

Catalytic Asymmetric Addition and Telomerization of Butadiene with Enamine Intermediate

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Supporting Information

Table of Contents

General information and materials	S2
Experimental section.....	S3
NMR spectra.....	S34
HPLC charts.....	S75

General information: All commercial reagents were used without further purification unless otherwise noted. Nuclear magnetic resonance (NMR) was recorded on Bruker AV-400 and AV-500 spectrometers. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were measured on a NMR instrument (400 and 500 MHz for ^1H NMR, 101 and 126 MHz for ^{13}C NMR) with solvent resonance as the internal standard (^1H NMR: CDCl_3 at 7.26 ppm; ^{13}C NMR: CDCl_3 at 77.16 ppm). ^1H NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, td = triplet of doublet, dt = doublet of triplet, dd = doublet of doublet), coupling constants (Hz), and integration. The enantiomeric excesses were determined by HPLC analysis on Chiral Daicel Chiralpak AD, IC, IA, AS-H, OJ-H columns. Optical rotation was measured on a commercial polarimeter and reported as follows: $[\alpha]_D^{25}$ (c = g/100 mL, solvent). Infrared Spectroscopy was conducted on Thermo Fisher Nicolet 6700. High resolution mass spectra were obtained using electrospray ionization (ESI), Atmospheric Pressure Chemical Ionization (APCI) and Electron Impact (EI) mass spectrometer. Silica gel (100-200 mesh) was used for column chromatography.

Materials: The corresponding β -ketocarbonyl substrates were prepared according to reported procedures.¹ The α -branched aldehydes were prepared following literature precedent.²

General procedure for reactions

Procedure A: To a flame-dried Schlenk tube equipped with a magnetic stir bar was added β -ketocarbonyl (**2**, 0.1 mmol), primary amine **1a**/TfOH (20 mol%, 7.0 mg), Pd(OAc)₂ precursor (5 mol%, 1.1 mg), DPEPhos (10 mol%, 5.40 mg), followed by butadiene (0.5 mL, 2M in THF). The reaction mixture was stirred at 60 °C, under Ar for 60 h. Then solvent was removed and the residue was purified by silica gel column (Hexane: EtOAc = 50 : 1) to give **4**. The **4/5** value was determined by NMR. The enantiometric excess was determined by GC or HPLC after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst.

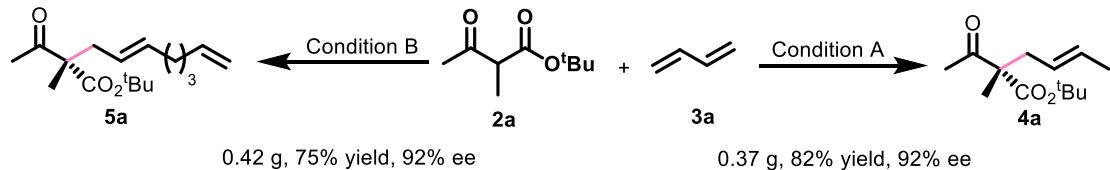
Procedure B: To a flame-dried Schlenk tube equipped with a magnetic stir bar was added β -ketocarbonyl (**2**, 0.1 mmol), primary amine **1a**/TfOH (20 mol%, 7.0 mg), Pd(C₃H₅)Cp precursor (5 mol%, 1.1 mg), Tri-*p*-tolylphosphine (10 mol%, 3.0 mg), followed by butadiene (0.5 mL, 2M in THF). The reaction mixture was stirred under Ar, at 60 °C for 60 h. Then solvent was removed and the residue was purified by silica gel column (Hexane: EtOAc = 50 : 1) to give **5**. The **5/4** value was determined by NMR. The enantiometric excess was determined by GC or HPLC after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst.

General procedure for reactions of α -branched aldehydes

To a flame-dried Schlenk tube equipped with a magnetic stir bar was added α -branched aldehydes (**6**, 0.1 mmol), primary amine **1c**/NHTf₂ (20 mol%, 11.2 mg), Pd(C₃H₅)Cp precursor (5 mol%, 1.1 mg), Tri-*p*-tolylphosphine (10 mol%, 3.0 mg), followed by butadiene (0.5 mL, 2M in THF). The reaction mixture was stirred under Ar, at 60 °C for 60 h. Then solvent was removed and the residue was purified by silica gel column (Hexane: EtOAc = 50 : 1) to give main product **8**. The **8/7** value was determined by NMR. The enantiometric excess was determined by HPLC after one

step transformation via olefin metathesis reaction with 2nd Grubbs catalyst.

General procedure for the larger scale experiments

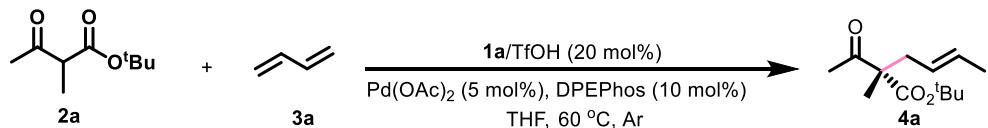


Procedure A: To a flame-dried Schlenk tube equipped with a magnetic stir bar was added β -ketocarbonyl (**2a**, 2.0 mmol), primary amine **1a**/TfOH (20 mol%, 140.0 mg), Pd(OAc)₂ precursor (5 mol%, 22.0 mg), DPEPhos (10 mol%, 108.0 mg), followed by butadiene (6.0 mL, 2M in THF). The reaction mixture was stirred at 60 °C, under Ar for 60 h. Then solvent was removed and the residue was purified by silica gel column (Hexane: EtOAc = 50 : 1) to give **4a** in 82% yield. The **4a/5a** value was determined by NMR. The enantiometric excess was determined by HPLC after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst.

Procedure B: To a flame-dried Schlenk tube equipped with a magnetic stir bar was added β -ketocarbonyl (**2a**, 2.0 mmol), primary amine **1a**/TfOH (20 mol%, 140.0 mg), Pd(C₃H₅)Cp precursor (5 mol%, 22.0 mg), Tri-*p*-tolylphosphine (10 mol%, 60.0 mg), followed by butadiene (0.5 mL, 2M in THF). The reaction mixture was stirred under Ar, at 60 °C for 60 h. Then solvent was removed and the residue was purified by silica gel column (Hexane: EtOAc = 50 : 1) to give **5a** in 75% yield. The **5a/4a** value was determined by NMR. The enantiometric excess was determined by HPLC after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst.

Optimization of Reaction Conditions for Pathway-A

Table 1: Screening for Standard Conditions ^a



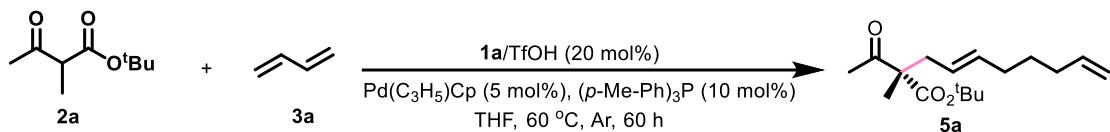
Entry	Variations	Yield (%)	<i>ee</i> (%)
1	None	83	93
2	[Pd(C ₃ H ₅)Cl] ₂	78	92
3	Pd(PCy ₃) ₂ Cl ₂	NR	/
4	Pd ₂ (dba) ₃	77	92
5	Pd(PPh ₃) ₄	62	90
6	Pd(C ₃ H ₅)Cp	80 (7:3)	90
7	Pd(acac) ₂	81	91
8	DPPB	NR	/
9	DPPP	NR	/
10	DPPM	NR	/
11	CHCl ₃	NR	/
12	DCM	71	79
13	Toluene	54 (4:1)	83
14	MeOH	80	86
15	CH ₃ CN	77	81

^a Reactions were performed at 60 °C with **2a** (0.1 mmol), **1a** (20 mol%) under Ar for 40-60 h.

Isolated yield. **4a/5a** > 19:1, was determined by NMR. Enantiomeric excess was determined by HPLC analysis after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst.

Optimization of Reaction Conditions for Pathway-B

Table 2: Screening for Standard Conditions ^a



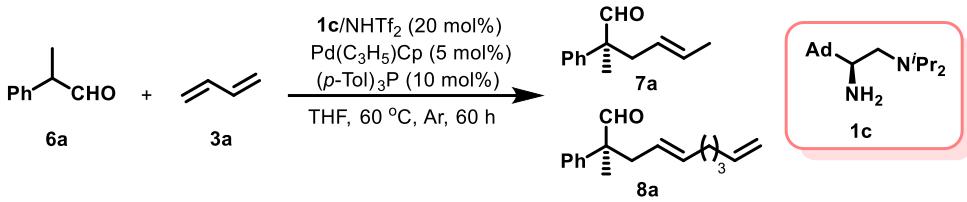
Entry	Variation from standard conditions	Yield (%) (5a : 4a)	<i>ee</i> (%)
1	none	80	93
2	PPh ₃	21	41
3	(o-Tol) ₃ P	71	29
4	(o-OMe-Ph) ₃ P	trace	/
5	PCy ₃	26	50
6	(p-F-Ph) ₃ P	40	70
7	(C ₆ F ₅) ₃ P	trace	/
8	(NMe ₂) ₃ P	trace	/
9	(OMe) ₃ P	95 (4:1)	91
10	(OPh) ₃ P	93 (4:1)	85
11		29 (7:1)	87
12	CHCl ₃	49	89
13	DCM	88	87
14	MeOH	95	75
15	CH ₃ CN	84	81

^a Reactions were performed at 60 °C with **2a** (0.1 mmol), **1a** (20 mol%) under Ar for 40-60 h.

Isolated yield. **5a**/**4a** > 19:1, was determined by NMR. Enantiomeric excess was determined by HPLC analysis after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst.

Optimization of Reaction Conditions for α -Branched Aldehyds

Table 3: Screening for Standard Conditions ^a



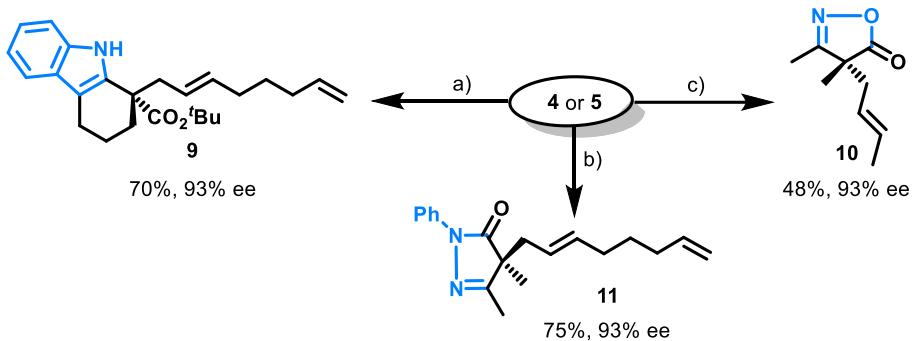
Entry	Variation from standard conditions	Yield (%)	ee (%)
1	none	62 (94:6)	83
2	1c /TfOH	74 (>19:1)	71
3	1a /TfOH	64 (94:6)	62
4	1b /TfOH	70 (87:13)	82
5	PPh ₃	71 (9:1)	82
6	(<i>p</i> -OMe-Ph) ₃ P	41 (9:1)	83
7	(<i>p</i> -F-Ph) ₃ P	71 (92:8)	82
8	(<i>o</i> -Me-Ph) ₃ P	55 (92:8)	83
9	(<i>m</i> -Me-Ph) ₃ P	71 (9:1)	82
10	(<i>o</i> -OMe-Ph) ₃ P	trace	/
11	(<i>m</i> -OMe-Ph) ₃ P	trace	/
12	Bu ₃ P	NR	/
13	Ph ₂ (Tol)P	71 (92:8)	83
14	(C ₆ F ₅) ₃ P	69 (4:1)	59
15	IMes	NR	/

^a Reactions were performed at r.t in 0.3 mL of MeCN with **6a** (0.1 mmol), **1c** (20 mol%) under Ar for 40-60 h. Isolated yield. **8a/7a** > 19:1, was determined by NMR. Enantiomeric excess was determined by HPLC analysis after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst.

Synthetic Transformations

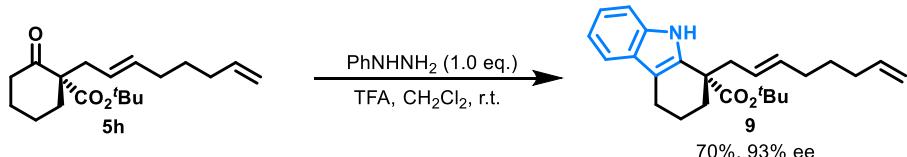
The synthetic utility of the allylation and telomerization compounds was demonstrated, and in this regard, we mainly focused on building molecular complexity. When treated with phenyl hydrazine,

adducts **5i** and **5a** underwent cyclo-condensation to form indole derivative **9** and pyrazolinone derivative **11**. Treating **4a** with hydroxylamine hydrochloride led to isoxazolone **10** with maintaining enantioselectivity. Both of these compounds are of privileged structural motif in pharmaceuticals.³



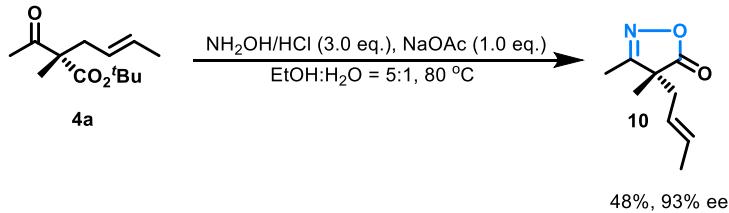
a) **5i**, PhNNH₂, TFA, CH₂Cl₂, room temperature, 12 h; b) **4a**, PhNNH₂, AcOH, EtOH, room temperature, 24 h. c) **4a**, NH₂OH/HCl, NaOAc, EtOH, H₂O, reflux, 72 h.

General procedure for products transformation

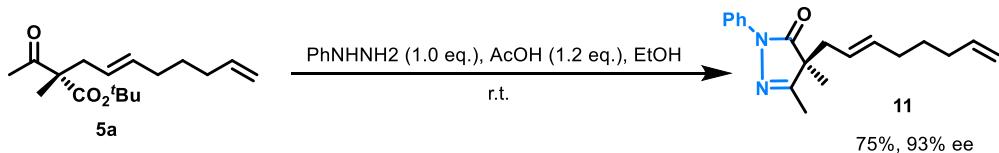


To a 10 mL tube equipped with a magnetic stir bar was added 0.1 mmol **5h**, 0.1 mmol PhNNH₂, 0.5 mL CH₂Cl₂, followed by 0.15 mmol. The reaction mixture was stirred at room temperature for 12 h. Then solvent was removed and the residue was purified by silica gel column (Hexane: EtOAc = 50 : 1) to give 26.5 mg **9** 70% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 5.86-5.76 (m, 1H), 5.57-5.50 (m, 1H), 5.43-5.30 (m, 1H), 5.03-4.96 (m, 2H), 2.81-2.65 (m, 3H), 2.54-2.49 (m, 1H), 2.37-2.24 (m, 1H), 2.12-1.76 (m, 7H), 1.52-1.41 (m, 11H). ¹³C NMR (101

MHz, CDCl₃) δ 173.8, 138.8, 136.1, 134.70, 134.5, 127.3, 125.2, 121.7, 119.1, 118.4, 114.7, 111.9, 110.9, 81.6, 47.9, 43.5, 33.3, 32.2, 31.1, 28.7, 28.3, 21.2, 20.5.



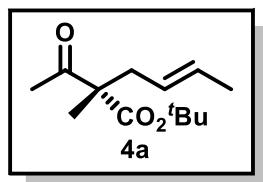
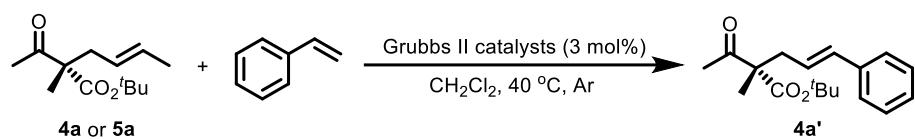
To a 10 mL tube equipped with a magnetic stir bar was added 0.1 mmol **4a**, 0.3 mmol NH₂OH/HCl, 0.1 mmol NaOAc, followed by 0.3 mL EtOH/H₂O (5:1). The reaction mixture was stirred at 80 °C for 72 h. Then solvent was removed and the residue was purified by silica gel column (Hexane: EtOAc = 8 : 1) to give 8.0 mg **10** in 48% yield. ¹H NMR (400 MHz, CDCl₃) δ 5.68-5.48 (m, 1H), 5.22-5.02 (m, 1H), 2.54-2.22 (m, 2H), 2.01 (s, 3H), 1.63 (ddd, *J* = 13.6, 7.2, 6.6 Hz, 3H), 1.31 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 180.8, 169.5, 131.8, 122.6, 51.0, 38.9, 20.1, 18.0, 12.0.



To a 10 mL tube equipped with a magnetic stir bar was added 0.1 mmol **5a**, 0.1 mmol PhNNHNH₂, 0.12 mmol AcOH, followed by 0.5 mL EtOH. The reaction mixture was stirred at room temperature for 24 h. Then solvent was removed and the residue was purified by silica gel column (Hexane: EtOAc = 50 : 1) to give 22.2 mg **11** 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 5.72-5.62 (m, 1H), 5.56-5.49 (m, 1H), 5.14-5.06 (m, 1H), 4.92-4.86 (m, 2H), 2.56-2.51 (m, 1H), 2.33-2.29 (m, 1H), 2.08 (s, 3H), 1.90 (p, *J* = 6.9 Hz, 4H), 1.36-1.24 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 175.9, 163.5, 138.6, 138.2, 135.5, 128.9, 124.9, 122.9, 118.8, 114.6, 55.0, 39.0, 33.0, 31.8, 28.4, 19.9, 13.9.

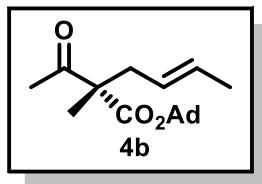
Determination of configuration

The absolute configuration of product **4a** and **5a** were confirmed by comparing HPLC of **4a'** derived from **4a** or **5a** through CM with known compound **4a'**.¹

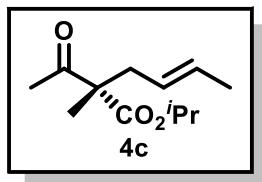


4a: Colorless oil (60 h, 17.0 mg, 75% yield, 95% ee). $[\alpha]_D^{25} = -22.1$ (*c* 1.50, CHCl₃). The ee was determined by GC. GC analysis: Rt-bDEXse, SPL 170 °C, Column 130 °C, FID 150 °C, flow rate

= 1.0 mL/min, retention time: 19.1 min (major), 19.4 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 5.52-5.47 (m, 1H), 5.29-5.22 (m, 1H), 2.54-2.36 (m, 2H), 2.13 (s, 3H), 1.63 (d, $J = 6.2$ Hz, 3H), 1.44 (s, 9H), 1.24 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.8, 171.9, 129.5, 125.3, 81.8, 60.4, 38.3, 28.0, 26.4, 19.0, 18.1. IR (thin film, cm^{-1}) 3003, 2944, 2293, 2253, 1710, 1443, 1419, 1375, 1039, 918, 749. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{22}\text{O}_3\text{Na}^+$: 249.1461, found: 249.1461.

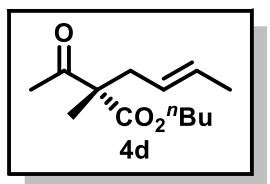


4b: Colorless oil (45 h, 20.6 mg, 68% yield, 92% *ee*). $[\alpha]_D^{25} = -19.0$ (c 2.00, CHCl_3). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak 2*OD, 1% *iso*-propanol/hexane, flow rate = 0.7 mL/min, $\lambda = 254$ nm, retention time: 25.2 min (minor), 27.7 min (major). ^1H NMR (400 MHz, CDCl_3) δ 5.52-5.45 (m, 1H), 5.29-5.22 (m, 1H), 2.53-2.35 (m, 2H), 2.16-2.08 (m, 12H), 1.73-1.57 (m, 9H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.9, 171.7, 129.5, 125.3, 81.9, 60.5, 41.3, 38.2, 36.2, 30.9, 26.4, 19.0, 18.1. IR (thin film, cm^{-1}) 2912, 2854, 1709, 1456, 1355, 1268, 1232, 1188, 1139, 1103, 1053, 987, 870, 747. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{28}\text{O}_3\text{Na}^+$: 327.1931, found: 327.1917.

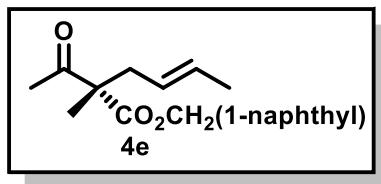


4c: Colorless oil (60 h, 14.0 mg, 66% yield, 91% *ee*). $[\alpha]_D^{25} = -28.0$ (c 1.40, CHCl_3). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst

and styrene. HPLC analysis: Daicel Chiralpak OJ, 2% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.0 min (major), 24.3 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 5.52-5.45 (m, 1H), 5.29-5.23 (m, 1H), 5.08-5.01 (m, 1H), 2.57-2.39 (m, 2H), 2.12 (s, 3H), 1.62 (d, J = 4.2 Hz, 4H), 1.28 (s, 3H), 1.22 (d, J = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.6, 172.3, 129.7, 125.1, 68.9, 59.8, 38.2, 26.4, 21.7, 19.0, 18.1. IR (thin film, cm^{-1}) 2984, 2937, 2256, 1709, 1454, 1376, 1356, 1274, 1240, 1199, 1101, 969, 907, 731, 649. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{20}\text{O}_3\text{Na}^+$: 235.1305, found: 235.1298.

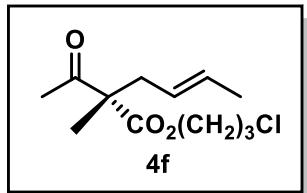


4d: Colorless oil (60 h, 17.0 mg, 75% yield, 90% *ee*). $[\alpha]_D^{25} = -19.0$ (c 1.70, CHCl_3). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak OJ, 2% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.4 min (major), 20.2 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 5.52-5.28 (m, 1H), 5.26-5.21 (m, 1H), 4.11 (t, J = 6.6 Hz, 2H), 2.58-2.40 (m, 2H), 2.12 (s, 3H), 1.63-1.60 (m, 5H), 1.38-1.24 (m, 5H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.5, 172.9, 129.8, 125.0, 65.3, 59.9, 38.3, 30.6, 26.5, 19.2, 19.0, 18.1, 13.8. IR (thin film, cm^{-1}) 2962, 2936, 2876, 2257, 1710, 1455, 1378, 1356, 1225, 1191, 1137, 1106, 968, 907, 728, 649. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{22}\text{O}_3\text{Na}^+$: 249.1461, found: 249.1455.

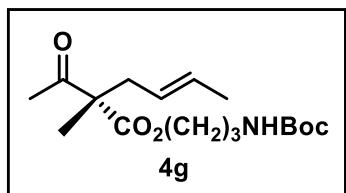


4e: Colorless oil (60 h, 20.0 mg, 65% yield, 87% *ee*). $[\alpha]_D^{25} = -22.2$ (c 2.00, CHCl_3). The *ee* was

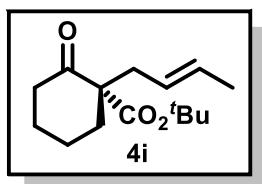
determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak 2*AD, 3% *iso*-propanol/hexane, flow rate = 0.7 mL/min, λ = 254 nm, retention time: 31.8 min (minor), 33.0 min (major). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.87 (t, *J* = 9.2 Hz, 2H), 7.63-7.38 (m, 4H), 5.62 (s, 2H), 5.42-5.34 (m, 1H), 5.22-5.14 (m, 1H), 2.57-2.38 (m, 2H), 1.99 (s, 3H), 1.54 (d, *J* = 5.7 Hz, 3H), 1.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 130.0, 129.7, 128.9, 128.0, 126.8, 125.4, 123.6, 65.5, 38.3, 26.4, 19.1, 18.1. IR (thin film, cm⁻¹) 2925, 2855, 2254, 1711, 1454, 1378, 1356, 1275, 1222, 1134, 1100, 904, 728, 650. HRMS (ESI) calcd for C₂₀H₂₂O₃Na⁺: 333.1461, found: 333.1453.



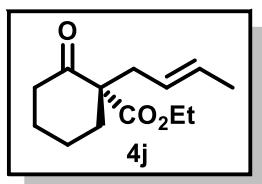
4f: Colorless oil (60 h, 18.7 mg, 76% yield, 85% *ee*). $[\alpha]_D^{25} = -10.6$ (*c* 1.88, CHCl₃). HPLC analysis: Daicel Chiralpak OJ, 15% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.6 min (minor), 19.2 min (major). ¹H NMR (400 MHz, CDCl₃) δ 5.55-5.47 (m, 1H), 5.28-5.21 (m, 1H), 4.27 (t, *J* = 6.0 Hz, 2H), 3.58 (t, *J* = 6.3 Hz, 2H), 2.59-2.41 (m, 2H), 2.18-2.04 (m, 5H), 1.64 (d, *J* = 6.4 Hz, 3H), 1.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 205.3, 172.7, 130.0, 124.8, 62.0, 59.9, 41.1, 38.3, 31.4, 29.8, 26.4, 19.1, 18.1. IR (thin film, cm⁻¹) 3021, 2985, 2938, 1711, 1451, 1378, 1357, 1215, 1137, 1106, 969, 908, 750, 732, 688, 651. HRMS (ESI) calcd for C₁₂H₁₉ClO₃Na⁺: 269.0915, found: 269.0905.



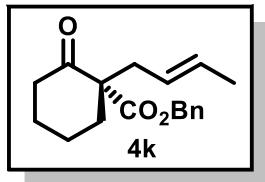
4g: Colorless oil (60 h, 28.3 mg, 87% yield, 85% *ee*). $[\alpha]_D^{25} = -10.9$ (*c* 1.83, CHCl₃). HPLC analysis: Daicel Chiraldak OJ, 15% *iso*-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 14.3 min (minor), 16.2 min (major). ¹H NMR (400 MHz, CDCl₃) δ 5.53-5.46 (m, 1H), 5.28-5.20 (m, 1H), 4.71 (s, 1H), 4.17 (t, *J* = 6.1 Hz, 2H), 3.16 (d, *J* = 6.1 Hz, 2H), 2.58-2.41 (m, 2H), 2.13 (s, 3H), 1.85-1.76 (m, 2H), 1.63 (d, *J* = 6.5 Hz, 3H), 1.42 (s, 9H), 1.30 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 205.5, 172.9, 156.0, 130.0, 124.9, 63.0, 59.9, 38.4, 37.5, 29.8, 29.2, 28.5, 26.5, 19.1, 18.1. IR (thin film, cm⁻¹) 3392, 3369, 2975, 2923, 2854, 1709, 1514, 1455, 1365, 1269, 1247, 1168, 1138, 1104, 1040, 1014, 969, 910, 864, 780, 732. HRMS (ESI) calcd for C₁₇H₂₉NO₅Na⁺: 350.1938, found: 350.1927.



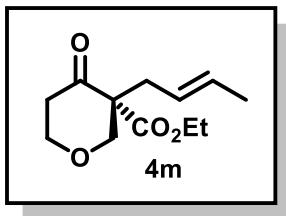
4i: Colorless oil (72 h, 20.2 mg, 80% yield, 94% *ee*). $[\alpha]_D^{25} = -89.0$ (*c* 2.00, CHCl₃). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak 2*OD, 1% *iso*-propanol/hexane, flow rate = 0.7 mL/min, $\lambda = 254$ nm, retention time: 20.9 min (minor), 35.9 min (major). ¹H NMR (400 MHz, CDCl₃) δ 5.51-5.29 (m, 2H), 2.56-2.33 (m, 4H), 2.20 (m, 1H), 2.00 (m, 1H), 1.76-1.52 (m, 7H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 208.2, 170.8, 128.7, 126.0, 81.88, 61.7, 41.4, 38.4, 36.2, 28.1, 27.8, 22.7, 18.0. IR (thin film, cm⁻¹) 3055, 2982, 2937, 2866, 1711, 1264, 1152, 735, 703. HRMS (ESI) calcd for C₁₅H₂₄O₃Na⁺: 275.1618, found: 275.1607.



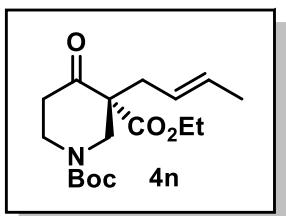
4j: Colorless oil (60 h, 16 mg, 71% yield, 92% *ee*). $[\alpha]_D^{25} = -43.3$ (*c* 1.60, CHCl₃). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak OJ, 3% *iso*-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 24.2 min (minor), 38.2 min (major). ¹H NMR (400 MHz, CDCl₃) δ 5.51-5.27 (m, 2H), 4.17 (q, *J* = 7.0 Hz, 2H), 2.56-2.39 (m, 4H), 2.25 (dd, *J* = 13.9, 7.4 Hz, 1H), 2.04-1.92 (m, 1H), 1.81-1.52 (m, 6H), 1.48-1.38 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 208.0, 171.8, 129.0, 125.8, 61.2, 41.3, 38.2, 35.9, 27.7, 22.6, 18.0, 14.3. IR (thin film, cm⁻¹) 3052, 3029, 2980, 2939, 2865, 1710, 1450, 1438, 1367, 1339, 1309, 1264, 1224, 1193, 1139, 1100, 1039, 970, 910, 864, 823, 734, 703. HRMS (ESI) calcd for C₁₃H₂₀O₃Na⁺: 247.1305, found: 247.1301.



4k: Colorless oil (60 h, 21.0 mg, 73% yield, 94% *ee*). $[\alpha]_D^{25} = -94.5$ (*c* 2.10, CHCl₃). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak AD, 2% *iso*-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 13.4 min (minor), 17.0 min (major). ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.28 (m, 5H), 5.40-5.28 (m, 2H), 5.20-5.07 (m, 2H), 2.58-2.23 (m, 5H), 2.01-1.88 (m, 1H), 1.77-1.61 (m, 3H), 1.57 (d, *J* = 5.6 Hz, 3H), 1.49-1.42 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 207.6, 171.6, 135.6, 129.2, 128.7, 128.5, 128.4, 125.5, 67.0, 61.4, 41.3, 38.1, 35.8, 27.7, 22.5, 18.0. IR (thin film, cm⁻¹) 2941, 2866, 2254, 1710, 1453, 1438, 1310, 1260, 1192, 1137, 971, 906, 728, 698, 649. HRMS (ESI) calcd for C₁₈H₂₂O₃Na⁺: 309.1461, found: 309.1453.

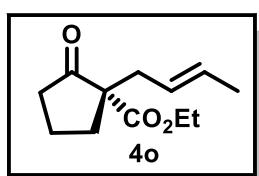


4m: Colorless oil (60 h, 16.1 mg, 71% yield, 90% *ee*). $[\alpha]_D^{25} = -81.3$ (*c* 1.60, CHCl_3). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak OJ, 15% *iso*-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 20.0 min (minor), 26.1 min (major). ¹H NMR (400 MHz, CDCl_3) δ 5.60-5.29 (m, 2H), 4.49 (d, *J* = 11.6 Hz, 1H), 4.29-4.15 (m, 3H), 3.72 (tt, *J* = 10.9, 5.5 Hz, 1H), 3.44 (d, *J* = 11.6 Hz, 1H), 2.90-2.74 (m, 1H), 2.58-2.41 (m, 2H), 2.33-2.20 (m, 1H), 1.63 (d, *J* = 5.9 Hz, 3H), 1.30-1.26 (m, 3H). ¹³C NMR (101 MHz, CDCl_3) δ 203.7, 170.4, 129.7, 124.7, 74.3, 68.8, 62.8, 61.7, 41.8, 34.0, 29.8, 18.0, 14.3. IR (thin film, cm^{-1}) 2976, 2920, 2856, 1715, 1468, 1449, 1423, 1379, 1367, 1221, 1207, 1176, 1134, 1098, 1035, 1012, 973, 906, 859, 727, 649, 549. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{18}\text{O}_4\text{Na}^+$: 249.1097, found: 249.1088.

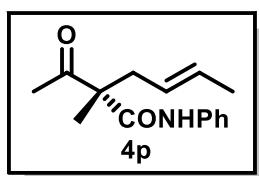


4n: Colorless oil (96 h, 13.1 mg, 40% yield, 93% *ee*, **4n/5n** = 2:1). $[\alpha]_D^{25} = -50.0$ (*c* 0.81, CHCl_3). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak 2OJ, 15% *iso*-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 19.9 min (major), 22.5 min (minor). ¹H NMR (400 MHz, CDCl_3) δ 5.82-5.72 (m, 0.38H, **5n**), 5.56-5.30 (m, 2H), 5.05-4.87 (m, 0.7H, **5n**), 4.45 (s, 1H), 4.26-3.93 (m, 3H), 3.40-3.01 (m, 2H), 2.68 (m, 1H), 2.57-2.29 (m, 3H), 2.00 (m, 1.5H,

5n), 1.63 (d, $J = 6.3$ Hz, 1.9H, **4n**), 1.52-1.36 (m, 9.7H), 1.25 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.0, 138.8, 135.3, 130.1, 124.8, 124.0, 114.7, 80.6, 61.7, 61.4, 40.0, 35.2, 33.3, 32.0, 29.8, 28.7, 28.4, 18.1, 14.3. IR (thin film, cm^{-1}) 2979, 2927, 2871, 1716, 1697, 1424, 1366, 1244, 1166, 973, 905, 729, 649. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{27}\text{NO}_5\text{Na}^+$: 348.1781, found: 348.1772.

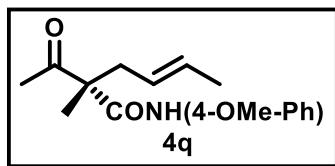


4o: Colorless oil (60 h, 12.5 mg, 60% yield, 85% ee). $[\alpha]_D^{25} = -15.1$ (c 1.20, CHCl_3). The ee was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak OJ, 5% iso-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 17.7 min (minor), 26.9 min (major). ^1H NMR (400 MHz, CDCl_3) δ 5.60-5.44 (m, 1H), 5.36-5.23 (m, 1H), 4.18-4.12 (m, 2H), 2.70-2.53 (m, 1H), 2.51-2.19 (m, 4H), 2.03-1.86 (m, 3H), 1.64 (dd, $J = 6.4, 1.5$ Hz, 3H). 1.24 (t, $J = 7.1$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 215.0, 171.2, 129.9, 125.5, 61.5, 60.4, 38.3, 36.8, 32.2, 19.6, 18.1, 14.3. IR (thin film, cm^{-1}) HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{18}\text{O}_3\text{Na}^+$: 233.1140, found: 233.1148.

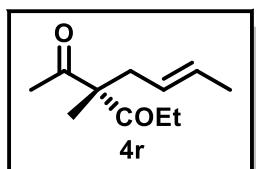


4p: Colorless oil (72 h, 22.1 mg, 90% yield, 84% ee). $[\alpha]_D^{25} = -12.9$ (c 2.00, CHCl_3). HPLC analysis: Daicel Chiraldak OJ, 5% iso-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 14.2 min (major), 15.4 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 7.55-7.43 (m, 2H), 7.32 (t, $J = 7.9$ Hz, 2H), 7.11 (t, $J = 7.4$ Hz, 1H), 5.60-5.55 (m, 1H), 5.36-5.28

(m, 1H), 2.64-2.61 (m, 2H), 2.26 (s, 3H), 1.65 (dd, J = 6.5, 1.0 Hz, 3H), 1.48 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 210.3, 169.3, 137.7, 130.5, 129.1, 125.0, 124.7, 120.2, 120.1, 60.3, 40.3, 27.4, 19.8, 18.2. IR (thin film, cm^{-1}) 3054, 3006, 2988, 1264, 896, 748, 703. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{19}\text{O}_2\text{NNa}^+$: 268.1308, found: 268.1299.

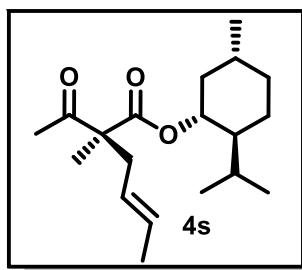


4q: Colorless oil (72 h, 23.7 mg, 86% yield, 87% *ee*). $[\alpha]_D^{25} = -15.0$ (*c* 2.37, CHCl_3). HPLC analysis: Daicel Chiraldak OJ, 10% iso-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 22.4 min (major), 24.1 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 7.99 (s, 1H), 7.38 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 5.61-5.52 (m, 1H), 5.35-5.27 (m, 1H), 3.78 (s, 3H), 2.71-2.56 (m, 2H), 2.25 (s, 3H), 1.65 (d, J = 6.2 Hz, 3H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 210.1, 169.2, 156.7, 130.8, 130.3, 125.1, 122.0, 122.0, 114.3, 60.2, 55.6, 40.2, 27.2, 19.7, 18.1. IR (thin film, cm^{-1}) 3054, 3006, 2989, 1263, 764, 749, 703. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{O}_3\text{NNa}^+$: 298.1414, found: 298.1406.

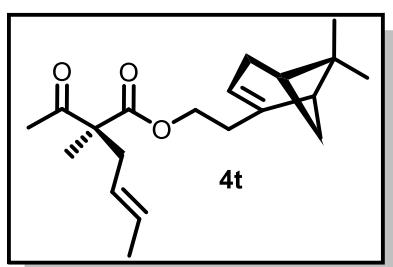


4r: Colorless oil (60 h, 15.0 mg, 73% yield, 89% *ee*, **4r/5r** = 1:1). $[\alpha]_D^{25} = -9.7$ (*c* 1.35, CHCl_3). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak OJ, 10% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 16.8 min (major), 20.7 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 5.80-5.74 (m, 0.5H, **5r**), 5.55-5.41 (m, 1H), 5.21-5.10 (m, 1H), 5.04-4.86 (m, 1H),

5r), 2.53 (dd, $J = 6.2, 2.2$ Hz, 2H), 2.39 (q, $J = 7.2$ Hz, 2H), 2.07 (s, 3H), 2.03-1.94 (m, 2H), 1.62 (dd, $J = 6.4, 1.3$ Hz, 1H)., 1.5H, **4r**), 1.45-1.34 (m, 1H), 1.29 (s, 3H), 1.03 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 209.9, 209.8, 207.3, 207.2, 138.7, 135.1, 129.8, 125.0, 124.2, 114.7, 76.8, 66.5, 37.9, 37.9, 33.3, 32.4, 32.1, 28.7, 26.9, 18.3, 18.3, 18.1, 8.1. IR (thin film, cm^{-1}) 2979, 2936, 2857, 1718, 1698, 1458, 1355, 1275, 1261, 1091, 969, 764, 749. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{18}\text{O}_2\text{Na}^+$: 205.1199, found: 205.1193.

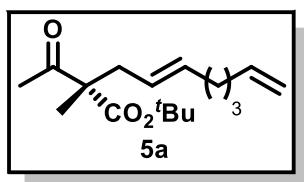


4s: Colorless oil (60 h, 26.7 mg, 87% yield, $>19:1$ *dr*). $[\alpha]_D^{25} = -60.1$ (c 2.50, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 5.53-5.48 (m, 1H), 5.28-5.20 (m, 1H), 4.69 (td, $J = 10.9, 4.3$ Hz, 1H), 2.59-2.40 (m, 2H), 2.12 (s, 3H), 2.01-1.95 (m, 1H), 1.87-1.75 (m, 1H), 1.69-1.62 (m, 5H), 1.57-1.24 (m, 6H), 1.07-0.86 (m, 8H), 0.73 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.4, 172.4, 129.9, 125.0, 75.6, 60.0, 46.9, 40.7, 38.2, 34.3, 31.5, 26.4, 26.0, 23.1, 22.1, 20.9, 19.0, 18.1, 15.9. IR (thin film, cm^{-1}) 2958, 2929, 2857, 2255, 1708, 1455, 1377, 1356, 1274, 1238, 1139, 1096, 967, 905, 729, 649. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{32}\text{O}_3\text{Na}^+$: 331.2244, found: 331.2235.

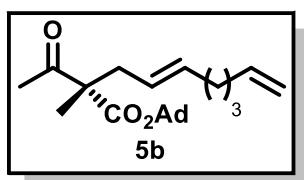


4t: Colorless oil (70 h, 30.0 mg, 94% yield, 14:1 *dr*). $[\alpha]_D^{25} = -13.5$ (c 2.50, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 5.54-5.45 (m, 1H), 5.33-5.14 (m, 2H), 4.19-4.07 (m, 2H), 2.57-2.40 (m, 2H),

2.38-2.33 (m, 1H), 2.32-2.16 (m, 4H), 2.12 (s, 3H), 2.10-2.00 (m, 2H), 1.63 (dd, J = 6.4, 1.3 Hz, 3H), 1.60 (d, J = 0.8 Hz, 1H), 1.31 (s, 1H), 1.27 (d, J = 7.0 Hz, 6H), 1.12 (d, J = 8.6 Hz, 1H), 0.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.4, 172.9, 143.9, 129.8, 127.9, 125.1, 124.2, 119.1, 63.6, 59.8, 45.8, 40.8, 38.3, 38.1, 36.0, 31.7, 31.5, 26.6, 26.4, 21.3, 19.0, 18.1. IR (thin film, cm^{-1}) 3027, 2985, 2917, 2885, 2834, 1712, 1453, 1434, 1380, 1355, 1268, 1223, 1185, 1136, 1106, 968, 736. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{30}\text{O}_3\text{Na}^+$: 341.2087, found: 341.2076.

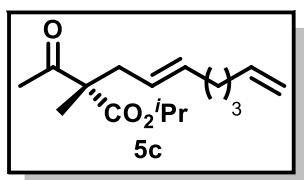


5a: Colorless oil (60 h, 22.4 mg, 80% yield, 93% *ee*). $[\alpha]_D^{25} = -20.0$ (c 2.99, CHCl_3). HPLC analysis: Daicel Chiraldak OJ, 5% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.8 min (major), 11.8 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 5.85-5.69 (m, 1H), 5.55-5.41 (m, 1H), 5.28-5.22 (m, 1H), 5.04-4.87 (m, 2H), 2.54-2.39 (m, 2H), 2.13 (s, 3H), 2.03-1.96 (m, 4H), 1.47-1.39 (m, 11H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.7, 171.9, 138.8, 134.8, 124.4, 114.7, 81.8, 60.37, 38.2, 33.3, 32.1, 28.7, 28.0, 26.4, 19.0. IR (thin film, cm^{-1}) 3077, 3063, 2979, 2931, 2856, 1710, 1641, 1457, 1369, 1264, 1150, 1114, 971, 911, 846, 735, 704. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{28}\text{O}_3\text{Na}^+$: 303.1931, found: 303.1926.

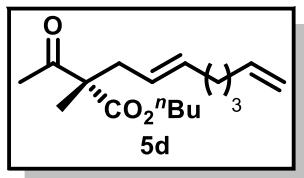


5b: Colorless oil (60 h, 23.2 mg, 65% yield, 91% *ee*). $[\alpha]_D^{25} = -20.5$ (c 2.32, CHCl_3). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak 2*OD, 1% *iso*-propanol/hexane, flow rate = 0.7

mL/min, $\lambda = 254$ nm, retention time: 25.8 min (minor), 28.2 min (major). ^1H NMR (400 MHz, CDCl_3) δ 5.83-5.73 (m, 1H), 5.51-5.44 (m, 1H), 5.28-5.21 (m, 1H), 5.01-4.92 (m, 2H), 2.54-2.37 (m, 2H), 2.19-2.07 (m, 12H), 2.01 (m, 4H), 1.65 (s, 6H), 1.47-1.38 (m, 2H), 1.24 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.8, 171.6, 138.8, 134.7, 124.5, 114.6, 81.9, 60.4, 41.3, 38.3, 36.3, 33.3, 32.1, 31.0, 28.7, 26.4, 19.0. IR (thin film, cm^{-1}) 3076, 2978, 2912, 2854, 1710, 1456, 1365, 1274, 1230, 1187, 1100, 1053, 968, 911, 868, 738, 704. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{34}\text{O}_3\text{Na}^+$: 381.2400, found: 381.2389.

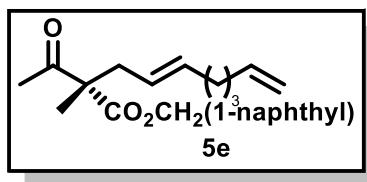


5c: Colorless oil (72 h, 17.0 mg, 65% yield, 92% ee). $[\alpha]_D^{25} = -21.6$ (c 1.70, CHCl_3). The ee was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak OJ, 2% *iso*-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 16.9 min (major), 24.1 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 5.83-5.73 (m, 1H), 5.51-5.44 (m, 1H), 5.28-5.20 (m, 1H), 5.10-4.89 (m, 3H), 2.58-2.39 (m, 2H), 2.13 (s, 3H), 2.13-1.96 (m, 4H), 1.47-1.35 (m, 2H), 1.28 (s, 3H), 1.23 (d, $J = 6.3$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.5, 172.3, 138.8, 135.0, 124.2, 114.7, 68.9, 59.8, 38.2, 33.3, 32.1, 28.7, 26.4, 21.7, 19.0. IR (thin film, cm^{-1}) 2983, 2931, 2856, 2255, 1708, 1455, 1376, 1358, 1239, 1101, 972, 906, 729, 649. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{26}\text{O}_3\text{Na}^+$: 289.1774, found: 289.1766.

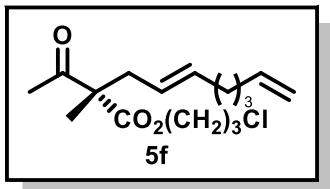


5d: Colorless oil (60 h, 21.2 mg, 76% yield, 93% ee). $[\alpha]_D^{25} = -20.3$ (c 2.12, CHCl_3). The ee was

determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak OJ, 2% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.1 min (major), 19.9 min (minor). ¹H NMR (400 MHz, CDCl₃) δ 5.81-5.72 (m, 1H), 5.50-5.44 (m, 1H), 5.26-5.22 (m, 1H), 5.08-4.86 (m, 2H), 4.11 (t, J = 6.6 Hz, 2H), 2.59-2.42 (m, 2H), 2.13 (s, 3H), 2.08-1.90 (m, 4H), 1.62-1.57 (m, 2H), 1.44-1.27 (m, 7H), 0.92 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 205.5, 172.9, 138.8, 135.1, 124.2, 114.7, 65.3, 59.9, 38.3, 33.3, 32.1, 30.6, 28.7, 26.5, 19.2, 19.0, 13.8. IR (thin film, cm⁻¹) 2962, 2932, 2875, 2857, 1710, 1640, 1458, 1377, 1356, 1225, 1099, 971, 906, 729, 649. HRMS (ESI) calcd for C₁₇H₂₈O₃Na⁺: 303.1931, found: 303.1924.

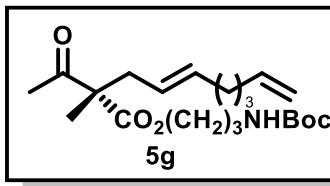


5e: Colorless oil (60 h, 27.0 mg, 74% yield, 90% ee). [α]_D²⁵ = -27.2 (*c* 2.20, CHCl₃). The ee was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak 2*AD, 3% *iso*-propanol/hexane, flow rate = 0.7 mL/min, λ = 254 nm, retention time: 31.3 min (minor), 32.6 min (major). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, J = 8.3 Hz, 1H), 7.87 (dd, J = 10.5, 8.5 Hz, 2H), 7.62-7.37 (m, 4H), 5.81-5.71 (m, 1H), 5.62 (s, 2H), 5.41-5.34 (m, 1H), 5.20-5.13 (m, 1H), 5.04-4.87 (m, 2H), 2.59-2.40 (m, 2H), 2.05-1.81 (m, 7H), 1.38-1.27 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 205.3, 172.7, 138.77, 135.2, 133.8, 131.7, 131.0, 129.6, 128.9, 128.0, 126.8, 126.1, 125.3, 124.0, 123.5, 114.7, 65.5, 60.1, 38.3, 33.3, 32.0, 28.6, 26.4, 19.0. IR (thin film, cm⁻¹) 3073, 3050, 2979, 2927, 2854, 1710, 1640, 1600, 1512, 1456, 1438, 1355, 1220, 1100, 971, 906, 800, 776, 728, 649. HRMS (ESI) calcd for C₂₄H₂₈O₃Na⁺: 387.1931, found: 387.1924.



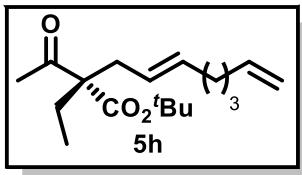
5f: Colorless oil (60 h, 15.0 mg, 50% yield, 86% *ee*, **5f/4f** = 9:1). $[\alpha]_D^{25} = -6.7$ (*c* 1.50, CHCl₃).

HPLC analysis: Daicel Chiraldak OJ, 15% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.6 min (minor), 19.2 min (major). ¹H NMR (400 MHz, CDCl₃) δ 5.83-5.73 (m, 0.9H, **5f**), 5.57-5.41 (m, 1H), 5.28-5.22 (m, 1H), 5.01-4.93 (m, 1.8H, **5f**), 4.27 (t, *J* = 5.9 Hz, 2H), 3.58 (t, *J* = 6.3 Hz, 2H), 2.60-2.42 (m, 2H), 2.21-1.89 (m, 8.6H), 1.64 (d, *J* = 6.4 Hz, 0.3H, **4f**), 1.42 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 205.3, 172.6, 138.8, 135.3, 124.0, 114.7, 62.0, 60.0, 41.1, 38.4, 33.3, 32.1, 31.4, 29.9, 28.7, 26.4, 19.1. IR (thin film, cm⁻¹) 2926, 2855, 2360, 2341, 2255, 1713, 1456, 1377, 1356, 1216, 1100, 972, 907, 757, 731, 668, 650. HRMS (ESI) calcd for C₁₆H₂₅ClO₃Na⁺: 323.1384, found: 323.1375.

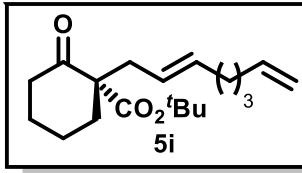


5g: Colorless oil (60 h, 20.0 mg, 53% yield, 86% *ee*). $[\alpha]_D^{25} = -15.0$ (*c* 2.00, CHCl₃). HPLC analysis: Daicel Chiraldak OJ, 15% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 14.3 min (minor), 16.3 min (major). ¹H NMR (400 MHz, CDCl₃) δ 5.83-5.74 (m, 1H), 5.53-5.44 (m, 1H), 5.32-5.17 (m, 1H), 5.00-4.92 (m, 2H), 4.69 (s, 1H), 4.18 (t, *J* = 5.2 Hz, 2H), 3.17 (d, *J* = 6.1 Hz, 2H), 2.59-2.43 (m, 2H), 2.14 (s, 3H), 2.04-1.96 (m, 4H), 1.86-1.76 (m, 2H), 1.43-1.40 (m, 11H), 1.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 205.5, 172.9, 160.0, 138.8, 135.3, 124.1, 114.7, 63.1, 60.0, 38.4, 37.5, 33.3, 32.1, 29.8, 29.2, 28.7, 28.5, 26.5, 19.1. IR (thin film, cm⁻¹) 3401, 2978, 2929, 2856, 2254, 1708, 1509, 1455, 1366, 1247, 1168, 1108, 971, 907,

729, 649. HRMS (ESI) calcd for $C_{21}H_{35}NO_5Na^+$: 404.2407, found: 404.2395.



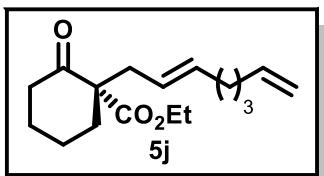
5h: Colorless oil (72 h, 7.0 mg, 24% yield, 95% *ee*). $[\alpha]_D^{25} = -12.5$ (*c* 0.60, CHCl₃). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak 2*OJ, 1% *iso*-propanol/hexane, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: 59.3 min (major), 75.4 min (minor). ¹H NMR (400 MHz, CDCl₃) δ 5.83-5.73 (m, 1H), 5.51-5.44 (m, 1H), 5.23-5.11 (m, 1H), 5.05-4.88 (m, 2H), 2.50 (dd, *J* = 7.4, 0.9 Hz, 2H), 2.11 (s, 3H), 2.05-1.95 (m, 4H), 1.91-1.78 (m, 2H), 1.50-1.34 (m, 11H), 0.76 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 205.4, 171.4, 138.8, 134.5, 124.2, 114.7, 81.8, 64.5, 34.0, 33.3, 32.1, 28.7, 28.0, 26.8, 24.1, 8.1. IR (thin film, cm⁻¹) 2976, 2928, 2855, 1711, 1369, 1255, 1154, 969, 911, 845, 735. HRMS (ESI) calcd for $C_{18}H_{30}O_3Na^+$: 317.2087, found: 317.2087.



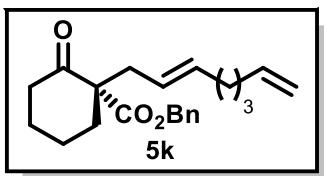
5i: Colorless oil (40 h, 25.4 mg, 83% yield, 93% *ee*). $[\alpha]_D^{25} = -90.0$ (*c* 2.50, CHCl₃). The *ee* was determined by GC. GC analysis: Rt-bDEXse, SPL 180 °C, Column 150 °C, FID 170 °C, flow rate = 1.0 mL/min, retention time: 19.9 min (major), 20.7 min (minor). ¹H NMR (400 MHz, CDCl₃) δ 5.81-5.73 (m, 1H), 5.52-5.29 (m, 2H), 5.06-4.84 (m, 2H), 2.54-2.38 (m, 4H), 2.27-2.22 (m, 1H), 2.05-1.95 (m, 5H), 1.75-1.55 (m, 4H), 1.43-1.40 (m, 11H). ¹³C NMR (101 MHz, CDCl₃) δ 208.1, 170.8, 138.9, 134.0, 125.1, 114.6, 81.9, 61.6, 41.4, 38.4, 36.0, 33.4, 32.1, 28.7, 28.1, 27.8, 22.7. IR

(thin film, cm^{-1}) 3076, 2877, 2932, 2664, 1710, 1453, 1438, 1369, 1250, 1151, 972, 910, 844, 737.

HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{30}\text{O}_3\text{Na}^+$: 329.2087, found: 329.2075.



5j: Colorless oil (60 h, 18.0 mg, 65% yield, 92% *ee*). $[\alpha]_D^{25} = -64.3$ (*c* 1.65, CHCl_3). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak OJ, 3% *iso*-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 24.6 min (minor), 38.9 min (major). ^1H NMR (400 MHz, CDCl_3) δ 5.83-5.72 (m, 1H), 5.47-5.29 (m, 2H), 5.06-4.85 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.55-2.41 (m, 4H), 2.29-2.24 (m, 1H), 2.04-1.94 (m, 5H), 1.78-1.60 (m, 4H), 1.48-1.37 (m, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 207.9, 171.7, 138.9, 134.3, 124.9, 114.6, 61.3, 61.2, 41.3, 38.3, 35.9, 33.3, 32.1, 28.8, 27.7, 22.6, 14.3. IR (thin film, cm^{-1}) 3076, 2978, 2932, 2863, 1713, 1439, 1137, 1094, 1023, 974, 910, 740. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{26}\text{O}_3\text{Na}^+$: 301.1774, found: 301.1763.



5k: Colorless oil (60 h, 27.0 mg, 79% yield, 94% *ee*). $[\alpha]_D^{25} = -82.4$ (*c* 2.70, CHCl_3). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak AD, 2% *iso*-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 13.4 min (minor), 17.0 min (major). ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.30 (m, 5H), 5.82-5.72 (m, 1H), 5.40-5.24 (m, 2H), 5.15 (dd, *J* = 10.7, 7.5 Hz, 2H),

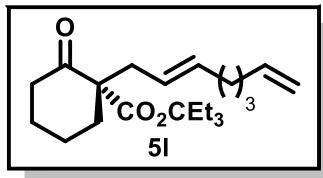
5.05-4.88 (m, 2H), 2.59-2.26 (m, 5H), 2.09-1.83 (m, 5H), 1.75-1.61 (m, 3H), 1.49-1.32 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 207.7, 171.6, 138.9, 135.6, 134.5, 128.7, 128.5, 128.4, 124.7,

114.6, 66.9, 61.4, 41.3, 38.2, 35.8, 33.3, 32.0, 28.7, 27.7, 22.6. IR (thin film, cm⁻¹) 2932, 2858,

1712, 1455, 1438, 1195, 1136, 973, 905, 728, 649. HRMS (ESI) calcd for C₂₂H₂₈O₃Na⁺: 363.1931,

found: 363.1921.



5l: Colorless oil (60 h, 26.0 mg, 75% yield, 97% ee). [α]_D²⁵ = -86.8 (c 2.70, CHCl₃). The ee was

determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst

and styrene. HPLC analysis: Daicel Chiraldak 2*OD, 5% *iso*-propanol/hexane, flow rate = 0.7

mL/min, λ = 254 nm, retention time: 12.4 min (minor), 14.9 min (major). ¹H NMR (400 MHz,

CDCl₃) δ 5.83-5.73 (m, 1H), 5.49-5.26 (m, 2H), 5.00-4.91 (m, 2H), 2.53-2.33 (m, 5H), 2.03-1.96

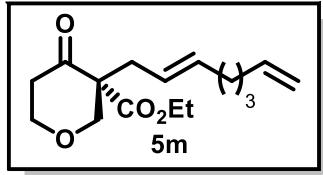
(m, 5H), 1.84-1.79 (m, 6H), 1.72-1.57 (m, 3H), 1.48-1.36 (m, 3H), 0.82 (t, J = 7.5 Hz, 9H). ¹³C

NMR (101 MHz, CDCl₃) δ 207.9, 170.6, 138.9, 134.3, 125.1, 114.6, 90.4, 61.5, 41.4, 38.5, 35.2,

33.4, 32.1, 28.7, 27.4, 27.3, 22.7, 8.0. IR (thin film, cm⁻¹) 2973, 2933, 2884, 2863, 1709, 1458,

1438, 1264, 1200, 1131, 973, 911, 874, 737, 704. HRMS (ESI) calcd for C₂₂H₃₆O₃Na⁺: 371.2556,

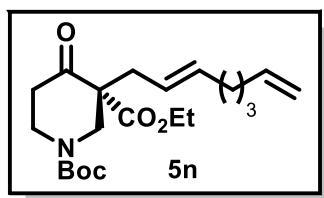
found: 371.2557.



5m: Colorless oil (60 h, 14.0 mg, 50% yield, 90% ee, **5m/4m** = 3:1). [α]_D²⁵ = -57.9 (c 1.21,

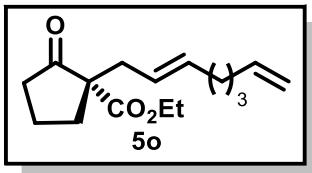
CHCl₃). The ee was determined after one step transformation via olefin metathesis reaction with

2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak OJ, 15% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 20.8 min (minor), 25.8 min (major). ¹H NMR (400 MHz, CDCl₃) δ 5.82-5.72 (m, 0.75H, **5m**), 5.59-5.31 (m, 2H), 5.10-4.88 (m, 1.5H, **5m**), 4.47 (d, J = 11.6 Hz, 1H), 4.30-4.15 (m, 3H), 3.74-3.63 (m, 1H), 3.51-3.41 (m, 1H), 2.92-2.75 (m, 1H), 2.59-2.42 (m, 2H), 2.38-2.23 (m, 1H), 2.02-1.97 (m, 2H, **5m**), 1.65 (d, J = 6.2 Hz, 0.75H, **4m**), 1.44 (m, 1.5H, **5m**), 1.28-1.25 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 203.6, 170.4, 138.8, 135.0, 124.7, 123.9, 114.7, 74.3, 68.8, 62.8, 61.7, 41.8, 34.1, 33.3, 32.0, 29.9, 28.7, 18.0, 14.3. IR (thin film, cm⁻¹) 2925, 2855, 2255, 1716, 1456, 1379, 1367, 1222, 1209, 1097, 974, 907, 730, 649, 549. HRMS (ESI) calcd for C₁₆H₂₄O₄Na⁺: 303.1567, found: 303.1556.



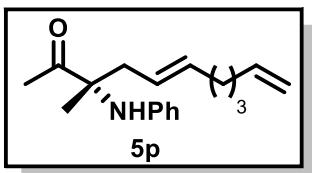
Colorless oil (96 h, 10.0 mg, 30% yield, 93% *ee*, **5n/4n** = 2:1). $[\alpha]_D^{25} = -68.5$ (*c* 0.54, CHCl₃). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak 2OJ, 15% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 19.8 min (major), 22.5 min (minor). ¹H NMR (400 MHz, CDCl₃) δ 5.81-5.74 (m, 0.63H, **5n**), 5.56-5.31 (m, 2H), 5.15-4.88 (m, 1.2H, **5n**), 4.46 (s, 1H), 4.20-4.03 (m, 3H), 3.38-3.08 (m, 2H), 2.72-2.67 (m, 1H), 2.54-2.35 (m, 3H), 2.05-1.91 (m, 2.5H, **5n**), 1.63 (d, J = 6.2 Hz, 1H, **4n**), 1.48 (s, 9H), 1.45-1.38 (m, 1.2H, **5n**), 1.27 (t, J = 7.1 Hz, 3H, **4n**). ¹³C NMR (101 MHz, CDCl₃) δ 205.0, 170.2, 154.4, 138.8, 135.3, 130.1, 124.8, 124.0, 114.7, 80.6, 61.7, 61.4, 40., 35.2, 33.3, 32.0, 29.8, 28.7, 28.4, 18.1, 14.3. IR (thin film, cm⁻¹) 2978, 2926, 2855, 2254, 1717, 1698, 1424, 1367, 1243, 1166, 973, 905, 728, 649. HRMS (ESI) calcd for

$C_{21}H_{33}NO_5Na^+$: 402.2251, found: 402.2242.



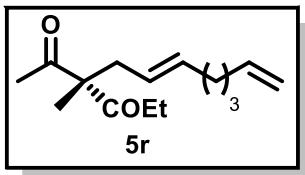
5o: Colorless oil (60 h, 15.8 mg, 60% yield, 85% *ee*, **5o/4o** = 4:1.). $[\alpha]_D^{25} = -12.4$ (*c* 1.50, CHCl₃).

The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak OJ, 5% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.8 min (minor), 26.9 min (major). ¹H NMR (400 MHz, CDCl₃) δ 5.83-5.73 (m, 0.81H, **5o**), 5.53-5.46 (m, 1H), 5.32-5.24 (m, 1H), 5.01-4.92 (m, 1.62H, **5o**), 4.18-4.12 (m, 2H), 2.65-2.55 (m, 1H), 2.45-2.17 (m, 4H), 2.06-1.87 (m, 6.24H, **5o**), 1.64 (dd, *J* = 6.4, 1.4 Hz, 0.57H, **4o**), 1.46-1.41 (m, 1.62H, **5o**), 1.24 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 214.9, 171.2, 138.8, 135.2, 129.9, 125.5, 124.7, 114.7, 76.8, 61.5, 60.4, 38.3, 36.9, 36.8, 33.3, 32.2, 32.0, 28.7, 19.6, 18.1, 14.3. IR (thin film, cm⁻¹) 2977, 2926, 2855, 1750, 1723, 1446, 1266, 1224, 1150, 1029, 973, 913, 737, 704. HRMS (ESI) calcd for C₁₆H₂₄O₃Na⁺: 287.1618, found: 287.1606.

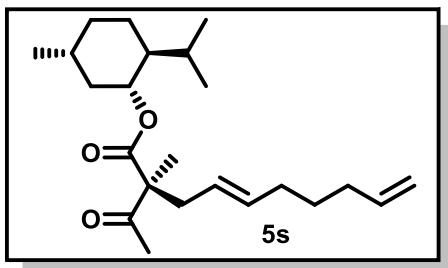


5p: Colorless oil (40 h, 61% yield, 33% *ee*, **5p/4p** = 7:1.). $[\alpha]_D^{25} = -13.9$ (*c* 1.83, CHCl₃). HPLC analysis: Daicel Chiralpak AD, 5% *iso*-propanol/hexane, flow rate = 0.5 mL/min, λ = 210 nm, retention time: 17.2 min (minor), 18.7 min (major). ¹H NMR (400 MHz, CDCl₃) δ 8.15 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.80-5.70 (m, 0.87H, **5p**), 5.59-5.52 (m, 1H), 5.34-5.27 (m, 1H), 4.99-4.91 (m, 1.74H, **5p**), 2.65-2.62 (m, 2H), 2.26 (s, 1H).

3H), 2.03-1.97 (m, 3.48H, **5p**), 1.65 (d, $J = 5.9$ Hz, 0.39H, **4p**), 1.49 (s, 3H), 1.45-1.36 (m, 2H, **5p**). ^{13}C NMR (101 MHz, CDCl_3) δ 210.3, 169.2, 138.7, 137.7, 135.7, 129.2, 124.7, 124.1, 120.2, 114.7, 60.3, 40.4, 33.3, 32.1, 28.7, 27.4, 19.8. IR (thin film, cm^{-1}) 3054, 2987, 1422, 1264, 896, 731, 703. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_2\text{Na}^+$: 343.1778, found: 322.1768.

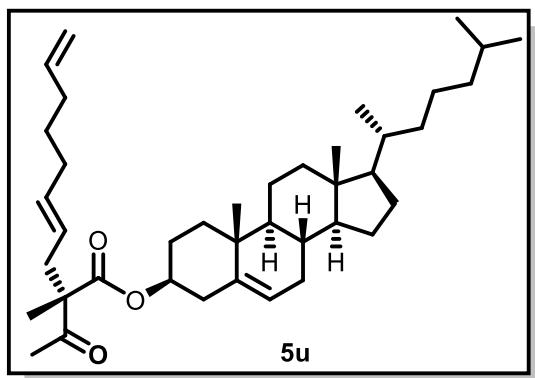


5r: Colorless oil (60 h, 18.2 mg, 77% yield, 87% ee, **5r/4r** = 19:1.). $[\alpha]_D^{25} = -5.2$ (c 1.70, CHCl_3). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak OJ, 10% *iso*-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 16.9 min (major), 20.8 min (minor). ^1H NMR (400 MHz, CDCl_3) δ 5.82-5.72 (m, 0.95H, **5r**), 5.52-5.42 (m, 1H), 5.21-5.13 (m, 1H), 5.03-4.88 (m, 1.9H, **5r**), 2.54 (d, $J = 7.2$ Hz, 2H), 2.39 (q, $J = 7.2$ Hz, 2H), 2.07 (s, 3H), 2.03-1.95 (m, 4H), 1.62 (d, $J = 6.4$ Hz, 0.15H, **4r**), 1.46-1.35 (m, 1.9H, **5r**), 1.30 (s, 3H), 1.03 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 209.8, 207.2, 138.8, 135.1, 124.2, 114.7, 66.5, 37.9, 33.3, 32.4, 32.1, 28.7, 26.9, 18.3, 8.1. IR (thin film, cm^{-1}) 2976, 2938, 2882, 1714, 1699, 1459, 1377, 1358, 1264, 1183, 1090, 975, 919, 747. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{24}\text{O}_2\text{Na}^+$: 259.1669, found: 259.1662.

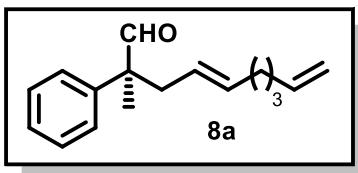


5s: Colorless oil (60 h, 14.5 mg, 40% yield, >19:1 *dr*). $[\alpha]_D^{25} = -48.5$ (c 1.40, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 5.83-5.73 (m, 1H), 5.53-5.45 (m, 1H), 5.26-1.19 (m, 1H), 5.08-4.86 (m, 2H),

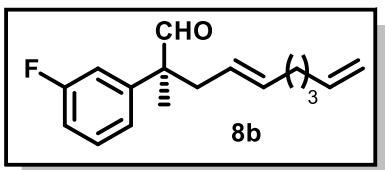
4.69 (td, $J = 10.9, 4.3$ Hz, 1H), 2.60-2.42 (m, 2H), 2.12 (s, 3H), 2.05-1.96 (m, 5H), 1.86-1.76 (m, 1H), 1.67 (dd, $J = 8.9, 6.7$ Hz, 2H), 1.54-1.28 (m, 8H), 1.06-0.87 (m, 8H), 0.73 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.4, 172.4, 138.8, 135.1, 124.1, 114.7, 75.6, 60.0, 46.9, 40.7, 38.2, 34.3, 33.3, 32.1, 31.5, 28.7, 26.5, 26.0, 23.1, 22.1, 21.0, 19.0, 15.9. IR (thin film, cm^{-1}) 2957, 2928, 2856, 2254, 1709, 1456, 1375, 1356, 1235, 971, 905, 729, 649. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{38}\text{O}_3\text{Na}^+$: 385.2713, found: 385.2703.



5u: Colorless oil (70 h, 51 mg, 86% yield, $>19:1$ *dr*). $[\alpha]_D^{25} = -6.4$ (c 2.51, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 5.83-75.73 (m, 1H), 5.52-5.44 (m, 1H), 5.37 (d, $J = 4.4$ Hz, 1H), 5.30-5.18 (m, 1H), 5.10-4.89 (m, 2H), 4.72-4.61 (m, 1H), 2.64-2.36 (m, 2H), 2.29 (d, $J = 7.1$ Hz, 2H), 2.13 (s, 3H), 2.00 (m, 5H), 1.84 (ddd, $J = 9.6, 7.7, 3.6$ Hz, 3H), 1.64-1.24 (m, 18H), 1.18-0.98 (m, 12H), 0.92-0.85 (m, 9H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 205.5, 172.2, 139.4, 138.8, 135.0, 124.3, 123.1, 114.7, 75.0, 59.9, 56.8, 56.3, 50.2, 42.5, 39.9, 39.7, 38.3, 37.0, 36.7, 36.3, 35.9, 33.3, 32.1, 32.1, 32.0, 28.7, 28.4, 28.2, 27.7, 26.4, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 19.0, 18.9, 12.0. IR (thin film, cm^{-1}) 3054, 2934, 2868, 2853, 1711, 1457, 1440, 1378, 1355, 1264, 1236, 1196, 1136, 1119, 996, 972, 912, 896, 735, 704. HRMS (ESI) calcd for $\text{C}_{40}\text{H}_{64}\text{O}_3\text{Na}^+$: 615.4748, found: 615.4747.

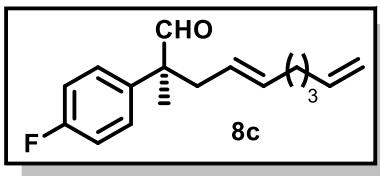


8a: Colorless oil (60 h, 62% yield, 16:1, 83% *ee*). $[\alpha]_D^{25} = +12.8$ (*c* 1.50, CHCl₃). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak OJ, 2% *iso*-propanol/hexane, flow rate = 0.5mL/min, $\lambda = 254$ nm, retention time: 22.4 min (minor), 23.2 min (major). ¹H NMR (400 MHz, CDCl₃) δ 9.53 (s, 1H), 7.38 (dd, *J* = 10.6, 4.4 Hz, 2H), 7.32-7.22 (m, 3H), 5.81-5.71 (m, 0.94H, **8a**), 5.47-5.40 (m, 1H), 5.23-5.12 (m, 1H), 4.99-4.91 (m, 1.88H, **8a**), 2.67-2.55 (m, 2H), 2.02-1.90 (m, 3.76H, **8a**), 1.60 (d, *J* = 6.4 Hz, 0.17H, **7a**), 1.44-1.34 [m, 4.88H (1.88H, **8a**)]. ¹³C NMR (101 MHz, CDCl₃) δ 202.5, 140.0, 138.9, 134.7, 128.9, 127.3, 127.3, 124.7, 114.6, 54.0, 39.5, 33.2, 32.1, 28.7, 19.2. IR (thin film, cm⁻¹) 3059, 3028, 2977, 2928, 2854, 1724, 1640, 1600, 1495, 1445, 1265, 971, 914, 736, 701. HRMS (ESI) calcd for C₁₇H₂₂ONa⁺: 265.1563, found: 265.1564.

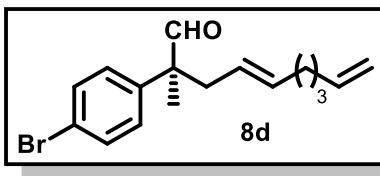


8b: Colorless oil (70 h, 78% yield, 16:1, 83% *ee*). $[\alpha]_D^{25} = +11.9$ (*c* 2.00, CHCl₃). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak 2*AS, 3% *iso*-propanol/hexane, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: 20.0 min (minor), 21.0 min (major). ¹H NMR (400 MHz, CDCl₃) δ 9.52 (s, 1H), 7.40-7.28 (m, 0.94H, **8b**), 7.09-6.90 (m, 3H), 5.81-5.71 (m, 1H), 5.48-5.41 (m, 1H), 5.23-5.08 (m, 1H), 5.02-4.85 (m, 1.88H, **8b**), 2.67-2.50 (m, 2H), 1.99-1.92 (m, 3.76H, **8b**), 1.61 (d, *J* = 6.4 Hz, 1H), 1.45-1.32 [m, 4.88H (1.88H, **8b**)]. ¹³C NMR (126 MHz, CDCl₃) δ

201.8, 163.3 (d, $J = 246.3$ Hz), 142.7 (d, $J = 6.9$ Hz), 138.8, 135.1, 130.3 (d, $J = 8.4$ Hz), 124.2, 123.1 (d, $J = 2.8$ Hz), 114.7, 114.4 (dd, $J = 23.9, 21.6$ Hz), 54.0, 39.6, 33.2, 32.1, 28.7, 19.2. IR (thin film, cm^{-1}) 3077, 2977, 2927, 2854, 2809, 2709, 2255, 1725, 1612, 1588, 1490, 1440, 1267, 1226, 1165, 970, 908, 784, 730, 697, 650. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{22}\text{FO}^+$: 261.1649, found: 261.1640.

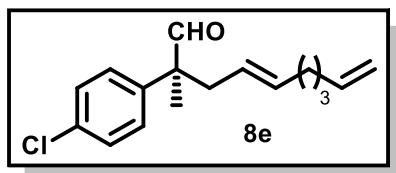


8c: Colorless oil (70 h, 54% yield, 12:1, 82% *ee*). $[\alpha]_D^{25} = +12.0$ (*c* 1.40, CHCl_3). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak 2*AS, 3% *iso*-propanol/hexane, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: 22.1 min (minor), 23.8 min (major). ¹H NMR (400 MHz, CDCl_3) δ 9.49 (s, 1H), 7.25-7.14 (m, 2H), 7.08-7.04 (m, 2H), 5.81-5.71 (m, 0.92H, **8c**), 5.47-5.39 (m, 1H), 5.21-5.07 (m, 1H), 4.99-4.91 (m, 1.84H, **8c**), 2.65-2.50 (m, 2H), 2.02-1.89 (m, 3.68H, **8c**), 1.60 (d, $J = 6.4$ Hz, 0.24H, **7c**), 1.46-1.31 [m, 4.84H, (1.84H, **8c**)]. ¹³C NMR (101 MHz, CDCl_3) δ 202.1, 162.1 (d, $J = 246.6$ Hz), 138.8, 135.6, 135.0, 129.0 (d, $J = 8.0$ Hz), 124.4, 115.8 (d, $J = 21.2$ Hz), 114.7, 53.5, 39.6, 33.2, 32.1, 28.7, 19.3. IR (thin film, cm^{-1}) 3077, 2977, 2927, 2854, 2808, 2707, 1724, 1640, 1602, 1510, 1457, 1439, 1236, 1166, 971, 910, 832. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{22}\text{FO}^+$: 261.1649, found: 261.1640.

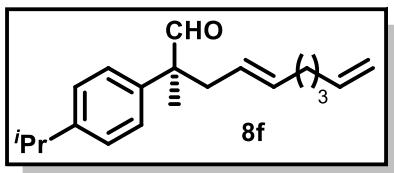


8d: Colorless oil (70 h, 41% yield, 9:1, 81% *ee*). $[\alpha]_D^{25} = +11.5$ (*c* 1.30, CHCl_3). The *ee* was

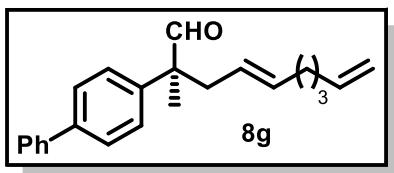
determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak 2*AS, 3% *iso*-propanol/hexane, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 25.2 min (minor), 27.7 min (major). ¹H NMR (400 MHz, CDCl₃) δ 9.50 (s, 1H), 7.55-7.44 (m, 2H), 7.17-7.06 (m, 2H), 5.81-5.71 (m, 0.9H, **8d**), 5.47-5.40 (m, 1H), 5.20-5.06 (m, 1H), 5.03-4.86 (m, 1.8H, **8d**), 2.65-2.48 (m, 2H), 2.02-1.89 (m, 3.6H, **8d**), 1.60 (d, J = 6.4 Hz, 0.3H, **7d**), 1.43-1.33 [m, 4.8H (1.8H, **8d**)]. ¹³C NMR (126 MHz, CDCl₃) δ 201.9, 139.0, 138.8, 135.2, 132.0, 129.1, 124.2, 121.6, 114.7, 53.8, 39.5, 33.2, 32.1, 28.7, 19.2. IR (thin film, cm⁻¹) 3076, 2976, 2926, 2853, 2707, 1726, 1640, 1491, 1456, 1439, 1398, 1108, 1009, 970, 910, 819, 735. HRMS (ESI) calcd for C₁₇H₂₂BrO⁺: 321.0849, found: 321.0849.



8e: Colorless oil (72 h, 91% yield, 12:1, 84% *ee*). $[\alpha]_D^{25} = +13.7$ (*c* 2.50, CHCl₃). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak 2*AS, 3% *iso*-propanol/hexane, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 23.6 min (minor), 25.6 min (major). ¹H NMR (400 MHz, CDCl₃) δ 9.50 (s, 1H), 7.39-7.31 (m, 2H), 7.21-7.12 (m, 2H), 5.79-5.71 (m, 0.92H, **8e**), 5.43 (m, 1H), 5.22-5.07 (m, 1H), 5.02-4.86 (m, 1.84H, **8e**), 2.63-2.51 (m, 2H), 2.01-1.88 (m, 3.68H, **8e**), 1.60 (d, J = 6.4 Hz, 0.24H, **7e**), 1.44-1.34 [m, 4.84H (1.84H, **8e**)]. ¹³C NMR (101 MHz, CDCl₃) δ 202.0, 138.8, 138.4, 135.1, 133.4, 129.0, 128.8, 124.2, 114.7, 53.7, 39.6, 33.2, 32.1, 28.7, 19.2. IR (thin film, cm⁻¹) 3076, 2977, 2926, 2853, 2807, 2707, 1725, 1640, 1494, 1457, 1439, 1402, 1276, 1261, 1097, 1013, 970, 911, 823, 750. HRMS (ESI) calcd for C₁₇H₂₂ClO⁺: 277.1354, found: 277.1348.

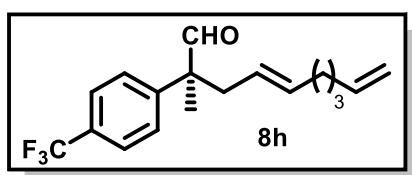


8f: Colorless oil (50 h, 70% yield, 12:1, 80% *ee*). $[\alpha]_D^{25} = +11.7$ (*c* 2.00, CHCl₃). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak OJ, 2% *iso*-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 13.0 min (minor), 14.1 min (major). ¹H NMR (400 MHz, CDCl₃) δ 9.51 (s, 1H), 7.26-7.15 (m, 4H), 5.81-5.71 (m, 0.95H, **8f**), 5.46-5.42 (m, 1H), 5.27-5.13 (m, 1H), 5.01-4.89 (m, 1.9H, **8f**), 2.94-2.87 (m, 1H), 2.60 (d, *J* = 7.2 Hz, 2H), 2.05-1.91 (m, 3.8H, **8f**), 1.61 (d, *J* = 6.4 Hz, 0.15H, **7f**), 1.43-1.35 [m, 4.9H (1.9H, **8f**)], 1.25 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 202.6, 147.9, 138.9, 137.2, 134.6, 127.2, 127.0, 124.9, 114.6, 53.7, 39.5, 33.8, 33.2, 32.1, 28.8, 24.0, 19.2. IR (thin film, cm⁻¹) 3076, 3054, 3026, 2962, 2928, 2871, 2856, 2807, 2708, 1723, 1640, 1509, 1459, 1416, 1385, 1265, 1017, 971, 911, 828, 738, 704. HRMS (ESI) calcd for C₂₀H₂₈ONa⁺: 307.2032, found: 307.2034.

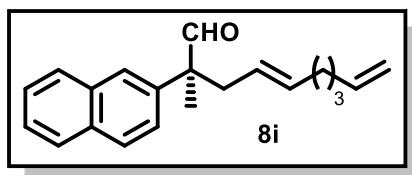


8g: Colorless oil (72 h, 82% yield, 16:1, 83% *ee*). $[\alpha]_D^{25} = +13.6$ (*c* 2.60, CHCl₃). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak 2*As, 3% *iso*-propanol/hexane, flow rate = 0.5 mL/min, $\lambda = 254$ nm, retention time: 27.8 min (minor), 31.1 min (major). ¹H NMR (400 MHz, CDCl₃) δ 9.57 (s, 1H), 7.63-7.59 (m, 4H), 7.48-7.43 (m, 2H), 7.38-7.32 (m, 3H), 5.80-5.72 (m, 0.94H, **8g**), 5.51-5.44 (m, 1H), 5.29-5.16 (m, 1H), 5.00-4.91 (m, 1.88H), 2.72-2.60 (m, 2H), 1.98

(m, 3.76H, **8g**), 1.63 (d, $J = 6.4$ Hz, 0.18H, **7g**), 1.49-1.36 [m, 4.88H (1.88H, **8g**)]. ^{13}C NMR (101 MHz, CDCl_3) δ 202.4, 140.6, 140.2, 138.9, 138.8, 134.8, 128.9, 127.8, 127.6, 127.2, 124.7, 114.6, 53.9, 39.5, 33.2, 32.1, 28.7, 19.2. IR (thin film, cm^{-1}) 3030, 2977, 2927, 2854, 2709, 1722, 1486, 1455, 1391, 1276, 1261, 971, 906, 835, 765, 729, 698, 649. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{27}\text{O}^+$: 319.2056, found: 319.2050.

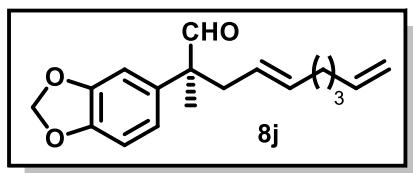


8h: Colorless oil (72 h, 83% yield, 12:1, 82% ee). $[\alpha]_D^{25} = +12.2$ (c 2.58, CHCl_3). The ee was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak OJ, 2% *iso*-propanol/hexane, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 22.0 min (minor), 22.8 min (major). ^1H NMR (400 MHz, CDCl_3) δ 9.55 (s, 1H), 7.63 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J = 8.3$ Hz, 2H), 5.80-5.70 (m, 0.92H, **8h**), 5.48-5.41 (m, 1H), 5.21-5.06 (m, 1H), 4.98-4.91 (m, 0.84H, **8h**), 2.71-2.53 (m, 2H), 1.99-1.92 (m, 3.68H, **8h**), 1.60 (d, $J = 6.4$ Hz, 0.24H, **7h**), 1.46 (s, 3H), 1.42-1.32 (m, 1.84H, **8h**). IR (thin film, cm^{-1}). ^{13}C NMR (101 MHz, CDCl_3) δ 201.7, 144.2, 138.7, 135.4, 127.8, 125.8 (d, $J = 3.8$ Hz), 123.9, 114.7, 54.2, 39.7, 33.2, 32.0, 28.7, 19.3. HRMS (ESI) 3076, 3056, 2979, 2855, 2812, 2711, 1727, 1641, 1618, 1456, 1440, 1412, 1328, 1265, 1168, 1127, 1080, 1016, 971, 912, 837, 739, 704. calcd for $\text{C}_{18}\text{H}_{22}\text{F}_3\text{O}^+$: 311.1617, found: 311.1617.



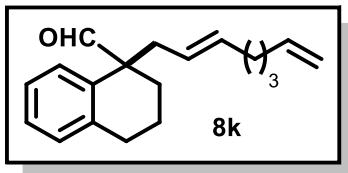
8i: Colorless oil (70 h, 74% yield, 9:1, 76% ee). $[\alpha]_D^{25} = +8.5$ (c 2.00, CHCl_3). The ee was

determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak 2*As, 1% *iso*-propanol/hexane, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 36.3 min (minor), 41.8 min (major). ¹H NMR (400 MHz, CDCl₃) δ 9.61 (s, 1H), 7.89-7.81 (m, 3H), 7.71 (d, J = 1.7 Hz, 1H), 7.53-7.46 (m, 2H), 7.37 (dd, J = 8.6, 1.9 Hz, 1H), 5.78-5.68 (m, 0.9H, **8i**), 5.51-5.44 (m, 1H), 5.24-5.17 (m, 1H), 4.96-4.90 (m, 1.8H, **8i**), 2.79-2.66 (m, 2H), 2.01-1.87 (m, 3.6H, **8i**), 1.60 (d, J = 6.4 Hz, 0.3H, **7i**), 1.54 (s, 3H), 1.41-1.32 (m, 1.8H, **8i**). ¹³C NMR (126 MHz, CDCl₃) δ 202.5, 138.8, 137.3, 134.8, 133.5, 132.5, 128.6, 128.1, 127.7, 126.5, 126.4, 126.3, 125.2, 124.7, 114.6, 54.2, 39.4, 33.2, 32.1, 28.7, 19.3. IR (thin film, cm⁻¹) 3059, 2976, 2926, 2853, 2705, 1722, 1639, 1598, 1508, 1455, 1437, 1374, 1274, 1131, 969, 909, 856, 817, 732, 659. HRMS (ESI) calcd for C₂₁H₂₅O⁺: 293.1900, found: 293.1889.



8j: Colorless oil (70 h, 75% yield, 9:1, 74% ee). $[\alpha]_D^{25} = +6.3$ (*c* 2.10, CHCl₃). The ee was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiraldak 2*As, 3% *iso*-propanol/hexane, flow rate = 0.5 mL/min, λ = 254 nm, retention time: 39.3 min (minor), 50.9 min (major). ¹H NMR (400 MHz, CDCl₃) δ 9.45 (s, 1H), 6.81 (d, J = 8.1 Hz, 1H), 6.74 (d, J = 1.9 Hz, 1H), 6.68 (dd, J = 8.1, 1.9 Hz, 1H), 5.96 (s, 2H), 5.80-5.73 (m, 0.9H, **8j**), 5.48-5.38 (m, 1H), 5.22-5.11 (m, 1H), 5.01-4.87 (m, 1.8H), 2.56-2.52 (m, 2H), 2.03-1.91 (m, 3.6H, **8j**), 1.61 (d, J = 6.4 Hz, 0.3H, **7j**), 1.41-1.34 [m, 4.8H (1.8H, **8j**)]. ¹³C NMR (126 MHz, CDCl₃) δ 202.1, 148.3, 146.8, 138.9, 134.7, 133.7, 124.7, 120.7, 114.6, 108.5, 107.9, 101.3, 53.7, 39.6, 33.2, 32.1, 28.7, 19.3. IR (thin film, cm⁻¹) 3077, 2977, 2925, 2854, 2706, 1722, 1505, 1487, 1436, 1237, 1108, 1040, 907, 810, 730, 650, 635.

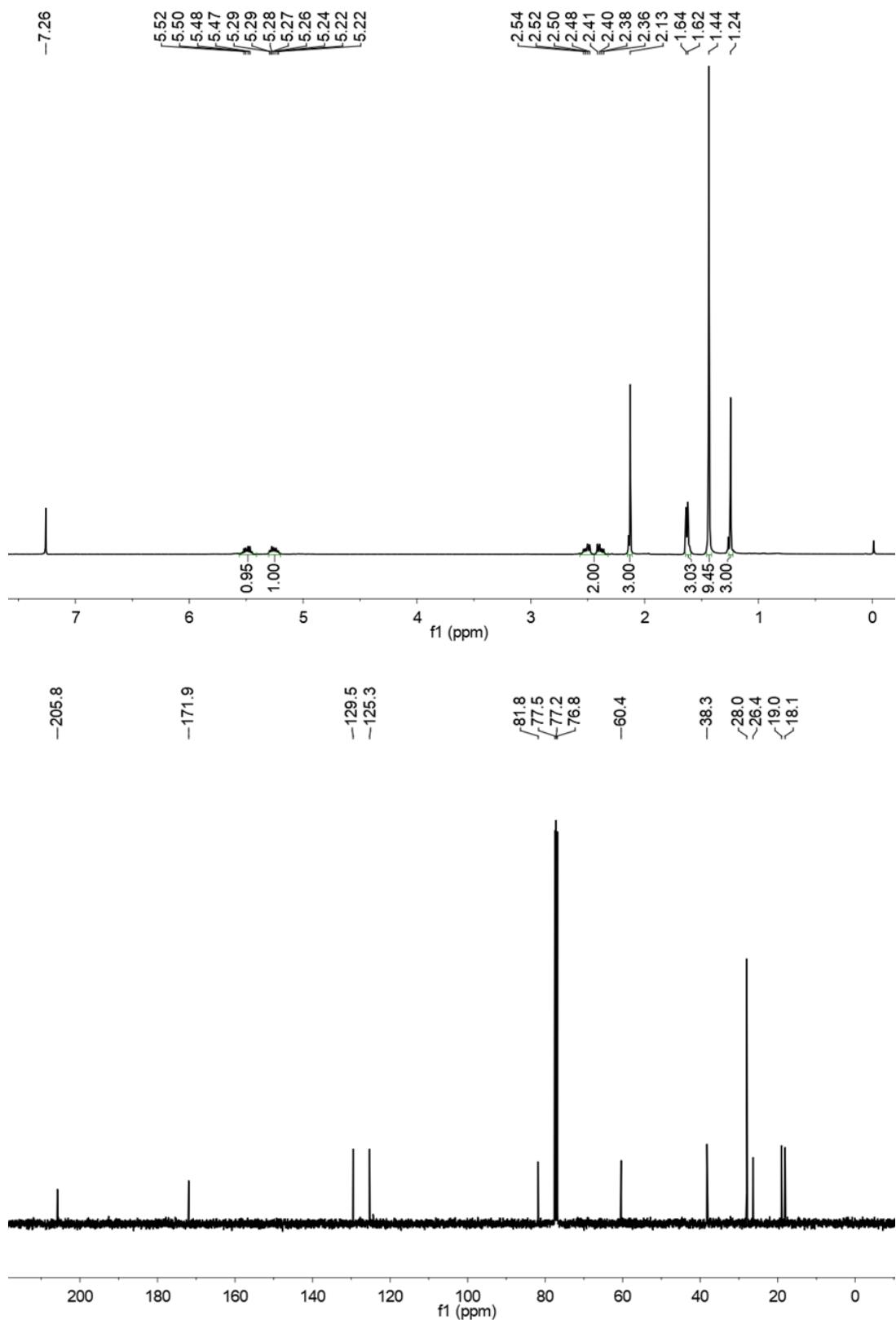
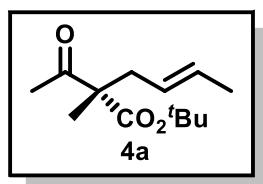
HRMS (ESI) calcd for C₁₈H₂₃O₃⁺: 287.1642, found: 287.1632.

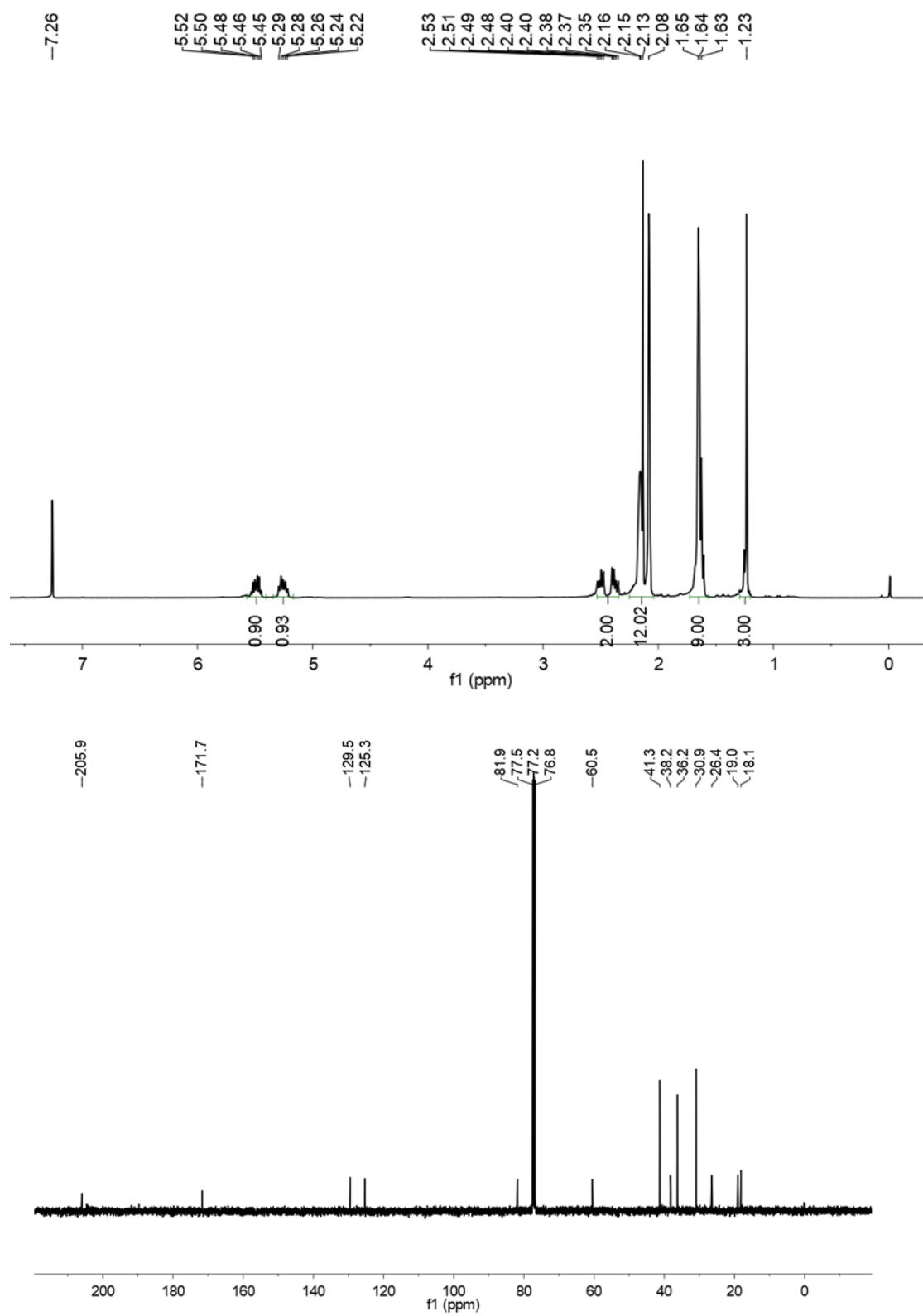
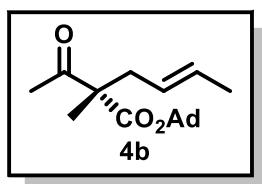


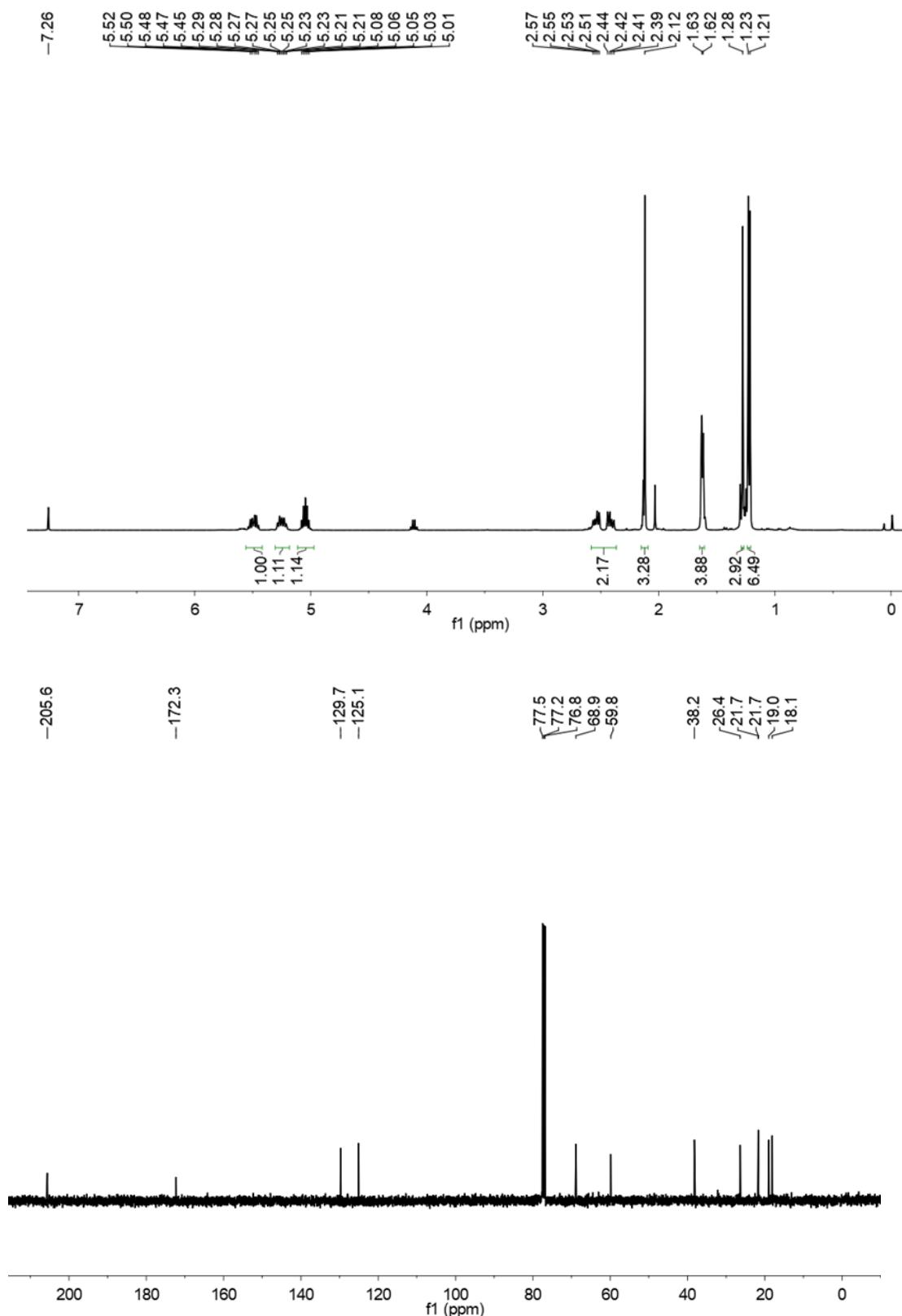
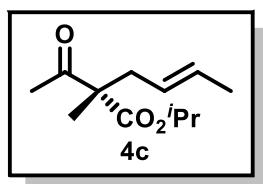
8k: Colorless oil (70 h, 81% yield, 16:1, 76% *ee*). [α]_D²⁵ = +7.9 (*c* 2.20, CHCl₃). The *ee* was determined after one step transformation via olefin metathesis reaction with 2nd Grubbs catalyst and styrene. HPLC analysis: Daicel Chiralpak OJ, 10% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 14.9 min (minor), 19.1 min (major). ¹H NMR (400 MHz, CDCl₃) δ 9.55 (s, 1H), 7.25-7.09 (m, 4H), 5.82-5.72 (m, 0.94H, **8k**), 5.48-5.41 (m, 1H), 5.25-5.19 (m, 1H), 5.04-4.86 (m, 1.88H, **8k**), 2.77 (t, *J* = 6.1 Hz, 2H), 2.56 (d, *J* = 7.2 Hz, 2H), 2.14-2.06 (m, 1H), 2.02-1.92 (m, 3.76H), 1.89-1.73 (m, 3H), 1.62 (d, *J* = 6.4 Hz, 0.19H, **7k**), 1.44-1.33 (m, 1.88H, **8k**). ¹³C NMR (126 MHz, CDCl₃) δ 202.5, 138.9, 138.8, 134.5, 129.9, 128.4, 127.0, 126.4, 125.2, 114.6, 53.4, 40.2, 33.2, 32.1, 30.1, 28.7, 28.0, 19.4. IR (thin film, cm⁻¹) 3064, 3018, 2929, 2853, 2842, 2710, 1720, 1640, 1489, 1443, 972, 908, 757, 731, 649. HRMS (ESI) calcd for C₁₉H₂₅O⁺: 269.1900, found: 269.1889.

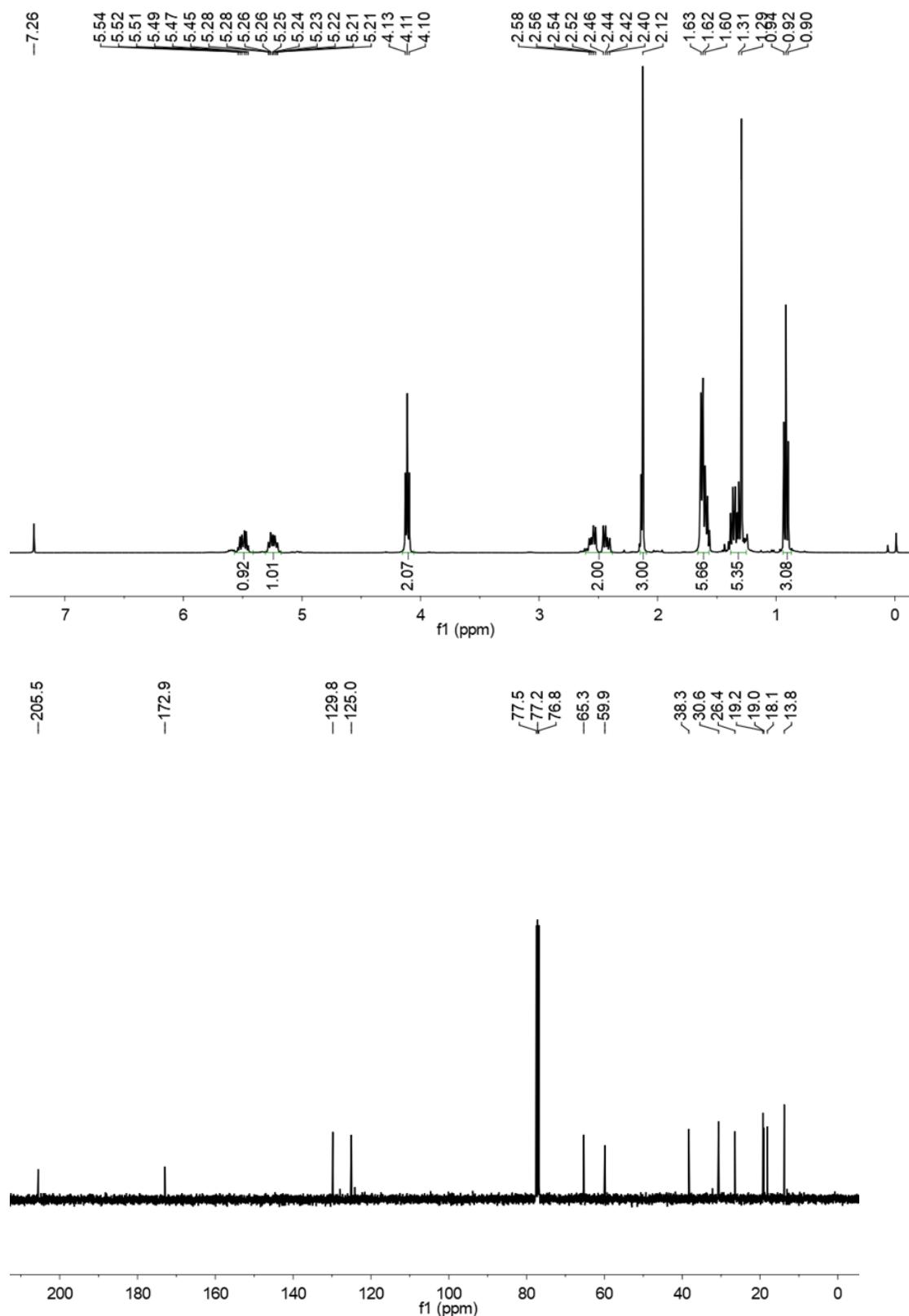
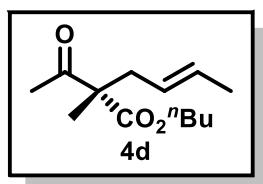
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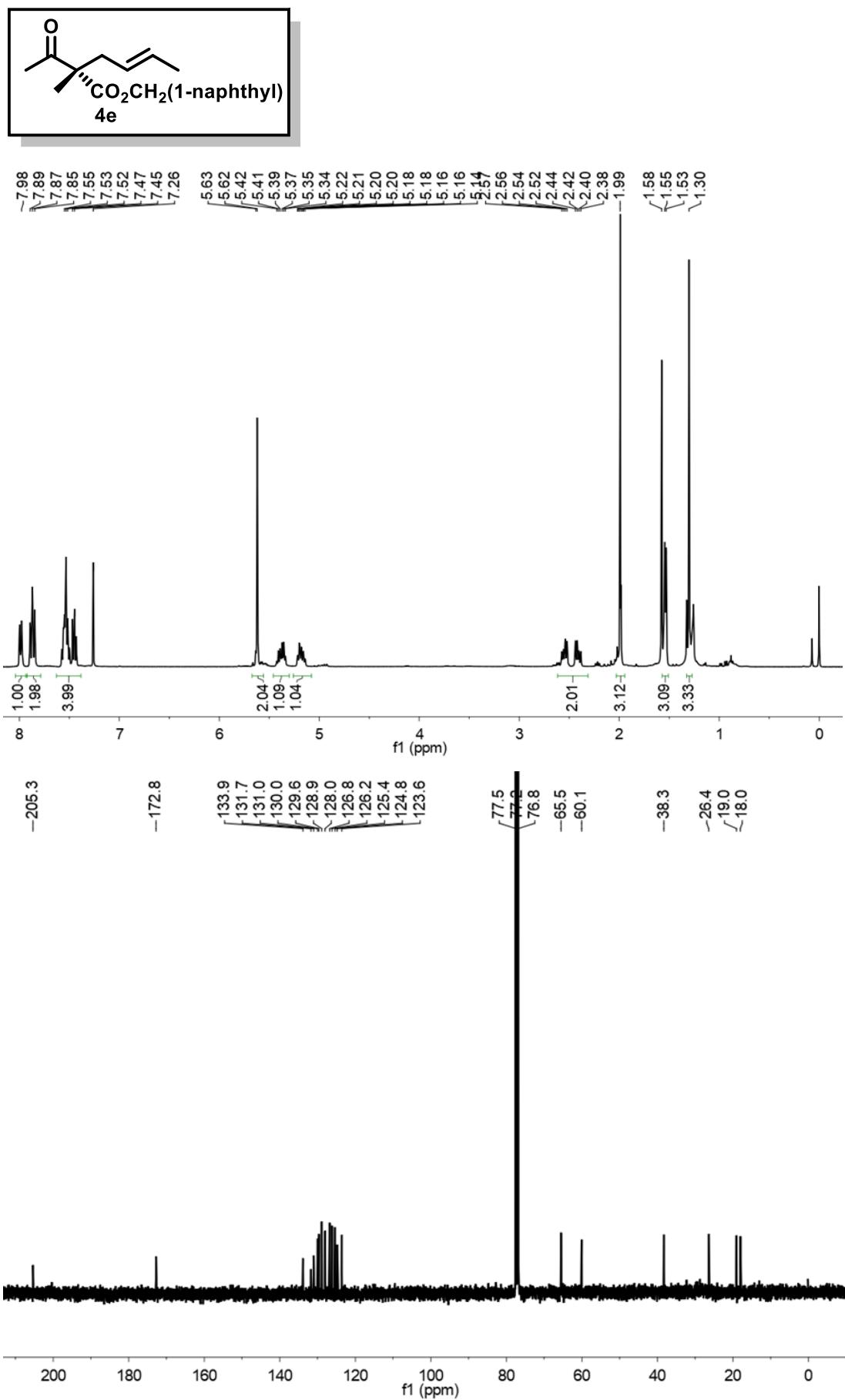
- (1) a) Zhou, H.; Wang, Y. ; Zhang, L.; Cai, M.; Luo, S. *J. Am. Chem. Soc.* **2017**, *139*, 3631. b)
Zhou, H.; Zhang, L.; Xu, C.; Luo, S. *Angew. Chem., Int. Ed.* **2015**, *54*, 12645.
- (2) Hoffmann, S.; Nicoletti, M.; List, B. *J. Am. Chem. Soc.* **2006**, *128*, 13074.
- (3) a) M. Penning, J. Christoffers, *Eur. J. Org. Chem.* **2013**, 389; b) K. Okamoto, K. Sasakura, T. Shimbayashi, K. Ohe, *Chem. Lett.* **2016**, *45*, 988.

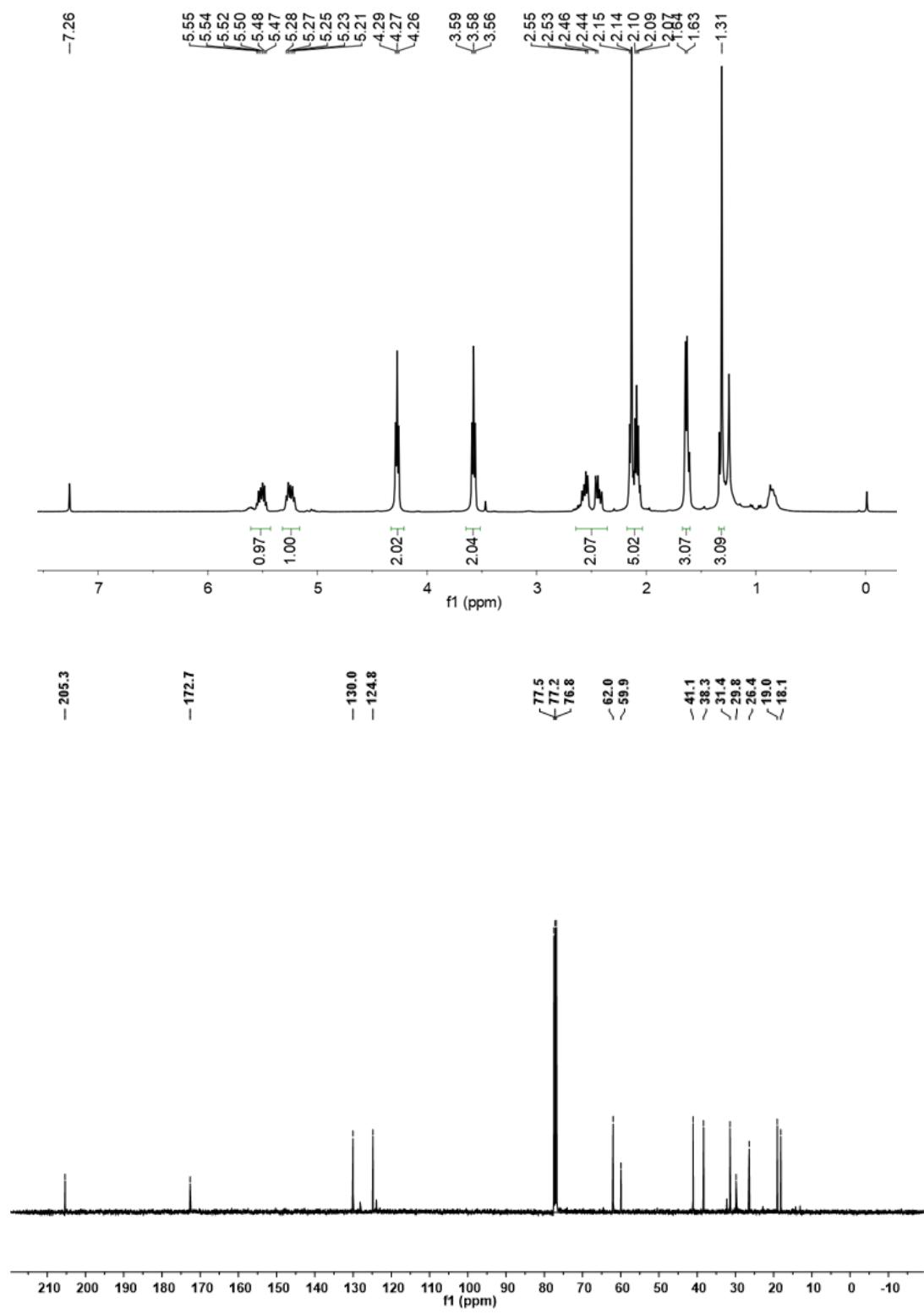
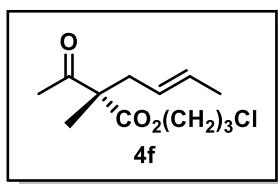


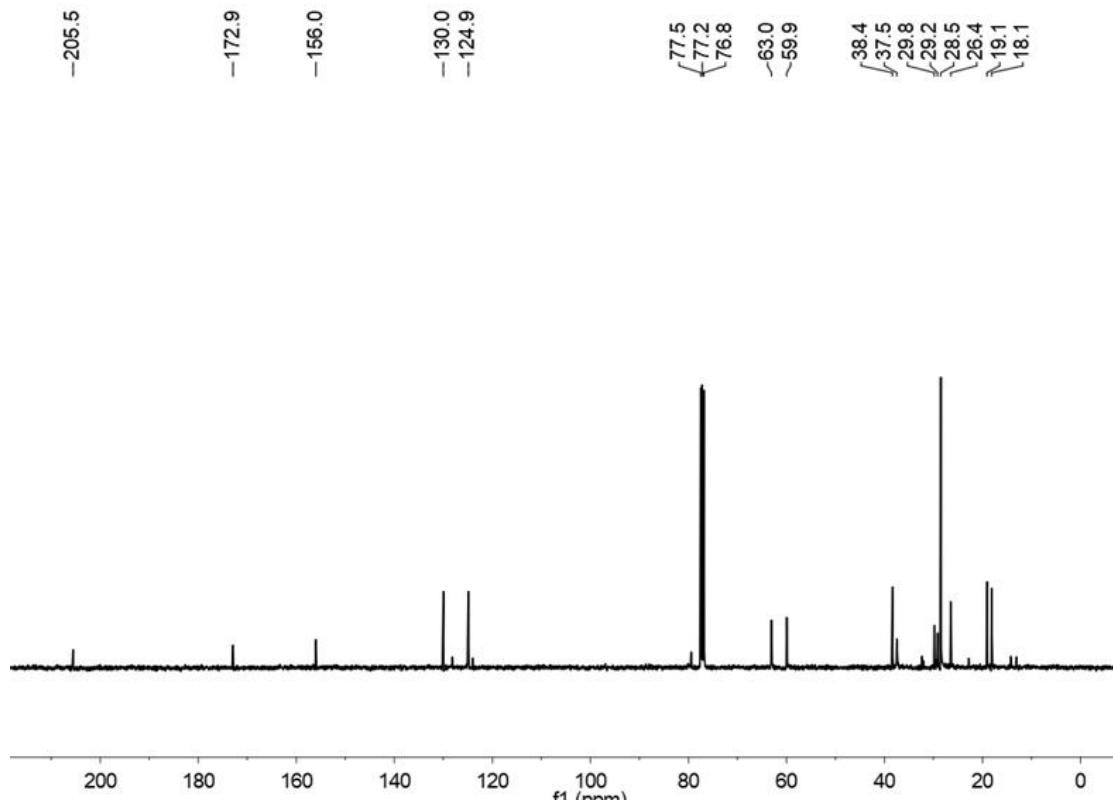
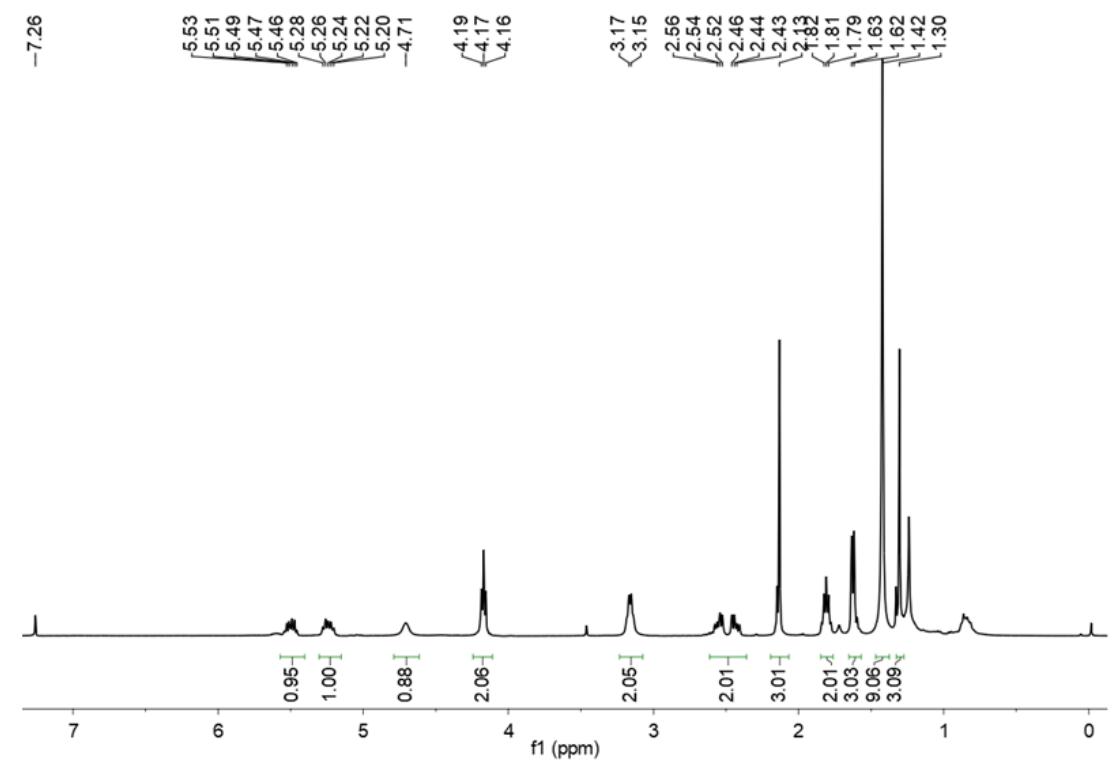
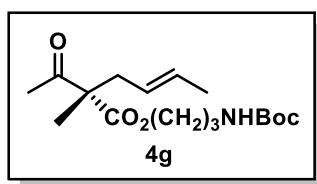


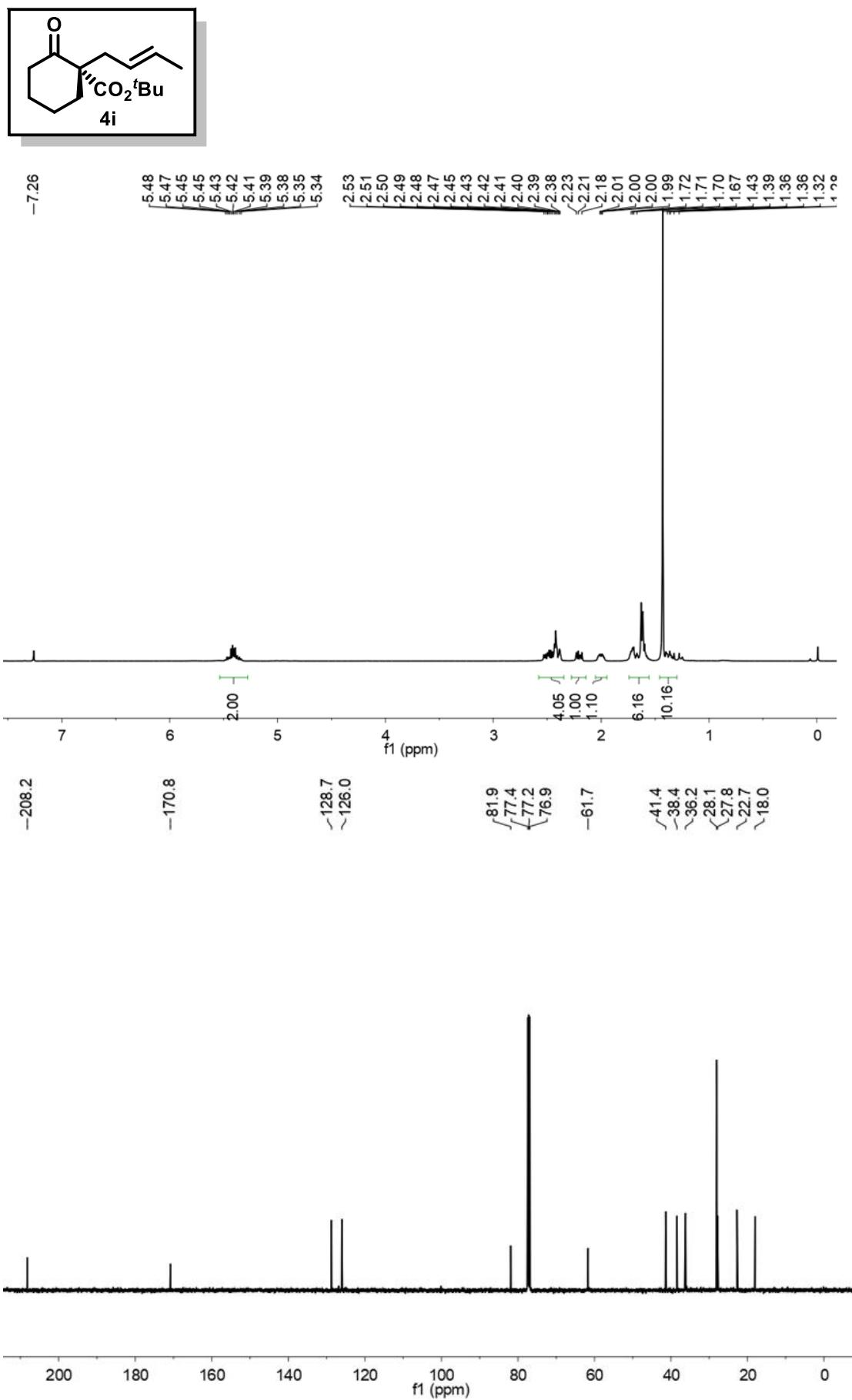


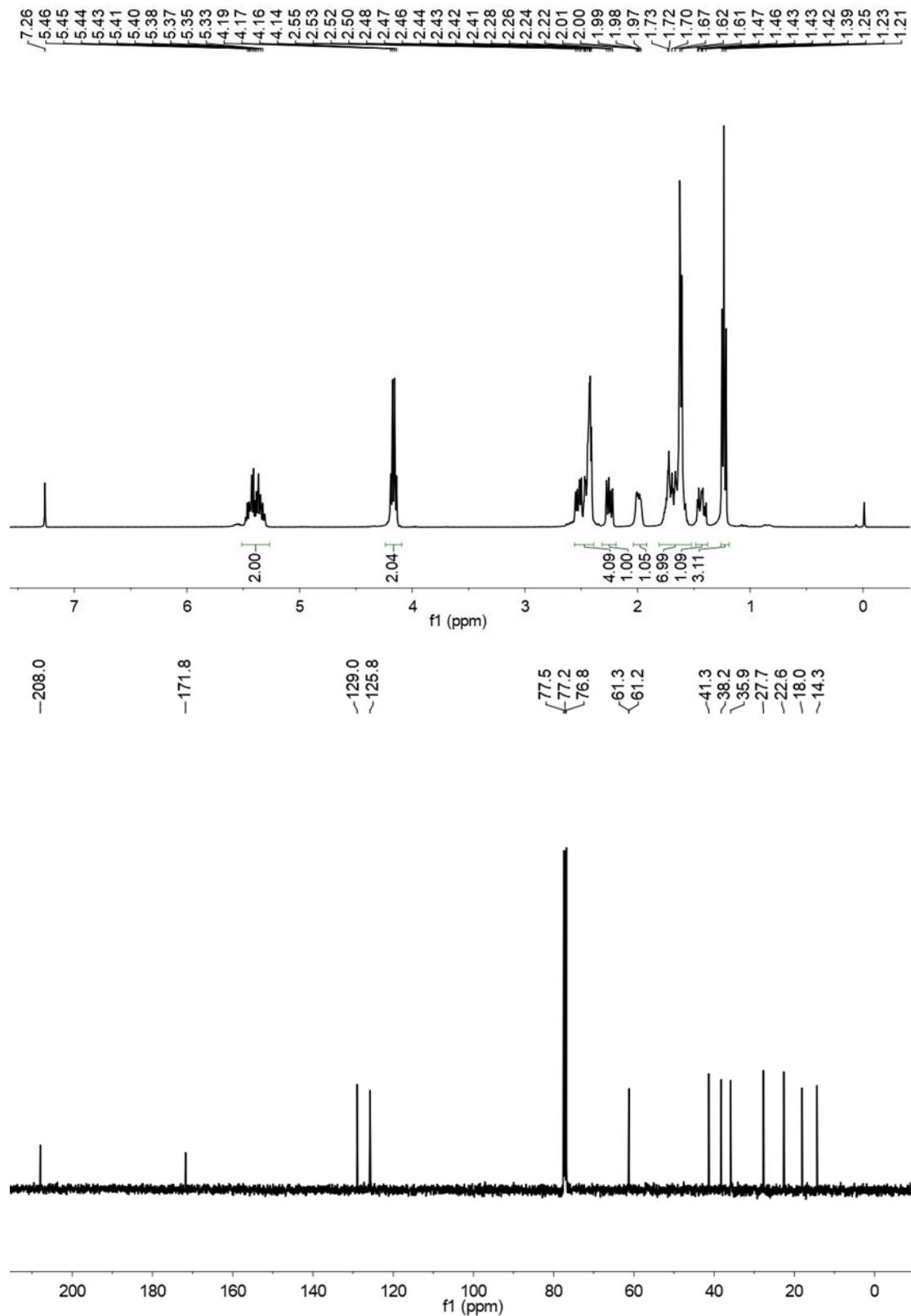
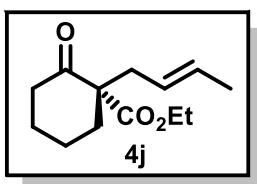


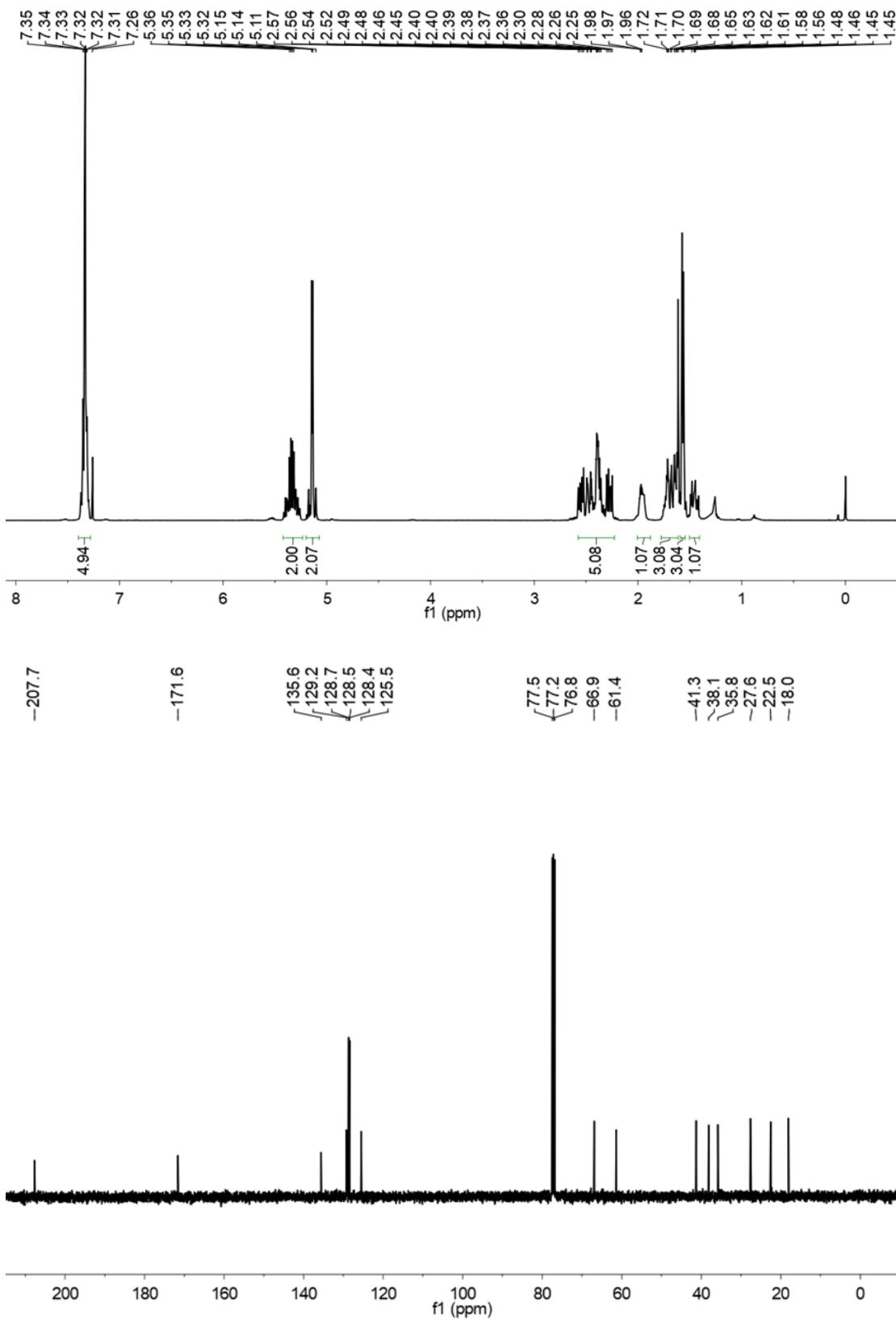
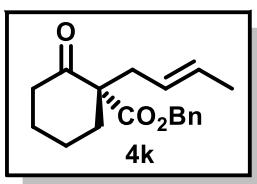


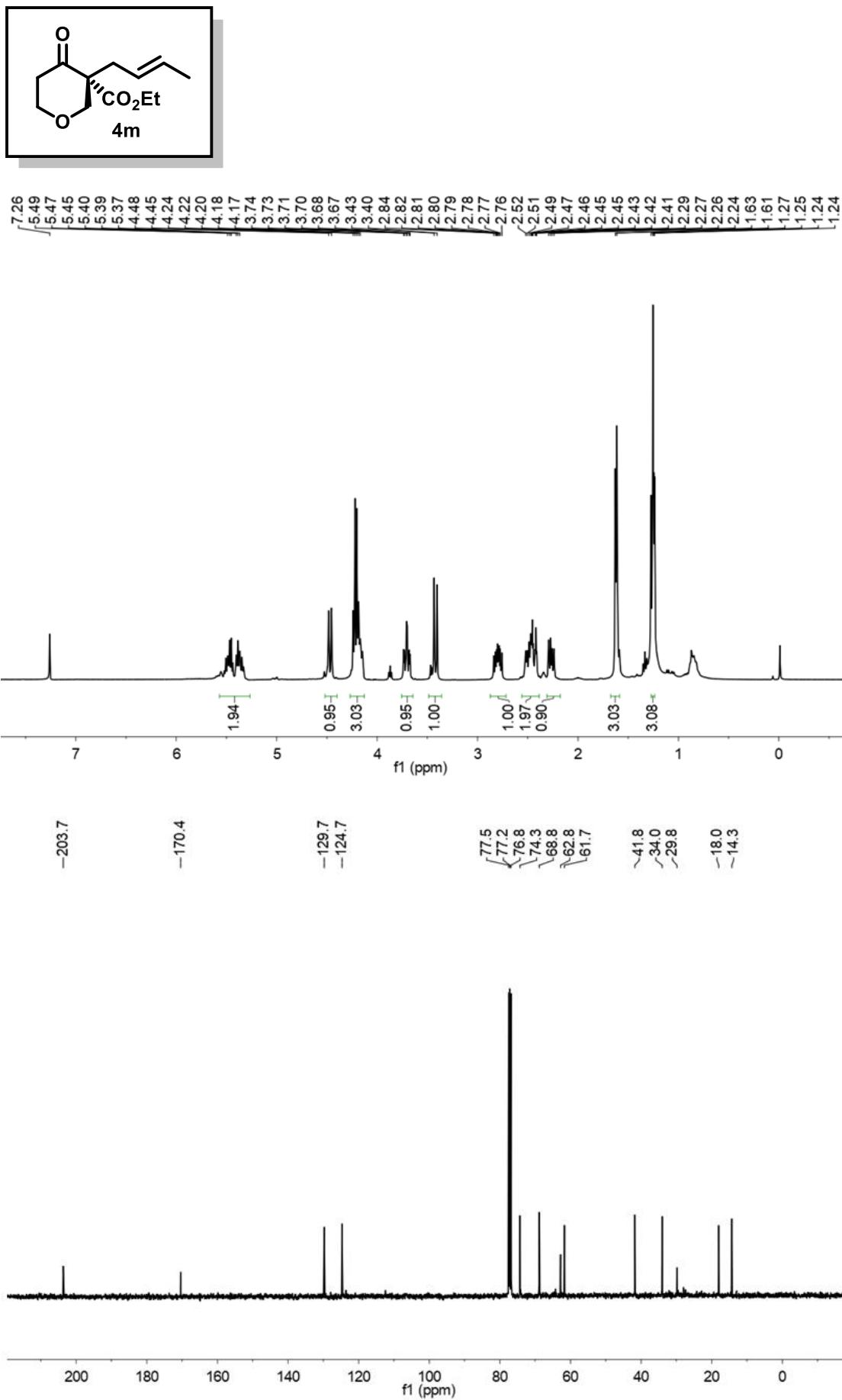


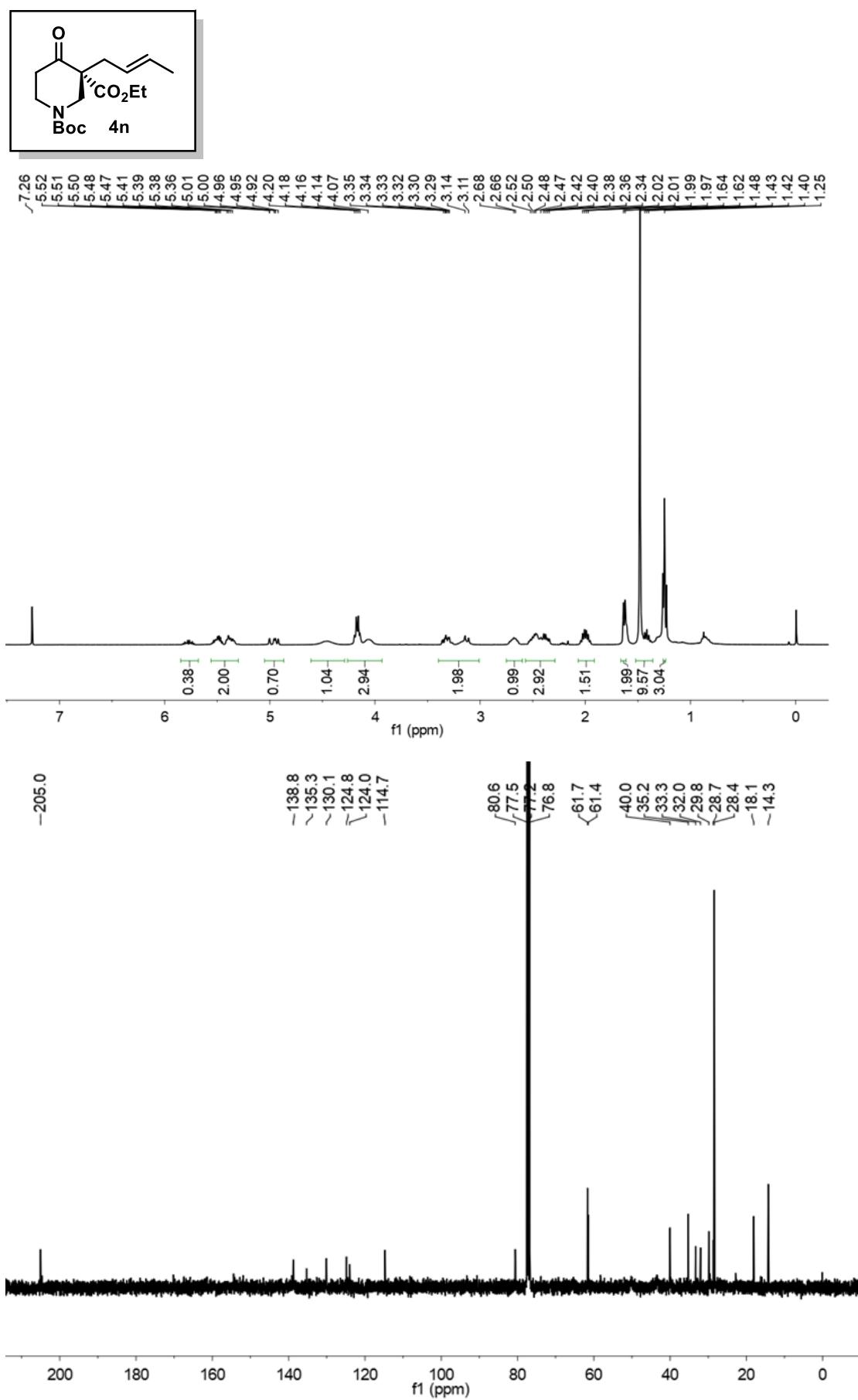


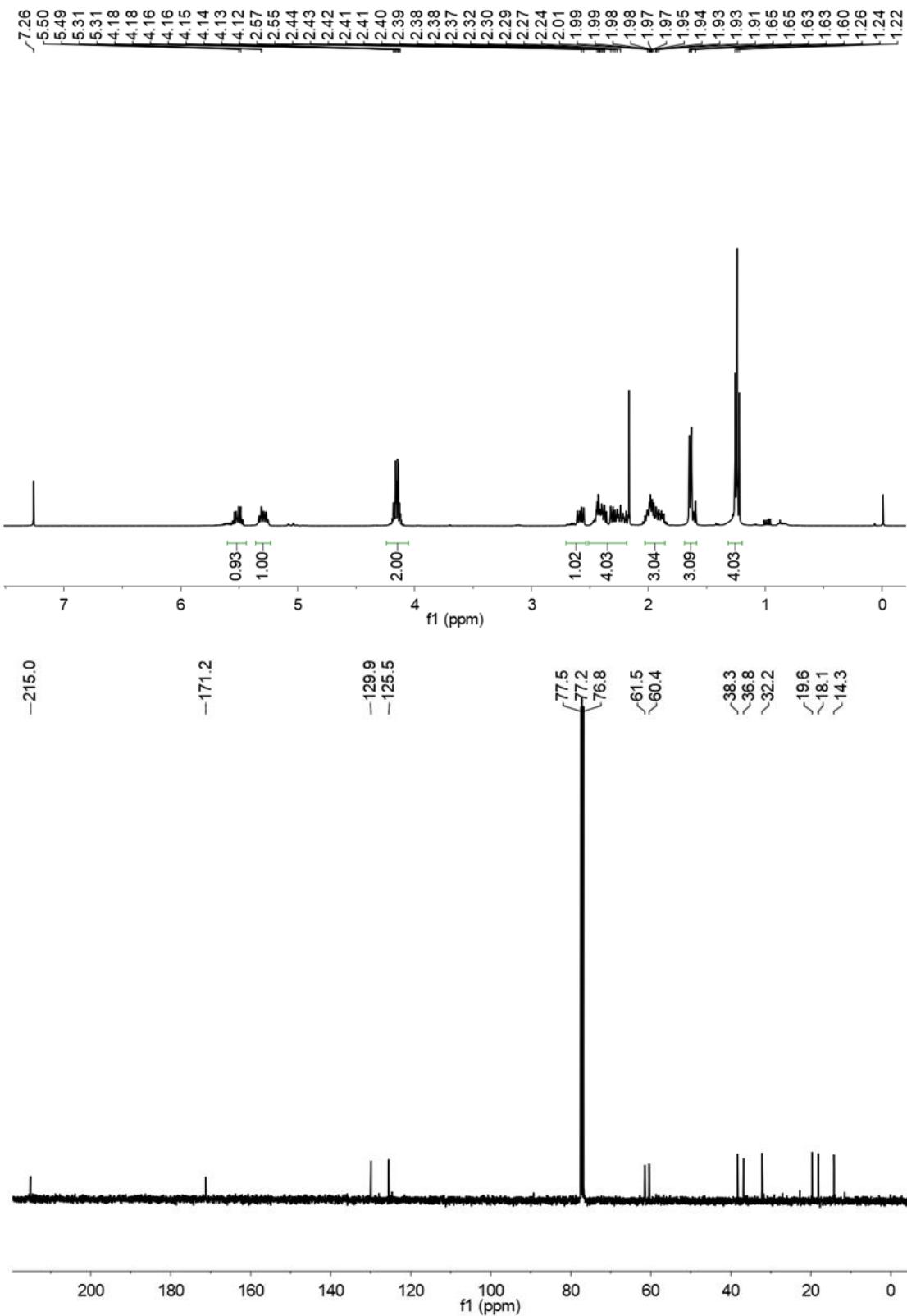
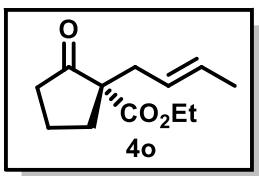


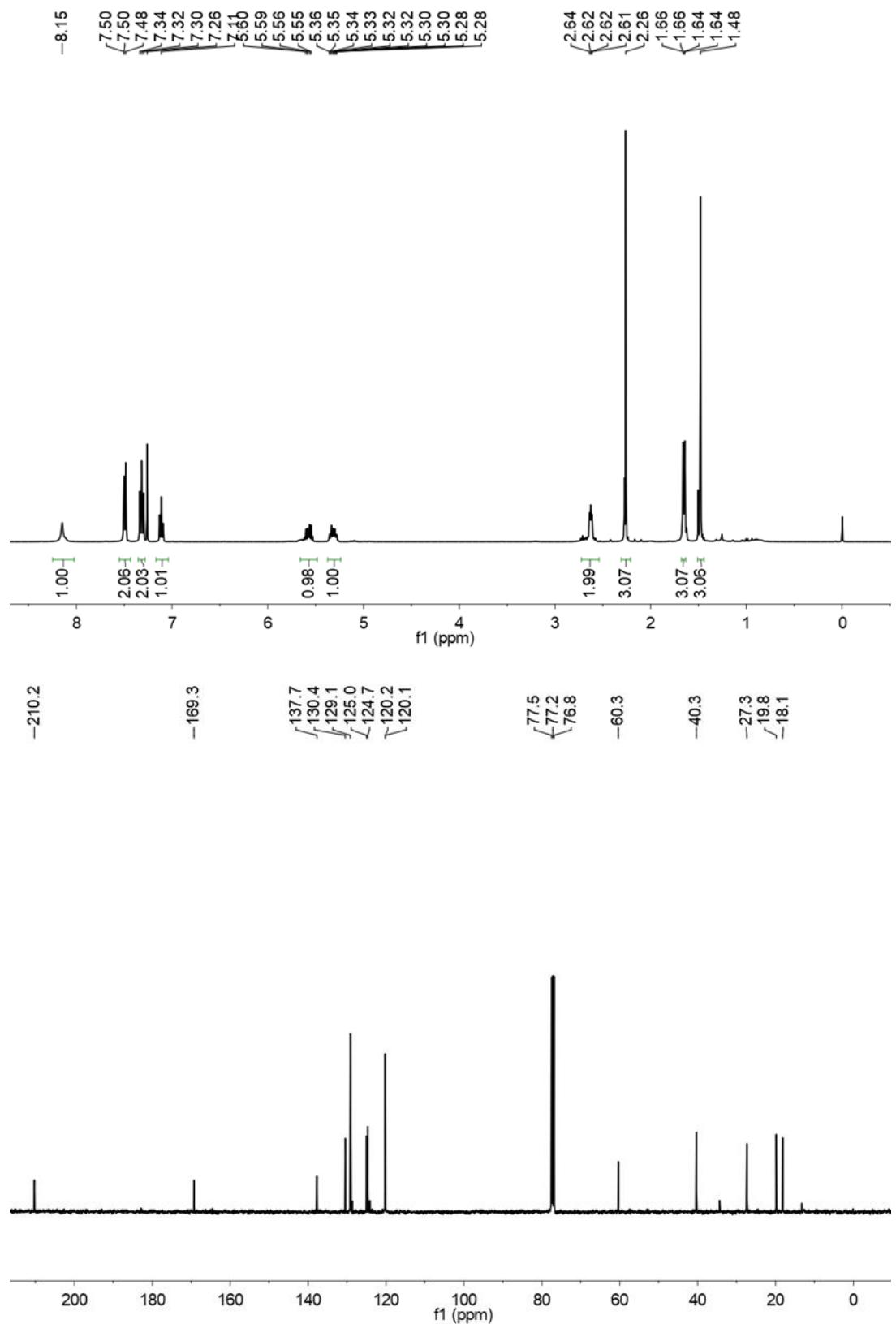
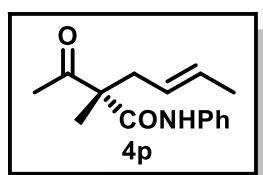


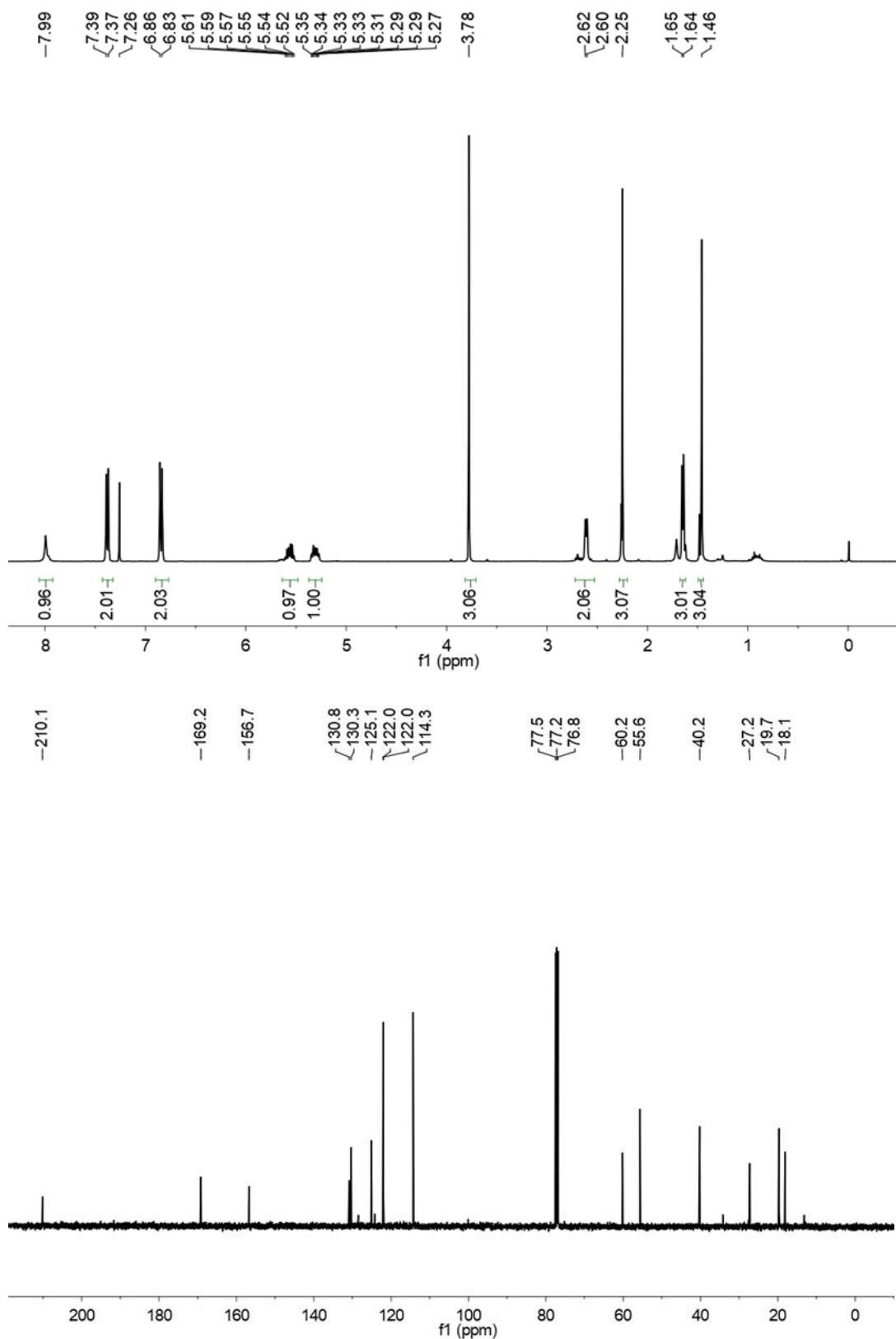
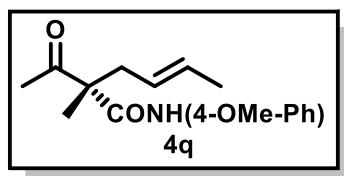


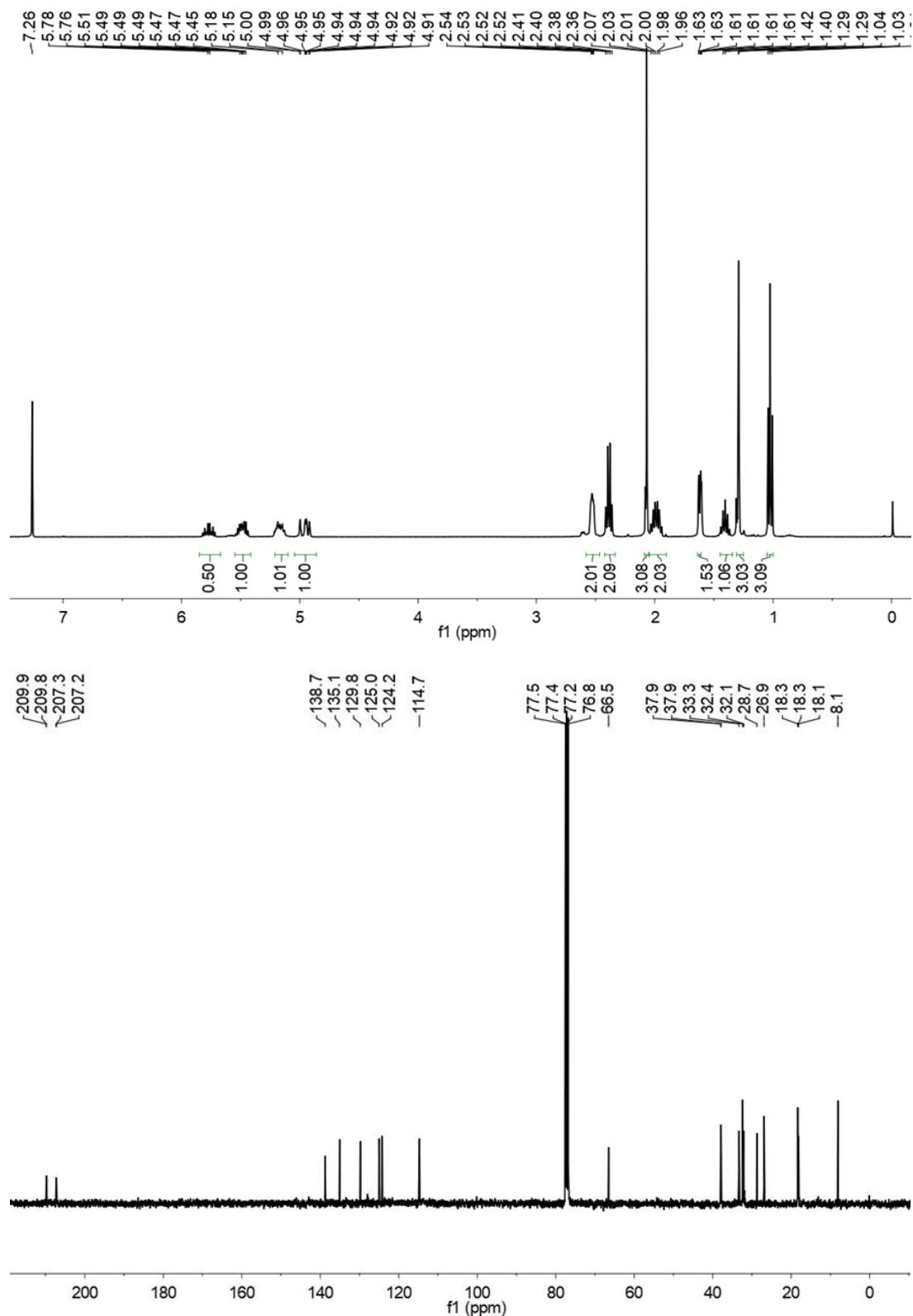
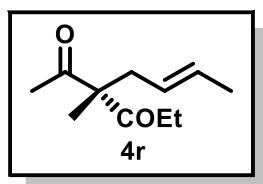


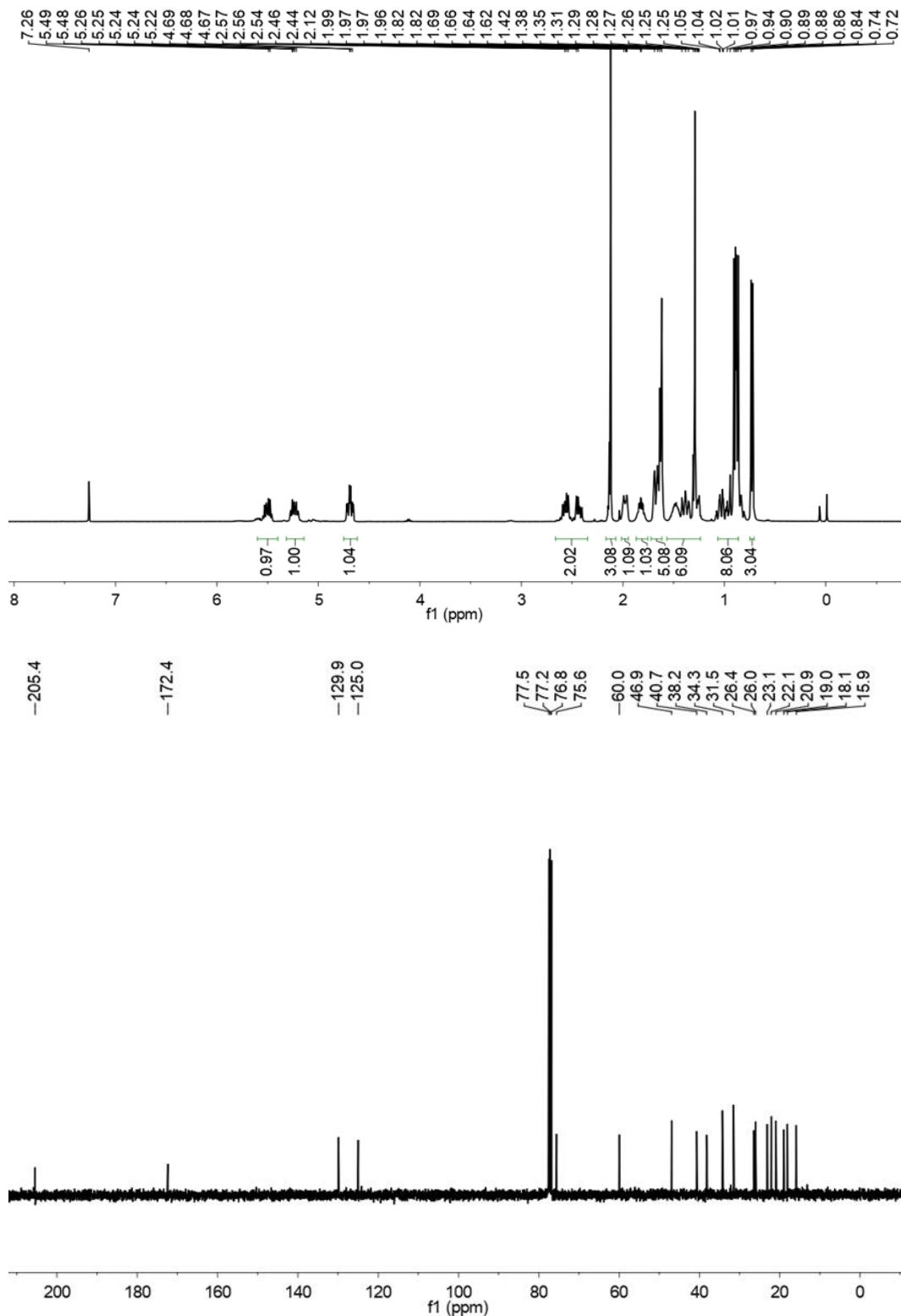
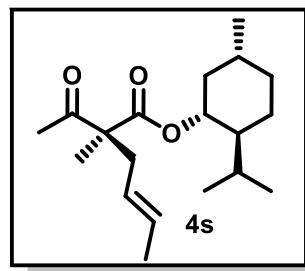


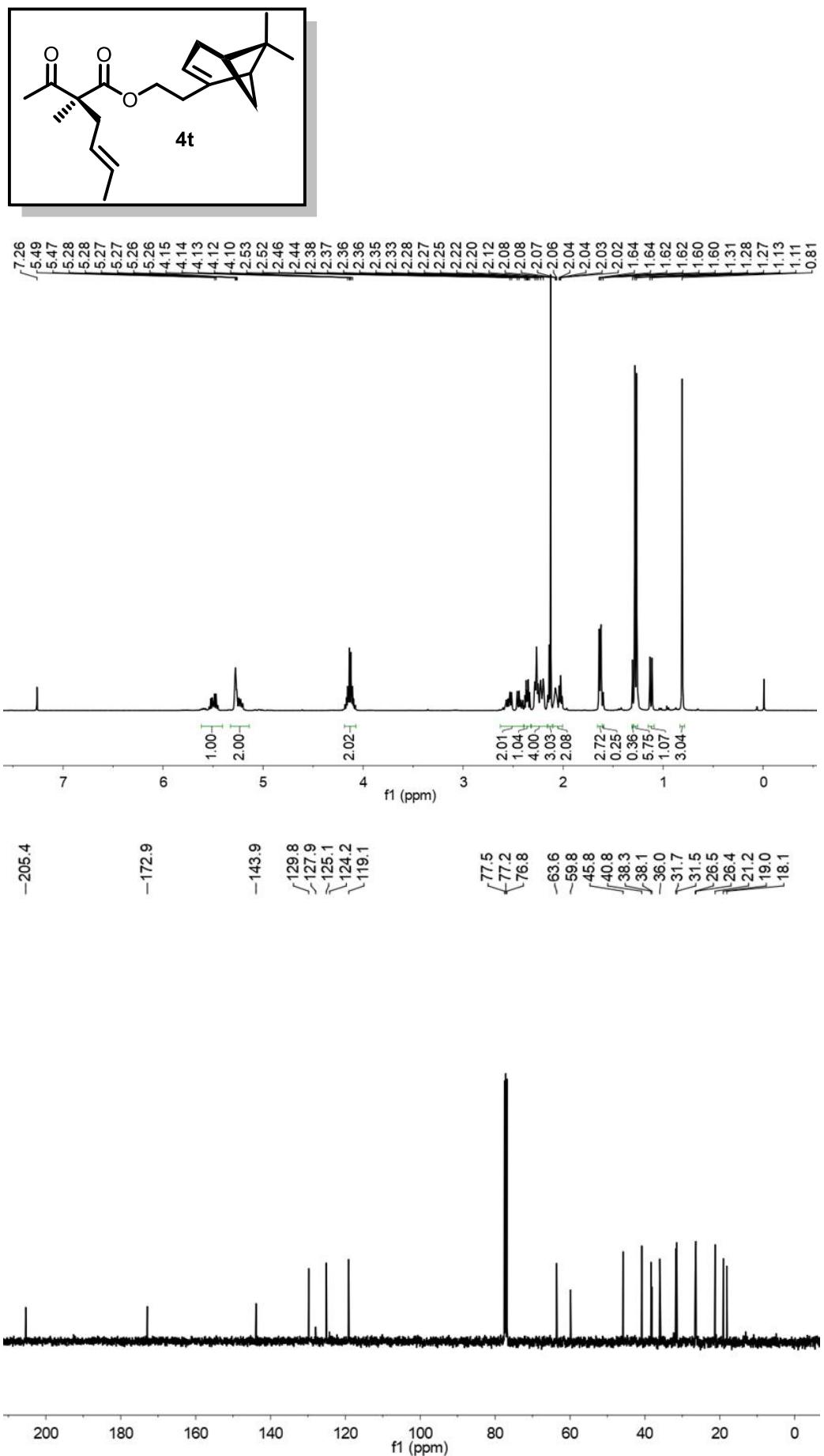


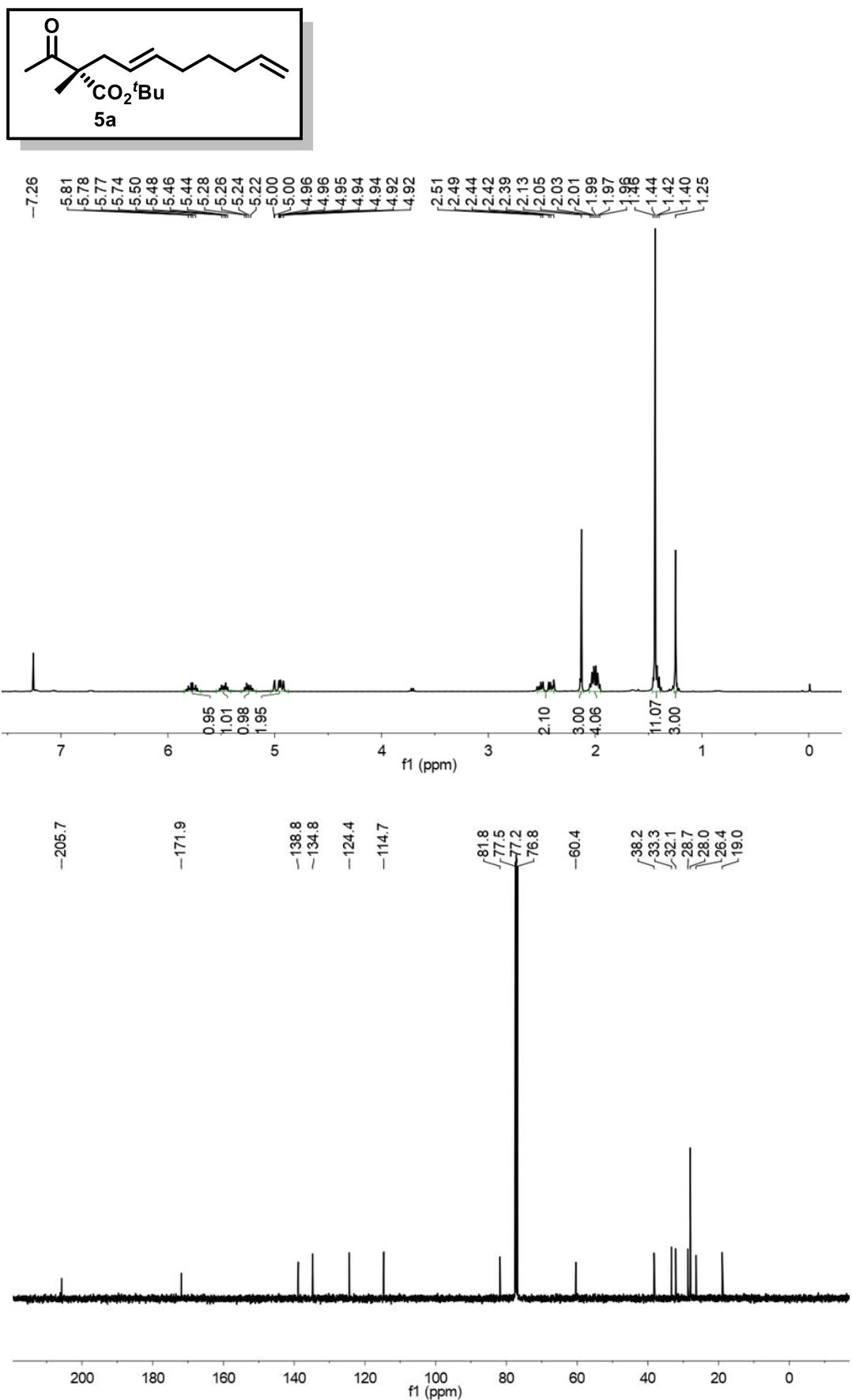


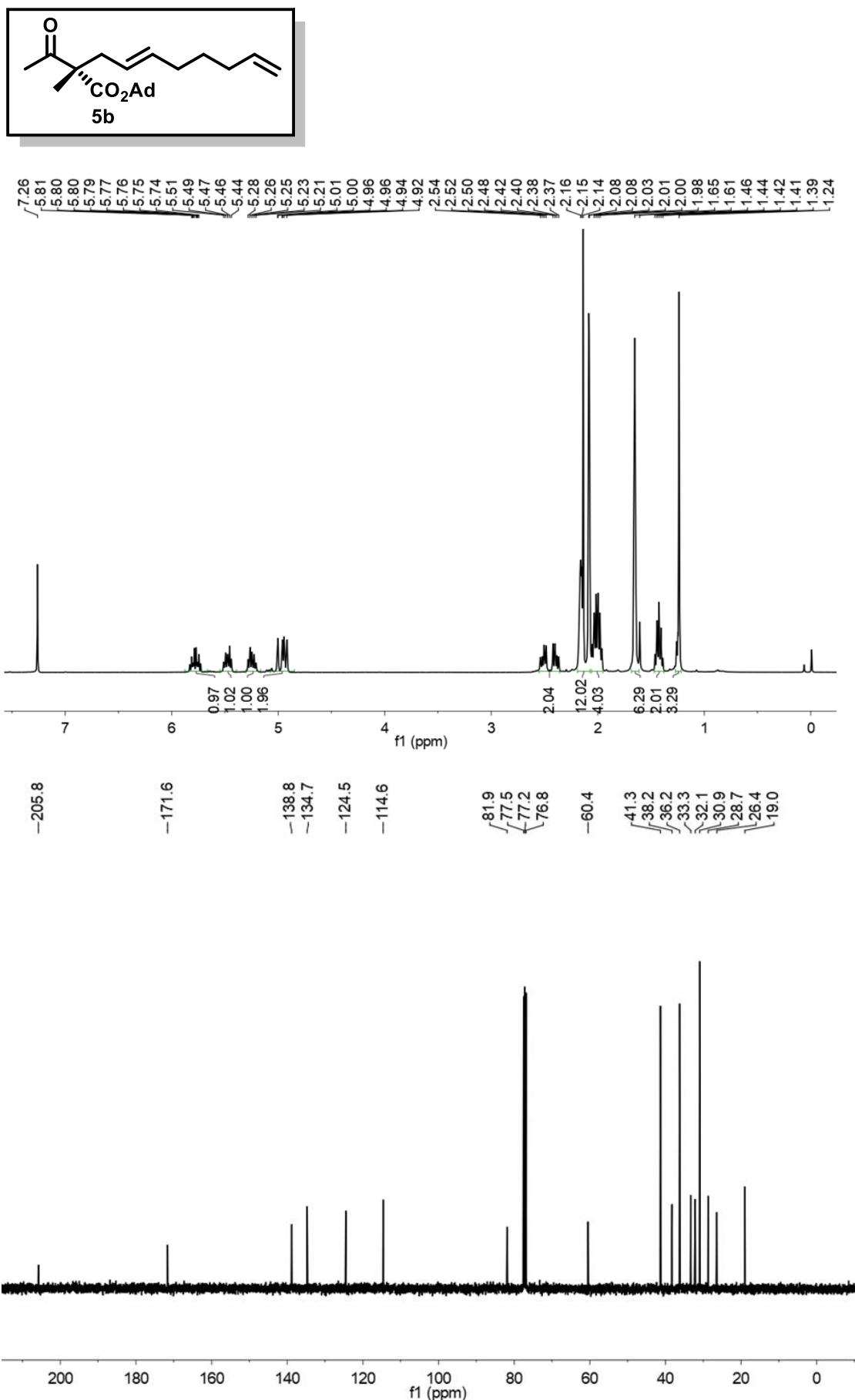


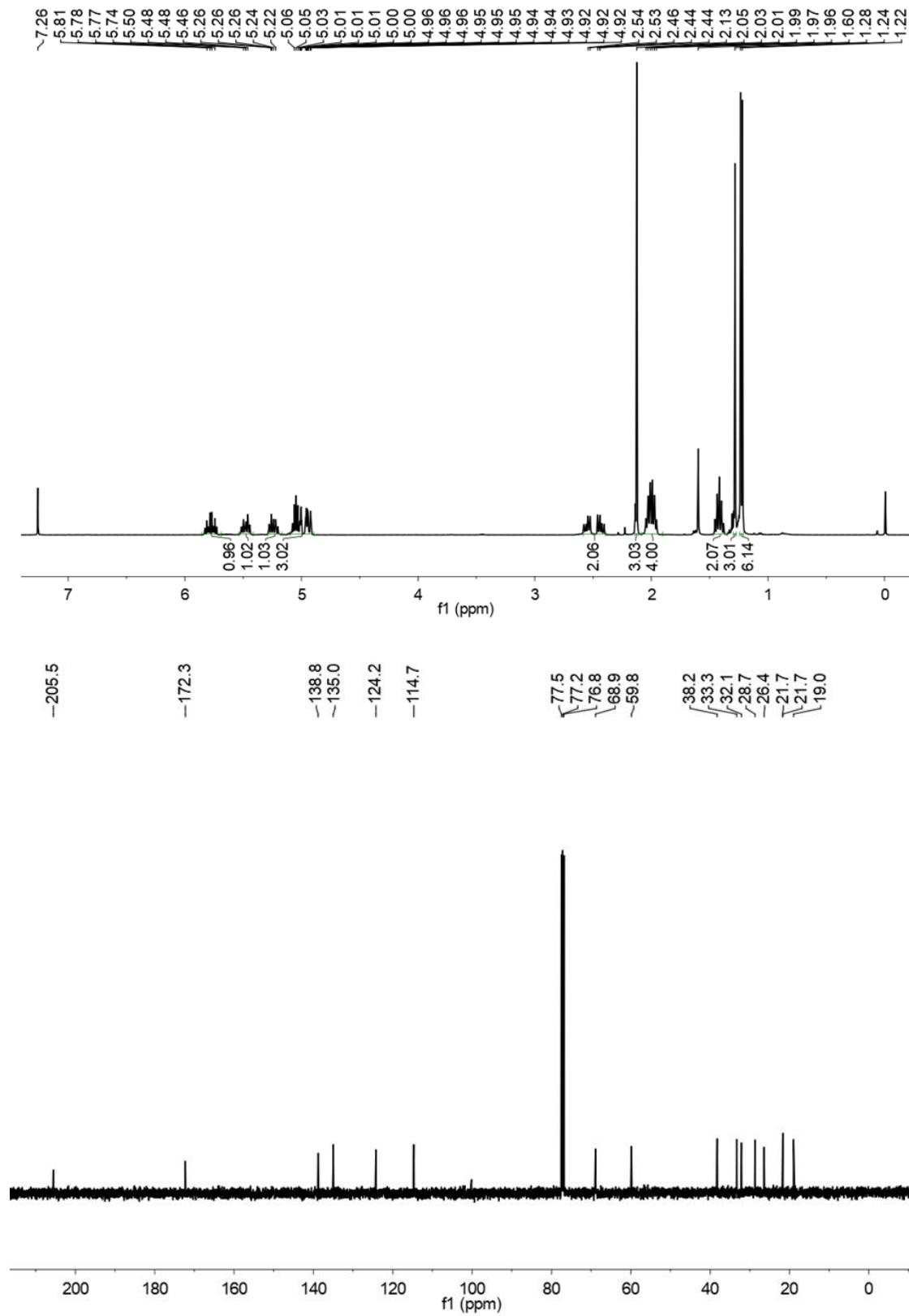
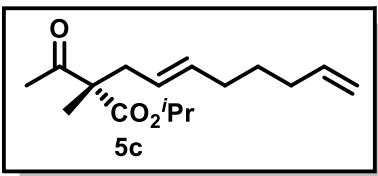


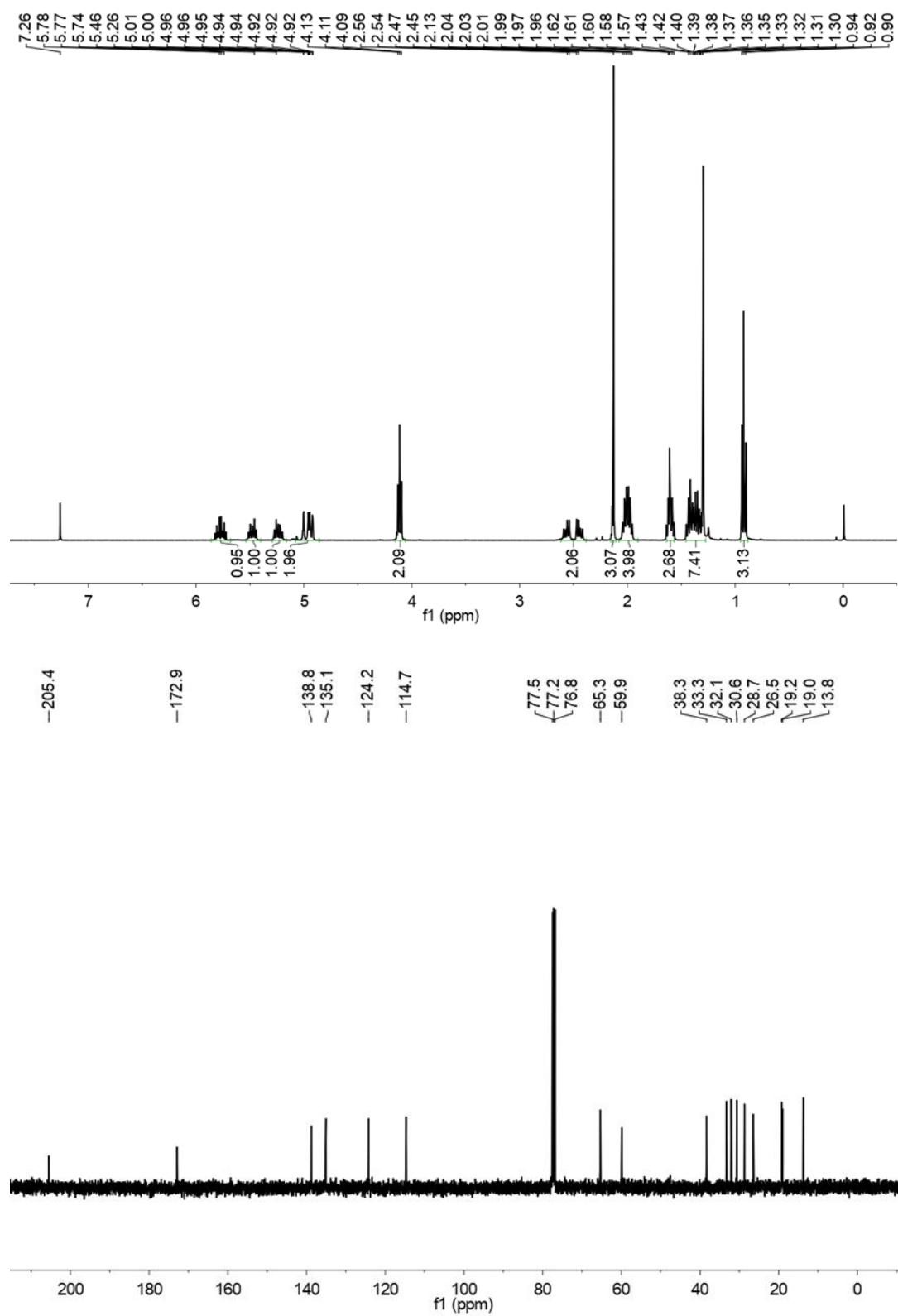
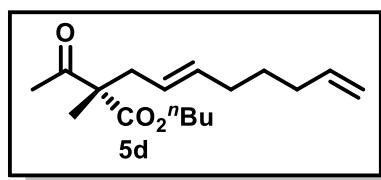


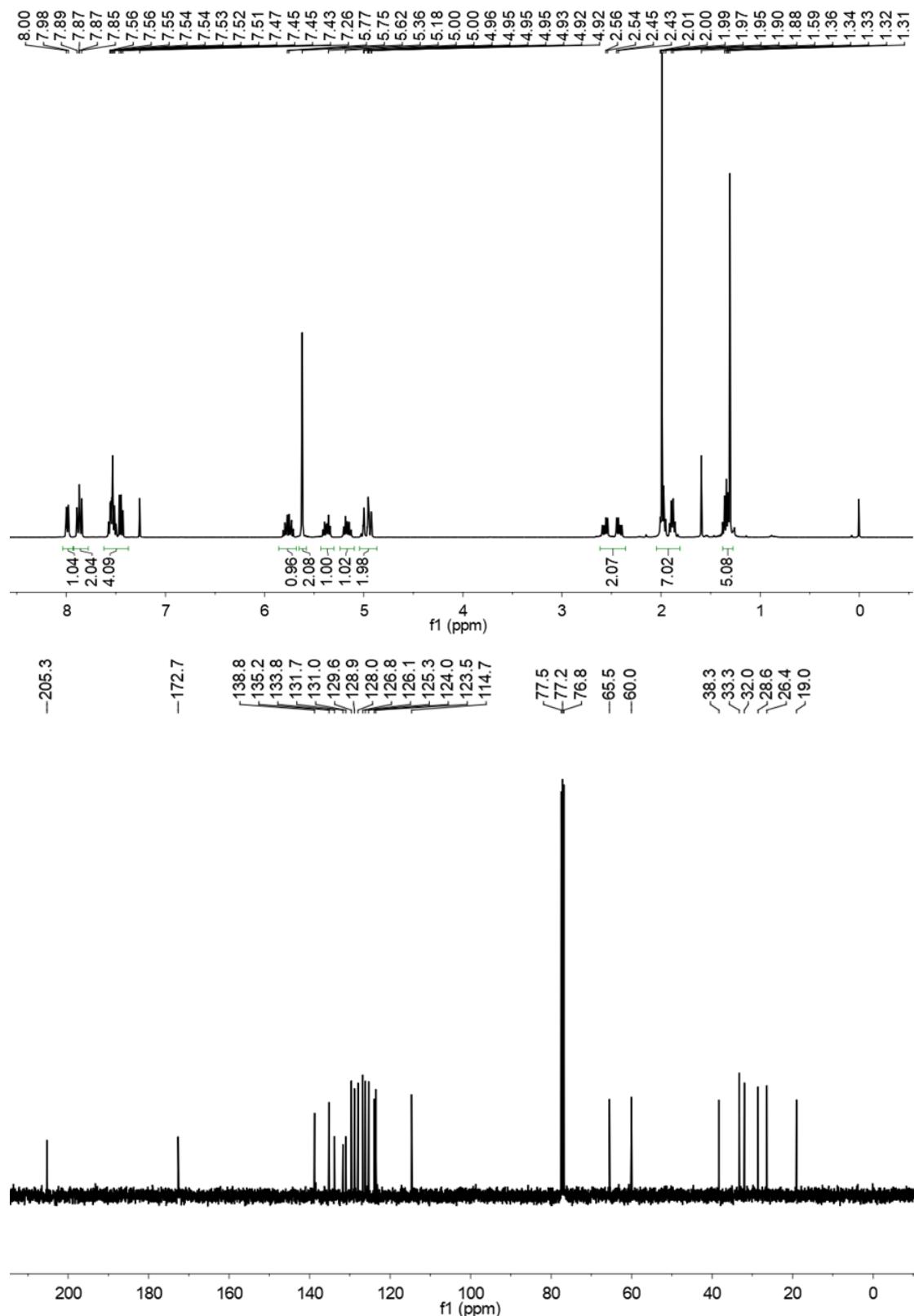
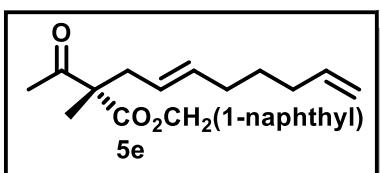


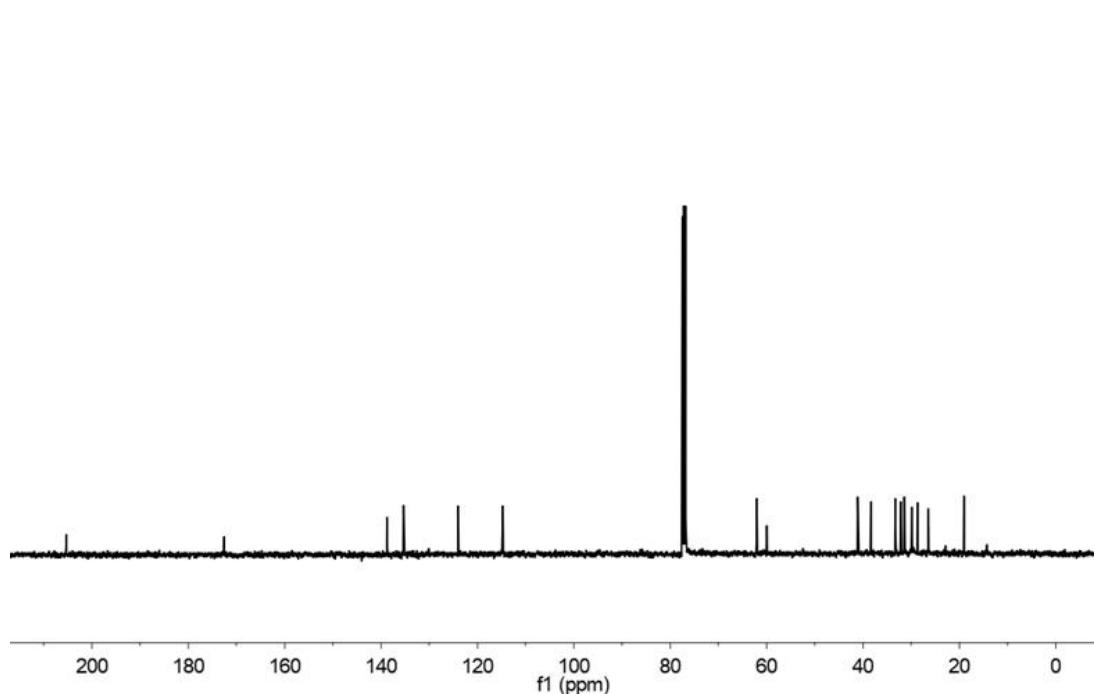
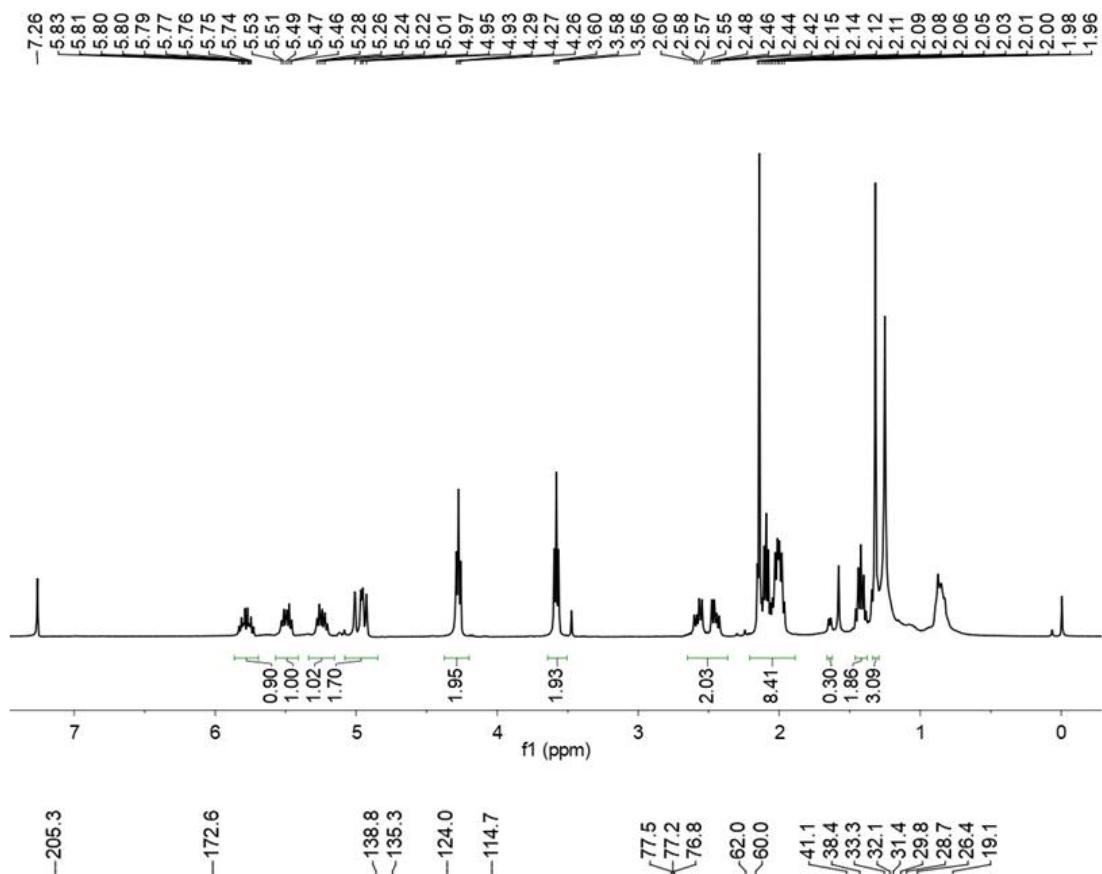
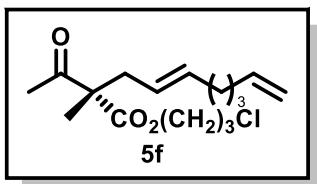


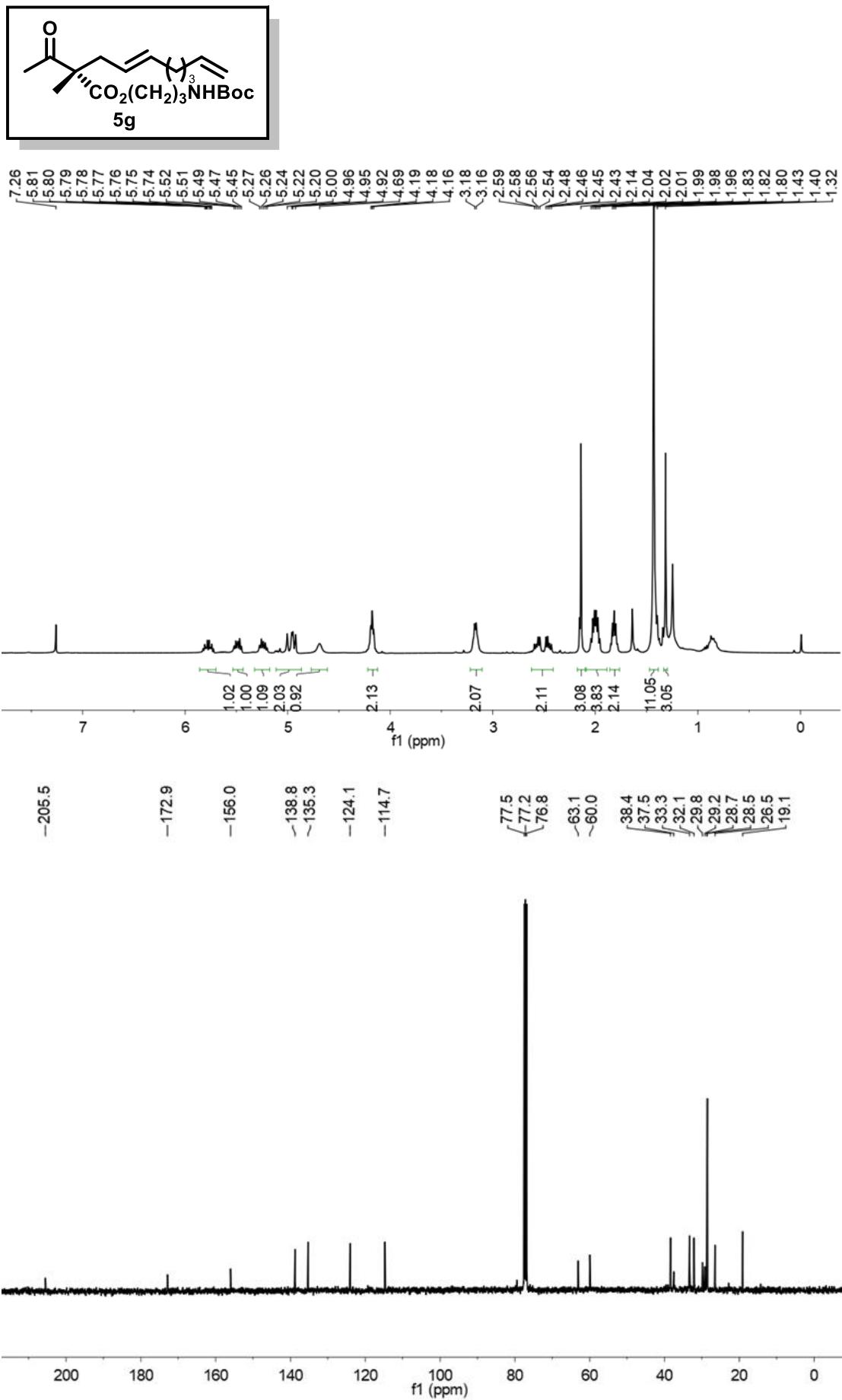


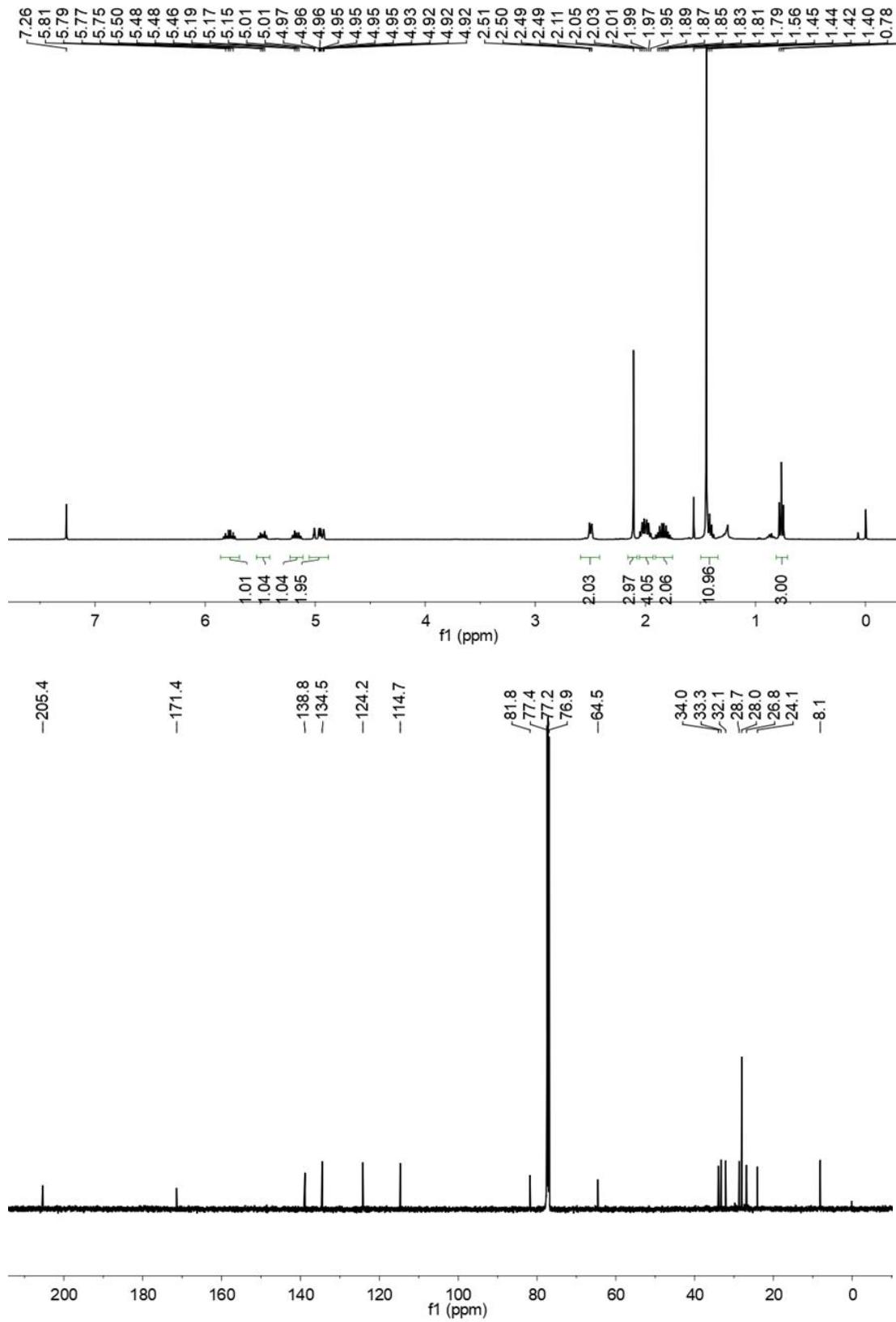
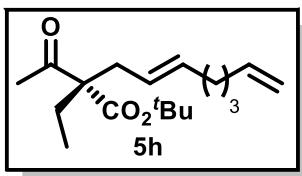


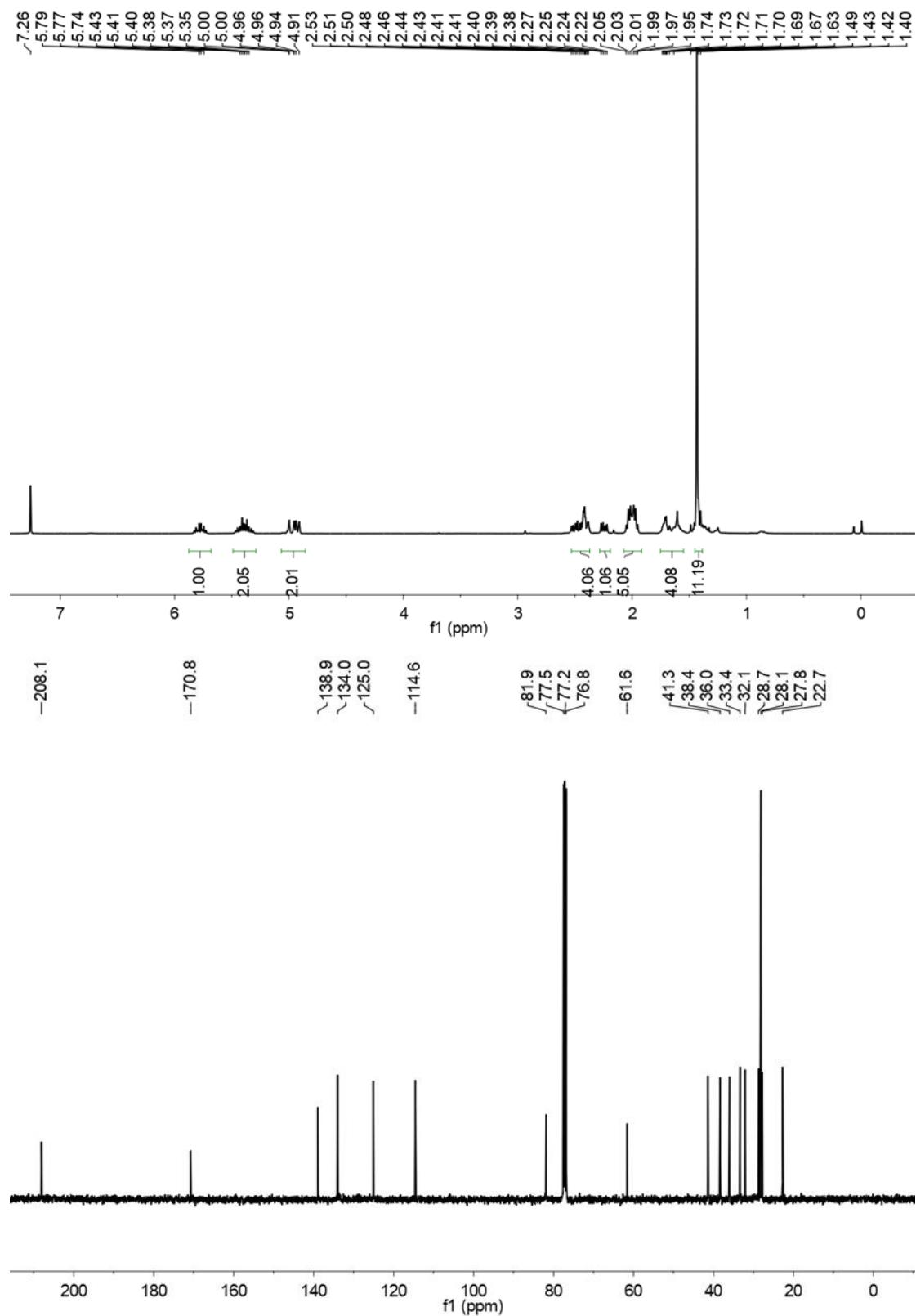
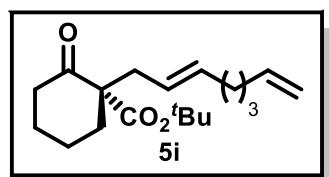


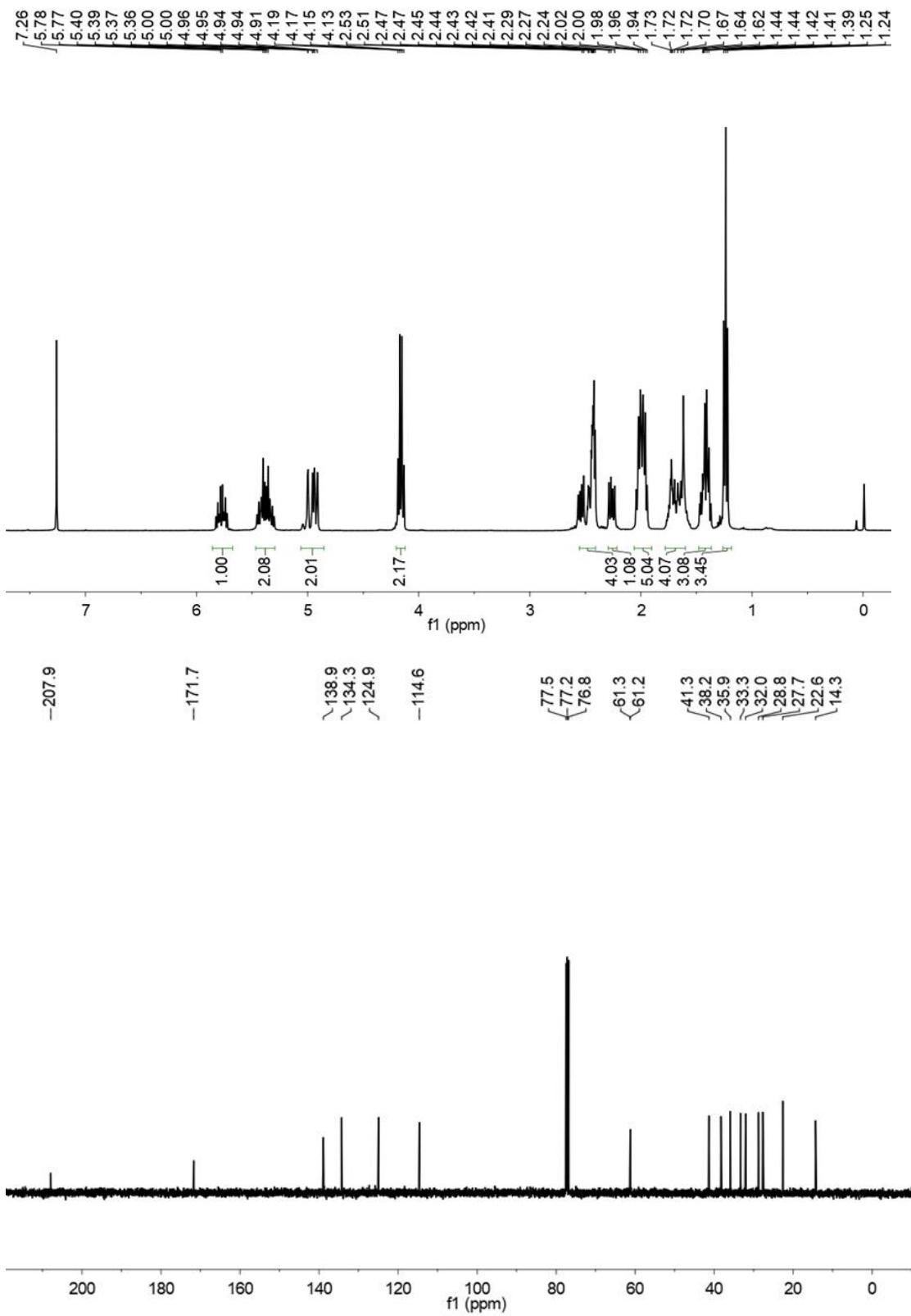
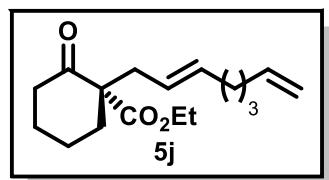


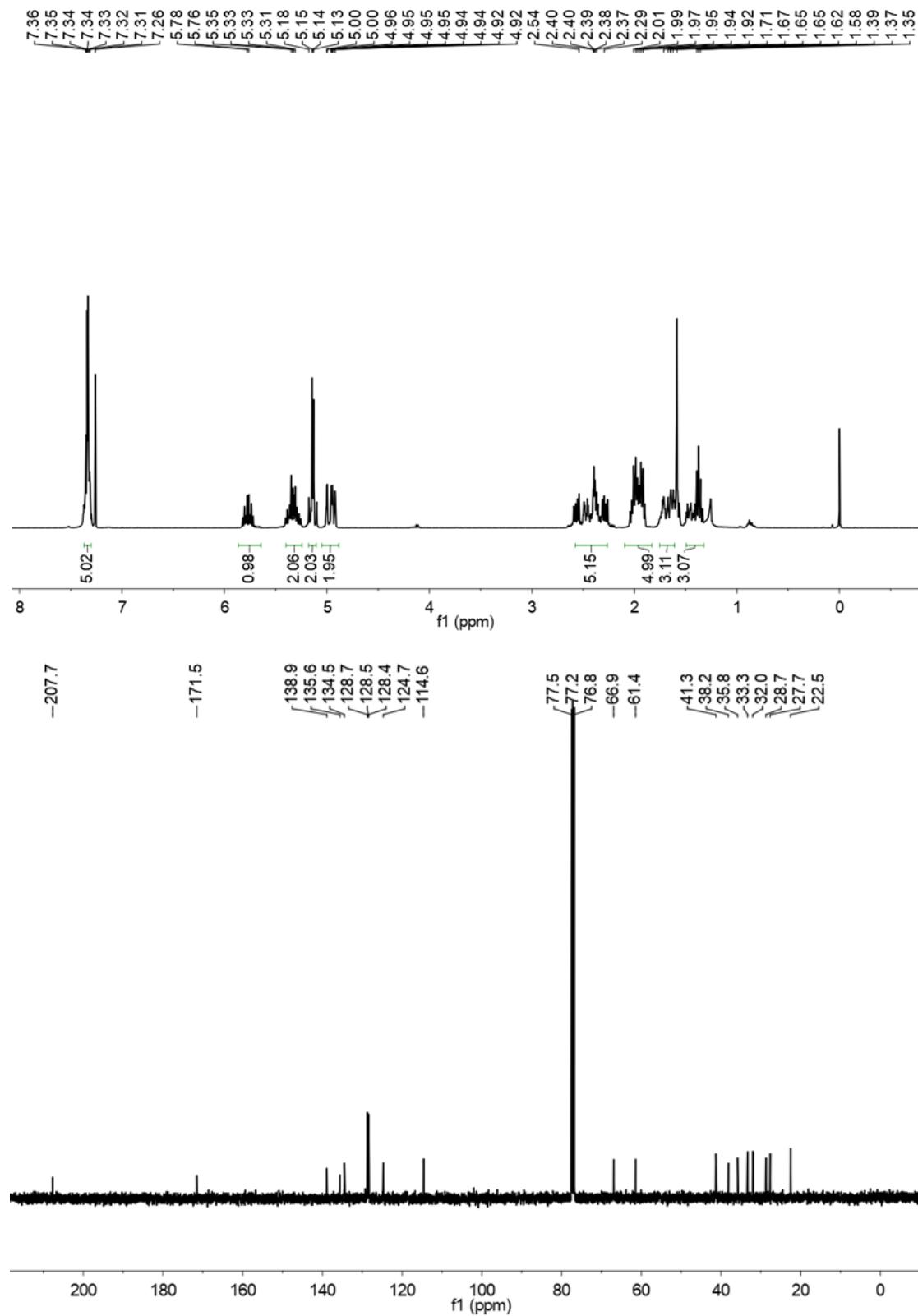
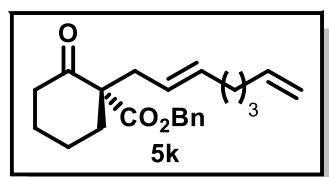


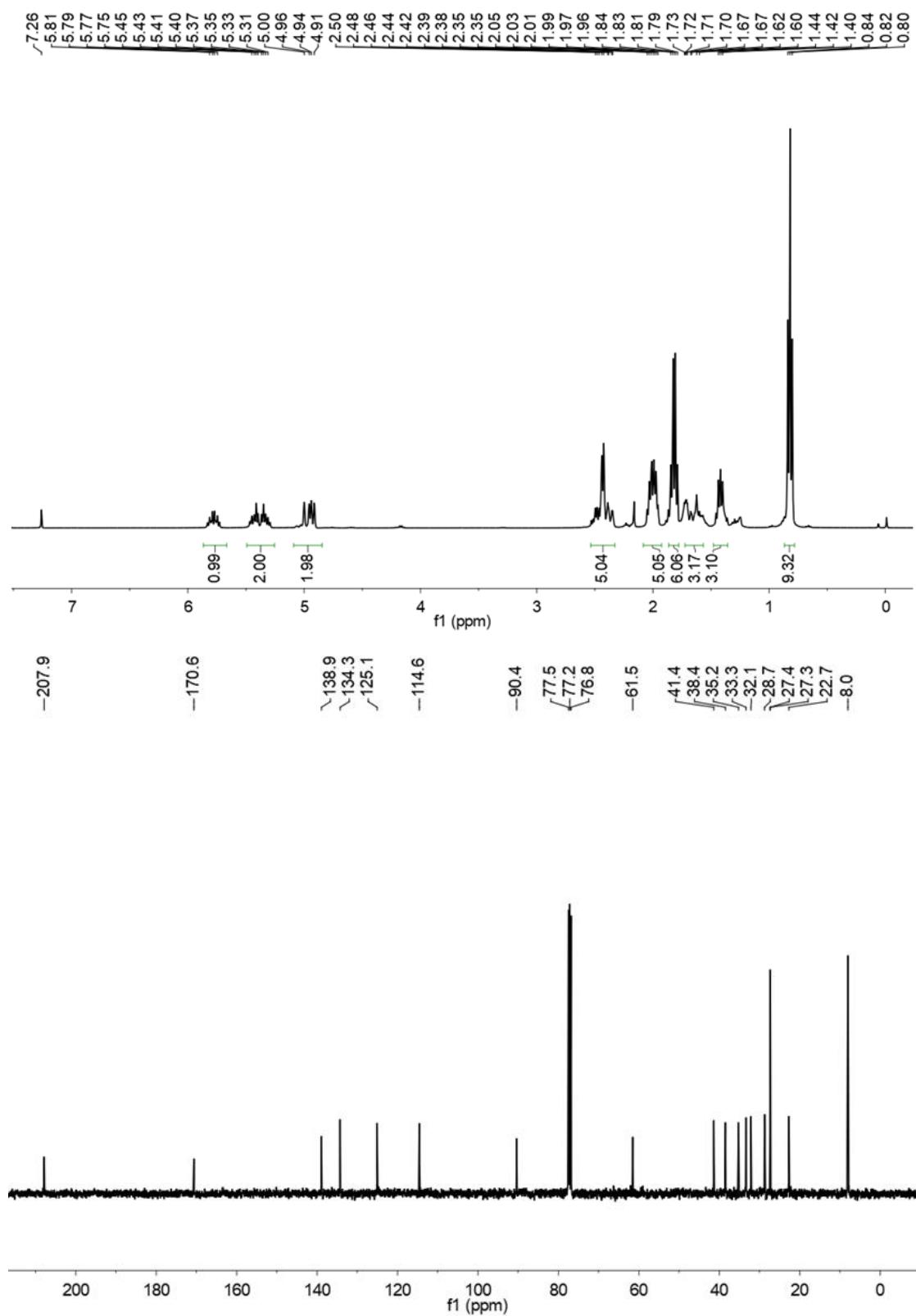
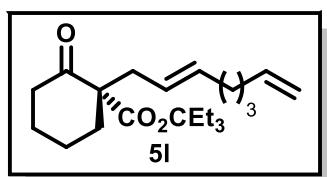


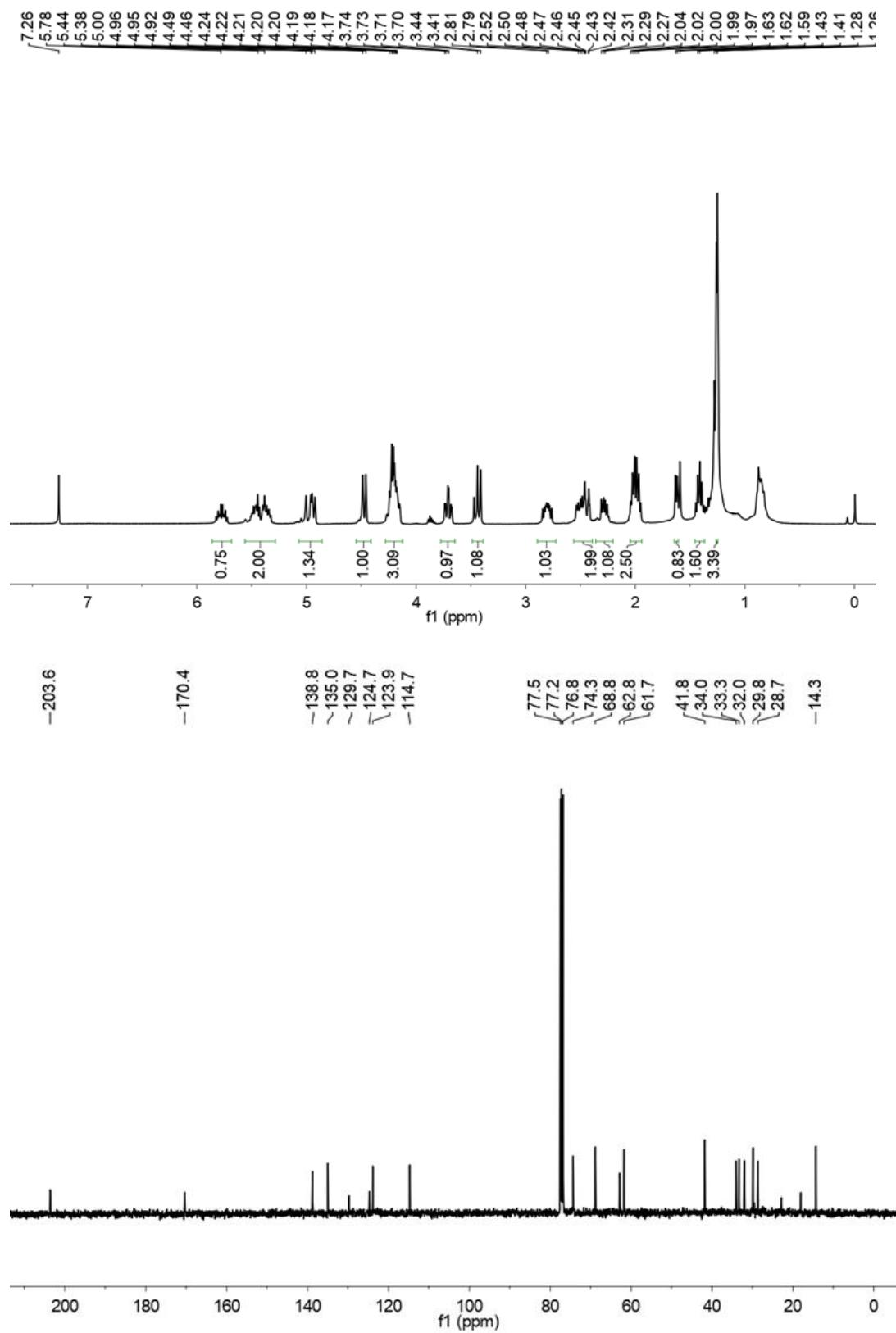
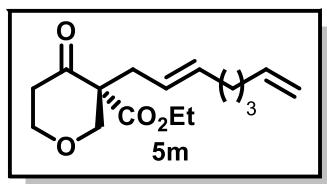


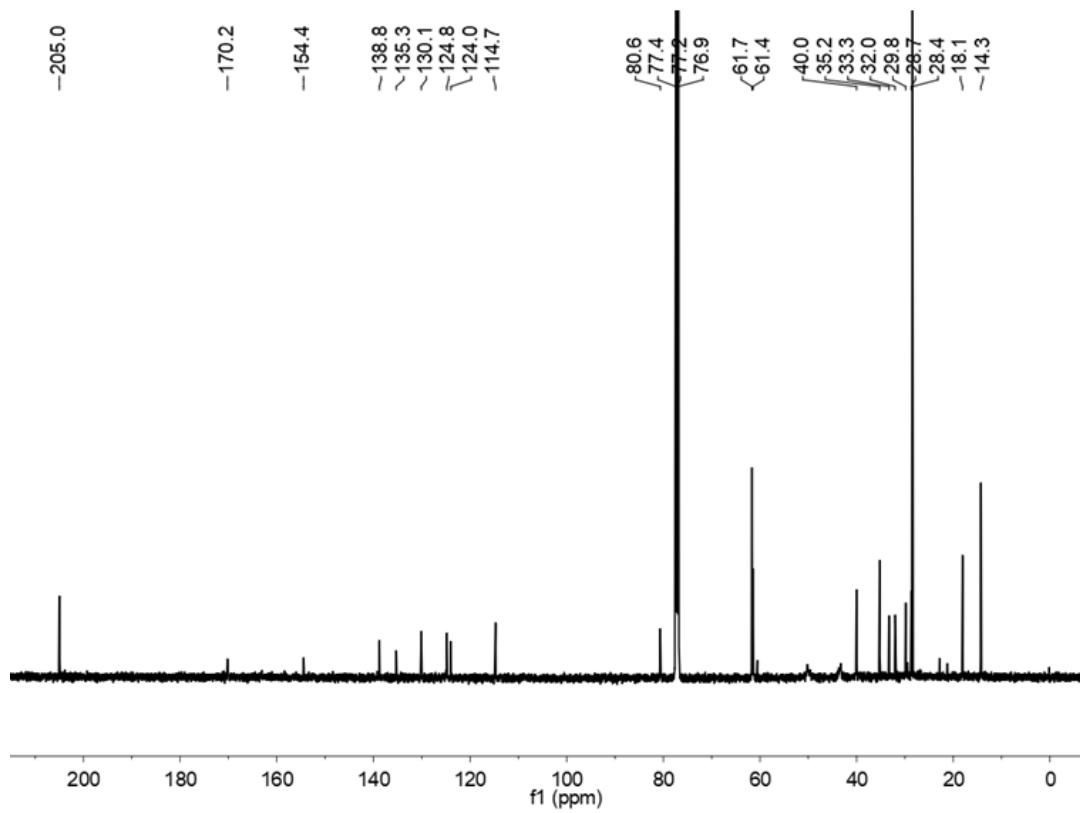
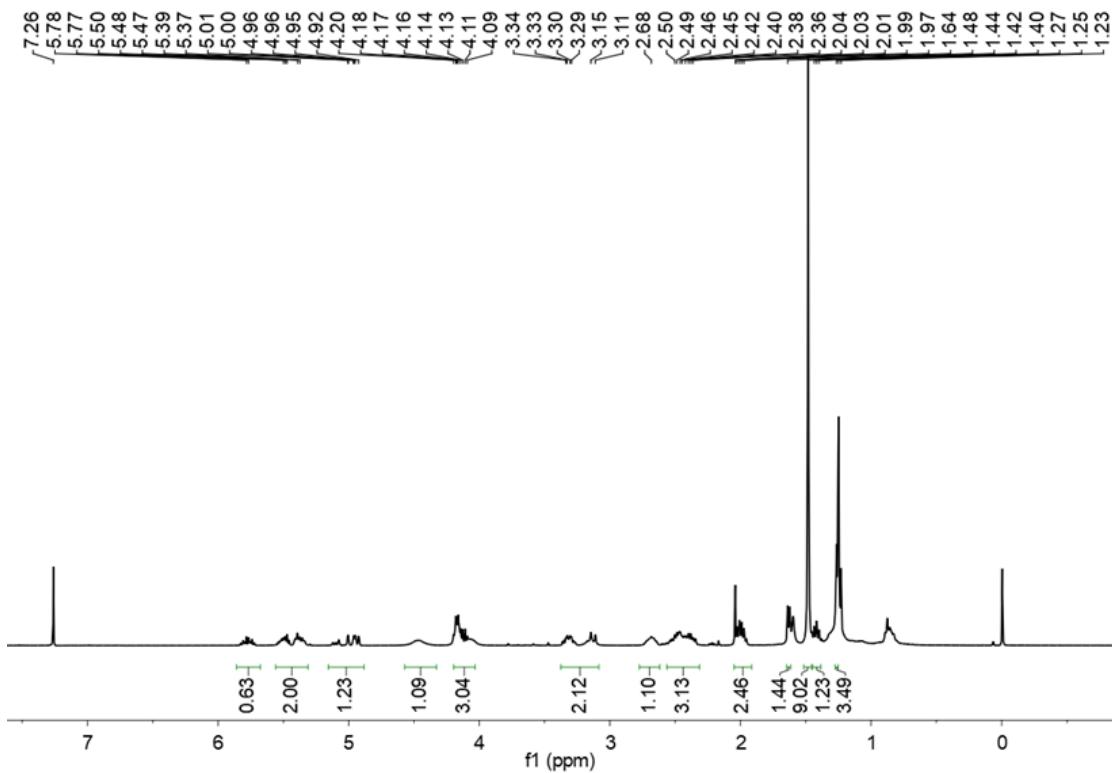
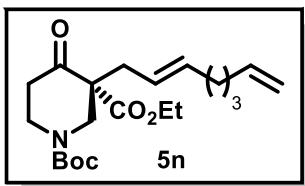


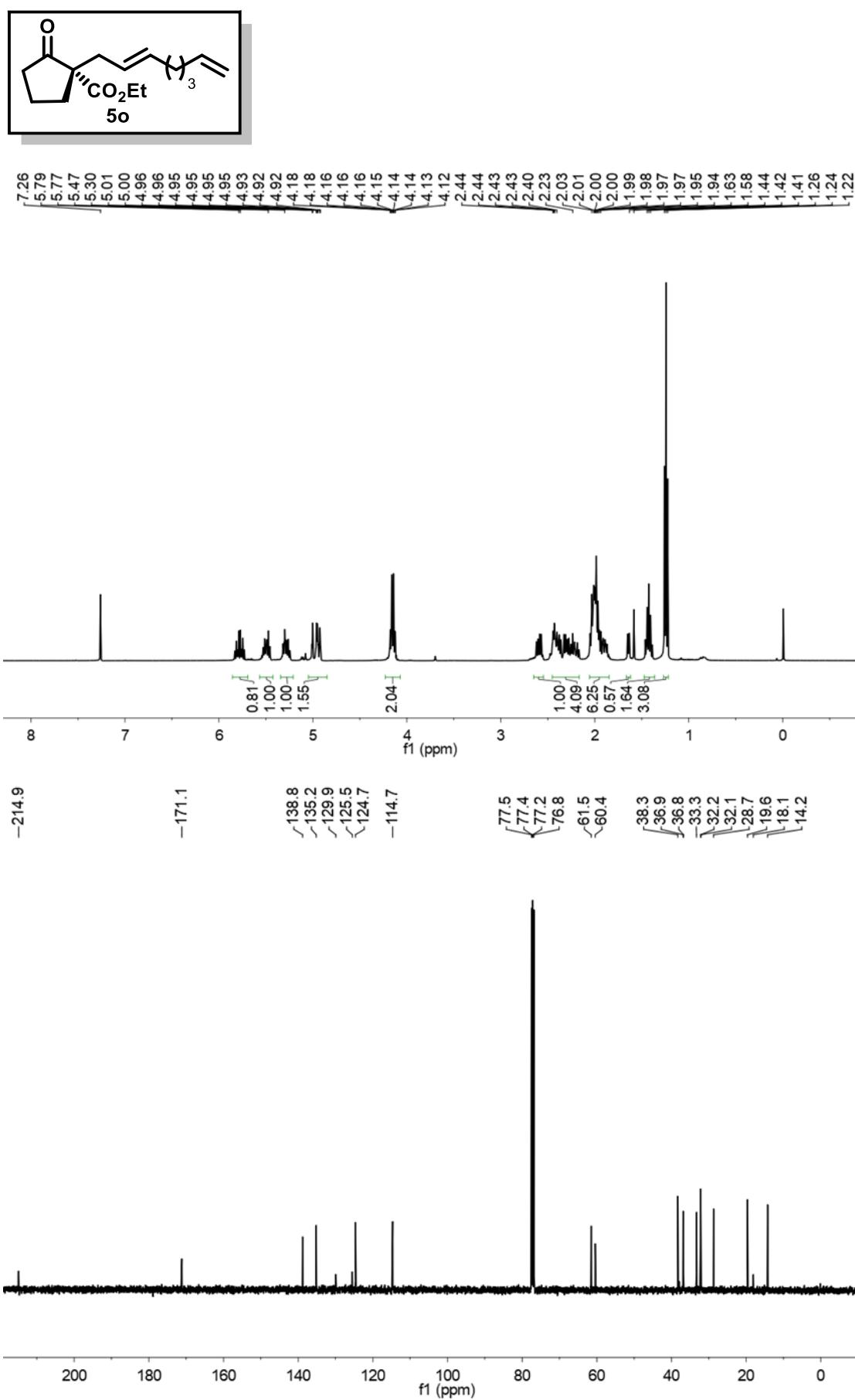


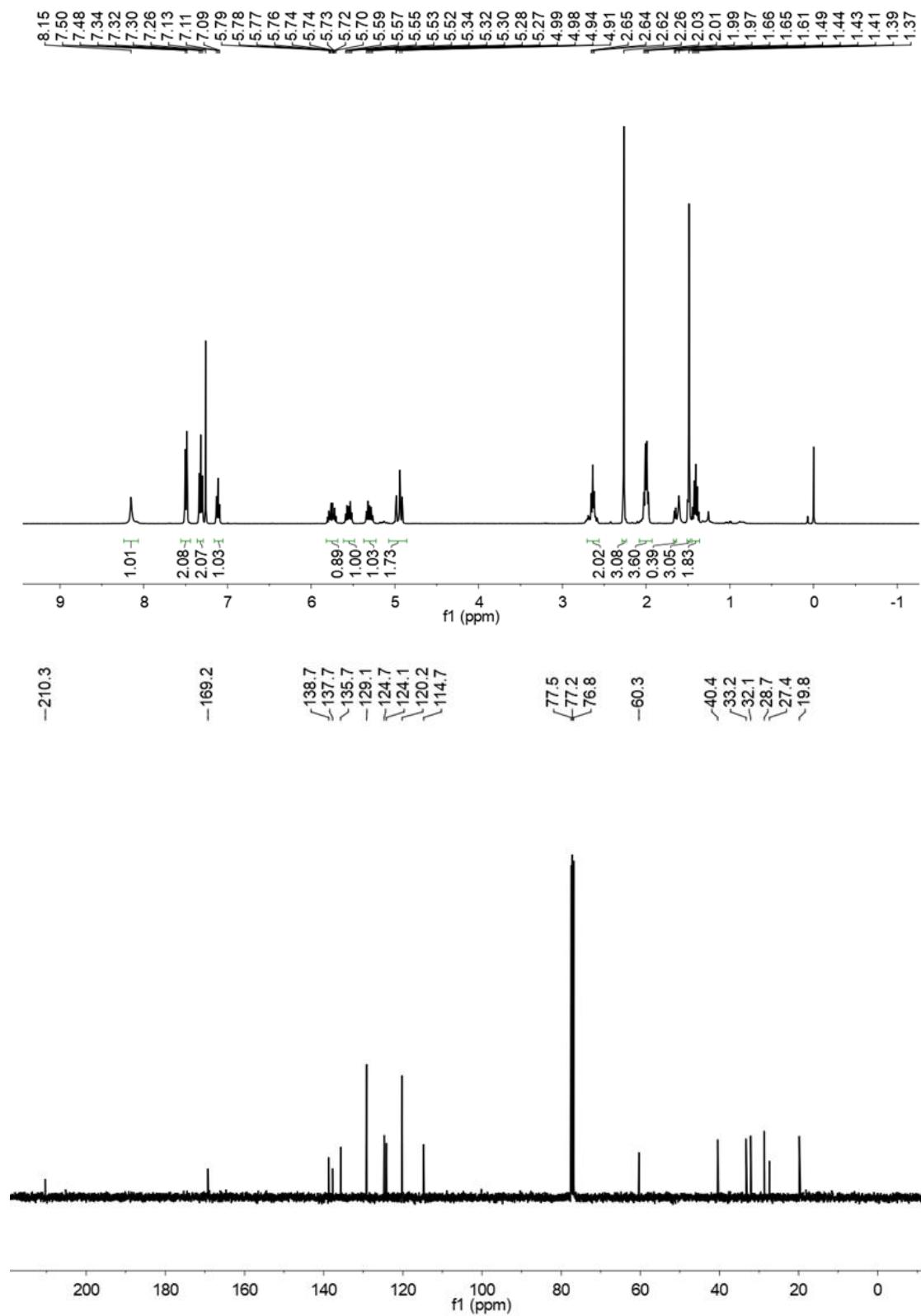
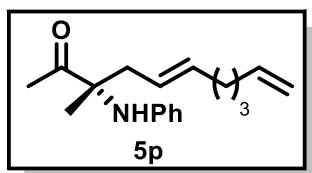


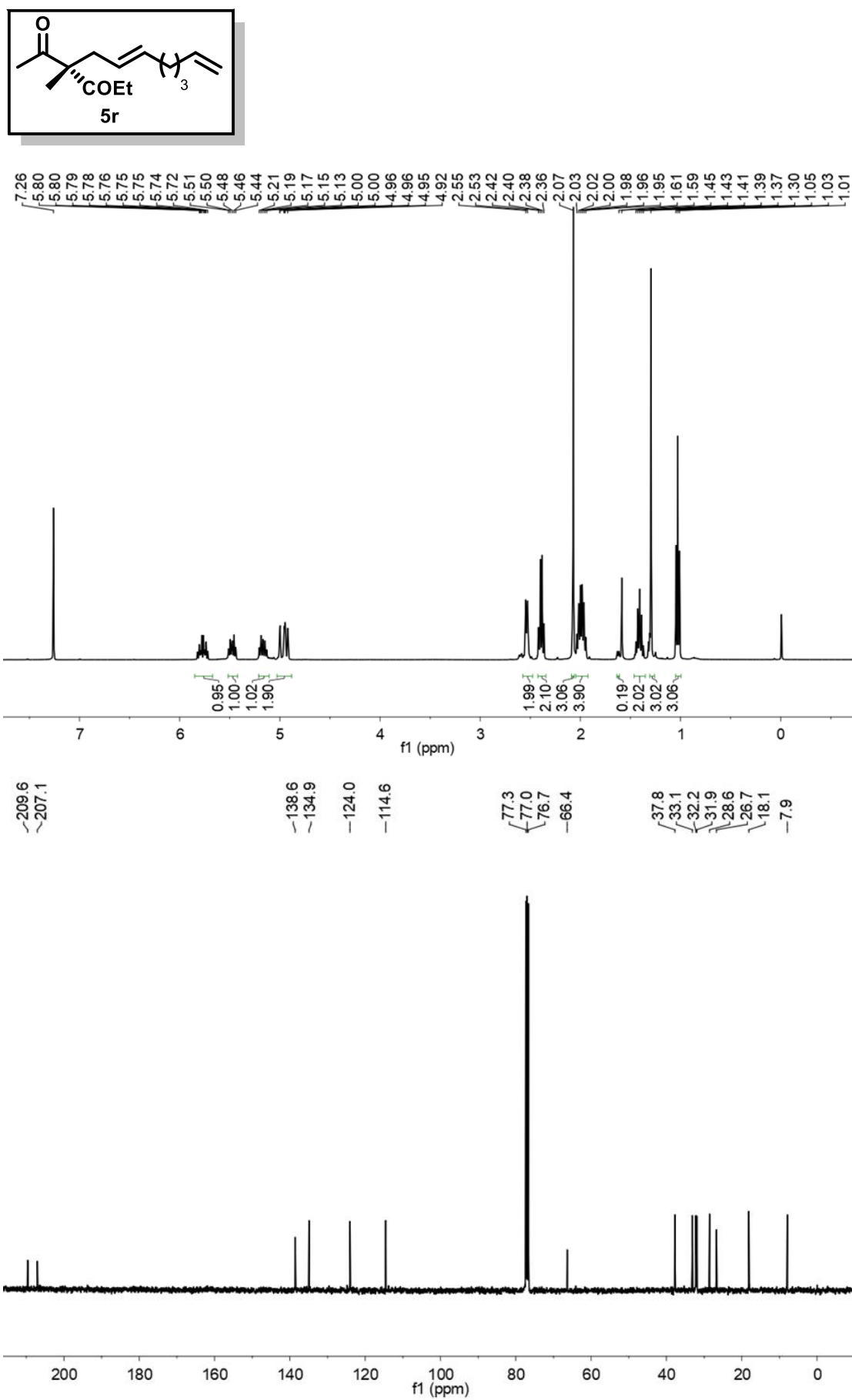


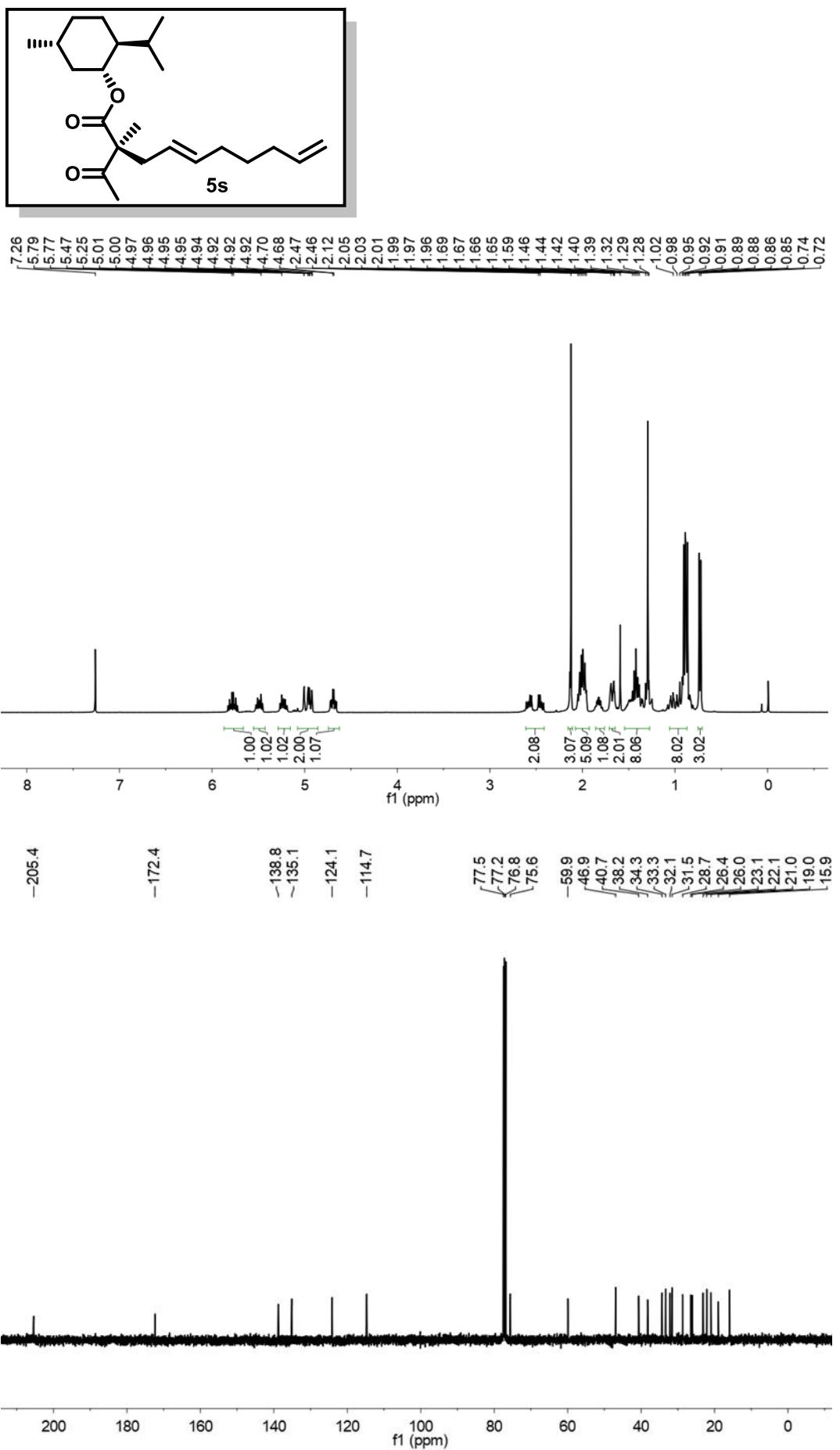


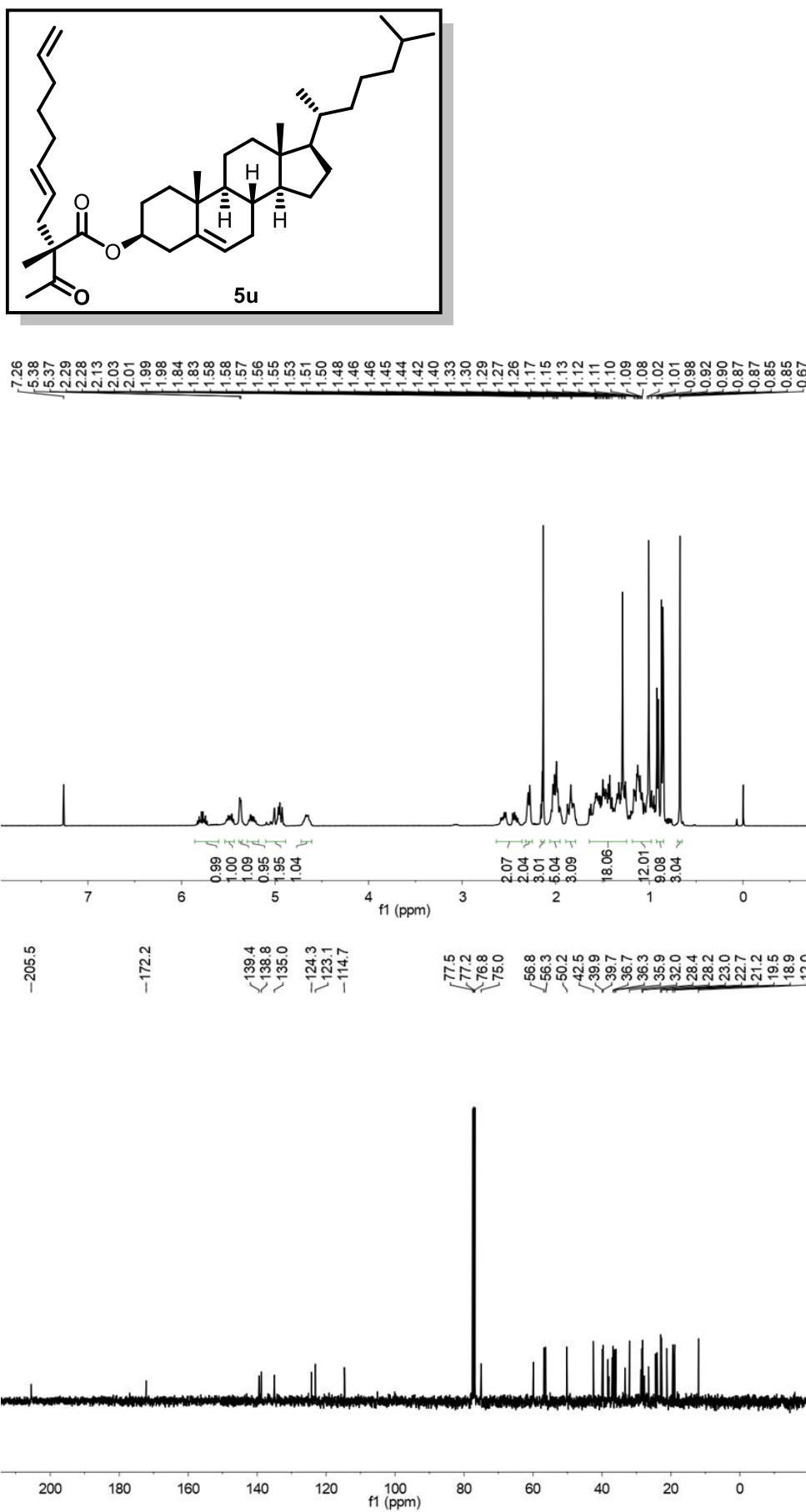


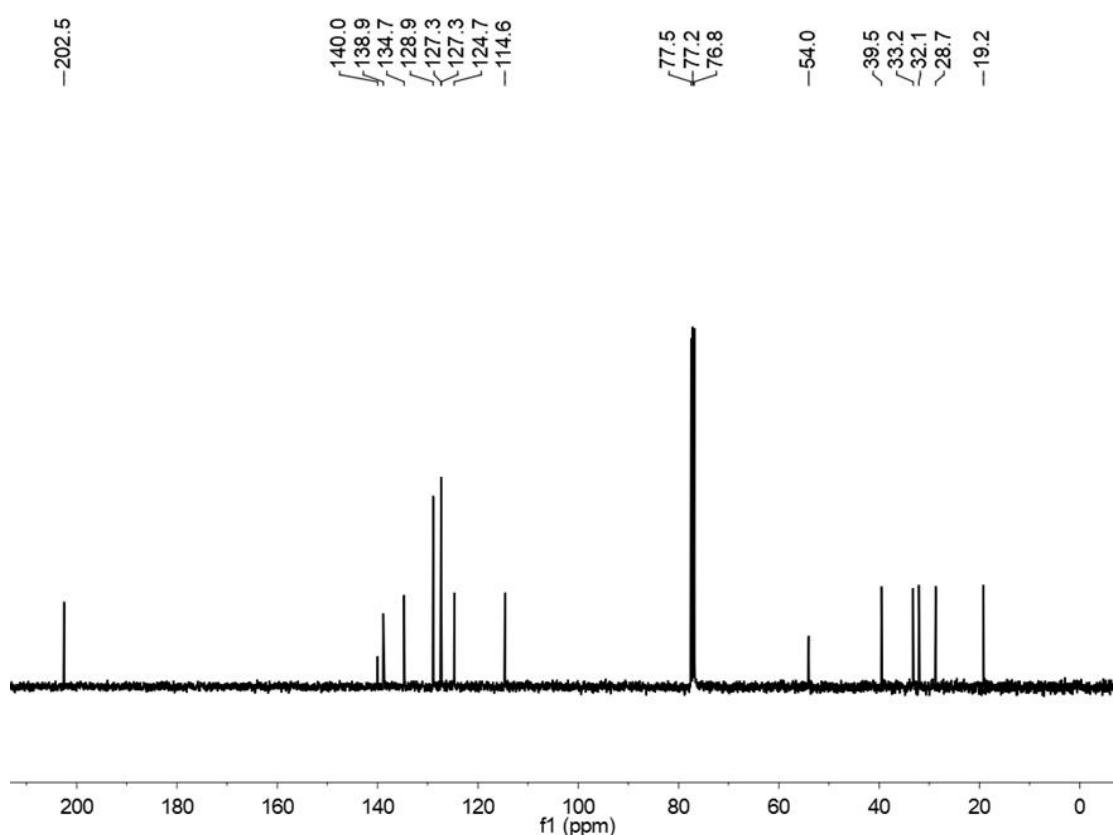
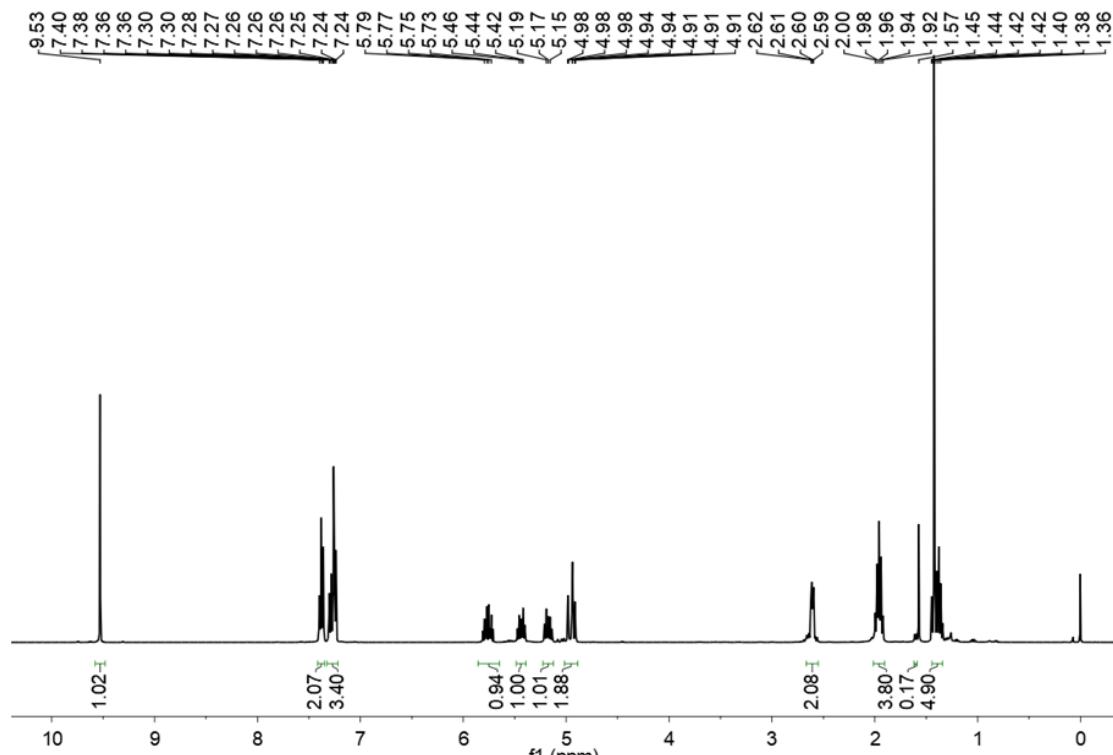
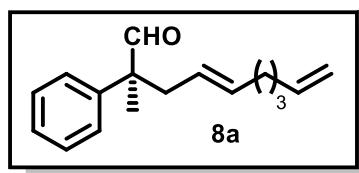


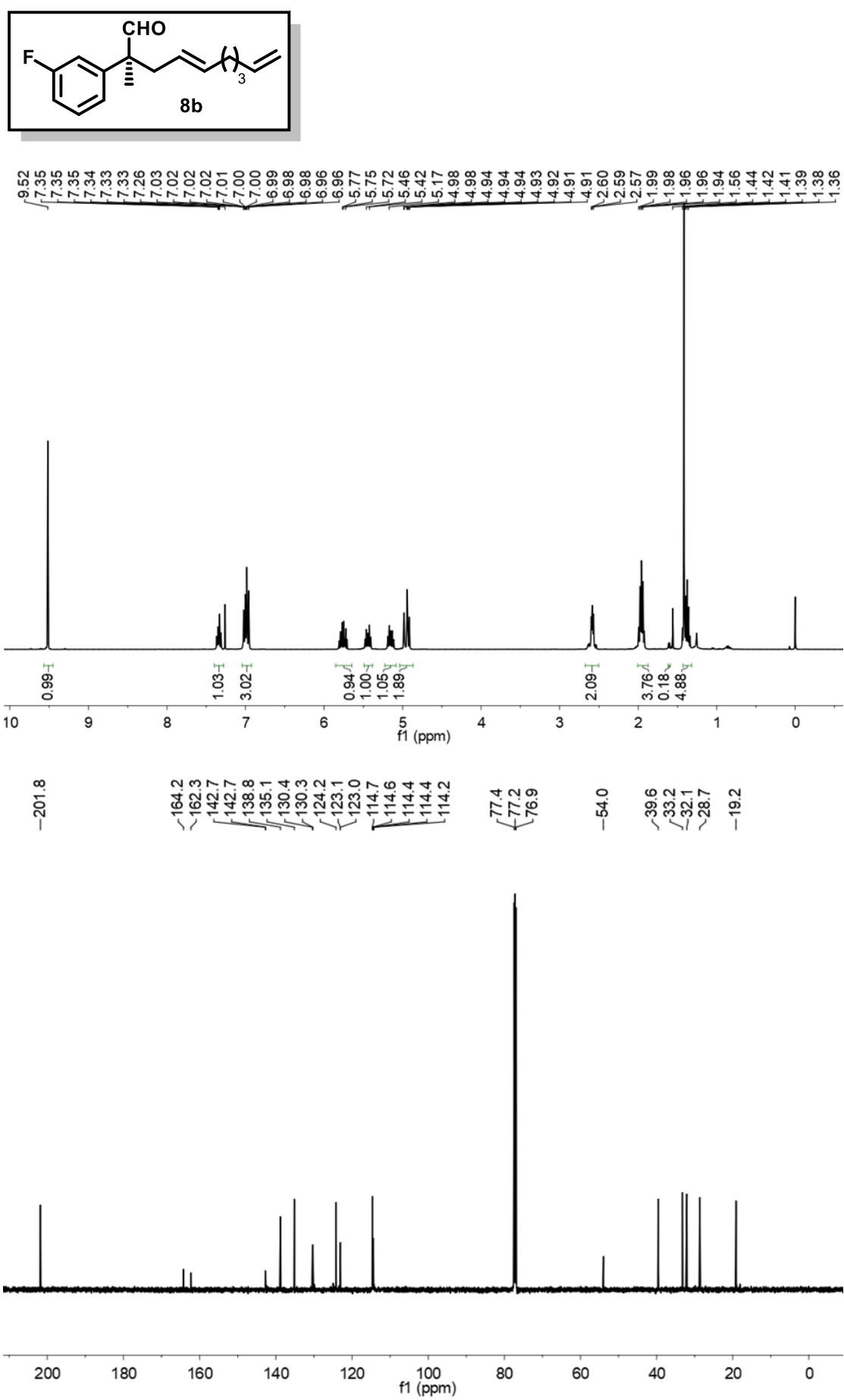




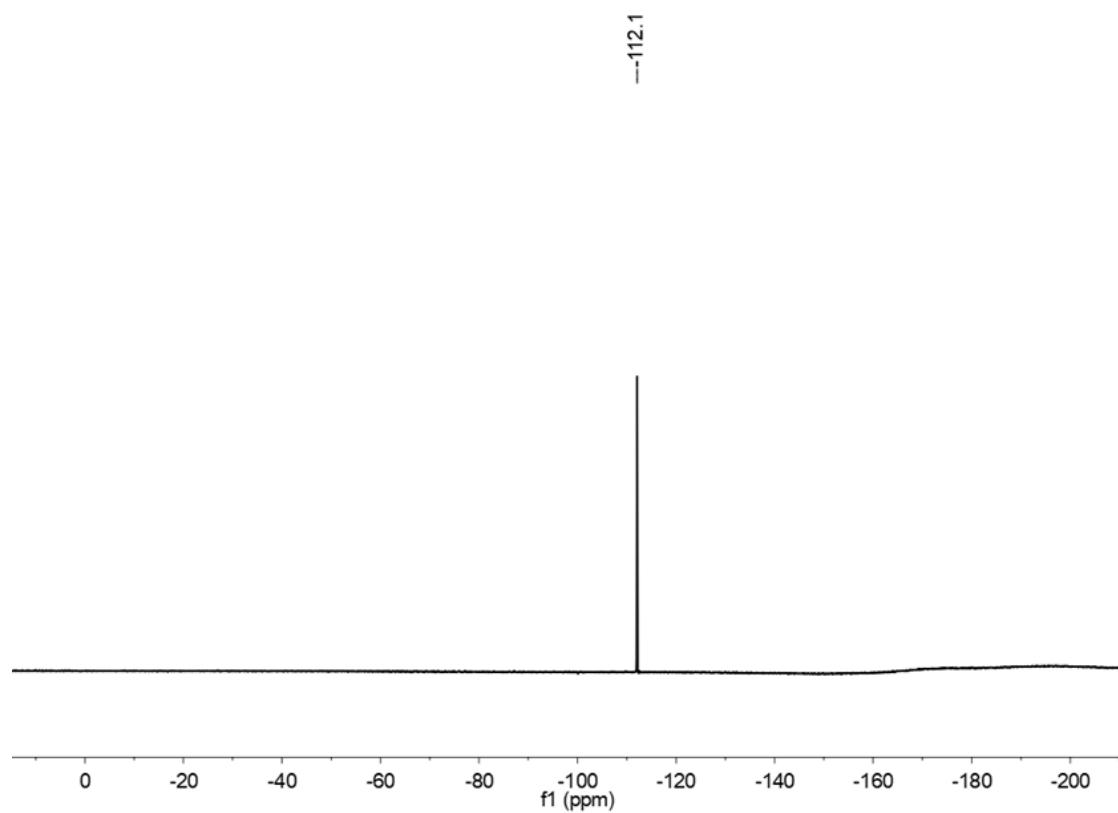


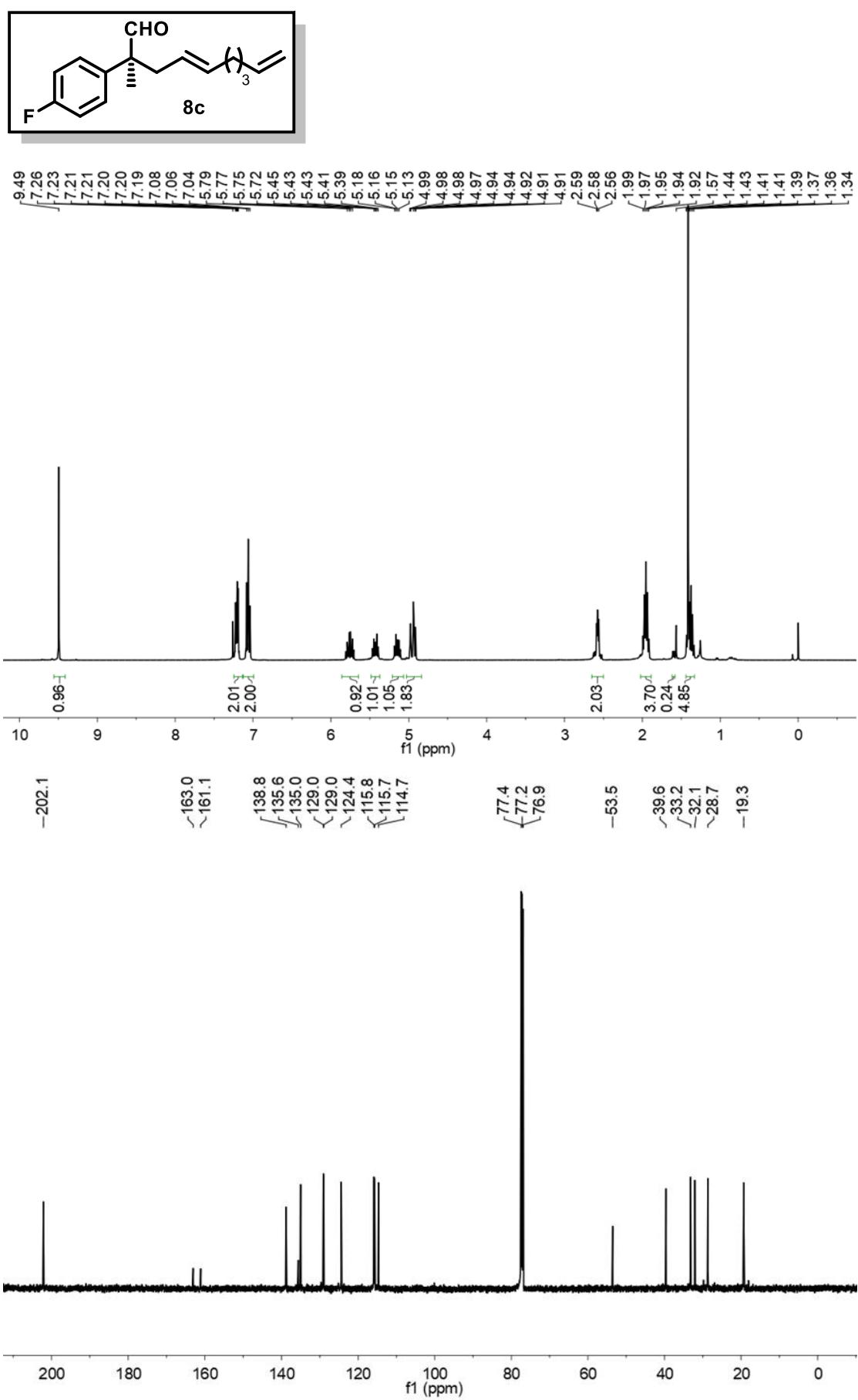




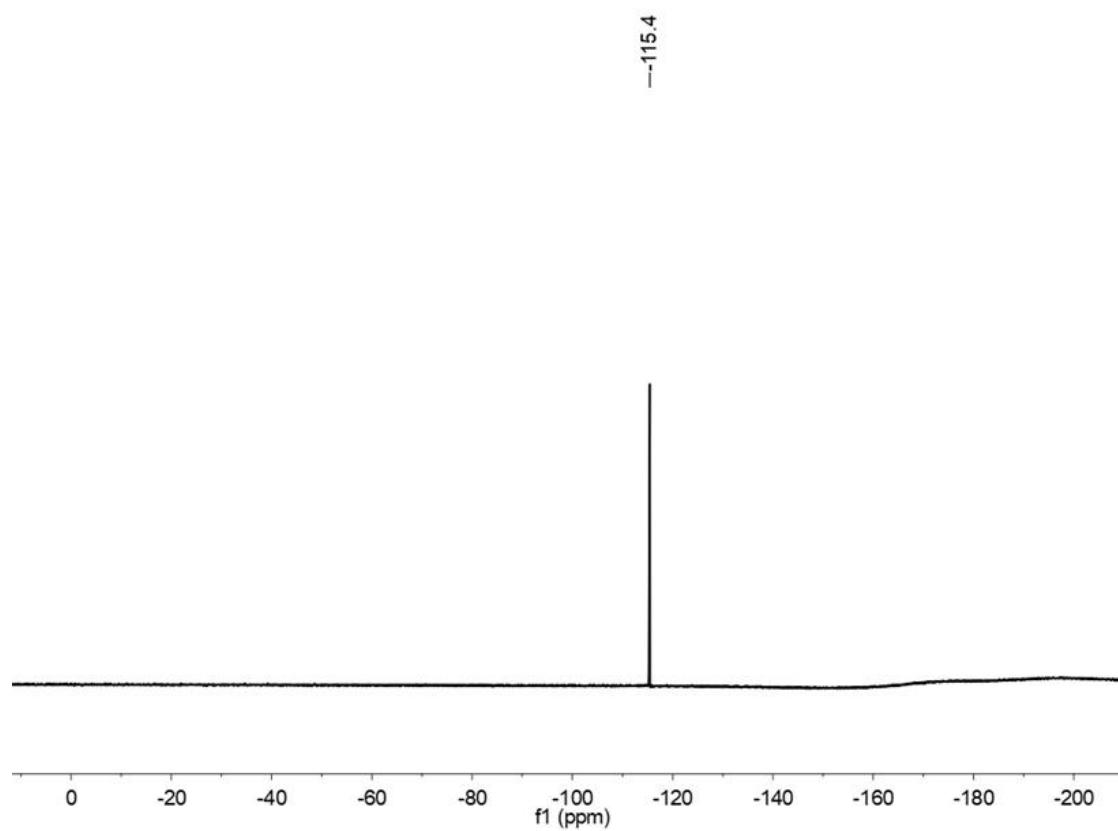


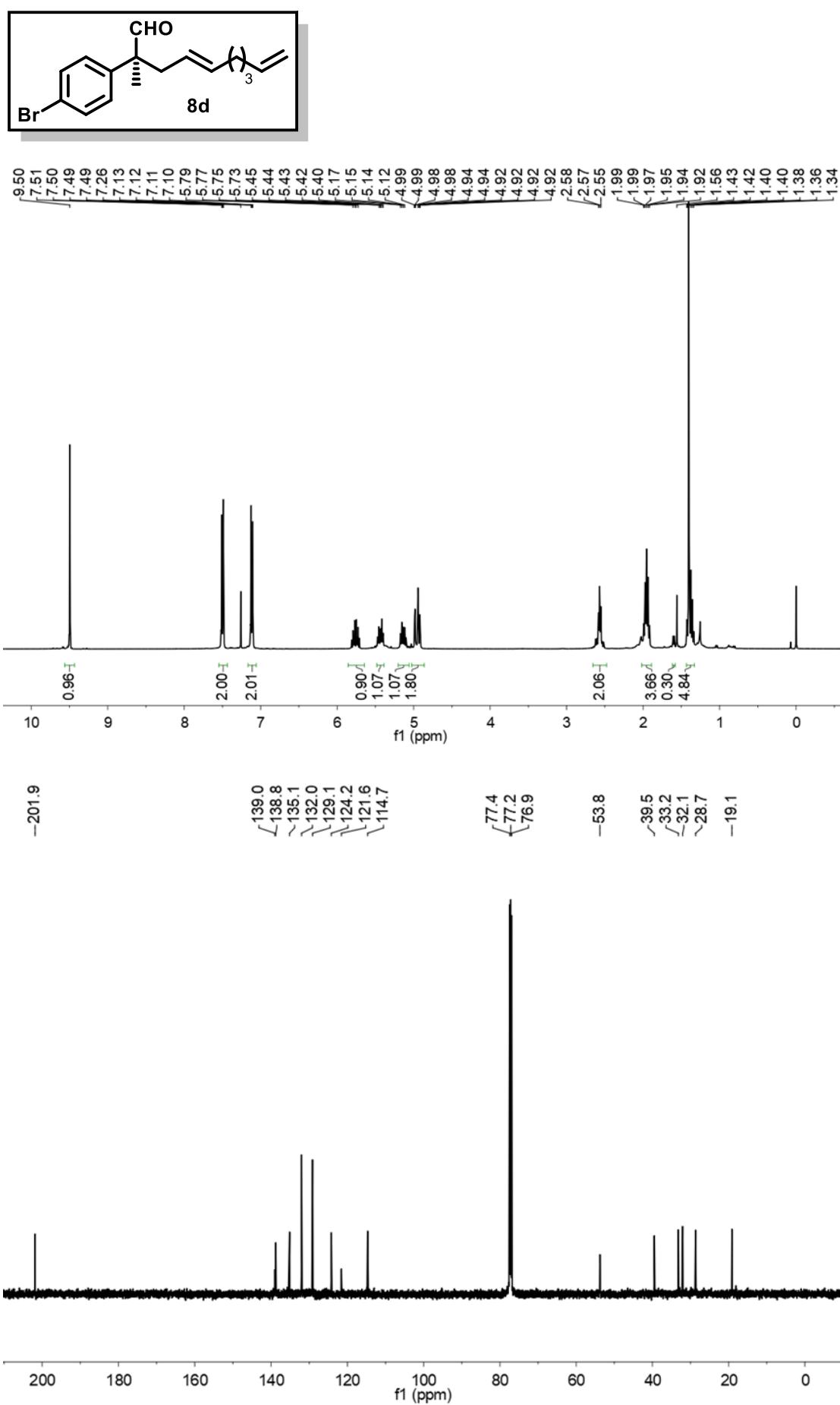
¹⁹F NMR

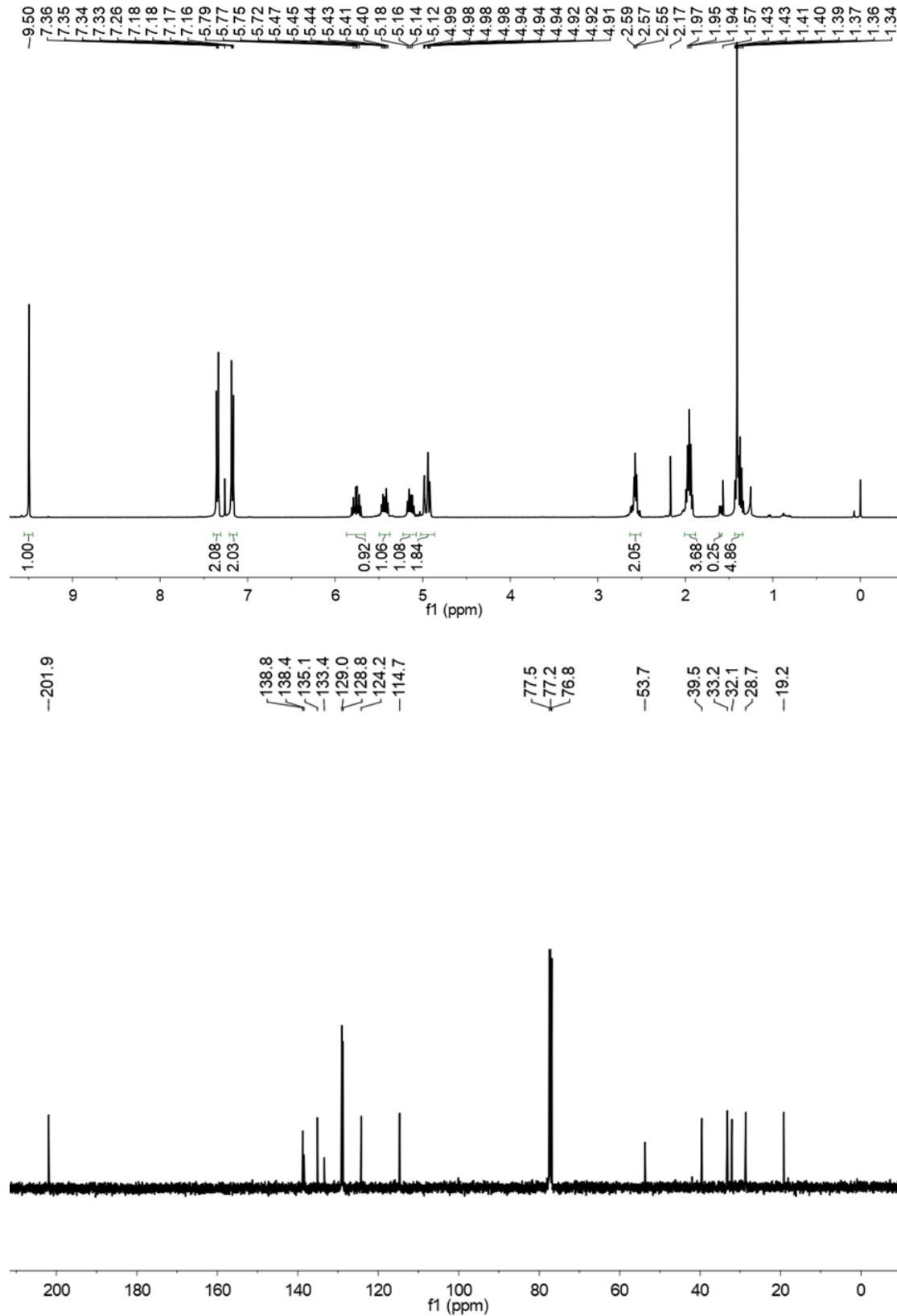
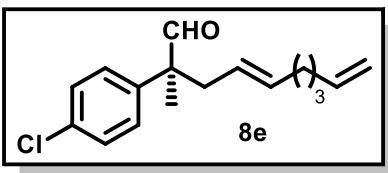


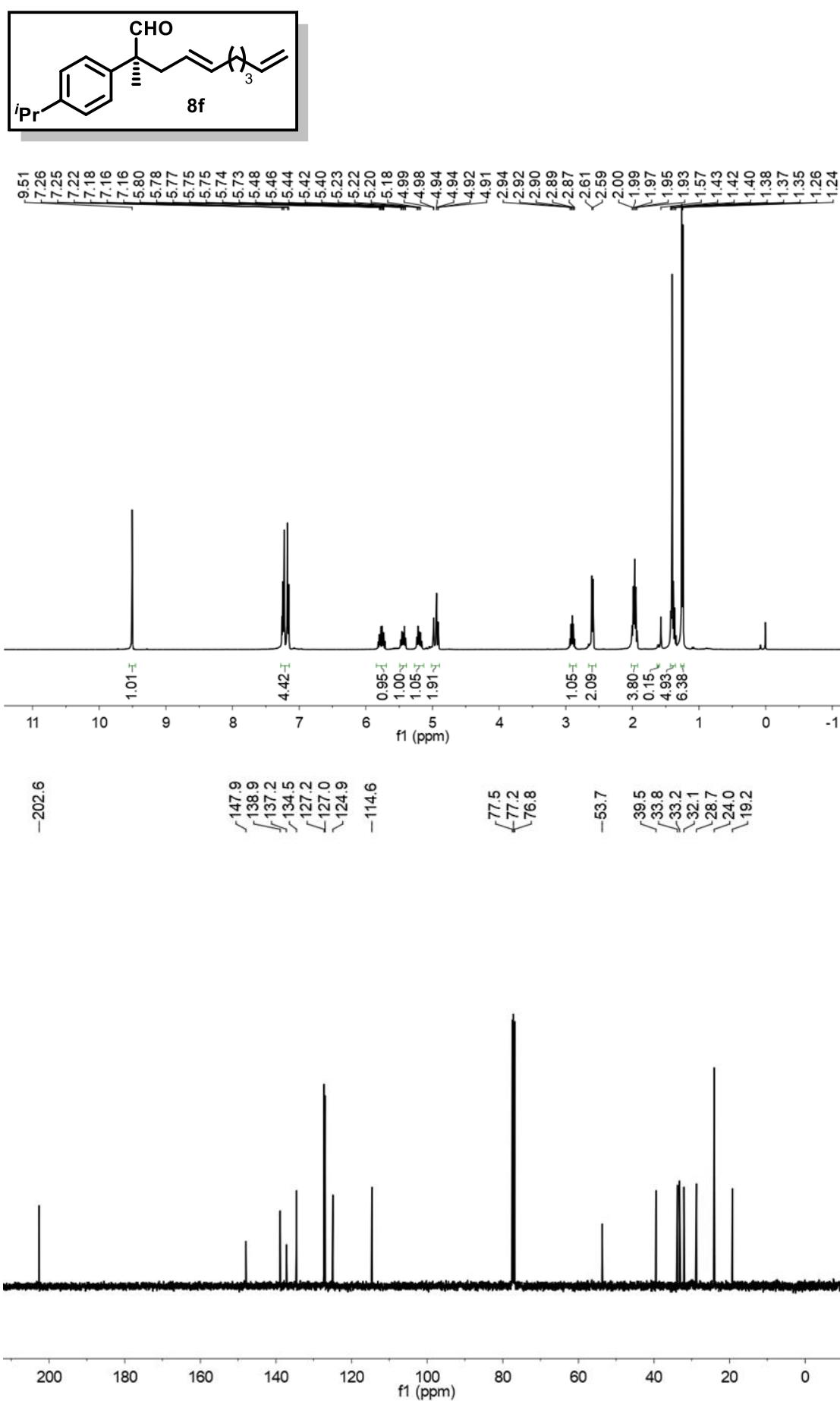


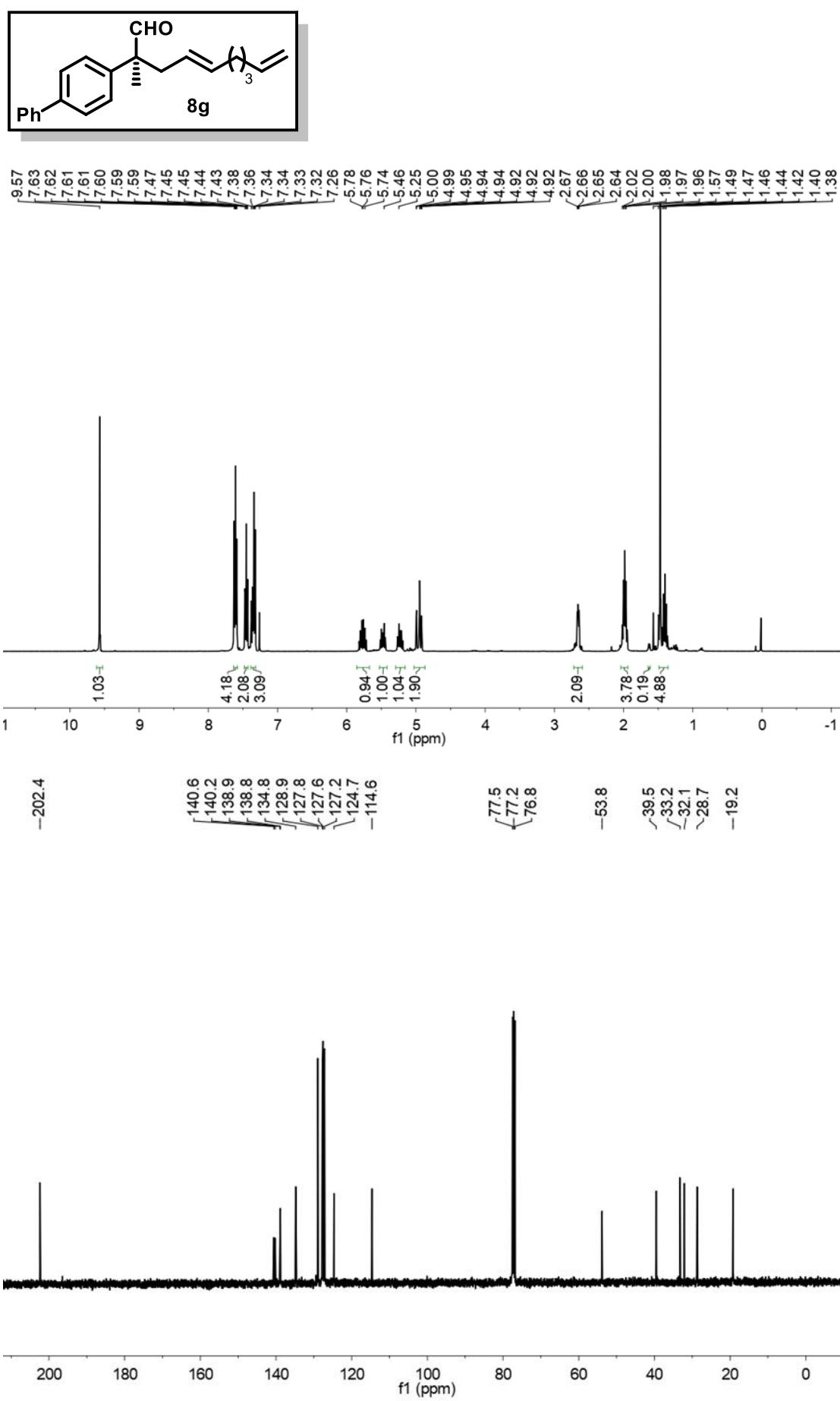
¹⁹F NMR

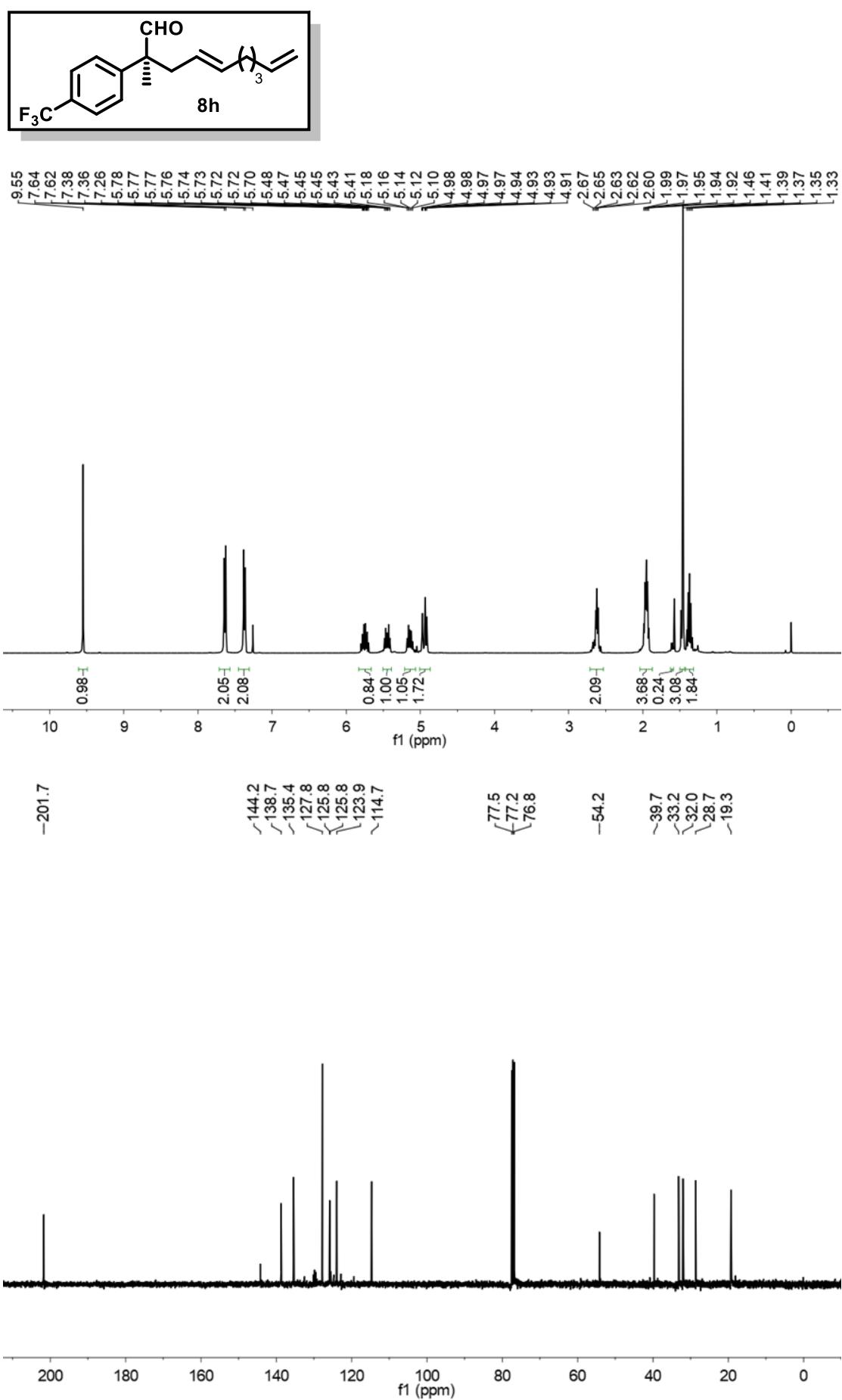




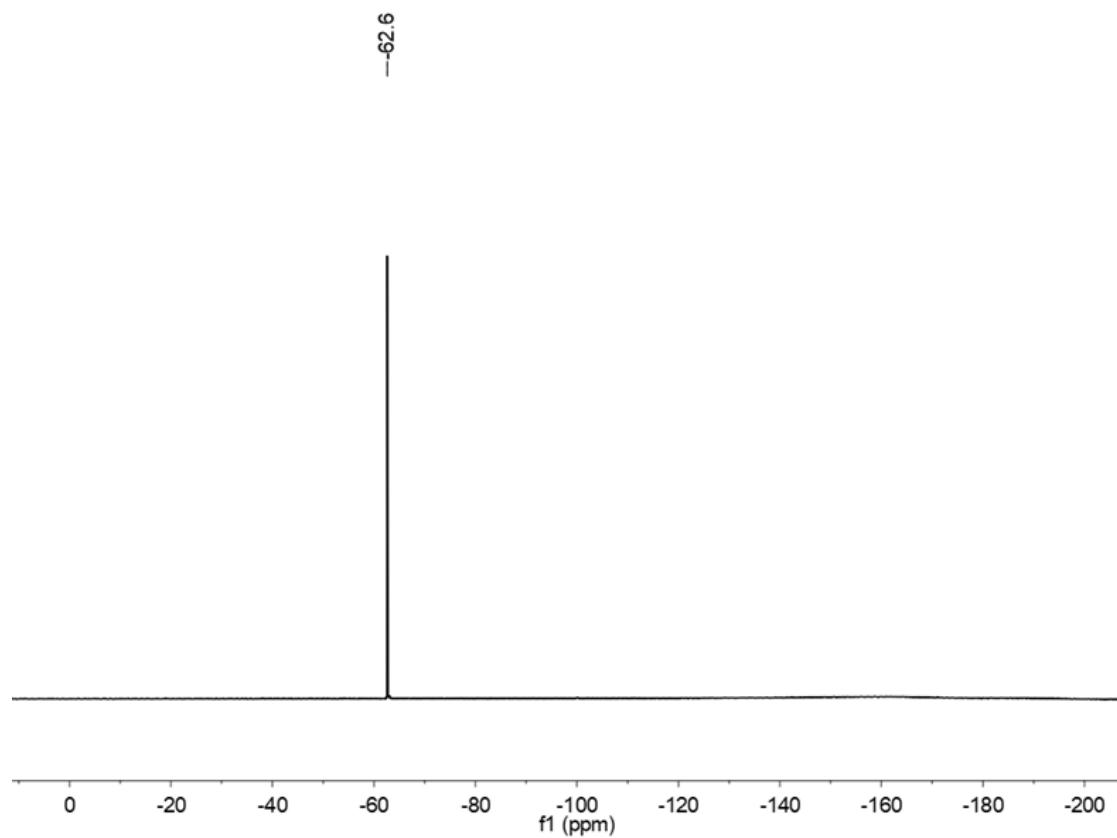


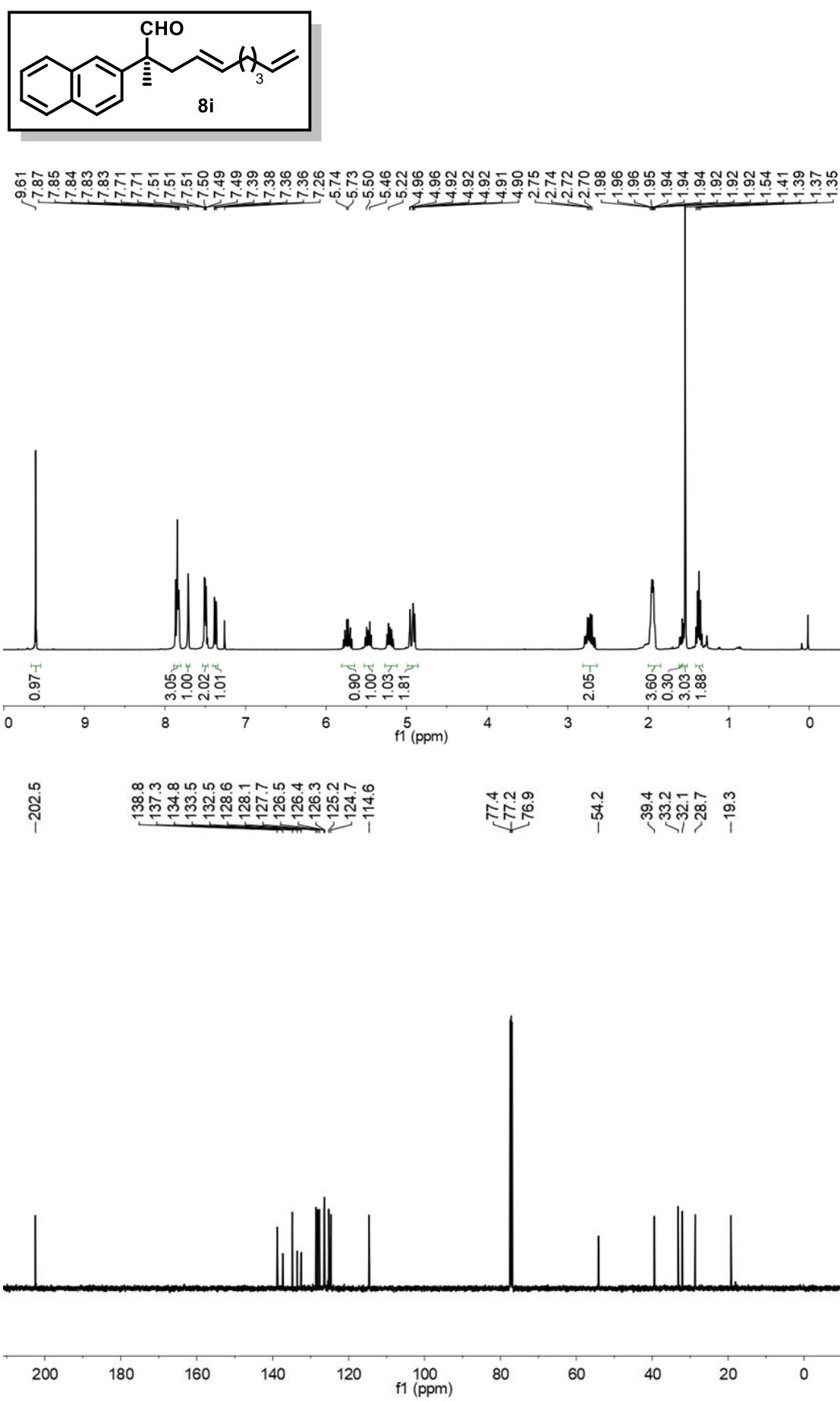


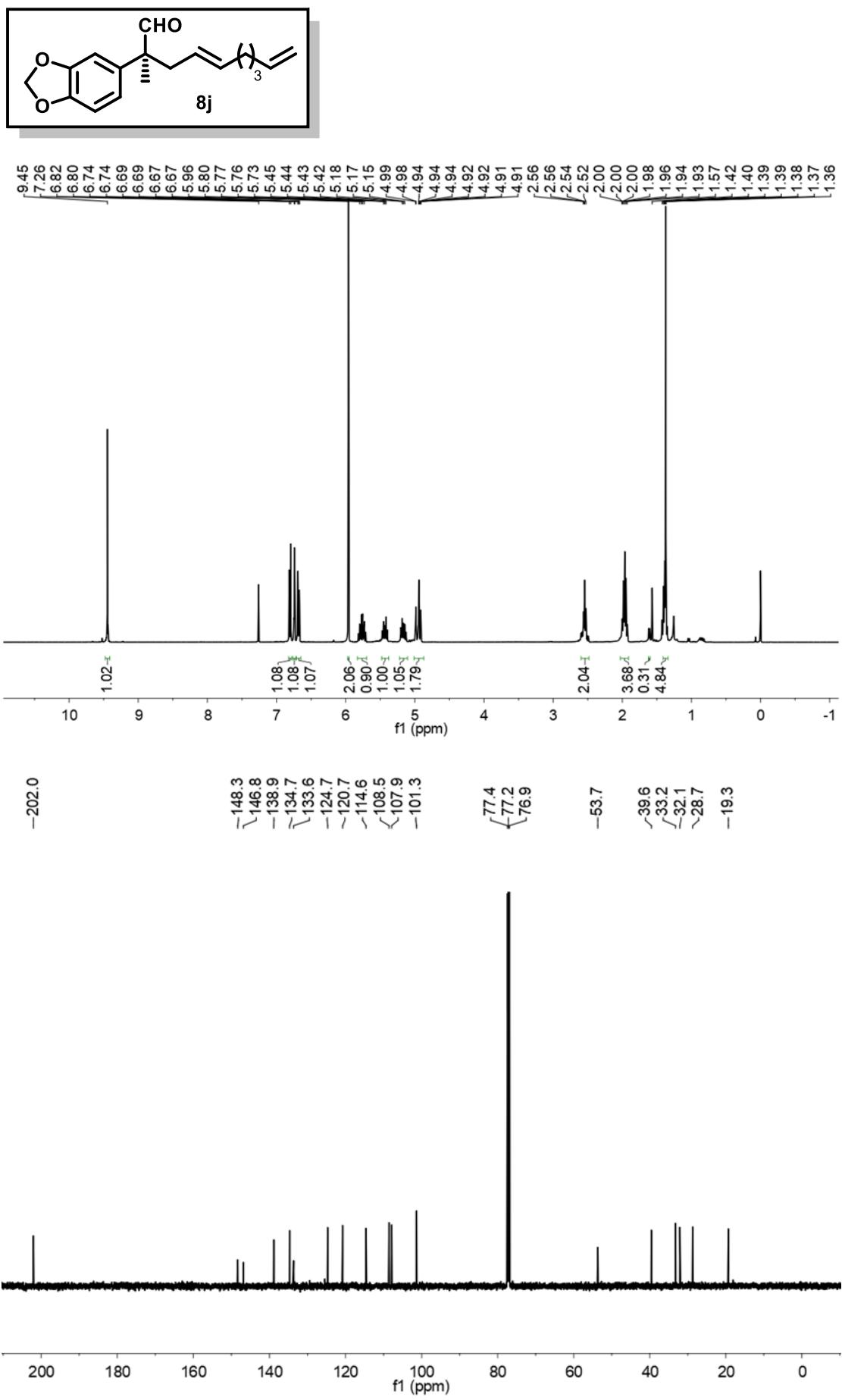


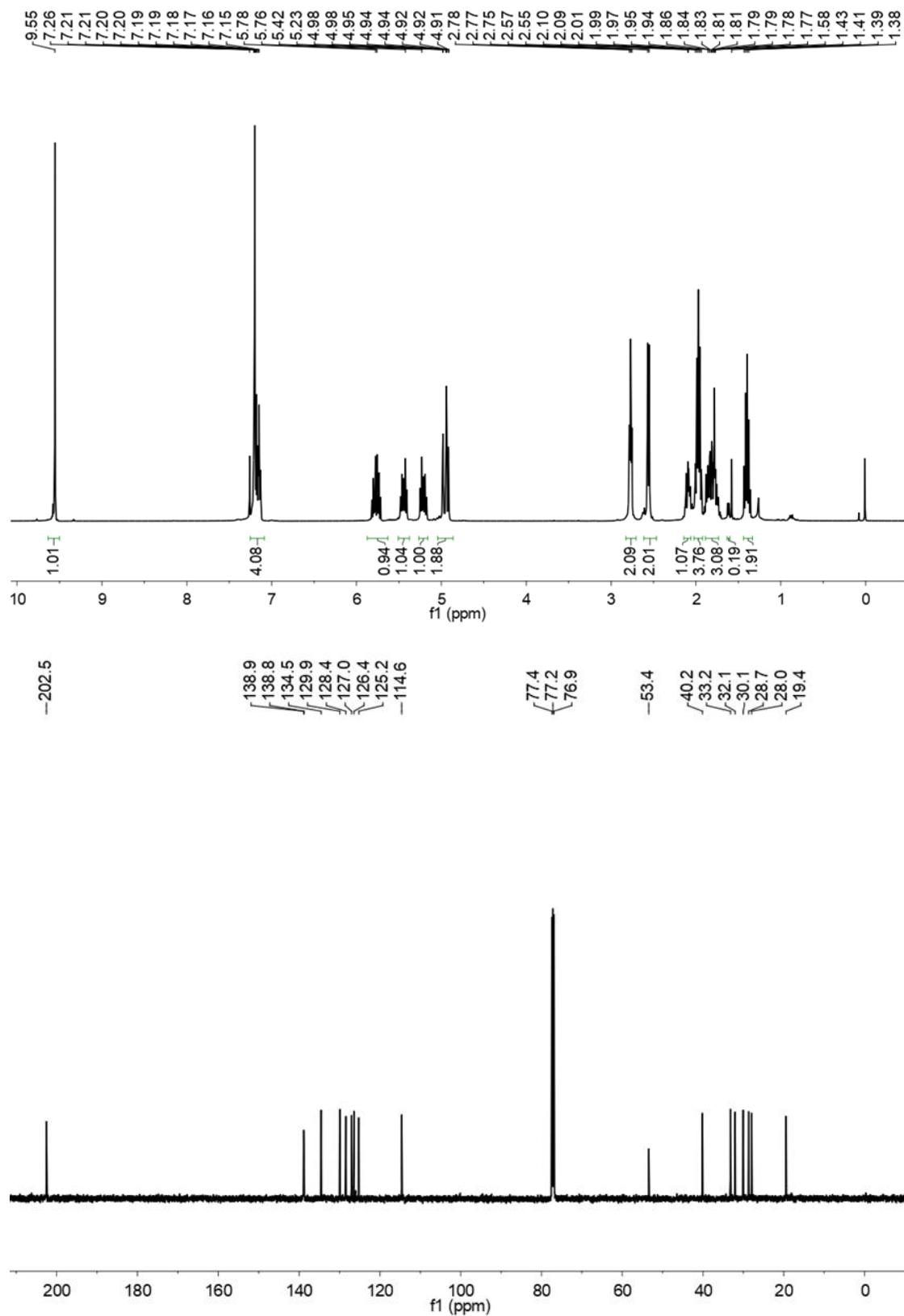
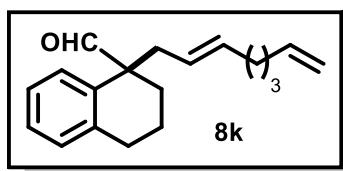


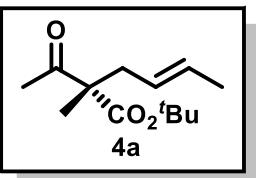
¹⁹F NMR





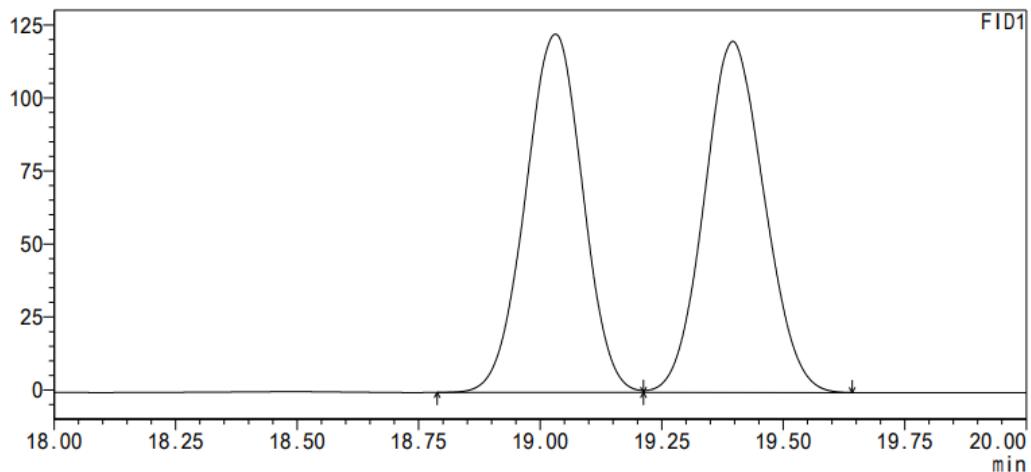






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mV



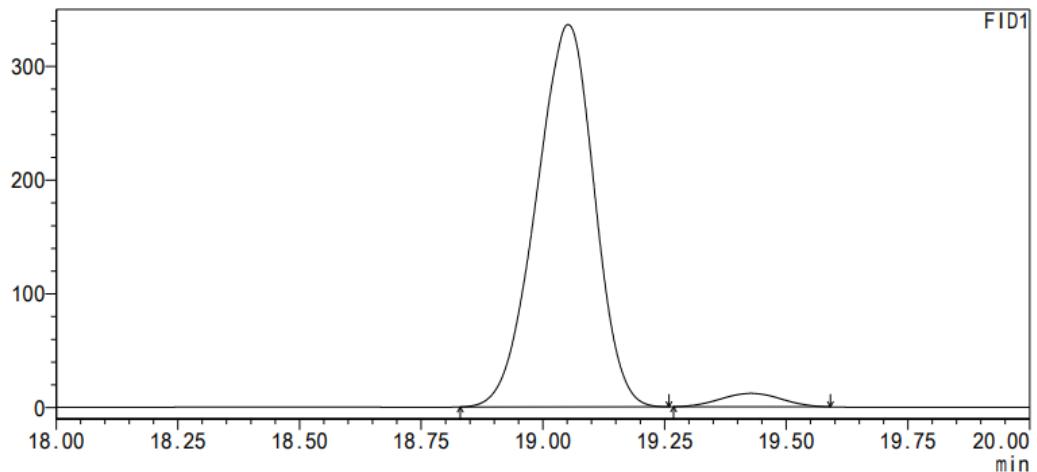
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FID1

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	19.031	122529	1007171	49.263
2	19.396	120192	1037322	50.737

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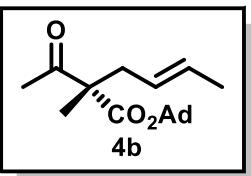
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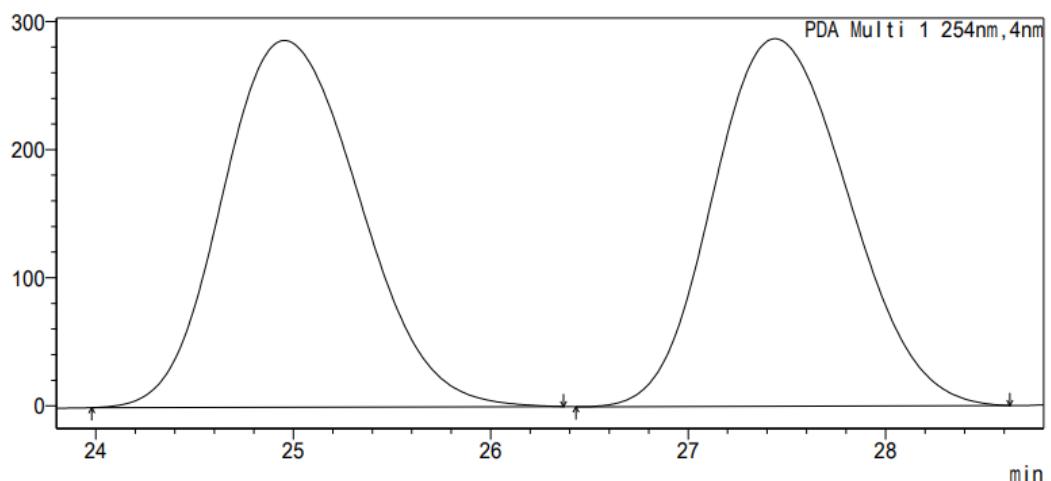
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Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	19.052	335999	2791593	96.446
2	19.427	11817	102869	3.554



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mAU



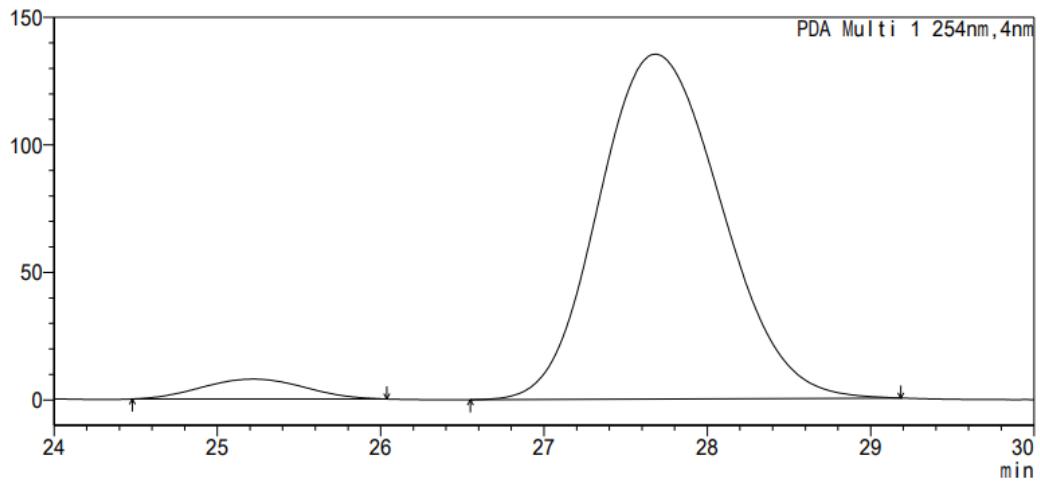
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PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	24.956	286210	13847124	50.280
2	27.440	286739	13693008	49.720

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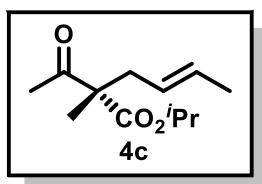
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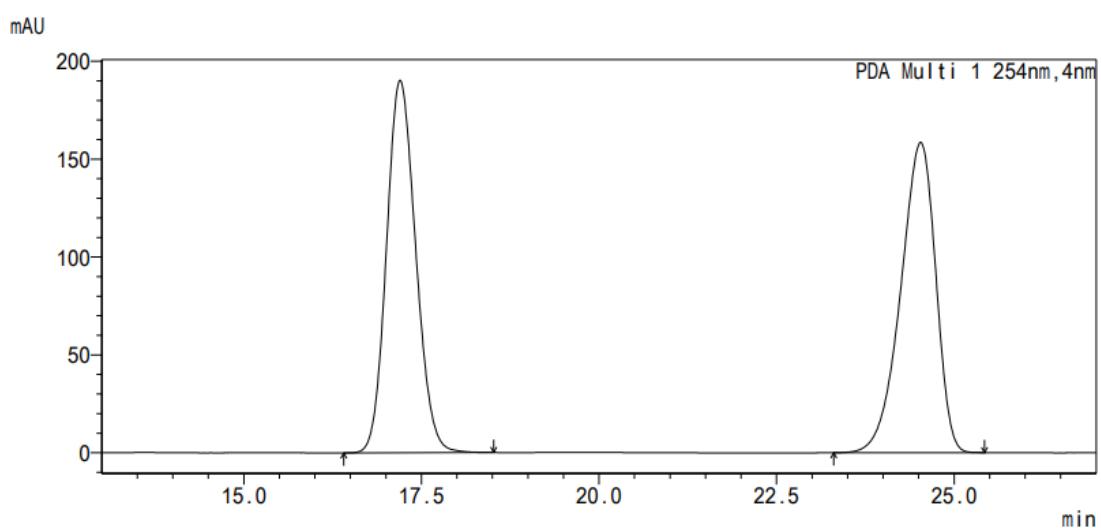
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PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	25.218	7790	342219	4.630
2	27.682	135215	7049402	95.370



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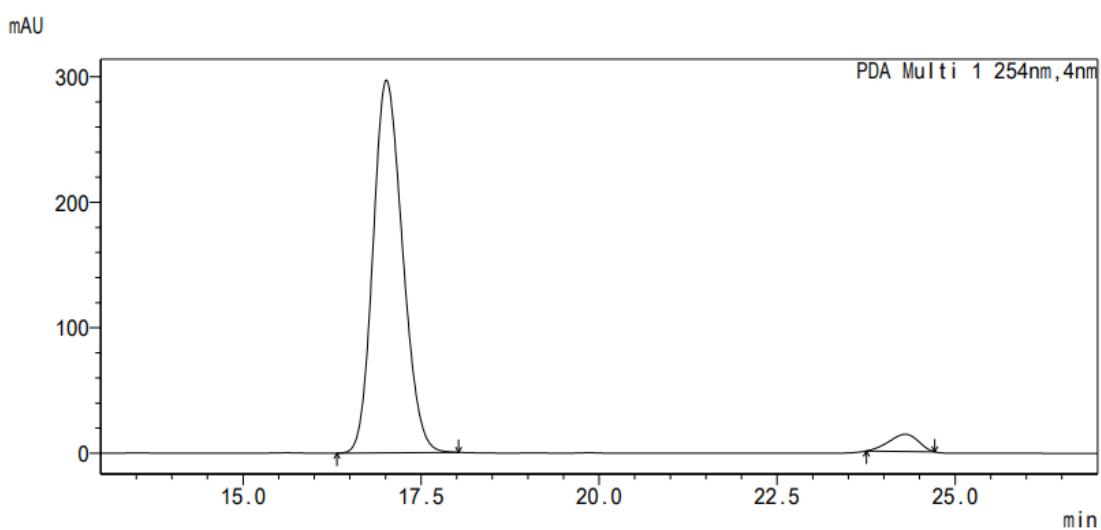


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.200	190206	5445183	50.037
2	24.529	158530	5437137	49.963

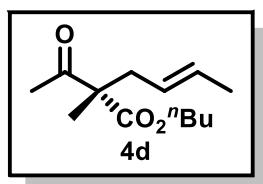
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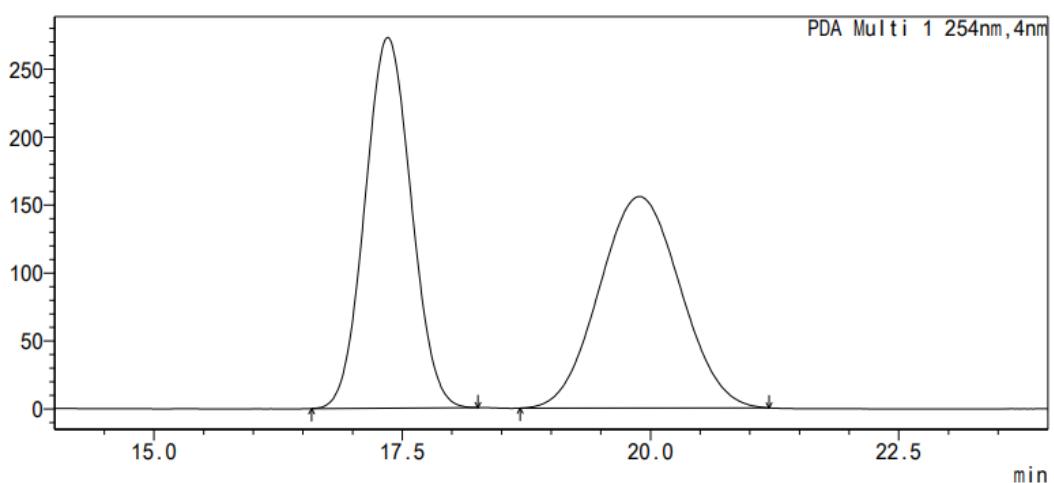
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1	17.013	297086	8553620	95.600
2	24.300	13740	393693	4.400



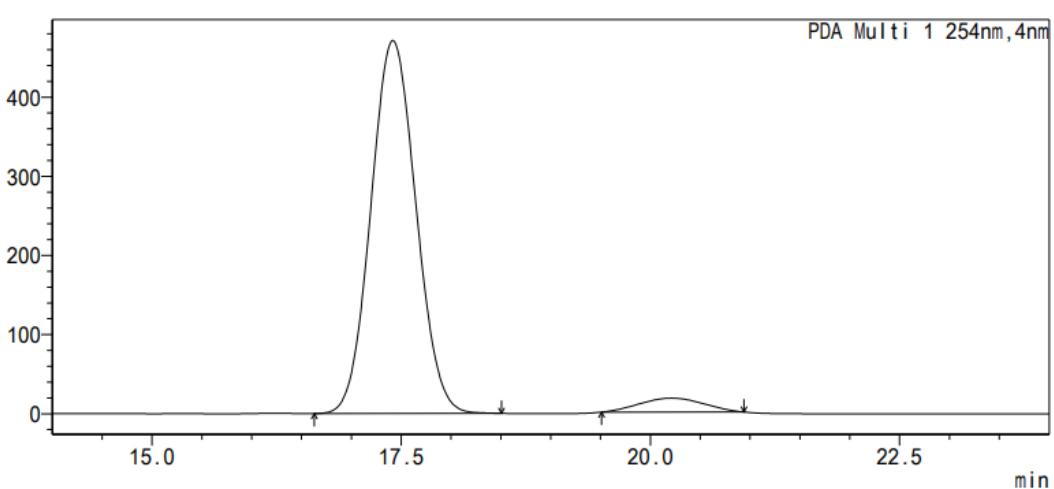
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mAU



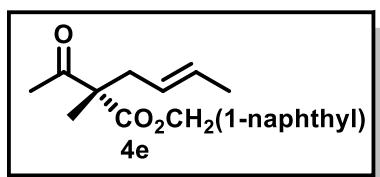
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PDA Ch1 254nm

mAU



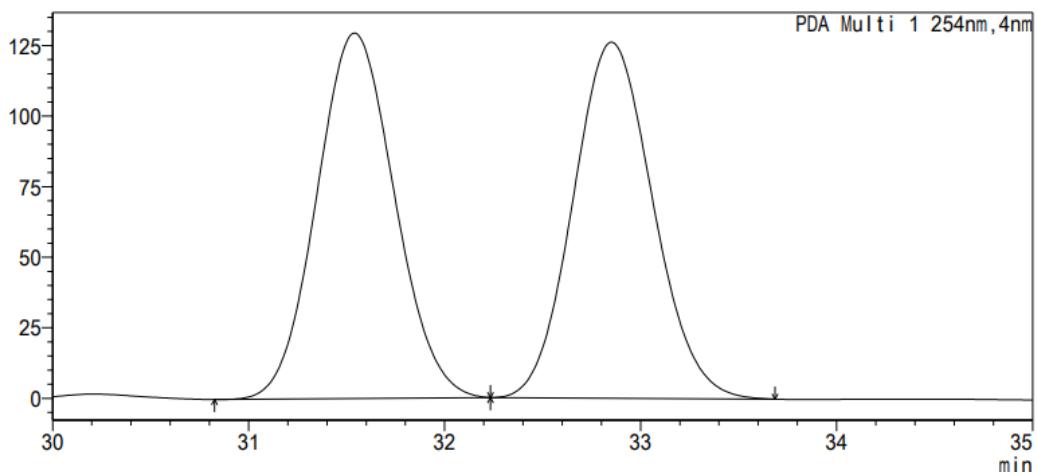
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PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.416	471354	14816779	94.944
2	20.213	17616	789032	5.056



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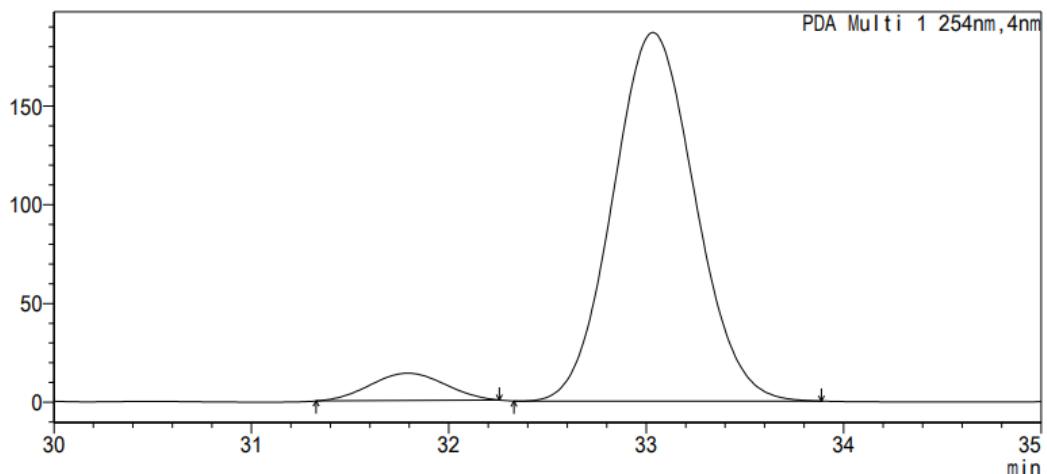
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PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	31.540	129446	3575287	49.977
2	32.852	126126	3578605	50.023

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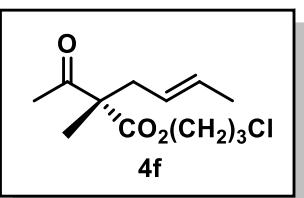
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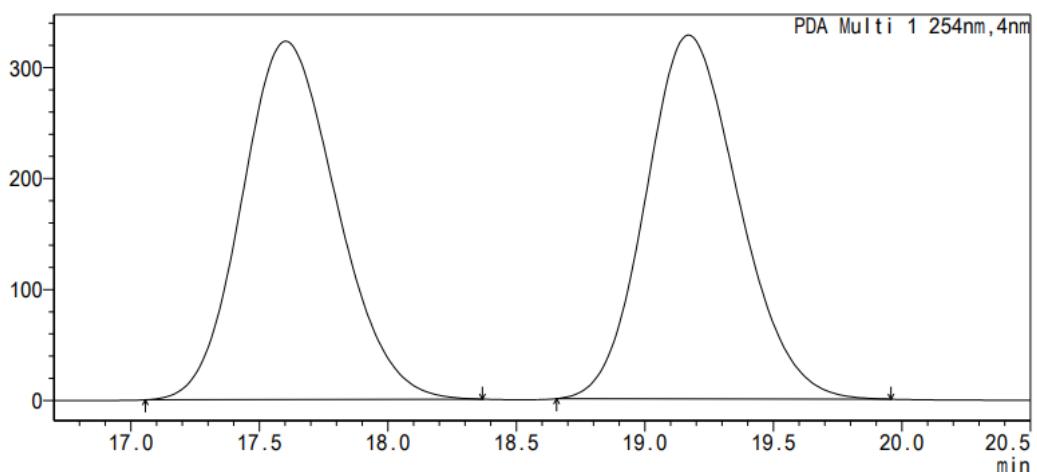
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PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	31.792	13855	366425	6.349
2	33.034	186636	5405114	93.651



mAU

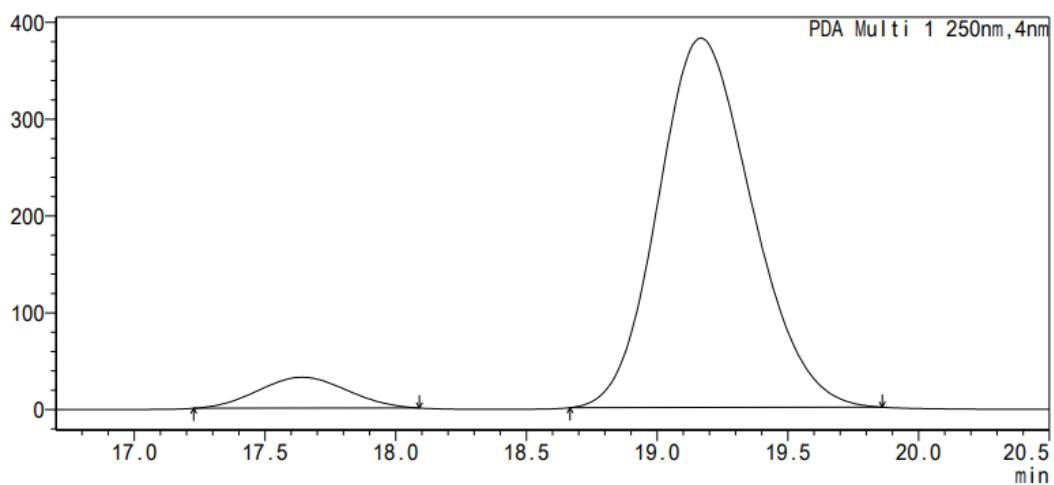


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.602	322888	8310536	50.090
2	19.169	327823	8280653	49.910

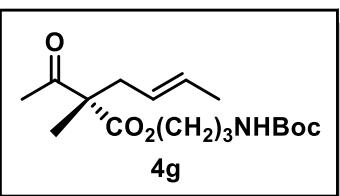
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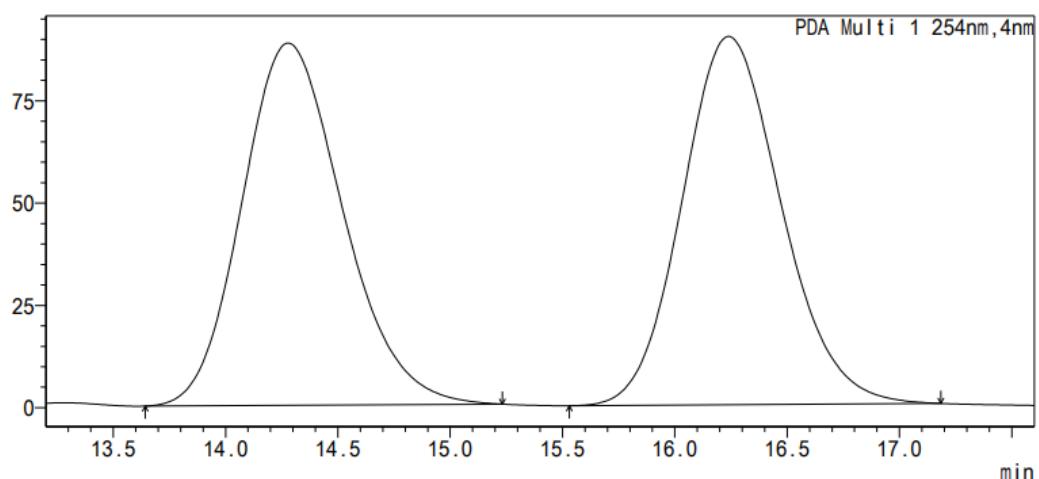
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PDA Ch1 250nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.642	31930	759527	7.351
2	19.167	381787	9572971	92.649



mAU

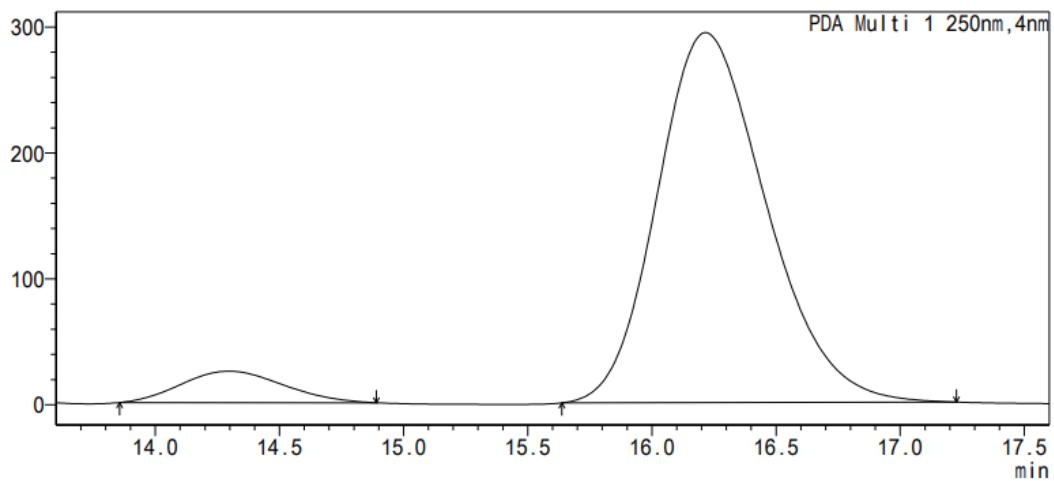


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PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	14.279	88530	2771223	50.007
2	16.240	90016	2770397	49.993

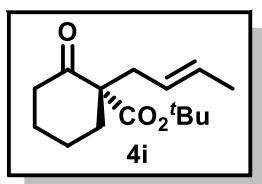
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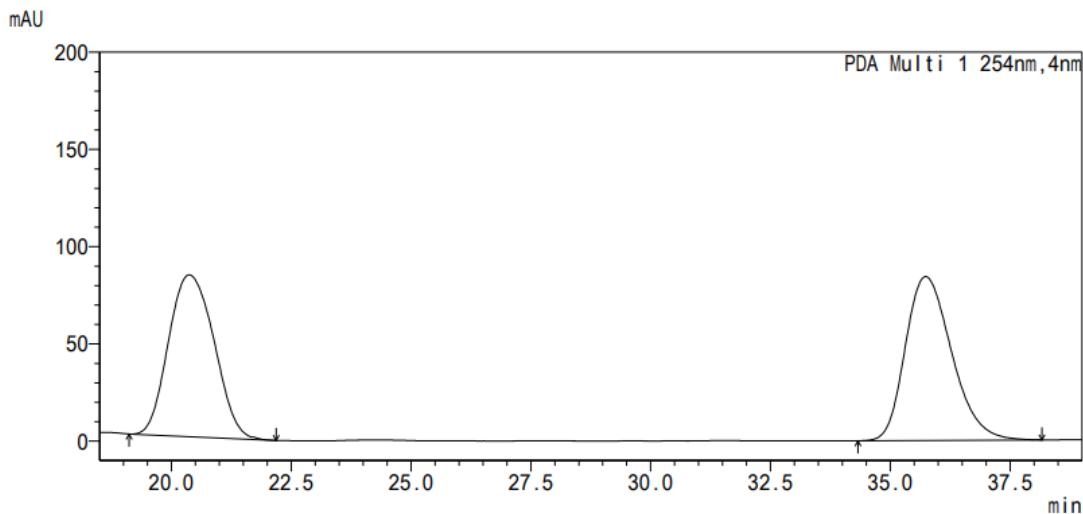
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PDA Ch1 250nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	14.296	24972	714427	7.368
2	16.216	293847	8982521	92.632



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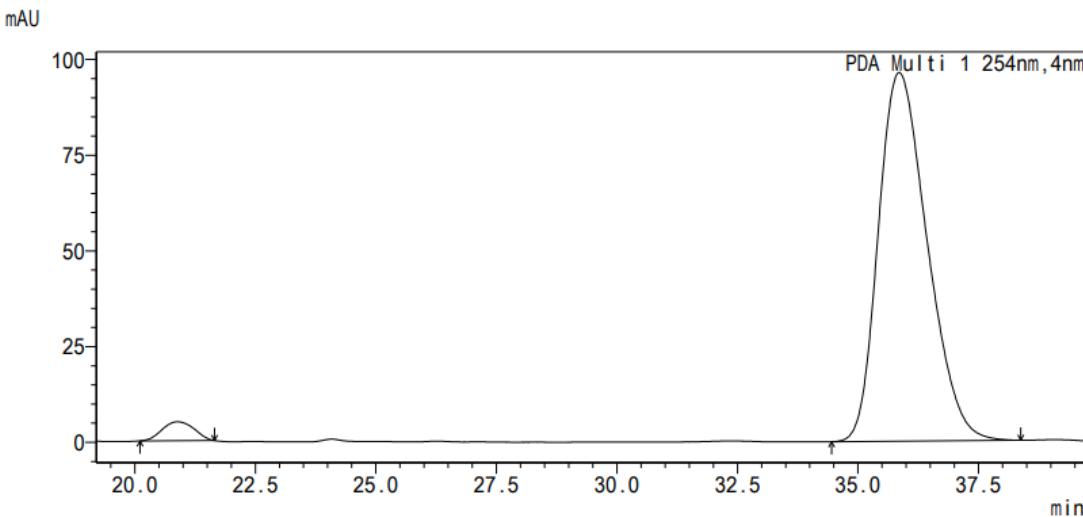


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PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	20.370	83198	5508966	49.268
2	35.737	84267	5672578	50.732

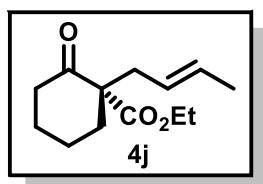
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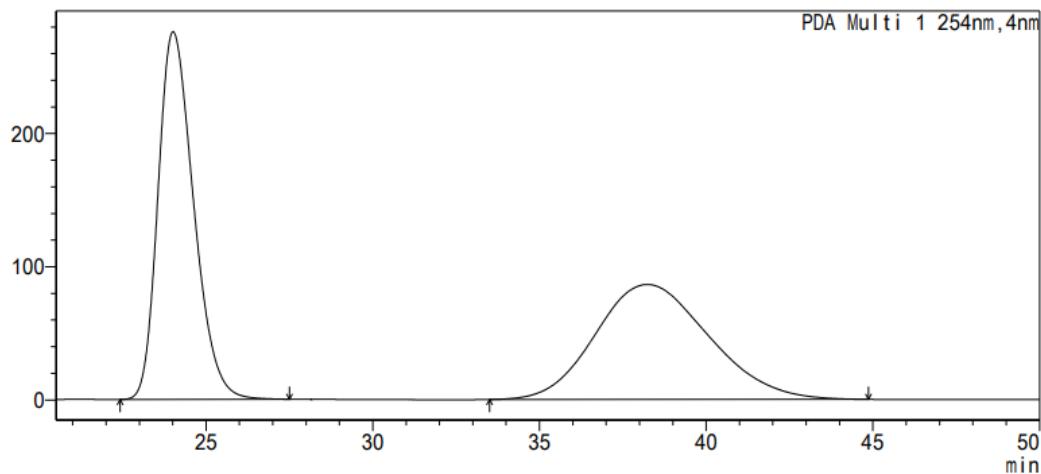
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	20.885	4946	227538	3.246
2	35.854	96308	6781416	96.754



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mAU



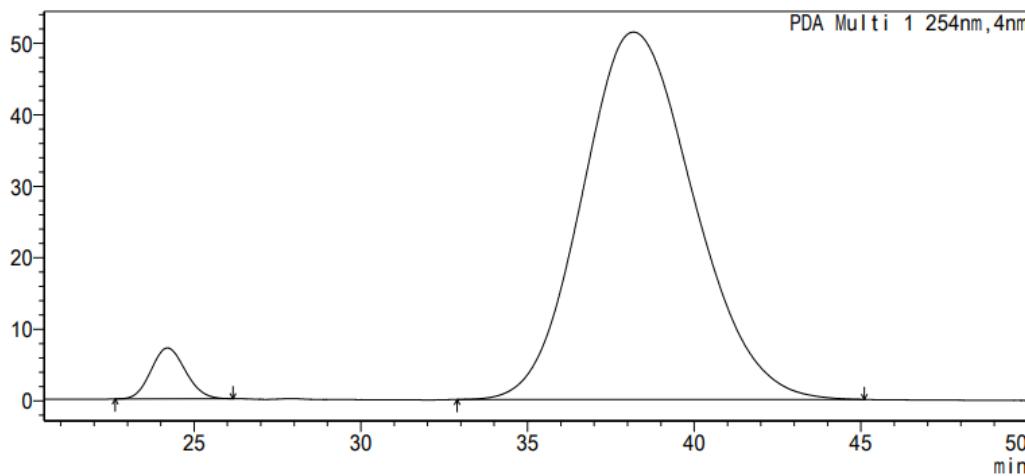
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Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	24.010	276192	20478833	50.020
2	38.240	86307	20462491	49.980

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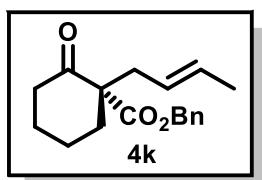
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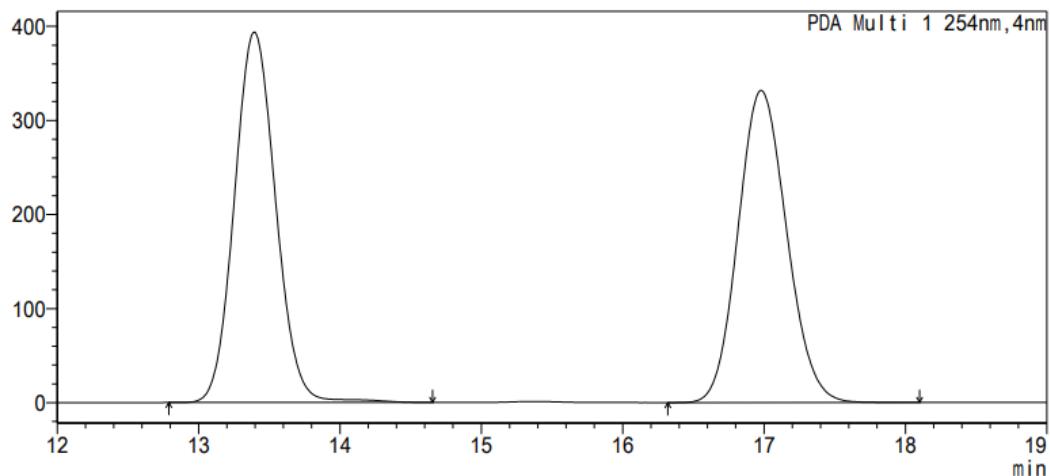
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	24.200	7123	510929	4.095
2	38.182	51414	11966226	95.905



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mAU



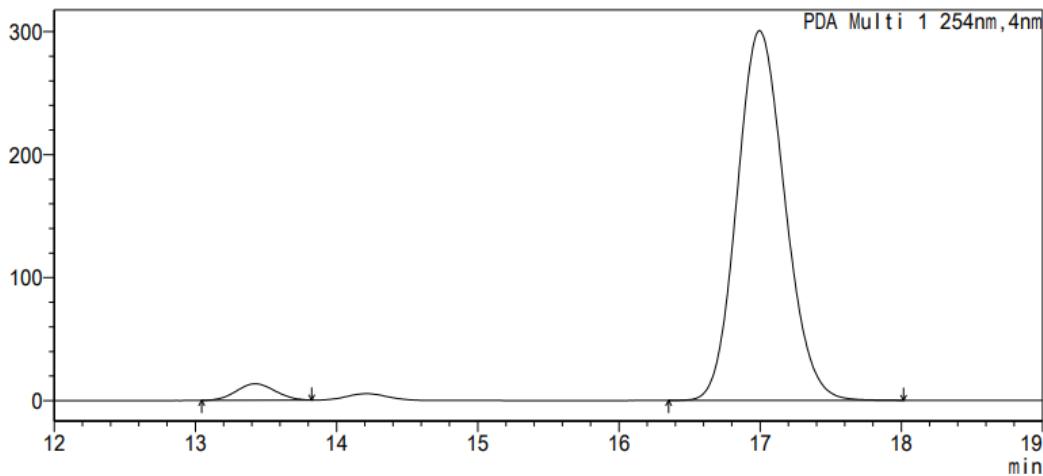
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PDA Ch1 254nm

Index	Time/min	Height /mAU	Quantity/Area	Area %/%
1	13.394	393728	7999835	50.226
2	16.979	331854	7927894	49.774

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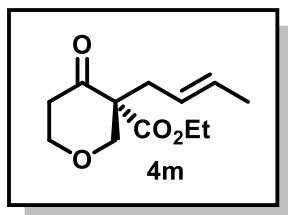
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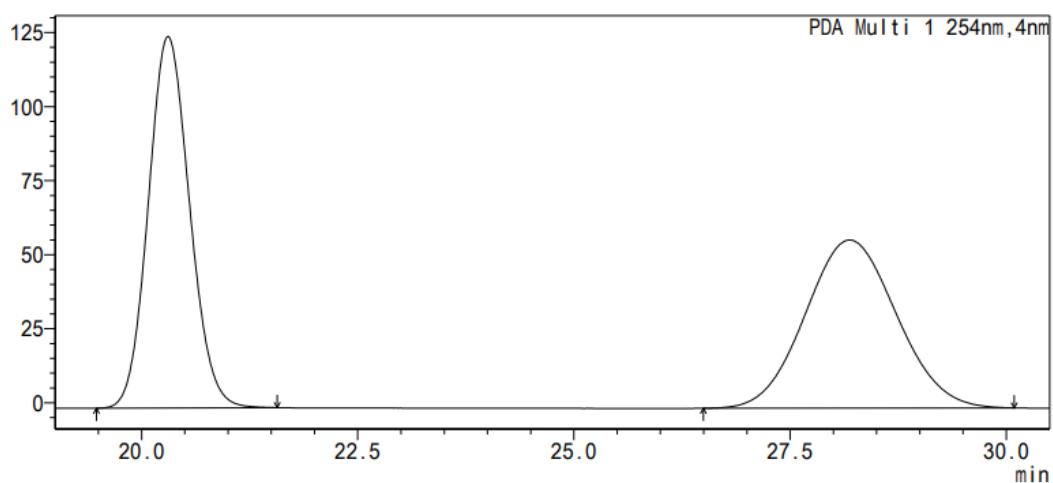
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PDA Ch1 254nm

Index	Time/min	Height /mAU	Quantity/Area	Area %/%
1	13.424	13341	254016	3.463
2	16.996	300656	7081836	96.537



mAU

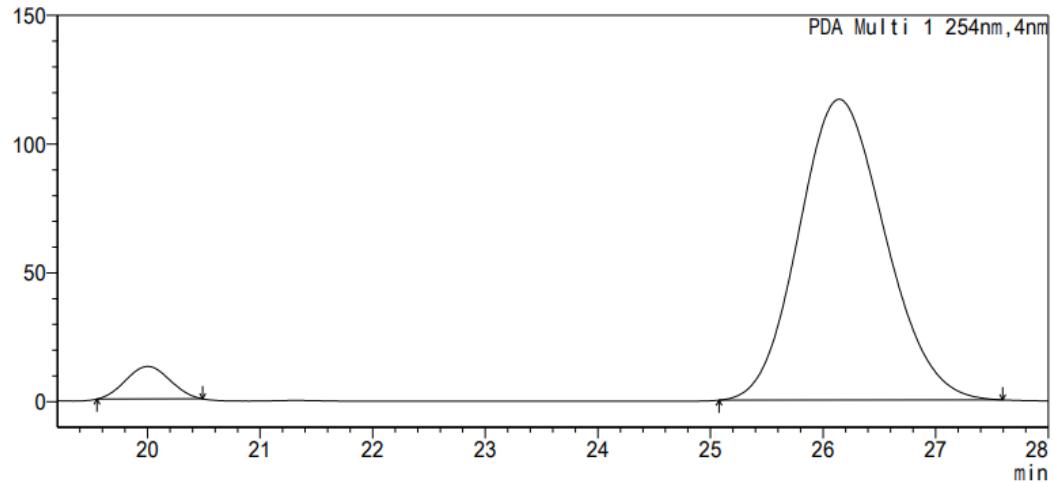


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PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	20.305	125436	4168433	49.991
2	28.189	56782	4169876	50.009

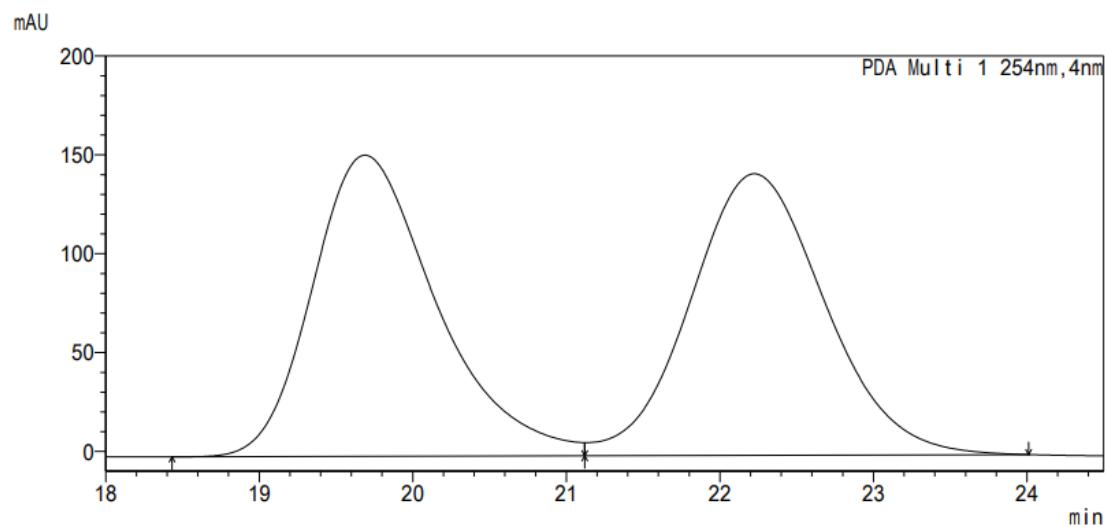
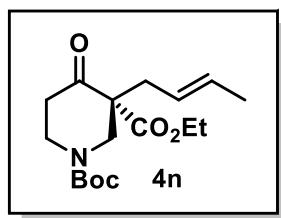
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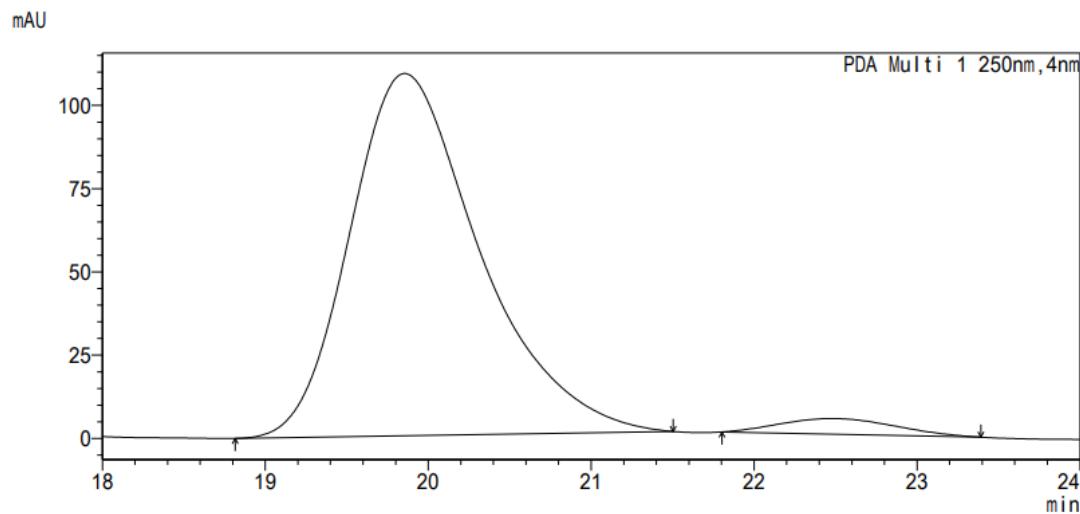
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1	20.001	12662	343760	5.233
2	26.144	116848	6224733	94.767



<Peak Results>

PDA Ch1 254nm

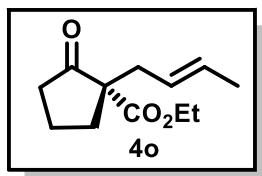
Index	Time/min	Height /mAU	Quantity/Area	Area %/%
1	19.689	152346	8559843	49.625
2	22.225	142400	8689097	50.375



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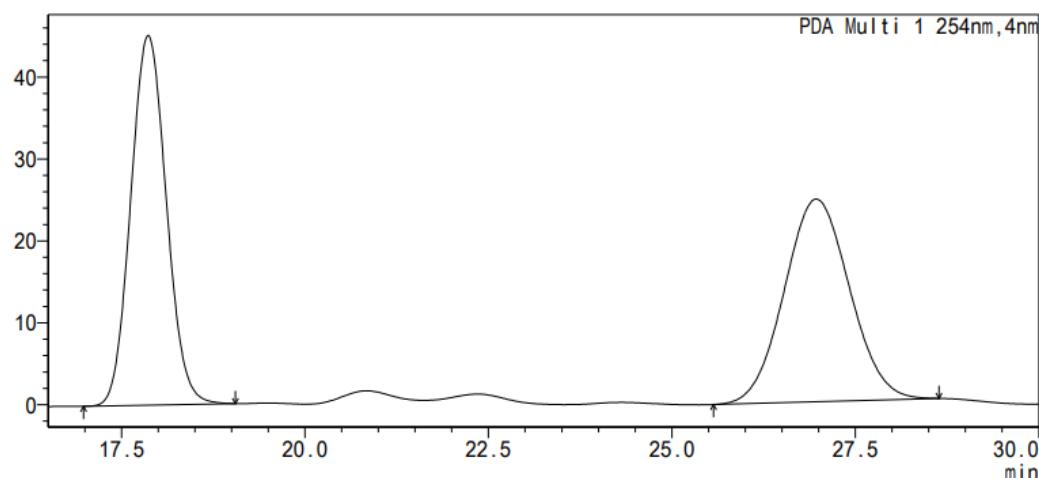
PDA Ch1 250nm

Index	Time/min	Height /mAU	Quantity/Area	Area %/%
1	19.855	108796	6017941	96.313
2	22.485	4695	230382	3.687



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mAU



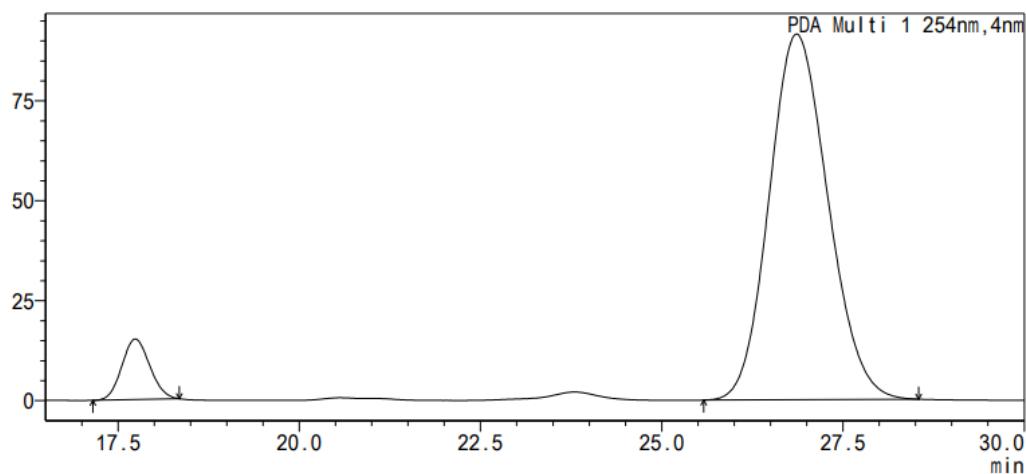
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PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.864	45147	1523474	49.883
2	26.965	24744	1530606	50.117

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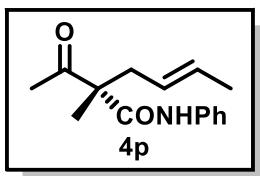
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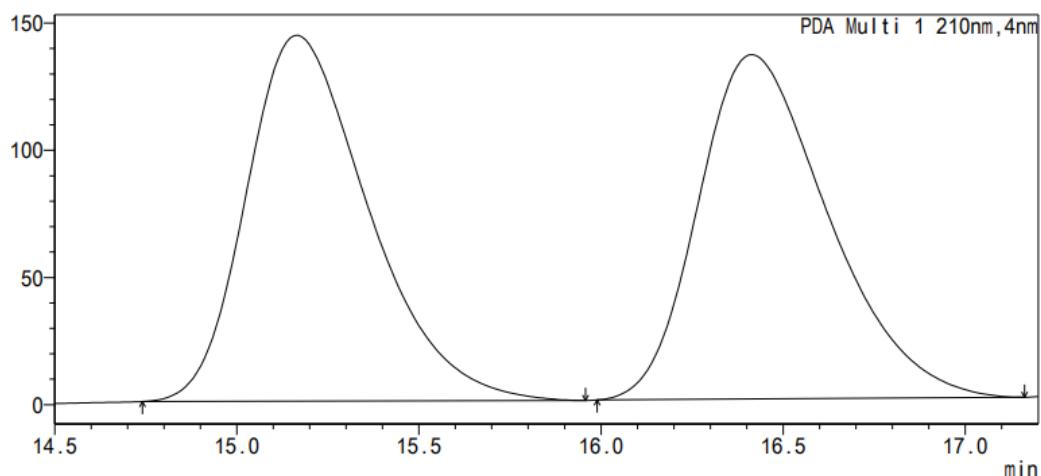
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.738	15162	406788	7.304
2	26.859	91495	5162297	92.696



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mAU



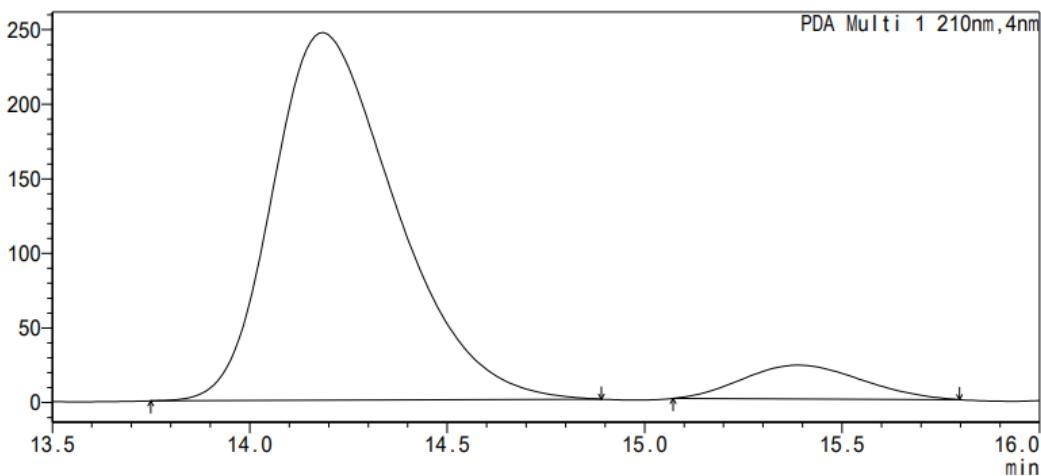
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PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	15.165	143843	3359200	49.974
2	16.414	135412	3362685	50.026

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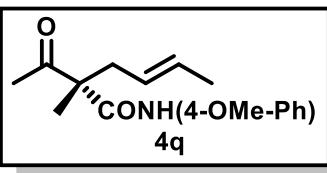
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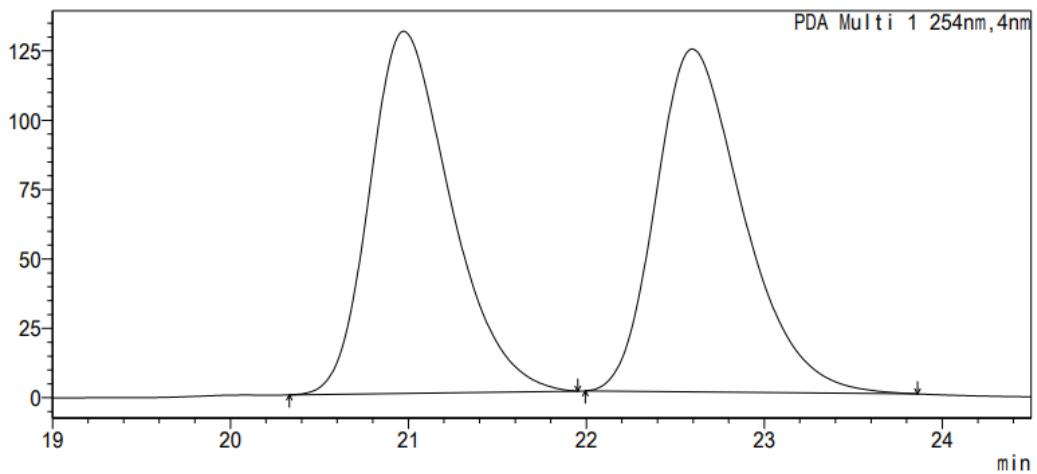
PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	14.184	246476	5345351	91.856
2	15.389	22658	473928	8.144



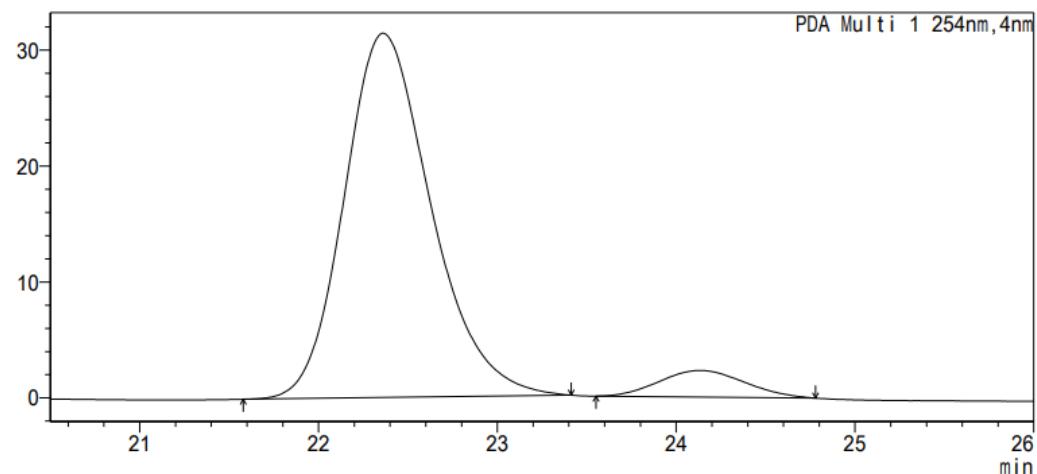
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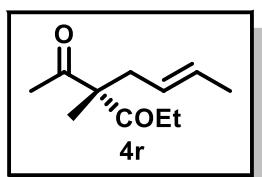
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PDA Ch1 254nm

mAU



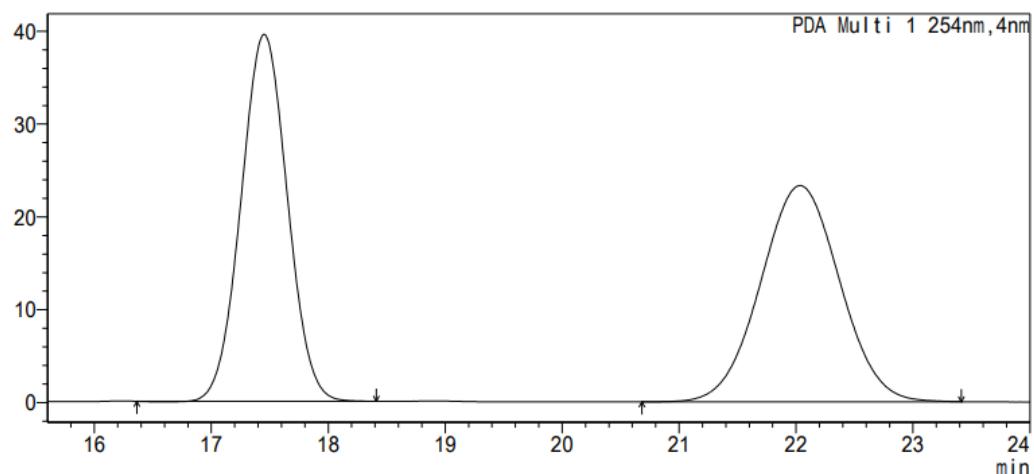
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PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	22.361	31432	1061051	93.303
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mAU



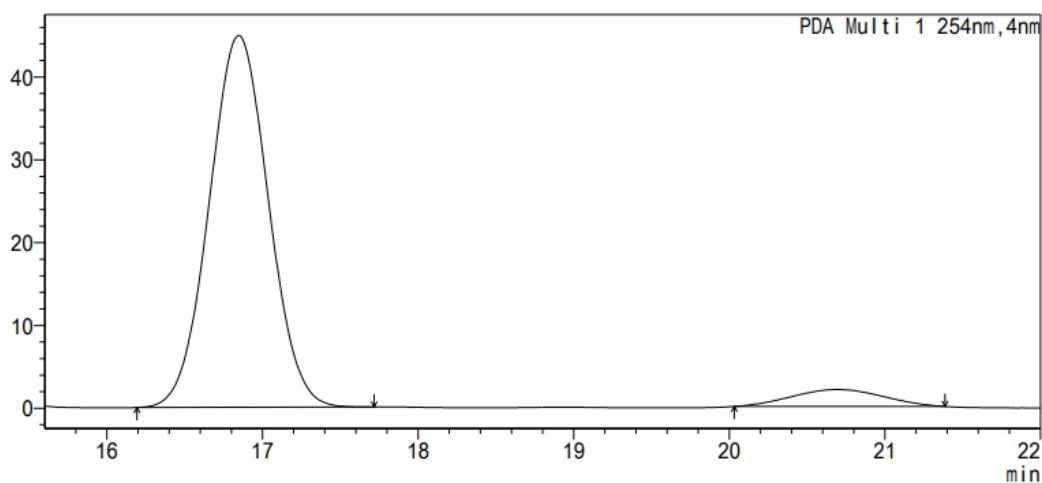
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PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.452	39539	1089389	49.836
2	22.034	23298	1096538	50.164

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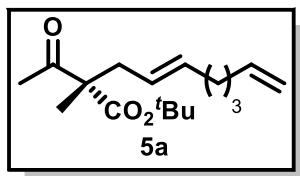
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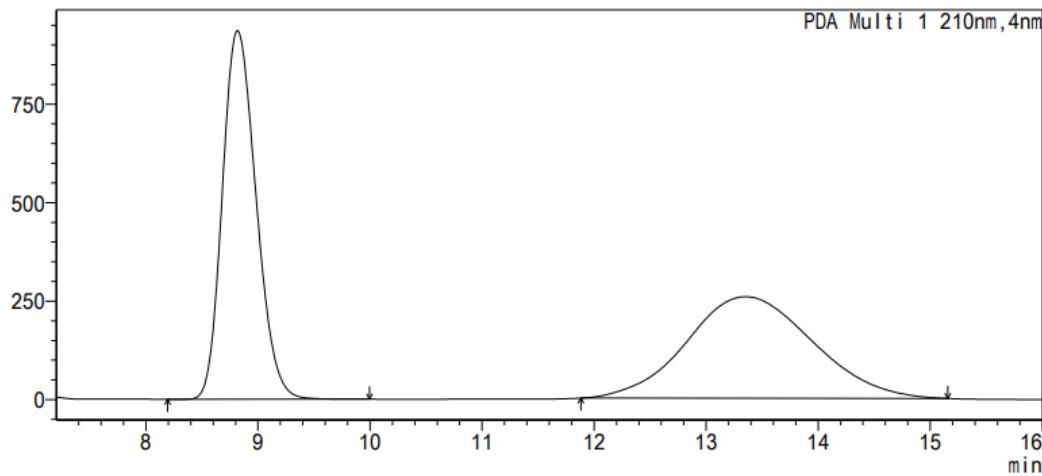
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	16.846	44911	1188284	93.423
2	20.692	2048	83654	6.577



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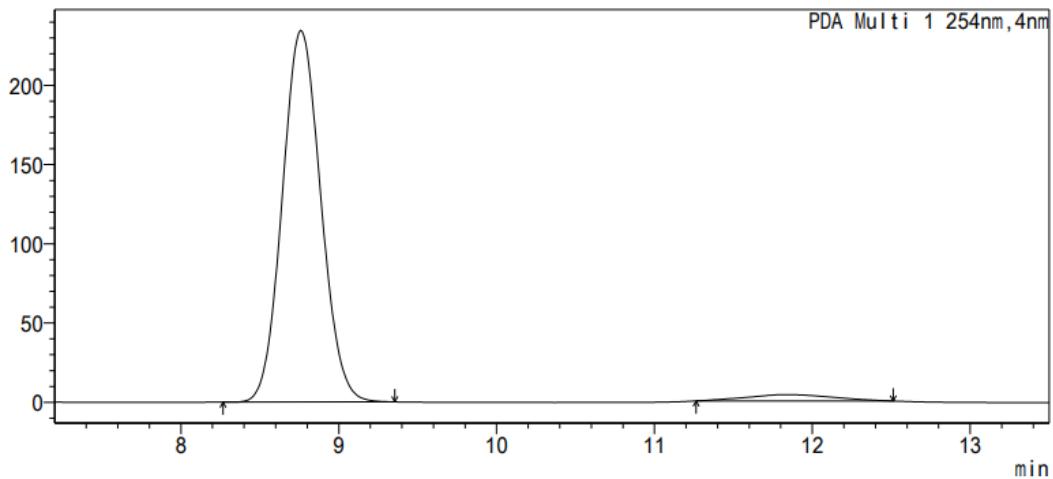
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PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
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2	13.352	257866	20188619	50.755

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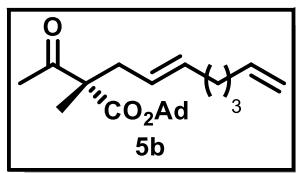
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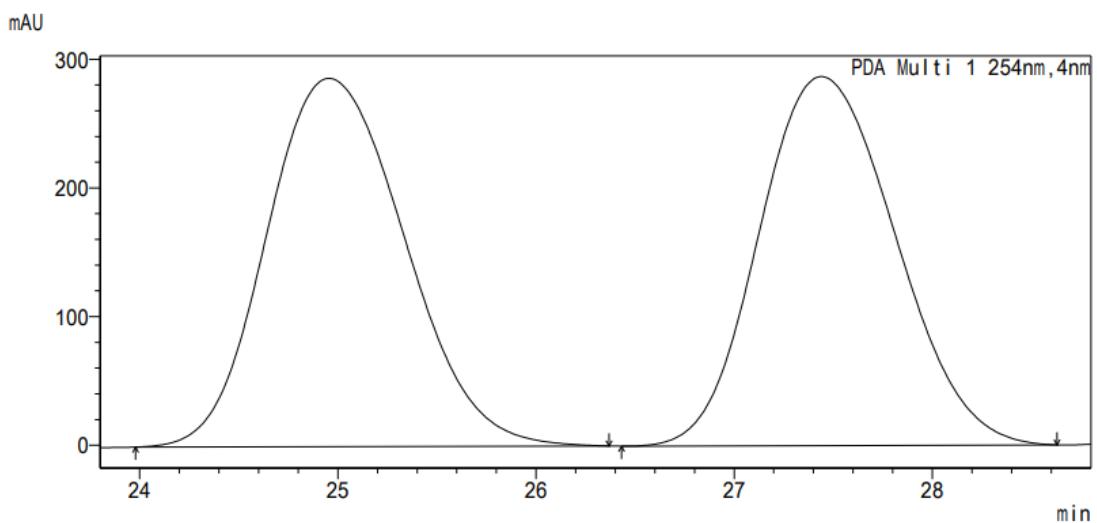
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PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
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2	11.842	4022	154405	3.733



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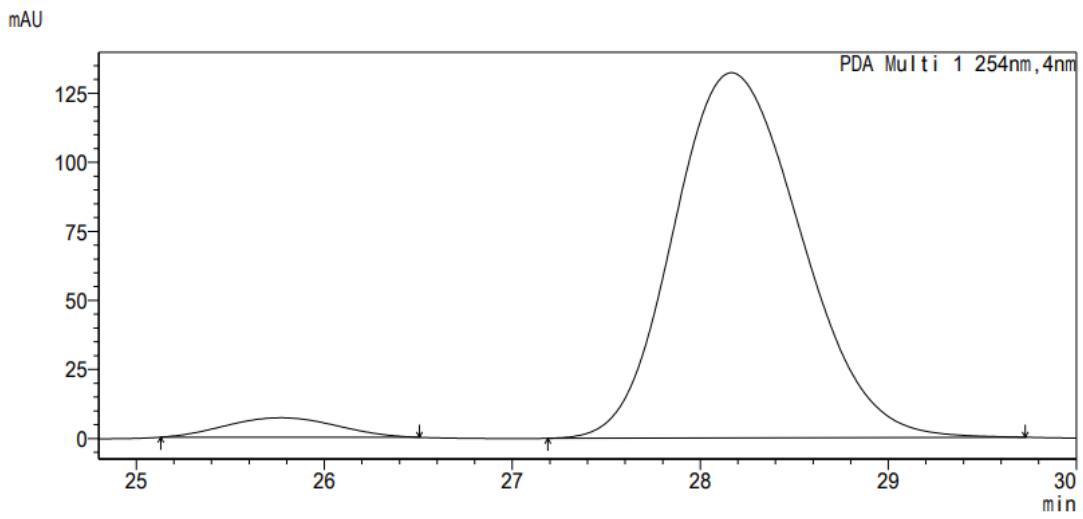


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	24.956	286210	13847124	50.280
2	27.440	286739	13693008	49.720

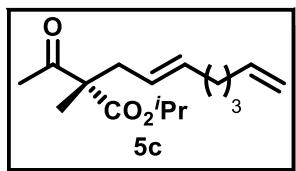
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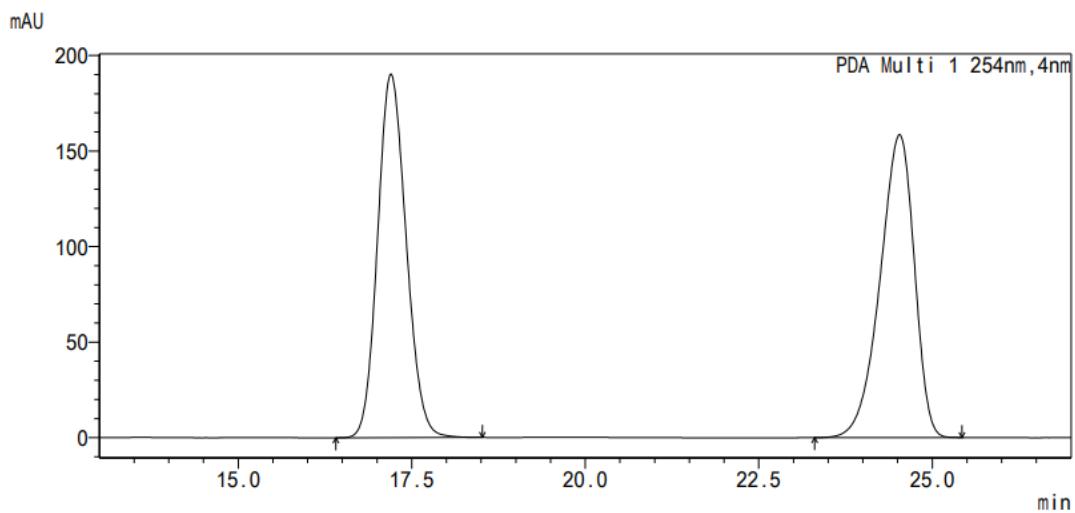
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	25.770	7054	289485	4.439
2	28.166	132207	6231882	95.561



<Chromatogram>

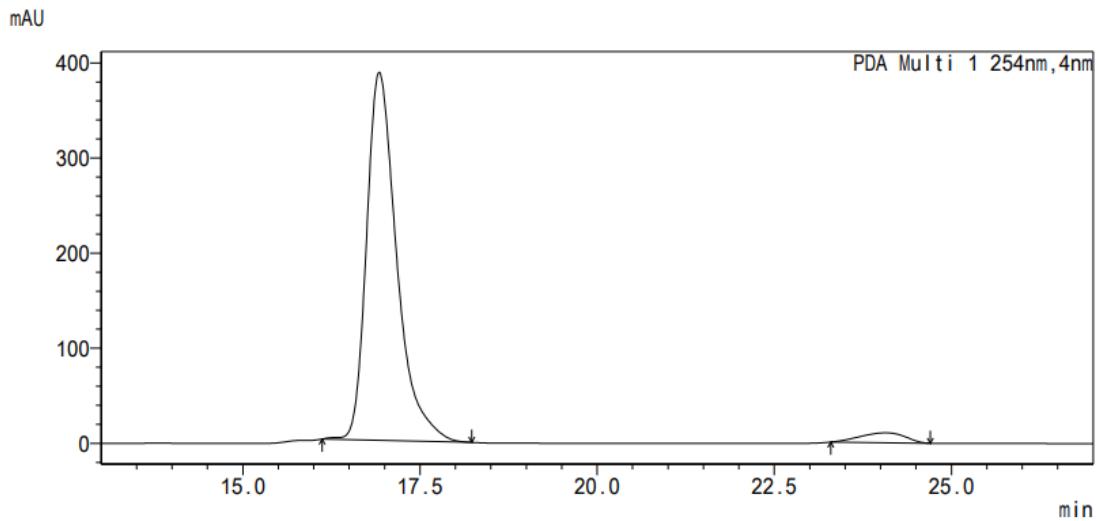


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.200	190206	5445183	50.037
2	24.529	158530	5437137	49.963

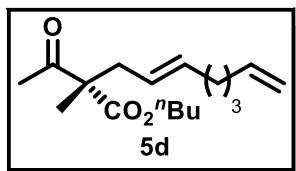
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<Peak Results>

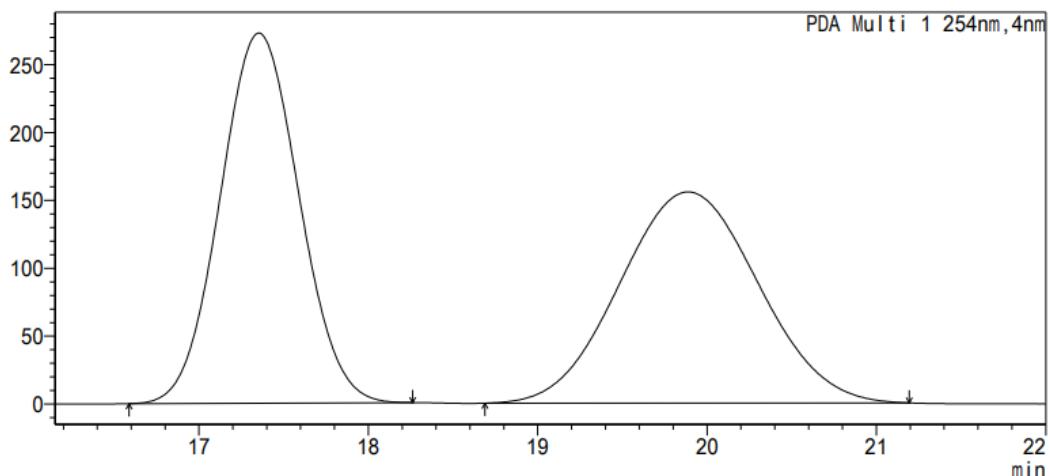
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	16.924	386808	11456609	96.134
2	24.069	10433	460671	3.866



<Chromatogram>

mAU



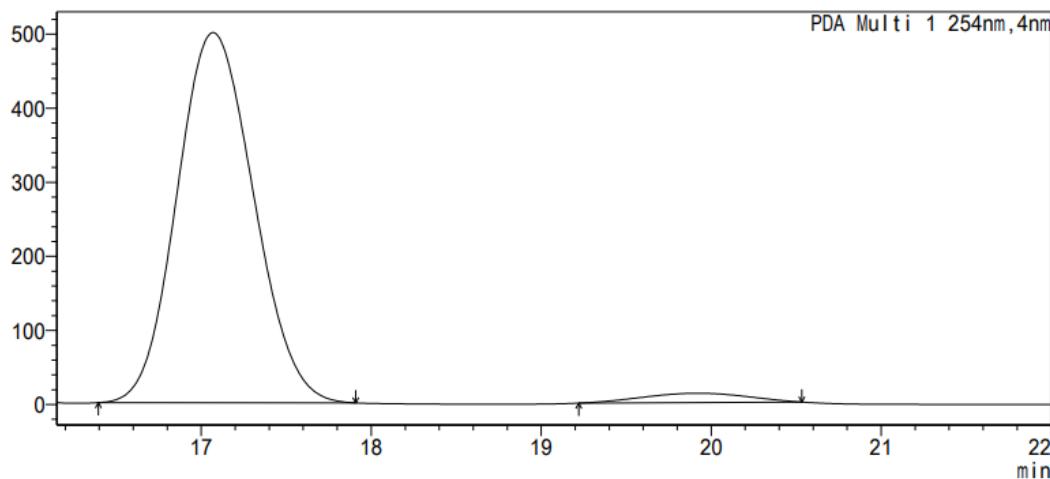
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.353	272751	8846459	50.009
2	19.888	155579	8843405	49.991

<Chromatogram>

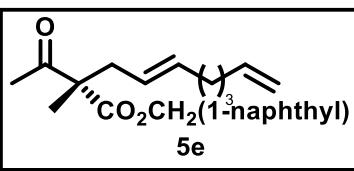
mAU



<Peak Results>

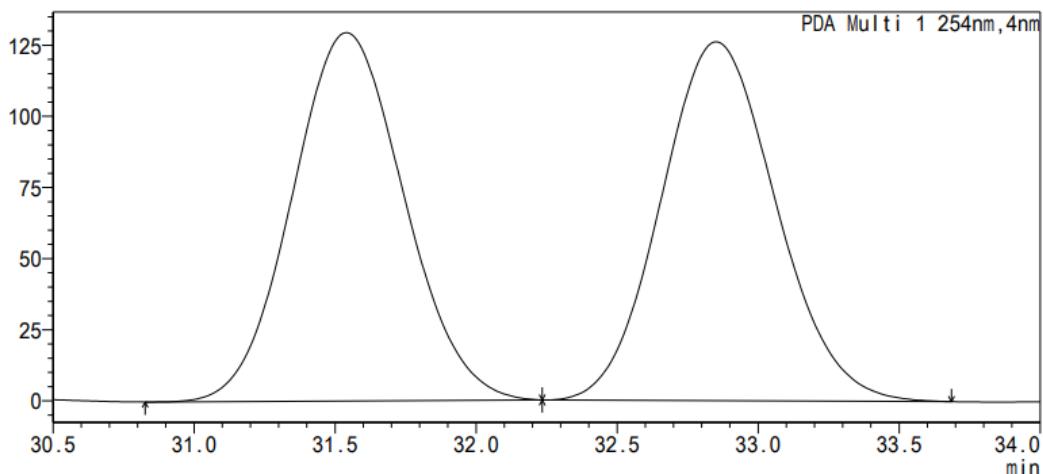
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.069	499725	15689065	96.682
2	19.920	12604	538384	3.318



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mAU



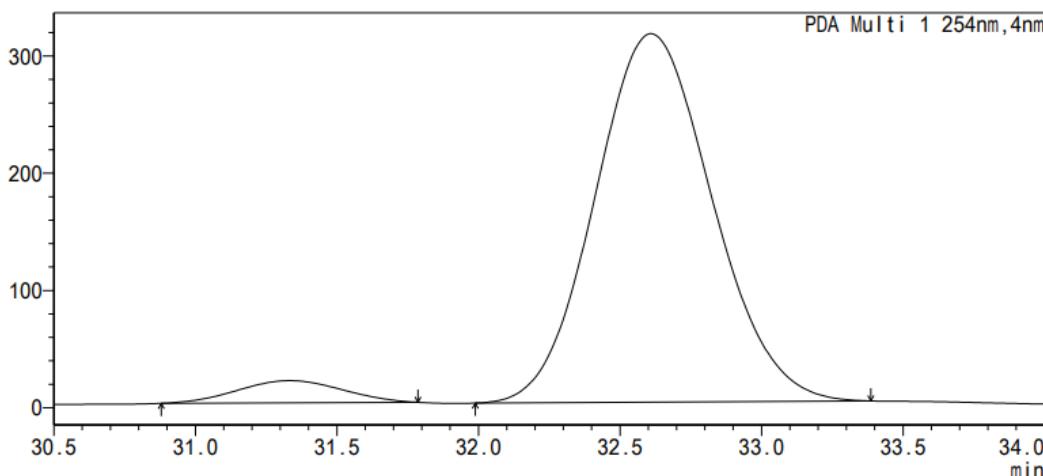
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	31.540	129446	3575287	49.977
2	32.852	126126	3578605	50.023

<Chromatogram>

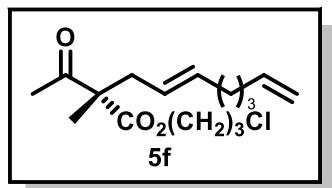
mAU



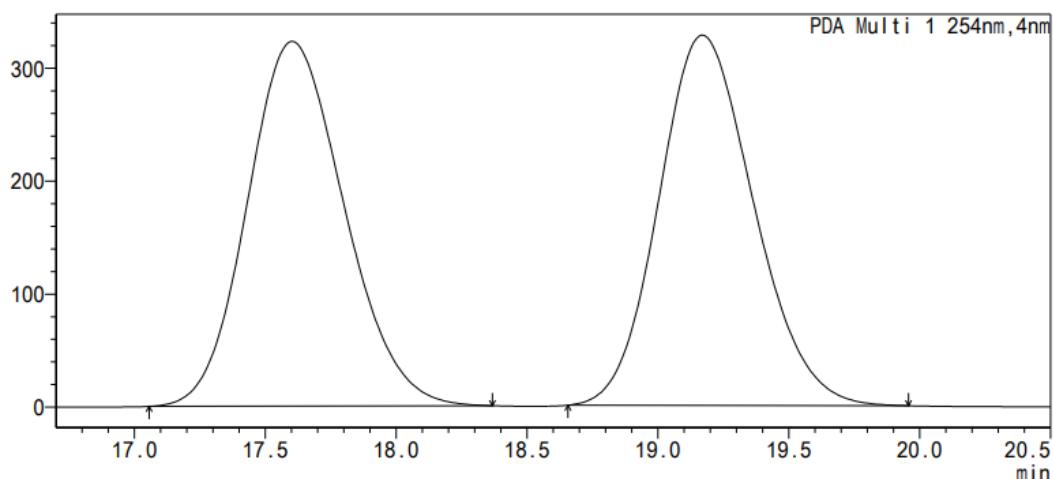
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	31.333	18936	488506	5.131
2	32.610	314416	9032301	94.869



mAU

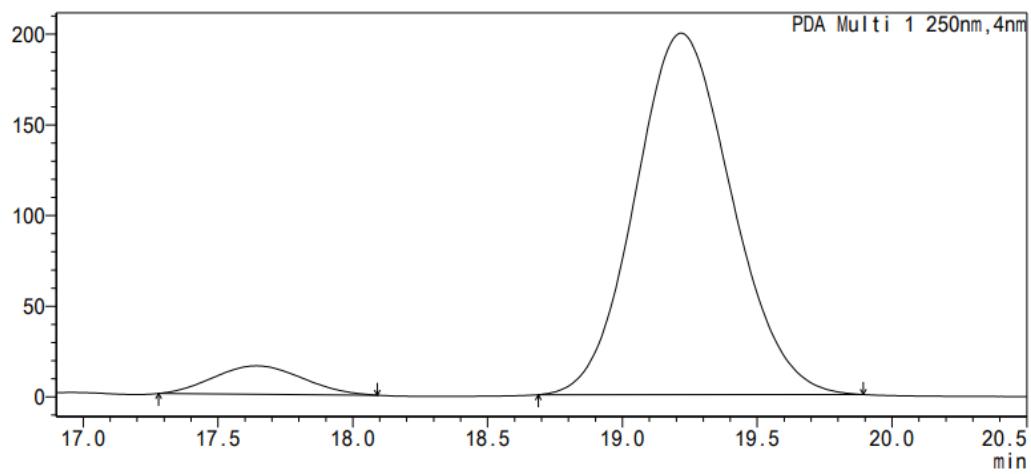


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.602	322888	8310536	50.090
2	19.169	327823	8280653	49.910

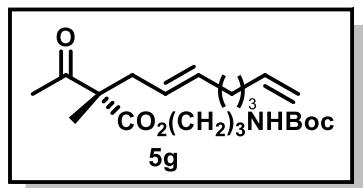
mAU



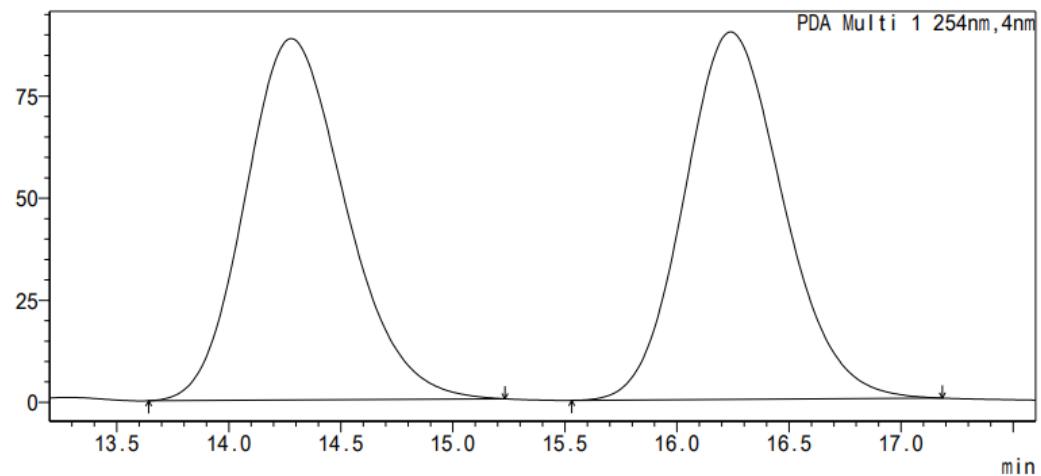
<Peak Results>

PDA Ch1 250nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.643	15663	359658	6.754
2	19.218	199320	4965745	93.246



mAU

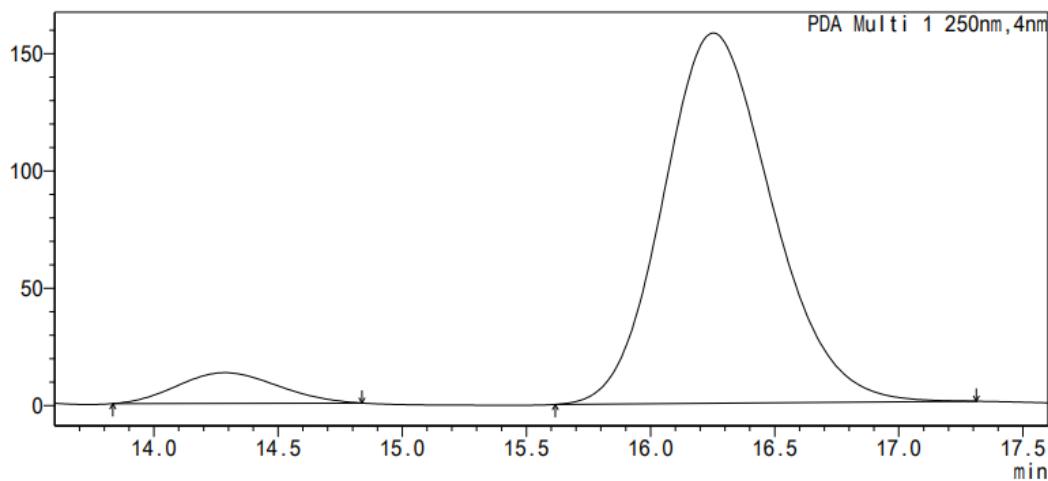


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	14.279	88530	2771223	50.007
2	16.240	90016	2770397	49.993

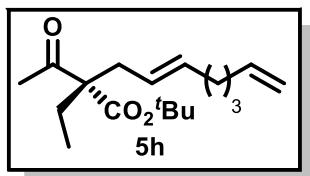
mAU



<Peak Results>

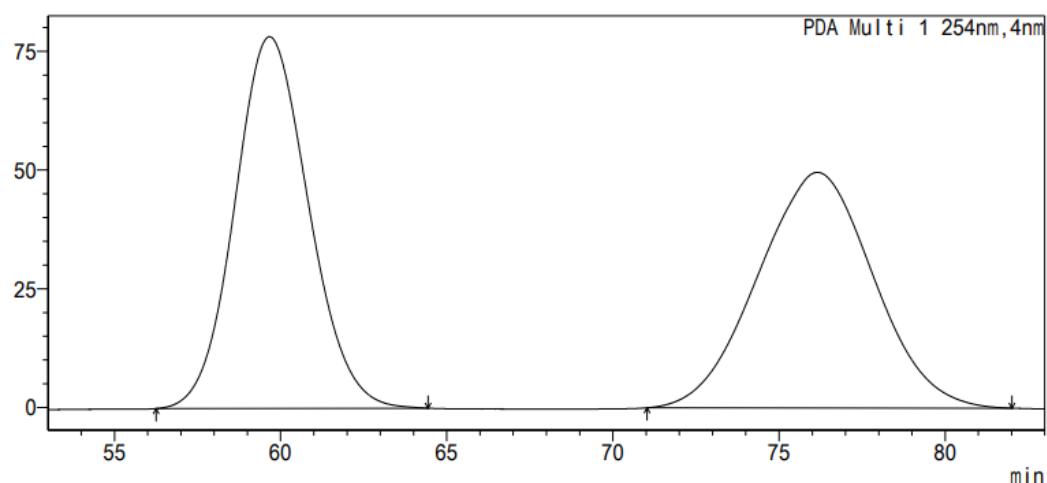
PDA Ch1 250nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	14.287	13053	367501	7.096
2	16.253	157761	4811210	92.904



<Chromatogram>

mAU



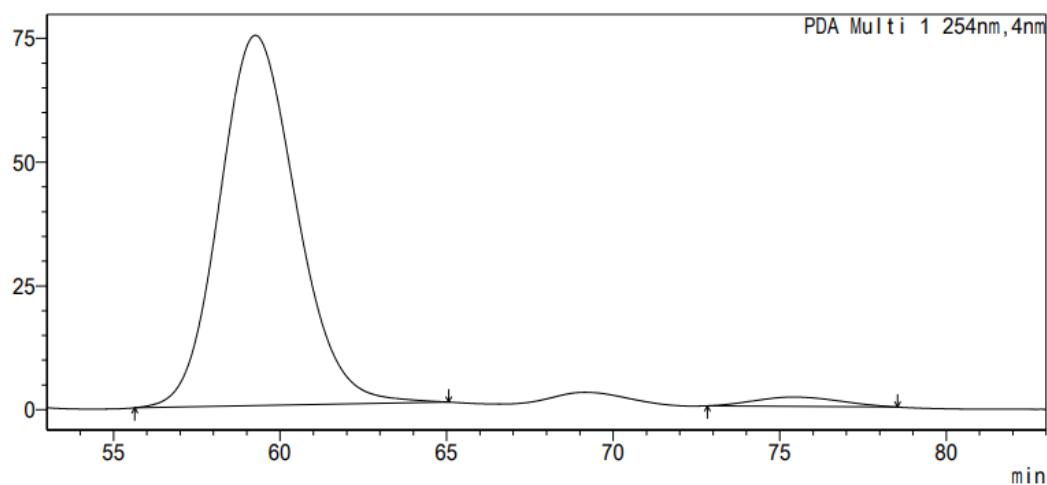
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	59.662	78287	12125243	50.227
2	76.146	49628	12015832	49.773

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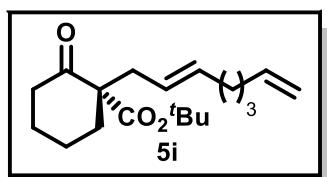
mAU



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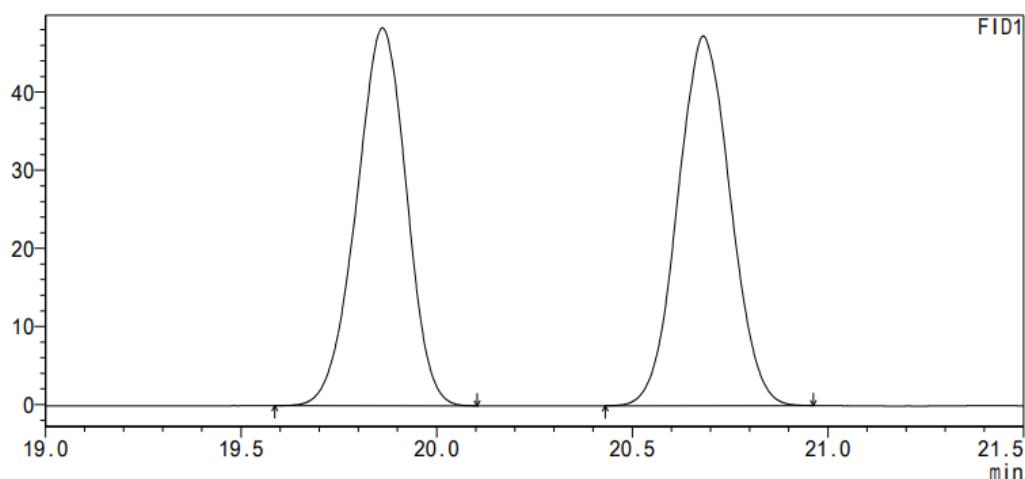
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	59.256	74785	12029274	97.281
2	75.443	1899	336252	2.719



<Chromatogram>

mV



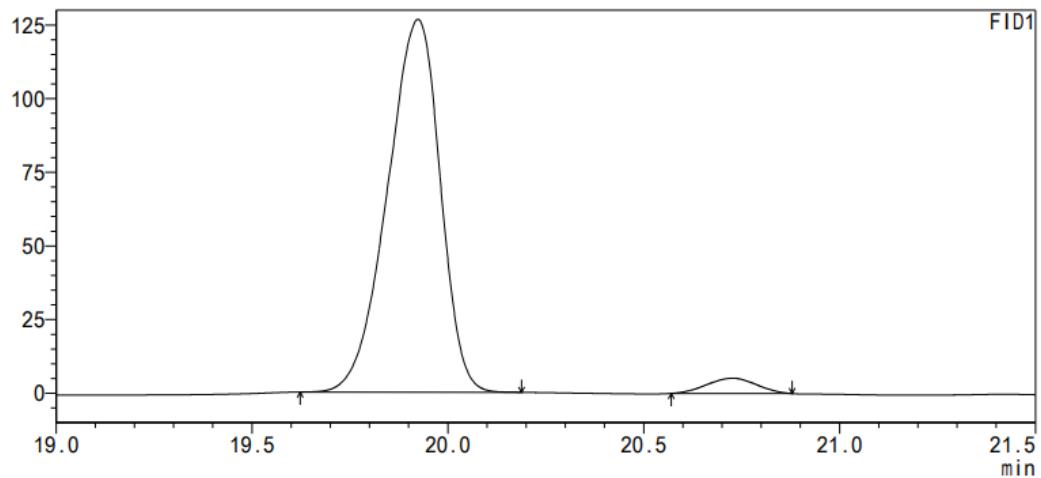
<Peak Results>

FID1

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	19.861	48345	430794	49.217
2	20.681	47313	444506	50.783

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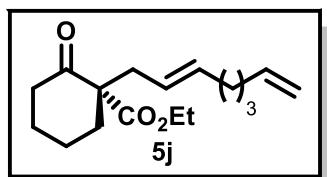
mV



<Peak Results>

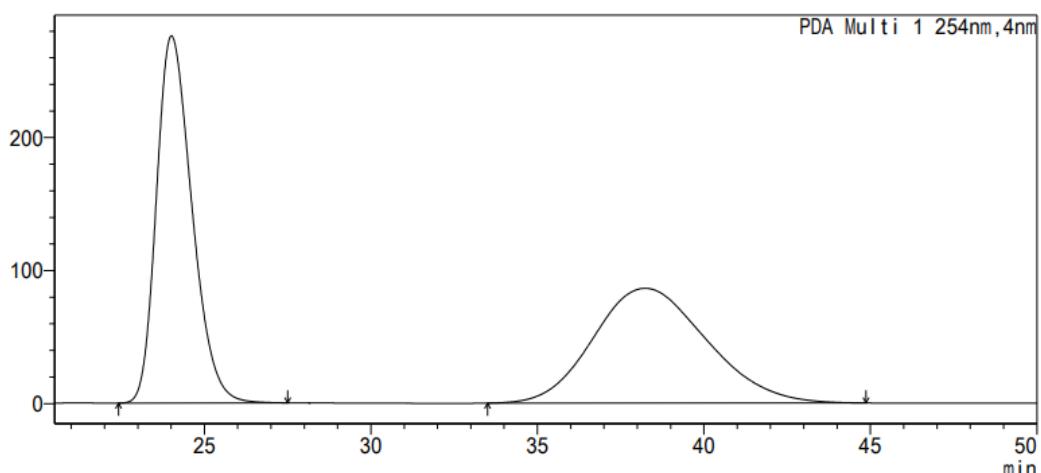
FID1

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	19.924	126524	1186743	96.311
2	20.728	5180	45459	3.689



<Chromatogram>

mAU



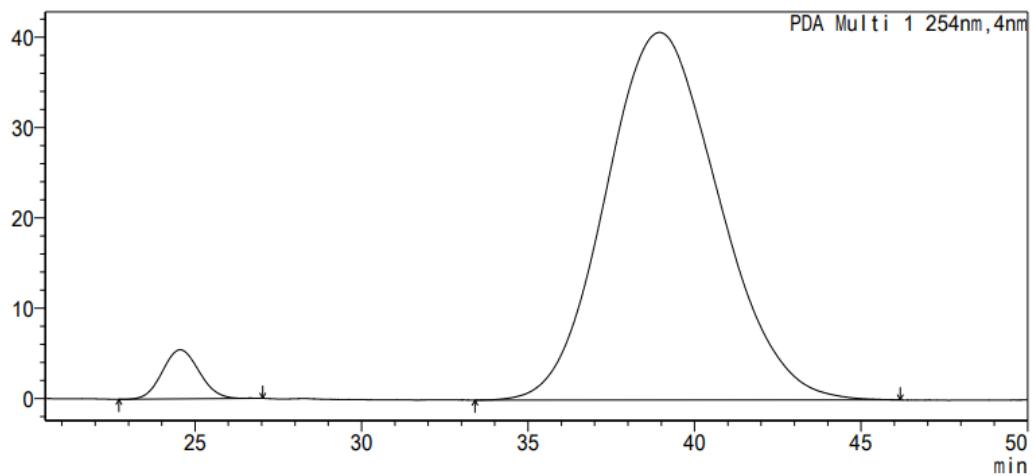
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	24.010	276192	20478833	50.020
2	38.240	86307	20462491	49.980

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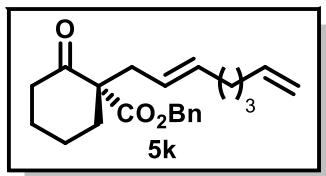
mAU



<Peak Results>

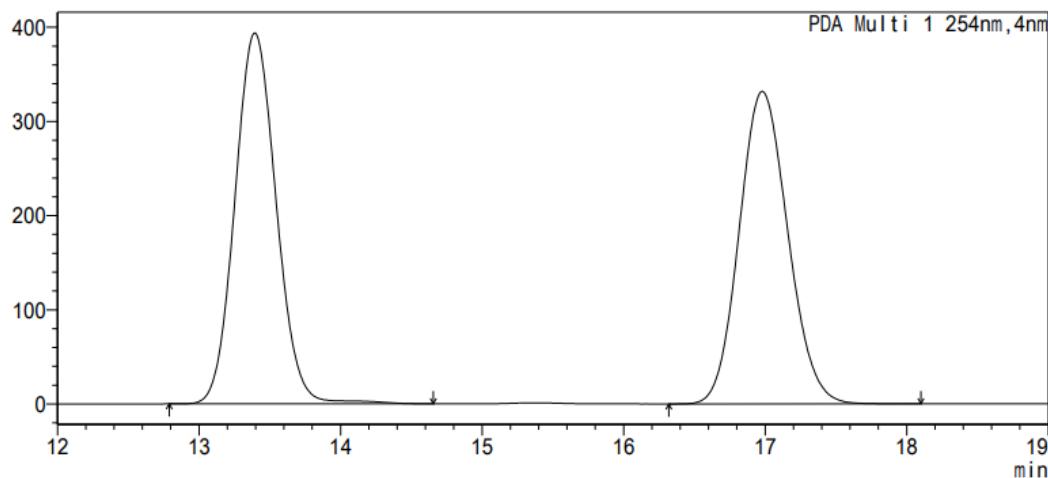
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	24.555	5439	417043	4.149
2	38.931	40715	9633600	95.851



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mAU



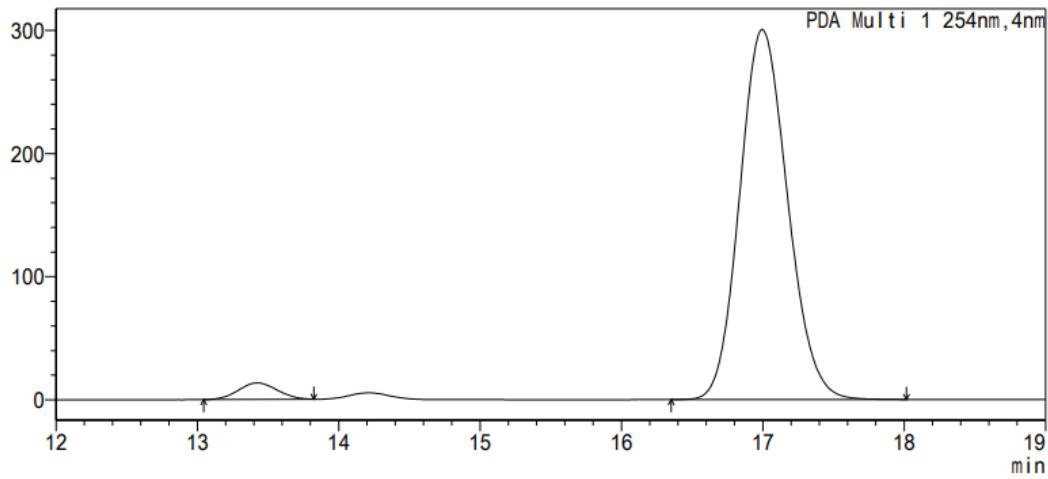
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	13.394	393728	7999835	50.226
2	16.979	331854	7927894	49.774

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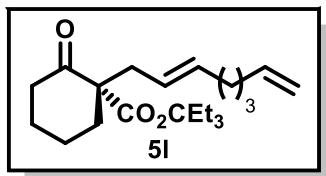
mAU



<Peak Results>

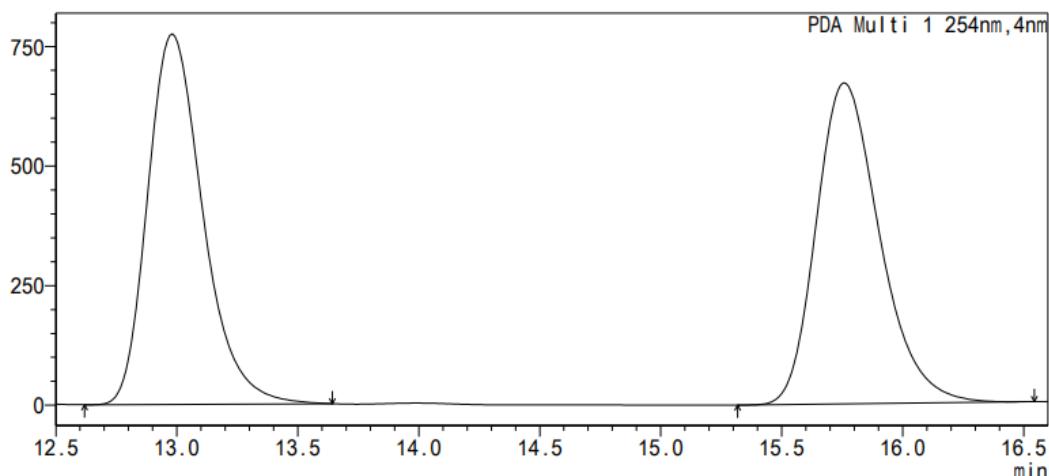
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	13.424	13341	254016	3.463
2	16.996	300656	7081836	96.537



<Chromatogram>

mAU



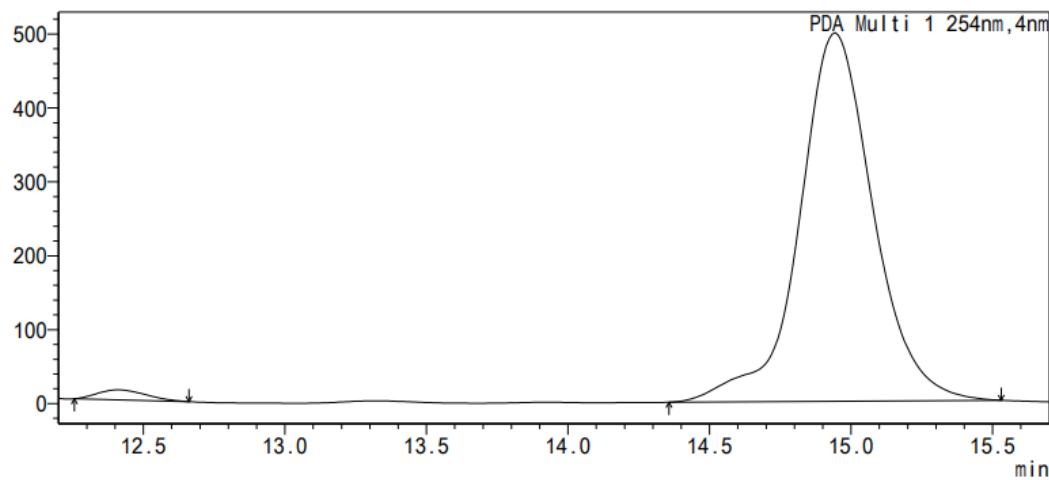
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	12.980	774502	12290741	50.076
2	15.758	671049	12253255	49.924

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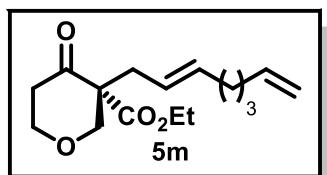
mAU



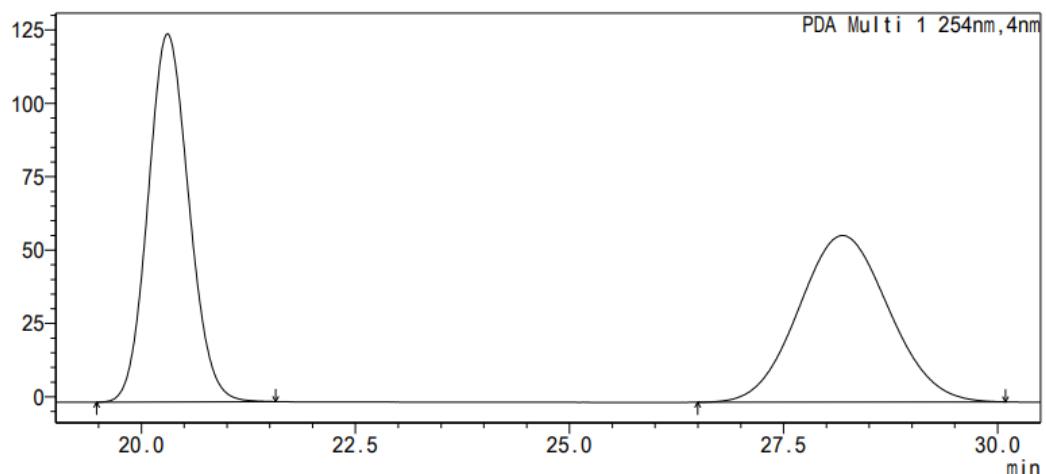
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	12.411	13640	161260	1.747
2	14.942	498503	9069903	98.253



mAU

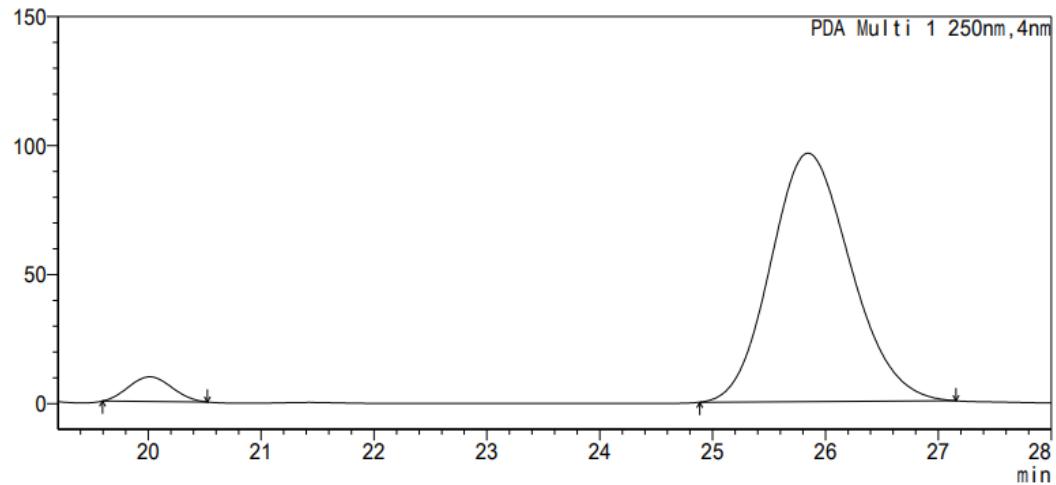


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	20.305	125436	4168433	49.991
2	28.189	56782	4169876	50.009

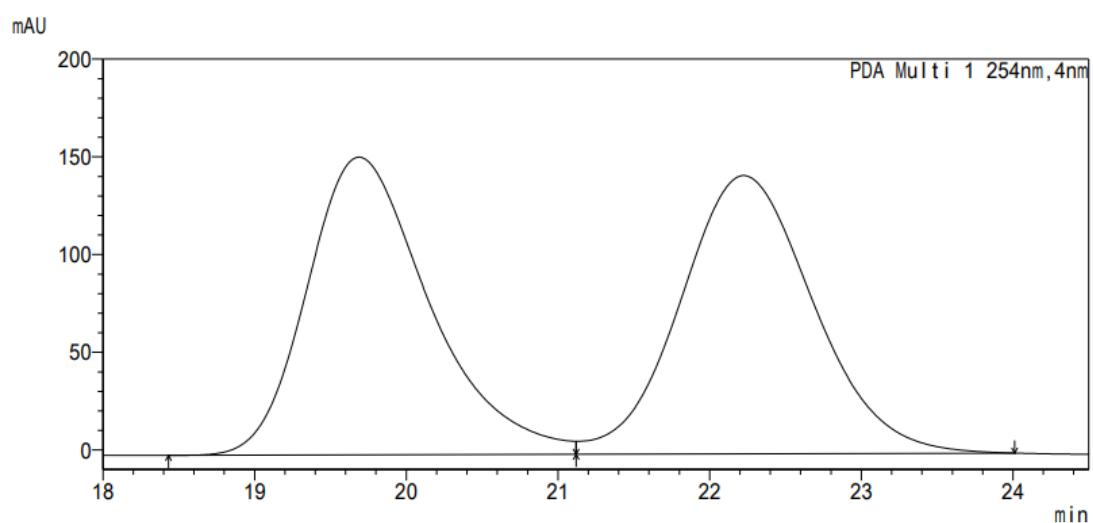
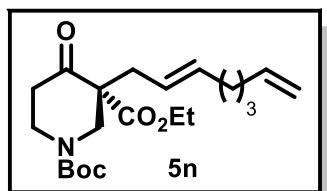
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<Peak Results>

PDA Ch1 250nm

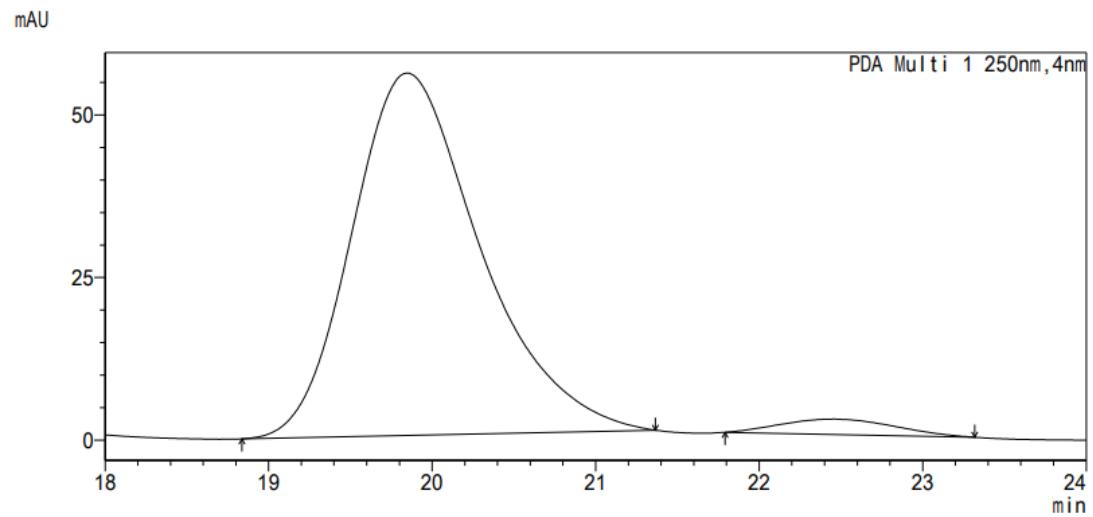
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	20.012	9586	255041	5.096
2	25.846	96325	4749628	94.904



<Peak Results>

PDA Ch1 254nm

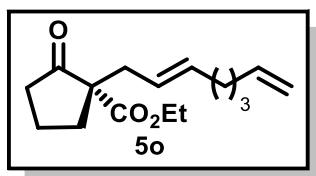
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	19.689	152346	8559843	49.625
2	22.225	142400	8689097	50.375



<Peak Results>

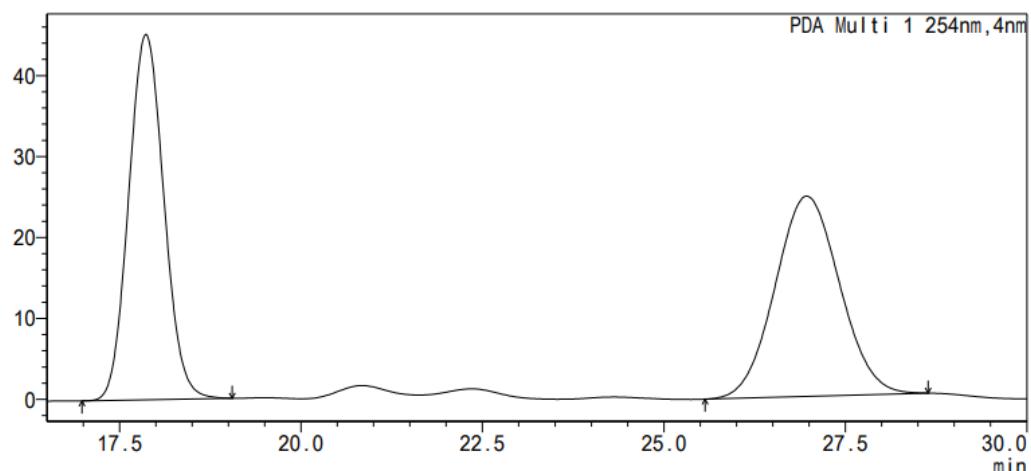
PDA Ch1 250nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	19.848	55701	3034026	96.368
2	22.460	2370	114343	3.632



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mAU



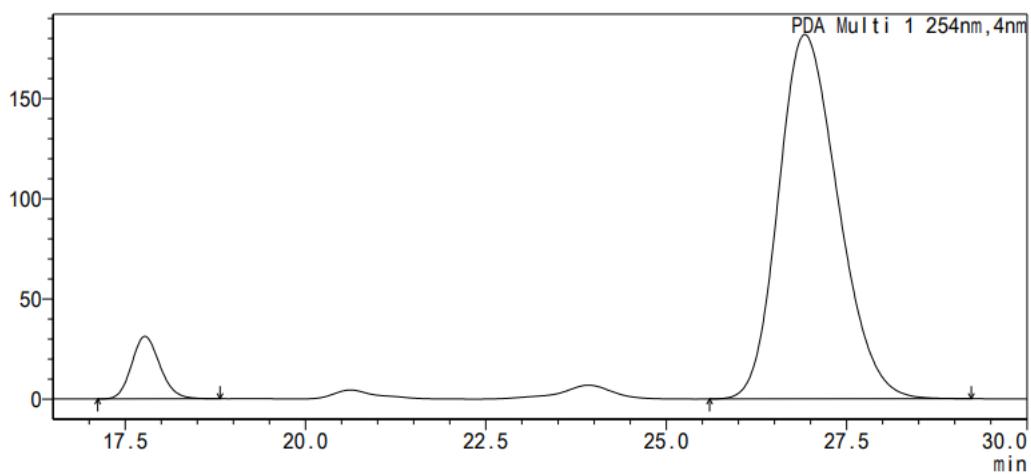
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.864	45147	1523474	49.883
2	26.965	24744	1530606	50.117

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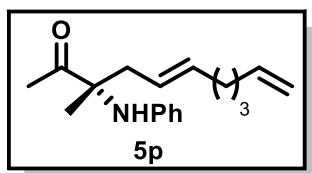
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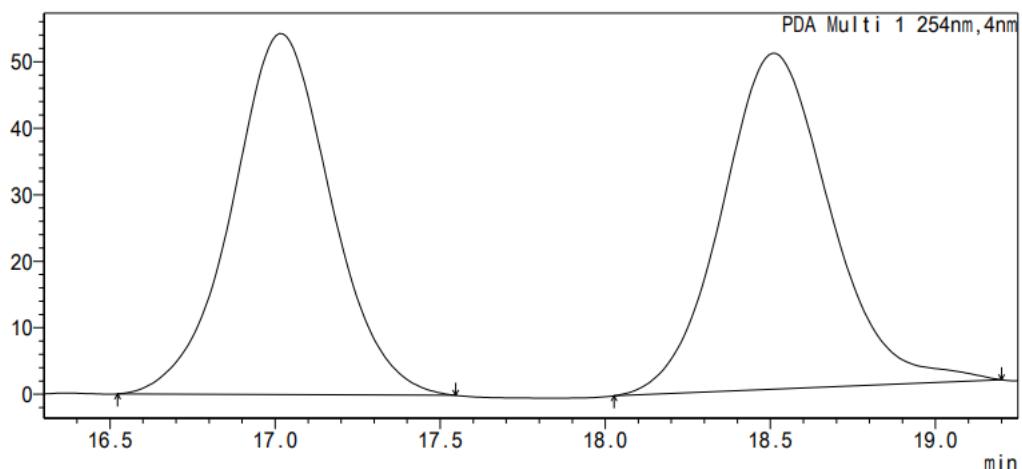
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.774	31216	853041	7.539
2	26.918	181788	10462634	92.461



<Chromatogram>

mAU



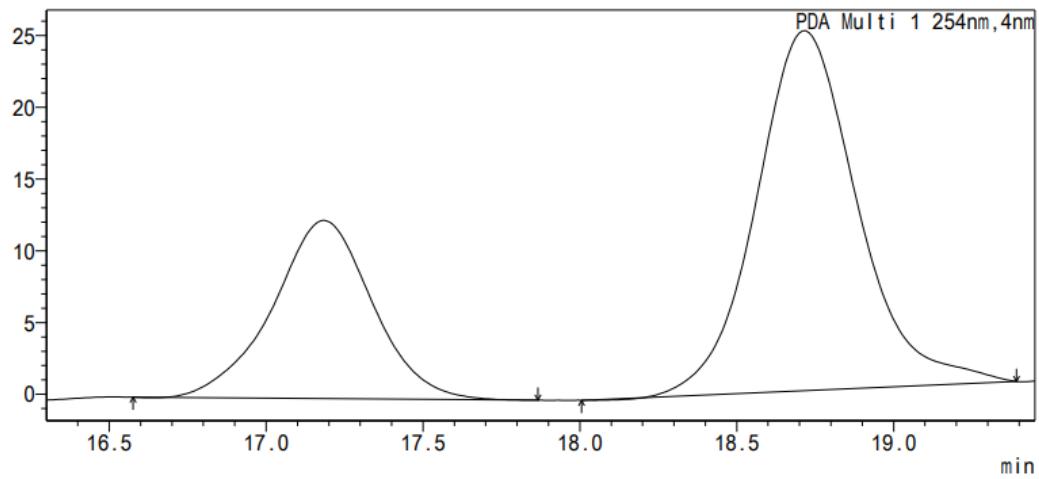
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.017	54282	1133307	49.531
2	18.510	50514	1154790	50.469

<Chromatogram>

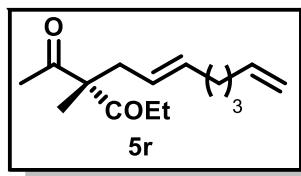
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<Peak Results>

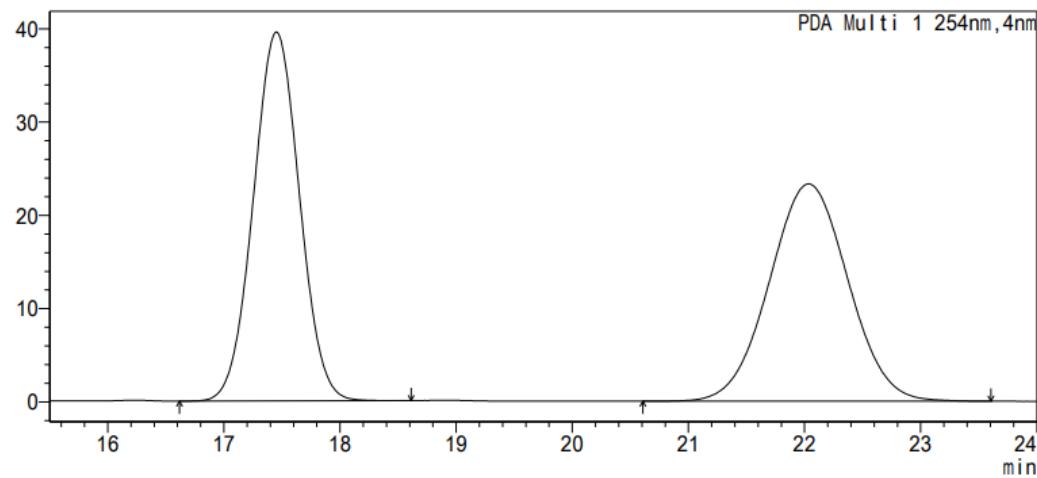
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.184	12429	274816	32.827
2	18.715	25083	562359	67.173



<Chromatogram>

mAU



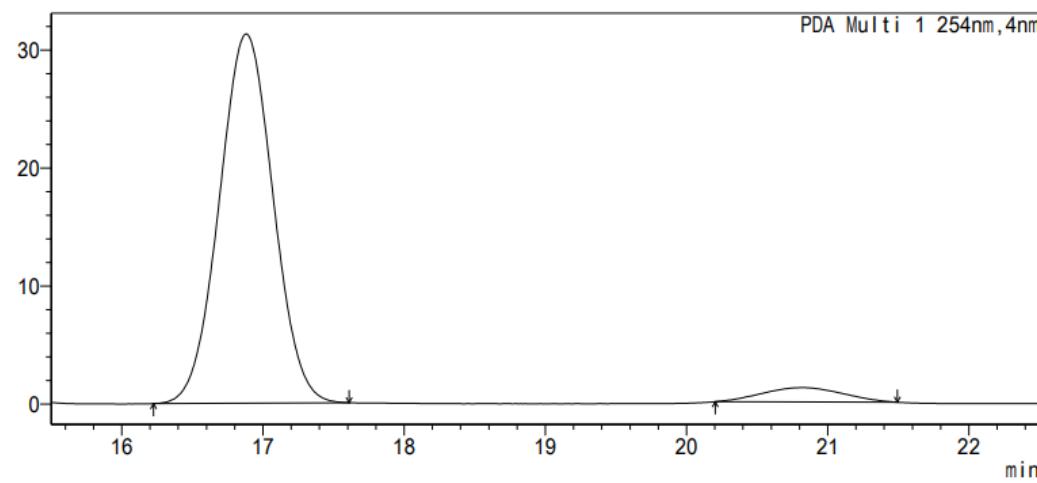
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.452	39573	1093474	49.900
2	22.034	23306	1097871	50.100

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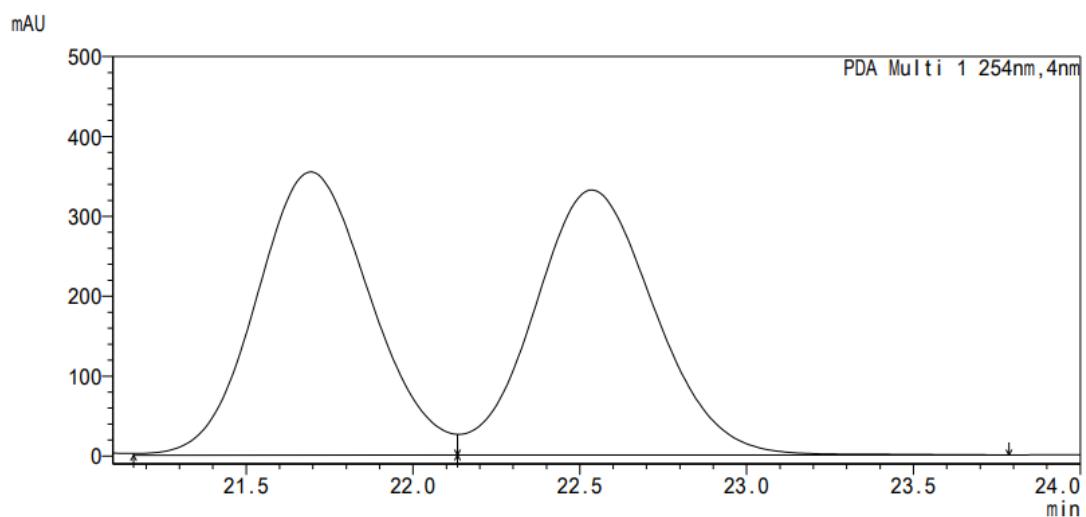
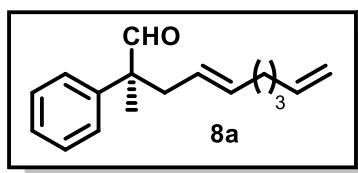
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<Peak Results>

PDA Ch1 254nm

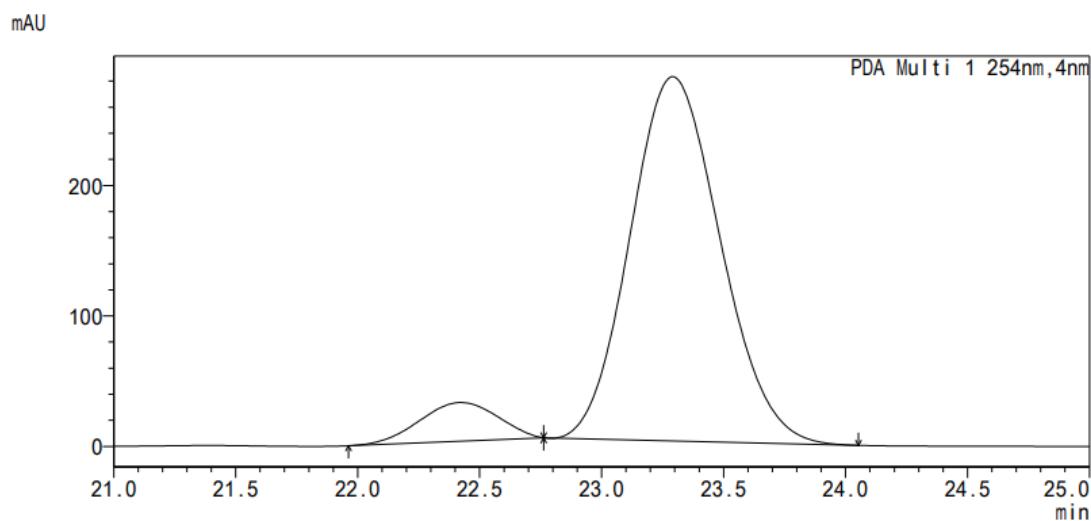
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	16.881	31307	831256	94.492
2	20.829	1217	48456	5.508



<Peak Results>

PDA Ch1 254nm

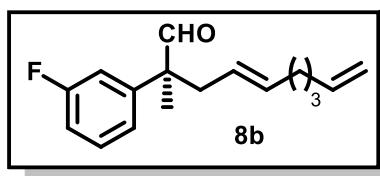
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	21.693	354666	8443467	50.338
2	22.536	331929	8329927	49.662



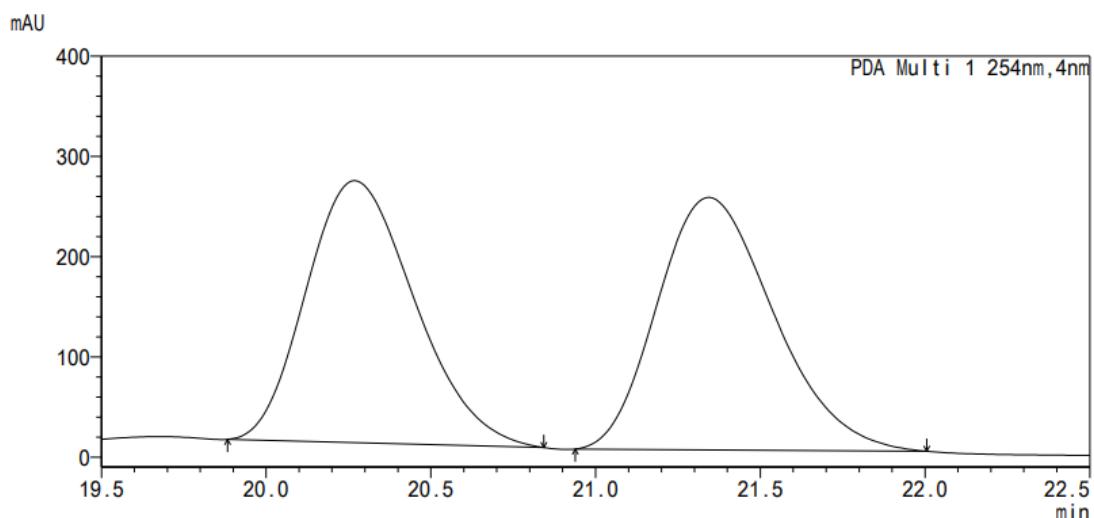
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	22.423	29721	662248	8.439
2	23.291	279164	7184954	91.561



<Chromatogram>

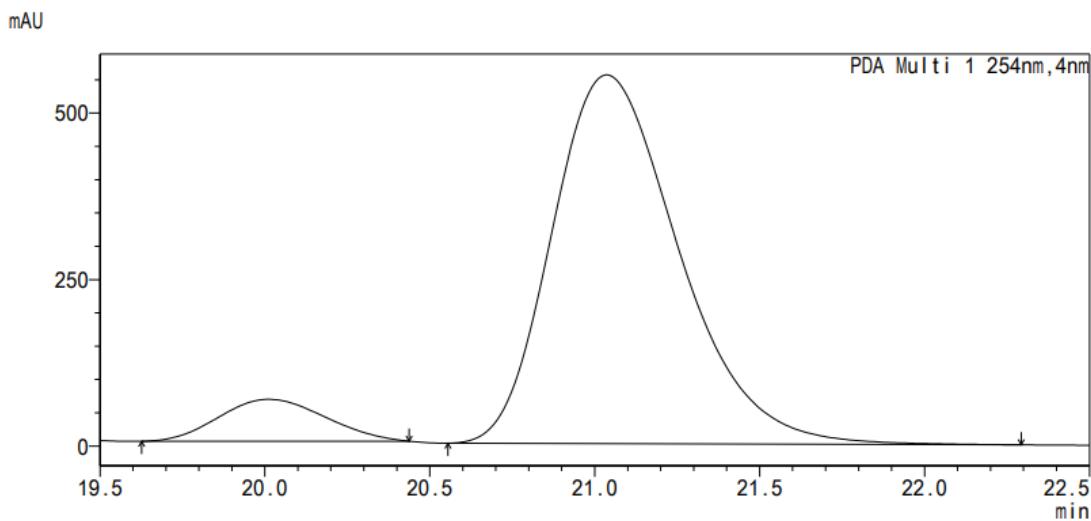


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	20.269	261493	5982460	49.147
2	21.343	252000	6190177	50.853

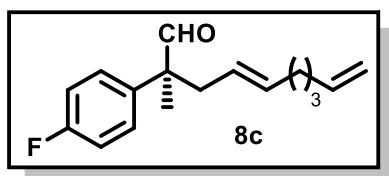
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<Peak Results>

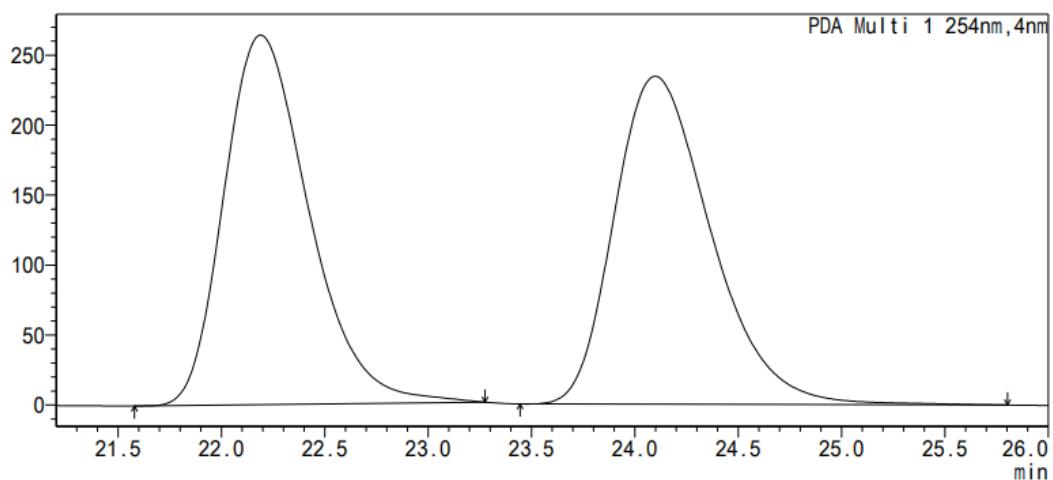
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	20.013	62991	1408763	8.694
2	21.036	553867	14795394	91.306



<Chromatogram>

mAU



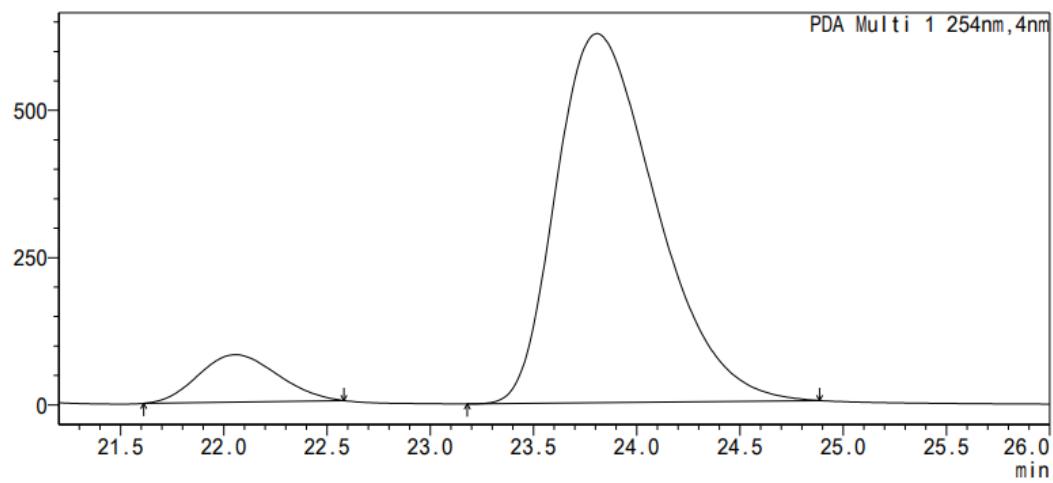
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	22.189	264225	7561332	49.715
2	24.098	234557	7648034	50.285

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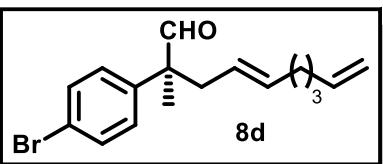
mAU



<Peak Results>

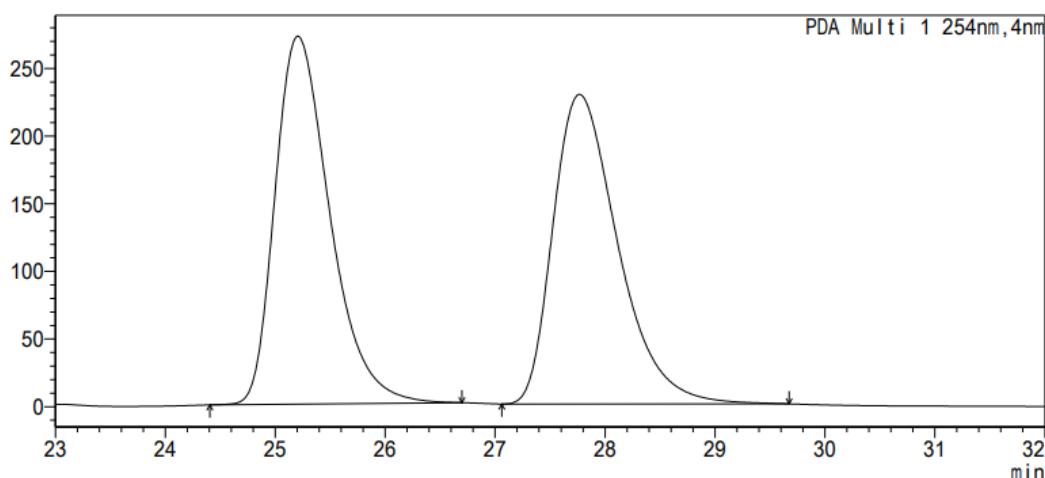
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	22.056	80409	2147549	9.207
2	23.807	626854	21176598	90.793



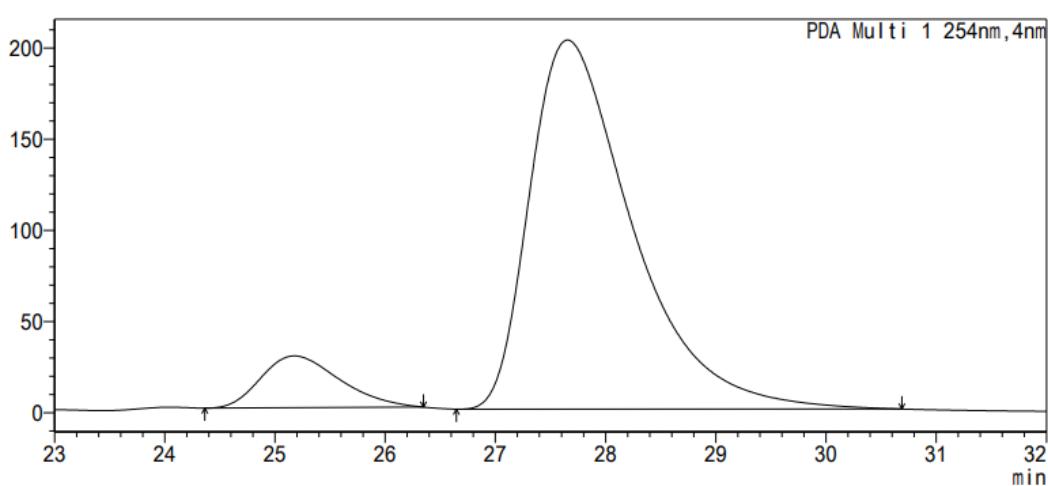
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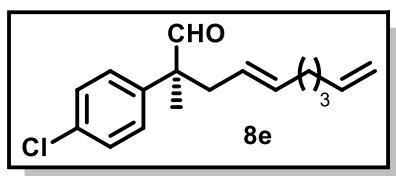
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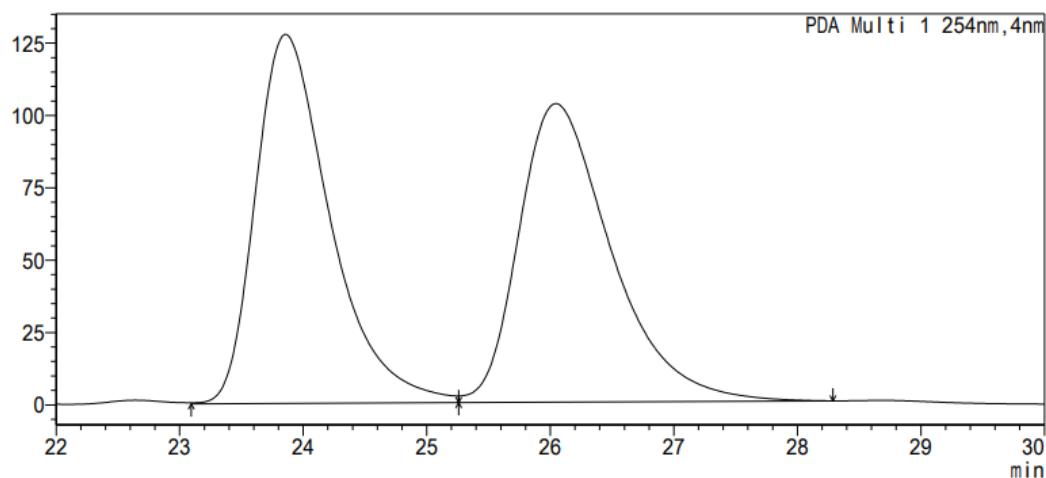
mAU





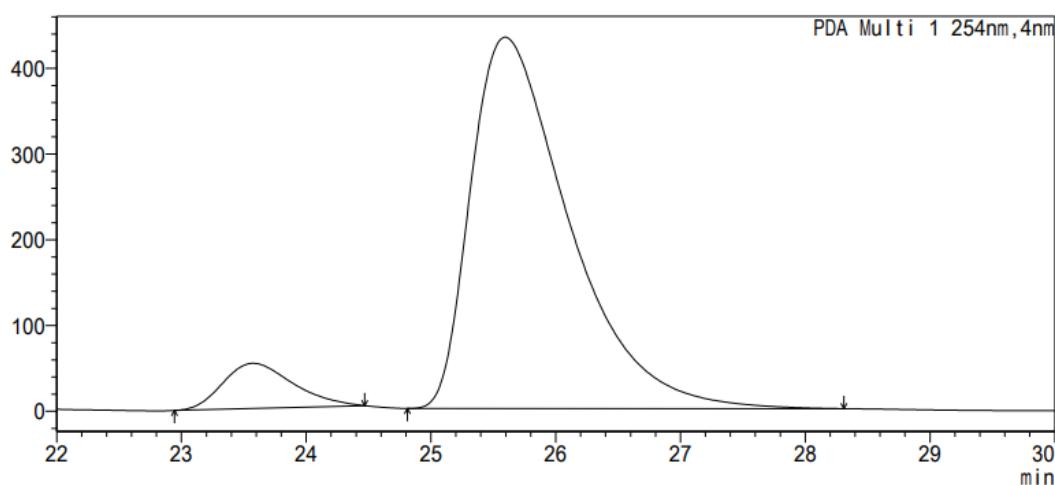
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mAU



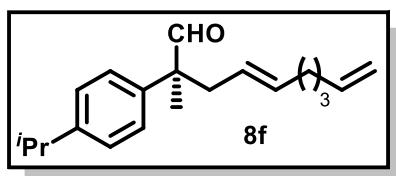
<Peak Results>
PDA Ch1 254nm

mAU



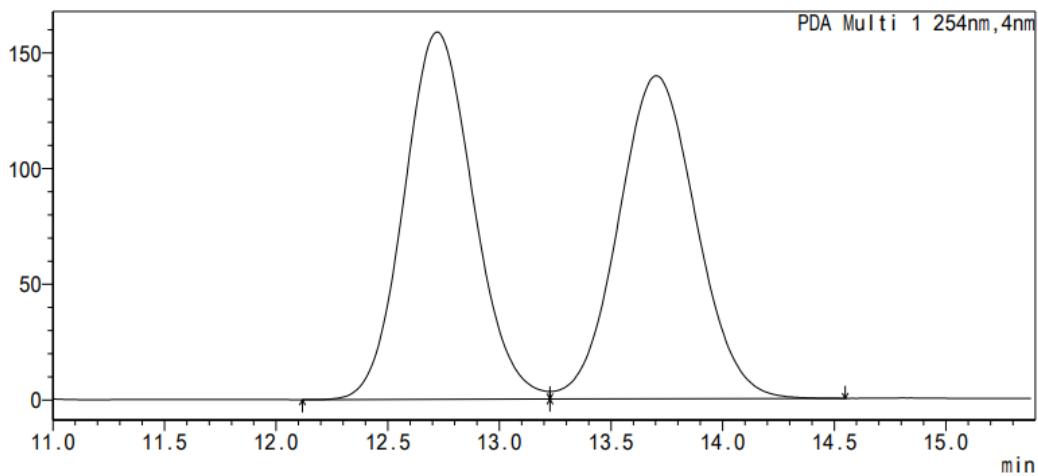
<Peak Results>
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	23.574	52692	2059435	7.969
2	25.595	433075	23783571	92.031



<Chromatogram>

mAU



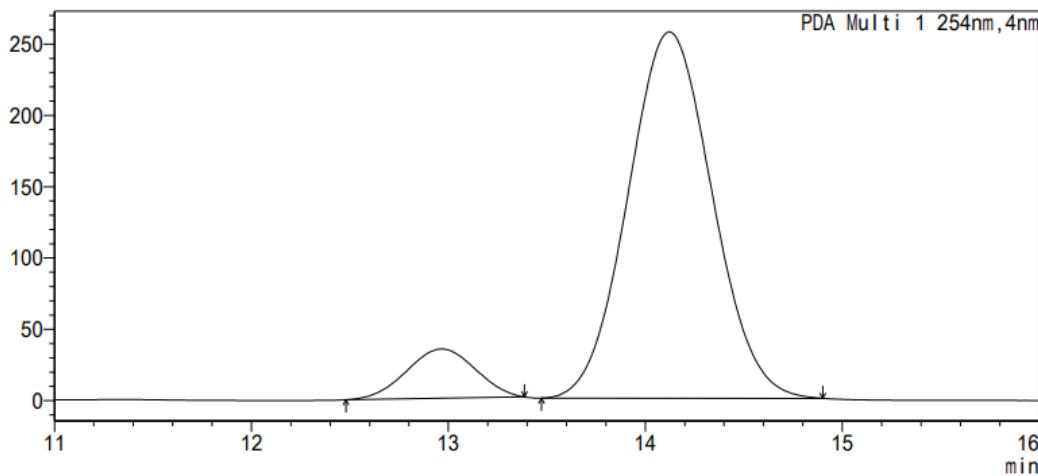
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	12.721	158758	3423389	50.254
2	13.703	139611	3388728	49.746

<Chromatogram>

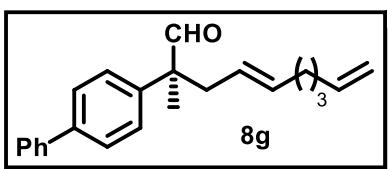
mAU



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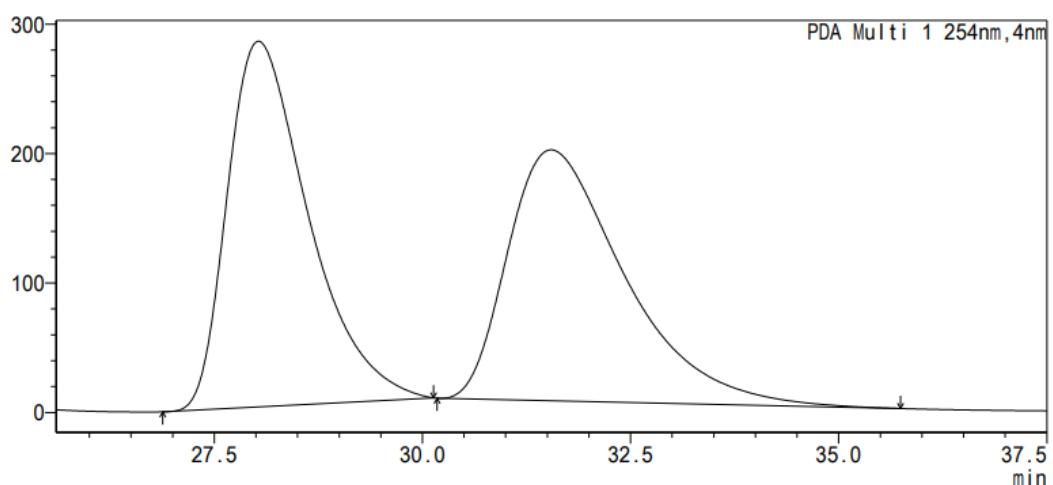
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	12.966	34543	837627	9.878
2	14.122	256899	7641681	90.122



<Chromatogram>

mAU



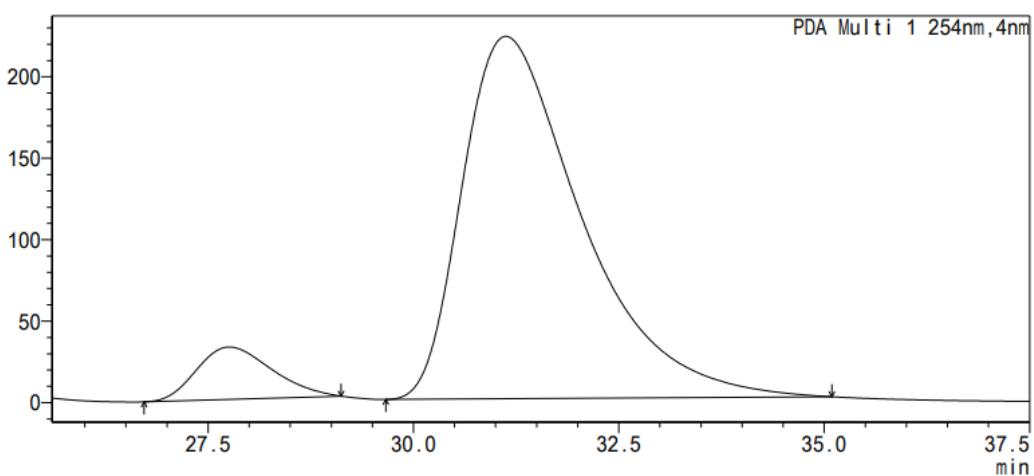
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	28.030	282537	19166016	50.320
2	31.545	193837	18922557	49.680

<Chromatogram>

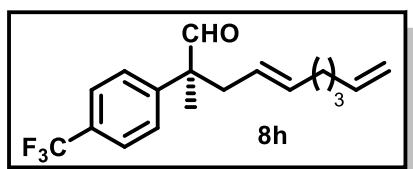
mAU



<Peak Results>

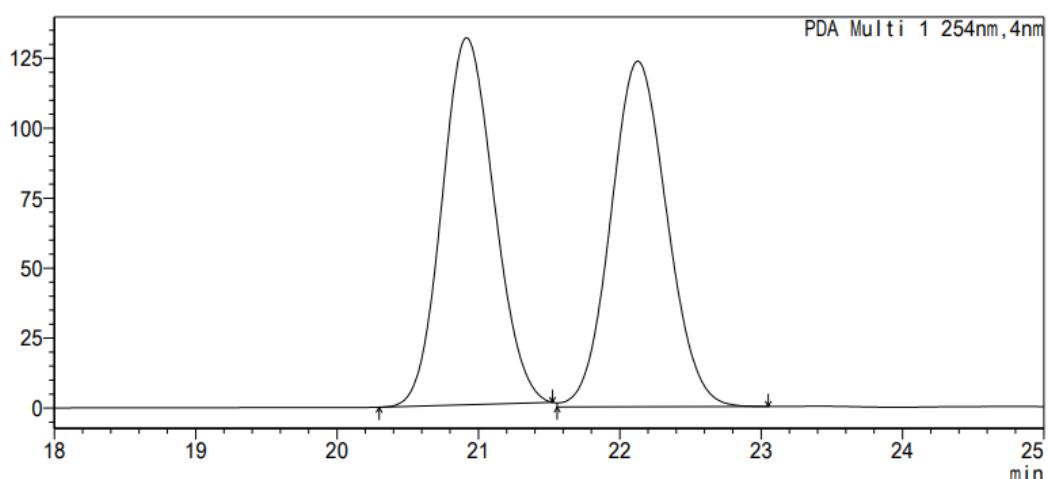
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	27.759	32123	2039267	8.302
2	31.125	222497	22525190	91.698



<Chromatogram>

mAU



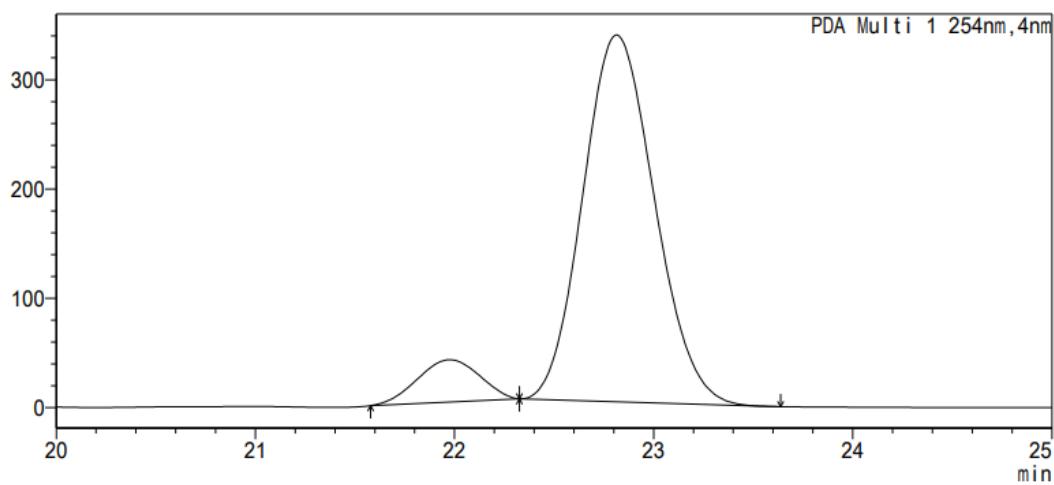
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	20.916	131181	3368741	49.648
2	22.128	123490	3416490	50.352

<Chromatogram>

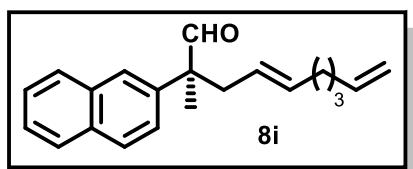
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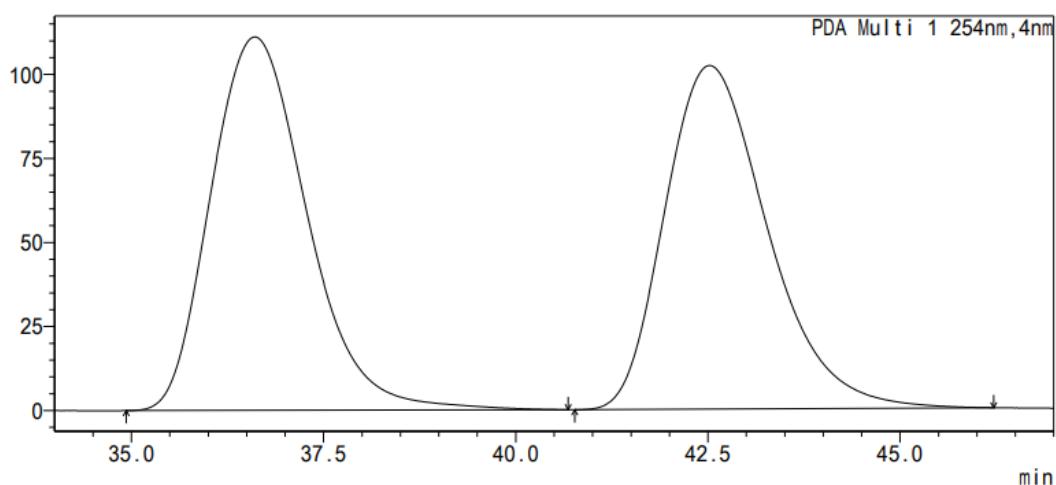
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	21.976	38669	835624	9.049
2	22.814	335731	8398419	90.951



<Chromatogram>

mAU



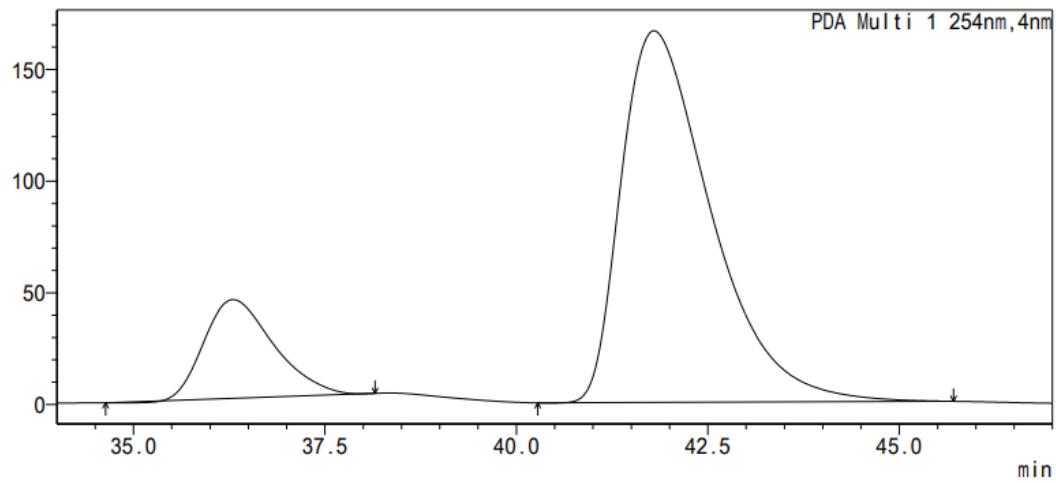
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	36.607	111140	9686087	50.459
2	42.520	102250	9509968	49.541

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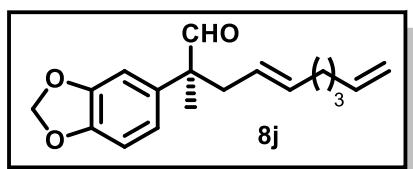
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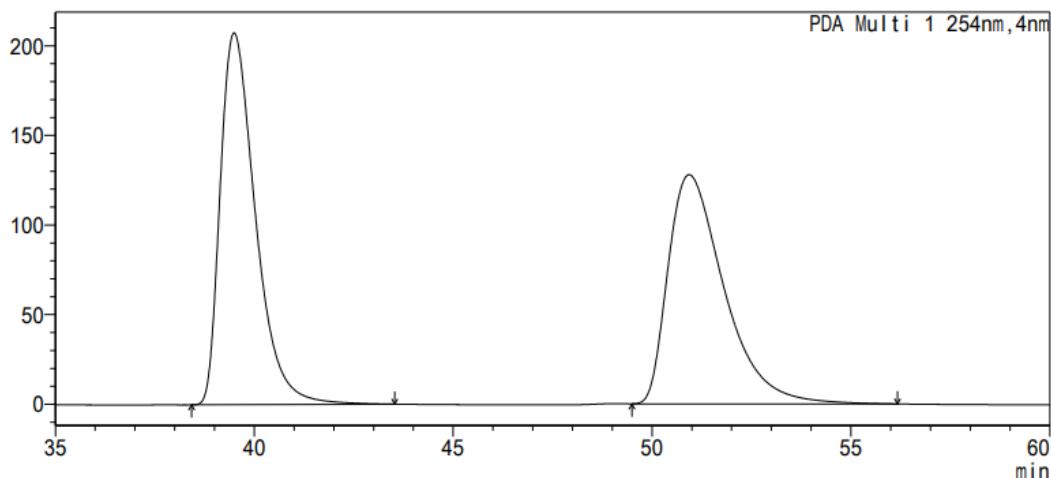
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	36.303	44252	2793557	17.006
2	41.796	166459	13633468	82.994



<Chromatogram>

mAU



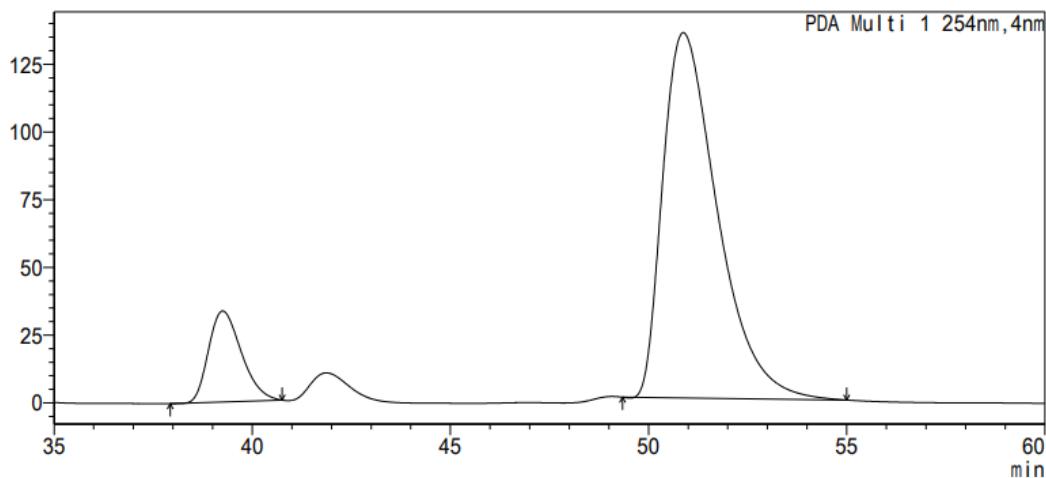
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	39.492	207497	12807996	50.526
2	50.932	127889	12541491	49.474

<Chromatogram>

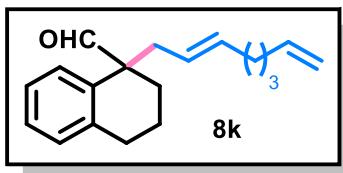
mAU



<Peak Results>

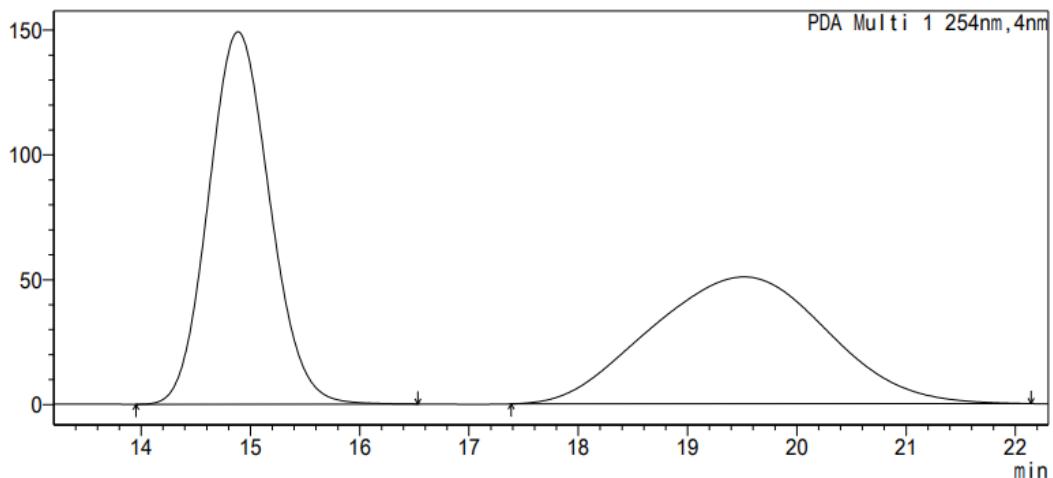
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	39.253	33557	1931463	12.981
2	50.875	134896	12947434	87.019



<Chromatogram>

mAU



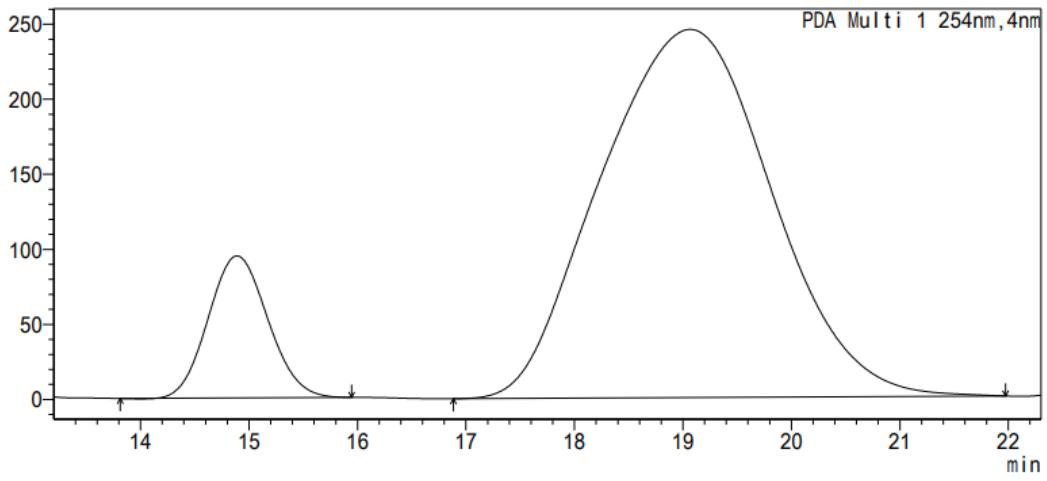
<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	14.886	149233	5817994	50.322
2	19.512	50842	5743523	49.678

<Chromatogram>

mAU



<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	14.889	94638	3609952	11.841
2	19.066	245264	26876632	88.159