

Supplementary Information

Enantioselective Switch in Asymmetric Michael Addition

Reactions using Phosponium Salts

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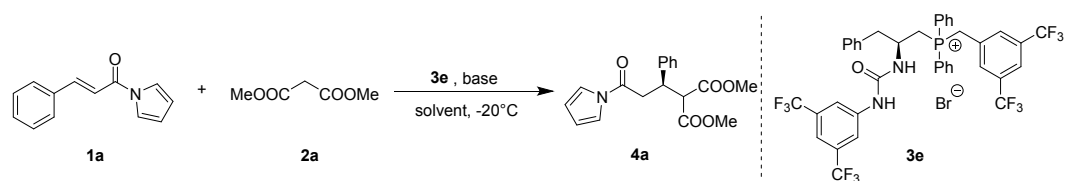
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The optimization of other reaction conditions

Table S1: Optimization of other reaction conditions A.^a



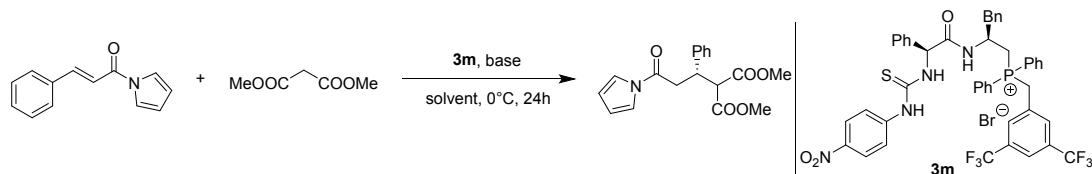
Entry	Solvent	Base	<i>t</i> (h)	Yield ^b (%)	<i>R/S</i>	ee ^c
1 ^d	toluene	K ₂ CO ₃	6	92	<i>R</i>	83%
2 ^e	toluene	K ₂ CO ₃	12	93	<i>R</i>	85%
3	toluene	K ₂ CO ₃	17	95	<i>R</i>	89%
4	m-Xylene	K ₂ CO ₃	16	92	<i>R</i>	91%
5	mesitylene	K ₂ CO ₃	22	97	<i>R</i>	94%
6	Et ₂ O	K ₂ CO ₃	21	92	<i>R</i>	82%
7	TBME	K ₂ CO ₃	17	95	<i>R</i>	83%
8	mesitylene	Cs ₂ CO ₃	17	93	<i>R</i>	91%
9	mesitylene	CsF	12	91	<i>R</i>	93%
10	mesitylene	KF	24	trace	-	-
11	mesitylene	K ₂ HPO ₄	24	trace	-	-
12	mesitylene	K ₃ PO ₄	21	94	<i>R</i>	93%
13	mesitylene	NaOH	8	91	<i>R</i>	92%
14	mesitylene	<i>t</i> BuOK	24	trace	-	-
15 ^f	mesitylene	<i>t</i> BuOK	2.5	94	<i>R</i>	94%
16 ^g	mesitylene	<i>t</i> BuOK	4.5	92	<i>R</i>	93%
17 ^f	mesitylene	<i>t</i> BuOLi	24	41	<i>R</i>	41%
18 ^f	mesitylene	<i>t</i> BuONa	6	93	<i>R</i>	91%
19 ^{f, h}	mesitylene	<i>t</i> BuOK	2.5	92	<i>R</i>	94.4%
20 ^{f, h, i}	mesitylene	<i>t</i> BuOK	7	89	<i>R</i>	94%

^a Unless otherwise noted, the reaction was performed with 0.1 mmol of **1a**, 0.2 mmol of **2a**, 3 equiv. of base, 3 mol% of **3e**, 1 mL of toluene, at -20 °C. Experiment process: **1a**, **2a** and **3e** were solved in mesitylene firstly at -20 °C. The mixture was stirred for 10 min, then *t*BuOK was added.

^b Isolated yield. ^c Determined by HPLC using chiral stationary phase. ^d 0.5 mmol of **2a** was used, reaction was performed at 0 °C. ^e Reaction was performed at 0 °C. ^f 0.02 mmol of base was used. ^g

0.005 mmol of base was used. ^h Experiment process: **2a** and *t*BuOK were solved in mesitylene firstly at -20 °C. The mixture was stirred for 20 min, then **3e** and **1a** were added. ⁱ 1 mol% of **3e** was used.

Table S2: Optimization of other reaction conditions B.^a



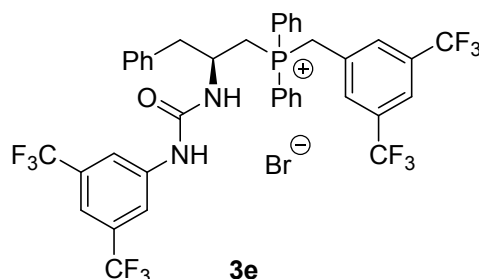
Entry	Solvent	Base	<i>t</i> (h)	Yield ^b (%)	<i>R/S</i>	ee ^c
1	toluene	K ₂ CO ₃	24	92	<i>S</i>	99%
2	m-Xylene	K ₂ CO ₃	17	90	<i>S</i>	98%
3	mesitylene	K ₂ CO ₃	20	91	<i>S</i>	99%
4	TBME	K ₂ CO ₃	36	80	<i>S</i>	94%
5	mesitylene	Cs ₂ CO ₃	14	95	<i>S</i>	84%
6	mesitylene	CsF	15	91	<i>S</i>	88%
7	mesitylene	KF	24	trace	-	-
8	mesitylene	K ₂ HPO ₄	24	trace	-	-
9	mesitylene	K ₃ PO ₄	24	90	<i>S</i>	99%
10	mesitylene	NaOH	24	93	<i>S</i>	89%
11 ^d	mesitylene	<i>t</i> BuOK	24	92	<i>S</i>	96%
12 ^e	mesitylene	K ₂ CO ₃	11	90	<i>S</i>	96%
13 ^f	mesitylene	K ₂ CO ₃	48	88	<i>S</i>	98%
14 ^g	mesitylene	K ₂ CO ₃	48	89	<i>S</i>	99%
15 ^h	mesitylene	K ₂ CO ₃	41	92	<i>S</i>	96%
16 ⁱ	mesitylene	K ₂ CO ₃	13	93	<i>S</i>	98%

^a Unless otherwise noted, the reaction was performed with 0.1 mmol of **1a**, 0.5 mmol of **2a**, 3 equiv. of K₂CO₃, 3 mol% of **3m**, 1 mL of toluene, at 0 °C. ^b Isolated yield. ^c Determined by HPLC using chiral stationary phase. ^d 0.02 mmol of base was used. ^e Reaction was performed at rt. ^f 0.01 mmol of K₂CO₃ was used. ^g The reaction was performed with 0.2 mmol of **2a**. ^h The reaction was performed with 1 mol% of **3m**. ⁱ The reaction was performed with 5 mol% of **3m**.

Synthesis of the catalysts 3.

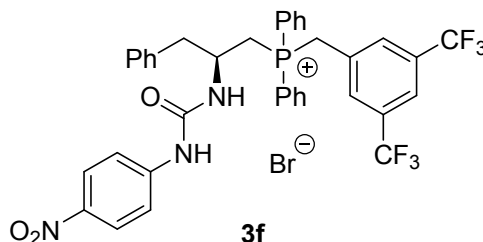
Phase-transfer catalysts **3a-3d**¹ and **3h-3m**² have been described, and the catalysts **3e-3g** were synthesized according to procedures reported previously.¹

(*S*)-(3,5-bis(trifluoromethyl)benzyl)(2-(3-(3,5-bis(trifluoromethyl)phenyl)ureido)-3-phenylpropyl)diphenylphosphonium bromide (**3e**)



White solid, m.p. 114-115 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.78 (s 1H), 7.78 (s, 2H), 7.72 (dd, *J* = 12.8, 7.6 Hz, 2H), 7.54-7.59 (m, 4H), 7.46-7.50 (m, 2H), 7.30-7.39 (m, 5H), 7.09-7.21 (m, 7H), 5.21 (t, *J* = 14.8 Hz, 1H), 4.58 (t, *J* = 14.8 Hz, 1H), 4.20-4.31 (m, 1H), 3.98-4.07 (m, 1H), 3.12-3.18 (m, 1H), 2.87 (dd, *J* = 13.2, 9.6 Hz, 1H), 2.73 (t, *J* = 14.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 154.4, 141.0, 137.0, 135.2 (d, *J*_{C-P} = 2.8 Hz), 133.6 (d, *J*_{C-P} = 9.7 Hz), 133.2 (d, *J*_{C-P} = 9.2 Hz), 132.2 (q, *J*_{C-F} = 33.6 Hz), 131.8, 131.5, 130.6 (2C), 130.4, 130.3, 130.2, 129.4, 129.0, 127.4, 123.4 (q, *J*_{C-F} = 271.0 Hz), 122.5 (q, *J*_{C-F} = 271.4 Hz), 122.2 (m), 118.0, 116.3, 116.0, 115.4, 115.2, 114.9, 114.8, 47.0 (d, *J*_{C-P} = 4.6 Hz), 43.5 (d, *J*_{C-P} = 13.6 Hz), 30.4 (d, *J*_{C-P} = 46.5 Hz), 25.7 (d, *J*_{C-P} = 50.7 Hz); ¹⁹F NMR (CDCl₃, 376 MHz) δ -62.9, -63.2; ³¹P NMR (CDCl₃, 162 MHz) δ 24.9; IR (Neat): 3217, 3061, 1694, 1569, 1474, 1439, 1389, 1373, 1278, 1133, 902, 881, 741, 704; HRMS (ESI): calcd for [M-Br]⁺ (C₃₉H₃₀F₁₂N₂OP)⁺ requires 801.1899; found 801.1899; [α]_D²⁵ = -25.8 (*c* = 1.0, CHCl₃).

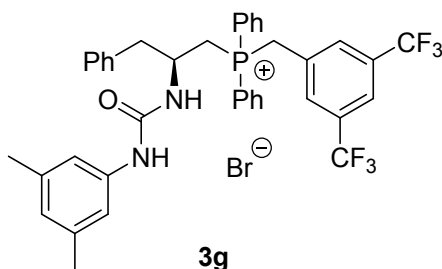
(*S*)-(3,5-bis(trifluoromethyl)benzyl)(2-(3-(4-nitrophenyl)ureido)-3-phenylpropyl)diphenylphosphonium bromide (**3f**)



Yellow solid, m.p. 116-117 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.90 (s 1H), 7.98 (s, 2H), 7.73 (dd, *J* = 12.8, 7.6 Hz, 2H), 7.54-7.62 (m, 3H), 7.37-7.51 (m, 7H), 7.31 (s 2H), 7.08-7.20 (m, 7H), 5.14 (t, *J* = 14.8 Hz, 1H), 4.54 (t, *J* = 14.8 Hz, 1H), 4.21-4.33 (m, 1H), 3.96-4.05 (m, 1H), 3.10-3.16 (m, 1H), 2.82-2.88 (m, 1H), 2.68 (t, *J* = 14.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 154.1, 145.9, 141.7, 136.9, 135.3 (q, *J*_{C-F} = 2.9 Hz), 133.6 (d, *J*_{C-P} = 9.7 Hz), 133.1 (d, *J*_{C-P} = 9.2 Hz), 132.2 (q,

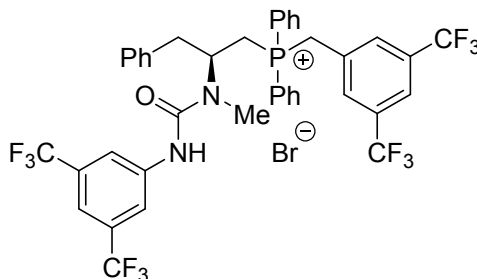
$J_{C-F} = 33.6$ Hz), 130.6, 130.5, 130.4, 130.3, 130.2, 129.4, 129.0, 127.2, 124.9, 122.5 (q, $J_{C-F} = 271.3$ Hz), 122.3 (m), 117.4, 116.0 (d, $J_{C-P} = 7.4$ Hz), 115.2 (d, $J_{C-P} = 6.1$ Hz), 46.9 (d, $J_{C-P} = 4.7$ Hz), 43.6 (d, $J_{C-P} = 13.7$ Hz), 30.4 (d, $J_{C-P} = 46.6$ Hz), 25.4 (d, $J_{C-P} = 50.4$ Hz); $^{19}\text{F NMR}$ (CDCl_3 , 376 MHz) δ -63.1; $^{31}\text{P NMR}$ (CDCl_3 , 162 MHz) δ 24.7; **IR** (Neat): 3207, 3060, 1698, 1597, 1557, 1505, 1438, 1373, 1329, 1303, 1279, 1232, 1177, 1137, 1110, 902, 854, 740, 705; **HRMS** (ESI): calcd for $[\text{M-Br}]^+$ ($\text{C}_{37}\text{H}_{31}\text{F}_6\text{N}_3\text{OP}$) $^+$ requires 710.2002; found 710.2002; $[\alpha]_{\text{D}}^{25} = -20.0$ ($c = 1.0$, CHCl_3).

(S)-(3,5-bis(trifluoromethyl)benzyl)(2-(3-(3,5-dimethylphenyl)ureido)-3-phenylpropyl)diphenylphosphonium bromide (3g)



Yellow solid, m.p. 120-121 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.86 (s 1H), 7.74-7.79 (m, 2H), 7.63-7.66 (m, 3H), 7.56-7.59 (m, 2H), 7.41-7.46 (m, 2H), 7.15-7.35 (m, 10H), 6.98 (s 2H), 6.59 (s 1H), 5.29 (td, $J = 15.2, 6.0$ Hz, 1H), 4.63 (t, $J = 14.8$ Hz, 1H), 4.28-4.40 (m, 1H), 4.04-4.15 (m, 1H), 3.17-3.24 (m, 1H), 2.87-2.93 (m, 1H), 2.70-2.78 (m, 1H), 2.22 (s 6H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 154.9, 139.1, 138.1, 137.4, 135.2 (3C), 135.1, 133.6 (d, $J_{C-P} = 9.6$ Hz), 133.2 (d, $J_{C-P} = 9.1$ Hz), 132.1 (q, $J_{C-F} = 33.8$ Hz), 130.9, 130.8, 130.7, 130.4, 130.3, 130.1, 129.5, 128.9, 126.9, 123.9, 122.5 (q, $J_{C-F} = 271.4$ Hz), 122.1 (m), 116.5, 116.4, 116.0, 115.6, 115.1, 46.9 (d, $J_{C-P} = 4.7$ Hz), 43.8 (d, $J_{C-P} = 13.9$ Hz), 30.0 (d, $J_{C-P} = 45.9$ Hz), 25.7 (d, $J_{C-P} = 50.4$ Hz), 21.3; $^{19}\text{F NMR}$ (CDCl_3 , 376 MHz) δ -63.1; $^{31}\text{P NMR}$ (CDCl_3 , 162 MHz) δ 25.4; **IR** (Neat): 3265, 3027, 2920, 1683, 1613, 1559, 1438, 1373, 1332, 1278, 1235, 1177, 1138, 921, 902, 839, 740, 705; **HRMS** (ESI): calcd for $[\text{M-Br}]^+$ ($\text{C}_{39}\text{H}_{36}\text{F}_6\text{N}_2\text{OP}$) $^+$ requires 693.2364; found 693.2364; $[\alpha]_{\text{D}}^{25} = -17.7$ ($c = 1.0$, CHCl_3).

(S)-(3,5-bis(trifluoromethyl)benzyl)(2-(3-(3,5-bis(trifluoromethyl)phenyl)-1-methylureido)-3-phenylpropyl)diphenylphosphonium bromide (3n)



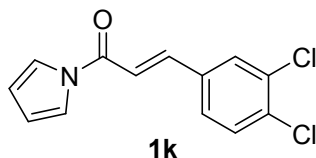
White solid, m.p. 103-104 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.08-8.11 (m, 4H), 7.99 (s, 1H), 7.68-7.73 (m, 2H), 7.63 (t, $J = 5.6$ Hz, 1H), 7.51-7.56 (m, 4H), 7.41-7.46 (m, 3H), 7.26-7.29 (m, 3H), 7.20-7.21 (m, 2H), 7.02-7.09 (m, 2H), 5.66 (t, $J = 11.2$ Hz, 1H), 4.86-5.07 (m, 1H), 4.70-4.77 (m, 1H), 4.47-4.64 (m, 1H), 3.19 (s, 3H), 2.97 (d, $J = 4.8$ Hz, 2H), 2.71 (t, $J = 11.6$ Hz, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 155.2, 140.9, 136.7, 135.1 (d, $J_{C-P} = 12.0$ Hz), 133.8 (d, $J_{C-P} = 10.2$ Hz), 133.1

(d, $J_{C-P} = 8.7$ Hz), 132.1 (2C), 131.8 (2C), 131.7, 131.5, 131.2, 131.1, 131.0 (2C), 130.9, 130.8, 130.7 (2C), 130.3, 130.1, 130.0, 129.5, 128.9, 127.2, 123.4 (q, $J_{C-F} = 271.0$ Hz), 122.5 (q, $J_{C-F} = 271.8$ Hz), 121.9 (m), 120.3, 119.3, 118.5, 116.3, 116.1, 115.8, 115.7, 115.0, 114.9, 51.2, 40.7 (d, $J_{C-P} = 13.7$ Hz), 30.9 (d, $J_{C-P} = 47.2$ Hz), 29.4 (d, $J_{C-P} = 38.2$ Hz), 22.4; **^{19}F NMR** (CDCl₃, 376 MHz) δ -62.9, -63.2; **^{31}P NMR** (CDCl₃, 162 MHz) δ 24.9; **IR** (Neat): 2910, 1691, 1374, 1278, 1178, 1134, 742, 704, 683; **HRMS** (ESI): calcd for [M-Br]⁺ (C₄₀H₃₂F₁₂N₂OP)⁺ requires 815.2055; found 815.2055; $[\alpha]_D^{25} = -38.0$ ($c = 1.0$, CHCl₃).

Synthesis of the substrate 1.

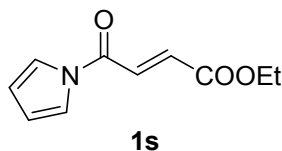
Compounds **1a-3c**,³ **1d**,⁴ **1e**,³ **1f**,³ **1g-1i**,⁴ **1j**,⁵ **1l**,⁵ **1m**,³ **1n**,³ **1o**,⁶ **1p**,⁷ **3q**,³ **3r**,³ **3t**,³ **3u**,³ **3v**,⁸ and **3x**⁹ were known. **3k**,⁶ **3n**,¹ **3s**,⁴ and **3w**³ were also synthesized according to procedures reported previously.

(*E*)-3-(3,4-dichlorophenyl)-1-(1H-pyrrol-1-yl)prop-2-en-1-one (**1k**)



White solid, m.p. 145-146 °C; **1H NMR** (CDCl₃, 400 MHz) δ 7.87 (d, $J = 15.6$ Hz, 1H), 7.71 (d, $J = 2.0$ Hz, 1H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.43-7.46 (m, 3H), 7.12 (d, $J = 15.6$ Hz, 1H), 6.38 (t, $J = 2.4$ Hz, 2H); **^{13}C NMR** (CDCl₃, 100 MHz) δ 162.3, 144.6, 134.9, 134.2, 133.4, 131.0, 129.7, 127.5, 119.2, 117.5, 113.7; **IR** (Neat): 1682, 1626, 1552, 1470, 1409, 1387, 1353, 1308, 1285, 1263, 1247, 1206, 1132, 1073, 1209, 974, 941, 851, 816, 749, 722; **HRMS** (ESI): calcd for [M+H]⁺ (C₁₃H₁₀Cl₂NO)⁺ requires 266.0134; found requires 266.0132.

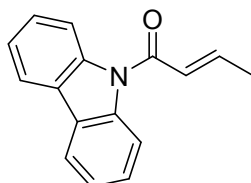
Ethyl (*E*)-4-oxo-4-(1H-pyrrol-1-yl)but-2-enoate (**1s**)



Light yellow solid, m.p. 72-73 °C; **1H NMR** (CDCl₃, 400 MHz) δ 7.60 (d, $J = 15.2$ Hz, 1H), 7.40 (t, $J = 2.0$ Hz, 2H), 7.10 (d, $J = 15.2$ Hz, 1H), 6.38 (t, $J = 2.0$ Hz, 2H), 4.31 (q, $J = 7.2$ Hz, 2H), 1.36 (t, $J = 7.2$ Hz, 3H); **^{13}C NMR** (CDCl₃, 100 MHz) δ 164.7, 161.2, 135.6, 131.3, 119.4, 114.3, 61.6, 14.1; **IR** (Neat): 3145, 2977, 1714, 1692, 1646, 1474, 1409, 1368, 1355, 1310, 1280, 1186, 1134, 1117, 1089, 1056, 963, 937, 875, 755, 722; **HRMS** (ESI): calcd for [M+H]⁺ (C₁₀H₁₂NO₃)⁺ requires

194.0812; found requires 194.0814.

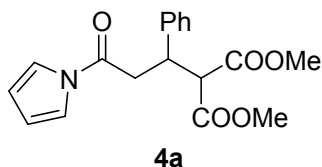
(E)-1-(9H-fluoren-9-yl)but-2-en-1-one (1w)



White solid, m.p. 57-58 °C; **¹H NMR** (CDCl₃, 400 MHz) δ 8.10 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 7.6 Hz, 2H), 7.45-7.49 (m, 2H), 7.36-7.39 (m, 2H), 7.23-7.32 (m, 1H), 6.80-6.85 (m, 1H), 3.11 (dd, *J* = 7.2, 1.6 Hz, 3H); **¹³C NMR** (CDCl₃, 100 MHz) δ 166.1, 145.5, 138.5, 127.0, 126.1, 126.0, 123.3, 119.9, 115.6, 18.6; **IR** (Neat): 3059, 1681, 1641, 1597, 1584, 1489, 1478, 1443, 1357, 1331, 1308, 1294, 1270, 1237, 1215, 1166, 1121, 1094, 1036, 1023, 977, 940, 891, 824, 806, 753, 723; **HRMS** (ESI): calcd for [M+H]⁺ (C₁₆H₁₄NO)⁺ requires 236.1075; found requires 236.1071.

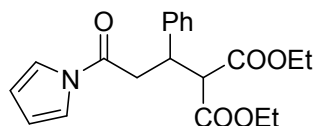
The spectral data of the products 4.

Dimethyl 2-(3-oxo-1-phenyl-3-(1H-pyrrol-1-yl)propyl)malonate (4a)



White solid, m.p. 93-94 °C; **¹H NMR** (CDCl₃, 400 MHz) δ 7.19-7.28 (m, 7H), 6.25 (s, 2H), 4.11-4.16 (m, 1H), 3.87 (d, *J* = 9.2 Hz, 1H), 3.73 (s, 3H), 3.42-3.51 (m, 4H), 3.30 (dd, *J* = 16.4, 9.2 Hz, 1H); **¹³C NMR** (CDCl₃, 100 MHz) δ 168.5, 168.1, 167.9, 139.5, 128.6, 127.9, 127.5, 119.0, 113.1, 56.8, 52.7, 52.5, 41.0, 38.4; **IR** (Neat): 2953, 1735, 1596, 1469, 1455, 1435, 1374, 1281, 1198, 1157, 1120, 1075, 1021, 960, 924, 744, 701; **HRMS** (ESI): calcd for [M+H]⁺ (C₁₈H₂₀NO₅)⁺ requires 330.1336; found 330.1336; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 80:20; Condition A : (*R*)-**4a**, 92% yield (30.4 mg), 94% ee, [α]_D²⁵ = -22.9 (*c* = 1.0, CHCl₃), retention time 14.9 min (major) and 18.9 min (minor); Condition B: (*S*)-**4a**, 91% yield (30.1 mg), 99% ee, [α]_D²⁵ = +25.0 (*c* = 1.0, CHCl₃); retention time 14.6 min (minor) and 18.8 min (major).

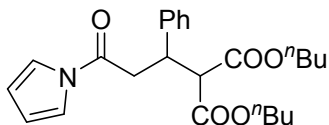
Diethyl 2-(3-oxo-1-phenyl-3-(1H-pyrrol-1-yl)propyl)malonate (4b)



4b

White solid, m.p. 105-106 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.18-7.29 (m, 7H), 6.25 (t, $J = 2.0$ Hz, 2H), 4.09-4.27 (m, 3H), 3.96 (q, $J = 7.2$ Hz, 2H), 3.83 (d, $J = 9.6$ Hz, 1H), 3.45 (dd, $J = 16.0$, 4.0 Hz, 1H), 3.28 (dd, $J = 16.0$, 9.6 Hz, 1H), 1.24 (t, $J = 6.8$ Hz, 3H), 1.01 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 168.2, 168.1, 167.5, 139.5, 128.5, 128.1, 127.5, 119.0, 113.1, 61.8, 61.5, 57.1, 41.1, 38.7, 14.0, 13.7; **IR** (Neat): 2982, 2936, 1729, 1496, 1469, 1455, 1405, 1369, 1281, 1249, 1174, 1119, 1095, 1074, 1029, 921, 863, 744, 700; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{20}\text{H}_{24}\text{NO}_5$)⁺ requires 358.1649; found 358.1649; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, $\lambda = 254$ nm, hexane/isopropanol = 80:20; Condition A : (*R*)-**4b**, 91% yield (32.3 mg), 96% ee, $[\alpha]_{\text{D}}^{25} = -18.2$ ($c = 1.0$, CHCl_3), retention time 13.2 min (major) and 25.3 min (minor); Condition B: (*S*)-**4b**, 93% yield (33.2 mg), 98% ee, $[\alpha]_{\text{D}}^{25} = +20.0$ ($c = 1.0$, CHCl_3); retention time 13.2 min (minor) and 25.1 min (major).

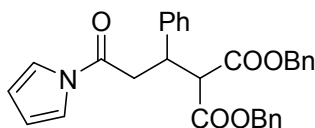
Dibutyl 2-(3-oxo-1-phenyl-3-(1H-pyrrol-1-yl)propyl)malonate (4c)



4c

White solid, m.p. 69-70 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.18-7.28 (m, 7H), 6.25 (t, $J = 2.0$ Hz, 2H), 4.09-4.20 (m, 3H), 3.84-3.92 (m, 3H), 3.45 (dd, $J = 16.4$, 4.4 Hz, 1H), 3.28 (dd, $J = 16.0$, 9.6 Hz, 1H), 1.55-1.62 (m, 2H), 1.28-1.40 (m, 4H), 1.14-1.24 (m, 2H), 0.91 (t, $J = 7.6$ Hz, 3H), 0.83 (t, $J = 7.6$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 168.3, 168.1, 167.6, 139.6, 128.5, 128.0, 127.5, 119.0, 113.1, 65.6, 65.3, 57.2, 41.1, 38.7, 30.4, 30.2, 19.0, 18.9, 13.6, 13.5; **IR** (Neat): 2960, 2934, 2874, 1730, 1469, 1406, 1374, 1281, 1248, 1170, 1119, 1073, 923, 743, 700; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{24}\text{H}_{32}\text{NO}_5$)⁺ requires 414.2275; found 414.2275; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, $\lambda = 254$ nm, hexane/isopropanol = 80:20; Condition A : (*R*)-**4c**, 99% yield (40.9 mg), 94% ee, $[\alpha]_{\text{D}}^{25} = -12.8$ ($c = 1.0$, CHCl_3), retention time 8.0 min (major) and 15.5 min (minor); Condition B: (*S*)-**4c**, 99% yield (40.8 mg), 99% ee, $[\alpha]_{\text{D}}^{25} = +14.2$ ($c = 1.0$, CHCl_3); retention time 8.0 min (minor) and 15.4 min (major).

Dimethyl 2-(3-oxo-1-phenyl-3-(1H-pyrrol-1-yl)propyl)malonate (4d)

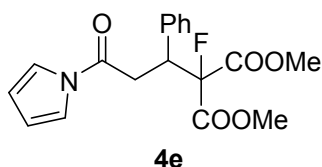


4d

White solid, m.p. 99-100 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.19-7.30 (m, 15H), 7.05-7.07 (m,

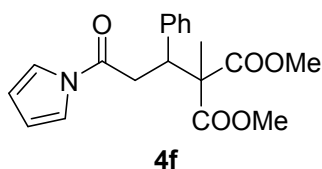
2H), 6.22 (t, $J = 2.4$ Hz, 2H), 5.10-5.18 (m, 2H), 4.91 (s, 2H), 4.13-4.18 (m, 1H), 3.95 (d, $J = 9.2$ Hz, 1H), 3.34 (dd, $J = 16.4, 4.4$ Hz, 1H), 3.24 (dd, $J = 16.4, 9.2$ Hz, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 168.0, 167.8, 167.2, 139.4, 135.0, 134.9, 128.6, 128.6, 128.5 (2C), 128.3 (2C), 128.2, 128.0, 127.5, 119.0, 113.1, 67.5, 67.3, 57.1, 41.0, 38.3; **IR** (Neat): 3064, 3032, 2954, 1731, 1497, 1469, 1455, 1374, 1281, 1215, 1152, 1120, 1002, 956, 924, 743; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{30}\text{H}_{28}\text{NO}_5$) $^+$ requires 482.1962; found 482.1960; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, $\lambda = 254$ nm, hexane/isopropanol = 50:50; Condition A : (*R*)-**4d**, 93% yield (44.6 mg), 91% ee, $[\alpha]_{\text{D}}^{25} = -5.3$ ($c = 1.0$, CHCl_3), retention time 16.6 min (major) and 30.8 min (minor); Condition B: (*S*)-**4d**, 90% yield (43.2 mg), 98% ee, $[\alpha]_{\text{D}}^{25} = +5.9$ ($c = 1.0$, CHCl_3); retention time 17.0 min (minor) and 31.3 min (major).

Dimethyl 2-fluoro-2-(3-oxo-1-phenyl-3-(1H-pyrrol-1-yl)propyl)malonate (**4e**)



White solid, m.p. 117-118 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.34-7.36 (m, 2H), 7.24-7.31 (m, 5H), 6.26 (t, $J = 2.4$ Hz, 2H), 4.47 (ddd, $J_{\text{H-F}} = 32.0$ Hz, $J = 9.6, 3.6$ Hz, 1H); 3.88 (s, 3H), 3.55 (s, 3H), 3.44 (dd, $J = 16.8, 9.6$ Hz, 1H), 3.32 (dd, $J = 17.2, 4.0$ Hz, 1H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 167.3, 165.7 (d, $J_{\text{C-F}} = 25.7$ Hz), 164.9 (d, $J_{\text{C-F}} = 26.2$ Hz), 136.1, 129.1 (d, $J_{\text{C-F}} = 2.1$ Hz), 128.6, 126.2, 119.0, 113.3, 97.0 (d, $J_{\text{C-F}} = 205.1$ Hz), 53.8, 53.1, 45.3 (d, $J_{\text{C-F}} = 18.4$ Hz), 35.7 (d, $J_{\text{C-F}} = 4.7$ Hz); $^{19}\text{F NMR}$ (CDCl_3 , 376 MHz) δ -173.5 (d, $J_{\text{C-F}} = 32.0$ Hz); **IR** (Neat): 2955, 1756, 17116, 1470, 1455, 1435, 1406, 1374, 1318, 1284, 1247, 1148, 1121, 1090, 1074, 1049, 961, 920, 744, 701; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{18}\text{H}_{19}\text{FNO}_5$) $^+$ requires 348.1242; found 348.1245; HPLC analysis Daicel Chiralpak AS-H, flow rate = 1.0 mL/min, $\lambda = 254$ nm, hexane/isopropanol = 80:20; Condition A : (*S*)-**4e**, 92% yield (31.8 mg), 99% ee, $[\alpha]_{\text{D}}^{25} = -45.9$ ($c = 1.0$, CHCl_3), retention time 10.2 min (minor) and 14.5 min (major); Condition B: (*R*)-**4e**, 97% yield (33.8 mg), 97% ee, $[\alpha]_{\text{D}}^{25} = +41.9$ ($c = 1.0$, CHCl_3); retention time 9.9 min (major) and 13.8 min (minor).

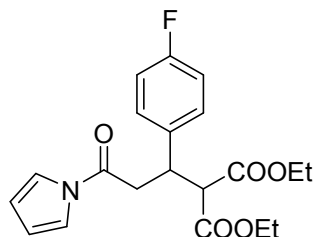
Dimethyl 2-methyl-2-(3-oxo-1-phenyl-3-(1H-pyrrol-1-yl)propyl)malonate (**4f**)



White solid, m.p. 86-87 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.33 (s, 2H), 7.19-7.28 (m, 5H), 6.25 (s, 2H), 4.10 (dd, $J = 9.6, 4.0$ Hz, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 3.47-3.59 (m, 2H), 1.41 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 171.9, 171.6, 168.5, 137.9, 129.1, 128.4, 127.7, 119.1, 112.9, 57.8, 52.7, 52.6, 46.1, 37.3, 19.6; **IR** (Neat): 2952, 1734, 1468, 1454, 1435, 1380, 1322, 1248, 1158, 1104,

1075, 965, 923, 747, 703; **HRMS** (ESI): calcd for $[M+H]^+$ ($C_{19}H_{22}NO_5$)⁺ requires 344.1492; found 344.1492; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 80:20; Condition A : (*S*)-**4f**, 87% yield (29.9 mg), 48% ee, $[\alpha]_D^{25} = -14.9$ ($c = 1.0$, $CHCl_3$), retention time 7.6 min (major) and 11.8 min (minor); Condition B: (*R*)-**4f**, 93% yield (31.8 mg), 98% ee, $[\alpha]_D^{25} = +30.8$ ($c = 1.0$, $CHCl_3$); retention time 7.8 min (minor) and 12.4 min (major).

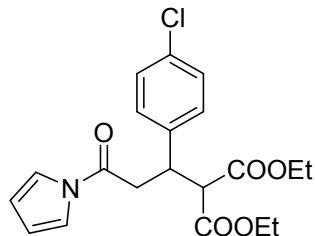
Diethyl 2-(1-(4-fluorophenyl)-3-oxo-3-(1H-pyrrol-1-yl)propyl)malonate (4g)



4g

White solid, m.p. 71-72 °C; **¹H NMR** ($CDCl_3$, 400 MHz) δ 7.23-7.28 (m, 4H), 6.96 (t, $J = 8.8$ Hz, 2H), 6.26 (t, $J = 2.4$ Hz, 2H), 4.17-4.27 (m, 2H), 4.08-4.15 (m, 1H), 3.98 (q, $J = 7.2$ Hz, 2H), 3.79 (d, $J = 9.6$ Hz, 1H), 3.44 (dd, $J = 16.0, 4.0$ Hz, 1H), 3.24 (dd, $J = 16.0, 10.0$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.04 (t, $J = 7.2$ Hz, 3H); **¹³C NMR** ($CDCl_3$, 100 MHz) δ 168.0 (2C), 167.4, 161.9 (d, $J_{C-F} = 244.8$ Hz), 135.2, 129.8 (d, $J_{C-F} = 8.1$ Hz), 119.0, 115.4 (d, $J_{C-F} = 21.3$ Hz), 113.3, 61.9, 61.6, 57.1, 40.4, 38.8, 14.0, 13.8; **¹⁹F NMR** ($CDCl_3$, 376 MHz) δ -114.8; **IR** (Neat): 2983, 2937, 1730, 1605, 1512, 1470, 1406, 1370, 1290, 1228, 1161, 1119, 1101, 1075, 1029, 919, 839, 744; **HRMS** (ESI): calcd for $[M+H]^+$ ($C_{20}H_{23}FNO_5$)⁺ requires 376.1555; found 376.1555; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 80:20; Condition A : (*R*)-**4g**, 94 yield (35.1 mg), 96% ee, $[\alpha]_D^{25} = -18.6$ ($c = 1.0$, $CHCl_3$), retention time 13.0 min (major) and 32.0 min (minor); Condition B: (*S*)-**4g**, 91% yield (34.0 mg), 99% ee, $[\alpha]_D^{25} = +19.7$ ($c = 1.0$, $CHCl_3$); retention time 13.2 min (minor) and 32.7 min (major).

Diethyl 2-(1-(4-chlorophenyl)-3-oxo-3-(1H-pyrrol-1-yl)propyl)malonate (4h)

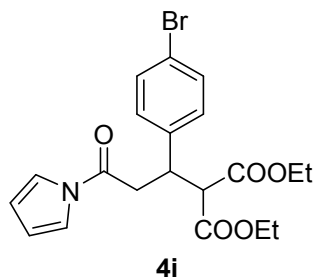


4h

White solid, m.p. 112-113 °C; **¹H NMR** ($CDCl_3$, 400 MHz) δ 7.20-7.28 (m, 6H), 6.26 (t, $J = 2.4$ Hz, 2H), 4.15-4.27 (m, 2H), 4.07-4.13 (m, 1H), 3.99 (q, $J = 7.2$ Hz, 2H), 3.79 (d, $J = 9.6$ Hz, 1H), 3.44 (dd, $J = 16.4, 4.0$ Hz, 1H), 3.25 (dd, $J = 16.4, 10.0$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.05 (t, $J = 7.2$ Hz, 3H); **¹³C NMR** ($CDCl_3$, 100 MHz) δ 168.0, 167.9, 167.3, 138.1, 133.3, 129.6, 128.7,

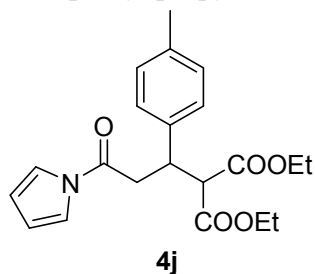
119.0, 113.3, 61.9, 61.7, 56.9, 40.4, 38.5, 14.0, 13.8; **IR** (Neat): 2982, 2936, 1729, 1492, 1469, 1407, 1369, 1286, 1249, 1175, 1120, 1108, 1094, 1075, 1014, 919, 829, 744; **HRMS** (ESI): calcd for $[M+H]^+$ ($C_{20}H_{23}ClNO_5$)⁺ requires 392.1259; found 392.1259; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 70:30; Condition A : (*R*)-**4h**, 96% yield (37.5 mg), 96% ee, $[\alpha]_D^{25} = -15.0$ ($c = 1.0$, $CHCl_3$), retention time 11.1 min (major) and 25.6 min (minor); Condition B: (*S*)-**4h**, 96% yield (37.6 mg), 99% ee, $[\alpha]_D^{25} = +15.7$ ($c = 1.0$, $CHCl_3$); retention time 11.2 min (minor) and 26.1 min (major).

Diethyl 2-(1-(4-bromophenyl)-3-oxo-3-(1H-pyrrol-1-yl)propyl)malonate (4i)



White solid, m.p. 106-107 °C; **¹H NMR** ($CDCl_3$, 400 MHz) δ 7.33 (d, $J = 8.4$ Hz, 2H), 7.21 (s, 2H), 7.09 (d, $J = 8.4$ Hz, 2H), 6.19 (t, $J = 2.0$ Hz, 2H), 4.07-4.20 (m, 2H), 3.99-4.04 (m, 1H), 3.92 (q, $J = 7.2$ Hz, 2H), 3.72 (d, $J = 9.6$ Hz, 1H), 3.37 (dd, $J = 16.4, 4.0$ Hz, 1H), 3.18 (dd, $J = 16.0, 9.6$ Hz, 1H), 1.18 (t, $J = 7.2$ Hz, 3H), 0.99 (t, $J = 7.2$ Hz, 3H); **¹³C NMR** ($CDCl_3$, 100 MHz) δ 167.9 (2C), 167.3, 138.6, 131.7, 129.9, 121.4, 119.0, 113.3, 61.9, 61.7, 56.8, 40.5, 38.4, 14.0, 13.8; **IR** (Neat): 2982, 2934, 1728, 1488, 1469, 1408, 1369, 1285, 1249, 1175, 1119, 1074, 1029, 1010, 919, 824, 744, 716; **HRMS** (ESI): calcd for $[M+H]^+$ ($C_{20}H_{23}BrNO_5$)⁺ requires 436.0754; found 436.0755; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 70:30; Condition A : (*R*)-**4i**, 99% yield (43.1 mg), 96% ee, $[\alpha]_D^{25} = -13.1$ ($c = 1.0$, $CHCl_3$), retention time 11.6 min (major) and 26.3 min (minor); Condition B: (*S*)-**4i**, 99% yield (43.5 mg), 99% ee, $[\alpha]_D^{25} = +13.8$ ($c = 1.0$, $CHCl_3$); retention time 11.7 min (minor) and 26.6 min (major).

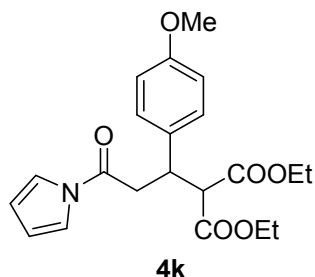
Diethyl 2-(3-oxo-3-(1H-pyrrol-1-yl)-1-(p-tolyl)propyl)malonate (4j)



White solid, m.p. 92-93 °C; **¹H NMR** ($CDCl_3$, 400 MHz) δ 7.29 (s, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.25 (t, $J = 2.0$ Hz, 2H), 4.16-4.27 (m, 2H), 4.05-4.11 (m, 1H), 3.97 (q, $J = 7.2$ Hz, 2H), 3.80 (d, $J = 9.6$ Hz, 1H), 3.43 (dd, $J = 16.0, 4.0$ Hz, 1H), 3.25 (dd, $J = 16.0, 9.6$ Hz, 1H), 2.27 (s, 3H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.04 (t, $J = 7.2$ Hz, 3H); **¹³C NMR** ($CDCl_3$, 100 MHz) δ 168.3, 168.2, 167.5, 137.1, 136.4, 129.2, 127.9, 119.0, 113.1, 61.8, 61.5, 57.3, 40.7, 38.8, 21.1, 14.0,

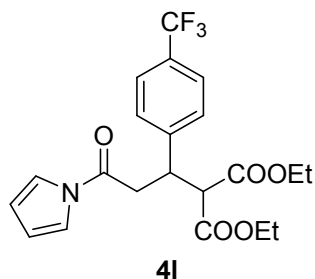
13.8; **IR** (Neat): 2982, 2935, 1730, 1515, 1469, 1405, 1369, 1283, 1249, 1175, 1115, 1074, 1030, 920, 817, 744; **HRMS** (ESI): calcd for $[M+H]^+$ ($C_{21}H_{26}NO_5$)⁺ requires 372.1805; found 372.1806; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 70:30; Condition A : (*R*)-**4j**, 92% yield (34.3 mg), 97% ee, $[\alpha]_D^{25} = -10.8$ ($c = 1.0$, $CHCl_3$), retention time 9.4 min (major) and 18.3 min (minor); Condition B: (*S*)-**4j**, 90% yield (33.3 mg), er 99% ee, $[\alpha]_D^{25} = +11.6$ ($c = 1.0$, $CHCl_3$); retention time 9.5 min (minor) and 18.5 min (major).

Diethyl 2-(1-(4-methoxyphenyl)-3-oxo-3-(1H-pyrrol-1-yl)propyl)malonate (4k)



White solid, m.p. 107-108 °C; **¹H NMR** ($CDCl_3$, 400 MHz) δ 7.29 (t, $J = 2.0$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.4$ Hz, 2H), 6.25 (t, $J = 2.0$ Hz, 2H), 4.15-4.27 (m, 2H), 4.04-4.10 (m, 1H), 3.97 (q, $J = 7.2$ Hz, 2H), 3.79 (d, $J = 9.6$ Hz, 1H), 3.75 (s, 3H), 3.42 (dd, $J = 16.0, 4.0$ Hz, 1H), 3.23 (dd, $J = 16.0, 10.0$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.04 (t, $J = 7.2$ Hz, 3H); **¹³C NMR** ($CDCl_3$, 100 MHz) δ 168.3, 168.2, 167.5, 158.7, 131.3, 129.1, 119.0, 113.9, 113.1, 61.8, 61.5, 57.3, 55.1, 40.4, 39.0, 14.0, 13.8; **IR** (Neat): 2982, 2936, 1729, 1612, 1584, 1514, 1469, 1405, 1369, 1288, 1251, 1179, 1113, 1074, 1032, 919, 862, 833, 744; **HRMS** (ESI): calcd for $[M+H]^+$ ($C_{21}H_{26}NO_6$)⁺ requires 388.1755; found 388.1755; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 60:40; Condition A : (*R*)-**4k**, 90% yield (34.9 mg), 97% ee, $[\alpha]_D^{25} = -12.6$ ($c = 1.0$, $CHCl_3$), retention time 11.1 min (major) and 27.1 min (minor); Condition B: (*S*)-**4k**, 86% yield (33.1 mg), 99% ee, $[\alpha]_D^{25} = +14.0$ ($c = 1.0$, $CHCl_3$); retention time 11.1 min (minor) and 27.2 min (major).

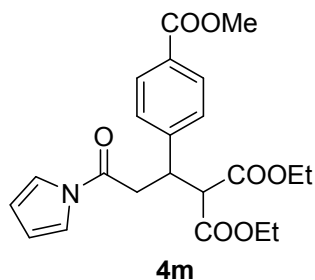
Diethyl 2-(3-oxo-3-(1H-pyrrol-1-yl)-1-(4-(trifluoromethyl)phenyl)propyl)malonate (4l)



White solid, m.p. 118-119 °C; **¹H NMR** ($CDCl_3$, 400 MHz) δ 7.47 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.20 (s, 2H), 6.19 (t, $J = 2.0$ Hz, 2H), 4.08-4.20 (m, 3H), 3.91 (q, $J = 7.2$ Hz, 2H), 3.77 (d, $J = 9.6$ Hz, 1H), 3.41 (dd, $J = 16.8, 4.0$ Hz, 1H), 3.25 (dd, $J = 16.0, 9.6$ Hz, 1H), 1.17 (t, $J = 7.2$ Hz, 3H), 0.95 (t, $J = 7.2$ Hz, 3H); **¹³C NMR** ($CDCl_3$, 100 MHz) δ 167.8, 167.7, 167.2, 143.8, 129.7 (q, $J_{C-F} = 32.4$ Hz), 128.6, 125.5 (q, $J_{C-F} = 3.7$ Hz), 123.9 (q, $J_{C-F} = 270.7$ Hz), 118.9, 113.4, 62.0,

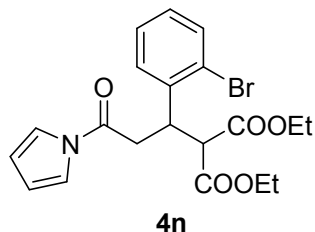
61.7, 56.7, 40.7, 38.2, 13.9, 13.7; **¹⁹F NMR** (CDCl₃, 376 MHz) δ -62.7; **IR** (Neat): 2984, 2940, 1730, 1619, 1470, 1422, 1407, 1370, 1326, 1282, 1250, 1166, 1114, 1070, 1018, 919, 845, 744; **HRMS** (ESI): calcd for [M+H]⁺ (C₂₁H₂₃F₃NO₅)⁺ requires 426.1523; found 426.1523; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 70:30; Condition A : (*R*)-**4l**, 99% yield (41.9 mg), 96% ee, [α]_D²⁵ = -18.0 (*c* = 1.0, CHCl₃), retention time 9.1 min (major) and 17.8 min (minor); Condition B: (*S*)-**4l**, 99% yield (41.8 mg), 98% ee, [α]_D²⁵ = +18.9 (*c* = 1.0, CHCl₃); retention time 9.0 min (minor) and 17.6 min (major).

Diethyl 2-(1-(4-(methoxycarbonyl)phenyl)-3-oxo-3-(1H-pyrrol-1-yl)propyl)malonate (4m)



White solid, m.p. 132-133 °C; **¹H NMR** (CDCl₃, 400 MHz) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 2H), 6.26 (t, *J* = 2.4 Hz, 2H), 4.13-4.27 (m, 3H), 3.97 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 3.84 (d, *J* = 9.6 Hz, 1H), 3.48 (dd, *J* = 16.4, 4.0 Hz, 1H), 3.31 (dd, *J* = 16.4, 9.6 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); **¹³C NMR** (CDCl₃, 100 MHz) δ 167.9, 167.8, 167.2, 166.7, 144.9, 129.8, 129.3, 128.3, 119.0, 113.3, 62.0, 61.7, 56.7, 52.1, 40.9, 38.3, 14.0, 13.8; **IR** (Neat): 2983, 1724, 1611, 1470, 1436, 1406, 1369, 1281, 1177, 1115, 1075, 1020, 920, 858, 775, 745, 707; **HRMS** (ESI): calcd for [M+H]⁺ (C₂₂H₂₆NO₇)⁺ requires 416.1704; found 416.1704; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 50:50; Condition A : (*R*)-**4m**, 99% yield (41.1 mg), 96% ee, [α]_D²⁵ = -15.2 (*c* = 1.0, CHCl₃), retention time 21.3 min (major) and 35.8 min (minor); Condition B: (*S*)-**4m**, 87% yield (36.3 mg), 98% ee, [α]_D²⁵ = +18.0 (*c* = 1.0, CHCl₃); retention time 22.6 min (minor) and 35.0 min (major).

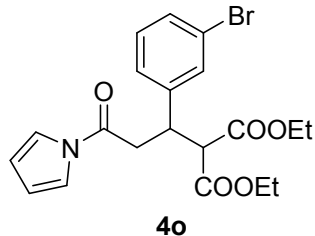
Diethyl 2-(1-(2-bromophenyl)-3-oxo-3-(1H-pyrrol-1-yl)propyl)malonate (4n)



Colorless oil; **¹H NMR** (CDCl₃, 400 MHz) δ 7.55 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.21-7.32 (m, 4H), 7.06-7.10 (m, 1H), 6.26 (t, *J* = 2.4 Hz, 2H), 4.59-4.64 (m, 1H), 4.03-4.24 (m, 5H), 3.43-3.55 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); **¹³C NMR** (CDCl₃, 100 MHz) δ 168.1 (2C), 167.5, 138.5, 133.5, 128.9, 127.6, 124.8, 119.1, 113.2, 61.8, 61.7, 55.0, 39.8, 36.7, 13.9, 13.8.; **IR** (Neat): 2982, 1730, 1470, 1442, 1405, 1369, 1341, 1283, 1247, 1176, 1116, 1095, 1074, 1026, 923, 744; **HRMS** (ESI): calcd for [M+H]⁺ (C₂₀H₂₃BrNO₅)⁺ requires 436.0754; found 436.0753; HPLC

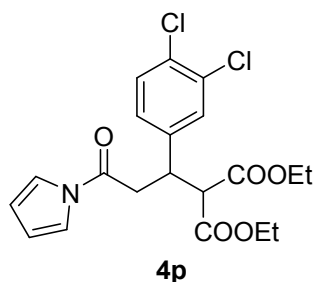
analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 70:30; Condition A : (*R*)-**4n**, 95% yield (41.5 mg), 73% ee, $[\alpha]_{\text{D}}^{25} = -23.8$ ($c = 1.0$, CHCl_3), retention time 7.2 min (major) and 16.7 min (minor); Condition B: (*S*)-**4n**, 95% yield (41.5 mg), 96% ee, $[\alpha]_{\text{D}}^{25} = +29.7$ ($c = 1.0$, CHCl_3); retention time 7.4 min (minor) and 17.2 min (major).

Diethyl 2-(1-(3-bromophenyl)-3-oxo-3-(1H-pyrrol-1-yl)propyl)malonate (4o)



Light yellow oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.43 (s, 1H), 7.34-7.36 (m, 1H), 7.22-7.29 (m, 3H), 7.15 (t, $J = 8.0$ Hz, 1H), 6.27 (t, $J = 2.0$ Hz, 2H), 4.14-4.26 (m, 2H), 4.07-4.12 (m, 1H), 4.00 (q, $J = 7.2$ Hz, 2H), 3.80 (d, $J = 9.6$ Hz, 1H), 3.45 (dd, $J = 16.4, 4.0$ Hz, 1H), 3.27 (dd, $J = 16.4, 9.6$ Hz, 1H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.06 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 167.9, 167.8, 167.3, 142.0, 131.2, 130.6, 130.1, 127.0, 122.5, 119.0, 113.3, 61.9, 61.7, 56.8, 40.5, 38.3, 14.0, 13.8; **IR** (Neat): 2982, 2937, 1728, 1568, 1470, 1430, 1406, 1369, 1283, 1249, 1176, 1120, 1097, 1075, 1029, 998, 920, 787, 744; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{20}\text{H}_{23}\text{BrNO}_5$)⁺ requires 436.0754; found 436.0753; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 70:30; Condition A : (*R*)-**4o**, 95% yield (41.3 mg), 95% ee, $[\alpha]_{\text{D}}^{25} = -19.9$ ($c = 1.0$, CHCl_3), retention time 8.7 min (major) and 10.5 min (minor); Condition B: (*S*)-**4o**, 98% yield (42.6 mg), 97% ee, $[\alpha]_{\text{D}}^{25} = +20.8$ ($c = 1.0$, CHCl_3); retention time 8.8 min (minor) and 10.6 min (major).

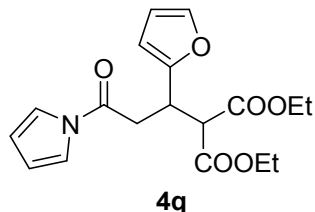
Diethyl 2-(1-(3,4-dichlorophenyl)-3-oxo-3-(1H-pyrrol-1-yl)propyl)malonate (4p)



White solid, m.p. 63-64 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.39 (d, $J = 2.0$ Hz, 1H), 7.35 (d, $J = 8.4$ Hz, 1H), 7.28 (s, 2H), 7.16 (dd, $J = 8.4, 2.0$ Hz, 1H), 6.28 (t, $J = 2.0$ Hz, 2H), 4.15-4.27 (m, 2H), 4.01-4.12 (m, 3H), 3.78 (d, $J = 9.6$ Hz, 1H), 3.45 (dd, $J = 16.8, 4.0$ Hz, 1H), 3.27 (dd, $J = 16.8, 9.6$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.09 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 167.8, 167.7, 167.2, 140.0, 132.5, 131.6, 130.5, 130.2, 127.8, 118.9, 113.4, 62.0, 61.8, 56.6, 40.0, 38.1, 14.0, 13.8; **IR** (Neat): 2982, 2937, 1729, 1470, 1407, 1369, 1285, 1176, 1154, 1119, 1074, 1030, 919, 743; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{NO}_5$)⁺ requires 426.0870; found 426.0870; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol

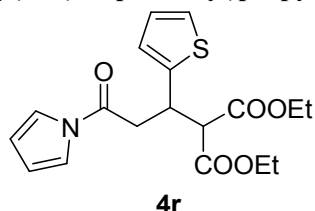
= 70:30; Condition A : (*R*)-**4p**, 96% yield (41.0 mg), 96% ee, $[\alpha]_{\text{D}}^{25} = -20.5$ ($c = 1.0$, CHCl_3), retention time 9.1 min (major) and 14.0 min (minor); Condition B: (*S*)-**4p**, 92% yield (39.4 mg), 95% ee, $[\alpha]_{\text{D}}^{25} = +21.1$ ($c = 1.0$, CHCl_3); retention time 9.1 min (minor) and 14.0 min (major)

Diethyl 2-(1-(furan-2-yl)-3-oxo-3-(1H-pyrrol-1-yl)propyl)malonate (**4q**)



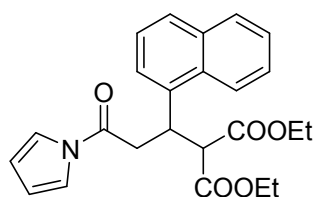
Colorless oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.30-7.32 (m, 3H), 6.25-6.28 (m, 3H), 6.16 (d, $J = 3.2$ Hz, 1H), 4.16-4.29 (m, 3H), 4.11 (q, $J = 7.2$ Hz, 2H), 3.91 (d, $J = 8.0$ Hz, 1H), 3.39 (d, $J = 6.8$ Hz, 2H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.17 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 168.1, 167.8, 167.5, 152.6, 141.9, 119.0, 113.2, 110.3, 107.4, 61.8, 61.7, 54.8, 36.0, 34.6, 14.0, 13.9; **IR** (Neat): 2982, 2935, 1731, 1470, 1406, 1369, 1283, 1259, 1175, 1119, 1097, 1075, 1015, 920, 803, 743; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{18}\text{H}_{22}\text{NO}_6$)⁺ requires 348.1442; found 348.1443; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, $\lambda = 254$ nm, hexane/isopropanol = 70:30; Condition A : (*R*)-**4q**, 95% yield (33.1 mg), 93% ee, $[\alpha]_{\text{D}}^{25} = -13.2$ ($c = 1.0$, CHCl_3), retention time 7.3 min (major) and 8.3 min (minor); Condition B: (*S*)-**4q**, 88% yield (30.5 mg), 98% ee, $[\alpha]_{\text{D}}^{25} = +13.8$ ($c = 1.0$, CHCl_3); retention time 7.3 min (minor) and 8.8 min (major).

Diethyl 2-(3-oxo-3-(1H-pyrrol-1-yl)-1-(thiophen-2-yl)propyl)malonate (**4r**)



Light yellow solid, m.p. 80-81 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.31 (s, 2H), 7.15 (d, $J = 4.8$ Hz, 1H), 6.87-6.94 (m, 2H), 6.27 (s, 2H), 4.44-4.50 (m, 1H), 4.14-4.27 (m, 2H), 4.07 (q, $J = 7.2$ Hz, 2H), 3.89 (d, $J = 8.0$ Hz, 1H), 3.48 (dd, $J = 16.4, 4.4$ Hz, 1H), 3.38 (dd, $J = 16.4, 8.8$ Hz, 1H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.13 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 167.9 (2C), 167.4, 142.6, 126.7, 126.0, 124.5, 119.0, 113.2, 61.8, 61.7, 57.4, 39.3, 36.3, 14.0, 13.8; **IR** (Neat): 2980, 2933, 1729, 1469, 1405, 1368, 1339, 1278, 1175, 1116, 1074, 1029, 920, 852, 746; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{18}\text{H}_{22}\text{NO}_5\text{S}$)⁺ requires 364.1213; found 364.1212; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, $\lambda = 254$ nm, hexane/isopropanol = 70:30; Condition A : (*R*)-**4r**, 91% yield (33.0 mg), 95% ee, $[\alpha]_{\text{D}}^{25} = -27.9$ ($c = 1.0$, CHCl_3), retention time 9.2 min (major) and 13.7 min (minor); Condition B: (*S*)-**4r**, 94% yield (34.2 mg), 99% ee, $[\alpha]_{\text{D}}^{25} = +28.2$ ($c = 1.0$, CHCl_3); retention time 9.2min (minor) and 13.7 min (major).

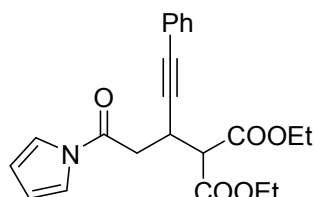
Diethyl 2-(1-(naphthalen-1-yl)-3-oxo-3-(1H-pyrrol-1-yl)propyl)malonate (**4s**)



4s

Colorless oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.23 (d, $J = 8.4$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.53-7.57 (m, 1H), 7.37-7.49 (m, 3H), 7.25-7.27 (m, 2H), 6.23 (s, 2H), 5.04-5.15 (m, 1H), 4.10-4.24 (m, 2H), 4.05 (d, $J = 8.4$ Hz, 2H), 3.86-3.91 (m, 2H), 3.51-3.65 (m, 2H), 1.19 (t, $J = 7.2$ Hz, 3H), 0.88 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 168.4, 168.3, 167.6, 136.1, 134.0, 131.4, 128.9, 128.0, 126.5, 125.7, 125.1, 122.9, 119.0, 113.1, 110.0, 61.8, 61.6, 56.6, 38.3, 34.6, 13.9, 13.6. **IR** (Neat): 2981, 2936, 1728, 1597, 1512, 1469, 1405, 1368, 1340, 1283, 1176, 1119, 1096, 1073, 1030, 924, 861, 798, 778, 744; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{24}\text{H}_{26}\text{NO}_5$) $^+$ requires 408.1805; found 408.1805; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, $\lambda = 254$ nm, hexane/isopropanol = 70:30; Condition A : (*R*)-**4s**, 95% yield (38.8 mg), 95% ee, $[\alpha]_{\text{D}}^{25} = -48.2$ ($c = 1.0$, CHCl_3), retention time 10.2 min (major) and 15.9 min (minor); Condition B: (*S*)-**4s**, 99% yield (40.2 mg), 97% ee, $[\alpha]_{\text{D}}^{25} = +49.3$ ($c = 1.0$, CHCl_3); retention time 10.2min (minor) and 15.8 min (major).

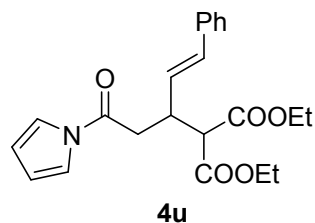
Diethyl 2-(5-oxo-1-phenyl-5-(1H-pyrrol-1-yl)pent-1-yn-3-yl)malonate (4t)



4t

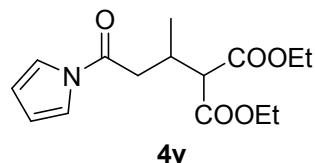
White solid, m.p. 80-81 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.24-7.38 (m, 7H), 6.31 (s, 2H), 4.22-4.29 (m, 4H), 4.00-4.07 (m, 1H), 3.84 (d, $J = 7.2$ Hz, 1H), 3.26-3.40 (m, 2H), 1.25-1.30 (m, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 167.8, 167.4, 167.2, 131.7, 128.1, 122.6, 119.2, 113.4, 110.0, 87.0, 84.0, 61.9, 54.9, 37.4, 28.3, 14.1; **IR** (Neat): 2982, 2937, 1732, 1490, 1470, 1444, 1407, 1369, 1342, 1284, 1255, 1175, 1121, 1096, 1072, 1029, 921, 757, 744; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{22}\text{H}_{24}\text{NO}_5$) $^+$ requires 382.1649; found 382.1649; HPLC analysis Daicel Chiralpak AS-H + PC-II, flow rate = 1.0 mL/min, $\lambda = 254$ nm, hexane/isopropanol = 90:10; Condition A : (*R*)-**4t**, 90% yield (34.4 mg), 92% ee, $[\alpha]_{\text{D}}^{25} = +0.3$ ($c = 1.0$, CHCl_3), retention time 19.9 min (minor) and 21.6 min (major); Condition B: (*S*)-**4t**, 95% yield (36.2 mg), 91% ee, $[\alpha]_{\text{D}}^{25} = -0.3$ ($c = 1.0$, CHCl_3); retention time 20.4 min (major) and 22.3 min (minor).

Diethyl (E)-2-(5-oxo-1-phenyl-5-(1H-pyrrol-1-yl)pent-1-en-3-yl)malonate (4u)



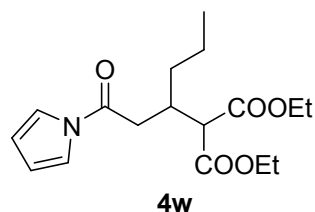
White solid, m.p. 126-127 °C; **¹H NMR** (CDCl₃, 400 MHz) δ 7.12-7.28 (m, 7H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.13-6.22 (m, 3H), 4.02-4.20 (m, 4H), 3.67 (d, *J* = 7.6 Hz, 1H), 3.53-3.60 (m, 1H), 3.20 (dd, *J* = 16.0, 4.4 Hz, 1H), 3.04 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); **¹³C NMR** (CDCl₃, 100 MHz) δ 168.4, 168.1, 168.0, 136.5, 133.3, 128.5, 127.7, 127.4, 126.4, 119.1, 113.3, 61.7, 61.6, 55.4, 39.2, 37.5, 14.0; **IR** (Neat): 2982, 1729, 1469, 1448, 1405, 1369, 1291, 1175, 1124, 1073, 1030, 968, 922, 744; **HRMS** (ESI): calcd for [M+H]⁺ (C₂₂H₂₆NO₅)⁺ requires 384.1805; found 384.1806; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 70:30; Condition A : (*S*)-**4u**, 86% yield (33.1 mg), 96% ee, [α]_D²⁵ = +3.3 (*c* = 1.0, CHCl₃), retention time 8.9 min (major) and 10.8 min (minor); Condition B: (*R*)-**4u**, 80% yield (30.7 mg), 99% ee, [α]_D²⁵ = -3.5 (*c* = 1.0, CHCl₃); retention time 8.9 min (minor) and 10.8 min (major).

Diethyl 2-(4-oxo-4-(1H-pyrrol-1-yl)butan-2-yl)malonate (**4v**)



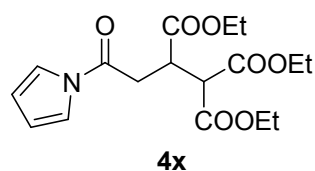
Colorless oil; **¹H NMR** (CDCl₃, 400 MHz) δ 7.30 (s, 2H), 6.22 (s, 2H), 4.09-4.18 (m, 4H), 3.41 (d, *J* = 6.8 Hz, 1H), 3.11 (dd, *J* = 16.0, 4.4 Hz, 1H), 2.81-2.91 (m, 1H), 2.70 (dd, *J* = 15.6, 8.8 Hz, 1H), 1.18-1.22 (m, 6H), 1.07 (d, *J* = 6.8 Hz, 3H); **¹³C NMR** (CDCl₃, 100 MHz) δ 169.1, 168.4 (2C), 119.1, 113.1, 61.5, 56.2, 38.7, 29.9, 17.6, 14.0; **IR** (Neat): 2980, 2934, 1731, 1470, 1371, 1302, 1262, 1177, 1095, 1071, 1031, 931, 864, 801, 744; **HRMS** (ESI): calcd for [M+H]⁺ (C₁₅H₂₂NO₅)⁺ requires 296.1492; found 296.1494; HPLC analysis Daicel Chiralpak IG, flow rate = 0.7 mL/min, λ = 214 nm, hexane/isopropanol = 90:10; Condition A : (*R*)-**4v**, 94% yield (27.8 mg), 82% ee, [α]_D²⁵ = -0.23 (*c* = 1.0, CHCl₃), retention time 17.9 min (minor) and 18.9 min (major); Condition B: (*S*)-**4v**, 95% yield (28.1 mg), 94% ee, [α]_D²⁵ = +1.3 (*c* = 1.0, CHCl₃); retention time 17.8 min (major) and 19.0 min (minor).

Diethyl 2-(1-oxo-1-(1H-pyrrol-1-yl)hexan-3-yl)malonate (**4w**)



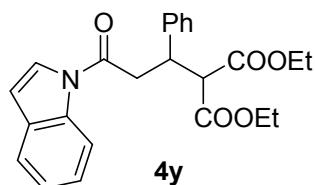
Colorless oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.37 (s, 2H), 6.29 (s, 2H), 4.16-4.23 (m, 4H), 3.66 (d, $J = 4.8$ Hz, 1H), 3.20 (dd, $J = 16.4, 4.4$ Hz, 1H), 2.80-2.94 (m, 2H), 1.33-1.53 (m, 4H), 1.23-1.29 (m, 6H), 0.91 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 169.5, 168.8, 168.6, 119.1, 113.1, 61.5, 61.3, 53.7, 36.2, 34.2, 34.1, 20.1, 14.0, 14.0, 13.9; **IR** (Neat): 2960, 2929, 2873, 1731, 1469, 1405, 1369, 1261, 1157, 1099, 1072, 1030, 924, 802, 743; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{17}\text{H}_{26}\text{NO}_5$) $^+$ requires 324.1805; found 324.1806; HPLC analysis Daicel Chiralpak IG, flow rate = 0.7 mL/min, $\lambda = 214$ nm, hexane/isopropanol = 90:10; Condition A : (*R*)-**4w**, 91% yield (29.5 mg), 78% ee, $[\alpha]_{\text{D}}^{25} = -1.4$ ($c = 1.0$, CHCl_3), retention time 14.9 min (minor) and 16.2 min (major); Condition B: (*S*)-**4w**, 93% yield (30.2 mg), 96% ee, $[\alpha]_{\text{D}}^{25} = +1.4$ ($c = 1.0$, CHCl_3); retention time 14.8 min (major) and 16.2 min (minor).

Triethyl 4-oxo-4-(1H-pyrrol-1-yl)butane-1,1,2-tricarboxylate (**4x**)



Colorless oil; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.32 (s, 2H), 6.30 (t, $J = 2.0$ Hz, 2H), 4.13-4.25 (m, 6H), 4.04 (d, $J = 6.0$ Hz, 1H), 3.77-3.82 (m, 1H), 3.48 (dd, $J = 17.2, 7.2$ Hz, 1H), 3.23 (dd, $J = 17.2, 4.8$ Hz, 1H), 1.20-1.29 (m, 9H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 171.4, 168.4, 167.8, 119.0, 113.3, 61.9 (2C), 61.6, 52.0, 39.8, 33.4, 13.9 (3C); **IR** (Neat): 2982, 2930, 2872, 1732, 1470, 1408, 1369, 1290, 1176, 1123, 1075, 922, 909, 859, 743; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{17}\text{H}_{24}\text{NO}_7$) $^+$ requires 354.1547; found 354.1547; HPLC analysis Daicel Chiralpak PC-II, flow rate = 1.0 mL/min, $\lambda = 254$ nm, hexane/isopropanol = 70:30; Condition A : (*R*)-**4x**, 95% yield (33.7 mg), 73% ee, $[\alpha]_{\text{D}}^{25} = -3.9$ ($c = 1.0$, CHCl_3), retention time 13.4 min (major) and 18.1 min (minor); Condition B: (*S*)-**4x**, 99% yield (34.8 mg), 92% ee, $[\alpha]_{\text{D}}^{25} = +5.8$ ($c = 1.0$, CHCl_3); retention time 13.3 min (minor) and 17.8 min (major).

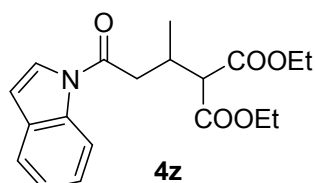
Diethyl 2-(3-(1H-indol-1-yl)-3-oxo-1-phenylpropyl)malonate (**4y**)



White solid, m.p. 82-83 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.35 (d, $J = 8.0$ Hz, 1H), 7.52-7.58 (m, 2H), 7.18-7.30 (m, 7H), 6.62 (d, $J = 3.6$ Hz, 1H), 4.14-4.27 (m, 3H), 3.97 (q, $J = 7.2$ Hz, 2H), 3.87 (d, $J = 9.6$ Hz, 1H), 3.56 (dd, $J = 15.6, 4.4$ Hz, 1H), 3.34 (dd, $J = 15.6, 9.6$ Hz, 1H), 1.23 (t, $J = 6.8$ Hz, 3H), 1.01 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 169.0, 168.3, 167.6, 139.6, 135.5, 130.3, 128.6, 128.1, 127.5, 125.0, 124.7, 123.6, 120.7, 116.6, 109.3, 61.9, 61.5, 57.2, 41.3, 40.0, 14.0, 13.8; **IR** (Neat): 2981, 2935, 1730, 1537, 1472, 1452, 1389, 1343, 1308, 1252, 1227, 1207, 1175, 1152, 1109, 1084, 1029, 751, 700; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{24}\text{H}_{26}\text{NO}_5$) $^+$ requires

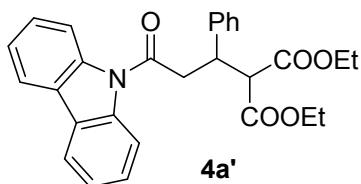
408.1805; found 408.1806; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 70:30; Condition A : (*R*)-**4y**, 97% yield (39.4 mg), 95% ee, $[\alpha]_{\text{D}}^{25}$ = +14.8 (c = 1.0, CHCl₃), retention time 15.1 min (major) and 31.3 min (minor); Condition B: (*S*)-**4y**, 89% yield (36.1 mg), 99% ee, $[\alpha]_{\text{D}}^{25}$ = -15.5 (c = 1.0, CHCl₃); retention time 15.2 min (minor) and 31.4 min (major).

Diethyl 2-(4-(1H-indol-1-yl)-4-oxobutan-2-yl)malonate (4z)



Colorless oil; **¹H NMR** (CDCl₃, 400 MHz) δ 8.40 (d, J = 8.4 Hz, 1H), 7.48-7.55 (m, 2H), 7.18-7.29 (m, 2H), 6.57 (d, J = 3.6 Hz, 1H), 4.12-4.17 (m, 4H), 3.45 (d, J = 6.4 Hz, 1H), 3.22 (dd, J = 15.6, 4.0 Hz, 1H), 2.86-2.94 (m, 1H), 2.75 (dd, J = 15.6, 8.8 Hz, 1H), 1.17-1.22 (m, 6H), 1.11 (d, J = 6.8 Hz, 3H); **¹³C NMR** (CDCl₃, 100 MHz) δ 170.0, 168.6, 168.5, 135.6, 130.4, 125.1, 124.9, 123.7, 120.8, 116.6, 109.2, 61.5, 56.3, 40.1, 30.0, 17.7, 14.1; **IR** (Neat): 2979, 2930, 2855, 1731, 1605, 1586, 1537, 1452, 1369, 1309, 1261, 1207, 1155, 1094, 1031, 802, 752; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ (C₁₉H₂₄NO₅)⁺ requires 346.1649; found 346.1649; HPLC analysis Daicel Chiralpak IG, flow rate = 0.7 mL/min, λ = 214 nm, hexane/isopropanol = 90:10; Condition A : (*R*)-**4z**, 95% yield (32.7 mg), 74% ee, $[\alpha]_{\text{D}}^{25}$ = -18.6 (c = 1.0, CHCl₃), retention time 24.0 min (minor) and 26.7 min (major); Condition B: (*S*)-**4z**, 90% yield (31.1 mg), 95% ee, $[\alpha]_{\text{D}}^{25}$ = +28.7 (c = 1.0, CHCl₃); retention time 23.7 min (major) and 27.0 min (minor).

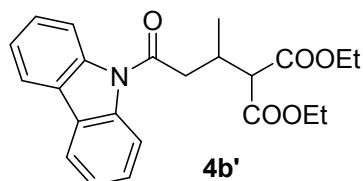
Diethyl 2-(3-(9H-carbazol-9-yl)-3-oxo-1-phenylpropyl)malonate (4a')



White solid, m.p. 91-92 °C; **¹H NMR** (CDCl₃, 400 MHz) δ 8.16 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.33-7.36 (m, 4H), 7.23-7.27 (m, 2H), 7.16-7.19 (m, 1H), 4.33-4.40 (m, 1H), 4.13-4.25 (m, 2H), 4.01 (q, J = 7.2 Hz, 2H), 3.95 (d, J = 8.8 Hz, 1H), 3.69-3.81 (m, 2H), 1.21 (t, J = 6.8 Hz, 3H), 1.06 (t, J = 7.2 Hz, 3H); **¹³C NMR** (CDCl₃, 100 MHz) δ 170.8, 168.4, 167.8, 140.5, 138.4, 128.5, 128.2, 127.3, 127.3, 126.3, 123.6, 119.8, 116.4, 61.7, 61.5, 57.3, 42.7, 40.7, 14.0, 13.8; **IR** (Neat): 3062, 3031, 1981, 2936, 1731, 1697, 1599, 1491, 1478, 1426, 1446, 1370, 1324, 1278, 1239, 1209, 1157, 1103, 1032, 980, 861, 755, 723, 700; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ (C₂₈H₂₈NO₅)⁺ requires 458.1962; found 458.1962; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, λ = 254 nm, hexane/isopropanol = 70:30; Condition A : (*R*)- **4a'**, 95% yield (43.3 mg), 96% ee, $[\alpha]_{\text{D}}^{25}$ = -30.8 (c = 1.0, CHCl₃), retention time 11.9 min (major) and 28.2 min (minor); Condition B: (*S*)- **4a'**, 90% yield (41.1 mg), 98% ee, $[\alpha]_{\text{D}}^{25}$ = -30.9

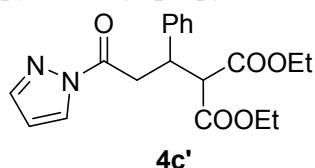
($c = 1.0$, CHCl_3); retention time 11.7 min (minor) and 27.7 min (major).

Diethyl 2-(4-(9H-carbazol-9-yl)-4-oxobutan-2-yl)malonate (**4b'**)



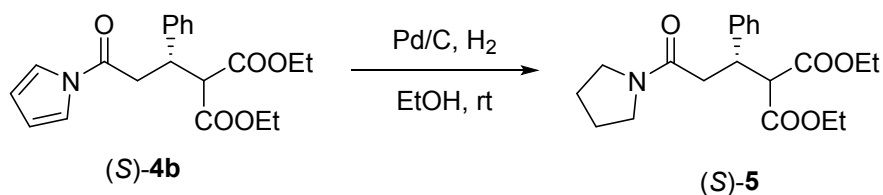
Colorless oil; **¹H NMR** (CDCl_3 , 400 MHz) δ 8.24 (d, $J = 8.4$ Hz, 2H), 7.98 (d, $J = 7.6$ Hz, 2H), 7.47 (t, $J = 8.0$ Hz, 2H), 7.37 (t, $J = 7.6$ Hz, 2H), 4.17-4.26 (m, 4H), 3.67 (d, $J = 5.6$ Hz, 1H), 3.43-3.50 (m, 1H), 3.15-3.23 (m, 2H), 1.22-1.30 (m, 9H); **¹³C NMR** (CDCl_3 , 100 MHz) δ 171.7, 168.8, 168.6, 138.4, 127.4, 126.4, 123.6, 119.8, 116.5, 61.4 (2C), 61.4, 56.0, 43.0, 29.7, 18.1, 14.1 (2C); **IR** (Neat): 2980, 2937, 1730, 1696, 1478, 1490, 1445, 1425, 1372, 1326, 1281, 1239, 1208, 1159, 1096, 1061, 1034, 755, 723; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{23}\text{H}_{26}\text{NO}_5$)⁺ requires 396.1805; found 396.1806; HPLC analysis Daicel Chiralpak IC, flow rate = 1.0 mL/min, $\lambda = 254$ nm, hexane/isopropanol = 80:20; Condition A : (*R*)-**4b'**, 94% yield (37.1 mg), 78% ee, $[\alpha]_{\text{D}}^{25} = +2.5$ ($c = 1.0$, CHCl_3), retention time 14.4 min (major) and 17.6 min (minor); Condition B: (*S*)-**4b'**, 95% yield (37.4 mg), 96% ee, $[\alpha]_{\text{D}}^{25} = -2.9$ ($c = 1.0$, CHCl_3); retention time 14.5 min (minor) and 17.7 min (major).

Diethyl 2-(3-oxo-1-phenyl-3-(1H-pyrazol-1-yl)propyl)malonate (**4c'**)



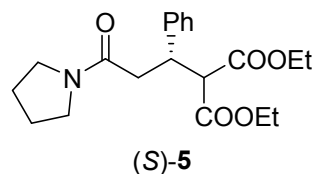
White solid, m.p. 98-99 °C; **¹H NMR** (CDCl_3 , 400 MHz) δ 8.12 (d, $J = 2.4$ Hz, 1H), 7.66 (s, 1H), 7.30-7.32 (m, 2H), 7.25 (t, $J = 7.6$ Hz, 2H), 7.16-7.20 (m, 1H), 6.37 (dd, $J = 2.8, 1.6$ Hz, 1H), 4.15-4.26 (m, 3H), 3.93 (q, $J = 7.2$ Hz, 2H), 3.74-3.84 (m, 2H), 3.59 (dd, $J = 17.2, 4.4$ Hz, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 0.98 (t, $J = 7.2$ Hz, 3H); **¹³C NMR** (CDCl_3 , 100 MHz) δ 169.6, 168.0, 167.5, 143.8, 139.9, 128.4, 128.3, 128.2, 127.3, 109.5, 61.7, 61.3, 57.4, 40.6, 38.3, 14.0, 13.7; **IR** (Neat): 3232, 2983, 2929, 1733, 1496, 1455, 1393, 1370, 1252, 1152, 1096, 1030, 860, 766, 701; **HRMS** (ESI): calcd for $[\text{M}+\text{H}]^+$ ($\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_5$)⁺ requires 359.1601; found 359.1600; HPLC analysis Daicel Chiralpak AD-H, flow rate = 1.0 mL/min, $\lambda = 254$ nm, hexane/isopropanol = 70:30; Condition A : (*R*)-**4c'**, 49% yield (17.5 mg), 92% ee, $[\alpha]_{\text{D}}^{25} = -46.0$ ($c = 1.0$, CHCl_3), retention time 10.9 min (major) and 14.6 min (minor); Condition B: (*S*)-**4c'**, 72% yield (25.7 mg), 83% ee, $[\alpha]_{\text{D}}^{25} = +42.8$ ($c = 1.0$, CHCl_3); retention time 11.1 min (minor) and 14.8 min (major).

Synthesis of compound (S)-5.



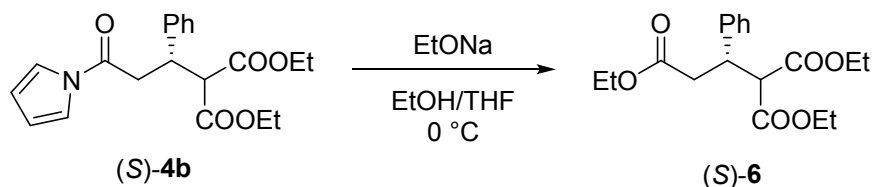
To solution of **(S)-4b** (0.15 mmol) in EtOH (4 mL) was added Pd/C (5 mg, 10%). Then reaction mixture was stirred under H₂ atmosphere (1 atm) at room temperature for 21 h. After completion of reaction, the Pd/C catalyst was removed by filtration. The filtrate was evaporated to remove the solvent and the crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether as eluent) to afford pure product **(S)-5**.

Diethyl (S)-2-(3-oxo-1-phenyl-3-(pyrrolidin-1-yl)propyl)malonate ((S)-5)



99% yield; white solid, m.p. 64-65 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.23-7.30 (m, 4H), 7.16-7.20 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.99-4.05 (m, 1H), 3.91-3.96 (m, 3H), 3.16-3.38 (m, 4H), 2.69-2.80 (m, 2H), 1.66-1.78 (m, 4H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 168.9, 168.3, 167.9, 140.7, 128.2, 128.2, 127.0, 61.5, 61.1, 56.8, 46.5, 45.5, 41.4, 38.7, 25.9, 24.2, 14.0, 13.7; IR (Neat): 2976, 2873, 1732, 1636, 1436, 1394, 1368, 1314, 1258, 1152, 1096, 1036, 764, 750, 702; HRMS (ESI): calcd for [M+H]⁺(C₂₀H₂₈NO₅)⁺ requires 362.1962; found 362.1963; 99% ee determined by HPLC (AD-H, hexane/*i*-PrOH 70/30, flow rate 1.0 mL/min; *t*_{major} = 9.6 min, *t*_{minor} = 8.1 min, λ = 220 nm); [α]_D²⁵ = +18.2 (*c* = 1.0, CHCl₃).

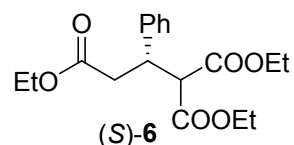
Synthesis of compound (S)-6.



To solution of **(S)-4b** (0.15 mmol) in mixed solvent of EtOH (2 mL) and THF (0.5 mmol) at 0 °C was added EtONa (0.23 mmol). The reaction mixture was stirred at same temperature for 2h. Then the reaction was quenched with saturated NH₄Cl aqueous solution (10 mL). And the mixture was

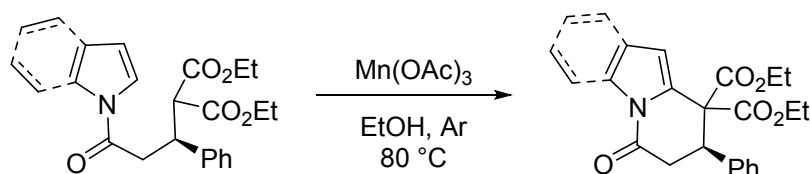
extracted with AcOEt (15 mL×3). The combined organic layers were washed with brine and dried with Na₂SO₄. After evaporating solvent in vacuo, the residue was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether as eluent) to afford product (*S*)-6.

Triethyl (*S*)-2-phenylpropane-1,1,3-tricarboxylate ((*S*)-6)



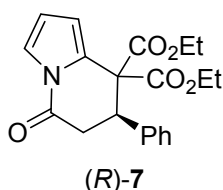
97% yield; colorless oil; ¹H NMR (CDCl₃, 400 MHz) δ 7.18-7.29 (m, 5H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.89-4.02 (m, 5H), 3.73 (d, *J* = 10.4 Hz, 1H), 2.85 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.72 (dd, *J* = 15.6, 10.0 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 171.0, 168.0, 167.5, 139.8, 128.3, 128.2, 127.2, 61.6, 61.3, 60.4, 57.3, 41.5, 38.7, 14.0, 14.0, 13.7; IR (Neat): 2982, 2937, 1725, 1454, 1369, 1254, 1150, 1096, 1031, 765, 701; HRMS (ESI): calcd for [M+H]⁺ (C₂₀H₂₈NO₅)⁺ requires 337.1646; found 337.1645; 99% ee determined by HPLC (AD-H, hexane/*i*-PrOH 80/20, flow rate 1.0 mL/min; *t*_{major} = 11.1 min, *t*_{minor} = 7.1 min, λ = 220 nm); [α]_D²⁵ = +15.7 (*c* = 1.0, CHCl₃).

Synthesis of compound (*R*)-7 and (*R*)-8^[10].



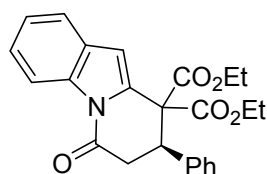
(*R*)-4d' (or (*R*)-4y, 0.15 mmol) and Mn(AcO)₃·2H₂O (0.45 mmol) were added into EtOH (2.0 mL) under Ar. Then the reaction mixture was stirred at 80 °C until the TLC analysis showed complete consumption of starting material. The solvent was evaporated in vacuo. The residue was dissolved in water (10 mL), and the mixture was extracted with EtOAc (15 mL×3). The organic layers were combined and washed with brine, then dried with Na₂SO₄. The solvent was removed in vacuo. The residue was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether as eluent) to yield product (*R*)-7 (or (*R*)-8).

Diethyl (*R*)-5-oxo-7-phenyl-6,7-dihydroindolizine-8,8(5*H*)-dicarboxylate((*R*)-7)



81% yield, colorless oil; **¹H NMR** (CDCl₃, 400 MHz) 7.52 (dd, *J* = 3.2, 1.6 Hz, 1H), 7.15-7.20 (m, 3H), 6.88-6.91 (m, 2H), 6.65 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.39 (t, *J* = 3.2 Hz, 1H), 4.11-4.28 (m, 3H), 3.87-4.02 (m, 2H), 3.65 (dd, *J* = 17.6, 6.0 Hz, 1H), 2.95 (dd, *J* = 17.6, 3.6 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H); **¹³C NMR** (CDCl₃, 100 MHz) δ 168.4, 167.2, 166.2, 139.1, 128.7, 127.9, 127.8, 126.2, 117.5, 116.5, 113.5, 62.4, 61.8, 57.6, 44.9, 37.7, 13.8, 13.6; **IR** (Neat): 2983, 1731, 1406, 1367, 1313, 1236, 1198, 1156, 1042, 700; **HRMS** (ESI): calcd for [M+H]⁺ (C₂₀H₂₂NO₅)⁺ requires 356.1492; found 356.1492; >99% ee determined by HPLC (AD-H, hexane/*i*-PrOH 95/5, flow rate 1.0 mL/min; *t*_{major} = 8.4 min, *t*_{minor} = 11.0 min, λ = 254 nm); [α]_D²⁵ = +52.7 (*c* = 1.0, CHCl₃).

Diethyl (*R*)-6-oxo-8-phenyl-7,8-dihydropyrido[1,2-*a*]indole-9,9(6*H*)-dicarboxylate ((*R*)-8)



(*R*)-8

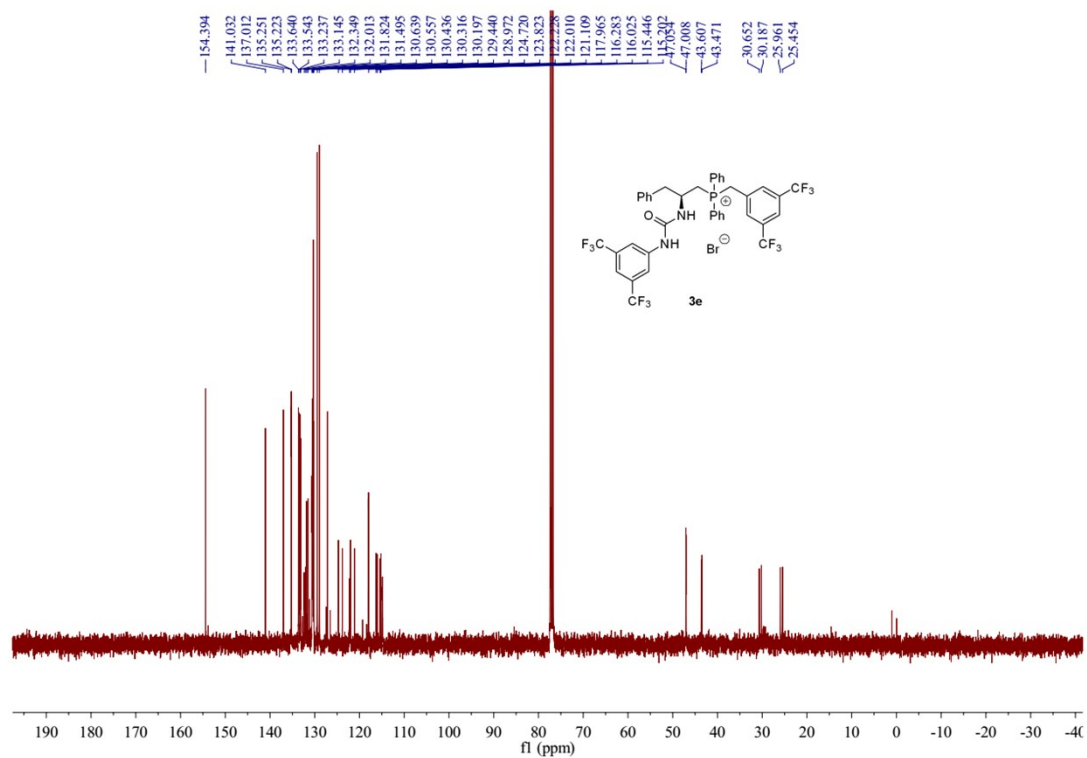
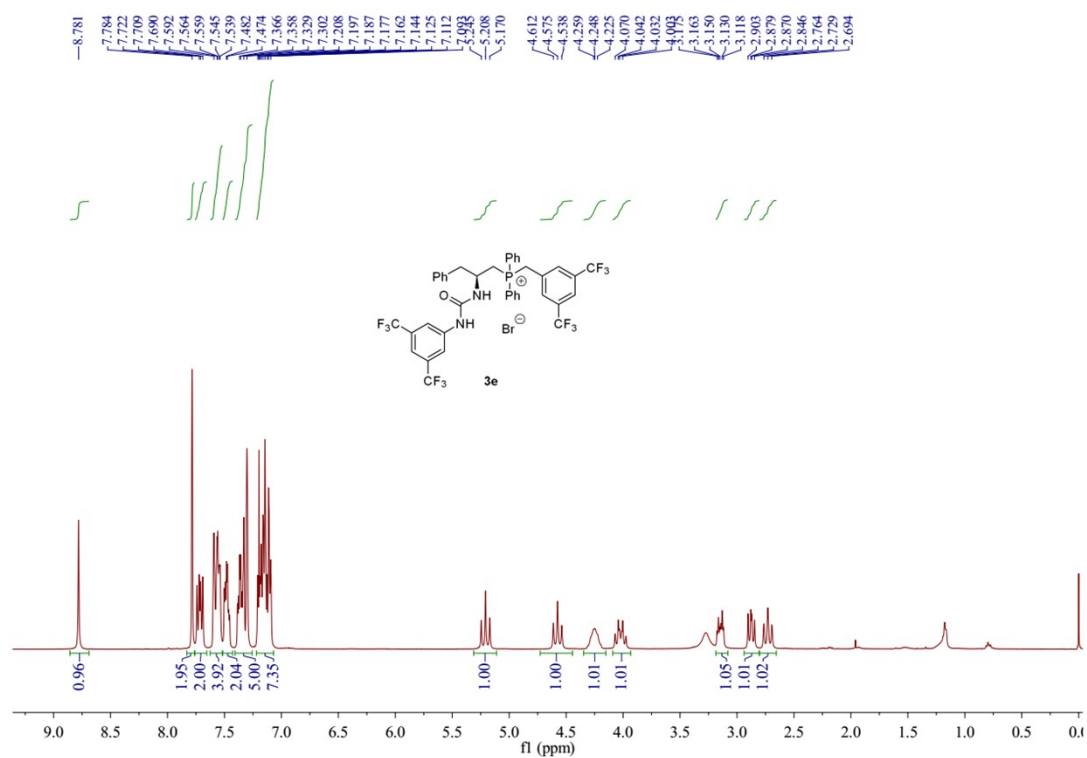
78% yield, colorless oil; **¹H NMR** (CDCl₃, 400 MHz) δ 8.55 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.37-7.41 (m, 1H), 7.31-7.35 (m, 1H), 7.14-7.22 (m, 3H), 7.05 (s, 1H), 6.94-6.98 (m, 2H), 4.24-4.32 (m, 2H), 4.11-4.19 (m, 1H), 3.93-4.06 (m, 2H), 3.74 (dd, *J* = 17.6, 6.0 Hz, 1H), 3.03 (dd, *J* = 17.6, 4.0 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); **¹³C NMR** (CDCl₃, 100 MHz) δ 168.8, 168.0, 167.6, 139.7, 135.6, 132.1, 130.2, 129.4, 128.6, 128.5, 126.2, 125.0, 121.6, 117.5, 113.4, 63.4, 62.7, 58.9, 45.2, 39.1, 14.5, 14.3; **IR** (Neat): 2937, 1737, 1712, 1453, 1371, 1349, 1321, 1236, 1204, 1160, 1096, 1070, 1012, 861, 753, 700; **HRMS** (ESI): calcd for [M+H]⁺ (C₂₄H₂₄NO₅)⁺ requires 406.1649; found 406.1649; 98% ee determined by HPLC (AD-H, hexane/*i*-PrOH 85/15, flow rate 1.0 mL/min; *t*_{major} = 24.5 min, *t*_{minor} = 13.7 min, λ = 254 nm); [α]_D²⁵ = +22.1 (*c* = 1.0, CHCl₃).

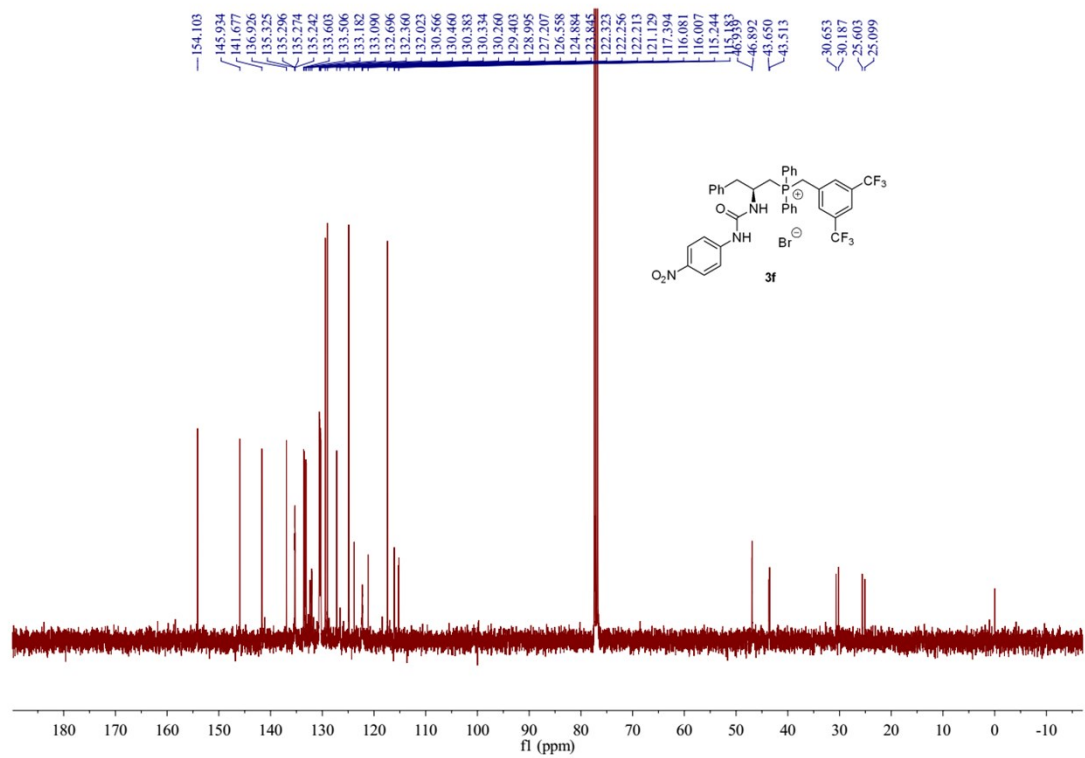
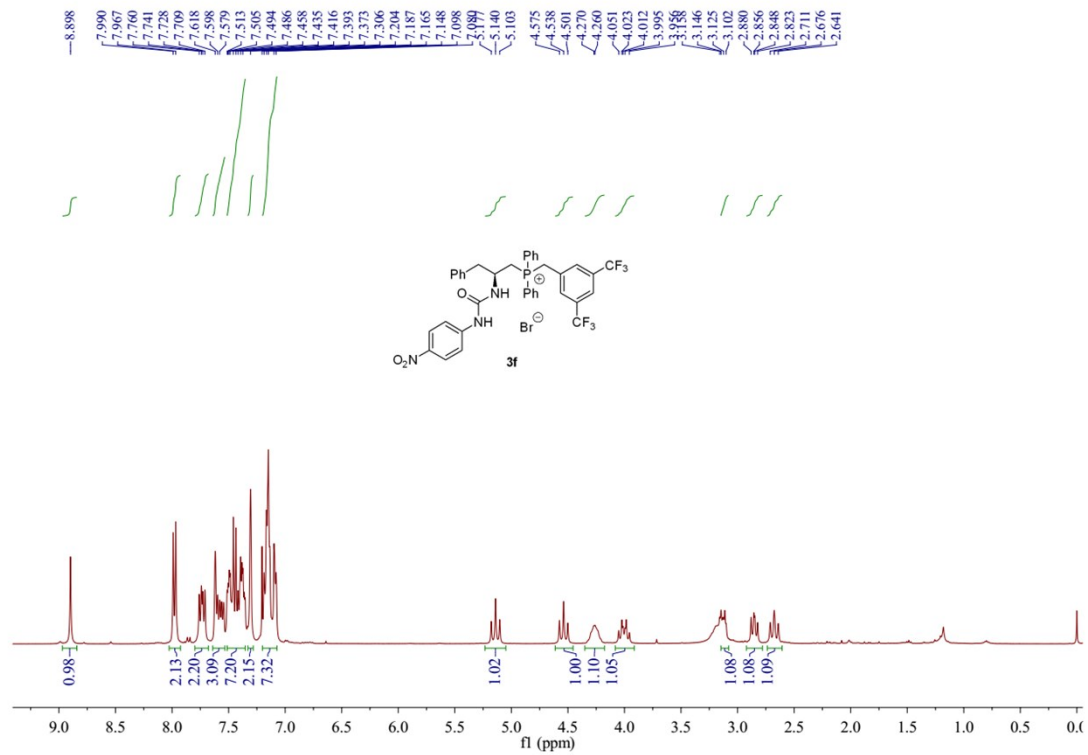
References

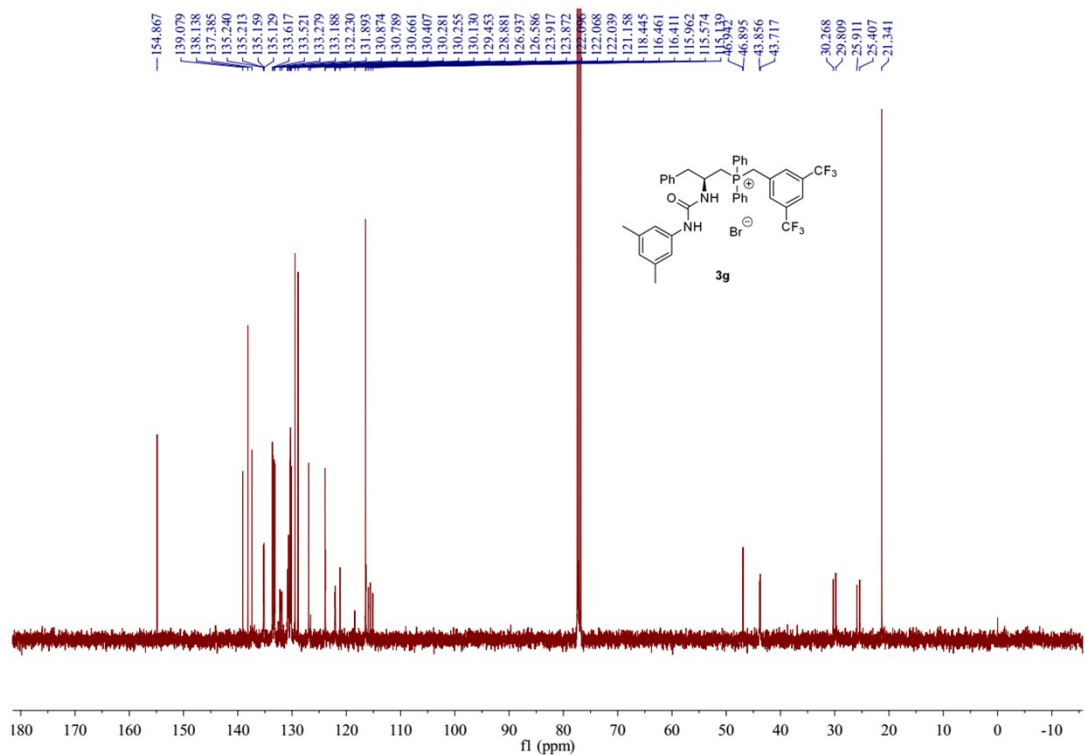
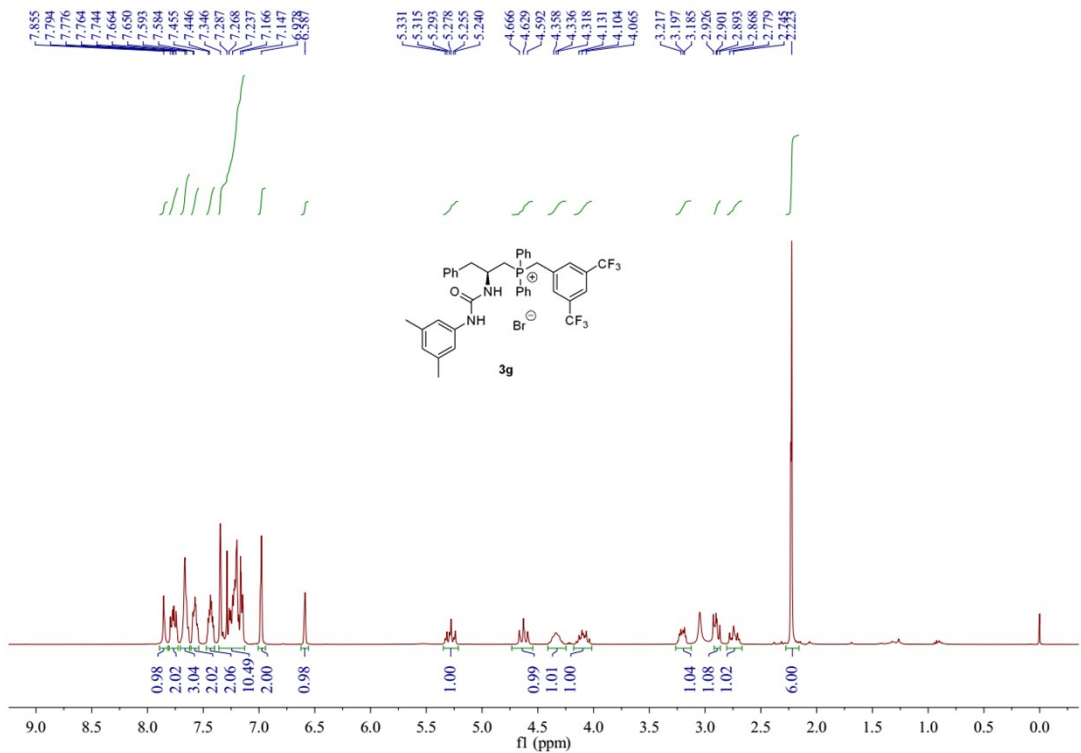
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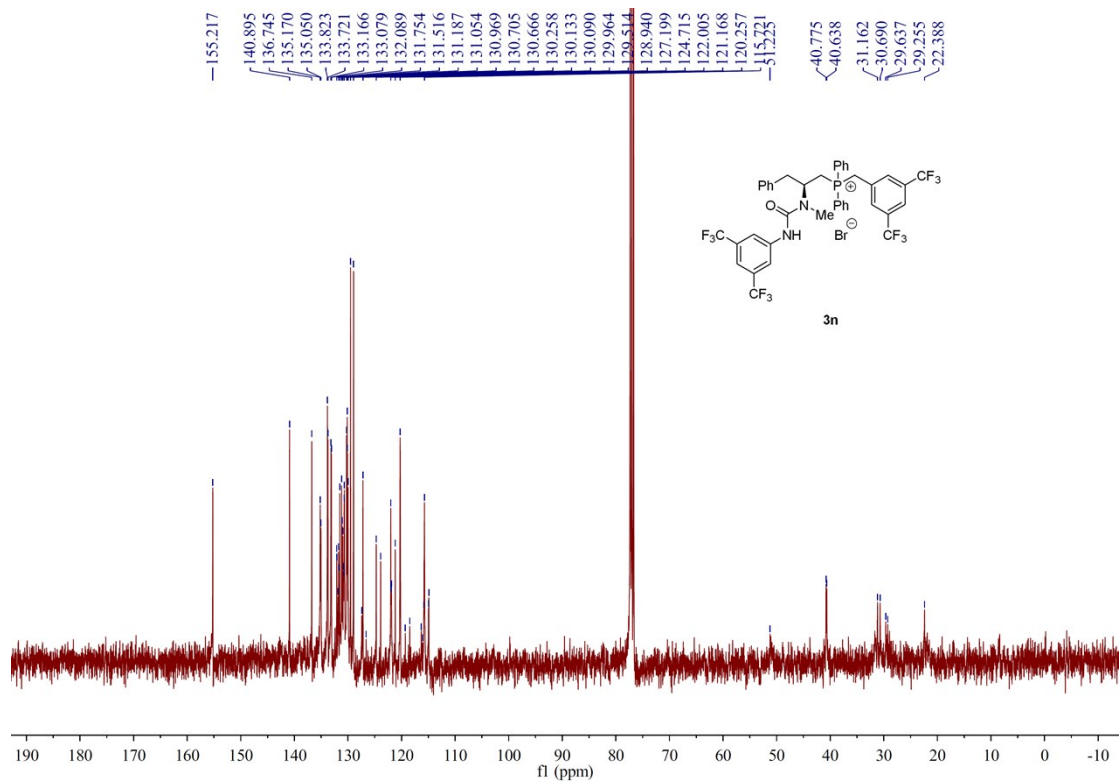
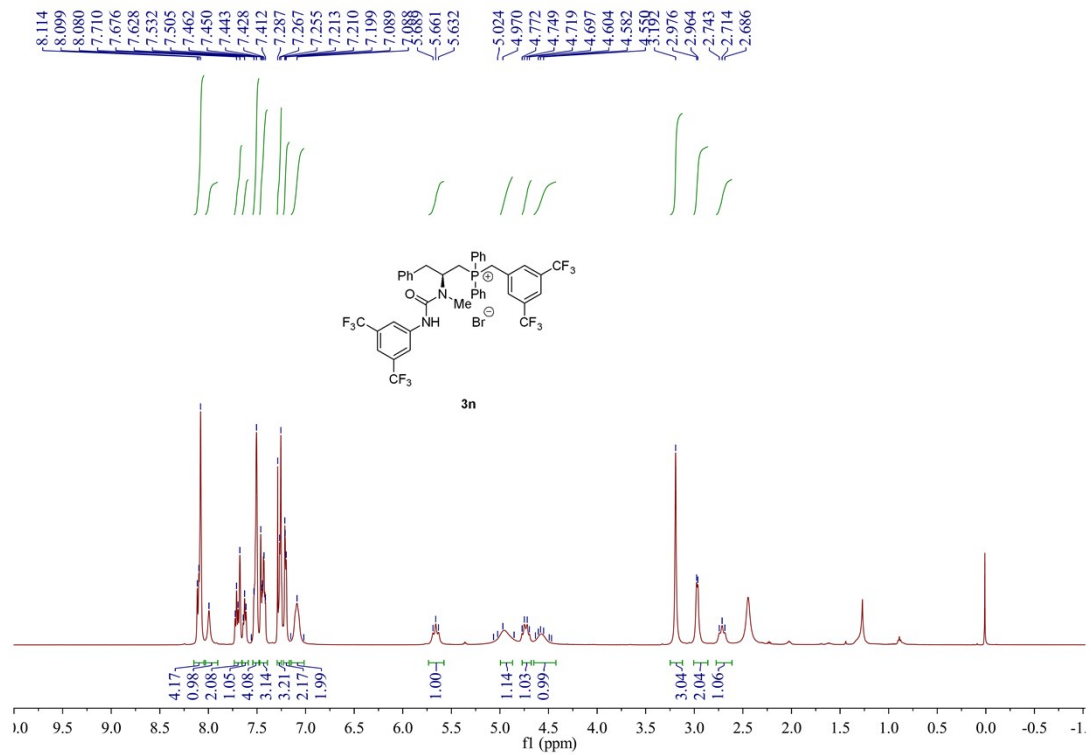
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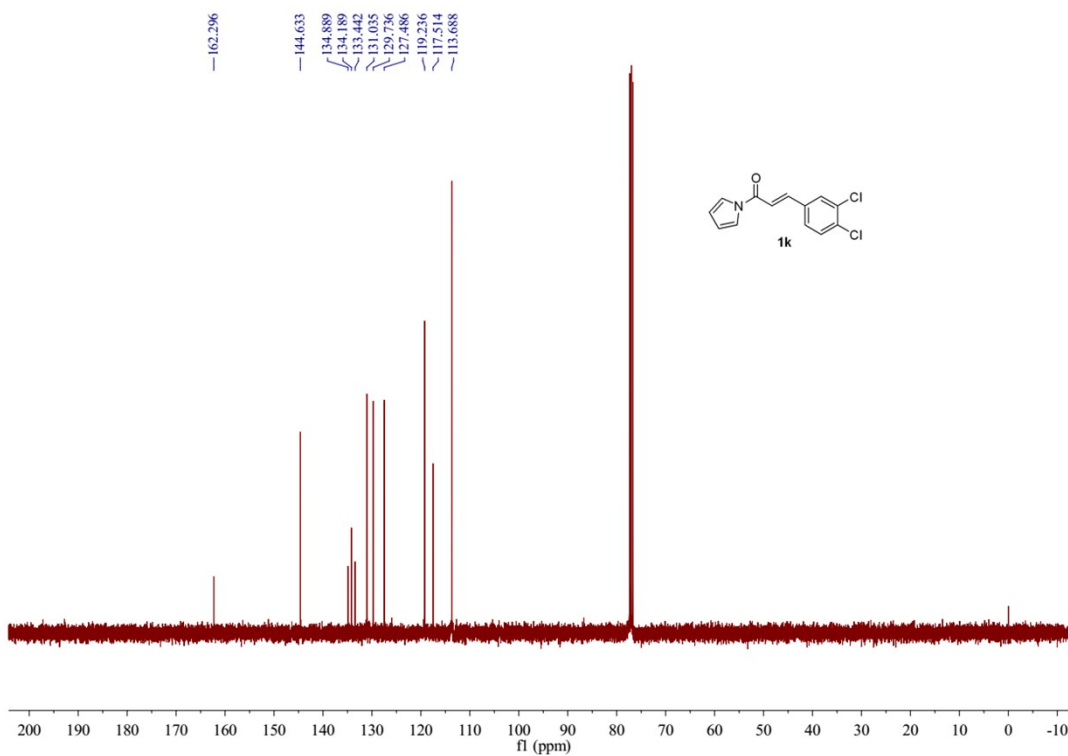
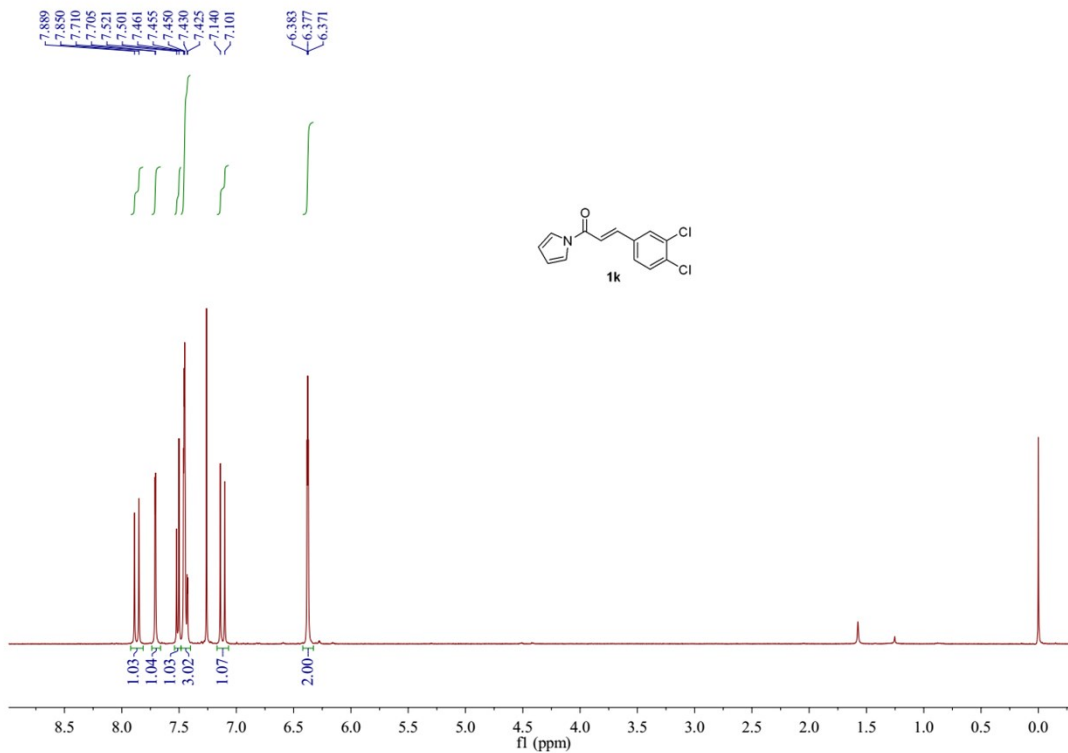
Copies of NMR spectra and HPLC traces

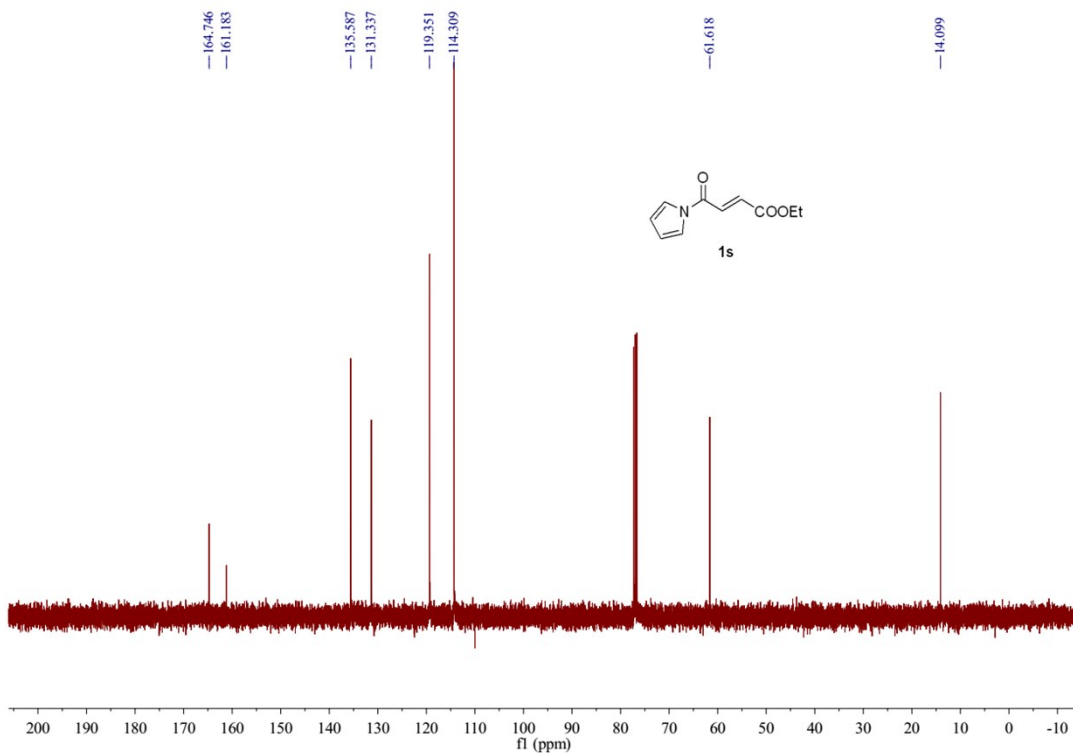
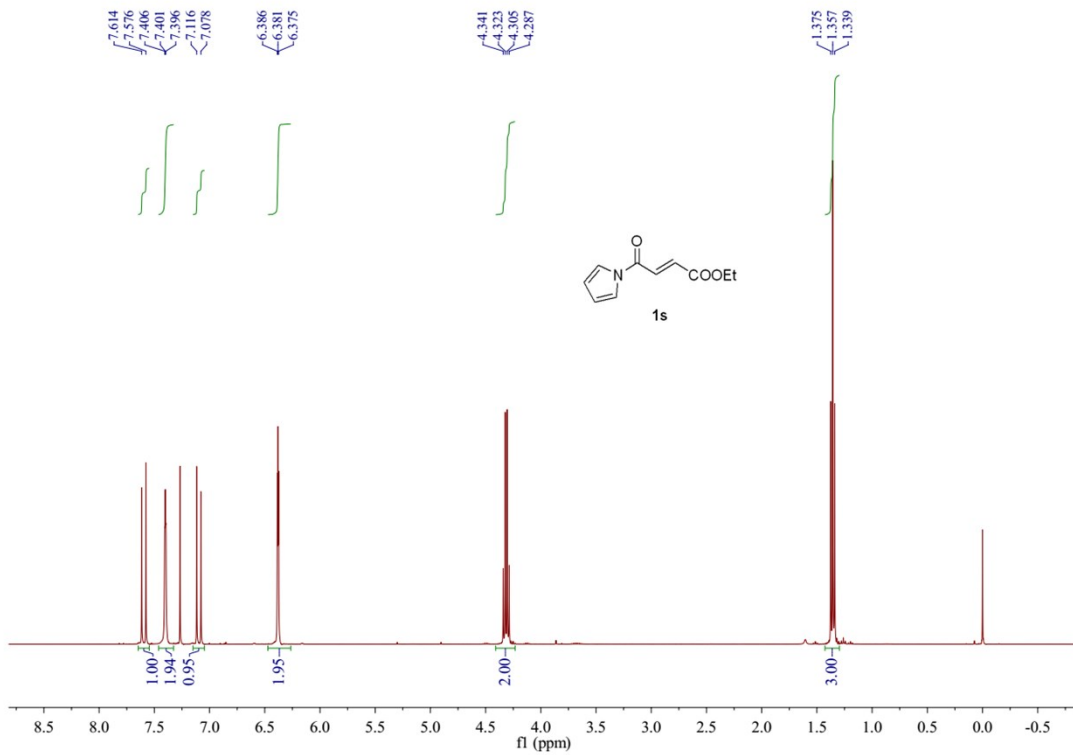


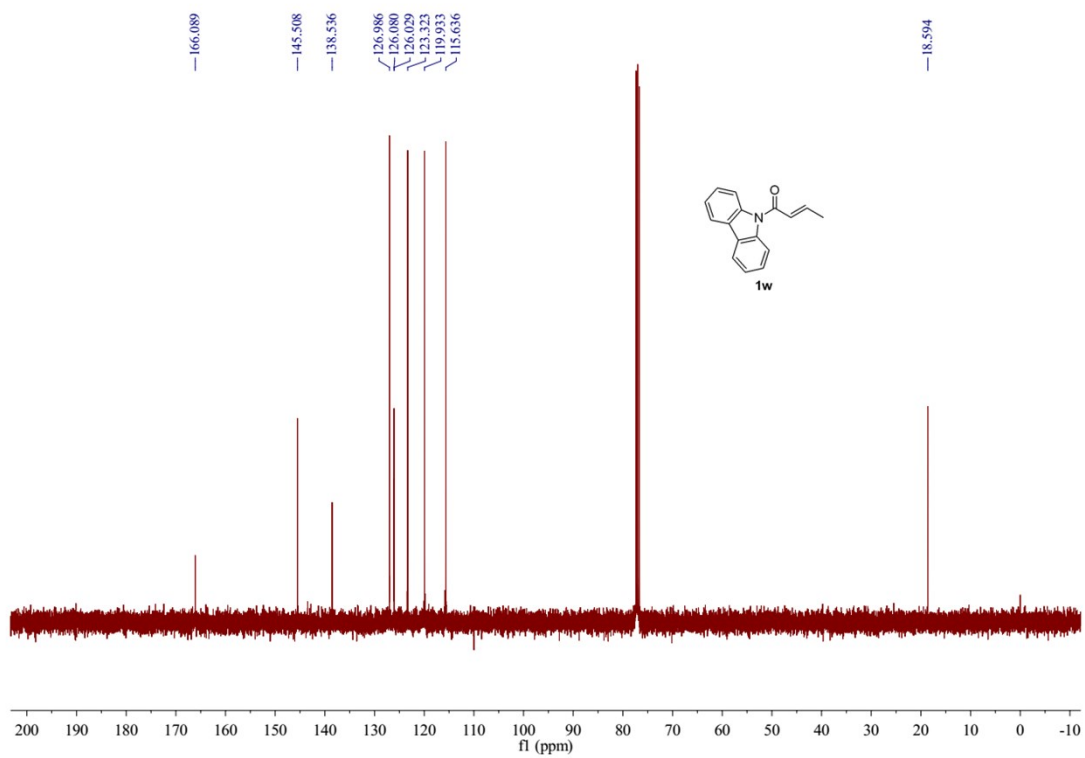
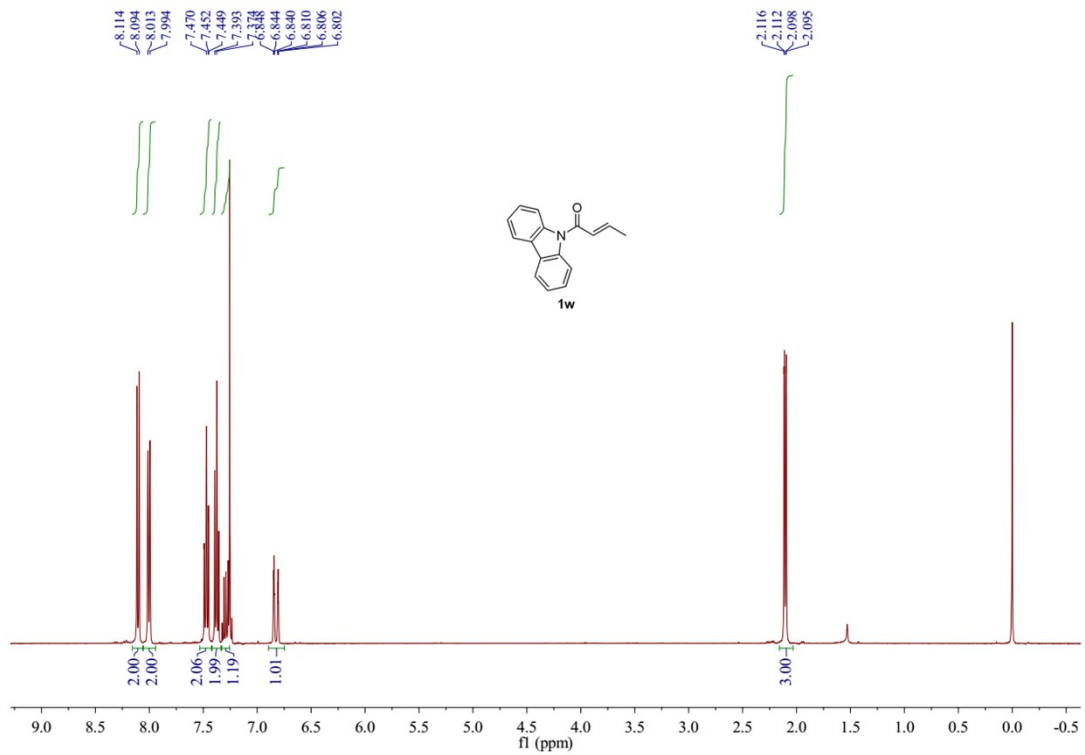


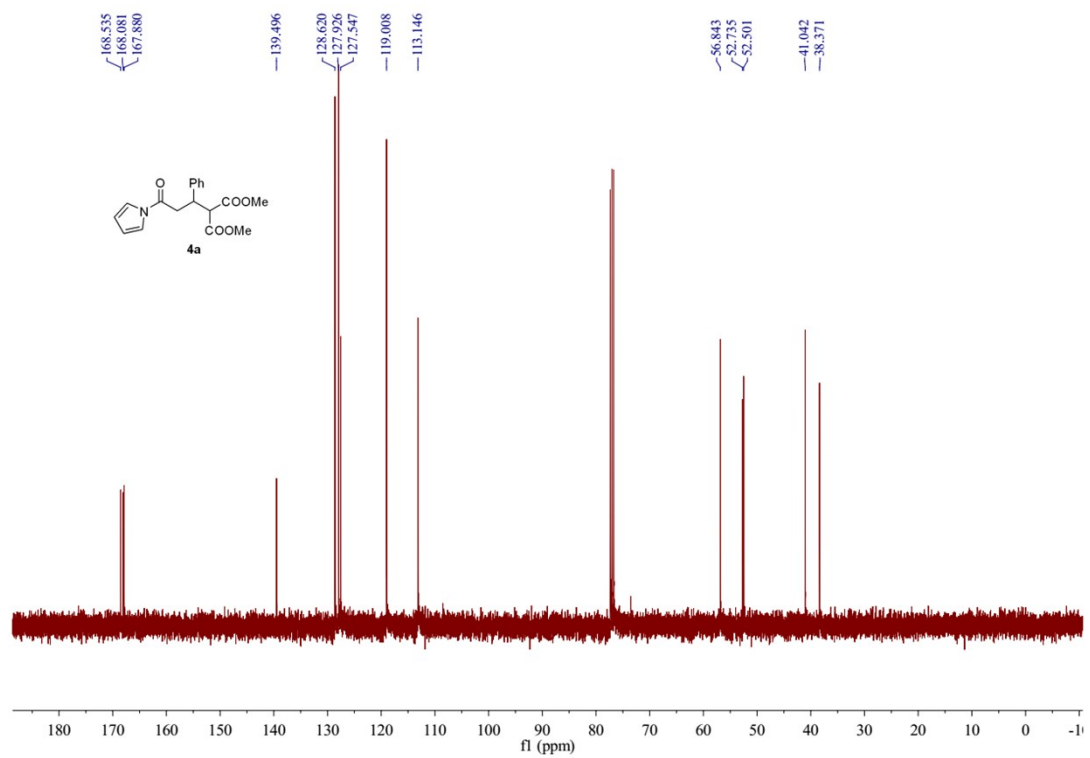
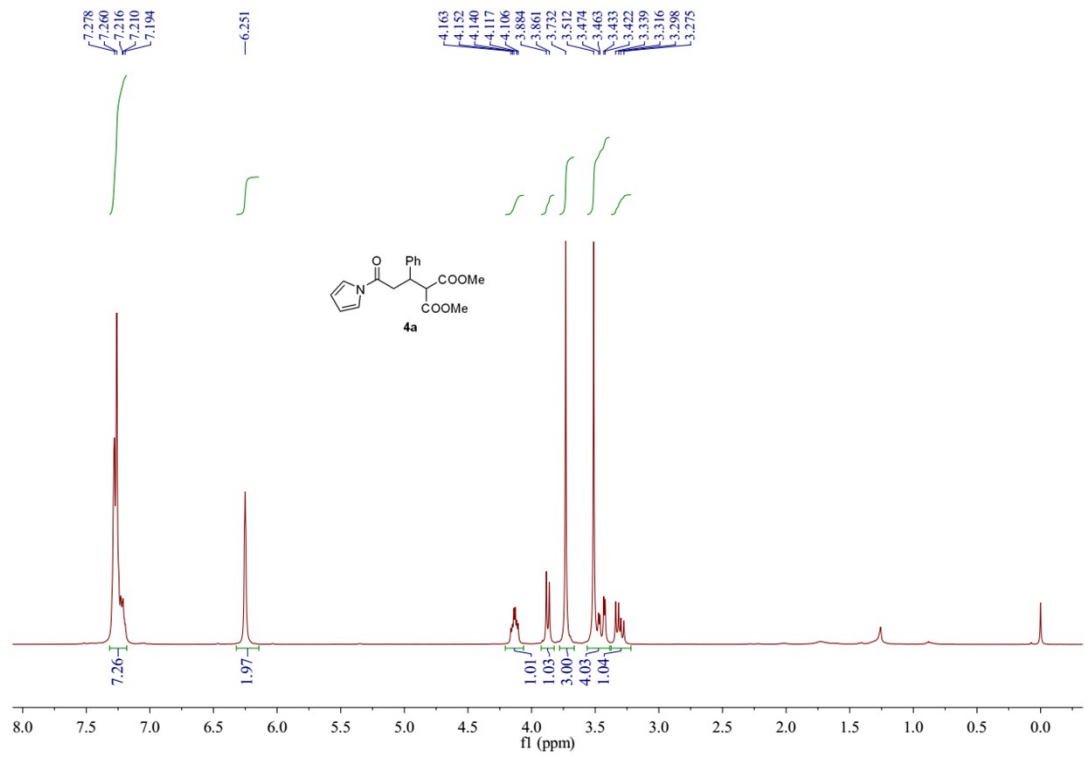


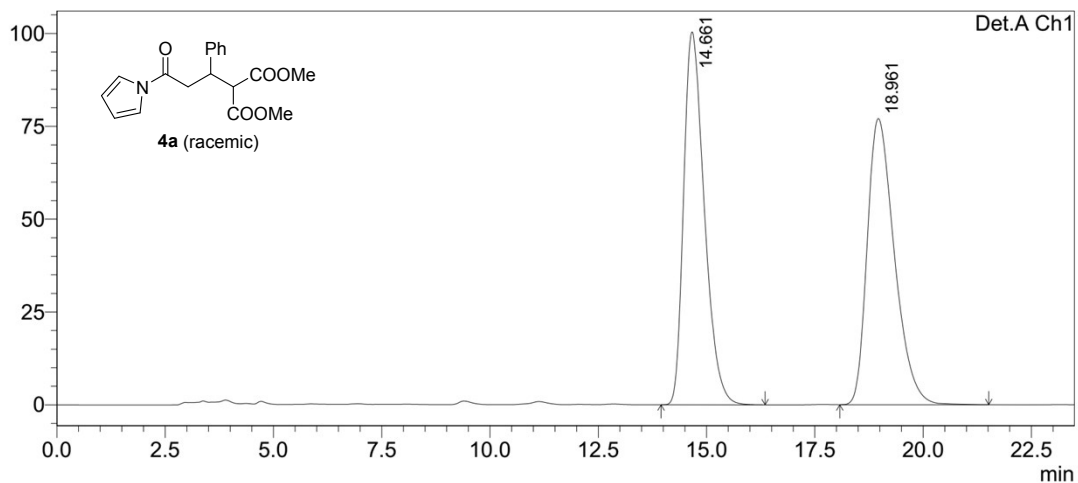










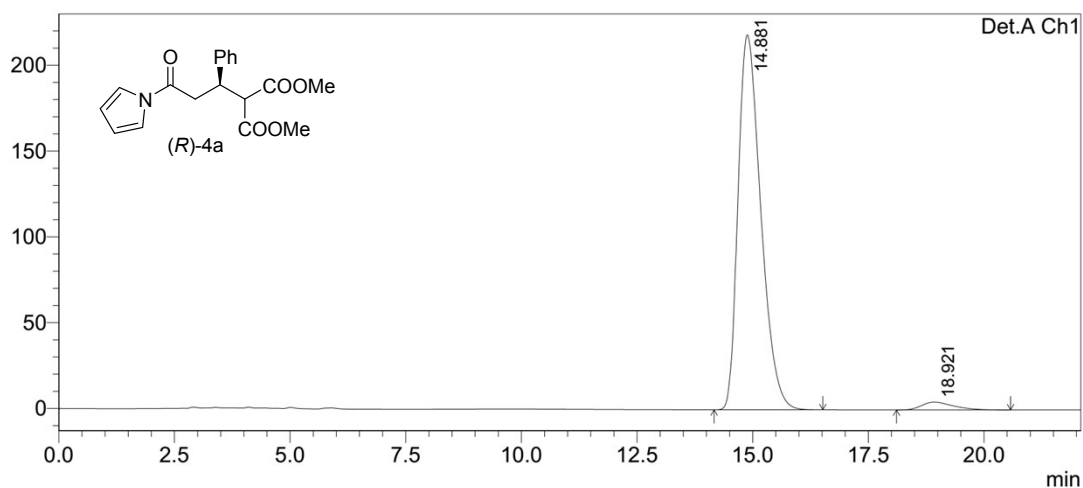


et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.661	3334705	100416	49.712	56.577
2	18.961	3373399	77068	50.288	43.423
Total		6708104	177484	100.000	100.000

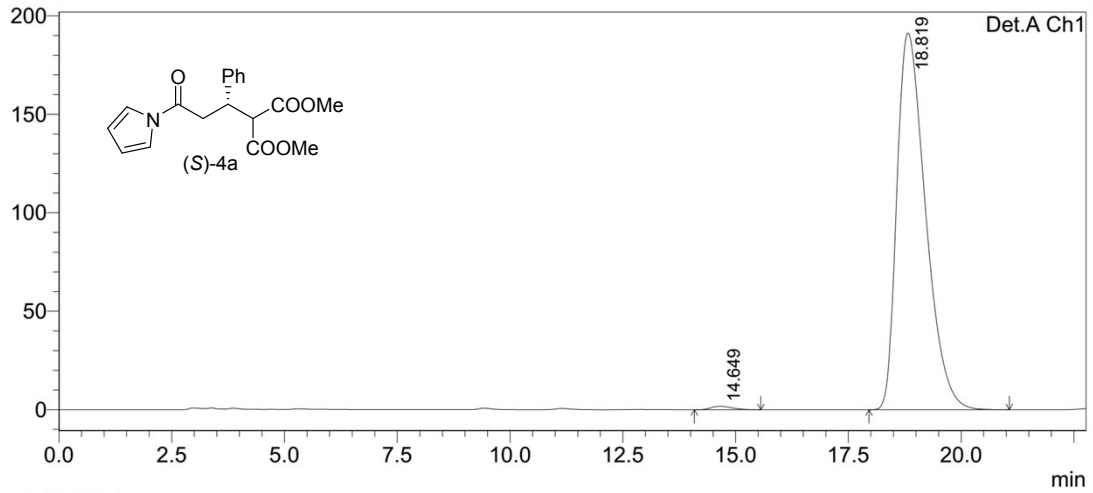


et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.881	7467297	218437	97.198	97.962
2	18.921	215286	4544	2.802	2.038
Total		7682583	222981	100.000	100.000

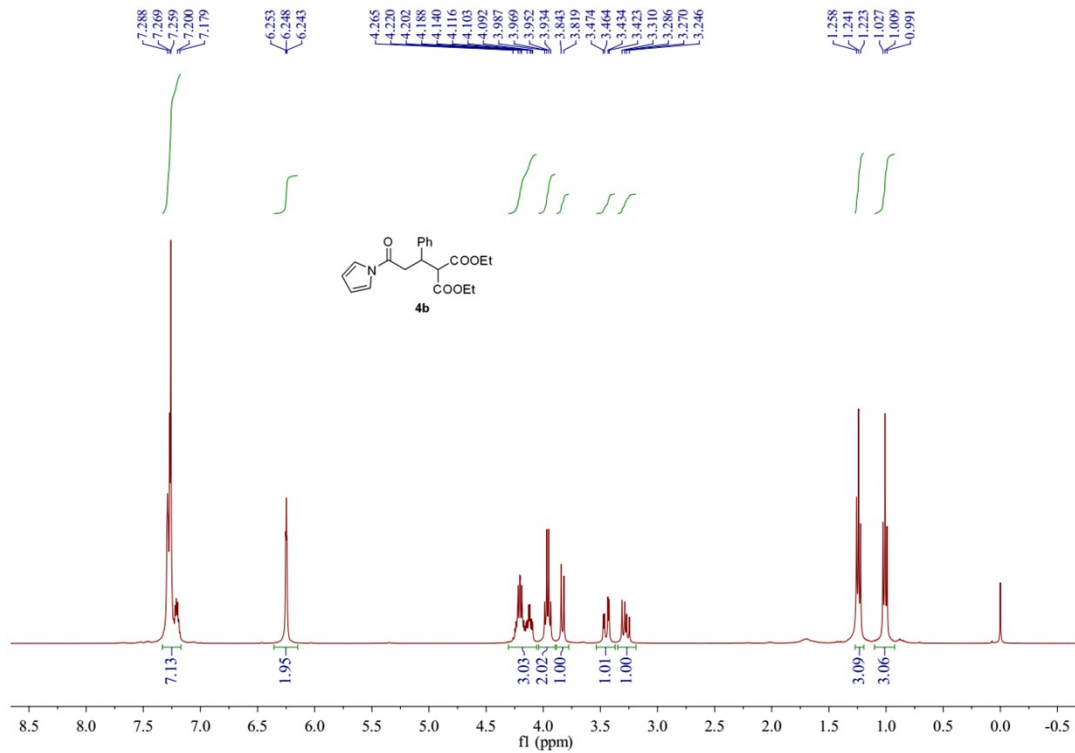


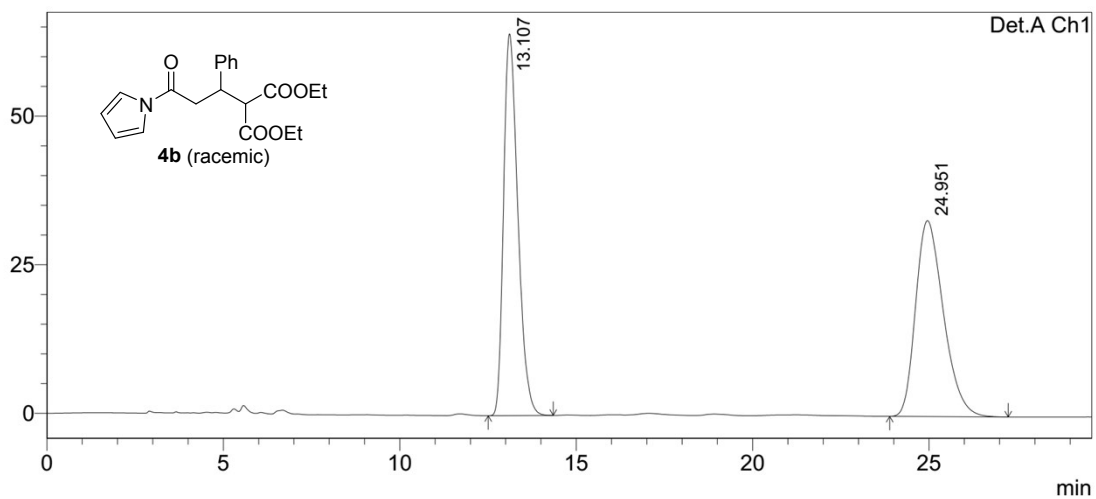
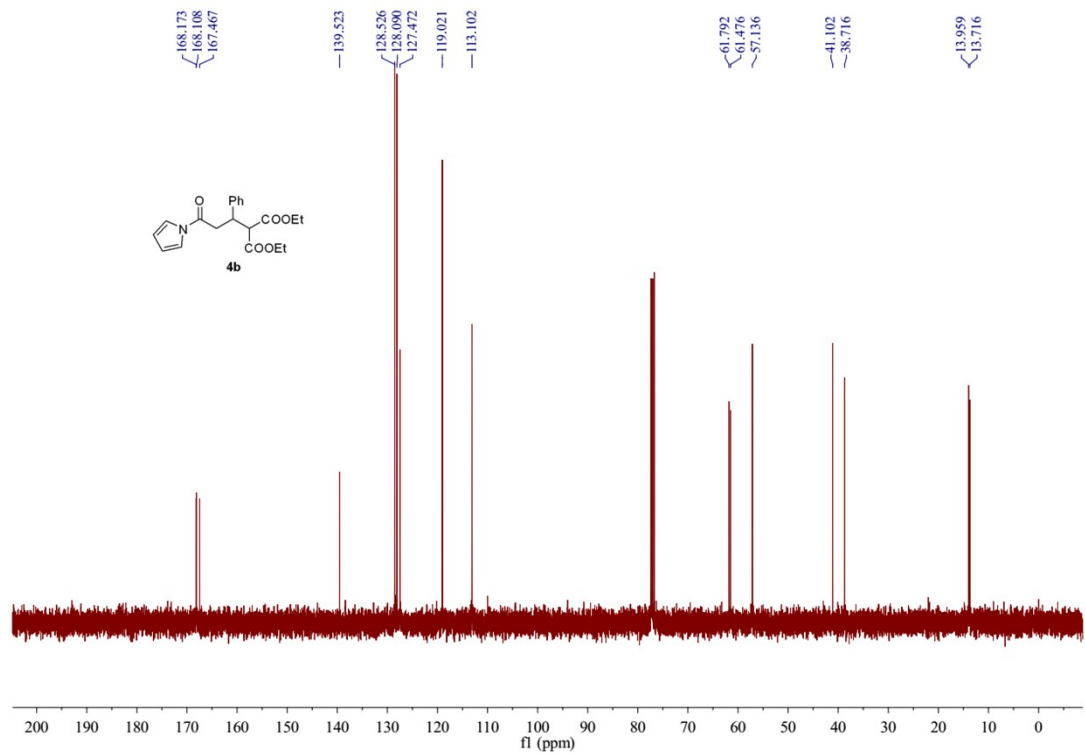
st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.649	56076	1779	0.658	0.922
2	18.819	8464571	191256	99.342	99.078
Total		8520647	193035	100.000	100.000



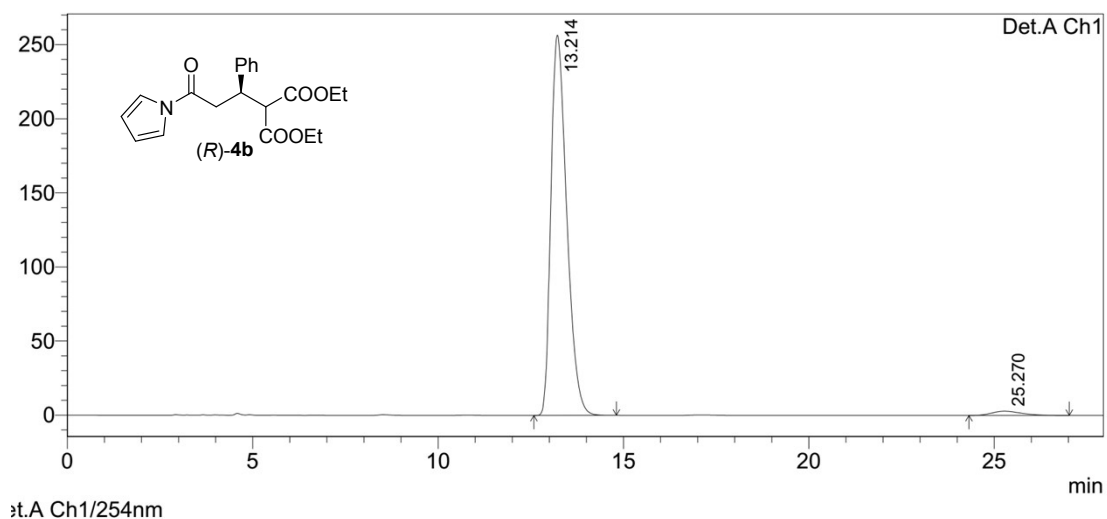


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.107	1806899	64243	49.975	66.091
2	24.951	1808672	32961	50.025	33.909
Total		3615571	97204	100.000	100.000

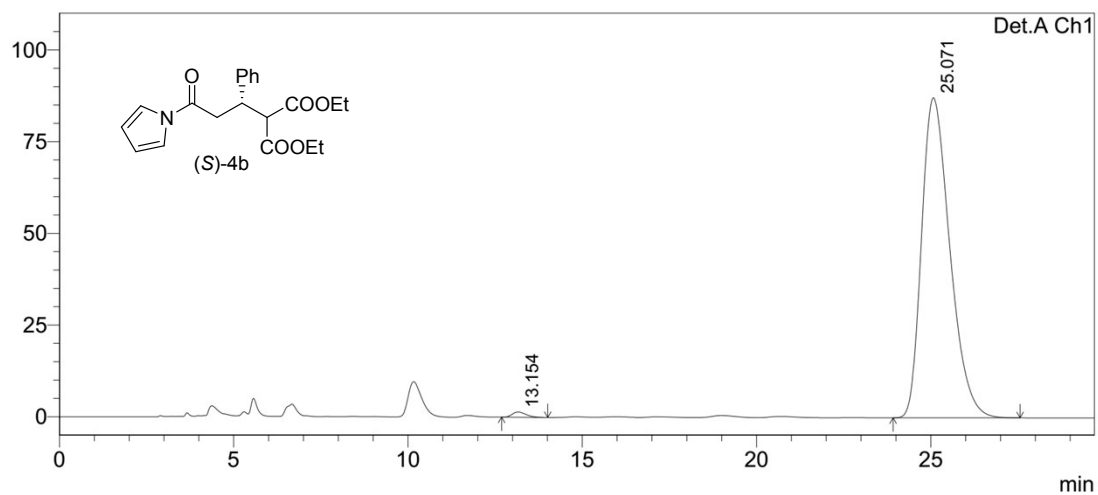


st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.214	7619623	256560	97.956	98.900
2	25.270	158976	2855	2.044	1.100
Total		7778599	259415	100.000	100.000

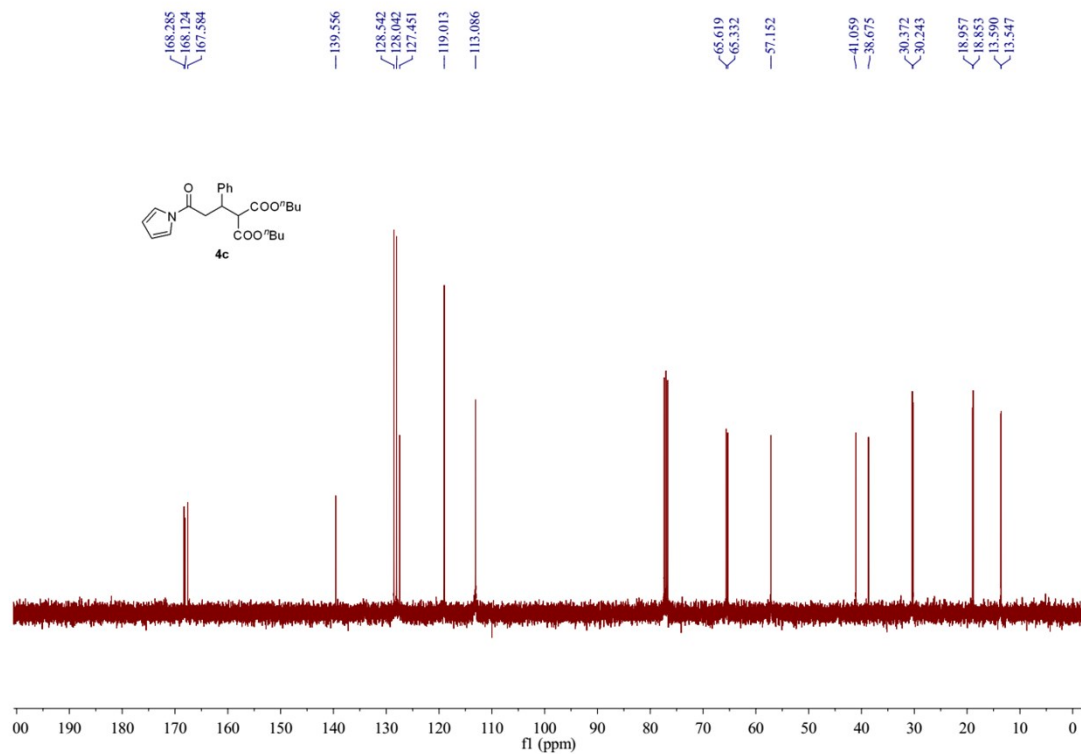
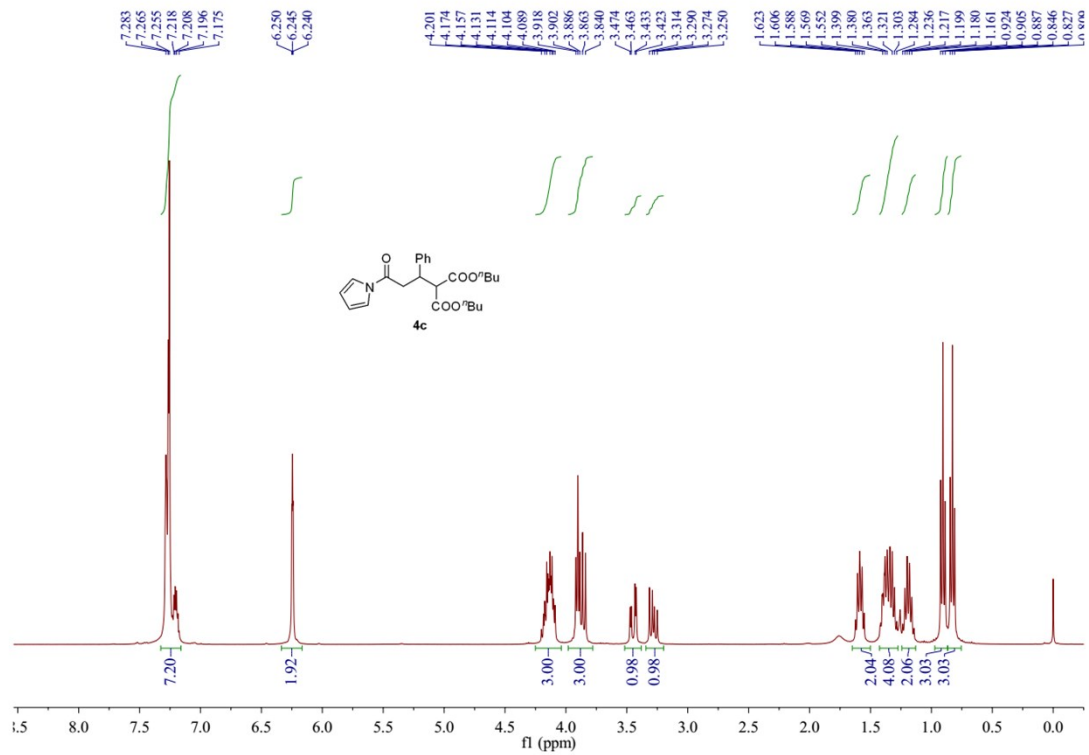


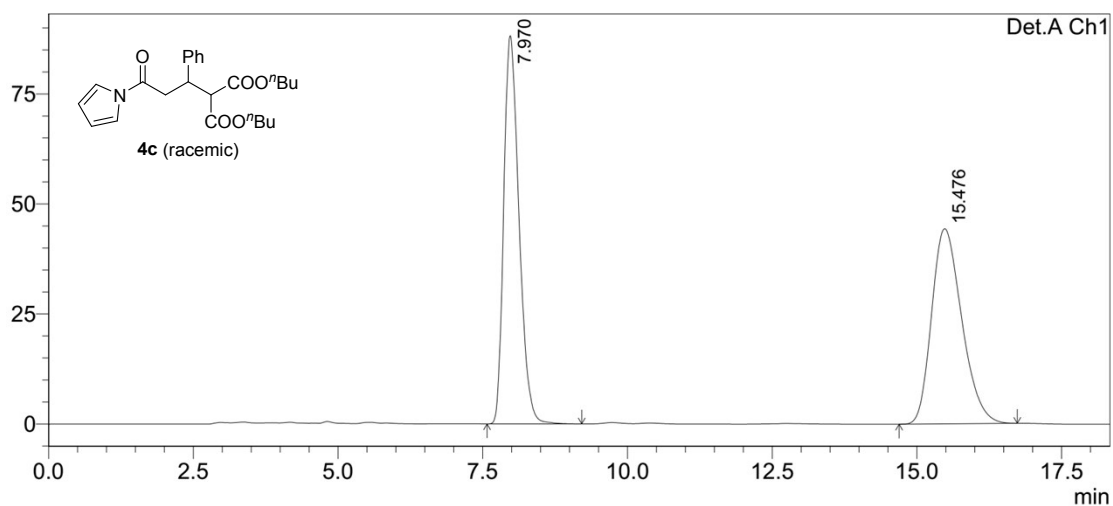
st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.154	39610	1434	0.799	1.616
2	25.071	4919877	87263	99.201	98.384
Total		4959487	88697	100.000	100.000

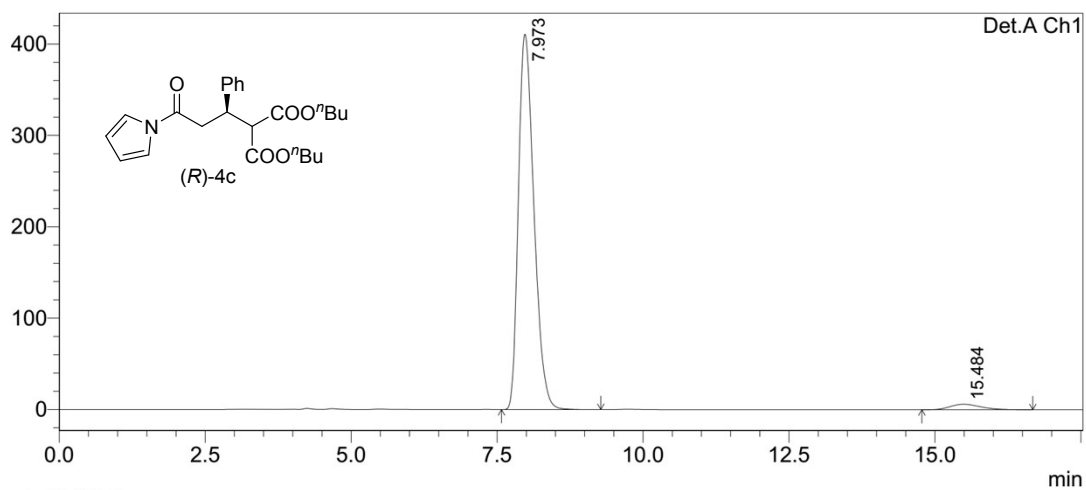




PeakTable

Detector A Ch1 254nm

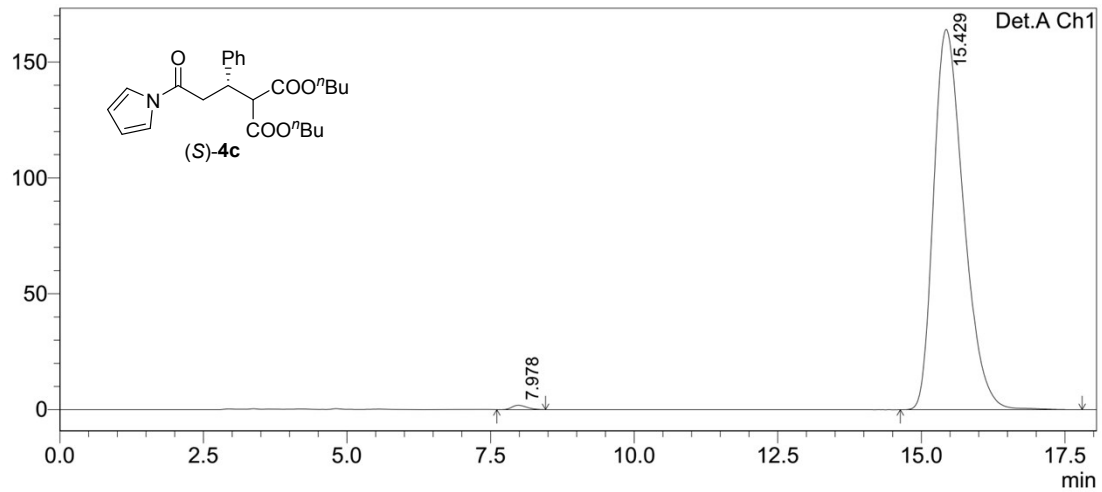
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.970	1617887	88229	50.184	66.549
2	15.476	1606052	44348	49.816	33.451
Total		3223939	132578	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.973	7614290	410924	97.243	98.565
2	15.484	215890	5983	2.757	1.435
Total		7830180	416907	100.000	100.000

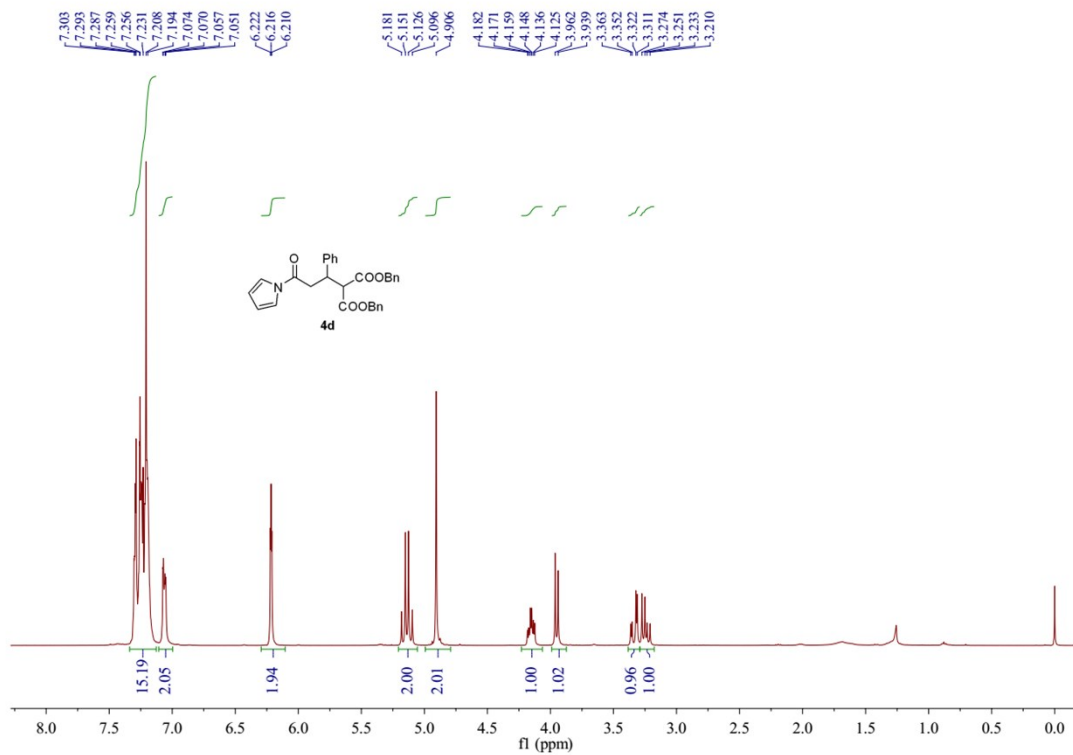


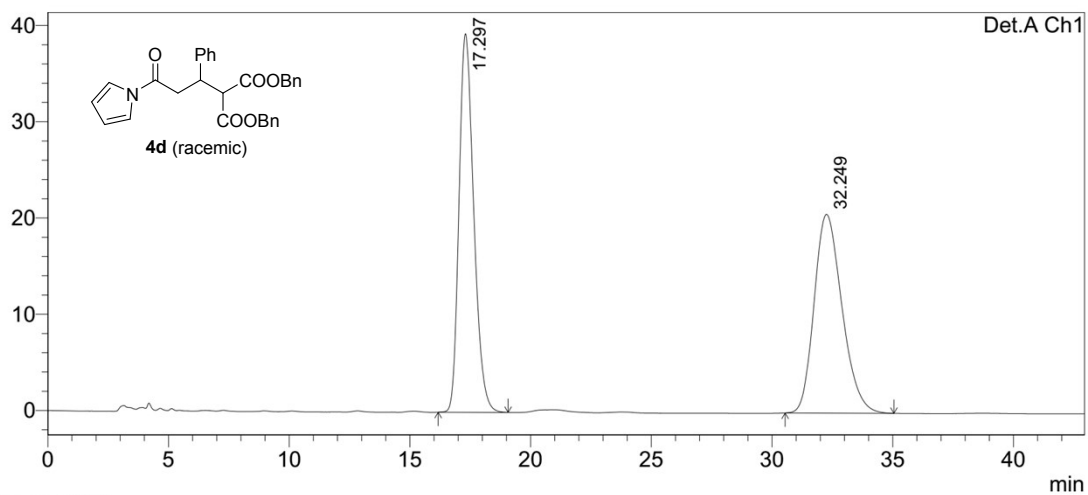
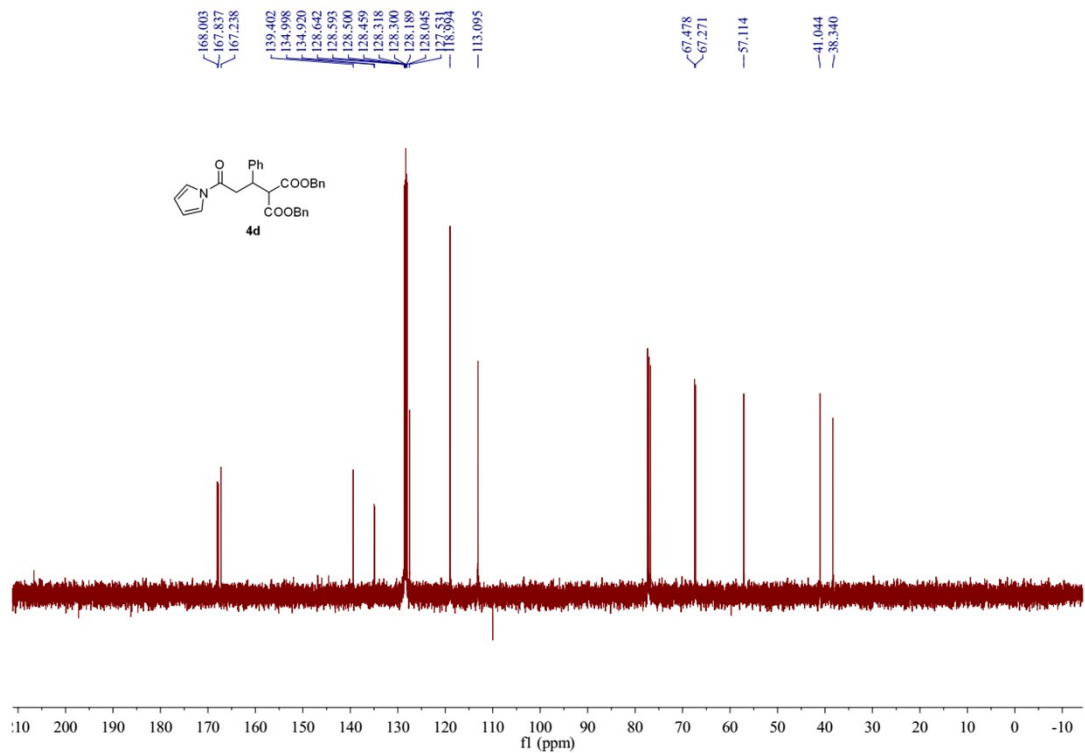
t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.978	33484	1873	0.558	1.129
2	15.429	5966529	164080	99.442	98.871
Total		6000013	165953	100.000	100.000



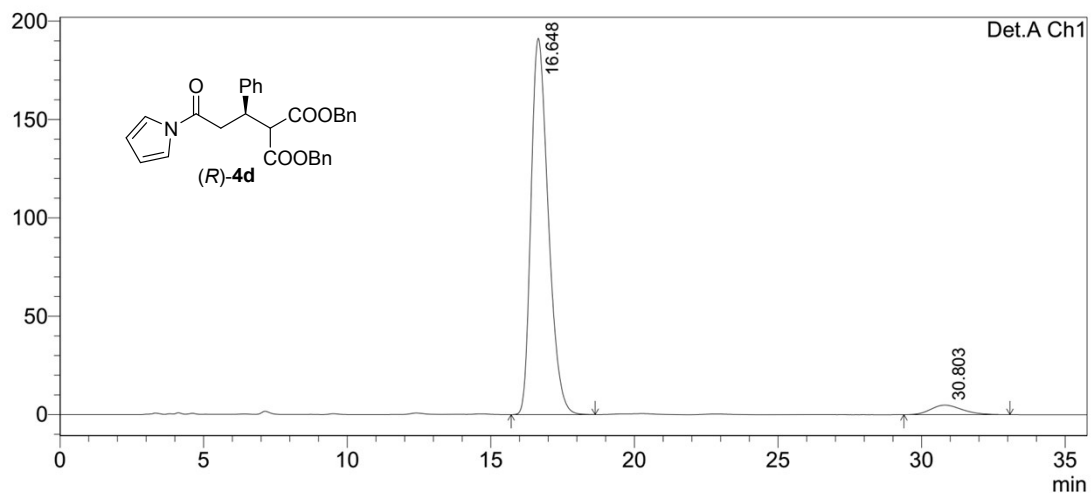


Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.297	1669075	39331	50.195	65.575
2	32.249	1656082	20648	49.805	34.425
Total		3325157	59979	100.000	100.000

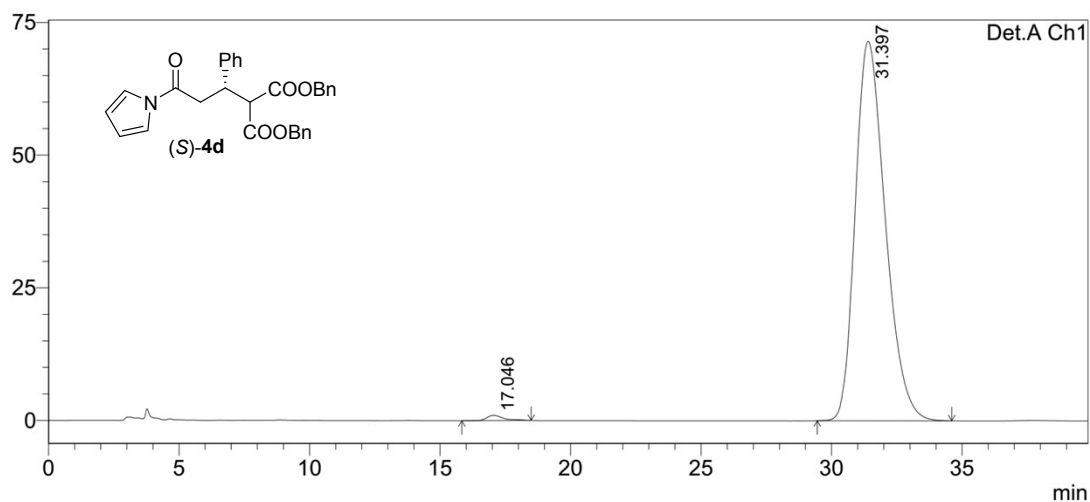


et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.648	7990254	191241	95.602	97.529
2	30.803	367611	4846	4.398	2.471
Total		8357865	196088	100.000	100.000

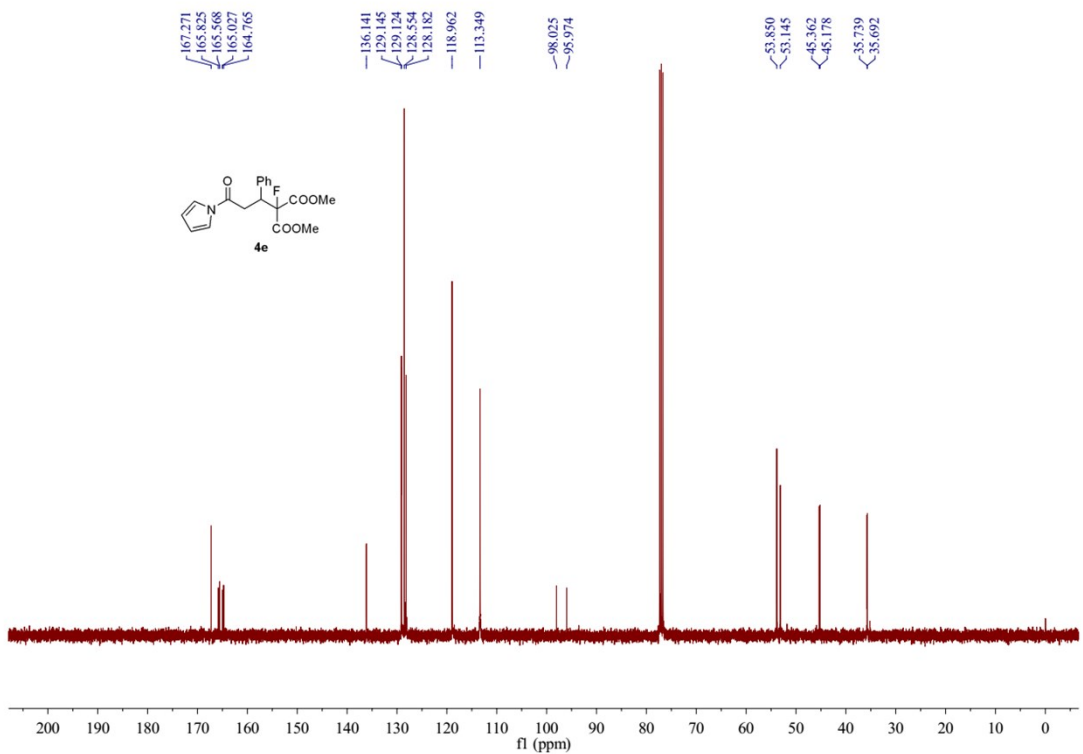
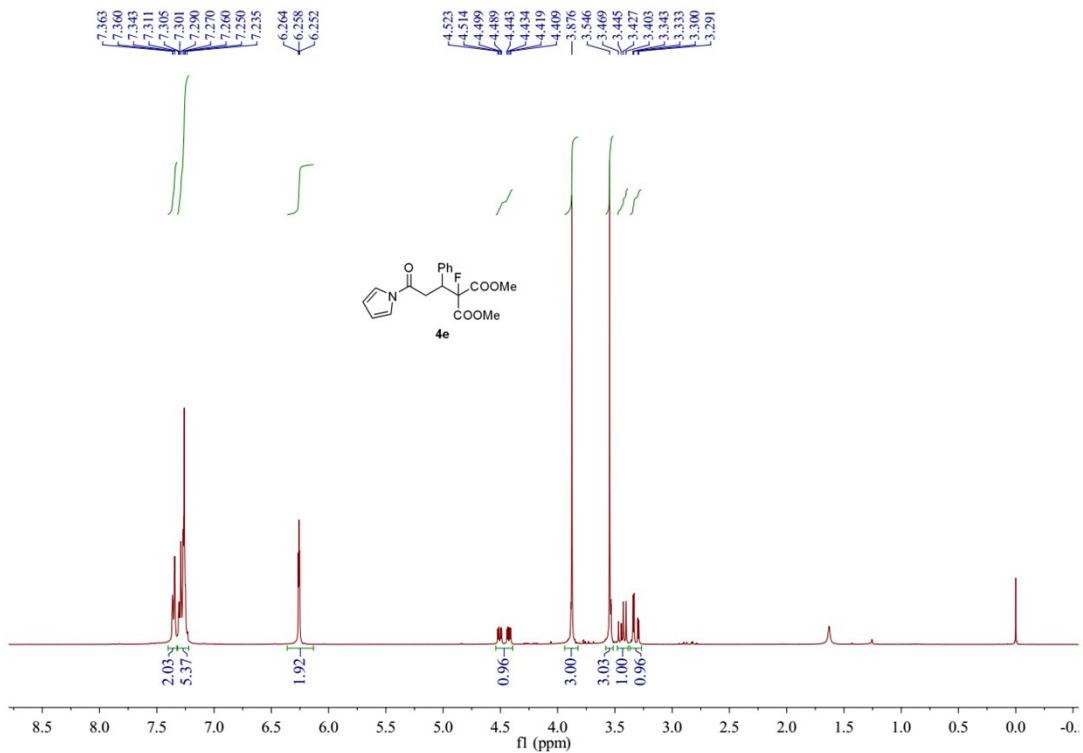


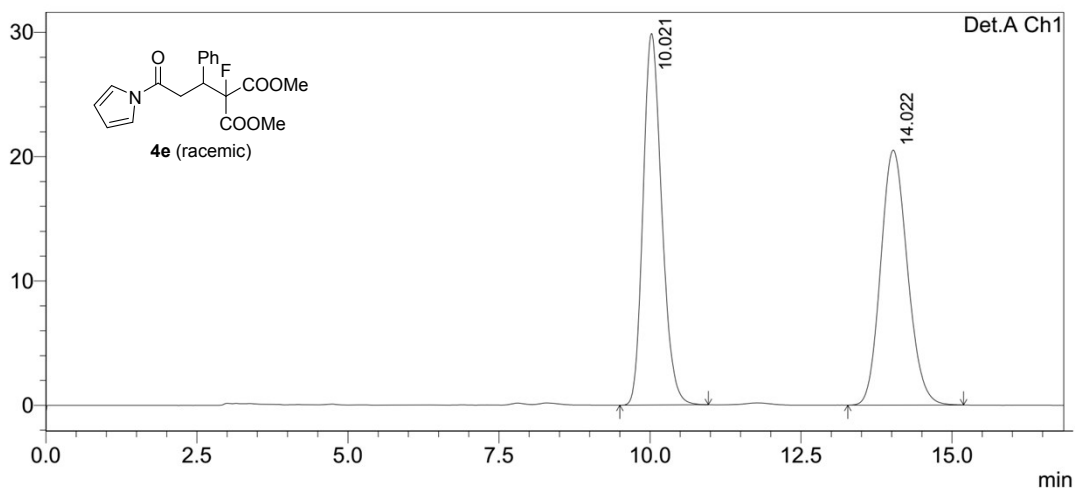
et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.046	44704	985	0.776	1.359
2	31.397	5714601	71508	99.224	98.641
Total		5759305	72493	100.000	100.000



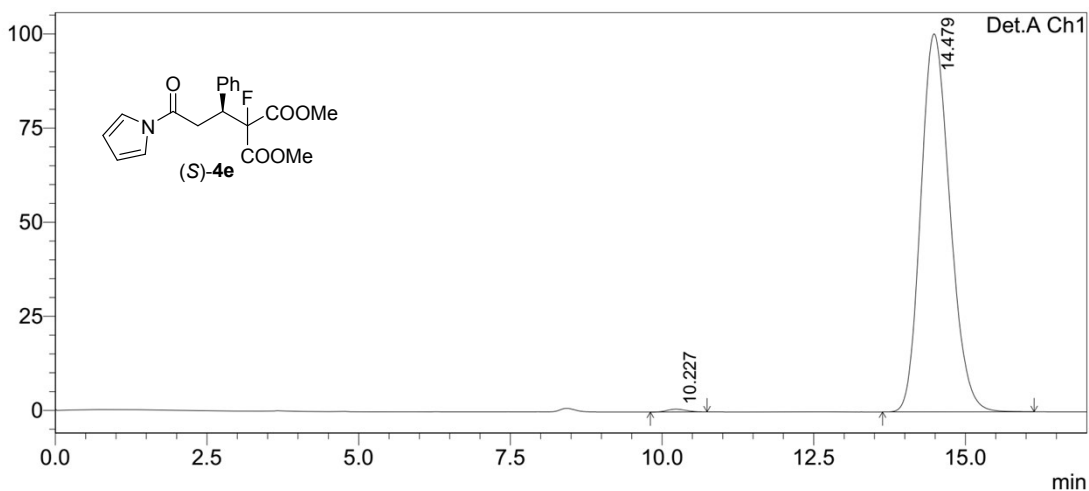


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.021	641334	29894	50.402	59.313
2	14.022	631112	20507	49.598	40.687
Total		1272446	50401	100.000	100.000

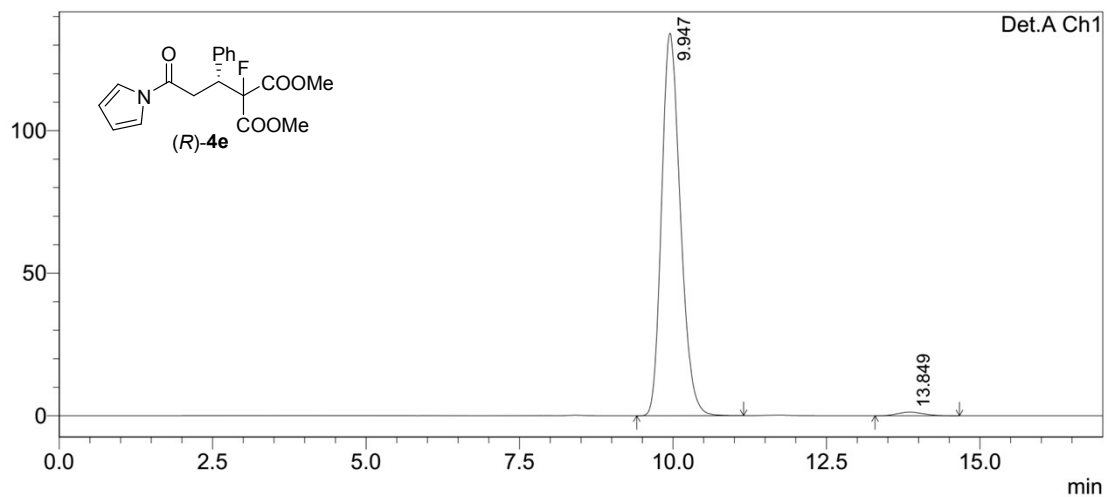


et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.227	16075	756	0.476	0.747
2	14.479	3358143	100452	99.524	99.253
Total		3374218	101208	100.000	100.000

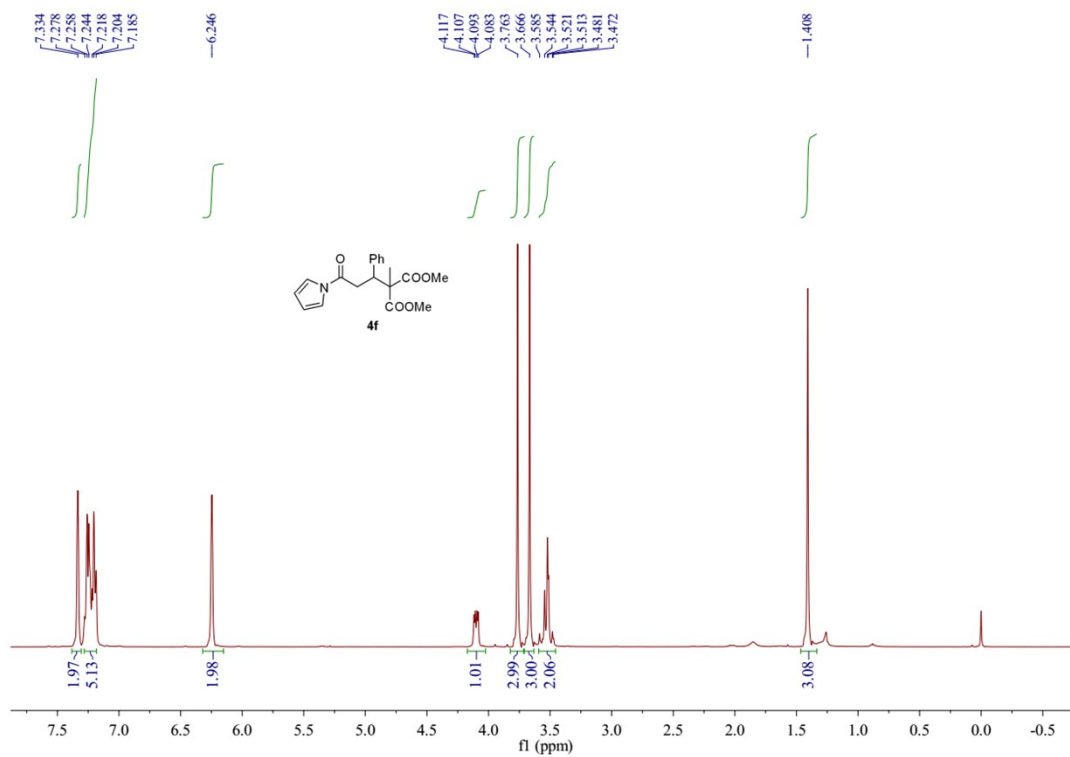


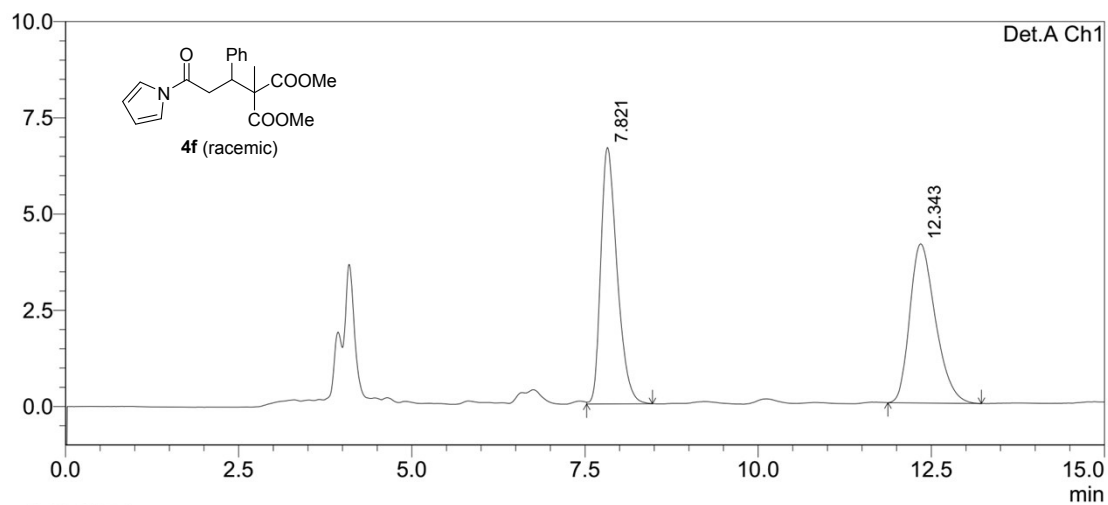
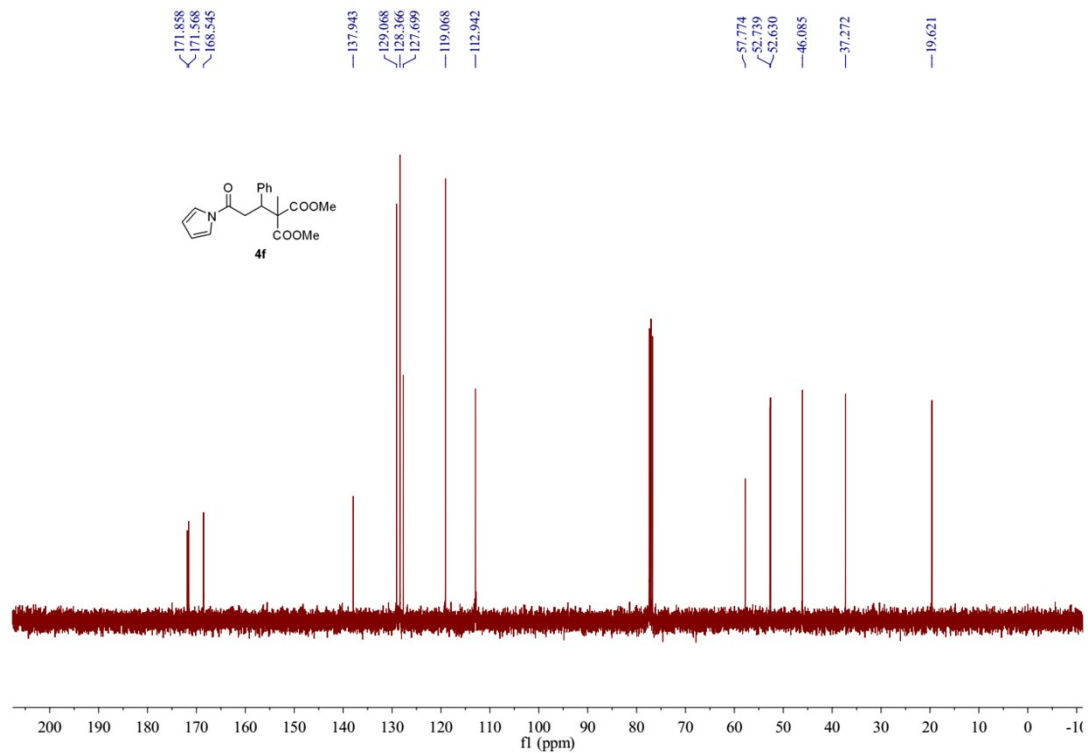
st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.947	2858328	134180	98.717	99.075
2	13.849	37143	1253	1.283	0.925
Total		2895471	135433	100.000	100.000



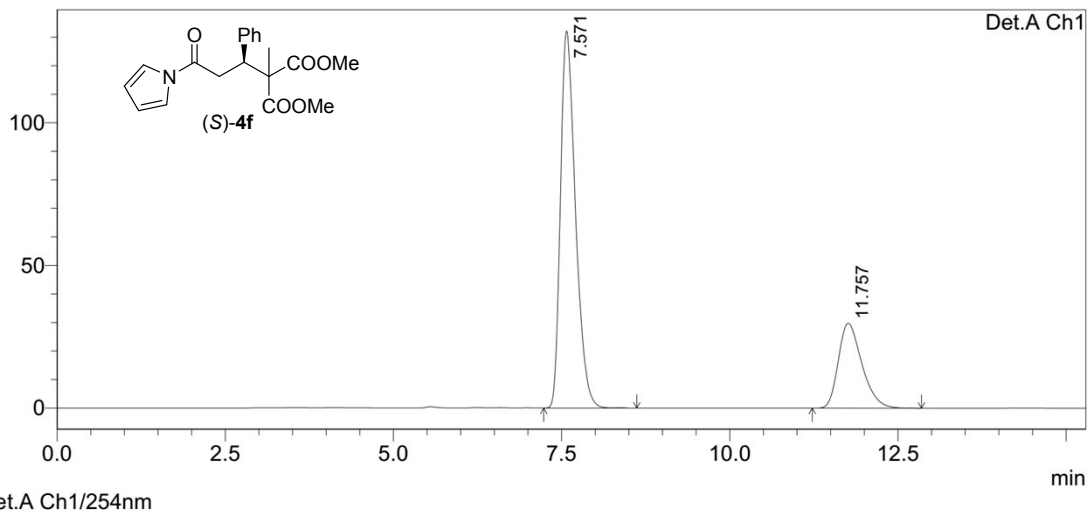


st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.821	109483	6664	50.678	61.711
2	12.343	106554	4135	49.322	38.289
Total		216037	10798	100.000	100.000

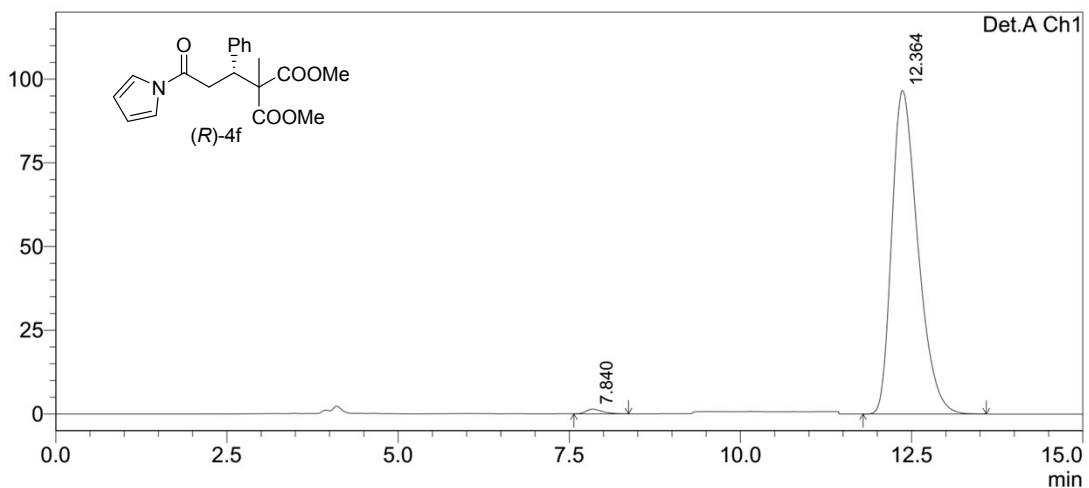


st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.571	2054751	132213	73.923	81.635
2	11.757	724836	29743	26.077	18.365
Total		2779587	161956	100.000	100.000

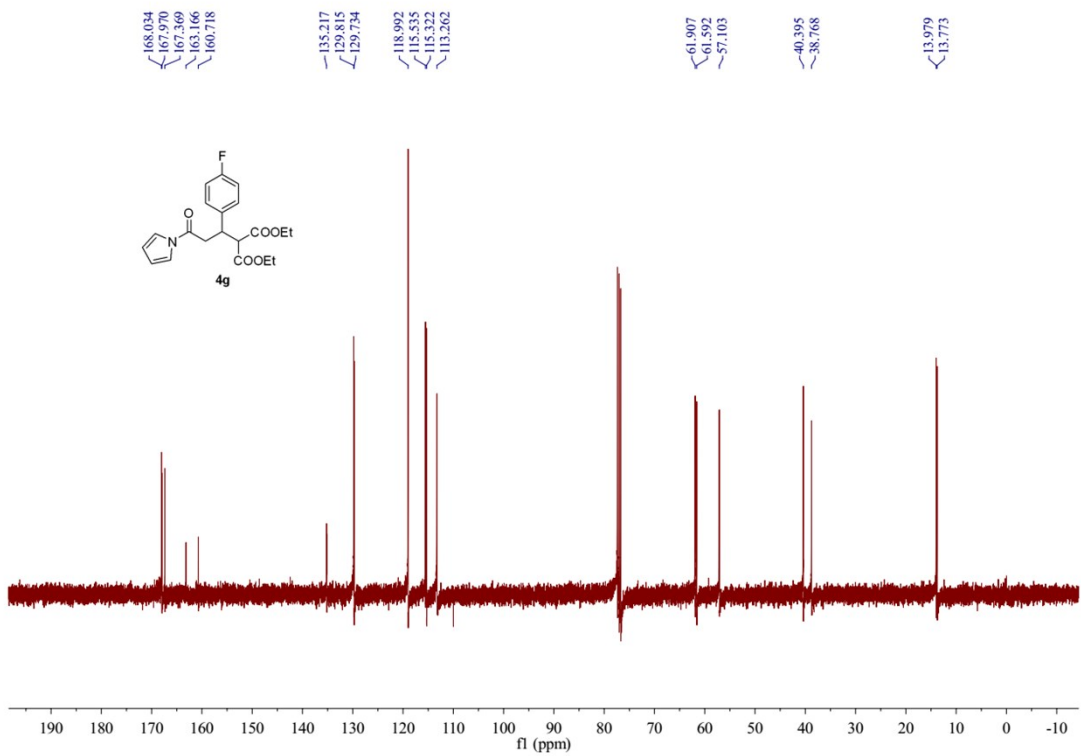
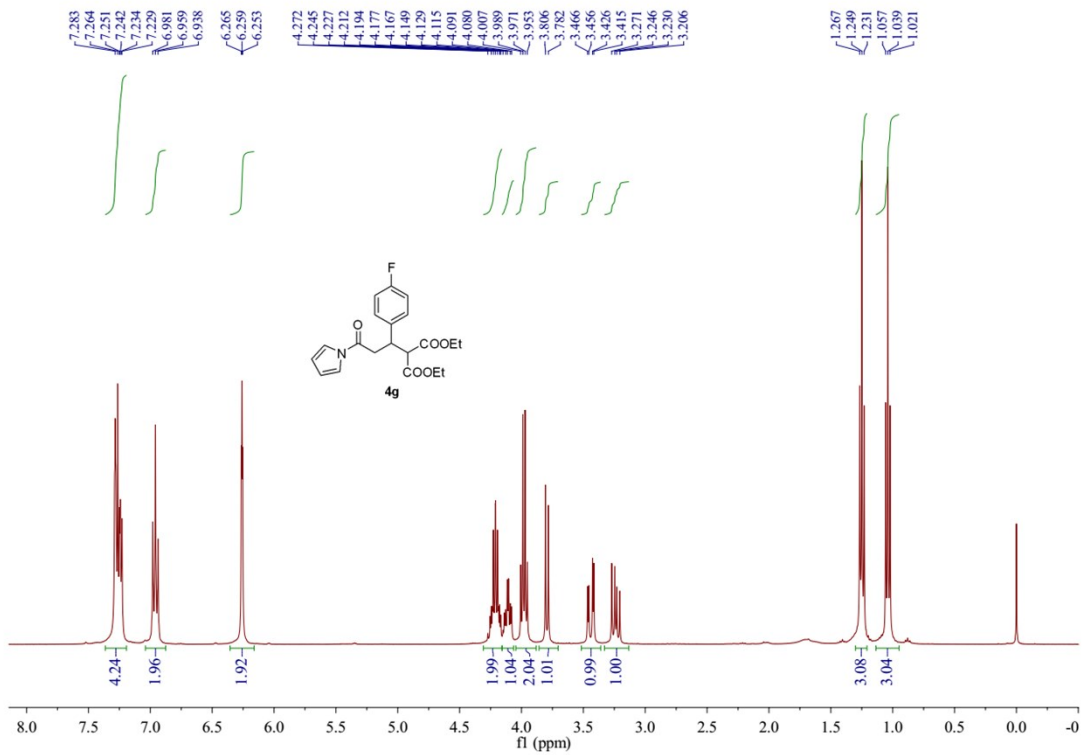


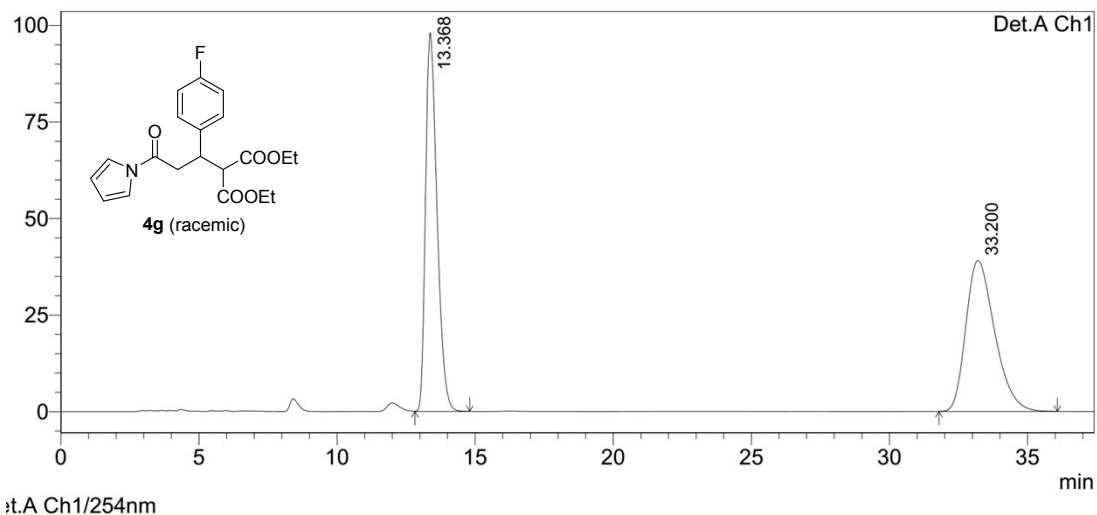
st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.840	23055	1402	0.891	1.429
2	12.364	2564105	96676	99.109	98.571
Total		2587160	98078	100.000	100.000

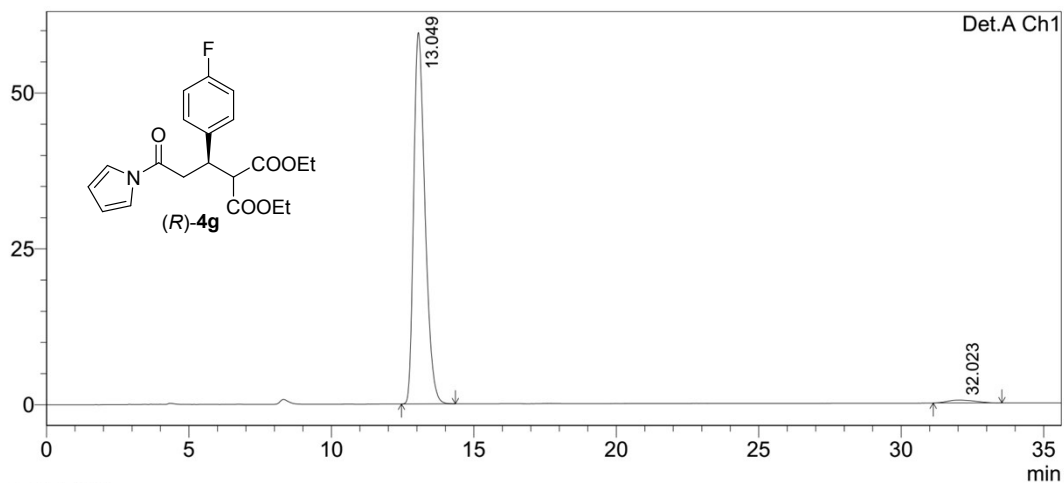




PeakTable

Detector A Ch1 254nm

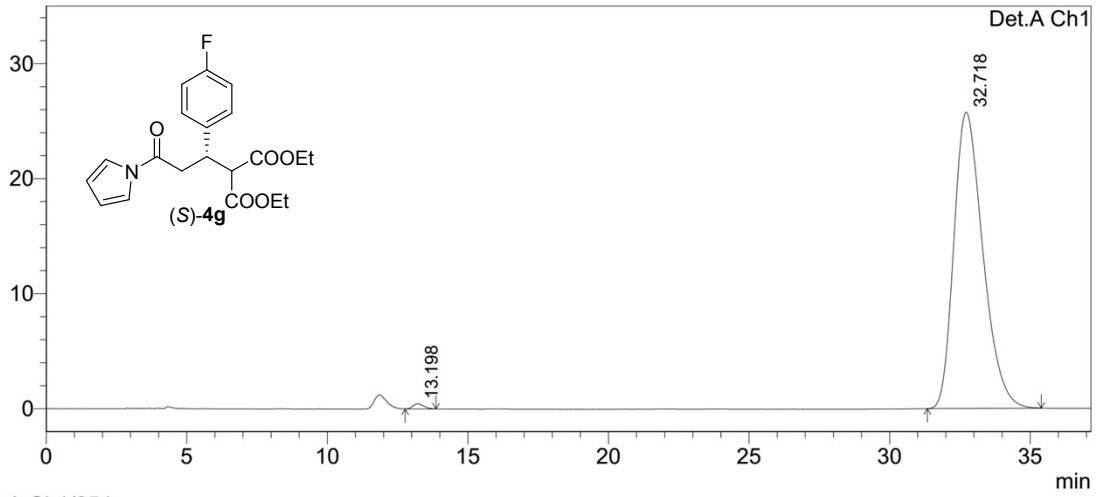
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.368	2831828	98107	49.927	71.526
2	33.200	2840150	39056	50.073	28.474
Total		5671978	137163	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.049	1640419	59571	98.114	99.188
2	32.023	31525	488	1.886	0.812
Total		1671944	60059	100.000	100.000

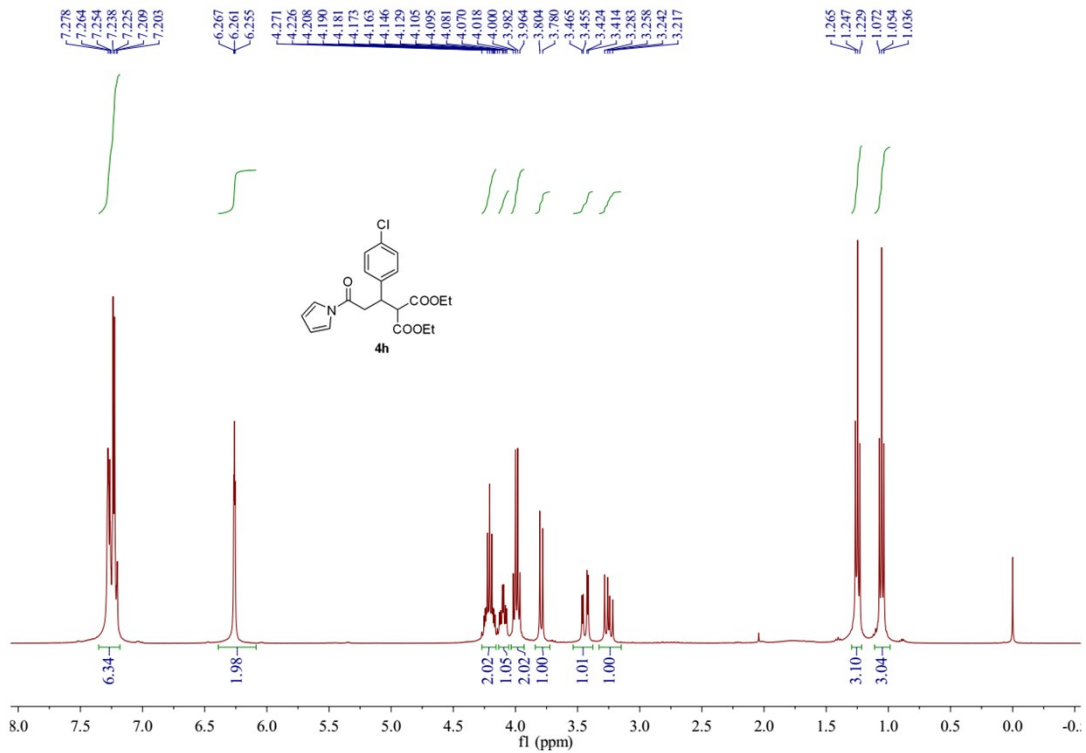


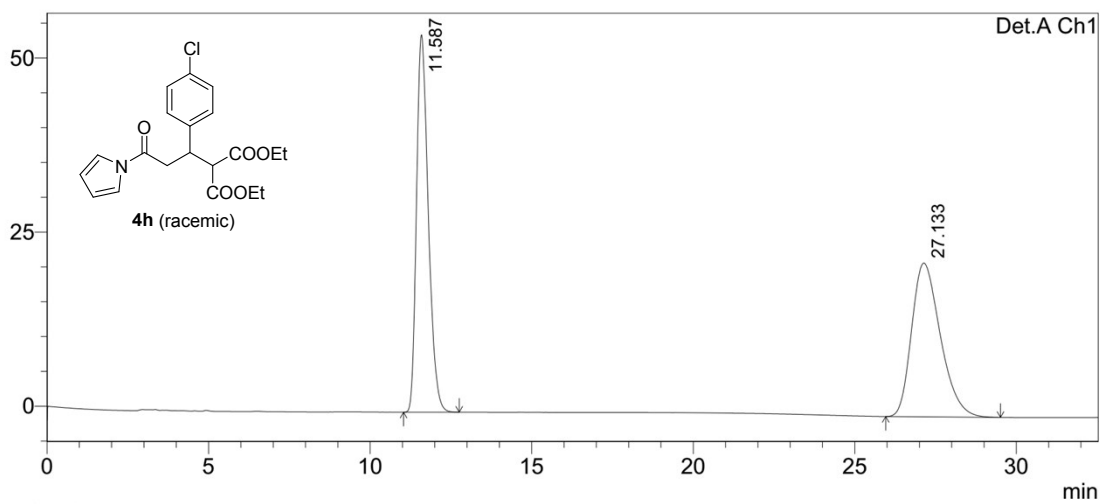
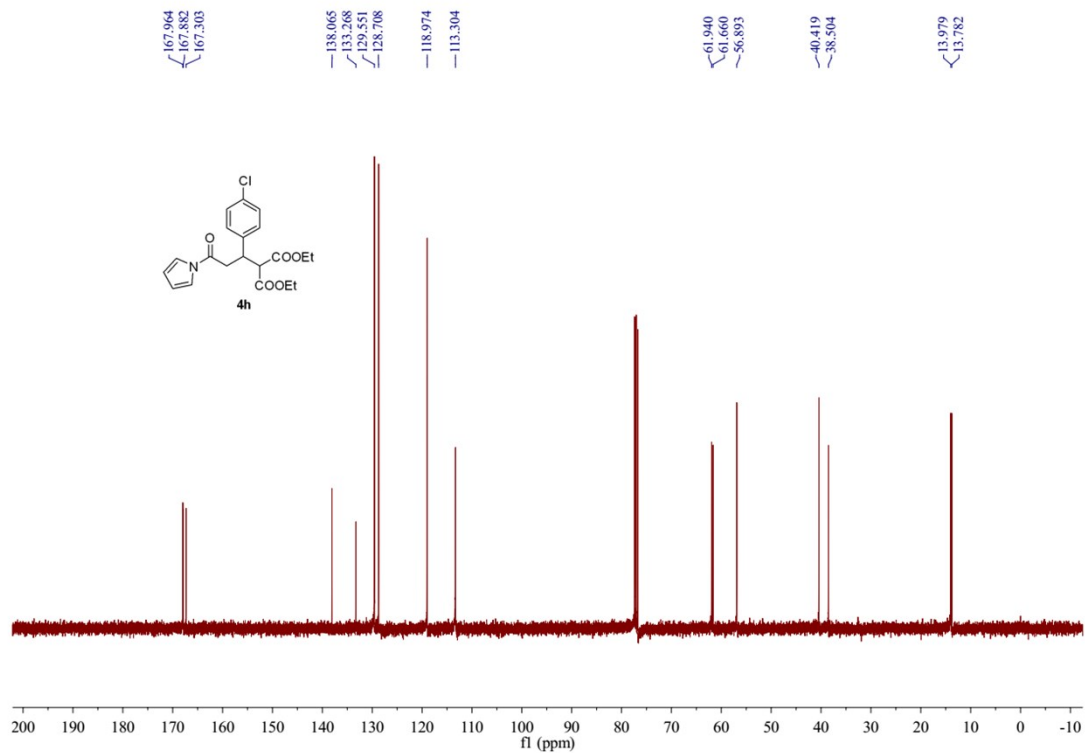
t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.198	11891	447	0.639	1.705
2	32.718	1849917	25760	99.361	98.295
Total		1861809	26207	100.000	100.000



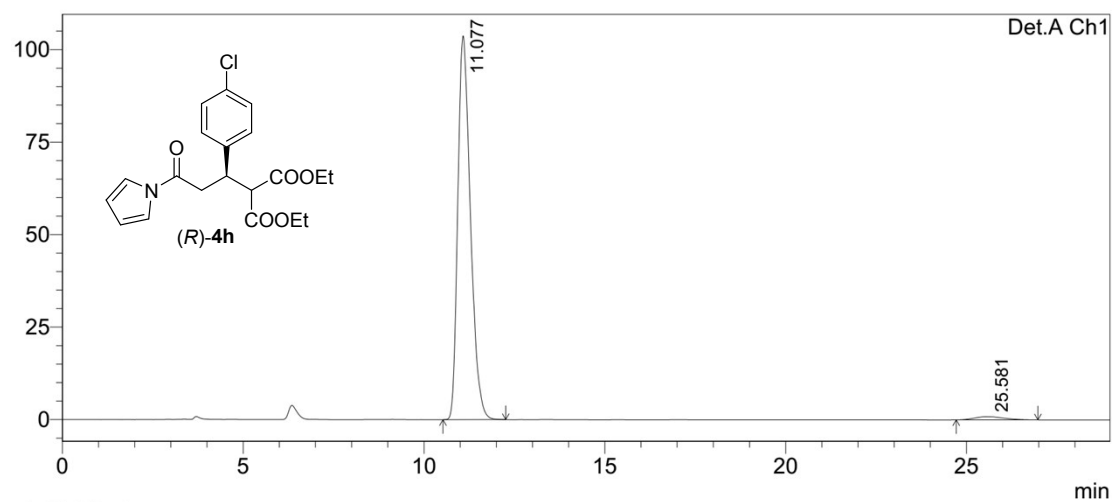


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.587	1374213	54208	50.145	71.059
2	27.133	1366255	22078	49.855	28.941
Total		2740468	76286	100.000	100.000

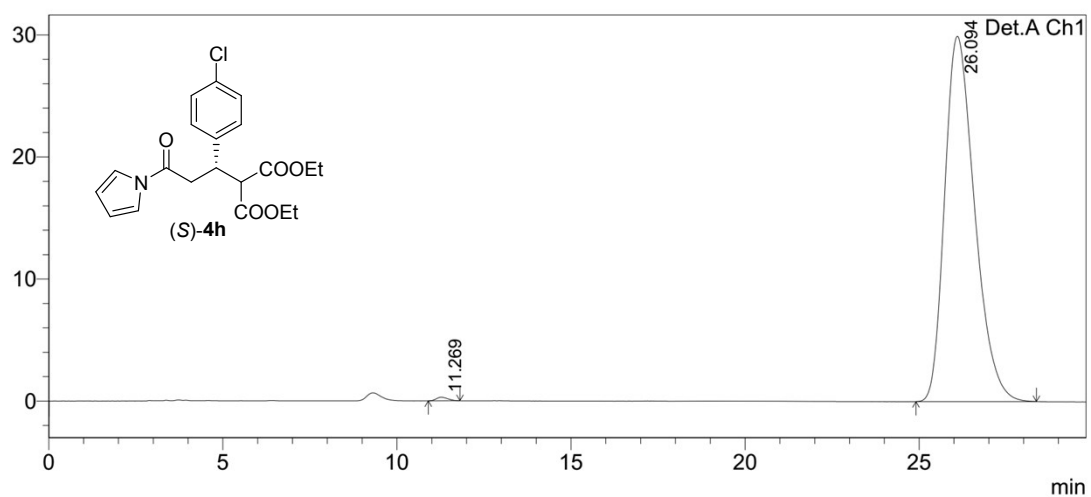


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.077	2516746	103733	98.101	99.166
2	25.581	48727	872	1.899	0.834
Total		2565472	104605	100.000	100.000

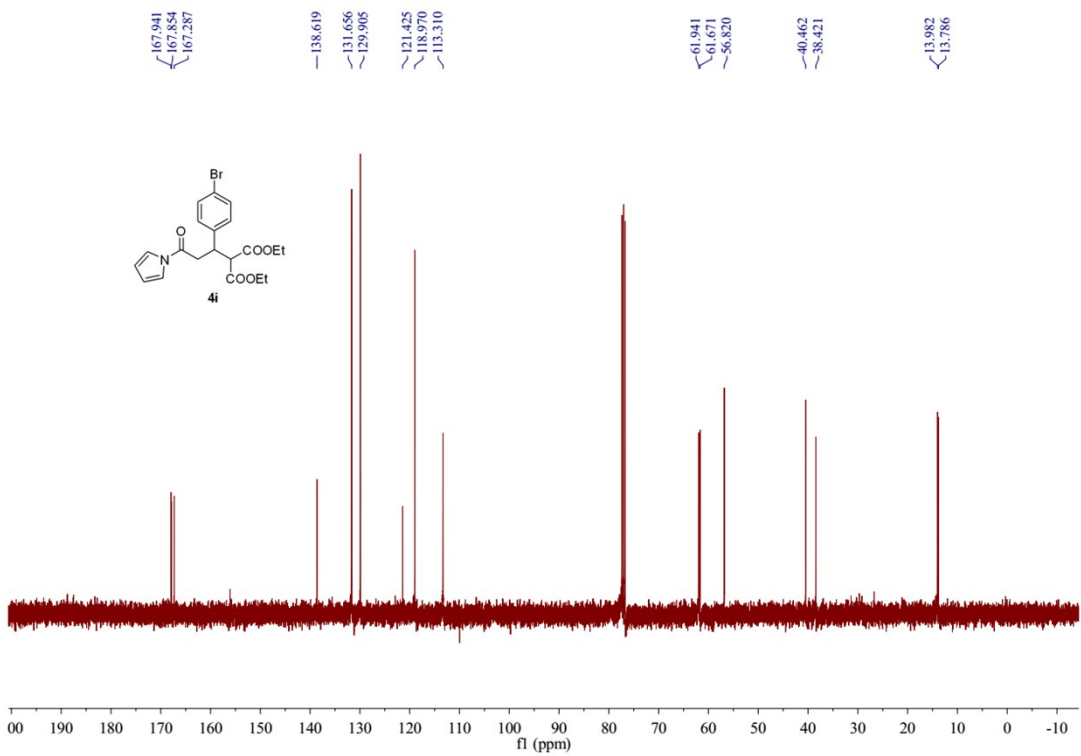
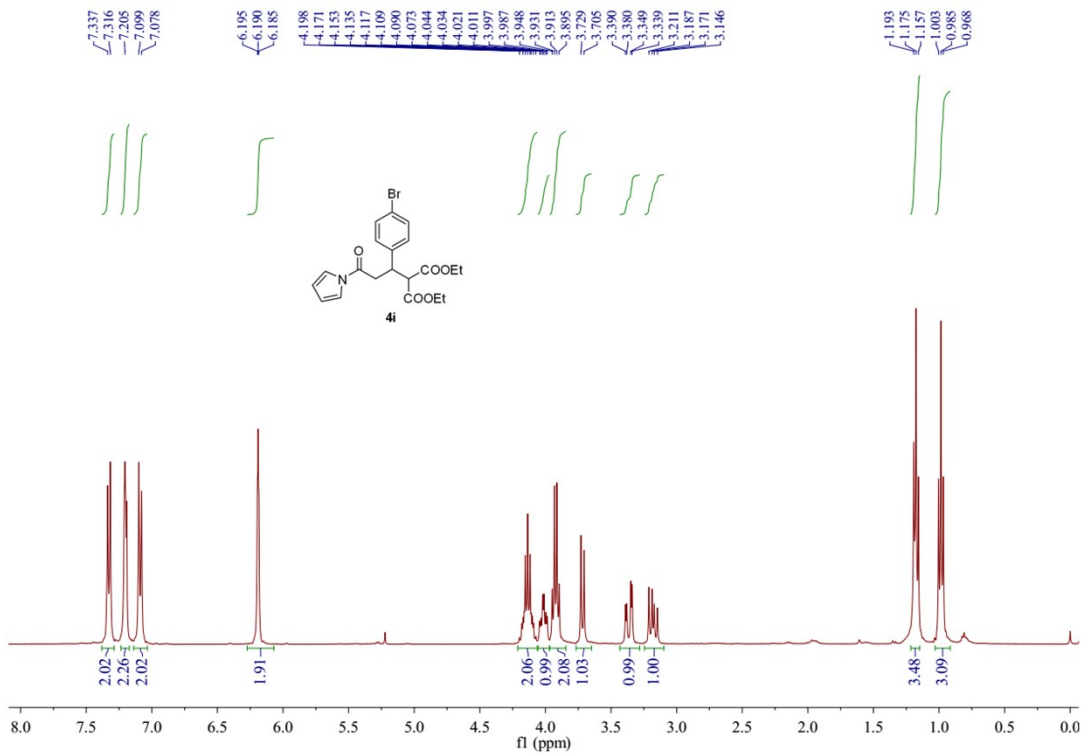


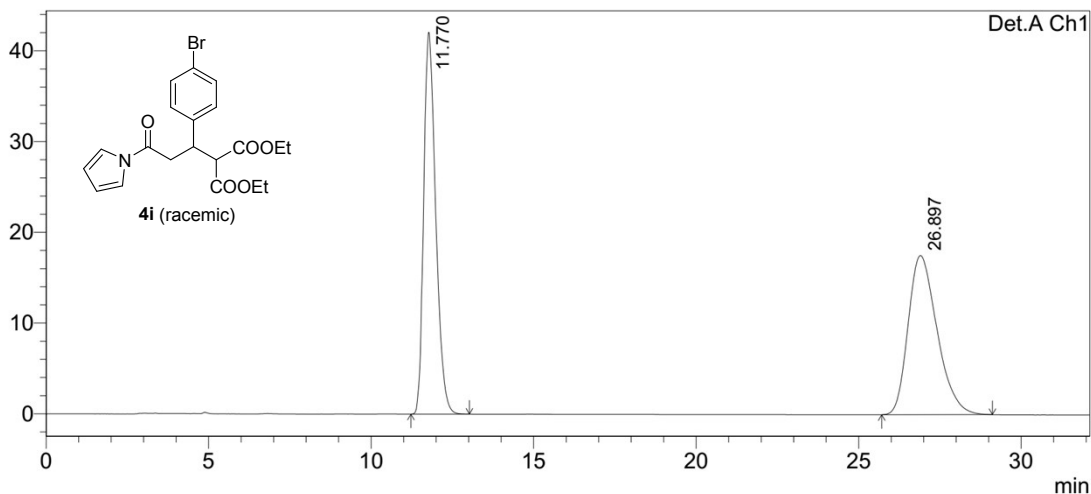
st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.269	6758	294	0.376	0.973
2	26.094	1790103	29931	99.624	99.027
Total		1796862	30225	100.000	100.000



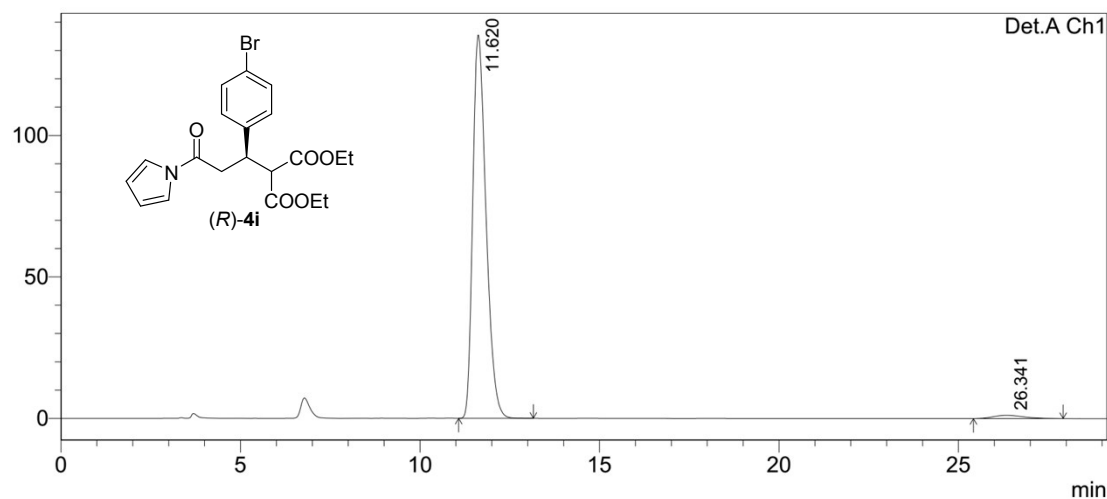


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.770	1084113	42094	49.965	70.588
2	26.897	1085622	17539	50.035	29.412
Total		2169735	59632	100.000	100.000

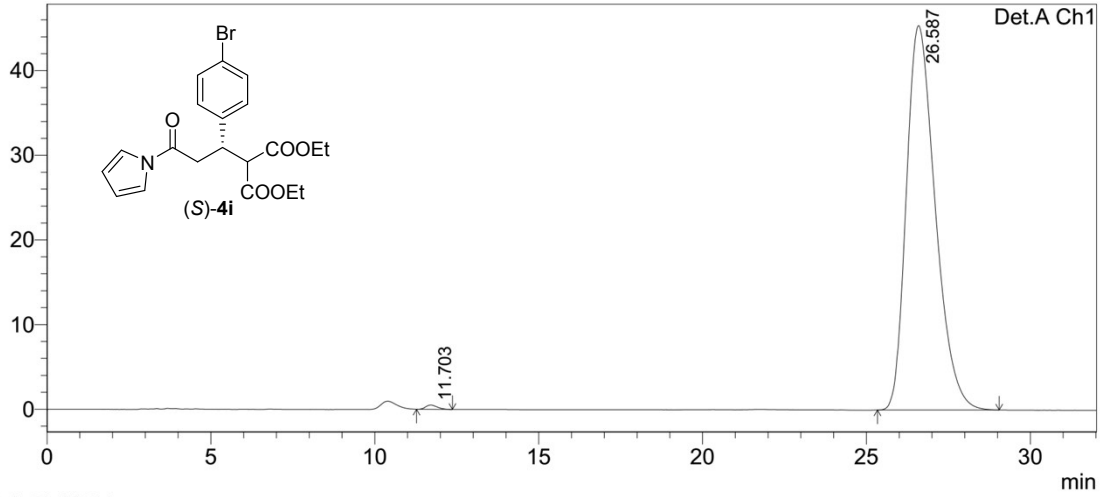


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.620	3476953	135511	98.073	99.145
2	26.341	68311	1169	1.927	0.855
Total		3545264	136680	100.000	100.000

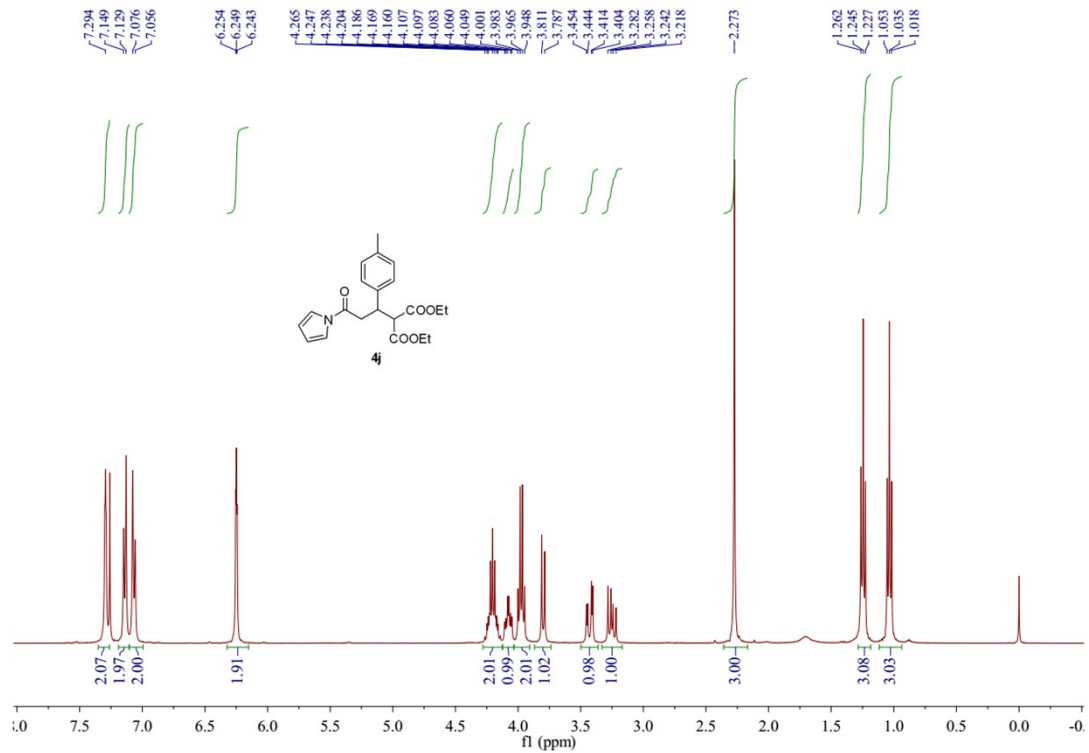


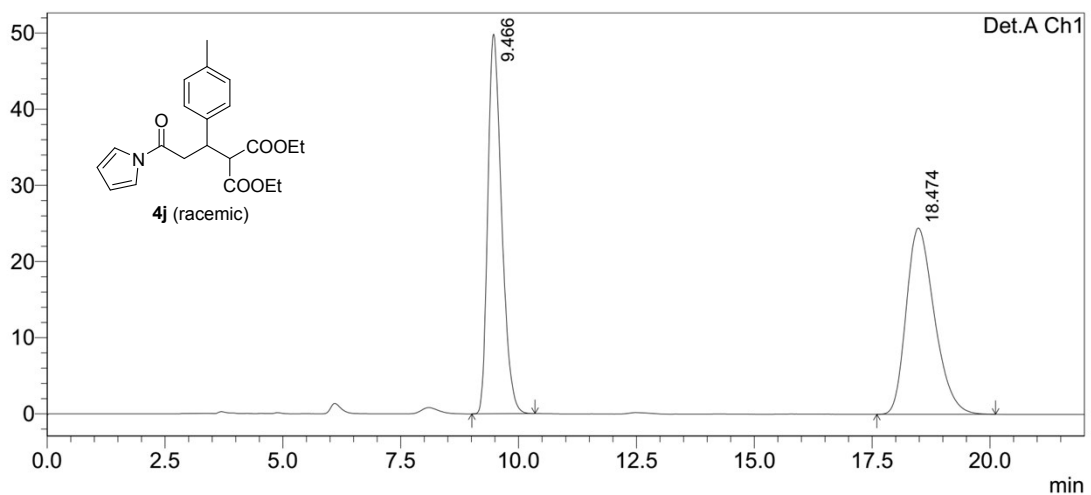
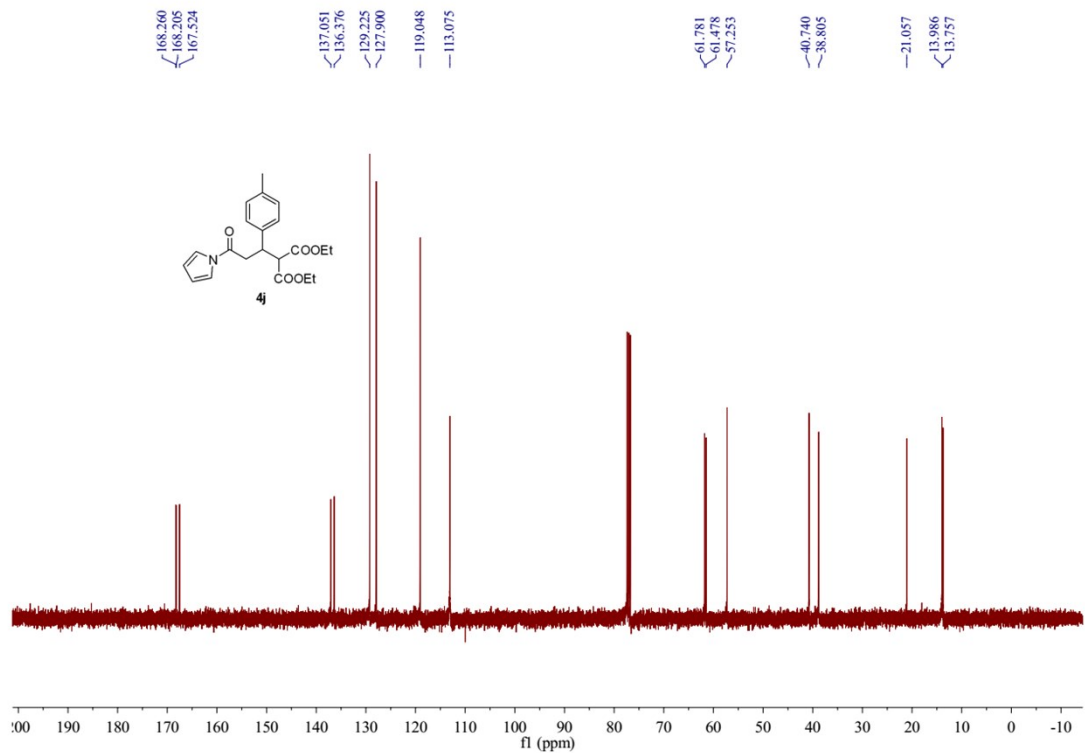
t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.703	12397	509	0.443	1.109
2	26.587	2787968	45411	99.557	98.891
Total		2800365	45920	100.000	100.000



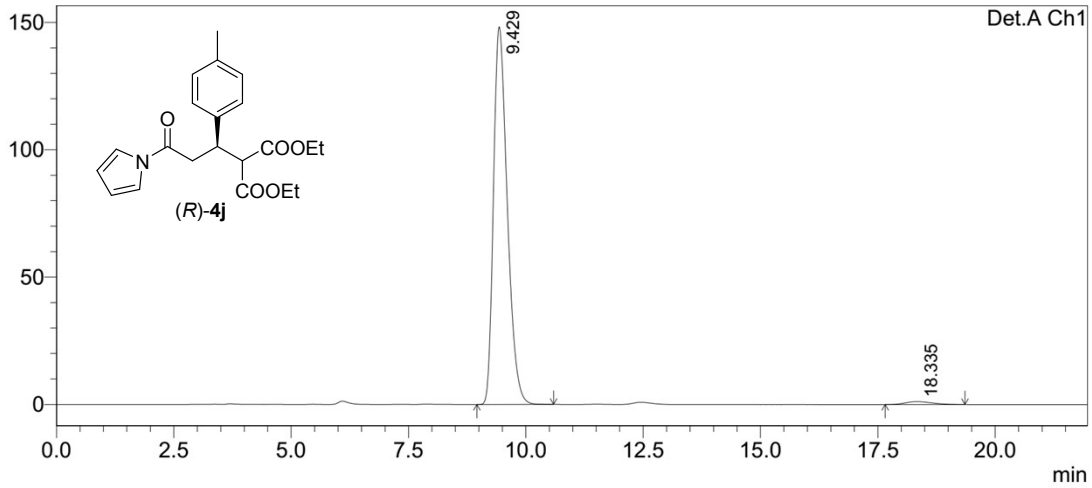


..A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.466	1016101	49835	49.932	67.079
2	18.474	1018879	24458	50.068	32.921
Total		2034980	74293	100.000	100.000

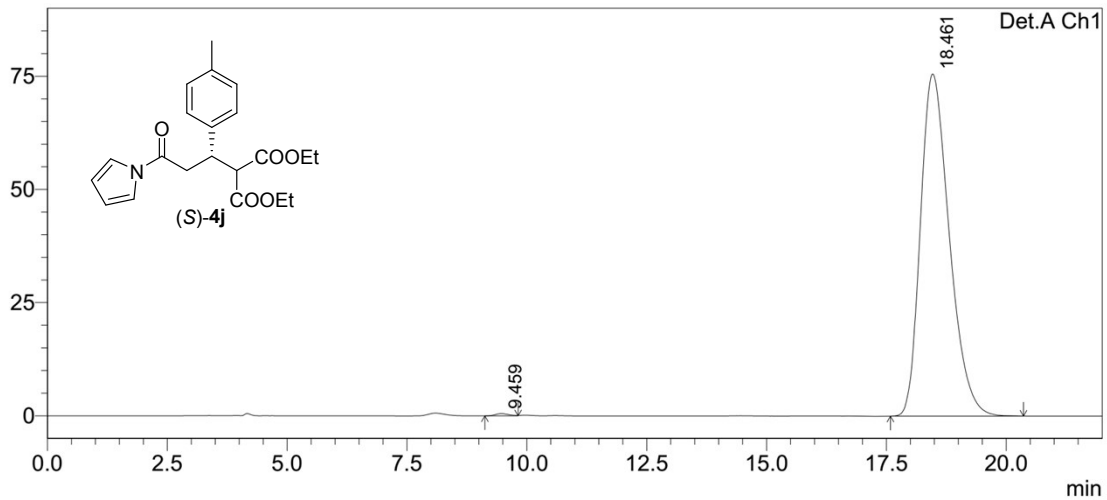


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.429	3038736	148291	98.515	99.239
2	18.335	45794	1137	1.485	0.761
Total		3084530	149427	100.000	100.000

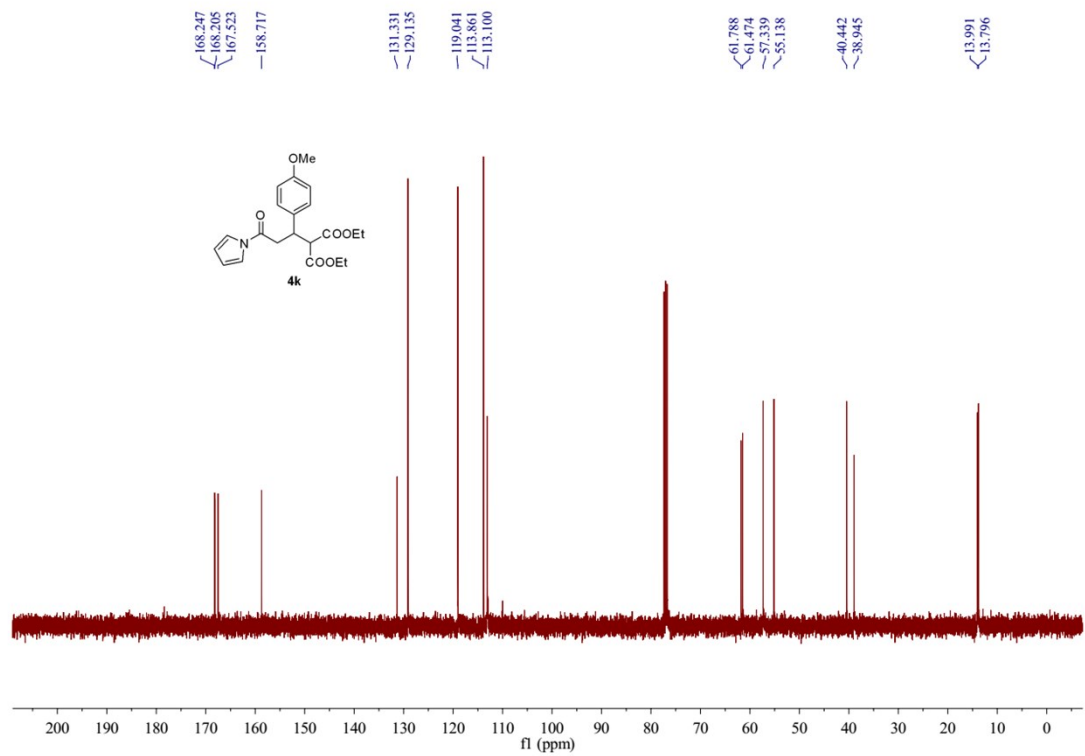
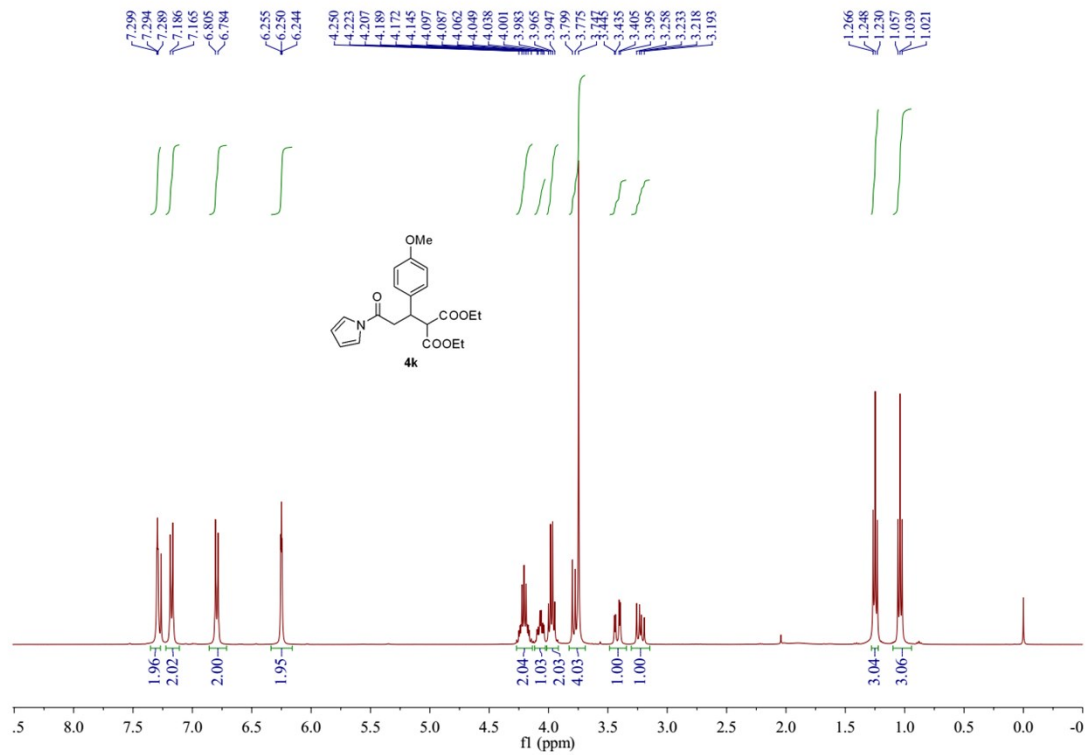


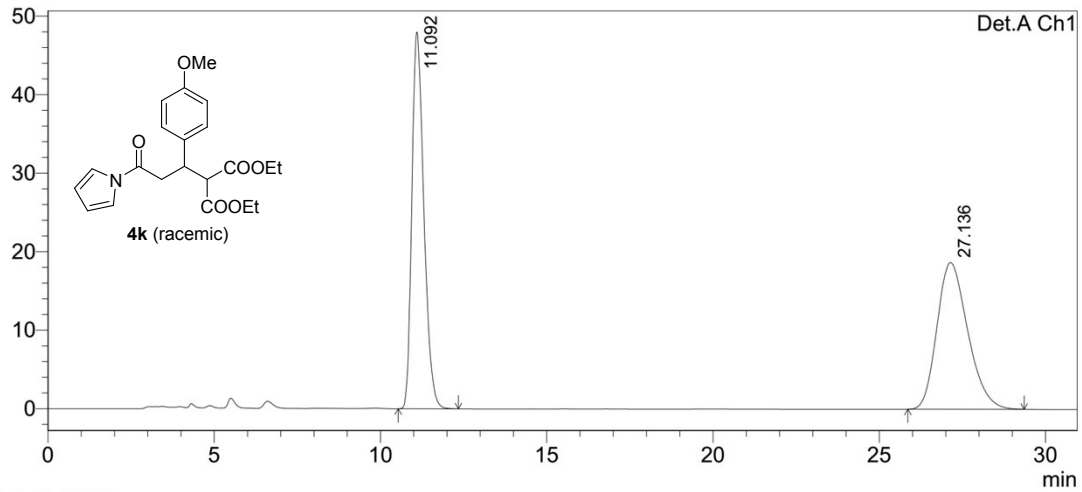
.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.459	10131	504	0.320	0.663
2	18.461	3159396	75573	99.680	99.337
Total		3169527	76078	100.000	100.000



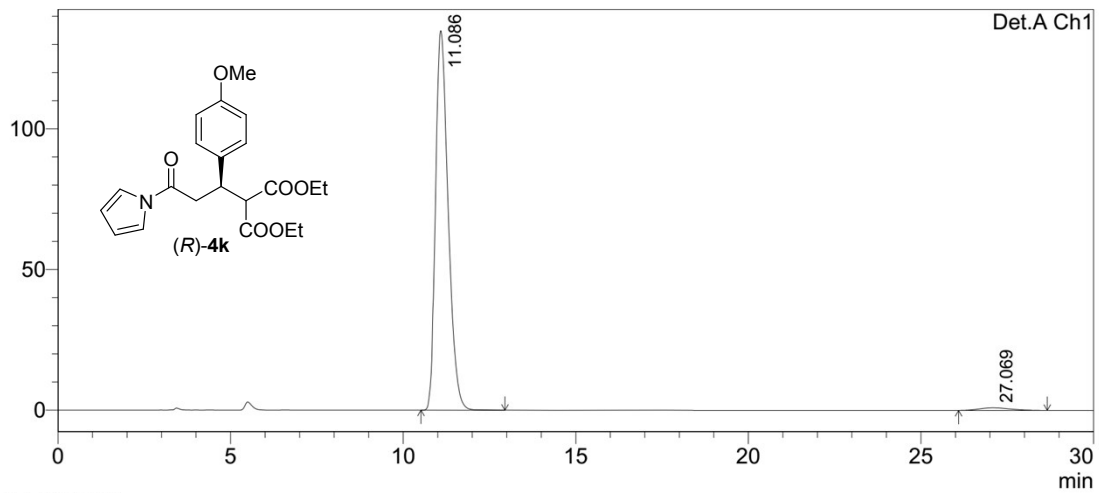


st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.092	1206290	47987	50.032	71.964
2	27.136	1204724	18695	49.968	28.036
Total		2411014	66682	100.000	100.000

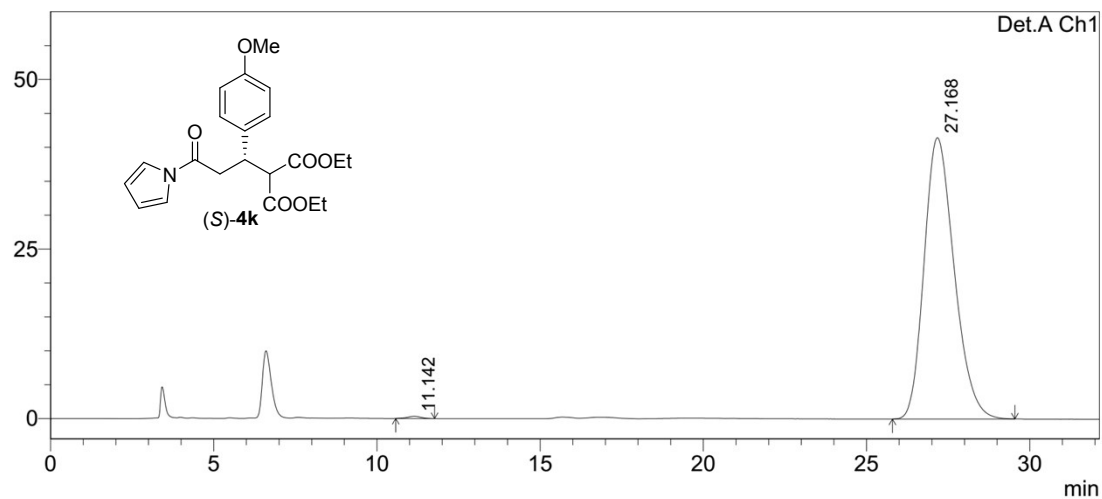


st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.086	3430238	134864	98.345	99.324
2	27.069	57717	918	1.655	0.676
Total		3487956	135782	100.000	100.000

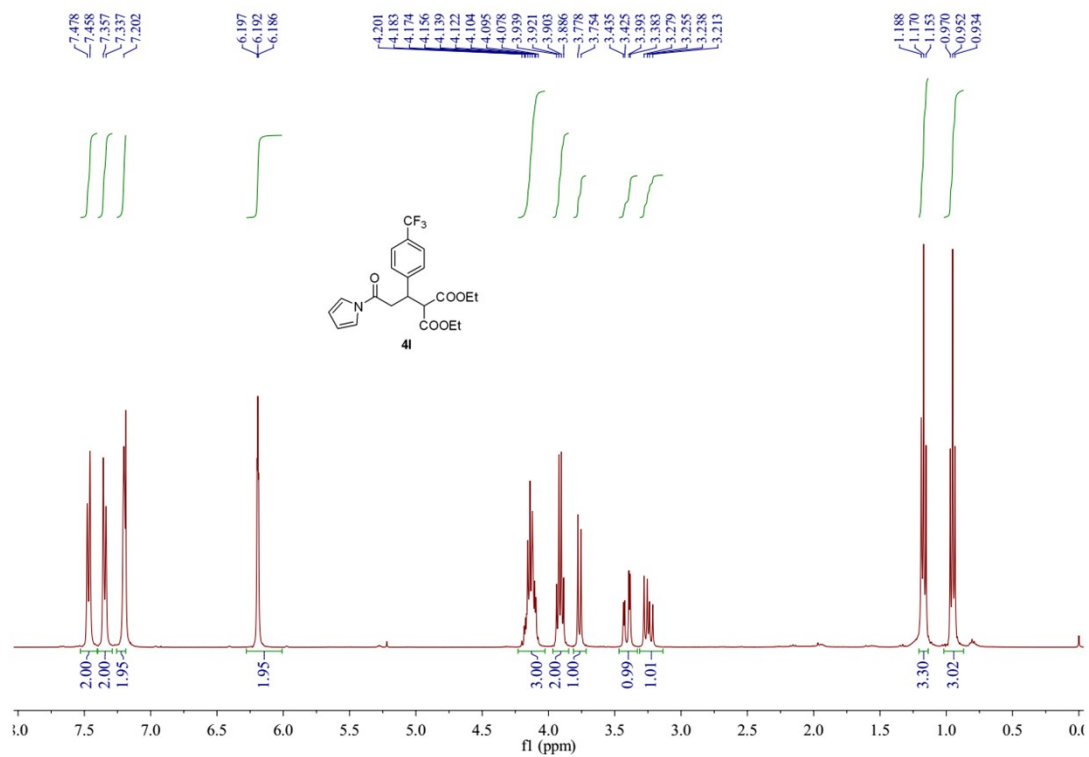


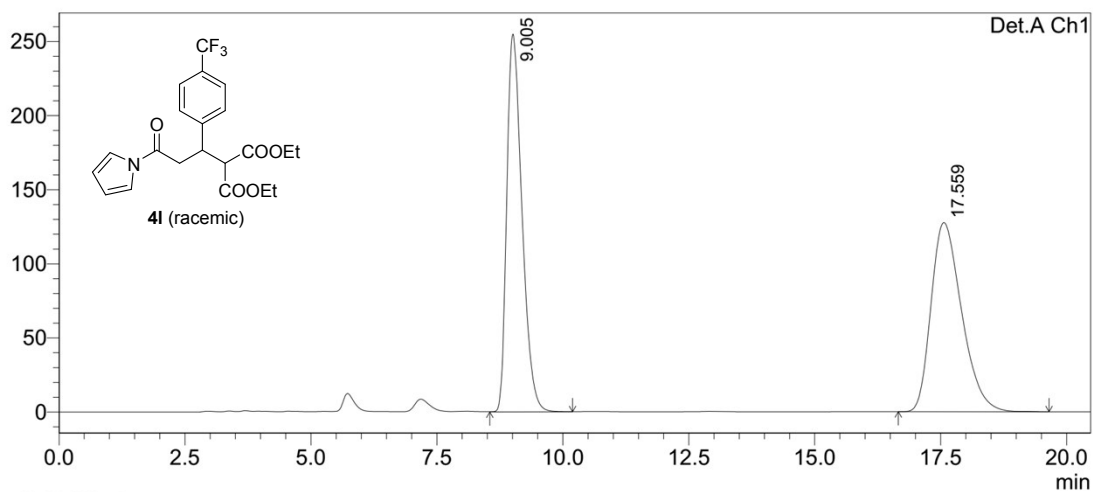
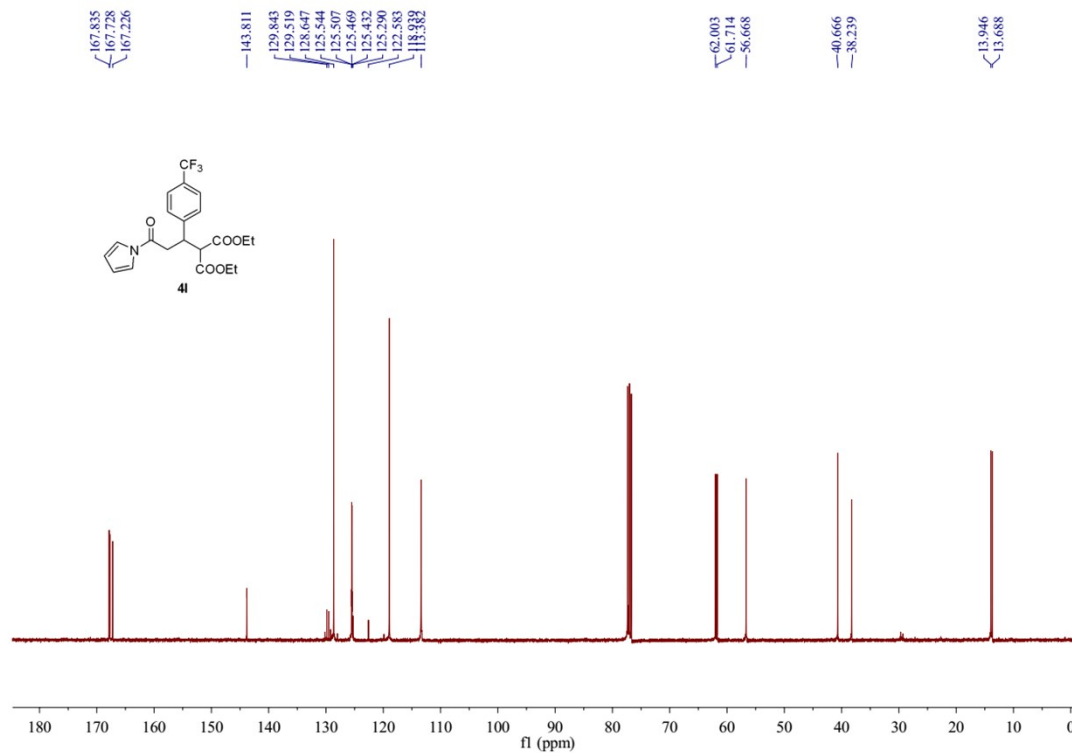
.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.142	9866	340	0.369	0.813
2	27.168	2660970	41484	99.631	99.187
Total		2670836	41825	100.000	100.000



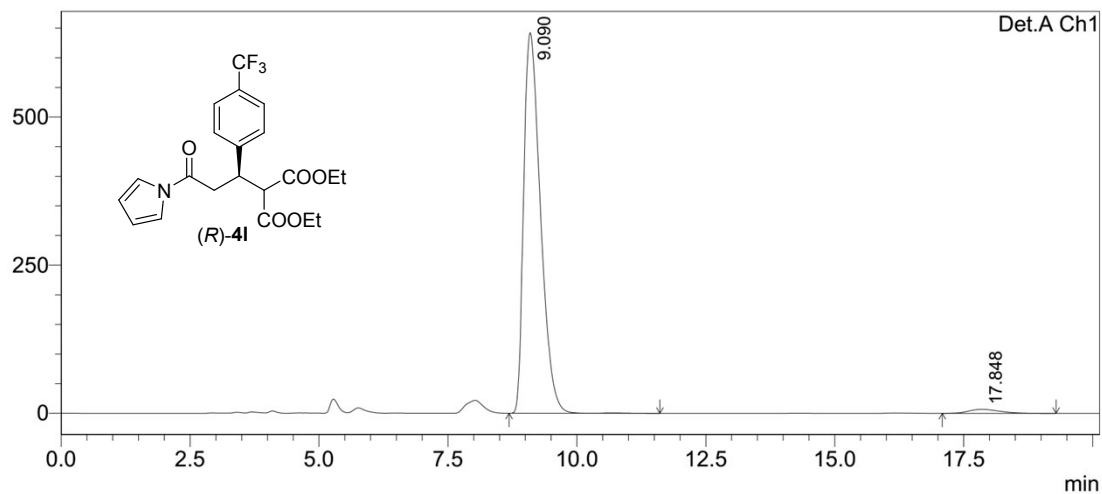


at.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.005	5363851	254902	49.839	66.634
2	17.559	5398407	127641	50.161	33.366
Total		10762258	382543	100.000	100.000

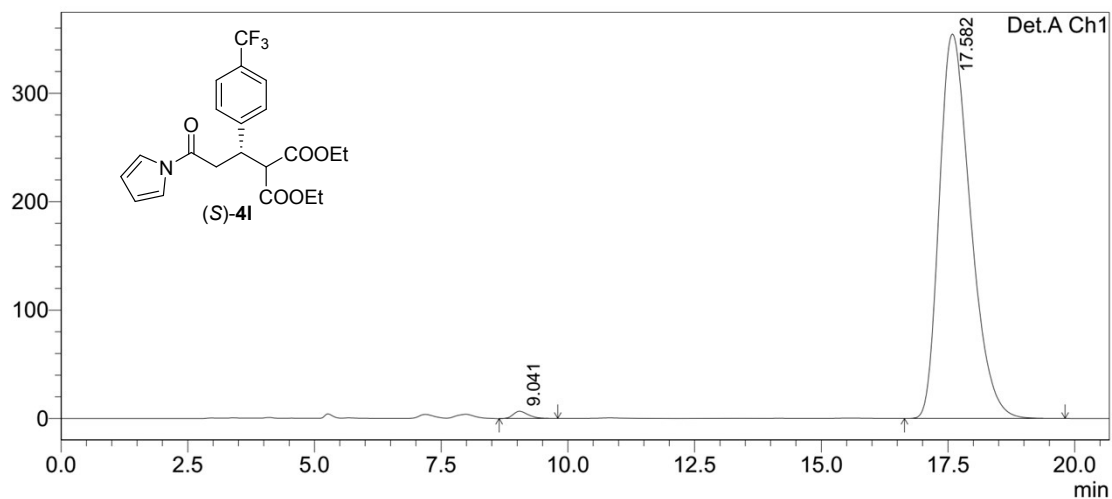


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.090	14508361	642347	98.102	98.963
2	17.848	280752	6734	1.898	1.037
Total		14789113	649081	100.000	100.000

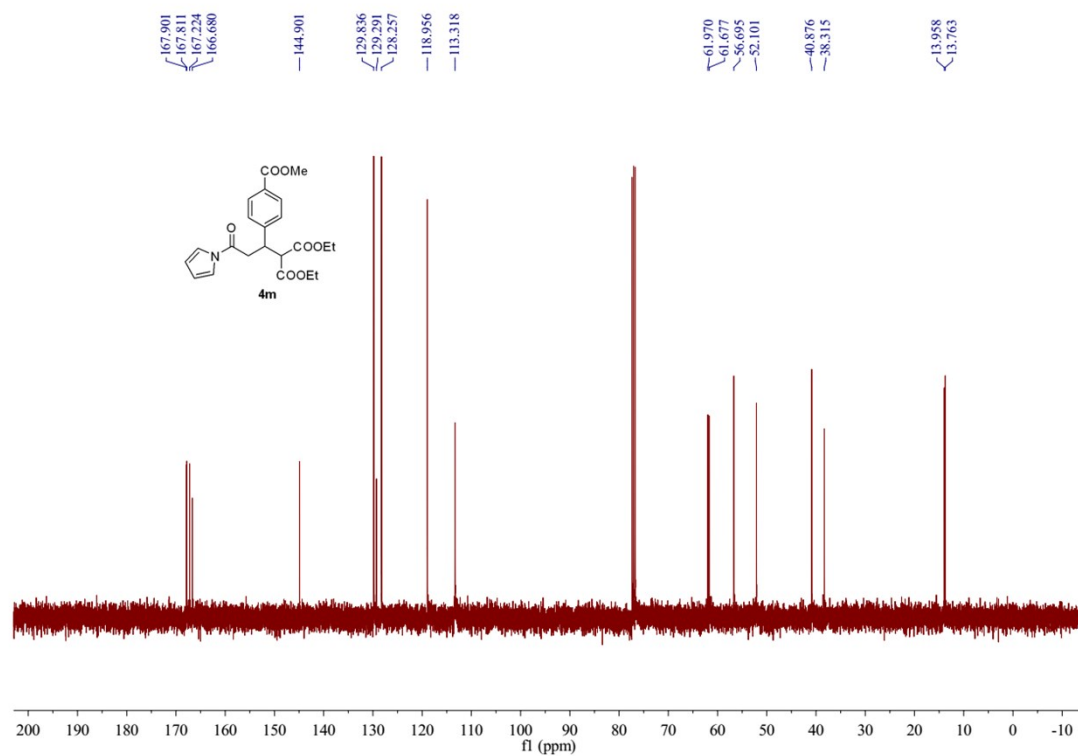
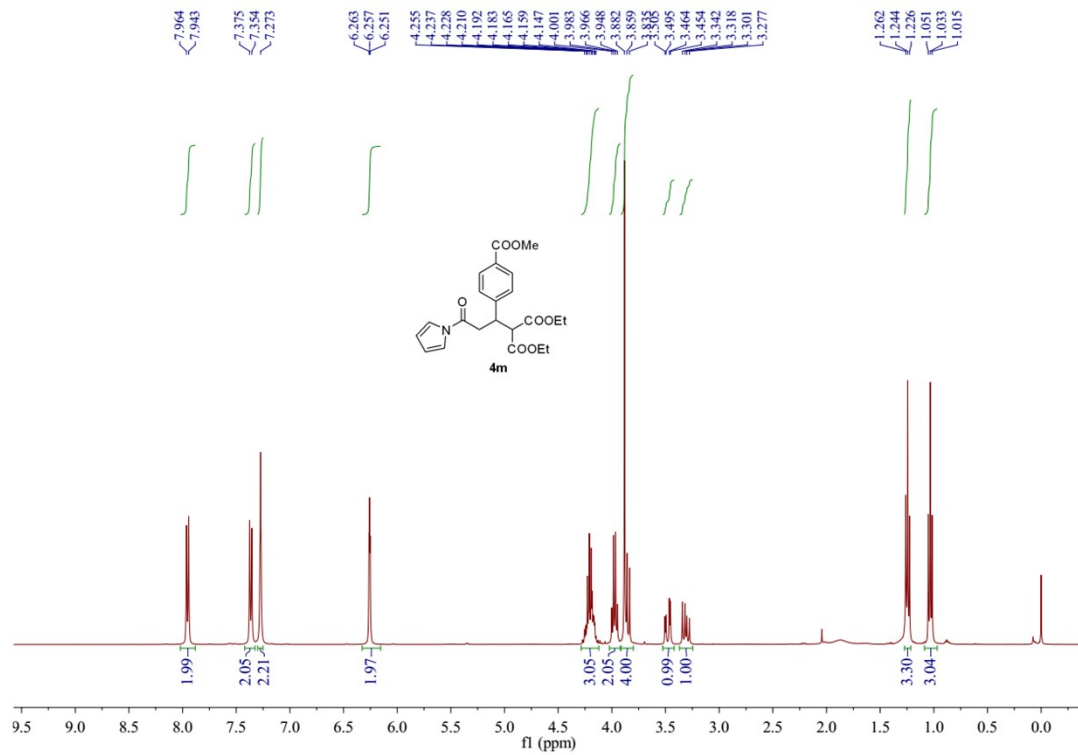


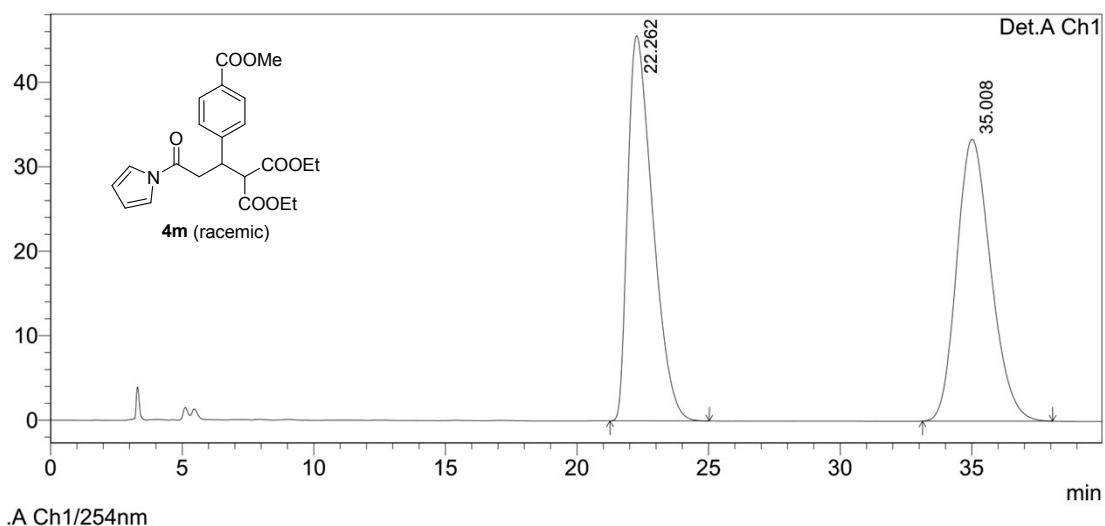
t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.041	134064	6569	0.875	1.819
2	17.582	15184545	354614	99.125	98.181
Total		15318609	361183	100.000	100.000



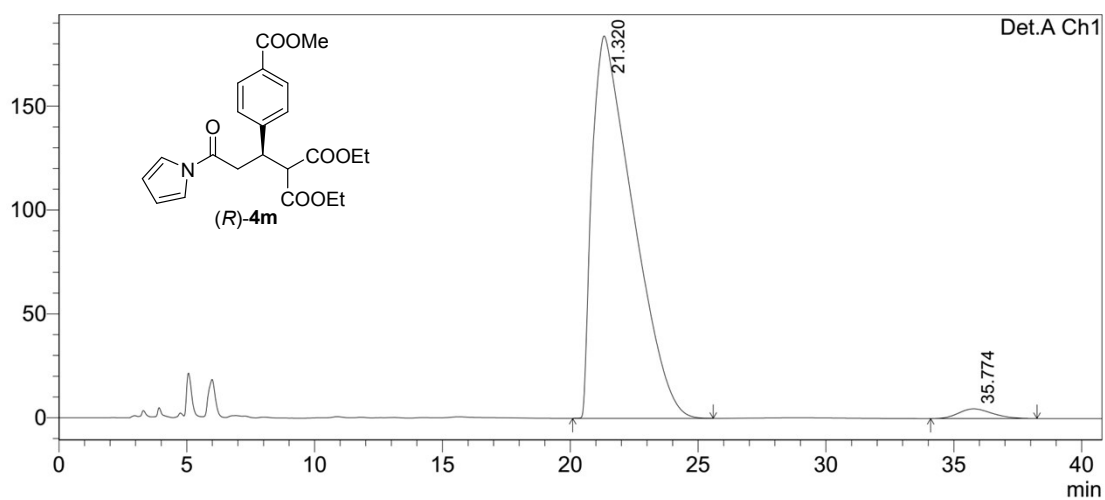


.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.262	3009357	45583	49.999	57.745
2	35.008	3009519	33355	50.001	42.255
Total		6018876	78938	100.000	100.000

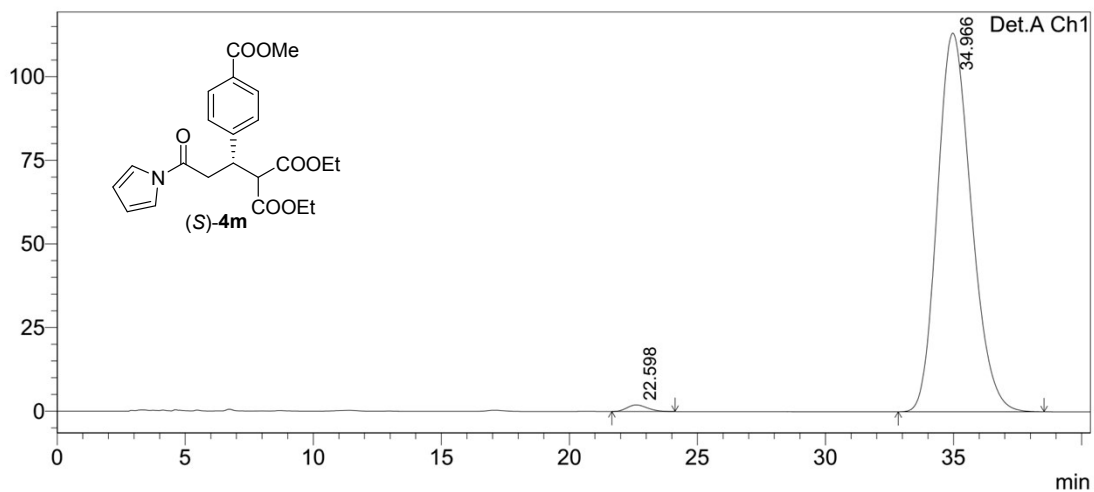


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.320	20392234	184032	97.938	97.529
2	35.774	429277	4663	2.062	2.471
Total		20821512	188696	100.000	100.000

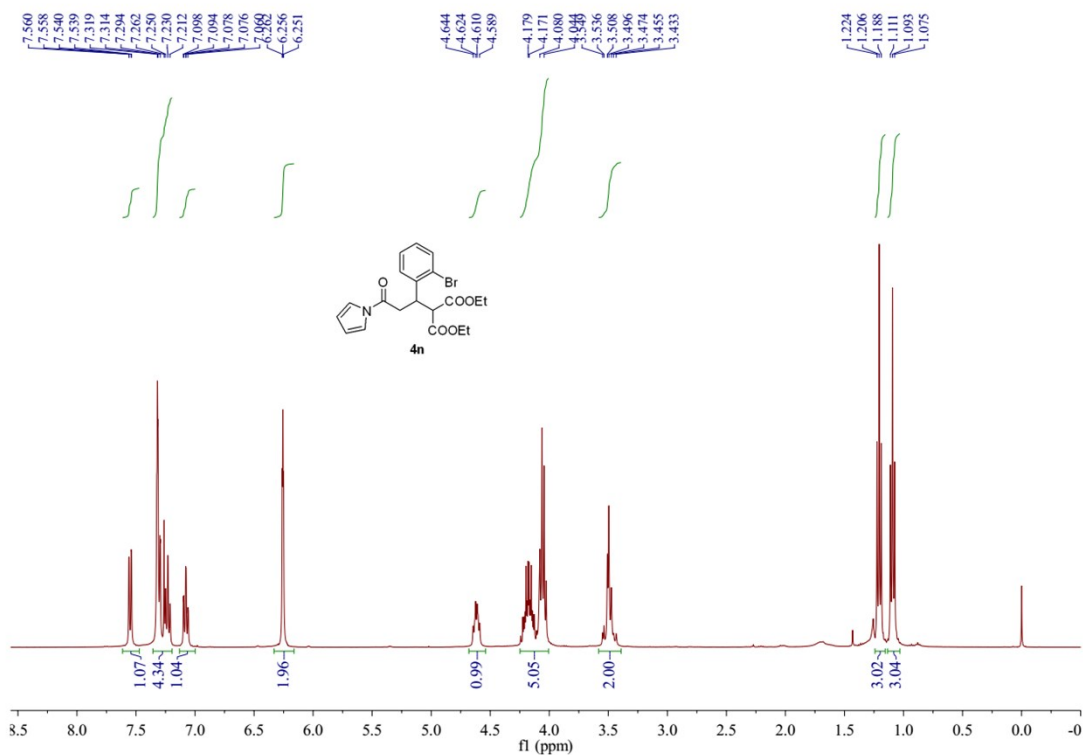


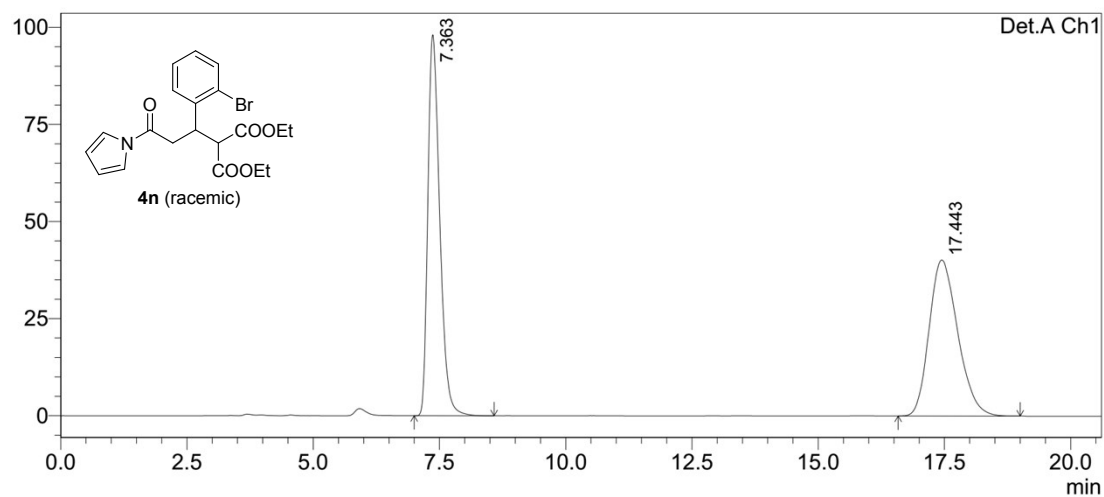
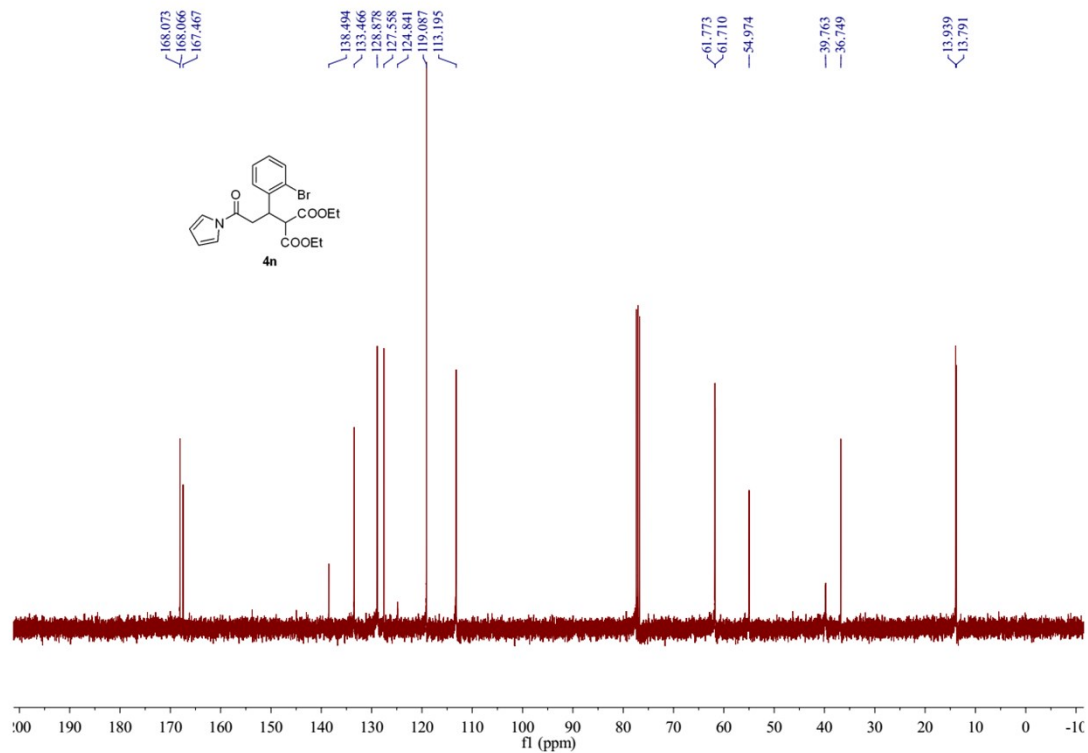
at.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.598	108392	1953	1.028	1.696
2	34.966	10437956	113207	98.972	98.304
Total		10546348	115160	100.000	100.000



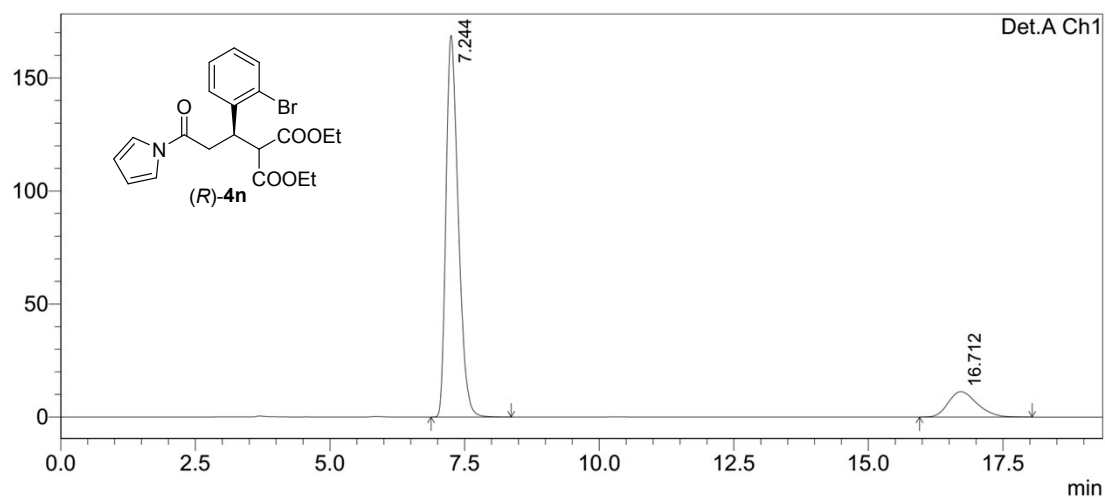


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.363	1605933	98124	50.338	70.947
2	17.443	1584394	40183	49.662	29.053
Total		3190327	138307	100.000	100.000

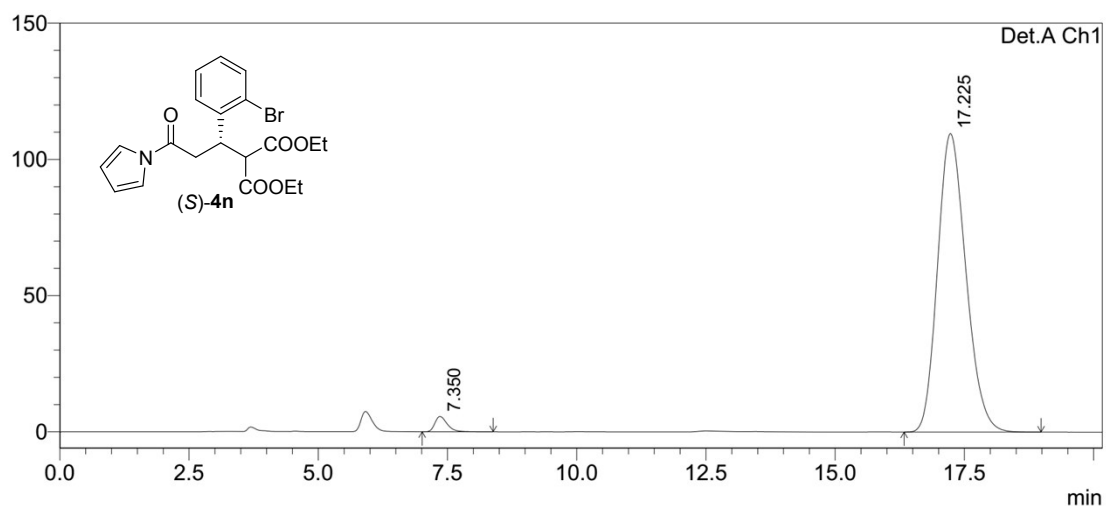


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.244	2681275	168851	86.481	93.750
2	16.712	419161	11257	13.519	6.250
Total		3100435	180108	100.000	100.000

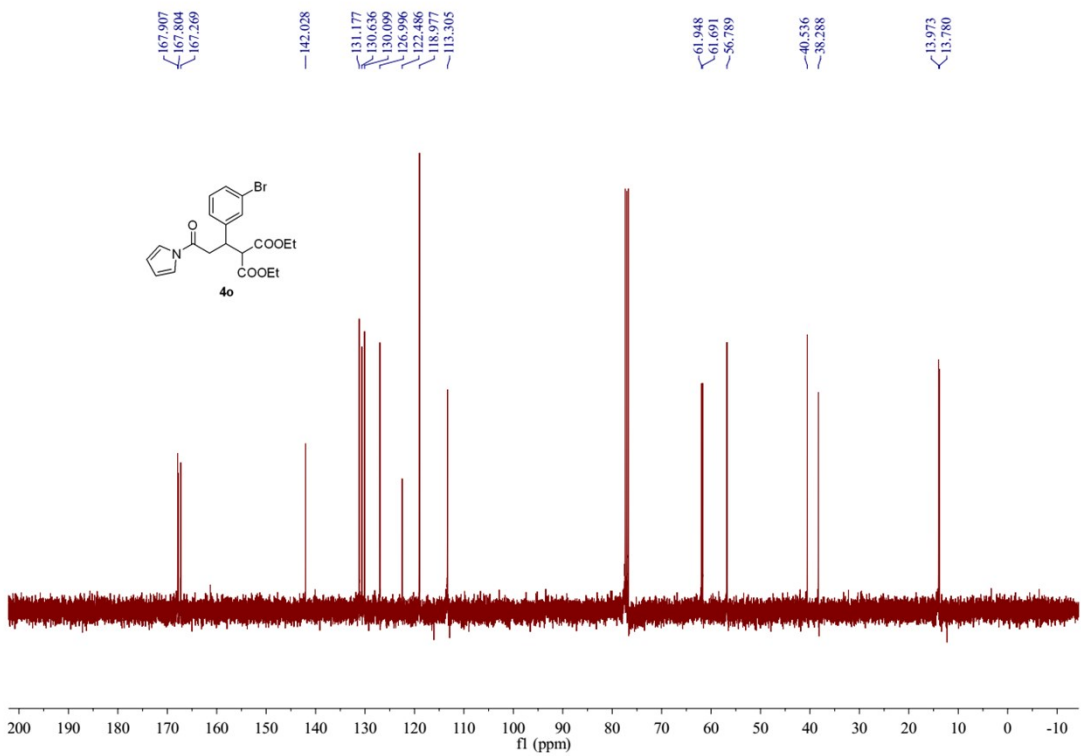
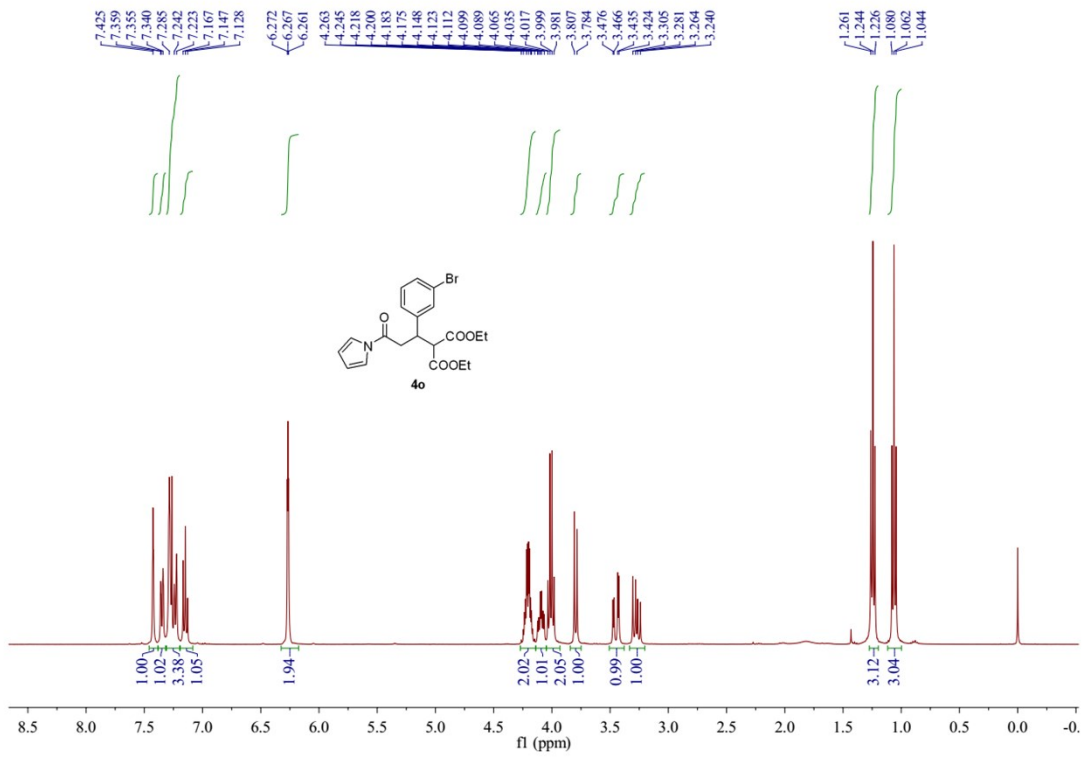


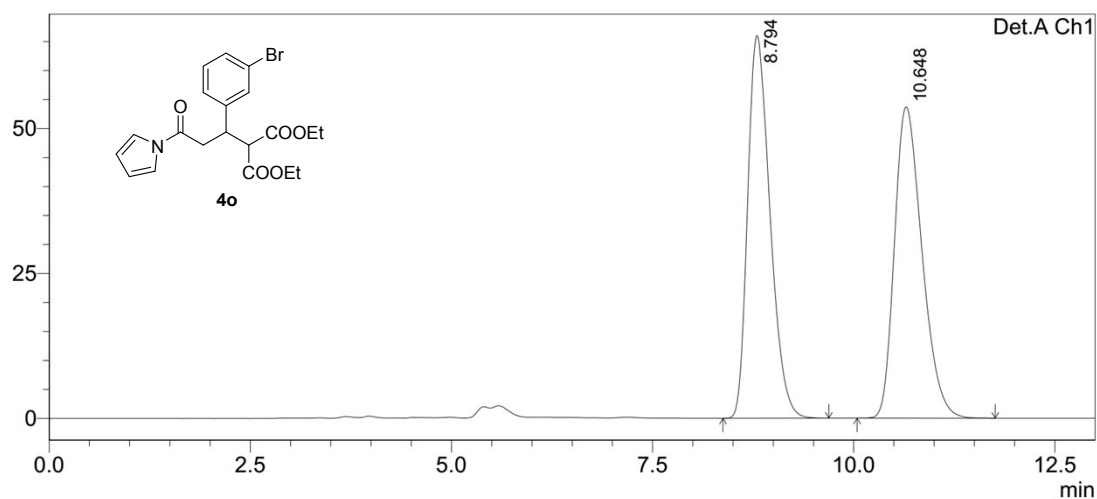
t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.350	93263	5620	2.184	4.880
2	17.225	4176835	109548	97.816	95.120
Total		4270098	115167	100.000	100.000



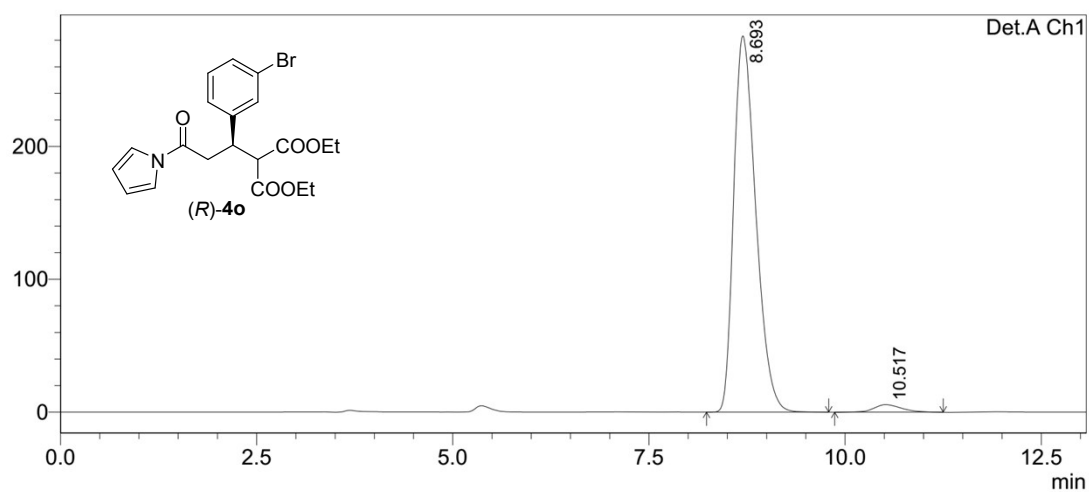


.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.794	1276672	66017	49.954	55.145
2	10.648	1279033	53698	50.046	44.855
Total		2555705	119715	100.000	100.000

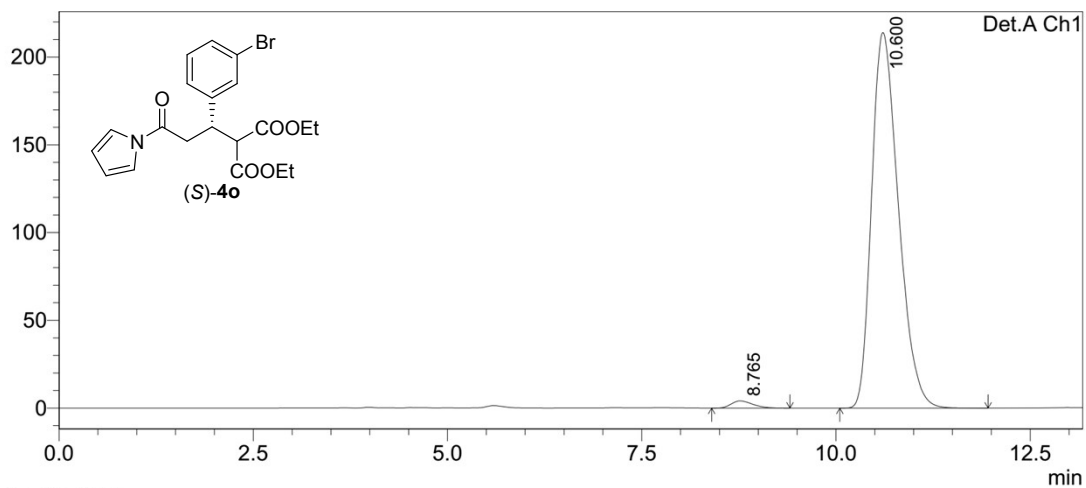


it.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

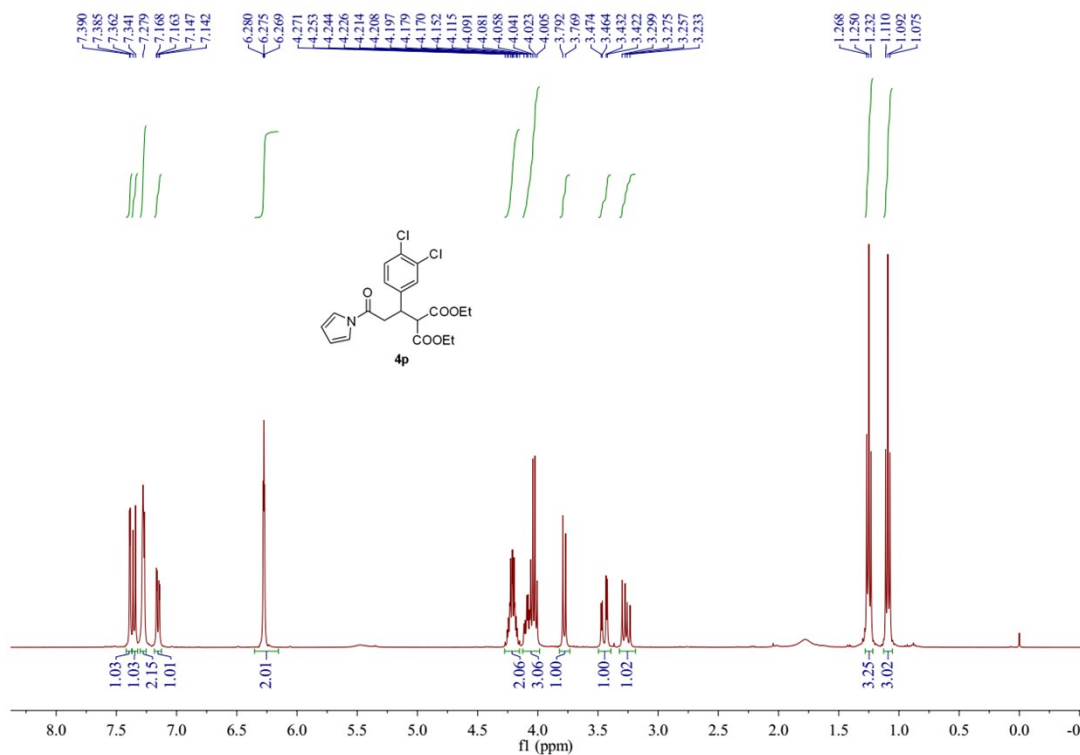
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.693	5545028	283249	97.668	98.061
2	10.517	132423	5600	2.332	1.939
Total		5677450	288849	100.000	100.000

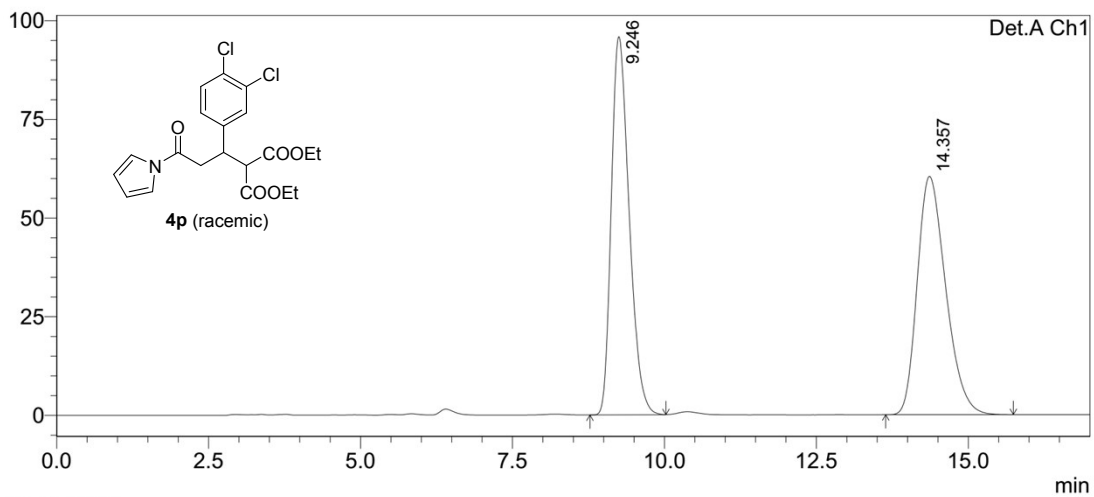
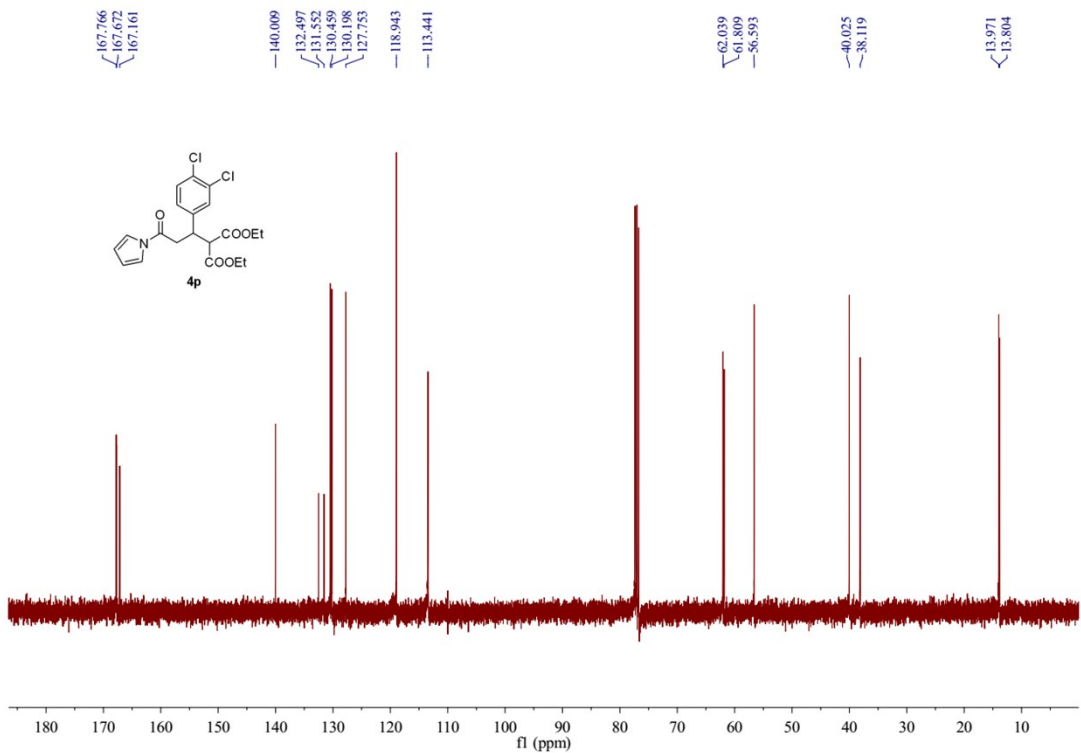


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.765	78368	4098	1.502	1.879
2	10.600	5138628	213964	98.498	98.121
Total		5216996	218062	100.000	100.000



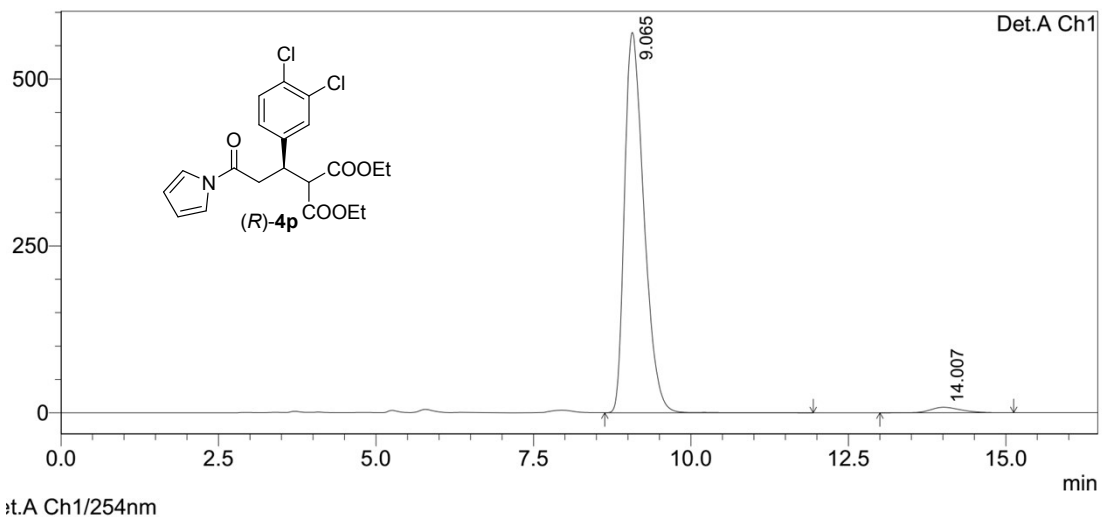


Det. A Ch1/254nm

PeakTable

Detector A Ch1 254nm

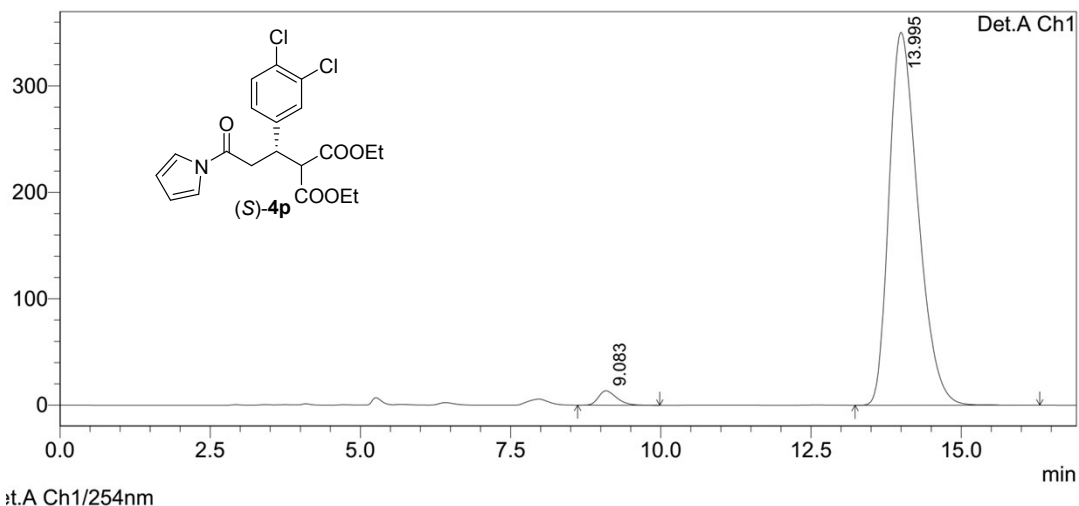
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.246	1959133	95883	49.908	61.358
2	14.357	1966338	60385	50.092	38.642
Total		3925471	156267	100.000	100.000



PeakTable

Detector A Ch1 254nm

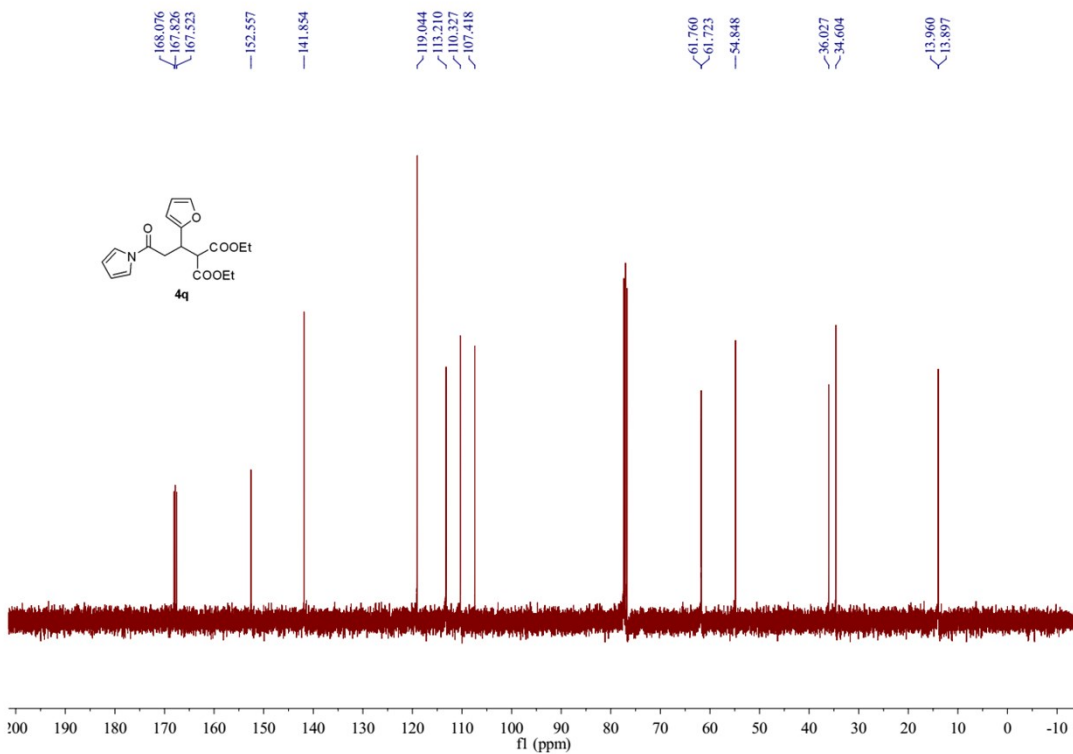
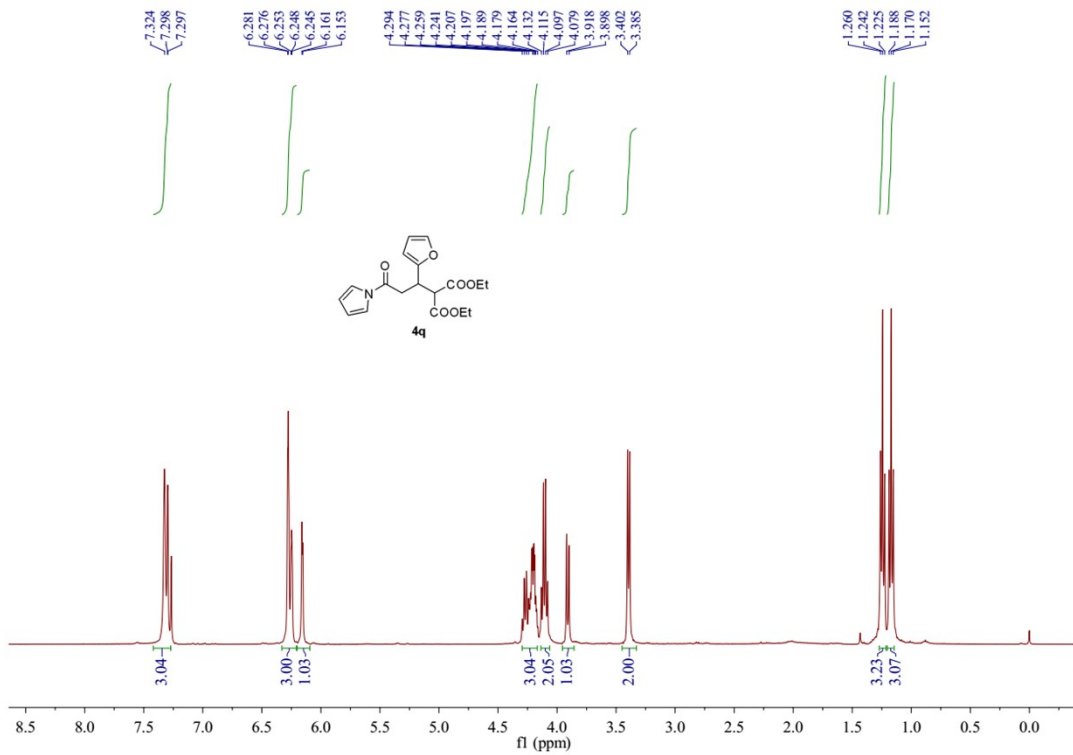
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.065	12194936	569798	97.802	98.573
2	14.007	274068	8248	2.198	1.427
Total		12469004	578046	100.000	100.000

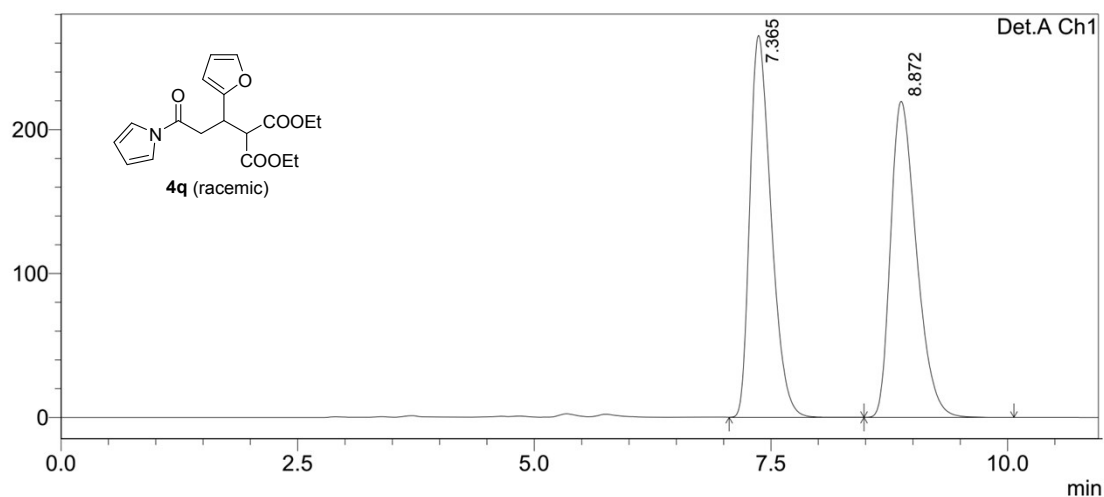


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.083	281349	13486	2.332	3.706
2	13.995	11782398	350370	97.668	96.294
Total		12063748	363856	100.000	100.000



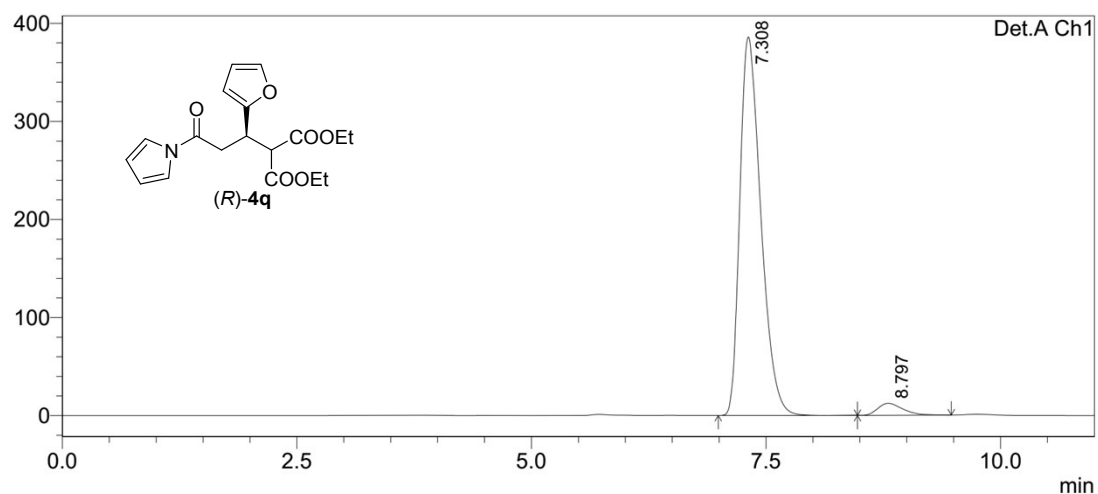


st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.365	4150090	265446	49.799	54.711
2	8.872	4183615	219728	50.201	45.289
Total		8333705	485174	100.000	100.000

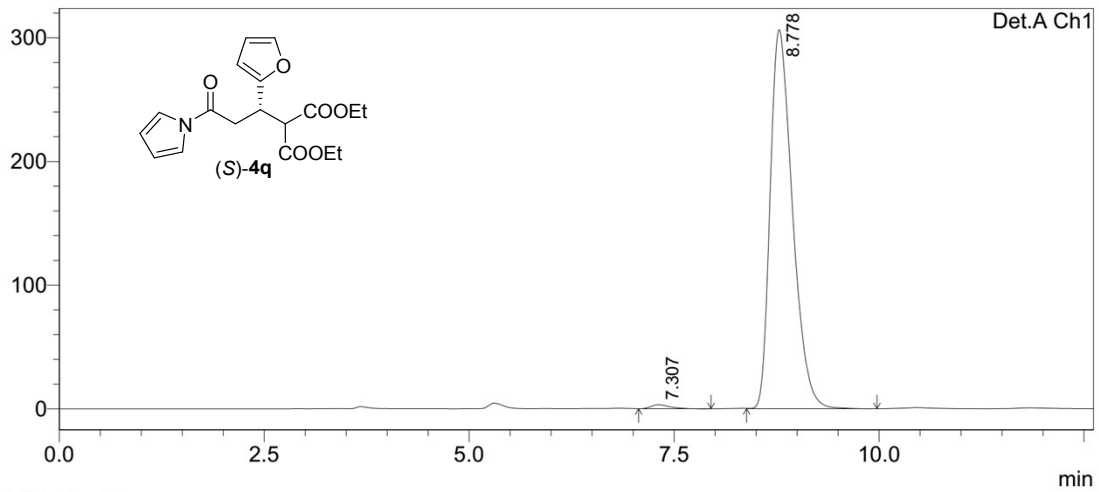


st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.308	6010711	385930	96.345	96.921
2	8.797	228036	12262	3.655	3.079
Total		6238747	398192	100.000	100.000

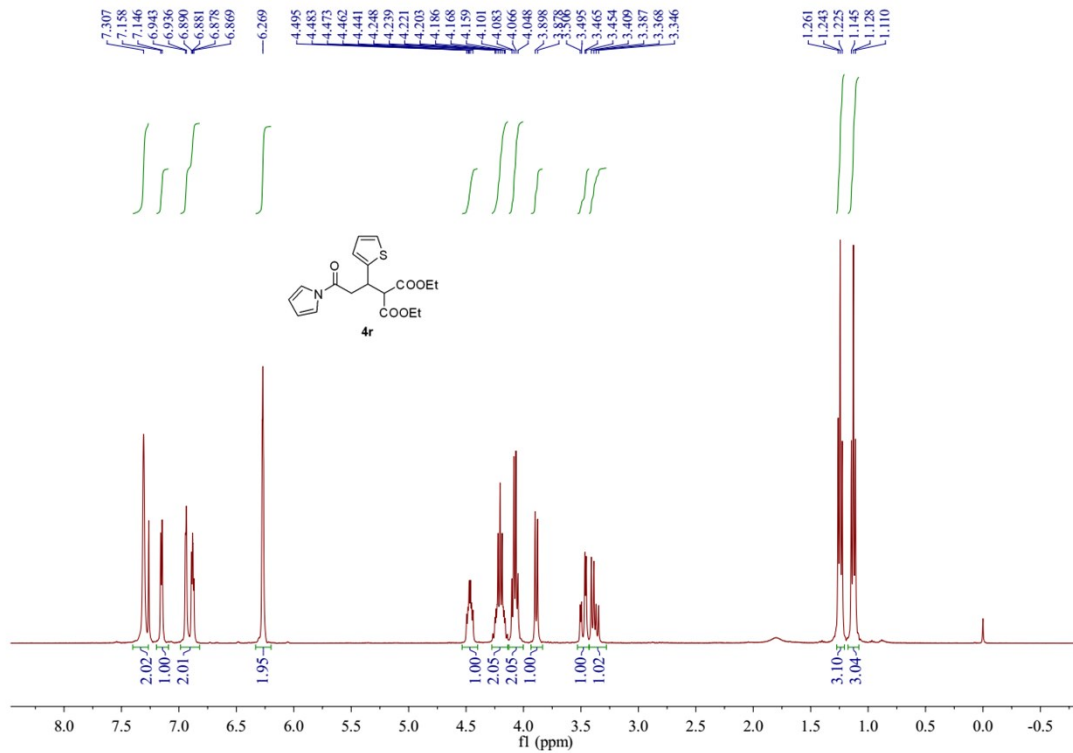


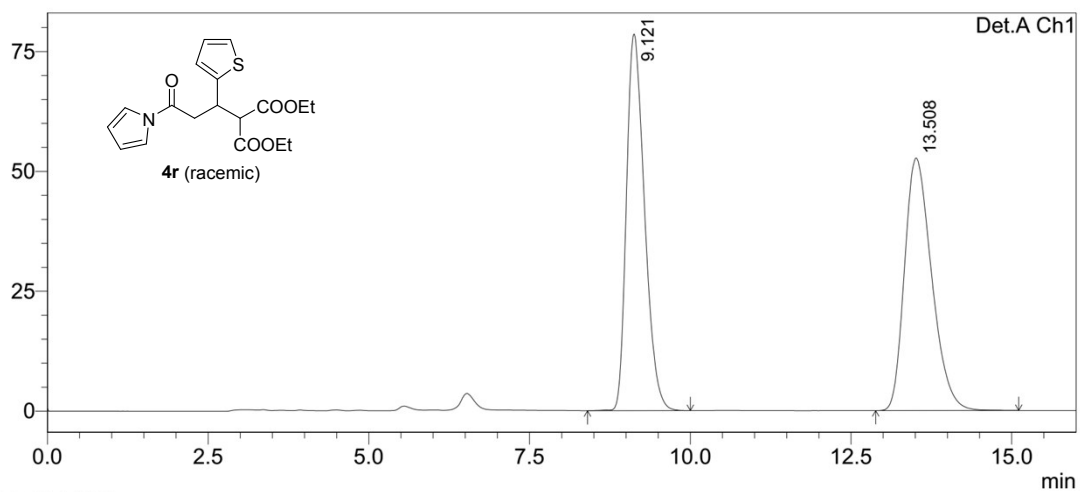
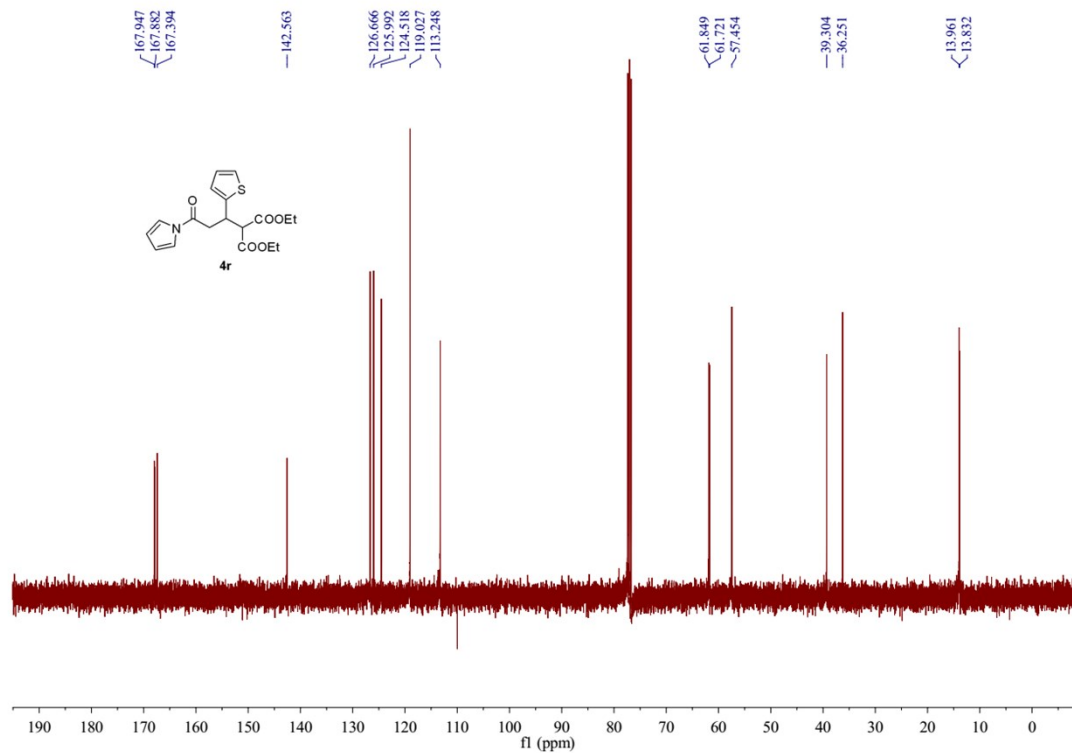
at.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.307	49536	3210	0.848	1.037
2	8.778	5789552	306463	99.152	98.963
Total		5839088	309673	100.000	100.000



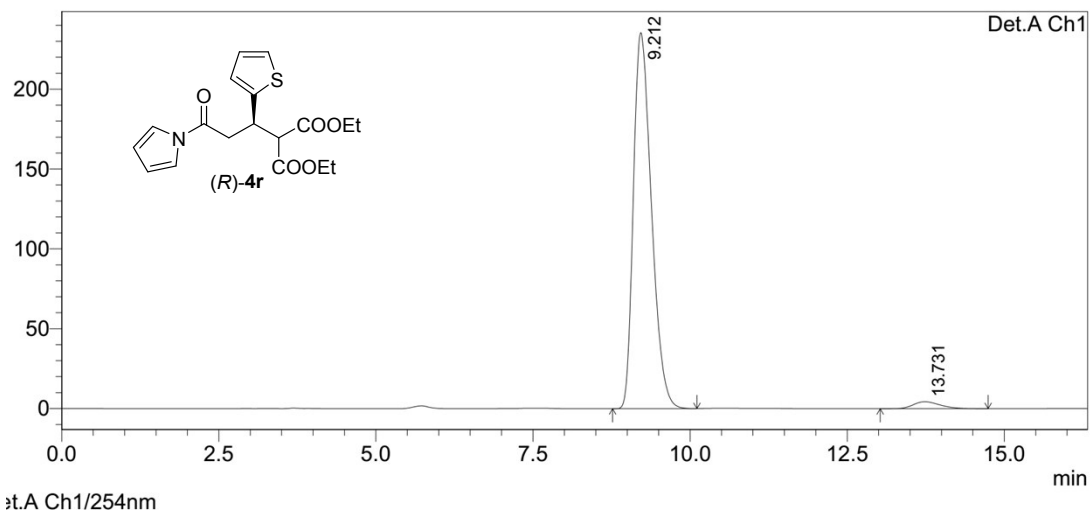


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.121	1539956	78554	49.851	59.869
2	13.508	1549156	52656	50.149	40.131
Total		3089112	131209	100.000	100.000

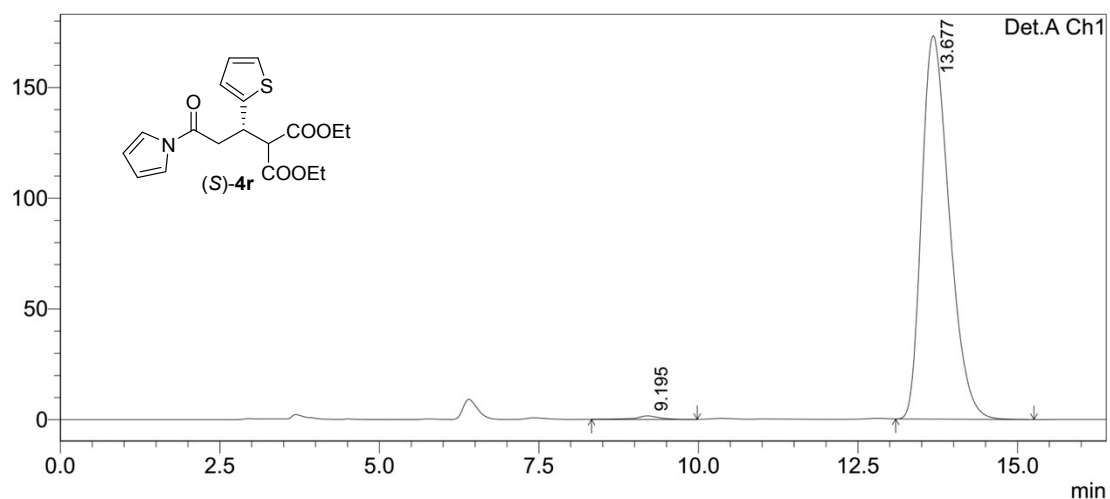


Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.212	4710976	235522	97.315	98.180
2	13.731	129986	4367	2.685	1.820
Total		4840962	239889	100.000	100.000

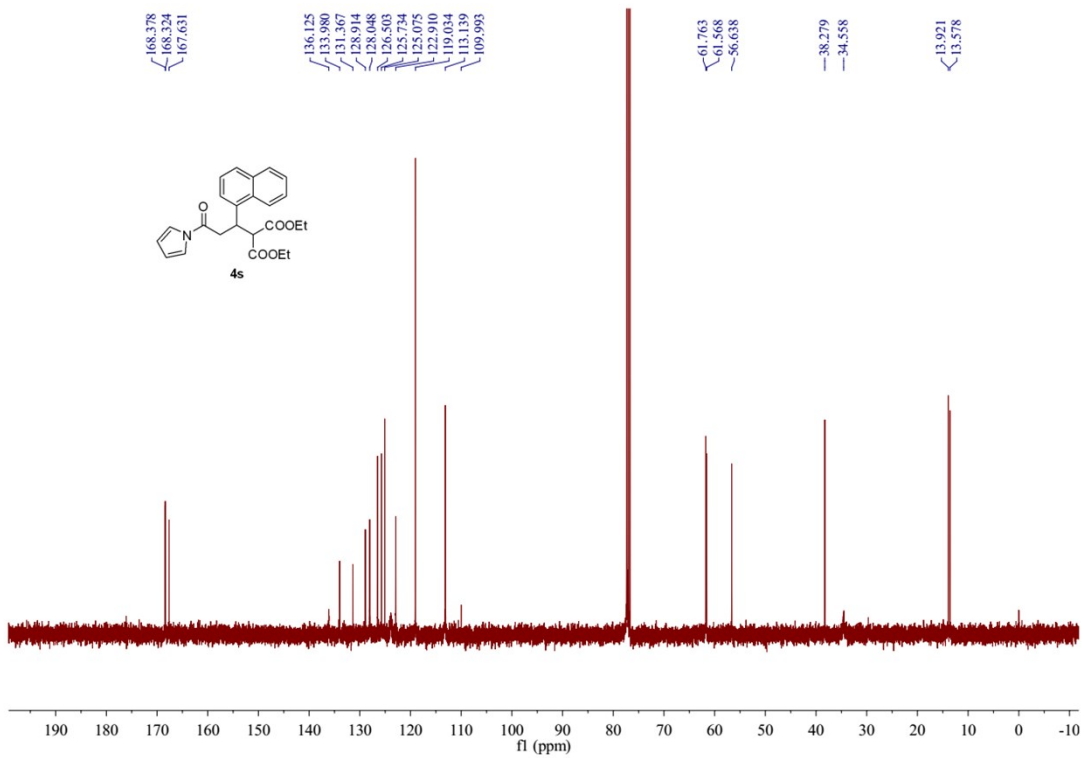
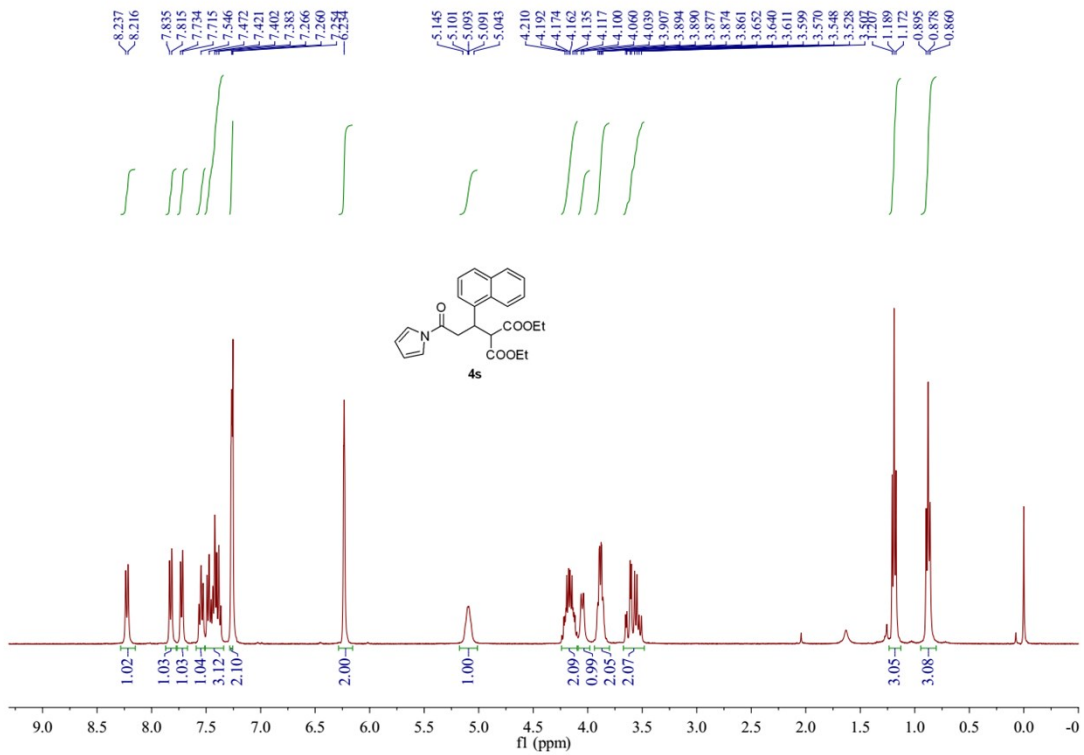


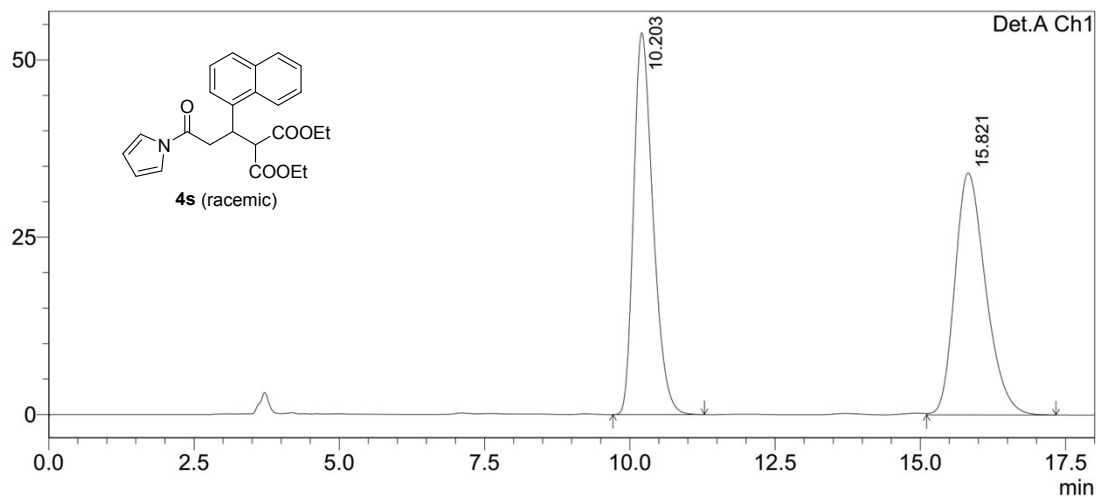
Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.195	39089	1574	0.745	0.902
2	13.677	5206564	173034	99.255	99.098
Total		5245653	174608	100.000	100.000



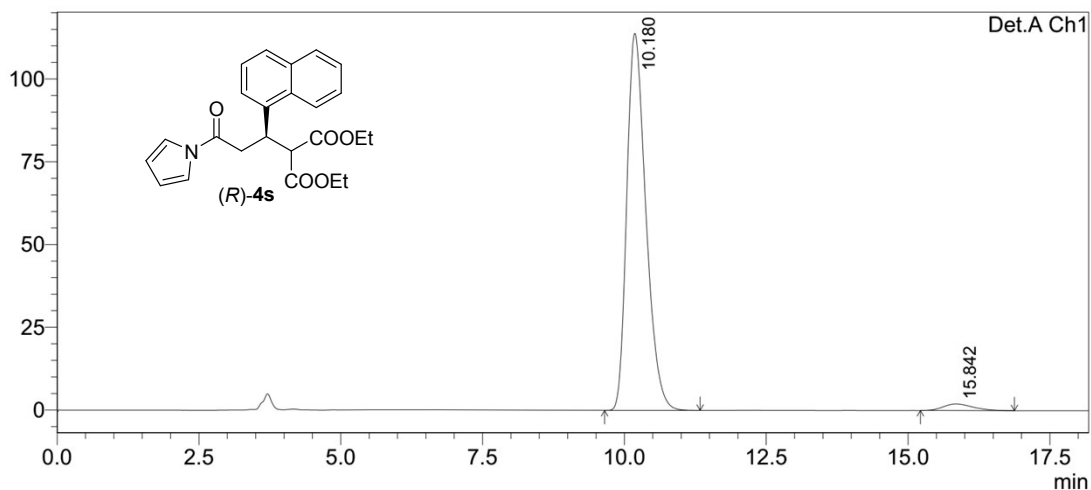


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.203	1251415	53848	49.830	61.206
2	15.821	1259958	34131	50.170	38.794
Total		2511373	87980	100.000	100.000

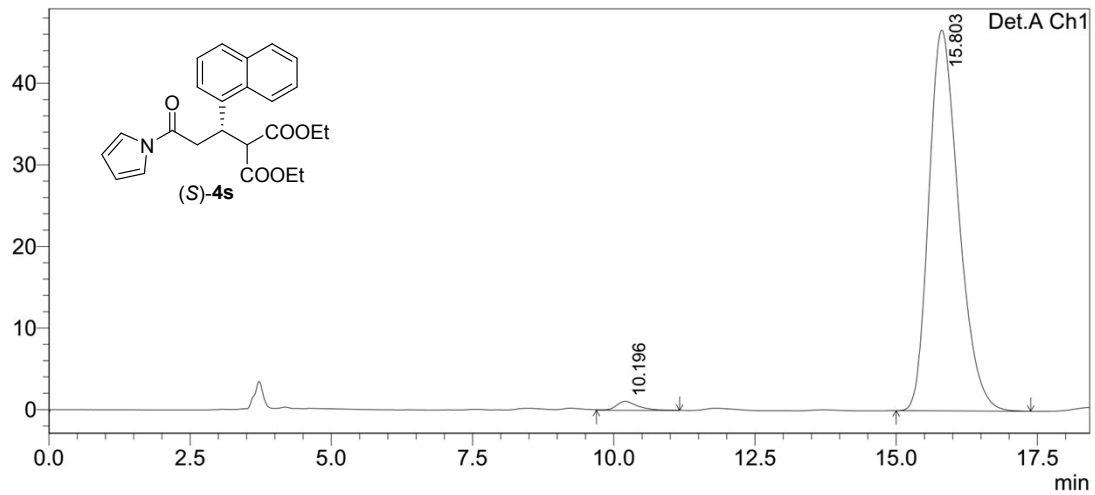


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.180	2669125	113900	97.364	98.278
2	15.842	72252	1995	2.636	1.722
Total		2741377	115896	100.000	100.000

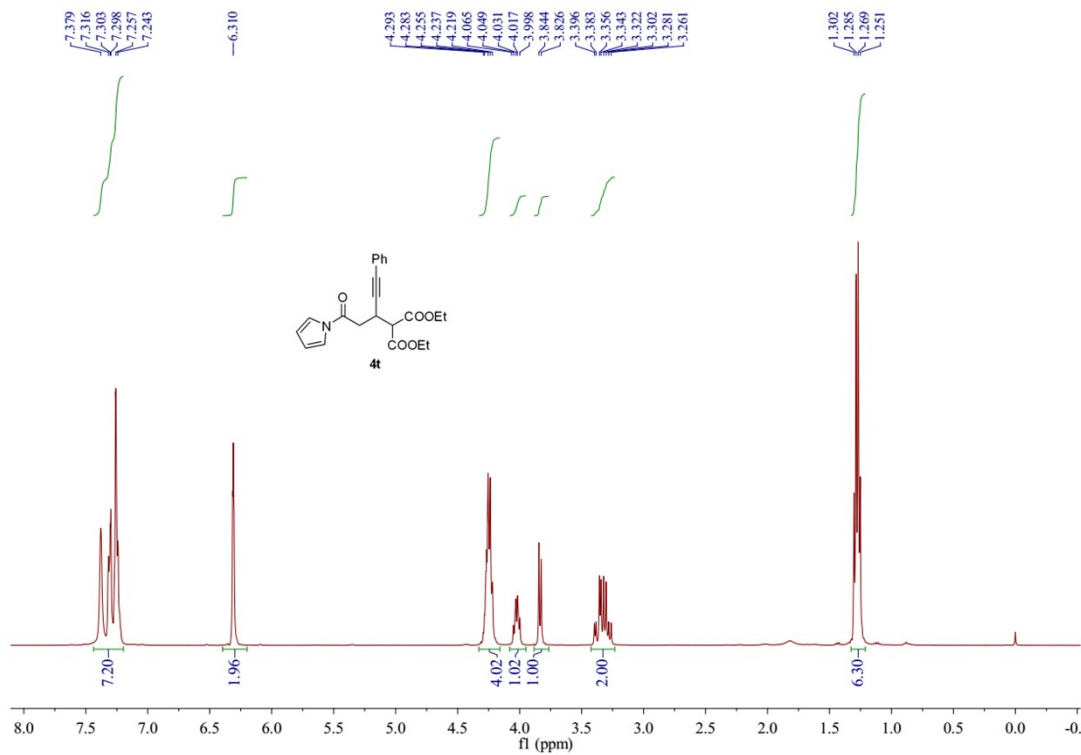


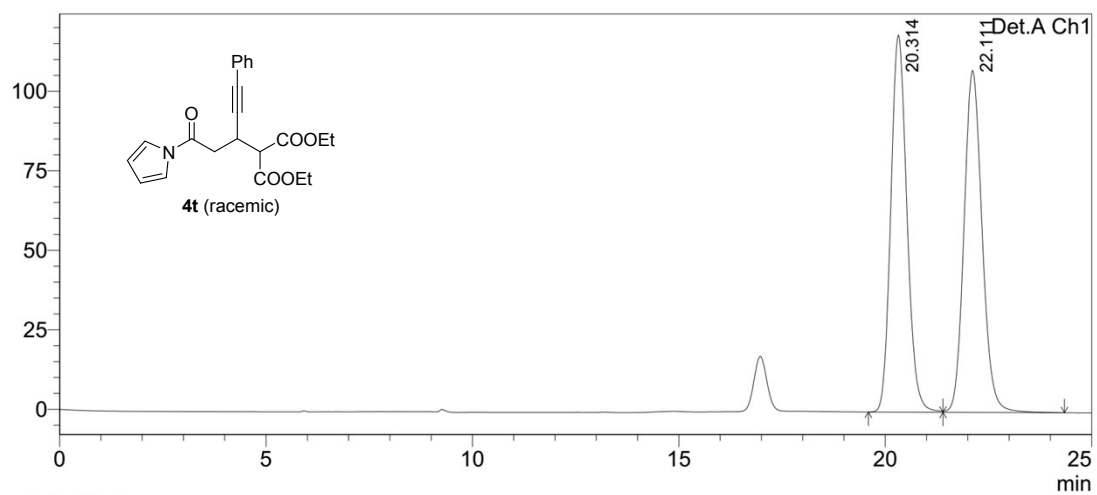
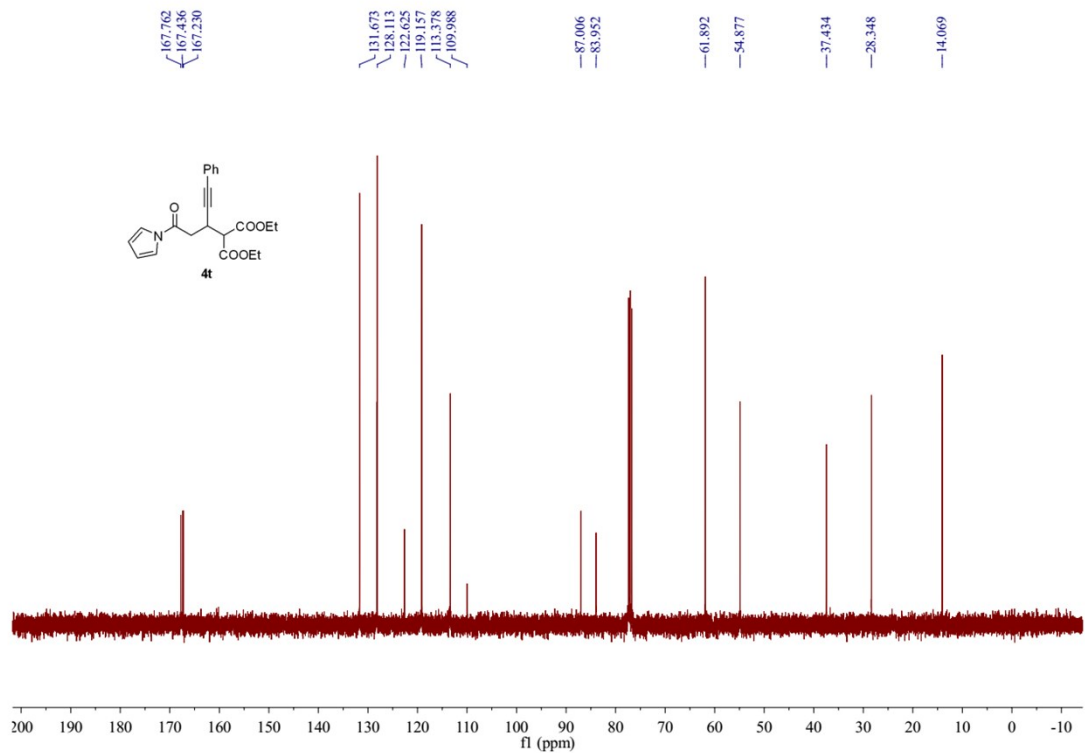
.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.196	29538	1109	1.693	2.321
2	15.803	1715658	46661	98.307	97.679
Total		1745195	47769	100.000	100.000



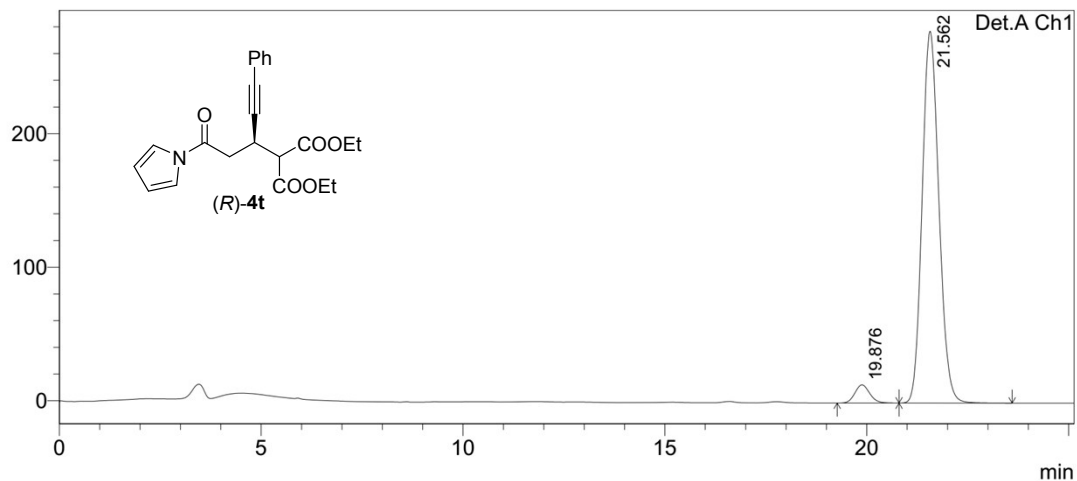


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.314	3215070	118552	49.490	52.439
2	22.111	3281296	107522	50.510	47.561
Total		6496366	226075	100.000	100.000

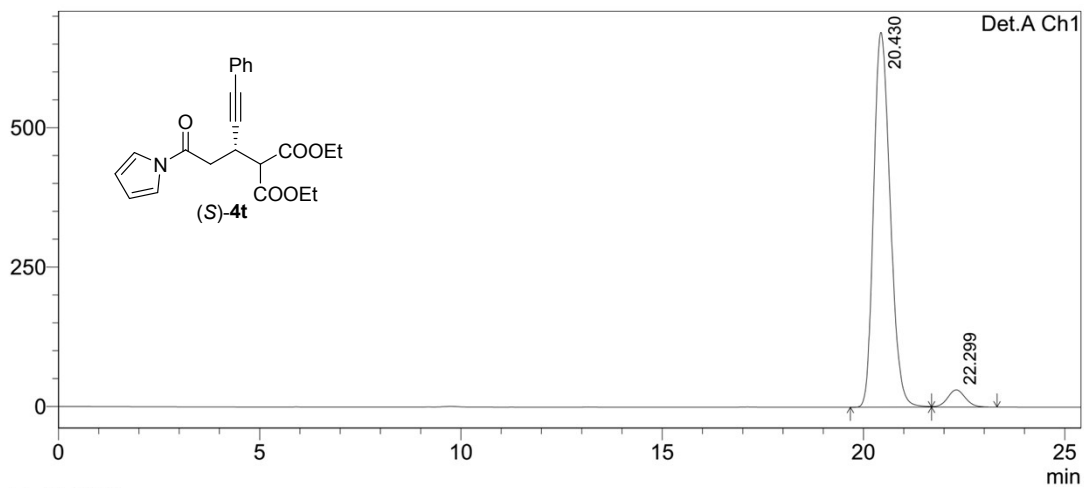


et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.876	346688	13638	4.149	4.668
2	21.562	8009058	278522	95.851	95.332
Total		8355746	292161	100.000	100.000

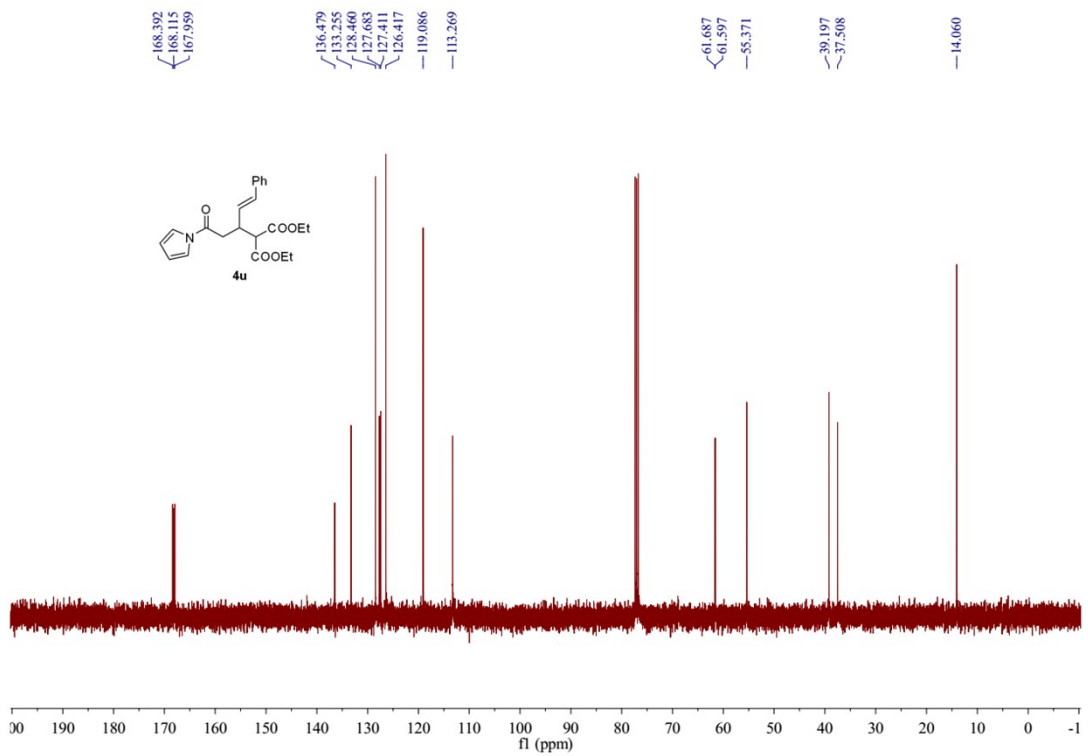
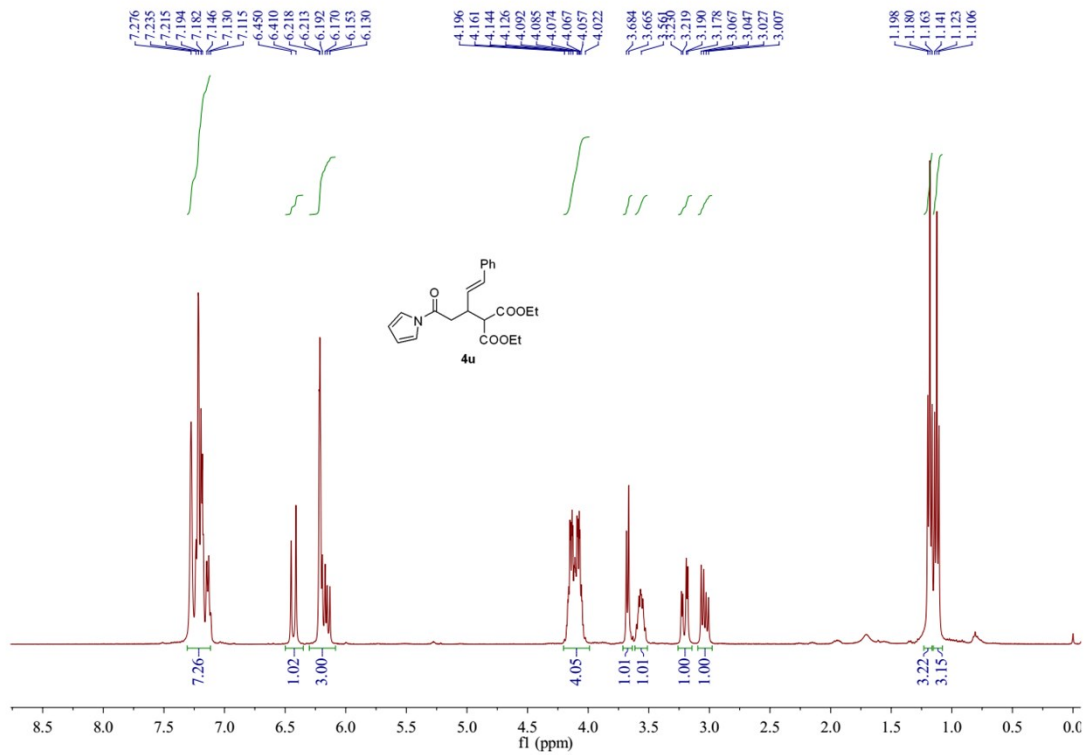


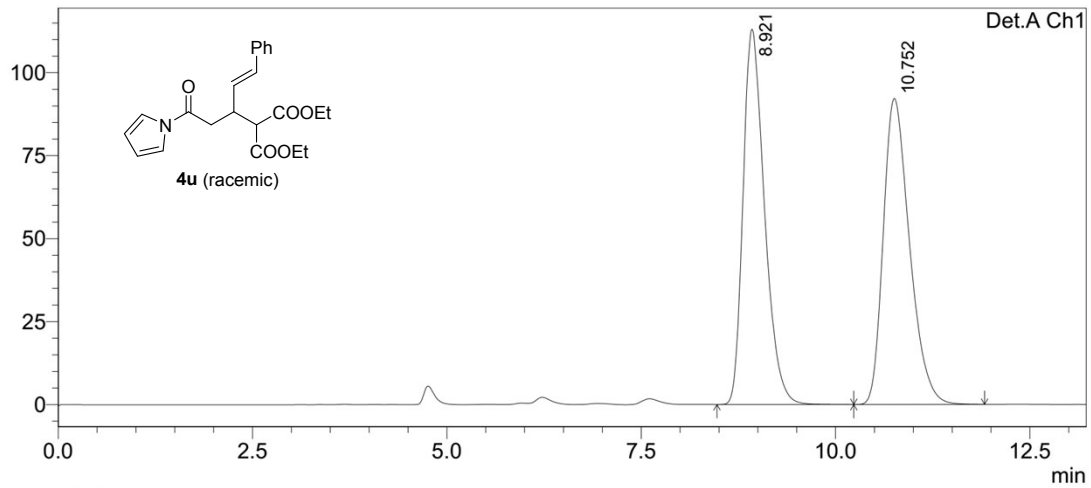
et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.430	19221714	672691	95.291	95.598
2	22.299	949936	30975	4.709	4.402
Total		20171649	703666	100.000	100.000



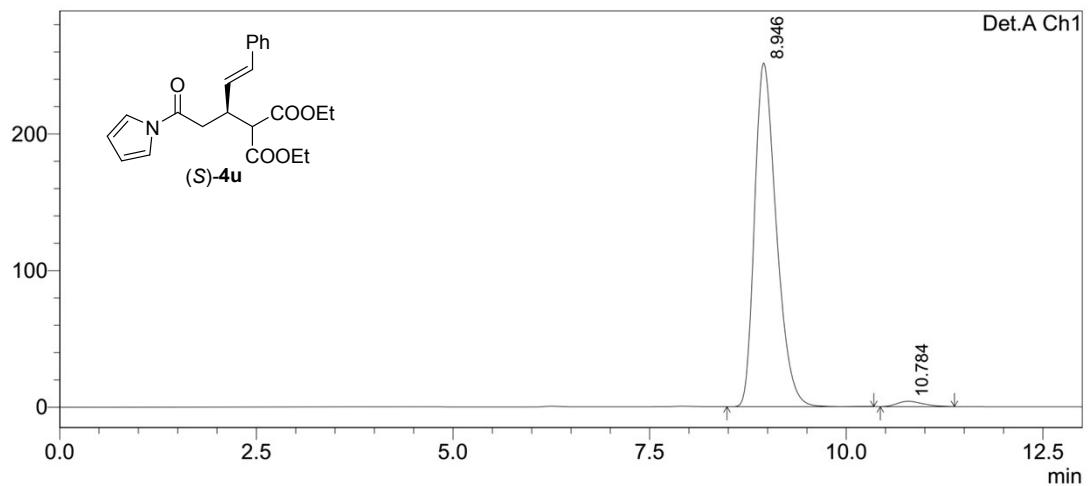


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.921	2172934	113114	50.071	55.092
2	10.752	2166812	92205	49.929	44.908
Total		4339746	205319	100.000	100.000

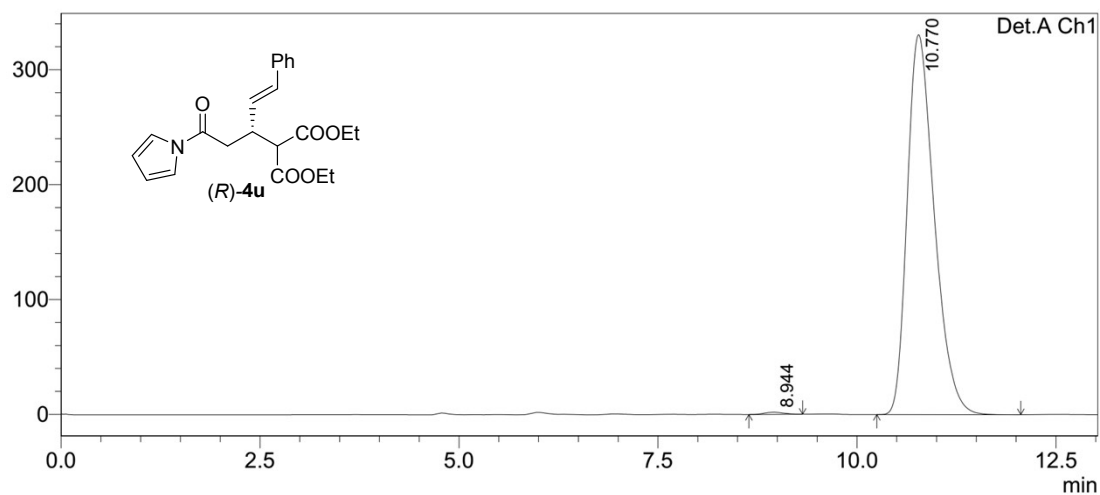


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.946	4854058	251559	98.187	98.466
2	10.784	89624	3919	1.813	1.534
Total		4943682	255478	100.000	100.000

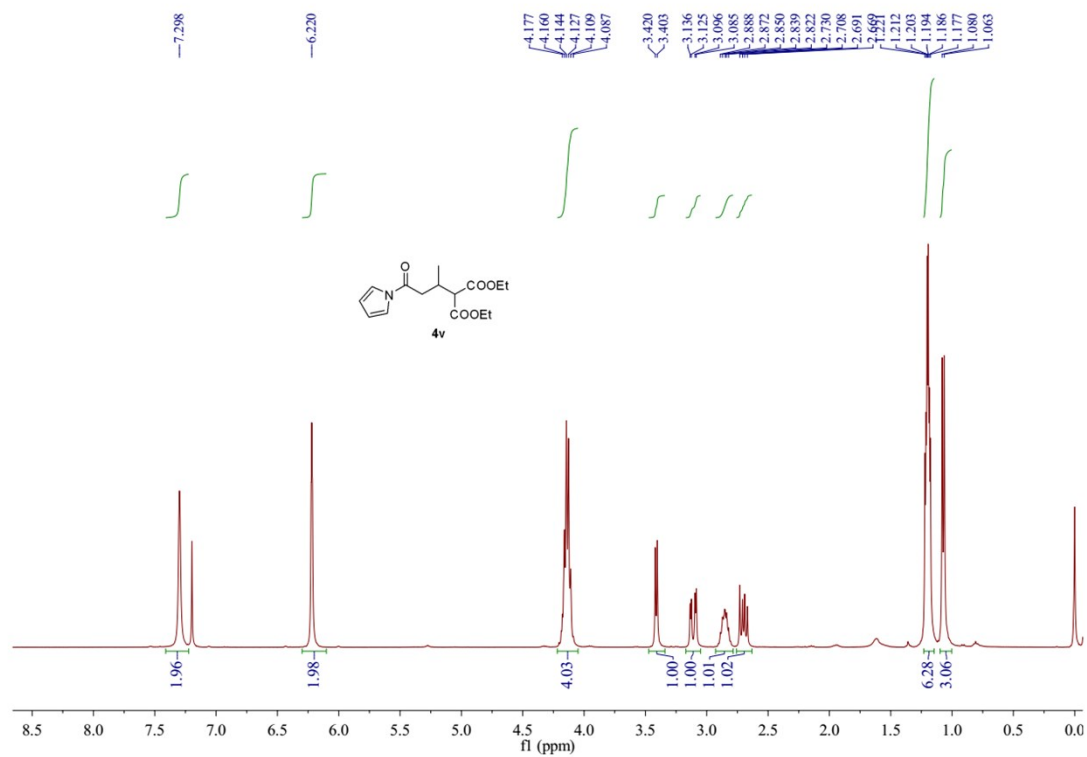


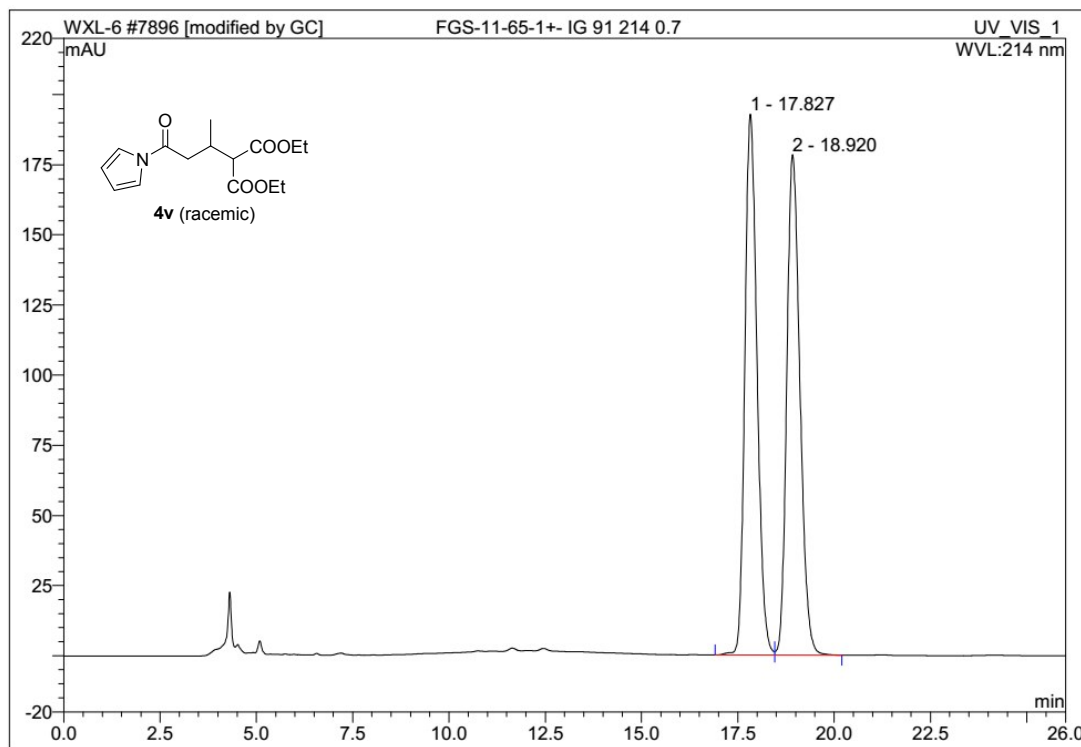
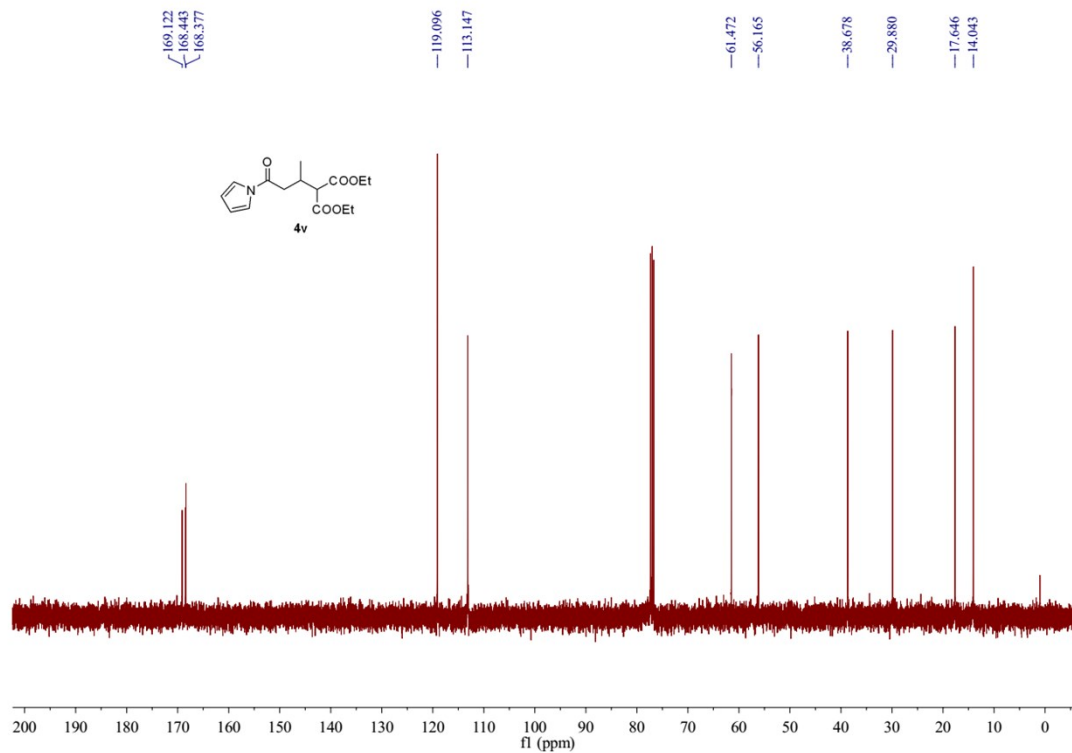
Det.A Ch1/254nm

PeakTable

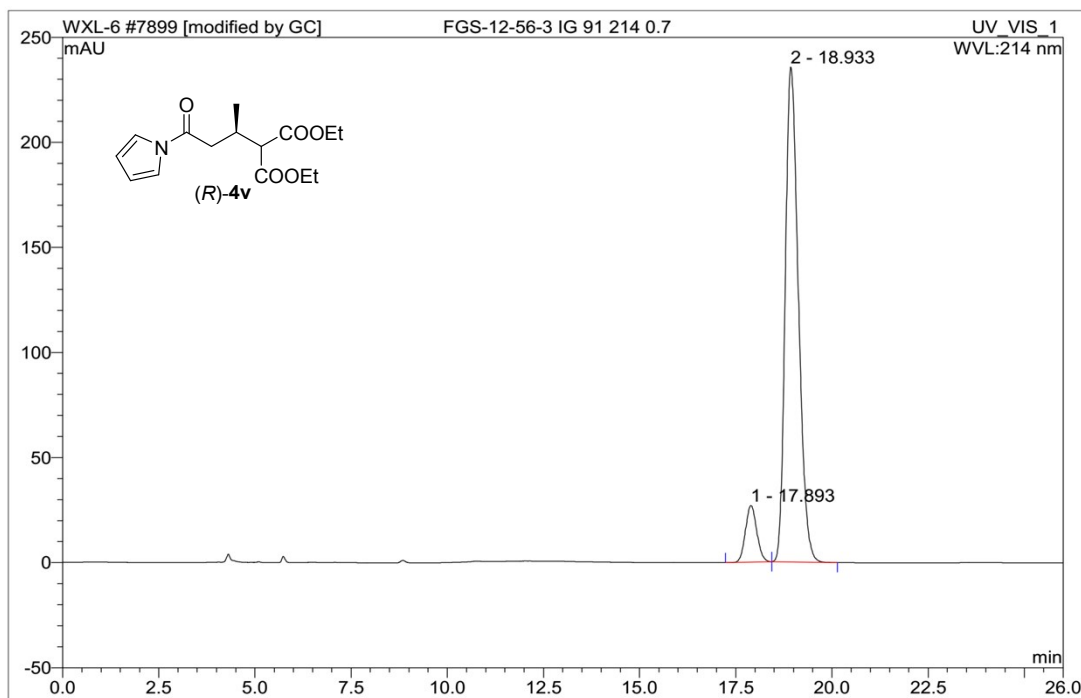
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.944	31176	1813	0.397	0.545
2	10.770	7815985	330756	99.603	99.455
Total		7847161	332569	100.000	100.000

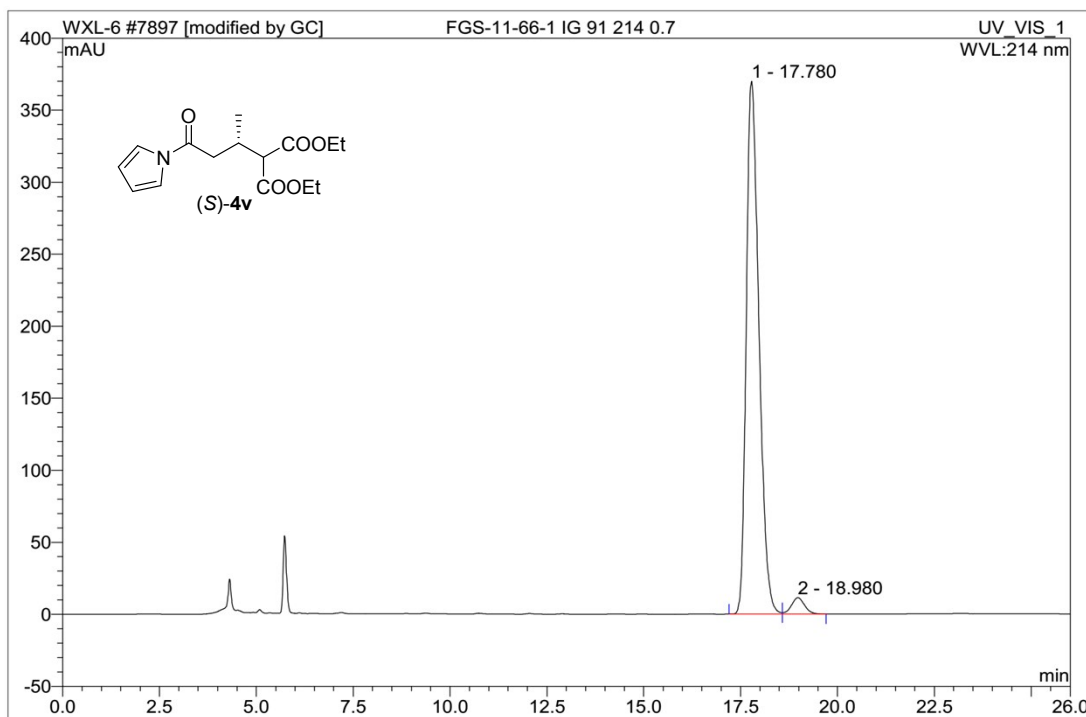




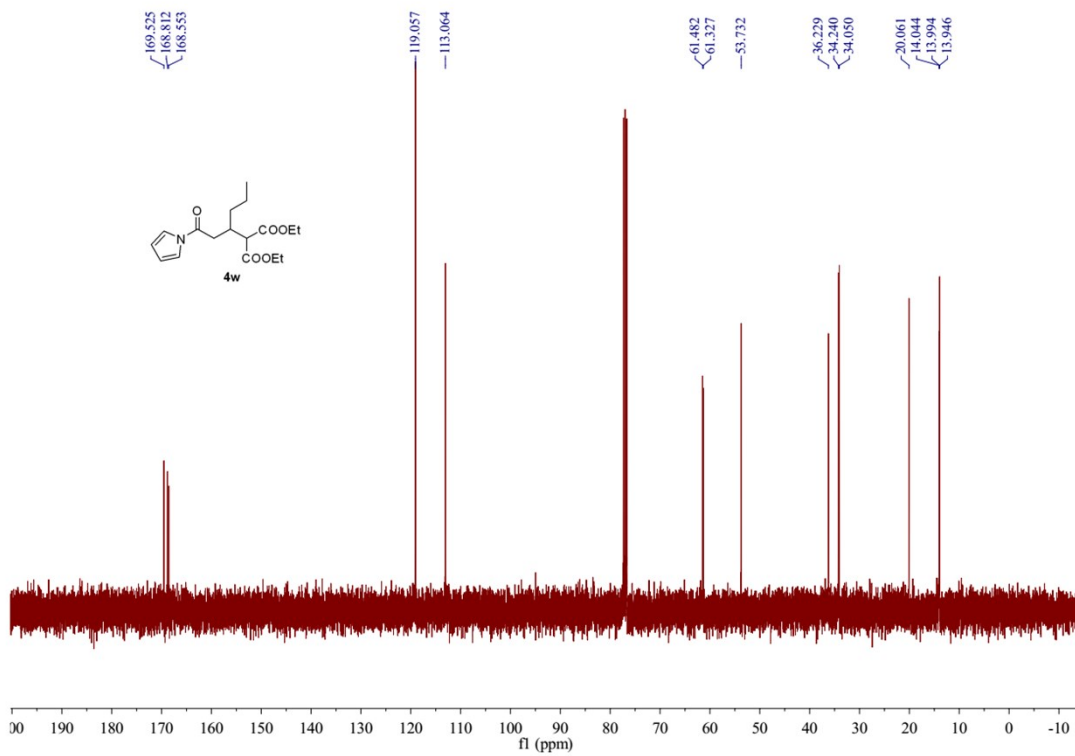
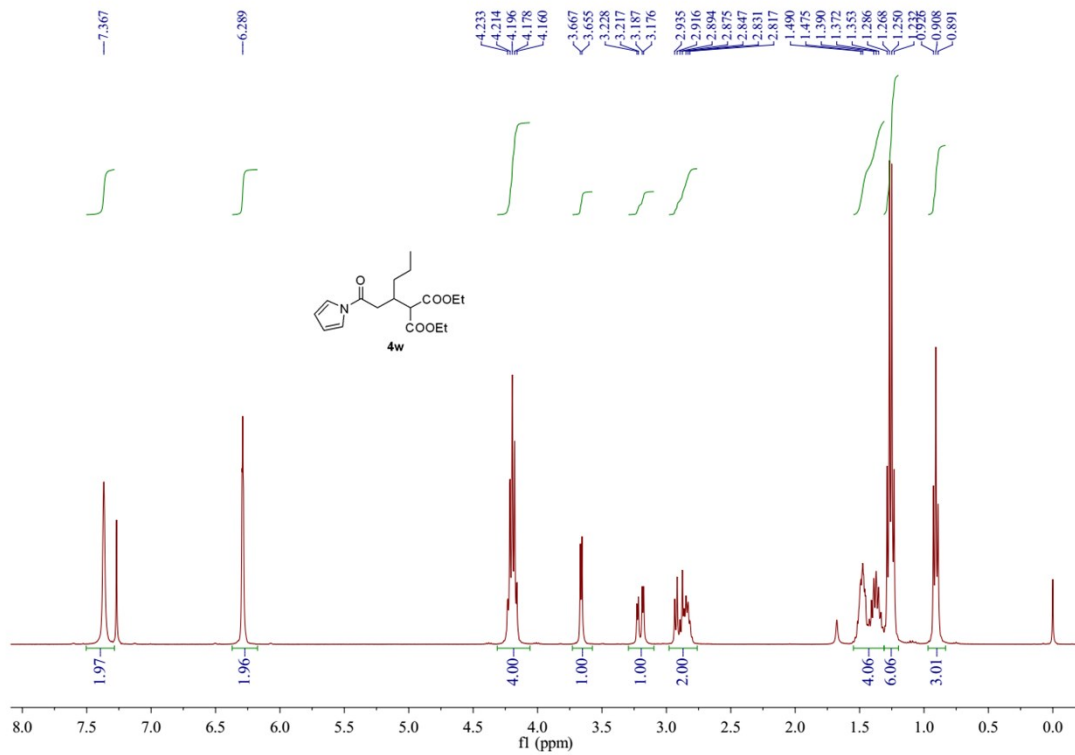
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.83	n.a.	192.878	70.521	49.96	n.a.	BM
2	18.92	n.a.	178.487	70.627	50.04	n.a.	MB
Total:			371.366	141.148	100.00	0.000	

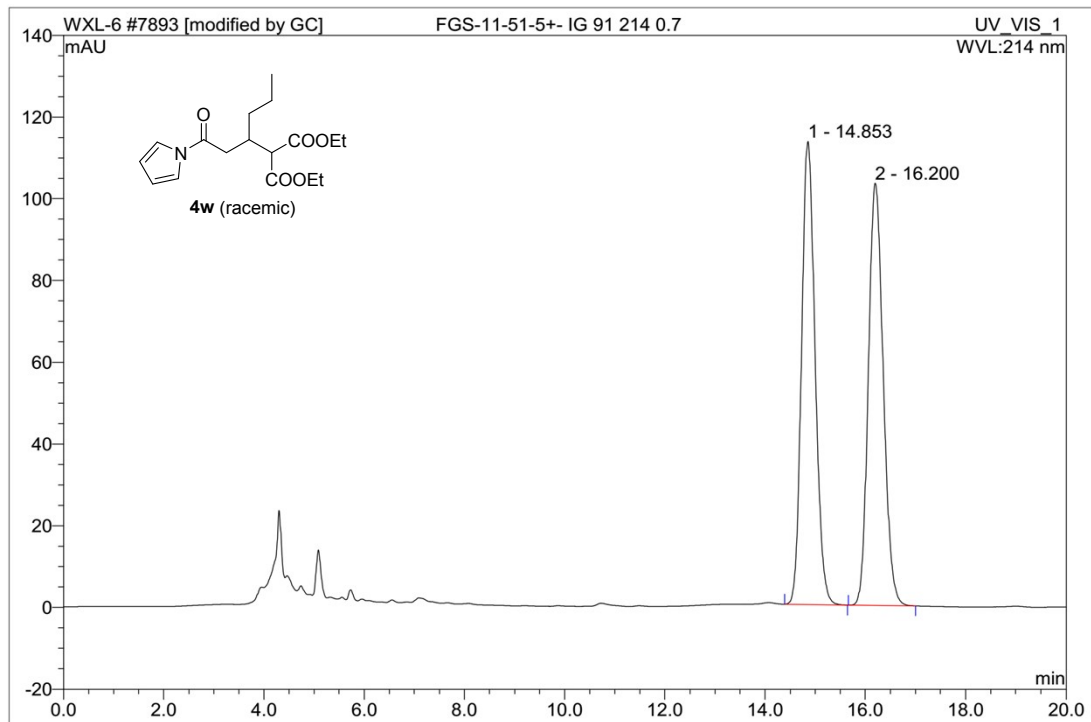


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.89	n.a.	27.024	9.230	9.01	n.a.	BMb*
2	18.93	n.a.	235.611	93.167	90.99	n.a.	bMB*
Total:			262.634	102.397	100.00	0.000	

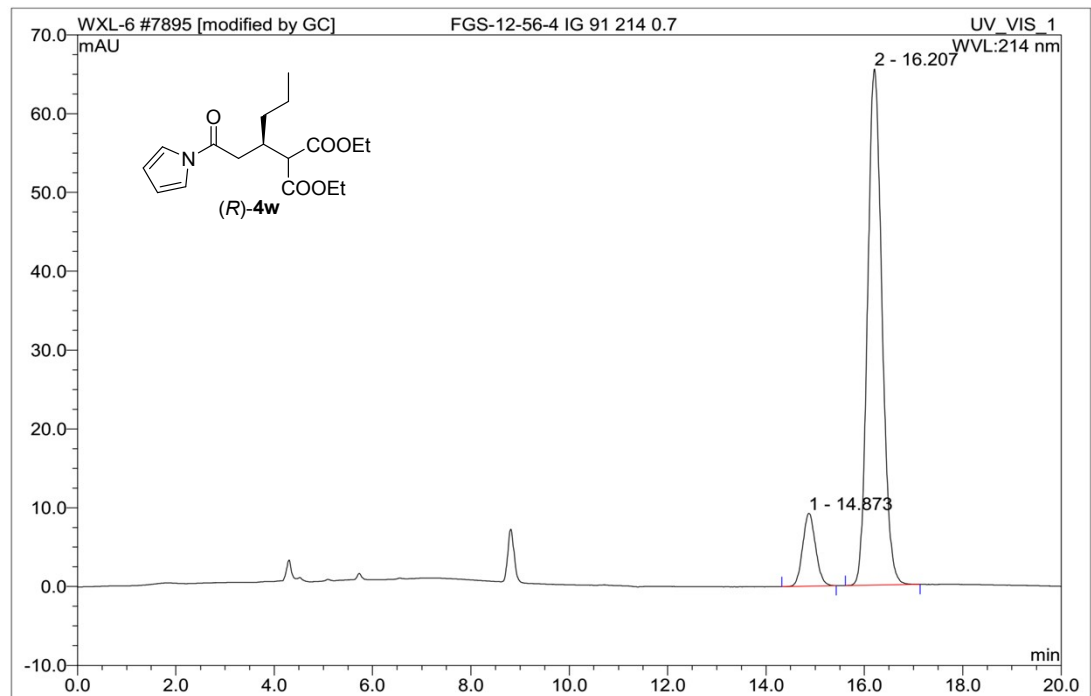


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.78	n.a.	369.920	140.083	96.92	n.a.	BM
2	18.98	n.a.	11.317	4.451	3.08	n.a.	MB
Total:			381.237	144.534	100.00	0.000	

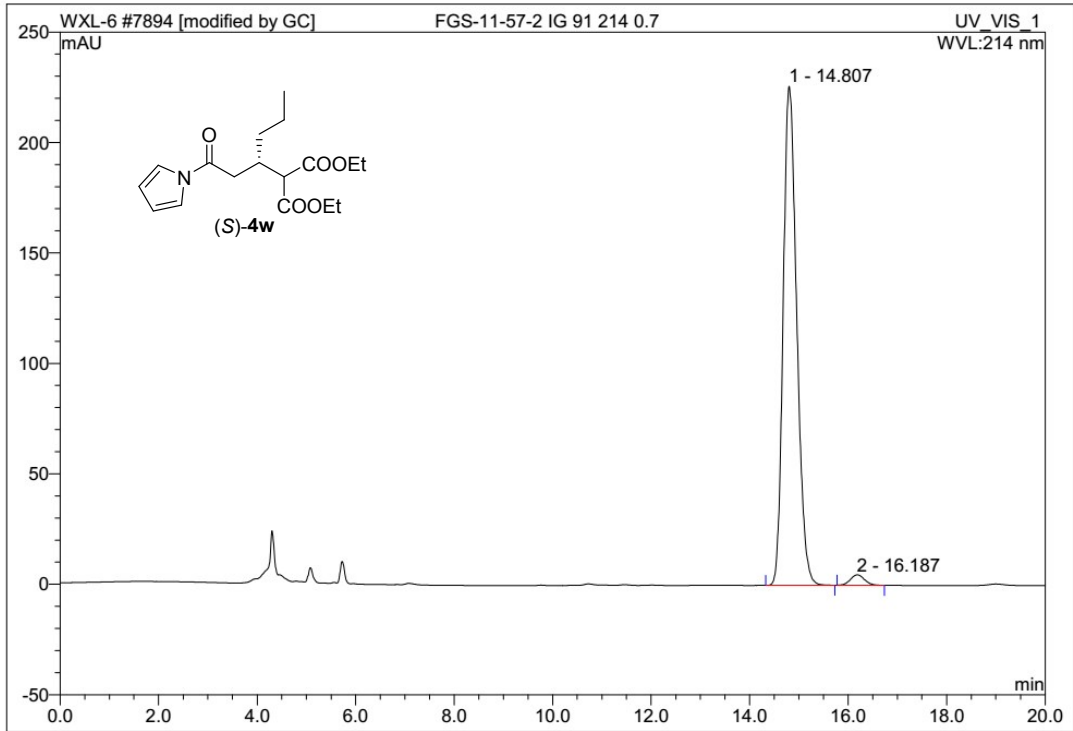




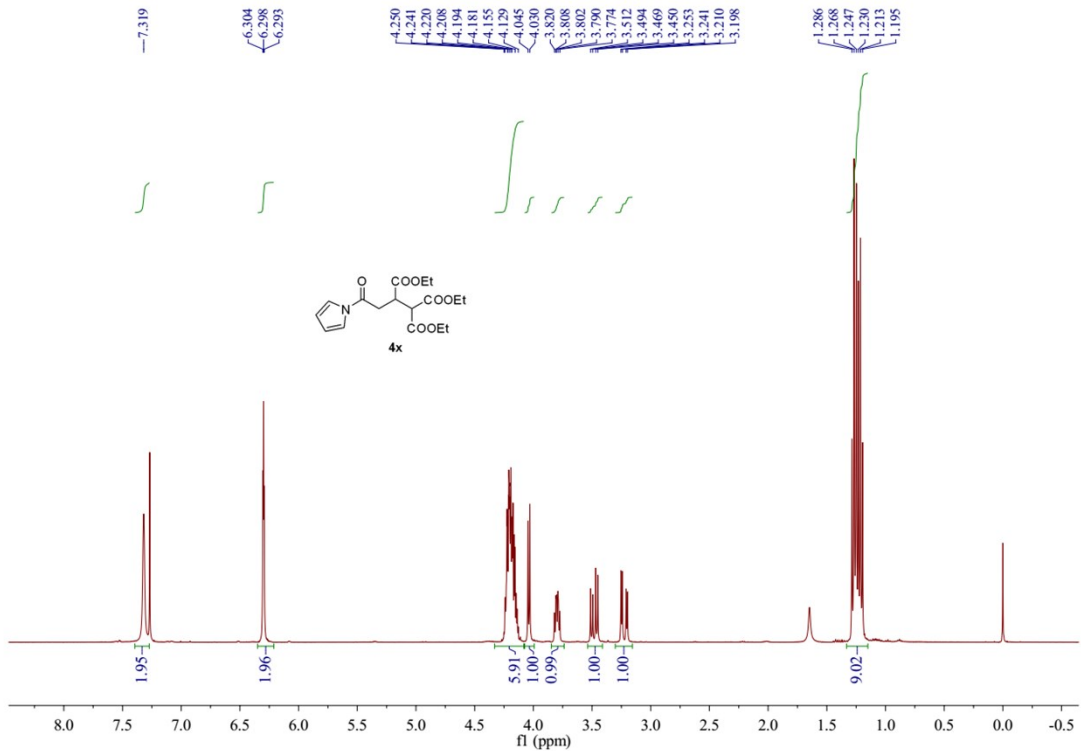
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.85	n.a.	113.360	35.462	49.95	n.a.	BMB
2	16.20	n.a.	103.332	35.536	50.05	n.a.	BMB
Total:			216.692	70.998	100.00	0.000	

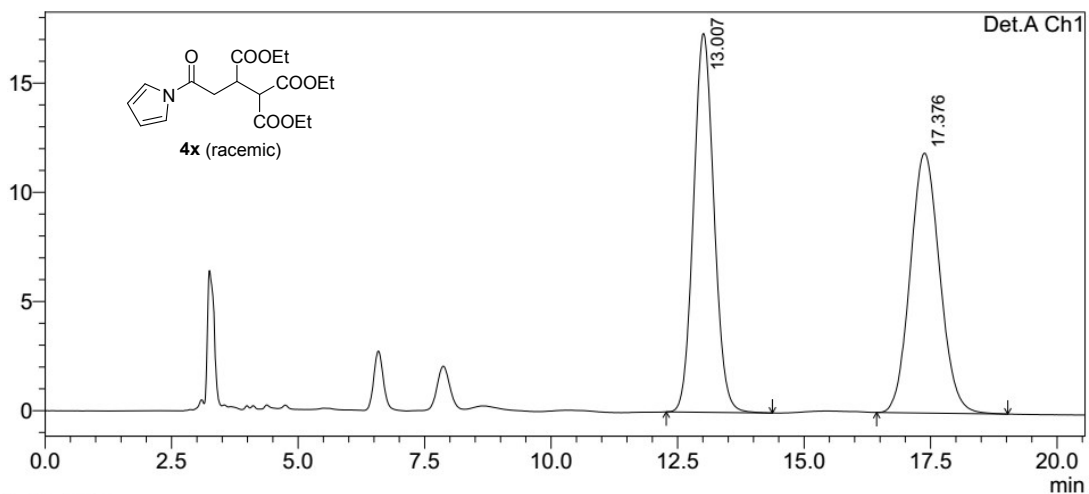
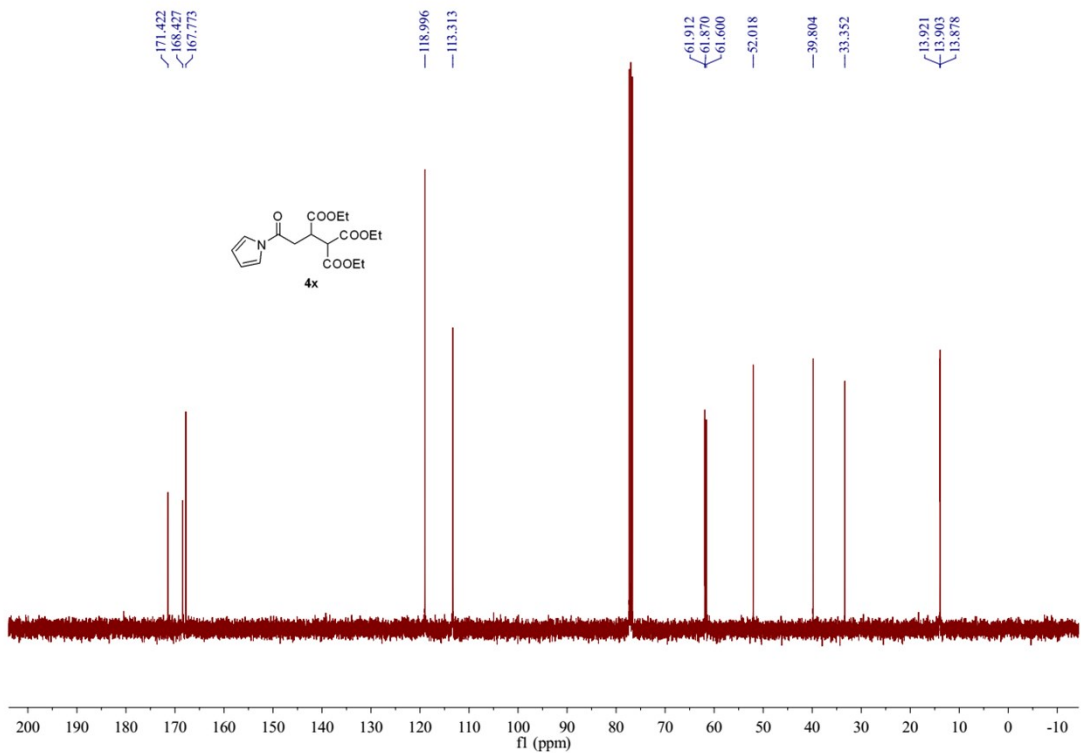


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.87	n.a.	9.256	2.803	11.18	n.a.	BMB*
2	16.21	n.a.	65.480	22.274	88.82	n.a.	BMB*
Total:			74.735	25.077	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.81	n.a.	225.984	71.914	97.86	n.a.	BMB
2	16.19	n.a.	4.754	1.569	2.14	n.a.	BMB
Total:			230.738	73.483	100.00	0.000	



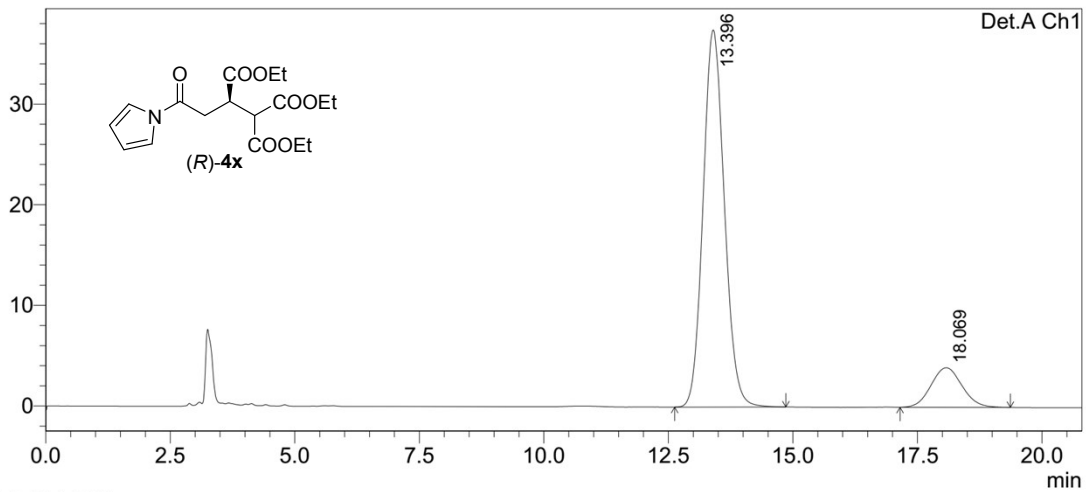


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.007	487077	17351	50.221	59.309
2	17.376	482786	11904	49.779	40.691
Total		969863	29256	100.000	100.000

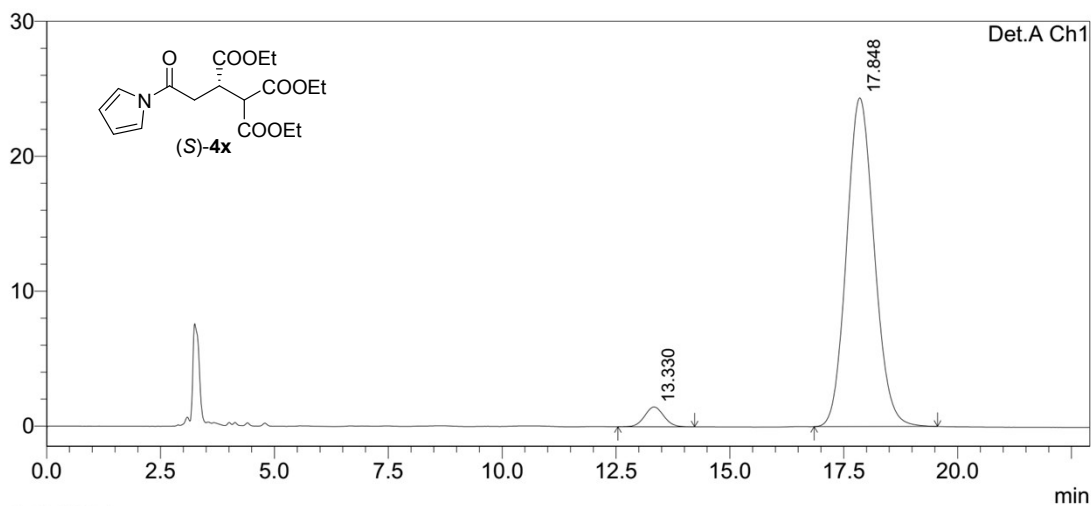


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.396	1112054	37475	86.719	90.476
2	18.069	170307	3945	13.281	9.524
Total		1282361	41420	100.000	100.000

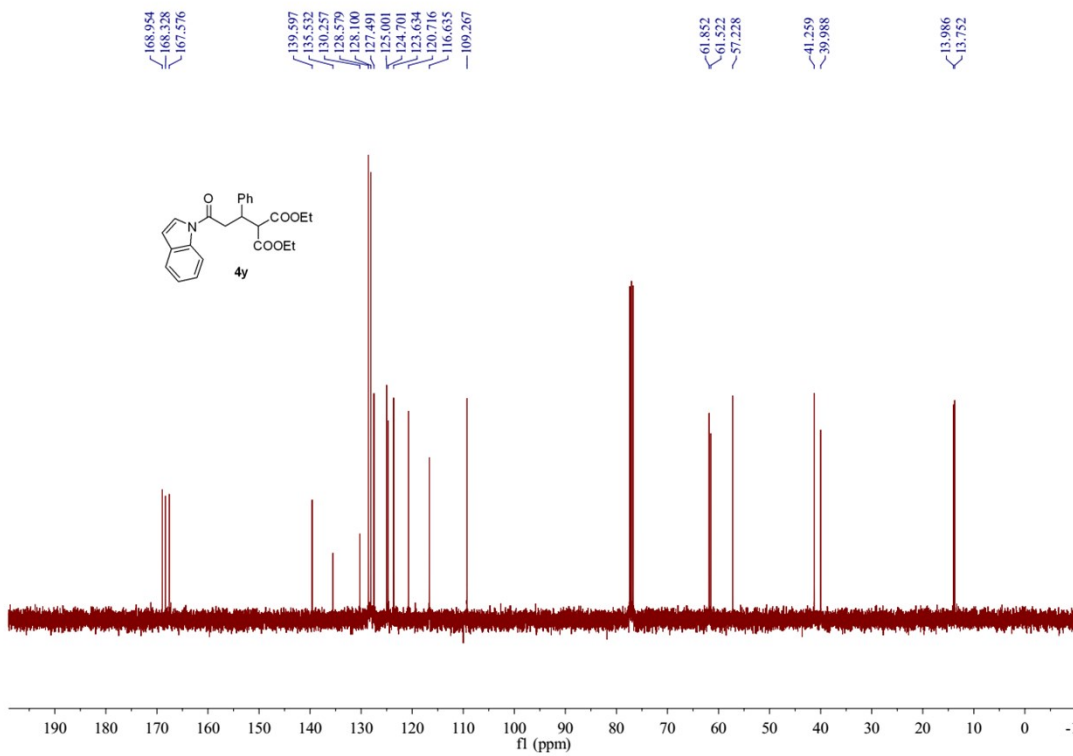
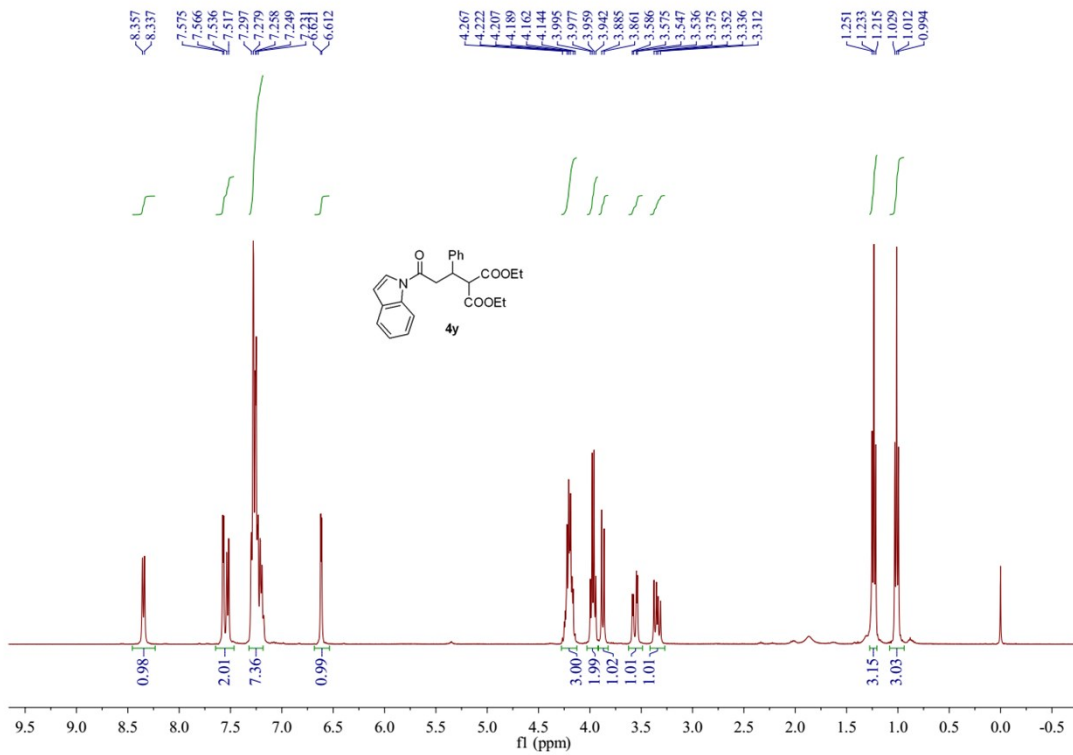


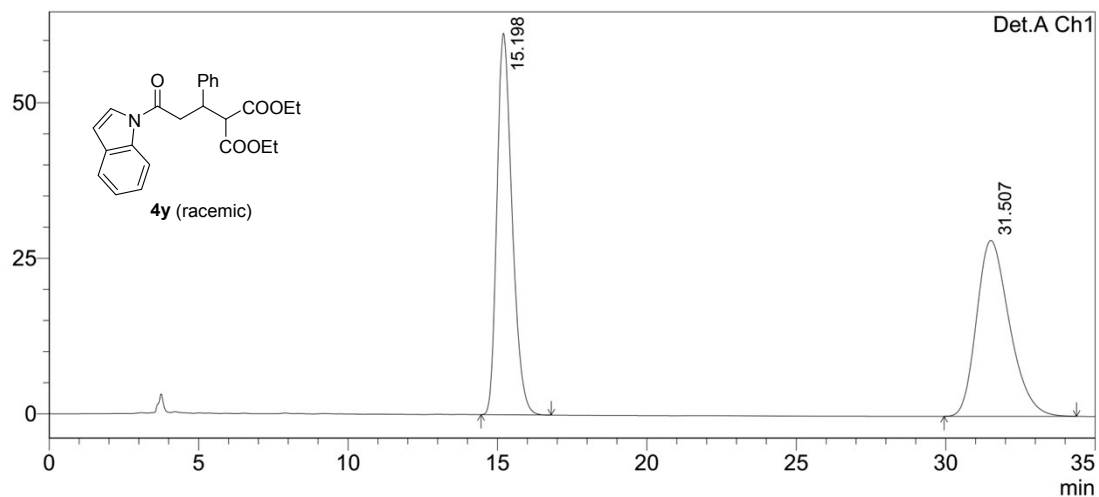
t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.330	42585	1466	3.965	5.675
2	17.848	1031406	24360	96.035	94.325
Total		1073991	25825	100.000	100.000



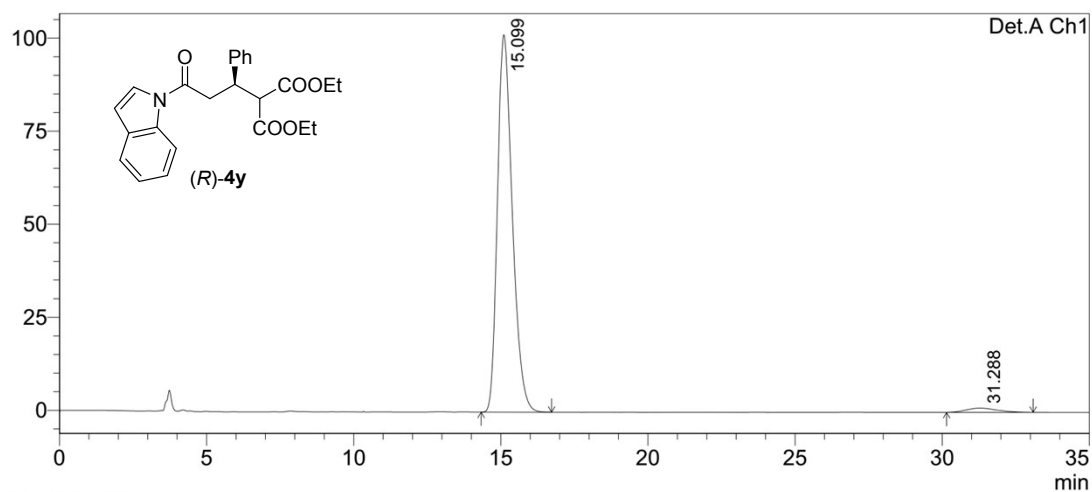


.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.198	2166453	61308	50.005	68.448
2	31.507	2166012	28260	49.995	31.552
Total		4332465	89568	100.000	100.000

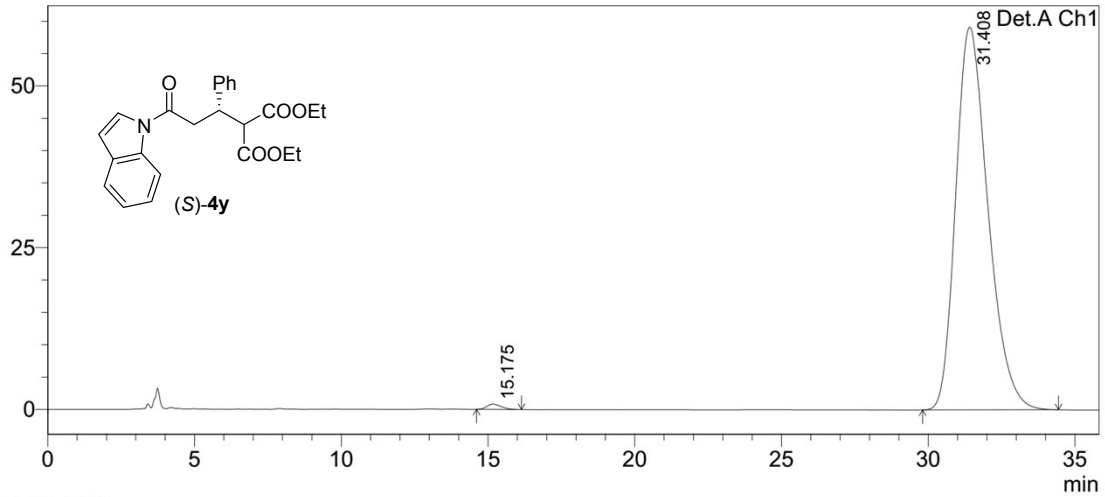


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.099	3576061	101399	97.741	98.895
2	31.288	82662	1133	2.259	1.105
Total		3658723	102532	100.000	100.000

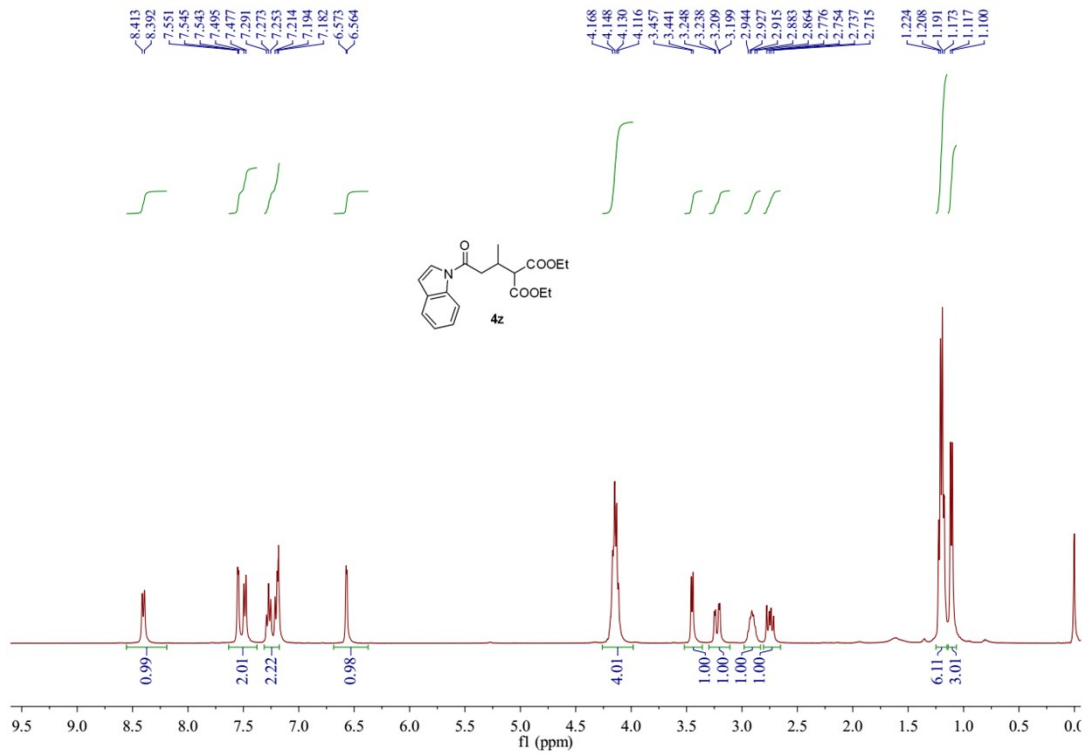


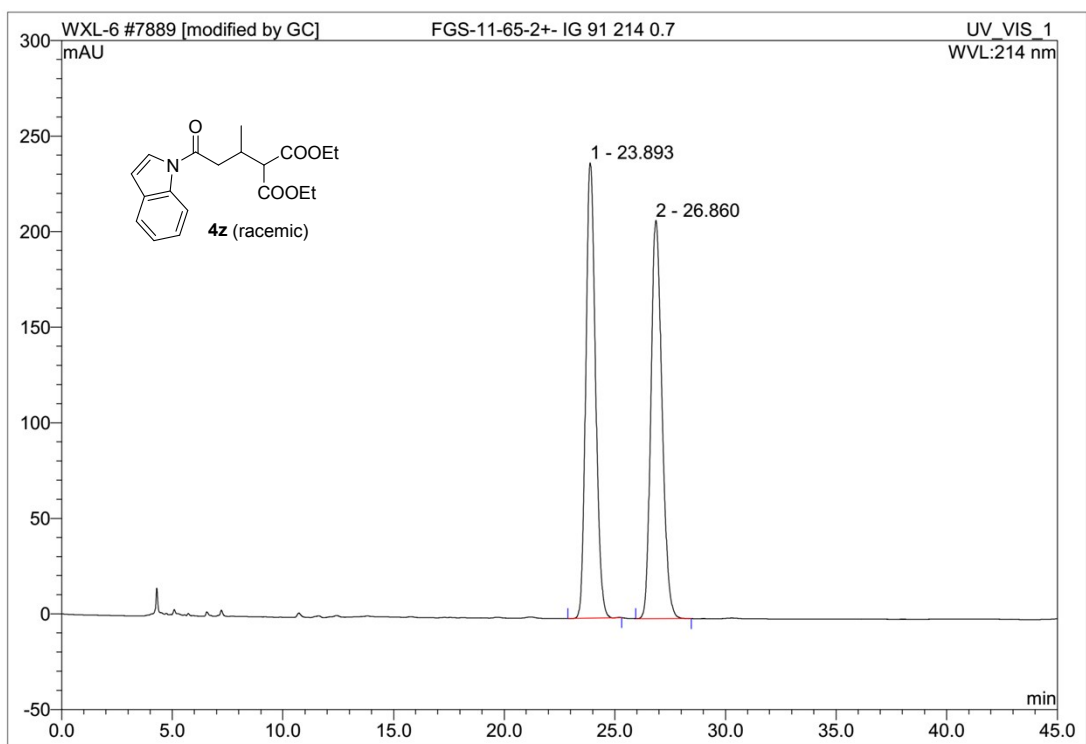
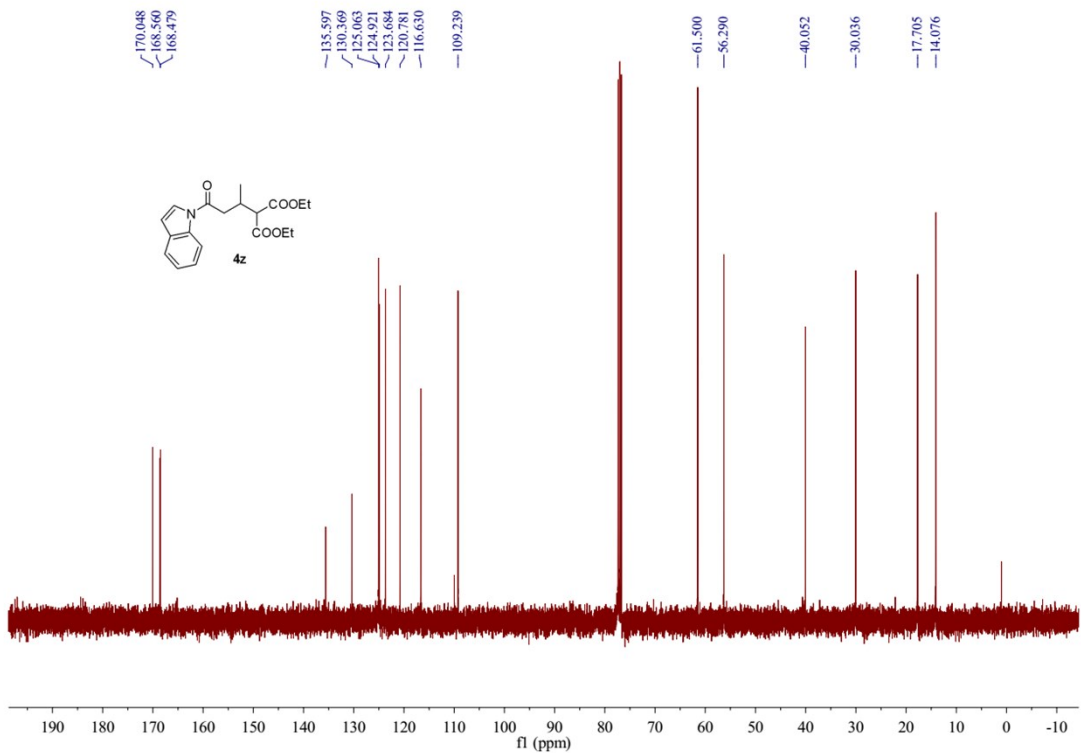
..A Ch1/254nm

PeakTable

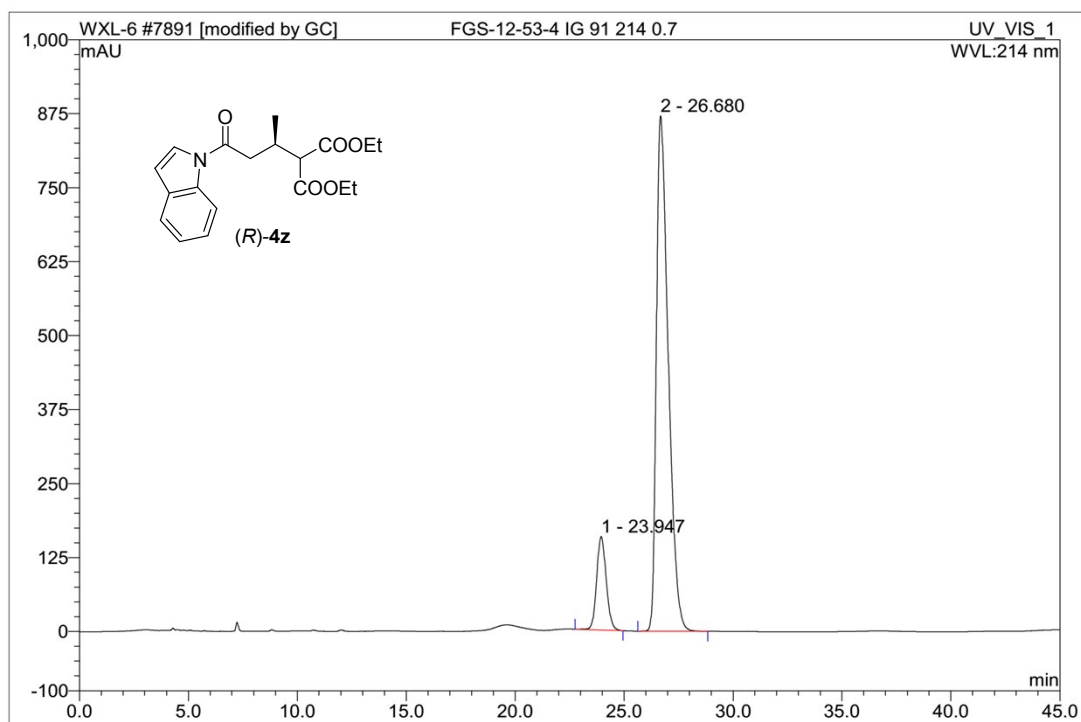
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.175	28337	825	0.623	1.375
2	31.408	4522973	59140	99.377	98.625
Total		4551309	59965	100.000	100.000

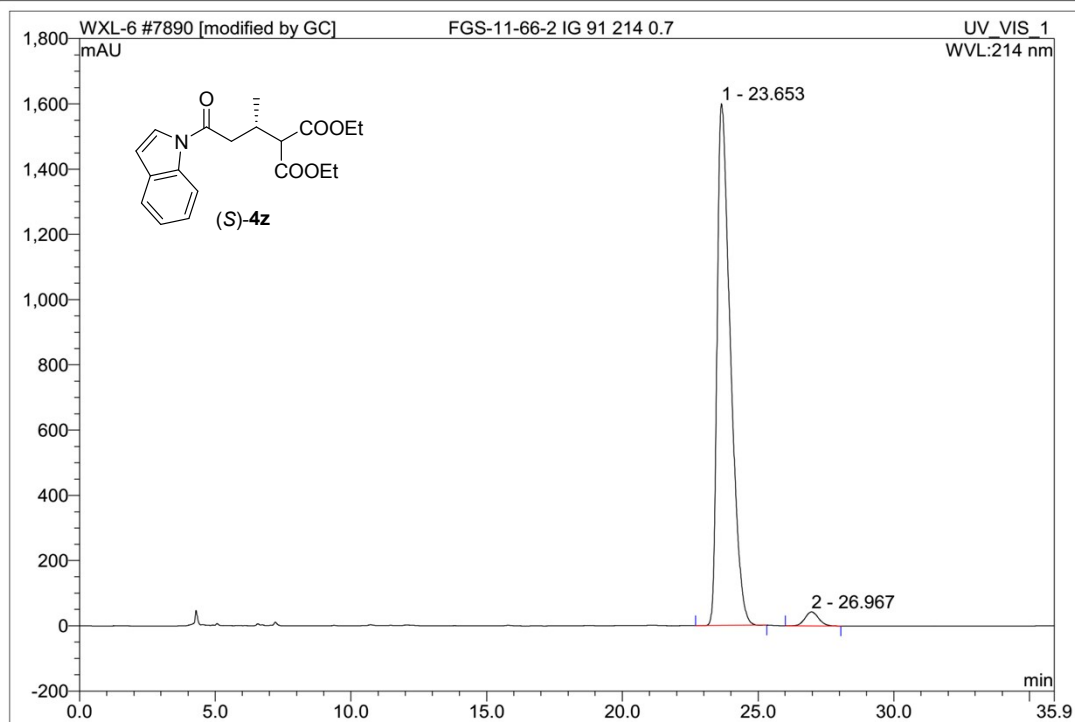




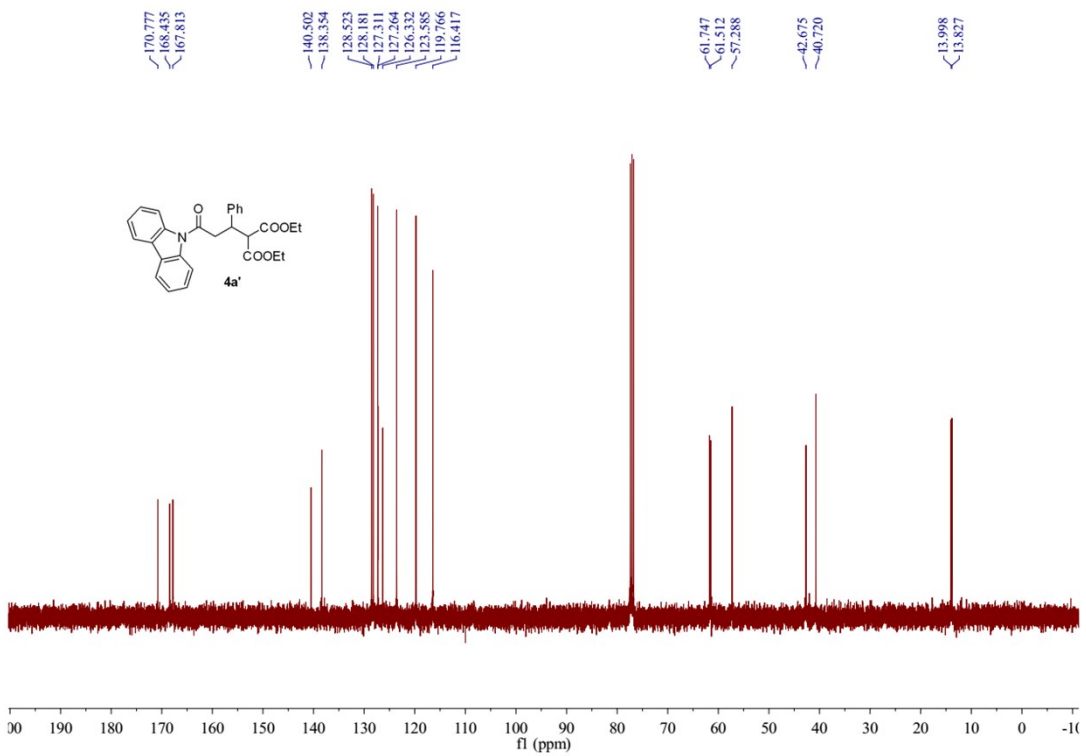
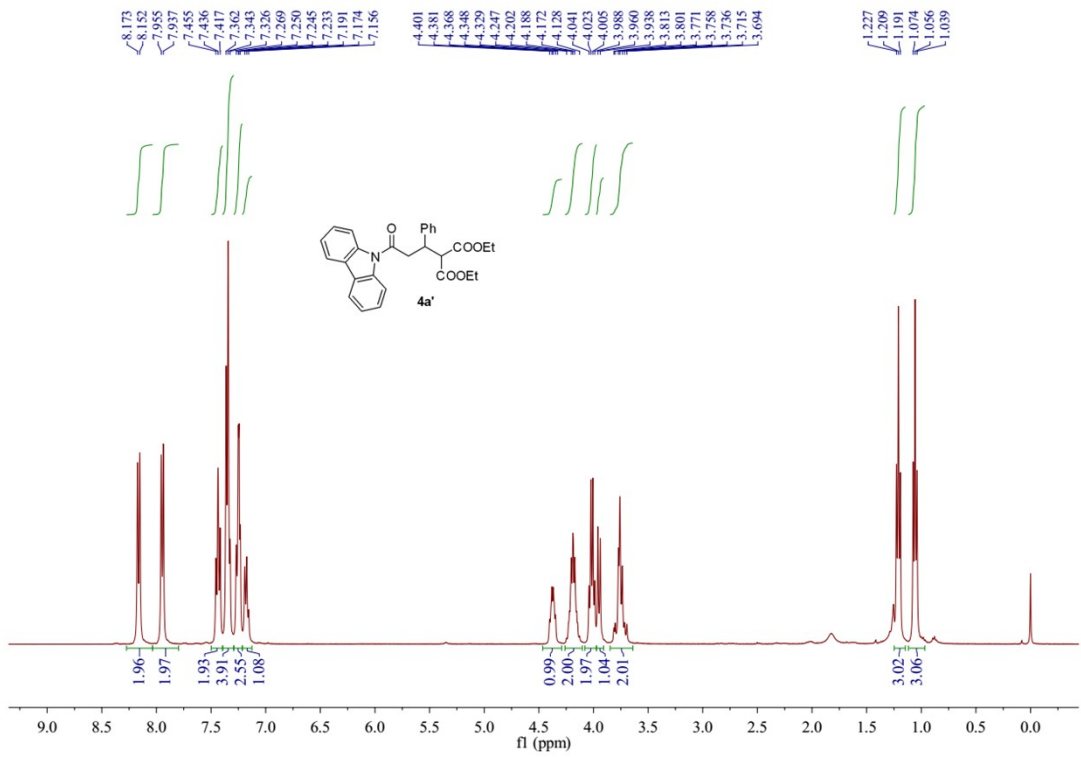
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.89	n.a.	238.319	120.831	49.85	n.a.	BMB*
2	26.86	n.a.	208.333	121.569	50.15	n.a.	BMB
Total:			446.653	242.400	100.00	0.000	

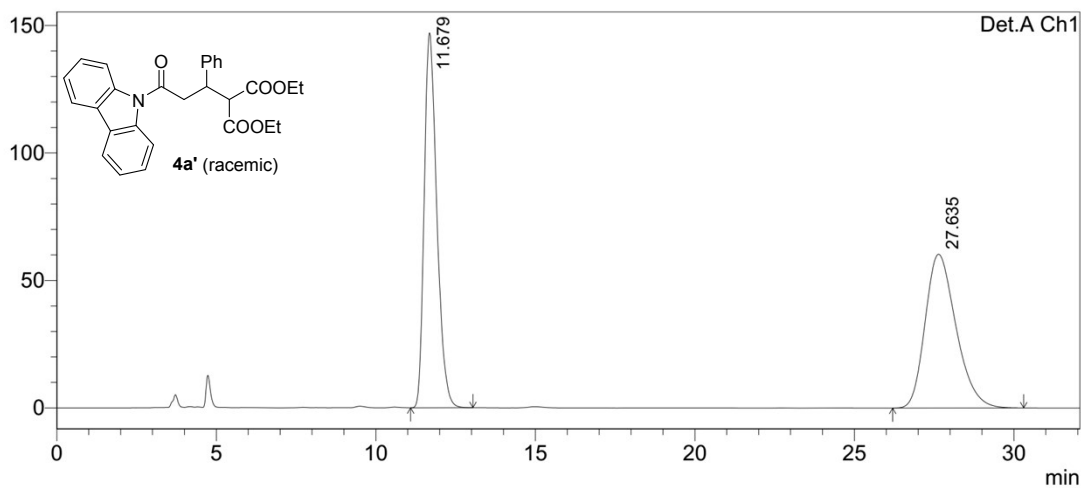


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.95	n.a.	158.140	80.444	12.76	n.a.	BMB*
2	26.68	n.a.	870.687	550.191	87.24	n.a.	BMB*
Total:			1028.826	630.634	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.65	n.a.	1600.056	906.022	97.32	n.a.	BMB*
2	26.97	n.a.	42.777	24.949	2.68	n.a.	BMB
Total:			1642.833	930.971	100.00	0.000	



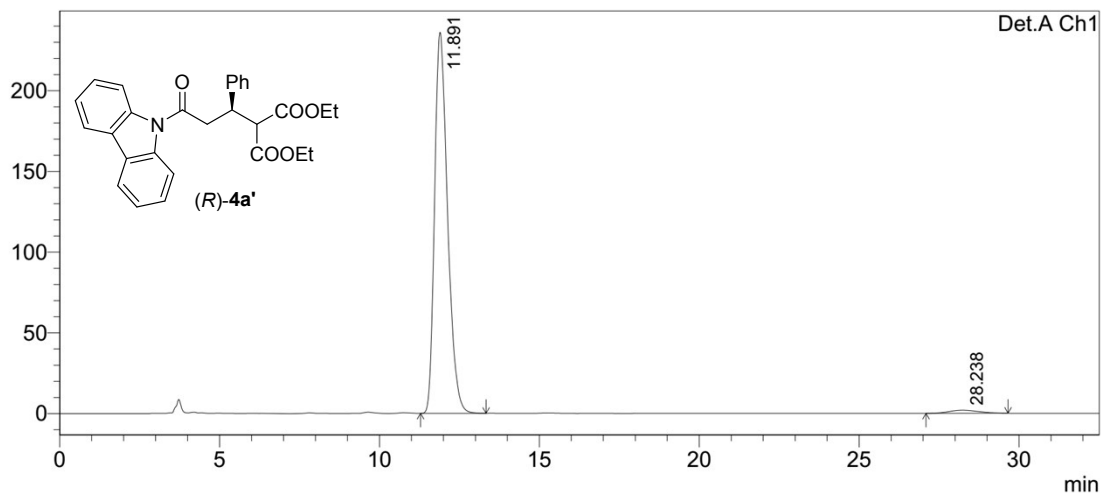


et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.679	4042296	147062	49.910	70.911
2	27.635	4056828	60329	50.090	29.089
Total		8099123	207391	100.000	100.000

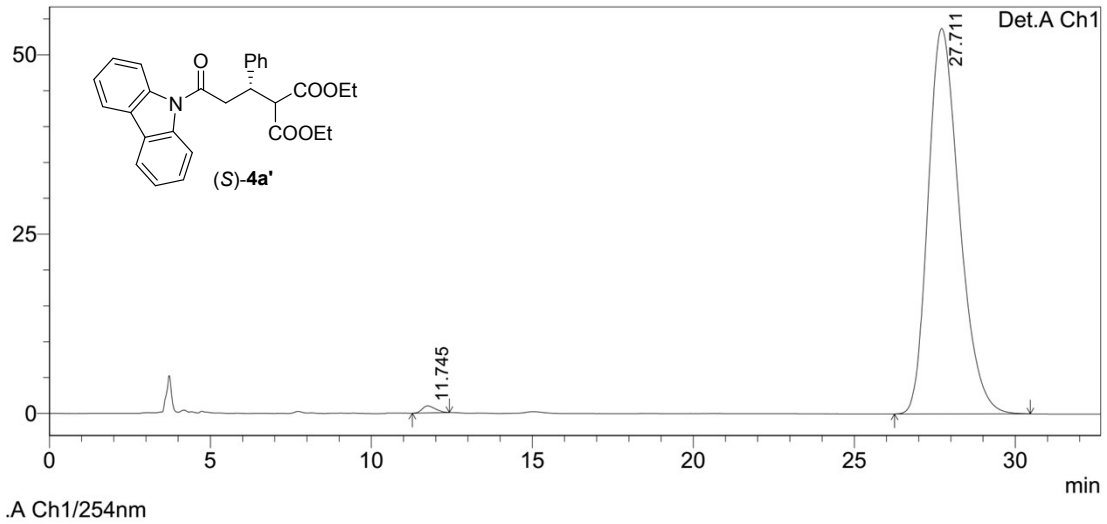


et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

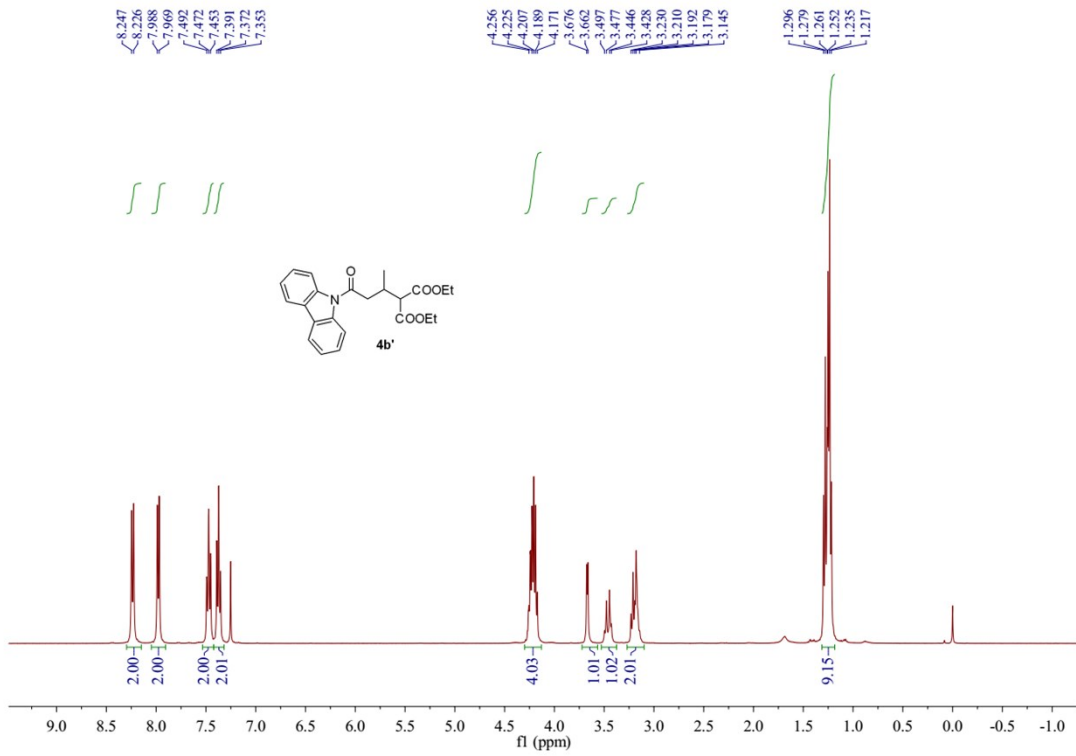
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.891	6659074	235984	98.195	99.206
2	28.238	122406	1888	1.805	0.794
Total		6781480	237871	100.000	100.000

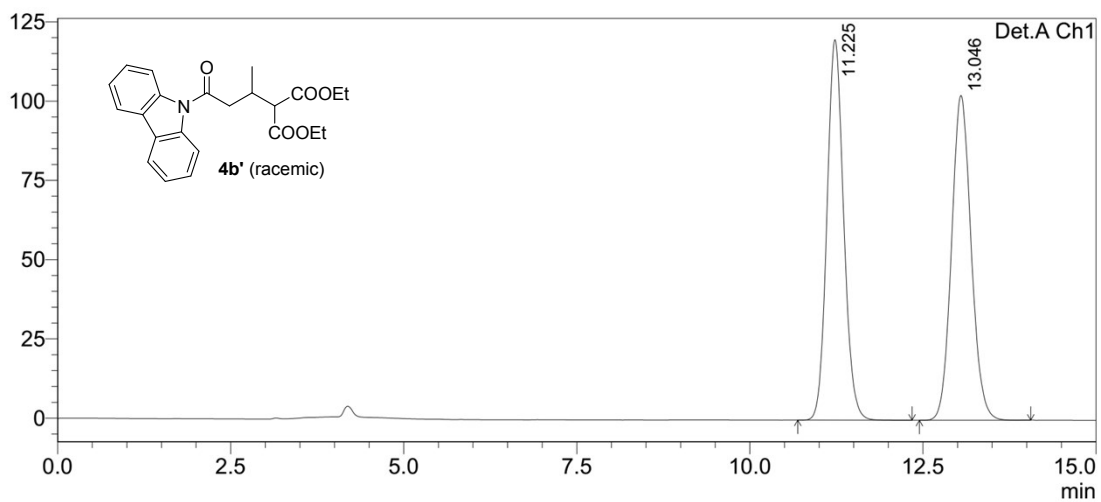
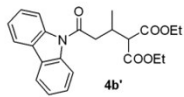
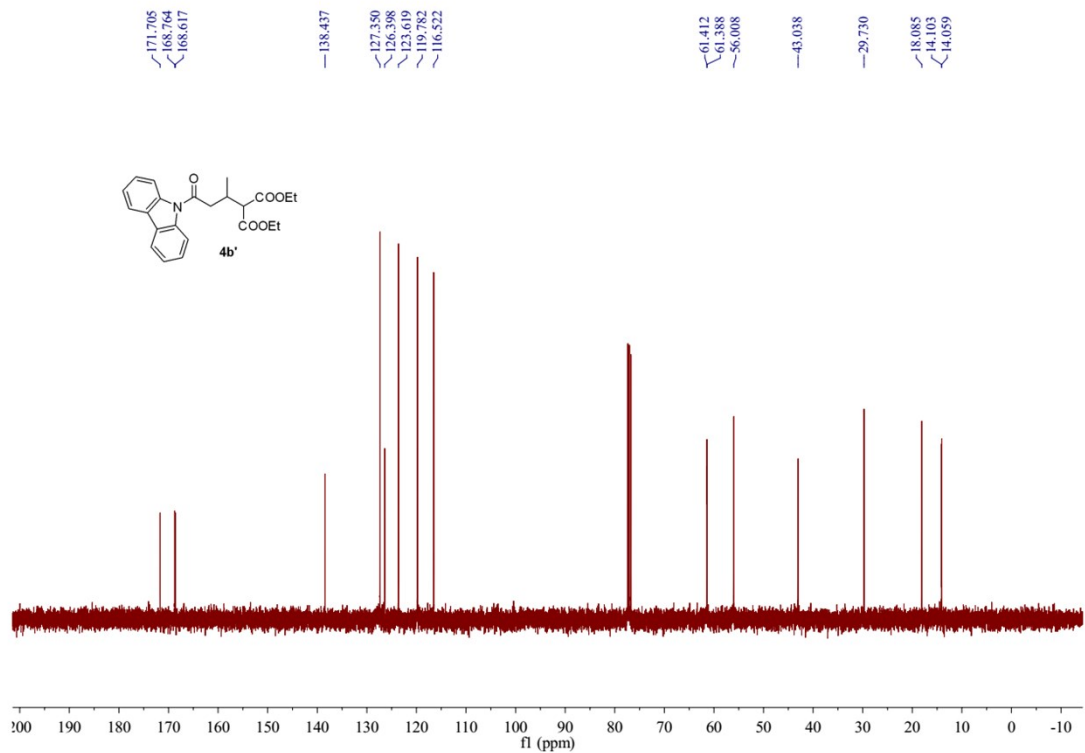


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.745	27735	981	0.759	1.793
2	27.711	3626338	53744	99.241	98.207
Total		3654073	54725	100.000	100.000



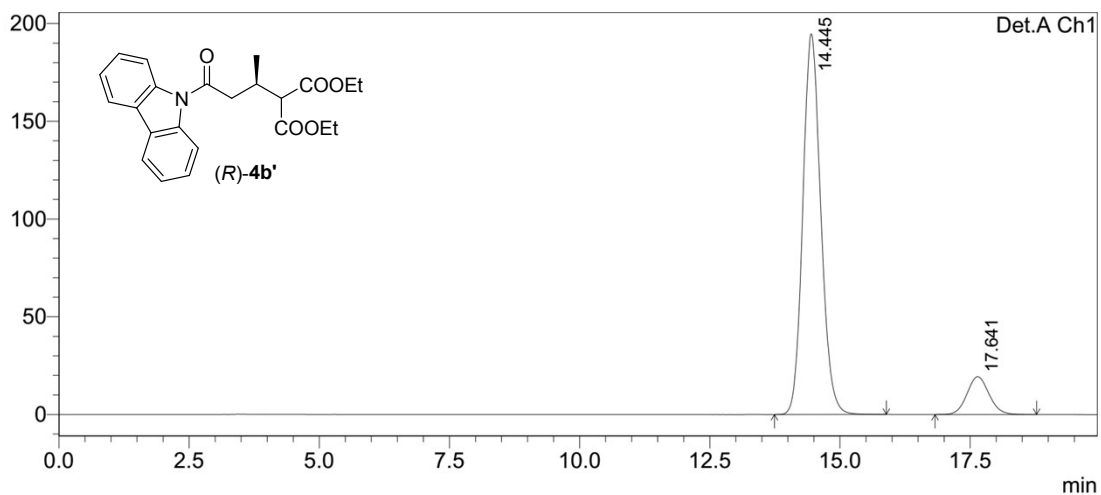


st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.225	2017232	120012	49.945	53.940
2	13.046	2021707	102479	50.055	46.060
Total		4038938	222491	100.000	100.000

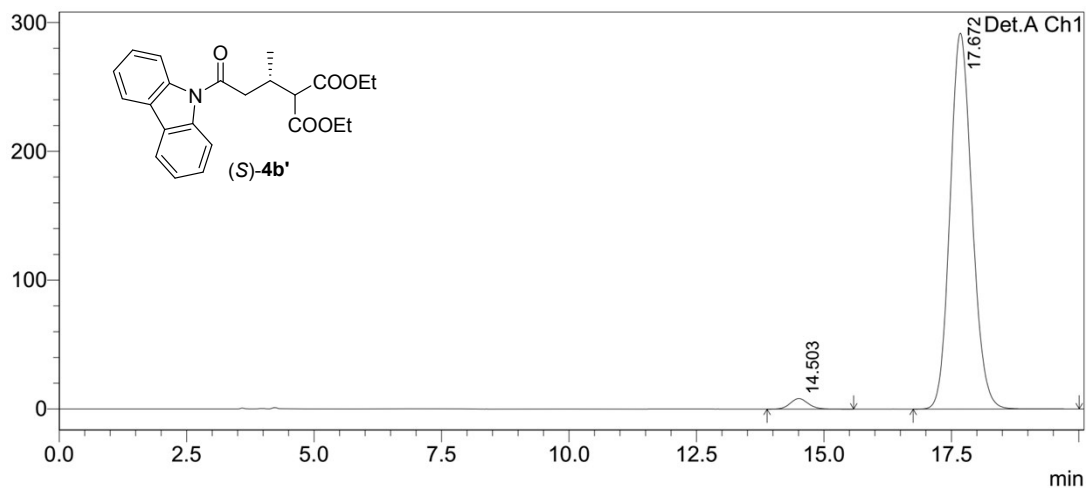


et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.445	4684427	194753	89.167	90.966
2	17.641	569097	19342	10.833	9.034
Total		5253524	214095	100.000	100.000

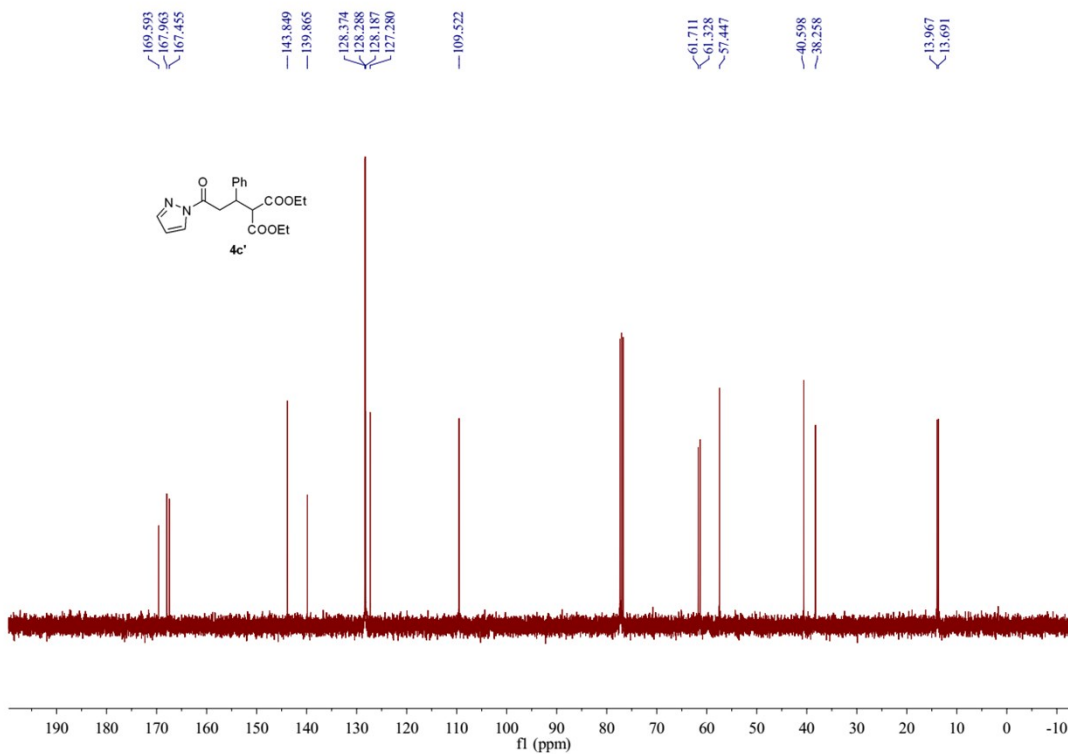
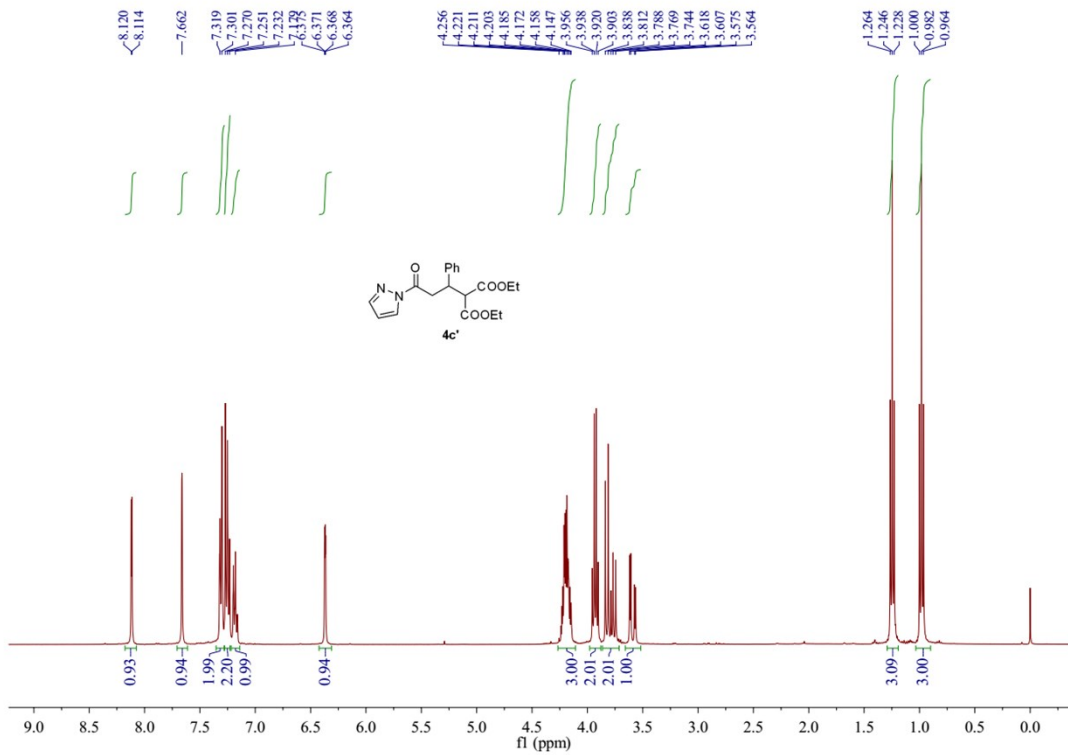


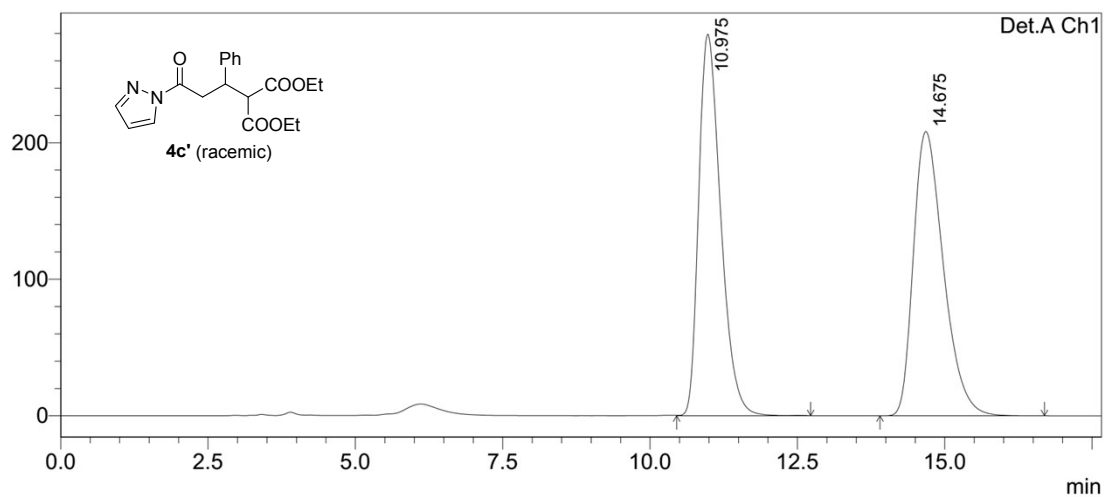
et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.503	199719	8153	2.230	2.718
2	17.672	8757099	291772	97.770	97.282
Total		8956818	299925	100.000	100.000



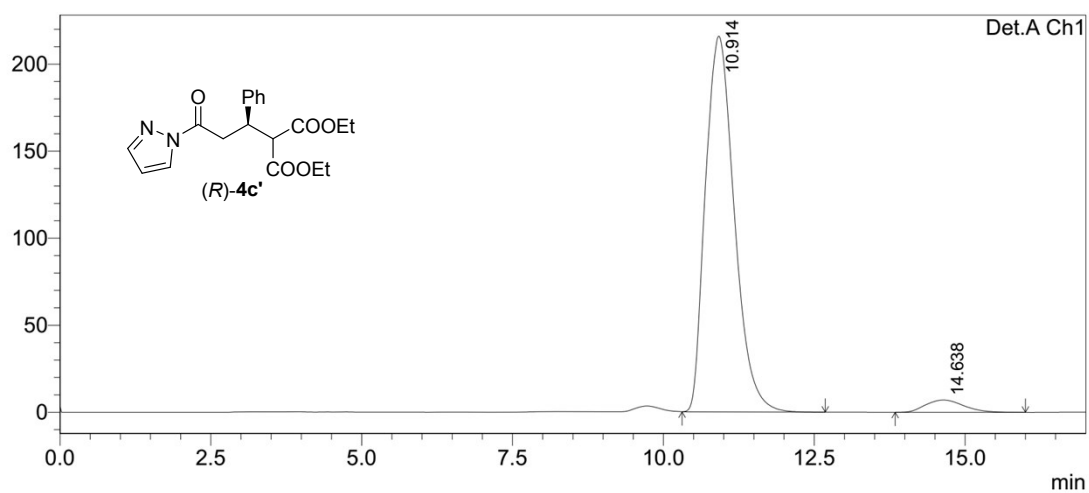


t.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.975	7262424	279337	49.606	57.297
2	14.675	7377909	208191	50.394	42.703
Total		14640333	487528	100.000	100.000

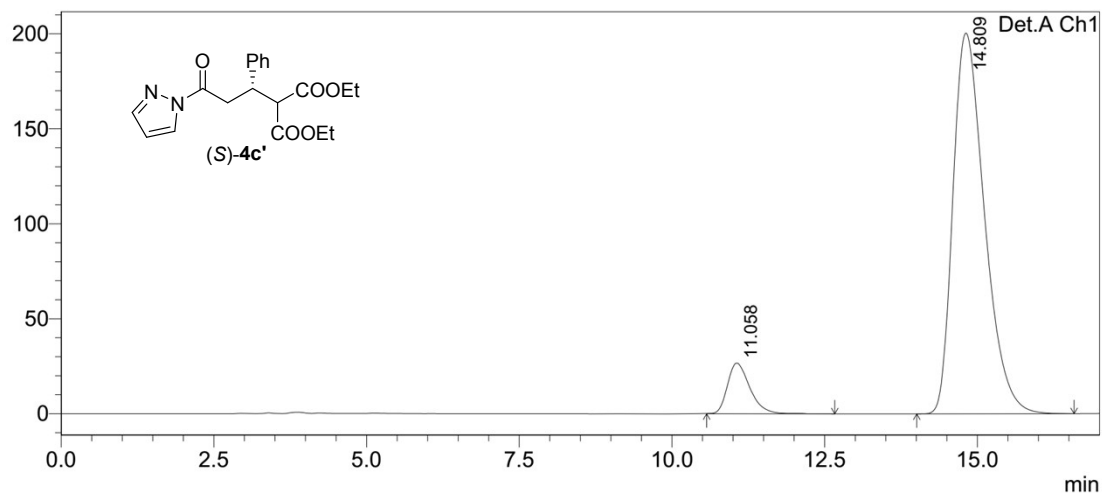


et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.914	7199511	215917	95.855	96.812
2	14.638	311308	7110	4.145	3.188
Total		7510820	223027	100.000	100.000

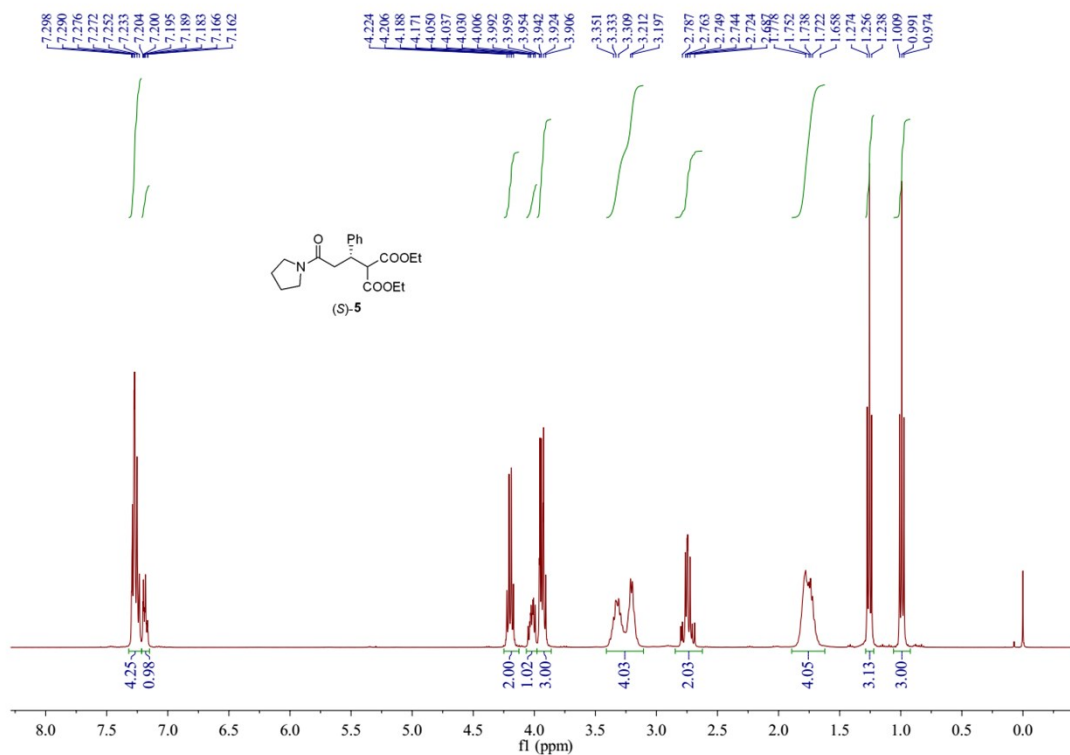


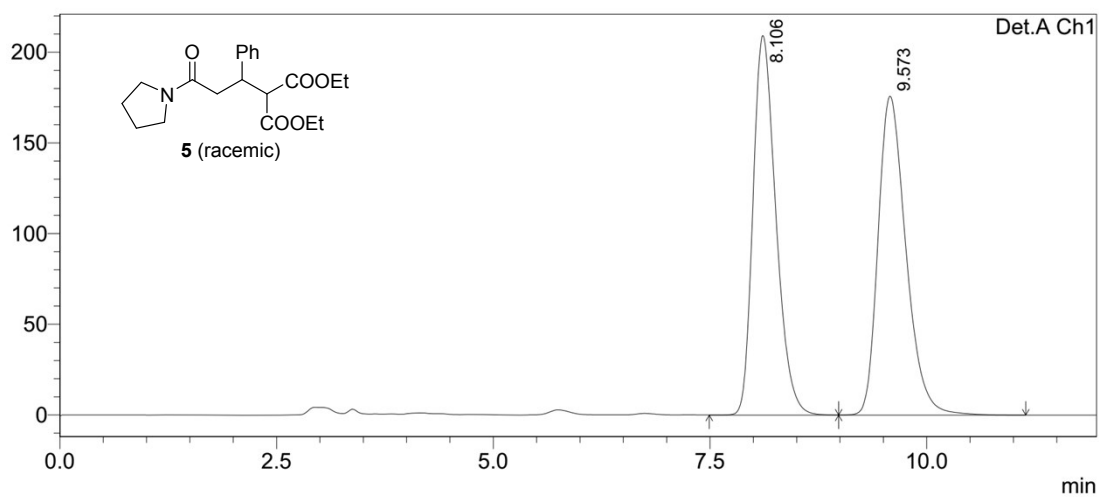
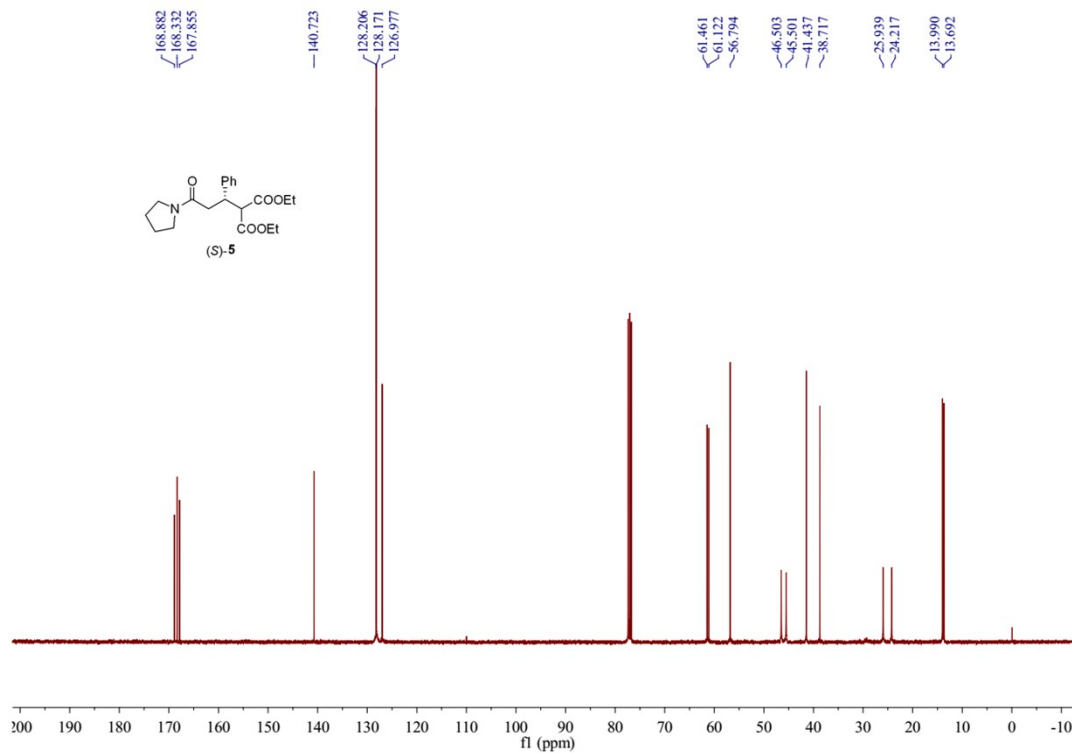
Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.058	681062	26701	8.646	11.753
2	14.809	7196471	200487	91.354	88.247
Total		7877534	227187	100.000	100.000



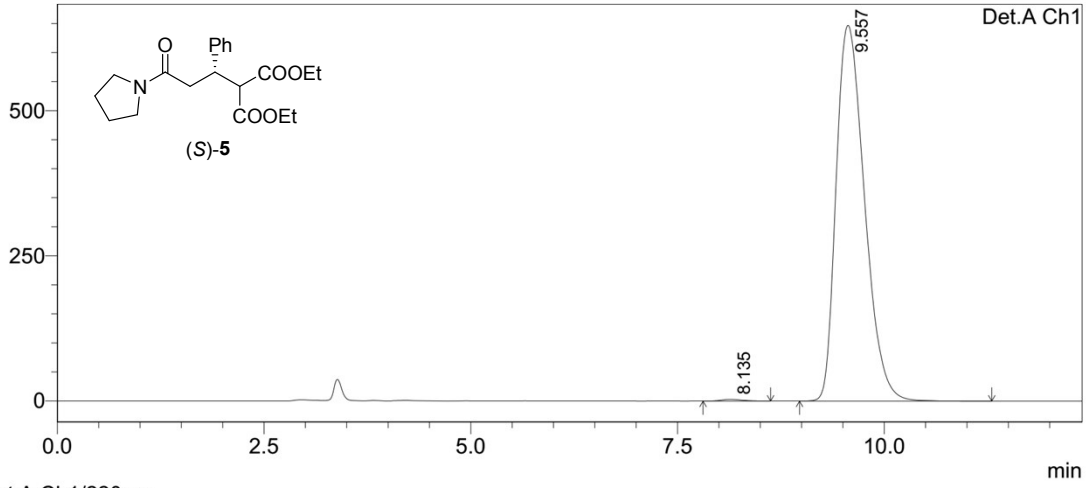


Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

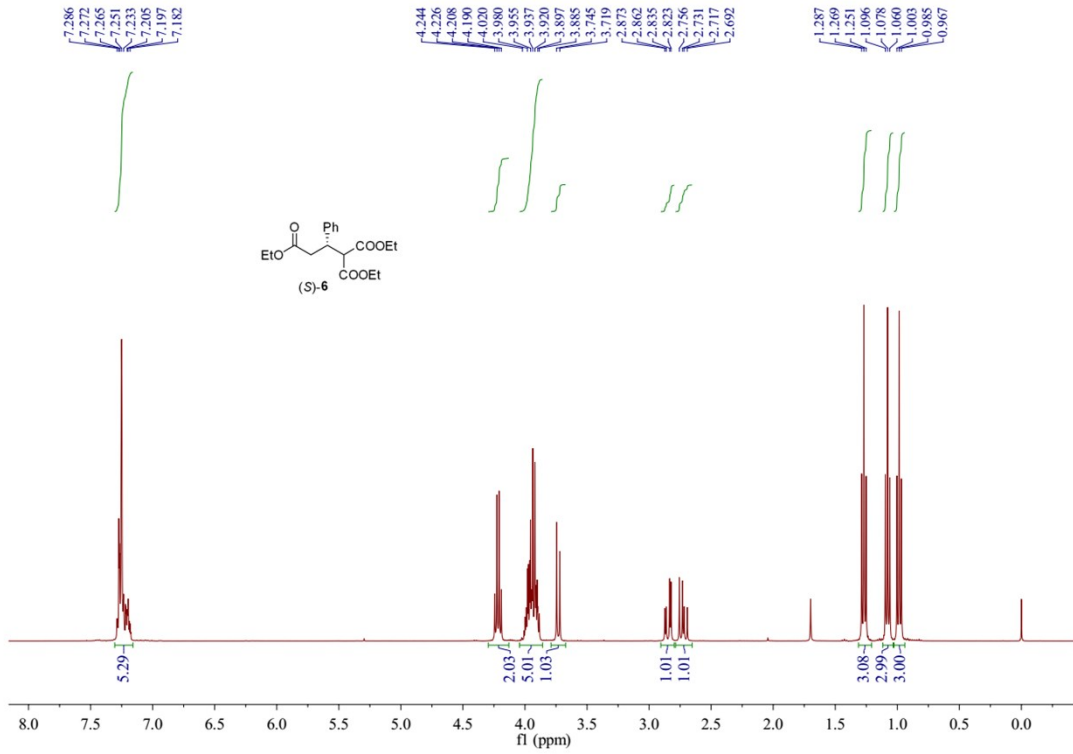
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.106	3851487	209340	49.481	54.346
2	9.573	3932276	175862	50.519	45.654
Total		7783763	385202	100.000	100.000

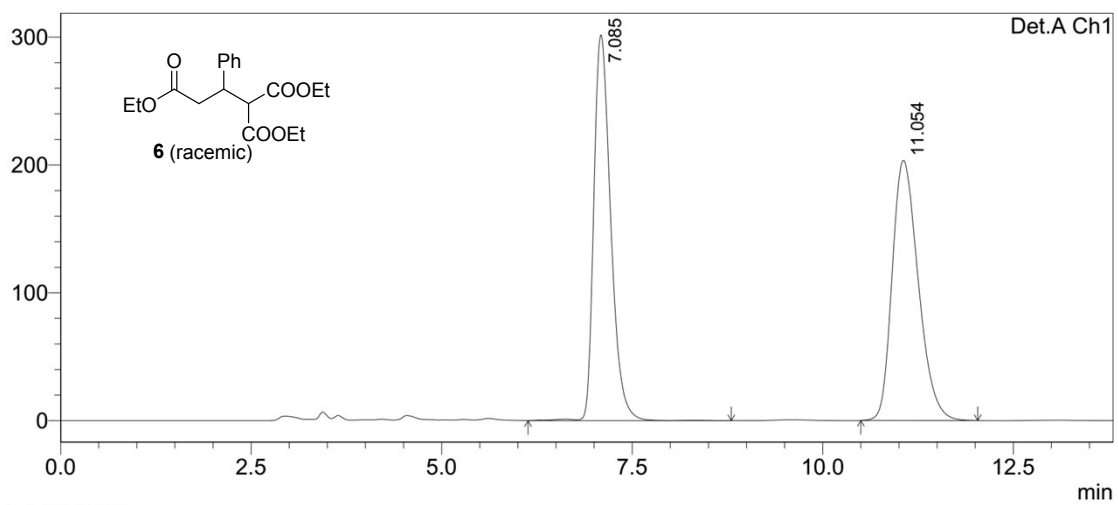
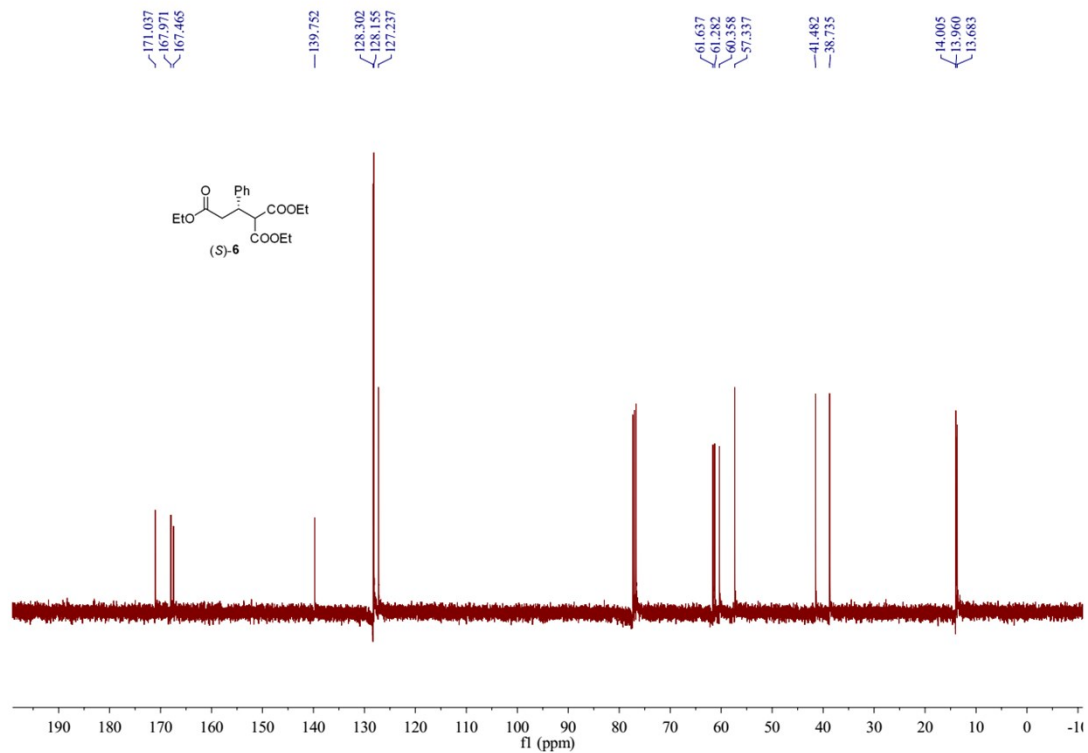


PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.135	51642	2865	0.333	0.441
2	9.557	15458504	647152	99.667	99.559
Total		15510146	650017	100.000	100.000



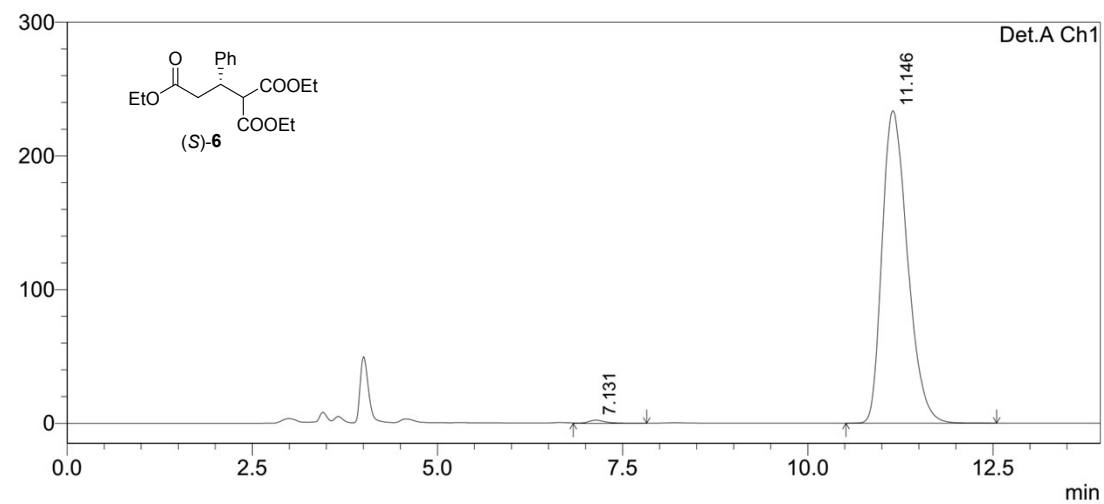


Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.085	4686019	301820	49.137	59.736
2	11.054	4850592	203435	50.863	40.264
Total		9536611	505255	100.000	100.000

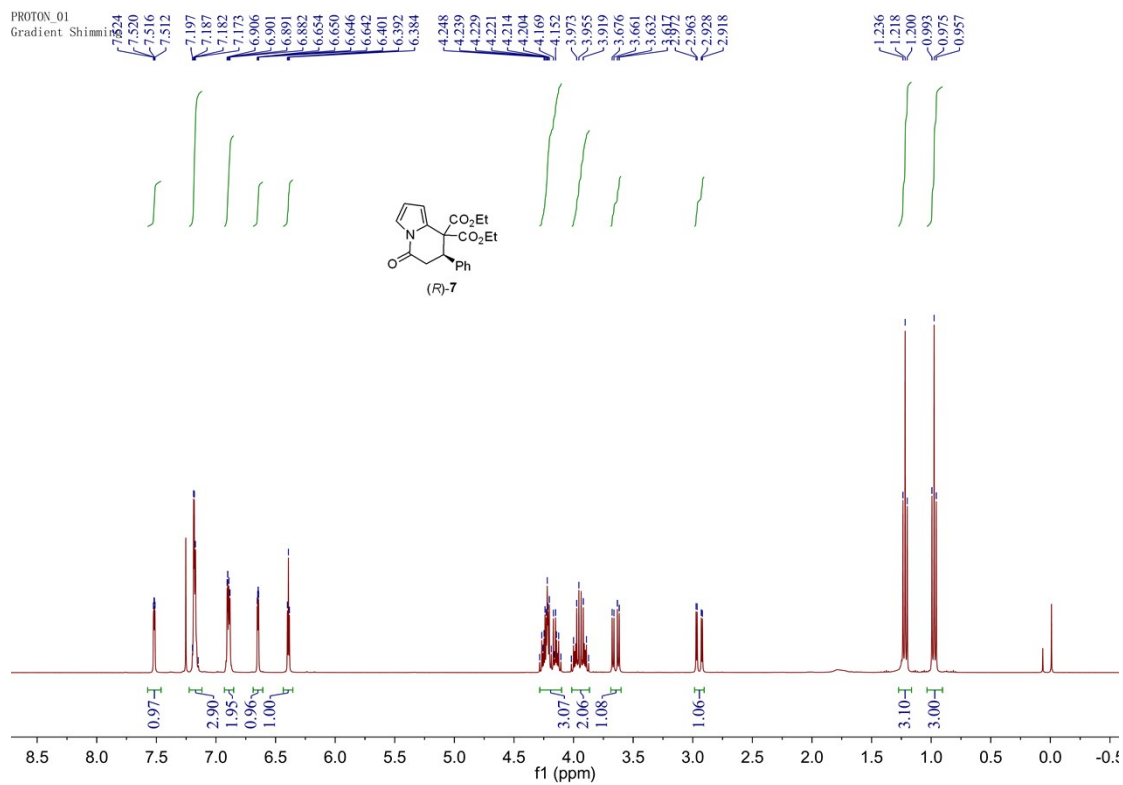


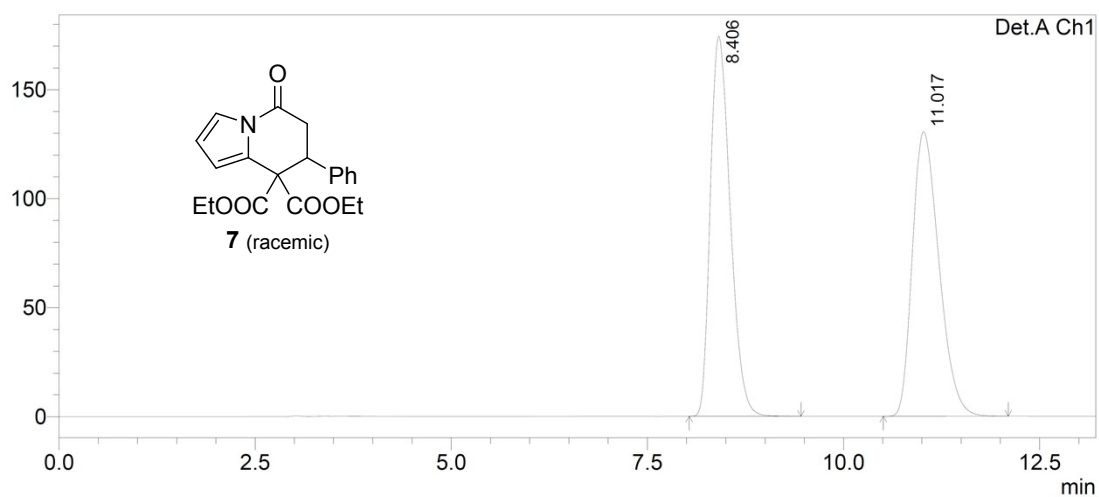
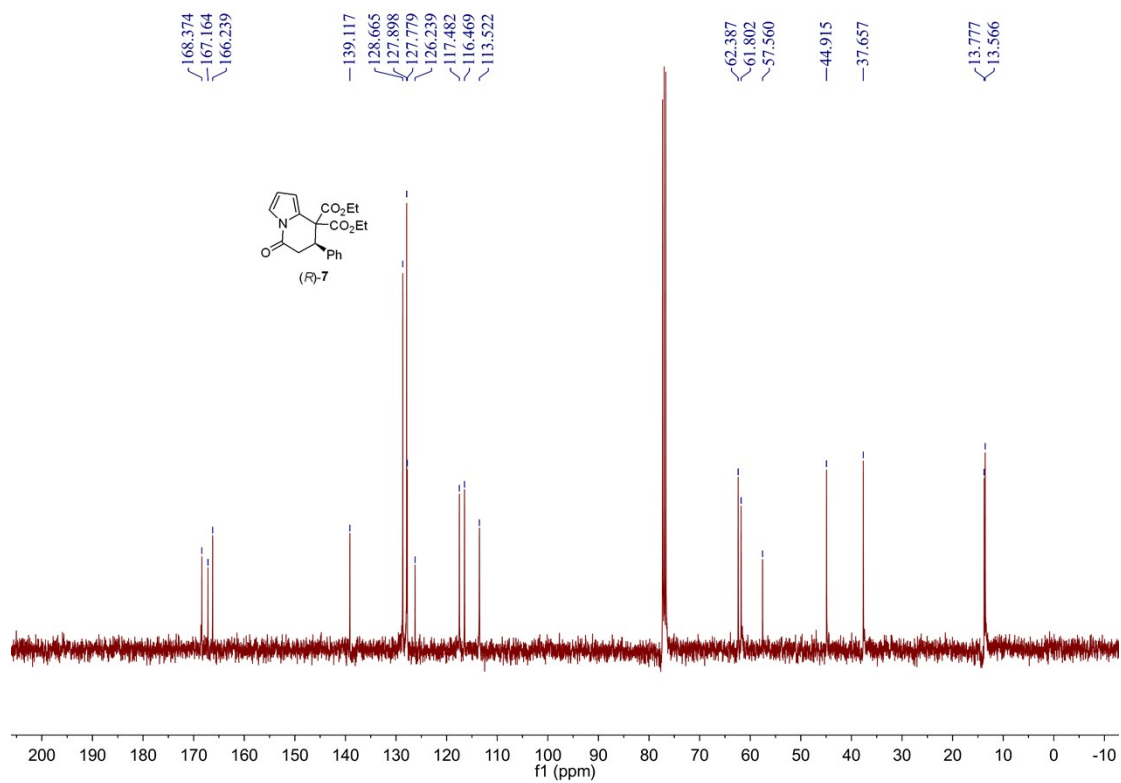
st.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.131	40348	2397	0.717	1.015
2	11.146	5588160	233761	99.283	98.985
Total		5628509	236158	100.000	100.000



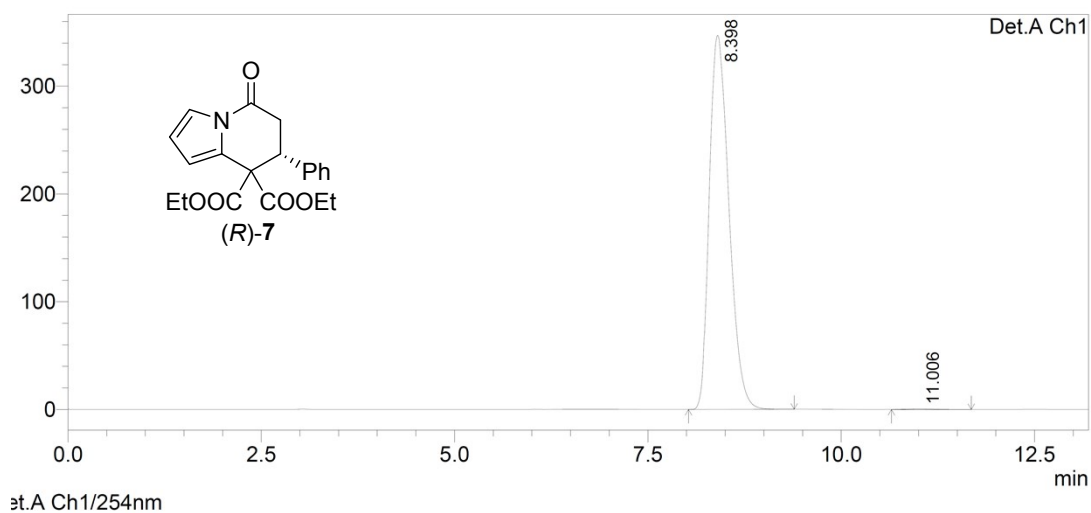


st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.406	3083101	174358	49.968	57.199
2	11.017	3087005	130471	50.032	42.801
Total		6170107	304828	100.000	100.000

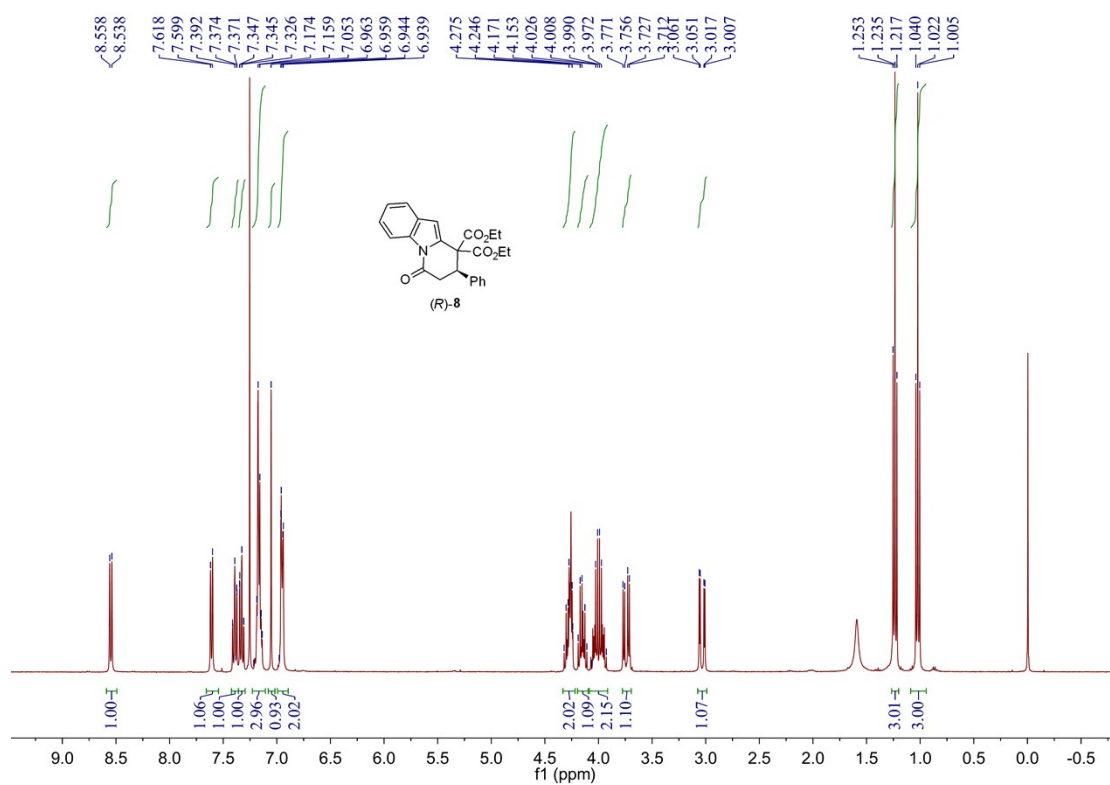


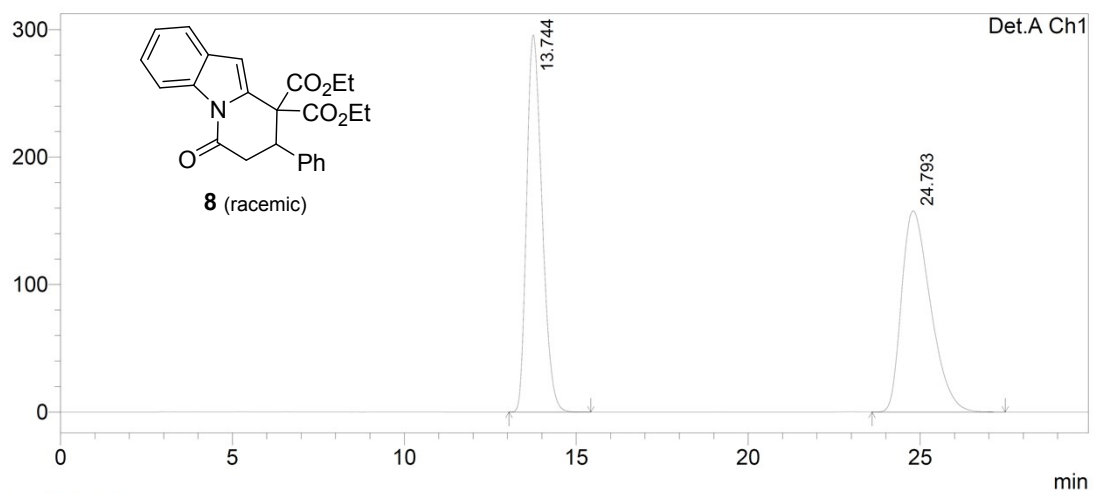
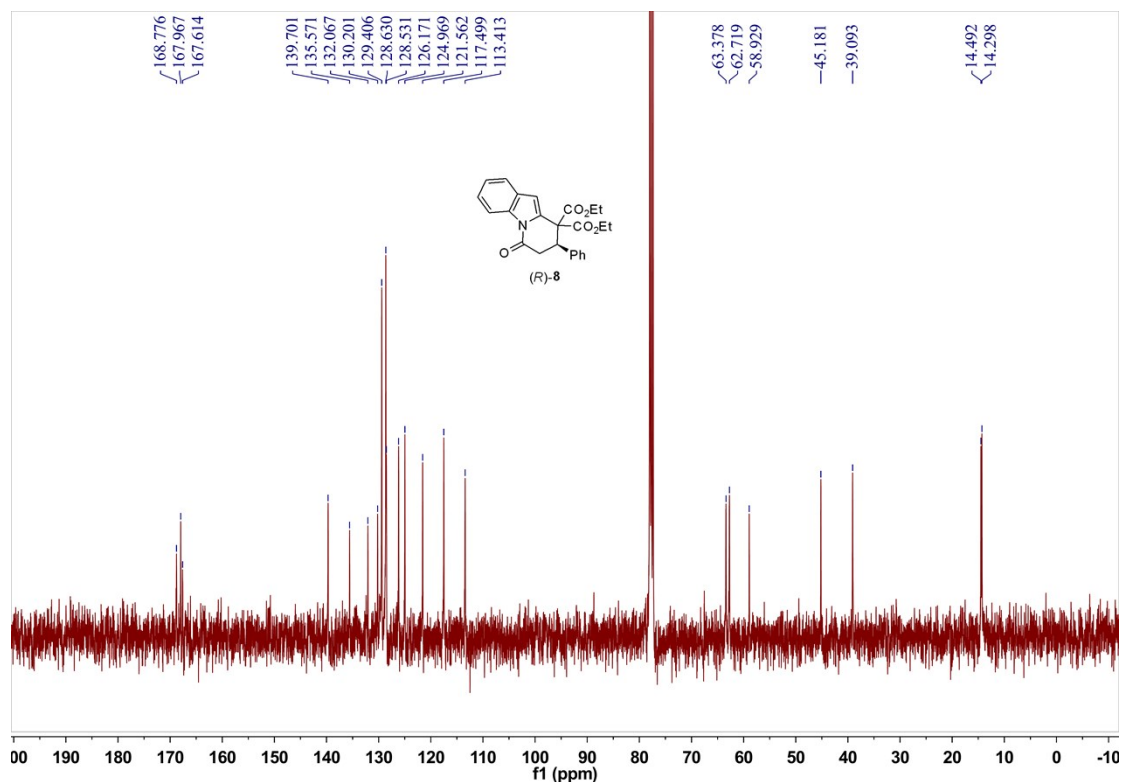
st.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.398	6152814	347216	99.811	99.854
2	11.006	11631	507	0.189	0.146
Total		6164445	347724	100.000	100.000



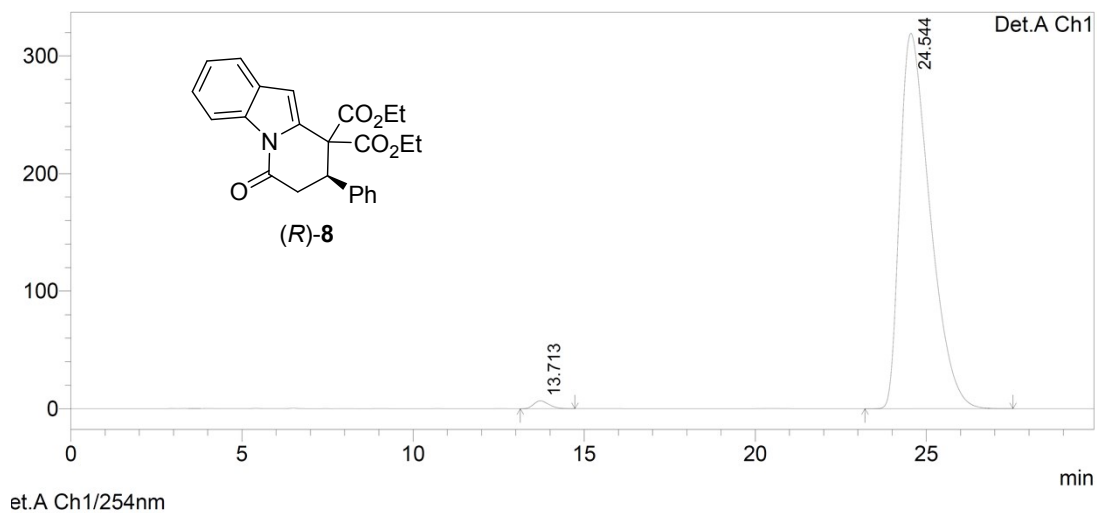


at.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.744	9227835	295997	49.893	65.210
2	24.793	9267539	157918	50.107	34.790
Total		18495374	453915	100.000	100.000



et.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.713	204686	6651	1.038	2.040
2	24.544	19523295	319401	98.962	97.960
Total		19727981	326052	100.000	100.000

The single crystal data of catalyst 3e and the product (S)-4i produced in condition B.

(1) Catalyst 3e (CCDC 1897269).

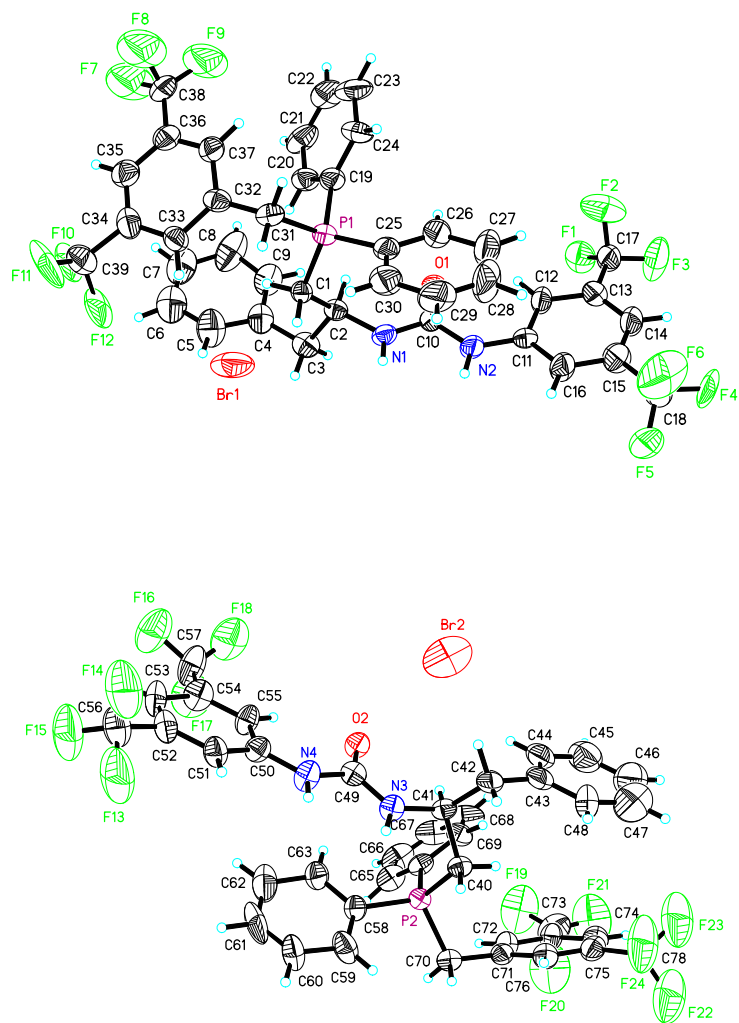


Table 1. Crystal data and structure refinement for 3e.

Identification code	3e	
Empirical formula	$C_{39}H_{32}BrF_{12}N_2O_2P$	
Formula weight	899.54	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 8.7747(4) Å	a = 72.036(2)°.
	b = 15.1721(9) Å	b = 88.944(2)°.

	$c = 16.4580(9) \text{ \AA}$	$g = 84.345(2)^\circ$.
Volume	$2073.94(19) \text{ \AA}^3$	
Z	2	
Density (calculated)	1.440 Mg/m^3	
Absorption coefficient	1.119 mm^{-1}	
F(000)	908	
Crystal size	$0.190 \times 0.130 \times 0.080 \text{ mm}^3$	
Theta range for data collection	$2.333 \text{ to } 24.998^\circ$.	
Index ranges	$-10 \leq h \leq 10, -18 \leq k \leq 18, -19 \leq l \leq 19$	
Reflections collected	31904	
Independent reflections	14162 [R(int) = 0.1088]	
Completeness to $\theta = 25.242^\circ$	97.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7153 and 0.5531	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14162 / 186 / 1079	
Goodness-of-fit on F^2	1.008	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1053, wR2 = 0.2673$	
R indices (all data)	$R1 = 0.1529, wR2 = 0.3269$	
Absolute structure parameter	0.187(13)	
Largest diff. peak and hole	0.702 and $-0.494 \text{ e. \AA}^{-3}$	

(1) The product (*S*)-**4i** produced in condition B. (CCDC 1897272).

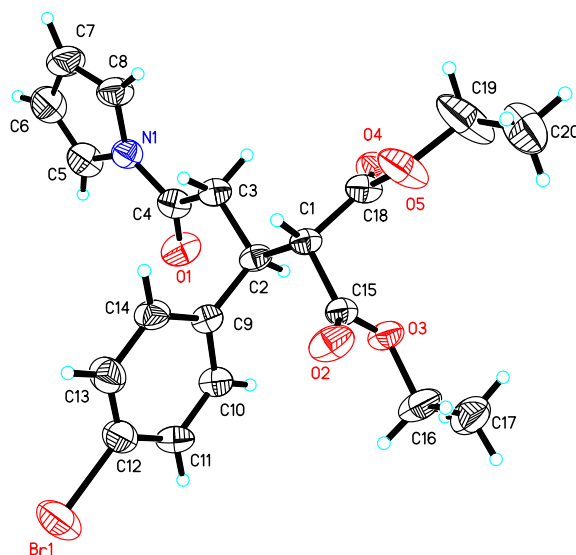


Table 1. Crystal data and structure refinement for (*S*)-**4i**

Identification code	(<i>S</i>)- 4i
Empirical formula	$\text{C}_{20}\text{H}_{22}\text{BrNO}_5$

Formula weight	436.29	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 12.3447(10) Å	a = 90°.
	b = 5.5630(5) Å	b = 104.256(2)°.
	c = 17.4342(15) Å	g = 90°.
Volume	1160.40(17) Å ³	
Z	2	
Density (calculated)	1.249 Mg/m ³	
Absorption coefficient	1.797 mm ⁻¹	
F(000)	448	
Crystal size	0.170 x 0.140 x 0.100 mm ³	
Theta range for data collection	1.702 to 25.496°.	
Index ranges	-14 ≤ h ≤ 14, -6 ≤ k ≤ 6, -21 ≤ l ≤ 21	
Reflections collected	16833	
Independent reflections	4286 [R(int) = 0.0491]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6022	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4286 / 1 / 247	
Goodness-of-fit on F ²	0.989	
Final R indices [I > 2σ(I)]	R1 = 0.0472, wR2 = 0.1126	
R indices (all data)	R1 = 0.0859, wR2 = 0.1270	
Absolute structure parameter	0.023(8)	
Extinction coefficient	0.011(3)	
Largest diff. peak and hole	0.401 and -0.323 e.Å ⁻³	