Supporting Information

Asymmetric Synthesis of 1*H*-Pyrrol-3(2*H*)-ones from 2,3-Diketoesters By Combination of Aldol Condensation With Benziylic Acid Rearrangement

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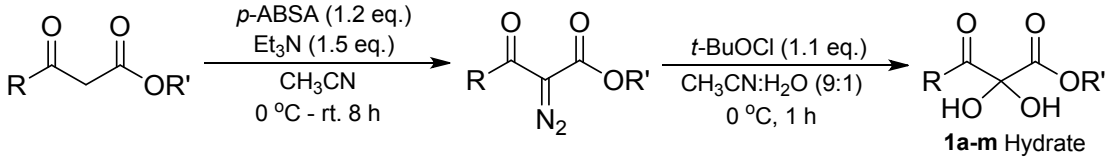
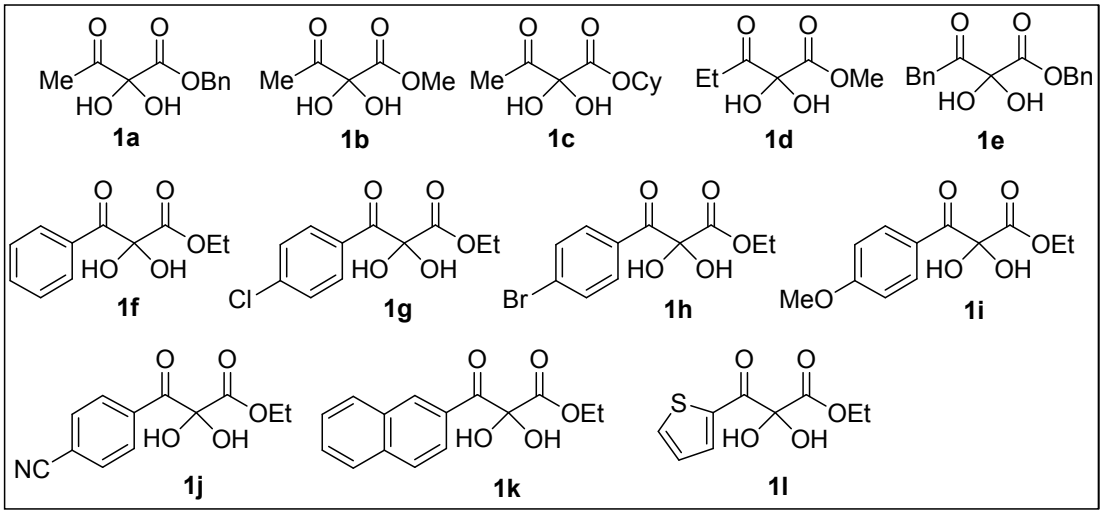
General. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on an Agilent DD2-500 MHz spectrometer. Chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (*J*) are given in Hertz (Hz). The peak information is described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were performed on a microTOF-ESI mass spectrometer using CsOAc as the standard. Melting points were obtained uncorrected from an Electrothermo Mel-Temp DLX 104 device.

General procedure for the synthesis of 2,3-diketoesters.





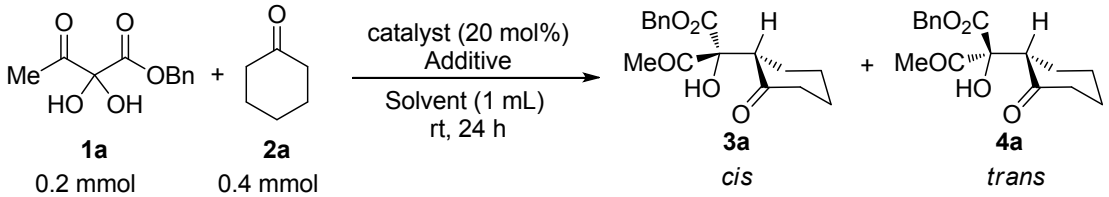
Preparation of α-Diazo-β-ketoesters:[1] A solution of β-ketoester (10 mmol, 1.0 eq.) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (2.8 g, 12 mmol, 1.2 eq.) in 75 mL of CH_3CN was added triethylamine (2.1 ml, 1.5 mmol, 1.5 eq.) at 0 °C, and the resulting solution was stirred at room temperature for 8 hours during which time the corresponding sulfonamide precipitated as a white solid. The white precipitate was filtered, and the resulting solution was concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2), eluting with hexane and ethyl acetate to provide α-diazo-β-ketoester.

General Procedure for the Synthesis of 2,3-Diketoesters 1a-m:[1a] A solution of α-diazo-β-ketoesters (5.0 mmol, 1.0 eq.) in 20 mL of solvent [$CH_3CN:H_2O$ (9:1)] at 0 °C was added tert-

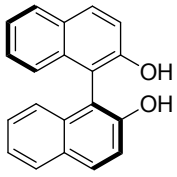
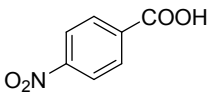
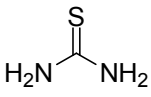
butyl hypochlorite (0.61 ml, 5.5 mmol) dropwise over 30 min via syringe pump. The reaction was stirred for an additional 30 min at room temperature and then concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2), eluting with hexane and ethyl acetate to provide compounds **1a-m** as their monohydrates. 2,3-Diketoesters **1a**,[1a] **1b**,[1a] **1d**,[2] **1f**,[3] **1g**,[3] **1i**[4] are known compounds, **1c**, **1e**, **1h**, **1j**, **1k**, **1l** are new compounds and characeterized in detail.

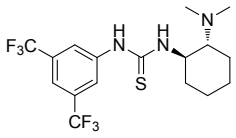
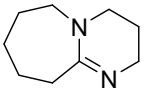
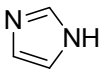
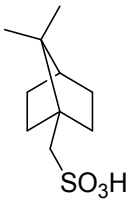
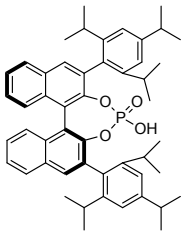
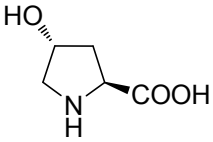
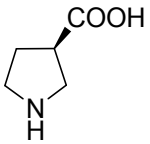
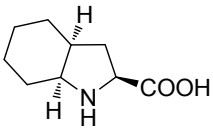
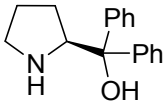
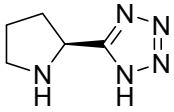
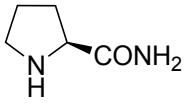
Optimization of the *L*-proline catalyzed aldol reaction.

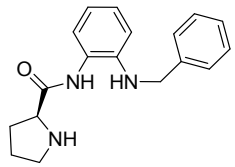
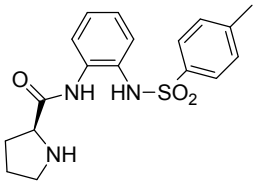
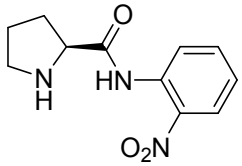
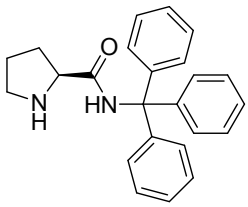
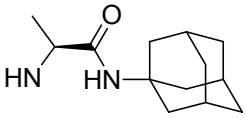
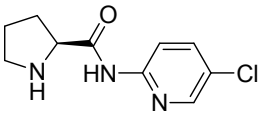
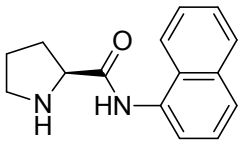
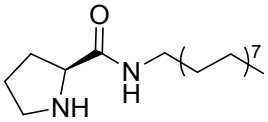
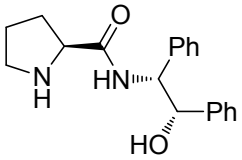
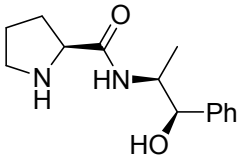
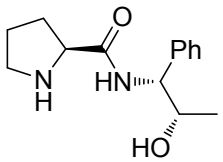
Various solvents, additives and organocatalysts were screened from which *L*-proline in DCM at room temperature gave the highest diastereoselectivity. Additives were not effective.

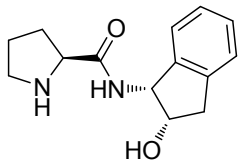
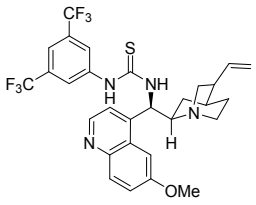


1a 0.2 mmol + **2a** 0.4 mmol → **3a** *cis* + **4a** *trans*

Entry	Catalyst[a]	Additive[b]	Solvent	Temp.	Yield (%)[c]	3a/4a d.r.[d]
1	*L*-proline	---	DMF	rt	90	65:35
2	*L*-proline	---	MeCN	rt	91	65:35
3	*L*-proline	---	THF	rt	67	65:35
4	*L*-proline	---	DCM	rt	92	74:26
5	*L*-proline	---	$CHCl_3$	rt	88	73:27
6	*L*-proline	---	DCE	rt	95	73:27
7[e]	*L*-proline	---	DCM	0 °C	72	74:26
8	*L*-proline	CF_3COOH	DCM	rt	34	65:35
9	*L*-proline	H_2O	DCM	rt	90	74:26
10	*L*-proline		DCM	rt	82	60:40
11	*L*-proline		DCM	rt	92	60:40
12	*L*-proline		DCM	rt	65	63:37

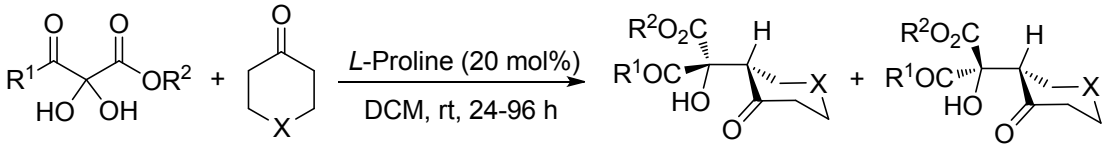
13	*L*-proline		DCM	rt	71	59:41
14	*L*-proline		DCM	rt	19	37:63
15	*L*-proline		DCM	rt	90	64:36
16	*L*-proline		DCM	rt	87	67:33
17	*L*-proline		DCM	rt	48	66:34
18		---	DCM	rt	trace	---
19		---	DCM	rt	trace	---
20		---	DCM	rt	85	50:50
21		---	DCM	rt	NR	---
22		---	DCM	rt	85	54:46
23		---	DCM	rt	86	36:64

24		---	DCM	rt	87	40:60
25		---	DCM	rt	79	48:52
26		---	DCM	rt	91	43:57
27		---	DCM	rt	95	53:47
28		---	DCM	rt	97	44:56
29		---	DCM	rt	94	50:50
30		---	DCM	rt	96	46:54
31		---	DCM	rt	93	49:51
32		---	DCM	rt	89	37:63
33		---	DCM	rt	88	36:64
34		---	DCM	rt	98	42:58

35		---	DCM	rt	95	37:63
36		---	DCM	rt	87	60:40

[a] 20 mol% catalyst was added. [b] 20 mol% additive was added. [c] Determined by crude ^{1}H NMR using CH_2I_2 as internal standard. [d] Determined by ^{1}H NMR. [e] Reaction was run for 48 h.

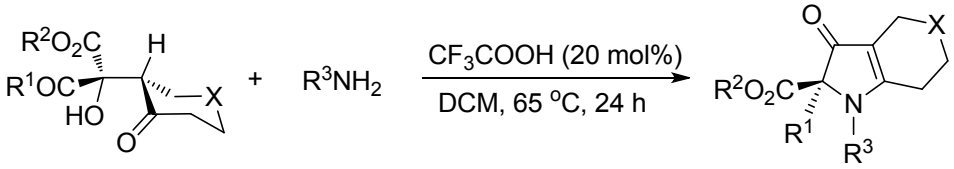
General procedure for the *L*-proline catalyzed aldol reaction.



1a-l **2a-b** **3a-m** **4a-m**

In a 25 mL one-neck flask containing a magnetic stirring bar, dichloromethane (5.0 mL), **1** (1.0 mmol), **2** (2.0 mmol) and *L*-proline (23.0 mg, 0.2 mmol) were added in sequence, then the reaction mixture was stirred at room temperature for 24-96 h. After reaction was complete, the product mixture was concentrated and its components were purified by flash column chromatography (SiO_2), eluding with hexane/ethyl acetate, to provide products **3** and **4**.

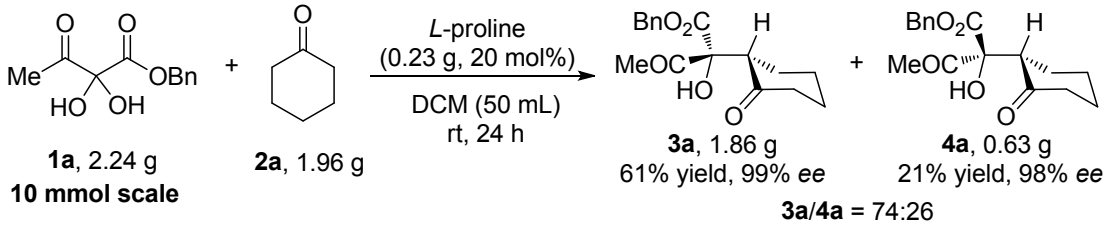
General procedure for TFA catalyzed ~~benzylic~~ benzilic acid rearrangement reaction.

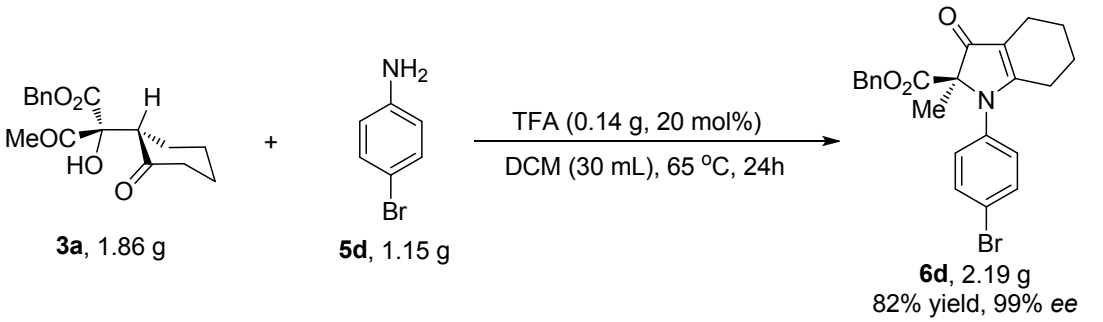


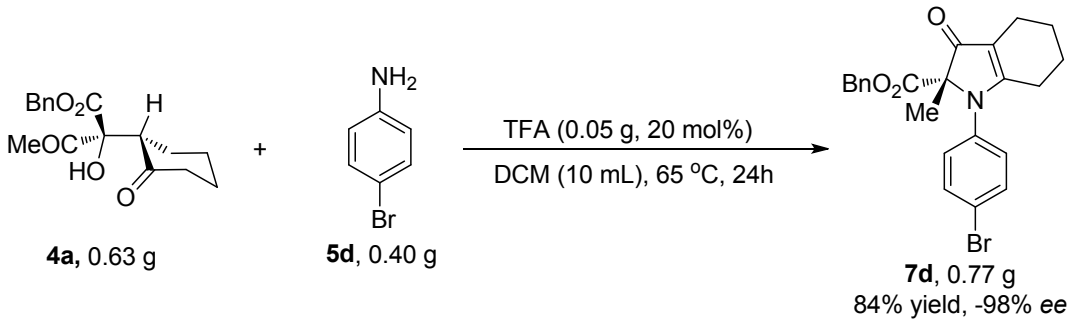
3a-i, k-m **5a-j** **6a-t**

In a 8 mL vial containing a magnetic stirring bar and a screw cap, a solution containing **3** (0.10 mmol, 1.0 eq.), **5** (0.11 mol, 1.1 eq.), trifluoroacetic aicd (2.28 mg, 0.02 mmol) in dichloromethane (0.5 mL) were stirred in an oil bath at 65 °C for 24 h. Then the reaction mixture was directly injected into the chromatography column (4g) and purified by flash column chromatography (SiO_2) eluding with hexanes/ethyl acetate to provide products **6**.

General procedures for gram-scale reactions.





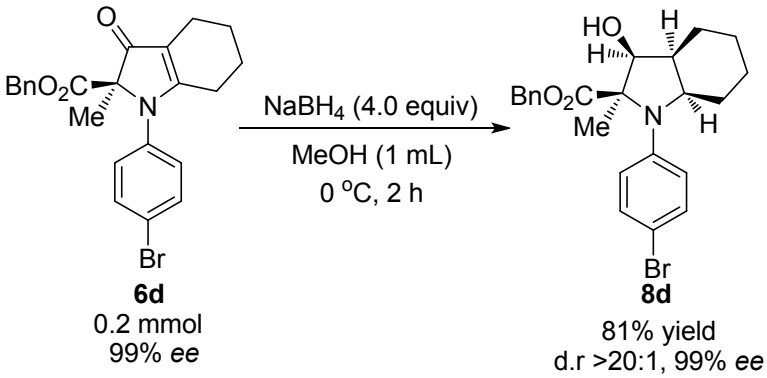


In a 100 mL one-neck flask containing a magnetic stirring bar, dichloromethane (50 mL), **1a** (2.24 g, 10 mmol), **2a** (1.96 g, 20 mmol) and *L*-proline (230 mg, 2 mmol) were added in sequence, then the reaction mixture was stirred at room temperature for 24h. After reaction was complete, the product mixture was concentrated and its components were purified by flash column chromatography (SiO_2), eluding with hexane/ethyl acetate, to provide products **3a** (1.86 g, 61% yield, 99% *ee*) and **4a** (0.63 g, 21% yield, 98% *ee*).

In a 100 mL one-neck flask containing a magnetic stirring bar and a condenser, dichloromethane (30 mL), **3a** (1.86 g), **5d** (1.15 g) and trifluoroacetic acid (0.14 g) were added in sequence, then the reaction mixture was stirred at 65 °C for 24 h. After reaction was complete, the mixture was concentrated andpurified by flash column chromatography (SiO_2), eluding with hexane/ethyl acetate, to provide **6d** (2.19 g, 82% yield, 99% *ee*).

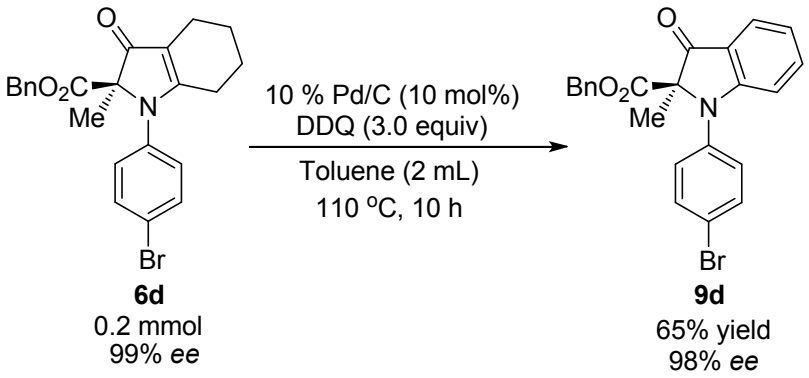
In a 25 mL one-neck flask containing a magnetic stirring bar and a condenser, dichloromethane (10 mL), **4a** (0.63 g), **5d** (0.40 g) and trifluoroacetic acid (0.05 g) was added in sequence, then the reaction mixture was stirred at 65 ^{o}C for 24 h. After reaction was complete, the mixture was concentrated and purified by flash column chromatography (SiO_2), eluding with hexane/ethyl acetate, to provide **7d** (0.77 g, 84% yield, -98% *ee*).

General procedure for reduction of 6d.



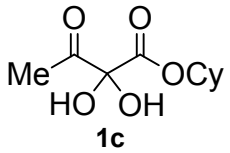
In a 8 mL vial containing a magnetic stirring bar, a solution containing **6d** (87.8 mg, 0.2 mmol) and methanol (1 mL) was stirred at 0°C. Then $NaBH_4$ (31 mg, 0.8 mmol) was added in three portions over 30 min, then the reaction mixture was stirred at 0°C for another 1.5 h after which 5 mL saturated Na_2CO_3 solution was added and the mixture was stirred at room temperature for 30 min. The reaction mixture was extracted three times (ethyl acetate 10 ml ×3) and the combined organic layer was dried using anhydrous Na_2SO_4, concentrated and purified by flash column chromatography (SiO_2), eluding with hexanes/ethyl acetate, to provide **8d** (71.8 mg, 81% yield, >20:1 d.r., 99% *ee*).

General procedure for aromatation of 6d.



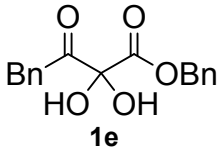
In a 8 mL vial containing a magnetic stirring bar and a screw cap, a solution containing **6d** (87.8 mg, 0.2 mmol), DDQ (135.6 mg, 0.6 mmol), 10% Pd/C (11.0 mg, 0.02 mmol) and toluene (2 mL) were stirred in oil bath at 110°C for 10 h. After this timethe reaction mixture was allowed to cool to room temperature, 5 mL saturated Na_2CO_3 solution was added, the mixture was stirred at room temperature for 5 min then was extracted three times (ethyl acetate 10 ml ×3). After drying the combined organic layer over anhydrous Na_2SO_4, the solution wasconcentrated and purified by flash column chromatography (SiO_2), eluding with hexanes/ethyl acetate, to provide **9d** (56.5 mg, 65% yield, 98% *ee*).

Characterization data of products 1, 3a-m, 4a-m, 6a-t.



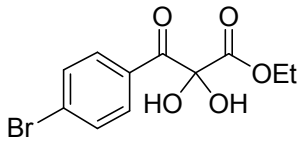
1c

Cyclohexyl 2,2-Dihydroxy-3-oxobutanoate (1c). White solid (73% yield); mp = 49.3-50.7 °C; TLC R_f = 0.29 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.08 (brs, 2H), 4.92-4.89 (m, 1H), 2.28 (s, 3H), 1.86-1.83 (comp, 2H), 1.71-1.67 (comp, 2H), 1.54-1.44 (comp, 3H), 1.44-1.33 (comp, 2H), 1.30-1.23 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.98, 168.41, 92.49, 76.24, 31.00, 25.03, 23.32, 23.04. HRMS (ESI) *m/z* calculated for $[C_{10}H_{16}O_5+Na]^+$ $[M+Na]^+$ 239.0890, found: 239.0890.



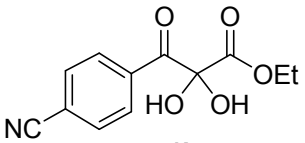
1e

Benzyl 2,2-Dihydroxy-3-oxo-4-phenylbutanoate (1e). Yellow solid (78% yield); mp = 78.6-82.4 °C; TLC R_f = 0.20 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.38 (comp, 3H), 7.32-7.28 (comp, 5H), 7.09-7.07 (comp, 2H), 5.15 (s, 2H), 5.03 (brs, 2H), 3.86 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.77, 168.74, 134.01, 132.11, 129.75, 128.99, 128.79, 128.59, 128.54, 127.42, 92.56, 68.77, 42.54. HRMS (ESI) *m/z* calculated for $[C_{17}H_{16}O_5+Na]^+$ $[M+Na]^+$ 323.0890, found: 323.0891.



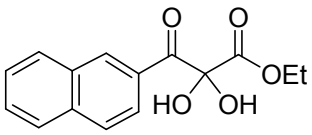
1h

Ethyl 3-(4-Bromophenyl)-2,2-dihydroxy-3-oxopropanoate (1h). White solid (75% yield); mp = 88.0-89.5 °C; TLC R_f = 0.37 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 5.37 (brs, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 1.12 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.83, 169.60, 132.18, 131.57, 130.23, 130.15, 91.74, 63.34, 13.71. HRMS (ESI) *m/z* calculated for $[C_{11}H_{11}BrO_5+Na]^+$ $[M+Na]^+$ 324.9682, found: 324.9681.



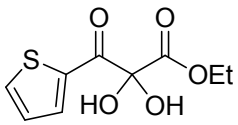
1j

Ethyl 3-(4-Cyanophenyl)-2,2-dihydroxy-3-oxopropanoate (1j). White solid (70% yield); mp = 102.9-106.9 °C; TLC R_f = 0.20 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 5.28 (brs, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 1.17 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.81, 169.12, 134.65, 132.48, 130.43, 117.68, 117.52, 91.96, 63.51, 13.70. HRMS (ESI) *m/z* calculated for $[C_{12}H_{11}NO_5+Na]^+$ $[M+Na]^+$ 272.0529, found: 272.0525.



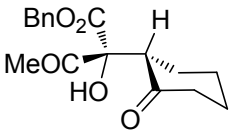
1k

Ethyl 2,2-Dihydroxy-3-(naphthalen-2-yl)-3-oxopropanoate (1k). Light yellow solid (71% yield); mp = 75.7-77.0 °C; TLC R_f = 0.33 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 5.52 (brs, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 1.07 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.51, 170.05, 136.15, 132.94, 132.28, 130.12, 129.47, 128.66, 127.79, 127.07, 124.79, 91.85, 63.24, 13.68. HRMS (ESI) *m/z* calculated for $[C_{15}H_{14}O_5+Na]^+$ $[M+Na]^+$ 297.0733, found: 297.0725.



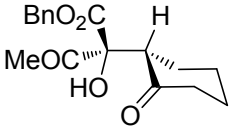
1l

Ethyl 2,2-Dihydroxy-3-oxo-3-(thiophen-2-yl)propanoate (1l). Yellow solid (77% yield); mp = 58.9-61.3 °C; TLC R_f = 0.26 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 4.0 Hz, 1.0 Hz, 1H), 7.79 (d, *J* = 4.0 Hz, 1H), 7.17 (t, *J* = 4.0 Hz, 1H), 5.30 (brs, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 1.16 (t, *J* = 7.0 Hz. 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.90, 169.70, 136.57, 136.29, 128.68, 109.99, 92.08, 63.41, 13.72. HRMS (ESI) *m/z* calculated for $[C_9H_{10}O_5S+Na]^+$ $[M+Na]^+$ 253.0141, found: 253.0136.



3a

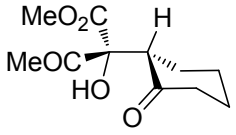
(*R*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (3a). Light yellow solid (68% yield); mp = 48.8-50.6 °C; TLC R_f = 0.30 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.36 (comp, 5H), 5.27 (d, *J* = 15.0 Hz, 1H), 5.20 (d, *J* = 15.0 Hz, 1H), 4.31 (s, 1H), 3.65 (dd, *J* = 15.0 Hz, 8.0 Hz, 1H), 2.44-2.30 (comp, 5H), 2.06-2.05 (m ,1H), 1.89-1.88 (m, 1H), 1.81-1.75 (comp, 2H), 1.69-1.61 (comp, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.52, 204.48, 169.57, 134.68, 128.71, 128.66, 128.25, 84.96, 68.40, 56.51, 41.87, 27.49, 26.71, 24.92, 24.48. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH = 80:20, flow rate 1.0 mL/min, 230 nm, major enantiomer tr = 7.6 min, minor enantiomer tr = 8.6 min). HRMS (ESI) *m/z* calculated for $[C_{17}H_{20}O_5+Na]^+$ $[M+Na]^+$ 327.1203, found: 327.1195.



4a

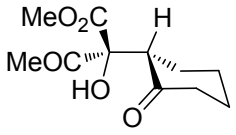
(*S*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (4a). Light yellow solid (24% yield); mp = 71.0-72.5 °C; TLC R_f = 0.40 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ

7.39-7.30 (comp, 5H), 5.22 (d, *J* = 15.0 Hz, 1H), 5.16 (d, *J* = 15.0 Hz, 1H), 4.09 (s, 1H), 3.62 (dd, *J* = 15.0 Hz, 7.5 Hz, 1H), 2.44-2.30 (comp, 2H), 2.25 (s, 3H), 2.10-2.07 (m, 1H), 1.92-1.83 (comp, 2H), 1.77-1.62 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.47, 205.72, 170.17, 134.92, 128.55, 128.43, 128.12, 84.75, 68.26, 55.84, 41.95, 27.58, 27.12, 25.85, 24.57. Enantiomeric excess: 97% (Diacel Chirapak OD-H, hexanes/i-PrOH = 80:20, flow rate 1.0 mL/min, 230 nm, major enantiomer tr = 6.4 min, minor enantiomer tr = 7.0 min). HRMS (ESI) *m/z* calculated for $[C_{17}H_{20}O_5+Na]^+$ $[M+Na]^+$ 327.1203, found: 327.1200.



3b

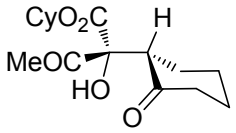
(*R*)-Methyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (3b). White solid (60% yield); mp = 64.5-65.6 °C; TLC R_f = 0.27 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.26 (s, 1H), 3.68 (s, 3H), 3.53 (dd, *J* = 12.0 Hz, 6.0 Hz, 1H), 2.34-2.16 (comp, 5H), 1.99-1.94 (m, 1H), 1.85-1.82 (m, 1H), 1.78-1.47 (comp, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.22, 204.56, 170.10, 84.86, 56.50, 53.61, 41.73, 27.50, 26.55, 24.79, 24.41. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH = 90:10, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 9.2 min, minor enantiomer tr = 9.8 min). HRMS (ESI) *m/z* calculated for $[C_{11}H_{16}O_5+Na]^+$ $[M+Na]^+$ 251.0890, found: 251.0882.



4b

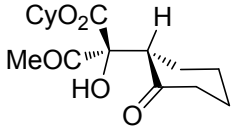
(*S*)-Methyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (4b). White solid (16%yield); mp = 71.6-72.8 °C; TLC R_f = 0.37(3:1hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ4.07 (s, 1H), 3.71 (s, 3H), 3.57-3.53 (m, 1H), 2.36-2.30 (comp, 2H), 2.24 (s, 3H), 2.05-2.03 (m, 1H), 1.87-1.86 (m, 1H), 1.78-1.77 (m, 1H), 1.71-1.61 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.28, 205.98, 170.79, 84.58, 55.85, 53.50, 41.93, 27.46, 27.01, 25.82, 24.55. Enantiomeric excess: 97% (Diacel Chirapak OD-H, hexanes/i-PrOH = 93:7, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 9.6 min, minor enantiomer tr = 10.0 min). HRMS (ESI) *m/z* calculated for

$[C_{11}H_{16}O_5+Na]^+$ $[M+Na]^+$ 251.0890, found: 251.0884.



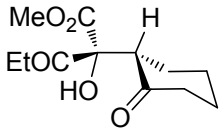
3c

(*R*)-Cyclohexyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (3c). Colorless liquid (67% yield); TLC R_f = 0.48 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86-4.80 (m, 1H), 4.25 (s, 1H), 3.61 (dd, *J* = 12.5 Hz, 6.0 Hz, 1H), 2.40-2.26 (comp, 5H), 2.06-2.03 (m, 1H), 1.93-1.91 (m, 1H), 1.86-1.75 (comp, 4H), 1.70-1.61 (comp, 4H), 1.52-1.23 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.32, 204.76, 169.16, 84.80, 75.65, 56.46, 41.87, 31.20, 31.07, 27.46, 26.72, 25.10, 24.92, 24.59, 23.38, 23.31. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH = 93:7, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 7.1 min, minor enantiomer tr = 8.4 min). HRMS (ESI) *m/z* calculated for $[C_{16}H_{24}O_5+Na]^+$ $[M+Na]^+$ 319.1516, found: 319.1516.



4c

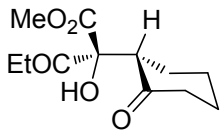
(*S*)-Cyclohexyl 2-Hydroxy-3-oxo-2-((*S*)-2-oxocyclohexyl)butanoate (4c). Colorless liquid (20% yield); TLC R_f = 0.57 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86-4.83 (m, 1H), 4.07 (s, 1H), 3.60 (dd, *J* = 11.5 Hz, 5.5 Hz, 1H), 2.43-2.30 (comp, 2H), 2.27 (s, 3H), 2.10-2.07 (m, 1H), 1.91-1.64 (comp, 9H), 1.52-1.26 (comp, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.26, 206.01, 169.70, 84.75, 75.25, 55.71, 42.03, 31.06, 31.02, 27.71, 27.20, 25.77, 25.22, 24.68, 23.41, 23.40. Enantiomeric excess: 98% (Diacel Chirapak OD-H, hexanes/i-PrOH = 98:2, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 8.3 min, minor enantiomer tr = 8.7 min). HRMS (ESI) *m/z* calculated for $[C_{16}H_{24}O_5+Na]^+$ $[M+Na]^+$ 319.1516, found: 319.1512.



3d

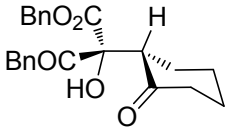
(*R*)-Methyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]pentanoate (3d). Colorless liquid (65%

yield); TLC R_f = 0.31 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.23 (s, 1H), 3.73 (s, 3H), 3.63-3.59 (m, 1H), 2.96-2.88 (m, 1H), 2.47-2.39 (m, 1H), 2.36-2.23 (comp, 2H), 2.03-1.99 (m, 1H), 1.91-1.88 (m, 1H), 1.80-1.53 (comp, 4H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.44, 207.30, 170.46, 84.76, 56.67, 53.70, 41.86, 30.25, 27.52, 26.66, 24.49, 7.56. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH = 95:5, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 9.9 min, minor enantiomer tr = 12.9 min). HRMS (ESI) *m/z* calculated for $[C_{12}H_{18}O_5+Na]^+$ $[M+Na]^+$ 265.1046, found: 265.1036.



4d

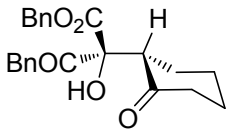
(*S*)-Methyl 2-Hydroxy-3-oxo-2-((*S*)-2-oxocyclohexyl)pentanoate (4d). White solid (19% yield); mp = 39.5-41.9 °C; TLC R_f = 0.45 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.02 (s, 1H), 3.71 (s, 3H), 3.58-3.55 (m, 1H), 2.75-2.67 (m, 1H), 2.63-2.55 (m, 1H), 2.39-2.28 (comp, 2H), 2.06-2.03 (m, 1H), 1.87-1.85 (m, 1H), 1.77-1.57 (comp, 4H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.48, 208.60, 170.98, 84.54, 56.18, 53.53, 41.95, 31.31, 27.56, 27.04, 24.57, 7.26. Enantiomeric excess: 97% (Diacel Chirapak AD-H, hexanes/i-PrOH = 80:20, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 7.8 min, minor enantiomer tr = 8.9 min). HRMS (ESI) *m/z* calculated for $[C_{12}H_{18}O_5+Na]^+$ $[M+Na]^+$ 265.1046, found: 265.1043.



3e

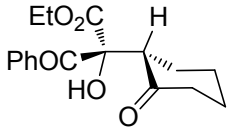
(*R*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-4-phenylbutanoate (3e). Yellow solid (59% yield); mp = 80.8-83.1 °C; TLC R_f = 0.33 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.37 (comp, 3H), 7.32-7.24 (comp, 5H), 7.14 (d, *J* = 6.5 Hz, 2H), 5.17 (d, *J* = 12.5 Hz, 1H), 5.10 (d, *J* = 12.5 Hz, 1H), 4.27 (s, 1H), 4.17 (d, *J* = 11.5 Hz, 1H), 4.02 (d, *J* = 11.5 Hz, 1H), 3.72 (dd, *J* = 12.5 Hz, 6.0 Hz, 1H), 2.45-2.42 (m, 1H), 2.35-2.28 (m, 1H), 2.06-2.03 (m, 1H), 1.88-1.87 (m,1H), 1.79-1.76 (m, 1H), 1.71-1.60 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.33, 204.20, 169.76, 134.66, 133.66, 129.92, 128.74, 128.70, 128.43, 128.33, 126.90, 84.75,

68.52, 57.21, 44.29, 41.92, 27.29, 26.77, 24.47. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH = 80:20, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 10.2 min, minor enantiomer tr = 11.8 min). HRMS (ESI) *m/z* calculated for $[C_{23}H_{24}O_5+Na]^+$ $[M+Na]^+$ 403.1516, found: 403.1517.



4e

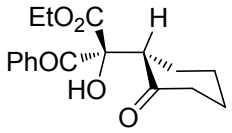
(*S*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-4-phenylbutanoate (4e). Yellow liquid (21% yield); TLC R_f = 0.43 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.35 (comp, 3H), 7.31-7.24 (comp, 5H), 7.07 (d, *J* = 7.5 Hz, 2H), 5.19 (d, *J* = 12.0 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 4.16 (s, 1H), 3.98 (d, *J* = 12.0 Hz, 1H), 3.90 (d, *J* = 12.0 Hz, 1H), 3.66 (dd, *J* = 12.0 Hz, 5.5 Hz, 1H), 2.42-2.40 (m, 1H), 2.35-2.30 (m, 1H), 2.10-2.08 (m, 1H), 1.87-1.78 (comp, 2H), 1.76-1.66 (comp, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.76, 204.85, 170.12, 134.91, 133.13, 129.75, 128.57, 128.44, 128.24, 127.00, 84.94, 68.32, 56.10, 44.30, 42.00, 27.84, 27.20, 24.61. Enantiomeric excess: 98% (Diacel Chirapak OD-H, hexanes/i-PrOH = 90:10, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 12.6 min, minor enantiomer tr = 14.5 min). HRMS (ESI) *m/z* calculated for $[C_{23}H_{24}O_5+Na]^+$ $[M+Na]^+$ 403.1516, found: 403.1516.



3f

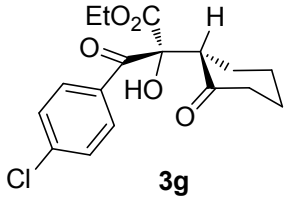
(*R*)-Ethyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-3-phenylpropanoate (3f). Clolorless liquid (51% yield); TLC R_f = 0.43 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 9.0 Hz, 2H), 7.57-7.53 (m, 1H), 7.45-7.42 (comp, 2H), 4.59 (s, 1H), 4.34-4.20 (comp, 2H), 3.85 (dd, *J* = 16.5 Hz, 6.5 Hz, 1H), 2.55-2.40 (comp, 2H), 2.18-2.13 (m, 1H), 2.00-1.63 (comp, 3H), 1.23 (t, *J* = 8.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.68, 195.74, 169.27, 134.68, 133.00, 129.76, 128.25, 84.73, 62.63, 56.08, 42.53, 28.49, 28.02, 24.95, 13.99. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH = 97:3, flow rate 1.0 mL/min, 230 nm, major enantiomer tr = 17.0 min, minor enantiomer tr = 20.1 min). HRMS (ESI) *m/z* calculated for $[C_{17}H_{20}O_5+Na]^+$

$[M+Na]^+$ 327.1203, found: 327.1200.



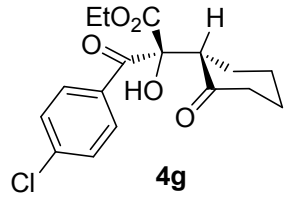
4f

(*S*)-Ethyl 2-Hydroxy-3-oxo-2-((*S*)-2-oxocyclohexyl)-3-phenylpropanoate (4f). Clolorless liquid (12% yield); TLC R_f = 0.50 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.0 Hz, 2H), 7.58-7.54 (m, 1H), 7.46-7.42 (comp, 2H), 4.30-4.21 (comp, 3H), 3.88-3.83 (m, 1H), 2.47-2.37 (comp, 2H), 2.14-2.10 (m, 1H), 2.04-2.00 (m, 1H), 1.93-1.92 (m, 1H), 1.86-1.67 (comp, 3H), 1.24 (t, *J* = 8.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.12, 197.09, 171.31, 135.92, 133.52, 130.29, 128.55, 85.72, 63.29, 57.43, 42.65, 28.81, 27.77, 25.18, 14.30. Enantiomeric excess: 98% (Diacel Chirapak OD-H, hexanes/i-PrOH = 99:1, flow rate 0.6 mL/min, 254 nm, major enantiomer tr = 31.1 min, minor enantiomer tr = 32.9 min). HRMS (ESI) *m/z* calculated for $[C_{17}H_{20}O_5+Na]^+$ $[M+Na]^+$ 327.1203, found: 327.1197.



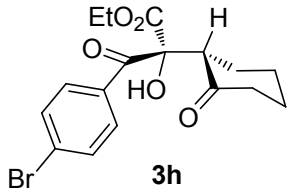
3g

(*R*)-Ethyl 3-(4-Chlorophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3g). Colorless liquid (58% yield); TLC R_f = 0.46 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 9.0 Hz, 2H), 4.55 (s, 1H), 4.27-4.19 (comp, 2H), 3.80 (dd, *J* = 12.5 Hz, 5.5 Hz, 1H), 2.50-2.44 (m, 1H), 2.39-2.36 (m, 1H), 2.14-2.10 (m, 1H), 1.97-1.89 (comp, 2H), 1.86-1.70 (comp, 2H), 1.68-1.59 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.67, 194.62, 169.07, 139.43, 133.00, 131.33, 128.54, 84.81, 62.76, 56.07, 42.48, 28.41, 27.99, 24.90, 14.01. Enantiomeric excess: 99% (Diacel Chirapak OJ-H, hexanes/i-PrOH = 80:20, flow rate 0.8 mL/min, 254 nm, major enantiomer tr = 9.1 min, minor enantiomer tr = 11.7 min). HRMS (ESI) *m/z* calculated for $[C_{17}H_{19}ClO_5+Na]^+$ $[M+Na]^+$ 361.0813, found: 361.0810.



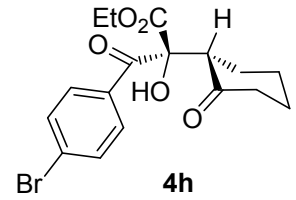
4g

(*S*)-Ethyl 3-(4-Chlorophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4g). Colorless liquid (7% yield); TLC R_f = 0.55 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.0 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 2H), 4.30-4.19 (comp, 3H), 3.82 (dd, *J* = 12.0 Hz, 5.5 Hz, 1H), 2.46-2.38 (comp, 2H), 2.13-2.11 (m, 1H), 2.00-2.19 (m, 1H), 1.92-1.91 (m, 1H), 1.83-1.70 (comp, 3H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.95, 195.31, 170.71, 139.71, 133.70, 131.57, 128.46, 85.47, 62.97, 57.02, 42.23, 28.47, 27.41, 24.76, 13.89. Enantiomeric excess: 94% (Diacel Chirapak OJ-H, hexanes/i-PrOH = 80:20, flow rate 0.8 mL/min, 254 nm, major enantiomer tr = 8.0 min, minor enantiomer tr = 10.0 min). HRMS (ESI) *m/z* calculated for $[C_{17}H_{19}ClO_5+Na]^+$ $[M+Na]^+$ 361.0813, found: 361.0811.



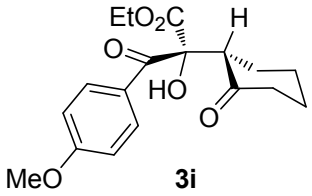
3h

(*R*)-Ethyl 3-(4-Bromophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3h). White solid (56% yield); mp = 61.7-63.1 °C; TLC R_f = 0.42 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 4.54 (s, 1H), 4.30-4.20 (comp, 2H), 3.81 (dd, *J* = 12.5 Hz, 6.0 Hz, 1H), 2.52-2.45 (m, 1H), 2.41-2.38 (m, 1H), 2.16-2.11 (m, 1H), 1.98-1.90 (comp, 2H), 1.88-1.60 (comp, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.68, 194.88, 169.06, 133.43, 131.56, 131.41, 128.26, 84.82, 62.79, 56.11, 42.50, 28.42, 28.00, 24.91, 14.03. Enantiomeric excess: 99% (Diacel Chirapak OJ-H, hexanes/i-PrOH = 80:20, flow rate 0.8 mL/min, 254 nm, major enantiomer tr = 9.5 min, minor enantiomer tr = 12.1 min). HRMS (ESI) *m/z* calculated for $[C_{17}H_{19}BrO_5+Na]^+$ $[M+Na]^+$ 405.0308, found: 405.0298.



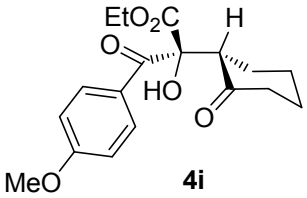
4h

(*S*)-Ethyl 3-(4-Bromophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4h). Colorless liquid (6% yield); TLC R_f = 0.36 (10:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 4.29-4.19 (comp, 3H), 3.81 (dd, *J* = 12.0 Hz, 5.5 Hz, 1H), 2.46-2.37 (comp, 2H), 2.13-2.10 (m, 1H), 2.02-1.99 (m, 1H), 1.92-1.91 (m, 1H), 1.82-1.68 (comp, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.93, 195.56, 170.68, 134.14, 131.62, 131.45, 128.51, 85.46, 62.98, 57.01, 42.22, 28.45, 27.39, 24.75, 13.89. Enantiomeric excess: 95% (Diacel Chirapak OJ-H, hexanes/i-PrOH = 80:20, flow rate 0.8 mL/min, 254 nm, major enantiomer tr = 8.5 min, minor enantiomer tr = 10.6 min). HRMS (ESI) *m/z* calculated for $[C_{17}H_{19}BrO_5+Na]^+$ $[M+Na]^+$ 405.0308, found: 405.0305.



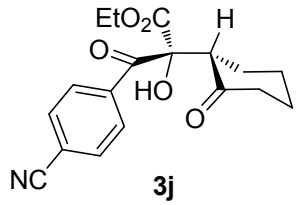
3i

(*R*)-Ethyl 2-Hydroxy-3-(4-methoxyphenyl)-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3i). Colorless liquid (25% yield); TLC R_f = 0.26 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.0 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 4.68 (s, 1H), 4.28-4.17 (comp, 2H), 3.85 (s, 3H), 3.80 (dd, *J* = 12.5 Hz, 5.0 Hz, 1H), 2.54-2.48 (m, 1H), 2.40-2.37 (m, 1H), 2.16-2.12 (m, 1H), 1.97-1.91 (comp, 2H), 1.90-1.84 (m, 1H), 1.81-1.62 (comp, 2H), 1.19 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.28, 193.49, 169.37, 163.54, 132.45, 127.19, 113.52, 84.77, 62.39, 55.66, 55.43, 42.68, 28.75, 28.26, 25.05, 14.02. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 70:30, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 15.2 min, minor enantiomer tr = 26.2 min). HRMS (ESI) *m/z* calculated for $[C_{18}H_{22}O_6+Na]^+$ $[M+Na]^+$ 357.1308, found: 357.1306.



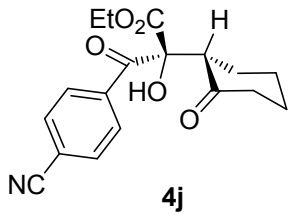
4i

(*S*)-Ethyl 2-Hydroxy-3-(4-methoxyphenyl)-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4i). Colorless liquid (4% yield); TLC R_f = 0.32 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 4.29 (s, 1H), 4.28-4.19 (comp, 2H), 3.89-3.83 (comp, 4H), 2.46-2.37 (comp, 2H), 2.12-2.09 (m, 1H), 2.00-1.99 (m, 1H), 1.91-1.89 (m, 1H), 1.82-1.71 (comp, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.90, 194.10, 171.20, 163.66, 132.78, 127.96, 113.43, 85.23, 62.70, 57.03, 55.45, 42.30, 28.46, 27.47, 24.80, 13.90. Enantiomeric excess: 98% (Diacel Chirapak AD-H, hexanes/i-PrOH = 70:30, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 12.0 min, minor enantiomer tr = 23.1 min). HRMS (ESI) *m/z* calculated for $[C_{18}H_{22}O_6+Na]^+$ $[M+Na]^+$ 357.1308, found: 357.1300.



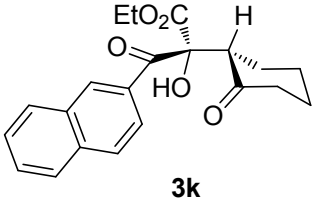
3j

(*R*)-Ethyl 3-(4-Cyanophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3j). White solid (70% yield); mp = 84.2-85.3 °C; TLC R_f = 0.29 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 4.40 (s, 1H), 4.33-4.23 (comp, 2H), 3.84 (dd, *J* = 12.5 Hz, 6.0 Hz, 1H), 2.49-2.39 (comp, 2H), 2.15-2.12 (m, 1H), 1.99-1.96 (m, 1H), 1.92-1.72 (comp, 3H), 1.68-1.60 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.91, 195.65, 169.00, 138.66, 131.94, 130.06, 118.02, 115.82, 84.82, 63.23, 56.79, 42.28, 28.02, 27.67, 24.75, 14.03. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH = 80:20, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 8.9 min, minor enantiomer tr = 9.9 min). HRMS (ESI) *m/z* calculated for $[C_{18}H_{19}NO_5+Na]^+$ $[M+Na]^+$ 352.1155, found: 352.1150.



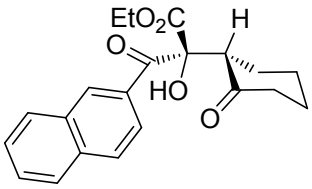
4j

(*S*)-Ethyl 3-(4-Cyanophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4j). White solid (13% yield); mp = 102.2-105.7 °C; TLC R_f = 0.39 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 4.31-4.20 (comp, 3H), 3.80 (dd, *J* = 12.0 Hz, 5.5 Hz, 1H), 2.47-2.37 (comp, 2H), 2.14-2.11 (m, 1H), 2.01-1.93 (comp, 2H), 1.82-1.67 (comp, 3H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.82, 195.92, 170.30, 138.94, 131.85, 130.30, 117.95, 116.12, 85.58, 63.21, 57.03, 42.16, 28.44, 27.33, 24.70, 13.89. Enantiomeric excess: 96% (Diacel Chirapak OD-H, hexanes/i-PrOH = 90:10, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 12.4 min, minor enantiomer tr = 13.5 min). HRMS (ESI) *m/z* calculated for $[C_{18}H_{19}NO_5+Na]^+$ $[M+Na]^+$ 352.1155, found: 352.1154.



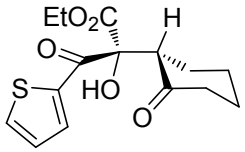
3k

(*R*)-Ethyl 2-Hydroxy-3-(naphthalen-2-yl)-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3k). Colorless liquid (45% yield); TLC R_f = 0.41 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.87-7.84 (comp, 2H), 7.60-7.51 (comp, 2H), 4.73 (s, 1H), 4.33-4.21 (comp, 2H), 3.91 (dd, *J* = 12.5 Hz, 5.0 Hz, 1H), 2.56-2.49 (m, 1H), 2.43-2.41 (m, 1H), 2.16-2.14 (m, 1H), 2.00-1.90 (comp, 3H), 1.84-1.64 (comp, 2H), 1.21 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.89, 195.42, 169.37, 135.45, 132.30, 131.89, 129.93, 128.60, 128.04, 127.64, 126.60, 125.34, 85.01, 62.64, 56.12, 42.59, 28.60, 28.10, 24.99, 14.05. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 70:30, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 30.2 min, minor enantiomer tr = 36.5 min). HRMS (ESI) *m/z* calculated for $[C_{21}H_{22}O_5+Na]^+$ $[M+Na]^+$ 377.1359, found: 377.1359.



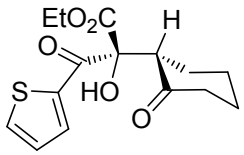
4k

(*S*)-Ethyl 2-Hydroxy-3-(naphthalen-2-yl)-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4k). Colorless liquid (12% yield); TLC R_f = 0.48 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.87-7.85 (comp, 2H), 7.72-7.59 (m, 1H), 7.56-7.53 (m, 1H), 4.39 (s, 1H), 4.32-4.22 (comp, 2H), 3.91 (dd, *J* = 12.0 Hz, 5.5 Hz, 1H), 2.48-2.40 (comp, 2H), 2.14-2.05 (comp, 2H), 1.94-1.91 (m, 1H), 1.88-1.67 (comp, 3H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.81, 196.28, 171.01, 135.44, 132.69, 132.25, 132.23, 130.01, 128.70, 127.84, 127.61, 126.61, 125.35, 85.57, 62.88, 57.14, 42.29, 28.49, 27.39, 24.80, 13.93. Enantiomeric excess: 97% (Diacel Chirapak AD-H, hexanes/i-PrOH = 70:30, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 12.5 min, minor enantiomer tr = 24.9 min). HRMS (ESI) *m/z* calculated for $[C_{21}H_{22}O_5+Na]^+$ $[M+Na]^+$ 377.1359, found: 377.1354.



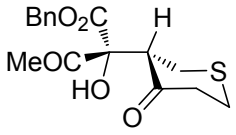
3l

(*R*)-Ethyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-3-(thiophen-2-yl)propanoate (3l). Yellow liquid (67% yield); TLC R_f = 0.32 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 4.0 Hz,1.0 Hz, 1H), 7.62 (dd, *J* = 5.0 Hz, 1.0 Hz, 1H), 7.06 (dd, *J* = 5.0 Hz, 4.0 Hz, 1H), 4.65 (s, 1H), 4.25-4.13 (comp, 2H), 3.77 (dd, *J* = 12.0 Hz, 6.0 Hz, 1H), 2.47-2.40 (m, 1H), 2.37-2.33 (m, 1H), 2.11-2.06 (m, 1H), 1.93-1.79 (comp, 3H), 1.77-1.68 (m, 1H), 1.66-1.57 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.98, 187.99, 169.07, 139.26, 135.32, 134.91, 127.89, 84.74, 62.79, 55.72, 42.42, 28.33, 27.87, 24.88, 13.97. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH = 90:10, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 12.6 min, minor enantiomer tr = 15.3 min). HRMS (ESI) *m/z* calculated for $[C_{15}H_{18}O_5S+Na]^+$ $[M+Na]^+$ 333.0767, found: 333.0766.



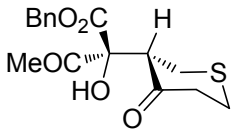
4l

(*S*)-Ethyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-3-(thiophen-2-yl)propanoate (4l). Yellow solid (9% yield); mp = 69.7-70.4 °C; TLC R_f = 0.42 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 4.0 Hz, 1.0 Hz, 1H), 7.69 (dd, *J* = 5.0 Hz, 1.0 Hz, 1H), 7.12 (dd, *J* = 5.0 Hz, 4.0 Hz, 1H), 4.36 (s, 1H), 4.27-4.17 (comp, 2H), 3.81 (dd, *J* = 12.0 Hz, 5.5 Hz, 1H), 2.45-2.36 (comp, 2H), 2.12-2.09 (m, 1H), 2.04-2.01 (m, 1H), 1.91-1.89 (m, 1H), 1.85-1.66 (comp, 3H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.22, 188.44, 170.59, 139.06, 136.38, 135.94, 127.80, 84.81, 62.99, 56.84, 42.19, 28.23, 27.40, 24.72, 13.86. Enantiomeric excess: 92% (Diacel Chirapak AD-H, hexanes/i-PrOH = 92:8, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 25.7 min, minor enantiomer tr = 27.5 min). HRMS (ESI) *m/z* calculated for $[C_{15}H_{18}O_5S+Na]^+$ $[M+Na]^+$ 333.0767, found: 333.0760.



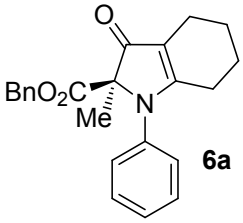
3m

(*R*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-4-oxotetrahydro-2*H*-thiopyran-3-yl]butanoate (3m). White solid (56% yield); mp = 92.4-94.0 °C; TLC R_f = 0.29 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.33 (comp, 5H), 5.28 (d, *J* = 12.0 Hz, 1H), 5.19 (d, *J* = 12.0 Hz, 1H), 3.94 (dd, *J* = 12.0 Hz, 4.5 Hz, 1H), 3.04-2.99 (m, 1H), 2.96-2.90 (m, 1H), 2.86-2.84 (m, 1H), 2.77-2.67 (comp, 2H), 2.53-2.50 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.56, 203.38, 169.21, 134.49, 128.90, 128.77, 128.36, 84.98, 68.71, 58.55, 44.37, 30.10, 29.59, 24.70. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH = 80:20, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 10.2 min, minor enantiomer tr = 12.2 min). HRMS (ESI) *m/z* calculated for $[C_{16}H_{18}O_5S+Na]^+$ $[M+Na]^+$ 345.0767, found: 345.0757.



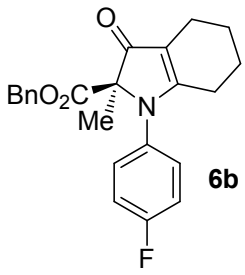
4m

(*S*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-4-oxotetrahydro-2*H*-thiopyran-3-yl]butanoate (4m). Yellow solid (17% yield); mp = 63.4-64.8 °C; TLC R_f = 0.42 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.33 (comp, 3H), 7.29-7.27 (comp, 2H), 5.19 (d, *J* = 12.5 Hz, 1H), 5.16 (d, *J* = 12.5 Hz, 1H), 4.16 (s, 1H), 3.95 (dd, *J* = 12.0 Hz, 4.5 Hz, 1H), 3.01-2.93 (comp, 2H), 2.90-2.86 (m, 1H), 2.74-2.64 (comp, 3H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.70, 204.79, 169.63, 134.67, 128.61, 128.21, 84.71, 68.50, 57.71, 44.55, 30.38, 30.10, 25.55, 25.54. Enantiomeric excess: 89% (Diacel Chirapak OD-H, hexanes/i-PrOH = 80:20, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 9.5 min, minor enantiomer tr = 11.1 min). HRMS (ESI) *m/z* calculated for $[C_{16}H_{18}O_5S+Na]^+$ $[M+Na]^+$ 345.0767, found: 345.0757.



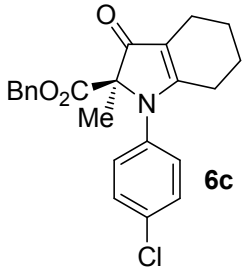
6a

(*R*)-Benzyl 2-Methyl-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6a). Yellow liquid (87% yield); TLC R_f = 0.33 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.18 (comp, 8H), 6.91-6.90 (comp, 2H), 5.13 (d,*J* = 12.0H, 1H), 5.04 (d, *J* = 12.0 Hz, 1H), 2.30-2.20 (comp, 4H), 1.67-1.55 (comp, 4H), 1.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.52, 174.87, 167.59, 137.24, 135.43, 129.24, 128.46, 128.17, 128.04, 127.98, 127.46, 107.56, 74.97, 67.30, 25.46, 22.16, 22.08, 18.99, 18.93. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 90:10, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 12.8 min, minor enantiomer tr = 14.5 min). HRMS (ESI) *m/z* calculated for $[C_{23}H_{23}NO_3+Na]^+$ $[M+Na]^+$ 384.1570, found: 384.1568.



6b

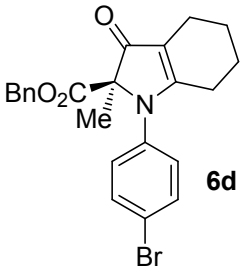
(*R*)-Benzyl 1-(4-Fluorophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6b). Yellow solid (84% yield); mp = 64.5-65.2 °C; TLC R_f = 0.31 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ7.33-7.26 (comp, 5H), 6.96-6.93 (comp, 4H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 2.30-2.23 (comp, 4H), 1.74-1.70 (comp, 4H), 1.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.38, 174.96, 167.39, 161.70 (d, *J* = 247 Hz), 135.34, 133.06, 133.04, 130.25 (d, *J* = 8.6 Hz), 128.52, 128.31, 128.20, 116.17 (d, *J* = 22.5 Hz), 107.45, 74.96, 67.39, 25.21, 22.06, 22.02, 18.95, 18.93. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 95:5, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 24.5 min, minor enantiomer tr = 26.3 min). HRMS (ESI) *m/z* calculated for $[C_{23}H_{22}FNO_3+Na]^+$ $[M+Na]^+$ 402.1476, found: 402.1474.



6c

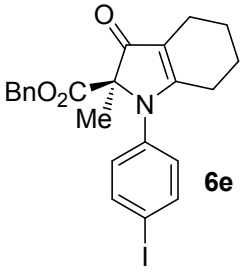
(*R*)-Benzyl 1-(4-Chlorophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6c). Yellow solid (84% yield); mp = 68.2-68.8 °C; TLC R_f = 0.36 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.33 (comp, 3H), 7.29-7.26 (comp, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.21 (d, *J* = 12.5 Hz, 1H), 5.08 (d, *J* = 12.5 Hz, 1H), 2.32-2.28 (comp, 4H), 1.76-1.66 (comp, 4H), 1.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.38, 174.54, 167.34, 135.76, 135.29, 133.26, 129.44, 129.22, 128.53, 128.33, 128.21, 108.15, 74.91, 67.45, 25.40, 22.11, 21.97, 19.04, 18.95. Enantiomeric excess: 99% (Diacel Chirapak IC-3, hexanes/i-PrOH = 70:30, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 22.3 min, minor enantiomer tr = 25.3 min). HRMS (ESI) *m/z* calculated for $[C_{23}H_{22}ClNO_3+Na]^+$ $[M+Na]^+$

418.1180, found: 418.1175.



6d

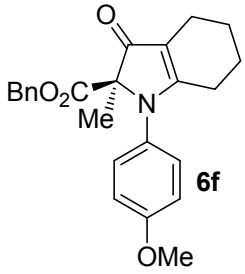
(*R*)-Benzyl 1-(4-Bromophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6d). Yellow liquid (82% yield); TLC R_f = 0.37 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.33 (comp, 5H), 7.29-7.26 (comp, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.09 (d, *J* = 12.0 Hz, 1H), 2.33-2.29 (comp, 4H), 1.76-1.67 (comp, 4H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.37, 174.47, 167.34, 136.28, 135.28, 132.44, 129.45, 128.54, 128.35, 128.22, 121.18, 108.25, 74.86, 67.47, 25.44, 22.12, 21.96, 19.07, 18.95. Enantiomeric excess: 99% (Diacel Chirapak IC-3, hexanes/i-PrOH = 70:30, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 23.0 min, minor enantiomer tr = 26.3 min). HRMS (ESI) *m/z* calculated for $[C_{23}H_{22}BrNO_3+Na]^+$ $[M+Na]^+$ 462.0675, found: 462.0672.



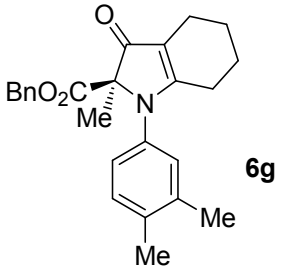
6e

(*R*)-Benzyl 1-(4-Iodophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6e). Yellow liquid (81% yield); TLC R_f = 0.40 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 9.0 Hz, 2H), 7.34-7.33 (comp, 3H), 7.27-7.26 (comp, 2H), 6.69 (d, *J* = 9.0 Hz, 2H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.07 (d, *J* = 12.0 Hz, 1H), 2.30-2.29 (comp, 4H), 1.74-1.67 (comp, 4H), 1.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.37, 174.36, 167.33, 138.42, 137.01, 135.28, 129.55, 128.54, 128.34, 128.19, 108.40, 92.41, 74.84, 67.46, 25.49, 22.13, 21.95, 19.07, 18.9. Enantiomeric excess: 99% (Diacel Chirapak IC-3, hexanes/i-PrOH = 70:30, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 24.3 min, minor enantiomer tr = 27.8 min). HRMS (ESI) *m/z*

calculated for $[C_{23}H_{22}IO_3+Na]^+$ $[M+Na]^+$ 510.0536, found: 510.0535.

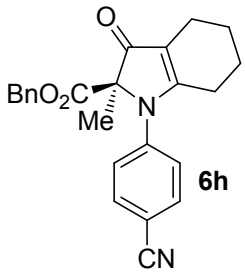


(*R*)-Benzyl 1-(4-Methoxyphenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6f). Yellow liquid (84% yield); TLC R_f = 0.23 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.26 (comp, 5H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 5.19 (d, *J* = 12.5 Hz, 1H), 5.08 (d, *J* = 12.5 Hz, 1H), 3.77 (s, 3H), 2.35-2.16 (comp, 4H), 1.71-1.63 (comp, 4H), 1.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ195.45, 175.61, 167.58, 158.98, 135.45, 129.87, 129.53, 128.48, 128.19, 128.10, 114.38, 106.55, 75.05, 67.23, 55.43, 25.15, 22.12, 22.07, 18.98, 18.89. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 90:10, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 17.6 min, minor enantiomer tr = 19.6 min). HRMS (ESI) *m/z* calculated for $[C_{24}H_{25}NO_4+Na]^+$ $[M+Na]^+$ 414.1676, found: 414.1677.

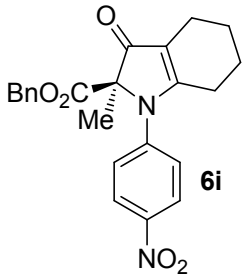


(*R*)-Benzyl 1-(3,4-Dimethylphenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6g). Yellow liquid (87% yield); TLC R_f = 0.35 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.26 (comp, 5H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.20 (d, *J* = 12.0 Hz, 1H), 5.10 (d, *J* = 12.0 Hz, 1H), 2.30-2.26 (comp, 4H), 2.22 (s, 3H), 2.13 (s, 3H), 1.73-1.64 (comp, 4H), 1.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.53, 175.23, 167.69, 137.66, 136.26, 135.55, 134.73, 130.25, 129.08, 128.45, 128.13, 128.04, 125.48, 106.90, 75.00, 67.21, 25.39, 22.15, 19.73, 19.28, 19.01, 18.89. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 90:10, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 9.4 min, minor enantiomer tr = 12.0 min). HRMS (ESI) *m/z* calculated for $[C_{25}H_{27}NO_3+Na]^+$

$[M+Na]^+$ 412.1883, found: 412.1884.

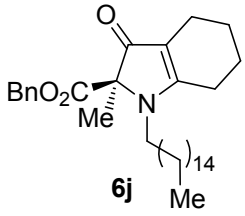


(*R*)-Benzyl 1-(4-Cyanophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6h). Yellow liquid (78% yield); TLC R_f = 0.25 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.34-7.32 (comp, 3H), 7.27-7.25 (comp, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 5.22 (d, *J* = 12.5 Hz, 1H), 5.08 (d, *J* = 12.5 Hz, 1H), 2.44-2.43 (comp, 2H), 2.33-2.31 (comp, 2H), 1.83-1.80 (comp, 2H), 1.71-1.67 (comp, 2H), 1.56 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ195.10, 172.92, 167.09, 141.62, 135.09, 133.16, 128.56, 128.50, 128.31, 126.02, 118.14, 111.02, 109.50, 74.76, 67.74, 26.25, 22.30, 21.70, 19.20, 18.97. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 90:10, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 30.3 min, minor enantiomer tr = 36.4 min). HRMS (ESI) *m/z* calculated for $[C_{24}H_{22}N_2O_3+Na]^+$ $[M+Na]^+$ 409.1522, found: 409.1522.



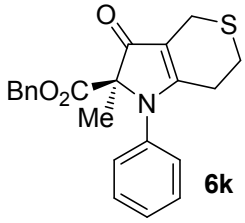
(*R*)-Benzyl 2-Methyl-1-(4-nitrophenyl)-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6i). Yellow liquid (85% yield); TLC R_f = 0.30 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.33-7.25 (comp, 5H), 6.98 (d, *J* = 8.5 Hz, 2H), 5.24 (d, *J* = 12.5 Hz, 1H), 5.08 (d, *J* = 12.5 Hz, 1H), 2.51-2.50 (comp, 2H), 2.35-2.34 (comp, 2H), 1.86-1.81 (comp, 2H), 1.74-1.67 (comp, 2H), 1.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.08, 172.76, 167.00, 144.72, 143.36, 134.99, 128.56, 128.38, 124.95, 124.85, 111.85, 74.82, 67.85, 26.56, 22.36, 21.61, 19.30, 19.01. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 90:10, flow

rate 1.0 mL/min, 210 nm, major enantiomer tr = 29.0 min, minor enantiomer tr = 33.3 min). HRMS (ESI) *m/z* calculated for $[C_{23}H_{22}N_2O_5+Na]^+$ $[M+Na]^+$ 429.1421, found: 429.1423.



6j

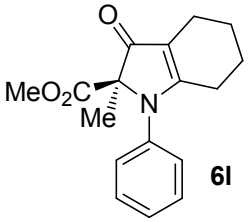
(*R*)-Benzyl 1-Hexadecyl-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6j). Yellow liquid (46% yield); TLC R_f = 0.34 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.28 (comp, 5H), 5.18 (d, *J* = 12.5 Hz, 1H), 5.14 (d, *J* = 12.5 Hz, 1H), 7.30-7.23 (m, 1H), 3.09-3.02 (m, 1H), 2.49-2.48 (m, 1H), 2.43-2.41 (m, 1H), 2.25-2.23 (comp, 2H), 1.80-1.79 (comp, 2H), 1.69-1.10 (comp, 2H), 1.59 (s, 3H), 1.47-1.45 (comp, 2H), 1.31-1.22 (comp, 26H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.27, 175.90, 168.05, 135.60, 128.47, 128.14, 127.82, 105.05, 73.89, 67.22, 44.14, 31.92, 30.37, 29.70, 29.66, 29.62, 29.55, 29.52, 29.36, 29.20, 27.02, 24.47, 22.69, 22.13, 22.05, 19.04, 18.80, 14.12. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 95:5, flow rate 1.0 mL/min, 230 nm, major enantiomer tr = 7.2 min, minor enantiomer tr = 9.2 min). HRMS (ESI) *m/z* calculated for $[C_{33}H_{51}NO_3+Na]^+$ $[M+Na]^+$ 532.3761, found: 532.3753.



6k

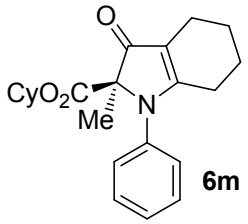
(*R*)-Benzyl 2-Methyl-3-oxo-1-phenyl-1,2,3,4,6,7-hexahydrothiopyrano[4,3-*b*]pyrrole-2-carboxylate (6k). Yellow liquid (91% yield); TLC R_f = 0.35 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.26 (comp, 8H), 7.00-6.98 (comp, 2H), 5.22 (d, *J* = 12.0 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 3.50 (d, *J* = 15.5 Hz, 1H), 3.40 (d, *J* = 15.5 Hz, 1H), 2.80-2.78 (comp, 2H), 2.57-2.55 (comp, 2H), 1.54 (s ,3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.23, 173.45, 167.05, 136.51, 135.22, 129.48, 128.58, 128.53, 128.33, 128.20, 128.19, 104.54, 74.28, 67.54, 27.57, 24.79, 21.13, 18.80. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 90:10, flow rate 1.0

mL/min, 230 nm, major enantiomer tr = 19.7 min, minor enantiomer tr = 25.5 min). HRMS (ESI) *m/z* calculated for $[C_{22}H_{21}NO_3S+Na]^+$ $[M+Na]^+$ 402.1134, found: 402.1127.



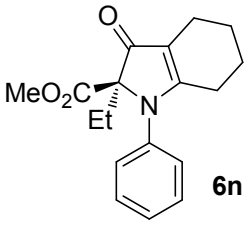
6l

(*R*)-Methyl 2-Methyl-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6l). Yellow solid (89% yield); mp = 96.5-97.9 °C; TLC R_f = 0.21 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (comp, 2H), 7.32-7.29 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.71 (s, 3H), 2.33-2.28 (comp, 4H), 1.76-1.65 (comp, 4H), 1.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.53, 175.08, 168.23, 137.31, 129.35, 128.15, 127.69, 107.33, 74.98, 52.84, 25.44, 22.10, 22.03, 19.08, 18.95. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 96:4, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 18.2 min, minor enantiomer tr = 19.8 min). HRMS (ESI) *m/z* calculated for $[C_{17}H_{19}NO_3+Na]^+$ $[M+Na]^+$ 308.1257, found: 308.1257.



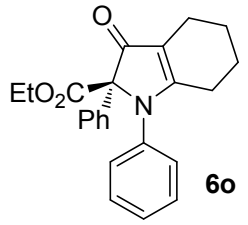
6m

(*R*)-Cyclohexyl 2-Methyl-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6m). Yellow liquid (88% yield); TLC R_f = 0.42 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.33 (comp, 2H), 7.28-7.26 (m, 1H), 7.12-7.10 (comp, 2H), 4.79-4.76 (m, 1H), 2.36-2.28 (comp, 4H), 1.78-1.56 (comp, 9H), 1.50 (s, 3H), 1.49-1.23 (comp, 7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.78, 174.61, 167.03, 137.49, 129.23, 127.72, 127.29, 107.57, 75.22, 73.91, 31.12, 30.98, 25.57, 25.31, 23.18, 23.09, 22.25, 22.12, 19.02, 18.71. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 95:5, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 12.2 min, minor enantiomer tr = 15.8 min). HRMS (ESI) *m/z* calculated for $[C_{22}H_{27}NO_3+Na]^+$ $[M+Na]^+$ 376.1883, found: 376.1874.



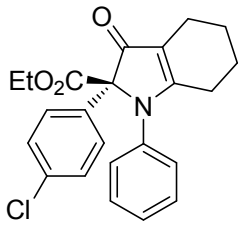
6n

(*R*)-Methyl 2-Ethyl-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6n). White solid (28% yield); mp = 121.0-123.0 °C; TLC R_f = 0.25 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.28 (comp, 2H), 7.23-7.19 (m, 1H), 7.04-7.02 (comp, 2H), 3.62 (s, 3H), 2.37-2.31 (comp, 3H), 2.25-2.24 (comp, 2H), 1.90-1.87 (m, 1H), 1.70-1.58 (comp, 5H), 0.69 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.62, 175.95, 167.99, 137.42, 129.30, 127.06, 126.97, 109.58, 79.19, 52.74, 25.78, 24.72, 22.30, 22.05, 18.85, 7.01. Enantiomeric excess: 99% (Diacel Chirapak IC-3, hexanes/i-PrOH = 70:30, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 21.8 min, minor enantiomer tr = 29.5 min). HRMS (ESI) *m/z* calculated for $[C_{18}H_{21}NO_3+Na]^+$ $[M+Na]^+$ 322.1413, found: 322.1414.



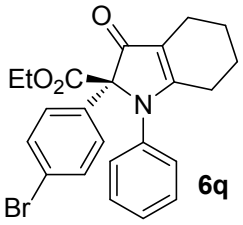
6o

(*R*)-Ethyl 3-Oxo-1,2-diphenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6o). Yellow solid (73% yield); mp = 126.6-128.8 °C; TLC R_f = 0.36 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.26 (comp, 3H), 7.21-7.19 (comp, 5H), 6.91-6.89 (comp, 2H), 4.19 (q, *J* = 7.0 Hz, 2H), 2.54-2.48 (m, 1H), 2.41-2.24 (comp, 3H), 1.86-1.68 (comp, 4H), 1.15 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.78, 175.70, 166.71, 137.73, 135.36, 128.78, 128.72, 128.30, 128.27, 128.20, 127.14, 108.05, 82.15, 62.24, 25.94, 22.26, 22.07, 19.12, 13.99. Enantiomeric excess: 99% (Diacel Chirapak AD-H, hexanes/i-PrOH = 90:10, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 9.4 min, minor enantiomer tr = 11.1 min). HRMS (ESI) *m/z* calculated for $[C_{23}H_{23}NO_3+Na]^+$ $[M+Na]^+$ 384.1570, found: 384.1563.



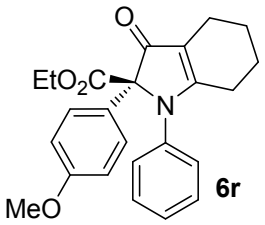
6p

(*R*)-Ethyl 2-(4-Chlorophenyl)-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6p). Yellow liquid (58% yield); TLC R_f = 0.42 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.19 (comp, 7H), 6.94 (d, *J* = 8.5 Hz, 2H), 4.19 (q, *J* = 7.0 Hz, 2H), 2.59-2.54 (m, 1H), 2.42-2.39 (m, 1H), 2.33-2.30 (comp, 2H), 1.86-1.85 (m, 1H), 1.75-1.70 (comp, 3H), 1.15 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.54, 175.92, 166.37, 137.63, 134.37, 133.76, 130.16, 128.95, 128.47, 127.77, 127.24, 108.35, 81.37, 62.40, 26.06, 22.26, 22.00, 19.10, 13.97. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH/MeOH = 94:4:2, flow rate 1.0 mL/min, 210 nm, major enantiomer tr = 8.0 min, minor enantiomer tr = 8.8 min). HRMS (ESI) *m/z* calculated for $[C_{23}H_{22}ClNO_3+Na]^+$ $[M+Na]^+$ 418.1180, found: 418.1174.

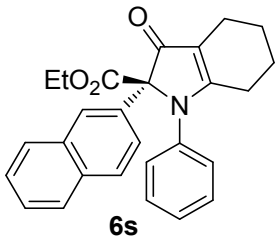


6q

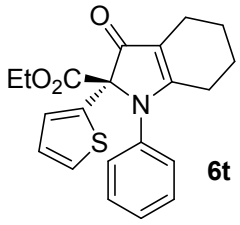
(*R*)-Ethyl 2-(4-Bromophenyl)-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6q). Yellow solid (46% yield); mp = 126.9-129.8 °C; TLC R_f = 0.43 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.25-7.23 (comp, 3H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.95-6.93 (comp, 2H), 4.18 (q, *J* = 7.0 Hz, 2H), 2.59-2.54 (m, 1H), 2.42-2.38 (m, 1H), 2.34-2.30 (comp, 2H), 1.87-1.84 (m, 1H), 1.78-1.70 (comp, 3H), 1.14 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.49, 175.92, 166.30, 137.63, 134.26, 131.42, 130.44, 128.96, 127.68, 127.22, 122.63, 108.42, 81.41, 62.40, 26.07, 22.26, 21.99, 19.10, 13.96. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH/MeOH = 94:4:2, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 8.2 min, minor enantiomer tr = 8.8 min). HRMS (ESI) *m/z* calculated for $[C_{23}H_{22}BrNO_3+Na]^+$ $[M+Na]^+$ 462.0675, found: 462.0672.



(*R*)-Ethyl 2-(4-Methoxyphenyl)-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6r). Yellow liquid (67% yield); TLC R_f = 0.22 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.22 (comp, 3H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.93-6.91 (comp, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.21 (q, *J* = 7.0 Hz, 2H), 3.80 (s, 3H), 2.53-2.49 (m, 1H), 2.44-2.33 (comp, 2H), 2.28-2.24 (m, 1H), 1.85-1.75 (comp, 4H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.85, 175.66, 166.89, 159.50, 137.72, 130.15, 128.73, 128.39, 127.49, 127.17, 113.74, 107.77, 81.83, 62.25, 55.28, 25.93, 22.26, 22.10, 19.15, 14.02. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH/MeOH = 90:8:2, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 10.7 min, minor enantiomer tr = 11.8 min). HRMS (ESI) *m/z* calculated for $[C_{24}H_{25}NO_4+Na]^+$ $[M+Na]^+$ 414.1676, found: 414.1675.

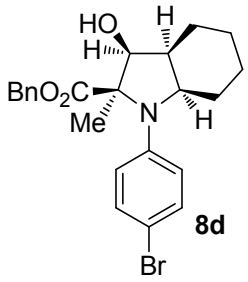


(*R*)-Ethyl 2-(Naphthalen-2-yl)-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6s). Yellow solid (61% yield); mp = 162.6-165.5 °C; TLC R_f = 0.33(3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.80 (d, *J* = 9.0 Hz, 2H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.50-7.46 (comp, 2H), 7.22-7.19 (comp, 4H), 6.96-6.94 (comp, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 2.61-2.56 (m, 1H), 2.48-2.31 (comp, 3H), 1.89-1.87 (m, 1H), 1.81-1.78 (comp, 3H), 1.19 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.73, 175.85, 166.73, 137.79, 133.12, 133.00, 132.69, 128.80, 128.49, 128.19, 127.77, 127.44, 127.19, 126.45, 126.34, 126.01, 108.22, 82.17, 77.30, 77.05, 76.80, 62.34, 26.02, 22.31, 22.09, 19.20, 14.03. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH = 90:10, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 9.6 min, minor enantiomer tr = 12.0 min). HRMS (ESI) *m/z* calculated for $[C_{27}H_{25}NO_3+Na]^+$ $[M+Na]^+$ 434.1726, found: 434.1721.



6t

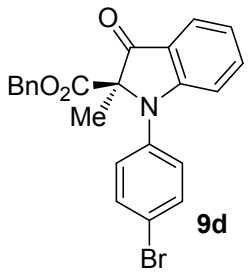
(*R*)-Ethyl 3-Oxo-1-phenyl-2-(thiophen-2-yl)-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6t). Yellow liquid (72% yield); TLC R_f = 0.34 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.25 (comp, 4H), 7.04 (dd, *J* = 4.0 Hz, 1.0 Hz, 1H), 7.00-6.98 (comp, 2H), 6.94 (dd, *J* = 4.0 Hz, 1.0 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 2.53-2.50 (m, 1H), 2.39-2.34 (comp, 3H), 1.83-1.76 (comp, 4H), 1.21 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.93, 175.62, 165.90, 137.61, 136.53, 128.93, 128.09, 127.51, 127.20, 126.31, 126.28, 107.16, 78.49, 62.60, 26.12, 22.27, 22.02, 19.16, 14.00. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH/MeOH = 90:8:2, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 9.1 min, minor enantiomer tr = 9.8 min). HRMS (ESI) *m/z* calculated for $[C_{21}H_{21}NO_3S+Na]^+$ $[M+Na]^+$ 390.1134, found: 390.1129.



8d

(2*R*,3*S*,3a*S*,7a*R*)-Benzyl 1-(4-Bromophenyl)-3-hydroxy-2-methyloctahydro-1*H*-indole-2-carboxylate (8d). White solid (81% yield); mp = 43.0-45.3 °C; TLC R_f = 0.20 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.28 (comp, 5H), 7.19 (d, *J* = 9.0 Hz, 2H), 6.37 (d, J = 9.0 Hz, 2H), 5.26 (d, *J* = 12.0 Hz, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 4.20-4.18 (t, *J* = 6.0 Hz, 1H), 3.91-3.87 (m, 1H), 2.46-2.40 (m, 1H), 2.31 (d, *J* = 7.0 Hz, 1H), 2.18-2.15 (m, 1H), 1.95-1.92 (m, 1H), 1.74-1.51 (comp, 8H), 1.23-1.20 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.29, 143.07, 135.46, 131.46, 128.50, 128.31, 128.27, 116.36, 108.36, 85.46, 72.64, 67.23, 58.77, 38.10, 27.21, 23.43, 22.31, 20.86. Enantiomeric excess: 99% (Diacel Chirapak OD-H, hexanes/i-PrOH = 95:5, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 8.4 min, minor enantiomer tr = 9.5

min). HRMS (ESI) *m/z* calculated for $[C_{23}H_{26}BrNO_3S+Na]^+$ $[M+Na]^+$ 466.0988, found: 466.0990.



9d

(*R*)-Benzyl 1-(4-Bromophenyl)-2-methyl-3-oxoindoline-2-carboxylate (9d). Yellow solid (65% yield); mp = 63.7-64.8 °C; TLC R_f =0.22 (3:1 hexanes/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.50-7.46 (m, 1H), 7.40 (d, *J* = 9.0 Hz, 2H), 7.34-7.32 (comp, 3H), 7.23-7.21 (comp, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 6.94-6.91 (comp, 2H), 5.24 (d, *J* = 12.5 Hz, 1H), 5.06 (d, *J* = 12.5 Hz, 1H), 1.60 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.36, 167.80, 159.30, 137.85, 137.61, 135.00, 132.83, 128.54, 128.44, 128.31, 127.28, 125.62, 119.93, 119.78, 111.35, 74.85, 67.72, 19.05. Enantiomeric excess: 98% (Diacel Chirapak AD-H, hexanes/i-PrOH = 90:10, flow rate 1.0 mL/min, 254 nm, major enantiomer tr = 10.2 min, minor enantiomer tr = 10.9 min). HRMS (ESI) *m/z* calculated for $[C_{23}H_{18}BrNO_3+Na]^+$ $[M+Na]^+$ 458.0368, found: 458.0366.

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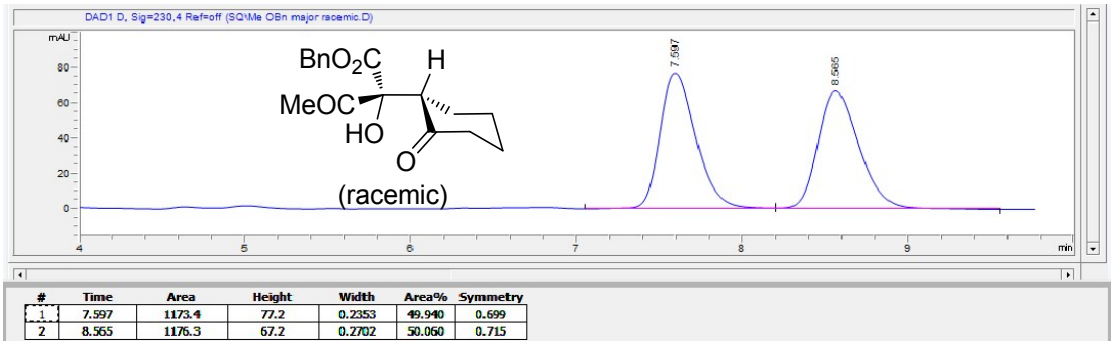
3. H. Wang, S. B. Ren, J. Zhang, W. Zhang and Y. K. Liu, *J. Org. Chem*., 2005, **80**, 6856.

4. H. Asahara and N. Nishiwaki, *J. Org. Chem*., 2014, **79**, 11735.

HPLC spectra of products 3a-m, 4a-m, 6a-t, 7d.

(*R*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (3a).



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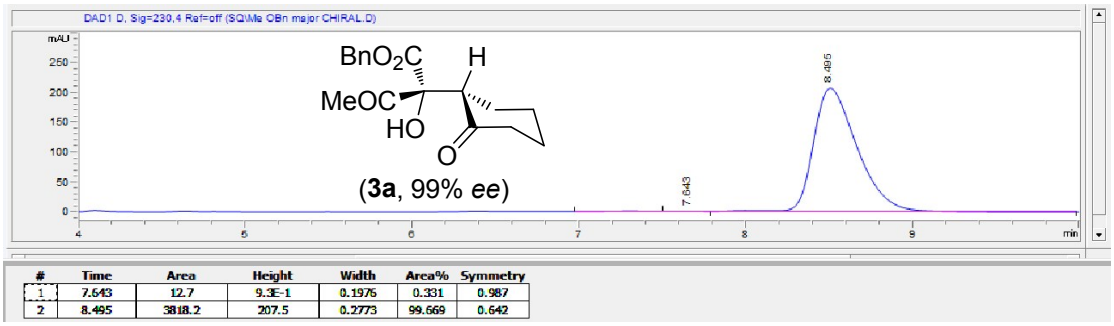

#	Time	Area	Height	Width	Area%	Symmetry
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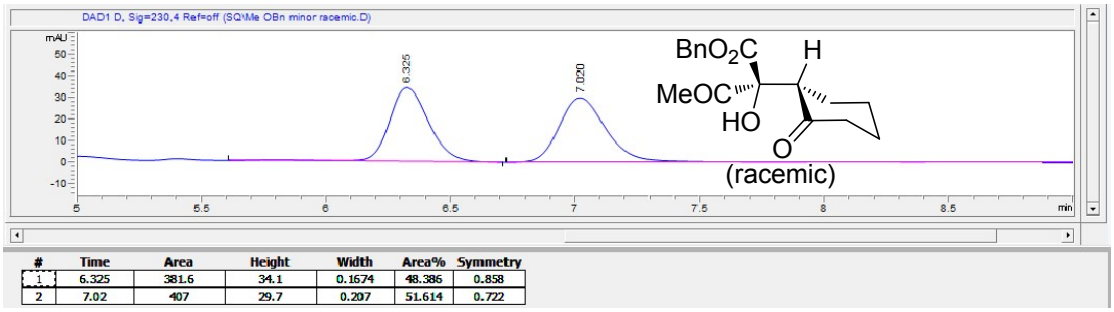
2	8.495	3818.2	207.5	0.2773	99.669	0.642

(*S*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (4a).



#	Time	Area	Height	Width	Area%	Symmetry
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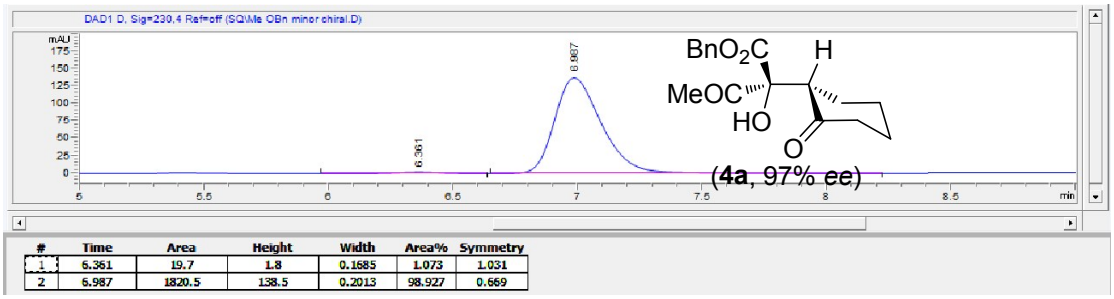

#	Time	Area	Height	Width	Area%	Symmetry
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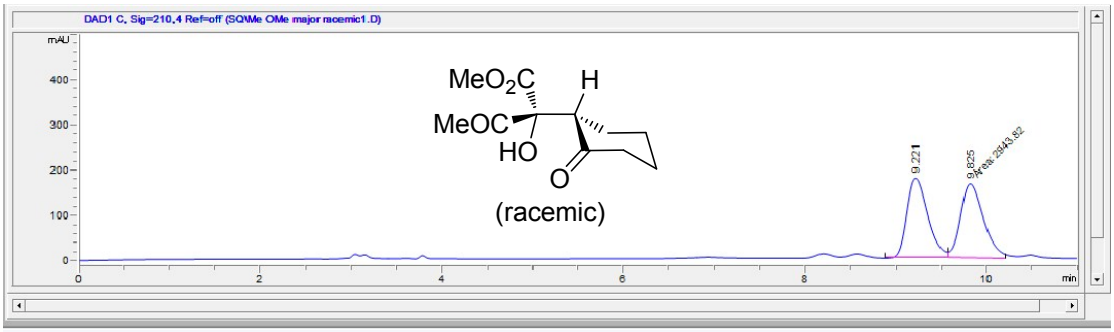
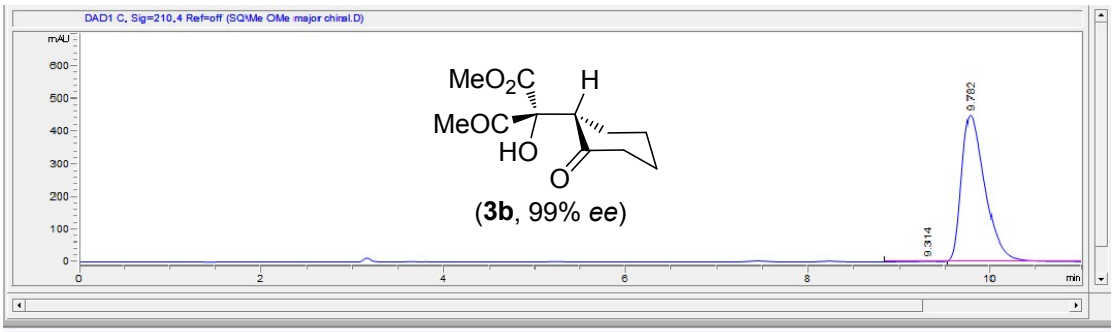
2	6.987	1820.5	138.5	0.2013	98.927	0.669

(*R*)-Methyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (3b).

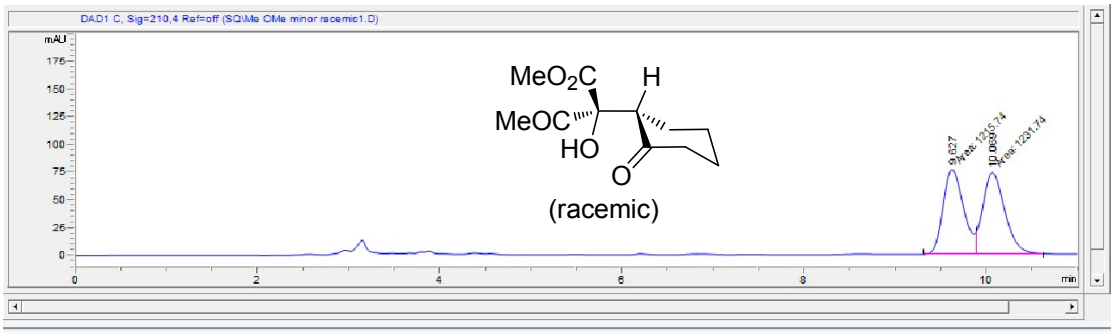


#	Time	Area	Height	Width	Area%	Symmetry
1	9.221	2852	176.7	0.2483	49.208	0.678
2	9.825	2943.8	165	0.2974	50.792	0.722

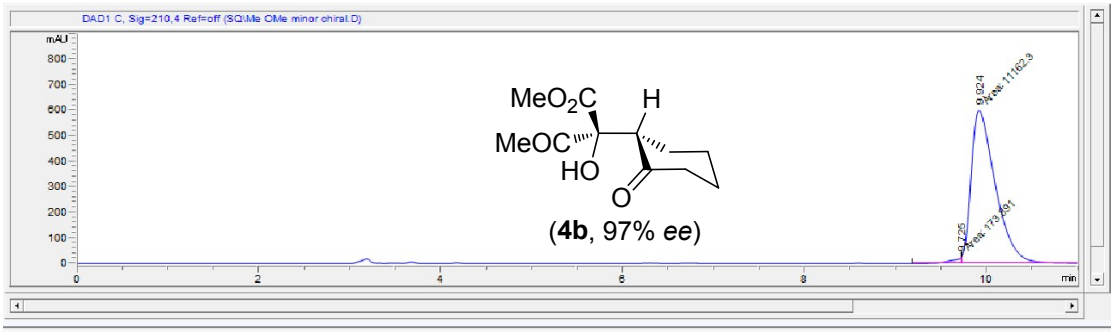


#	Time	Area	Height	Width	Area%	Symmetry
1	9.314	37.8	1.8	0.2877	0.461	2.026
2	9.782	8165.1	446.6	0.2773	99.539	0.569

(*S*)-Methyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (4b).

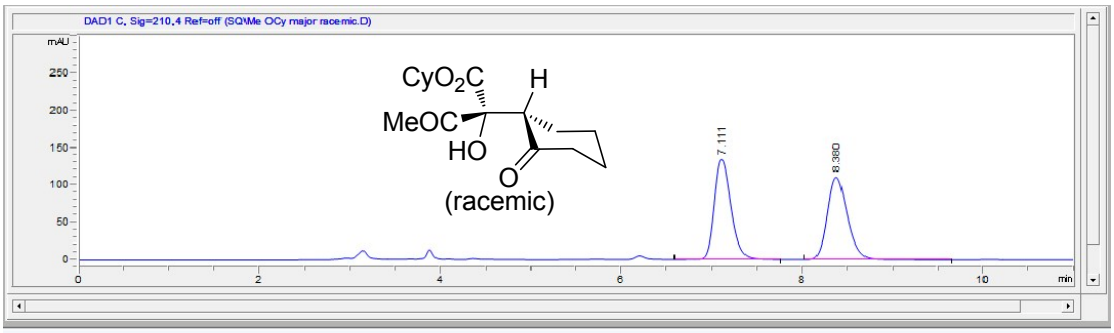


#	Time	Area	Height	Width	Area%	Symmetry
1	9.627	1215.7	76.5	0.2648	49.673	0
2	10.069	1231.7	73.5	0.2794	50.327	0.726

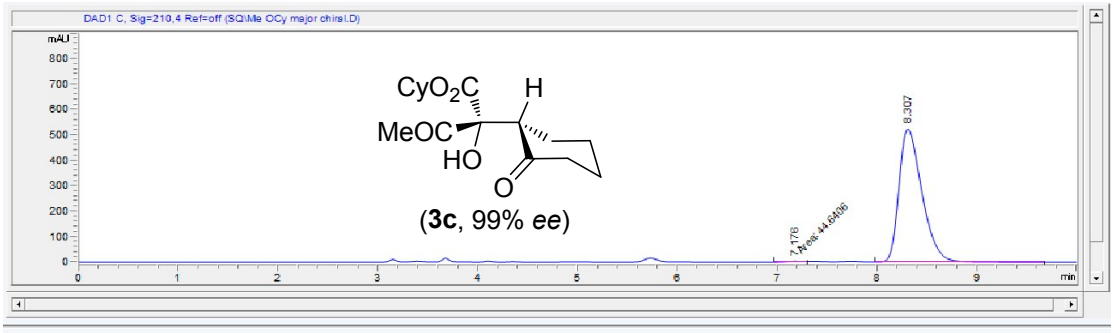


#	Time	Area	Height	Width	Area%	Symmetry
1	9.725	173.9	24.5	0.1184	1.534	354.874
2	9.924	11162.3	599.1	0.3105	98.466	0.487

(*R*)-Cyclohexyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (3c).

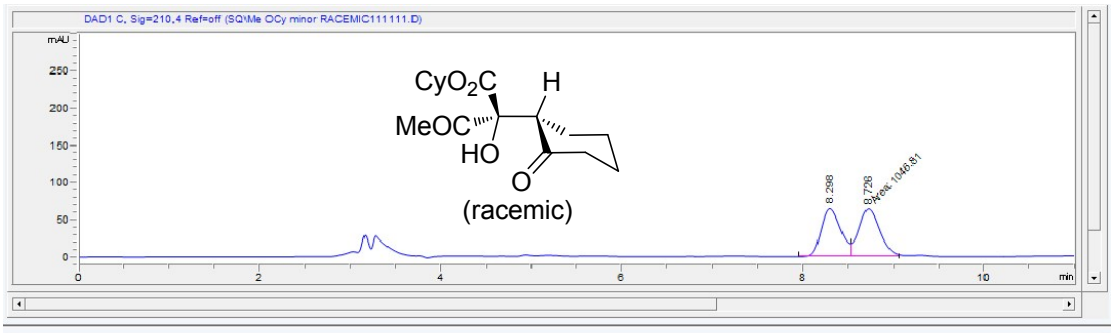


#	Time	Area	Height	Width	Area%	Symmetry
1	7.111	1717.4	134.2	0.1953	50.000	0.737
2	8.38	1717.4	110.5	0.2414	50.000	0.76

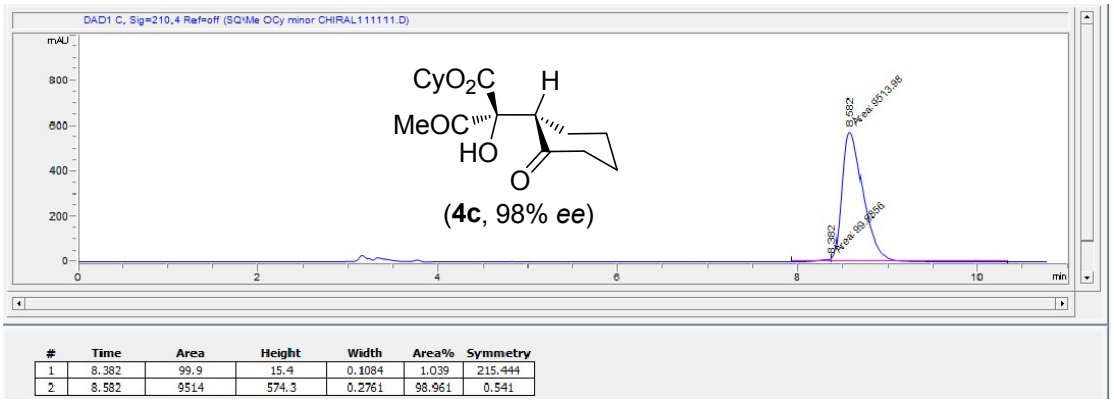


#	Time	Area	Height	Width	Area%	Symmetry
1	7.176	44.6	3.4	0.2159	0.529	1.016
2	8.307	8389.8	524.2	0.2447	99.471	0.601

(*S*)-Cyclohexyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (4c).

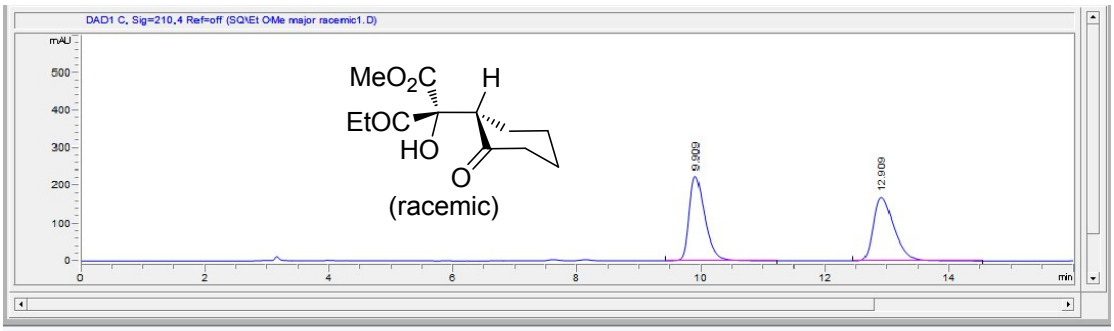


#	Time	Area	Height	Width	Area%	Symmetry
1	8.298	969.8	64.4	0.2338	48.090	0.777
2	8.726	1046.8	64.1	0.2721	51.910	0.827

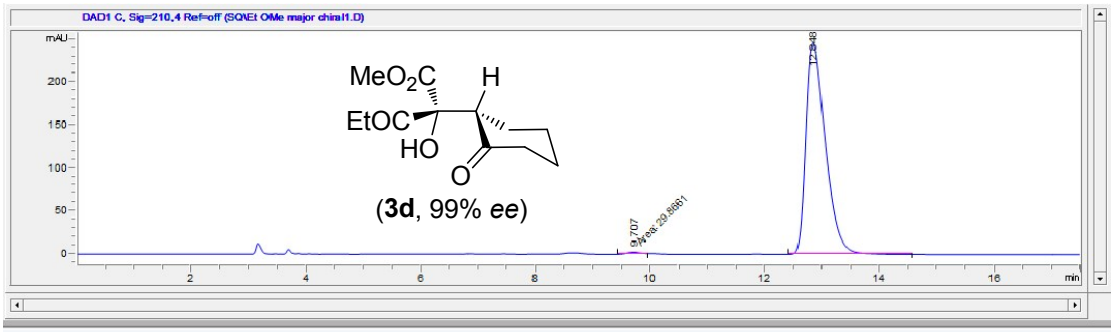


#	Time	Area	Height	Width	Area%	Symmetry
1	8.382	99.9	15.4	0.1084	1.039	215.444
2	8.582	9514	574.3	0.2761	98.961	0.541

(*R*)-Methyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]pentanoate (3d).

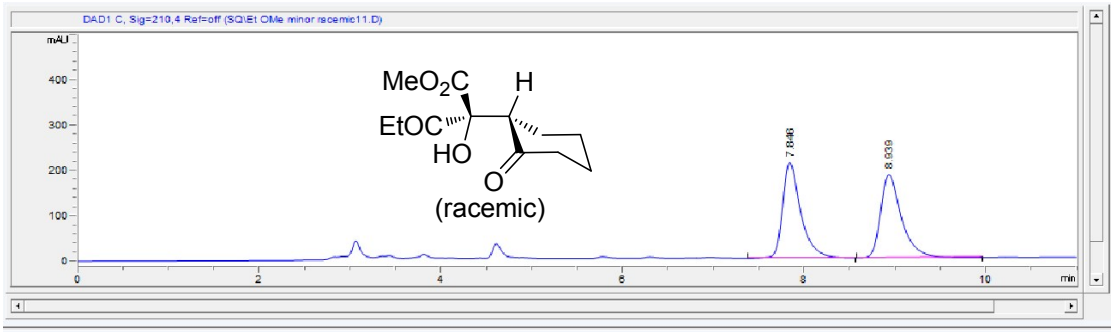


#	Time	Area	Height	Width	Area%	Symmetry
1	9.909	4022	225.9	0.2697	50.345	0.603
2	12.909	3966.9	170.4	0.3556	49.655	0.597

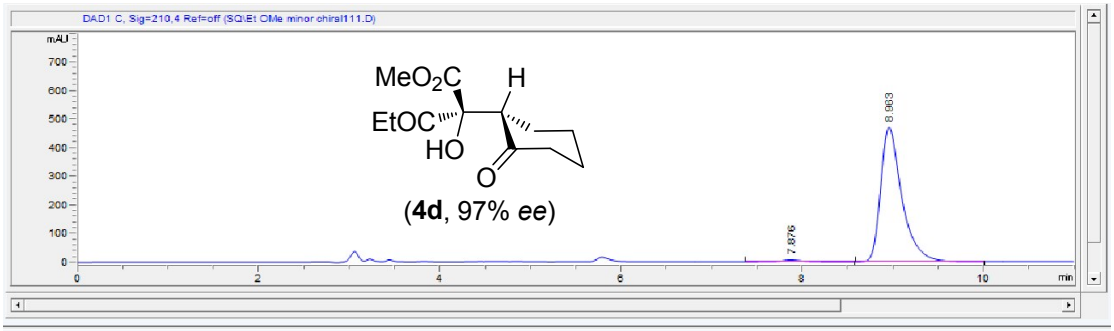


#	Time	Area	Height	Width	Area%	Symmetry
1	9.707	29.9	2.1	0.2394	0.509	1.07
2	12.848	5832.3	246.2	0.3624	99.491	0.542

(*S*)-Methyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]pentanoate (4d).

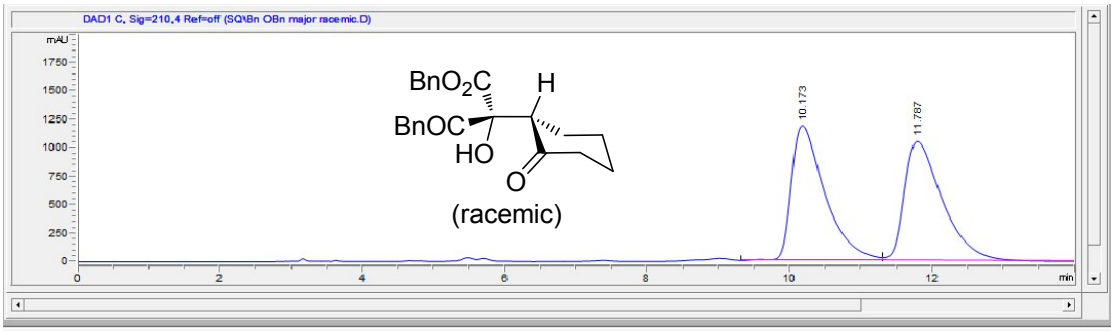


#	Time	Area	Height	Width	Area%	Symmetry
1	7.846	2940.4	210.8	0.2067	50.179	0.613
2	8.939	2919.4	183	0.2381	49.821	0.613

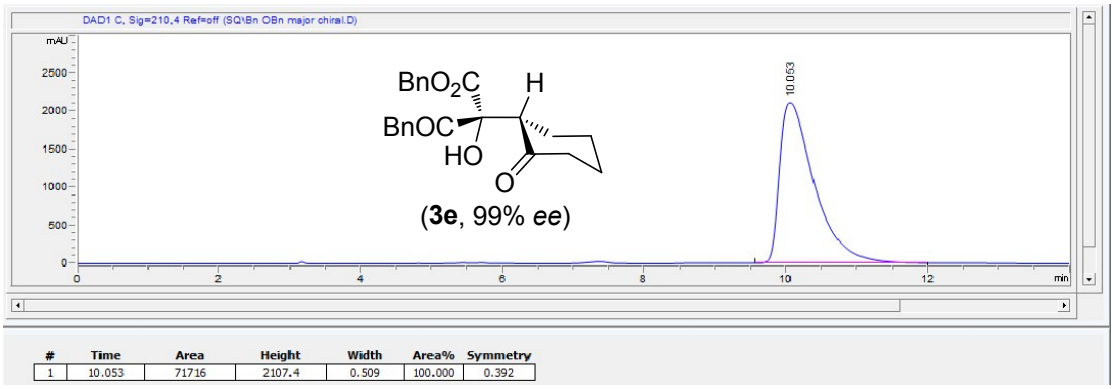


#	Time	Area	Height	Width	Area%	Symmetry
1	7.876	113.5	6.9	0.235	1.463	0.926
2	8.963	7648.1	472.6	0.2408	98.537	0.603

(*R*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-4-phenylbutanoate (3e).

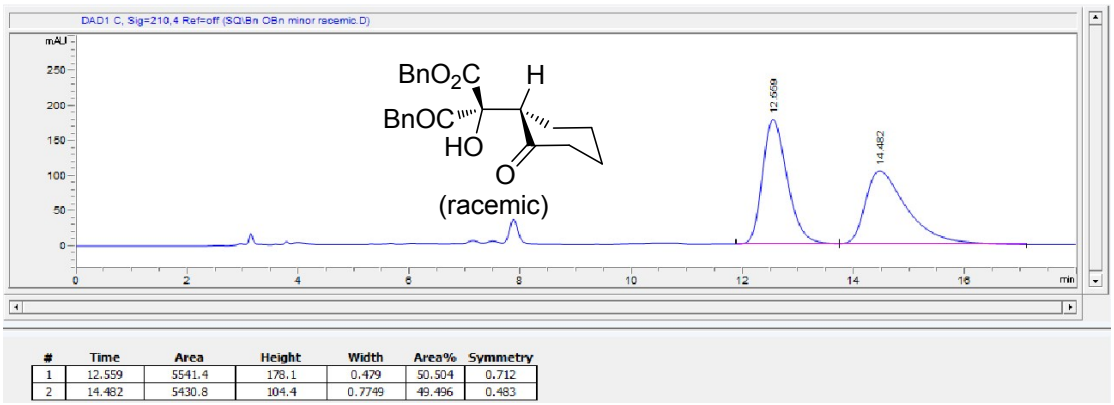


#	Time	Area	Height	Width	Area%	Symmetry
1	10.173	39229.2	1186.3	0.4904	49.875	0.46
2	11.787	39426.1	1049.5	0.5643	50.125	0.483

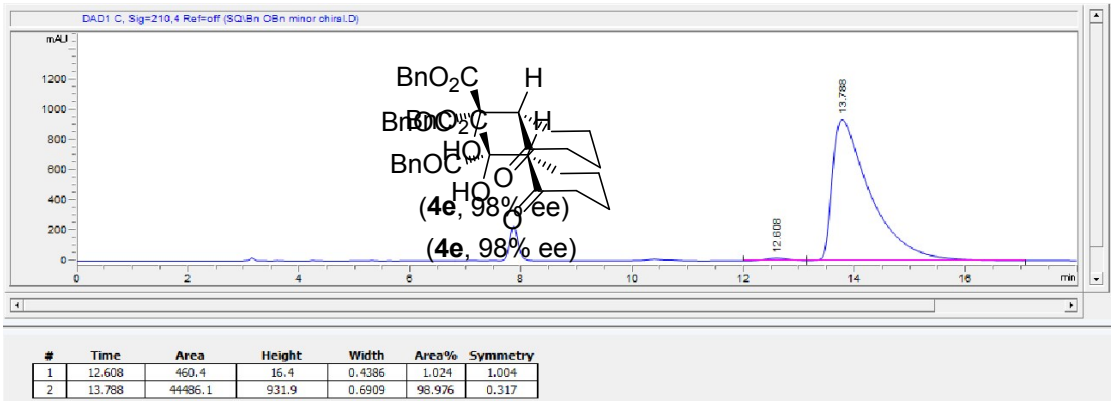


#	Time	Area	Height	Width	Area%	Symmetry
1	10.053	71716	2107.4	0.509	100.000	0.392

(*S*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-4-phenylbutanoate (4e).

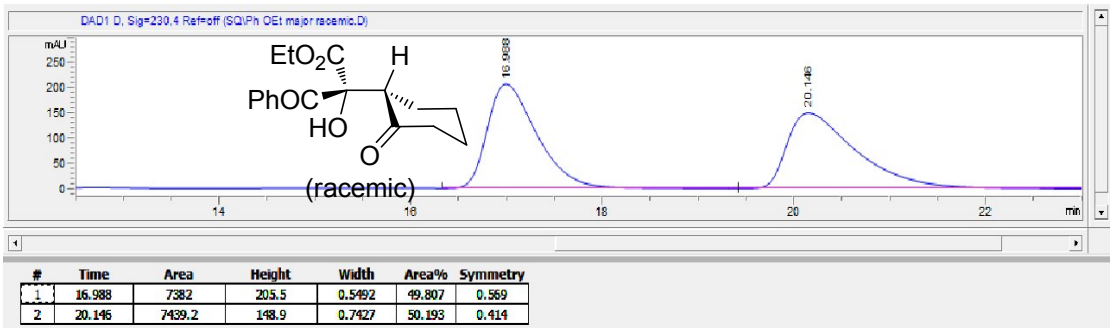


#	Time	Area	Height	Width	Area%	Symmetry
1	12.559	5541.4	178.1	0.479	50.504	0.712
2	14.482	5430.8	104.4	0.7749	49.496	0.483

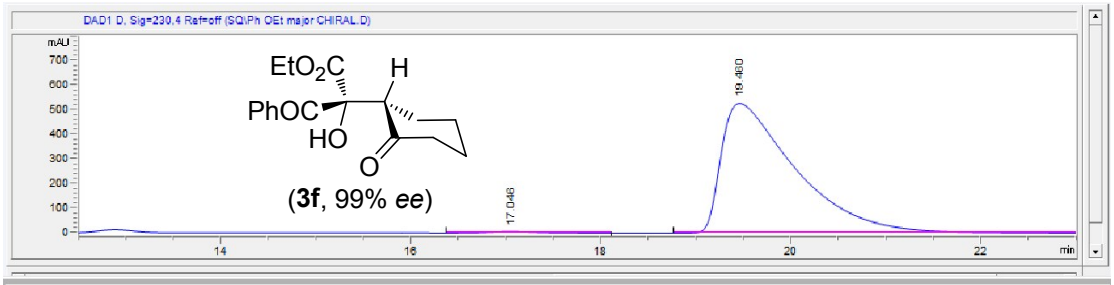


#	Time	Area	Height	Width	Area%	Symmetry
1	12.608	460.4	16.4	0.4386	1.024	1.004
2	13.788	44486.1	931.9	0.6909	98.976	0.317

(*R*)-Ethyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-3-phenylpropanoate (3f).

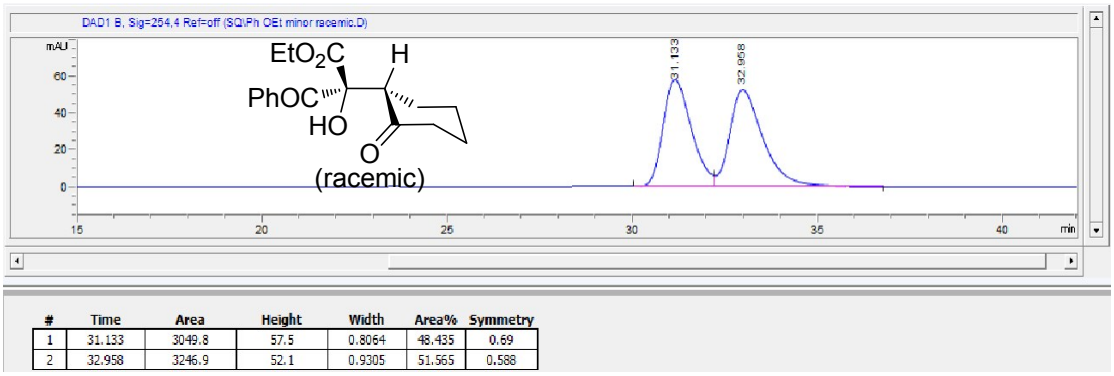


#	Time	Area	Height	Width	Area%	Symmetry
1	16.988	7382	205.5	0.5492	49.807	0.569
2	20.146	7439.2	148.9	0.7427	50.193	0.414

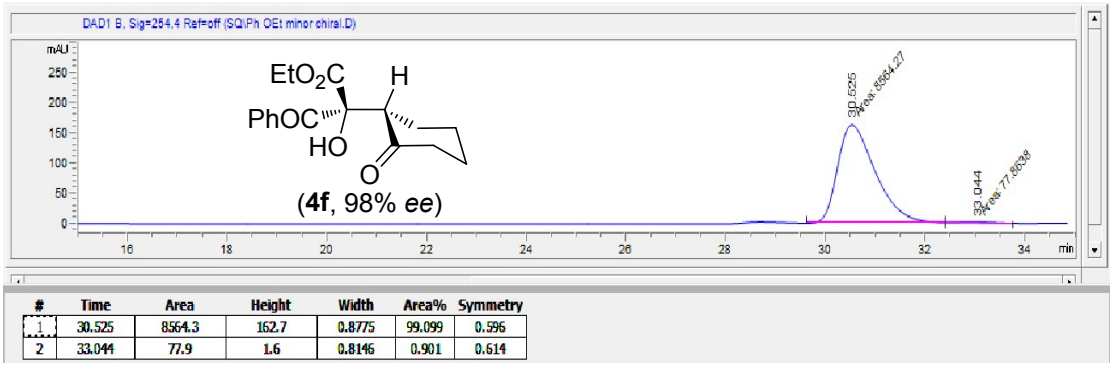


#	Time	Area	Height	Width	Area%	Symmetry
1	17.046	182.8	5.4	0.5139	0.628	0.814
2	19.46	28899	532.4	0.7912	99.372	0.301

(*S*)-Ethyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-3-phenylpropanoate (4f).

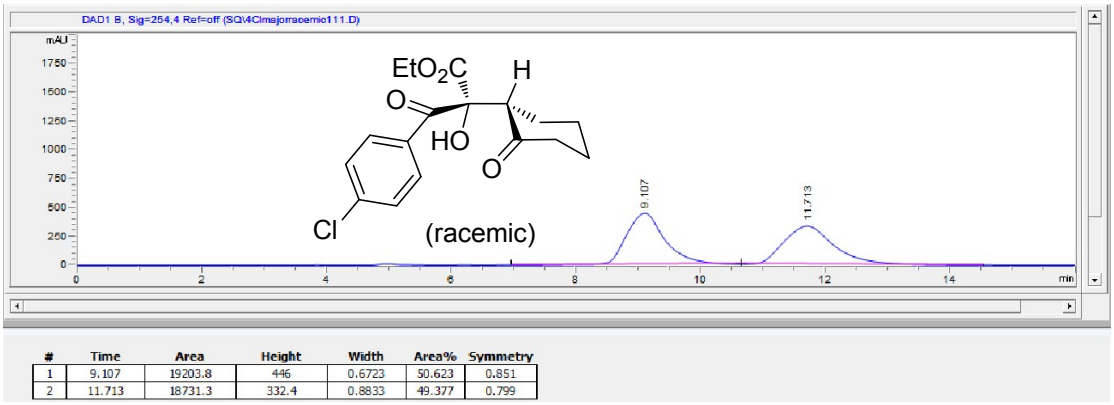


#	Time	Area	Height	Width	Area%	Symmetry
1	31.133	3049.8	57.5	0.8064	48.435	0.69
2	32.958	3246.9	52.1	0.9305	51.565	0.588

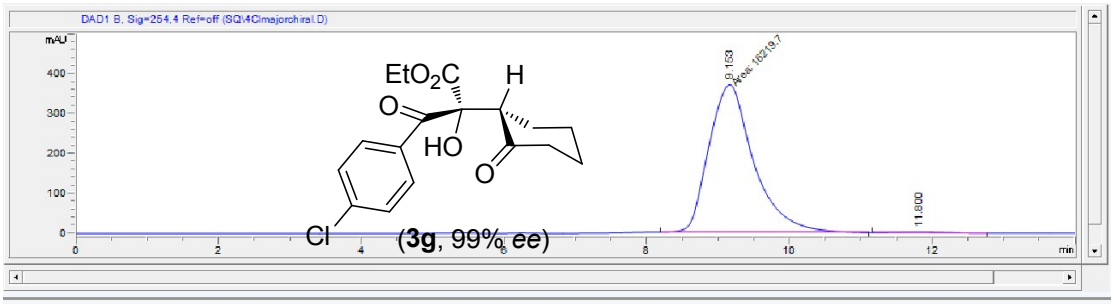


#	Time	Area	Height	Width	Area%	Symmetry
1	30.525	8564.3	162.7	0.8775	99.099	0.596
2	33.044	77.9	1.6	0.8146	0.901	0.614

(*R*)-Ethyl 3-(4-Chlorophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3g).

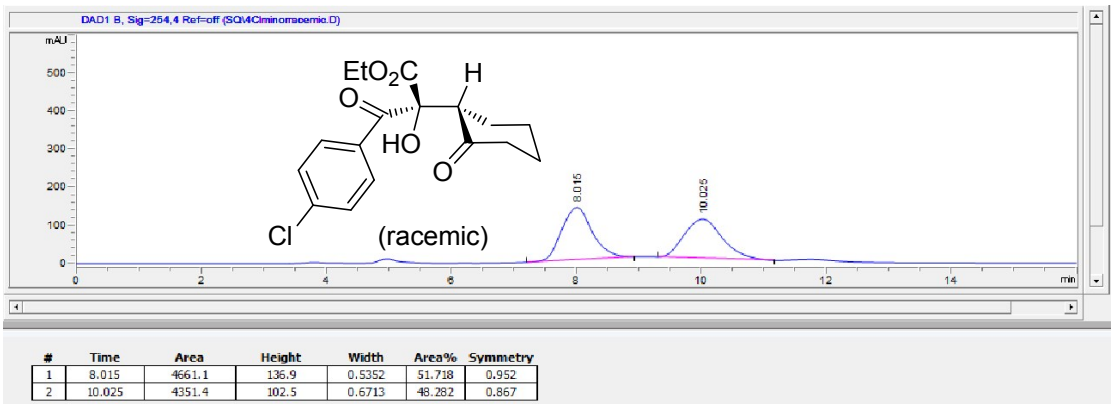


#	Time	Area	Height	Width	Area%	Symmetry
1	9.107	19203.8	446	0.6723	50.623	0.851
2	11.713	18731.3	332.4	0.8833	49.377	0.799

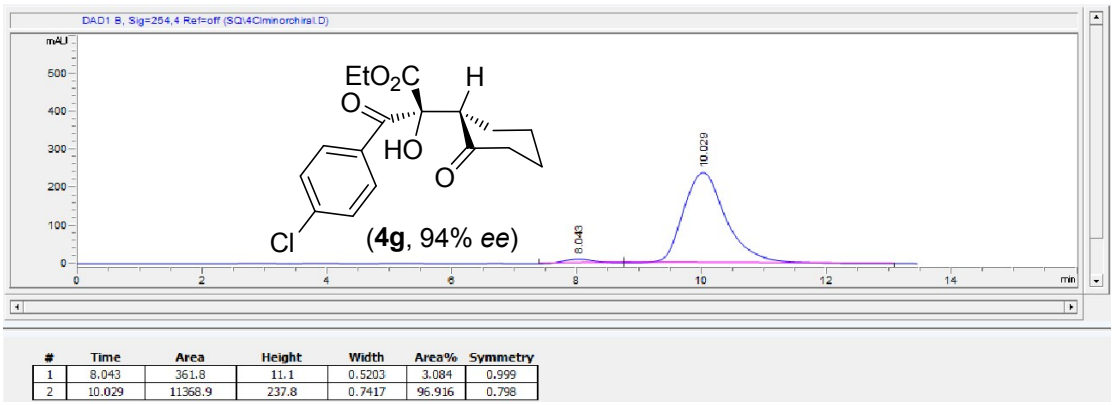


#	Time	Area	Height	Width	Area%	Symmetry
1	9.153	16219.7	371.3	0.7281	99.415	0.819
2	11.8	95.4	2.2	0.5379	0.585	0.779

(*S*)-Ethyl 3-(4-Chlorophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4g).

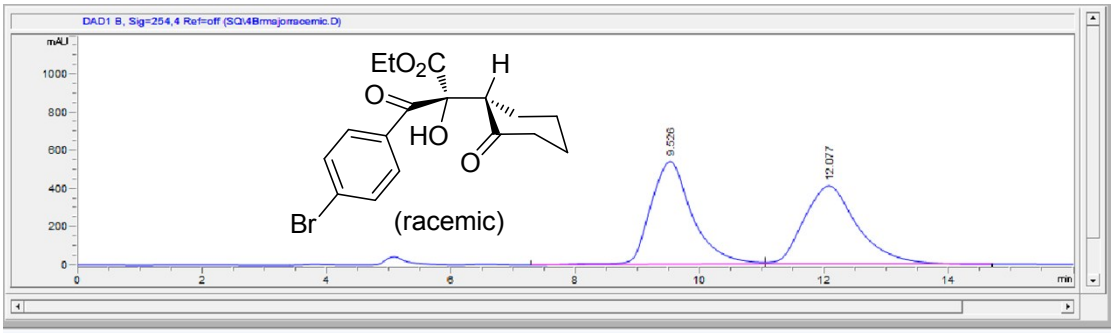


#	Time	Area	Height	Width	Area%	Symmetry
1	8.015	4661.1	136.9	0.5352	51.718	0.952
2	10.025	4351.4	102.5	0.6713	48.282	0.867

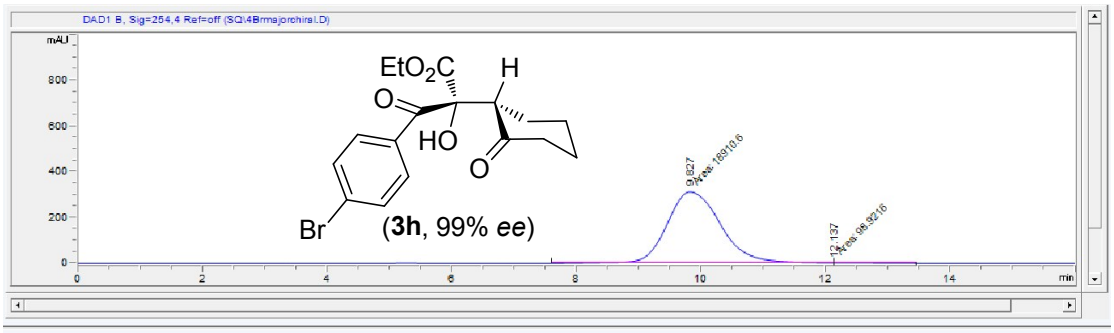


#	Time	Area	Height	Width	Area%	Symmetry
1	8.043	361.8	11.1	0.5203	3.084	0.999
2	10.029	11368.9	237.8	0.7417	96.916	0.798

(*R*)-Ethyl 3-(4-Bromophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3h).

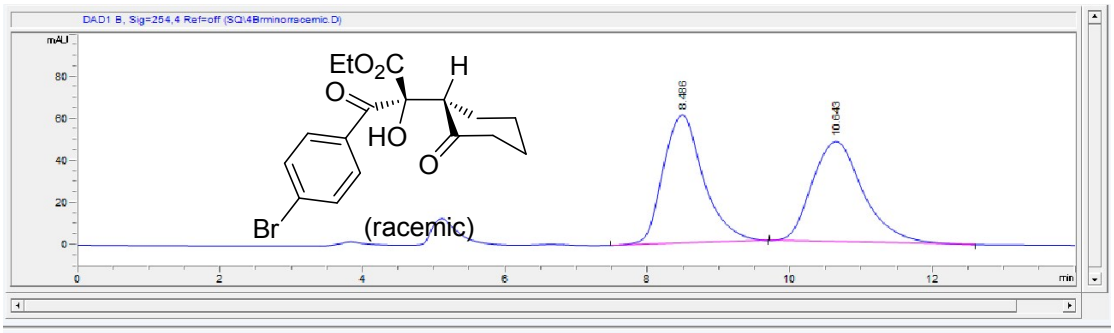


#	Time	Area	Height	Width	Area%	Symmetry
1	9.526	25498.6	541.1	0.7298	50.642	0.828
2	12.077	24852.4	412.1	0.9376	49.358	0.807

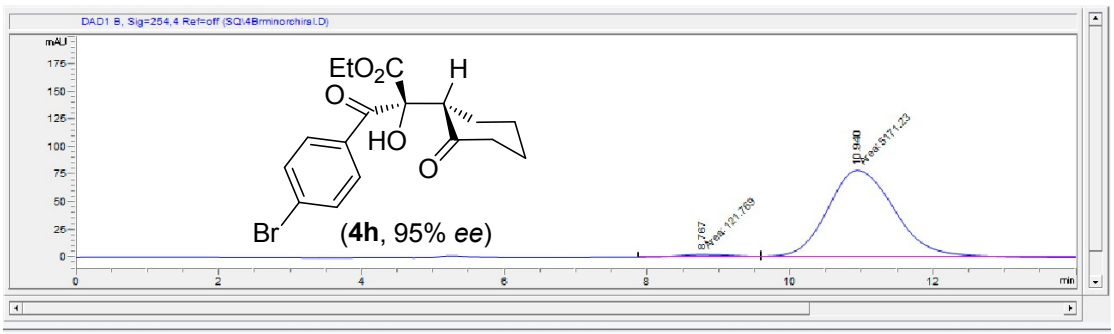


#	Time	Area	Height	Width	Area%	Symmetry
1	9.827	18910.6	313.8	1.0044	99.480	0.736
2	12.137	98.9	2.1	0.7824	0.520	0

(*S*)-Ethyl 3-(4-Bromophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4h).

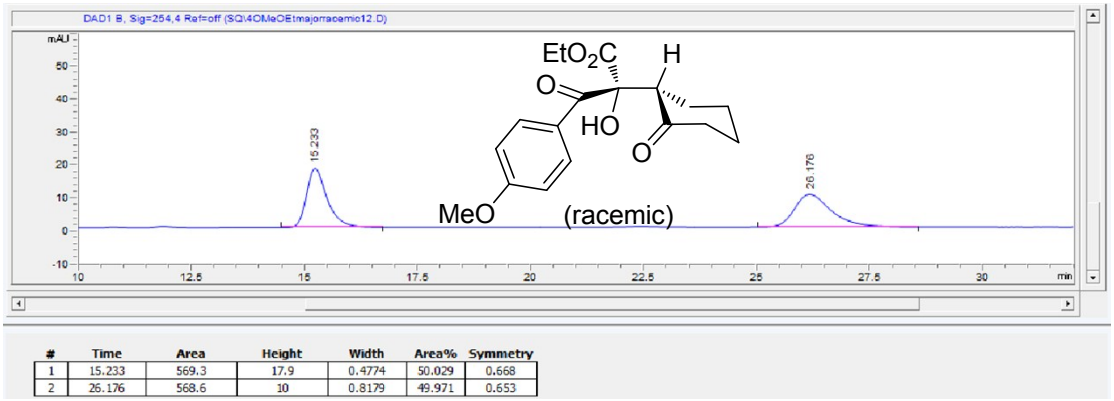


#	Time	Area	Height	Width	Area%	Symmetry
1	8.486	2402.2	61.1	0.6105	50.166	0.841
2	10.643	2386.3	47.7	0.7771	49.834	0.812

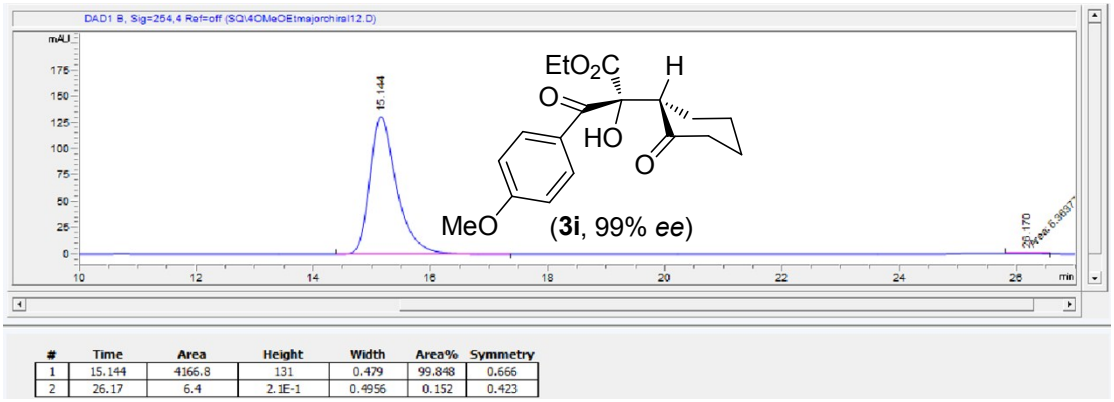


#	Time	Area	Height	Width	Area%	Symmetry
1	8.767	121.8	2.1	0.9462	2.301	0
2	10.94	5171.2	78.6	1.0961	97.699	0.79

(*R*)-Ethyl 2-Hydroxy-3-(4-methoxyphenyl)-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3i).

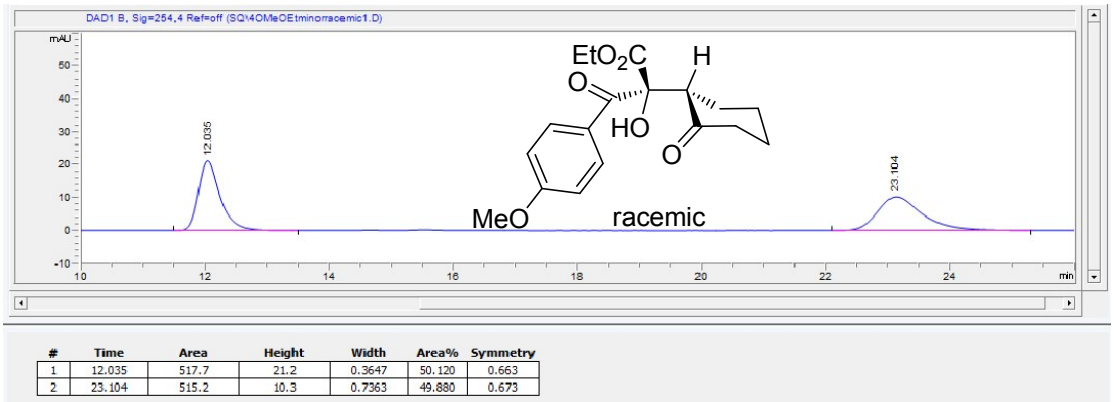


#	Time	Area	Height	Width	Area%	Symmetry
1	15.233	569.3	17.9	0.4774	50.029	0.668
2	26.176	568.6	10	0.8179	49.971	0.653

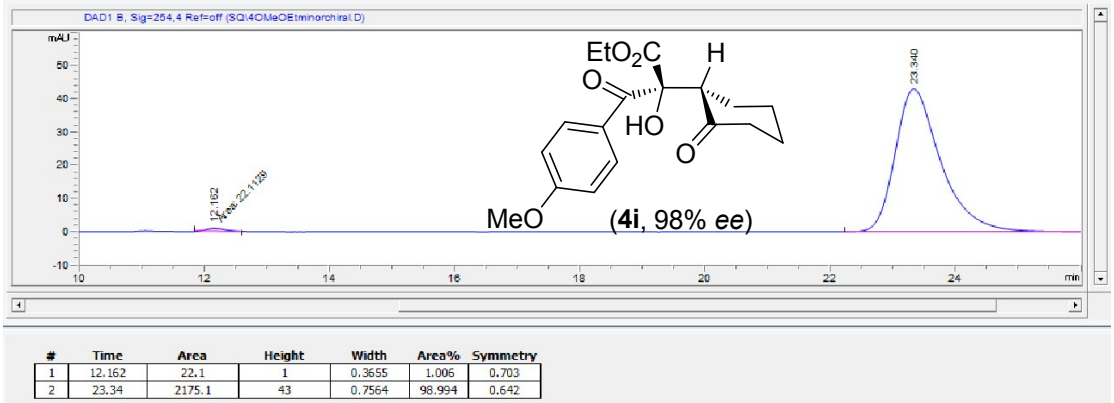


#	Time	Area	Height	Width	Area%	Symmetry
1	15.144	4166.8	131	0.479	99.848	0.666
2	26.17	6.4	2.1E-1	0.4956	0.152	0.423

(*S*)-Ethyl 2-Hydroxy-3-(4-methoxyphenyl)-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4i).

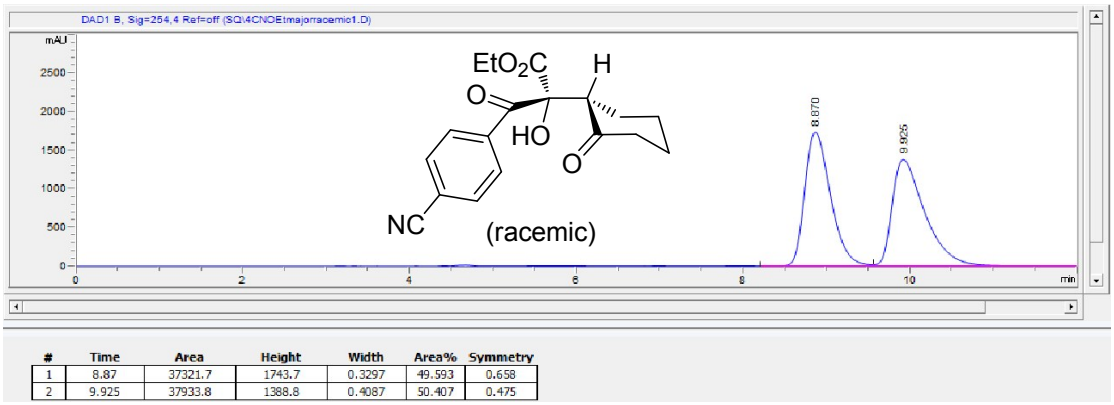


#	Time	Area	Height	Width	Area%	Symmetry
1	12.035	517.7	21.2	0.3647	50.120	0.663
2	23.104	515.2	10.3	0.7363	49.880	0.673

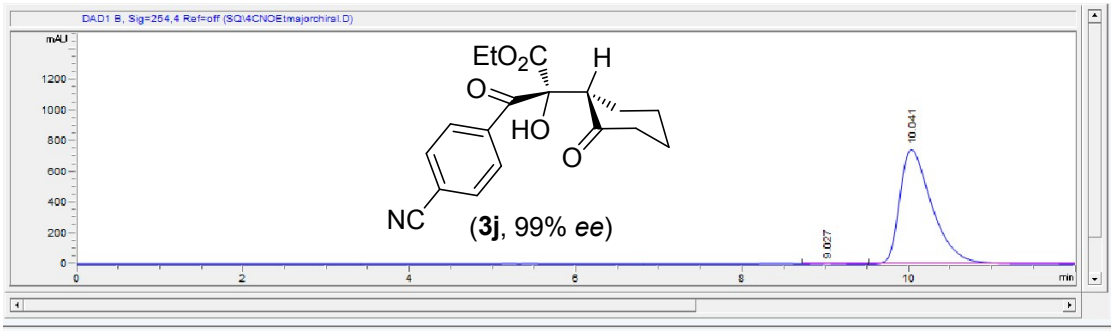


#	Time	Area	Height	Width	Area%	Symmetry
1	12.162	22.1	1	0.3655	1.006	0.703
2	23.34	2175.1	43	0.7564	98.994	0.642

(*R*)-Ethyl 3-(4-Cyanophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3j).

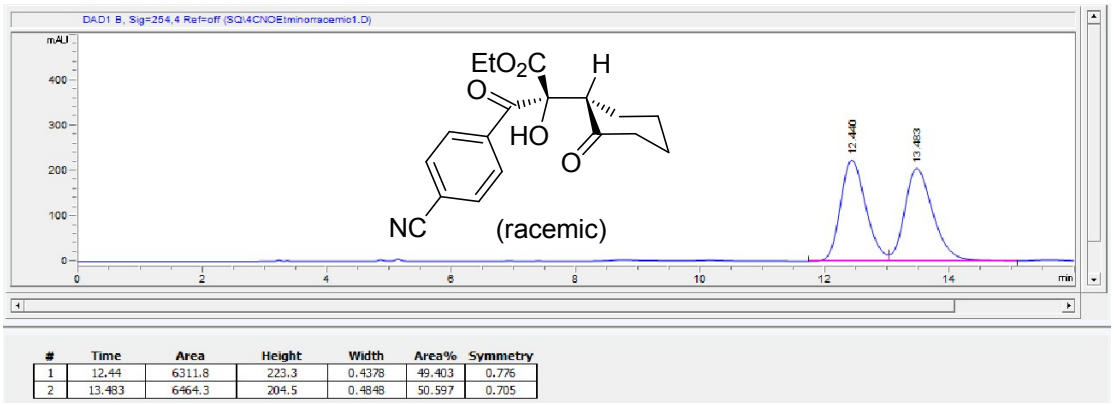


#	Time	Area	Height	Width	Area%	Symmetry
1	8.87	37321.7	1743.7	0.3297	49.593	0.658
2	9.925	37933.8	1388.8	0.4087	50.407	0.475

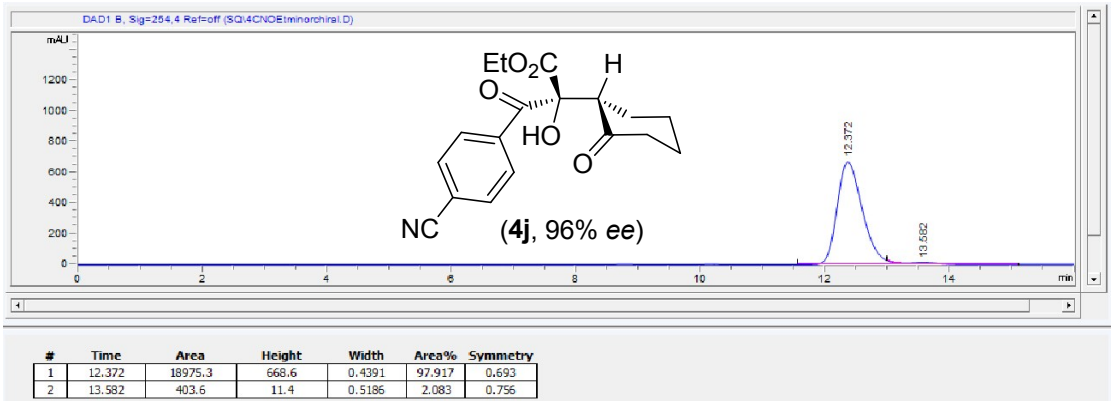


#	Time	Area	Height	Width	Area%	Symmetry
1	9.027	47	2.4	0.3008	0.232	0.786
2	10.041	20248.8	745.8	0.4108	99.768	0.525

(*S*)-Ethyl 3-(4-Cyanophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4j).

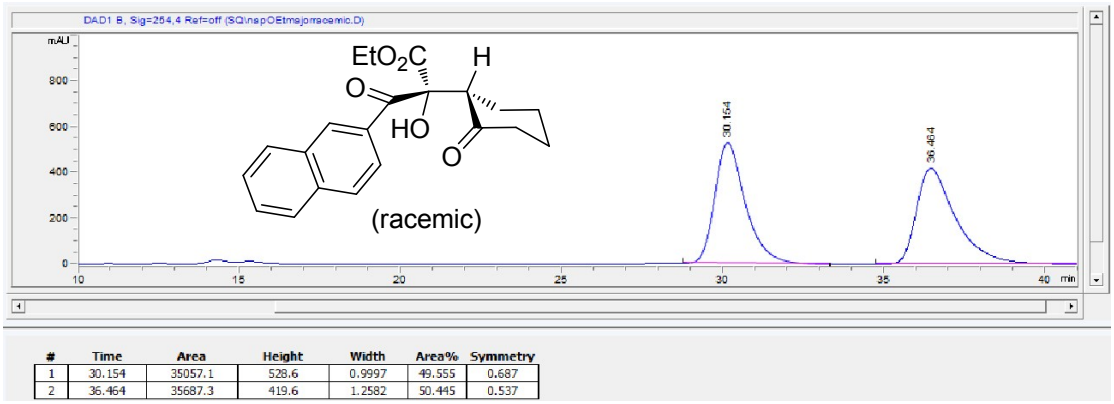


#	Time	Area	Height	Width	Area%	Symmetry
1	12.44	6311.8	223.3	0.4378	49.403	0.776
2	13.483	6464.3	204.5	0.4848	50.597	0.705

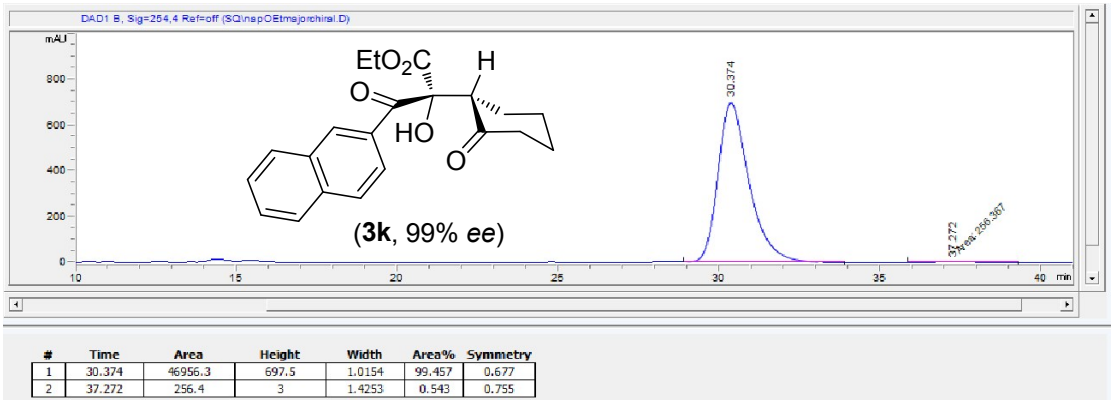


#	Time	Area	Height	Width	Area%	Symmetry
1	12.372	18975.3	668.6	0.4391	97.917	0.693
2	13.582	403.6	11.4	0.5186	2.083	0.756

(*R*)-Ethyl 2-Hydroxy-3-(naphthalen-2-yl)-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3k).

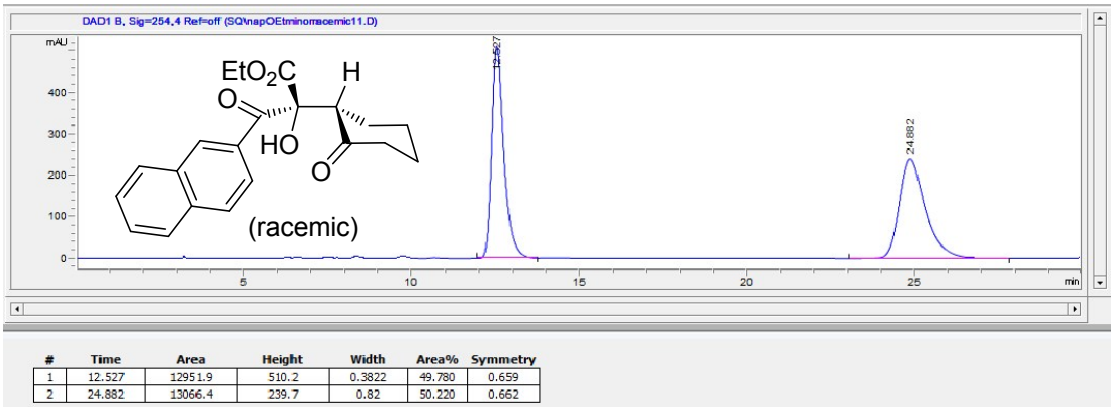


#	Time	Area	Height	Width	Area%	Symmetry
1	30.154	35057.1	528.6	0.9997	49.555	0.687
2	36.464	35687.3	419.6	1.2582	50.445	0.537

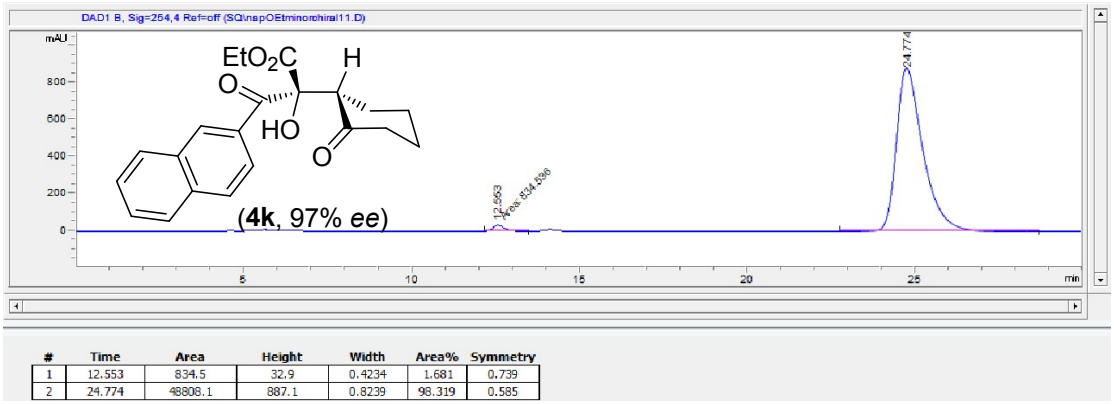


#	Time	Area	Height	Width	Area%	Symmetry
1	30.374	46956.3	697.5	1.0154	99.457	0.677
2	37.272	256.4	3	1.4253	0.543	0.755

(*S*)-Ethyl 2-Hydroxy-3-(naphthalen-2-yl)-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4k).

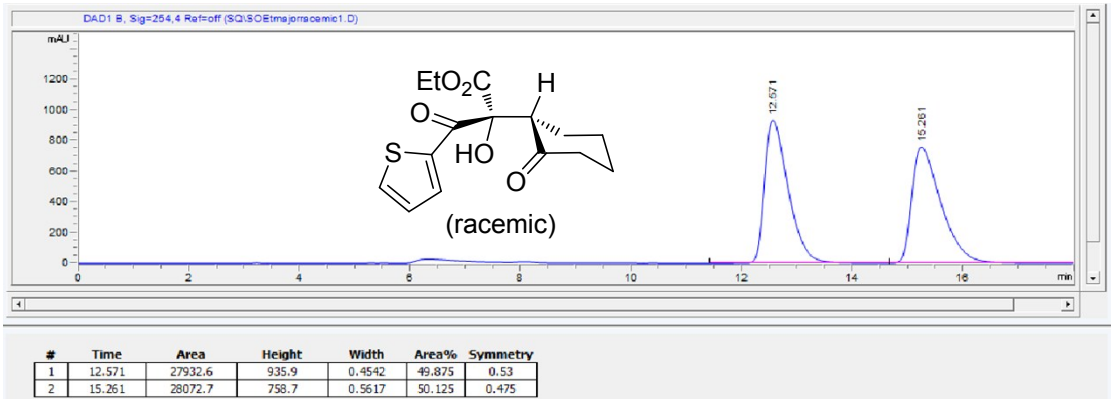


#	Time	Area	Height	Width	Area%	Symmetry
1	12.527	12951.9	510.2	0.3822	49.780	0.659
2	24.882	13066.4	239.7	0.82	50.220	0.662

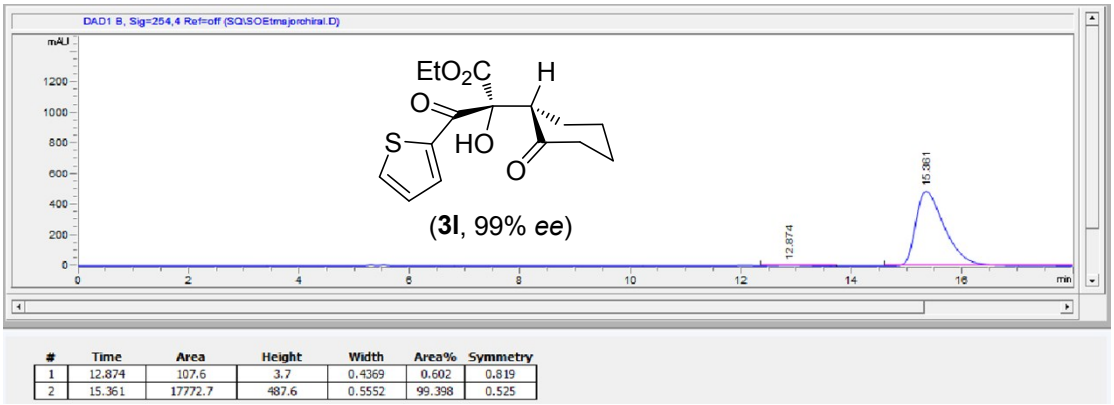


#	Time	Area	Height	Width	Area%	Symmetry
1	12.553	834.5	32.9	0.4234	1.681	0.739
2	24.774	48808.1	887.1	0.8239	98.319	0.585

(*R*)-Ethyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-3-(thiophen-2-yl)propanoate (3l).

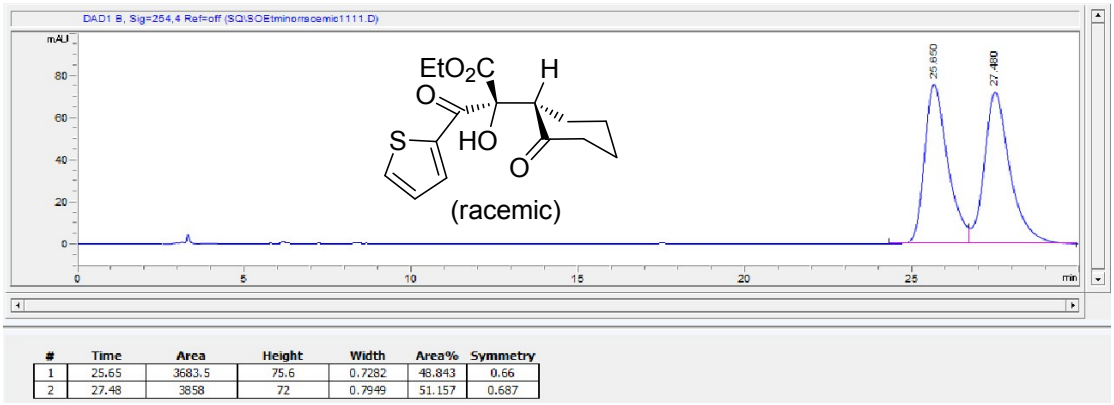


#	Time	Area	Height	Width	Area%	Symmetry
1	12.571	27932.6	935.9	0.4542	49.875	0.53
2	15.261	28072.7	758.7	0.5617	50.125	0.475

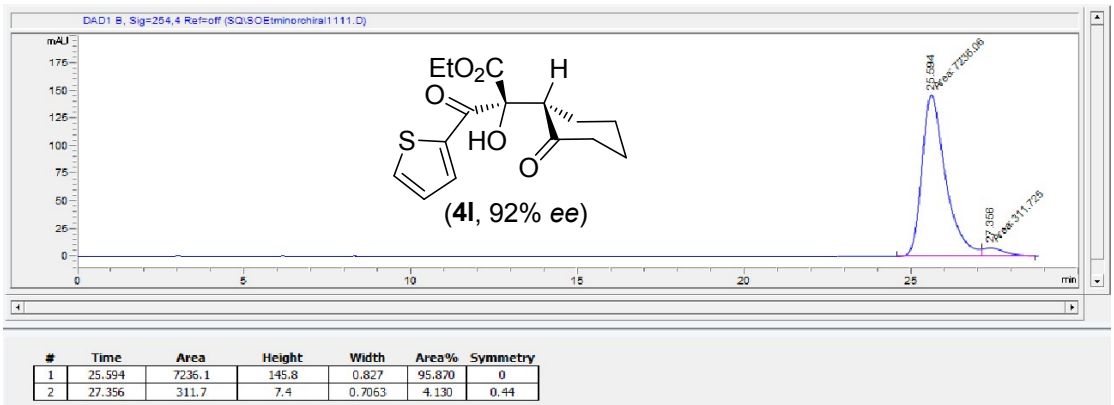


#	Time	Area	Height	Width	Area%	Symmetry
1	12.874	107.6	3.7	0.4369	0.602	0.819
2	15.361	17772.7	487.6	0.5552	99.398	0.525

(*S*)-Ethyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-3-(thiophen-2-yl)propanoate (4l).

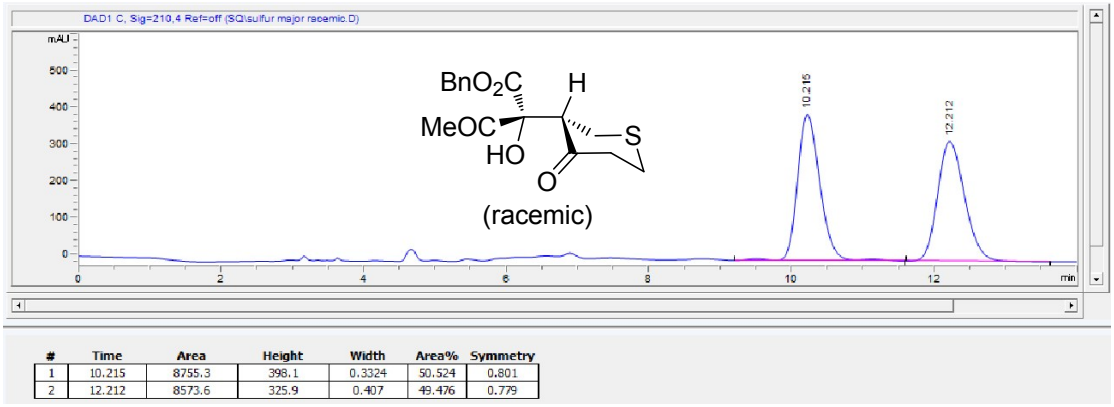


#	Time	Area	Height	Width	Area%	Symmetry
1	25.65	3683.5	75.6	0.7282	48.843	0.66
2	27.48	3858	72	0.7949	51.157	0.687

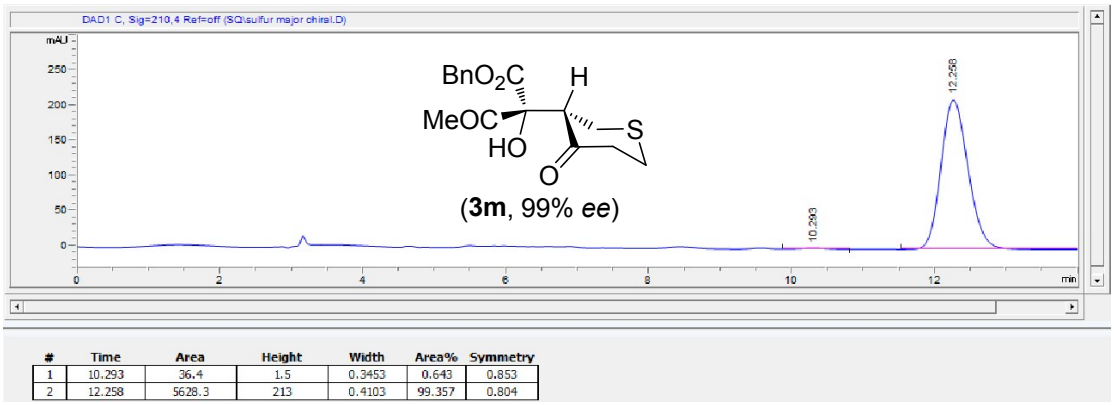


#	Time	Area	Height	Width	Area%	Symmetry
1	25.594	7236.1	145.8	0.827	95.870	0
2	27.356	311.7	7.4	0.7063	4.130	0.44

(*R*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-4-oxotetrahydro-2*H*-thiopyran-3-yl]butanoate (3m).

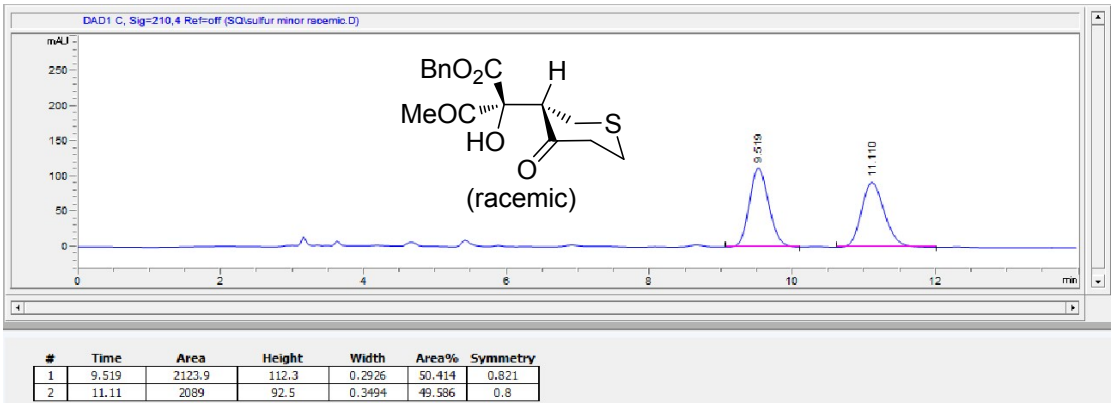


#	Time	Area	Height	Width	Area%	Symmetry
1	10.215	8755.3	398.1	0.3324	50.524	0.801
2	12.212	8573.6	325.9	0.407	49.476	0.779

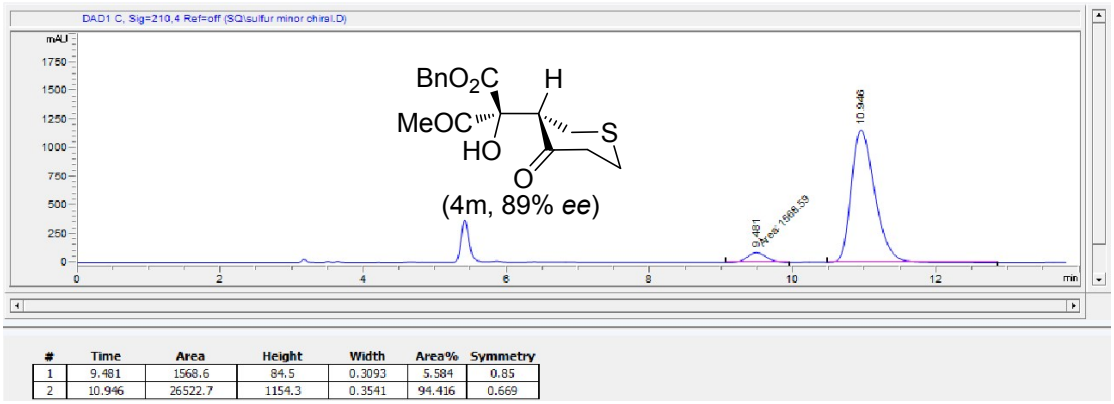


#	Time	Area	Height	Width	Area%	Symmetry
1	10.293	36.4	1.5	0.3453	0.643	0.853
2	12.258	5628.3	213	0.4103	99.357	0.804

(*S*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-4-oxotetrahydro-2*H*-thiopyran-3-yl]butanoate (4m).

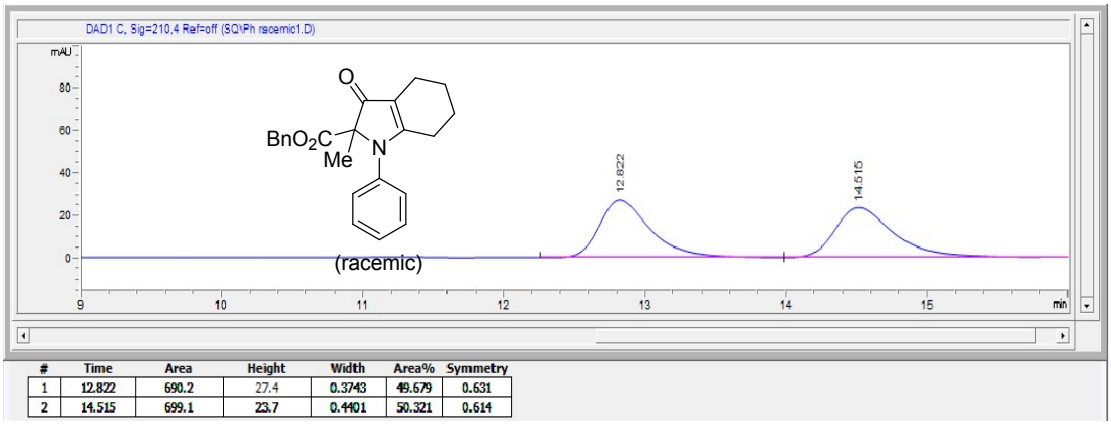


#	Time	Area	Height	Width	Area%	Symmetry
1	9.519	2123.9	112.3	0.2926	50.414	0.821
2	11.11	2089	92.5	0.3494	49.586	0.8

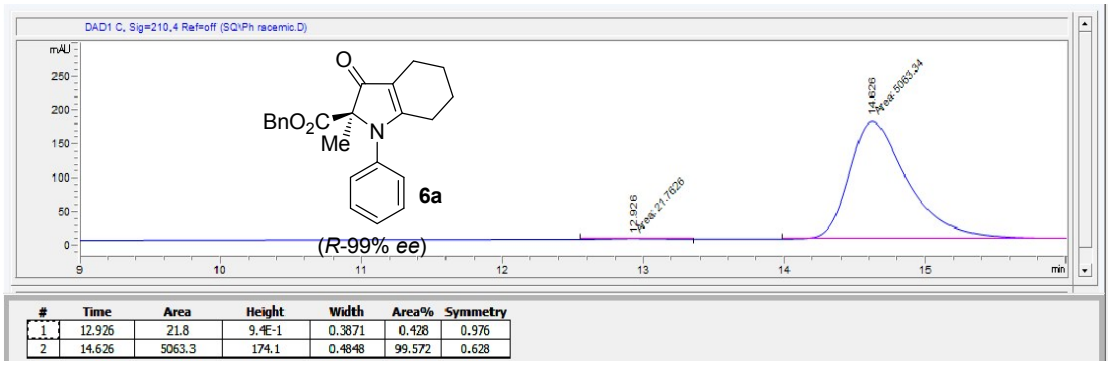


#	Time	Area	Height	Width	Area%	Symmetry
1	9.481	1568.6	84.5	0.3093	5.584	0.85
2	10.946	26522.7	1154.3	0.3541	94.416	0.669

(*R*)-Benzyl 2-Methyl-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6a).

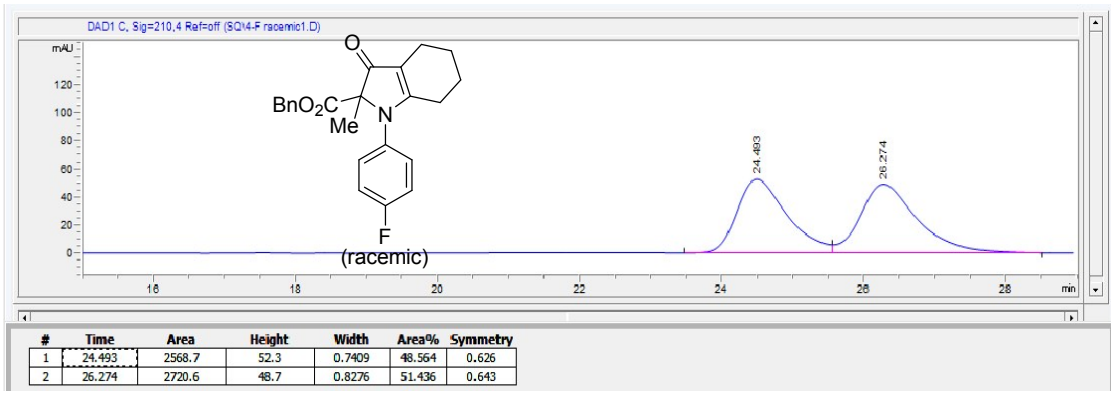


#	Time	Area	Height	Width	Area%	Symmetry
1	12.822	690.2	27.4	0.3743	49.679	0.631
2	14.515	699.1	23.7	0.4401	50.321	0.614

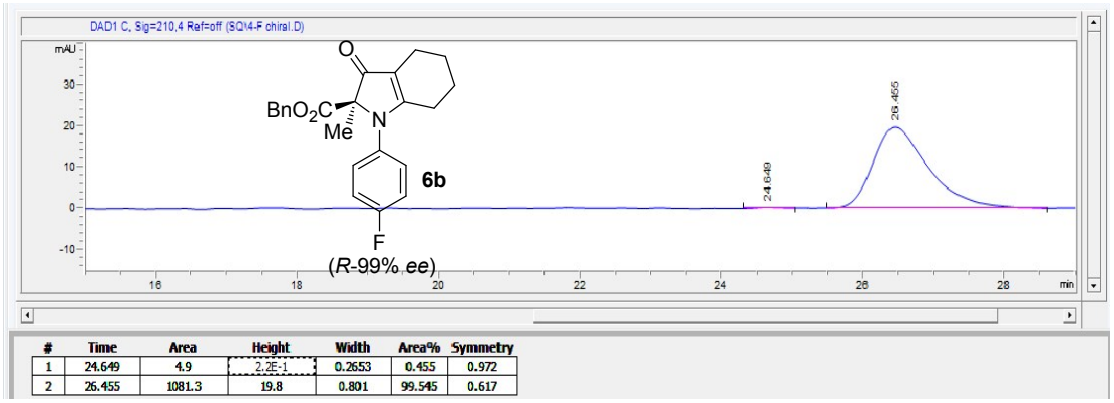


#	Time	Area	Height	Width	Area%	Symmetry
1	12.926	21.8	9.4E-1	0.3871	0.428	0.976
2	14.626	5063.3	174.1	0.4848	99.572	0.628

(*R*)-Benzyl 1-(4-Fluorophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6b).

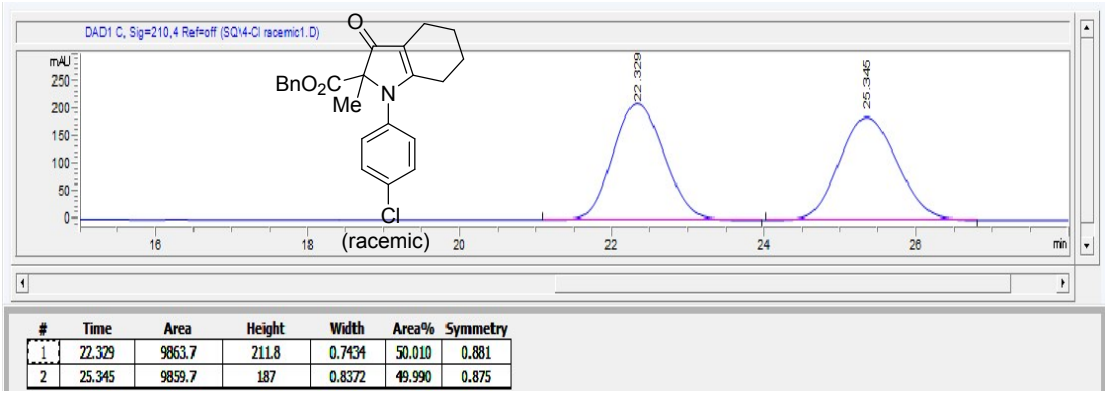


#	Time	Area	Height	Width	Area%	Symmetry
1	24.493	2568.7	52.3	0.7409	48.564	0.626
2	26.274	2720.6	48.7	0.8276	51.436	0.643

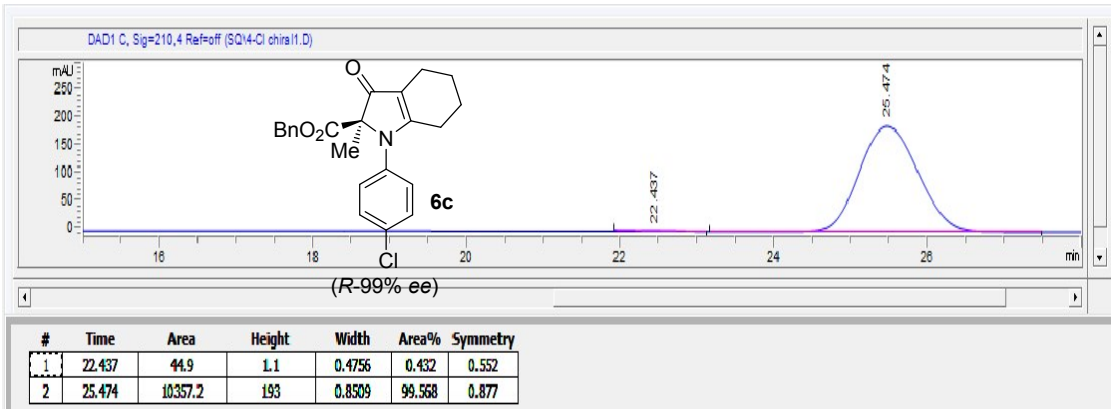


#	Time	Area	Height	Width	Area%	Symmetry
1	24.649	4.9	2.2E-1	0.2653	0.455	0.972
2	26.455	1081.3	19.8	0.801	99.545	0.617

(*R*)-Benzyl 1-(4-Chlorophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6c).

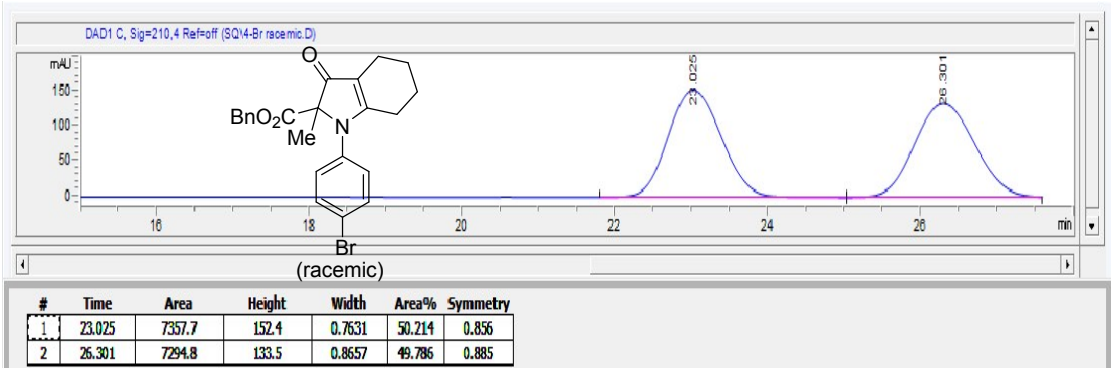


#	Time	Area	Height	Width	Area%	Symmetry
1	22.329	9863.7	211.8	0.7434	50.010	0.881
2	25.345	9859.7	187	0.8372	49.990	0.875

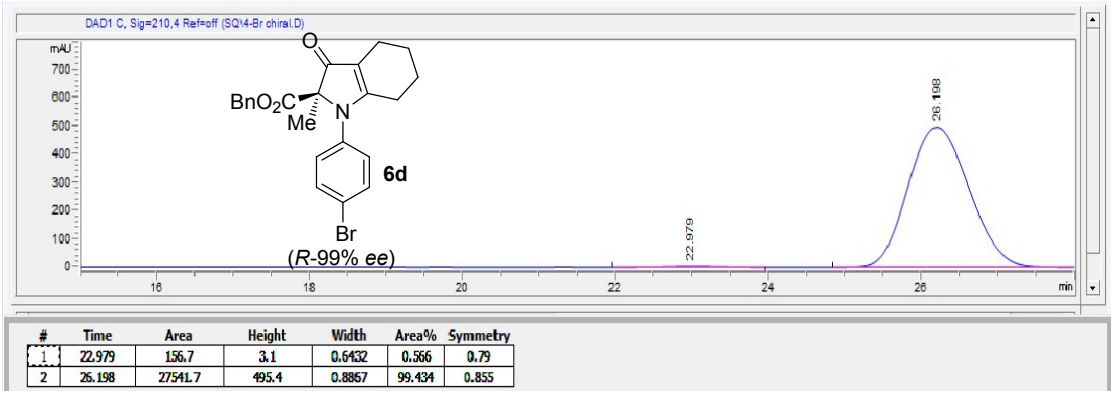


#	Time	Area	Height	Width	Area%	Symmetry
1	22.437	44.9	1.1	0.4756	0.432	0.552
2	25.474	10357.2	193	0.8509	99.568	0.877

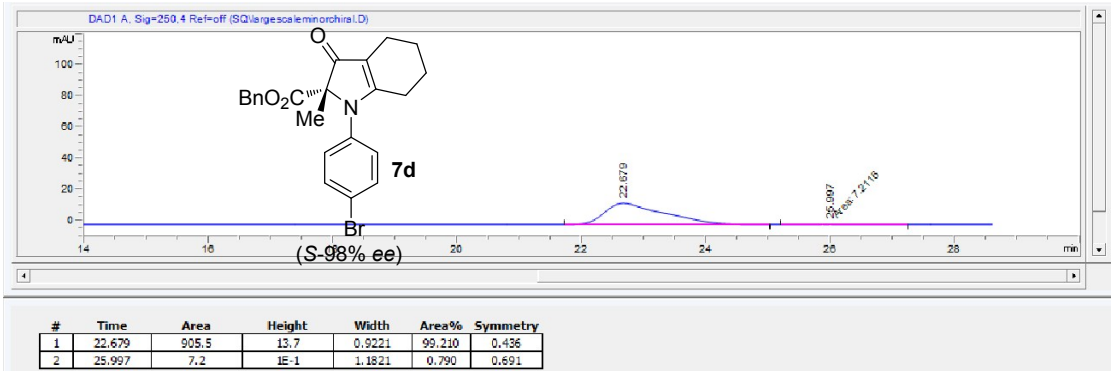
(*R*)-Benzyl 1-(4-Bromophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6d).



#	Time	Area	Height	Width	Area%	Symmetry
1	23.025	7357.7	152.4	0.7631	50.214	0.856
2	26.301	7294.8	133.5	0.8657	49.786	0.885

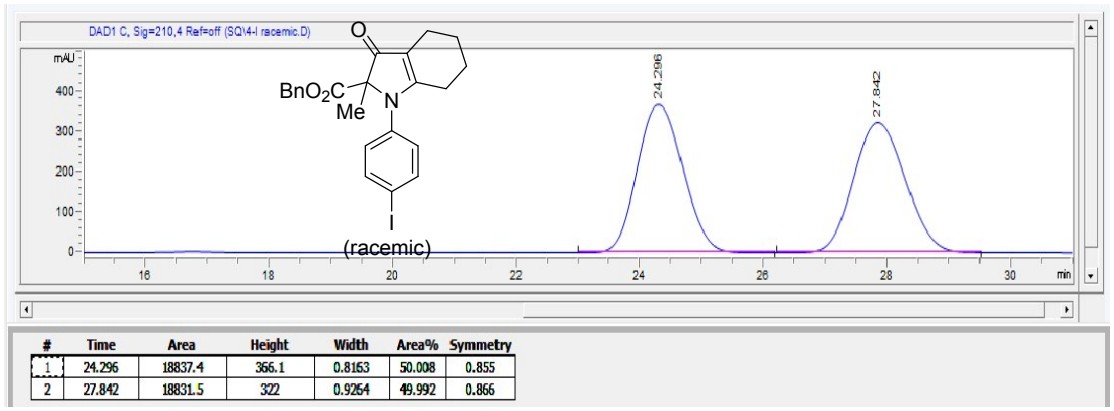


#	Time	Area	Height	Width	Area%	Symmetry
1	22.979	156.7	3.1	0.6432	0.566	0.79
2	26.198	27541.7	495.4	0.8867	99.434	0.855

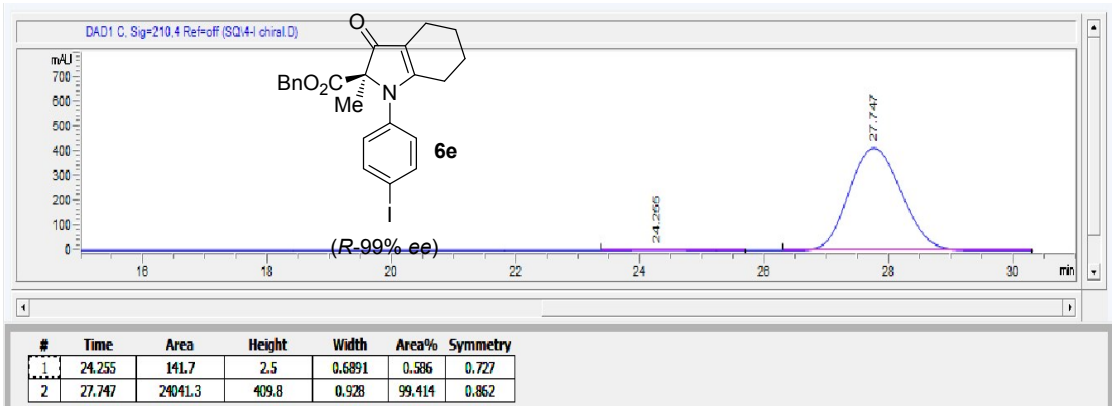


#	Time	Area	Height	Width	Area%	Symmetry
1	22.679	905.5	13.7	0.9221	99.210	0.436
2	25.997	7.2	1E-1	1.1821	0.790	0.691

(*R*)-Benzyl 1-(4-Iodophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6e).

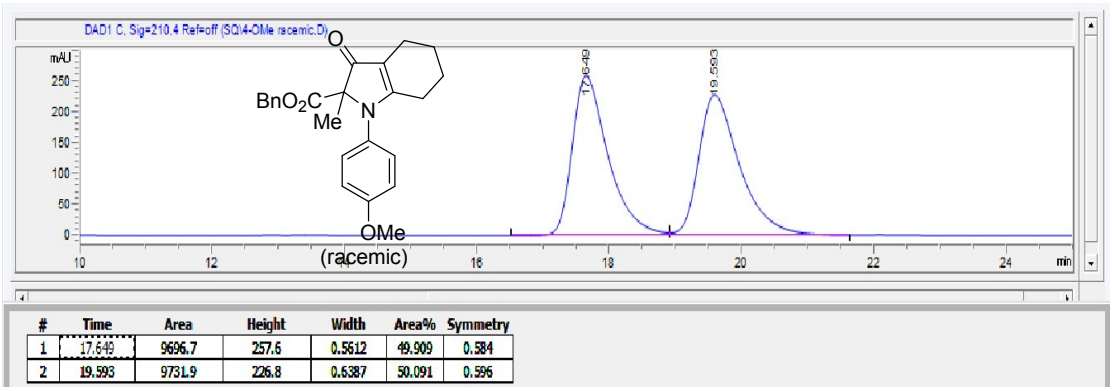


#	Time	Area	Height	Width	Area%	Symmetry
1	24.296	18837.4	366.1	0.8163	50.008	0.855
2	27.842	18831.5	322	0.9264	49.992	0.866

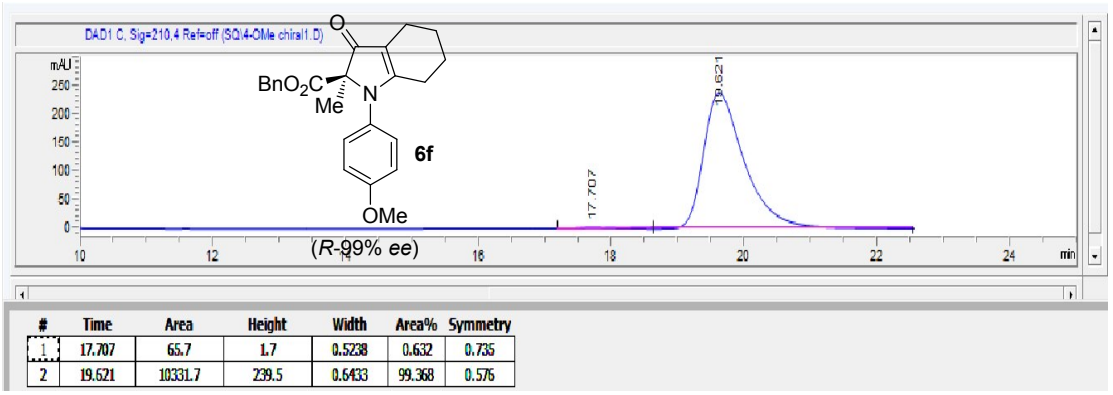


#	Time	Area	Height	Width	Area%	Symmetry
1	24.255	141.7	2.5	0.6891	0.586	0.727
2	27.747	24041.3	409.8	0.928	99.414	0.862

(*R*)-Benzyl 1-(4-Methoxyphenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6f).

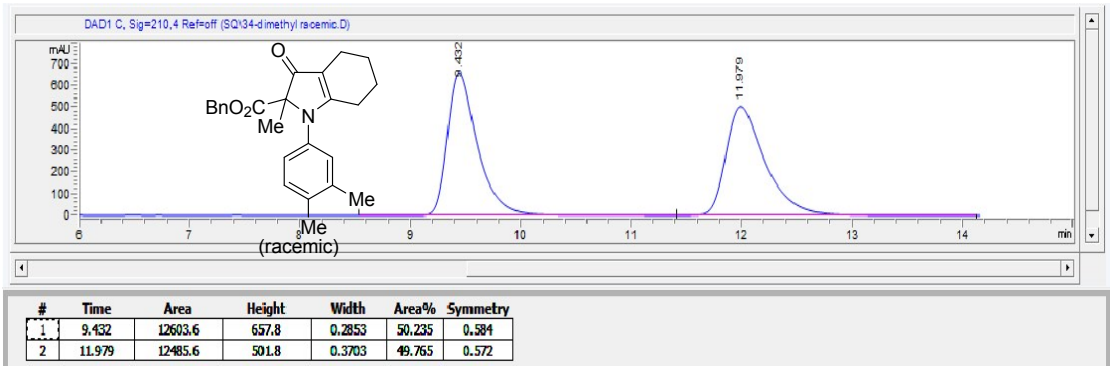


#	Time	Area	Height	Width	Area%	Symmetry
1	17.649	9696.7	257.6	0.5612	49.909	0.584
2	19.593	9731.9	226.8	0.6387	50.091	0.596

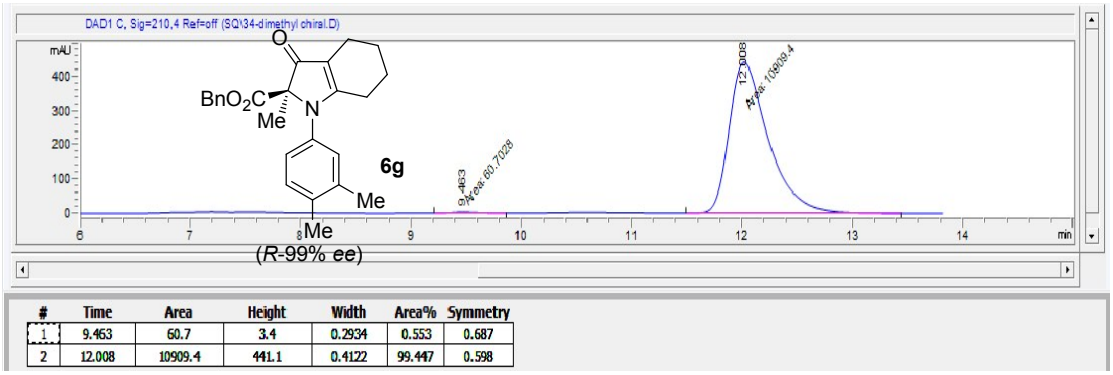


#	Time	Area	Height	Width	Area%	Symmetry
1	17.707	65.7	1.7	0.5238	0.632	0.735
2	19.621	10331.7	239.5	0.6433	99.368	0.576

(*R*)-Benzyl 1-(3,4-Dimethylphenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6g).

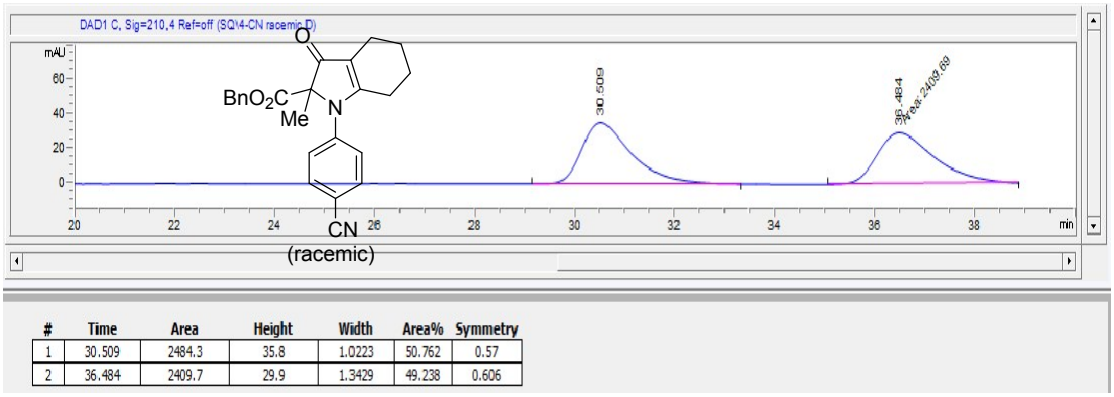


#	Time	Area	Height	Width	Area%	Symmetry
1	9.432	12603.6	657.8	0.2853	50.235	0.584
2	11.979	12485.6	501.8	0.3703	49.765	0.572

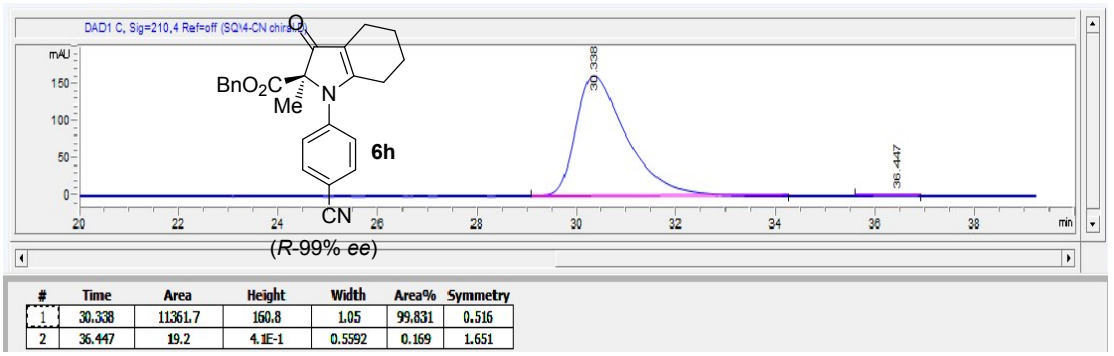


#	Time	Area	Height	Width	Area%	Symmetry
1	9.463	60.7	3.4	0.2934	0.553	0.687
2	12.008	10909.4	441.1	0.4122	99.447	0.598

(*R*)-Benzyl 1-(4-Cyanophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6h).

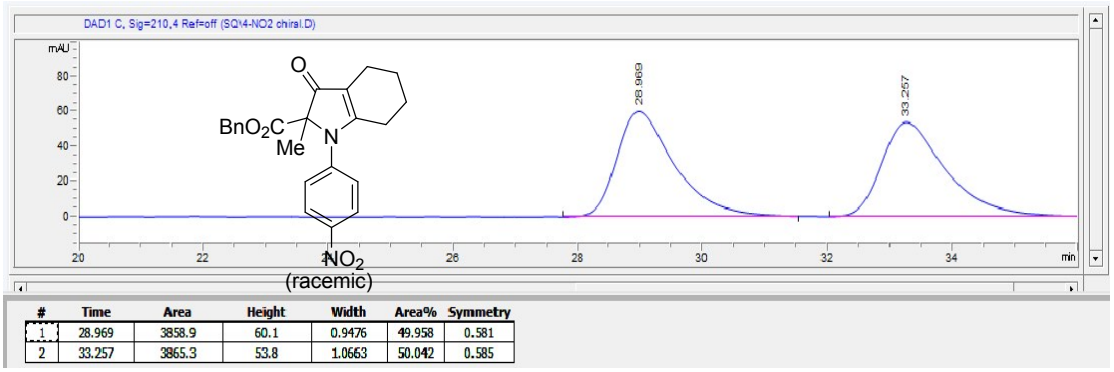


#	Time	Area	Height	Width	Area%	Symmetry
1	30.509	2484.3	35.8	1.0223	50.762	0.57
2	36.484	2409.7	29.9	1.3429	49.238	0.606

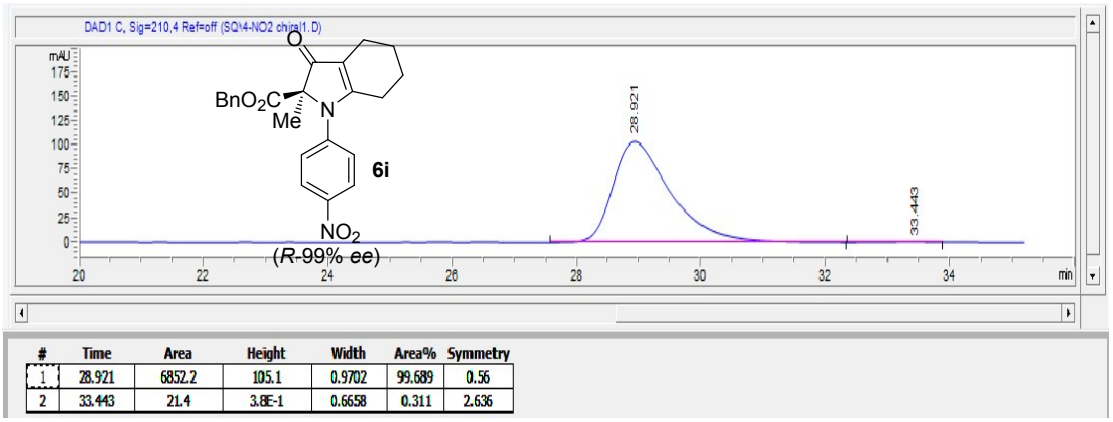


#	Time	Area	Height	Width	Area%	Symmetry
1	30.338	11361.7	160.8	1.05	99.831	0.516
2	36.447	19.2	4.1E-1	0.5592	0.169	1.651

(*R*)-Benzyl 2-Methyl-1-(4-nitrophenyl)-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6i).

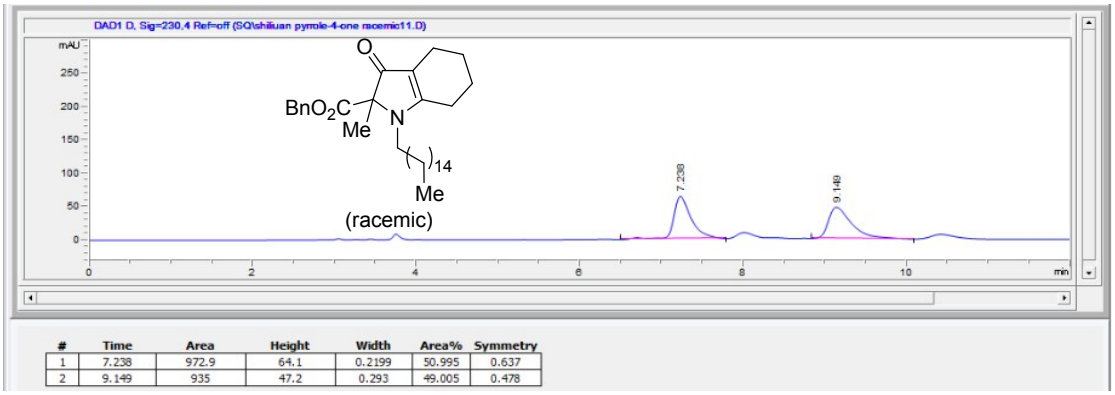


#	Time	Area	Height	Width	Area%	Symmetry
1	28.969	3858.9	60.1	0.9476	49.958	0.581
2	33.257	3865.3	53.8	1.0663	50.042	0.585

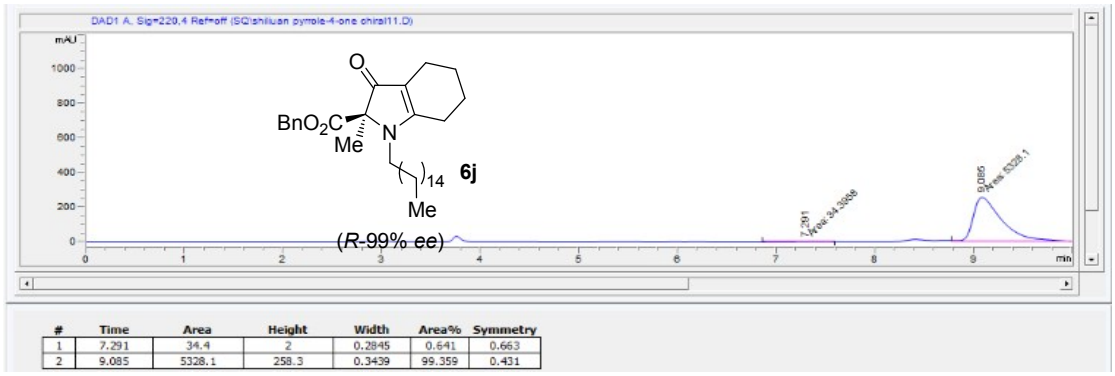


#	Time	Area	Height	Width	Area%	Symmetry
1	28.921	6852.2	105.1	0.9702	99.689	0.56
2	33.443	21.4	3.8E-1	0.6658	0.311	2.636

(*R*)-Benzyl 1-Hexadecyl-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6j).

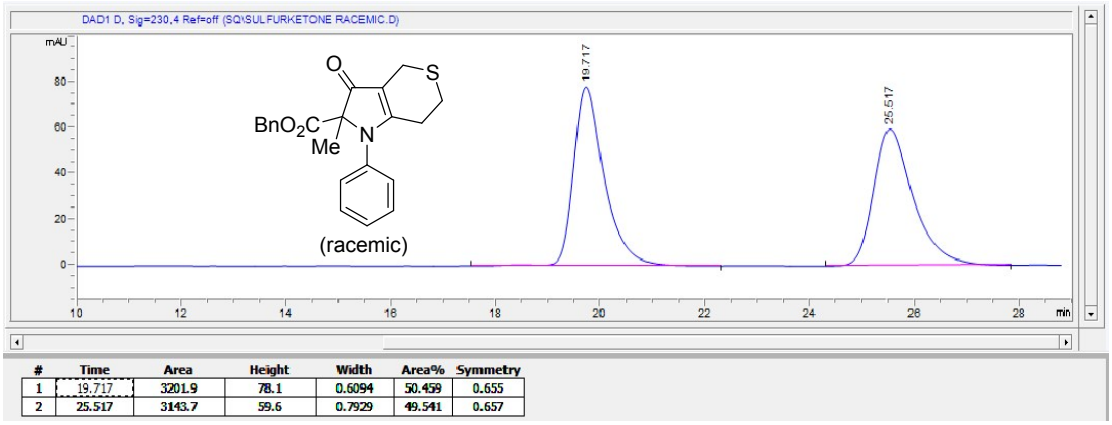


#	Time	Area	Height	Width	Area%	Symmetry
1	7.238	972.9	64.1	0.2199	50.995	0.637
2	9.149	935	47.2	0.293	49.005	0.478

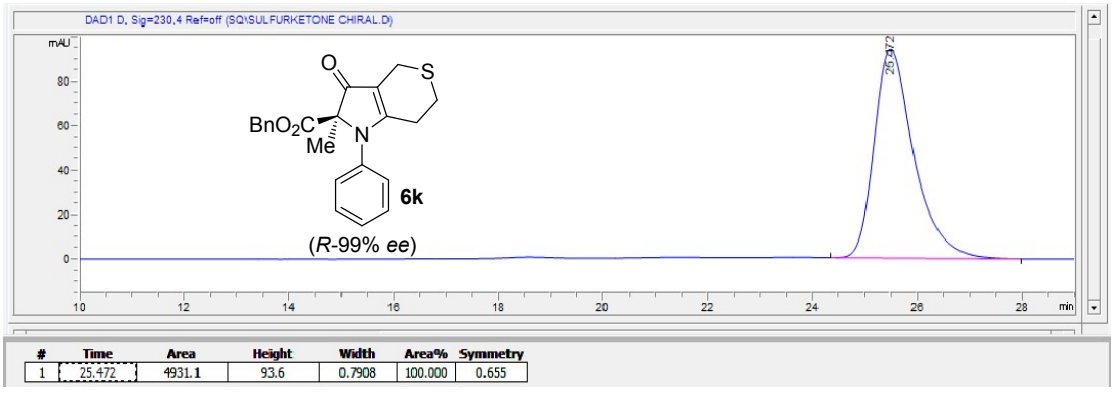


#	Time	Area	Height	Width	Area%	Symmetry
1	7.291	34.4	2	0.2845	0.641	0.663
2	9.085	5328.1	258.3	0.3439	99.359	0.431

(*R*)-Benzyl 2-Methyl-3-oxo-1-phenyl-1,2,3,4,6,7-hexahydrothiopyrano[4,3-*b*]pyrrole-2-carboxylate (6k).

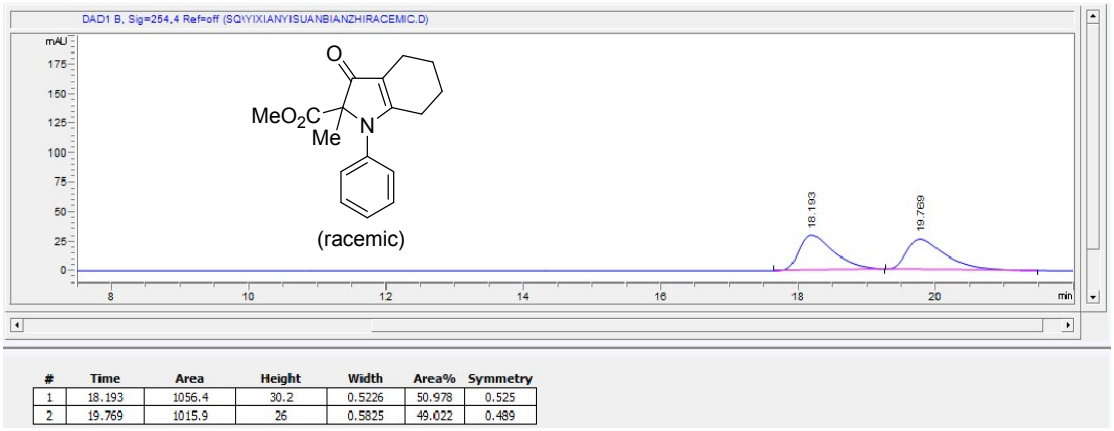


#	Time	Area	Height	Width	Area%	Symmetry
1	19.717	3201.9	78.1	0.6094	50.459	0.655
2	25.517	3143.7	59.6	0.7929	49.541	0.657

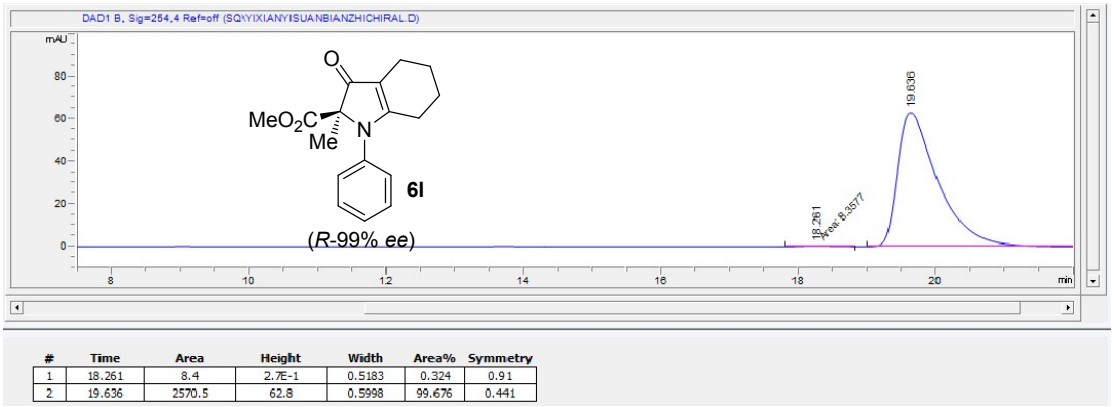


#	Time	Area	Height	Width	Area%	Symmetry
1	25.472	4931.1	93.6	0.7908	100.000	0.655

(*R*)-Methyl 2-Methyl-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6l).

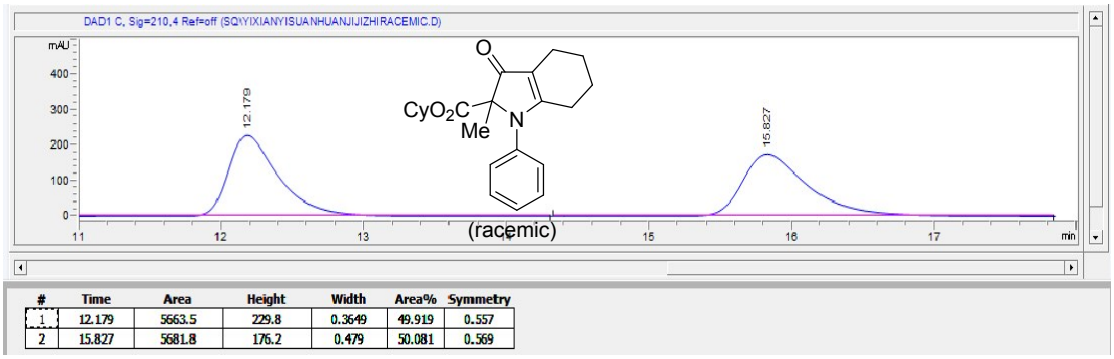


#	Time	Area	Height	Width	Area%	Symmetry
1	18.193	1056.4	30.2	0.5226	50.978	0.525
2	19.769	1015.9	26	0.5825	49.022	0.489

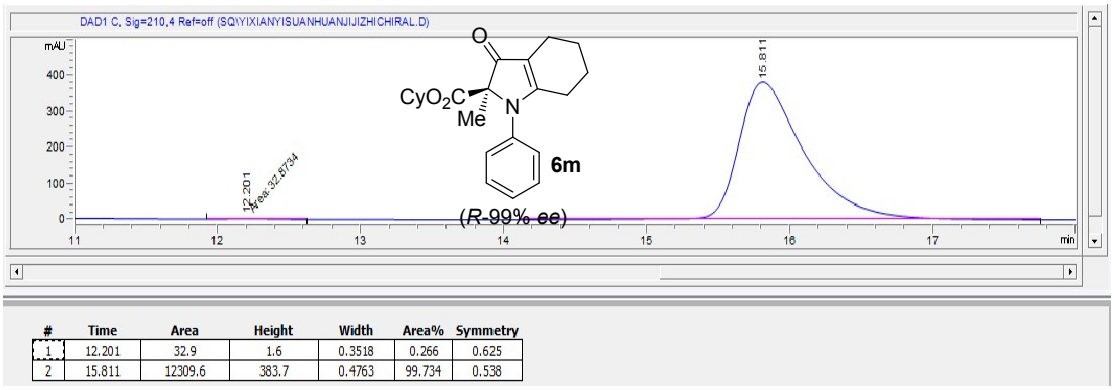


#	Time	Area	Height	Width	Area%	Symmetry
1	18.261	8.4	2.7E-1	0.5183	0.324	0.91
2	19.636	2570.5	62.8	0.5998	99.676	0.441

(*R*)-Cyclohexyl 2-Methyl-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6m).

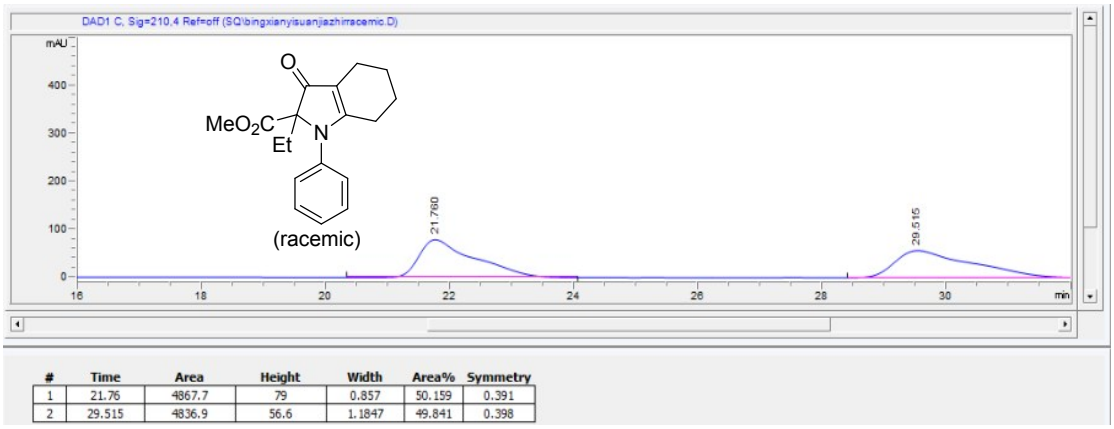


#	Time	Area	Height	Width	Area%	Symmetry
1	12.179	5663.5	229.8	0.3649	49.919	0.557
2	15.827	5681.8	176.2	0.479	50.081	0.569

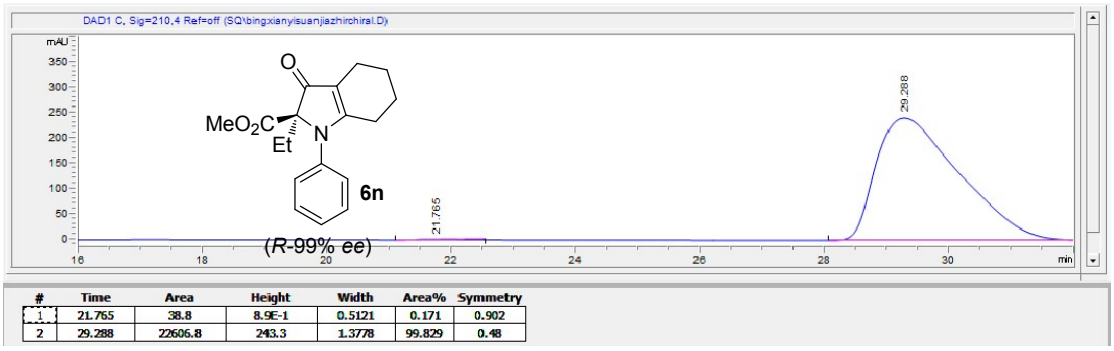


#	Time	Area	Height	Width	Area%	Symmetry
1	12.201	32.9	1.6	0.3518	0.266	0.625
2	15.811	12309.6	383.7	0.4763	99.734	0.538

(*R*)-Methyl 2-Ethyl-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6n).

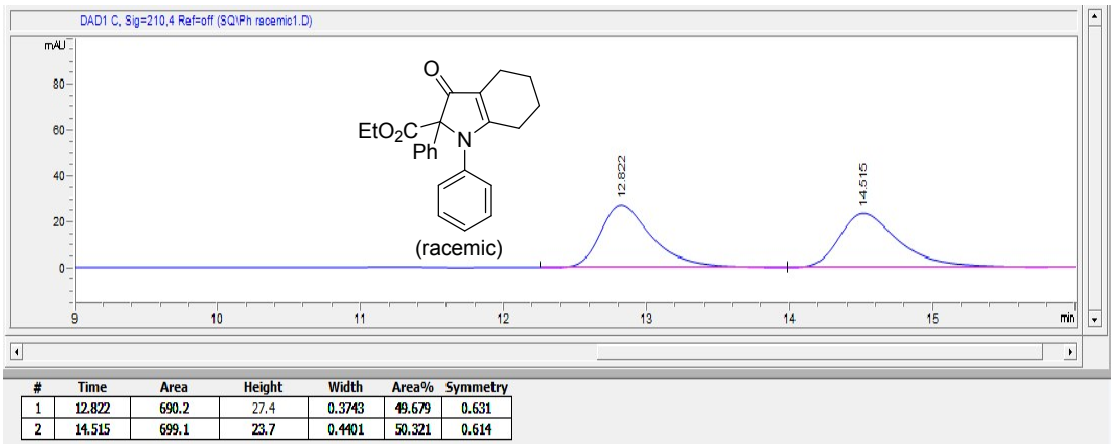


#	Time	Area	Height	Width	Area%	Symmetry
1	21.76	4867.7	79	0.857	50.159	0.391
2	29.515	4836.9	56.6	1.1847	49.841	0.398

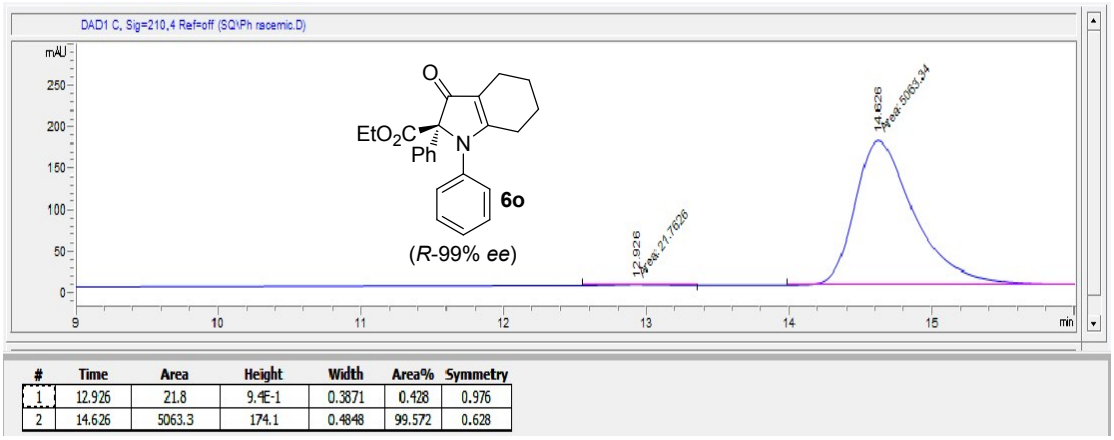


#	Time	Area	Height	Width	Area%	Symmetry
1	21.765	38.8	8.9E-1	0.5121	0.171	0.902
2	29.288	22606.8	243.3	1.3778	99.829	0.48

(*R*)-Ethyl 3-Oxo-1,2-diphenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6o).

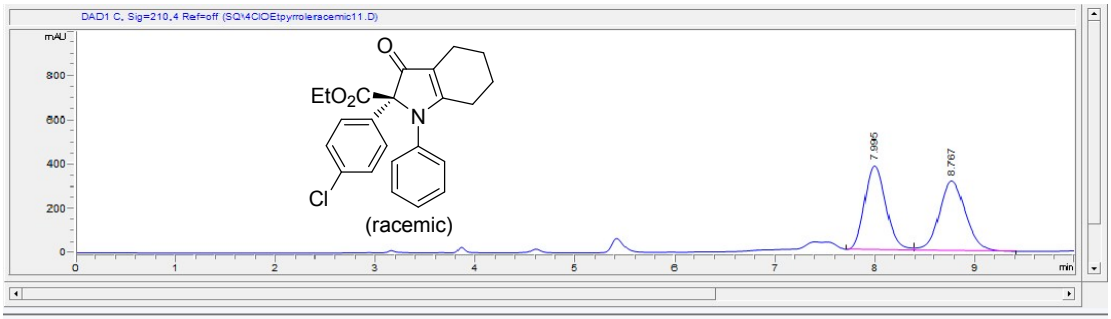


#	Time	Area	Height	Width	Area%	Symmetry
1	12.822	690.2	27.4	0.3743	49.679	0.631
2	14.515	699.1	23.7	0.4401	50.321	0.614

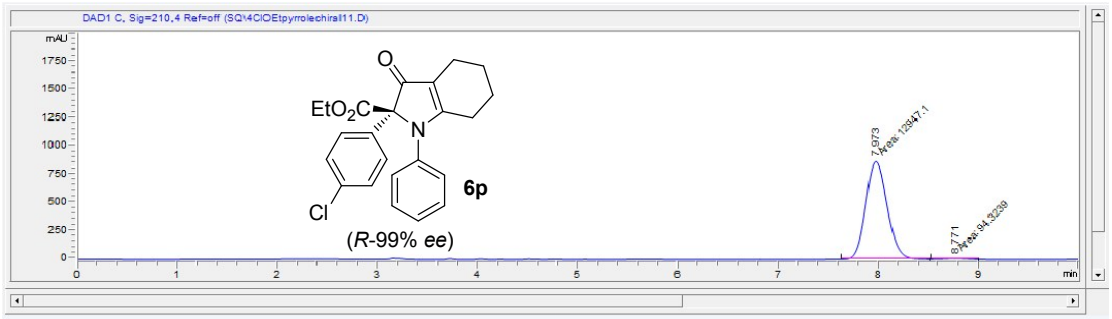


#	Time	Area	Height	Width	Area%	Symmetry
1	12.926	21.8	9.4E-1	0.3871	0.428	0.976
2	14.626	5063.3	174.1	0.4848	99.572	0.628

(*R*)-Ethyl 2-(4-Chlorophenyl)-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6p).

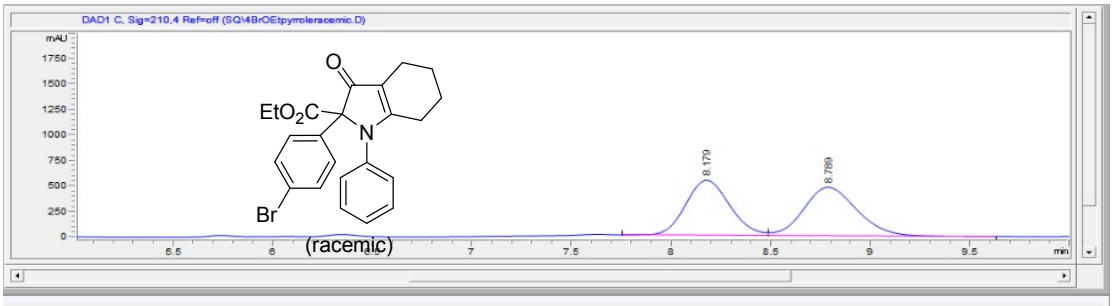


#	Time	Area	Height	Width	Area%	Symmetry
1	7.995	5710.2	381.8	0.2325	49.463	0.831
2	8.767	5834.2	315.4	0.2838	50.537	0.868

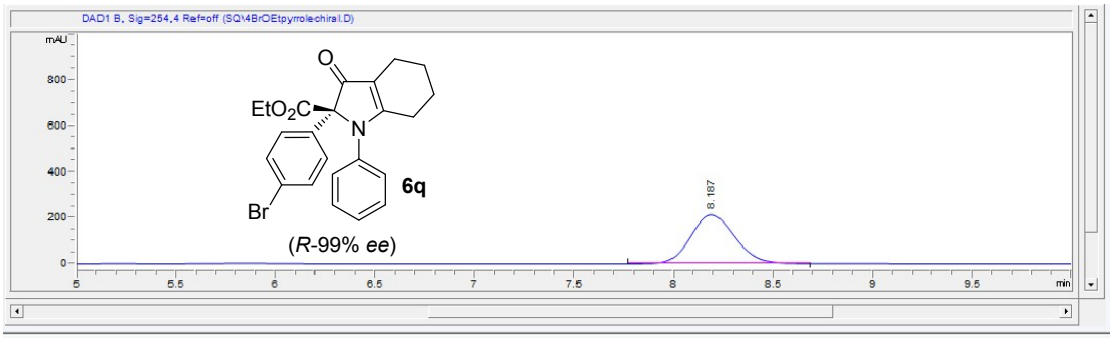


#	Time	Area	Height	Width	Area%	Symmetry
1	7.973	12947.1	868.2	0.2485	99.277	0.861
2	8.771	94.3	6.6	0.2397	0.723	0.969

(*R*)-Ethyl 2-(4-Bromophenyl)-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6q).

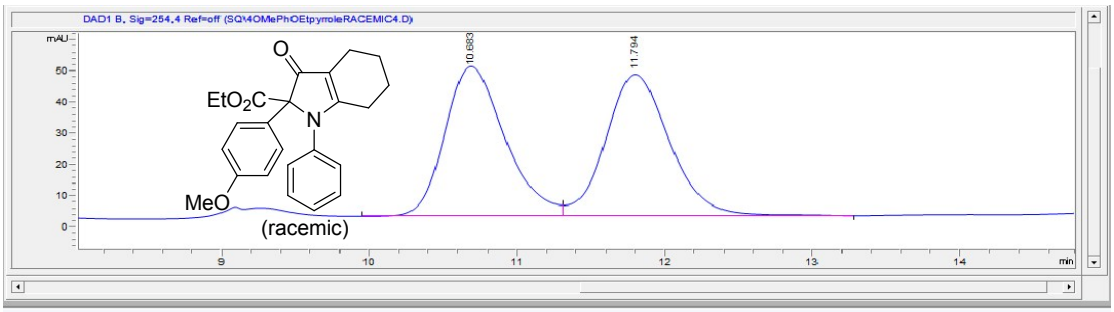


#	Time	Area	Height	Width	Area%	Symmetry
1	8.179	8298.8	539.3	0.2395	48.382	0.868
2	8.789	8854	475.7	0.2871	51.618	0.806

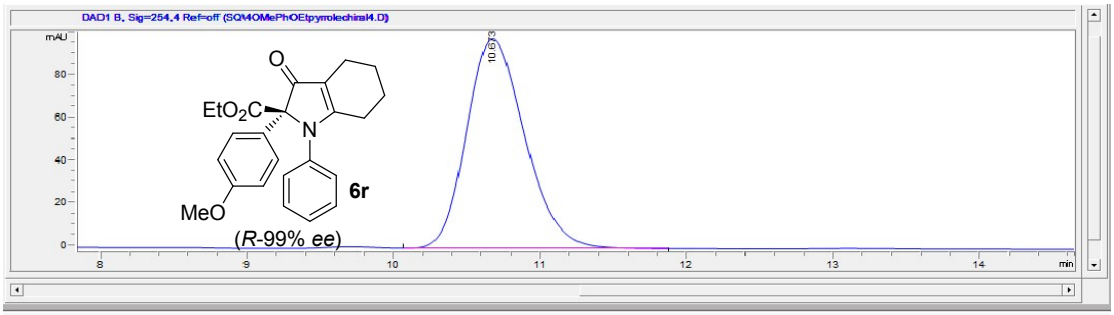


#	Time	Area	Height	Width	Area%	Symmetry
1	8.187	3323.7	214.1	0.2411	100.000	0.86

(*R*)-Ethyl 2-(4-Methoxyphenyl)-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6r).

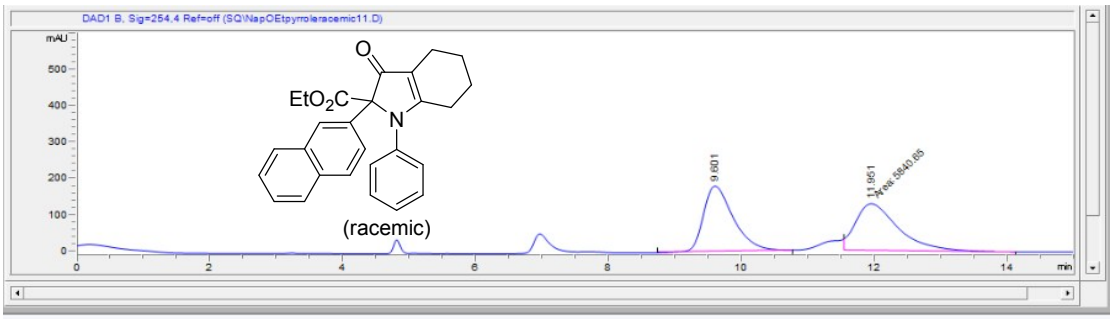


#	Time	Area	Height	Width	Area%	Symmetry
1	10.683	1360.6	48	0.4329	49.867	0.733
2	11.794	1367.8	45.3	0.4622	50.133	0.819

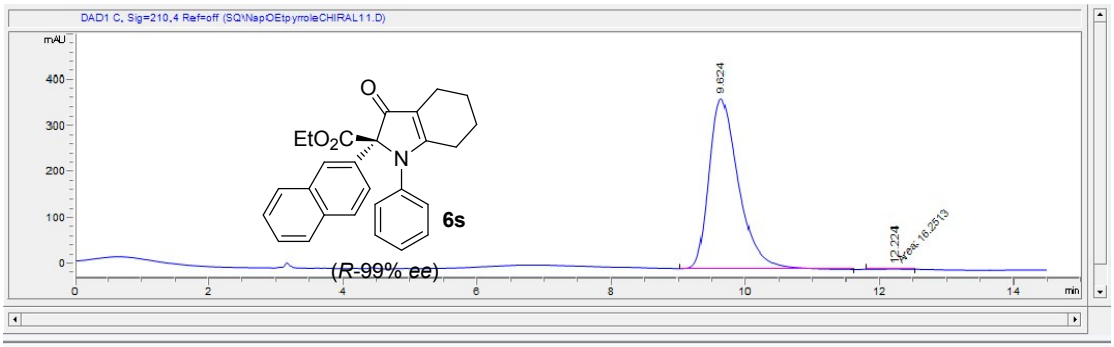


#	Time	Area	Height	Width	Area%	Symmetry
1	10.673	2722.1	98.4	0.4308	100.000	0.771

(*R*)-Ethyl 2-(Naphthalen-2-yl)-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6s).

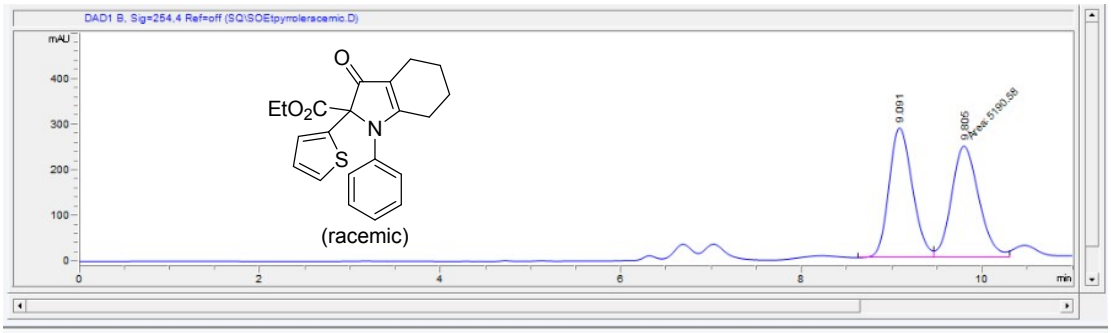


#	Time	Area	Height	Width	Area%	Symmetry
1	9.601	5643.8	180.2	0.4754	49.143	0.604
2	11.951	5840.6	129.3	0.753	50.857	0.554

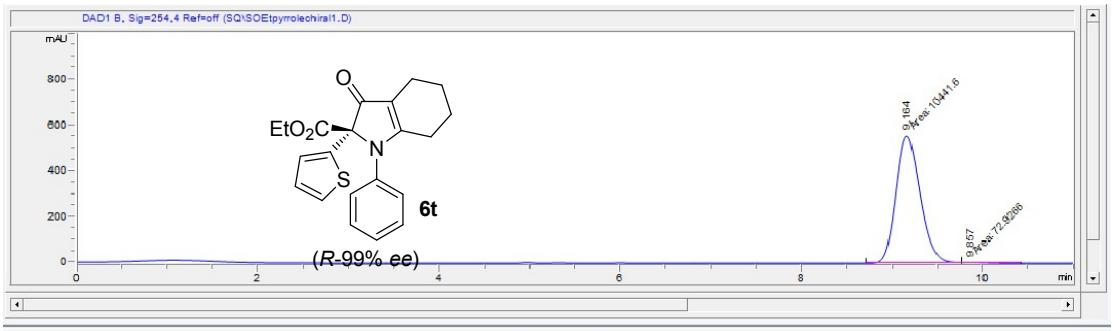


#	Time	Area	Height	Width	Area%	Symmetry
1	9.624	11429.8	369.7	0.4707	99.858	0.635
2	12.224	16.3	6.1E-1	0.4463	0.142	0.679

(*R*)-Ethyl 3-Oxo-1-phenyl-2-(thiophen-2-yl)-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6t).

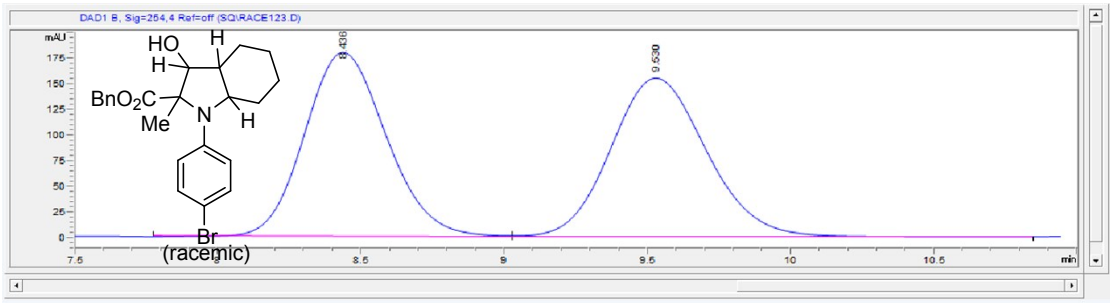


#	Time	Area	Height	Width	Area%	Symmetry
1	9.091	5154.2	285.3	0.2807	49.824	0.794
2	9.805	5190.6	245	0.353	50.176	0

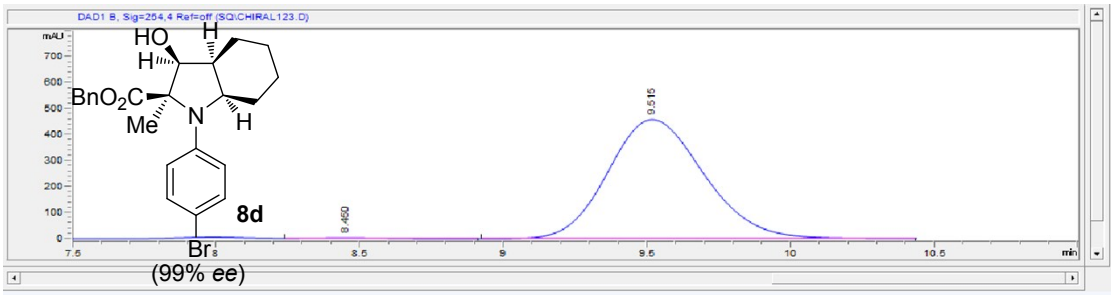


#	Time	Area	Height	Width	Area%	Symmetry
1	9.164	10441.6	558	0.3119	99.306	0.79
2	9.857	72.9	3.8	0.3164	0.694	0.408

(2*R*,3*S*,3a*S*,7a*R*)-Benzyl 1-(4-Bromophenyl)-3-hydroxy-2-methyloctahydro-1*H*-indole-2-carboxylate (8d).

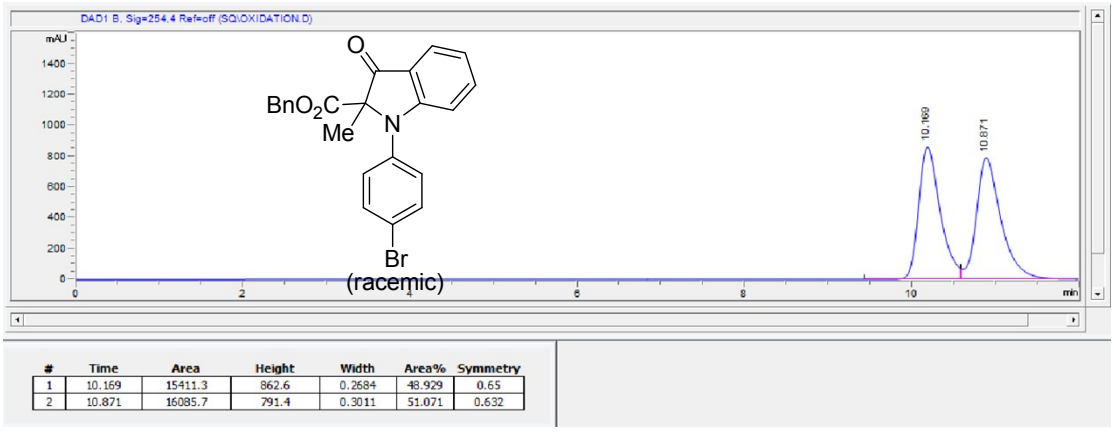


#	Time	Area	Height	Width	Area%	Symmetry
1	8.436	3612.6	181	0.3108	49.896	0.853
2	9.53	3627.7	155.7	0.3618	50.104	0.858

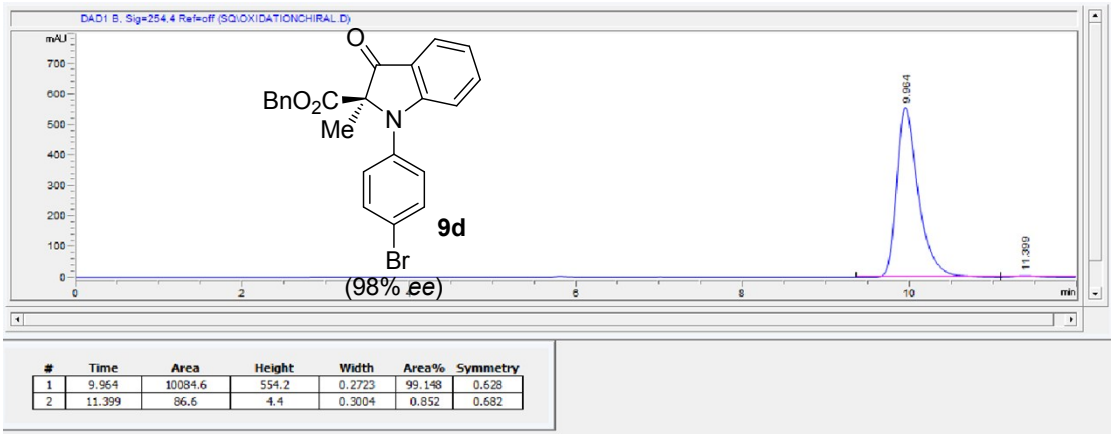


#	Time	Area	Height	Width	Area%	Symmetry
1	8.45	56.2	2.9	0.2898	0.526	0.917
2	9.515	10623.7	457.2	0.3611	99.474	0.83

(*R*)-Benzyl 1-(4-Bromophenyl)-2-methyl-3-oxoindoline-2-carboxylate (9d).



#	Time	Area	Height	Width	Area%	Symmetry
1	10.169	15411.3	862.6	0.2684	48.929	0.65
2	10.871	16085.7	791.4	0.3011	51.071	0.632

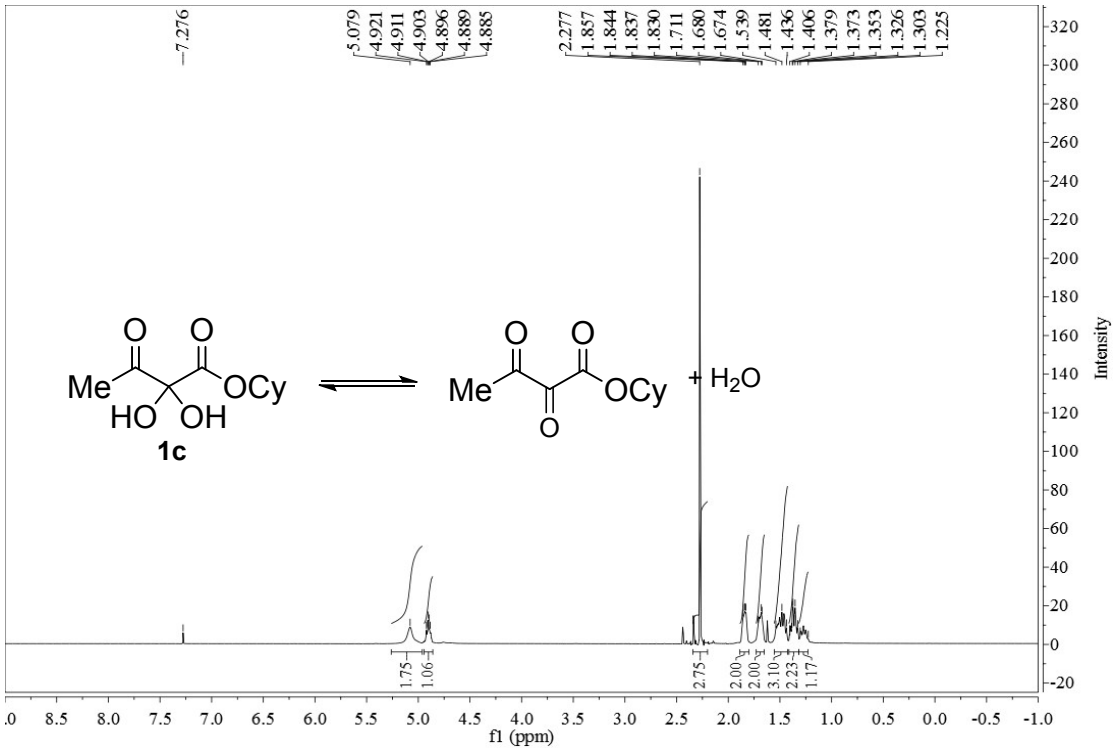


#	Time	Area	Height	Width	Area%	Symmetry
1	9.964	10084.6	554.2	0.2723	99.148	0.628
2	11.399	86.6	4.4	0.3004	0.852	0.682

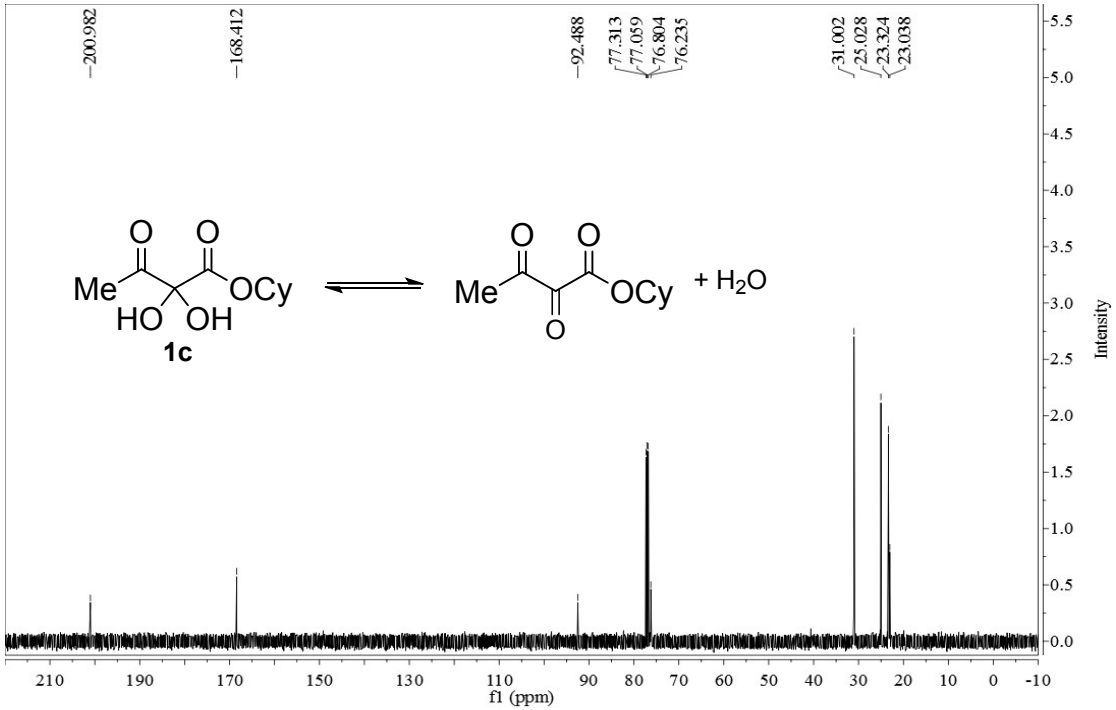
^{1}H NMR and ^{13}C NMR spectra of products 3a-m, 4a-m, 6a-t.

Cyclohexyl 2,2-Dihydroxy-3-oxobutanoate (1c).

^{1}HNMR (500 MHz, $CDCl_3$)

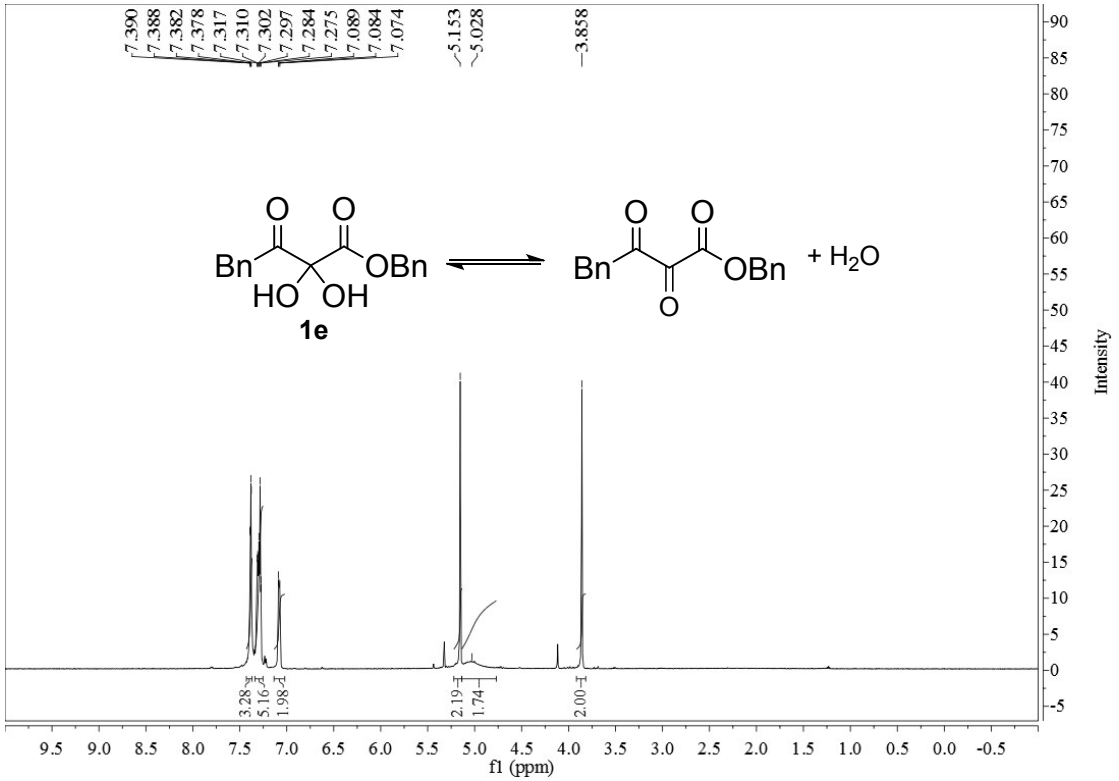


^{13}C NMR (125 MHz, $CDCl_3$)

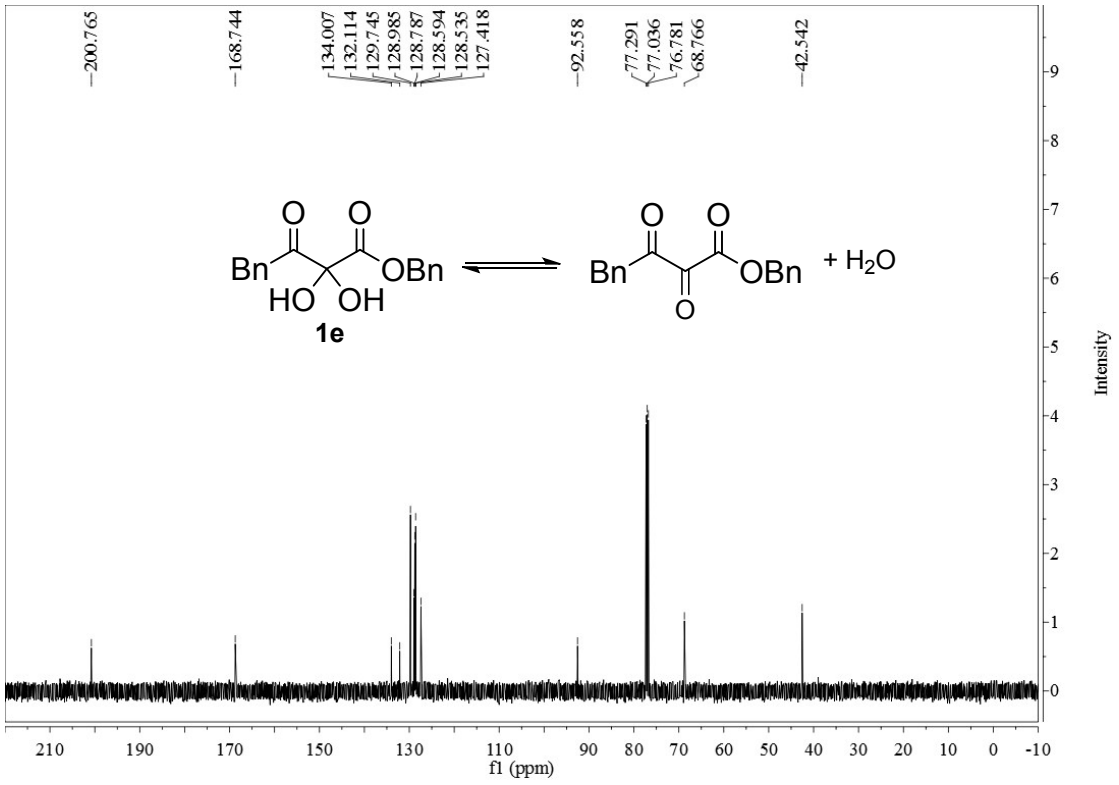


Benzyl 2,2-Dihydroxy-3-oxo-4-phenylbutanoate (1e).

^{1}HNMR (500 MHz, $CDCl_3$)

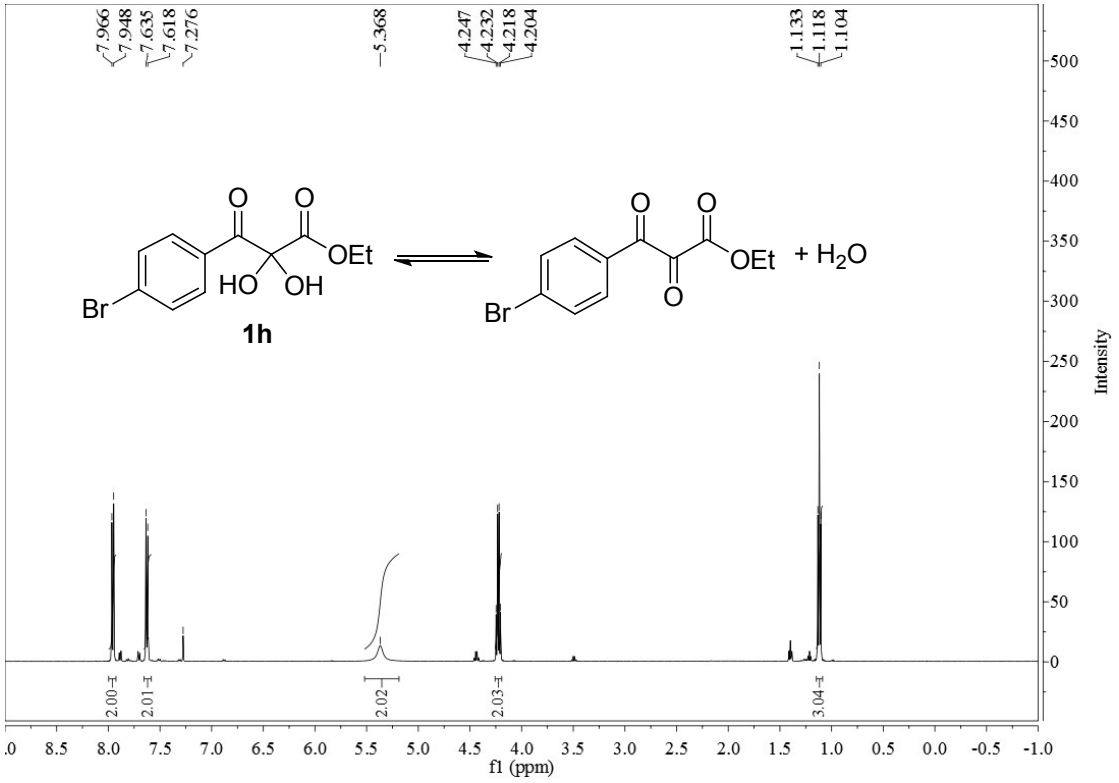


^{13}C NMR (125 MHz, $CDCl_3$)

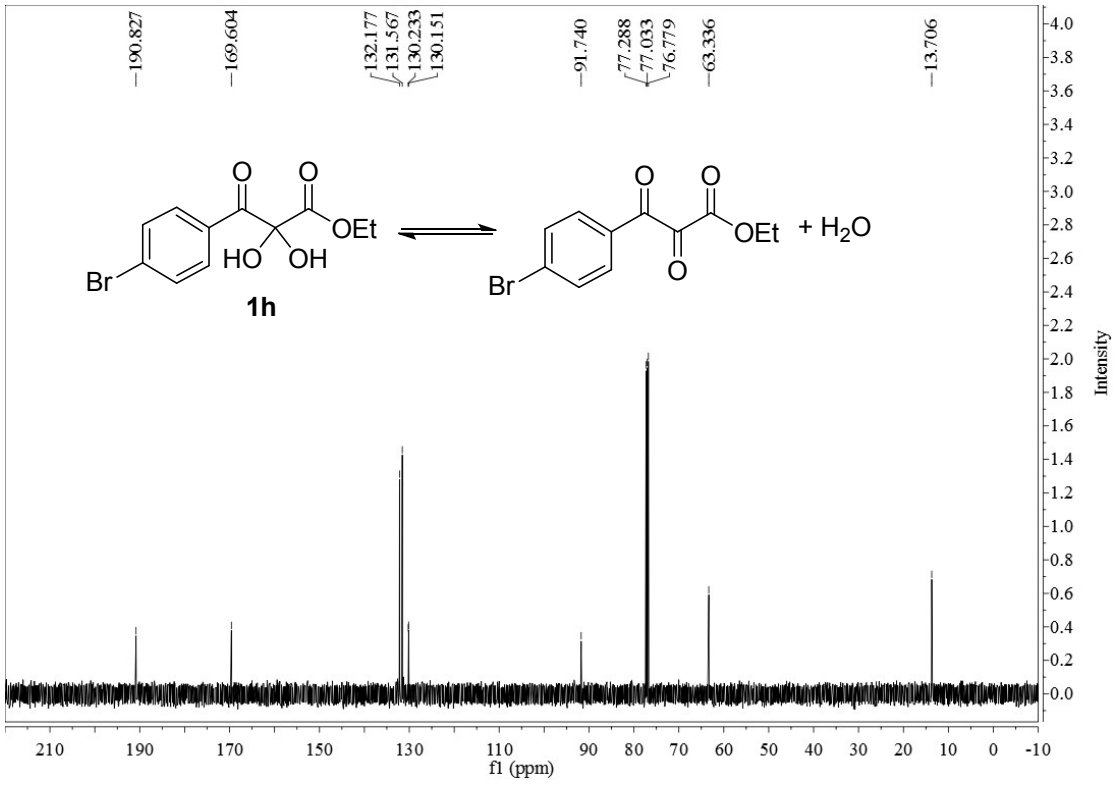


Ethyl 3-(4-Bromophenyl)-2,2-dihydroxy-3-oxopropanoate (1h).

^{1}HNMR (500 MHz, $CDCl_3$)

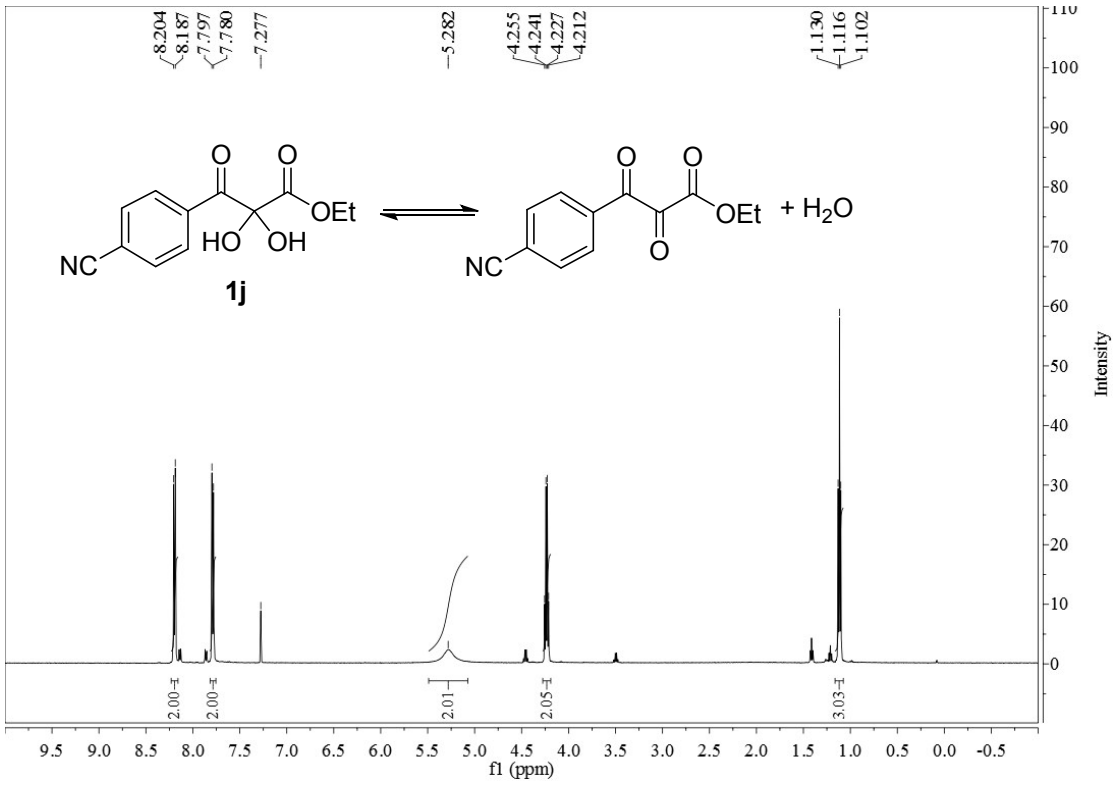


^{13}C NMR (125 MHz, $CDCl_3$)

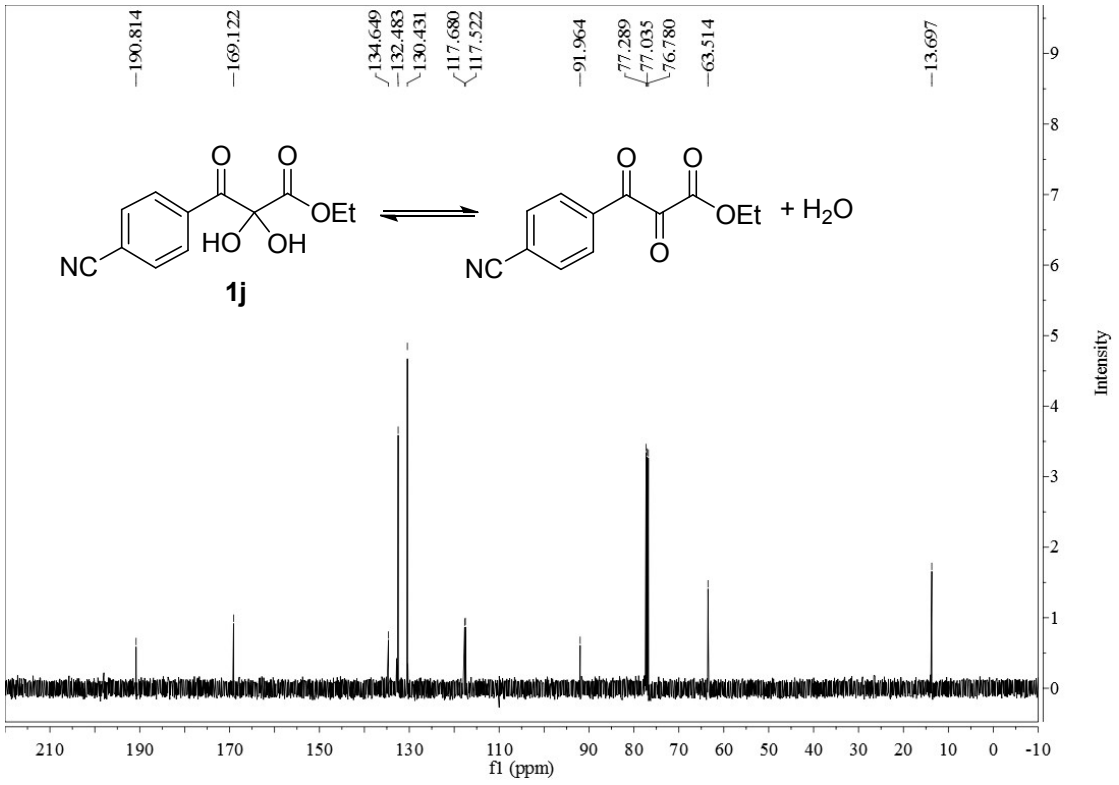


Ethyl 3-(4-Cyanophenyl)-2,2-dihydroxy-3-oxopropanoate (1j).

^{1}HNMR (500 MHz, $CDCl_3$)

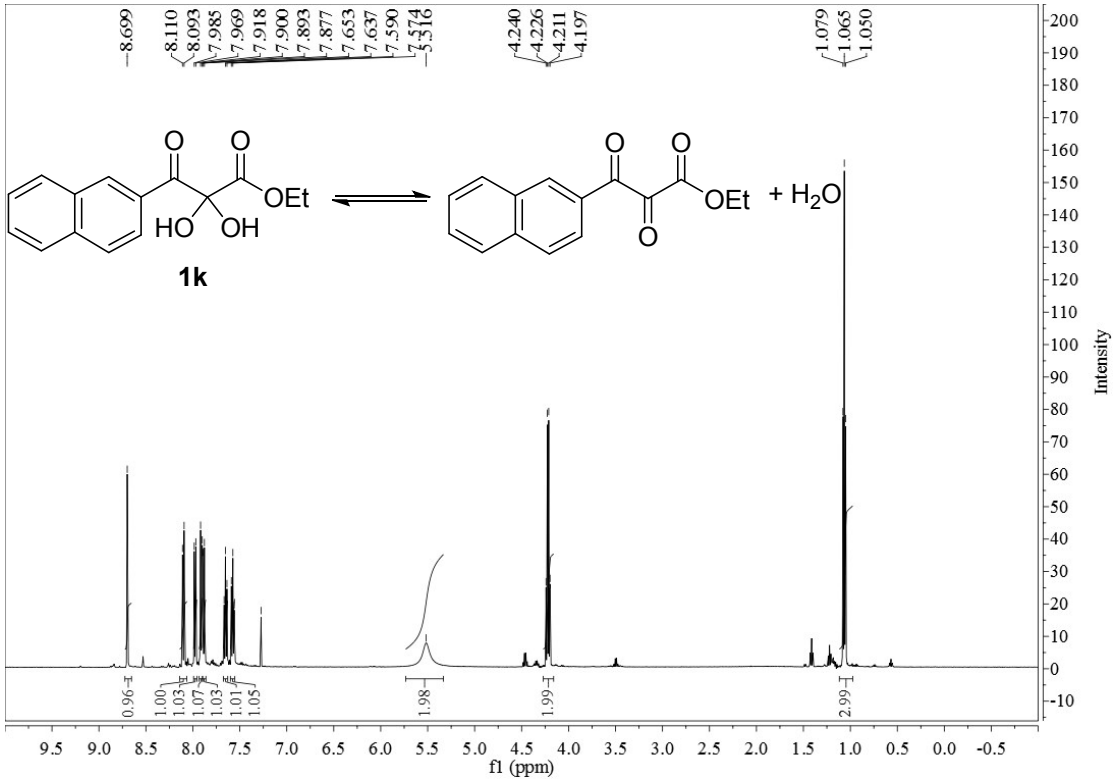


^{13}C NMR (125 MHz, $CDCl_3$)

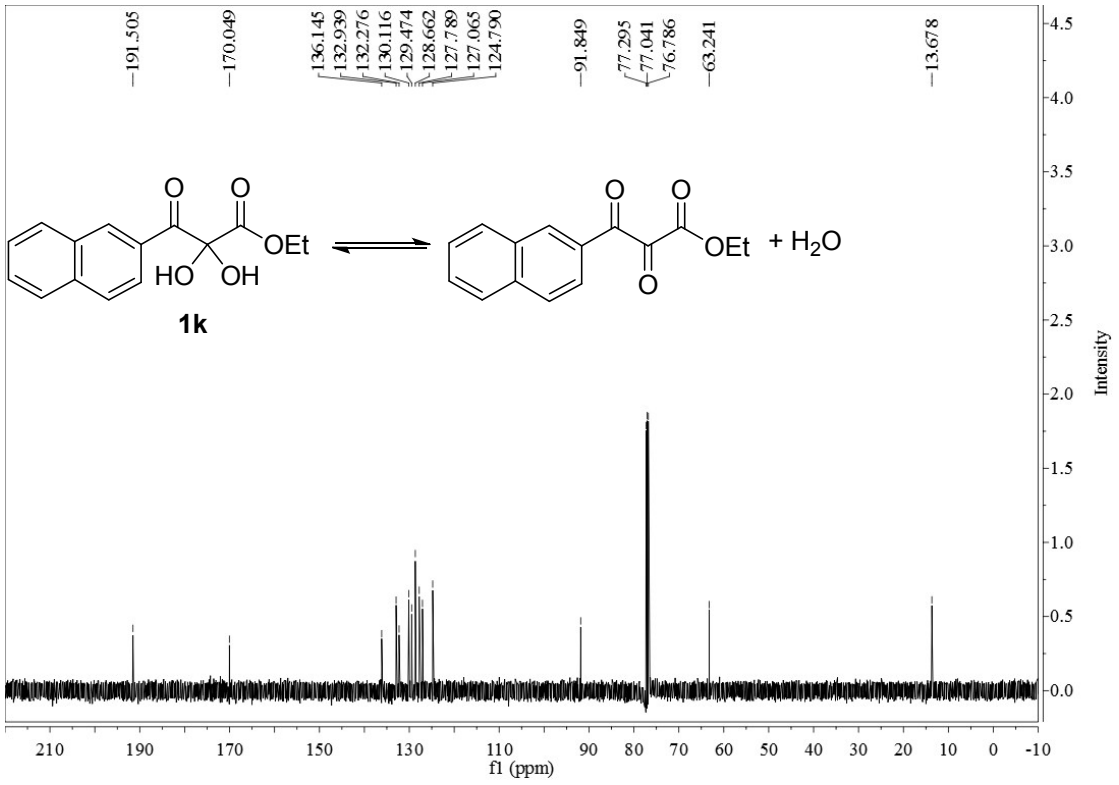


Ethyl 2,2-Dihydroxy-3-(naphthalen-2-yl)-3-oxopropanoate (1k).

^{1}HNMR (500 MHz, $CDCl_3$)

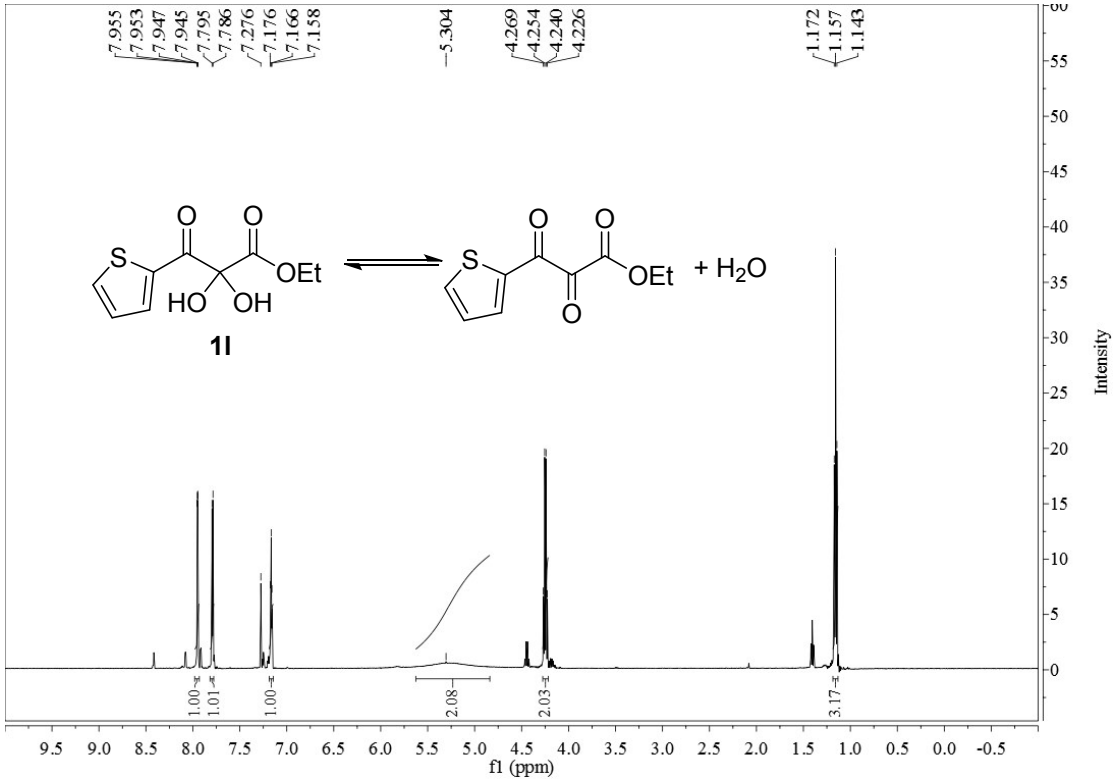


^{13}C NMR (125 MHz, $CDCl_3$)

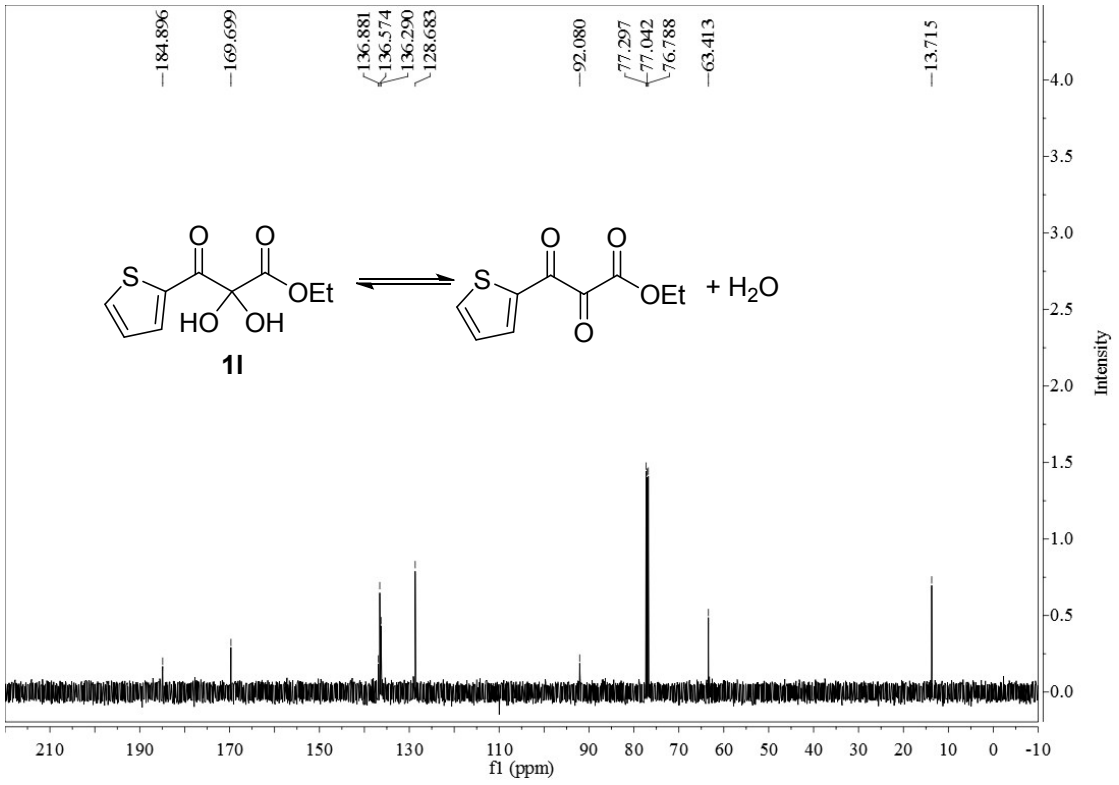


Ethyl 2,2-Dihydroxy-3-oxo-3-(thiophen-2-yl)propanoate (1l).

^{1}HNMR (500 MHz, $CDCl_3$)

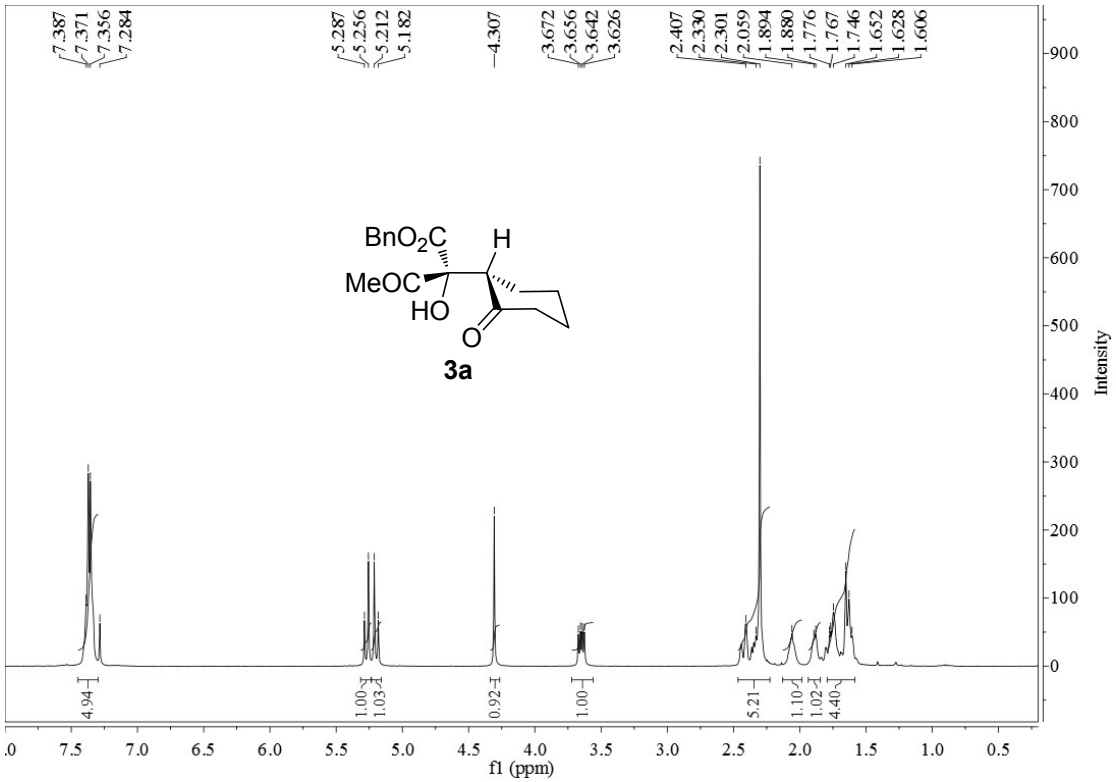


^{13}C NMR (125 MHz, $CDCl_3$)

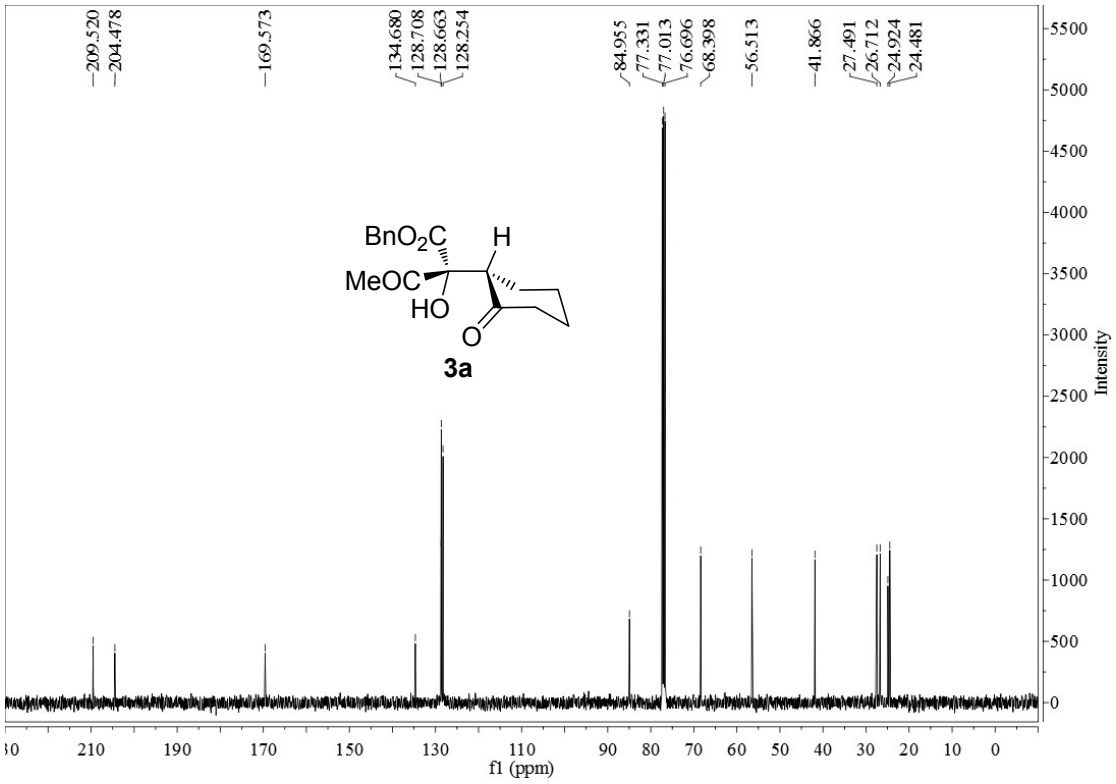


(*R*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (3a).

^{1}HNMR (500 MHz, $CDCl_3$)

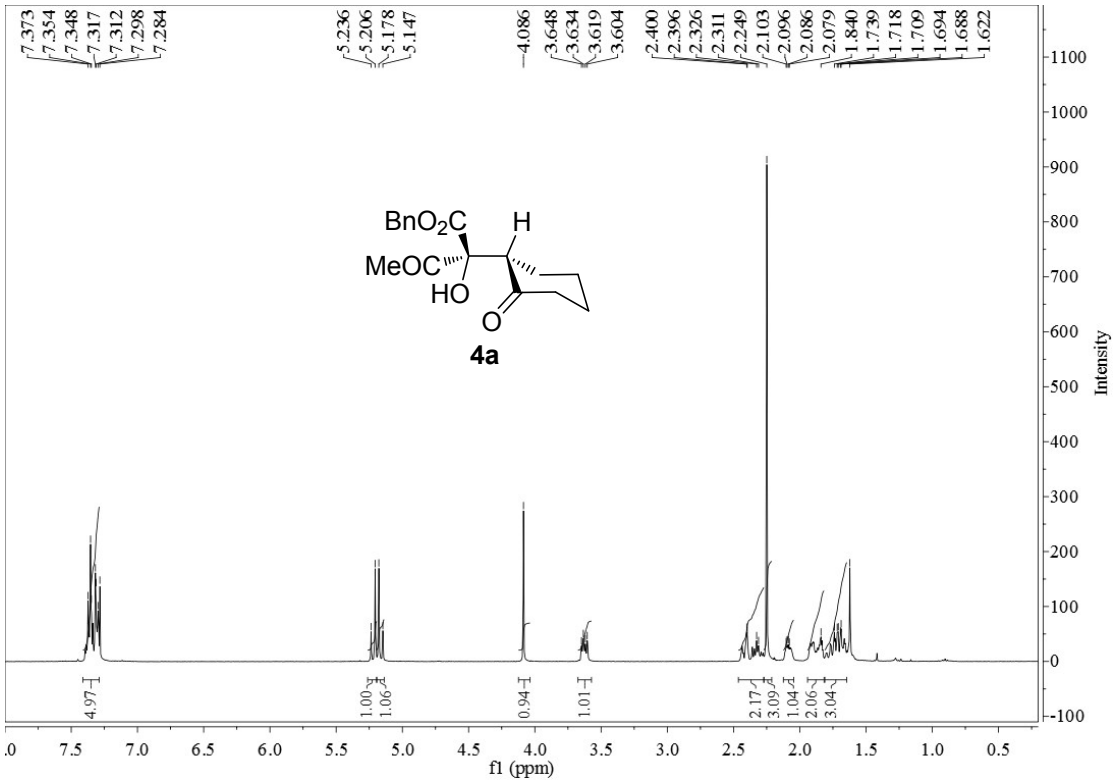


^{13}C NMR (125 MHz, $CDCl_3$)

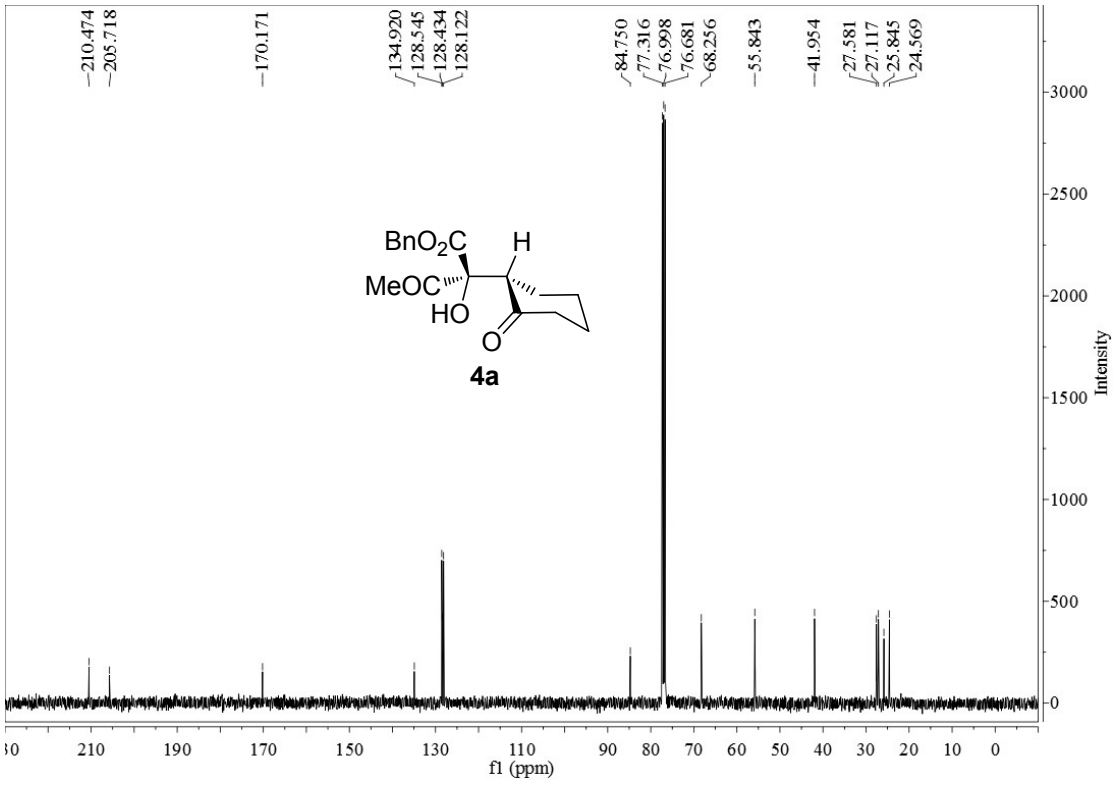


(*S*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (4a).

^{1}HNMR (500 MHz, $CDCl_3$)

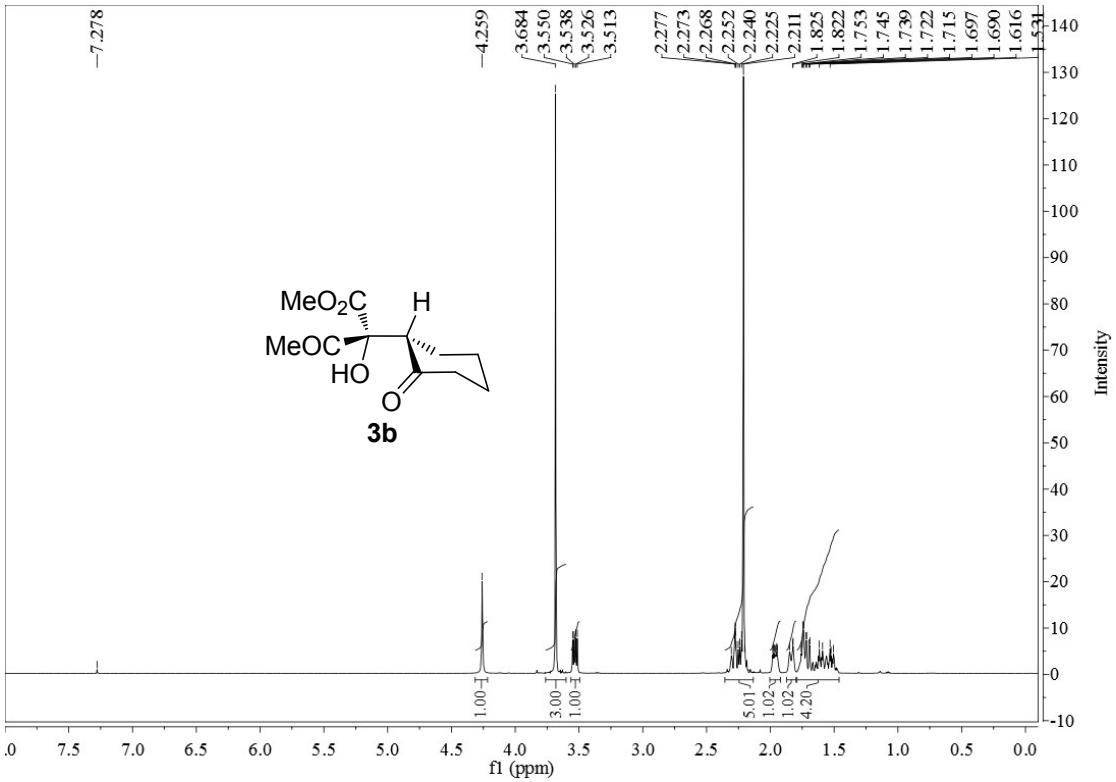


^{13}C NMR (125 MHz, $CDCl_3$)

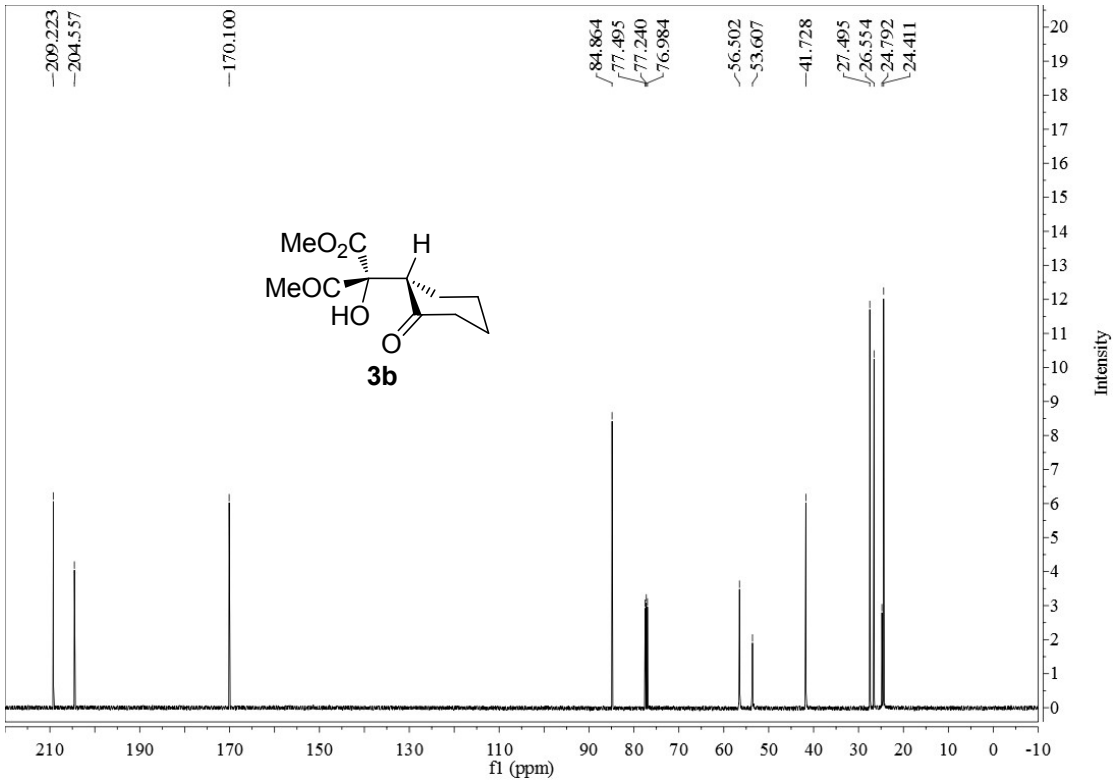


(*R*)-Methyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (3b).

^{1}HNMR (500 MHz, $CDCl_3$)

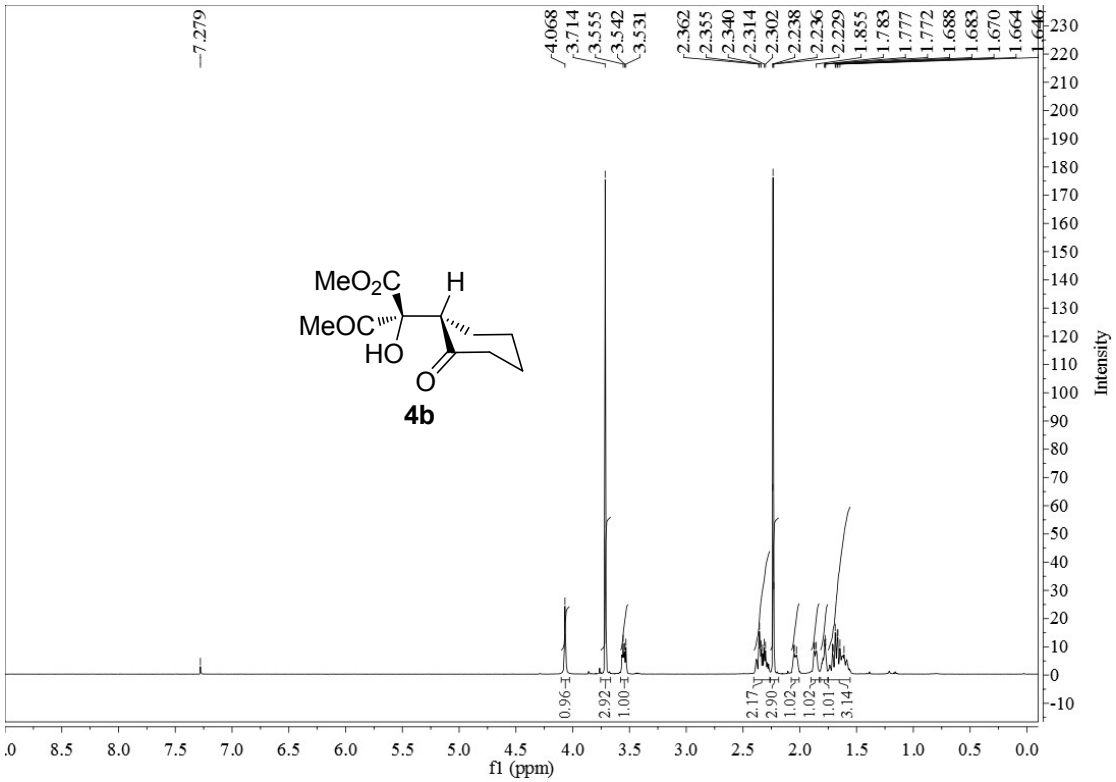


^{13}C NMR (125 MHz, $CDCl_3$)

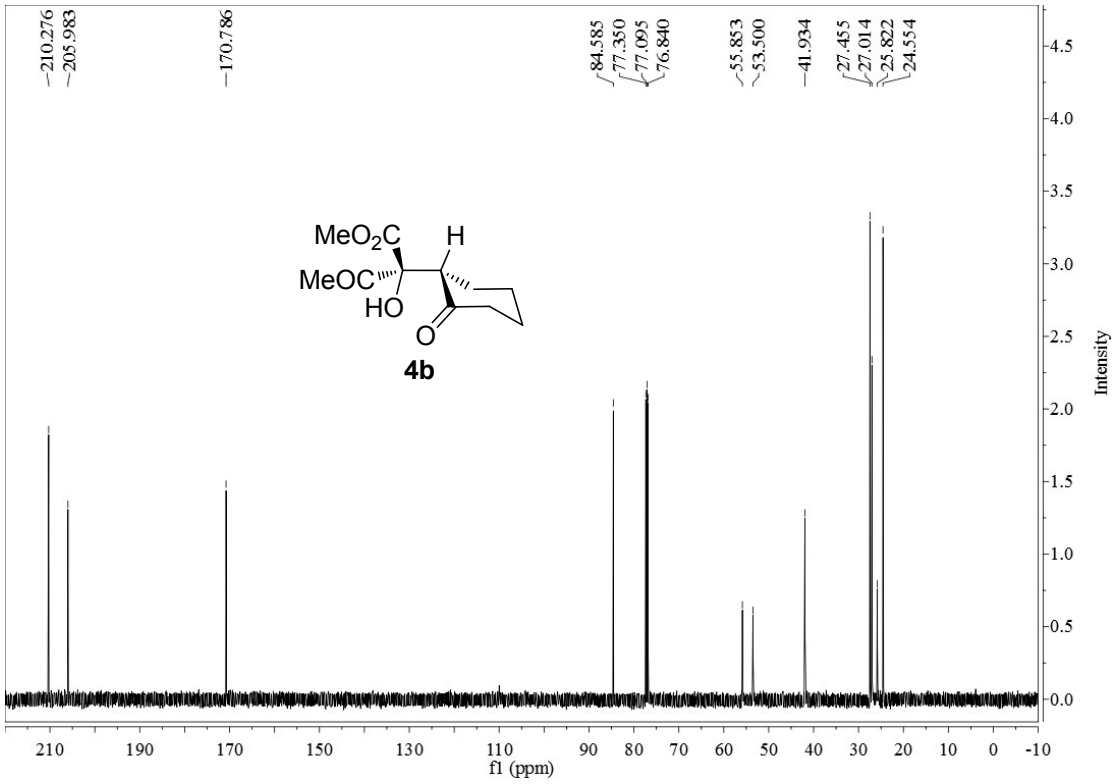


(*S*)-Methyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (4b).

^{1}HNMR (500 MHz, $CDCl_3$)

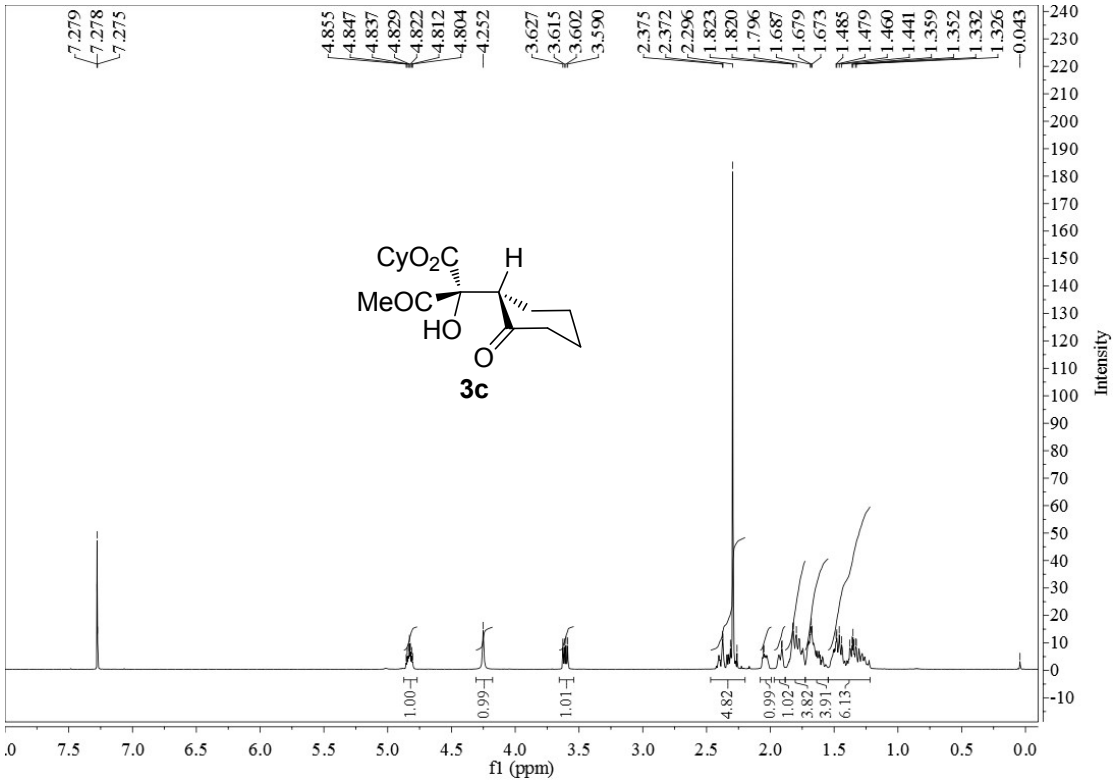


^{13}C NMR (125 MHz, $CDCl_3$)

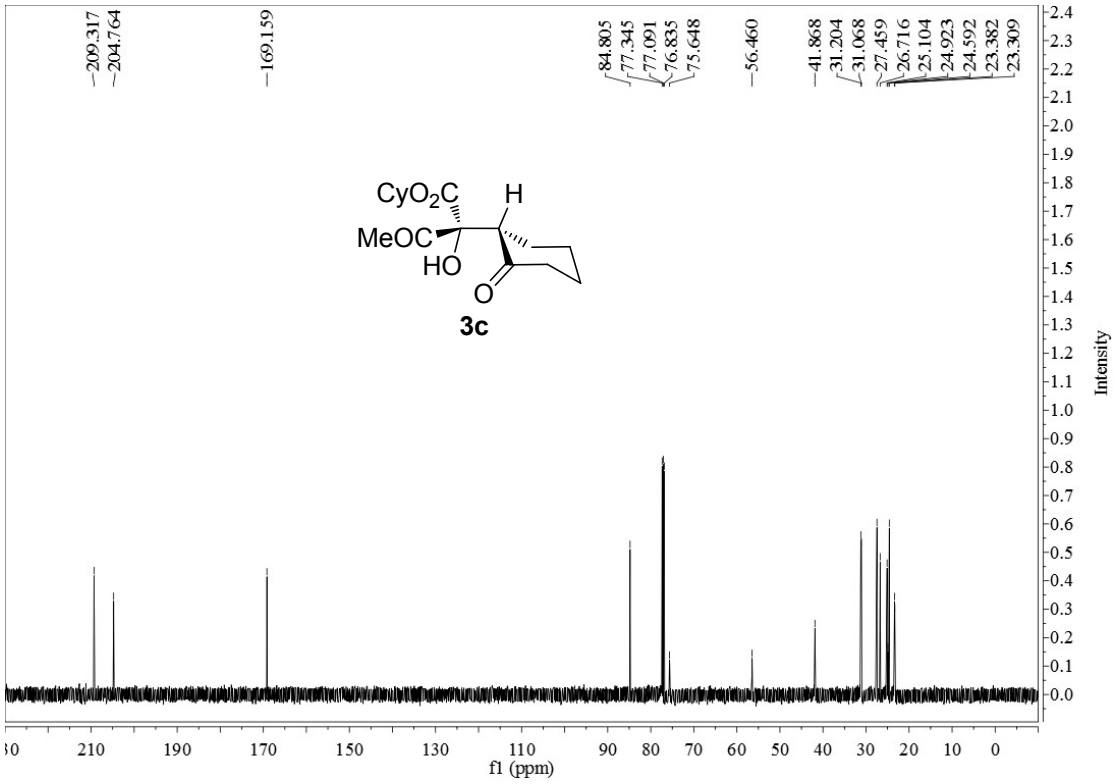


(*R*)-Cyclohexyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (3c).

^{1}HNMR (500 MHz, $CDCl_3$)

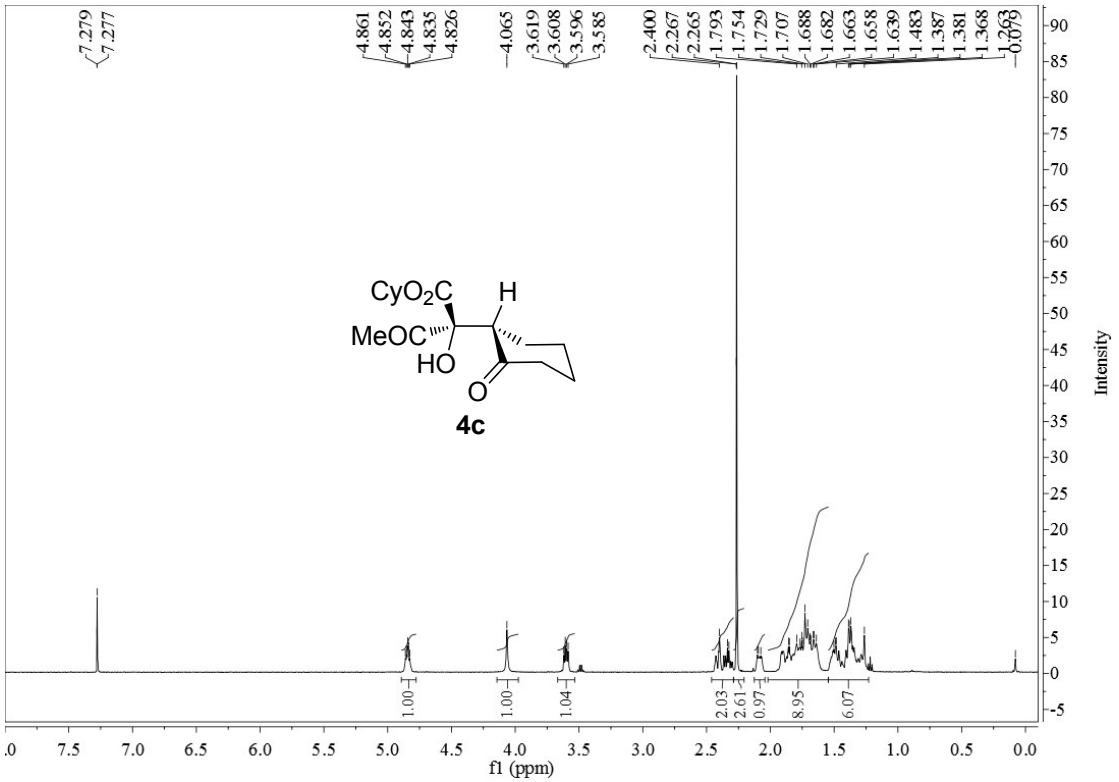


^{13}C NMR (125 MHz, $CDCl_3$)

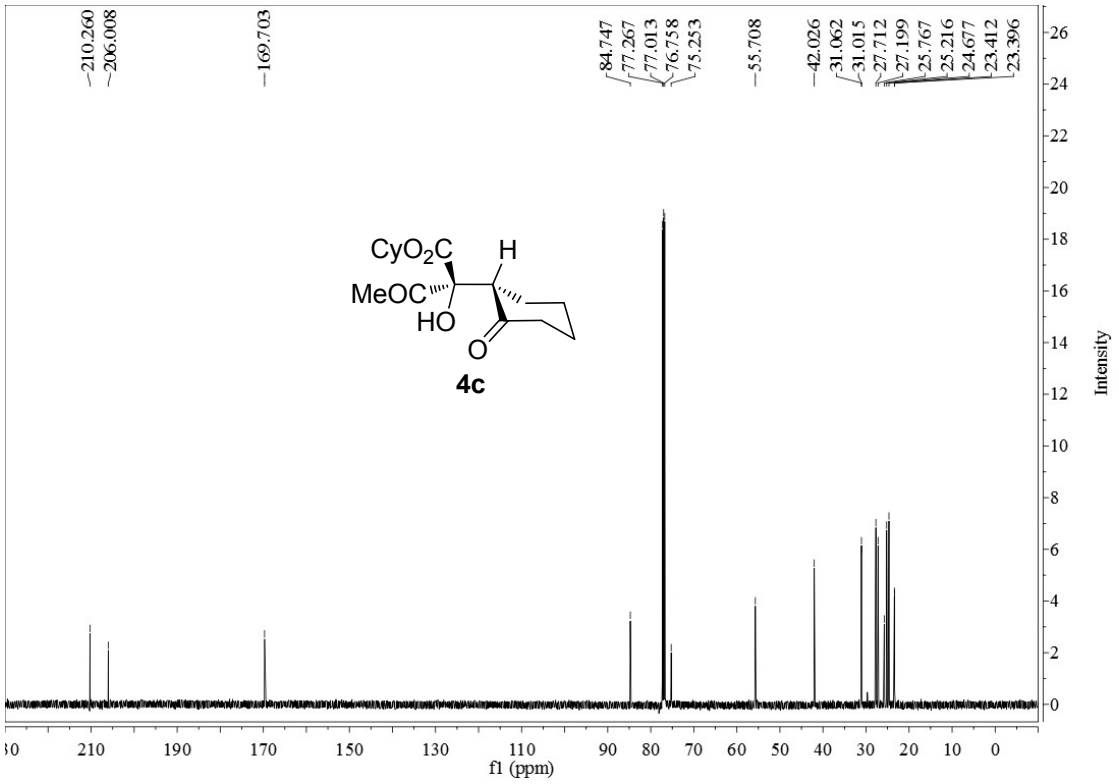


(*S*)-Cyclohexyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]butanoate (4c).

^{1}HNMR (500 MHz, $CDCl_3$)

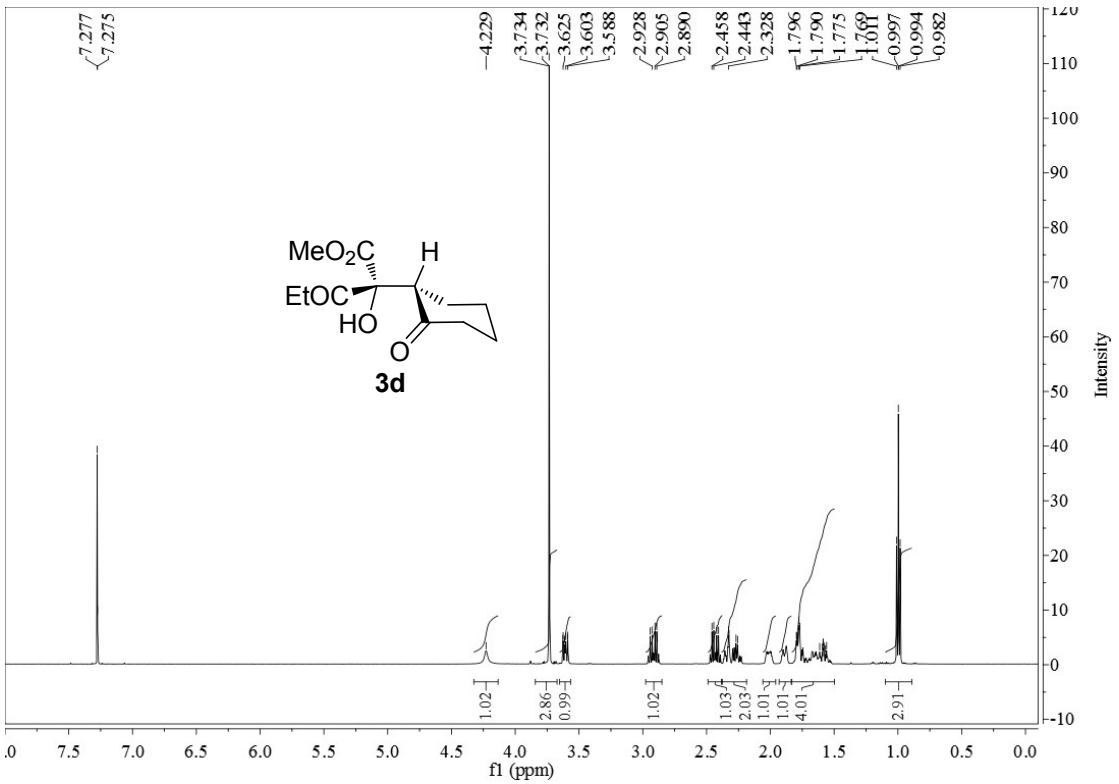


^{13}C NMR (125 MHz, $CDCl_3$)

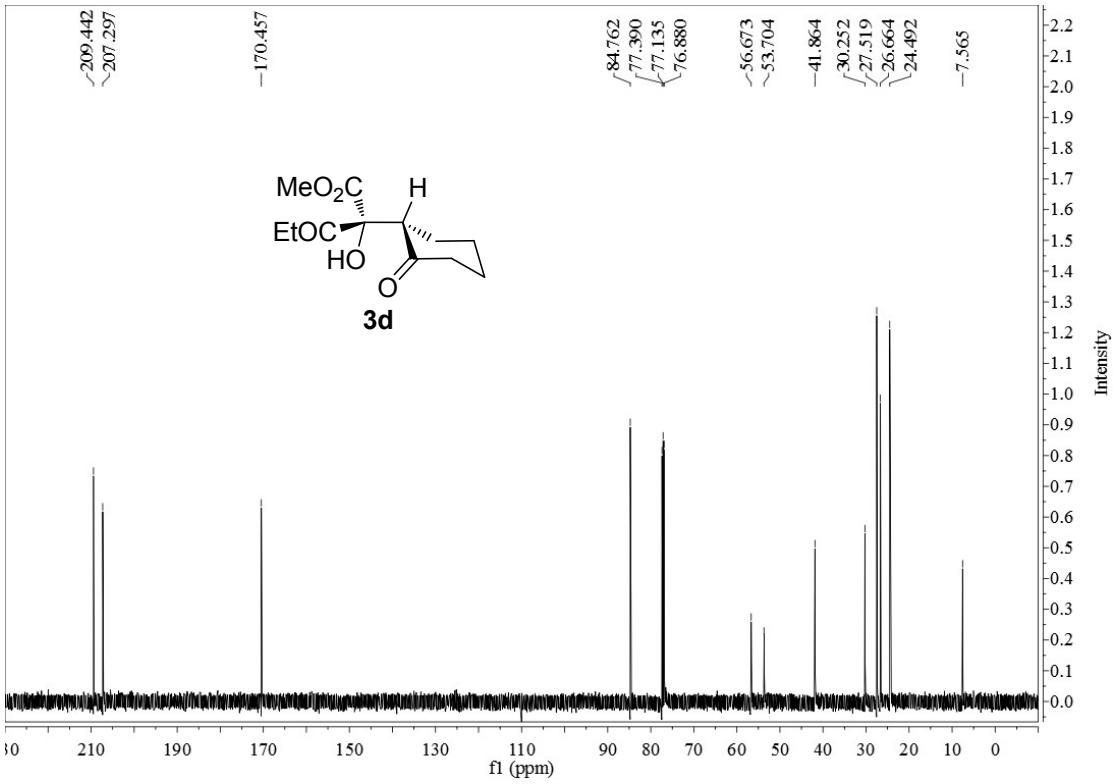


(*R*)-Methyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]pentanoate (3d).

^{1}HNMR (500 MHz, $CDCl_3$)

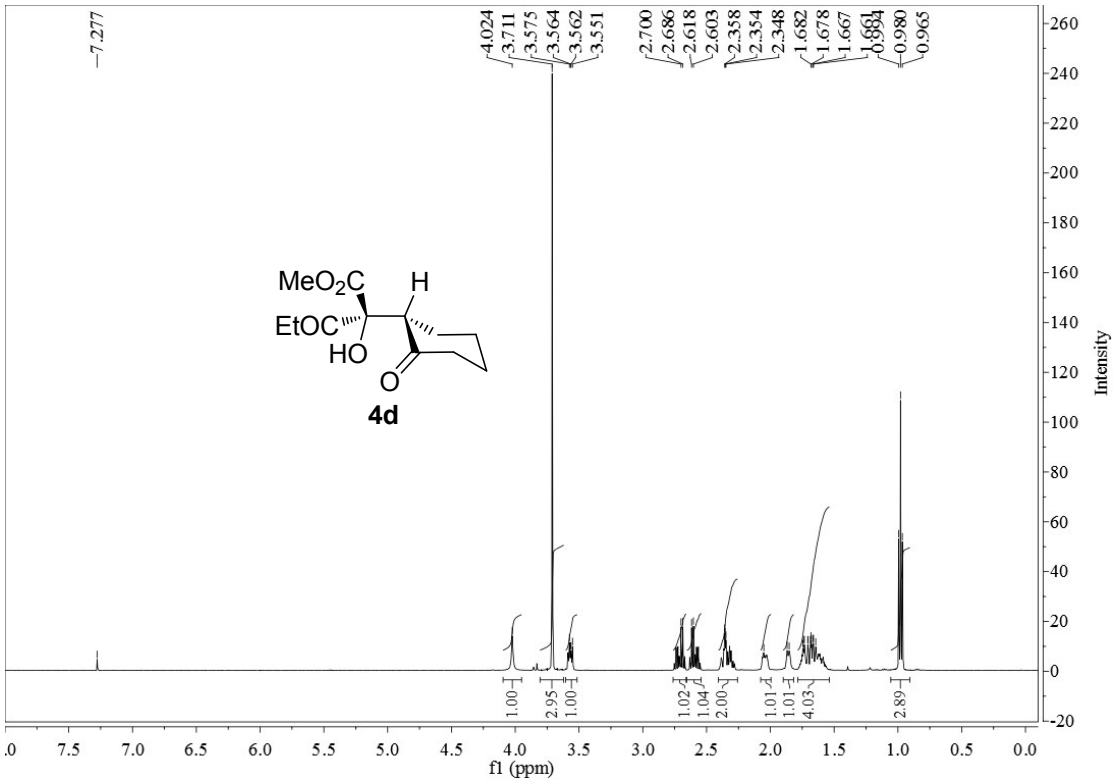


^{13}C NMR (125 MHz, $CDCl_3$)

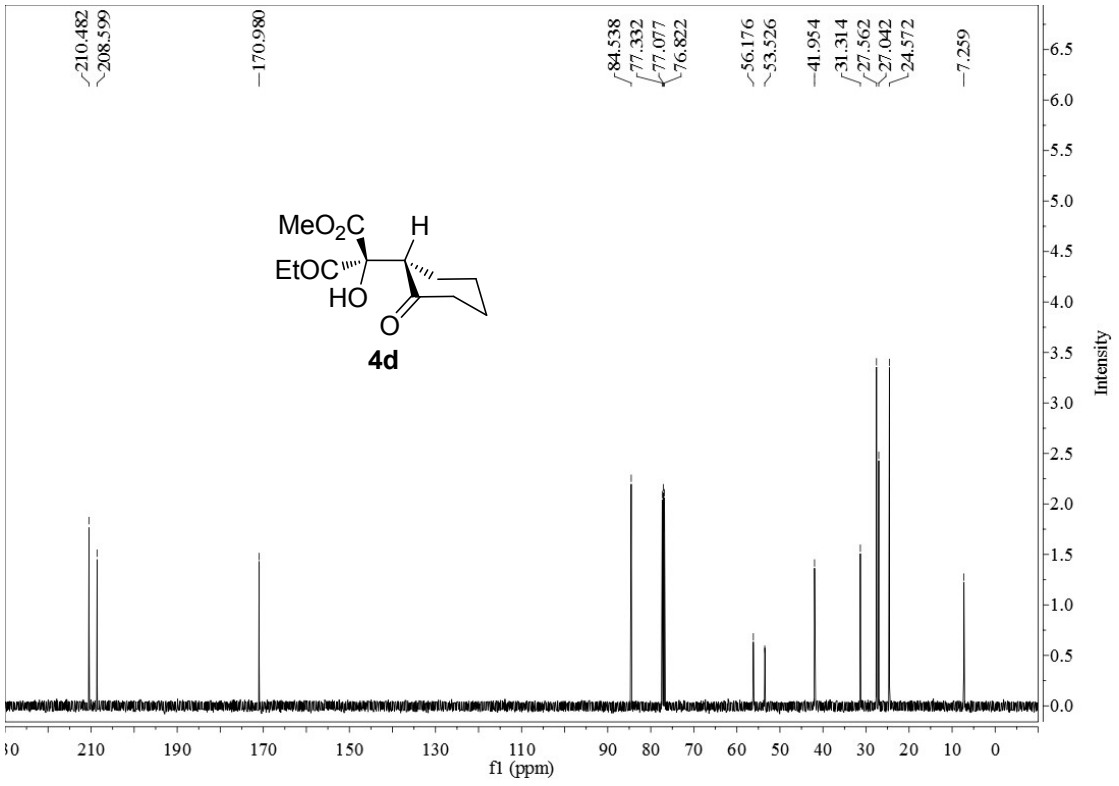


(*S*)-Methyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]pentanoate (4d).

^{1}HNMR (500 MHz, $CDCl_3$)

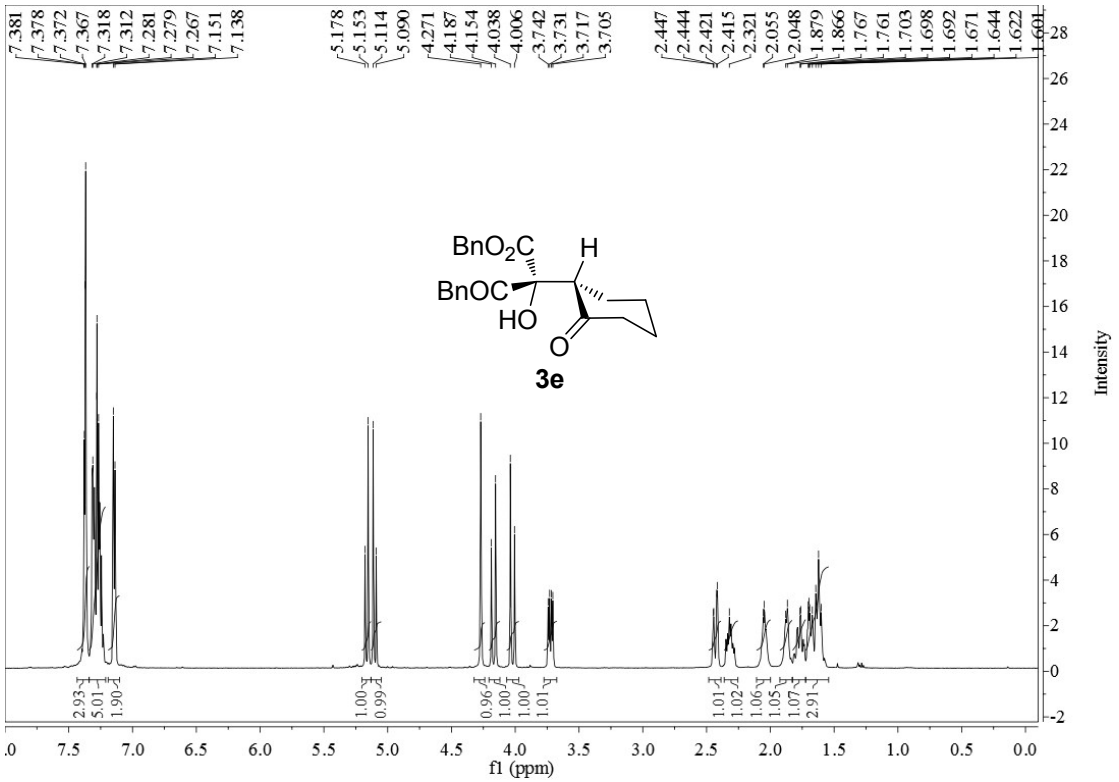


^{13}C NMR (125 MHz, $CDCl_3$)

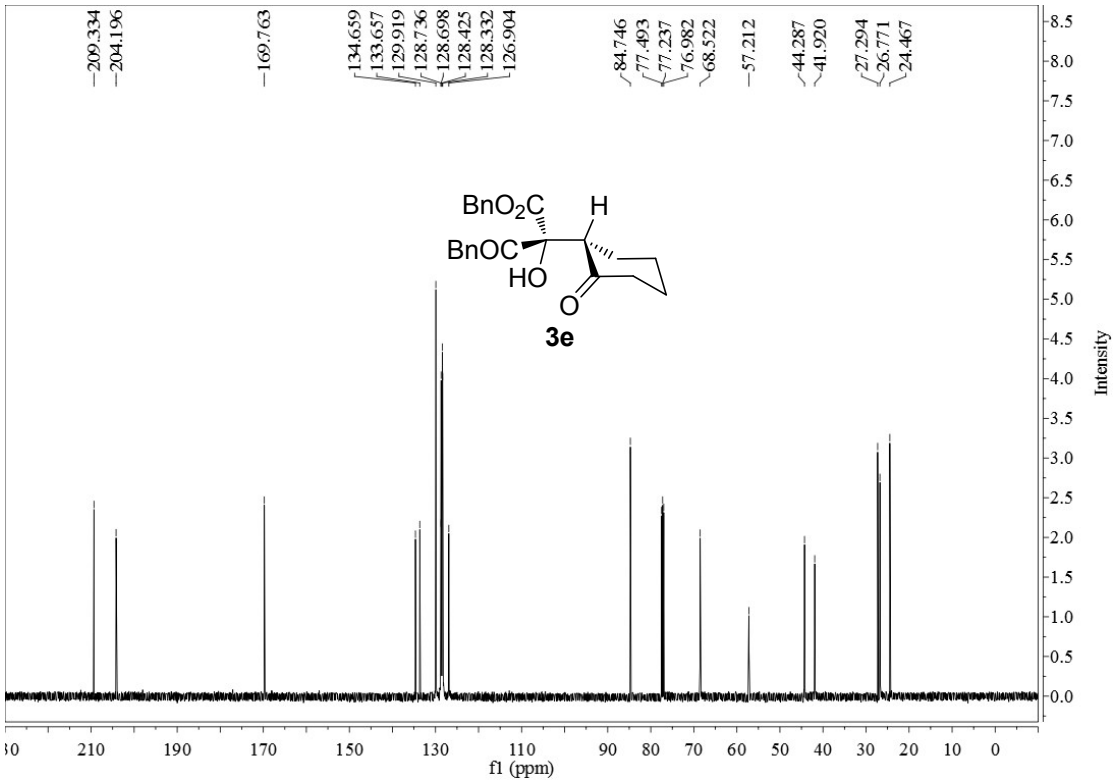


(*R*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-4-phenylbutanoate (3e).

^{1}HNMR (500 MHz, $CDCl_3$)

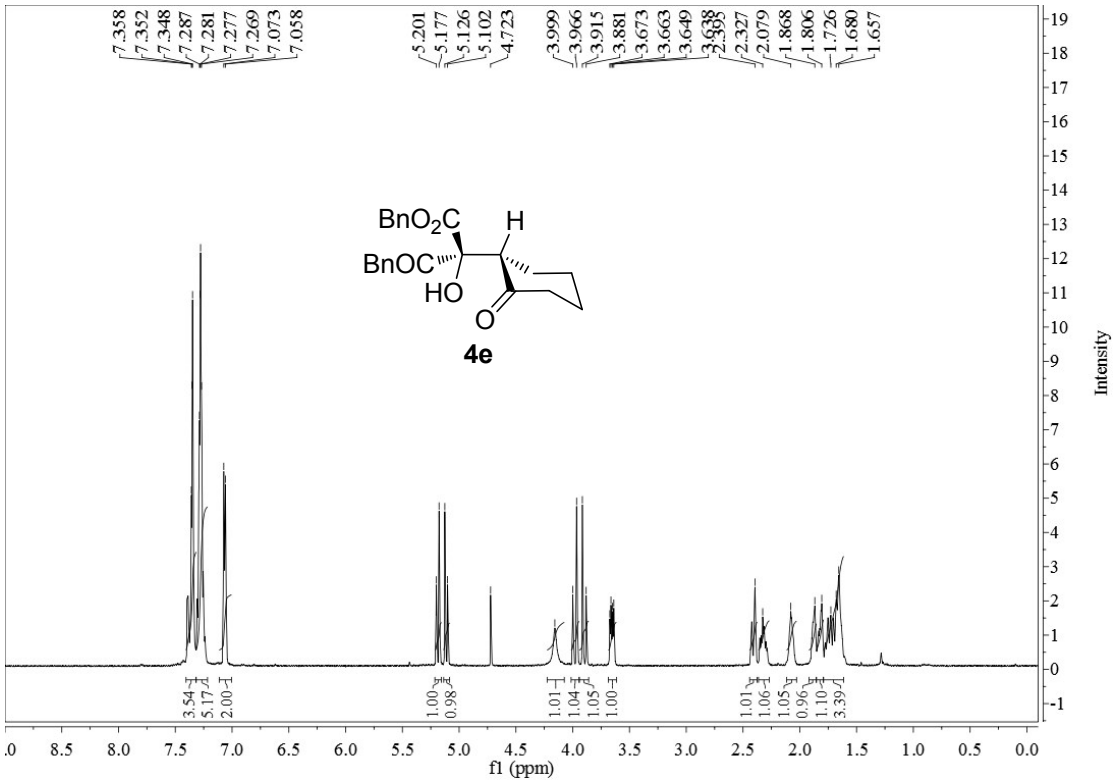


^{13}C NMR (125 MHz, $CDCl_3$)

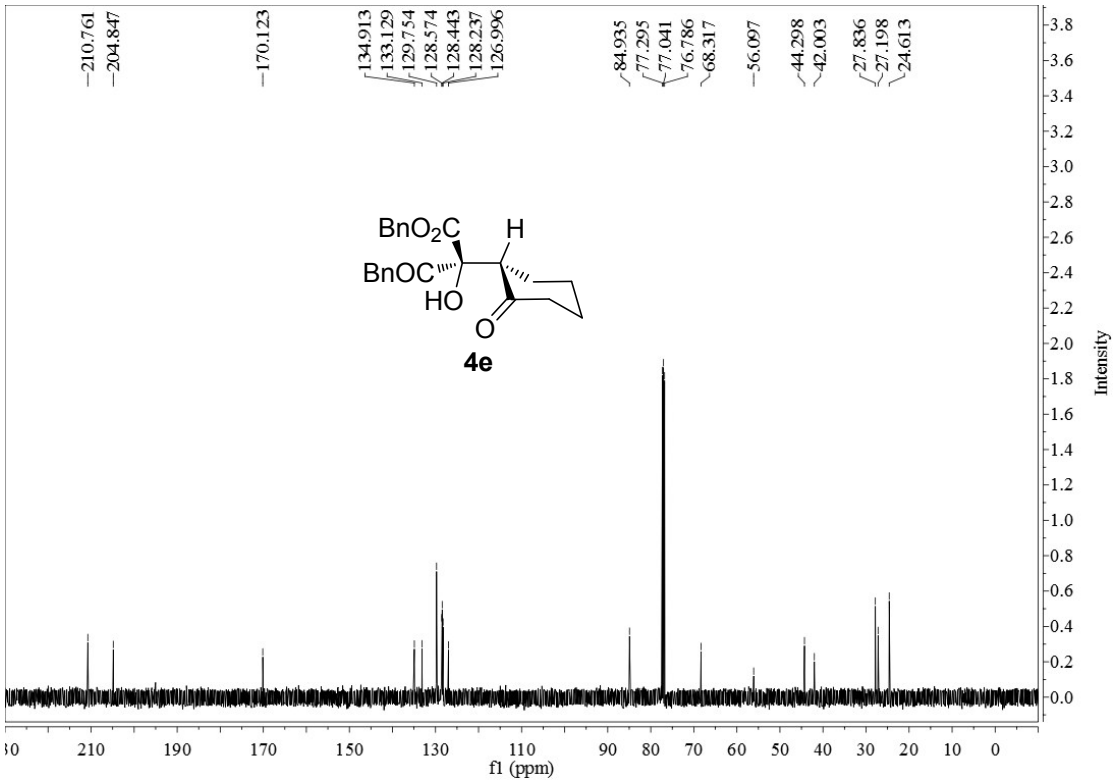


(*S*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-4-phenylbutanoate (4e).

^{1}HNMR (500 MHz, $CDCl_3$)

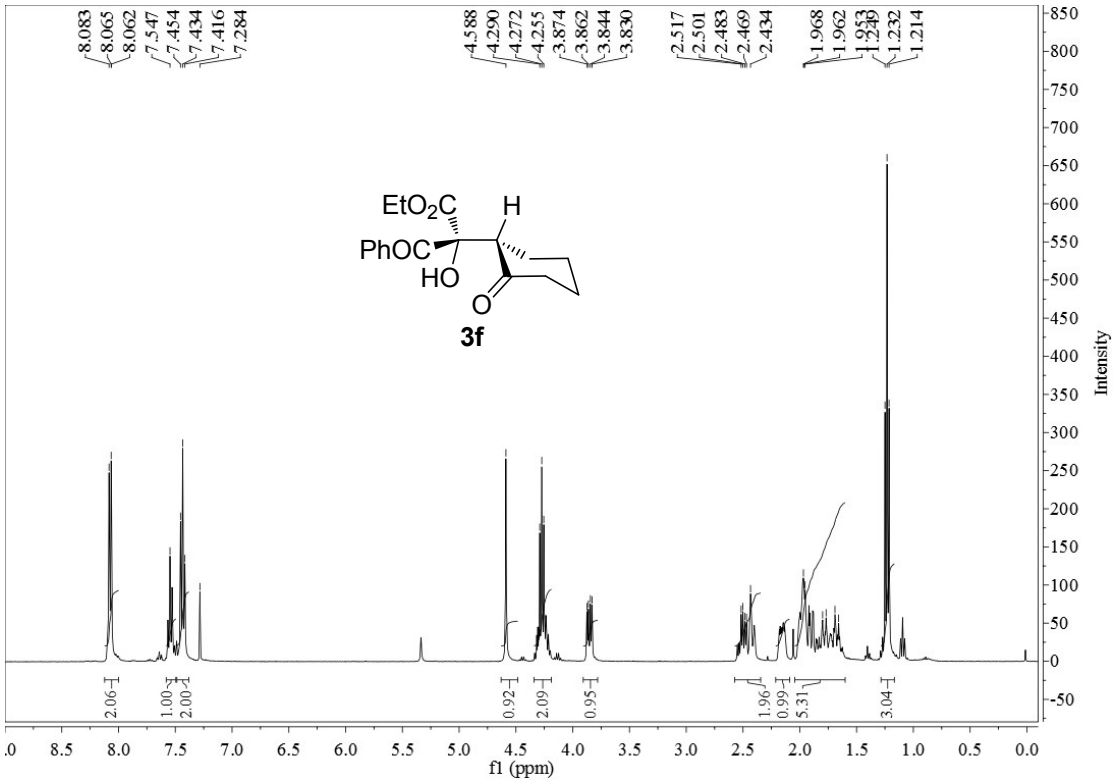


^{13}C NMR (125 MHz, $CDCl_3$)

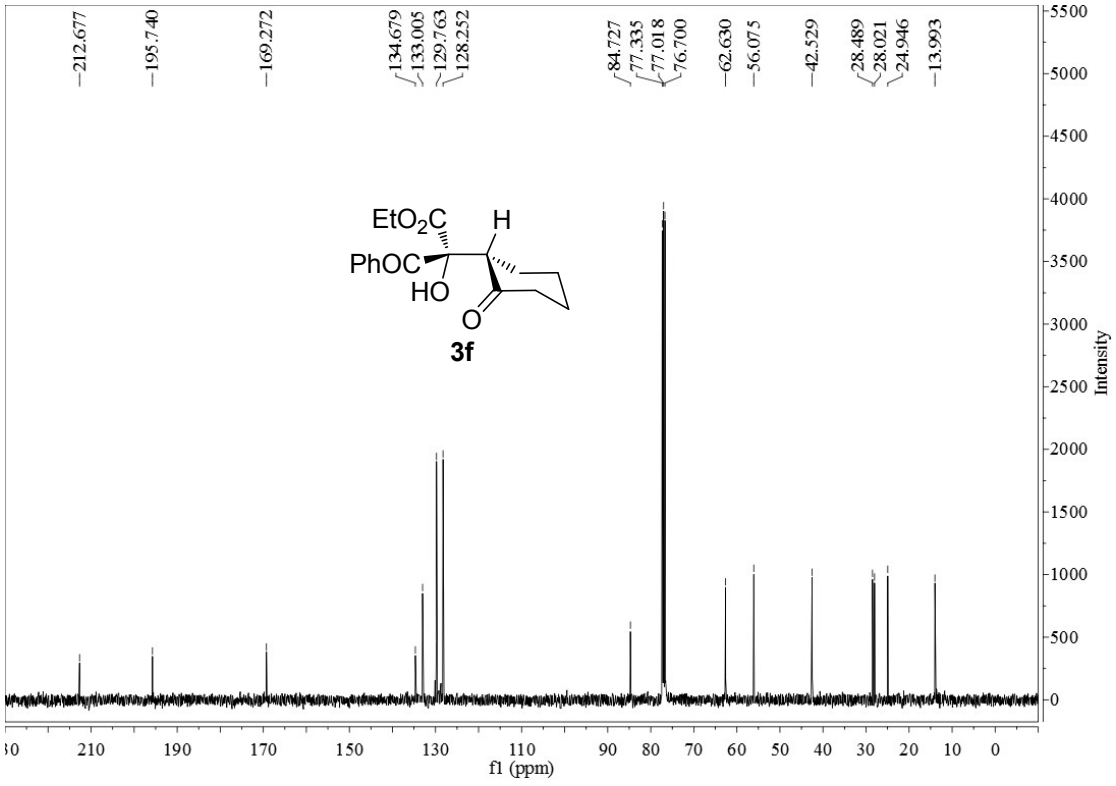


(*R*)-Ethyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-3-phenylpropanoate (3f).

^{1}HNMR (500 MHz, $CDCl_3$)

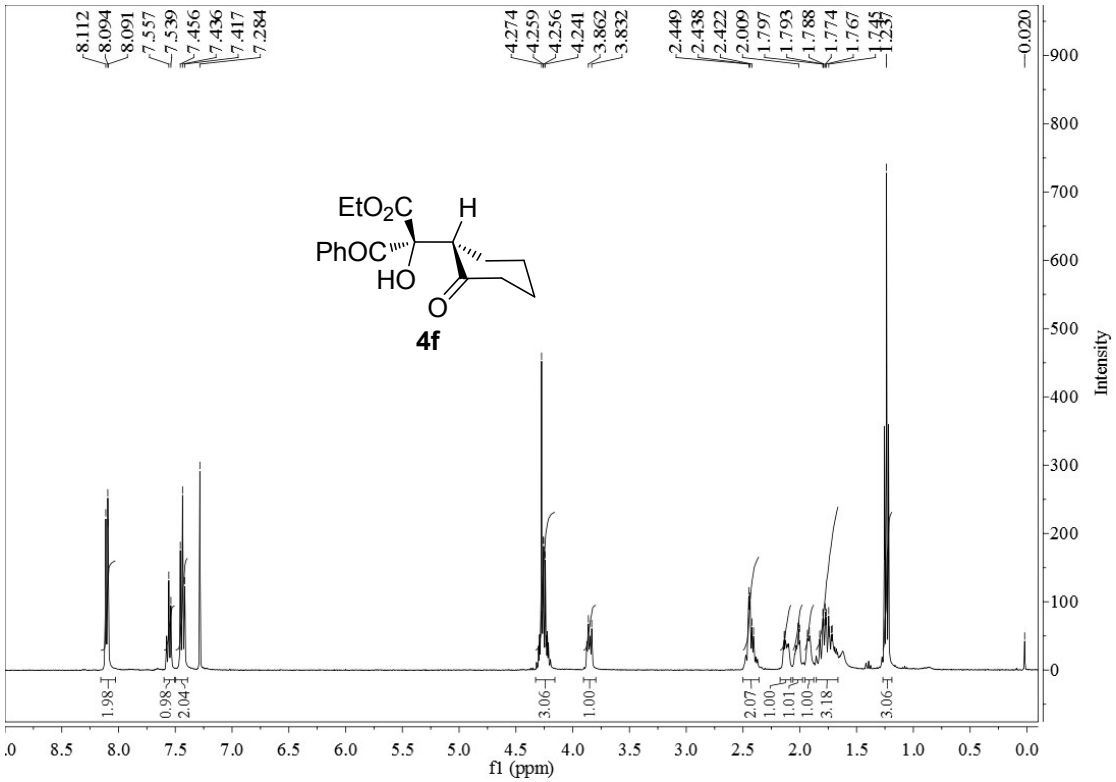


^{13}C NMR (125 MHz, $CDCl_3$)

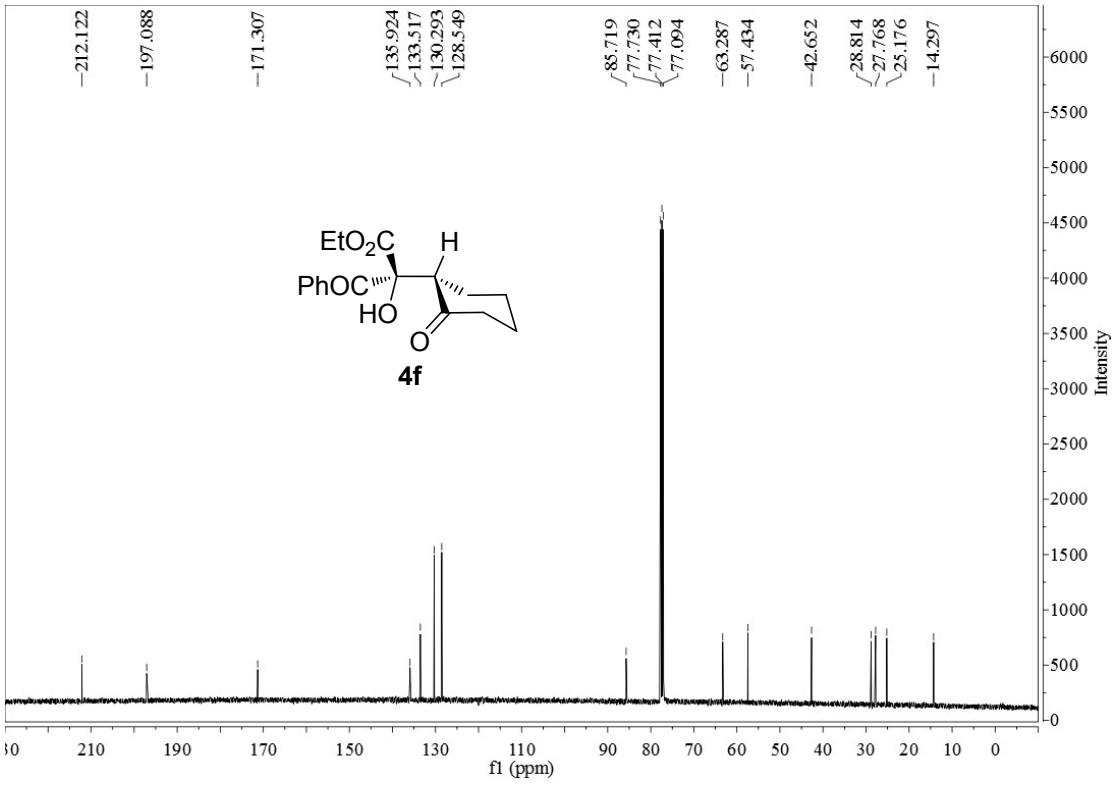


(*S*)-Ethyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-3-phenylpropanoate (4f).

^{1}HNMR (500 MHz, $CDCl_3$)

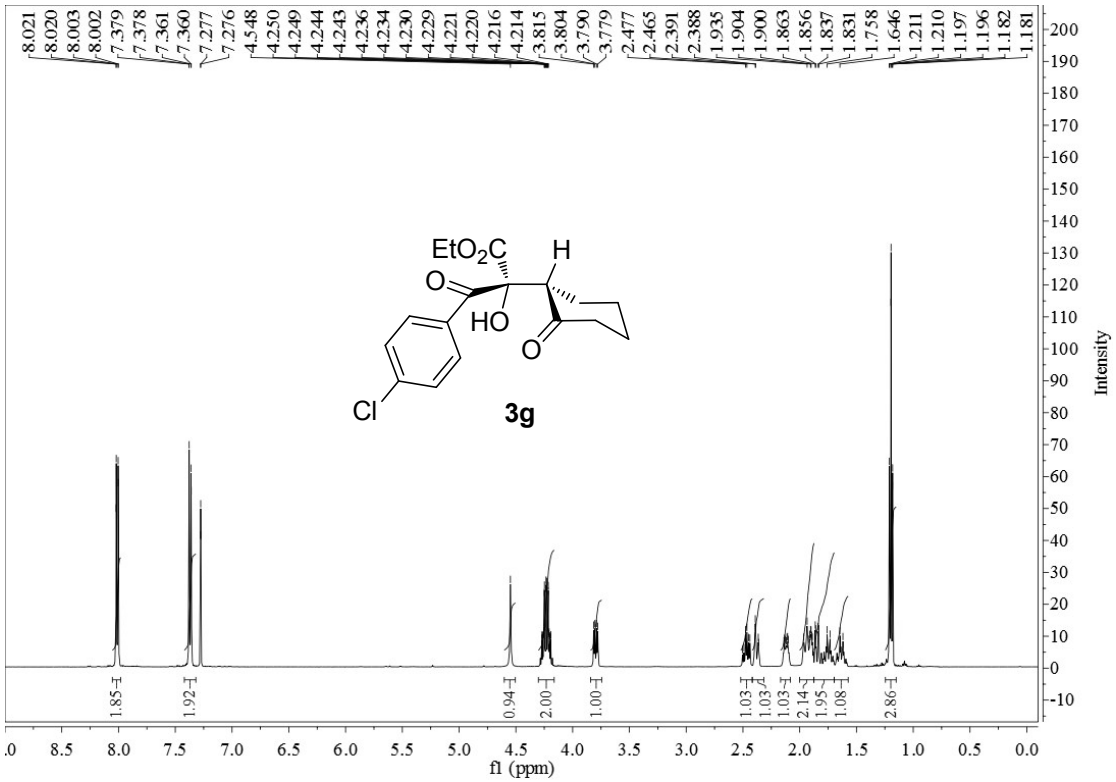


^{13}C NMR (125 MHz, $CDCl_3$)

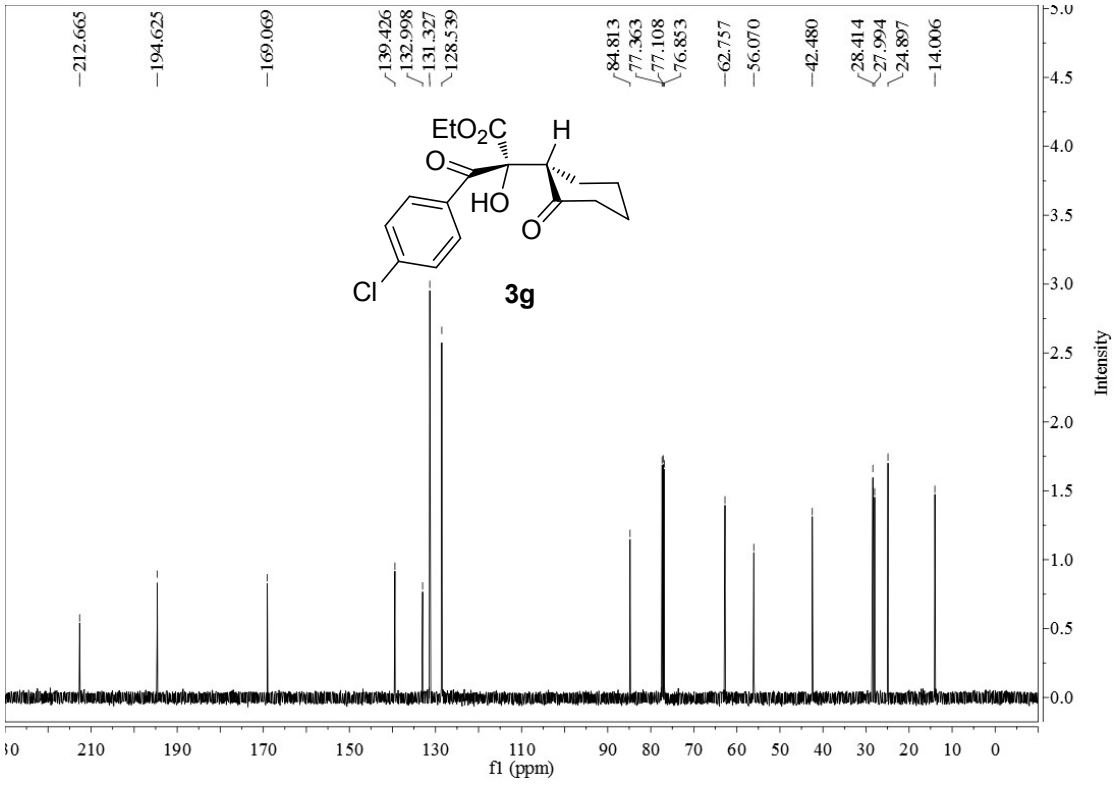


(*R*)-Ethyl 3-(4-Chlorophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3g).

^{1}HNMR (500 MHz, $CDCl_3$)

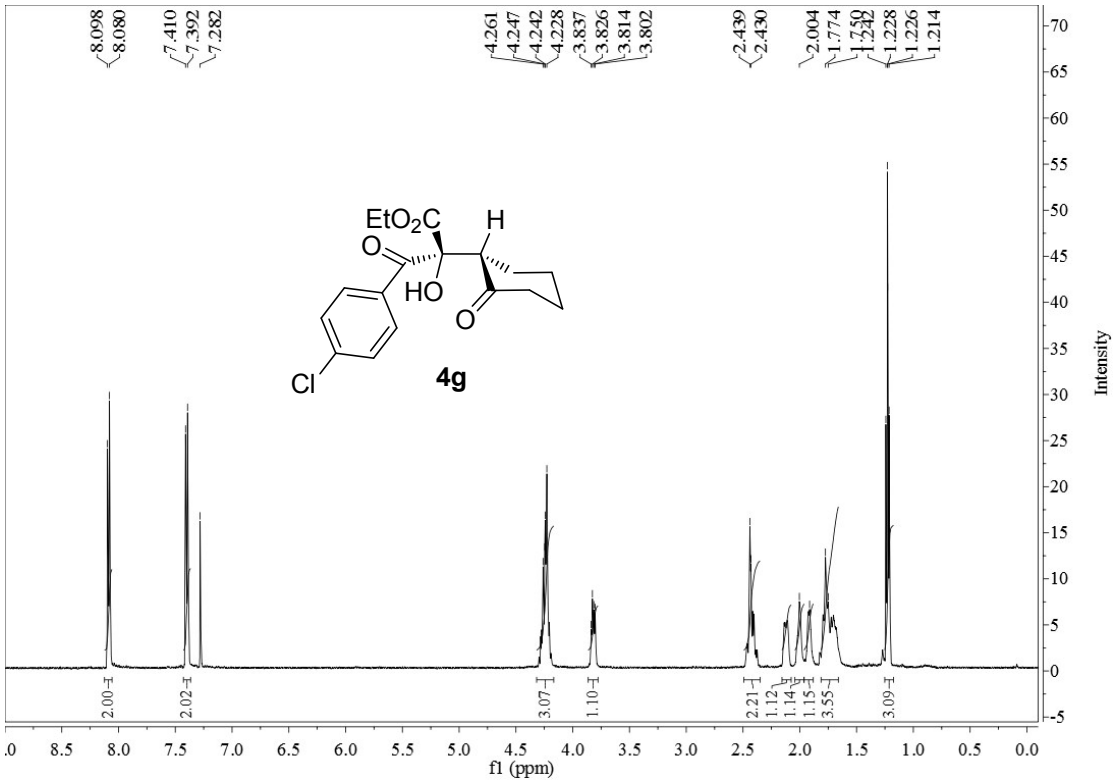


^{13}C NMR (125 MHz, $CDCl_3$)

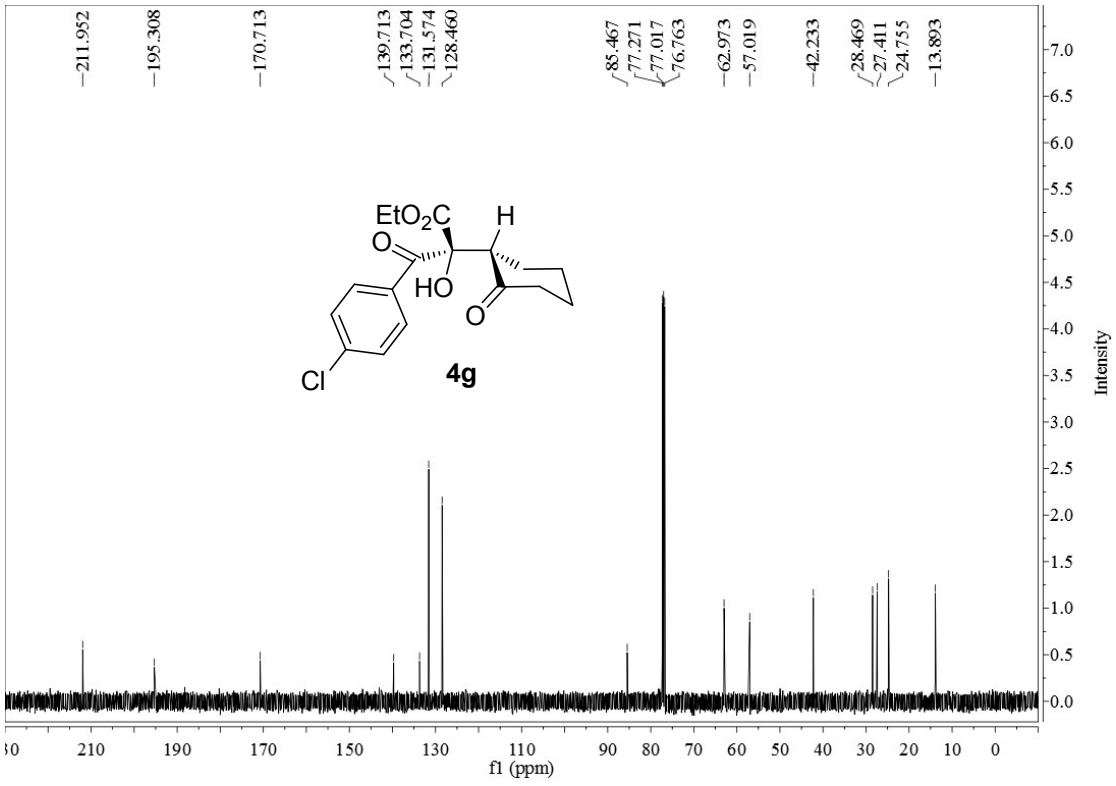


(*S*)-Ethyl 3-(4-Chlorophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4g).

^{1}HNMR (500 MHz, $CDCl_3$)

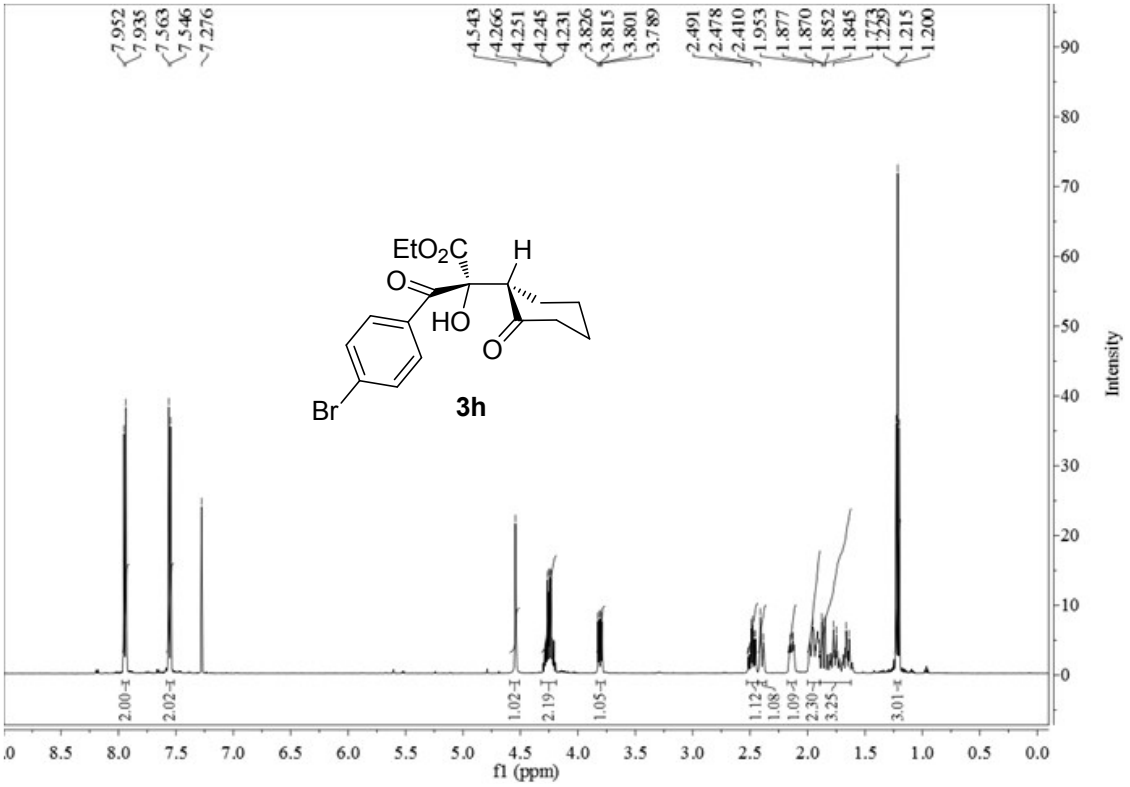


^{13}C NMR (125 MHz, $CDCl_3$)

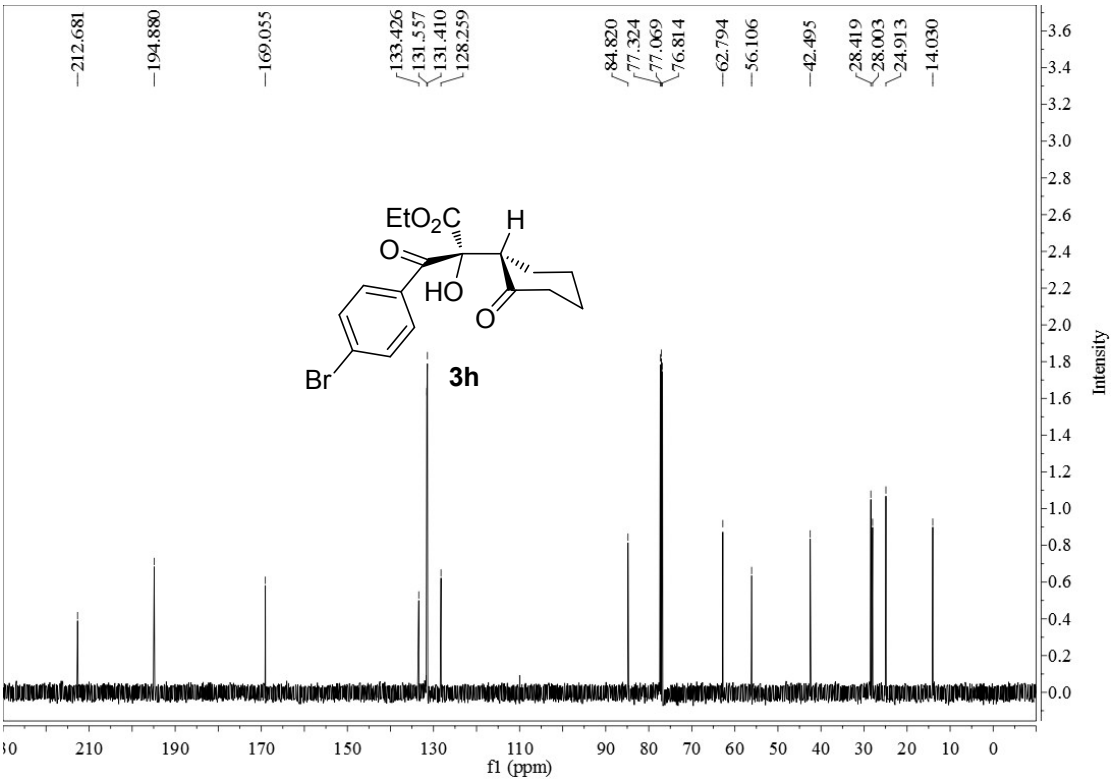


(*R*)-Ethyl 3-(4-Bromophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3h).

^{1}HNMR (500 MHz, $CDCl_3$)

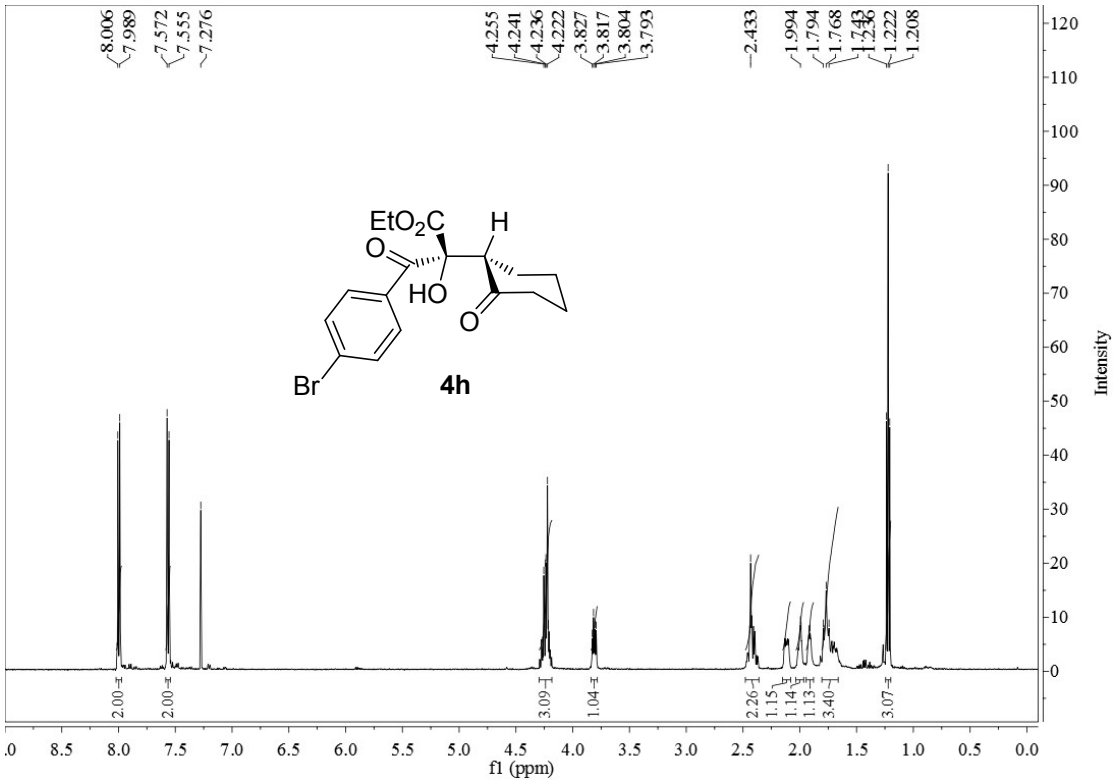


^{13}C NMR (125 MHz, $CDCl_3$)

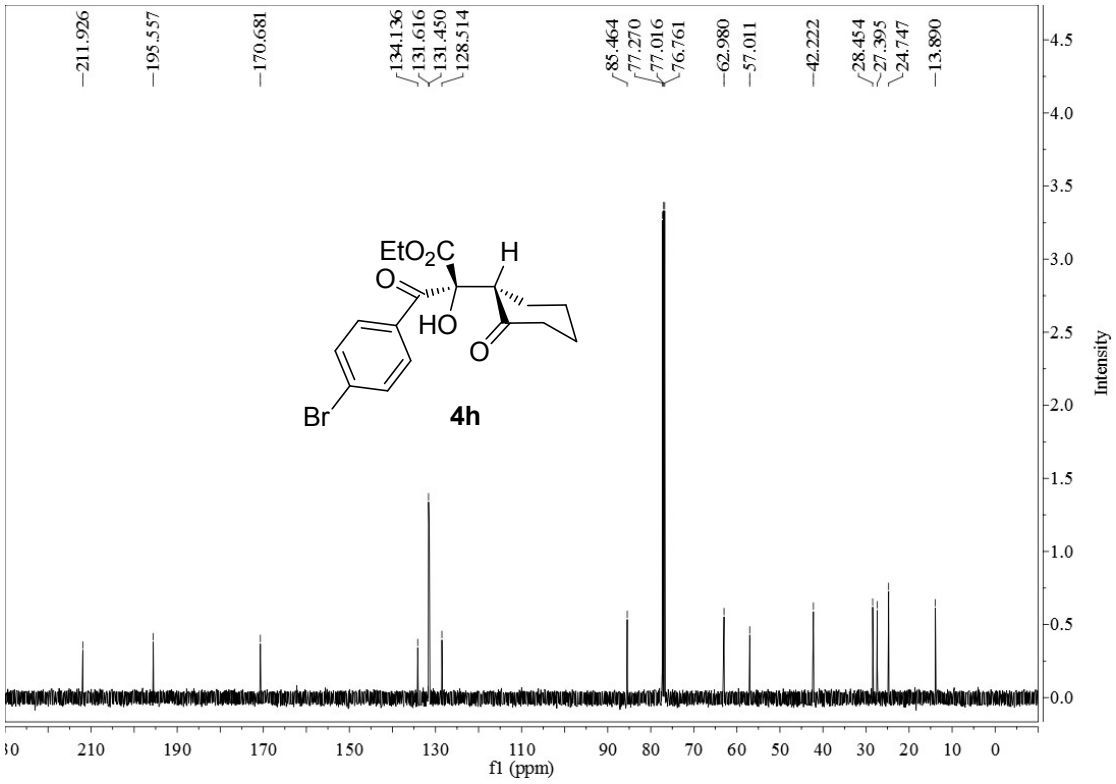


(*S*)-Ethyl 3-(4-Bromophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4h).

^{1}HNMR (500 MHz, $CDCl_3$)

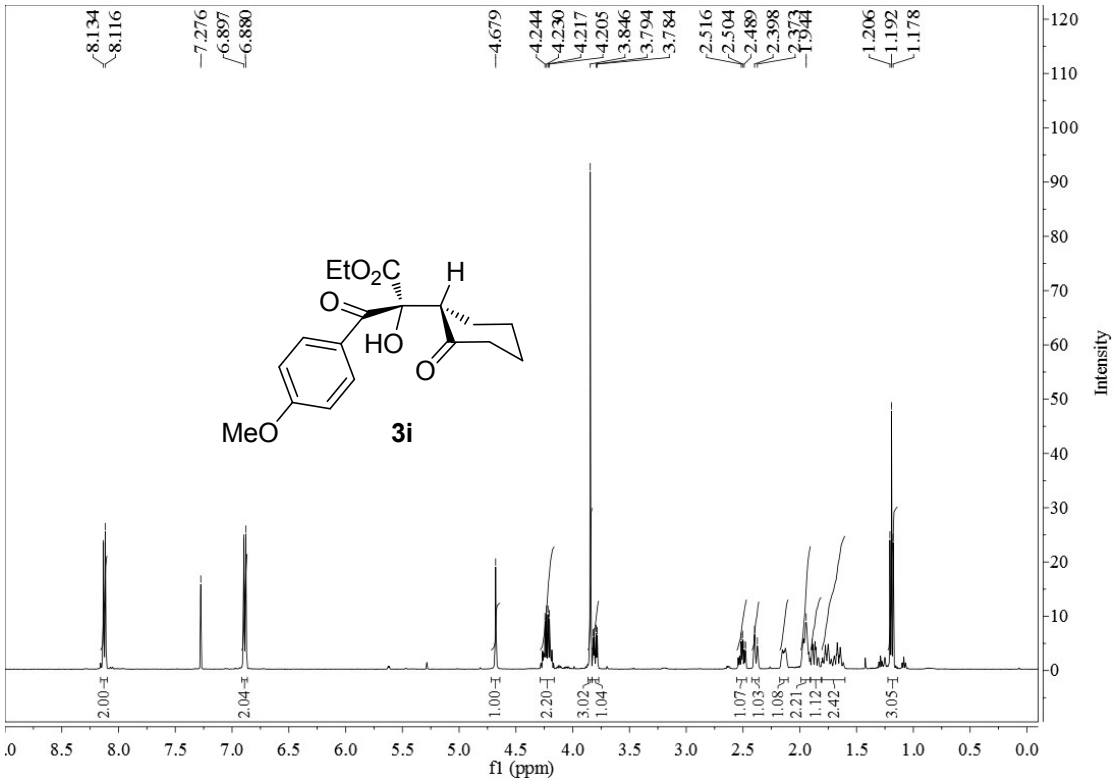


^{13}C NMR (125 MHz, $CDCl_3$)

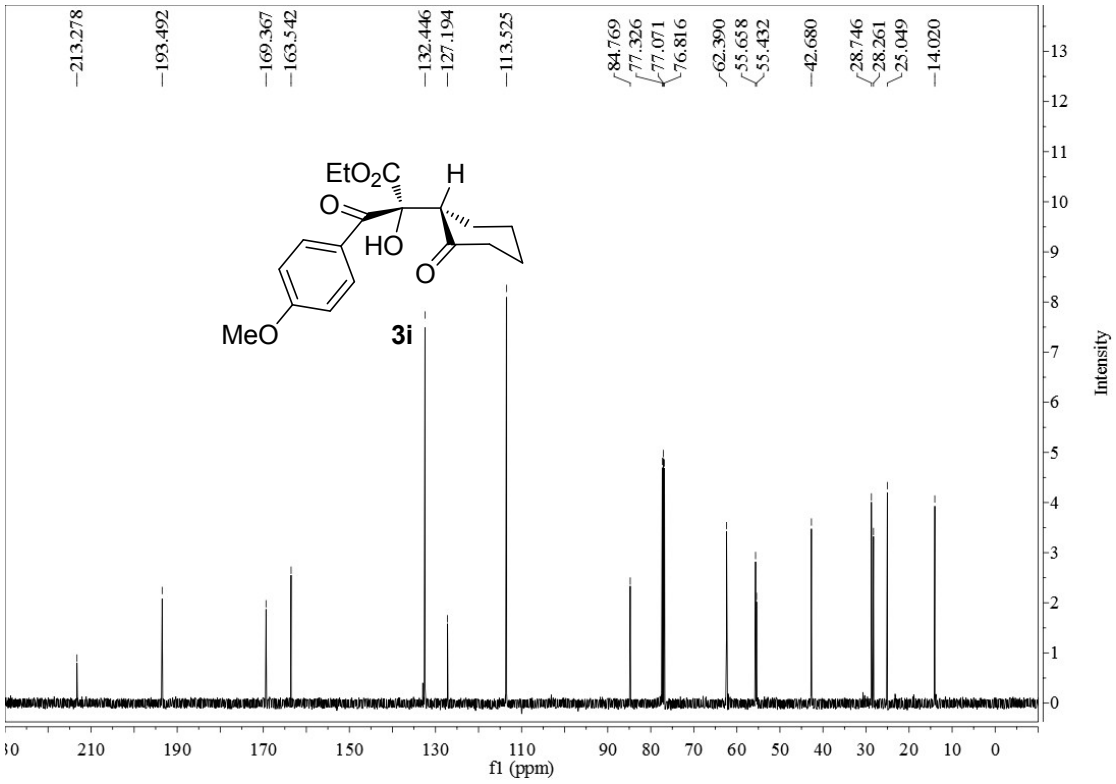


(*R*)-Ethyl 2-Hydroxy-3-(4-methoxyphenyl)-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3i).

^{1}HNMR (500 MHz, $CDCl_3$)

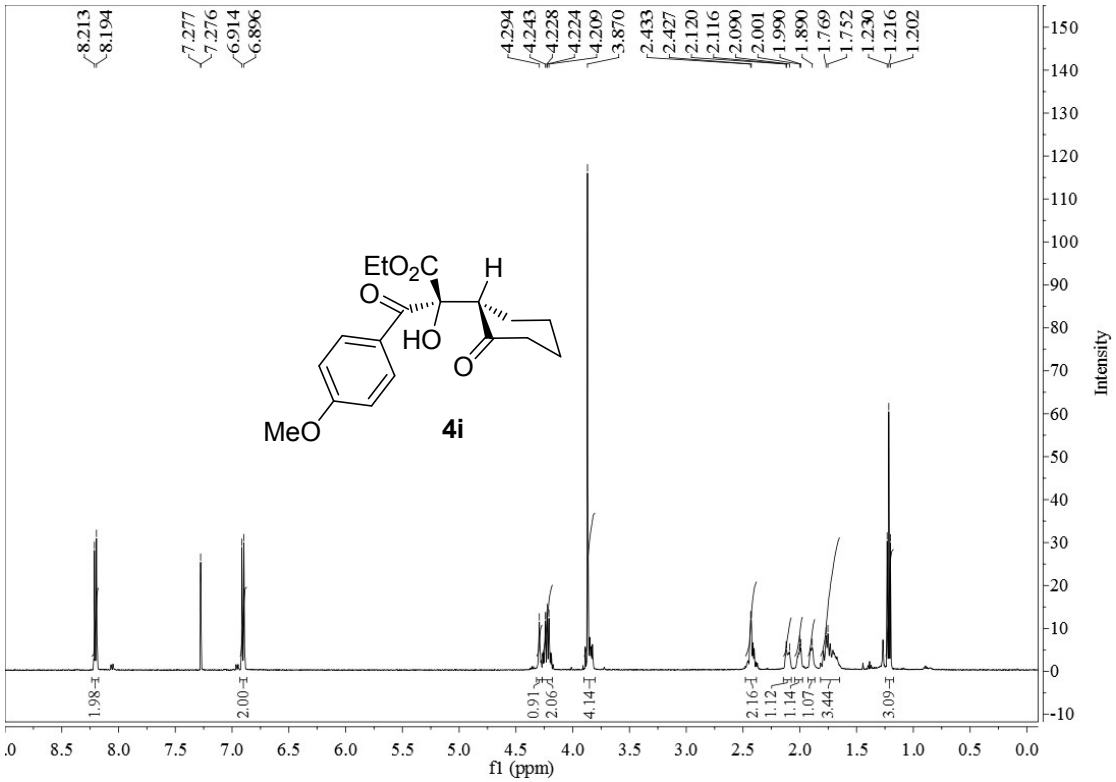


^{13}C NMR (125 MHz, $CDCl_3$)

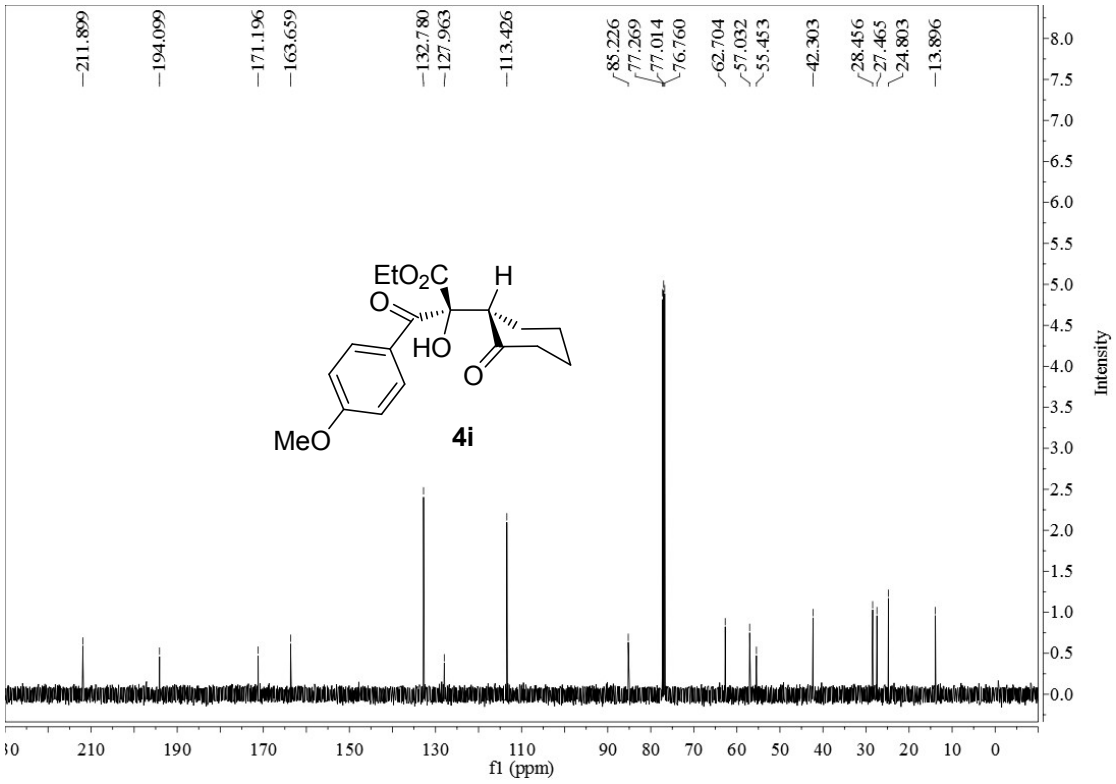


(*S*)-Ethyl 2-Hydroxy-3-(4-methoxyphenyl)-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4i).

^{1}HNMR (500 MHz, $CDCl_3$)

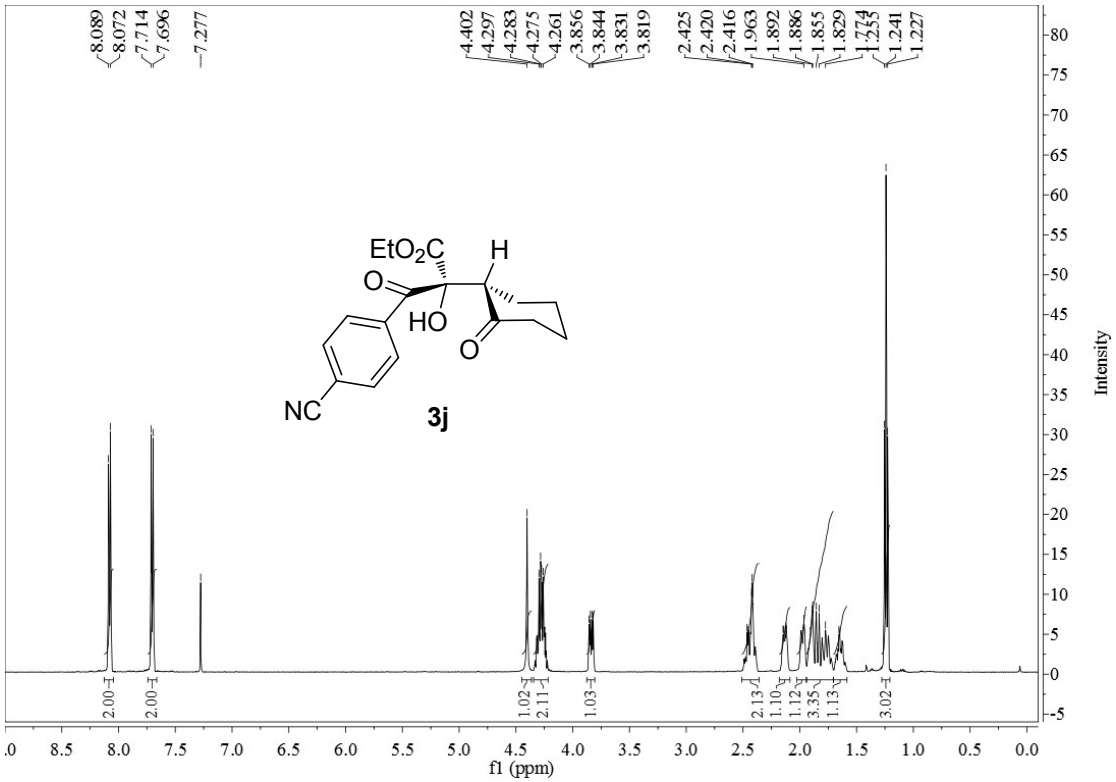


^{13}C NMR (125 MHz, $CDCl_3$)

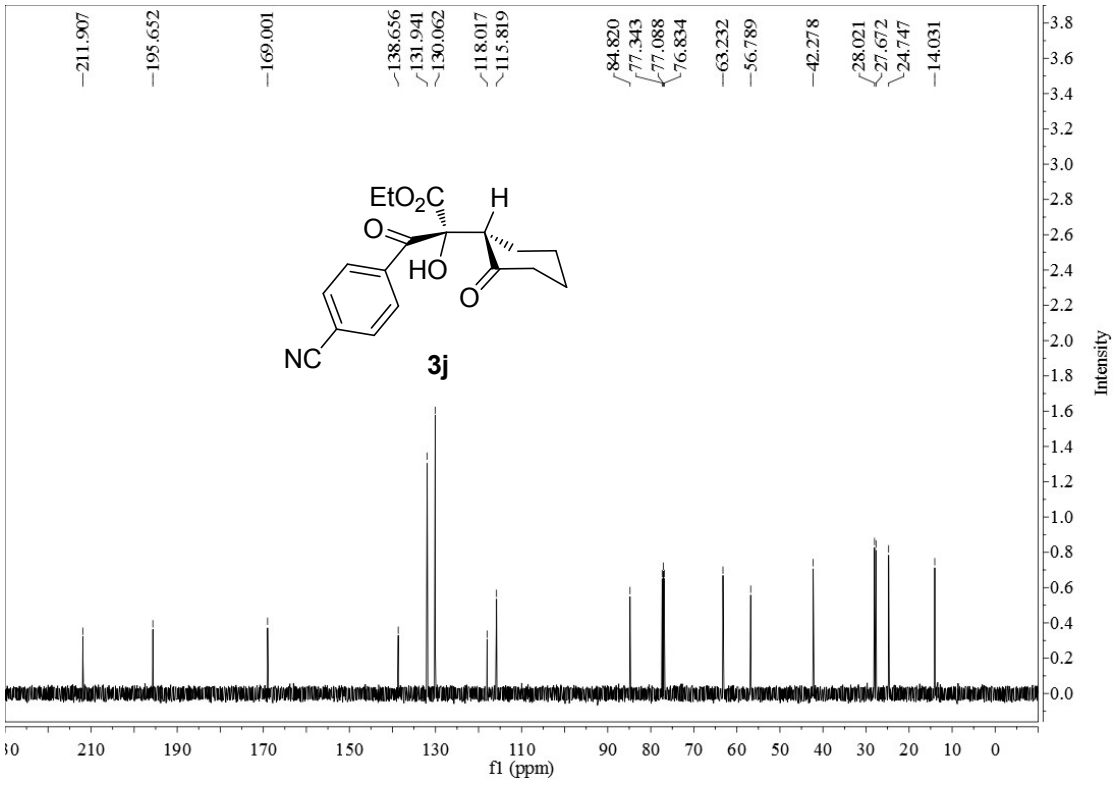


(*R*)-Ethyl 3-(4-Cyanophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3j).

^{1}HNMR (500 MHz, $CDCl_3$)

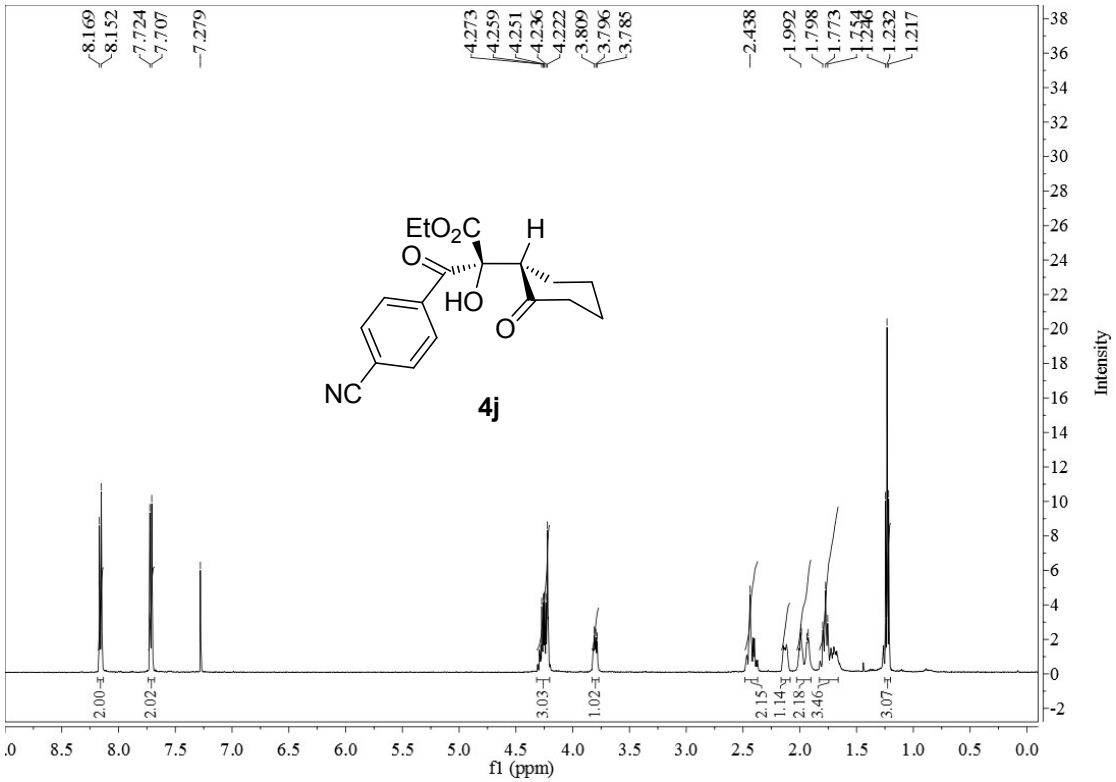


^{13}C NMR (125 MHz, $CDCl_3$)

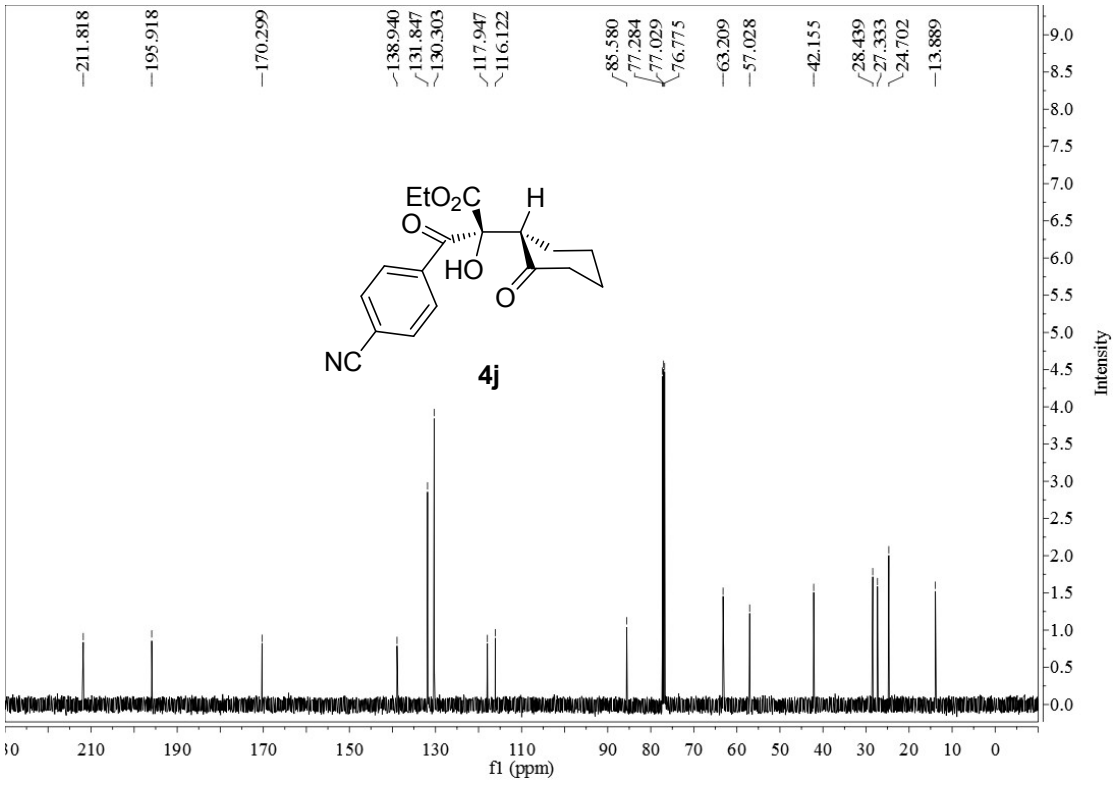


(*S*)-Ethyl 3-(4-Cyanophenyl)-2-hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4j).

^{1}HNMR (500 MHz, $CDCl_3$)

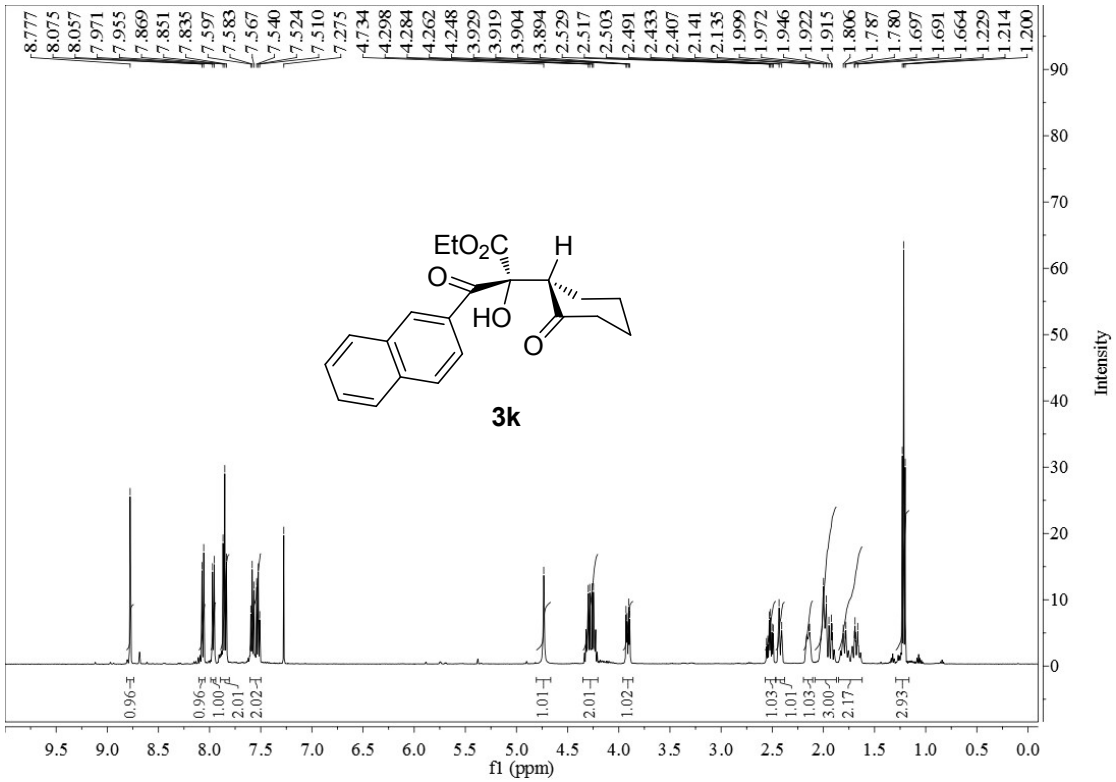


^{13}C NMR (125 MHz, $CDCl_3$)

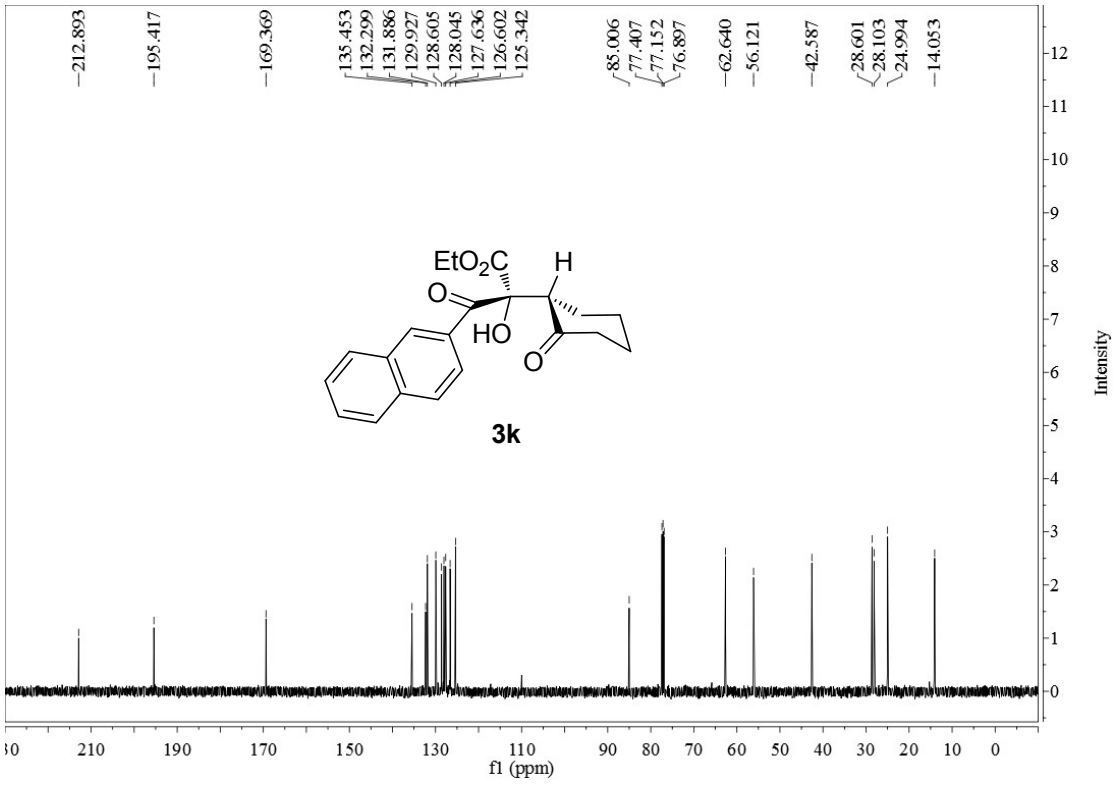


(*R*)-Ethyl 2-Hydroxy-3-(naphthalen-2-yl)-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (3k).

^{1}HNMR (500 MHz, $CDCl_3$)

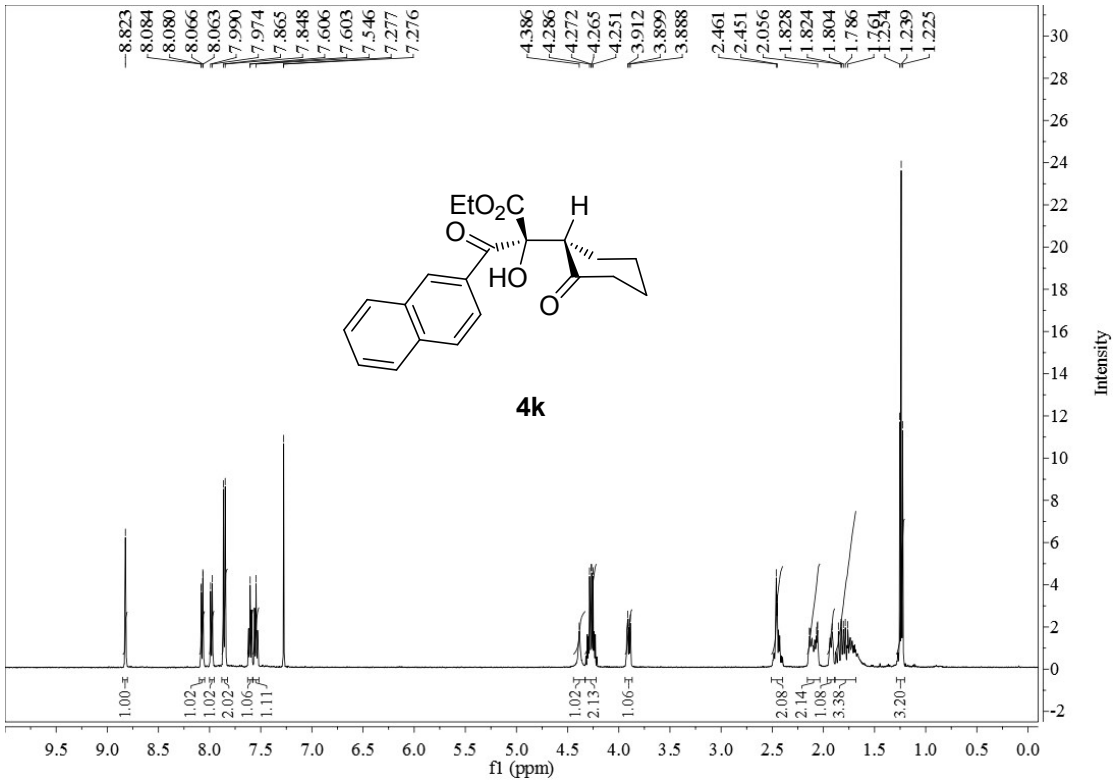


^{13}C NMR (125 MHz, $CDCl_3$)

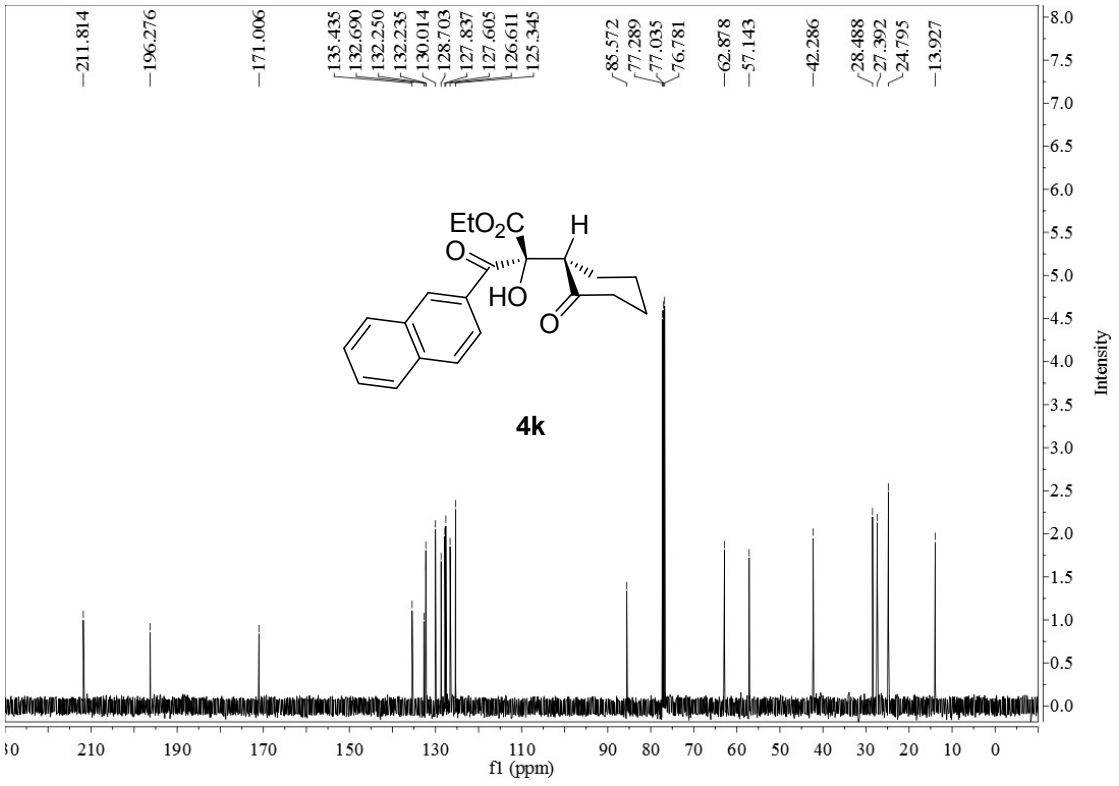


(*S*)-Ethyl 2-Hydroxy-3-(naphthalen-2-yl)-3-oxo-2-[(*S*)-2-oxocyclohexyl]propanoate (4k).

^{1}HNMR (500 MHz, $CDCl_3$)

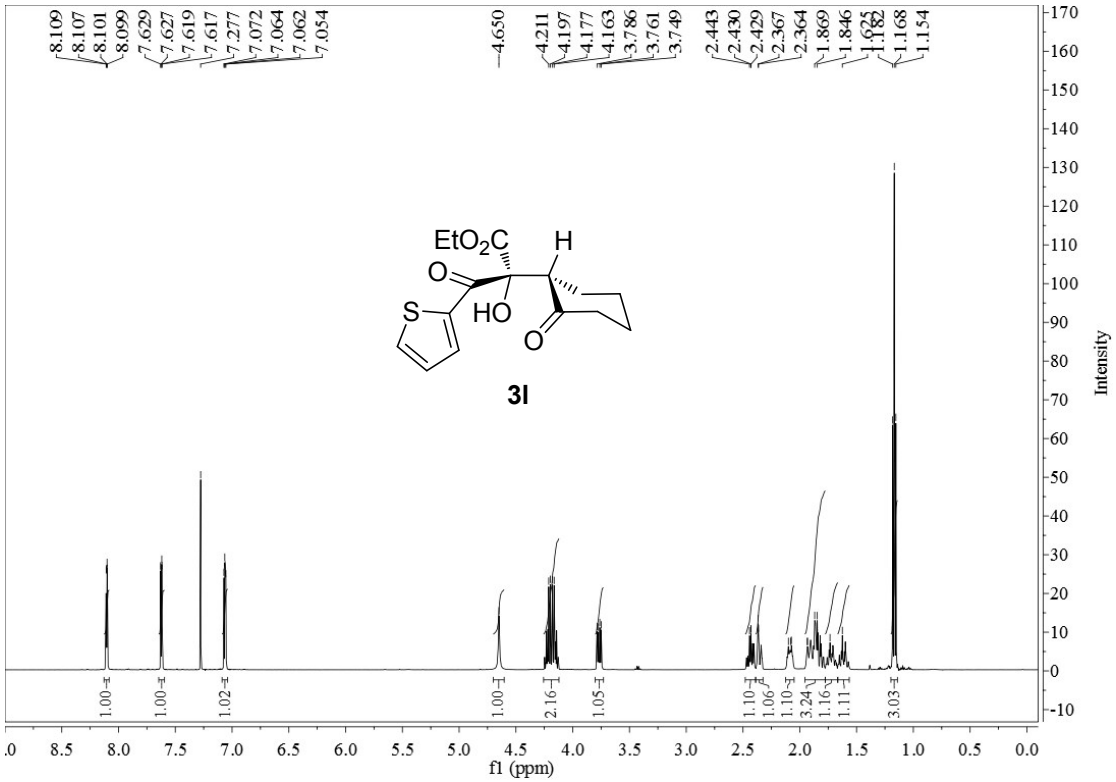


^{13}C NMR (125 MHz, $CDCl_3$)

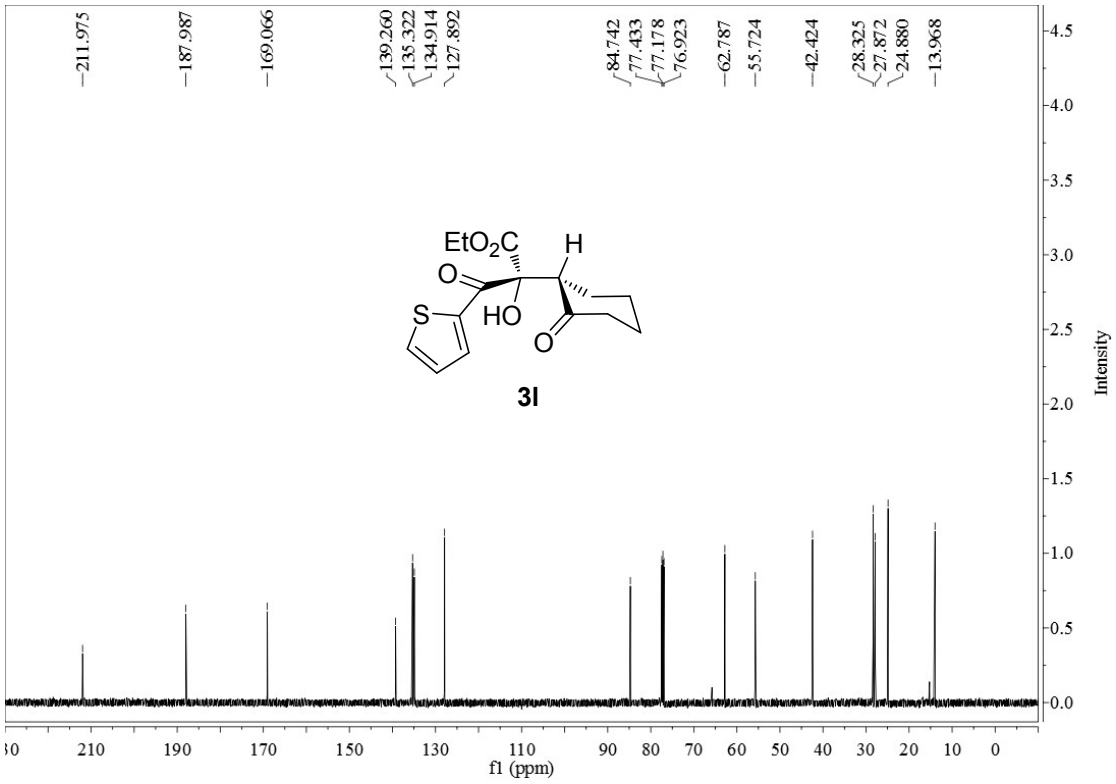


(*R*)-Ethyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-3-(thiophen-2-yl)propanoate (3l).

^{1}HNMR (500 MHz, $CDCl_3$)

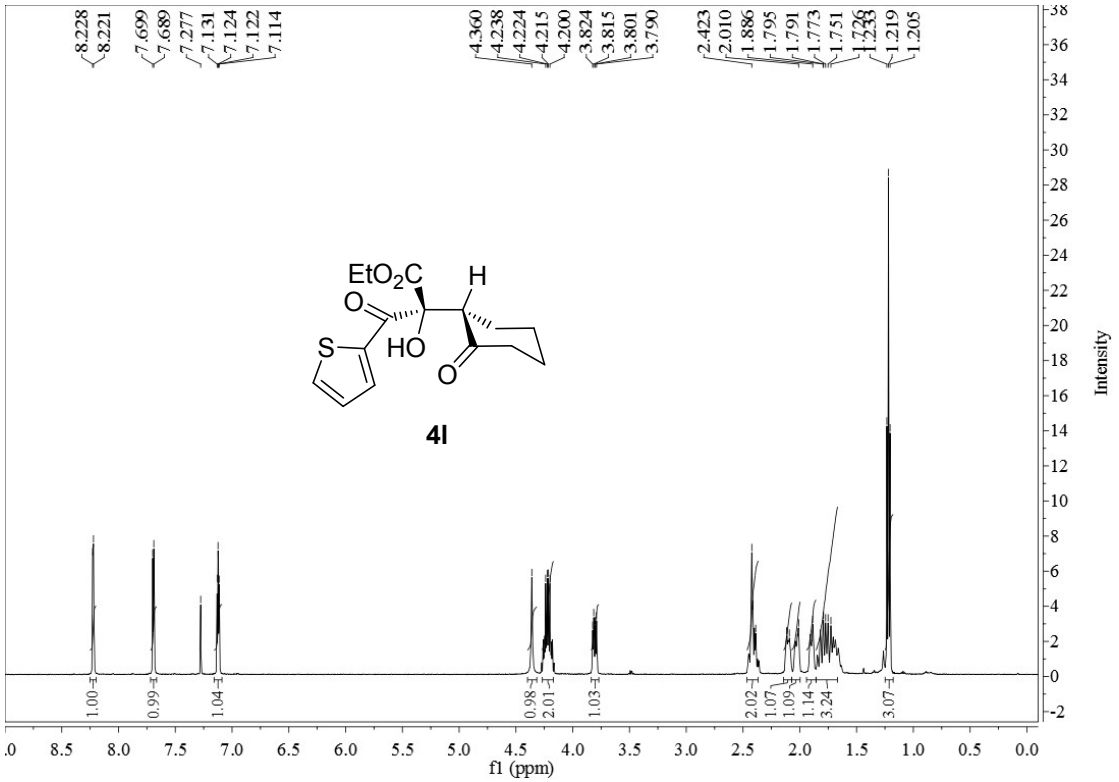


^{13}C NMR (125 MHz, $CDCl_3$)

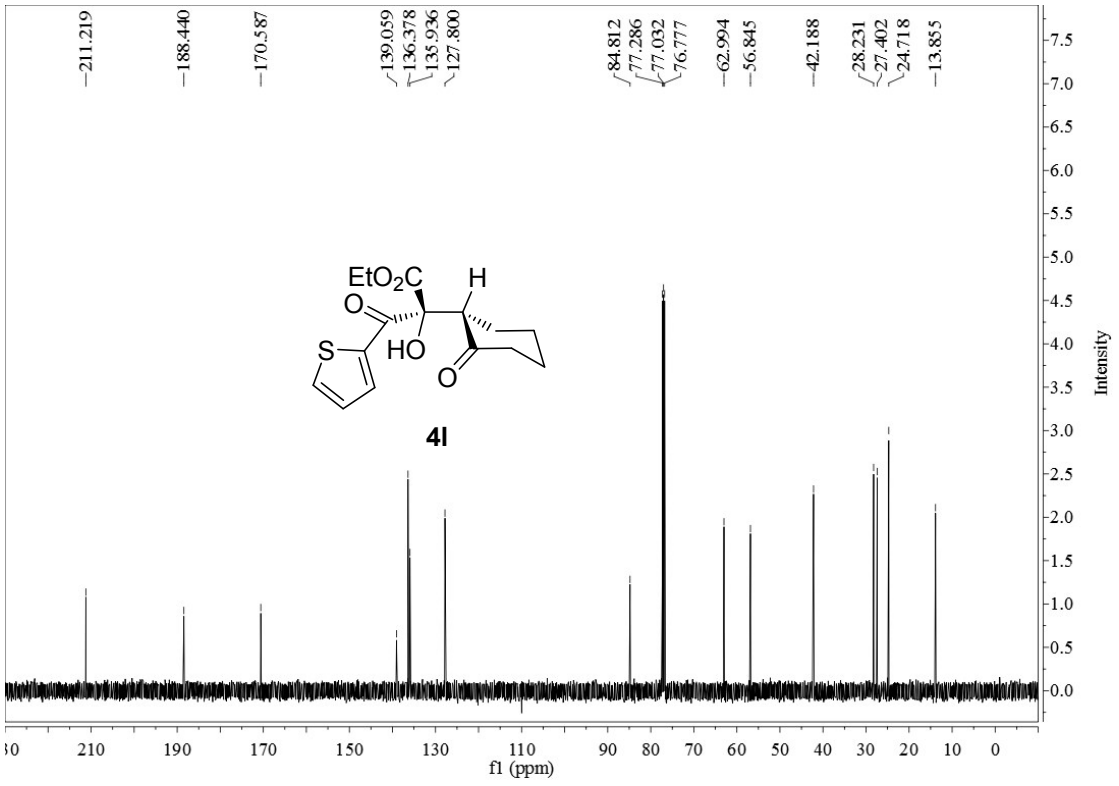


(*S*)-Ethyl 2-Hydroxy-3-oxo-2-[(*S*)-2-oxocyclohexyl]-3-(thiophen-2-yl)propanoate (4l).

^{1}HNMR (500 MHz, $CDCl_3$)

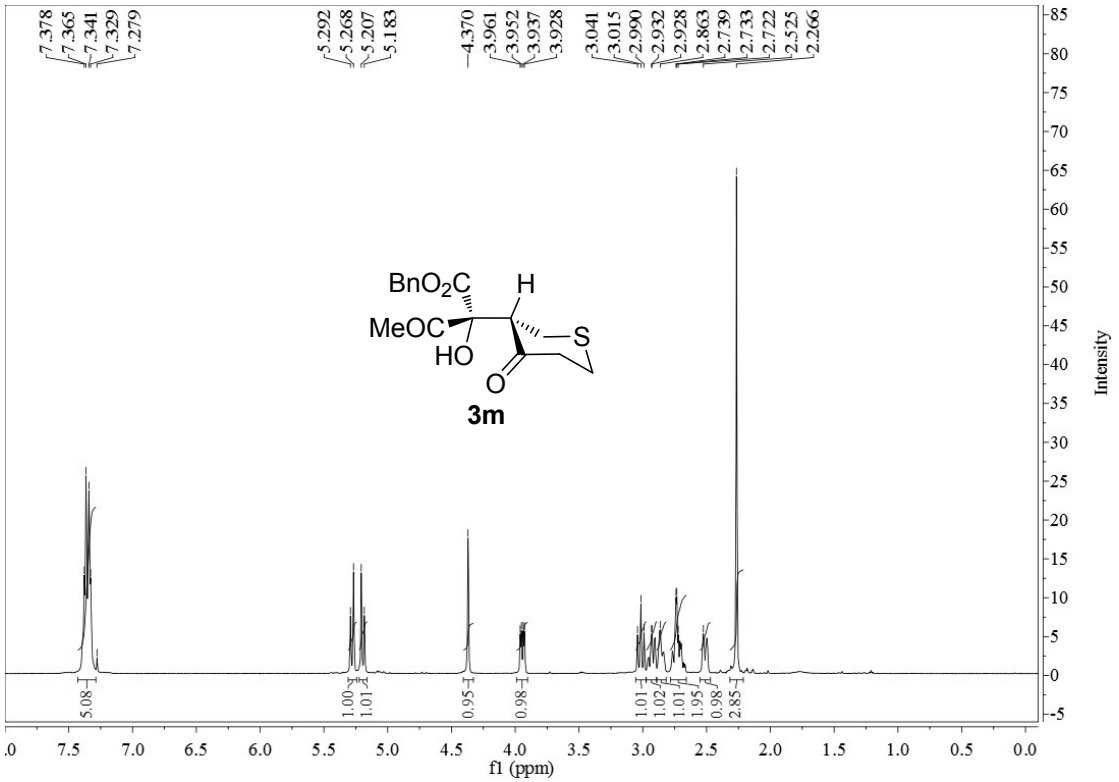


^{13}C NMR (125 MHz, $CDCl_3$)

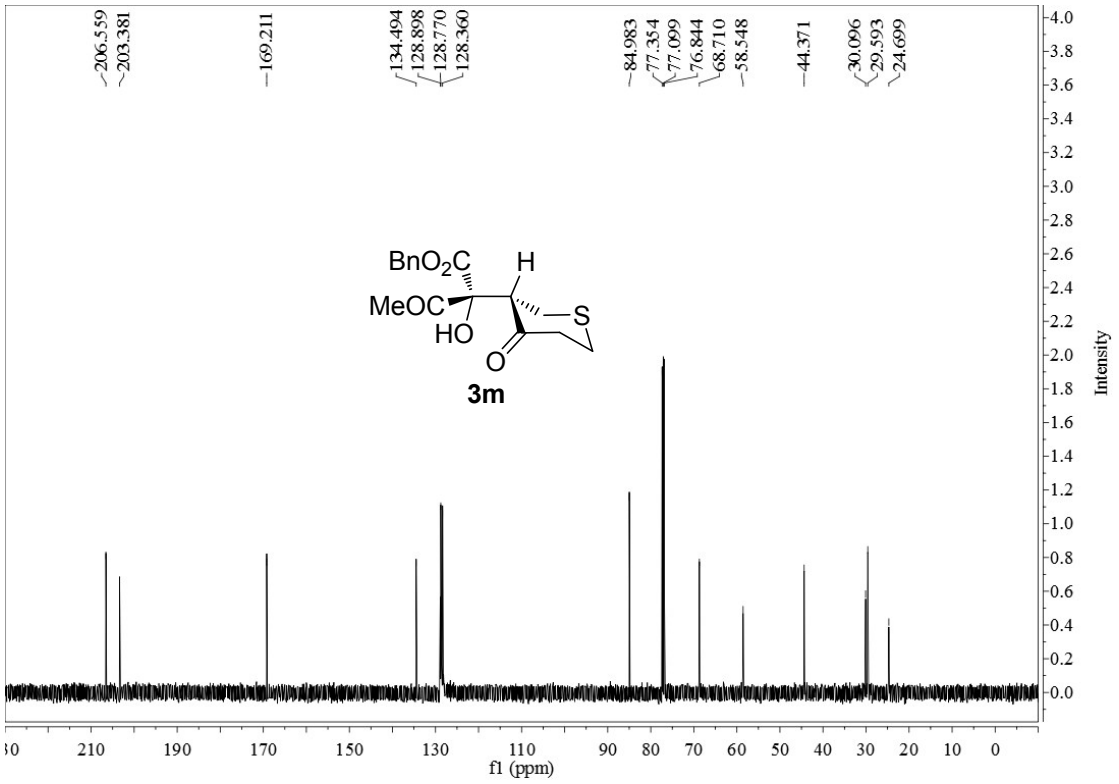


(*R*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-4-oxotetrahydro-2*H*-thiopyran-3-yl]butanoate (3m).

^{1}HNMR (500 MHz, $CDCl_3$)

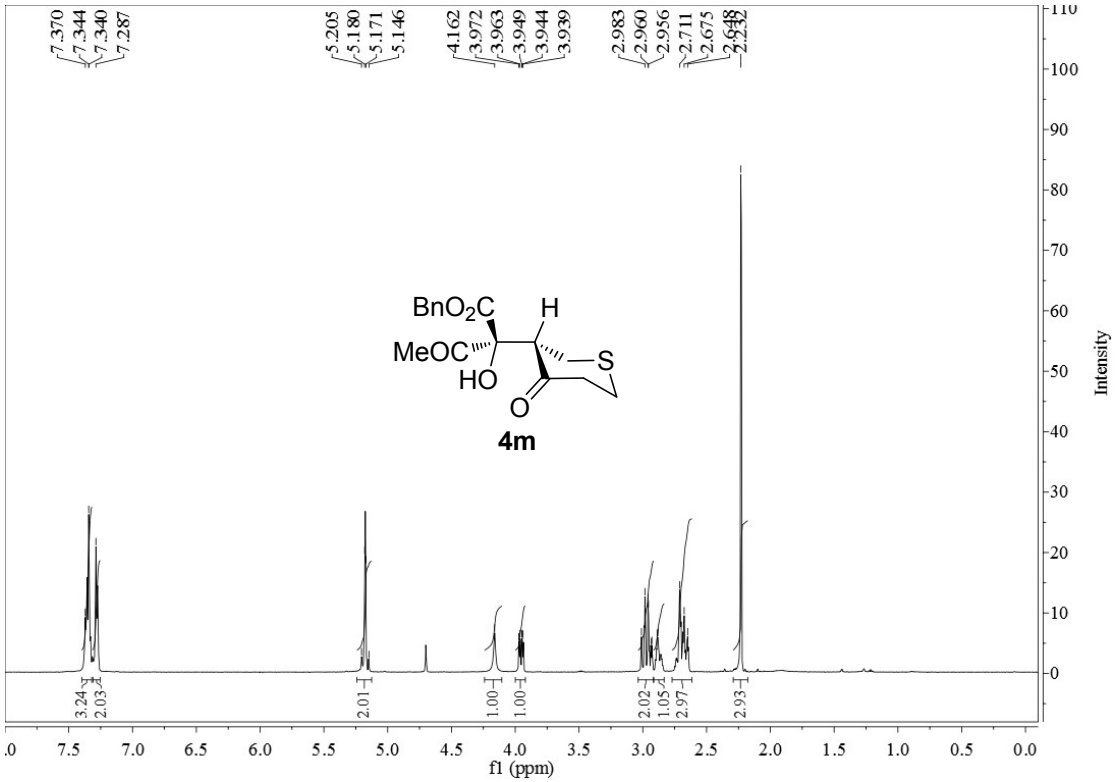


^{13}C NMR (125 MHz, $CDCl_3$)

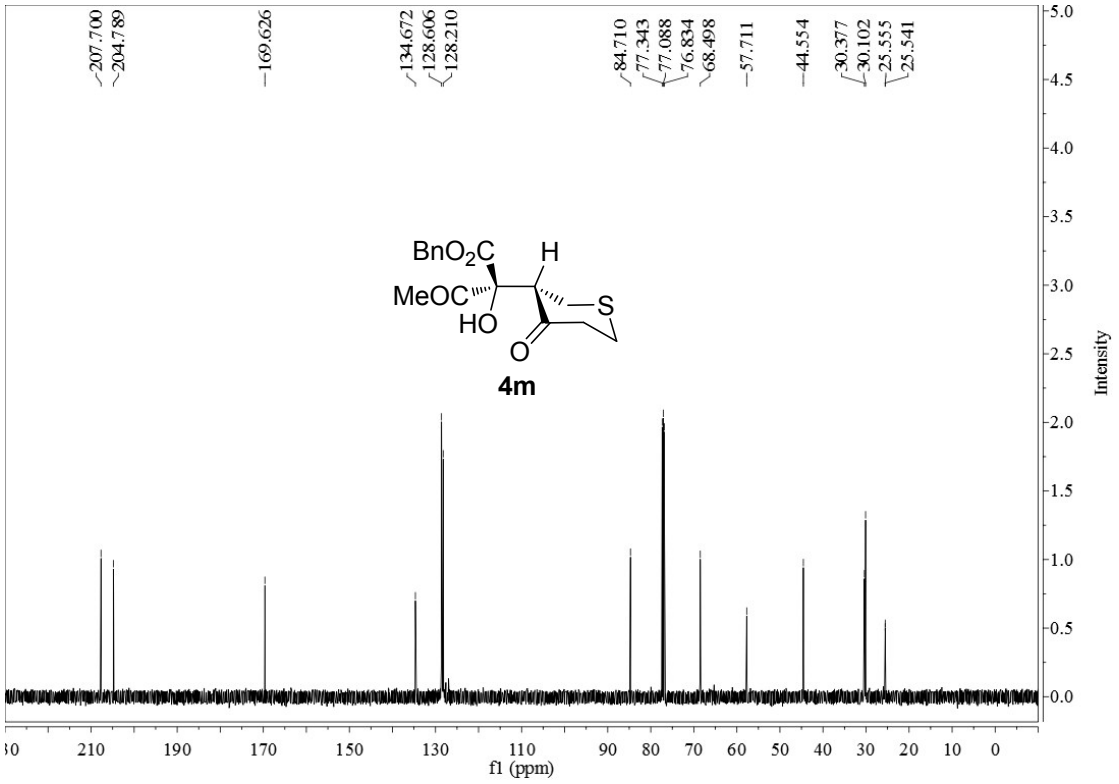


(*S*)-Benzyl 2-Hydroxy-3-oxo-2-[(*S*)-4-oxotetrahydro-2*H*-thiopyran-3-yl]butanoate (4m).

^{1}HNMR (500 MHz, $CDCl_3$)

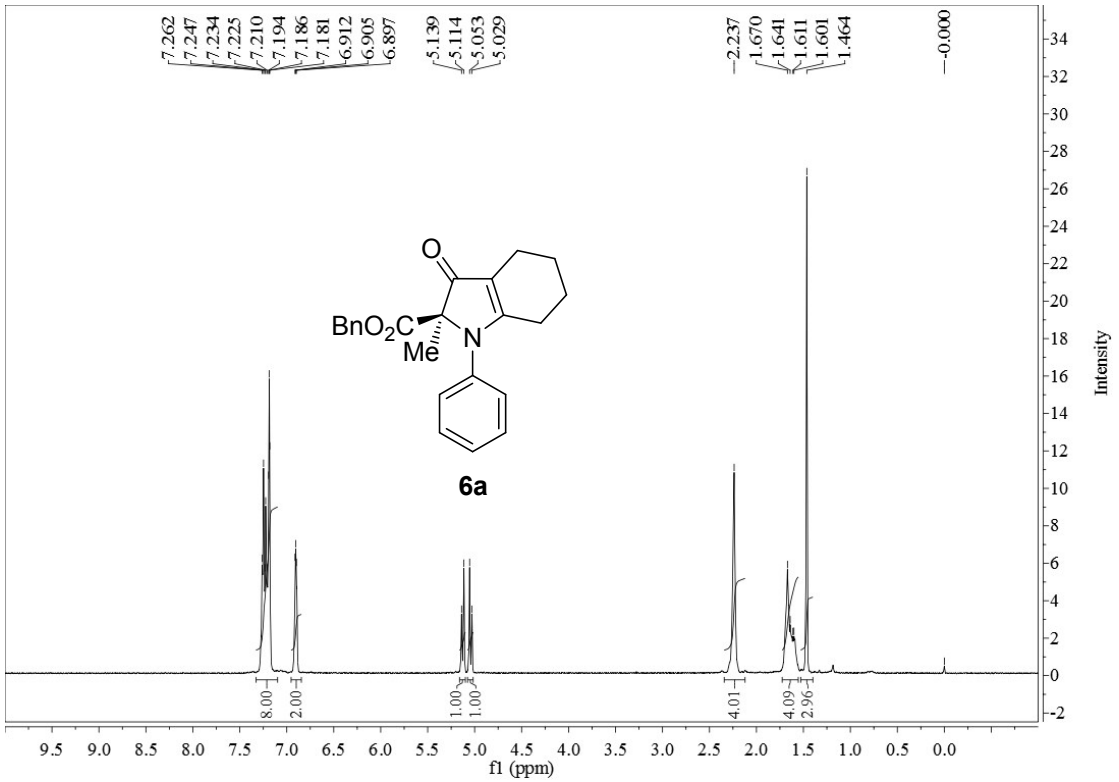


^{13}C NMR (125 MHz, $CDCl_3$)

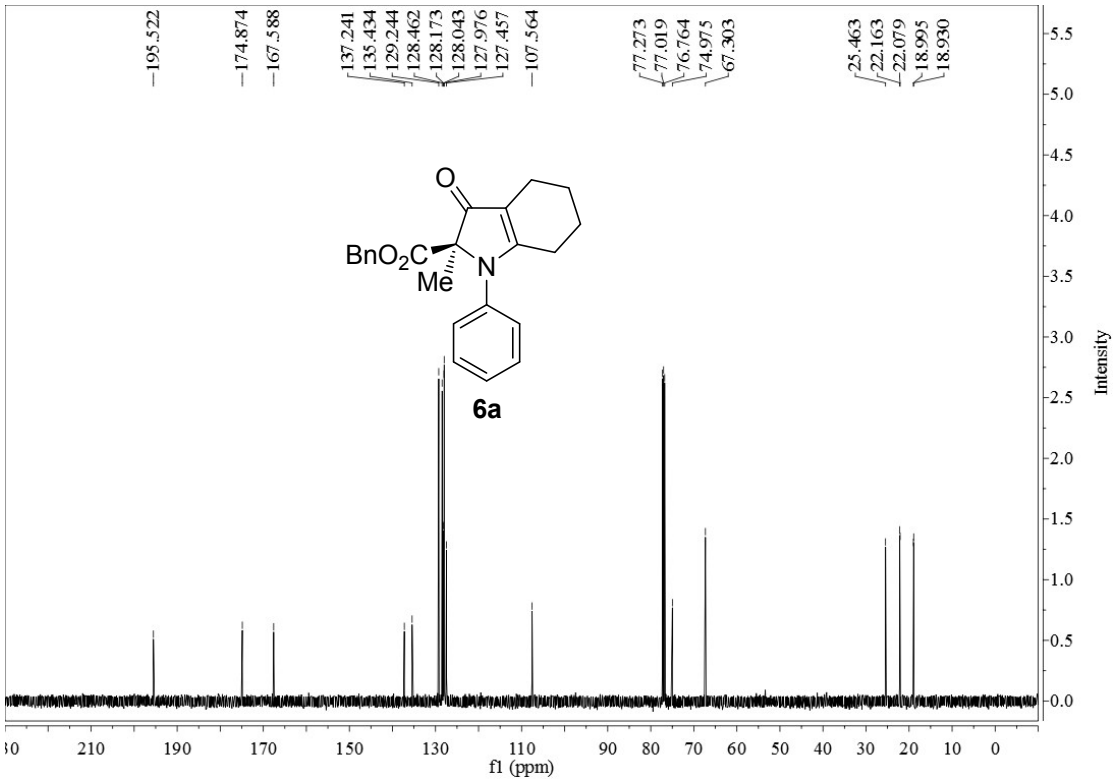


(*R*)-Benzyl 2-Methyl-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6a).

^{1}HNMR (500 MHz, $CDCl_3$)

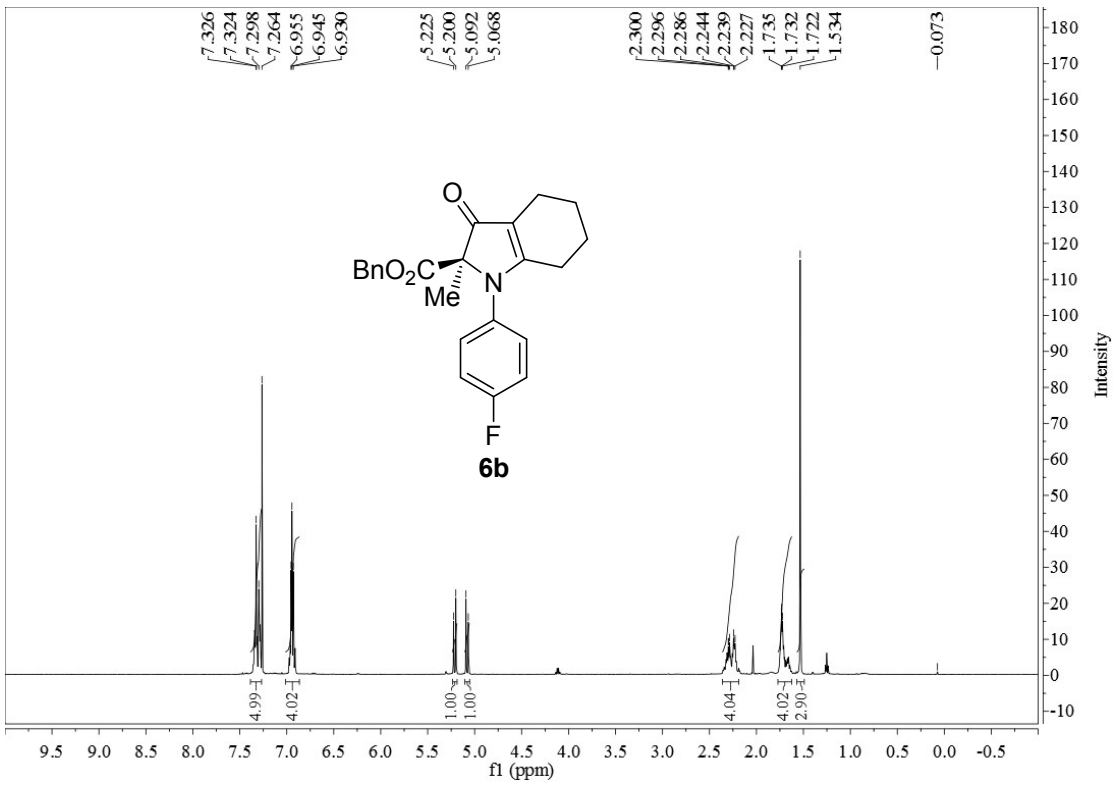


^{13}C NMR (125 MHz, $CDCl_3$)

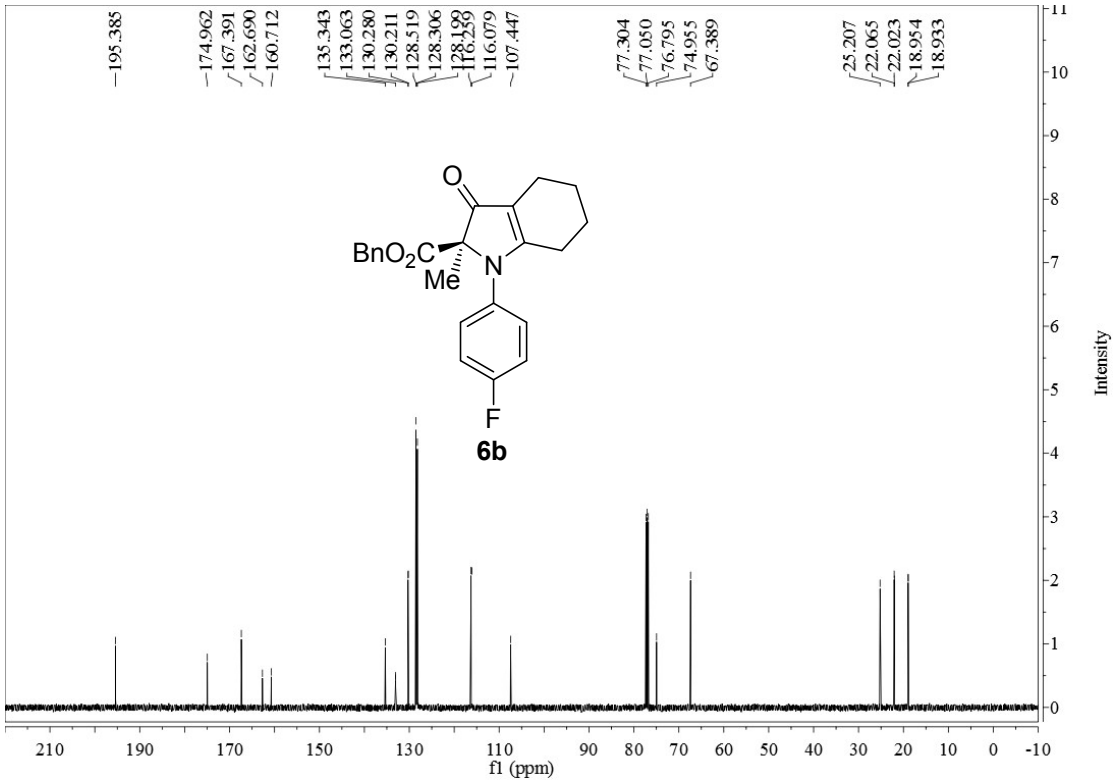


(*R*)-Benzyl 1-(4-Fluorophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6b).

^{1}HNMR (500 MHz, $CDCl_3$)

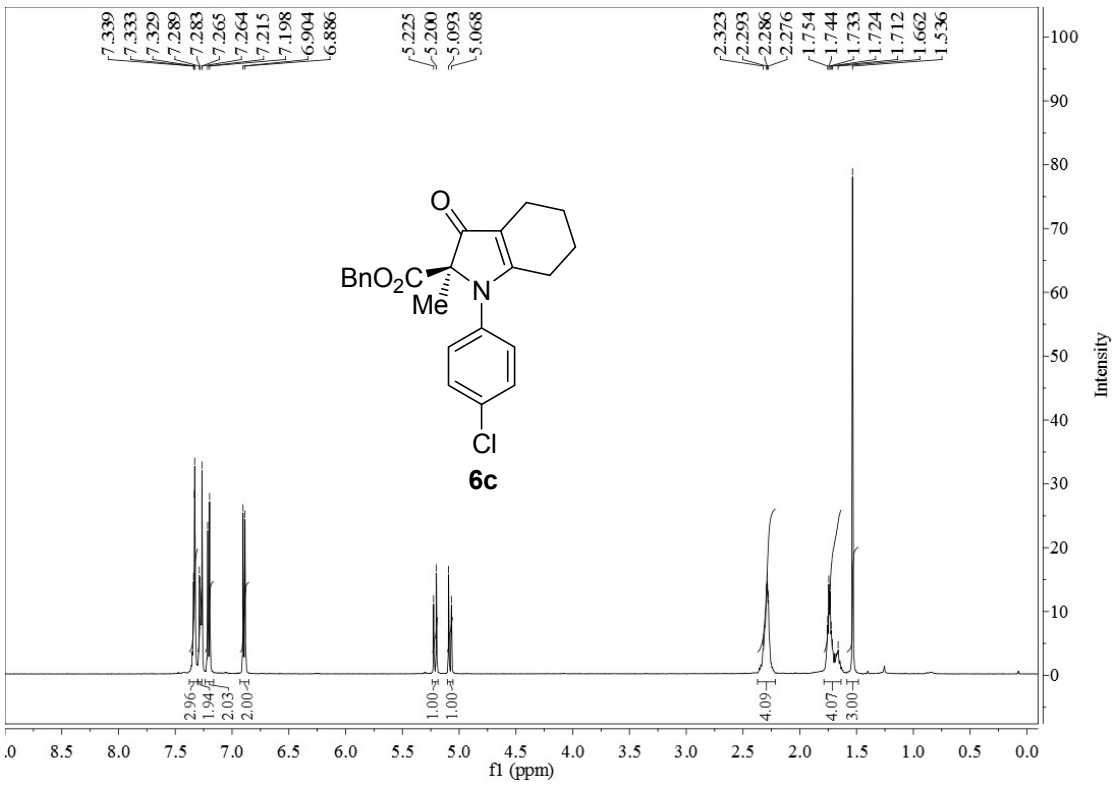


^{13}C NMR (125 MHz, $CDCl_3$)

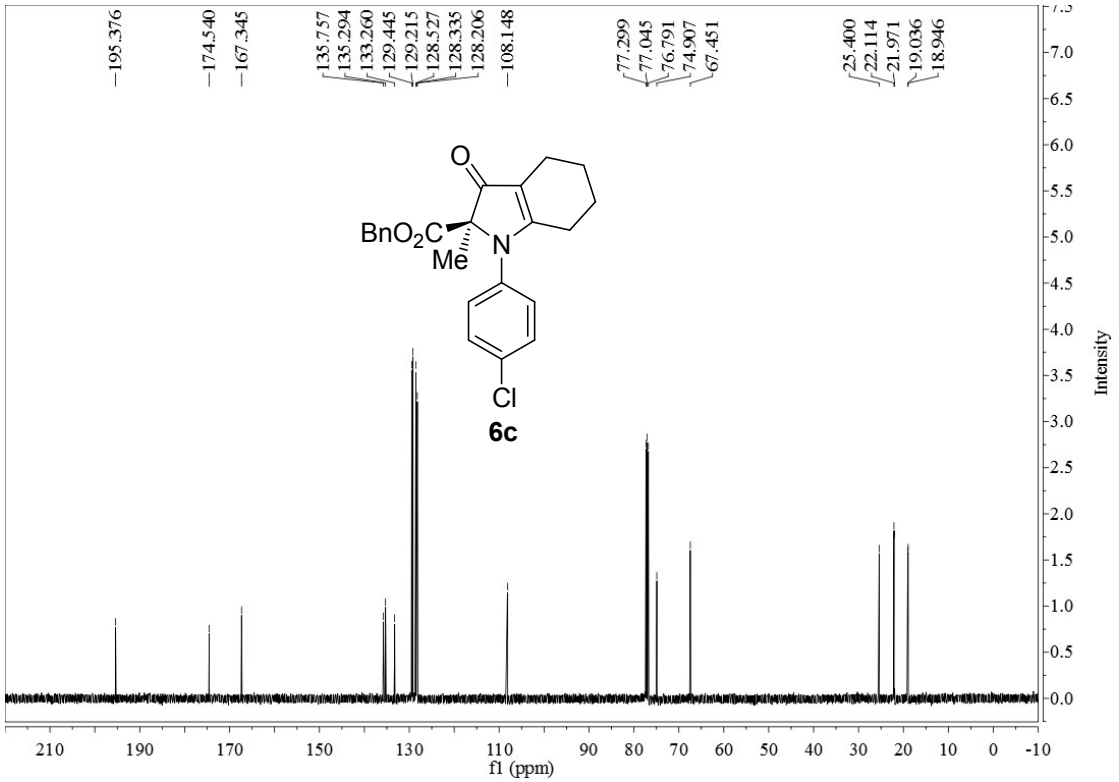


(*R*)-Benzyl 1-(4-chlorophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6c).

^{1}HNMR (500 MHz, $CDCl_3$)

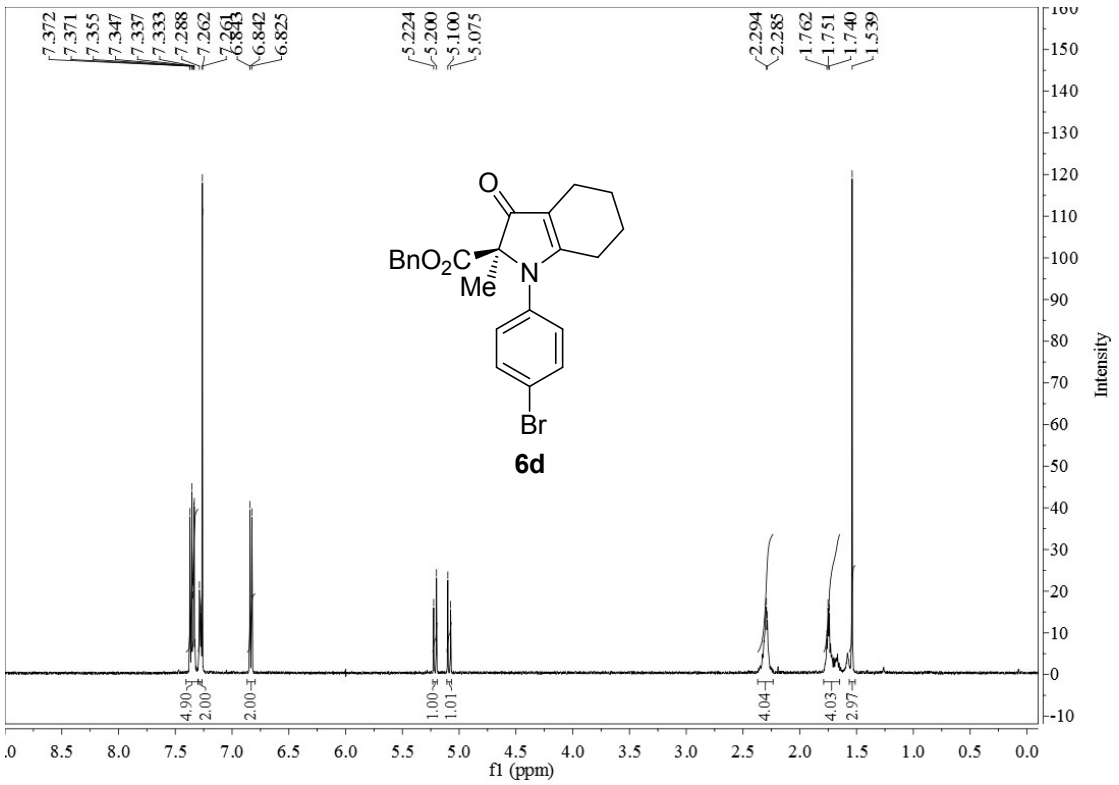


^{13}C NMR (125 MHz, $CDCl_3$)

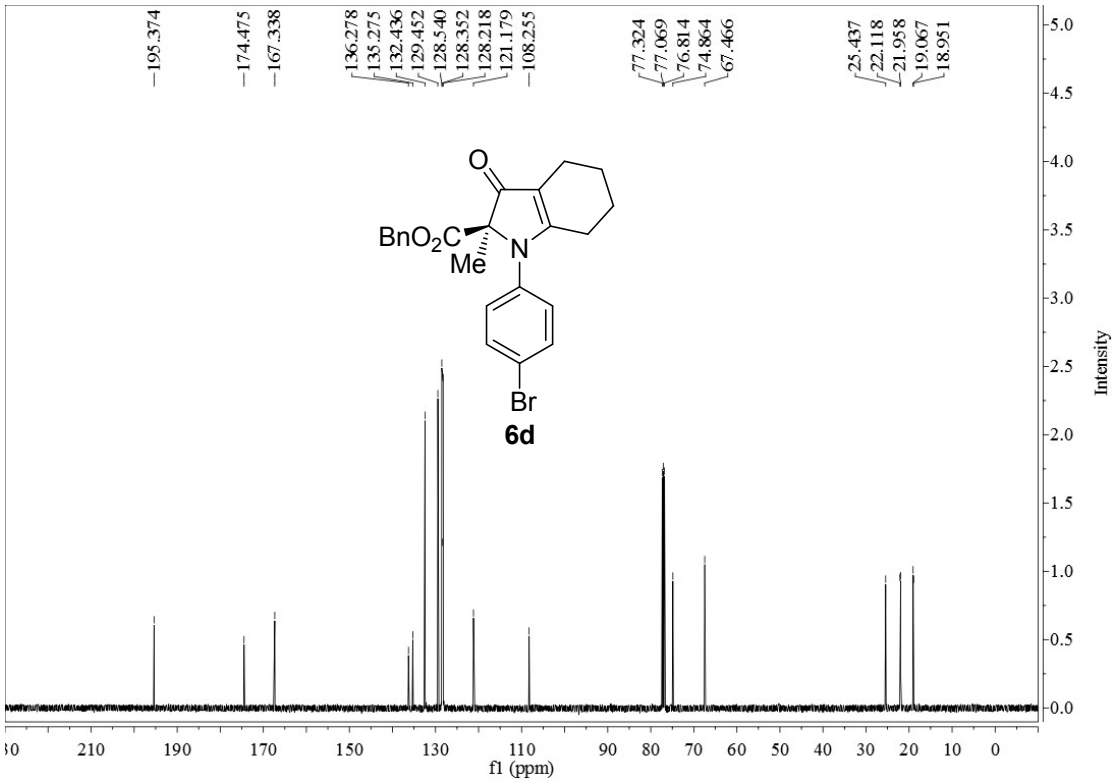


(*R*)-Benzyl 1-(4-Bromophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6d).

^{1}HNMR (500 MHz, $CDCl_3$)

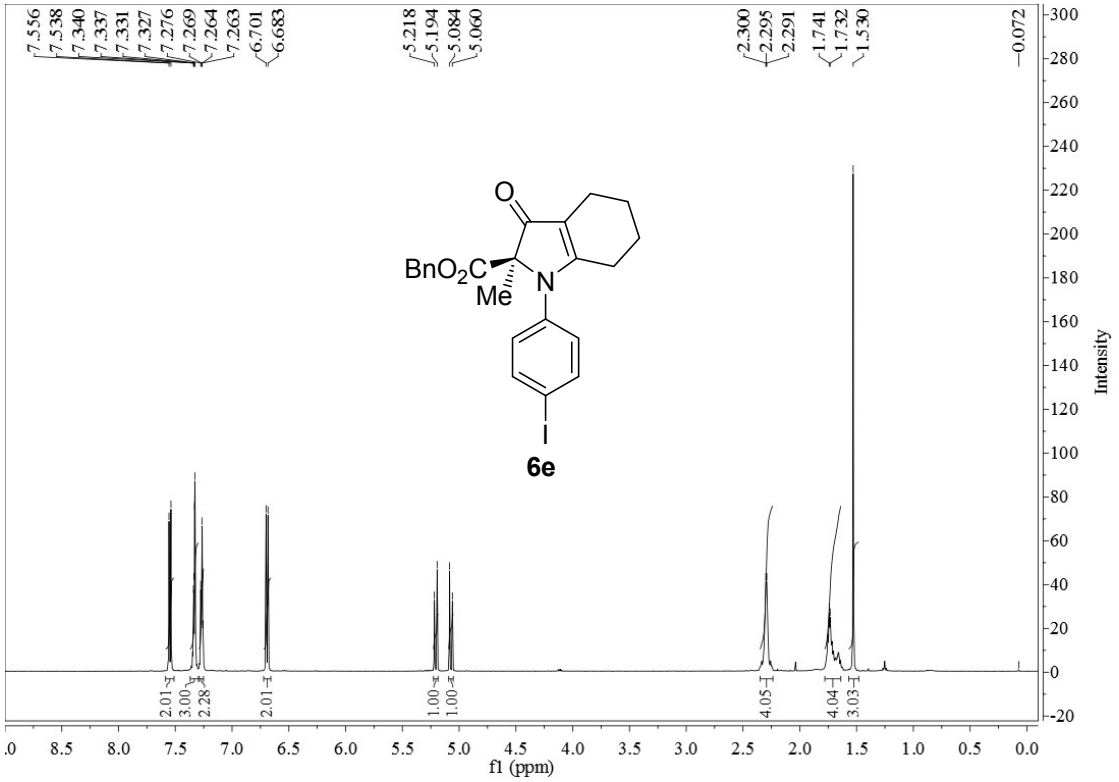


^{13}C NMR (125 MHz, $CDCl_3$)

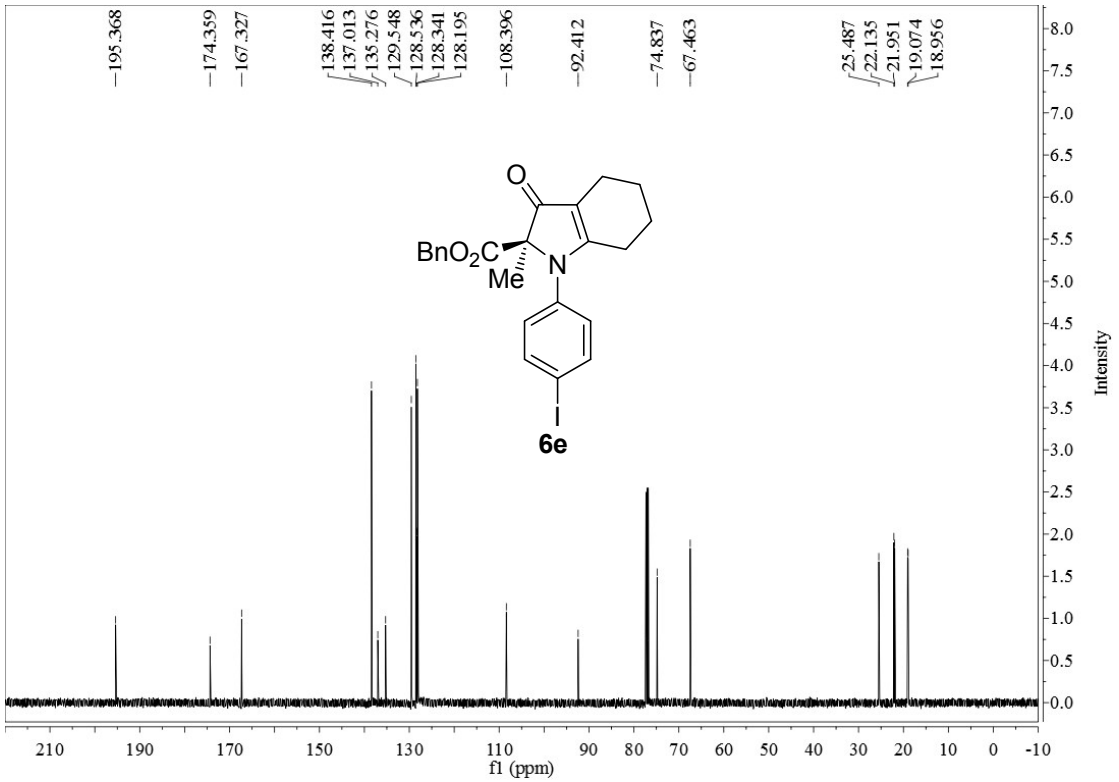


(*R*)-Benzyl 1-(4-Iodophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6e).

^{1}HNMR (500 MHz, $CDCl_3$)

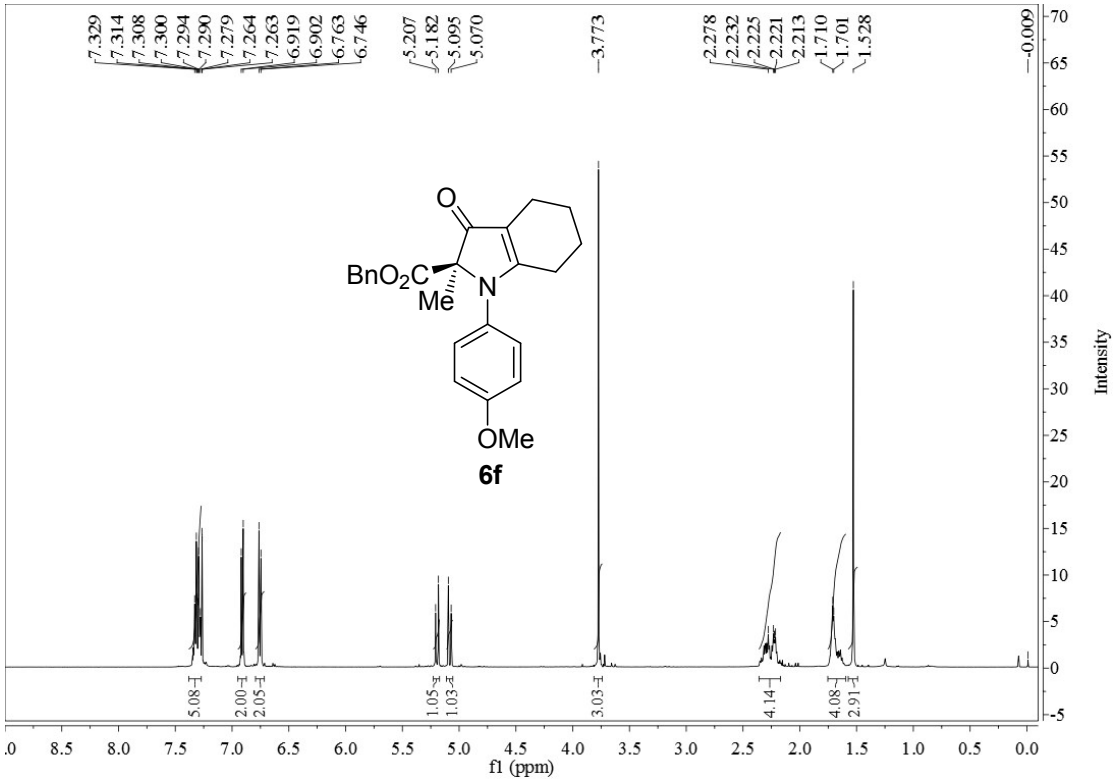


^{13}C NMR (125 MHz, $CDCl_3$)

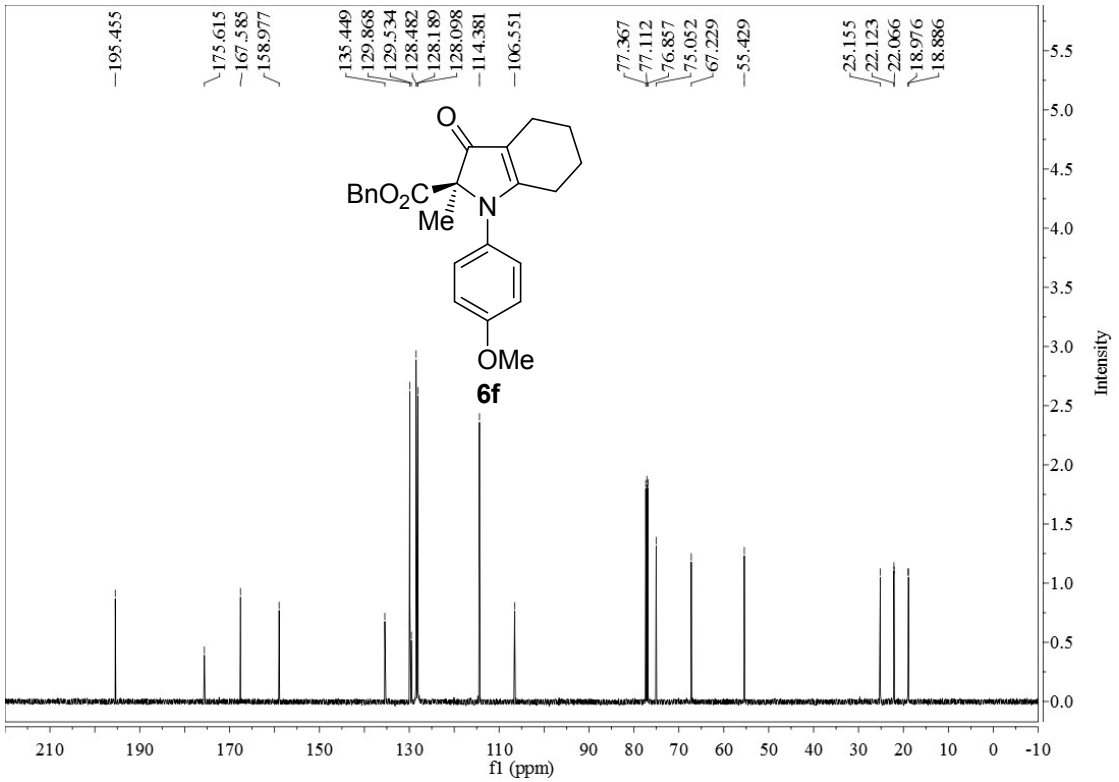


(*R*)-Benzyl 1-(4-Methoxyphenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6f).

^{1}HNMR (500 MHz, $CDCl_3$)

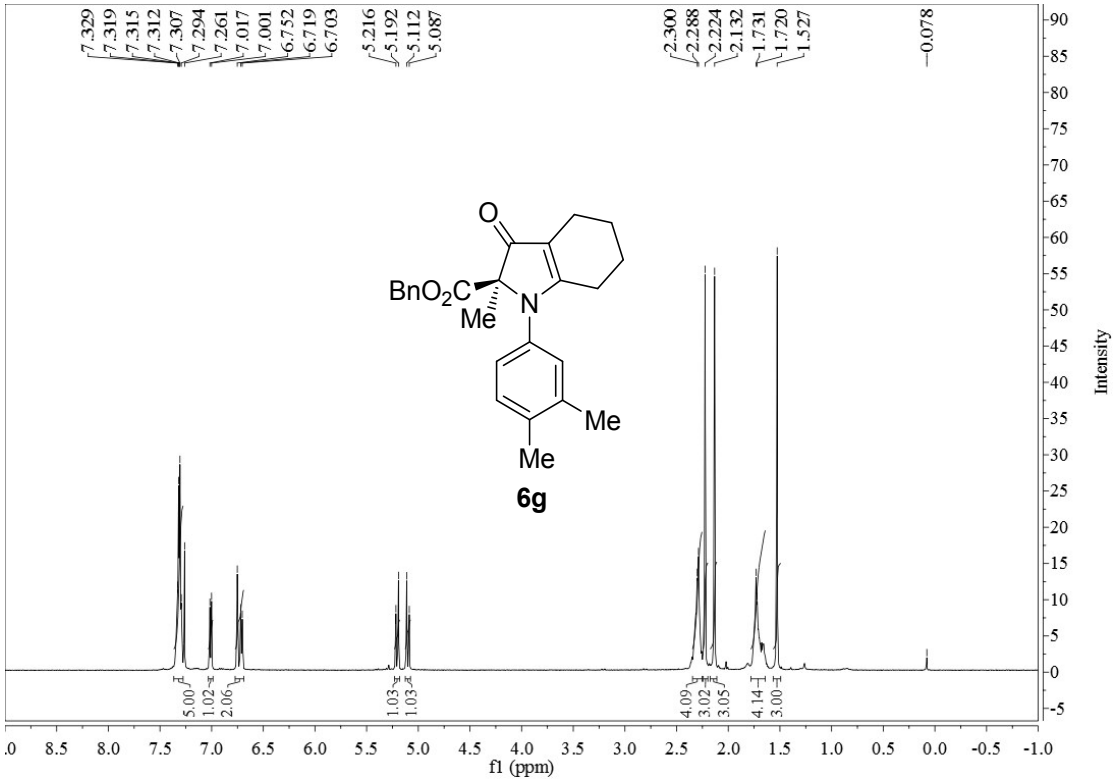


^{13}C NMR (125 MHz, $CDCl_3$)

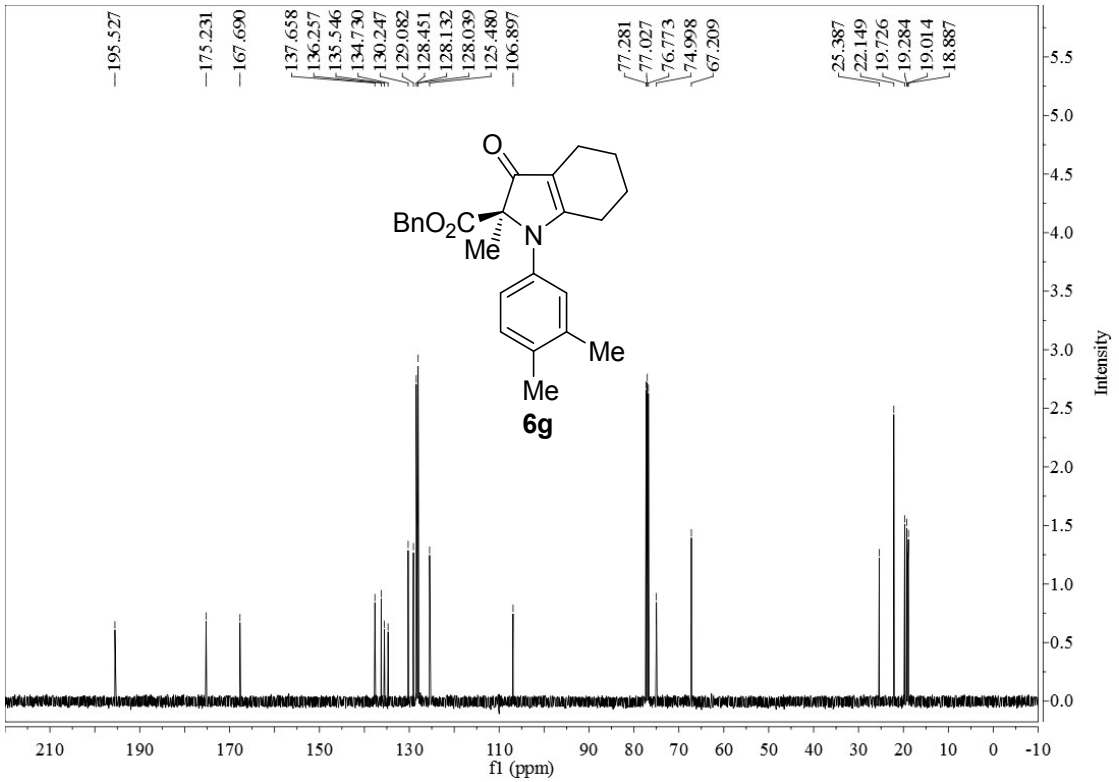


(*R*)-Benzyl 1-(3,4-Dimethylphenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6g).

^{1}HNMR (500 MHz, $CDCl_3$)

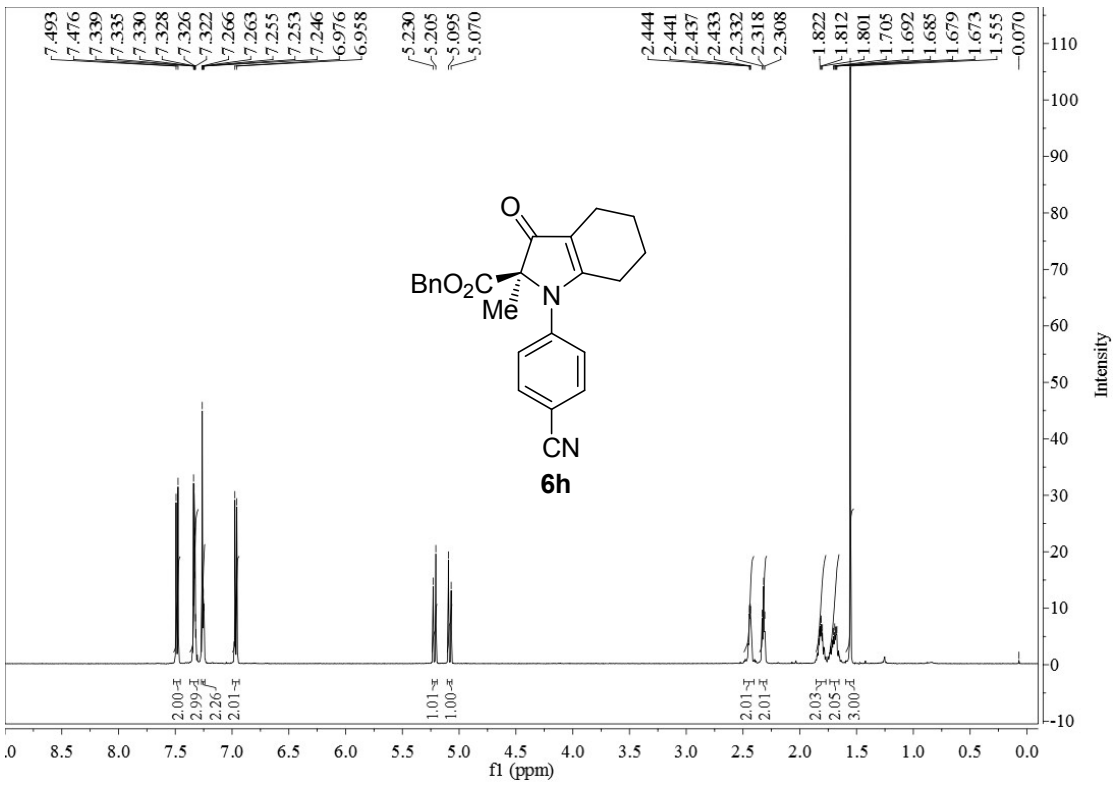


^{13}C NMR (125 MHz, $CDCl_3$)

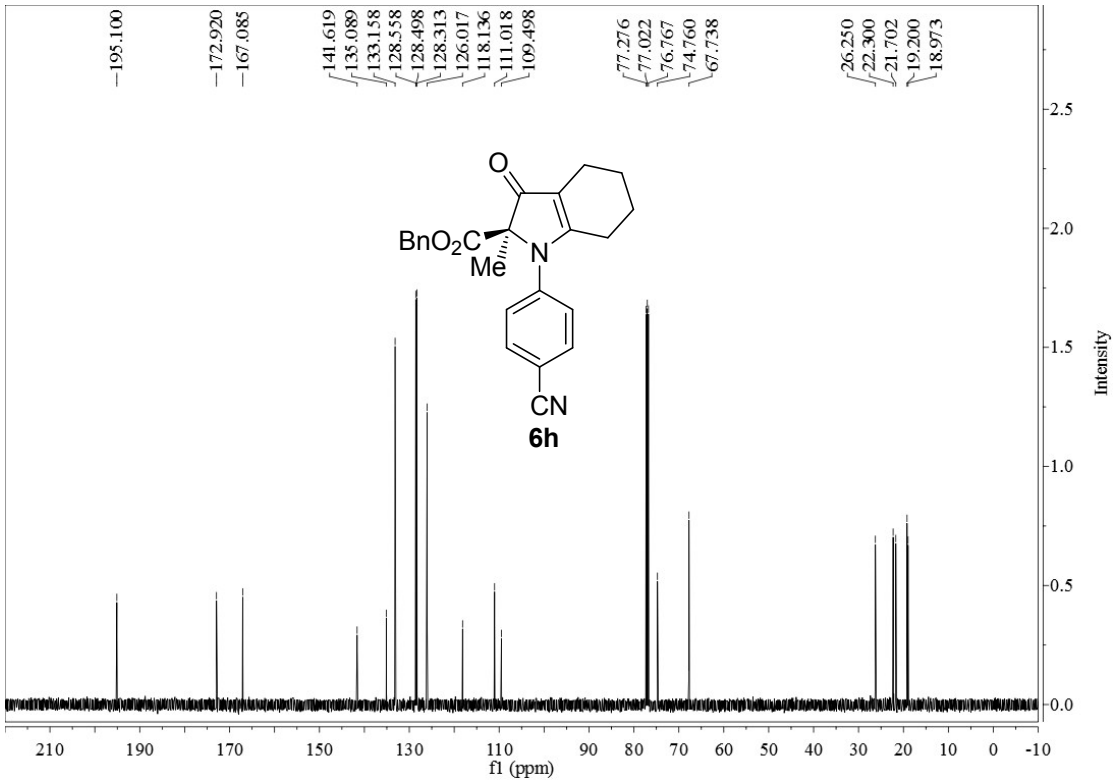


(*R*)-Benzyl 1-(4-Cyanophenyl)-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6h).

^{1}HNMR (500 MHz, $CDCl_3$)

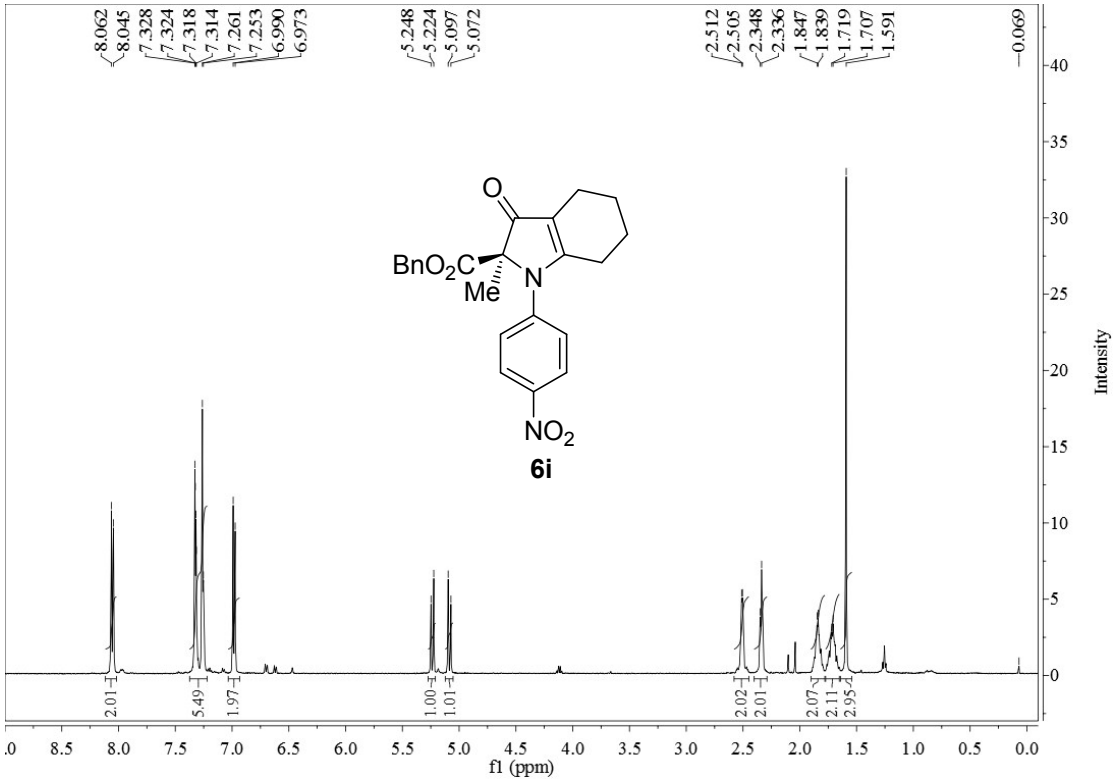


^{13}C NMR (125 MHz, $CDCl_3$)

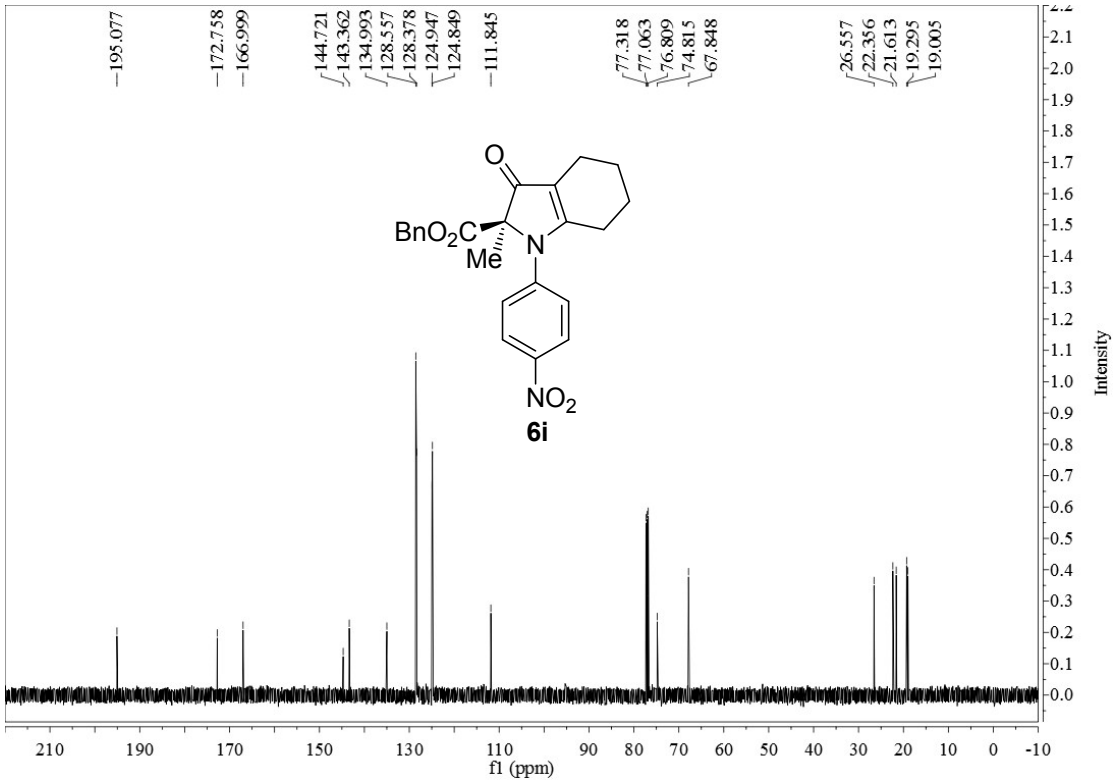


(*R*)-Benzyl 2-Methyl-1-(4-nitrophenyl)-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6i).

^{1}HNMR (500 MHz, $CDCl_3$)

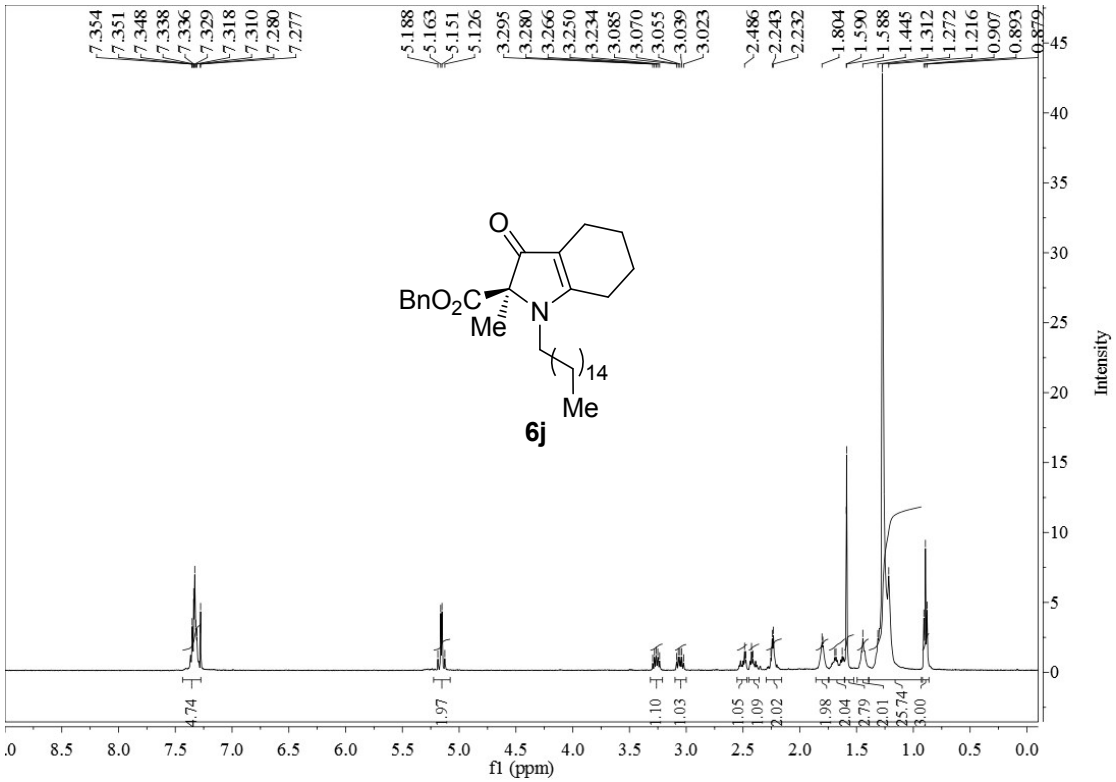


^{13}C NMR (125 MHz, $CDCl_3$)

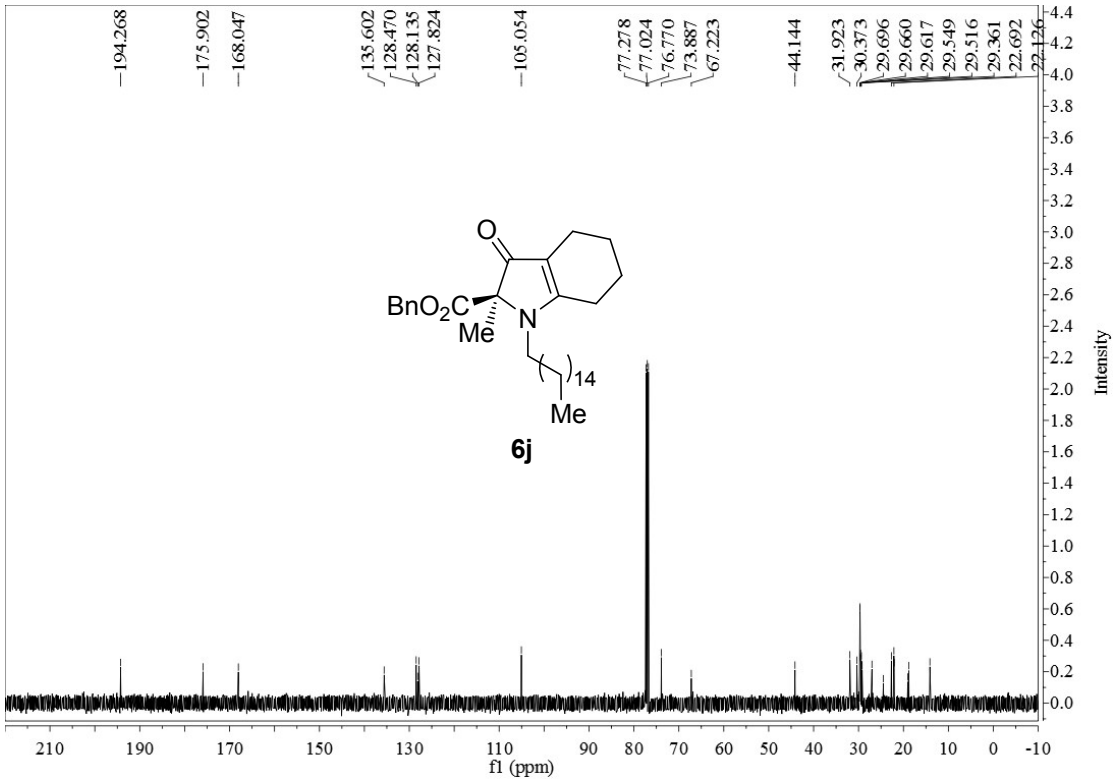


(*R*)-Benzyl 1-Hexadecyl-2-methyl-3-oxo-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6j).

^{1}HNMR (500 MHz, $CDCl_3$)

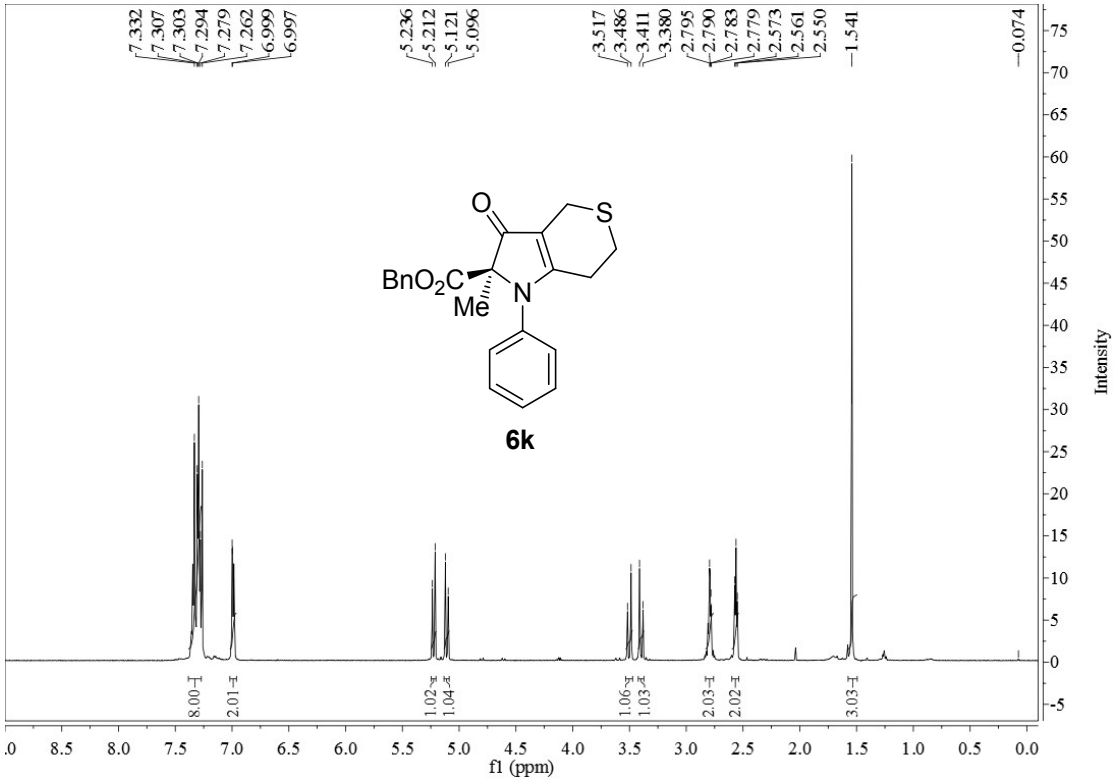


^{13}C NMR (125 MHz, $CDCl_3$)

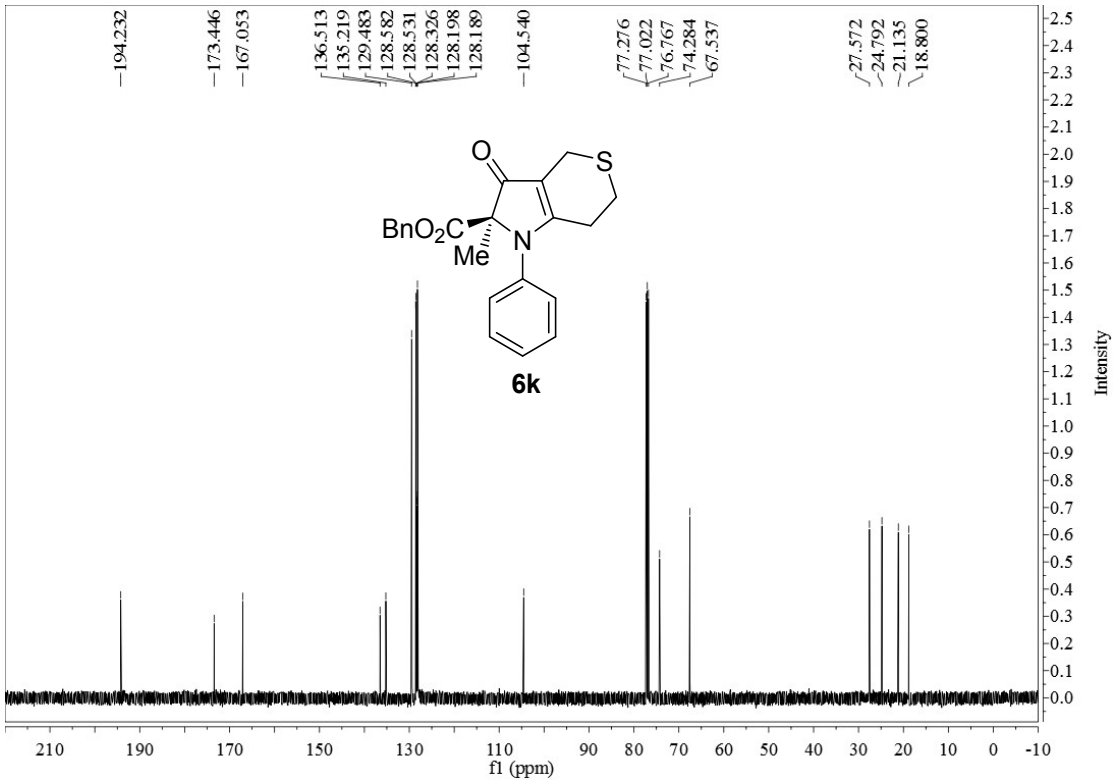


(*R*)-Benzyl 2-Methyl-3-oxo-1-phenyl-1,2,3,4,6,7-hexahydrothiopyrano[4,3-*b*]pyrrole-2-carboxylate (6k).

^{1}HNMR (500 MHz, $CDCl_3$)

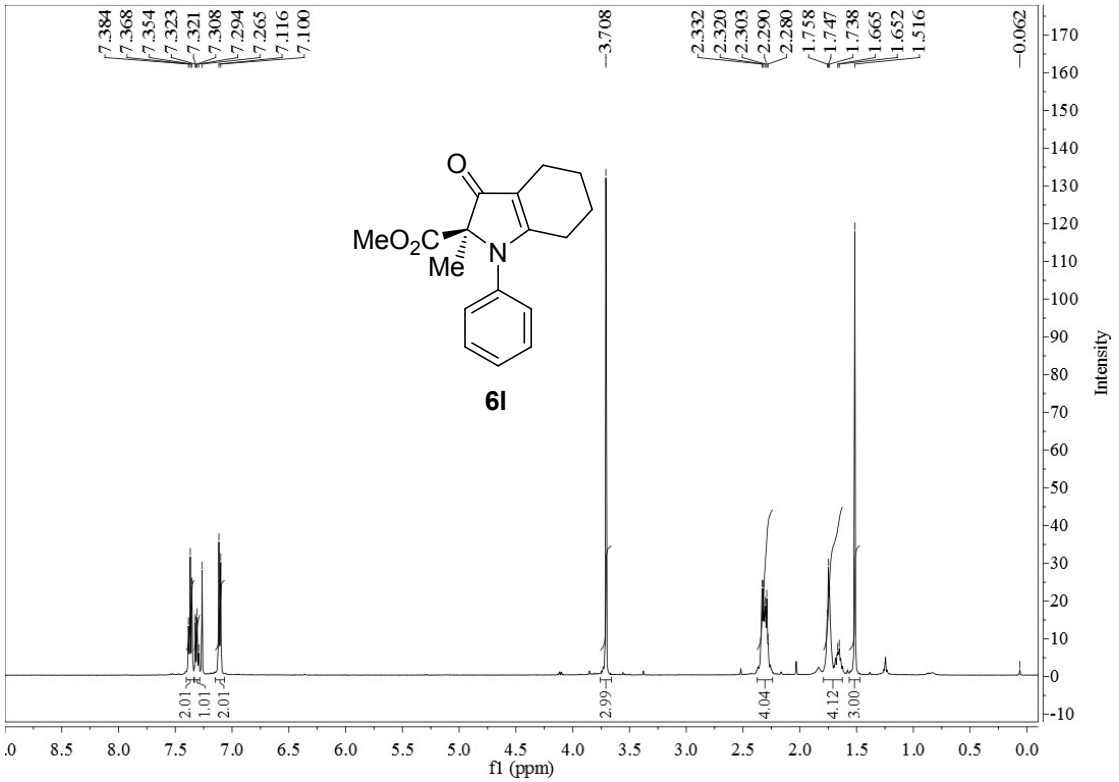


^{13}C NMR (125 MHz, $CDCl_3$)

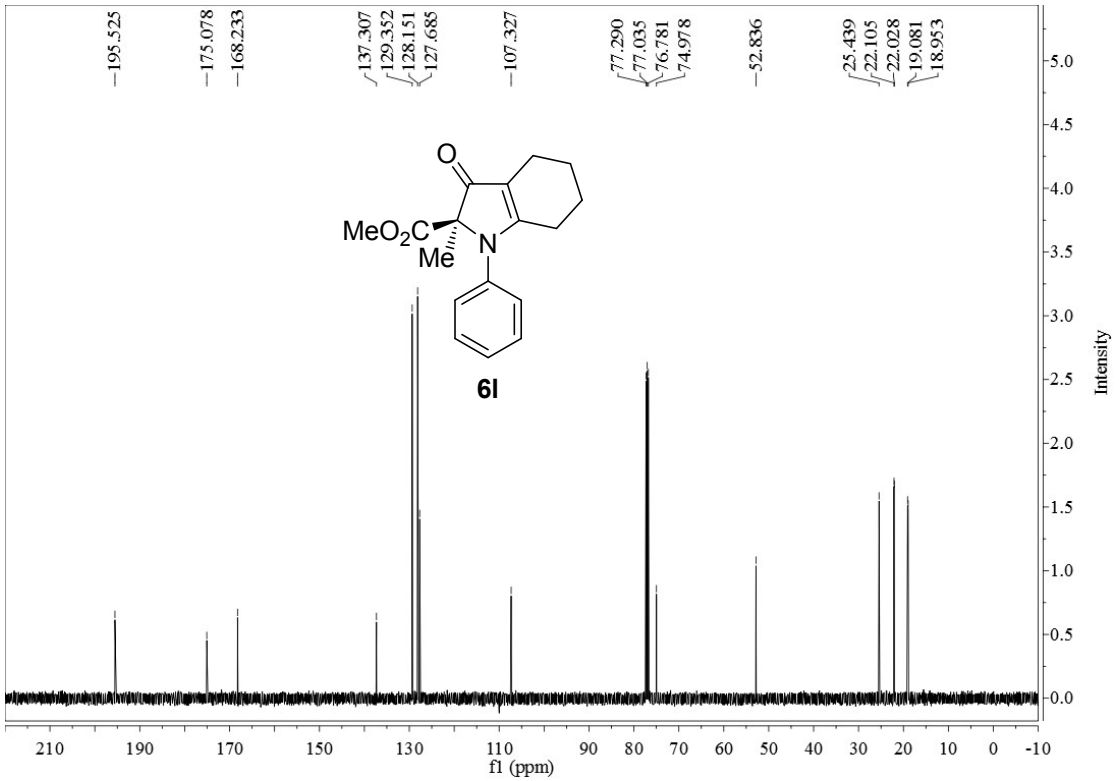


(*R*)-Methyl 2-Methyl-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6l).

^{1}HNMR (500 MHz, $CDCl_3$)

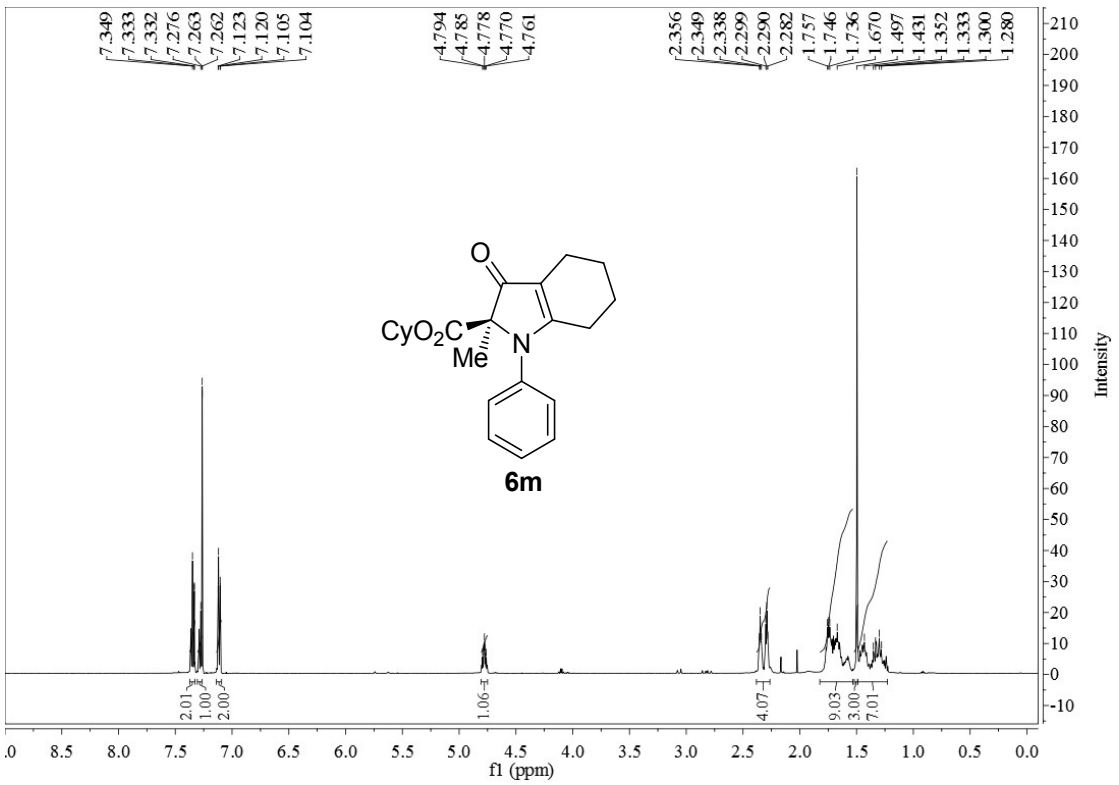


^{13}C NMR (125 MHz, $CDCl_3$)

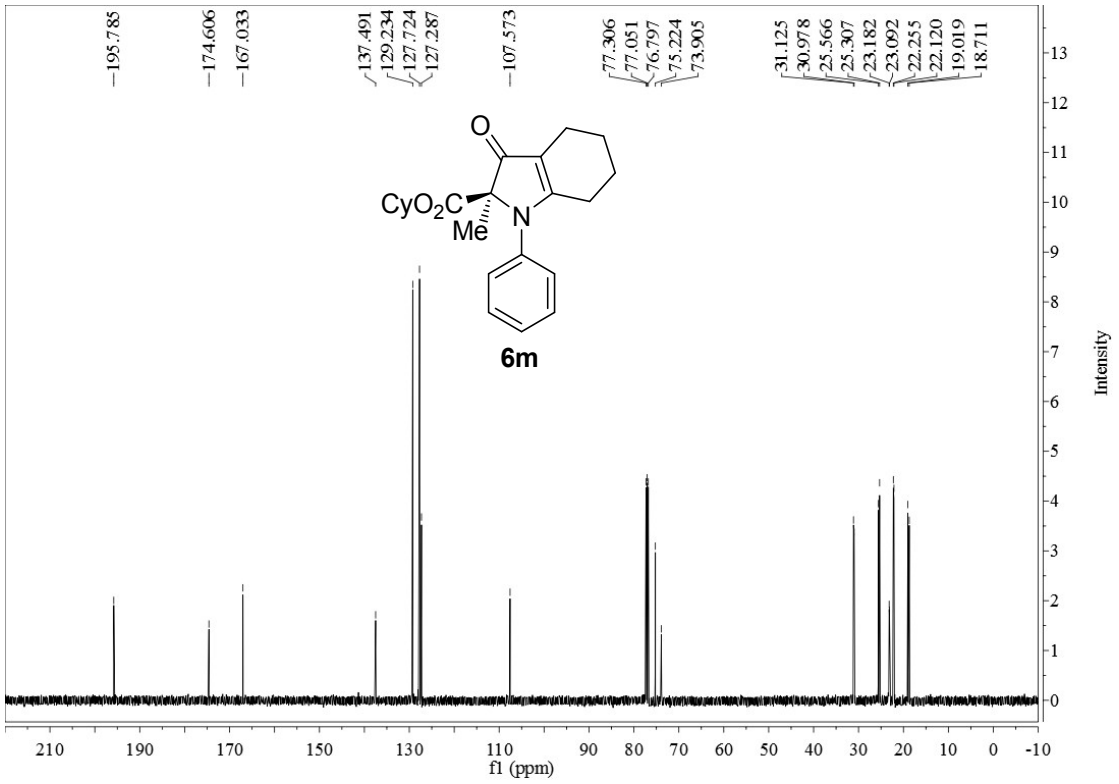


(*R*)-Cyclohexyl 2-Methyl-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6m).

^{1}HNMR (500 MHz, $CDCl_3$)

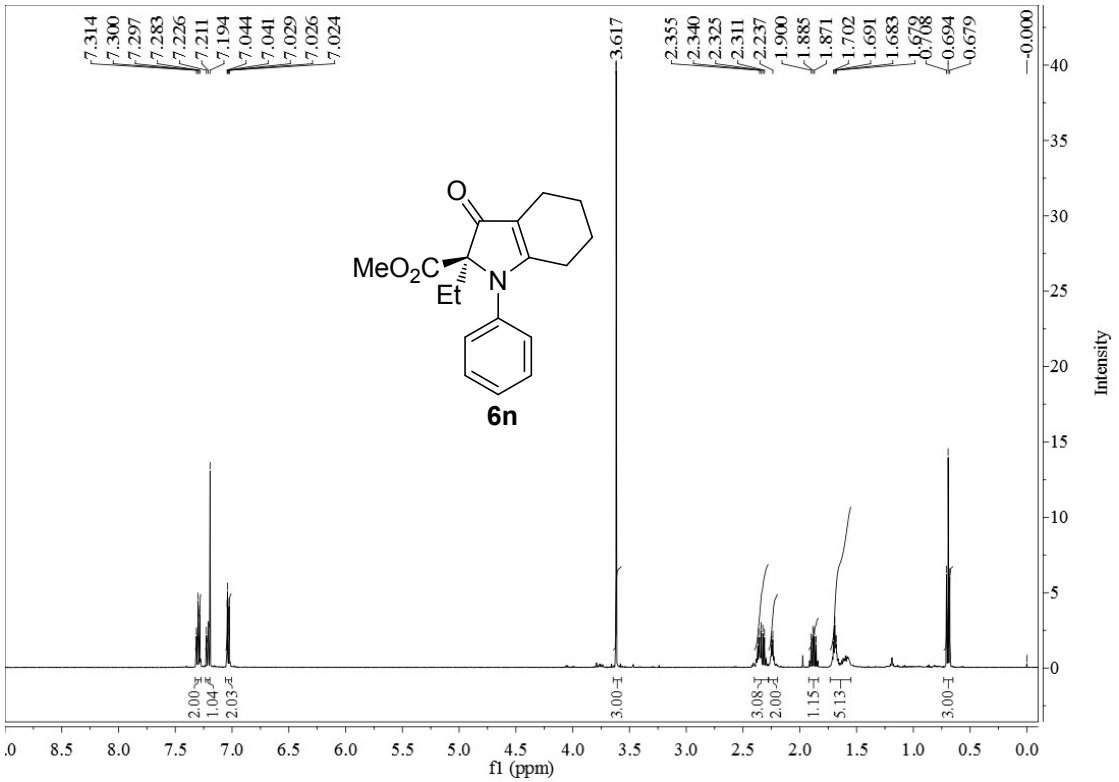


^{13}C NMR (125 MHz, $CDCl_3$)

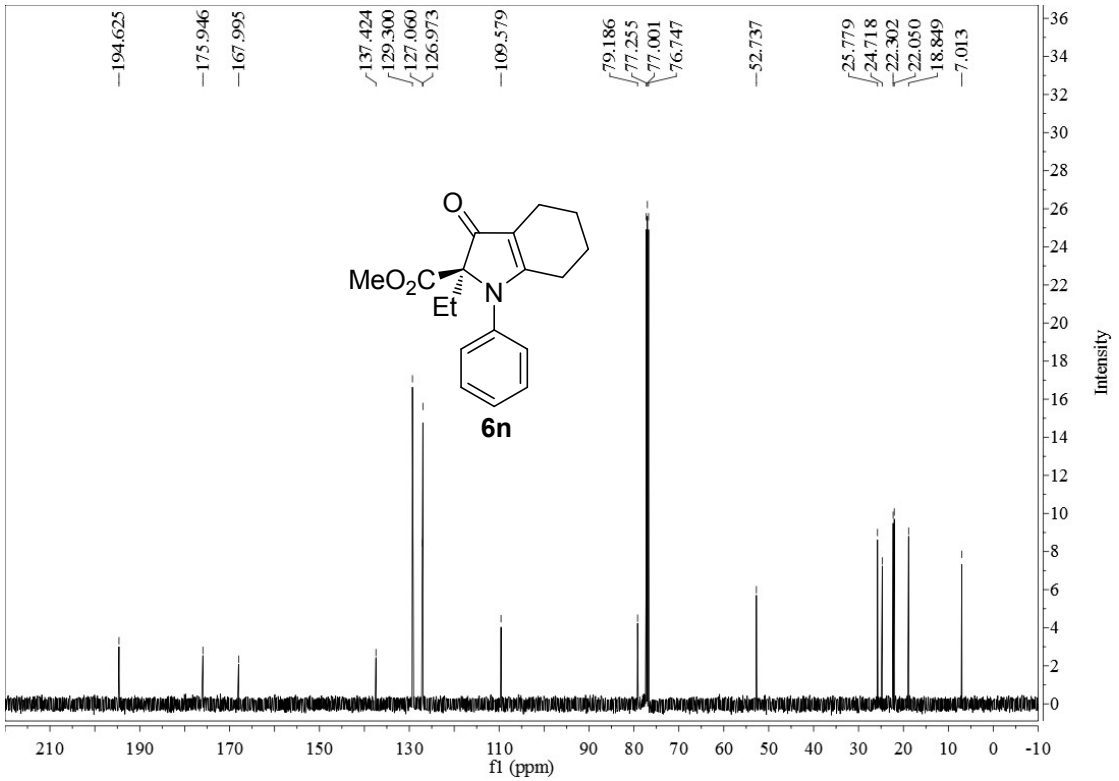


(*R*)-Methyl 2-Ethyl-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6n).

^{1}HNMR (500 MHz, $CDCl_3$)

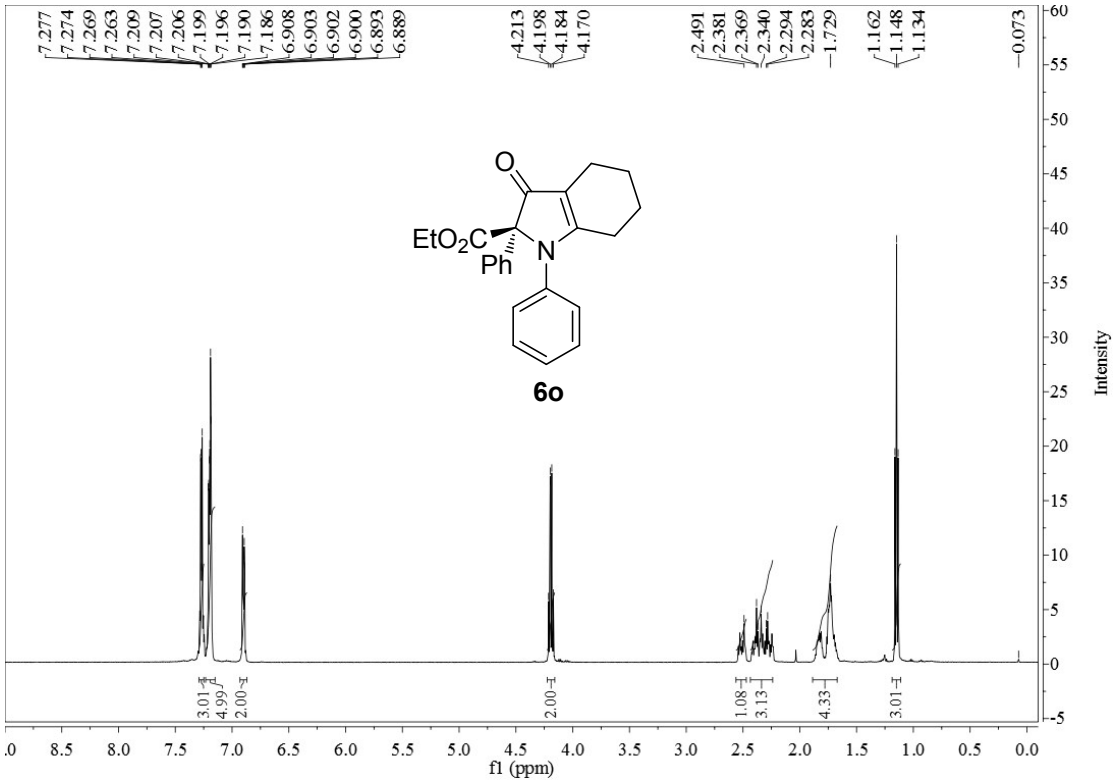


^{13}C NMR (125 MHz, $CDCl_3$)

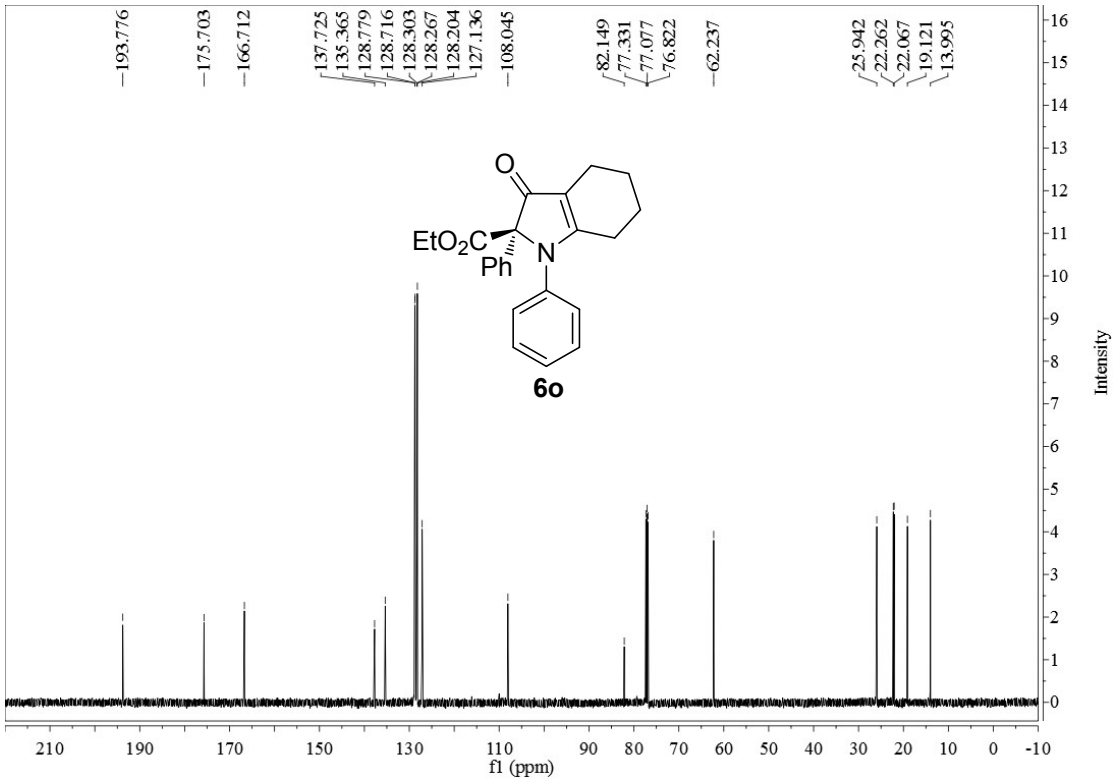


(*R*)-Ethyl 3-Oxo-1,2-diphenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6o).

^{1}HNMR (500 MHz, $CDCl_3$)

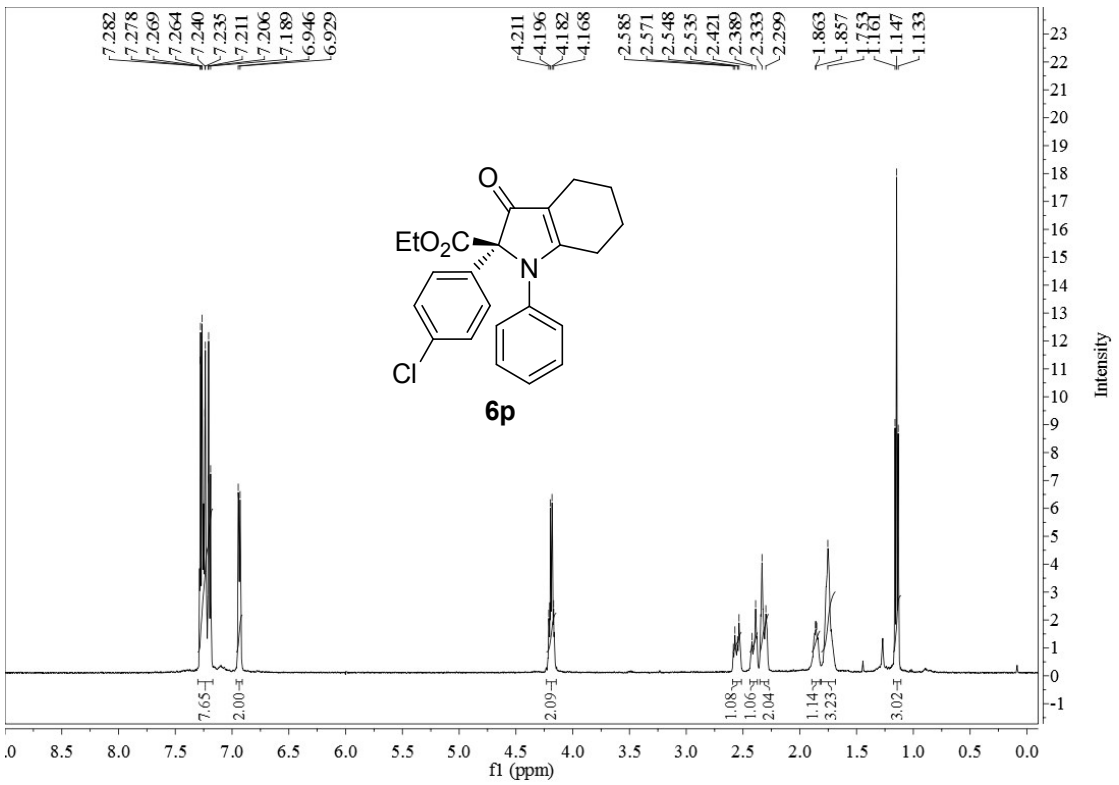


^{13}C NMR (125 MHz, $CDCl_3$)

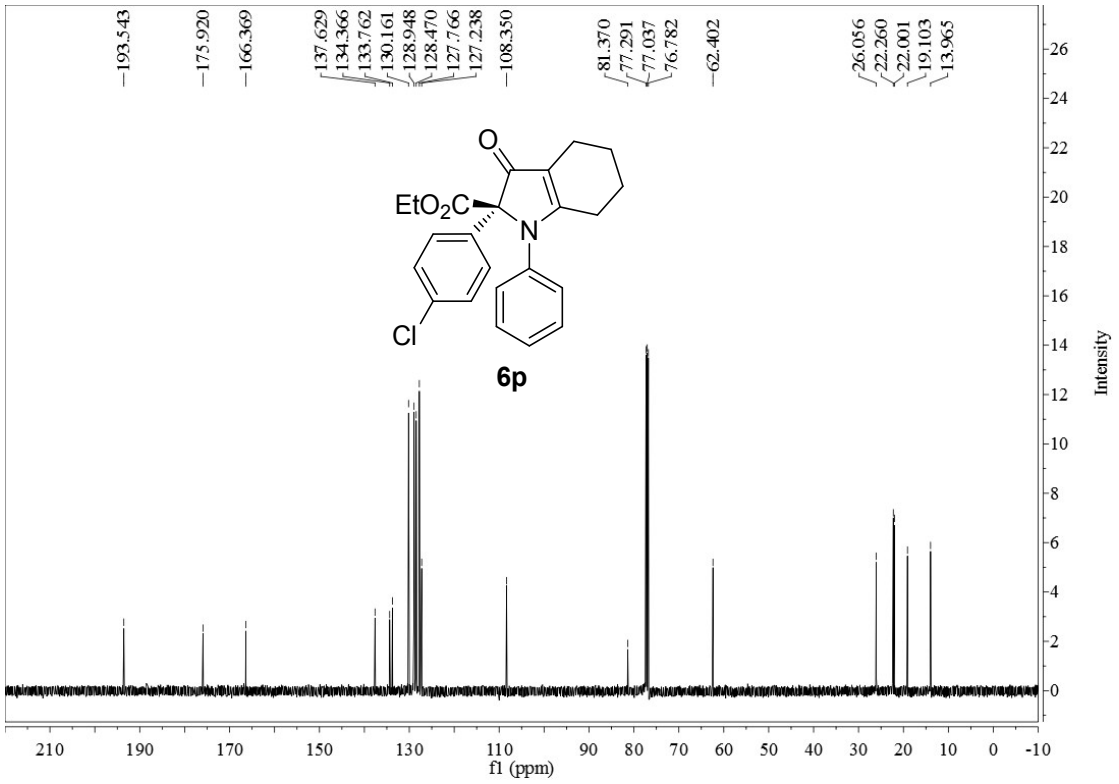


(*R*)-Ethyl 2-(4-Chlorophenyl)-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6p).

^{1}HNMR (500 MHz, $CDCl_3$)

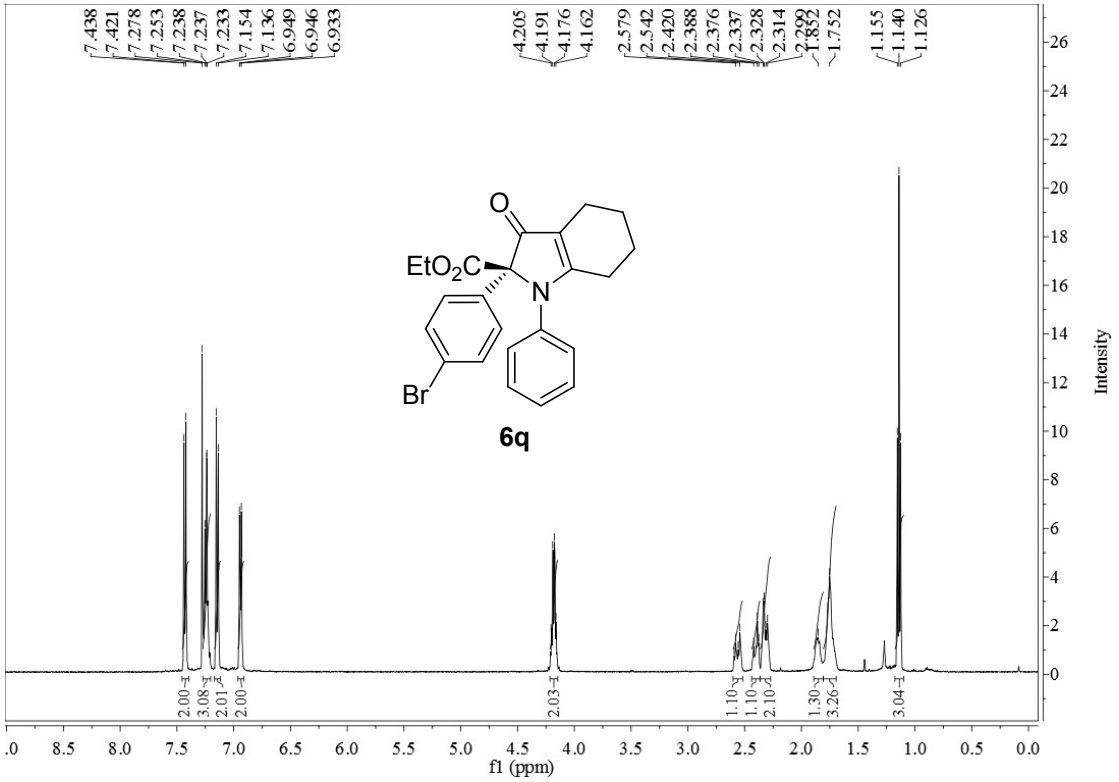


^{13}C NMR (125 MHz, $CDCl_3$)

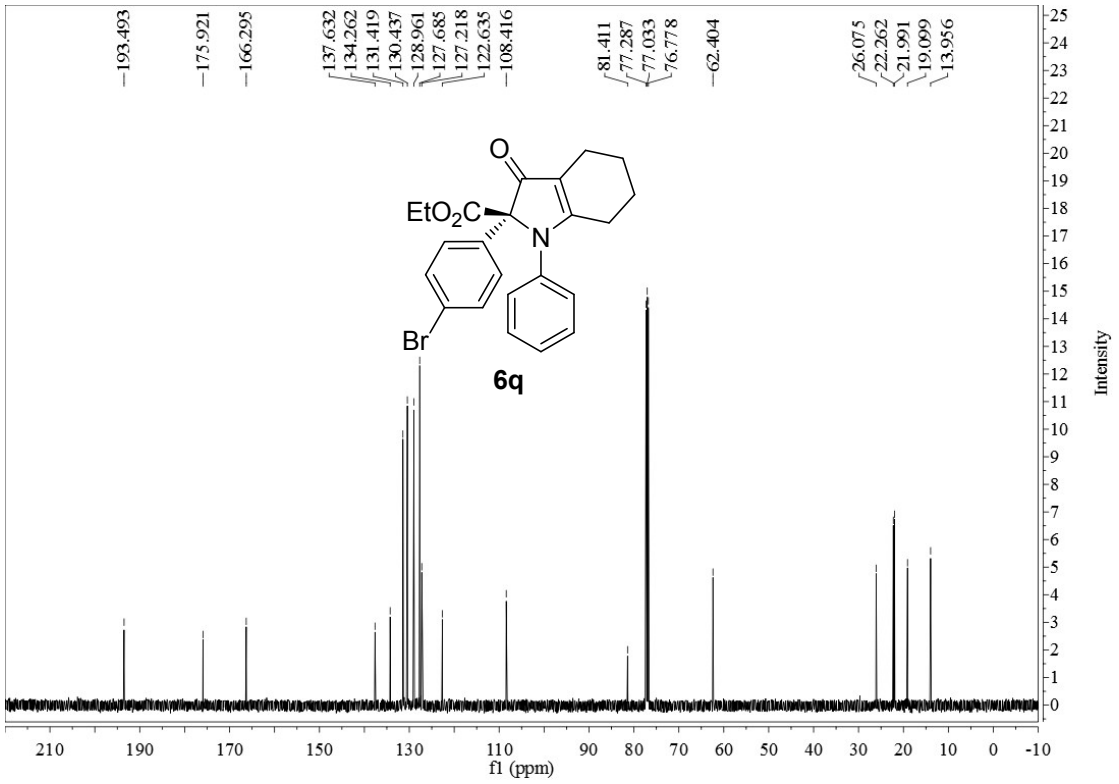


(*R*)-Ethyl 2-(4-Bromophenyl)-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6q).

^{1}HNMR (500 MHz, $CDCl_3$)

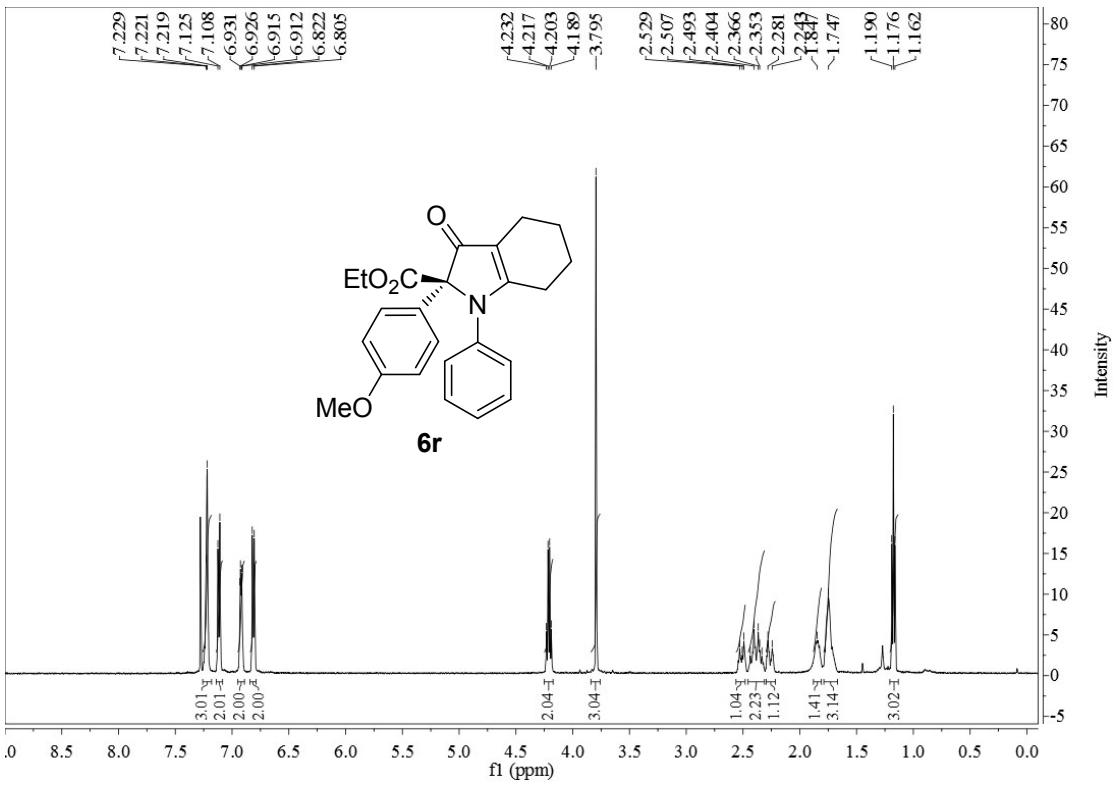


^{13}C NMR (125 MHz, $CDCl_3$)

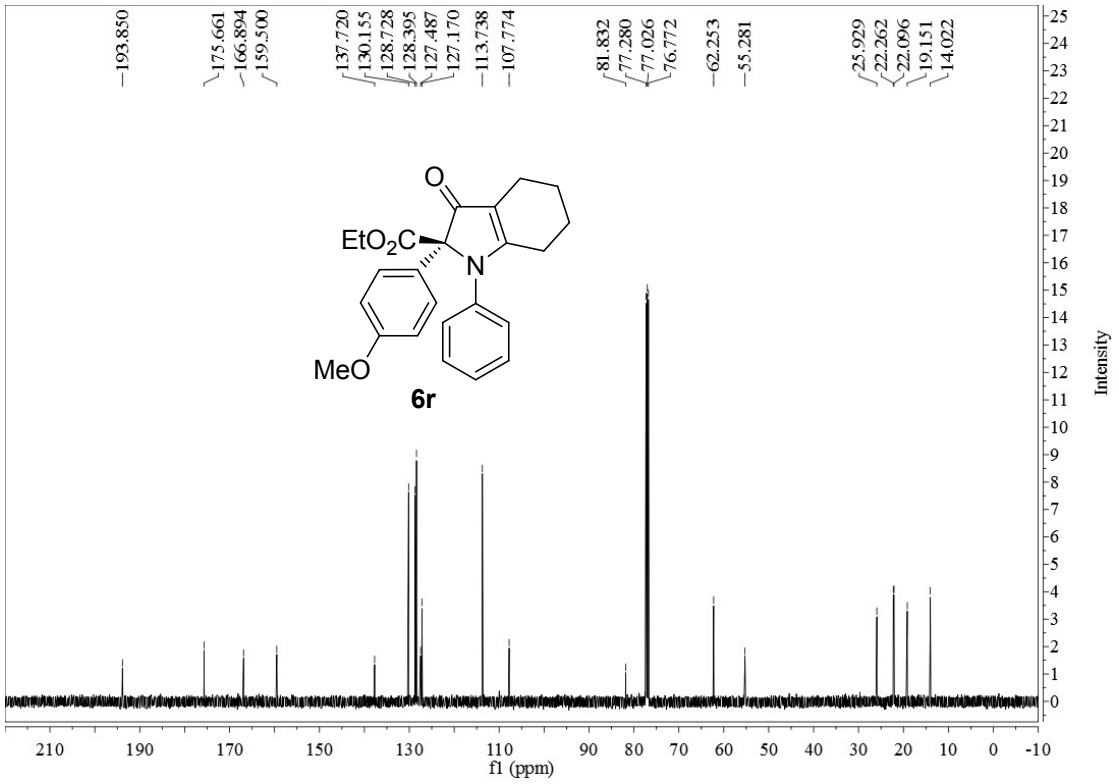


(*R*)-Ethyl 2-(4-Methoxyphenyl)-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6r).

^{1}HNMR (500 MHz, $CDCl_3$)

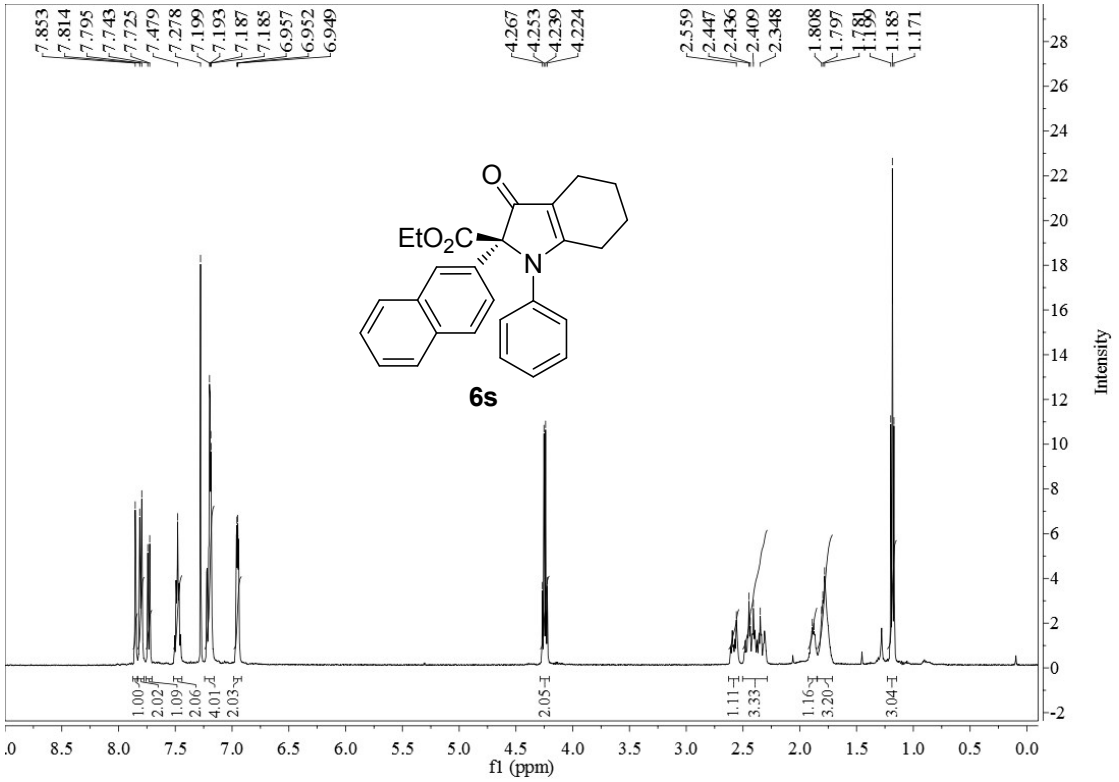


^{13}C NMR (125 MHz, $CDCl_3$)

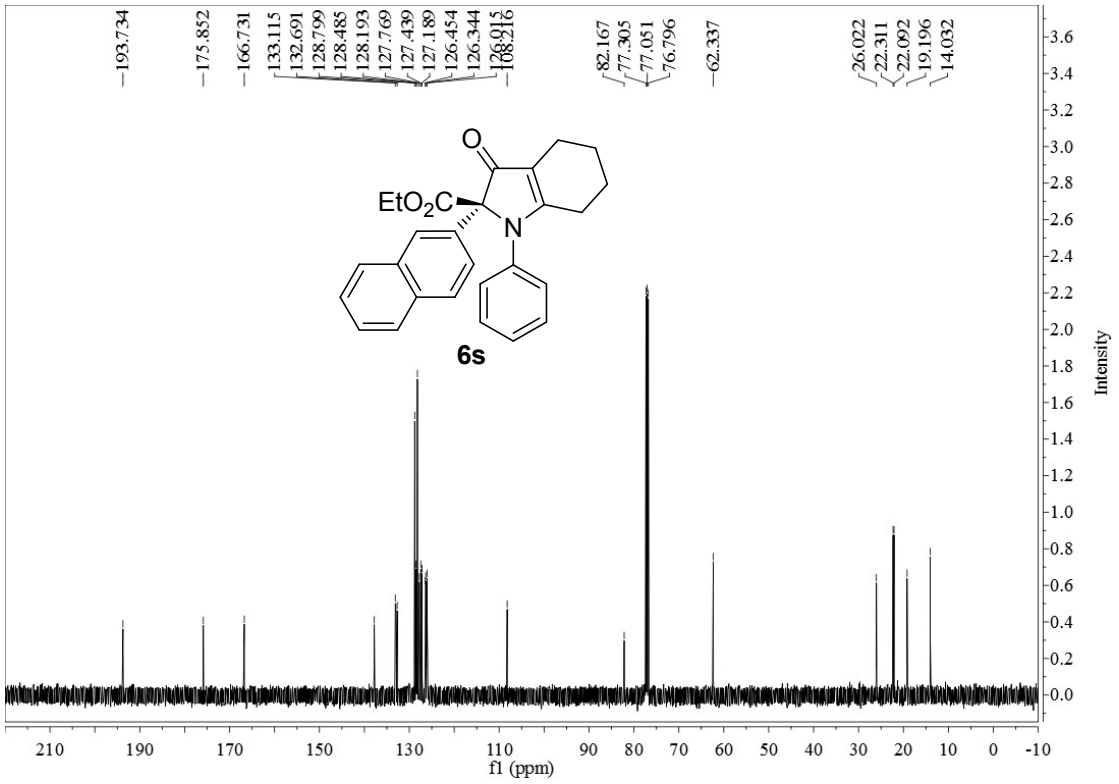


(*R*)-Ethyl 2-(Naphthalen-2-yl)-3-oxo-1-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6s).

^{1}HNMR (500 MHz, $CDCl_3$)

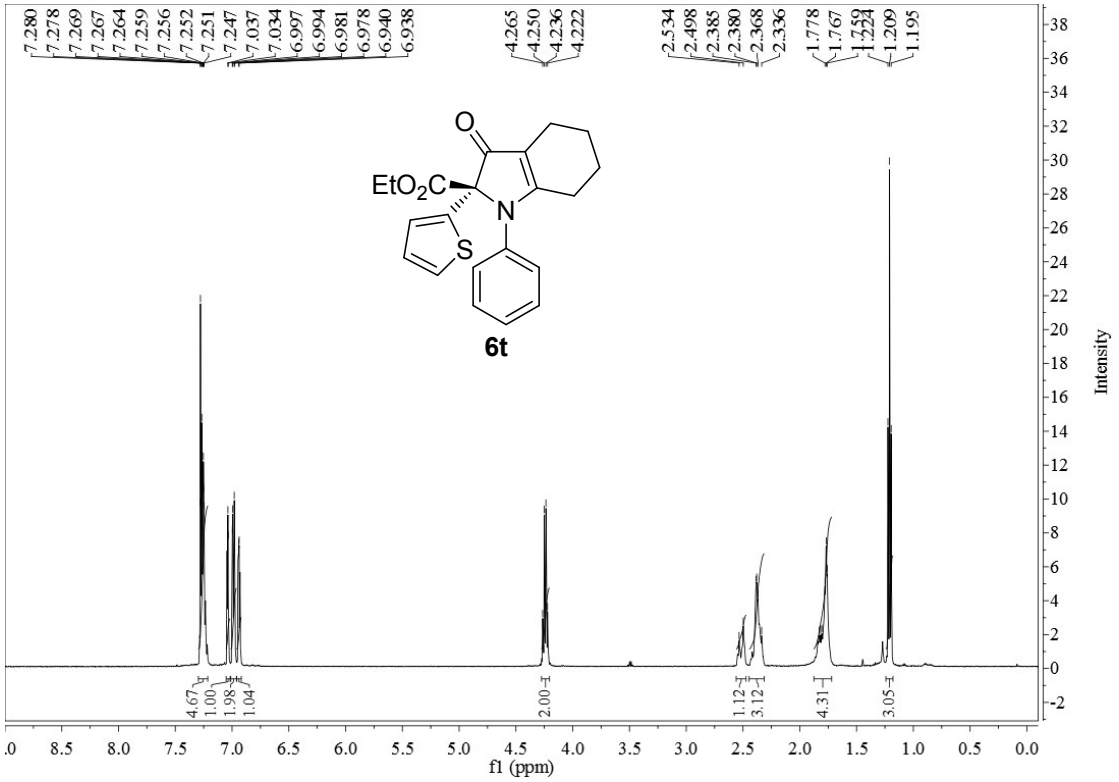


^{13}C NMR (125 MHz, $CDCl_3$)

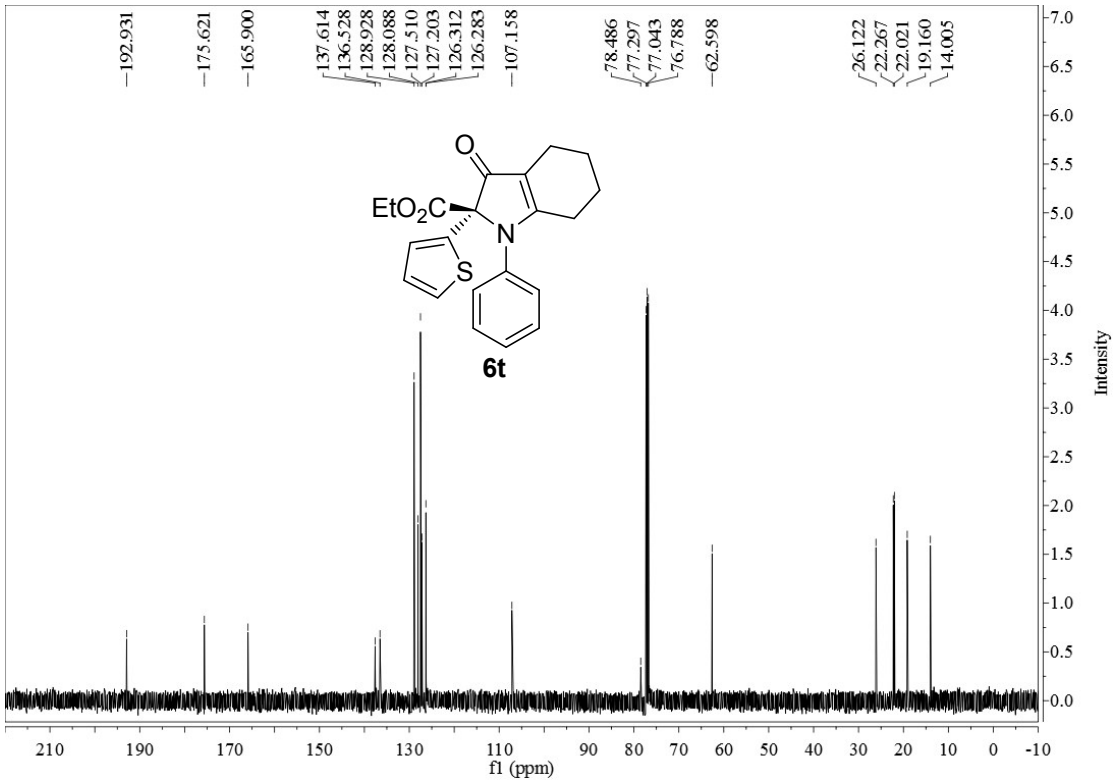


(*R*)-Ethyl 3-Oxo-1-phenyl-2-(thiophen-2-yl)-2,3,4,5,6,7-hexahydro-1*H*-indole-2-carboxylate (6t).

^{1}HNMR (500 MHz, $CDCl_3$)

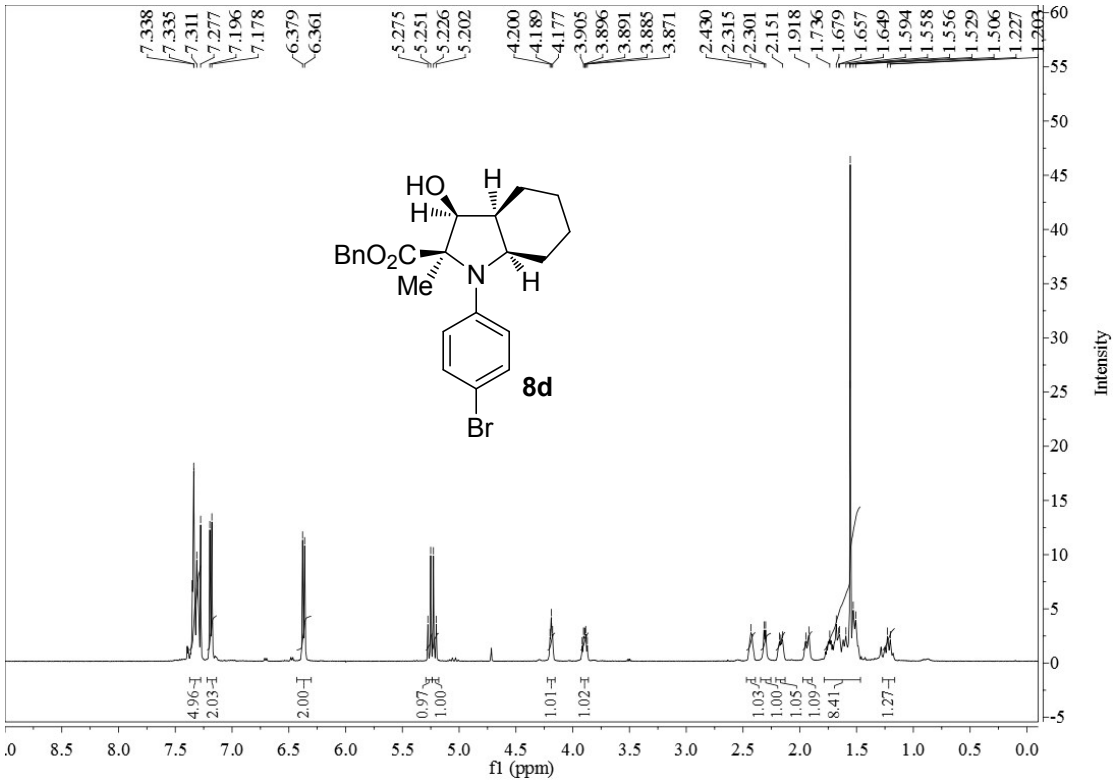


^{13}C NMR (125 MHz, $CDCl_3$)

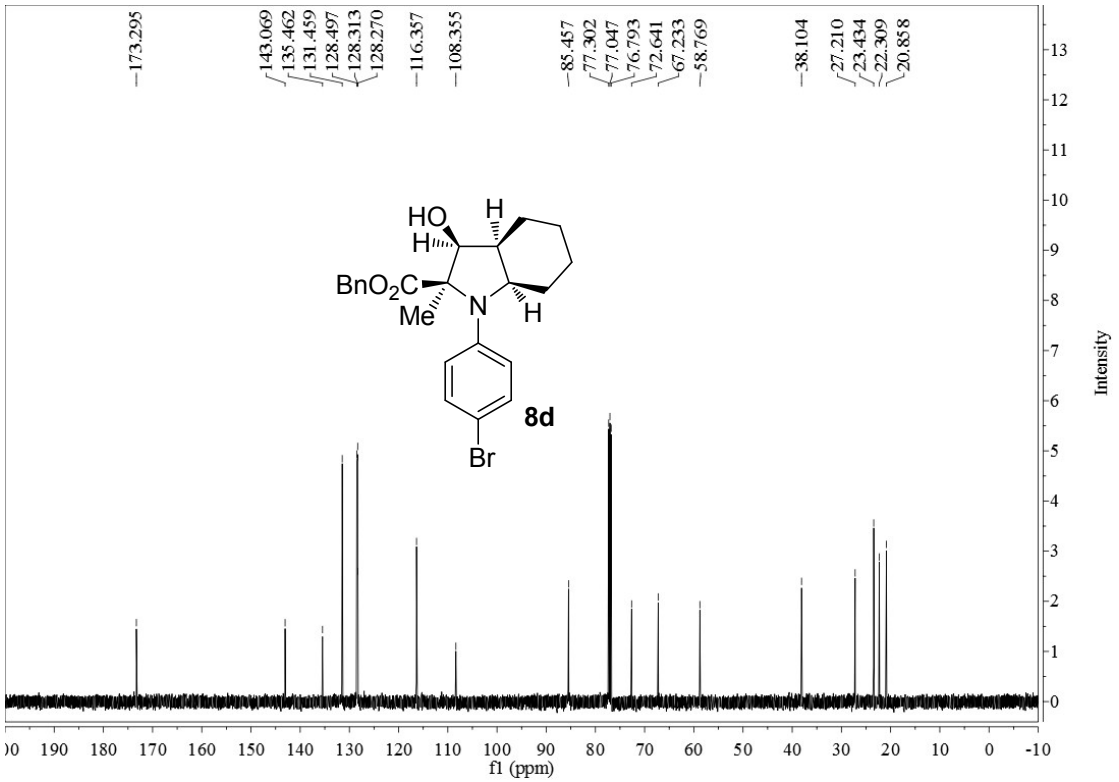


(2*R*,3*S*,3a*S*,7a*R*)-Benzyl 1-(4-Bromophenyl)-3-hydroxy-2-methyloctahydro-1*H*-indole-2-carboxylate (8d).

^{1}HNMR (500 MHz, $CDCl_3$)

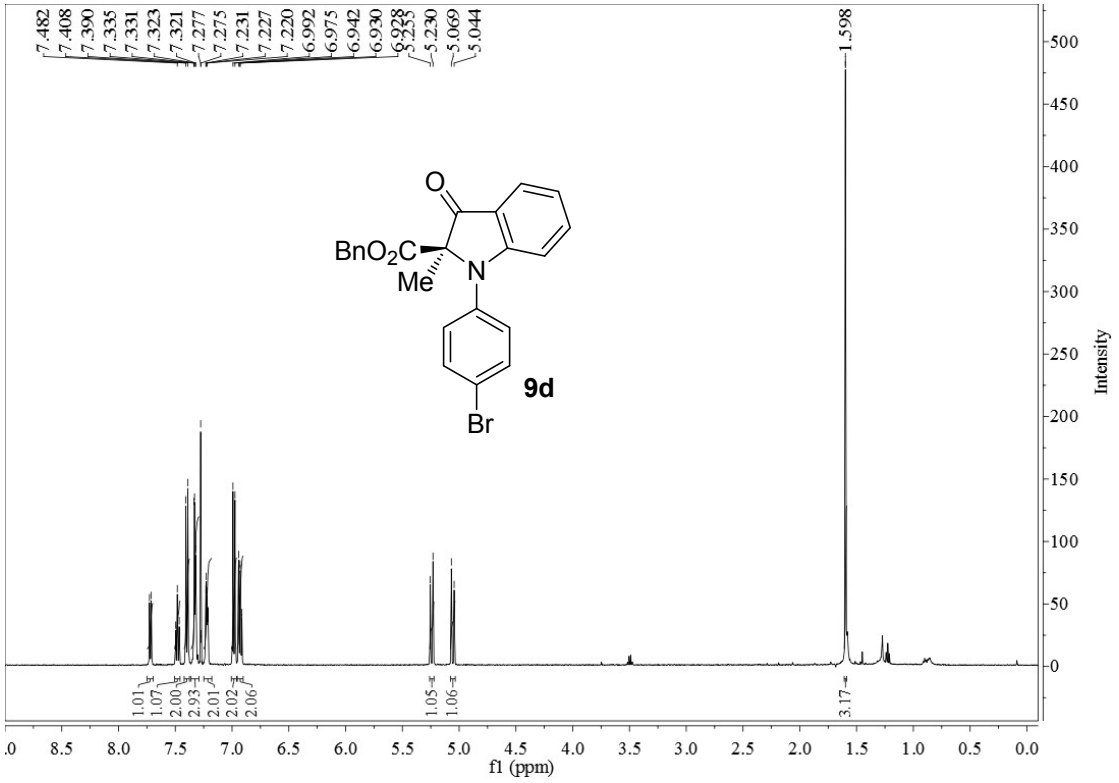


^{13}C NMR (125 MHz, $CDCl_3$)

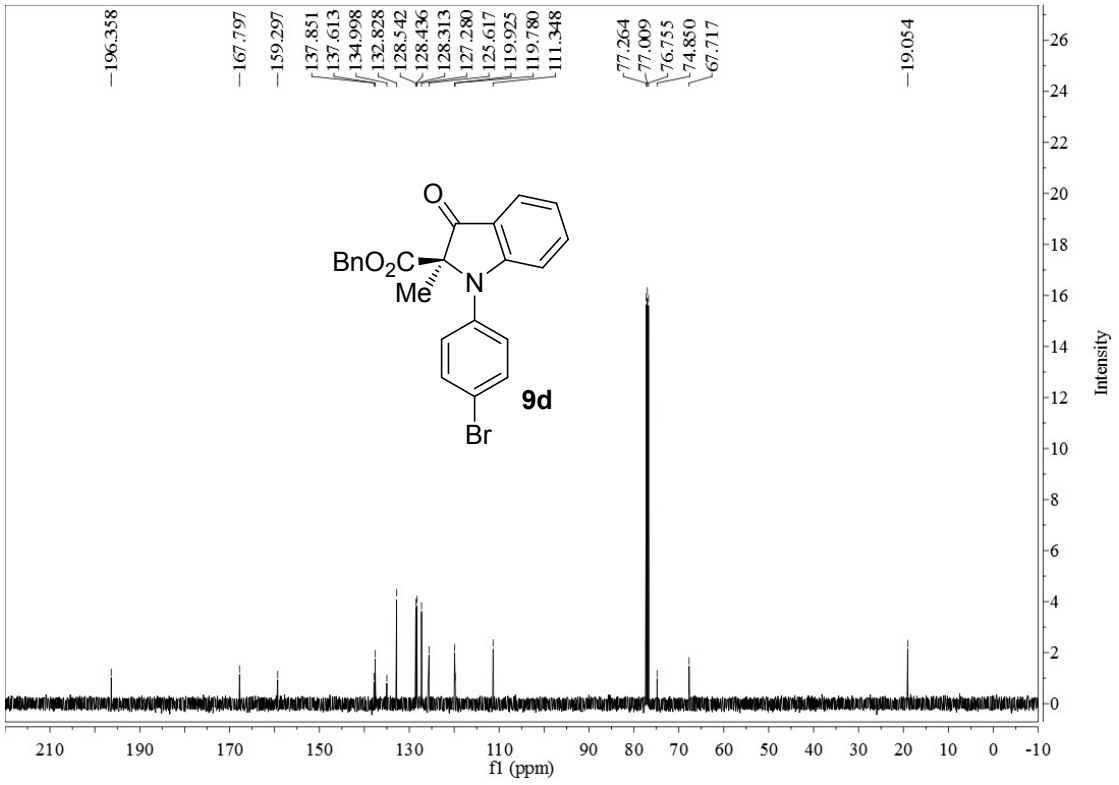


(*R*)-Benzyl 1-(4-Bromophenyl)-2-methyl-3-oxoindoline-2-carboxylate (9d).

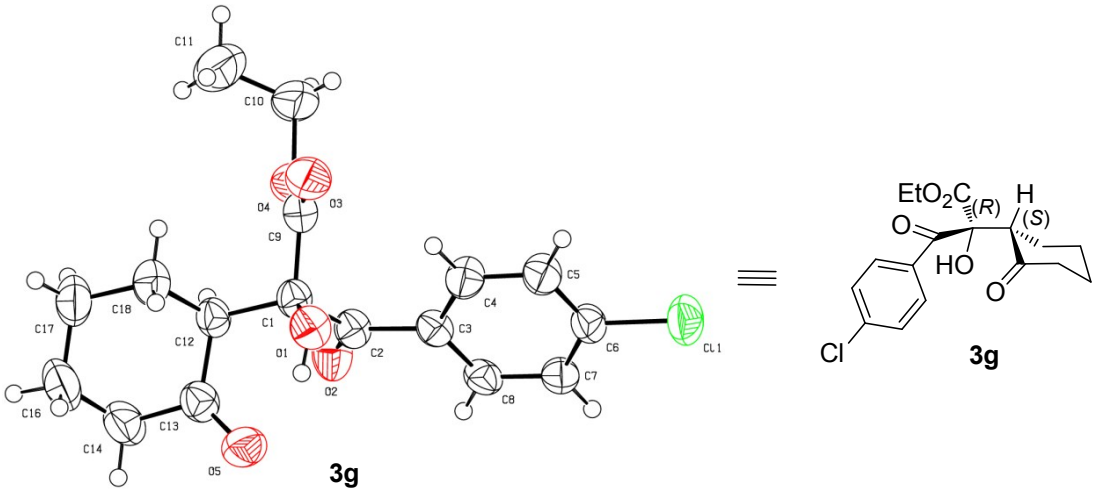
^{1}HNMR (500 MHz, $CDCl_3$)

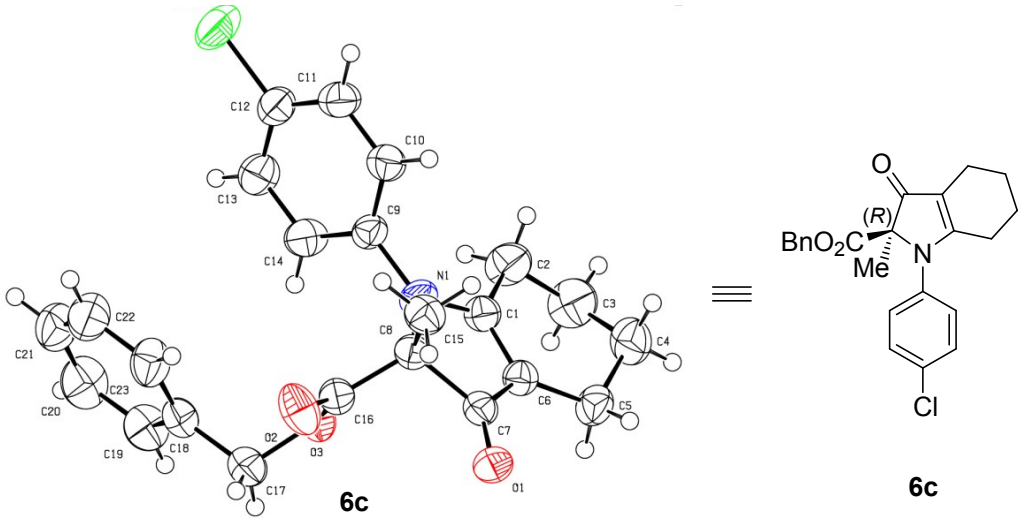


^{13}C NMR (125 MHz, $CDCl_3$)



Crystallographic datas for compound 3g and 6c





Single crystals of **3g** ($C_{17}H_{19}ClO_5$)and **6c** ($C_{23}H_{22}ClNO_3$)wereprepared by slow evaporation of ethyl ether and hexane.Suitable colorless prism-like crystals of both compounds, with dimensions of 0.50 x 0.47 x 0.30 mm and 0.50 x 0.40 x 0.23 mm, resepectively, were mounted in epoxy onto glass fibers. The data were collected at 293(2) K using a Rigaku AFC12/Saturn 724 CCD fitted with Mo Kα radiation (λ= 0.71073 Å). Data collection and unit cell refinement were performed using *Crystal Clear* software.[1] The total number of data were measured in the range 4.6< 2θ < 50.1° using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors (0.512, 1.000 and 0.872, 1.000, respectively), were accomplished with *Crystal Clear* and *ABSCOR*,[2] respectively. The structure, using Olex2,[3] was solved with the ShelXT[4] structure solution program using direct methods and refined (on F^2) with the ShelXL[5]

refinement package using full-matrix, least-squares techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were determined by geometry and refined by a riding model.

Crystallographic data and Structure Refinement Table

Compound	**6c**	**3g**
Empirical formula	$C_{23}H_{22}ClNO_3$	$C_{17}H_{19}ClO_5$
Formula weight	395.86	338.77
Crystal system	orthorhombic	monoclinic
Space Group	$P2_12_12_1$	$C2$
a(Å)	9.258(2)	21.410(6)
b(Å)	9.554(2)	9.115(3)
c(Å)	22.789(5)	8.678(3)
α(°)	90	90
β(°)	90	90.827(4)
γ(°)	90	90
Volume(Å^3)	2015.8(9)	1693.5(9)
Z, Z'	4,1	4,1
ρ(calc.)	1.304	1.329
λ	0.71075	0.71075
Temp.(K)	293	293
F(000)	832	712
μ(mm^{-1})	0.213	0.248
T_{min}, T_{max}	0.512, 1.000	0.872, 1.000
$2\theta_{range}$(°)	4.624- 50.484	4.694- 50.096
Reflections Collected	7560	5190
Independent reflections	3718	2420
Completeness	99.0%	98.0%
Data / restraints / parameters	3718/ 0/ 255	2420/ 1/ 210
Observed data [I > 2σ(I)]	3490	2350
$wR(F^2$ all data)	0.1149	0.0924
$R(F$ obsd data)	0.0421	0.0340
Goodness-of-fit on F^2	1.062	1.050
largest diff. peak and hole, e Å^{-3}	0.20/-0.27	0.20/-0.25

$$wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

1. *CrystalClear*, User Manual. Rigaku/MSC Inc., Rigaku Corporation, The Woodlands, TX, 2011.

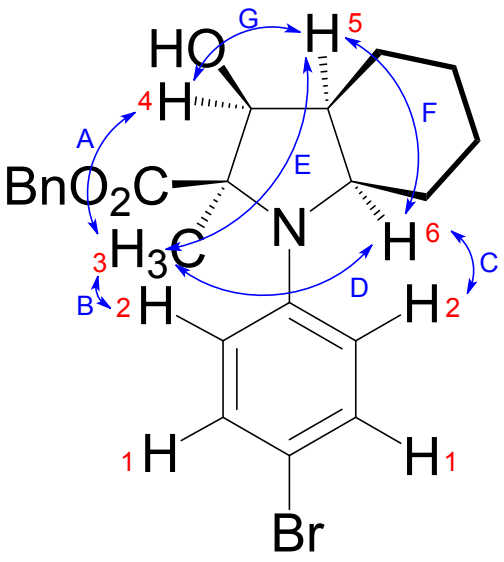
2. Higashi, *ABSCOR*, Rigaku Corporation, Tokyo, Japan, 1995.

3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339.

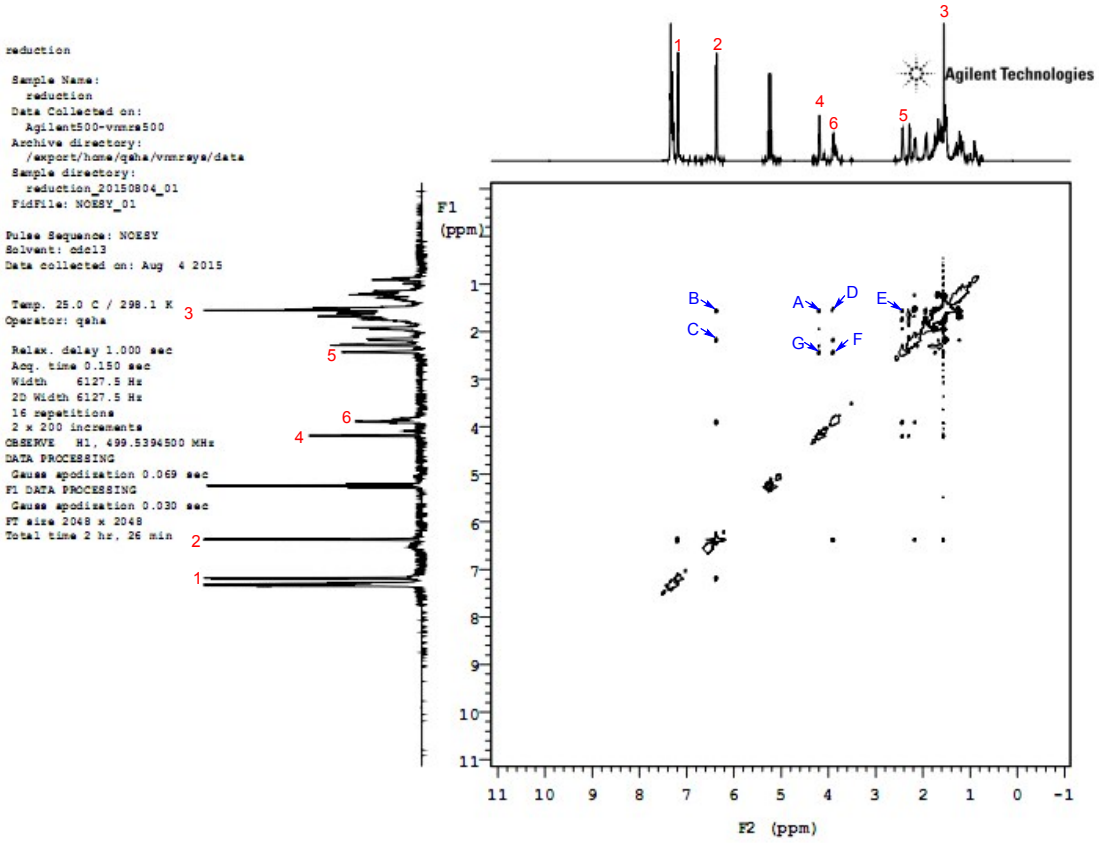
4. G.M.Sheldrick, *Acta Cryst*., 2015, *A71*, 3.

5. G.M.Sheldrick, *Acta Cryst*., 2008, *A64*, 112.

NOE spectrum of 8d.


G
HO
H
5
4
H
A
F
E
BnO2C
N
H3C
H
6
C
3
D
B
2
H
H
2
1
H
H
1
Br

8d


reduction
Sample Name:
reduction
Data Collected on:
Agilent500-vnmrs500
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Sample directory:
reduction_20150804_01
FidFile: NOESY_01
Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Aug 4 2015
Temp. 25.0 C / 298.1 K
Operator: qaha
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 6127.5 Hz
2D Width 6127.5 Hz
16 repetitions
2 x 200 increments
OBSERVE H1, 499.5394500 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.030 sec
FT size 2048 x 2048
Total time 2 hr, 26 min
Agilent Technologies
F1 (ppm)
F2 (ppm)