Alkenyl Carbonyl Derivatives in Enantioselective Redox Relay Heck Reactions: Accessing *α,β*-Unsaturated Systems

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Supporting Information

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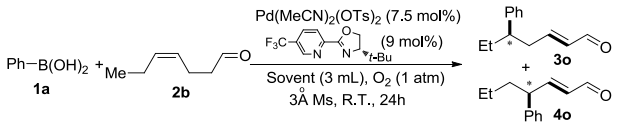
Computational and Correlative Studies

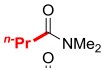
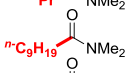
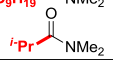
A. Effects of Dimethylamide Solvents on Site Selectivity

i. DFT Calculations

For computationally derived IR vibration values, dimethyl amides were geometrically optimized and their frequencies and intensities were calculated using Gaussian 09 software.[1] The functional used for DFT calculation is M06-2x. A triple zeta potential basis-set (jun-cc-pvtz) was chosen based on the evaluation of the M06-2x functional for organic molecules, as triple zeta quality basis sets mostly result to quantitative correlations.[2] Subsequently, Sterimol values of the X group of the dimethyl amide were calculated for the geometry optimized structures using Molecular Modeling Pro®.[3] NBO charges were obtained using NBO Version 3.1 in Gaussian 09.[4]

Table S1. Effect of Different Solvent on the Reaction of 1a and 2b.[a]



Entry	Solvent	yield of **3o**[b]	**3o**:**4o**[c]
1		44%	3.61 and 3.64
2		50%	6.04 and 5.99
3		35%	4.78 and 4.84
4		21%	6.73 and 6.71
5		< 10%	7.11 and 6.91
6		< 10%	7.82 and 7.90

[a]**1a** (0.75 mmol, 3.0 eq), **2b** (0.25 mmol, 1.0 eq), $Pd(MeCN)_2(OTs)_2$ (0.01875 mmol, 7.5 mol%), (S)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (0.0225 mmol, 9 mol%), solvent (3 mL),3Å Ms (50 mg),O_2 (1 atm), room temperature, 24 h. [b] Isolated yield.[c] Determined by NMR.

ii. Model Development

First, parameters that describe the steric and electronic perturbations induced by the substituents on the X group of the solvent were identified. Using MATLAB® R2014a software[5], a multiple linear regression model was developed toutilize the normalized steric and electronic parameters in predicting the difference in transition state energies ($\Delta\Delta G^{\ddagger}$).These predicted

$\Delta\Delta G^{\ddagger}$values were then compared to the measured $\Delta\Delta G^{\ddagger}$ values obtained from an average of two experimental results. A good correlation between the two indicates that the predicted $\Delta\Delta G^{\ddagger}$ approximates the measured $\Delta\Delta G^{\ddagger}$ adequately. The resulting model was then evaluated for accuracy and precision using Leave-One-Out (LOO) validation.[6]

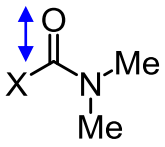


Figure S1.Carbonyl stretch of dimethyl amide.

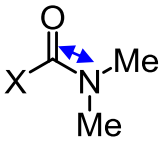


Figure S2.C-N stretch of dimethyl amide.

Table S2. (a) Regioselectivity ratios of **3o**:**4o** of two trial runs. (b) Average of the regioselectivity ratios of two trials[a]. (c) Difference in $\Delta\Delta G^{\ddagger}$ calculated from regioselectivityratios[a]. (d) $\Delta\Delta G^{\ddagger}$ calculated from average regioselectivityratios[b]. (e) Standard deviation of the measured $\Delta\Delta G^{\ddagger}$[c].

X	Trial1 3o:4o[a]	Trial 2 3o:4o[a]	Average 3o:4o[b]	Trial 1 $\Delta\Delta G^{\ddagger}$[c] (kcal mol^{-1})	Trial 2 $\Delta\Delta G^{\ddagger}$[c] (kcal mol^{-1})	Average $\Delta\Delta G^{\ddagger}$[d] (kcal mol^{-1})	*s* $\Delta\Delta G^{\ddagger}$[e] (kcal mol^{-1})
H	3.61	3.64	3.63	0.76	0.77	0.76	0.003
Me	6.04	5.99	6.02	1.07	1.06	1.06	0.003
NMP	4.84	4.78	4.81	0.93	0.93	0.93	0.005
^{n}-Pr	6.73	6.71	6.72	1.13	1.13	1.13	0.001
^{i}-Pr	7.82	7.90	7.86	1.22	1.22	1.22	0.004
^{n}-C_9H_{19}	7.11	6.91	7.01	1.16	1.15	1.15	0.012

Table S3. Crude values of electronic and steric parameters of dimethyl amides including IR frequencies (*v*) and intensities (*I*) of C-N stretch and carbonyl (C=O) stretch of the dimethyl amide solvents together with the Sterimol values (B_1, B_5, and L) of the X group.

X	v_{C-N}	I_{C-N}	$v_{C=O}$	$I_{C=O}$	B_1	B_5	*L*
H	1554.90	46.56	1798.86	551.66	1.17	1.17	2.27
Me	1558.66	98.83	1766.67	426.05	1.70	2.21	3.08
NMP	1549.78	30.88	1812.44	495.70	1.71	3.79	6.61
^{n}-Pr	1555.15	98.35	1762.47	364.73	1.72	3.58	5.19
^{i}-Pr	1555.71	98.24	1755.70	350.01	2.06	3.36	4.30
^{n}-C_9H_{19}	1554.64	106.88	1762.50	350.28	1.72	7.82	11.50

Table S4. Normalized values of electronic and steric parameters of dimethyl amides. Shown are normalized IR frequencies (ν) and intensities (I) of C-N stretch and carbonyl (C=O) stretch of the dimethyl amide solvents together with the Sterimol values (B_1, B_5, and L) of the X group.

X	ν_{C-N}	I_{C-N}	$\nu_{C=O}$	$I_{C=O}$	B_1	B_5	L
H	0.03	-1.03	0.96	1.52	-1.78	-1.10	-0.97
Me	1.34	0.58	-0.42	0.04	0.07	-0.64	-0.73
NMP	-1.75	-1.51	1.55	0.86	0.10	0.06	0.34
$^{n-}$Pr	0.12	0.57	-0.60	-0.69	0.14	-0.03	-0.09
$^{i-}$Pr	0.32	0.56	-0.89	-0.86	1.33	-0.13	-0.36
$^{n-}C_9H_{19}$	-0.06	0.83	-0.60	-0.86	0.14	1.84	1.81

Equation S1. Crude (a) and normalized (b)linear regression model relating the IR intensity ($I_{C=O}$) of the carbonyl stretch of the dimethyl amide solvents to the $\Delta\Delta G^{\ddagger}$.

(a) Crude Regression Model: $\Delta\Delta G^{\ddagger} = 1.88 - 0.0020\boldsymbol{I}_{C=O}$

(b) Normalized Regression Model: $\Delta\Delta G^{\ddagger} = 1.04 - 0.17\boldsymbol{I}_{C=O}$

Table S5.Measured and Predicted differences in transition state energies ($\Delta\Delta G^{\ddagger}$) derived using equation S1.

X	**Measured $\Delta\Delta G^{\ddagger}$ (kcal mol^{-1})**	**Predicted $\Delta\Delta G^{\ddagger}$ (kcal mol^{-1})**
H	0.76	0.78
Me	1.06	1.03
NMP	0.93	0.89
$^{n-}$Pr	1.13	1.16
$^{i-}$Pr	1.22	1.19
$^{n-}C_9H_{19}$	1.15	1.19

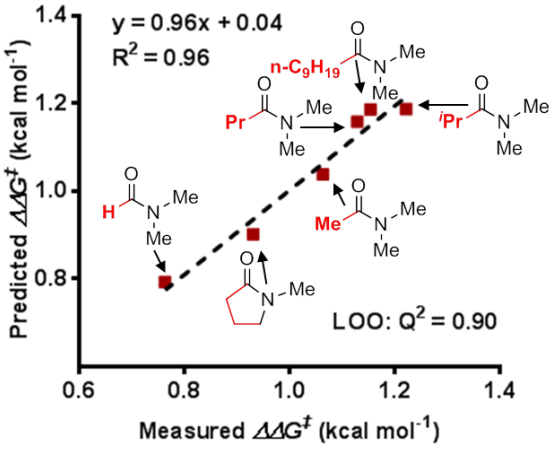


Figure S3. Comparison of predicted difference in $\Delta\Delta G^{\ddagger}$ derived using equation S1 that related the IR intensity of the carbonyl stretch ($I_{C=O}$) of various dimethyl amide solvents, with the measured $\Delta\Delta G^{\ddagger}$.

Table S6. Measured and Leave-One-Out (LOO) predicted $\Delta\Delta G^{\ddagger}$ as validation to the linear regression models obtained using equation S1.

X	Measured $\Delta\Delta G^{\ddagger}$(kcal mol^{-1})	LOO Predicted $\Delta\Delta G^{\ddagger}$(kcal mol^{-1})
H	0.76	0.84
Me	1.06	1.03
NMP	0.93	0.89
$^{n-}$Pr	1.13	1.17
$^{i-}$Pr	1.22	1.17
$^{n-}C_9H_{19}$	1.15	1.20

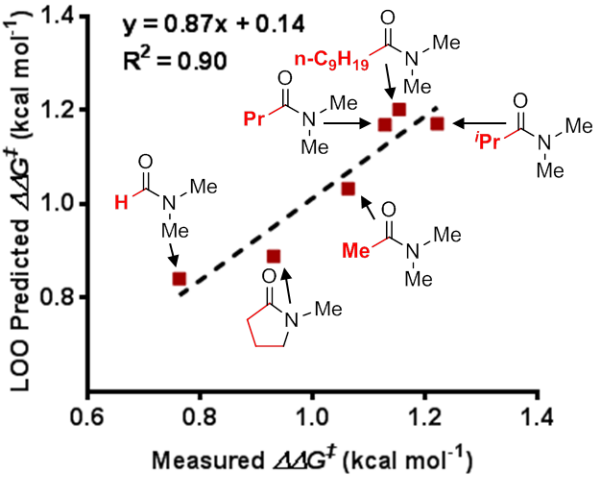


Figure S4. Leave-One-Out (LOO) validation of linear regression model based on equation S1 relating the predicted $\Delta\Delta G^{\ddagger}$ in response to the IR intensities of the carbonyl stretch ($I_{C=O}$) of various dimethylamide solvents.

Equation S2. Crude (a) and normalized (b) multivariate linear regression model relating the IR intensities of the carbonyl stretch ($I_{C=O}$) and the Sterimol B1 values of the X group of the dimethylamide to the $\Delta\Delta G^{\ddagger}$.

(a) Crude Regression Model: $\Delta\Delta G^{\ddagger} = 1.37 - 0.0015\boldsymbol{I}_{C=O} + 0.17B_1$

(b) Normalized Regression Model: $\Delta\Delta G^{\ddagger} = 1.04 - 0.13\boldsymbol{I}_{C=O} + 0.051B_1$

Table S7. Measured and predicted $\Delta\Delta G^{\ddagger}$ derived using equation S2.

X	Measured $\Delta\Delta G^{\ddagger}$ (kcal mol^{-1})	Predicted $\Delta\Delta G^{\ddagger}$ (kcal mol^{-1})
H	0.76	0.76
Me	1.06	1.04
NMP	0.93	0.94
$^{n-}$Pr	1.13	1.14
$^{i-}$Pr	1.22	1.22

$^{n-}C_9H_{19}$	1.15	1.16

Table S8. Measured and Leave-One-Out (LOO) predicted $\Delta\Delta G^{\ddagger}$ as validation to the linear regression models obtained using equation S2.

X	Measured $\Delta\Delta G^{\ddagger}$ (kcal mol^{-1})	LOO Predicted $\Delta\Delta G^{\ddagger}$ (kcal mol^{-1})
H	0.76	0.82
Me	1.06	1.08
NMP	0.93	0.89
^{n-}Pr	1.13	1.14
^{i-}Pr	1.22	1.24
$^{n-}C_9H_{19}$	1.15	1.13

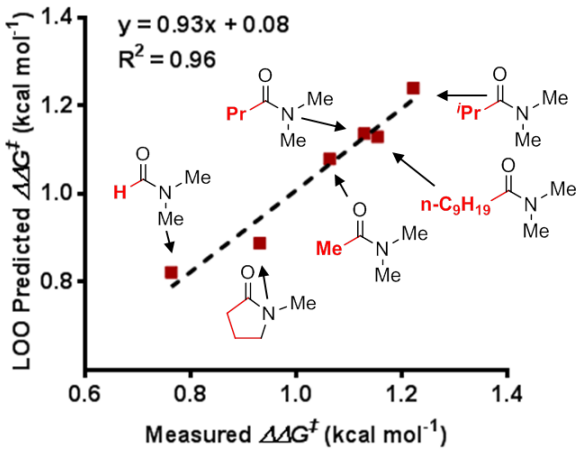


Figure S5. Leave-One-Out (LOO) validation of multiple linear regression model, based onequation S2, relating the IR intensities of the carbonyl stretch ($I_{C=O}$) and the Sterimol B1 values of the X group of the dimethylamide solvents to the $\Delta\Delta G^{\ddagger}$.

B. Functional Group Changes on Substrate 2a

i. DFT Calculations

For computationally derived IR vibration values, dimethyl amides were geometrically optimized and their frequencies and intensities were calculated using Gaussian 09 software.[1] The functional used for DFT calculation is M06-2x. A triple zeta potential basis-set (TZVP) was chosen based on the evaluation of the M06-2x functional for organic molecules, as triple zeta quality basis sets mostly result to quantitative correlations.[2] Subsequently, Sterimol values of the X group of the dimethylamide were calculated for the geometry optimized structures using Molecular Modeling Pro®.[3] NBO charges were obtained using NBO Version 3.1 in Gaussian 09.[4]

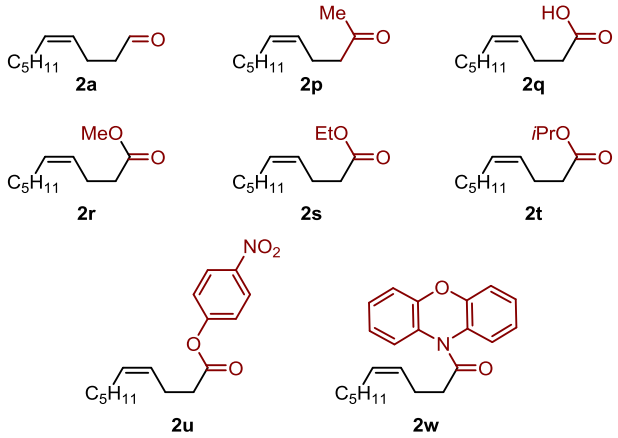


Figure S6. Substrates with C_5H_{11} substituents bound to the alkene.

Table S9. Site selectivity ratios of δ:γ and corresponding measured $\Delta\Delta G^{\ddagger}$.

Substrate	Ratio δ:γ	Measured ΔΔG‡ (kcal mol^{-1})
2a	15.1	1.61
2p	11.2	1.43
2q	7.9	1.22
2r	9.4	1.33
2s	8.5	1.27
2t	7.0	1.15
2u	12.0	1.47
2w	7.0	1.15

Table S10. Crude values of electronic and steric parameters of substrates including IR frequencies (ν) and intensities (I) of C=C, carbonyl (C=O), and C-H symmetric and asymmetric stretches together with ^{13}C NMR shifts and NBO charges on the alkene and the carbonyl groups.

substrate	$\nu_{C=C}$	$I_{C=C}$	$\nu_{C=O}$	$I_{C=O}$	$\nu_{C-H,sym}$	$I_{C-H,sym}$	$\nu_{C-H,asym}$	$I_{C=O,asym}$
2a	1760.47	3.50	1862.07	160.83	3167.94	39.14	3145.25	12.90
2p	1756.43	2.94	1851.46	159.31	3169.11	35.92	3149.76	6.76
2q	1758.15	3.06	1876.75	277.08	3176.86	27.81	3153.08	8.49
2r	1759.51	1.82	1856.32	299.28	3171.34	35.49	3146.55	8.44
2s	1762.86	1.38	1854.60	288.42	3172.13	34.54	3160.20	3.54
2t	1753.87	0.92	1847.84	283.22	3175.07	24.14	3155.73	7.01
2u	1752.78	1.76	1892.87	250.29	3174.84	24.18	3152.01	4.28
2w	1751.78	2.51	1797.31	321.59	3171.86	16.98	3150.74	3.29

substrate	$^{13}C_{\gamma}$	$^{13}C_{\delta}$	$^{13}C_{\gamma-\delta}$	$^{13}C_{C=O}$	$NBO_{C\gamma}$	$NBO_{C\delta}$	$NBO_{C\delta-\gamma}$	$NBO_{O,carbonyl}$	$NBO_{C,carbonyl}$
2a	131.94	127.22	4.72	202.41	-0.203	-0.155	0.048	-0.523	0.440
2p	131.31	127.54	3.77	208.54	-0.201	-0.158	0.043	-0.539	0.589
2q	131.89	126.86	5.03	179.72	-0.201	-0.161	0.040	-0.574	0.780
2r	131.62	127.22	4.40	173.68	-0.197	-0.164	0.033	-0.581	0.779
2s	131.50	127.30	4.20	173.24	-0.196	-0.165	0.031	-0.581	0.784
2t	131.43	127.39	4.04	173.01	-0.193	-0.170	0.023	-0.588	0.789
2u	155.50	145.30	10.20	170.70	-0.205	-0.166	0.039	-0.543	0.793
2w	131.60	127.37	4.23	171.69	-0.204	-0.159	0.045	-0.581	0.690

Table S11. Crude values of NBO charge on carbonyl oxygen and the measured site selectivity ($\Delta\Delta G^{\ddagger}$).

substrate	NBO	Measured $\Delta\Delta G^{\ddagger}$ (kcal mol^{-1})
2a	-0.523	1.61
2p	-0.539	1.43
2q	-0.574	1.22
2r	-0.581	1.33
2s	-0.581	1.27
2t	-0.588	1.15
2u	-0.543	1.47
2w	-0.581	1.15

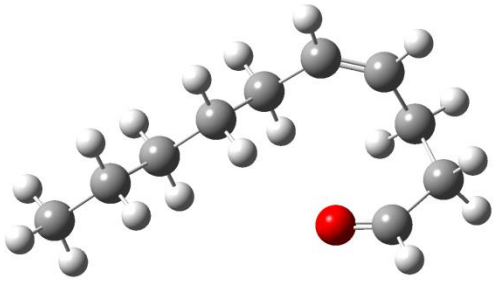


Figure S7. Geometry optimized structure of 2a.

References

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(3) Quinn, J. A.; ChemSW, Inc.: Fairfield , CA.

(4) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.

(5) In MATLAB NBO Version, 3.1 *(R2014a)*; The MathWorks, Inc.: Natick, MA, 2014.

(6) Arlot, S.; Celisse, A. *Statist. Surv.* **2010**, *4*, 40.

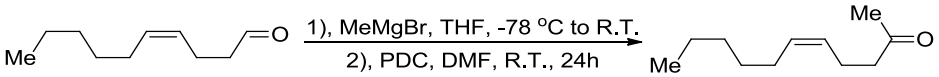
Experimental section

General Remarks:

All manipulations were conducted using Schlenk techniques .^{1}H-NMR spectra were obtained at 300 MHz, or 500 MHz, chemical shifts are reported in ppm, and referenced to the tetramethylsilane (δ = 0 ppm). ^{13}C-NMR spectra were obtained at 75 MHz, or 125 MHz and referenced to $CDCl_3$ (δ = 77.00 ppm). IR spectra were recorded using a Thermo Nicolet FT-IR. High resolution mass spectrometry (HRMS) data were obtained on a Waters LCP Premier XE instrument by ESI/TOF. SFC (supercritical fluid chromatography) analysis was performed at 40 ^{o}C, using a Thar instrument fitted with a S2 chiral stationary phase as indicated. Optical rotations were measured (Na D line) on a Perkin Elmer Model 343 Polarimeter fitted with a micro cell with a 1 dm path length; concentrations are reported in g/100 mL. Dry DMA were purchased from Aldrich and stored over activated 3 Å molecular sieves (3 Å MS). Powdered 3 Å MS were activated by flowing N_2 through a glass tube of sieves maintained at 200 °C. Alkene substrates were purchased from Aldrich, TCI or Acros, or synthesized according to the procedures outlined below. Alkyne precursors to alkene substrates were purchased from Aldrich. $Pd(CH_3CN)_2(OTs)_2$ was synthesized according to the literature procedure.[1]The ligand was synthesized according to the literature procedure.[2]

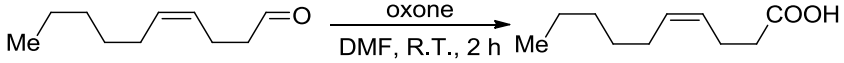
Synthesis of alkene substrates

1) Preparation of (*Z*)-undec-5-en-2-one:



Procedure: (*Z*)-dec-4-enal (10 mmol, 1.54g) and THF (50 mL) mixed in a dry round bottom flask. After coolingto-78^{o}C, MeMgBr (11 mmol, 3M in THF) was addeddropwise. This reaction mixture was allowed to warm to room temperature and stirred overnight. To this mixture, 1mL methanol was added. After removing the organic solvent, DMF (50 mL) and pyridinium dichromate (50 mmol, 18.81g) were added. This reaction mixture was stirredat room temperature overnight. The mixture was diluted with EtOAc (100 mL) and water (50 mL). The aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were washed with brine (50 mL), and dried over sodium sulfate. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatographyto afford (*Z*)-undec-5-en-2-one 1.48g (yield = 88%). Rf = 0.9 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.43-5.38 (m, 1H), 5.33-5.28 (m, 1H), 2.48 (t, *J* = 7.5 Hz, 2H), 2.31 (q, *J* = 7.5 Hz, 2H), 2.15 (s, 3H), 2.03 (q, *J* = 7.5 Hz, 2H), 1.36-1.27 (m, 6H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 208.5, 131.3, 127.5, 43.6, 31.5, 29.9, 29.3, 27.1, 22.6, 21.7, 14.0 ppm; IR (neat): ν = 2957, 2927, 2857, 1719, 1361, 1160 cm^{-1}; HRMS m/z (ESI) calcd for $C_{11}H_{21}O$ $(M + H)^{+}$ 169.1592, found 169.1597.

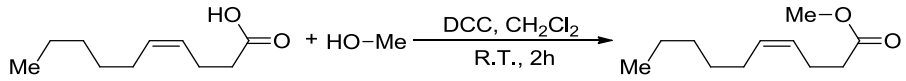
2) Preparation of (*Z*)-dec-4-enoic acid:



Procedure: (*Z*)-dec-4-enal (10 mmol, 1.54g), monopersulfate compound (20 mmol, 6.15g) and

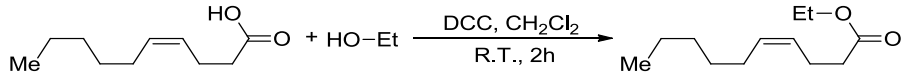
DMF (50 mL) were combined in a dry round bottom flask. This reaction mixture was stirred at room temperature for 2 h. The mixture was diluted with EtOAc (100 mL) and water (50 mL). The aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were washed with brine (50 mL), and dried over sodium sulfate. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography to afford (*Z*)-dec-4-enoic acid 748.4 mg (yield% = 44%). Rf = 0.3 (V_{Hexane}:$V_{ethyl\ acetate}$ = 2:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 11.28 (brs, 1H), 5.44 (dd, J_1 = 15 Hz, J_2 = 10 Hz, 1H), 5.34 (dd, J_1 = 15 Hz, J_2 = 10 Hz, 1H), 2.41-2.36 (m, 4H), 2.04 (dd, J_1 = 15 Hz, J_2 = 5 Hz, 2H), 1.37-1.26 (m, 6H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 179.7, 131.9, 126.9, 34.2, 31.5, 29.3, 27.2, 22.6, 22.5, 14.0 ppm; IR (neat): ν = 3008, 2957, 2925, 2857, 1710, 1412, 1279, 1211 cm^{-1}; HRMS m/z (ESI) calcd for $C_{10}H_{18}O_2Na$ $(M + Na)^+$ 193.1204, found 193.1213.

3) Preparation of (*Z*)-methyl dec-4-enoate:



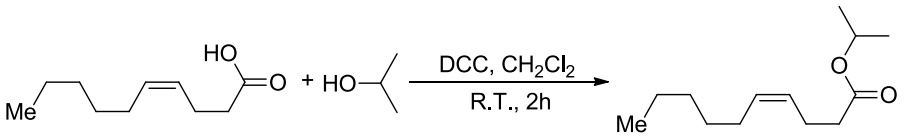
Procedure: (*Z*)-dec-4-enoic acid (5mmol, 851 mg), N,N-dicyclohexylcarbodiimide (5.5mmol, 1134 mg), methanol (5.5 mmol, 176 mg) and DCM (30 mL) were combined in a dry round bottom flask. This reaction mixture was stirred at room temperature for 3 h. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography to afford (*Z*)-methyl dec-4-enoate 875 mg (yield = 95%). Rf = 0.9 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.42 (dd, J_1 = 17.5, J_2 = 7.5 Hz, 1H), 5.37-5.31 (m, 1H), 3.67 (s, 3H), 2.38-2.32 (m, 4H), 2.05 (t, J = 7.5 Hz, 2H), 1.34-1.29 (m, 6H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 173.7, 131.6, 127.2, 51.5, 34.2, 31.5, 29.3, 27.1, 22.8, 22.6, 14.0 ppm; IR (neat): ν = 2954, 2925, 2856, 1740, 1436, 1195, 1162 cm^{-1}; HRMS m/z (ESI) calcd for $C_{11}H_{20}O_2Na$ $(M + Na)^+$ 207.1361, found 207.1366.

4) Preparation of (*Z*)-ethyl dec-4-enoate:



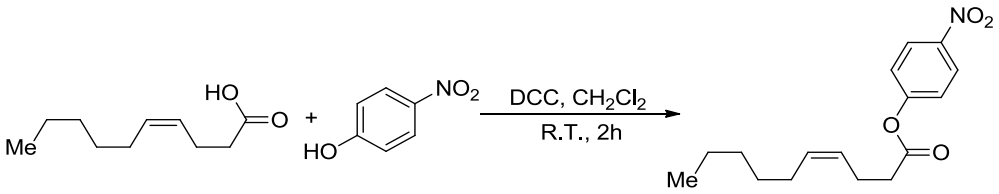
Procedure: (*Z*)-dec-4-enoic acid (5 mmol, 851 mg), N,N-dicyclohexylcarbodiimide (5.5 mmol, 1134 mg), ethanol (5.5 mmol, 253 mg) and DCM (30 mL) were combined in a dry round bottom flask. This reaction mixture was stirred at room temperature for 3 h. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography to afford (*Z*)-ethyl dec-4-enoate 942 mg (yield = 95%). Rf = 0.9 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.42 (dd, J_1= 17.5 Hz, J_2 = 7.5 Hz, 1H), 5.32 (dd, J_1 = 15Hz, J_2 = 7.5 Hz, 1H), 4.13 (q, J = 5 Hz, 2H), 2.38-2.32 (m, 4H), 2.04 (dd, J_1 = 15 Hz, J_2 = 5 Hz, 2H), 1.28-1.24 (m, 9H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 173.2, 131.5, 127.3, 60.3, 34.4, 31.5, 29.3, 27.1, 22.8, 22.5, 14.2, 14.0 ppm; IR (neat): ν = 2957, 2926, 2857, 1736, 1461, 1371, 1160 cm^{-1}; HRMS m/z (ESI) calcd for $C_{12}H_{22}O_2Na$ $(M + Na)^+$ 221.1517, found 221.1520.

5) Preparation of (*Z*)-isopropyl dec-4-enoate:



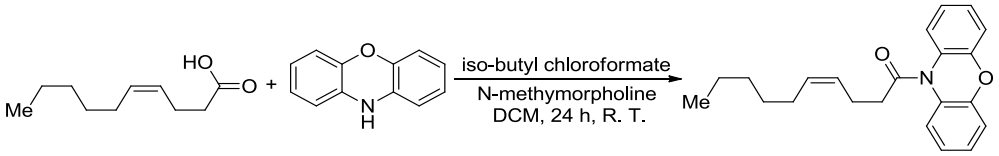
Procedure: (*Z*)-dec-4-enoic acid (5 mmol, 851 mg), N,N-dicyclohexylcarbodiimide (5.5 mmol, 1134 mg), propan-2-ol (5.5 mmol, 330 mg) and DCM (30 mL) were combined in a dry round bottom flask. This reaction mixture was stirred at room temperature for 3 h. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography to afford (*Z*)-isopropyl dec-4-enoate 1019 mg (yield = 96%). Rf = 0.9 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.44-5.39 (m, 1H), 5.35-5.30 (m, 1H), 5.03-4.98 (m, 1H), 2.36-2.29 (m, 4H), 2.06-2.02 (m, 2H), 1.33-1.22 (m, 12H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 173.0, 131.4, 127.4, 67.5, 34.7, 31.5, 29.3, 27.2, 22.9, 22.6, 21.9, 14.1 ppm; IR (neat): ν = 2957, 2925, 2857, 1732, 1373, 1167, 1108 cm^{-1}; HRMS m/z (ESI) calcd for $C_{13}H_{24}O_2Na$ $(M + Na)^+$ 235.1674, found 235.1679.

6) Preparation of(*Z*)-4-nitrophenyl dec-4-enoate:



Procedure: (*Z*)-dec-4-enoic acid (5 mmol, 851 mg), N,N-dicyclohexylcarbodiimide (5.5 mmol, 1134 mg), 4-nitrophenol (5.5 mmol, 765 mg) and DCM (30 mL) were combined in a dry round bottom flask. This reaction mixture was stirred at room temperature for 3 h. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography to afford (*Z*)-4-nitrophenyl dec-4-enoate1355 mg (yield = 93%). Rf = 0.2 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.27 (dt, J_1 = 10 Hz, J_2 = 2.5 Hz, 2H), 7.28 (dt, J_1 = 10 Hz, J_2 = 2.5 Hz, 2H), 5.51 (dd, J_1 = 20 Hz, J_2 = 5 Hz, 1H), 5.40 (dd, J_1 = 17.5 Hz, J_2 = 7.5 Hz, 1H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.50 (q, *J* = 5 Hz, 2H), 2.1-2.05 (m, 2H), 1.35-1.26 (m, 6H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.7, 155.5, 145.3, 132.4, 126.4, 125.2, 122.4, 34.4, 31.5, 29.2, 27.2, 22.6, 22.5, 14.0 ppm; IR (neat): ν = 2956, 2925, 1765, 1523, 1345, 1105 cm^{-1}; HRMS m/z (ESI) calcd for $C_{16}H_{21}NO_4Na$ $(M + Na)^+$ 314.1368, found 314.1370.

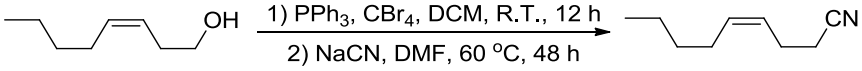
7) Preparation of (*Z*)-1-(10H-phenoxazin-10-yl) dec-4-en-1-one:



Procedure: (*Z*)-dec-4-enoic acid (3.2 mmol, 555 mg), *N*-methylmorpholine (4.0 mmol, 404 mg) and DCM (50 mL) were combined in a dry round bottom flask at 0 ^{o}C followed by the addition of *iso*-butyl chloroformate (4.0 mmol, 546.4 mg). This reaction mixture was stirred at 0 ^{o}C for 0.5 h. To this, 10H-phenoxazine (4.0 mmol, 732.8 mg) was added and stirred for 12 h. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica

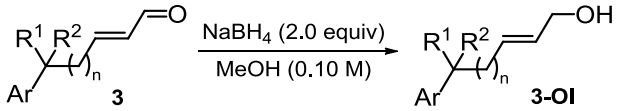
gel chromatography to afford (*Z*)-1-(10H-phenoxazin-10-yl)dec-4-en-1-one 773 mg (yield% = 72%). Rf = 0.3 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.50-7.47 (m, 2H), 7.25-7.17 (m, 2H), 7.13-7.10 (m, 4H), 5.41-5.28 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.40 (q, *J* = 6.3 Hz, 2H), 1.98 (q, *J* = 6.3 Hz, 2H) 1.32-1.19 (m, 6H), 0.86 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.7, 151.2, 131.6, 129.4, 127.4, 126.8, 125.2, 123.3, 116.9, 34.3, 31.4, 29.2, 27.1, 23.2, 22.5, 14.0 ppm; IR (neat): ν = 2955, 2925, 1681, 1480, 1265, 751 cm^{-1}; HRMS m/z (ESI) calcd for $C_{22}H_{25}NO_2Na$ $(M + Na)^+$ 358.1783, found 358.1787.

8) Preparation of (*Z*)-non-4-enenitrile:



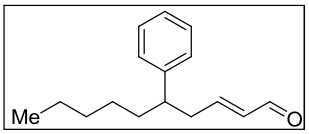
Procedure: The first step: (*Z*)-oct-3-en-1-ol (10 mmol, 1.28 g), PPh_3 (11 mmol, 2.89 g), CBr_4 (11 mmol, 3.65 g) and DCM (50 mL) were combined in a dry round bottom flask. This reaction mixture was stirred at room temperature for 12 h. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography to afford (*Z*)-1-bromooct-3-ene 1.72g (yield = 90%). The second step: (*Z*)-1-bromooct-3-ene (5.23 mmol, 1g), NaCN (15.7 mmol, 1.02 g) and DMF (30 mL) were combined in a dry round bottom flask. This reaction mixture was stirred at 60 °C for 2 h. The mixture was diluted with EtOAc (100 mL) and water (50 mL). The aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were washed with brine (50 mL), and dried over sodium sulfate. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel chromatography to afford (*Z*)-non-4-enenitrile 0.51 g (yield = 71%). Rf = 0.9 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.61-5.52 (m, 1H), 5.40-5.32 (m, 1H), 2.44-2.35 (m, 4H), 2.07-2.05 (m, 2H), 1.36-1.30 (m, 4H), 0.94-0.88 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ =133.7, 124.8, 119.4, 31.6, 27.0, 23.2, 22.3, 17.6, 13.9 ppm; IR (neat): ν = 2957, 2928, 2246, 1457, 1427, 719 cm^{-1}; HRMS m/z (ESI) calcd for $C_9H_{15}NNa$ $(M + Na)^+$ 160.1102, found 160.1111.

General procedure of reduction (used in some cases for chiral separations)

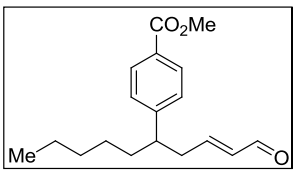


The aldehyde product was dissolved in MeOH (0.1 M) in a 20 mL scintillation vial equipped with a stir bar. The mixture was cooled to 0 °C. Sodium borohydride (2.0equiv) was added, and the resulting mixture was stirred for 30 min. The solvent was removed under reduced pressure, and the resulting residue was transferred to a separatory funnel using diethyl ether (100 mL) and water (20 mL). The aqueous layer was extracted with diethyl ether (2 x 50 mL), and the combined organic layers were washed with water (20 mL), and brine (20 mL). The organic layer was then dried over sodium sulfate, and concentrated under reduced pressure. The resulting mixture was purified using silica gel flash chromatography with 10–20% EtOAc in hexanes as the eluent to give the alcohol product.

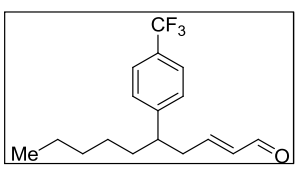
Analytical data for product:



1) (*E*)-5-phenyldec-2-enal (**3a**): Typical procedure: $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), 3Å MS (50 mg), and DMA (3 mL) were combined and placed under O_2 (1 atm).The resulting mixture was stirred for 15 min. To this, (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv) and phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv) were added. The resulting mixture was stirred for 24 h at room temperature. The mixture was diluted with diethyl ether (100 mL) and water (25 mL). The aqueous layer was extracted with diethyl ether (2 x 25 mL). The combined organic layers were washed with brine (1 x 10 mL), and dried over sodium sulfate. The organic extracts were concentrated under reduced pressure, and the resulting residue was purified by silica gel flash chromatography using 1% EtOAc in hexanes to afford 45.0mg **3a** (78% yield) with 99:1 er value. The regioselectivity of **3a**:**4a** was 15:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction).**3a**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.41 (d, *J* = 9.0 Hz, 1H), 7.35-7.21 (m, 3H), 7.16 (d, *J* = 9.0 Hz, 2H), 6.70-6.64 (m, 1H), 6.10-6.00 (m, 1H), 2.80-2.60 (m, 3H), 1.68-1.63 (m, 2H), 1.28-1.19 (m, 6H), 0.86-0.80 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.0, 157.0, 134.0, 128.5, 127.4, 126.5, 45.2, 40.0, 36.4, 31.8, 27.0, 22.5, 14.0 ppm; IR (neat): ν = 3027, 2927, 2856, 1690, 1453, 700 cm^{-1}; HRMS m/z (ESI) calcd for $C_{16}H_{22}ONa$ $(M + Na)^+$ 253.1568, found 253.1563; $[\alpha]_D^{20}$ = -19 (c = 0.1, $CHCl_3$).

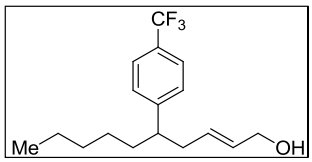


2) (*E*)-methyl 4-(1-oxodec-2-en-5-yl)benzoate (**3b**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6mg, 0.25 mmol, 1.0 equiv), (4-(methoxycarbonyl)phenyl)boronic acid (134.9mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 40.0mg **3b** (55% yield) with 97:3 er value. The regioselectivity of **3b**:**4b** was more than 30:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3b**: Light yellow liquid; Rf = 0.2 (V_{Hexane}:$V_{ethyl\ acetate}$ = 5:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.39 (d, *J* = 9.0 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 2H), 7.23 (d, *J* = 9.0 Hz, 2H), 6.70-6.57 (m, 1H), 6.07-5.99 (m, 1H), 3.91 (s, 3H), 2.84-2.56 (m, 3H), 1.72-1.64 (m, 2H), 1.26-1.16 (m, 6H), 0.83 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 193.7, 166.9, 155.9, 149.4, 134.2, 129.9, 128.5, 127.5, 52.0, 45.2, 39.6, 36.1, 31.6, 26.9, 22.4, 14.0 ppm; IR (neat): ν = 2954, 2928, 2857, 1720, 1691, 1279, 1112 cm^{-1}; HRMS m/z (ESI) calcd for $C_{18}H_{24}O_3Na$ $(M + Na)^+$ 311.1623, found 253.1622; $[\alpha]_D^{20}$ =-38(c = 0.1, $CHCl_3$).

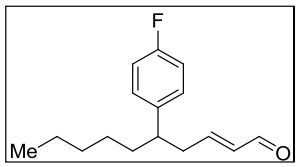


3) (*E*)-5-(4-(trifluoromethyl)phenyl)dec-2-enal (**3c**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazol (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6mg, 0.25 mmol, 1.0 equiv), (4-(trifluoromethyl)phenyl)boronic acid (142.4mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 36.0 mg **3c** (48% yield) with 95:5er value. The regioselectivity of **3c**:**4c** was more than 30:1 (Based on crude ^{1}H

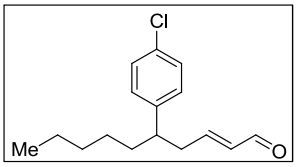
NMR (500 MHz) of this reaction). **3c**:Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.41 (d, *J* = 9.0 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 6.66-6.58 (m, 1H), 6.10-6.00 (m, 1H), 2.88-2.56 (m, 3H), 1.70-1.65 (m, 2H), 1.26-1.17 (m, 6H), 0.84 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 193.7, 155.7, 134.3, 127.8, 125.5 (q, *J* = 3.75 Hz), 45.1, 39.6, 36.2, 31.7, 26.9, 22.4, 14.0 ppm; IR (neat): ν = 2930, 2859, 1693, 1325, 1164, 1122, 1069, 838 cm^{-1}; HRMS m/z (ESI) calcd for $C_{17}H_{21}OF_3Na$ $(M + Na)^+$ 321.1442, found 321.1435; $[\alpha]_D^{20}$ =-19 (c = 0.1, $CHCl_3$).



3-ol) (*E*)-5-(4-(trifluoromethyl)phenyl)dec-2-en-1-ol (**3c-Ol**): Light yellow liquid; 95:5er value. Rf = 0.2 (V_{Hexane}:$V_{ethyl\ acetate}$ = 5:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54 (d, *J* = 5.0 Hz, 2H), 7.24 (d, *J* = 5.0 Hz, 2H), 5.61-5.47 (m, 2H), 4.01 (d, *J* = 10 Hz, 2H), 2.68-2.63 (m, 1H), 2.42-2.29 (m, 2H), 1.71-1.51 (m, 3H), 1.25-1.08 (m, 6H), 0.83 (t, *J* = 5.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 149.5, 130.9, 130.5, 127.97, 127.90, 125.2, (q, *J* = 3.75 Hz), 123.3, 63.5, 45.9, 39.4, 35.8, 31.8, 27.0, 22.5, 14.0 ppm; IR (neat): ν = 2928, 2858, 1618, 1325, 1163, 1123, 1069, 1018 cm^{-1}; HRMS m/z (ESI) calcd for $C_{17}H_{23}OF_3Na$ $(M + Na)^+$ 323.1599, found 323.1599; $[\alpha]_D^{20}$ = -0.013 (c = 0.1, EtOH).

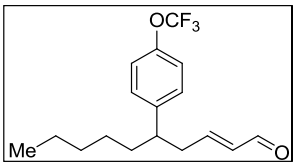


4) (*E*)-5-(4-fluorophenyl)dec-2-enal (**3d**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), (4-fluorophenyl)boronic acid (104.9 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 44.0 mg **3d** (71% yield) with less than 1:99er value. The regioselectivity of **3d**:**4d** was more than 30:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3d**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.39 (d, *J* = 6.0 Hz, 1H), 7.27-7.07 (m, 2H), 7.02-6.96 (m, 2H), 6.68-6.58 (m, 1H), 6.07-5.99 (m, 1H), 2.78-2.50 (m, 3H), 1.68-1.57 (m, 2H), 1.26-1.15 (m, 6H), 0.83 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 193.9, 156.5, 139.8, 134.1, 128.8 (d, *J* = 3.0 Hz), 115.5 (d, *J* = 6.0 Hz), 44.5, 40.1, 36.5, 31.7, 27.0, 22.5, 14.0 ppm; IR (neat): ν = 2928, 2857, 1691, 1509, 1223, 1159, 833 cm^{-1}; HRMS m/z (ESI) calcd for $C_{16}H_{21}OFNa$ $(M + Na)^+$ 271.1474, found 271.1484; $[\alpha]_D^{20}$ =-14 (c = 0.1, $CHCl_3$).

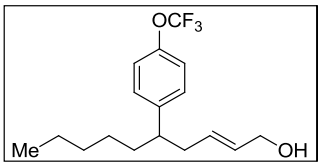


5) (*E*)-5-(4-chlorophenyl)dec-2-enal (**3e**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), (4-chlorophenyl)boronic acid (117.3 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 42.4 mg **3e** (64% yield) with more than 98:2 er value. The regioselectivity of **3e**:**4e**was more than 30:1 (Based on crude^1 H NMR (500 MHz) of this reaction). **3e**:Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.40 (d, *J* = 9.0 Hz, 1H), 7.30-7.26 (m, 2H), 7.10-7.06 (m, 2H), 6.62-6.59 (m, 1H), 6.07-5.99 (m, 1H), 2.73-2.55 (m, 3H), 1.67-1.58 (m, 2H), 1.25-1.16 (m, 6H), 0.83 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 193.8, 156.2, 142.4, 134.2, 132.1,

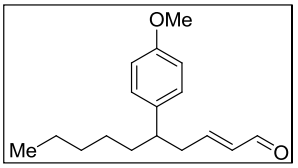
128.8, 128.7, 44.6, 39.8, 36.3, 31.7, 26.9, 22.5, 14.0 ppm; IR (neat): ν = 2927, 2856, 1691, 1491, 1092, 1014, 826 cm^{-1}; HRMS m/z (ESI) calcd for $C_{16}H_{21}OClNa$ $(M + Na)^+$287.1179, found 287.1180; $[\alpha]_D^{20}$ =-30 (c = 0.1, $CHCl_3$).



6) (*E*)-5-(4-(trifluoromethoxy)phenyl)dec-2-enal (**3f**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), (4-(trifluoromethoxy)phenyl)boronic acid (154.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 34.0 mg **3f** (43% yield) with more than 99:1 er value. The regioselectivity of **3f**:**4f** was12:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). For procedure with copper co-catalyst: $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), $Cu(OTf)_2$ (4.5 mg, 0.013mmol, 5mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (9.5 mg, 0.035 mmol, 14mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), (4-(trifluoromethoxy)phenyl)boronic acid (154.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 47.2 mg **3f** (60% yield) with 98:2er value. The regioselectivity of **3f**:**4f** was 11:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3f**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.41 (d, *J* = 6.0 Hz, 1H), 7.20-7.15 (m, 4H), 6.67-6.59 (m, 1H), 6.09-6.01 (m, 1H), 2.81-2.53 (m, 3H), 1.70-1.58 (m, 2H), 1.30-1.57 (m, 6H), 0.84 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 193.7, 156.0, 142.6, 134.2, 128.6, 121.0, 44.6, 39.8, 36.3, 31.7, 26.9, 22.4, 14.0 ppm; IR (neat): ν = 2939, 2858, 1693, 1509, 1257, 1222, 1164, 975 cm^{-1}; HRMS m/z (ESI) calcd for $C_{17}H_{21}O_2F_3Na$ $(M + Na)^+$337.1391, found 337.1398; $[\alpha]_D^{20}$ =-22 (c = 0.1, $CHCl_3$).

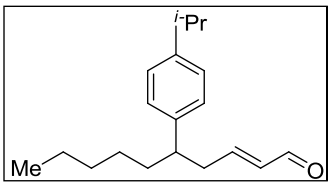


6-ol) (*E*)-5-(4-(trifluoromethoxy)phenyl)dec-2-en-1-ol (**3f-Ol**): Light yellow liquid; more than 99:1er value; Rf = 0.2 (V_{Hexane}:$V_{ethyl\ acetate}$ = 5:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.16-7.10 (m, 4H), 5.60-5.48 (m, 2H), 4.02 (d, *J* = 5.0 Hz, 2H), 2.63-2.57 (m, 1H), 2.39-2.26 (m, 2H), 1.68-1.49 (m, 3H), 1.24-1.12 (m, 6H), 0.83 (t, *J* = 5.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 144.0, 130.8, 130.7, 128.8, 120.7, 63.6, 45.4, 39.6, 36.0, 31.8, 27.0, 22.5, 14.0 ppm; IR (neat): ν = 2928, 2856, 1653, 1559, 1507, 1257, 1222, 669 cm^{-1}; HRMS m/z (ESI) calcd for $C_{17}H_{23}O_2F_3Na$ $(M + Na)^+$339.1548, found339.1533; $[\alpha]_D^{20}$ = -0.017 (c = 0.1, EtOH).

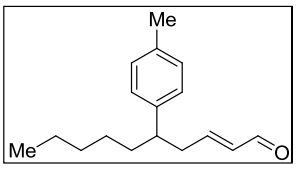


7) (*E*)-5-(4-methoxyphenyl)dec-2-enal (**3g**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), (4-methoxyphenyl)boronic acid (113.9 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 28.0 mg **3g** (43% yield) with 98:2 er value. The regioselectivity of **3g**:**4g** was9.1:1 (Based on crude^{1}H NMR (500 MHz) of this reaction). **3g**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 5:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.39 (d, *J* = 9.0 Hz, 1H), 7.06 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.70-6.60

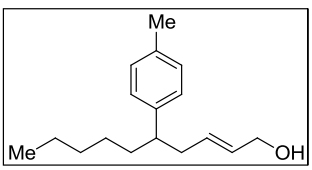
(m, 1H), 6.07-5.99 (m, 1H), 3.80 (s, 3H), 2.70-2.55 (m, 3H), 1.64-1.59 (m, 2H), 1.25-1.17 (m, 6H), 0.83 (t, *J* = 9.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.0, 158.1, 157.2, 135.9, 133.9, 128.3, 113.9, 55.2, 44.4, 40.2, 36.5, 31.8, 27.0, 22.5, 14.0 ppm; IR (neat): ν = 2926, 2855, 1688, 1511, 1245, 1177, 1036, 829 cm^{-1}; HRMS m/z (ESI) calcd for $C_{17}H_{24}O_2Na$ $(M + Na)^+$ 283.1674, found 283.1678; $[\alpha]_D^{20}$ =-36 (c = 0.1, $CHCl_3$).



8) (*E*)-5-(4-isopropylphenyl)dec-2-enal (**3h**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), (4-isopropylphenyl)boronic acid (123.0 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 37.0 mg **3h** (54% yield) with 95:5er value. The regioselectivity of **3h**:**4h** was14:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3h**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.40 (d, *J* = 9.0 Hz, 1H), 7.18-7.12 (m, 2H), 7.07-7.02 (m, 2H), 6.72-6.63 (m, 1H), 6.09-5.99 (m, 1H), 2.93-2.56 (m, 4H), 1.63-1.59 (m, 2H), 1.27-1.22 (m, 12H), 0.83 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.1, 157.3, 146.9, 141.2, 133.9, 127.2, 126.5, 44.7, 40.0, 36.3, 33.6, 31.8, 27.0, 24.0, 22.5, 14.0 ppm; IR (neat): ν = 2958, 2927, 2858, 1693, 1508, 1458, 1135, 974, 668 cm^{-1}; HRMS m/z (ESI) calcd for $C_{19}H_{28}ONa$ $(M + Na)^+$ 295.2038, found 295.2040; $[\alpha]_D^{20}$ =-21 (c = 0.1, $CHCl_3$).

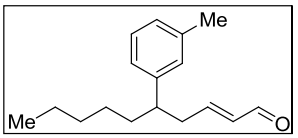


9) (*E*)-5-(*p*-tolyl)dec-2-enal (**3i**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), *p*-tolylboronic acid (102.0 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 49.0 mg **3i** (80% yield) with 98:2er value. The regioselectivity of **3i**:**4i** was19:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3i**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.39 (d, *J* = 9.0 Hz, 1H), 7.12 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 6.0 Hz, 2H), 6.71-6.61 (m, 1H), 6.08-6.00 (m, 1H), 2.75-2.60 (m, 3H), 2.33 (s, 3H), 1.63-1.57 (m, 2H), 1.25-1.18 (m, 6H), 0.83 (t, *J* = 9.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.1, 157.2, 140.8, 136.0, 133.9, 129.2, 127.3, 44.8, 40.1, 36.4, 31.8, 27.0, 22.5, 21.0, 14.0 ppm; IR (neat): ν = 2926, 2857, 1724, 1692, 1514, 1457, 975, 816 cm^{-1}; HRMS m/z (ESI) calcd for $C_{17}H_{24}ONa$ $(M + Na)^+$267.1725, found 267.1730; $[\alpha]_D^{20}$ = -19 (c = 0.1, $CHCl_3$).

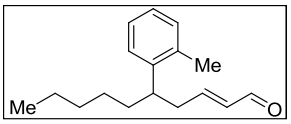


9-ol) (*E*)-5-(p-tolyl)dec-2-en-1-ol (**3i-Ol**): Light yellow liquid;98:2er value; Rf = 0.2 (V_{Hexane}:$V_{ethyl\ acetate}$ = 5:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.09 (d, *J* = 5.0 Hz, 2H), 7.02 (d, *J* = 5.0 Hz, 2H), 5.60-5.50 (m, 2H), 4.00 (d, *J* = 5.0 Hz, 2H), 2.56-2.50 (m, 1H), 2.36-2.26 (m, 5H), 1.65-1.48 (m, 3H), 1.24-1.11 (m, 6H), 0.83 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 142.3, 135.3, 131.7, 130.2, 128.9, 127.5, 63.7, 45.5, 39.7, 36.0, 31.9, 27.1, 22.5, 21.0, 14.1 ppm; IR (neat): ν = 2925, 2861, 1621, 1507, 1270, 814, 668 cm^{-1}; HRMS m/z (ESI) calcd for $C_{17}H_{26}ONa$ $(M + Na)^+$ 269.1881, found 269.1879;

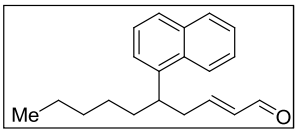
$[\alpha]_D^{20}$ = -0.016 (c = 0.1, EtOH).



10) (*E*)-5-(*m*-tolyl)dec-2-enal (**3j**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), *m*-tolylboronic acid (102.0 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 40.0 mg **3j** (65% yield) with lower than 1:99 er value. The regioselectivity of **3j**:**4j**was9.3:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3j**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.40 (d, *J* = 9.0 Hz, 1H), 7.22-7.17 (m, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.95-6.93 (m, 2H), 6.71-6.61 (m, 1H), 6.10-6.01 (m, 1H), 2.71-2.58 (m, 3H), 2.34 (s, 3H), 1.66-1.58 (m, 2H), 1.25-1.22 (m, 6H), 0.84 (t, *J* = 9.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.0, 157.1, 143.9, 138.0, 133.9, 128.3, 128.2, 127.2, 124.4, 45.1, 40.0, 36.4, 31.8, 27.0, 22.5, 21.5, 14.0 ppm; IR (neat): ν = 2926, 2856, 1718, 1692, 1606, 1457, 974, 784, 784, 705 cm^{-1}; HRMS m/z (ESI) calcd for $C_{17}H_{24}ONa$ $(M + Na)^+$ 267.1725, found 267.1724; $[\alpha]_D^{20}$ = -18 (c = 0.1, $CHCl_3$).

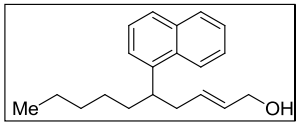


11) (*E*)-5-(o-tolyl)dec-2-enal (**3ka**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), *o*-tolylboronic acid (102.0 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 37.0 mg **3k** (60% yield) with 3:97 er value. The regioselectivity of **3k**:**4k** was 21:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3k**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.40 (d, *J* = 9.0 Hz, 1H), 7.20-7.08 (m, 4H), 6.68-6.63 (m, 1H), 6.09-6.01 (m, 1H), 3.12-3.03 (m, 1H), 2.70-2.55 (m, 2H), 2.30 (s, 3H), 1.68-1.64 (m, 2H), 1.26-1.22 (m, 6H), 0.83 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 193.9, 156.9, 142.2, 135.8, 134.0, 130.4, 126.3, 126.0, 125.5, 39.6, 39.4, 36.1, 31.9, 26.9, 22.5, 19.9, 14.0 ppm; IR (neat): ν = 2927, 2856, 1724, 1692, 1490, 1459, 974, 758, 728 cm^{-1}; HRMS m/z (ESI) calcd for $C_{17}H_{24}ONa$ $(M + Na)^+$ 267.1725, found 267.1728; $[\alpha]_D^{20}$ = -4 (c = 0.1, $CHCl_3$).

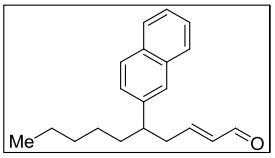


12) (*E*)-5-(naphthalen-1-yl)dec-2-enal (**3l**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), naphthalen-1-ylboronic acid (129.0 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 29.0 mg **3l** (41% yield) with 4:96 er value. The regioselectivity of **3l**:**4l** is more than 30:1 (Based on crude^{1}H NMR (500 MHz) of this reaction). For procedure with copper co-catalyst: $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), $Cu(OTf)_2$ (4.5 mg, 0.013mmol, 5mol%), (*S*)-4-(tert- butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (9.5 mg, 0.035 mmol, 14mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), (4-(trifluoromethoxy)phenyl)boronic acid (154.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) were combined under O_2 (1 atm) for 24 h. Afforded 39.1 mg **3l** (56%

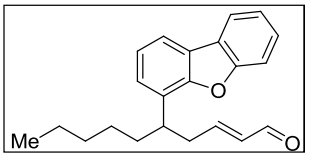
yield) with 4:96 er value. The regioselectivity of **3l**:**4l** was more than 30:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3l**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.33 (d, *J* = 6.0 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 6.0 Hz, 1H), 7.53-7.47 (m, 3H), 7.37 (d, *J* = 6.0 Hz, 1H), 6.70-6.63 (m, 1H), 6.12-6.04 (m, 1H), 3.73 (t, *J* = 6.0 Hz, 1H), 2.81 (t, *J* = 6.0 Hz, 2H), 1.86-1.79 (m, 2H), 1.25-1.19 (m, 6H), 0.82 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 193.9, 156.8, 139.9, 134.1, 132.0, 129.1, 126.9, 126.0, 125.5, 122.7, 39.4, 35.8, 31.9, 27.0, 22.5, 14.0 ppm; IR (neat): ν = 2928, 2856, 1690, 1136, 974, 798, 778 cm^{-1}; HRMS m/z (ESI) calcd for $C_{20}H_{24}ONa$ (M + Na)$^+$303.1725, found 303.1734; $[\alpha]_D^{20}$ = +45 (c = 0.1, $CHCl_3$).



12-ol) (*E*)-5-(naphthalen-1-yl)dec-2-en-1-ol (**3l-Ol**): Light yellow liquid; 4:96 er value; Rf = 0.2 (V_{Hexane}:$V_{ethyl\ acetate}$ = 5:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.11 (d, *J* = 10 Hz, 1H), 7.86 (d, *J* = 10.0, 1H), 7.71 (d, *J* = 5.0 Hz, 1H), 7.51-7.44 (m, 3H), 7.36 (d, *J* = 10.0 Hz, 1H), 5.58-5.56 (m, 2H), 3.94 (t, *J* = 4.0 Hz, 2H), 3.58-3.52 (m, 1H), 2.51-2.49 (m, 2H), 1.82-1.74 (m, 3H), 1.25-1.18 (m, 6H), 0.81 (t, *J* = 5.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 141.4, 133.9, 132.3, 131.4, 130.5, 129.0, 126.3, 125.6, 125.5, 125.2, 123.2, 63.6, 39.1, 35.4, 32.1, 27.1, 22.5, 14.0 ppm; IR (neat): ν = 2927, 2856, 1508, 1457, 1396, 969, 778, 668 cm^{-1}; HRMS m/z (ESI) calcd for $C_{20}H_{26}ONa$ (M + Na)$^+$305.1881, found 305.1879; $[\alpha]_D^{20}$ = +0.010 (c = 0.1, EtOH).

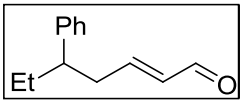


13) (*E*)-5-(naphthalen-2-yl)dec-2-enal (**3m**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), naphthalen-2-ylboronic acid (129.0 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 35.0 mg **3m** (50% yield) with 98:2 er value. The regioselectivity of **3m**:**4m** was 14:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3m**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.35 (d, *J* = 6.0 Hz, 1H), 7.82-7.77 (m, 3H), 7.57 (s, 1H), 7.48-7.43 (m, 2H), 7.33-7.31 (m, 1H), 6.68-6.63 (m, 1H), 6.10-6.02 (m, 1H), 2.95-2.85 (m, 1H), 2.74-2.69 (m, 2H), 1.73 (q, *J* = 6.0 Hz, 2H), 1.25-1.22 (m, 6H), 0.82 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 193.9, 156.8, 141.3, 134.0, 133.4, 132.4, 128.3, 127.6, 127.5, 126.2, 126.1, 125.5, 125.4, 45.4, 39.9, 36.3, 31.7, 27.1, 22.5, 14.0 ppm; IR (neat): ν = 2926, 2855, 1688, 1635, 1507, 1126, 974, 818, 747 cm^{-1}; HRMS m/z (ESI) calcd for $C_{20}H_{24}ONa$ (M + Na)$^+$ 303.1725, found 303.1731; $[\alpha]_D^{20}$ = -25 (c = 0.1, $CHCl_3$).

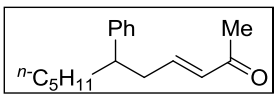


14) (*E*)-5-(dibenzo[*b*,*d*]furan-4-yl)dec-2-enal (**3n**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enal (38.6 mg, 0.25 mmol, 1.0 equiv), dibenzo[*b*,*d*]furan-4-ylboronic acid (159.0 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 40.0 mg **3n** (50% yield) with more than 99:1er value. The regioselectivity of **3n**:**4n** was more than30:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3n**: Light yellow liquid; Rf = 0.2 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H

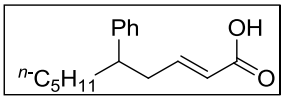
NMR ($CDCl_3$, 300 MHz): δ = 9.44 (m, 1H), 7.97-7.94 (m, 1H), 7.84-7.81 (m, 1H), 7.60-7.57 (m, 1H), 7.46 (t, *J* = 6.0 Hz, 1H), 7.37-7.22 (m, 3H), 6.77-6.67 (m, 1H), 6.10-6.02 (m, 1H), 3.44-3.38 (m, 1H), 2.95-2.82 (m, 2H), 1.94-1.78 (m, 2H), 1.30-1.16 (m, 6H), 0.81 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.0, 156.9, 154.4, 134.0, 127.9, 127.1, 125.7, 124.4, 122.9, 122.7, 120.7, 118.7, 111.7, 39.9, 38.6, 34.9, 31.7, 27.2, 22.5, 14.0 ppm; IR (neat): ν = 2928, 2856, 1691, 1451, 1422, 1185, 753 cm^{-1}; HRMS m/z (ESI) calcd for $C_{22}H_{24}O_2Na$ $(M + Na)^+$ 343.1674, found 343.1676; $[\alpha]_D^{20}$ = +10 (c = 0.1, $CHCl_3$).



15) (*E*)-5-phenylhept-2-enal (**3o**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-hept-4-enal (28.0 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 23.5 mg **3o** (50% yield) with 2:98 er value. The regioselectivity of **3o**:**4o** was 6.1:1 (Based on crude ^1H NMR (500 MHz) of this reaction). **3o**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^1H NMR ($CDCl_3$, 500 MHz): δ = 9.39 (d, *J* = 10.0 Hz, 1H), 7.32-7.26 (m, 2H), 7.22 (t, *J* = 10.0 Hz, 1H), 7.15 (d, *J* = 5.0 Hz, 2H), 6.69-6.66 (m, 1H), 6.07-6.02 (m, 1H), 2.70-2.60 (m, 3H), 1.73-1.61 (m, 2H), 0.81 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 193.9, 156.8, 143.6, 134.0, 128.5, 127.5, 126.5, 46.9, 39.6, 29.3, 11.9 ppm; IR (neat): ν = 2960, 2927, 1722, 1689, 1494, 1453, 760, 700 cm^{-1}; HRMS m/z (ESI) calcd for $C_{13}H_{16}ONa$ $(M + Na)^+$211.1099, found 211.1104; $[\alpha]_D^{20}$ = -30 (c = 0.1, $CHCl_3$).

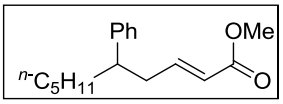


16) (*E*)-6-phenylundec-3-en-2-one (**3p**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-undec-5-en-2-one (42.1 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 42.6 mg **3p** (70% yield) with 98:2er value. The regioselectivity of **3p**:**4p** was 11:1 (Based on crude ^1H NMR (500 MHz) of this reaction). **3p**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.31-7.25 (m, 2H), 7.21-7.18 (m, 1H), 7.15-7.11 (m, 2H), 6.67-6.57 (m, 1H), 5.99 (d, *J* = 15.0 Hz, 1H), 2.74-2.63 (m, 1H), 2.54-2.47 (m, 2H), 2.14 (s, 3H), 1.66-1.60 (m, 2H), 1.26-1.13 (m, 6H), 0.83 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 198.5, 146.6, 144.2, 132.3, 128.4, 127.4, 126.3, 45.3, 39.9, 36.1, 31.7, 27.0, 27.7, 22.4, 14.0 ppm; IR (neat): ν = 2955, 2926, 2856, 1699, 1675, 1627, 1361, 1252, 979, 700 cm^{-1}; HRMS m/z (ESI) calcd for $C_{17}H_{24}ONa$ $(M + Na)^+$267.1725, found 267.1730; $[\alpha]_D^{20}$ = -14 (c = 0.1, $CHCl_3$).

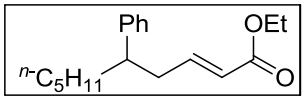


17) (*E*)-5-phenyldec-2-enoic acid (**3q**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-4-enoic acid (42.5 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 37.4 mg **3q** (61% yield) with 97:3 er value. The regioselectivity of **3q**:**4q** was 7.9:1 (Based on crude ^1H NMR (500 MHz) of this reaction). **3q**: Light yellow liquid; Rf = 0.4

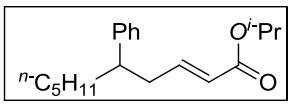
(V_{Hexane}:$V_{ethyl\ acetate}$ = 2:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 11.0 (brs, 1H), 7.30-7.26 (m, 2H), 7.21-7.12 (m, 3H), 6.95-6.89 (m, 1H), 5.74 (d, *J* = 15.0 Hz, 1H), 2.72-2.66 (m, 1H), 2.55-2.47 (m, 2H), 1.67-1.60 (m, 2H), 1.25-1.19 (m, 6H), 0.84 (t, *J* = 12.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 150.4, 144.3, 128.5, 127.5, 126.4, 121.7, 45.1, 39.8, 36.1, 31.8, 27.0, 22.5, 14.0 ppm; IR (neat): ν = 2926, 2856, 1701, 1650, 1452, 1285, 760, 699 cm^{-1}; HRMS m/z (ESI) calcd for $C_{16}H_{22}O_2Na$ $(M + Na)^+$269.1517, found 269.1511; $[\alpha]_D^{20}$ = -16 (c = 0.1, $CHCl_3$).



18) (*E*)-methyl 5-phenyldec-2-enoate (**3r**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-methyl dec-4-enoate (46.0 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 39.0 mg **3r** (60% yield) with 95:5 er value. The regioselectivity of **3r**:**4r** was 9.4:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3r**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.30-7.25 (m, 2H), 7.20-7.12 (m, 3H), 6.83 (dt, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 1H), 5.76 (dt, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 1H), 3.68 (s, 3H), 2.70-2.65 (m, 1H), 2.50-2.47 (m, 2H), 1.64-1.58 (m, 2H), 1.27-1.21 (m, 6H), 0.82 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.9, 147.8, 144.4, 128.4, 127.5, 126.3, 122.1, 51.3, 45.2, 39.7, 36.1, 31.8, 27.0, 22.5, 14.0 ppm; IR (neat): ν = 2953, 2927, 2857, 1726, 1453, 1435, 1273, 1161, 760, 700 cm^{-1}; HRMS m/z (ESI) calcd for $C_{17}H_{24}O_2Na$ $(M + Na)^+$283.1674, found 283.1672; $[\alpha]_D^{20}$ = -18 (c = 0.1, $CHCl_3$).

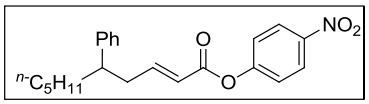


19) (*E*)-ethyl 5-phenyldec-2-enoate (**3s**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-ethyl dec-4-enoate (49.6 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 42.0 mg **3s** (61% yield) with 96:4 er value. The regioselectivity of **3s**:**4s** was 8.5:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3s**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.28 (dd, J_1 = 15.0 Hz, J_2 = 10.0 Hz, 2H), 7.20-7.13 (m, 3H), 6.86-6.80 (m, 1H), 5.77-5.74 (m, 1H), 4.14 (q, *J* = 5.0 Hz, 2H), 2.71-2.65 (m, 1H), 2.50-2.46 (m, 2H), 1.67-1.58 (m, 2H), 1.26-1.22 (m, 9H), 0.82 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.5, 147.4, 144.5, 128.4, 127.5, 126.2, 122.5, 60.1, 45.2, 39.7, 36.0, 31.8, 27.0, 22.5, 14.2, 14.0 ppm; IR (neat): ν = 2956, 2927, 2857, 1721, 1453, 1266, 1159, 1638, 700 cm^{-1}; HRMS m/z (ESI) calcd for $C_{18}H_{26}O_2Na$ $(M + Na)^+$ 297.1831, found 297.1829; $[\alpha]_D^{20}$ = -15 (c = 0.1, $CHCl_3$).

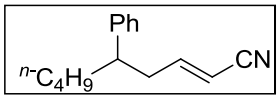


20) (*E*)-isopropyl 5-phenyldec-2-enoate (**3t**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-isopropyl dec-4-enoate (53.1 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 36.0 mg **3t** (50% yield) with 97:3er value. The regioselectivity of **3t**:**4t**was 7.0:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3t**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:V_{ethyl}

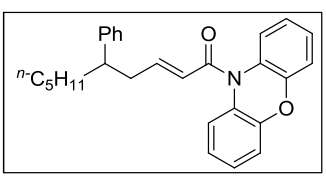
$_{acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.30-7.26 (m, 2H), 7.20-7.12 (m, 3H), 6.84-6.78 (m, 1H), 5.75-5.71 (m, 1H), 5.04-4.99 (m, 1H), 2.70-2.64 (m, 1H), 2.49-2.45 (m, 2H), 1.69-1.56 (m, 2H), 1.26-1.19 (m, 12H), 0.82 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.0, 147.1, 144.6, 128.4, 127.5, 126.2, 122.9, 67.3, 45.2, 39.7, 35.9, 31.8, 27.0, 22.5, 21.8, 14.0 ppm; IR (neat): ν = 2957, 2927, 2857, 1731, 1718, 1373, 1109, 700 cm^{-1}; HRMS m/z (ESI) calcd for $C_{19}H_{28}O_2Na$ $(M + Na)^+$ 311.1987, found 311.1992; $[\alpha]_D^{20}$ = -12 (c = 0.1, $CHCl_3$).



21) (*E*)-4-nitrophenyl 5-phenyldec-2-enoate (**3u**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihyd rooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-4-nitrophenyl dec-4-enoate (72.8 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 52.0 mg **3u** (57% yield) with 96:4er value. The regioselectivity of **3u**:**4u** was12:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3u**: Light yellow liquid; Rf = 0.3 (V_{Hexane}:$V_{ethyl\ acetate}$ = 5:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.25 (d, *J* = 10.0 Hz, 2H), 7.31 (q, *J* = 10.0 Hz, 2H), 7.26-7.22 (m, 3H), 7.17 (d, *J* = 5.0 Hz, 2H), 7.11-7.05 (m, 1H), 5.95 (d, *J* = 15.0 Hz, 1H), 2.78-2.72 (m, 1H), 2.63-2.56 (m, 2H), 1.72-1.61 (m, 2H), 1.27-1.18 (m, 6H), 0.84 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 163.6, 155.5, 151.7, 144.1, 128.5, 127.4, 126.5, 125.1, 122.4, 120.8, 45.1, 40.0, 36.2, 31.8, 27.0, 22.5, 14.0 ppm; IR (neat): ν = 2955, 2927, 2857, 1742, 1524, 1491, 1346, 1208, 1114 cm^{-1}; HRMS m/z (ESI) calcd for $C_{22}H_{25}NO_4Na$ $(M + Na)^+$ 390.1681, found 390.1690; $[\alpha]_D^{20}$ = -46 (c = 0.1, $CHCl_3$).

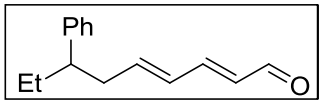


22) (*E*)-5-phenylnon-2-enenitrile (**3v**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-non-4-enenitrile (34.3 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 25.0 mg **3v** (47% yield) with 5:95er value. Z-product:E-product = 1:5; the regioselectivity of **3v**:**4v** was 16:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3v**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.32-7.29 (m, 2H), 7.23-7.21 (m, 1H), 7.20-7.16 (m, 2H), 5.97 (dt, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 1H), 5.34 (dt, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 1H), 3.26 (dd, J_1 = 15.0 Hz, J_2 = 10.0 Hz, 1H), 3.07-3.06 (m, 2H), 1.73-1.68 (m, 2H), 1.31-1.17 (m, 4H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 143.7, 139.9, 128.5, 127.5, 126.4, 117.7, 116.8, 48.6, 35.2, 29.7, 22.6, 20.4, 14.0 ppm; IR (neat): ν = 2957, 2929, 2858, 2250, 1735, 1493, 1453, 970, 700 cm^{-1}; HRMS m/z (ESI) calcd for $C_{15}H_{19}NNa$ $(M + Na)^+$ 236.1415, found 236.1411; $[\alpha]_D^{20}$ = -13 (c = 0.1, $CHCl_3$).

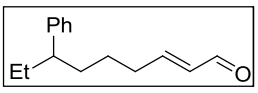


23) (*E*)-1-(10H-phenoxazin-10-yl)-5-phenyldec-2-en-1-one (**3w**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydroo xazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-1-(10H-phenoxazin-10-yl)dec-4-en-1-one (83.9 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 57.4 mg **3w** (56% yield) with 96:4 er value. The

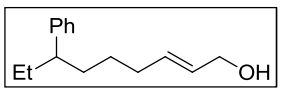
regioselectivity of **3w**:**4w** was 7.0:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3w**: Light yellow liquid; Rf = 0.2 (V_{Hexane}:$V_{ethyl\ acetate}$ = 5:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.34-7.23 (m, 5H), 7.17-7.03 (m, 8H), 6.99 (dd, J_1 = 15.0 Hz, J_2 = 10.0 Hz, 1H), 6.10 (dd, J_1 = 15.0 Hz, J_2 = 5.0 Hz, 1H), 2.75-2.69 (m, 1H), 2.55-2.40 (m, 2H), 1.66-1.62 (m, 2H), 1.26-1.17 (m, 6H), 0.83 (t, J = 5.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 164.1, 150.6, 146.3, 144.6, 129.3, 128.4, 127.6, 126.5, 126.2, 124.8, 123.3, 122.8, 116.6, 45.3, 40.2, 36.1, 31.8, 27.1, 22.5, 14.0 ppm; IR (neat): ν = 2927, 2856, 1674, 1481, 1456, 1268, 1210, 1148, 757, 700 cm^{-1}; HRMS m/z (ESI) calcd for $C_{28}H_{29}NO_2Na$ $(M + Na)^+$ 434.2096, found 434.2103; $[\alpha]_D^{20}$ = +59 (c = 0.1, $CHCl_3$).



24) (2*E*,4*E*)-7-phenylnona-2,4-dienal (**3x**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (2*E*,6*Z*)-nona-2,6-dienal (34.6 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 27.4 mg **3x** (51% yield) with 1:99er value. The regioselectivity of **3x**:**4x**was 9.1:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3x**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.49 (d, J = 5.0 Hz, 1H), 7.30 (dd, J_1 = 10.0 Hz, J_2 = 5.0 Hz, 2H), 7.22 (d, J = 5.0 Hz, 1H), 7.15-7.13 (m, 2H), 6.98 (dd, J_1 = 15.0 Hz, J_2 = 15.0 Hz, 1H), 6.26 (dd, J_1 = 15.0 Hz, J_2 = 10.0 Hz, 1H), 6.13-6.00 (m, 2H), 2.60-2.49 (m, 3H), 1.73-1.58 (m, 2H), 0.80 (t, J = 10.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 193.8, 152.5, 145.2, 144.2, 130.2, 129.8, 128.4, 127.6, 126.3, 47.5, 40.2, 29.0, 12.0 ppm; IR (neat): ν = 2961, 2926, 2874, 1683, 1639, 1119, 1012, 988, 701 cm^{-1}; HRMS m/z (ESI) calcd for $C_{15}H_{18}ONa$ $(M + Na)^+$ 237.1255, found 237.1257; $[\alpha]_D^{20}$ = -97 (c = 0.1, $CHCl_3$).

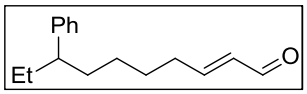


25) (*E*)-7-phenylnon-2-enal (**3y**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-non-6-enal (35.0 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 22.2 mg **3y** and **4y** (41% yield) with 7:93er value. The regioselectivity of **3y**:**4y** was2.1:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3y**: Light yellow liquid; Rf = 0.4 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.46 (d, J = 5.0 Hz, 1H), 7.29 (t, J = 10.0 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 5.0 Hz, 2H), 6.77-6.74 (m, 1H), 6.07-6.03 (m, 1H), 2.42-2.24 (m, 3H), 1.70-1.56 (m, 4H), 1.40-1.30 (m, 2H), 0.77 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 194.1, 158.7, 145.2, 133.0, 128.3, 127.6, 126.0, 47.7, 35.9, 32.7, 29.7, 25.9, 12.2 ppm; IR (neat): ν = 2928, 2859, 1725, 1690, 1494, 1452, 1133, 973, 701 cm^{-1}; HRMS m/z (ESI) calcd for $C_{15}H_{20}ONa$ $(M + Na)^+$ 239.1412, found 239.1415; $[\alpha]_D^{20}$ = -7 (c = 0.1, $CHCl_3$).

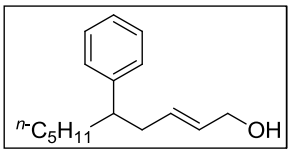


25-ol) (*E*)-7-phenylnon-2-en-1-ol (**3y-Ol**): Light yellow liquid;7:93er value. Rf = 0.2 (V_{Hexane}:$V_{ethyl\ acetate}$ = 5:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.29-7.26 (m, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 5.0 Hz, 2H), 5.64-5.54 (m, 2H), 4.05 (t, J = 5.0 Hz, 2H), 2.41-2.36 (m, 1H), 2.40-1.96 (m, 2H), 1.67-1.50 (m, 5H), 1.28-1.20 (m, 3H), 0.76 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 145.7, 133.3, 128.9, 128.2, 127.7, 125.8, 63.8, 47.8, 36.0, 32.3, 29.7, 27.2, 12.2 ppm; IR (neat): ν = 2927,

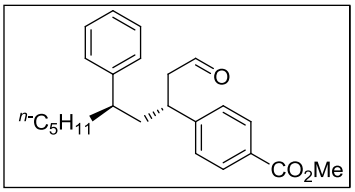
2857, 1653, 1507, 1456, 1090, 967, 700 cm^{-1}; HRMS m/z (ESI) calcd for $C_{15}H_{22}ONa$ (M + Na)$^+$241.1568, found241.1575; $[\alpha]_D^{20}$ = -0.015 (c = 0.1, EtOH).



26) (*E*)-8-phenyldec-2-enal (**3z**): $Pd(CH_3CN)_2(OTs)_2$ (10.0 mg, 0.019 mmol, 7.5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (6.1 mg, 0.025 mmol, 9 mol%), (*Z*)-dec-7-enal (38.6 mg, 0.25 mmol, 1.0 equiv), phenylboronic acid (91.4 mg, 0.75 mmol, 3.0 equiv), 3Å MS (50 mg), and DMA (3 mL) under O_2 (1 atm) for 24 h. Afforded 21.3 mg **3z** and **4z** (37% yield) with 98:2 er value. The regioselectivity of **3z**:**4z** was 1.5:1 (Based on crude ^{1}H NMR (500 MHz) of this reaction). **3z**: Light yellow liquid; Rf = 0.5 (V_{Hexane}:$V_{ethyl\ acetate}$ = 10:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.46 (d, *J* = 10.0 Hz, 1H), 7.30-7.20 (m, 2H), 7.18-7.11 (m, 3H), 6.79-6.74 (m, 1H), 6.10-6.03 (m, 1H), 2.50-2.25 (m, 3H), 1.60-1.45 (m, 6H), 1.26-1.13 (m, 2H), 0.76 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 194.1, 158.8, 145.6, 132.9, 128.3, 128.2, 127.7, 127.6, 125.9, 47.8, 45.6, 36.3, 36.1, 32.6, 29.7, 27.9, 27.1, 20.7, 14.1, 12.2 ppm; IR (neat): ν = 2927, 2857, 1690, 1494, 1452, 1136, 974, 700 cm^{-1}; HRMS m/z (ESI) calcd for $C_{16}H_{22}ONa$ (M + Na)$^+$253.1568, found 253.1566; $[\alpha]_D^{20}$ = -10 (c = 0.1, $CHCl_3$).

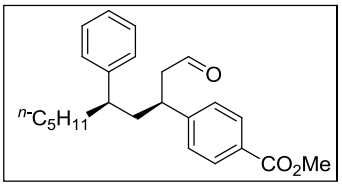


27) (*E*)-5-phenyldec-2-en-1-ol (**5**): **3a** (0.25 mmol, 57.6 mg) and dichloromethane (10 ml) were added into a dry 25 mL round bottom flask. Under -78^{o}C, 0.375 mmoldiisobutylaluminum hydride (1.0 M in heptanes) were slowly added. And then, the reaction system was warmed into room temperature, and stirred for 1 hour. After that, 0.5 mL H_2O was added to quench the reaction. This reaction afforded 52.9 mg **5** (91% yield). Light yellow liquid; Rf = 0.2 (V_{Hexane}:$V_{ethyl\ acetate}$ = 5:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.27 (dd, J_1 = 10.0 Hz, J_2 = 5.0 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 10.0 Hz, 2H), 5.60-5.51 (m, 2H), 4.00 (t, *J* = 5.0 Hz, 2H), 2.60-2.54 (m, 1H), 2.39-2.30 (m, 2H), 1.67-1.52 (m, 3H), 1.25-1.08 (m, 6H), 0.83 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 145.3, 131.5, 130.3, 128.2, 127.7, 126.0, 63.7, 46.0, 39.7, 36.0, 31.9, 27.1, 22.5, 14.1 ppm; IR (neat): ν = 2926, 2856, 1456, 1270, 970, 760, 700 cm^{-1}; HRMS m/z (ESI) calcd for $C_{16}H_{24}ONa$ (M + Na)$^+$ 255.1725, found 255.1725; $[\alpha]_D^{20}$ = +30 (c = 0.1, $CHCl_3$).



28) methyl 4-((3*R*,5*R*)-1-oxo-5-phenyldecan-3-yl)benzoate(**6 (R, R)**): Mix Pd_2Dba_3 (5.2 mg, 0.005 mmol, 5 mol%), (*S*)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (3.3 mg, 0.012 mmol, 12 mol%), 3Å MS (20 mg), and DMF (1.5 mL) under N_2 (1 atm).The resulting mixture was stirred for 15 min. Then,**5** (23.2 mg, 0.1 mmol, 1.0 equiv) and 4-(methoxycarbonyl)benzenediazoniumhexafluorophosphate (62.5 mg, 0.25 mmol, 2.5 equiv) were added. The resulting mixture was stirred for 24 h at room temperature. Afforded 19.0 mg**6 (R, R)** (52% yield) with 5.5:94.5 dr value (Based on ^{1}H NMR (500 MHz) of this reaction). Light yellow liquid; Rf = 0.3 (V_{Hexane}:$V_{ethyl\ acetate}$ = 5:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.50 (t, *J* = 5.0 Hz, 1H), 7.99 (d, *J* = 5.0 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 5.0 Hz, 2H), 7.01 (d, *J* = 5.0 Hz, 2H), 3.92 (s, 3H), 2.97-2.90 (m, 1H), 2.65-2.60 (m, 2H), 2.20-2.10 (m, 1H), 2.01-1.95 (m, 2H), 1.50-1.44 (m, 2H), 1.20-1,04 (m, 6H), 0.77 (t, *J* = 7.5 Hz,

3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 201.0, 166.9, 148.8, 144.5, 130.0, 128.5, 127.9, 127.8, 126.3, 52.1, 51.1, 43.2, 42.5, 37.9, 37.7, 31.7, 27.0, 22.4, 14.0 ppm; IR (neat): ν = 2927, 1724, 1653, 1559, 1286, 1271, 1108, 760, 701 cm^{-1}; HRMS m/z (ESI) calcd for $C_{24}H_{30}O_3Na$ (M + Na)$^+$389.2093, found 389.2095; $[\alpha]_D^{20}$ = -93 (c = 0.1, $CHCl_3$).



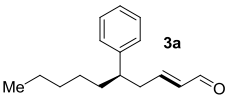
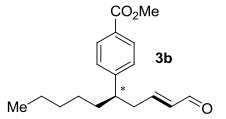
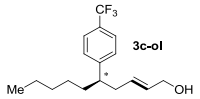
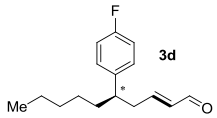
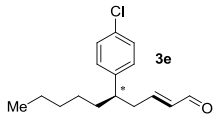
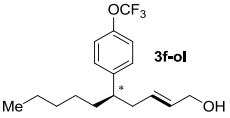
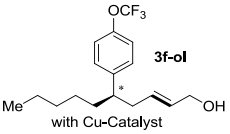
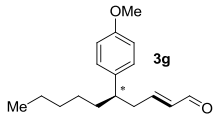
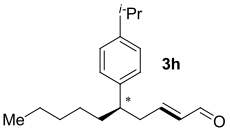
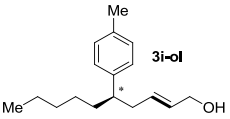
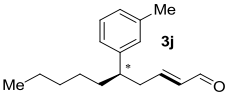
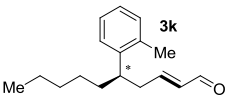
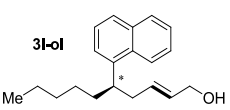
29) methyl 4-((3R,5R)-1-oxo-5-phenyldecan-3-yl)benzoate(**6 (R, S)**): Mix Pd_2Dba_3 (5.2 mg, 0.005 mmol, 5 mol%), (R)-4-(tert-butyl)-2-(5-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (3.3 mg, 0.012 mmol, 12 mol%), 3Å MS (20 mg), and DMF (1.5 mL) under N_2 (1 atm).The resulting mixture was stirred for 15 min. Then,**5** (23.2 mg, 0.1 mmol, 1.0 equiv) and 4-(methoxycarbonyl)benzenediazoniumhexafluorophosphate (62.5 mg, 0.25 mmol, 2.5 equiv) were added. The resulting mixture was stirred for 24 h at room temperature. Afforded 17.0 mg**6 (R, S)** (46% yield) with 91.0:9.0 dr value (Based on ^{1}H NMR (500 MHz) of this reaction). Light yellow liquid; Rf = 0.3 (V_{Hexane}:$V_{ethyl\ acetate}$ = 5:1), ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.56 (t, *J* = 4.0 Hz, 1H), 7.95 (d, *J* = 5.0 Hz, 2H), 7.27-7.24 (m, 2H), 7.19-7.18 (m, 3H), 7.04 (d, *J* = 10 Hz, 2H), 3.90 (s, 3H), 3.22 (dd, J_1 = 20 Hz, J_2 = 5.0 Hz, 1H), 2.74-2.71 (m, 2H), 2.41-2.36 (m, 1H), 2.07-1.87 (m, 2H), 1.59-1.40 (m, 2H), 1.19-1.03 (m, 6H), 0.8 (t, *J* = 7.5 Hz, 3H);^{13}C NMR ($CDCl_3$, 125 MHz): δ = 201.1, 166.9, 149.4, 145.0, 130.0, 128.5, 127.43, 127.41, 126.2, 52.1, 49.6, 43.7, 43.1, 37.7, 36.0, 31.8, 26.9, 22.5, 14.0 ppm; IR (neat): ν = 2927, 2856, 1724, 1436, 1281, 1112, 701, 668 cm^{-1}; HRMS m/z (ESI) calcd for $C_{24}H_{30}O_3Na$ (M + Na)$^+$ 389.2093, found 389.2099; $[\alpha]_D^{20}$ = -0.008 (c = 0.1, EtOH).

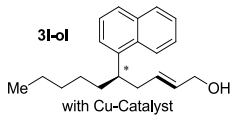
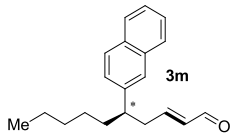
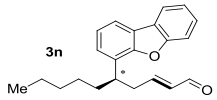
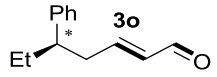
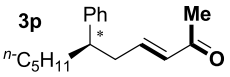
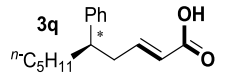
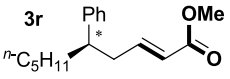
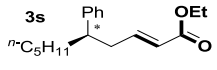
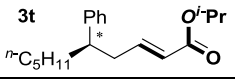
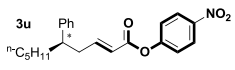
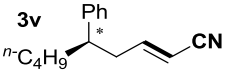
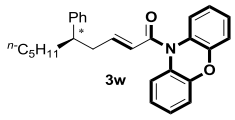
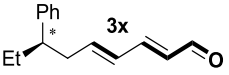
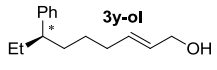
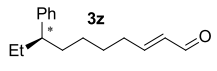
Reference:

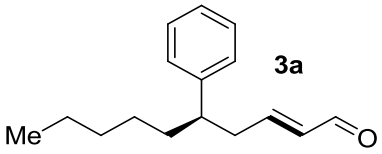
(1) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.*, **1991**, *417*, 235.

(2) Werner, E. W.; Mei, T.-S.; Burckle, A. J.; Sigman, M. S.*Science*,**2012**, *338*, 1455.

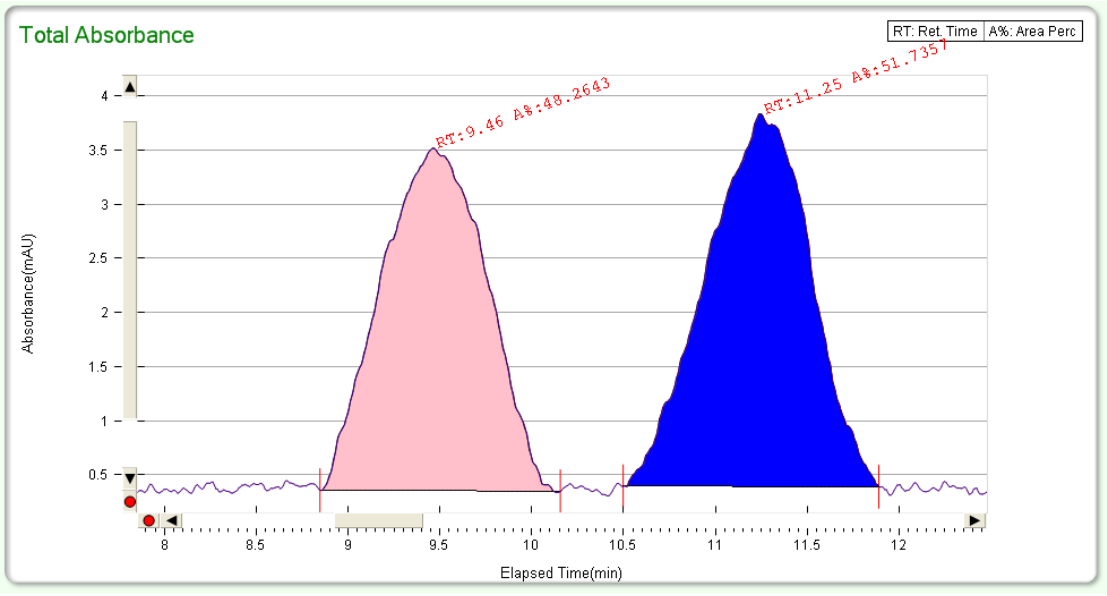
Enantiomeric ratio of products

Entry	Compound	Conditions	Retention time	er
1		Column OD, 40 °C, MeOH:CO_2 1:99-2:98 (25 min), 2mL/min	9.2 and 10.9 min	1:99
2		Column AY-H, 40 °C, ^{i}-PrOH:CO_2 1:99-3:97 (25 min), 2mL/min	12.7 and 14.1 min	97:3
3		Column AD-H, 40 °C, ^{i}-PrOH:CO_2 6:94, 1mL/min	12.3 and 13.9 min	95:5
4		Column Whelko, 40 °C, ^{i}-PrOH:CO_2 0:100-2:98 (25 min), 2mL/min	12.4 and 13.1 min	<1:99
5		Column AS-H, 40 °C, ^{i}-PrOH:CO_2 1:99-3:97 (25 min), 2mL/min	4.3 and 4.9 min	98:2
6		Column AD-H, 40 °C, ^{i}-PrOH:CO_2 5:95-20:80 (25 min), 2mL/min	18.9 and 21.3 min	>99:1
6-Cu		Column AD-H, 40 °C, ^{i}-PrOH:CO_2 5:95-20:80 (25 min), 2mL/min	18.8 and 21.0 min	98:2
7		Column Whelko, 40 °C, ^{i}-PrOH:CO_2 0:100-5:95 (25 min), 2mL/min	14.5 and 15.6 min	98:2
8		Column OJ-H, 40 °C, ^{i}-PrOH:CO_2 0:100-2:98 (25 min), 2mL/min	17.2 and 20.5 min	95:5
9		Column AD-H, 40 °C, ^{i}-PrOH:CO_2 5:95, 2mL/min	17.3 and 18.6 min	98:2
10		Column OD, 40 °C, ^{i}-PrOH:CO_2 0:100-2:98 (25 min), 2mL/min	20.4 and 25.0 min	1:99
11		Column OZ, 40 °C, ^{i}-PrOH:CO_2 0:100-2:98 (25 min), 2mL/min	15.1 and 16.2 min	3:97
12		Column AD-H, 40 °C, ^{i}-PrOH:CO_2 5:95-20:80 (25 min), 2mL/min	12.1 and 13.1 min	4:96

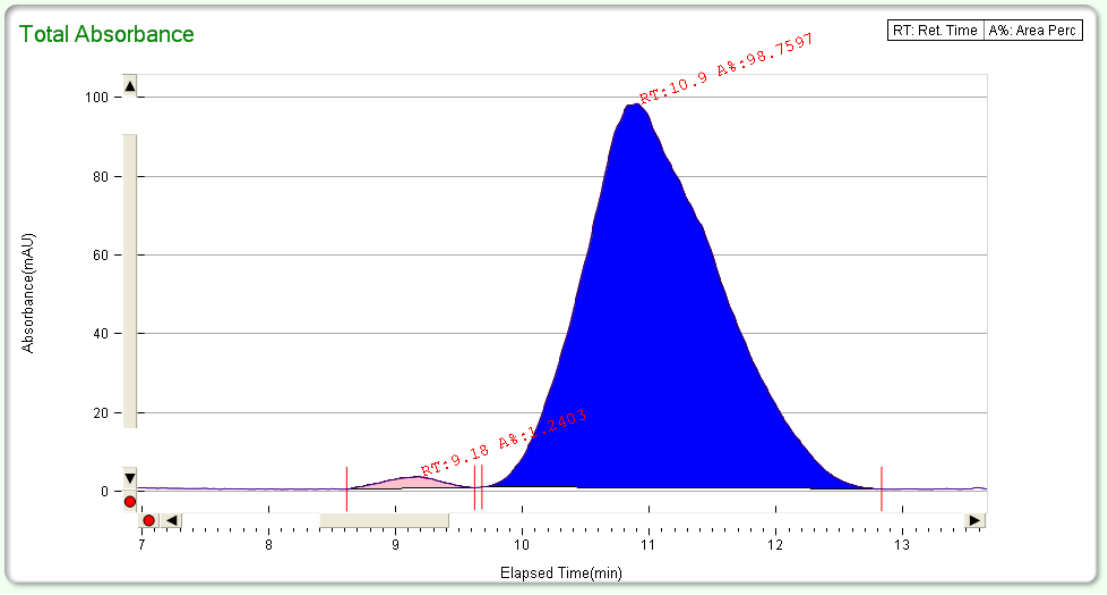
12-Cu		Column AD-H, 40 °C, ^{i}-PrOH:CO_2 5:95-20:80 (25 min), 2mL/min	12.1 and 13.1 min	4:96
13		Column OJ-H, 40 °C, MeOH:CO_2 0:100-5:95 (25 min), 2mL/min	18.1 and 19.4 min	98:2
14		Column AY-H, 40 °C, MeOH:CO_2 0:100-5:95 (25 min), 2mL/min	6.0 and 7.0 min	>99:1
15		Column OD, 40 °C, ^{i}-PrOH:CO_2 0:100-5:95 (25 min), 2mL/min	12.1 and 13.7 min	2:98
16		Column AY-H, 40 °C, ^{i}-PrOH:CO_2 0:100-1:99 (25 min), 2mL/min	4.5 and 6.4 min	98:2
17		Column OZ-H, 40 °C, ^{i}-PrOH:CO_2 1:99-5:95 (25 min), 2mL/min	21.1 and 23.7 min (esterification)	97:3
18		Column OZ-H, 40 °C, ^{i}-PrOH:CO_2 1:99-5:95 (25 min), 2mL/min	20.3 and 25.4 min (transformation)	95:5
19		Column OZ-H, 40 °C, ^{i}-PrOH:CO_2 1:99-5:95 (25 min), 2mL/min	20.3 and 25.4 min (transformation)	96:4
20		Column OZ-H, 40 °C, ^{i}-PrOH:CO_2 1:99-5:95 (25 min), 2mL/min	20.2 and 25.3 min (transformation)	97:3
21		Column OZ-H, 40 °C, ^{i}-PrOH:CO_2 1:99-5:95 (25 min), 2mL/min	18.9 and 23.4 min	96:4
22		Column OJ-H, 40 °C, ^{i}-PrOH:CO_2 0:100-1:99 (25 min), 2mL/min	25.3 and 27.7 min	5:95
23		Column OZ-H, 40 °C, ^{i}-PrOH:CO_2 1:99-5:95 (25 min), 2mL/min	20.2 and 25.3 min (transformation)	96:4
24		Column OD, 40 °C, ^{i}-PrOH:CO_2 0:100-2:98 (25 min), 2mL/min	16.4 and 17.5 min	1:99
25		Column OJ-H, 40 °C, ^{i}-PrOH:CO_2 5:95, 2mL/min	11.6 and 13.6 min	7:93
26		Column AY-H, 40 °C, ^{i}-PrOH:CO_2 0:100-5:95 (25 min), 2mL/min	5.4 and 6.2 min	98:2



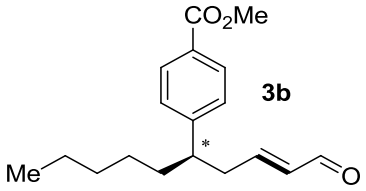
Separation of enantiomers by SFC. Chiralcel® Column OD, 40 °C, 1:99-2:98 (25 min) (MeOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 9.2 min, t_2 = 10.9 min.



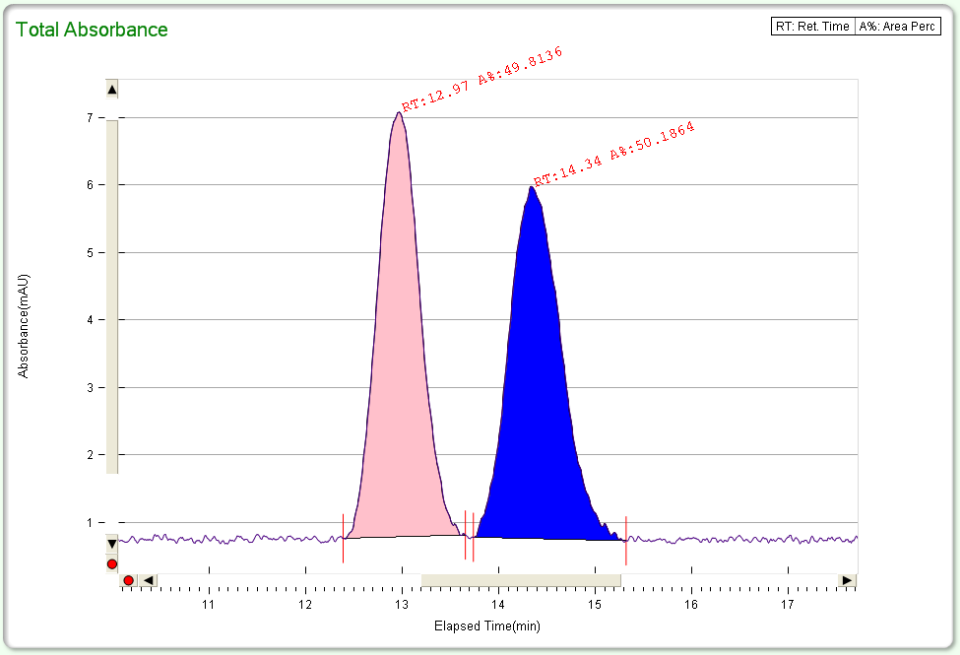
(±)-3a



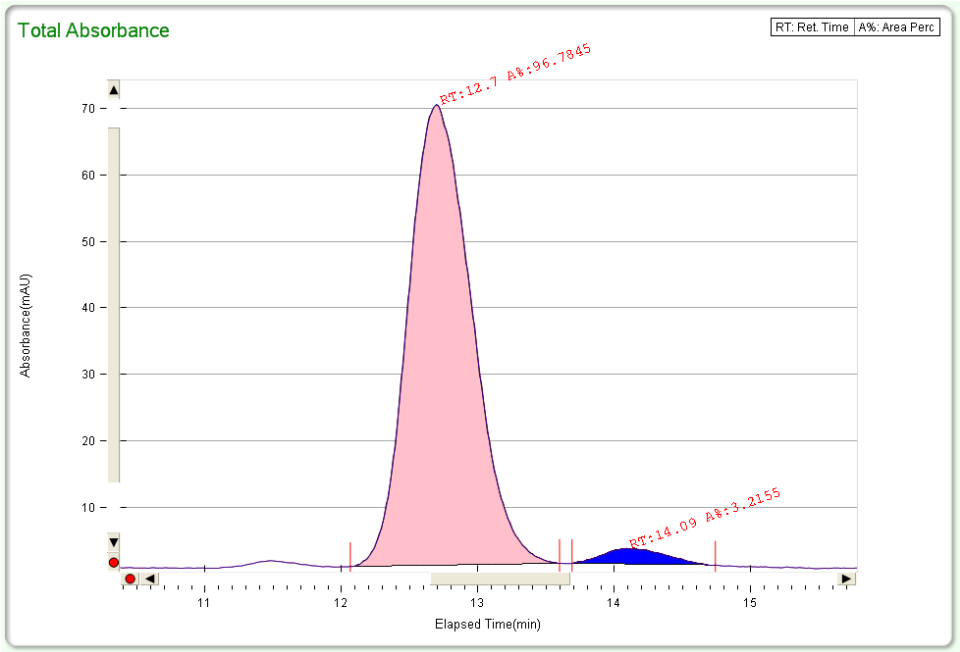
(±)-3a



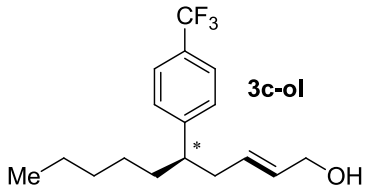
Separation of enantiomers by SFC. Chiralcel® Column AY-H, 40 °C, 1:99-3:97 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 12.7 min, t_2 = 14.1 min.



(±)-3b

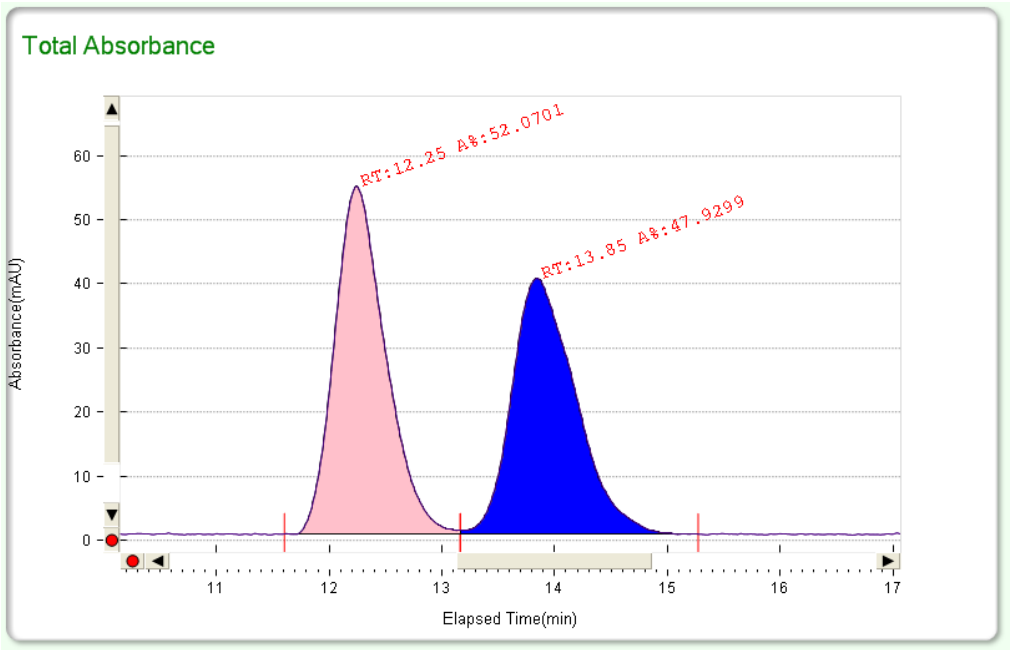


3b

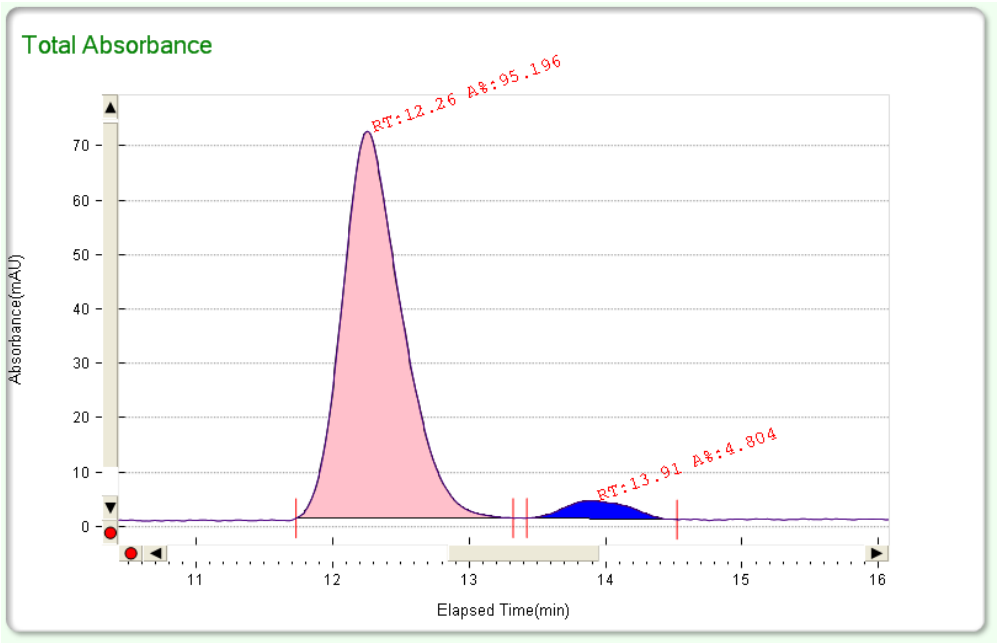


3c-ol

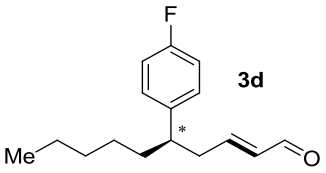
Separation of enantiomers by SFC. Chiralcel® Column AD-H, 40 °C, 6:94 (25 min) (^{i}PrOH:CO_2), 1mL/min, 160 bar, and 40°C; t_1 = 12.3 min, t_2 = 13.9 min.



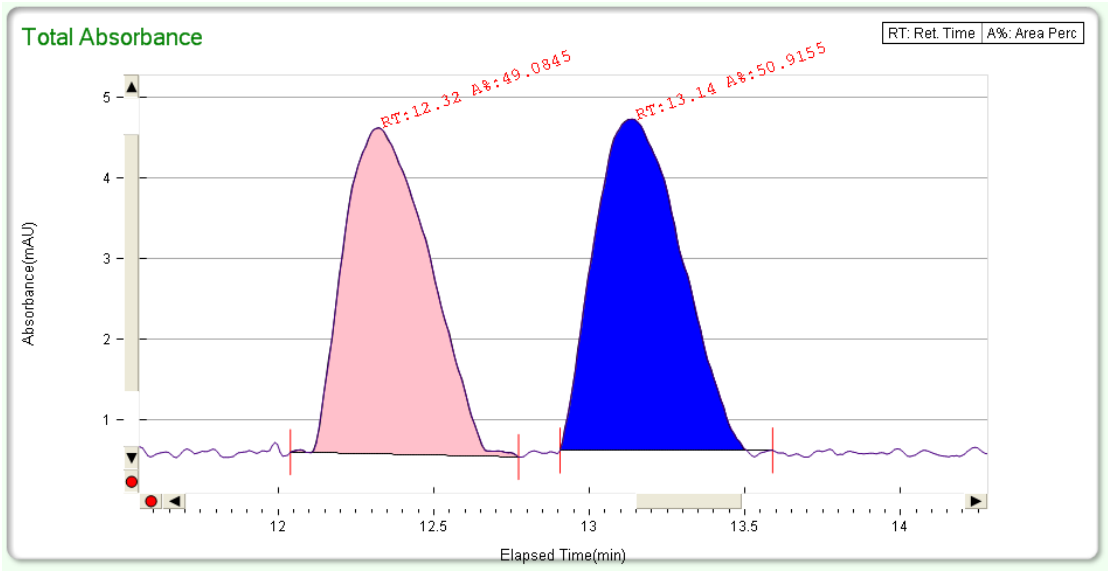
(±)-3c-ol



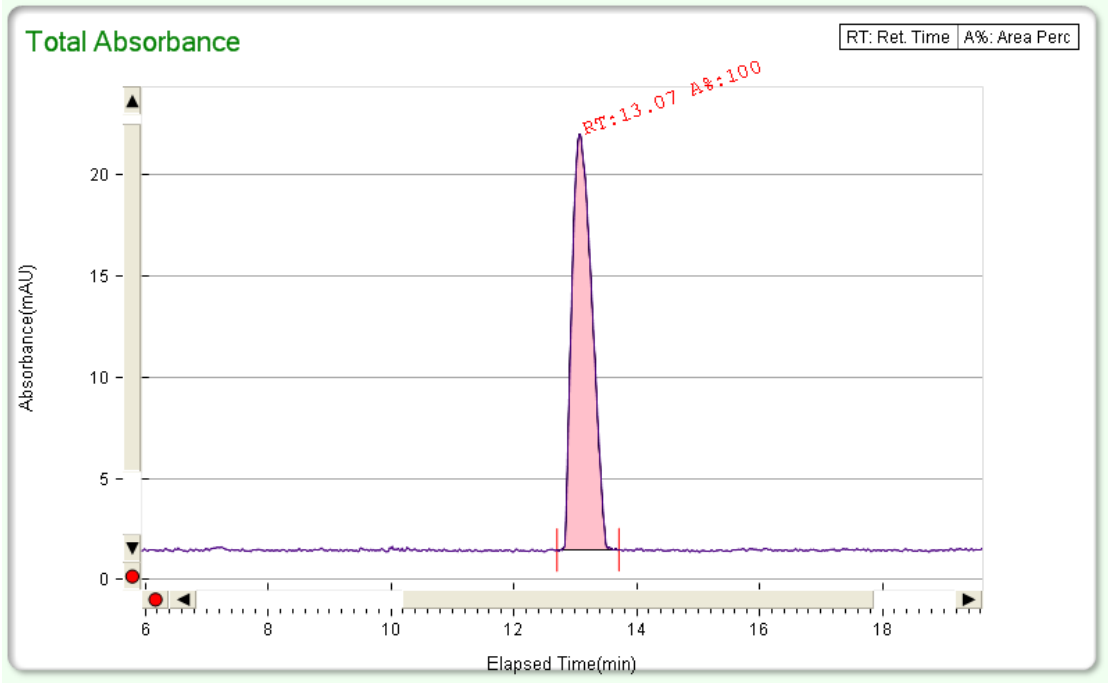
3c-ol



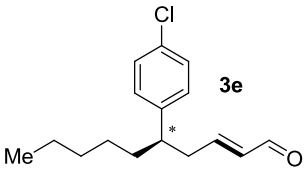
Separation of enantiomers by SFC. Chiralcel® Column whelko, 40 °C, 0:100-2:98 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 12.4 min, t_2 = 13.1 min.



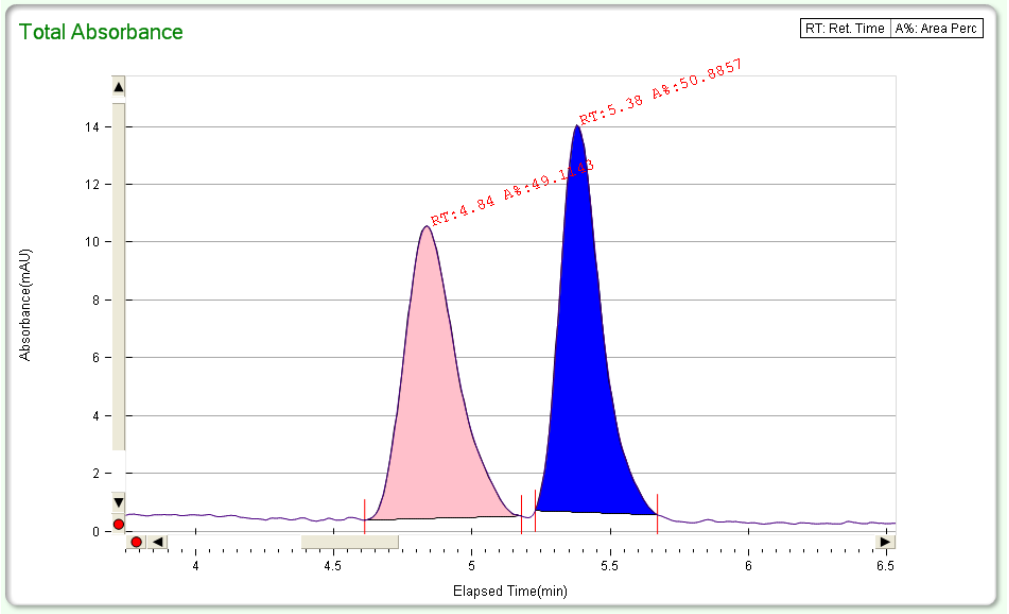
(±)-3d



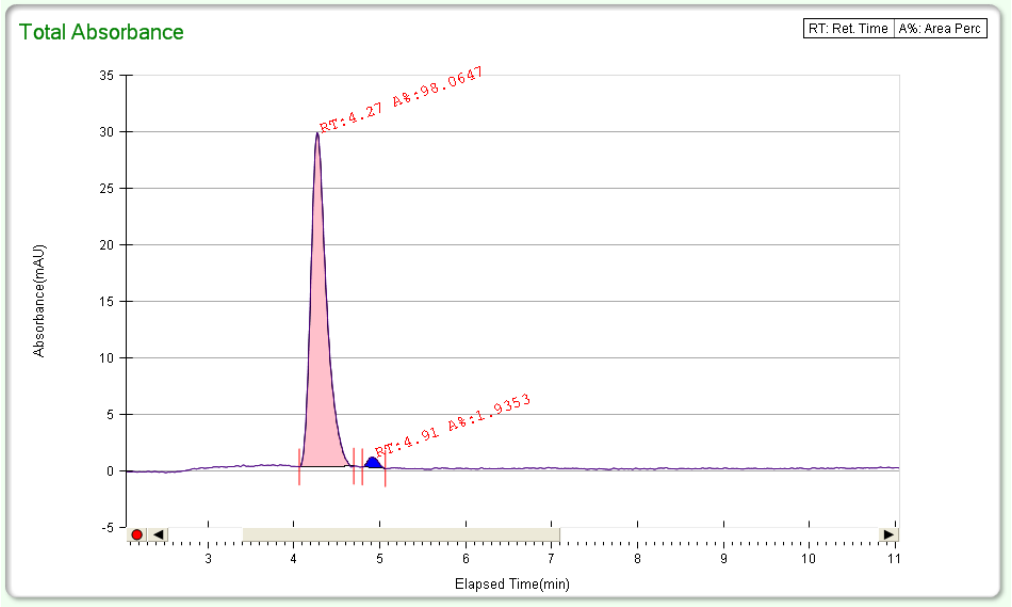
3d



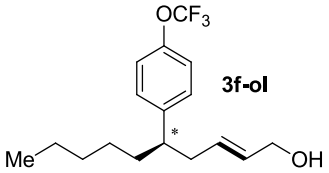
Separation of enantiomers by SFC. Chiralcel® Column AS-H, 40 °C, 1:99-3:97 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 4.3 min, t_2 = 4.9 min.



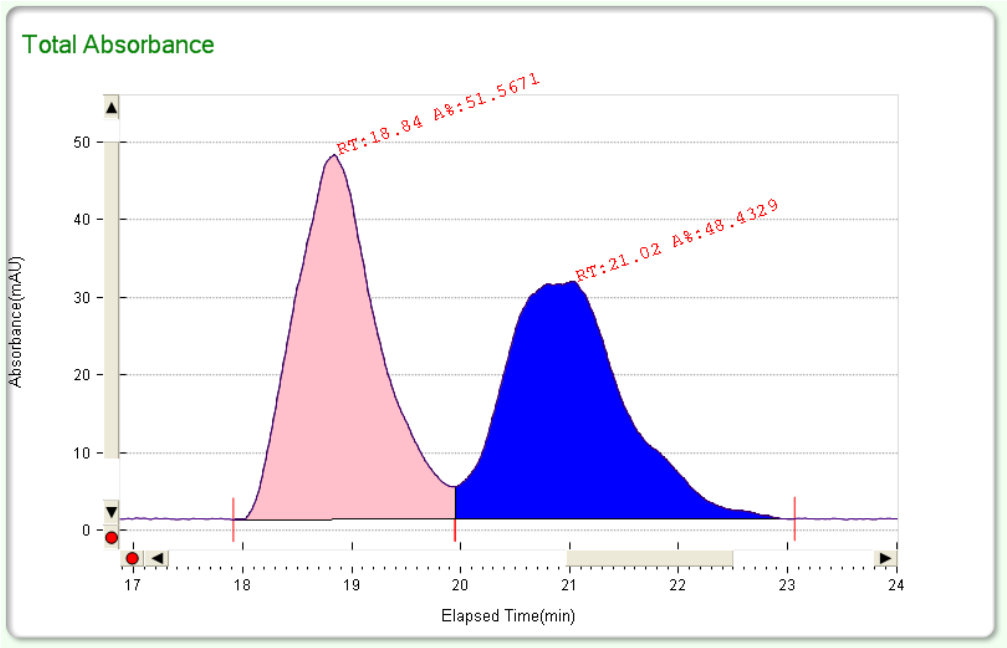
(±)-3e



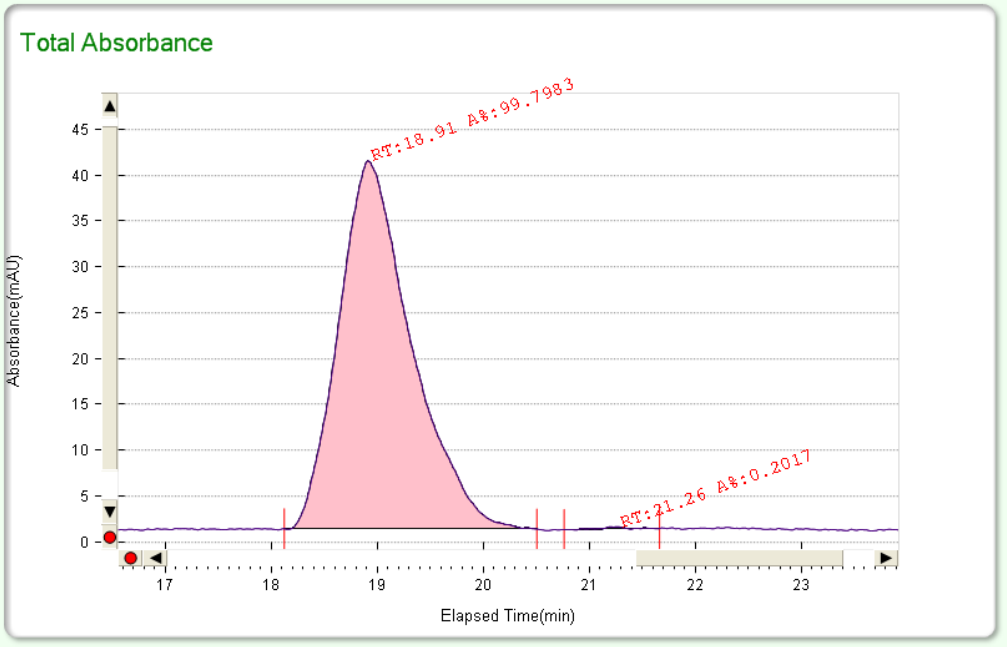
3e



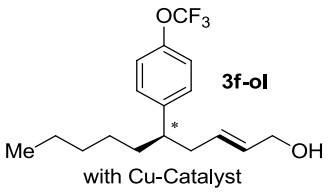
Separation of enantiomers by SFC. Chiralcel® Column AD-H, 40 °C, 5:95-20:80 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 18.9 min, t_2 = 21.3 min.



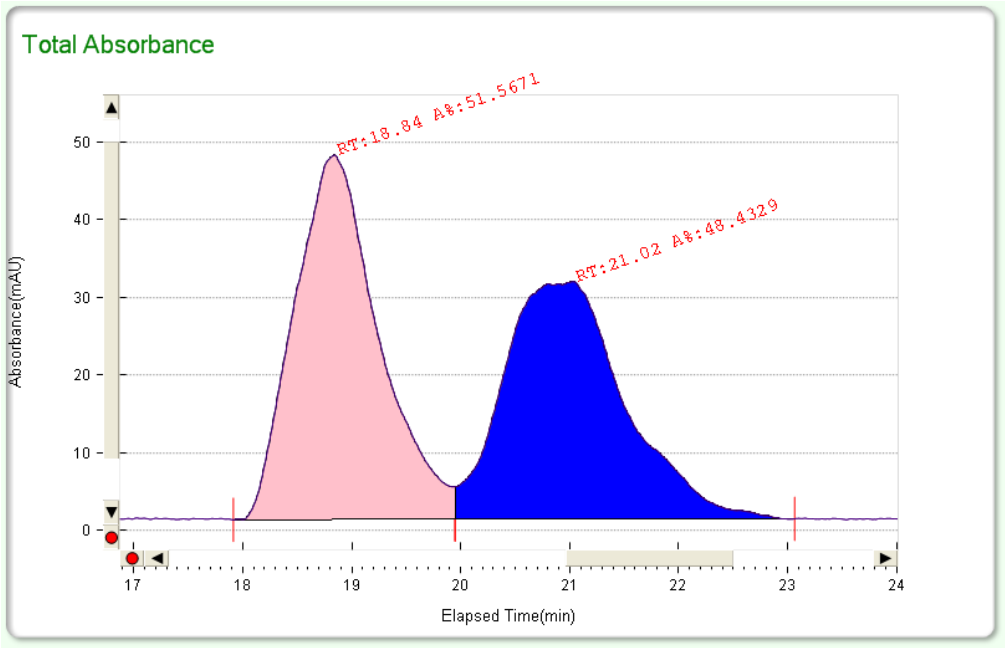
(±)-3f-ol



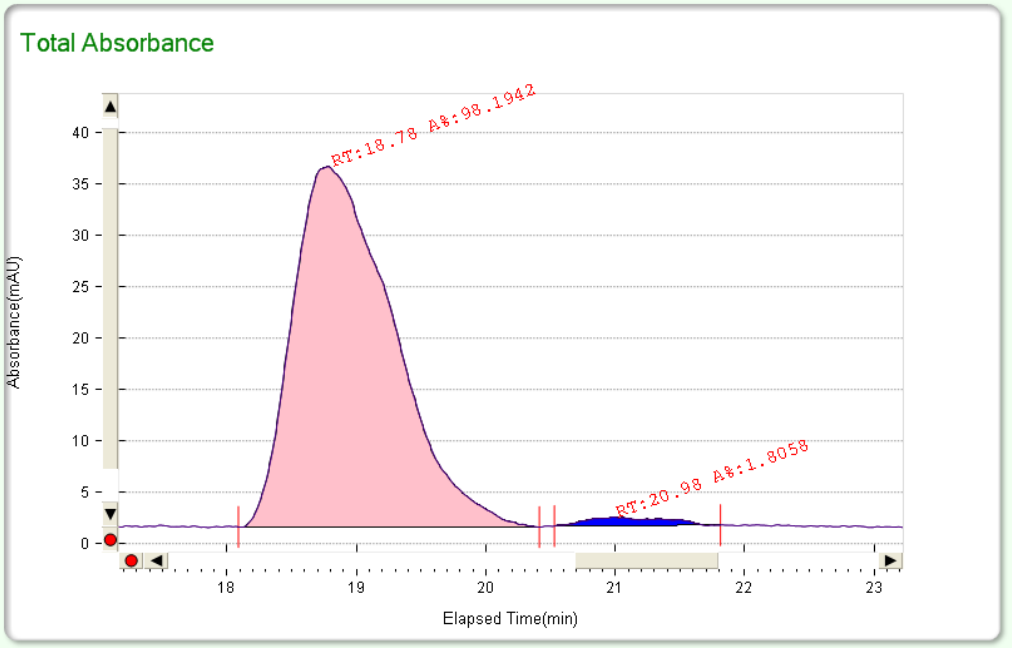
3f-ol



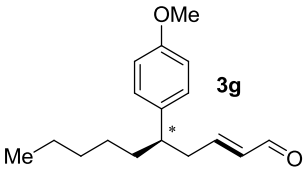
Separation of enantiomers by SFC. Chiralcel® Column AD-H, 40 °C, 5:95-20:80 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 18.8 min, t_2 = 21.0 min.



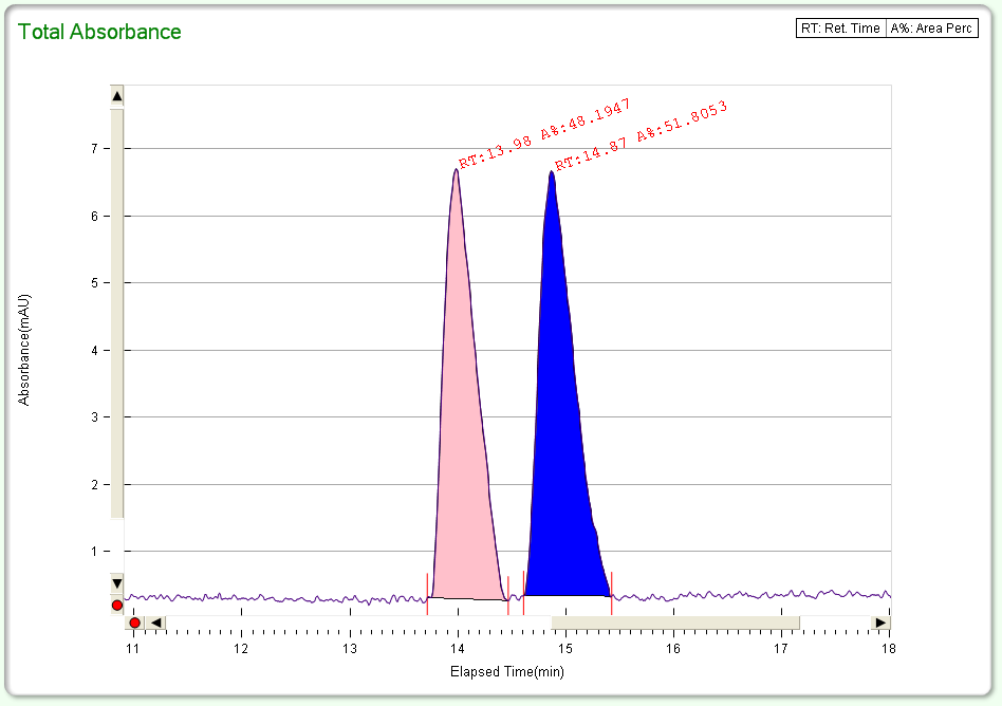
(±)-3f-ol



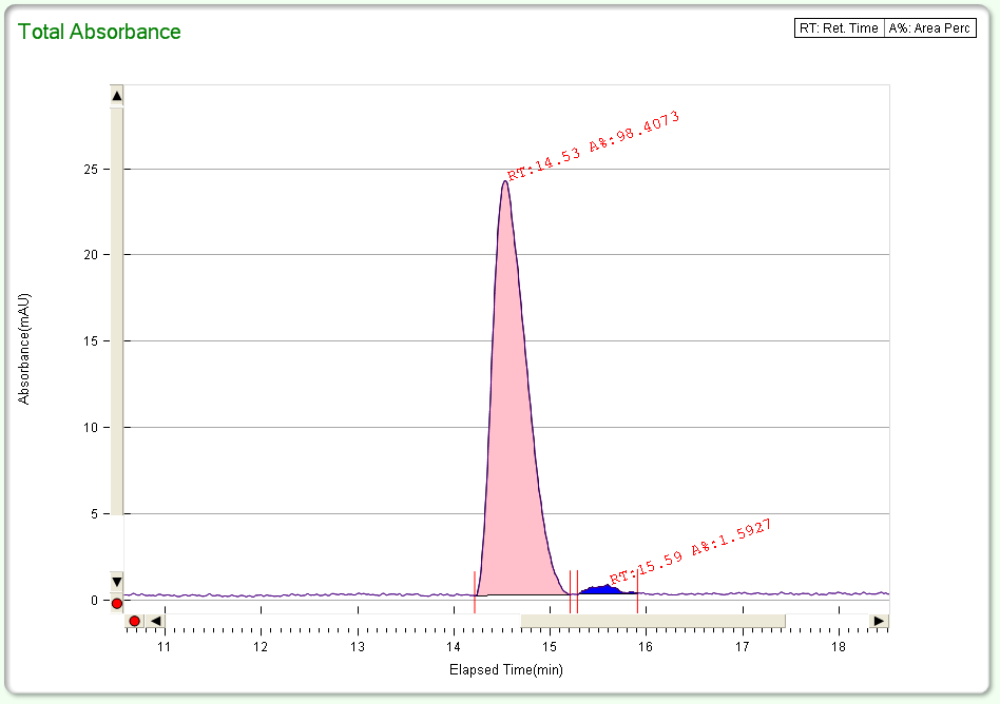
3f-ol (With Cu-Catalyst)



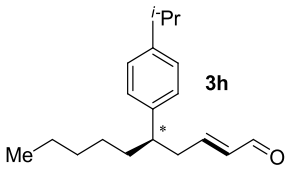
Separation of enantiomers by SFC. Chiralcel® Column whelko, 40 °C, 0:100-5:95 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 14.5 min, t_2 = 15.6 min.



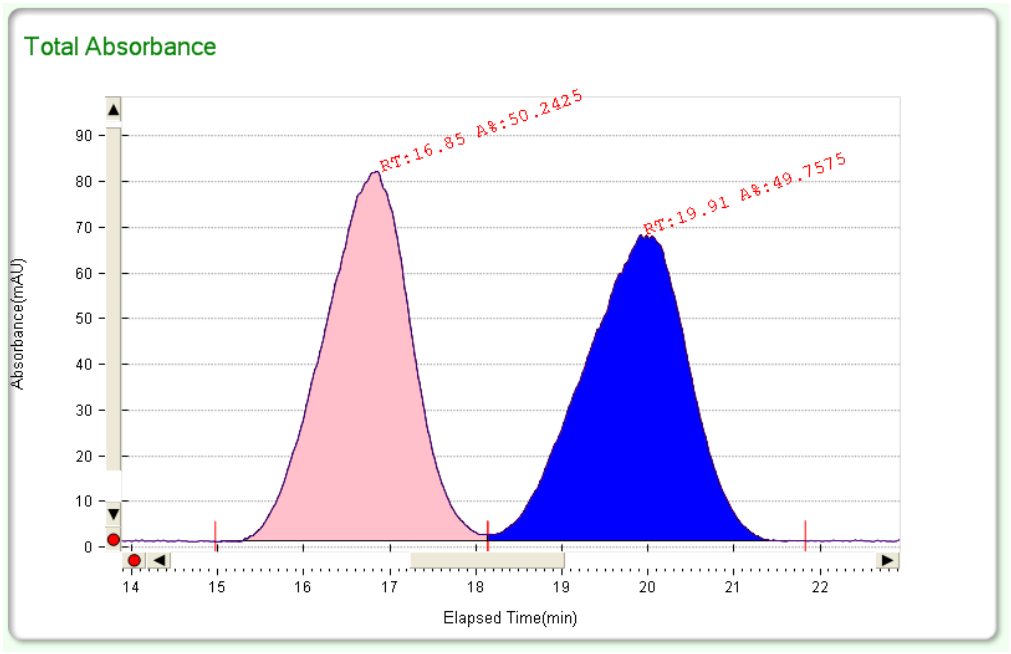
(±)-3g



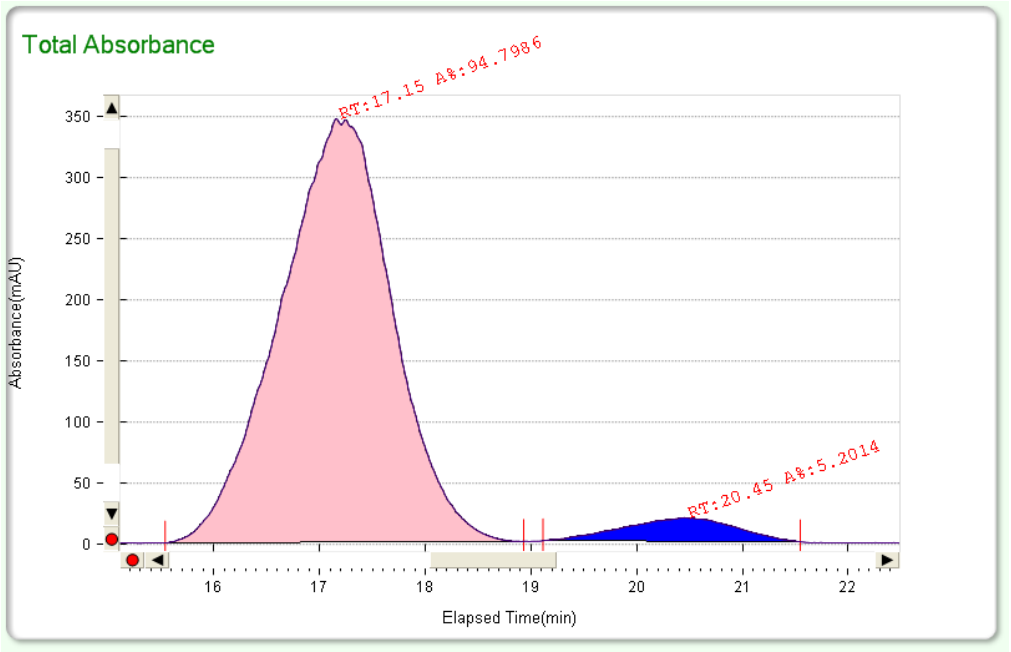
3g



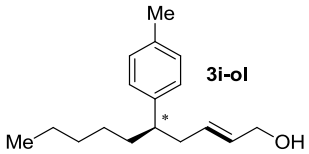
Separation of enantiomers by SFC. Chiralcel® Column OJ-H, 40 °C, 0:100-2:98 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 17.2 min, t_2 = 20.5 min.



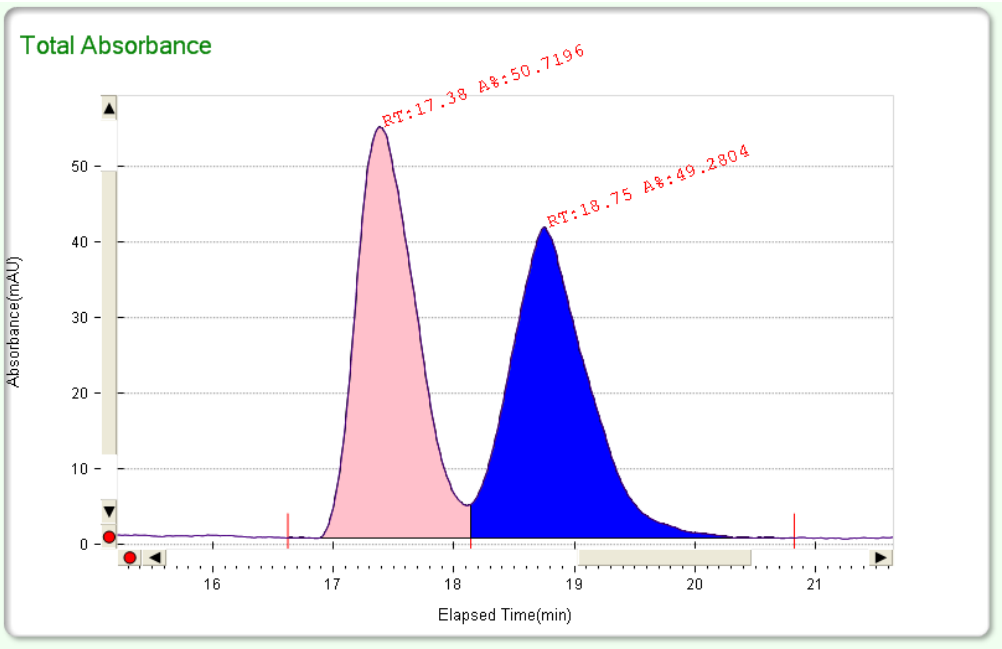
(±)-3h



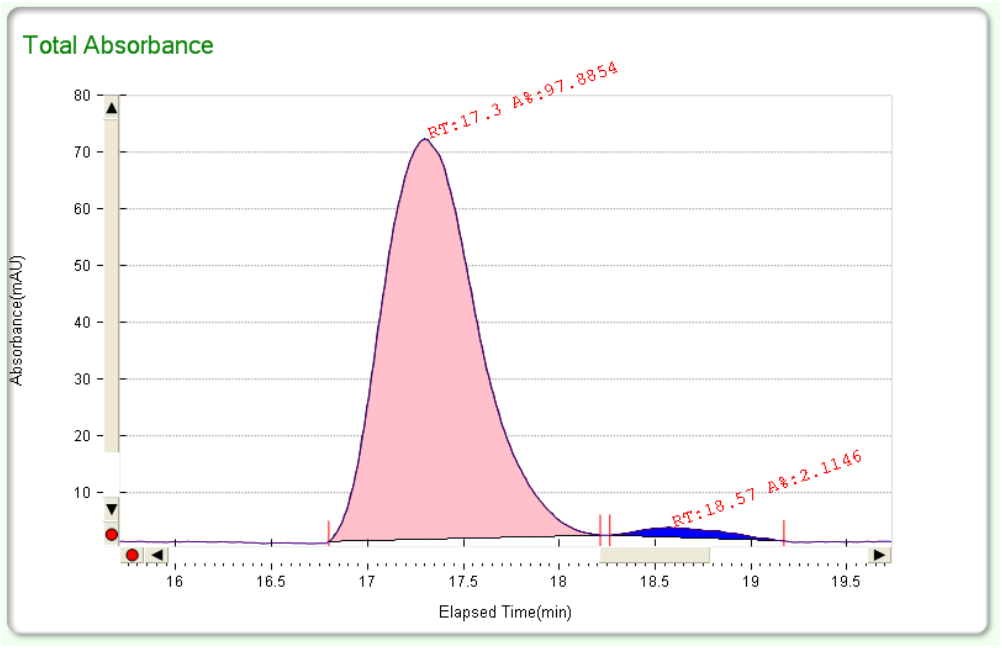
3h



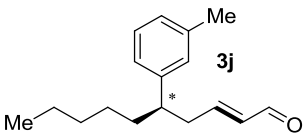
Separation of enantiomers by SFC. Chiralcel® Column AD-H, 40 °C, 5:95 (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 17.3 min, t_2 = 18.6 min.



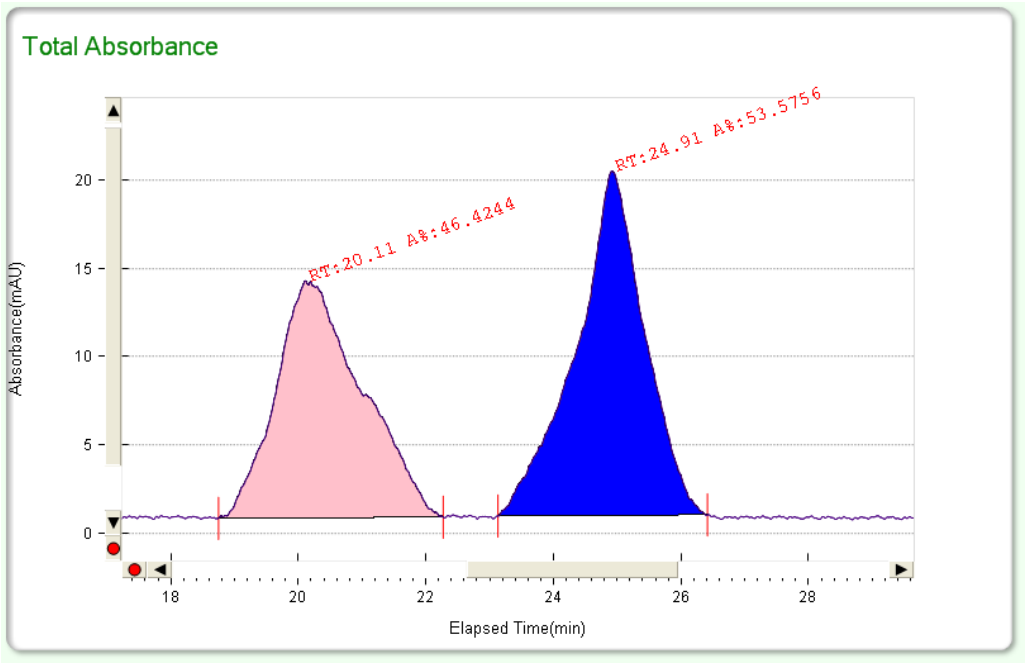
(±)-3i-ol



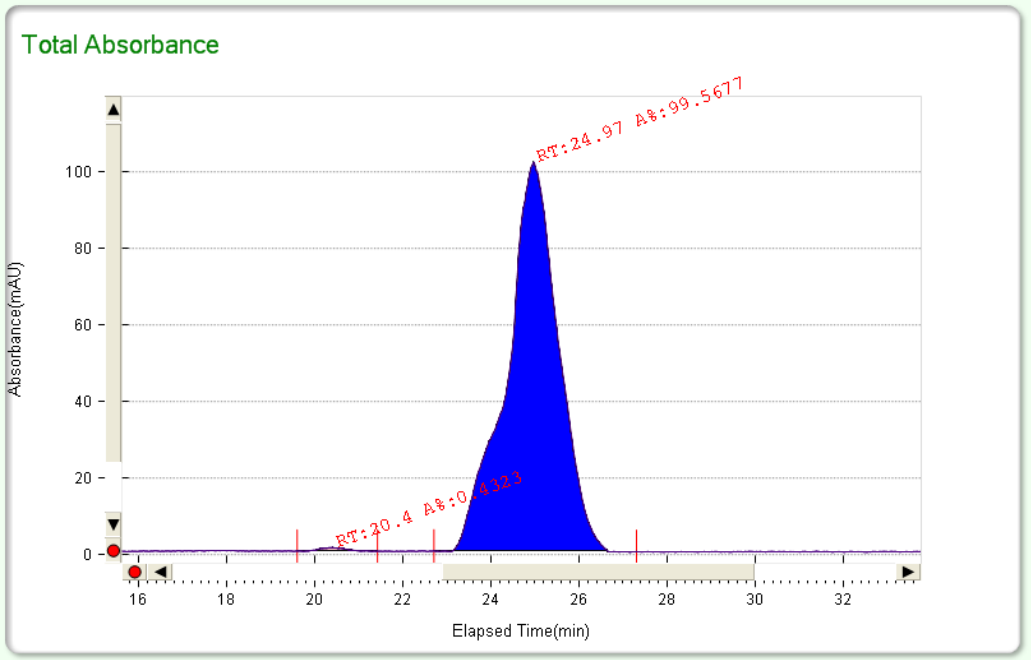
3i-ol



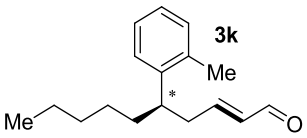
Separation of enantiomers by SFC. Chiralcel® Column OD, 40 °C, 0:100-2:98 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 20.4 min, t_2 = 25.0 min.



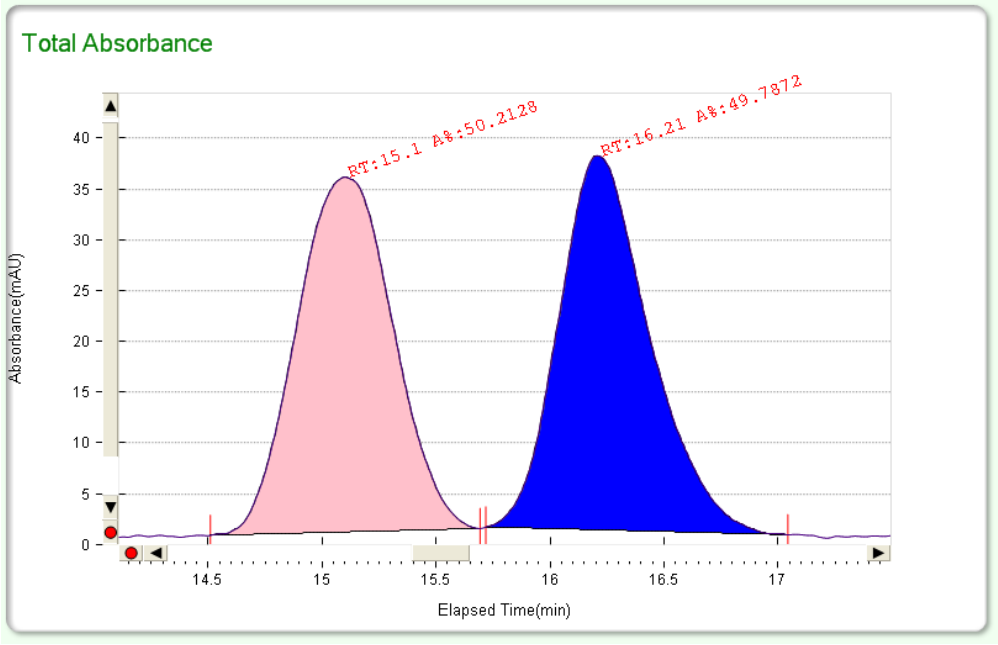
(±)-3j



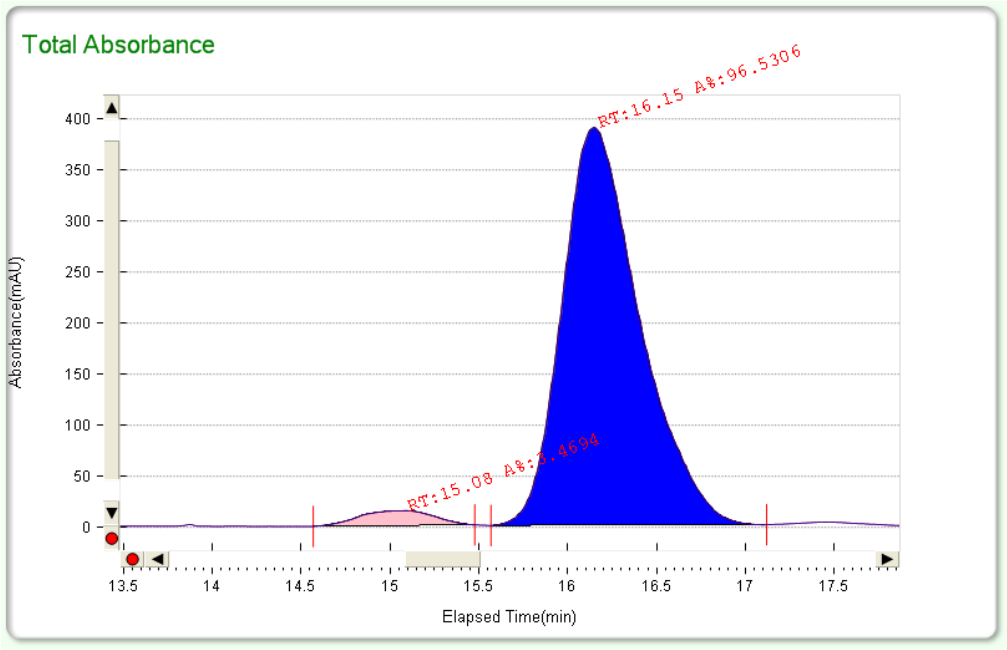
3j



Separation of enantiomers by SFC. Chiralcel® Column OZ, 40 °C, 0:100-2:98 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 15.1 min, t_2 = 16.2 min.

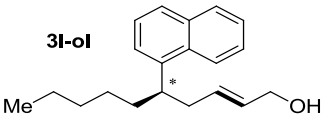


(±)-3k

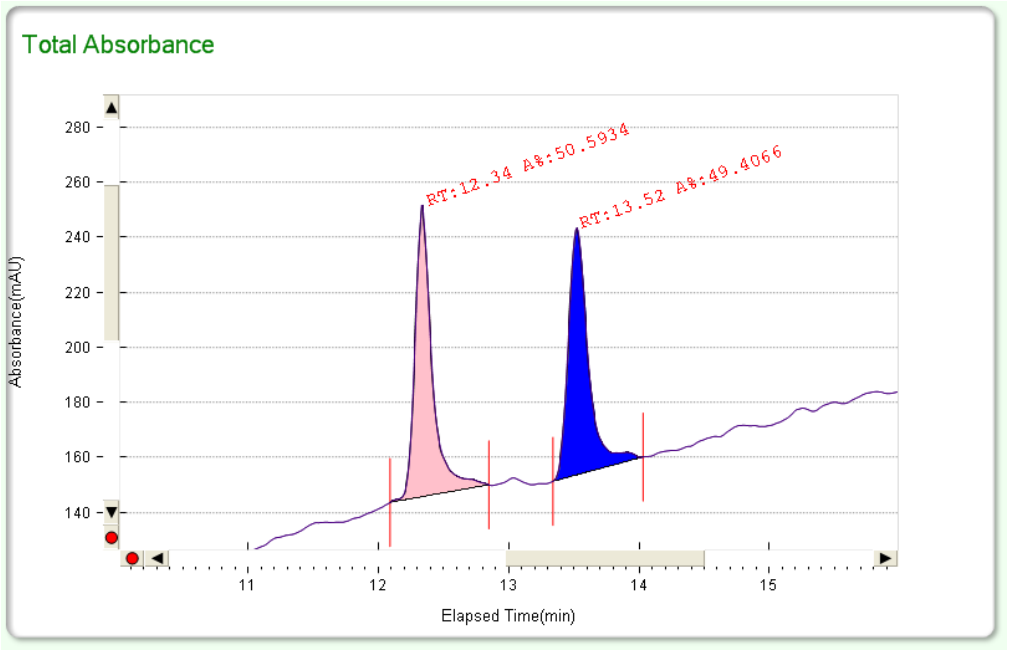


3k

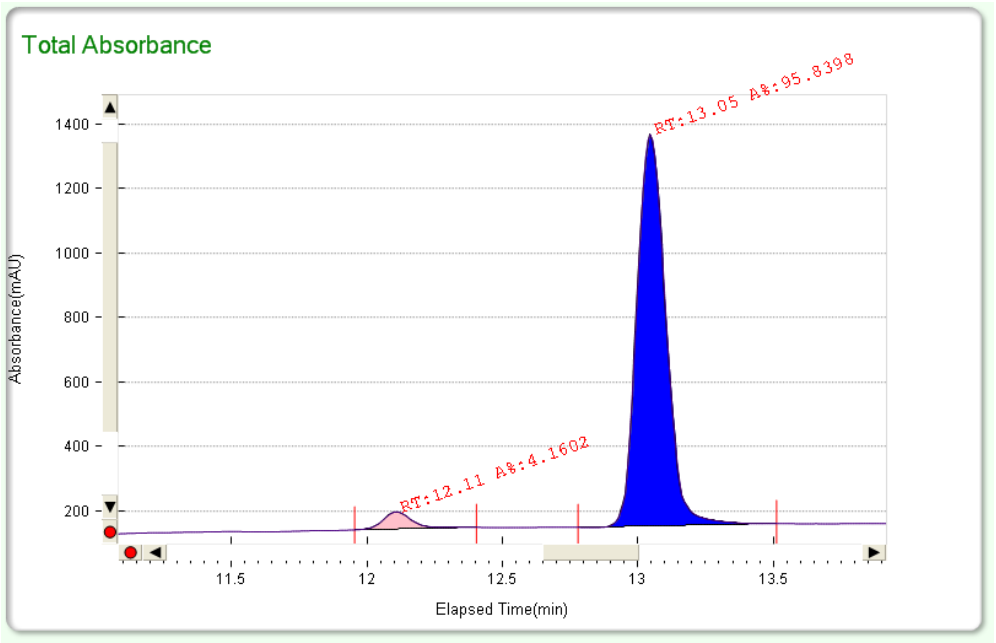
3l-ol



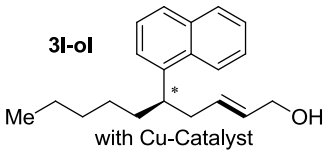
Separation of enantiomers by SFC. Chiralcel® Column AD-H, 40 °C, 5:95-20:80 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 12.1 min, t_2 = 13.1 min.



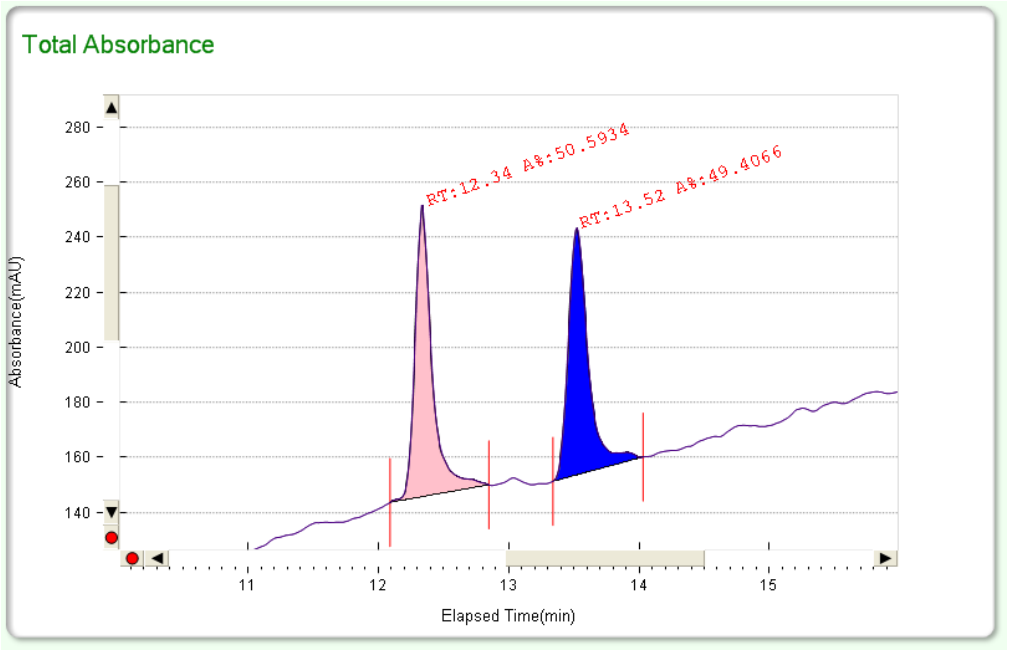
(±)-3l-ol



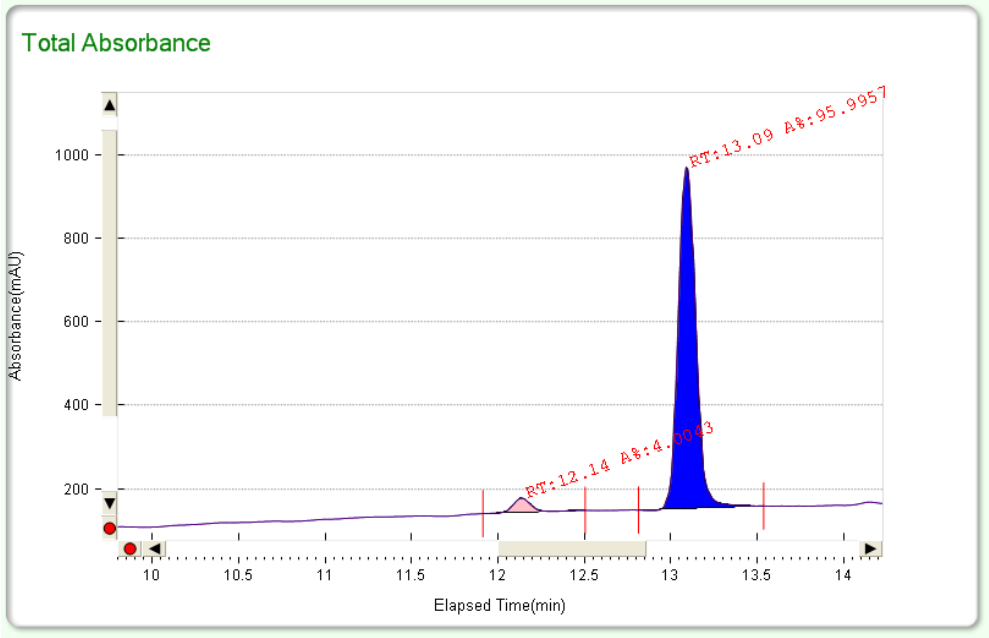
3l-ol



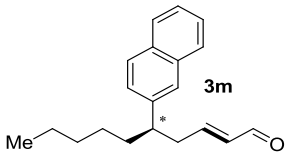
Separation of enantiomers by SFC. Chiralcel® Column AD-H, 40 °C, 5:95-20:80 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 12.1 min, t_2 = 13.1 min.



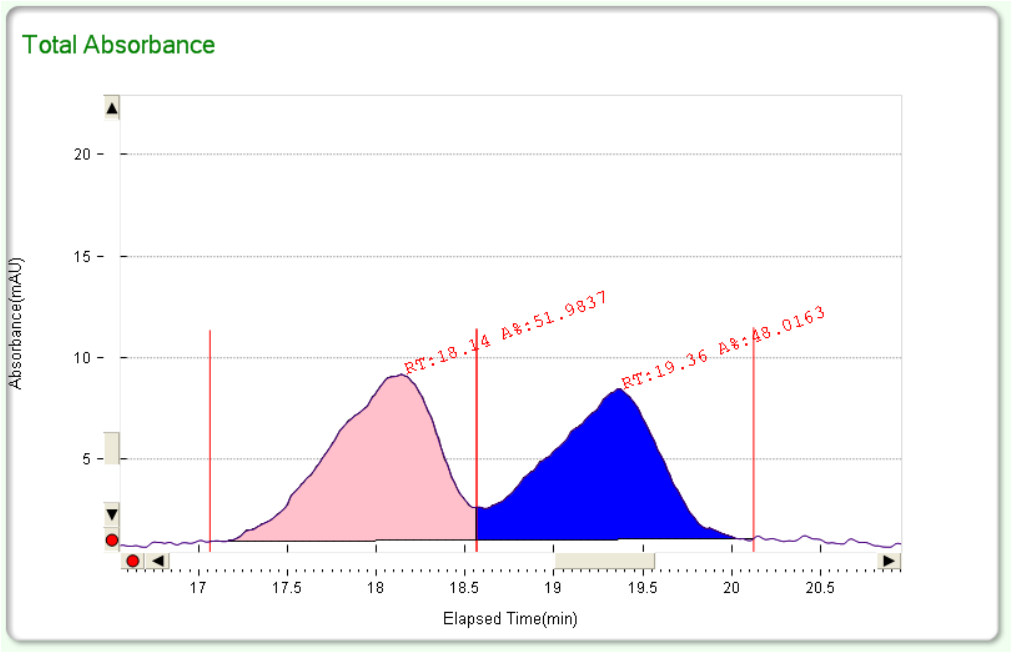
(±)-3l-ol



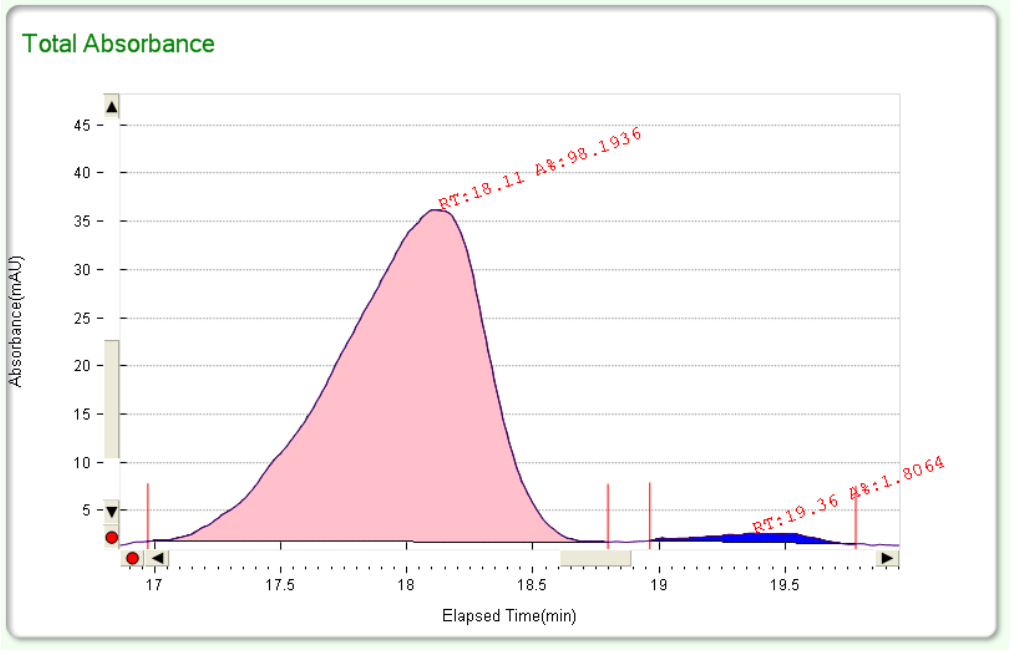
3l-ol (with Cu-Catalyst)



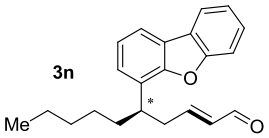
Separation of enantiomers by SFC. Chiralcel® Column OJ-H, 40 °C, 0:100-5:95 (25 min) (MeOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 18.1 min, t_2 = 19.4 min.



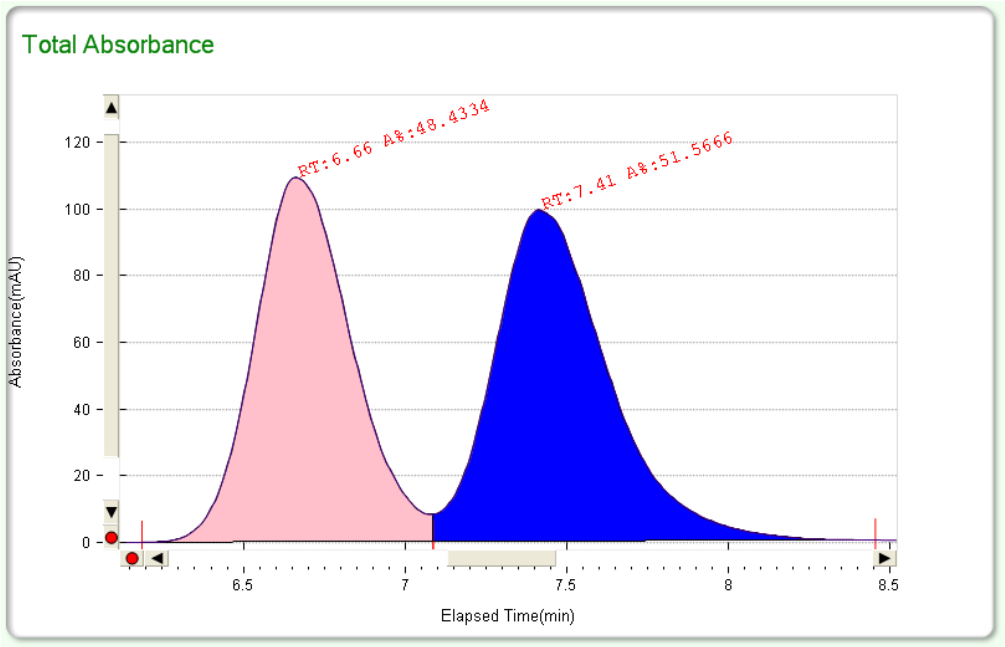
(±)-3m



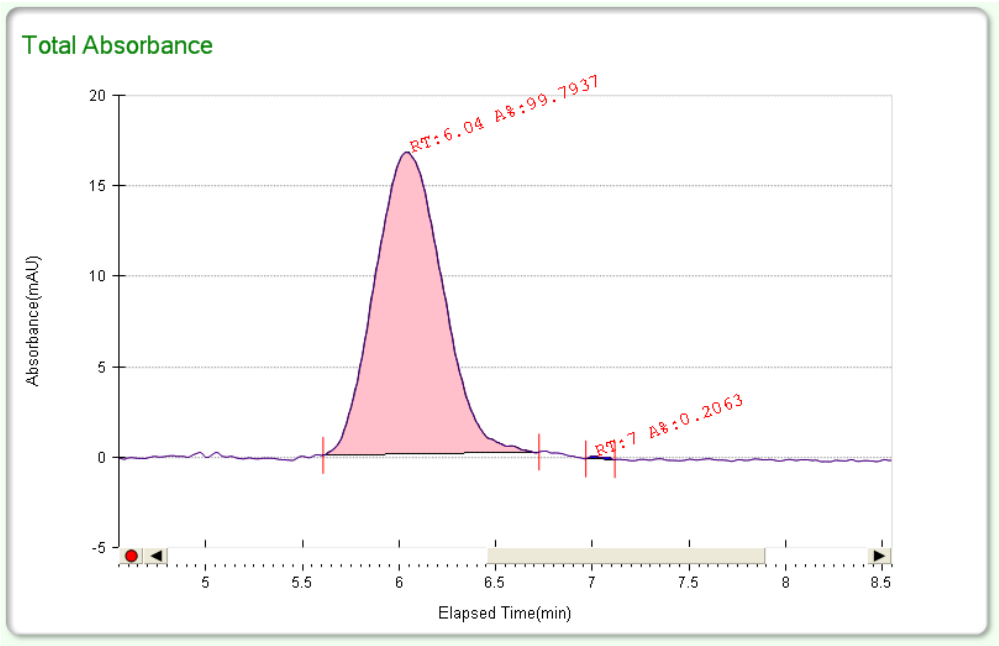
3m



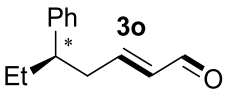
Separation of enantiomers by SFC. Chiralcel® Column AY-H, 40 °C, 0:100-5:95 (25 min) (MeOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 6.0 min, t_2 = 7.0 min.



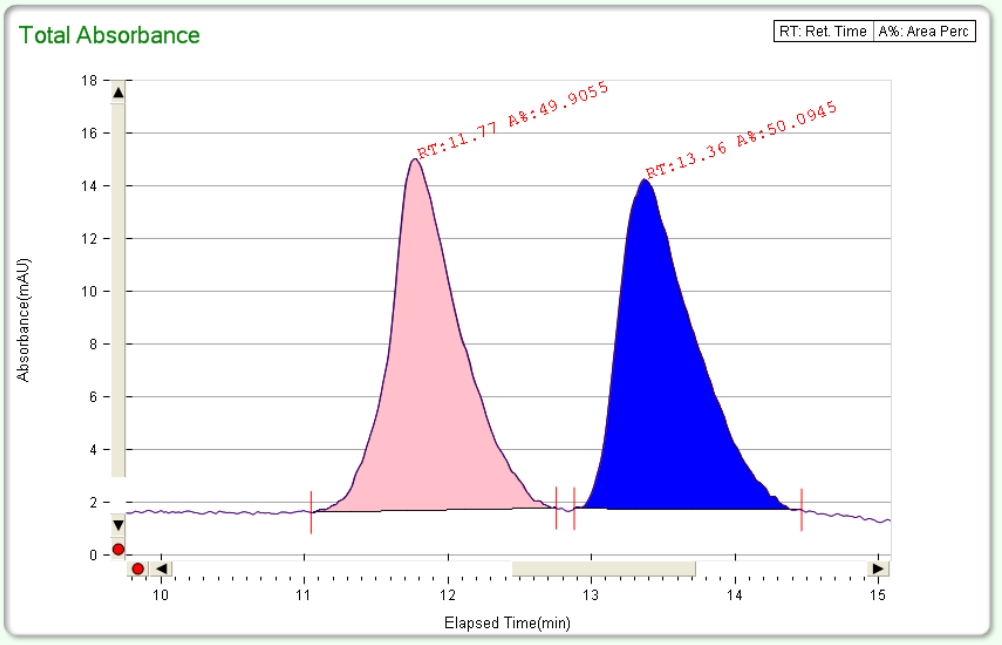
(±)-3n



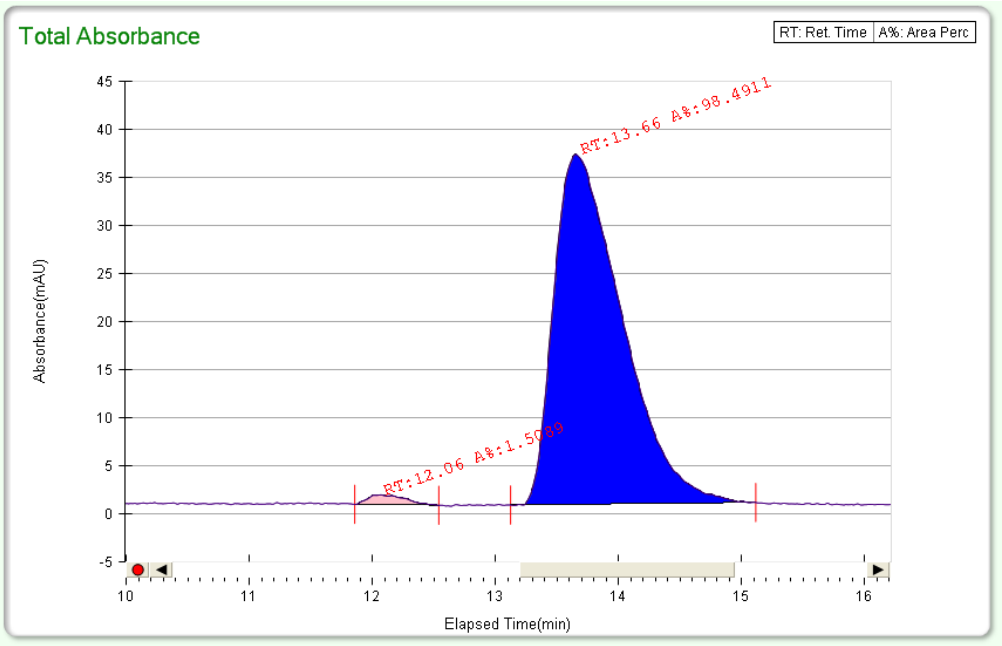
3n



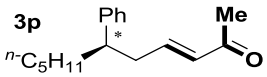
Separation of enantiomers by SFC. Chiralcel® ColumnOD, 40 °C, 0:100-5:95 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 12.1 min, t_2 = 13.7 min.



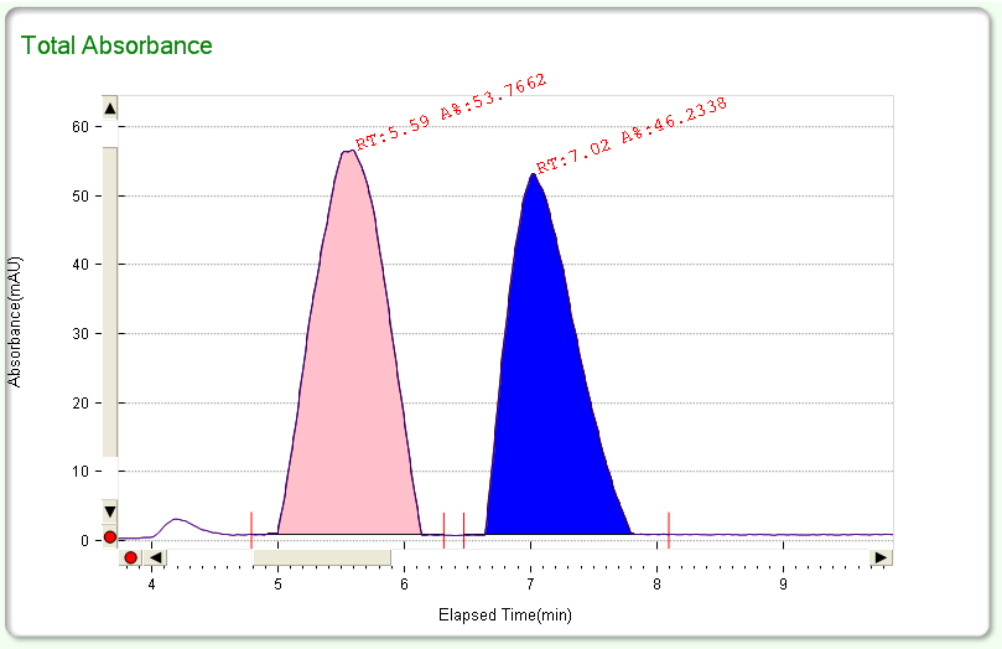
(±)-3o



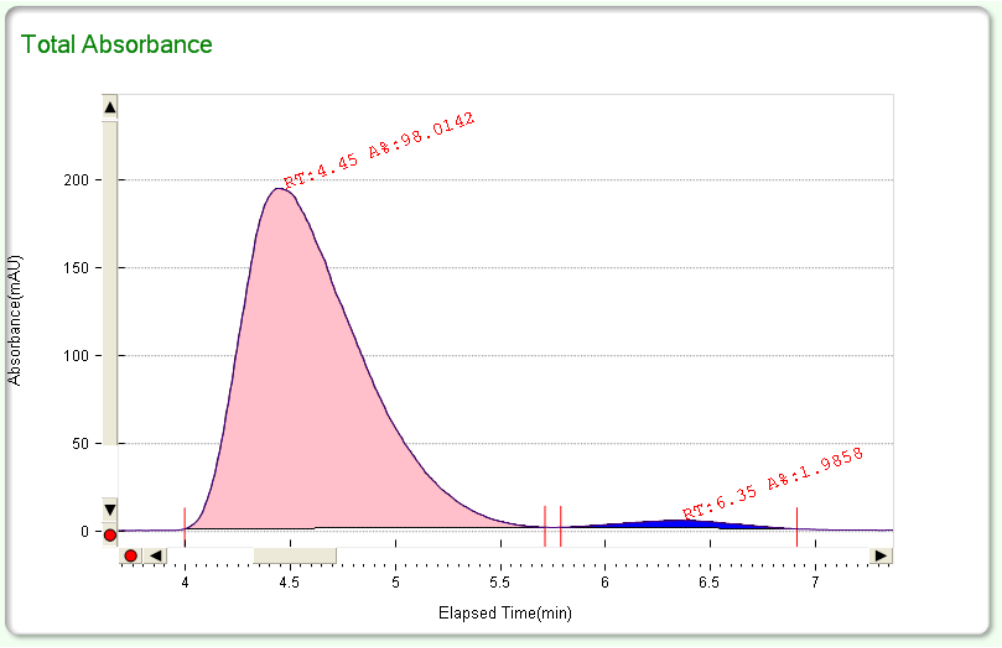
3o



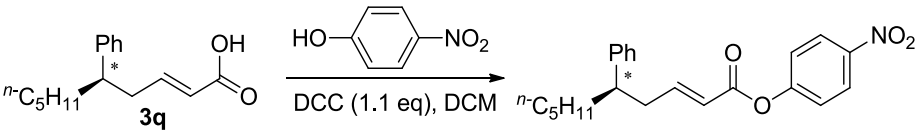
Separation of enantiomers by SFC. Chiralcel® Column AY-H, 40 ^{o}C, 0:100-1:99 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 4.5 min, t_2 = 6.4 min.



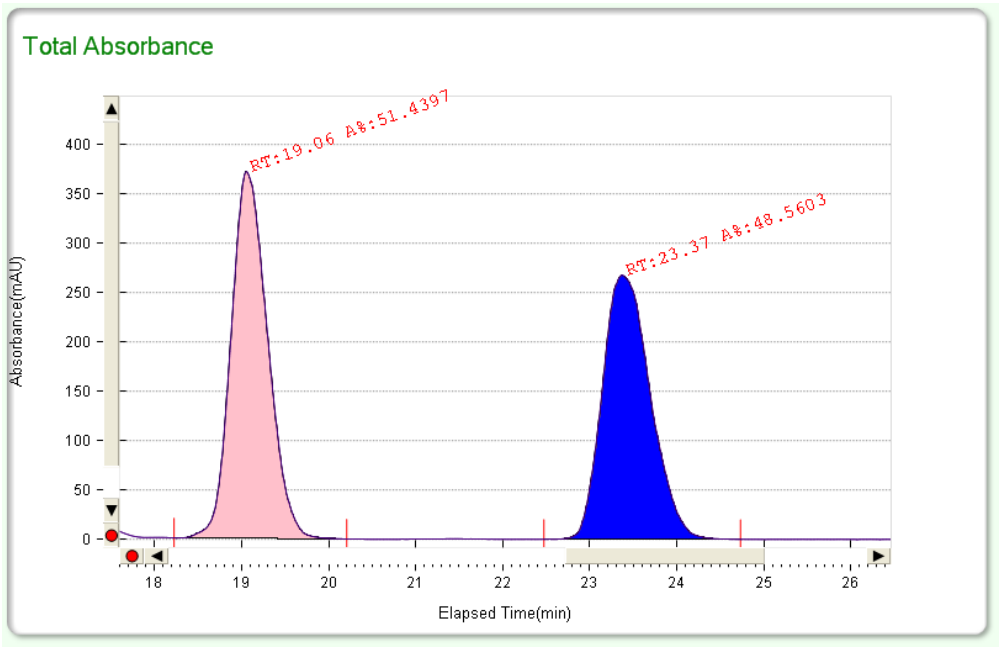
(±)-3p



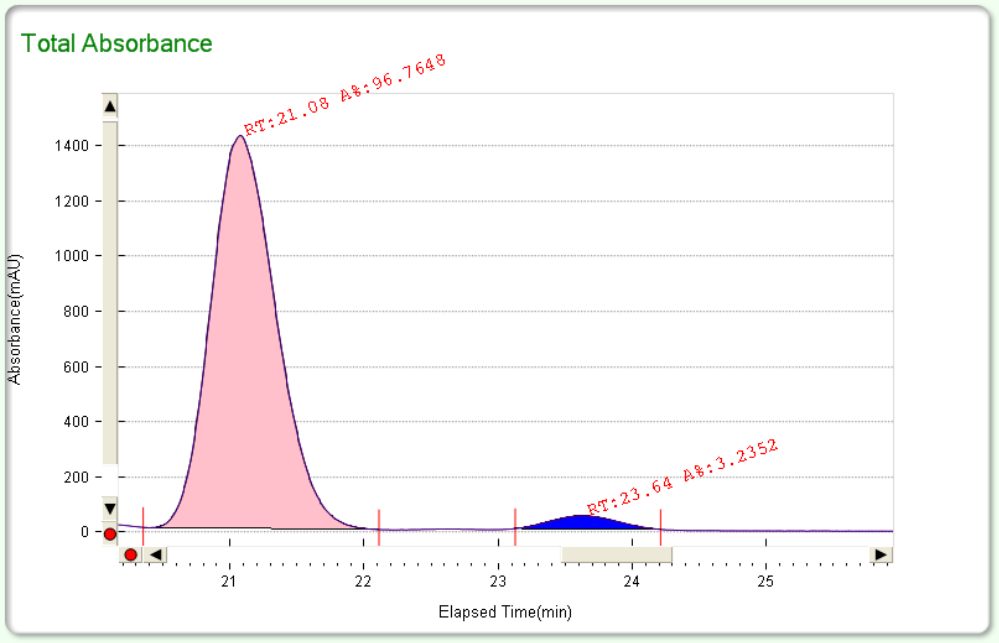
3p



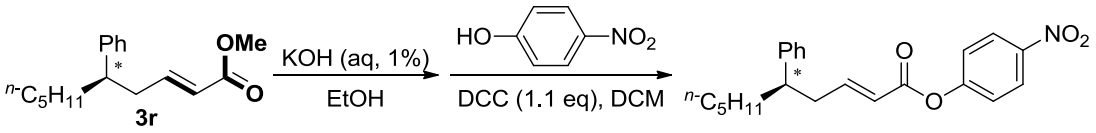
Separation of enantiomers by SFC. Chiralcel® Column OZ-H, 40 °C, 1:99-5:95 (25 min) (^{i}-PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 21.1 min, t_2 = 23.7 min.



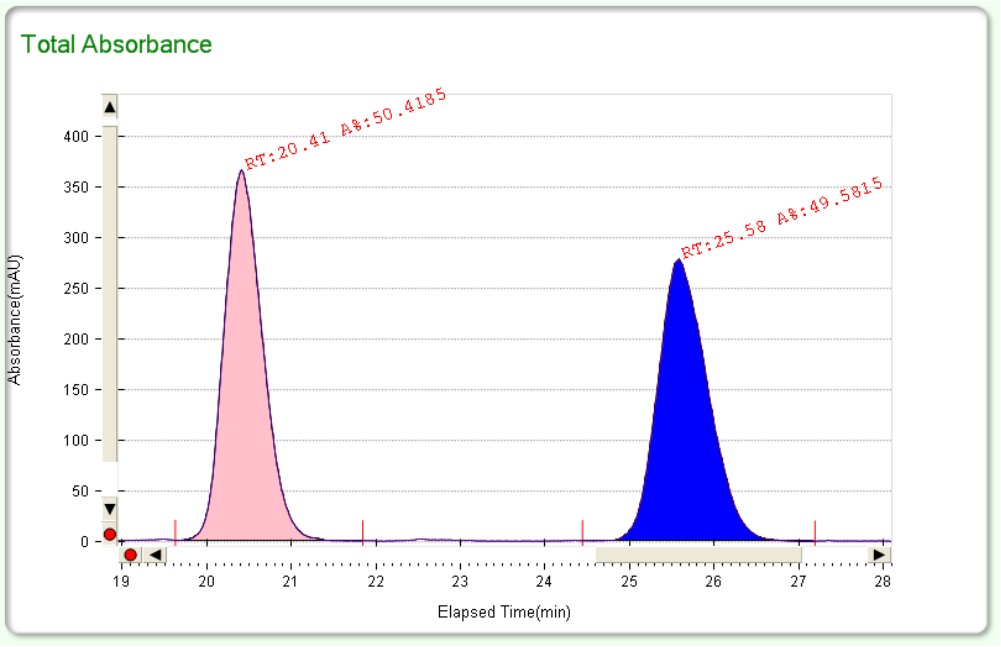
(±)-3q-esterification



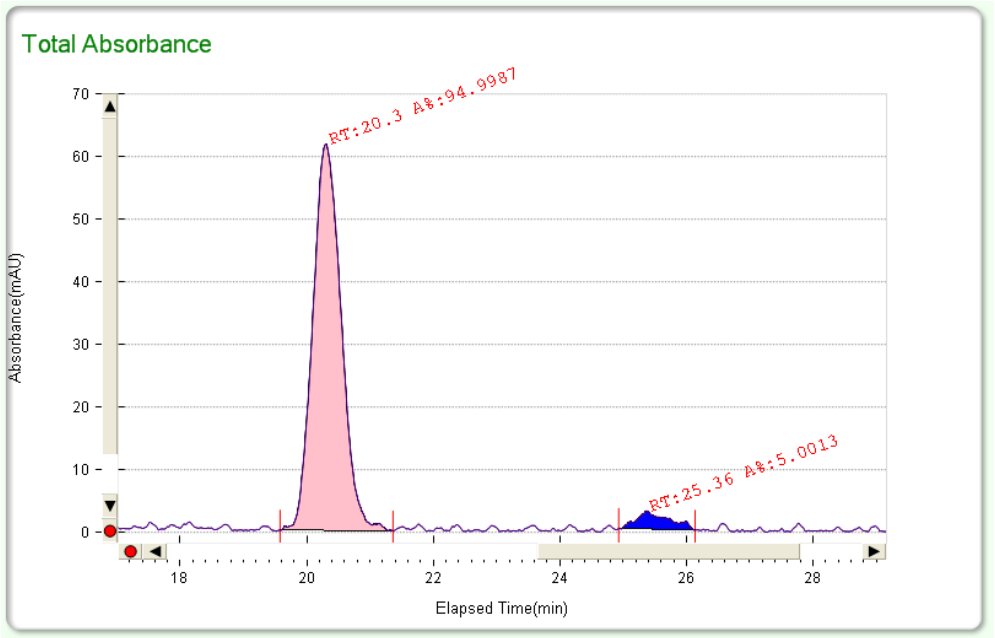
3q-esterification



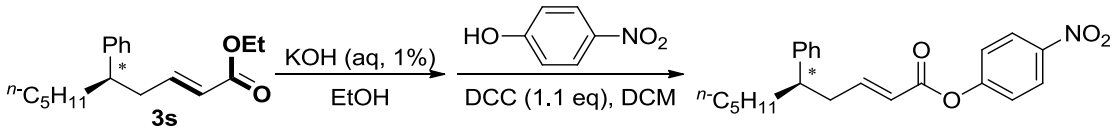
Separation of enantiomers by SFC. Chiralcel® Column OZ-H, 40 °C, 1:99-5:95 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 20.3 min, t_2 = 25.4 min.



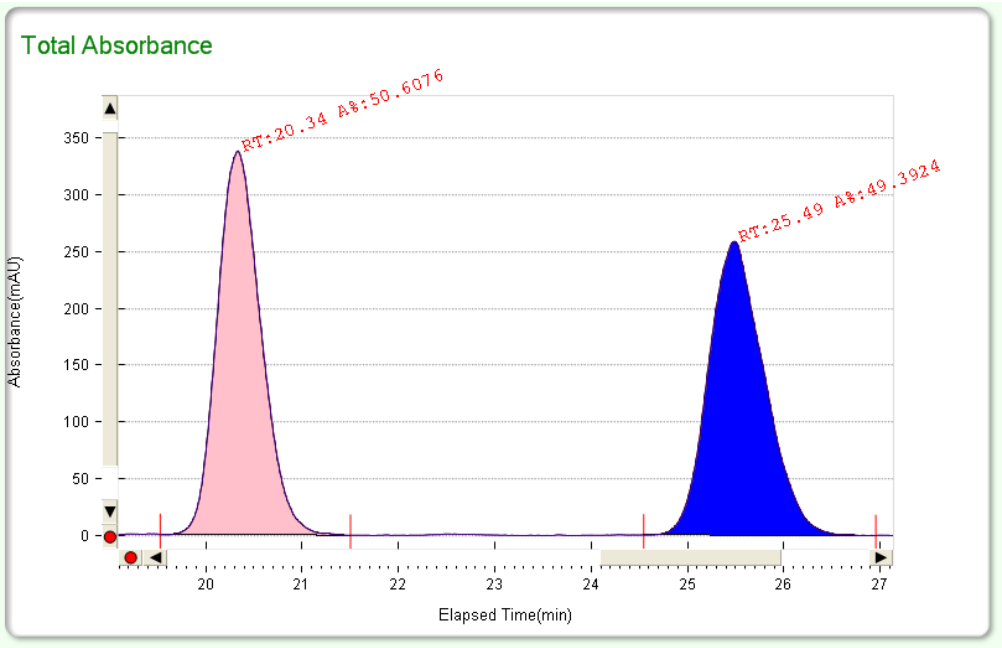
(±)-3r-transformation



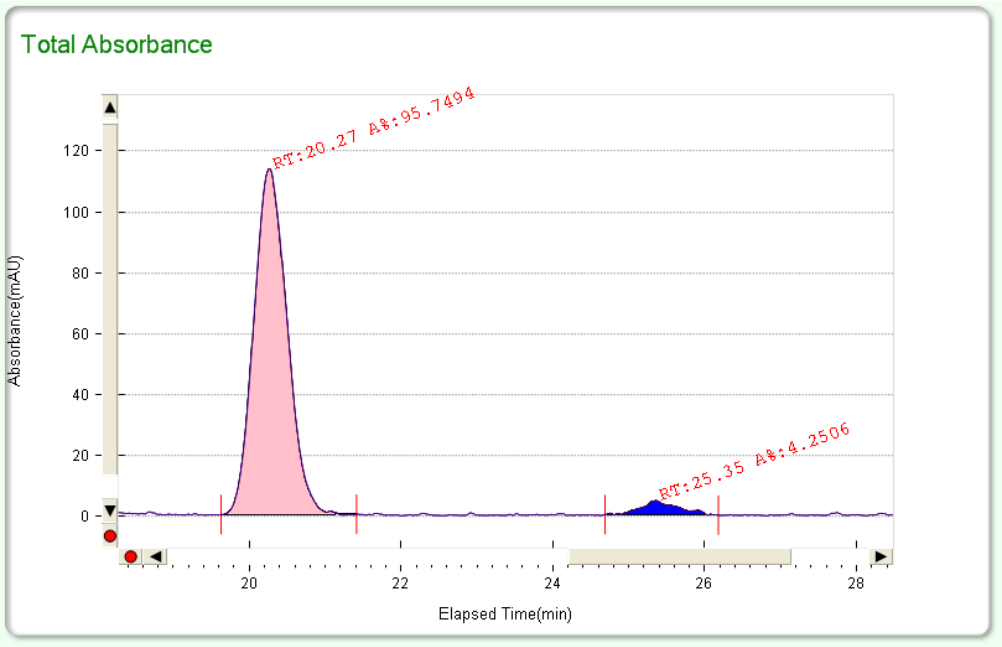
3r-transformation



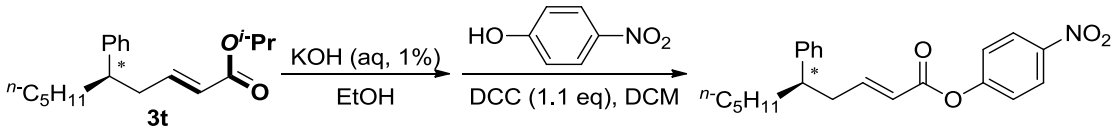
Separation of enantiomers by SFC. Chiralcel® Column OZ-H, 40 °C, 1:99-5:95 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 20.3 min, t_2 = 25.4 min.



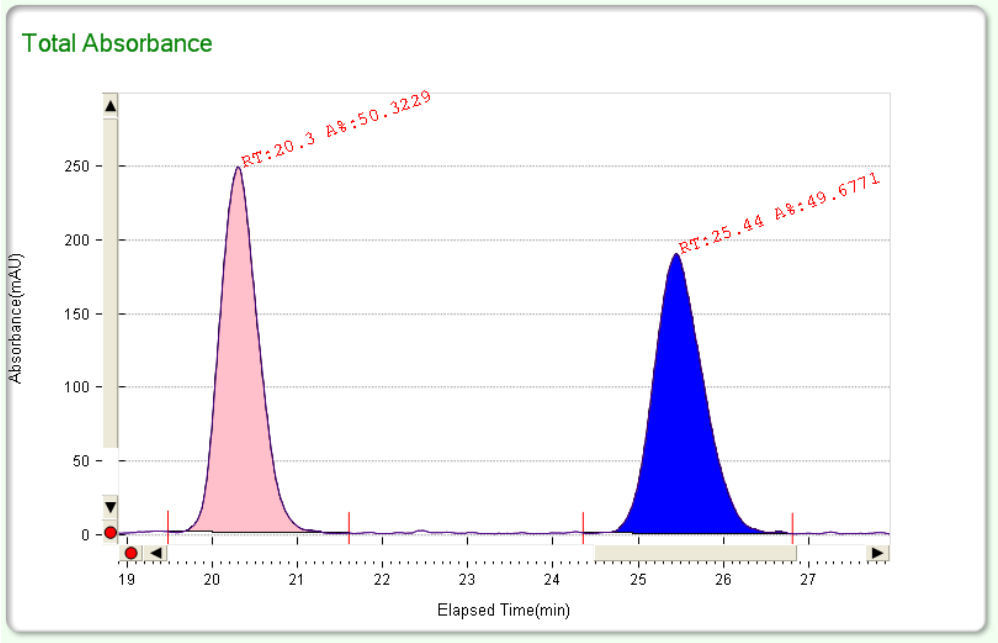
(±)-3s-transformation



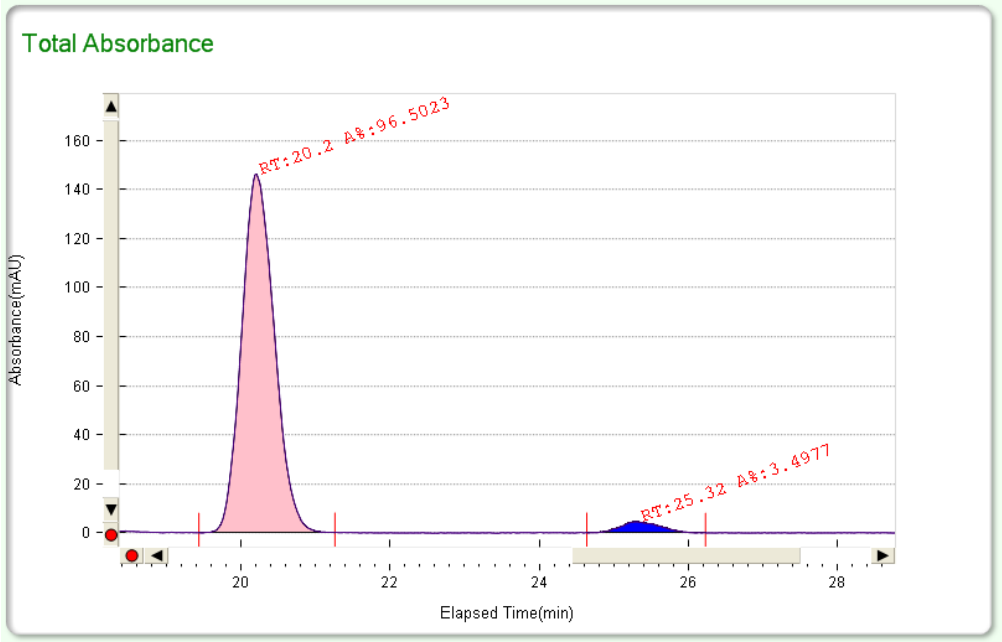
3s-transformation



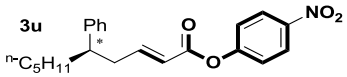
Separation of enantiomers by SFC. Chiralcel® Column OZ-H, 40 °C, 1:99-5:95 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 20.2 min, t_2 = 25.3 min.



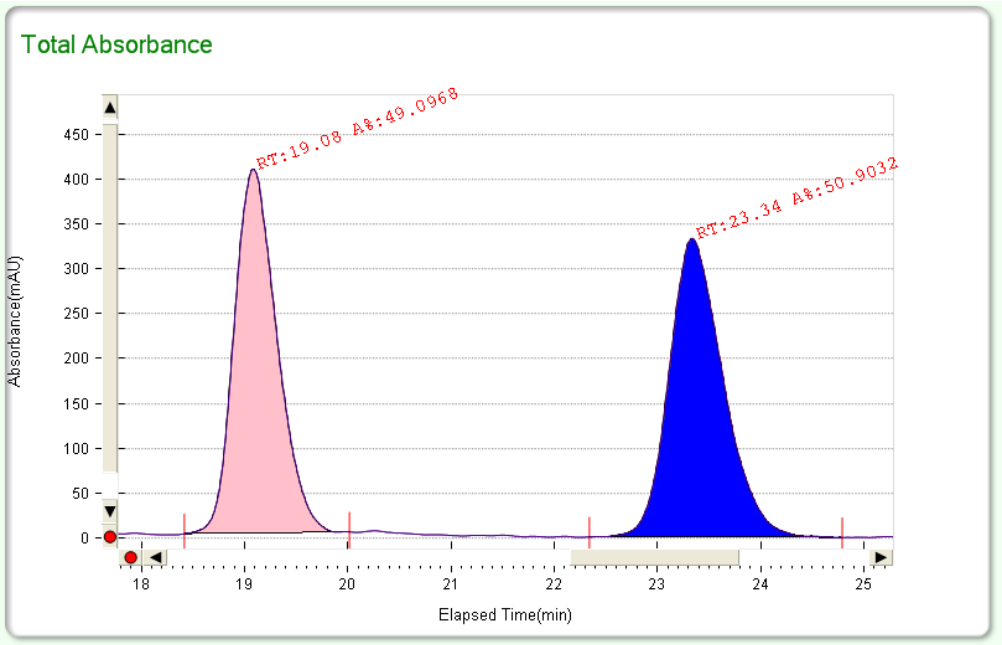
(±)-3t-transformation



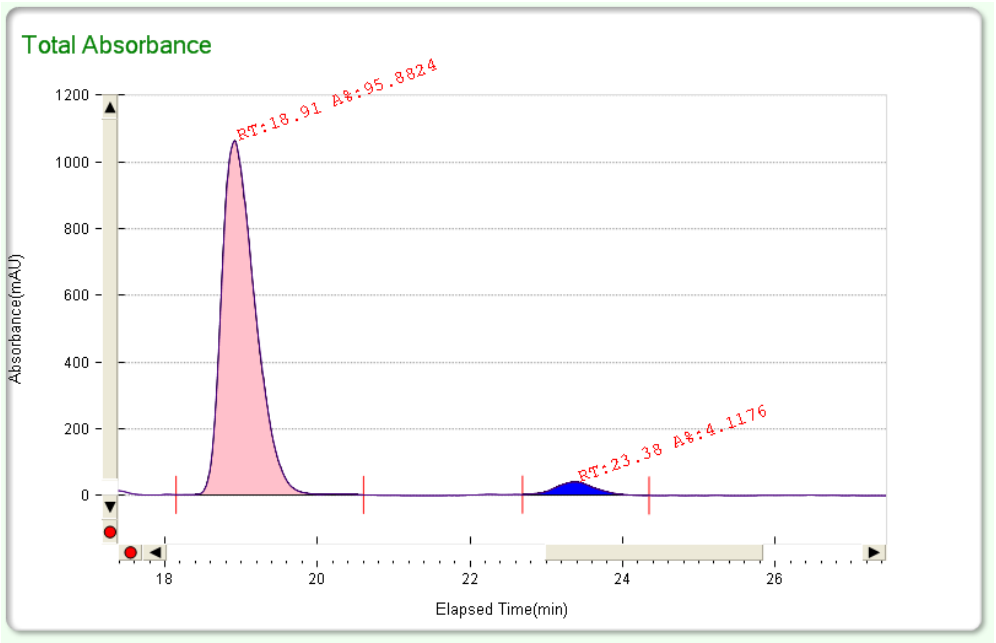
3t-transformation



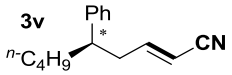
Separation of enantiomers by SFC. Chiralcel® Column OZ-H, 40 °C, 1:99-5:95 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 18.9 min, t_2 = 23.4 min.



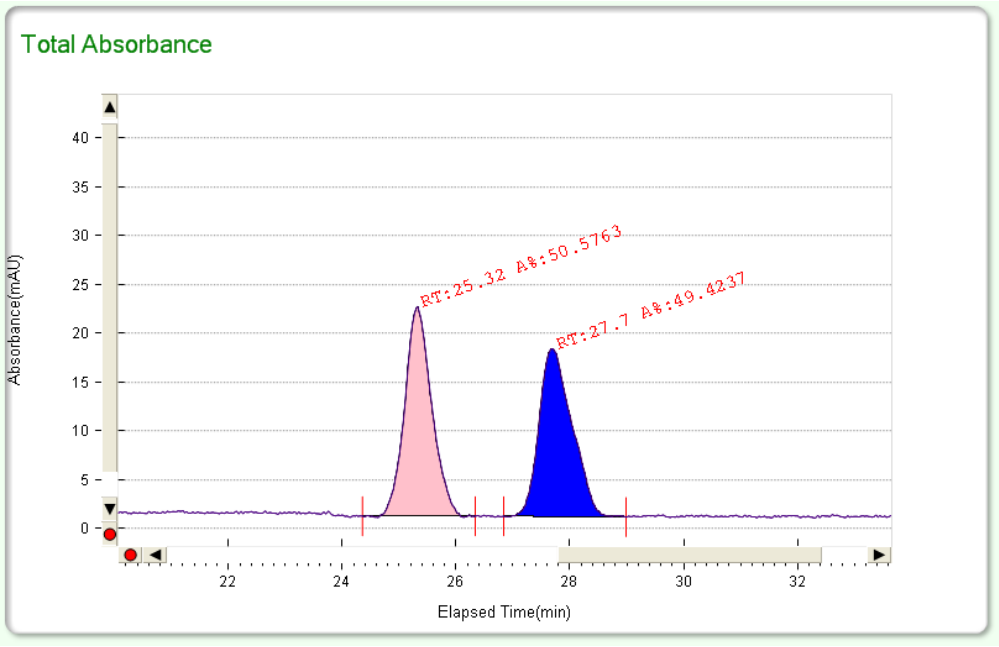
(±)-3u



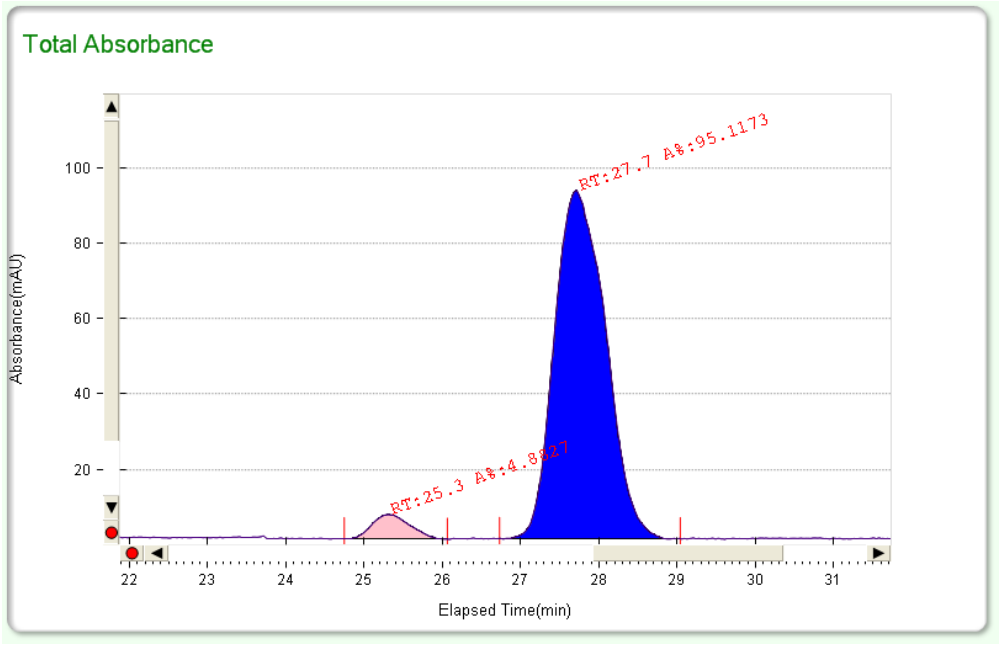
3u



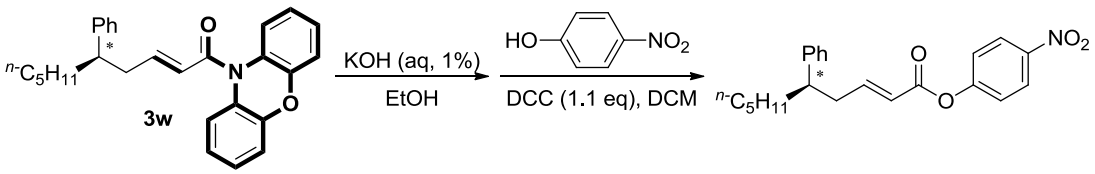
Separation of enantiomers by SFC. Chiralcel® Column OJ-H, 40 °C, 0:100-1:99 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 25.3 min, t_2 = 27.7 min.



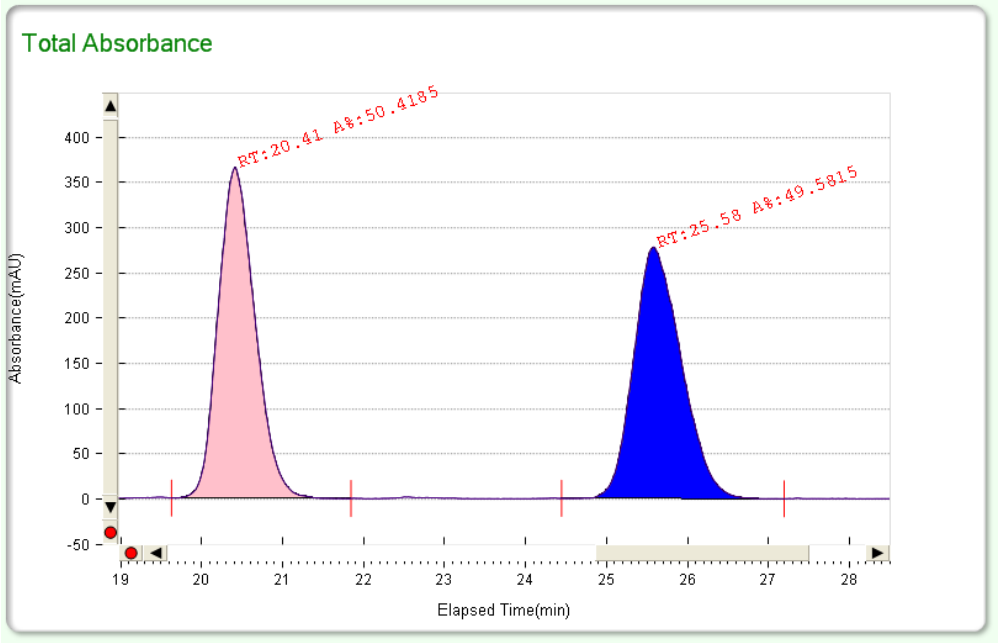
(±)-3v



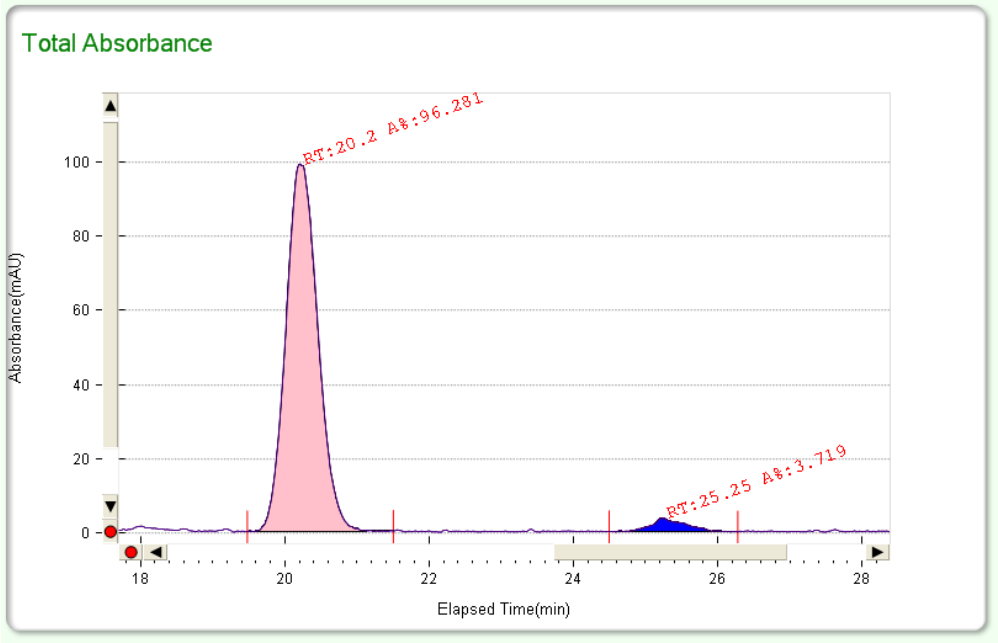
3v



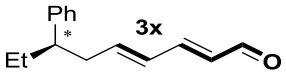
Separation of enantiomers by SFC. Chiralcel® Column OZ-H, 40 °C, 1:99-5:95 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 20.2 min, t_2 = 25.3 min.



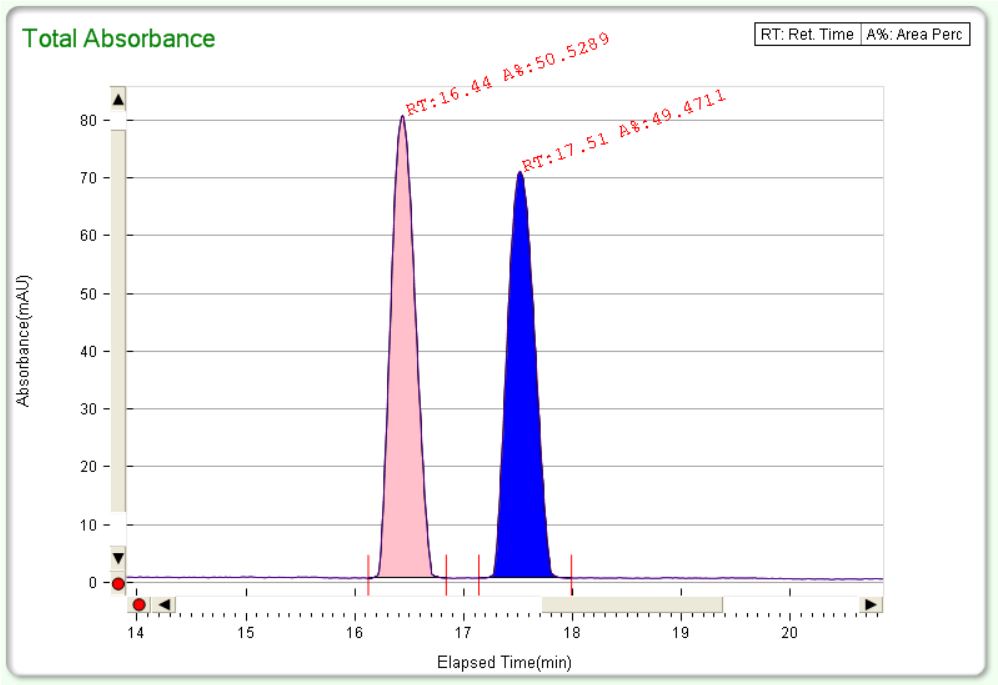
(±)-3w-transformation



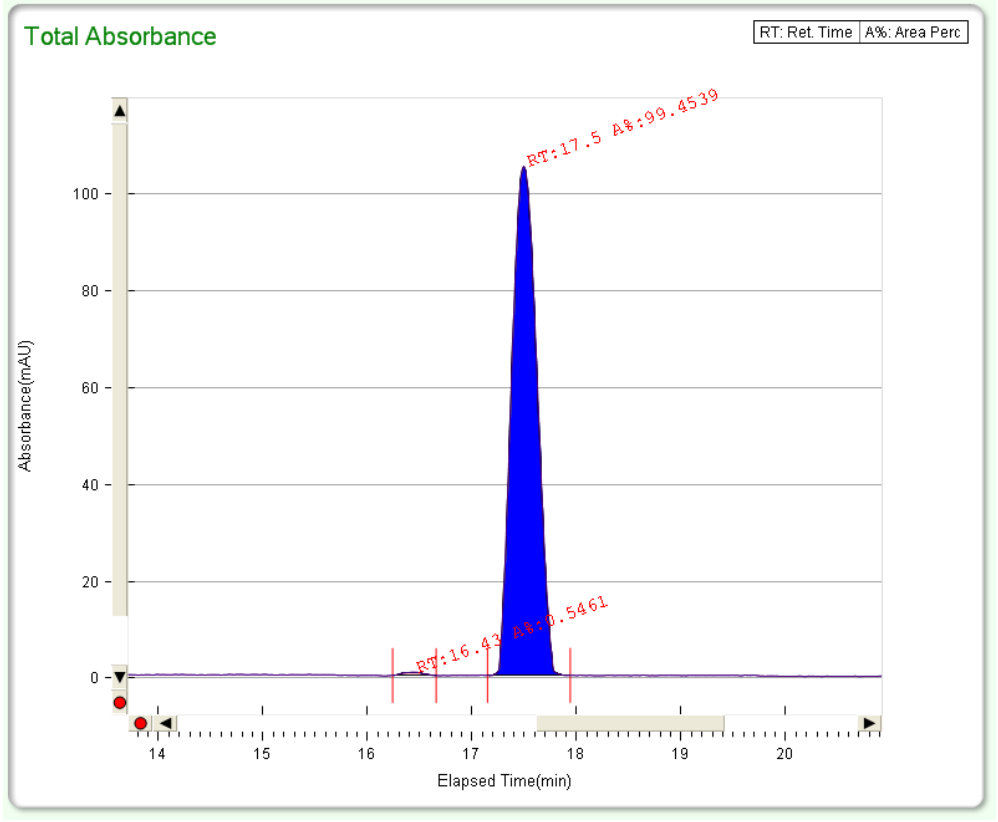
3w-transformation



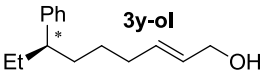
Separation of enantiomers by SFC. Chiralcel® Column OD, 40 °C, 0:100-2:98 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 16.4 min, t_2 = 17.5 min.



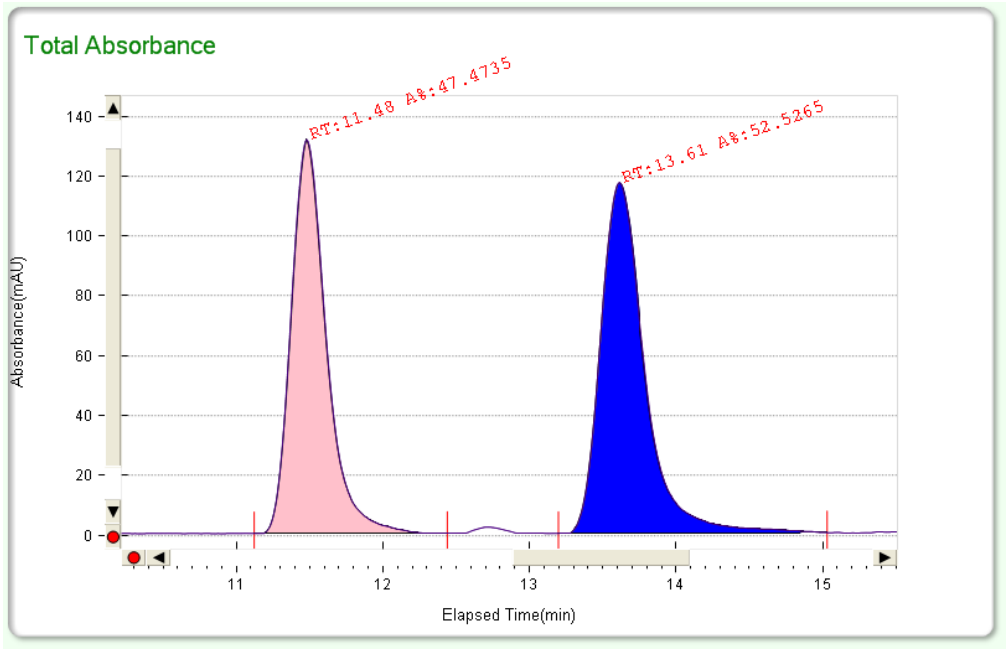
(±)-3x



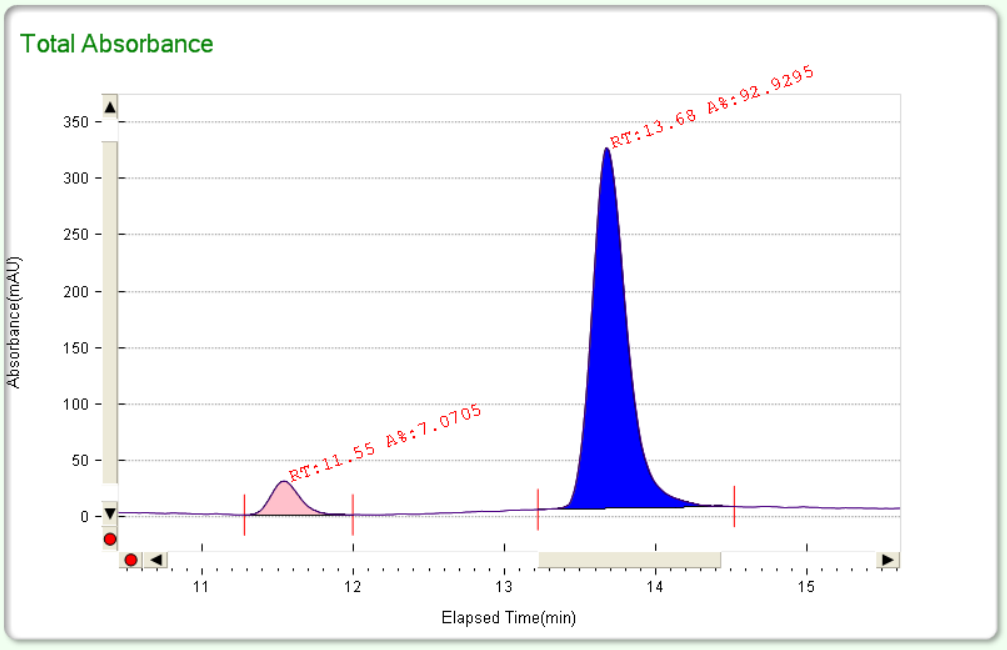
3x



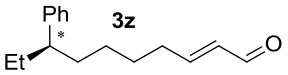
Separation of enantiomers by SFC. Chiralcel® Column OJ-H, 40 °C, 5:95 (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 11.6 min, t_2 = 13.6 min.



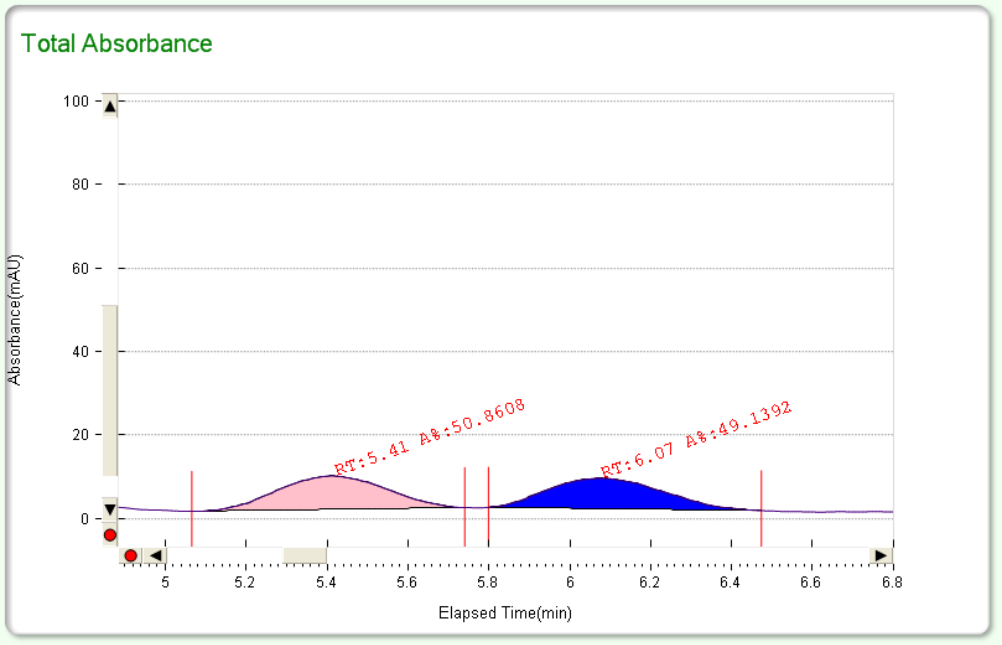
(±)-3y-ol



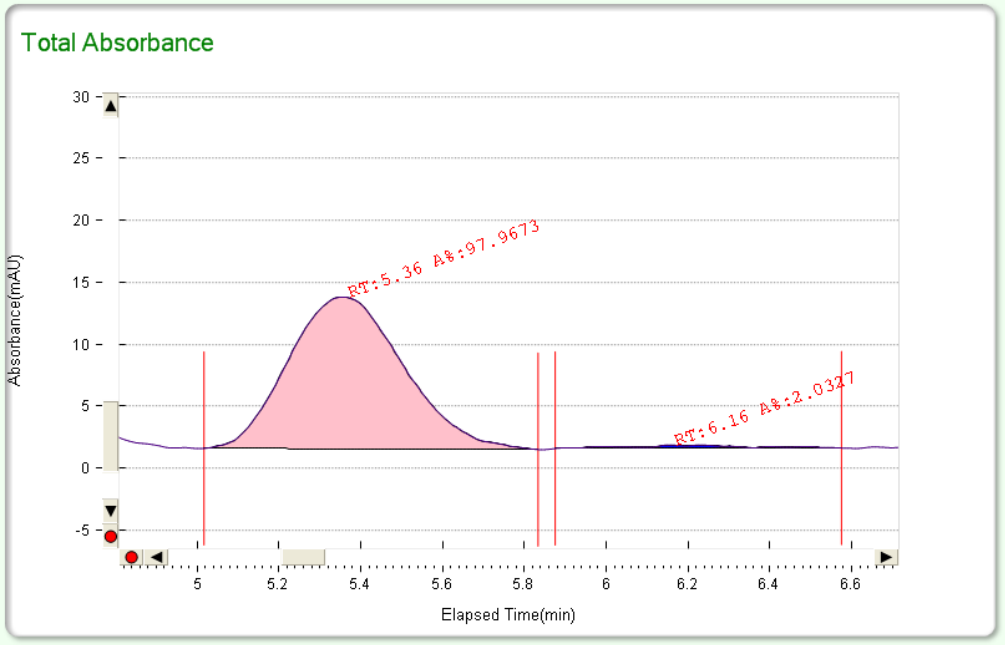
3y-ol



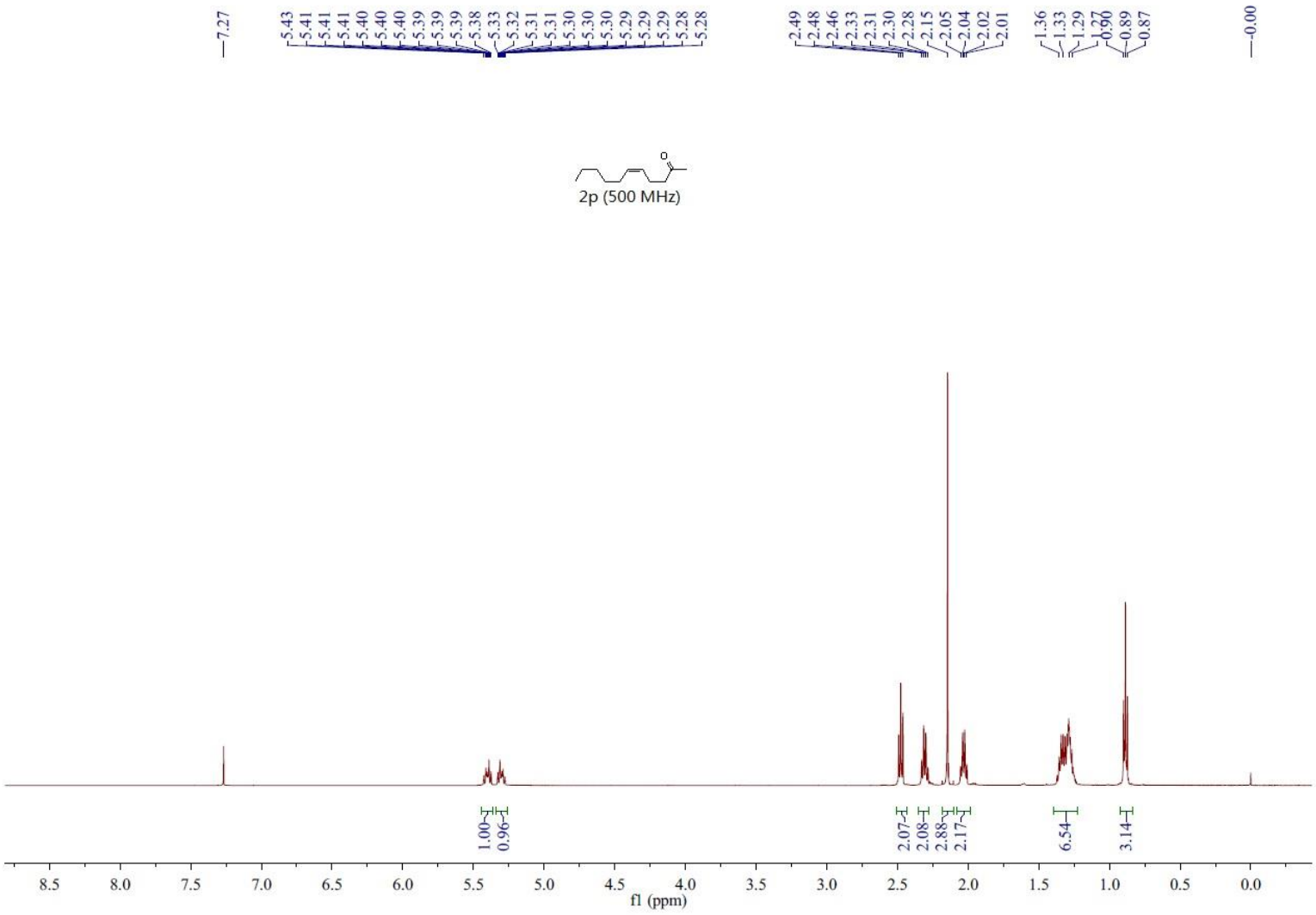
Separation of enantiomers by SFC. Chiralcel® Column AY-H, 40 °C, 0:100-5:99 (25 min) (^{i}PrOH:CO_2), 2mL/min, 160 bar, and 40°C; t_1 = 5.4 min, t_2 = 6.2 min.

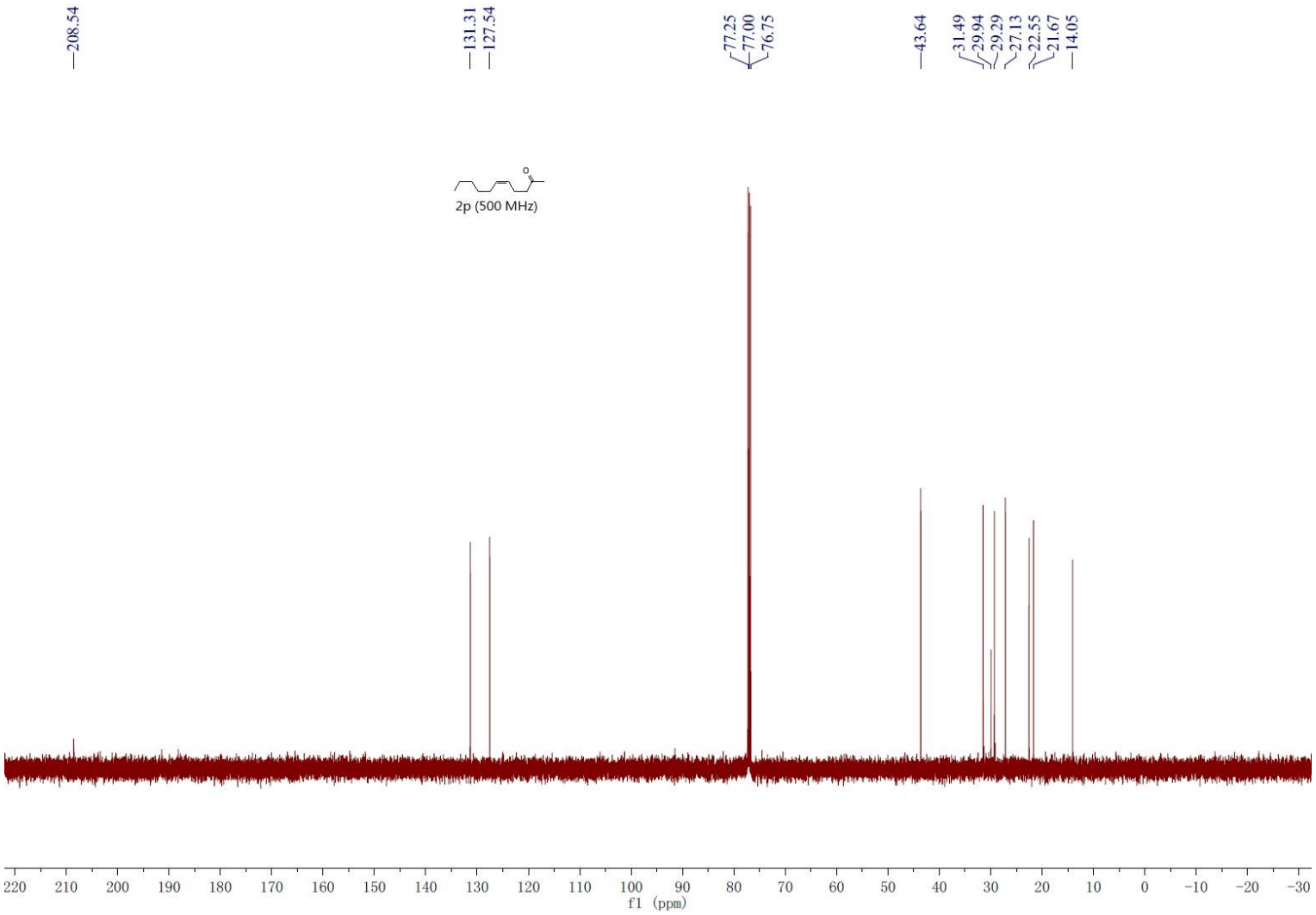


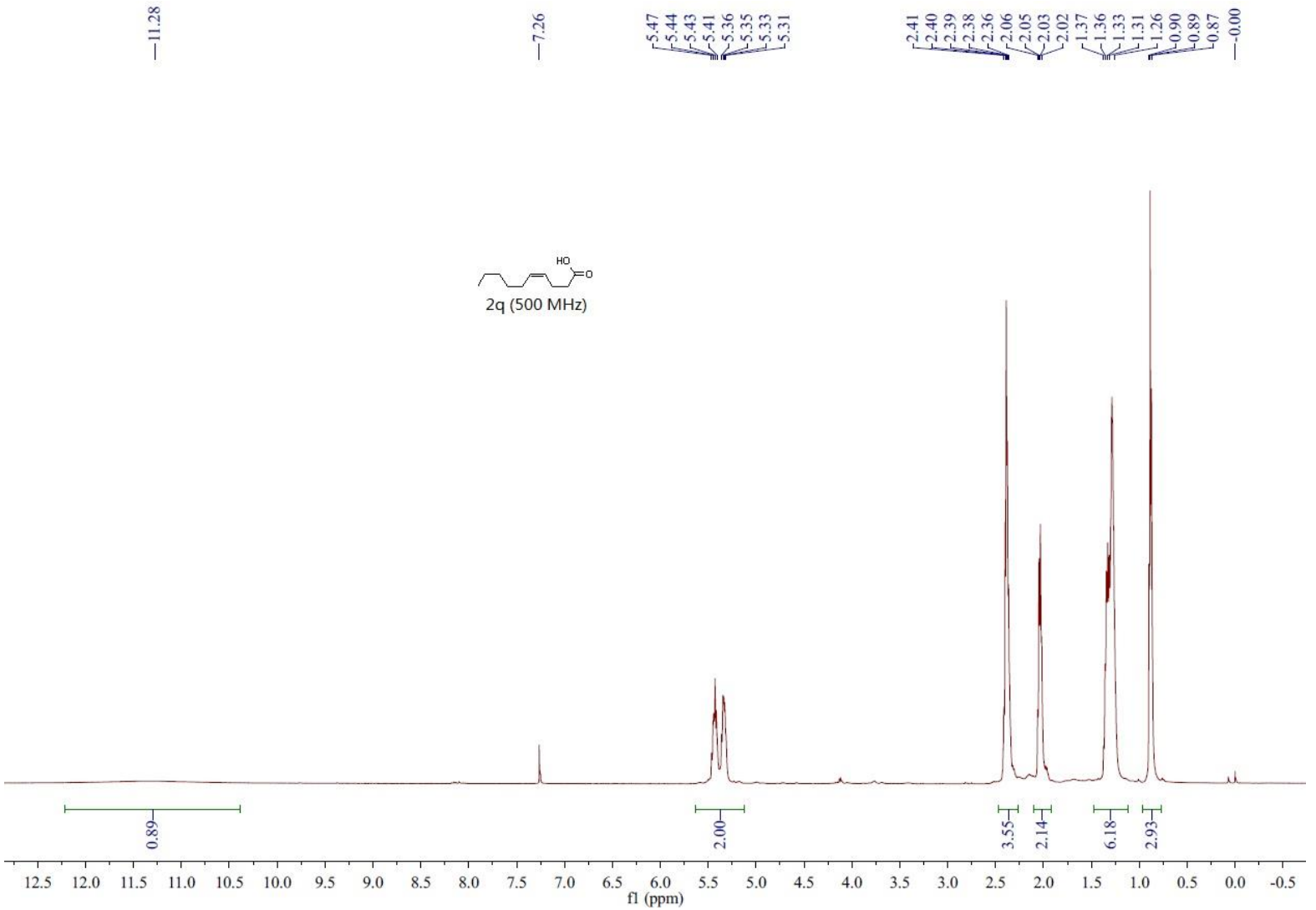
(±)-3z

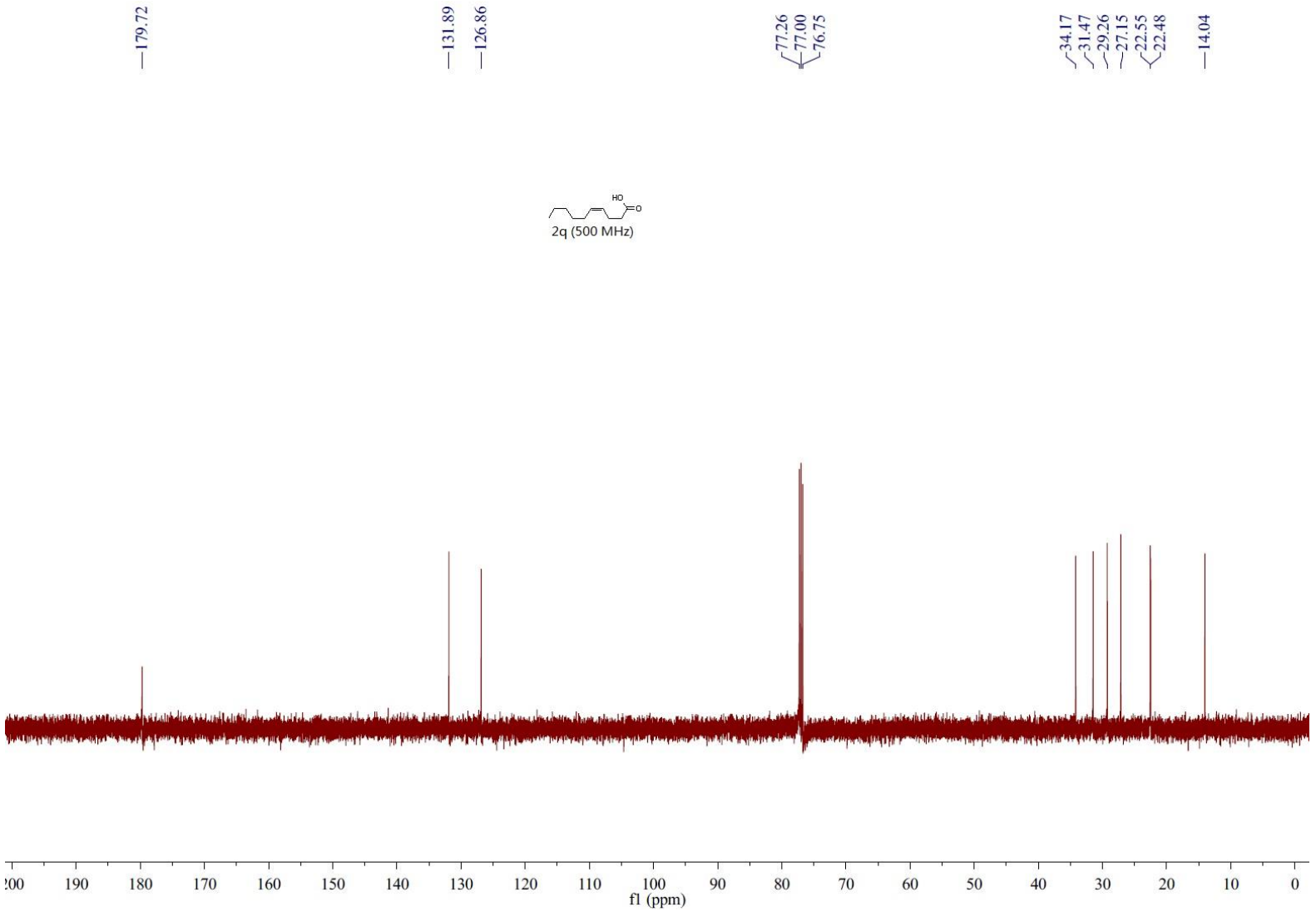


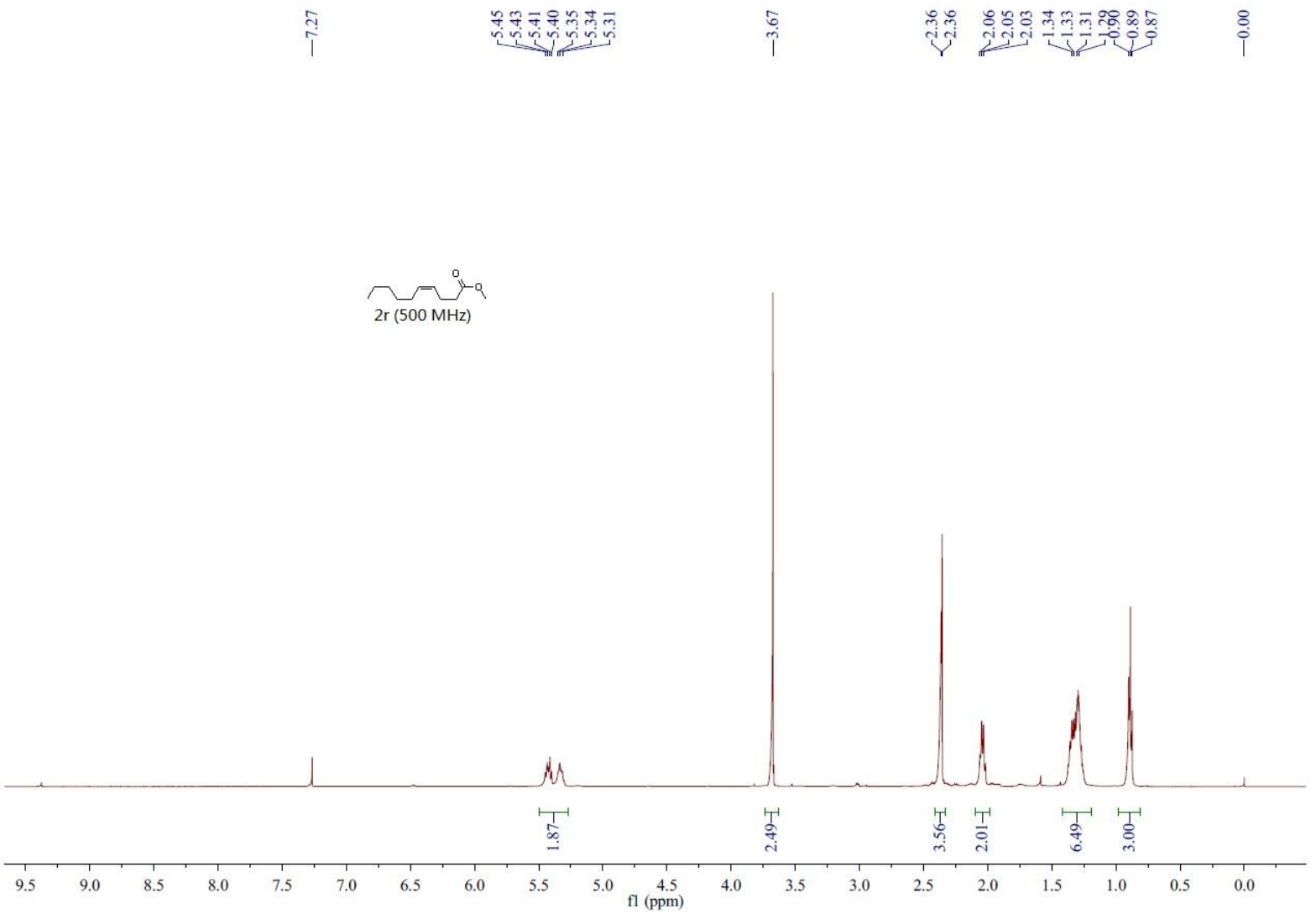
3z

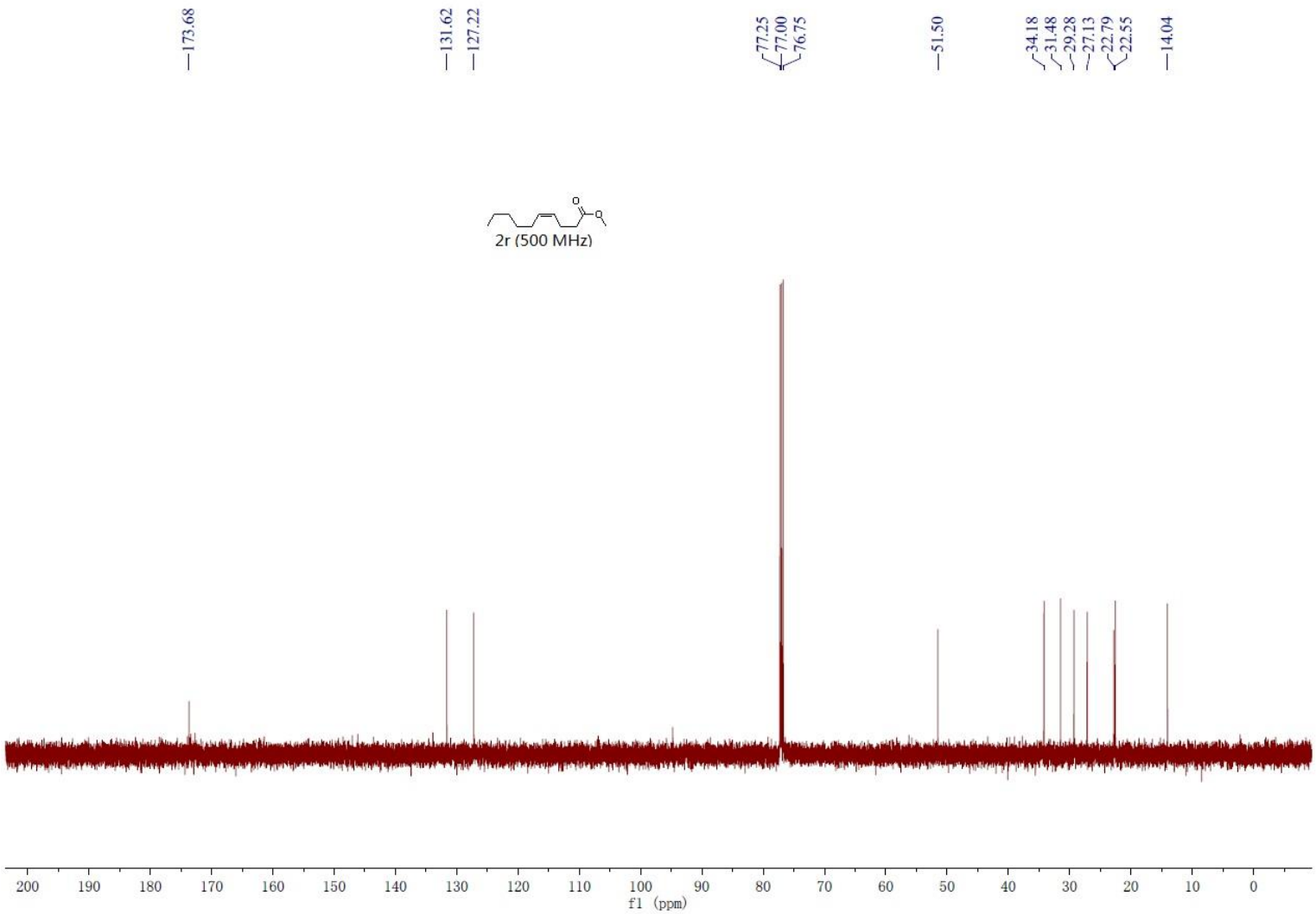

7.27
5.43
5.41
5.41
5.41
5.40
5.40
5.40
5.39
5.39
5.39
5.38
5.33
5.32
5.31
5.31
5.30
5.30
5.30
5.29
5.29
5.29
5.28
5.28
2.49
2.48
2.46
2.33
2.31
2.30
2.28
2.15
2.05
2.04
2.02
2.01
1.36
1.33
1.29
1.27
0.90
0.89
0.87
0.00
O
2p (500 MHz)
1.00
0.96
2.07
2.08
2.88
2.17
6.54
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

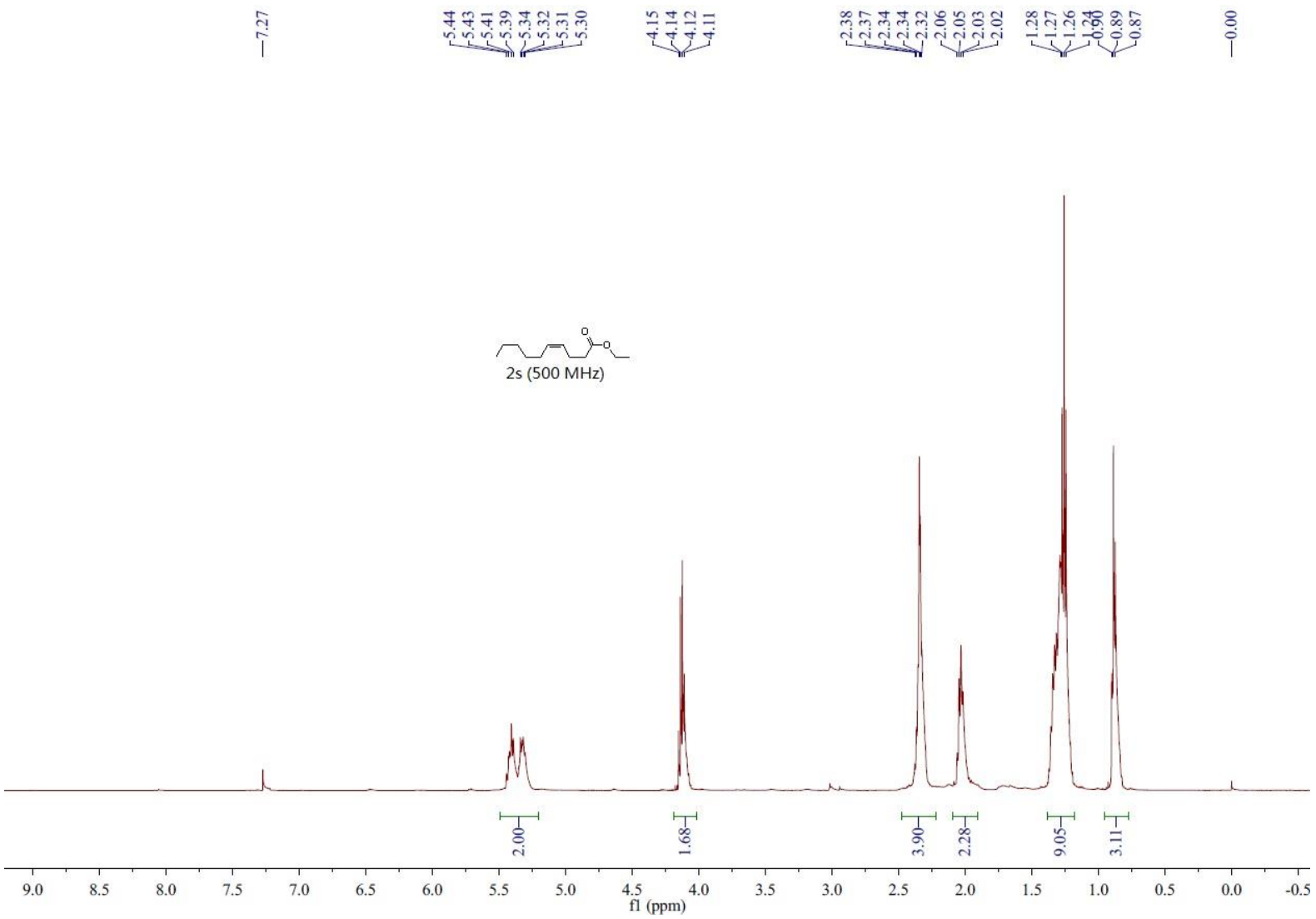

208.54
131.31
127.54
77.25
77.00
76.75
43.64
31.49
29.94
29.29
27.13
22.55
21.67
14.05
2p (500 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)

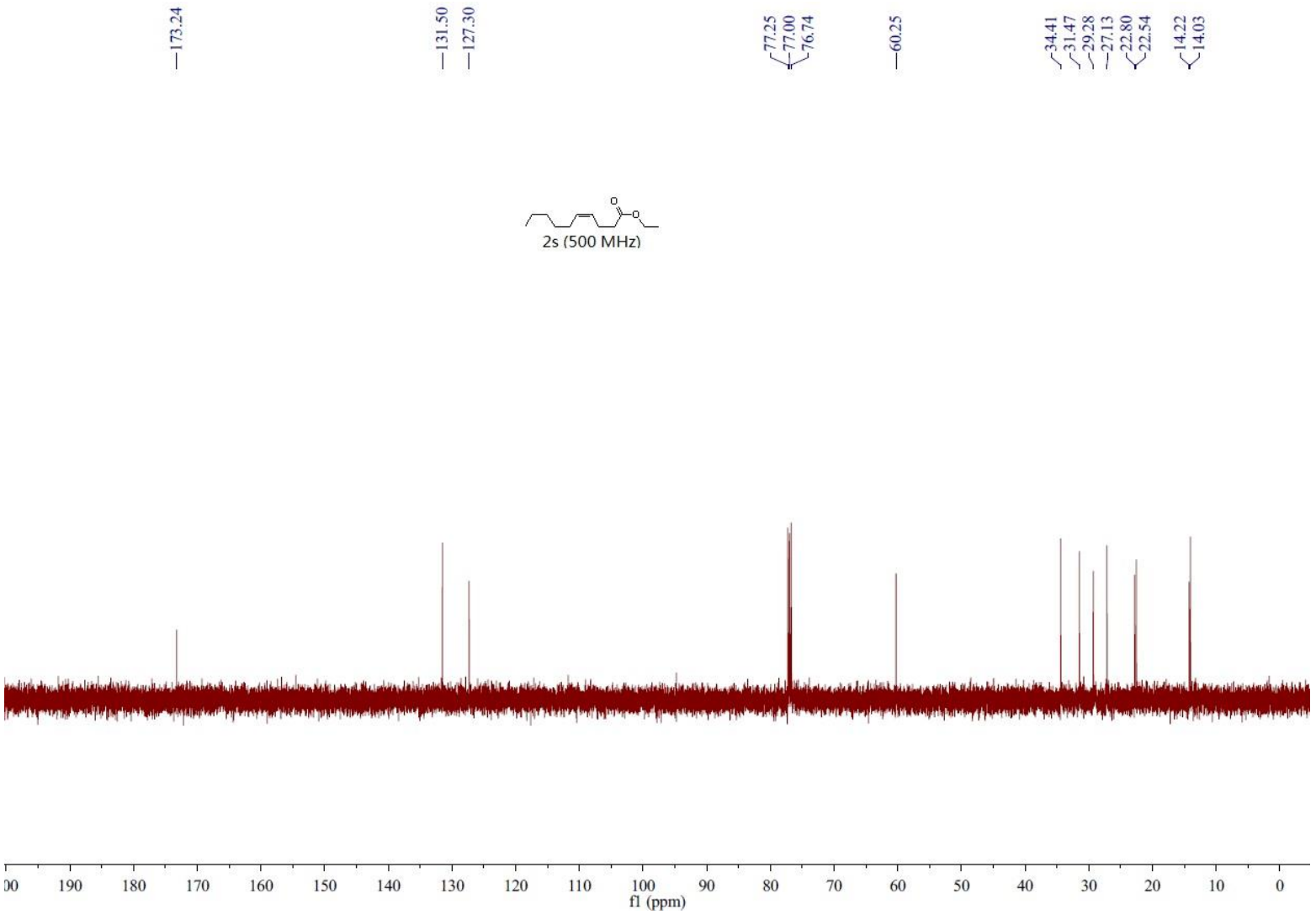

11.28
7.26
5.47
5.44
5.43
5.41
5.36
5.35
5.33
5.31
2.41
2.40
2.39
2.38
2.36
2.06
2.05
2.03
2.02
1.37
1.36
1.33
1.31
1.26
0.90
0.89
0.87
-0.00
HO
O
2q (500 MHz)
0.89
2.00
3.55
2.14
6.18
2.93
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

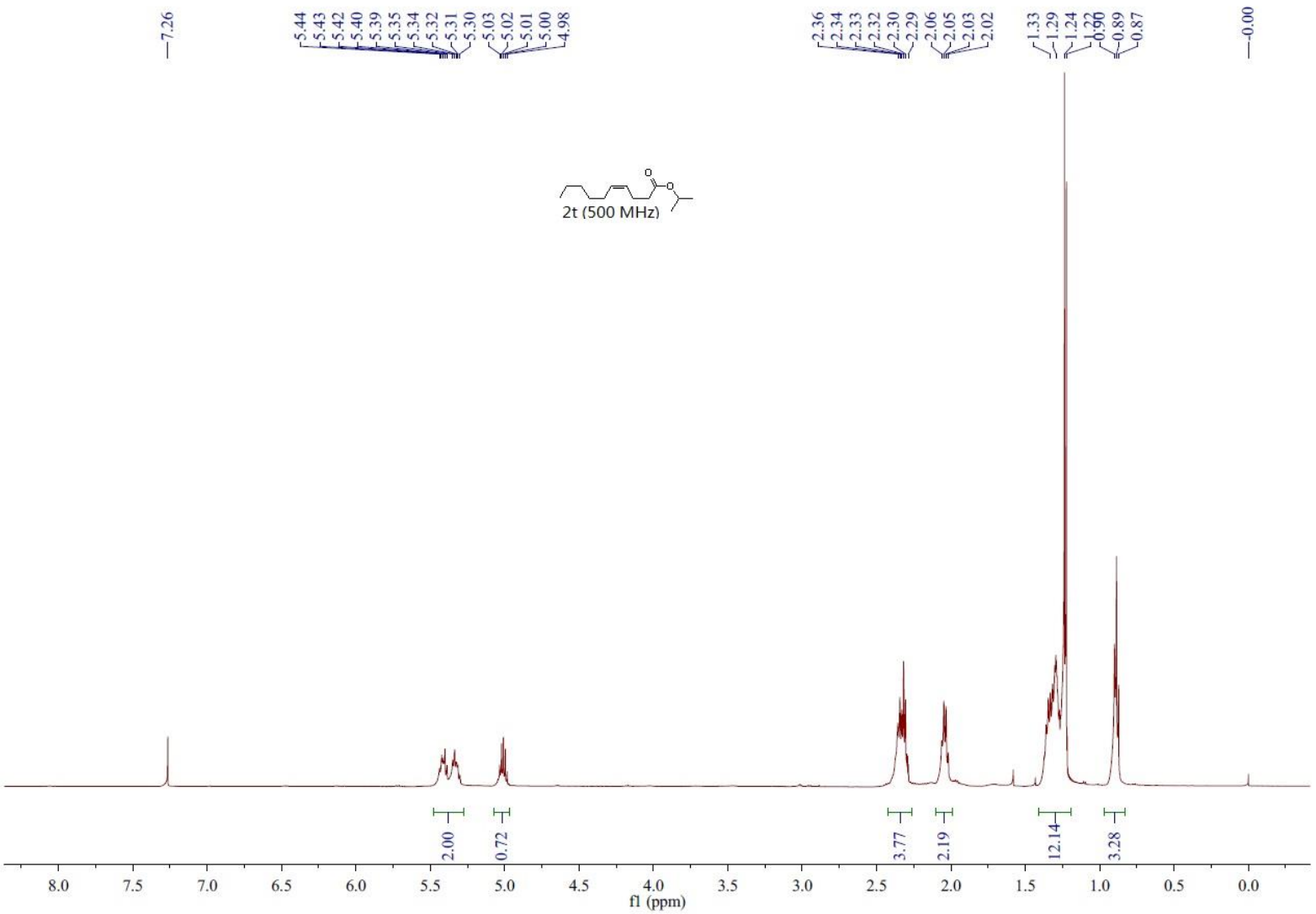

179.72
131.89
126.86
77.26
77.00
76.75
34.17
31.47
29.26
27.15
22.55
22.48
14.04
HO
O
2q (500 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

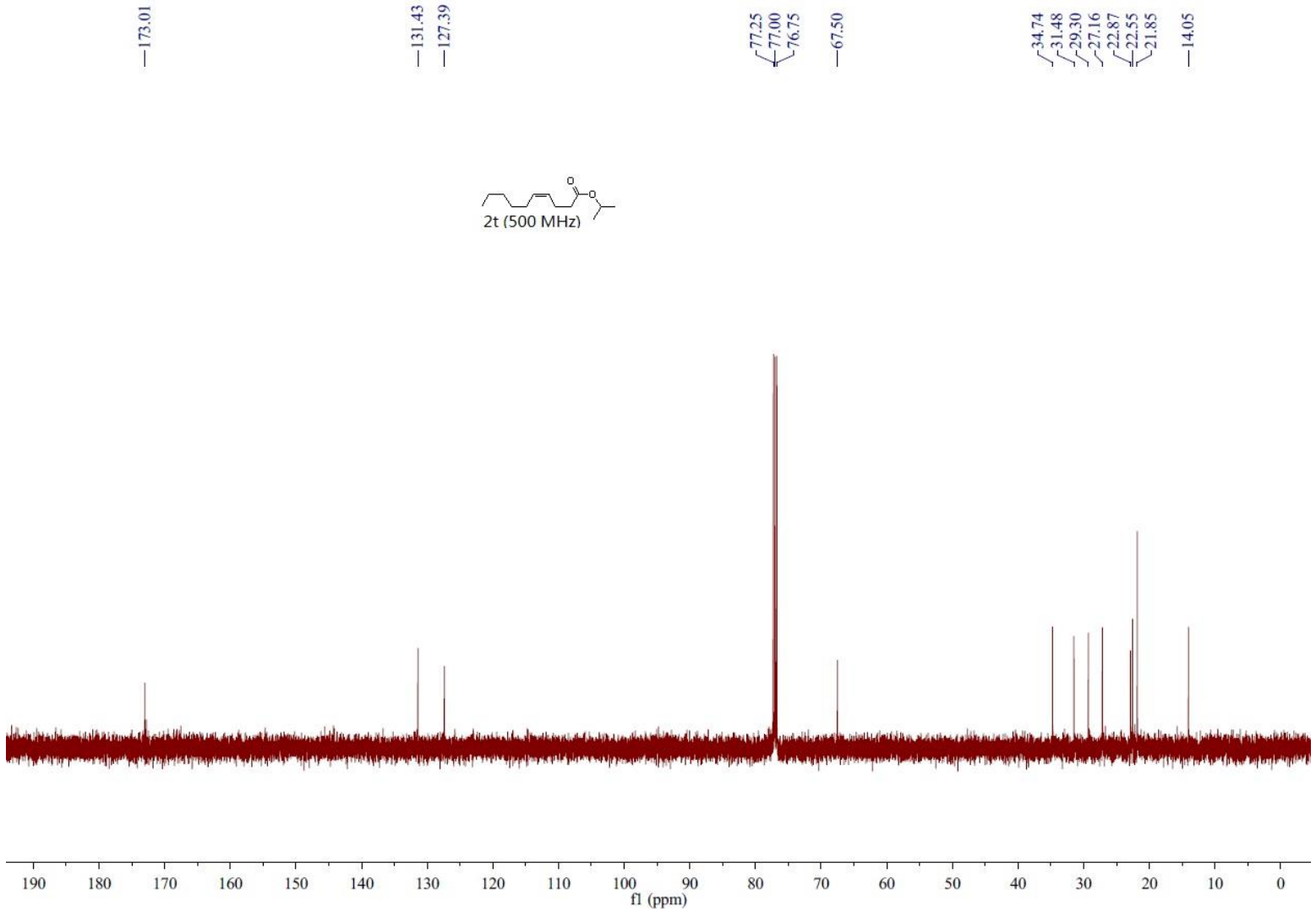

7.27
5.45
5.43
5.41
5.40
5.35
5.34
5.31
3.67
2.36
2.36
2.06
2.05
2.03
1.34
1.33
1.31
1.29
0.90
0.89
0.87
0.00
2r (500 MHz)
1.87
2.49
3.56
2.01
6.49
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

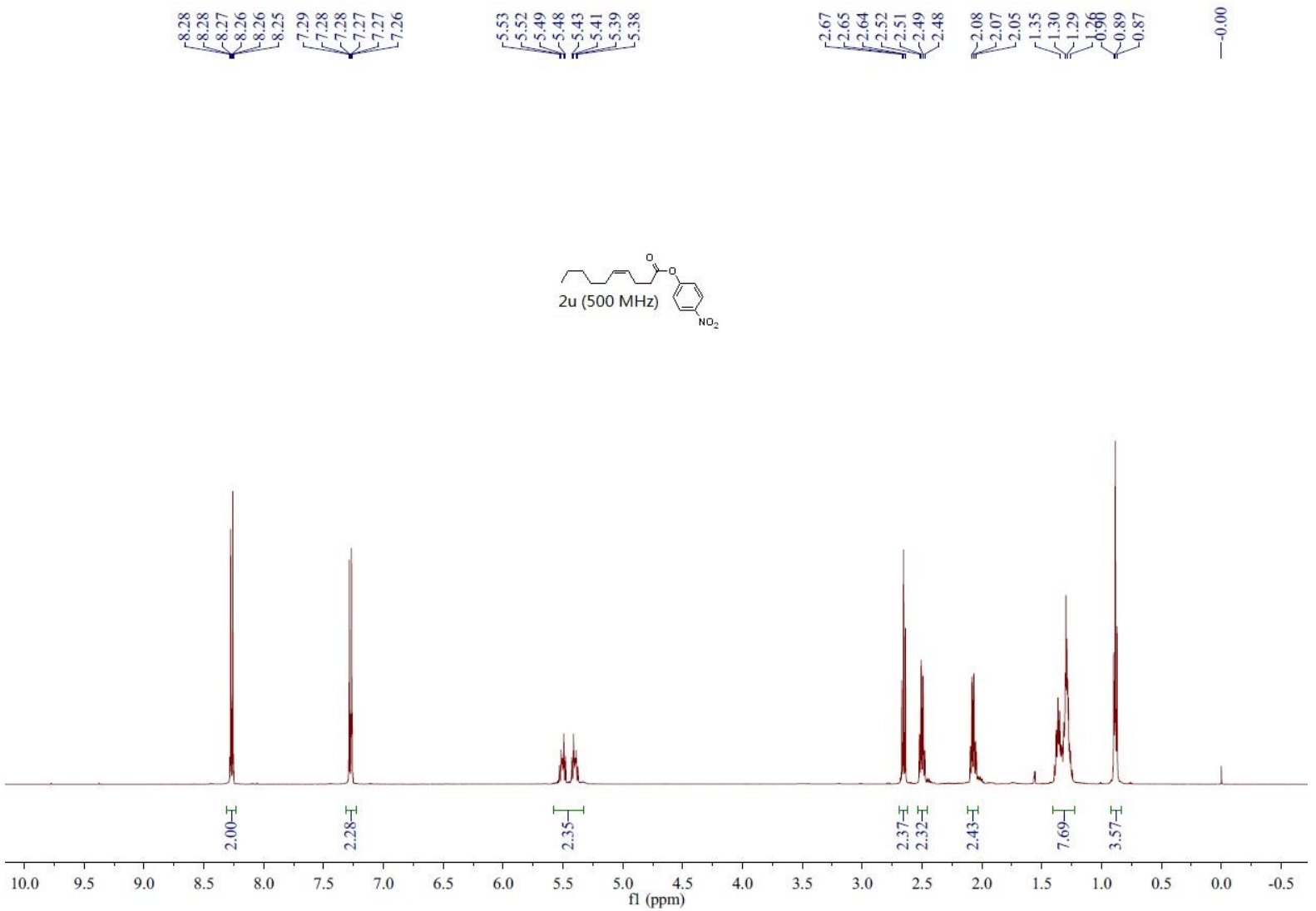

173.68
131.62
127.22
77.25
77.00
76.75
51.50
34.18
31.48
29.28
27.13
22.79
22.55
14.04
2r (500 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

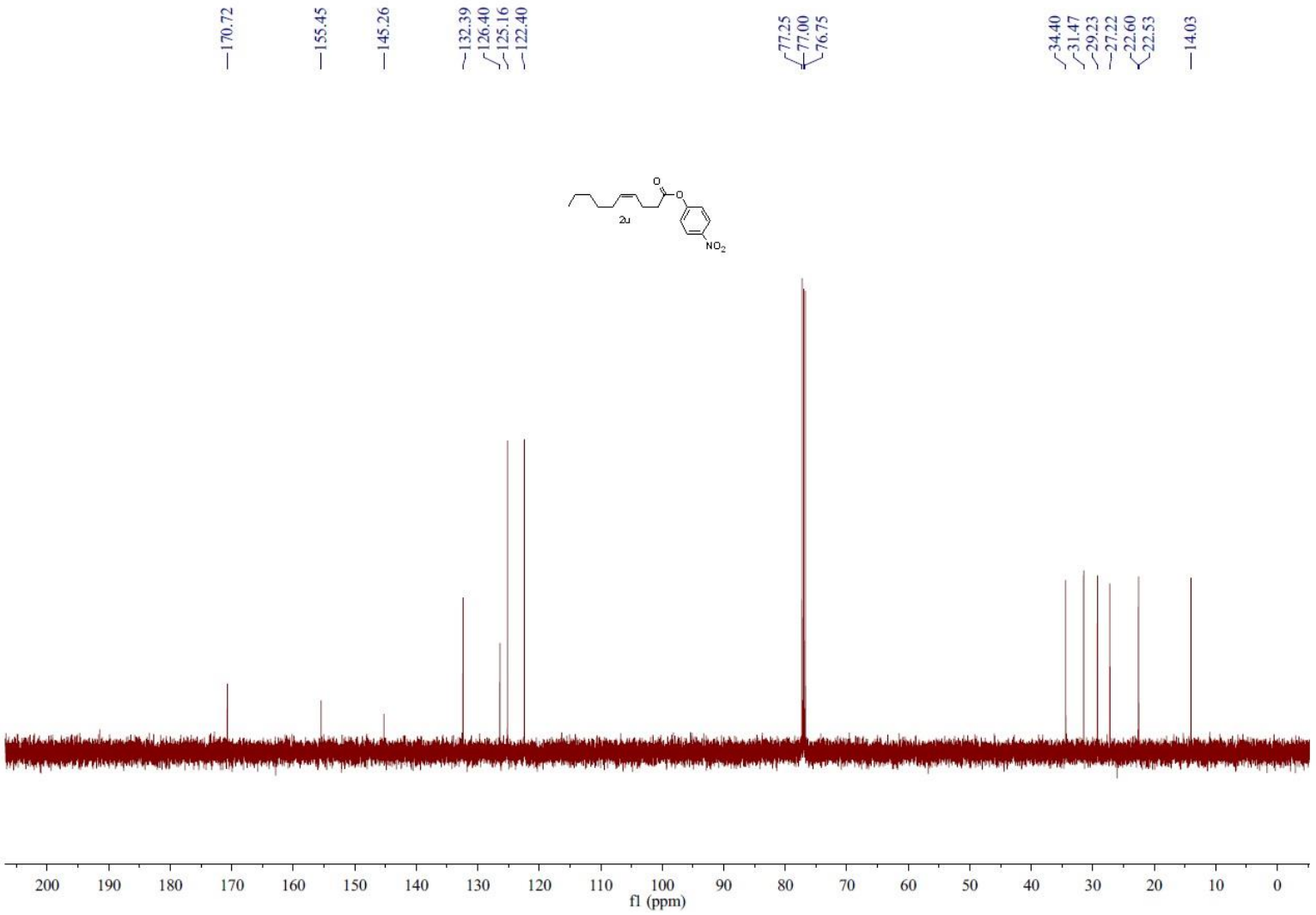

7.27
5.44
5.43
5.41
5.39
5.34
5.32
5.31
5.30
4.15
4.14
4.12
4.11
2.38
2.37
2.34
2.34
2.32
2.06
2.05
2.03
2.02
1.28
1.27
1.26
0.90
0.89
0.87
0.00
2s (500 MHz)
2.00
1.68
3.90
2.28
9.05
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

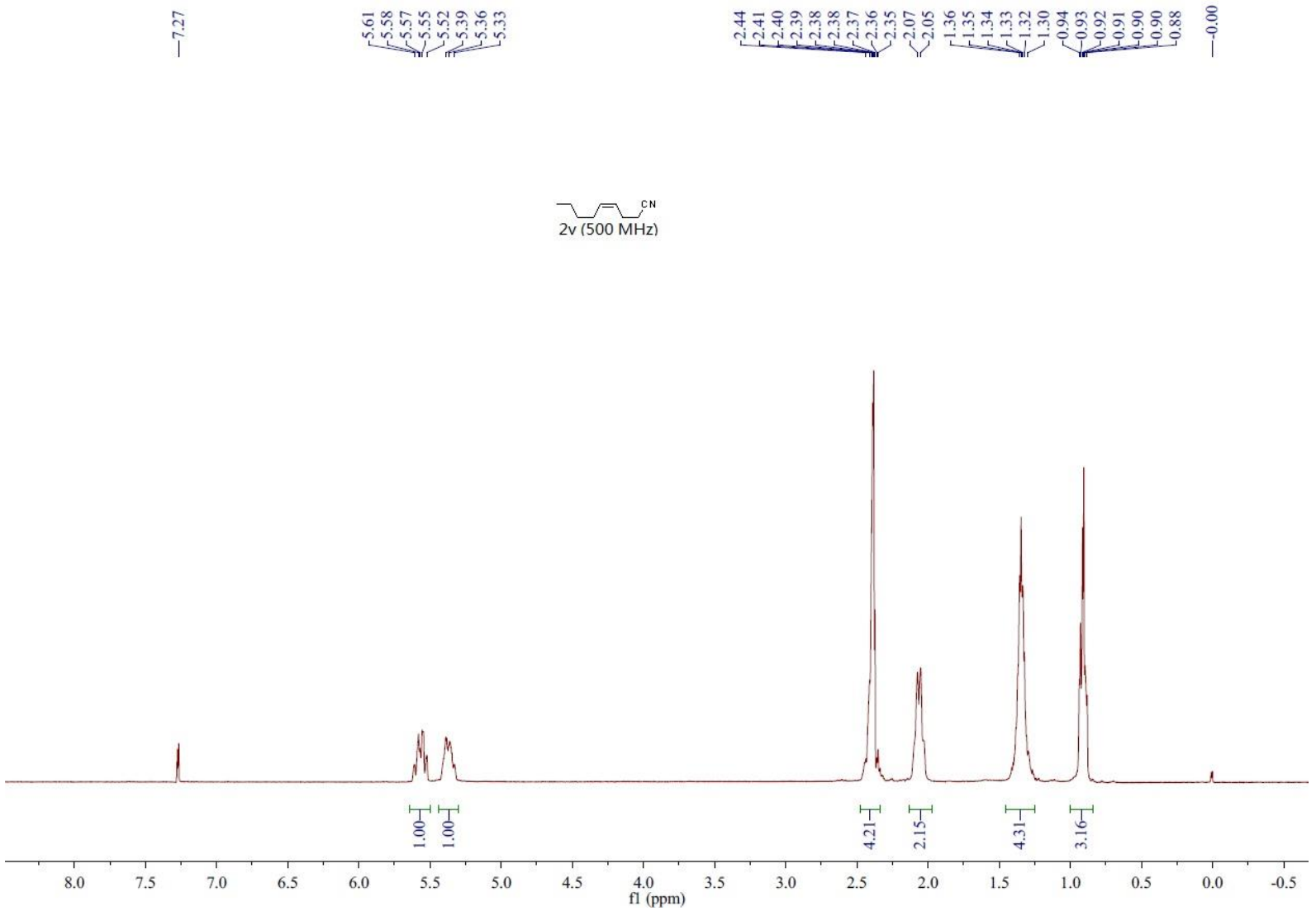

173.24
131.50
127.30
77.25
77.00
76.74
60.25
34.41
31.47
29.28
27.13
22.80
22.54
14.22
14.03
2s (500 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

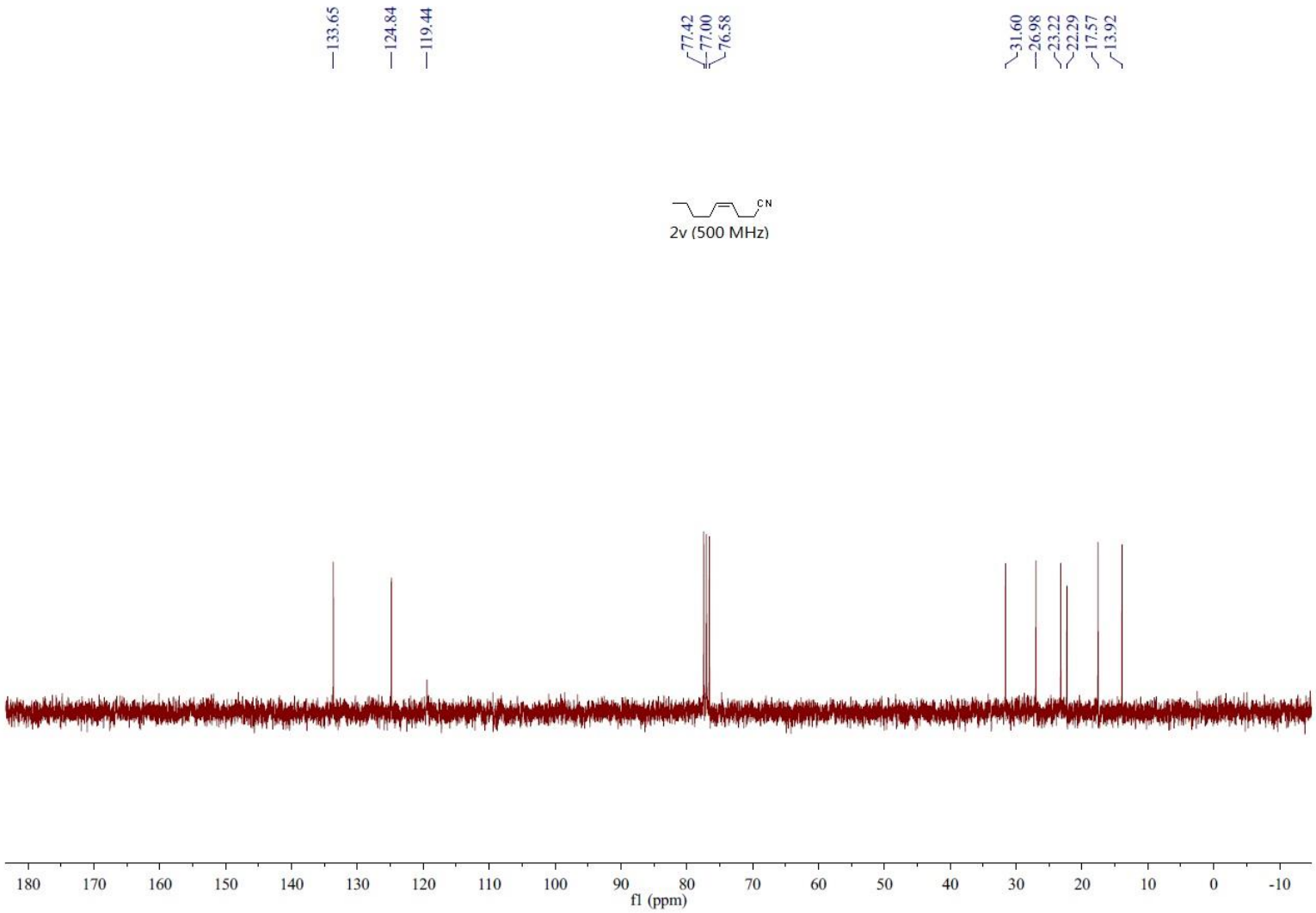

7.26
5.44
5.43
5.42
5.40
5.39
5.35
5.34
5.32
5.31
5.30
5.03
5.02
5.01
5.00
4.98
2.36
2.34
2.33
2.32
2.30
2.29
2.06
2.05
2.03
2.02
1.33
1.29
1.24
0.90
0.89
0.87
0.00
2t (500 MHz)
2.00
0.72
3.77
2.19
12.14
3.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

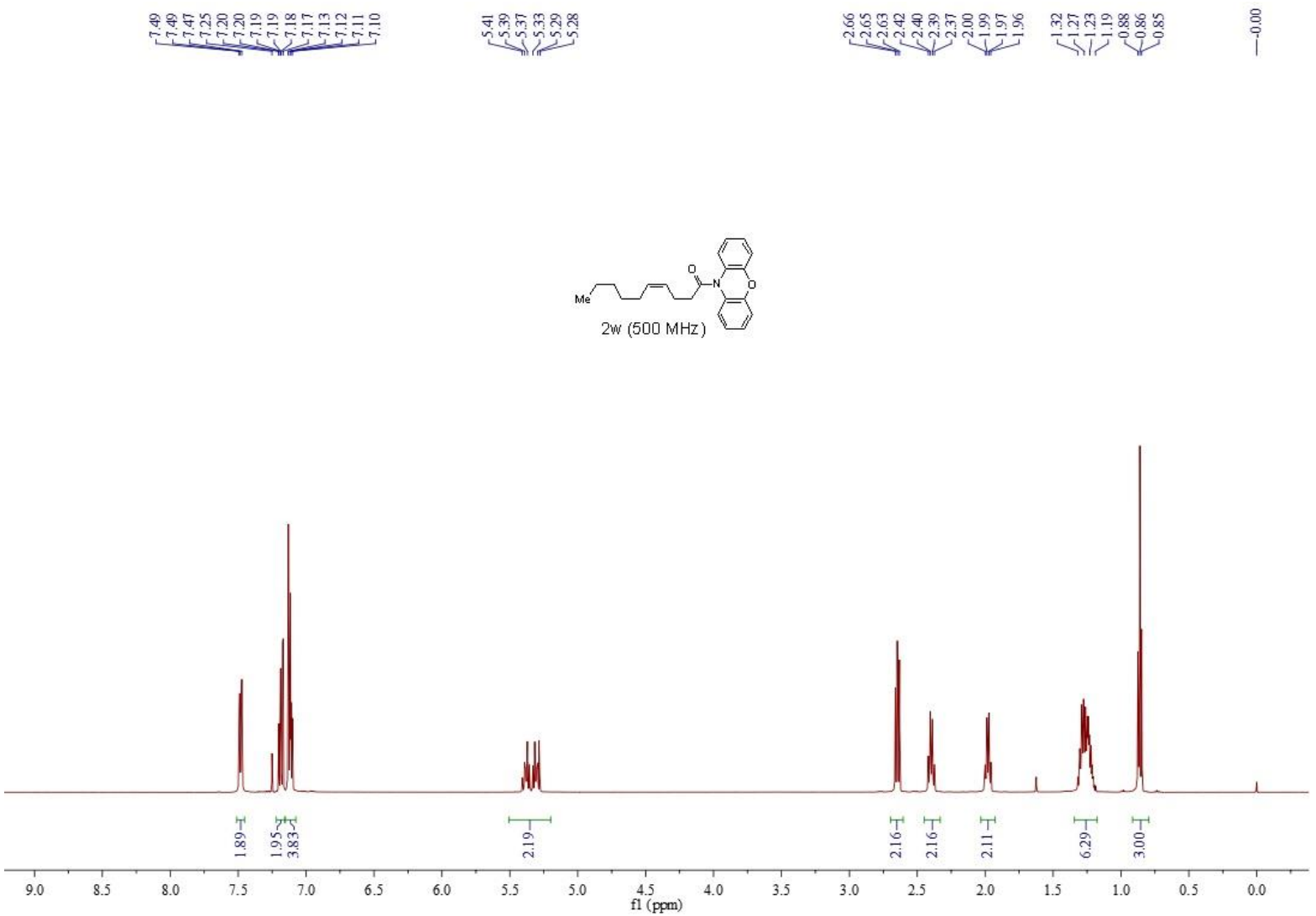

173.01
131.43
127.39
77.25
77.00
76.75
67.50
34.74
31.48
29.30
27.16
22.87
22.55
21.85
14.05
2t (500 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

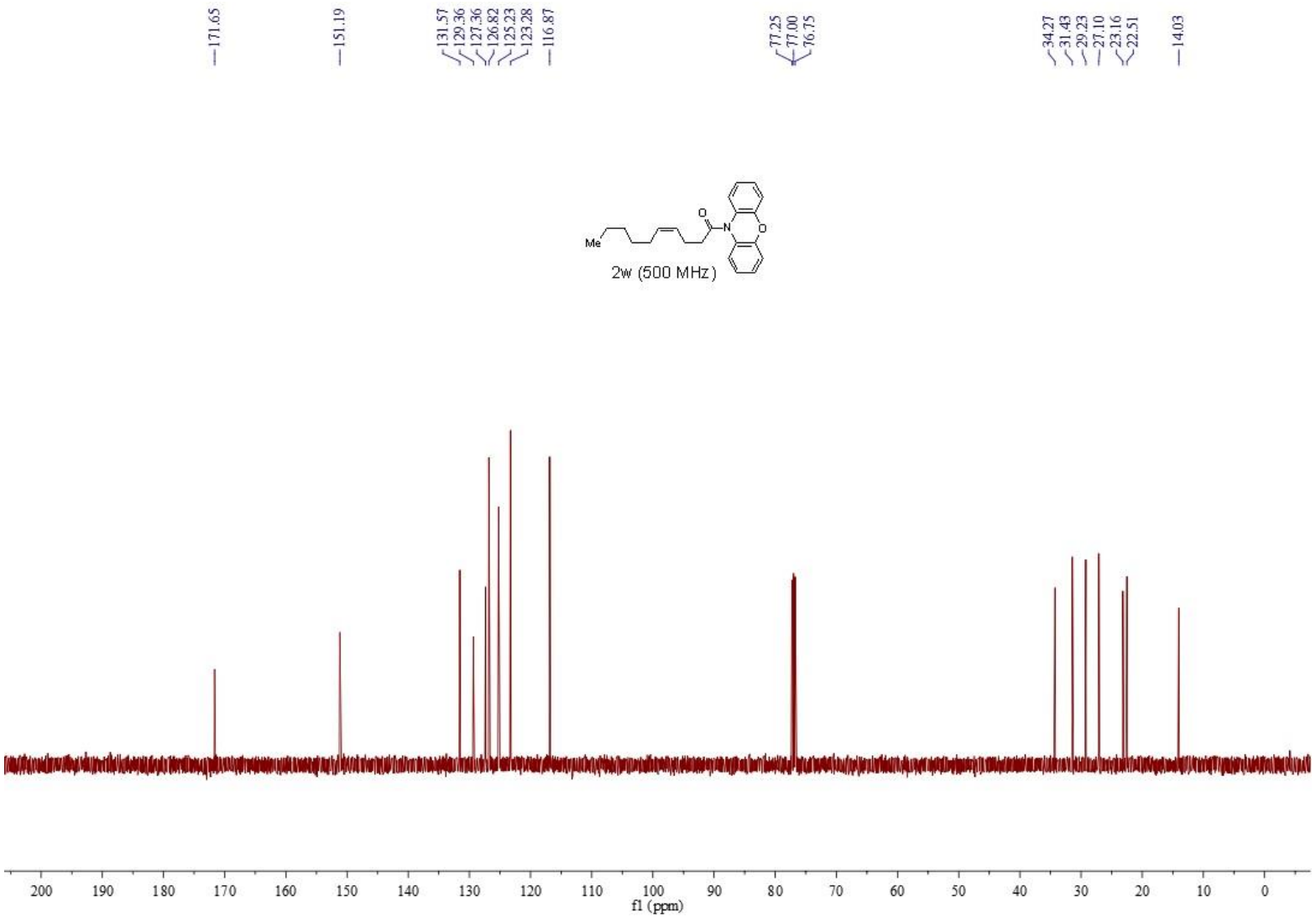

8.28
8.28
8.27
8.26
8.26
8.25
7.29
7.28
7.28
7.27
7.27
7.26
5.53
5.52
5.49
5.48
5.43
5.41
5.39
5.38
2.67
2.65
2.64
2.52
2.51
2.49
2.48
2.08
2.07
2.05
1.35
1.30
1.29
0.90
0.89
0.87
0.00
2u (500 MHz)
O
O
NO2
2.00
2.28
2.35
2.37
2.32
2.43
7.69
3.57
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


170.72
155.45
145.26
132.39
126.40
125.16
122.40
77.25
77.00
76.75
34.40
31.47
29.23
27.22
22.60
22.53
14.03
2u
NO2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

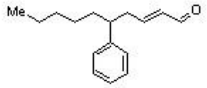

7.27
5.61
5.58
5.57
5.55
5.52
5.39
5.36
5.33
2.44
2.41
2.40
2.39
2.38
2.38
2.37
2.36
2.35
2.07
2.05
1.36
1.35
1.34
1.33
1.32
1.30
0.94
0.93
0.92
0.91
0.90
0.90
0.88
0.00
CN
2v (500 MHz)
1.00
1.00
4.21
2.15
4.31
3.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


133.65
124.84
119.44
77.42
77.00
76.58
31.60
26.98
23.22
22.29
17.57
13.92
CN
2v (500 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

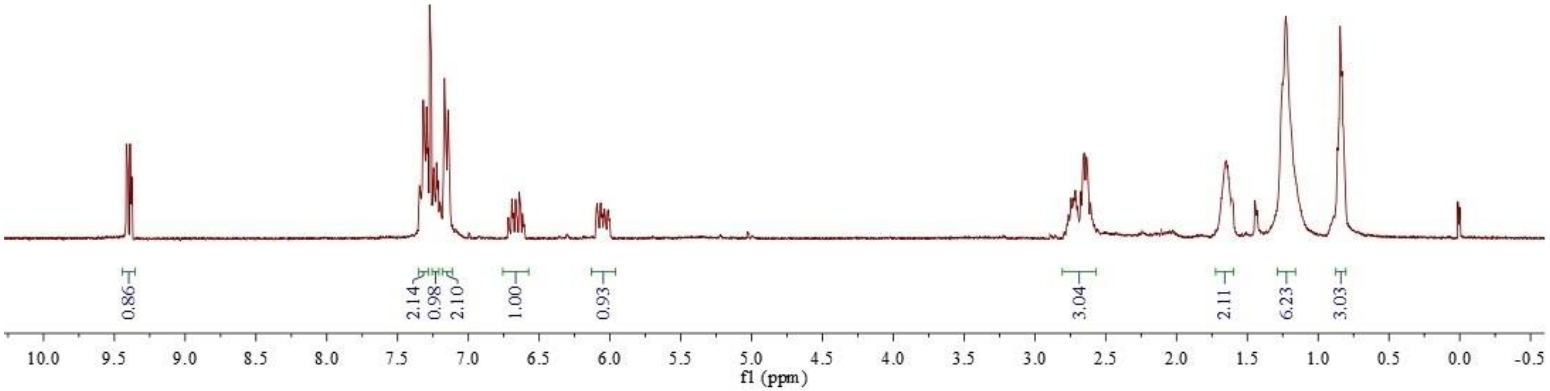

7.49
7.49
7.47
7.25
7.20
7.20
7.19
7.19
7.18
7.17
7.13
7.12
7.11
7.10
5.41
5.39
5.37
5.33
5.29
5.28
2.66
2.65
2.63
2.42
2.40
2.39
2.37
2.00
1.99
1.97
1.96
1.32
1.27
1.23
1.19
0.88
0.86
0.85
0.00
Me
O
N
O
2w (500 MHz)
1.89
1.95
3.83
2.19
2.16
2.16
2.11
6.29
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

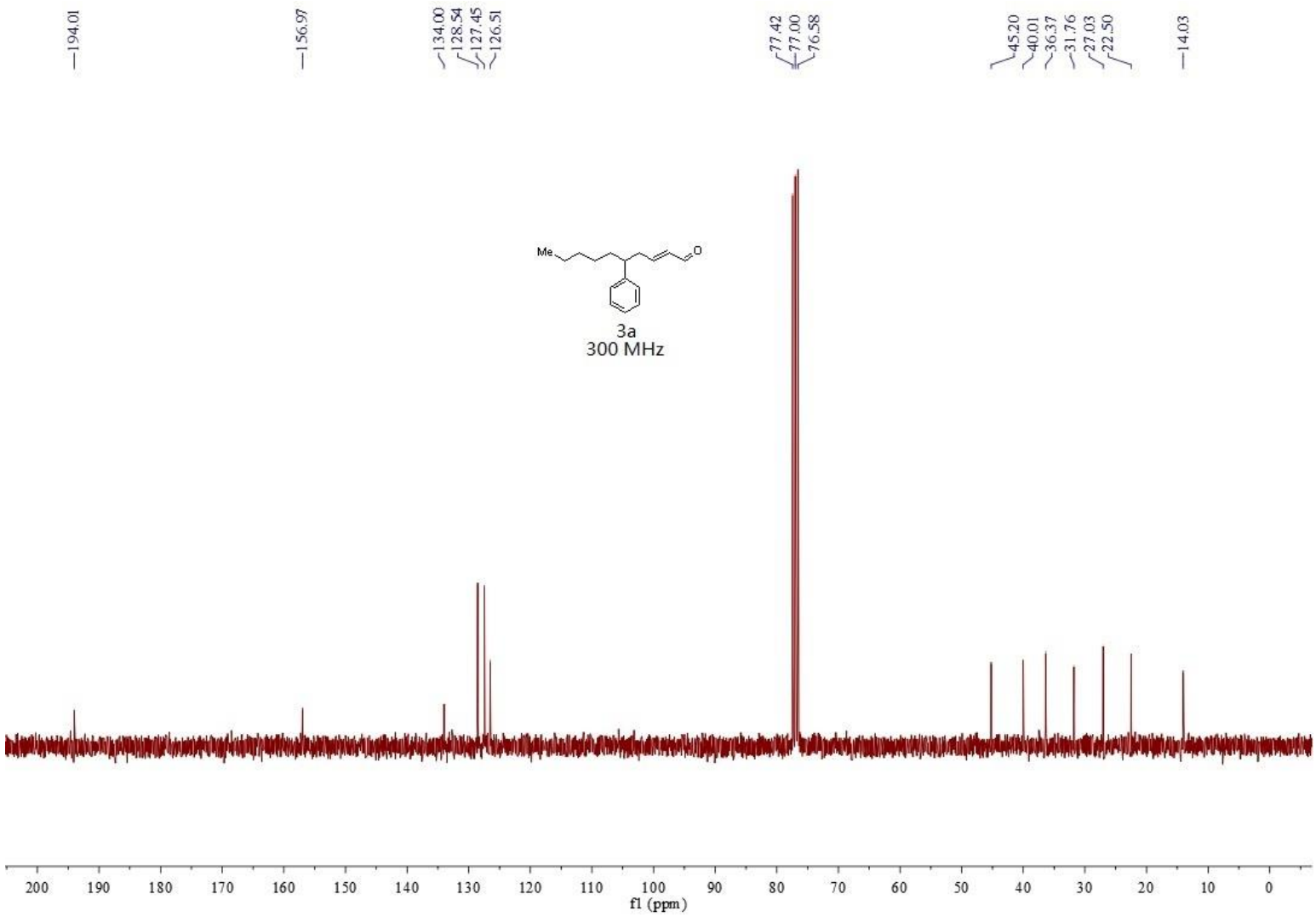

171.65
151.19
131.57
129.36
127.36
126.82
125.23
123.28
116.87
77.25
77.00
76.75
34.27
31.43
29.23
27.10
23.16
22.51
14.03
Me
O
N
O
2w (500 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

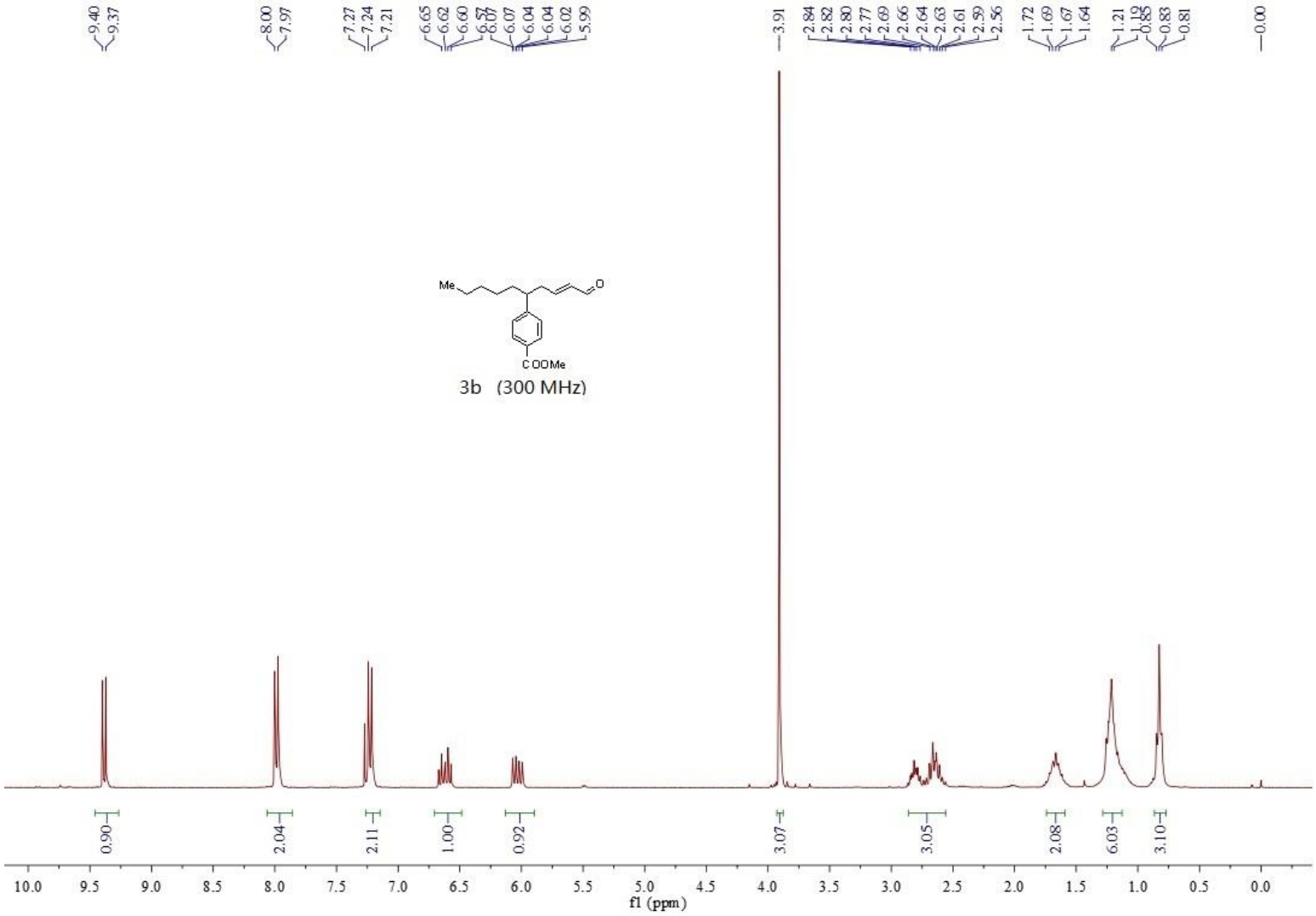

9.42
9.39
7.35
7.32
7.31
7.30
7.28
7.26
7.25
7.25
7.24
7.23
7.21
7.17
7.14
6.69
6.67
6.07
6.06
6.04
6.03
6.01
6.00
2.79
2.77
2.74
2.71
2.70
2.67
2.66
2.63
2.61
1.67
1.65
1.64
1.63
1.27
1.25
1.24
1.23
1.22
1.19
0.85

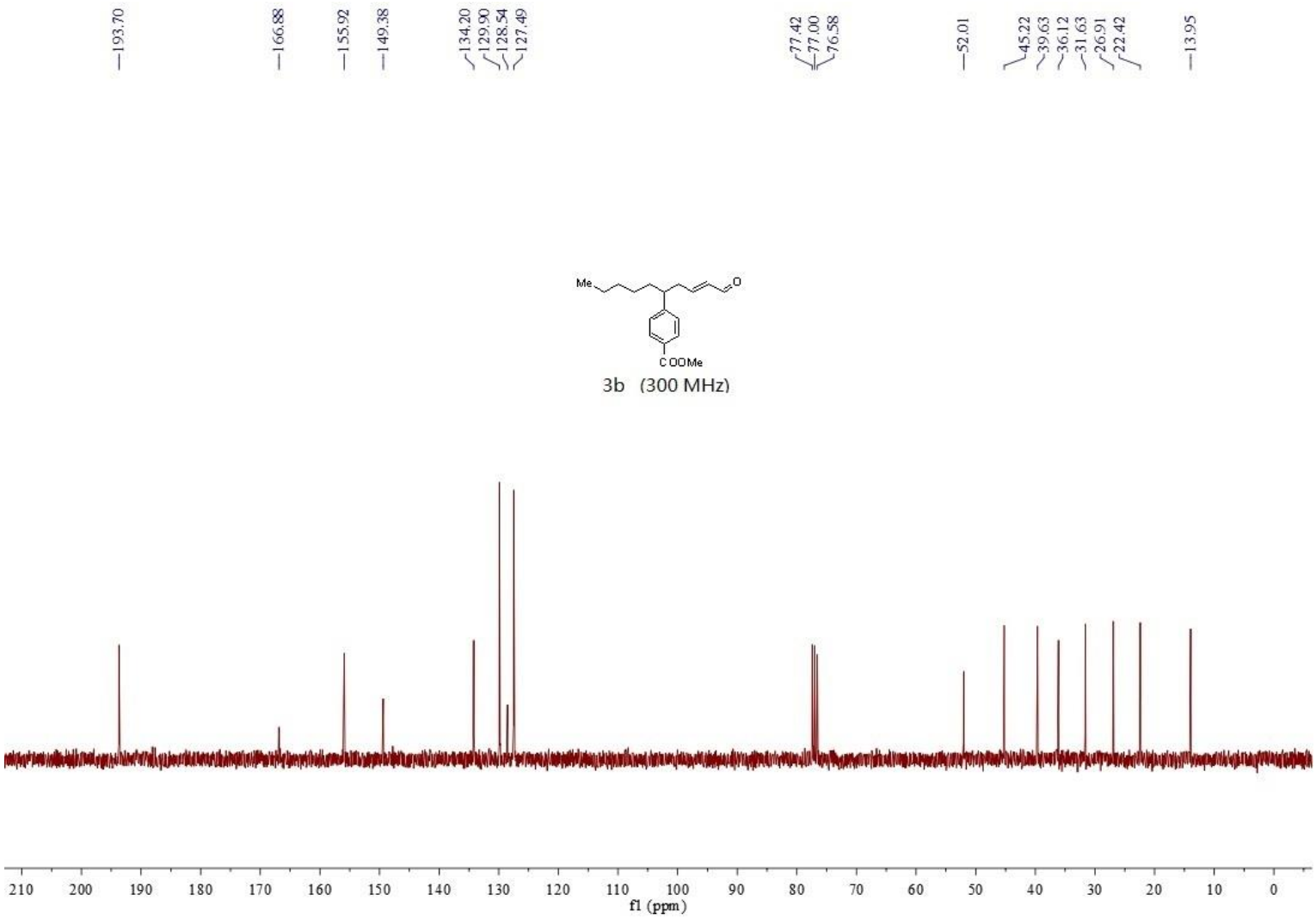

Me
O

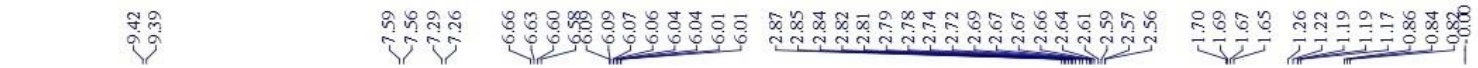
3a
300 MHz

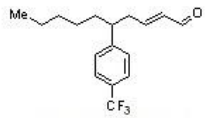

0.86
2.14
0.98
2.10
1.00
0.93
3.04
2.11
6.23
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


194.01
156.97
134.00
128.54
127.45
126.51
77.42
77.00
76.58
45.20
40.01
36.37
31.76
27.03
22.50
14.03
Me
O
3a
300 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

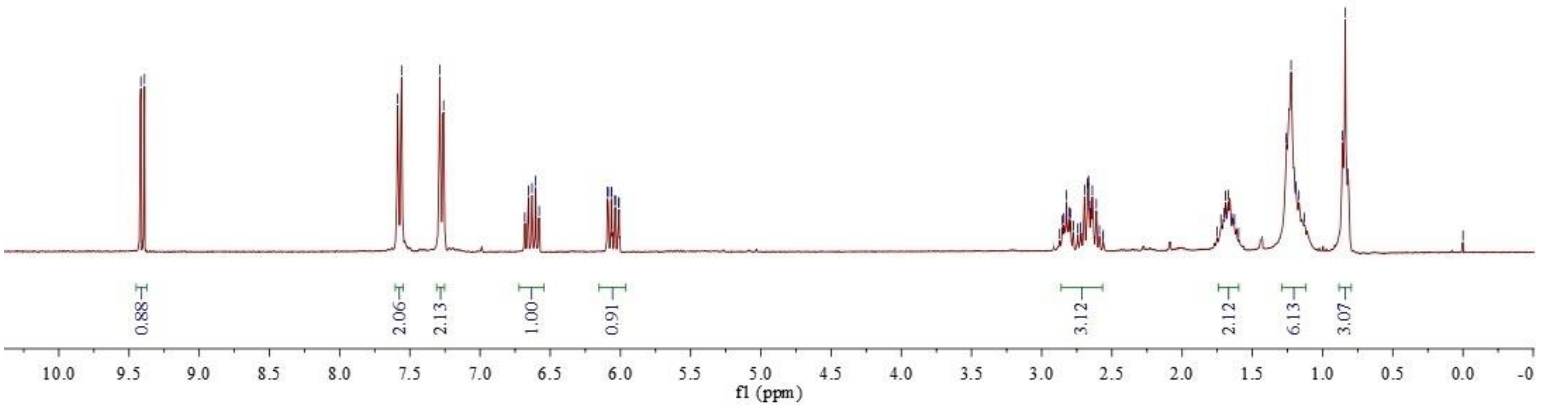

9.40
9.37
8.00
7.97
7.27
7.24
7.21
6.65
6.62
6.60
6.57
6.07
6.04
6.04
6.02
5.99
3.91
2.84
2.82
2.80
2.77
2.69
2.66
2.64
2.63
2.61
2.59
2.56
1.72
1.69
1.67
1.64
1.21
1.19
0.85
0.83
0.81
0.00
Me
O
COOMe
3b (300 MHz)
0.90
2.04
2.11
1.00
0.92
3.07
3.05
2.08
6.03
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

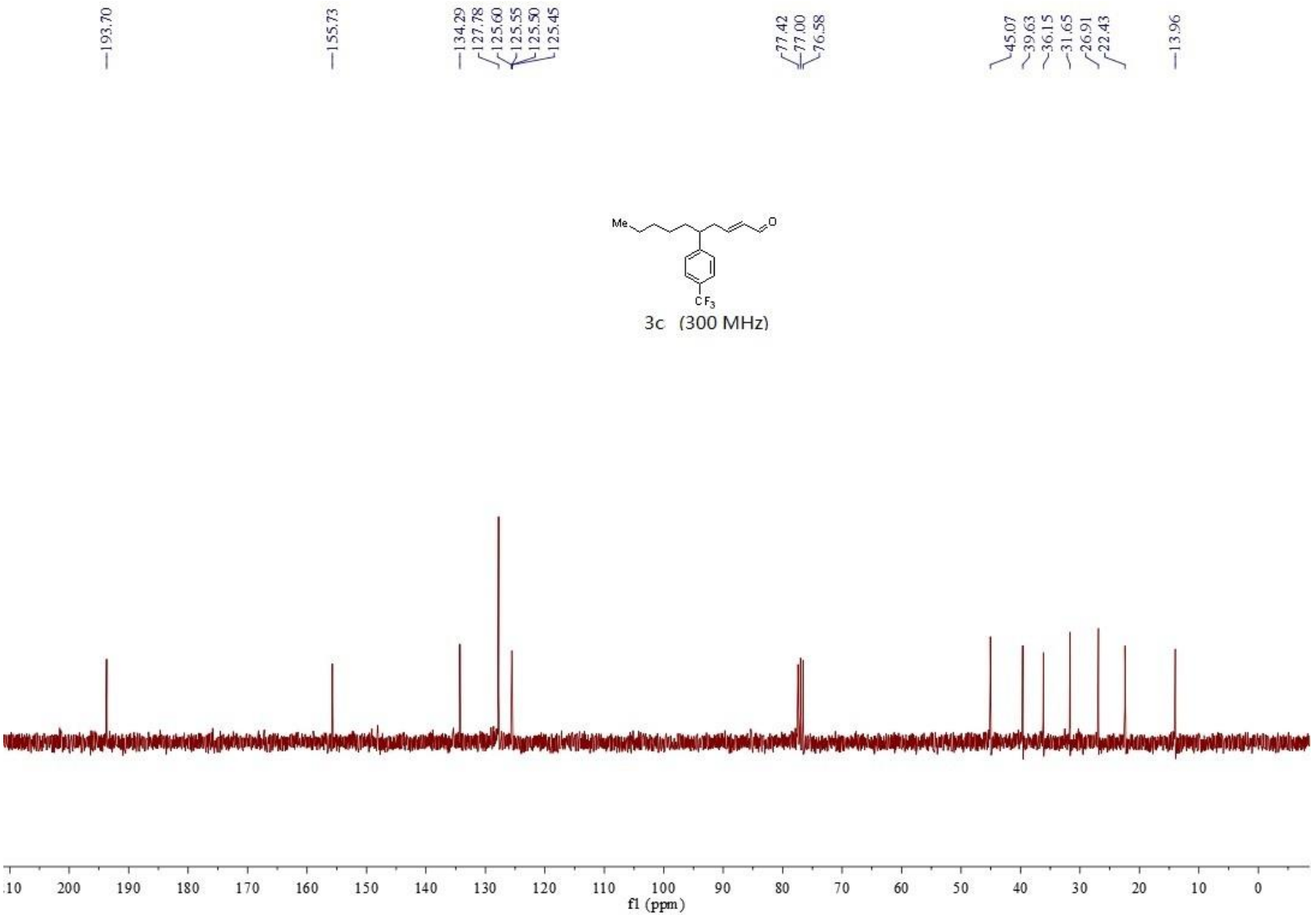

193.70
166.88
155.92
149.38
134.20
129.90
128.54
127.49
77.42
77.00
76.58
52.01
45.22
39.63
36.12
31.63
26.91
22.42
13.95
Me
O
COOMe
3b (300 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

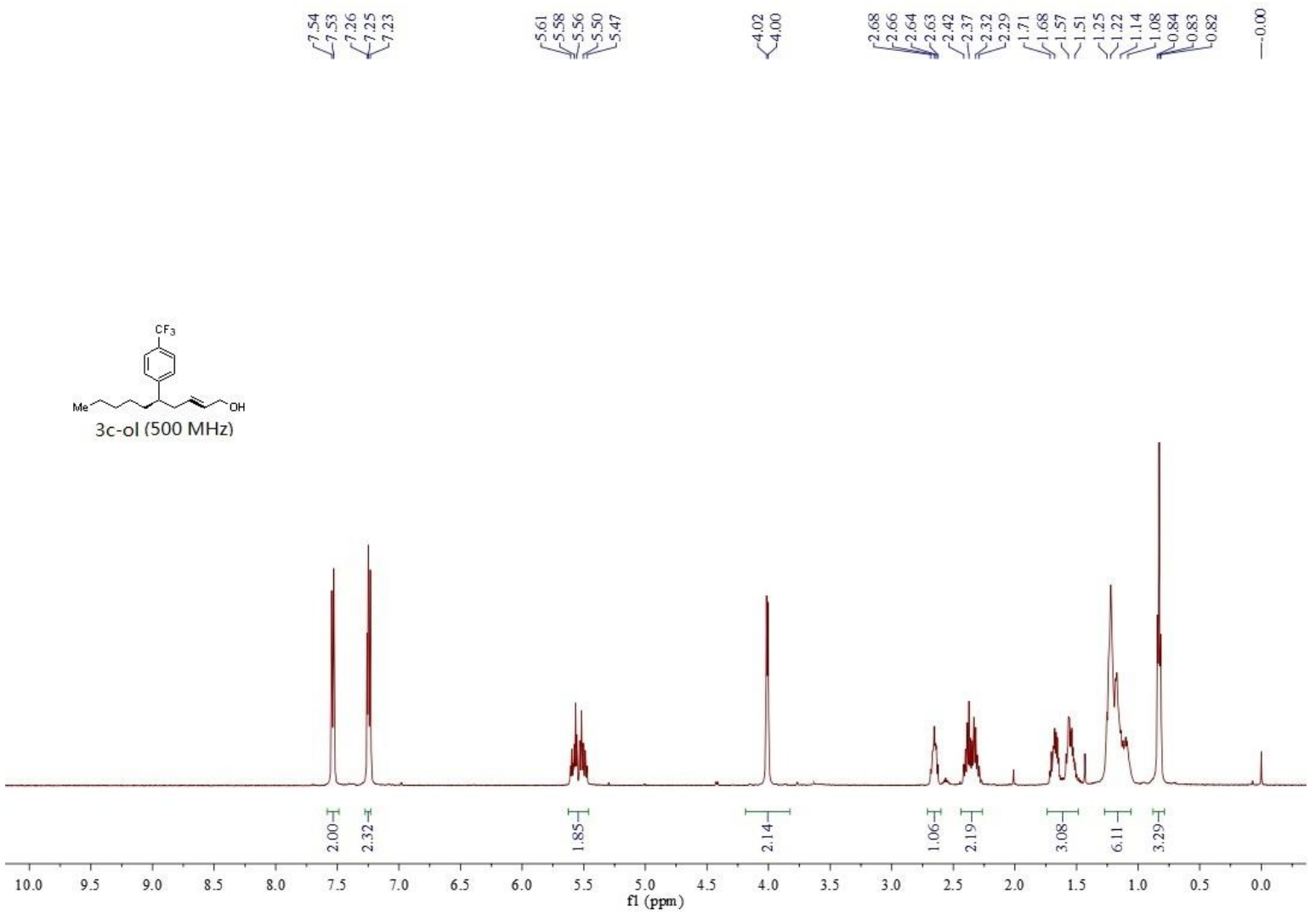

9.42
9.39
7.59
7.56
7.29
7.26
6.66
6.63
6.60
6.09
6.07
6.06
6.04
6.04
6.01
6.01
2.87
2.85
2.84
2.82
2.81
2.79
2.78
2.74
2.72
2.69
2.67
2.67
2.66
2.64
2.61
2.59
2.57
2.56
1.70
1.69
1.67
1.65
1.26
1.22
1.19
1.19
1.17
0.86
0.84
0.82
0.00

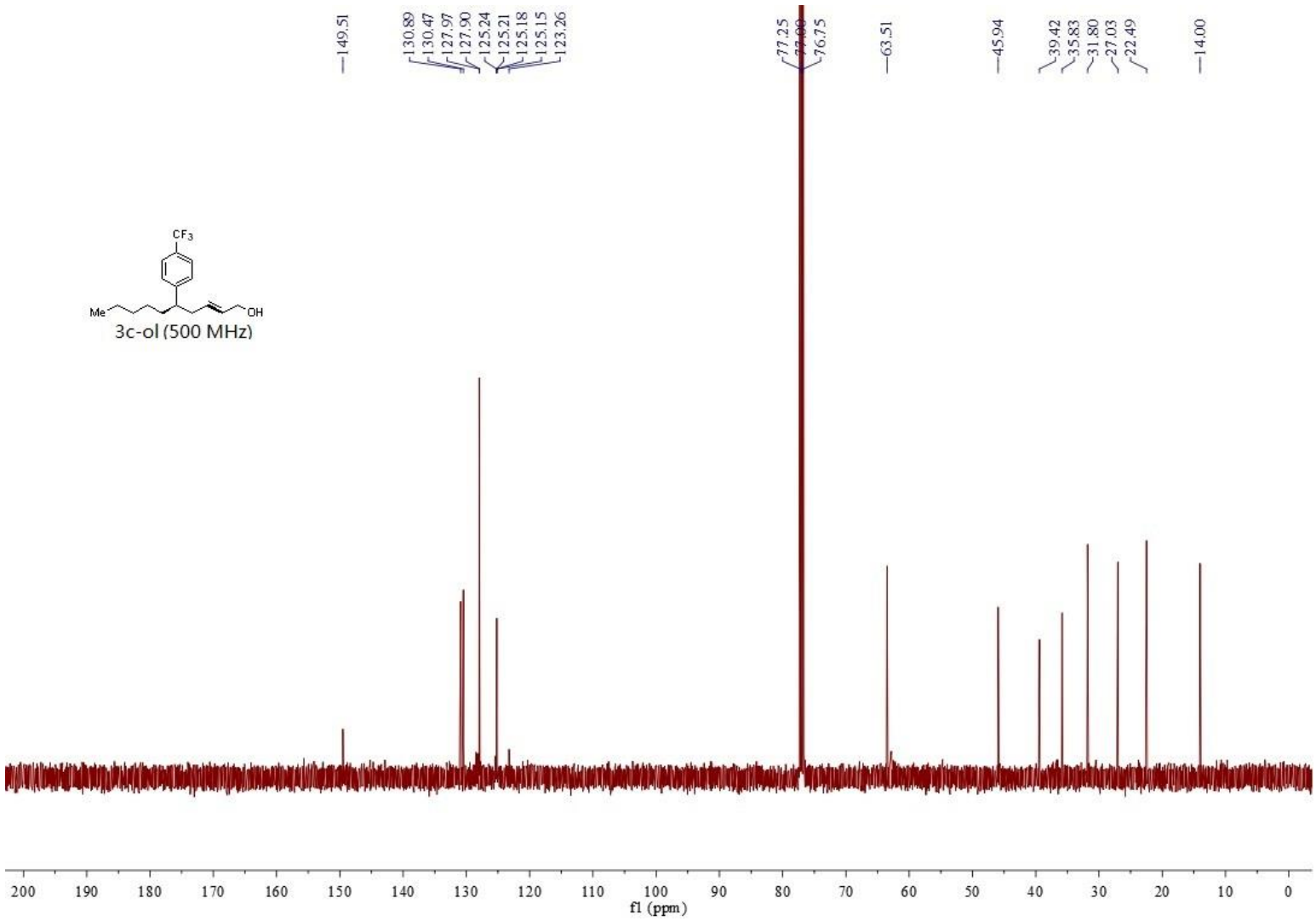

Me
O
CF3

3c (300 MHz)

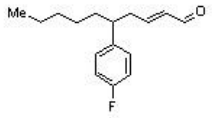

0.88
2.06
2.13
1.00
0.91
3.12
2.12
6.13
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


193.70
155.73
134.29
127.78
125.60
125.55
125.50
125.45
77.42
77.00
76.58
45.07
39.63
36.15
31.65
26.91
22.43
13.96
Me
O
CF3
3c (300 MHz)
f1 (ppm)

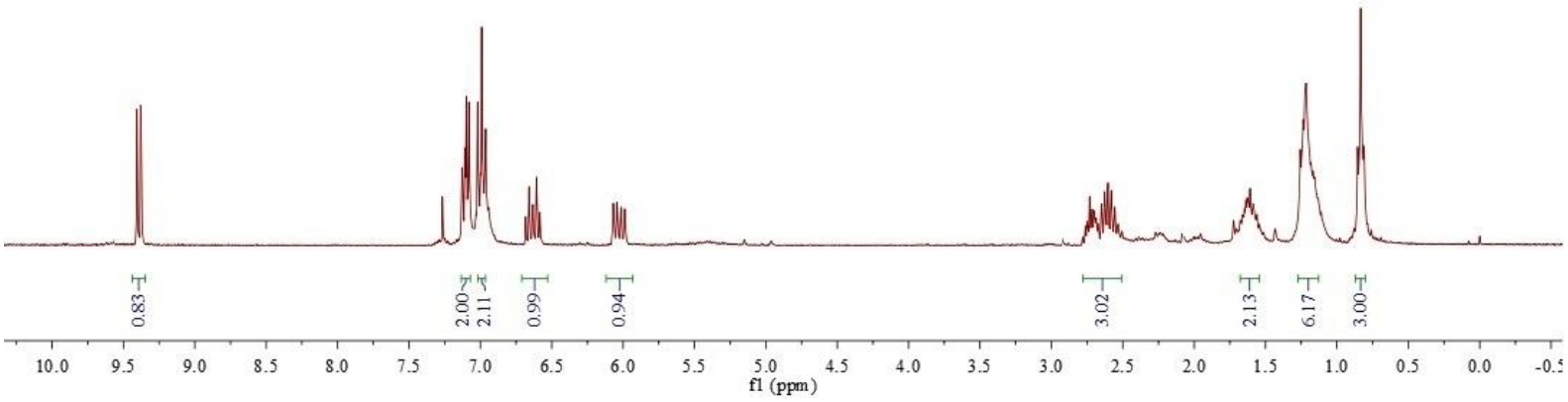

7.54
7.53
7.26
7.25
7.23
5.61
5.58
5.56
5.50
5.47
4.02
4.00
2.68
2.66
2.64
2.63
2.42
2.37
2.32
2.29
1.71
1.68
1.57
1.51
1.25
1.22
1.14
1.08
0.84
0.83
0.82
0.00
CF3
Me
OH
3c-ol (500 MHz)
2.00
2.32
1.85
2.14
1.06
2.19
3.08
6.11
3.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

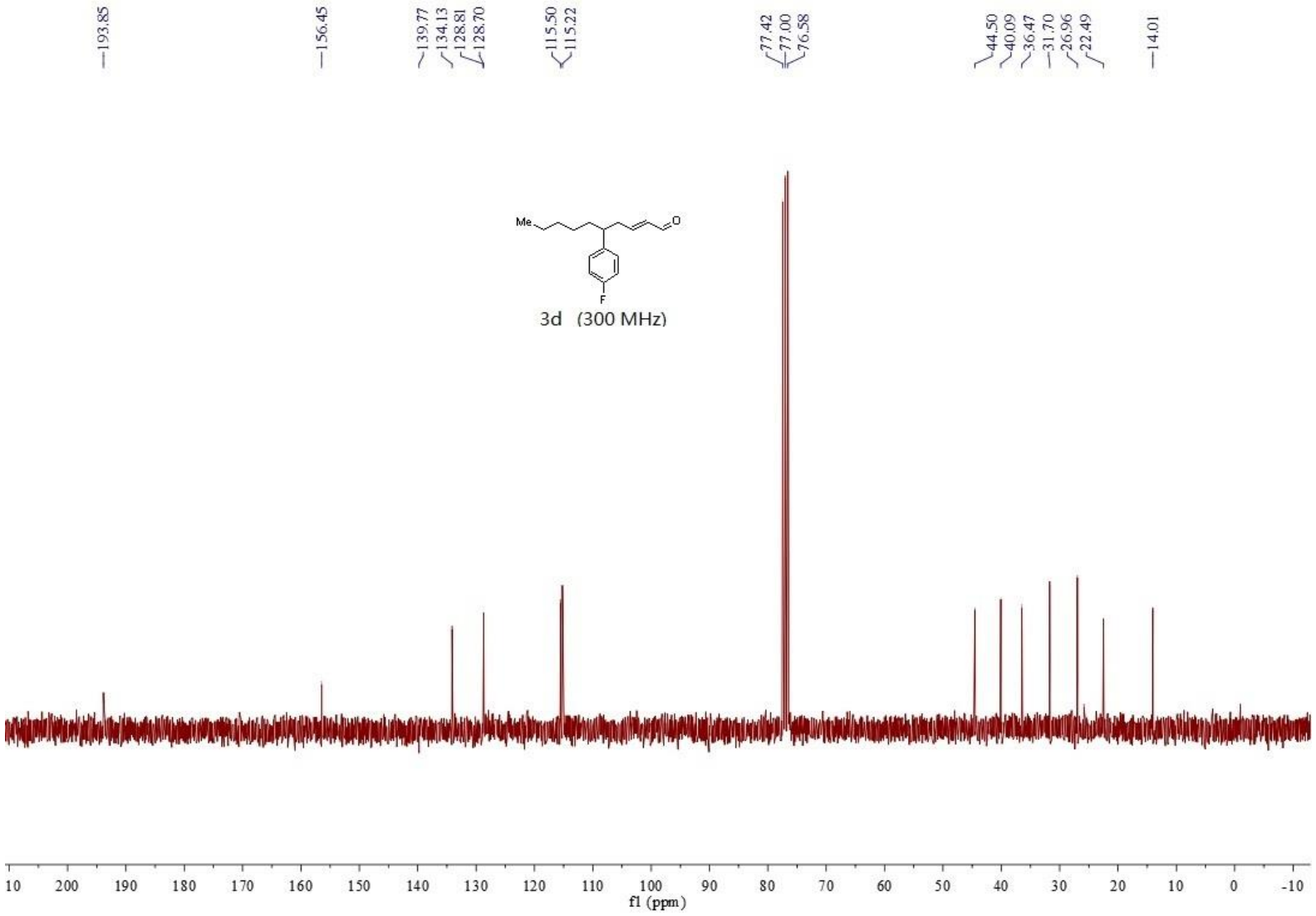

149.51
130.89
130.47
127.97
127.90
125.24
125.21
125.18
125.15
123.26
77.25
77.00
76.75
63.51
45.94
39.42
35.83
31.80
27.03
22.49
14.00
CF3
Me
OH
3c-ol (500 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

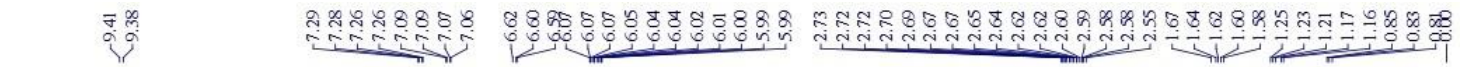

9.40
9.38
7.27
7.13
7.11
7.10
7.08
7.07
7.02
7.00
6.99
6.98
6.96
6.68
6.66
6.63
6.61
6.58
6.07
6.04
6.01
5.99
2.78
2.76
2.74
2.72
2.69
2.66
2.63
2.60
2.58
2.55
2.53
2.50
1.61
1.59
1.26
1.24
1.22
1.21
1.20
1.17
1.15
0.86
0.83
0.81
0.00

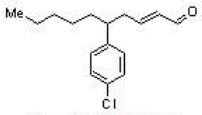

Me
O
F

3d (300 MHz)

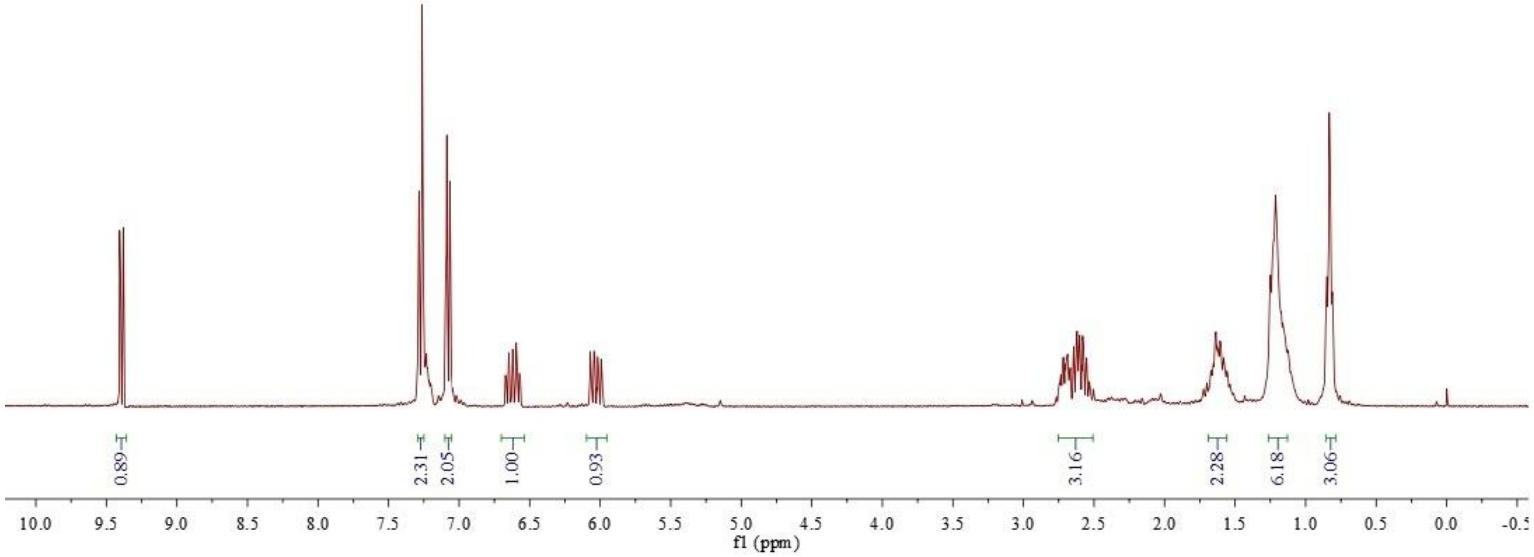

0.83
2.00
2.11
0.99
0.94
3.02
2.13
6.17
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

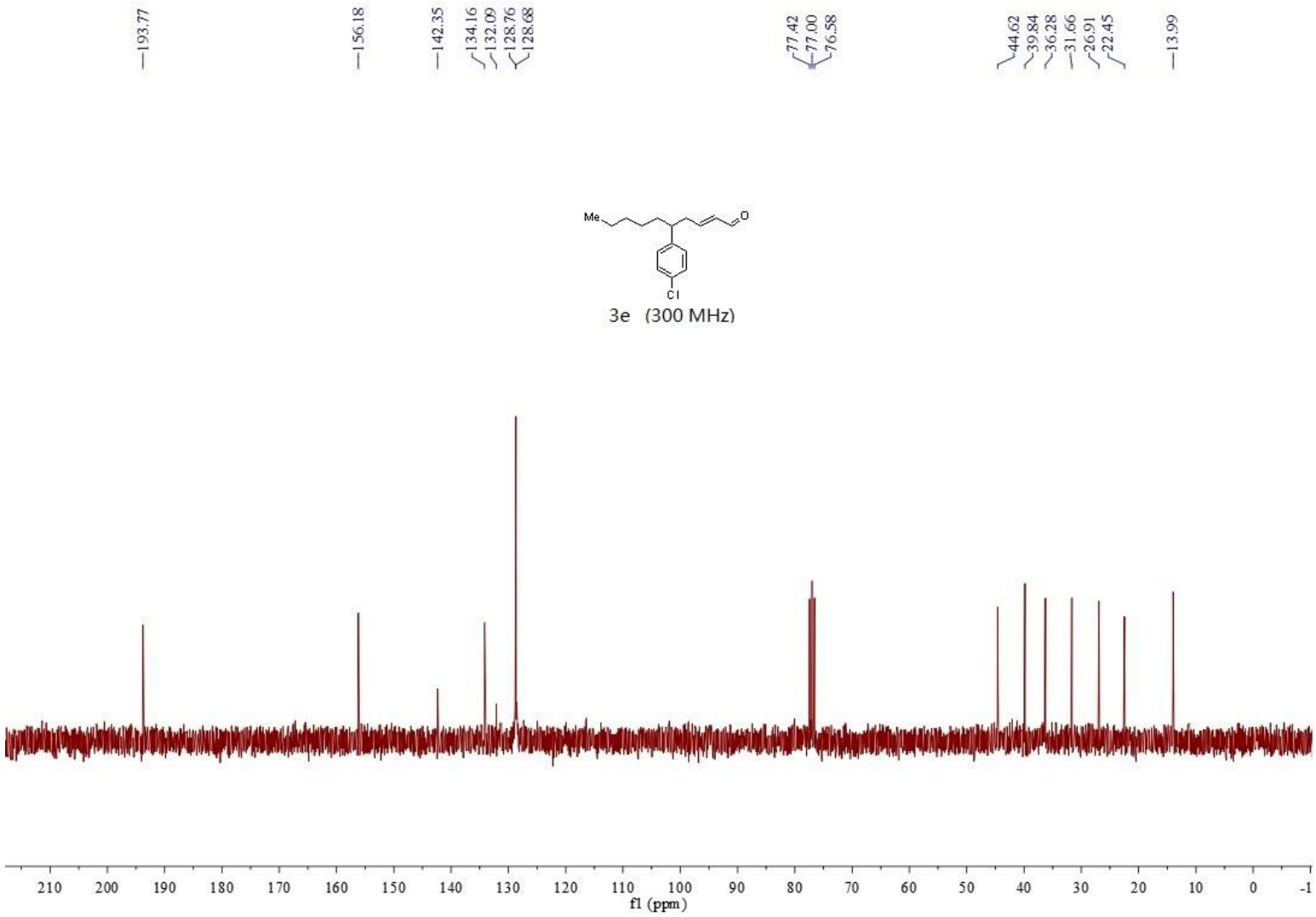

193.85
156.45
139.77
134.13
128.81
128.70
115.50
115.22
77.42
77.00
76.58
44.50
40.09
36.47
31.70
26.96
22.49
14.01
Me
O
F
3d (300 MHz)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

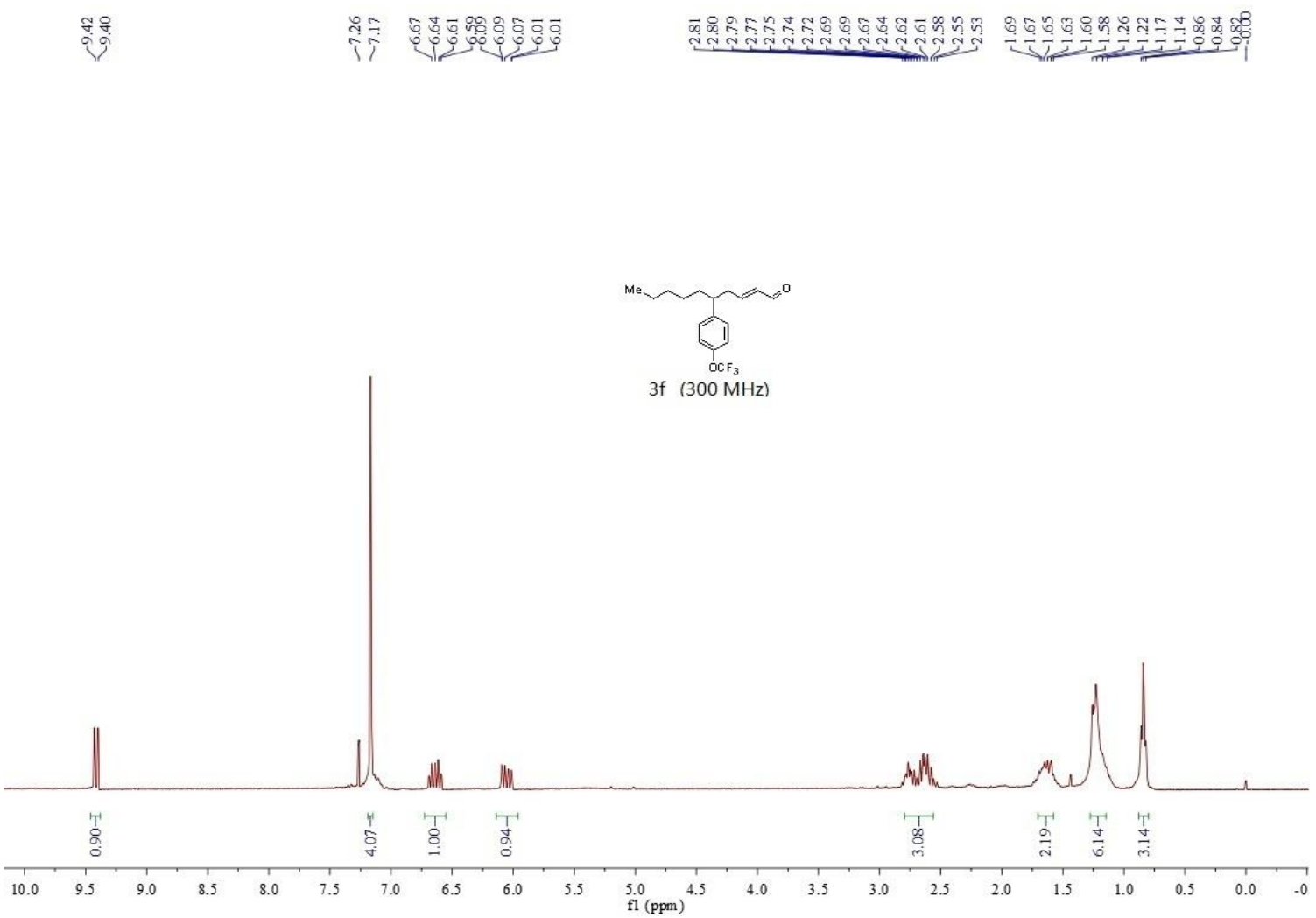

9.41
9.38
7.29
7.28
7.26
7.26
7.09
7.09
7.07
7.06
6.62
6.60
6.07
6.07
6.05
6.04
6.04
6.02
6.01
6.00
5.99
5.99
2.73
2.72
2.72
2.70
2.69
2.67
2.67
2.65
2.64
2.62
2.62
2.60
2.59
2.58
2.58
2.55
1.67
1.64
1.62
1.60
1.58
1.25
1.23
1.21
1.17
1.16
0.85
0.83
0.81
0.80

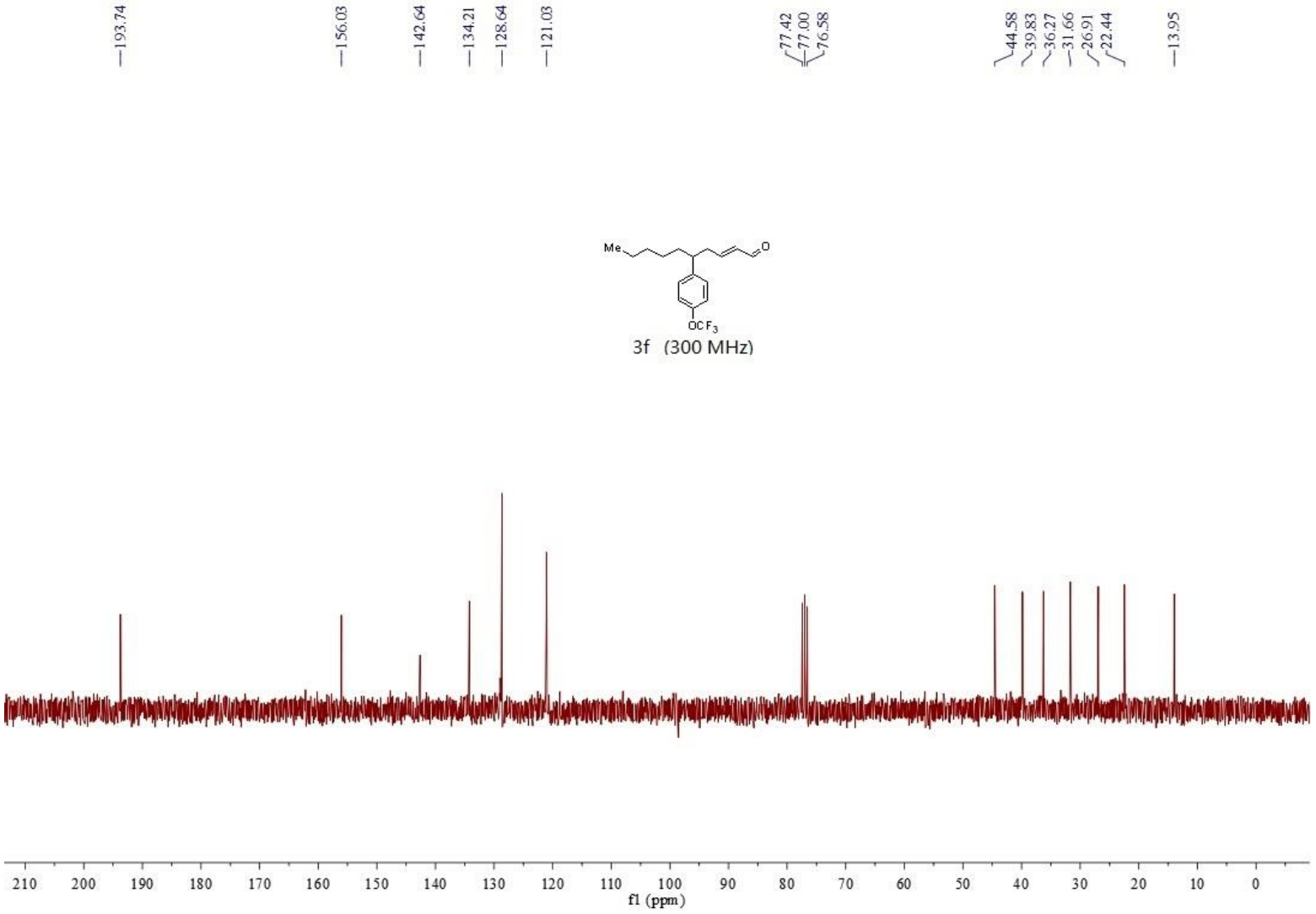

Me
O
Cl

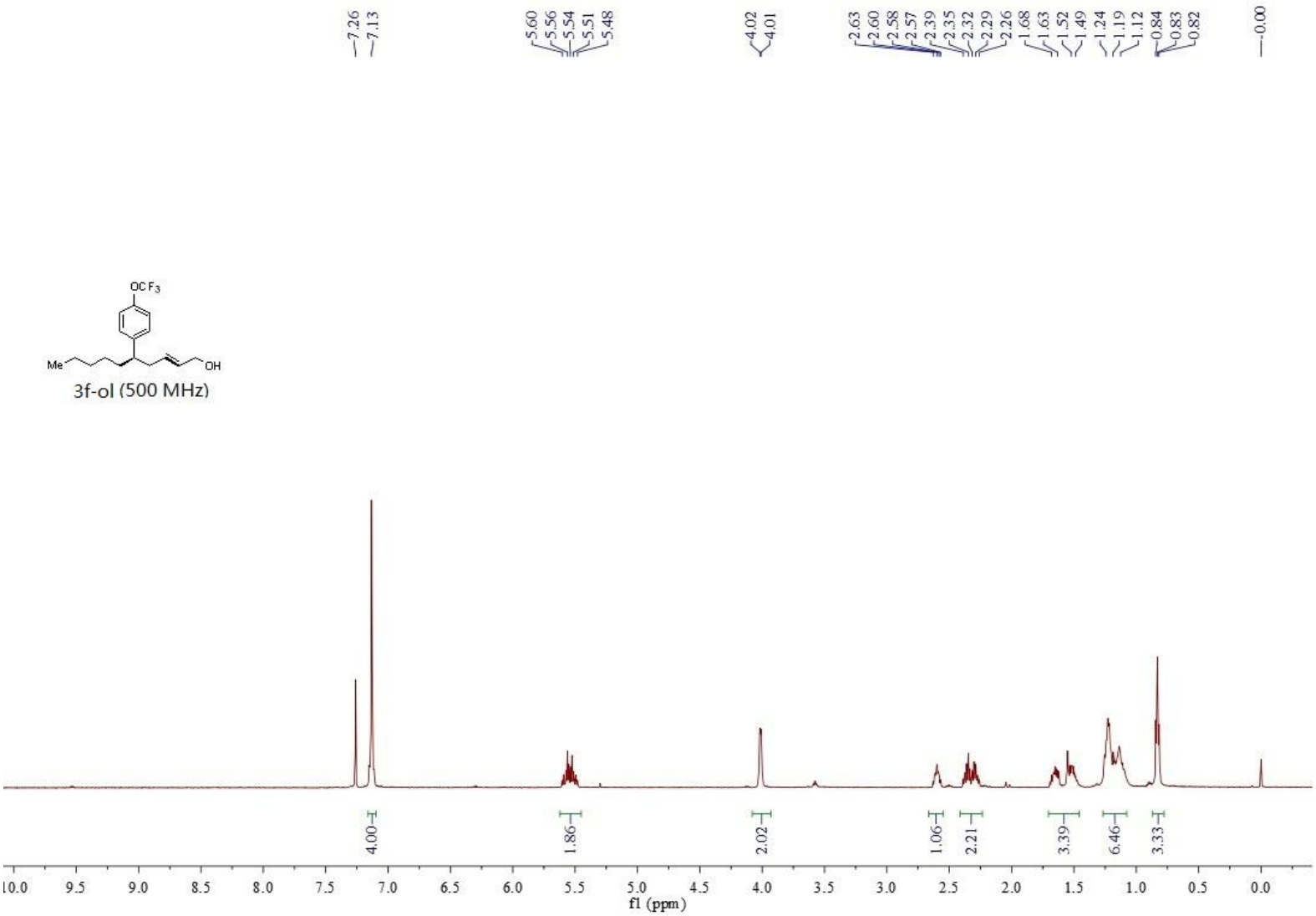
3e (300 MHz)

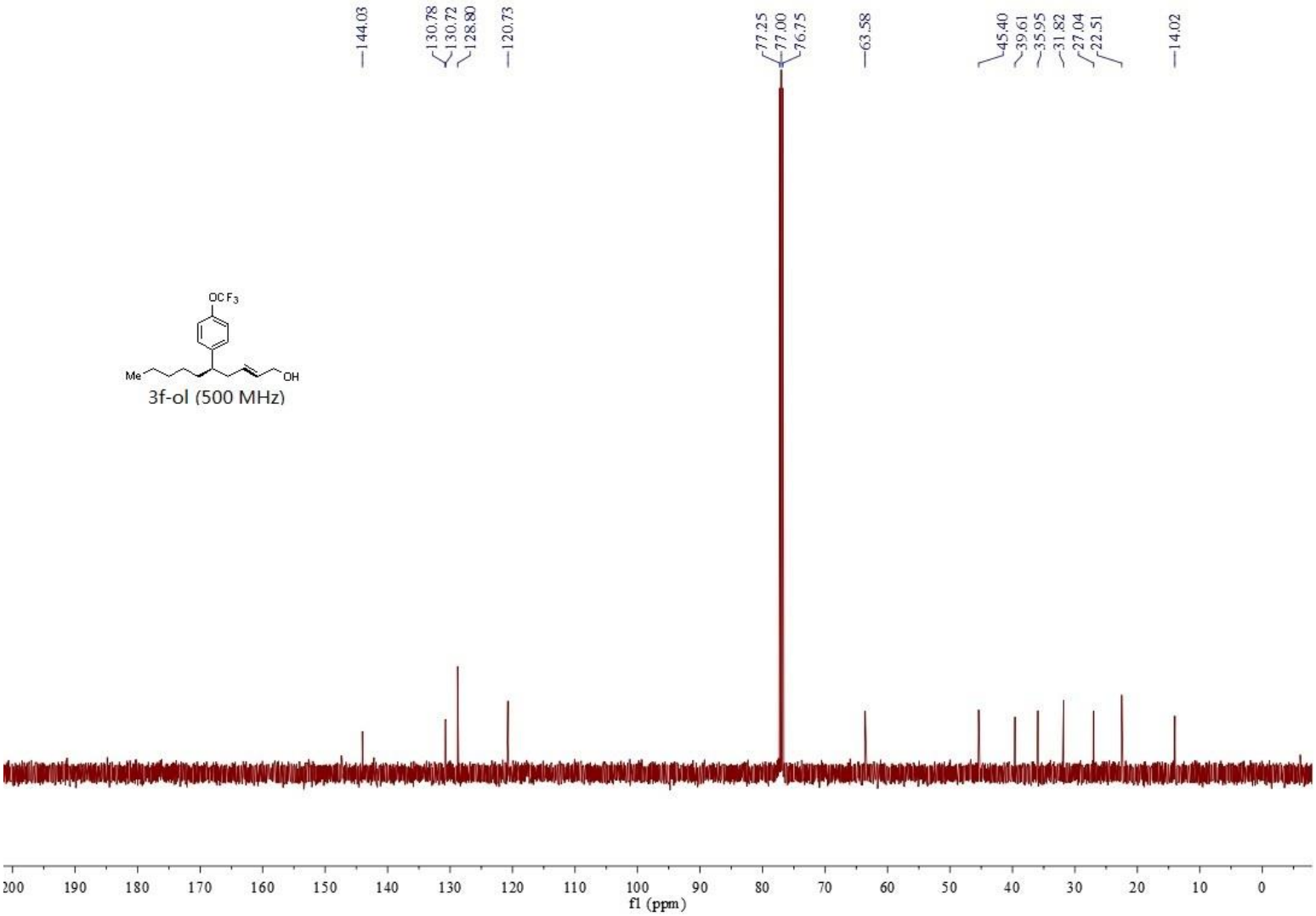

0.89
2.31
2.05
1.00
0.93
3.16
2.28
6.18
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

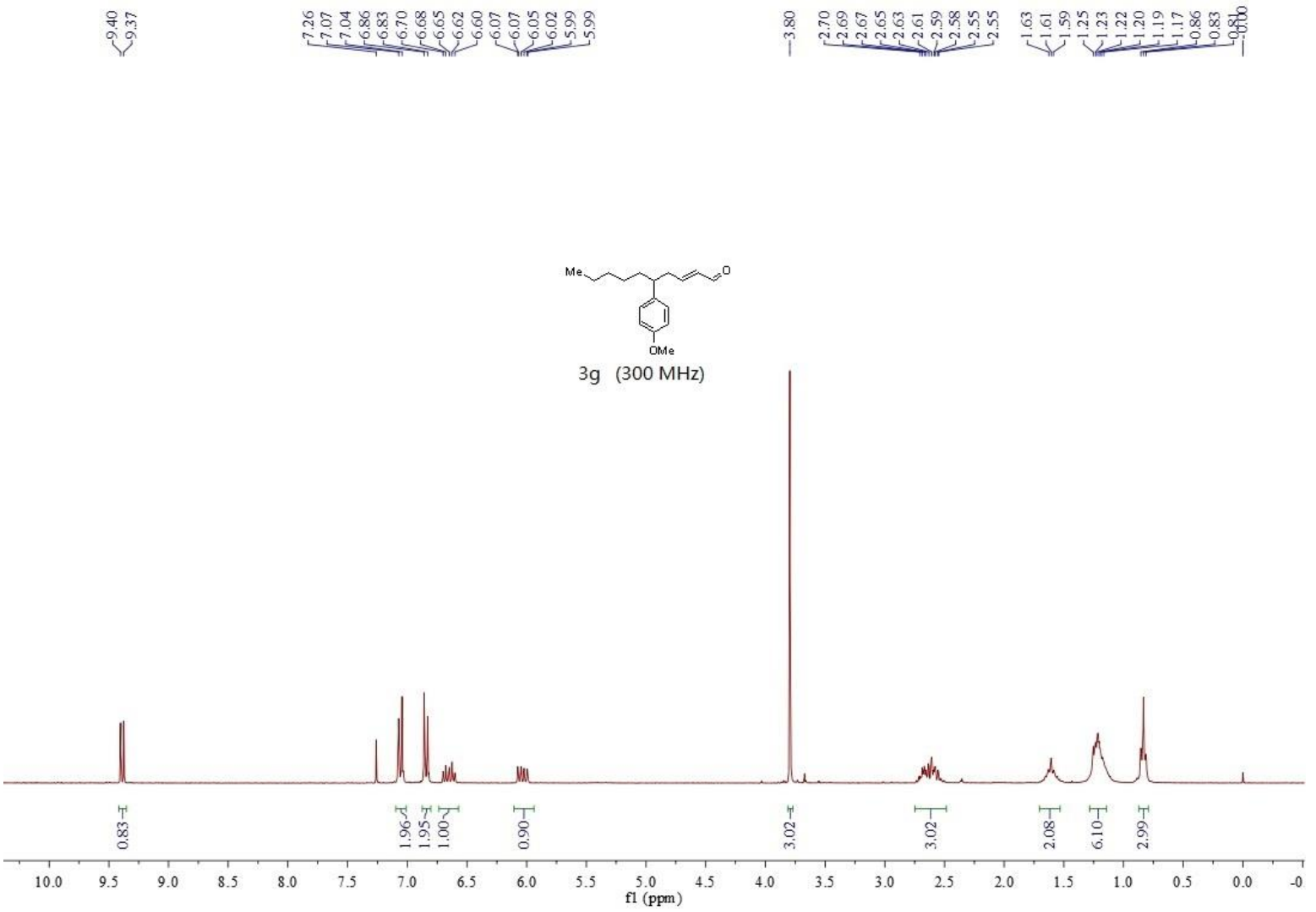

193.77
156.18
142.35
134.16
132.09
128.76
128.68
77.42
77.00
76.58
44.62
39.84
36.28
31.66
26.91
22.45
13.99
Me
O
Cl
3e (300 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

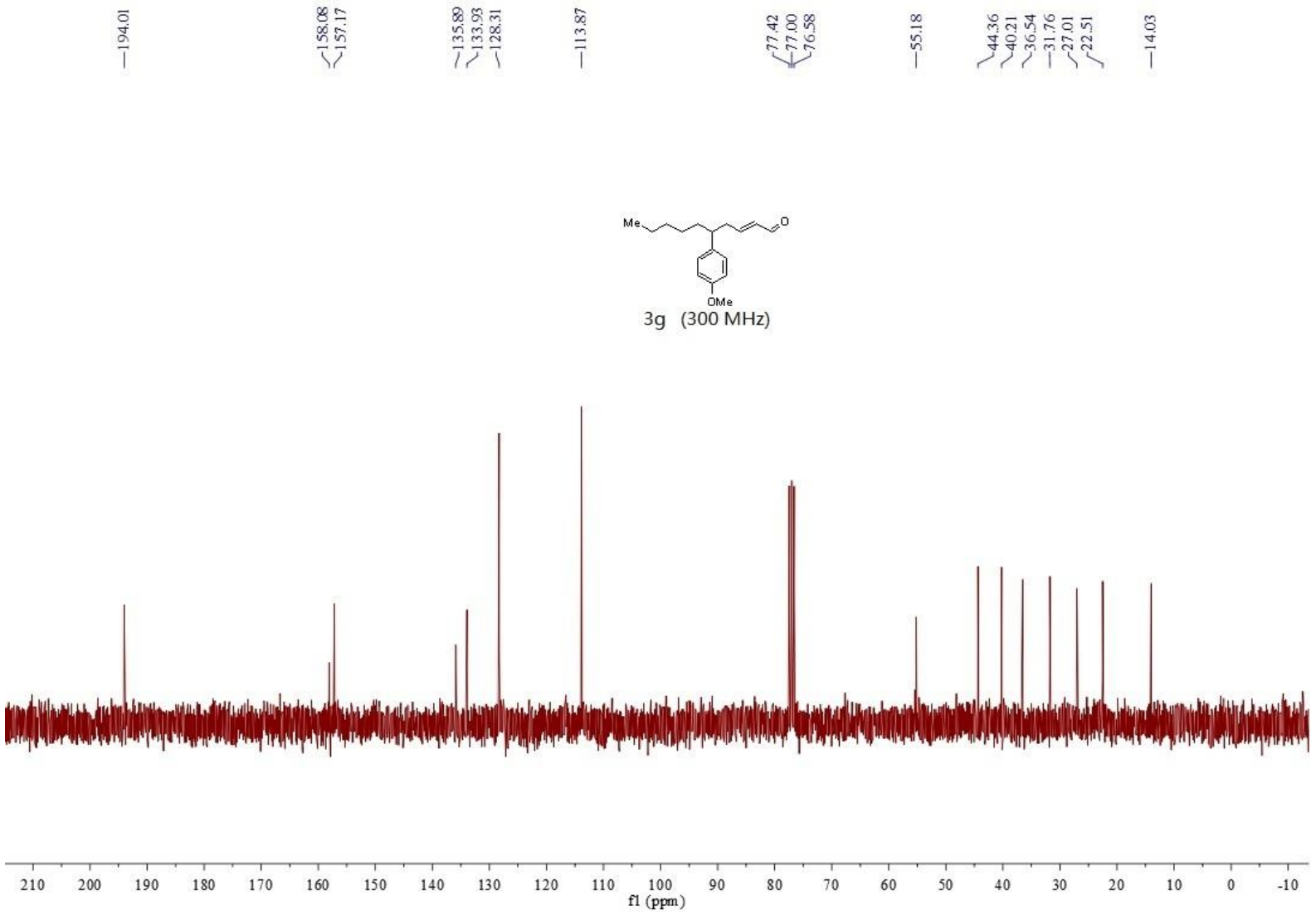

9.42
9.40
7.26
7.17
6.67
6.64
6.61
6.58
6.09
6.07
6.01
6.01
2.81
2.80
2.79
2.77
2.75
2.74
2.72
2.69
2.69
2.67
2.64
2.62
2.61
2.58
2.55
2.53
1.69
1.67
1.65
1.63
1.60
1.58
1.26
1.22
1.17
1.14
0.86
0.84
0.82
0.00
Me
O
OCF3
3f (300 MHz)
0.90
4.07
1.00
0.94
3.08
2.19
6.14
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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
0.0
-0
f1 (ppm)

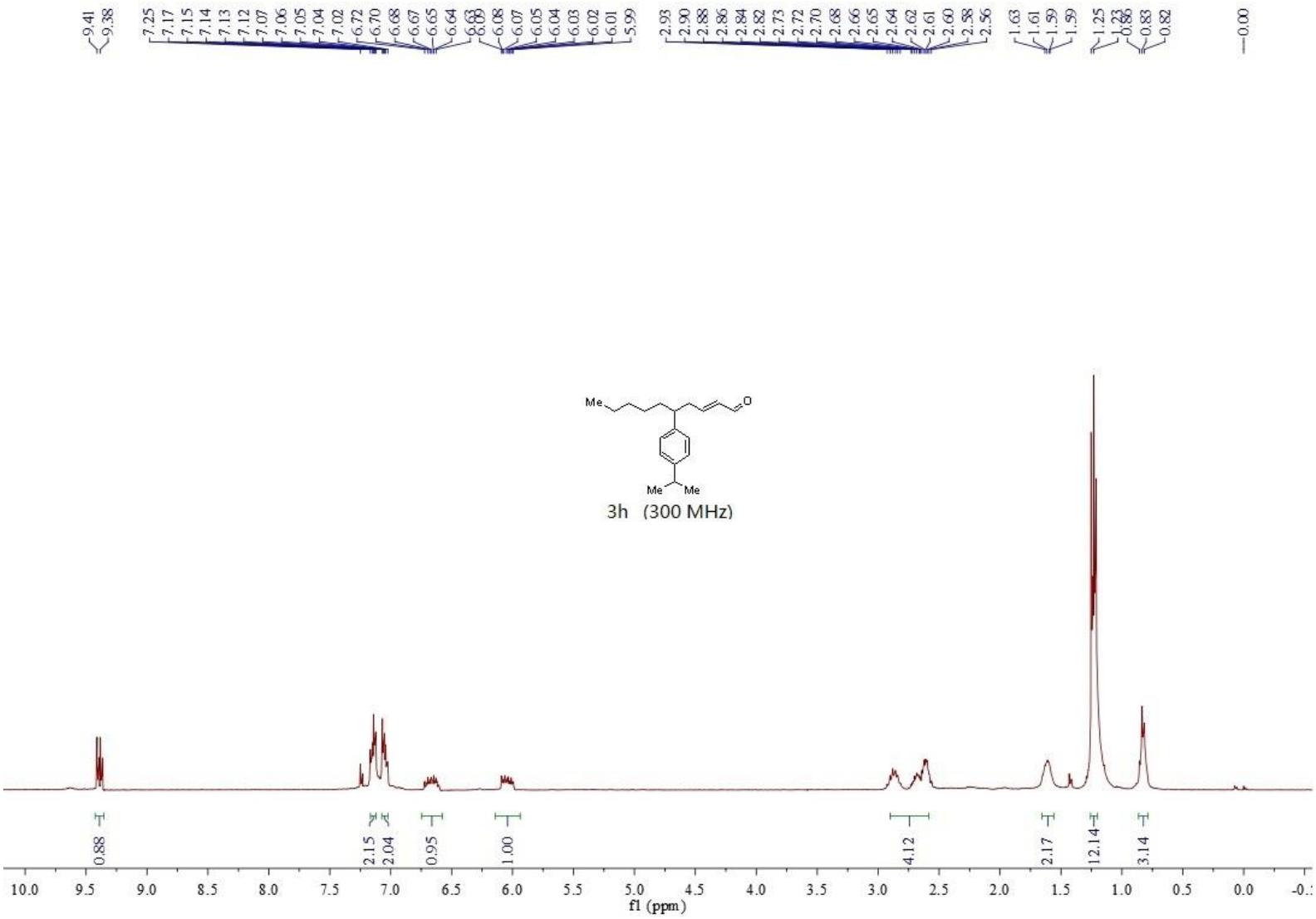

193.74
156.03
142.64
134.21
128.64
121.03
77.42
77.00
76.58
44.58
39.83
36.27
31.66
26.91
22.44
13.95
Me
O
OCF3
3f (300 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

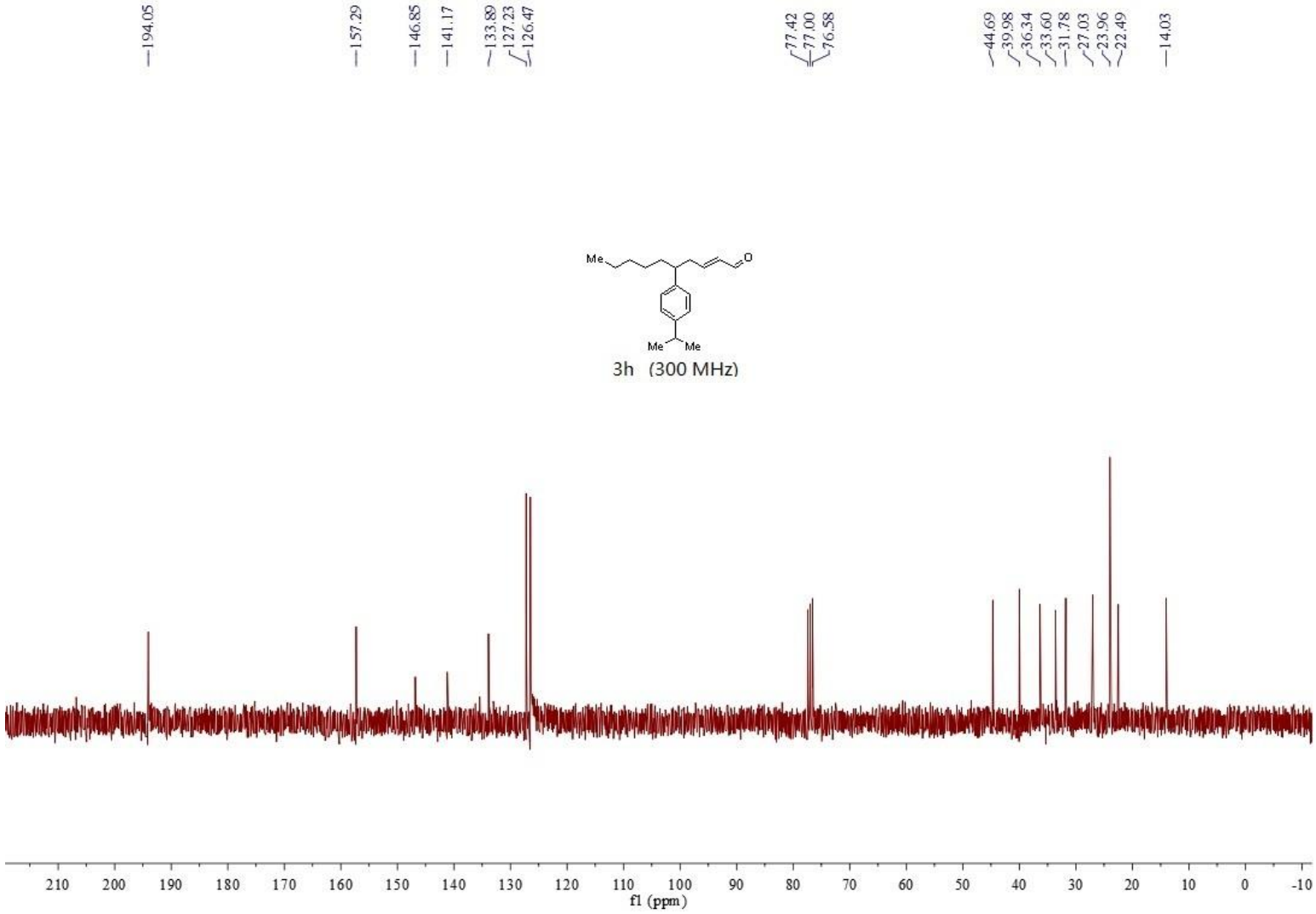

7.26
7.13
5.60
5.56
5.54
5.51
5.48
4.02
4.01
2.63
2.60
2.58
2.57
2.39
2.35
2.32
2.29
2.26
1.68
1.63
1.52
1.49
1.24
1.19
1.12
0.84
0.83
0.82
0.00
OCF3
Me
OH
3f-ol (500 MHz)
4.00
1.86
2.02
1.06
2.21
3.39
6.46
3.33
f1 (ppm)

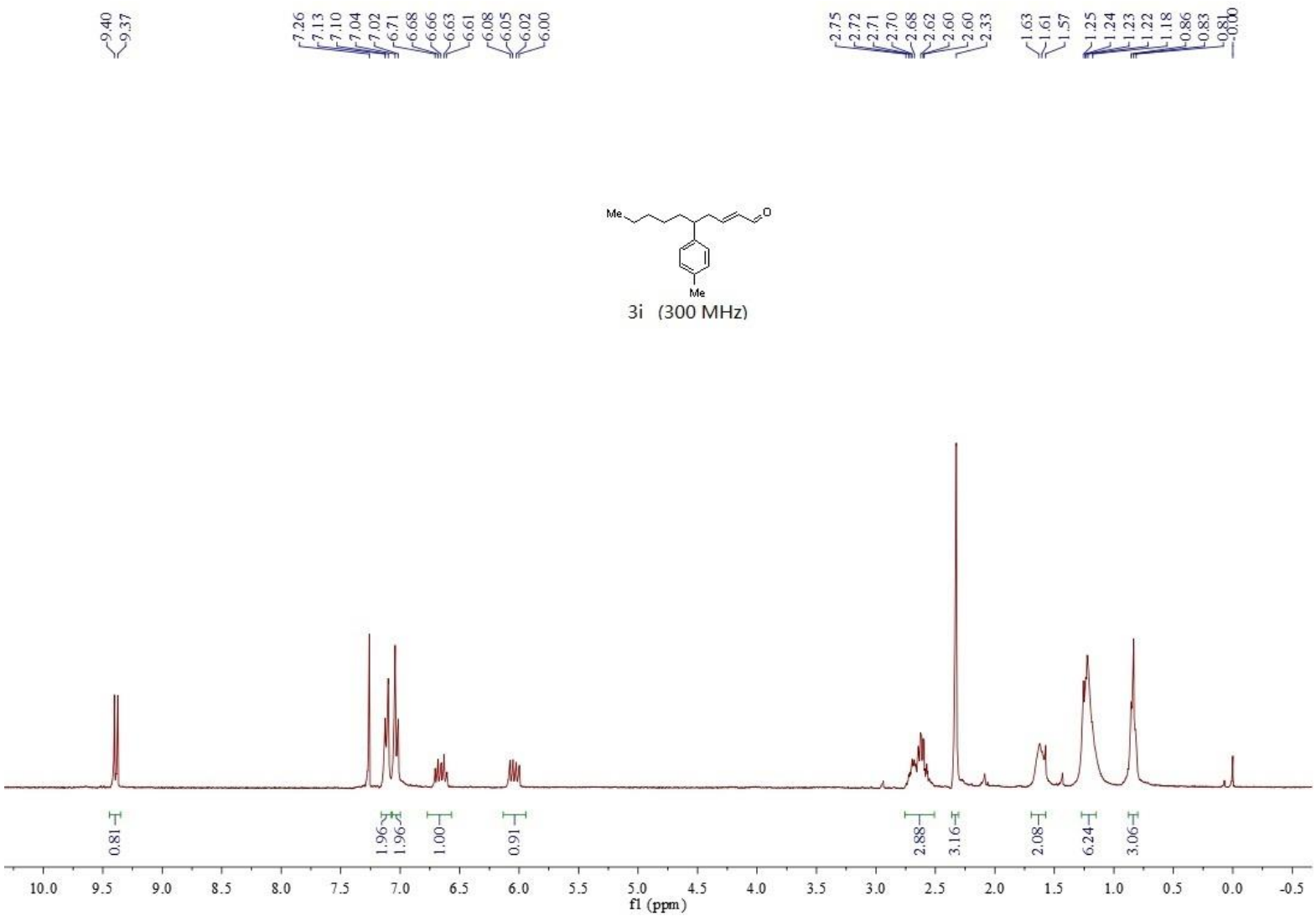

144.03
130.78
130.72
128.80
120.73
77.25
77.00
76.75
63.58
45.40
39.61
35.95
31.82
27.04
22.51
14.02
OCF3
Me
OH
3f-ol (500 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.40
9.37
7.26
7.07
7.04
6.86
6.83
6.70
6.68
6.65
6.62
6.60
6.07
6.07
6.05
6.02
5.99
5.99
3.80
2.70
2.69
2.67
2.65
2.63
2.61
2.59
2.58
2.55
2.55
1.63
1.61
1.59
1.25
1.23
1.22
1.20
1.19
1.17
0.86
0.83
0.81
0.00
Me
O
OMe
3g (300 MHz)
0.83
1.96
1.95
1.00
0.90
3.02
3.02
2.08
6.10
2.99
10.0 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 0.0 -0
f1 (ppm)

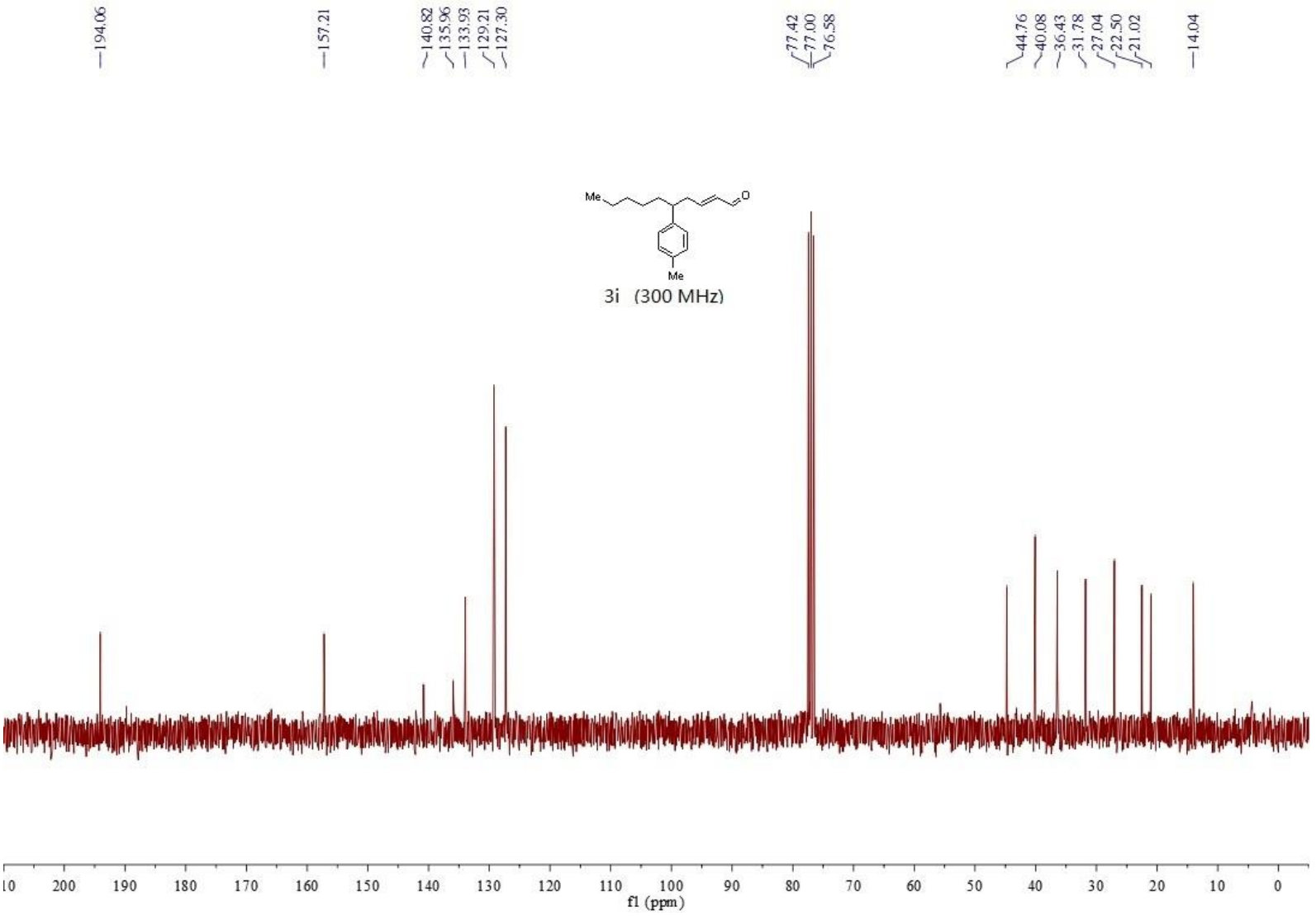

194.01
158.08
157.17
135.89
133.93
128.31
113.87
77.42
77.00
76.58
55.18
44.36
40.21
36.54
31.76
27.01
22.51
14.03
Me
O
OMe
3g (300 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

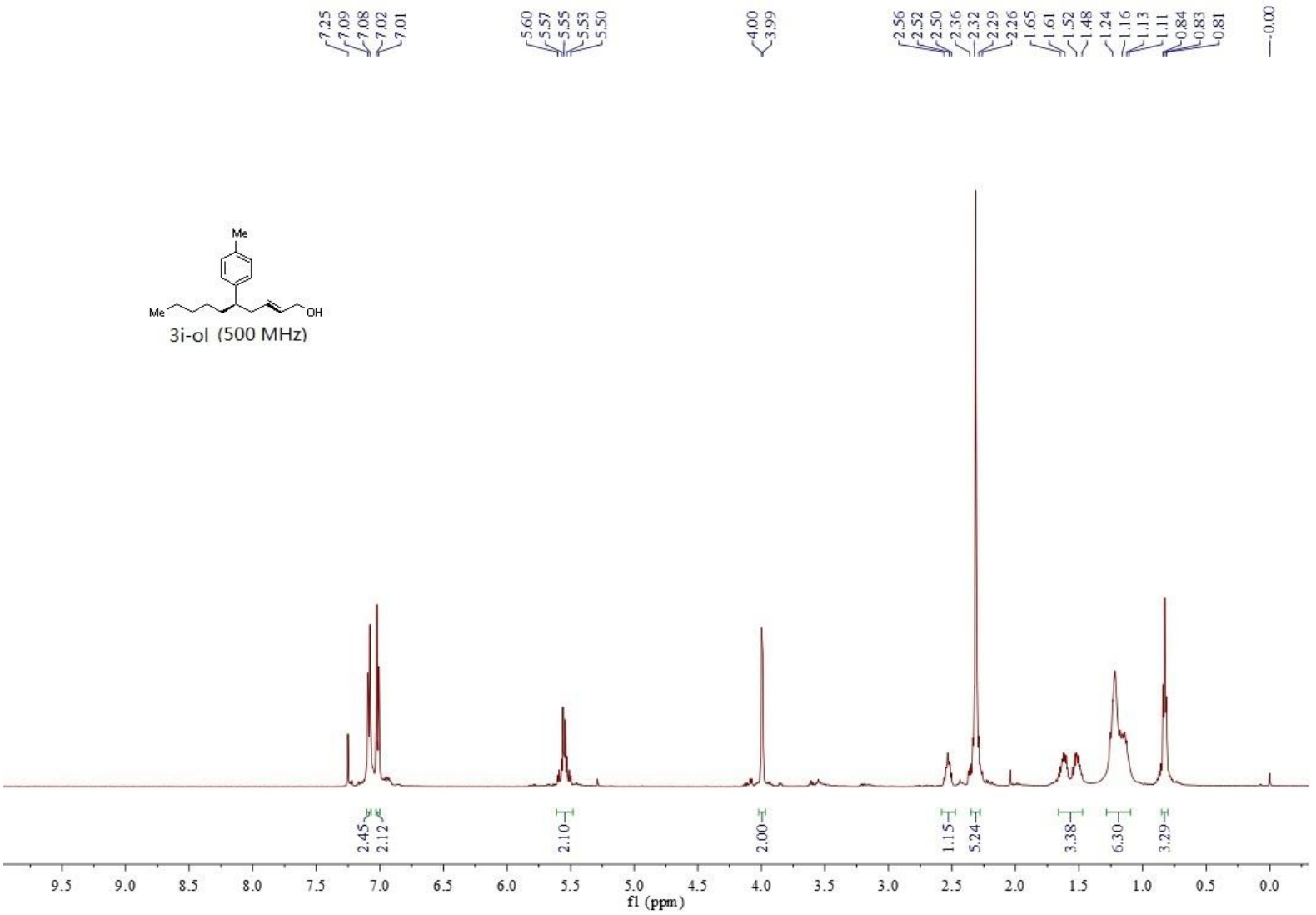

9.41
9.38
7.25
7.17
7.15
7.14
7.13
7.12
7.07
7.06
7.05
7.04
7.02
6.72
6.70
6.68
6.67
6.65
6.64
6.08
6.07
6.05
6.04
6.03
6.02
6.01
5.99
2.93
2.90
2.88
2.86
2.84
2.82
2.73
2.72
2.70
2.68
2.66
2.65
2.64
2.62
2.61
2.60
2.58
2.56
1.63
1.61
1.59
1.59
1.25
0.88
0.83
0.82
0.00
Me
O
Me
Me
3h (300 MHz)
0.88
2.15
2.04
0.95
1.00
4.12
2.17
12.14
3.14
10.0
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
0.0
f1 (ppm)

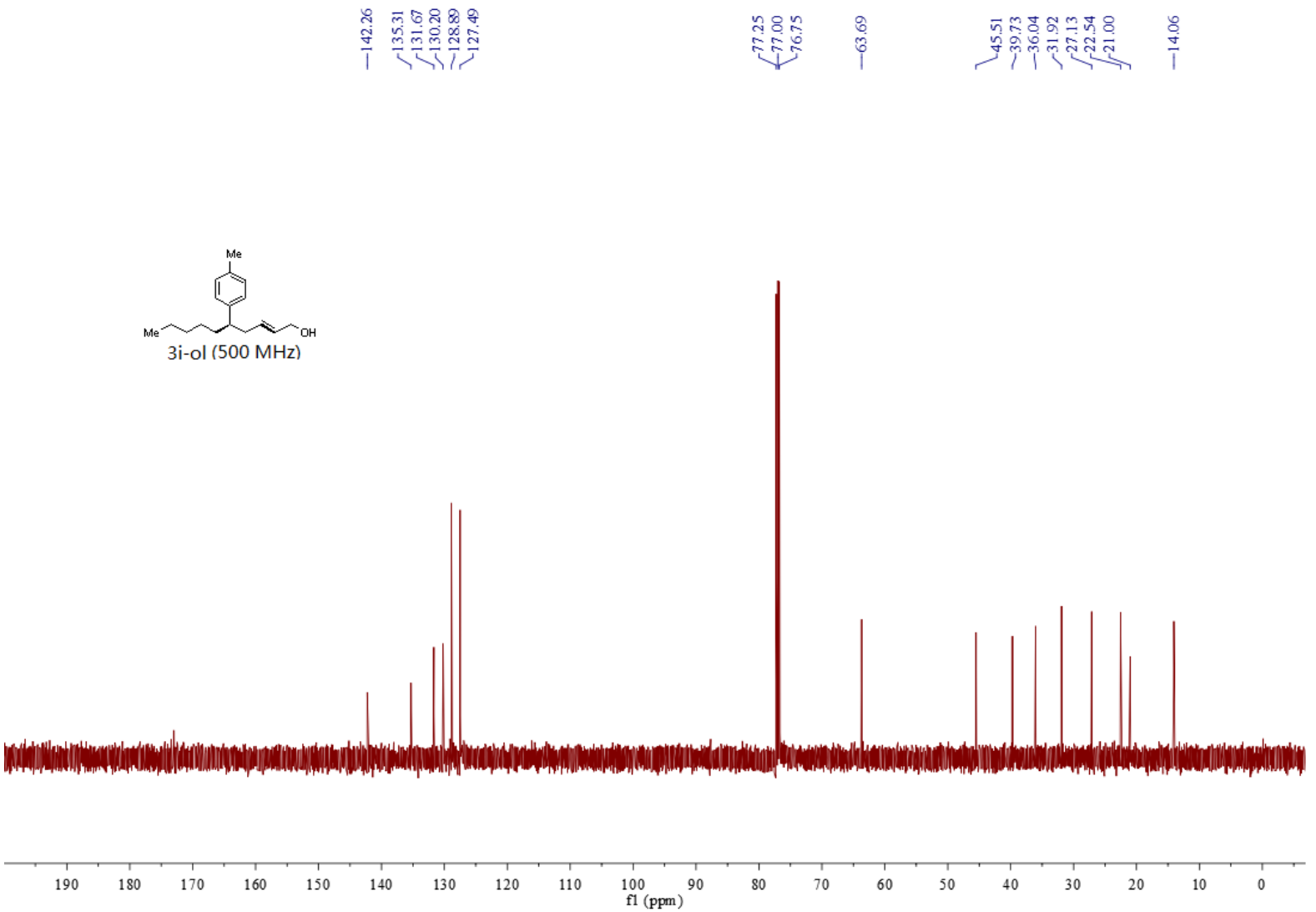

194.05
157.29
146.85
141.17
133.89
127.23
126.47
77.42
77.00
76.58
44.69
39.98
36.34
33.60
31.78
27.03
23.96
22.49
14.03
Me
O
Me
Me
3h (300 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

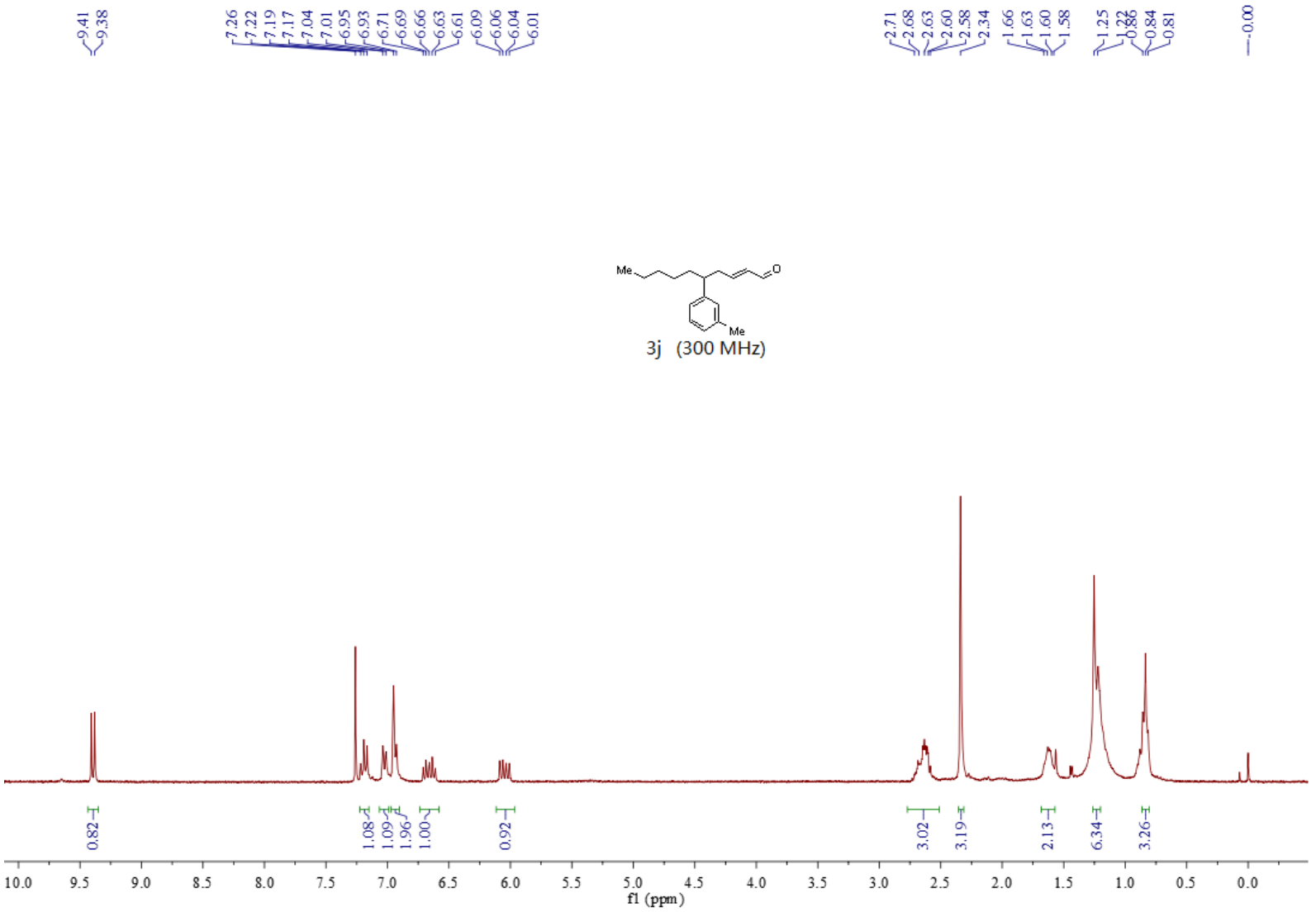

9.40
9.37
7.26
7.13
7.10
7.04
7.02
6.71
6.68
6.66
6.63
6.61
6.08
6.05
6.02
6.00
2.75
2.72
2.71
2.70
2.68
2.62
2.60
2.60
2.33
1.63
1.61
1.57
1.25
1.24
1.23
1.22
1.18
0.86
0.83
0.81
0.00
Me
O
Me
0.81
1.96
1.96
1.00
0.91
2.88
3.16
2.08
6.24
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

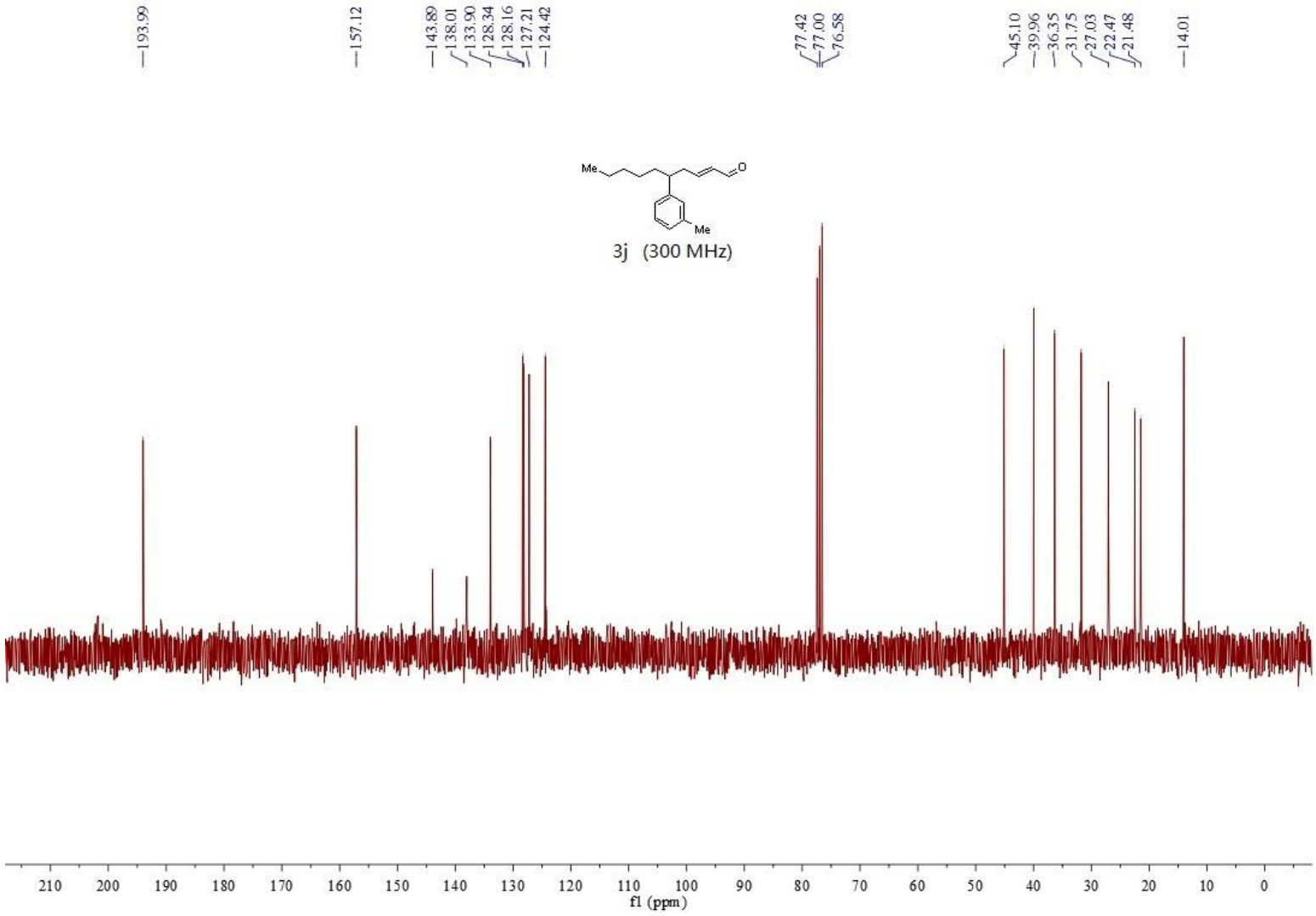
3i (300 MHz)

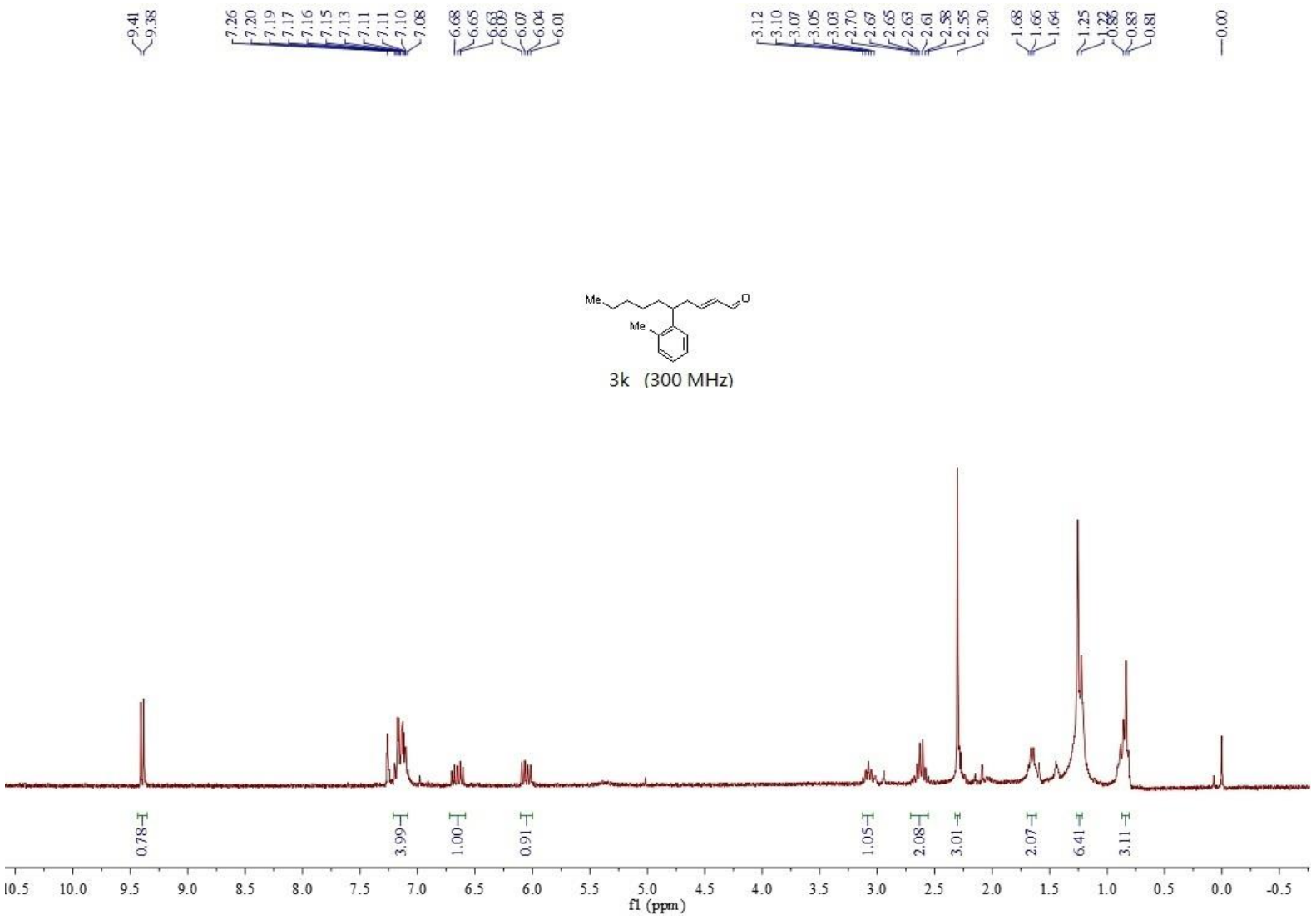

194.06
157.21
140.82
135.96
133.93
129.21
127.30
77.42
77.00
76.58
44.76
40.08
36.43
31.78
27.04
22.50
21.02
14.04
Me
O
Me
3i (300 MHz)
f1 (ppm)

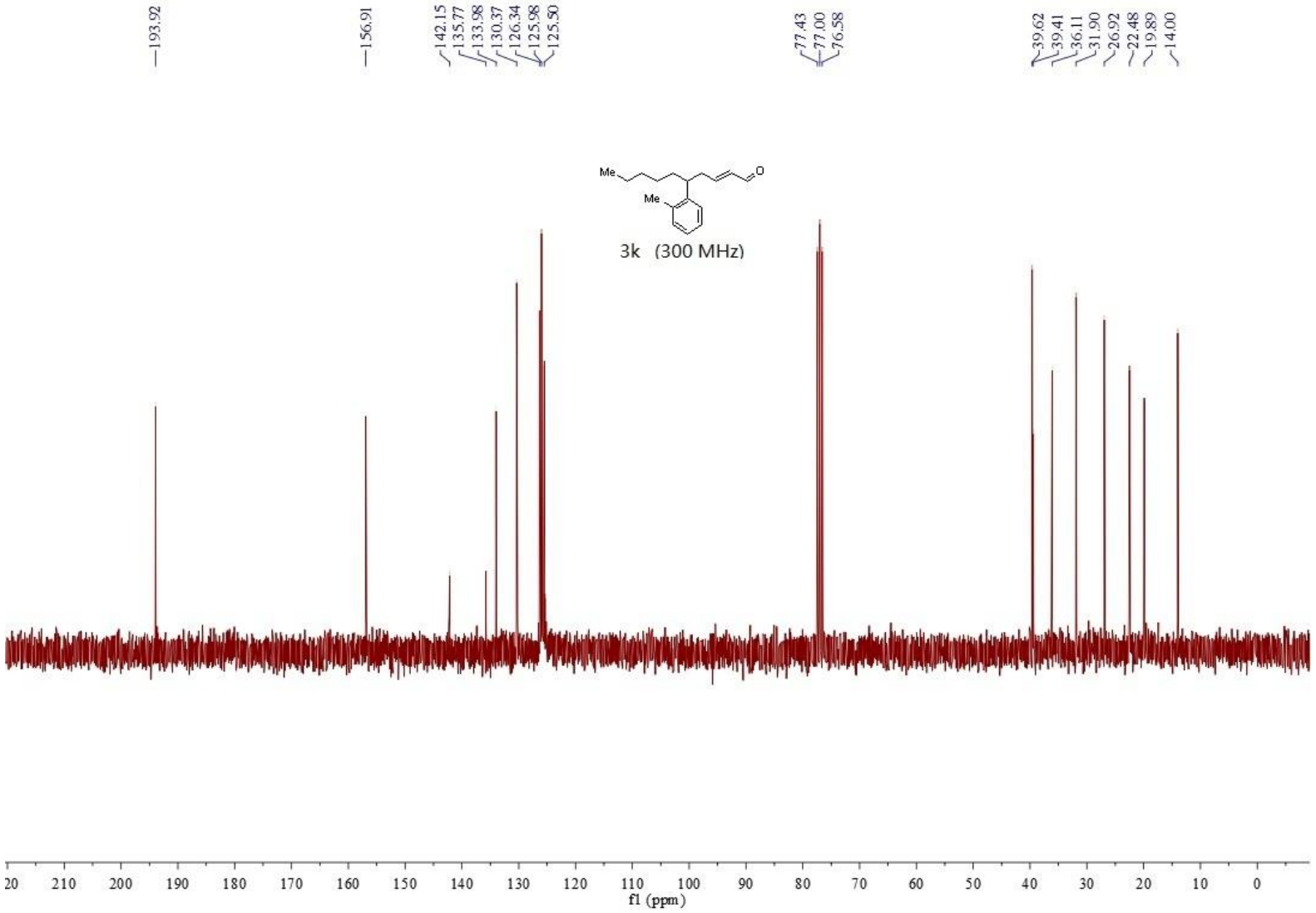

7.25
7.09
7.08
7.02
7.01
5.60
5.57
5.55
5.53
5.50
4.00
3.99
2.56
2.52
2.50
2.36
2.32
2.29
2.26
1.65
1.61
1.52
1.48
1.24
1.16
1.13
1.11
0.84
0.83
0.81
0.00
Me
Me
OH
3i-ol (500 MHz)
2.45
2.12
2.10
2.00
1.15
5.24
3.38
6.30
3.29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

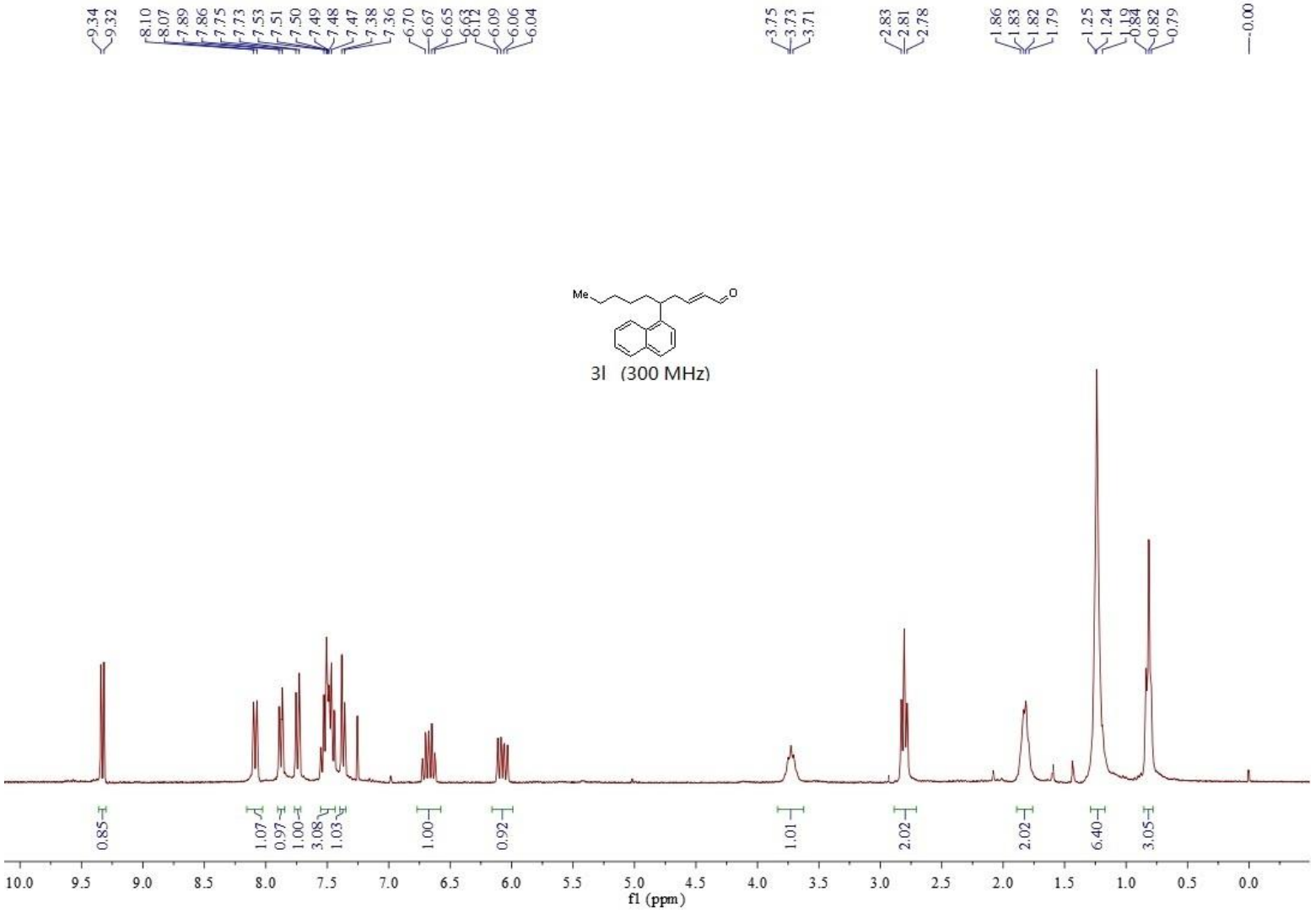

142.26
135.31
131.67
130.20
128.89
127.49
77.25
77.00
76.75
63.69
45.51
39.73
36.04
31.92
27.13
22.54
21.00
14.06
Me
Me
OH
3i-ol (500 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

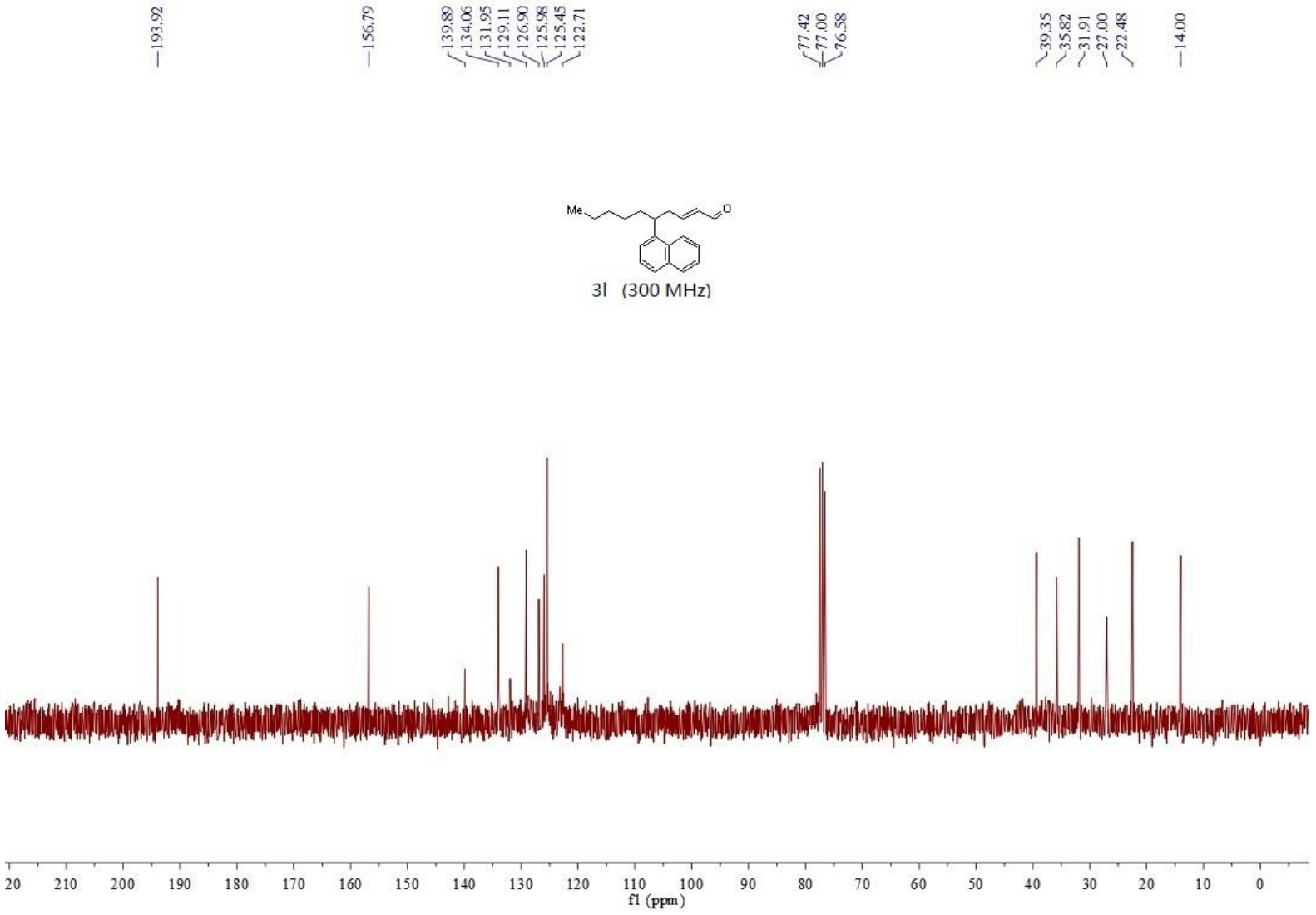

9.41
9.38
7.26
7.22
7.19
7.17
7.04
7.01
6.95
6.93
6.71
6.69
6.66
6.63
6.61
6.09
6.06
6.04
6.01
2.71
2.68
2.63
2.60
2.58
2.34
1.66
1.63
1.60
1.58
1.25
1.22
0.86
0.84
0.81
0.00
Me
O
Me
3j (300 MHz)
0.82
1.08
1.09
1.96
1.00
0.92
3.02
3.19
2.13
6.34
3.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

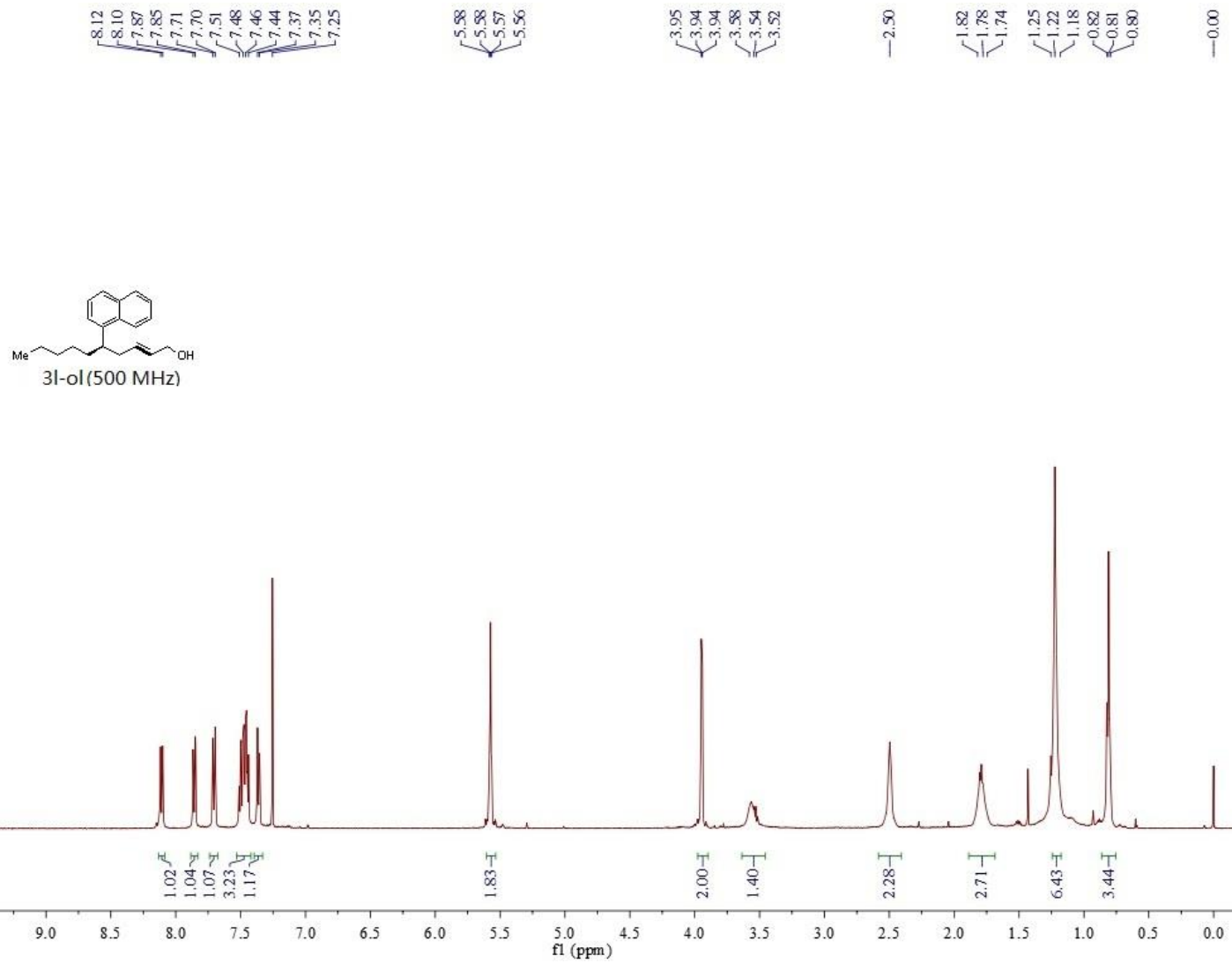

193.99
157.12
143.89
138.01
133.90
128.34
128.16
127.21
124.42
77.42
77.00
76.58
45.10
39.96
36.35
31.75
27.03
22.47
21.48
14.01
Me
Me
O
3j (300 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

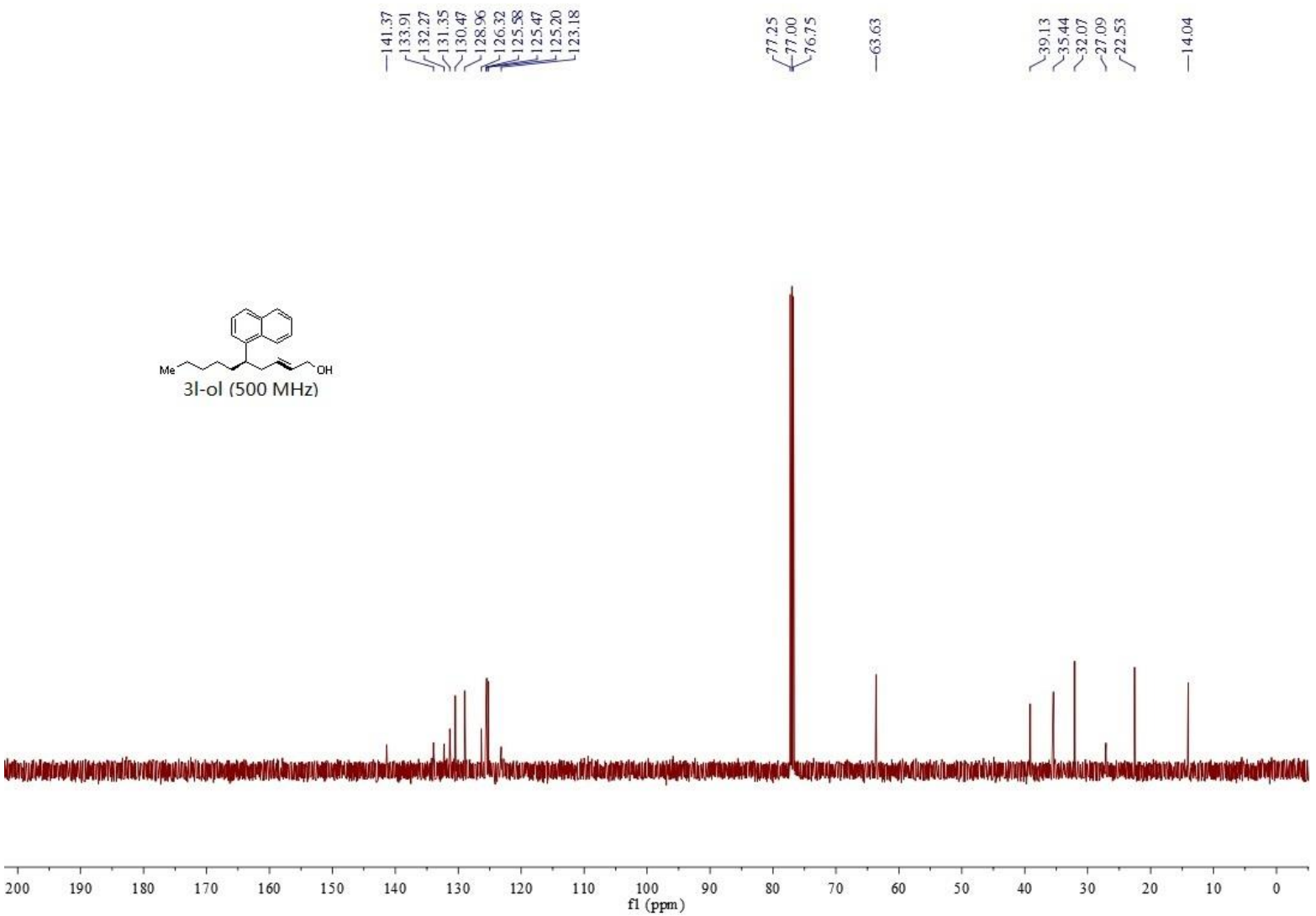

9.41
9.38
7.26
7.20
7.19
7.17
7.16
7.15
7.13
7.11
7.11
7.10
7.08
6.68
6.65
6.63
6.60
6.07
6.04
6.01
3.12
3.10
3.07
3.05
3.03
2.70
2.67
2.65
2.63
2.61
2.58
2.55
2.30
1.68
1.66
1.64
1.25
1.22
0.86
0.83
0.81
0.00
Me
Me
O
3k (300 MHz)
0.78
3.99
1.00
0.91
1.05
2.08
3.01
2.07
6.41
3.11
f1 (ppm)

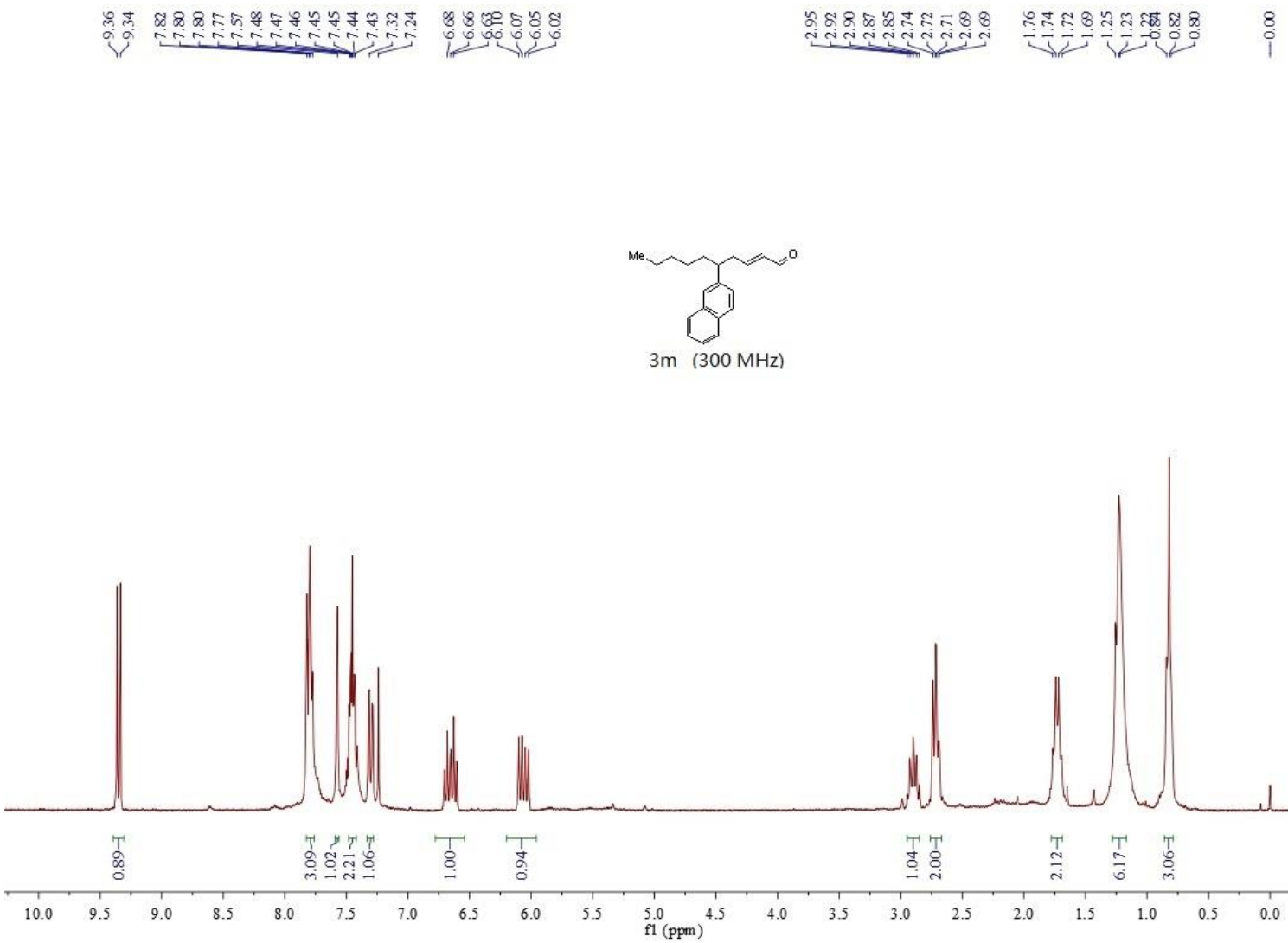

193.92
156.91
142.15
135.77
133.98
130.37
126.34
125.98
125.50
77.43
77.00
76.58
39.62
39.41
36.11
31.90
26.92
22.48
19.89
14.00
Me
Me
O
3k (300 MHz)
f1 (ppm)

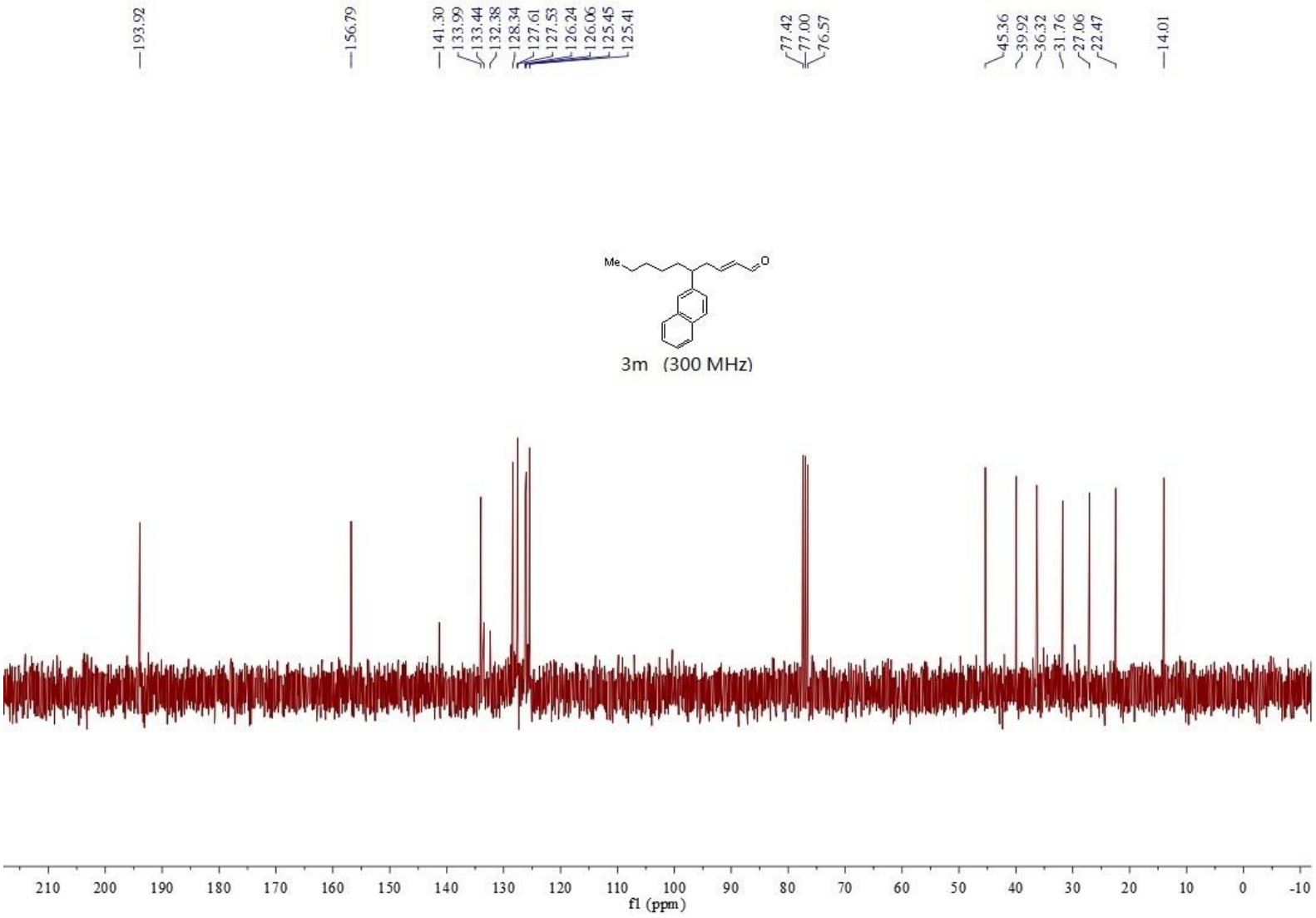

9.34
9.32
8.10
8.07
7.89
7.86
7.75
7.73
7.53
7.51
7.50
7.49
7.48
7.47
7.38
7.36
6.70
6.67
6.65
6.63
6.12
6.09
6.06
6.04
3.75
3.73
3.71
2.83
2.81
2.78
1.86
1.83
1.82
1.79
1.25
1.24
1.19
0.84
0.82
0.79
0.00
Me
O
3l (300 MHz)
0.85
1.07
0.97
1.00
3.08
1.03
1.00
0.92
1.01
2.02
2.02
6.40
3.05
10.0
9.5
9.0
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
0.0
f1 (ppm)

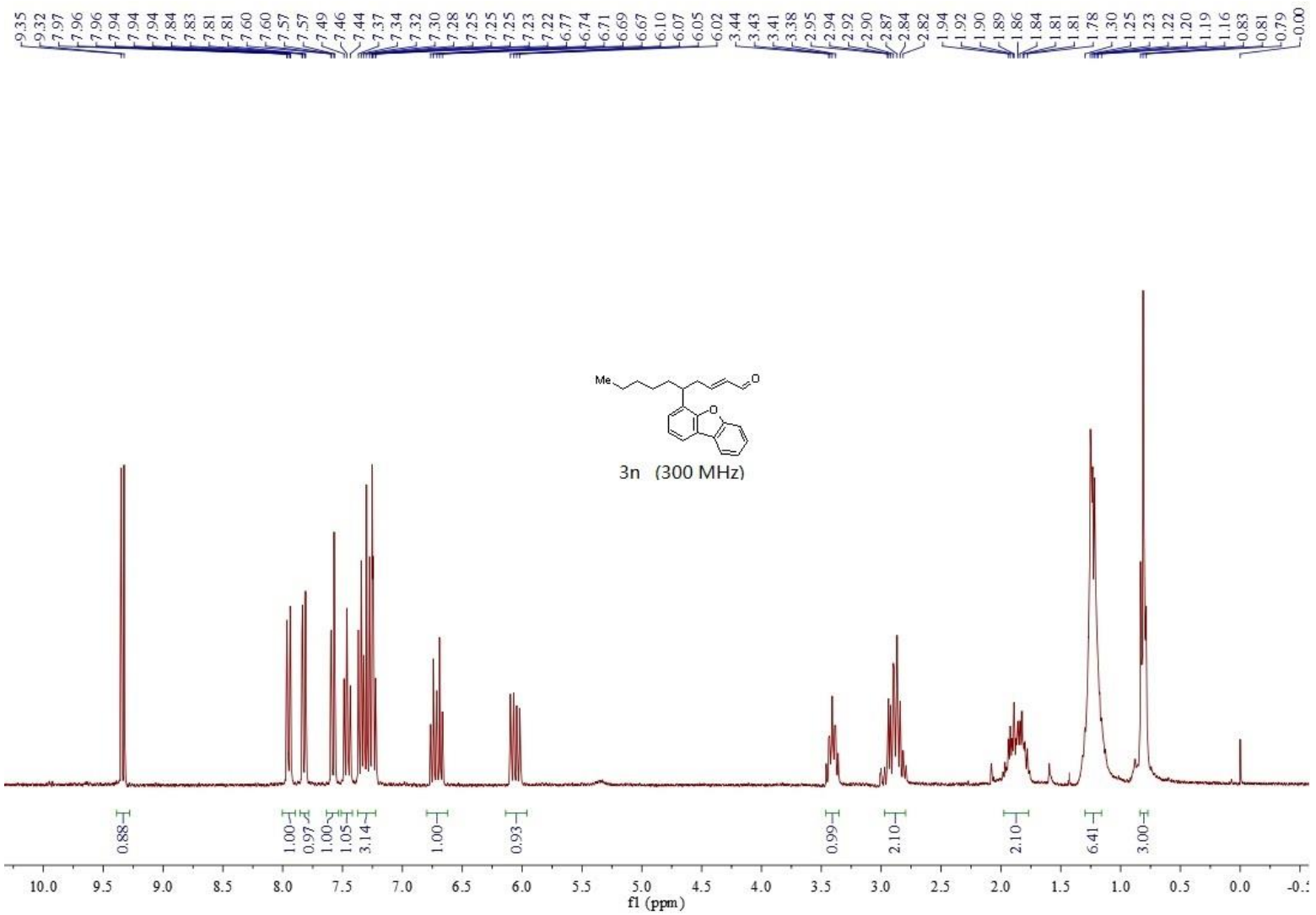

193.92
156.79
139.89
134.06
131.95
129.11
126.90
125.98
125.45
122.71
77.42
77.00
76.58
39.35
35.82
31.91
27.00
22.48
14.00
Me
O
3l (300 MHz)
f1 (ppm)

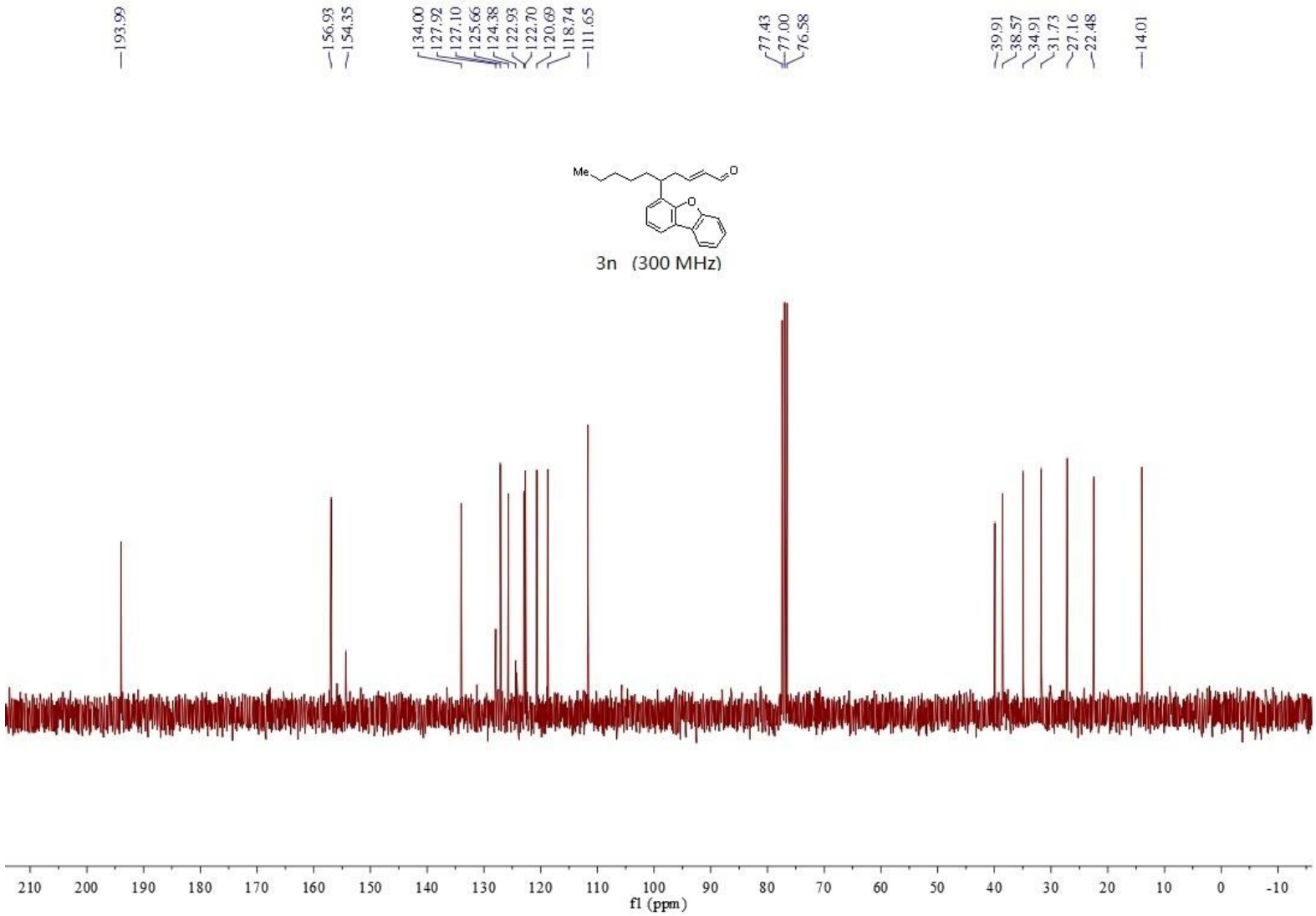

8.12
8.10
7.87
7.85
7.71
7.70
7.51
7.48
7.46
7.44
7.37
7.35
7.25
5.58
5.58
5.57
5.56
3.95
3.94
3.94
3.58
3.54
3.52
2.50
1.82
1.78
1.74
1.25
1.22
1.18
0.82
0.81
0.80
0.00
Me
OH
3l-ol (500 MHz)
1.02
1.04
1.07
3.23
1.17
1.83
2.00
1.40
2.28
2.71
6.43
3.44
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

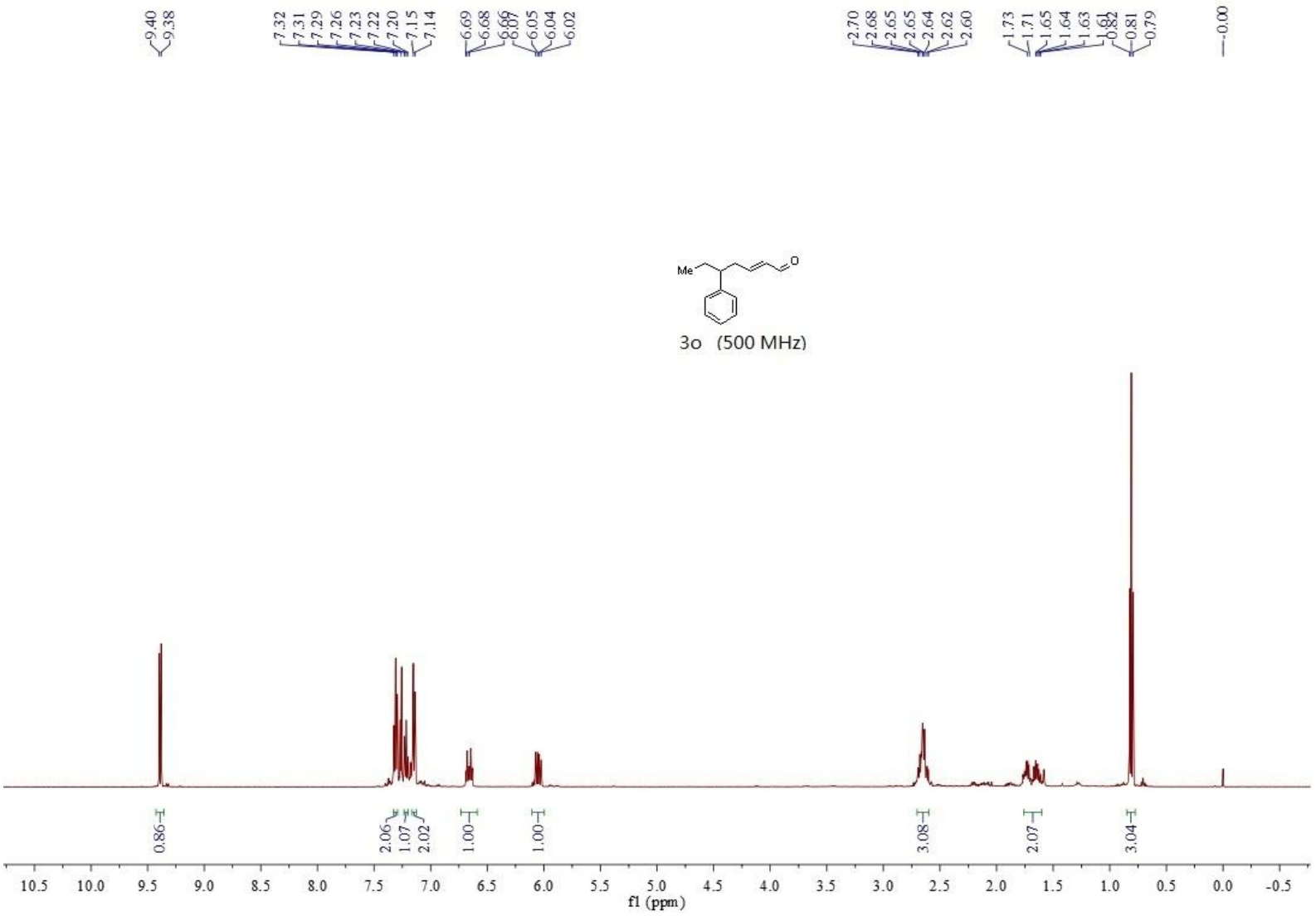

141.37
133.91
132.27
131.35
130.47
128.96
126.32
125.58
125.47
125.20
123.18
77.25
77.00
76.75
63.63
39.13
35.44
32.07
27.09
22.53
14.04
Me
OH
3l-ol (500 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

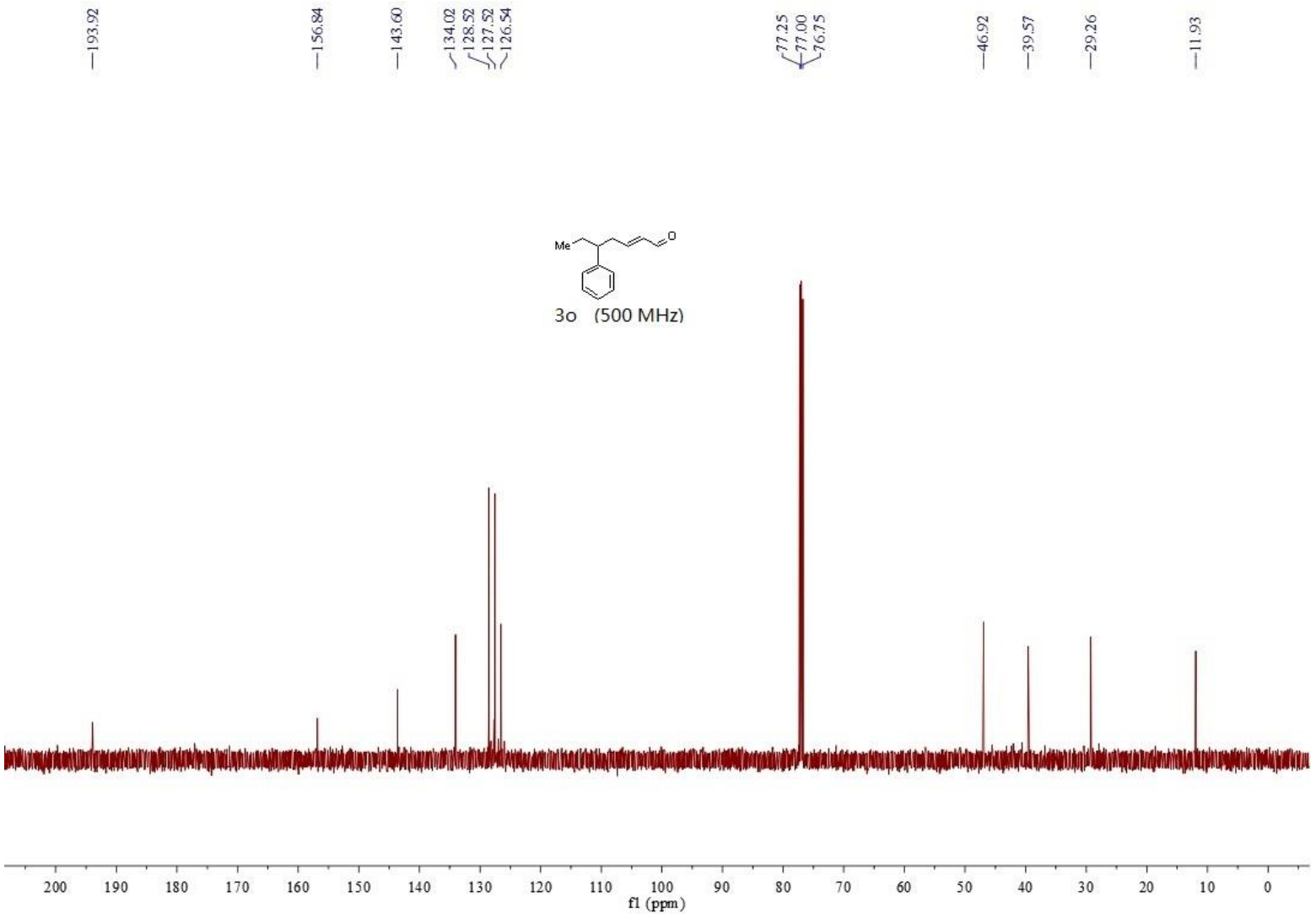

9.36
9.34
7.82
7.80
7.80
7.77
7.57
7.48
7.47
7.46
7.45
7.45
7.44
7.43
7.32
7.24
6.68
6.66
6.63
6.10
6.07
6.05
6.02
2.95
2.92
2.90
2.87
2.85
2.74
2.72
2.71
2.69
2.69
1.76
1.74
1.72
1.69
1.25
1.23
0.82
0.80
0.00
Me
O
3m (300 MHz)
0.89
3.09
1.02
2.21
1.06
1.00
0.94
1.04
2.00
2.12
6.17
3.06
10.0
9.5
9.0
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
0.0
-0.5
f1 (ppm)

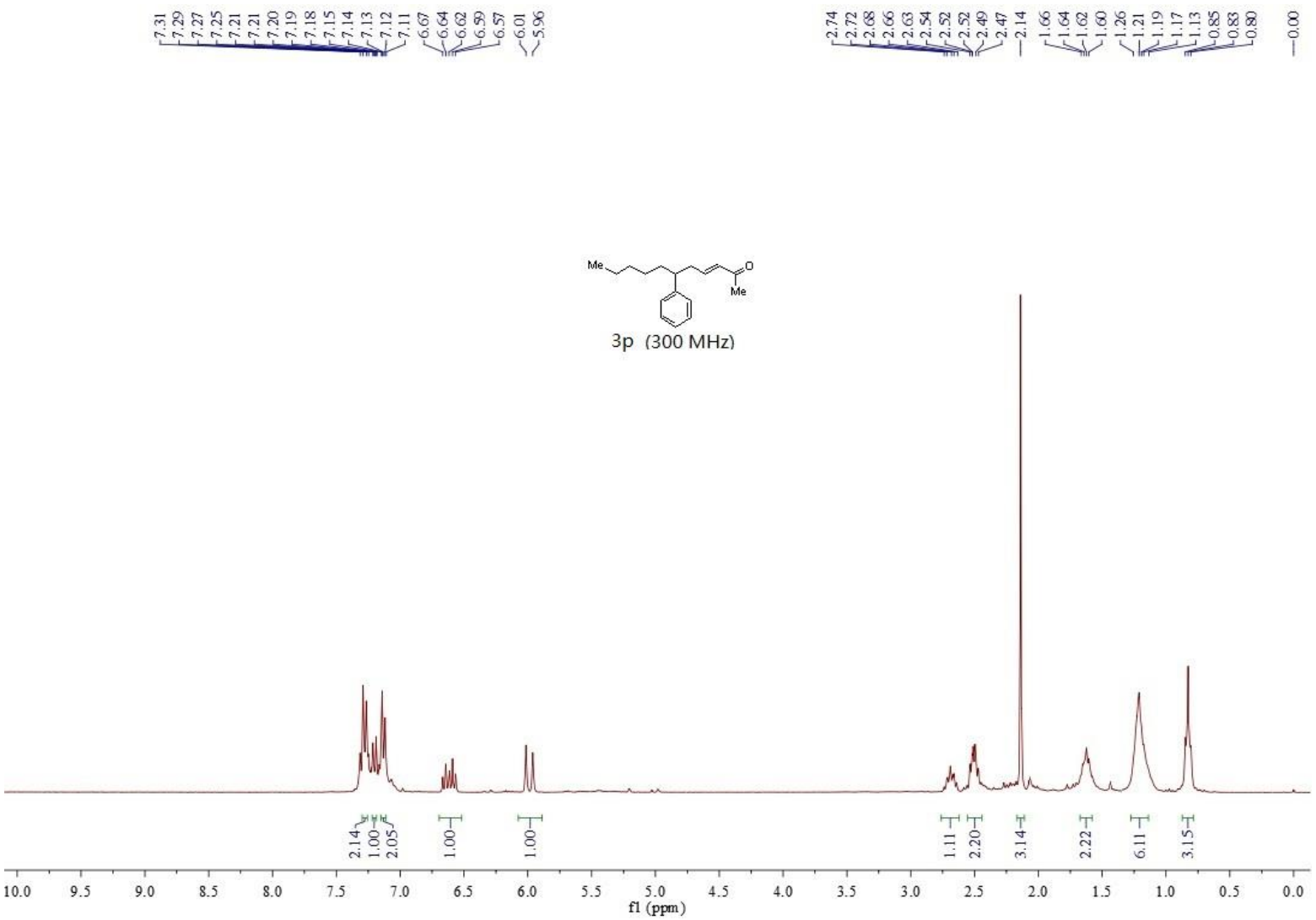

193.92
156.79
141.30
133.99
133.44
132.38
128.34
127.61
127.53
126.24
126.06
125.45
125.41
77.42
77.00
76.57
45.36
39.92
36.32
31.76
27.06
22.47
14.01
Me
O
3m (300 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

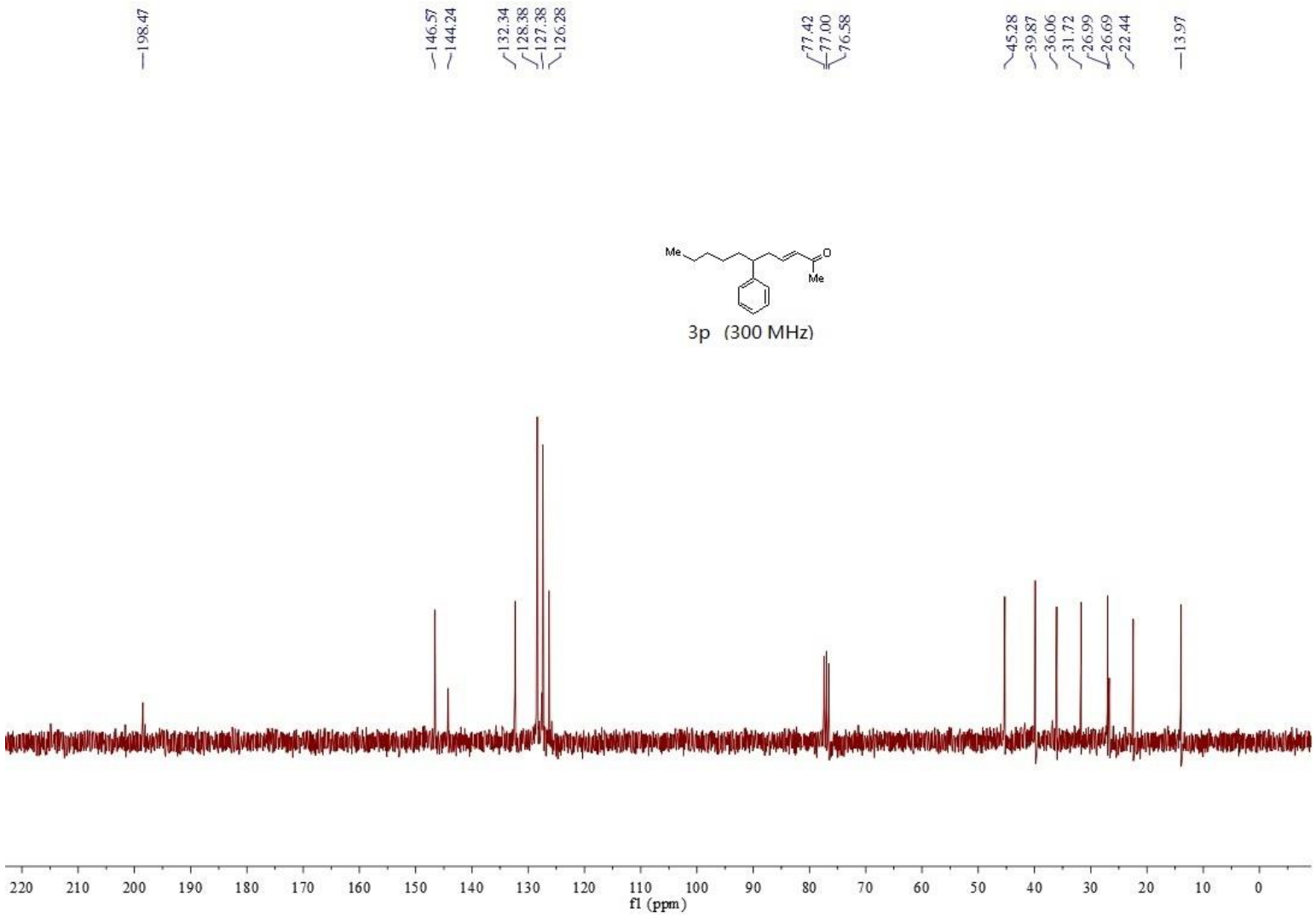

9.35
9.32
7.97
7.96
7.96
7.94
7.94
7.94
7.84
7.83
7.81
7.81
7.60
7.60
7.57
7.57
7.49
7.46
7.44
7.37
7.34
7.32
7.30
7.28
7.25
7.25
7.25
7.23
7.22
6.77
6.74
6.71
6.69
6.67
6.10
6.07
6.05
6.02
3.44
3.43
3.41
3.38
2.95
2.94
2.92
2.90
2.87
2.84
2.82
1.94
1.92
1.90
1.89
1.86
1.84
1.81
1.81
1.78
1.30
1.25
1.23
1.22
1.20
1.19
1.16
0.83
0.81
0.79
0.00
Me
O
O
3n (300 MHz)
0.88
1.00
0.97
1.00
1.05
3.14
1.00
0.93
0.99
2.10
2.10
6.41
3.00
10.0
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
0.0
f1 (ppm)

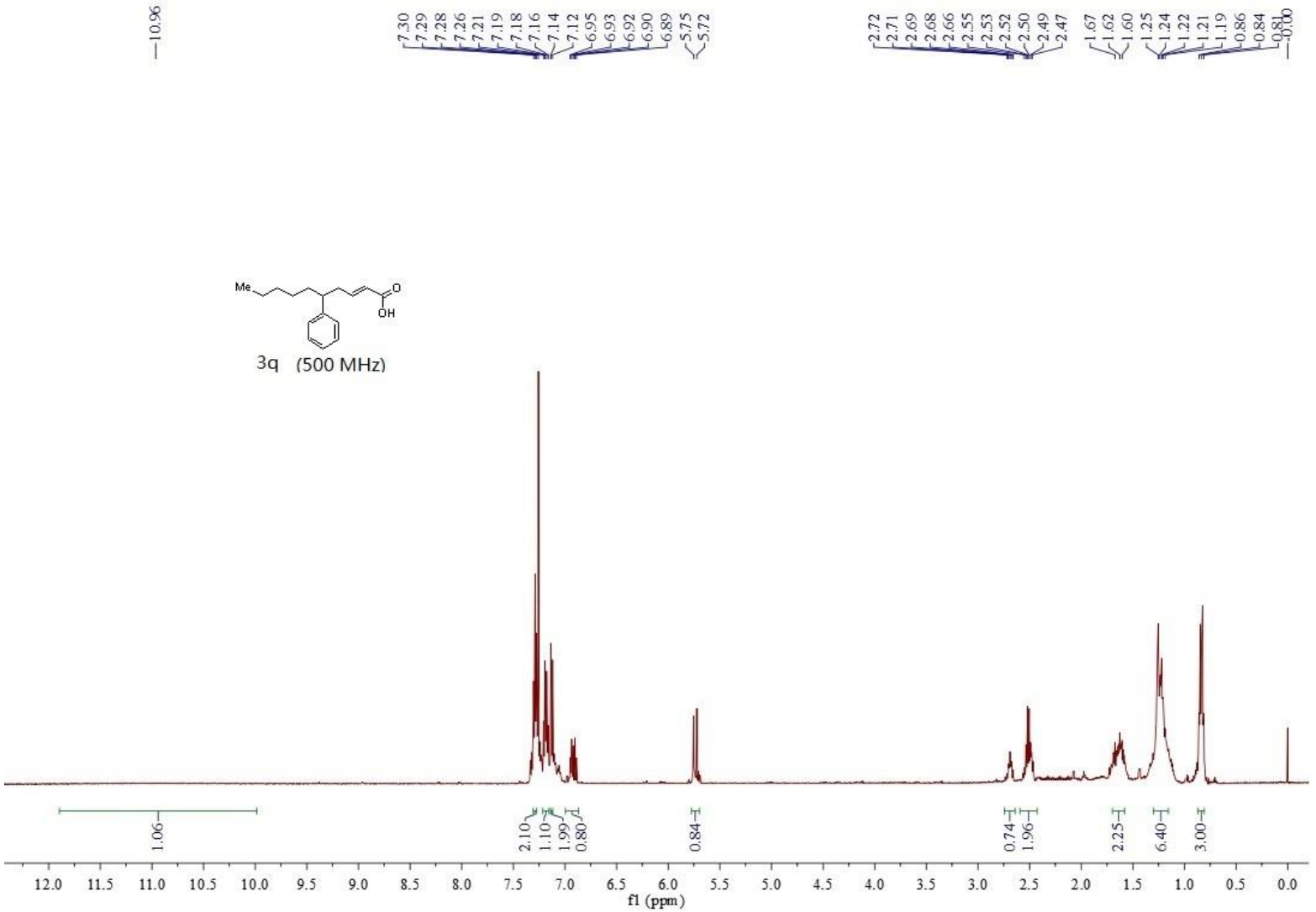

193.99
156.93
154.35
134.00
127.92
127.10
125.66
124.38
122.93
122.70
120.69
118.74
111.65
77.43
77.00
76.58
39.91
38.57
34.91
31.73
27.16
22.48
14.01
Me
O
O
3n (300 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

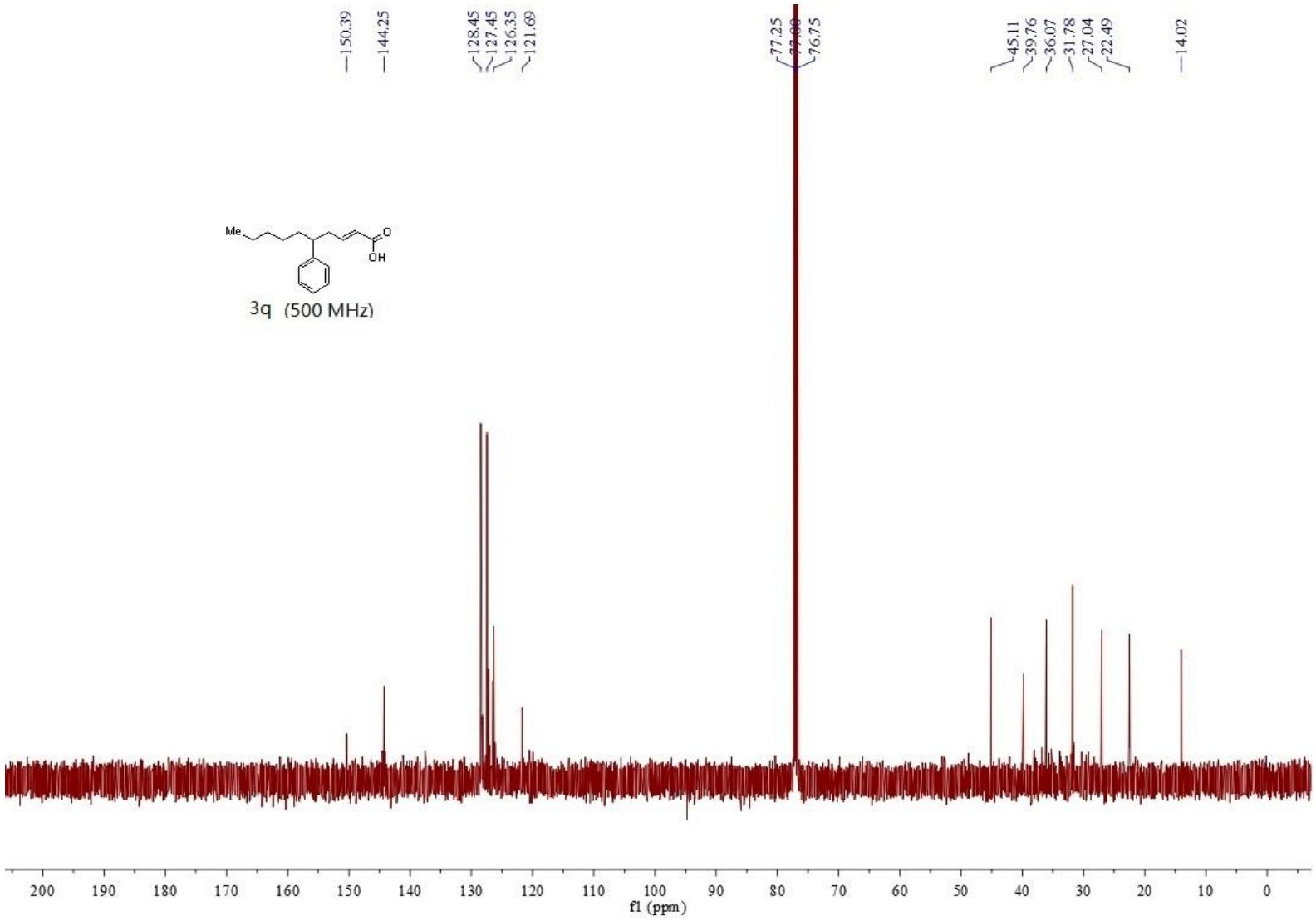

9.40
9.38
7.32
7.31
7.29
7.26
7.23
7.22
7.20
7.15
7.14
6.69
6.68
6.66
6.07
6.05
6.04
6.02
2.70
2.68
2.65
2.65
2.64
2.62
2.60
1.73
1.71
1.65
1.64
1.63
1.61
0.82
0.81
0.79
-0.00
Me
O
3o (500 MHz)
0.86
2.06
1.07
2.02
1.00
1.00
3.08
2.07
3.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

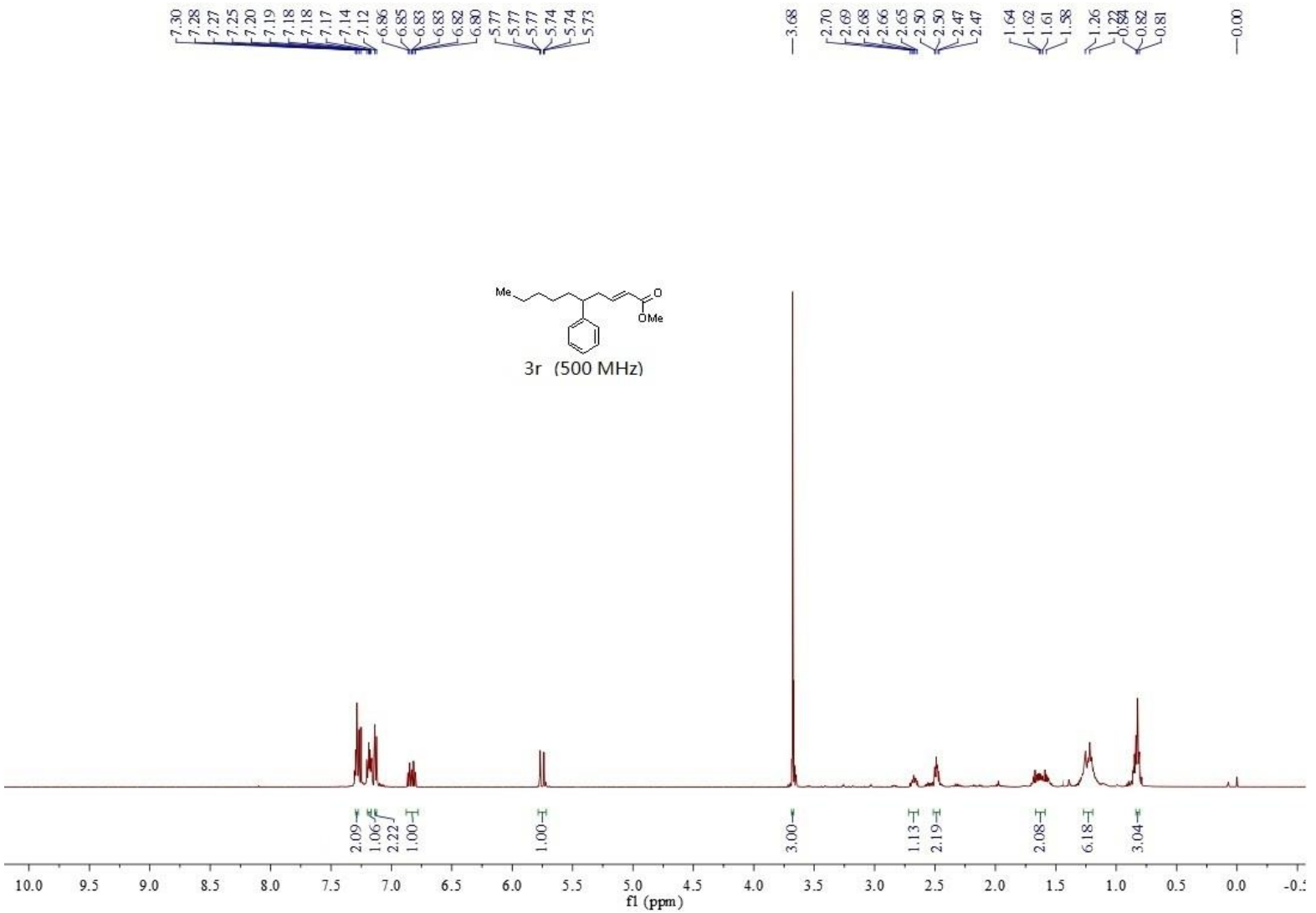

193.92
156.84
143.60
134.02
128.52
127.52
126.54
77.25
77.00
76.75
46.92
39.57
29.26
11.93
Me
O
3o (500 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

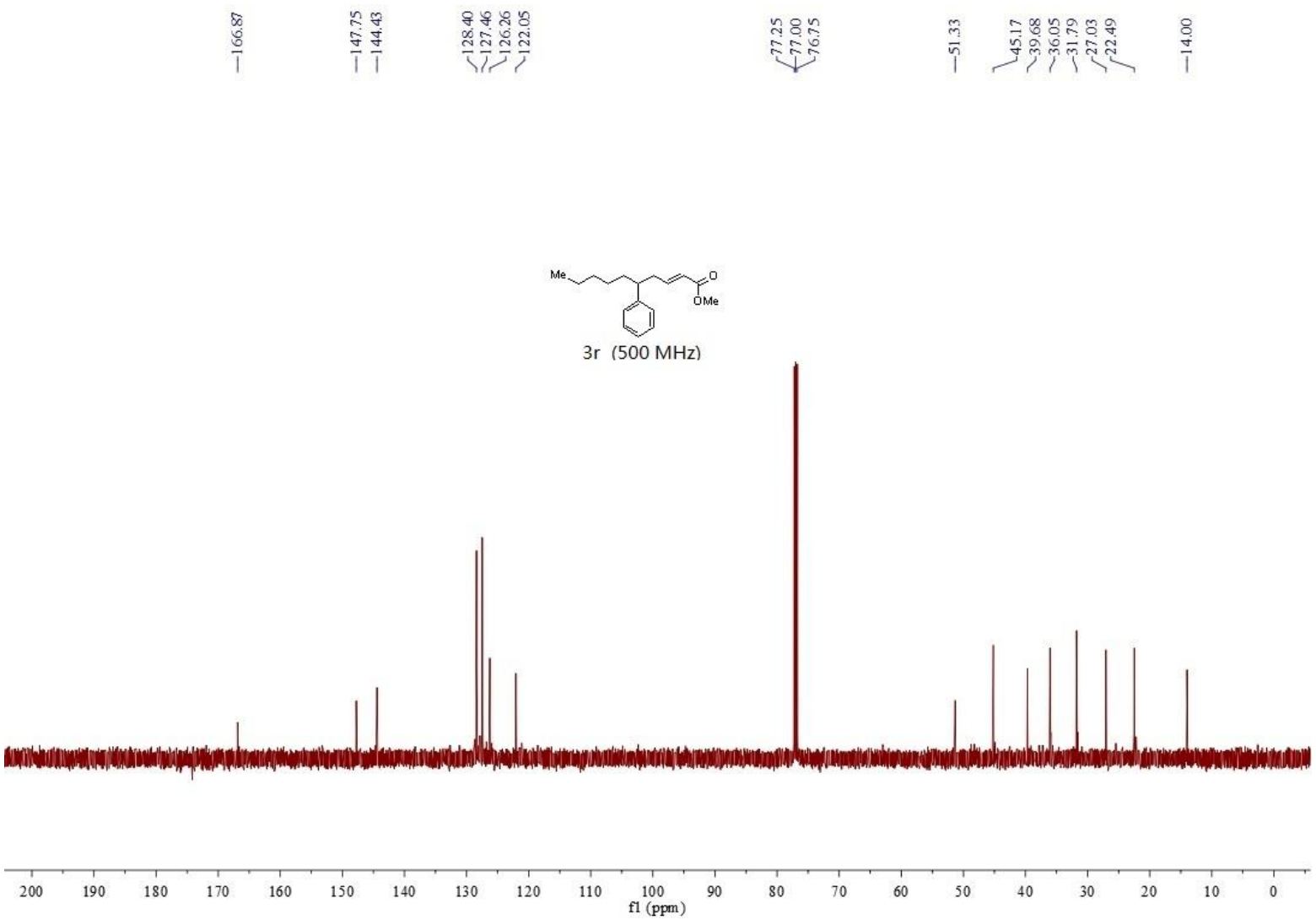

7.31
7.29
7.27
7.25
7.21
7.21
7.20
7.19
7.18
7.15
7.14
7.13
7.12
7.11
6.67
6.64
6.62
6.59
6.57
6.01
5.96
2.74
2.72
2.68
2.66
2.63
2.54
2.52
2.52
2.49
2.47
2.14
1.66
1.64
1.62
1.60
1.26
1.21
1.19
1.17
1.13
0.85
0.83
0.80
0.00
Me
O
Me
3p (300 MHz)
2.14
1.00
2.05
1.00
1.00
1.11
2.20
3.14
2.22
6.11
3.15
10.0
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
0.0
f1 (ppm)

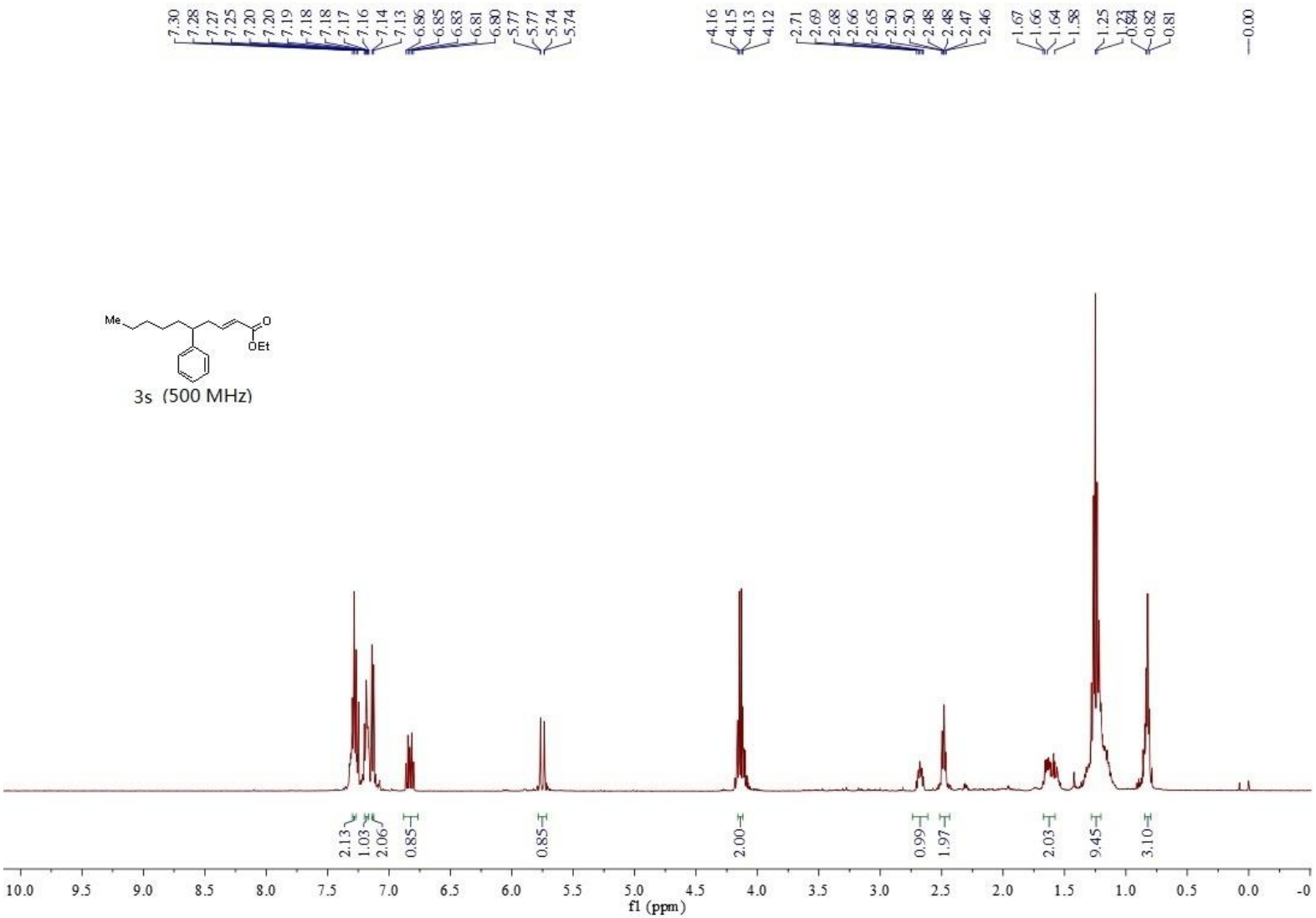

198.47
146.57
144.24
132.34
128.38
127.38
126.28
77.42
77.00
76.58
45.28
39.87
36.06
31.72
26.99
26.69
22.44
13.97
Me
O
Me
3p (300 MHz)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

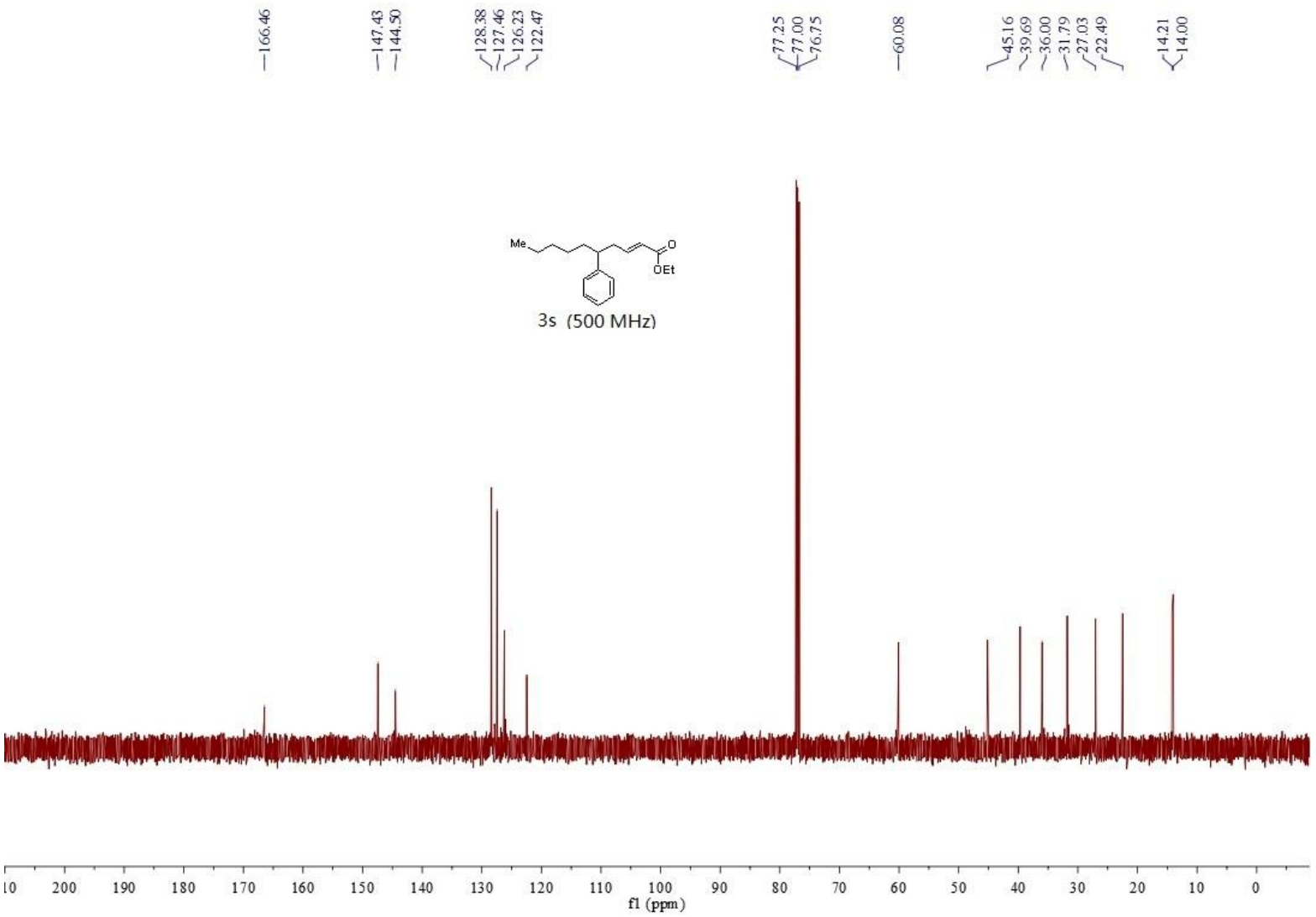

10.96
7.30
7.29
7.28
7.26
7.21
7.19
7.18
7.16
7.14
7.12
6.95
6.93
6.92
6.90
6.89
5.75
5.72
2.72
2.71
2.69
2.68
2.66
2.55
2.53
2.52
2.50
2.49
2.47
1.67
1.62
1.60
1.25
1.24
1.22
1.21
1.19
0.86
0.84
0.81
0.00
Me
O
OH
3q (500 MHz)
1.06
2.10
1.10
1.99
0.80
0.84
0.74
1.96
2.25
6.40
3.00
12.0 11.5 11.0 10.5 10.0 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 0.0
f1 (ppm)

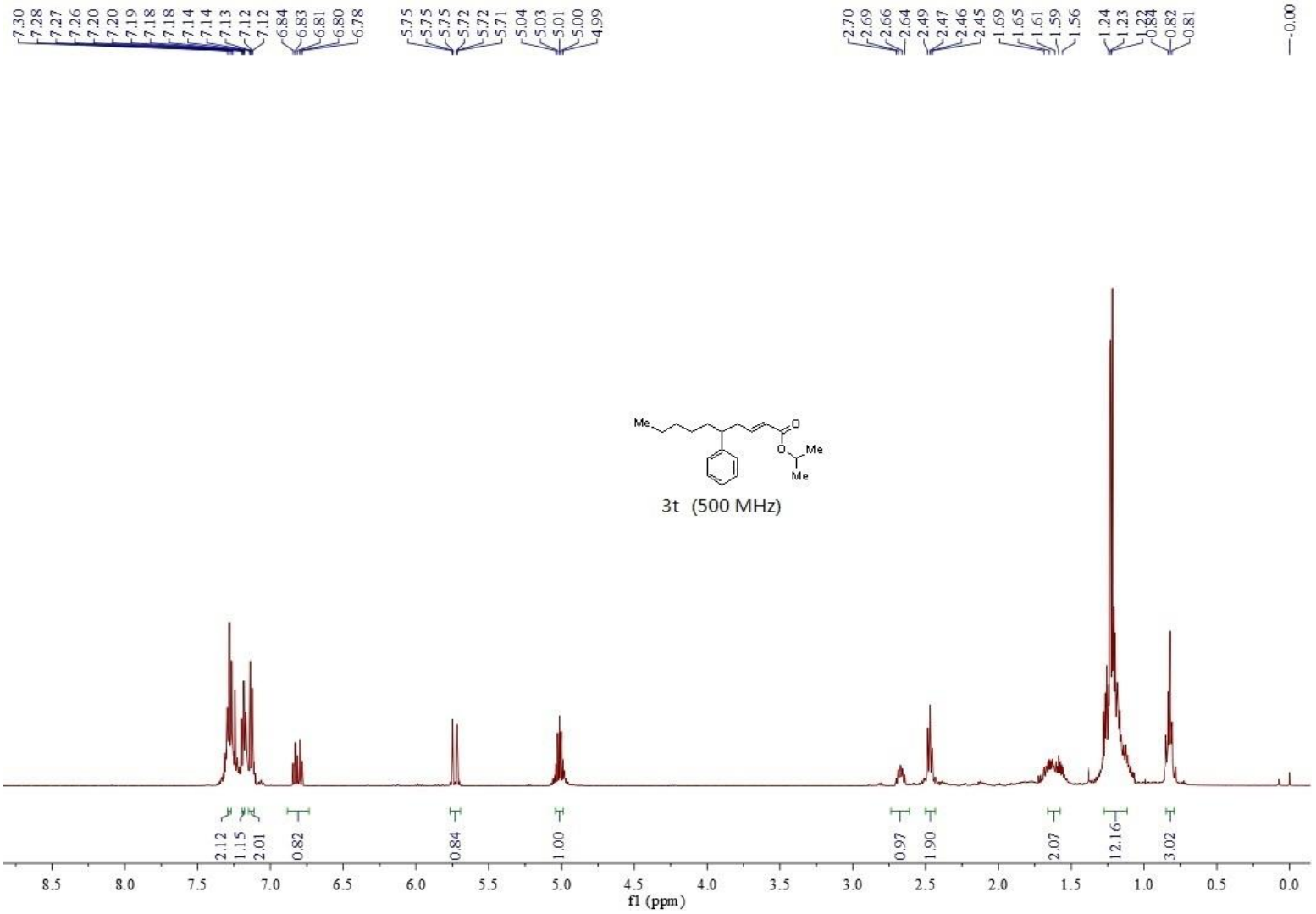

150.39
144.25
128.45
127.45
126.35
121.69
77.25
76.75
45.11
39.76
36.07
31.78
27.04
22.49
14.02
Me
O
OH
3q (500 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

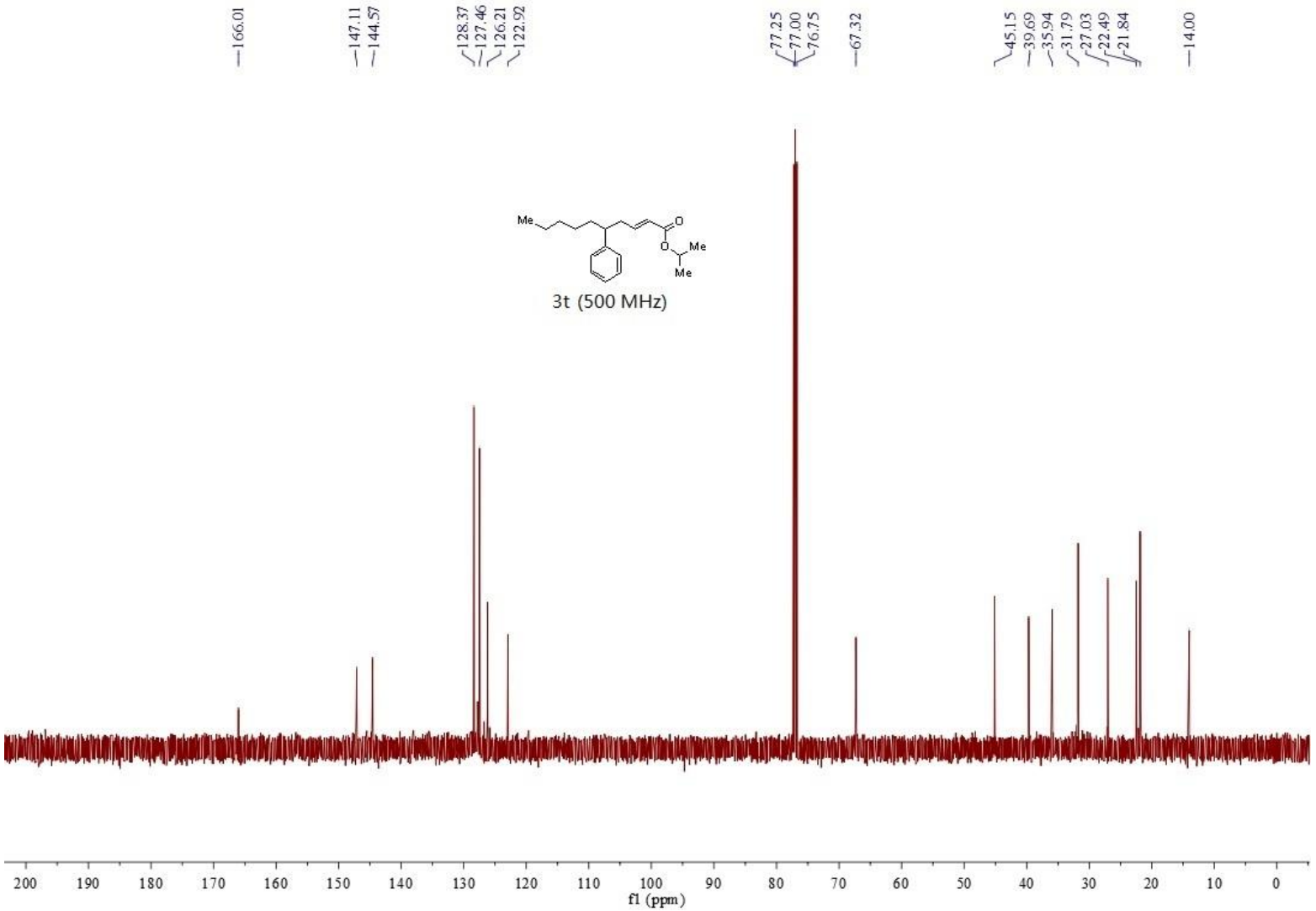

7.30
7.28
7.27
7.25
7.20
7.19
7.18
7.18
7.17
7.14
7.12
6.86
6.85
6.83
6.83
6.82
6.80
5.77
5.77
5.77
5.74
5.74
5.73
3.68
2.70
2.69
2.68
2.66
2.65
2.50
2.50
2.47
2.47
1.64
1.62
1.61
1.58
1.26
0.82
0.81
0.00
Me
O
OMe
3r (500 MHz)
2.09
1.06
2.22
1.00
1.00
3.00
1.13
2.19
2.08
6.18
3.04
10.0
9.5
9.0
8.5
8.0
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
0.0
f1 (ppm)


166.87
147.75
144.43
128.40
127.46
126.26
122.05
77.25
77.00
76.75
51.33
45.17
39.68
36.05
31.79
27.03
22.49
14.00
Me
O
OMe
3r (500 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

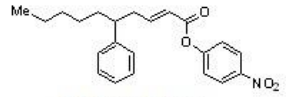

7.30
7.28
7.27
7.25
7.20
7.20
7.19
7.18
7.18
7.17
7.16
7.14
7.13
6.86
6.85
6.83
6.81
6.80
5.77
5.77
5.74
5.74
4.16
4.15
4.13
4.12
2.71
2.69
2.68
2.66
2.65
2.50
2.50
2.48
2.48
2.47
2.46
1.67
1.66
1.64
1.58
1.25
0.84
0.82
0.81
0.00
Me
O
OEt
3s (500 MHz)
2.13
1.03
2.06
0.85
0.85
2.00
0.99
1.97
2.03
9.45
3.10
10.0
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
0.0
-0
f1 (ppm)


166.46
147.43
144.50
128.38
127.46
126.23
122.47
77.25
77.00
76.75
60.08
45.16
39.69
36.00
31.79
27.03
22.49
14.21
14.00
Me
O
OEt
3s (500 MHz)
f1 (ppm)

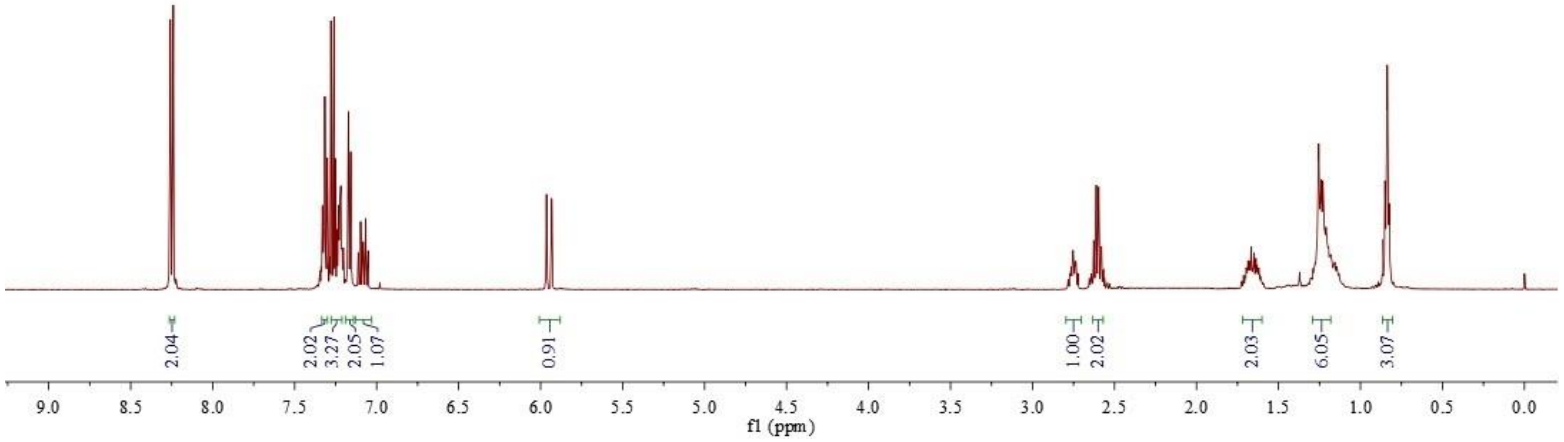

7.30
7.28
7.27
7.26
7.20
7.20
7.19
7.18
7.18
7.14
7.14
7.13
7.12
7.12
6.84
6.83
6.81
6.80
6.78
5.75
5.75
5.75
5.72
5.72
5.71
5.04
5.03
5.01
5.00
4.99
2.70
2.69
2.66
2.64
2.49
2.47
2.46
2.45
1.69
1.65
1.61
1.59
1.56
1.24
1.23
0.84
0.82
0.81
-0.00
Me
O
O
Me
Me
3t (500 MHz)
2.12
1.15
2.01
0.82
0.84
1.00
0.97
1.90
2.07
12.16
3.02
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
0.0
f1 (ppm)

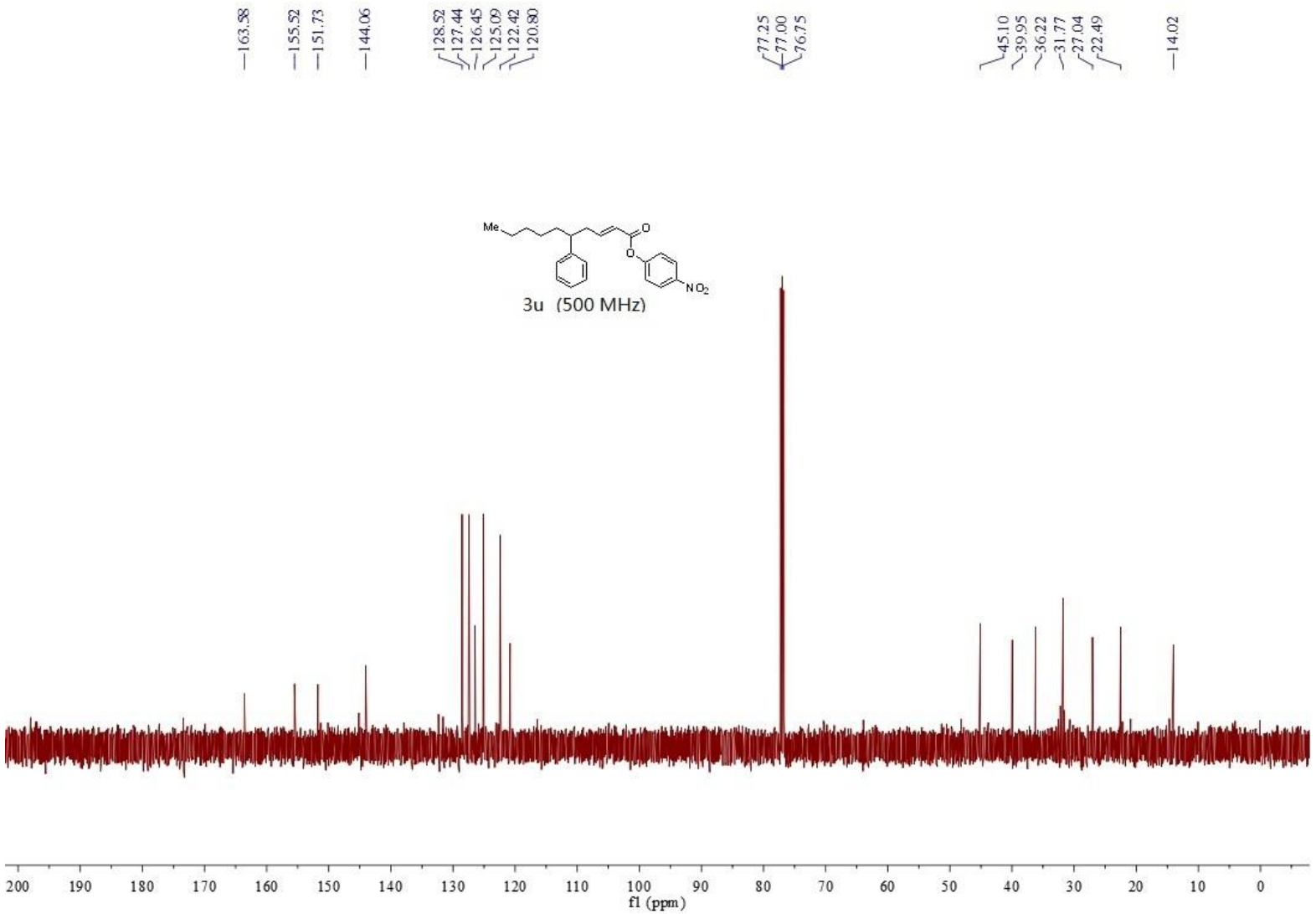

166.01
147.11
144.57
128.37
127.46
126.21
122.92
77.25
77.00
76.75
67.32
45.15
39.69
35.94
31.79
27.03
22.49
21.84
14.00
Me
O
O
Me
Me
3t (500 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

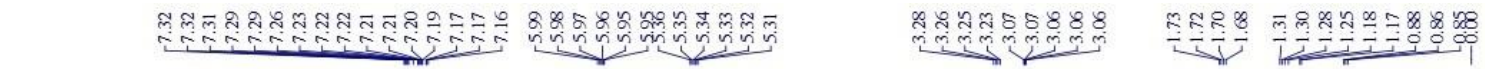

8.26
8.24
7.33
7.32
7.30
7.28
7.26
7.23
7.22
7.17
7.16
7.11
7.10
7.08
7.07
7.05
5.96
5.93
2.78
2.76
2.74
2.72
2.63
2.60
2.58
2.56
1.72
1.69
1.66
1.61
1.25
1.23
1.18
0.85
0.84
0.82
0.00

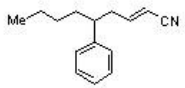

Me
O
O
NO2

3u (500 MHz)

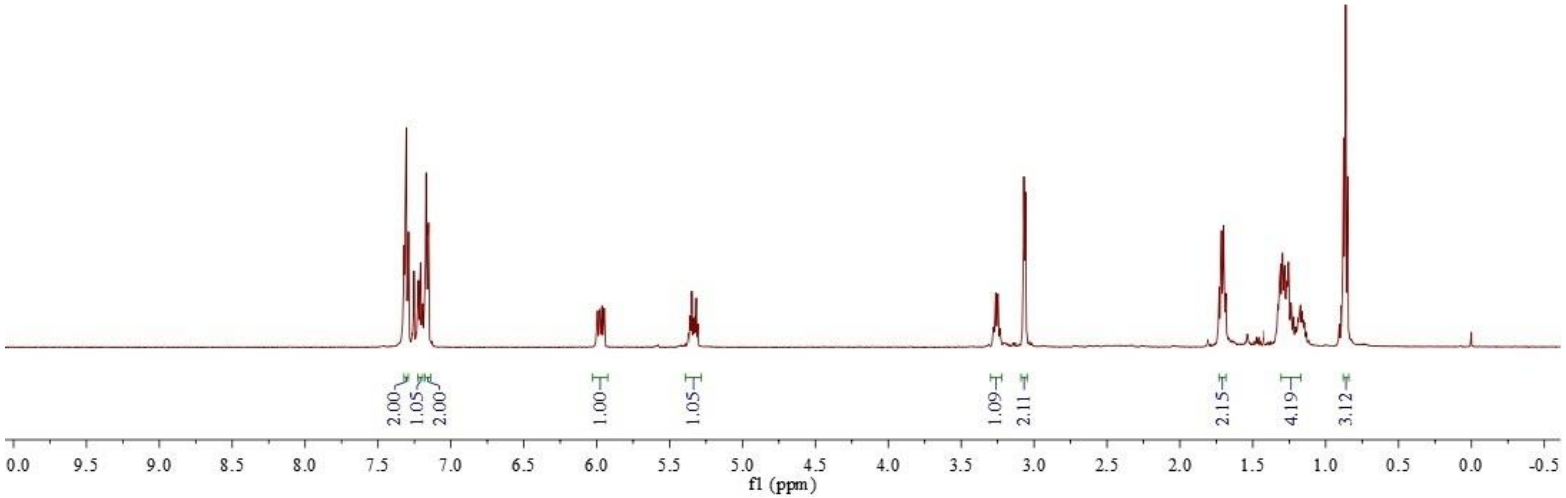

2.04
2.02
3.27
2.05
1.07
0.91
1.00
2.02
2.03
6.05
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

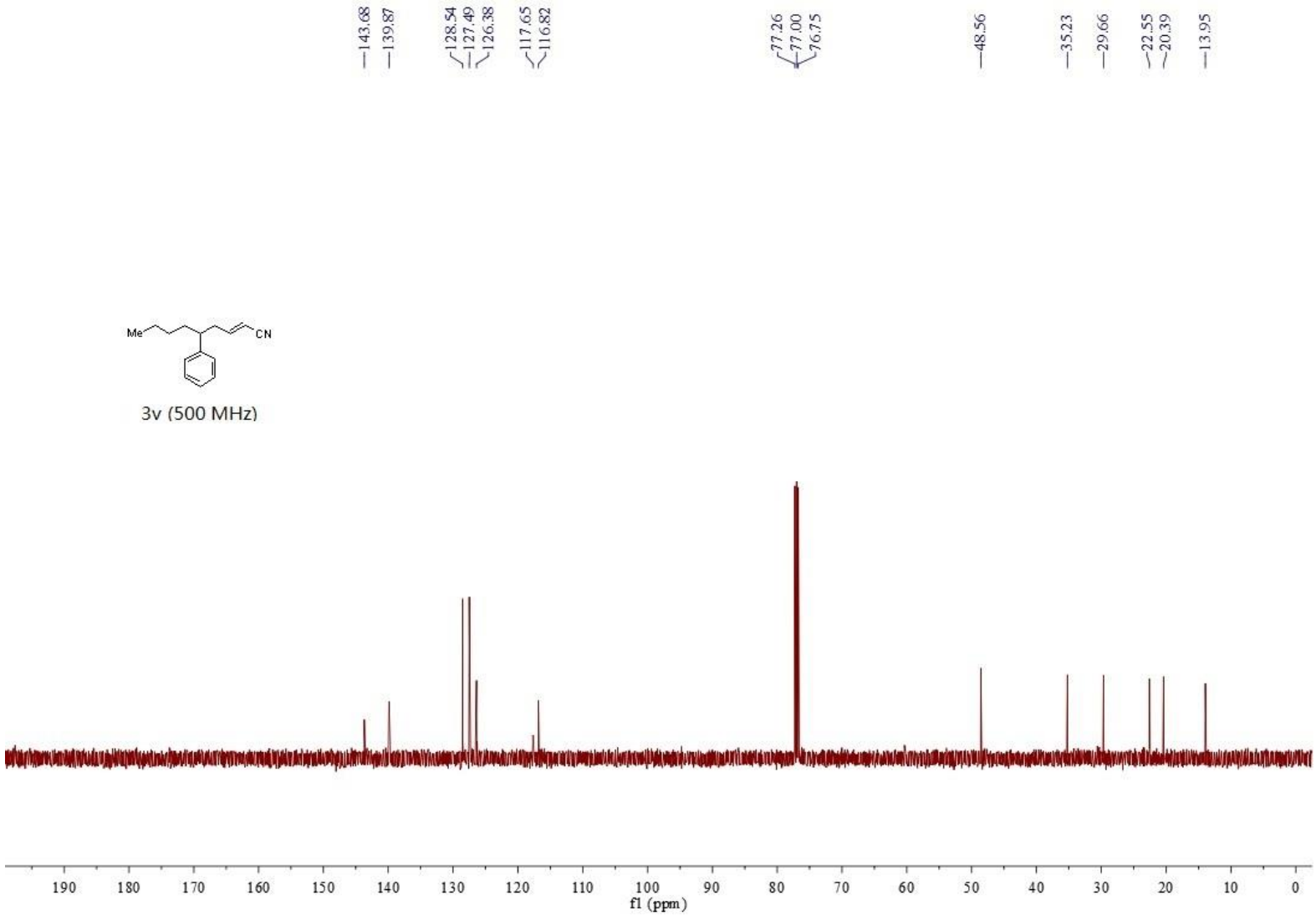

163.38
155.52
151.73
144.06
128.52
127.44
126.45
125.09
122.42
120.80
77.25
77.00
76.75
45.10
39.95
36.22
31.77
27.04
22.49
14.02
Me
O
O
NO2
3u (500 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

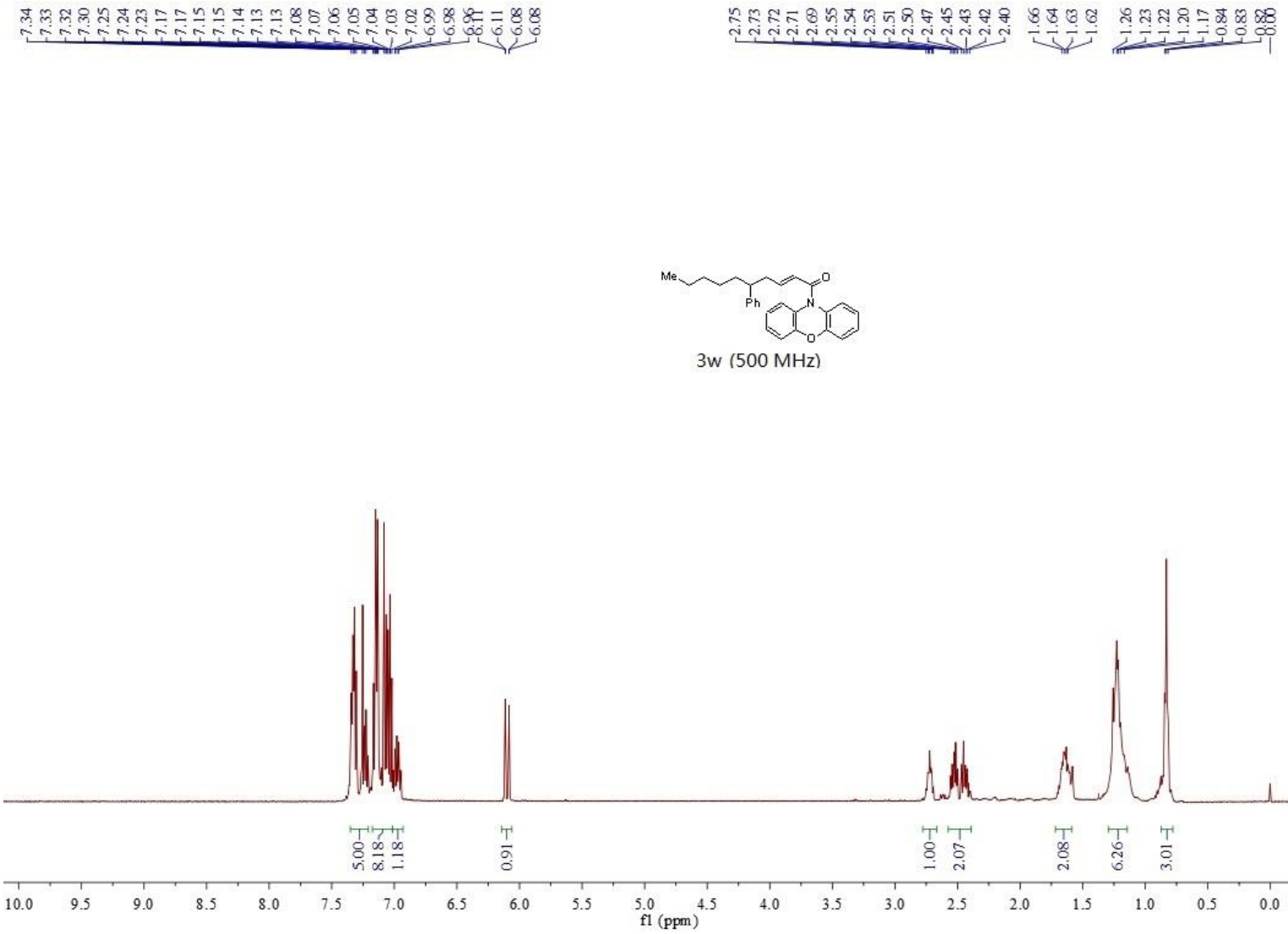

7.32
7.32
7.31
7.29
7.29
7.26
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.17
7.17
7.16
5.99
5.98
5.97
5.96
5.95
5.35
5.35
5.34
5.33
5.32
5.31
3.28
3.26
3.25
3.23
3.07
3.07
3.06
3.06
3.06
1.73
1.72
1.70
1.68
1.31
1.30
1.28
1.25
1.18
1.17
0.88
0.86
0.85
0.85

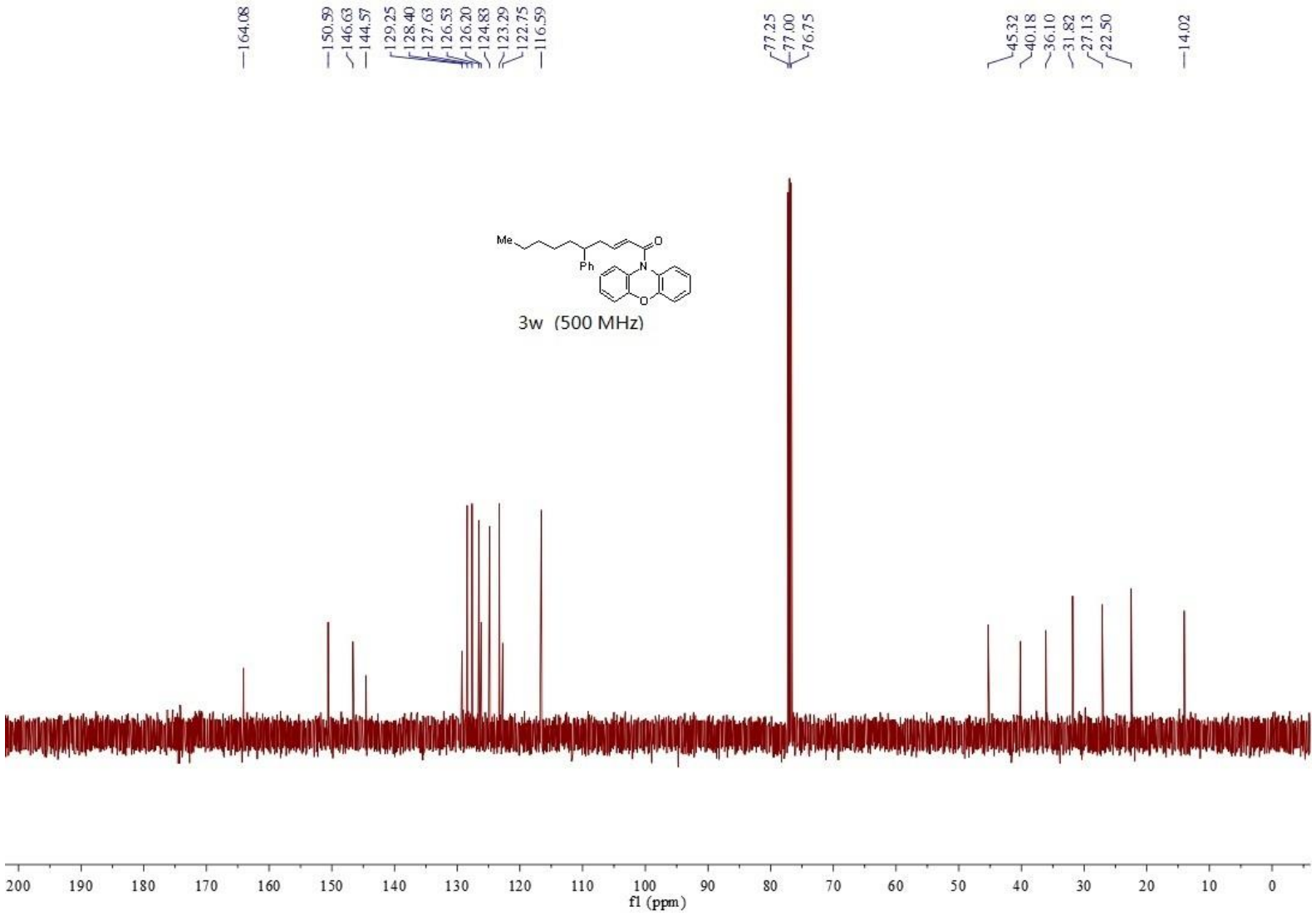

Me
CN

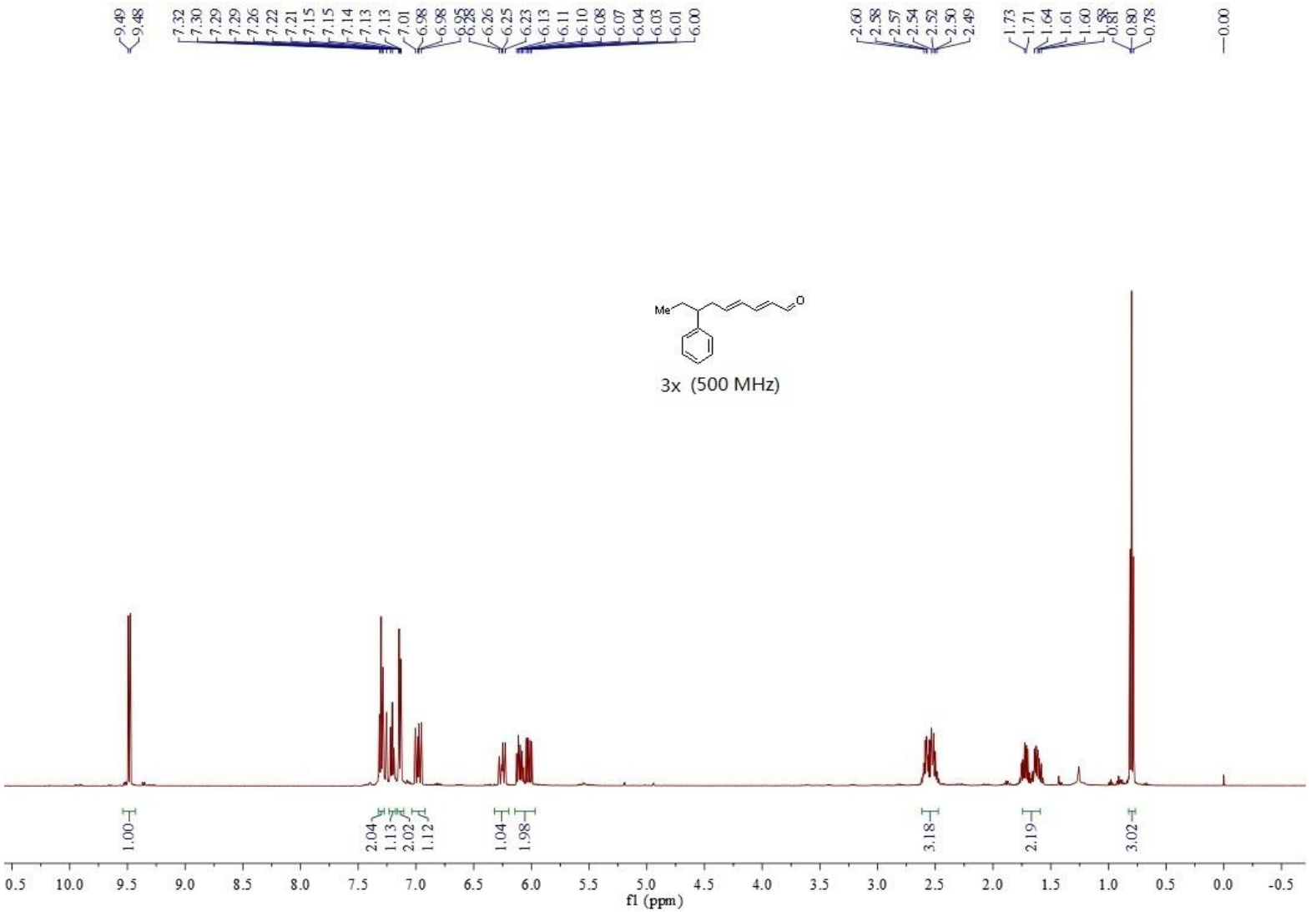
3v (500 MHz)

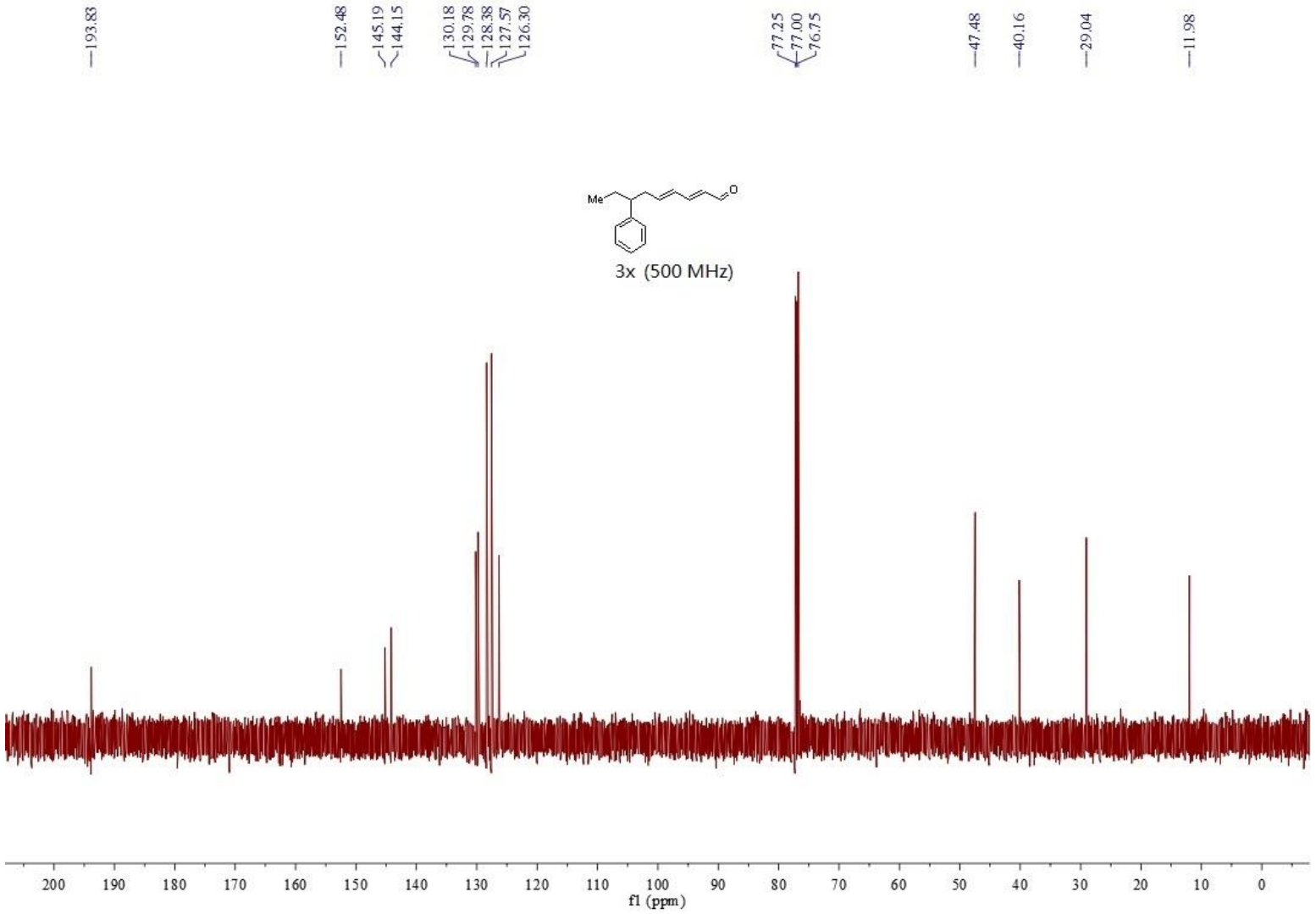

2.00
1.05
2.00
1.00
1.05
1.09
2.11
2.15
4.19
3.12
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

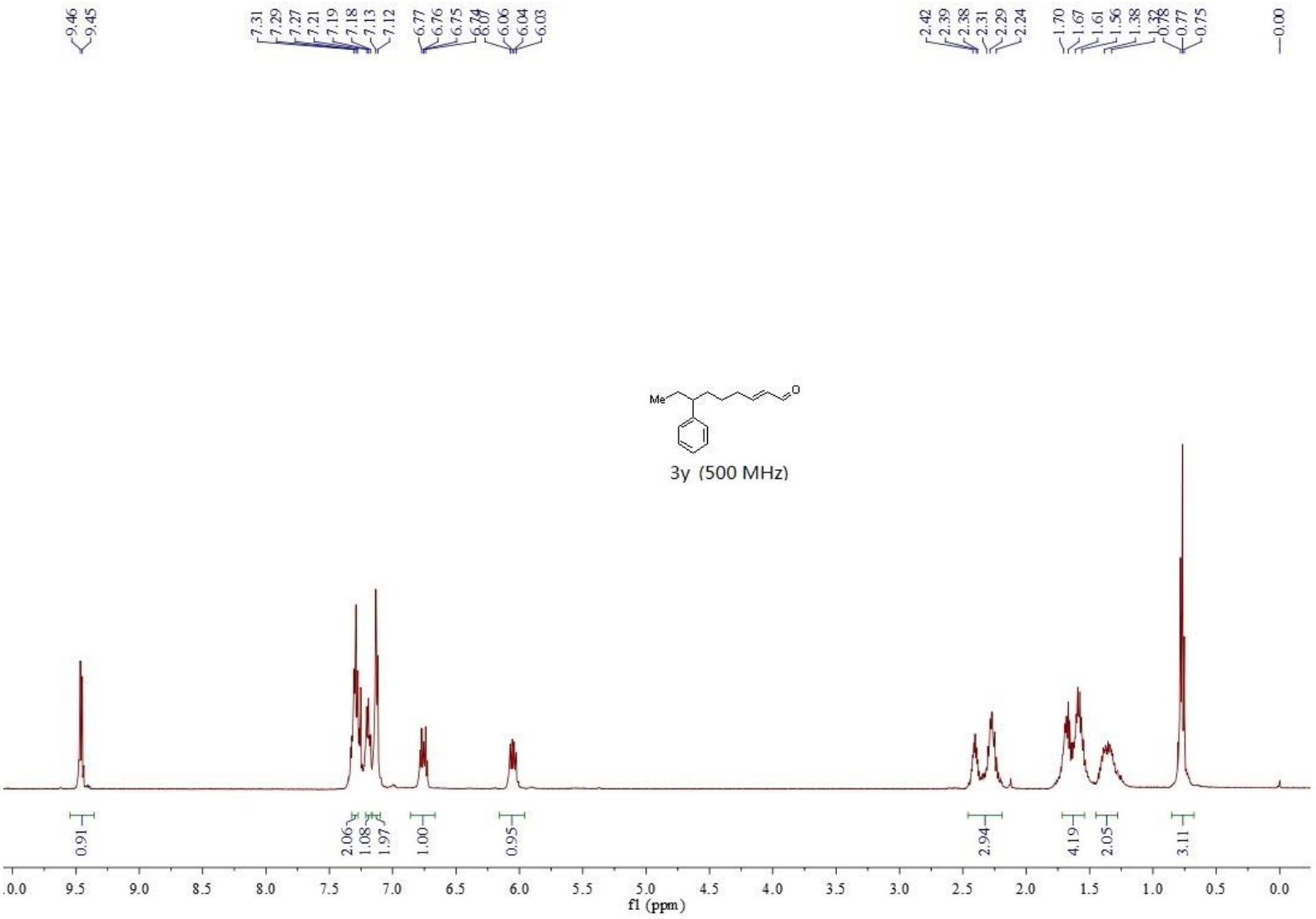

143.68
139.87
128.54
127.49
126.38
117.65
116.82
77.26
77.00
76.75
48.56
35.23
29.66
22.55
20.39
13.95
Me
CN
3v (500 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

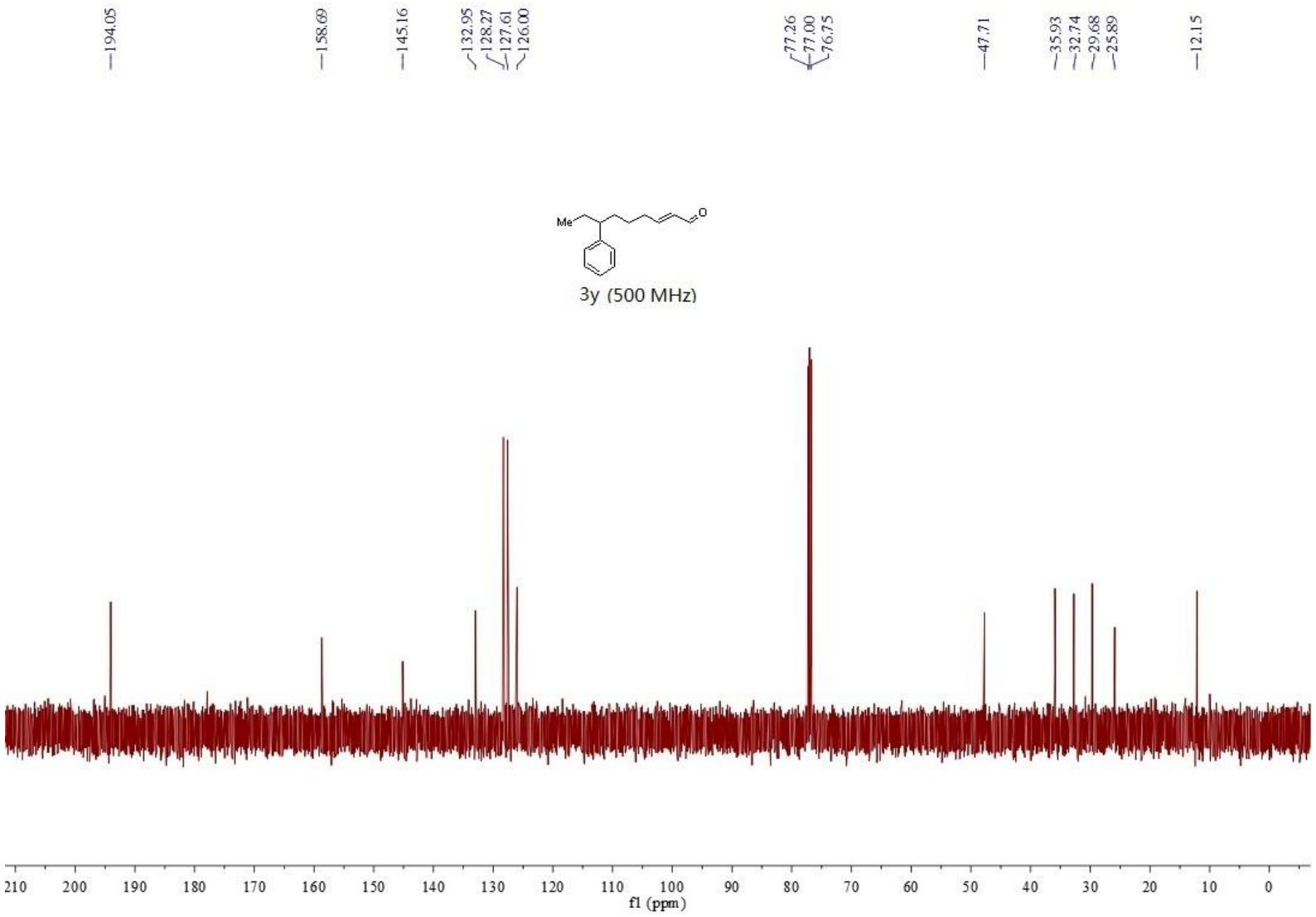

7.34
7.33
7.32
7.30
7.25
7.24
7.23
7.17
7.17
7.15
7.15
7.14
7.13
7.13
7.08
7.07
7.06
7.05
7.04
7.03
7.02
6.99
6.98
6.96
6.11
6.08
6.08
2.75
2.73
2.72
2.71
2.69
2.55
2.54
2.53
2.51
2.50
2.47
2.45
2.43
2.42
2.40
1.66
1.64
1.63
1.62
1.26
1.23
1.22
1.20
1.17
0.84
0.83
0.82
0.00
Me
Ph
O
N
O
3w (500 MHz)
5.00
8.18
1.18
0.91
1.00
2.07
2.08
6.26
3.01
10.0
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
0.0
-0.
f1 (ppm)

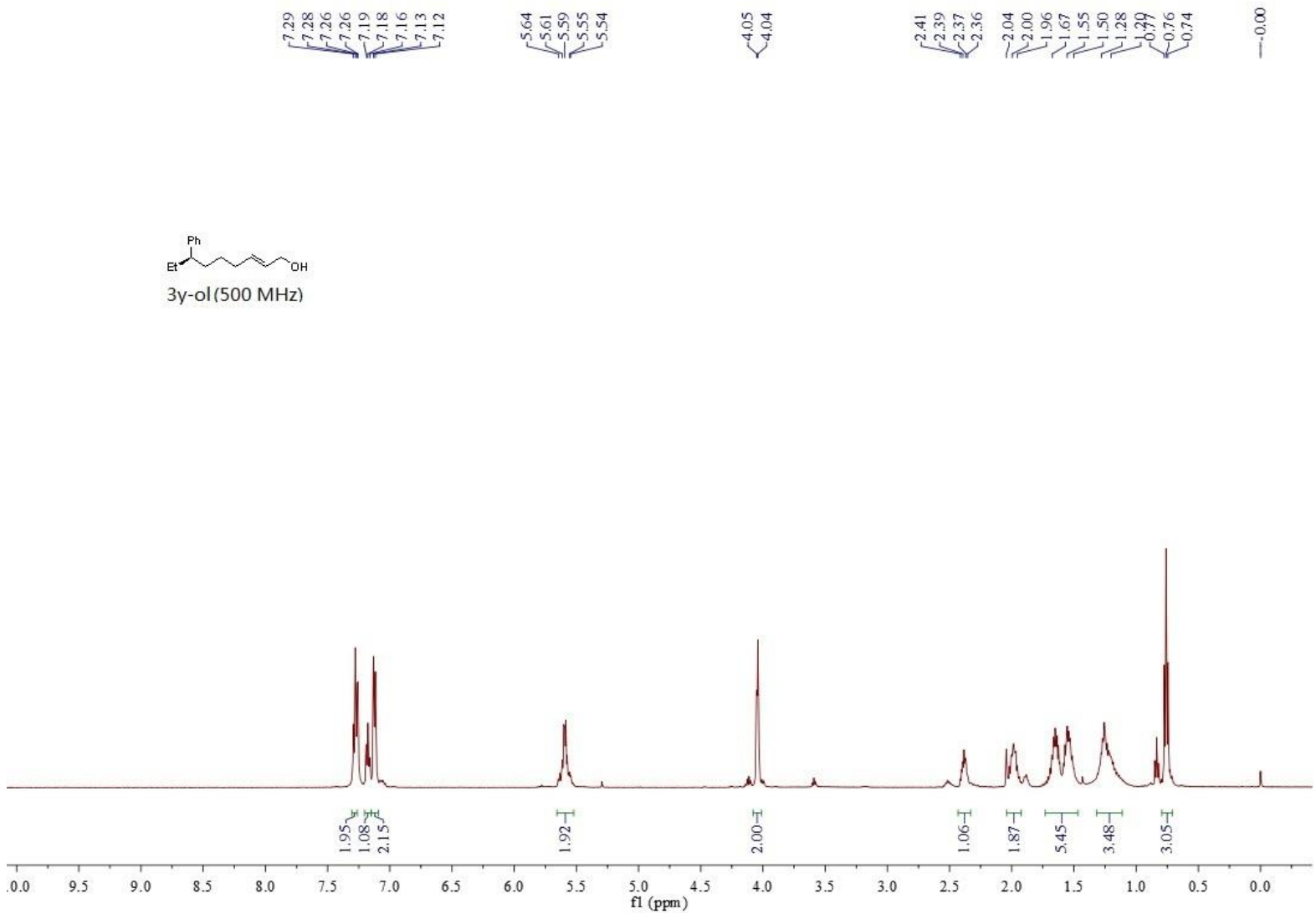

164.08
150.99
146.63
144.57
129.25
128.40
127.63
126.53
126.20
124.83
123.29
122.75
116.59
77.25
77.00
76.75
45.32
40.18
36.10
31.82
27.13
22.50
14.02
Me
Ph
O
N
O
3w (500 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

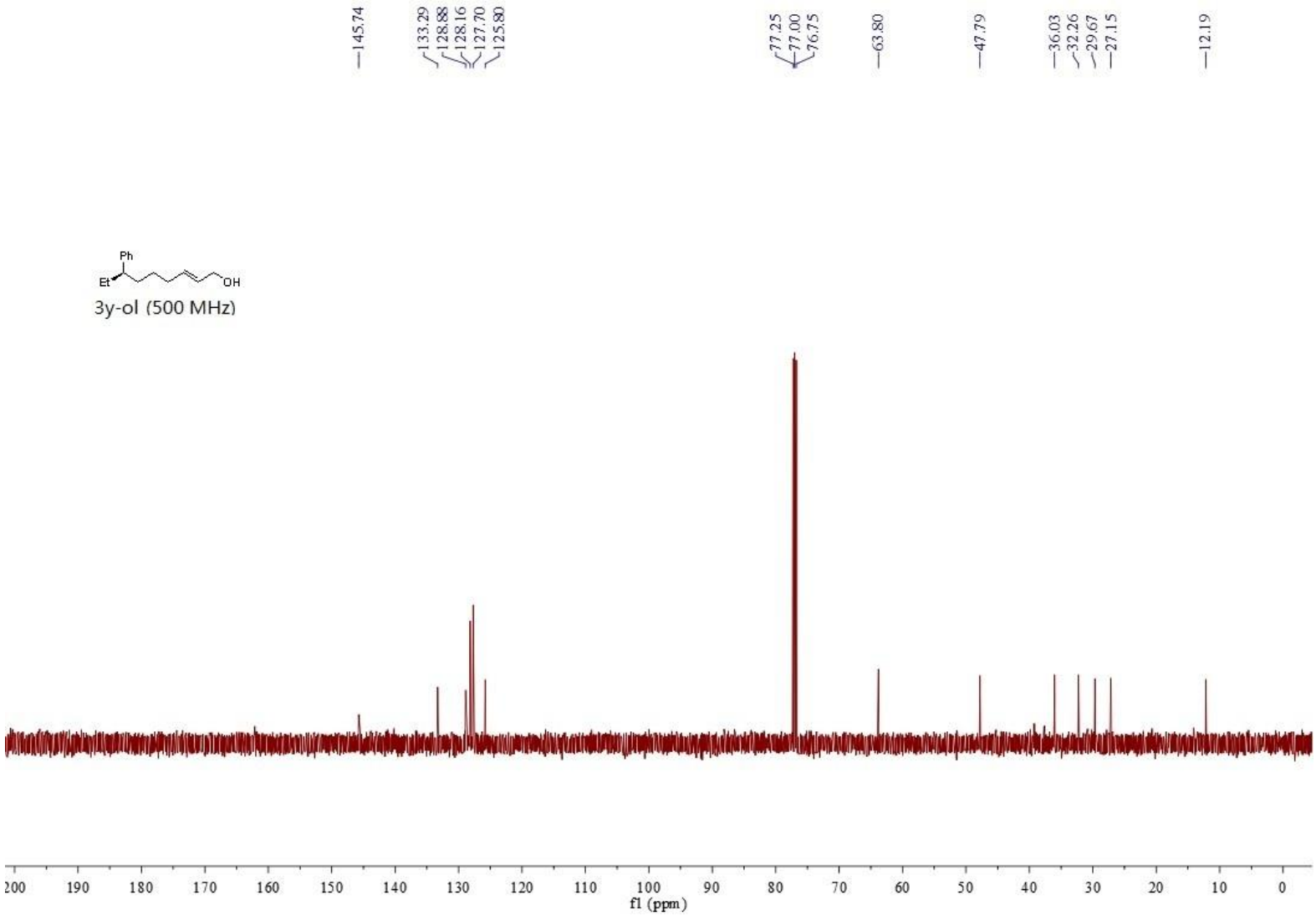

9.49
9.48
7.32
7.30
7.29
7.29
7.26
7.22
7.21
7.15
7.15
7.14
7.13
7.13
7.01
6.98
6.98
6.95
6.28
6.26
6.25
6.23
6.13
6.11
6.10
6.08
6.07
6.04
6.03
6.01
6.00
2.60
2.58
2.57
2.54
2.52
2.50
2.49
1.73
1.71
1.64
1.61
1.60
1.58
0.81
0.80
0.78
0.00
Me
O
3x (500 MHz)
1.00
2.04
1.13
2.02
1.12
1.04
1.98
3.18
2.19
3.02
0.5
10.0
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
0.0
-0.5
f1 (ppm)

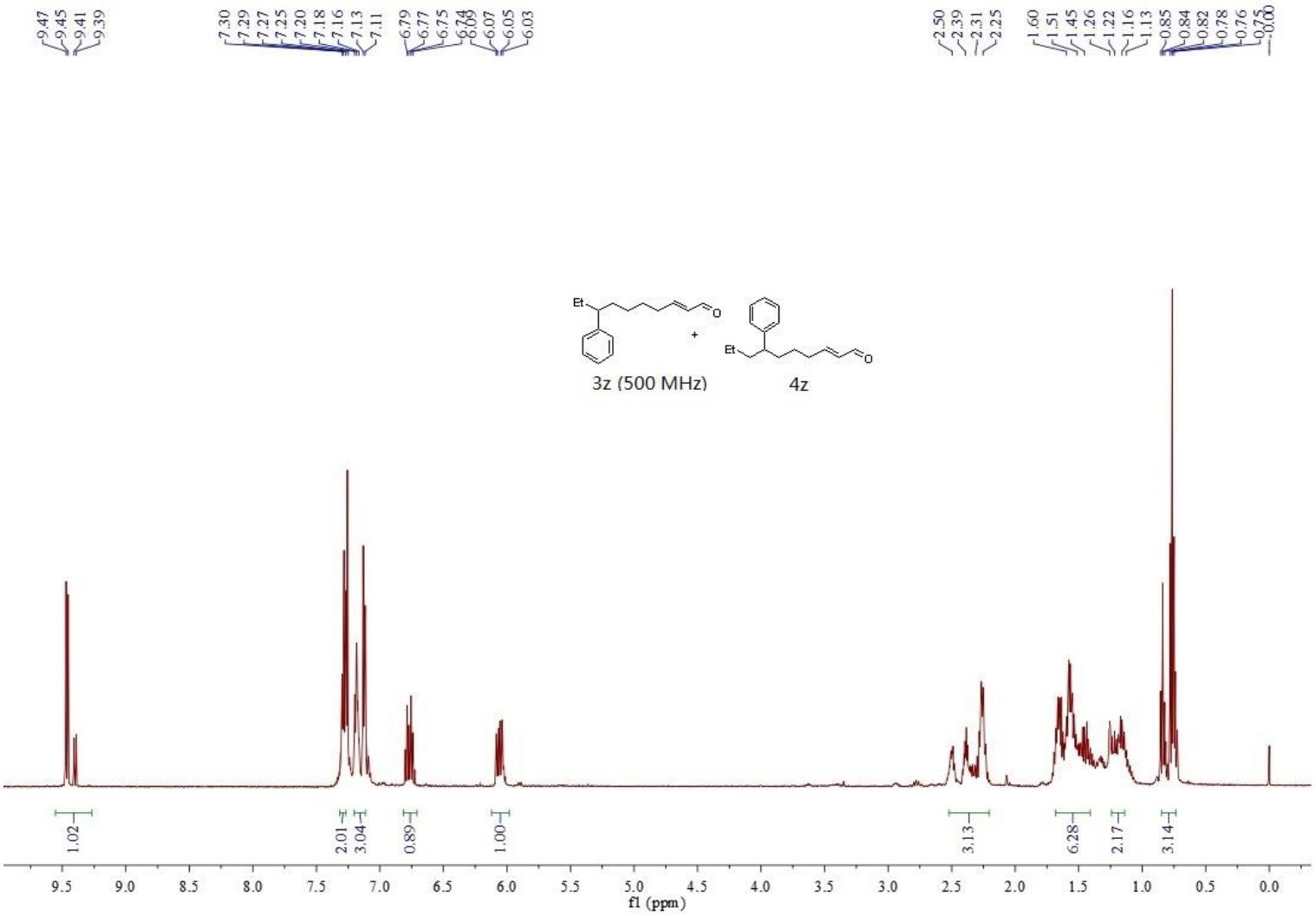

193.83
152.48
145.19
144.15
130.18
129.78
128.38
127.57
126.30
77.25
77.00
76.75
47.48
40.16
29.04
11.98
Me
O
3x (500 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

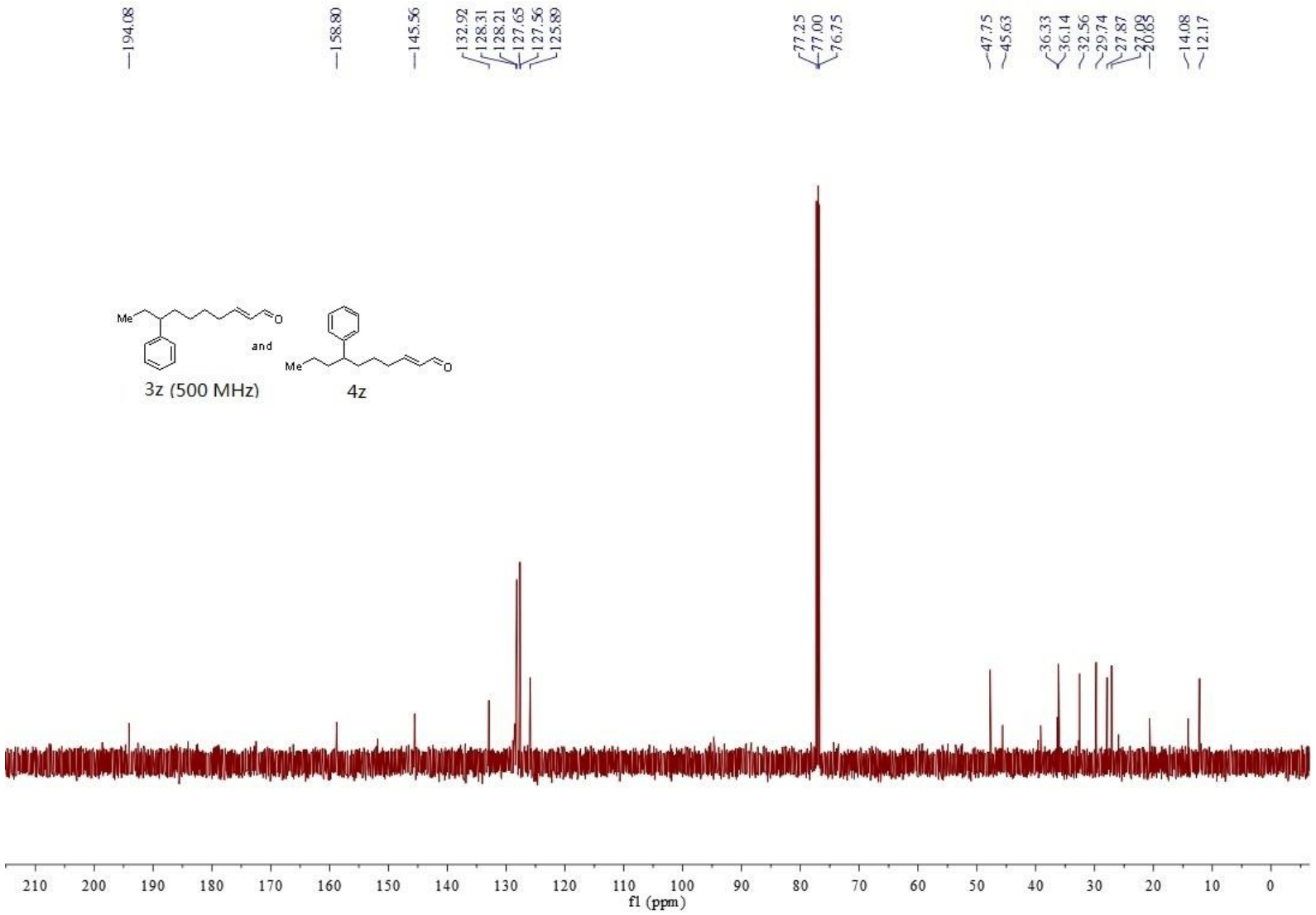

9.46
9.45
7.31
7.29
7.27
7.21
7.19
7.18
7.13
7.12
6.77
6.76
6.75
6.06
6.04
6.03
2.42
2.39
2.38
2.31
2.29
2.24
1.70
1.67
1.61
1.56
1.38
0.78
0.77
0.75
0.00
Me
O
3y (500 MHz)
0.91
2.06
1.08
1.97
1.00
0.95
2.94
4.19
2.05
3.11
f1 (ppm)

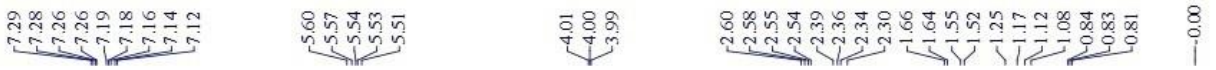

194.05
158.69
145.16
132.95
128.27
127.61
126.00
77.26
77.00
76.75
47.71
35.93
32.74
29.68
25.89
12.15
Me
O
3y (500 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

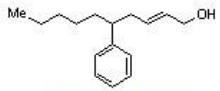

7.29
7.28
7.26
7.26
7.19
7.18
7.16
7.13
7.12
5.64
5.61
5.59
5.55
5.54
4.05
4.04
2.41
2.39
2.37
2.36
2.04
2.00
1.96
1.67
1.55
1.50
1.28
0.77
0.76
0.74
0.00
Ph
Et
OH
3y-ol (500 MHz)
1.95
1.08
2.15
1.92
2.00
1.06
1.87
5.45
3.48
3.05
f1 (ppm)


145.74
133.29
128.88
128.16
127.70
125.80
77.25
77.00
76.75
63.80
47.79
36.03
32.26
29.67
27.15
12.19
Ph
Et
OH
3y-ol (500 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

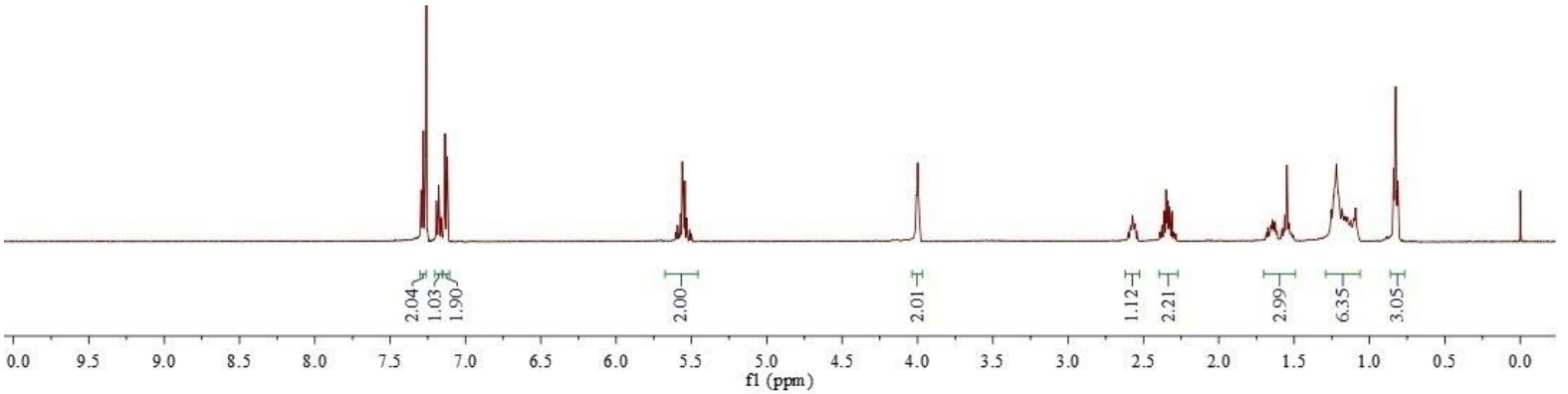

9.47
9.45
9.41
9.39
7.30
7.29
7.27
7.25
7.20
7.18
7.16
7.13
7.11
6.79
6.77
6.75
6.74
6.09
6.07
6.05
6.03
2.50
2.39
2.31
2.25
1.60
1.51
1.45
1.26
1.22
1.16
1.13
0.85
0.84
0.82
0.78
0.76
0.75
0.00
Et
O
+
Et
O
3z (500 MHz)
4z
1.02
2.01
3.04
0.89
1.00
3.13
6.28
2.17
3.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

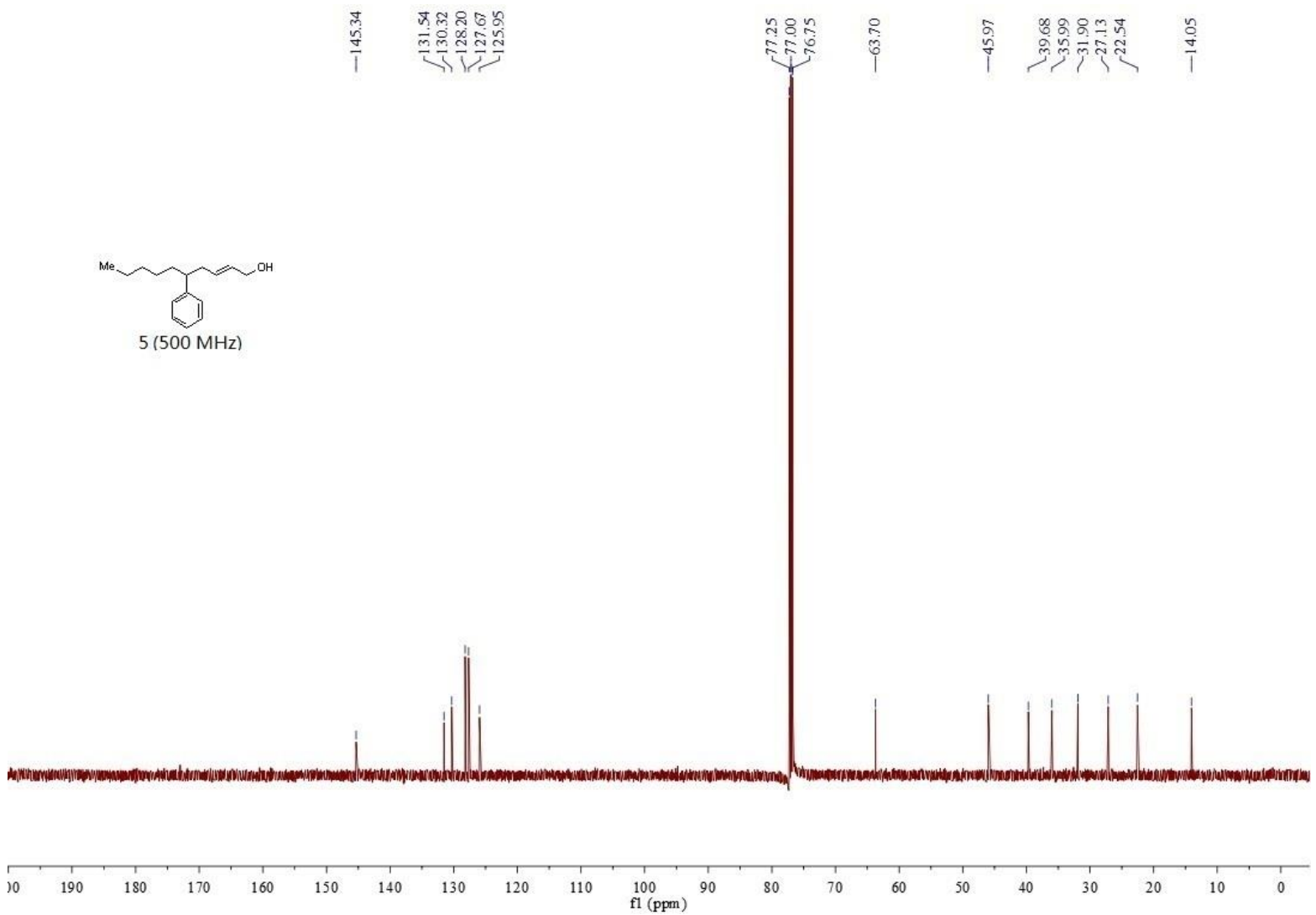

194.08
158.80
145.56
132.92
128.31
128.21
127.65
127.56
125.89
77.25
77.00
76.75
47.75
45.63
36.33
36.14
32.56
29.74
27.87
27.08
20.03
14.08
12.17
Me
O
and
Me
O
3z (500 MHz)
4z
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

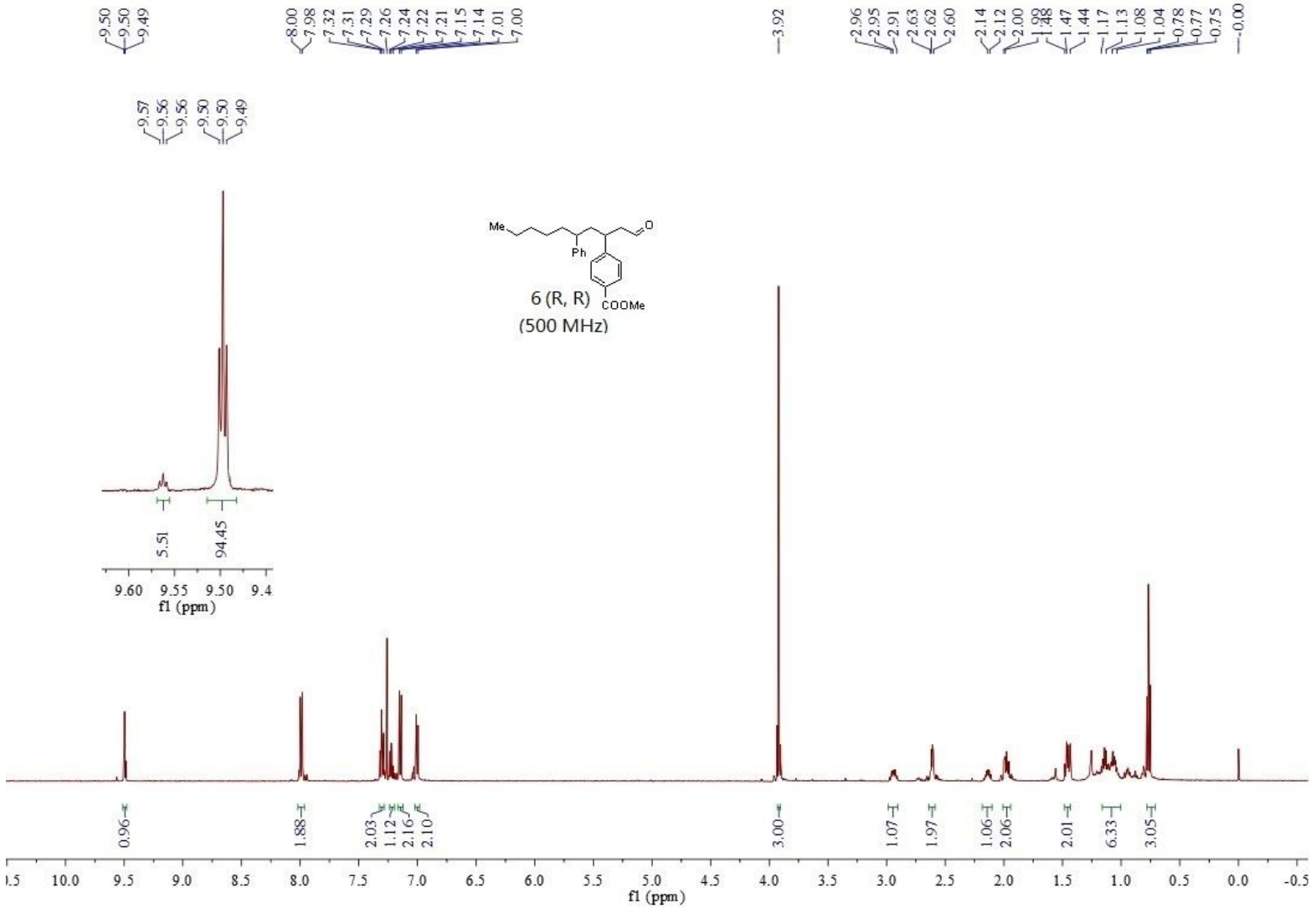

7.29
7.28
7.26
7.26
7.19
7.18
7.16
7.14
7.12
5.60
5.57
5.54
5.53
5.51
4.01
4.00
3.99
2.60
2.58
2.55
2.54
2.39
2.36
2.34
2.30
1.66
1.64
1.55
1.52
1.25
1.17
1.12
1.08
0.84
0.83
0.81
0.00

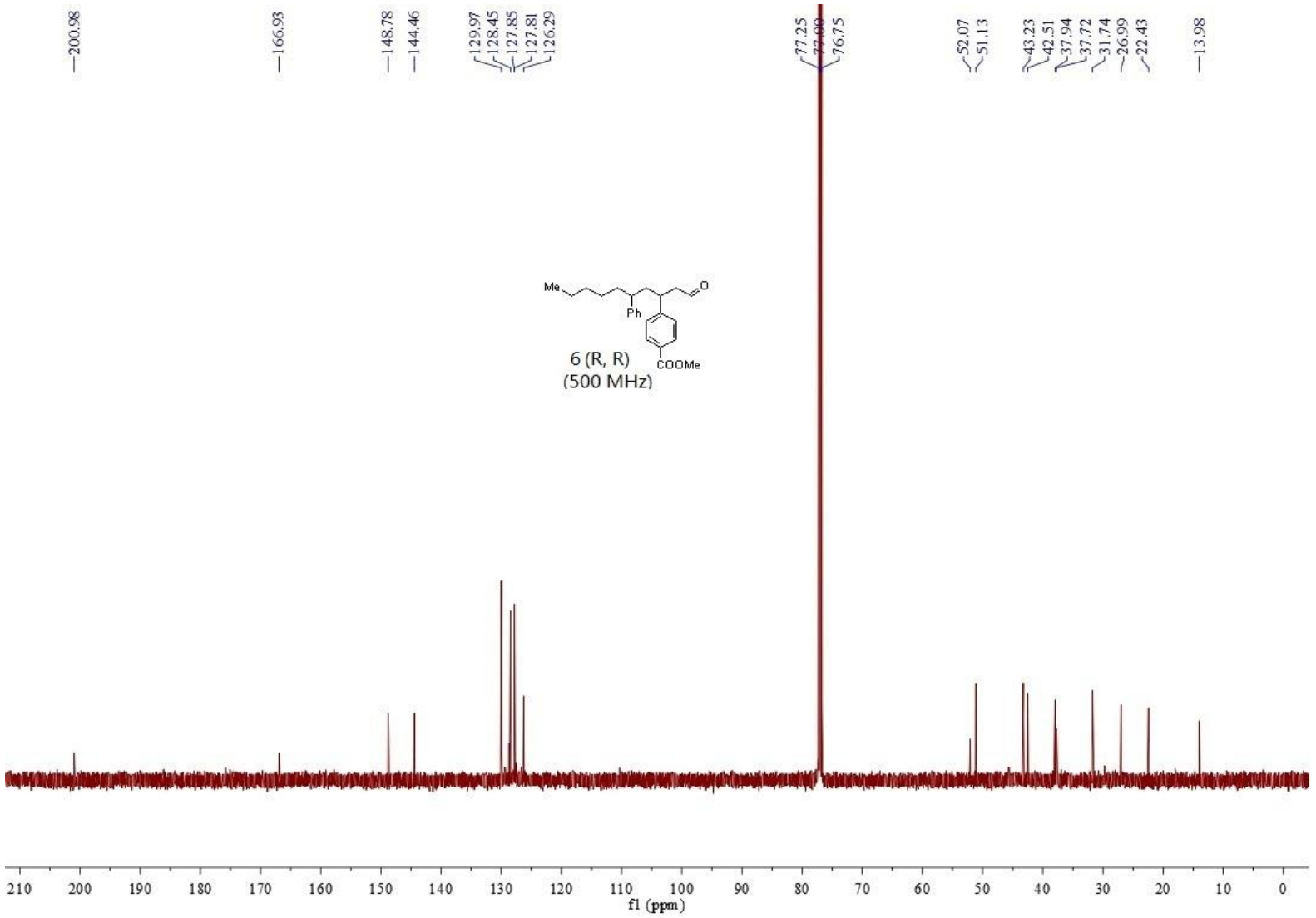

Me
OH

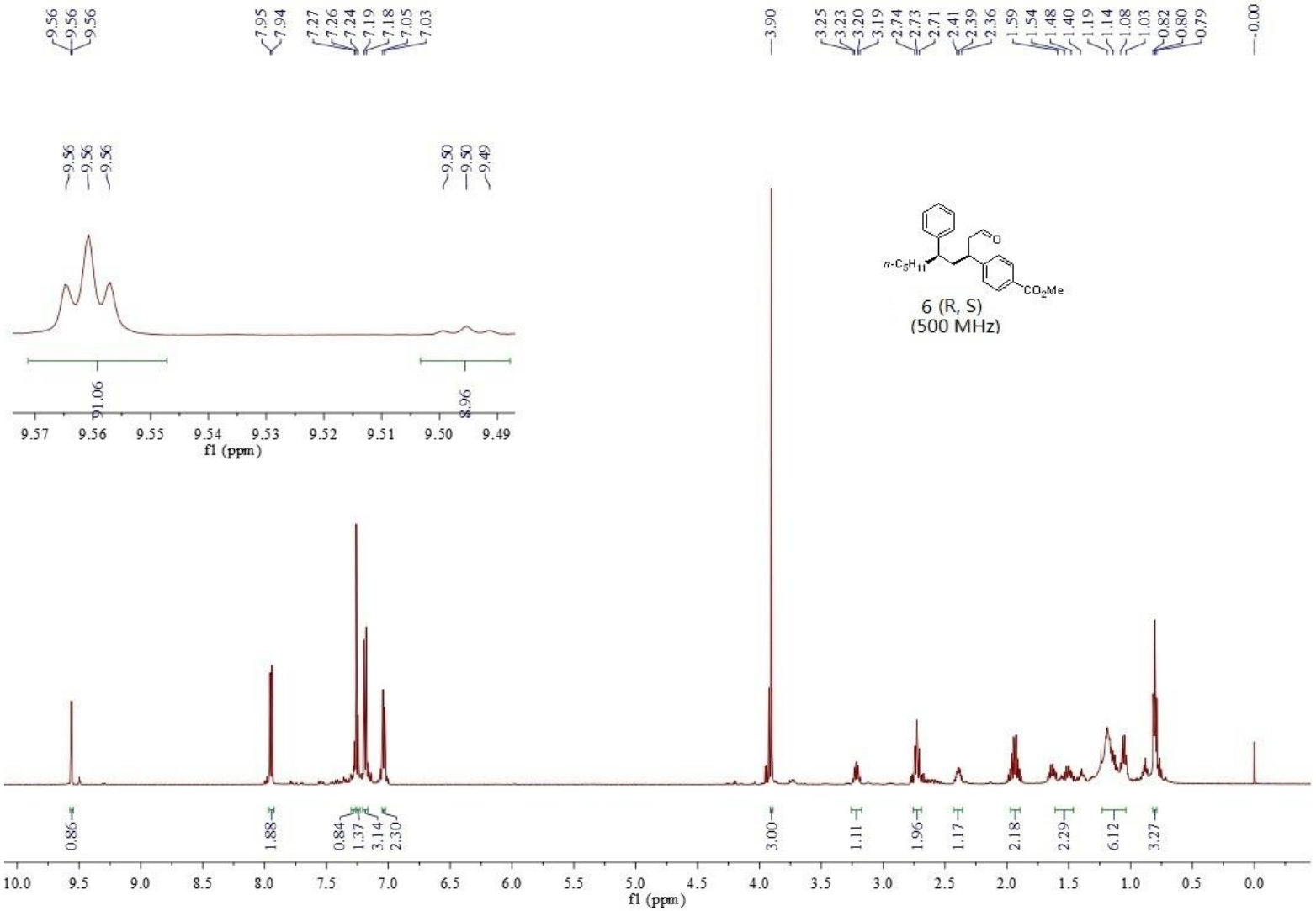
5 (500 MHz)

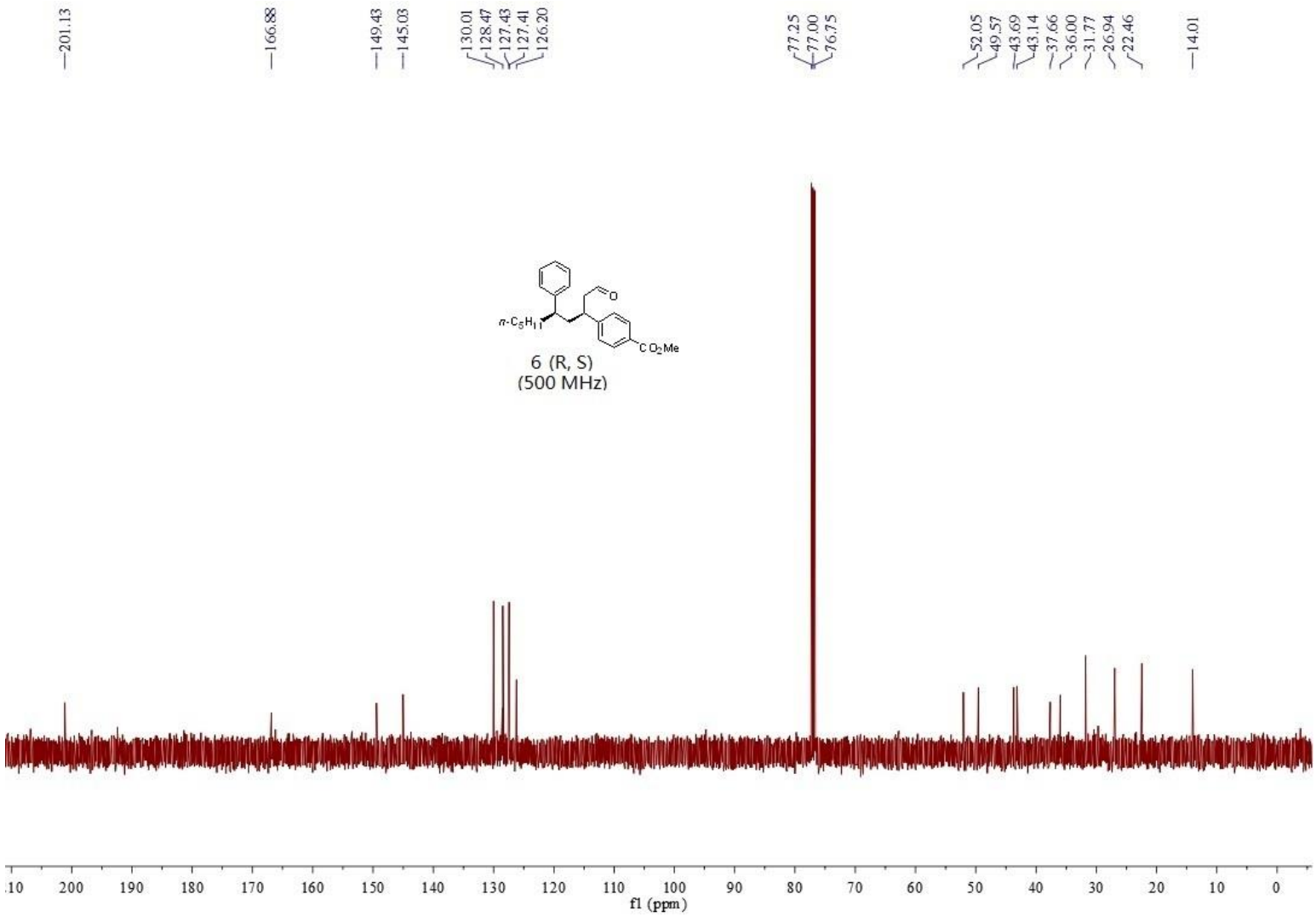

2.04
1.03
1.90
2.00
2.01
1.12
2.21
2.99
6.35
3.05
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


145.34
131.54
130.32
128.20
127.67
125.95
77.25
77.00
76.75
63.70
45.97
39.68
35.99
31.90
27.13
22.54
14.05
Me
OH
5 (500 MHz)
f1 (ppm)


6 (R, R)
(500 MHz)
Me
Ph
O
COOMe
f1 (ppm)


200.98
166.93
148.78
144.46
129.97
128.45
127.85
127.81
126.29
77.25
77.00
76.75
52.07
51.13
43.23
42.51
37.94
37.72
31.74
26.99
22.43
13.98
Me
Ph
O
COOMe
6 (R, R)
(500 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.56
9.56
9.56
7.95
7.94
7.27
7.26
7.24
7.19
7.18
7.05
7.03
3.90
3.25
3.23
3.20
3.19
2.74
2.73
2.71
2.41
2.39
2.36
1.59
1.54
1.48
1.40
1.19
1.14
1.08
1.03
0.82
0.80
0.79
0.00
9.56
9.56
9.56
9.50
9.50
9.49
1.06
0.96
9.57 9.56 9.55 9.54 9.53 9.52 9.51 9.50 9.49
f1 (ppm)
n-C5H11
CO2Me
6 (R, S)
(500 MHz)
0.86
1.88
0.84
1.37
3.14
2.30
3.00
1.11
1.96
1.17
2.18
2.29
6.12
3.27
10.0 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 0.0
f1 (ppm)


201.13
166.88
149.43
145.03
130.01
128.47
127.43
127.41
126.20
77.25
77.00
76.75
52.05
49.57
43.69
43.14
37.66
36.00
31.77
26.94
22.46
14.01
n-C5H11
O
CO2Me
6 (R, S)
(500 MHz)
f1 (ppm)