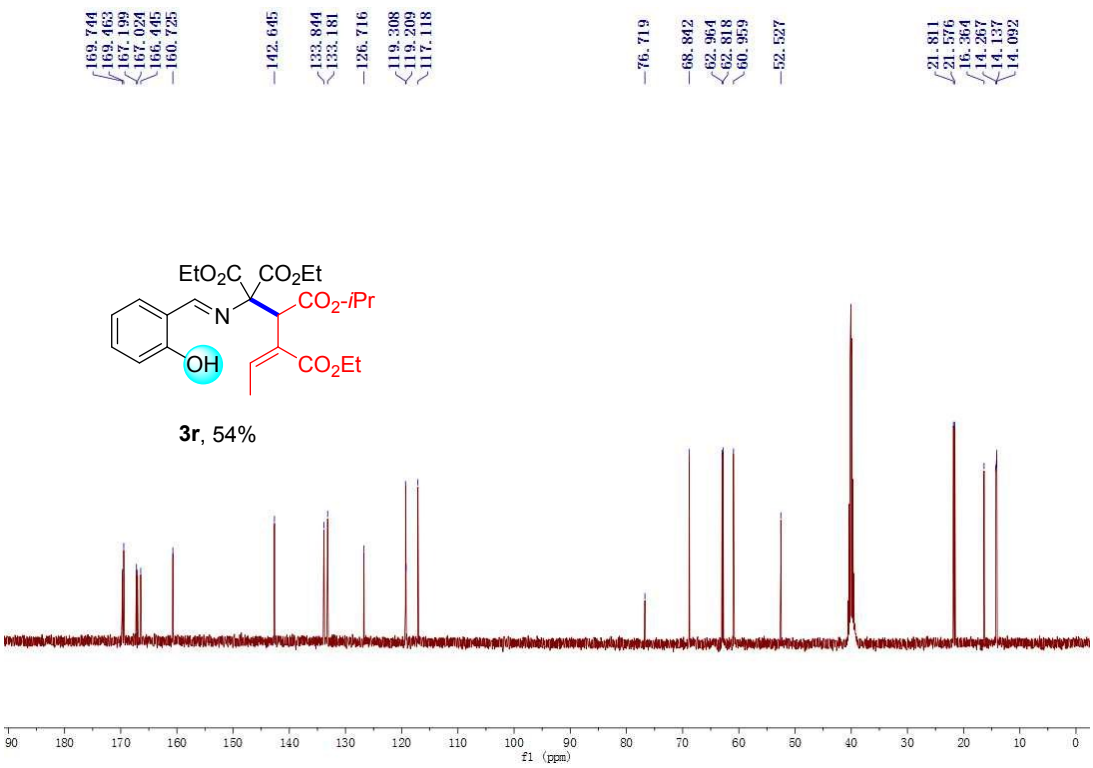


3q, 60%

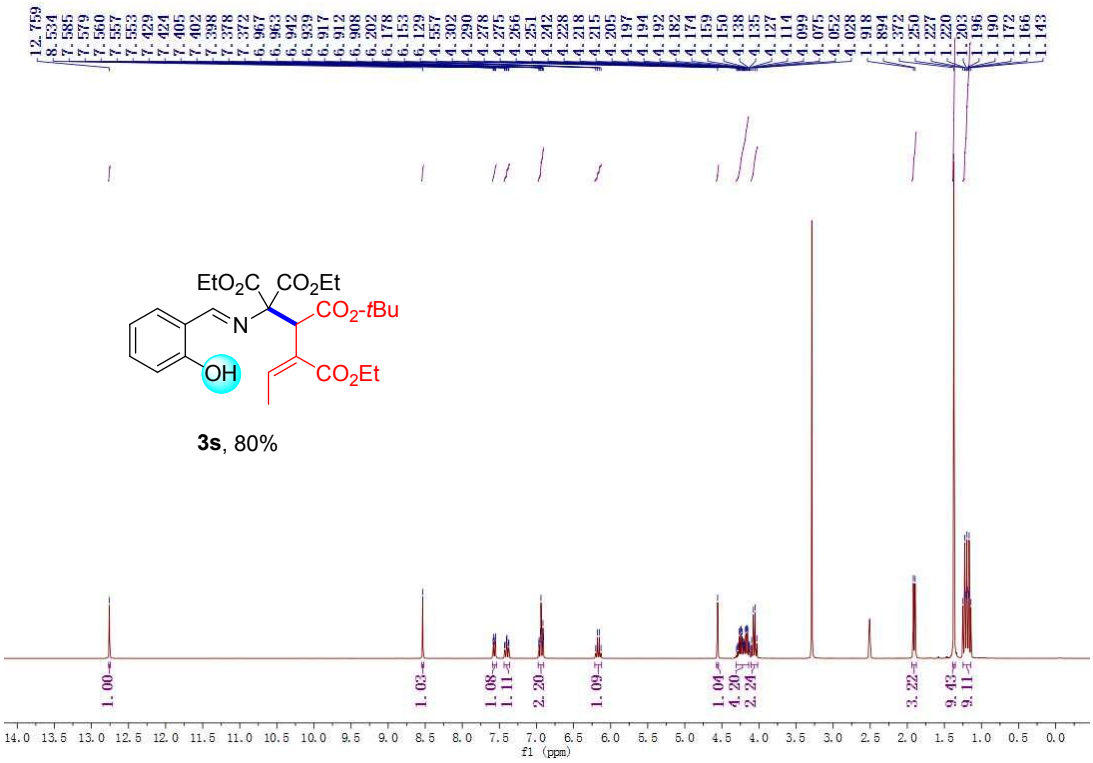



12.689
8.548
7.575
7.569
7.550
7.544
7.430
7.424
7.405
7.402
7.399
7.397
7.378
7.372
6.968
6.964
6.943
6.939
6.935
6.934
6.931
6.918
6.915
6.908
6.906
6.904
6.204
6.202
6.180
6.178
4.927
4.907
4.886
4.595
4.281
4.257
4.234
4.223
4.211
4.200
4.188
4.176
4.164
4.152
4.140
4.089
4.080
4.065
4.056
4.041
4.032
4.017
4.009
1.922
1.898
1.244
1.233
1.220
1.209
1.205
1.196
1.185
1.181
1.174
1.157
1.143
1.134
1.122
EtO2C
CO2Et
CO2-iPr
N
OH
CO2Et
1.00
0.99
1.06
1.09
2.19
1.08
1.12
1.05
4.14
2.16
3.18
9.22
6.01
f1 (ppm)

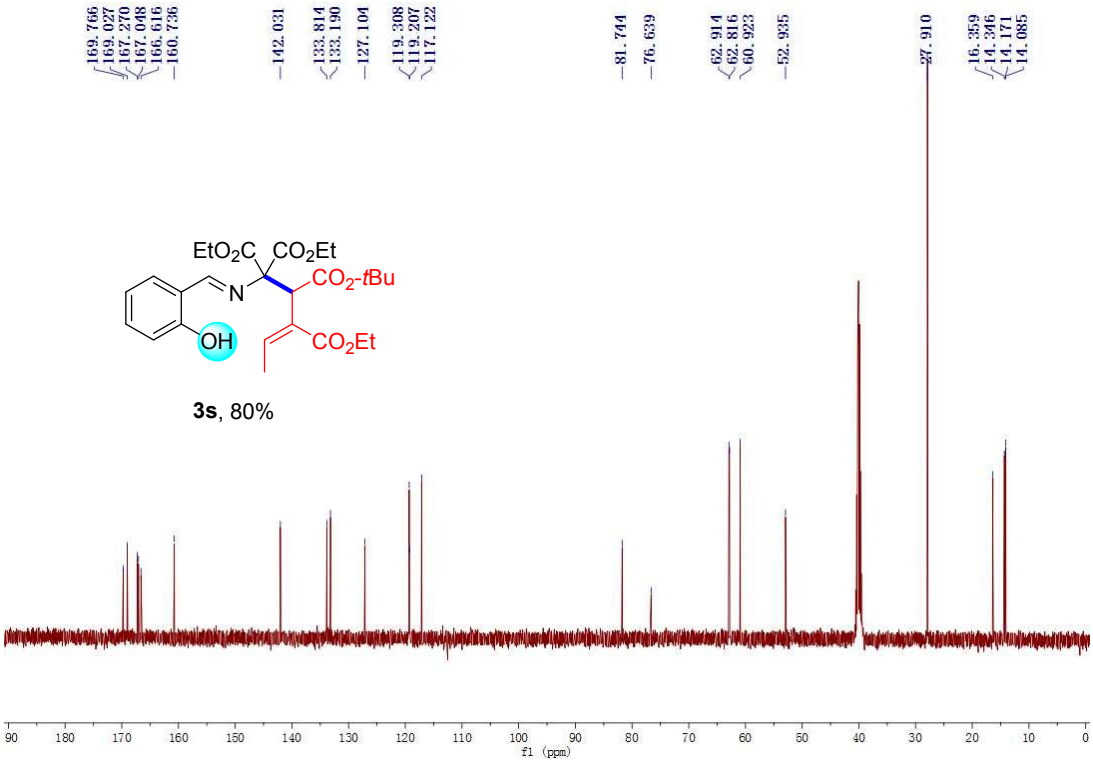
3r, 54%


169.744
169.463
167.199
167.024
166.445
160.725
142.645
133.844
133.181
126.716
119.308
119.209
117.118
76.719
68.842
62.964
62.818
60.959
52.527
21.811
21.576
16.364
14.267
14.137
14.092
EtO2C
CO2Et
CO2-iPr
N
OH
CO2Et
f1 (ppm)

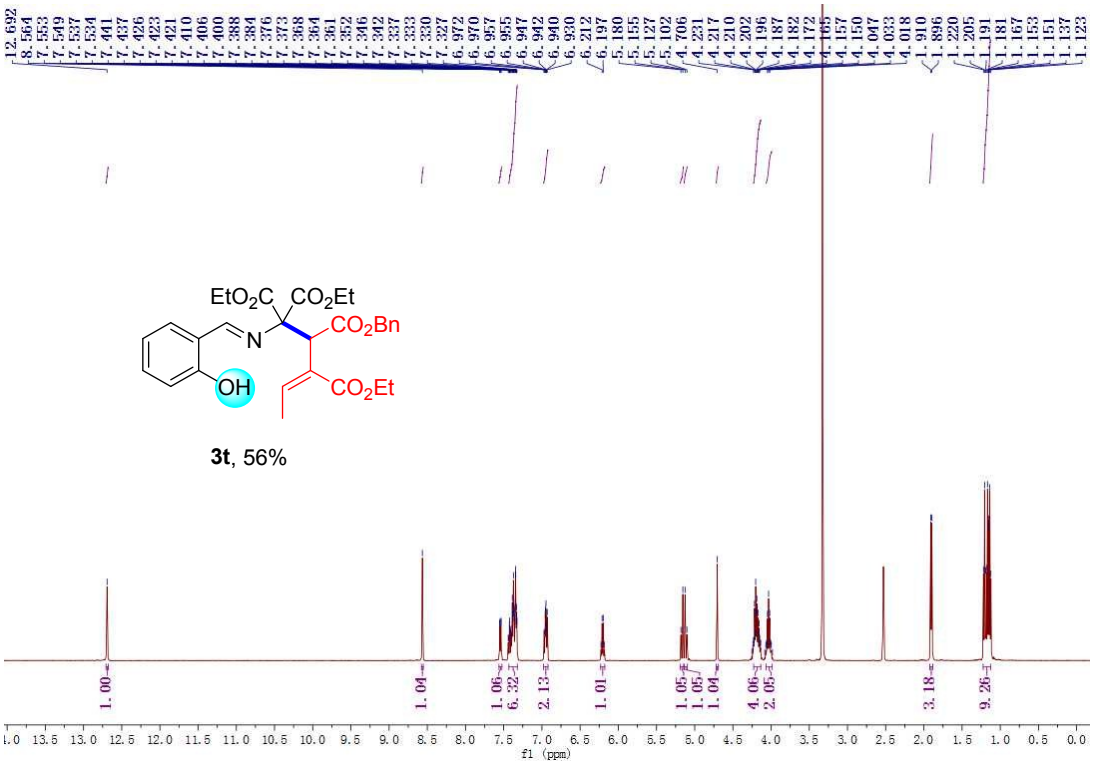
3r, 54%


12.759
8.534
8.585
7.579
7.560
7.557
7.553
7.429
7.424
7.405
7.402
7.398
7.378
7.372
6.967
6.963
6.942
6.939
6.917
6.912
6.908
6.202
6.178
6.153
6.129
4.557
4.302
4.290
4.278
4.275
4.266
4.251
4.242
4.228
4.218
4.215
4.205
4.197
4.194
4.192
4.182
4.174
4.159
4.150
4.138
4.135
4.127
4.114
4.099
4.075
4.052
4.028
1.918
1.894
1.372
1.250
1.227
1.220
1.203
1.196
1.190
1.172
1.166
1.143
EtO2C
CO2Et
CO2-tBu
N
OH
CO2Et
1.00
1.03
1.08
1.11
2.20
1.09
1.04
4.20
2.24
3.22
9.43
9.11
f1 (ppm)

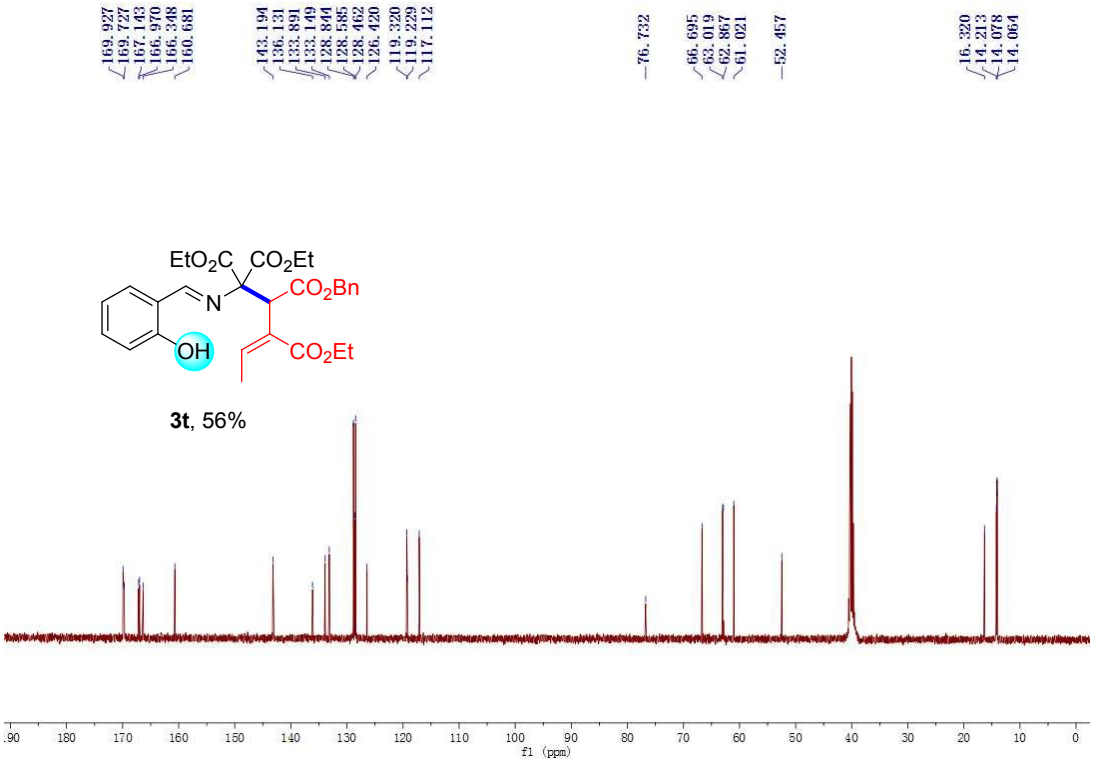
3s, 80%


169.766
169.027
167.270
167.048
166.616
160.736
142.031
133.814
133.190
127.104
119.308
119.207
117.122
81.744
76.639
62.914
62.816
60.923
52.935
27.910
16.359
14.346
14.171
14.085
EtO2C
CO2Et
CO2-tBu
N
OH
CO2Et
f1 (ppm)

3s, 80%

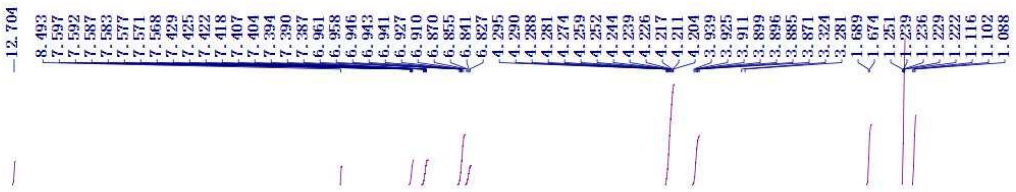

12.692
8.564
7.553
7.549
7.537
7.534
7.441
7.437
7.426
7.423
7.421
7.410
7.406
7.400
7.388
7.384
7.376
7.373
7.368
7.364
7.361
7.352
7.346
7.342
7.337
7.333
7.330
7.327
6.972
6.970
6.957
6.955
6.947
6.942
6.940
6.930
6.212
6.197
5.180
5.155
5.127
5.102
4.706
4.231
4.217
4.210
4.202
4.196
4.187
4.182
4.172
4.165
4.157
4.150
4.047
4.033
4.018
1.910
1.896
1.220
1.205
1.191
1.181
1.167
1.153
1.151
1.137
1.123
EtO2C
CO2Et
CO2Bn
N
OH
CO2Et
1.00
1.04
1.06
6.32
2.13
1.01
1.05
1.05
1.04
4.06
2.05
3.18
9.26
f1 (ppm)

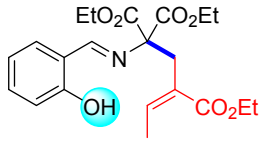
3t, 56%


169.927
169.727
167.143
166.970
166.348
160.681
143.194
136.131
133.891
133.149
128.844
128.585
128.462
126.420
119.320
119.229
117.112
76.732
66.695
63.019
62.867
61.021
52.457
16.320
14.213
14.078
14.064
f1 (ppm)

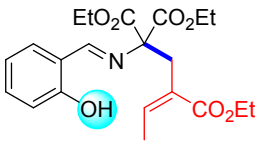
EtO2C
CO2Et
CO2Bn
N
OH
CO2Et

3t, 56%

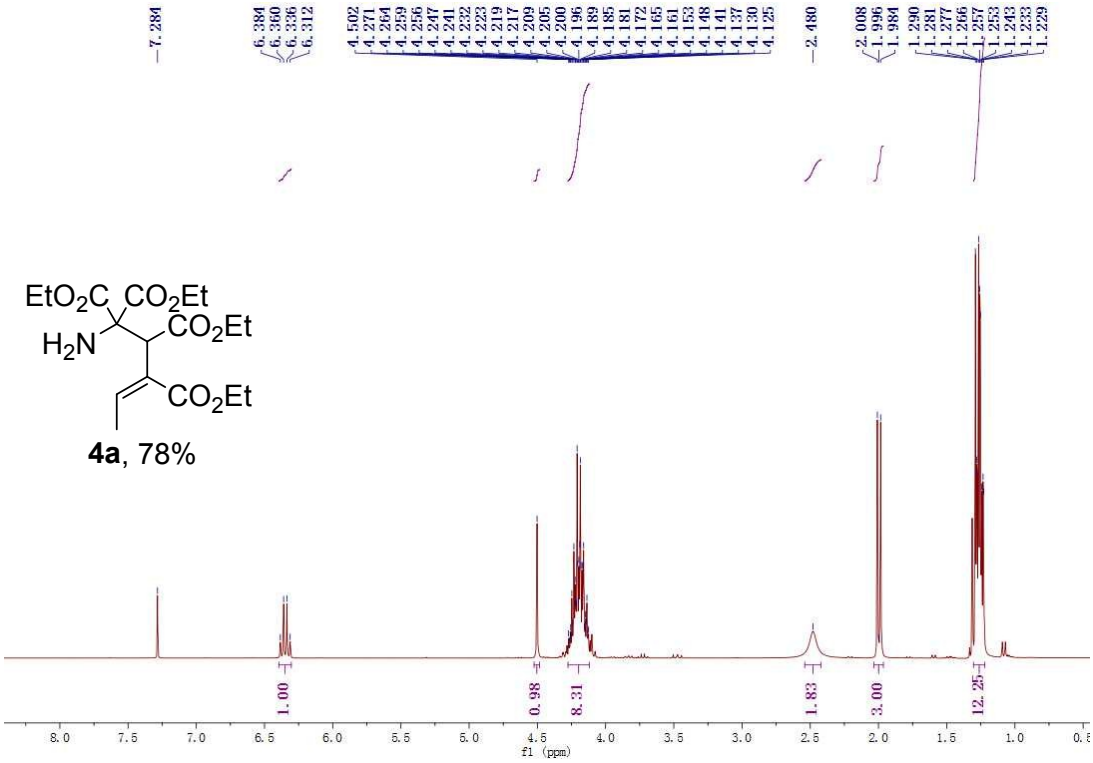


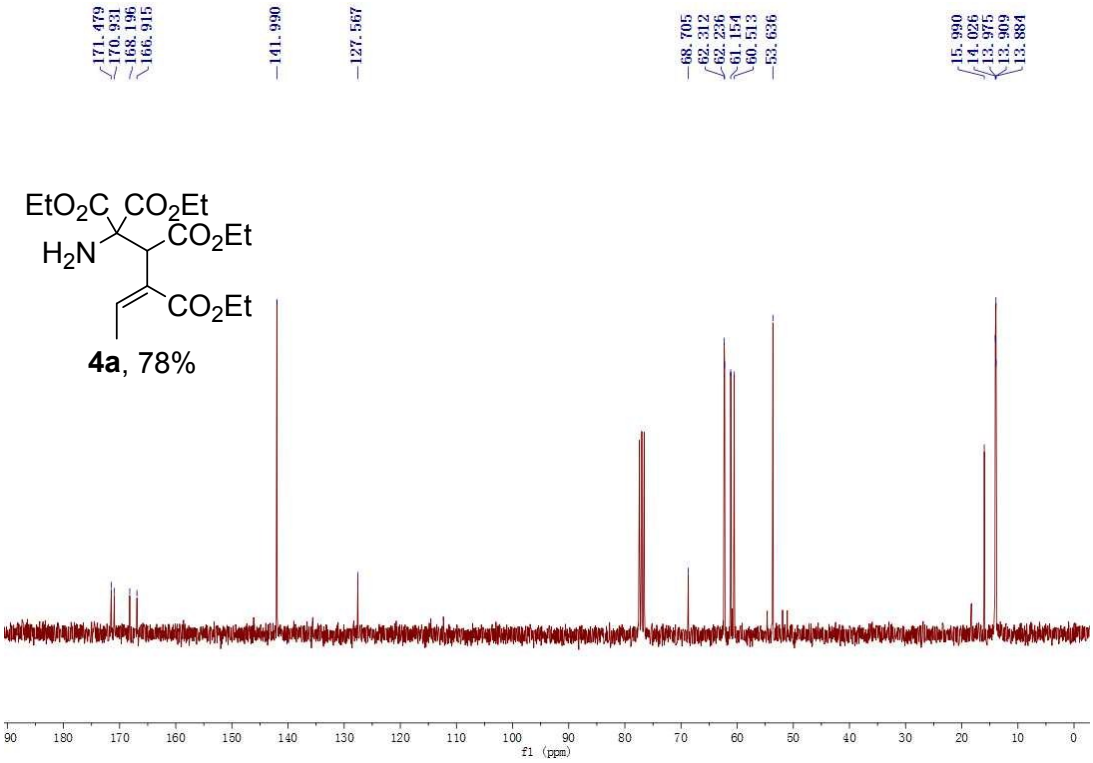


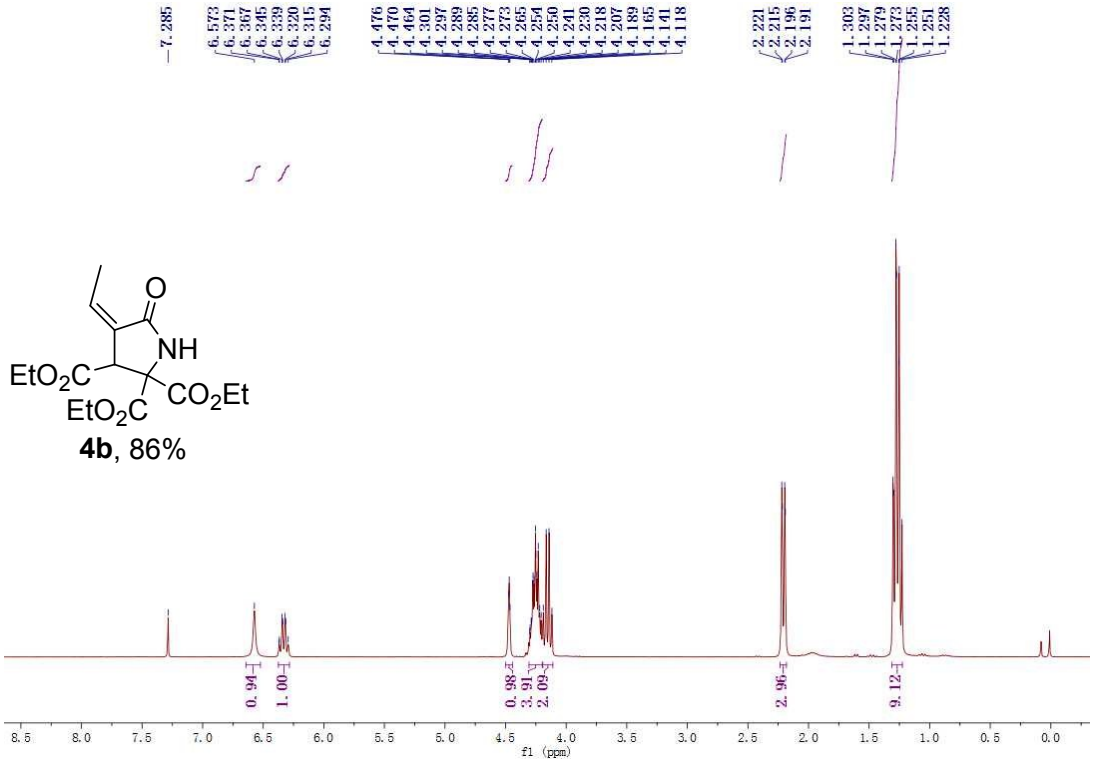
3v, 88%

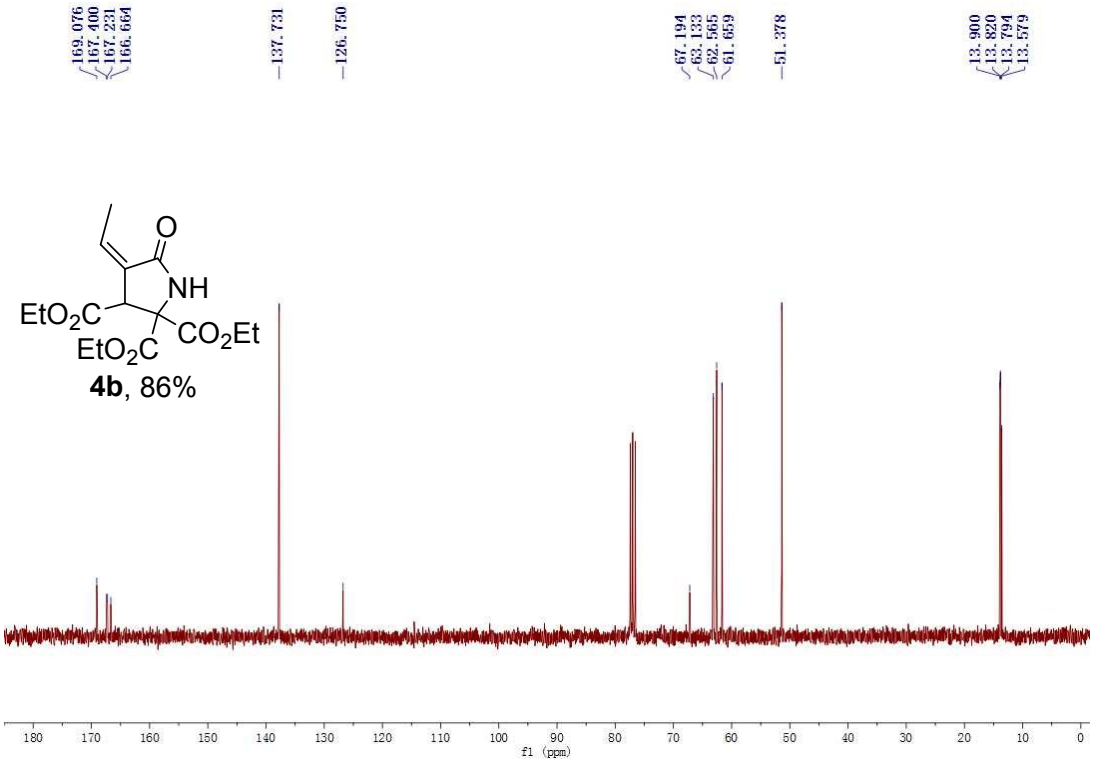


3v, 88%

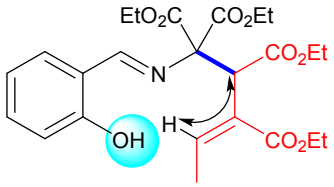

7.284
6.384
6.360
6.336
6.312
4.502
4.271
4.264
4.259
4.256
4.247
4.241
4.232
4.223
4.219
4.217
4.209
4.205
4.200
4.196
4.189
4.185
4.181
4.172
4.165
4.161
4.153
4.148
4.141
4.137
4.130
4.125
2.480
2.008
1.996
1.984
1.290
1.281
1.277
1.266
1.257
1.253
1.243
1.233
1.229
EtO2C CO2Et
H2N
CO2Et
CO2Et
4a, 78%
1.00
0.98
8.31
1.83
3.00
12.25
f1 (ppm)


171.479
170.931
168.196
166.915
141.990
127.567
68.705
62.312
62.236
61.154
60.513
53.636
15.990
14.026
13.975
13.909
13.884
EtO2C CO2Et
H2N
CO2Et
CO2Et
4a, 78%
f1 (ppm)

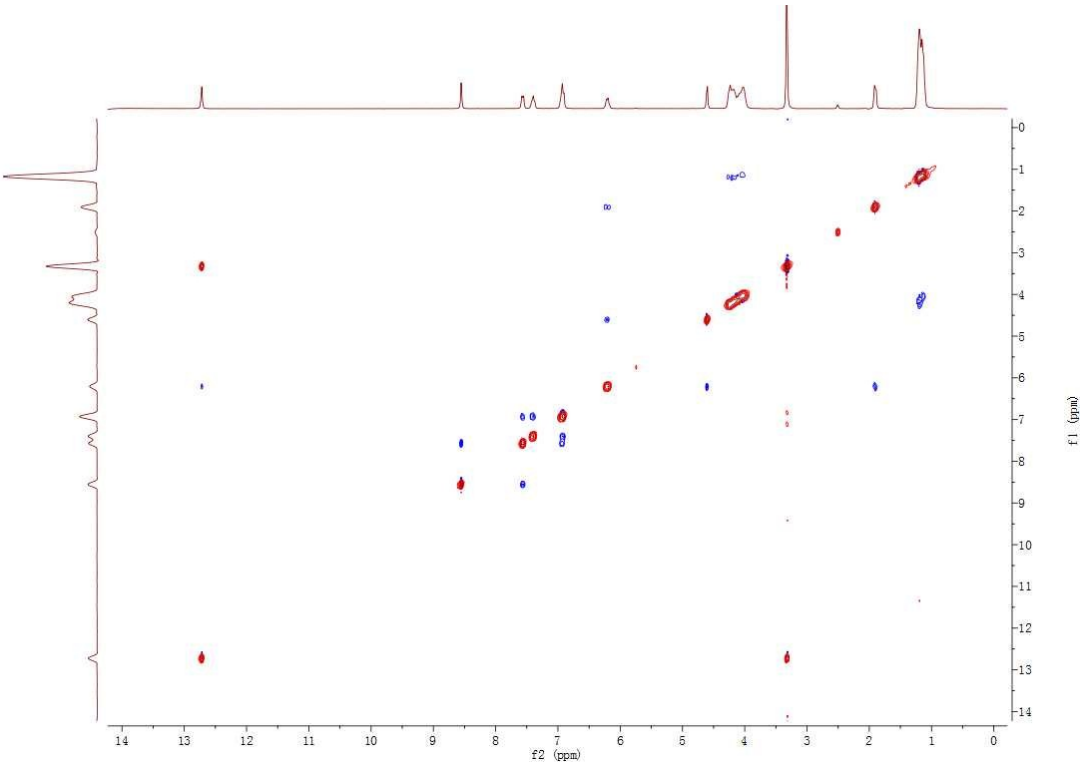

7.285
6.573
6.371
6.367
6.345
6.339
6.320
6.315
6.294
4.476
4.470
4.464
4.301
4.297
4.289
4.285
4.277
4.273
4.265
4.254
4.250
4.241
4.230
4.218
4.207
4.189
4.165
4.141
4.118
2.221
2.215
2.196
2.191
1.303
1.297
1.279
1.273
1.255
1.251
1.228
O
NH
EtO2C
CO2Et
EtO2C
4b, 86%
0.94
1.00
0.98
3.91
2.09
2.96
9.12
f1 (ppm)


169.076
167.400
167.231
166.664
137.731
126.750
67.194
63.133
62.565
61.659
51.378
13.900
13.820
13.794
13.579
O
NH
EtO2C
CO2Et
EtO2C
4b, 86%
f1 (ppm)

5. Copy of NOESY Spectra



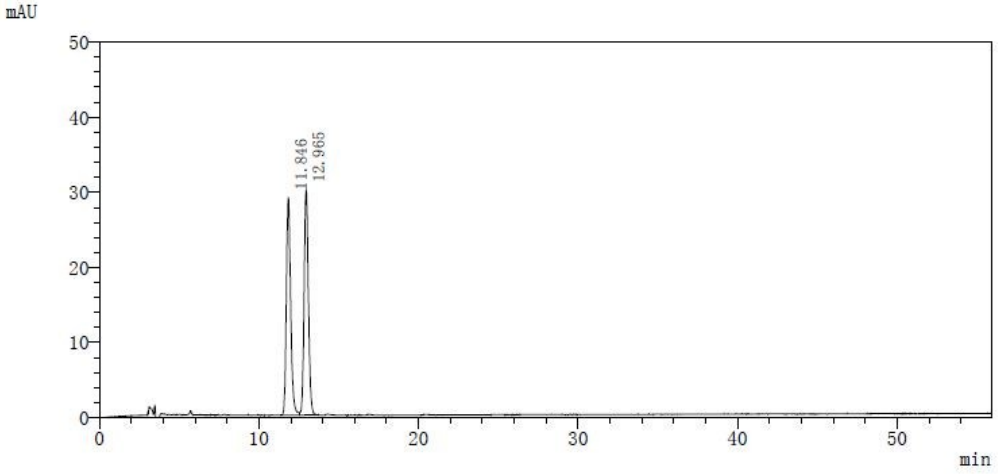
3a



6. Copy of HPLC Traces

Retention of the chiral center was evidenced through HPLC analysis against the racemic and enantiopure compound **3** using a Daicel chiral column (eluent: 1 mL/min 5% isopropanol in hexane).

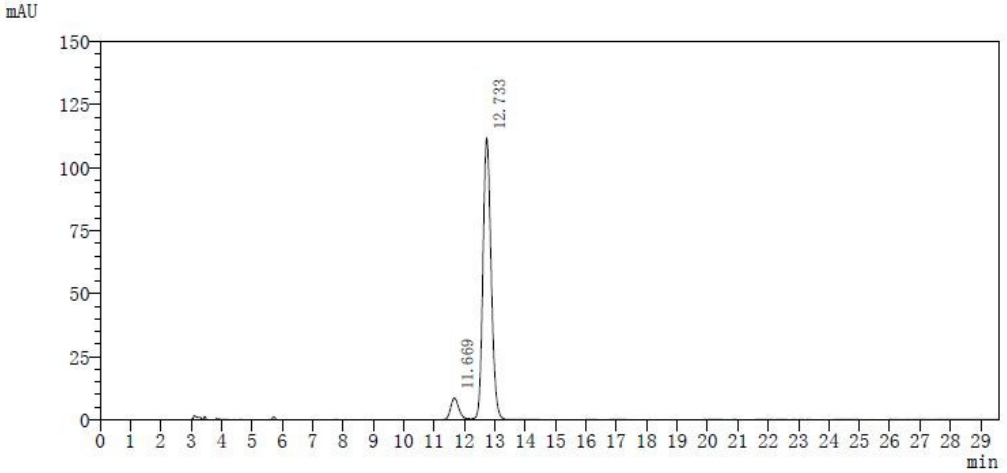
HPLC chromatogram of racemic **3a**



PDA Ch1 254nm

	Retention Time	Area	Area %	Height	Height %
	11.846	546343	49.622	28933	49.210
	12.965	554673	50.378	29862	50.790
Total		1101016	100.000	58796	100.000

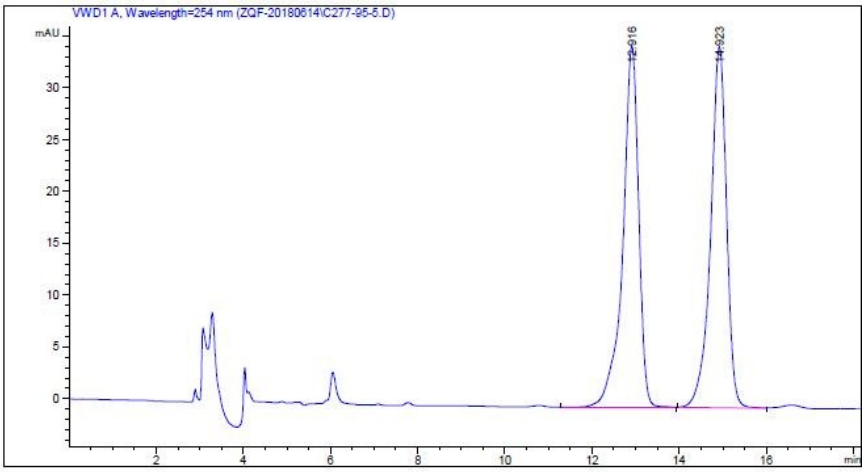
HPLC chromatogram of enantiopure **3a**



PDA Ch1 254nm

	Retention Time	Area	Area %	Height	Height %
	11.669	162213	7.169	8550	7.114
	12.733	2100504	92.831	111628	92.886
Total		2262717	100.000	120178	100.000

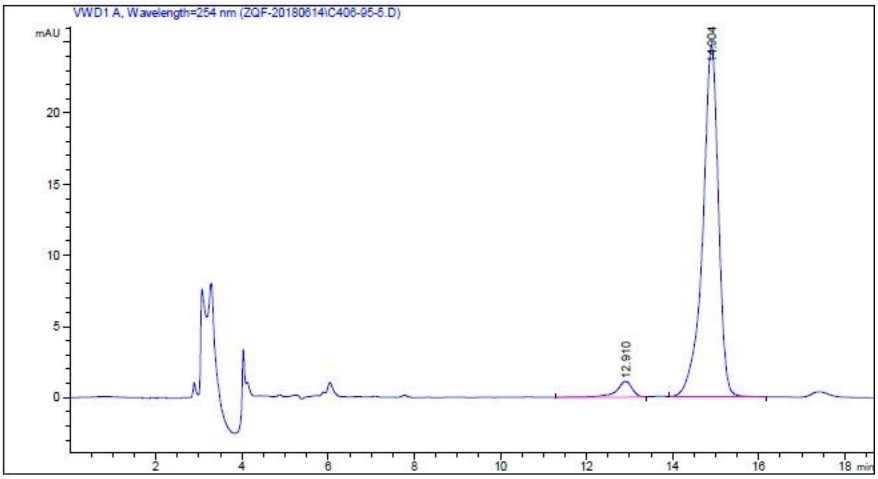
HPLC chromatogram of racemic **3p**



PDA Ch1 254nm

	Retention Time	Area	Area %	Height	Height %
	12.916	883.081	49.989	34.895	50.025
	14.923	883.473	50.011	34.860	49.975
Total		1766.554	100.000	69.755	100.000

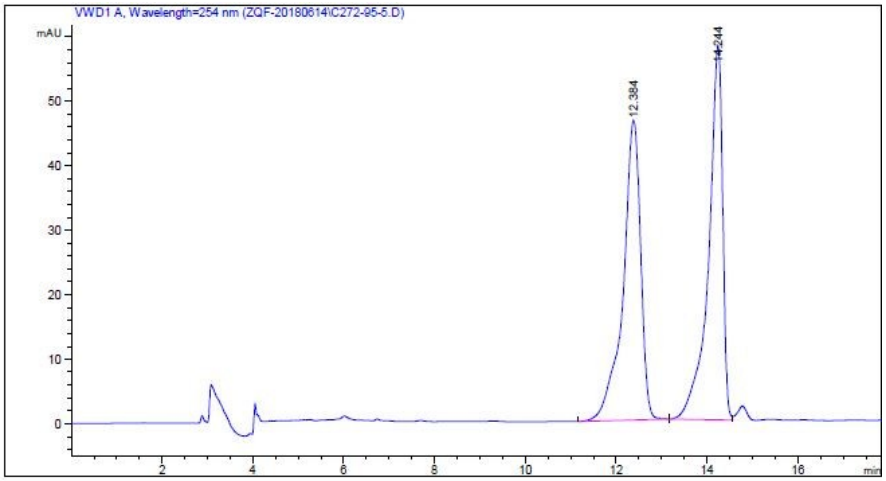
HPLC chromatogram of enantiopure **3p**



PDA Ch1 254nm

	Retention Time	Area	Area %	Height	Height %
	12.910	29.177	4.423	1.116	4.322
	14.904	630.433	95.577	24.706	95.678
Total		659.610	100.000	25.822	100.000

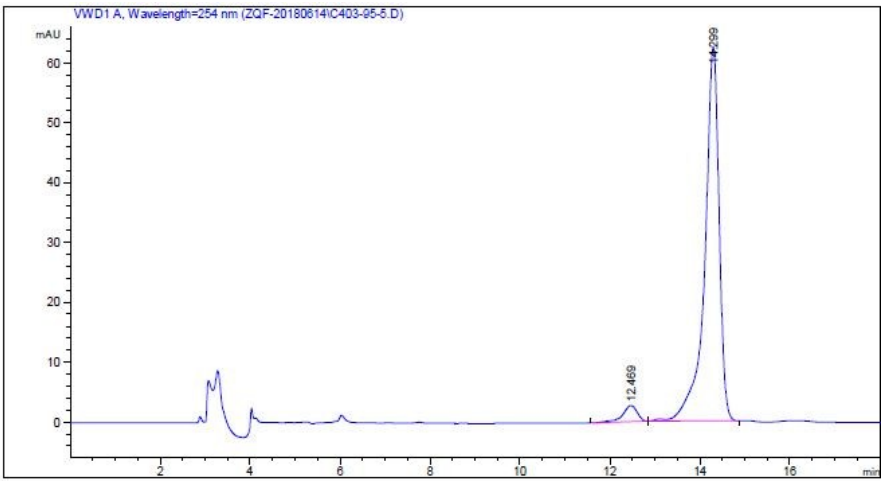
HPLC chromatogram of racemic **3q**



PDA Ch1 254nm

	Retention Time	Area	Area %	Height	Height %
	12.384	1249.479	50.042	46.420	44.444
	14.244	1247.379	49.958	58.025	55.556
Total		2496.858	100.000	104.445	100.000

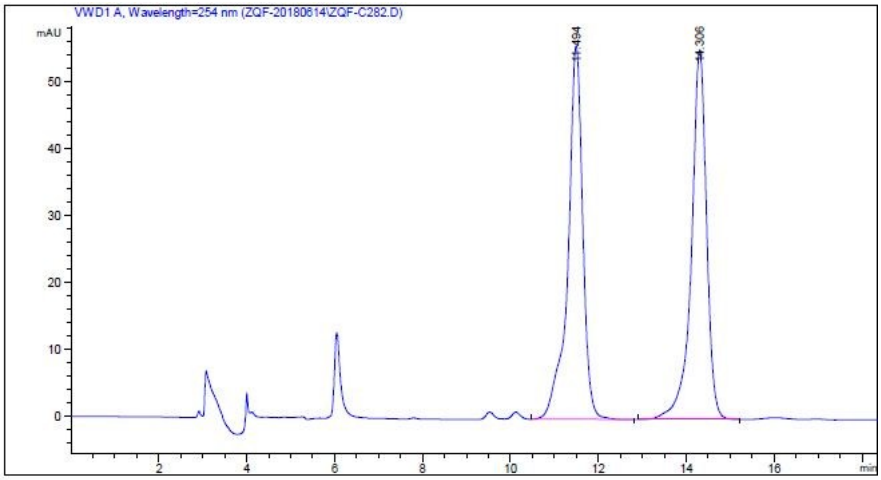
HPLC chromatogram of enantiopure **3q**



PDA Ch1 254nm

	Retention Time	Area	Area %	Height	Height %
	12.469	61.465	4.242	2.726	4.180
	14.299	1387.650	95.758	62.486	95.820
Total		1449.115	100.000	65.212	100.000

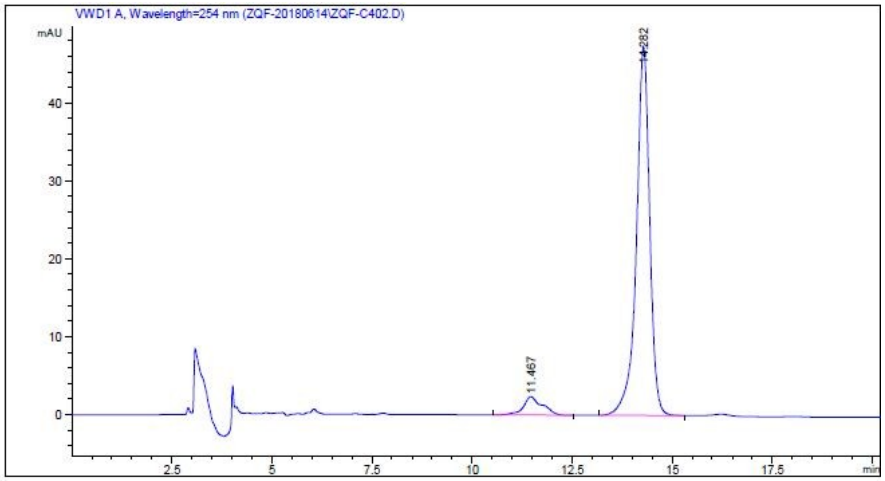
HPLC chromatogram of racemic **3r**



PDA Ch1 254nm

	Retention Time	Area	Area %	Height	Height %
	11.494	1316.459	49.782	55.928	50.273
	14.306	1328.013	50.218	55.320	49.727
Total		2644.472	100.000	111.248	100.000

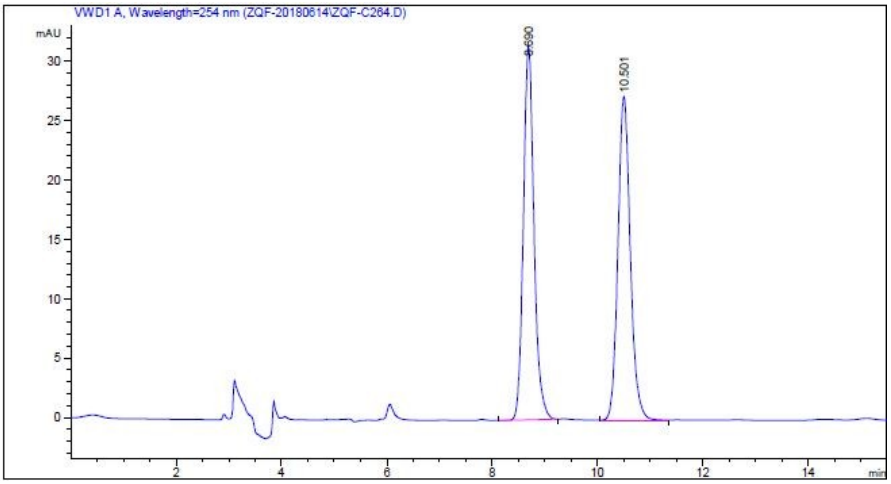
HPLC chromatogram of enantiopure **3r**



PDA Ch1 254nm

	Retention Time	Area	Area %	Height	Height %
	11.467	78.056	6.634	2.374	4.772
	14.282	1098.553	93.366	47.377	95.228
Total		1176.609	100.000	49.751	100.000

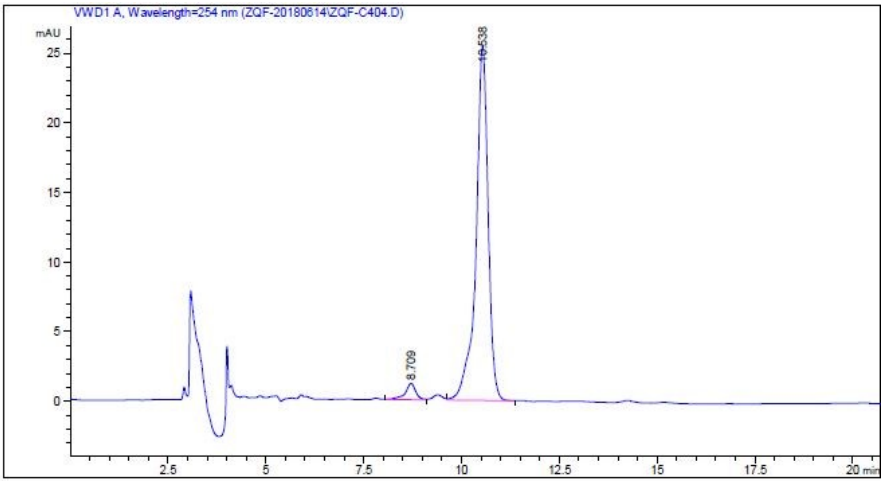
HPLC chromatogram of racemic **3s**



PDA Ch1 254nm

	Retention Time	Area	Area %	Height	Height %
	8.690	441.489	49.814	31.504	53.621
	10.501	444.794	50.186	27.249	46.379
Total		889.283	100.000	58.753	100.000

HPLC chromatogram of enantiopure **3s**



PDA Ch1 254nm

	Retention Time	Area	Area %	Height	Height %
	8.709	21.804	3.800	1.168	4.378
	10.538	552.034	96.200	25.510	95.622
Total		573.838	100.000	26.678	100.000