Electronic Supplementary Information

Phosphine-catalyzed γ-addition of nitroacetates to allenoates for enantioselective creation of α,α-disubstituted α-amino acids precursors

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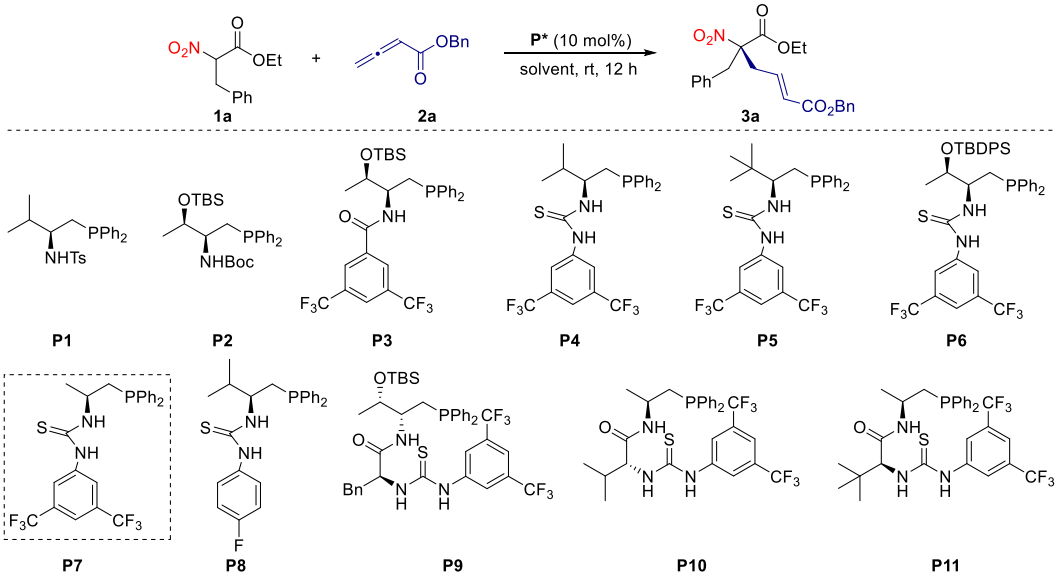
I. General remarks

Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere. $CHCl_3$ were used without further purification. All chemicals were used without further purification as commercially available unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (300–400 mesh). NMR spectra were recorded on a Bruker AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm) The ^1H NMR (500 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ = 7.26 ppm). The ^{13}C NMR (125 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.16 ppm). All high resolution mass spectra (HRMS) were obtained on a Finnigan/MAT 95XL-T spectrometer. Optical rotations were measured using an Anton Paar MCP-100 polarimeter. Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase. The racemic sample was prepared by $MePPh_2$ catalysis. Catalysts were synthesized by following our previously reported procedures.[1] Nitroacetates were prepared according to the literatures.[2]

II. Optimization of the reaction conditions

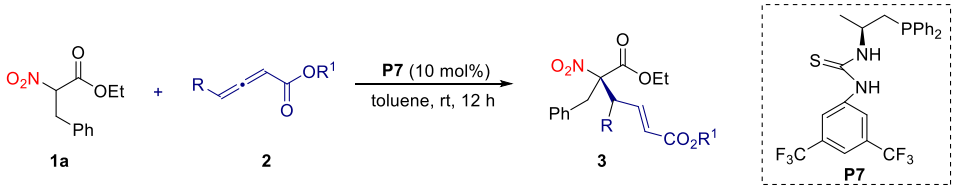
Table S1: Optimization of the phosphine-catalyzed enantioselective γ-addition of ethyl 2-nitro-3-phenylpropanoate **1a** with benzyl buta-2,3-dienoate **2a**[a]

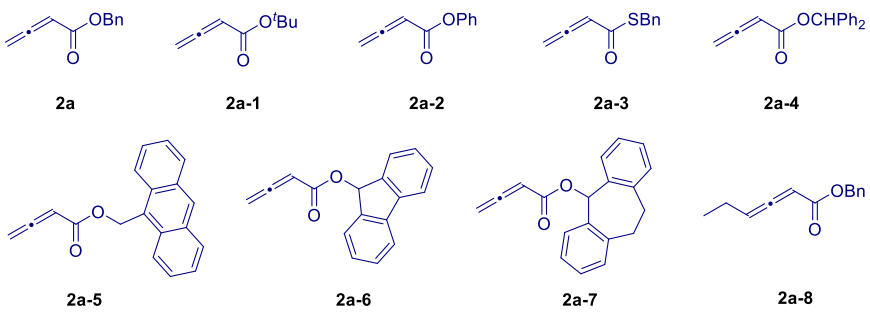


Entry	Cat. (mol%)	Solvent	Yield (%)[b]	*Ee* (%)[c]
1	$MePPh_2$ (10)	toluene	90	--
2	**P1** (10)	toluene	91	27
3	**P2** (10)	toluene	89	19
4	**P3** (10)	toluene	75	7
5	**P4** (10)	toluene	93	65
6	**P5** (10)	toluene	87	17
7	**P6** (10)	toluene	86	36
8	**P7 (10)**	**toluene**	**94**	**77**
9	**P8** (10)	toluene	68	39
10	**P9** (10)	toluene	65	9
11	**P10** (10)	toluene	89	3
12	**P11** (10)	toluene	trace	--
13	**P7** (10)	CH_2Cl_2	90	66
14	**P7** (10)	$CHCl_3$	89	72
15	**P7** (10)	THF	n.d.	--
16	**P7** (10)	Et_2O	90	73
17	**P7** (10)	EtOAc	89	55
18	**P7** (10)	CH_3CN	81	38
19	**P7** (10)	PhCl	90	75
20	**P7** (10)	dioxane	88	63
21	**P7** (10)	$PhCF_3$	88	72
22[d]	**P7** (10)	toluene	89	64
23[e]	**P7** (10)	toluene	91	68
24[f]	**P7** (10)	toluene	92	76
25[g]	**P7** (10)	toluene	91	75
26[h]	**P7** (10)	toluene	88	72

[a] Reaction conditions: **1a** (0.05 mmol), **2a** (0.075 mmol, 1.5 equiv.) and cat. in solvent (1.0 mL) at room temperature for 12 h. [b] Yield of isolated **3a**. [c] The *ee* values of **3a** was determined by HPLC analysis on a chiral-stationary-phase column. [d] PhOH (0.5 equiv.) was used as the additive. [e] PhCOOH (0.1 equiv.) was used as the additive. [f] 0 °C for 24 h. [g] -10 °C for 72 h. [h] 4 Å MS (50.0 mg) was used as the additive. n.d. = not detected.

Table S2: Optimization of the phosphine-catalyzed enantioselective γ-addition of ethyl 2-nitro-3-phenylpropanoate **1a** with allenoates **2**[a]

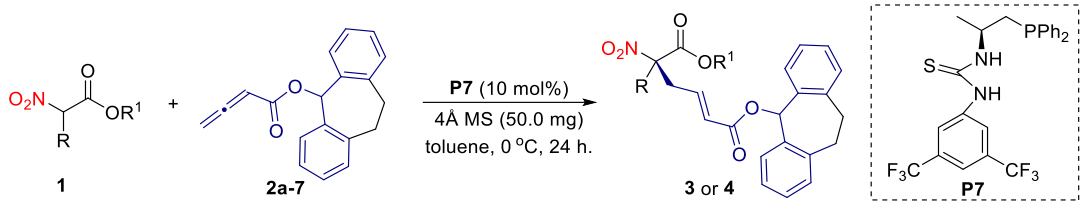




Entry	Allenoate (**2**)	Product (**3**)	Yield (%)[b]	*Ee* (%)[c]
1	**2a**	**3a**	94	77
2	**2a-1**	**3a-1**	96	68
3	**2a-2**	**3a-2**	97	66
4	**2a-3**	**3a-3**	90	63
5	**2a-4**	**3a-4**	93	80
6	**2a-5**	**3a-5**	91	83
7	**2a-6**	**3a-6**	91	83
8	**2a-7**	**3a-7**	92	80
9	**2a-7**	**3a-8**	n.d.	--
10[d]	**2a-6**	**3a-6**	91	83
11[e]	**2a-7**	**3a-7**	92	87
12[d,e]	**2a-7**	**3a-7**	**93**	**90**
13[e,f]	**2a-7**	**3a-7**	91	85
14	**2a-8**	**3a-8**	n.d.	--

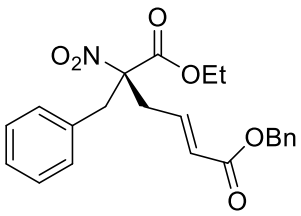
[a] Reaction conditions: **1a** (0.05 mmol), **2** (0.075 mmol, 1.5 equiv.) and **P7** (10.0 mol%) in toluene (1.5 mL) at room temperature for 12 h. [b] Yield of isolated **3**. [c] The *ee* values of **3** was determined by HPLC analysis on a chiral-stationary-phase column. [d] 0 °C for 24 h. [e] 4 Å MS (50.0 mg) was used as the additive. [f] -10 °C for 72 h. n.d. = not detected.

III. Representative procedure for the enantioselective phosphine-catalyzed *γ*-addition of nitroacetates with allenoates



A dried tube with a magnetic stir bar was charged with nitroacetates **1** (0.05 mmol, 1.0 equiv.), catalyst **P7** (0.005 mmol, 10 mol%), 4 Å MS (50.0 mg), followed by the addition of toluene (1.0 mL). Then allenoate **2a-7** (0.075 mmol, 1.5 equiv.) was dissolved in toluene (0.5 mL) and dropwise added into the reaction mixture at 0 °C. The reaction mixture was then stirred at that temperature for 24 hours. Then the solvent was evaporated and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to afford the *γ*-addition products **3** or **4**.

IV. Experimental data for the described substances



1-Benzyl 6-ethyl (*S*,*E*)-5-benzyl-5-nitrohex-2-enedioate (3a)

Colourless oil; $[\alpha]^{25}_{D}$ = -4.6 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.30 (m, 8H), 7.11–7.08 (m, 2H), 6.86 (dt, *J* = 15.0, 7.5 Hz, 1H), 5.99 (d, *J* = 16.0 Hz, 1H), 5.20 (s, 2H), 4.30–4.23 (m, 2H), 3.62 (d, *J* = 23.5 Hz, 1H), 3.50 (d, *J* = 24.0 Hz, 1H), 2.95 (d, *J* = 12.5 Hz, 2H), 1.25 (t, *J* = 12.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.78, 165.28, 139.82, 135.87, 132.62, 130.04, 129.04, 128.74, 128.48, 128.42, 128.30, 126.70, 95.42, 66.63, 63.35, 40.12, 36.13, 13.92 ppm. HRMS (ESI) m/z calcd for $C_{22}H_{23}NNaO_6$ $[M+Na]^+$ 420.1418, found 420.1410. The *ee* value was 77%, t_R (minor) = 13.997 min, t_R (major) = 15.594 min (Chiralpak IF, λ = 220 nm, 2.5% *i*PrOH/hexane, flow rate = 1.0 mL/min).

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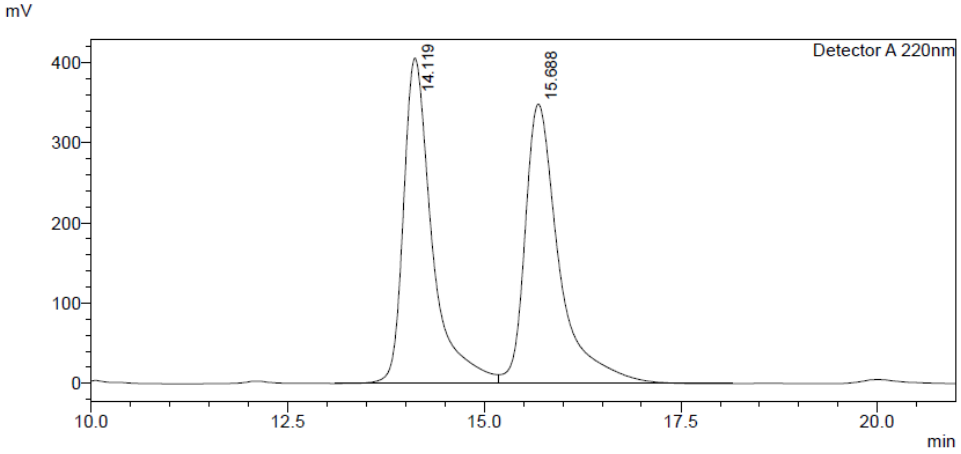

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Detector A 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	14.119	10289698	405641	49.493	49.493	
2	15.688	10500476	348450	50.507	50.507	
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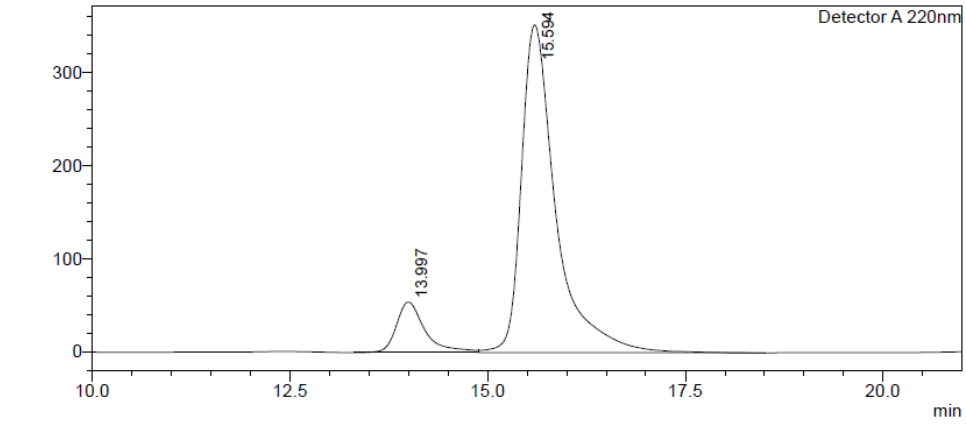

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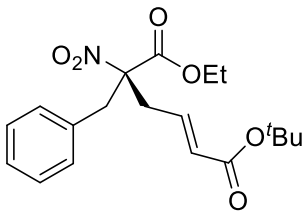
Detector A 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	13.997	1373174	54313	11.358	11.358	
2	15.594	10716939	352070	88.642	88.642	
Total		12090112	406383	100.000		



1-(*tert*-Butyl) 6-ethyl (*S*,*E*)-5-benzyl-5-nitrohex-2-enedioate (3a-1)

Colourless oil; $[\alpha]^{25}_{D}$ = -3.1 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.30 (m, 3H), 7.10–7.09 (m, 2H), 6.70 (dt, *J* = 15.0, 7.5 Hz, 1H), 5.87 (dt, *J* = 15.5, 1.0 Hz, 1H), 4.31–4.24 (m, 2H), 3.61 (d, *J* = 14.0 Hz, 1H), 3.49 (d, *J* = 14.5 Hz, 1H), 2.91 (d, *J* = 7.5 Hz, 2H), 1.48 (s, 9H), 1.27 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.87,

164.83, 137.75, 132.70, 130.04, 129.02, 128.85, 128.26, 95.50, 81.08, 63.29, 39.95, 35.88, 28.23, 13.95 ppm. HRMS (ESI) m/z calcd for $C_{19}H_{25}NNaO_6$ $[M+Na]^+$ 386.1574, found 386.1574. The *ee* value was 68%, t_R (minor) = 7.134 min, t_R (major) = 7.906 min (Chiralpak IF, λ = 220 nm, 2.5% *i*PrOH/hexane, flow rate = 1.0 mL/min).

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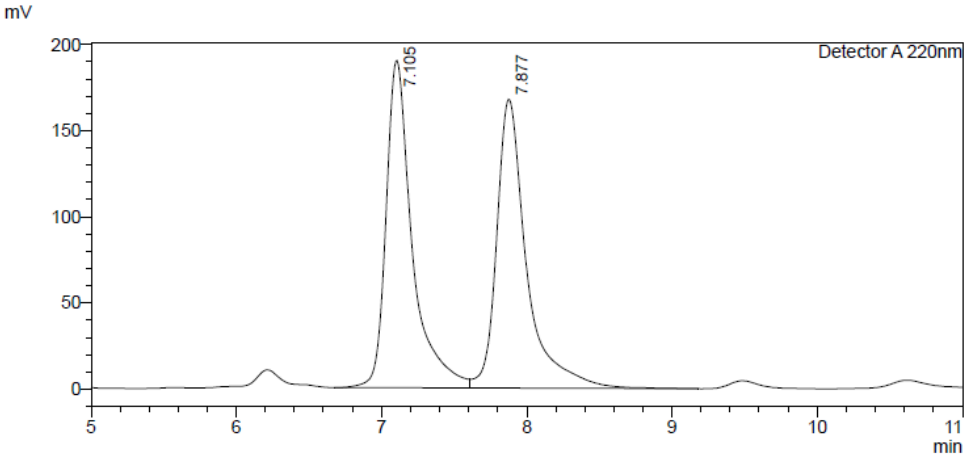

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Detector A 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	7.105	2388026	190032	49.727	49.727	
2	7.877	2414250	167815	50.273	50.273	
Total		4802276	357846	100.000		

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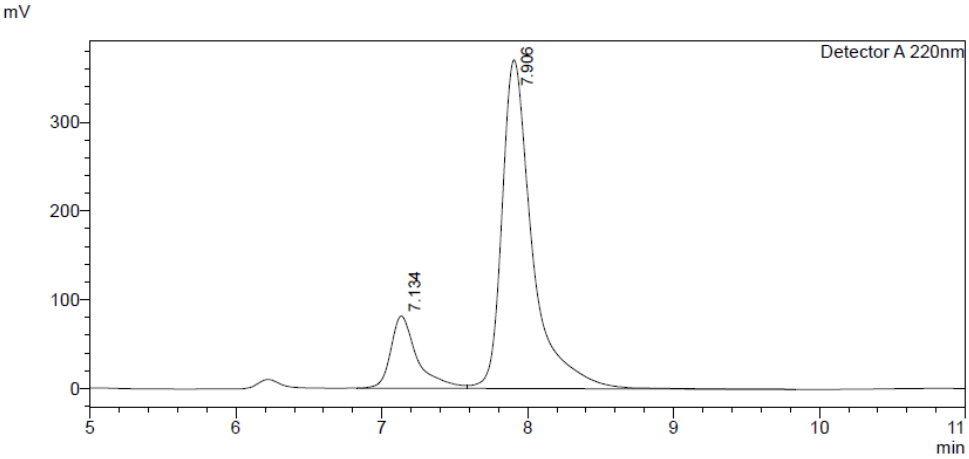

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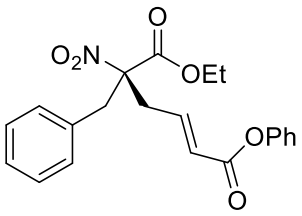
Detector A 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	7.134	1028612	81419	16.093	16.093	
2	7.906	5363224	370656	83.907	83.907	
Total		6391836	452074	100.000		



6-Ethyl 1-phenyl (*S*,*E*)-5-benzyl-5-nitrohex-2-enedioate (3a-2)

Colourless oil; $[\alpha]^{25}_{D}$ = -3.9 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 (t, J = 8.0 Hz, 2H) 7.35–7.33 (m, 3H), 7.27–7.24 (m, 1H), 7.14–7.11 (m, 4H), 7.01 (dt, J = 15.0, 7.5 Hz, 1H), 6.14 (d, J = 15.5 Hz, 1H), 4.36–4.26 (m, 2H), 3.66 (d, J = 14.5 Hz, 1H), 3.55 (d, J = 14.0 Hz, 1H), 3.03 (dd, J = 7.5, 1.0 Hz, 2H), 1.30 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.76, 163.82, 150.61, 141.43, 132.55, 130.05, 129.59, 129.10, 128.37, 126.23, 126.10, 121.61, 95.38, 63.45, 40.25, 36.30, 13.98 ppm. HRMS (ESI) m/z calcd for $C_{21}H_{21}NNaO_6$ $[M+Na]^+$ 406.1261, found 406.1258. The *ee* value was 66%, t_R (major) = 25.602 min, t_R (minor) = 29.580 min (Chiralpak IC, λ = 254 nm, 2.5% *i*PrOH/hexane, flow rate = 1.0 mL/min).

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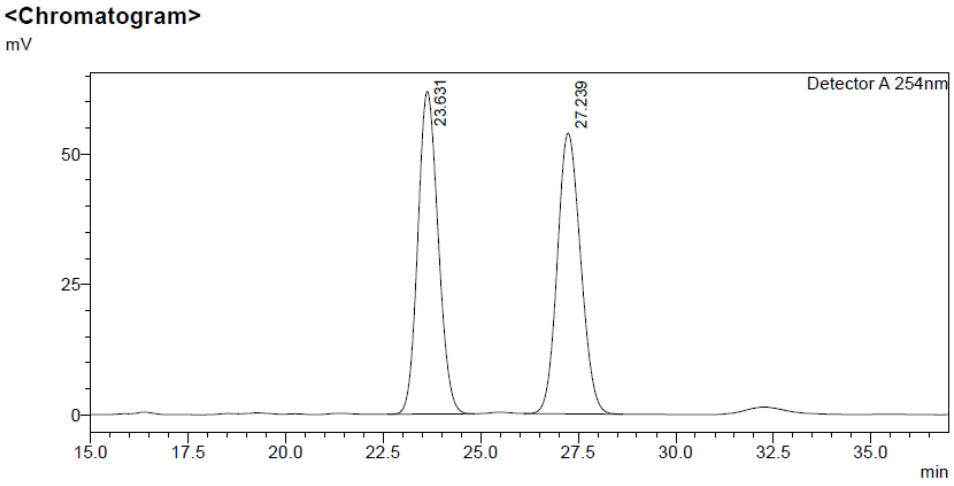

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Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Mark
1	23.631	2243691	61880	50.069	50.069	
2	27.239	2237474	53820	49.931	49.931	
Total		4481165	115700	100.000		

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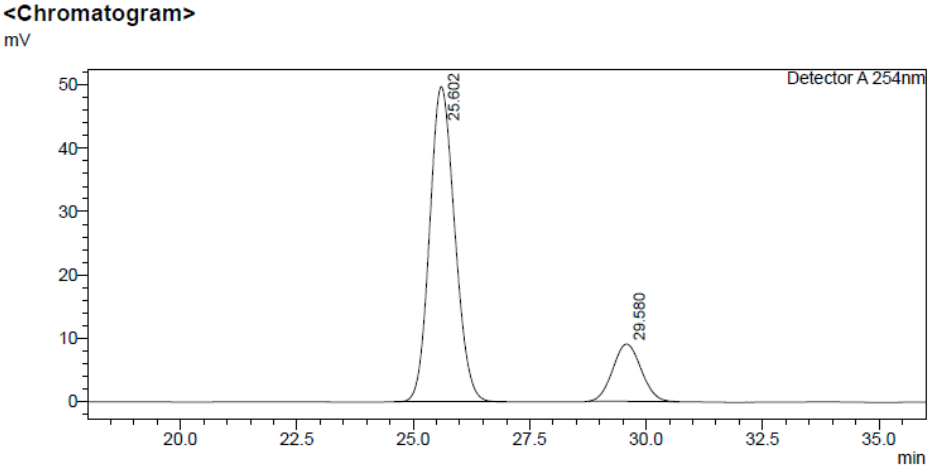

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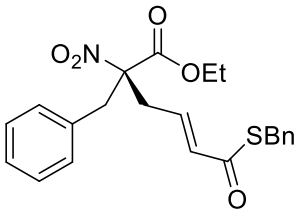
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	25.602	1867444	49714	82.950	82.950	
2	29.580	383852	9040	17.050	17.050	
Total		2251296	58754	100.000		



Ethyl (*S*,*E*)-2-benzyl-6-((benzylthio)oxy)-2-nitro-6-oxohexenoate (3a-3)

Colourless oil; $[\alpha]^{25}_{D}$ = -0.8 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.22 (m, 8H), 7.09–7.07 (m, 2H), 6.75 (dt, *J* = 15.0, 7.5 Hz, 1H), 6.19 (dt, *J* = 15.5, 1.0 Hz, 1H), 4.31–4.24 (m, 2H), 4.20 (s, 2H), 3.62 (d, *J* = 14.0 Hz, 1H), 3.50 (d, *J* = 14.5 Hz, 1H), 2.92–2.90 (m, 2H), 1.26 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.51, 165.76, 137.29, 135.55, 133.09, 132.53, 130.03, 129.08, 129.05, 128.83, 128.35, 127.56, 95.38, 63.43, 40.24, 36.12, 33.35, 13.97 ppm. HRMS (ESI) m/z calcd for $C_{22}H_{23}NNaO_6S$ $[M+Na]^+$ 452.1138, found 452.1139. The *ee* value was 63%, t_R (minor) = 15.161 min, t_R (major) = 22.561 min (Chiralpak IF, λ = 254 nm, 2.5% *i*PrOH/hexane, flow rate = 1.0 mL/min).

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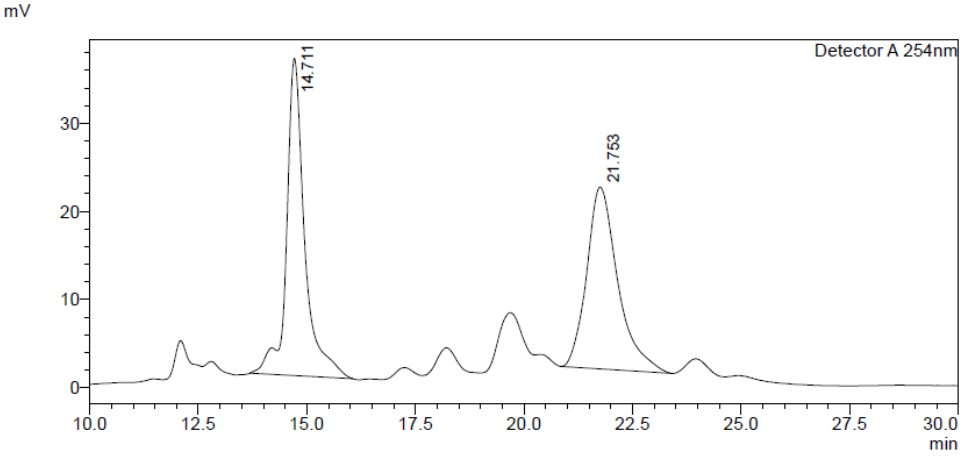

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	14.711	1041313	35976	50.355	50.355	
2	21.753	1026630	20624	49.645	49.645	
Total		2067942	56601	100.000		

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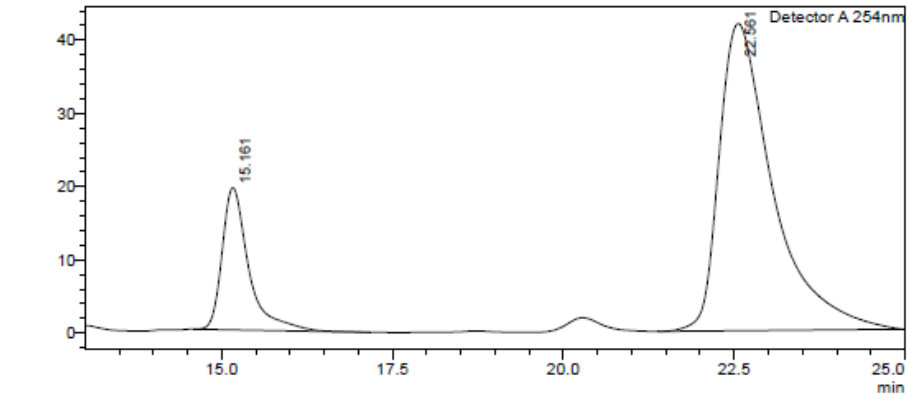

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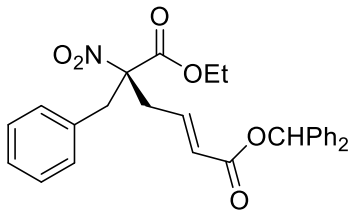
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	15.161	526888	19416	18.675	18.675	
2	22.561	2294467	41953	81.325	81.325	
Total		2821356	61369	100.000		



1-Benzhydryl 6-ethyl (*S*,*E*)-5-benzyl-5-nitrohex-2-enedioate (3a-4)

Colourless oil; $[\alpha]^{25}_{D}$ = -4.1 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.28 (m, 13H), 7.10–7.09 (m, 2H), 6.95 (s, 1H), 6.91 (dt, *J* = 15.0, 7.5 Hz, 1H), 6.07 (d, *J* = 15.5 Hz, 1H), 4.28–4.23 (m, 2H), 3.63 (d, *J* = 14.5 Hz, 1H), 3.51 (d, *J* = 14.5 Hz, 1H), 2.96 (d, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.80, 164.49, 140.21, 140.10, 132.59, 130.04, 129.04, 128.68, 128.31, 128.15, 127.25, 127.24,

126.71, 95.40, 77.37, 63.36, 40.22, 36.18, 13.92 ppm. HRMS (ESI) m/z calcd for $C_{28}H_{27}NNaO_6$ $[M+Na]^+$ 496.1731, found 496.1728. The *ee* value was 80%, t_R (minor) = 16.809 min, t_R (major) = 22.078 min (Chiralpak IC, λ = 254 nm, 2.5% *i*PrOH/hexane, flow rate = 1.0 mL/min).

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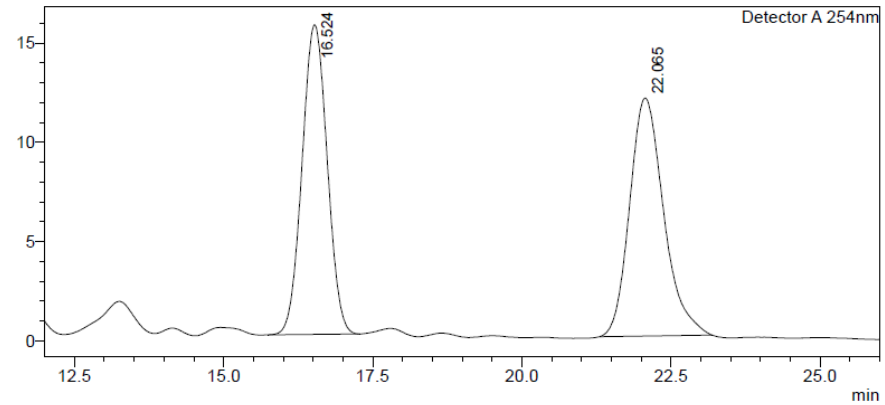
mV



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	16.524	457713	15608	49.016	49.016	
2	22.065	476099	11992	50.984	50.984	
Total		933813	27600	100.000		

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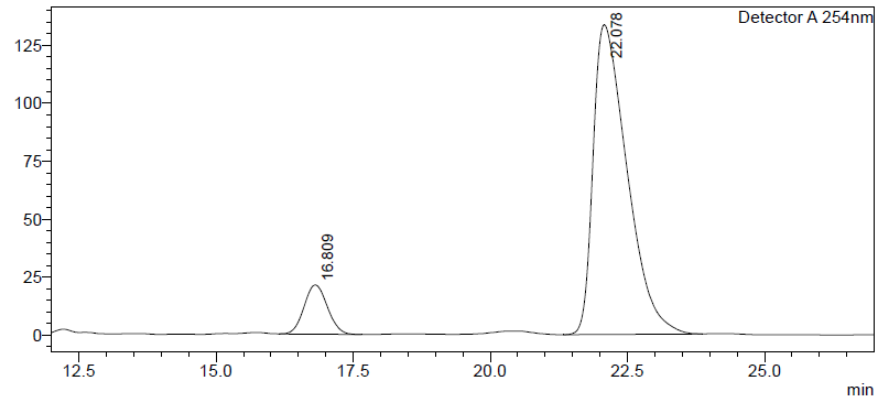
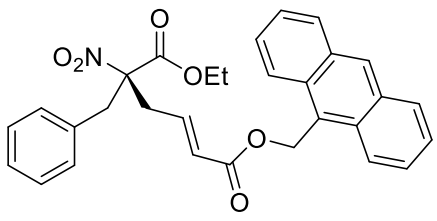


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	16.809	629079	21244	9.858	9.858	
2	22.078	5752404	133580	90.142	90.142	
Total		6381483	154824	100.000		

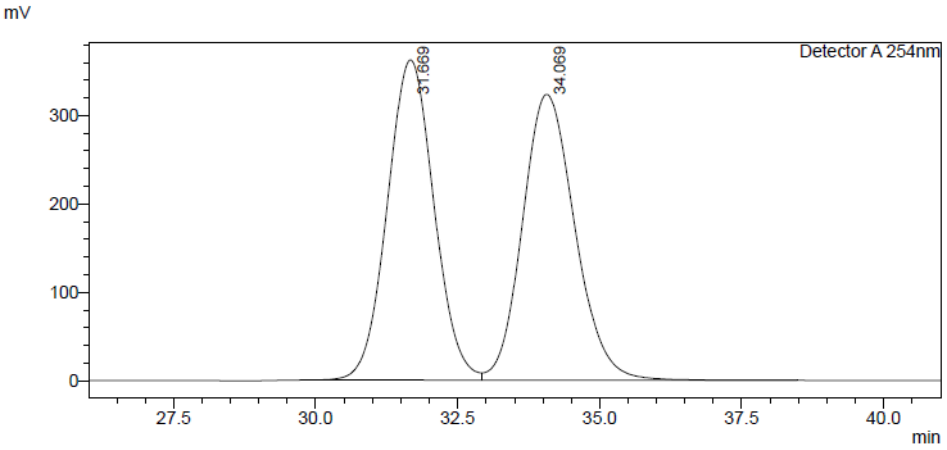


1-(Anthracen-9-ylmethyl) 6-ethyl (*S*,*E*)-5-benzyl-5-nitrohex-2-enedioate (3a-5)

Pale yellow solid; $[\alpha]^{25}_D$ = -4.7 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 8.53 (s, 1H), 8.35 (d, *J* = 9 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.61–7.58 (m, 2H), 7.52–7.49 (m,

2H), 7.26–7.25 (m, 3H), 7.05–7.03 (m, 2H), 6.84 (dt, *J* = 15.0, 7.5 Hz, 1H), 6.24 (s, 2H), 5.95 (d, *J* = 15.5 Hz, 1H), 4.23–4.16 (m, 2H), 3.58 (d, *J* = 14.0 Hz, 1H), 3.45 (d, *J* = 14.5 Hz, 1H), 2.89 (d, *J* = 7.5 Hz, 2H), 1.15 (t, *J* = 7.5 Hz, 3H). ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.73, 165.65, 139.97, 132.54, 131.52, 131.21, 129.98, 129.46, 129.27, 128.99, 128.24, 126.85, 126.59, 126.08, 125.28, 124.03, 95.32, 63.31, 59.24, 40.02, 36.01, 13.82 ppm. HRMS (ESI) m/z calcd for $C_{30}H_{27}NNaO_6$ $[M+Na]^+$ 520.1731, found 520.1736. The *ee* value was 83%, t_R (major) = 35.054 min, t_R (minor) = 32.562 min (Chiralpak IC, λ = 254 nm, 2.5% *i*PrOH/hexane, flow rate = 1.0 mL/min).

<Chromatogram>

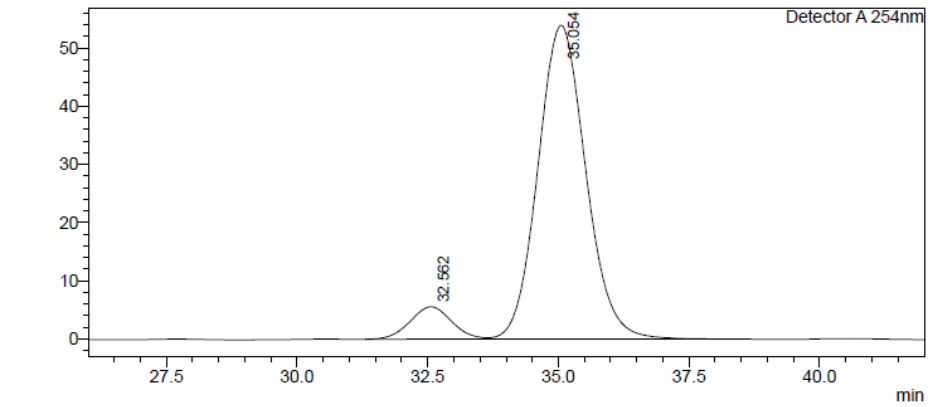


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	31.669	20760269	362171	49.955	49.955	
2	34.069	20797311	323392	50.045	50.045	
Total		41557580	685563	100.000		

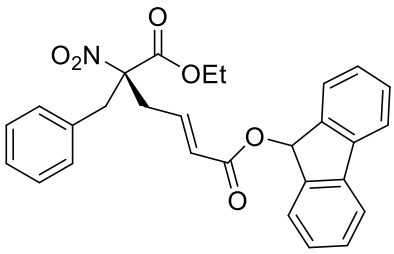
<Chromatogram>



<Peak Table>

Detector A 254nm

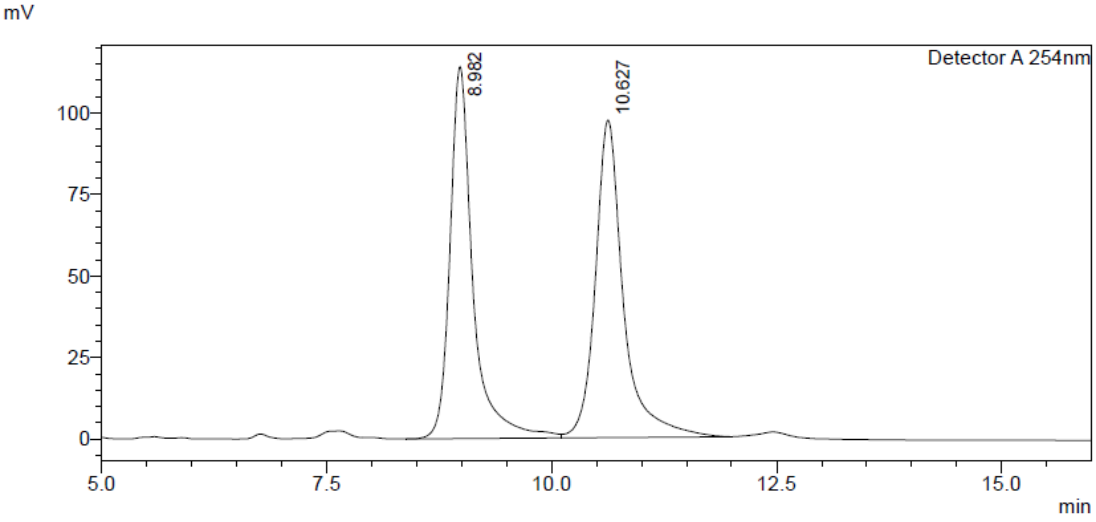
Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	32.562	307533	5556	8.220	8.220	
2	35.054	3433724	53907	91.780	91.780	
Total		3741257	59463	100.000		



6-Ethyl 1-(9*H*-fluoren-9-yl) (*S*,*E*)-5-benzyl-5-nitrohex-2-enedioate (3a-6)

Colourless oil; $[\alpha]^{25}_{D}$ = -5.5 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.31–7.28 (m, 5H), 7.10–7.08 (m, 2H), 6.92 (dt, *J* = 15.0, 7.5 Hz, 1H), 6.86 (s, 1H), 6.04 (d, *J* = 15.5 Hz, 1H), 4.31–4.22 (m, 2H), 3.63 (d, *J* = 14.0 Hz, 1H), 3.51 (d, *J* = 14.0 Hz, 1H), 2.96 (d, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.18, 165.77, 142.00, 141.20, 140.39, 132.57, 130.04, 129.72, 129.05, 128.31, 128.03, 126.58, 126.11, 126.10, 120.20, 95.37, 75.55, 63.37, 40.17, 36.20, 13.94 ppm. HRMS (ESI) m/z calcd for $C_{28}H_{25}NNaO_6$ $[M+Na]^+$ 494.1574, found 494.1577. The *ee* value was 83%, t_R (major) = 9.039 min, t_R (minor) = 10.727 min (Chiralpak IA, λ = 254 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

<Chromatogram>

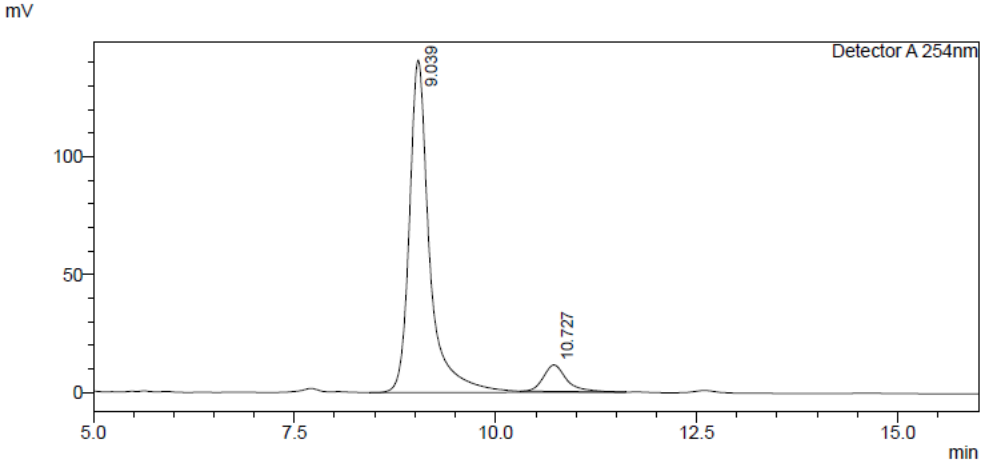


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	8.982	2029242	114076	49.001	49.001	
2	10.627	2111962	97395	50.999	50.999	
Total		4141203	211471	100.000		

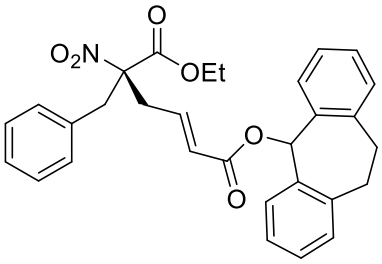
<Chromatogram>



<Peak Table>

Detector A 254nm

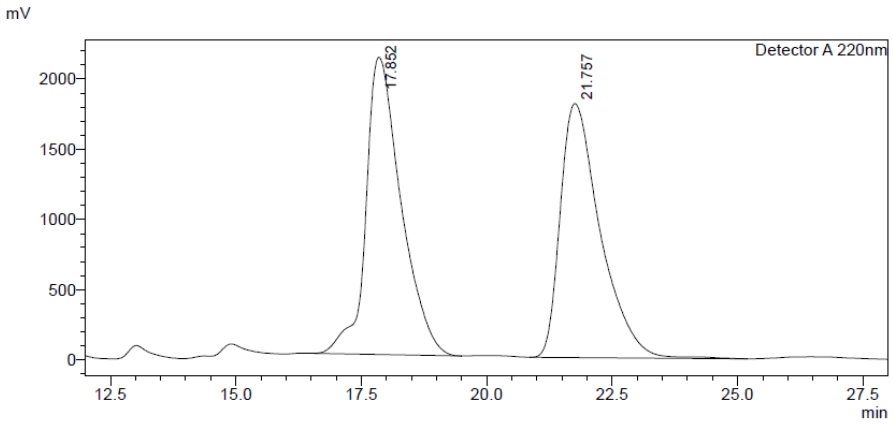
Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	9.039	2489900	140837	91.736	91.736	
2	10.727	224315	11197	8.264	8.264	
Total		2714215	152034	100.000		



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-benzyl-5-nitrohex-2-enedioate (3a-7)

Colourless oil; $[\alpha]^{25}_{D}$ = -2.9 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.43 (m, 2H), 7.30–7.24 (m, 5H), 7.20–7.17 (m, 4H), 7.08–7.06 (m, 2H), 6.95 (s, 1H), 6.83 (dt, *J* = 15.0, 7.5 Hz, 1H), 5.98 (dt, *J* = 15.5, 1.0 Hz, 1H), 4.28–4.18 (m, 2H), 3.60 (d, *J* = 14.0 Hz, 1H), 3.60–3.54 (m, 2H), 3.47 (d, *J* = 14.5 Hz, 1H), 3.08–3.02 (m, 2H), 2.92 (dt, *J* = 8.0, 1.5 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.79, 164.31, 140.25, 139.78, 136.49, 132.57, 130.49, 130.01, 129.97, 129.01, 128.27, 126.99, 126.31, 95.35, 79.68, 63.34, 40.12, 36.06, 32.52, 13.85 ppm. HRMS (ESI) m/z calcd for $C_{30}H_{29}NNaO_6$ $[M+Na]^+$ 522.1887, found 522.1877. The *ee* value was 90%, t_R (major) = 18.458 min, t_R (minor) = 22.496 min (Chiralpak IC, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

<Chromatogram>

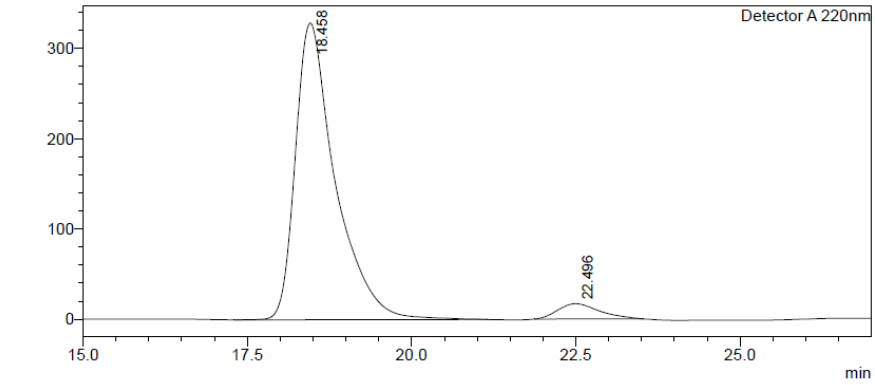


<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.	Name
1	17.852	103623724	2115446	50.795	50.795	
2	21.757	100380178	1808203	49.205	49.205	
Total		204003902	3923649	100.000		

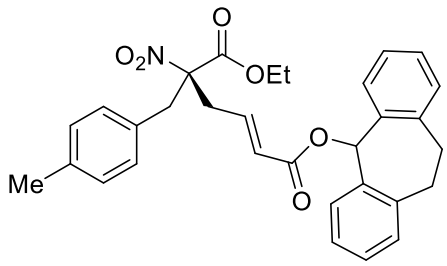
<Chromatogram>



<Peak Table>

Detector A 220nm

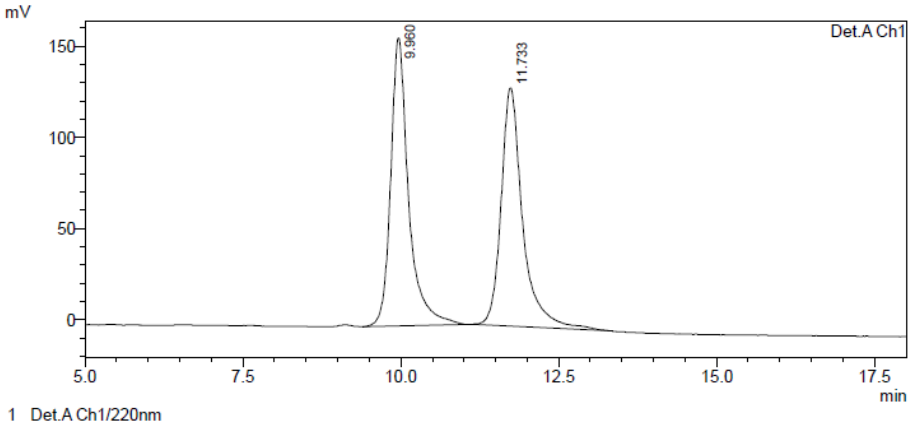
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Height%	Area%
1	18.458	13899189	328840	94.859		M	95.074	94.859
2	22.496	753334	17039	5.141		M	4.926	5.141
Total		14652523	345879				100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-(4-methylbenzyl)-5-nitrohex-2-enedioate (3b)

Colourless oil; $[\alpha]^{25}_{D}$ = -4.4 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (d, J = 7.5 Hz, 2H), 7.27–7.24 (m, 2H), 7.20–7.17 (m, 4H), 7.10 (d, J = 7.5 Hz, 2H), 6.96–6.94 (m, 3H), 6.83 (dt, J = 15.0, 7.5 Hz, 1H), 5.97 (d, J = 15.5 Hz, 1H), 4.26–4.20 (m, 2H), 3.60–3.54 (m, 2H), 3.57 (d, J = 14.5 Hz, 1H), 3.43 (d, J = 14.5 Hz, 1H), 3.08–3.02 (m, 2H), 2.92–2.90 (m, 2H), 2.31 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H) ppm. ^{13}C

NMR (125 MHz, $CDCl_3$): δ = 165.84, 164.33, 140.23, 139.90, 138.04, 136.49, 130.48, 129.96, 129.84, 129.70, 129.38, 128.99, 126.91, 126.30, 95.40, 79.64, 63.28, 39.73, 35.98, 32.51, 21.18, 13.86 ppm. HRMS (ESI) m/z calcd for $C_{31}H_{31}NNaO_6$ $[M+Na]^+$ 536.2044, found 536.2036. The *ee* value was 90%, t_R (major) = 9.987 min, t_R (minor) = 11.792 min (Chiralpak IA, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

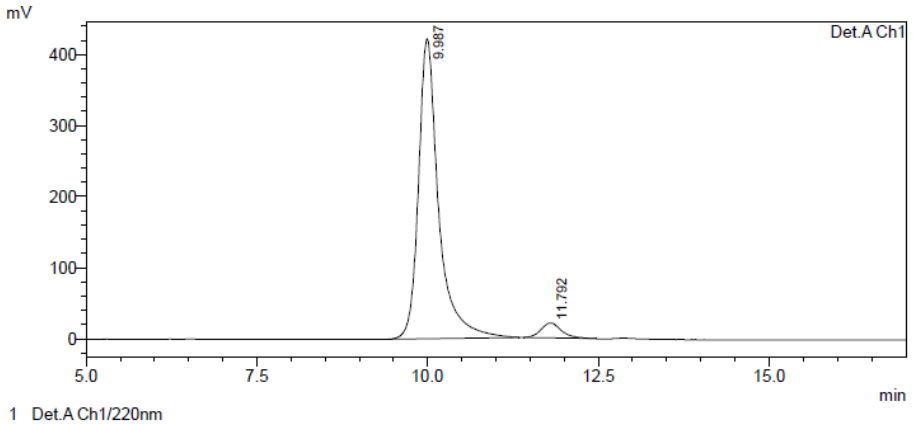


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.960	3118924	157876	50.164	54.703
2	11.733	3098548	130731	49.836	45.297
Total		6217473	288607	100.000	100.000

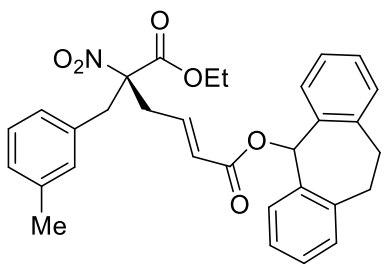


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

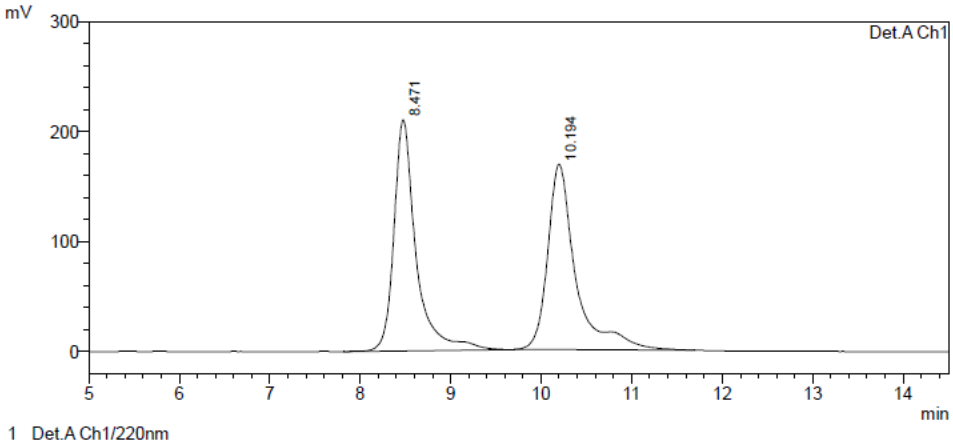
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.987	8665485	421992	95.263	95.290
2	11.792	430898	20859	4.737	4.710
Total		9096382	442851	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-(3-methylbenzyl)-5-nitrohex-2-enedioate (3c)

Colourless oil; $[\alpha]^{25}_D$ = -5.3 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.43 (m, 2H),

7.27–7.24 (m, 2H), 7.20–7.16 (m, 5H), 7.09 (d, J = 7.5 Hz, 1H), 6.95 (s, 1H), 6.87–6.80 (m, 3H), 5.96 (d, J = 15.5 Hz, 1H), 4.26–4.20 (m, 2H), 3.60–3.53 (m, 2H), 3.56 (d, J = 14.5 Hz, 1H), 3.44 (d, J = 14.5 Hz, 1H), 3.08–3.02 (m, 2H), 2.91 (d, J = 7.5 Hz, 2H), 2.29 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.84, 164.33, 140.23, 139.89, 138.69, 136.50, 132.45, 130.73, 130.49, 129.94, 129.01, 128.99, 128.87, 127.02, 126.96, 126.31, 95.39, 79.64, 63.30, 40.05, 36.09, 32.52, 21.45, 13.87 ppm. HRMS (ESI) m/z calcd for $C_{31}H_{31}NNaO_6$ $[M+Na]^+$ 536.2044, found 536.2049. The *ee* value was 89%, t_R (major) = 8.457 min, t_R (minor) = 10.187 min (Chiralpak IA, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

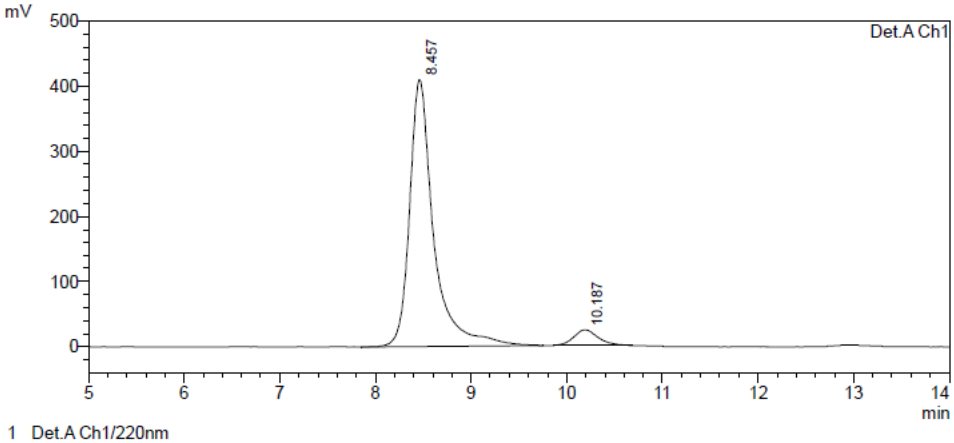


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.471	3572107	210350	49.270	55.447
2	10.194	3678008	169021	50.730	44.553
Total		7250115	379372	100.000	100.000

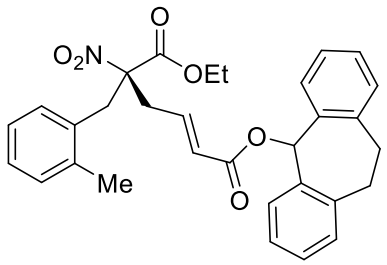


1 Det.A Ch1/220nm

PeakTable

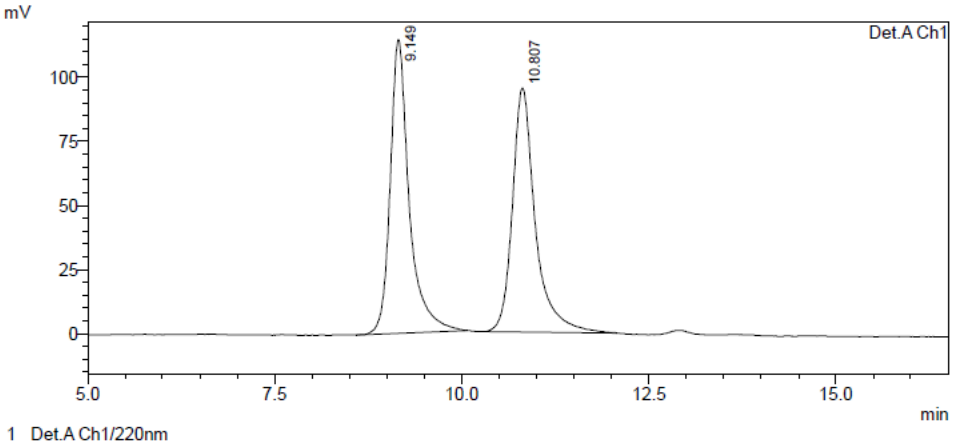
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.457	7146978	409594	94.504	94.549
2	10.187	415653	23614	5.496	5.451
Total		7562630	433208	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-(2-methylbenzyl)-5-nitrohex-2-enedioate (3d)

Colourless oil; $[\alpha]^{25}_{D}$ = -6.9 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.5 Hz, 2H), 7.26–7.23 (m, 2H), 7.20–7.09 (m, 7H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.94 (s, 1H), 6.83 (dt, *J* = 15.0, 7.5 Hz, 1H), 5.91 (d, *J* = 15.5 Hz, 1H), 4.25–4.14 (m, 2H), 3.69–3.61 (m, 2H), 3.58–3.52 (m, 2H), 3.07–3.01 (m, 2H), 2.99–2.90 (m, 2H), 2.26 (s, 3H), 1.15 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.12, 164.27, 140.20, 140.06, 137.49, 136.52, 131.25, 131.20, 130.46, 130.10, 129.88, 128.95, 128.11, 126.67, 126.44, 126.29, 95.59, 79.50, 63.33, 36.81, 36.64, 32.52, 19.90, 13.76 ppm. HRMS (ESI) m/z calcd for $C_{31}H_{31}NNaO_6$ $[M+Na]^+$ 536.2044, found 536.2041. The *ee* value was 90%, t_R (major) = 9.124 min, t_R (minor) = 10.771 min (Chiralpak IA, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

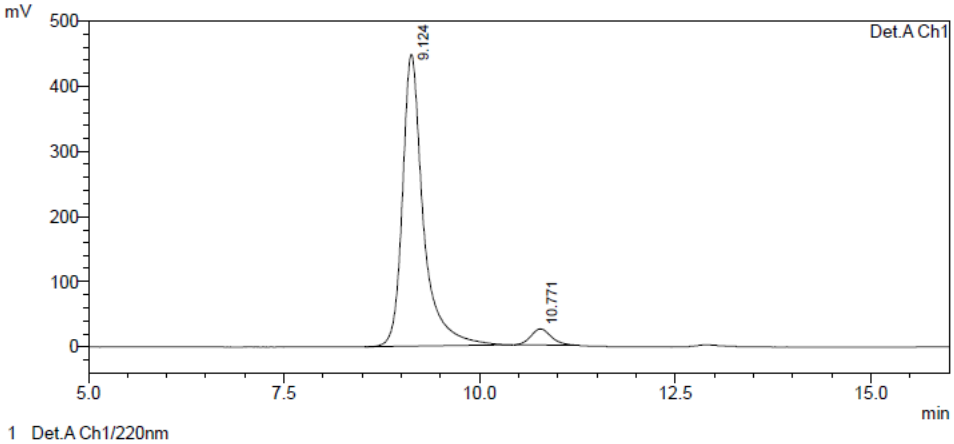


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.149	2029311	114503	50.032	54.585
2	10.807	2026690	95267	49.968	45.415
Total		4056001	209769	100.000	100.000

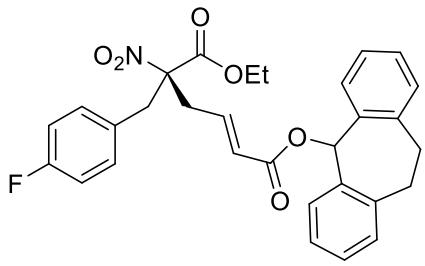


1 Det.A Ch1/220nm

PeakTable

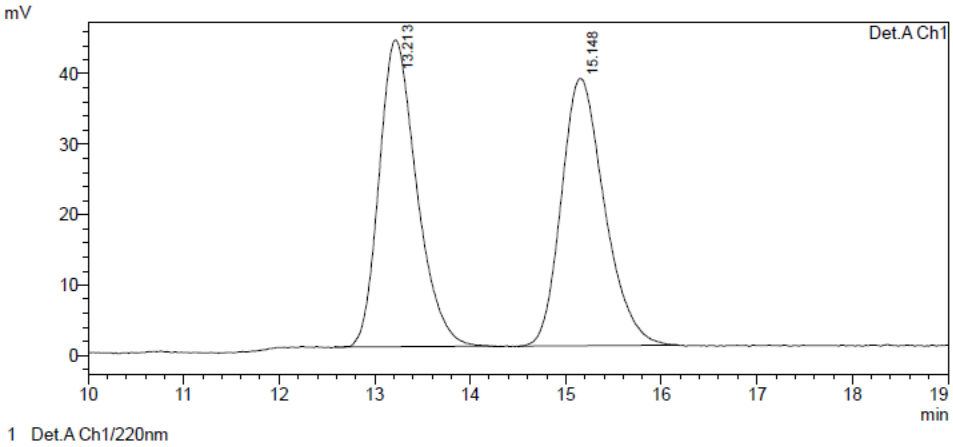
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.124	8336038	448196	94.910	94.770
2	10.771	447017	24732	5.090	5.230
Total		8783055	472928	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-(4-fluorobenzyl)-5-nitrohex-2-enedioate (3e)

Colourless oil; $[\alpha]^{25}_{D}$ = -5.5 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.42 (m, 2H), 7.27–7.24 (m, 2H), 7.19 (d, J = 7.0 Hz, 4H), 7.06–7.03 (m, 2H), 7.00–6.96 (m, 2H), 6.94 (s, 1H), 6.80 (dt, J = 15.0, 7.5 Hz, 1H), 5.98 (d, J = 15.5 Hz, 1H), 4.26–4.19 (m, 2H), 3.60–3.65 (m, 2H), 3.56 (d, J = 14.5 Hz, 1H), 3.43 (d, J = 14.5 Hz, 1H), 3.07–3.01 (m, 2H), 2.96–2.86 (m, 2H), 1.19 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.67, 164.27, 162.29 (d, J = 246.3 Hz), 140.29, 139.51, 136.43, 131.66 (d, J = 8.8 Hz), 130.50, 130.05 (d, J = 1.3 Hz), 129.04, 128.08, 127.12, 126.33, 116.00 (d, J = 21.3 Hz), 95.21, 79.82, 63.43, 39.36, 36.09, 32.53, 13.86 ppm. HRMS (ESI) m/z calcd for $C_{30}H_{28}FNNaO_6$ $[M+Na]^+$ 540.1793, found 540.1792. The *ee* value was 87%, t_R (major) = 13.152 min, t_R (minor) = 15.077 min (Chiralpak IC, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

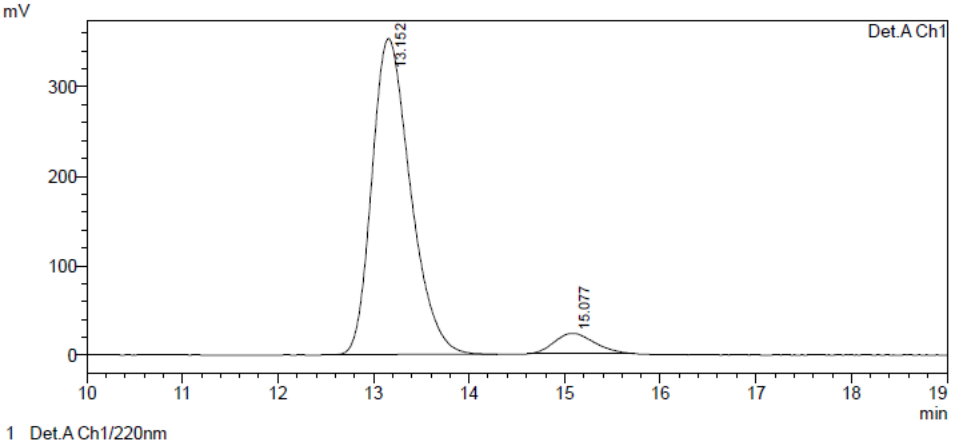


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.213	1193400	43543	50.050	53.426
2	15.148	1190995	37958	49.950	46.574
Total		2384395	81501	100.000	100.000

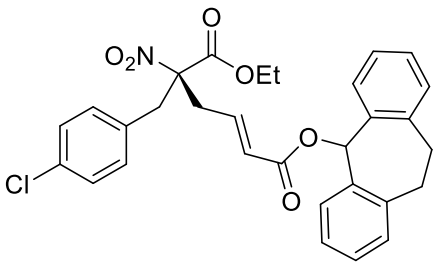


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

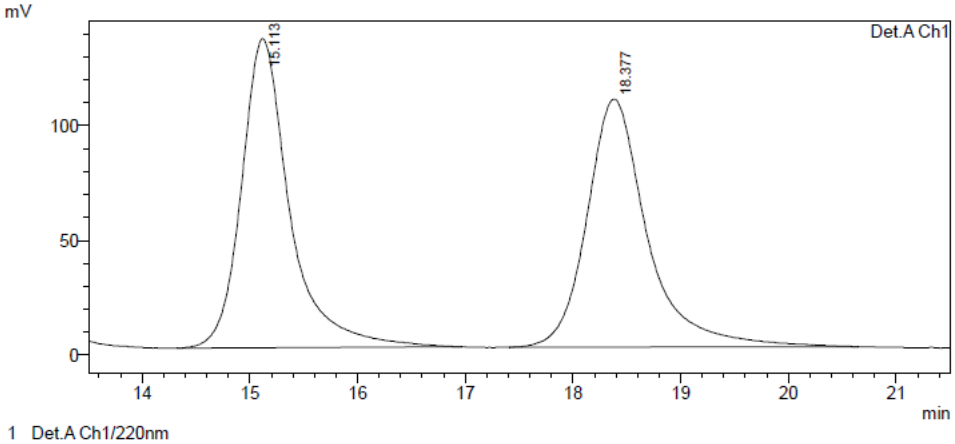
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.152	9922485	353510	93.687	93.940
2	15.077	668616	22806	6.313	6.060
Total		10591101	376316	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-(4-chlorobenzyl)-5-nitrohex-2-enedioate (3f)

Colourless oil; $[\alpha]^{25}_{D}$ = -1.5 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, J = 7.5 Hz, 2H), 7.26–7.25 (m, 4H), 7.19 (d, J = 7.5 Hz, 4H), 7.00 (d, J = 8.5 Hz, 2H), 6.95 (s, 1H), 6.80 (dt, J = 15.0, 7.5 Hz, 1H), 5.98 (d, J = 15.5 Hz, 1H), 4.27–4.20 (m, 2H), 3.60–3.55 (m, 2H), 3.56 (d, J = 14.5 Hz, 1H), 3.43 (d, J = 14.5 Hz, 1H), 3.08–3.02 (m, 2H), 2.96–2.86 (m, 2H), 1.19 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.58, 164.25, 140.29, 139.40, 136.42, 134.42, 131.34, 130.50, 130.05, 129.22,

129.04, 128.08, 127.18, 126.32, 95.08, 79.84, 63.48, 39.47, 36.10, 32.53, 13.86 ppm. HRMS (ESI) m/z calcd for $C_{30}H_{28}{}^{35}ClNNaO_6$ $[M+Na]^+$ 556.1497, found 556.1487, $C_{30}H_{28}{}^{37}ClNNaO_6$ $[M+Na]^+$ 557.1531, found 557.1538. The *ee* value was 86%, t_R (major) = 14.471 min, t_R (minor) = 17.427 min (Chiralpak IA, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

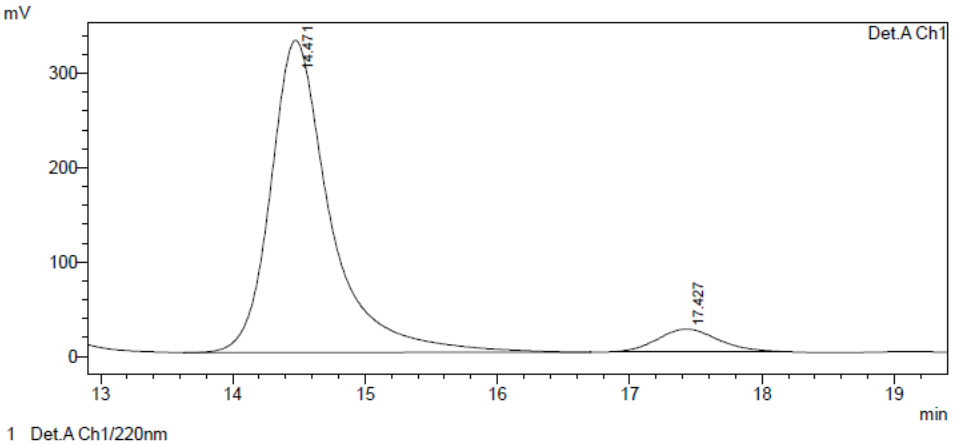


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.113	4223399	134715	49.973	55.487
2	18.377	4227895	108070	50.027	44.513
Total		8451294	242785	100.000	100.000

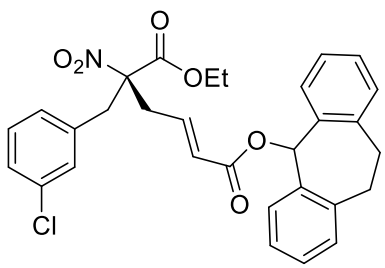


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

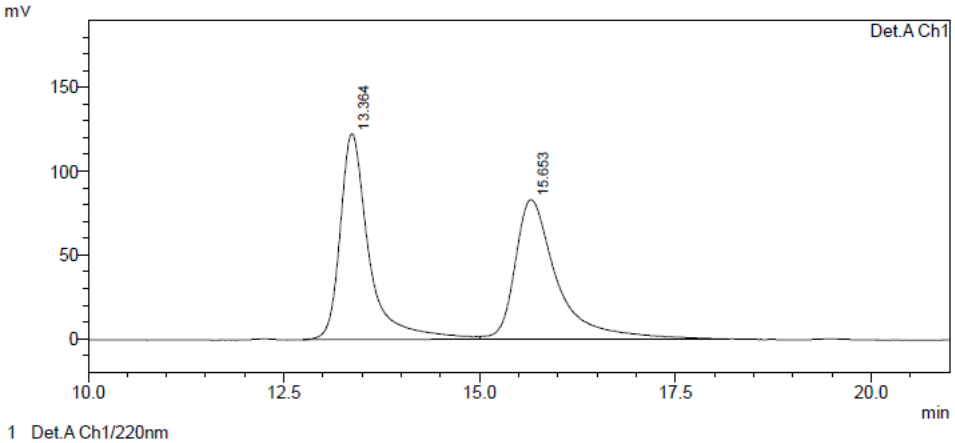
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.471	10413879	331131	93.193	93.243
2	17.427	760665	23997	6.807	6.757
Total		11174544	355128	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-(3-chlorobenzyl)-5-nitrohex-2-enedioate (3g)

Colourless oil; $[\alpha]^{25}_D$ = -6.3 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.42 (m, 2H),

7.27–7.22 (m, 4H), 7.19 (d, *J* = 7.0 Hz, 4H), 7.08 (s, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.94 (s, 1H), 6.79 (dt, *J* = 15.0, 7.5 Hz, 1H), 5.98 (d, *J* = 15.5 Hz, 1H), 4.28–4.19 (m, 2H), 3.60–3.55 (m, 2H), 3.55 (d, *J* = 14.5 Hz, 1H), 3.45 (d, *J* = 14.5 Hz, 1H), 3.07–3.02 (m, 2H), 2.92 (d, *J* = 7.5 Hz, 2H), 1.20 (t, *J* = 7.0 Hz, 3H). ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.53, 164.23, 140.27, 139.34, 136.45, 134.83, 134.59, 130.50, 130.26, 130.19, 130.00, 129.02, 128.55, 128.19, 127.25, 126.32, 95.05, 79.78, 63.53, 39.70, 36.24, 32.53, 13.86 ppm. HRMS (ESI) m/z calcd for $C_{30}H_{28}{}^{35}ClNNaO_6$ $[M+Na]^+$ 556.1497, found 556.1501, $C_{30}H_{28}{}^{37}ClNNaO_6$ $[M+Na]^+$ 557.1531, found 557.1528. The *ee* value was 87%, t_R (minor) = 13.456 min, t_R (major) = 15.758 min (Chiralpak IF, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

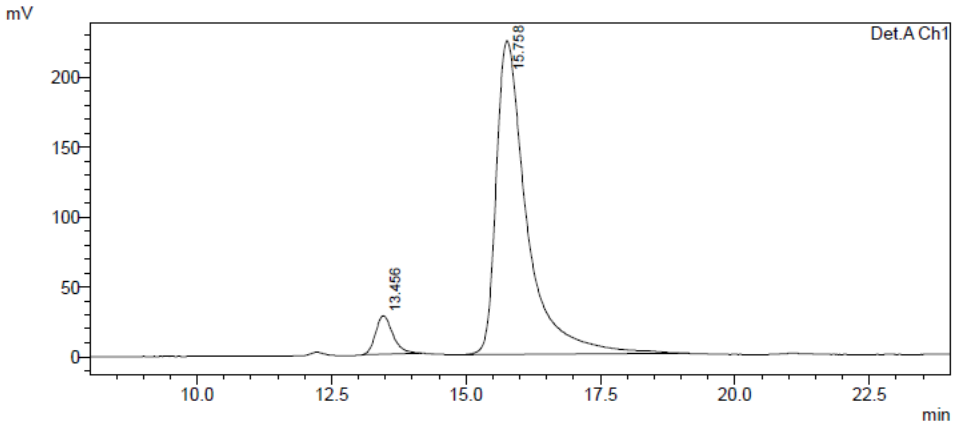


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.364	3164540	122972	50.352	59.584
2	15.653	3120304	83413	49.648	40.416
Total		6284844	206385	100.000	100.000

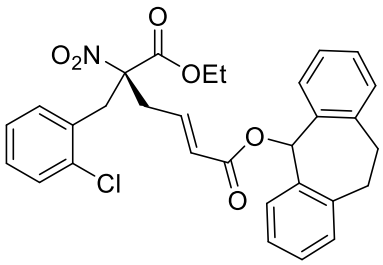


1 Det.A Ch1/220nm

PeakTable

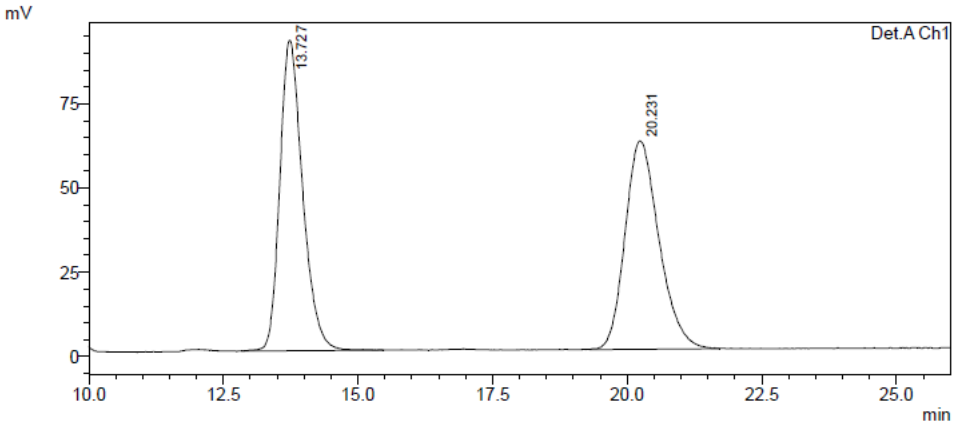
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.456	616064	27527	6.457	10.924
2	15.758	8925456	224465	93.543	89.076
Total		9541520	251991	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-(2-chlorobenzyl)-5-nitrohex-2-enedioate (3h)

Colourless oil; $[\alpha]^{25}_{D}$ = -3.1 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.0 Hz, 2H), 7.36–7.34 (m, 1H), 7.26–7.23 (m, 2H), 7.20–7.15 (m, 6H), 7.12–7.10 (m, 1H), 6.93 (s, 1H), 6.87 (dt, J = 15.0, 7.5 Hz, 1H), 5.92 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.26–4.16 (m, 2H), 3.87 (d, *J* = 15.0 Hz, 1H), 3.74 (d, *J* = 15.0 Hz, 1H), 3.58–3.51 (m, 2H), 3.07–3.01 (m, 2H), 2.97 (dt, *J* = 7.5, 1.5 Hz, 2H), 1.15 (t, *J* = 7.0 Hz, 3H).ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.71, 164.27, 140.17, 140.10, 136.58, 135.36, 131.53, 131.05, 130.44, 130.13, 129.82, 129.67, 128.92, 127.47, 126.55, 126.28, 95.61, 79.37, 63.45, 37.07, 36.45, 32.52, 13.77 ppm. HRMS (ESI) m/z calcd for $C_{30}H_{28}{}^{35}ClNNaO_6$ $[M+Na]^+$ 556.1497, found 556.1493, $C_{30}H_{28}{}^{37}ClNNaO_6$ $[M+Na]^+$ 557.1531, found 557.1531. The *ee* value was 81%, t_R (major) = 13.677 min, t_R (minor) = 20.152 min (Chiralpak IC, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

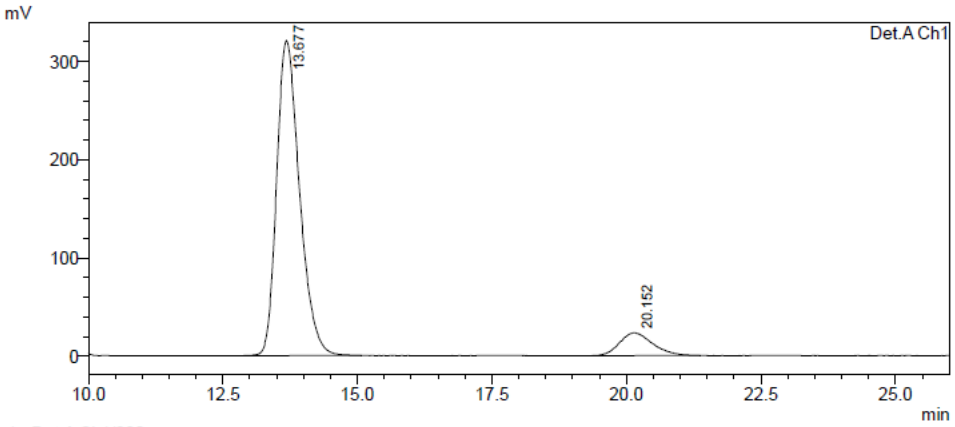


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.727	2724415	92080	50.121	59.826
2	20.231	2711304	61833	49.879	40.174
Total		5435719	153913	100.000	100.000

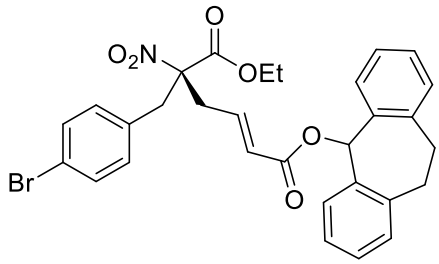


1 Det.A Ch1/220nm

PeakTable

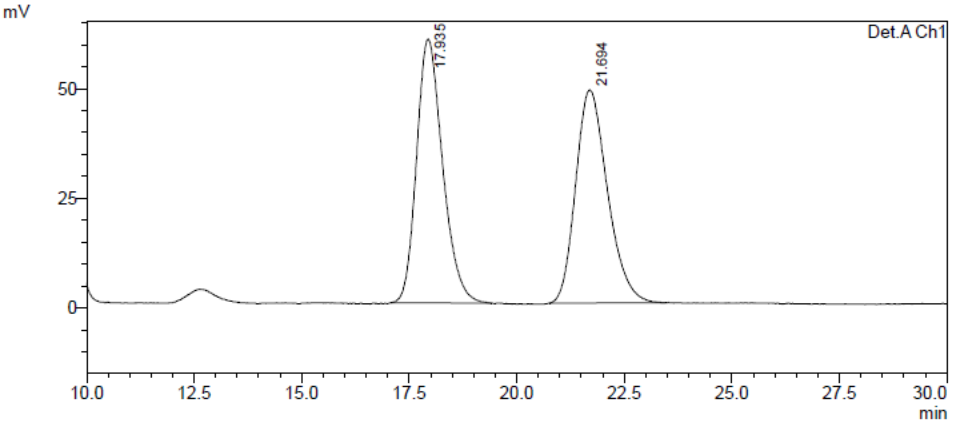
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.677	9487178	320623	90.508	93.273
2	20.152	994917	23124	9.492	6.727
Total		10482094	343747	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-(4-bromobenzyl)-5nitrohex-2-enedioate (3i)

Colourless oil; $[\alpha]^{25}_{D}$ = -1.6 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56–7.55 (m, 1H), 7.52–7.51 (m, 1H), 7.45–7.43 (m, 2H), 7.37–7.34 (m, 1H), 7.27–7.24 (m, 1H), 7.19 (d, *J* = 7.0 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.95 (s, 1H), 6.86 (dt, *J* = 15.5, 7.5 Hz, 1H), 6.00 (d, *J* = 16.0 Hz, 1H), 4.29–4.20 (m, 2H), 3.64 (d, *J* = 14.5 Hz, 1H), 3.60–3.55 (m, 2H), 3.51 (d, *J* = 14.5 Hz, 1H), 3.07–3.02 (m, 2H), 2.07–2.95 (m, 2H), 1.20 (t, *J* = 7.0 Hz, 3H).ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.81, 164.33, 141.19, 140.26, 139.78, 136.50, 131.51, 130.60, 129.99, 128.96, 128.09, 127.69, 127.17, 126.33, 95.35, 79.73, 63.40, 39.81, 36.13, 32.53, 13.89 ppm. HRMS (ESI) m/z calcd for $C_{30}H_{28}{}^{79}BrNNaO_6$ $[M+Na]^+$ 600.0992, found 600.0996, $C_{30}H_{28}{}^{81}BrNNaO_6$ $[M+Na]^+$ 602.0972, found 602.0979. The *ee* value was 86%, t_R (minor) = 18.335 min, t_R (major) = 22.068 min (Chiralpak IC, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

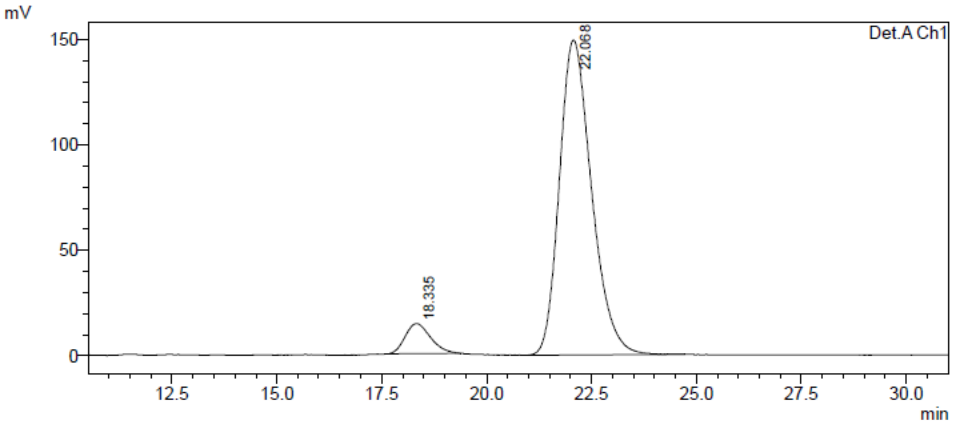


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.935	2542231	60126	50.385	55.310
2	21.694	2503366	48581	49.615	44.690
Total		5045597	108706	100.000	100.000

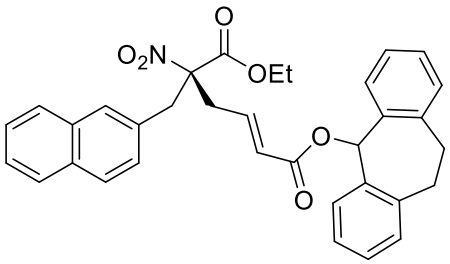


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

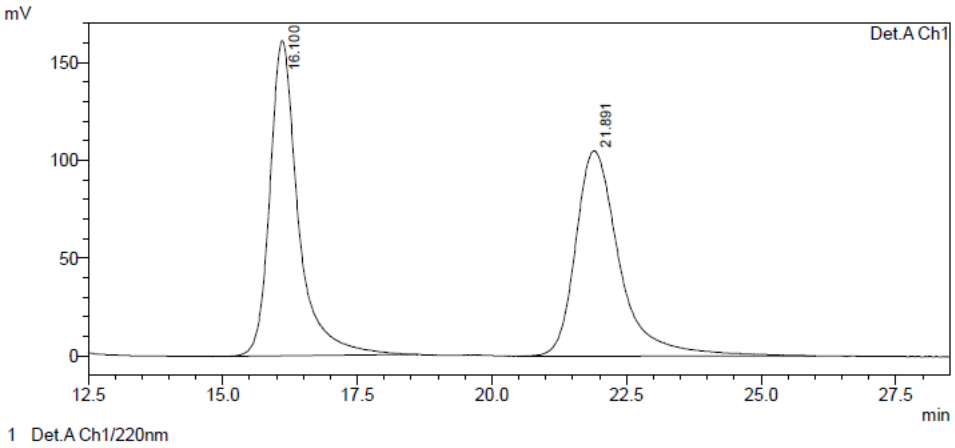
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.335	591284	14157	6.901	8.665
2	22.068	7976990	149231	93.099	91.335
Total		8568274	163388	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-(naphthalen-2-ylmethyl)-5-nitrohex-2-enedioate (3j)

Colourless oil; $[\alpha]^{25}_{D}$ = -3.8 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.0 Hz, 1H), 7.56 (s, 1H), 7.50–7.44 (m, 4H), 7.28–7.25 (m, 2H), 7.21–7.15 (m, 7H), 6.97 (s, 1H), 6.89 (dt, J = 15.0, 7.5 Hz, 1H), 5.99 (d, J = 14.5 Hz, 1H), 4.25 (q, J = 7.0 Hz, 2H), 3.78 (d, J = 14.5 Hz, 1H), 3.65 (d, J = 14.5 Hz, 1H), 3.61–3.56 (m, 2H), 3.08–3.03 (m, 2H), 2.95 (d, J = 7.5 Hz, 2H), 1.19 (t, J = 7.0 Hz, 3H).ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.83, 164.33, 140.24, 139.78, 136.51, 133.40, 132.95, 130.50,

129.96, 129.39, 129.01, 128.78, 128.07, 127.86, 127.77, 127.38, 127.10, 126.63, 126.51, 126.32, 95.41, 79.69, 63.40, 40.28, 36.20, 32.53, 13.88 ppm. HRMS (ESI) m/z calcd for $C_{34}H_{31}NNaO_6$ $[M+Na]^+$ 572.2044, found 572.2049. The *ee* value was 87%, t_R (major) = 16.090 min, t_R (minor) = 21.884 min (Chiralpak IA, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

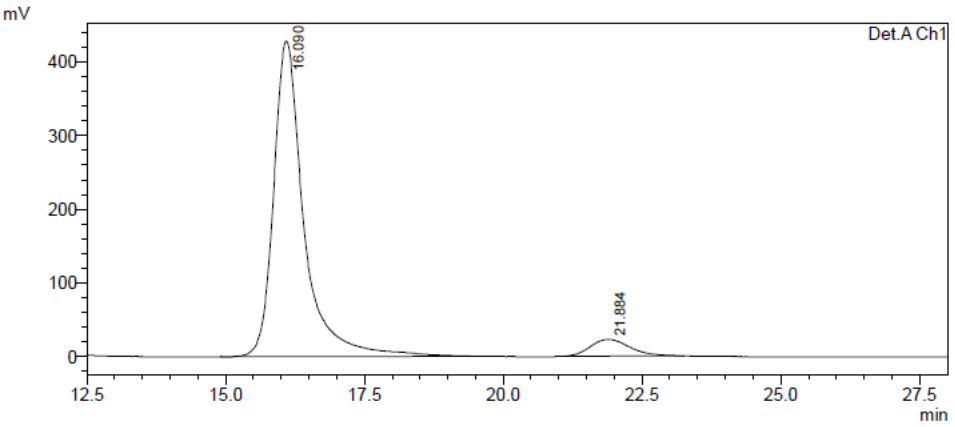


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.100	5941399	160974	49.904	60.562
2	21.891	5964232	104827	50.096	39.438
Total		11905631	265801	100.000	100.000

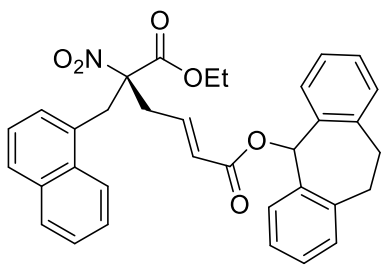


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

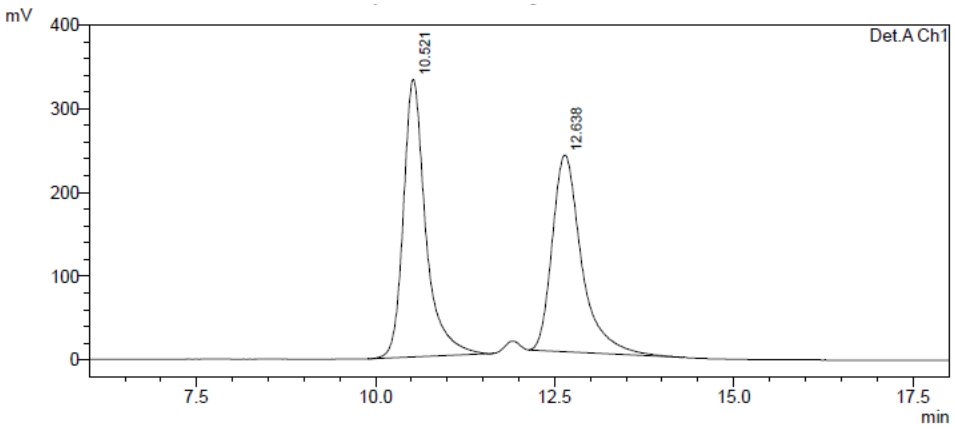
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.090	16296595	428191	93.521	94.955
2	21.884	1129056	22748	6.479	5.045
Total		17425651	450939	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-(naphthalen-1-ylmethyl)-5-nitrohex-2-enedioate (3k)

Colourless oil; $[\alpha]^{25}_D$ = -2.8 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.94–7.92 (m, 1H),

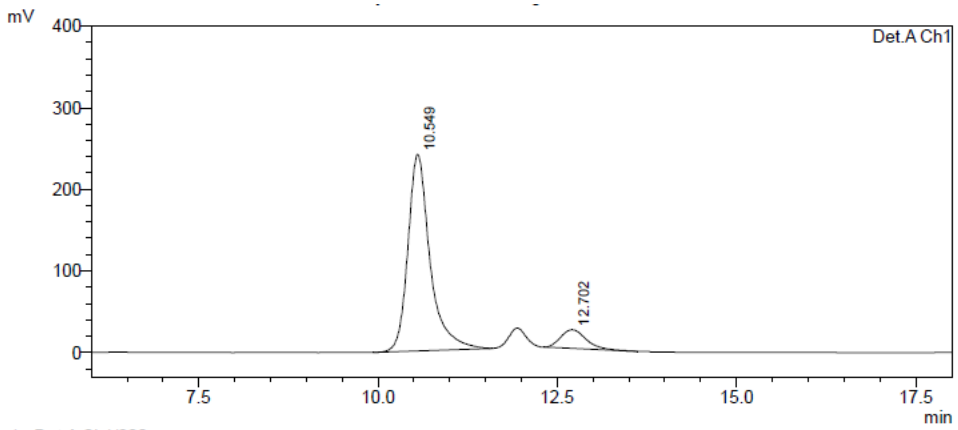
7.83–7.81 (m, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.48–7.40 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.28–7.22 (m, 2H), 7.21–7.16 (m, 6H), 6.93 (s, 1H), 6.80 (dt, *J* = 15.0, 7.5 Hz, 1H), 5.79 (d, *J* = 15.5 Hz, 1H), 4.15 (d, *J* = 15.0 Hz, 1H), 4.15–4.06 (m, 2H), 4.02 (d, *J* = 15.0 Hz, 1H), 3.57–3.52 (m, 2H), 3.06–3.01 (m, 2H), 2.90 (d, *J* = 7.0 Hz, 2H), 1.08 (t, *J* = 7.0 Hz, 3H).ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.09, 164.26, 140.24, 139.94, 136.56, 134.05, 132.61, 130.46, 130.31, 129.93, 128.97, 128.51, 128.09, 127.19, 126.70, 126.59, 126.30, 126.06, 125.43, 123.24, 95.90, 79.48, 63.37, 36.81, 35.88, 32.54, 13.66 ppm. HRMS (ESI) m/z calcd for $C_{34}H_{31}NNaO_6$ $[M+Na]^+$ 572.2044, found 572.2038. The *ee* value was 80%, t_R (major) = 10.549 min, t_R (minor) = 12.702 min (Chiralpak IA, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.521	7222507	332029	51.811	58.578
2	12.638	6717482	234784	48.189	41.422
Total		13939989	566814	100.000	100.000

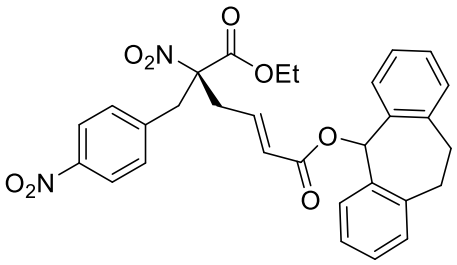


1 Det.A Ch1/220nm

PeakTable

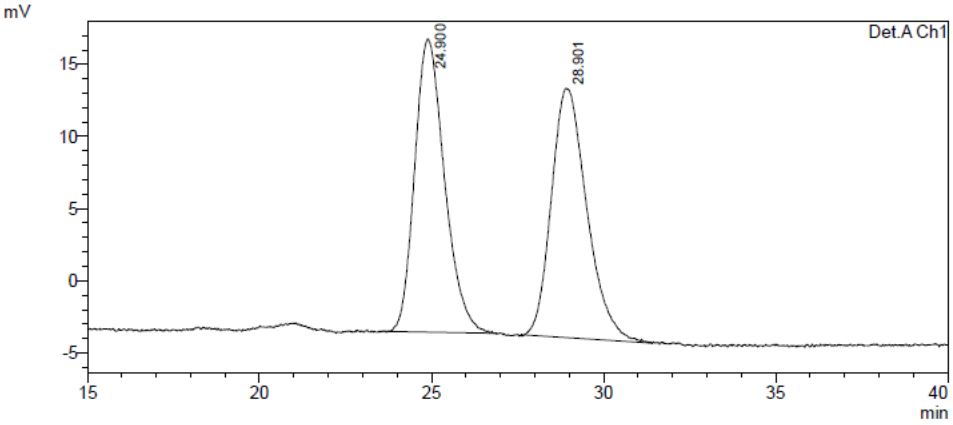
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.549	5174053	240838	90.097	91.298
2	12.702	568686	22956	9.903	8.702
Total		5742739	263794	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-nitro-5-(4-nitrobenzyl)hex-2-enedioate (3l)

Colourless oil; $[\alpha]^{25}_{D}$ = -4.6 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, J = 9.0 Hz, 2H), 7.43 (d, J = 7.5 Hz, 2H), 7.28–7.24 (m, 4H), 7.20–7.17 (m, 4H), 6.94 (s, 1H), 6.78 (dt, J = 15.0, 7.5 Hz, 1H), 5.99 (d, J = 15.5 Hz, 1H), 4.27–4.20 (m, 2H), 3.67 (d, J = 14.5 Hz, 1H), 3.60–3.55 (m, 2H), 3.54 (d, J = 14.5 Hz, 1H), 3.06–3.01 (m, 2H), 2,99–2.88 (m, 2H), 1.19 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.25, 164.15, 147.96, 140.35, 140.12, 138.78, 136.31, 131.10, 130.53, 130.16, 129.11, 127.56, 126.35, 124.08, 94.75, 80.07, 63.76, 39.79, 36.40, 32.54, 13.86 ppm. HRMS (ESI) m/z calcd for $C_{30}H_{28}N_2NaO8$ $[M+Na]^+$ 567.1738, found 567.1731. The *ee* value was 75%, t_R (minor) = 25.480 min, t_R (major) = 29.696 min (Chiralpak IC, λ = 220 nm, 20.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

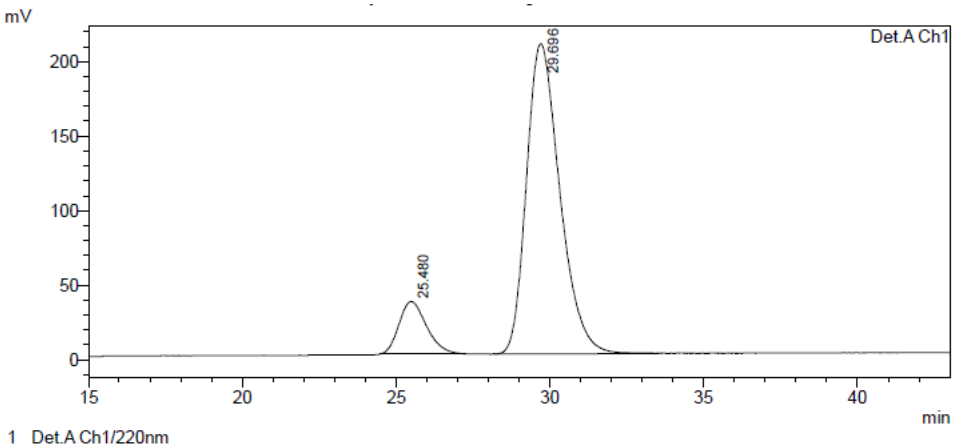


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.900	1230213	20321	49.826	54.049
2	28.901	1238784	17277	50.174	45.951
Total		2468997	37598	100.000	100.000

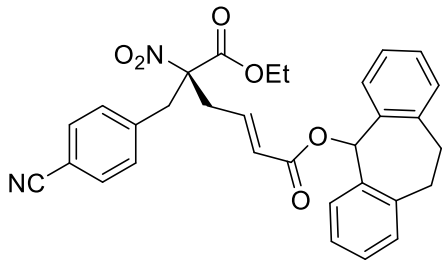


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

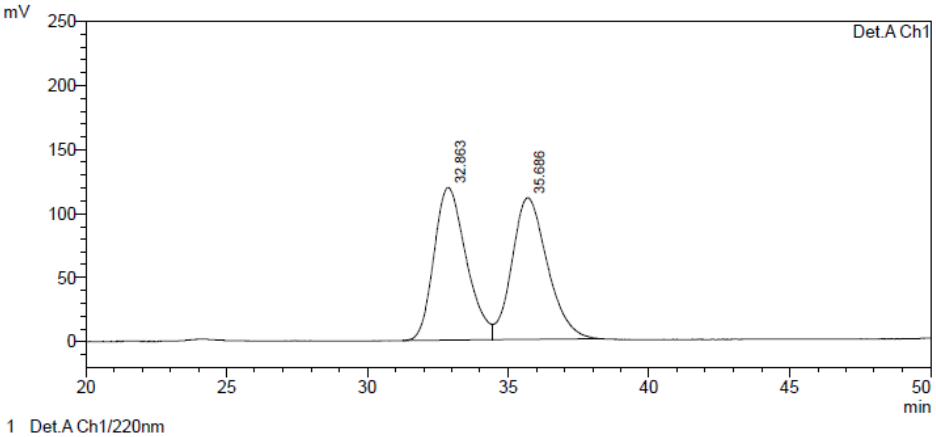
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.480	2206737	35262	12.297	14.484
2	29.696	15738738	208197	87.703	85.516
Total		17945475	243459	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-(4-cyanobenzyl)-5-nitrohex-2-enedioate (3m)

Colourless oil; $[\alpha]^{25}_{D}$ = -4.7 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 7.5 Hz, 2H), 7.28–7.24 (m, 2H), 7.21–7.17 (m, 6H), 6.94 (s, 1H), 6.77 (dt, J = 15.5, 7.5 Hz, 1H), 5.98 (dt, J = 15.5, 1.0 Hz, 1H), 4.27–4.18 (m, 2H), 3.63 (d, J = 14.5 Hz, 1H), 3.60–3.55 (m, 2H), 3.50 (d, J = 14.5 Hz, 1H), 3.07–3.01 (m, 2H), 2.97–2.86 (m, 2H), 1.18 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.29, 164.15, 140.34, 138.87, 138.13, 136.32, 132.67, 130.90, 130.52, 130.15,

129.10, 127.47, 126.33, 118.31, 112.48, 94.77, 80.03, 63.69, 40.06, 36.34, 32.53, 13.84 ppm. HRMS (ESI) m/z calcd for $C_{31}H_{28}N_2NaO_6$ $[M+Na]^+$ 547.1840, found 547.1843. The *ee* value was 76%, t_R (major) = 33.533 min, t_R (minor) = 36.555 min (Chiralpak IC, λ = 220 nm, 20.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

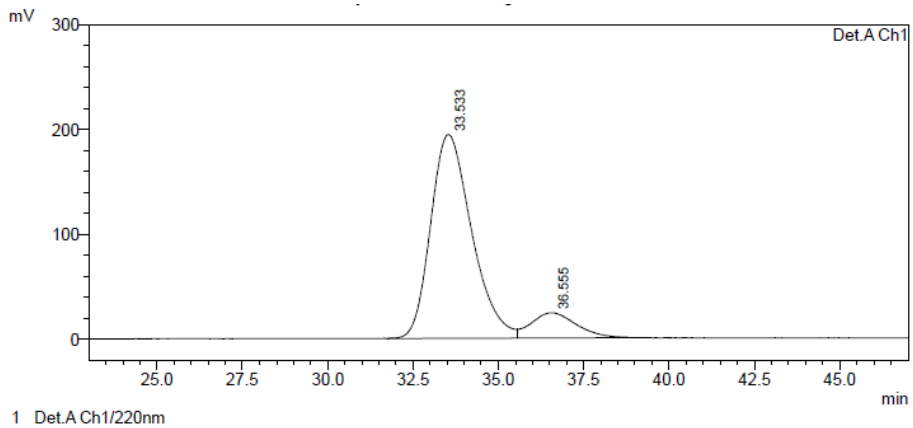


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.863	9533020	119244	49.523	51.847
2	35.686	9716627	110748	50.477	48.153
Total		19249647	229992	100.000	100.000

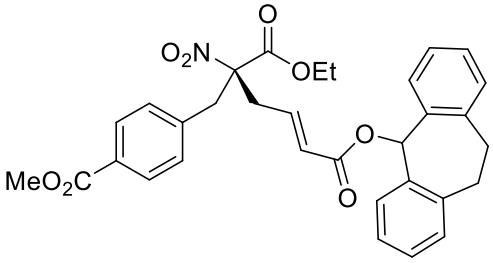


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

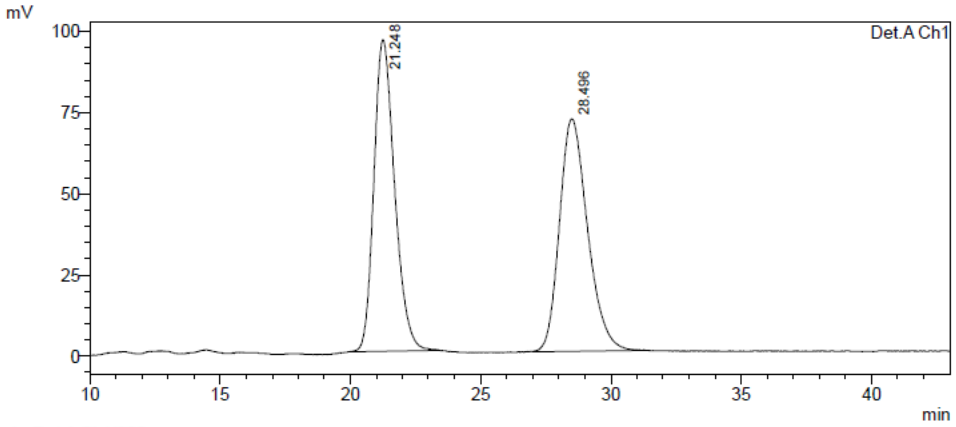
Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.533	16257290	194473	88.072	88.994
2	36.555	2201827	24051	11.928	11.006
Total		18459117	218524	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-(4-(methoxycarbonyl)benzyl)-5-nitrohex-2-enedioate (3n)

Colourless oil; $[\alpha]^{25}_D$ = -3.4 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97 (d, J = 8.0 Hz, 2H), 7.44–7.42 (m, 2H), 7.27–

7.24 (m, 2H), 7.20–7.14 (m, 6H), 6.94 (s, 1H), 6.81 (dt, J = 15.0, 7.5 Hz, 1H), 5.98 (d, J = 15.5 Hz, 1H), 4.26–4.19 (m, 2H), 3.91 (s, 3H), 3.63 (d, J = 14.0 Hz, 1H), 3.60–3.55 (m, 2H), 3.51 (d, J = 14.5 Hz, 1H), 3.06–3.01 (m, 2H), 2.95–2.86 (m, 2H), 1.19 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.63, 165.50, 164.23, 140.28, 139.31, 137.77, 136.41, 130.50, 130.19, 130.11, 130.03, 129.03, 127.28, 126.32, 95.02, 79.84, 63.52, 52.34, 39.97, 36.16, 32.52, 13.85 ppm. HRMS (ESI) m/z calcd for $C_{32}H_{31}NNaO_8$ $[M+Na]^+$ 580.1942, found 580.1936. The *ee* value was 87%, t_R (minor) = 21.168 min, t_R (major) = 28.264 min (Chiralpak IC, λ = 220 nm, 20.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

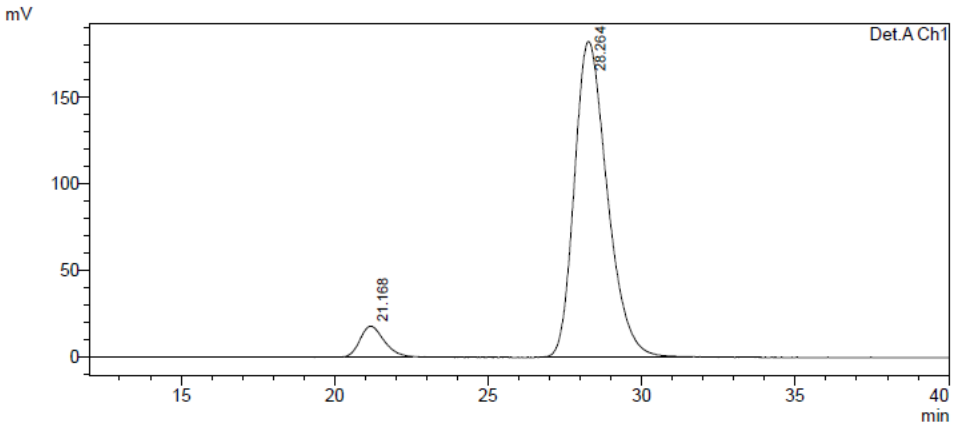


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.248	5324056	95889	49.747	57.268
2	28.496	5378272	71550	50.253	42.732
Total		10702328	167438	100.000	100.000

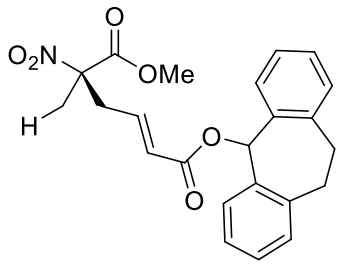


1 Det.A Ch1/220nm

PeakTable

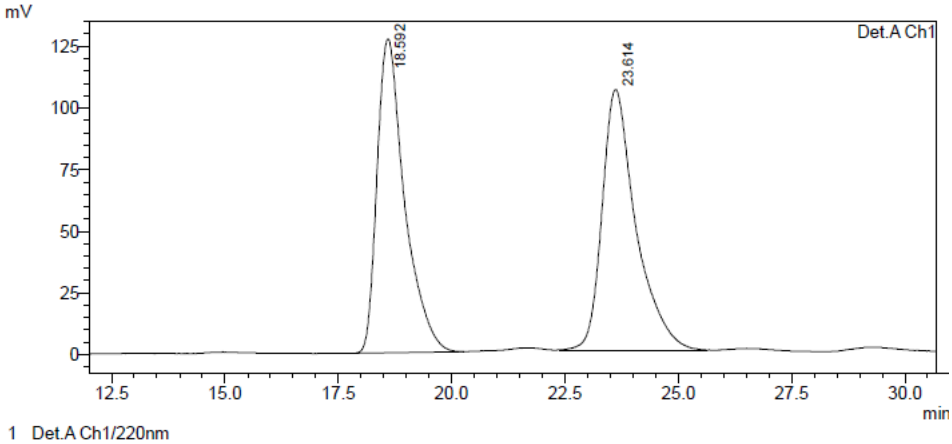
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.168	919434	17404	6.355	8.718
2	28.264	13548785	182230	93.645	91.282
Total		14468219	199634	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-methyl (*R*,*E*)-5-methyl-5-nitrohex-2-enedioate (4a)

Colourless oil; $[\alpha]^{25}_{D}$ = 5.6 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.5 Hz, 2H), 7.27–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.93 (s, 1H), 6.76 (dt, *J* = 15.5, 7.5 Hz, 1H), 5.99 (dt, *J* = 15.5, 1.0 Hz, 1H), 3.80 (s, 3H), 3.60–3.53 (m, 2H), 3.12–2.98 (m, 4H), 1.77 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.13, 164.30, 140.30, 139.40, 136.45, 130.50, 130.03, 129.02, 127.37, 126.32, 91.43, 79.73, 53.89, 39.18, 32.53, 21.50 ppm. HRMS (ESI) m/z calcd for $C_{23}H_{23}NNaO_6$ $[M+Na]^+$ 432.1418, found 432.1421. The *ee* value was 91%, t_R (major) = 18.466 min, t_R (minor) = 23.410 min (Chiralpak IC, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

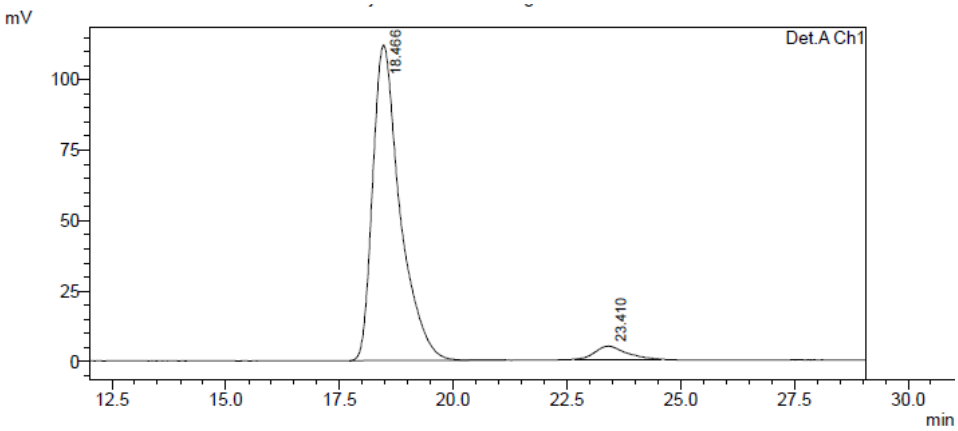


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.592	5381460	127254	49.515	54.632
2	23.614	5486857	105673	50.485	45.368
Total		10868317	232927	100.000	100.000

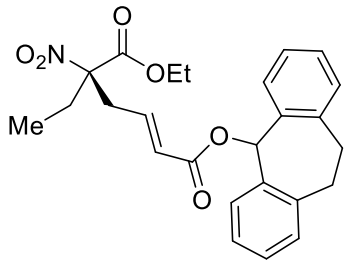


1 Det.A Ch1/220nm

PeakTable

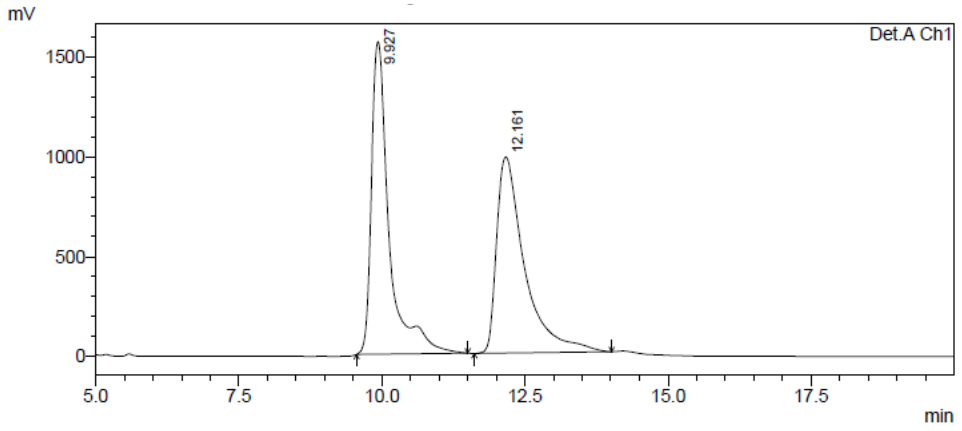
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.466	4666507	111866	95.674	96.041
2	23.410	211010	4611	4.326	3.959
Total		4877516	116477	100.000	100.000

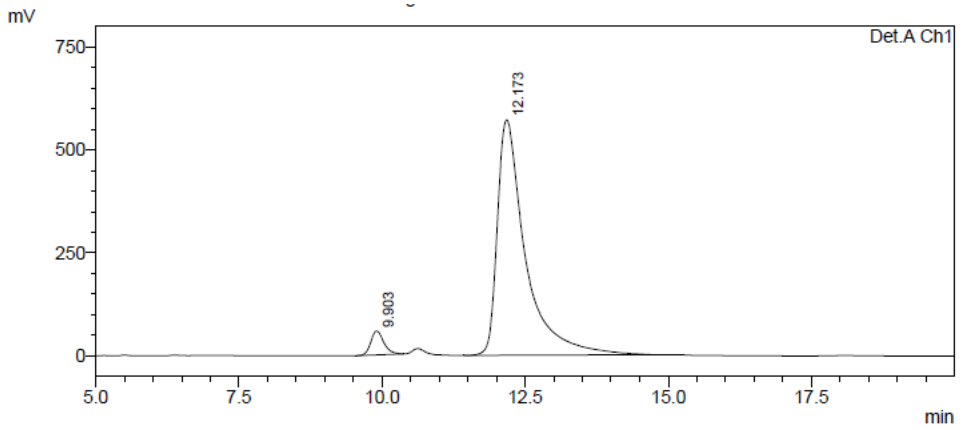


1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*R*,*E*)-5-ethyl-5-nitrohex-2-enedioate (4b)

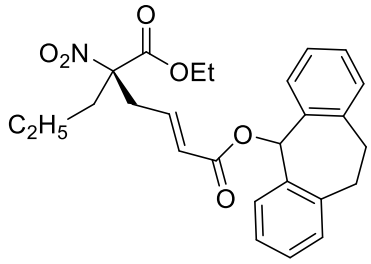
Colourless oil; $[\alpha]^{25}_{D}$ = 3.8 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.0 Hz, 2H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.93 (s, 1H), 6.73 (dt, *J* = 15.5, 7.5 Hz, 1H), 5.97 (d, *J* = 15.5 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 3.59–3.53 (m, 2H), 3.06 –3.01 (m, 4H), 2.30–2.14 (m, 2H), 1.23 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.06, 164.31, 140.27, 139.62, 136.47, 130.48, 130.00, 128.99, 126.89, 126.30, 95.38, 79.65, 63.13, 36.13, 32.51, 27.44, 13.93, 8.04 ppm. HRMS (ESI) m/z calcd for $C_{25}H_{27}NNaO_6$ $[M+Na]^+$ 460.1731, found 460.1737. The *ee* value was 91%, t_R (minor) = 9.903 min, t_R (major) = 12.173 min (Chiralpak IF, λ = 220 nm, 10.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.927	33619401	1565760	50.222	61.443
2	12.161	33322261	982553	49.778	38.557
Total		66941661	2548314	100.000	100.000

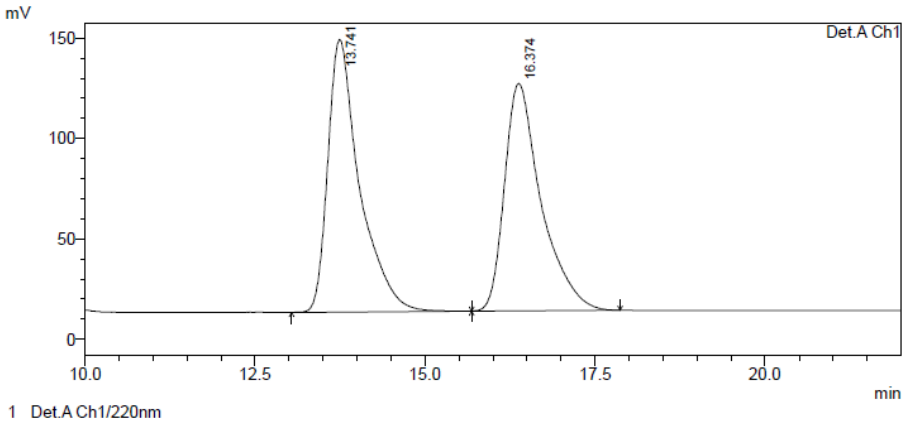


Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.903	924042	58053	4.511	9.221
2	12.173	19561535	571553	95.489	90.779
Total		20485578	629606	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*R*,*E*)-5-nitro-5-propylhex-2-enedioate (4c)

Colourless oil; $[\alpha]^{25}_{D}$ = 0.8 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.5 Hz, 2H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.93 (s, 1H), 6.74 (dt, *J* = 15.5, 7.5 Hz, 1H), 5.96 (dt, *J* = 15.5, 1.0 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 3.59–3.53 (m, 2H), 3.06–3.00 (m, 4H), 2.21–2.07 (m, 2H), 1.33–1.19 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 3H), 0.95 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.16, 164.34, 140.26, 139.74, 136.51, 136.48, 130.49, 129.98, 128.99, 126.83, 126.31, 94.96, 79.65, 63.14, 36.70, 36.12, 32.52, 17.09, 14.00, 13.92 ppm. HRMS (ESI) m/z calcd for $C_{26}H_{29}NNaO_6$ $[M+Na]^+$ 474.1887, found 474.1881. The *ee* value was 90%, t_R (minor) = 13.693 min, t_R (major) = 16.276 min (Chiralpak IC, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

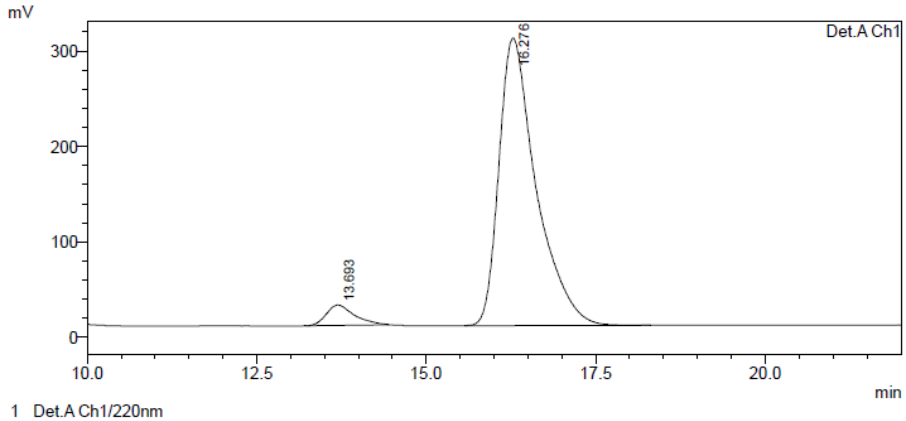


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.741	4424091	135824	50.997	54.501
2	16.374	4251192	113392	49.003	45.499
Total		8675283	249216	100.000	100.000

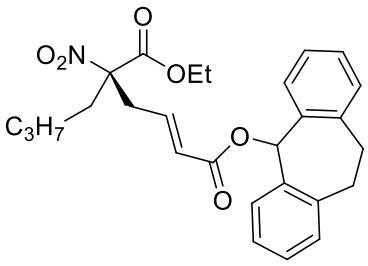


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

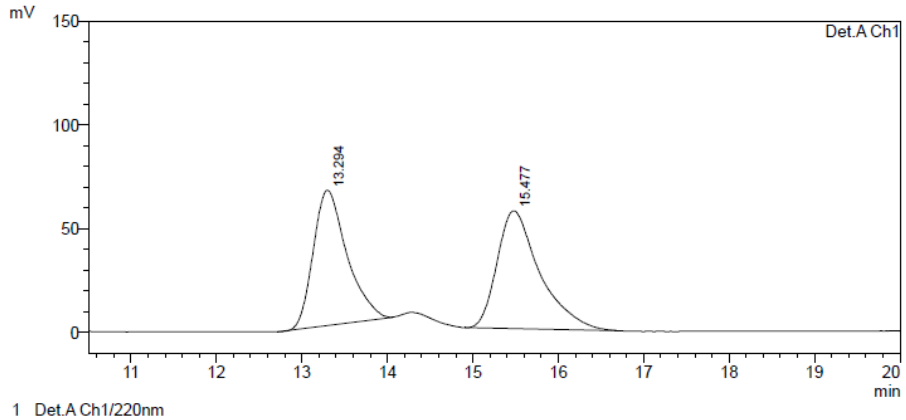
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.693	611812	21304	5.055	6.606
2	16.276	11491217	301201	94.945	93.394
Total		12103029	322505	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*R*,*E*)-5-butyl-5-nitrohex-2-enedioate (4d)

Colourless oil; $[\alpha]^{25}_{D}$ = 3.3 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.5 Hz, 2H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.94 (s, 1H), 6.74 (dt, *J* = 15.5, 7.5 Hz, 1H), 5.96 (dt, *J* = 15.5, 1.0 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 3.58–3.52 (m, 2H), 3.07–3.00 (m, 4H), 2.23–2.10 (m, 2H), 1.38–1.31 (m, 2H), 1.27–1.13 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.16, 164.32, 140.24, 139.72, 136.49, 130.48, 129.94, 128.98, 126.83, 126.30, 95.01, 79.62, 63.13, 36.61, 33.77, 32.51, 25.61, 22.55, 13.92, 13.79 ppm.

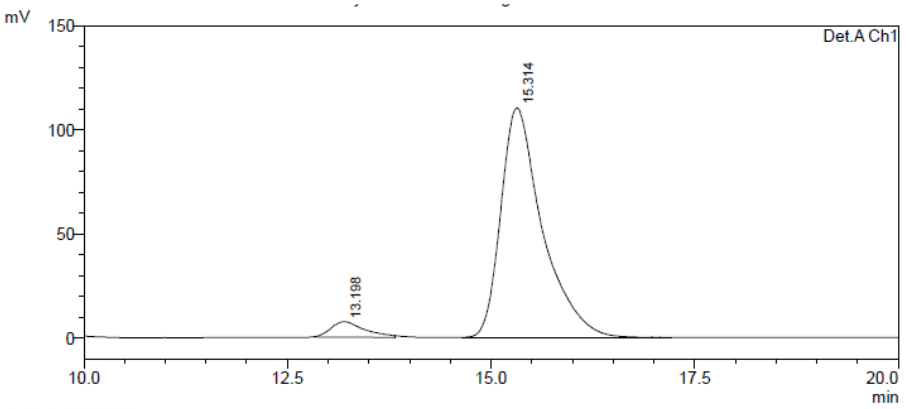
HRMS (ESI) m/z calcd for $C_{27}H_{31}NNaO_6$ $[M+Na]^+$ 488.2044, found 488.2044. The *ee* value was 90%, t_R (minor) = 13.198 min, t_R (major) = 15.314 min (Chiralpak IC, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 220nm

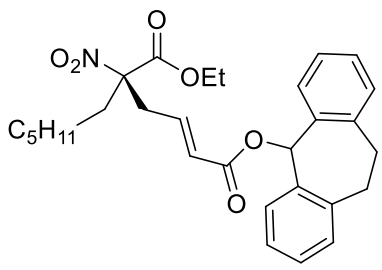
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.294	1789723	65251	47.430	53.430
2	15.477	1983657	56873	52.570	46.570
Total		3773380	122124	100.000	100.000



PeakTable

Detector A Ch1 220nm

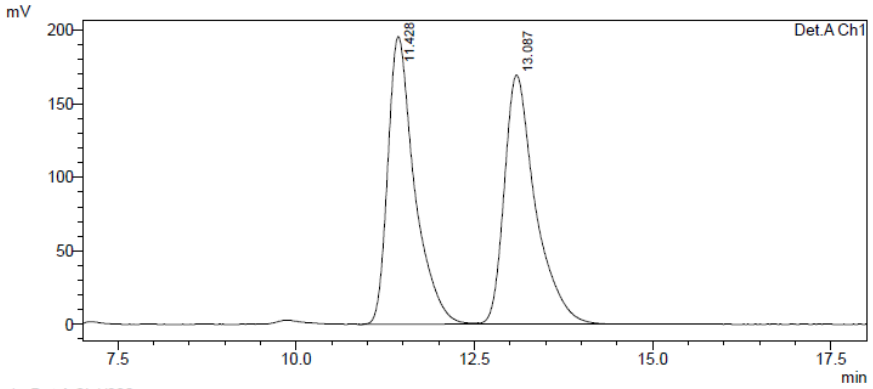
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.198	208241	7313	5.045	6.214
2	15.314	3919325	110371	94.955	93.786
Total		4127566	117684	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*R*,*E*)-5-hexyl-5-nitrohex-2-enedioate (4e)

Colourless oil; $[\alpha]^{25}_D$ = 1.8 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.0 Hz, 2H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.93 (s, 1H), 6.74 (dt, J = 15.5, 7.5 Hz, 1H), 5.96 (dt, J = 15.5, 1.0 Hz, 1H), 4.23 (q, J = 7.0 Hz, 2H), 3.58–3.52 (m, 2H), 3.09–3.99 (m, 4H), 2.22–2.09 (m, 2H), 1.34–1.15 (m, 8H),

1.22 (t, J = 7.0 Hz, 3H), 0.86 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.17, 164.33, 140.25, 139.75, 136.50, 130.48, 129.96, 128.99, 126.83, 126.31, 95.03, 79.63, 63.13, 36.64, 34.05, 32.52, 31.40, 29.04, 23.47, 22.54, 14.07, 13.93 ppm. HRMS (ESI) m/z calcd for $C_{29}H_{35}NNaO_6$ $[M+Na]^+$ 516.2357, found 516.2349. The *ee* value was 90%, t_R (minor) = 11.318 min, t_R (major) = 12.933 min (Chiralpak IC, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

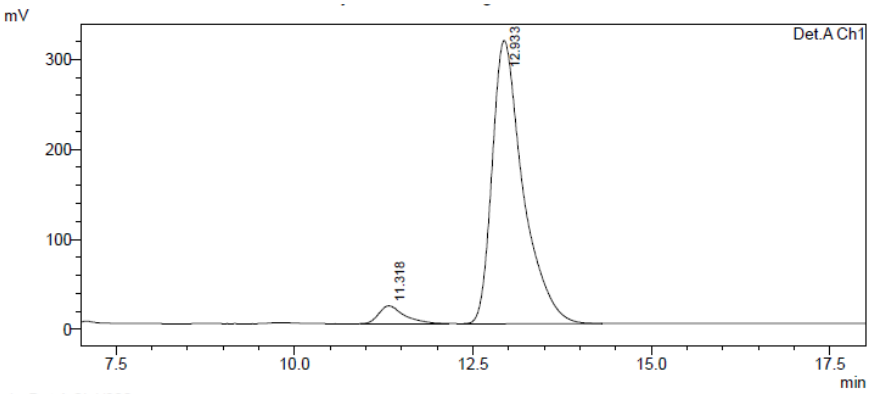


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.428	5100203	195205	49.919	53.601
2	13.087	5116696	168973	50.081	46.399
Total		10216898	364178	100.000	100.000

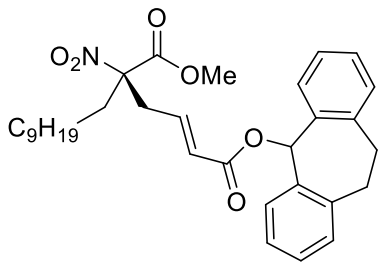


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

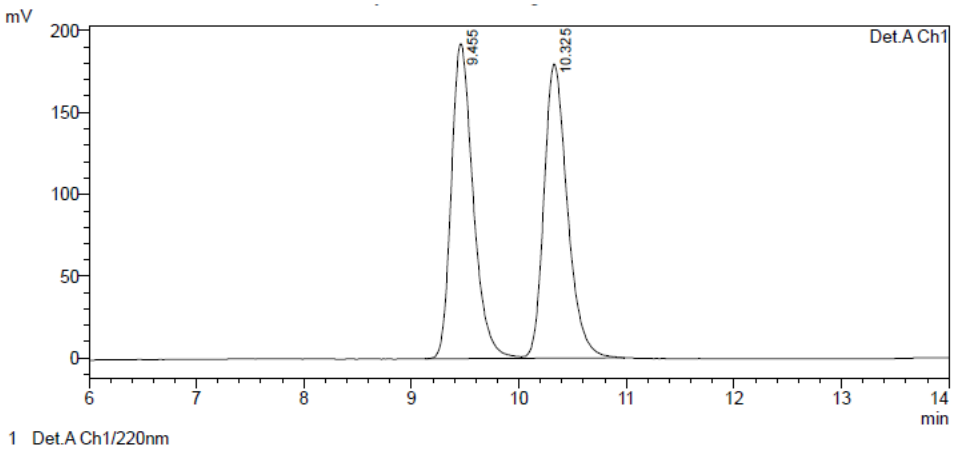
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.318	491501	19821	4.944	5.930
2	12.933	9448967	314416	95.056	94.070
Total		9940468	334237	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-methyl (*R*,*E*)-5-decyl-5-nitrohex-2-enedioate (4f)

Colourless oil; $[\alpha]^{25}_D$ = 1.8 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.5 Hz, 2H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.93 (s, 1H),

6.72 (dt, J = 15.5, 7.5 Hz, 1H), 5.96 (dt, J = 15.5, 1.0 Hz, 1H), 3.77 (s, 3H), 3.59–3.52 (m, 2H), 3.10–3.00 (m, 4H), 2.22–2.09 (m, 2H), 1.31–1.13 (m, 16H), 0.88 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.73, 164.34, 140.24, 139.59, 136.52, 136.49, 130.50, 129.95, 129.00, 126.90, 126.32, 95.06, 79.66, 53.66, 36.66, 34.06, 32.52, 32.00, 29.61, 29.54, 29.40, 29.28, 23.60, 22.80, 14.25 ppm. HRMS (ESI) m/z calcd for $C_{32}H_{41}NNaO_6$ $[M+Na]^+$ 558.2826, found 558.2827. The *ee* value was 90%, t_R (minor) = 9.299 min, t_R (major) = 10.036 min (Chiralpak IB, λ = 220 nm, 2.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

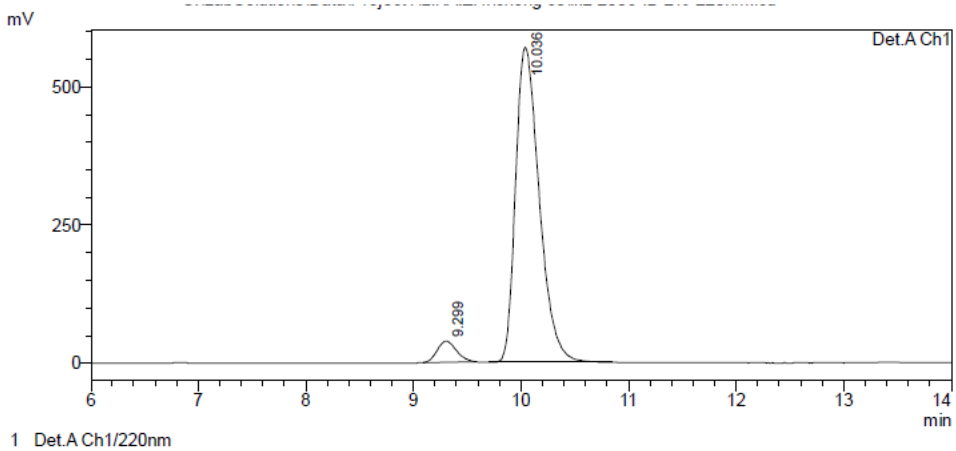


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.455	2715128	192165	49.998	51.702
2	10.325	2715377	179515	50.002	48.298
Total		5430505	371680	100.000	100.000

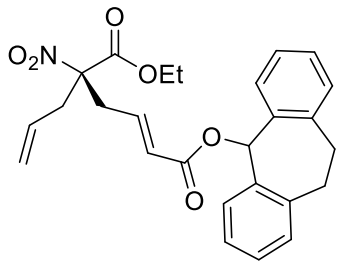


1 Det.A Ch1/220nm

PeakTable

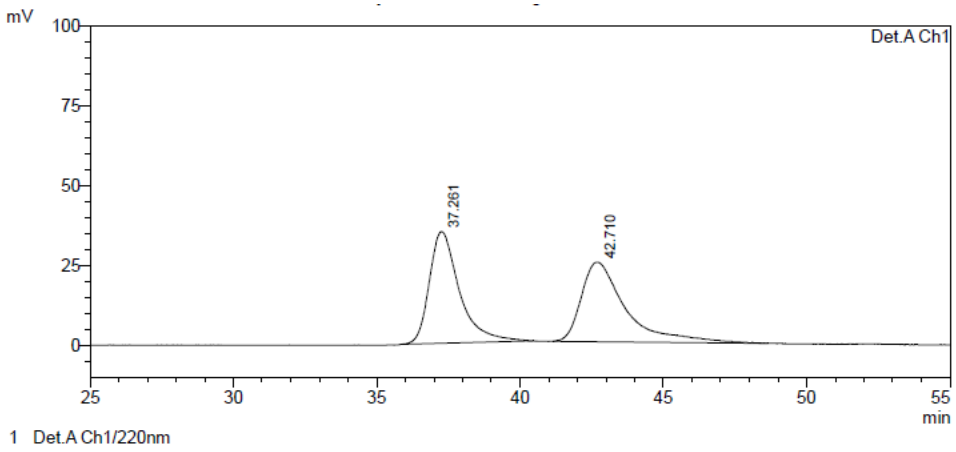
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.299	475292	38220	5.148	6.291
2	10.036	8757691	569345	94.852	93.709
Total		9232983	607565	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*R*,*E*)-5-allyl-5-nitrohex-2-enedioate (4g)

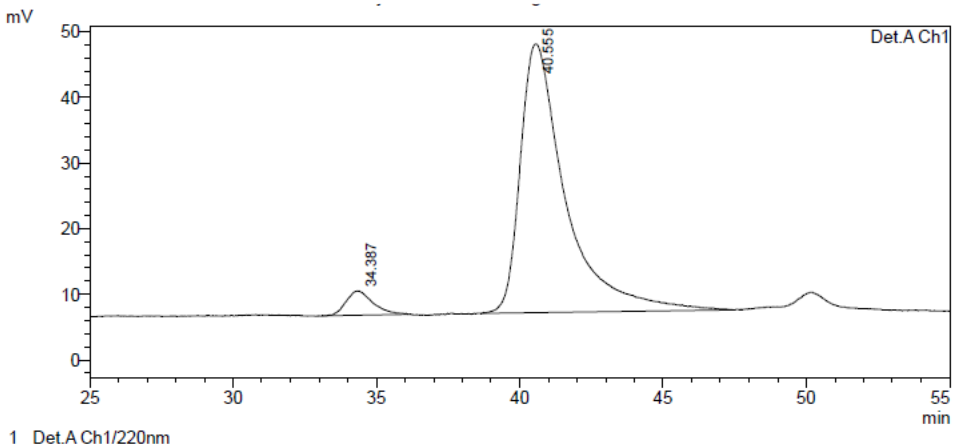
Colourless oil; $[\alpha]^{25}_{D}$ = -4.1 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.0 Hz, 2H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.93 (s, 1H), 6.75 (dt, *J* = 15.5, 7.5 Hz, 1H), 5.97 (dt, *J* = 15.5, 1.0 Hz, 1H), 5.63–5.55 (m, 1H), 5.24–5.19 (m, 2H), 4.24 (q, *J* = 7.0 Hz, 2H), 3.59–3.54 (m, 2H), 3.06–3.01 (m, 4H), 2.97 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.88 (dd, *J* = 14.5, 7.5 Hz, 1H), 1.22 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.62, 164.29, 140.25, 139.44, 136.47, 130.48, 129.97, 129.00, 128.08, 127.11, 126.31, 122.15, 94.23, 79.68, 63.30, 38.64, 36.46, 32.52, 13.94 ppm. HRMS (ESI) m/z calcd for $C_{26}H_{27}NNaO_6$ $[M+Na]^+$ 472.1731, found 472.1738. The *ee* value was 90%, t_R (minor) = 34.387 min, t_R (major) = 40.555 min (Chiralpak IF, λ = 220 nm, 1,0% *i*PrOH/hexane, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.261	2570624	34999	49.131	58.414
2	42.710	2661516	24917	50.869	41.586
Total		5232140	59916	100.000	100.000

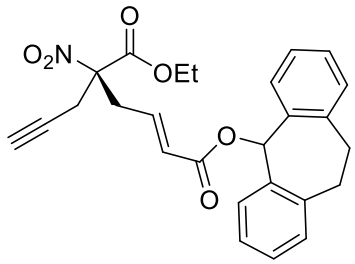


1 Det.A Ch1/220nm

PeakTable

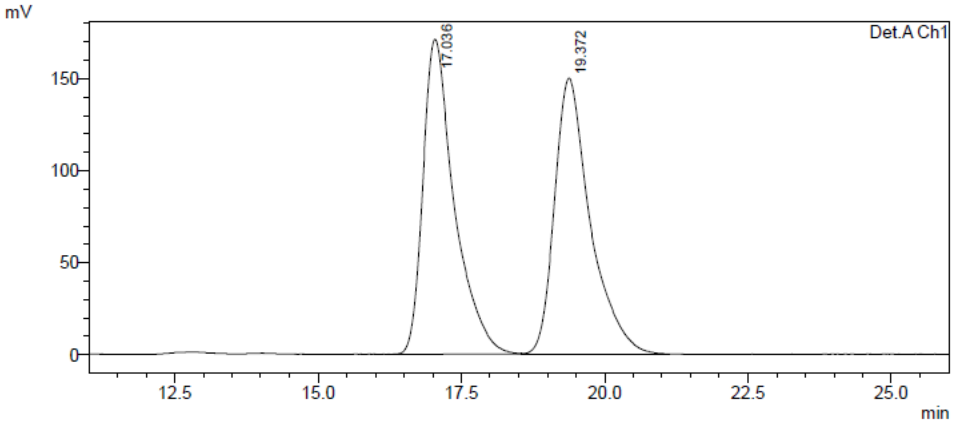
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.387	241244	3696	5.094	8.284
2	40.555	4494242	40918	94.906	91.716
Total		4735486	44614	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*S*,*E*)-5-nitro-5-(prop-2-yn-1-yl)hex-2-enedioate (4h)

Colourless oil; $[\alpha]^{25}_{D}$ = -0.8 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, J = 7.5 Hz, 2H), 7.27–7.24 (m, 2H), 7.19–7.16 (m, 4H), 6.94 (s, 1H), 6.74 (dt, J = 15.5, 7.5 Hz, 1H), 6.04 (d, J = 15.5 Hz, 1H), 4.27 (q, J = 7.0 Hz, 2H), 3.59–3.53 (m, 2H), 3.23–3.18 (m, 3H), 3.08–3.01 (m, 3H), 2.14 (t, J = 2.5 Hz, 1H), 1.24 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.64, 164.23, 140.30, 138.80, 136.45, 136.43, 130.49, 130.05, 129.03, 127.63, 126.31, 92.60, 79.78, 75.37, 74.05, 63.75, 36.02, 32.53, 25.10, 13.87 ppm. HRMS (ESI) m/z calcd for $C_{26}H_{25}NNaO_6$ $[M+Na]^+$ 470.1574, found 470.1577. The *ee* value was 89%, t_R (major) = 16.977 min, t_R (minor) = 19.319 min (Chiralpak IC, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

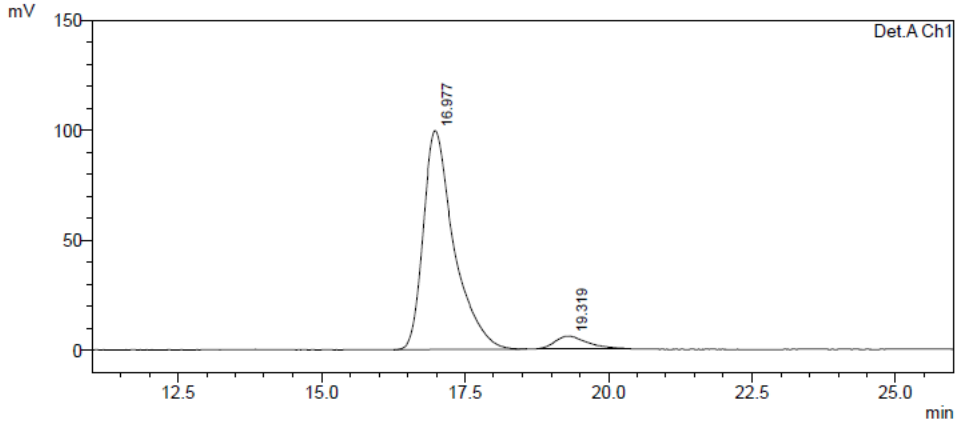


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.036	6511787	171203	50.014	53.284
2	19.372	6508158	150100	49.986	46.716
Total		13019945	321302	100.000	100.000

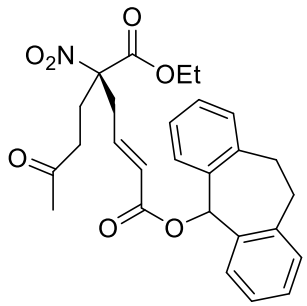


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

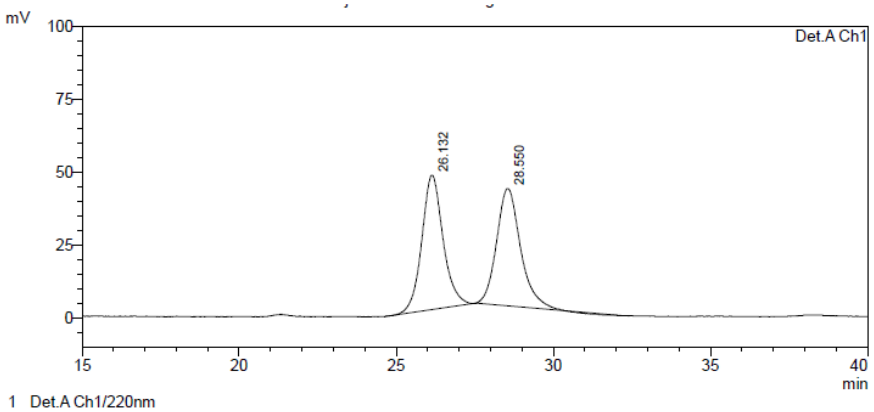
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.977	3711443	99646	94.426	94.609
2	19.319	219090	5678	5.574	5.391
Total		3930534	105323	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*R*,*E*)-5-nitro-5-(3-oxobutyl)hex-2-enedioate (4i)

Colourless oil; $[\alpha]^{25}_{D}$ = 0.6 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.0 Hz, 2H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.92 (s, 1H), 6.74 (dt, J = 15.5, 7.5 Hz, 1H), 5.97 (d, J = 15.5 Hz, 1H), 4.26–4.20 (m, 2H), 3.58–3.52 (m, 2H), 3.06–2.99 (m, 4H), 2.55–2.52 (m, 2H), 2.45–2.41 (m, 2H), 2.13 (s, 3H), 1.23 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 205.40, 165.75, 164.18, 140.28, 139.13, 136.44, 130.48, 130.03, 129.00, 127.23, 126.30, 94.09, 79.75,

63.41, 38.01, 37.78, 32.52, 30.00, 28.33, 13.89 ppm. HRMS (ESI) m/z calcd for $C_{27}H_{29}NNaO_7$ $[M+Na]^+$ 502.1836, found 502.1826. The *ee* value was 86%, t_R (minor) = 26.166 min, t_R (major) = 28.500 min (Chiralpak IA, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

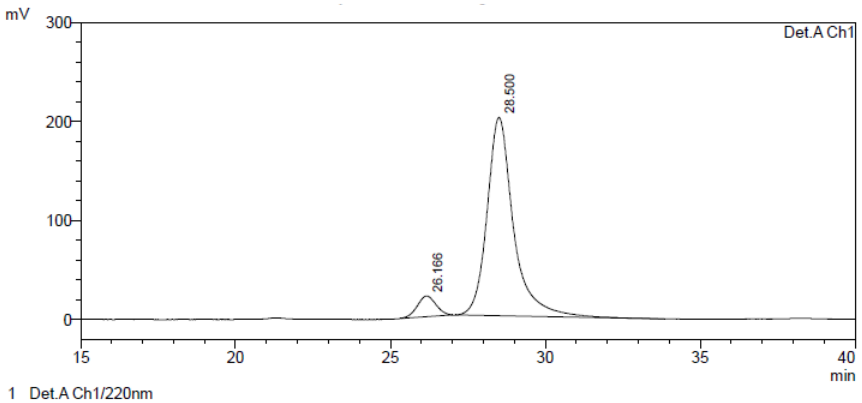


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.132	2175670	46150	50.678	53.370
2	28.550	2117486	40323	49.322	46.630
Total		4293156	86473	100.000	100.000

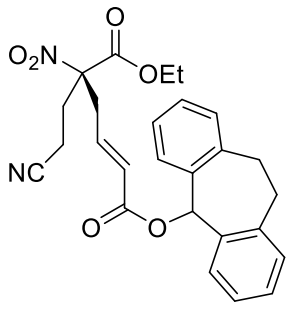


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

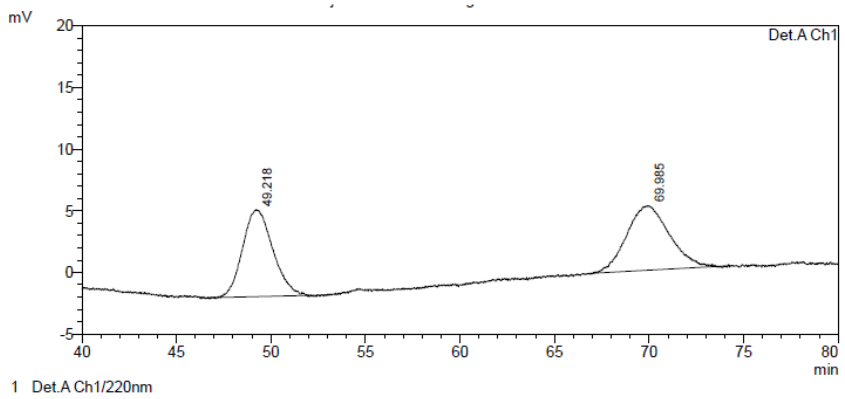
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.166	883559	20984	6.874	9.467
2	28.500	11969322	200667	93.126	90.533
Total		12852881	221652	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*R*,*E*)-5-(2-cyanoethyl)-5-nitrohex-2-enedioate (4j)

Colourless oil; $[\alpha]^{25}_D$ = 3.9 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.5 Hz, 2H), 7.27–7.24 (m, 2H), 7.20–7.17 (m, 4H), 6.93 (s, 1H), 6.69 (dt, *J* = 15.5, 7.5 Hz, 1H), 6.02 (d, *J* = 15.5 Hz, 1H), 4.32–4.27 (m, 2H), 3.60–3.54 (m, 2H), 3.14–3.00 (m, 4H), 2.55–2.44 (m, 4H), 1.26 (t, *J* = 7.0 Hz, 3H) ppm.

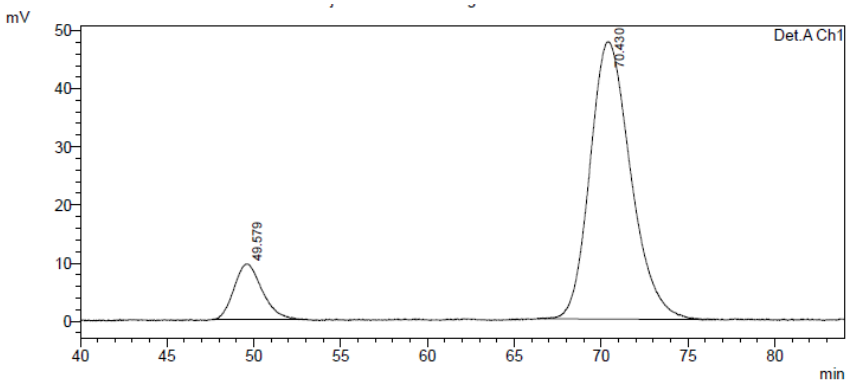
^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.77, 163.98, 140.35, 137.95, 136.28, 136.25, 130.52, 130.17, 129.09, 128.04, 126.32, 117.62, 92.97, 80.09, 64.04, 37.69, 32.52, 30.33, 13.85, 12.81 ppm. HRMS (ESI) m/z calcd for $C_{26}H_{26}N_2NaO_6$ $[M+Na]^+$ 485.1683, found 485.1687. The *ee* value was 76%, t_R (minor) = 49.579 min, t_R (major) = 70.430 min (Chiralpak IC, λ = 220 nm, 20.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 220nm

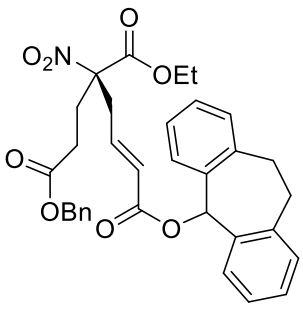
Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.218	781448	7042	48.664	57.342
2	69.985	824361	5239	51.336	42.658
Total		1605810	12281	100.000	100.000



PeakTable

Detector A Ch1 220nm

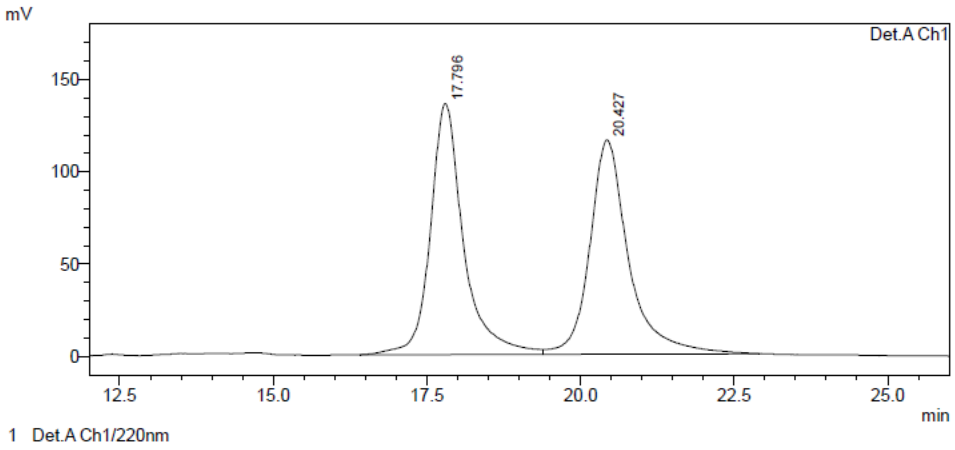
Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.579	1079342	9540	12.165	16.657
2	70.430	7793379	47729	87.835	83.343
Total		8872721	57269	100.000	100.000



1-Benzyl 6-(10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 3-ethyl (*R*,*E*)-3-nitrohex-5-ene-1,3,6-tricarboxylate (4k)

Colourless oil; $[\alpha]^{25}_D$ = 1.3 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.5 Hz, 2H), 7.36–7.33 (m,

5H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.93 (s, 1H), 6.74 (dt, J = 15.5, 7.5 Hz, 1H), 5.97 (d, J = 15.5 Hz, 1H), 5.11 (s, 2H), 4.25–4.20 (m, 2H), 3.59–3.54 (m, 2H), 3.05–3.02 (m, 4H), 2.55–2.42 (m, 4H), 1.21 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.31, 165.55, 164.17, 140.28, 139.00, 136.42, 135.54, 130.49, 130.02, 129.00, 128.75, 128.57, 128.52, 127.31, 126.30, 93.93, 79.75, 67.00, 63.48, 37.59, 32.52, 29.49, 28.88, 13.87 ppm. HRMS (ESI) m/z calcd for $C_{33}H_{33}NNaO_8$ $[M+Na]^+$ 594.2098, found 594.2089. The *ee* value was 85%, t_R (minor) = 17.799 min, t_R (major) = 20.407 min (Chiralpak IA, λ = 220 nm, 10.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

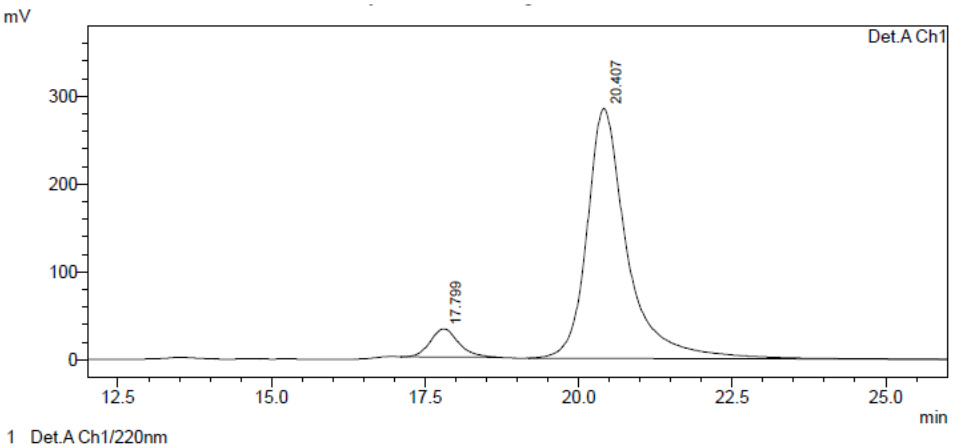


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.796	5112479	135750	50.034	53.956
2	20.427	5105512	115843	49.966	46.044
Total		10217991	251593	100.000	100.000

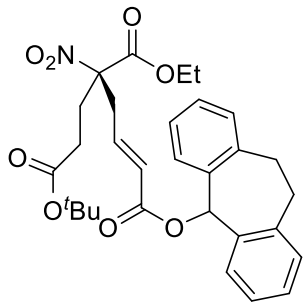


1 Det.A Ch1/220nm

PeakTable

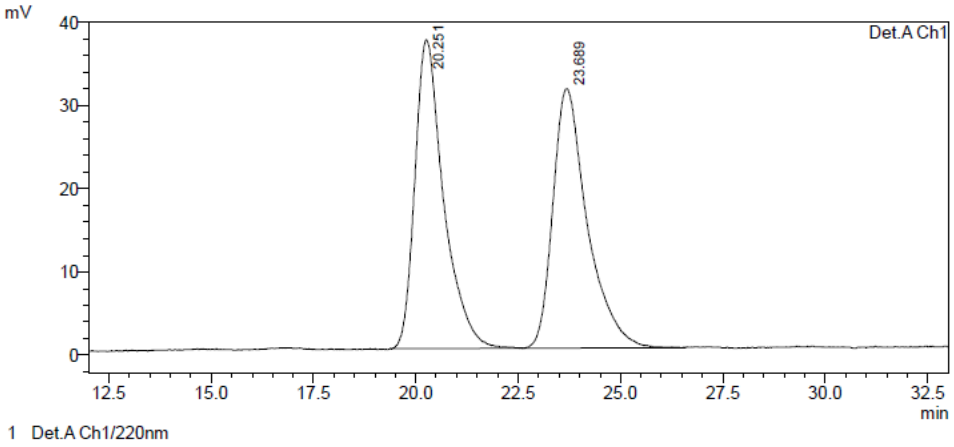
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.799	1034228	32214	7.345	10.160
2	20.407	13045641	284849	92.655	89.840
Total		14079869	317063	100.000	100.000



1-(*tert*-Butyl) 6-(10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 3-ethyl (*R*,*E*)-3-nitrohex-5-ene-1,3,6-tricarboxylate (4l)

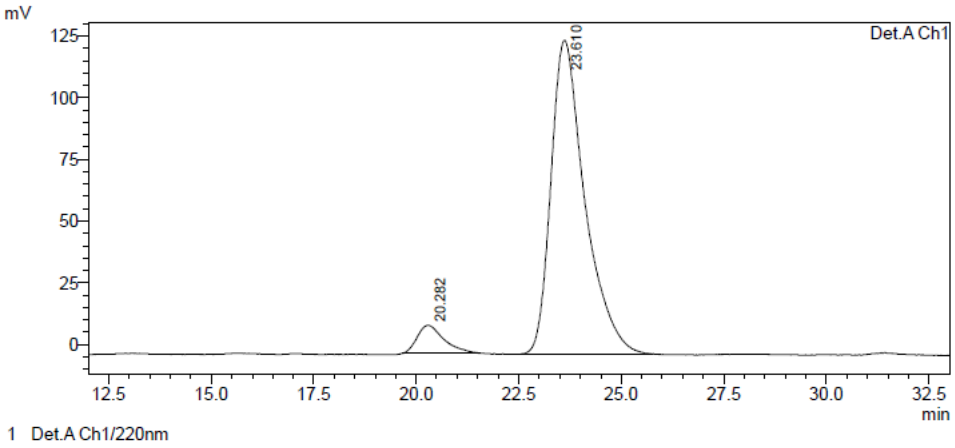
Colourless oil; $[\alpha]^{25}_{D}$ = 1.6 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.5 Hz, 2H), 7.26–7.23 (m, 2H), 7.18–7.16 (m, 4H), 6.93 (s, 1H), 6.75 (dt, *J* = 15.5, 7.5 Hz, 1H), 5.97 (d, *J* = 15.5 Hz, 1H), 4.26–4.22 (m, 2H), 3.58–3.54 (m, 2H), 3.04–3.02 (m, 4H), 2.48–2.44 (m, 2H), 2.30–2.26 (m, 2H), 1.42 (s, 9H), 1.23 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.65, 165.68, 164.21, 140.27, 139.19, 136.47, 130.49, 130.01, 129.00, 127.22, 126.30, 94.09, 81.49, 79.72, 63.40, 37.45, 32.53, 29.92, 29.56, 28.14, 13.90 ppm. HRMS (ESI) m/z calcd for $C_{30}H_{35}NNaO_8$ $[M+Na]^+$ 560.2255, found 560.2257. The *ee* value was 87%, t_R (minor) = 20.282 min, t_R (major) = 23.610 min (Chiralpak IC, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.251	1813722	37126	49.879	54.350
2	23.689	1822521	31183	50.121	45.650
Total		3636243	68309	100.000	100.000

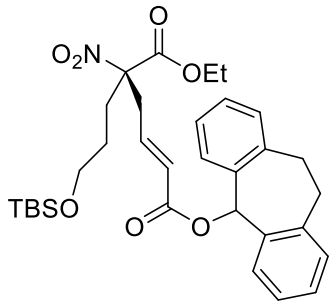


1 Det.A Ch1/220nm

PeakTable

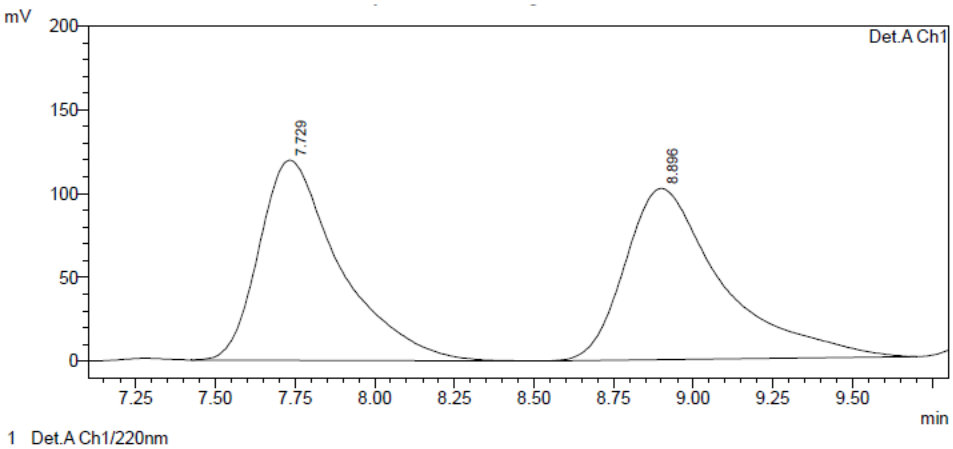
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.282	508813	11274	6.496	8.144
2	23.610	7324419	127158	93.504	91.856
Total		7833232	138432	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*R*,*E*)-5-(3-((*tert*-butyldimethylsilyl)oxy) propyl)-5-nitrohex-2-enedioate (4m)

Colourless oil; $[\alpha]^{25}_{D}$ = 4.9 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.5 Hz, 2H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.93 (s, 1H), 6.74 (dt, *J* = 15.5, 7.5 Hz, 1H), 5.97 (d, *J* = 15.5 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 3.61–3.52 (m, 4H), 3.06–2.99 (m, 4H), 2.29–2.18 (m, 2H), 1.51–1.36 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 3H), 0.85 (s, 9H), 0.01 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.08, 164.26, 140.27, 139.58, 136.49, 130.47, 130.01, 128.98, 126.94, 126.29, 94.84, 79.62, 63.17, 62.07, 36.83, 32.53, 30.97, 27.00, 25.96, 18.35, 13.92, -5.27 ppm. HRMS (ESI) m/z calcd for $C_{32}H_{43}NNaO_7Si$ $[M+Na]^+$ 604.2701, found 604.2706. The *ee* value was 93%, t_R (minor) = 7.520 min, t_R (major) = 8.650 min (Chiralpak IC, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

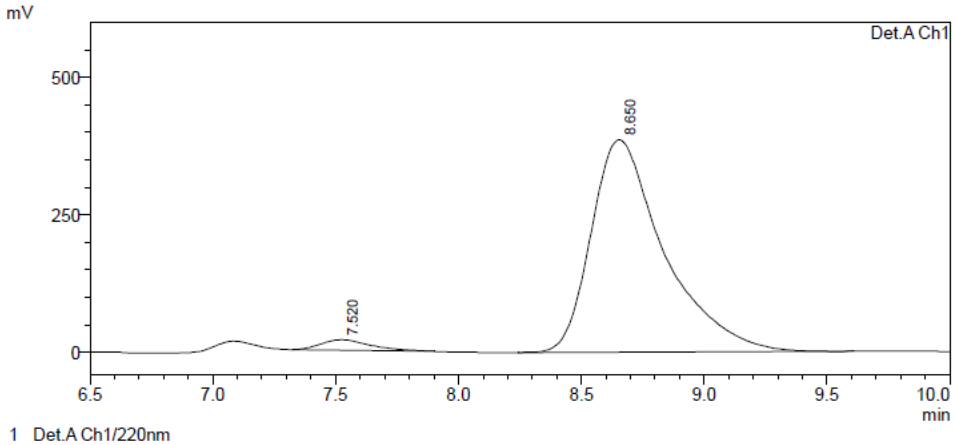


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.729	2107076	119488	49.291	53.901
2	8.896	2167717	102194	50.709	46.099
Total		4274793	221681	100.000	100.000

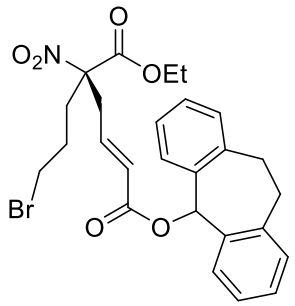


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

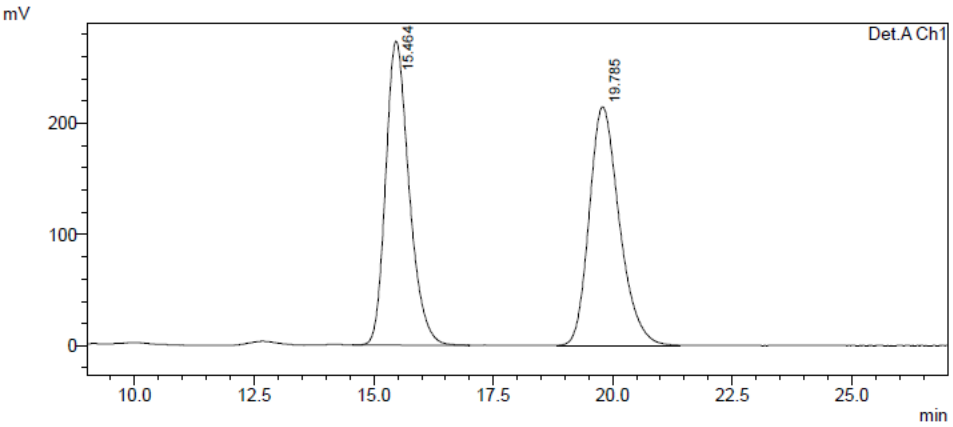
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.520	267178	19039	3.241	4.702
2	8.650	7976515	385852	96.759	95.298
Total		8243693	404891	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*R*,*E*)-5-(3-bromopropyl)-5-nitrohex-2-enedioate (4n)

Colourless oil; $[\alpha]^{25}_{D}$ = -1.9 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.5 Hz, 2H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.93 (s, 1H), 6.73 (dt, J = 15.5, 7.5 Hz, 1H), 5.99 (d, J = 15.5 Hz, 1H), 4.26 (q, J = 7.0 Hz, 2H), 3.58–3.52 (m, 2H), 3.41–3.34 (m, 2H), 3.10–3.00 (m, 4H), 2.37–2.27 (m, 2H), 1.89–1.76 (m, 2H), 1.24 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.73, 164.19, 140.28, 138.98, 136.44, 130.50, 130.00, 129.01, 127.34, 126.32, 94.23, 79.76, 63.45, 36.99, 32.97, 32.55, 31.96, 26.95, 13.94 ppm. HRMS (ESI) m/z calcd for

$C_{26}H_{28}{}^{79}BrNNaO_6$ $[M+Na]^+$ 552.0992, found 552.0997, $C_{26}H_{28}{}^{81}BrNNaO_6$ $[M+Na]^+$ 554.0972, found 554.0968. The *ee* value was 89%, t_R (minor) = 15.478 min, t_R (major) = 19.785 min (Chiralpak IC, λ = 220 nm, 10.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

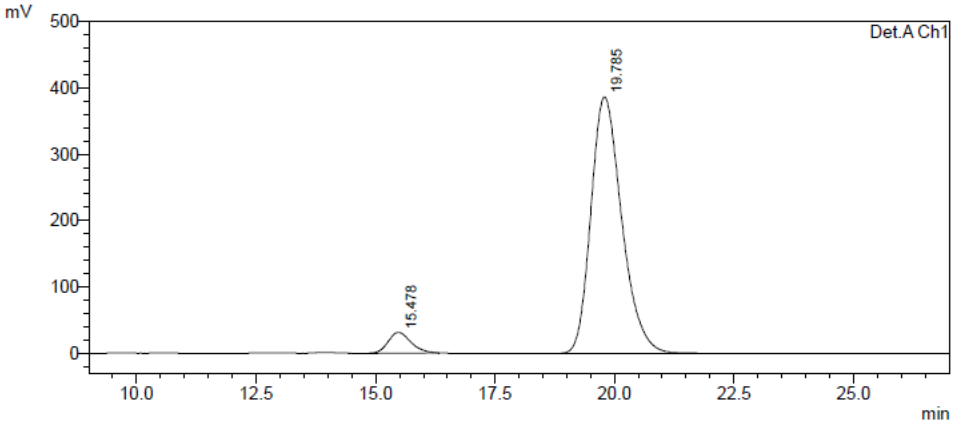


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.464	9323376	273593	49.776	56.027
2	19.785	9407119	214731	50.224	43.973
Total		18730496	488324	100.000	100.000

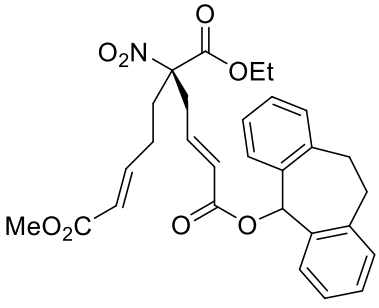


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

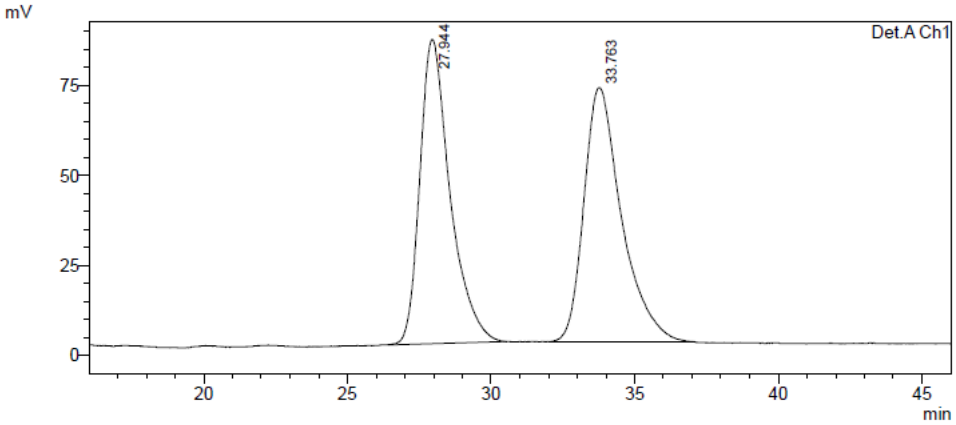
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.478	1023678	31192	5.567	7.469
2	19.785	17365867	386421	94.433	92.531
Total		18389545	417613	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 4-ethyl 8-methyl (*R*,1*E*,7*E*)-4-nitroocta-1,7-diene-1,4,8-tricarboxylate (4o)

Colourless oil; $[\alpha]^{25}_D$ = 1.5 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 (d, J = 7.5 Hz, 2H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.92 (s, 1H),

6.85 (dt, *J* = 15.5, 6.5 Hz, 1H), 6.71 (dt, *J* = 15.5, 7.5 Hz, 1H), 5.98 (d, *J* = 15.5 Hz, 1H), 5.84 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.73 (s, 3H), 3.58–3.52 (m, 2H), 3.07–3.00 (m, 4H), 2.37–2.16 (m, 4H), 1.23 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.54, 165.62, 164.17, 145.44, 140.30, 138.99, 136.38, 130.50, 130.07, 129.03, 127.30, 126.31, 122.72, 94.15, 79.86, 63.48, 51.73, 37.06, 32.56, 32.52, 26.35, 13.91 ppm. HRMS (ESI) m/z calcd for $C_{29}H_{31}NNaO_8$ $[M+Na]^+$ 544.1942, found 544.1947. The *ee* value was 84%, t_R (minor) = 27.627 min, t_R (major) = 33.201 min (Chiralpak IC, λ = 220 nm, 20.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

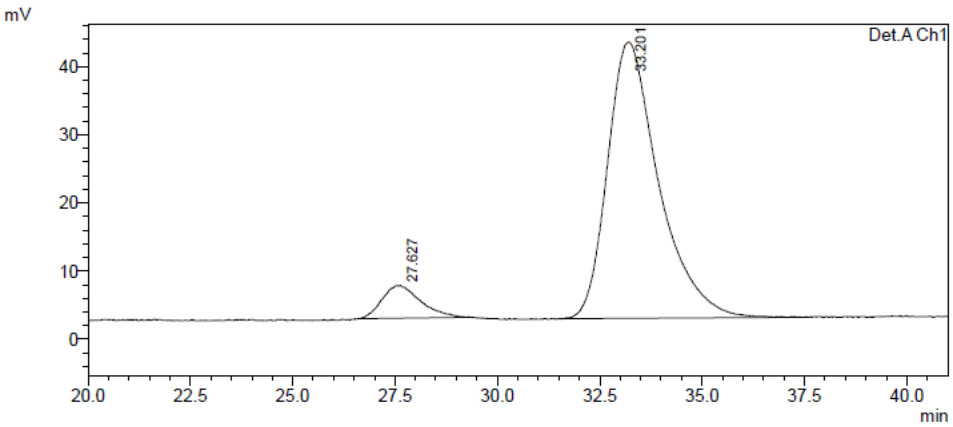


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.944	6183086	84528	49.002	54.453
2	33.763	6434825	70702	50.998	45.547
Total		12617911	155230	100.000	100.000

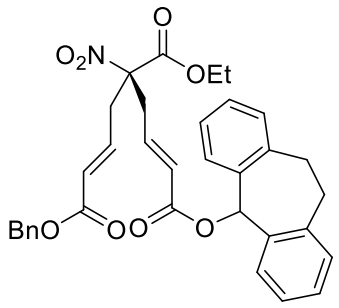


1 Det.A Ch1/220nm

PeakTable

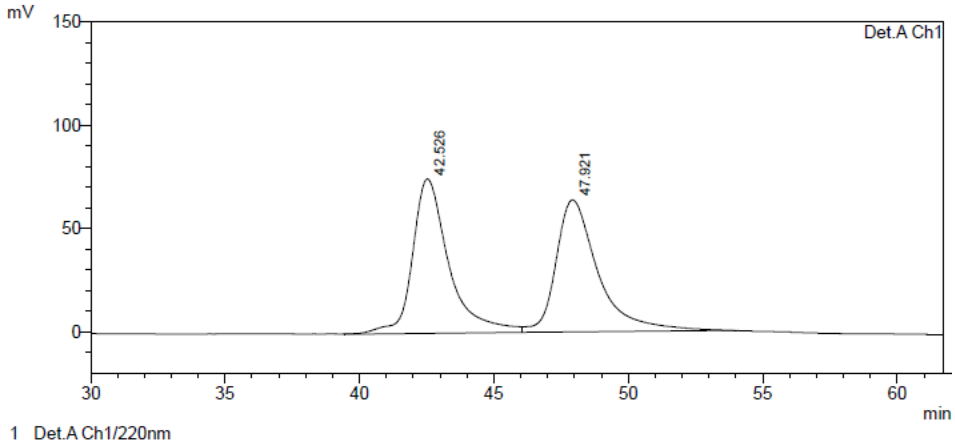
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.627	313237	4795	8.166	10.587
2	33.201	3522670	40493	91.834	89.413
Total		3835907	45288	100.000	100.000



1-Benzyl 7-(10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 4-ethyl (*R*,1*E*,6*E*)-4-nitrohepta-1,6-diene-1,4,7-tricarboxylate (4p)

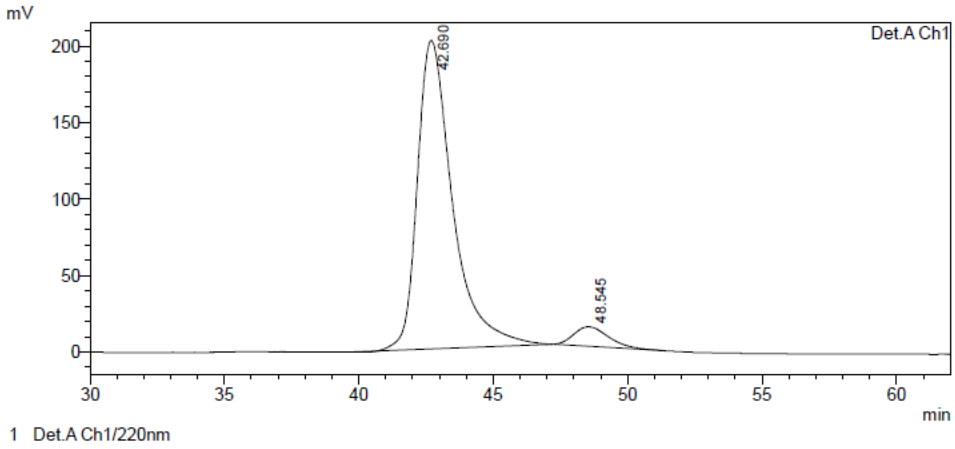
Colourless oil; $[\alpha]^{25}_{D}$ = -1.2 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.0 Hz, 2H), 7.39–7.32 (m, 5H), 7.27–7.24 (m, 2H), 7.19–7.16 (m, 4H), 6.93 (s, 1H), 6.77–6.69 (m, 2H), 6.01–5.97 (m, 2H), 5.17 (s, 2H), 4.25 (q, J = 7.0 Hz, 2H), 3.58–3.52 (m, 2H), 3.10–2.99 (m, 6H), 1.21 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.12, 165.08, 164.12, 140.29, 138.75, 138.65, 136.37, 135.73, 130.50, 130.04, 129.03, 128.72, 128.49, 128.43, 127.57, 127.17, 126.30, 93.57, 79.85, 66.68, 63.68, 36.89, 36.83, 32.50, 13.88 ppm. HRMS (ESI) m/z calcd for $C_{34}H_{33}NNaO_8$ $[M+Na]^+$ 606.2098, found 606.2091. The *ee* value was 88%, t_R (major) = 42.690 min, t_R (minor) = 48.545 min (Chiralpak IF, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.526	7060116	74671	50.182	53.885
2	47.921	7008950	63904	49.818	46.115
Total		14069067	138576	100.000	100.000

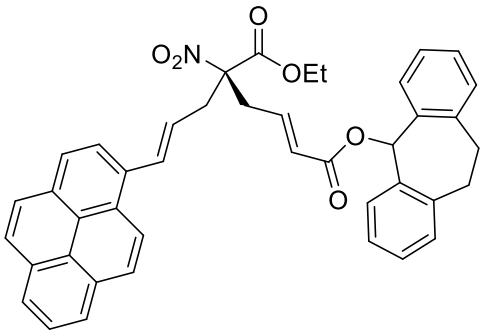


1 Det.A Ch1/220nm

PeakTable

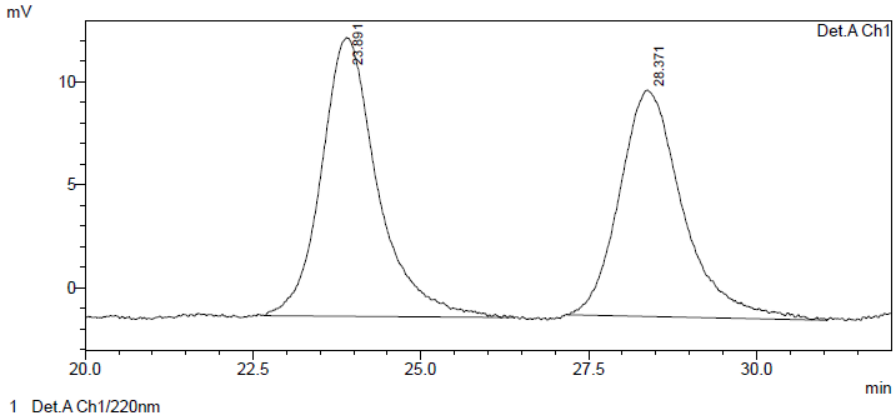
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.690	18426673	201562	94.105	94.048
2	48.545	1154260	12755	5.895	5.952
Total		19580933	214318	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*R*,*E*)-5-nitro-5-((*E*)-3-(pyren-1-yl)allyl)hex-2-enedioate (4q)

Yellow oil; $[\alpha]^{25}_{D}$ = 1.0 (c = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 9.0 Hz, 1H), 8.18 (t, *J* = 8.5 Hz, 2H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.07–7.99 (m, 5H), 7.55 (d, *J* = 15.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.28–7.24 (m, 2H), 7.19–7.18 (m, 4H), 6.98 (s, 1H), 6.92–6.84 (m, 1H), 6.15 (dt, *J* = 15.0, 7.5 Hz, 1H), 6.08 (d, *J* = 15.5 Hz, 1H), 4.30 (q, *J* = 7.0 Hz, 2H), 3.59–3.54 (m, 2H), 3.36–3.24 (m, 2H), 3.20 (d, *J* = 7.5 Hz, 2H), 3.05–3.00 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H). ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.77, 164.35, 140.28, 139.52, 136.50, 134.22, 131.55, 131.30, 130.96, 130.88, 130.51, 130.50, 130.03, 129.02, 128.22, 128.02, 127.65, 127.50, 127.26, 126.33, 126.18, 125.56, 125.32, 125.12, 124.93, 124.25, 123.43, 122.83, 94.61, 79.80, 63.45, 38.63, 36.87, 32.53, 14.00 ppm. HRMS (ESI) m/z calcd for $C_{42}H_{35}NNaO_6$ $[M+Na]^+$ 672.2357, found 672.2348. The *ee* value was 90%, t_R (minor) = 23.691 min, t_R (major) = 28.031 min (Chiralpak IA, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

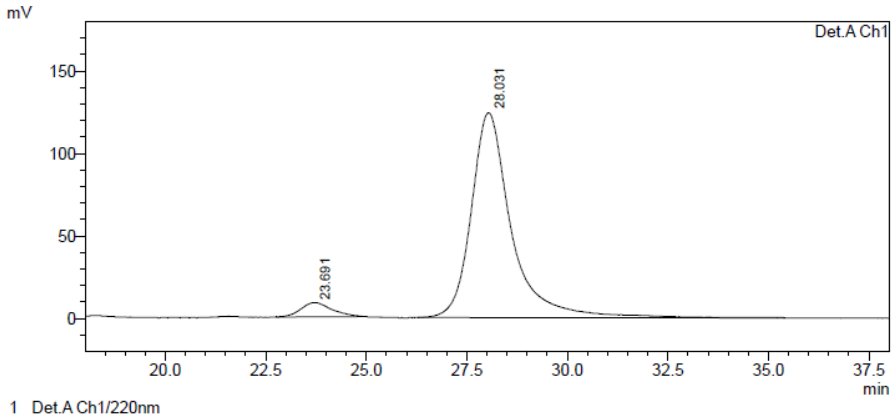


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.891	784034	13546	52.240	55.185
2	28.371	716789	11001	47.760	44.815
Total		1500823	24547	100.000	100.000

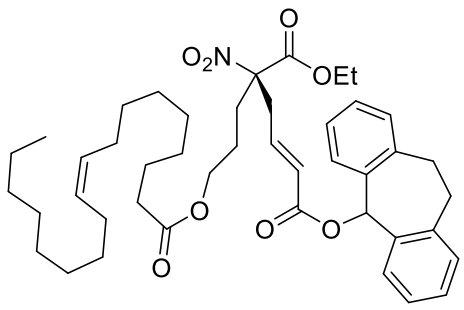


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

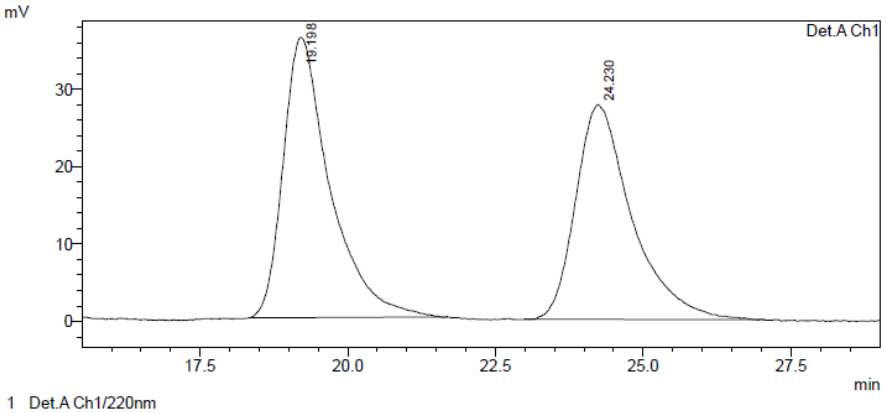
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.691	460030	8620	5.040	6.480
2	28.031	8668170	124409	94.960	93.520
Total		9128200	133029	100.000	100.000



1-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl) 6-ethyl (*R*,*E*)-5-nitro-5-(3-(oleoyloxy) propyl)hex-2-enedioate (4r)

Colourless oil; $[\alpha]^{25}_{D}$ = 1.4 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 (d, J = 7.5 Hz, 2H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.93 (s, 1H), 6.73 (dt, J = 15.5, 7.5 Hz, 1H), 5.98 (d, J = 15.5 Hz, 1H), 5.36–5.34 (m, 2H), 4.25 (q, J = 7.0 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H), 3.58–3.52 (m, 2H), 3.06–3.00 (m, 4H), 2.30–2.17 (m, 4H), 2.04–2.00 (m, 4H), 1.65–1.51 (m, 5H), 1.33–1.27 (m, 19H), 1.23 (t, J = 7.0 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.78, 165.80, 164.21, 140.26, 139.23, 136.46, 136.43, 130.49, 130.14,

130.00, 129.89, 129.02, 127.14, 126.31, 94.44, 79.73, 63.36, 63.03, 36.86, 34.25, 32.52, 32.04, 31.02, 29.91, 29.85, 29.66, 29.46, 29.45, 29.31, 29.26, 29.24, 27.36, 27.32, 25.01, 23.19, 22.81, 14.25, 13.92 ppm. HRMS (ESI) m/z calcd for $C_{44}H_{61}NNaO_8$ $[M+Na]^+$ 754.4289, found 754.4283. The *ee* value was 92%, t_R (minor) = 19.458 min, t_R (major) = 24.672 min (Chiralpak IC, λ = 220 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

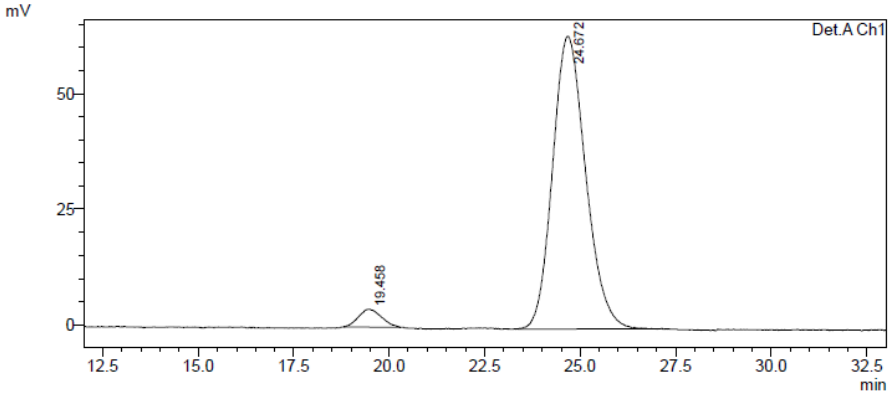


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.198	1997595	36212	52.121	56.620
2	24.230	1835006	27745	47.879	43.380
Total		3832601	63957	100.000	100.000



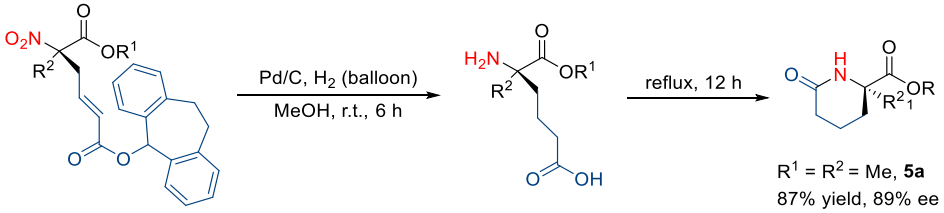
1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.458	161668	3883	4.054	5.774
2	24.672	3826479	63356	95.946	94.226
Total		3988147	67238	100.000	100.000

V. Synthetic manipulation of the product.

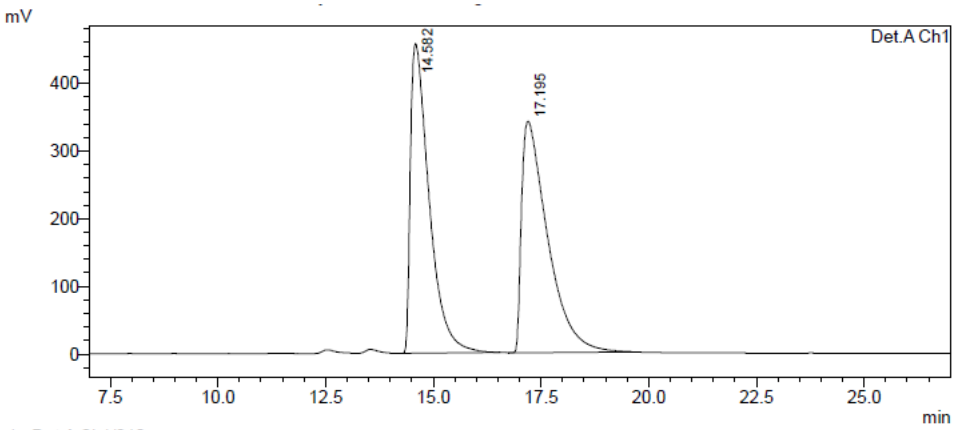


$R^1 = R^2$ = Me, **4a** (90% ee)
$R^1 = R^2$ = Et, **4b** (90% ee)

$R^1 = R^2$ = Me, **4a**-1
$R^1 = R^2$ = Et, **4b**-1

$R^1 = R^2$ = Me, **5a**
87% yield, 89% ee
$R^1 = R^2$ = Et, **5b**
92% yield, 90% ee

A stirred solution of **4a** (40.9 mg, 0.1 mmol) in MeOH (2 mL) was added Pd/C (10 mg) under the H_2 balloon. The mixture was stirred at room temperature for 6 h, and then the mixture was refluxed directly at 70 °C for 12 h. After completion of the reaction indicated by TLC, the mixture to a silica gel chromatography column (silica gel, PE/EtOAc = 1/1) to afford the desired product **5a** as colorless oil (14.9 mg, 87% yield); $[\alpha]^{25}_D$ = 3.3 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.81 (s, 3H), 2.47–2.37 (m, 2H), 2.32–2.25 (m, 1H), 2.23–2.17 (m, 1H), 1.80 (s, 3H), 1.73–1.64 (m, 1H), 1.61–1.52 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.52, 167.86, 92.41, 53.70, 35.80, 33.39, 21.35, 19.01 ppm. HRMS (ESI) m/z calcd for $C_8H_{13}NNaO_3$ $[M+Na]^+$ 194.0788, found 194.0787. The *ee* value was 89%, t_R (minor) = 14.945 min, t_R (major) = 16.874 min (Chiralpak ID, λ = 210 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

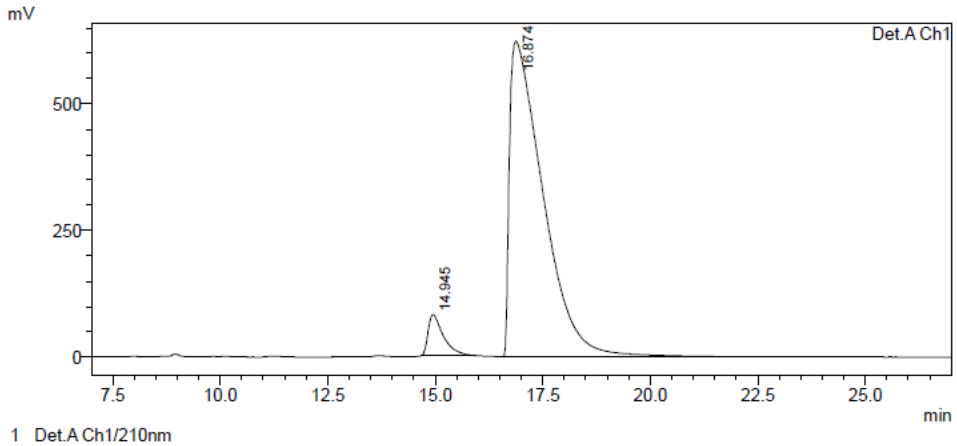


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.582	13866471	456992	48.973	57.232
2	17.195	14448201	341499	51.027	42.768
Total		28314672	798491	100.000	100.000



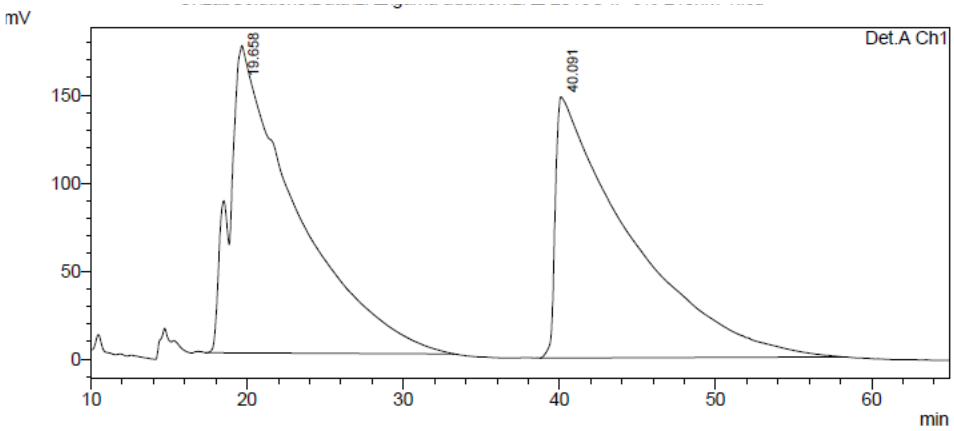
1 Det.A Ch1/210nm

PeakTable

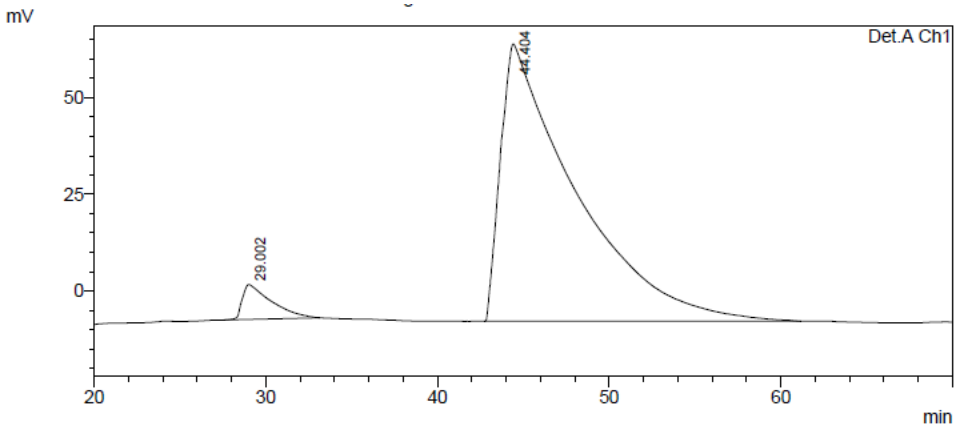
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.945	1997493	80979	5.600	11.507
2	16.874	33672672	622781	94.400	88.493
Total		35670166	703760	100.000	100.000

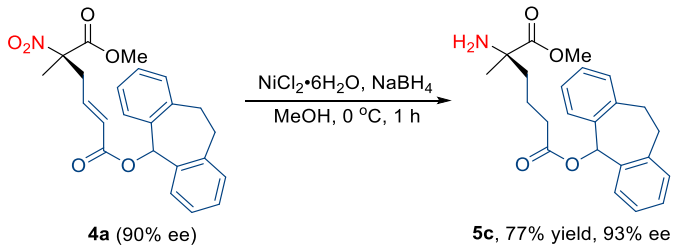
A stirred solution of **4b** (50.0 mg, 0.11 mmol) in MeOH (2 mL) was added Pd/C (10 mg) under the H_2 balloon. The mixture was stirred at room temperature for 6 h, and then the mixture was refluxed directly at 70 ºC for 12 h. After completion of the reaction indicated by TLC, the mixture to a silica gel chromatography column (silica gel, PE/EtOAc = 1/1) to afford the desired product **5b** as colorless oil (21.1 mg, 92% yield); $[\alpha]^{25}_{D}$ = -2.5 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.27 (q, J = 7.0 Hz, 2H), 2.42 (td, J = 7.0, 2.0 Hz, 2H), 2.35–2.18 (m, 4H), 1.65–1.47 (m, 2H), 1.29 (t, J = 7.0 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.87, 166.83, 96.36, 62.87, 33.29, 32.44, 27.07, 18.76, 14.00, 8.01 ppm. HRMS (ESI) m/z calcd for $C_{10}H_{17}NNaO_3$ $[M+Na]^+$ 222.1101, found 222.1110. The *ee* value was 90%, t_R (minor) = 29.002 min, t_R (major) = 44.404 min (Chiralpak IF, λ = 210 nm, 5.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.658	52405375	174622	51.700	54.071
2	40.091	48959682	148328	48.300	45.929
Total		101365056	322950	100.000	100.000



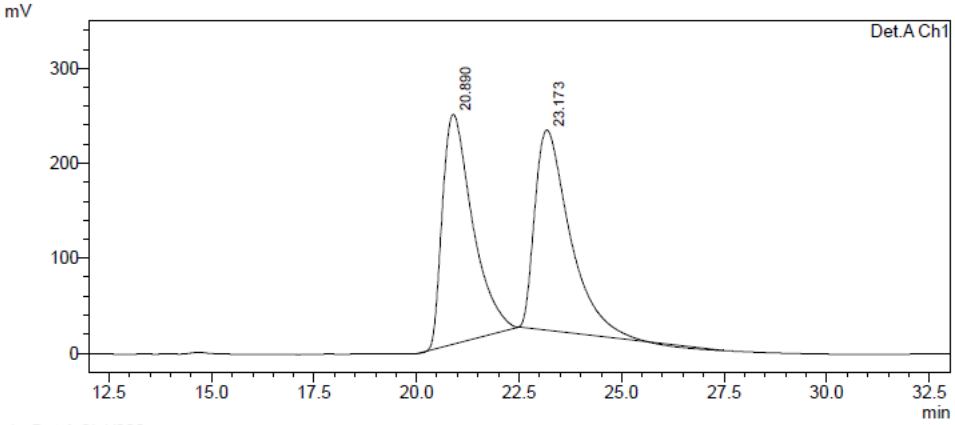
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.002	1055449	9032	4.660	11.182
2	44.404	21593915	71742	95.340	88.818
Total		22649365	80774	100.000	100.000



4a (90% ee) **5c**, 77% yield, 93% ee

To a solution of **4a** (40.9 mg, 0.1 mmol) in MeOH (2.0 mL), $NiCl_2 \cdot 6H_2O$ (23.8 mg, 0.1 mmol) and $NaBH_4$ (19.0 mg, 0.5 mmol) was added at 0 °C. The reaction mixture was stirred at 0 °C for 90 min. Then, $NaHCO_3$ was added dropwise until the solution attained pH 9. Methanol was removed by evaporation, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, After evaporation under reduced pressure, the residue was purified by silica gel flash column chromatography (hexane/ ethyl acetate = 2/1) to give **5c** as colorless oil (29.4 mg, 77%yield). $[\alpha]^{25}_D$ = -1.8 (c = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.0 Hz, 2H), 7.25–7.22 (m, 2H), 7.18–7.15 (m, 4H), 6.90 (s, 1H), 3.66 (s, 3H), 3.59–3.52 (m, 2H), 3.05–2.99 (m, 2H), 2.34 (t, J = 6.0 Hz, 2H), 1.66–1.62 (m, 2H), 1.53–1.49 (m, 2H), 1.27 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.58, 172.08, 140.20, 136.76, 130.41, 129.84, 128.86, 126.28, 79.10, 57.78, 52.37, 40.17, 34.62, 32.53, 26.12, 19.76 ppm. HRMS (ESI) m/z calcd for

$C_{23}H_{27}NNaO_4$ $[M+Na]^+$ 404.1832, found 404.1830. The *ee* value was 93%, t_R (minor) = 21.522 min, t_R (major) = 23.468 min (Chiralpak IF, λ = 220 nm, 10.0% *i*PrOH/hexane, flow rate = 1.0 mL/min).

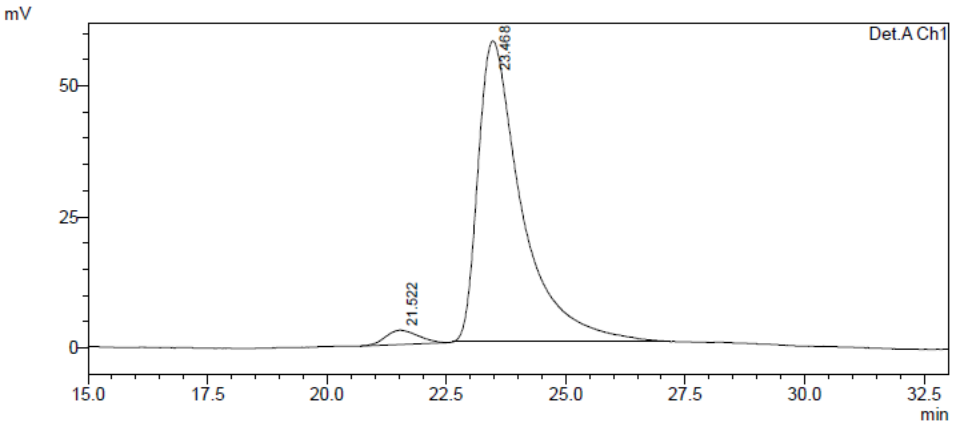


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.890	12384024	242012	49.664	53.431
2	23.173	12551757	210927	50.336	46.569
Total		24935780	452940	100.000	100.000



1 Det.A Ch1/220nm

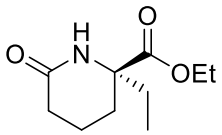
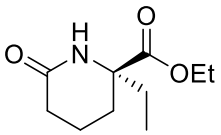
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.522	128346	2740	3.382	4.555
2	23.468	3667044	57428	96.618	95.445
Total		3795390	60169	100.000	100.000

VI. Determination of the absolute configuration of 5b.

The absolute configuration of products **5b** was established through the comparison of its value of specific rotation with that of a known compound reported in the literature.[3]

(R)-product in this work	*(R)*-product in literature
 ethyl (*R*)-2-ethyl-6-oxopiperidine-2-carboxylate	 ethyl (*R*)-2-ethyl-6-oxopiperidine-2-carboxylate
Specific rotation: $[\alpha]D^{20}$ = -2.5 (c = 1.9, $CHCl_3$)	Reported specific rotation: $[\alpha]D^{20}$ = -8.3 (c = 1.9, $CHCl_3$)

VII. References

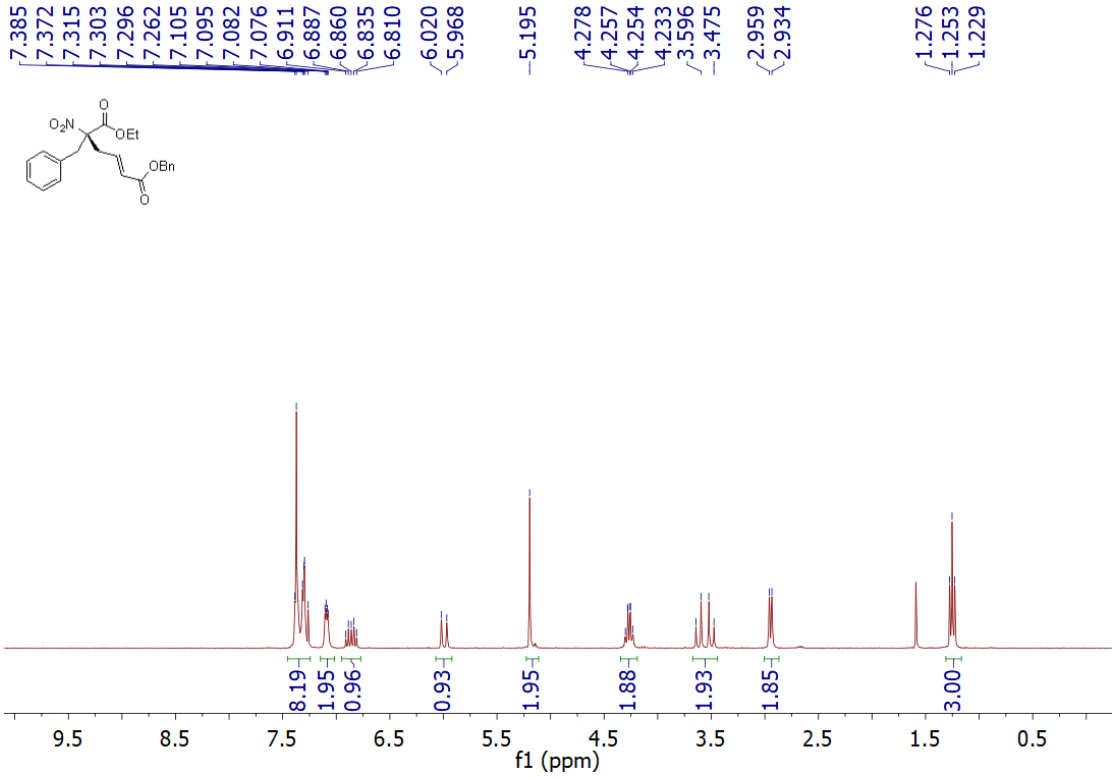
1 (*a*) X. Han, Y. Wang, F. Zhong and Y. Lu, Enantioselective [3 + 2] Cycloaddition of Allenes to Acrylates Catalyzed by Dipeptide-Derived Phosphines: Facile Creation of Functionalized Cyclopentenes Containing Quaternary Stereogenic Centers, *J. Am. Chem. Soc.,* 2011, **133**, 1726–1728; (*b*) F. Zhong, X. Han, Y. Wang and Y. Lu, Highly Enantioselective [3 + 2] Annulation of Morita–Baylis–Hillman Adducts Mediated by *L*-Threonine-Derived Phosphines: Synthesis of 3-Spirocyclopentene-2-oxindoles having Two Contiguous Quaternary Centers, *Angew. Chem., Int. Ed.,* 2011, **50**, 7837–7841; (*c*) F. Zhong, X. Han, Y. Wang and Y. Lu, Highly enantioselective [4 + 2] annulations catalyzed by amino acid-based phosphines: Synthesis of functionalized cyclohexenes and 3-spirocyclohexene-2-oxindoles, *Chem. Sci.,* 2012, **3**, 1231–1234; (*d*) X. Han, F. Zhong, Y. Wang and Y. Lu, Versatile Enantioselective [3 + 2] Cyclization between Imines and Allenoates Catalyzed by Dipeptide-Based Phosphines, *Angew. Chem., Int. Ed.,* 2012, **51**, 767–770; (*e*) F. Zhong, J. Luo, G.-Y. Chen, X. Dou and Y. Lu, Highly Enantioselective Regiodivergent Allylic Alkylations of MBH Carbonates with Phthalides, *J. Am. Chem. Soc.,* 2012, **134**, 10222–10227; (*f*) F. Zhong, X. Dou, X. Han, W. Yao, Q. Zhu, Y. Meng and Y. Lu, Chiral Phosphine Catalyzed Asymmetric Michael Addition of Oxindoles, *Angew. Chem., Int. Ed.,* 2013, **52**, 943–947; (*g*) X. Han, W. Yao, T. Wang, Y. R. Tan, Z. Yan, J. Kwiatkowski and Y. Lu, Asymmetric Synthesis of Spiropyrazolones through Phosphine-Catalyzed [4 + 1] Annulation, *Angew. Chem., Int. Ed.,* 2014, **53**, 5643–5647; (*h*) W. Yao, X. Dou and Y. Lu, Highly Enantioselective Synthesis of 3,4-Dihydropyrans through a Phosphine-Catalyzed [4 + 2] Annulation of Allenones and β,γ-Unsaturated α-Keto Esters, *J. Am. Chem. Soc.,* 2015, **137**, 54–57; (*i*) T. Wang, Z. Yu, D. L. Hoon, C. Y. Phee, Y. Lan and Y. Lu, Regiodivergent

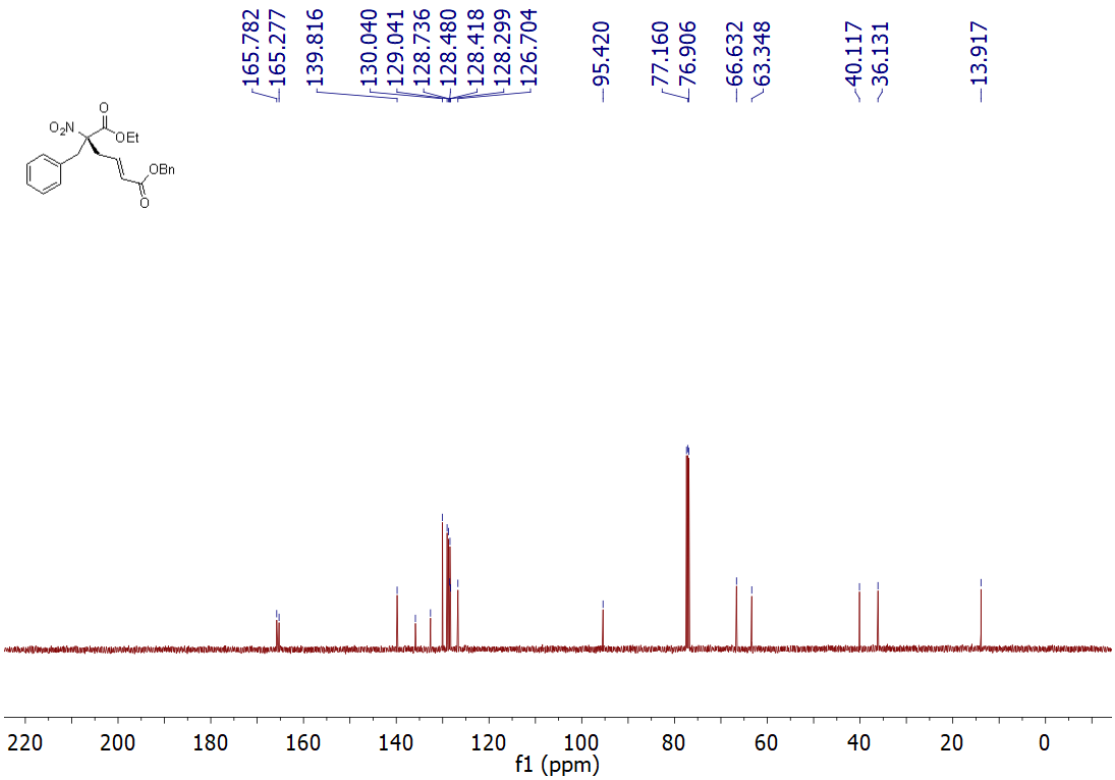
Enantioselective γ-Additions of Oxazolones to 2,3-Butadienoates Catalyzed by Phosphines: Synthesis of α,α-Disubstituted α-Amino Acids and *N,O*-Acetal Derivatives, *J. Am. Chem. Soc.,* 2016, **138**, 265–271.

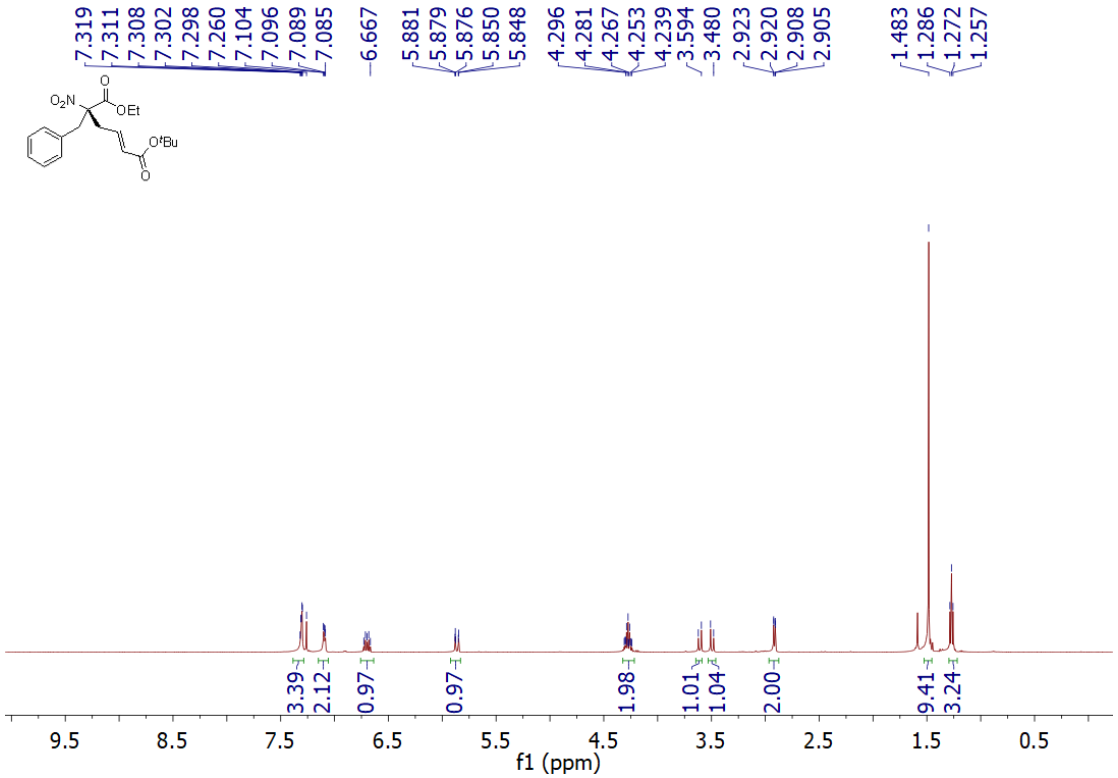
2 D. F. González, J. P. Brand and J. Waser, Ethynyl-1,2-benziodoxol-3(1 *H*)-one (EBX): An Exceptional Reagent for the Ethynylation of Keto, Cyano, and Nitro Esters, *Chem. –Eur. J.,* 2010*,* **16***,* 9457–9461.

3 B. Westermann and I. Gedrath, Facile Synthesis of Completely Protected Enantiomerically Pure α,α-Disubstituted α-Amino Acids, *Synlett,* 1996, 665–666.

VIII. Copies of ^{1}H and ^{13}C NMR spectra



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5.876
5.850
5.848
4.296
4.281
4.267
4.253
4.239
3.594
3.480
2.923
2.920
2.908
2.905
1.483
1.286
1.272
1.257
O2N
OEt
OtBu
O
3.39
2.12
0.97
0.97
1.98
1.01
1.04
2.00
9.41
3.24
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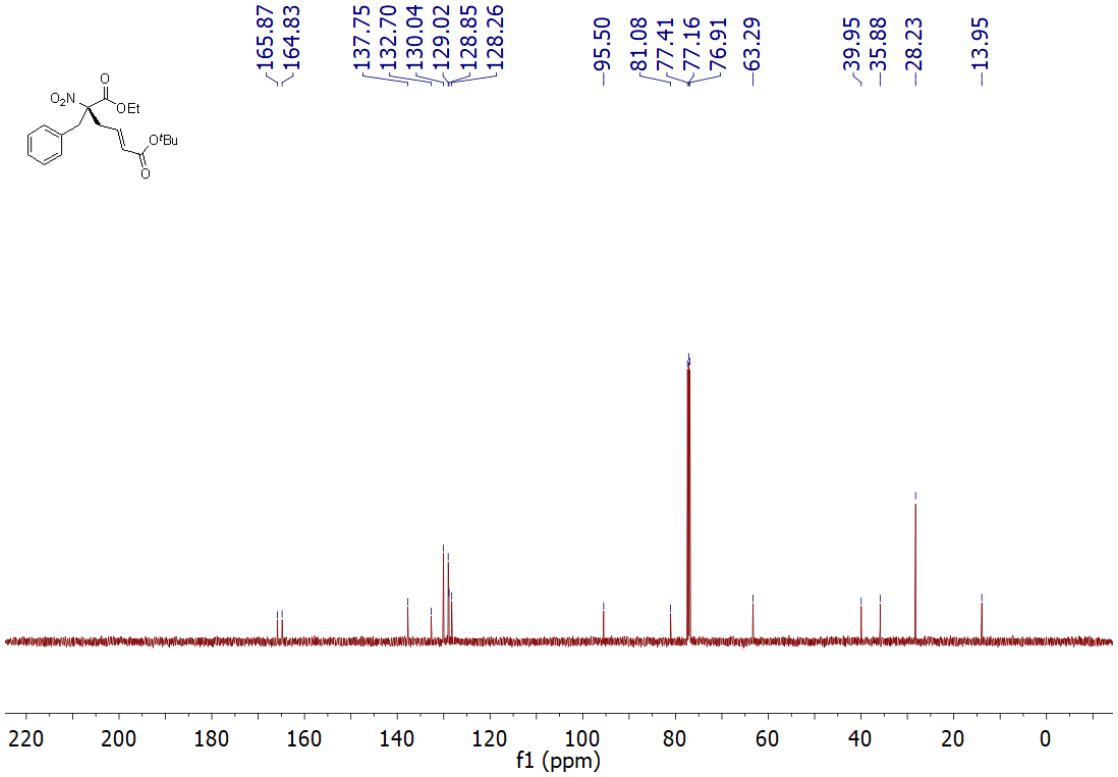
f1 (ppm)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63.29
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28.23
13.95
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OtBu
O
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180
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140
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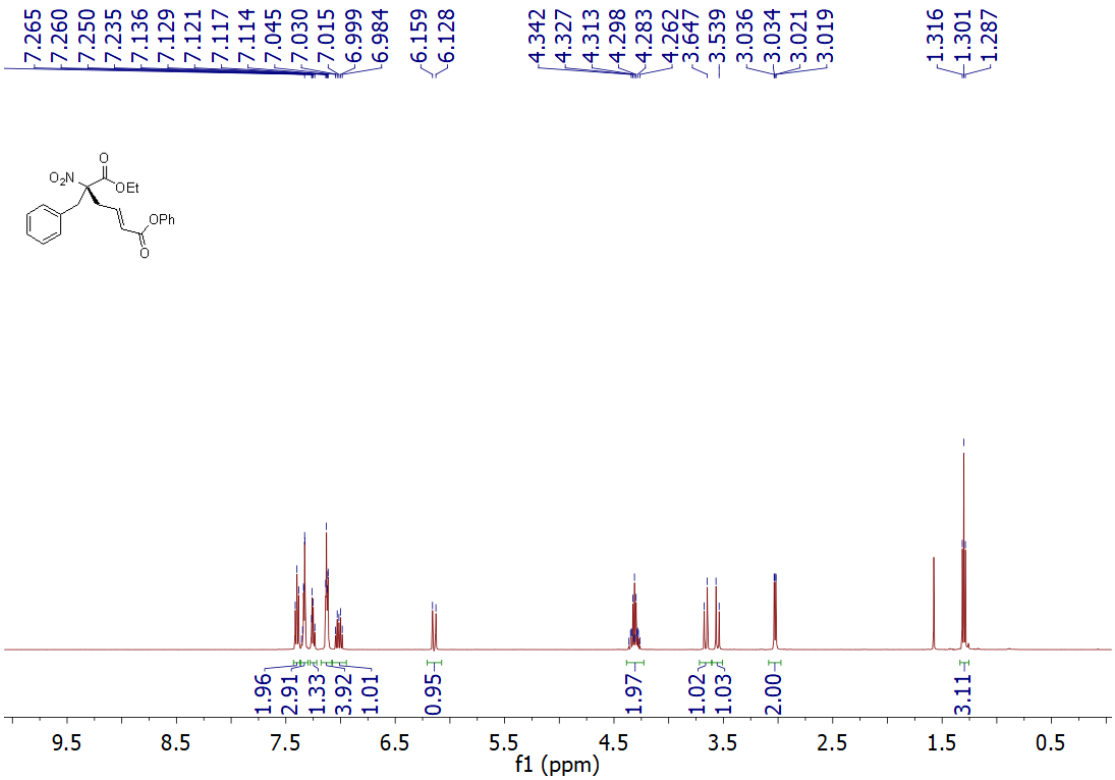
100
80
60
40
20
0
f1 (ppm)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4.313
4.298
4.283
4.262
3.647
3.539
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3.034
3.021
3.019
1.316
1.301
1.287
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OEt
OPh
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2.91
1.33
3.92
1.01
0.95
1.97
1.02
1.03
2.00
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1.5
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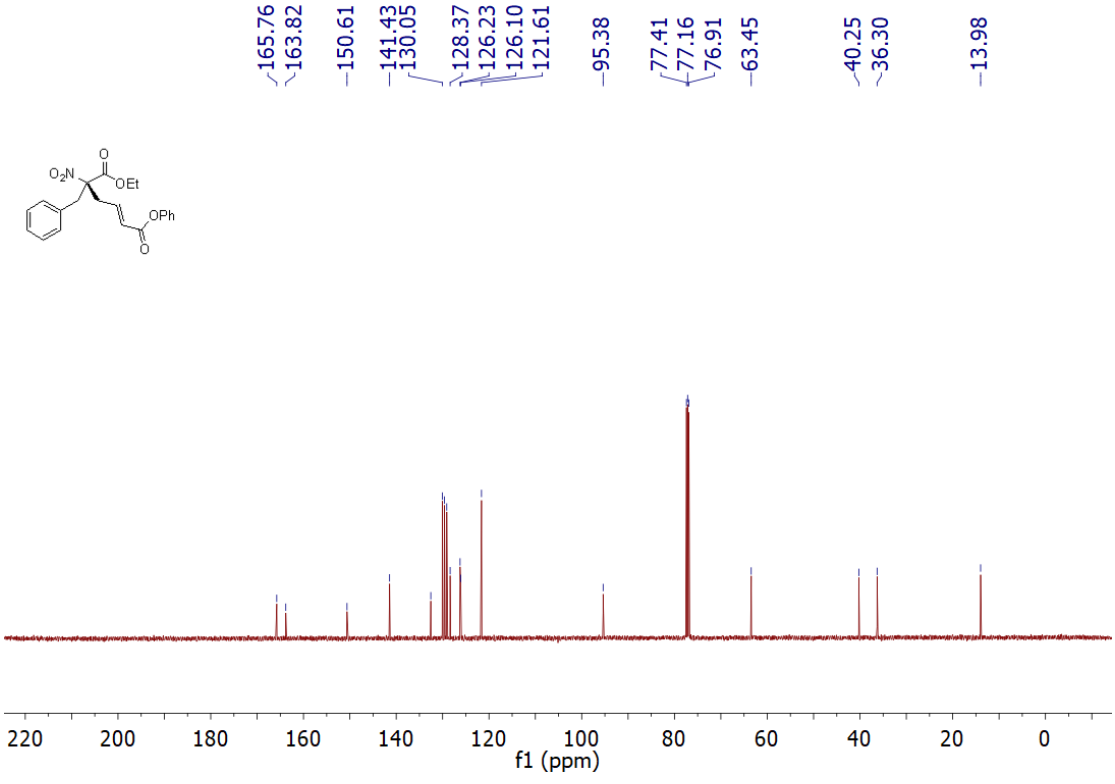
f1 (ppm)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40.25
36.30
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O2N
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180
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100
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20
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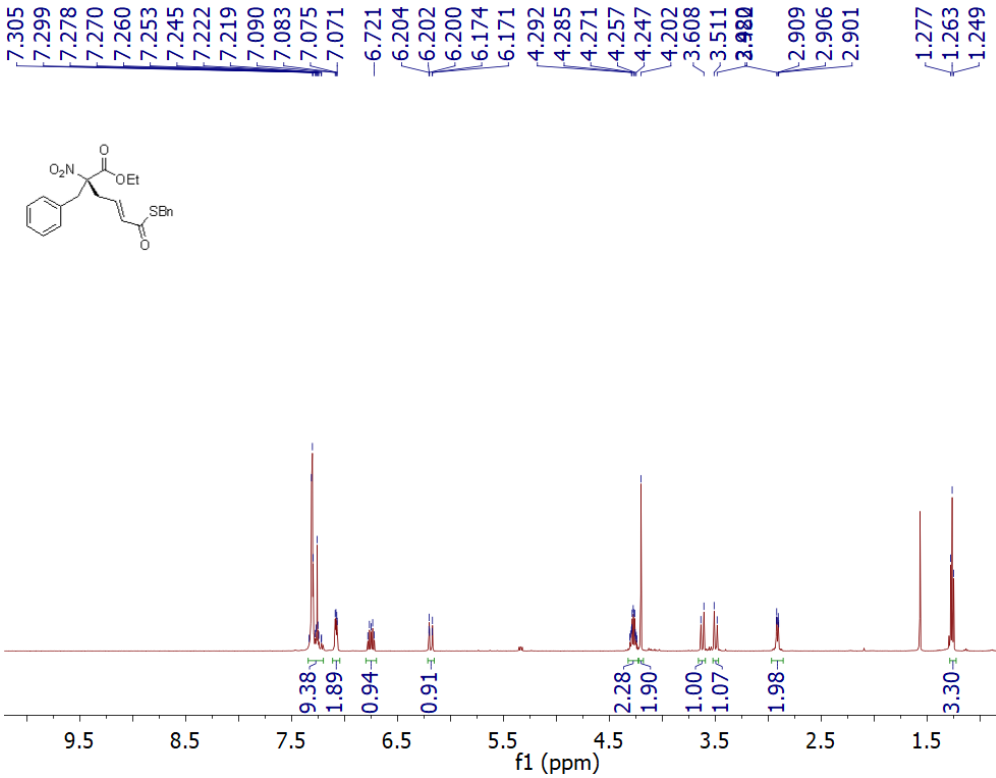
f1 (ppm)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6.202
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3.608
3.511
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2.906
2.901
1.277
1.263
1.249
O2N
OEt
SBn
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0.91
2.28
1.90
1.00
1.07
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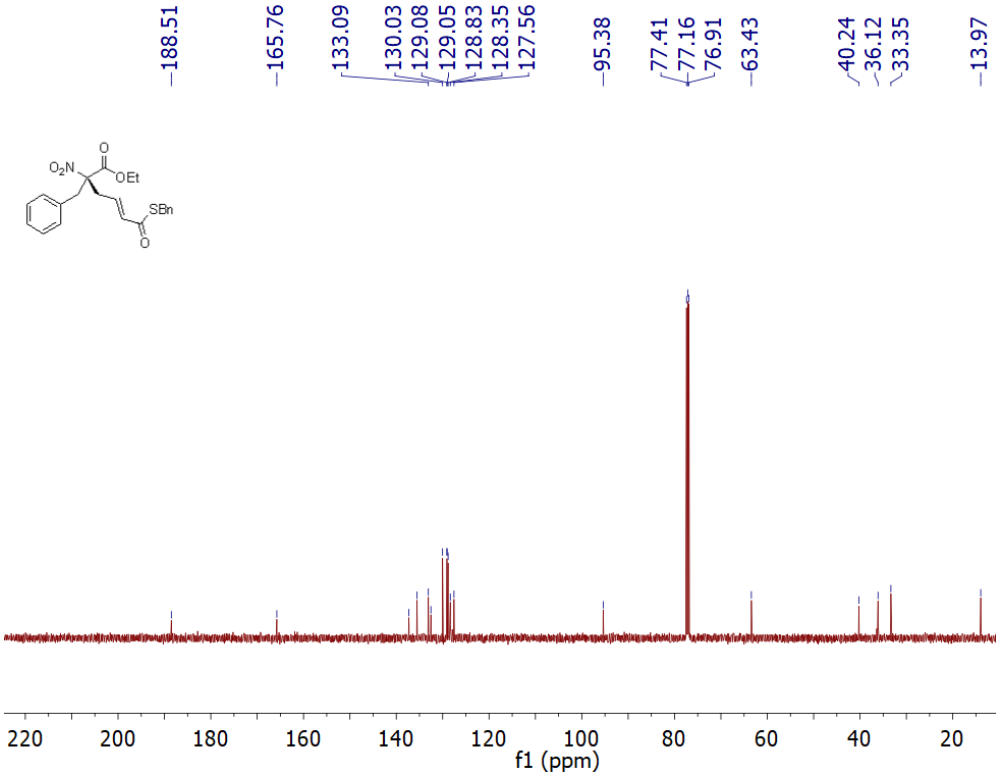
f1 (ppm)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40.24
36.12
33.35
13.97
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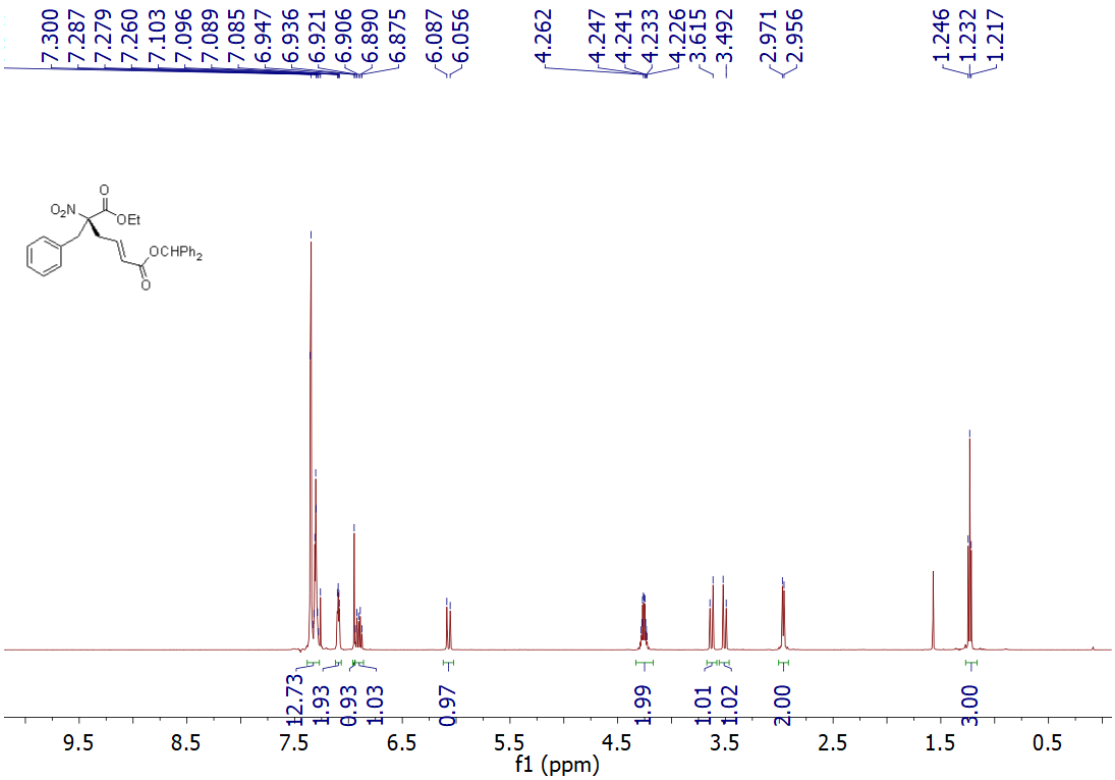
f1 (ppm)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6.875
6.087
6.056
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4.241
4.233
4.226
3.615
3.492
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2.956
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OEt
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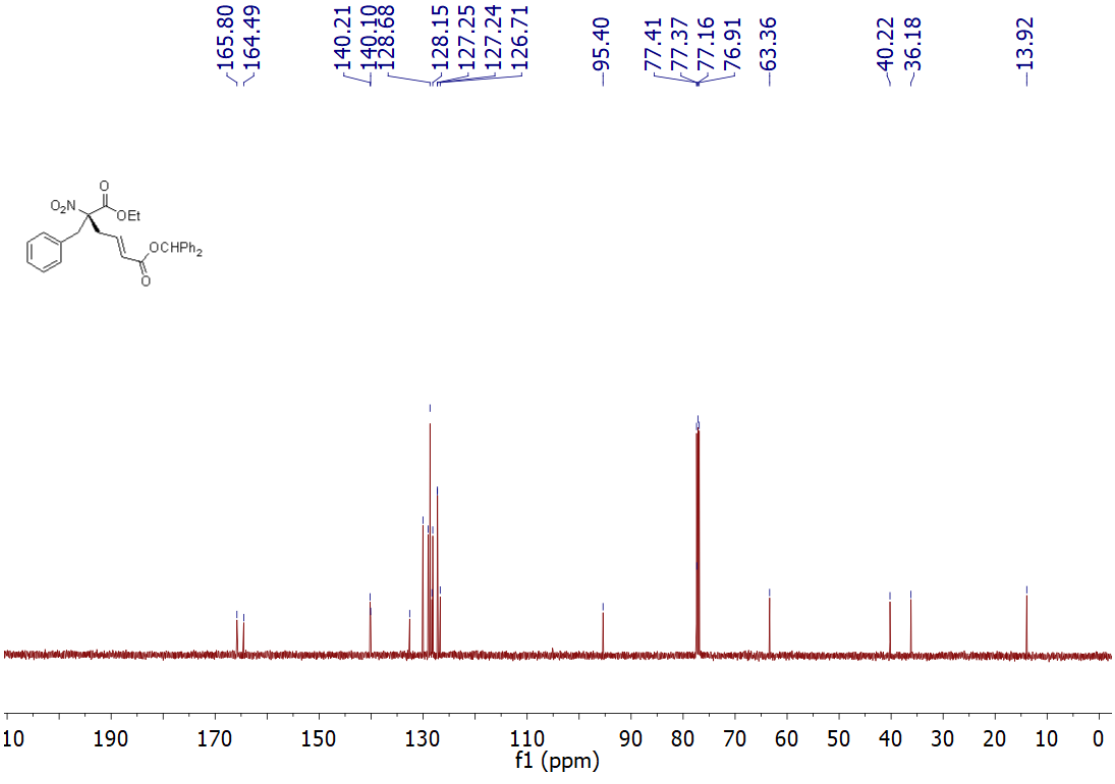
f1 (ppm)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77.16
76.91
63.36
40.22
36.18
13.92
O2N
OEt
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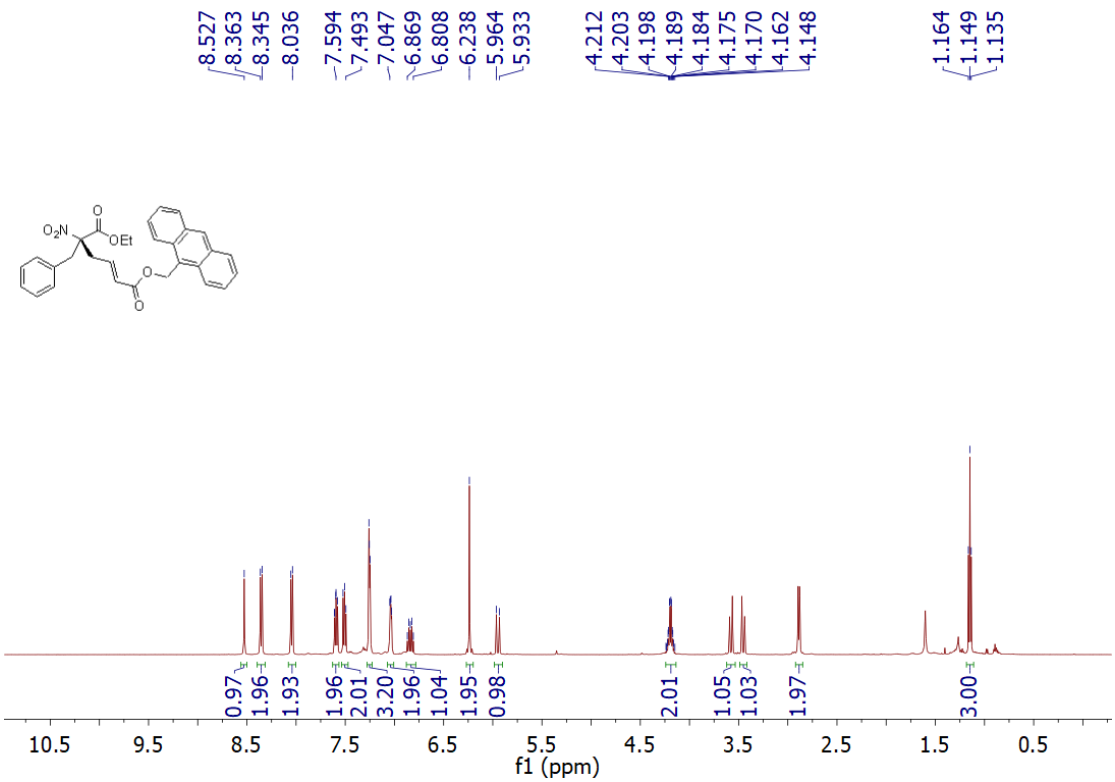
f1 (ppm)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4.170
4.162
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1.135
O2N
OEt
O
O
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1.96
1.93
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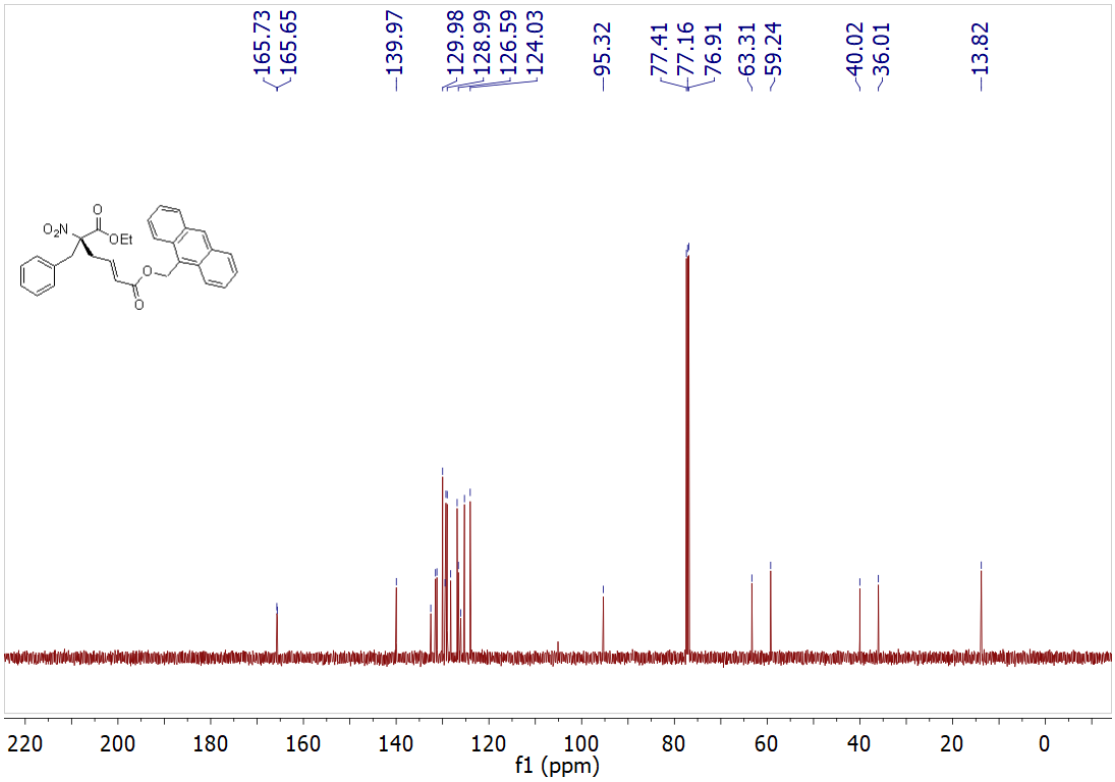
f1 (ppm)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36.01
13.82
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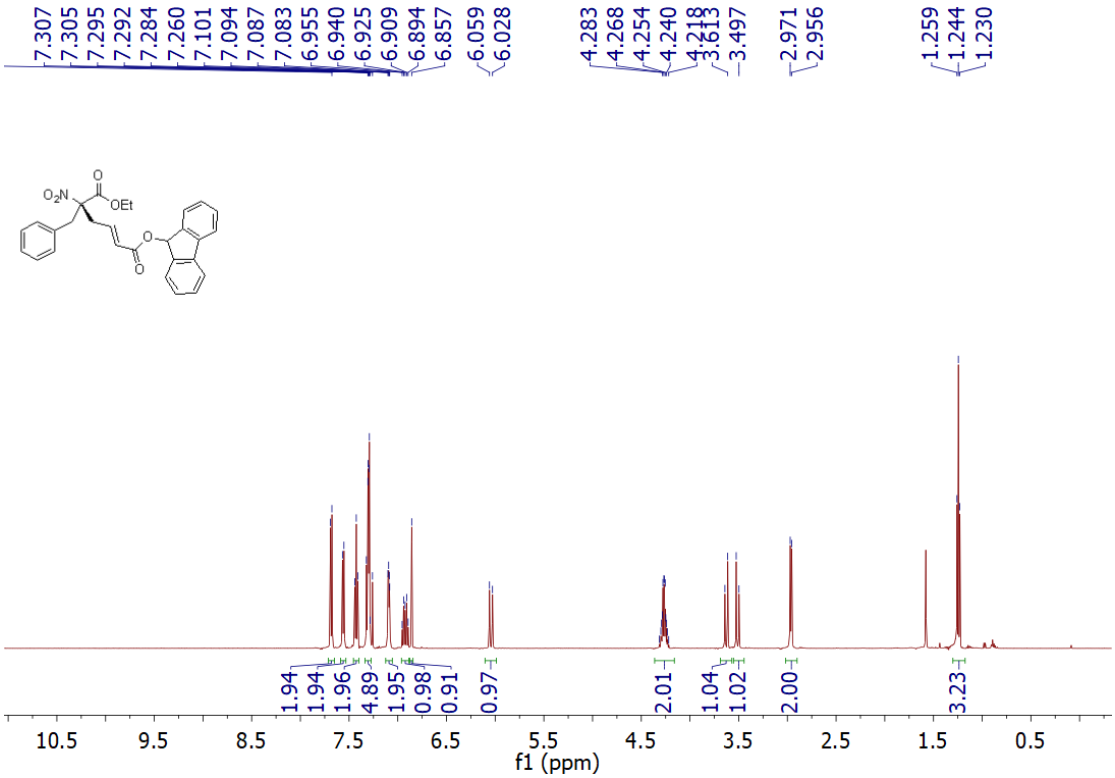
60
40
20
0
f1 (ppm)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1.94
1.96
4.89
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0.91
0.97
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1.04
1.02
2.00
3.23
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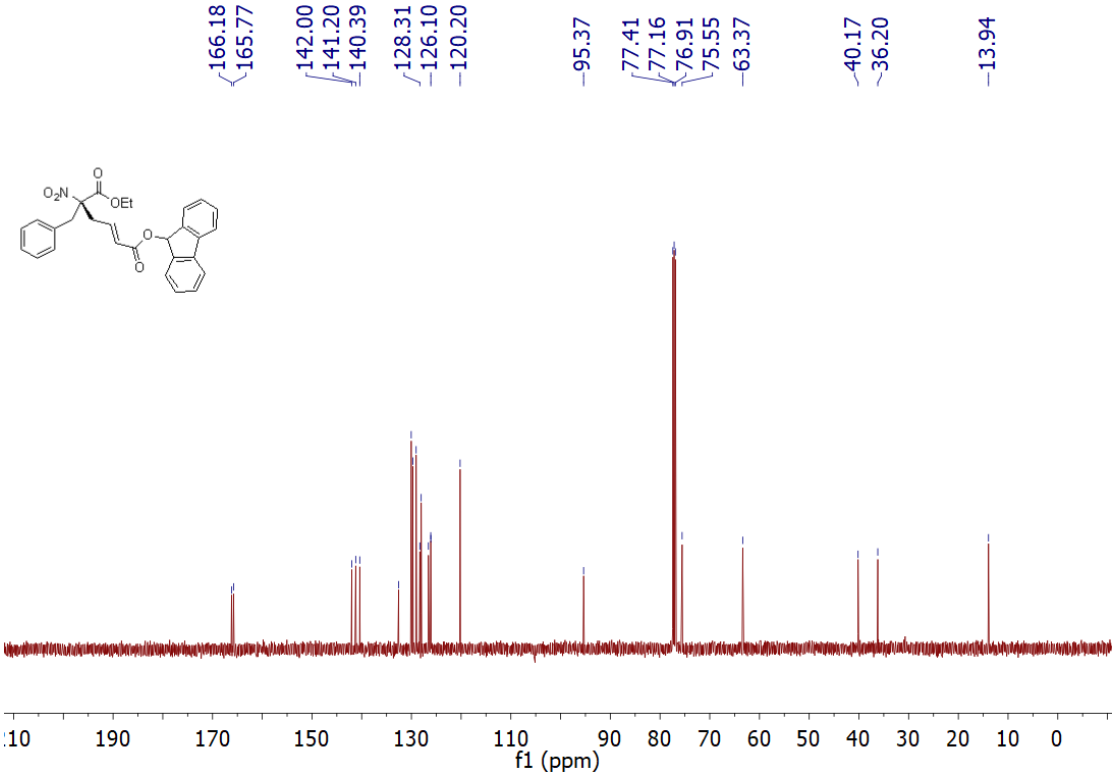
f1 (ppm)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210
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170
150
130
110
90
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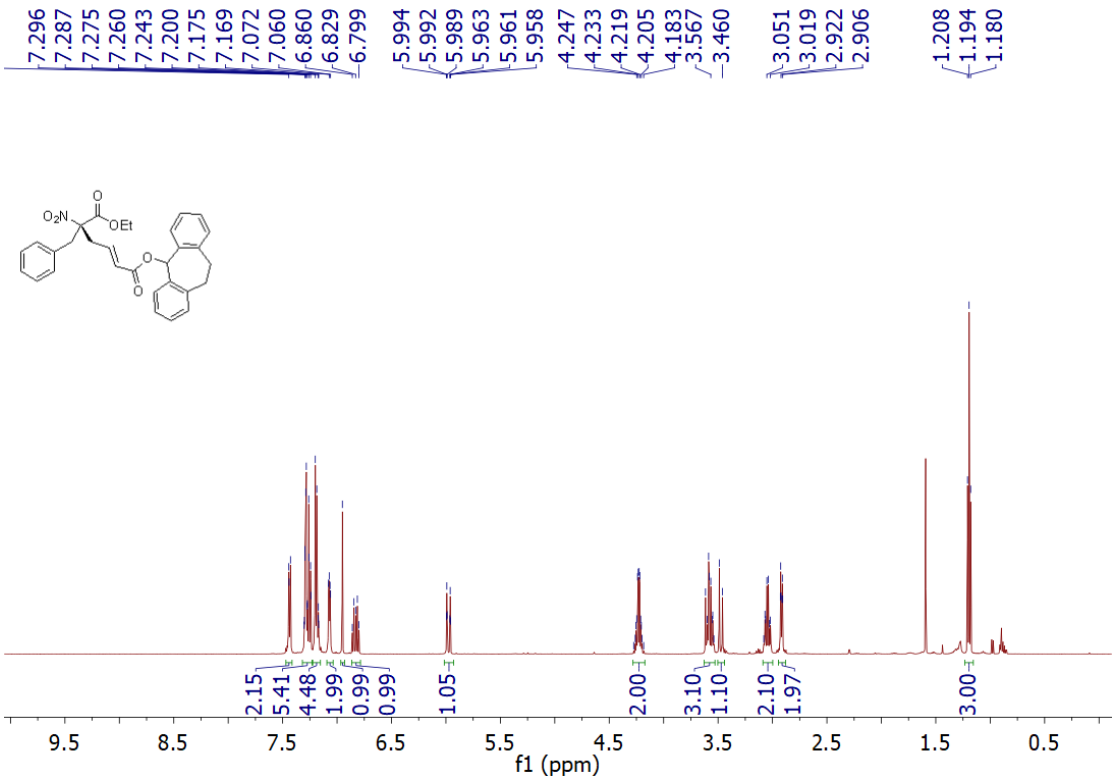
70
60
50
40
30
20
10
0
f1 (ppm)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6.799
5.994
5.992
5.989
5.963
5.961
5.958
4.247
4.233
4.219
4.205
4.183
3.567
3.460
3.051
3.019
2.922
2.906
1.208
1.194
1.180
O2N
OEt
O
O
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5.41
4.48
1.99
0.99
0.99
1.05
2.00
3.10
1.10
2.10
1.97
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5.5
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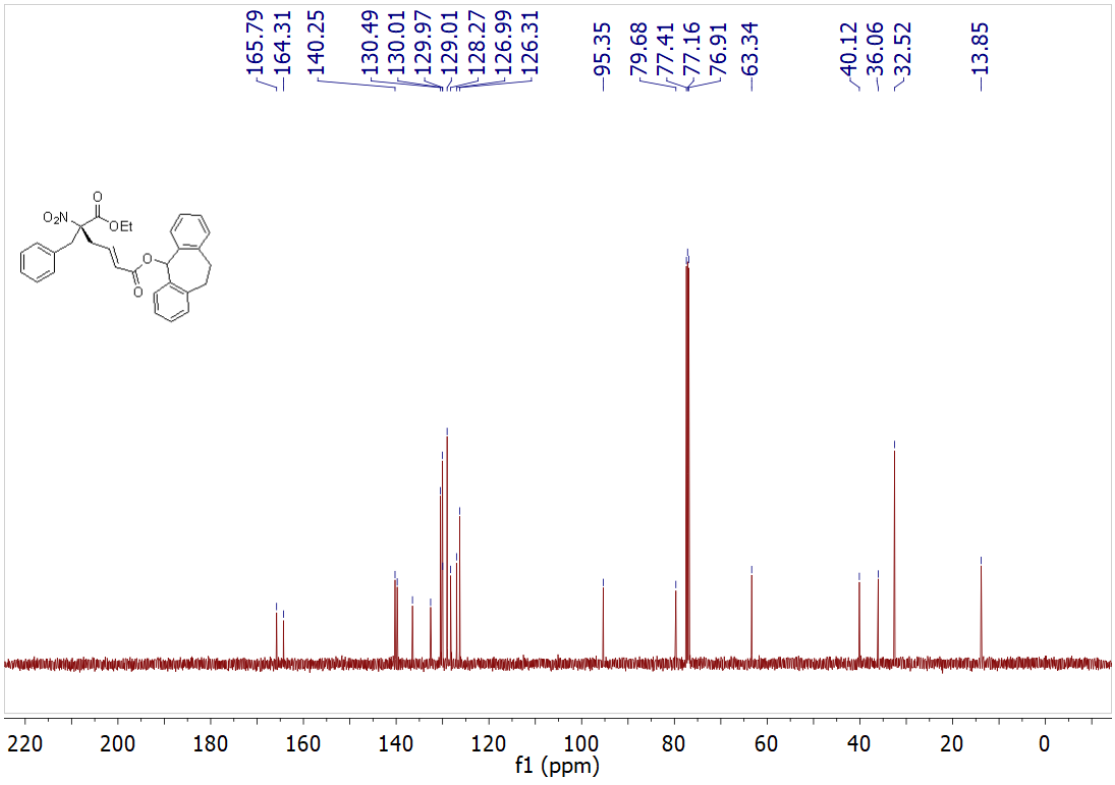
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128.27
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126.31
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77.41
77.16
76.91
63.34
40.12
36.06
32.52
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O
O
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140
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100
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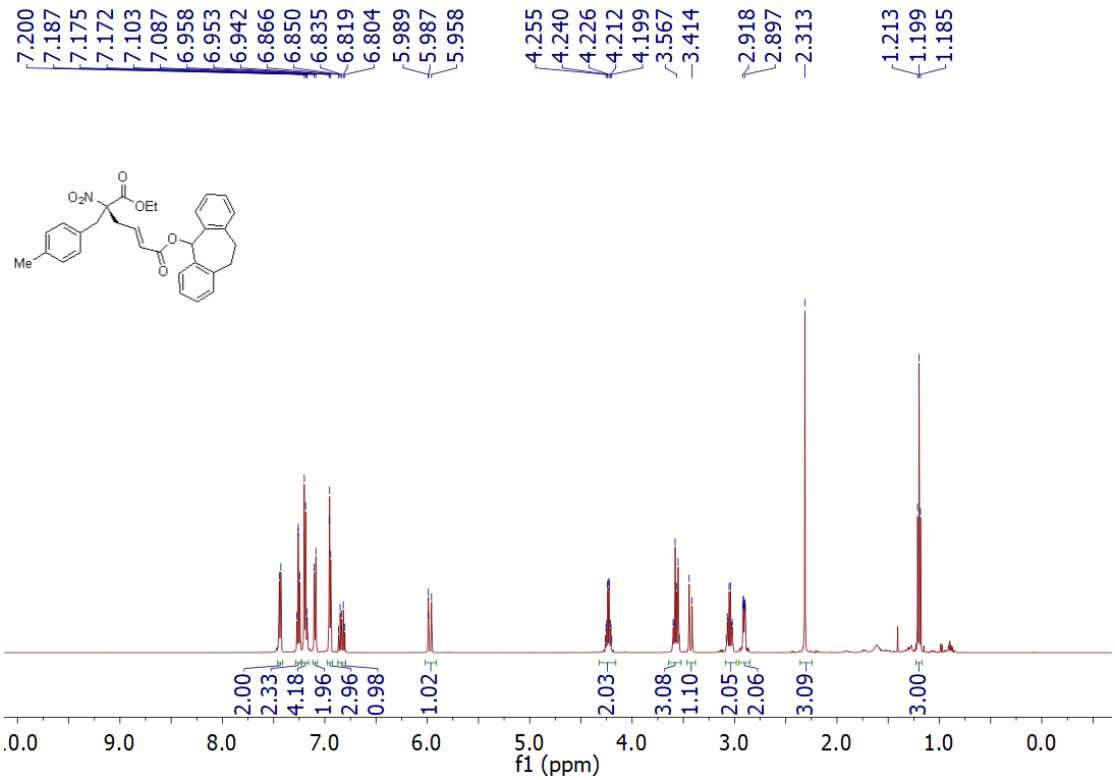
0
f1 (ppm)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6.850
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6.804
5.989
5.987
5.958
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4.240
4.226
4.212
4.199
3.567
3.414
2.918
2.897
2.313
1.213
1.199
1.185
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OEt
Me
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4.18
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3.08
1.10
2.05
2.06
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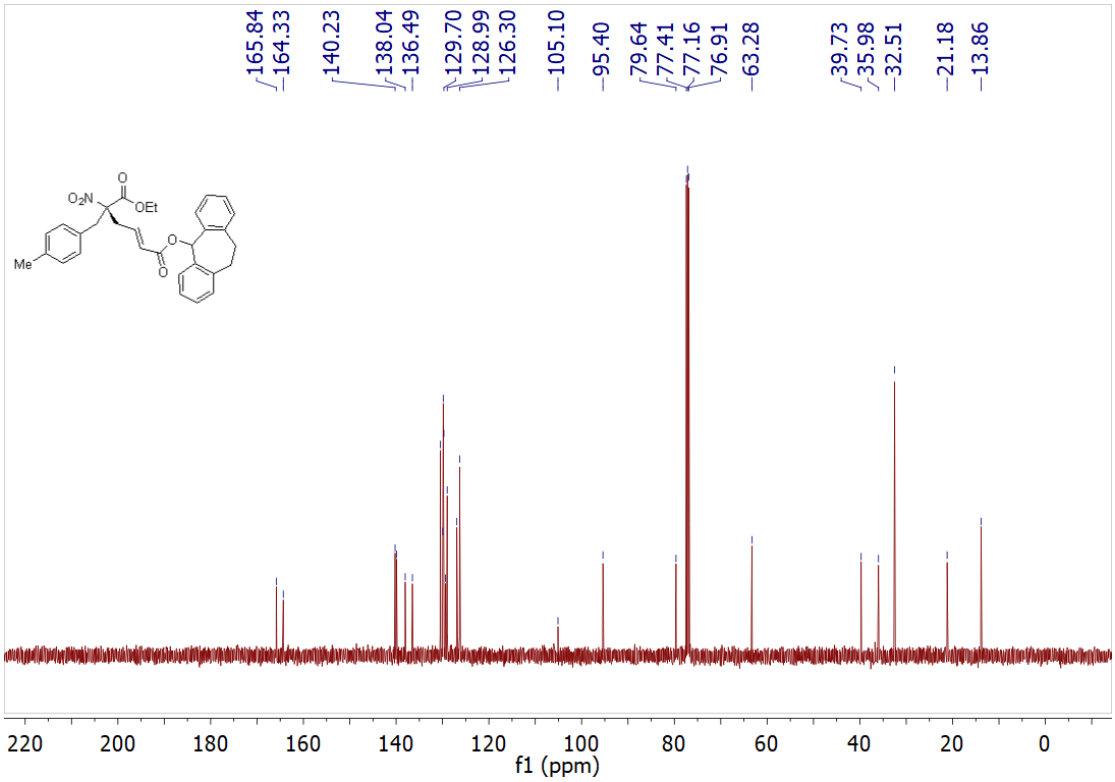
3.00
f1 (ppm)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77.41
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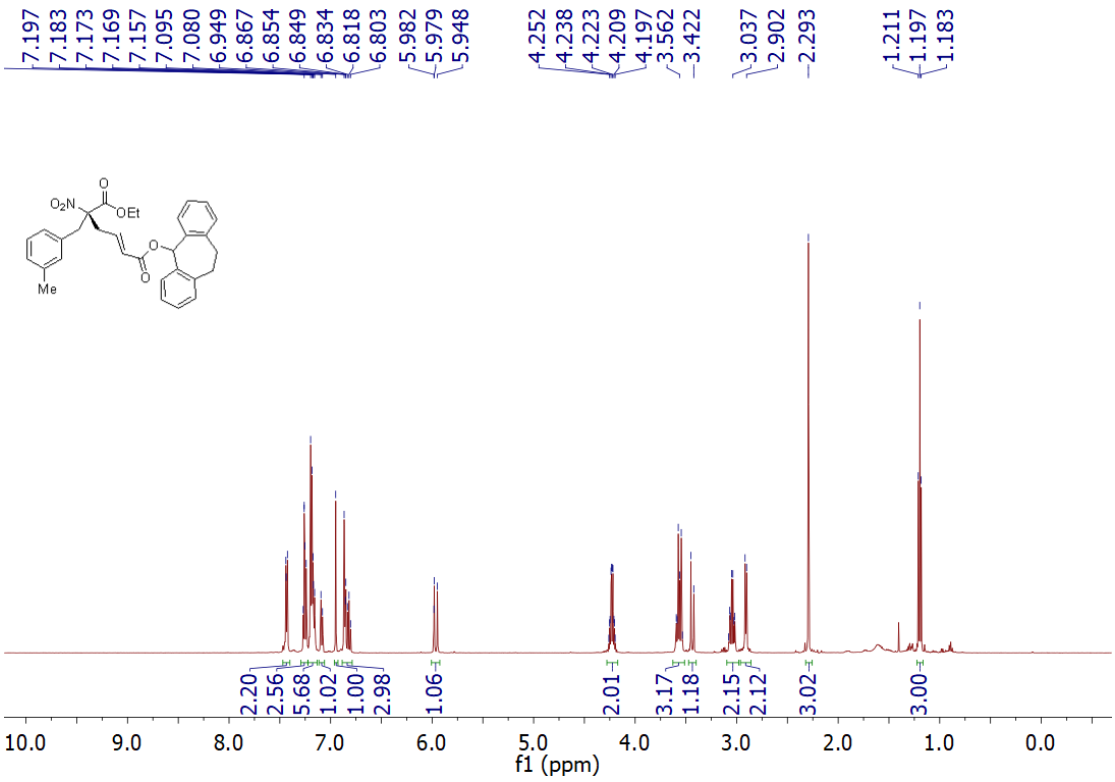
32.51
21.18
13.86
O2N
OEt
Me
f1 (ppm)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6.854
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6.803
5.982
5.979
5.948
4.252
4.238
4.223
4.209
4.197
3.562
3.422
3.037
2.902
2.293
1.211
1.197
1.183
O2N
OEt
O
O
Me
2.20
2.56
5.68
1.02
1.00
2.98
1.06
2.01
3.17
1.18
2.15
2.12
3.02
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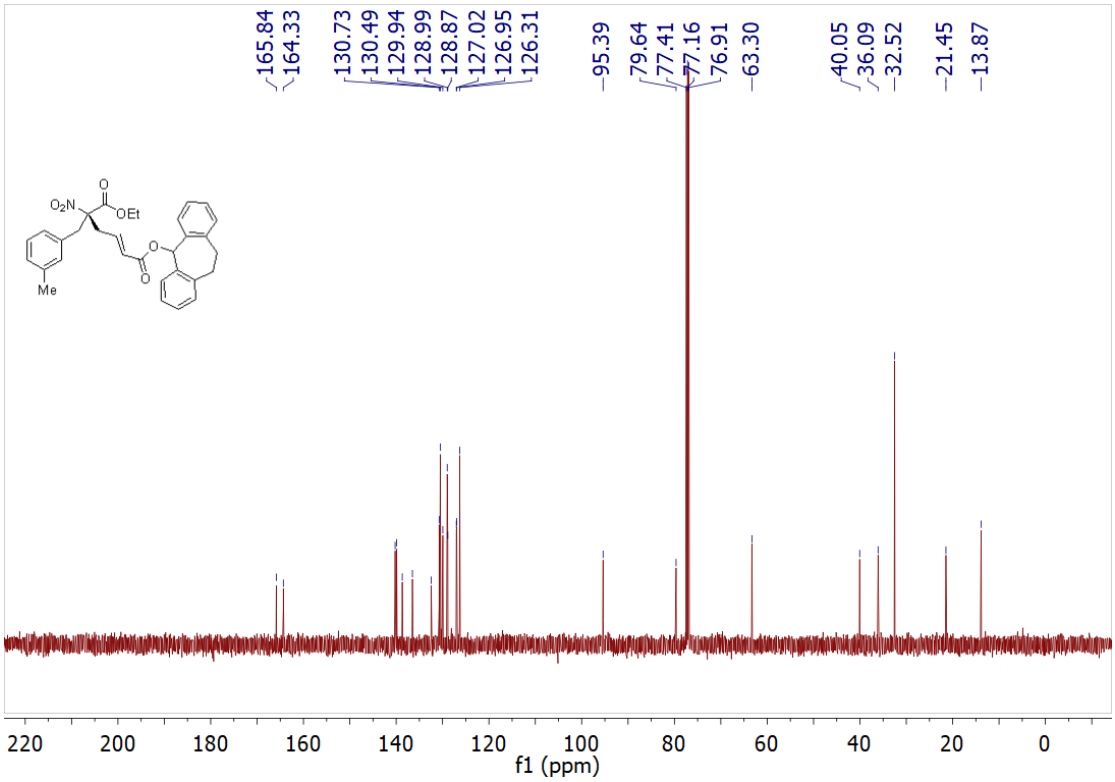
f1 (ppm)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77.16
76.91
63.30
40.05
36.09
32.52
21.45
13.87
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O
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100
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60
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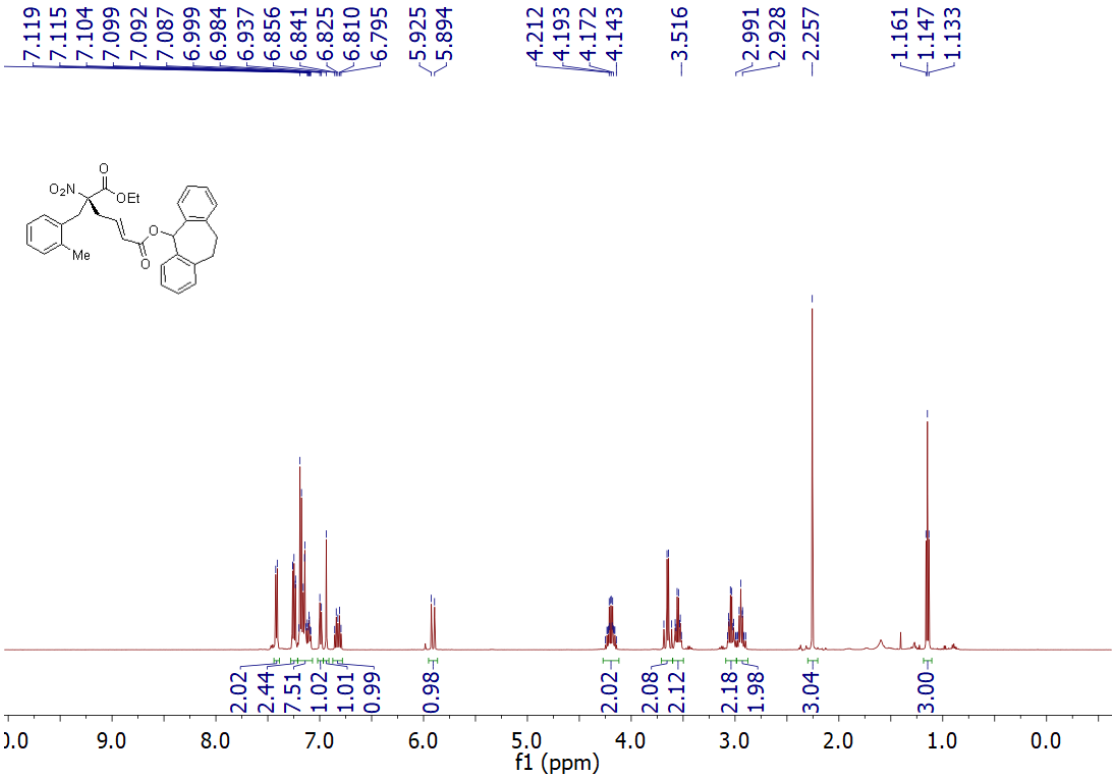
f1 (ppm)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6.810
6.795
5.925
5.894
4.212
4.193
4.172
4.143
3.516
2.991
2.928
2.257
1.161
1.147
1.133
O2N
OEt
O
Me
2.02
2.44
7.51
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1.01
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0.98
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2.08
2.12
2.18
1.98
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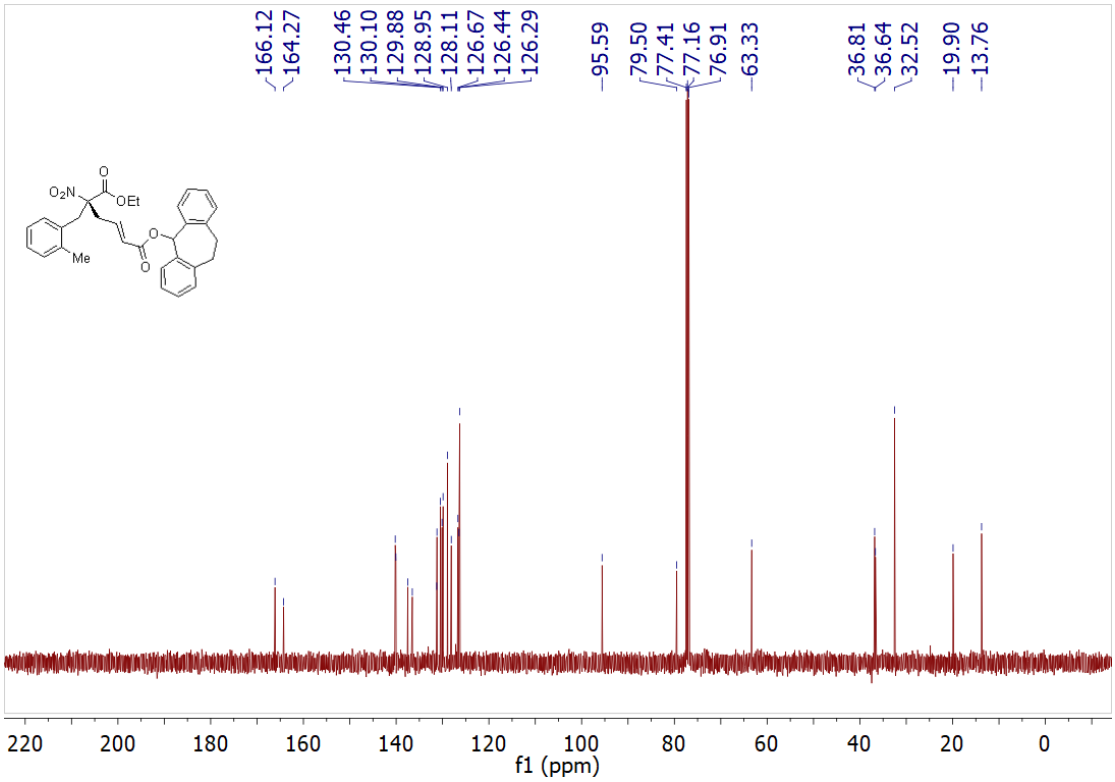
3.00
f1 (ppm)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77.41
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36.64
32.52
19.90
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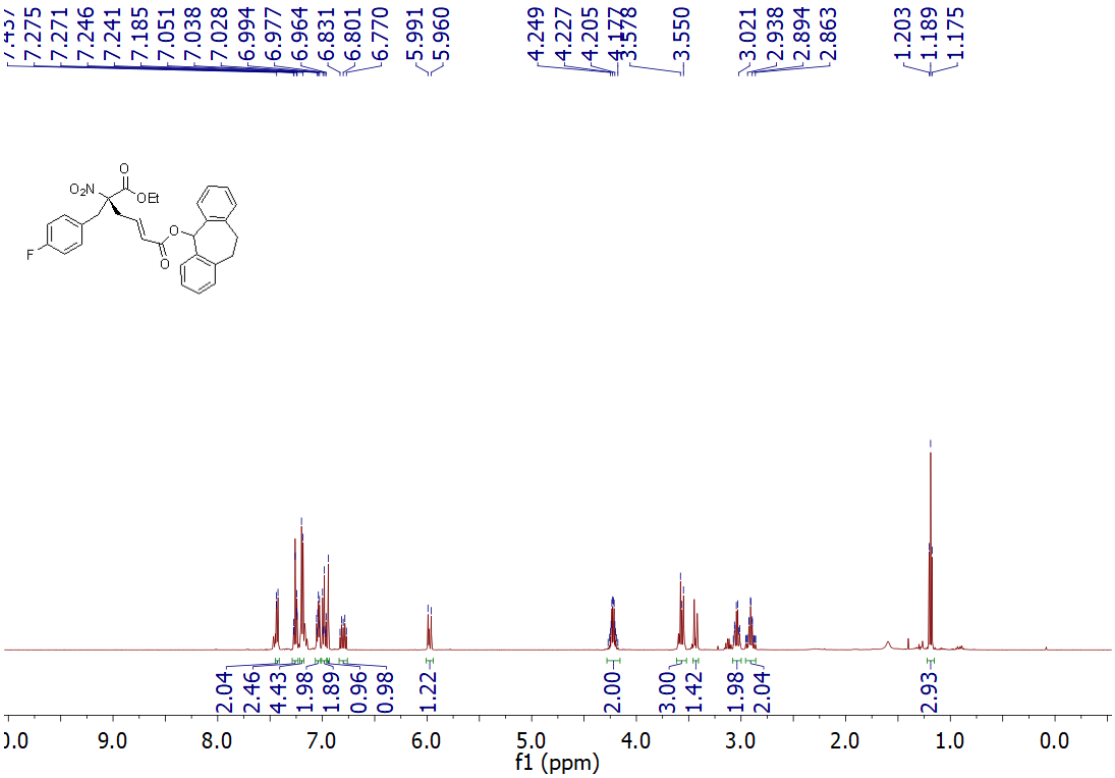
OEt
O
Me
f1 (ppm)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6.770
5.991
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4.205
3.578
3.550
3.021
2.938
2.894
2.863
1.203
1.189
1.175
O2N
OEt
F
O
2.04
2.46
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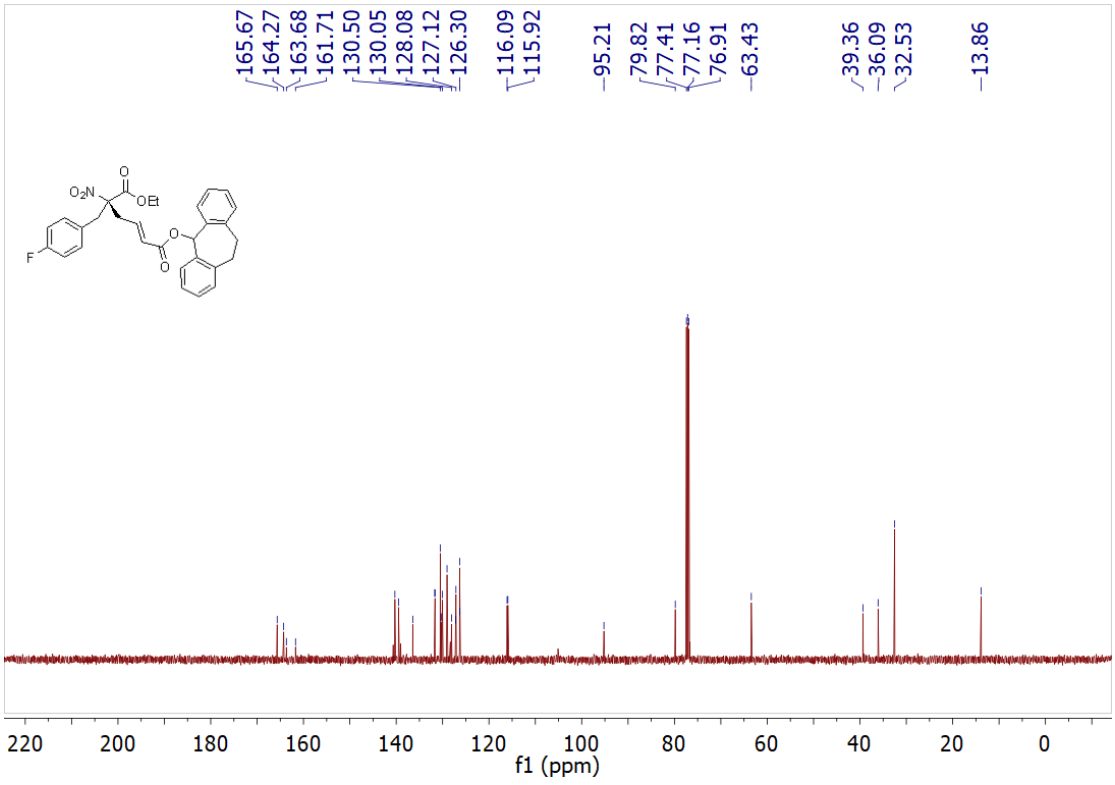
2.93
f1 (ppm)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115.92
95.21
79.82
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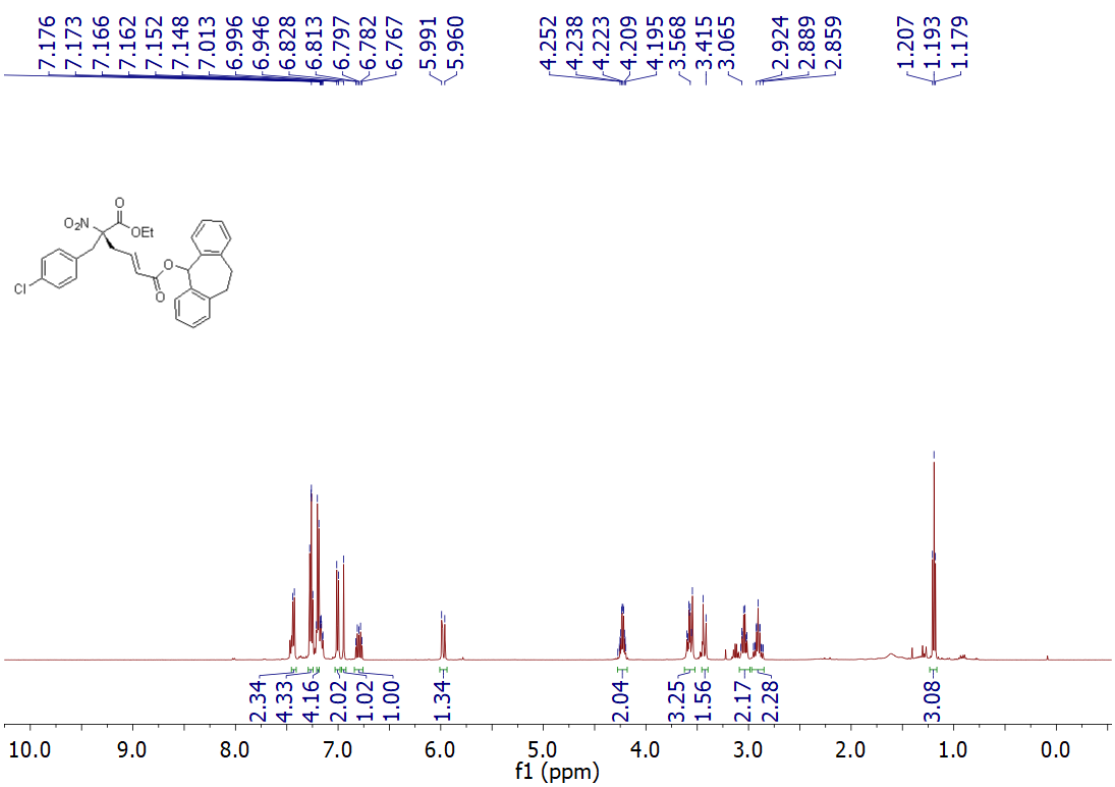
63.43
39.36
36.09
32.53
13.86
O2N
OEt
F
O
f1 (ppm)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6.782
6.767
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5.960
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4.238
4.223
4.209
4.195
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3.415
3.065
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2.889
2.859
1.207
1.193
1.179
O2N
OEt
Cl
2.34
4.33
4.16
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1.02
1.00
1.34
2.04
3.25
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2.28
3.08
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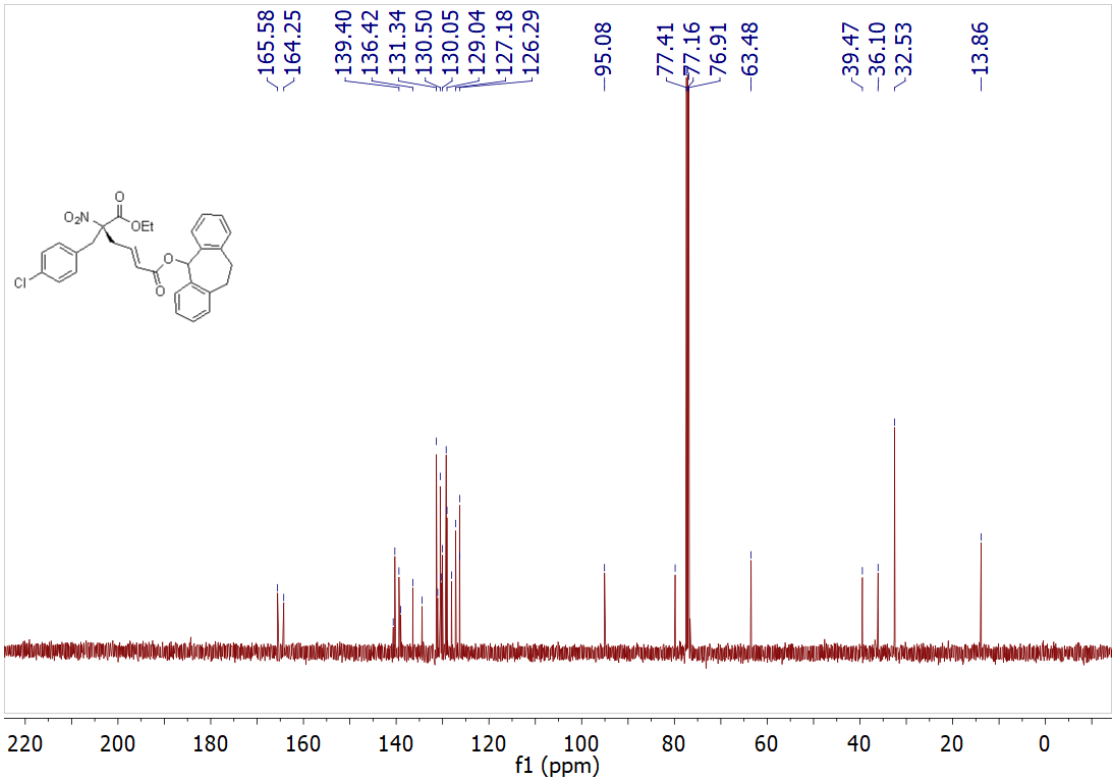
f1 (ppm)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95.08
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76.91
63.48
39.47
36.10
32.53
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O2N
OEt
Cl
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180
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140
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100
80
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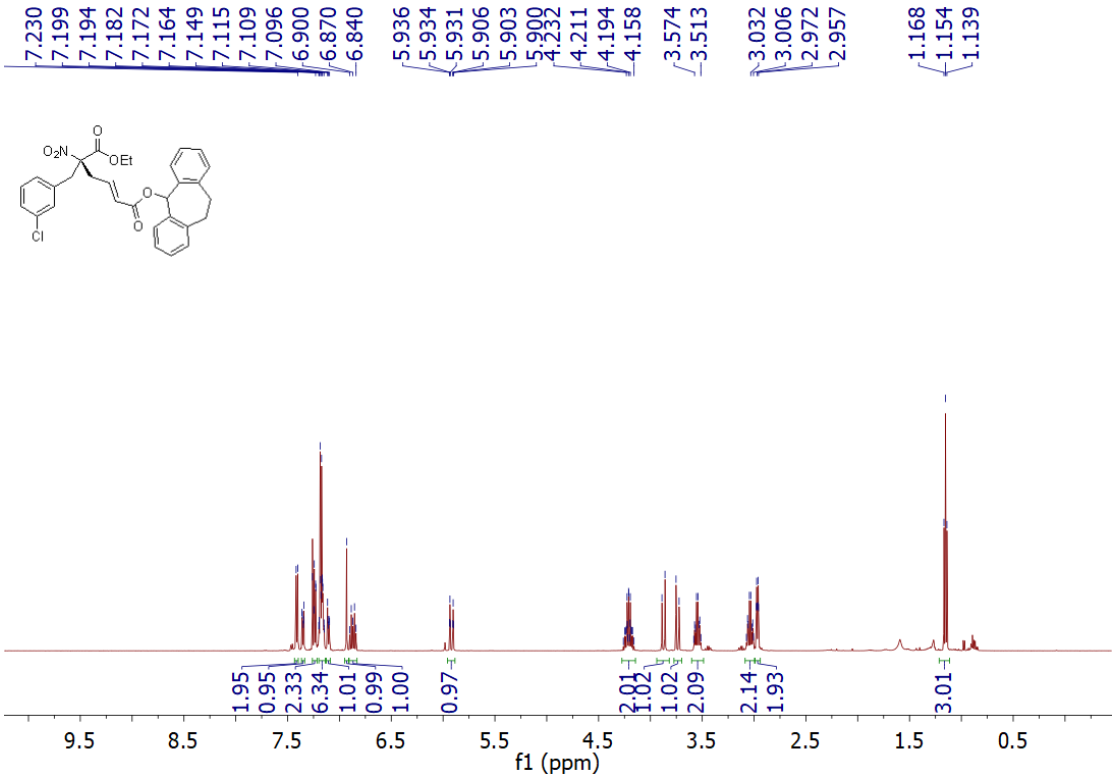
20
0
f1 (ppm)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5.900
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1.154
1.139
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O
O
Cl
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0.95
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1.01
0.99
1.00
0.97
2.01
1.02
1.02
2.09
2.14
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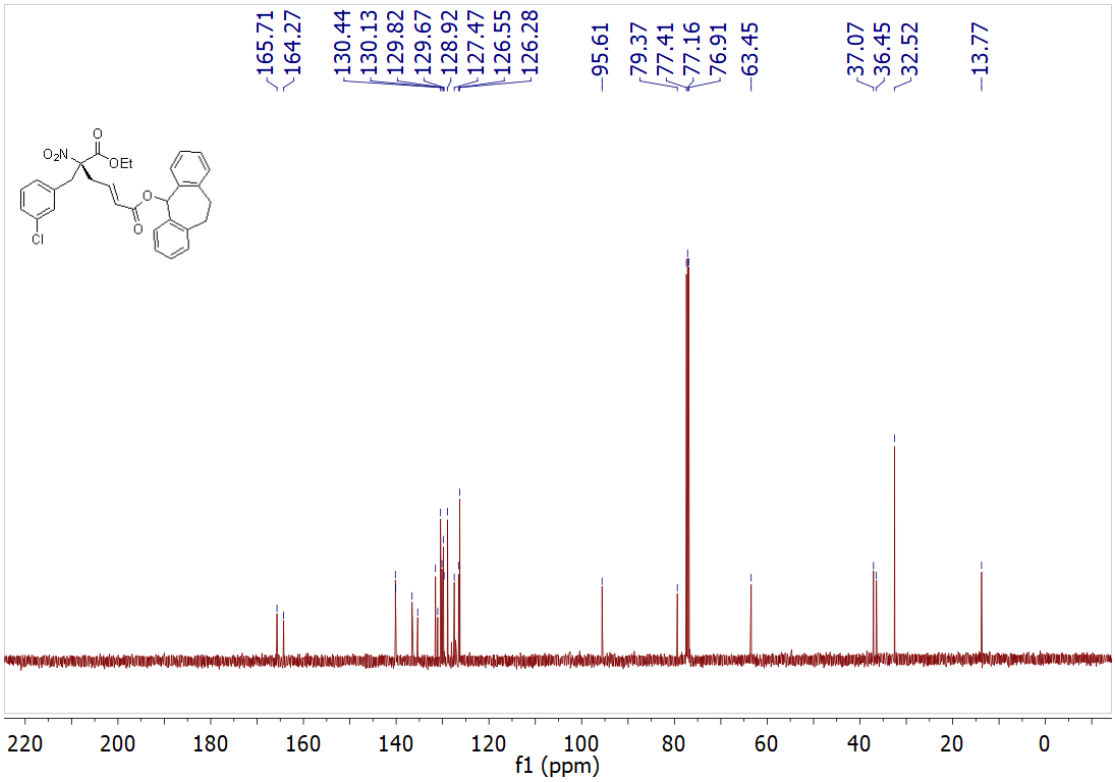
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76.91
63.45
37.07
36.45
32.52
13.77
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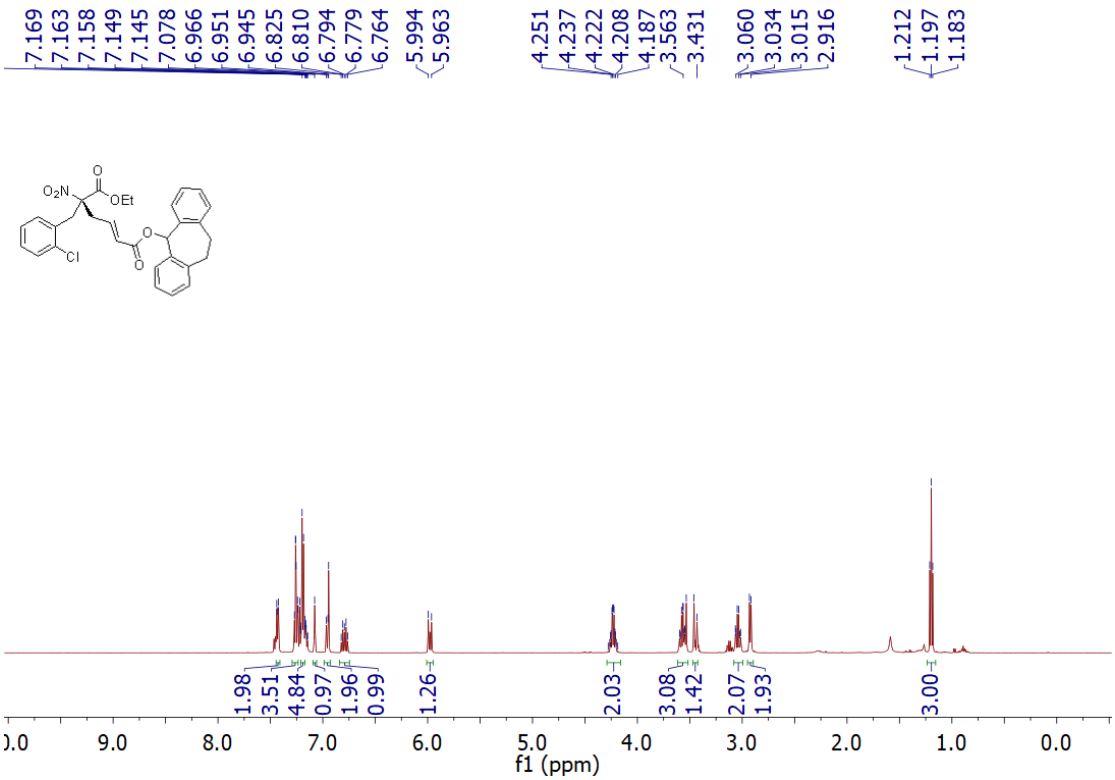
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6.764
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1.183
O2N
OEt
Cl
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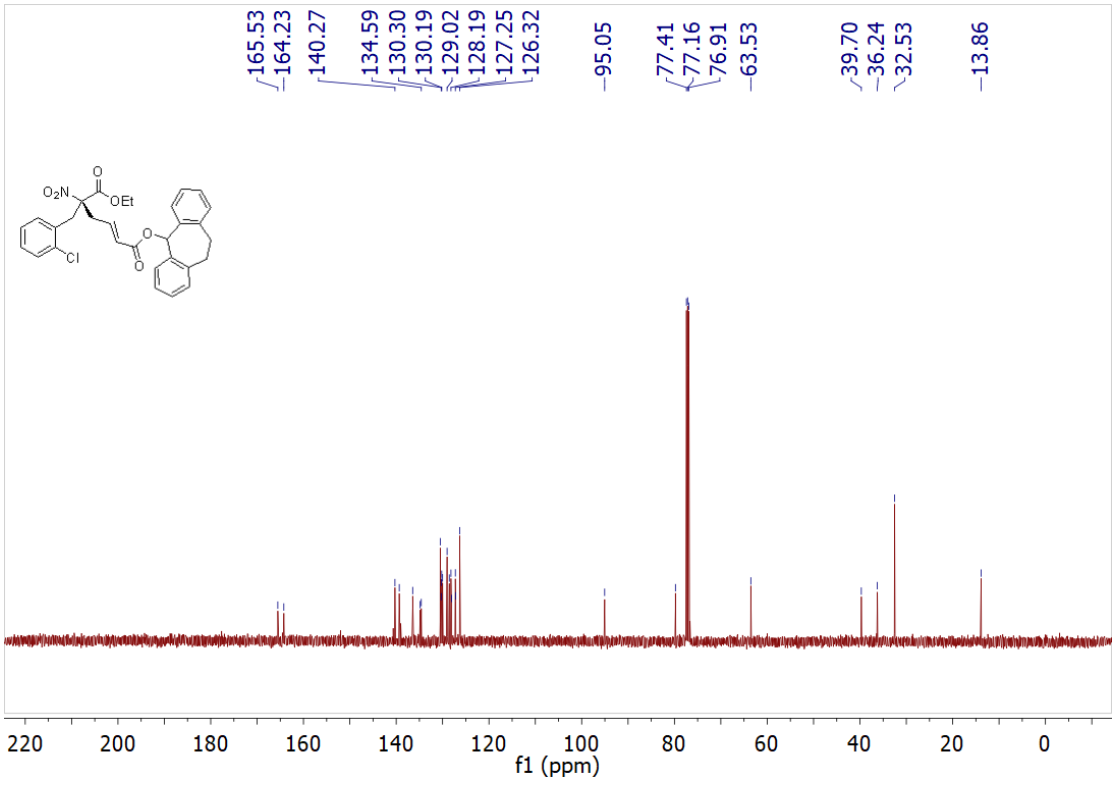
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126.32
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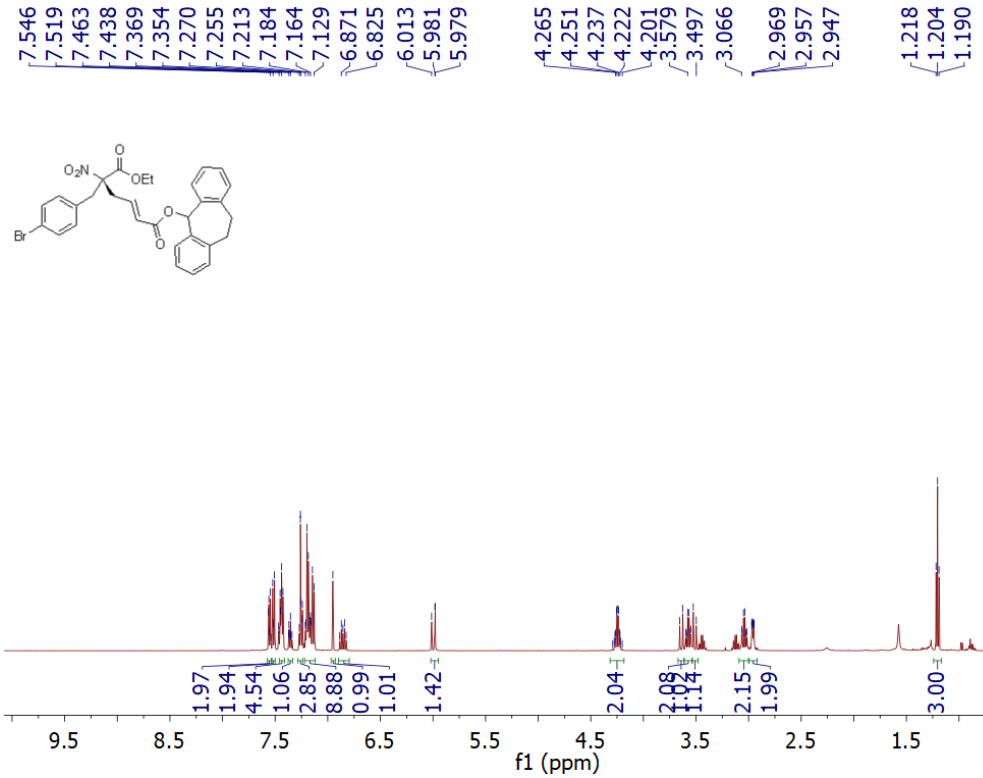
76.91
63.53
39.70
36.24
32.53
13.86
O2N
OEt
Cl
f1 (ppm)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2.947
1.218
1.204
1.190
O2N
OEt
Br
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4.54
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2.85
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1.01
1.42
2.04
2.08
1.02
1.14
2.15
1.99
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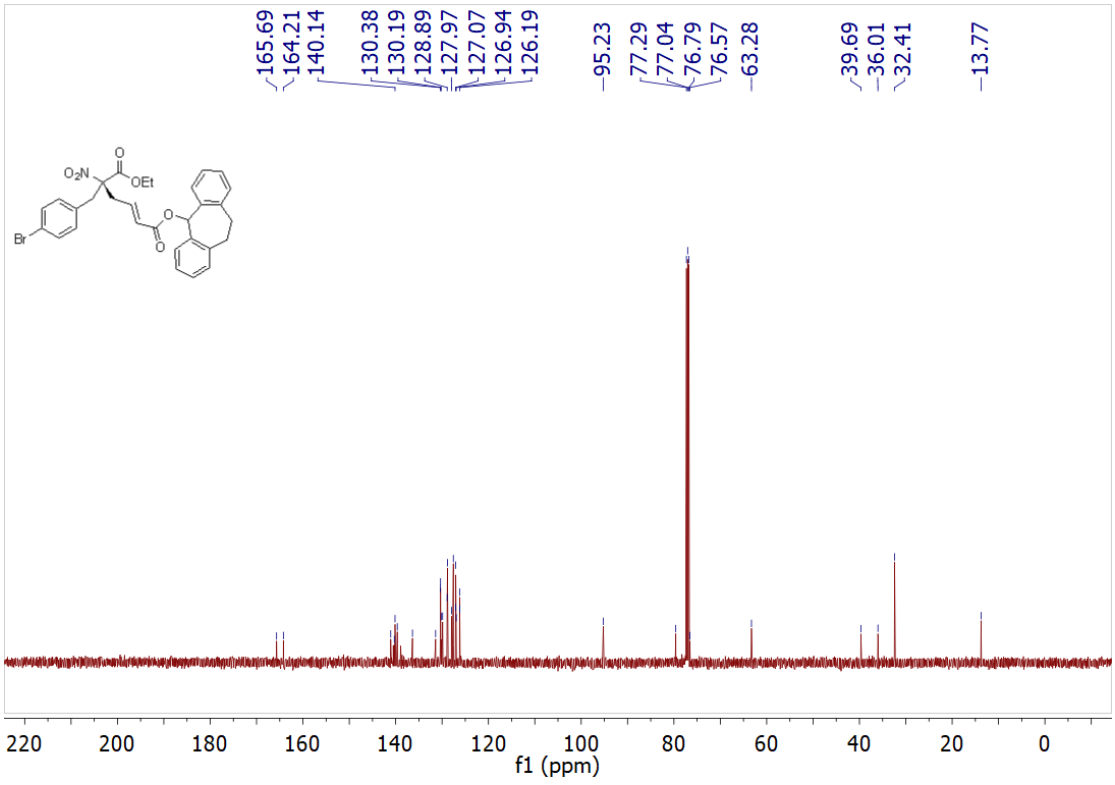
f1 (ppm)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126.19
95.23
77.29
77.04
76.79
76.57
63.28
39.69
36.01
32.41
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Br
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200
180
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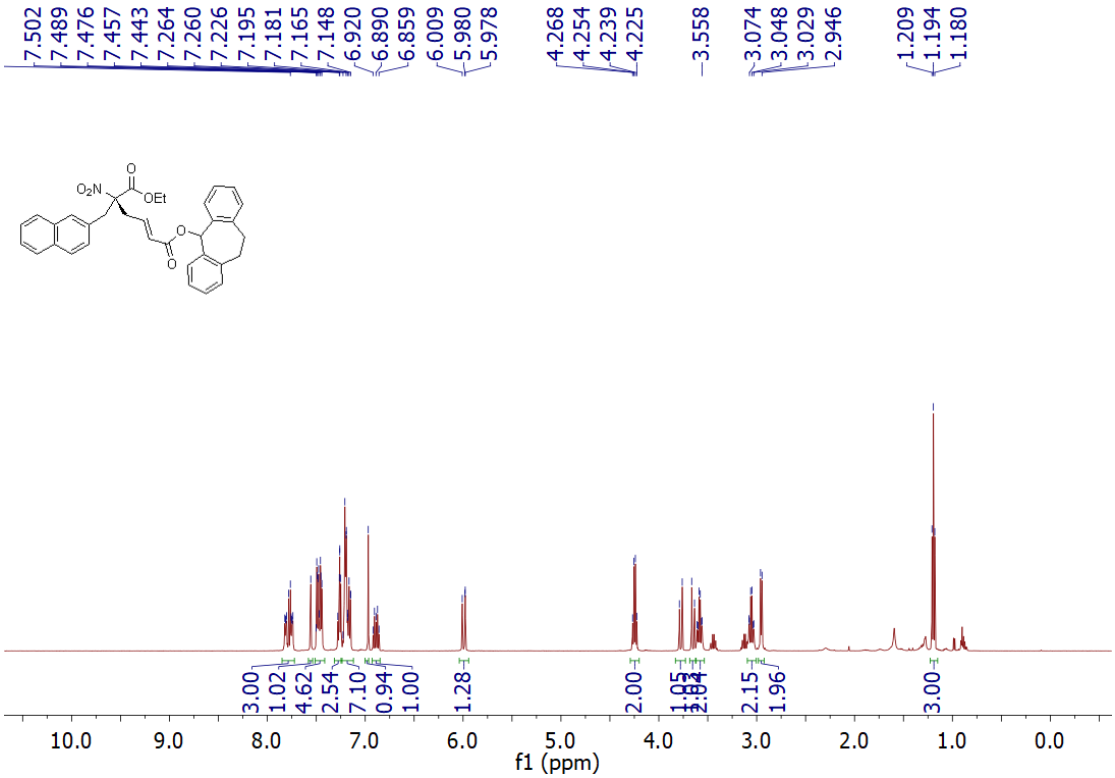
140
120
100
80
60
40
20
0
f1 (ppm)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4.239
4.225
3.558
3.074
3.048
3.029
2.946
1.209
1.194
1.180
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O
O
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1.02
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1.28
2.00
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3.00
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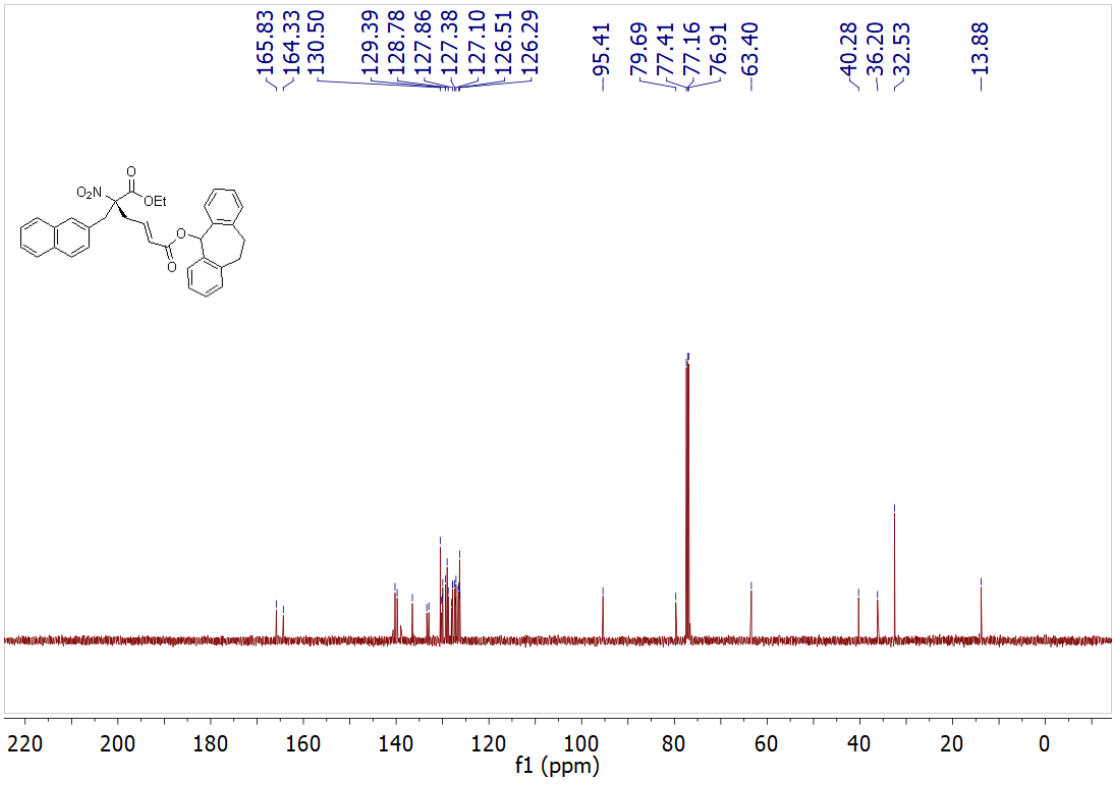
f1 (ppm)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126.29
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77.16
76.91
63.40
40.28
36.20
32.53
13.88
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O
O
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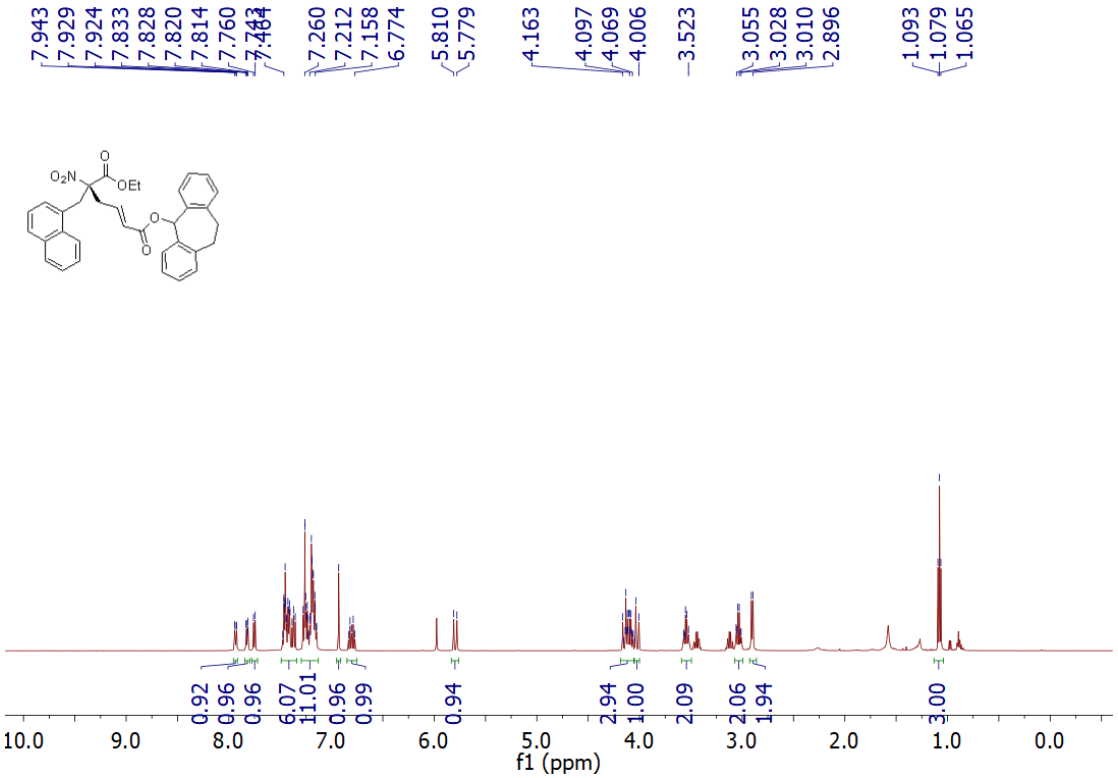
100
80
60
40
20
0
f1 (ppm)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5.810
5.779
4.163
4.097
4.069
4.006
3.523
3.055
3.028
3.010
2.896
1.093
1.079
1.065
O2N
OEt
O
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0.96
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11.01
0.96
0.99
0.94
2.94
1.00
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2.06
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3.00
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2.0
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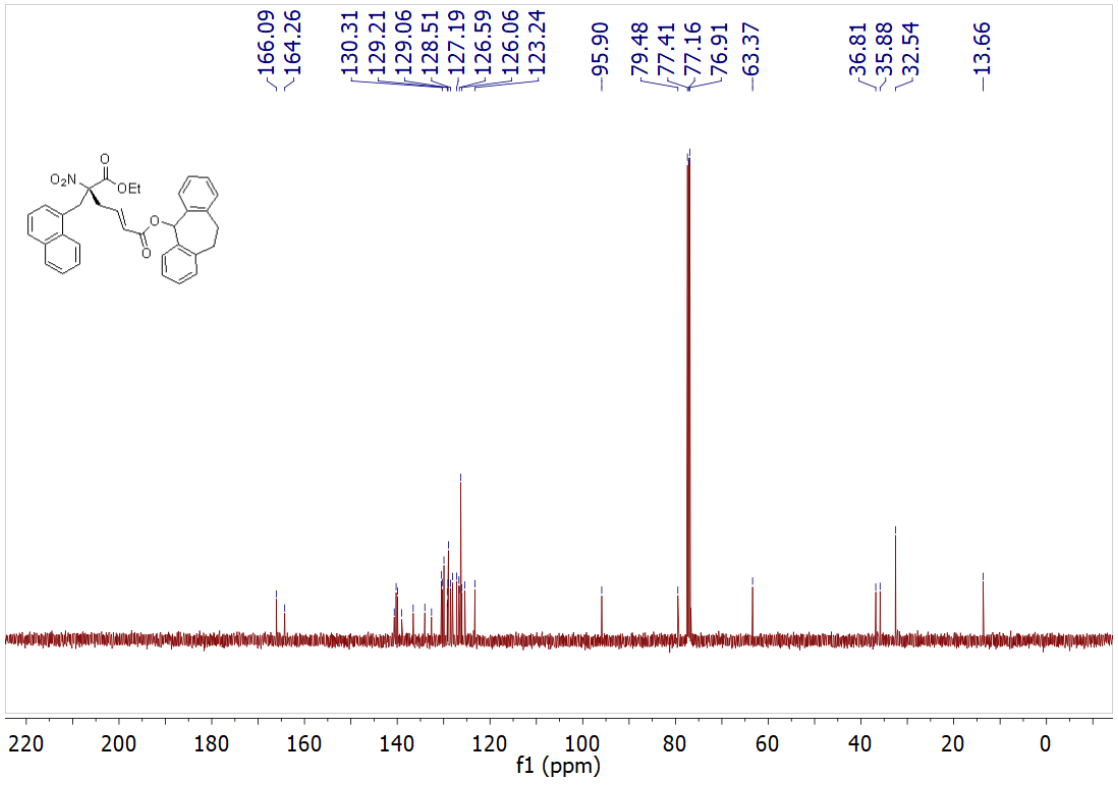
0.0
f1 (ppm)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77.41
77.16
76.91
63.37
36.81
35.88
32.54
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OEt
O
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200
180
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140
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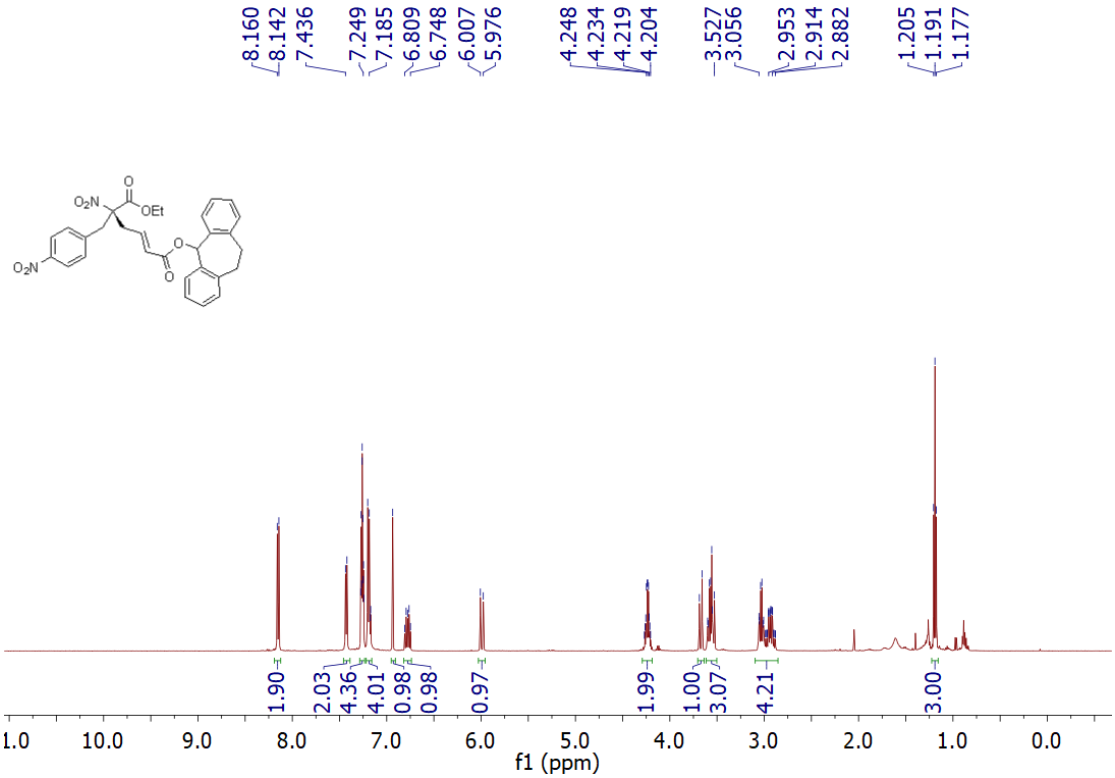
100
80
60
40
20
0
f1 (ppm)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4.219
4.204
3.527
3.056
2.953
2.914
2.882
1.205
1.191
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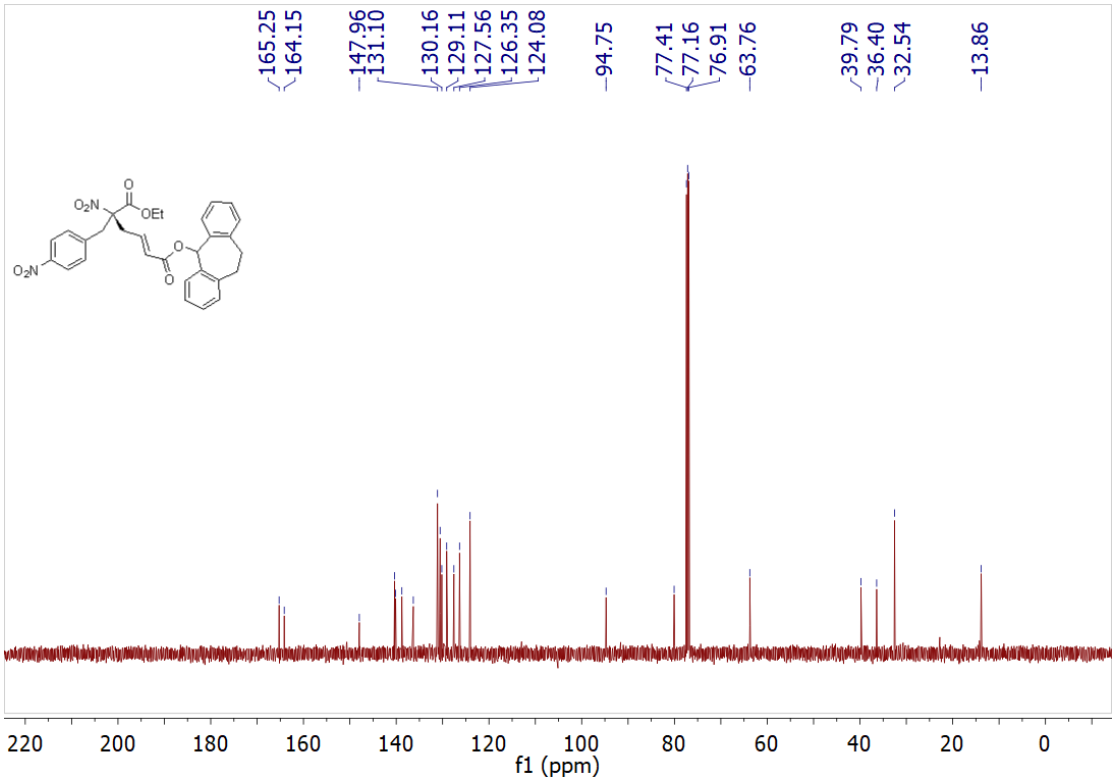
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36.40
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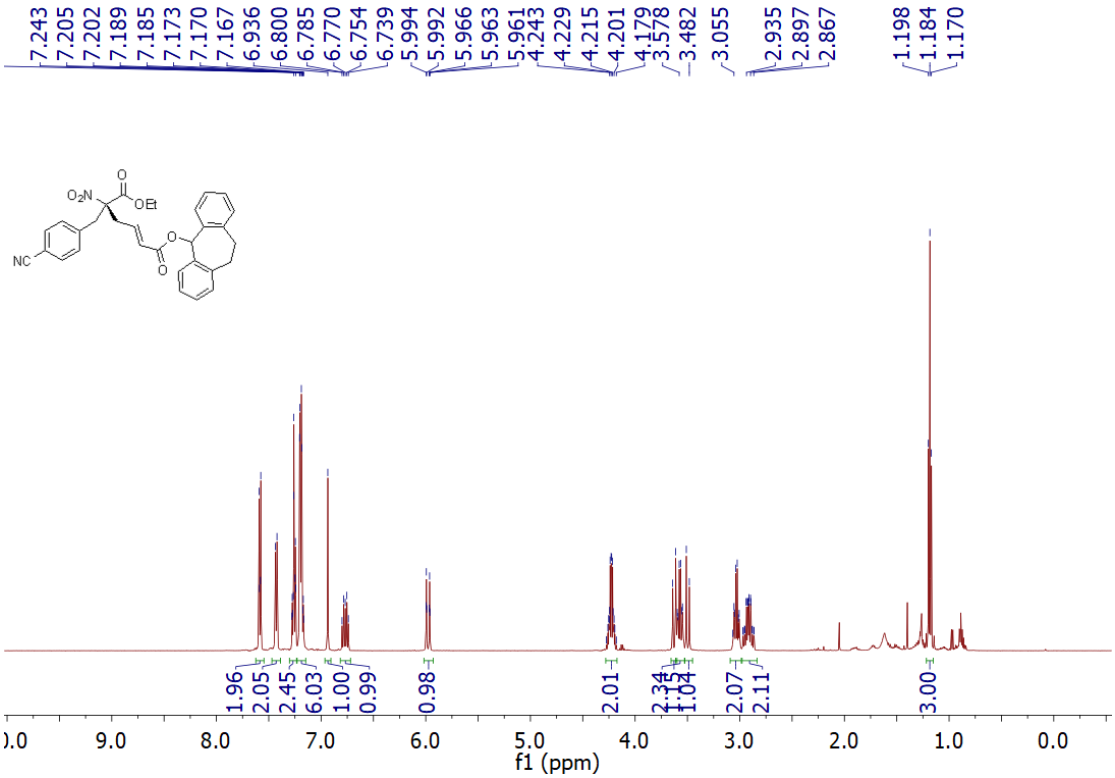
13.86
f1 (ppm)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7.170
7.167
6.936
6.800
6.785
6.770
6.754
6.739
5.994
5.992
5.966
5.963
5.961
4.243
4.229
4.215
4.201
4.179
3.578
3.482
3.055
2.935
2.897
2.867
1.198
1.184
1.170
O2N
OEt
NC
1.96
2.05
2.45
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0.98
2.01
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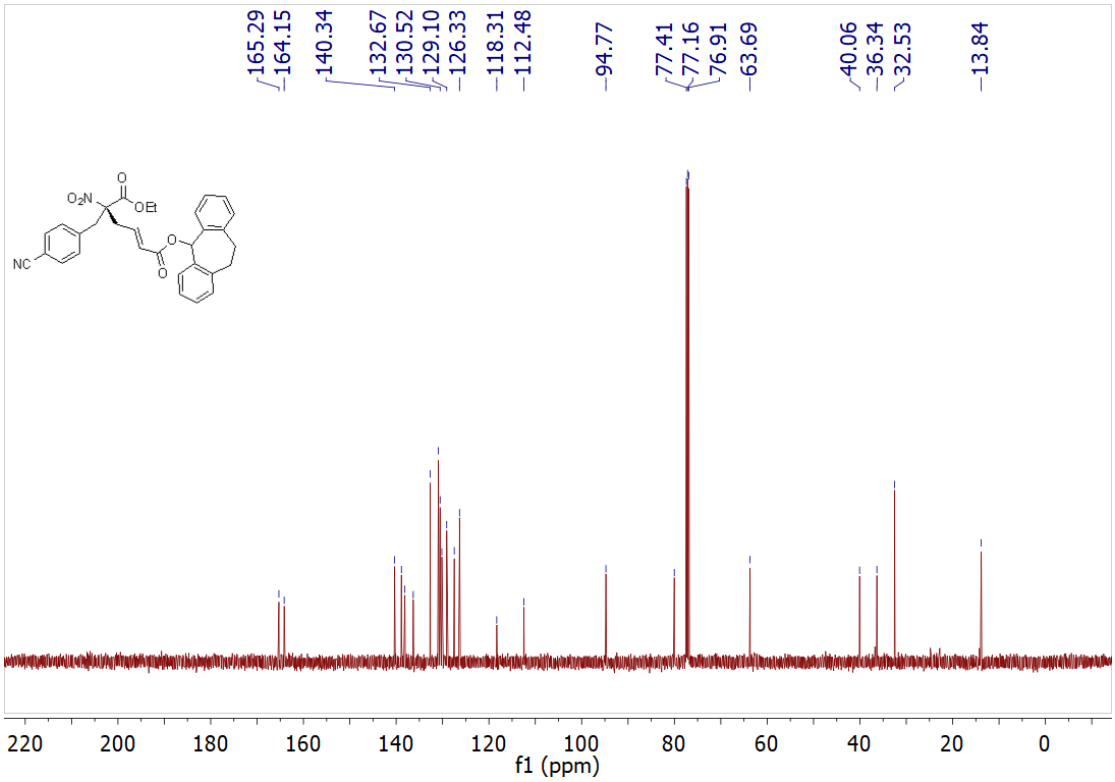
1.04
2.07
2.11
3.00
f1 (ppm)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129.10
126.33
118.31
112.48
94.77
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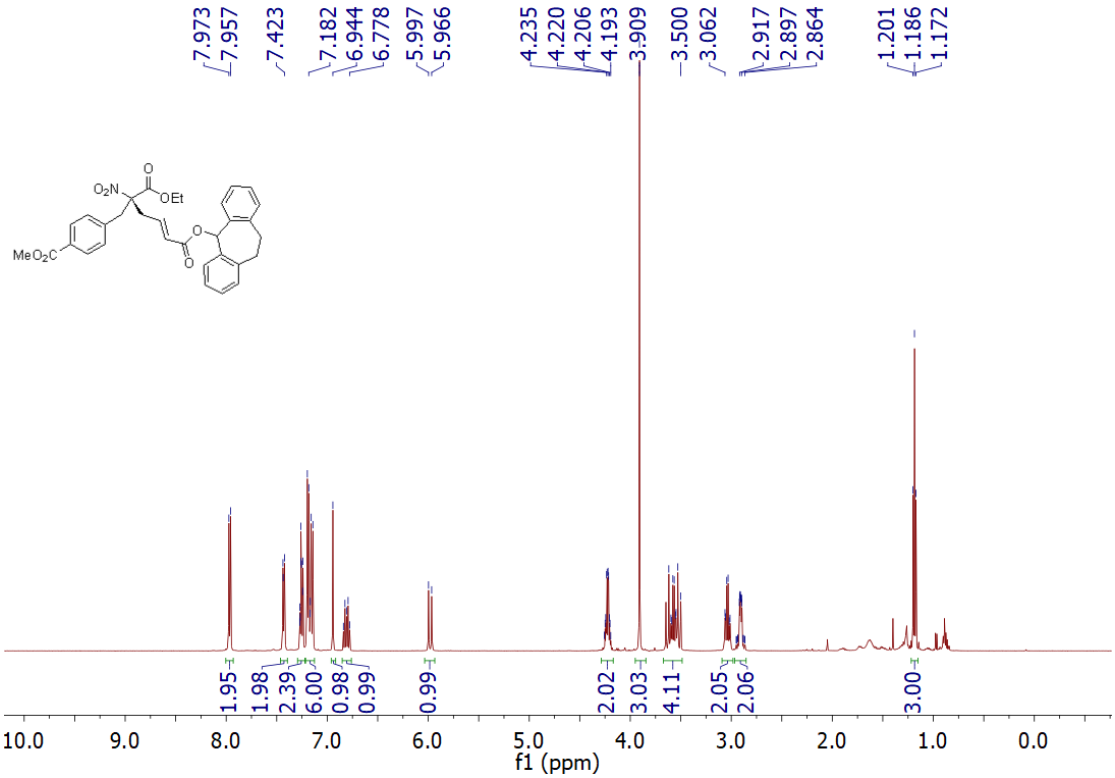
76.91
63.69
40.06
36.34
32.53
13.84
O2N
OEt
NC
f1 (ppm)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4.206
4.193
3.909
3.500
3.062
2.917
2.897
2.864
1.201
1.186
1.172
1.95
1.98
2.39
6.00
0.98
0.99
0.99
2.02
3.03
4.11
2.05
2.06
3.00
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6.0
5.0
4.0
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2.0
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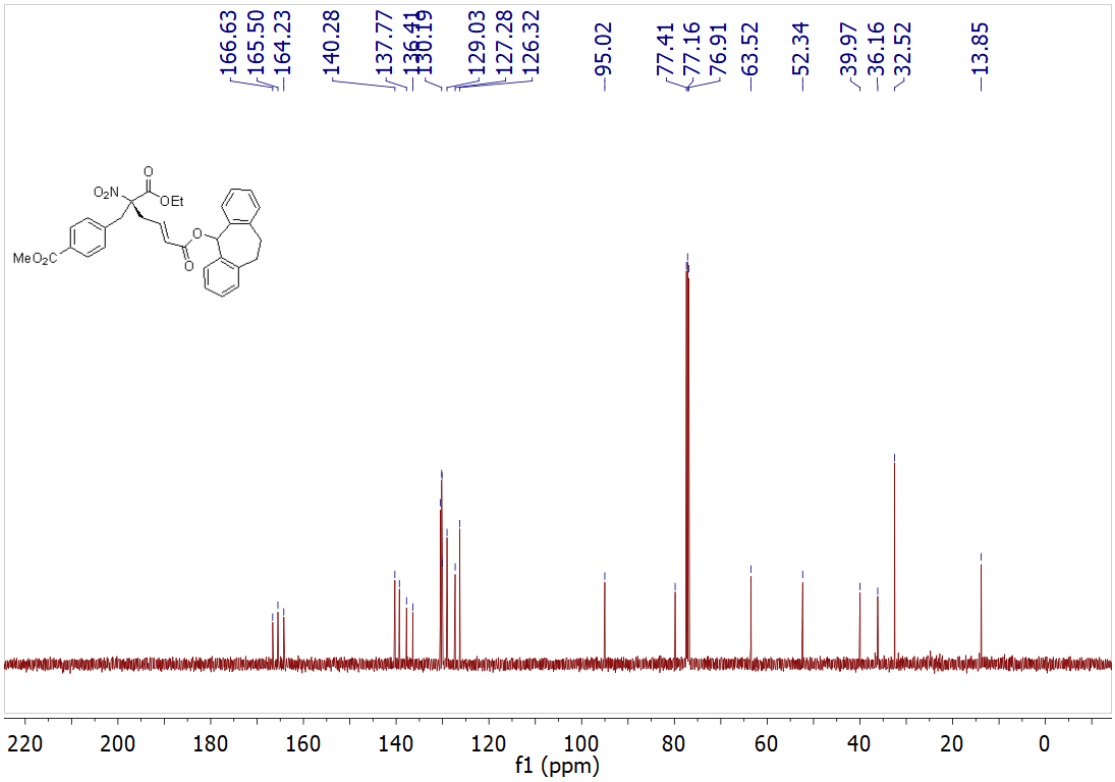
f1 (ppm)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126.32
95.02
77.41
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76.91
63.52
52.34
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140
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100
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20
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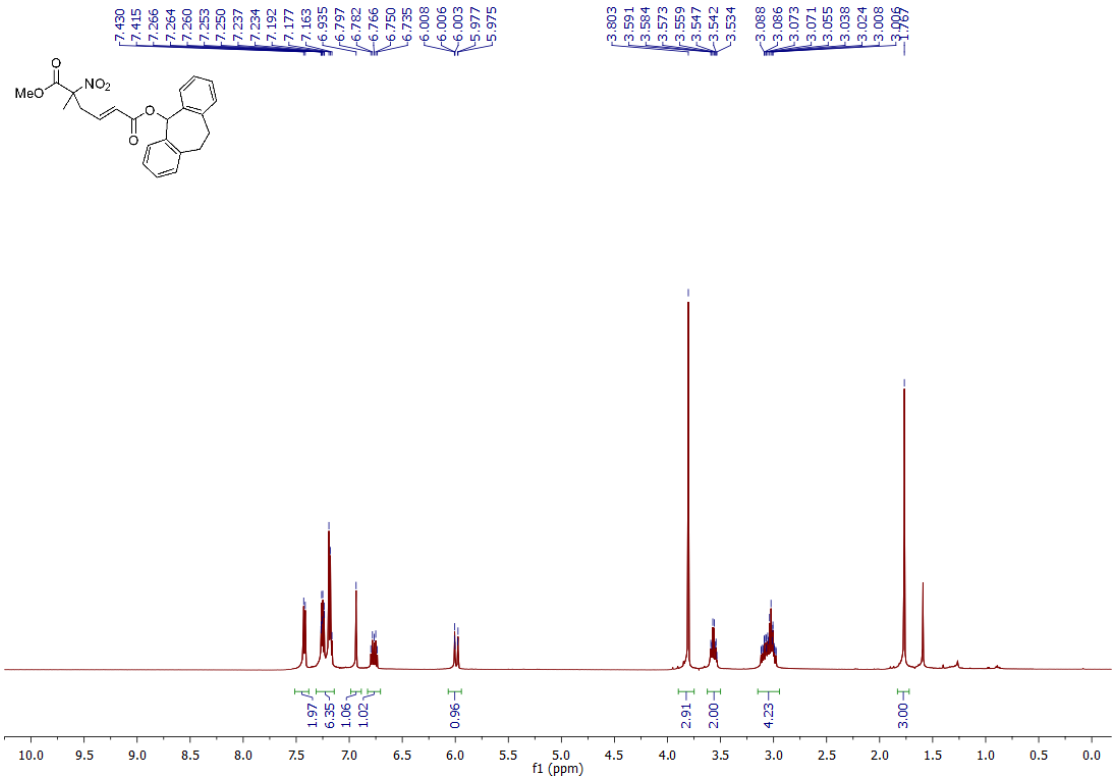
f1 (ppm)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7.264
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7.253
7.250
7.237
7.234
7.192
7.177
7.163
6.935
6.797
6.782
6.766
6.750
6.735
6.008
6.006
6.003
5.977
5.975
3.803
3.591
3.584
3.573
3.559
3.547
3.542
3.534
3.088
3.086
3.073
3.071
3.055
3.038
3.024
3.008
3.006
1.767
MeO
NO2
O
O
O
1.97
6.35
1.06
1.02
0.96
2.91
2.00
4.23
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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1.0
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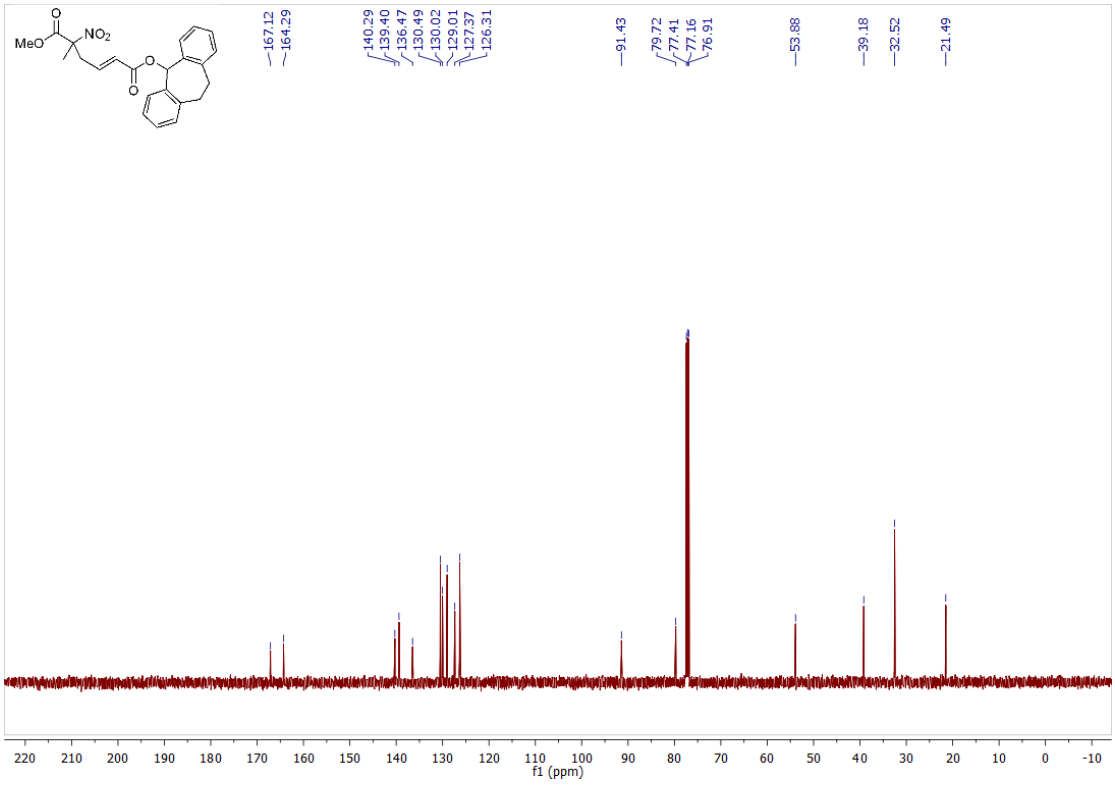
0.0
f1 (ppm)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NO2
O
O
O
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136.47
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130.02
129.01
127.37
126.31
91.43
79.72
77.41
77.16
76.91
53.88
39.18
32.52
21.49
220
210
200
190
180
170
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100
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80
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40
30
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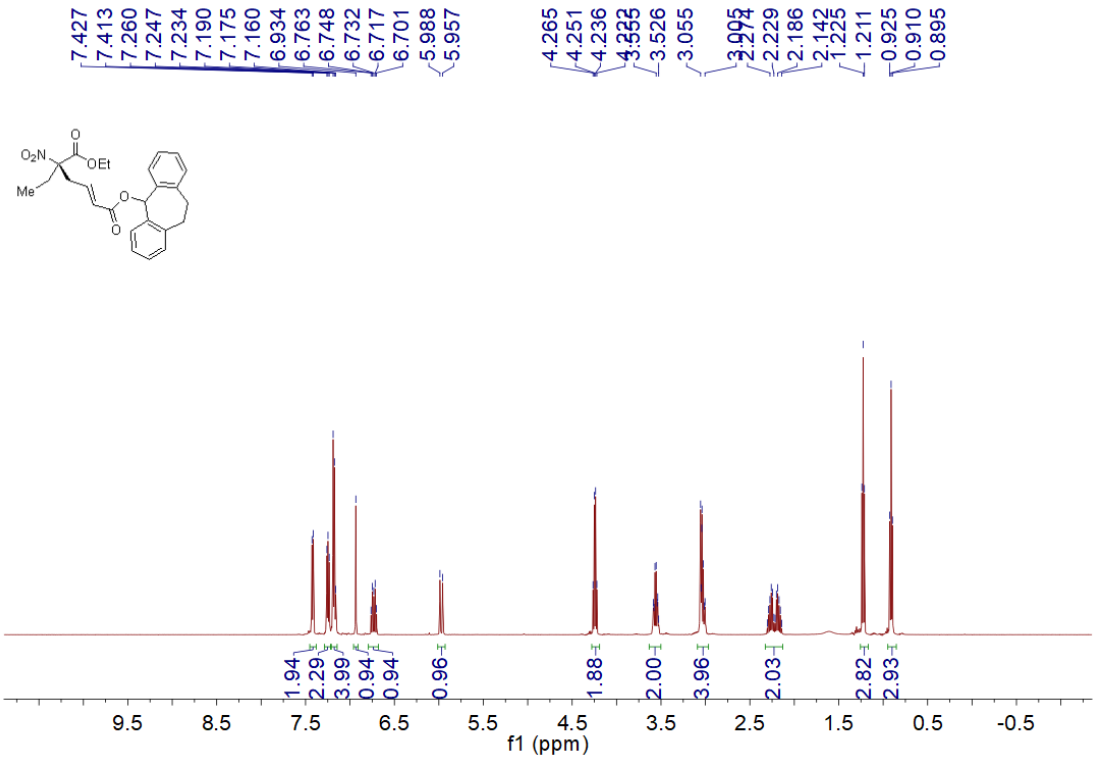
f1 (ppm)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7.260
7.247
7.234
7.190
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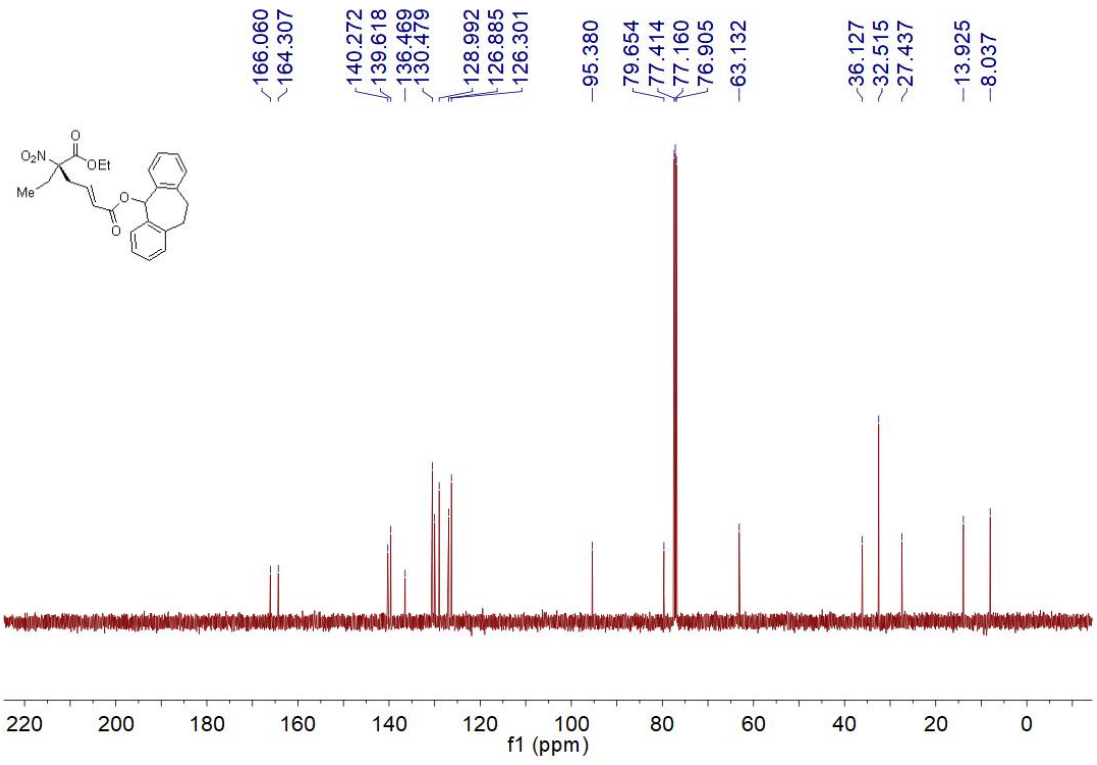
7.160
6.934
6.763
6.748
6.732
6.717
6.701
5.988
5.957
4.265
4.251
4.236
3.526
3.055
2.229
2.186
2.142
2.225
1.211
0.925
0.910
0.895
O2N
OEt
Me
1.94
2.29
3.99
0.94
0.94
0.96
1.88
2.00
3.96
2.03
2.82
2.93
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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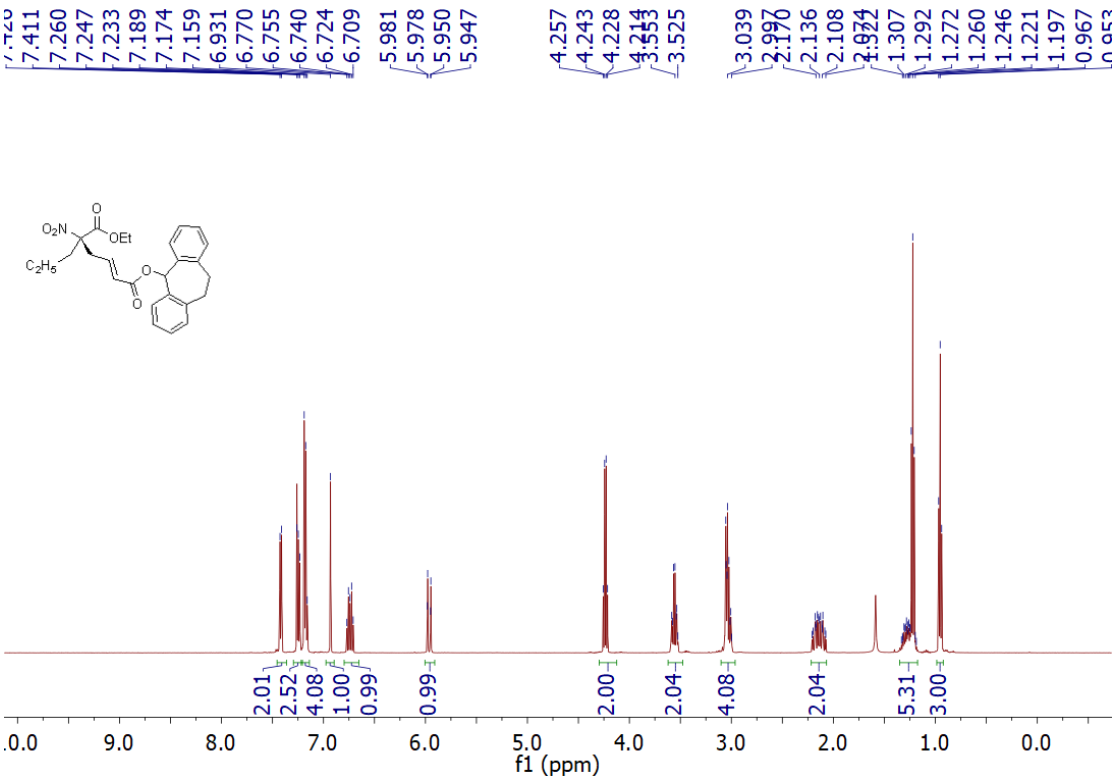
164.307
140.272
139.618
136.469
130.479
128.992
126.885
126.301
95.380
79.654
77.414
77.160
76.905
63.132
36.127
32.515
27.437
13.925
8.037
O2N
OEt
Me
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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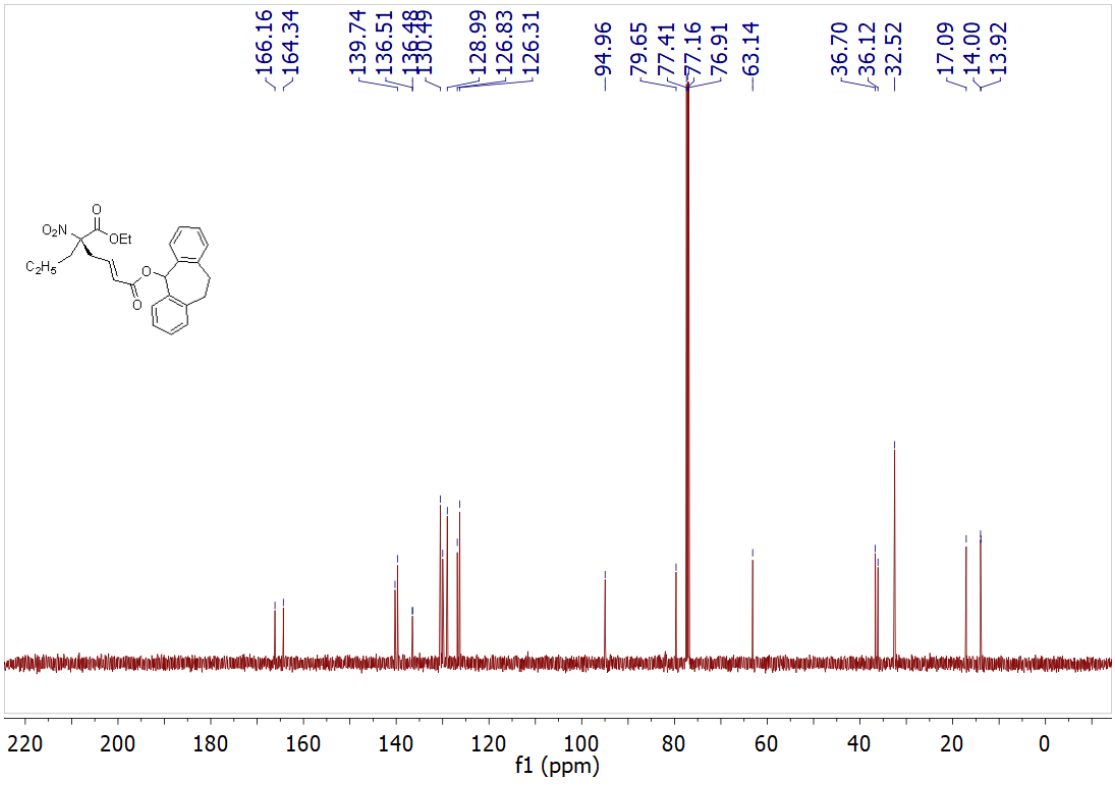
7.174
7.159
6.931
6.770
6.755
6.740
6.724
6.709
5.981
5.978
5.950
5.947
4.257
4.243
4.228
3.525
3.039
2.170
2.136
2.108
1.307
1.292
1.272
1.260
1.246
1.221
1.197
0.967
O2N
OEt
C2H5
O
2.01
2.52
4.08
1.00
0.99
0.99
2.00
2.04
4.08
2.04
5.31
3.00
f1 (ppm)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164.34
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126.31
94.96
79.65
77.41
77.16
76.91
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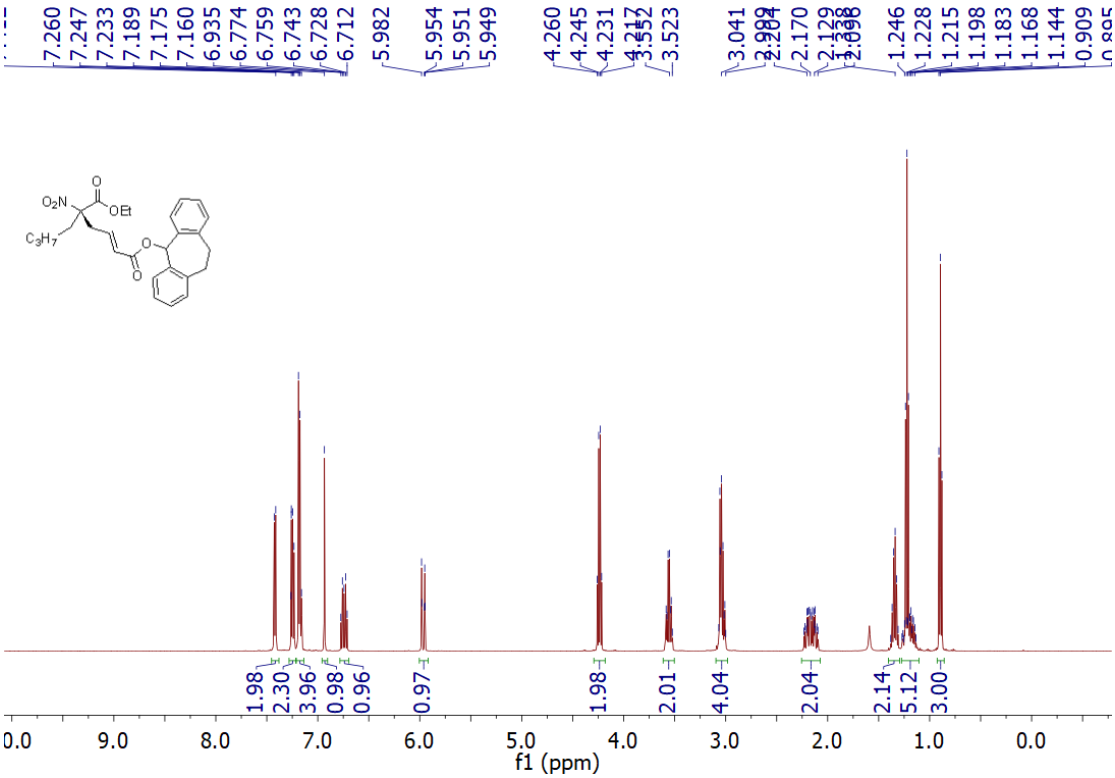
36.12
32.52
17.09
14.00
13.92
O2N
OEt
C2H5
O
f1 (ppm)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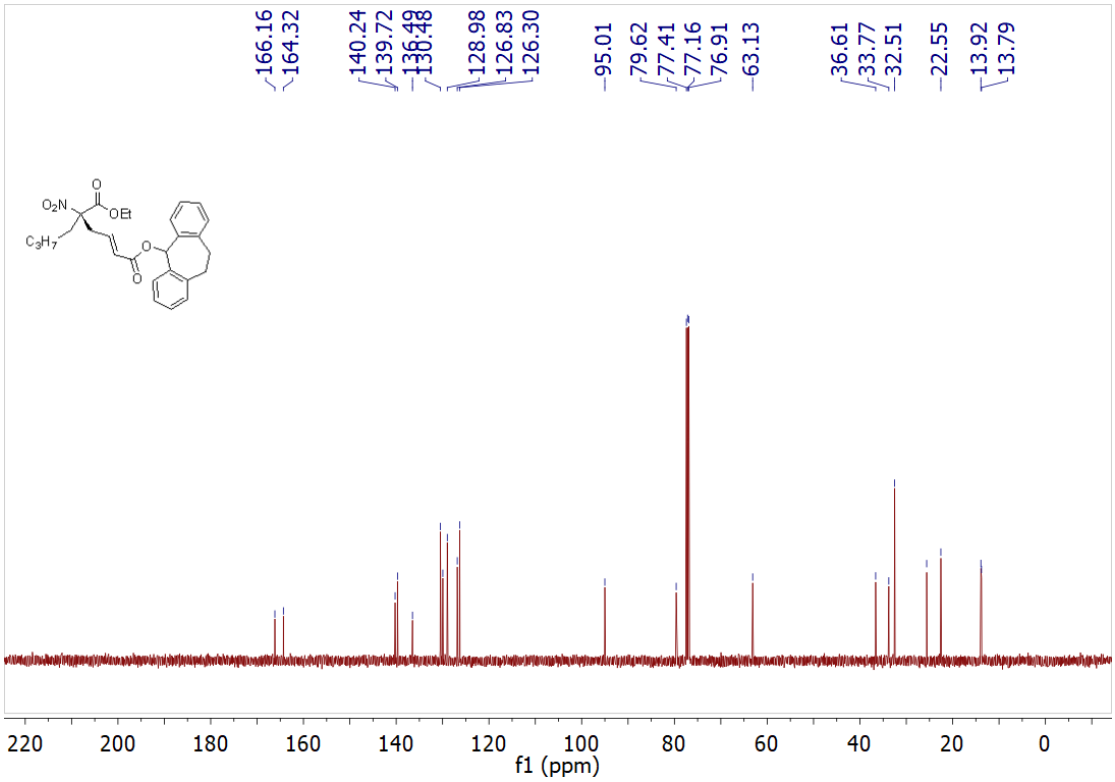
6.774
6.759
6.743
6.728
6.712
5.982
5.954
5.951
5.949
4.260
4.245
4.231
3.523
3.041
2.170
2.129
1.246
1.228
1.215
1.198
1.183
1.168
1.144
0.909
1.98
2.30
3.96
0.98
0.96
0.97
1.98
2.01
4.04
2.04
2.14
5.12
3.00
f1 (ppm)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164.32
140.24
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126.83
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95.01
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77.41
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76.91
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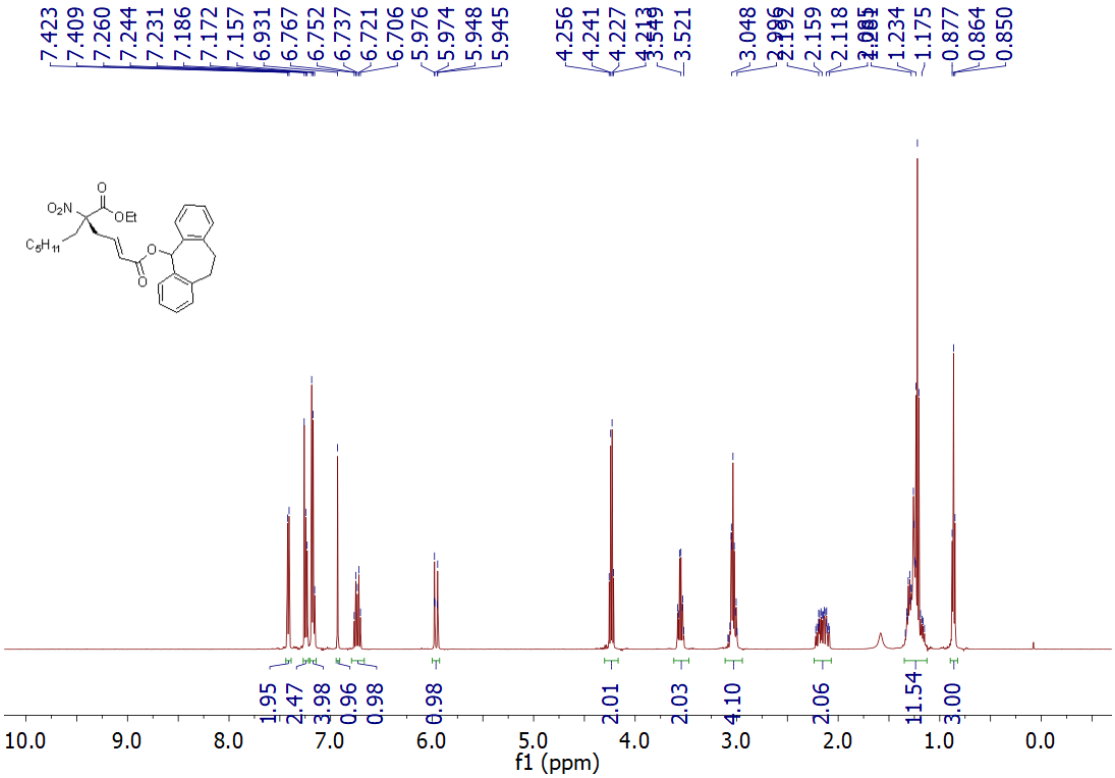
32.51
22.55
13.92
13.79
f1 (ppm)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7.244
7.231
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6.767
6.752
6.737
6.721
6.706
5.976
5.974
5.948
5.945
4.256
4.241
4.227
3.521
3.048
2.159
2.118
1.234
1.175
0.877
0.864
0.850
1.95
2.47
3.98
0.96
0.98
0.98
2.01
2.03
4.10
2.06
11.54
3.00
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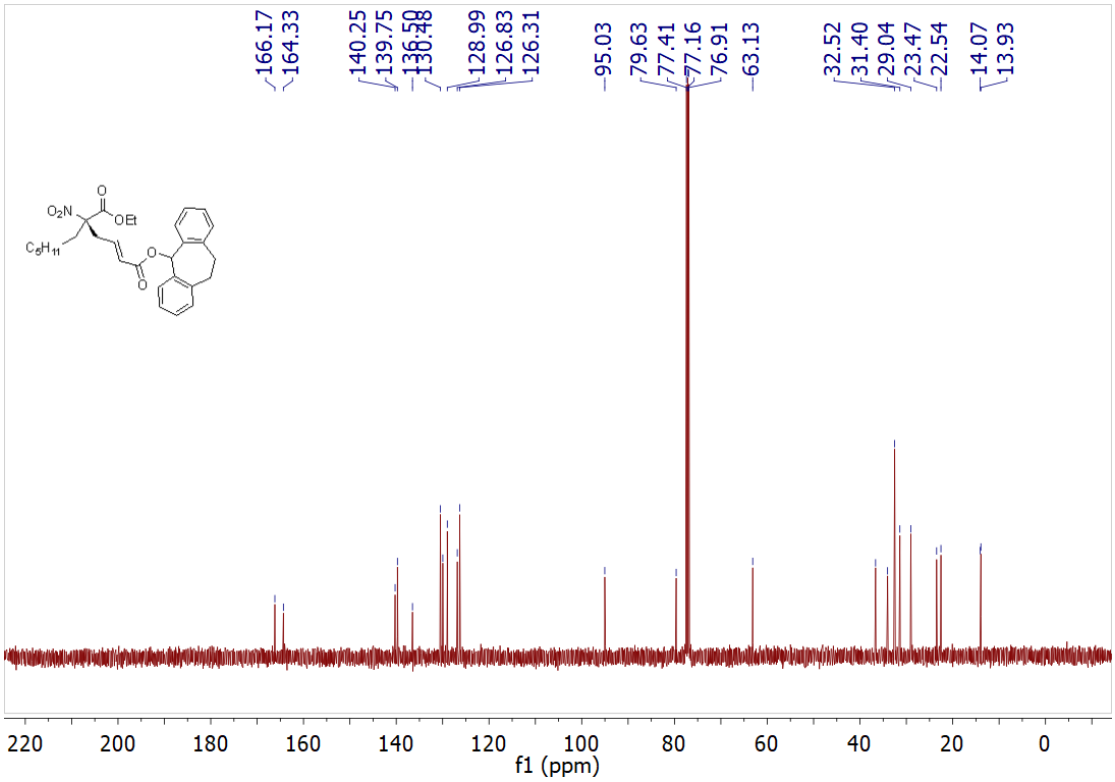
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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126.31
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77.41
77.16
76.91
63.13
32.52
31.40
29.04
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140
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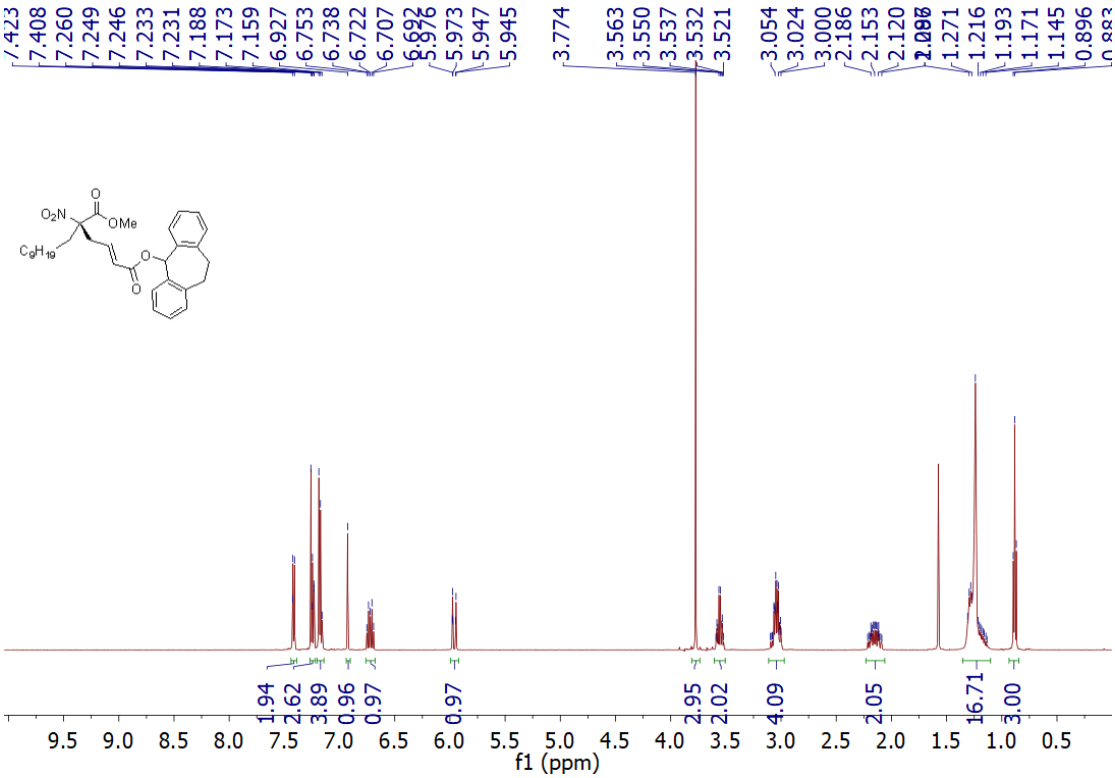
100
80
60
40
20
0
f1 (ppm)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7.246
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7.231
7.188
7.173
7.159
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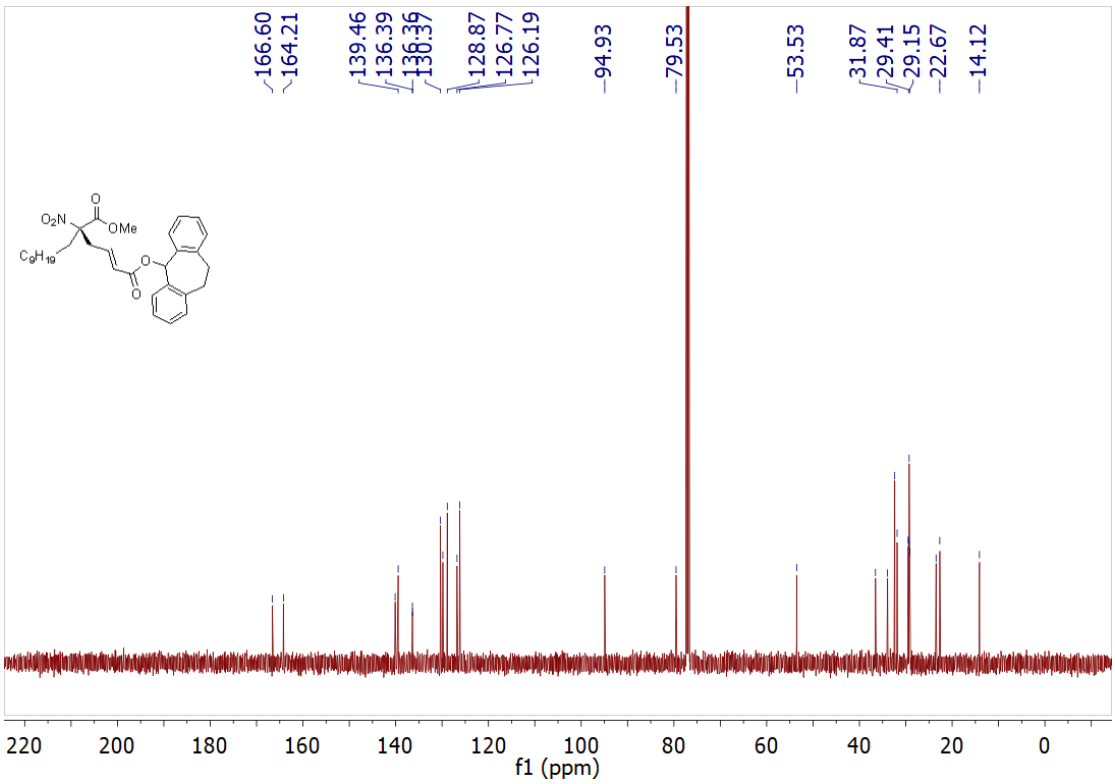
6.753
6.738
6.722
6.707
6.692
5.976
5.973
5.947
5.945
3.774
3.563
3.550
3.537
3.532
3.521
3.054
3.024
3.000
2.186
2.153
2.120
1.271
1.216
1.193
1.171
1.145
0.896
1.94
2.62
3.89
0.96
0.97
0.97
2.95
2.02
4.09
2.05
16.71
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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136.37
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126.77
126.19
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79.53
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31.87
29.41
29.15
22.67
14.12
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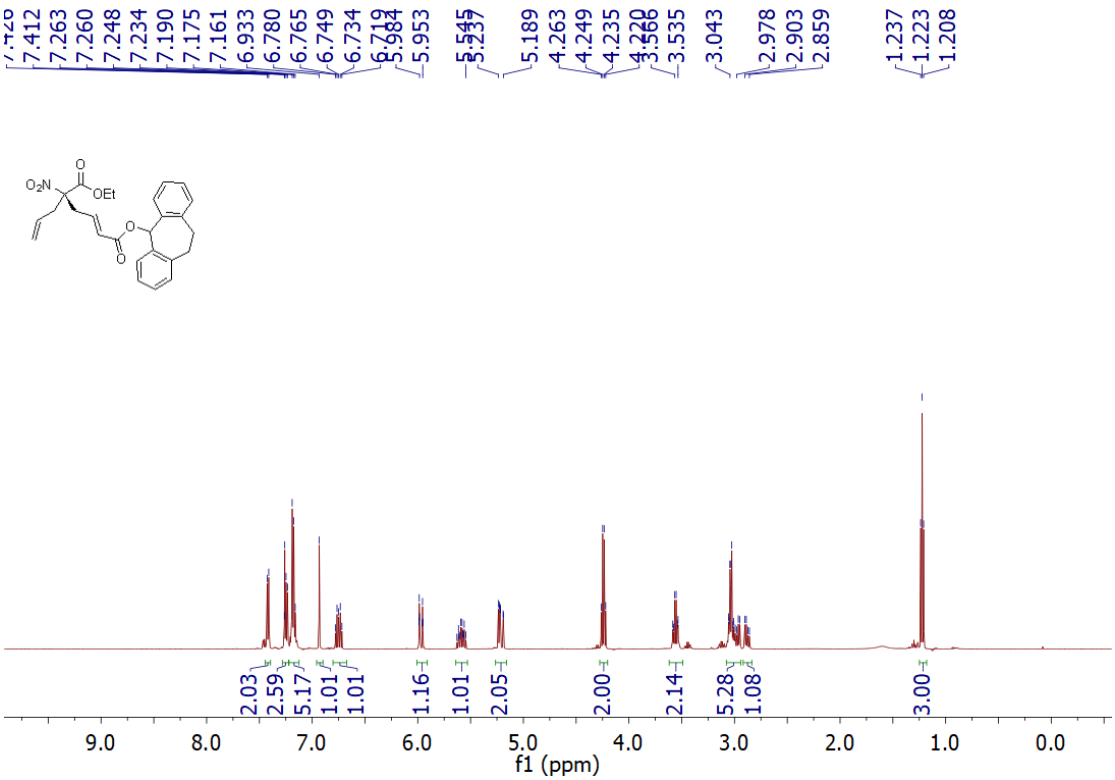
f1 (ppm)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6.734
5.953
5.189
4.263
4.249
4.235
3.535
3.043
2.978
2.903
2.859
1.237
1.223
1.208
O2N
OEt
2.03
2.59
5.17
1.01
1.01
1.16
1.01
2.05
2.00
2.14
5.28
1.08
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5.0
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2.0
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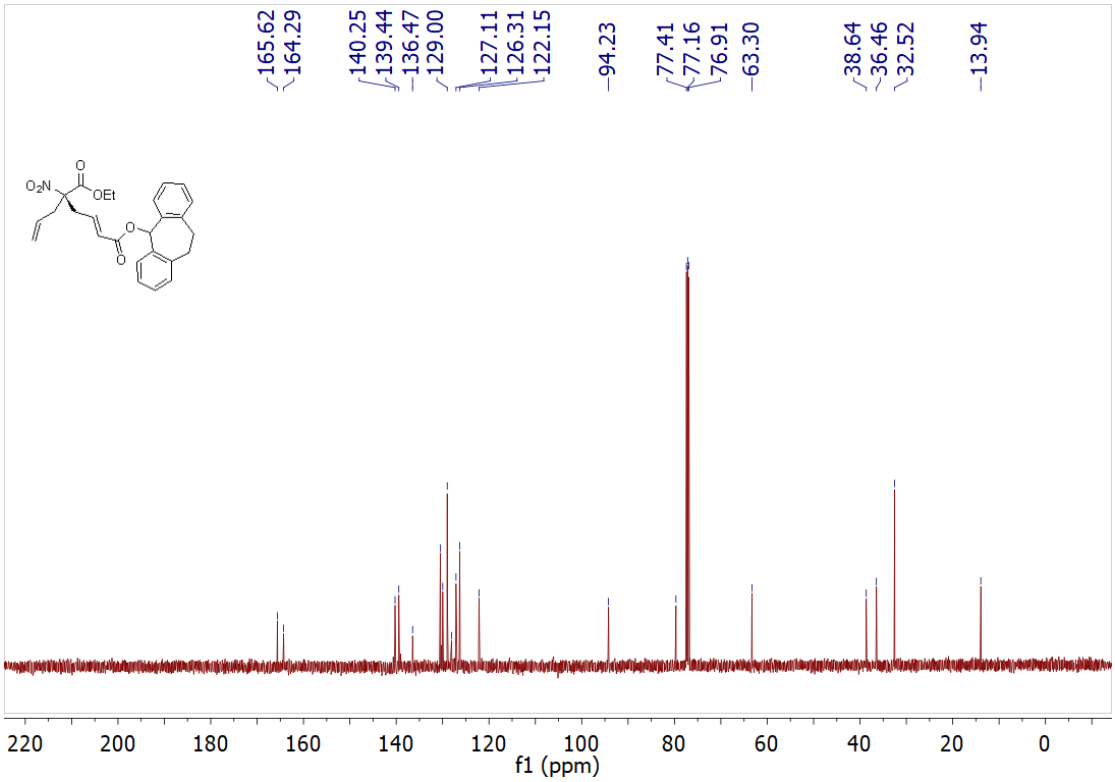
0.0
f1 (ppm)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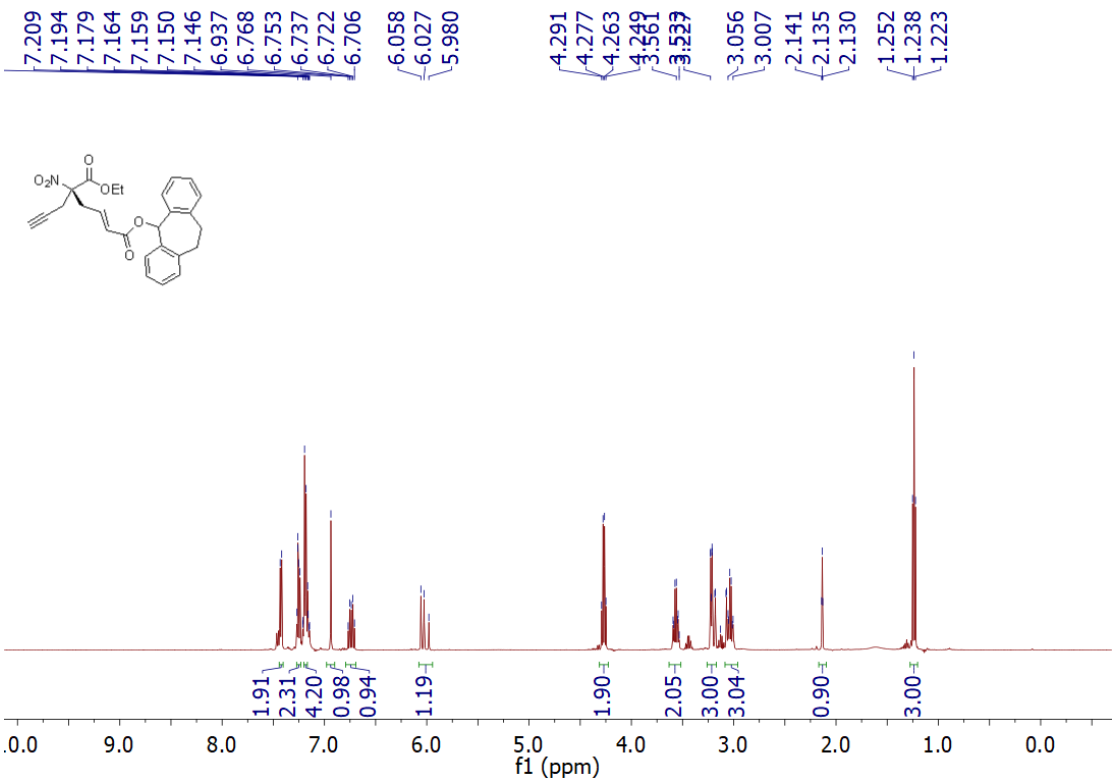
122.15
94.23
77.41
77.16
76.91
63.30
38.64
36.46
32.52
13.94
O2N
OEt
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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6.706
6.058
6.027
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3.533
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3.056
3.007
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2.130
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1.238
1.223
1.91
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0.94
1.19
1.90
2.05
3.00
3.04
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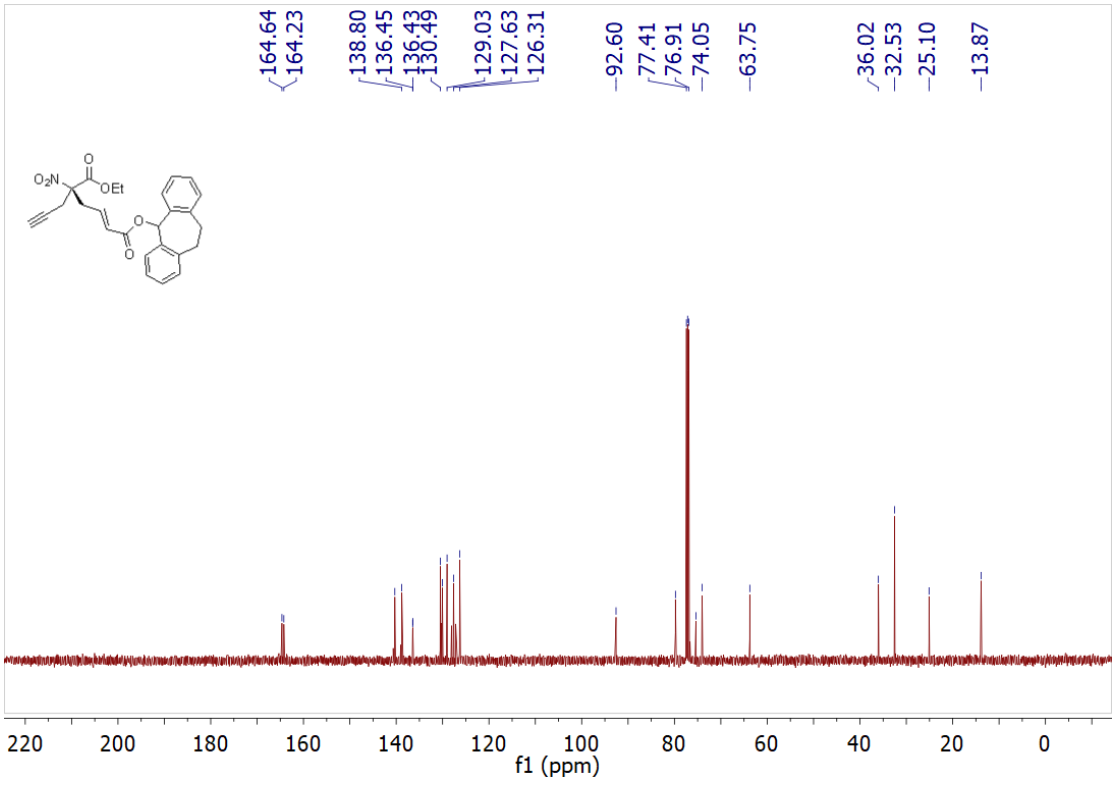
3.00
f1 (ppm)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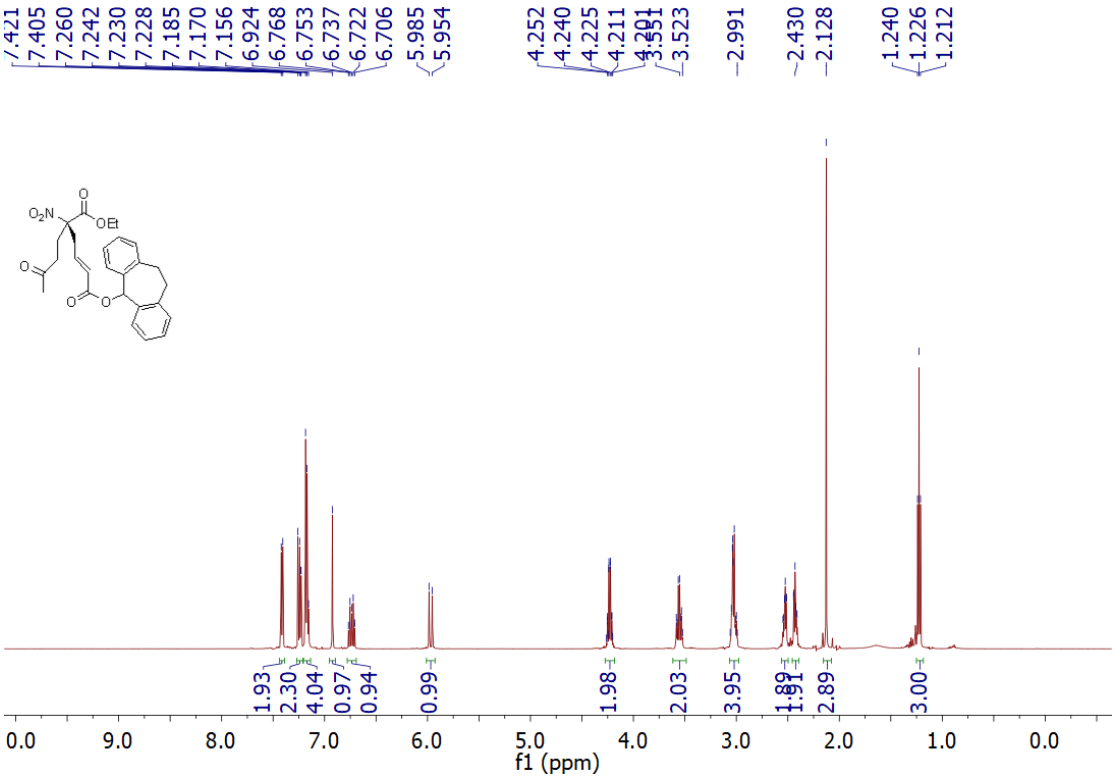
13.87
f1 (ppm)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6.768
6.753
6.737
6.722
6.706
5.985
5.954
4.252
4.240
4.225
4.211
3.551
3.523
2.991
2.430
2.128
1.240
1.226
1.212
1.93
2.30
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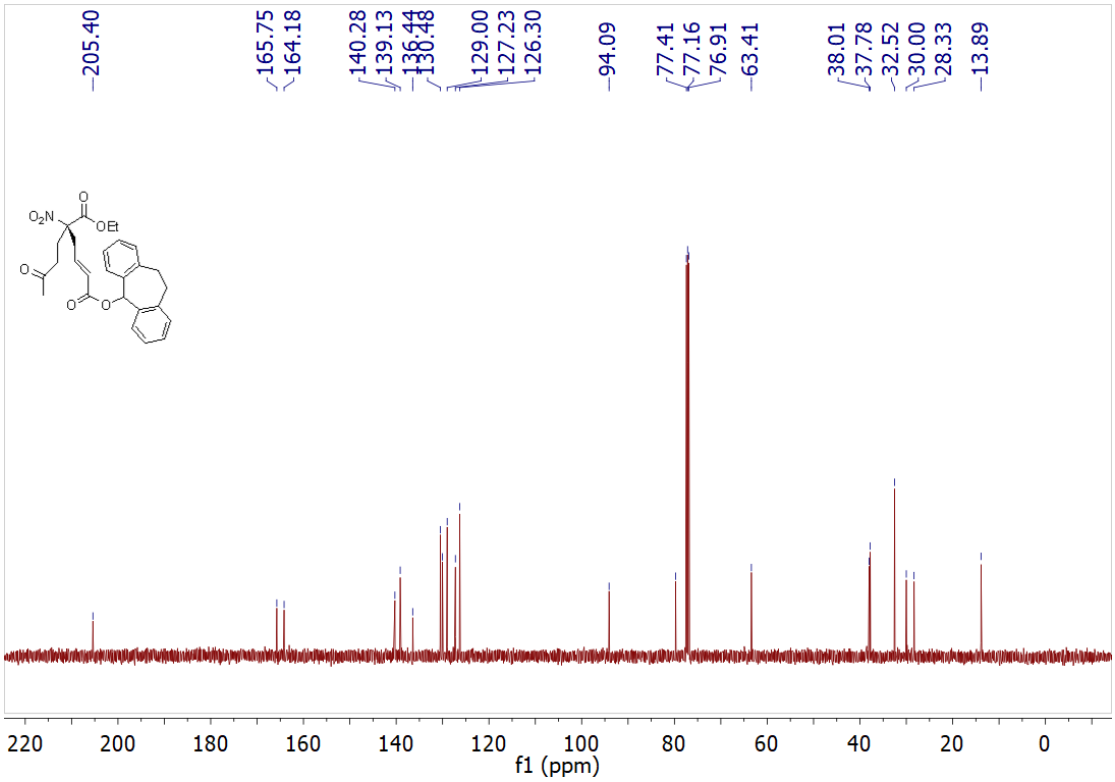
0.99
1.98
2.03
3.95
1.89
1.91
2.89
3.00
f1 (ppm)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126.30
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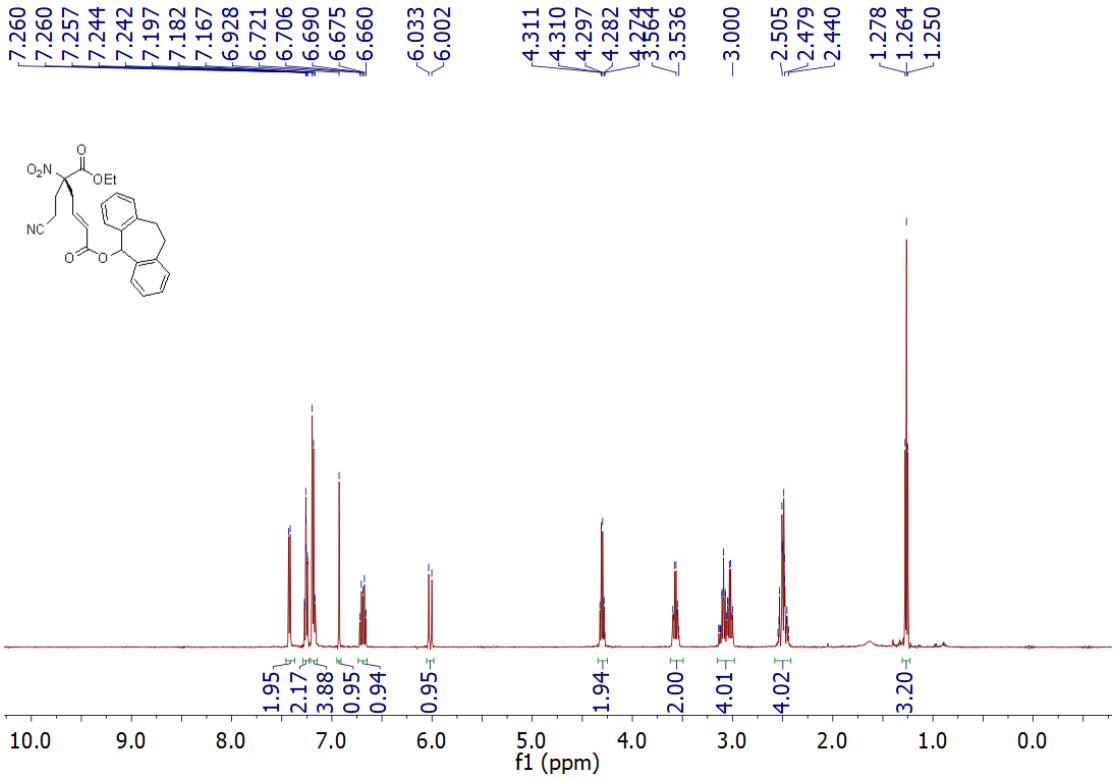
76.91
63.41
38.01
37.78
32.52
30.00
28.33
13.89
f1 (ppm)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4.310
4.297
4.282
4.274
4.264
3.536
3.000
2.505
2.479
2.440
1.278
1.264
1.250
O2N
OEt
NC
O
O
1.95
2.17
3.88
0.95
0.94
0.95
1.94
2.00
4.01
4.02
3.20
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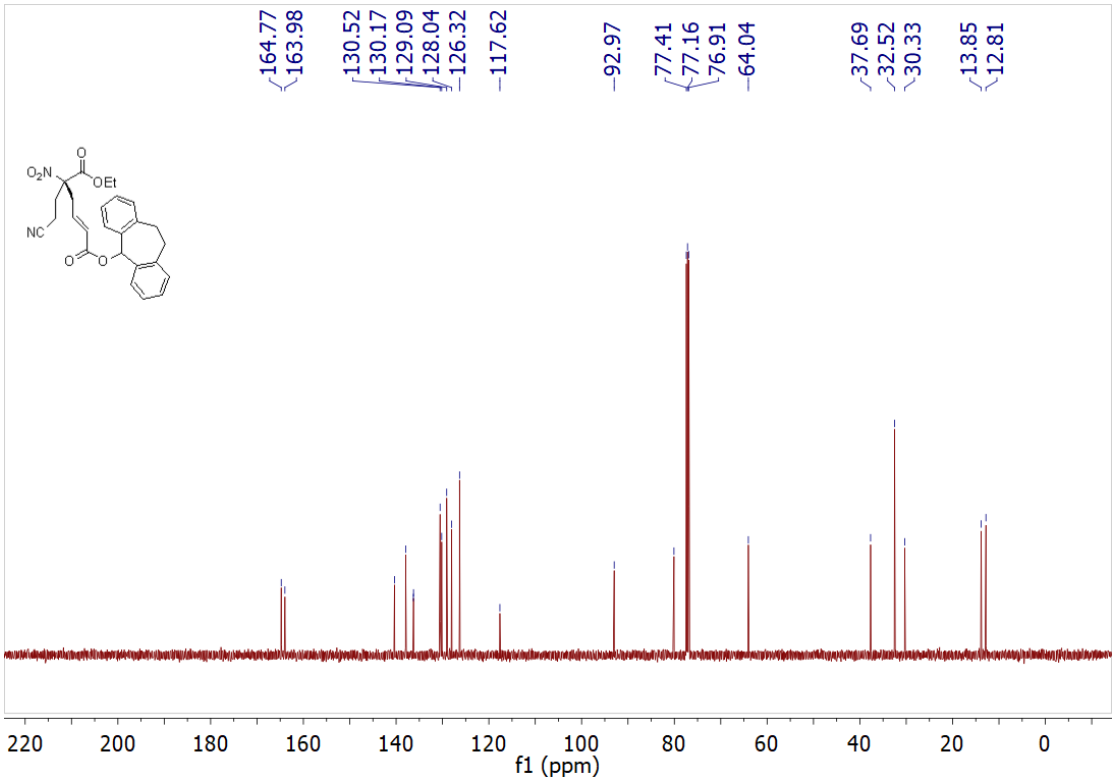
f1 (ppm)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77.16
76.91
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37.69
32.52
30.33
13.85
12.81
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OEt
NC
O
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220
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140
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100
80
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40
20
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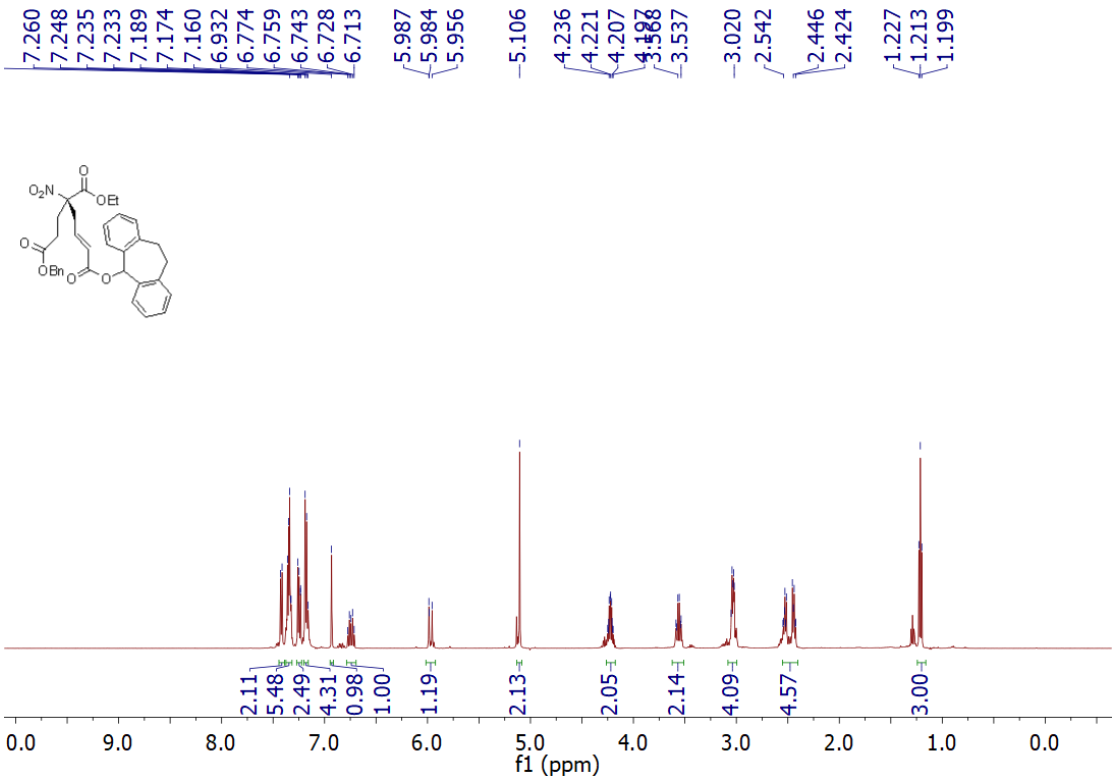
f1 (ppm)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4.207
3.537
3.020
2.542
2.446
2.424
1.227
1.213
1.199
O2N
OEt
OBn
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2.05
2.14
4.09
4.57
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
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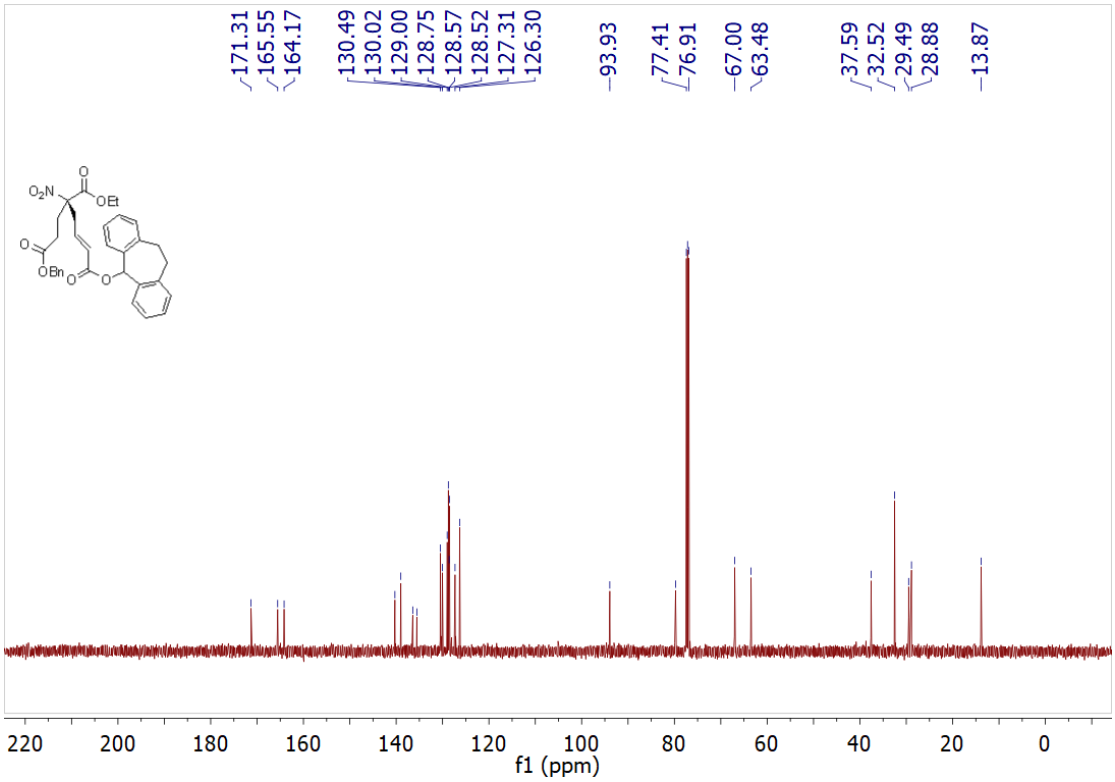
f1 (ppm)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128.57
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127.31
126.30
93.93
77.41
76.91
67.00
63.48
37.59
32.52
29.49
28.88
13.87
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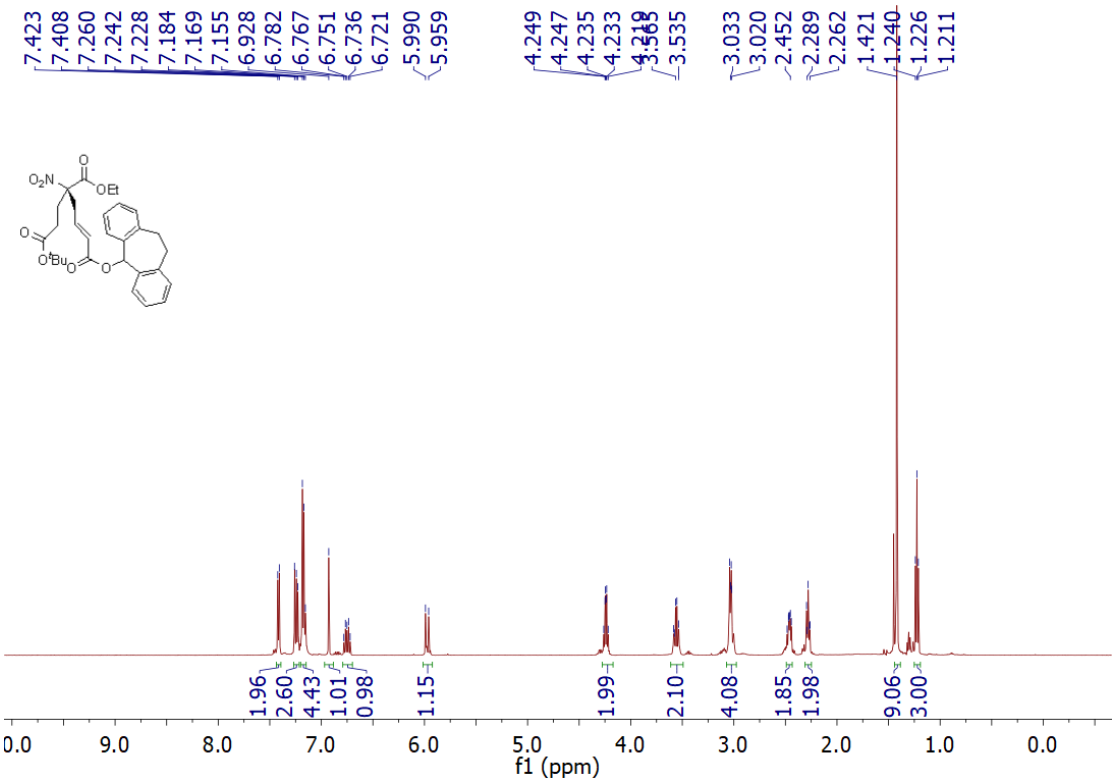
OEt
OBn
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.169
7.155
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6.782
6.767
6.751
6.736
6.721
5.990
5.959
4.249
4.247
4.235
4.233
3.535
3.033
3.020
2.452
2.289
2.262
1.421
1.240
1.226
1.211
1.96
2.60
4.43
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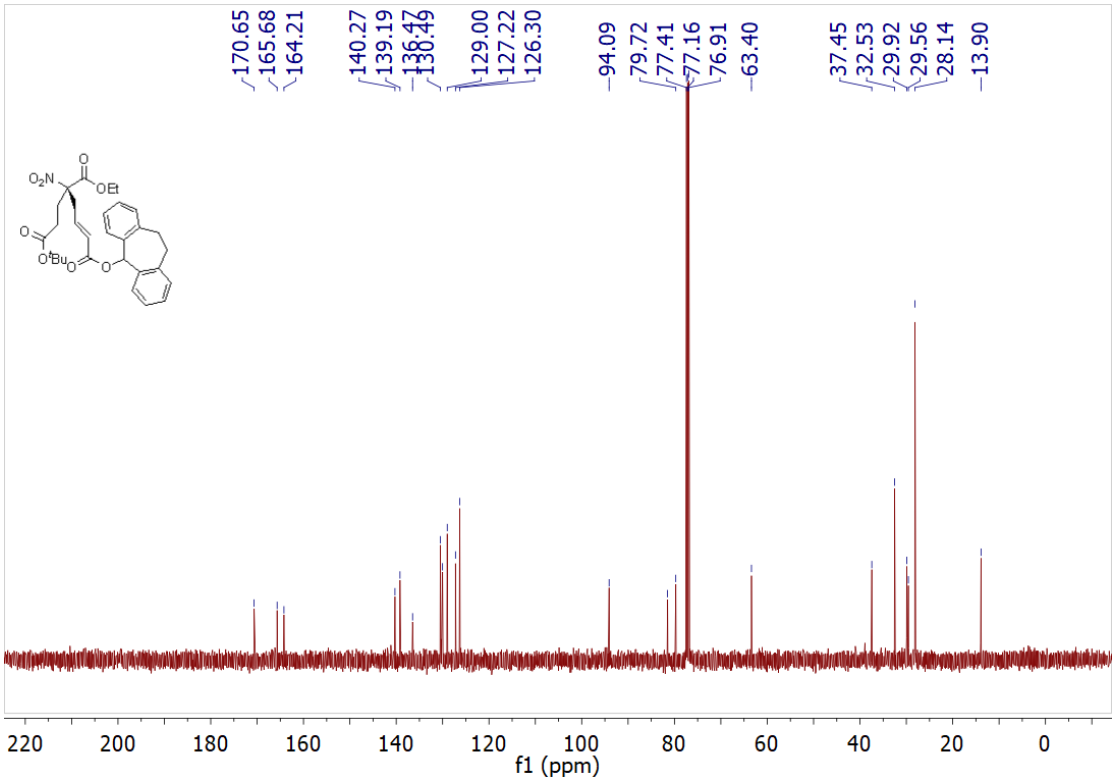
1.15
1.99
2.10
4.08
1.85
1.98
9.06
3.00
f1 (ppm)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126.30
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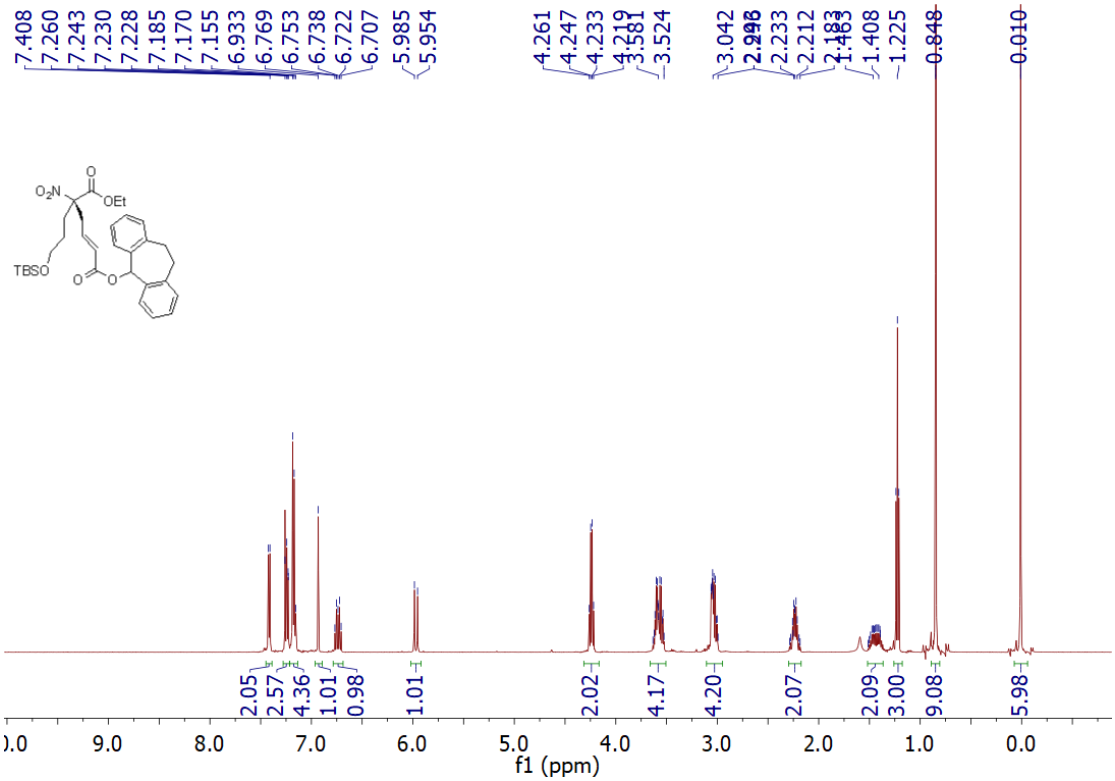
76.91
63.40
37.45
32.53
29.92
29.56
28.14
13.90
f1 (ppm)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7.185
7.170
7.155
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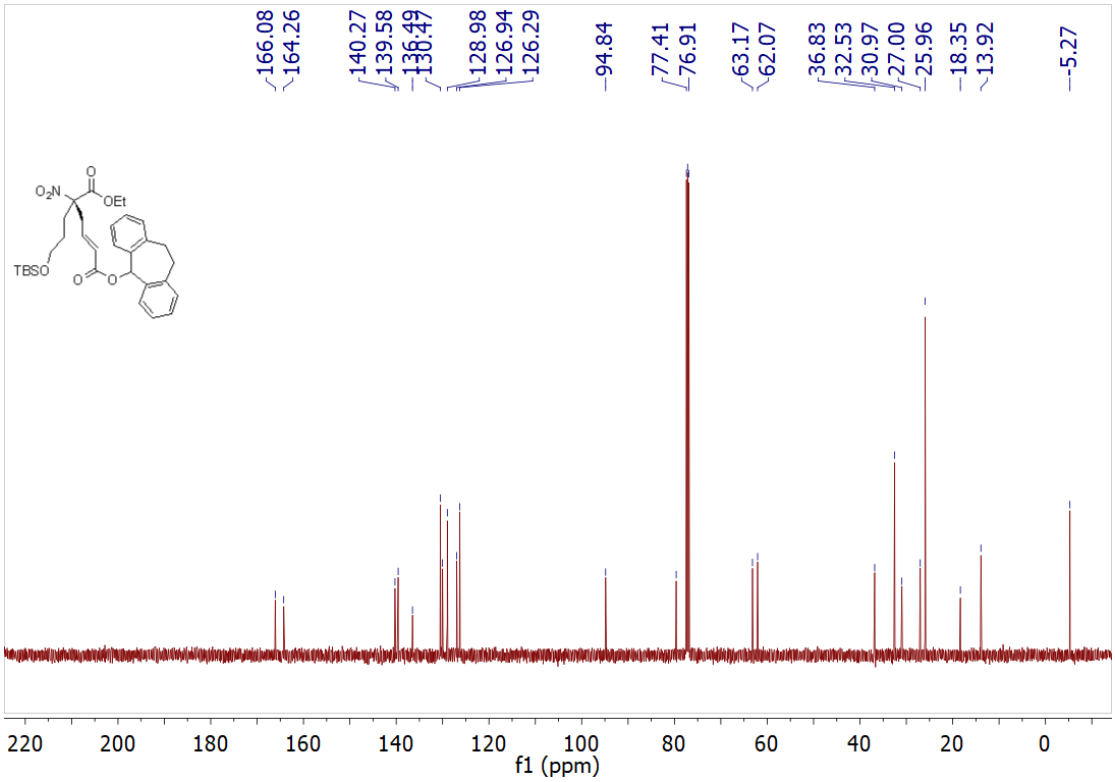
6.753
6.738
6.722
6.707
5.985
5.954
4.261
4.247
4.233
4.219
4.201
3.581
3.524
3.042
2.233
2.212
1.408
1.225
0.848
0.010
O2N
OEt
TBSO
2.05
2.57
4.36
1.01
0.98
1.01
2.02
4.17
4.20
2.07
2.09
3.00
9.08
5.98
f1 (ppm)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139.58
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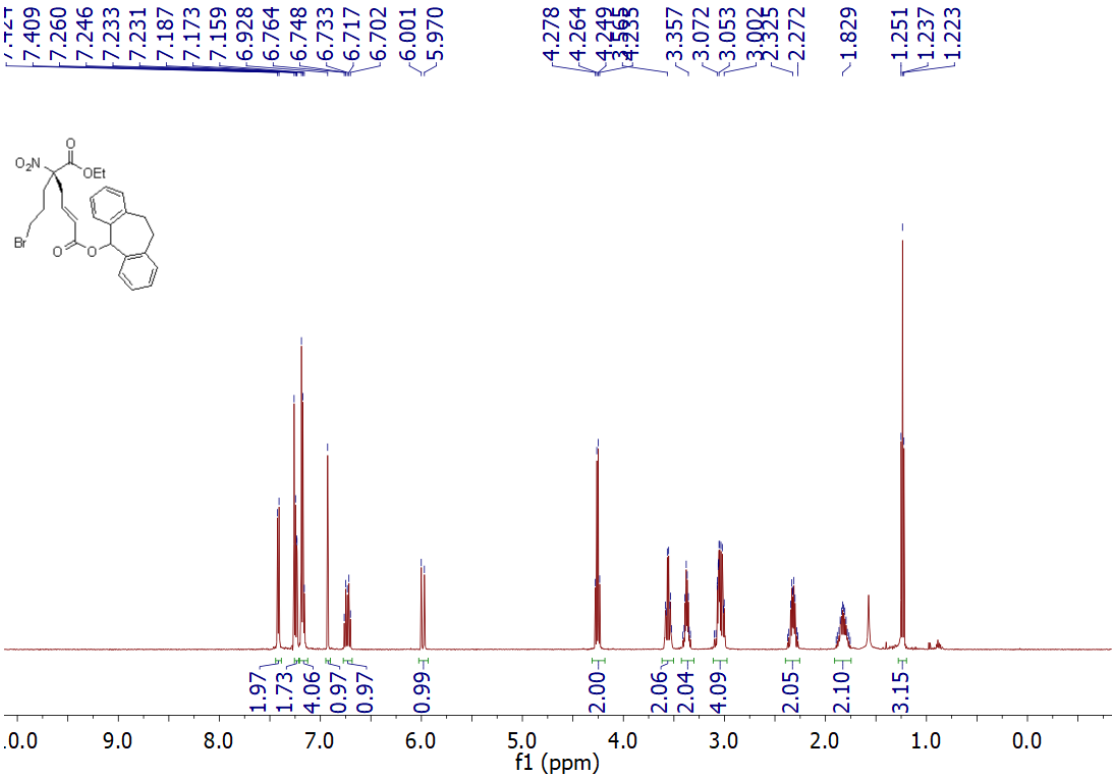
126.94
126.29
94.84
77.41
76.91
63.17
62.07
36.83
32.53
30.97
27.00
25.96
18.35
13.92
-5.27
O2N
OEt
TBSO
f1 (ppm)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7.246
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7.231
7.187
7.173
7.159
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6.764
6.748
6.733
6.717
6.702
6.001
5.970
4.278
4.264
3.357
3.072
3.053
2.272
1.829
1.251
1.237
1.223
1.97
1.73
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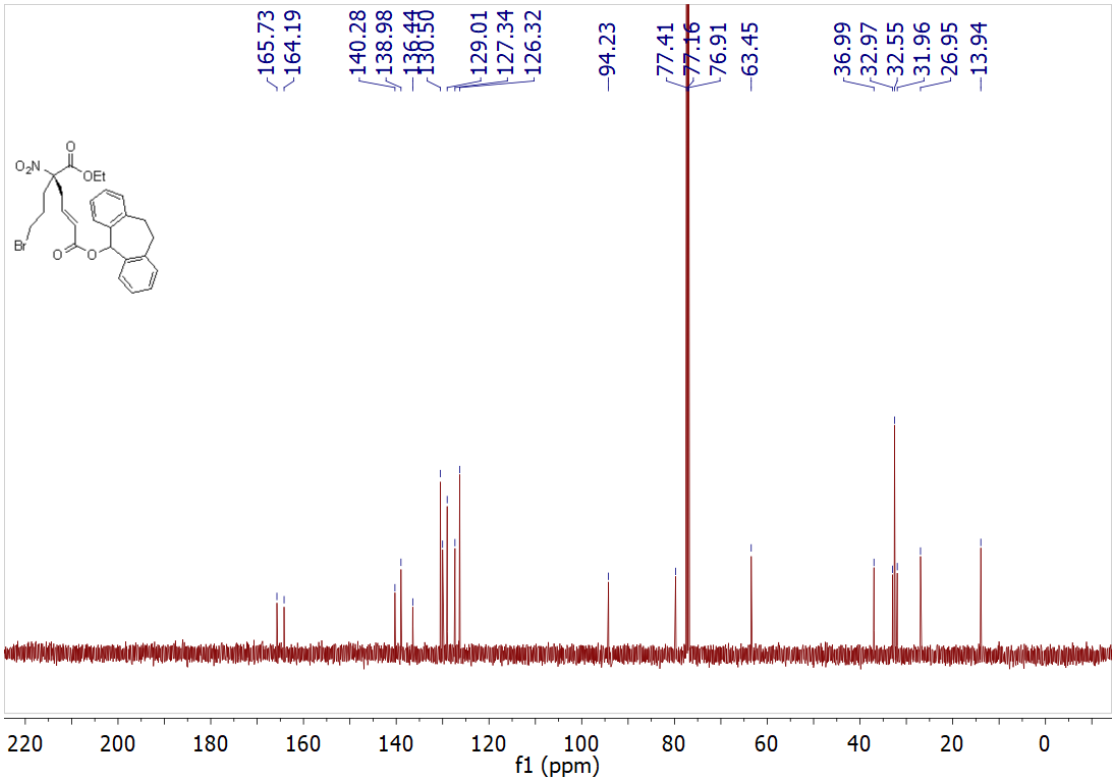
0.97
0.97
0.99
2.00
2.06
2.04
4.09
2.05
2.10
3.15
f1 (ppm)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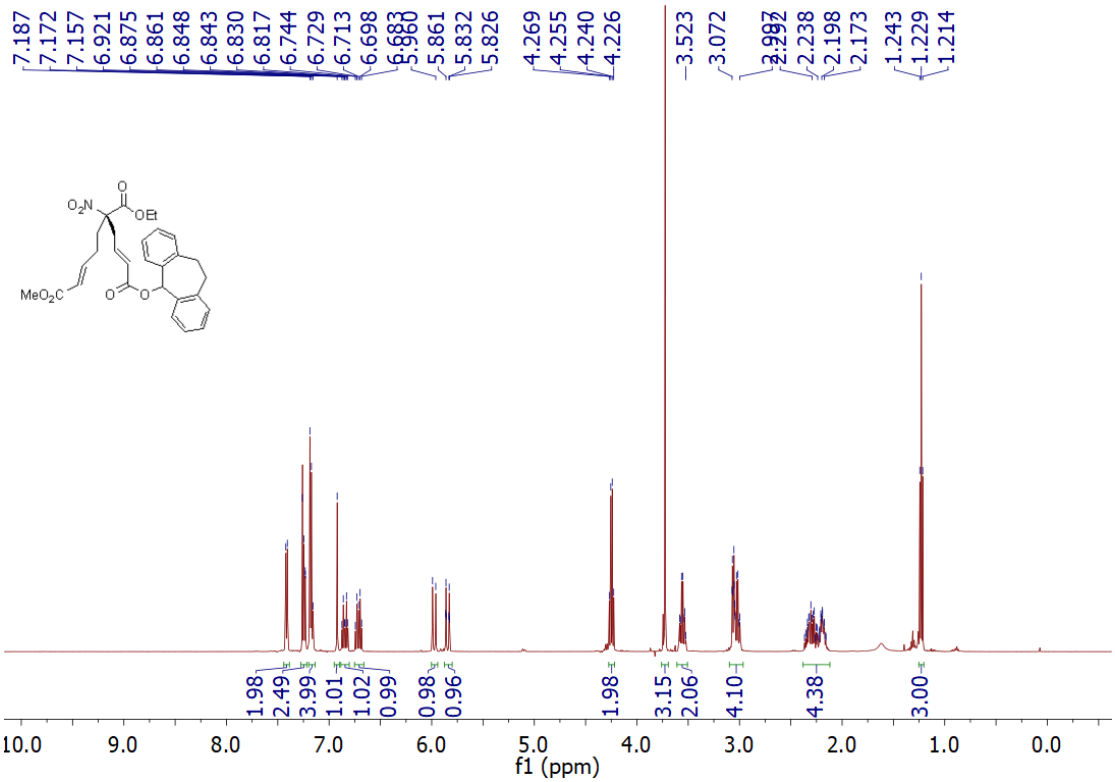
127.34
126.32
94.23
77.41
77.16
76.91
63.45
36.99
32.97
32.55
31.96
26.95
13.94
f1 (ppm)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7.157
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6.875
6.861
6.848
6.843
6.830
6.817
6.744
6.729
6.713
6.698
5.861
5.832
5.826
4.269
4.255
4.240
4.226
3.523
3.072
2.238
2.198
2.173
1.243
1.229
1.214
1.98
2.49
3.99
1.01
1.02
0.99
0.98
0.96
1.98
3.15
2.06
4.10
4.38
3.00
10.0
9.0
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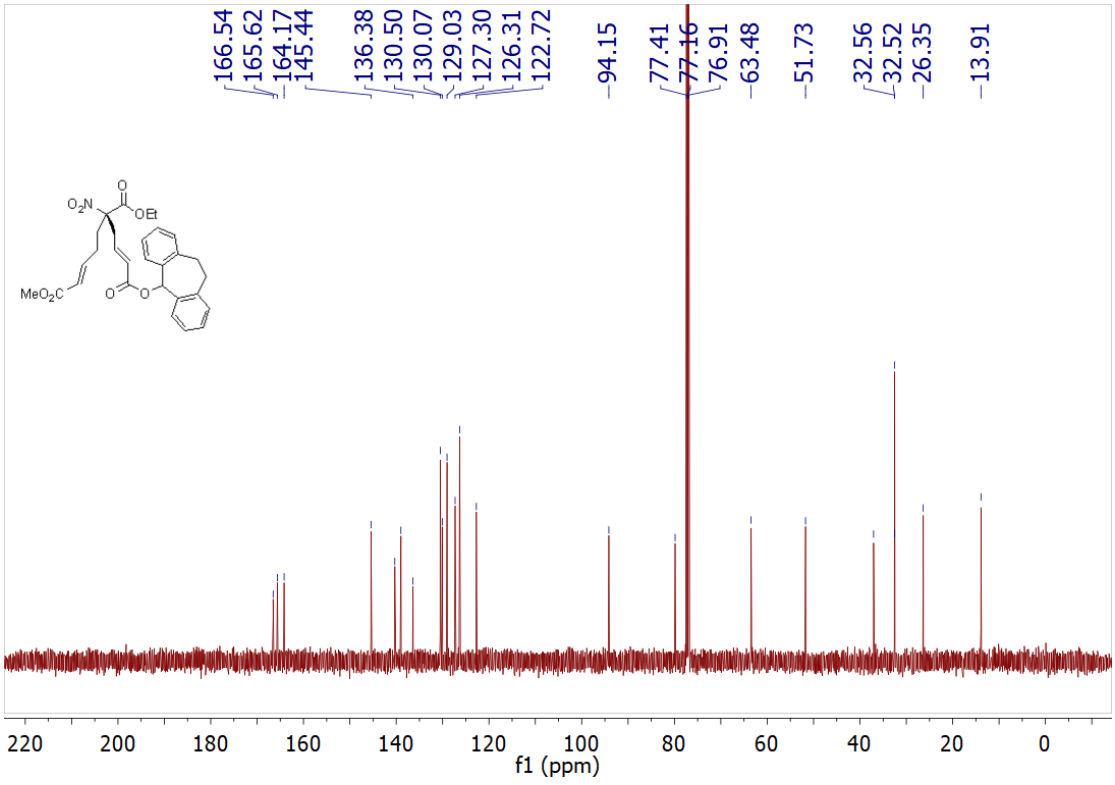
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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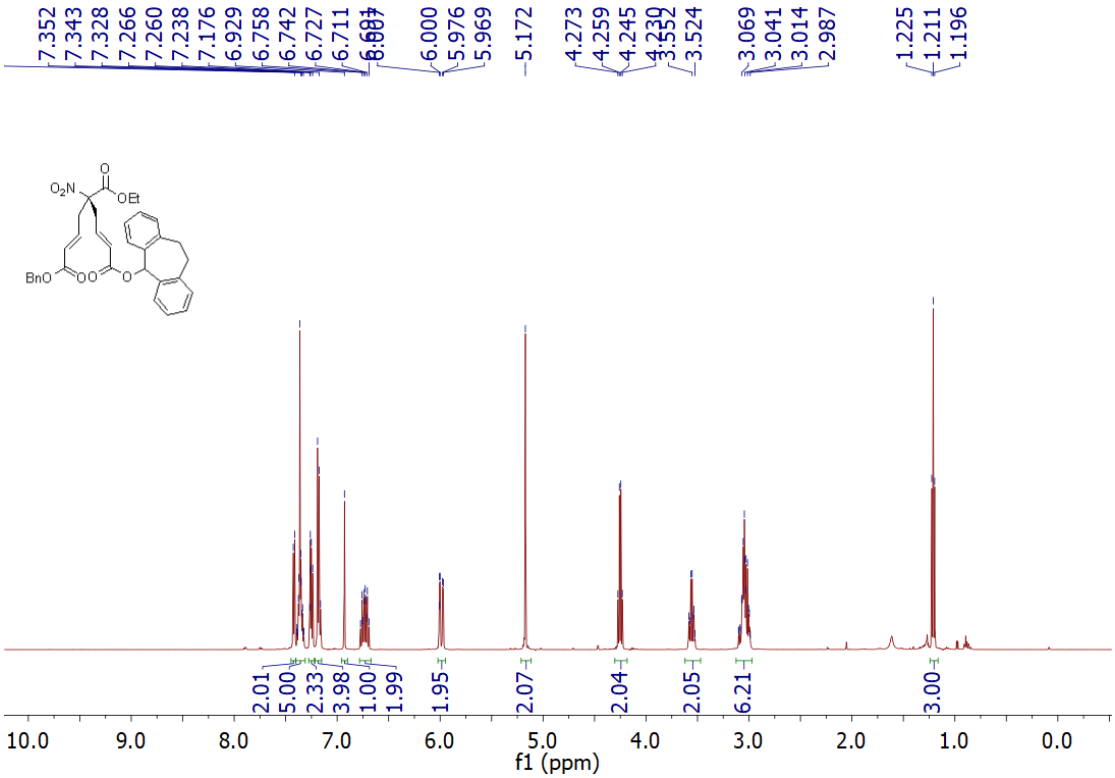
145.44
136.38
130.50
130.07
129.03
127.30
126.31
122.72
94.15
77.41
77.16
76.91
63.48
51.73
32.56
32.52
26.35
13.91
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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6.758
6.742
6.727
6.711
6.000
5.976
5.969
5.172
4.273
4.259
4.245
4.230
3.552
3.524
3.069
3.041
3.014
2.987
1.225
1.211
1.196
O2N
OEt
BnO
2.01
5.00
2.33
3.98
1.00
1.99
1.95
2.07
2.04
2.05
6.21
3.00
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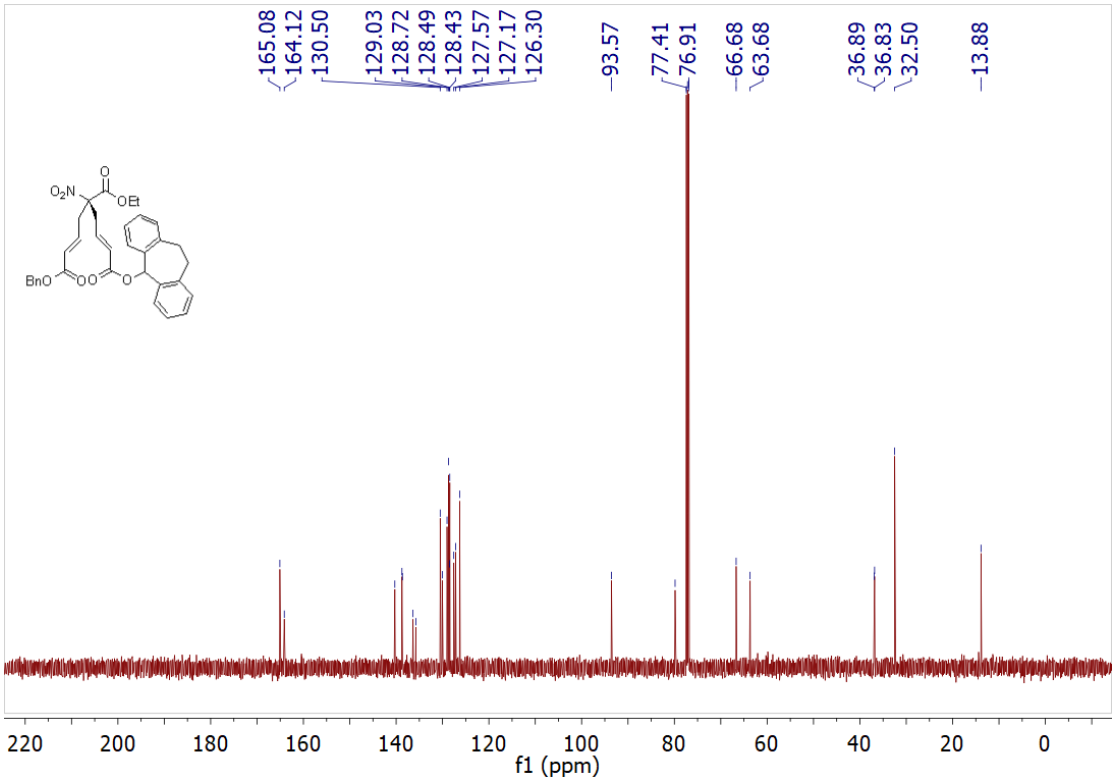
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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164.12
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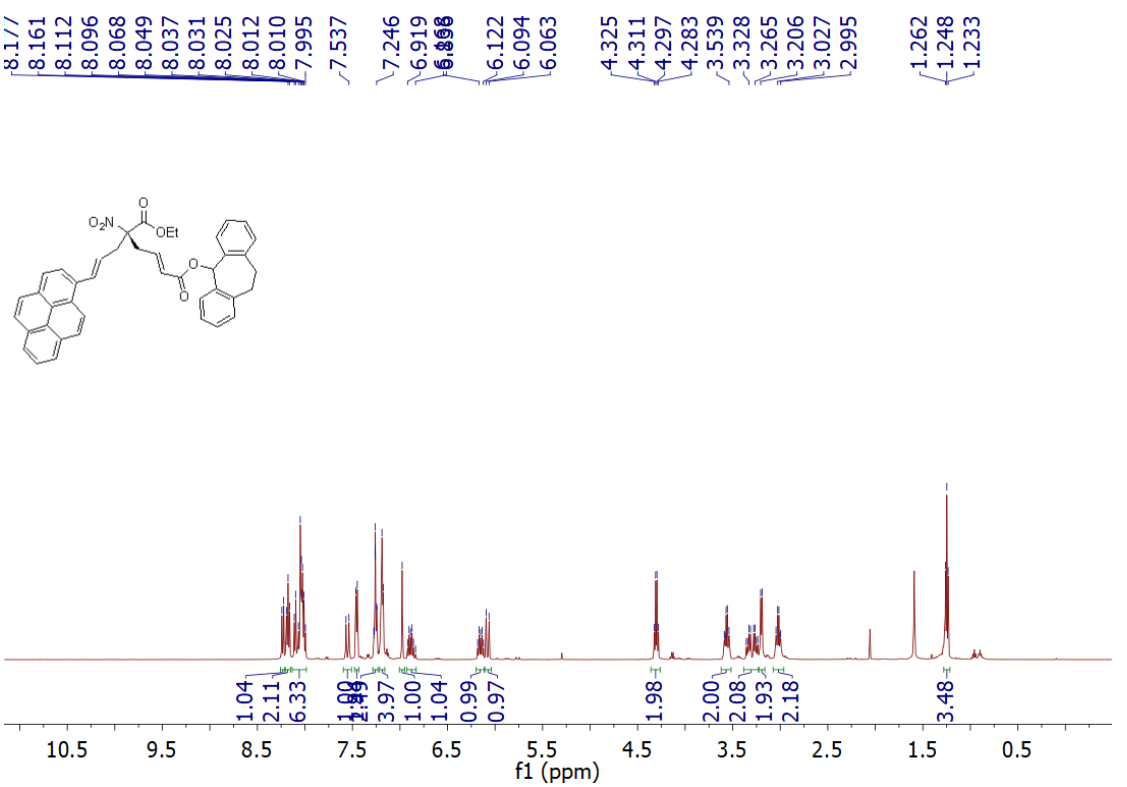
128.49
128.43
127.57
127.17
126.30
93.57
77.41
76.91
66.68
63.68
36.89
36.83
32.50
13.88
O2N
OEt
BnO
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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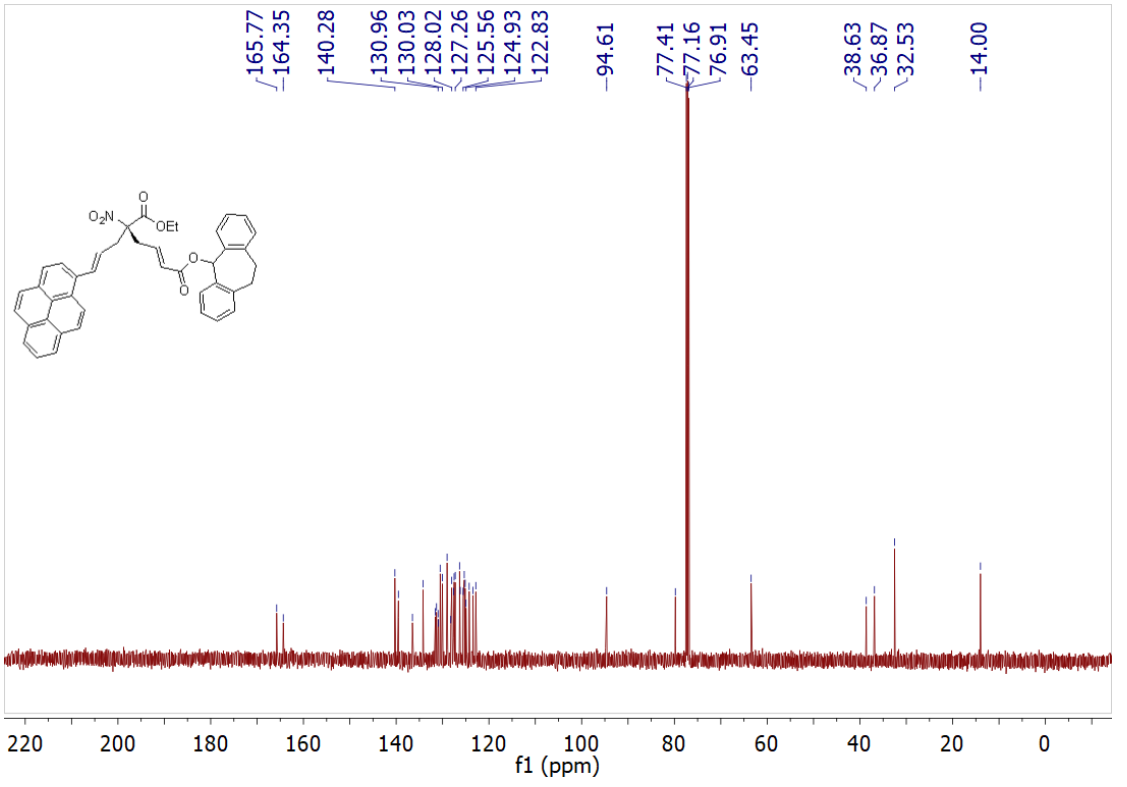
8.037
8.031
8.025
8.012
8.010
7.995
7.537
7.246
6.919
6.122
6.094
6.063
4.325
4.311
4.297
4.283
3.539
3.328
3.265
3.206
3.027
2.995
1.262
1.248
1.233
O2N
OEt
O
O
1.04
2.11
6.33
3.97
1.00
1.04
0.99
0.97
1.98
2.00
2.08
1.93
2.18
3.48
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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128.02
127.26
125.56
124.93
122.83
94.61
77.41
77.16
76.91
63.45
38.63
36.87
32.53
14.00
O2N
OEt
O
O
220
200
180
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140
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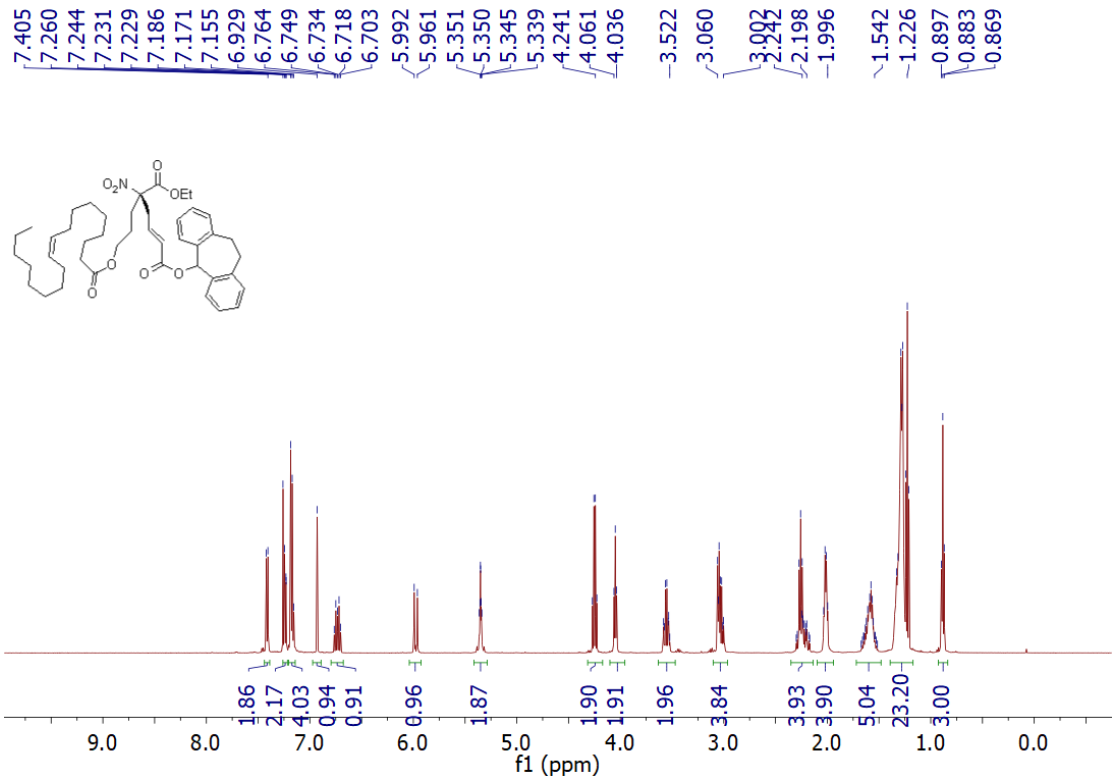
100
80
60
40
20
0
f1 (ppm)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6.749
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6.718
6.703
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5.961
5.351
5.350
5.345
5.339
4.241
4.061
4.036
3.522
3.060
3.002
2.242
2.198
1.996
1.542
1.226
0.897
0.883
0.869
1.86
2.17
4.03
0.94
0.91
0.96
1.87
1.90
1.91
1.96
3.84
3.93
3.90
5.04
23.20
3.00
9.0
8.0
7.0
6.0
5.0
4.0
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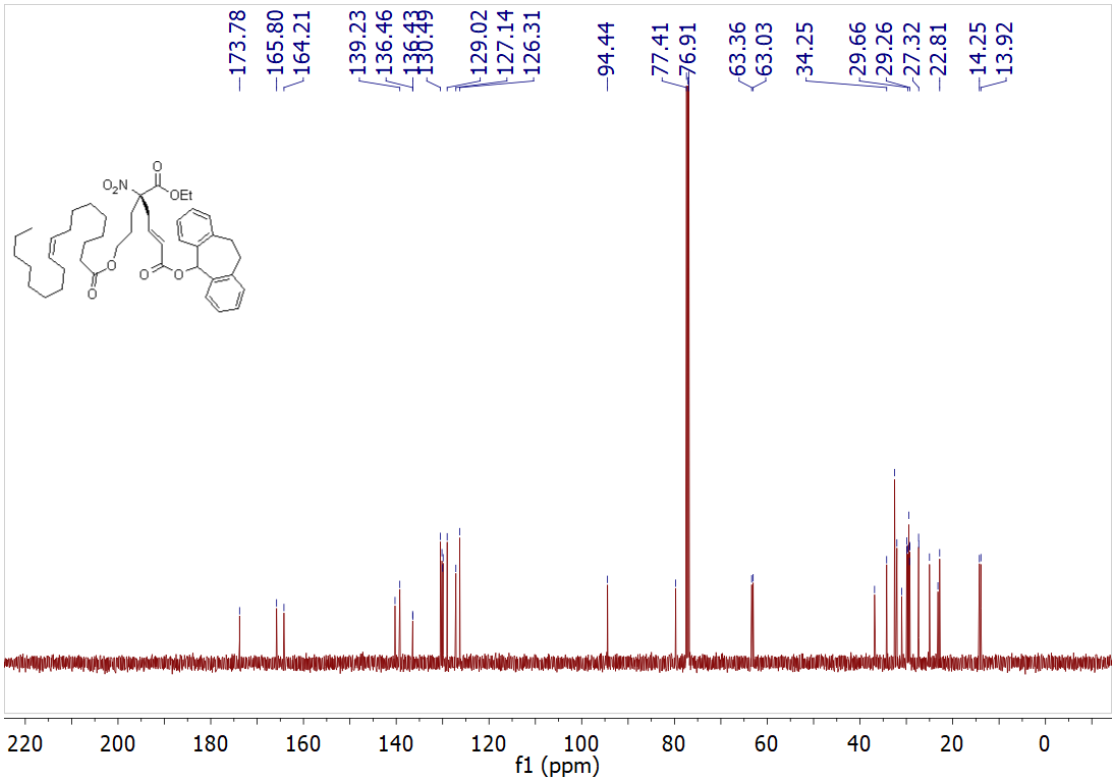
2.0
1.0
0.0
f1 (ppm)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129.02
127.14
126.31
94.44
77.41
76.91
63.36
63.03
34.25
29.66
29.26
27.32
22.81
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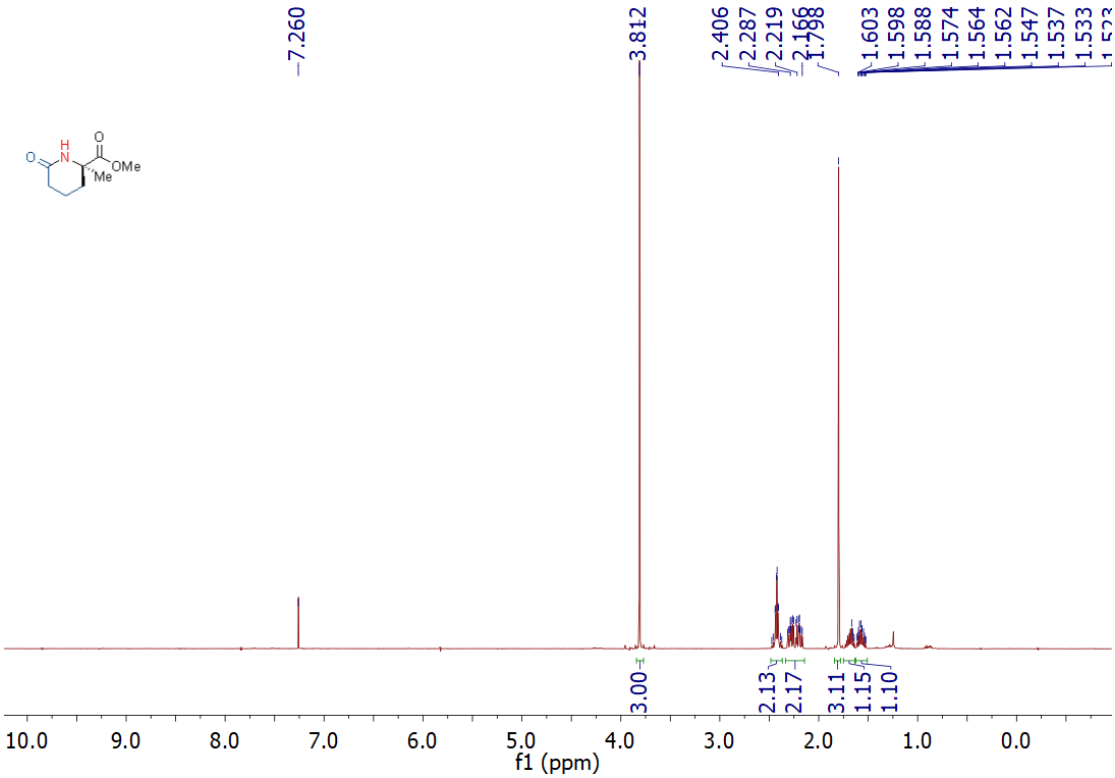
13.92
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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1.588
1.574
1.564
1.562
1.547
1.537
1.533
OMe
Me
3.00
2.13
2.17
3.11
1.15
1.10
10.0
9.0
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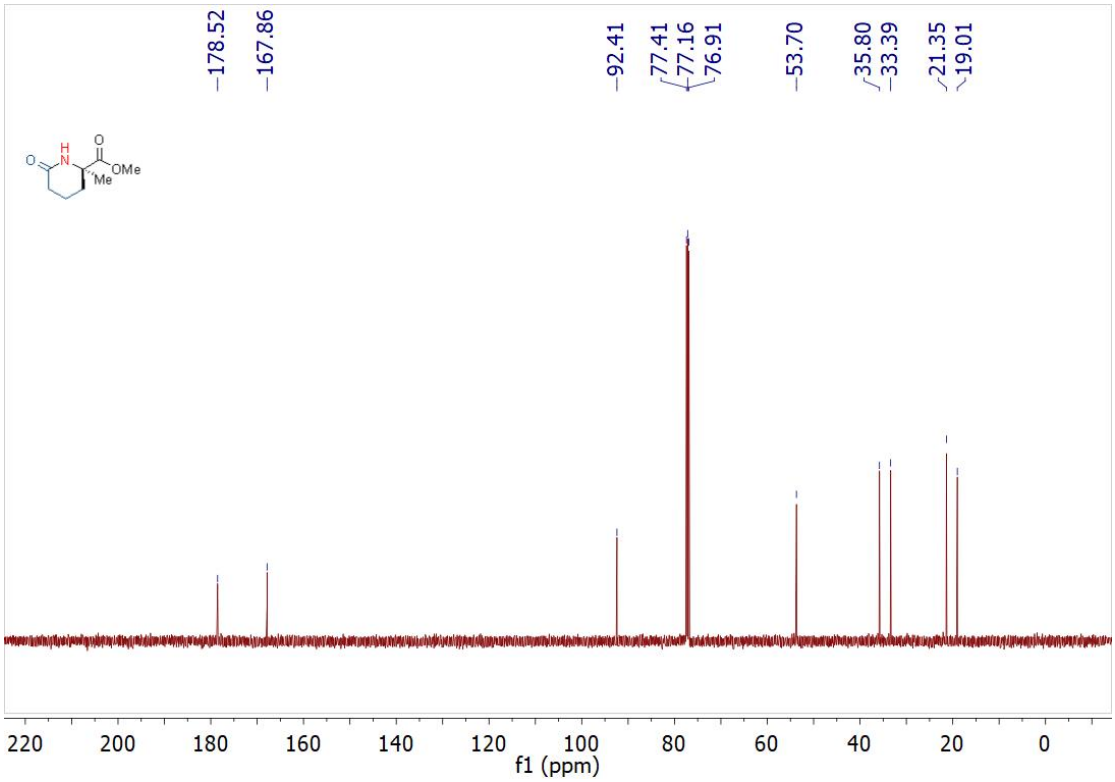
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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77.41
77.16
76.91
53.70
35.80
33.39
21.35
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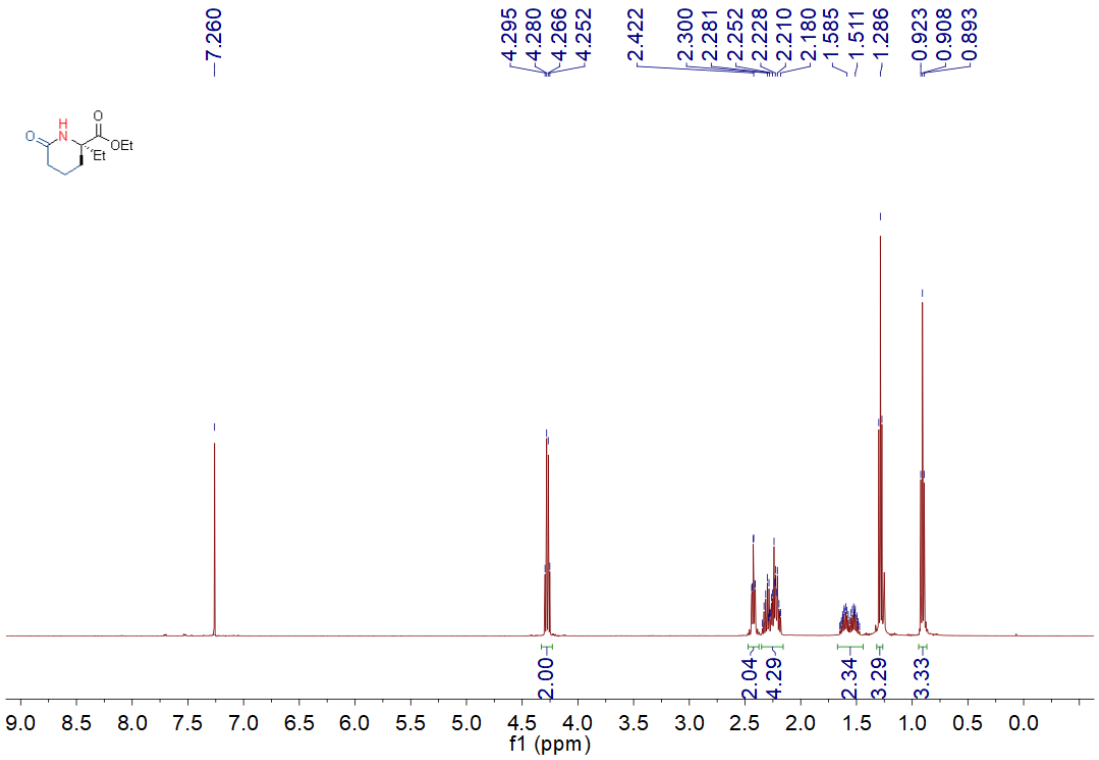
OMe
Me
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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4.266
4.252
2.422
2.300
2.281
2.252
2.228
2.210
2.180
1.585
1.511
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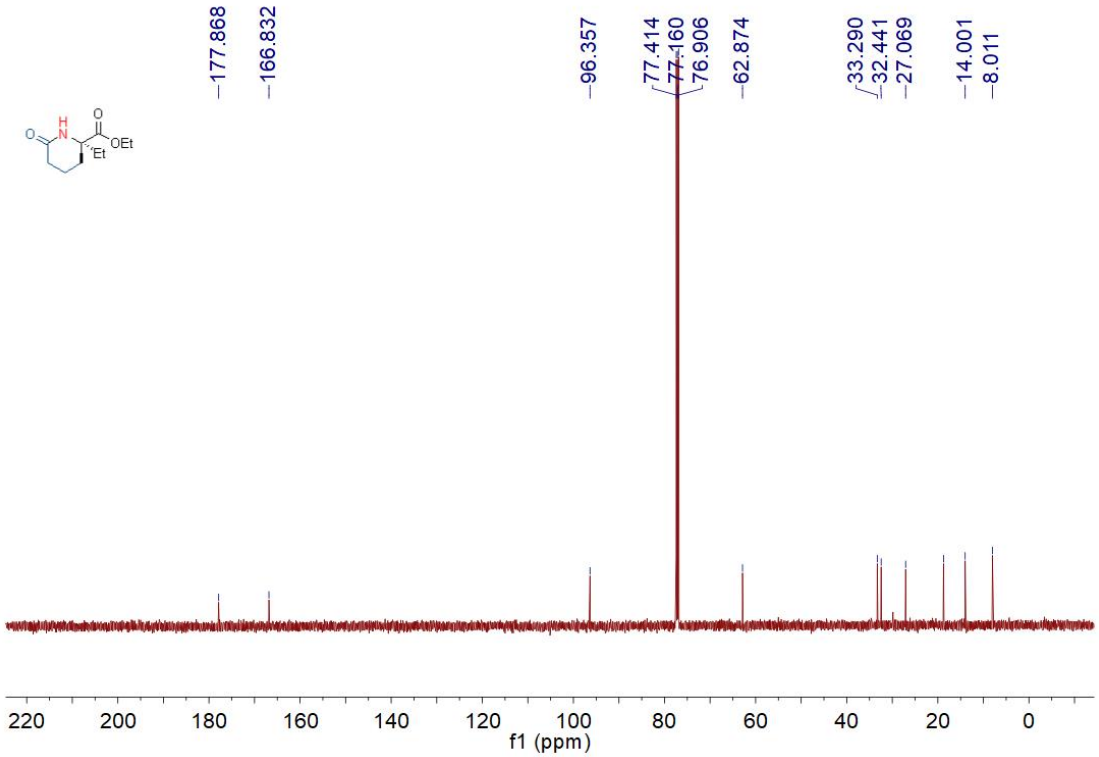
0.908
0.893
2.00
2.04
4.29
2.34
3.29
3.33
f1 (ppm)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32.441
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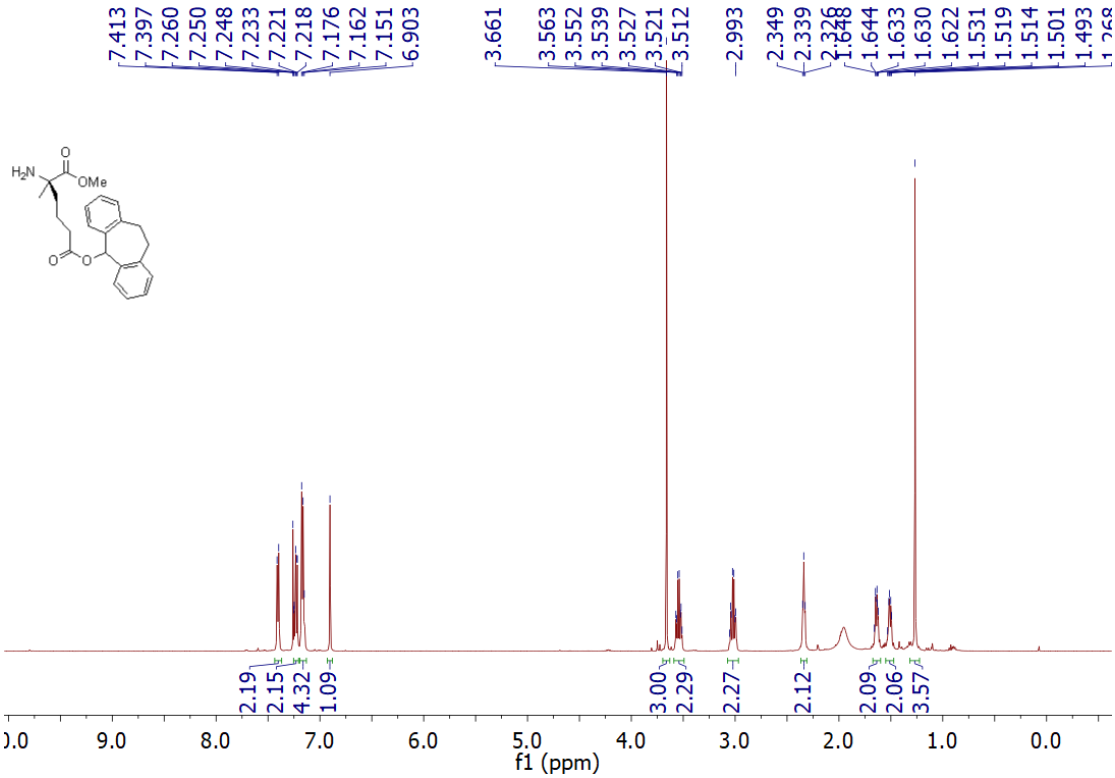
8.011
f1 (ppm)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7.218
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7.162
7.151
6.903
3.661
3.563
3.552
3.539
3.527
3.521
3.512
2.993
2.349
2.339
1.644
1.633
1.630
1.622
1.531
1.519
1.514
1.501
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1.09
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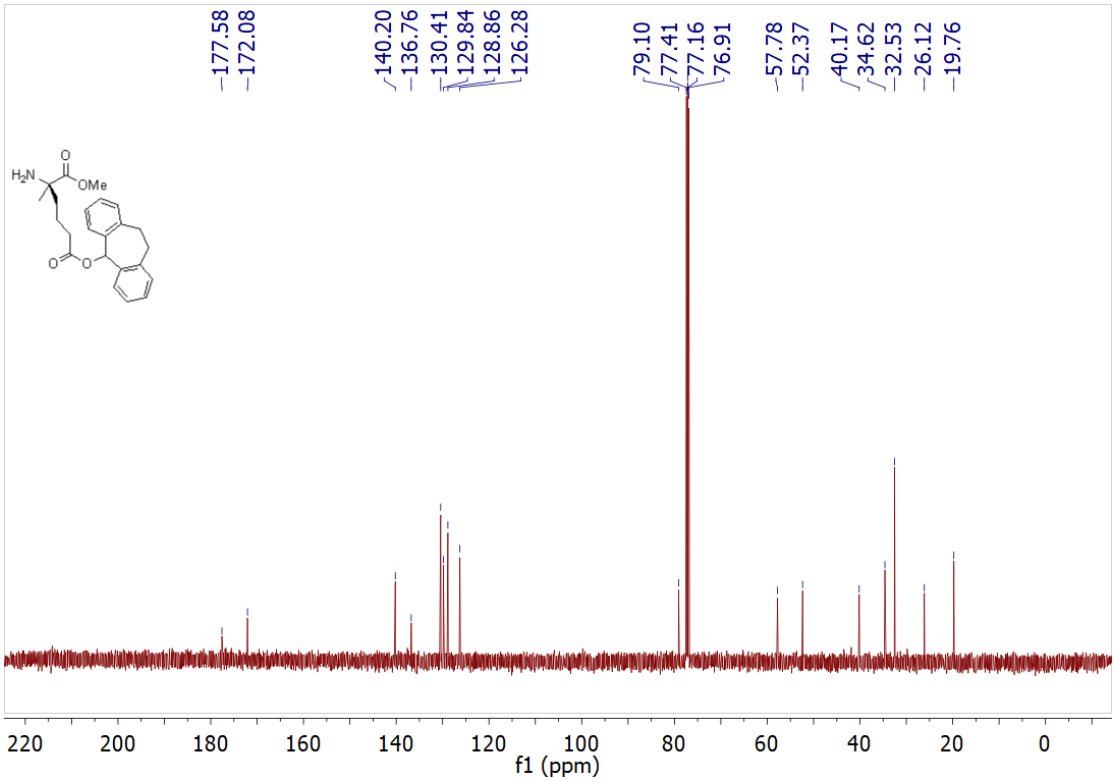
2.09
2.06
3.57
f1 (ppm)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79.10
77.41
77.16
76.91
57.78
52.37
40.17
34.62
32.53
26.12
19.76
f1 (ppm)