Electronic Supplementary Information for:

Remote Carbamate-directed Site-selective Benzylic C-H Oxygenation via Synergistic Copper/TEMPO Catalysis at Room Temperature

Jiaming Chen,[†] Fang Wang,[†] Yanping Huang,[†,‡] Xiaoqi, Jia,[†] Dailin Zhuang,[†] Zhenyang Wan,[†] and Ziyuan Li[*,†]*

[†] Department of Pharmaceutical and Biological Engineering, School of Chemical Engineering, Sichuan University, No.24 South Section 1, Yihuan Road, Chengdu 610065, China

[‡] Engineering Experimental Teaching Centre, School of Chemical Engineering, Sichuan University, No.24 South Section 1, Yihuan Road, Chengdu 610065, China

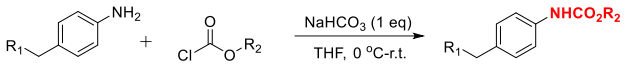
[*]E-mail: liziyuan@scu.edu.cn; Fax: (+86)28-85405221

Table of Contents

General Remarks

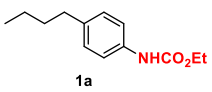
All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar, Acros, J&K Chemicals, Adamas-beta, Accela ChemBio and Aladdin Chemicals. CuOTf (99%, CAS No. 42152-44-3), TEMPO (98%+, CAS No. 2564-83-2), NFSI (97%+, CAS No. 133745-75-2), MeCN (99.9%, SafeDry, water < 50 ppm) and 1,1-diphenylethene (98%+, CAS No. 530-48-3) were purchased from Adamas. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Carbamate substrates were prepared via condensation between corresponding anilines and chloroformates according to literature reported methods.[1] Products were purified by flash chromatography on silica gel using petroleum ether, ethyl acetate and dichloromethane as the eluents. ^{1}H-NMR spectra were recorded on Bruker AVANCE III-400 or JNM-ECZ400S/L1 spectrometers. Chemical shifts (in ppm) were referenced with TMS in $CDCl_3$ (0 ppm). ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm) or DMSO-d_6 (δ = 39.50 ppm). High resolution mass spectra were obtained from an Agilent 6520B Q-TOF mass spectrometer with electron spray ionization (ESI) as the ion source.

Preparation and ^{1}H-NMR data of Substrates



Typical Procedure: To a 100 mL flask charged with a solution of 4-alkyl aniline (10 mmol) in THF (20 mL) was added $NaHCO_3$ (10 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 15 minutes and was added hexyl choroformate (10 mmol). After stirred overnight at 25 °C, the reaction was quenched with saturated NH_4Cl, extracted with ethyl acetate, washed with water, dried over Na_2SO_4, and concentrated *in vacuo* to give yellow residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent on silical gel to afford 4-alkyl carbamate **1a-g**, **1n** and **1p-r** in 79-92% yield.

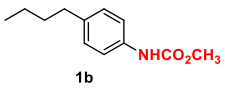
Ethyl (4-butylphenyl)carbamate (1a)



1a

Yield 92%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.27 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.63 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.39-1.27 (m, 5H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm.

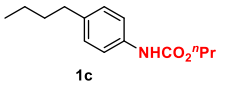
Methyl (4-butylphenyl)carbamate (1b)



1b

Yield 89%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.27 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.70 (s, 1H), 3.76 (s, 3H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.38-1.28 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm.

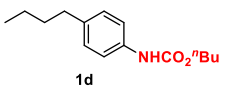
Propyl (4-butylphenyl)carbamate (1c)



1c

Yield 85%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.27 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.59 (s, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 2.56 (t, *J* = 8.6 Hz, 2H), 1.73-1.64 (m, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.38-1.28 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm.

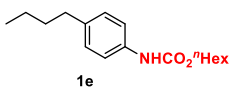
Butyl (4-butylphenyl)carbamate (1d)



1d

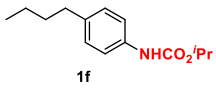
Yield 91%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.28 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.65 (s, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.63 (p, *J* = 7.0 Hz, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.45-1.28 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 5.5 Hz, 3H) ppm.

Hexyl (4-butylphenyl)carbamate (1e)



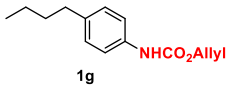
Yield 89%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.27 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.59 (s, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 2.56 (t, *J* = 8.6 Hz, 2H), 1.73-1.64 (m, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.38-1.28 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm.

Isopropyl (4-butylphenyl)carbamate (1f)



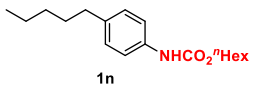
Yield 81%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.27 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.52 (s, 1H), 5.01 (hept, *J* = 6.3 Hz, 1H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.37-1.30 (m, 2H), 1.30 (s, 3H), 1.28 (s, 3H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm.

Allyl (4-butylphenyl)carbamate (1g)



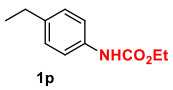
Yield 79%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = .28 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.61 (s, 1H), 5.97 (m, 1H), 5.36 (m, 1H), 5.25 (m, 1H), 4.66 (d, *J* = 5.7 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.38-1.28 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm.

Hexyl (4-pentylphenyl)carbamate (1n)



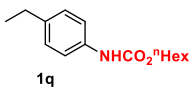
Yield 81%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.28 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.60 (s, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.66 (p, *J* = 6.8 Hz, 2H), 1.58 (p, *J* = 7.6 Hz, 2H), 1.41-1.28 (m, 10H), 0.92-0.85 (m, 6H) ppm.

Ethyl (4-ethylphenyl)carbamate (1p)



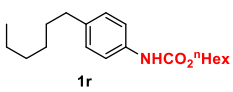
Yield 82%. **^{1}H NMR (CDCl$_3$, 400 MHz):** 7.28 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.68 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.6 Hz, 3H) ppm.

Hexyl (4-ethylphenyl)carbamate (1q)

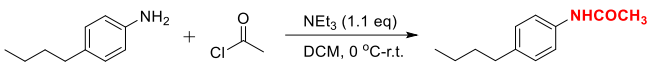


Yield 88%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.28 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.60 (s, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.66 (p, *J* = 6.8 Hz, 2H), 1.40-1.29 (m, 6H), 1.21 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H) ppm.

Hexyl (4-hexylphenyl)carbamate (1r)

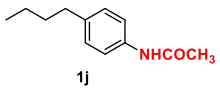


Yield 89%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.28 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.60 (s, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.66 (p, *J* = 6.8 Hz, 2H), 1.40-1.29 (m, 6H), 1.21 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H) ppm.



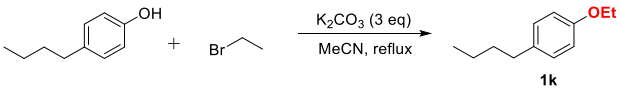
Typical Procedure: To a 100 mL flask charged with a solution of 4-butylaniline (5 mmol) in DCM (10 mL) was added triethylamine (5.5 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes and was added a solution of acetyl chloride (5.5 mmol) in DCM (5 mL). After stirred overnight at 25 °C, the reaction was extracted with DCM, washed with water, dried over Na_2SO_4, and concentrated *in vacuo* to give yellow residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (15:1, *v*/*v*) as the eluent on silical gel to afford *N*-(4-butylphenyl) acetamide (**1j**) in 78% yield.

***N*-(4-Butylphenyl)acetamide (1j)**



1j

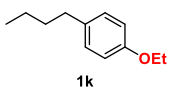
Yield 78%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.56 (s, 1H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.14 (s, 3H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.37-1.28 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm.



1k

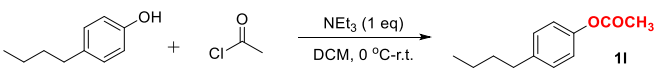
Typical Procedure: To a 100 mL flask charged with a solution of 4-butylphenol (5 mmol) in MeCN (10 mL) was added K_2CO_3 (15 mmol) at 25 °C. The reaction mixture was stirred at 25 °C for 5 minutes and was added bromoethane (10 mmol). After stirred at 25 °C for 2 hours, the reaction was quenched with saturated NH_4Cl, extracted with ethyl acetate, washed with water, dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (15:1 to 10:1, *v*/*v*) as the eluent on silical gel to afford 1-butyl-4-ethoxybenzene (**1k**) in 79% yield.

1-Butyl-4-ethoxybenzene (1k)



1k

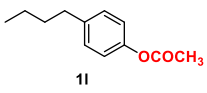
Yield 78%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.07 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.00 (q, *J* = 7.0 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.42 – 1.28 (m, 5H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm.



Typical Procedure: To a 100 mL flask charged with a solution of 4-butylphenol (5 mmol) in DCM (10 mL) was added triethylamine (5.5 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes and

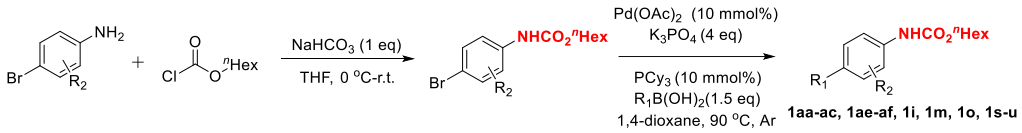
was added a solution of acetyl chloride (5.5 mmol) in DCM (5 mL). After stirred at 25 °C for 2 hours, the reaction was extracted with DCM, washed with water, dried over Na_2SO_4, and concentrated *in vacuo* to give yellow residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (15:1 to 10:1, *v*/*v*) as the eluent on silical gel to afford 4-butylphenyl acetate (**1k**) in 82% yield.

4-Butylphenyl acetate (1l)



1l

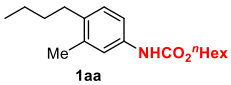
Yield 79%. **^{1}H NMR ($CDCl_3$, 400 MHz):** 7.17 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.28 (s, 3H), 1.58 (p, *J* = 7.5 Hz, 2H), 1.39-1.30 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm.



Typical Procedure: To a 100 mL flask charged with a solution of corresponding bromoaniline (10 mmol) in THF (20 mL) was added $NaHCO_3$ (10 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 15 minutes and was added hexyl choroformate (10 mmol). After stirred overnight at 25 °C, the reaction mixture was quenched with saturated NH_4Cl, extracted with ethyl acetate, washed with water, dried over Na_2SO_4, and concentrated *in vacuo* to give yellow residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (8:1, *v*/*v*) as the eluent on silical gel to afford corresponding hexyl-(bromophenyl)-carbamate intermediates in 70-81% yield.

To a reaction flask charged with K_3PO_4 (20 mmol), palladium(II) acetate (10 mol%) and tricyclohexyl phosphine (10 mol%) was added a solution of corresponding alkyl boric acid (7.5 mmol) and the above hexyl-(bromophenyl)-carbamate intermediates (5 mmol) in anhydrous 1,4-dioxane (20 mL) via a syringe under argon (1 atm). After stirred at 90 °C for 4 hours, the reaction mixture was quenched with water, extracted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (25:1, *v*/*v*) as the eluent on silical gel to afford corresponding hexyl-(butylphenyl)-carbamates **1aa-ac**, **1ae-af**, **1i**, **1m**, **1o**, **1s-u** in 46-60% yield (21-37% total yield of two steps).

Hexyl (4-butyl-3-methylphenyl)carbamate (1aa)

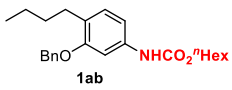


1aa

Total yield 42%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ =7.16 (s, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.49 (s, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 2.54 (t, *J* = 7.7

Hz, 2H), 2.27 (s, 3H), 1.66 (m, 2H), 1.51 (m, 2H), 1.43-1.27 (m, 8H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H) ppm.

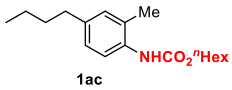
Hexyl (3-(benzyloxy)-4-butylphenyl)carbamate (1ab)



1ab

Total yield 41%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = (d, *J* = 6.9 Hz, 2H), 7.41-7.35 (m, 2H), 7.32 (dt, *J* = 8.1 Hz, 2.0 Hz, 1H), 7.29 (dt, *J* = 11.2 Hz, 1.4 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.71 (dd, *J* = 8.0 Hz, 2.1 Hz, 1H), 6.59 (s, 1H), 5.06 (s, 2H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.61 (d, *J* = 7.6 Hz, 2H), 1.66 (p, *J* = 6.8 Hz, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.42-1.28 (m, 8H), 0.93-0.87 (m, 6H) ppm.

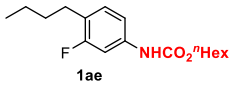
Hexyl (4-butyl-2-methylphenyl)carbamate (1ac)



1ac

Total yield 37%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.62 (s, 1H), 7.01 (dd, *J* = 8.3 Hz, 1.8 Hz, 1H), 6.97 (s, 1H), 6.29 (s, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 2.53 (d, *J* = 7.6 Hz, 2H), 2.22 (s, 3H), 1.66 (p, *J* = 6.8 Hz, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.42-1.28 (m, 8H), 0.91 (m, 6H) ppm.

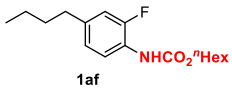
Hexyl (4-butyl-3-fluorophenyl)carbamate (1ae)



1ae

Total yield 21%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.22 (t, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 8.3 Hz, 1H), 6.94 (dd, *J* = 8.2 Hz, 1.5 Hz, 1H), 6.60 (s, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.57 (td, *J* = 7.6 Hz, 1.1 Hz, 2H), 1.66 (p, *J* = 6.8 Hz, 2H), 1.55 (p, *J* = 7.5 Hz, 2H), 1.43-1.28 (m, 8H), 0.94-0.87 (m, 6H) ppm.

Hexyl (4-butyl-3-fluorophenyl)carbamate (1af)



1af

Total yield 31%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 8.01 (d, *J* = 26 Hz, 1H), 6.92 (dd, *J* = 8.5 Hz, 2.1 Hz, 1H), 6.88 (dd, *J* = 12.0 Hz, 1.9 Hz, 1H), 6.73 (s, 1H), 4.16 (t, *J* = 6.7 Hz, 3H), 2.55 (d, *J* = 7.6 Hz, 2H), 1.67 (m, 3H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.43-1.29 (m, 8H), 0.95-0.87 (m, 6H) ppm.

Hexyl (4-butylphenyl)(methyl)carbamate (1i)

1i

Total yield 35%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.13 (s, 4H), 4.08 (t, *J* = 6.6 Hz, 2H), 3.28 (s, 3H), 2.59 (t, *J* = 7.7 Hz, 2H), 1.62-1.56 (m, 4H), 1.36 (p, *J* = 7.4 Hz, 2H), 1.30-1.24 (m, 6H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 6.7 Hz, 3H) ppm.

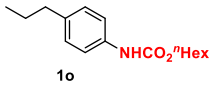
Hexyl (4-isobutylphenyl)carbamate (1m)

1m

Total yield 37%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.28 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J*

= 8.5 Hz, 2H), 6.59 (s, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.82 (m, 1H), 1.66 (p, *J* = 6.8 Hz, 2H), 1.40-1.28 (m, 6H), 0.92-0.86 (m, 9H) ppm.

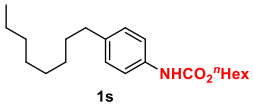
Hexyl (4-propylphenyl)carbamate (1o)



1o

Total yield 37%. **^{1}H NMR (CDCl$_3$, 400 MHz):**δ = 7.28 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.60 (s, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.53 (d, *J* = 7.4 Hz, 2H), 1.69-1.55 (m, 4H), 1.42-1.35 (m, 2H), 1.34-1.28 (m, 4H), 0.93-0.87 (m, 6H) ppm.

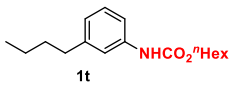
Hexyl (4-propylphenyl)carbamate (1s)



1s

Total yield 44%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.27 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.57 (s, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.55 (d, *J* = 7.5 Hz, 2H), 1.66 (p, *J* = 6.9 Hz, 2H), 1.57 (p, *J* = 7.4 Hz, 2H), 1.43-1.21 (m, 16H), 0.94-0.84 (m, 6H) ppm.

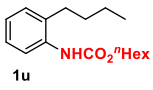
Hexyl (3-butylphenyl)carbamate (1t)



1t

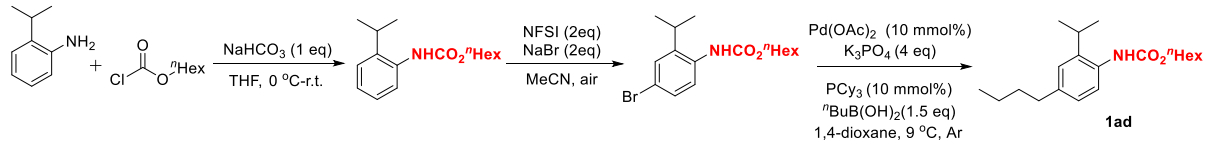
Total yield 30%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.24 (s, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 3.4 Hz, 1H), 6.89- 6.86 (m, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.58 (t, *J* = 7.9 Hz, 2H), 1.71 -1.62 (m, 2H), 1.58 (p, *J* = 7.5 Hz, 2H), 1.42 -1.28 (m, 8H), 0.94 -0.87 (m, 6H) ppm.

Hexyl (2-butylphenyl)carbamate (1u)



1u

Total yield 31%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.75 (s, 1H), 7.20 (td, *J* = 7.9, 1.6 Hz, 1H), 7.15 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.05 (td, *J* = 7.5, 1.2 Hz, 1H), 6.40 (s, 1H), 4.16 (t, *J* = 6.8 Hz, 2H), 2.56 (t, *J* = 7.64 Hz, 2H), 1.72 - 1.63 (m, 2H), 1.61-1.53 (m, 2H), 1.44 -1.29 (m, 8H), 0.95 (t, *J* = 7.30 Hz, 3H), 0.91 (t, *J* = 6.68 Hz, 3H)ppm.

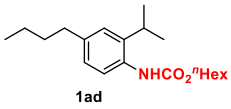


Typical Procedure: To a 100 mL flask charged with a solution of 2-isopropylaniline (10 mmol) in THF (20 mL) was added $NaHCO_3$ (10 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 15 minutes and was added hexyl choroformate (10 mmol). After stirred overnight at 25 °C, the reaction mixture was quenched with saturated NH_4Cl, extracted with ethyl acetate, washed with water, dried over Na_2SO_4, and concentrated *in vacuo* to give yellow residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (8:1, *v*/*v*) as the eluent on silical gel to afford hexyl (2-isopropylphenyl)carbamate in 87% yield.

To a 100 mL flask charged with a solution of the above hexyl (3-isopropylphenyl)carbamate (5 mmol) in MeCN (20 mL) was added NFSI (2 mmol) and NaBr (2 mmol) at 25 °C. After stirred at 25 °C overnight, the reaction mixture was quenched with saturated Na_2CO_3, extracted with ethyl acetate, washed with water, dried over Na_2SO_4, and concentrated *in vacuo* to give yellow residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent on silical gel to afford hexyl (4-bromo-2-isopropylphenyl)carbamate in 63% yield.

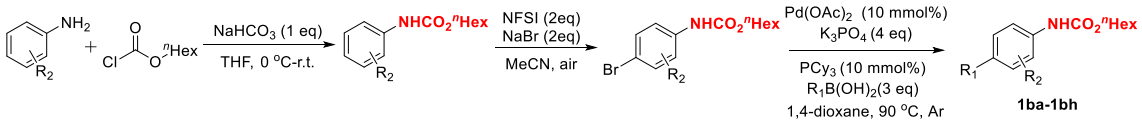
To a reaction flask charged with K_3PO_4 (20 mmol), palladium(II) acetate (10 mol%) and tricyclohexyl phosphine (10 mol%) was added a solution of butyl boric acid (7.5 mmol) and the above hexyl (4-bromo-2-isopropylphenyl)carbamate (5 mmol) in anhydrous 1,4-dioxane (20 mL) via a syringe under argon (1 atm). After stirred at 90 °C for 4 hours, the reaction mixture was quenched with water, extracted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (35:1, *v*/*v*) as the eluent on silical gel to afford hexyl (4-butyl-2-isopropylphenyl)carbamate (**1ad)** in 54% yield (29% total yield of three steps).

Hexyl (4-butyl-2-isopropylphenyl)carbamate (1ad)



1ad

Total yield 29%. **^{1}H NMR (CDCl$_3$, 400 MHz):**δ = 7.51 (s, 1H), 7.05 (d, *J* = 2.0 Hz, 1H), 7.00 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.32 (s, 1H), 4.14 (t, *J* = 6.8 Hz, 2H), 3.03 (hept, *J* = 6.4 Hz, 1H), 2.57 (d, *J* = 7.7 Hz, 2H), 1.67 (p, *J* = 6.9, 6.4 Hz, 3H), 1.56 (p, *J* = 7.8 Hz, 2H), 1.41-1.28 (m, 8H), 1.23 (d, *J* = 6.8 Hz, 6H), 0.93 (t, *J* = 7.3 Hz, 3H) , 0.89 (t, *J* = 4.5 Hz, 3H) ppm.



1ba-1bh

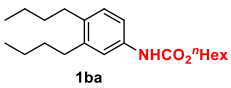
Typical Procedure: To a 100 mL flask charged with a solution of corresponding bromoanilines (10 mmol) in THF (20 mL) was added $NaHCO_3$ (10 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 15 minutes and was added hexyl choroformate (10 mmol). After stirred overnight at 25 °C, the reaction mixture was quenched with saturated NH_4Cl, extracted with ethyl acetate, washed with water, dried over Na_2SO_4, and concentrated *in vacuo* to give yellow residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent on silical gel to afford corresponding hexyl (bromophenyl)carbamates in 81-83% yield.

To a 100 mL flask charged with a solution of the above hexyl (bromophenyl)carbamates (5 mmol) in

MeCN (20 mL) was added NFSI (2 mmol) and NaBr (2 mmol) at 25 °C. After stirred at 25 °C overnight, the reaction mixture was quenched with saturated Na_2CO_3, extracted with ethyl acetate, washed with water, dried over Na_2SO_4, and concentrated *in vacuo* to give yellow residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent on silical gel to afford corresponding hexyl (dibromophenyl)carbamates in 66-68% yield.

To a reaction flask charged with K_3PO_4 (20 mmol), palladium(II) acetate (10 mol%) and tricyclohexyl phosphine (10 mol%) was added a solution of corresponding alkyl boric acid (15 mmol) and the above hexyl (dibromophenyl)carbamates (5 mmol) in anhydrous 1,4-dioxane (20 mL) via a syringe under argon (1 atm). After stirred at 90 °C for 4 hours, the reaction mixture was quenched with water, extracted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (35:1, *v*/*v*) as the eluent on silical gel to afford corresponding hexyl carbamate substrates **1ba-bh** in 32-51% yield (17-28% total yield of three steps).

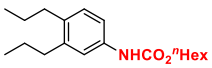
Hexyl (3,4-dibutylphenyl)carbamate (1ba)



1ba

Total yield 27%. **^{1}H NMR (CDCl$_3$, 400 MHz):**δ = 7.18 (s, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.53 (s, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 2.56 (q, *J* = 7.9 Hz, 4H), 1.70-1.61 (m, 2H), 1.60-1.49 (m, 4H), 1.45-1.27 (m, 10H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H) ppm.

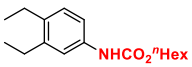
Hexyl (3,4-dipropylphenyl)carbamate (1bb)



1bb

Total yield 28%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.17 (s, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.52 (s, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 2.57-2.51 (m, 4H), 1.69-1.55 (m, 6H), 1.42-1.27 (m, 6H), 0.99-0.94 (m, 6H), 0.91-0.88 (m, 3H) ppm.

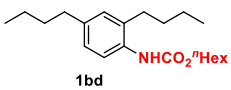
Hexyl (3,4-diethylphenyl)carbamate (1bc)



1bc

Total yield 27%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.19 (s, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.55 (s, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.65-2.57 (m, 4H), 1.69-1.62 (m, 2H), 1.42-1.29 (m, 6H), 1.25-1.16 (m, 6H), 0.93-0.87 (m, 3H) ppm.

Hexyl (2,4-dibutylphenyl)carbamate (1bd)

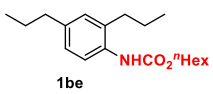


1bd

Total yield 23%. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.59 (s, 1H), 7.01 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.96 (d, *J* = 1.9 Hz, 1H), 6.30 (s, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 2.58-2.50 (m, 4H), 1.67 (p, *J* = 6.8 Hz, 2H), 1.62-1.50 (m, 4H), 1.43-1.31 (m, 10H), 0.97-0.93 (m, 3H),

0.93-0.87 (m, 6H) ppm.

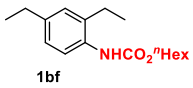
Hexyl (2,4-dipropylphenyl)carbamate (1be)



1be

Total yield 24%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.60 (s, 1H), 7.01 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.96 (d, *J* = 1.9 Hz, 1H), 6.30 (s, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 2.54-2.49 (m, 4H), 1.70-1.56 (m, 6H), 1.39-1.29 (m, 6H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.95-0.88 (m, 6H) ppm.

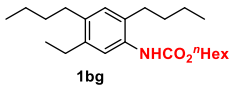
Hexyl (2,4-diethylphenyl)carbamate (1bf)



1bf

Total yield 17%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.61 (s, 1H), 7.04 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.01 (d, *J* = 1.7 Hz, 1H), 6.29 (s, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 2.64-2.55 (m, 4H), 1.71-1.62 (m, 2H), 1.40-1.29 (m, 6H), 1.24-1.19 (m, 6H), 0.92-0.88 (t, *J* = 6.8 Hz, 3H) ppm.

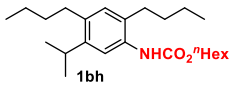
Hexyl (2,4-dibutyl-5-ethylphenyl)carbamate (1bg)



1bg

Total yield 25%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.51 (s, 1H), 6.91 (s, 1H), 6.28 (s, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 2.61 (q, *J* = 7.5 Hz, 2H), 2.57-2.47 (m, 4H), 1.67 (p, *J* = 6.8 Hz, 2H), 1.53 (p, *J* = 7.4 Hz, 4H), 1.44-1.28 (m, 12H), 1.21 (t, *J* = 7.6 Hz, 3H), 0.99-0.9 (m, 9H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm.

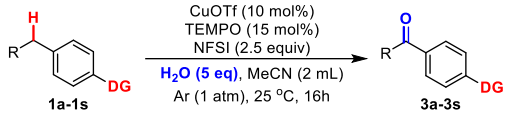
Hexyl (2,4-dibutyl-5-isopropylphenyl)carbamate (1bh)



1bh

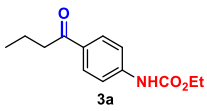
Total yield 25%. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.62 (s, 1H), 6.89 (s, 1H), 6.30 (s, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 3.11 (p, *J* = 6.8 Hz, 1H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.49 (t, *J* = 7.7 Hz, 2H), 1.67 (p, *J* = 6.8 Hz, 2H), 1.60-1.46 (m, 4H), 1.43-1.34 (m, 6H), 1.32-1.29 (m, 4H), 1.23 (s, 3H), 1.22 (s, 3H), 0.96-0.92 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H) ppm.

Experimental Procedure and Characterization Data



Typical Procedure: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of substrates **1a-1s** (0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and water (27 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silical gel to afford corresponding phenone products **3a-3s**.

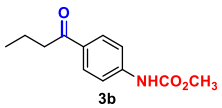
Ethyl (4-butyrylphenyl)carbamate (3a):



The benzylic oxygenation of 0.3 mmol of ethyl (4-butylphenyl)carbamate (**1a**, 66.4 mg) afforded 58.9 mg of **3a** (84%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 81.8-85.4 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.94 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.22 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 1.76 (sext, *J* = 7.4 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 199.41, 153.22, 142.42, 135.75, 129.51, 117.51, 61.47, 40.17, 17.82, 14.40, 13.84 ppm. **HRMS *m/z* (ESI)** calcd for $[C_{13}H_{17}NO_3+H]^+$ 236.1281, found 236.1278.

Methyl (4-butyrylphenyl)carbamate (3b):

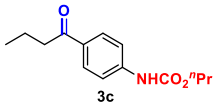


The benzylic oxygenation of 0.3 mmol of methyl (4-butylphenyl)carbamate (**1b**, 62.2 mg) afforded 50.0 mg of **3b** (75%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent.

White soild, m.p. 113.7-118.5 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.94 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* =

8.8 Hz, 2H), 7.07 (s, 1H), 3.80 (s, 3H), 2.91 (t, *J* = 7.3 Hz, 2H), 1.76 (sext, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 199.29, 153.58, 142.17, 132.05, 129.56, 117.60, 52.56, 40.24, 17.87, 13.87 ppm. **HRMS m/z (ESI)** calcd for $[C_{12}H_{15}NO_3+H]^+$ 222.1125, found 222.1121.

Propyl (4-butyrylphenyl)carbamate (3c):

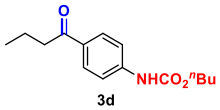


3c

The benzylic oxygenation of 0.3 mmol of propyl (4-butylphenyl)carbamate (**1c**, 70.5 mg) afforded 54.1 mg of **3c** (72%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 104.8-105.9 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.93 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 6.95 (s, 1H), 4.15 (d, *J* = 6.7 Hz, 2H), 2.91 (d, *J* = 7.2 Hz, 2H), 1.81-1.66 (m, 4H), 1.02-0.96 (m, 6H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 199.21, 153.24, 142.30, 132.02, 129.56, 117.57, 67.19, 40.24, 22.17, 17.89, 13.88, 10.28 ppm. **HRMS m/z (ESI)** calcd for $[C_{14}H_{19}NO_3+H]^+$ 250.1438, found 250.1438.

Butyl (4-butyrylphenyl)carbamate (3d):

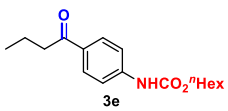


3d

The benzylic oxygenation of 0.3 mmol of butyl (4-butylphenyl)carbamate (**1d**, 74.8 mg) afforded 60.9 mg of **3d** (77%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 95.8-97.0 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.93 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.17 (s, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.76 (sext, *J* = 7.4 Hz, 2H), 1.66 (p, *J* = 7.1 Hz, 2H), 1.41 (sext, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 199.31, 153.32, 142.43, 131.89, 129.52, 117.57, 65.39, 40.21, 30.82, 18.98, 17.87, 13.84, 13.63 ppm. **HRMS m/z (ESI)** calcd for $[C_{15}H_{21}NO_3+H]^+$ 264.1594, found 264.1590.

Hexyl (4-butyrylphenyl)carbamate (3e):



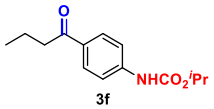
3e

The benzylic oxygenation of 0.3 mmol of hexyl (4-butylphenyl)carbamate (**1e**, 83.2 mg) afforded 80.1 mg of **3e** (92%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 96.2-98.4 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.93 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.15 (s, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 1.76 (sext, *J* = 7.4 Hz, 2H),

1.67 (p, *J* = 7.1 Hz, 2H), 1.39 – 1.29 (m, 6H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 199.32, 153.31, 142.40, 131.85, 129.53, 117.54, 65.70, 40.20, 31.36, 28.75, 25.43, 22.48, 17.86, 13.94, 13.85 ppm. **HRMS m/z (ESI)** calcd for $[C_{17}H_{25}NO_3+H]^+$ 292.1907, found 292.1903.

Isopropyl (4-butyrylphenyl)carbamate (3f):

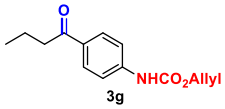


3f

The benzylic oxygenation of 0.3 mmol of isopropyl (4-butylphenyl)carbamate (**1f**, 70.5 mg) afforded 55.6 mg of **3f** (74%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 118.8-122.5 ºC. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.93 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 6.90 (s, 1H), 5.04 (hept, *J* = 6.3 Hz, 1H), 2.91 (t, *J* = 7.3 Hz, 2H), 1.76 (sext, *J* = 7.4 Hz, 2H), 1.31 (d, *J* = 6.3 Hz, 6H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 199.25, 152.73, 142.41, 131.88, 129.56, 117.50, 69.24, 40.23, 22.00, 17.88, 13.88 ppm. **HRMS m/z (ESI)** calcd for $[C_{14}H_{19}NO_3+H]^+$ 250.1438, found 250.1433.

Allyl (4-butyrylphenyl)carbamate (3g):

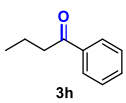


3g

The benzylic oxygenation of 0.3 mmol of allyl (4-butylphenyl)carbamate (**1g**, 70.2 mg) afforded 39.3 mg of **3g** (53%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent.

Yellow soild, m.p. 100.9-103.2 ºC. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.94 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.22 (s, 1H), 6.00-5.91 (m, 1H), 5.37 (dd, *J* = 17.2 Hz, 1.5 Hz, 1H), 5.27 (dd, *J* = 10.4 Hz, 1.2 Hz, 1H), 4.68 (d, *J* = 5.7 Hz, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 1.76 (sext, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 199.34, 152.83, 142.19, 132.03, 129.54, 118.53, 117.65, 66.09, 40.22, 17.85, 13.86 ppm. **HRMS m/z (ESI)** calcd for $[C_{14}H_{17}NO_3+H]^+$ 248.1281, found 248.1277.

1-Phenylbutan-1-one (3h) [2]**:**



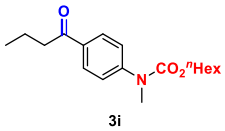
3h

The benzylic oxygenation of 0.3 mmol of butylbenzene (**1h**, 40.2 mg) afforded 3.7 mg of **3h** (8%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (20:1, *v*/*v*) as the eluent.

Colorless oil. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.97-7.95 (m, 2H), 7.57-7.53 (m, 1H), 7.47-7.44 (m, 2H),

2.95 (t, *J* = 7.3 Hz, 2H), 1.77 (sext, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 200.41, 137.04, 132.83, 128.50, 127.99, 40.46, 17.71, 13.84. **GC-MS m/z (EI)** calcd for [$C_{12}H_{14}O_3$] 148.1 found 148.1.

Hexyl (4-butyrylphenyl)(methyl)carbamate (3i):

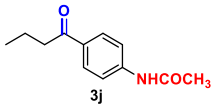


3i

The benzylic oxygenation of 0.3 mmol of hexyl (4-butylphenyl)(methyl)carbamate (**1i**, 87.4 mg) afforded 49.6 mg of **3i** (54%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent.

Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.95 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 4.14 (t, *J* = 6.7 Hz, 2H), 3.35 (s, 3H), 2.93 (t, *J* = 7.3 Hz, 2H), 1.77 (sext, *J* = 7.4 Hz, 2H), 1.65-1.59 (m, 2H), 1.35-1.26 (m, 6H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 199.33, 155.23, 147.34, 133.77, 128.66, 124.49, 66.26, 40.37, 36.97, 31.29, 28.69, 25.49, 22.45, 17.75, 13.91, 13.83 ppm. **HRMS m/z (ESI)** calcd for $[C_{18}H_{27}NO_3+H]^+$ 306.2064, found 306.2059.

***N*-(4-Butyrylphenyl)acetamide (3j):**

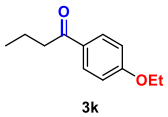


3j

The benzylic oxygenation of 0.3 mmol of *N*-(4-butylphenyl)acetamide (**1j**, 57.3 mg) afforded 25.6 mg of **3j** (42%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 116.9-120.8 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.01 (s, 1H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 2.21 (s, 3H), 1.76 (sext, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 199.54, 168.87, 142.25, 132.67, 129.40, 118.92, 40.30, 24.67, 17.88, 13.85 ppm. **HRMS m/z (ESI)** calcd for $[C_{12}H_{15}NO_2+H]^+$ 206.1176, found 206.1173.

1-(4-Ethoxyphenyl)butan-1-one (3k) [3]**:**



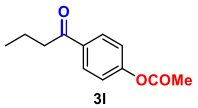
3k

The benzylic oxygenation of 0.3 mmol of 1-butyl-4-ethoxybenzene (**1k**, 53.4 mg) afforded 30.9 mg of **3k** (54%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (8:1, *v*/*v*) as the eluent.

Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ= 7.85 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 4.01 (q, *J* = 7.0 Hz, 2H), 2.81 (t, *J* = 7.3 Hz, 2H), 1.67 (sext, *J* = 7.4 Hz, 2H), 1.35 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 199.06, 162.67, 130.23, 129.94, 114.01, 63.63,

40.10, 17.94, 14.60, 13.87 ppm. **GC-MS m/z (EI)** calcd for [$C_{12}H_{16}O_2$] 192.1 found 192.1.

4-Butyrylphenyl acetate (3l) [4]**:**

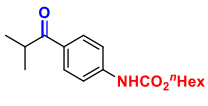


3l

The benzylic oxygenation of 0.3 mmol of 4-butylphenyl acetate (**1l**, 57.6 mg) afforded 41.8 mg of **3k** (68%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent.

Light yellow oil. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 8.00 (d, *J* = 8.9 Hz, 2H), 7.19 (d, *J* = 9.0 Hz, 2H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.32 (s, 3H), 1.77 (sext, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 199.09, 168.88, 154.10, 134.63, 129.61, 121.69, 40.42, 21.10, 17.67, 13.81 ppm. **GC-MS m/z (EI)** calcd for [$C_{12}H_{14}O_3$] 206.1 found 206.0.

Hexyl (4-isobutyrylphenyl)carbamate (3m):

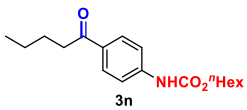


3m

The benzylic oxygenation of 0.3 mmol of hexyl (4-isobutylphenyl)carbamate (**1m**, 83.2 mg) afforded 62.3 mg of **3m** (71%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 59.5-60.9 °C. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.94 (d, *J* = 8.9 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.29 (s, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 3.53 (hept, *J* = 6.8 Hz, 1H), 1.66 (p, *J* = 7.1 Hz, 2H), 1.41-1.28 (m, 6H), 1.21 (d, *J* = 6.8 Hz, 6H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 203.39, 153.36, 142.44, 130.76, 129.78, 117.64, 65.66, 34.95, 31.34, 28.73, 25.41, 22.45, 19.17, 13.91 ppm. **HRMS m/z (ESI)** calcd for [$C_{17}H_{25}NO_3$+H]$^+$ 292.1907, found 292.1906.

Hexyl (4-pentanoylphenyl)carbamate (3n):

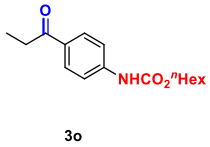


3n

The benzylic oxygenation of 0.3 mmol of hexyl (4-pentylphenyl)carbamate (**1n**, 87.4 mg) afforded 80.3 mg of **3n** (88%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1 to 20:1, *v*/*v*) as the eluent.

White soild, m.p. 80.2-81.6 °C. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.93 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.24 (s, 1H), 4.17 (t, *J* = 6.8 Hz, 2H), 2.93 (t, *J* = 7.5 Hz, 2H), 1.75-1.62 (m, 4H), 1.45-1.28 (m, 8H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 199.49, 153.33, 142.45, 131.80, 129.53, 117.55, 65.68, 38.01, 31.35, 28.74, 26.58, 25.42, 22.46, 22.43, 13.92, 13.88 ppm. **HRMS m/z (ESI)** calcd for [$C_{18}H_{27}NO_3$+H]$^+$ 306.2064, found 306.2062.

Hexyl (4-propionylphenyl)carbamate (3o):

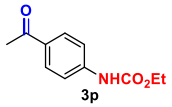


3o

The benzylic oxygenation of 0.3 mmol of hexyl (4-propylphenyl)carbamate (**1o**, 79.0 mg) afforded 60.9 mg of **3o** (73%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 10:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 102.2-104.3 °C. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.86 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.15 (s, 1H), 4.09 (t, *J* = 6.7 Hz, 2H), 2.89 (q, *J* = 7.3 Hz, 2H), 1.58 (p, *J* = 7.1 Hz, 2H), 1.33-1.20 (m, 6H), 1.14 (t, *J* = 7.3 Hz, 3H), 0.81 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 199.75, 153.33, 142.45, 131.63, 129.43, 117.55, 65.68, 31.43, 31.35, 28.74, 25.42, 22.46, 13.92, 8.29 ppm. **HRMS m/z (ESI)** calcd for $[C_{16}H_{23}NO_3+H]^+$ 278.1751, found 278.1748.

Ethyl (4-acetylphenyl)carbamate (3p):

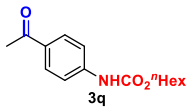


3p

The benzylic oxygenation of 0.3 mmol of ethyl (4-ethylphenyl)carbamate (**1p**, 57.9 mg) afforded 55.0 mg of **3p** (89%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 10:1, *v*/*v*) as the eluent.

White soild, m.p. 62.4-64.8 °C. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.93 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.10 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.57 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 197.00, 153.16, 142.58, 132.02, 129.84, 117.56, 61.56, 26.33, 14.43 ppm. **HRMS m/z (ESI)** calcd for $[C_{12}H_{14}O_3+H]^+$ 208.0968 found 208.0965.

Hexyl (4-acetylphenyl)carbamate (3q):

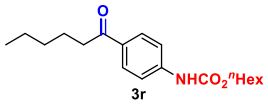


3q

The benzylic oxygenation of 0.3 mmol of hexyl (4-ethylphenyl)carbamate (**1q**, 74.8 mg) afforded 65.0 mg of **3q** (82%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 87.1-90.4 °C. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.93 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 6.96 (s, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 2.57 (s, 3H), 1.68 (p, *J* = 7.1 Hz, 2H), 1.40-1.30 (m, 6H), 0.90 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 196.93, 153.21, 142.51, 132.05, 129.87, 117.51, 65.80, 31.39, 28.78, 26.37, 25.47, 22.51, 13.98 ppm. **HRMS m/z (ESI)** calcd for $[C_{15}H_{21}NO_3+H]^+$ 264.1594, found 264.1595.

Hexyl (4-hexanoylphenyl)carbamate (3r):

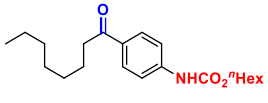


3r

The benzylic oxygenation of 0.3 mmol of hexyl (4-hexylphenyl)carbamate (**1r**, 91.6 mg) with CuI (5.7 mg, 0.03 mol) instead of CuOTf for 24 hours afforded 83.0 mg of **3r** (87%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 10:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 77.1-78.8 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.93 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.9 Hz, 2H), 7.29 (s, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 2.92 (t, *J* =7.4 Hz, 2H), 1.77-1.62 (m, 4H), 1.38-1.28 (m, 10H), 0.92-0.87 (m, 6H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 199.52, 153.34, 142.48, 131.78, 129.52, 117.55, 65.66, 38.25, 31.49, 31.34, 28.74, 25.41, 24.17, 22.45, 13.91, 13.88 ppm. **HRMS m/z (ESI)** calcd for $[C_{19}H_{29}NO_3+H]^+$ 320.2220, found 320.2218.

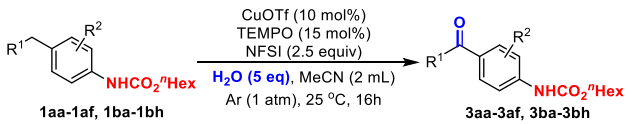
Hexyl (4-octanoylphenyl)carbamate (3s):



3s

The benzylic oxygenation of 0.3 mmol of hexyl (4-octylphenyl)carbamate (**1s**, 100.0 mg) with CuI (5.7 mg, 0.03 mol) instead of CuOTf for 24 hours afforded 86.8 mg of **3s** (83%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, *v*/*v*) as the eluent.

White soild, m.p. 90.6-92.2 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.93 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.22 (s, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 1.76-1.63 (m, 4H), 1.39-1.27 (m, 14H), 0.91-0.86 (m, 6H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 199.50, 153.32, 142.44, 131.82, 129.53, 117.55, 65.68, 38.31, 31.65, 31.36, 29.30, 29.09, 28.75, 25.43, 24.50, 22.55, 22.47, 14.01, 13.92 ppm. **HRMS m/z (ESI)** calcd for $[C_{21}H_{33}NO_3+H]^+$ 348.2533, found 348.2536.

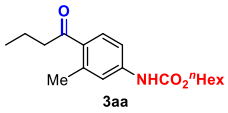


1aa-1af, 1ba-1bh　　3aa-3af, 3ba-3bh

Typical Procedure: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of substrates **1aa-1af** or **1ba-1bh** (0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and water (27 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4, and concentrated *in*

vacuo to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silical gel to afford corresponding phenone products **1aa-1af** or **1ba-1bh**.

Hexyl (4-butyryl-3-methylphenyl)carbamate (3aa):

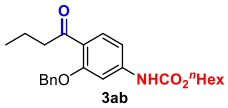


3aa

The benzylic oxygenation of 0.3 mmol of hexyl (4-butyl-3-methylphenyl)carbamate (**1aa**, 87.4 mg) afforded 69.8 mg of **3aa** (76%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 10:1, *v*/*v*) as the eluent.

Light orange soild, m.p. 51.8-52.7 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.68 (d, *J* = 8.5 Hz, 1H), 7.39 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.22 (d, *J* = 2.6 Hz, 1H), 6.98 (s, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 2.86 (t, *J* = 7.3 Hz, 2H), 2.51 (s, 3H), 1.77-1.63 (m, 4H), 1.39-1.29 (m, 6H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 202.88, 153.38, 140.69, 140.57, 132.27, 130.59, 121.06, 114.78, 65.62, 42.86, 31.38, 28.77, 25.45, 22.49, 21.96, 18.02, 13.94, 13.80 ppm. **HRMS m/z (ESI)** calcd for $[C_{18}H_{27}NO_3+H]^+$ 306.2064, found 306.2065.

Hexyl (3-(benzyloxy)-4-butyrylphenyl)carbamate (3ab):

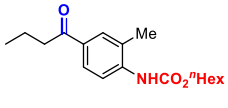


3ab

The benzylic oxygenation of 0.3 mmol of hexyl (3-(benzyloxy)-4-butylphenyl) carbamate (**1ab**, 115.0 mg) afforded 77.2 mg of **3ab** (65%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 83.1-85.3 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.01 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.79-7.73 (m, 1H), 7.61-7.57 (m, 1H), 7.45-7.36 (m, 4H), 7.10 (s, 1H), 6.76 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.13 (s, 2H), 4.16 (t, *J* = 6.7 Hz, 2H), 2.90 (t, *J* = 7.5 Hz, 2H), 1.70-1.57 (m, 4H), 1.41-1.30 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H), 0.81 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 201.23, 159.16, 153.36, 143.14, 135.82, 131.69, 129.76, 129.42, 128.55, 127.88, 123.02, 110.16, 102.06, 70.67, 65.67, 45.88, 31.36, 28.75, 25.43, 22.48, 17.96, 13.95, 13.69 ppm. **HRMS m/z (ESI)** calcd for $[C_{24}H_{31}NO_4+Na]^+$ 420.2145, found 420.2138.

Hexyl (4-butyryl-2-methylphenyl)carbamate (3ac):



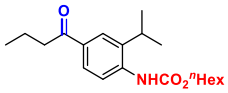
3ac

The benzylic oxygenation of 0.3 mmol of hexyl (4-butyl-2-methylphenyl)carbamate (**1ac**, 87.4 mg) with CuI (5.7 mg, 0.03 mol) instead of CuOTf for 24 hours afforded

67.6 mg of **3ac** (74%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 10:1, *v*/*v*) as the eluent.

Light orange soild, m.p. 50.8-53.6 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.08 (d, *J* = 8.5 Hz, 1H), 7.82 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.79 (d, *J* = 2.1 Hz, 1H), 6.62 (s, 1H), 4.19 (t, *J* = 6.8 Hz, 2H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 1.80-1.66 (m, 4H), 1.43-1.31 (m, 6H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 199.52, 153.33, 140.50, 131.88, 130.24, 127.62, 125.41, 118.49, 65.83, 40.23, 31.40, 28.78, 25.47, 22.51, 17.92, 17.61, 13.97, 13.88 ppm. **HRMS m/z (ESI)** calcd for $[C_{18}H_{27}NO_3+H]^+$ 306.2064, found 306.2061.

Hexyl (4-butyryl-2-isopropylphenyl)carbamate (3ad):

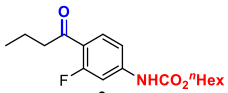


3ad

The benzylic oxygenation of 0.3 mmol of hexyl (4-butyl-2-isopropylphenyl) carbamate (**1ad**, 95.8 mg) for 24 hours afforded 67.2 mg of **3ad** (67%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (20:1 to 15:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 60.4-63.6 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.01 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 2.1 Hz, 1H), 7.80 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.77 (s, 1H), 4.18 (t, *J* = 6.8 Hz, 2H), 3.01 (hept, *J* = 6.8 Hz, 1H), 2.92 (t, *J* = 7.3 Hz, 2H), 1.81-1.65 (m, 4H), 1.43-1.32 (m, 6H), 1.30 (d, *J* = 6.8 Hz, 6H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 199.59, 153.68, 138.96, 136.72, 132.54, 127.01, 125.37, 120.13, 65.76, 40.20, 31.37, 28.75, 27.60, 25.43, 22.59, 22.47, 17.86, 13.93, 13.85 ppm. **HRMS m/z (ESI)** calcd for $[C_{17}H_{24}FNO_3+H]^+$ 334.2377, found 334.2376.

Hexyl (4-butyryl-3-fluorophenyl)carbamate (3ae):



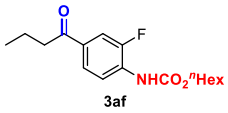
3ae

The benzylic oxygenation of 0.3 mmol of hexyl (4-butyl-3-fluorophenyl)carbamate (**1ae**, 88.6 mg) at 50 °C afforded 81.4 mg of **3ae** (88%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1 to 20:1, *v*/*v*) as the eluent.

White soild, m.p. 100.4-102.1 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.84 (t, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 13.6 Hz, 2.1 Hz, 1H), 7.23 (s, 1H), 7.05 (dd, *J* = 8.6 Hz, 2.1 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 2.93 (td, *J* = 7.3, 3.2 Hz, 2H), 1.78-1.63 (m, 4H), 1.41-1.25 (m, 6H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 197.63 (d, *J* = 4.7 Hz), 162.98 (d, *J* = 252.4 Hz), 153.09, 143.91 (d, *J* = 12.3 Hz), 131.51 (d, *J* = 4.2 Hz), 120.11 (d, *J* = 13.4 Hz), 113.59, 105.63 (d, *J* = 30.2 Hz), 65.94,

45.23 (d, *J* = 7.2 Hz), 31.35, 28.71, 25.42, 22.48, 17.45 (d, *J* = 2.2 Hz), 13.93, 13.76 ppm. **HRMS m/z (ESI)** calcd for $[C_{17}H_{24}FNO_3+Na]^+$ 332.1632, found 332.1629.

Hexyl (4-butyryl-2-fluorophenyl)carbamate (3af):

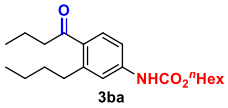


3af

The benzylic oxygenation of 0.3 mmol of hexyl (4-butyl-2-fluorophenyl)carbamate (**1af**, 88.6 mg) at 50 °C afforded 63.3 mg of **3af** (68%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, *v*/*v*) as the eluent.

White soild, m.p. 64.2-67.8 °C. **^{1}H NMR (DMSO-*d*$_6$, 400 MHz):** δ = 9.67 (s, 1H), 7.91 (t, *J* = 8.2 Hz, 1H), 7.75 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 7.69 (dd, *J* = 11.8, 1.9 Hz, 1H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.91 (t, *J* = 7.2, 2H), 1.60-1.54 (m, 4H), 1.32-1.22 (m, 6H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.83 (t, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR (DMSO-*d*$_6$, 100 MHz):** δ = 198.00, 153.68, 152.54 (d, *J* = 245.2 Hz), 132.48 (d, *J* = 5.3 Hz), 131.19 (d, *J* = 11.4 Hz), 124.66 (d, *J* = 3.1 Hz), 121.77, 114.72 (d, *J* = 20.12 Hz), 64.91, 39.56, 30.92, 28.40, 24.99, 22.06, 17.25, 13.89, 13.59 ppm. **HRMS m/z (ESI)** calcd for $[C_{17}H_{24}FNO_3+Na]^+$ 332.1632, found 332.1635.

Hexyl (3-butyl-4-butyrylphenyl)carbamate (3ba):

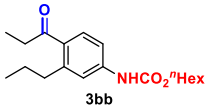


3ba

The benzylic oxygenation of 0.3 mmol of hexyl (3,4-dibutylphenyl)carbamate (**1ba**, 100.0 mg) afforded 94.4 mg of **3ba** (91%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1 to 20:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 60.2-61.8 °C. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.61 (d, *J* = 8.5 Hz, 1H), 7.35 (dd, *J* = 8.5 Hz, 2.2 Hz, 1H), 7.24 (d, *J* = 2.3 Hz, 1H), 6.92 (s, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 2.86-2.81 (m, 4H), 1.76-1.65 (m, 4H), 1.53 (p, *J* = 7.7 Hz, 2H), 1.41-1.29 (m, 8H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.92-0.88 (m, 6H) ppm. **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 203.37, 153.40, 145.09, 140.49, 132.66, 130.32, 120.25, 114.81, 65.60, 43.37, 33.96, 33.86, 31.39, 28.79, 25.47, 22.76, 22.50, 18.01, 13.94, 13.81 ppm. **HRMS m/z (ESI)** calcd for $[C_{21}H_{33}NO_3+H]^+$ 348.2533, found 348.2536.

Hexyl (4-propionyl-3-propylphenyl)carbamate (3bb):

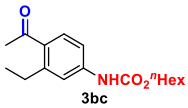


3bb

The benzylic oxygenation of 0.3 mmol of hexyl (3,4-dipropylphenyl)carbamate (**1bb**, 91.6 mg) afforded 69.2 mg of **3bb** (72%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (20:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 47.2-49.3 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.63 (d, *J* = 8.6 Hz, 1H), 7.37 (dd, *J* = 8.5 Hz, 2.2 Hz, 1H), 7.23 (d, *J* = 2.3 Hz, 1H), 6.94 (s, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 2.90 (q, *J* = 7.3 Hz, 2H), 2.81 (t, *J* = 7.8 Hz, 2H), 1.67 (p, *J* = 7.1 Hz, 2H), 1.57 (sext, *J* = 7.7 Hz, 2H), 1.42-1.29 (m, 6H), 1.18 (t, *J* = 7.3 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 203.66, 153.41, 144.89, 140.51, 132.37, 130.30, 120.33, 114.87, 65.61, 36.28, 34.45, 31.38, 28.78, 25.46, 24.73, 22.49, 14.11, 13.94, 8.56 ppm. **HRMS m/z (ESI)** calcd for $[C_{19}H_{29}NO_3+H]^+$ 320.2220, found 320.2218.

Hexyl (4-acetyl-3-ethylphenyl)carbamate (3bc):

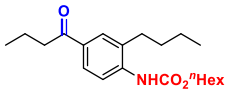


3bc

The benzylic oxygenation of 0.3 mmol of hexyl (3,4-diethylphenyl)carbamate (**1bc**, 83.2 mg) afforded 61.4 mg of **3bc** (70%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (20:1, *v*/*v*) as the eluent.

White soild, m.p. 58.3-60.4 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.70 (d, *J* = 8.6 Hz, 1H), 7.40 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.25 (d, *J* = 2.3 Hz, 1H), 7.01 (s, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 2.92 (q, *J* = 7.4 Hz, 2H), 2.56 (s, 3H), 1.67 (p, *J* = 7.1 Hz, 2H), 1.42-1.29 (m, 6H), 1.20 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 200.20, 153.37, 147.01, 141.17, 131.71, 131.58, 119.60, 114.76, 65.64, 31.38, 29.39, 28.78, 27.56, 25.46, 22.49, 15.58, 13.95 ppm. **HRMS m/z (ESI)** calcd for $[C_{17}H_{25}NO_3+H]^+$ 292.1907, found 292.1906.

Hexyl (2-butyl-4-butyrylphenyl)carbamate (3bd):

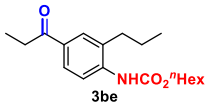


3bd

The benzylic oxygenation of 0.3 mmol of hexyl (2,4-dibutylphenyl)carbamate (**1bd**, 100.0 mg) for 24 hours afforded 76.4 mg of **3bd** (73%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1 to 20:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 66.3-68.6 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.06 (d, *J* = 8.5 Hz, 1H), 7.81 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.78 (d, *J* = 2.0 Hz, 1H), 6.70 (s, 1H), 4.19 (t, *J* = 6.8 Hz, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 2.60 (t, *J* = 7.8 Hz, 2H), 1.81-1.57 (m, 6H), 1.46-1.30 (m, 8H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 200.20, 153.37, 147.01, 141.17, 131.71, 131.58, 119.60, 114.76, 65.64, 31.38, 29.39, 28.78, 27.56, 25.46, 22.49, 15.58, 13.95 ppm. **HRMS m/z (ESI)** calcd for $[C_{21}H_{33}NO_3+H]^+$ 348.2533, found 348.2529.

Hexyl (4-propionyl-2-propylphenyl)carbamate (3be):

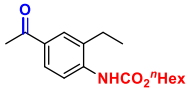


3be

The benzylic oxygenation of 0.3 mmol of hexyl (2,4-dipropylphenyl)carbamate (**1be**, 91.6 mg) afforded 61.5 mg of **3be** (64%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 69.4-71.3 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.06 (d, *J* = 8.5 Hz, 1H), 7.82 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.79 (d, *J* = 2.1 Hz, 1H), 6.66 (s, 1H), 4.19 (t, *J* = 6.8 Hz, 2H), 2.97 (q, *J* = 7.3 Hz, 2H), 2.58 (t, *J* = 7.7 Hz, 2H), 1.73-1.64 (m, 4H), 1.43-1.31 (m, 6H), 1.21 (t, *J* = 7.3 Hz, 3H), 1.01 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.0, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 200.00, 153.49, 139.92, 131.86, 130.05, 129.32, 127.38, 119.28, 65.84, 33.13, 31.50, 31.41, 28.79, 25.47, 22.51, 22.36, 13.97, 13.89, 8.37 ppm. **HRMS m/z (ESI)** calcd for $[C_{19}H_{29}NO_3+H]^+$ 320.2220, found 320.2217.

Hexyl (4-acetyl-2-ethylphenyl)carbamate (3bf):

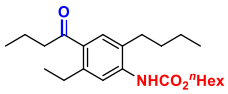


3bf

The benzylic oxygenation of 0.3 mmol of hexyl (2,4-diethylphenyl)carbamate (**1bf**, 83.2 mg) afforded 54.4 mg of **3bf** (62%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 74.8-77.9 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.09 (d, *J* = 9.1 Hz, 1H), 7.83-7.80 (m, 2H), 6.72 (s, 1H), 4.19 (t, *J* = 6.8 Hz, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.57 (s, 3H), 1.69 (p, *J* = 7.1 Hz, 2H), 1.43-1.27 (m, 9H), 0.90 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 197.30, 153.43, 140.07, 135.80, 132.19, 131.34, 128.43, 127.86, 119.02, 65.82, 31.38, 28.75, 26.36, 25.44, 24.00, 22.48, 13.95, 13.39 ppm. **HRMS m/z (ESI)** calcd for $[C_{17}H_{25}NO_3+H]^+$ 292.1907, found 292.1906.

Hexyl (2-butyl-4-butyryl-5-ethylphenyl)carbamate (3bg):



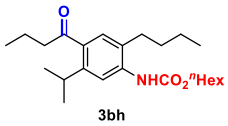
3bg

The benzylic oxygenation of 0.3 mmol of hexyl (2,4-dibutyl-5-ethylphenyl) carbamate (**1bg**, 108.4 mg) afforded 67.3 mg of **3bg** (60%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (20:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 36.2-37.6 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.86 (s, 1H), 7.38 (s, 1H), 6.54 (s, 1H), 4.18 (t, *J* = 6.8 Hz, 2H), 2.86-2.80 (m, 4H), 2.56 (t, *J* = 7.8 Hz, 2H), 1.77-1.66 (m, 4H), 1.58 (p, *J* = 7.6 Hz, 2H), 1.46-1.32 (m, 8H), 1.21 (t, *J* = 7.5 Hz, 4H), 1.00-0.95 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H) ppm.**^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 203.88, 153.68, 143.60, 137.98, 133.33, 129.95, 127.74, 121.91,

65.71, 43.52, 31.58, 31.41, 30.53, 28.81, 27.00, 25.49, 22.51, 22.46, 17.92, 15.89, 13.96, 13.86, 13.83 ppm. **HRMS m/z (ESI)** calcd for $[C_{23}H_{37}NO_3+H]^+$ 376.2846, found 376.2846.

Hexyl (2-butyl-4-butyryl-5-isopropylphenyl)carbamate (3bh):



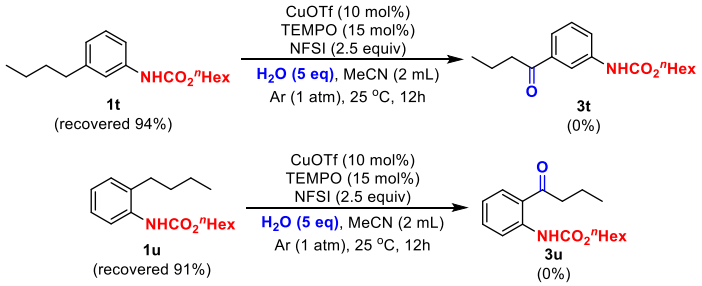
3bh

The benzylic oxygenation of 0.3 mmol of hexyl (2,4-dibutyl-5-isopropylphenyl) carbamate (**1bh**, 112.6 mg) afforded 79.2 mg of **3bh** (68%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (20:1, *v*/*v*) as the eluent.

Light yellow soild, m.p. 44.9-46.5 °C. **^{1}H NMR (CDCl3, 400 MHz):** δ = 7.97 (s, 1H), 7.24 (s, 1H), 6.54 (s, 1H), 4.19 (t, *J* = 6.8 Hz, 2H), 3.40 (hept, *J* = 6.8 Hz, 1H), 2.81 (t, *J* = 7.3 Hz, 2H), 2.55 (t, *J* = 7.8 Hz, 2H), 1.77-1.66 (m, 4H), 1.58 (p, *J* = 7.6 Hz, 2H), 1.46-1.30 (m, 8H), 1.24 (d, *J* = 6.8 Hz, 6H), 1.00-0.95 (m, 6H), 0.90 (t, *J* = 7.0 Hz, 3H) ppm.**^{13}C NMR (CDCl3, 100 MHz):** δ = 205.46, 153.82, 147.14, 137.79, 134.34, 128.71, 127.92, 118.59, 65.70, 44.45, 31.56, 31.41, 30.51, 29.26, 28.82, 25.50, 24.09, 22.51, 22.48, 17.92, 13.96, 13.86, 13.78 ppm. **HRMS m/z (ESI)** calcd for $[C_{24}H_{39}NO_3+H]^+$ 390.3003, found 390.2999.

Significance of the Carbamate Directing Group

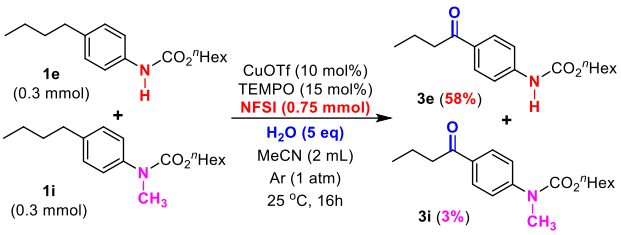
(1) Significance of the position of the directing group (Scheme 2a)



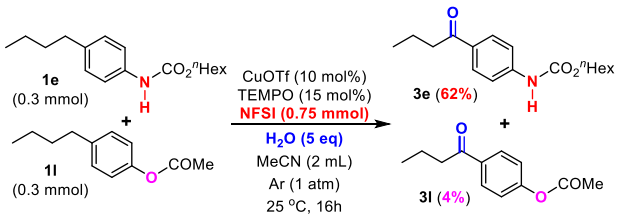
Typical Procedure for Reaction of 1t: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of **1t** (83.1 mg, 0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and water (27 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo* to give dark residue. ^{1}H-NMR of this residue suggested no oxygenated product **3t** was generated, and 77.8 mg of **1t** (94%) could be recovered from this residue via flash chromatography using petroleum ether and ethyl acetate as the eluent (25:1 to 20:1, *v*/*v*) on silical gel.

Typical Procedure for Reaction of 1u: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of **1u** (83.1 mg, 0.3 mmol) and TEMPO (7.0 mg, 0.045 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo* to give dark residue. ^{1}H-NMR of this residue suggested no oxygenated product **3u** was generated, and 75.4 mg of **1u** (91%) could be recovered from this residue via flash chromatography using petroleum ether and ethyl acetate as the eluent (25:1 to 15:1, *v*/*v*) on silical gel.

(2) Significance of the free N-H bond in the directing group (Scheme 2b)

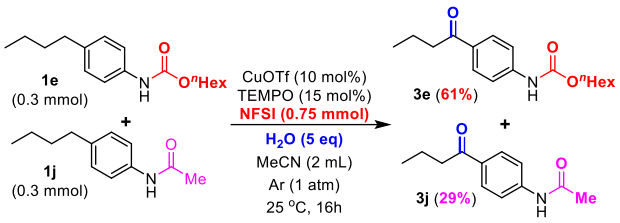


Typical Procedure for Competitive Experiment of 1e and 1i: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of **1e** (83.1 mg, 0.3 mmol), **1i** (87.4 mg, 0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and water (27 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (15:1 to 10:1, *v*/*v*) on silical gel, affording 53 mg of the mixture of **3e** and **3i**. ^{1}H-NMR analysis of this mixture suggested the ratio of **3e** to **3i** was 96:4, and the amounts of **3e** and **3i** in this mixture were calculated accordingly as 0.1744 mmol (50.8 mg, 58 %) and 0.0073 mmol (2.2 mg, 3 %), respectively.



Typical Procedure for Competitive Experiment of 1e and 1l: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of **1e** (83.1 mg, 0.3 mmol), **1l** (57.6 mg, 0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and water (27 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was analyzed by ^{1}H-NMR using dibromomethane (CH_2Br_2) as an internal standard to determine the yields of **3e** and **3l** as 62% and 4%, respectively.

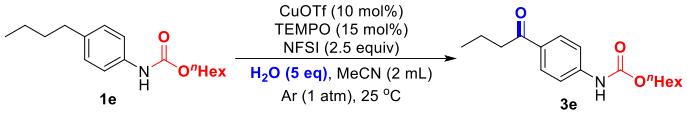
(3) Preference on carbamate over amide as the directing group (Scheme 2c)



Typical Procedure for Competitive Experiment of 1e and 1j: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of **1e** (83.1 mg, 0.3 mmol), **1j** (57.3 mg, 0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and water (27 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was analyzed by ^{1}H-NMR using dibromomethane (CH_2Br_2) as an internal standard to determine the yields of **3e** and **3j** as 61% and 29%, respectively.

Kinetic Studies

(1) Kinetic profiles for conversion from 1e to 2e under synergistic catalysis (Figure 1)



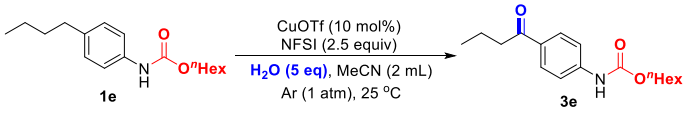
Typical Procedure: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of **1e** (83.1 mg, 0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and water (27 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for designated time as shown in Table S1.

Table S1. Detailed Results for Coversion from 1e to 3e under Synergistic Catalysis

Time (h)	1	2	3	4	6	8	10	12	14	16
Recovery of 1e	90.3	77.8	71.2	59.9	43.7	30.8	18.4	10.3	6.8	3.2
Yield of 3e	2.3	5.6	10.6	28.1	50.6	66.7	76.4	87.1	89.6	91.0

After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then analyzed with ^{1}H-NMR to determine the recoveries of **1e** and the yield of **3e** as summarized in Table S1, using dibromomethane (CH_2Br_2) as an internal standard.

(2) Kinetic profiles for conversion from 1e to 2e under copper catalysis without TEMPO (Figure 1)



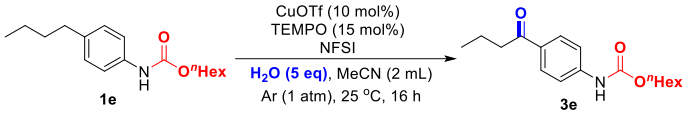
Typical Procedure: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of **1e** (83.1 mg, 0.3 mmol) and water (27 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for designated time as shown in Table S2.

Table S2. Detailed Results for Coversion from 1e to 3e under Copper Catalysis without TEMPO

Time (h)	1	2	3	4	6	8	10	12	14	16
Recovery of 1e	94.0	85.8	81.3	77.9	63.8	48.2	39.3	34.9	27.8	24.1
Yield of 3e	0	2.1	3.4	4.9	7.7	8.3	10.3	12.3	13.5	15.9

After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then analyzed with ^{1}H-NMR to determine the recoveries of **1e** and the yield of **3e** as summarized in Table S2, using dibromomethane (CH_2Br_2) as an internal standard.

(3) Influence of the loading of NFSI under synergistic catalysis (Figure 2)



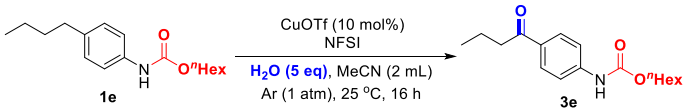
Typical Procedure: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and designated amount of NFSI as shown in Table S3 was added a solution of **1e** (83.1 mg, 0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and water (27 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours.

Table S3. Influence of the loading of NFSI under Synergistic Catalysis

NFSI (equiv)	**0.5**	**1**	**1.5**	**2**
Recovery of 1e	80.6	58.3	42.2	18.9
Yield of 3e	12.8	33.4	49.1	71.2

After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then analyzed with ^{1}H-NMR to determine the recoveries of **1e** and the yield of **3e** as summarized in Table S3, using dibromomethane (CH_2Br_2) as an internal standard.

(4) Influence of the loading of NFSI under copper catalysis without TEMPO (Figure 2)



Typical Procedure: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and designated amount of NFSI as shown in Table S3 was added a solution of **1e** (83.1 mg, 0.3 mmol) and water (27 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours.

After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then analyzed with ^{1}H-NMR to determine the recoveries of **1e** and the yield of **3e** as summarized in Table S4, using dibromomethane

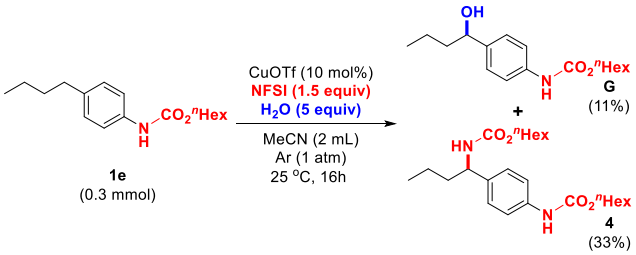
(CH_2Br_2) as an internal standard.

Table S4. Influence of the loading of NFSI under Copper Catalysis without TEMPO

NFSI (equiv)	**0.5**	**1**	**1.5**	**2**
Recovery of 1e	63.8	48.1	40.5	30.0
Yield of 3e	5.2	7.8	10.6	15.1

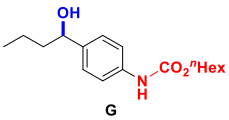
Control Experiments

(1) Byproducts from the reaction of 1e with an insufficient loading of NFSI in the absence of TEMPO (Scheme 3a)



Typical Procedure: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and NFSI (141.9 mg, 0.45 mmol) was added a solution of **1e** (83.1 mg, 0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and water (27 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (8:1 to 6:1, *v*/*v*) on silical gel, affording 9.8 mg of the benzylic hydroxylated product **G** (11%) and 21.1 mg of the benzyl carbamate **4** (33 %, calculated based on the theoretical yield of **4** as 0.15 mmol).

Hexyl (4-(1-hydroxybutyl)phenyl)carbamate (G):



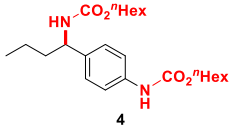
G

Light yellow soild, m.p. 53.6-54.9 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.35 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.69 (s, 1H), 4.63 (t, *J* = 6.7 Hz, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 1.95 (s, 1H), 1.82-1.62 (m, 4H), 1.43-1.29 (m, 8H), 0.93-0.88 (m, 6H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 153.76, 139.85, 137.21, 126.62, 118.62, 73.94, 65.42, 41.07, 31.41, 28.85, 25.49, 22.51, 18.97, 13.97, 13.91 ppm. **HRMS *m/z* (ESI)** calcd for $[C_{17}H_{27}NO_3+Na]^+$ 316.1883, found 316.1879.

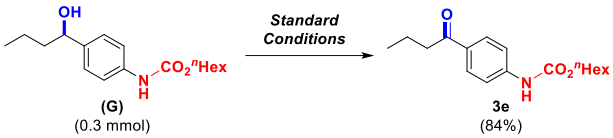
Hexyl (4-(1-(((hexyloxy)carbonyl)amino)butyl)phenyl)carbamate (4):

Light yellow soild, m.p. 101.6-104.3 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.34 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H) 6.94 (s, 1H), 5.07 (d, *J* = 8.2 Hz, 1H), 4.61 (d, *J* = 7.9 Hz, 1H), 4.14 (t, *J* = 6.8 Hz, 2H),

4.07-3.96 (m, 2H), 1.75-1.55 (m, 6H), 1.39-1.26 (m, 14H), 0.92-0.85 (m, 9H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 156.11, 153.80, 137.80, 137.03, 126.92, 118.74, 65.29, 64.96, 54.46, 38.71, 31.38, 28.89, 28.83, 25.44, 22.47, 19.31, 13.92, 13.69 ppm. **HRMS *m/z* (ESI)** calcd for $[C_{24}H_{40}N_2O_4+Na]^+$ 443.2880, found 443.2876.

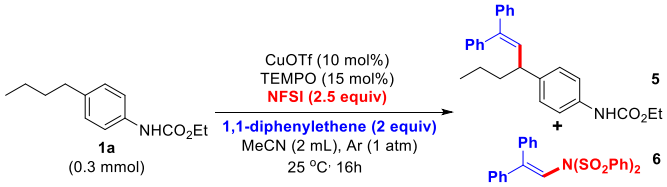


4



Typical Procedure: To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of alcohol **G** (87.9 mg, 0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and water (27 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silical gel to afford 73.6 mg of **3e** (84%).

(2) Radical trapping experiments with 1,1-diphenylethene (Scheme 3b)



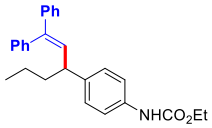
Typical Procedure (Scheme 3b, entry 1): To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of **1a** (66.3 mg, 0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and 1,1-diphenylethene (108.1 mg, 0.6 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (15:1 to 10:1, *v*/*v*) on silical gel, affording 29.6 mg of the benzyl alkene **5** (25%) and 62.4 mg of the imidyl alkene **6** (22 %, calculated based on the theoretical yield of **6** as 0.6 mmol).

Typical Procedure (Scheme 3b, entry 2): To a reaction tube charged with CuOTf (6.4 mg, 0.03 mmol)

and NFSI (236.5 mg, 0.75 mmol) was added a solution of **1a** (66.3 mg, 0.3 mmol) and 1,1-diphenylethene (108.1 mg, 0.6 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4 and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (15:1 to 10:1, *v*/*v*) on silical gel, affording 51.1 mg of the benzyl alkene **5** (43%) and 46.2 mg of the imidyl alkene **6** (16 %, calculated based on the theoretical yield of **6** as 0.6 mmol).

Typical Procedure (Scheme 3b, entry 3): To a reaction tube charged with NFSI (236.5 mg, 0.75 mmol) was added a solution of **1a** (66.3 mg, 0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and 1,1-diphenylethene (108.1 mg, 0.6 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 16 hours, and only trace amount of the imidyl alkene **6** could be observed on TLC while no benzyl alkene **5** was generated.

Ethyl (4-(1,1-diphenylhex-1-en-3-yl)phenyl)carbamate (5):



5

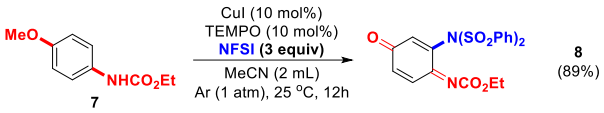
Light yellow oil. **^{1}H NMR (DMSO-*d*$_6$, 400 MHz)**: δ = 7.40-7.31 (m, 6H), 7.33-7.11 (m, 6H), 7.04-7.02 (m, 4H), 6.24 (d, *J* = 10.4 Hz, 1H), 4.06 (q, *J* = 10.6 Hz, 2H), 3.19 (dt, *J* = 10.2 Hz, 7.0 Hz, 1H), 1.66-1.52 (m, 2H), 1.21-1.17 (m, 5H), 0.70 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (DMSO-*d*$_6$, 100 MHz)**: δ = 153.58, 141.75, 139.84, 139.57, 138.83, 137.16, 133.17, 129.37, 128.37, 128.23, 127.31, 127.16, 127.01, 126.74, 118.54, 60.02, 43.99, 38.94, 20.15, 14.52, 13.71 ppm. **HRMS *m/z* (ESI)** calcd for $[C_{27}H_{29}NO_2+H]^+$ 400.2271, found 400.2276.

***N*-(2,2-Diphenylvinyl)-*N*-(phenylsulfonyl)benzenesulfonamide (6):**

6

Light yellow soild, m.p. 145.1-146.7 °C. **^{1}H NMR (CDCl$_3$, 400 MHz)**: δ = 7.70-7.68 (m, 4H), 7.54-7.52 (m, 2H), 7.39-7.19 (m, 14H), 6.13 (s, 1H) ppm. **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ = 152.44, 139.95, 138.72, 136.89, 134.01, 130.03, 129.29, 128.96, 128.86, 128.79, 128.55, 128.44, 128.34, 116.40 ppm. **HRMS *m/z* (ESI)** calcd for $[C_{26}H_{21}NO_4S_2+Na]^+$ 498.0804, found 498.0804.

(3) Oxidative dearomatization under similar synergistic catalysed conditions (Scheme 3c)



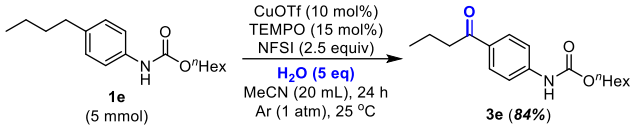
Typical Procedure (Scheme 3c): To a reaction tube charged with CuI (5.7 mg, 0.03 mmol) and NFSI (283.8 mg, 0.9 mmol) was added a solution of **7** (58.5 mg, 0.3 mmol) and TEMPO (4.7 mg, 0.03 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 12 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (6:1 to 3:1, *v*/*v*) on silical gel, affording 126.3 mg of the dearomative imidation product **8** (89 %).

Ethyl (4-oxo-2-(*N*-(phenylsulfonyl)phenylsulfonamido)cyclohexa-2,5-dien-1-ylidene)carbamate (8):

Yellow soild, m.p. 52.5-53.6 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 8.03 (d, *J* = 7.6 Hz, 4H), 7.69 (t, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 4H), 6.95 (d, *J* = 10.2 Hz, 1H), 6.65 (dd, *J* = 10.2 Hz, 2.0 Hz, 1H), 6.53 (d, *J* = 2.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 185.69, 160.55, 154.91, 142.66, 138.40, 137.67, 134.43, 134.27, 130.52, 129.21, 128.96, 63.54, 14.35 ppm. **HRMS *m/z* (ESI)** calcd for $[C_{21}H_{18}N_2O_7S_2+Na]^+$ 497.0448, found 497.0447.

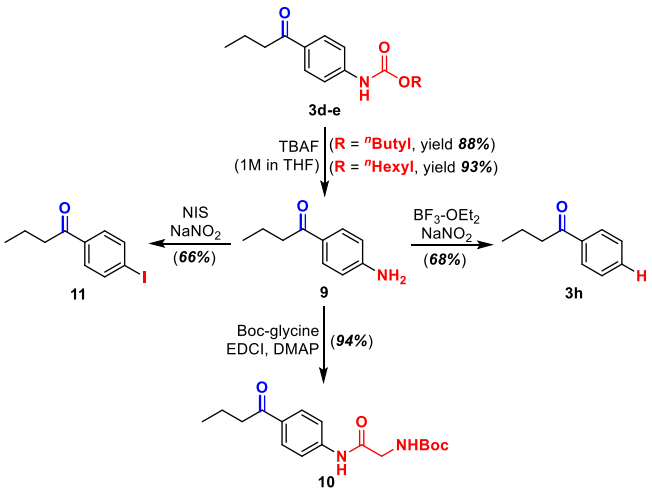
Application Potentials

(1) Gram-scale synthesis (Scheme 5a)



Typical Procedure: To a reaction tube charged with CuOTf (106.3 mg, 0.5 mmol) and NFSI (3.94 g, 12.5 mmol) was added a solution of **1e** (1.39 g, 5 mmol), TEMPO (117.2 mg, 0.75 mmol) and water (450 μl, 25 mmol) in anhydrous MeCN (20 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 24 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (6:1, *v*/*v*) on silical gel, affording 1.22 g of the oxygenated product **3e** (84%).

(2) The convertible carbamate directing group (Scheme 5b)

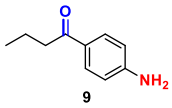


Typical Procedure for Deprotection of 3d: To a reaction tube charged with **3d** (263.2 mg, 1 mmol) was added a solution of TBAF (1M in THF, 5 mmol, 5 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 65 °C for 18 hours. After cooling to room temperature, the mixture was extracted with ethyl acetate. The combined organic phase was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (6:1, *v*/*v*) on silical gel, affording 142.8 mg of the aniline

product **9** (88%).

Typical Procedure for Deprotection of 3e: To a reaction tube charged with **3e** (291.2 mg, 1 mmol) was added a solution of TBAF (1M in THF, 5 mmol, 5 mL) in 1,4-dioxane (6 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 80 °C for 18 hours. After cooling to room temperature, the mixture was extracted with ethyl acetate. The combined organic phase was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (6:1, *v*/*v*) on silical gel, affording 151.4 mg of the aniline product **9** (93%).

1-(4-Aminophenyl)butan-1-one (9) [5]**:**

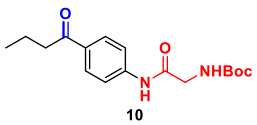


9

Light yellow soild, m.p. 90.2-91.5 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.81 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 4.22 (s, 2H), 2.84 (t, *J* = 7.4 Hz, 2H), 1.74 (sext, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 198.87, 151.05, 130.43, 127.43, 113.63, 39.83, 18.16, 13.91 ppm. **GC-MS *m/z* (EI)** calcd for [$C_{10}H_{13}NO$] 163.1, found 163.0.

Typical Procedure for Acylation of 9 with Amino Acid: To a reaction tube charged with DCM (1.5 mL) was successively added Boc-glycine (52.6 mg, 0.3 mmol), DMAP (91.6 mg, 0.75 mmol) and EDCI-HCl (86.3 mg, 0.45 mmol) at 0 °C. After stirring for 15 minutes, a solution of **9** (48.9 mg, 0.3 mmol) in DCM (0.5 mL) was added at 0 °C. Then the reaction mixture was stirred at room temperature for 12 hours and was extracted with DCM. The combined organic phase was washed with saturated NH_4Cl (aq.) and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (3:1, *v*/*v*) on silical gel, affording 89.9 mg of the amide **10** (94%).

***Tert*-Butyl (2-((4-butyrylphenyl)amino)-2-oxoethyl)carbamate (10):**

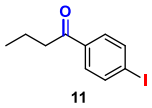


10

White soild, m.p. 85.1-87.3 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 9.12 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 5.77 (t, *J* = 5.8 Hz, 1H), 4.01 (d, *J* = 5.8 Hz, 1H), 2.89 (t, *J* = 7.3 Hz, 2H), 1.74 (sext, *J* = 7.4 Hz, 2H), 1.46 (s, 9H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 199.38, 168.44, 156.68, 141.83, 132.70, 129.27, 119.05, 80.63, 45.25, 40.21, 28.20, 17.77, 13.79 ppm. **HRMS *m/z* (ESI)** calcd for $[C_{17}H_{24}N_2O_4+Na]^+$ 343.1628, found 343.1627.

Typical Procedure for Deaminative Iodination of 9: To a reaction tube charged with DMF (1.5 mL) was successively added **9** (81.6 mg, 0.5 mmol) and $NaNO_2$ (86.3 mg, 1.25 mmol) at 0 °C. After stirring for 5 minutes, a solution of NIS (225.0 mg, 1 mmol) in DMF (0.5 mL) was added at 0 °C. Then the reaction mixture was stirred at room temperature for 12 hours and was extracted with ethyl acetate. The combined organic phase was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (15:1, *v*/*v*) on silical gel, affording 90.1 mg of the iodinated product **11** (66%).

1-(4-Iodophenyl)butan-1-one (11) [6]**:**

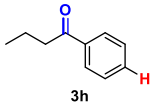


11

Light yellow soild, m.p. 62.4-64.8 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.82 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 1.76 (sext, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 199.62, 137.83, 136.27, 129.46, 100.74, 40.37, 17.61, 13.80 ppm. **GC-MS *m/z* (EI)** calcd for [$C_{10}H_{11}IO$] 273.99, found 273.9.

Typical Procedure for Deamination of 9: To a reaction tube charged with DMF (1.5 mL) was successively added **9** (81.6 mg, 0.5 mmol) and $NaNO_2$ (51.8 mg, 0.75 mmol) at 0 °C. After stirring for 5 minutes, a solution of BF_3-Et_2O (295.6 mg, 1 mmol) in DMF (0.5 mL) was added at 0 °C. Then the reaction mixture was stirred at room temperature for 4 hours and was extracted with ethyl acetate. The combined organic phase was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (15:1, *v*/*v*) on silical gel, affording 50.6 mg of the iodinated product **3h** (68%).

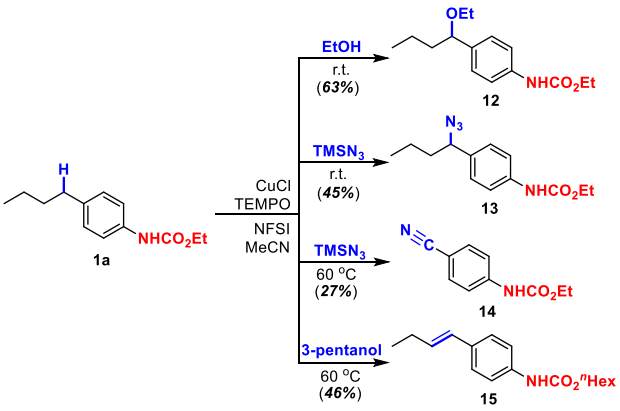
1-Phenylbutan-1-one (3h) [2]**:**



3h

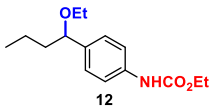
Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.97-7.95 (m, 2H), 7.57-7.53 (m, 1H), 7.47-7.44 (m, 2H), 2.95 (t, *J* = 7.3 Hz, 2H), 1.77 (sext, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 200.41, 137.04, 132.83, 128.50, 127.99, 40.46, 17.71, 13.84 ppm. **GC-MS *m/z* (EI)** calcd for [$C_{10}H_{12}O$] 148.1, found 148.1.

(3) Other benzylic functionalizations under development in our lab (Scheme 5c)



Typical Procedure for Benzylic C-H Alkoxylation of 1a: To a reaction tube charged with CuCl (3.0 mg, 0.03 mmol) and NFSI (283.8 mg, 0.9 mmol) was added a solution of **1a** (66.3 mg, 0.3 mmol), TEMPO (4.7 mg, 0.03 mmol) and EtOH (132 μl, 2.25 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 20 °C for 12 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (10:1, *v*/*v*) on silical gel, affording 49.7 mg of the iodinated product **12** (63%).

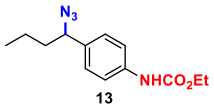
Ethyl (4-(1-ethoxybutyl)phenyl)carbamate (12):



White solid, m.p. 74.6-75.9 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.35 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.78 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.16 (t, *J* = 6.8 Hz, 1H), 3.39-3.26 (m, 2H), 1.82-1.73 (m, 1H), 1.60-1.53 (m, 1H), 1.43-1.21 (m, 4H), 1.15 (t, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 153.70, 138.18, 137.03, 127.24, 118.59, 81.40, 63.83, 61.13, 40.32, 19.00, 15.26, 14.49, 13.88 ppm. **HRMS *m/z* (ESI)** calcd for $[C_{15}H_{23}NO_3\text{-}H]^-$ 264.1605, found 264.1599.

Typical Procedure for Benzylic C-H Azidation of 1a: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189.2 mg, 0.6 mmol) was added a solution of **1a** (66.3 mg, 0.3 mmol), TEMPO (7.0 mg, 0.045 mmol) and $TMSN_3$ (79 μl, 0.6 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 12 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (15:1 to 10:1, *v*/*v*) on silical gel, affording 35.1 mg of the iodinated product **13** (45%).

Ethyl (4-(1-azidobutyl)phenyl)carbamate (13):

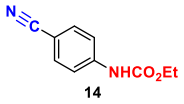


13

Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.40 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.83 (s, 1H), 4.37 (t, *J* = 7.3 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.85-1.76 (m, 1H), 1.73-1.64 (m, 1H), 1.43-1.29 (m, 5H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 153.59, 137.84, 134.59, 127.59, 118.73, 65.59, 61.24, 38.01, 19.38, 14.46, 13.60 ppm. **HRMS *m/z* (ESI)** calcd for $[C_{13}H_{18}N_4O_2+H]^+$ 263.1503, found 263.1496.

Typical Procedure for Benzylic Dealkylative Cyanation of 1a: To a reaction tube charged with CuCl (3.0 mg, 0.03 mmol) and NFSI (378.4 mg, 1.2 mmol) was added a solution of **1a** (66.3 mg, 0.3 mmol), TEMPO (2.3 mg, 0.015 mmol) and $TMSN_3$ (158 μl, 1.2 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 25 °C for 12 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (10:1 to 6:1, *v*/*v*) on silical gel, affording 15.2 mg of the iodinated product **14** (27%).

Ethyl (4-cyanophenyl)carbamate (14):

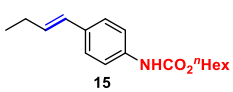


14

Light yellow solid, m.p. 93.5-94.9 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.59 (d, *J* = 8.9 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.00 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 191.03, 152.94, 142.20, 133.32, 118.19, 106.06, 61.80, 14.40 ppm. **HRMS *m/z* (ESI)** calcd for $[C_{10}H_{10}N_2O_2+H]^+$ 191.0815, found 191.0811.

Typical Procedure for Benzylic Dehydrogenation of 1e: To a reaction tube charged with CuCl (1.5 mg, 0.015 mmol) and NFSI (189.2 mg, 0.6 mmol) was added a solution of **1e** (83.1 mg, 0.3 mmol), TEMPO (4.7 mg, 0.03 mmol) and 3-pentanol (162 μl, 1.5 mmol) in anhydrous MeCN (2 mL) via a syringe under argon (1 atm). The reaction mixture was stirred at 60 °C for 12 hours. After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (15:1, *v*/*v*) on silical gel, affording 38.2 mg of the iodinated product **15** (46%).

Hexyl (*E*)-(4-(but-1-en-1-yl)phenyl)carbamate (15):



15

Light yellow solid, m.p. 56.6-59.3 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ = 7.32-7.26 (m, 4H), 6.63 (s, 1H), 6.32 (dt, *J* = 15.8 Hz, 1.5 Hz, 1H), 6.18 (dt, *J* = 15.8 Hz, 6.4 Hz, 1H), 4.15 (t, *J* = 7.2 Hz, 2H), 2.21 (p, *J* = 7.5 Hz, 2H), 1.69-1.62 (m, 2H), 1.40-1.29 (m, 6H), 1.08 (t, *J*

= 7.4 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ = 153.65, 136.57, 133.21, 131.53, 128.03, 126.46, 118.60, 65.38, 31.42, 28.86, 26.00, 25.50, 22.52, 13.98, 13.66 ppm. **HRMS *m/z* (ESI)** calcd for $[C_{17}H_{25}NO_2+H]^+$ 276.1958, found 276.1950.

References

[1] (a) Tran, V. H.; Kim, H.-K. *New. J. Chem.* **2019**, *43*, 14093-14101. (b) Shao, Z.; Wang, F.; Shi, J.; Ma, L.; Li, Z. *Org. Chem. Front.* **2021**, *8*, 3298-3307.

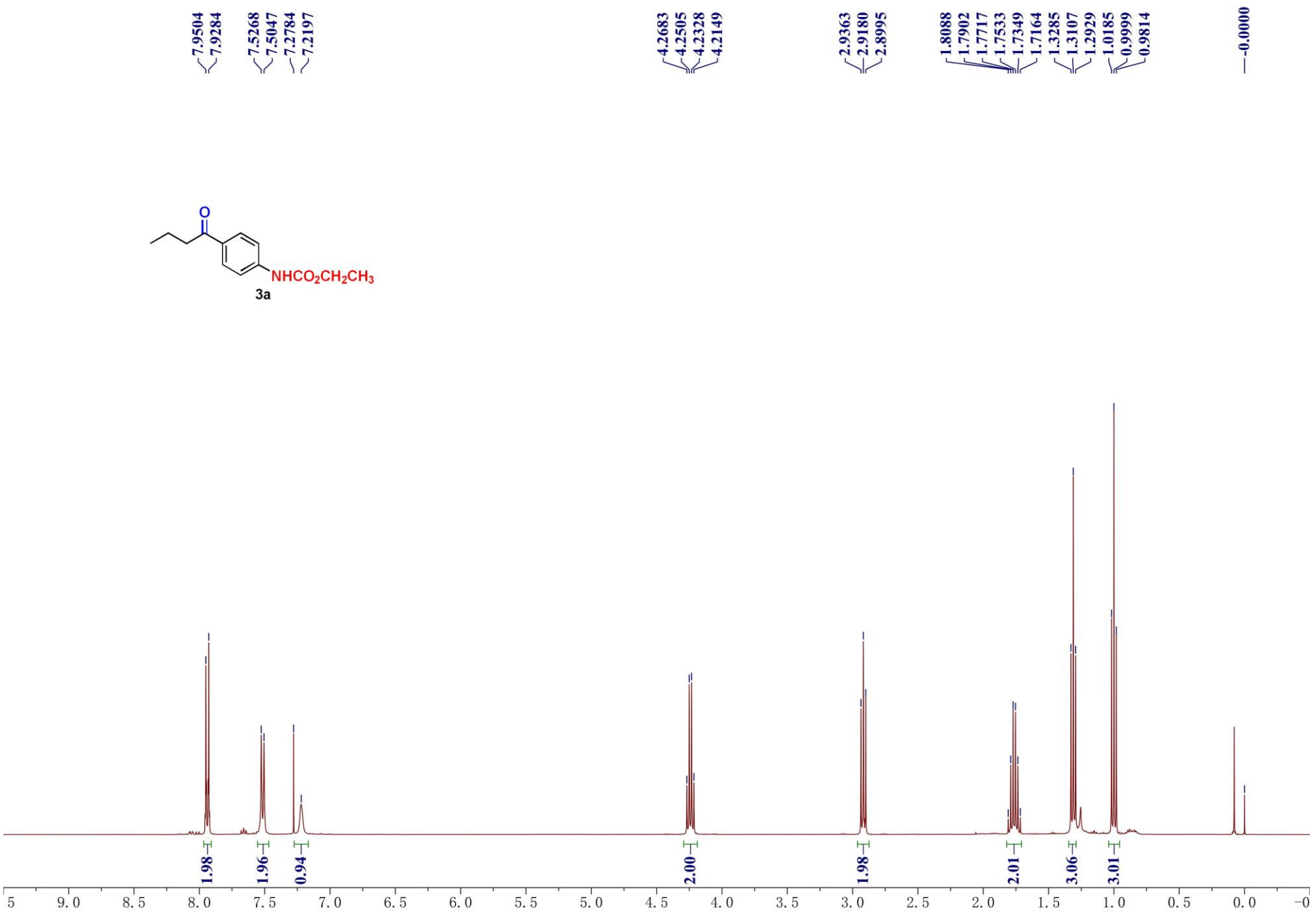
[2] Zhu, X.; Liu, Y.; Liu, C.; Yang, H.; Fu, H. *Green Chem.* **2020**, *22*, 4357-4363.

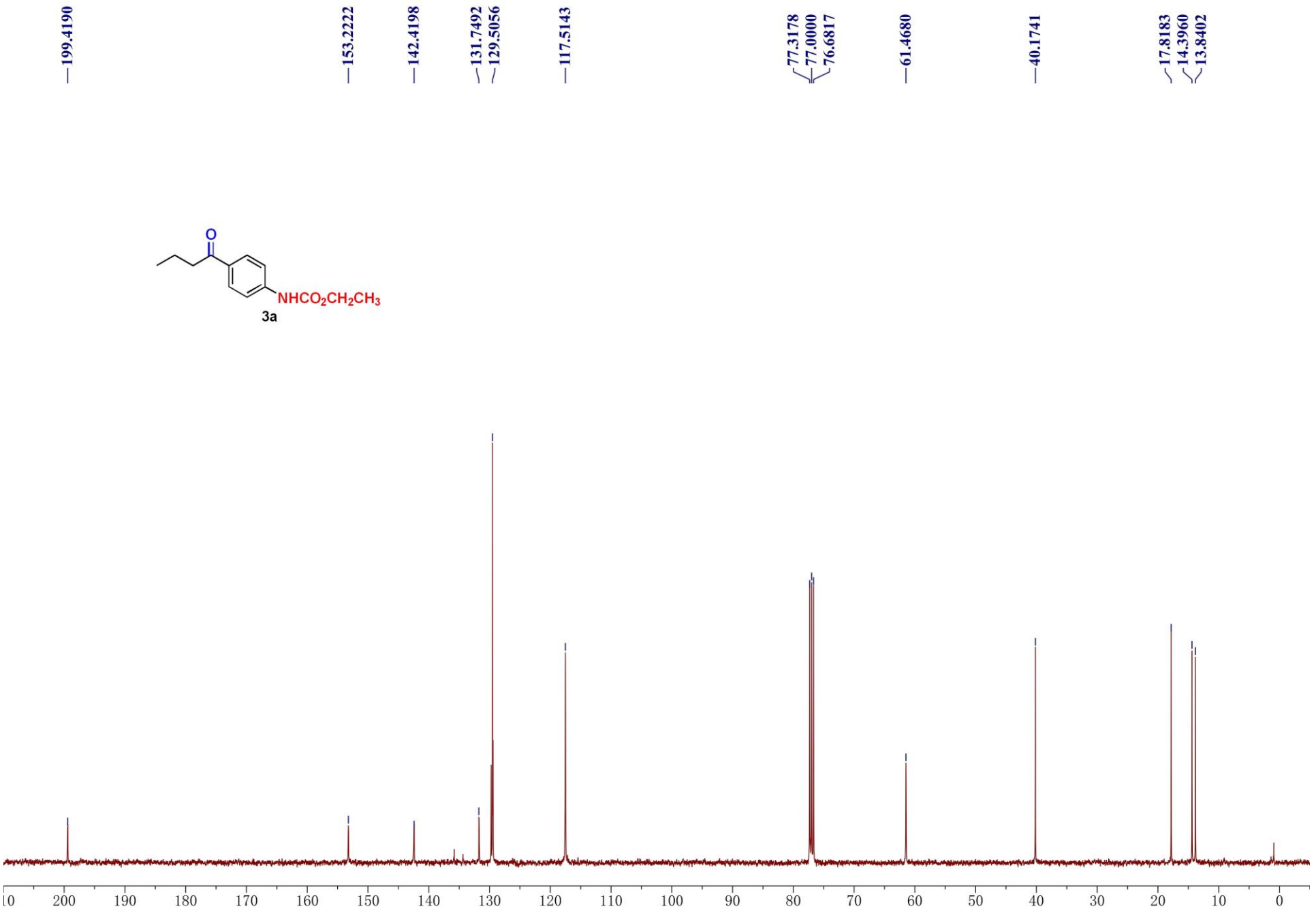
[3] Tran, P. H.; Hansen, P. E.; Hoang, H. M.; Chau, D.-K. N.; Le, T. N. *Tetrahedron Lett.* **2015**, *56*, 2187-2192.

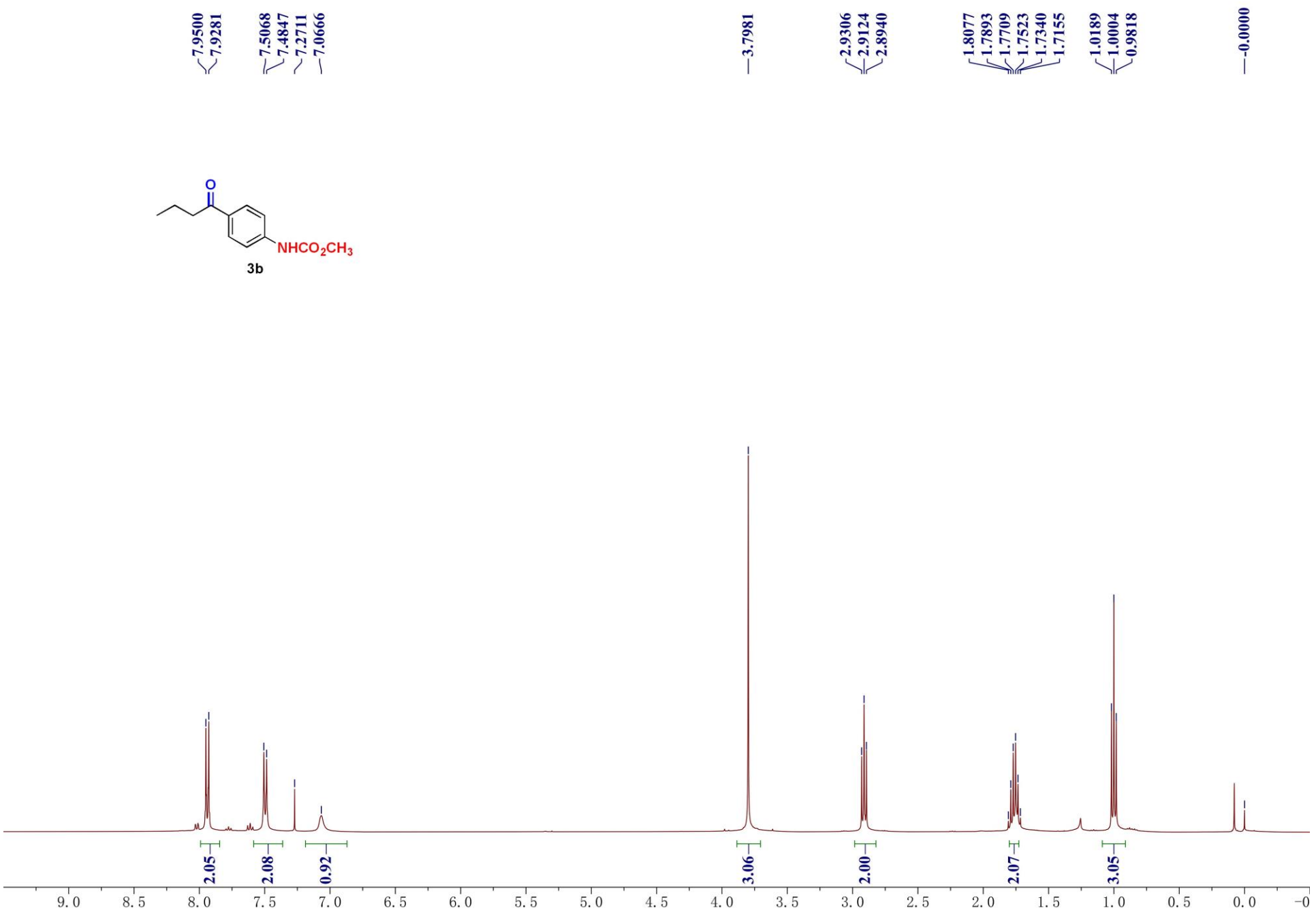
[4] (a) Baum, E. J.; Wan, J. K. S.; Pitts, Jr., J. N. *J. Am. Chem. Soc.* **1966**, *88*, 2652-2659. (b) Pitts, Jr., J. N.; Burley, D. R.; Mani, J. C.; Broadbent, A. D. *J. Am. Chem. Soc.* **1968**, *90*, 5902-5903.

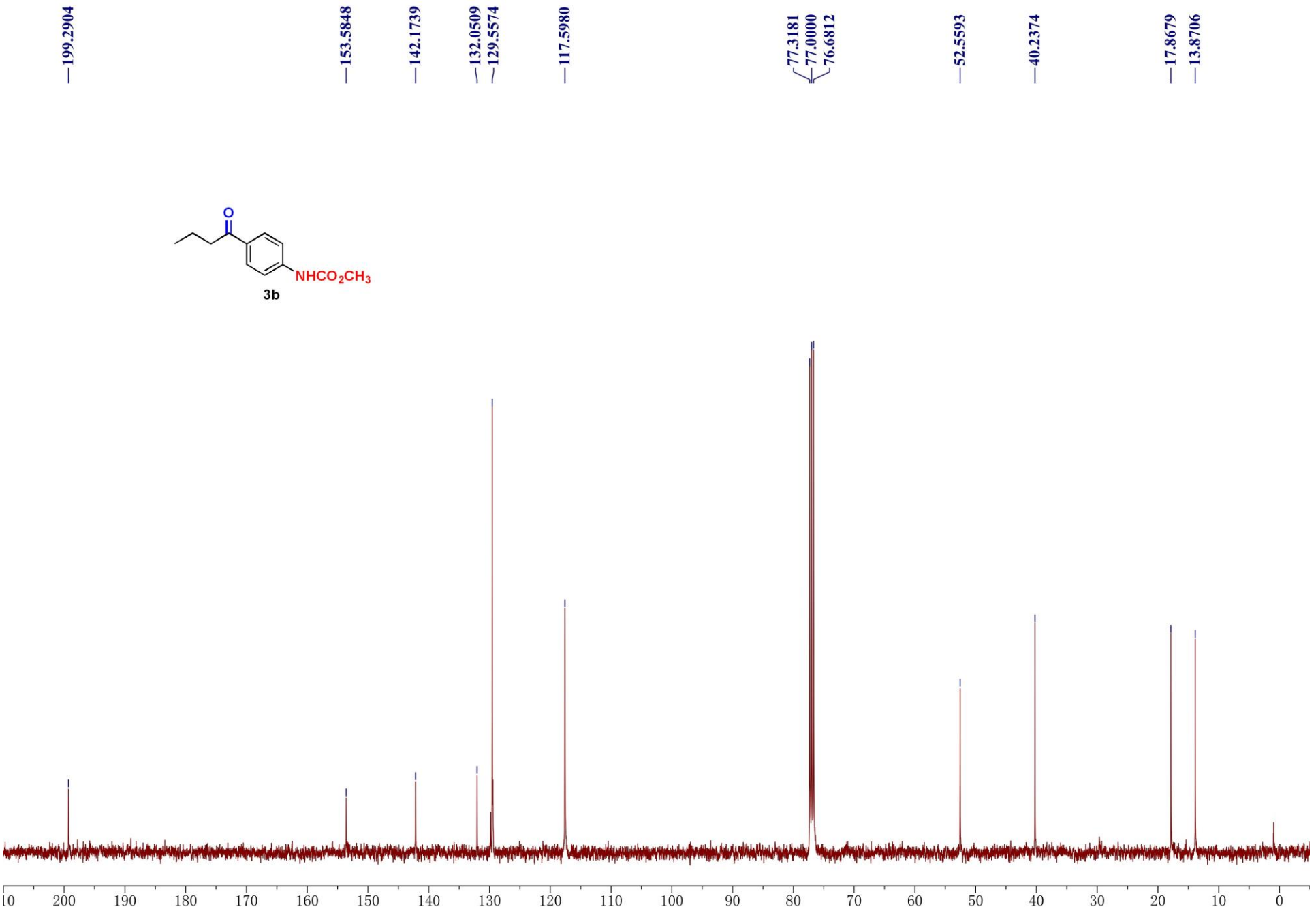
[5] Liu, Y.; Yao, B.; Deng, C.-L.; Tang, R.-Y.; Zhang, X.-G.; Li, J.-H. *Org. Lett.* **2011**, *13*, 2184-2187.

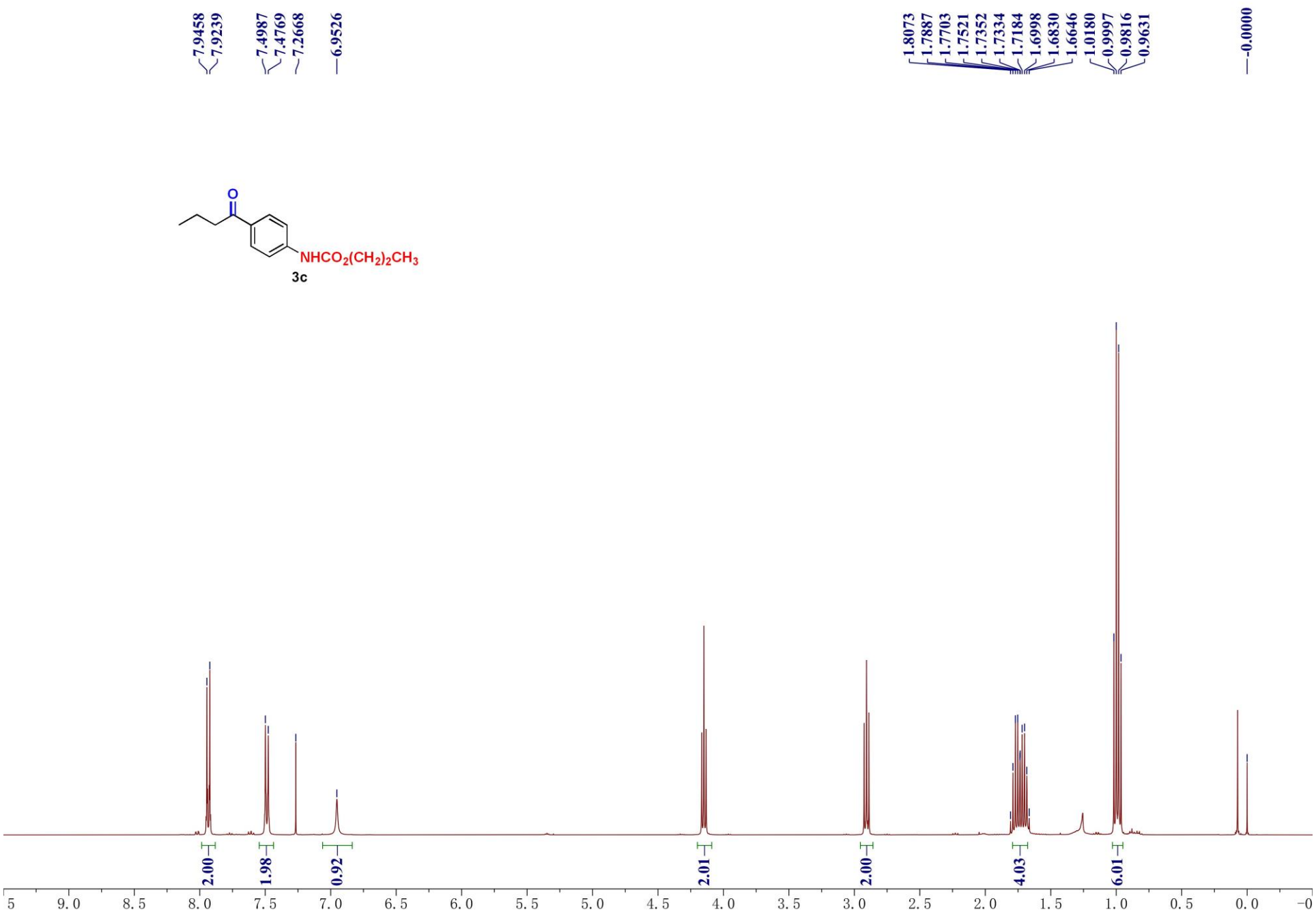
[6] Miyazawa, H.; Yokokura, H.; Ohkubo, Y.; Kondo, Y.; Yoshino, N. *J. Fluorine Chem.* **2005**, *126*, 301-306.

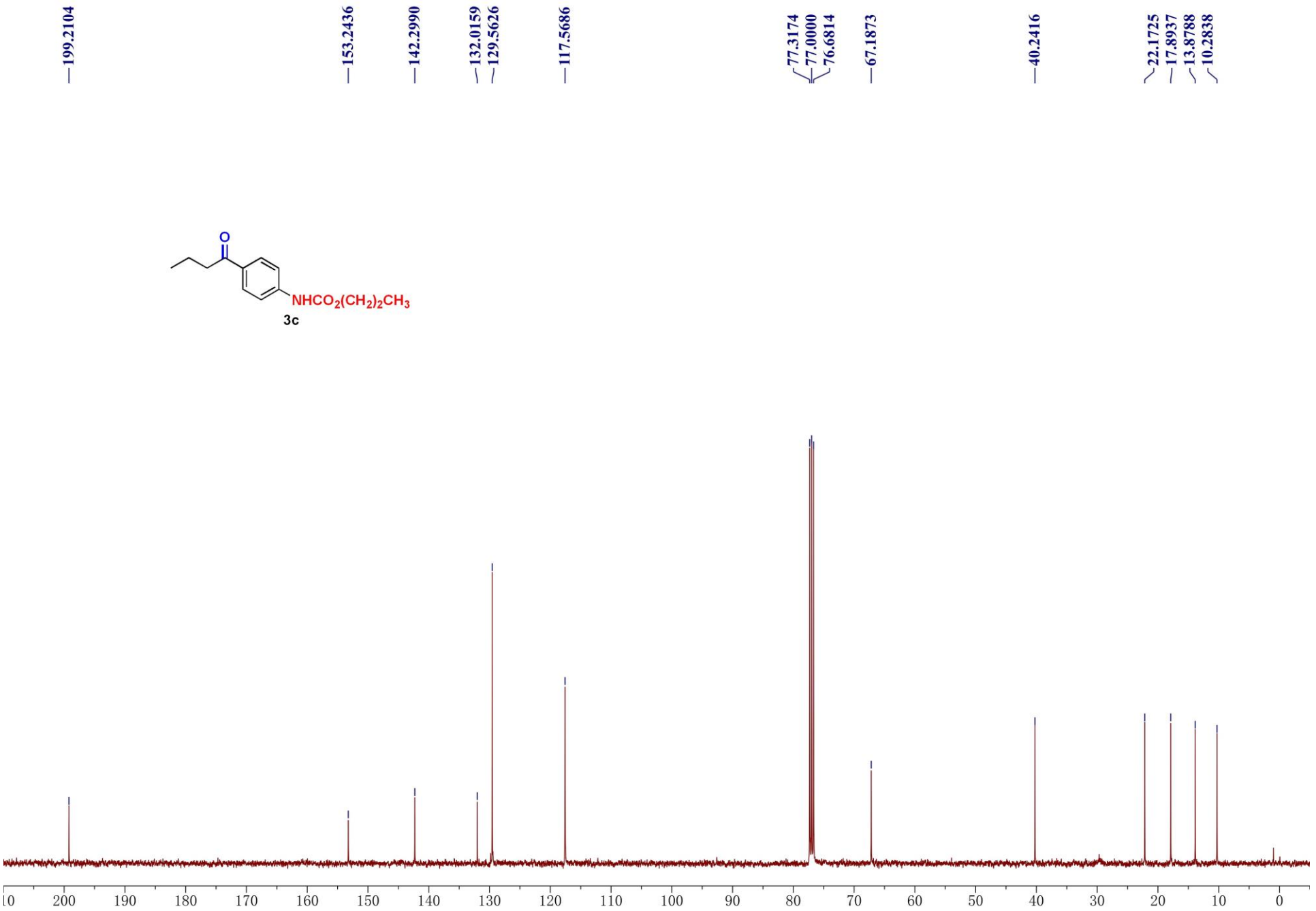

7.9504
7.9284
7.5268
7.5047
7.2784
7.2197
4.2683
4.2505
4.2328
4.2149
2.9363
2.9180
2.8995
1.8088
1.7902
1.7717
1.7533
1.7349
1.7164
1.3285
1.3107
1.2929
1.0185
0.9999
0.9814
-0.0000
O
NHCO2CH2CH3
3a
1.98
1.96
0.94
2.00
1.98
2.01
3.06
3.01
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

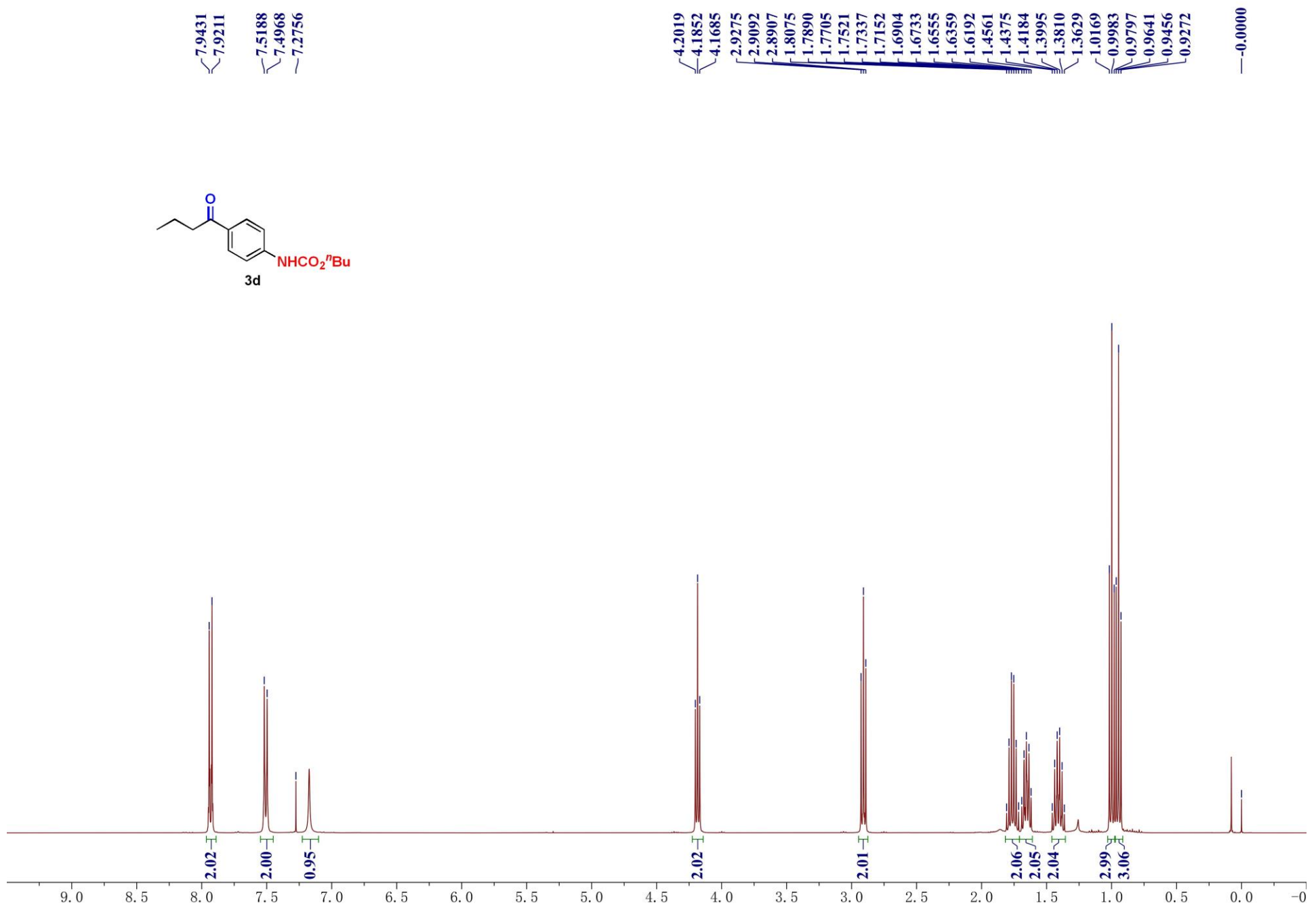

199.4190
153.2222
142.4198
131.7492
129.5056
117.5143
77.3178
77.0000
76.6817
61.4680
40.1741
17.8183
14.3960
13.8402
O
NHCO2CH2CH3
3a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

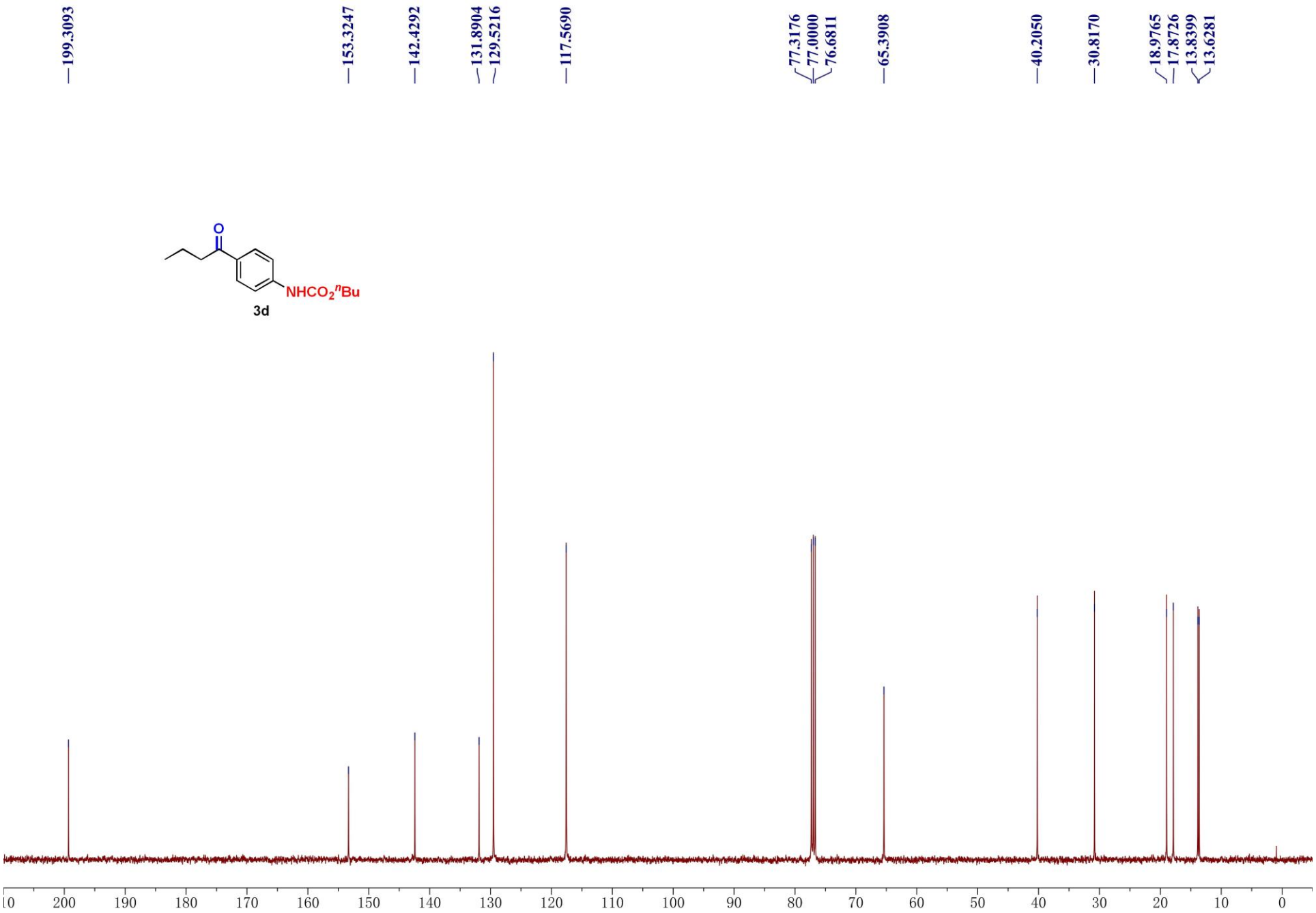

7.9500
7.9281
7.5068
7.4847
7.2711
7.0666
3.7981
2.9306
2.9124
2.8940
1.8077
1.7893
1.7709
1.7523
1.7340
1.7155
1.0189
1.0004
0.9818
-0.0000
O
NHCO2CH3
3b
2.05
2.08
0.92
3.06
2.00
2.07
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

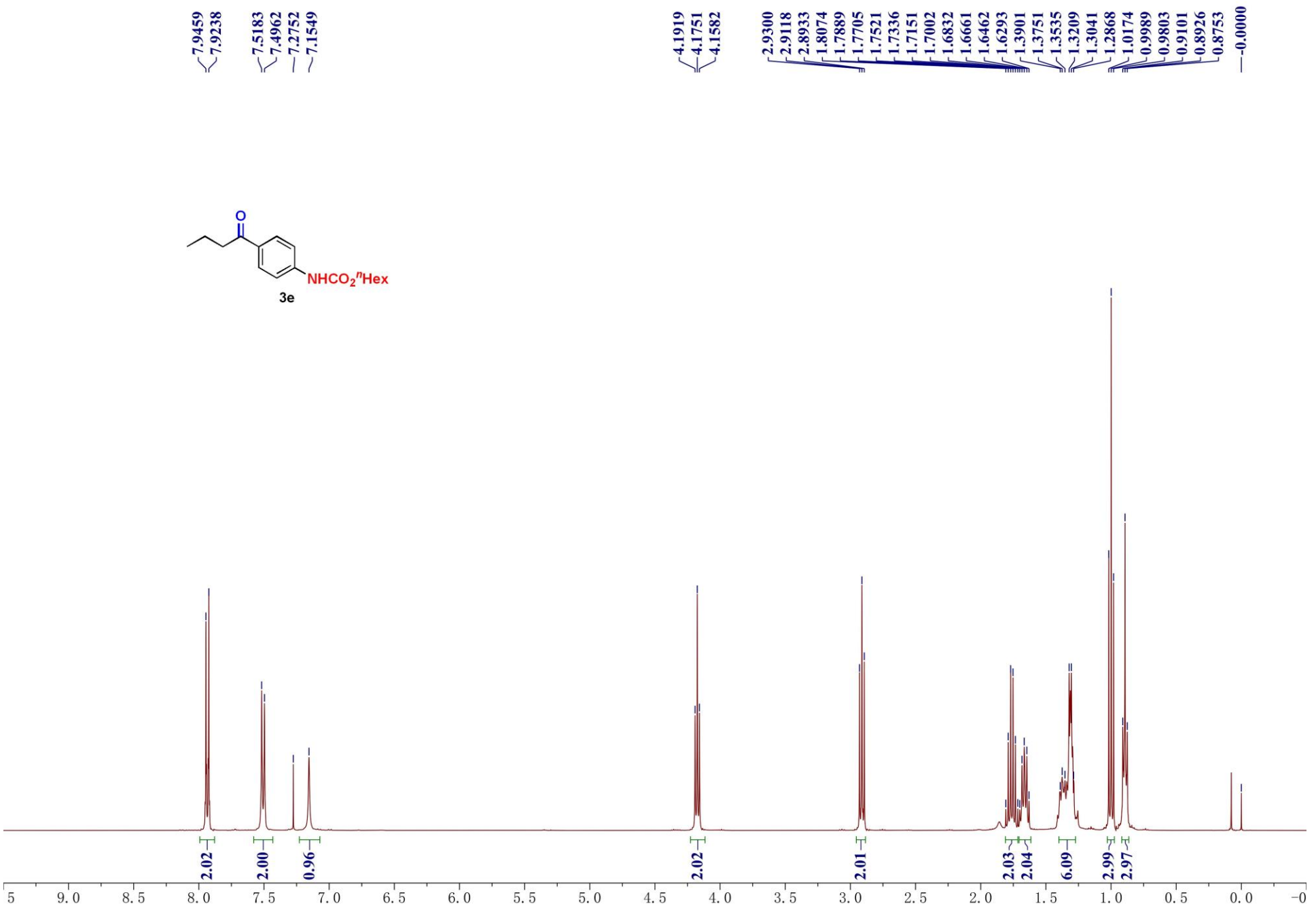

199.2904
153.5848
142.1739
132.0509
129.5574
117.5980
77.3181
77.0000
76.6812
52.5593
40.2374
17.8679
13.8706
O
NHCO2CH3
3b
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

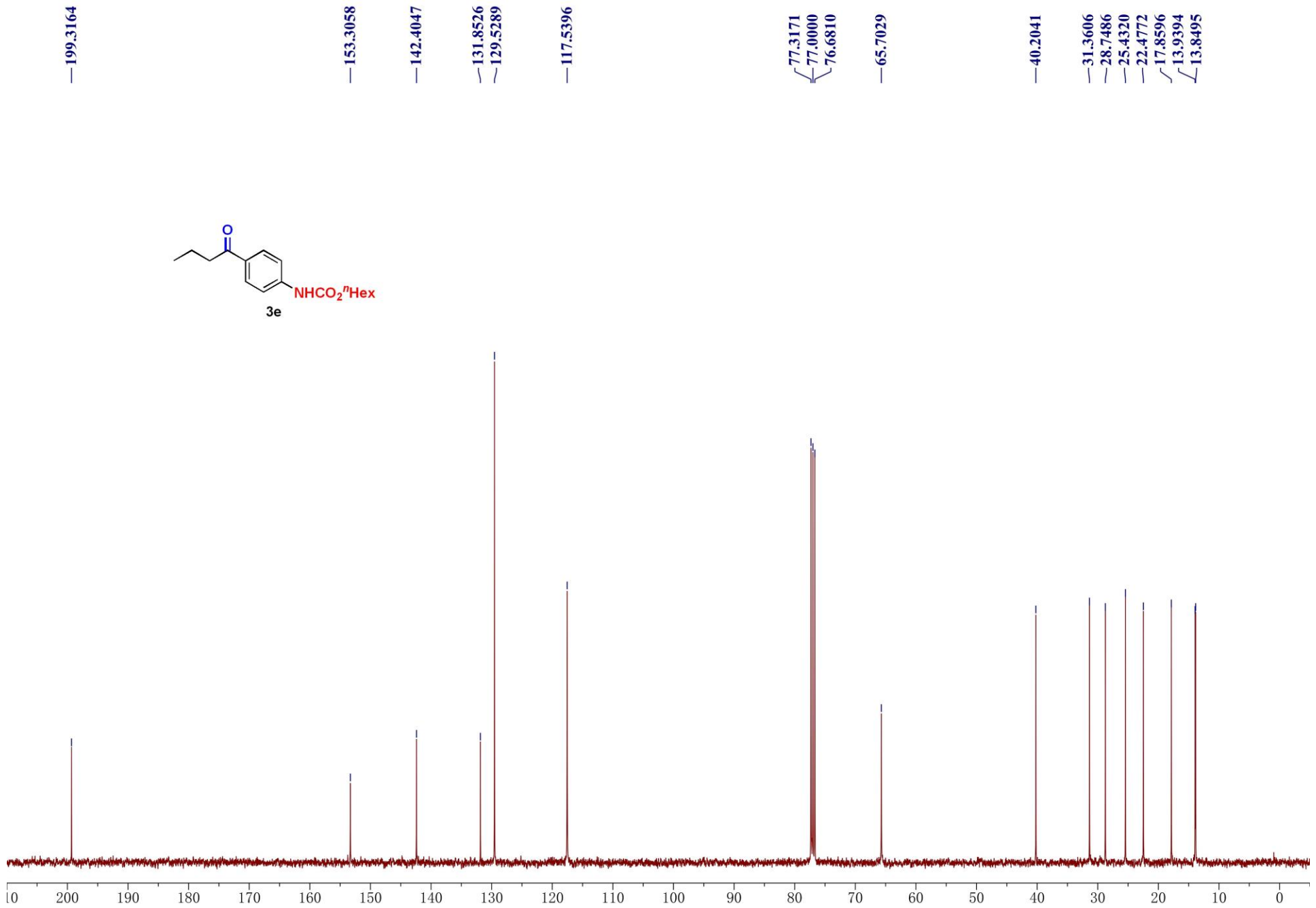

7.9458
7.9239
7.4987
7.4769
7.2668
6.9526
1.8073
1.7887
1.7703
1.7521
1.7352
1.7334
1.7184
1.6998
1.6830
1.6646
1.0180
0.9997
0.9816
0.9631
-0.0000
O
NHCO2(CH2)2CH3
3c
2.00
1.98
0.92
2.01
2.00
4.03
6.01
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

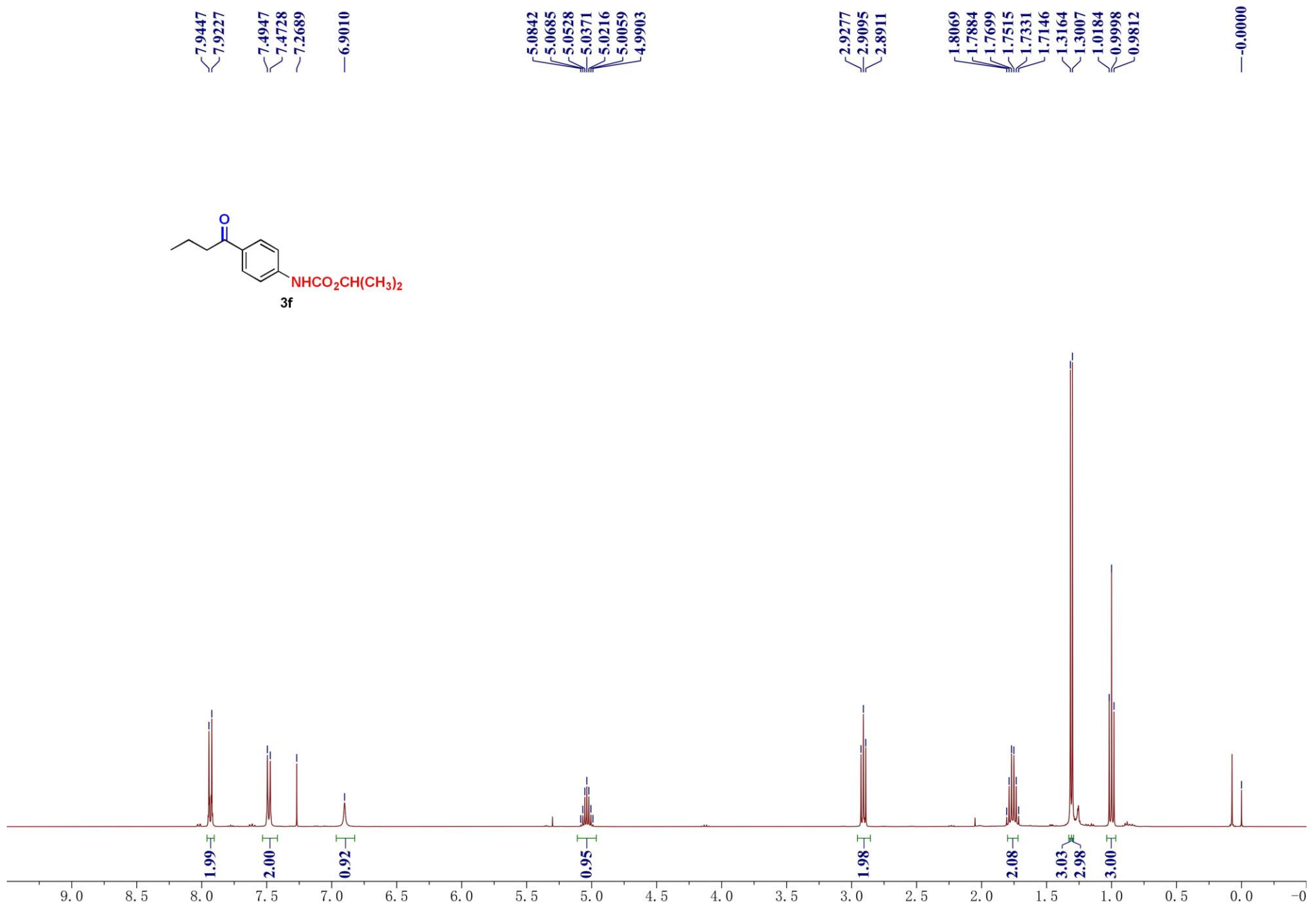

199.2104
153.2436
142.2990
132.0159
129.5626
117.5686
77.3174
77.0000
76.6814
67.1873
40.2416
22.1725
17.8937
13.8788
10.2838
O
NHCO2(CH2)2CH3
3c
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

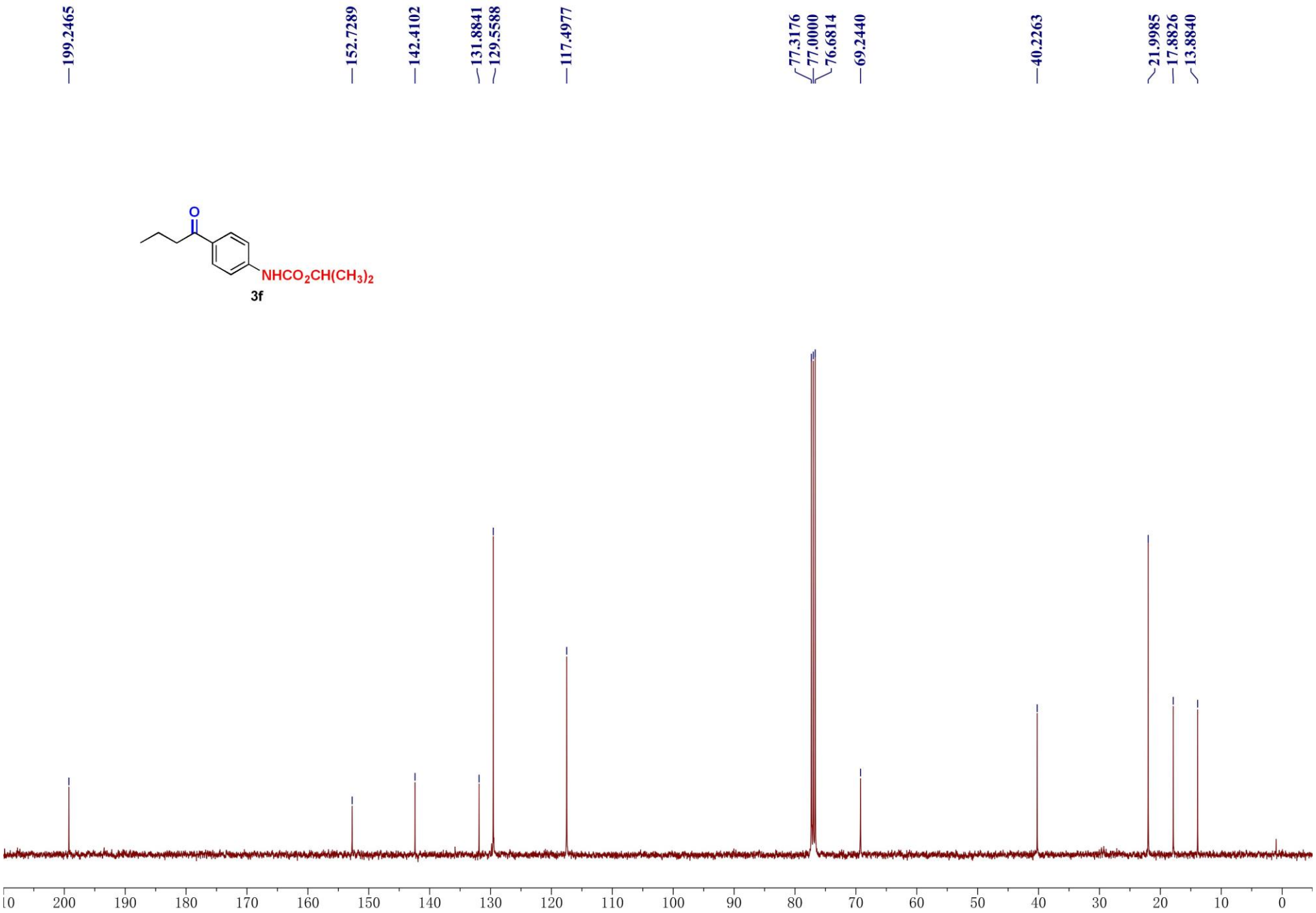

7.9431
7.9211
7.5188
7.4968
7.2756
4.2019
4.1852
4.1685
2.9275
2.9092
2.8907
1.8075
1.7890
1.7705
1.7521
1.7337
1.7152
1.6904
1.6733
1.6555
1.6359
1.6192
1.4561
1.4375
1.4184
1.3995
1.3810
1.3629
1.0169
0.9983
0.9797
0.9641
0.9456
0.9272
-0.0000
O
NHCO2nBu
3d
2.02
2.00
0.95
2.02
2.01
2.06
2.05
2.04
2.99
3.06
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

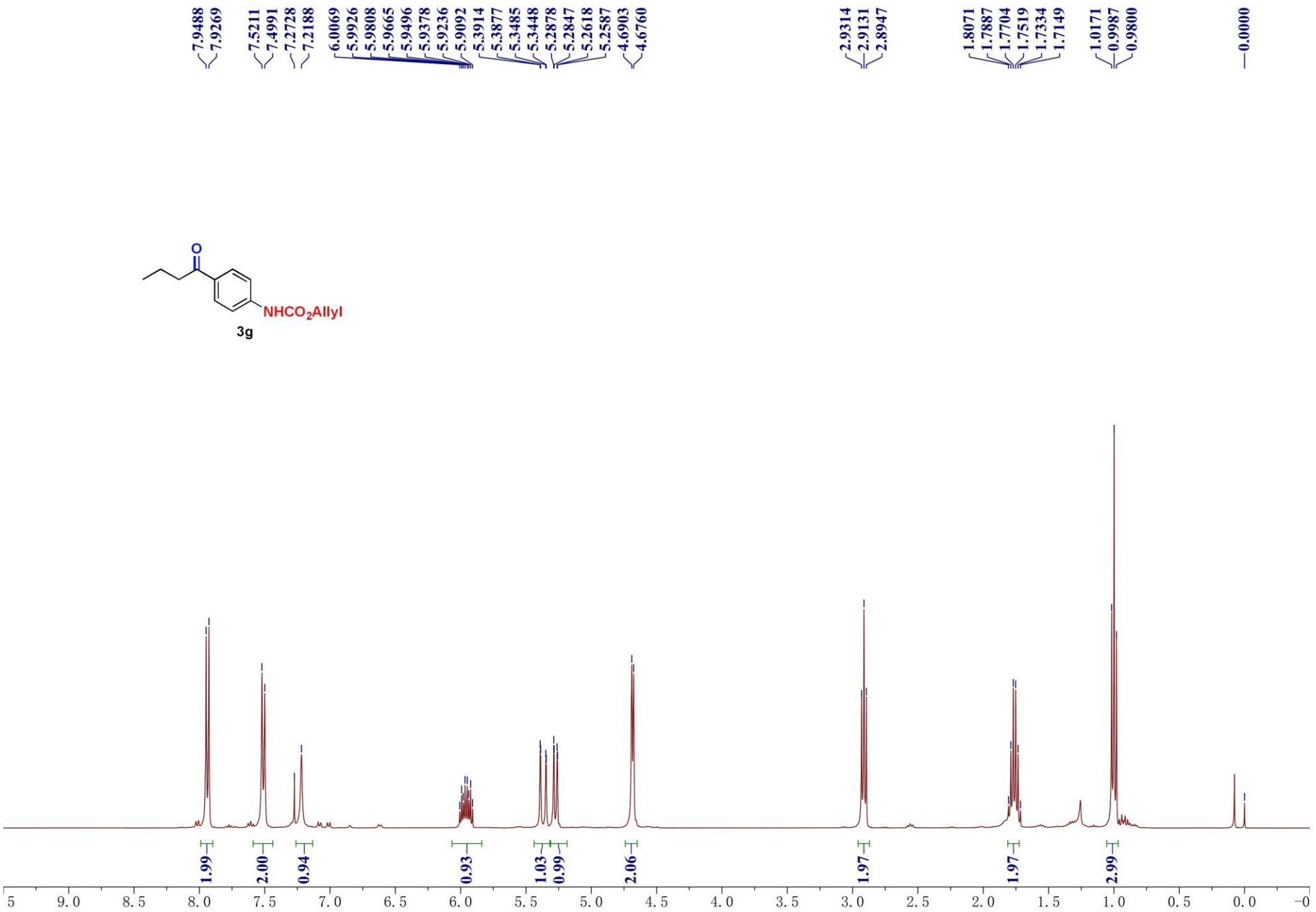

199.3093
153.3247
142.4292
131.8904
129.5216
117.5690
77.3176
77.0000
76.6811
65.3908
40.2050
30.8170
18.9765
17.8726
13.8399
13.6281
O
NHCO2nBu
3d
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

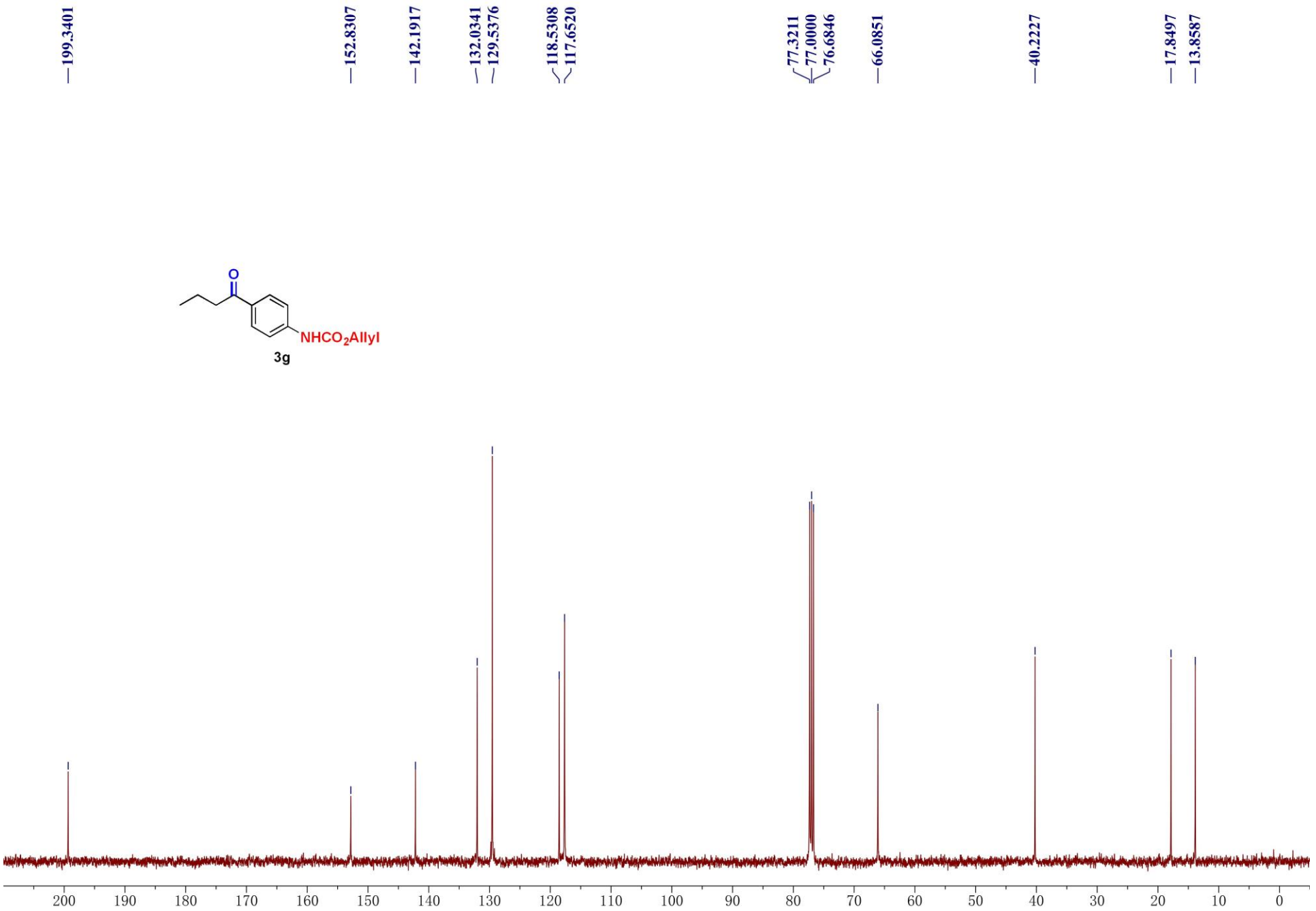

7.9459
7.9238
7.5183
7.4962
7.2752
7.1549
4.1919
4.1751
4.1582
2.9300
2.9118
2.8933
1.8074
1.7889
1.7705
1.7521
1.7336
1.7151
1.7002
1.6832
1.6661
1.6462
1.6293
1.3901
1.3751
1.3535
1.3209
1.3041
1.2868
1.0174
0.9989
0.9803
0.9101
0.8926
0.8753
-0.0000
O
NHCO2nHex
3e
2.02
2.00
0.96
2.02
2.01
2.03
2.04
6.09
2.99
2.97
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

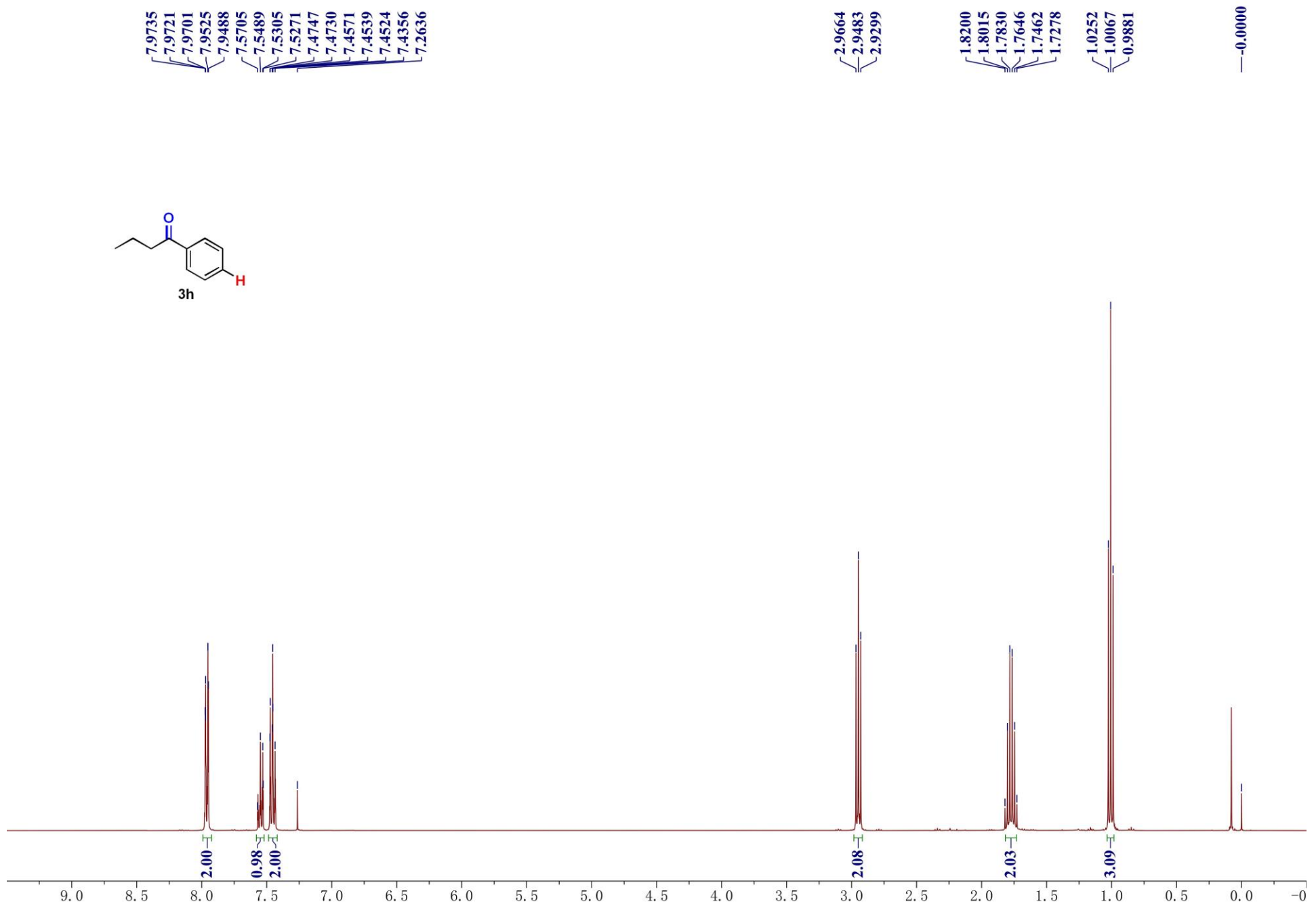

199.3164
153.3058
142.4047
131.8526
129.5289
117.5396
77.3171
77.0000
76.6810
65.7029
40.2041
31.3606
28.7486
25.4320
22.4772
17.8596
13.9394
13.8495
O
NHCO2nHex
3e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.9447
7.9227
7.4947
7.4728
7.2689
6.9010
5.0842
5.0685
5.0528
5.0371
5.0216
5.0059
4.9903
2.9277
2.9095
2.8911
1.8069
1.7884
1.7699
1.7515
1.7331
1.7146
1.3164
1.3007
1.0184
0.9998
0.9812
-0.0000
O
NHCO2CH(CH3)2
3f
1.99
2.00
0.92
0.95
1.98
2.08
3.03
2.98
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
-0

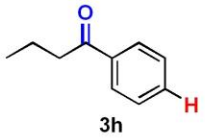

199.2465
152.7289
142.4102
131.8841
129.5588
117.4977
77.3176
77.0000
76.6814
69.2440
40.2263
21.9985
17.8826
13.8840
O
NHCO2CH(CH3)2
3f
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.9488
7.9269
7.5211
7.4991
7.2728
7.2188
6.0069
5.9926
5.9808
5.9665
5.9496
5.9378
5.9236
5.9092
5.3914
5.3877
5.3485
5.3448
5.2878
5.2847
5.2618
5.2587
4.6903
4.6760
2.9314
2.9131
2.8947
1.8071
1.7887
1.7704
1.7519
1.7334
1.7149
1.0171
0.9987
0.9800
0.0000
O
NHCO2Allyl
3g
1.99
2.00
0.94
0.93
1.03
0.99
2.06
1.97
1.97
2.99
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

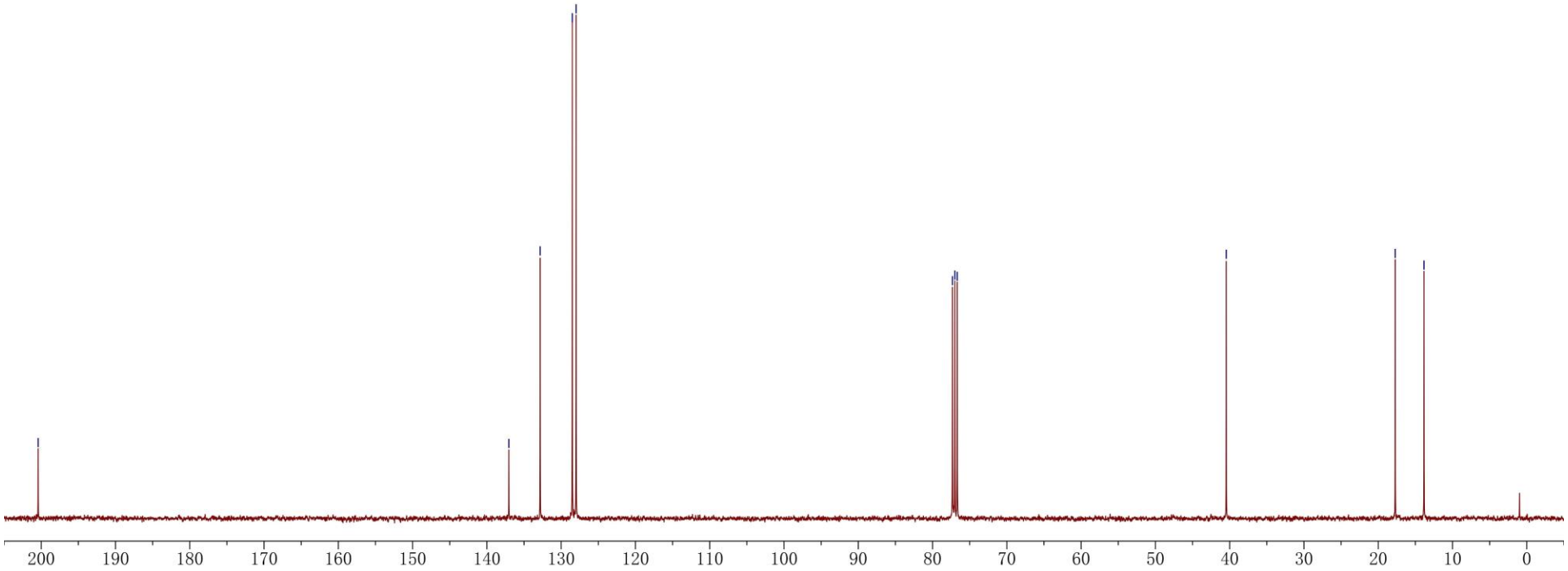

199.3401
152.8307
142.1917
132.0341
129.5376
118.5308
117.6520
77.3211
77.0000
76.6846
66.0851
40.2227
17.8497
13.8587
O
NHCO2Allyl
3g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

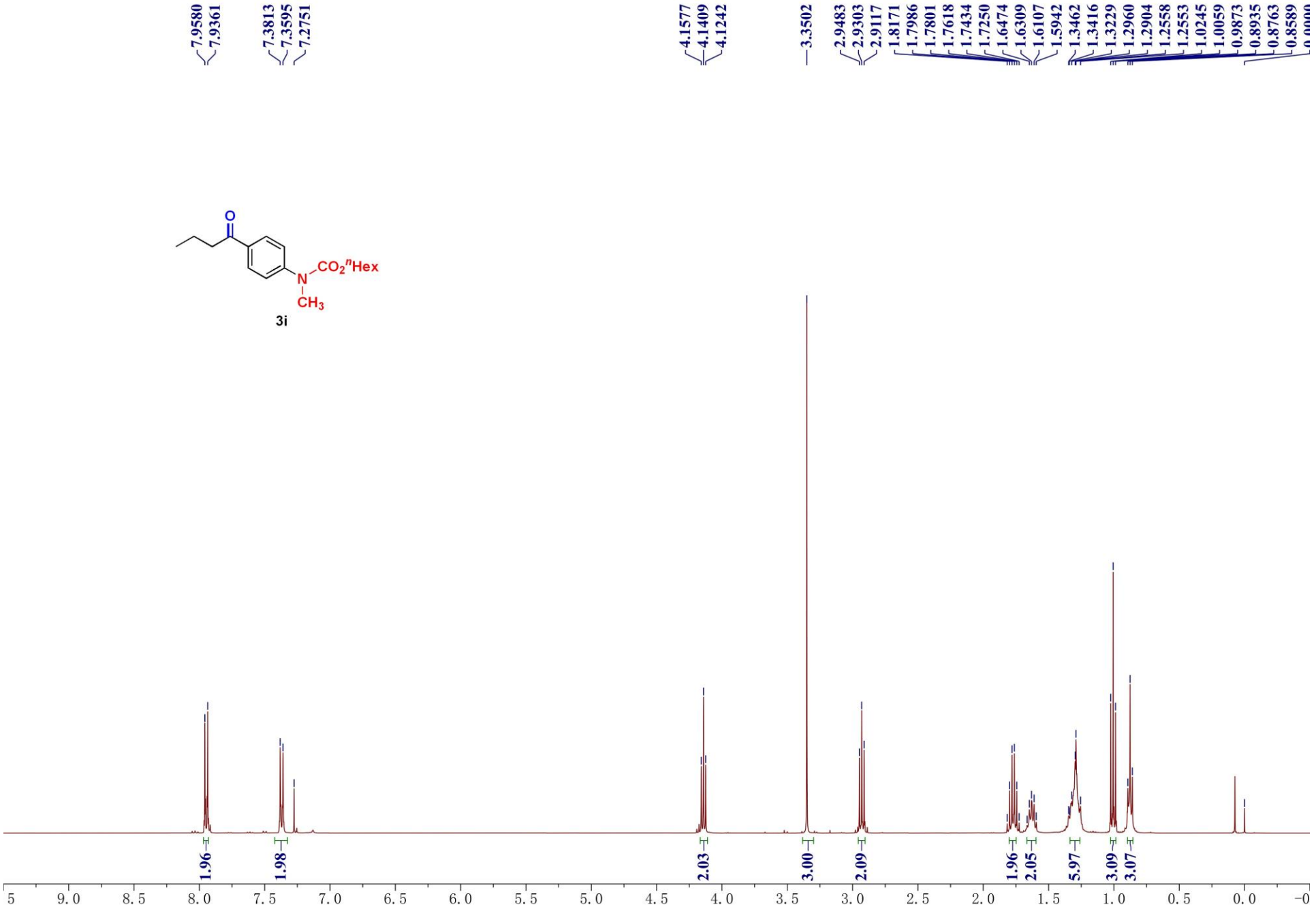

7.9735
7.9721
7.9701
7.9525
7.9488
7.5705
7.5489
7.5305
7.5271
7.4747
7.4730
7.4571
7.4539
7.4524
7.4356
7.2636
2.9664
2.9483
2.9299
1.8200
1.8015
1.7830
1.7646
1.7462
1.7278
1.0252
1.0067
0.9881
-0.0000
O
H
3h
2.00
0.98
2.00
2.08
2.03
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

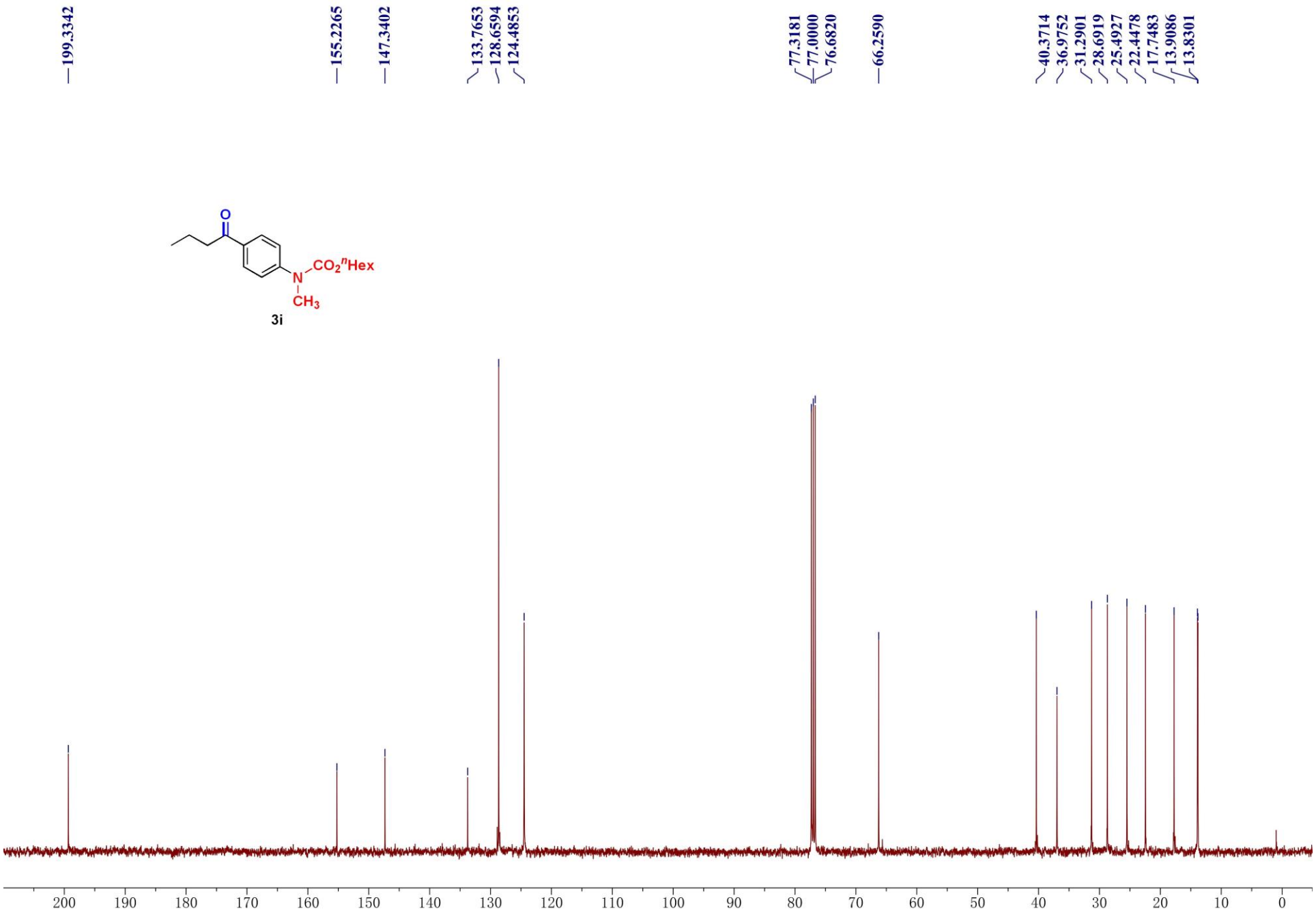
200.4144
137.0416
132.8291
128.4976
127.9894
77.3186
77.0000
76.6826
40.4618
17.7101
13.8380

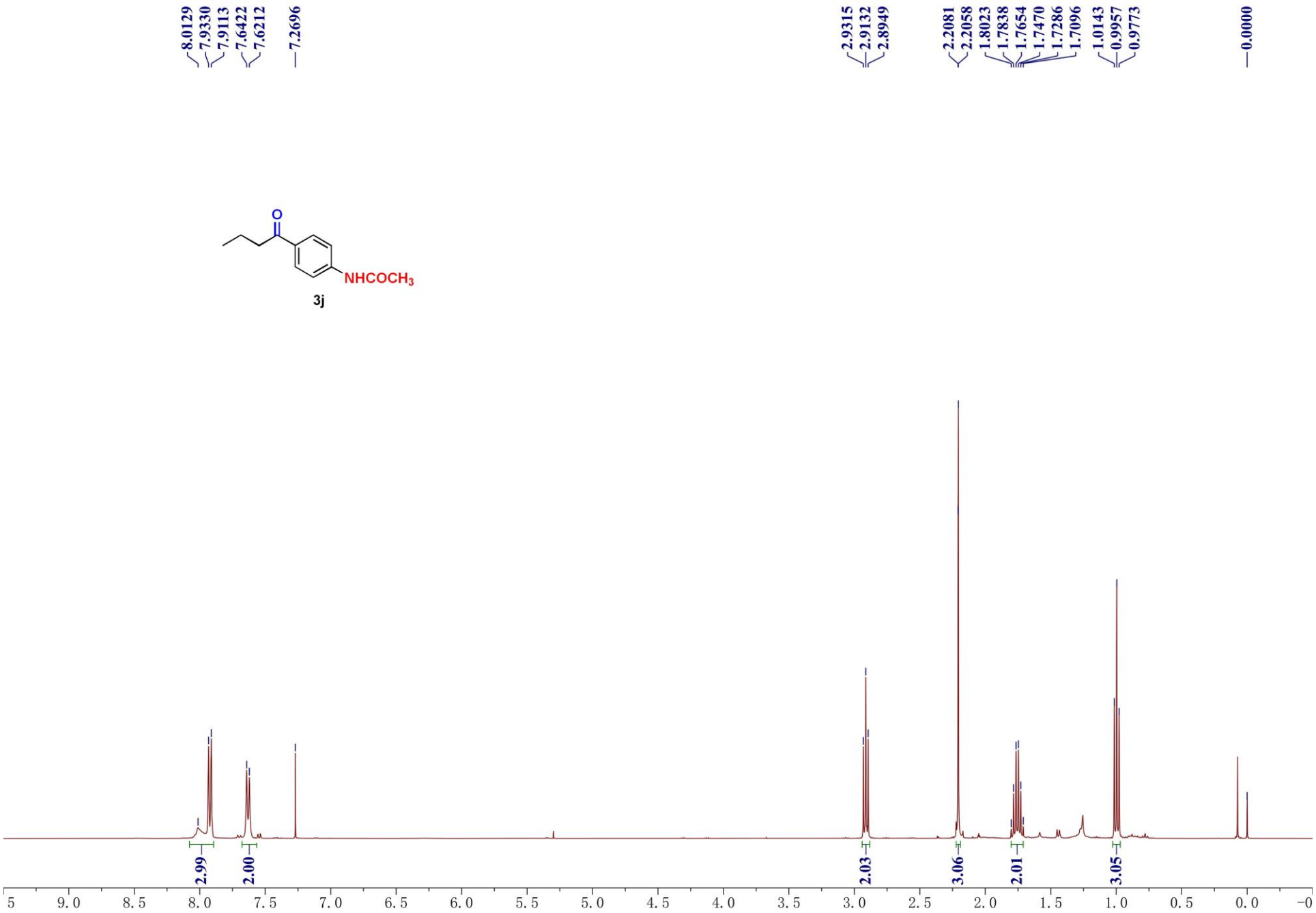


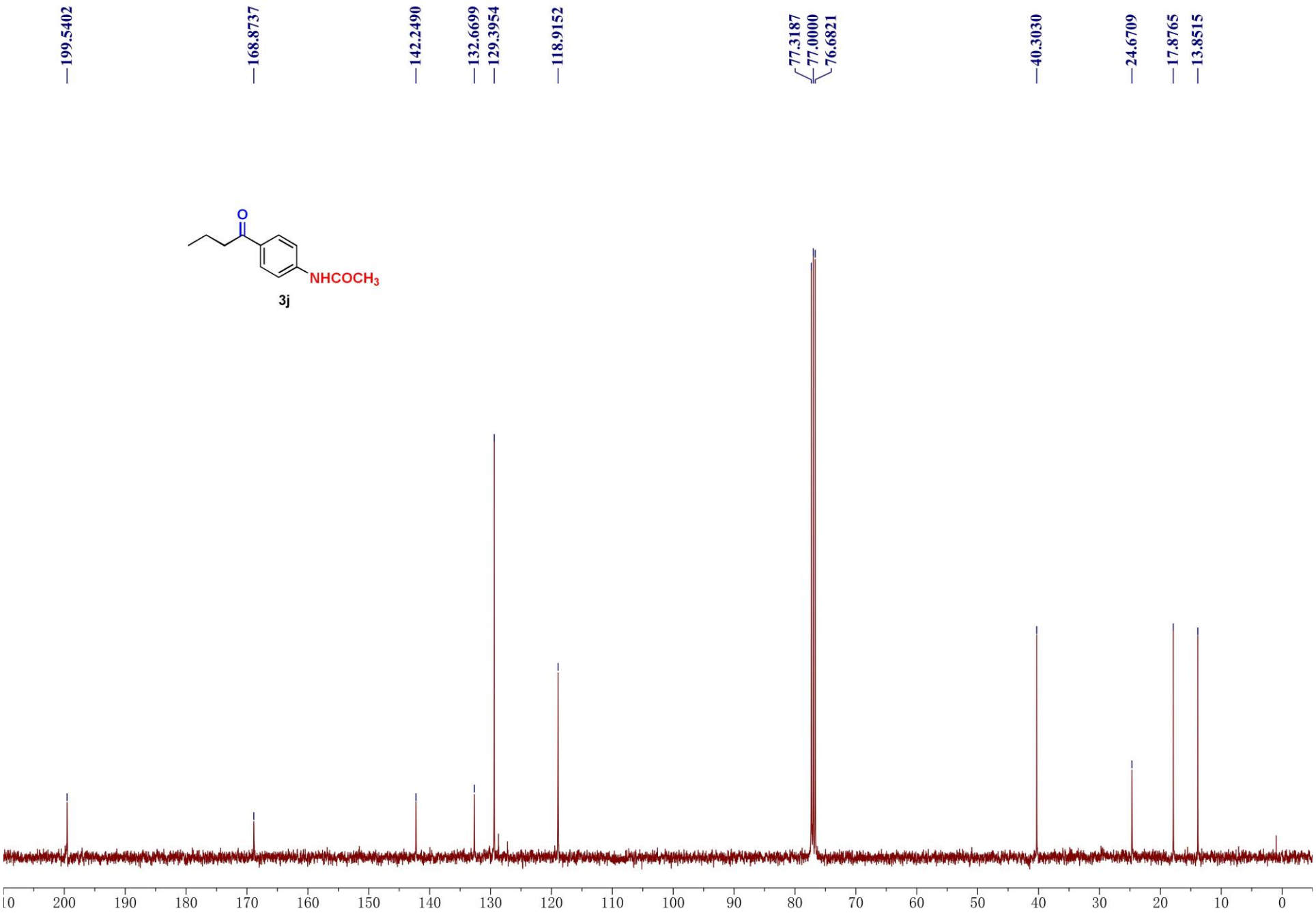
3h

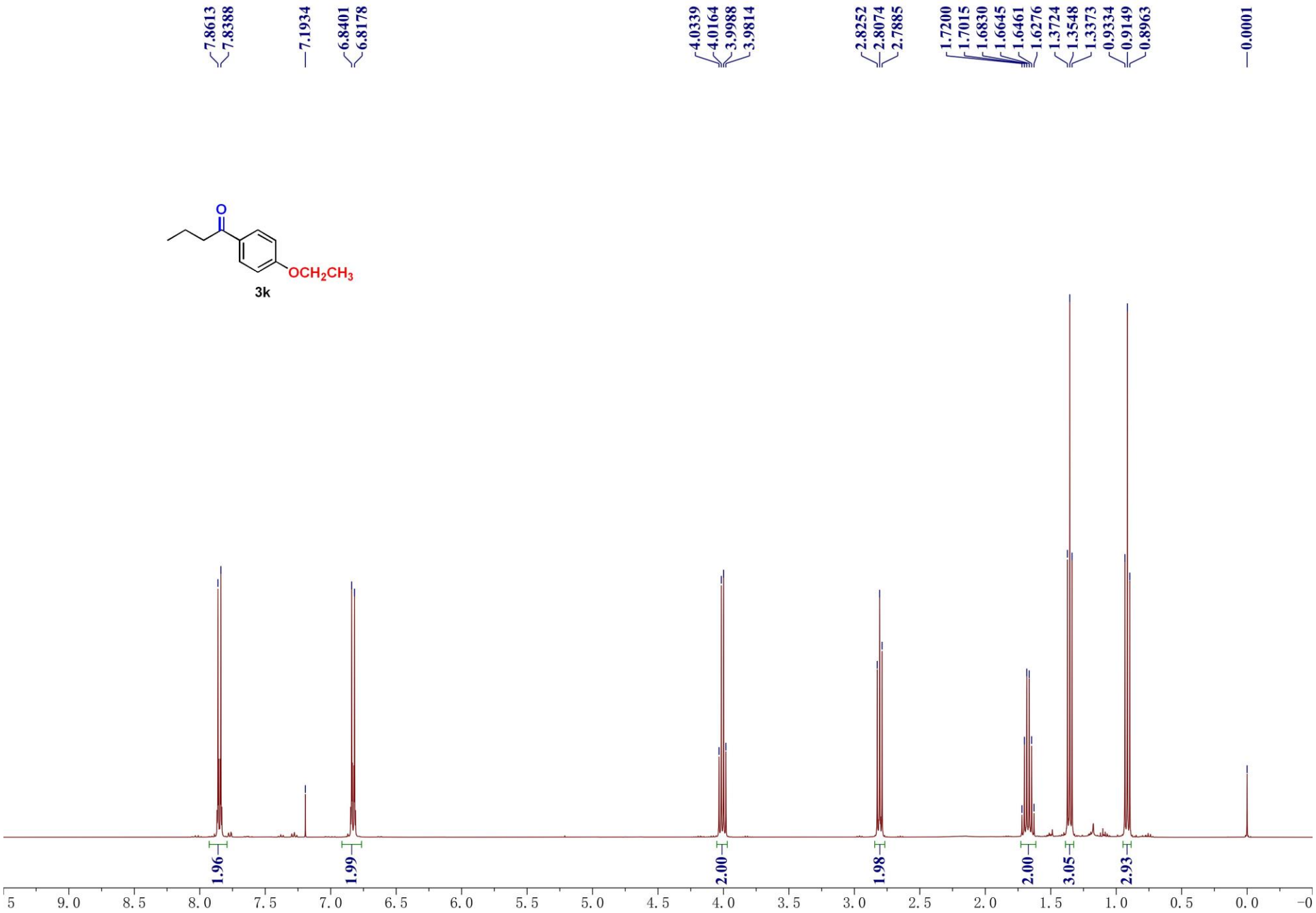


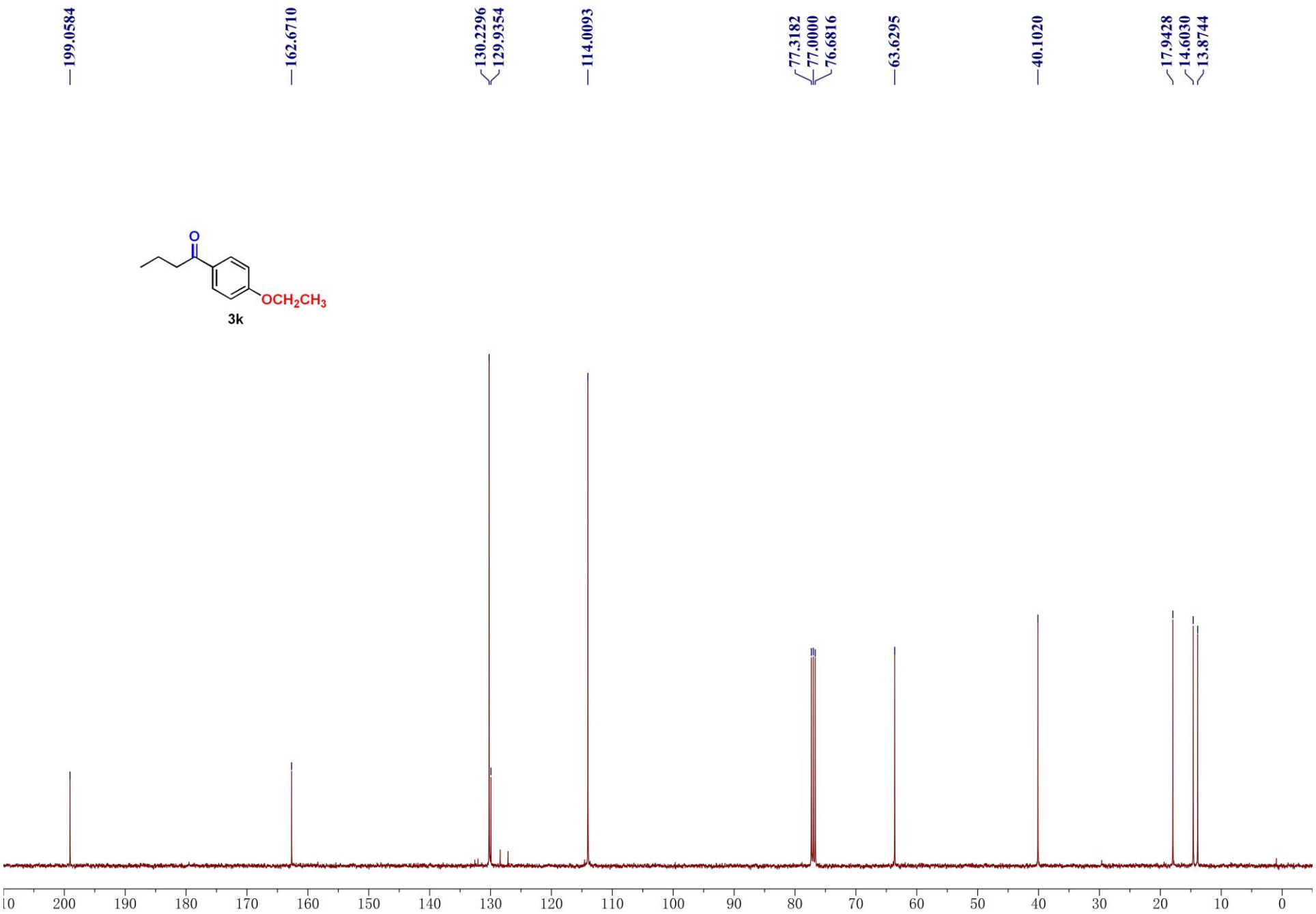

7.9580
7.9361
7.3813
7.3595
7.2751
4.1577
4.1409
4.1242
3.3502
2.9483
2.9303
2.9117
1.8171
1.7986
1.7801
1.7618
1.7434
1.7250
1.6474
1.6309
1.6107
1.5942
1.3462
1.3416
1.3229
1.2960
1.2904
1.2558
1.2553
1.0245
1.0059
0.9873
0.8935
0.8763
0.8589
O
CO2nHex
N
CH3
3i
1.96
1.98
2.03
3.00
2.09
1.96
2.05
5.97
3.09
3.07
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

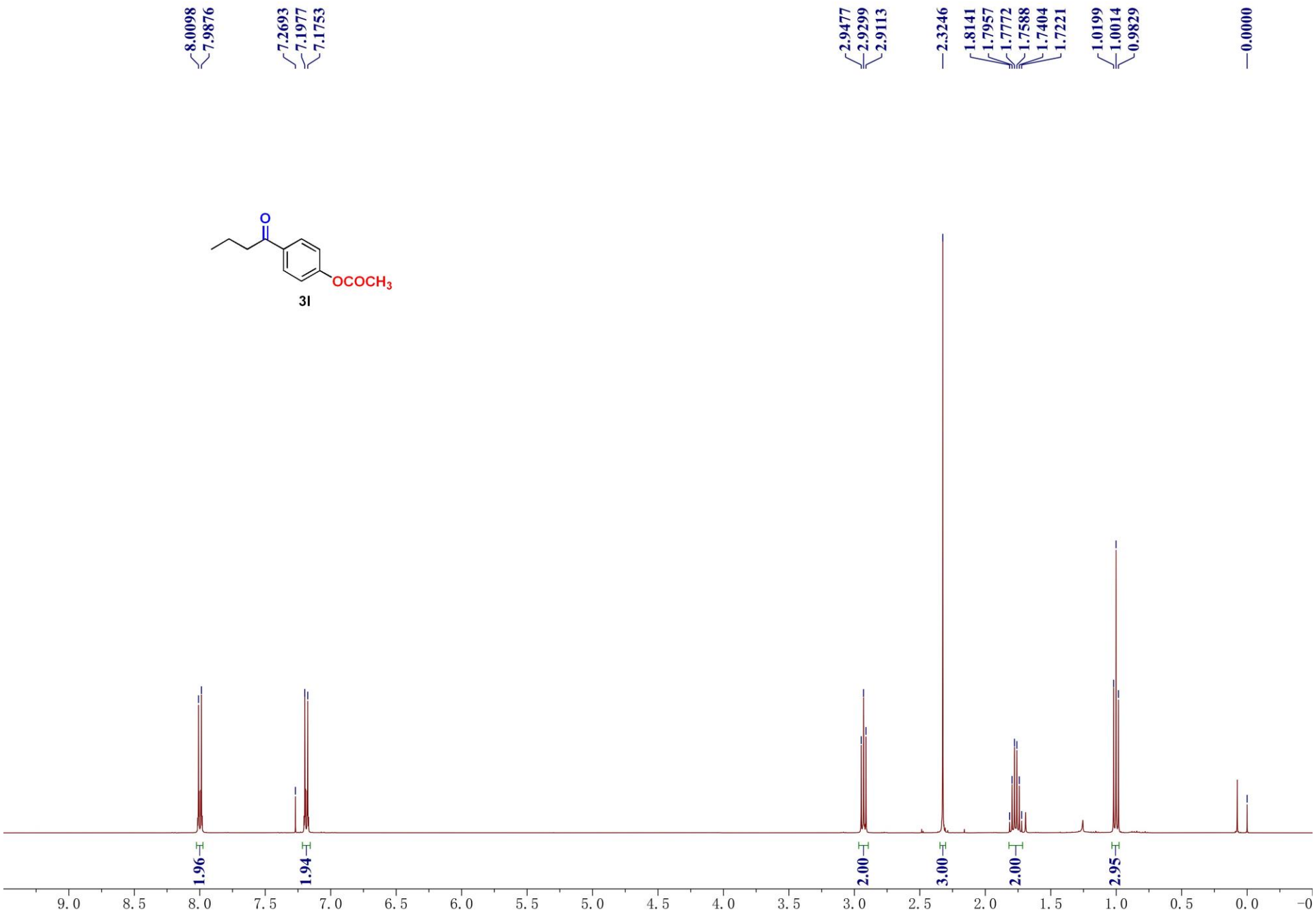

199.3342
155.2265
147.3402
133.7653
128.6594
124.4853
77.3181
77.0000
76.6820
66.2590
40.3714
36.9752
31.2901
28.6919
25.4927
22.4478
17.7483
13.9086
13.8301
O
CO2nHex
N
CH3
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

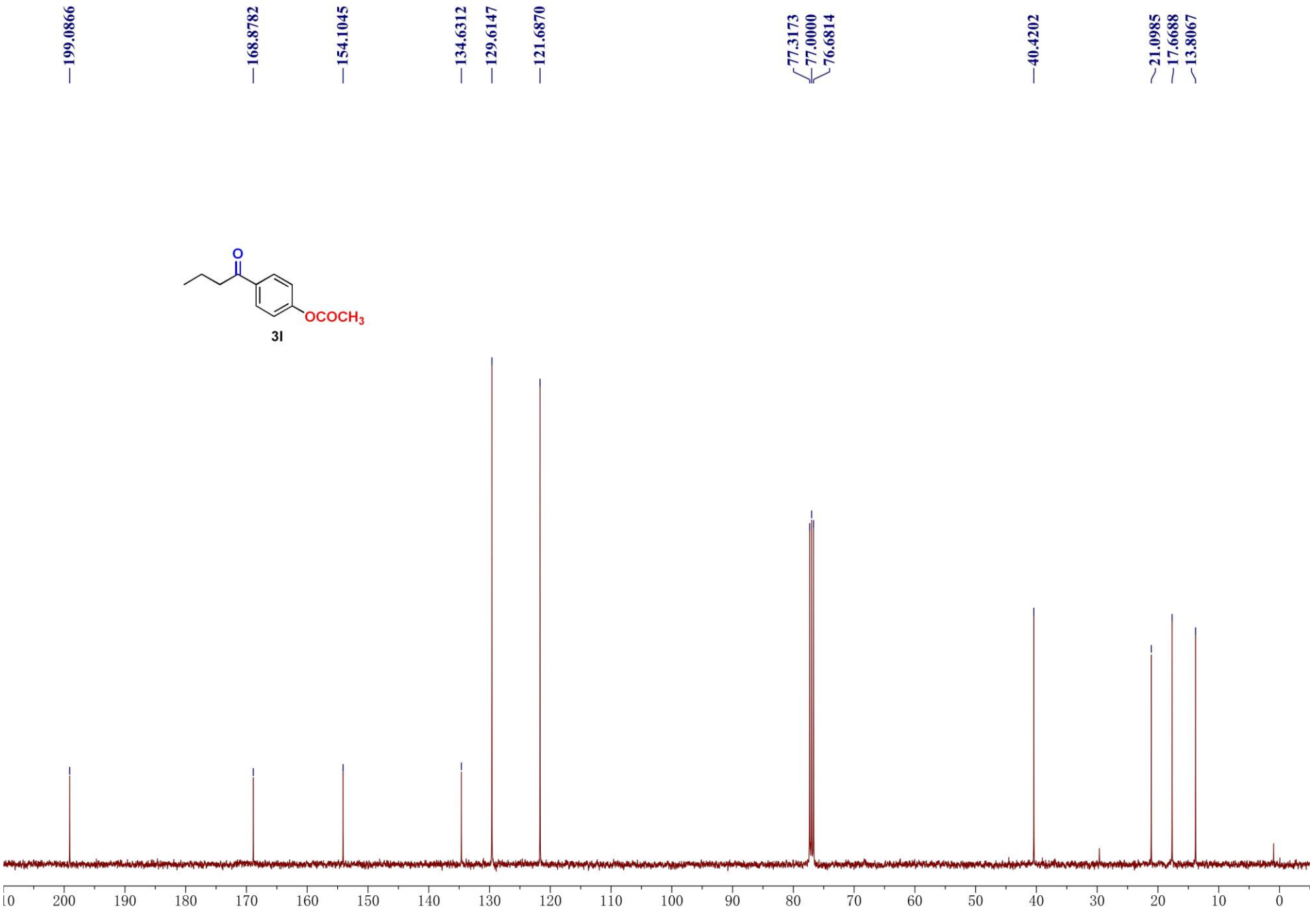

8.0129
7.9330
7.9113
7.6422
7.6212
7.2696
2.9315
2.9132
2.8949
2.2081
2.2058
1.8023
1.7838
1.7654
1.7470
1.7286
1.7096
1.0143
0.9957
0.9773
0.0000
O
NHCOCH3
3j
2.99
2.00
2.03
3.06
2.01
3.05
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0

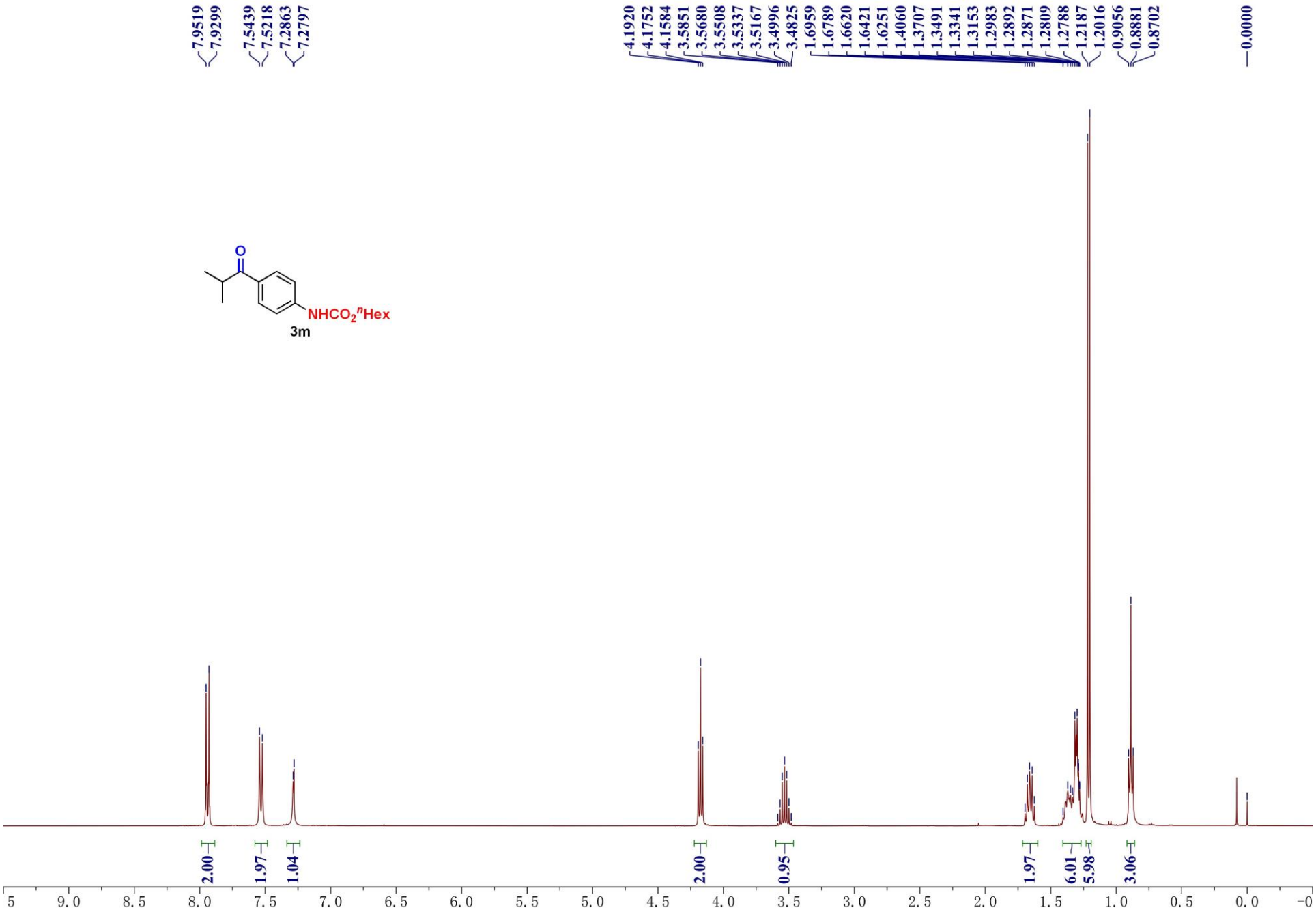

199.5402
168.8737
142.2490
132.6699
129.3954
118.9152
77.3187
77.0000
76.6821
40.3030
24.6709
17.8765
13.8515
O
NHCOCH3
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

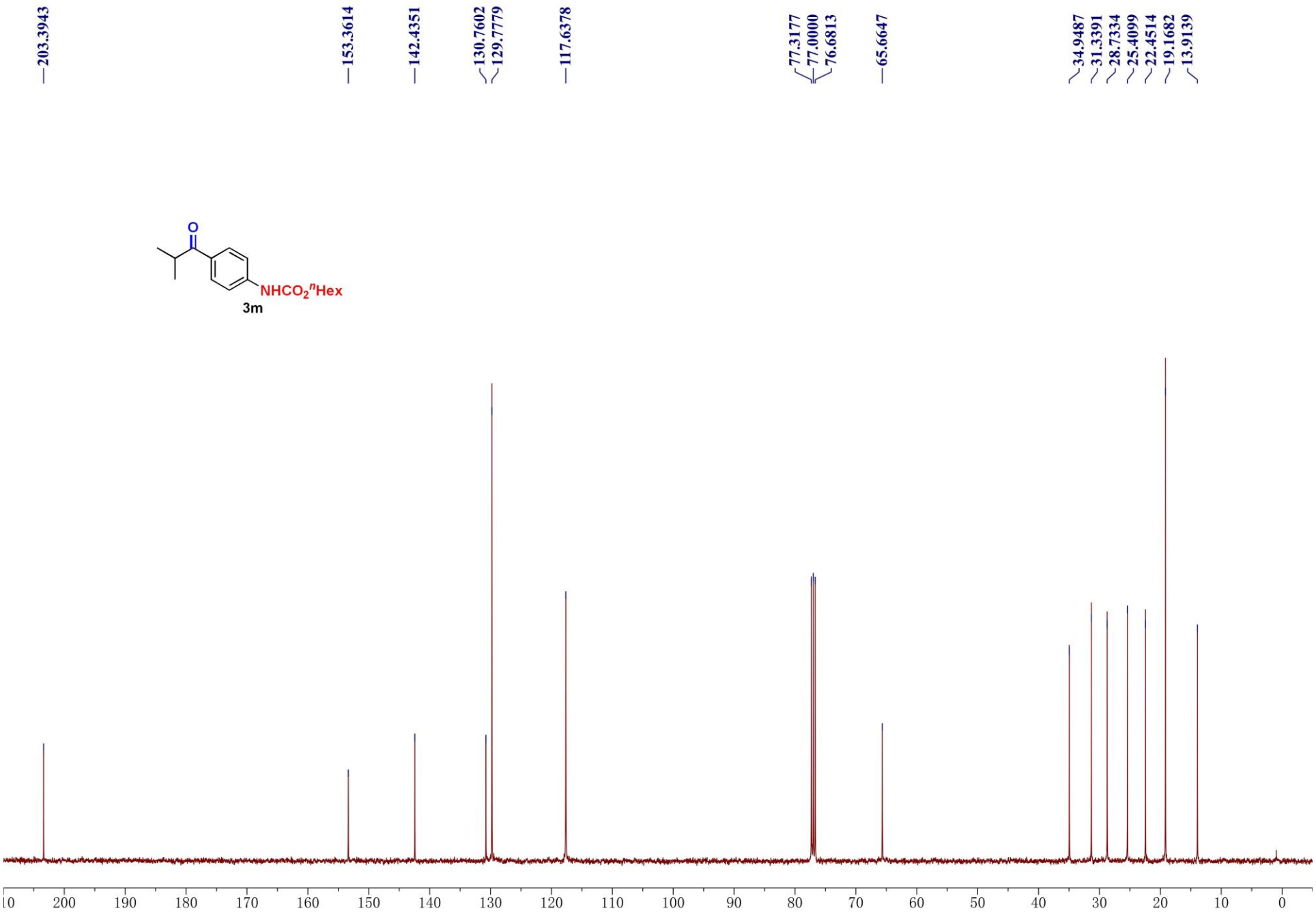

7.8613
7.8388
7.1934
6.8401
6.8178
4.0339
4.0164
3.9988
3.9814
2.8252
2.8074
2.7885
1.7200
1.7015
1.6830
1.6645
1.6461
1.6276
1.3724
1.3548
1.3373
0.9334
0.9149
0.8963
0.0001
O
OCH2CH3
3k
1.96
1.99
2.00
1.98
2.00
3.05
2.93
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0

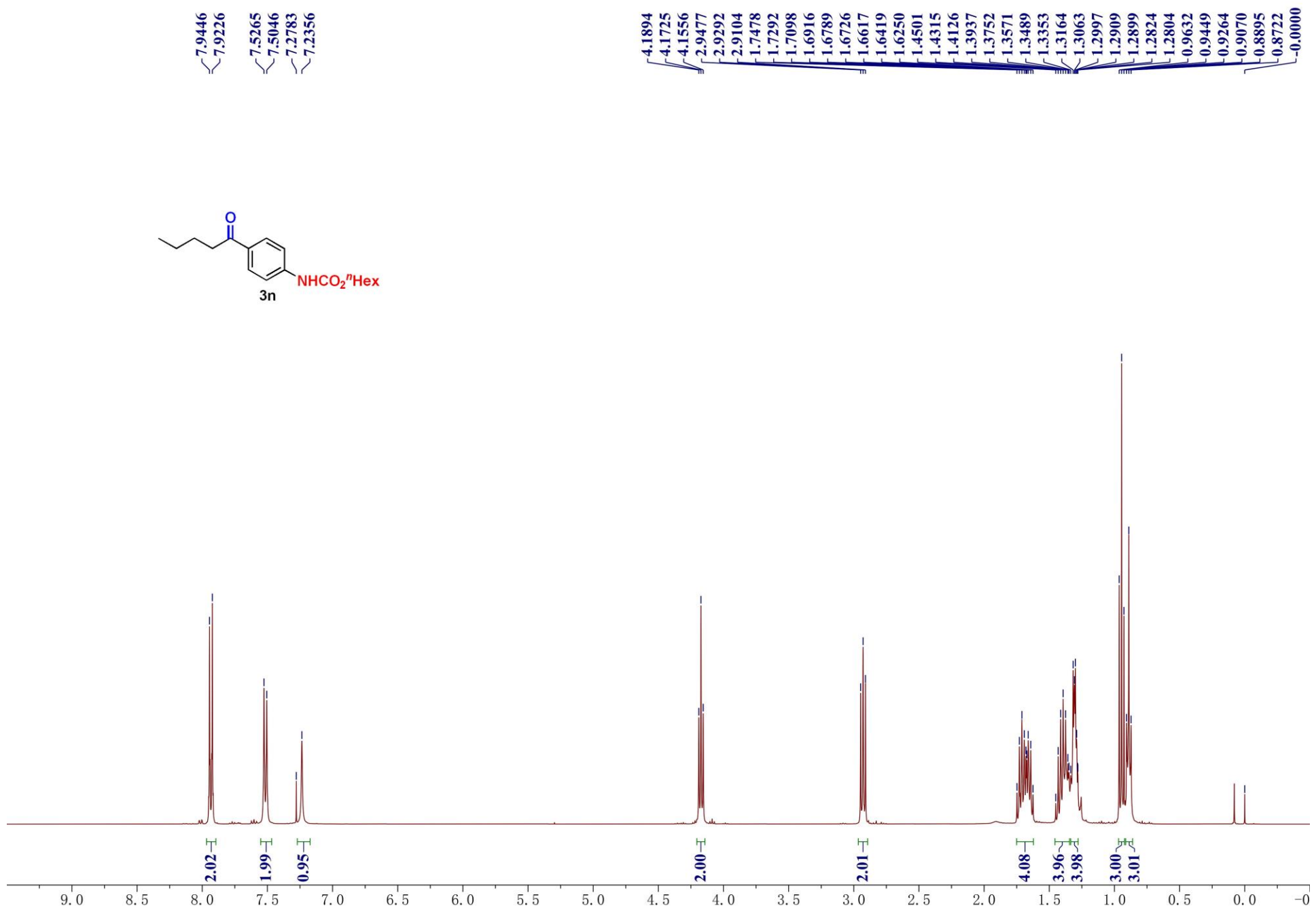

199.0584
162.6710
130.2296
129.9354
114.0093
77.3182
77.0000
76.6816
63.6295
40.1020
17.9428
14.6030
13.8744
O
OCH2CH3
3k
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

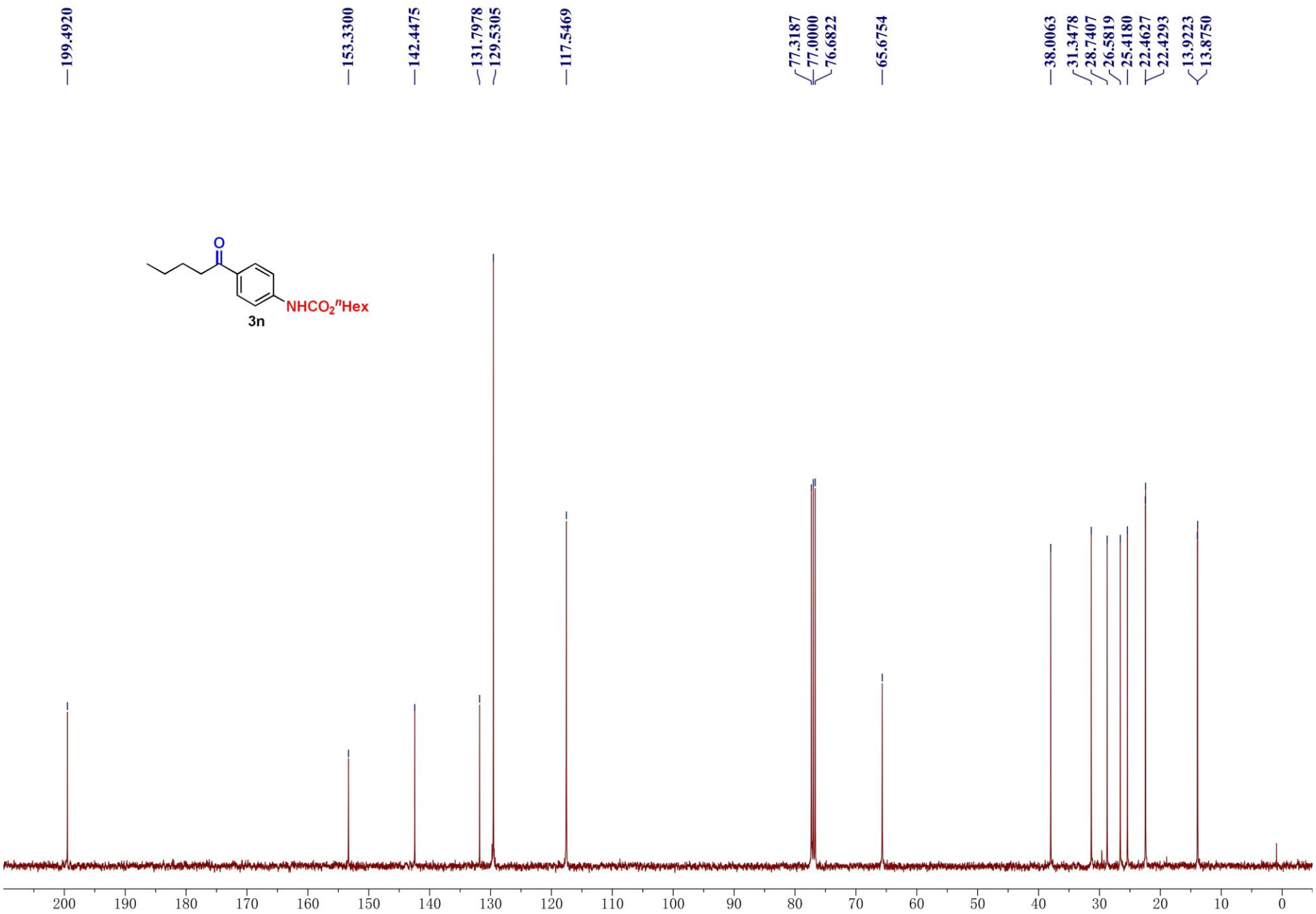

8.0098
7.9876
7.2693
7.1977
7.1753
2.9477
2.9299
2.9113
2.3246
1.8141
1.7957
1.7772
1.7588
1.7404
1.7221
1.0199
1.0014
0.9829
0.0000
O
OCOCH3
3l
1.96
1.94
2.00
3.00
2.00
2.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0

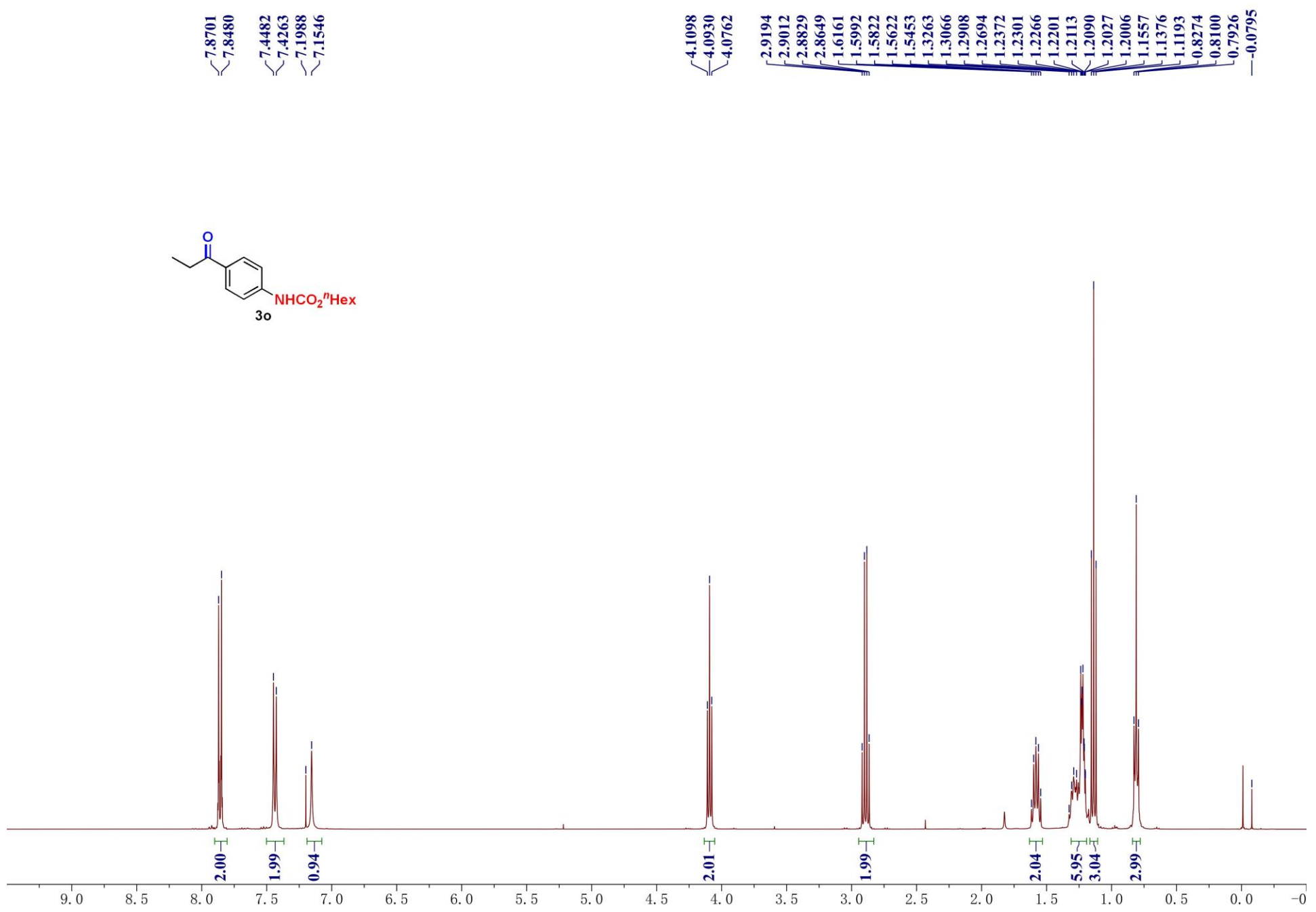

199.0866
168.8782
154.1045
134.6312
129.6147
121.6870
77.3173
77.0000
76.6814
40.4202
21.0985
17.6688
13.8067
O
OCOCH3
3l
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

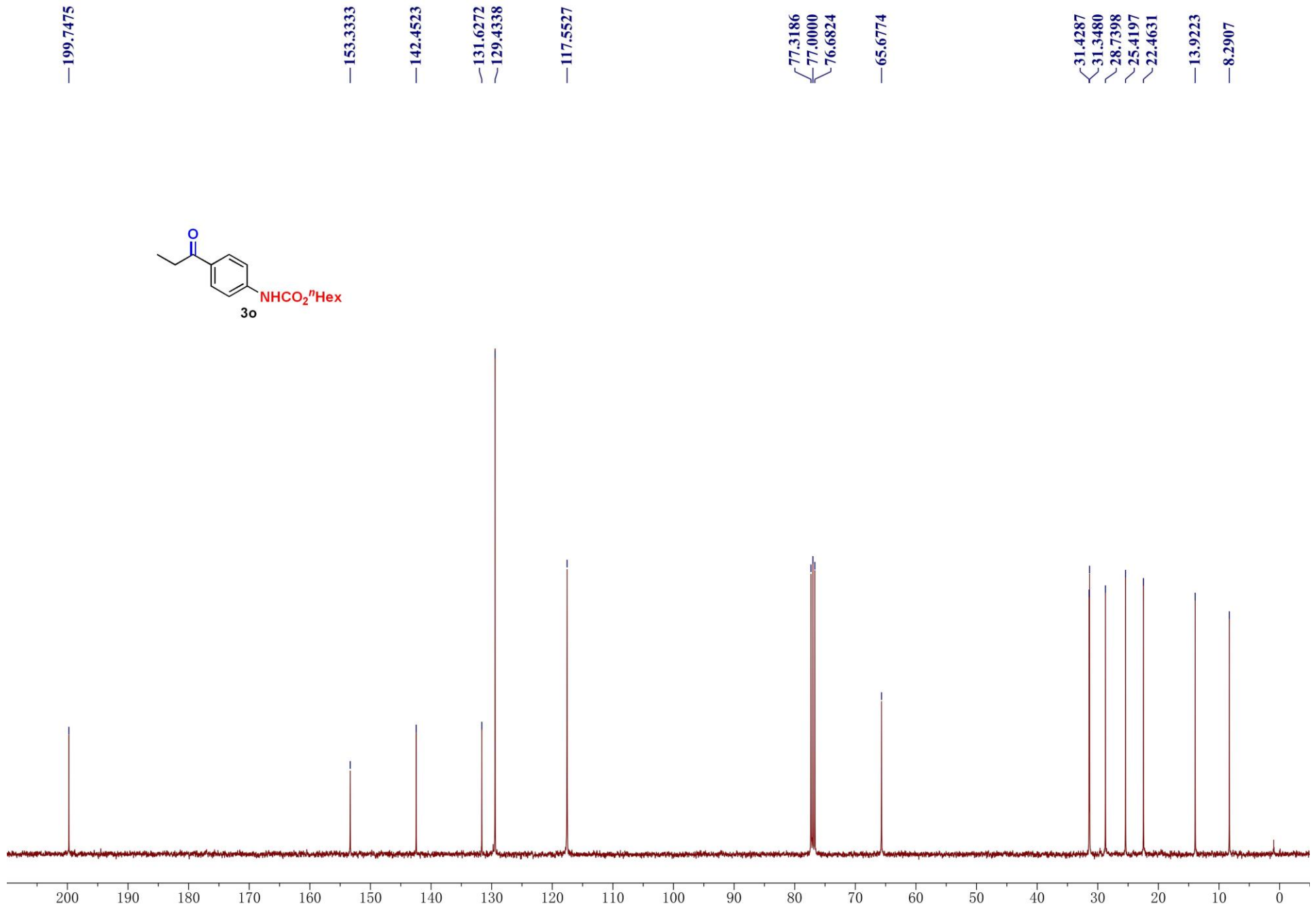

7.9519
7.9299
7.5439
7.5218
7.2863
7.2797
4.1920
4.1752
4.1584
3.5851
3.5680
3.5508
3.5337
3.5167
3.4996
3.4825
1.6959
1.6789
1.6620
1.6421
1.6251
1.4060
1.3707
1.3491
1.3341
1.3153
1.2983
1.2892
1.2871
1.2809
1.2788
1.2187
1.2016
0.9056
0.8881
0.8702
0.0000
O
NHCO2nHex
3m
2.00
1.97
1.04
2.00
0.95
1.97
6.01
5.98
3.06
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

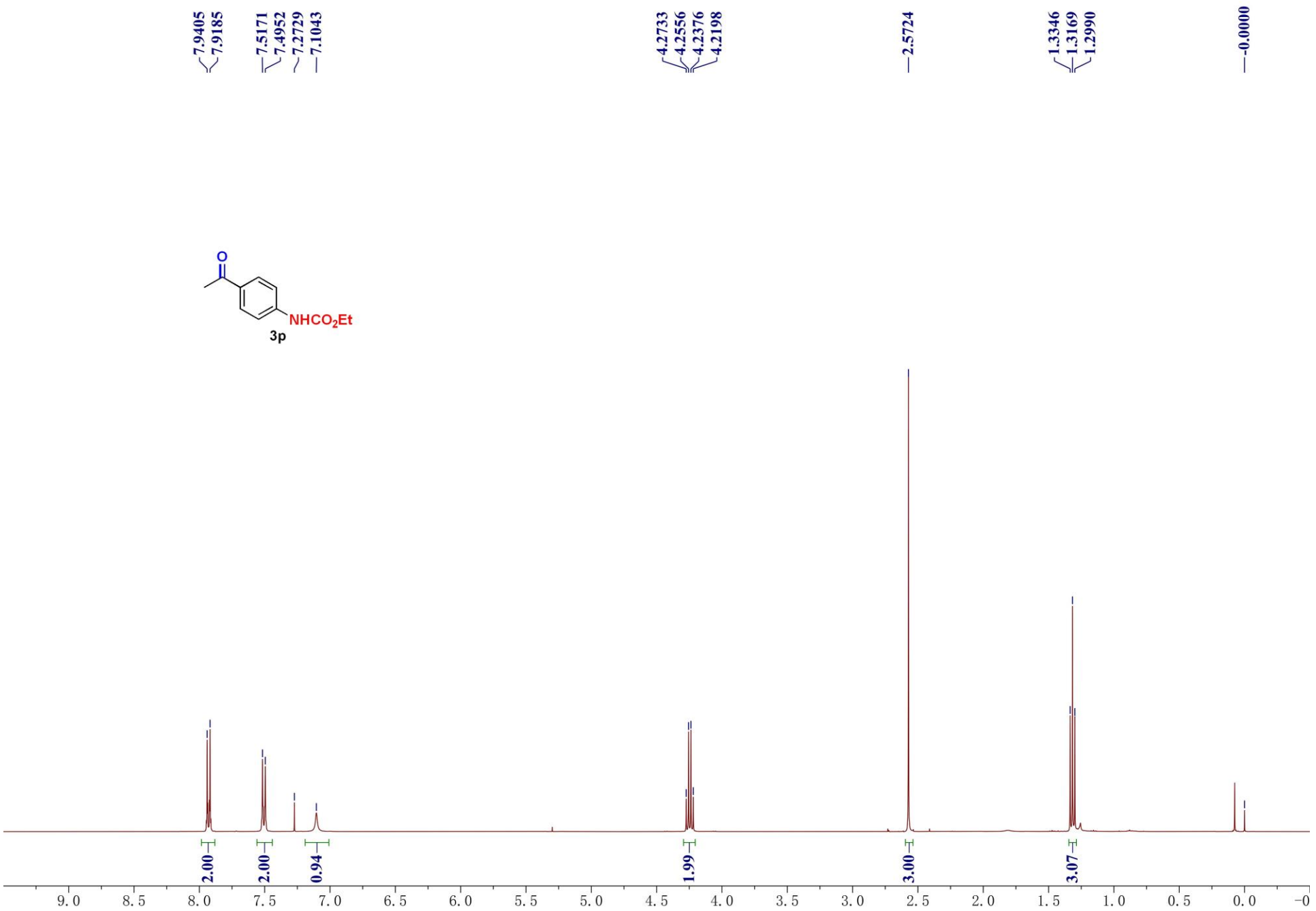

203.3943
153.3614
142.4351
130.7602
129.7779
117.6378
77.3177
77.0000
76.6813
65.6647
34.9487
31.3391
28.7334
25.4099
22.4514
19.1682
13.9139
O
NHCO2nHex
3m
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

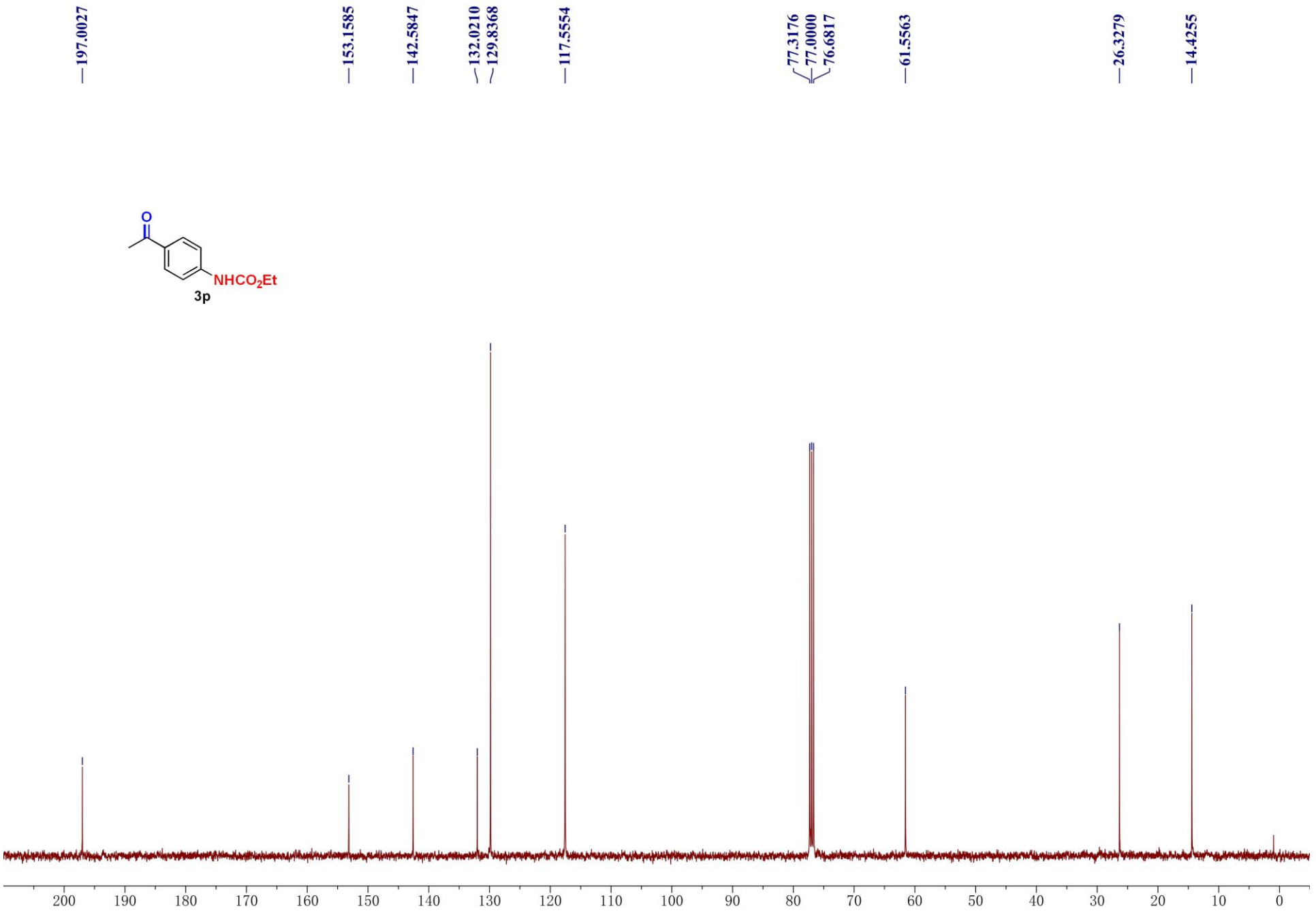

7.9446
7.9226
7.5265
7.5046
7.2783
7.2356
4.1894
4.1725
4.1556
2.9477
2.9292
2.9104
1.7478
1.7292
1.7098
1.6916
1.6789
1.6726
1.6617
1.6419
1.6250
1.4501
1.4315
1.4126
1.3937
1.3752
1.3571
1.3489
1.3353
1.3164
1.3063
1.2997
1.2909
1.2899
1.2824
1.2804
0.9632
0.9449
0.9264
0.9070
0.8895
0.8722
-0.0000
O
NHCO2nHex
3n
2.02
1.99
0.95
2.00
2.01
4.08
3.96
3.98
3.00
3.01
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

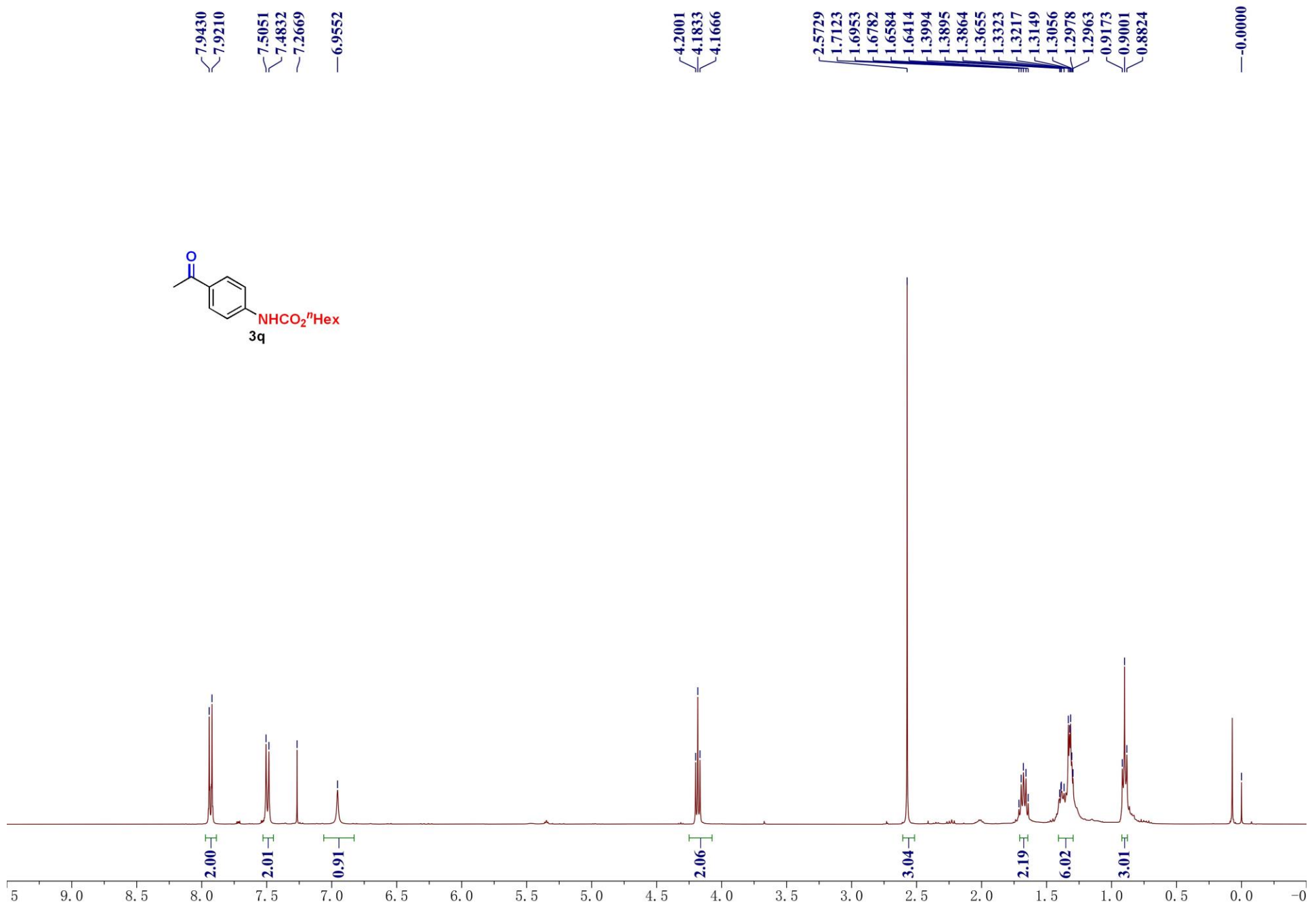

199.4920
153.3300
142.4475
131.7978
129.5305
117.5469
77.3187
77.0000
76.6822
65.6754
38.0063
31.3478
28.7407
26.5819
25.4180
22.4627
22.4293
13.9223
13.8750
O
NHCO2nHex
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

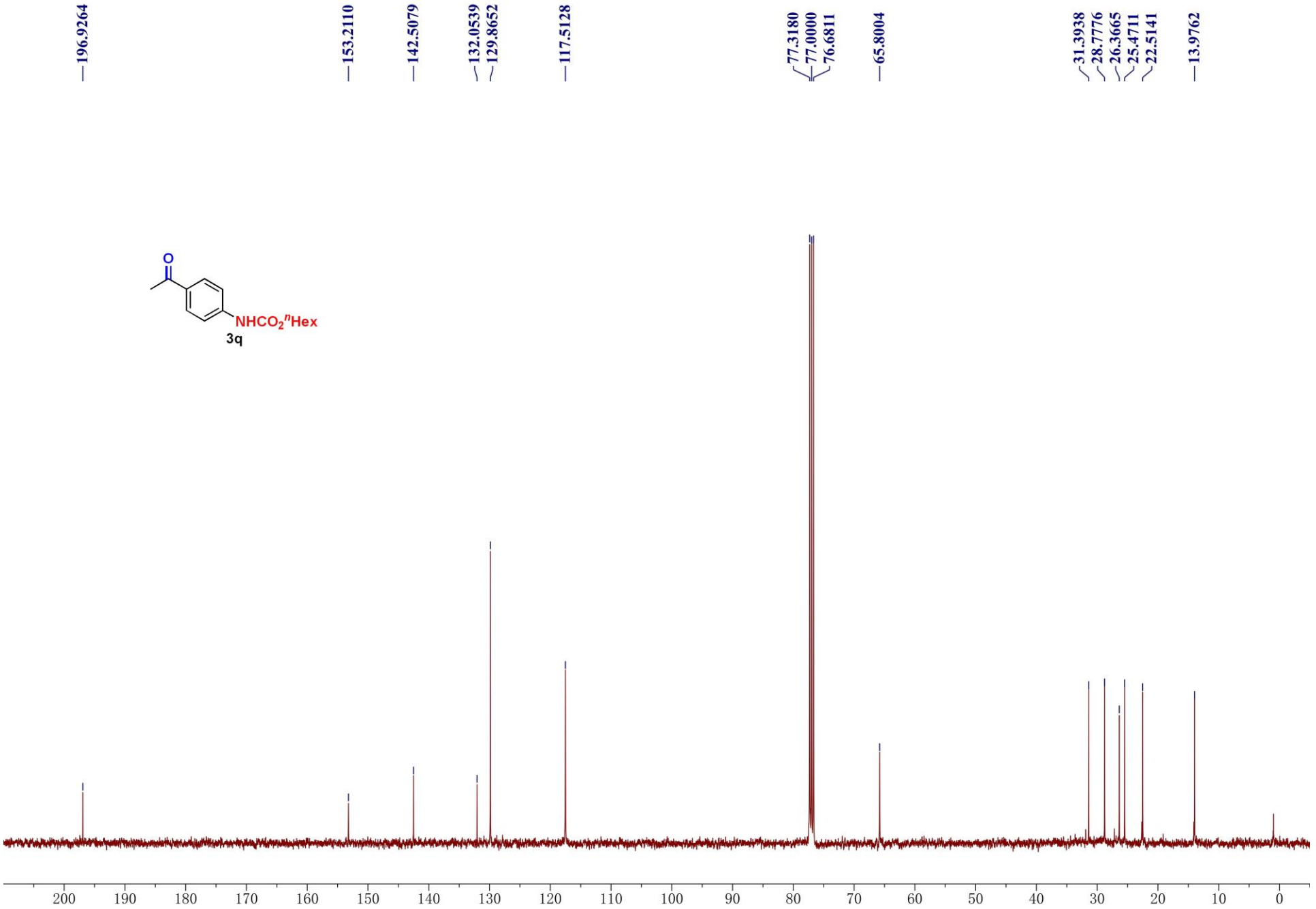

7.8701
7.8480
7.4482
7.4263
7.1988
7.1546
4.1098
4.0930
4.0762
2.9194
2.9012
2.8829
2.8649
1.6161
1.5992
1.5822
1.5622
1.5453
1.3263
1.3066
1.2908
1.2694
1.2372
1.2301
1.2266
1.2201
1.2113
1.2090
1.2027
1.2006
1.1557
1.1376
1.1193
0.8274
0.8100
0.7926
-0.0795
O
NHCO2nHex
3o
2.00
1.99
0.94
2.01
1.99
2.04
5.95
3.04
2.99
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

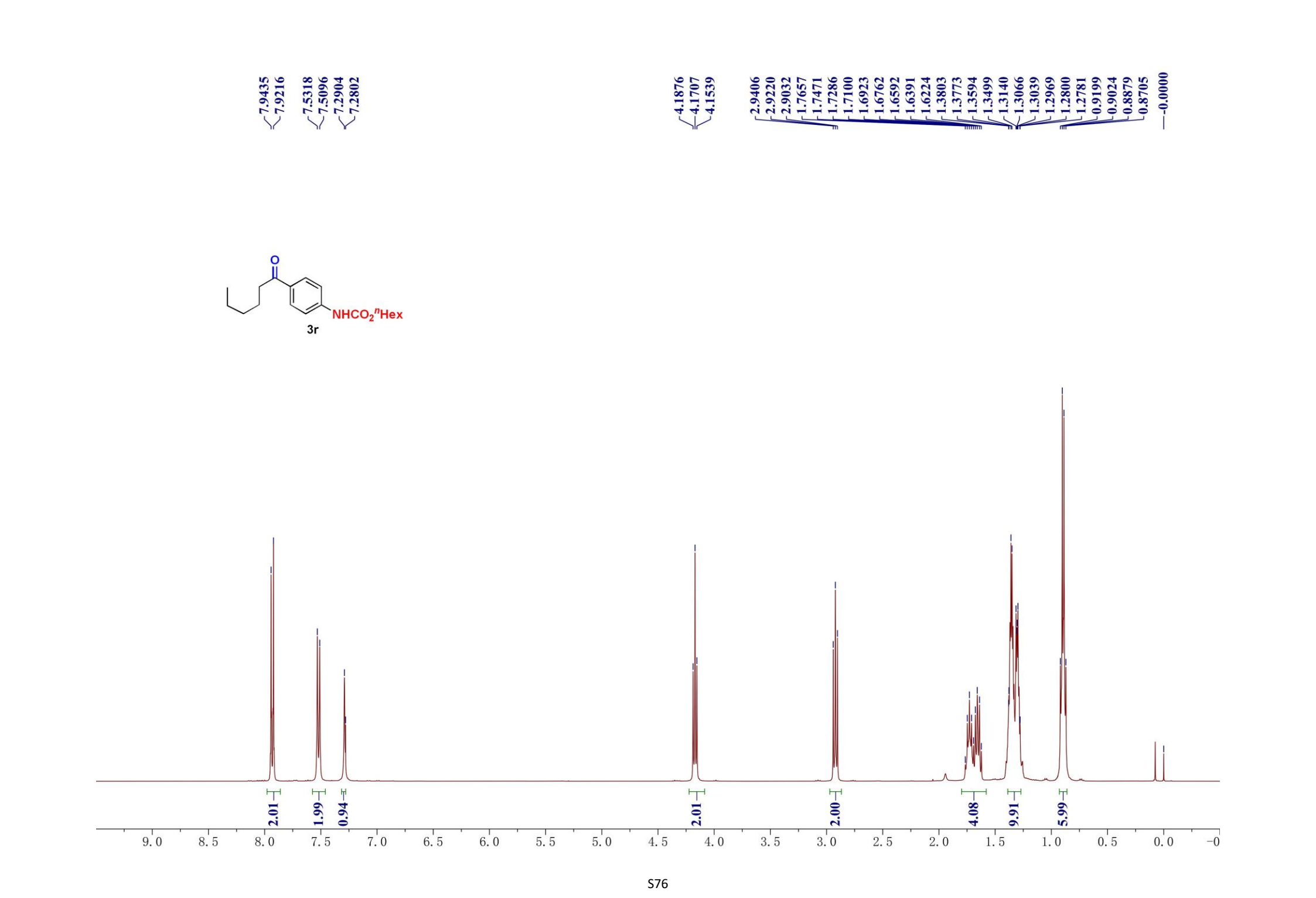

199.7475
153.3333
142.4523
131.6272
129.4338
117.5527
77.3186
77.0000
76.6824
65.6774
31.4287
31.3480
28.7398
25.4197
22.4631
13.9223
8.2907
O
NHCO2nHex
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

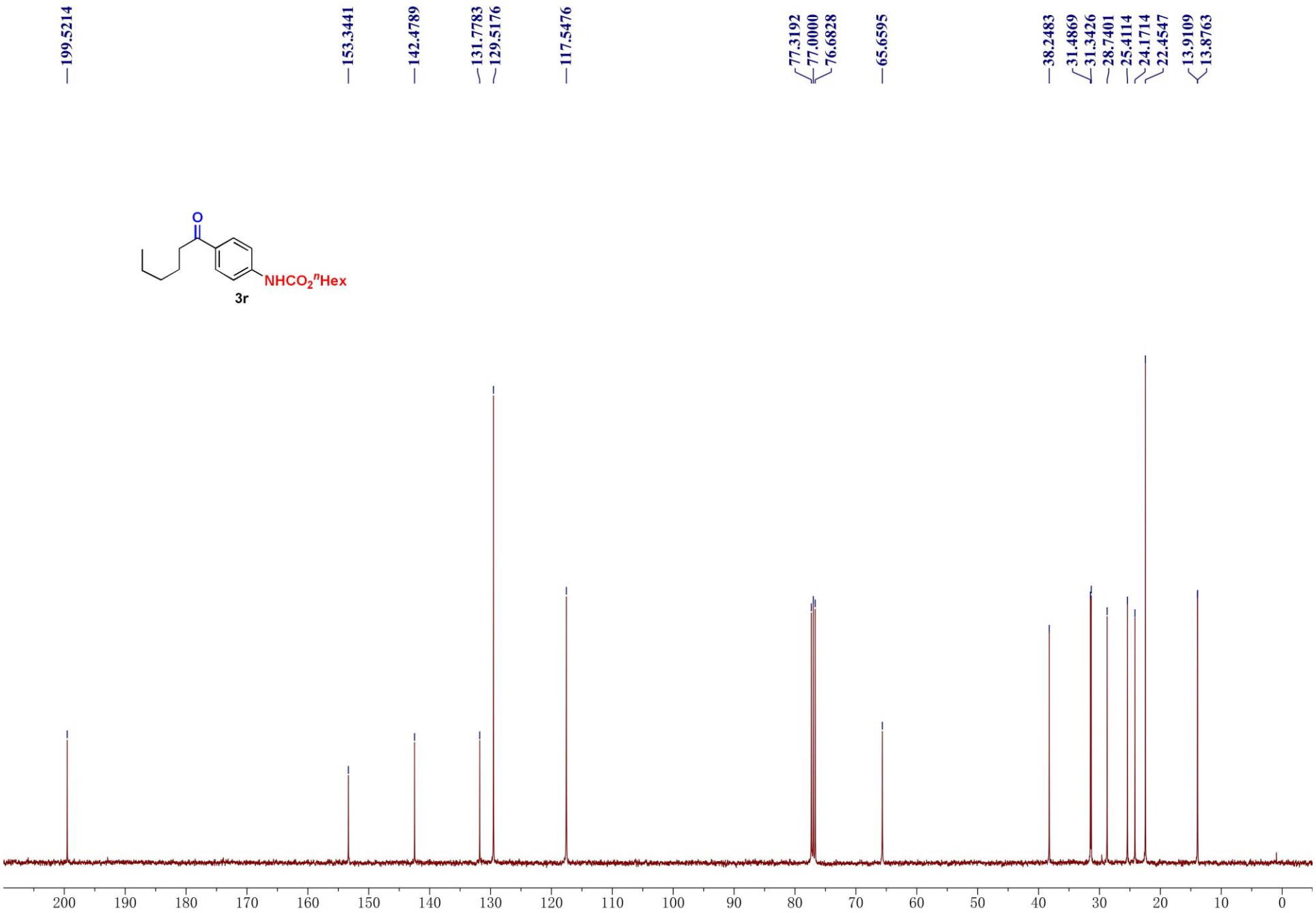

7.9405
7.9185
7.5171
7.4952
7.2729
7.1043
4.2733
4.2556
4.2376
4.2198
2.5724
1.3346
1.3169
1.2990
-0.0000
O
NHCO2Et
3p
2.00
2.00
0.94
1.99
3.00
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

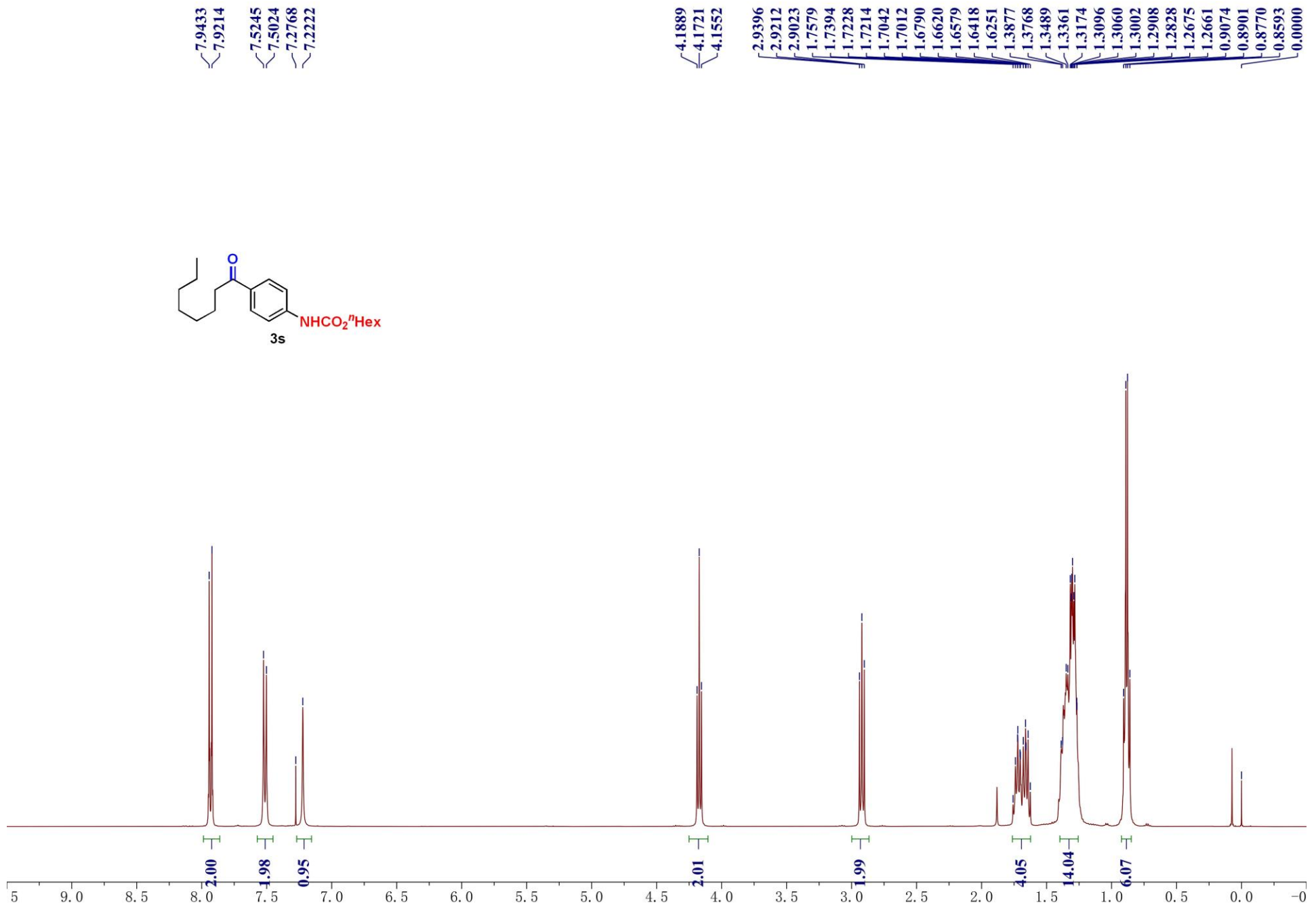

197.0027
153.1585
142.5847
132.0210
129.8368
117.5554
77.3176
77.0000
76.6817
61.5563
26.3279
14.4255
O
NHCO2Et
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

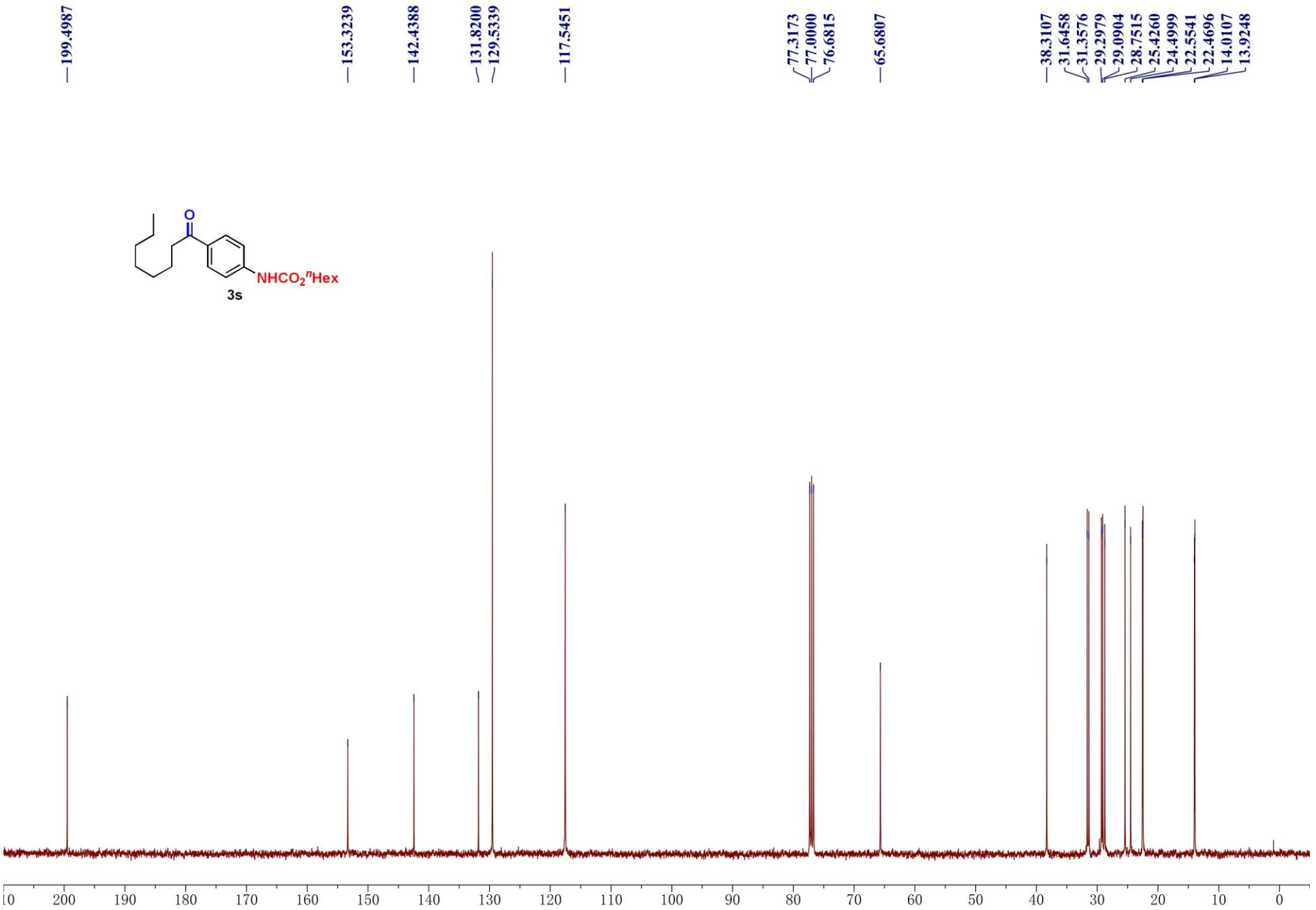

7.9430
7.9210
7.5051
7.4832
7.2669
6.9552
4.2001
4.1833
4.1666
2.5729
1.7123
1.6953
1.6782
1.6584
1.6414
1.3994
1.3895
1.3864
1.3655
1.3323
1.3217
1.3149
1.3056
1.2978
1.2963
0.9173
0.9001
0.8824
-0.0000
O
NHCO2nHex
3q
2.00
2.01
0.91
2.06
3.04
2.19
6.02
3.01
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

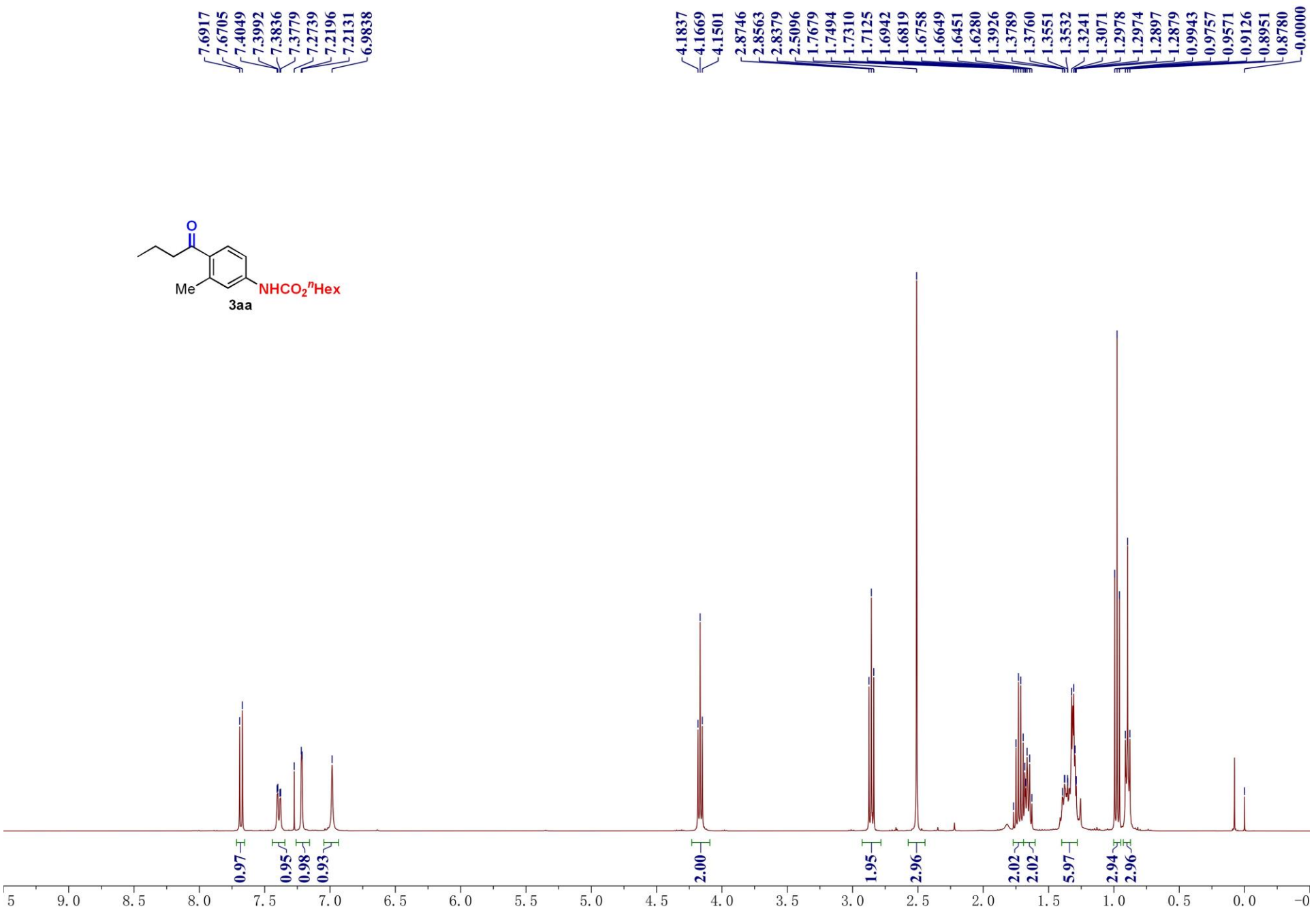

196.9264
153.2110
142.5079
132.0539
129.8652
117.5128
77.3180
77.0000
76.6811
65.8004
31.3938
28.7776
26.3665
25.4711
22.5141
13.9762
O
NHCO2nHex
3q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.9435
7.9216
7.5318
7.5096
7.2904
7.2802
4.1876
4.1707
4.1539
2.9406
2.9220
2.9032
1.7657
1.7471
1.7286
1.7100
1.6923
1.6762
1.6592
1.6391
1.6224
1.3803
1.3773
1.3594
1.3499
1.3140
1.3066
1.3039
1.2969
1.2800
1.2781
0.9199
0.9024
0.8879
0.8705
-0.0000
O
NHCO2nHex
3r
2.01
1.99
0.94
2.01
2.00
4.08
9.91
5.99
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

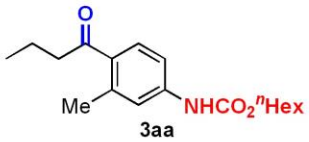

199.5214
153.3441
142.4789
131.7783
129.5176
117.5476
77.3192
77.0000
76.6828
65.6595
38.2483
31.4869
31.3426
28.7401
25.4114
24.1714
22.4547
13.9109
13.8763
O
NHCO2nHex
3r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.9433
7.9214
7.5245
7.5024
7.2768
7.2222
4.1889
4.1721
4.1552
2.9396
2.9212
2.9023
1.7579
1.7394
1.7228
1.7214
1.7042
1.7012
1.6790
1.6620
1.6579
1.6418
1.6251
1.3877
1.3768
1.3489
1.3361
1.3174
1.3096
1.3060
1.3002
1.2908
1.2828
1.2675
1.2661
0.9074
0.8901
0.8770
0.8593
0.0000
O
NHCO2nHex
3s
2.00
1.98
0.95
2.01
1.99
4.05
14.04
6.07

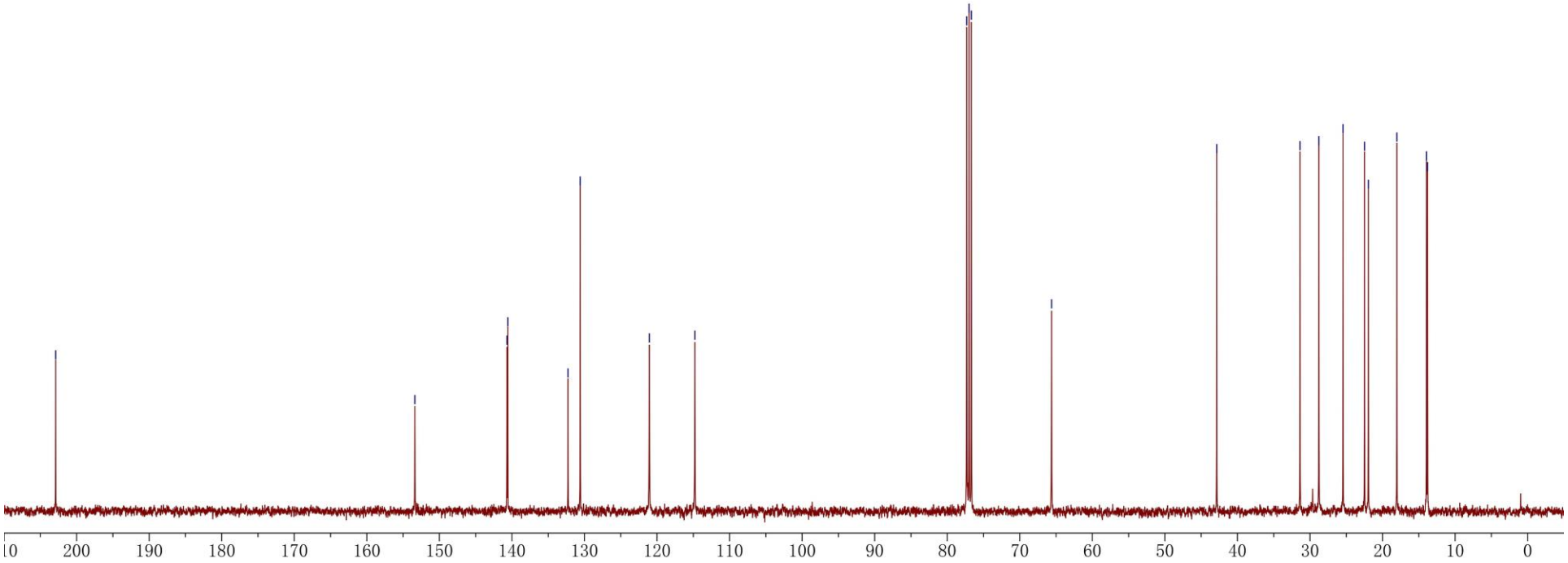

199.4987
153.3239
142.4388
131.8200
129.5339
117.5451
77.3173
77.0000
76.6815
65.6807
38.3107
31.6458
31.3576
29.2979
29.0904
28.7515
25.4260
24.4999
22.5541
22.4696
14.0107
13.9248
O
NHCO2nHex
3s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

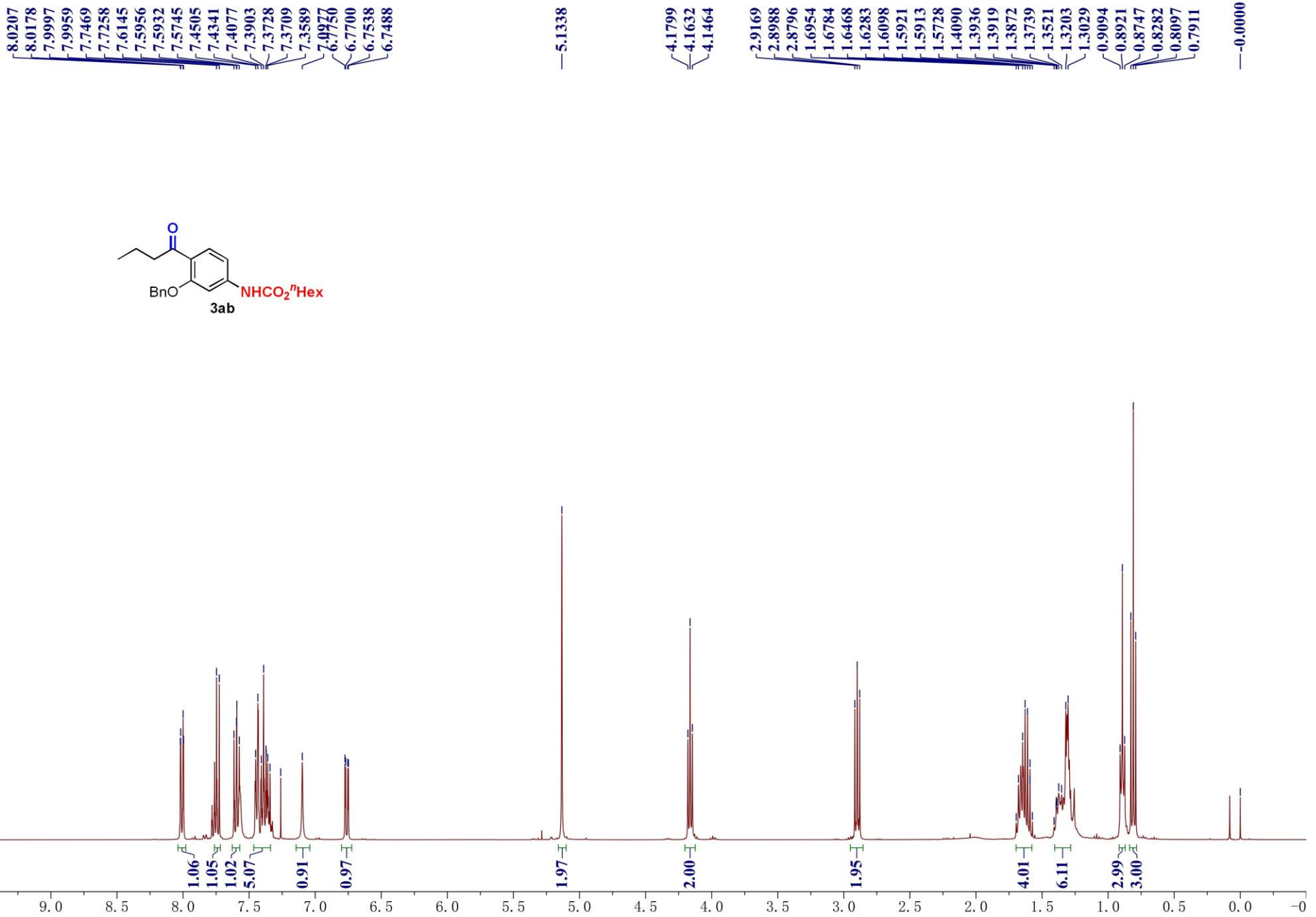

7.6917
7.6705
7.4049
7.3992
7.3836
7.3779
7.2739
7.2196
7.2131
6.9838
4.1837
4.1669
4.1501
2.8746
2.8563
2.8379
2.5096
1.7679
1.7494
1.7310
1.7125
1.6942
1.6819
1.6758
1.6649
1.6451
1.6280
1.3926
1.3789
1.3760
1.3551
1.3532
1.3241
1.3071
1.2978
1.2974
1.2897
1.2879
0.9943
0.9757
0.9571
0.9126
0.8951
0.8780
-0.0000
O
Me
NHCO2nHex
3aa
0.97
0.95
0.98
0.93
2.00
1.95
2.96
2.02
2.02
5.97
2.94
2.96
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

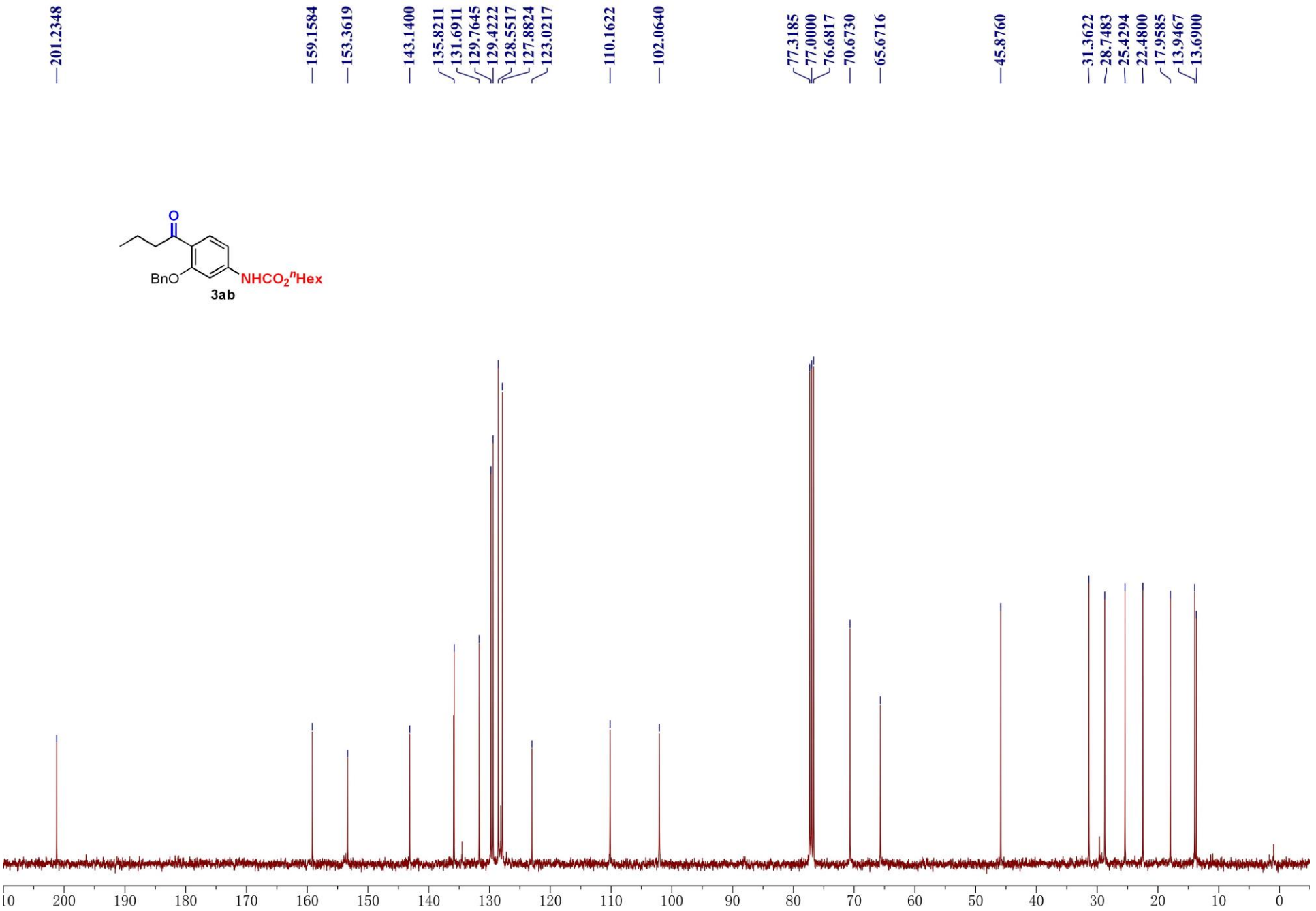
202.8810
153.3803
140.6873
140.5694
132.2739
130.5856
121.0648
114.7828
77.3190
77.0000
76.6829
65.6234
42.8585
31.3750
28.7699
25.4484
22.4864
21.9576
18.0212
13.9428
13.8019

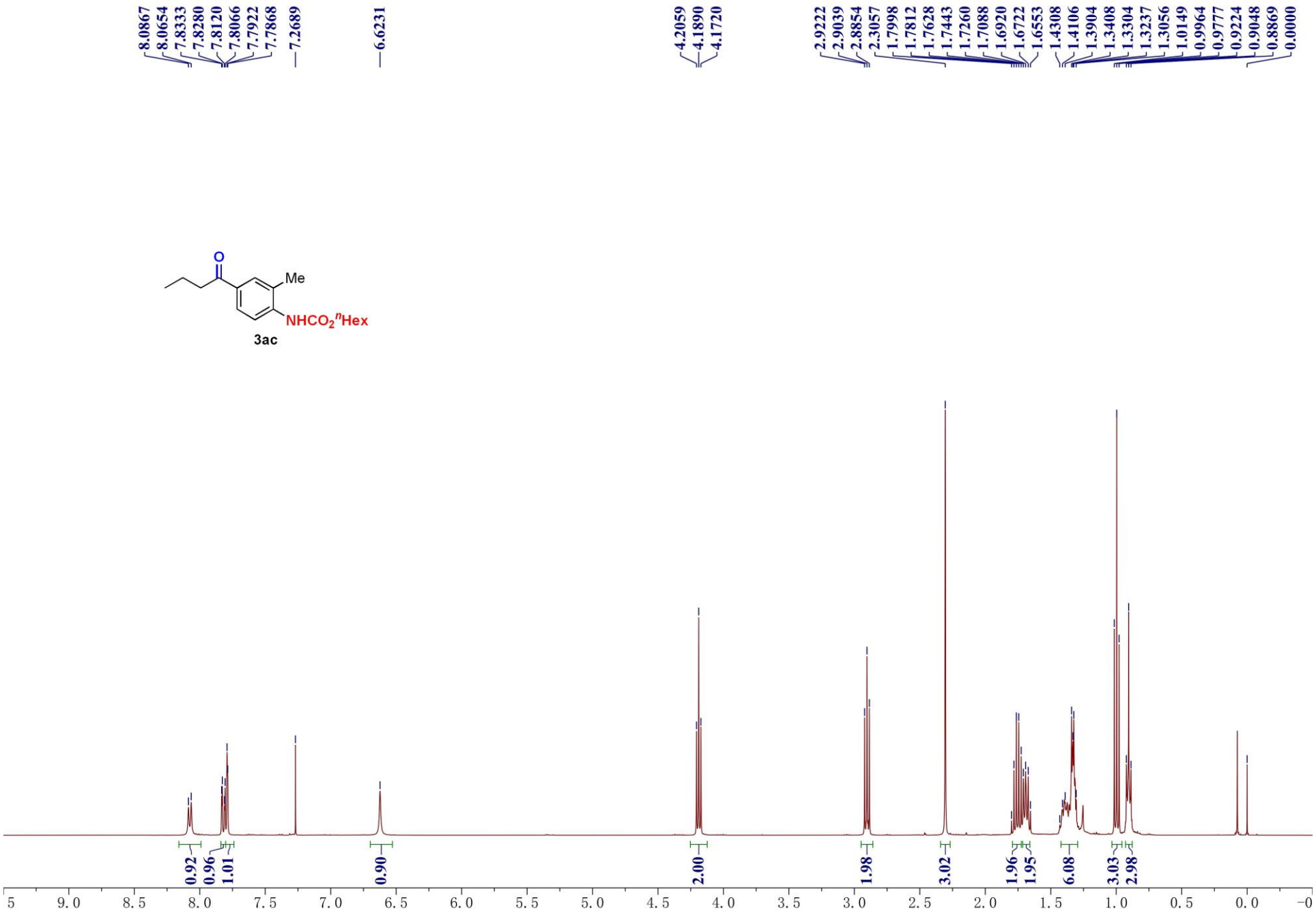


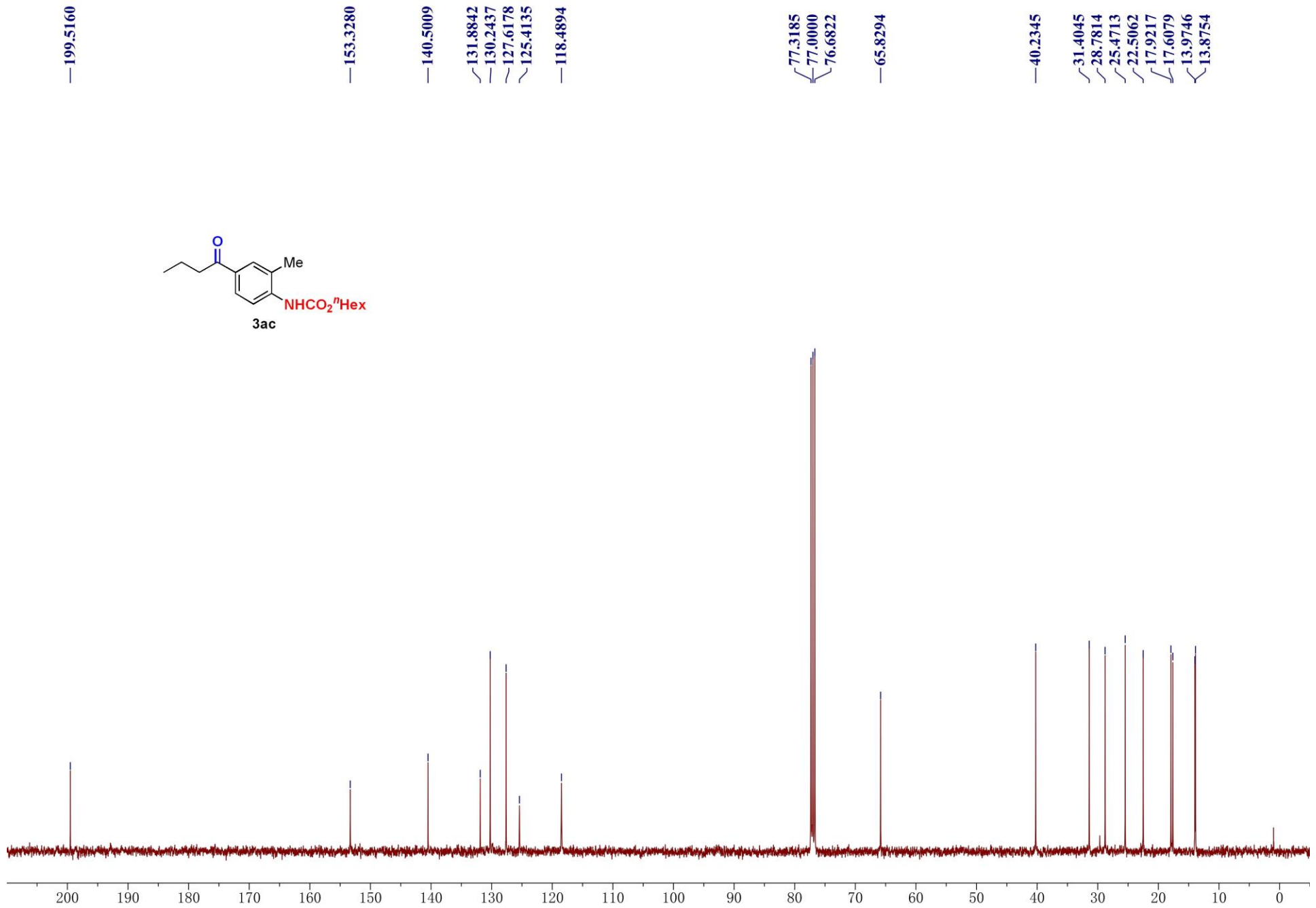
3aa

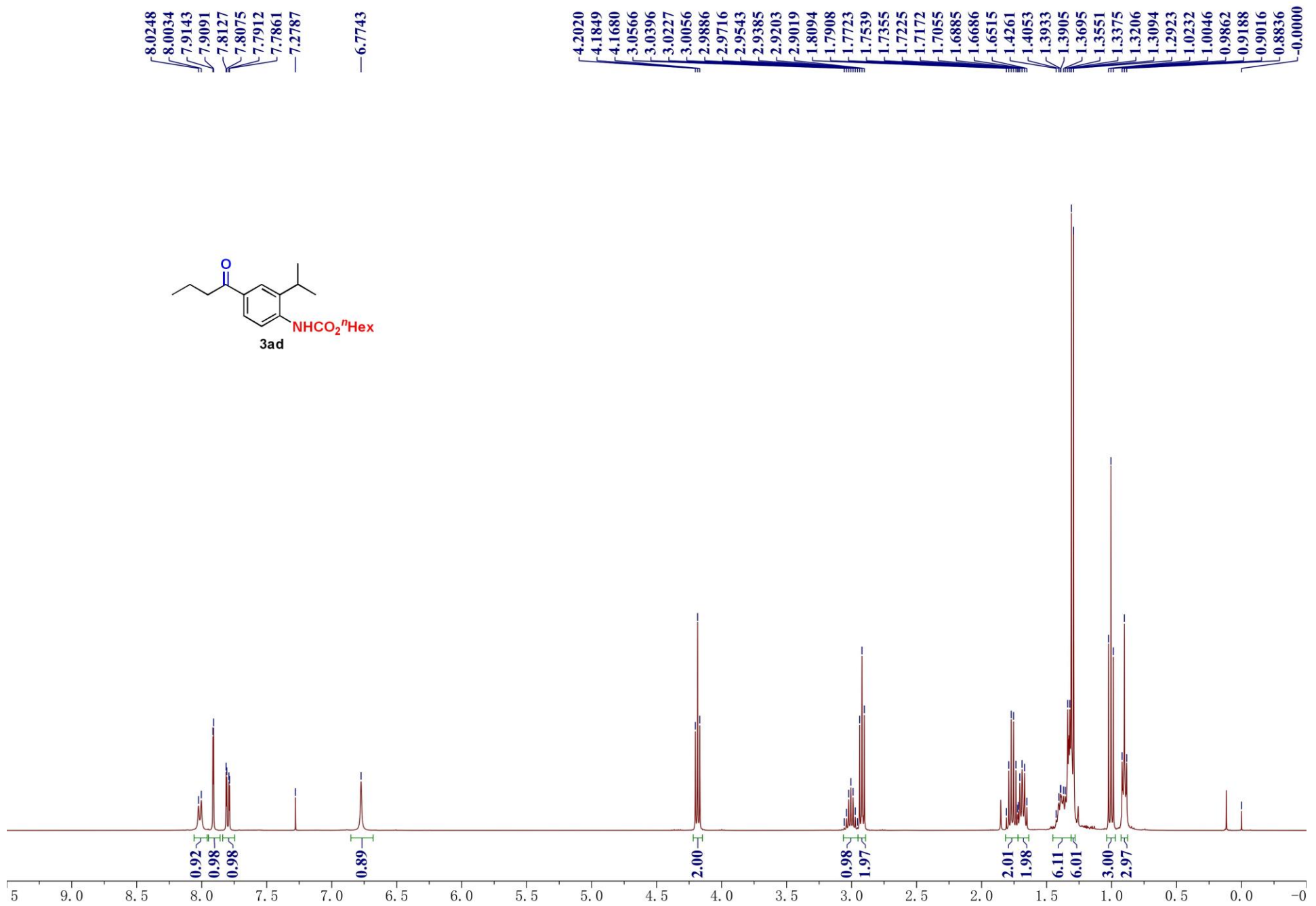


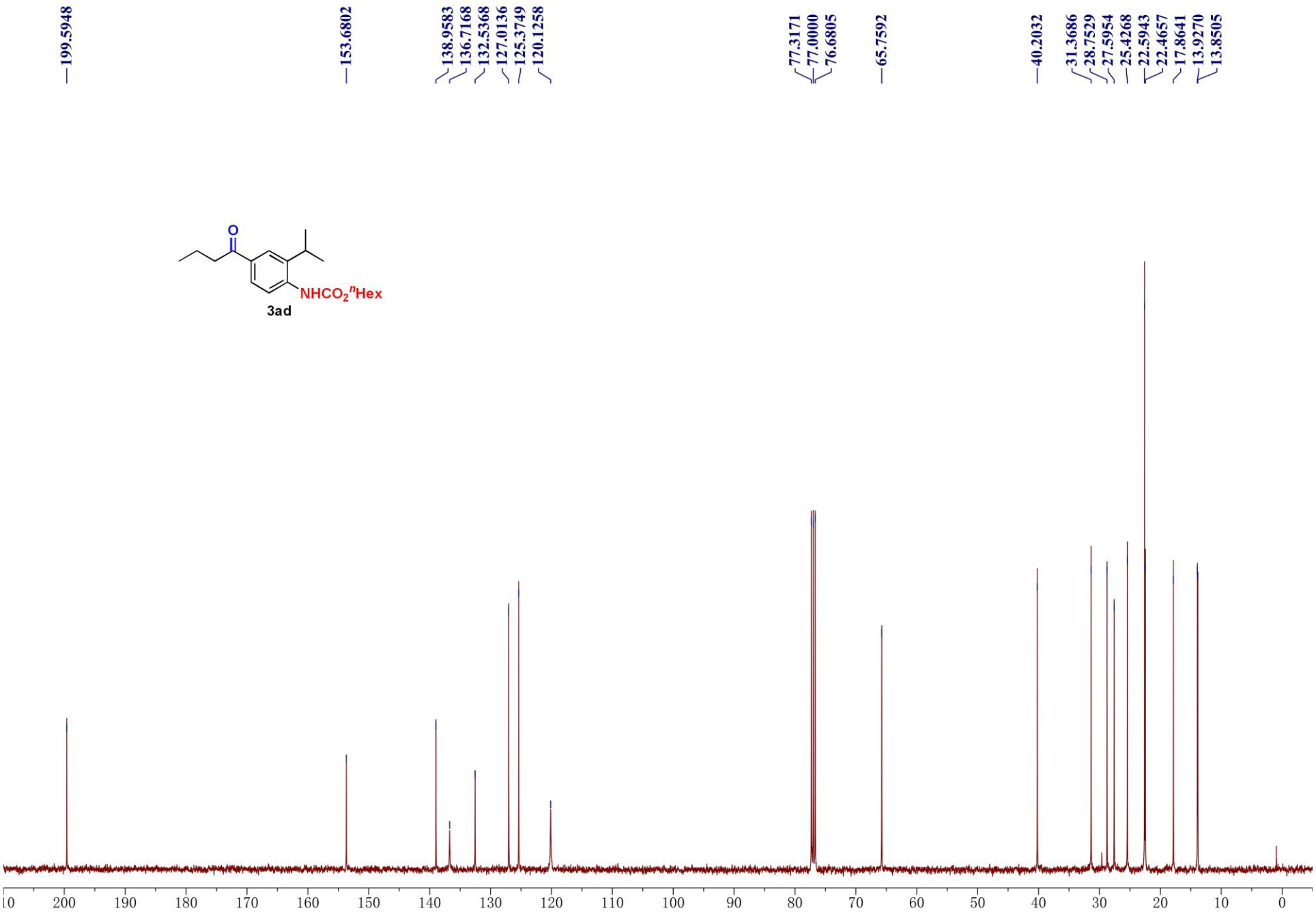

8.0207
8.0178
7.9997
7.9959
7.7469
7.7258
7.6145
7.5956
7.5932
7.5745
7.4505
7.4341
7.4077
7.3903
7.3728
7.3709
7.3589
7.0977
6.7750
6.7700
6.7538
6.7488
5.1338
4.1799
4.1632
4.1464
2.9169
2.8988
2.8796
1.6954
1.6784
1.6468
1.6283
1.6098
1.5921
1.5913
1.5728
1.4090
1.3936
1.3919
1.3872
1.3739
1.3521
1.3203
1.3029
0.9094
0.8921
0.8747
0.8282
0.8097
0.7911
-0.0000
O
BnO
NHCO2nHex
3ab
1.06
1.05
1.02
5.07
0.91
0.97
1.97
2.00
1.95
4.01
6.11
2.99
3.00

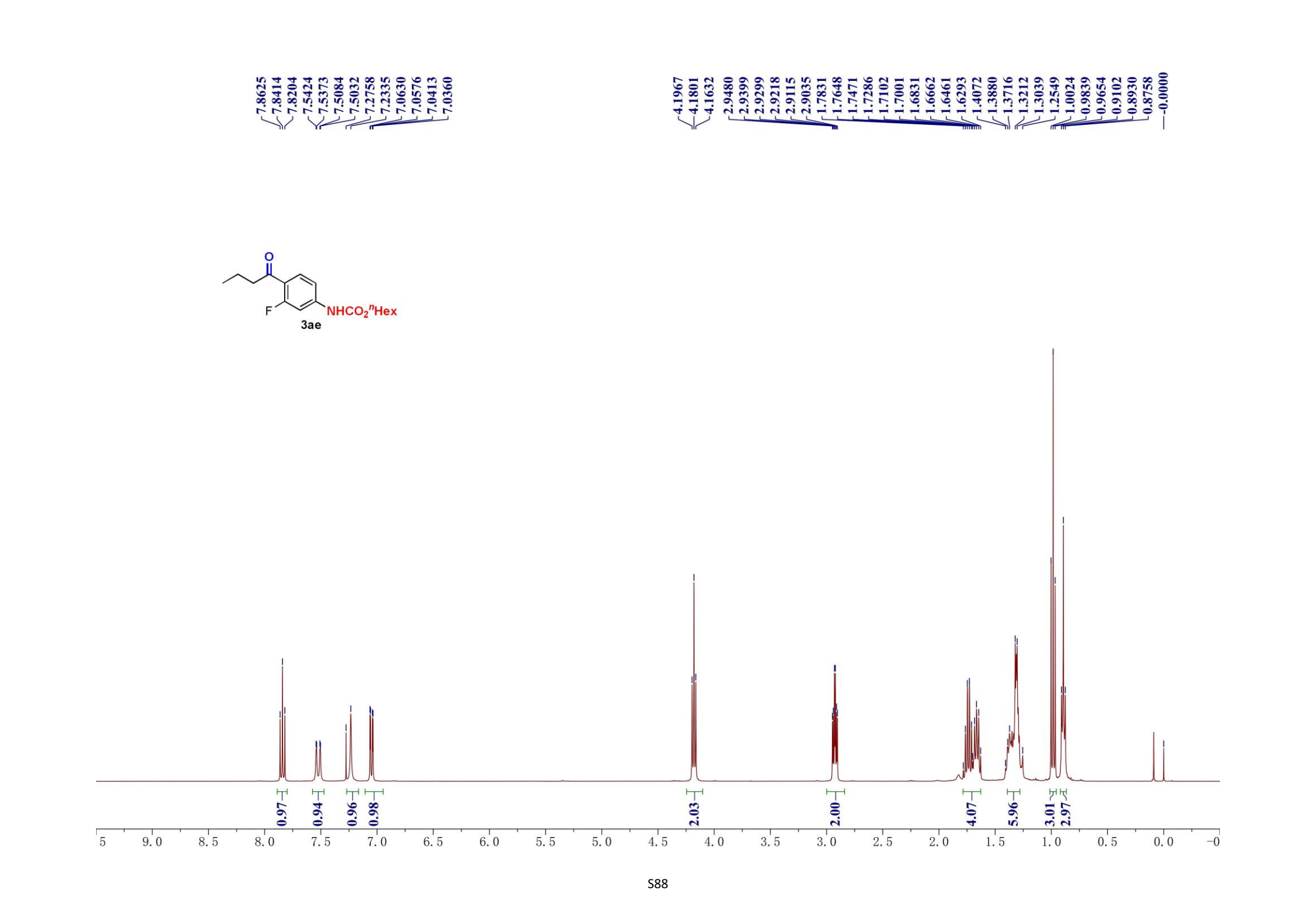

201.2348
159.1584
153.3619
143.1400
135.8211
131.6911
129.7645
129.4222
128.5517
127.8824
123.0217
110.1622
102.0640
77.3185
77.0000
76.6817
70.6730
65.6716
45.8760
31.3622
28.7483
25.4294
22.4800
17.9585
13.9467
13.6900
O
BnO
NHCO2nHex
3ab
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

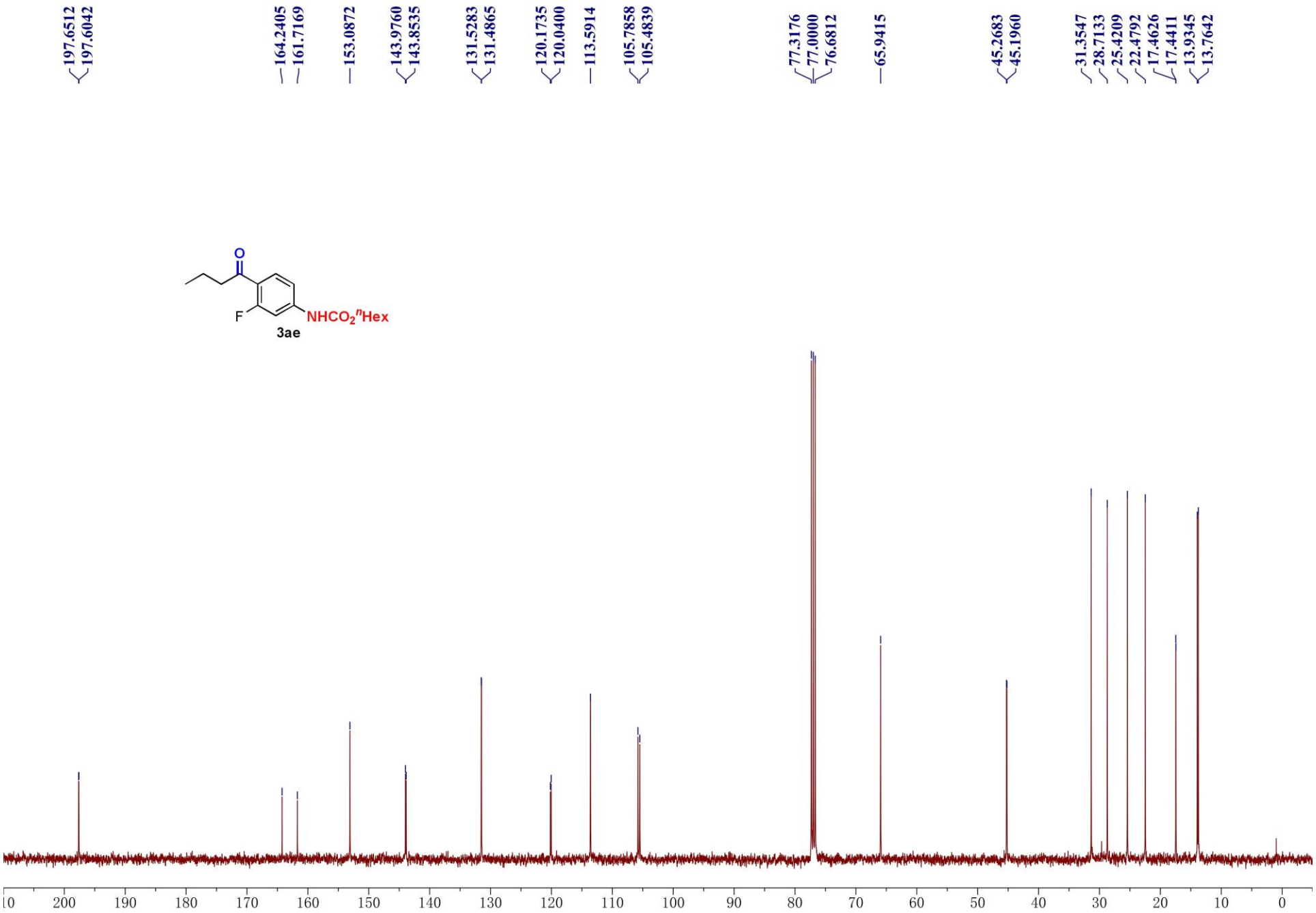

8.0867
8.0654
7.8333
7.8280
7.8120
7.8066
7.7922
7.7868
7.2689
6.6231
4.2059
4.1890
4.1720
2.9222
2.9039
2.8854
2.3057
1.7998
1.7812
1.7628
1.7443
1.7260
1.7088
1.6920
1.6722
1.6553
1.4308
1.4106
1.3904
1.3408
1.3304
1.3237
1.3056
1.0149
0.9964
0.9777
0.9224
0.9048
0.8869
0.0000
O
Me
NHCO2nHex
3ac
0.92
0.96
1.01
0.90
2.00
1.98
3.02
1.96
1.95
6.08
3.03
2.98

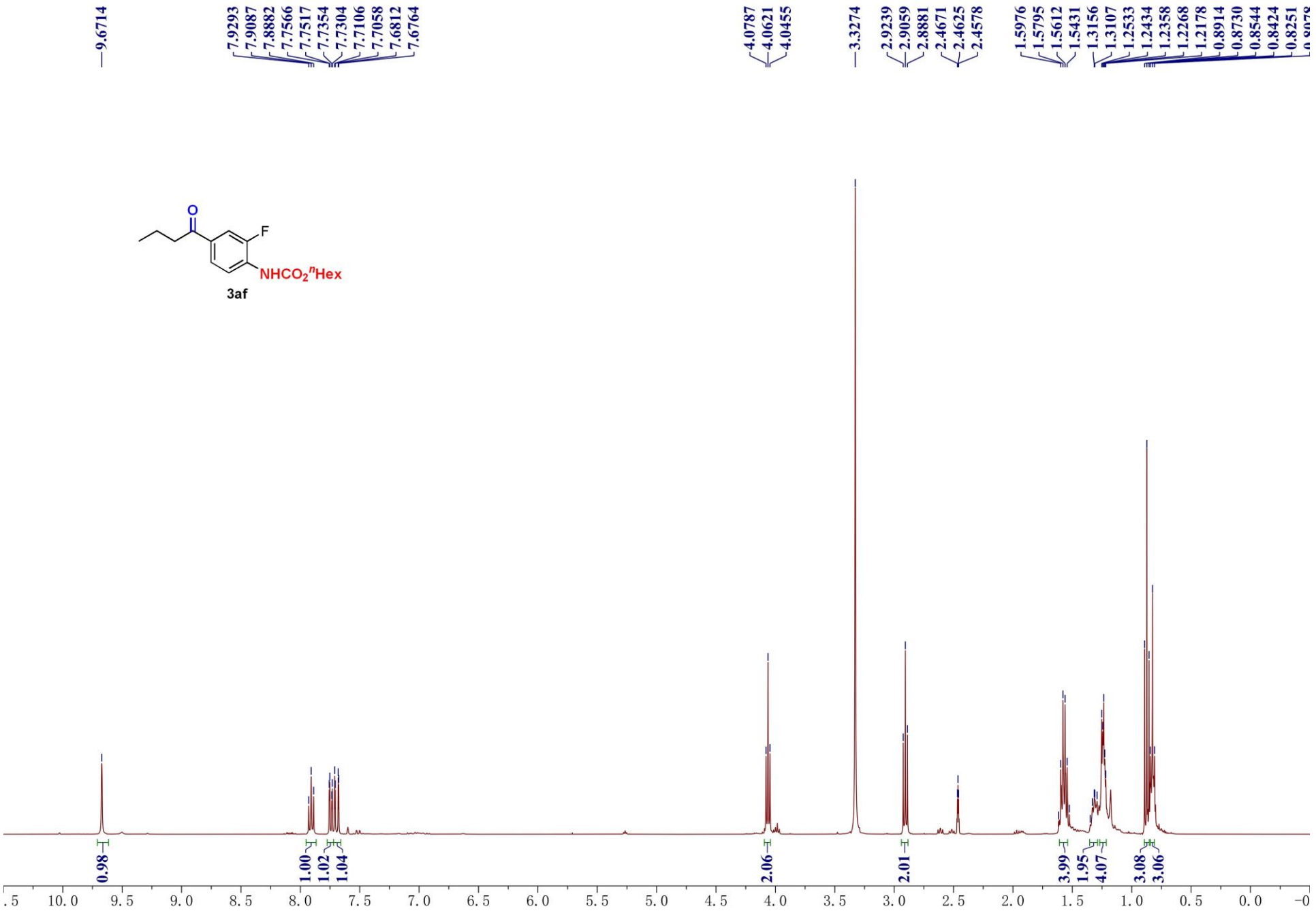

199.5160
153.3280
140.5009
131.8842
130.2437
127.6178
125.4135
118.4894
77.3185
77.0000
76.6822
65.8294
40.2345
31.4045
28.7814
25.4713
22.5062
17.9217
17.6079
13.9746
13.8754
O
Me
NHCO2nHex
3ac
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

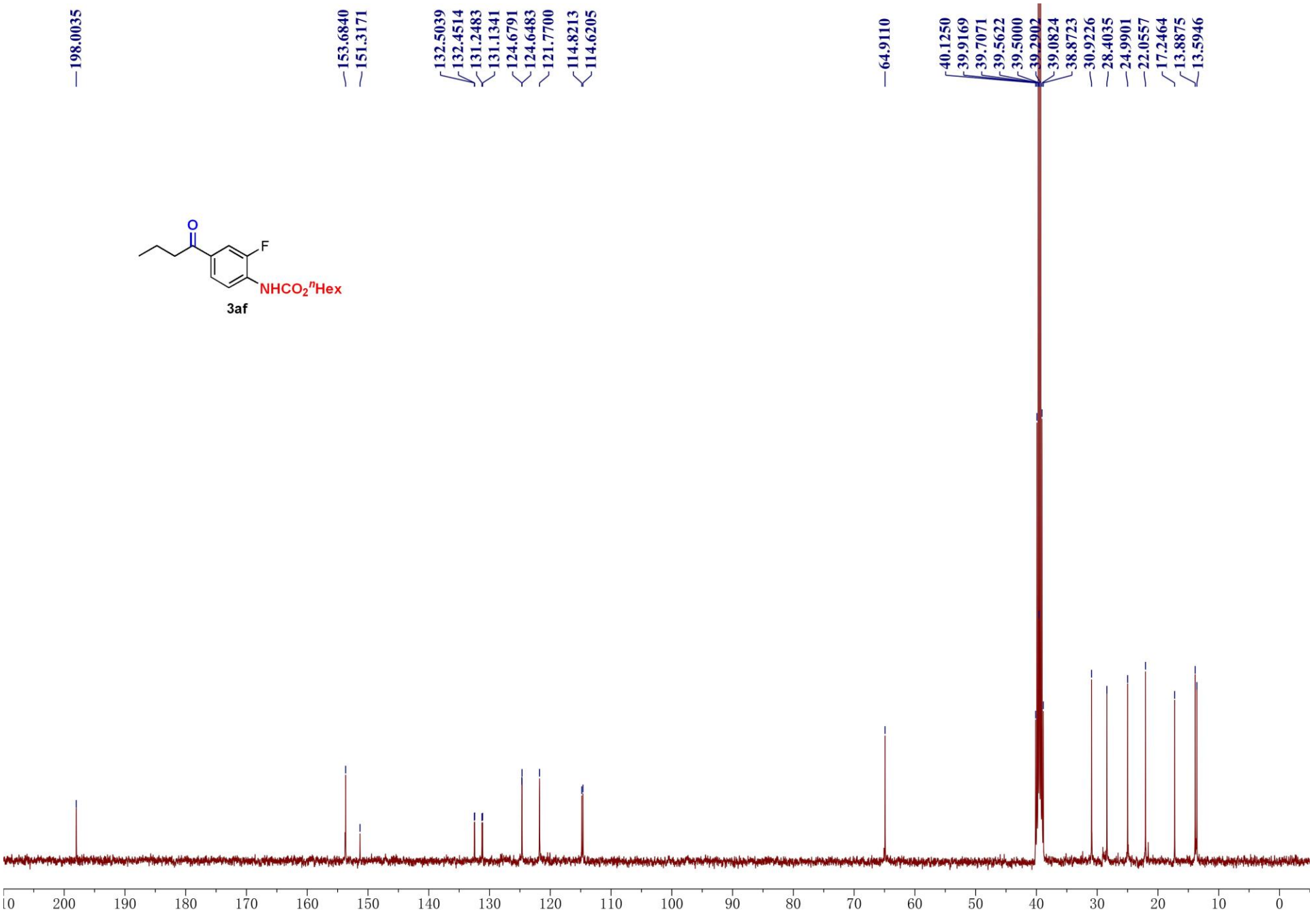

8.0248
8.0034
7.9143
7.9091
7.8127
7.8075
7.7912
7.7861
7.2787
6.7743
4.2020
4.1849
4.1680
3.0566
3.0396
3.0227
3.0056
2.9886
2.9716
2.9543
2.9385
2.9203
2.9019
1.8094
1.7908
1.7723
1.7539
1.7355
1.7225
1.7172
1.7055
1.6885
1.6686
1.6515
1.4261
1.4053
1.3933
1.3905
1.3695
1.3551
1.3375
1.3206
1.3094
1.2923
1.0232
1.0046
0.9862
0.9188
0.9016
0.8836
-0.0000
O
NHCO2nHex
3ad
0.92
0.98
0.98
0.89
2.00
0.98
1.97
2.01
1.98
6.11
6.01
3.00
2.97
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

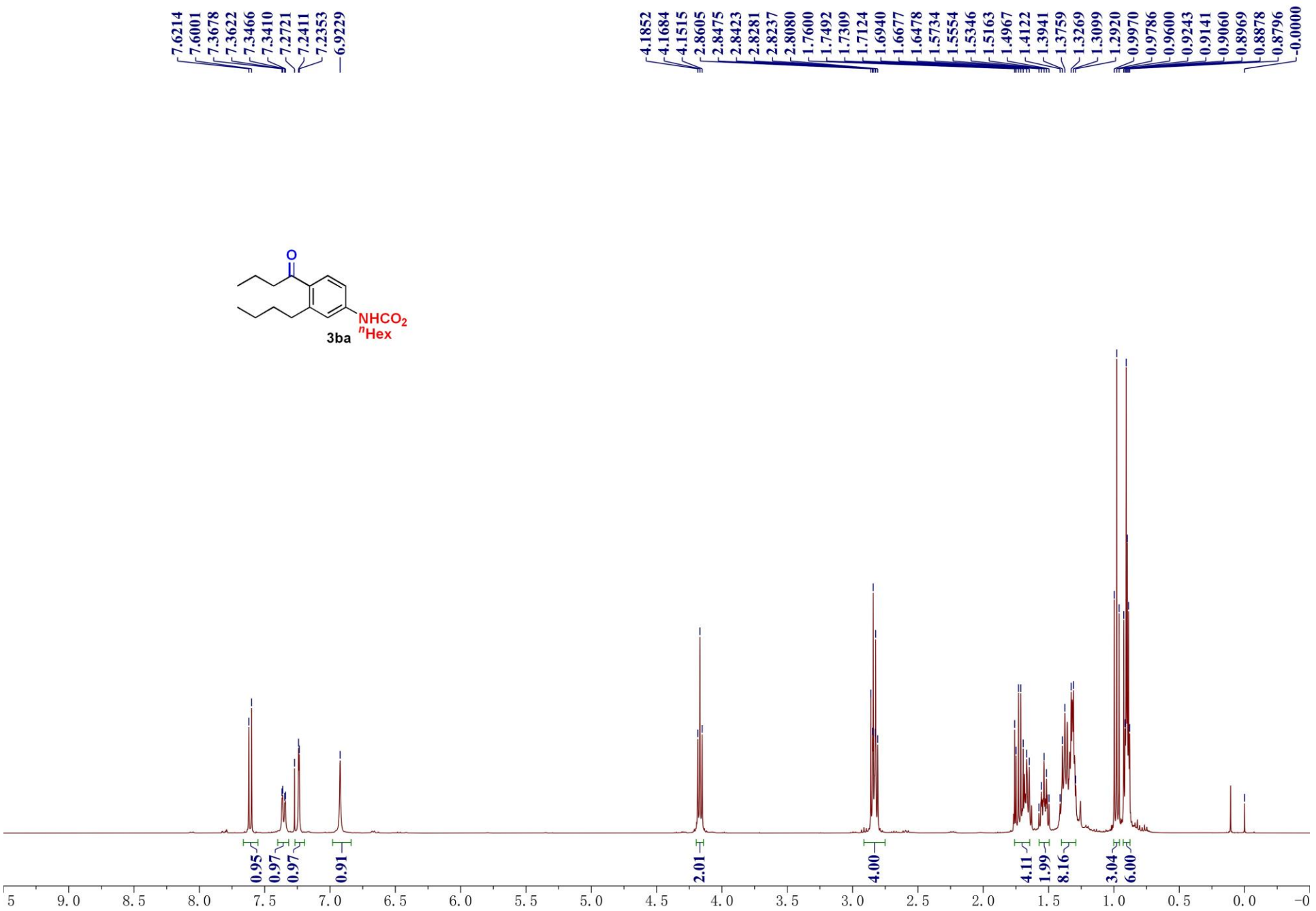

199.5948
153.6802
138.9583
136.7168
132.5368
127.0136
125.3749
120.1258
77.3171
77.0000
76.6805
65.7592
40.2032
31.3686
28.7529
27.5954
25.4268
22.5943
22.4657
17.8641
13.9270
13.8505
O
NHCO2nHex
3ad
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

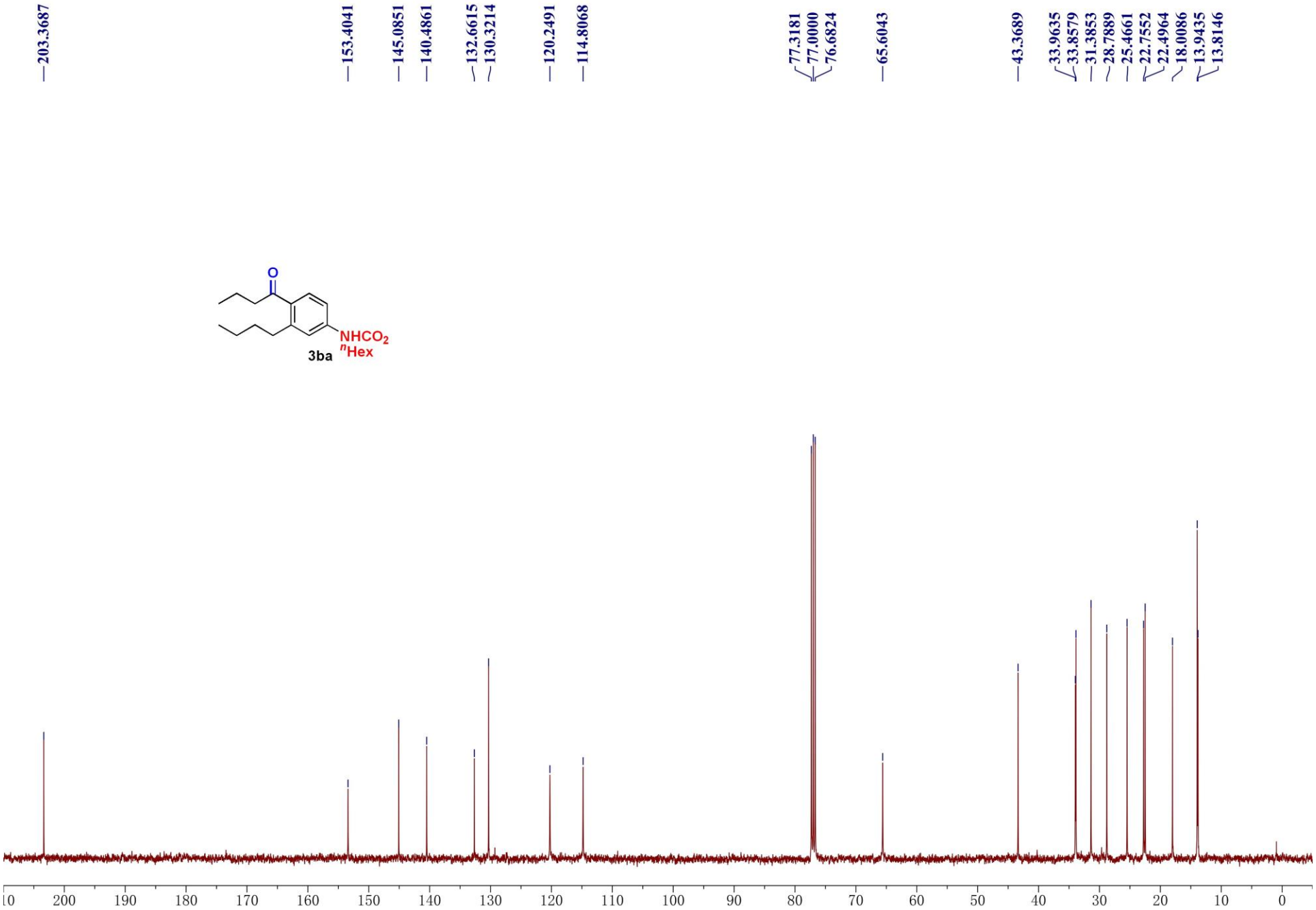

7.8625
7.8414
7.8204
7.5424
7.5373
7.5084
7.5032
7.2758
7.2335
7.0630
7.0576
7.0413
7.0360
4.1967
4.1801
4.1632
2.9480
2.9399
2.9299
2.9218
2.9115
2.9035
1.7831
1.7648
1.7471
1.7286
1.7102
1.7001
1.6831
1.6662
1.6461
1.6293
1.4072
1.3880
1.3716
1.3212
1.3039
1.2549
1.0024
0.9839
0.9654
0.9102
0.8930
0.8758
-0.0000
O
F
NHCO2nHex
3ae
0.97
0.94
0.96
0.98
2.03
2.00
4.07
5.96
3.01
2.97

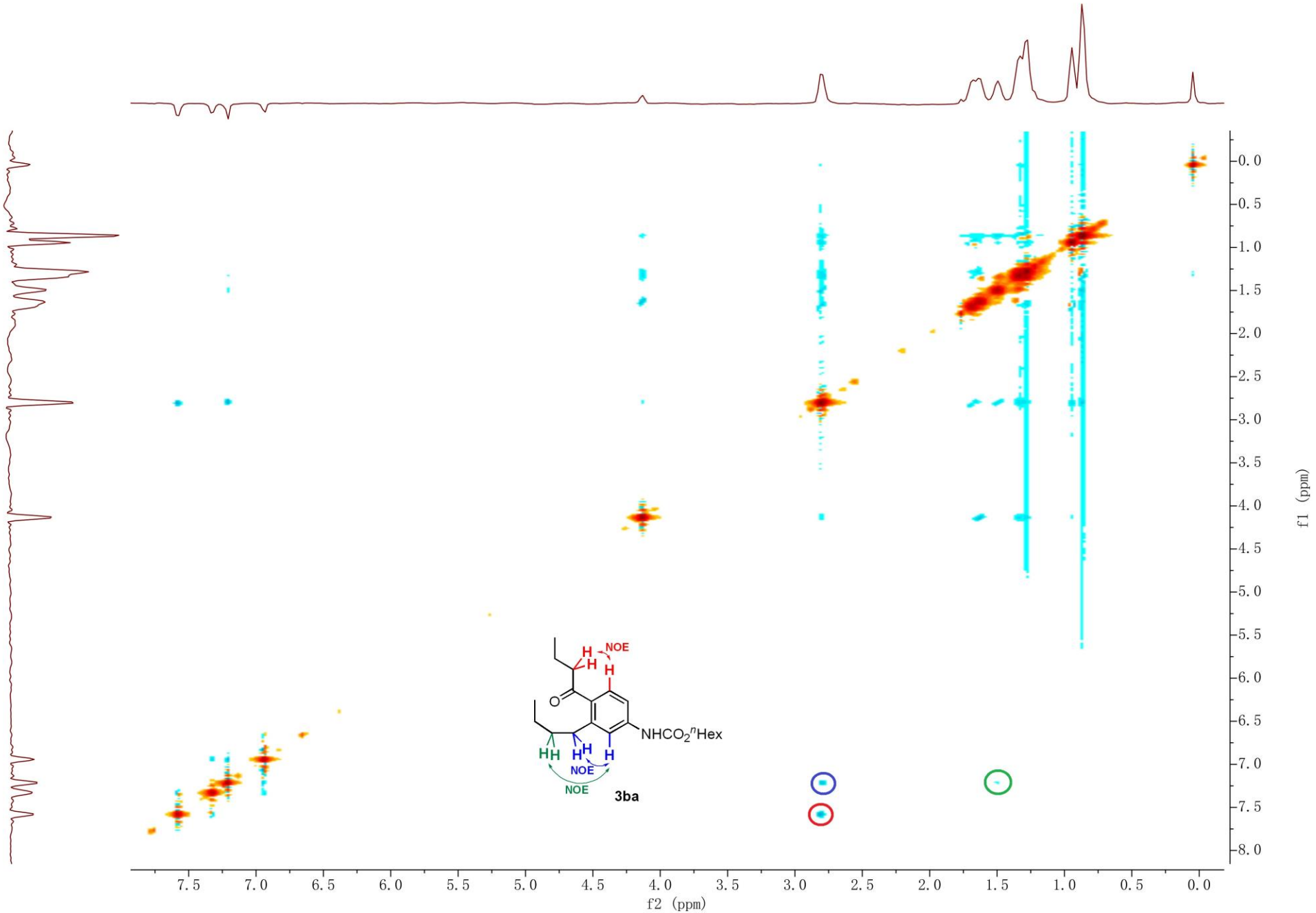

197.6512
197.6042
164.2405
161.7169
153.0872
143.9760
143.8535
131.5283
131.4865
120.1735
120.0400
113.5914
105.7858
105.4839
77.3176
77.0000
76.6812
65.9415
45.2683
45.1960
31.3547
28.7133
25.4209
22.4792
17.4626
17.4411
13.9345
13.7642
O
F
NHCO2nHex
3ae
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

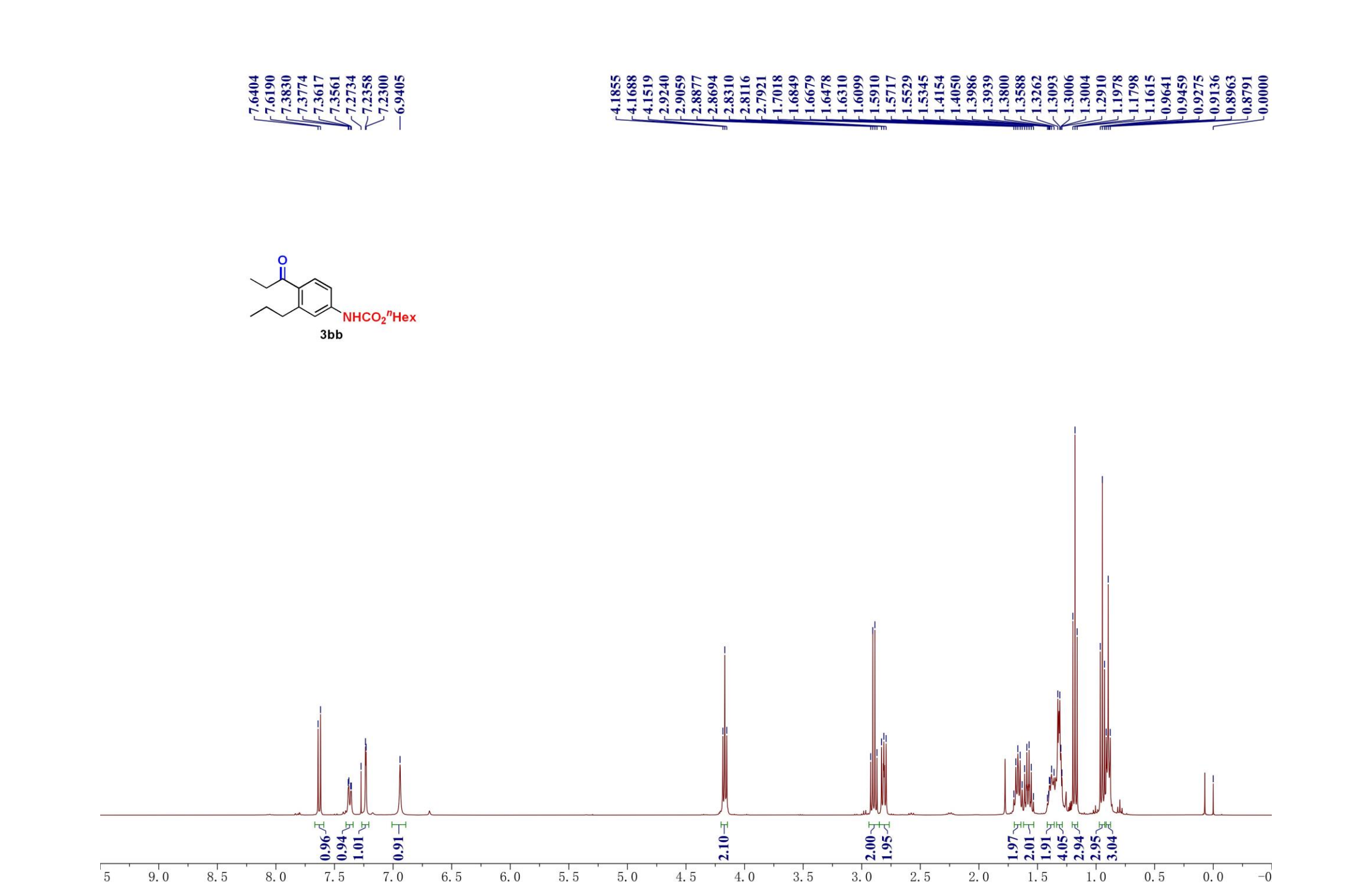

9.6714
7.9293
7.9087
7.8882
7.7566
7.7517
7.7354
7.7304
7.7106
7.7058
7.6812
7.6764
4.0787
4.0621
4.0455
3.3274
2.9239
2.9059
2.8881
2.4671
2.4625
2.4578
1.5976
1.5795
1.5612
1.5431
1.3156
1.3107
1.2533
1.2434
1.2358
1.2268
1.2178
0.8914
0.8730
0.8544
0.8424
0.8251
O
F
NHCO2nHex
3af
0.98
1.00
1.02
1.04
2.06
2.01
3.99
1.95
4.07
3.08
3.06

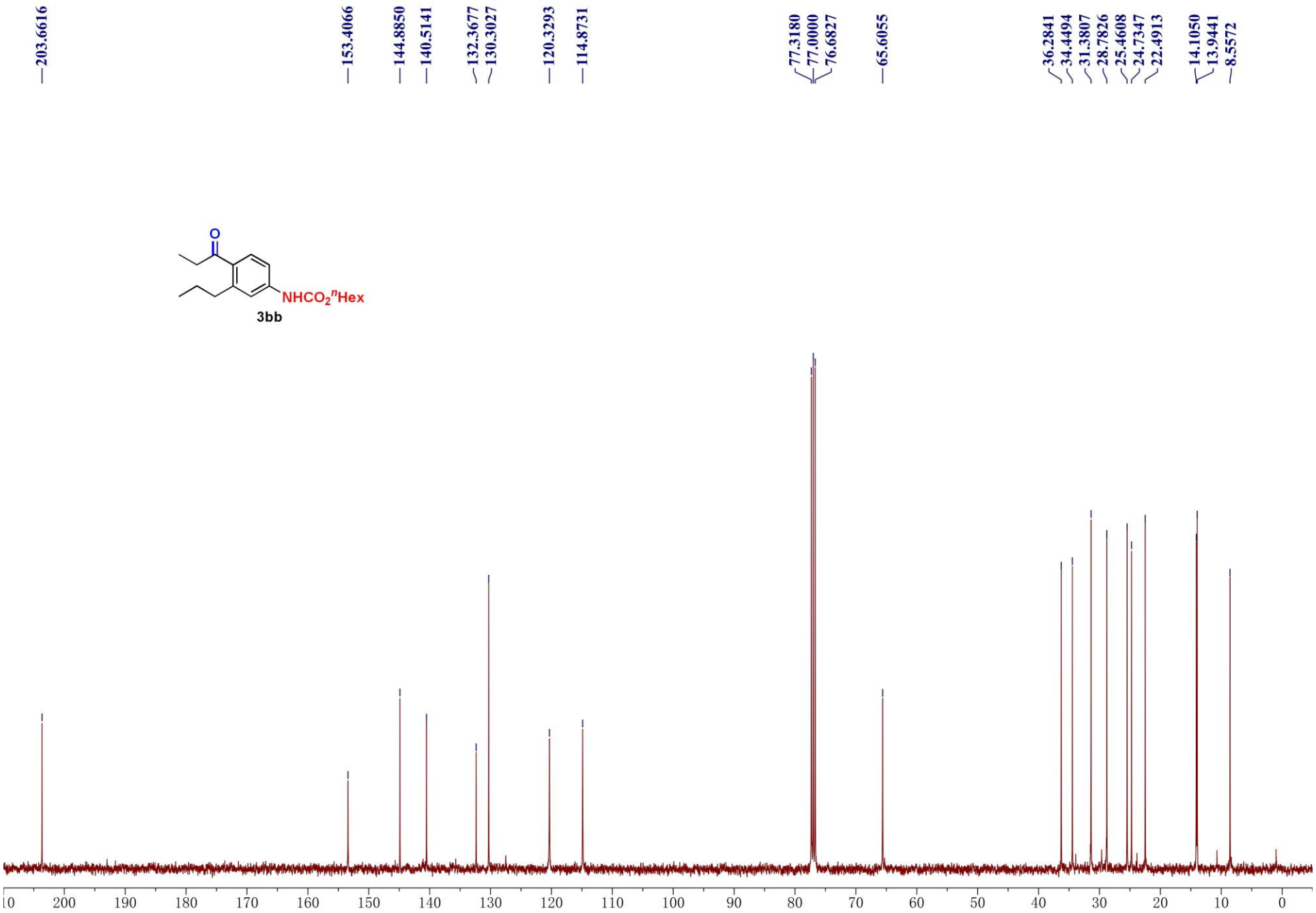

198.0035
153.6840
151.3171
132.5039
132.4514
131.2483
131.1341
124.6791
124.6483
121.7700
114.8213
114.6205
64.9110
40.1250
39.9169
39.7071
39.5622
39.5000
39.2902
39.0824
38.8723
30.9226
28.4035
24.9901
22.0557
17.2464
13.8875
13.5946
O
F
NHCO2nHex
3af
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

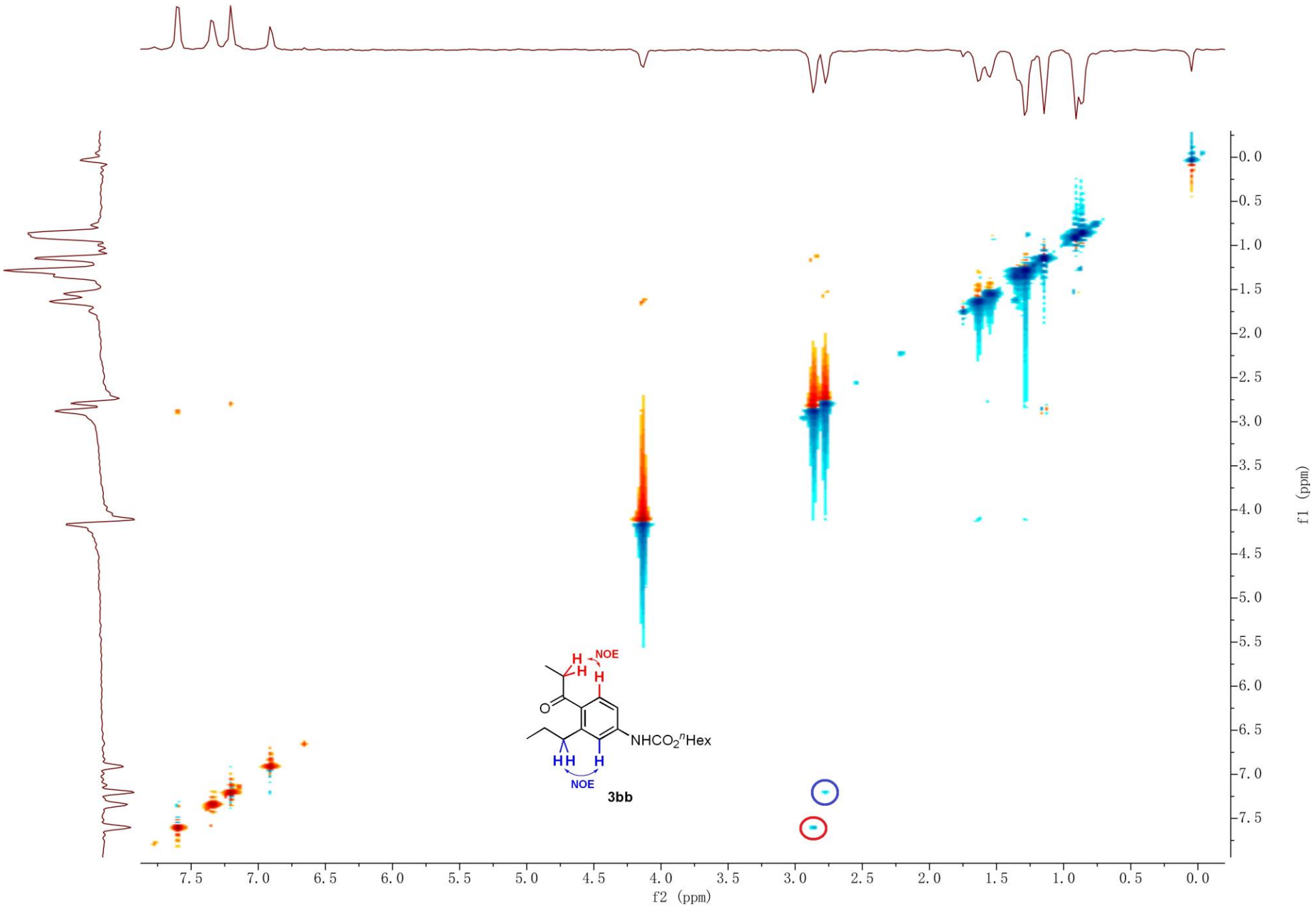

7.6214
7.6001
7.3678
7.3622
7.3466
7.3410
7.2721
7.2411
7.2353
6.9229
4.1852
4.1684
4.1515
2.8605
2.8475
2.8423
2.8281
2.8237
2.8080
1.7600
1.7492
1.7309
1.7124
1.6940
1.6677
1.6478
1.5734
1.5554
1.5346
1.5163
1.4967
1.4122
1.3941
1.3759
1.3269
1.3099
1.2920
0.9970
0.9786
0.9600
0.9243
0.9141
0.9060
0.8969
0.8878
0.8796
-0.0000
O
NHCO2
nHex
3ba
0.95
0.97
0.97
0.91
2.01
4.00
4.11
1.99
8.16
3.04
6.00

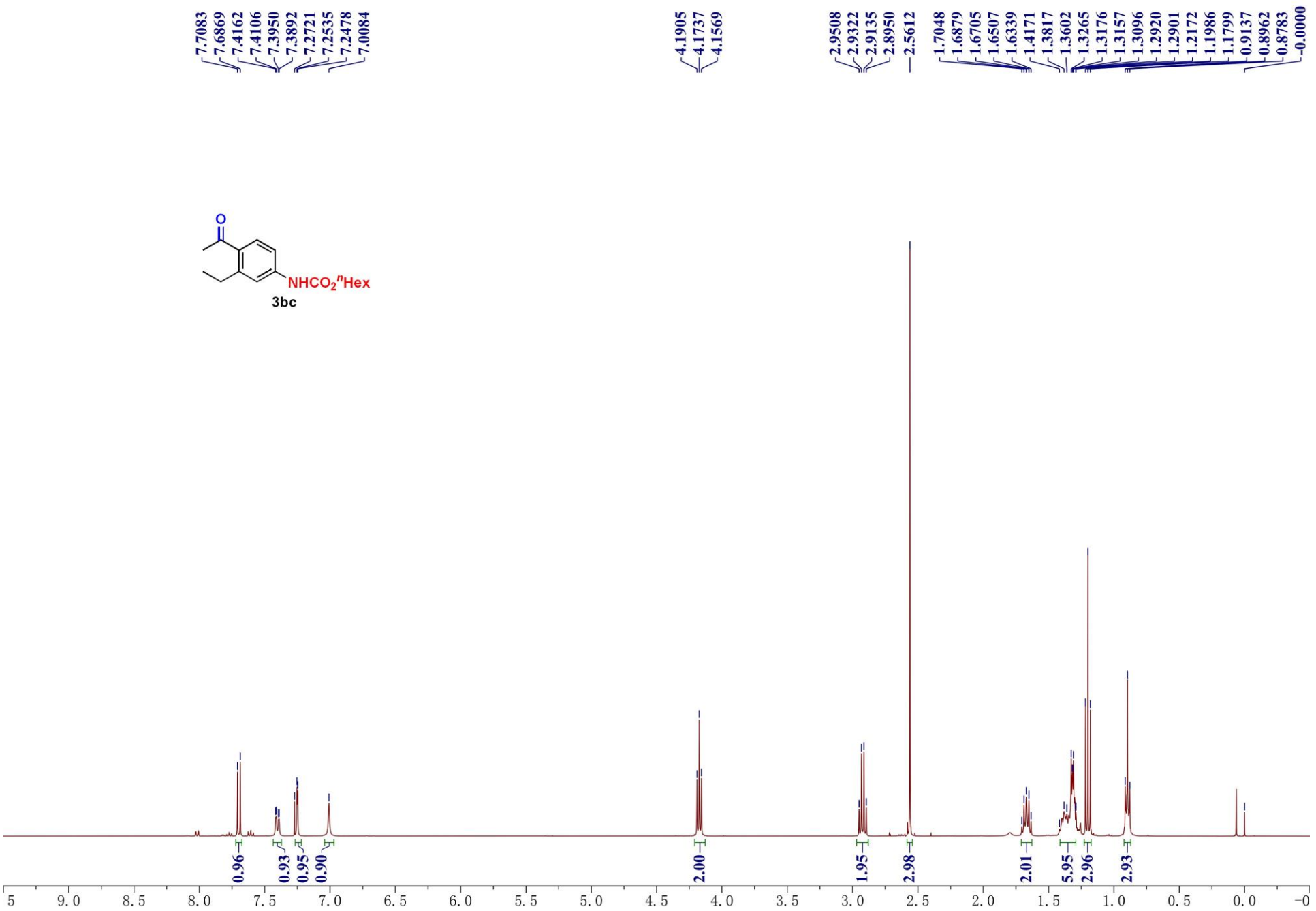

203.3687
153.4041
145.0851
140.4861
132.6615
130.3214
120.2491
114.8068
77.3181
77.0000
76.6824
65.6043
43.3689
33.9635
33.8579
31.3853
28.7889
25.4661
22.7552
22.4964
18.0086
13.9435
13.8146
O
NHCO2
nHex
3ba
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

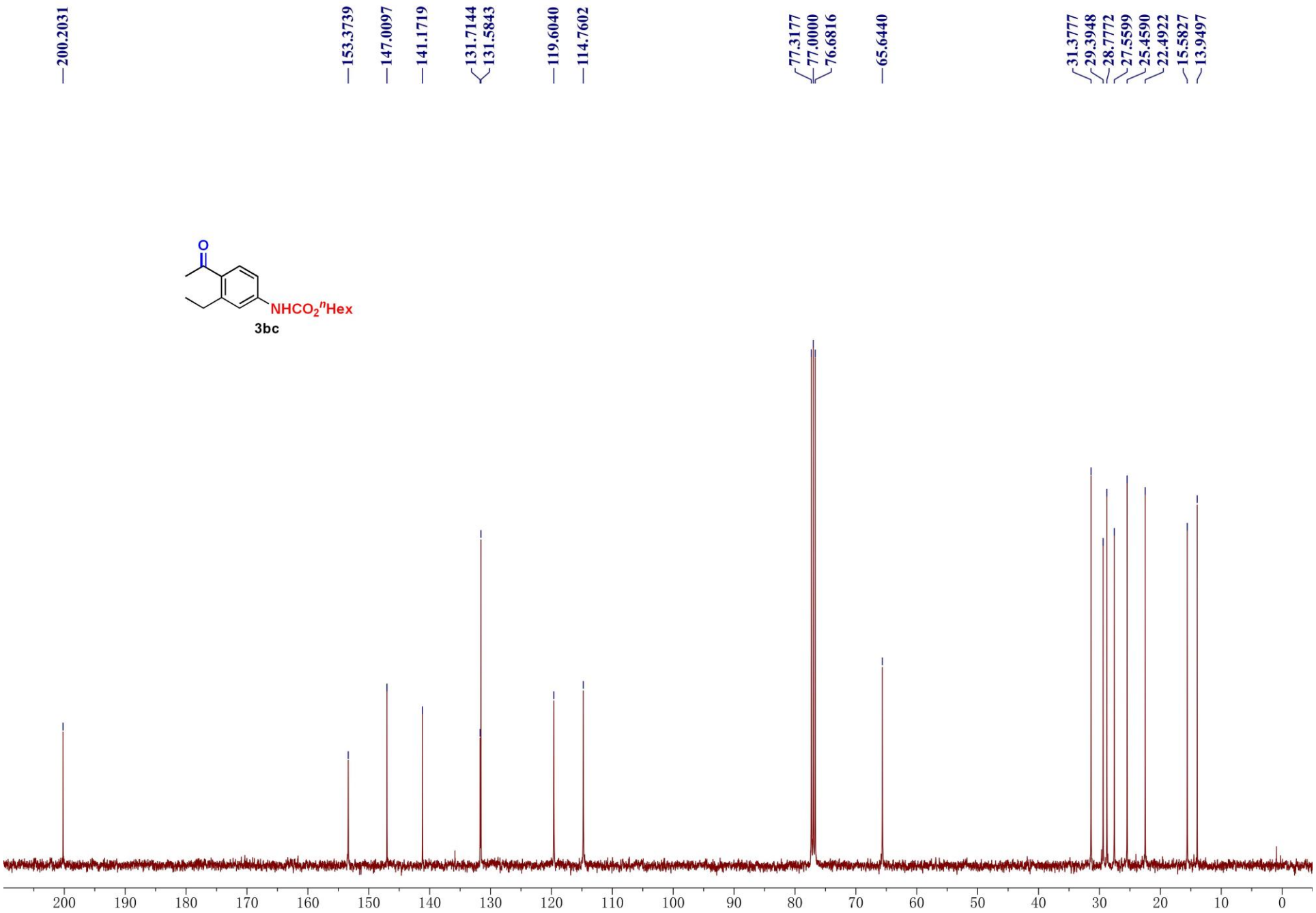

NOE
NOE
NOE
NHCO2nHex
3ba
f2 (ppm)
f1 (ppm)

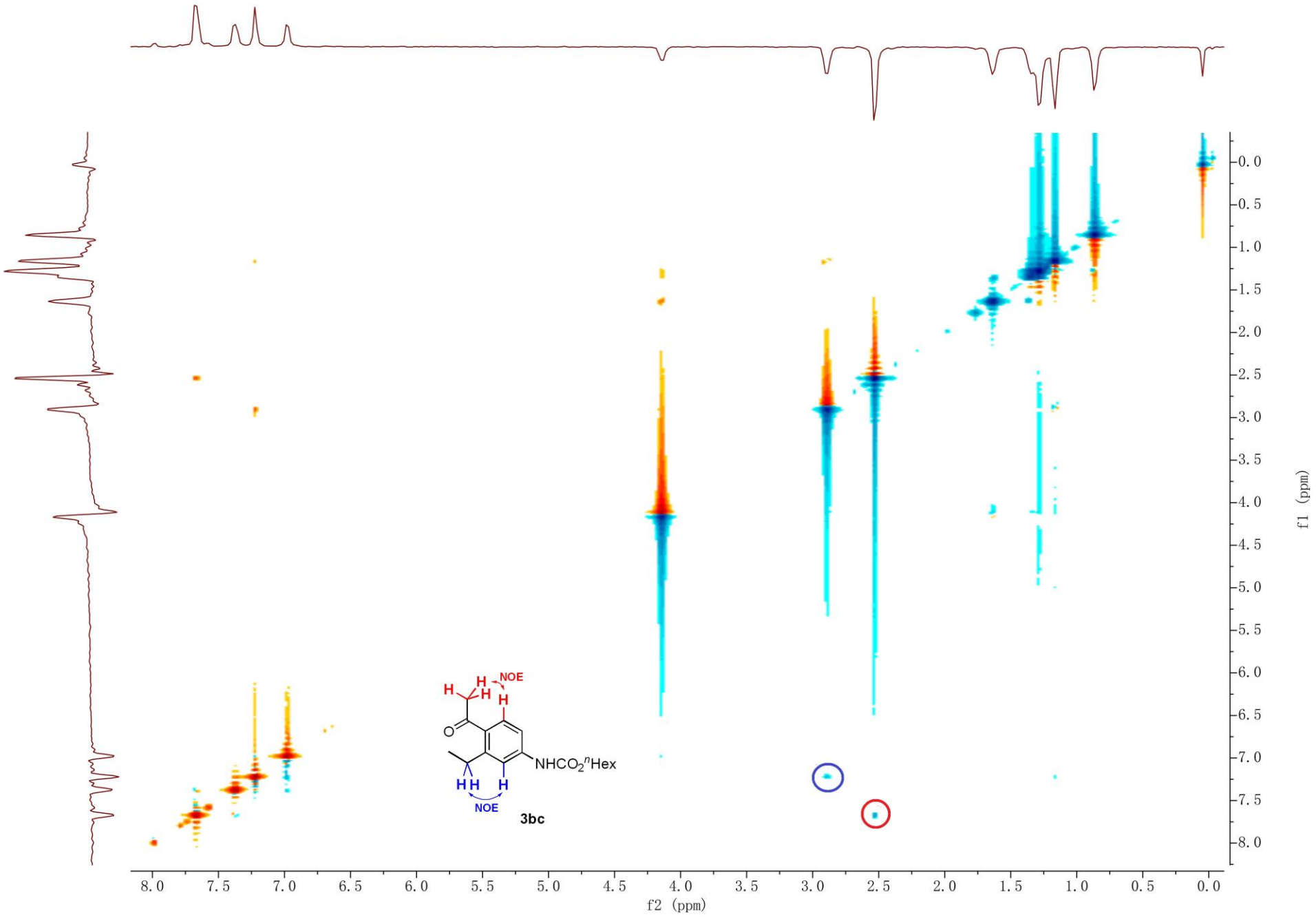

7.6404
7.6190
7.3830
7.3774
7.3617
7.3561
7.2734
7.2358
7.2300
6.9405
4.1855
4.1688
4.1519
2.9240
2.9059
2.8877
2.8694
2.8310
2.8116
2.7921
1.7018
1.6849
1.6679
1.6478
1.6310
1.6099
1.5910
1.5717
1.5529
1.5345
1.4154
1.4050
1.3986
1.3939
1.3800
1.3588
1.3262
1.3093
1.3006
1.3004
1.2910
1.1978
1.1798
1.1615
0.9641
0.9459
0.9275
0.9136
0.8963
0.8791
0.0000
O
NHCO2nHex
3bb
0.96
0.94
1.01
0.91
2.10
2.00
1.95
1.97
2.01
1.91
4.05
2.94
2.95
3.04
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

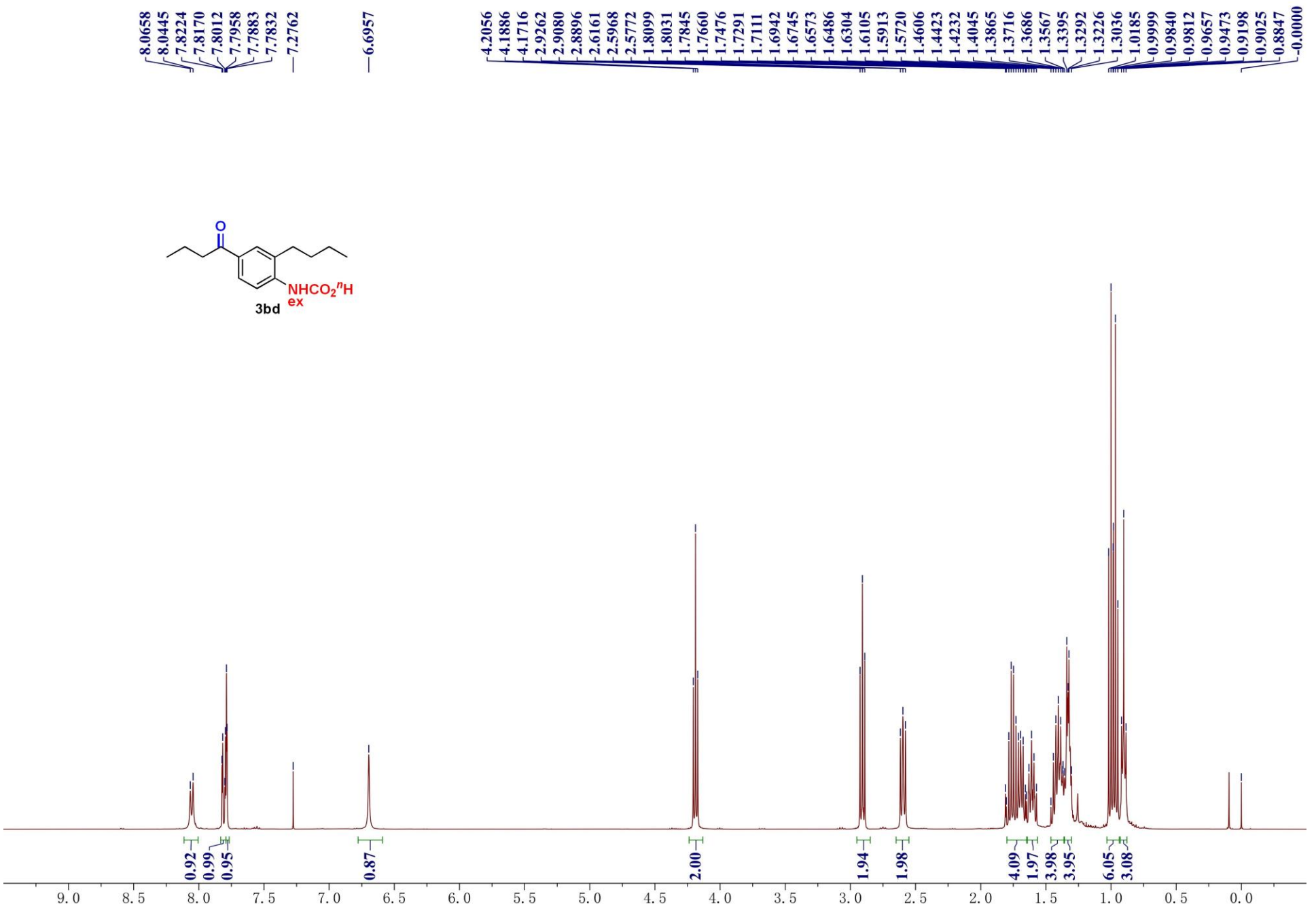

203.6616
153.4066
144.8850
140.5141
132.3677
130.3027
120.3293
114.8731
77.3180
77.0000
76.6827
65.6055
36.2841
34.4494
31.3807
28.7826
25.4608
24.7347
22.4913
14.1050
13.9441
8.5572
O
NHCO2nHex
3bb
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

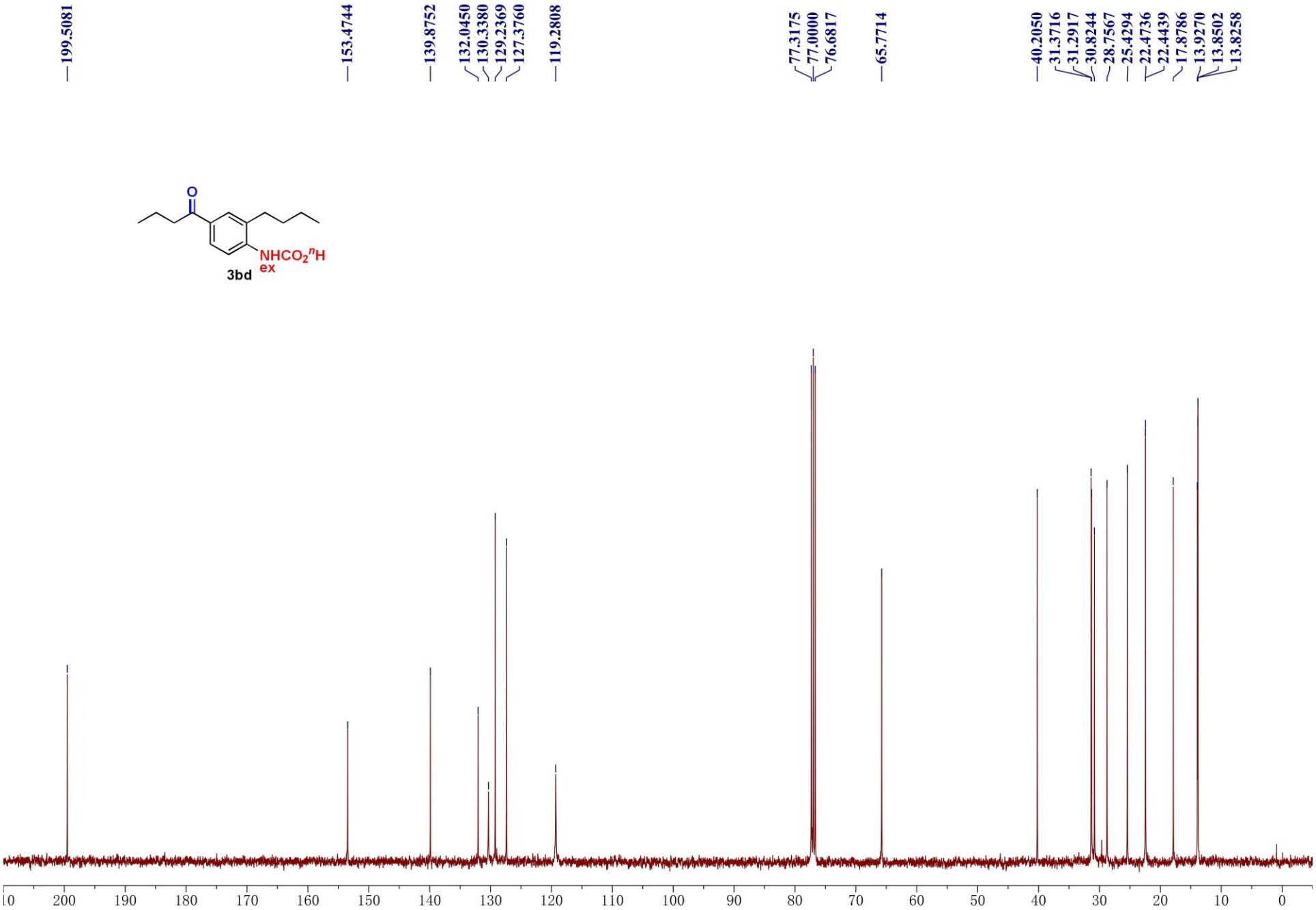

NOE
NOE
NHCO2nHex
3bb
f2 (ppm)
f1 (ppm)

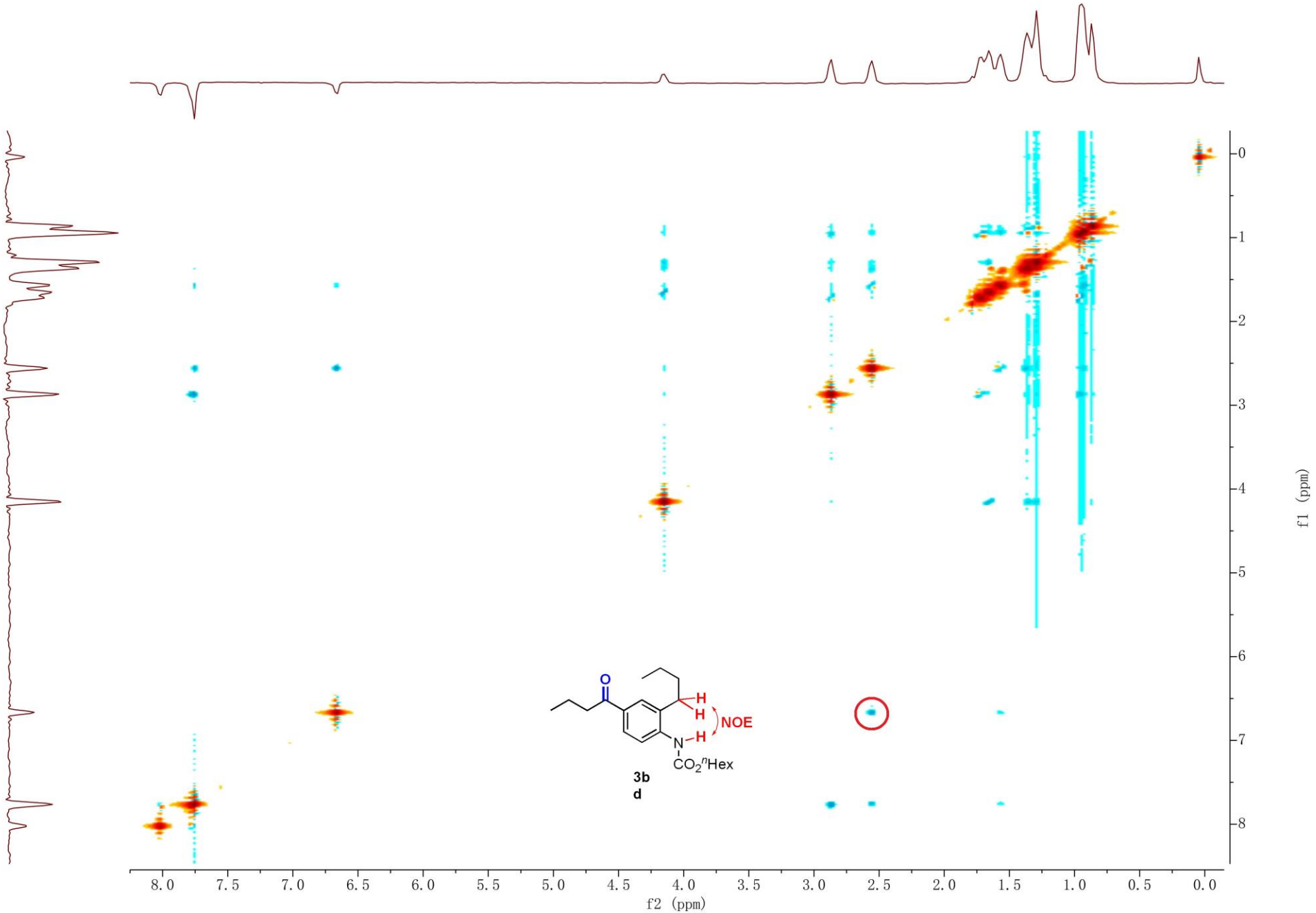

7.7083
7.6869
7.4162
7.4106
7.3950
7.3892
7.2721
7.2535
7.2478
7.0084
4.1905
4.1737
4.1569
2.9508
2.9322
2.9135
2.8950
2.5612
1.7048
1.6879
1.6705
1.6507
1.6339
1.4171
1.3817
1.3602
1.3265
1.3176
1.3157
1.3096
1.2920
1.2901
1.2172
1.1986
1.1799
0.9137
0.8962
0.8783
-0.0000
O
NHCO2nHex
3bc
0.96
0.93
0.95
0.90
2.00
1.95
2.98
2.01
5.95
2.96
2.93
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

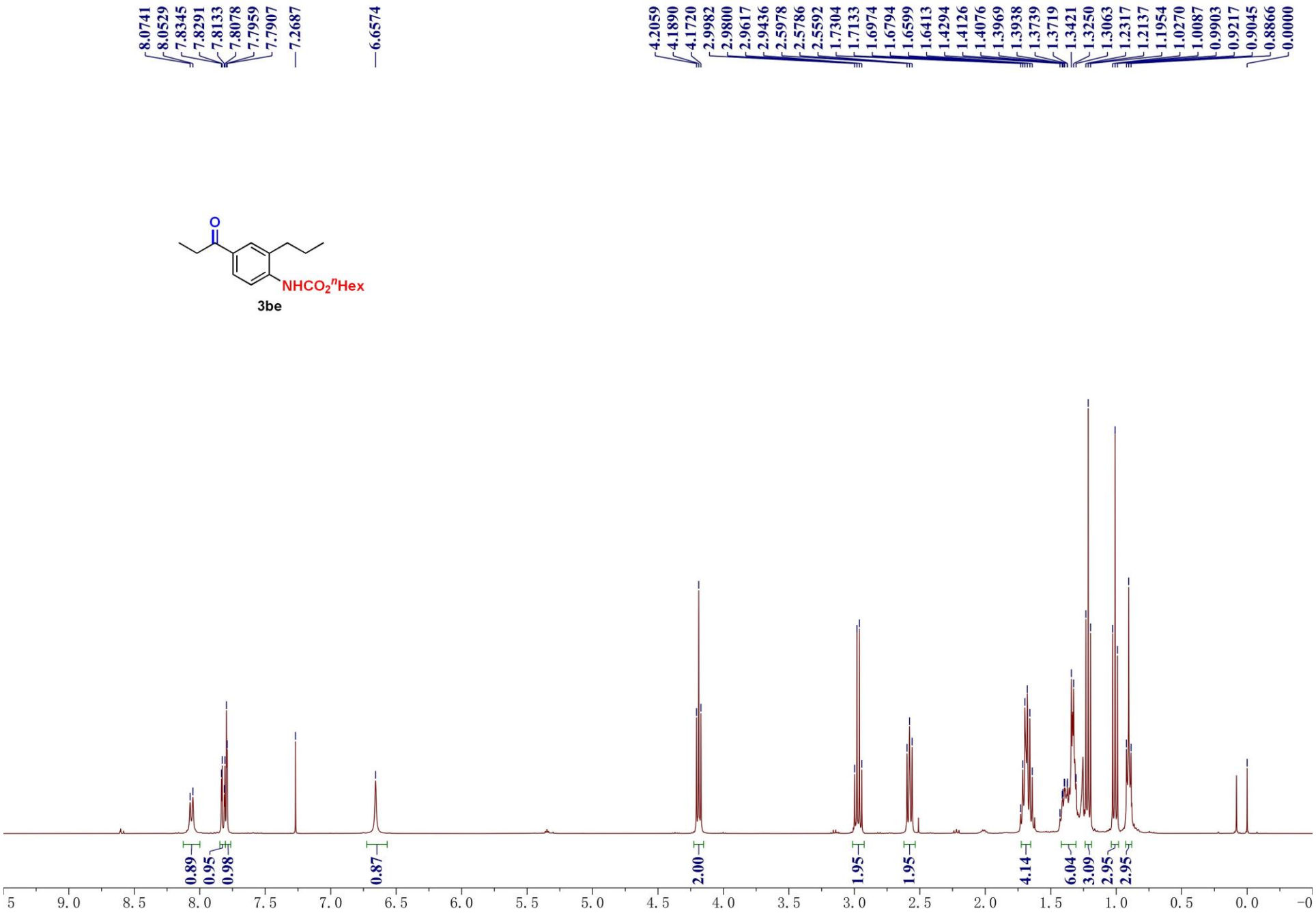

200.2031
153.3739
147.0097
141.1719
131.7144
131.5843
119.6040
114.7602
77.3177
77.0000
76.6816
65.6440
31.3777
29.3948
28.7772
27.5599
25.4590
22.4922
15.5827
13.9497
O
NHCO2nHex
3bc
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

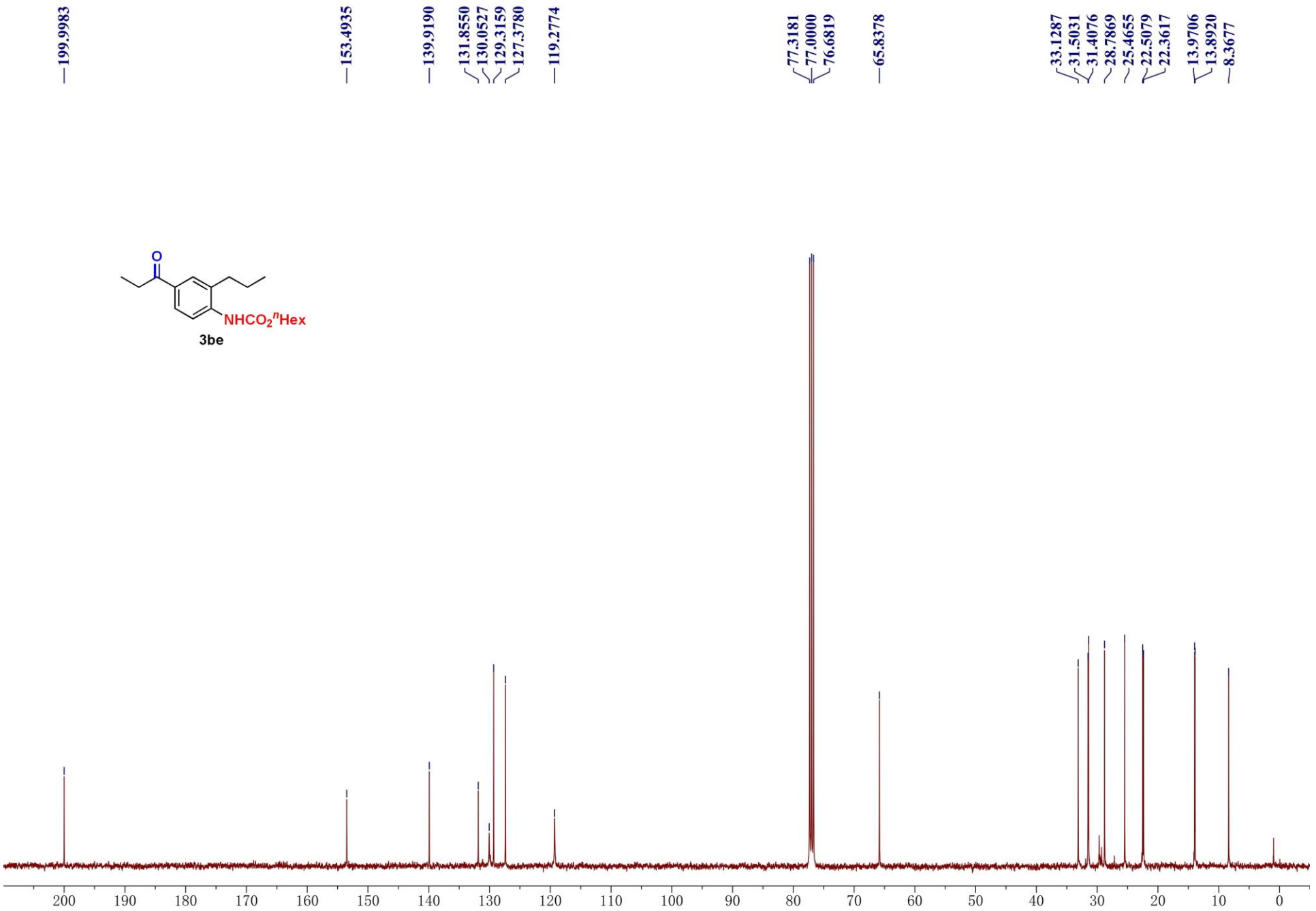

NOE
NHCO2nHex
NOE
3bc
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
f1 (ppm)

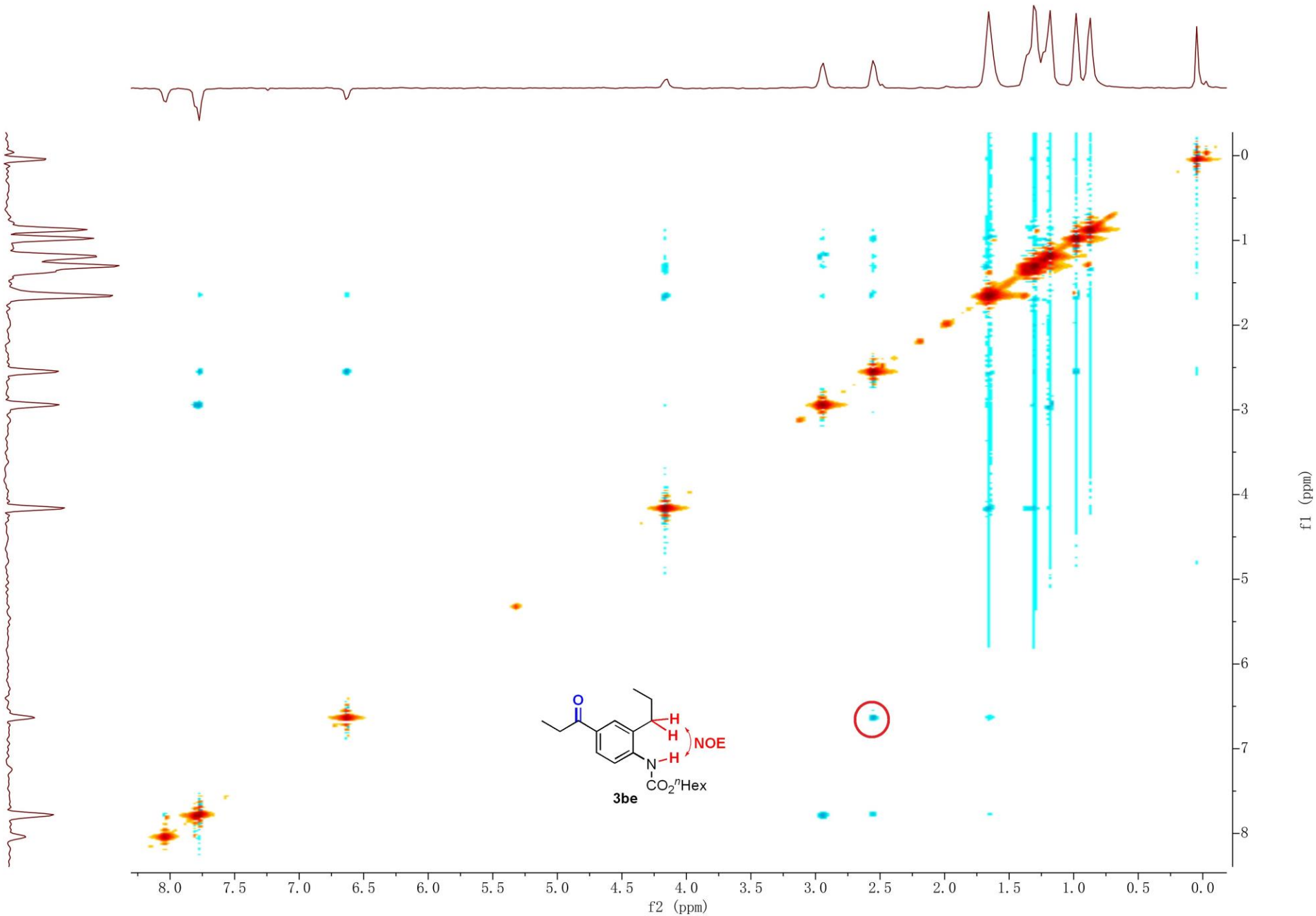

8.0658
8.0445
7.8224
7.8170
7.8012
7.7958
7.7883
7.7832
7.2762
6.6957
4.2056
4.1886
4.1716
2.9262
2.9080
2.8896
2.6161
2.5968
2.5772
1.8099
1.8031
1.7845
1.7660
1.7476
1.7291
1.7111
1.6942
1.6745
1.6573
1.6486
1.6304
1.6105
1.5913
1.5720
1.4606
1.4423
1.4232
1.4045
1.3865
1.3716
1.3686
1.3567
1.3395
1.3292
1.3226
1.3036
1.0185
0.9999
0.9840
0.9812
0.9657
0.9473
0.9198
0.9025
0.8847
-0.0000
O
NHCO2nH
ex
3bd
0.92
0.99
0.95
0.87
2.00
1.94
1.98
4.09
1.97
3.98
3.95
6.05
3.08
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

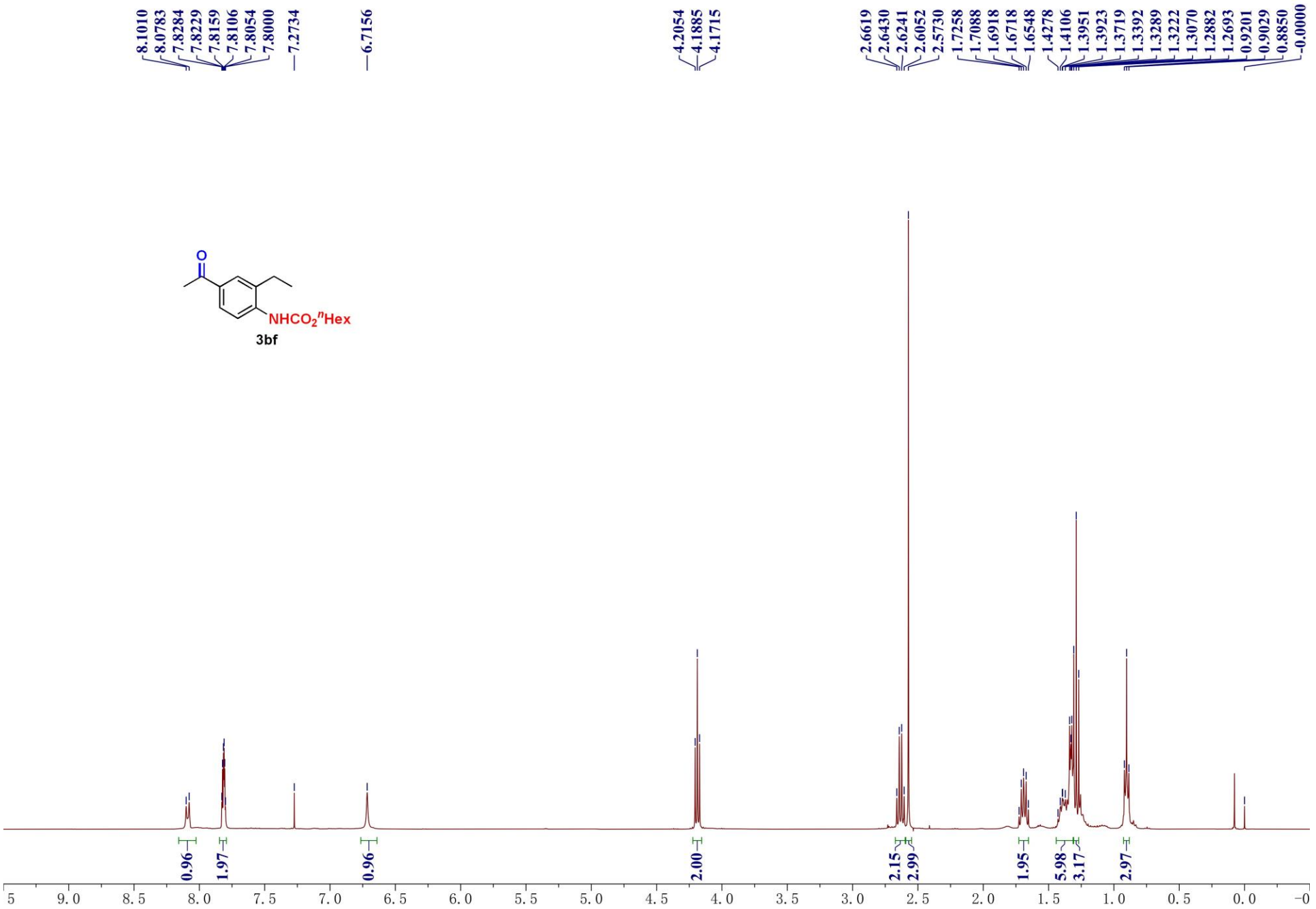

199.5081
153.4744
139.8752
132.0450
130.3380
129.2369
127.3760
119.2808
77.3175
77.0000
76.6817
65.7714
40.2050
31.3716
31.2917
30.8244
28.7567
25.4294
22.4736
22.4439
17.8786
13.9270
13.8502
13.8258
O
NHCO2nH
ex
3bd
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

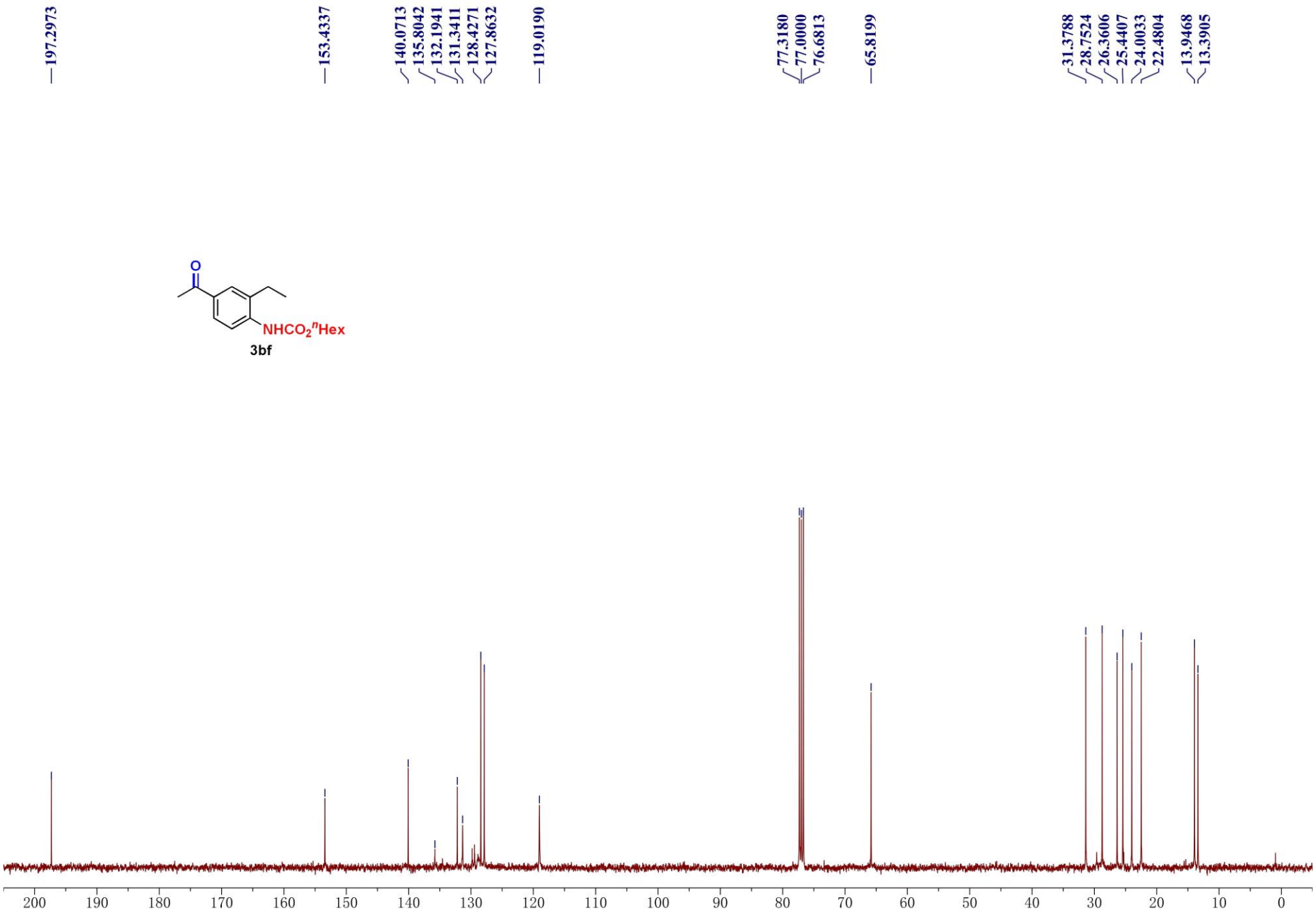

O
H
H
NOE
N
H
CO2nHex
3b
d
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

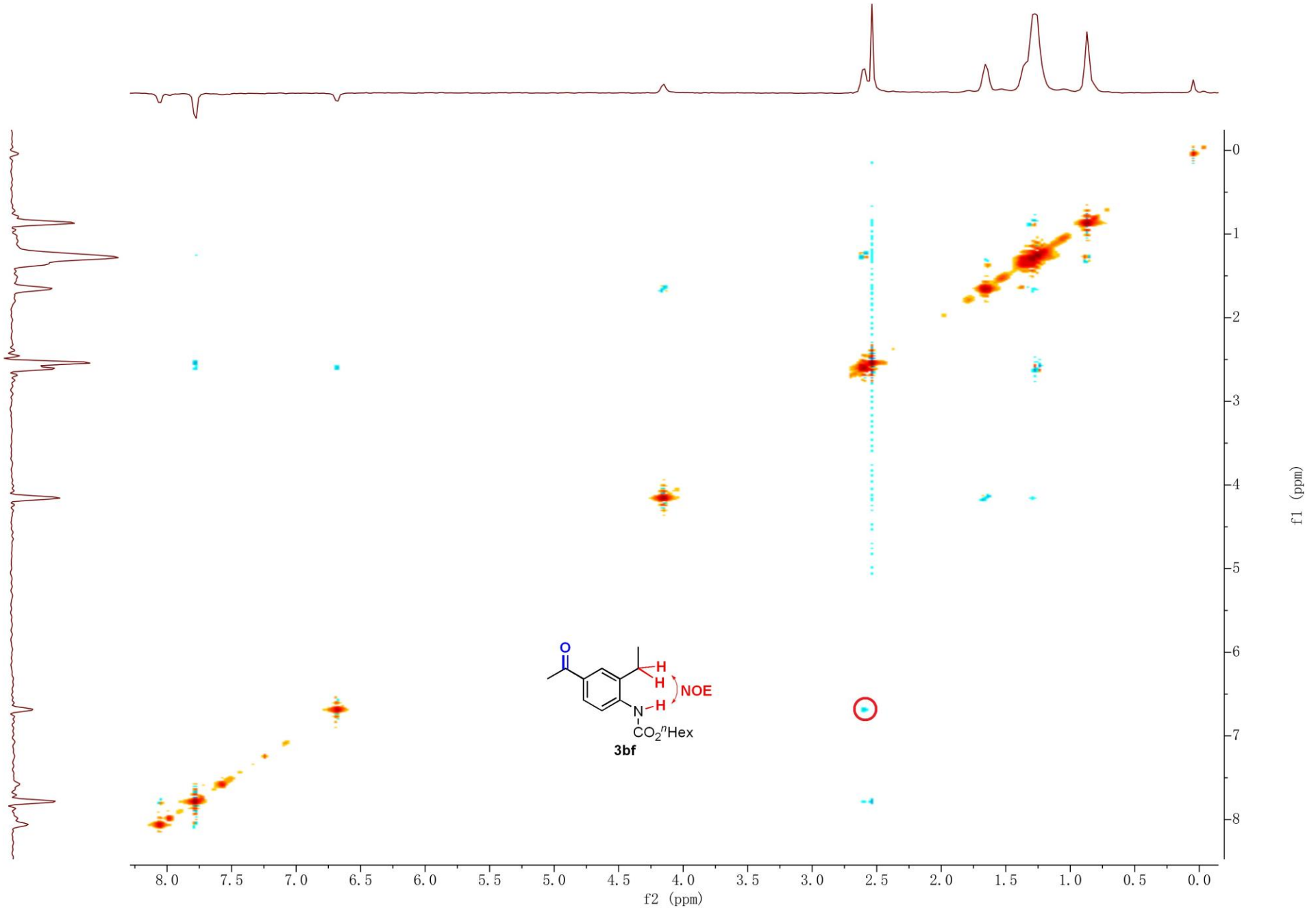

8.0741
8.0529
7.8345
7.8291
7.8133
7.8078
7.7959
7.7907
7.2687
6.6574
4.2059
4.1890
4.1720
2.9982
2.9800
2.9617
2.9436
2.5978
2.5786
2.5592
1.7304
1.7133
1.6974
1.6794
1.6599
1.6413
1.4294
1.4126
1.4076
1.3969
1.3938
1.3739
1.3719
1.3421
1.3250
1.3063
1.2317
1.2137
1.1954
1.0270
1.0087
0.9903
0.9217
0.9045
0.8866
0.0000
O
NHCO2nHex
3be
0.89
0.95
0.98
0.87
2.00
1.95
1.95
4.14
6.04
3.09
2.95
2.95
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

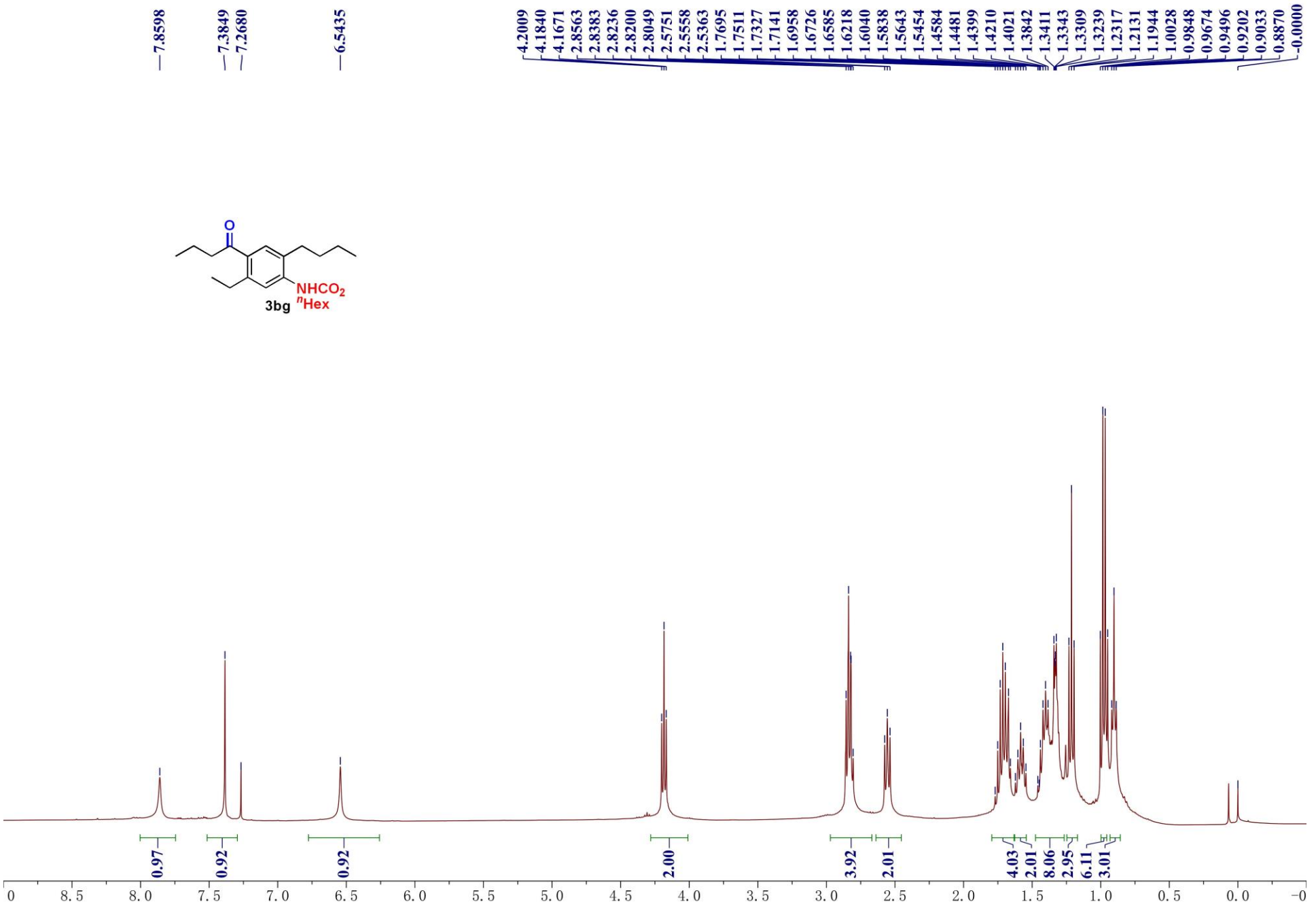

199.9983
153.4935
139.9190
131.8550
130.0527
129.3159
127.3780
119.2774
77.3181
77.0000
76.6819
65.8378
33.1287
31.5031
31.4076
28.7869
25.4655
22.5079
22.3617
13.9706
13.8920
8.3677
O
NHCO2nHex
3be
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

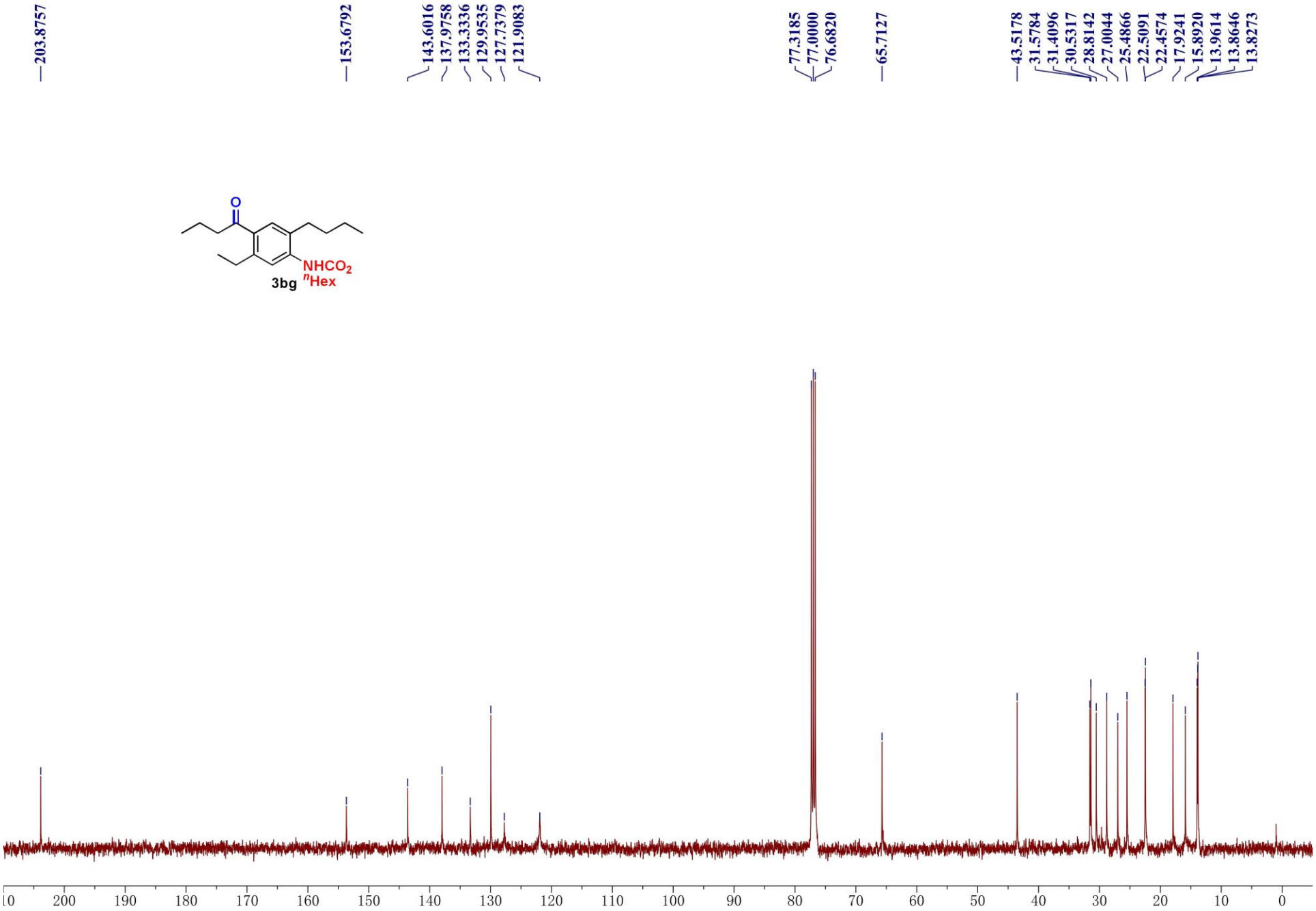

O
H
H
NOE
N
H
CO2nHex
3be
f2 (ppm)
f1 (ppm)

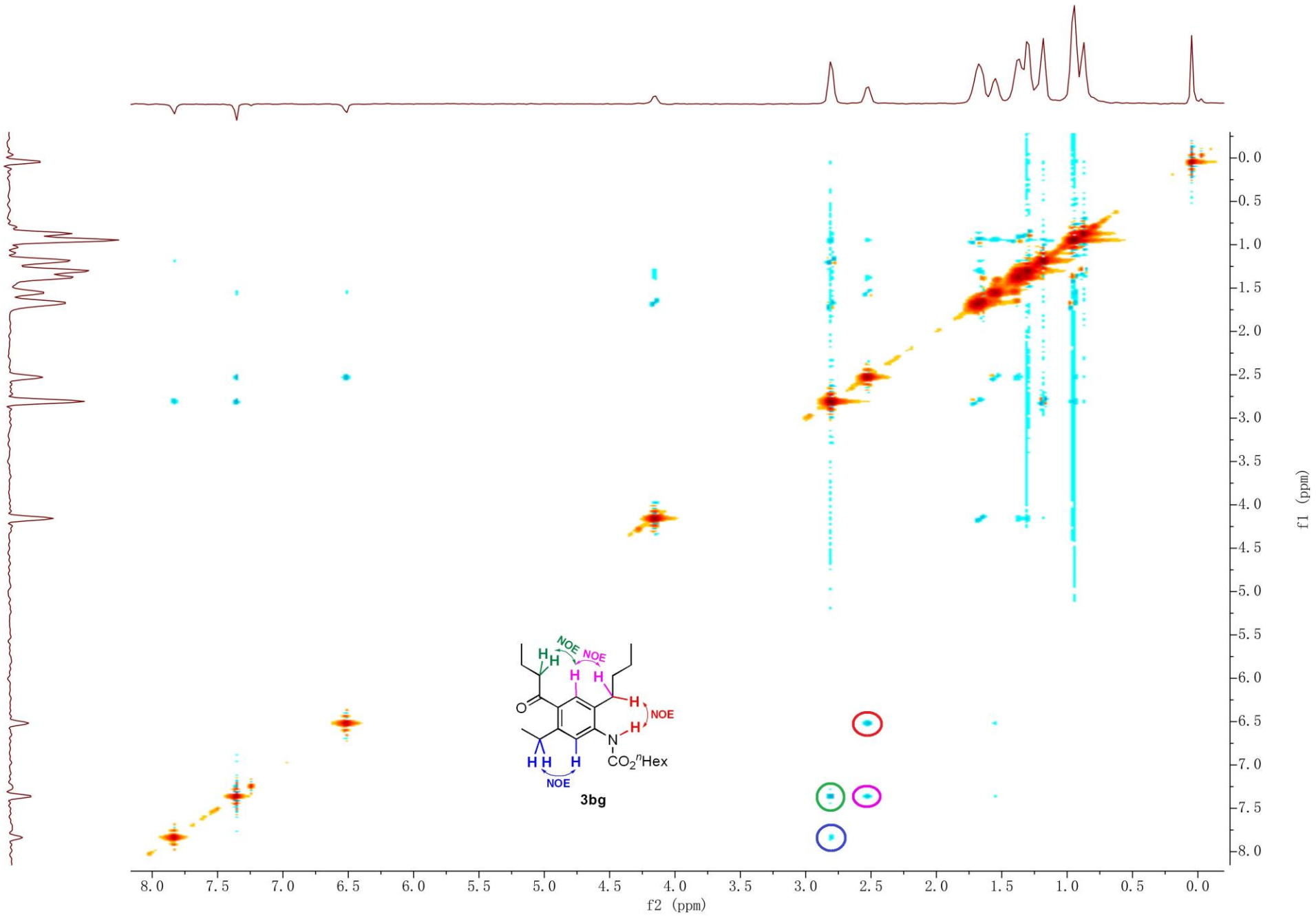

8.1010
8.0783
7.8284
7.8229
7.8159
7.8106
7.8054
7.8000
7.2734
6.7156
4.2054
4.1885
4.1715
2.6619
2.6430
2.6241
2.6052
2.5730
1.7258
1.7088
1.6918
1.6718
1.6548
1.4278
1.4106
1.3951
1.3923
1.3719
1.3392
1.3289
1.3222
1.3070
1.2882
1.2693
0.9201
0.9029
0.8850
-0.0000
O
NHCO2nHex
3bf
0.96
1.97
0.96
2.00
2.15
2.99
1.95
5.98
3.17
2.97
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

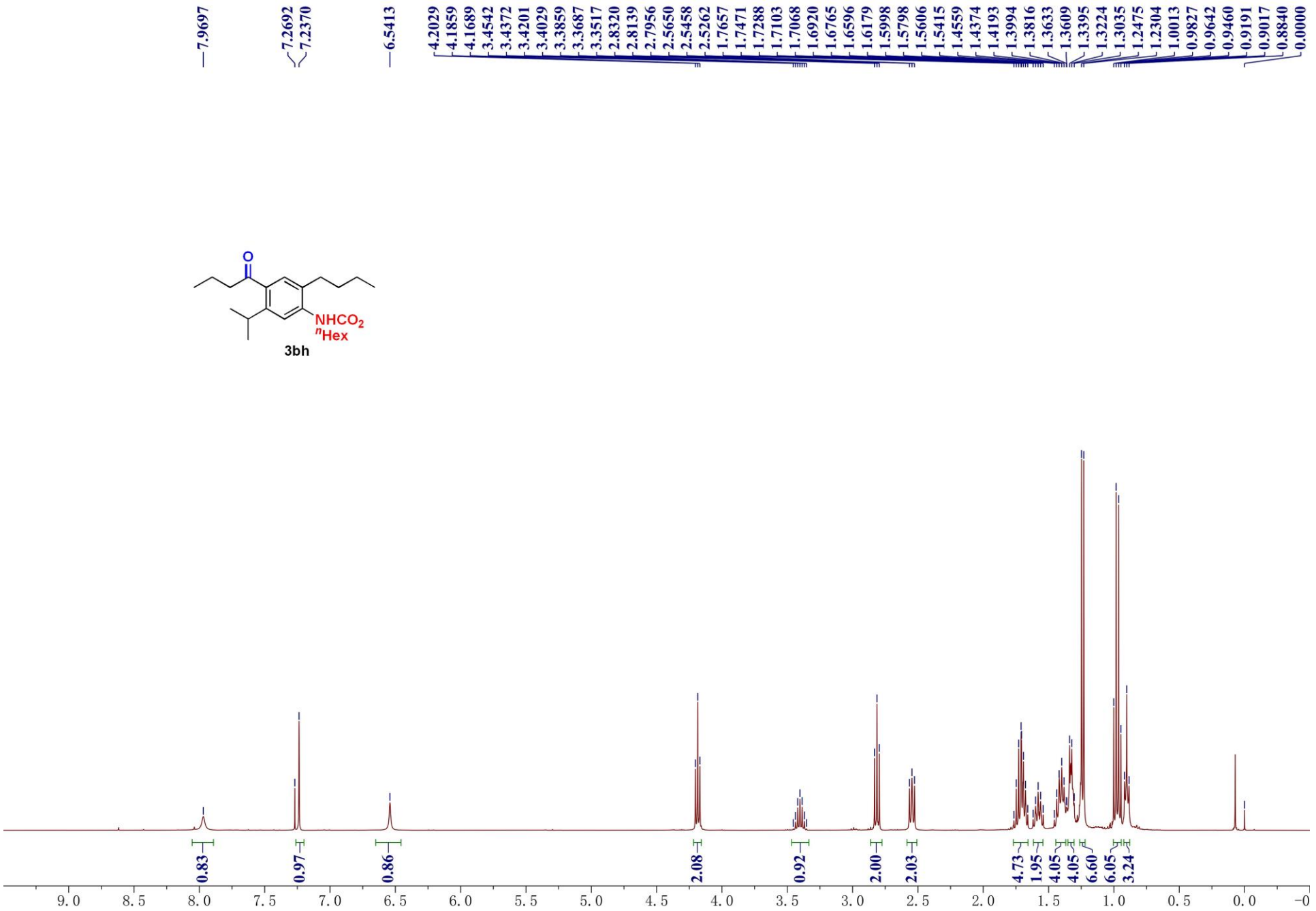

197.2973
153.4337
140.0713
135.8042
132.1941
131.3411
128.4271
127.8632
119.0190
77.3180
77.0000
76.6813
65.8199
31.3788
28.7524
26.3606
25.4407
24.0033
22.4804
13.9468
13.3905
O
NHCO2nHex
3bf
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

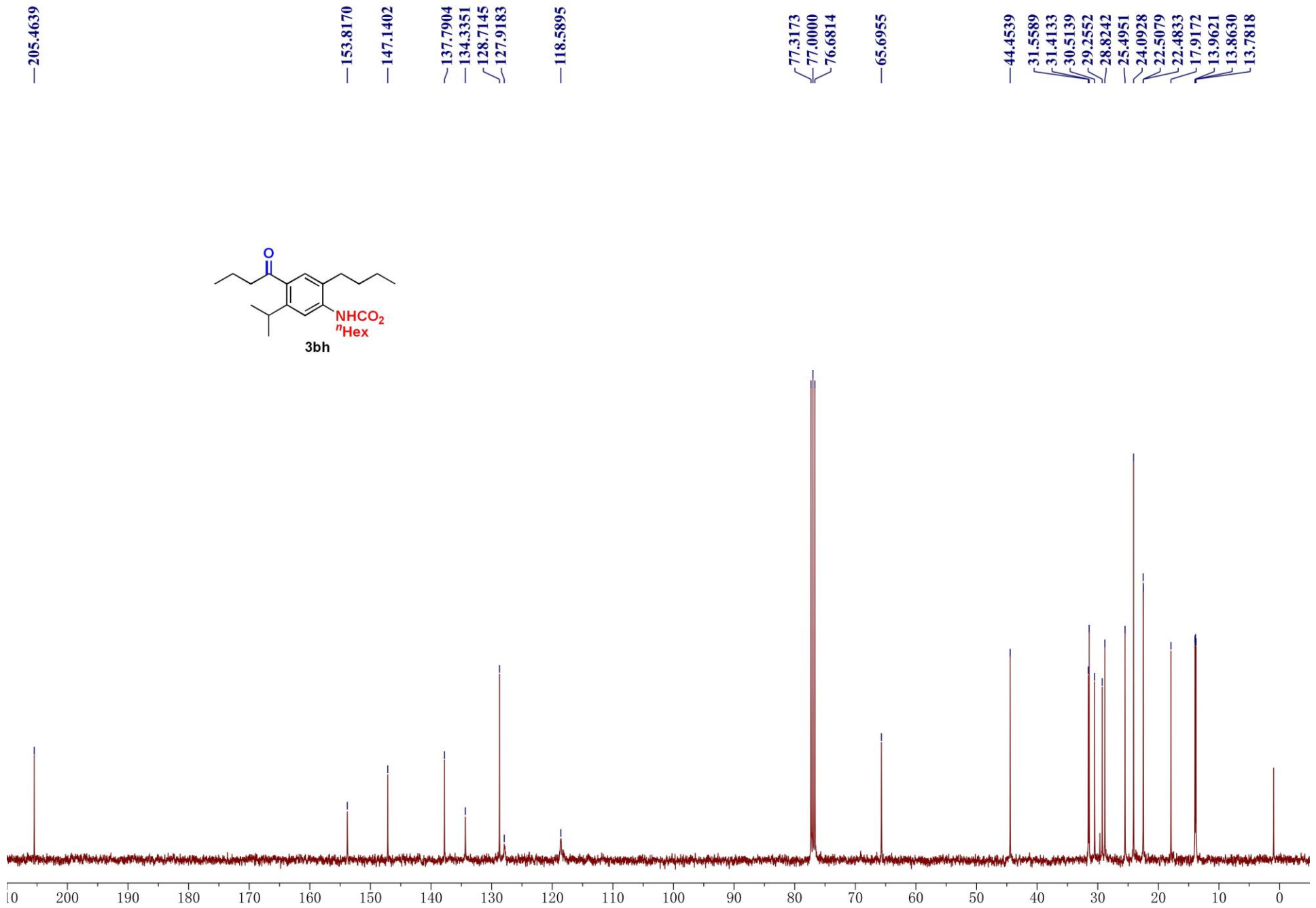

O
H
H
NOE
N
H
CO2nHex
3bf
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

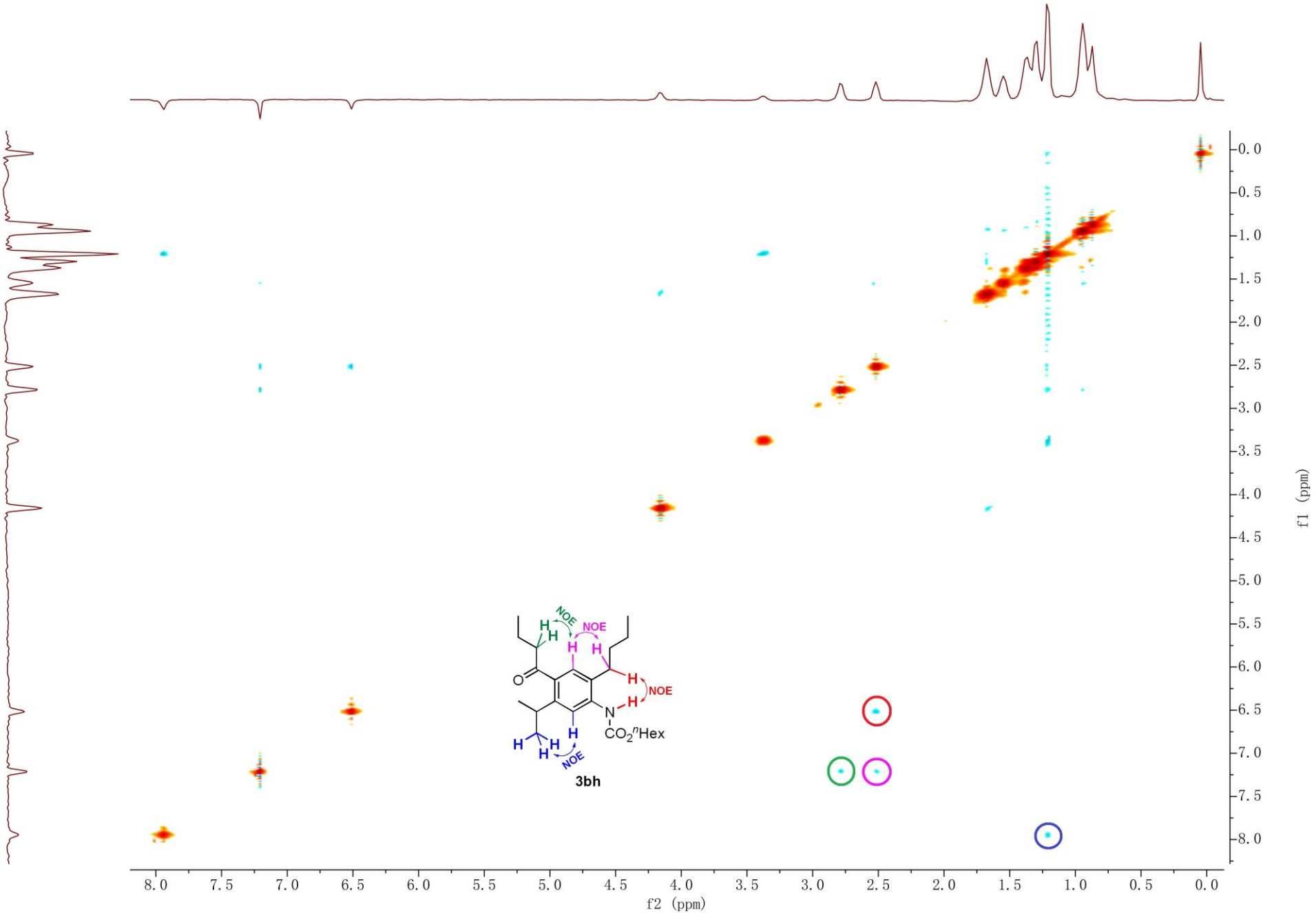

7.8598
7.3849
7.2680
6.5435
4.2009
4.1840
4.1671
2.8563
2.8383
2.8236
2.8200
2.8049
2.5751
2.5558
2.5363
1.7695
1.7511
1.7327
1.7141
1.6958
1.6726
1.6585
1.6218
1.6040
1.5838
1.5643
1.5454
1.4584
1.4481
1.4399
1.4210
1.4021
1.3842
1.3411
1.3343
1.3309
1.3239
1.2317
1.2131
1.1944
1.0028
0.9848
0.9674
0.9496
0.9202
0.9033
0.8870
-0.0000
O
NHCO2
nHex
3bg
0.97
0.92
0.92
2.00
3.92
2.01
4.03
2.01
8.06
2.95
6.11
3.01
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

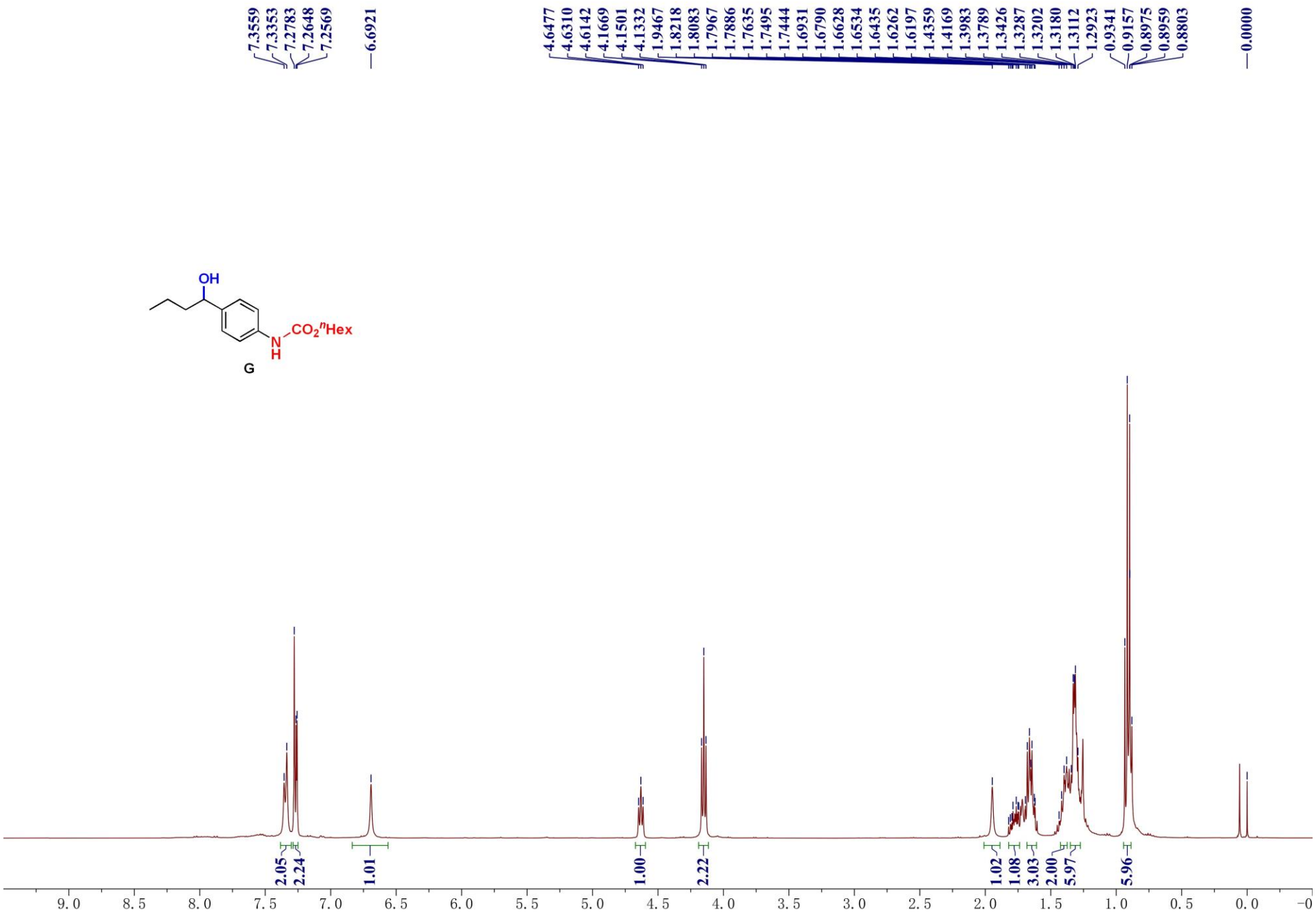

203.8757
153.6792
143.6016
137.9758
133.3336
129.9535
127.7379
121.9083
77.3185
77.0000
76.6820
65.7127
43.5178
31.5784
31.4096
30.5317
28.8142
27.0044
25.4866
22.5091
22.4574
17.9241
15.8920
13.9614
13.8646
13.8273
O
NHCO2
3bg nHex
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

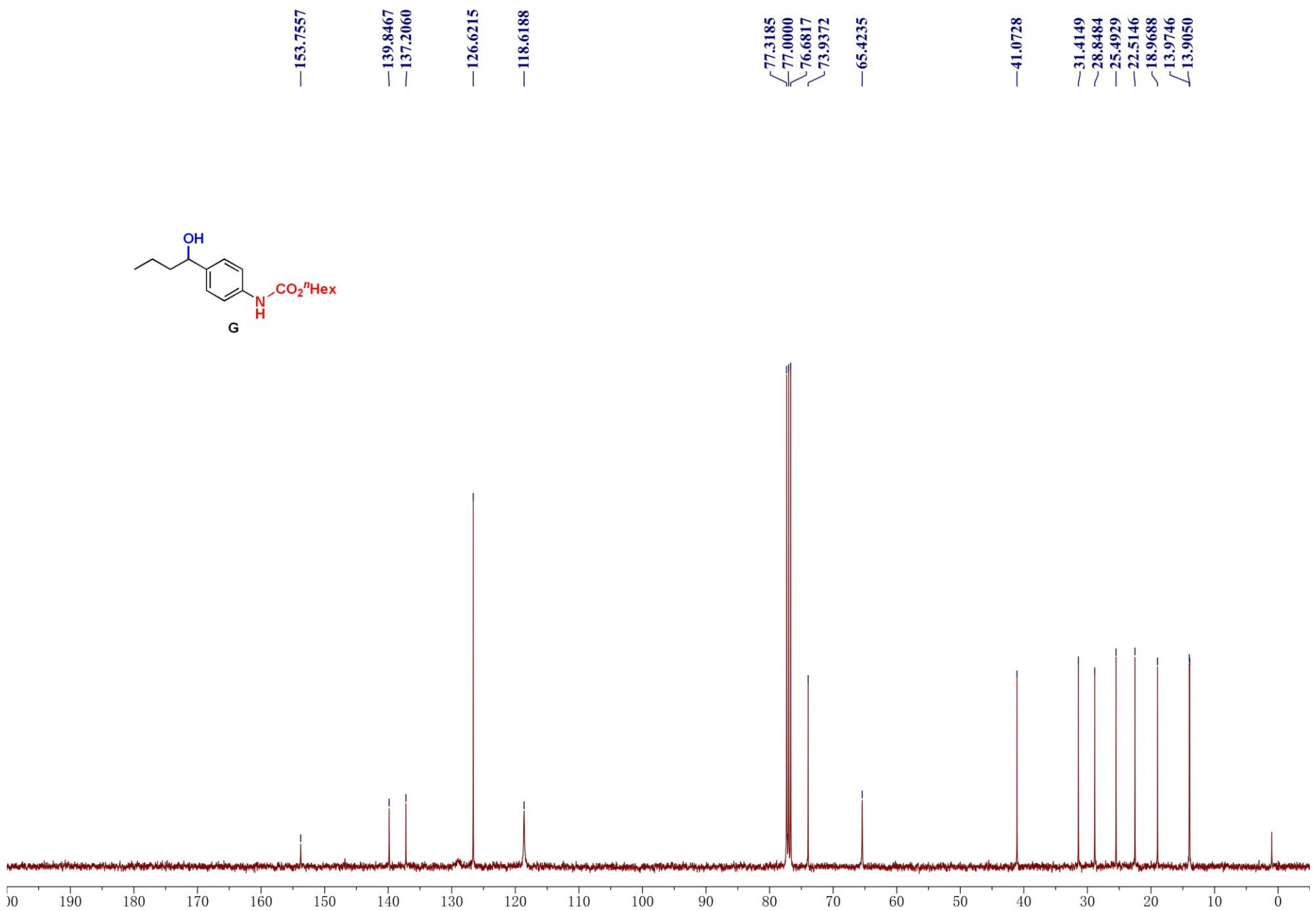

NOE
NOE
NOE
NOE
O
N
$CO_2{}^nHex$
3bg
f2 (ppm)
f1 (ppm)

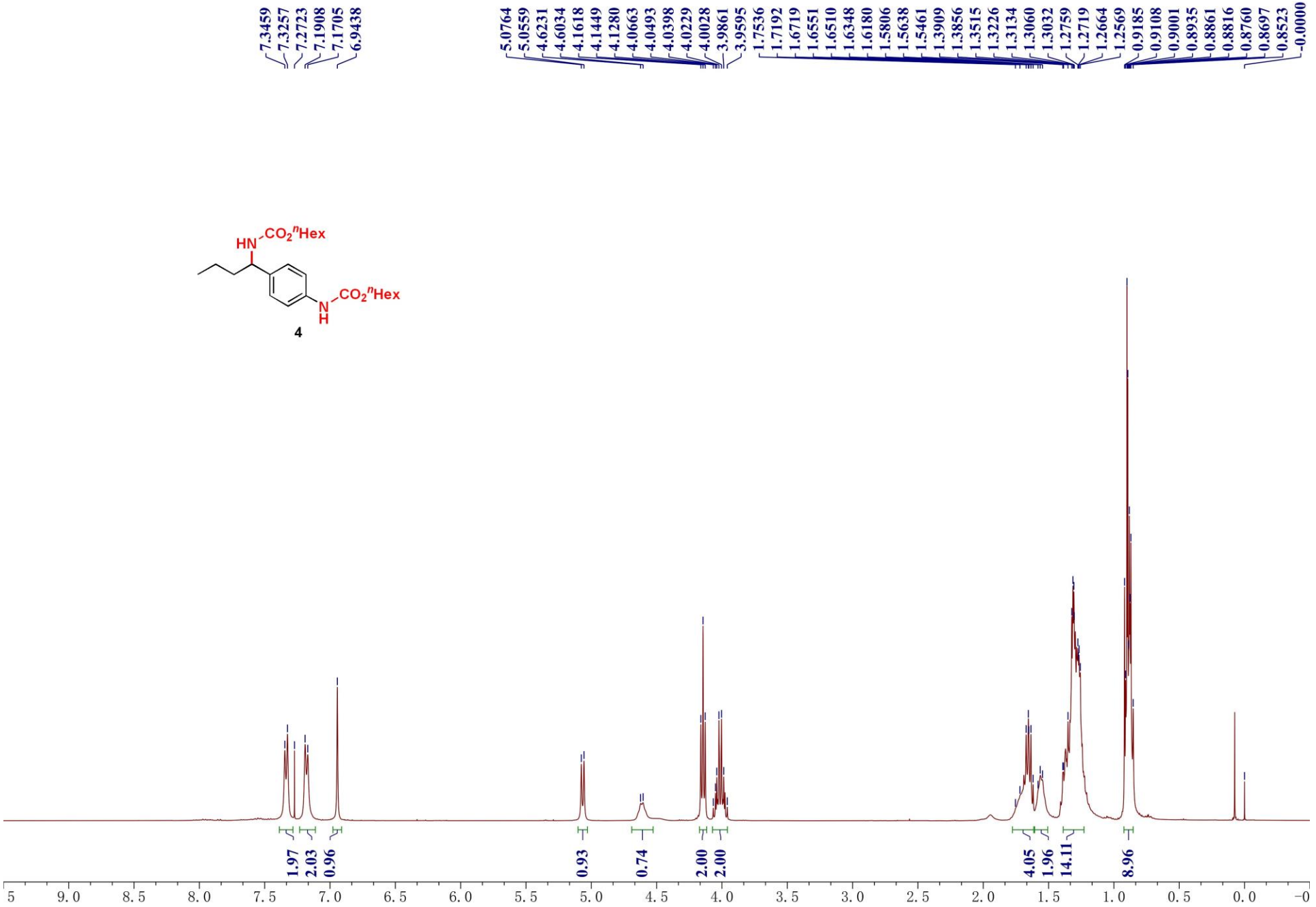

7.9697
7.2692
7.2370
6.5413
4.2029
4.1859
4.1689
3.4542
3.4372
3.4201
3.4029
3.3859
3.3687
3.3517
2.8320
2.8139
2.7956
2.5650
2.5458
2.5262
1.7657
1.7471
1.7288
1.7103
1.7068
1.6920
1.6765
1.6596
1.6179
1.5998
1.5798
1.5606
1.5415
1.4559
1.4374
1.4193
1.3994
1.3816
1.3633
1.3609
1.3395
1.3224
1.3035
1.2475
1.2304
1.0013
0.9827
0.9642
0.9460
0.9191
0.9017
0.8840
0.0000
O
NHCO2
nHex
3bh
0.83
0.97
0.86
2.08
0.92
2.00
2.03
4.73
1.95
4.05
4.05
6.60
6.05
3.24
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

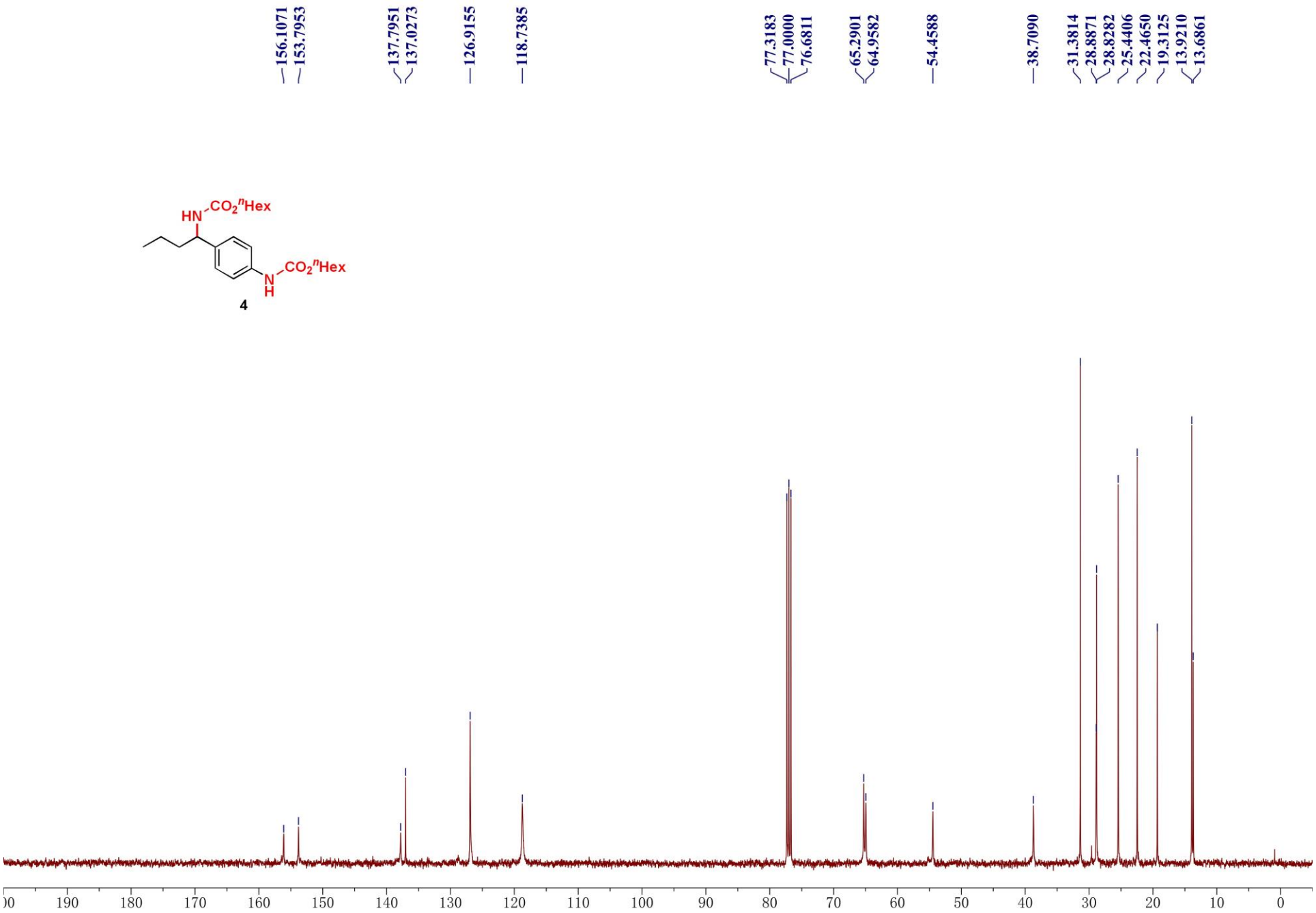

205.4639
153.8170
147.1402
137.7904
134.3351
128.7145
127.9183
118.5895
77.3173
77.0000
76.6814
65.6955
44.4539
31.5589
31.4133
30.5139
29.2552
28.8242
25.4951
24.0928
22.5079
22.4833
17.9172
13.9621
13.8630
13.7818
O
NHCO2
nHex
3bh
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

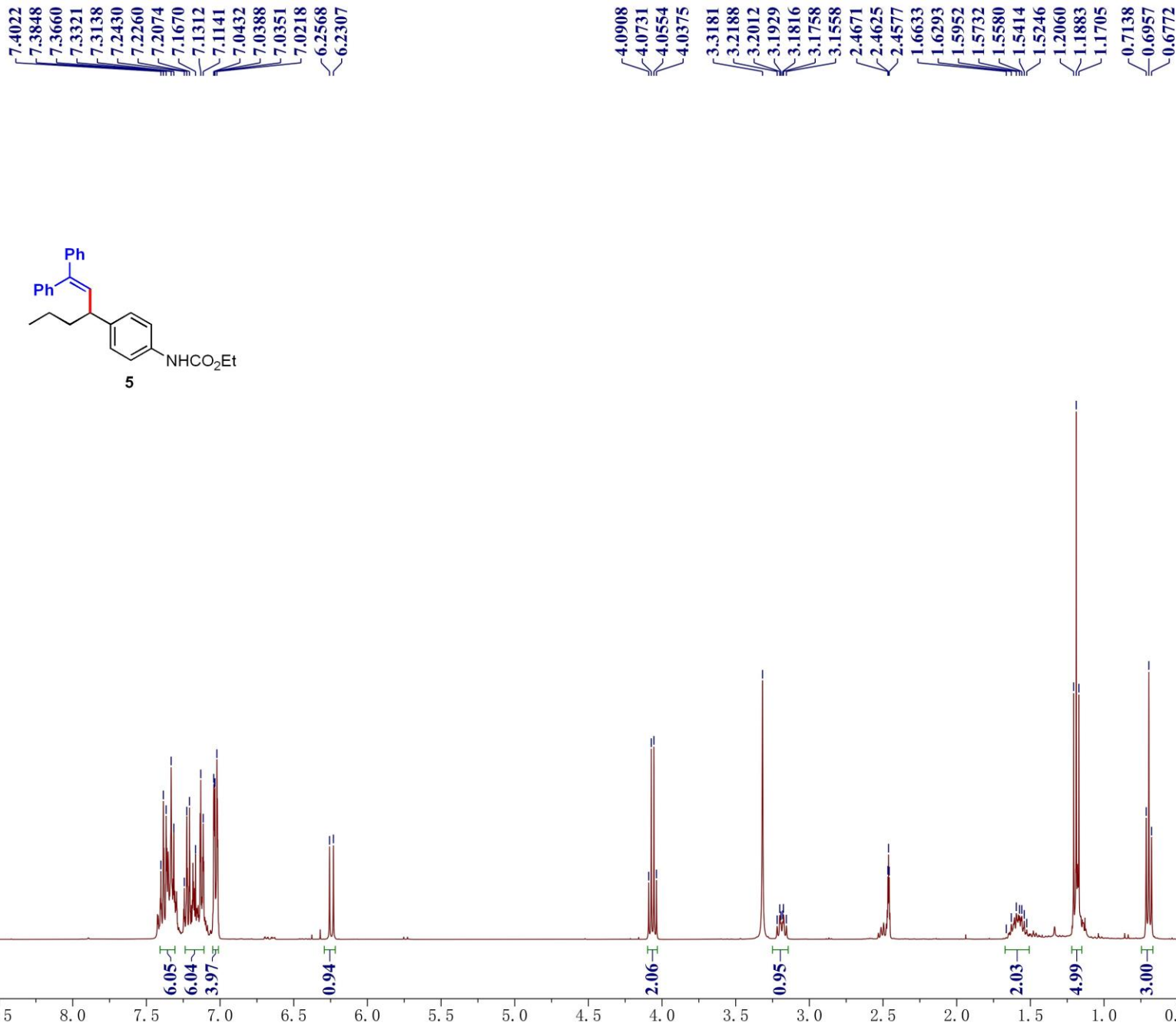

NOE
NOE
NOE
NOE
NOE
O
N
$CO_2{}^nHex$
3bh
f2 (ppm)
f1 (ppm)


7.3559
7.3353
7.2783
7.2648
7.2569
6.6921
4.6477
4.6310
4.6142
4.1669
4.1501
4.1332
1.9467
1.8218
1.8083
1.7967
1.7886
1.7635
1.7495
1.7444
1.6931
1.6790
1.6628
1.6534
1.6435
1.6262
1.6197
1.4359
1.4169
1.3983
1.3789
1.3426
1.3287
1.3202
1.3180
1.3112
1.2923
0.9341
0.9157
0.8975
0.8959
0.8803
0.0000
OH
CO2nHex
N
H
G
2.05
2.24
1.01
1.00
2.22
1.02
1.08
3.03
2.00
5.97
5.96
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


153.7557
139.8467
137.2060
126.6215
118.6188
77.3185
77.0000
76.6817
73.9372
65.4235
41.0728
31.4149
28.8484
25.4929
22.5146
18.9688
13.9746
13.9050
OH
N
H
CO2nHex
G
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.3459
7.3257
7.2723
7.1908
7.1705
6.9438
5.0764
5.0559
4.6231
4.6034
4.1618
4.1449
4.1280
4.0663
4.0493
4.0398
4.0229
4.0028
3.9861
3.9595
1.7536
1.7192
1.6719
1.6551
1.6510
1.6348
1.6180
1.5806
1.5638
1.5461
1.3909
1.3856
1.3515
1.3226
1.3134
1.3060
1.3032
1.2759
1.2719
1.2664
1.2569
0.9185
0.9108
0.9001
0.8935
0.8861
0.8816
0.8760
0.8697
0.8523
-0.0000
HN
CO2nHex
CO2nHex
N
H
4
1.97
2.03
0.96
0.93
0.74
2.00
2.00
4.05
1.96
14.11
8.96
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


156.1071
153.7953
137.7951
137.0273
126.9155
118.7385
77.3183
77.0000
76.6811
65.2901
64.9582
54.4588
38.7090
31.3814
28.8871
28.8282
25.4406
22.4650
19.3125
13.9210
13.6861
HN
CO2nHex
CO2nHex
N
H
4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

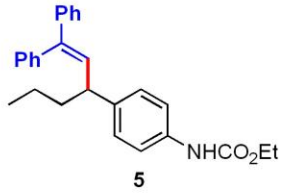

7.4022
7.3848
7.3660
7.3321
7.3138
7.2430
7.2260
7.2074
7.1670
7.1312
7.1141
7.0432
7.0388
7.0351
7.0218
6.2568
6.2307
4.0908
4.0731
4.0554
4.0375
3.3181
3.2188
3.2012
3.1929
3.1816
3.1758
3.1558
2.4671
2.4625
2.4577
1.6633
1.6293
1.5952
1.5732
1.5580
1.5414
1.5246
1.2060
1.1883
1.1705
0.7138
0.6957
0.6772
Ph
Ph
NHCO2Et
5
6.05
6.04
3.97
0.94
2.06
0.95
2.03
4.99
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
−0

153.5791
141.7492
139.8441
139.5691
138.8291
137.1574
133.1708
129.3669
128.3664
128.2254
127.3105
127.1563
127.0131
126.7399
118.5384

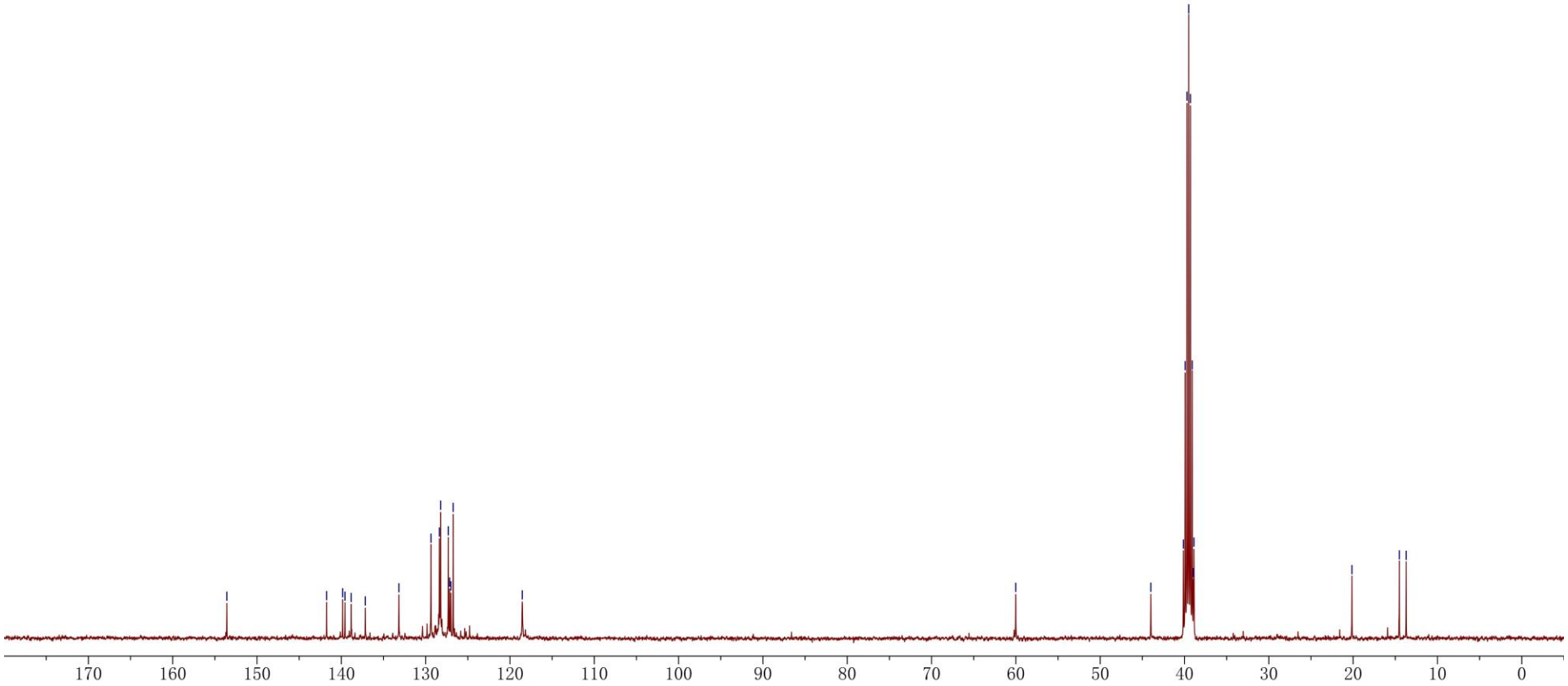
60.0186

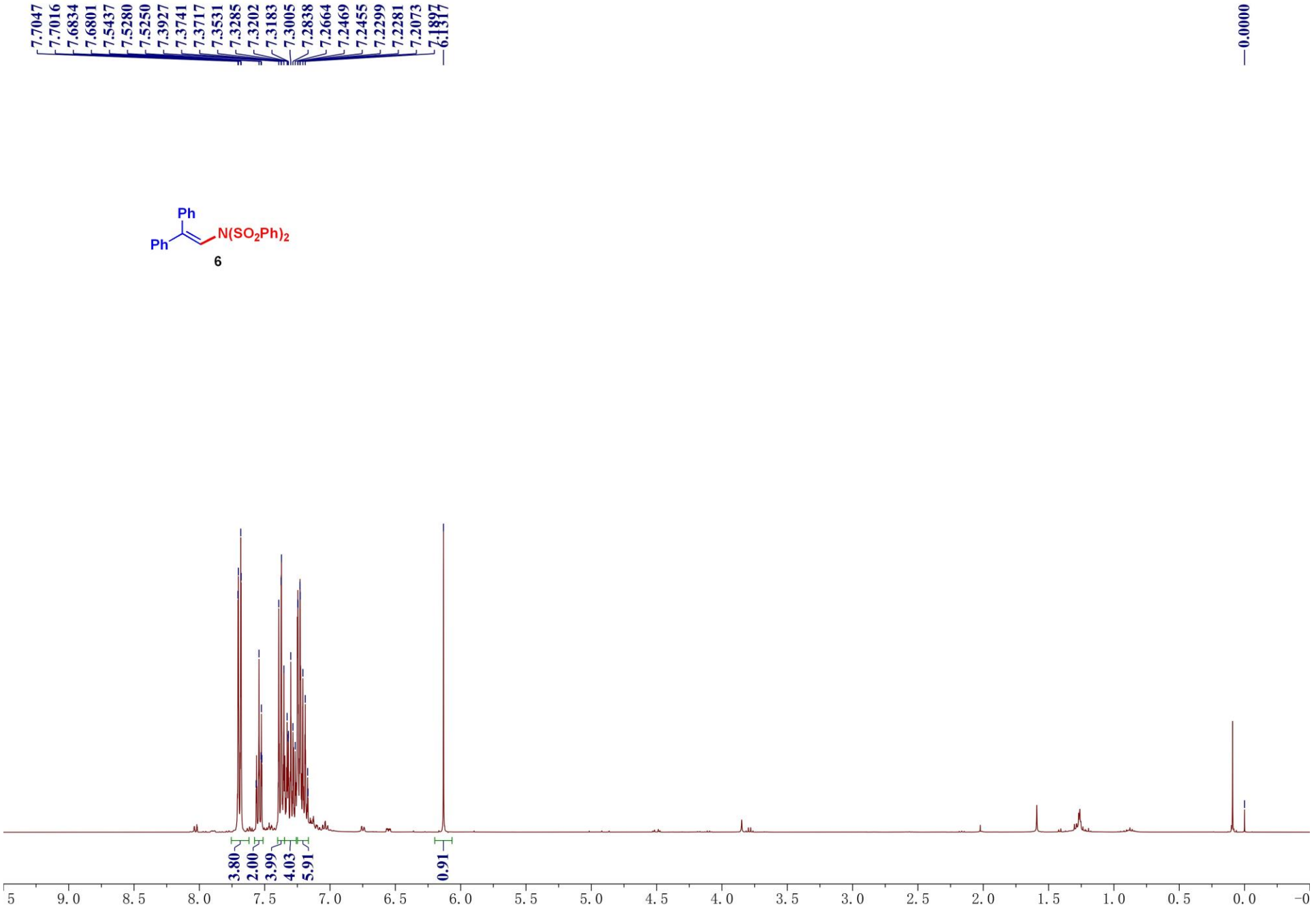
43.9941
40.1289
39.9217
39.7108
39.5022
39.2939
39.0846
38.9354
38.8770

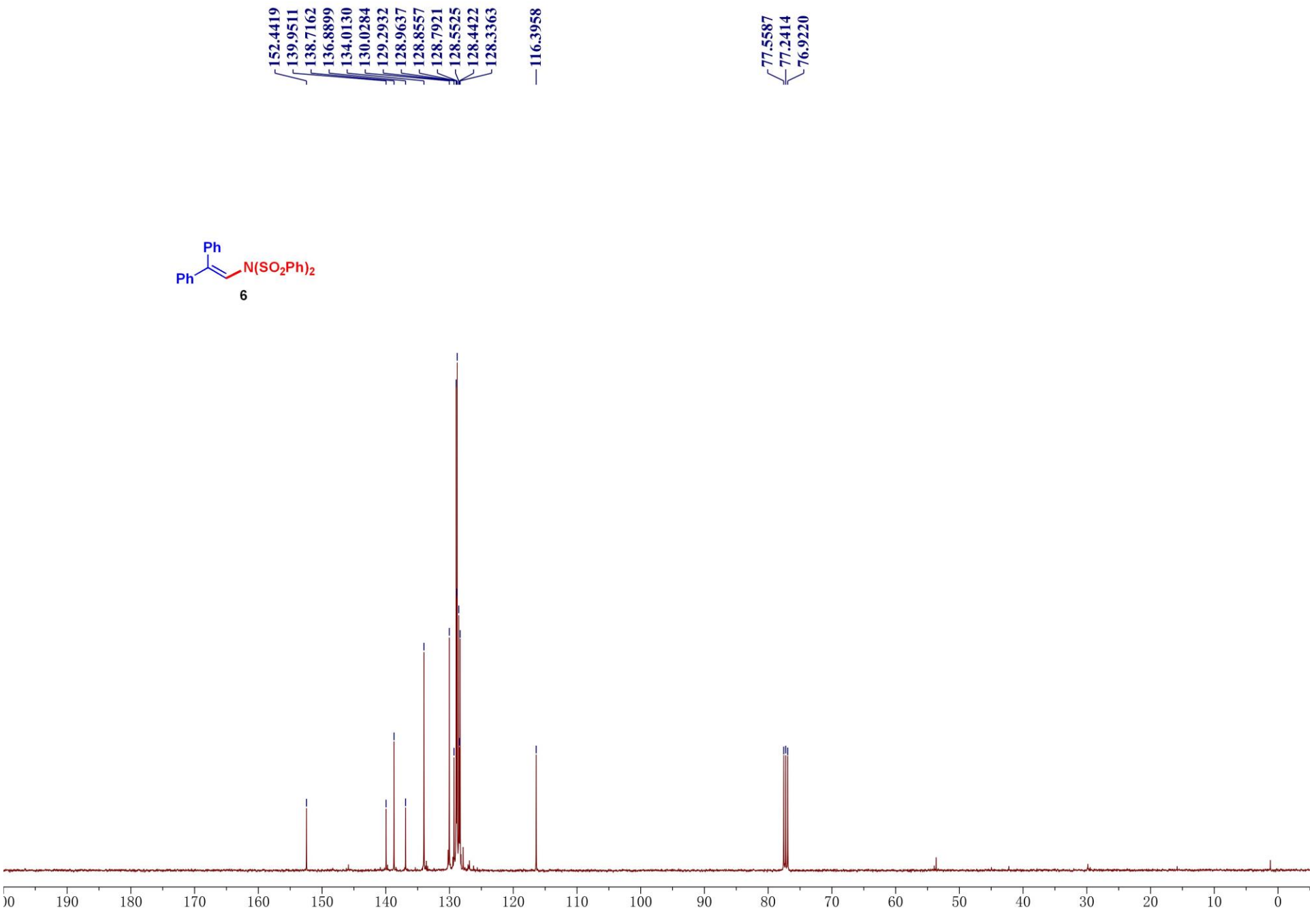
20.1470
14.5214
13.7108

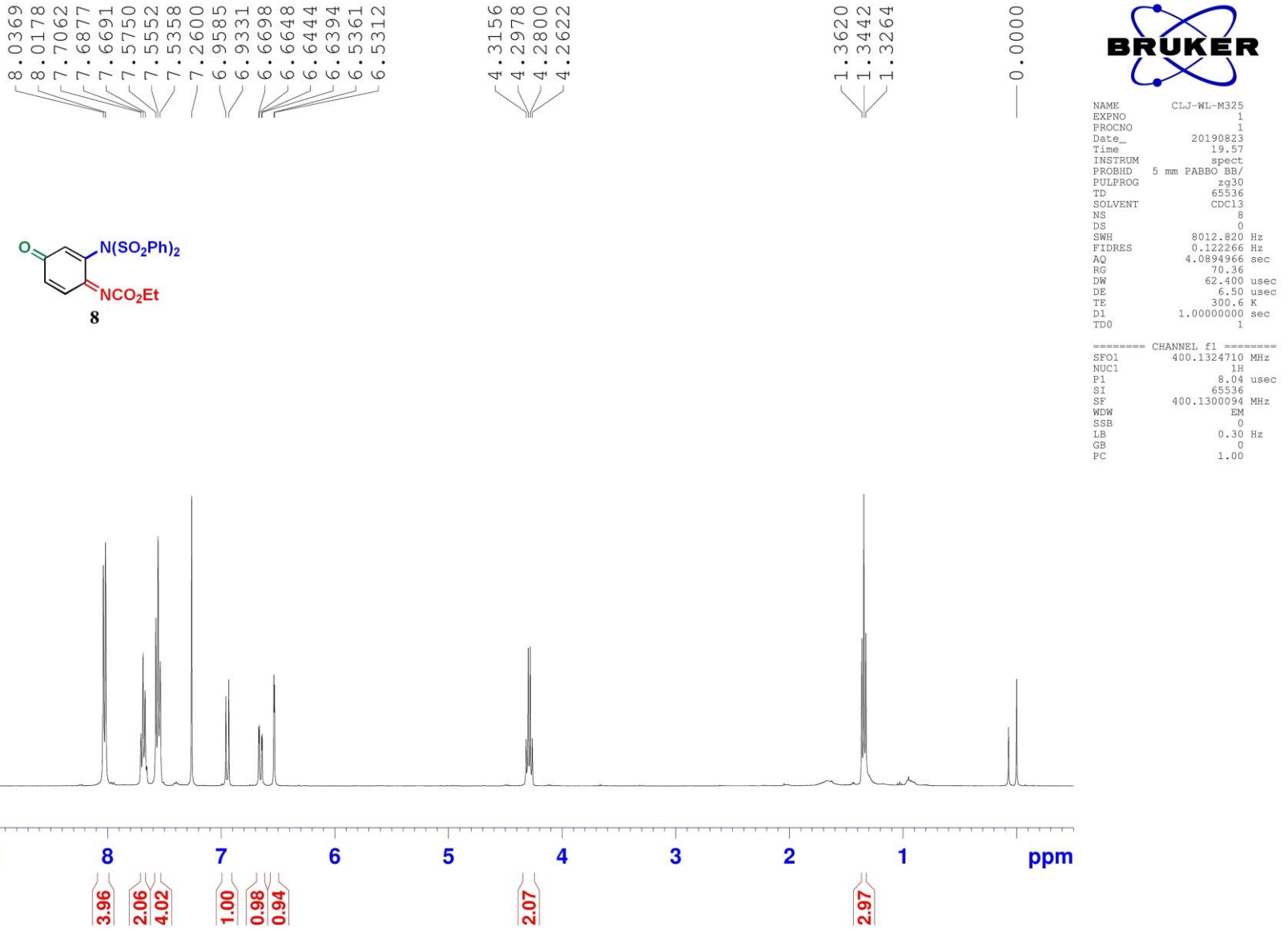


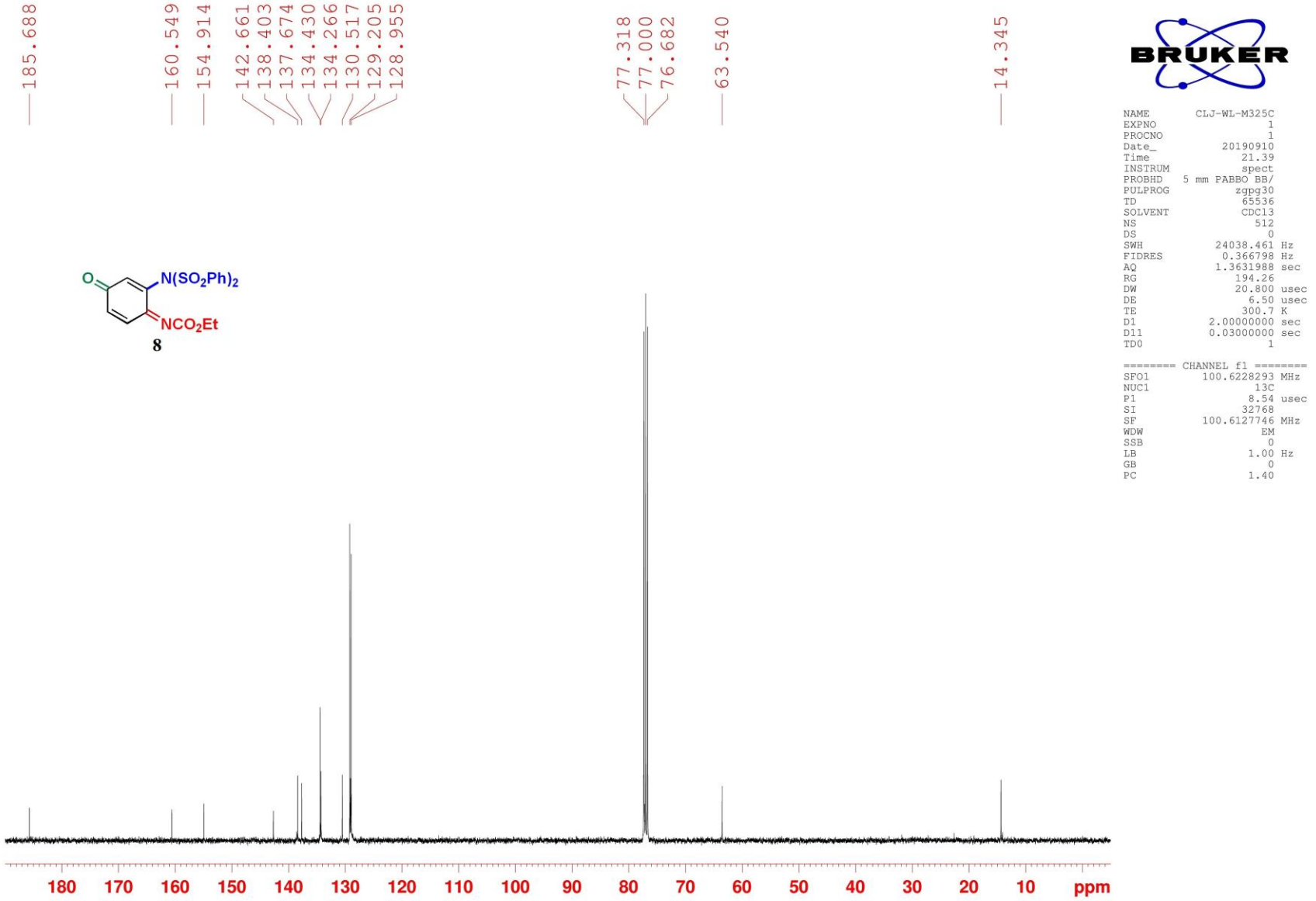
5




7.7047
7.7016
7.6834
7.6801
7.5437
7.5280
7.5250
7.3927
7.3741
7.3717
7.3531
7.3285
7.3202
7.3183
7.3005
7.2838
7.2664
7.2469
7.2455
7.2299
7.2281
7.2073
7.1897
7.1317
6.1317
0.0000
Ph
Ph
N(SO2Ph)2
6
3.80
2.00
3.99
4.03
5.91
0.91
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

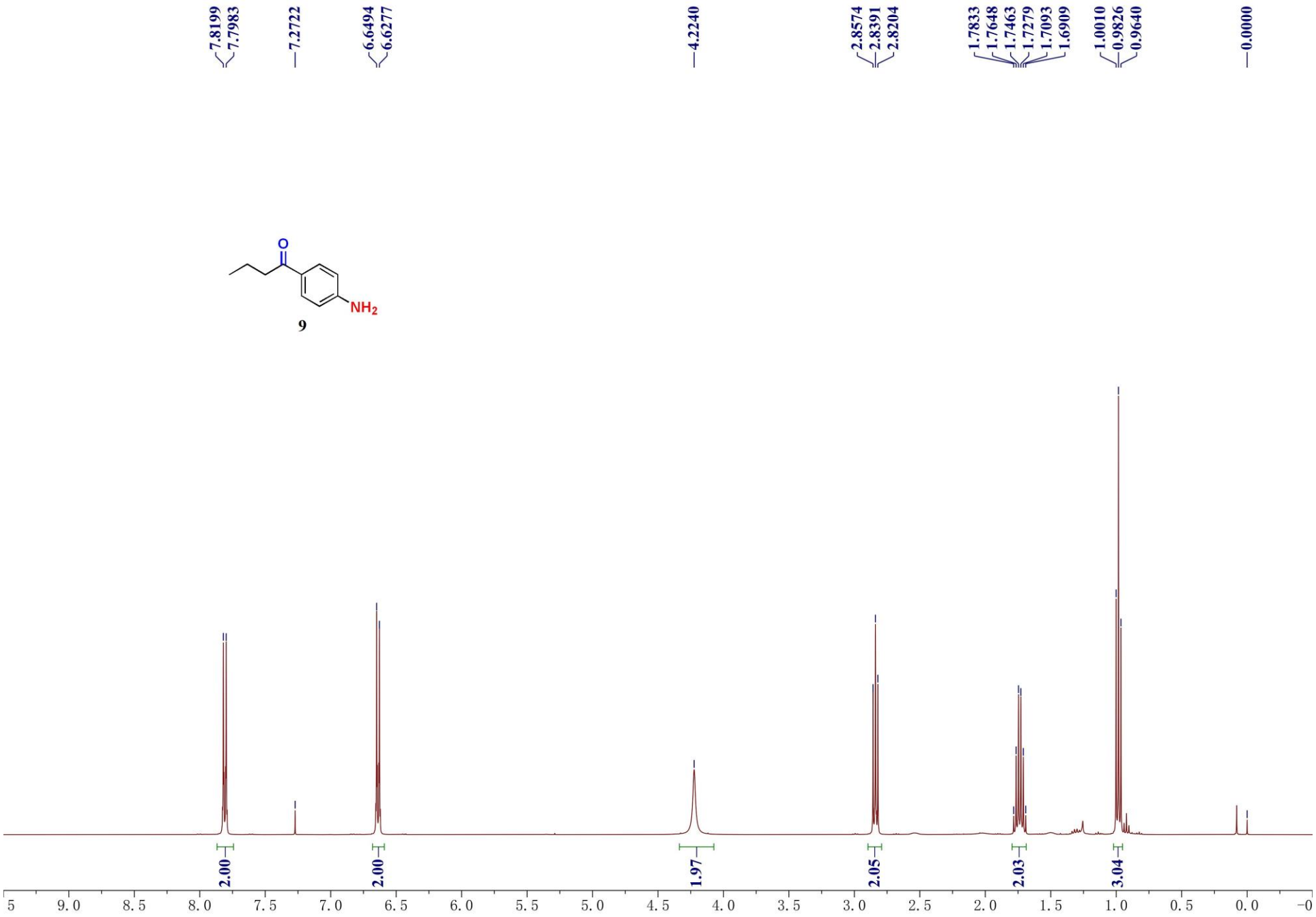

152.4419
139.9511
138.7162
136.8899
134.0130
130.0284
129.2932
128.9637
128.8557
128.7921
128.5525
128.4422
128.3363
116.3958
77.5587
77.2414
76.9220
Ph
Ph
N(SO2Ph)2
6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

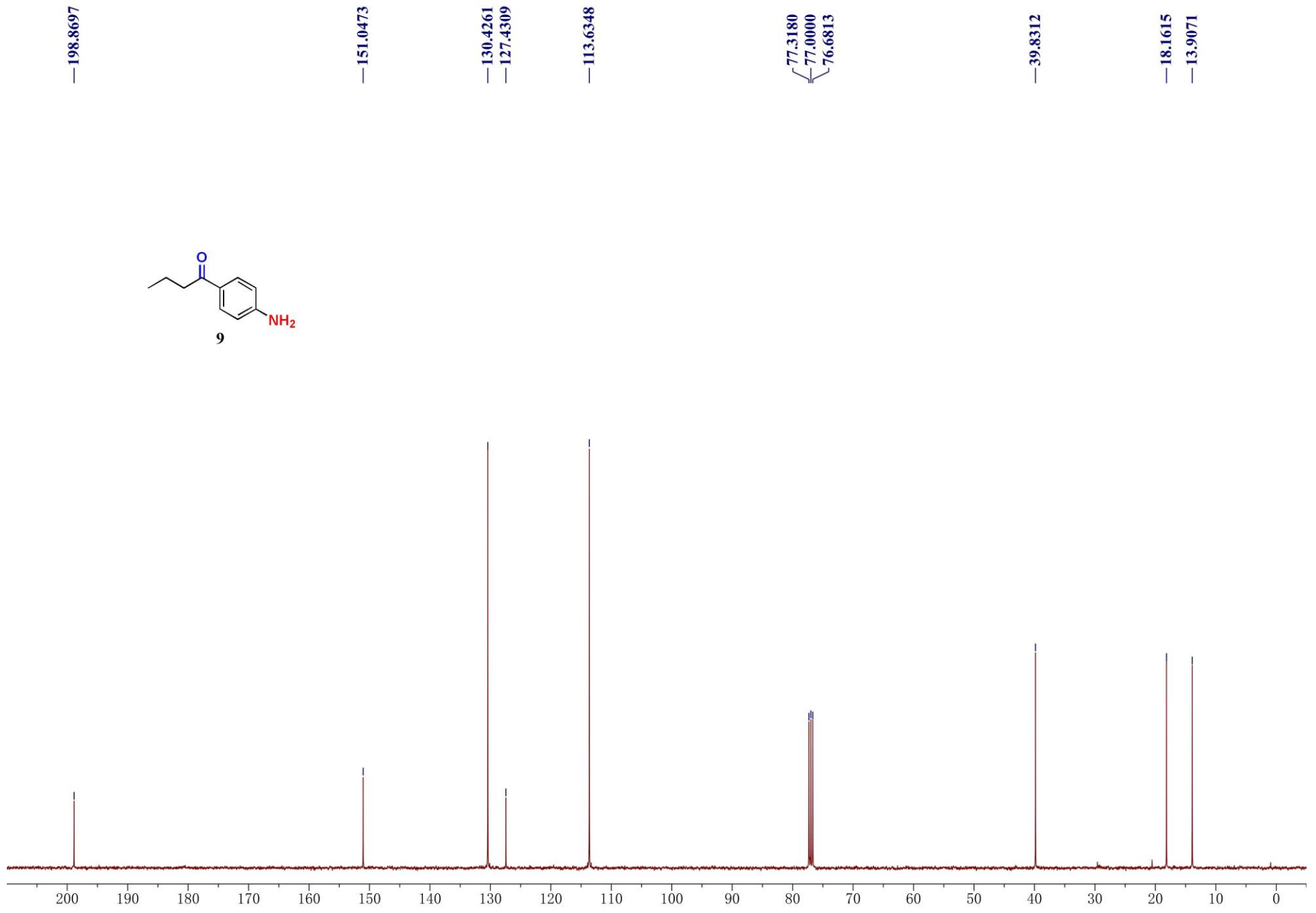

8.0369
8.0178
7.7062
7.6877
7.6691
7.5750
7.5552
7.5358
7.2600
6.9585
6.9331
6.6698
6.6648
6.6444
6.6394
6.5361
6.5312
4.3156
4.2978
4.2800
4.2622
1.3620
1.3442
1.3264
0.0000
BRUKER
NAME CLJ-WL-M325
EXPNO 1
PROCNO 1
Date_ 20190823
Time 19.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 70.36
DW 62.400 usec
DE 6.50 usec
TE 300.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 8.04 usec
SI 65536
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
N(SO2Ph)2
NCO2Et
8
9
8
7
6
5
4
3
2
1
ppm
3.96
2.06
4.02
1.00
0.98
0.94
2.07
2.97

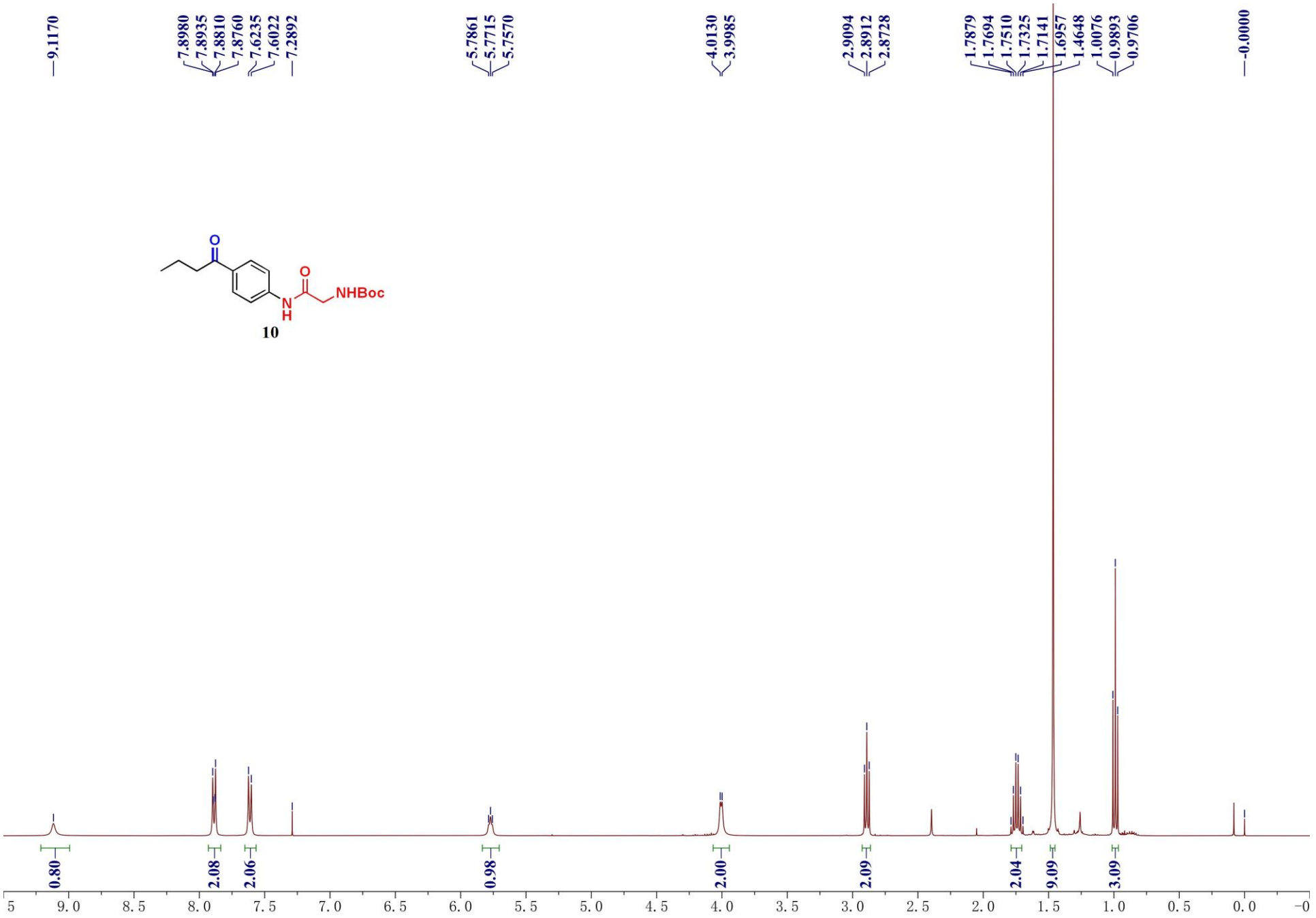


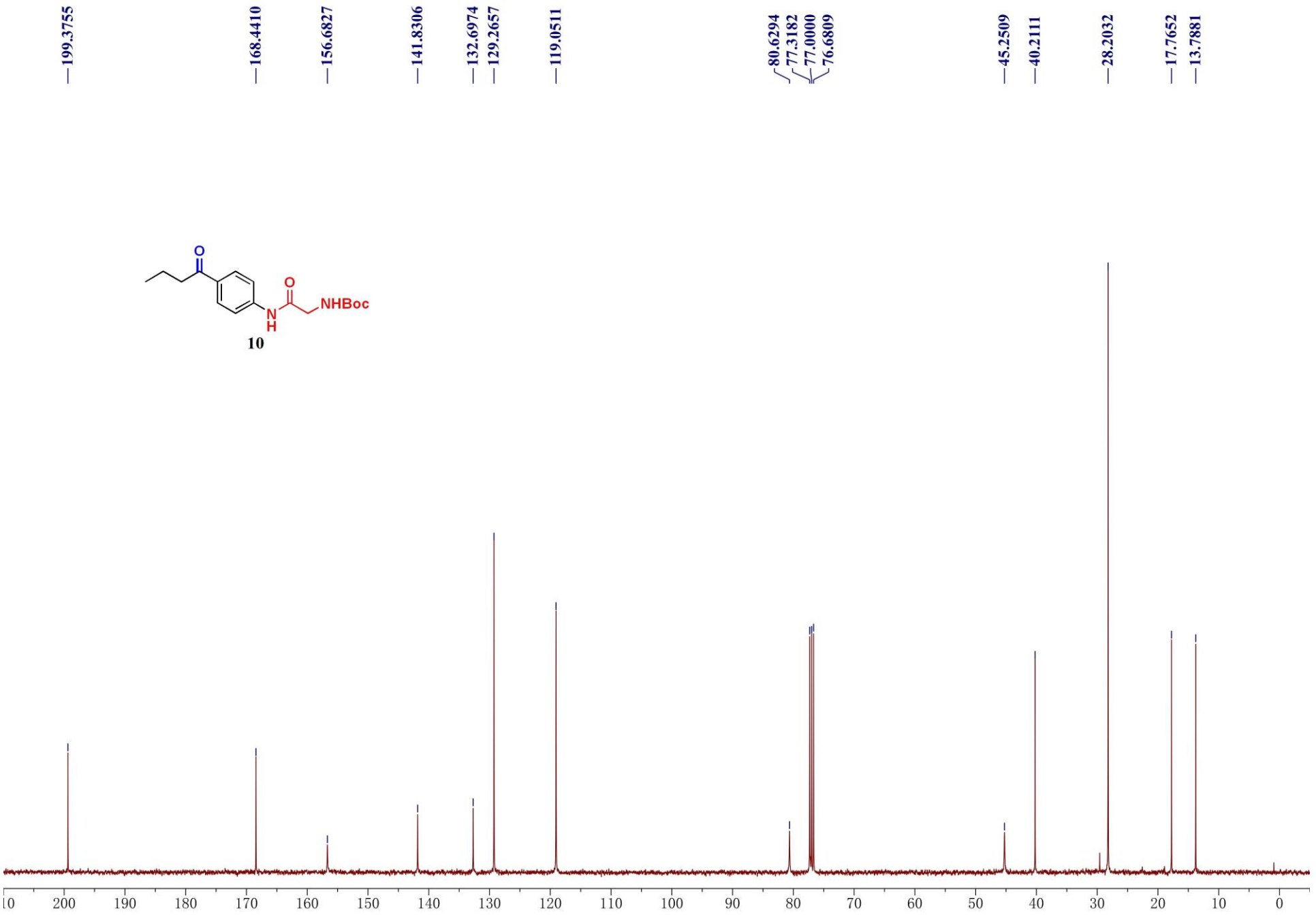
BRUKER

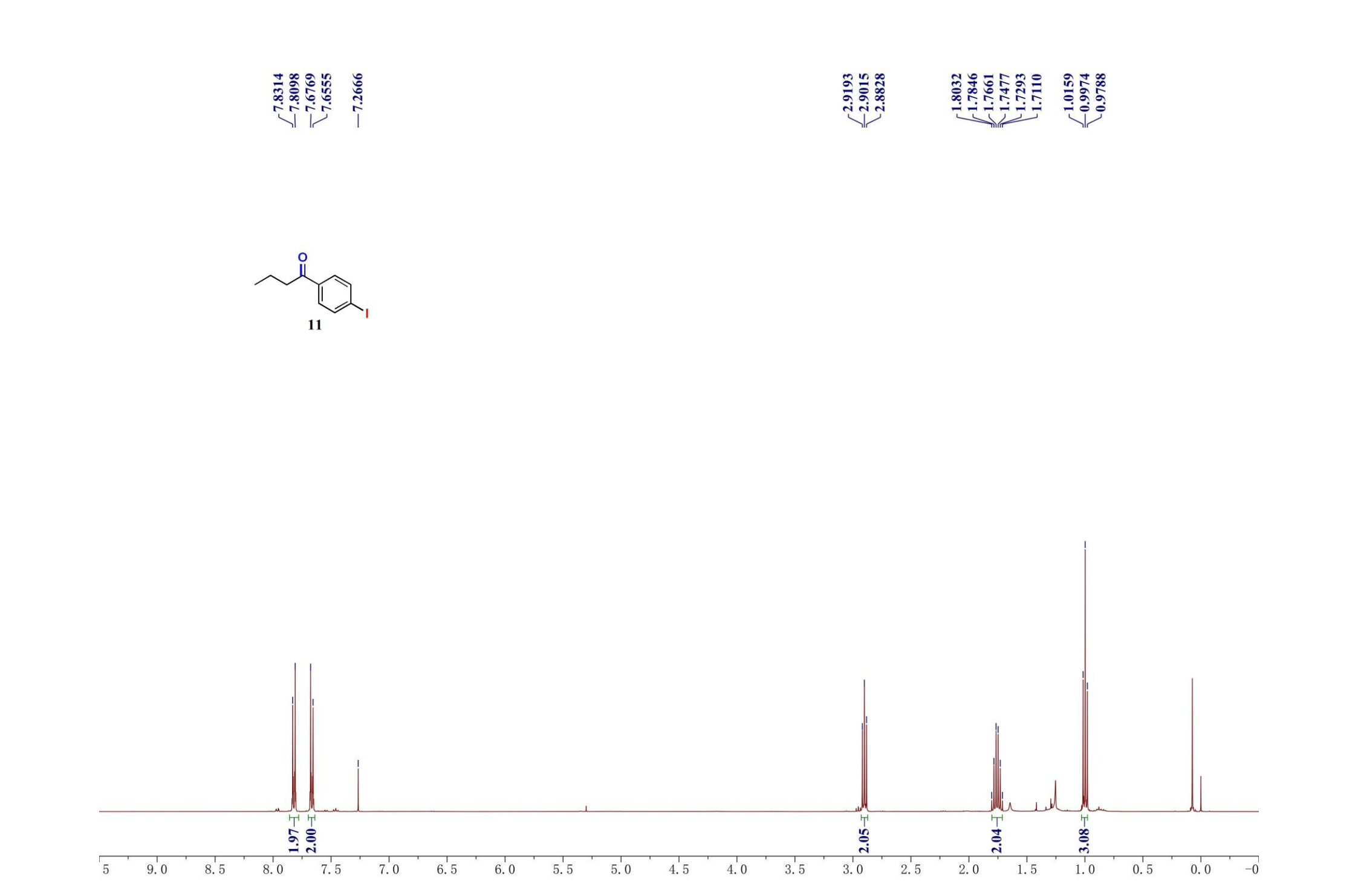
NAME	CLJ-WL-M325C
EXPNO	1
PROCNO	1
Date_	20190910
Time	21.39
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	0
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	194.26
DW	20.800 usec
DE	6.50 usec
TE	300.7 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228293 MHz
NUC1	13C
P1	8.54 usec
SI	32768
SF	100.6127746 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40


7.8199
7.7983
7.2722
6.6494
6.6277
4.2240
2.8574
2.8391
2.8204
1.7833
1.7648
1.7463
1.7279
1.7093
1.6909
1.0010
0.9826
0.9640
0.0000
O
NH2
9
2.00
2.00
1.97
2.05
2.03
3.04
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

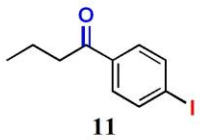

198.8697
151.0473
130.4261
127.4309
113.6348
77.3180
77.0000
76.6813
39.8312
18.1615
13.9071
O
NH2
9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


9.1170
7.8980
7.8935
7.8810
7.8760
7.6235
7.6022
7.2892
5.7861
5.7715
5.7570
4.0130
3.9985
2.9094
2.8912
2.8728
1.7879
1.7694
1.7510
1.7325
1.7141
1.6957
1.4648
1.0076
0.9893
0.9706
-0.0000
O
O
N
H
NHBoc
10
0.80
2.08
2.06
0.98
2.00
2.09
2.04
9.09
3.09
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

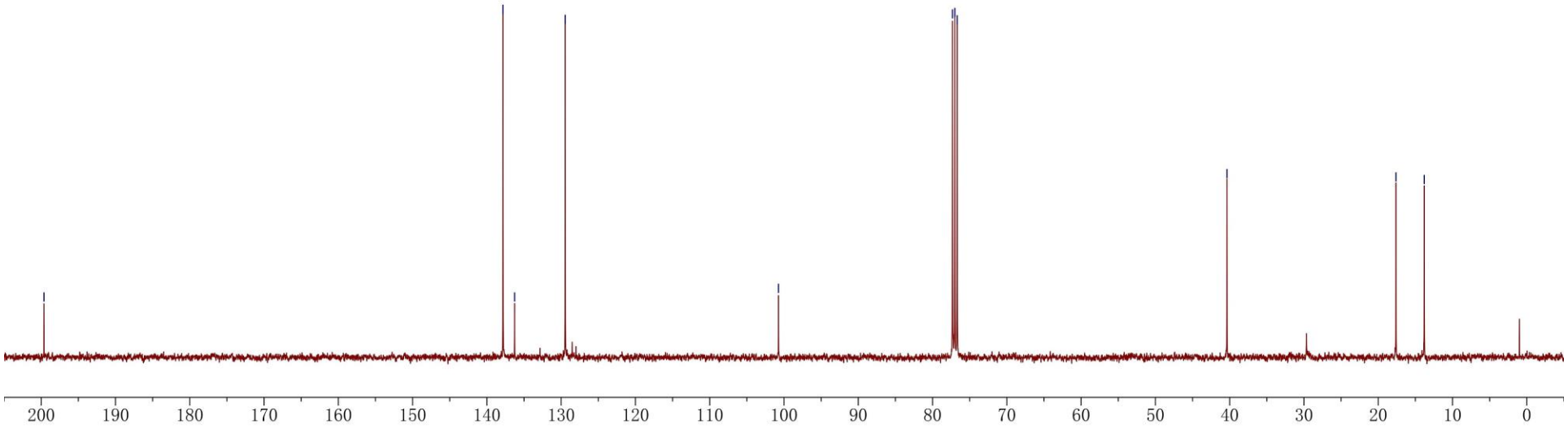

199.3755
168.4410
156.6827
141.8306
132.6974
129.2657
119.0511
80.6294
77.3182
77.0000
76.6809
45.2509
40.2111
28.2032
17.7652
13.7881
O
O
NHBoc
N
H
10
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

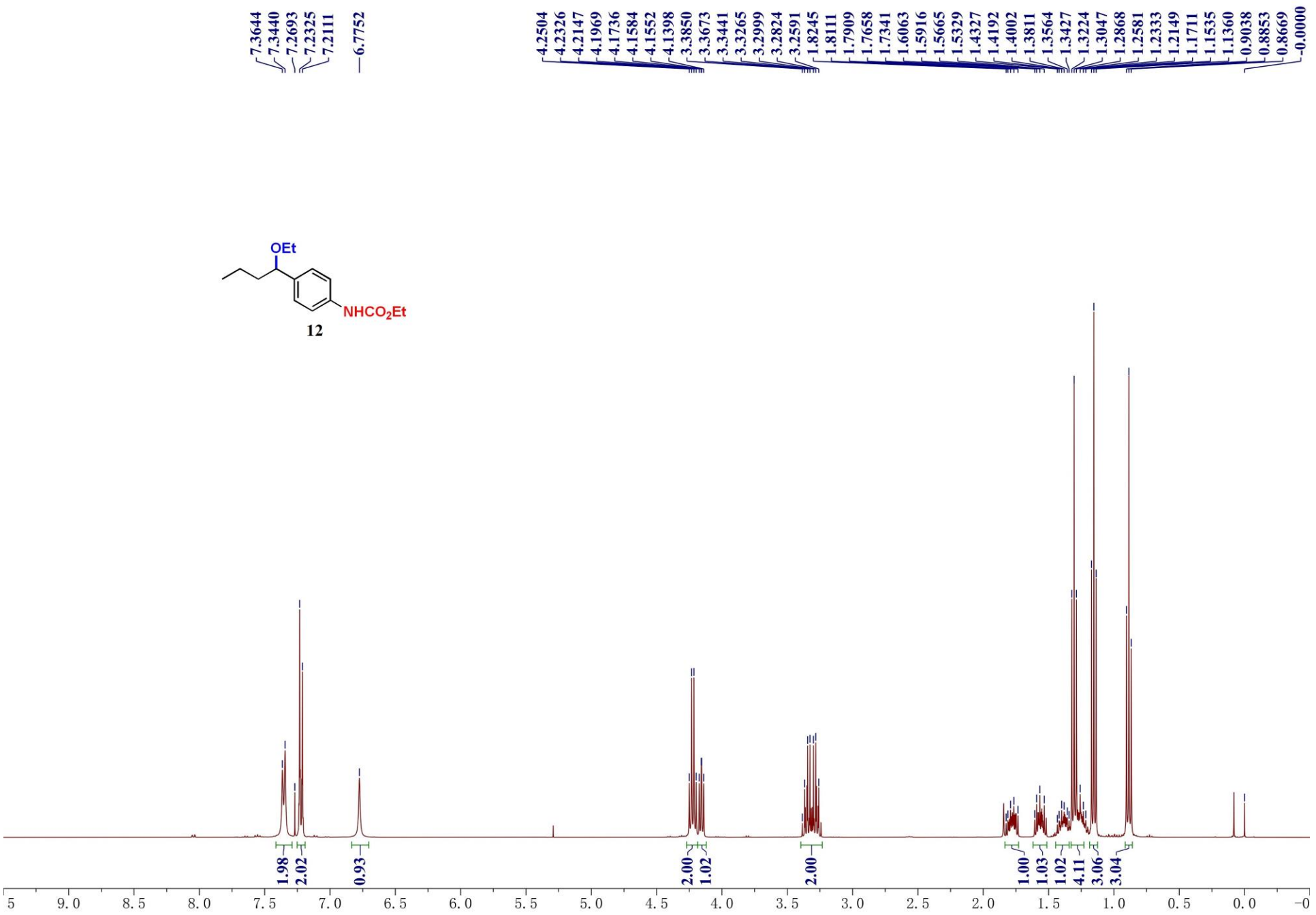

7.8314
7.8098
7.6769
7.6555
7.2666
2.9193
2.9015
2.8828
1.8032
1.7846
1.7661
1.7477
1.7293
1.7110
1.0159
0.9974
0.9788
O
I
11
1.97
2.00
2.05
2.04
3.08
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0

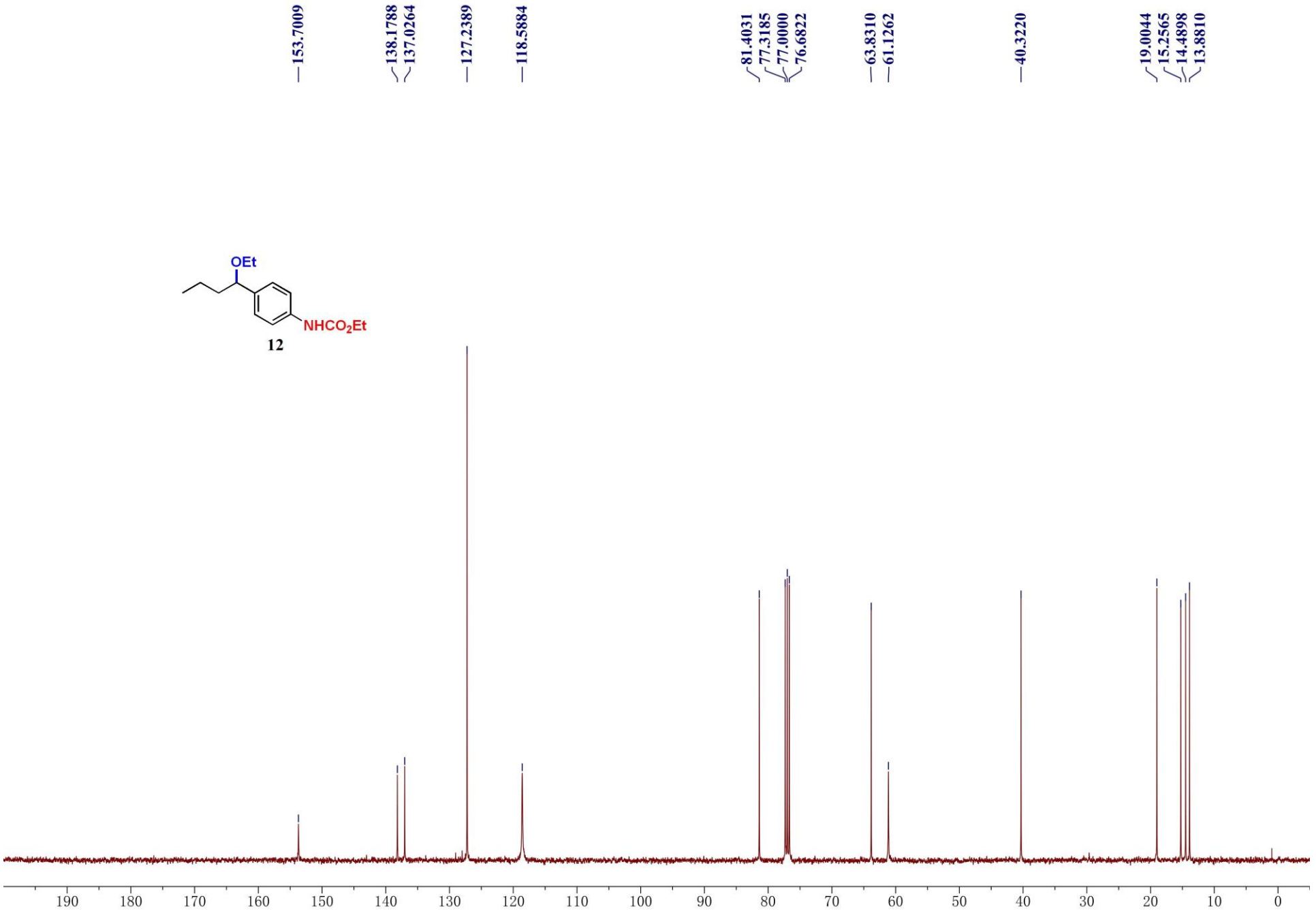
199.6248
137.8293
136.2670
129.4557
100.7399
77.3175
77.0000
76.6821
40.3673
17.6110
13.8021

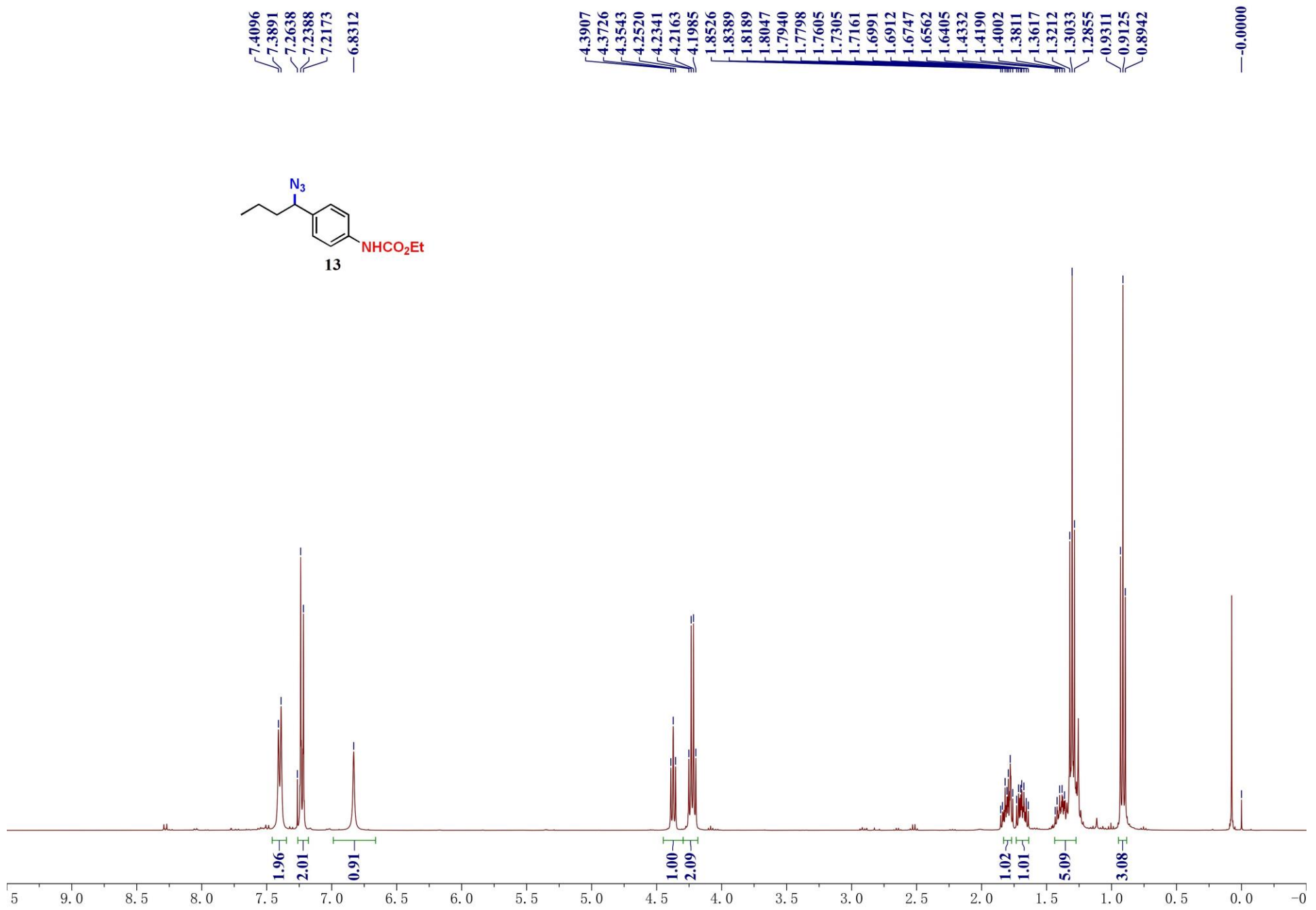


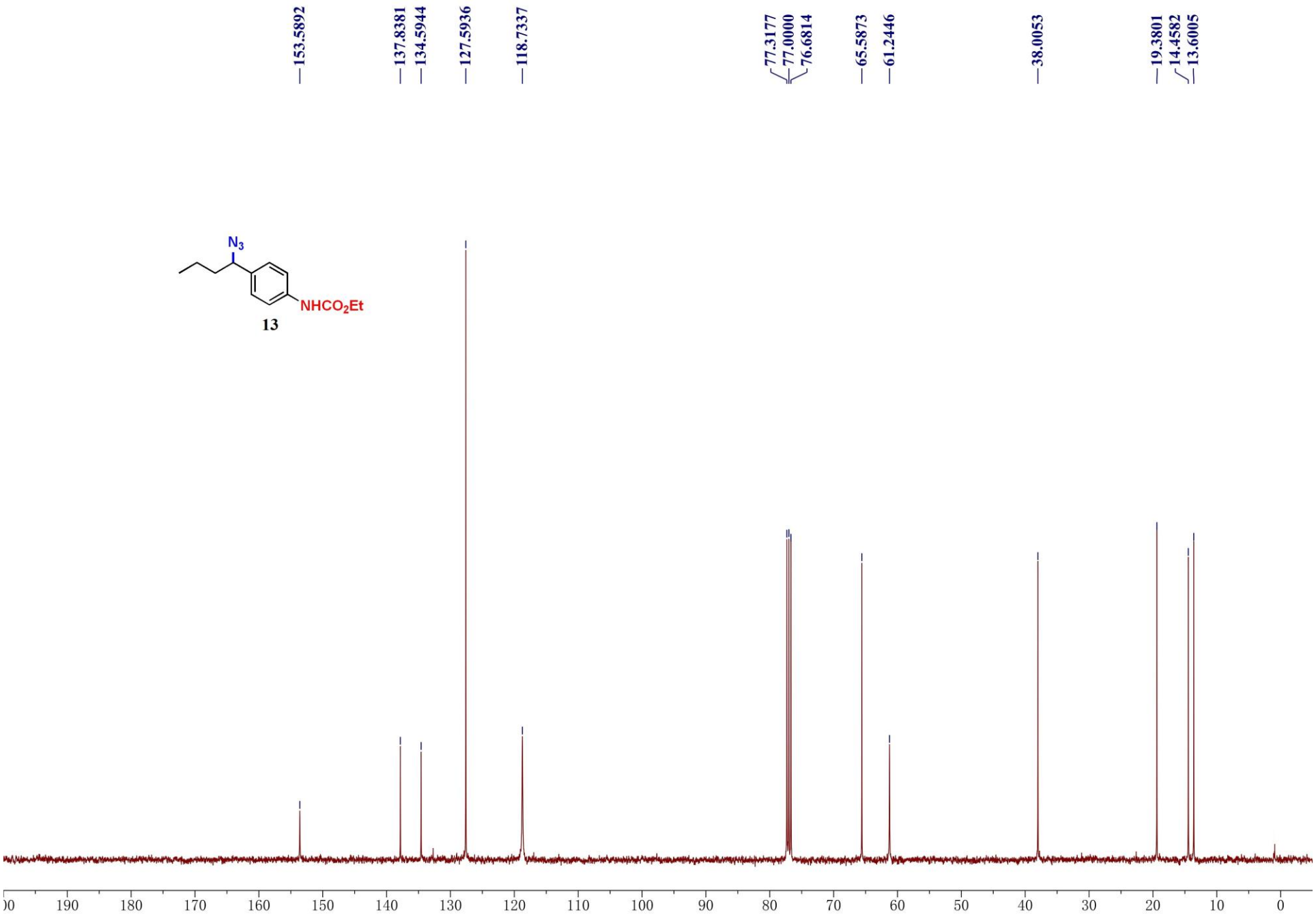
11

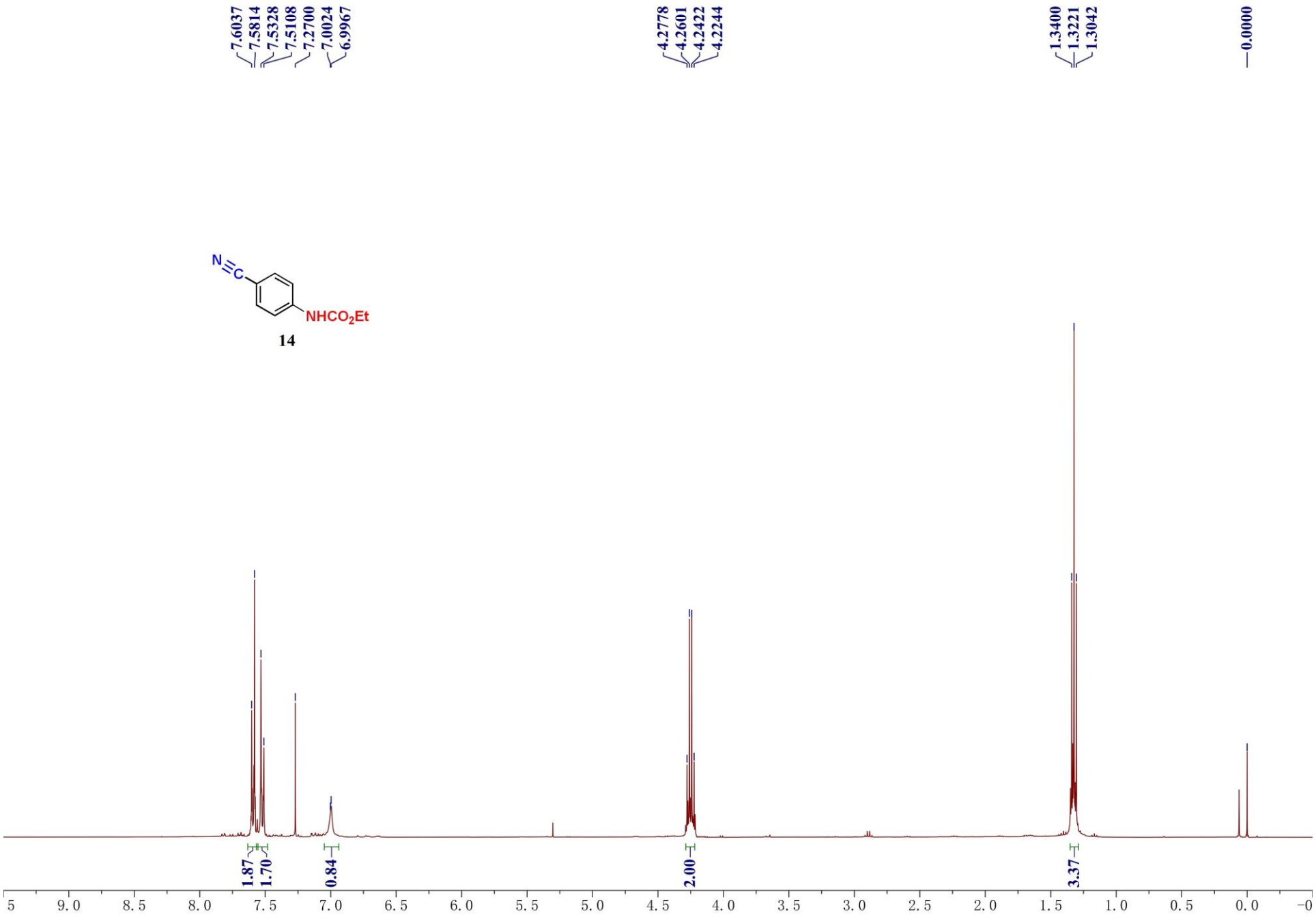


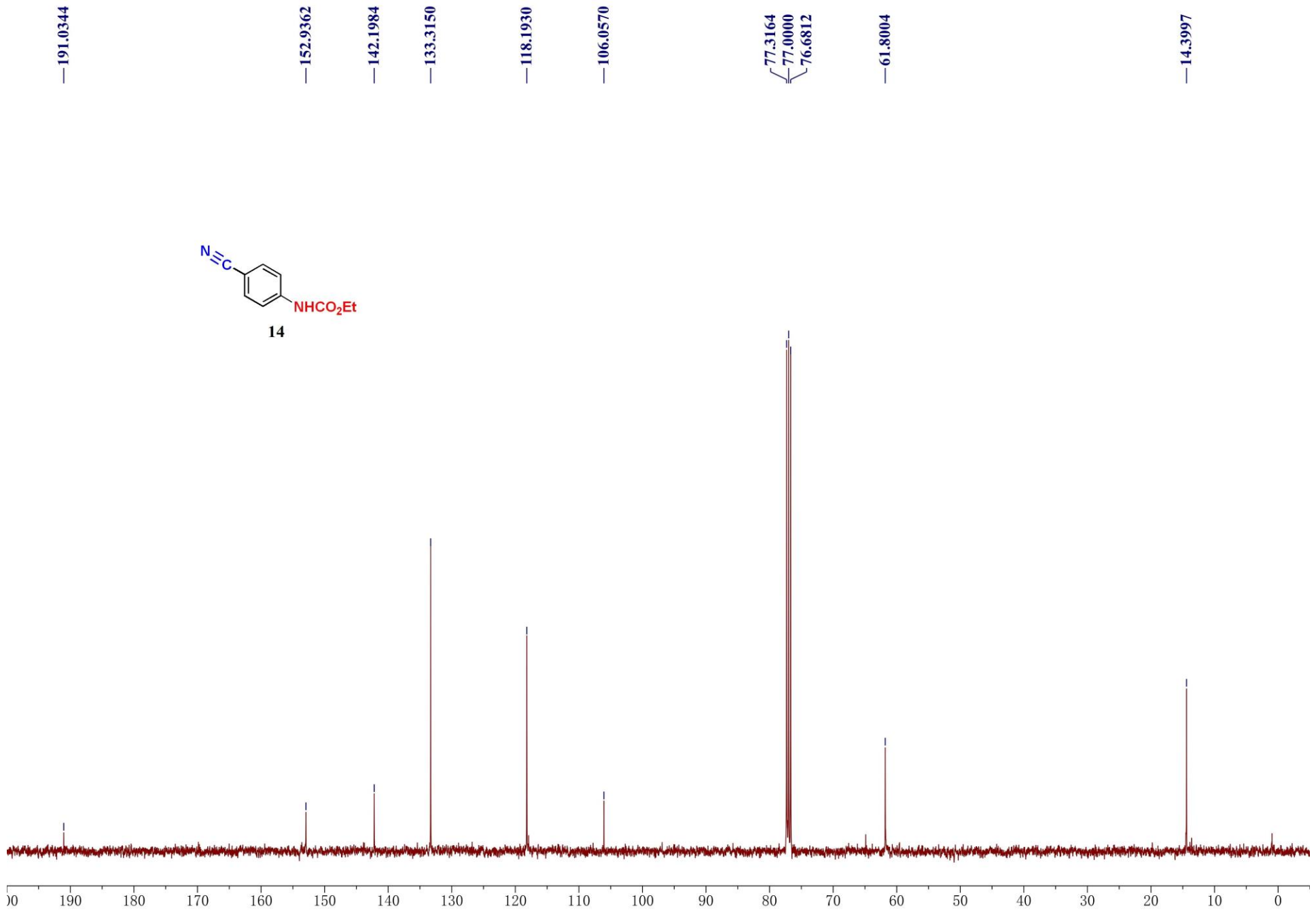

7.3644
7.3440
7.2693
7.2325
7.2111
6.7752
4.2504
4.2326
4.2147
4.1969
4.1736
4.1584
4.1552
4.1398
3.3850
3.3673
3.3441
3.3265
3.2999
3.2824
3.2591
1.8245
1.8111
1.7909
1.7658
1.7341
1.6063
1.5916
1.5665
1.5329
1.4327
1.4192
1.4002
1.3811
1.3564
1.3427
1.3224
1.3047
1.2868
1.2581
1.2333
1.2149
1.1711
1.1535
1.1360
0.9038
0.8853
0.8669
-0.0000
OEt
NHCO2Et
12
1.98
2.02
0.93
2.00
1.02
2.00
1.00
1.03
1.02
4.11
3.06
3.04
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


153.7009
138.1788
137.0264
127.2389
118.5884
81.4031
77.3185
77.0000
76.6822
63.8310
61.1262
40.3220
19.0044
15.2565
14.4898
13.8810
OEt
NHCO2Et
12
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

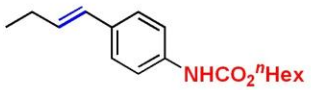

7.4096
7.3891
7.2638
7.2388
7.2173
6.8312
4.3907
4.3726
4.3543
4.2520
4.2341
4.2163
4.1985
1.8526
1.8389
1.8189
1.8047
1.7940
1.7798
1.7605
1.7305
1.7161
1.6991
1.6912
1.6747
1.6562
1.6405
1.4332
1.4190
1.4002
1.3811
1.3617
1.3212
1.3033
1.2855
0.9311
0.9125
0.8942
-0.0000
N3
NHCO2Et
13
1.96
2.01
0.91
1.00
2.09
1.02
1.01
5.09
3.08


153.5892
137.8381
134.5944
127.5936
118.7337
77.3177
77.0000
76.6814
65.5873
61.2446
38.0053
19.3801
14.4582
13.6005
N3
NHCO2Et
13
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

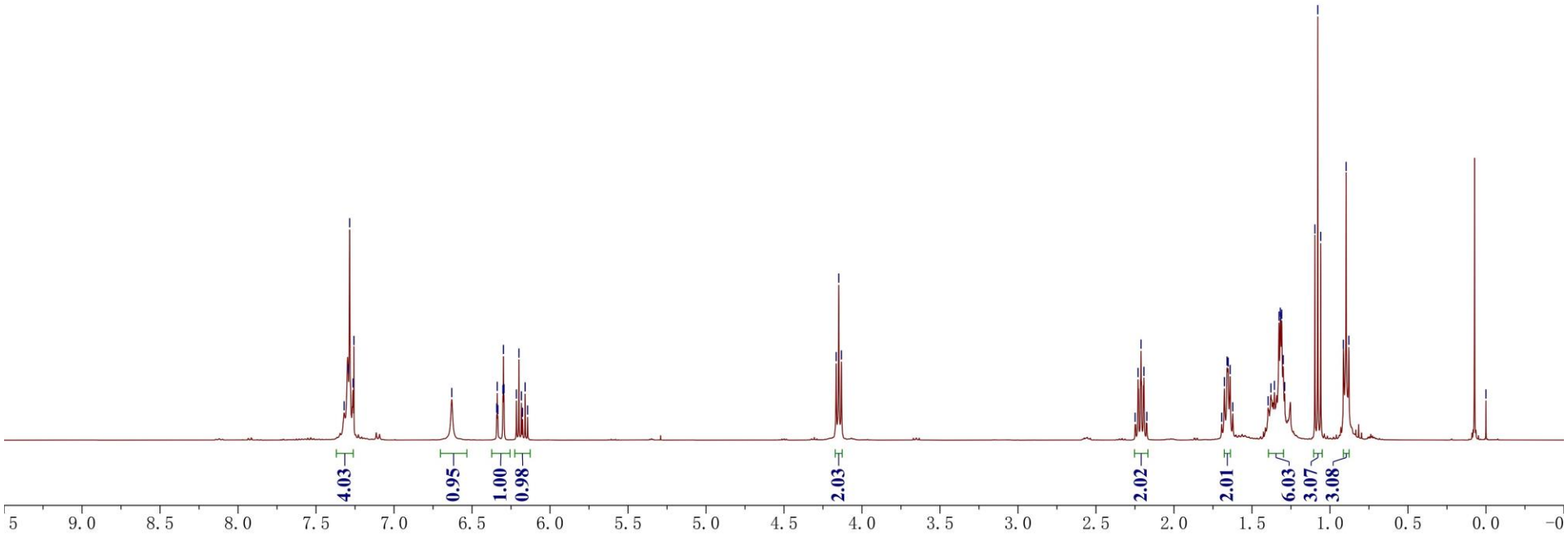

7.6037
7.5814
7.5328
7.5108
7.2700
7.0024
6.9967
4.2778
4.2601
4.2422
4.2244
1.3400
1.3221
1.3042
0.0000
N≡C
NHCO2Et
14
1.87
1.70
0.84
2.00
3.37
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0


191.0344
152.9362
142.1984
133.3150
118.1930
106.0570
77.3164
77.0000
76.6812
61.8004
14.3997
N≡C
NHCO2Et
14
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

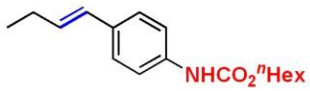

7.3198
7.2931
7.2845
7.2628
7.2573
6.6300
6.3418
6.3381
6.3344
6.3023
6.2986
6.2949
6.2154
6.1994
6.1833
6.1758
6.1599
6.1438
4.1657
4.1488
4.1320
2.2490
2.2302
2.2113
2.1924
2.1736
1.6938
1.6769
1.6598
1.6523
1.6398
1.6230
1.3965
1.3784
1.3563
1.3264
1.3180
1.3158
1.3095
1.2995
1.2903
1.0966
1.0780
1.0594
0.9139
0.8964
0.8791
-0.0000


NHCO2nHex

15


4.03
0.95
1.00
0.98
2.03
2.02
2.01
6.03
3.07
3.08
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

153.6549
136.5720
133.2129
131.5253
128.0282
126.4630
118.5970
77.3176
77.0000
76.6825
65.3835
31.4238
28.8619
25.9957
25.5022
22.5222
13.9810
13.6552



15