Organocatalytic Sequential Michael Reactions: Stereoselective Synthesis of Multifunctionalized Tetrahydroindan Derivatives

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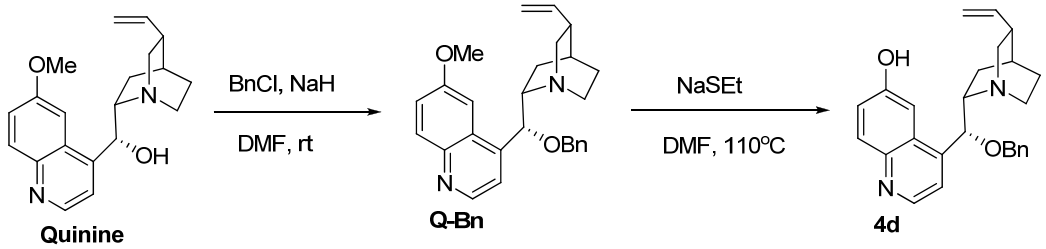
1. General information

^{1}H NMR spectra were recorded on commercial instruments (400 or 600 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (100 or 150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0). Enantiomeric excesses (*ee*) were determined by HPLC analysis using the corresponding commercial chiralpak column as stated in the experimental procedures at 23 ^{o}C. Optical rotations were reported as follows: $[a]_D^{20}$ (*c*: g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). All catalytic reactions were run in dried glassware, THF, toluene and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled over CaH_2. The cyclic-γ,δ-unstaturated-β-ketoesters **1**[1] and nitroolefins[2] were prepared according to the literature procedures.

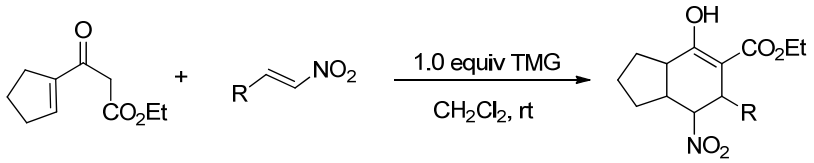
2. Typical procedure for catalysts preparation (4c, 4d, 4e)

Preparation of 4d[3] (4e was prepared from quinidine in the same procedure):



To a solution of quinine (4.0 g, 12.4 mmol) in DMF (40 mL) under nitrogen atmosphere, NaH (1.36 g, 57% suspension in mineral oil, 32.3 mmol) was added in small portions and the resulting mixture was stirred at room temperature for 2 h. Then BnCl (1.56 mL, 13.6 mmol) was added dropwise via a syringe in 10 min. The mixture was stirred at room temperature overnight. After the starting material was completely consumed, brine (40 mL) was added carefully and the resulting mixture was extracted with ethyl acetate (300 mL). The organic phase was washed with H_2O (3×100 mL), brine (100 mL) and dried over Na_2SO_4. The solvent was removed in *vacuo* to afford a light yellow oil (5.1 g, 99%). This crude product (**Q-Bn**) was used without further purification. Under N_2 atmosphere, a suspension of Q-Bn (5.1 g, 12.3 mmol) and NaSEt (4.2 g, 50.0 mmol) in dry DMF (60 mL) was stirred at 110 ^{o}C for 8-12 hours. The reaction mixture was cooled to room temperature, and the reaction was quenched with H_2O (60 mL). The solution was acidified to pH =2 by conc. HCl. This aqueous solution was washed by ethyl acetate (2×100 mL) and its pH value was adjusted to 8 by conc. ammonium hydroxide. The resulting mixture was extracted with ethyl acetate (2×150 mL). The combined organic phase was dried over Na_2SO_4, and concentrated in *vacuo* to afford a yellowish solid. This solid was washed by CH_2Cl_2 (2×30 mL) and then dissolved in aqueous HCl (2 N, 150 mL). The resulting solution was washed by ethyl acetate (50 mL) and adjusted to pH = 7 by conc. ammonium hydroxide. The aqueous phase was extracted by ethyl acetate (3×80 mL). The organic phase was dried with Na_2SO_4. After concentration, **4d** was obtained as a white powder (3.97g, 80%).

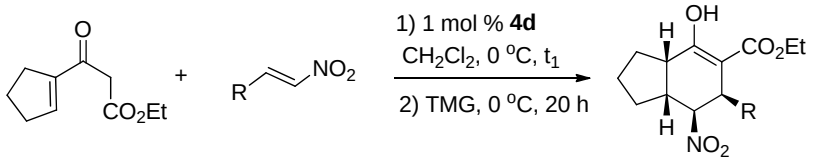
3. Typical procedure for racemic samples preparation



1 **2a-s** **3a-s**

To a test tube, the nitroolefin **2** (0.1 mmol), cyclic-γ,δ-unstaturated-β-ketoester **1** (0.15 mmol, 1.5 equiv) and TMG (1.0 equiv, 12 μL) in CH_2Cl_2 (1.0 mL) was stirred at room temperature for 20 h. Racemic product **3** was isolated via column chromatography (1/2, CH_2Cl_2/petroleum ether).

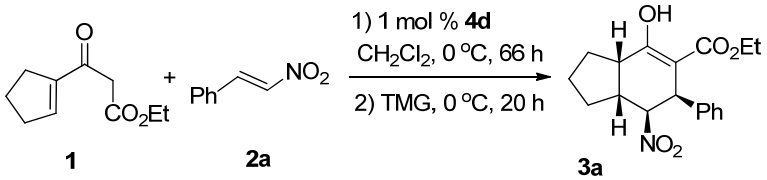
4. Typical procedure for catalytic sequential Michael reactions



1 **2a-s** **3a-s**

To a test tube, the nitroolefin **2** (0.1 mmol) and catalyst **4d** (1 mol %, 0.4 mg) in CH_2Cl_2 (0.5 mL) was stirred at 30 °C for 30 min, then cyclic-γ,δ-unstaturated-β-ketoester **1** (0.15 mmol, 1.5 equiv) was added and the mixture were stirred for the stated reaction time (20-84 h) at 0 °C. If the catalyst loading was 0.5 mol % (**Table 2**, entries 1, 3, 6, 7, 8 and 15), the solution of catalyst in CH_2Cl_2 was used. After the nitroolefin was completely consumed (monitored by TLC), TMG (1.0 equiv, 12 μL) was added under 0 °C, and the reaction mixture was stirred for further 20 h. Product **3** was isolated via column chromatography (1/2, CH_2Cl_2/petroleum ether). Unreacted nitroolefin should be separated by column chromatography (EtOAc/petroleum ether) to avoid the byproduct in the second Michael reaction (**Table 2**, entries 2, 12, 13, 18 and 19). Then CH_2Cl_2 (1.5 mL), TMG (1.0 equiv, 12 μL) was added under 0 °C and the reaction was stirred for further 20 h. Product **3** was isolated via column chromatography (1/2, CH_2Cl_2/petroleum ether).

5. Typical procedure for gram-scale synthesis and transformations of the product

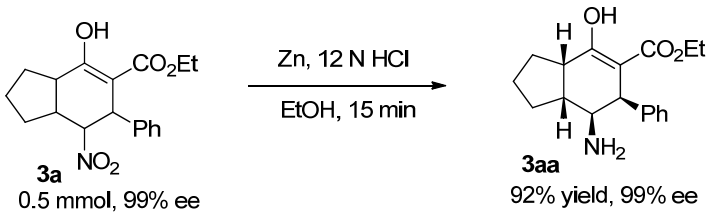


1 **2a** **3a**

12 mmol, 2.19 g 8 mmol, 1.19g

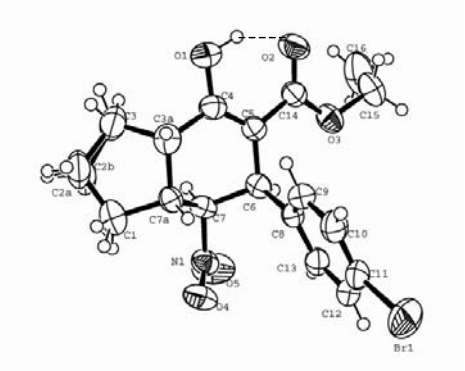
2.25 g, 85% yield, 97% ee
after recrystallization
65% yield, 99% ee, >99:1 dr

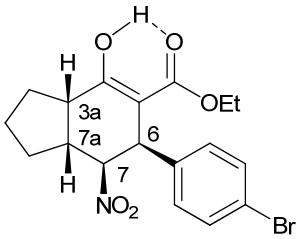
To a round bottom flasks, the nitroolefin **2a** (8 mmol, 1.19g) and catalyst **4e** (1 mol %, 32 mg) in CH_2Cl_2 (5 mL) was stirred at 30 °C for 30 min, then cyclic-γ,δ-unstaturated-β-ketoester **1** (12 mmol, 1.5 equiv) was added. The mixture was stirred for 66 h at 0 °C. Then TMG (300 μL) was added in small portions under 0 °C, and the reaction mixture was stirred for further 20 h. Product **3a** was isolated in 85% yield (2.25 g) with 97% ee. After a simple recrystallization (CH_2Cl_2/petroleum ether = 1:10) the product could be isolated in 65% yield with 99% ee.



To a solution of the product **3a** (0.5 mmol, 165.5 mg) in EtOH (3 mL) was added zinc powder (15 equiv, 0.49g), the reaction was heated to 60 ^{o}C and HCl (12M, 54 equiv) was added. 15 Minutes later, the reaction mixture was cooled to room temperature and the solution was made weakly basic (pH = 8) with NaOH (2M) and the aqueous layer was extracted with CH_2Cl_2 (3×15 mL). The combined organic layer was washed once with brine, dried (Mg_2SO_4) and evaporated to give yellow oil. Flash silica gel column chromatography (EtOAc/petroleum ether = 1:3) to afford the product **3aa** (138.5 mg, 92% yield) as colorless oil.

6. Crystal data and structure refinement for product 3i



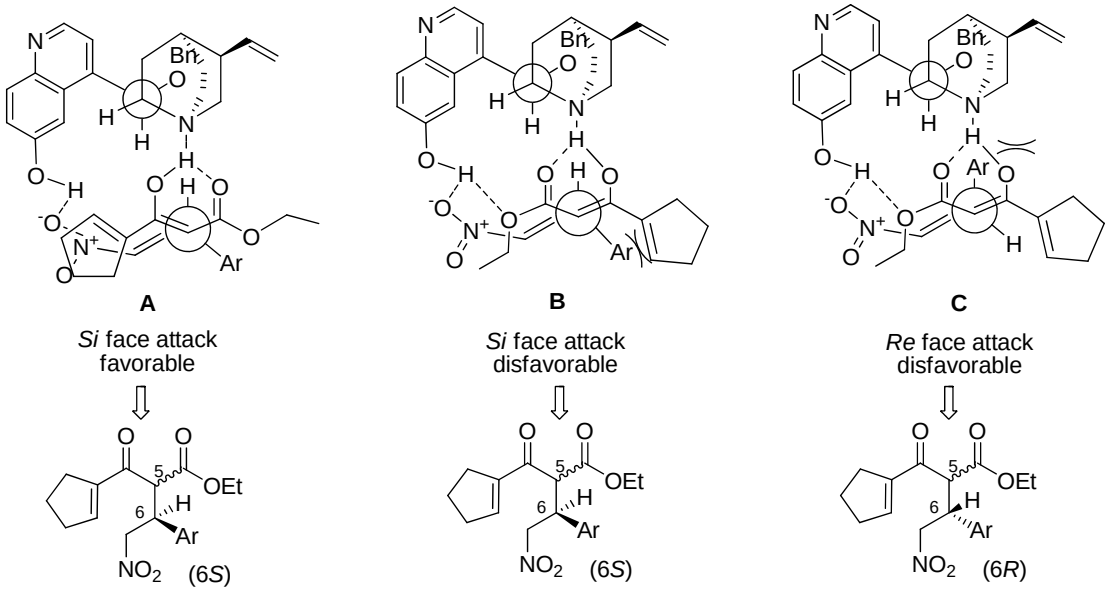


3i (3a*S*, 6*R*, 7*S*, 7a*R*)

Identification code	**3i**
Empirical formula	$C_{18}H_{20}BrNO_5$
Formula weight	410.26
Temperature / K	293.0
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 6.4249(4) A alpha = 90.00
	b = 13.8112(5) A beta = 90.00
	c = 20.5311(8) A gamma = 90.00
Volume / A^3	1821.85(15)
Z	4
Caluculated density / mg mm^{-3}	1.496
μ / mm^{-1}	2.284
F(000)	840
Crystal size / mm^3	0.35 × 0.32 × 0.30
Theta range for data collection	2.95 to 26.37^{o}
Index ranges	-5<=h<=8, -17<=k<=16, -25<=l<=15
Reflections collected	7595
Independent reflections	3708 [R(int) = 0.0247]

Data / restraints / parameters	3708 / 0 / 235
Goodness-of-fit on F^2	1.018
Final R indexes [I>2 sigma (I)]	R_1 = 0.0473, wR_2 = 0.0806
Final R indexes [all data]	R_1 = 0.0825, wR_2 = 0.0938
Largest diff. peak/hole / e A^{-3}	0.302/-0.389
CCDC	803725

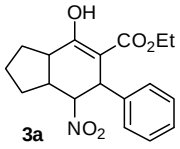
7. Proposed transition state



We think that the transition **A** should be more reasonable which gave the (6*S*)-product as the major. In transition state **B**, although the *Si* face attackment would result in (6*S*)-product, there was steric repulsion between the cyclopentene and substituent on nitroolefin. Similarly, transition state **C** should also be disfavorable which generated minor (6*R*)-product for the steric hindrance between the Ar group of nitroolefin and quinuclidine moiety of the catalysts.

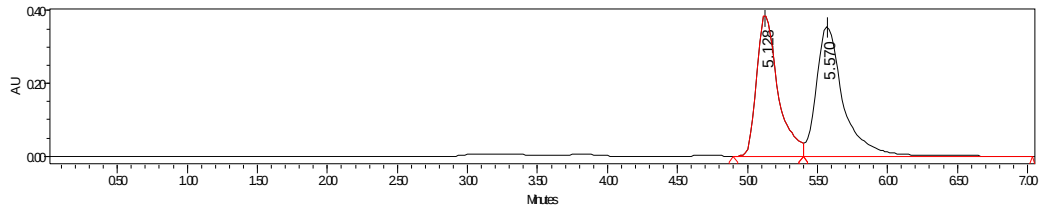
8. Analytical and spectral characterization data for the products

Ethyl 4-hydroxy-7-nitro-6-phenyl-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3a:

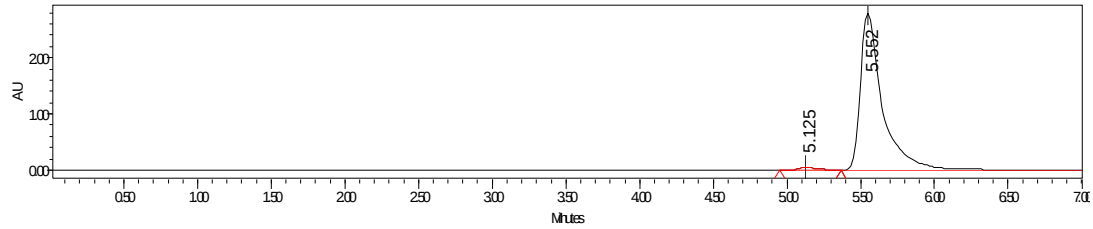


3a

white solid; 32.8 mg, 97% yield; $[a]_D^{20}$ = -286.3 (*c* = 0.40 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 97% ee, determined by HPLC analysis [Daicel chiralpak IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.13 min, t (major) = 5.56 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.55 (s, 1H), 7.30–7.25 (m, 3H), 7.05–7.01 (m, 2H), 4.62 (dd, *J* = 12.3, 5.3 Hz, 1H), 4.54 (d, *J* = 5.3 Hz, 1H), 4.11 (m, 1H), 4.02 (m, 1H), 3.07 (dd, *J* = 18.3, 9.1 Hz, 1H), 2.88 (m, 1H), 2.41–2.31 (m, 1H), 2.11–2.01 (m, 1H), 1.87–1.77 (m, 1H), 1.64 (m, 2H), 1.42–1.32 (m, 1H), 1.08 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101MHz, $CDCl_3$) δ = 173.87, 171.07, 136.89, 128.37, 128.28, 127.87, 97.85, 89.54, 60.91, 44.25, 43.57, 34.49, 31.59, 30.92, 24.76, 13.87 ppm; ESI-HRMS: calcd for ($C_{18}H_{21}NO_5$+Na^+): 354.1312, found: 354.1327.

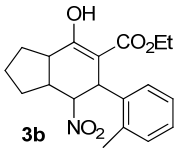


	Retention Time	Area	% Area
1	5.128	3588460	49.11
2	5.570	3718230	50.89



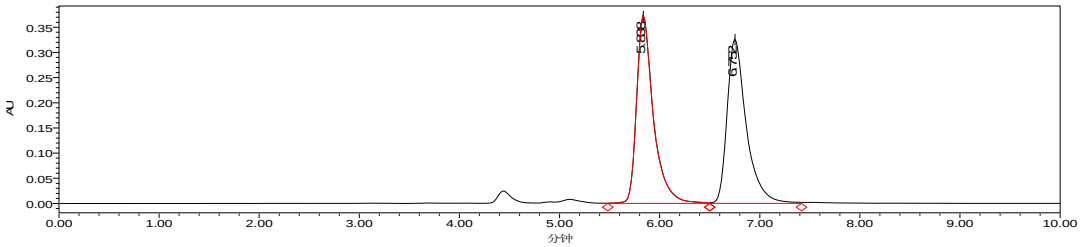
	Retention Time	Area	% Area
1	5.125	391236	1.33
2	5.552	29104452	98.67

Ethyl 4-hydroxy-7-nitro-6-(o-tolyl)-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3b:

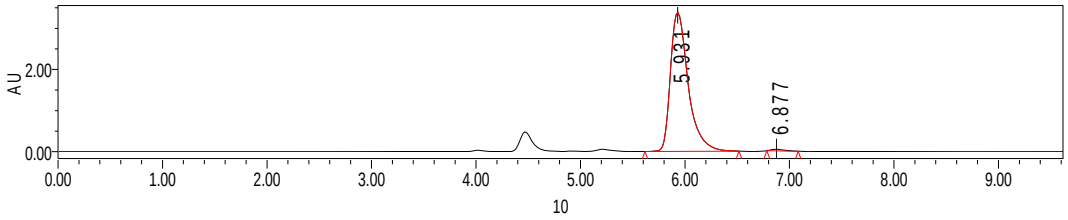


3b

white solid; 22.1 mg, 64% yield; $[a]_D^{20}$ = -305.6 (*c* = 0.25 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 98% ee, determined by HPLC analysis [Daicel chiralcel ADH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 6.88 min, t (major) = 5.93 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.47 (s, 1H), 7.16–7.09 (m, 3H), 7.00 (m, 1H), 4.98 (d, *J* = 5.3, 1H), 4.69 (dd, *J* = 11.8, 5.3, 1H), 4.18–3.96 (m, 2H), 3.15–3.04 (m, 2H), 2.40–2.32 (m, 1H), 2.29 (s, 3H), 2.06–1.97 (m, 1H), 1.84 (m, 1H), 1.66 (m, 2H), 1.35 (m, 1H), 1.12 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.49, 171.06, 137.46, 135.47, 130.69, 128.22, 127.38, 125.51, 99.13, 88.87, 60.98, 43.57, 38.64, 35.13, 31.66, 30.45, 24.68, 19.13, 13.85 ppm; ESI-HRMS: calcd for ($C_{19}H_{23}NO_5$+Na^+): 368.1468, found: 368.1473.

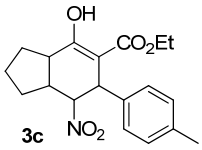


	Retention Time	Area	% Area
1	5.838	435884	50.07
2	6.752	434692	49.93

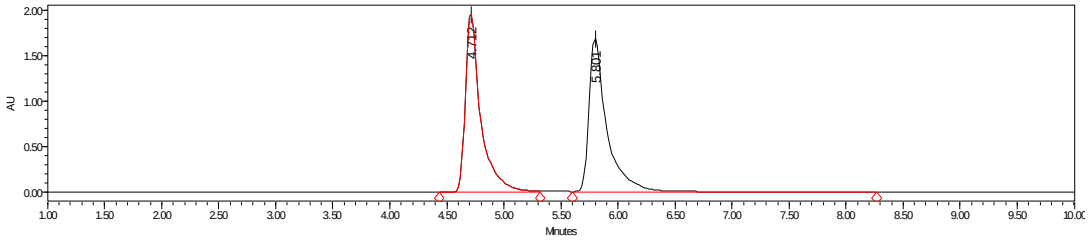


	Retention Time	Area	% Area
1	5.931	39880012	99.14
2	6.877	347195	0.86

Ethyl 4-hydroxy-7-nitro-6-(p-tolyl)-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3c:



white solid; 33.8 mg, 98% yield; $[a]_D^{20}$ = -328.1 (*c* = 0.33 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 95% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 4.74 min, t (major) = 5.85 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.54 (s, 1H), 7.07 (d, *J* = 7.9, 2H), 6.91 (d, *J* = 8.0, 2H), 4.59 (dd, *J* = 12.4, 5.2, 1H), 4.51 (d, *J* = 5.2, 1H), 4.13 (m, 1H), 4.00 (m, 1H), 3.05 (dd, *J* = 18.5, 9.1, 1H), 2.89–2.83 (m, 1H), 2.34 (m, 1H), 2.30 (s, 3H), 2.08–2.02 (m, 1H), 1.81 (m, 1H), 1.67–1.59 (m, 2H), 1.36 (m, 1H), 1.10 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 173.74, 171.12, 137.51, 133.78, 129.09, 128.12, 97.96, 89.64, 60.91, 43.89, 43.55, 34.48, 31.58, 30.92, 24.77, 21.08, 13.90 ppm; ESI-HRMS: calcd for ($C_{19}H_{23}NO_5$+Na^+): 368.1468, found: 368.1486.



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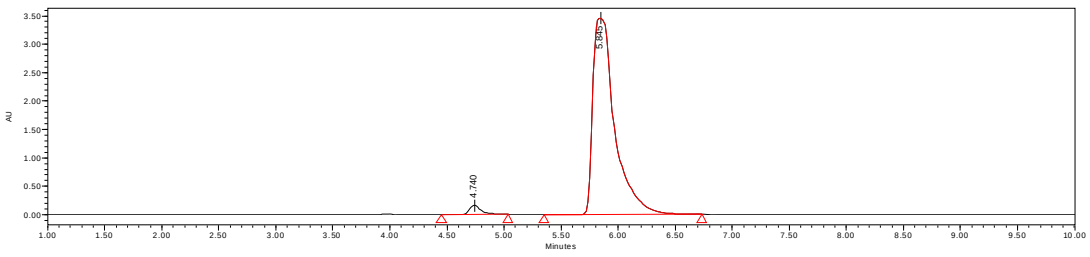
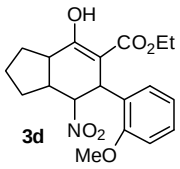
1	4.712	18295905	49.57
2	5.801	18613477	50.43



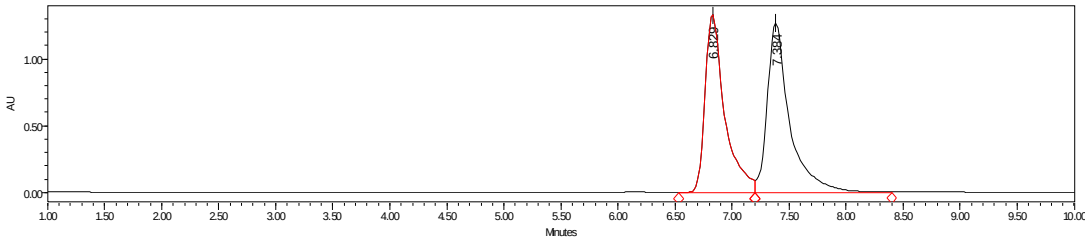
	Retention Time	Area	% Area
1	4.740	1103771	2.31
2	5.845	46612431	97.69

Ethyl 4-hydroxy-6-(2-methoxyphenyl)-7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3d:

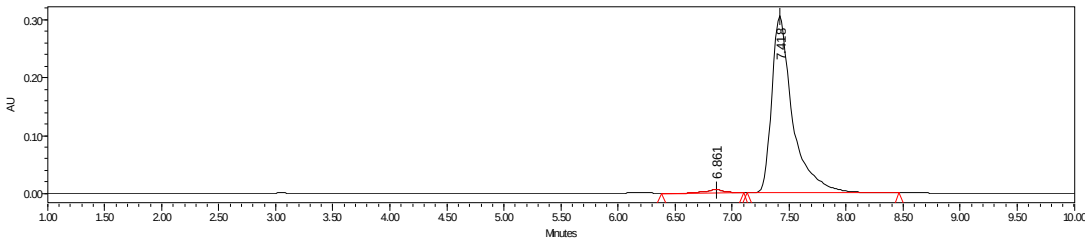


3d

white solid; 28.9 mg, 80% yield; $[a]_D^{20}$ = -321.7 (*c* = 0.16 in CH_2Cl_2); >99:1 dr, determined by NMR analysis ; 96% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 6.86 min, t (major) = 7.42 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.52 (s, 1H), 7.23 (t, *J* = 7.7, 1H), 6.97 (d, *J* = 7.3, 1H), 6.89 (t, *J* = 7.4, 1H), 6.82 (d, *J* = 8.2, 1H), 5.16 (d, *J* = 4.8, 1H), 4.65 (m, 1H), 4.09 (m, 1H), 4.01 (dq, *J* = 10.8, 7.1, 1H), 3.71 (s, 3H), 3.02 (dd, *J* = 18.1, 9.0, 1H), 2.84–2.78 (m, 1H), 2.35–2.29 (m, 1H), 1.91 (m, 1H), 1.85–1.77 (m, 1H), 1.66–1.60 (m, 2H), 1.33 (m, 1H), 1.06 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 174.07, 171.12, 158.27, 128.95, 128.72, 125.68, 119.95, 110.50, 98.12, 88.94, 60.76, 55.38, 43.55, 35.83, 31.24, 29.85, 24.57, 13.81 ppm; ESI-HRMS: calcd for ($C_{19}H_{23}NO_6$+Na^+): 384.1418, found: 384.1429.

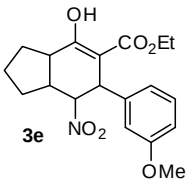


	Retention Time	Area	% Area
1	6.829	13980076	49.06
2	7.384	14514890	50.94



	Retention Time	Area	% Area
1	6.861	70856	1.75
2	7.418	3974772	98.25

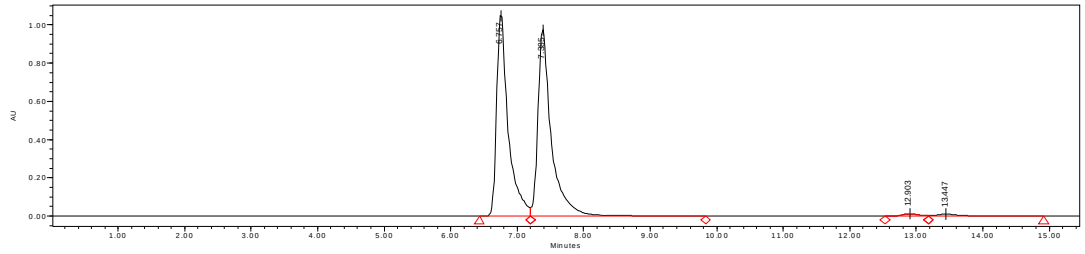
Ethyl 4-hydroxy-6-(3-methoxyphenyl)-7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3e:



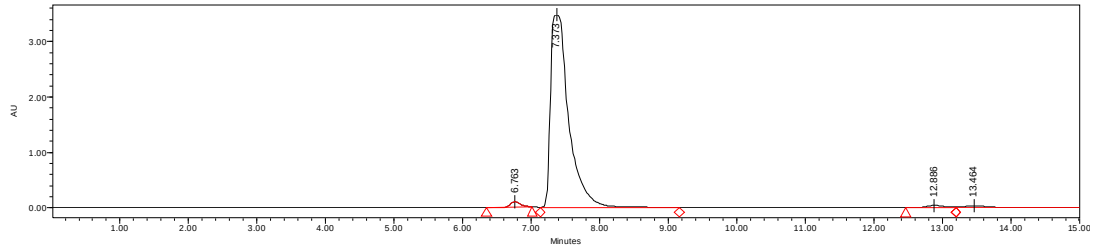
3e

white solid; 28.9 mg, 80% yield; $[a]_D^{20}$ = -346.2 (*c* = 0.24 in CH_2Cl_2); 98:2 dr, determined by HPLC analysis; 96% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 6.76 min, t (major) = 7.37 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.54 (s, 1H), 7.19 (t, *J* = 7.9, 1H), 6.79 (dd, *J* = 8.2, 2.2, 1H), 6.62 (d, *J* = 7.7, 1H), 6.57 (s, 1H), 4.59 (dd, *J* = 12.4, 5.3, 1H), 4.52 (d, *J* = 5.3, 1H), 4.13 (m, 1H), 4.05–3.99 (m, 1H), 3.77 (s, 3H), 3.06 (dd, *J* = 18.4, 9.1, 1H), 2.92–2.86 (m, 1H), 2.34 (m, 1H), 2.09–2.03 (m, 1H), 1.84–1.78 (m, 1H), 1.67–1.59 (m, 2H), 1.36 (m, 1H), 1.10 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 173.87, 171.04, 159.43, 138.54, 129.32, 120.81, 114.58, 112.54, 97.82, 89.49, 60.92, 55.16,

44.21, 43.54, 34.52, 31.57, 30.98, 24.78, 13.91 ppm; ESI-HRMS: calcd for ($C_{19}H_{23}NO_6$+Na^+): 384.1418, found: 384.1419.

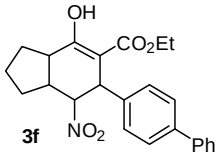


	Retention Time	Area	% Area
1	6.757	11839213	49.11
2	7.385	11987930	49.72
3	12.903	147341	0.61
4	13.447	135120	0.56



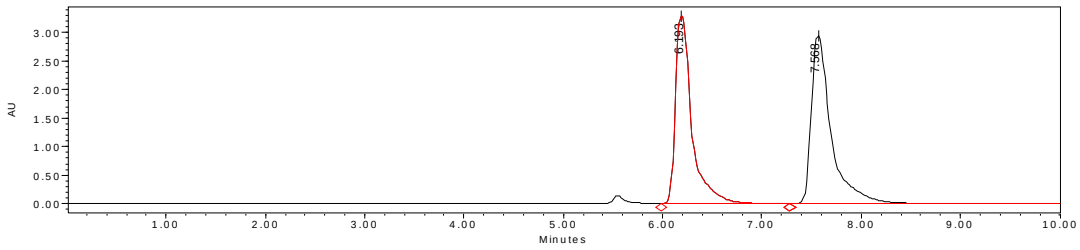
	Retention Time	Area	% Area
1	6.763	1313412	1.95
2	7.373	64557144	95.63
3	12.886	750070	1.11
4	13.464	883998	1.31

Ethyl 6-([1,1′-biphenyl]-4-yl)-4-hydroxy-7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3f:

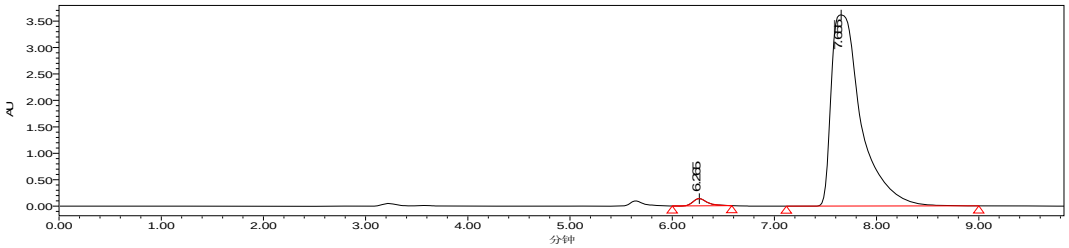


3f

white solid; 36.5 mg, 95% yield; $[a]_D^{20}$ = -231.2 (*c* = 0.52 in CH_2Cl_2); >99:1 dr; 96% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 6.26 min, t (major) = 7.66 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.57 (s, 1H), 7.56 (d, *J* = 7.4, 2H), 7.50 (d, *J* = 8.1, 2H), 7.42 (t, *J* = 7.6, 2H), 7.33 (t, *J* = 7.4, 1H), 7.09 (d, *J* = 8.1, 2H), 4.64 (dd, *J* = 12.3, 5.2, 1H), 4.59 (d, *J* = 5.2, 1H), 4.14 (m, 1H), 4.03 (m, 1H), 3.09 (dd, *J* = 18.2, 9.1, 1H), 2.95–2.89 (m, 1H), 2.40–2.33 (m, 1H), 2.11–2.04 (m, 1H), 1.82 (m, 1H), 1.68–1.60 (m, 2H), 1.43–1.35 (m, 1H), 1.10 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.92, 171.08, 140.60, 140.48, 135.95, 128.76, 128.73, 127.36, 127.04, 127.02, 97.87, 89.56, 60.99, 43.96, 43.61, 34.56, 31.61, 30.99, 24.79, 13.92 ppm; ESI-HRMS: calcd for ($C_{24}H_{25}NO_5$+Na^+): 430.1625, found: 430.1642.

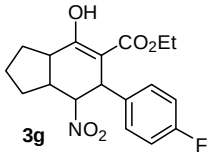


	Retention Time	Area	% Area
1	6.193	38022026	48.13
2	7.568	40971135	51.87



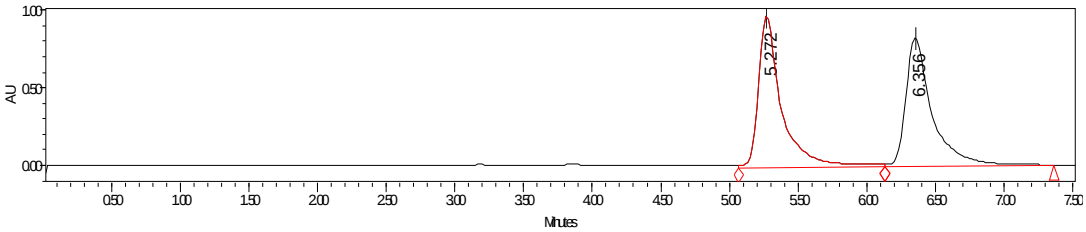
	Retention Time	Area	% Area
1	6.265	1420278	1.89
2	7.655	73528686	98.11

Ethyl 6-(4-fluorophenyl)-4-hydroxy-7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3g:

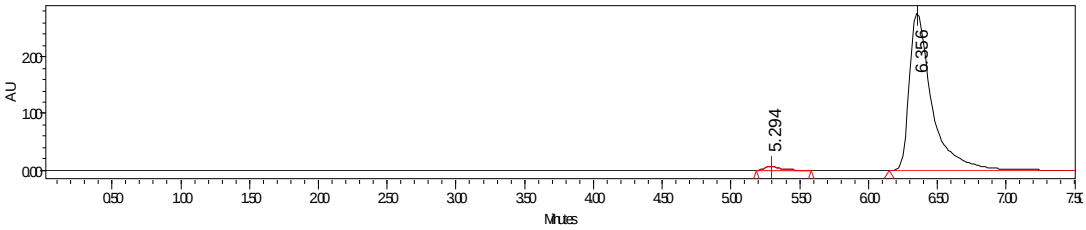


3g

white solid; 33.3 mg, 95% yield; $[a]_D^{20}$ = -214.4 (*c* = 0.36 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 97% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.29 min, t (major) = 6.36 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.53 (s, 1H), 6.98 (m, 4H), 4.60 (dd, *J* = 12.4, 5.3, 1H), 4.53 (d, *J* = 5.3, 1H), 4.15–4.01 (m, 2H), 3.05 (dd, *J* = 18.4, 9.1, 1H), 2.87–2.81 (m, 1H), 2.34 (m, 1H), 2.06 (m, 1H), 1.86–1.79 (m, 1H), 1.69–1.59 (m, 2H), 1.41–1.34 (m, 1H), 1.08 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.87, 170.93, 132.73, 132.70, 129.85, 129.77, 115.44, 115.22, 97.76, 89.36, 60.97, 43.52, 43.50, 34.39, 31.56, 30.86, 24.67, 13.87 ppm; ESI-HRMS: calcd for ($C_{18}H_{20}FNO_5$+Na^+): 372.1218, found: 372.1229.

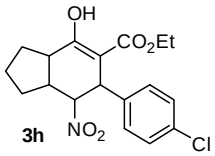


	Retention Time	Area	% Area
1	5.272	11303651	51.03
2	6.356	10846650	48.97



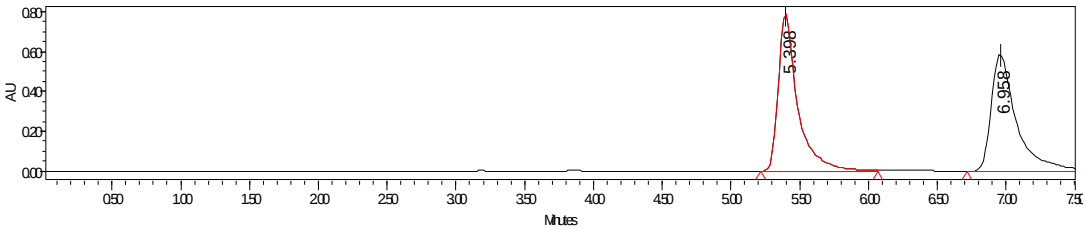
	Retention Time	Area	% Area
1	5.294	495562	1.53
2	6.356	31914258	98.47

Ethyl 6-(4-chorophenyl)-4-hydroxy-7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3h:

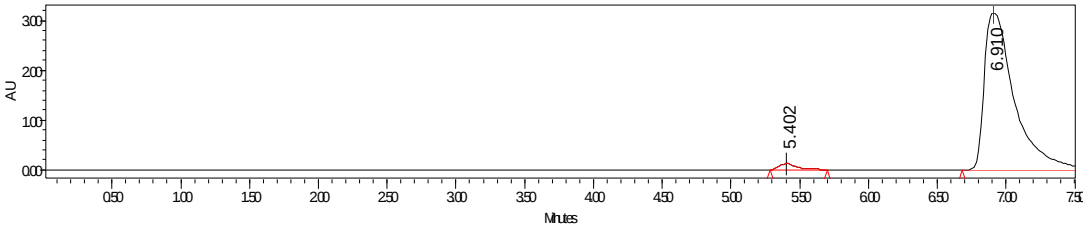


3h

yellow oil; 35.0 mg, 96% yield; $[a]_D^{20}$ = -209.5 (*c* = 0.43 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 96% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 5.40 min, t (major) = 6.91 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.54 (s, 1H), 7.25 (d, *J* = 8.4, 2H), 6.97 (d, *J* = 8.4, 2H), 4.61 (dd, *J* = 12.5, 5.3, 1H), 4.51 (d, *J* = 5.3, 1H), 4.15–4.00 (m, 2H), 3.05 (dd, *J* = 18.5, 9.0, 1H), 2.86–2.79 (m, 1H), 2.34 (m, 1H), 2.06 (m, 1H), 1.85–1.79 (m, 1H), 1.64 (m, 2H), 1.41–1.34 (m, 1H), 1.09 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.02, 170.87, 135.55, 133.82, 129.58, 128.61, 97.57, 89.26, 61.03, 43.64, 43.51, 34.42, 31.55, 30.87, 24.68, 13.89 ppm; ESI-HRMS: calcd for ($C_{18}H_{20}ClNO_5$+Na^+): 388.0922, found: 388.0934.



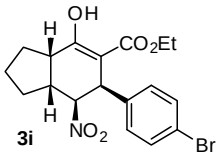
	Retention Time	Area	% Area
1	5.398	7763640	50.37
2	6.958	7649710	49.63



	Retention Time	Area	% Area
1	5.402	1036321	2.08
2	6.910	48807252	97.92

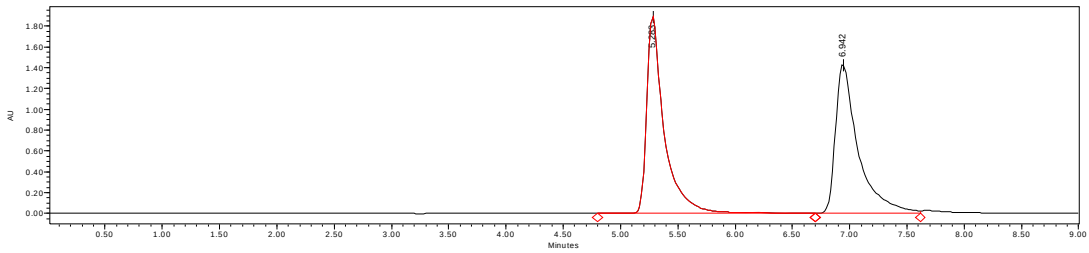
(3aS,6R,7S,7aR)-ethyl

6-(4-bromophenyl)-4-hydroxy-7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3i:

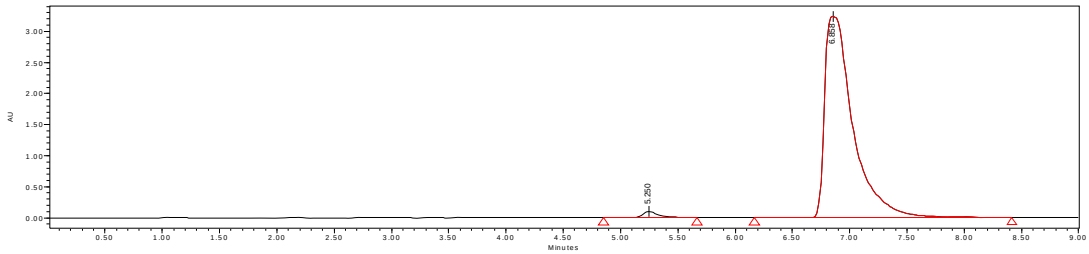


3i

yellow oil; 34.8 mg, 85% yield; $[a]_D^{20}$ = -197.1 (*c* = 0.63 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 96% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.25 min, t (major) = 6.86 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.54 (s, 1H), 7.40 (d, *J* = 8.3, 2H), 6.91 (d, *J* = 8.3, 2H), 4.61 (dd, *J* = 12.4, 5.3, 1H), 4.50 (d, *J* = 5.3, 1H), 4.17–3.98 (m, 2H), 3.05 (dd, *J* = 18.4, 9.0, 1H), 2.87–2.77 (m, 1H), 2.34 (m, 1H), 2.11–2.05 (m, 1H), 1.82 (m, 1H), 1.67–1.51 (m, 2H), 1.37 (m, 1H), 1.09 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.05, 170.85, 136.08, 131.57, 129.93, 122.02, 97.46, 89.20, 61.05, 43.71, 43.52, 34.43, 31.56, 30.88, 24.69, 13.90 ppm; ESI-HRMS: calcd for ($C_{18}H_{20}BrNO_5$+Na^+): 432.0417, found: 432.0433.

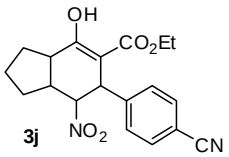


	Retention Time	Area	% Area
1	5.283	20247158	50.70
2	6.942	19687684	49.30



	Retention Time	Area	% Area
1	5.250	1016285	1.79
2	6.858	55632413	98.21

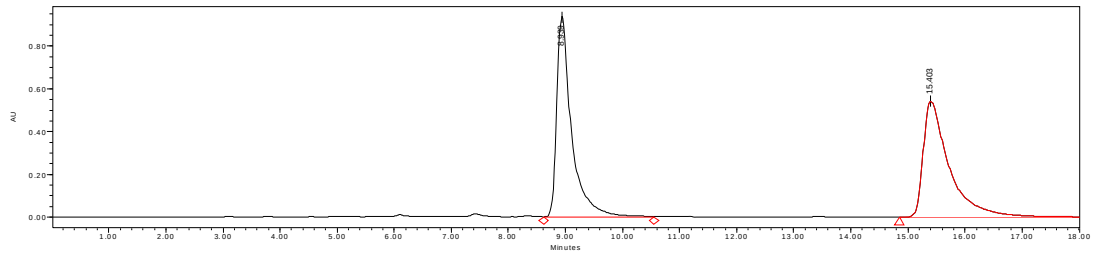
Ethyl 6-(4-cyanophenyl)-4-hydroxy-7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3j:



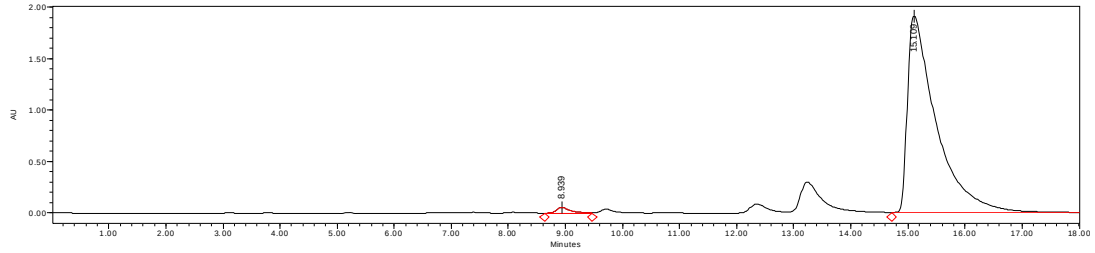
3j

white solid; 24.9 mg, 70% yield; $[a]_D^{20}$ = -236.5 (*c* = 0.40 in CH_2Cl_2); 89:11 dr, determined by NMR analysis; 97% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 8.94 min, t (major) = 15.10 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.56 (s, 1H), 7.58 (d, *J* = 8.2, 2H), 7.16 (d, *J* = 8.2, 2H), 4.66 (dd, *J* = 12.4, 5.4, 1H), 4.58 (d, *J* = 5.4, 1H), 4.15–3.99 (m, 2H), 3.07 (dd, *J* = 18.5, 8.9, 1H), 2.85–2.76 (m, 1H), 2.36 (m, 1H), 2.12–2.02 (m, 1H), 1.88–1.80 (m, 1H), 1.72–1.60 (m, 2H), 1.42–1.34 (m, 1H), 1.07 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.49, 170.59, 142.70, 132.59, 132.23, 129.11, 118.49, 111.97, 96.87, 88.99, 61.16, 44.19, 43.54, 34.53, 31.54, 30.82, 24.61, 13.88 ppm; ESI-HRMS:

calcd for ($C_{19}H_{20}N_2O_5$+Na^+): 379.1264, found: 379.1263.

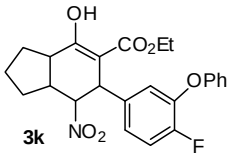


	Retention Time	Area	% Area
1	8.939	17122181	49.83
2	15.403	17241994	50.17



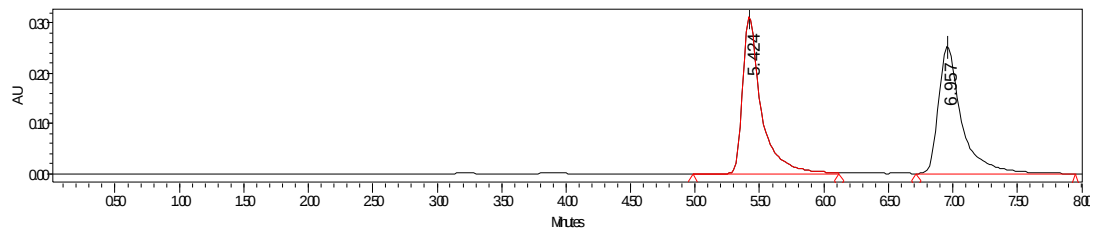
	Retention Time	Area	% Area
1	8.939	977971	1.43
2	15.109	67473341	98.57

Ethyl6-(4-fluoro-3-phenoxyphenyl)-4-hydroxy-7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3k:

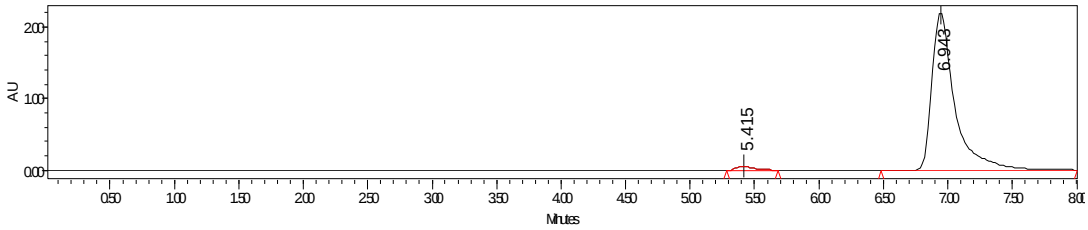


3k

yellow oil; 37.9 mg, 86% yield; $[a]_D^{20}$ = -185.0 (*c* = 0.4 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 97% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.41 min, t (major) = 6.94 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.50 (s, 1H), 7.33 (t, *J* = 8.0, 2H), 7.09 (m, 2H), 6.92 (d, *J* = 8.0, 2H), 6.83–6.78 (m, 1H), 6.76 (m, 1H), 4.57 (dd, *J* = 12.4, 5.3, 1H), 4.46 (d, *J* = 5.3, 1H), 4.15–4.05 (m, 2H), 2.95 (dd, *J* = 18.4, 9.1, 1H), 2.87–2.79 (m, 1H), 2.32 (m, 1H), 2.06 (m, 1H), 1.85–1.78 (m, 1H), 1.66–1.56 (m, 2H), 1.42–1.34 (m, 1H), 1.11 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.97, 170.82, 157.35, 155.17, 152.69, 143.21, 143.09, 133.98, 129.70, 124.55, 123.11, 122.15, 117.06, 116.83, 97.41, 89.17, 61.01, 43.56, 43.37, 34.44, 31.51, 30.84, 24.61, 13.93 ppm; ESI-HRMS: calcd for ($C_{24}H_{24}FNO_6$+Na^+): 464.1480, found: 464.1488.

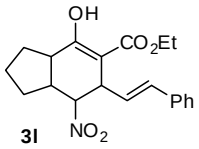


	Retention Time	Area	% Area
1	5.424	3169603	50.38
2	6.957	3122215	49.62



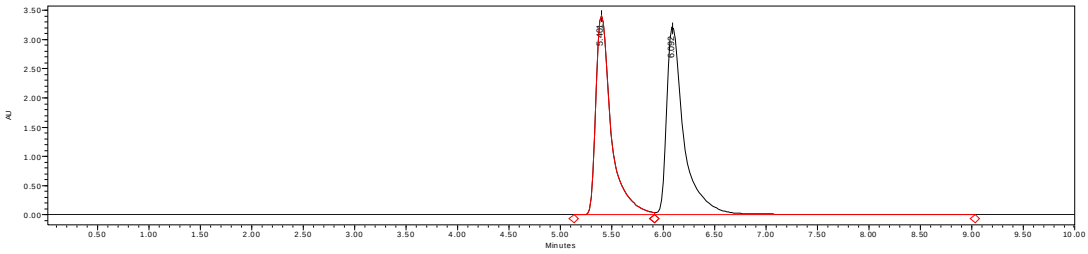
	Retention Time	Area	% Area
1	5.415	489316	1.78
2	6.943	26970571	98.22

(E)-ethyl 4-hydroxy-7-nitro-6-styryl-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3l:

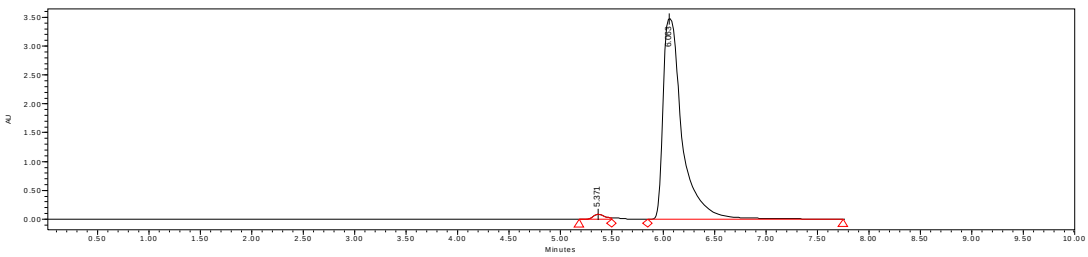


3l

yellow oil; 21.4 mg, 60% yield; $[a]_D^{20}$ = -365.8 (*c* = 0.26 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 97% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.37 min, t (major) = 6.06 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.55 (s, 1H), 7.32–7.27 (m, 4H), 7.24–7.20 (m, 1H), 6.37 (d, *J* = 15.6, 1H), 5.94 (dd, *J* = 15.6, 8.1, 1H), 4.49 (dd, *J* = 12.3, 4.9, 1H), 4.25–4.19 (m, 2H), 4.09 (dd, *J* = 8.0, 4.9, 1H), 3.10–3.04 (m, 1H), 2.96 (dd, *J* = 18.2, 9.5, 1H), 2.32–2.26 (m, 1H), 2.13 (m, 1H), 1.84–1.78 (m, 1H), 1.68–1.54 (m, 2H), 1.44 (m, 1H), 1.27 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 173.80, 171.22, 136.52, 133.88, 128.54, 127.82, 126.54, 124.50, 96.80, 89.17, 60.99, 43.19, 41.64, 35.33, 31.38, 31.07, 24.66, 14.18 ppm; ESI-HRMS: calcd for ($C_{20}H_{23}NO_5$+Na^+): 380.1468, found: 380.1462.

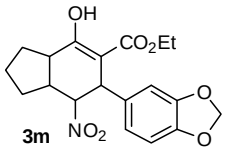


	Retention Time	Area	% Area
1	5.401	35561245	48.48
2	6.092	37788729	51.52



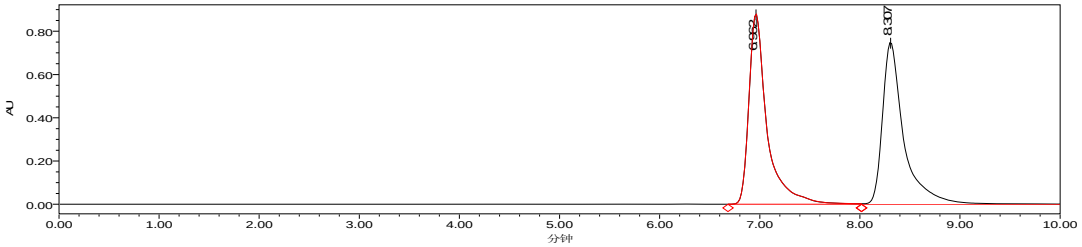
	Retention Time	Area	% Area
1	5.371	733165	1.61
2	6.063	44823018	98.39

Ethyl 6-(benzo[*d*][1,3]dioxol-5-yl)-4-hydroxy-7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3m:

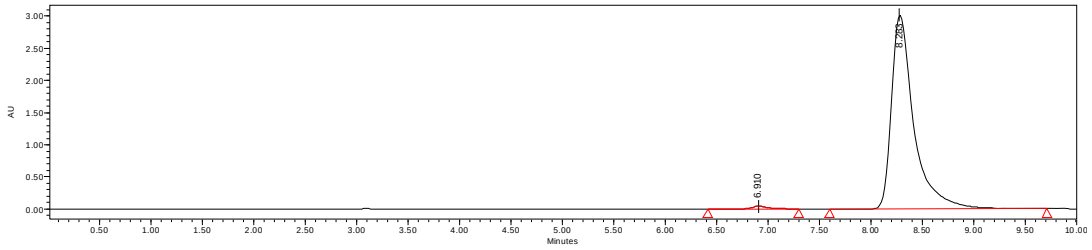


3m

white solid; 24.8 mg, 66% yield; $[a]_D^{20}$ = -310.5 (*c* = 0.36 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 98% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 6.91 min, t (major) = 8.28 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.52 (s, 1H), 6.70 (d, *J* = 7.9, 1H), 6.50 (m, 2H), 5.95–5.93 (m, 2H), 4.56 (dd, *J* = 12.4, 5.2, 1H), 4.46 (d, *J* = 5.2, 1H), 4.17–4.12 (m, 1H), 4.04 (m, 1H), 3.04 (dd, *J* = 18.8, 8.9, 1H), 2.92–2.86 (m, 1H), 2.37–2.31 (m, 1H), 2.07 (m, 1H), 1.85–1.78 (m, 1H), 1.66–1.56 (m, 2H), 1.41–1.34 (m, 1H), 1.12 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 173.69, 171.02, 147.65, 147.23, 130.68, 121.81, 108.45, 108.13, 101.13, 98.00, 89.57, 60.92, 43.98, 43.48, 34.46, 31.57, 30.95, 24.71, 13.93 ppm; ESI-HRMS: calcd for ($C_{19}H_{21}NO_7$+Na^+): 398.1210, found: 398.1217.

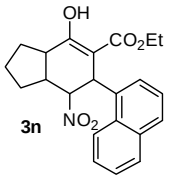


	Retention Time	Area	% Area
1	6.962	11099934	49.99
2	8.307	11105143	50.01



	Retention Time	Area	% Area
1	6.910	506239	1.09
2	8.283	46094698	98.91

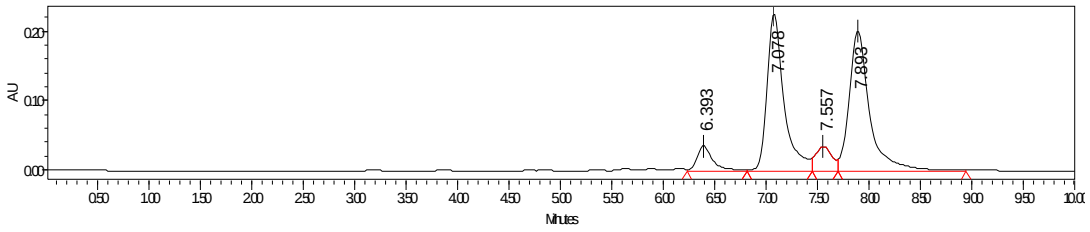
Ethyl 4-hydroxy-6-(naphthalen-1-yl)- 7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3n:



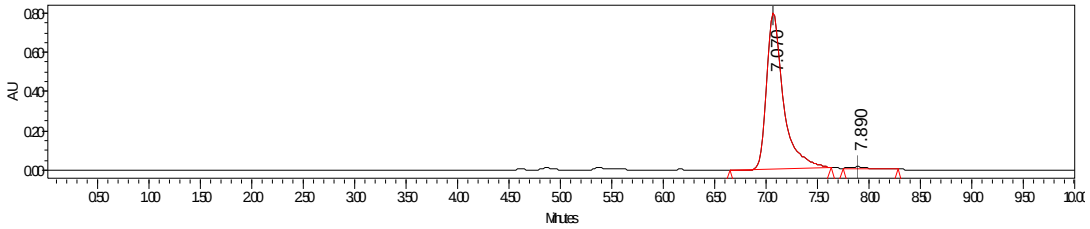
3n

white solid; 27.8 mg, 73% yield; $[a]_D^{20}$ = -332.0 (*c* = 0.24 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 95% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 7.89 min, t (major) = 7.07 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.47 (s, 1H), 8.10 (d, *J* = 8.3, 1H), 7.82 (d, *J* = 7.6, 1H), 7.76 (d, *J* = 8.2, 1H), 7.45 (m, 3H), 7.23 (d, *J* = 7.2, 1H), 5.64 (d, *J* = 5.3, 1H), 4.82 (dd, *J* = 12.2, 5.3, 1H), 4.00 (m, 1H), 3.81 (m, 1H), 3.18 (dd, *J* = 18.0, 8.4, 1H), 3.12–3.04 (m, 1H), 2.45–2.34 (m, 1H), 2.07–1.96 (m, 1H), 1.91–1.80 (m, 1H), 1.68 (m, 2H), 1.35 (m, 1H), 0.79 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.59, 171.00, 133.70, 133.55, 132.55, 128.70, 128.42, 126.31, 126.14, 125.73, 124.53, 122.12, 99.31, 88.73, 60.83, 43.59, 37.33, 35.28, 31.58, 30.40, 24.71, 13.56 ppm; ESI-HRMS: calcd for

($C_{22}H_{23}NO_5$+Na^+): 404.1468, found: 404.1474.

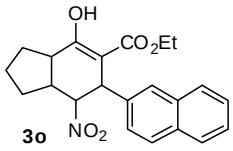


	Retention Time	Area	% Area
1	6.393	392398	6.34
2	7.078	2610672	42.18
3	7.557	392299	6.34
4	7.893	2793925	45.14



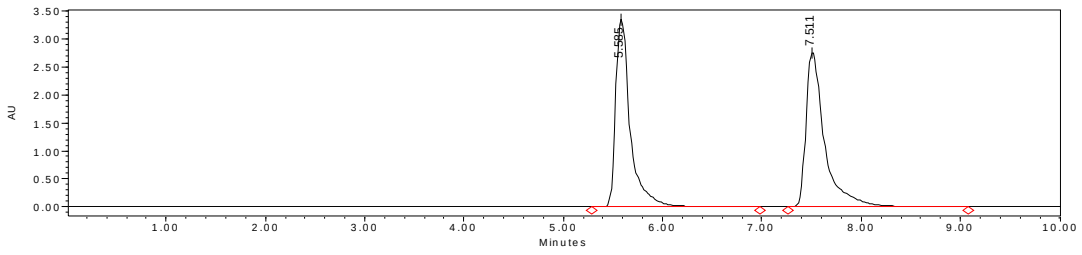
	Retention Time	Area	% Area
1	7.070	9048374	98.97
2	7.890	93962	1.03

Ethyl 4-hydroxy-6-(naphthalen-2-yl)- 7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3o:

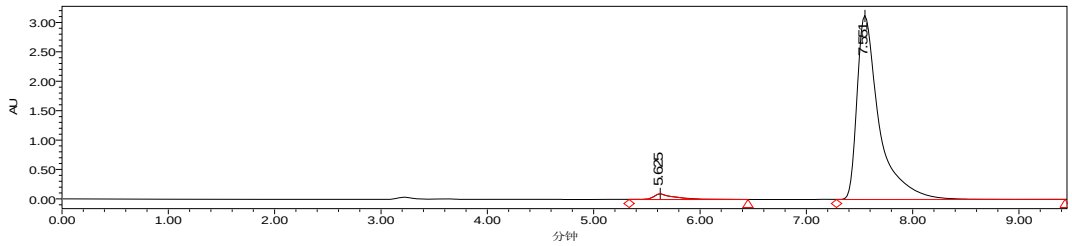


3o

white solid; 37.7 mg, 99% yield; $[a]_D^{20}$ = -284.9 (*c* = 0.47 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 95% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.62 min, t (major) = 7.55 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.62 (s, 1H), 7.79 (m, 2H), 7.75 (d, *J* = 8.5, 1H), 7.50 – 7.43 (m, 3H), 7.15 (d, *J* = 8.4, 1H), 4.73 (d, *J* = 5.2, 1H), 4.68 (dd, *J* = 12.3, 5.3, 1H), 4.12 (m, 1H), 3.98–3.91 (m, 1H), 3.15 (dd, *J* = 18.1, 9.2, 1H), 2.97–2.90 (m, 1H), 2.38 (m, 1H), 2.05 (m, 1H), 1.87–1.79 (m, 1H), 1.69–1.60 (m, 2H), 1.37 (m, 1H), 1.04 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.02, 171.12, 134.53, 133.14, 132.98, 128.13, 128.01, 127.64, 127.40, 126.25, 126.18, 126.06, 97.95, 89.58, 60.98, 44.34, 43.68, 34.63, 31.63, 30.96, 24.79, 13.88 ppm; ESI-HRMS: calcd for ($C_{22}H_{23}NO_5$+Na^+): 404.1468, found: 404.1478.

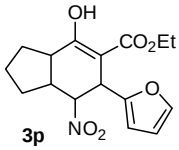


	Retention Time	Area	% Area
1	5.585	34101810	48.81
2	7.511	35759883	51.19



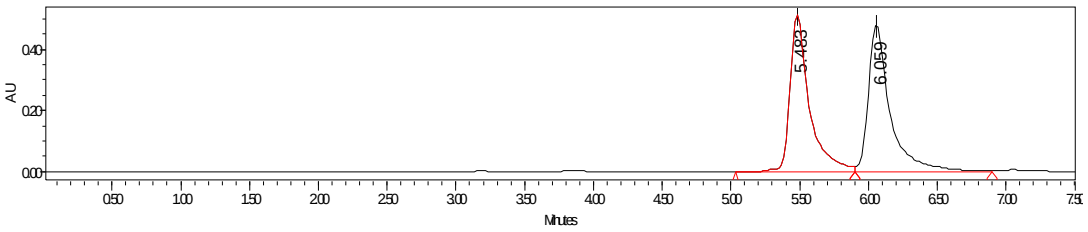
	Retention Time	Area	% Area
1	5.625	1170484	2.52
2	7.551	45250162	97.48

Ethyl 6-(furan-2-yl)-4-hydroxy-7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3p:

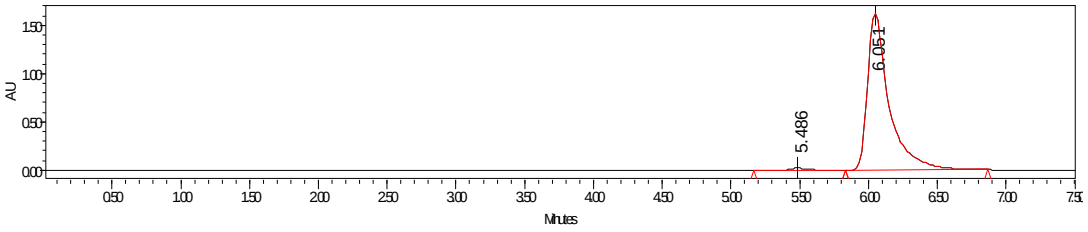


3p

yellow oil; 25.7 mg, 80% yield; $[a]_D^{20}$ = -204.8 (*c* = 0.40 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 96% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.49 min, t (major) = 6.05 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.53 (s, 1H), 7.31 (s, 1H), 6.27 (s, 1H), 6.05 (d, *J* = 3.1, 1H), 4.68 (d, *J* = 4.8, 1H), 4.50 (dd, *J* = 11.9, 4.8, 1H), 4.21–4.11 (m, 2H), 3.06 (dd, *J* = 18.0, 9.6, 1H), 3.02–2.98 (m, 1H), 2.30 (m, 1H), 2.10 (m, 1H), 1.84–1.76 (m, 1H), 1.68–1.55 (m, 2H), 1.39 (m, 1H), 1.20 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 174.56, 170.86, 150.75, 142.77, 110.32, 108.76, 95.77, 88.47, 61.02, 43.24, 38.33, 35.65, 31.30, 31.16, 24.88, 14.03 ppm; ESI-HRMS: calcd for ($C_{16}H_{19}NO_6$+Na^+): 344.1105, found: 344.1113.

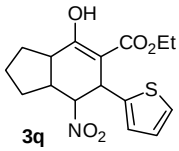


	Retention Time	Area	% Area
1	5.483	4998749	49.00
2	6.059	5202464	51.00



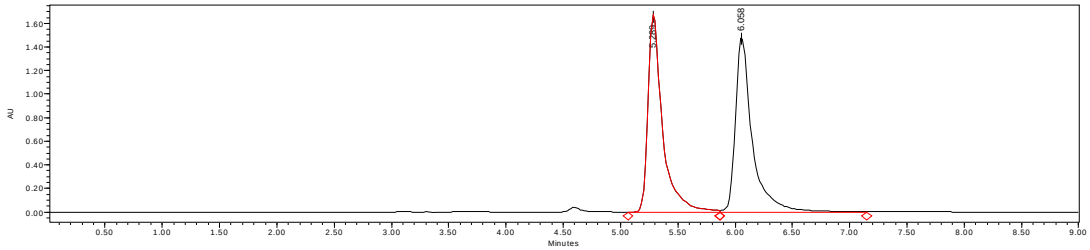
	Retention Time	Area	% Area
1	5.486	200571	1.11
2	6.051	17830577	98.89

Ethyl 4-hydroxy-7-nitro-6-(thiophen-2-yl)-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3q:

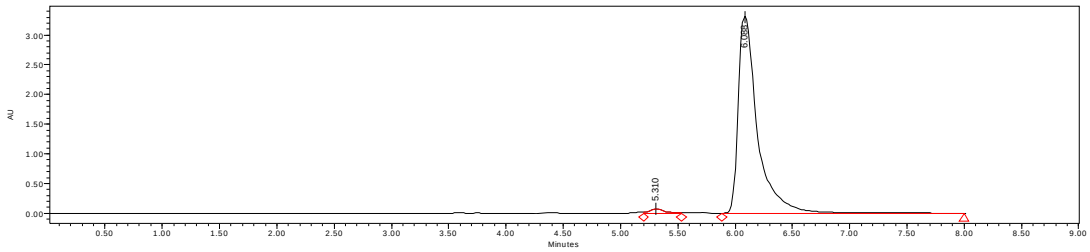


3q

colorless oil; 24.3 mg, 72% yield; $[a]_D^{20}$ = -277.6 (*c* = 0.33 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 97% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.31 min, t (major) = 6.09 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.53 (s, 1H), 7.18 (d, *J* = 5.1, 1H), 6.95–6.91 (m, 1H), 6.73 (d, *J* = 3.4, 1H), 4.87 (d, *J* = 4.9, 1H), 4.56 (dd, *J* = 11.8, 5.0, 1H), 4.21–4.06 (m, 2H), 3.11–2.95 (m, 2H), 2.37–2.27 (m, 1H), 2.13 (m, 1H), 1.85 (m, 1H), 1.70–1.51 (m, 2H), 1.43–1.33 (m, 1H), 1.15 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.78, 170.88, 140.99, 127.32, 126.20, 125.10, 99.02, 89.45, 61.07, 43.21, 39.67, 34.75, 31.49, 31.31, 24.94, 13.96 ppm; ESI-HRMS: calcd for ($C_{16}H_{19}NO_5S$+Na^+): 360.0876, found: 360.0885.

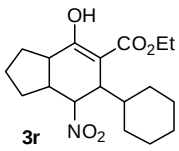


	Retention Time	Area	% Area
1	5.289	14904222	49.33
2	6.058	15310359	50.67



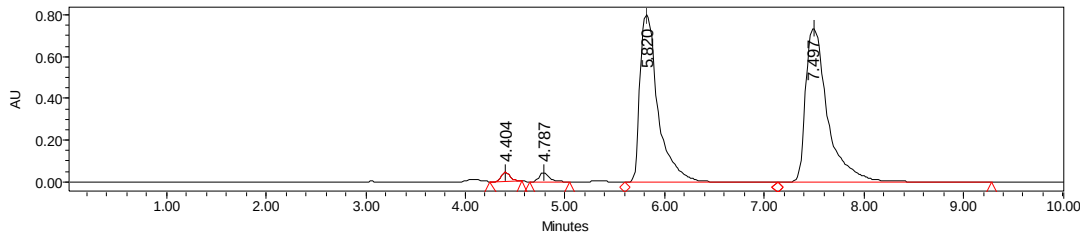
	Retention Time	Area	% Area
1	5.309	577550	1.47
2	6.088	38746424	98.53

Ethyl 6-cyclohexyl-4-hydroxy-7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3r:

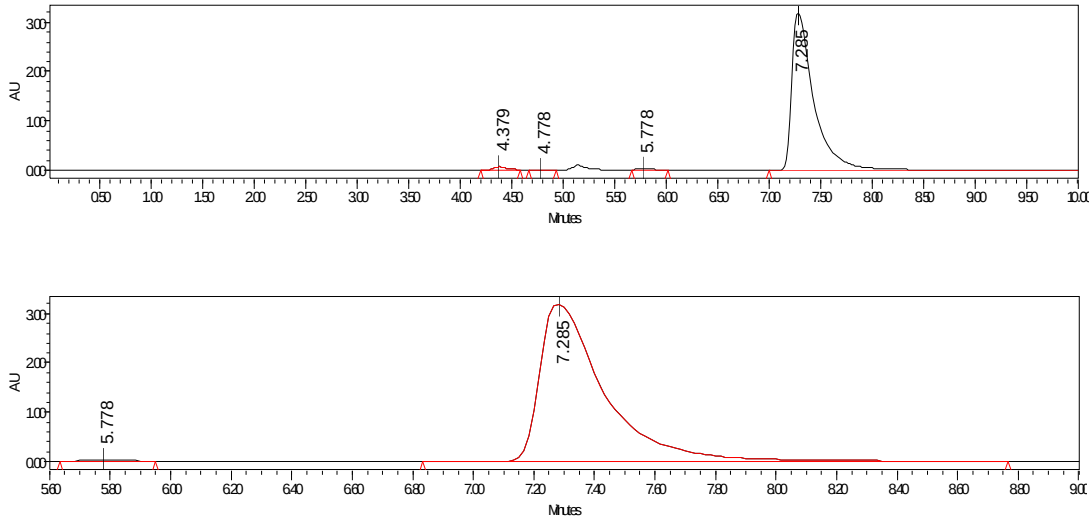


3r

white soild; 20.9 mg, 62% yield; $[a]_D^{20}$ = 51.7 (*c* = 0.41 in CH_2Cl_2); 99:1 dr, determined by HPLC analysis; 99% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.78 min, t (major) = 7.29 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.77 (s, 1H), 5.04 (dd, *J* = 7.2, 4.2, 1H), 4.30–4.21 (m, 1H), 4.16–4.08 (m, 1H), 3.16 (dd, *J* = 13.2, 4.2, 1H), 2.82–2.67 (m, 2H), 2.15 (dt, *J* = 13.1, 6.6, 1H), 2.00–1.84 (m, 4H), 1.77–1.73 (m, 4H), 1.67 (m, 2H), 1.51–1.45 (m, 2H), 1.28 (t, *J* = 7.1, 3H), 1.20–1.00 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.48, 172.35, 95.45, 84.90, 60.53, 44.71, 42.19, 40.92, 36.52, 31.08, 30.70, 29.91, 27.91, 26.53, 26.28, 26.22, 25.87, 14.18 ppm; ESI-HRMS: calcd for ($C_{18}H_{27}NO_5$+Na^+): 360.1781, found: 360.1789.

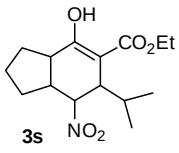


	Retention Time	Area	% Area
1	4.404	245167	1.14
2	4.787	260974	1.21
3	5.820	9929175	46.01
4	7.497	11147286	51.65



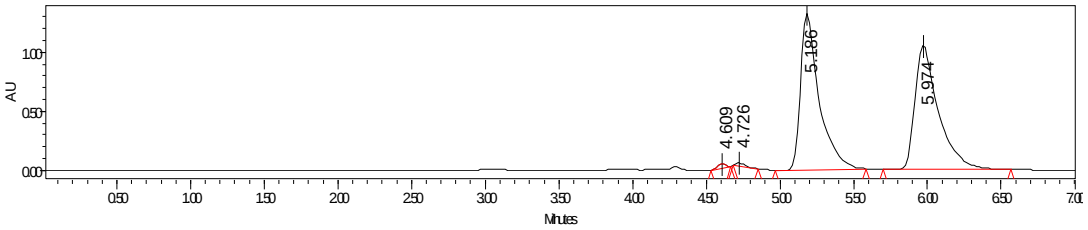
	Retention Time	Area	% Area
1	4.379	451719	0.94
2	4.778	4683	0.01
3	5.778	240981	0.50
4	7.285	47275366	98.55

Ethyl 4-hydroxy-6-isopropyl-7-nitro-2,3,3a,6,7,7a-hexahydro-1*H*-indene-5-carboxylate 3s:

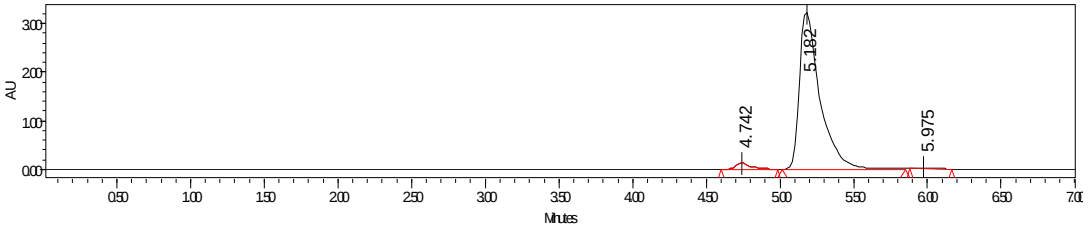


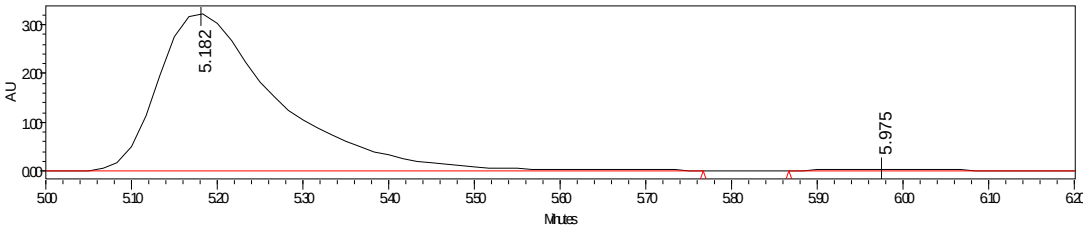
3s

white solid; 14.8 mg, 50% yield; $[a]_D^{20}$ = 71.5 (*c* = 0.13 in CH_2Cl_2); 97:3 dr, determined by HPLC analysis; 99% ee, determined by HPLC analysis [Daicel chiralcel ADH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 5.97 min, t (major) = 5.18 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.78 (s, 1H), 5.02 (dd, *J* = 5.3, 3.0, 1H), 4.29–4.24 (m, 1H), 4.12 (m, 1H), 3.12 (dd, *J* = 8.9, 2.9, 1H), 2.78 (m, 1H), 2.74–2.68 (m, 1H), 2.14 (m, 1H), 2.01–1.94 (m, 2H), 1.89–1.84 (m,1H), 1.66 (m, 1H), 1.55–1.44 (m, 2H), 1.28 (t, *J* = 7.1, 3H), 1.00 (d, *J* = 6.7, 3H), 0.94 (d, *J* = 6.8, 3H) ppm; ^{13}C NMR (150 MHz, CDCl3): δ = 175.40, 172.30, 95.82, 85.09, 60.54, 45.54, 40.99, 36.70, 32.45, 29.89, 27.87, 25.71, 20.88, 20.17, 14.15 ppm; ESI-HRMS: calcd for ($C_{15}H_{23}NO_5$+Na^+): 320.1468, found: 320.1474.



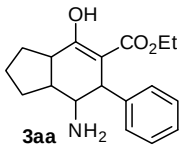
	Retention Time	Area	% Area
1	4.609	126638	0.54
2	4.726	114974	0.49
3	5.186	11560663	49.39
4	5.974	11606759	49.58





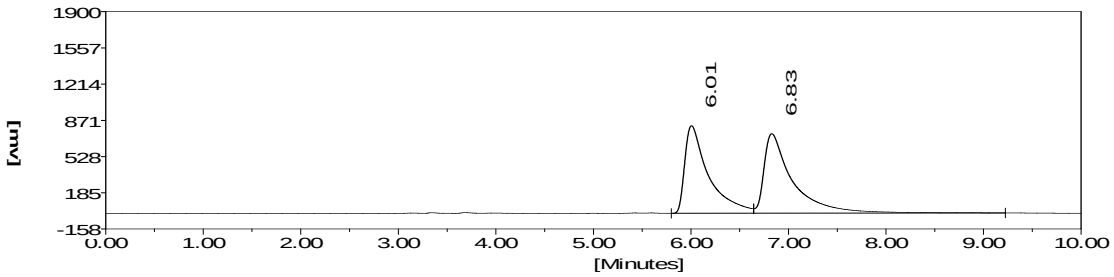
	Retention Time	Area	% Area
1	4.742	898891	2.77
2	5.182	31453900	96.83
3	5.975	132096	0.41

Ethyl 7-amino-4-oxo-6-phenyloctahydro-1*H*-indene-5-carboxylate 3aa:

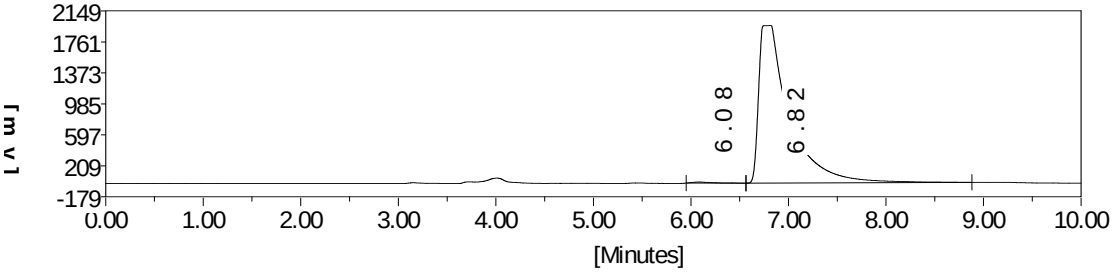


3aa

colorless oil; 25.7 mg, 92% yield; $[a]_D^{20}$ = -141.7 (*c* = 1.5 in CH_2Cl_2); >99:1 dr, determined by NMR analysis; 99% ee, determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 6.08 min, t (major) = 6.82 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 12.49 (s, 1H), 7.29 (t, *J* = 7.2, 2H), 7.22 (t, *J* = 7.2, 1H), 7.16 (d, *J* = 7.2, 2H), 4.10–4.05 (m, 1H), 4.01–3.95 (m, 1H), 3.87 (d, *J* = 4.8, 1H), 2.89 (dd, *J* = 8.0, 2.4, 1H), 2.77 (dd, *J* = 8.0, 5.4, 1H), 2.29–2.26 (m, 1H), 1.95–1.90 (m, 1H), 1.87–1.83 (m, 1H), 1.84–1.77 (m, 1H), 1.63–1.51 (m, 3H), 1.17–1.35 (br, 2H), 1.08 (t, *J* = 7.2, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.75, 172.01, 139.81, 129.64, 128.73, 127.83, 127.64, 126.61, 100.29, 60.29, 53.27, 46.96, 44.28, 40.39, 31.29, 30.08, 24.96, 13.92. ESI-HRMS: calcd for ($C_{18}H_{23}NO_3$+H^+): 302.1751, found: 302.1754.

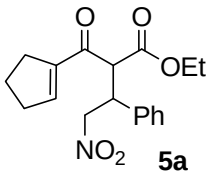


	Retention Time	Area	% Area
1	6.01	14034.23	47.6292
2	6.83	15431.39	52.3708



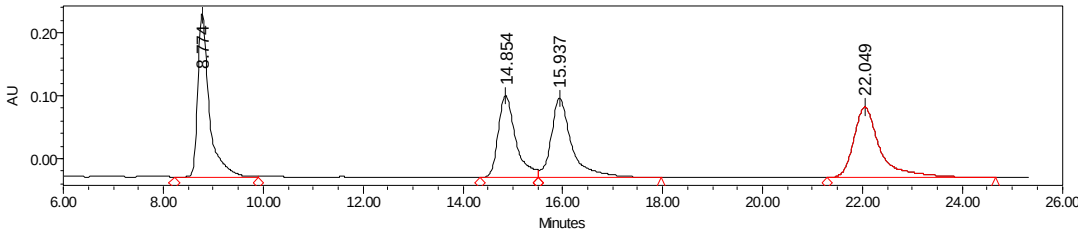
	Retention Time	Area	% Area
1	6.08	132.26	0.3107
2	6.82	42433.84	99.6893

Ethyl 2-(cyclopent-1-enecarbonyl)-4-nitro-3-phenylbutanoate 5a:



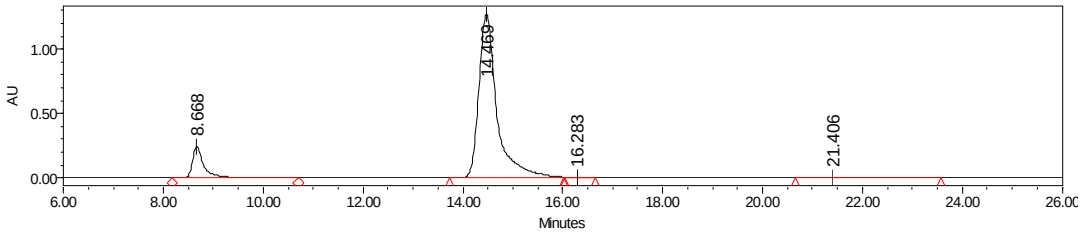
5a

white solid; 32.8 mg, 99% yield; 81:19 dr, determined by NMR analysis; 98% ee (minor 92% ee), determined by HPLC analysis [Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, major diastereomer: t (minor) = 16.28 min, t (major) = 14.47 min; minor diastereomer: t (minor) = 21.41 min, t (major) = 8.67 min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.32–7.16 (m, 5H), 6.85–6.78 (m, 1H), 4.89 (m, 2H), 4.51 (d, *J* = 9.5, 1H), 4.32–4.26 (td, *J* = 9.4, 4.7, 1H), 4.19 (q, *J* = 7.1, 2H), 2.64–2.56 (m, 1H), 2.56–2.46 (m, 1H), 2.45–2.37 (m, 1H), 2.33–2.26 (m, 1H), 1.88–1.76 (m, 2H), 1.24 (t, *J* = 7.1, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = (190.40, 190.33, 1C), (167.93, 167.32, 1C), (147.90, 1C), (146.70, 1C), (145.15, 145.11, 2C), (136.82, 136.45, 2C), (128.88, 128.82, 2C), (128.21, 128.04, 1C), (77.91, 77.86, 1C), (62.02, 61.75, 1C), (57.66, 57.26, 1C), (43.14, 42.85, 1C), (34.39, 34.16, 1C), (30.74, 30.57, 1C), 22.54, (13.98, 13.65, 1C) ppm; ESI-HRMS: calcd for ($C_{18}H_{21}NO_5$+Na^+): 354.1312, found: 354.1310.



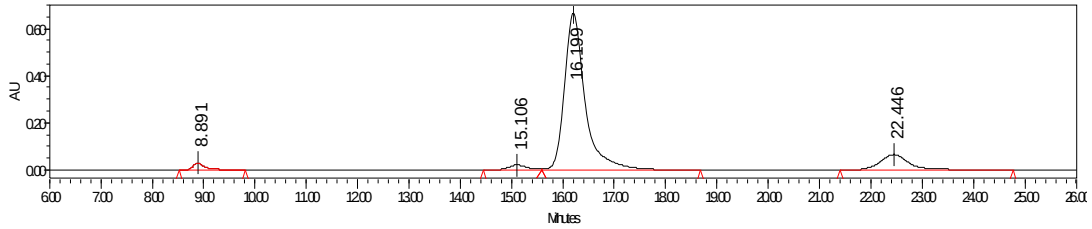
	Retention Time	Area	% Area
1	8.774	4171425	27.64

2	14.854	3178286	21.06
3	15.937	3596360	23.83
4	22.049	4144206	27.46



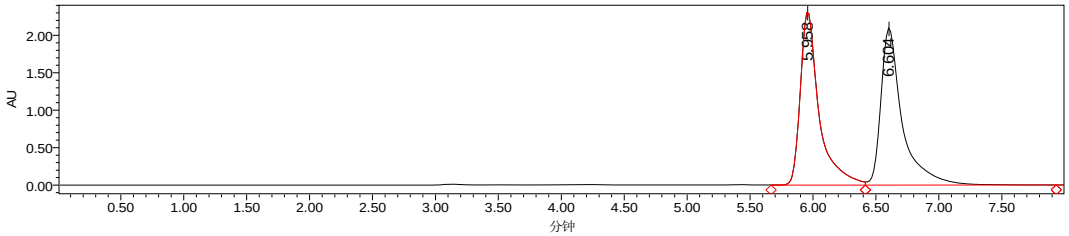
	Retention Time	Area	% Area
1	8.668	3758571	10.60
2	14.469	31454265	88.73
3	16.283	20492	0.06
4	21.406	217669	0.61

HPLC spectra of **5a** catalyzed by **4e** (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm):



	Retention Time	Area	% Area
1	8.891	464867	2.11
2	15.106	509709	2.32
3	16.199	18467603	83.98
4	22.446	2547953	11.59

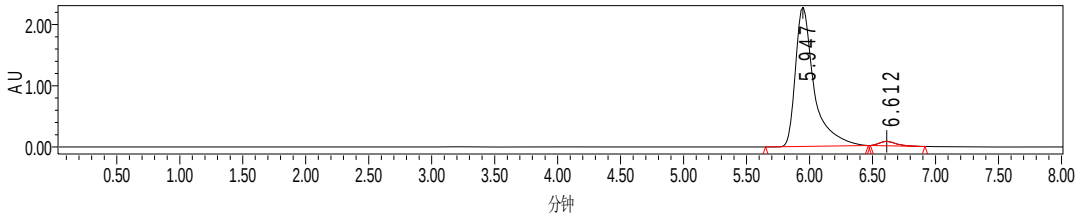
HPLC spectra of racemic **3a** catalyzed by TMG (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min,λ=254nm):



	Retention Time	Area	% Area
1	5.958	24006699	49.29
2	6.604	24695633	50.71

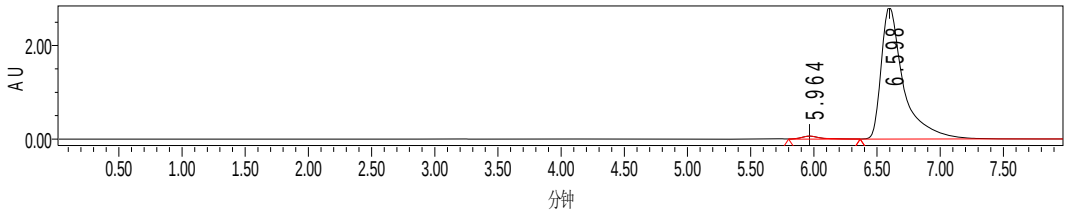
HPLC spectra of 3a catalyzed by **4e** (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min,

λ=254nm):



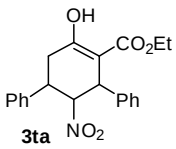
	Retention Time	Area	% Area
1	5.947	23365394	97.26
2	6.612	657571	2.74

HPLC spectra of **3a** catalyzed by **4d** (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ=254nm):



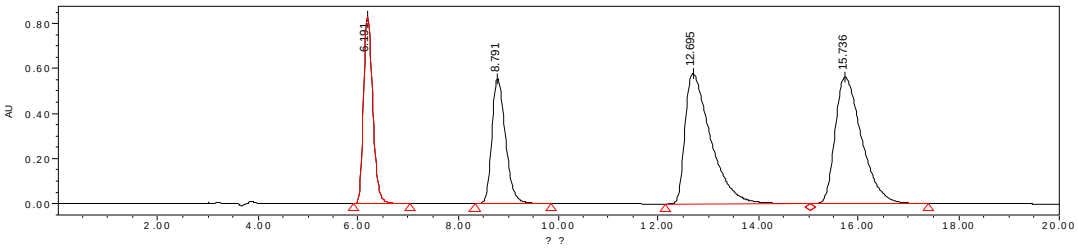
	Retention Time	Area	% Area
1	5.964	649942	1.85
2	6.598	34558793	98.15

Ethyl 2-hydroxy-5-nitro-4,6-diphenylcyclohex-1-enecarboxylate 3ta:[4]



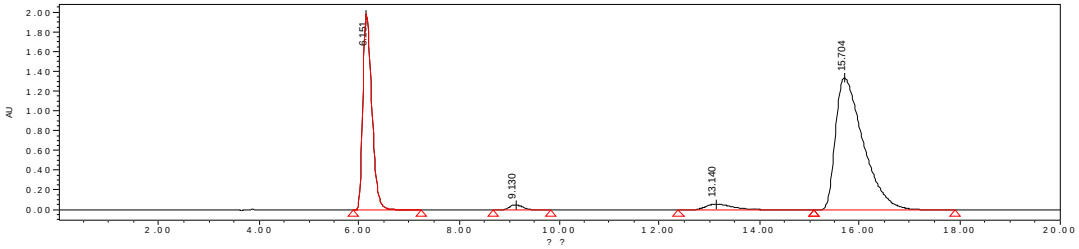
3ta

yellow oil; 29.7 mg, 75% yield; 68:32 dr, determined by HPLC analysis; 92% ee (minor 92% ee), determined by HPLC analysis [Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, major diastereomer: t (minor) = 13.14 min, t (major) = 15.70 min; minor diastereomer: t (minor) = 9.13 min, t (major) = 6.15 min]; major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.48 (s, 1H), 7.36–7.10 (m, 10H), 5.30 (dd, *J* = 12.4, 5.6, 1H), 4.64 (d, *J* = 5.6, 1H), 4.12–3.99 (m, 2H), 3.68–3.58 (m, 1H), 2.98 (dd, *J* = 19.6, 7.2, 1H), 2.64 (dd, *J* = 19.2, 11.2, 1H), 1.04 (t, *J* = 7.2, 3H) ppm; minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.71 (s, 1H), 7.35–7.23 (m, 8H), 7.05 (d, *J* = 6.8, 2H), 4.95–4.92 (m, 1H), 4.55 (s, 1H), 4.10–3.97 (m, 2H), 3.43 (m, 1H), 3.32 (dd, *J* = 18.4, 12.0, 1H), 2.78 (dd, *J* = 18.4, 6.4, 1H), 0.97 (t, *J* = 7.2, 3H) ppm.



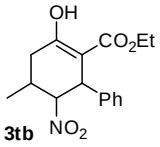
	Retention Time	Area	% Area

1	6.191	10665536	17.01
2	8.791	10563902	16.85
3	12.695	20742785	33.09
4	15.736	20712773	33.04



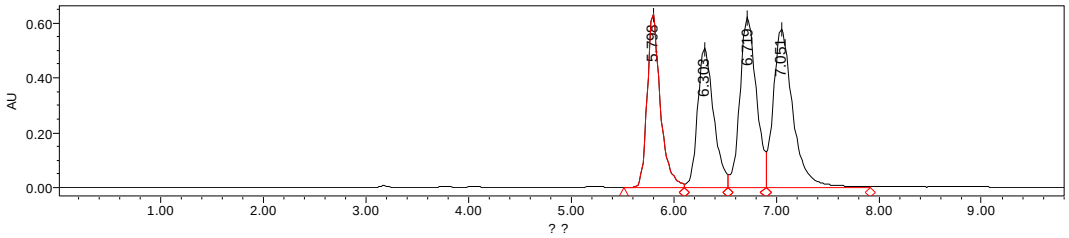
	Retention Time	Area	% Area
1	6.151	24710737	30.89
2	9.130	1053897	1.32
3	13.140	2532009	3.17
4	15.704	51697343	64.63

Ethyl 3-hydroxy-5-methyl-6-nitro-1,4,5,6-tetrahydro-[1, 1'-biphenyl]-2-carboxylate 3tb:[4]

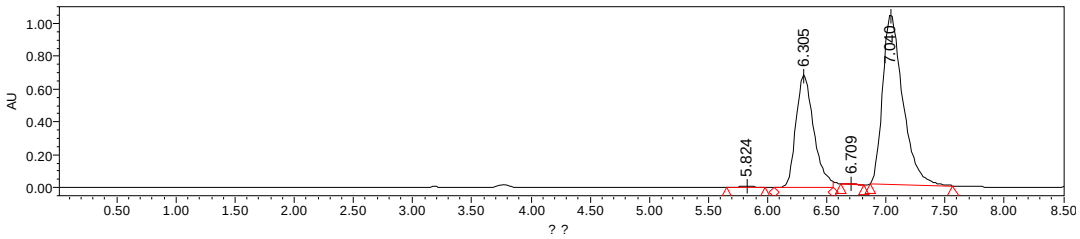


3tb

yellow oil; 18.4 mg, 60% yield; 64:36 dr, determined by HPLC analysis; 99% ee (minor 98% ee), determined by HPLC analysis [Daicel chiralcel ODH, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, major diastereomer: t (minor) = 6.71 min, t (major) = 7.04 min; minor diastereomer: t (minor) = 5.82 min, t (major) = 6.31 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.58 (s, 1H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.28 (s, 1H), 7.22 (d, *J* = 7.2 Hz, 2H), 4.65 (t, *J* = 2.9 Hz, 1H), 4.46 (d, *J* = 2.2 Hz, 1H), 4.06 – 3.94 (m, 2H), 2.57 (dd, *J* = 18.6, 6.9 Hz, 1H), 2.47 (dd, *J* = 18.6, 10.1 Hz, 1H), 2.32 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.93 (t, *J* = 7.1 Hz, 3H).

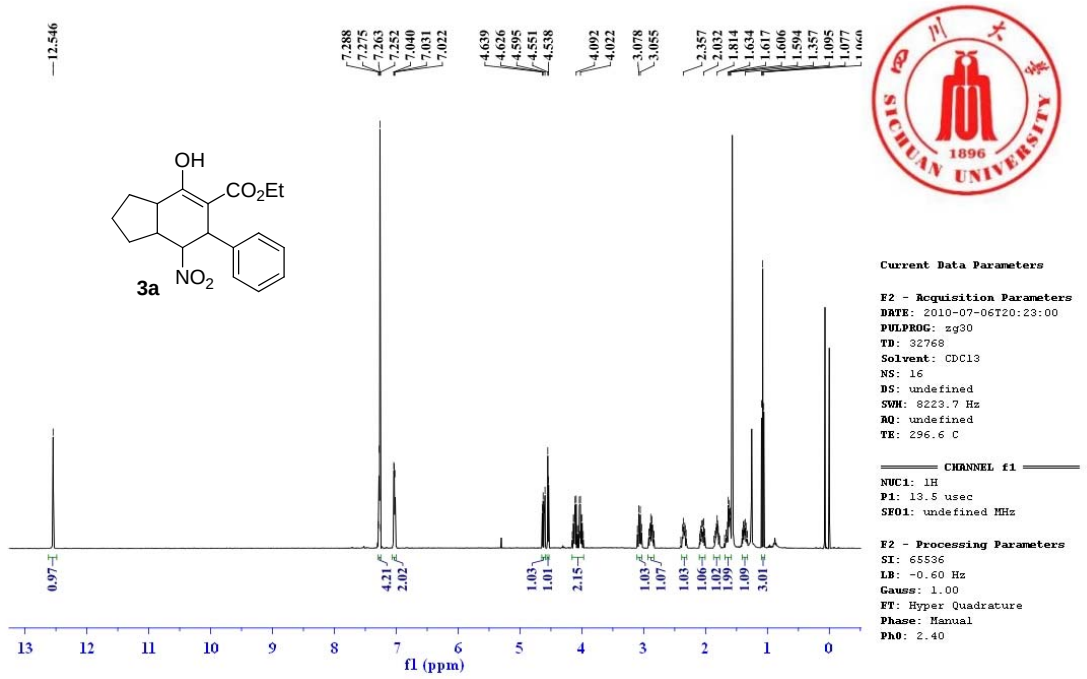


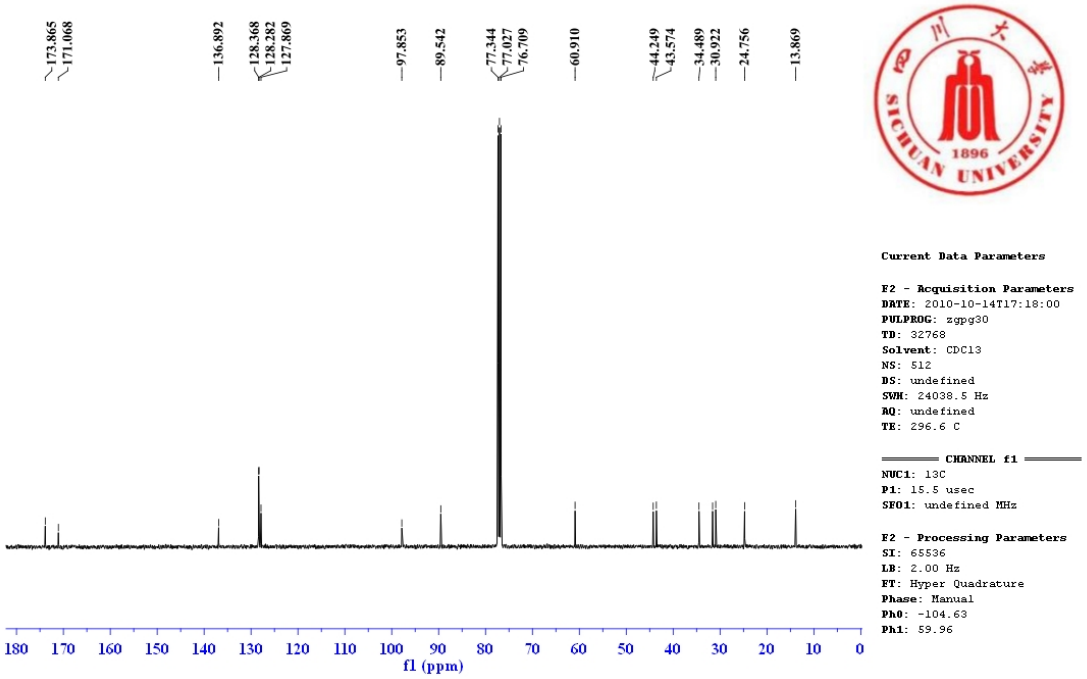
	Retention Time	Area	% Area
1	5.798	5609625	21.76
2	6.303	5554190	21.54
3	6.719	6933645	26.89
4	7.051	7683646	29.80

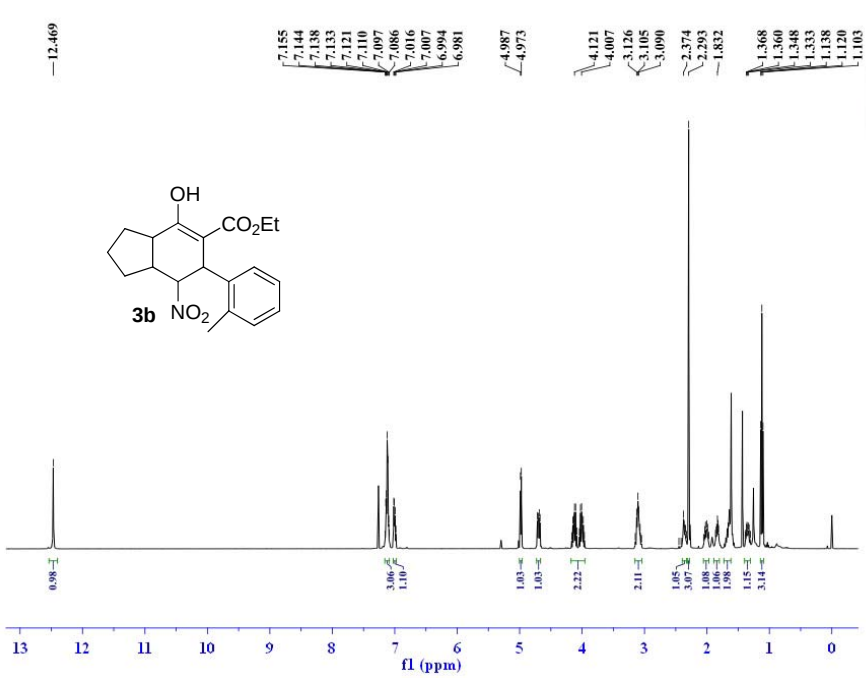


	Retention Time	Area	% Area
1	5.824	70569	0.35
2	6.305	6961043	34.40
3	6.709	16265	0.08
4	7.040	13190221	65.18

9. Copies of NMR spectra for the products





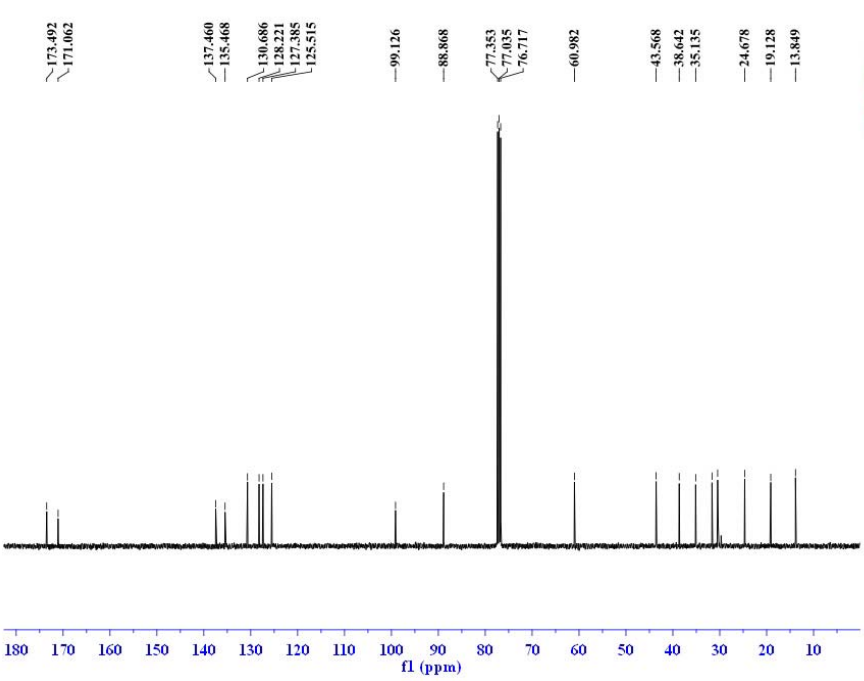


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-13T10:30:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296 C

CHANNEL f1
NUC1: 1H
P1: 13.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.30 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -353.02
Ph1: 19.60

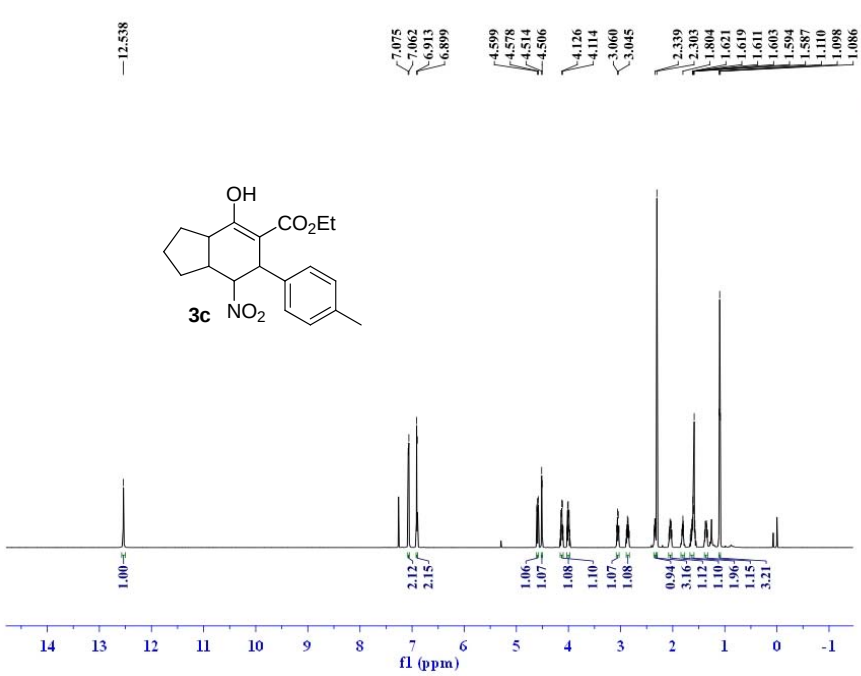


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-13T10:52:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 384
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.5 C

CHANNEL f1
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -107.56
Ph1: 68.37

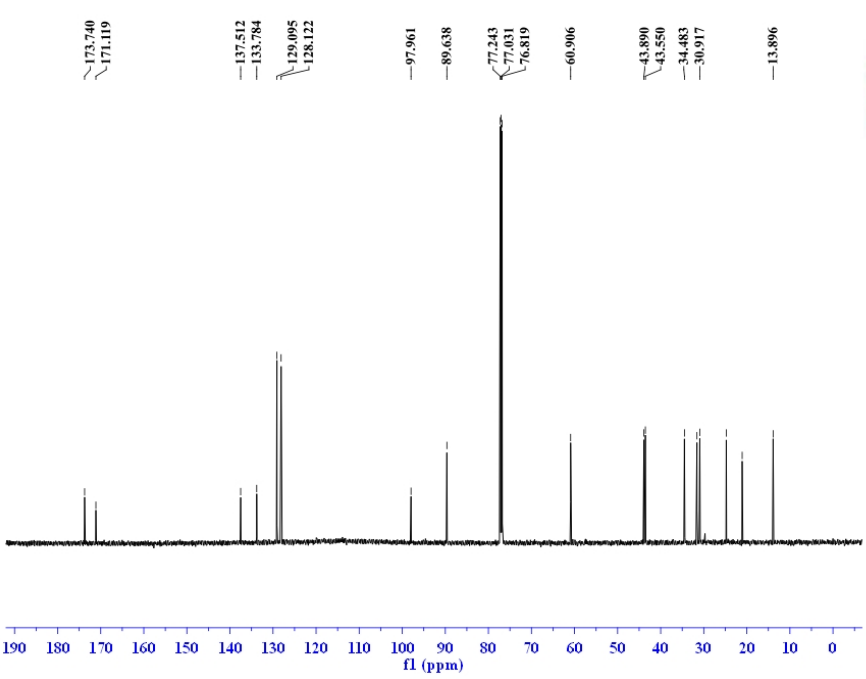


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-02T11:28:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.4 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.60 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 72.88
Ph1: 31.38

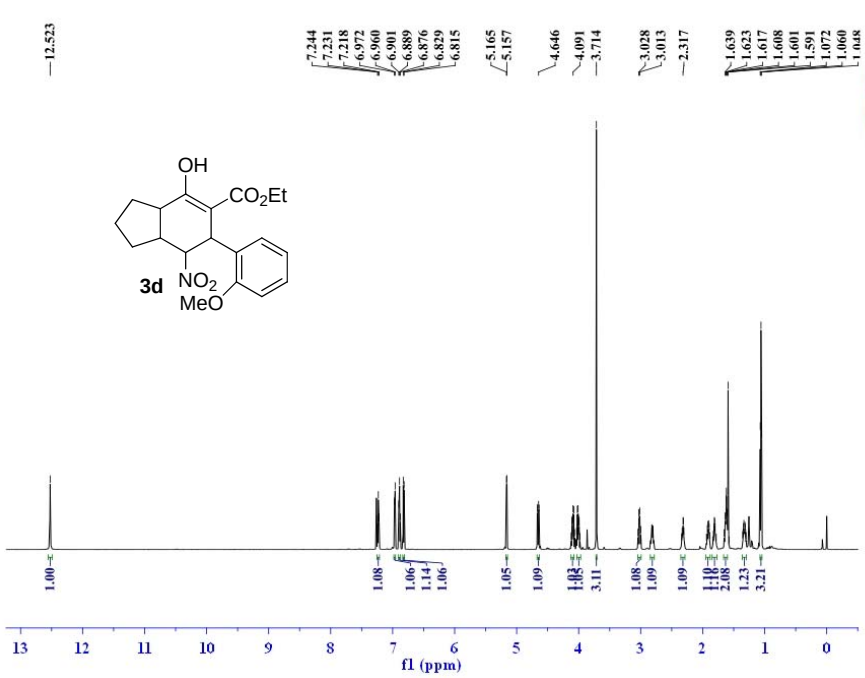


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-02T11:49:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 411
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 295.9 C

CHANNEL f1
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 2.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 58.85
Ph1: 81.80

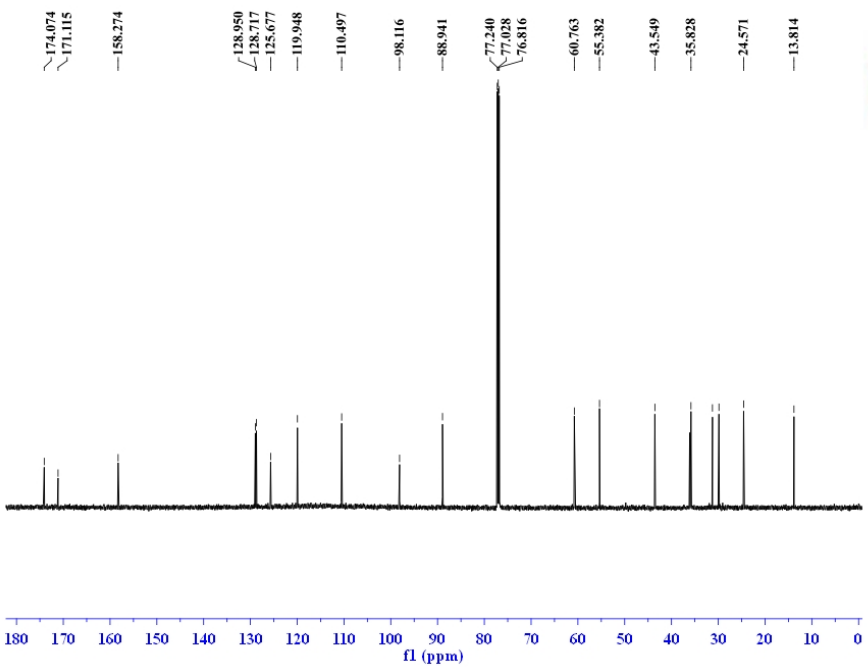


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-02T12:40:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.6 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.60 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 87.84
Ph1: 31.29

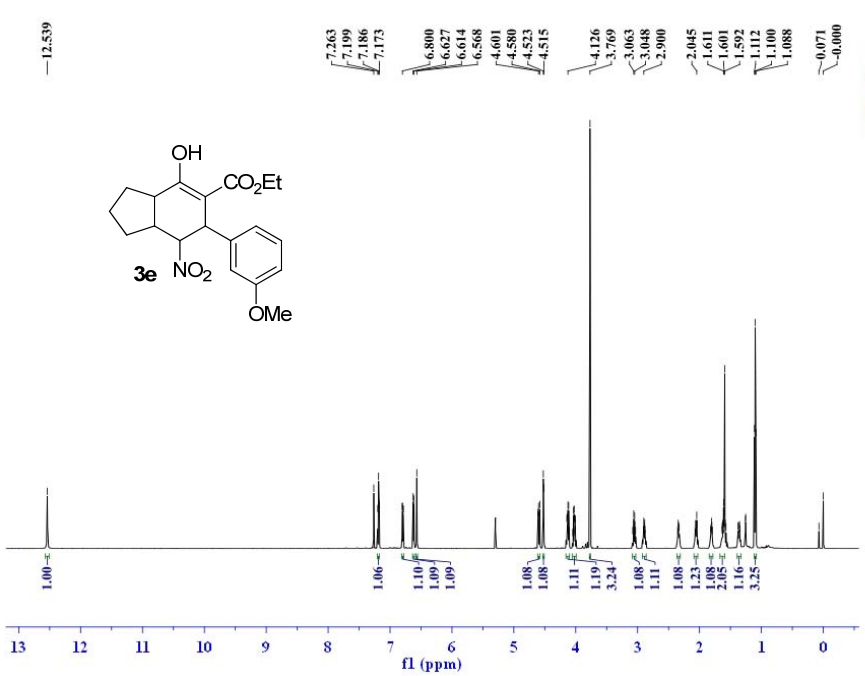


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-02T13:05:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 296 C

CHANNEL f1
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 57.82
Ph1: 87.38

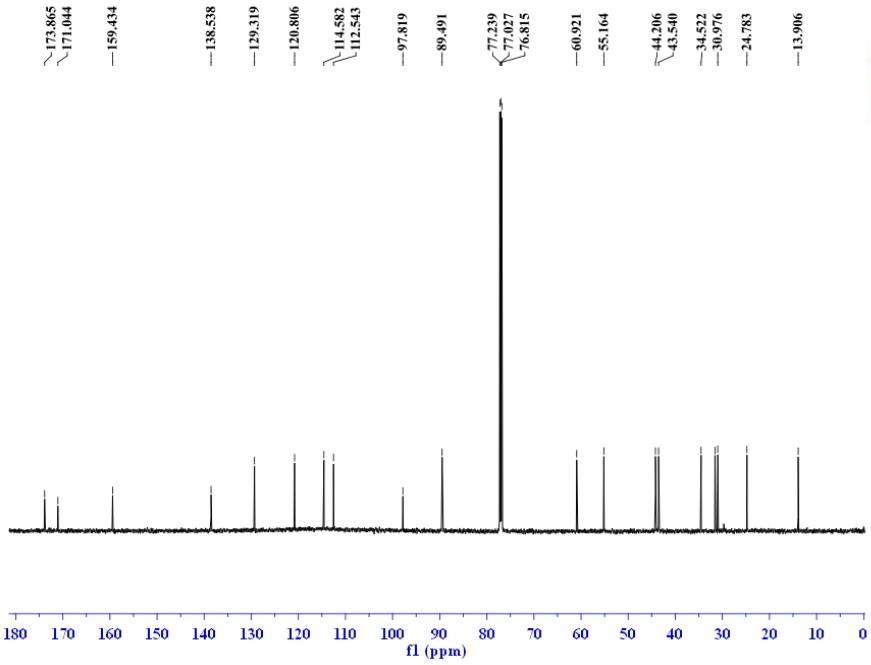


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-02T11:54:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.6 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.60 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 94.48
Ph1: 31.38



Current Data Parameters

F2 - Acquisition Parameters
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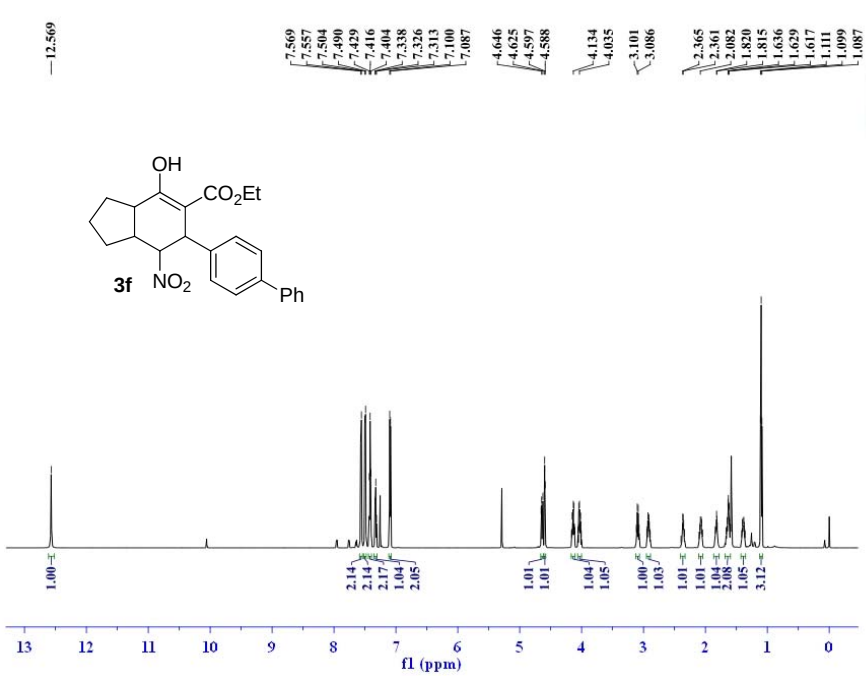
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 444
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 295.9 C

CHANNEL f1
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 2.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 64.28
Ph1: 75.62

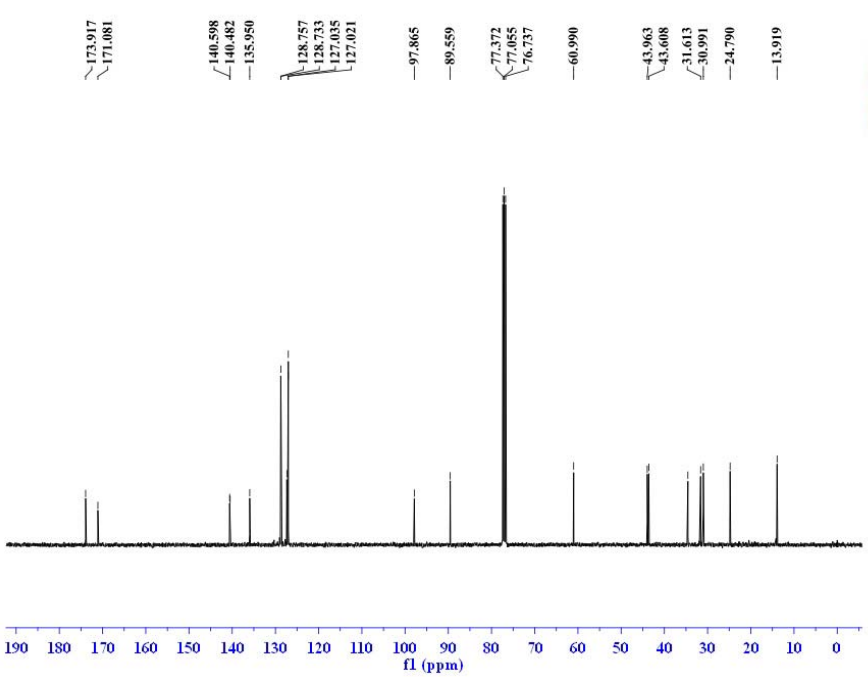


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-08-06T15:24:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 296 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.60 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -83.37
Ph1: 33.13

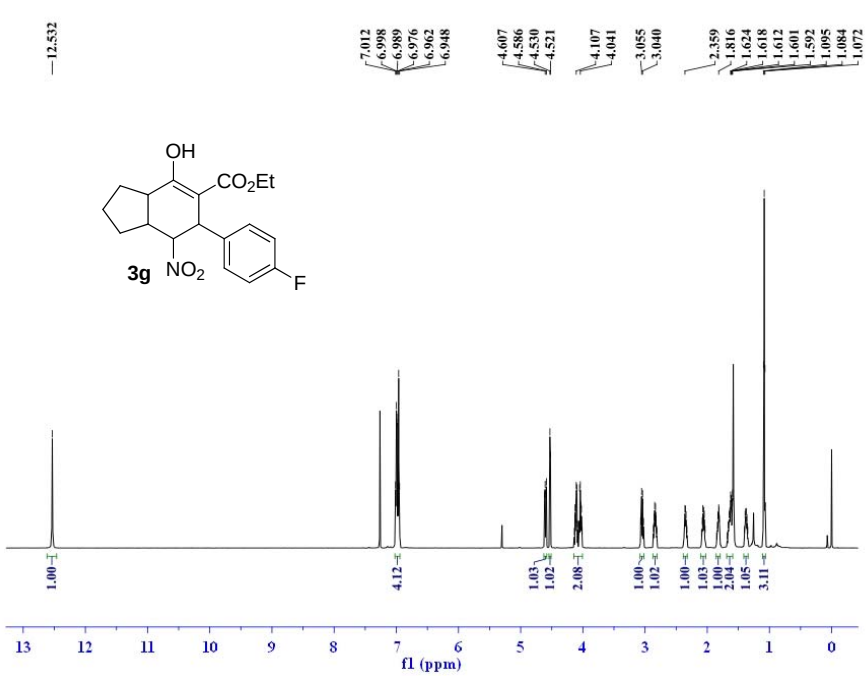


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-07T11:00:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 433
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.4 C

CHANNEL f1
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -115.64
Ph1: 76.26

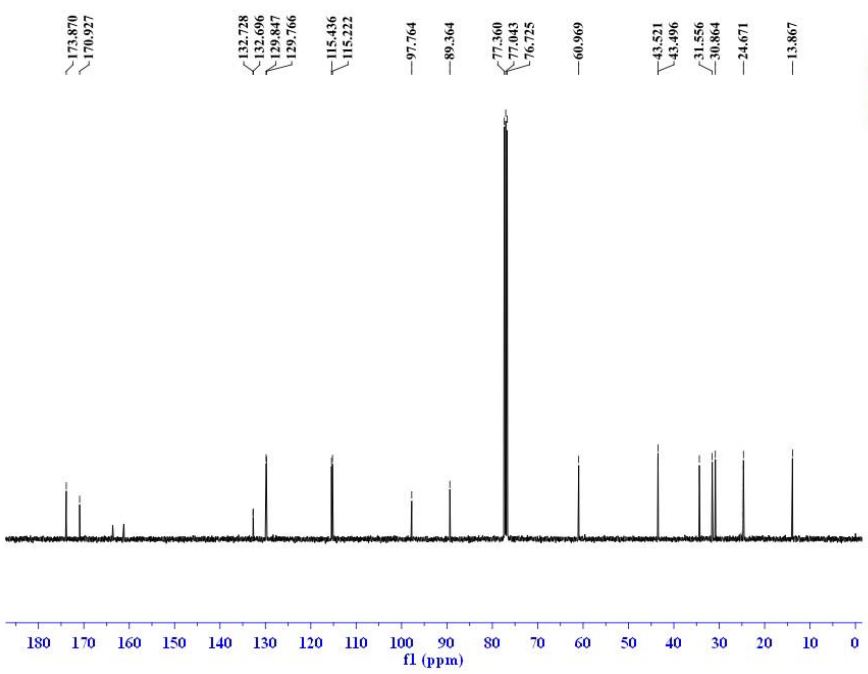


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-08-06T14:49:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.8 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.60 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -86.31
Ph1: 31.28

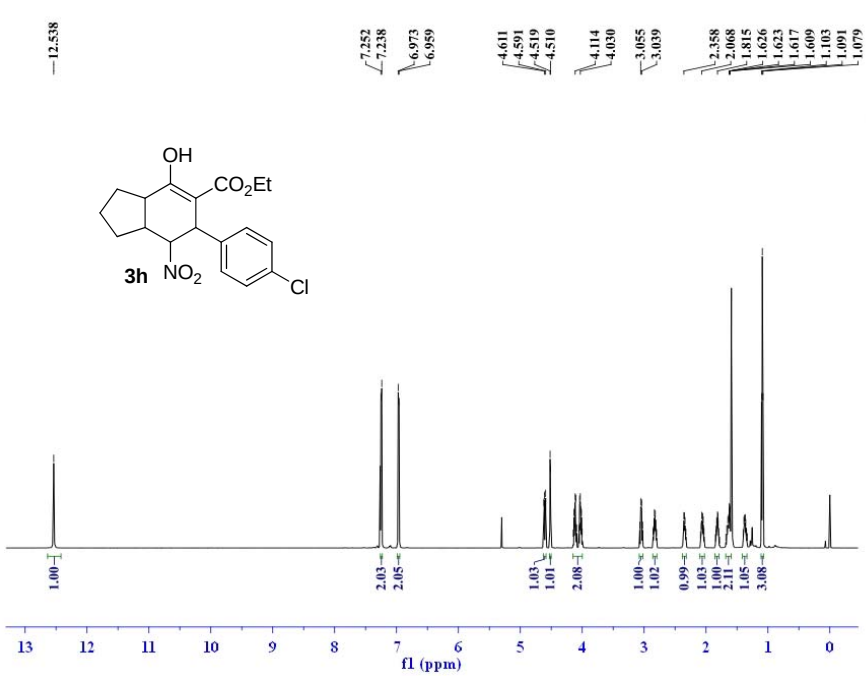


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-07T15:55:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 405
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.9 C

CHANNEL f1
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -104.73
Ph1: 70.12

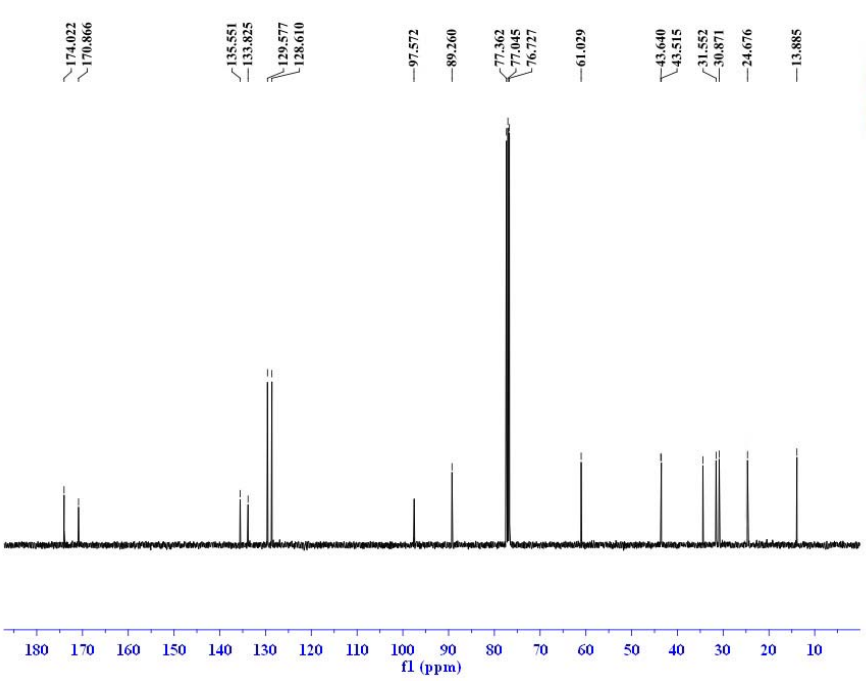


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-08-06T14:57:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.9 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.60 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -78.47
Ph1: 31.25

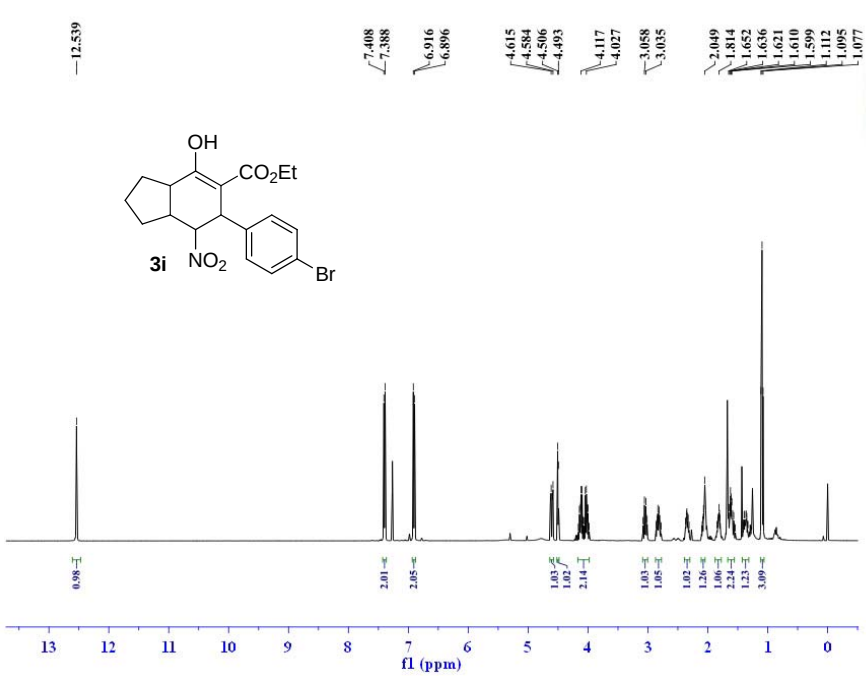


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-07T11:46:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 280
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.3 C

CHANNEL f1
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -111.97
Ph1: 73.19

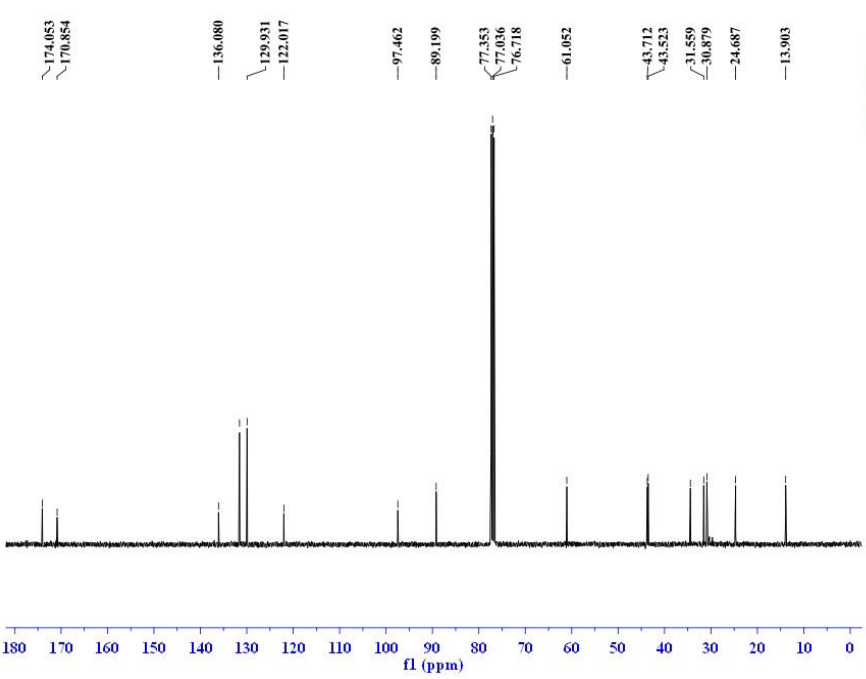


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-13T11:03:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295.8 C

CHANNEL f1
NUC1: 1H
P1: 13.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.30 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -347.31
Ph1: 15.27

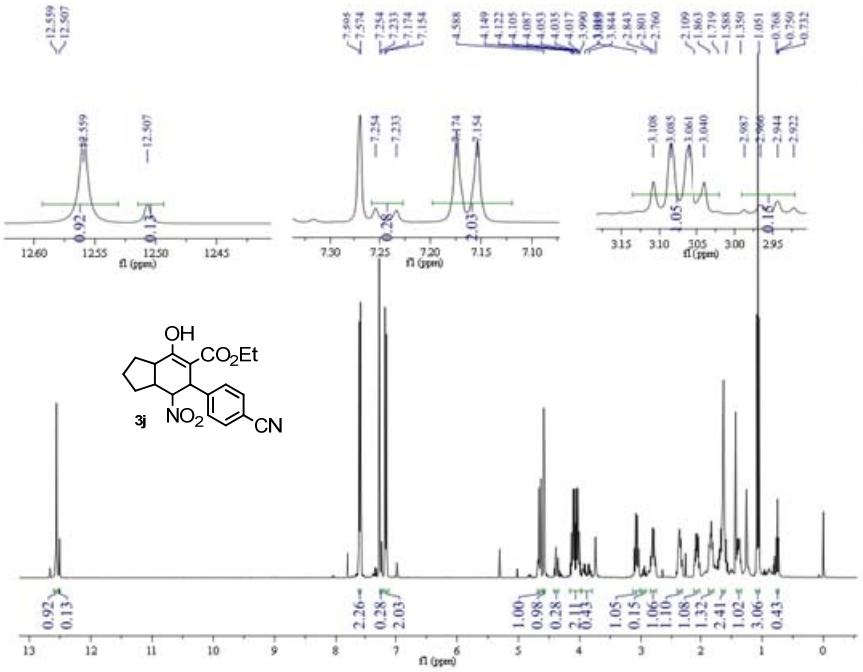


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-13T11:25:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 383
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.5 C

CHANNEL f1
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -107.56
Ph1: 68.37

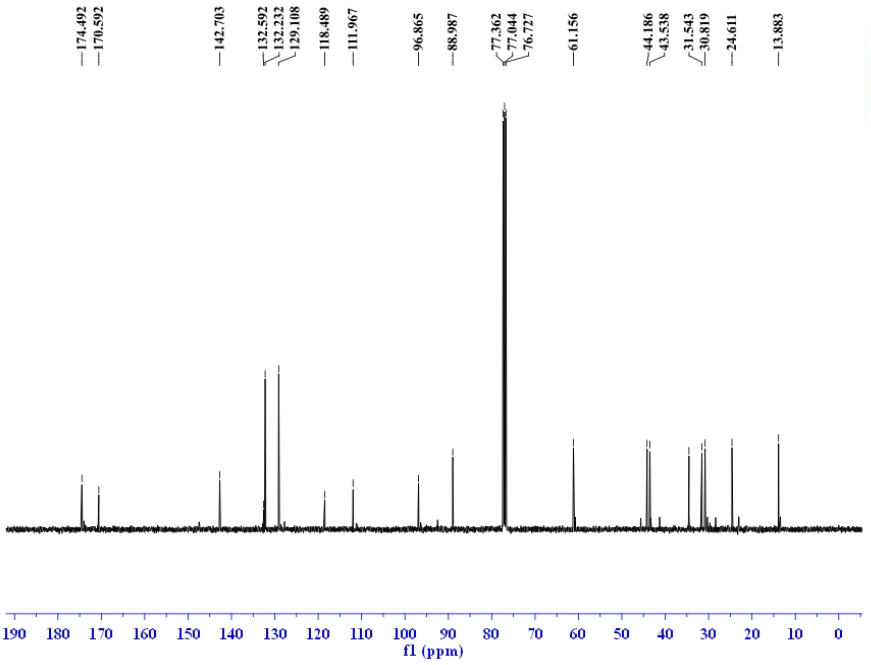


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-07T18:12:16
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296 C

CHANNEL f1
NUC1: 1H
P1: 13.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
BC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -207.21
Ph1: 18.70

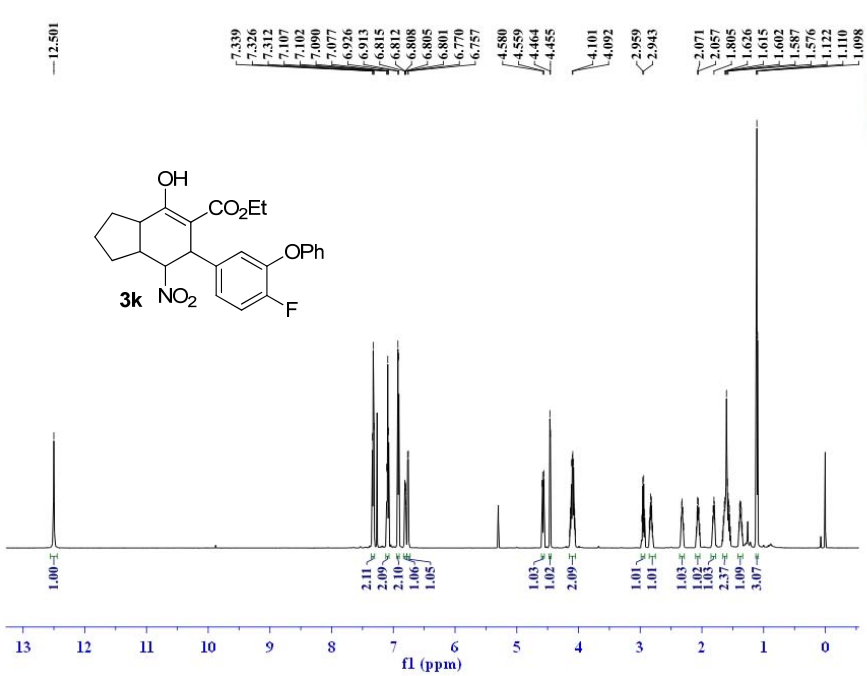


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-07T12:34:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 390
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.9 C

CHANNEL f1
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -122.15
Ph1: 90.70

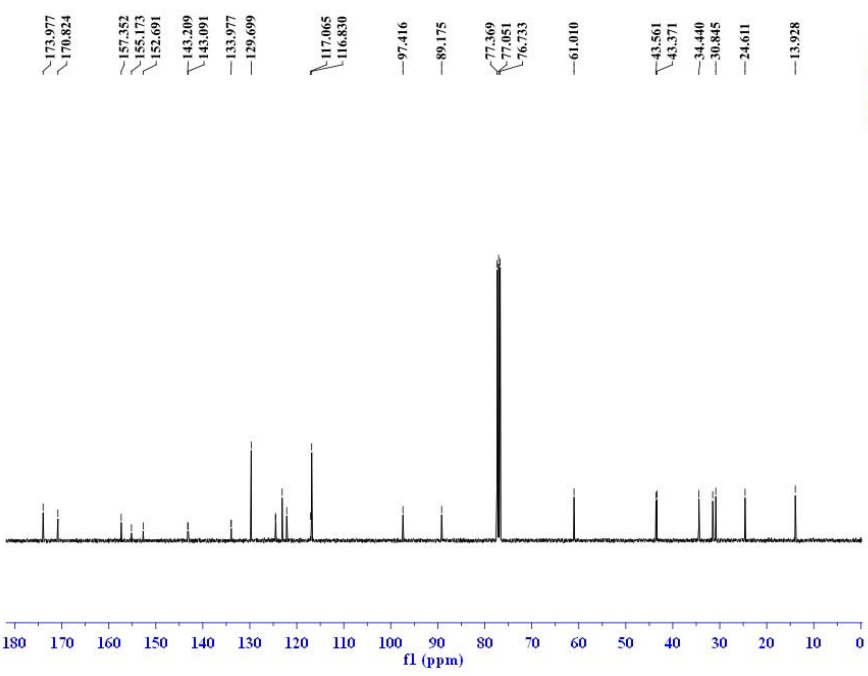


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-08-06T15:14:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.9 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.60 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -85.15
Ph1: 31.31

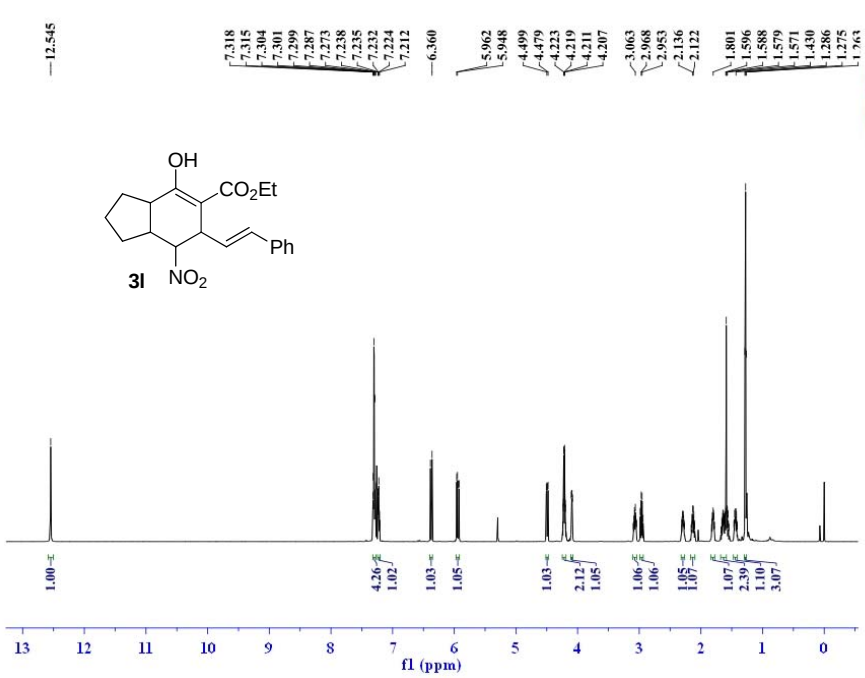


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-07T11:26:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 412
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.5 C

CHANNEL f1
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -106.72
Ph1: 70.33

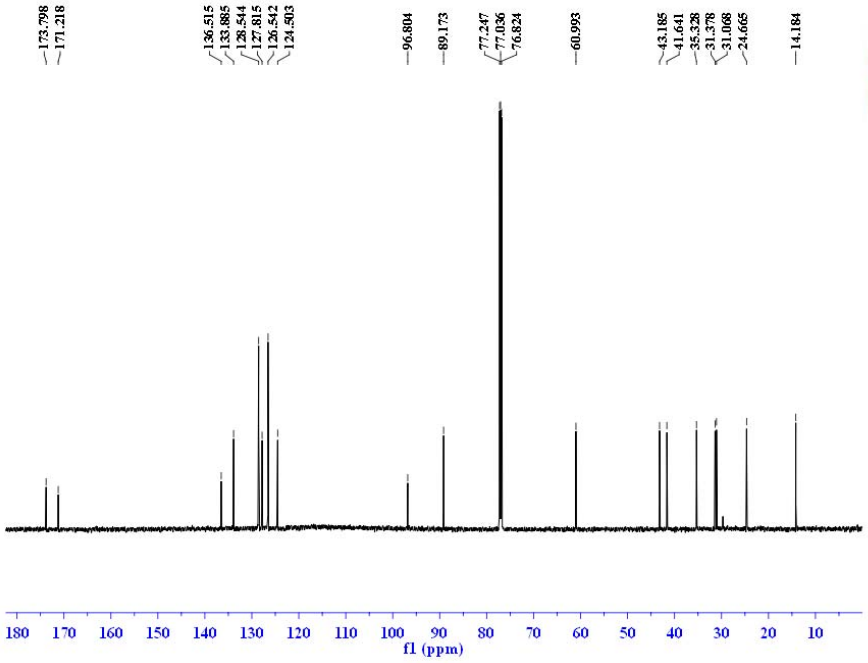


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-02T10:49:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.5 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.60 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 112.36
Ph1: 31.27

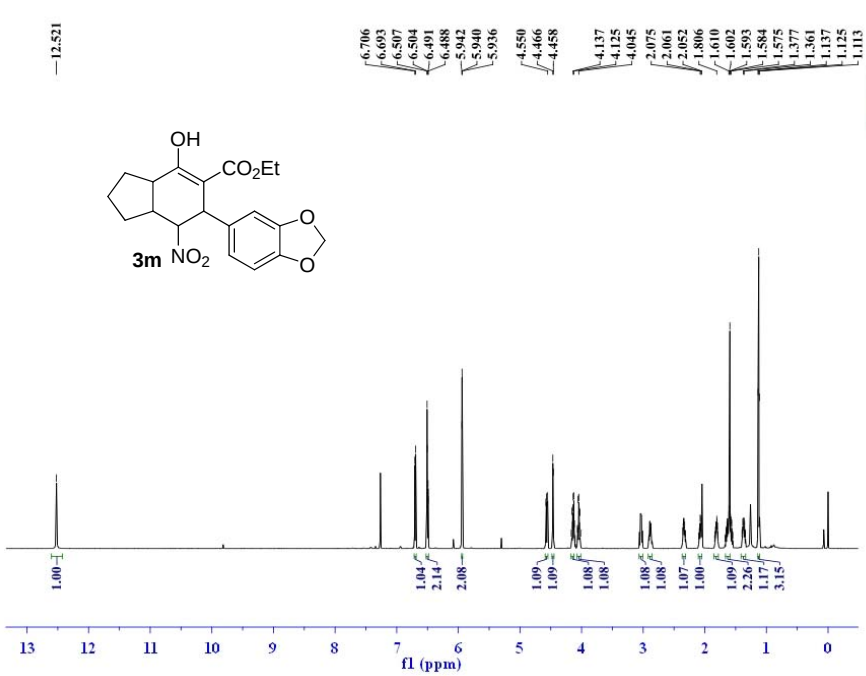


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-02T11:14:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 295.7 C

CHANNEL f1
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 2.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 75.69
Ph1: 53.25

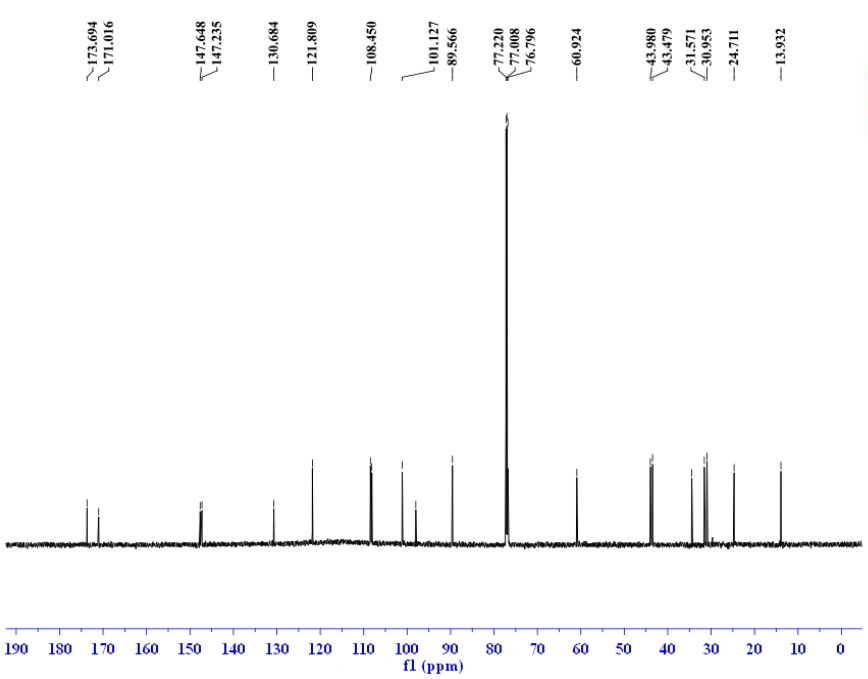


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-01T17:47:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.9 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.60 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 70.86
Ph1: 31.51

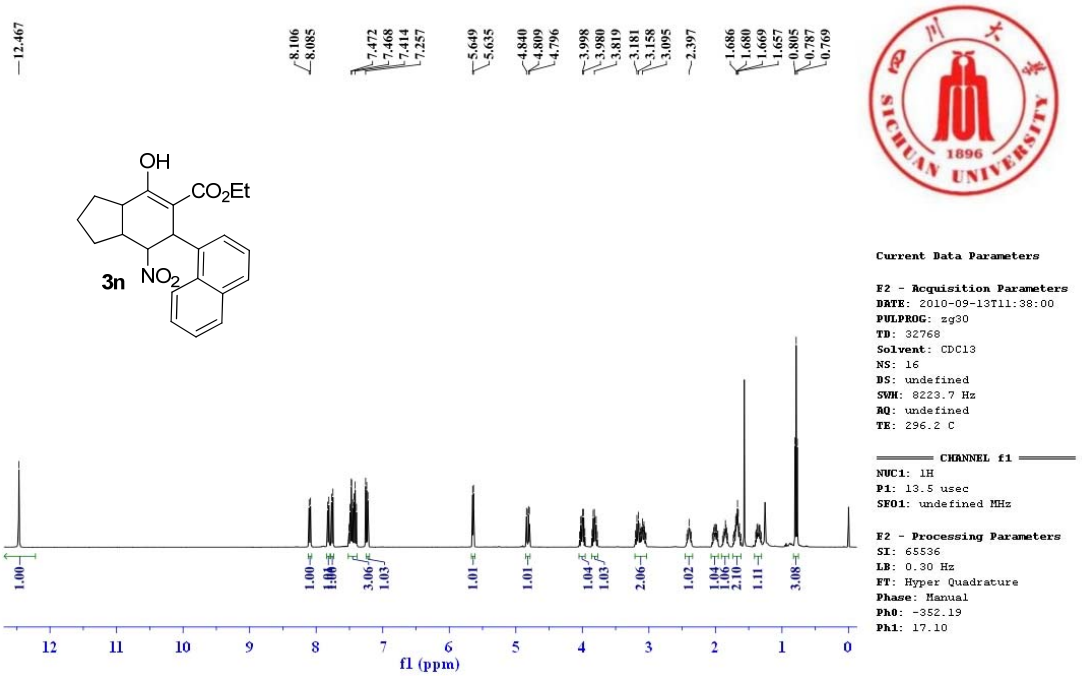


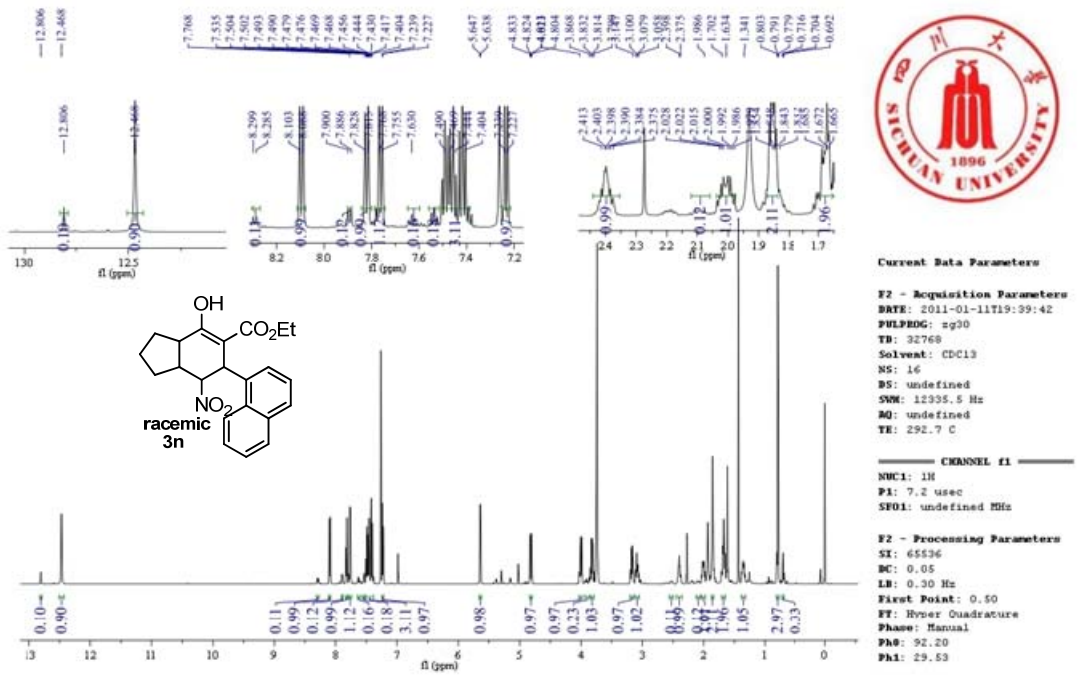
Current Data Parameters

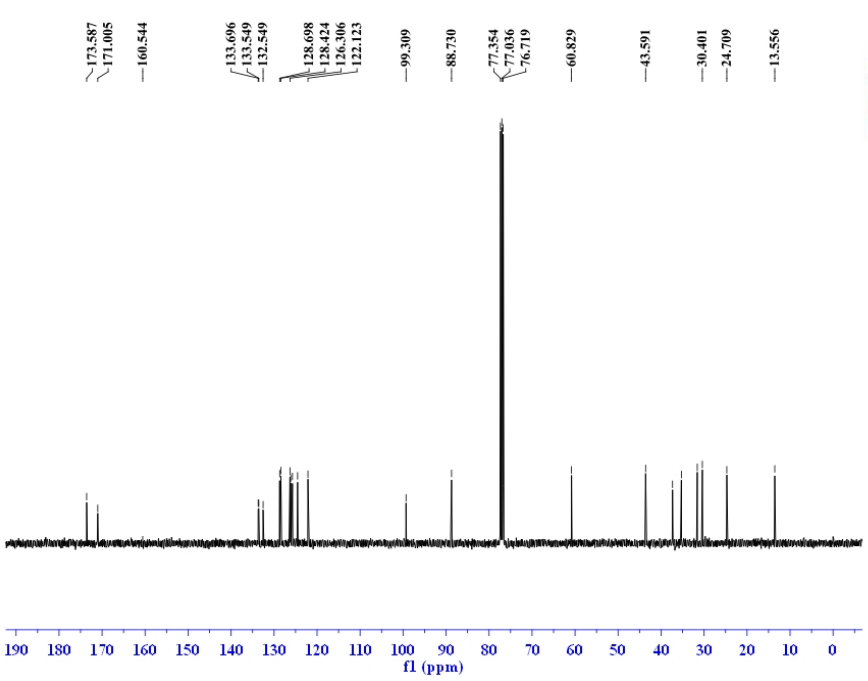
F2 - Acquisition Parameters
DATE: 2010-09-01T18:13:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 297.2 C

CHANNEL f1
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 2.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 72.31
Ph1: 60.00


OH
CO2Et
NO2
3n
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2010-09-13T11:38:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296.2 C
CHANNEL f1
NUC1: 1H
P1: 13.5 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
LB: 0.30 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -352.19
Ph1: 17.10
f1 (ppm)


OH
CO2Et
NO2
racemic
3n
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2011-01-11T19:39:42
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 292.7 C
CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
BC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 92.20
Ph1: 29.53
f1 (ppm)

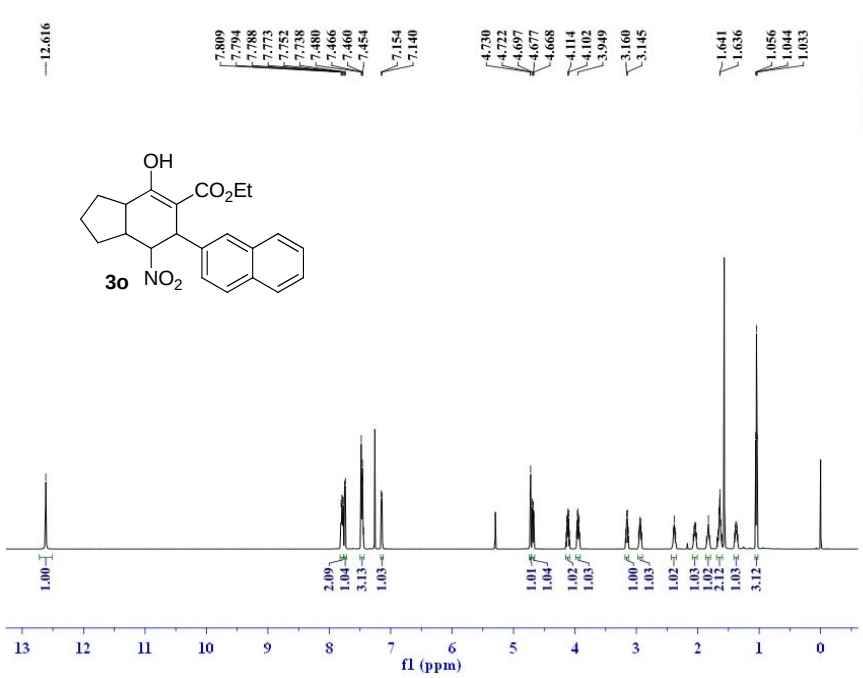


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-13T11:53:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 280
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 297.3 C

CHANNEL f1
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -118.22
Ph1: 80.29

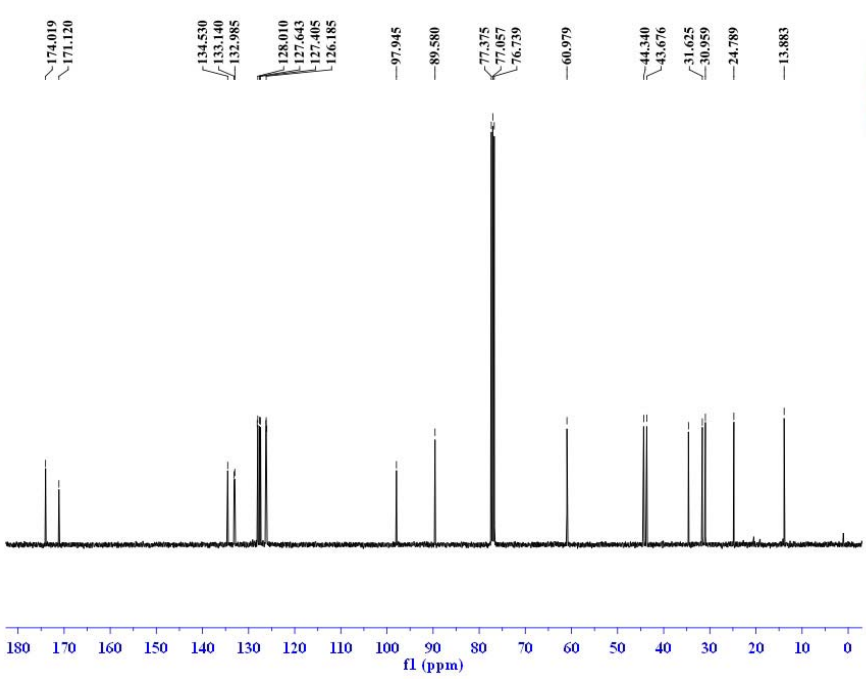


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-08-06T15:01:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.9 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.60 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -85.60
Ph1: 31.28

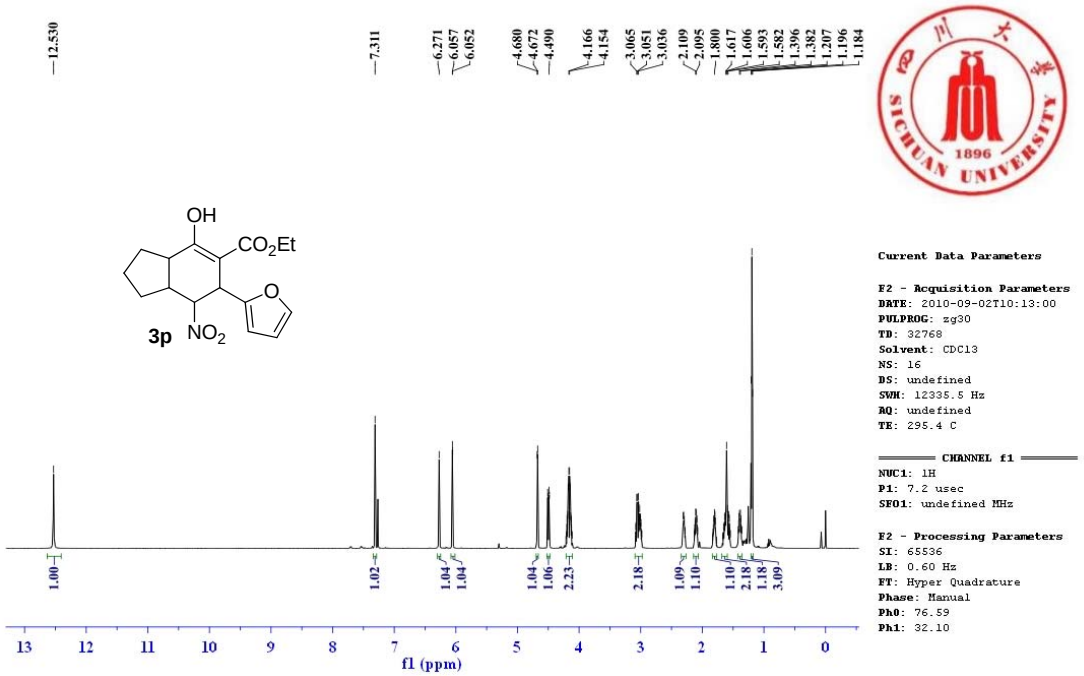


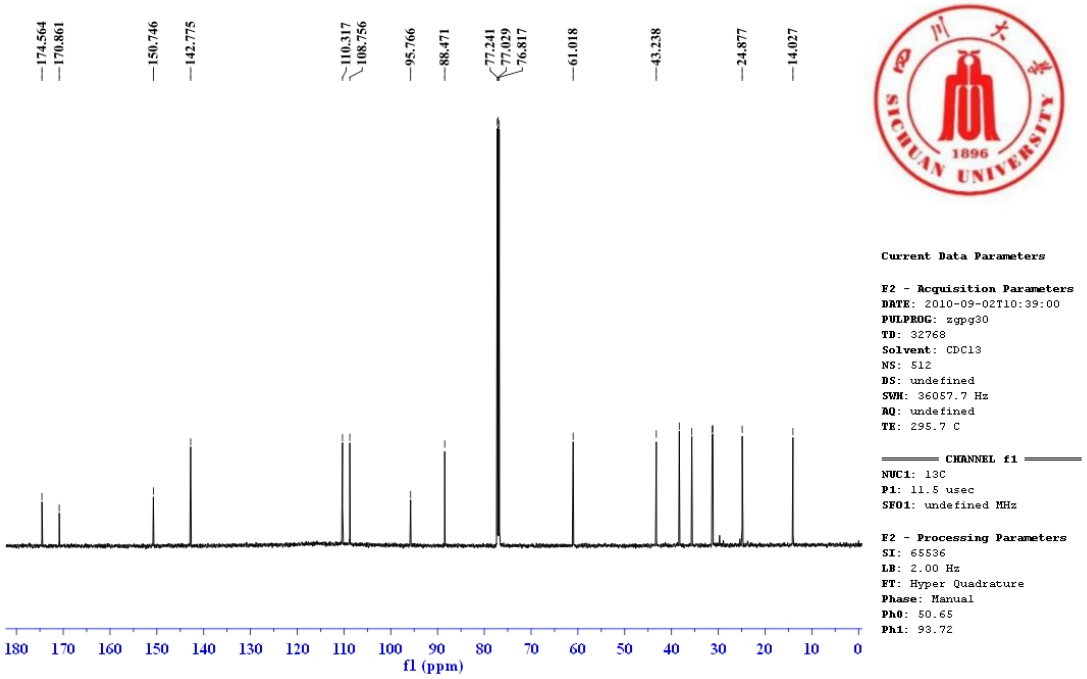
Current Data Parameters

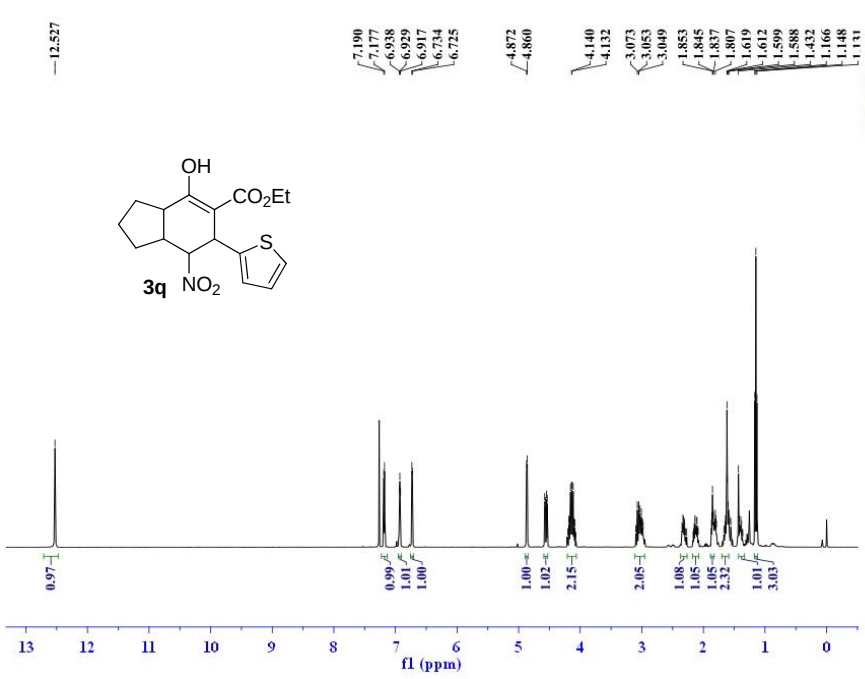
F2 - Acquisition Parameters
DATE: 2010-09-07T13:06:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 492
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 297 C

CHANNEL f1
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -110.12
Ph1: 78.54


12.530
7.311
6.271
6.057
6.052
4.680
4.672
4.490
4.166
4.154
3.065
3.051
3.036
2.109
2.095
1.800
1.617
1.606
1.593
1.582
1.396
1.382
1.207
1.196
1.184
OH
CO2Et
O
3p
NO2
1.00
1.02
1.04
1.04
1.04
1.06
2.23
2.18
1.09
1.10
1.10
2.18
1.18
3.09
13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2010-09-02T10:13:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.4 C
CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
LB: 0.60 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 76.59
Ph1: 32.10


174.564
170.861
150.746
142.775
110.317
108.756
95.766
88.471
77.241
77.029
76.817
61.018
43.238
24.877
14.027
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2010-09-02T10:39:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 295.7 C
CHANNEL f1
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
LB: 2.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 50.65
Ph1: 93.72

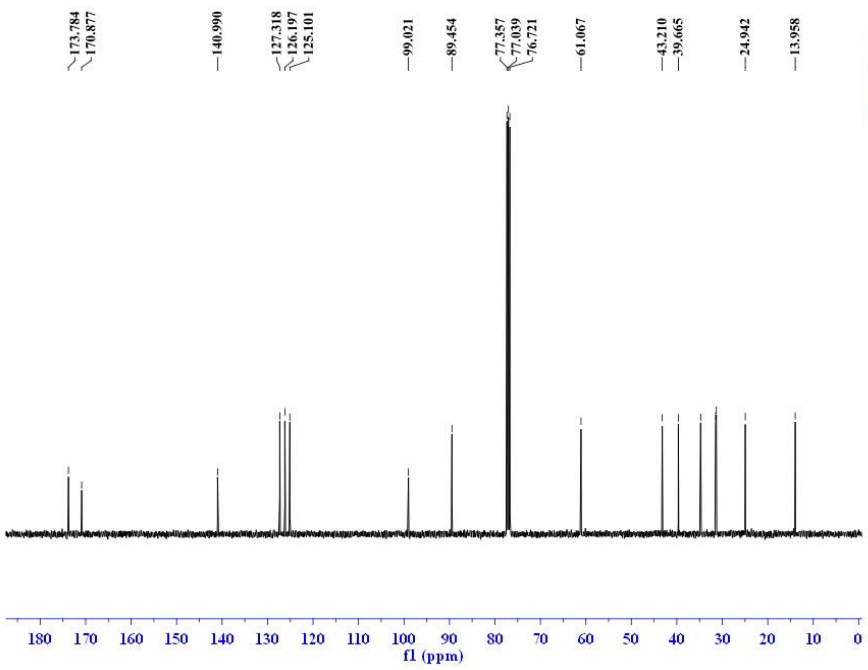


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-07T11:50:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296.3 C

CHANNEL f1
NUC1: 1H
P1: 13.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.30 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -209.16
Ph1: 18.07

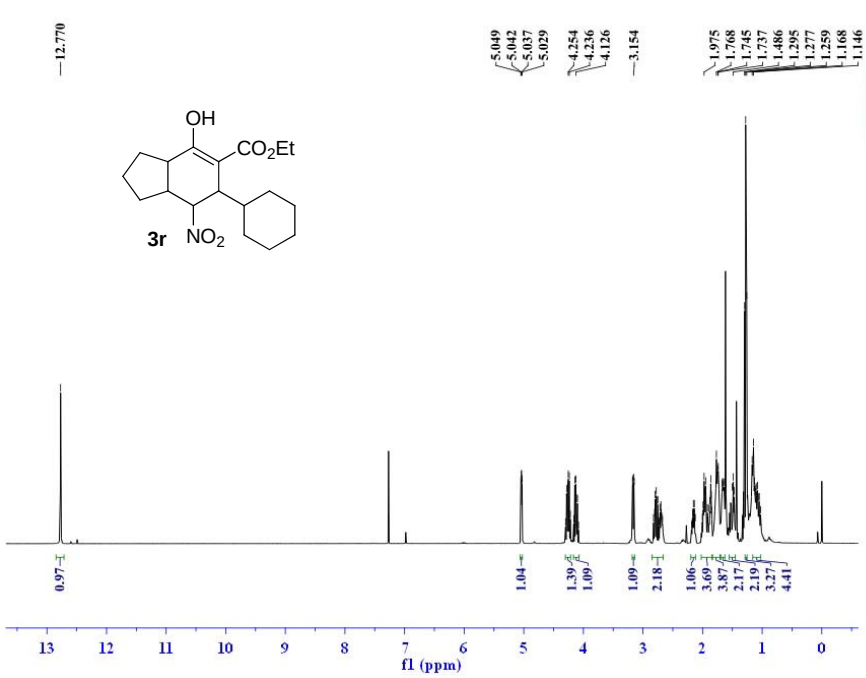


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-07T12:07:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 286
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.5 C

CHANNEL f1
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -110.78
Ph1: 71.07

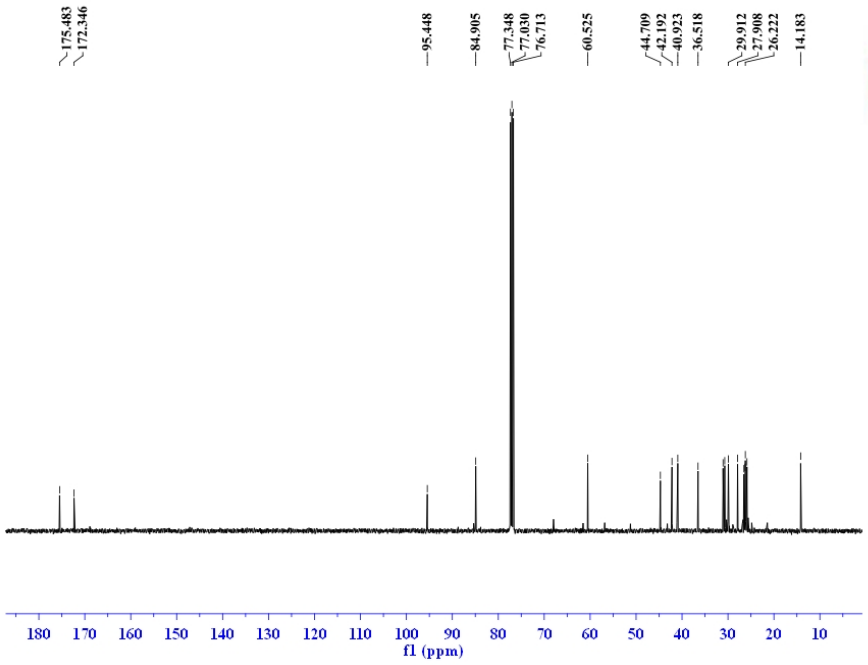


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-18T14:16:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 296.4 C

CHANNEL f1
NUC1: 1H
P1: 13.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: -0.20 Hz
Gauss: 1.00
FT: Hyper Quadrature
Phase: Manual
Ph0: -1.05
Ph1: 19.21

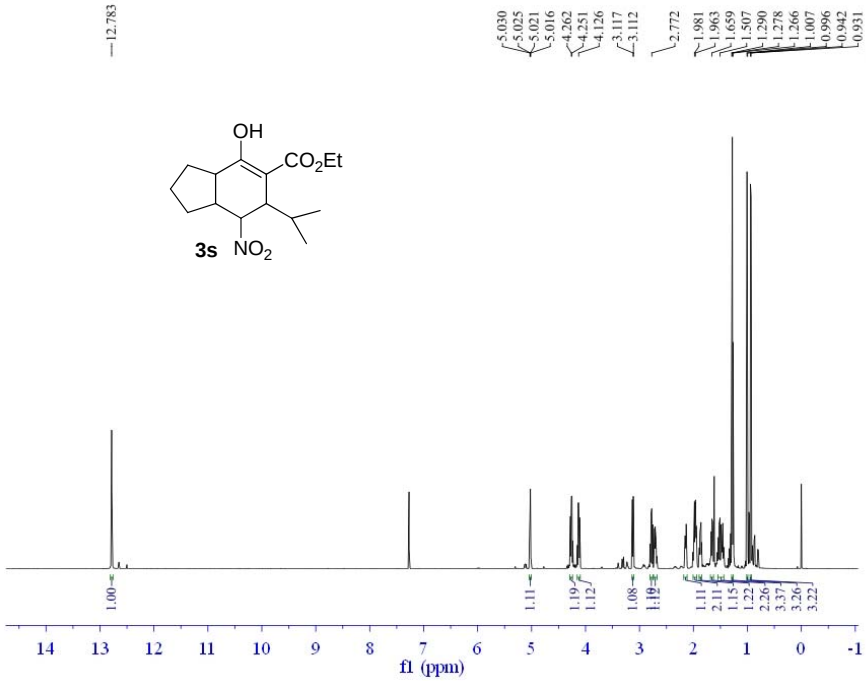


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-18T14:45:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 297.1 C

CHANNEL f1
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -109.25
Ph1: 65.91

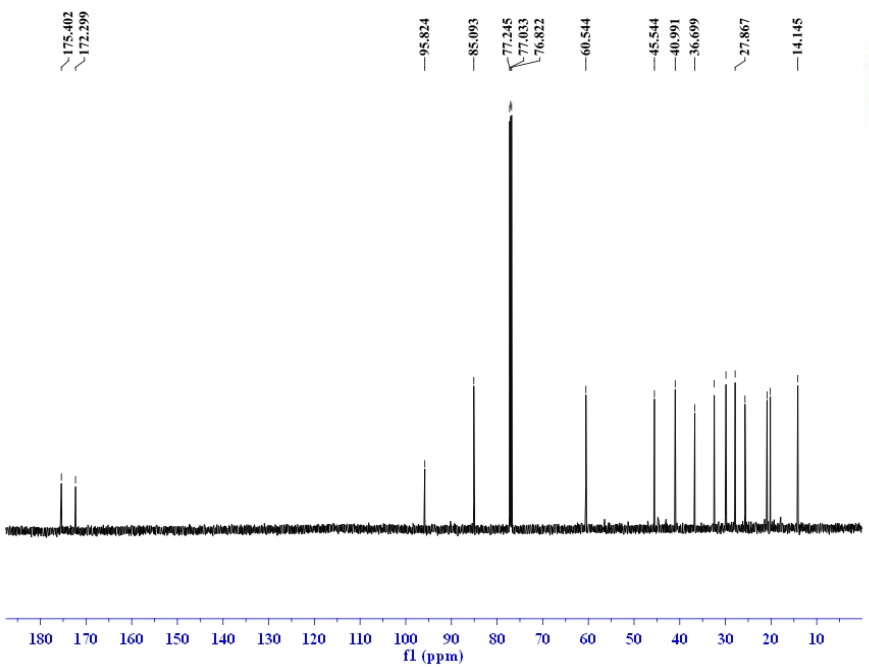


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-10-18T18:10:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.5 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -160.87
Ph1: 31.25

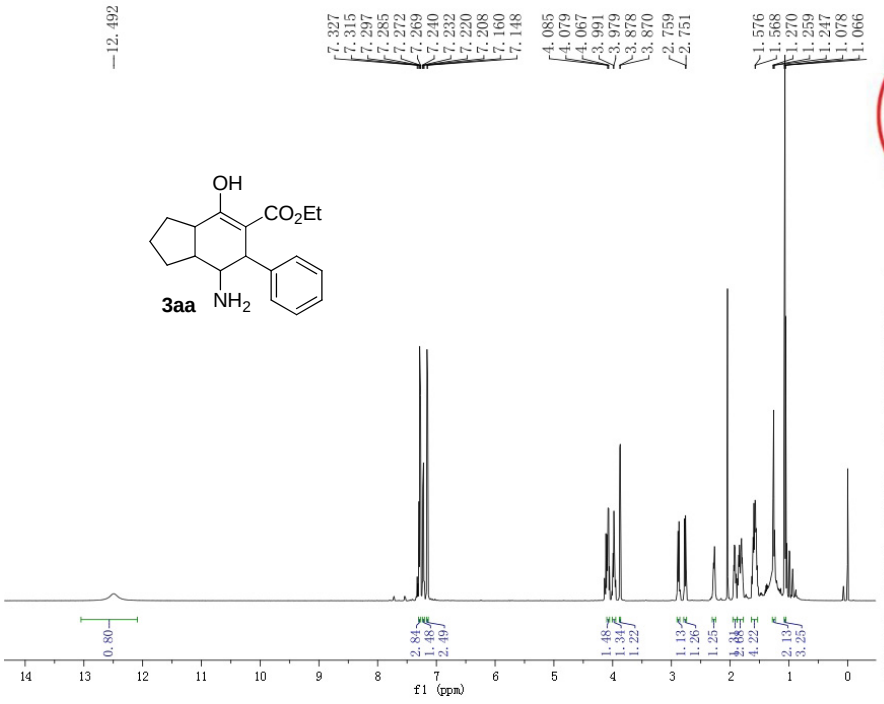


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-10-18T18:15:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 91
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 295.7 C

CHANNEL f1
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 45.00
Ph1: 97.13

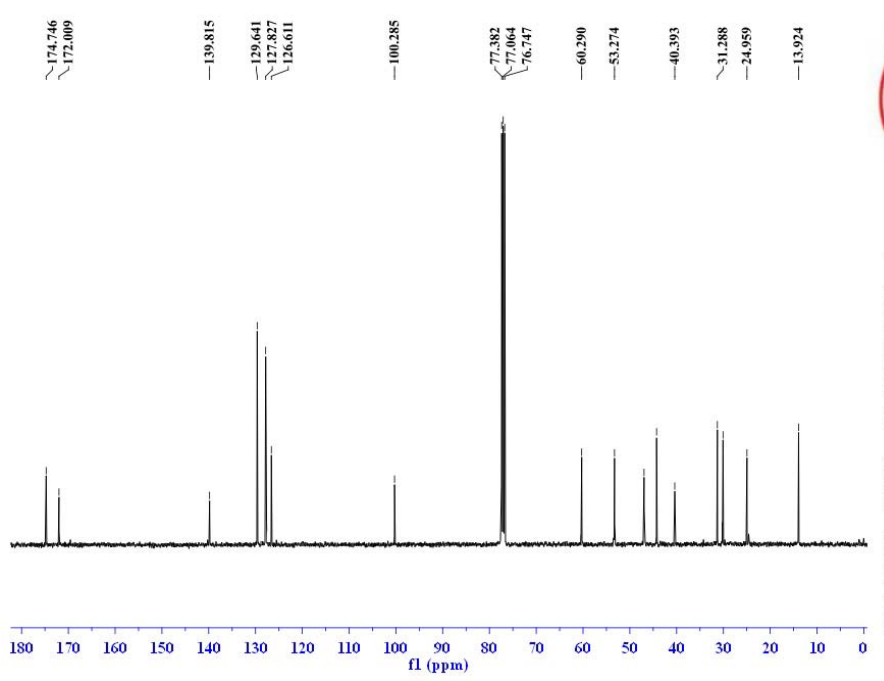


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-11-22T17:01:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295 C

CHANNEL f1
NUC1: 1H
P1: 7.6 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -210.56
Ph1: 31.88

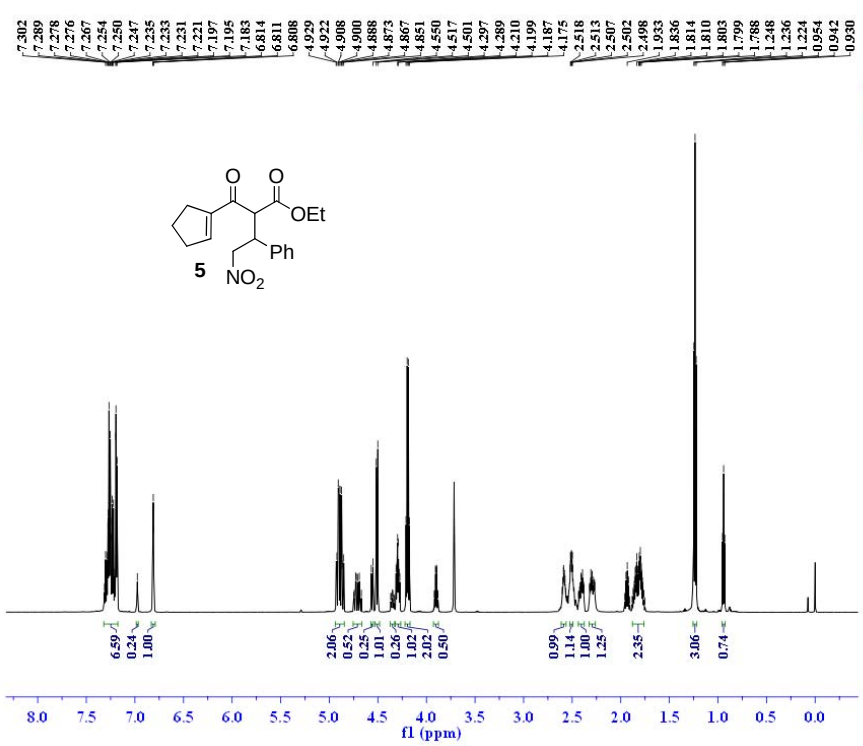


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-10-20T23:46:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 299 C

CHANNEL f1
NUC1: 13C
P1: 15.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 2.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -101.76
Ph1: 73.53

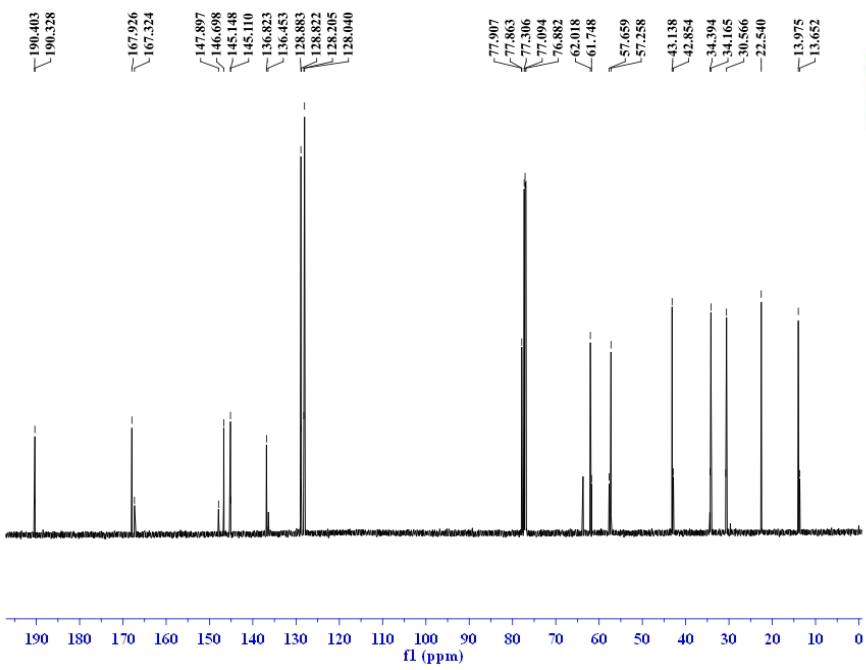


Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-10-18T17:54:00
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.3 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 0.30 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: -142.34
Ph1: 31.53

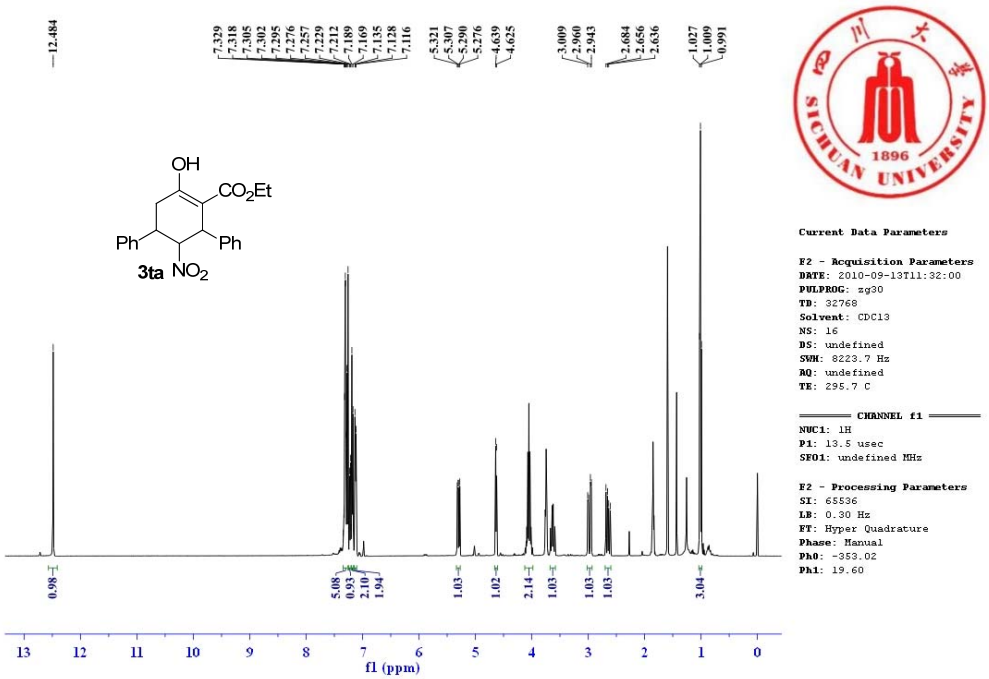


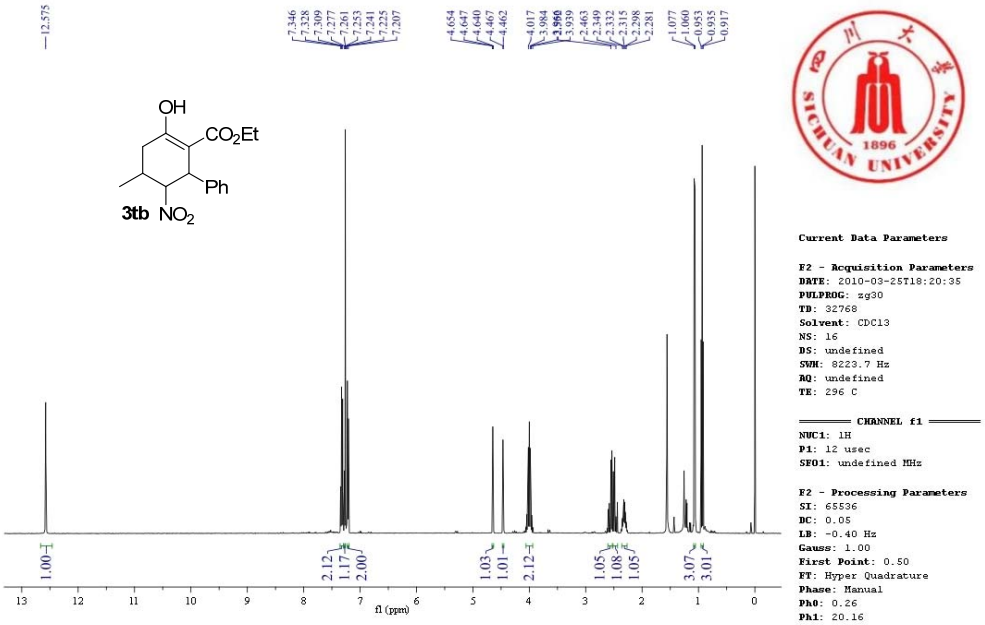
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-10-18T18:03:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 180
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 295.6 C

CHANNEL f1
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
Ph0: 49.36
Ph1: 88.34





10. References

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