Supporting Information

Zinc-Catalyzed Asymmetric Nitrooxylation of β-Keto Esters/Amides with a Benziodoxole-Derived Nitrooxy Transfer Reagent

Bin Li,‡ Xuan Cheng,‡ Zhen-Yu Guan, Si-Yuan Li, Tao Huo, Guo Cheng, Yan-Hui Fan, Fang-Shuai Zhou and Qing-Hai Deng*

The Education Ministry Key Lab of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, Shanghai 200234, P. R. China

E-mail: qinghaideng@shnu.edu.cn

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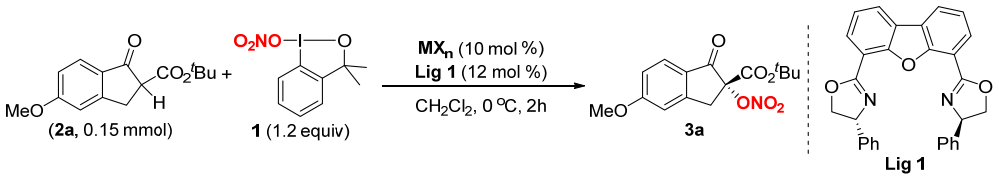
I. General Information

All manipulations were maintained under an atmosphere of nirogen unless otherwise stated. Commercially available reagents were used without further purification. Solvents were pre-dried over activated 4 Å molecular sieves and were refluxed over sodium-benzophenone (toluene, tetrahydrofurane), phosphorus pentoxide (chloroform) or calcium hydride (dichloromethane, dichloroethane, acetonitrile) under an nitrogen atmosphere and collected by distillation. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer and ^{13}C NMR spectra were recorded on a 101 MHz NMR spectrometer. Infrared spectra were prepared as KBr pellets and were recorded on a Varian Excalibur 3100 series FT-IR spectrometer. Mass spectra were recorded by the mass spectrometry service of Shanghai Institute of Organic Chemistry. HPLC analyses on a Waters 1596 or Shimadzu SPD-15C. Optical rotations were measured with Rudolph Research Analytical in a 1 dm cuvette.I. **L1-5**[1], **L6** [2], **L7**[3], **L8**[4], **L9**[5], **L10**[6], **L14**[7], **L15**[2], **L16**[8] and **L20**[7] were synthesized according to the literature procedures, and others ligands were commercially available. The substrates β-Keto Esters[9] and Amides[10] were synthesized according to the literature procedures.

II. Optimization of Asymmetric Nitrooxylation of β-Keto Esters

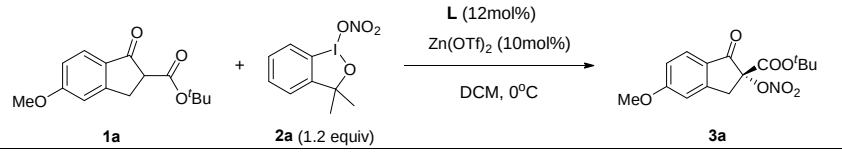
Table S1. Optimization of the Reaction Conditions (Metal Salts) for the Asymmetric Nitrooxylation



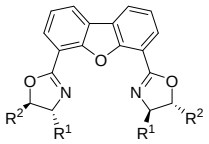
entry	MX_n	yield (%)[b]	ee (%)[c]
1[d]	-	60	-
2	$Mg(OTf)_2$	90	0
3	$Cu(OTf)_2$	94	-1
4	$Zn(OTf)_2$	88	52
5	$Ni(ClO_4)_2{\cdot}6H_2O$	82	-5
6	$Fe(OTf)_2$	94	7
7	$Co(OAc)_2{\cdot}4H_2O$	>99	-2
8	$Sc(OTf)_3$	94	0
9	$Ni(OTf)_2$	88	3
10	$Ca(OTf)_2$	78	0
11	LiOTf	77	0
12	$Al(OTf)_3$	82	1
13	$Y(OTf)_3$	91	0
14	$In(OTf)_3$	78	2

[a]Reaction conditions: **2a** (0.15 mmol), **1** (1.2 equiv.), MX_n (10 mol %), **Lig 1** (12 mol %), DCM (2.0 mL), 0 °C, N_2 atmosphere. [b]The yields of isolated products. [c]Determined by HPLC analysis. [d] Carried out at rt for 5 h.

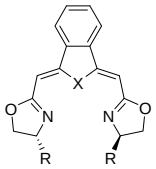
Table S2. Optimization of the Reaction Conditions (Ligands) for the Asymmetric Nitrooxylation



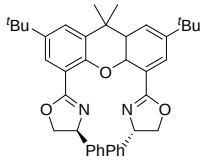
1a **2a** (1.2 equiv) **3a**



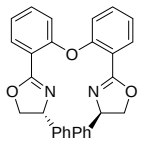
L 1 R^1 = Ph, R^2 = H 88% yield, 52% *ee*
L 2 R^1 = Bn, R^2 = H 86% yield, 2% *ee*
L 3 R^1 = ^{t}Bu, R^2 = H 57% yield, 0% *ee*
L 4 R^1 = ^{i}Pr , R^2 = H 52% yield, 41% *ee*
L 5 R^1 = Ph R^2 = Ph 79% yield, 38% *ee*



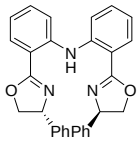
L 6 X = O, R = Ph 86% yield, 42% *ee*
L 15 X = O, R = ^{i}Pr 94% yield, 3% *ee*
L 16 X = NH, R = Ph 92% yield, 1% *ee*



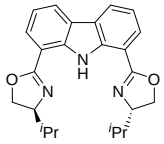
L 7
56% yield, -33% *ee*



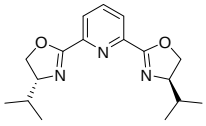
L 8
73% yield, 46% *ee*



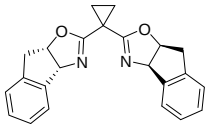
L 9
77% yield, 10% *ee*



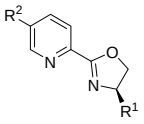
L 10
73% yield, -15% *ee*



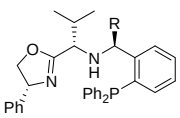
L 11
89% yield, 15% ee



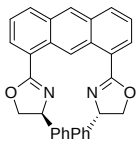
L 12
85% yield, -21% ee



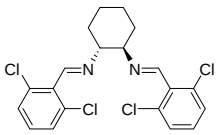
L 13 R^1 = ^{t}Bu, R^2 = H 83% yield, 17% *ee*
L 17 R^1 = ^{t}Bu, R^2 = NO_2 87% yield, 8% *ee*
L 18 R^1 = ^{t}Bu, R^2 = CF_3 85% yield, 11% *ee*
L 19 R^1 = Ph, R^2 = CF_3 82% yield, 11% *ee*



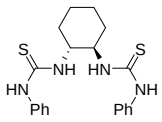
L 14 R = H 94% yield, 8% *ee*
L 20 R = Ph 94% yield, -2% *ee*



L 21
88% yield, 0% ee



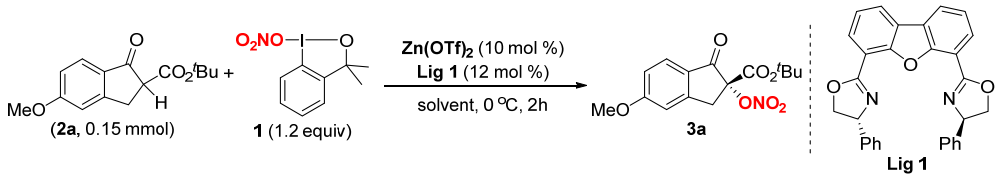
L 22
73% yield, 0% ee



L 23
62% yield, 0% ee

[a]Reaction conditions: **2a** (0.15 mmol), **1** (1.2 equiv.), $Zn(OTf)_2$ (10 mol %), **Lig** (12 mol %), DCM (2.0 mL), 0 °C, N_2 atmosphere.

Table S3. Optimization of the Reaction Conditions (solvent) for the Asymmetric Nitrooxylation

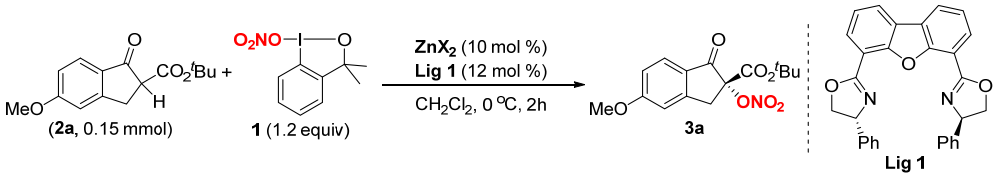


entry	solvent	yield (%)[b]	ee (%)[c]
1	DCM	88	52
2	DCE	86	45
3	MeCN	95	19
4	THF	90	1

5	$CHCl_3$	90	11
6	DME	89	5
7	chlorobenzene	97	9
8	1,2-dibromoethane	78	3
9	DCE/Et_2O	84	43
10	DCE/MeOH	trace	-

[a]Reaction conditions: **2a** (0.15 mmol), **1** (1.2 equiv.), $Zn(OTf)_2$ (10 mol %), **Lig 1** (12 mol %), solvent (2.0 mL), 0 °C, N_2 atmosphere. [b]The yields of isolated products. [c]Determined by HPLC analysis.

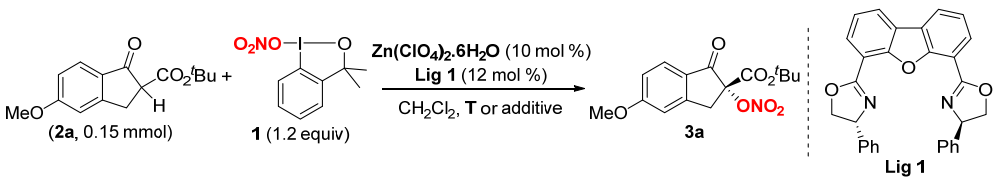
Table S4. Optimization of the Reaction Conditions ("Zn" salts) for the Asymmetric Nitrooxylation



entry	ZnX_2	yield (%)[b]	ee (%)[c]
1	$Zn(OTf)_2$	88	52
2	$Zn(NTf_2)_2$	95	23
3	$Zn(BF_4)_2{\cdot}xH_2O$	83	62
4[d]	$Zn(SbF_6)_2$	89	64
5	$Zn(ClO_4)_2{\cdot}6H_2O$	99	72
6	$Zn(OAc)_2$	87	11
7	$Zn(O_2CCF_3)_2$	83	11
8[e]	$Zn(O_2CPh)_2$	87	3

[a]Reaction conditions: **2a** (0.15 mmol), **1** (1.2 equiv.), $\mathbf{MX_n}$ (10 mol %), **Lig 1** (12 mol %), DCM (2.0 mL), 0 °C, N_2 atmosphere. [b]The yields of isolated products. [c]Determined by HPLC analysis. [d]$Zn(SbF_6)_2$ was prepared *in stu* by the reaction of $AgSbF_6$ with $ZnCl_2$ in DCM. [e]$Zn(O_2CPh)_2$ was prepared *in stu* by the reaction of AgO_2CPh with $ZnCl_2$ in DCM.

Table S5. Optimization of the Reaction Conditions (temperature and additive) for the Asymmetric Nitrooxylation

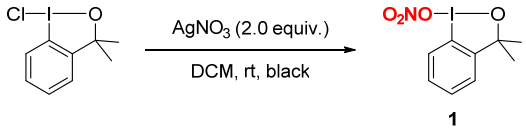


entry	T (°C)	additive	Time (h)	yield (%)[b]	ee (%)[c]
1	-20	-	5	83	53
2	0	-	2	99	72
3	rt	-	1.5	88	52
4	0	4 Å	2	76	1

[a]Reaction conditions: **2a** (0.15 mmol), **1** (1.2 equiv.), $Zn(ClO_4)_2{\cdot}6H_2O$ (10 mol %), **Lig 1** (12 mol %),

DCM (2.0 mL), 0 °C, N_2 atmosphere. [b]The yields of isolated products. [c]Determined by HPLC analysis.

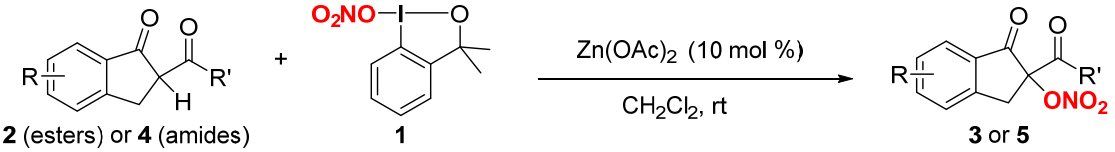
III. Preparation of reagent 1[11]



1

To an over-dried flask were added 1-chloro-3,3-dimethyl-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (10 mmol, 1.0 equiv.), $AgNO_3$ (20 mmol, 2.0 equiv.) and DCM (80 mL) at room temperature under N_2 atomasphere. After that the reaction was protected from light and stirred for 12 h at ambient temperature. Upon completion, the suspension was filtered over celite, and the filtrate was removed the solvent under reduced pressure to afford crude product as a yellow solid. The pure **reagent 1** was obtained via recrystallization in 95% yield (3.07 g, 9.5 mmol, pale yellow solid). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 1.60 (s, 6H); **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 149.0, 131.4, 131.3, 129.9, 126.8, 117.2, 89.3, 28.7; **IR *v* (KBr, cm^{-1})**: 3101, 2982, 2924, 1495, 1462, 1441, 1260, 635.

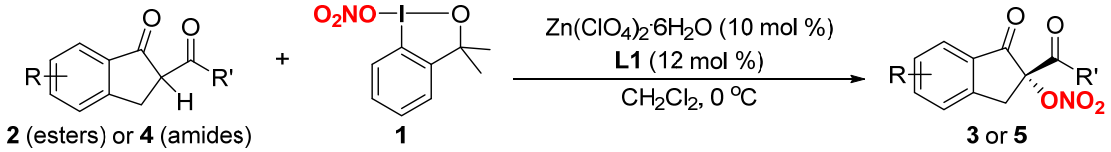
IV. General Procedure for racemic Nitrooxylation of β-Keto Esters/Amides



2 (esters) or **4** (amides) **1** **3** or **5**

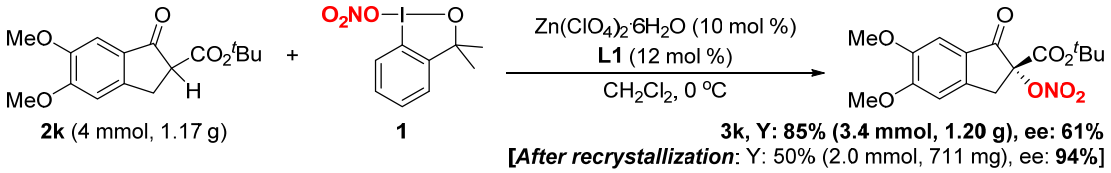
To an over-dried flask was charged with **2** or **4** (0.15 mmol, 1.0 equiv.), **reagent 1** (58.2 mg, 0.18 mmol, 1.2 equiv.), $Zn(OAc)_2$ (0.015 mmol, 10 mol %) and anhydrous CH_2Cl_2 (2 ml) under N_2 atmosphere. After that the reaction mixture was stirred at room temperature for 2 hours as monitoring by TLC. Upon completion the crude product was purified by colum chromatography via silica gel to afford the desired product **3** or **5**.

V. General Procedure for Catalytic Asymmetric Nitrooxylation



To an over-dried flask was charged with $Zn(ClO_4)_2 \cdot 6H_2O$ (0.015 mmol, 10 mol %), **L1** (0.018 mmol, 12 mol %) and anhydrous dichloromethane (2 mL) under N_2 atmosphere, then stirred at room temperature for 2 h. Substrates **2** or **4** (0.15 mmol, 1.0 equiv.) was added and stirred for 30 min at 0 °C. After that, to the mixture, **reagent 1** (0.18 mmol, 1.2 equiv.) was added and the reaction was keep in 0 °C under N_2 atmosphere as monitoring by TLC. Upon completion, the crude product was purified by column chromatography via silica gel to afford the desired asymmetric product **3** or **5**.

VI. General Procedure for Gram Scale:



2k (4 mmol, 1.17 g) **1**

3k, Y: 85% (3.4 mmol, 1.20 g), ee: 61%
[*After recrystallization*: Y: 50% (2.0 mmol, 711 mg), ee: 94%]

To an over-dried flask was charged with $Zn(ClO_4)_2 \cdot 6H_2O$ (0.4 mmol, 10 mol %), **L1** (0.48 mmol, 12 mol %) and anhydrous dichloromethane (5 mL) under N_2 atomsphere, then stirred at room temperature for 2 h. **2k** (4 mmol, 1.0 equiv.) was added and stirred for 30 min at 0 °C. After that, to the mxiture, **reagent 1** (4.8 mmol, 1.2 equiv.) was added and the reaction was keep in 0 °C under N_2 atmosphere as monitoring by TLC. Upon completion, the crude product was purified by column chromatography via silica gel to afford the desired asymmetric product **3k** in 85% yield (1.20 g, 3.4 mmol, ee: 61%). After recrystallization, the product ee value up to 94% in 50% yield (711 mg, 2.0 mmol), (Figure. S1).

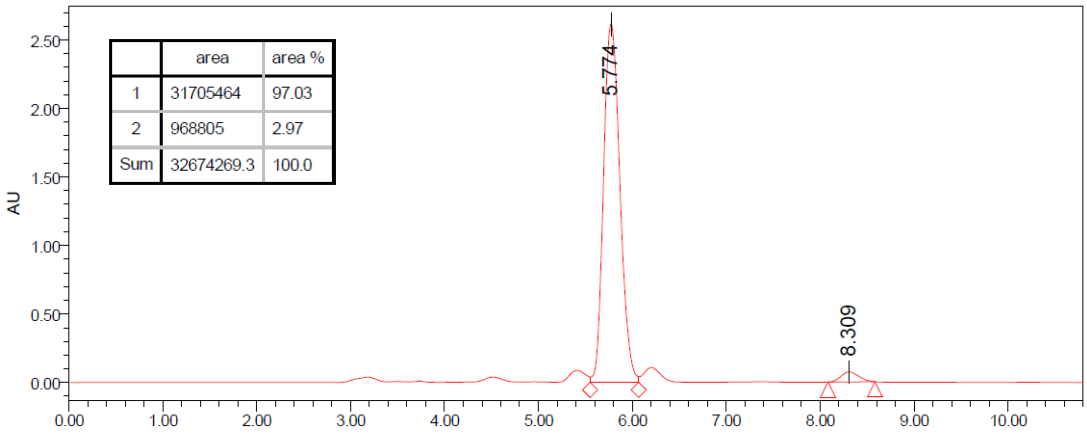
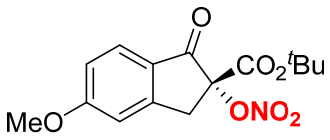
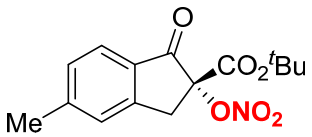


Figure S1. the HPLC spectra of **3k** after recrystallization



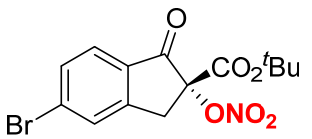
3a

(*R*)-*tert*-butyl-5-methoxy-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 99% yield (48.0 mg, 0.149 mmol); white solid (m.p. : 118-120 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.4 Hz, 1H), 6.97 (dd, *J* = 2.2, 8.6 Hz, 1H), 6.92 (s, 1H), 4.18 (d, *J* = 17.6 Hz, 1H), 3.92 (s, 3H), 3.33 (d, *J* = 17.6 Hz, 1H), 1.45 (s, 9H)； **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 189.1, 167.2, 164.4, 155.0, 127.8, 125.9, 117.0, 109.6, 89.6, 85.0, 56.1, 38.5, 27.8; **IR *v* (KBr, cm^{-1})**: 2978, 2933, 1746, 1719, 1649, 1600, 1295, 1263, 844; **HPLC**: (OD-H, Hexane/ ^{i}PrOH = 95/5, 1.0 mL/min, 254 nm), t_R (major-isomer) = 9.44 min, t_R (minor-isomer) = 10.56 min (72% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{15}H_{18}NO_7^+$ $[M+H]^+$: 324.1078, found: 324.1080.



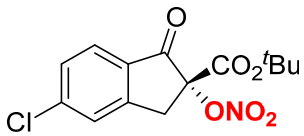
3b

(*R*)-*tert*-butyl-5-methyl-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 95% yield (43.7 mg, 0.143 mmol); white solid (m.p. : 108-110 °C); **H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.31 (s, 1H), 7.26 (d, *J*=7.6 Hz, 1H), 4.17 (d, *J* = 17.6 Hz, 1H), 3.34 (d, *J* = 17.6 Hz, 1H), 2.48 (s, 3H), 1.44 (s, 9H)； **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 190.7, 164.2, 152.3, 149.0, 130.5, 130.1, 126. 8, 125.7, 89.5, 85.0, 38.3, 27. 8, 22.5; **IR *v* (KBr, cm^{-1}):** 2980, 2928, 1753, 1721, 1656, 1295, 1150, 844, 824; **HPLC**: (OD-H, Hexane/ ^{i}PrOH = 95/5, 1.0 mL/min, 254 nm), t_R (major-isomer) = 6.4 min, t_R (minor-isomer) = 6.8 min (62% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{15}H_{18}NO_6^+$ $[M+H]^+$: 308.1129, found: 308.1132.



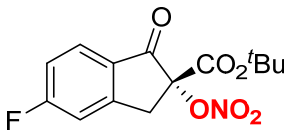
3c

(*R*)-*tert*-butyl-5-bromo-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 97% yield (54.2 mg, 0.146 mmol)； white solid (m.p. : 106-109 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 4.20 (d, *J* = 17.6 Hz, 1H), 3.39 (d, *J* = 17.6 Hz, 1H), 1.44 (s, 9H)； **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 190.3, 163.7, 153.1, 132.8, 132.5, 131.7, 129.9, 126.9, 89.0, 85.5, 38.1, 27.8； **IR *v* (KBr, cm^{-1})**: 2983, 2933, 1759, 1731, 1671, 1597, 1295, 1150, 1056, 839, 712; **HPLC**: (AD-H, Hexane/ ^{i}PrOH = 99/1, 1.0 mL/min, 254 nm), t_R (major-isomer) = 8.8 min, t_R (minor-isomer) = 11.0 min (40% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{14}H_{14}BrNNaO_6^+$ $[M+Na]^+$: 393.9897, found: 393.9896.



3d

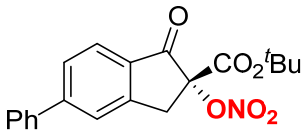
(*R*)-*tert*-butyl-5-chloro-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 93% yield (45.7 mg, 0.140 mmol); white solid (m.p. : 122-125 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.53 (s, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 4.20 (d, *J* = 18.0 Hz, 1H), 3.38 (d, *J* = 17.6 Hz, 1H), 1.44 (s, 9H)； **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 189.5, 169.8, 167.2, 163.9, 154.8, 128.5, 117.5, 113.6, 89.2, 85.4, 38.4, 27.8; **IR *v* (KBr, cm^{-1})**: 2980, 2930, 1761, 1729, 1654, 1594, 1295, 1150, 826; **HPLC**: (OD-H, Hexane/ ^{i}PrOH = 99/1, 1.0 mL/min, 254 nm), t_R (major-isomer) = 12.2 min, t_R (minor-isomer) = 13.6 min (46% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{14}H_{14}ClNNaO_6^+$ $[M+Na]^+$: 350.0402, found: 350.0398.



3e

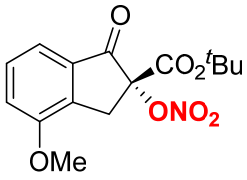
(*R*)-*tert*-butyl-5-fluoro-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 96% yield (44.8 mg, 0.144 mmol)； white solid (m.p. : 107-112 °C) ; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (dd, *J* = 5.2, 8.4 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 4.22 (d, *J* = 17.6 Hz, 1H), 3.39 (d, *J* = 18.0 Hz, 1H), 1.44 (d, *J* = 1.6 Hz,

9H); **$^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$)** δ 189.5, 168.5 (d, *J* = 261.6 Hz), 163.9, 154.8(d, *J* = 11.1 Hz), 129.3 (d, *J* = 2.0 Hz), 128.4(d, *J* = 11.1 Hz), 117.3 (d, *J* = 23.2 Hz), 113.4 (d, *J* = 23.2 Hz), 89.2, 85.4, 38.4 (d, *J* = 2.0 Hz), 27.8; **HPLC**: (AD-H, Hexane/ ^{i}PrOH = 99/1, 1.0 mL/min, 254 nm), t_R (major-isomer) = 11.3 min, t_R (minor-isomer) = 12.7 min (62% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{14}H_{15}FNO_6^+$ $[M+H]^+$: 312.0878, found: 312.0870.



3f

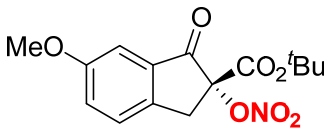
(*R*)-*tert*-butyl-2-(nitrooxy)-1-oxo-5-phenyl-2,3-dihydro-1*H*-indene-2-carboxylate; 98% yield (54.3 mg, 0.147 mmol); white solid (m.p. : 86-89 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.60 (m, 4H), 7.48 (dt, *J* = 13.5, 7.0 Hz, 3H), 4.28 (d, *J* = 17.6 Hz, 1H), 3.45 (d, *J* = 17.6 Hz, 1H), 1.47 (s, 9H); **$^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$)** δ 190.8, 164.2, 152.5, 150.3, 139.6, 131.7, 129.2, 128.2, 127.7, 126.3, 124.8, 89.5, 85.2, 38.5, 27.8; **HPLC**: (AD-H, Hexane/ ^{i}PrOH = 95/5, 1.0 mL/min, 254 nm), t_R (major-isomer) = 9.8 min, t_R (minor-isomer) = 19.1 min (55% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{20}H_{20}NO_6^+$ $[M+H]^+$: 370.1285, found: 370.1280.



3g

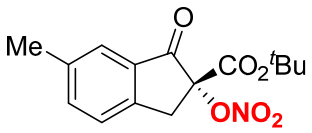
(*R*)-*tert*-butyl-4-methoxy-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 97% yield (47.0 mg, 0.146 mmol)； white solid (m.p: 75-77 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.35 (m, 2H), 7.14 (dd, *J* = 7.2, 1.6 Hz, 1H), 4.14 (dd, *J* = 18.0, 4.8 Hz, 1H), 3.92 (d, *J* = 2.8 Hz, 3H), 3.26 (dd, *J* = 18.2, 3.4 Hz, 1H), 1.44 (d, *J* = 4.0 Hz, 9H); **$^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$)** δ 191.7, 164.1, 156.7, 140.8, 134.1, 130.3, 117.01, 116.99, 89.1, 85.0, 55.8, 35.3, 27.8; **HPLC**: (OD-H, Hexane/ ^{i}PrOH = 99/1, 1.0 mL/min, 254 nm), t_R (major-isomer) = 8.1 min, t_R (minor-isomer) = 10.7 min

(55% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{15}H_{18}NO_7^+$ $[M+H]^+$: 324.1078, found: 324.1082.



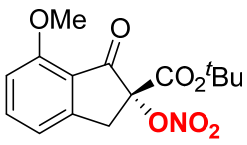
3h

(*R*)-tert-butyl-6-methoxy-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 92% yield (44.6 mg, 0.138 mmol); white solid (m.p. : 85-87 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 (d, *J* = 8.4 Hz, 1H), 7.29 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 4.14 (d, *J* = 17.6 Hz, 1H), 3.84 (s, 3H), 3.32 (d, *J* = 17.6 Hz, 1H), 1.44 (s, 9H); **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 191.4, 164.1, 160.3, 144.9, 134.0, 127.2, 126.7, 106.6, 89.9, 85.1, 55.8, 37.8, 27.8; **IR *v* (KBr, cm^{-1})**: 2980, 2937, 1756; 1759; 1667; 1301; 1203; 1153; 1063; 840; **HPLC**: (OD-H, Hexane/ ^{i}PrOH = 95/5, 1.0 mL/min, 254 nm), t_R (major-isomer) = 7.4 min, t_R (minor-isomer) = 8.6 min (55% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{15}H_{18}NO_7^+$ $[M+H]^+$: 324.1078, found: 324.1087.



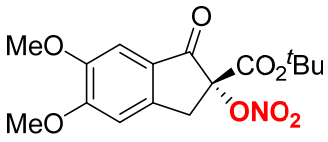
3i

(*R*)-*tert*-butyl-6-methyl-2-(nitrooxy)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate;92% yield (42.4 mg, 0.138 mmol); light yellow oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 4.17 (d, *J* = 17.6 Hz, 1H), 3.34 (d, *J* = 17.6 Hz, 1H), 2.42 (s, 3H), 1.43 (s, 9H); **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 191.4, 164.2, 149.3, 138.9, 138.4, 133.0, 126.2, 125.7, 89.6, 85.0, 38.2, 27.8, 21.2; **HPLC**: (OD-H, Hexane/ ^{i}PrOH = 99.2/0.8, 1.0 mL/min, 254 nm), t_R (major-isomer) = 9.0 min, t_R (minor-isomer) = 13.0 min (55% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{15}H_{18}NO_6^+$ $[M+H]^+$: 308.1129, found: 308.1125.



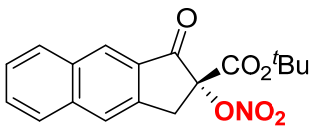
3j

(*R*)-*tert*-butyl-7-methoxy-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 92% yield (44.6 mg, 0.138 mmol); white solid (m.p. : 127-130 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (t, *J* = 8.2 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 4.16 (d, *J* = 17.6 Hz, 1H), 3.95 (s, 3H), 3.32 (d, *J* = 17.6 Hz, 1H), 1.44 (s, 9H)； **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 188.3, 164.4, 159.8, 153.8, 138.9, 121.3, 118.07, 110.3, 89.4, 85.0, 56.2, 38.0, 27.9; **HPLC**: (AD-H, Hexane/ ^{i}PrOH = 90/10, 1.0 mL/min, 254 nm), t_R (major-isomer) = 9.3 min, t_R (minor-isomer) = 12.0 min (78% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{15}H_{18}NO_7^+$ $[M+H]^+$: 324.1078, found: 324.1081.



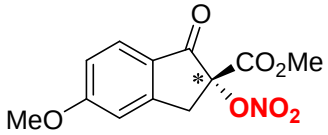
3k

(*R*)-*tert*-butyl-5,6-dimethoxy-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 99% yield (52.5 mg, 0.149 mmol); white solid (m.p. : 116-119 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.18 (d, *J* = 1.6 Hz, 1H), 6.90 (s, 1H), 4.13 (d, *J* = 17.6 Hz, 1H), 4.00 (s, 3H), 3.90 (s, 3H), 3.29 (d, *J* = 17.6 Hz, 1H), 1.44 (d, *J* = 1.6 Hz, 9H); **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** 189.5, 164.4, 157.5, 150.4, 148.0, 125.4, 107.1, 105.6, 89.6, 85.0, 56.7, 56.3, 38.2, 27.8; **IR *v* (KBr, cm^{-1})**: 2978, 2935, 1756, 1741, 1638, 1270, 1265, 1148, 836, 774; **HPLC**: (AD-H, Hexane/ ^{i}PrOH = 80/20, 1.0 mL/min, 254 nm), t_R (major-isomer) = 5.8 min, t_R (minor-isomer) = 8.4 min (61% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{16}H_{19}NNaO_8^+$ $[M+Na]^+$: 376.1003, found: 376.1010.



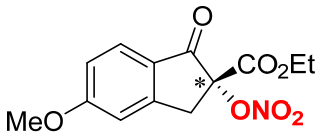
3l

(*R*)-*tert*-butyl-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-cyclopenta[b]naphthalene-2-carboxylate; 94% yield (48.4 mg, 0.141 mmol); white solid (m.p: 149-154 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.43 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.94 – 7.84 (m, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 4.40 (d, *J* = 17.6 Hz, 1H), 3.58 (d, *J* = 17.6 Hz, 1H), 1.43 (s, 9H); **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 191.7, 164.2, 143.3, 138.3, 132.8, 130.7, 130.4, 130.1, 128.2, 127.6, 127.1, 124.8, 89.9, 85.2, 38.1, 27.8; **IR *v* (KBr, cm^{-1})**: 2975, 2928, 1739, 1724, 1647, 1295, 1150, 1133, 844, 749; **HPLC**: (OD-H, Hexane/ ^{i}PrOH = 97/3, 1.0 mL/min, 254 nm), t_R (major-isomer) = 9.5 min, t_R (minor-isomer) = 11.0 min (44% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{18}H_{17}NNaO_6^+$ $[M+Na]^+$: 366.0948, found: 366.0939.



3m

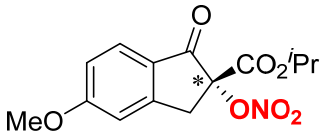
(*R*)-Methyl-5-methoxy-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 88% yield (42.7 mg, 0.132 mmol); white solid (m.p. : 105-110 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 9.6 Hz, 1H), 6.94 (s, 1H), 4.22 (d, *J* = 17.6 Hz, 1H), 3.93 (s, 3H), 3.81 (s, 3H), 3.37 (d, *J* = 17.6 Hz, 1H); **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 188.5, 167.4, 166.1, 154.8, 127.9, 125.6, 117.2, 109.7, 89.3, 56.1, 54.0, 38.4; **HPLC**: (AD-H, Hexane/ ^{i}PrOH = 95/5, 1.0 mL/min, 254 nm), t_R (major-isomer) = 17.6 min, t_R (minor-isomer) = 18.7 min (6% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{12}H_{11}NNaO_7^+$ $[M+Na]^+$: 304.0428, found: 304.0431.



3n

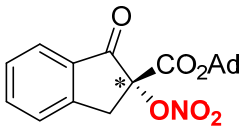
(*R*)-Ethyl-5-methoxy-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 92% yield (40.7 mg, 0.138 mmol); white solid (m.p. : 109-113 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.4 Hz, 1H), 6.98 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.94 (s, 1H), 4.28 (qd, *J* = 7.1, 2.3 Hz, 2H), 4.22 (d, *J* = 17.6 Hz, 1H), 3.93 (s, 3H), 3.36 (d, *J* = 17.6 Hz,

1H), 1.26 (t, *J* = 7.2 Hz, 3H); **$^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$)** δ 188.6, 167.4, 165.5, 154.9, 127.9, 125.7, 117.2, 109.7, 89.3, 63.4, 56.1, 38.4, 14.1; **HPLC**: (OD-H, Hexane/ ^{i}PrOH = 97/3, 1.0 mL/min, 254 nm), t_R (minor - isomer) = 21.2 min, t_R (major - isomer) = 24.1 min (21% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{13}H_{14}NO_7^+$ $[M+H]^+$: 296.0765, found: 296.0771.



3o

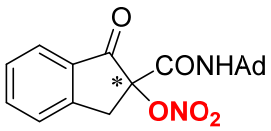
(*R*)-Isopropyl-5-methoxy-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 96% yield (44.5 mg, 0.144 mmol); white solid (m.p. : 116-119 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.8 Hz, 1H), 6.98 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.93 (s, 1H), 5.11 (m, 1H), 4.22 (d, *J* = 18.0 Hz, 1H), 3.93 (s, 3H), 3.35 (d, *J* = 17.6 Hz, 1H), 1.29 (d, *J* = 6.4 Hz, 3H), 1.22 (d, *J* = 6.0 Hz, 3H); **$^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$)** δ 188.7, 167.3, 154.9, 127.9, 125.8, 117.1, 109.7, 89.3, 71.7, 56.1, 38.4, 21.7, 21.5; **HPLC**: (AD-H, Hexane/ ^{i}PrOH = 94/6, 1.0 mL/min, 254 nm), t_R (major-isomer) = 15.4 min, t_R (minor-isomer) = 16.7 min (14% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{14}H_{16}NO_7^+$ $[M+H]^+$: 310.0921, found: 310.0919.



3p

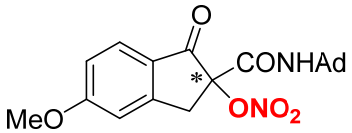
(3*r*)-adamantan-1-yl-(2*R*)-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate; 88% yield (49.0 mg, 0.132 mmol); white solid (m.p. : 126-129 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.0, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 4.22 (d, *J* = 18.0 Hz, 1H), 3.41 (d, *J* = 17.6 Hz, 1H), 2.16 (s, 3H), 2.06 (d, *J* = 2.8 Hz, 6H), 1.63 (t, *J* = 3.0 Hz, 6H); **$^{13}C\{^{1}H\}$NMR (101 MHz, $CDCl_3$)** δ 191.5, 163.6, 151.8, 137.0, 132.9, 128.7, 126.5, 125.9, 89.2, 85.2, 41.1, 38.5, 36.0, 31.1; **HPLC**： (AD-H, Hexane/ ^{i}PrOH = 97/3, 1.0 mL/min, 254 nm), t_R

(major-isomer) = 11.0 min, t_R (minor-isomer) = 14.8 min (24% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{20}H_{22}NO_6^+$ $[M+H]^+$: 372.1442, found: 372.1448.



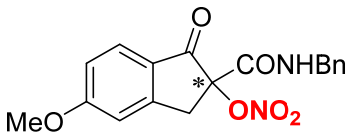
5a

2-(((3*r*)-adamantan-1-yl)carbamoyl)-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate; 90% yield (50.0 mg, 0.135 mmol)； white solid (m.p. : 140-142 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.0 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 6.12 (s, 1H), 4.31 (d, *J* = 17.2 Hz, 1H), 3.27 (d, *J* = 16.8 Hz, 1H), 2.07 (s, 3H), 1.98 (s, 5H), 1.66 (d, *J* = 2.8 Hz, 7H); **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 195.2, 161.2, 152.1, 136.9, 133.0, 128.5, 126.6, 125.5, 91.3, 53.2, 41.3, 36.3, 35.5, 29.5; **HPLC**: (AD-H, Hexane/ ^{i}PrOH = 95/5, 1.0 mL/min, 254 nm), t_R (minor - isomer) = 8.3 min, t_R (major-isomer) = 11.7 min (14% *ee*); **HRMS (ESI, m/z):** calcd for $C_{20}H_{23}N_2O_5^+$ $[M+H]^+$: 371.1601, found: 371.1607.



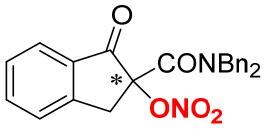
5b

2-(((3*r*)-adamantan-1-yl)carbamoyl)-5-methoxy-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate; 89% yield (53.6 mg, 0.134 mmol); white solid (m.p. : 97-101 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 - 7.69 (m, 1H), 7.01 – 6.88 (m, 2H), 6.14 (s, 1H), 4.28 (d, *J* = 16.8 Hz, 1H), 3.90 (s, 3H), 3.20 (d, *J* = 17.2 Hz, 1H), 2.10 – 1.92 (m, 9H), 1.71 – 1.62 (m, 6H); **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 192.7, 167.2, 161.6, 155.2, 127.4, 125.9, 116.9, 109.6, 91.6, 56.0, 53.1, 41.2, 36.3, 35.4, 29.5; **HPLC:** (OD-H, Hexane/ ^{i}PrOH = 90/10, 1.0 mL/min, 254 nm), t_R (major-isomer) = 6.3 min, t_R (minor-isomer) = 11.0 min (12% *ee*); **HRMS (ESI, m/z):** calcd for $C_{21}H_{25}N_2O_6^+$ $[M+H]^+$: 401.1707, found: 401.1711.



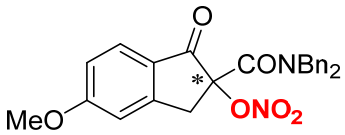
5c

2-(benzylcarbamoyl)-5-methoxy-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate; 91% yield (48.8 mg, 0.137 mmol); white solid (m.p. : 97-101 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 – 7.72 (m, 1H), 7.37 – 7.22 (m, 5H), 7.00 – 6.93 (m, 2H), 6.81 (s, 1H), 4.55 – 4.47 (m, 1H), 4.45 – 4.33 (m, 1H), 3.92 (s, 3H), 3.28 (d, *J* = 17.6 Hz, 1H); **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 192.1, 167.3, 163.2, 155.2, 137.1, 128.9, 127.9, 127.7, 127.5, 125.8, 117.1, 109.7, 91.3, 56.1, 44.4, 35.7; HPLC: (AD-H, Hexane/ ^{i}PrOH = 92/8, 1.0 mL/min, 254 nm), t_R (major-isomer) = 29.3 min, t_R (minor-isomer) = 34.1 min (6% *ee*); **HRMS (ESI, m/z):** calcd for $C_{18}H_{17}N_2O_6^+$ $[M+H]^+$: 357.1081, found: 357.1089.



5d

2-(dibenzylcarbamoyl)-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate; 84% yield (52.5 mg, 0.126 mmol); white solid (m.p. : 87-91 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 – 7.63 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 7.23 (td, *J* = 7.4, 1.2 Hz, 1H), 7.19 – 7.11 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 5.07 (d, *J* = 16.0 Hz, 1H), 4.97 (d, *J* = 14.8 Hz, 1H), 4.80 (d, *J* = 14.8 Hz, 1H), 4.56 (d, *J* = 17.6 Hz, 1H), 4.38 (d, *J* = 15.6 Hz, 1H), 3.56 (d, *J* = 17.6 Hz, 1H); **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 202.7, 167.9, 154.9, 136.5, 135.7, 134.3, 133.3, 131.5, 128.9, 128.1, 128.0, 127.8, 127.7, 127.5, 126.3, 126.2, 125.7, 124.9, 61.9, 51.2, 50.7, 38.8; HPLC: (AD-H, Hexane/ ^{i}PrOH = 85/15, 1.0 mL/min, 254 nm), t_R (major-isomer) = 20.2 min, t_R (minor-isomer) = 30.1 min (20% *ee*); **HRMS (ESI, m/z):** calcd for $C_{24}H_{21}N_2O_5^+$ $[M+H]^+$: 417.1445, found: 417.1447.

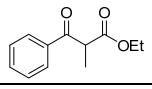
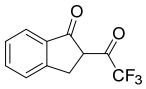
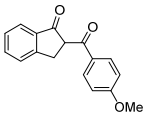
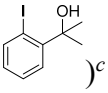
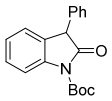


5e

2-(dibenzylcarbamoyl)-5-methoxy-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate; 87% yield (58.3 mg, 0.131 mmol); white solid (m.p. : 95-100 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 8.8 Hz, 1H), 7.41 – 7.31 (m, 5H), 7.30 – 7.27 (m, 1H), 7.24 – 7.11 (m, 3H), 7.06 (d, *J* = 2.0 Hz, 1H), 6.99 – 6.89 (m, 2H), 5.07 (d, *J* = 15.6 Hz, 1H), 4.95 (d, *J* = 14.8 Hz, 1H), 4.80 (d, *J* = 14.8 Hz, 1H), 4.50 (d, *J* = 17.6 Hz, 1H), 4.35 (d, *J* = 16.0 Hz, 1H), 3.94 (s, 3H), 3.49 (d, *J* = 17.6 Hz, 1H); **^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$)** δ 200.8, 168.1, 166.2, 158.0, 136.5, 134.7, 131.5, 128.9, 128.0, 127.7, 127.6, 127.38, 127.37, 126.3, 126.1, 124.9, 116.3, 109.4, 62.2, 55.9, 51.2, 50.7, 38.7; **HPLC**: (AD-H, Hexane/ ^{i}PrOH = 92/8, 1.0 mL/min, 254 nm), t_R (major-isomer) = 13.3 min, t_R (minor-isomer) = 38.8 min (12% *ee*); **HRMS (ESI, m/z)**: calcd for $C_{25}H_{23}N_2O_6^+$ $[M+H]^+$: 447.1551, found: 447.1558.

VII. Limited Substrates

Table S6: The results for limited substrates

Entry	Substrates	The result for racemic conditions[a]	The result for asymmtric conditions[b]
1		23% of yield	No reaction
2		No reaction	No reaction
3		~56% of yield (impurity with by-product )[c]	~43% of yield (impurity with by-product )
4		The substrate was decomposed	The substrate was decomposed

[a] Reaction conditions: **substrate** (0.15 mmol), **1** (1.2 equiv), $Zn(OAc)_2$ (10 mol %), CH_2Cl_2 (1.5 mL), rt, nitrogen. [b] Reaction conditions: **substrate** (0.15 mmol), **1** (1.2 equiv), $Zn(ClO_4)_2 \cdot 6H_2O$ (10 mol %), ligand **1** (12 mol %), CH_2Cl_2 (1.5 mL), 0 °C, nitrogen. [c] The ^{1}H NMR Spectrum is shown in Figure S2.

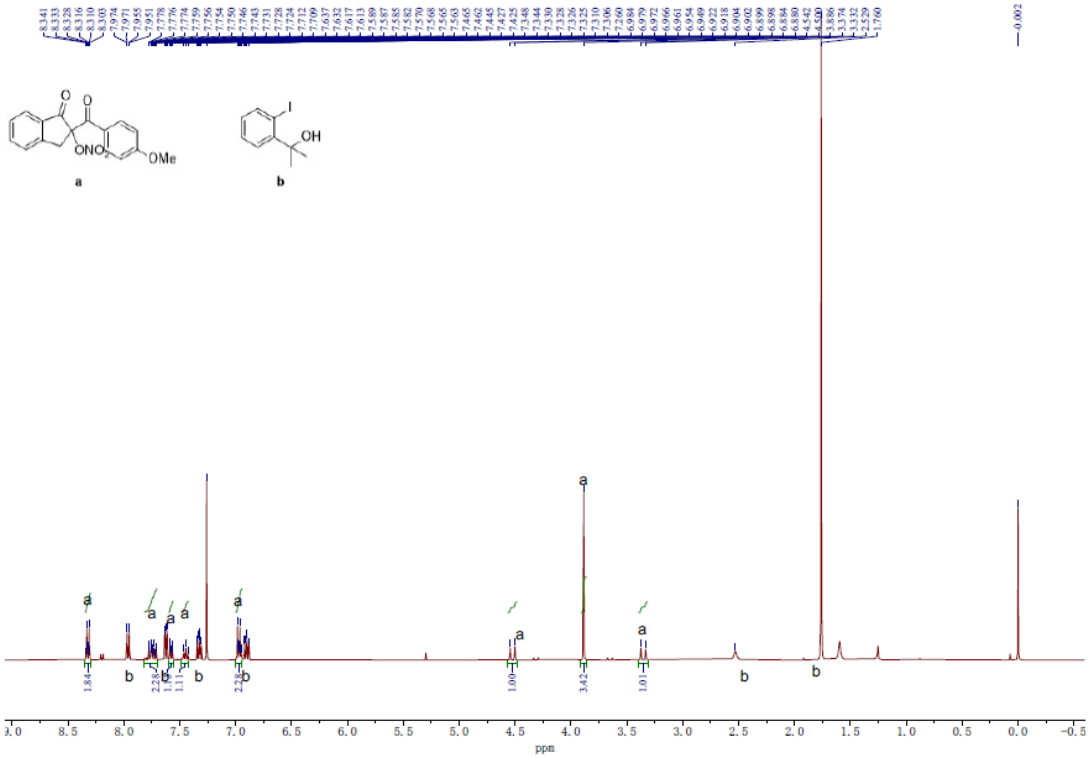
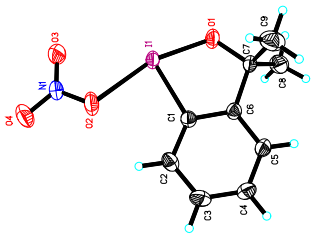
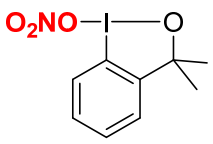


Figure S2. The ^{1}H NMR Spectrum of impure product

VIII. Crystallographic Data





reagent 1

Identification code	cd17385	
Empirical formula	C9 H10 I N O4	
Formula weight	323.08	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.0323(15) Å	α= 65.902(3)°.
	b = 8.5118(16) Å	β= 68.342(3)°.
	c = 9.7664(19) Å	γ = 68.126(3)°.
Volume	546.78(18) $Å^3$	
Z	2	
Density (calculated)	1.962 Mg/m^3	
Absorption coefficient	2.922 mm^{-1}	
F(000)	312	
Crystal size	0.200 x 0.170 x 0.140 mm^3	
Theta range for data collection	2.716 to 25.498°.	
Index ranges	-9<=h<=7, -10<=k<=10, -11<=l<=11	
Reflections collected	3146	
Independent reflections	2031 [R(int) = 0.0281]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.3346	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2031 / 0 / 139	
Goodness-of-fit on F^2	1.100	
Final R indices [I>2sigma(I)]	R1 = 0.0283, wR2 = 0.0715	
R indices (all data)	R1 = 0.0293, wR2 = 0.0722	
Extinction coefficient	0.065(4)	
Largest diff. peak and hole	0.759 and -1.056 e.$Å^{-3}$	

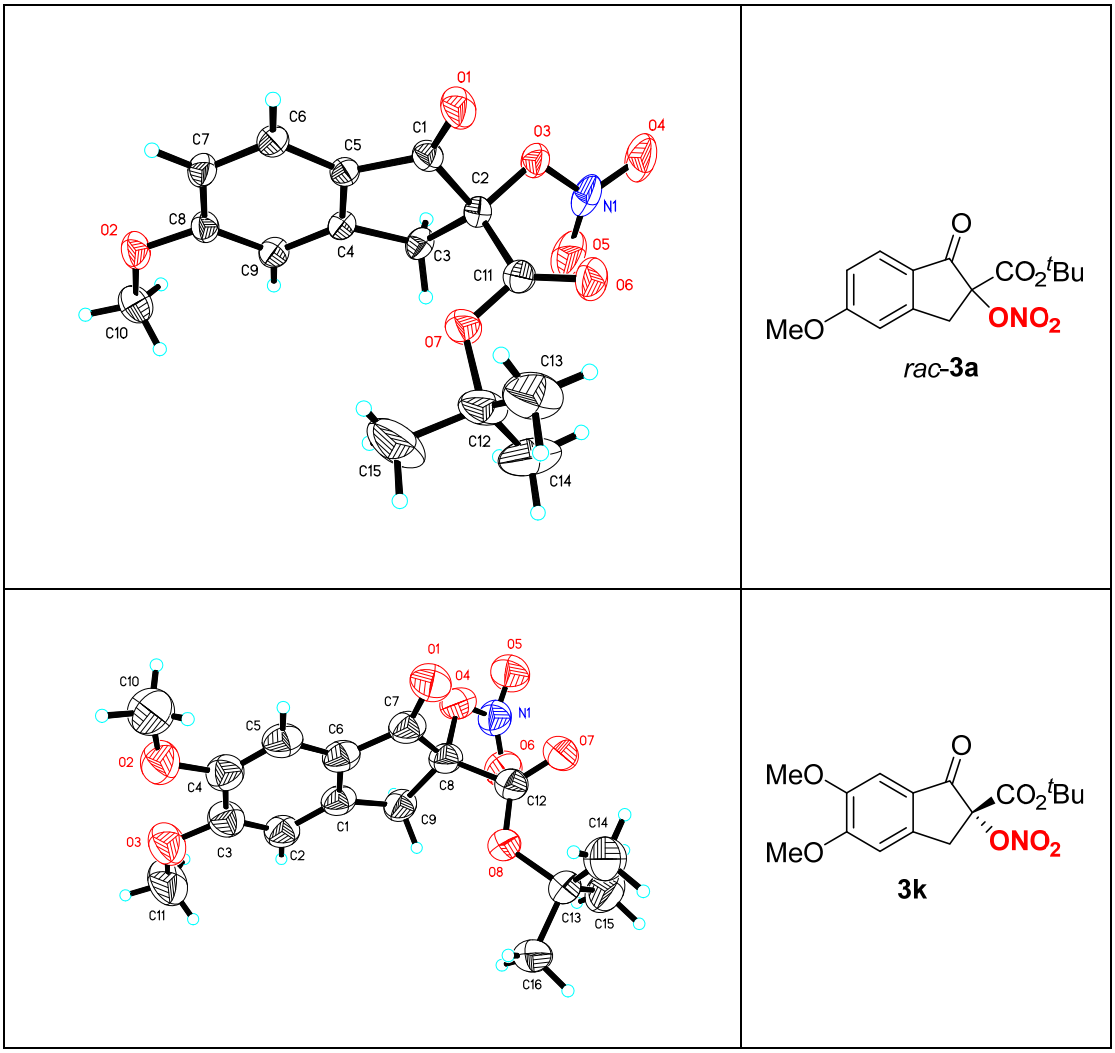


Table S7. Crystal data and structure refinement for *rac*-**3a** and **3k**.

	rac-**3a**	**3k**
Identification code	d8v17641	cu_d8v20406_0m
Empirical formula	C15 H17 N O7	C16 H19 N O8
Formula weight	323.29	353.32
Temperature	296(2) K	293(2) K
Wavelength	0.71073 Å	1.54178 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 21/c	P 21
Unit cell dimensions	a = 12.1197(6) Å, α = 90°. b = 13.2870(6) Å, β= 103.695(2)°. c = 10.6235(5) Å, γ = 90°.	a = 15.3075(5) Å, α = 90°. b = 12.2353(4) Å, β= 91.236(2)°. c = 19.3019(6) Å, γ = 90°.
Volume	1662.11(14) $Å^3$	3614.2(2) $Å^3$
Z	4	8
Density (calculated)	1.292 Mg/m^3	1.299 Mg/m^3
Absorption coefficient	0.104 mm^{-1}	0.898 mm^{-1}
F(000)	680	1488
Crystal size	0.180 x 0.130 x 0.080 mm^3	0.200 x 0.120 x 0.100 mm^3

Theta range for data collection	2.311 to 25.496°.	2.289 to 67.500°.
Index ranges	-14<=h<=14, -16<=k<=16, -12<=l<=12	-18<=h<=17, -14<=k<=13, -23<=l<=23
Reflections collected	26364	83425
Independent reflections	3093 [R(int) = 0.0611]	12861 [R(int) = 0.0627]
Completeness to theta = 25.242°	99.7 %	99.3 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6251	0.7533 and 0.4869
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3093 / 0 / 213	12861 / 2 / 922
Goodness-of-fit on F^2	1.028	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1278	R1 = 0.0680, wR2 = 0.1861
R indices (all data)	R1 = 0.0605, wR2 = 0.1411	R1 = 0.0871, wR2 = 0.2146
Absolute structure parameter	-	-0.09(6)
Extinction coefficient	0.032(5)	0.0186(15)
Largest diff. peak and hole	0.257 and -0.265 e.Å^{-3}	0.519 and -0.285 e.Å^{-3}

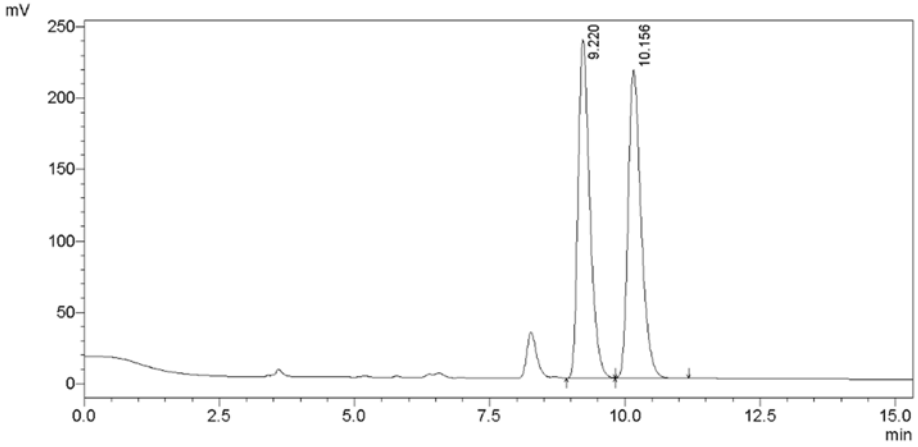
IX. HPLC Data

Compound 3a

HPLC Conditions

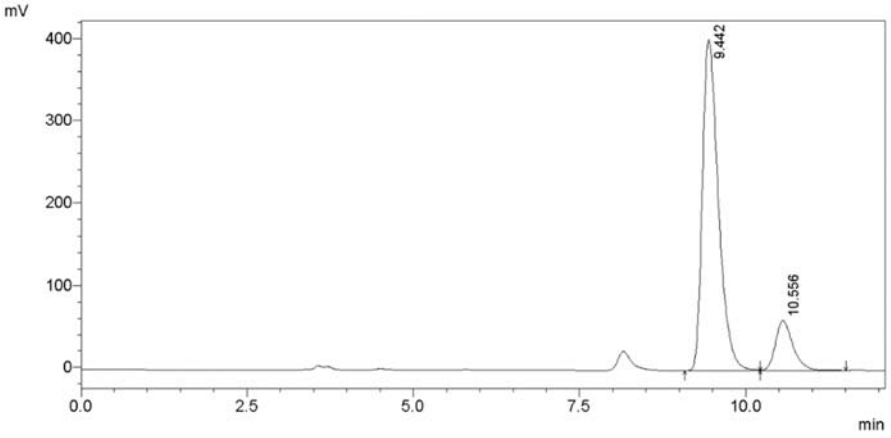
Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (95:5)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



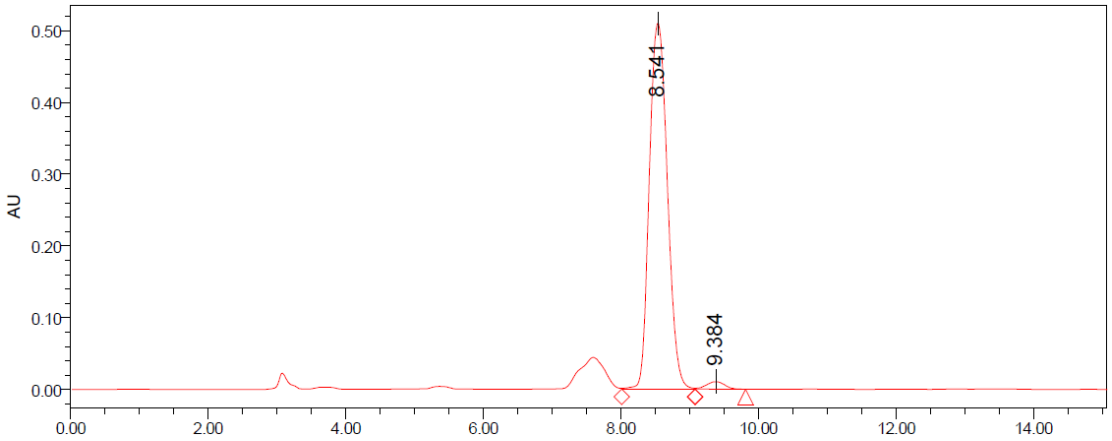
Peak#	Ret. Time	Area %
1	9.220	49.82
2	10.156	50.18

Chiral



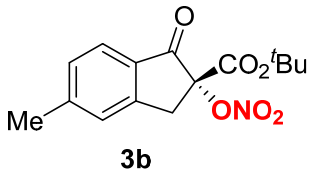
Peak#	Ret. Time	Area %
1	9.442	85.89
2	10.556	14.11

recrystallization



	area	area %
1	9314734	97.95
2	195036	2.05
Sum	9509770.0	100.0

Compound 3b

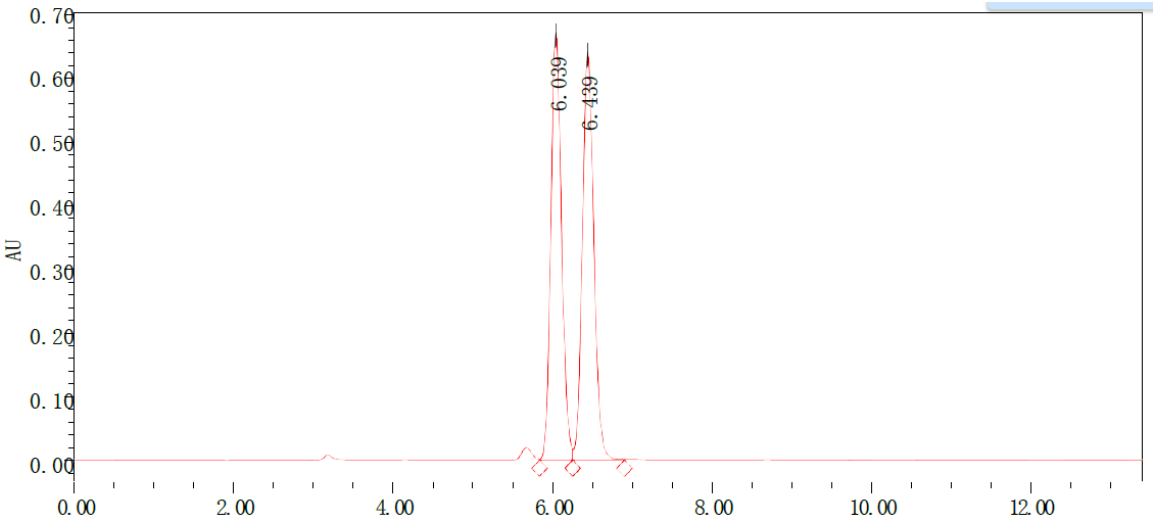


3b

HPLC Conditions

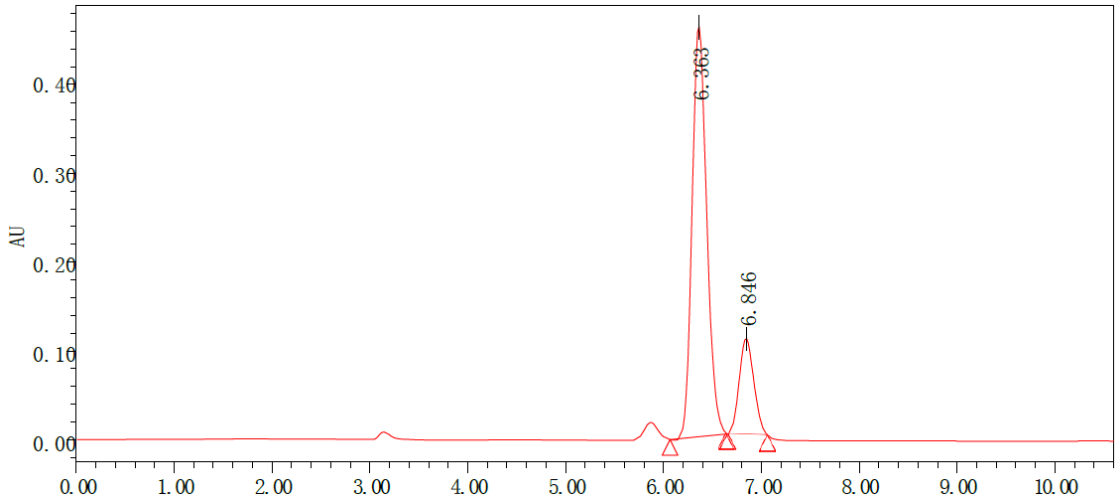
Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (95:5)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



Peak#	Ret. time	Area	Area %
1	6.039	6257175	49.58
2	6.439	6372536	50.42
		12639711	100.00

Chiral



Peak#	Ret. time	Area	Area %
1	6.363	4811985	81.08
2	6.846	1122729	18.92
		5934714	100.00

Compound 3c

HPLC Conditions

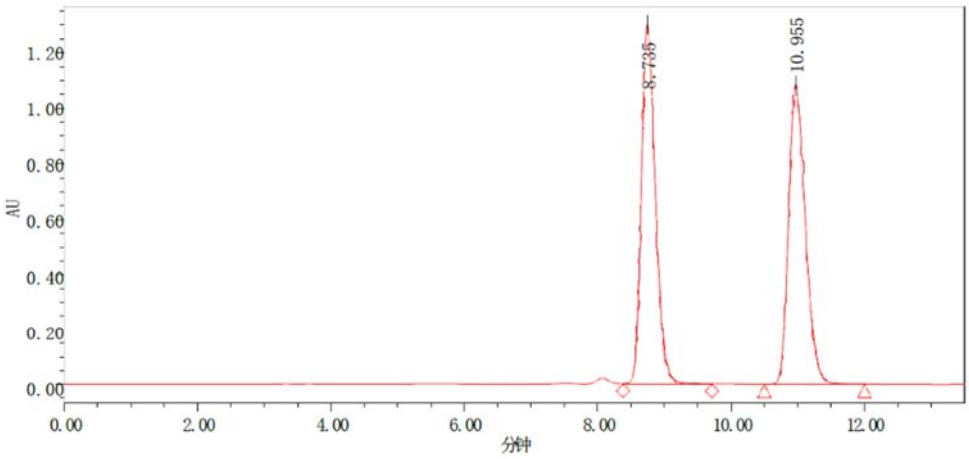
Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.

Eluent: Hexanes / isopropanol (99: 1)

Flow rate: 1.0 mL/min

Detection: UV 254 nm

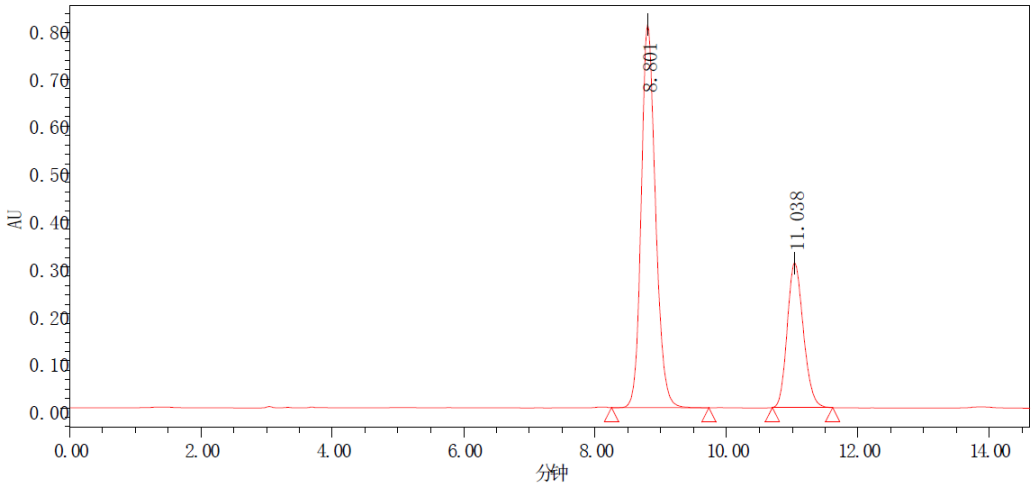
Racemic



Detector A Ch1 254nm

Peak#	Ret.time	Area	Area %
1	8.735	19151805	50.26
2	10.955	18954848	49.74
		38106653	100.00

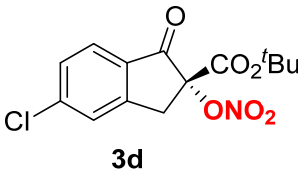
Chiral



Detector A Ch1 254nm

Peak#	Ret.time	Area	Area %
1	8.801	12377414	70.20
2	11.038	5253417	29.80
		17630831	100.00

Compound 3d

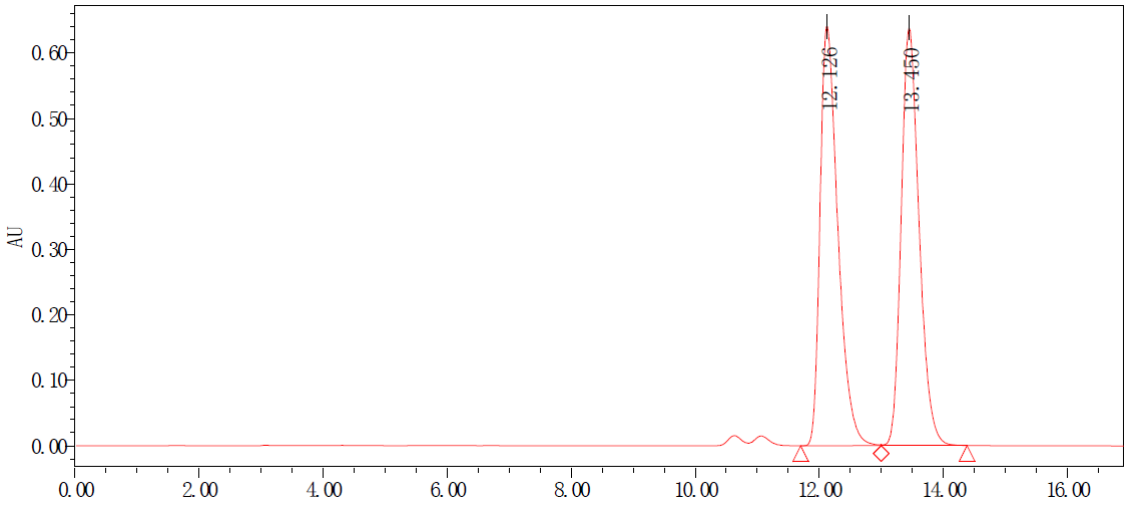


3d

HPLC Conditions

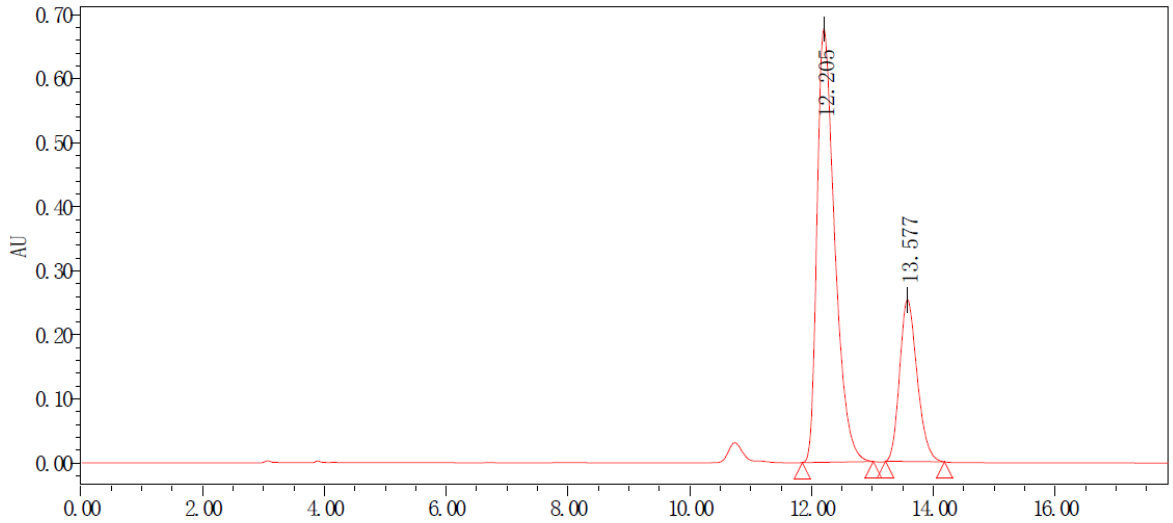
Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (99:1)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



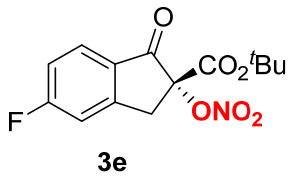
Peak#	Ret. Time	Area	Area %
1	12.126	1281279	50.00
2	13.450	12821450	50.00

Chiral



Peak#	Ret. Time	Area	Area %
1	12.126	13679808	73.01
2	13.577	5057318	26.99

Compound 3e

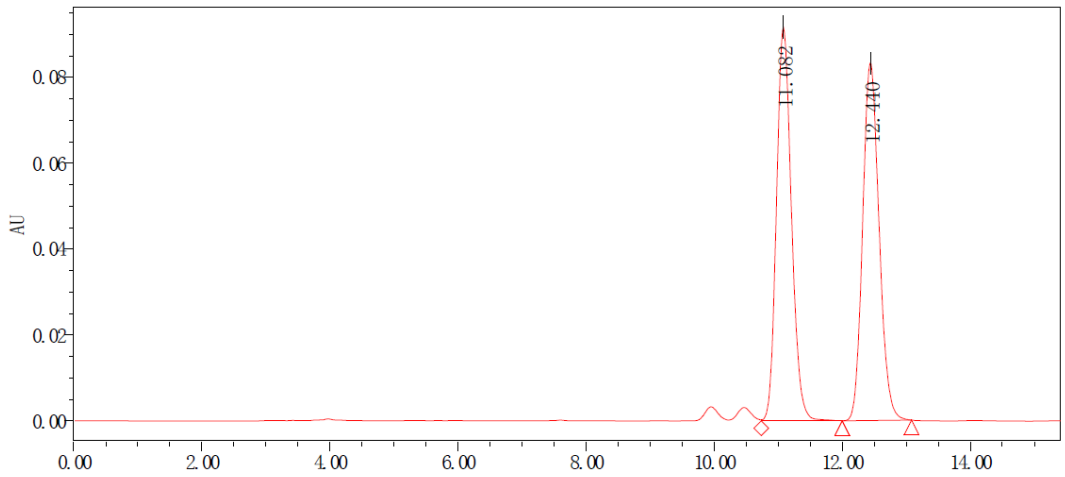


3e

HPLC Conditions

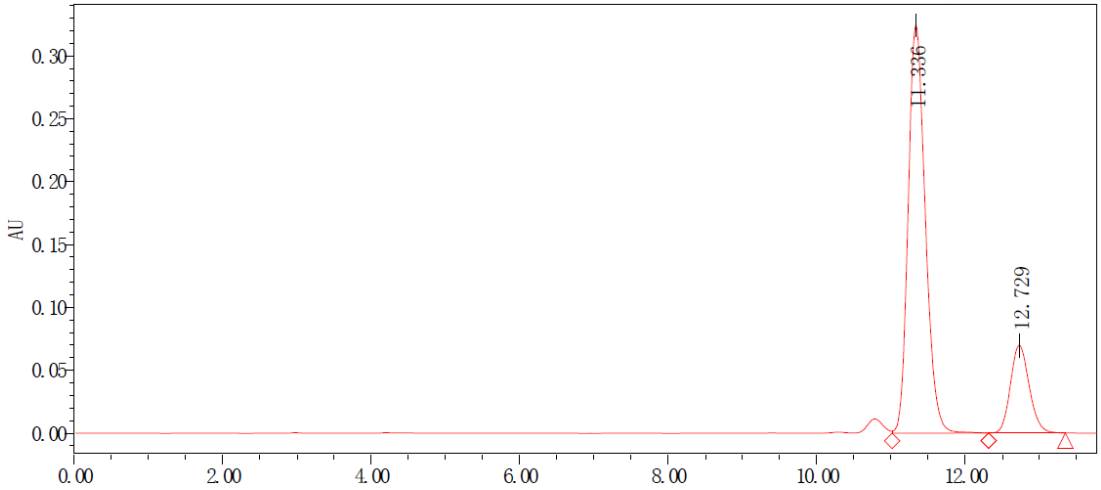
Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (99:1)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



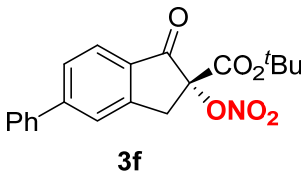
Peak#	Ret. Time	Area	Area %
1	11.082	1485829	50.05
2	12.440	1482827	49.95

Chiral



Peak#	Ret. Time	Area	Area %
1	11.336	5200006	80.96
2	12.729	1223145	19.04

Compound 3f

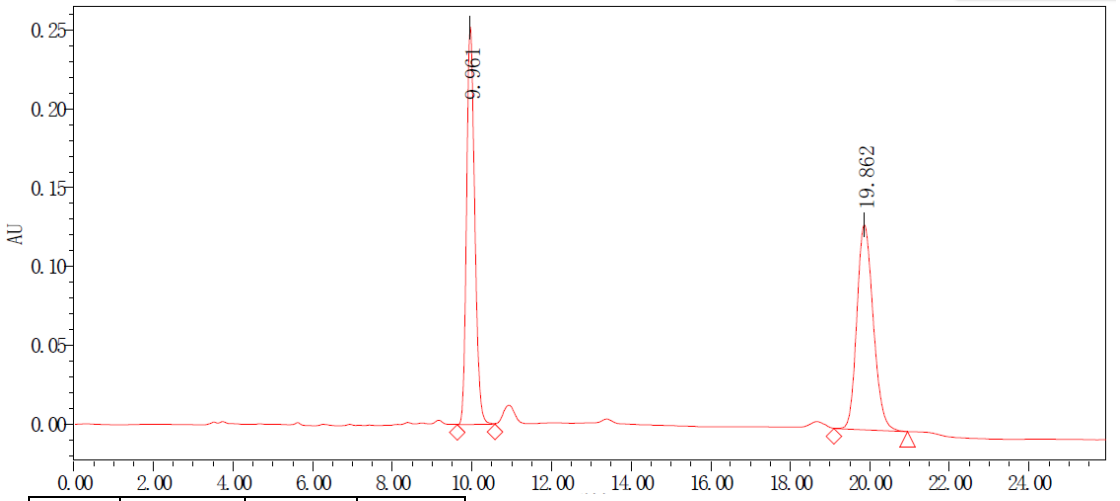


3f

HPLC Conditions

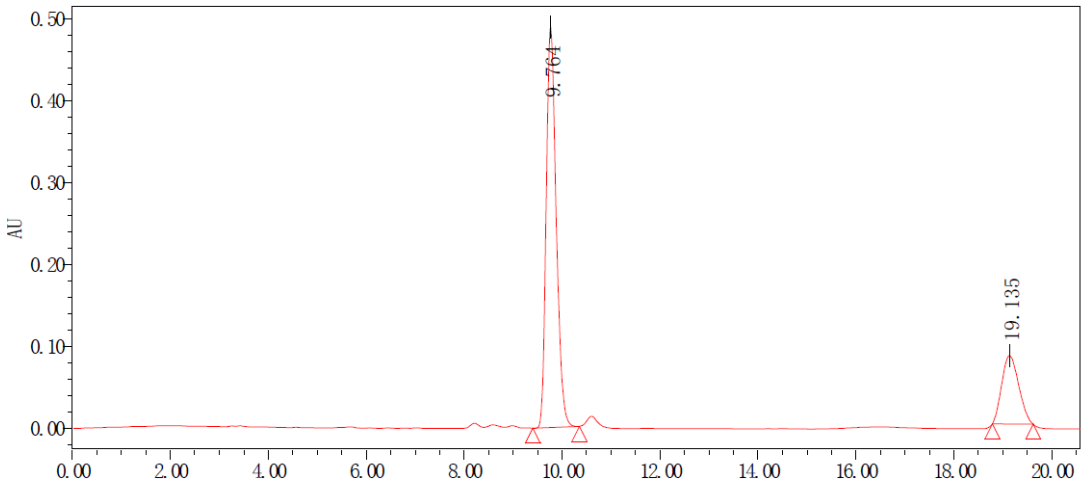
Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (95:5)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



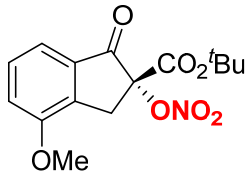
	Ret. Time	Area	Area %
1	9.961	3589515	49.11
2	19.862	3719734	50.89

Chiral



Peak#	Ret. Time	Area	Area %
1	9.764	6912334	77.53
2	19.135	2003453	22.47

Compound 3g

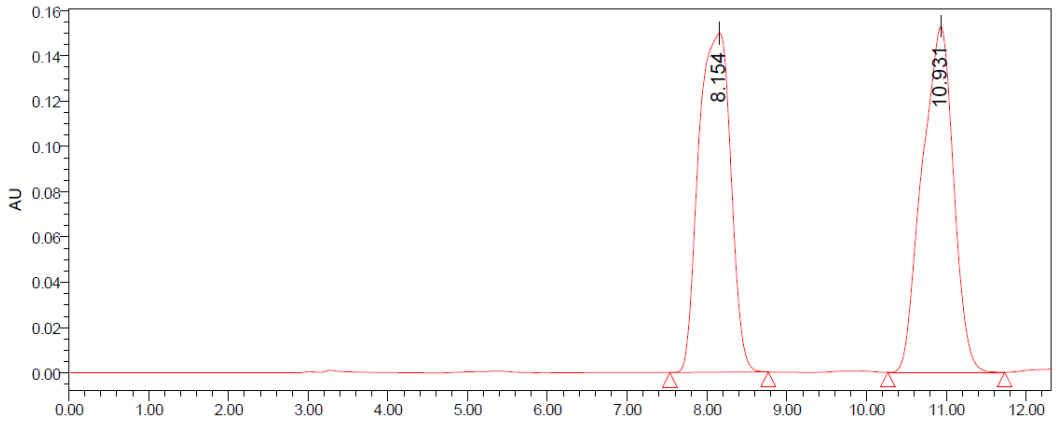


3g

HPLC Conditions

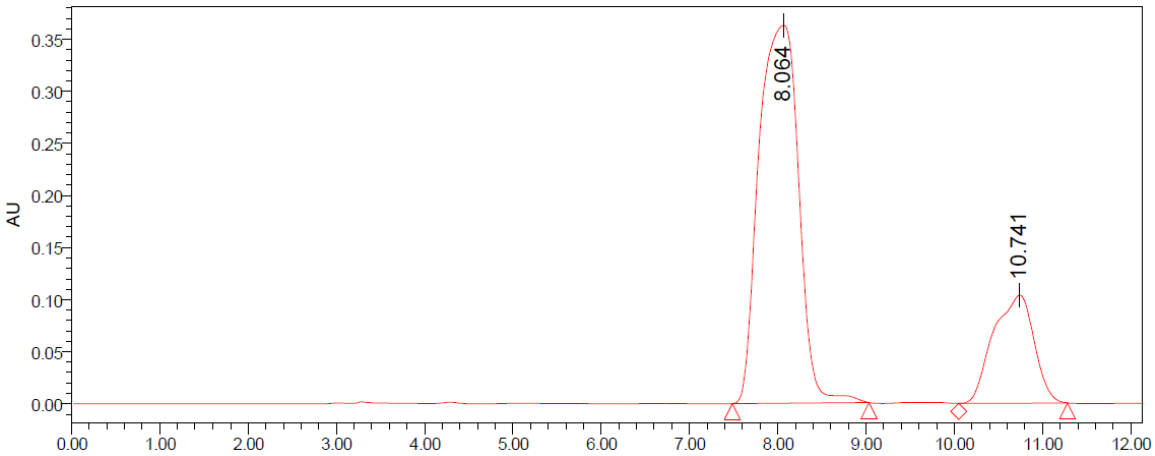
Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (99:1)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



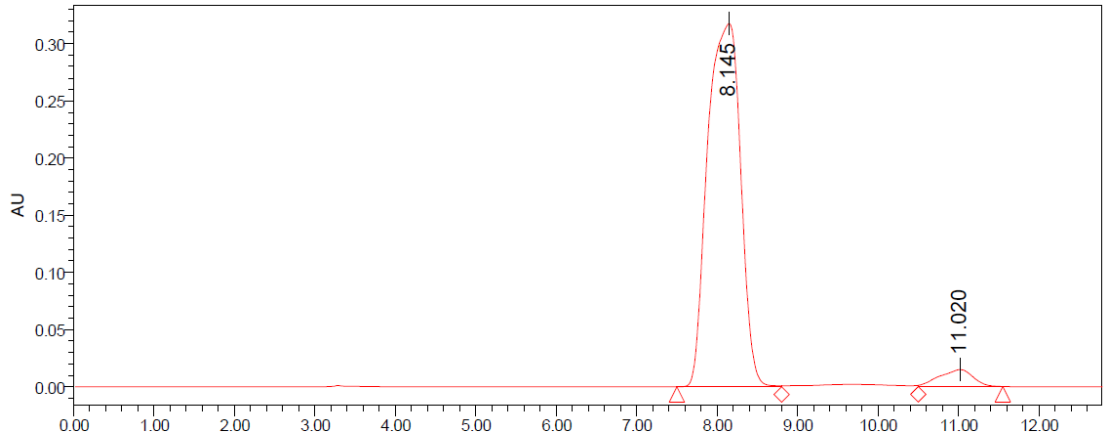
	area	area %
1	4185001	50.00
2	4184555	50.00
Sum	8369556.2	100.0

Chiral



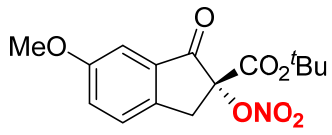
	area	area %
1	11390460	77.44
2	3317810	22.56
Sum	14708269.6	100.0

Recrystallization



	area	area %
1	9054498	95.43
2	433182	4.57
Sum	9487680.2	100.0

Compound 3h

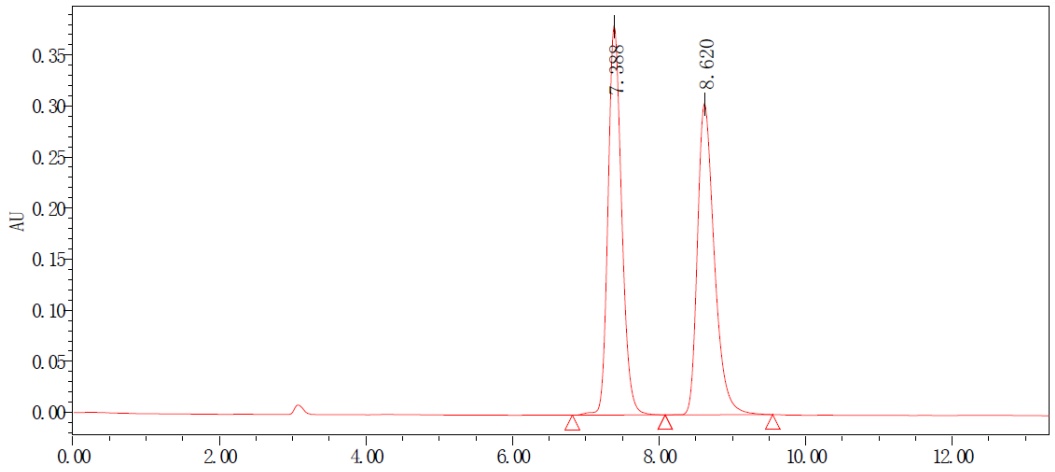


3h

HPLC Conditions

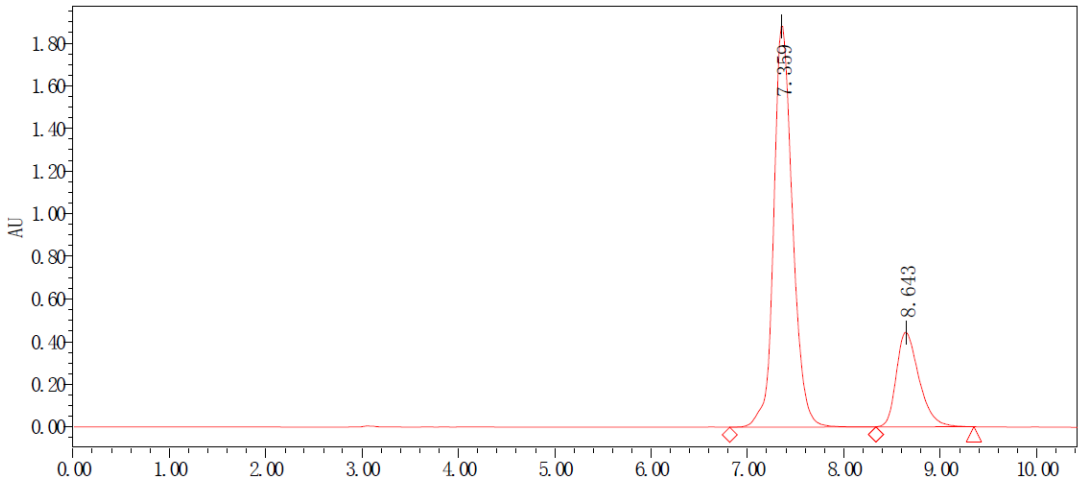
Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (95:5)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



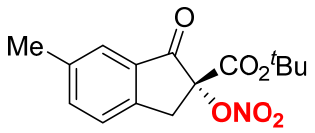
Peak#	Ret. Time	Area	Area %
1	7.388	4936242	50.31
2	8.620	4874954	49.69

Chiral



Peak#	Ret. Time	Area	Area %
1	7.359	25531157	77.83
2	8.643	7273980	22.17

Compound 3i

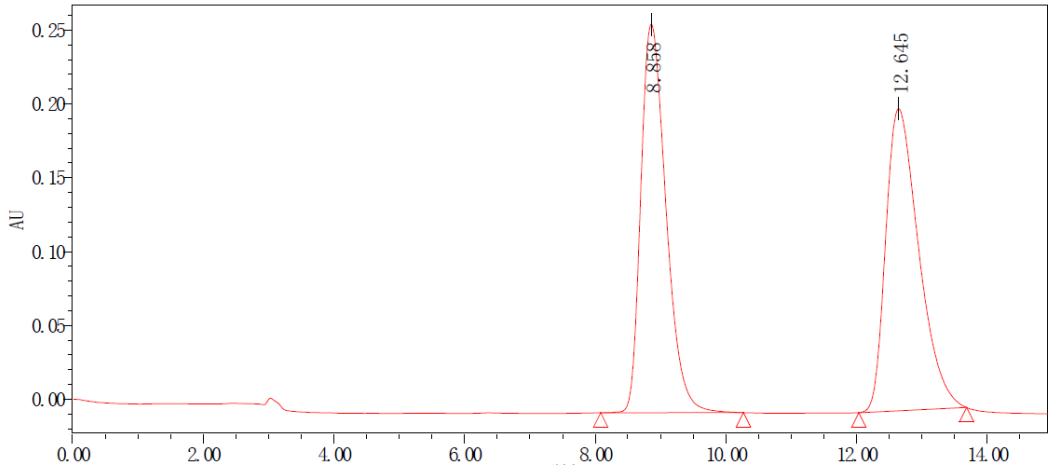


3i

HPLC Conditions

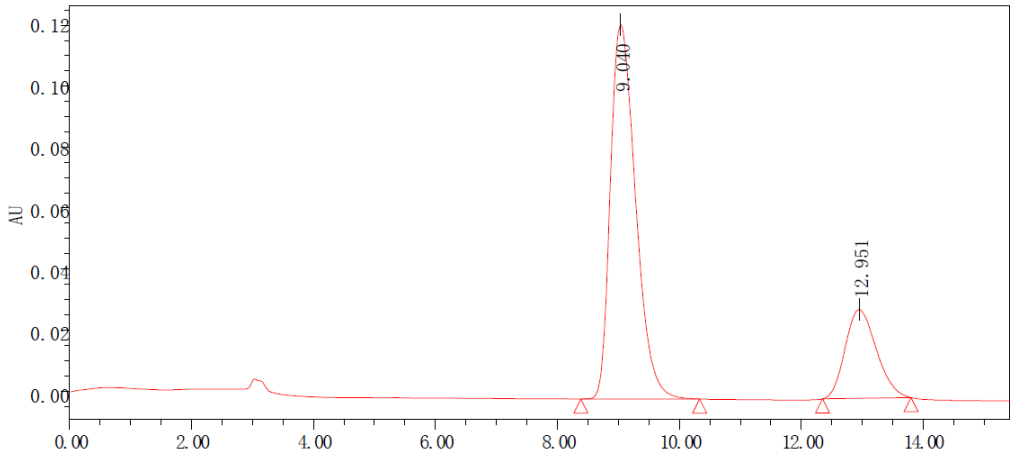
Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (99.2:0.8)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



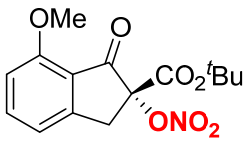
Peak#	Ret. time	Area	Area %
1	8.858	7068595	49.59
2	12.645	7186790	50.41
		14255385	100.00

Chiral



Peak#	Ret. time	Area	Area %
1	9.040	3528256	77.28
2	12.951	1037229	22.72
		4565485	100.00

Compound 3j

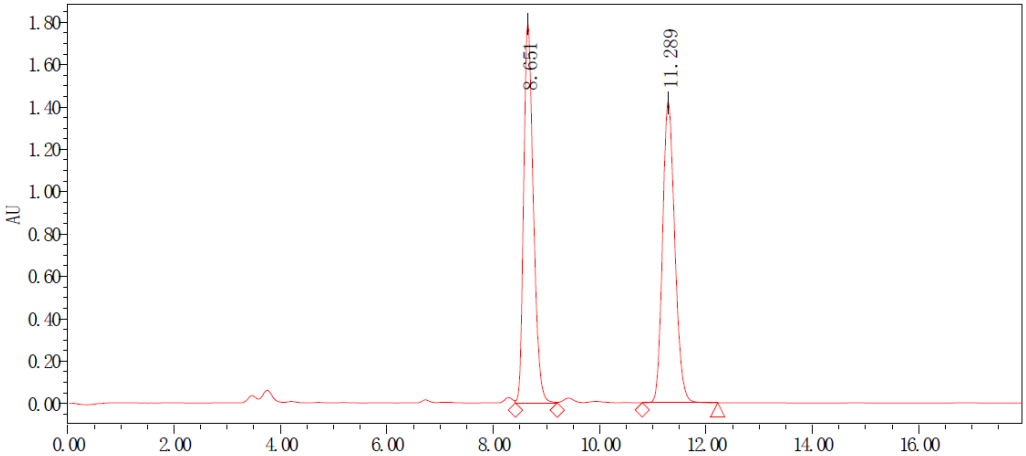


3j

HPLC Conditions

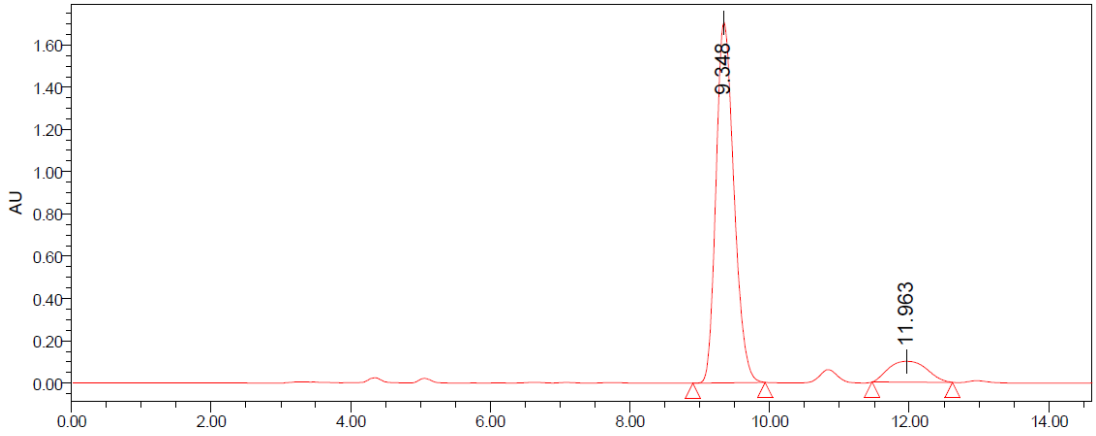
Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (90:10)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



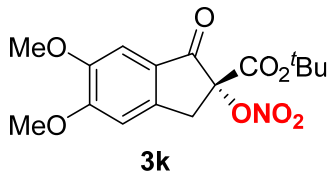
Peak#	Ret. Time	Area	Area %
1	8.651	22668872	49.98
2	11.289	22685438	50.02

Chiral



	ret.time	area	area %
1	9.348	30481020	88.973
2	11.963	3777759	11.027
Sum		34258779	100.000

Compound 3k

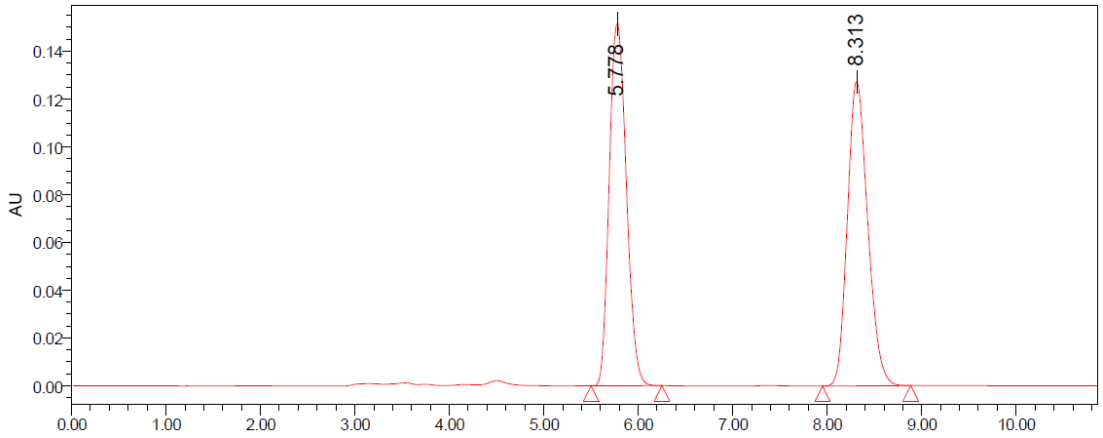


3k

HPLC Conditions

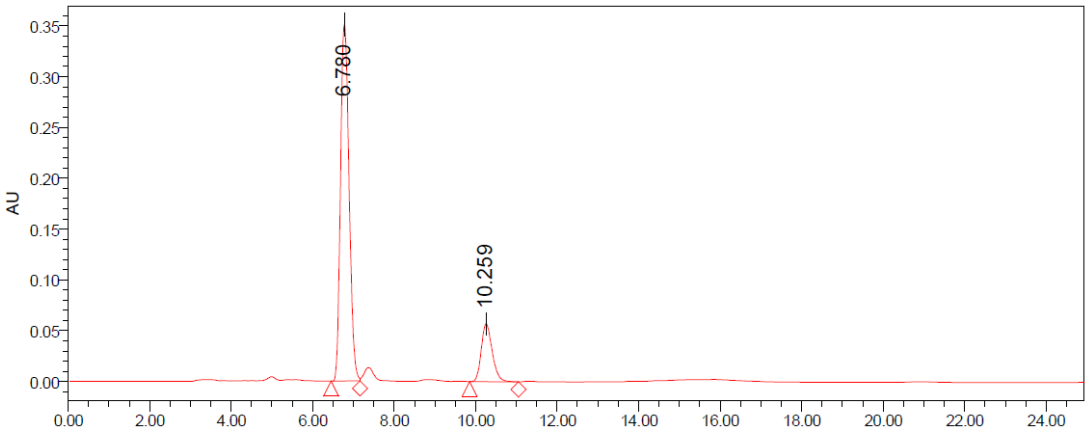
Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (80:20)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



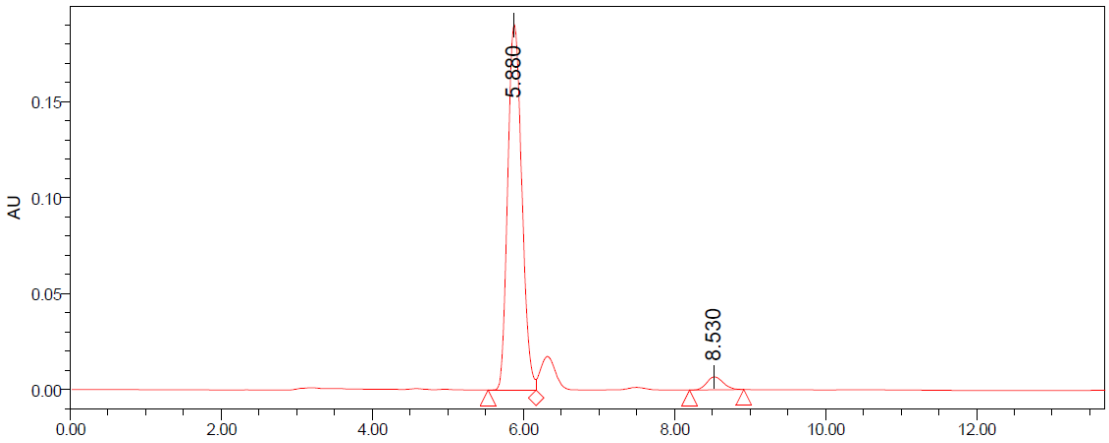
	area	area %
1	1904213	49.93
2	1909636	50.07
Sum	3813849.3	100.0

Chiral



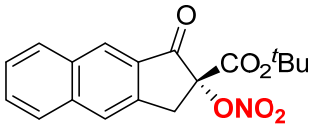
	ret.time	area	area %
1	6.780	5133799	82.847
2	10.259	1062946	17.153
Sum		6196744	100.000

Recrystallization



	area	area %
1	2463388	95.99
2	103024	4.01
Sum	2566412.8	100.0

Compound 3l

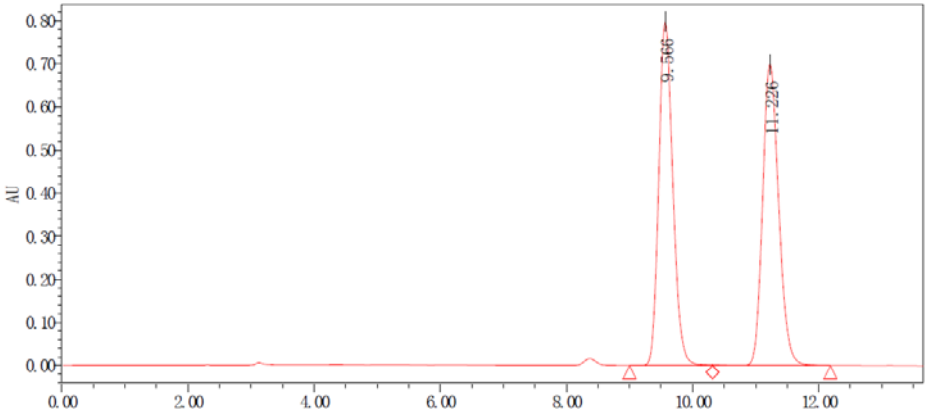


3l

HPLC Conditions

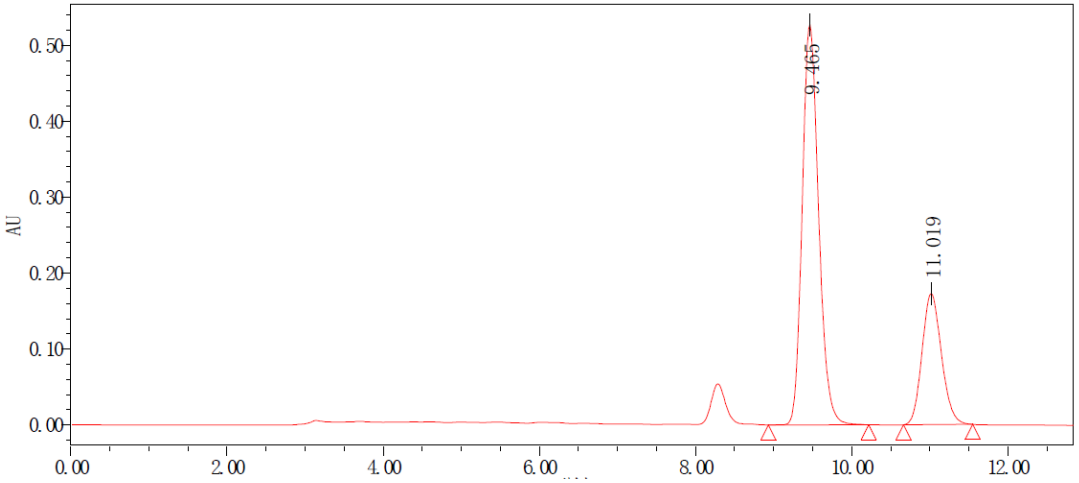
Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (97:3)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



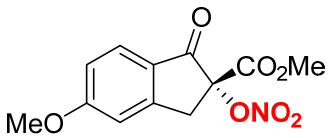
Peak#	Ret. Time	Area	Area %
1	9.566	12375809	49.94
2	11.226	12403843	50.06

Chiral



Peak#	Ret. Time	Area	Area %
1	9.465	77002788	72.11
2	11.019	2979354	27.89

Compound 3m

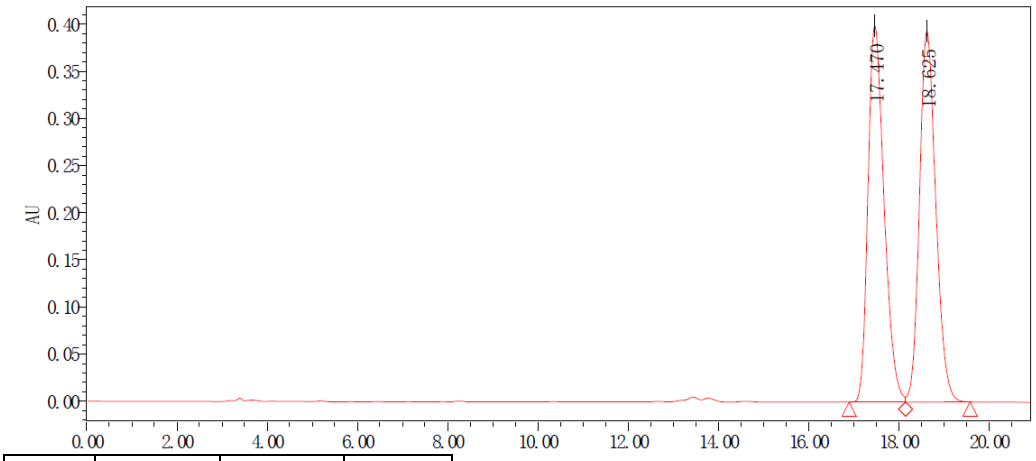


3m

HPLC Conditions

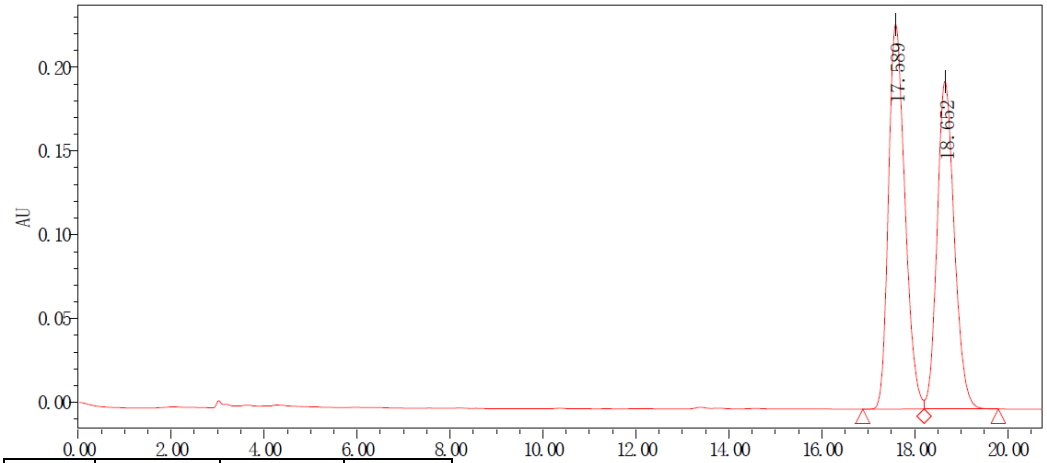
Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (95:5)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



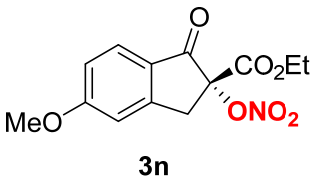
Peak#	Ret. Time	Area	Area %
1	17.470	9917609	50.05
2	18.625	9899466	49.95

Chiral



Peak#	Ret. Time	Area	Area %
1	17.589	5670749	52.91
2	18.652	5047070	47.09

Compound 3n

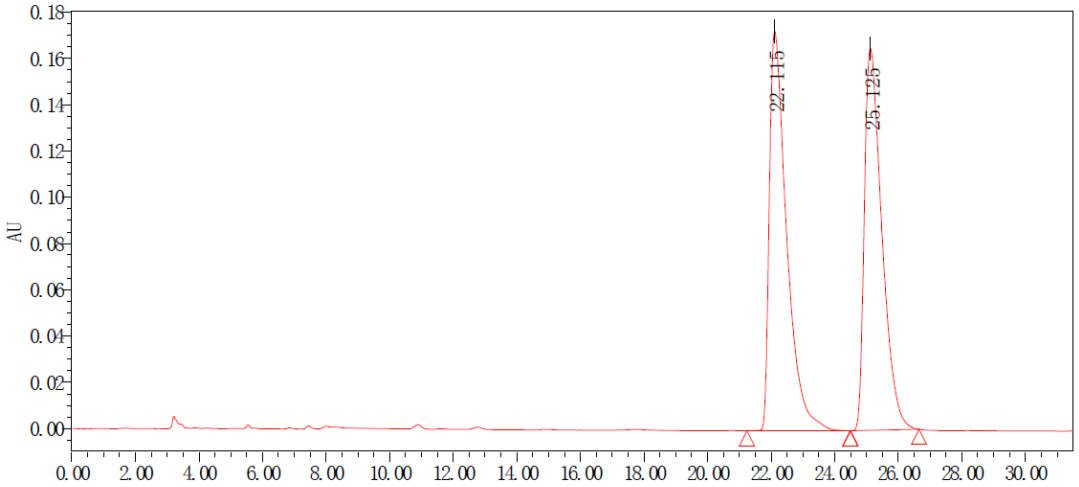


3n

HPLC Conditions

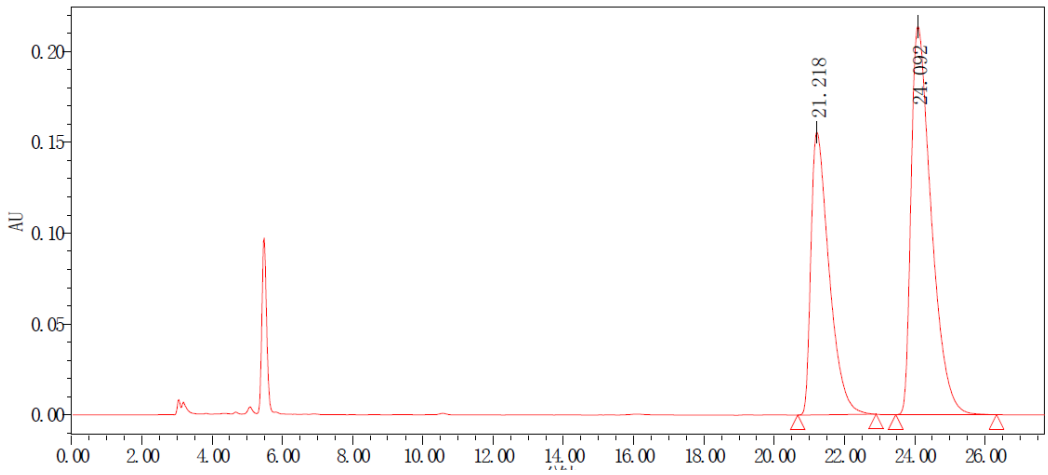
Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (97:3)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



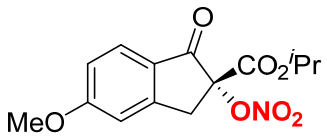
Peak#	Ret. Time	Area	Area %
1	22.115	6522875	50.77
2	25.125	6326113	49.23

Chiral



Peak#	Ret. Time	Area	Area %
1	21.218	5595907	39.72
2	24.092	8492683	60.28

Compound 3o

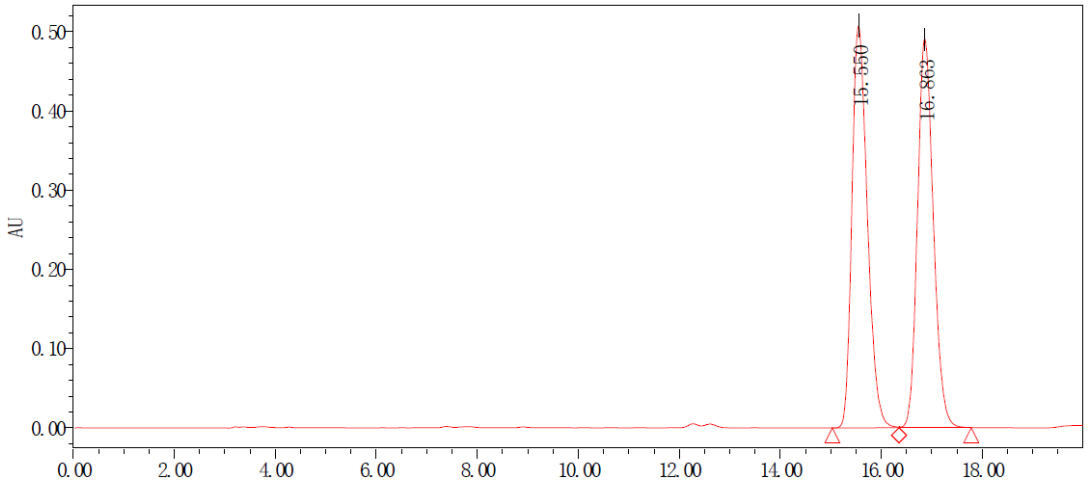


3o

HPLC Conditions

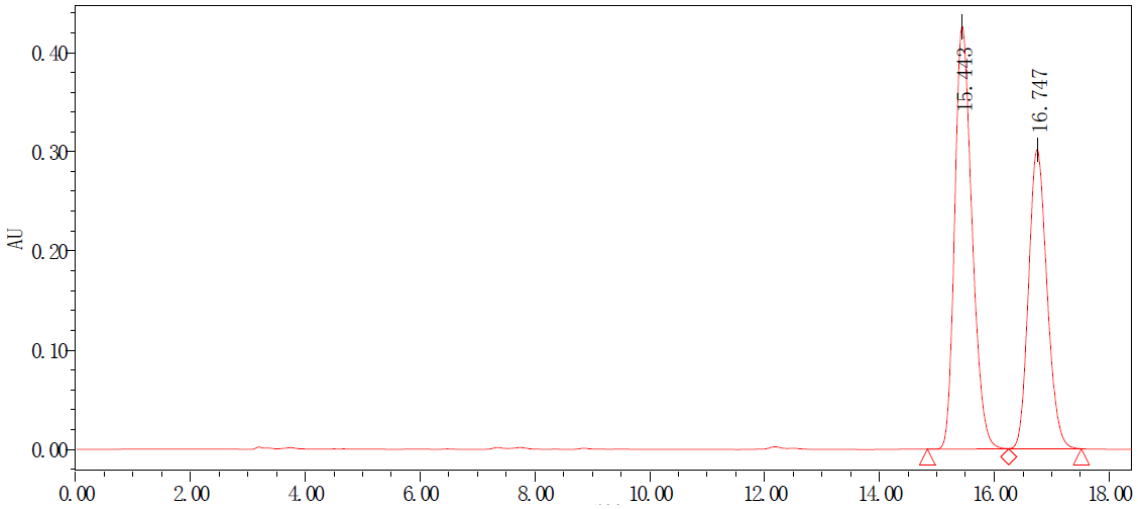
Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (94:6)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



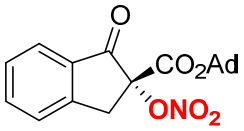
Peak#	Ret. Time	Area	Area %
1	15.550	10758177	50.06
2	16.863	10731872	49.94

Chiral



Peak#	Ret. Time	Area	Area %
1	15.443	8950780	57.01
2	16.747	6750550	42.99

Compound 3p

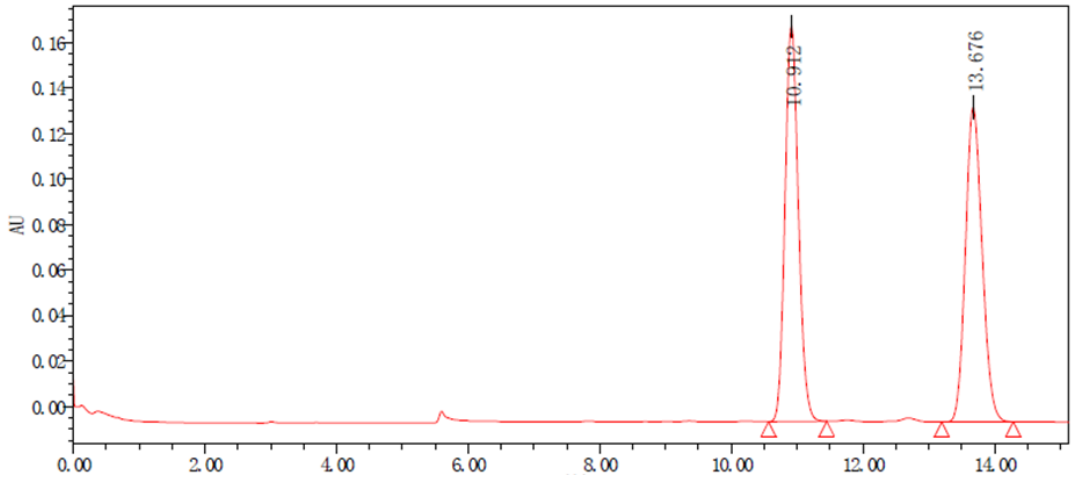


3p

HPLC Conditions

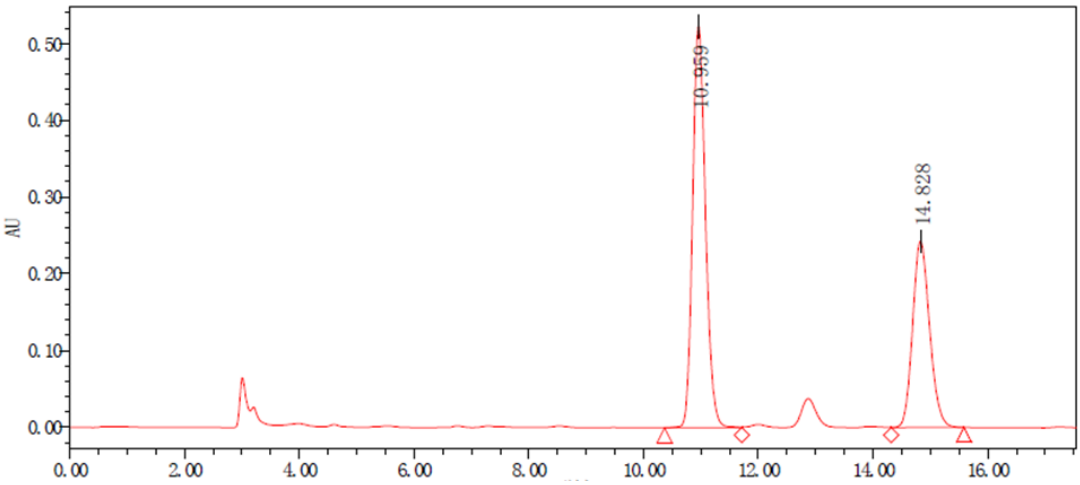
Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (97:3)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



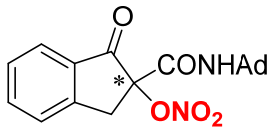
Peak#	Ret. Time	Area	Area %
1	10.912	2459607	50.18
2	13.676	2442359	49.82

Chiral



Peak#	Ret. Time	Area	Area %
1	10.959	8141253	62.03
2	14.828	4983529	37.97

Compound 5a

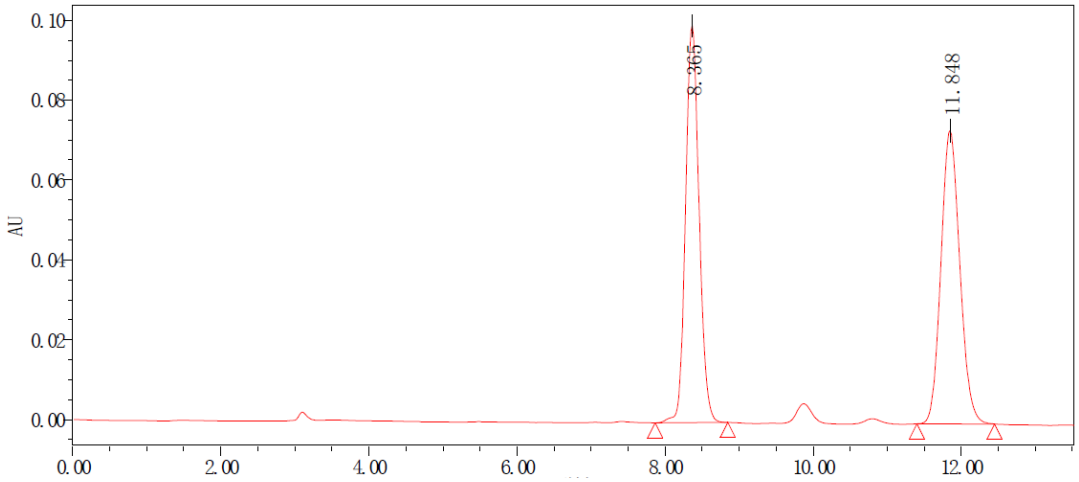


5a

HPLC Conditions

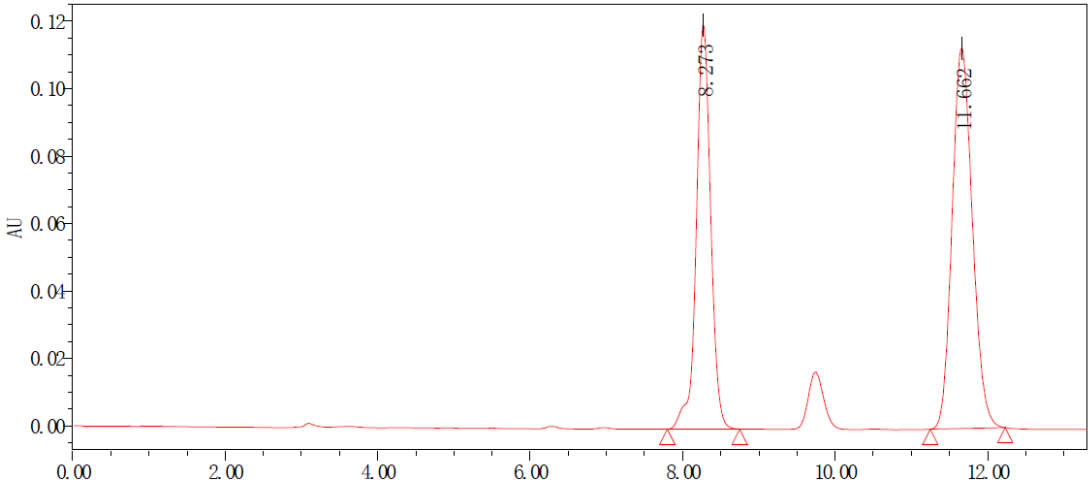
Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (95:5)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



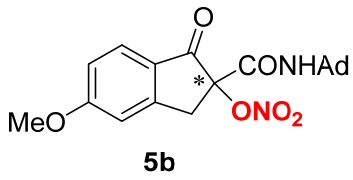
Peak#	Ret. Time	Area	Area %
1	8.651	1262155	49.25
2	11.848	1300349	50.75

Chiral



Peak#	Ret. Time	Area	Area %
1	8.273	1574192	42.94
2	11.662	2091813	57.06

Compound 5b

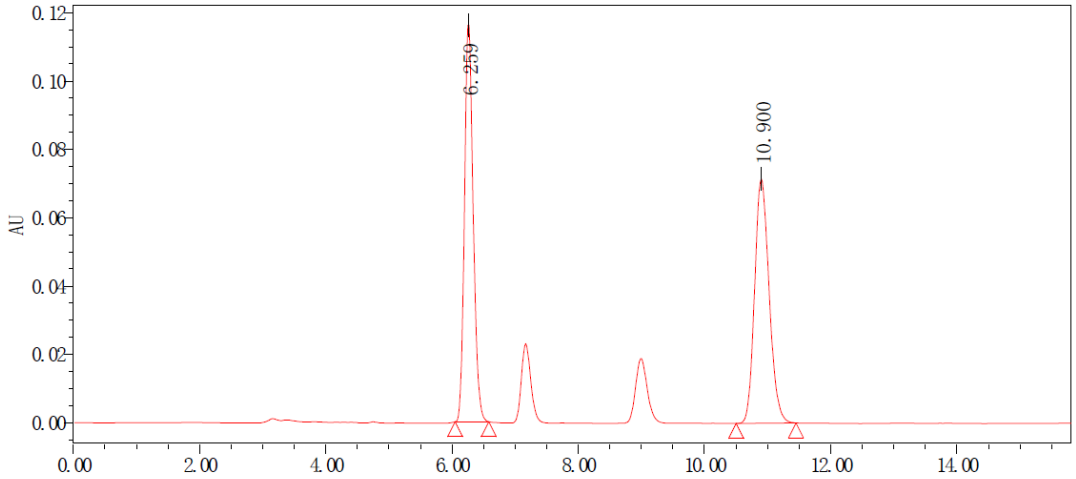


5b

HPLC Conditions

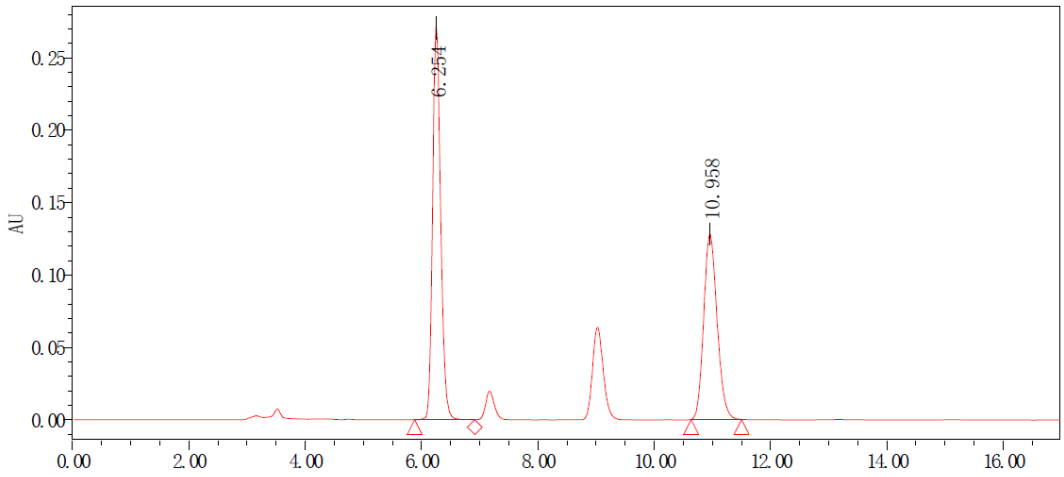
Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (90:10)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



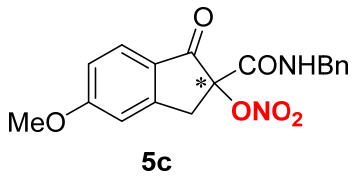
Peak#	Ret. Time	Area	Area %
1	6.259	1119440	49.57
2	10.900	1138802	50.43

Chiral



Peak#	Ret. Time	Area	Area %
1	6.254	2629186	56.19
2	10.985	2049785	43.81

Compound 5c

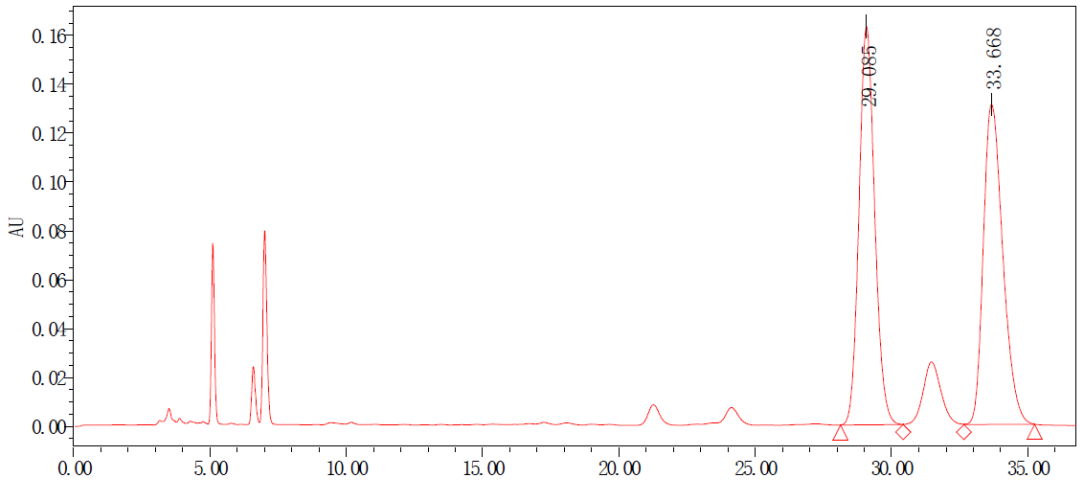


5c

HPLC Conditions

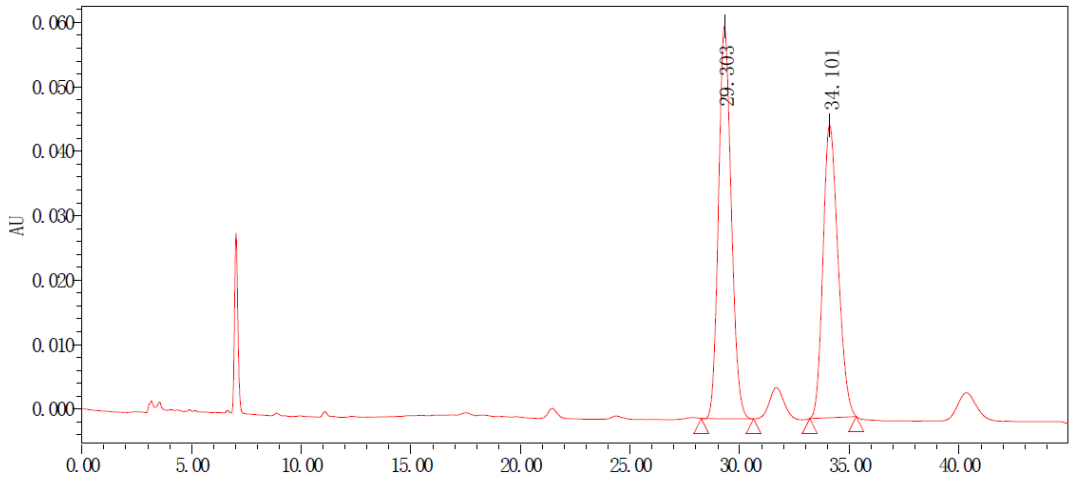
Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (92:8)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



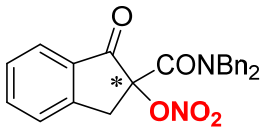
Peak#	Ret. Time	Area	Area %
1	29.085	6523499	50.03
2	33.668	6515156	49.97

Chiral



Peak#	Ret. Time	Area	Area %
1	29.303	2465018	53.24
2	34.101	2164964	46.76

Compound 5d

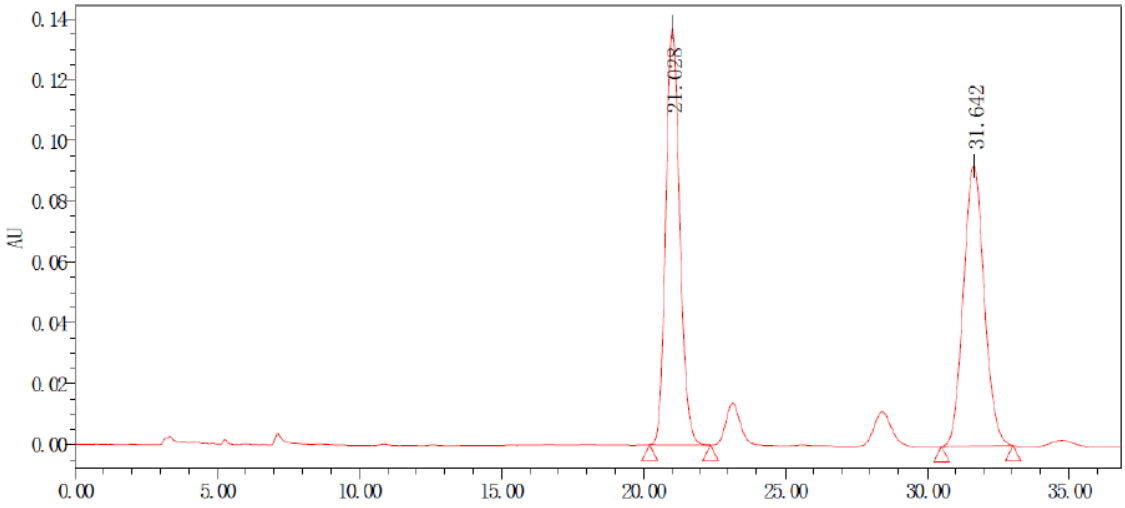


5d

HPLC Conditions

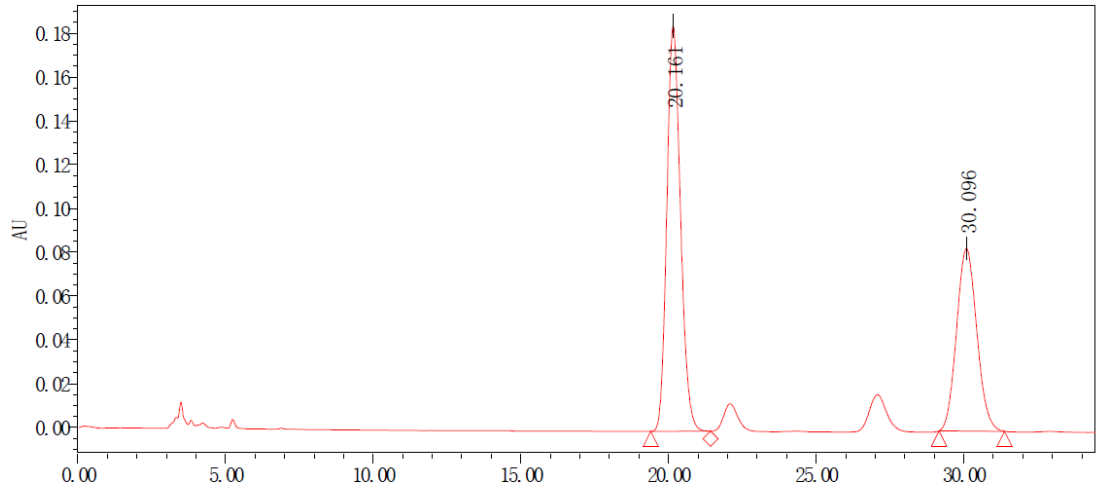
Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (85:15)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



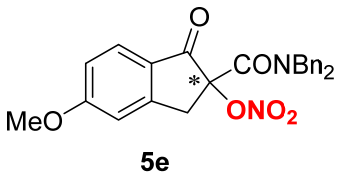
Peak#	Ret. time	Area	Area %
1	21.028	4723091	50.07
2	31.642	4709688	49.93
		9432779	100.00

Chiral



Peak#	Ret. Time	Area	Area %
1	20.161	5959315	60.04
2	30.096	3966504	39.96

Compound 5e

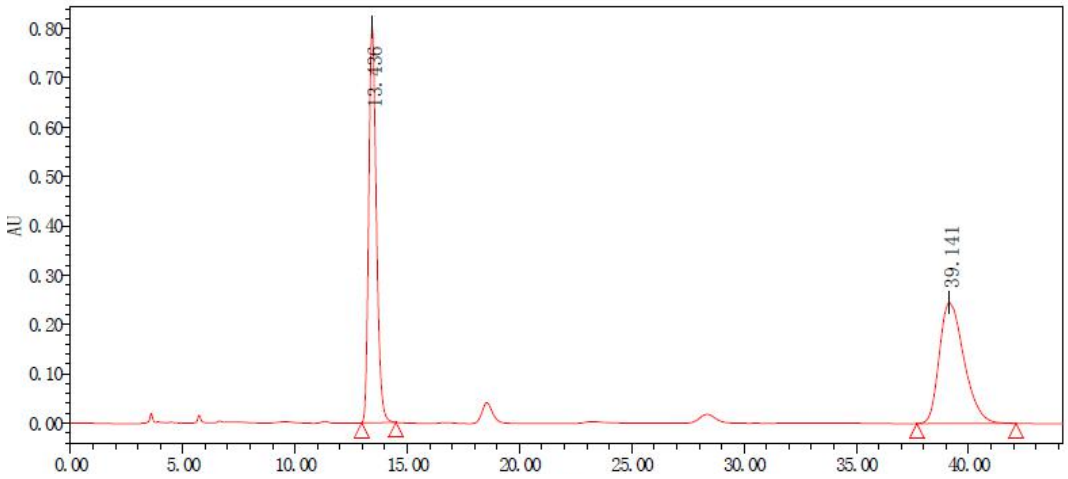


5e

HPLC Conditions

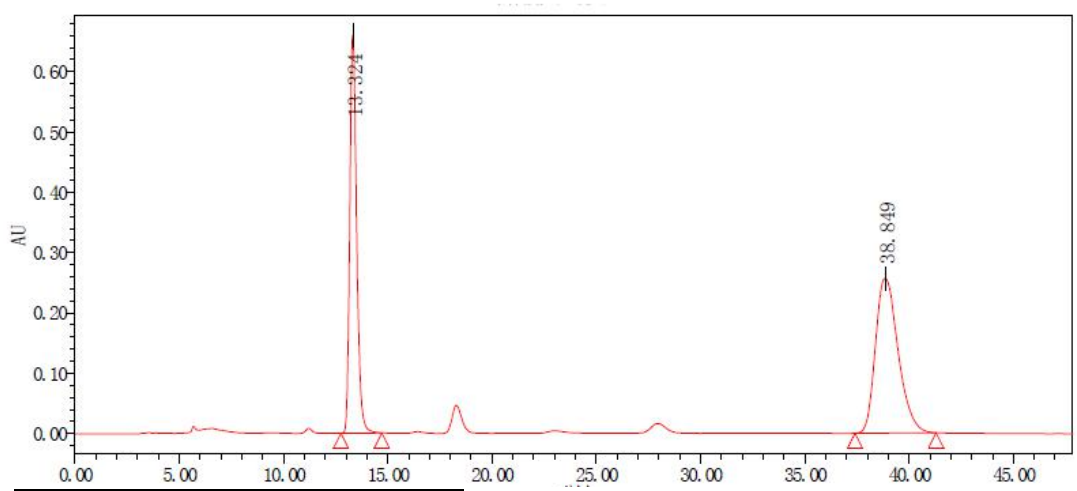
Column: Chiralcel AD-H, Daicel Chemical Industries, Ltd.
Eluent: Hexanes / isopropanol (92:8)
Flow rate: 1.0 mL/min
Detection: UV 254 nm

Racemic



Peak#	Ret. Time	Area	Area %
1	13.436	19074785	50.49
2	39.141	18706156	49.51

Chiral



Peak#	Ret. Time	Area	Area %
1	13.324	15110948	43.81
2	38.849	19378069	56.19

X. Reference

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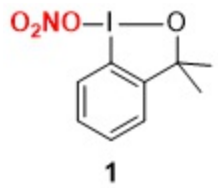
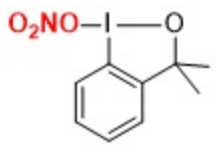


1

XI. NMR Spectra of New Compounds (^{1}H NMR, ^{13}C NMR)

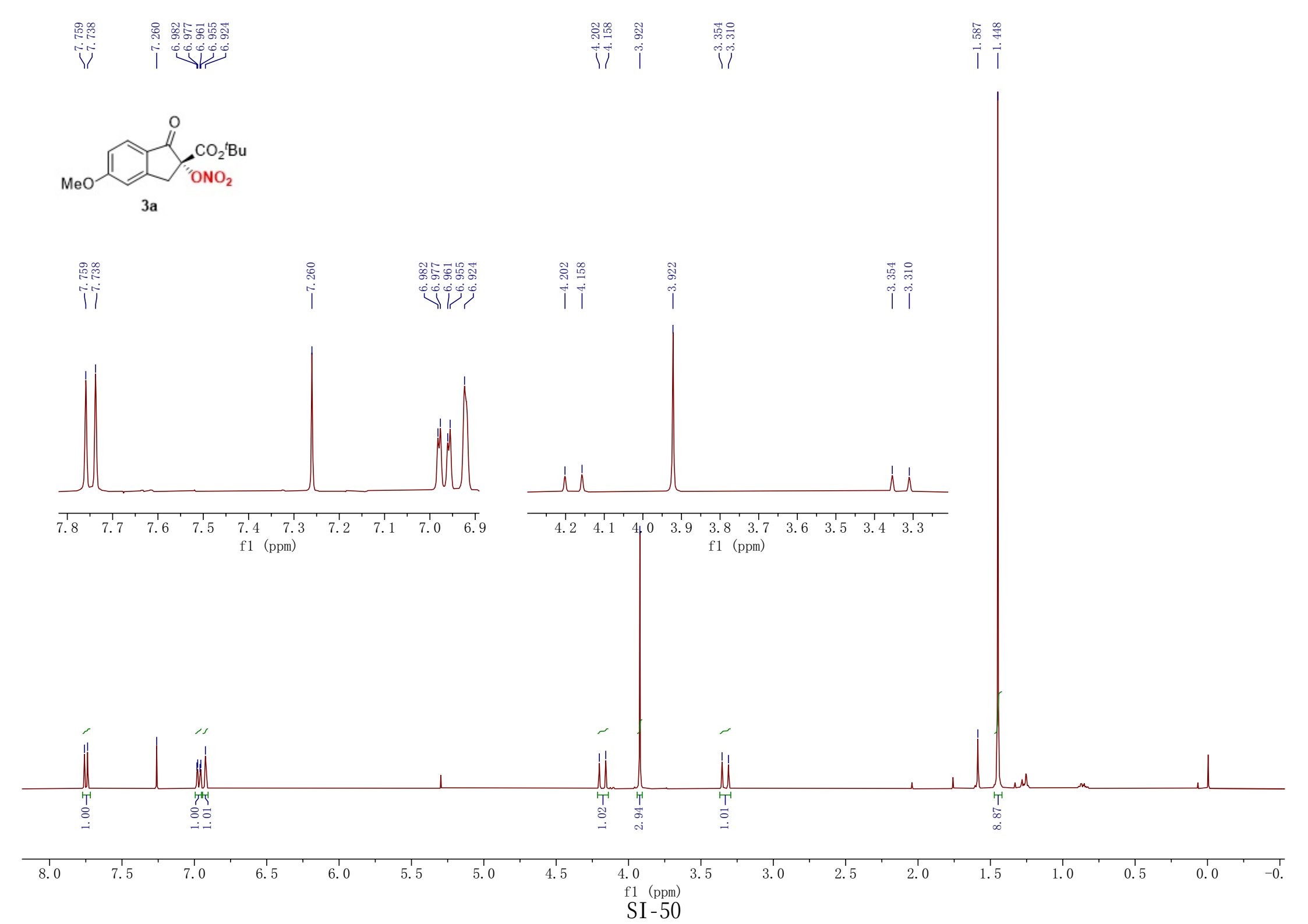


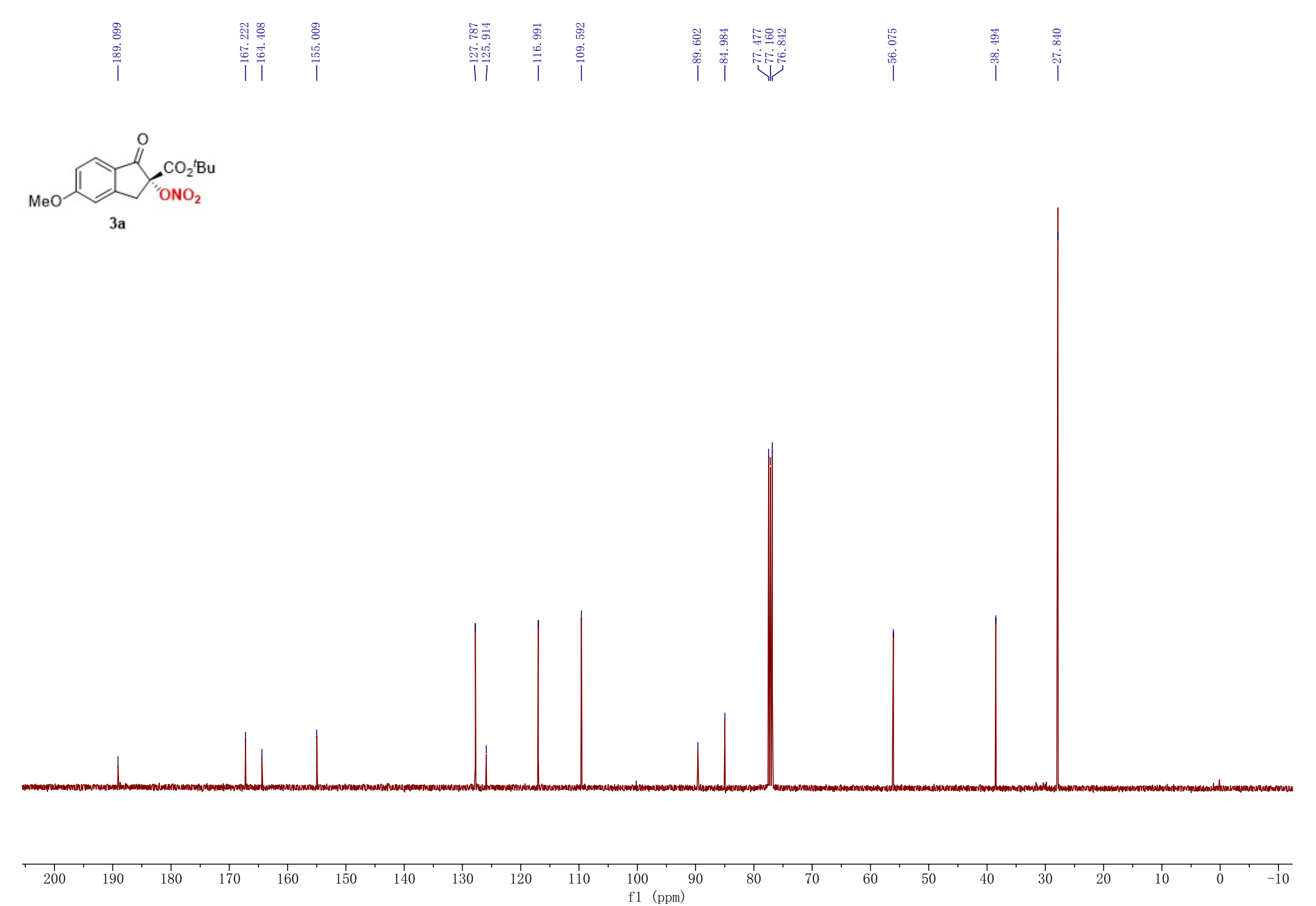
1

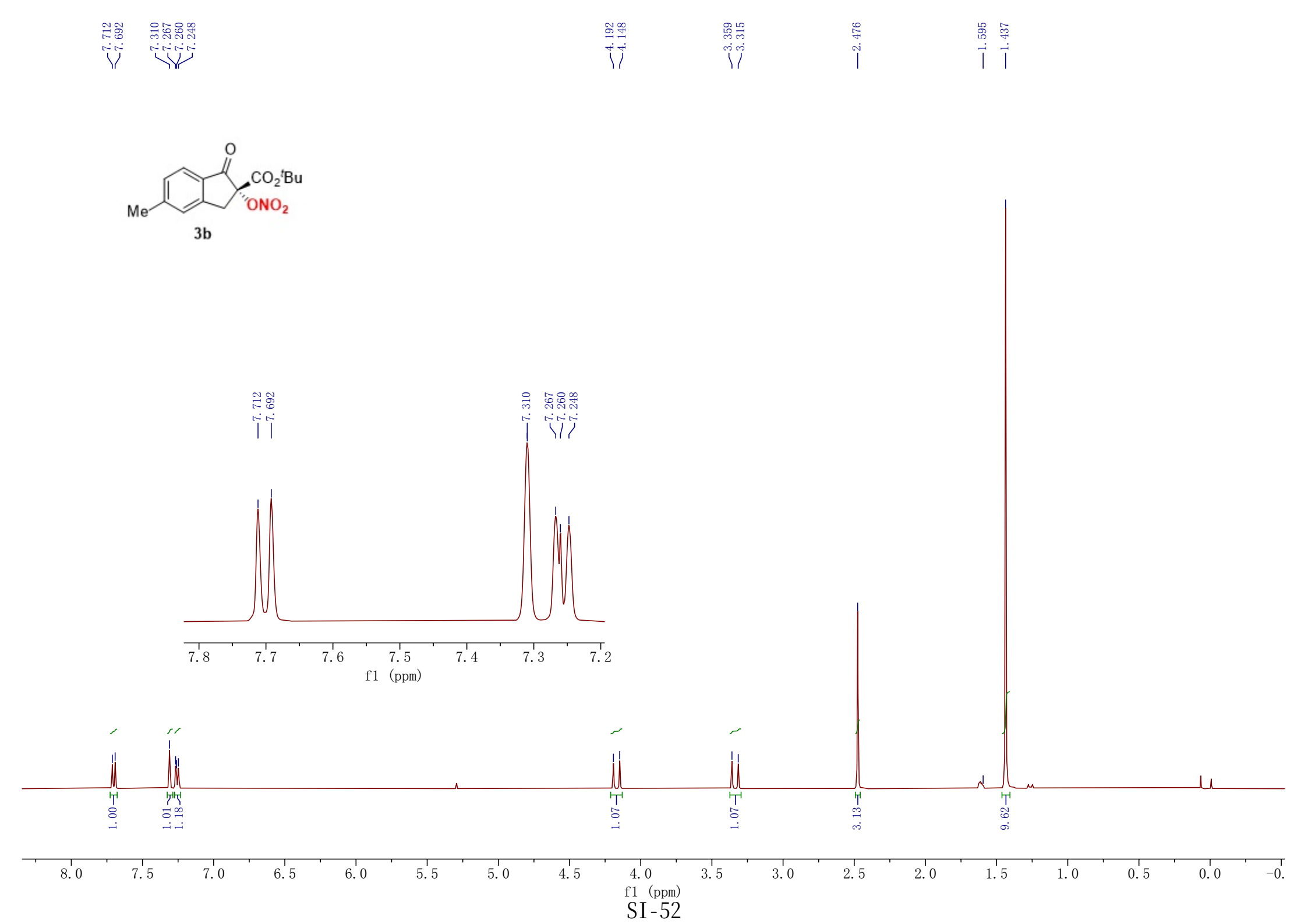
148.987
131.395
131.258
129.902
126.789
117.188
89.268
77.478
77.160
76.842
28.701

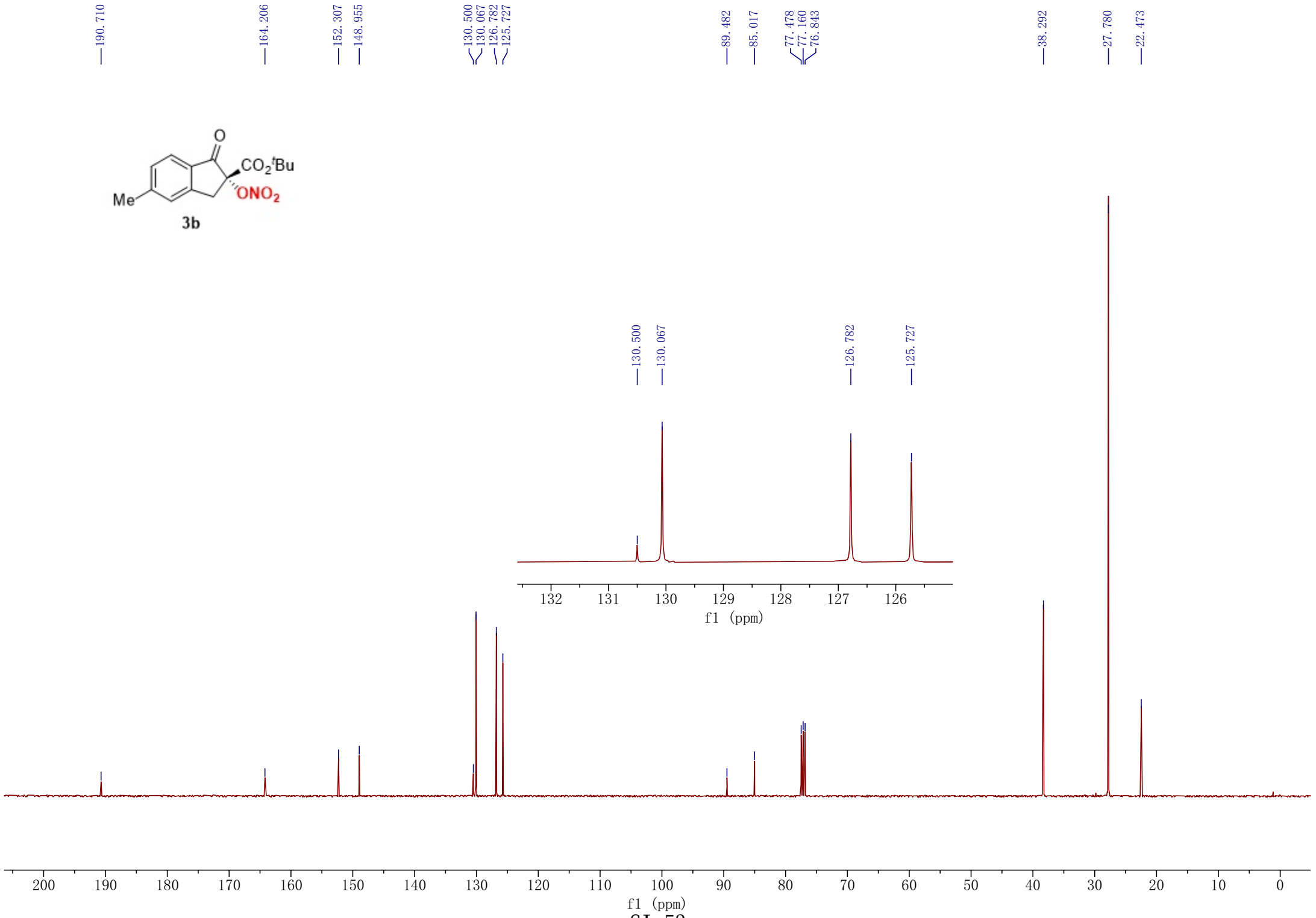
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

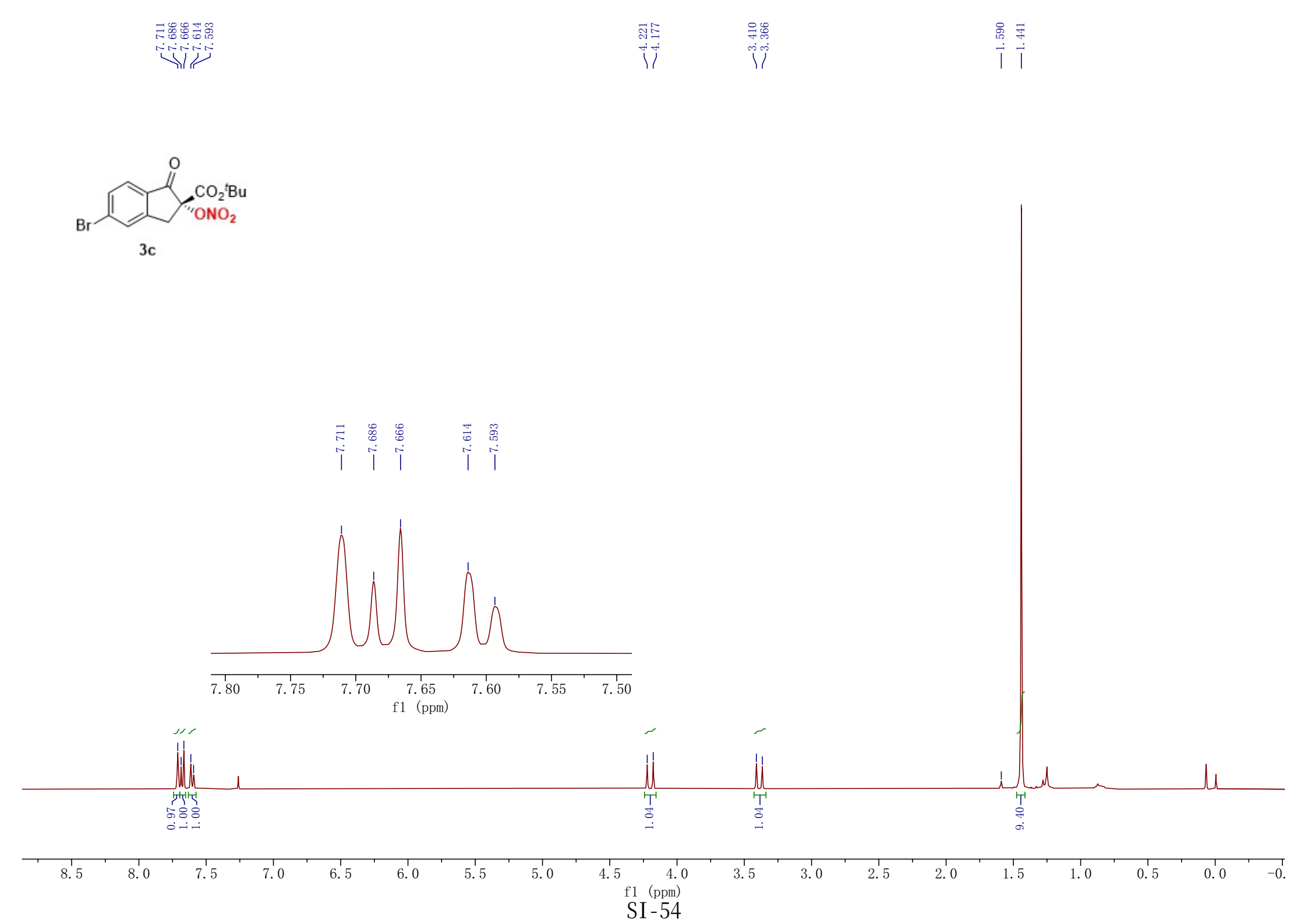
ppm

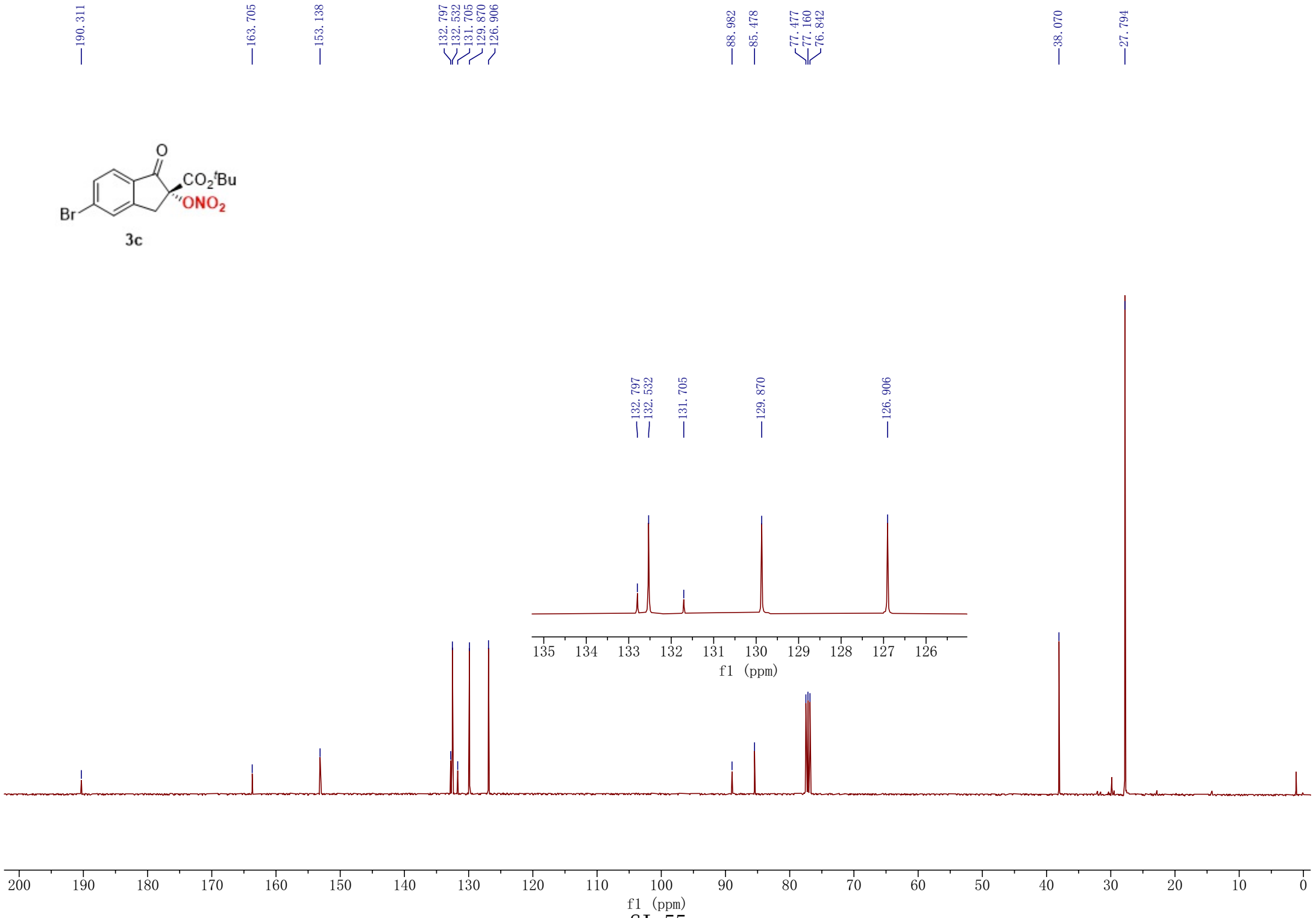

7.759
7.738
7.260
6.982
6.977
6.961
6.955
6.924
4.202
4.158
3.922
3.354
3.310
1.587
1.448
O
CO2tBu
MeO
ONO2
3a
f1 (ppm)
1.00
1.00
1.01
1.02
2.94
1.01
8.87

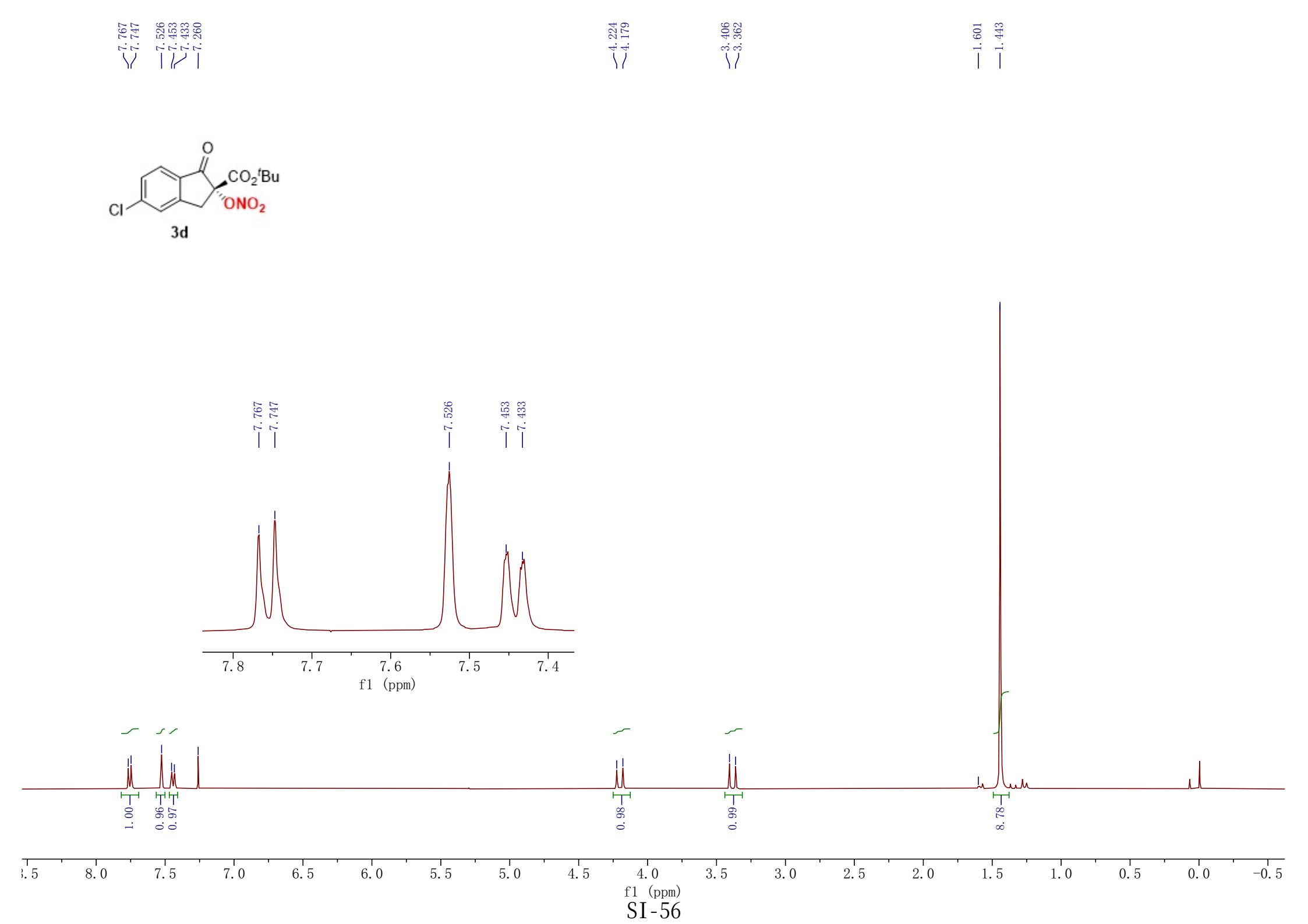

189.099
167.222
164.408
155.009
127.787
125.914
116.991
109.592
89.602
84.984
77.477
77.160
76.842
56.075
38.494
27.840
O
CO2tBu
ONO2
MeO
3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.712
7.692
7.310
7.267
7.260
7.248
4.192
4.148
3.359
3.315
2.476
1.595
1.437
O
CO2tBu
ONO2
Me
3b
f1 (ppm)
1.00
1.01
1.18
1.07
1.07
3.13
9.62
f1 (ppm)


190.710
164.206
152.307
148.955
130.500
130.067
126.782
125.727
89.482
85.017
77.478
77.160
76.843
38.292
27.780
22.473
O
CO2tBu
ONO2
Me
3b
130.500
130.067
126.782
125.727
132
131
130
129
128
127
126
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

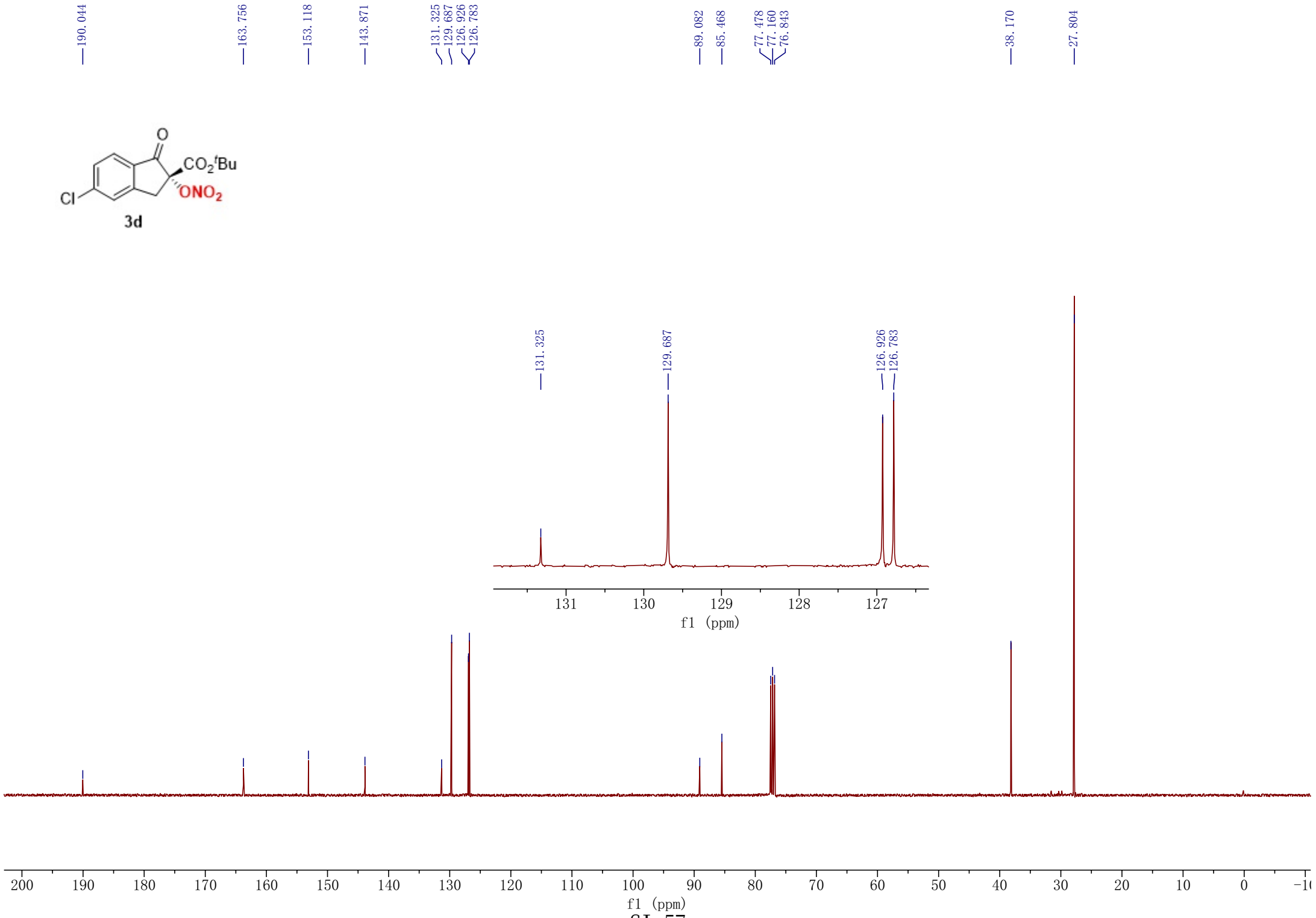

7.711
7.686
7.666
7.614
7.593
4.221
4.177
3.410
3.366
1.590
1.441
O
CO2tBu
ONO2
Br
3c
7.80
7.75
7.70
7.65
7.60
7.55
7.50
f1 (ppm)
0.97
1.00
1.00
1.04
1.04
9.40
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

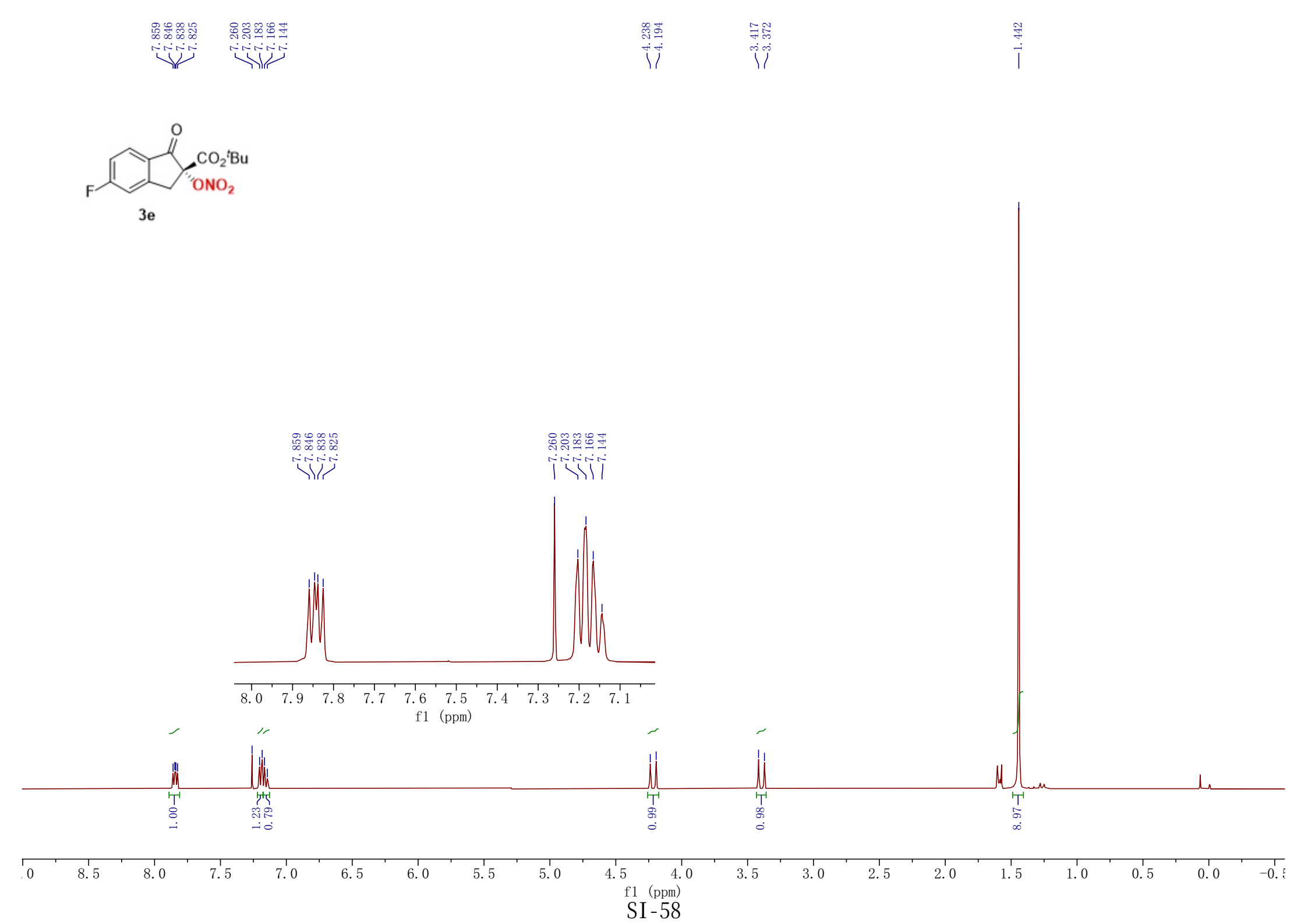

190.311
163.705
153.138
132.797
132.532
131.705
129.870
126.906
88.982
85.478
77.477
77.160
76.842
38.070
27.794
O
CO2tBu
ONO2
Br
3c
f1 (ppm)

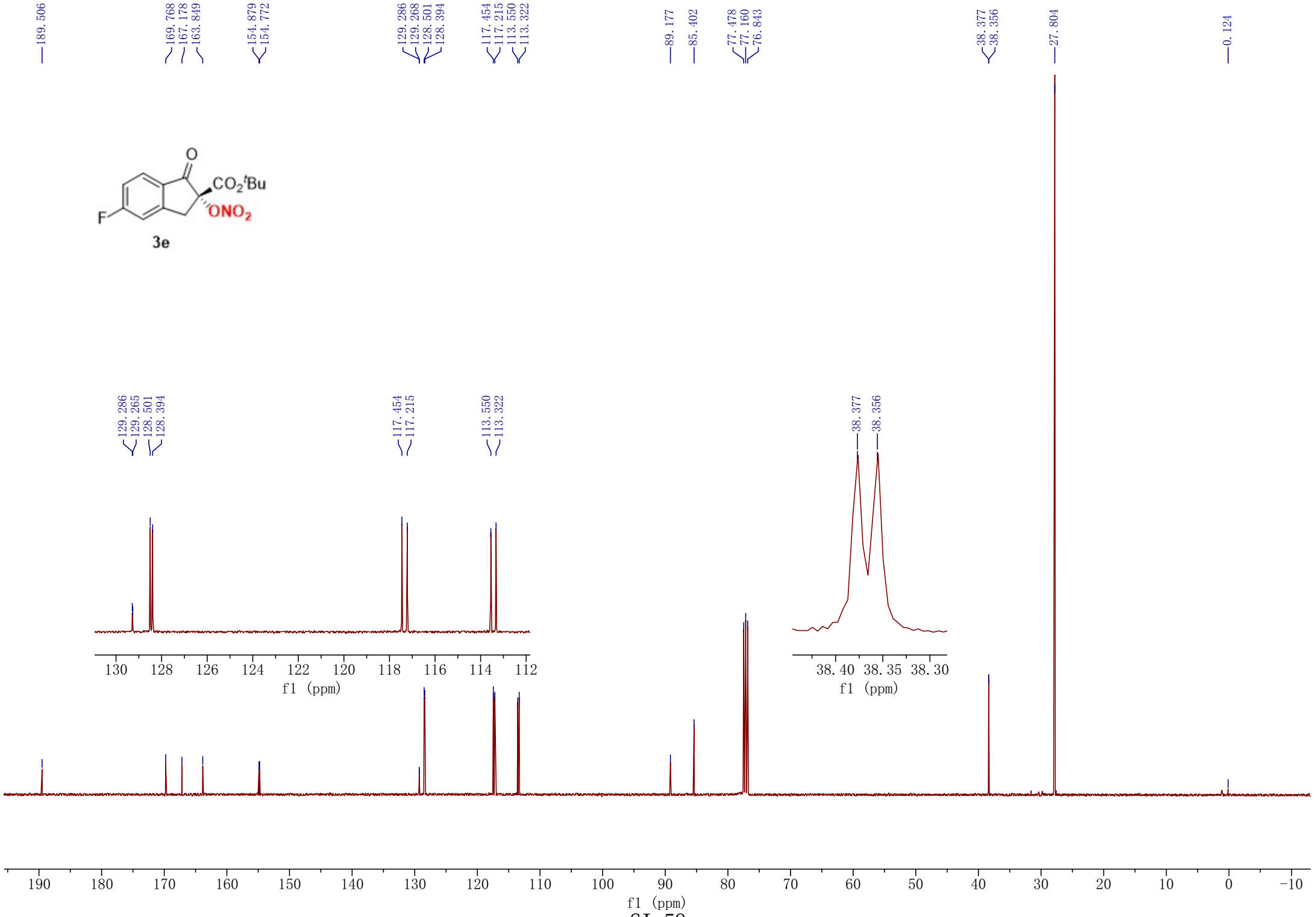

7.767
7.747
7.526
7.453
7.433
7.260
4.224
4.179
3.406
3.362
1.601
1.443
O
CO2tBu
ONO2
Cl
3d
f1 (ppm)
1.00
0.96
0.97
0.98
0.99
8.78

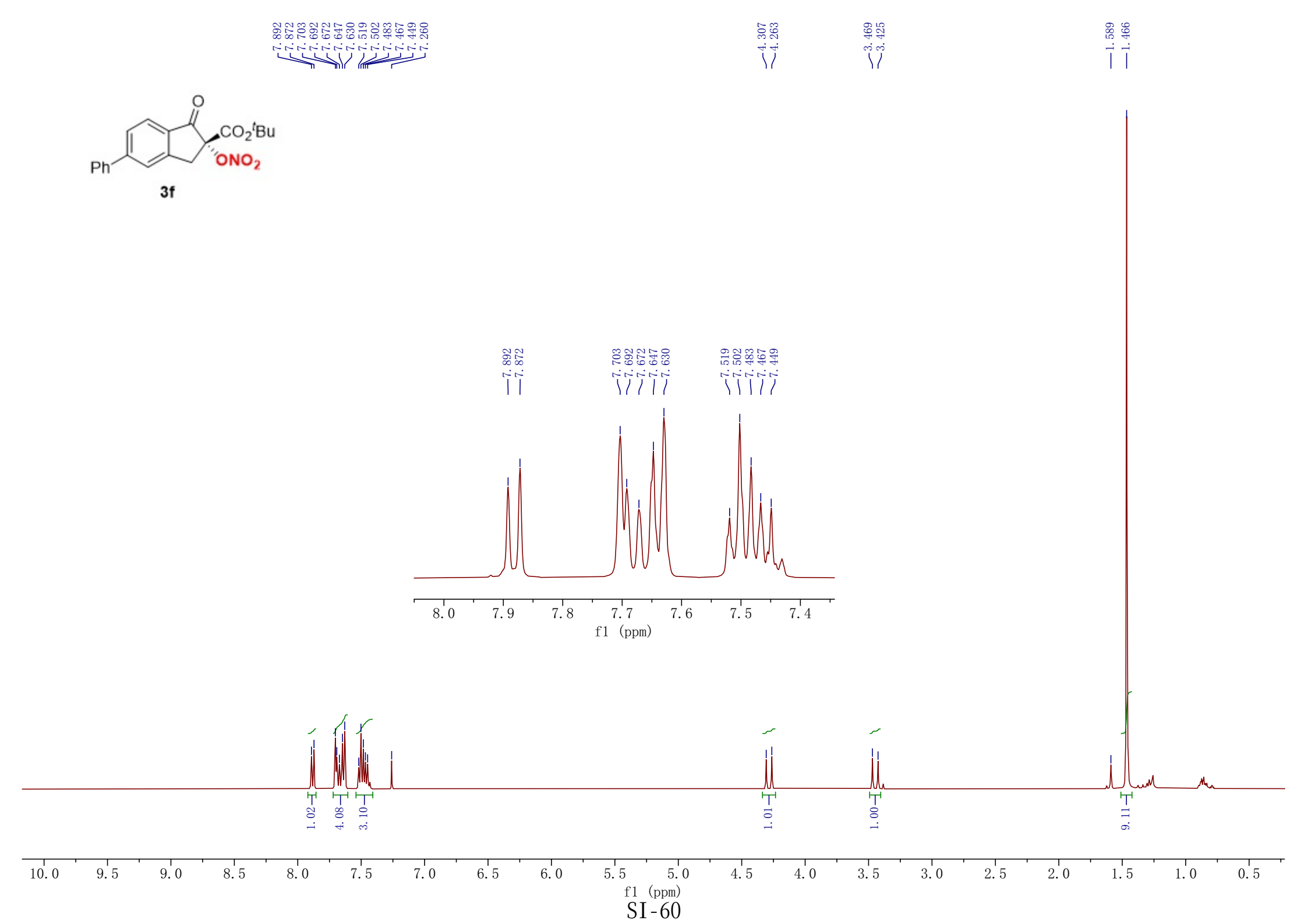
O
$CO_2{}^tBu$
Cl
ONO_2

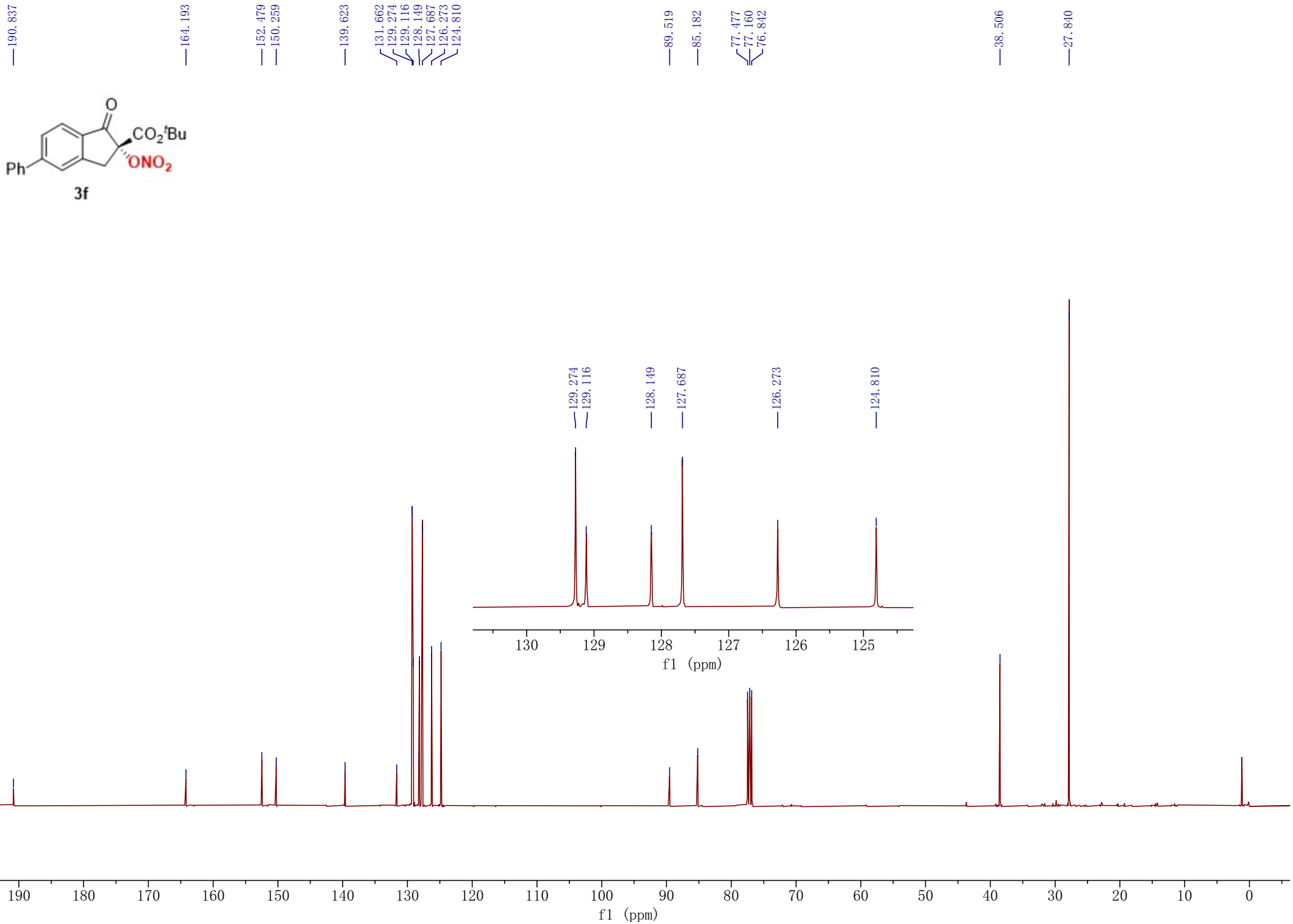
3d

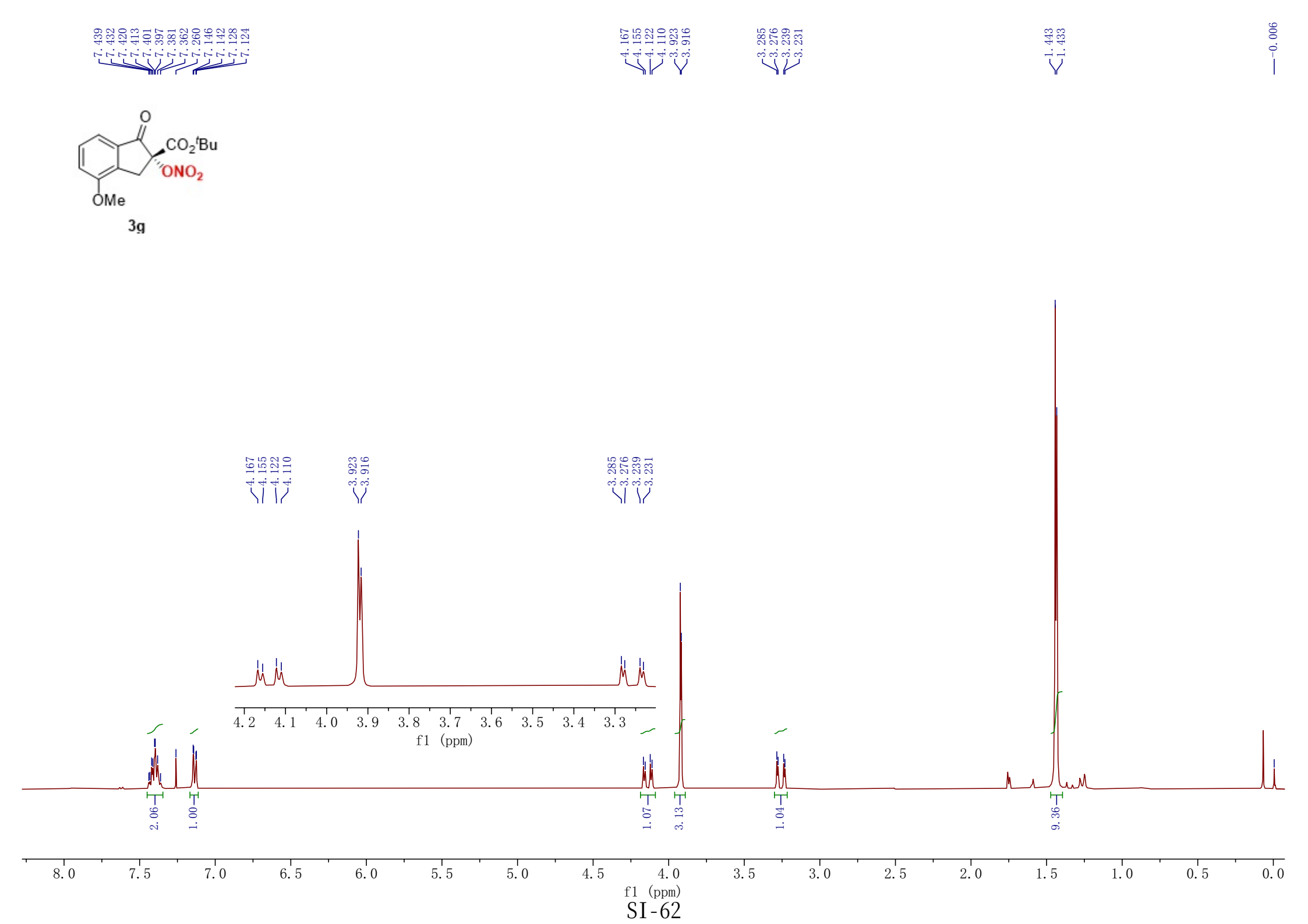

190.044
163.756
153.118
143.871
131.325
129.687
126.926
126.783
89.082
85.468
77.478
77.160
76.843
38.170
27.804
131
130
129
128
127
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

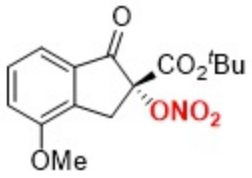

7.859
7.846
7.838
7.825
7.260
7.203
7.183
7.166
7.144
4.238
4.194
3.417
3.372
1.442
O
CO2tBu
F
ONO2
3e
f1 (ppm)
1.00
1.23
0.79
0.99
0.98
8.97
f1 (ppm)


189.506
169.768
167.178
163.849
154.879
154.772
129.286
129.268
128.501
128.394
117.454
117.215
113.550
113.322
89.177
85.402
77.478
77.160
76.843
38.377
38.356
27.804
0.124
O
CO2tBu
ONO2
F
3e
129.286
129.265
128.501
128.394
117.454
117.215
113.550
113.322
38.377
38.356
130 128 126 124 122 120 118 116 114 112
f1 (ppm)
38.40 38.35 38.30
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.892
7.872
7.703
7.692
7.672
7.647
7.630
7.519
7.502
7.483
7.467
7.449
7.260
4.307
4.263
3.469
3.425
1.589
1.466
O
CO2tBu
Ph
ONO2
3f
f1 (ppm)
1.02
4.08
3.10
1.01
1.00
9.11
f1 (ppm)


190.837
164.193
152.479
150.259
139.623
131.662
129.274
129.116
128.149
127.687
126.273
124.810
89.519
85.182
77.477
77.160
76.842
38.506
27.840
O
CO2tBu
Ph
ONO2
3f
f1 (ppm)
f1 (ppm)


7.439
7.432
7.420
7.413
7.401
7.397
7.381
7.362
7.260
7.146
7.142
7.128
7.124
4.167
4.155
4.122
4.110
3.923
3.916
3.285
3.276
3.239
3.231
1.443
1.433
0.006
O
CO2tBu
ONO2
OMe
3g
f1 (ppm)
2.06
1.00
1.07
3.13
1.04
9.36

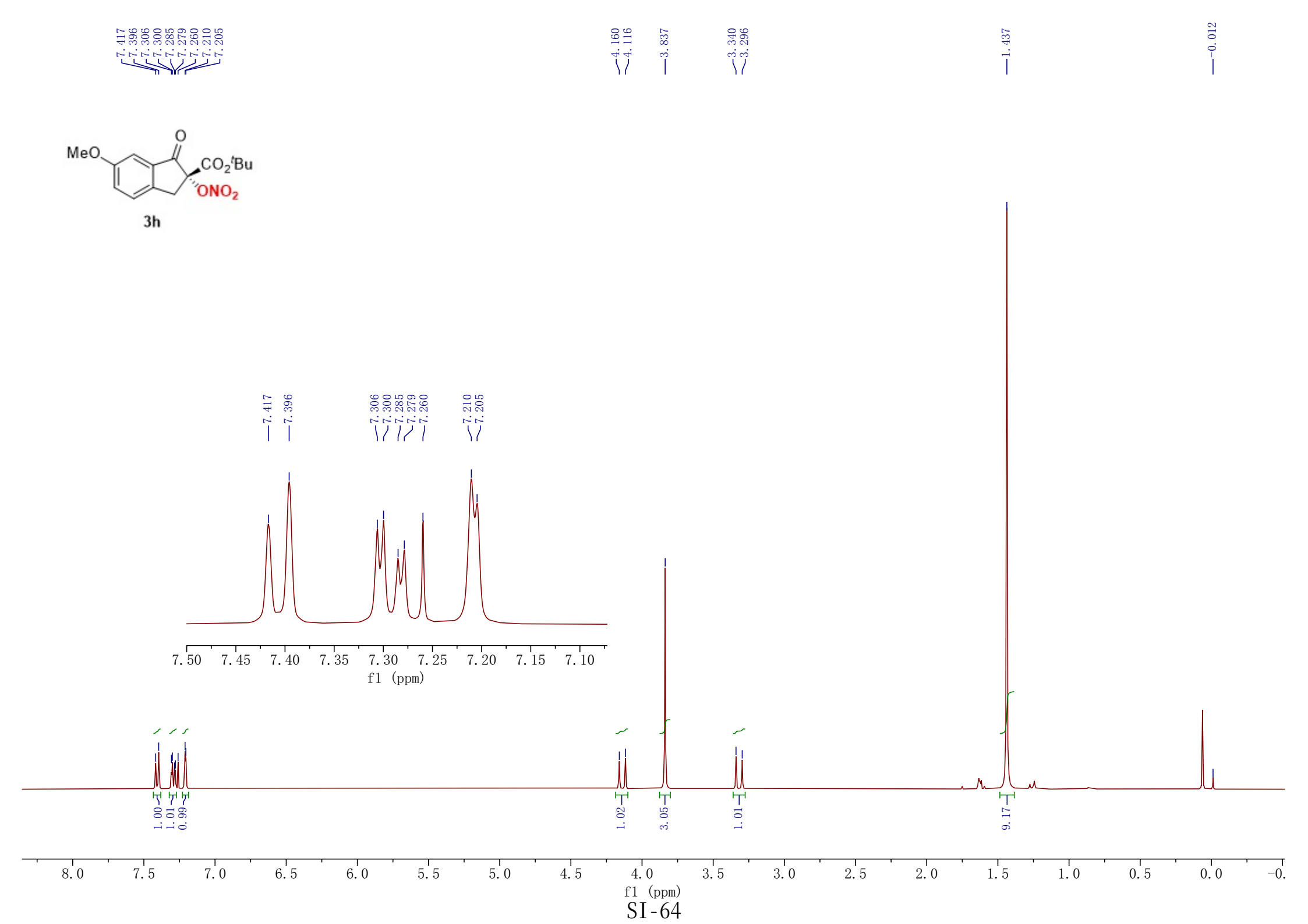


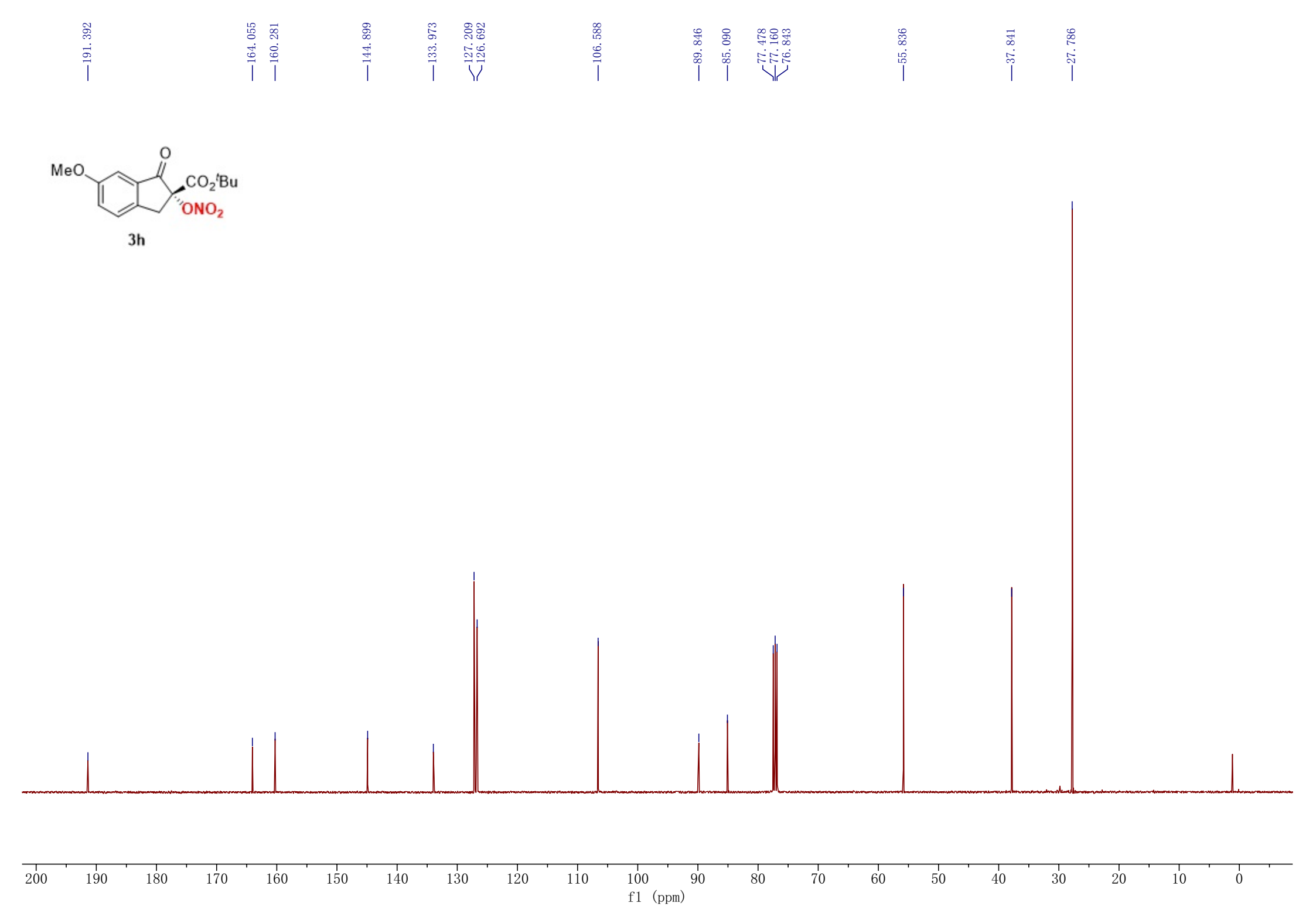
3g

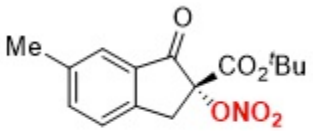
191.684
164.100
156.743
140.844
134.094
130.286
117.037
116.985
89.090
85.028
77.478
77.160
76.842
55.791
35.320
27.769

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

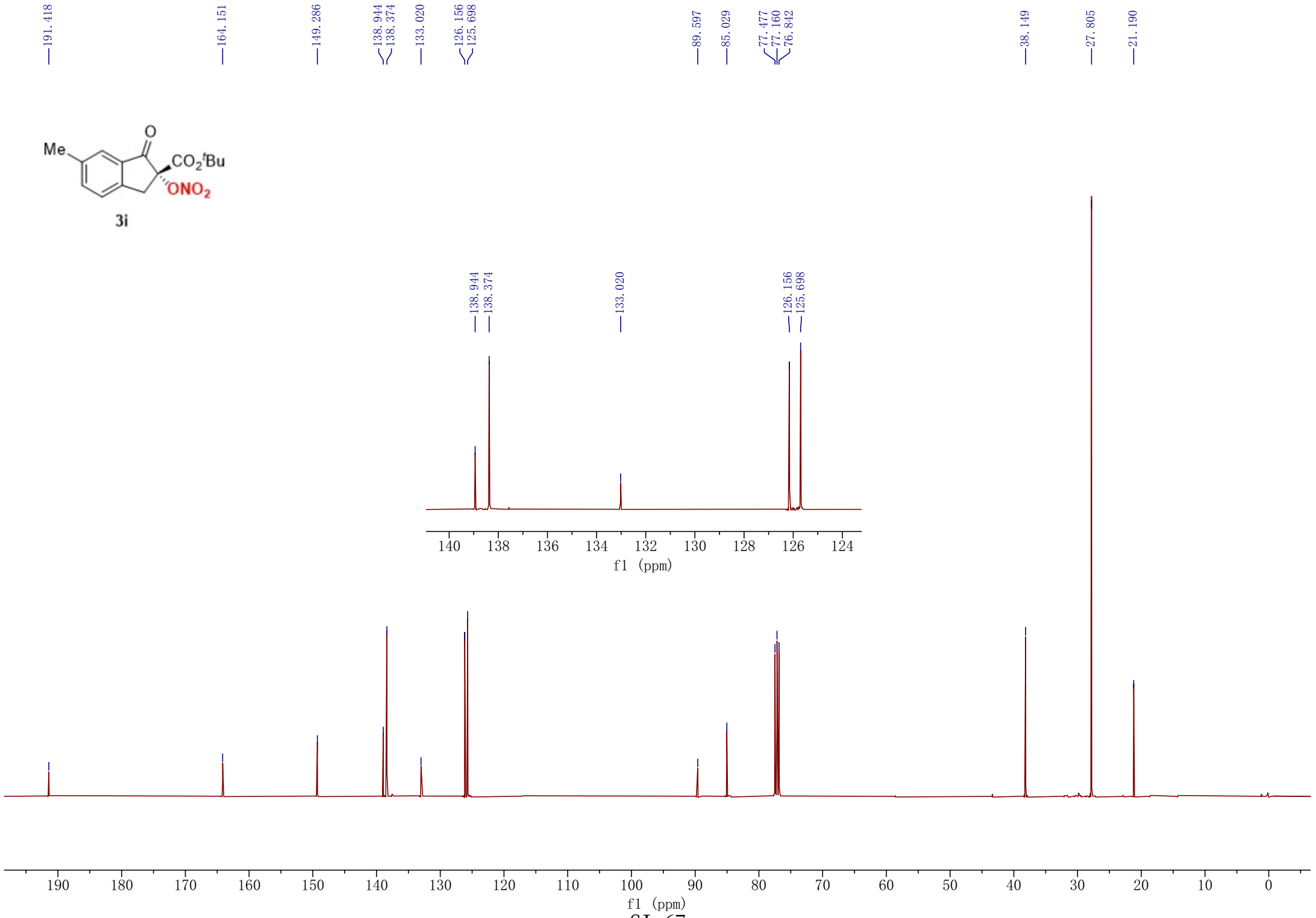
f1 (ppm)

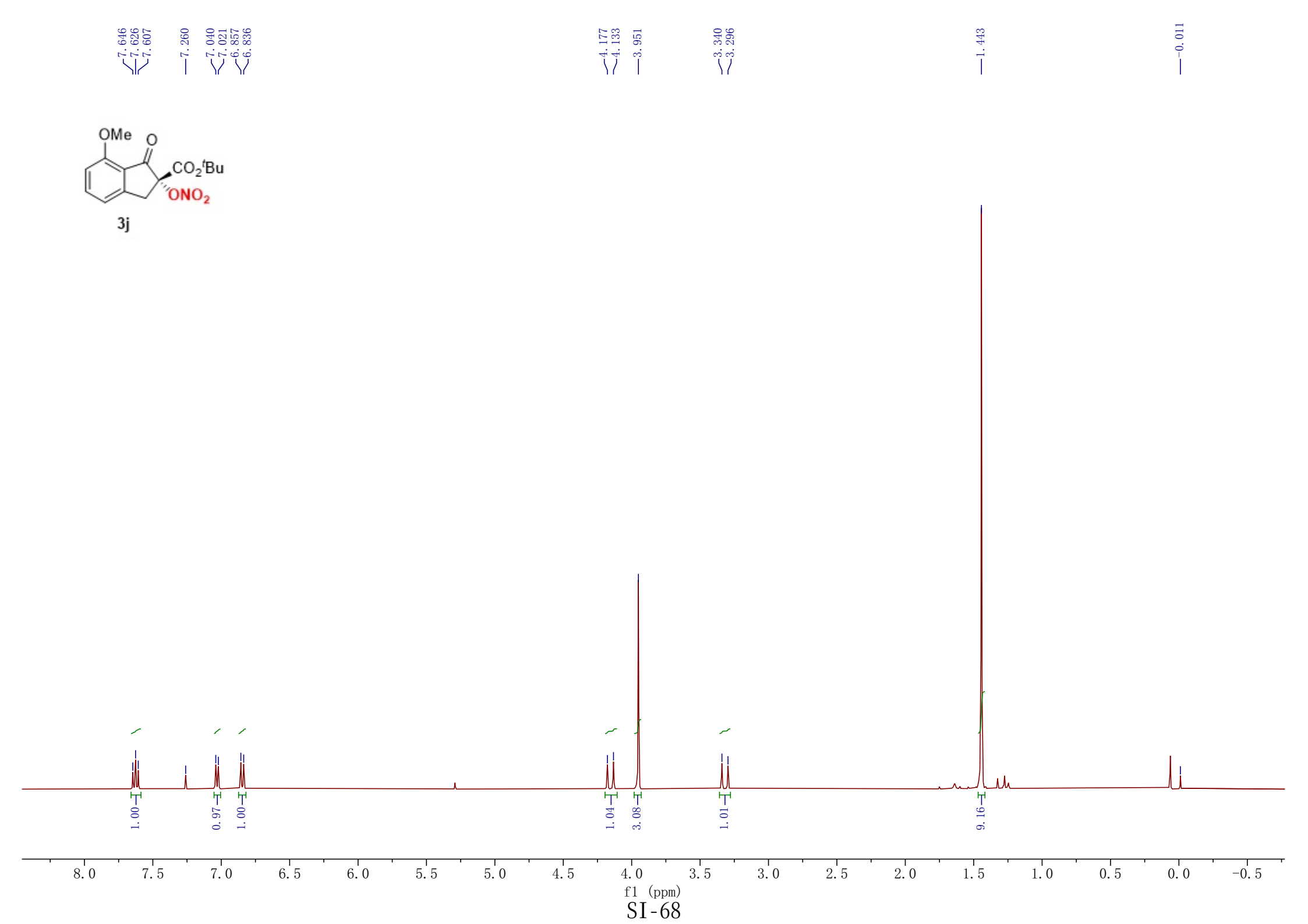

7.417
7.396
7.306
7.300
7.285
7.279
7.260
7.210
7.205
4.160
4.116
3.837
3.340
3.296
1.437
-0.012
MeO
O
CO2tBu
ONO2
3h
f1 (ppm)
1.00
1.01
0.99
1.02
3.05
1.01
9.17

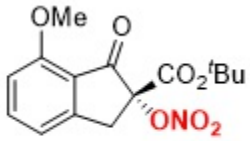

191.392
164.055
160.281
144.899
133.973
127.209
126.692
106.588
89.846
85.090
77.478
77.160
76.843
55.836
37.841
27.786
MeO
O
CO2tBu
ONO2
3h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3i


191.418
164.151
149.286
138.944
138.374
133.020
126.156
125.698
89.597
85.029
77.477
77.160
76.842
38.149
27.805
21.190
Me
O
CO2tBu
ONO2
3i
f1 (ppm)
f1 (ppm)


7.646
7.626
7.607
7.260
7.040
7.021
6.857
6.836
4.177
4.133
3.951
3.340
3.296
1.443
0.011
OMe
O
CO2tBu
ONO2
3j
1.00
0.97
1.00
1.04
3.08
1.01
9.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

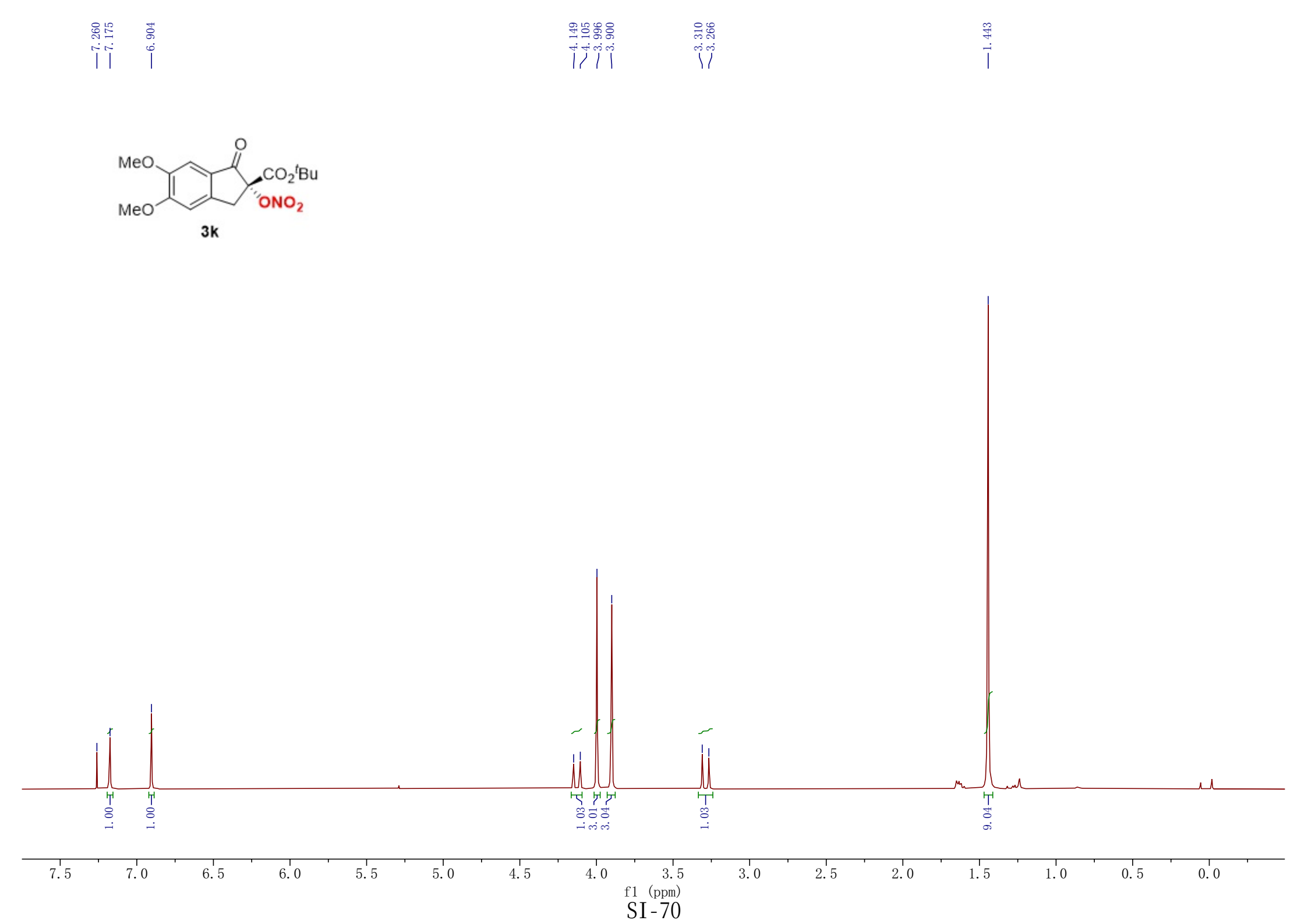


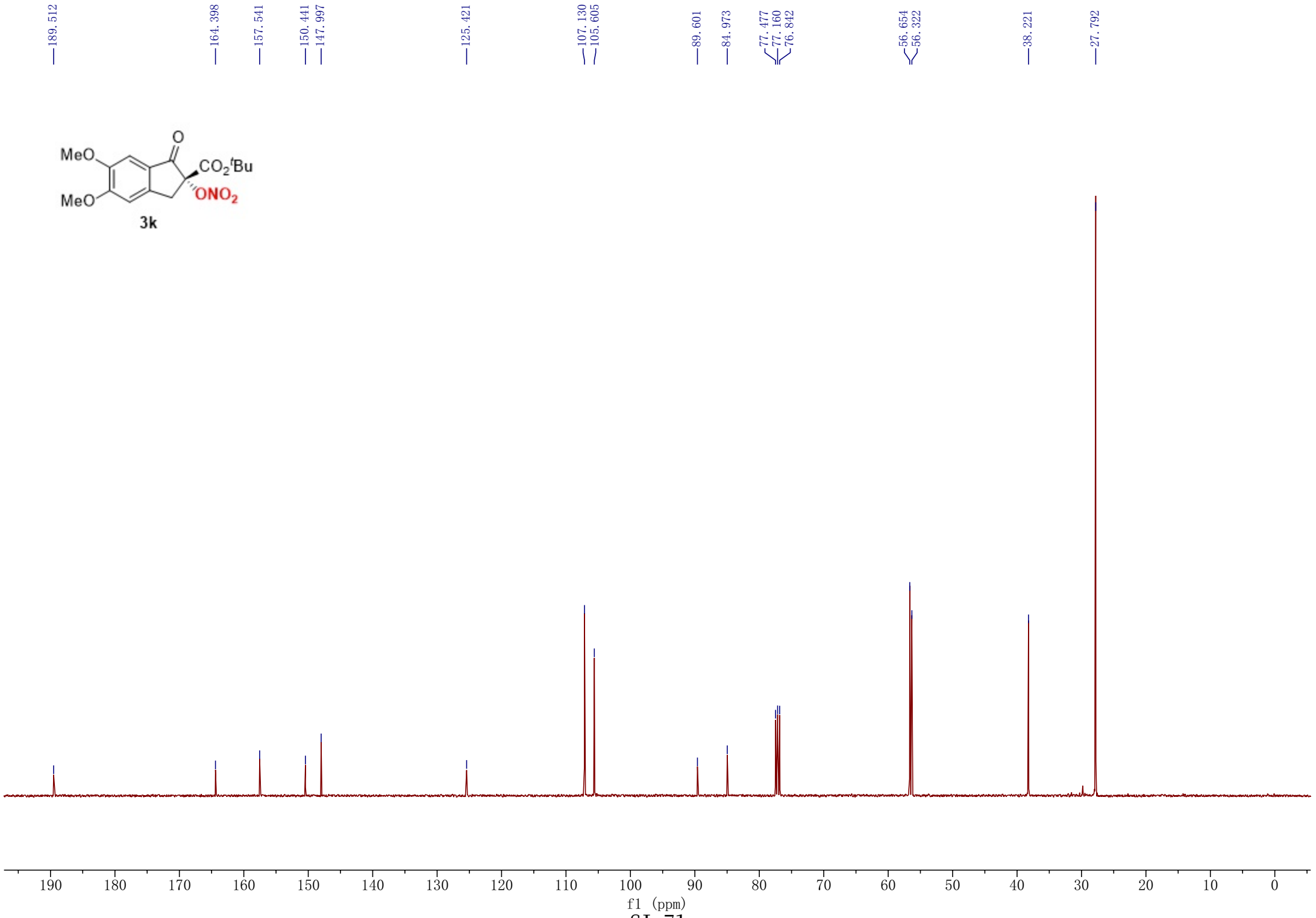
3j

188.271
164.404
159.803
153.776
138.937
121.317
118.067
110.272
89.440
85.019
77.578
77.260
76.943
56.208
38.023
27.926

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

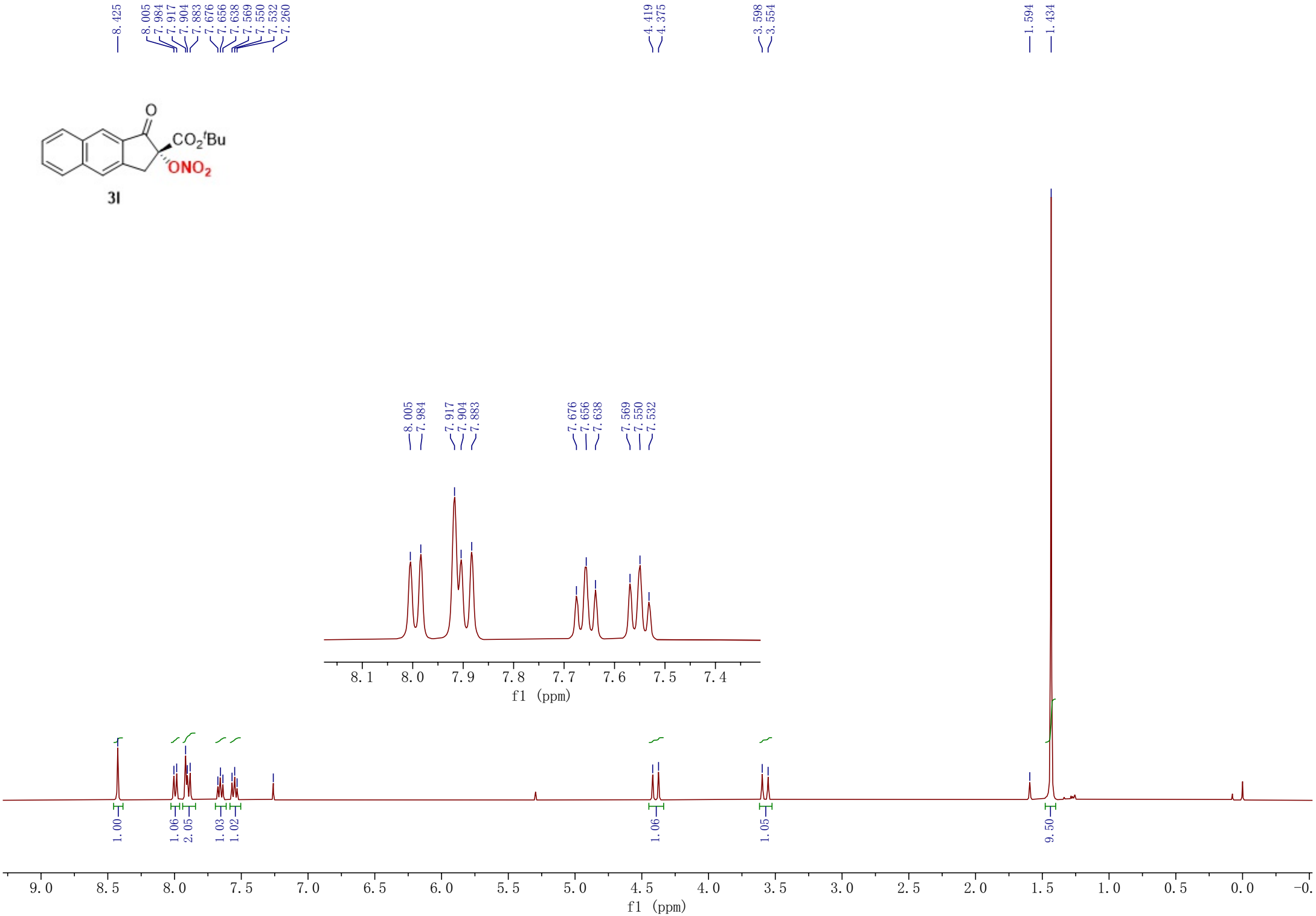
f1 (ppm)

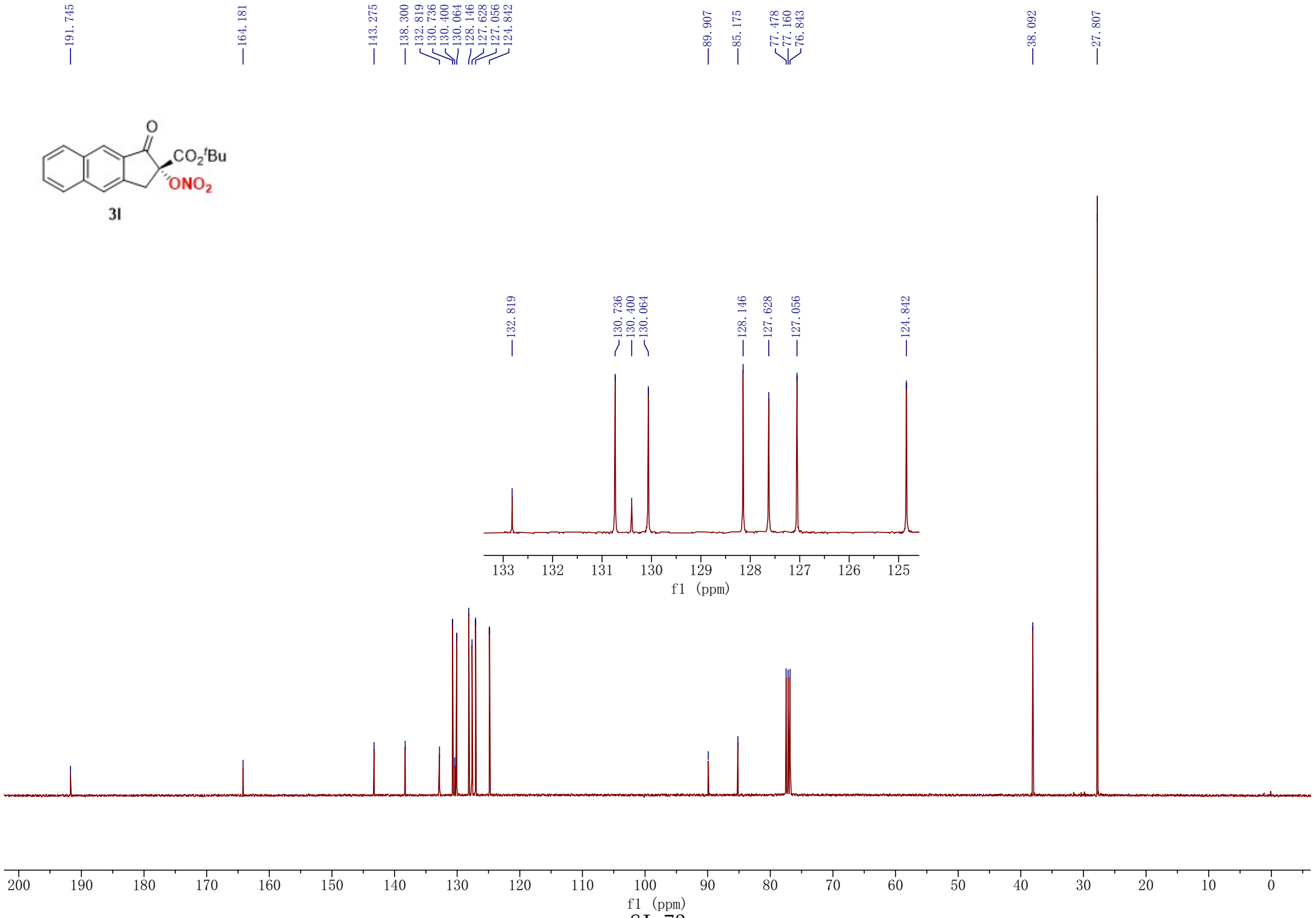

7.260
7.175
6.904
4.149
4.105
3.996
3.900
3.310
3.266
1.443
MeO
MeO
O
CO2tBu
ONO2
3k
1.00
1.00
1.03
3.01
3.04
1.03
9.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

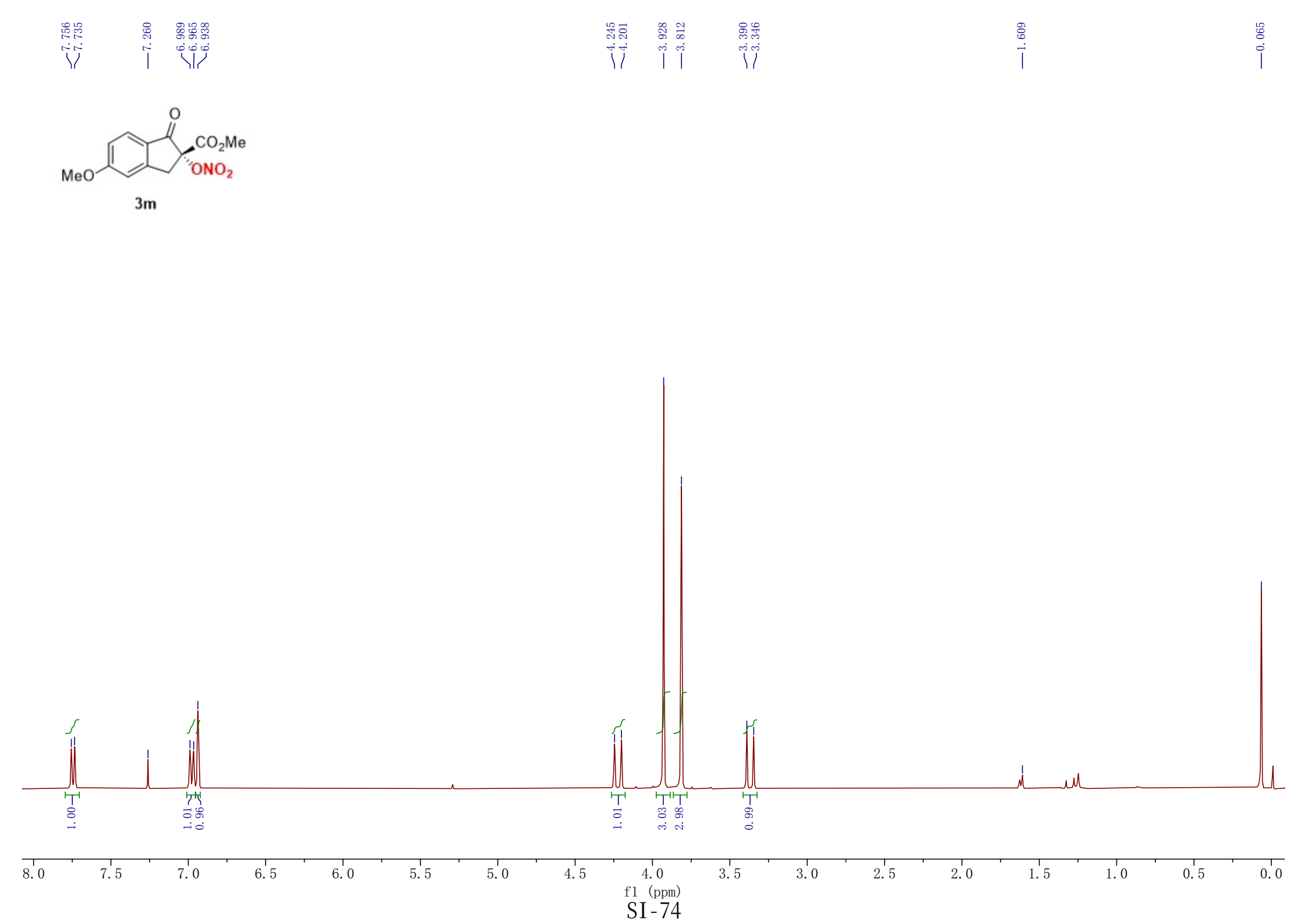

189.512
164.398
157.541
150.441
147.997
125.421
107.130
105.605
89.601
84.973
77.477
77.160
76.842
56.654
56.322
38.221
27.792
MeO
MeO
O
CO2tBu
ONO2
3k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

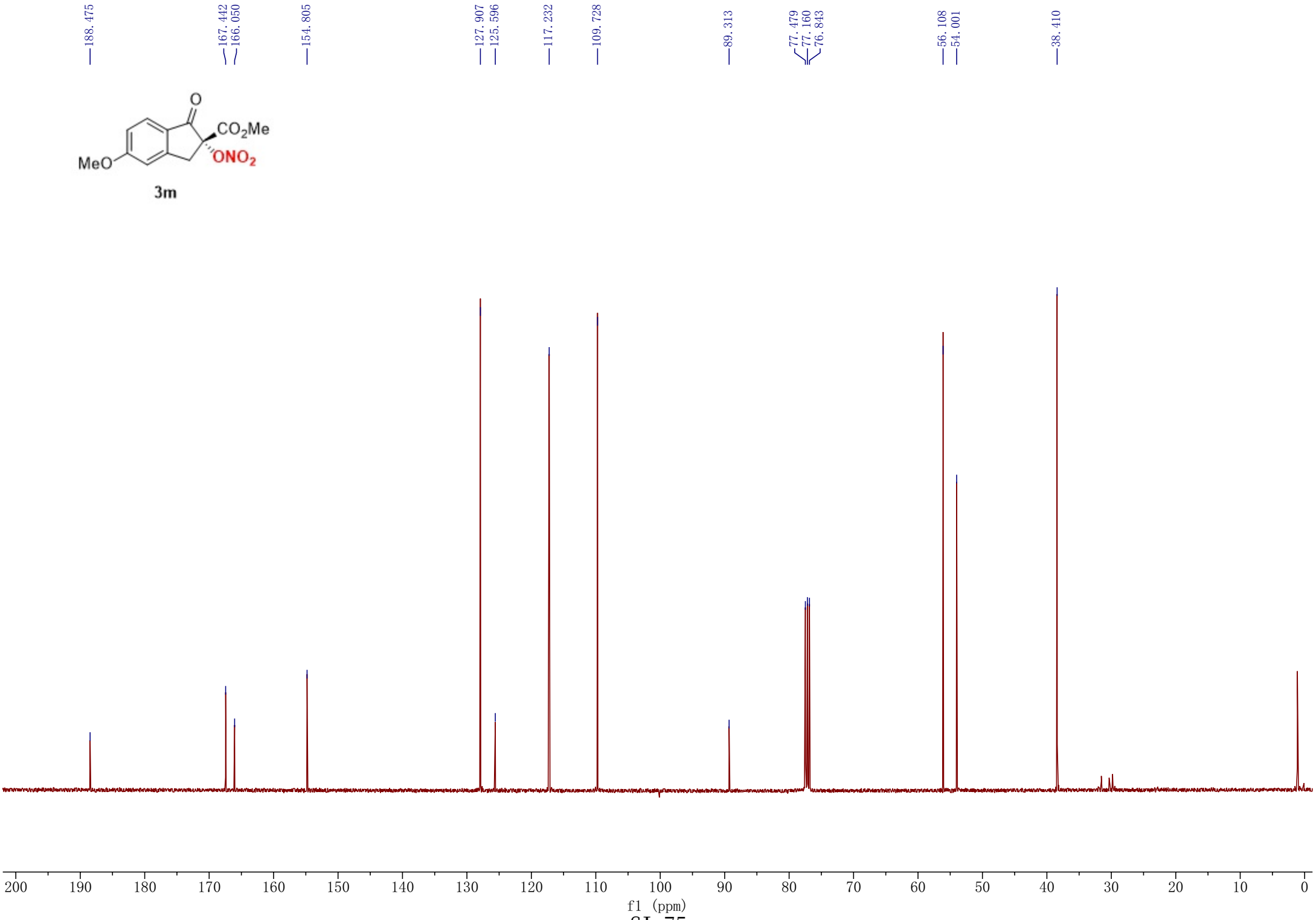
O
CO2tBu
ONO2

3l


8.425
8.005
7.984
7.917
7.904
7.883
7.676
7.656
7.638
7.569
7.550
7.532
7.260
4.419
4.375
3.598
3.554
1.594
1.434
1.00
1.06
2.05
1.03
1.02
1.06
1.05
9.50
f1 (ppm)


191.745
164.181
143.275
138.300
132.819
130.736
130.400
130.064
128.146
127.628
127.056
124.842
89.907
85.175
77.478
77.160
76.843
38.092
27.807
O
CO2tBu
ONO2
3l
f1 (ppm)


7.756
7.735
7.260
6.989
6.965
6.938
4.245
4.201
3.928
3.812
3.390
3.346
1.609
0.065
O
CO2Me
MeO
ONO2
3m
1.00
1.01
0.96
1.01
3.03
2.98
0.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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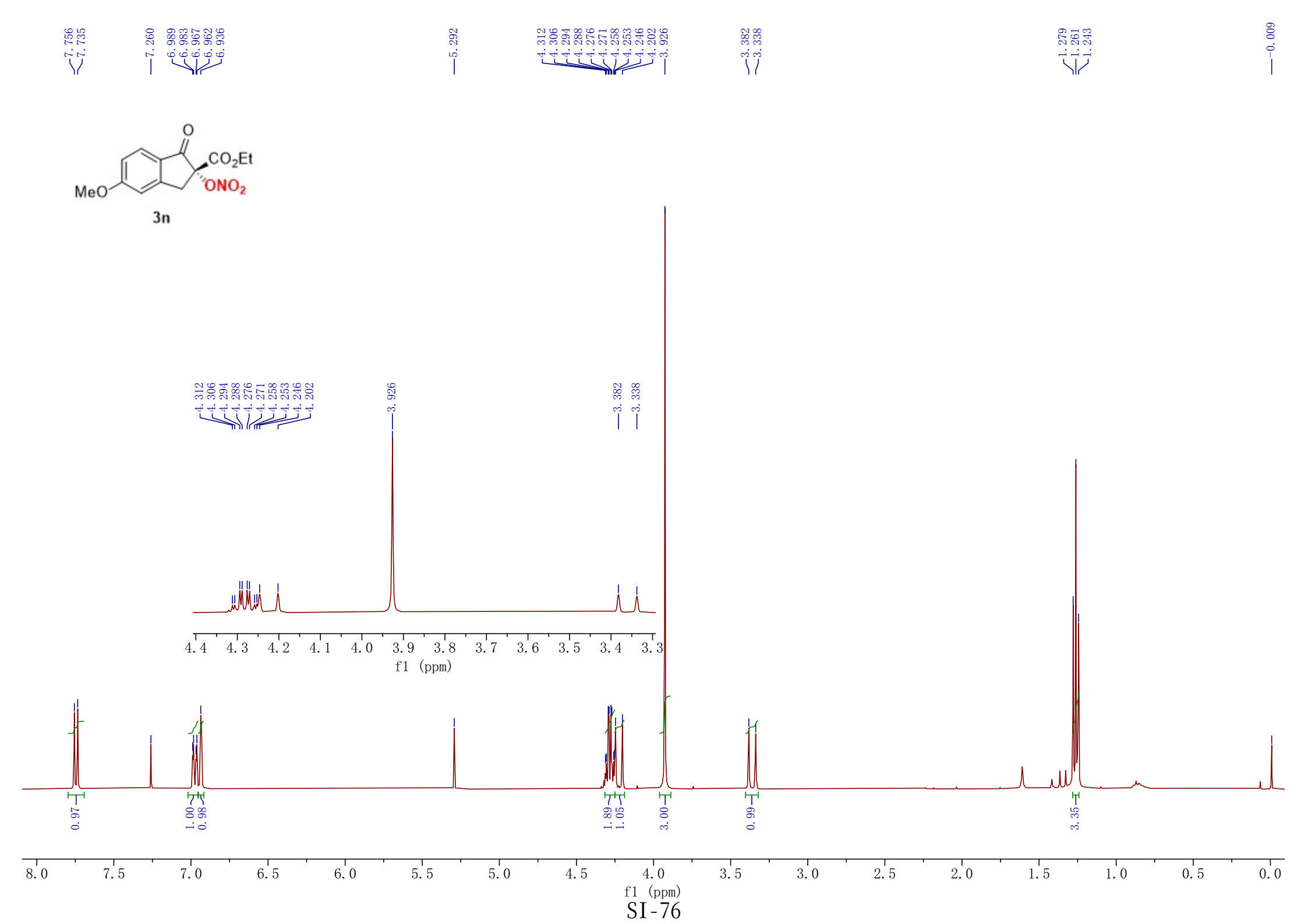
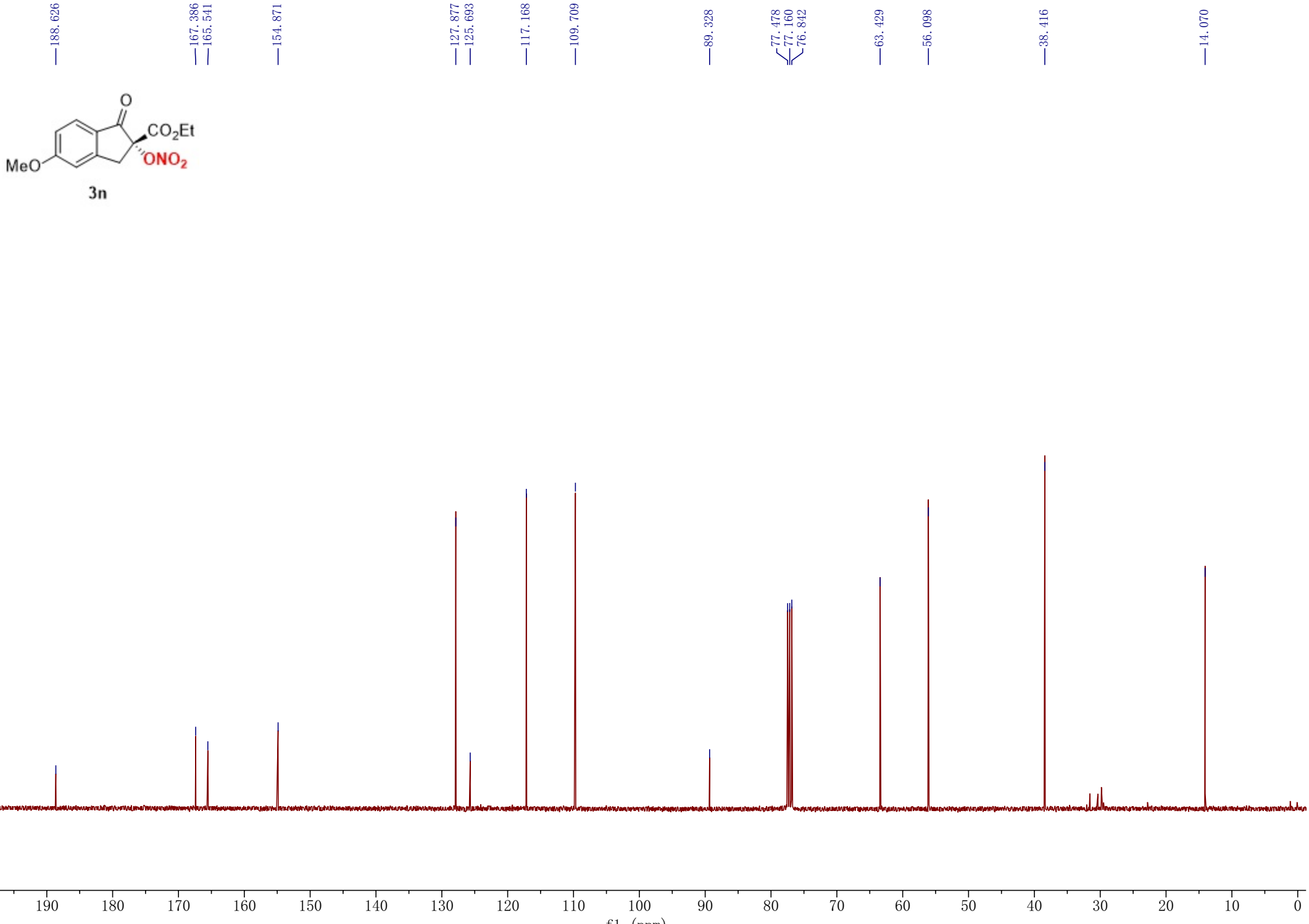
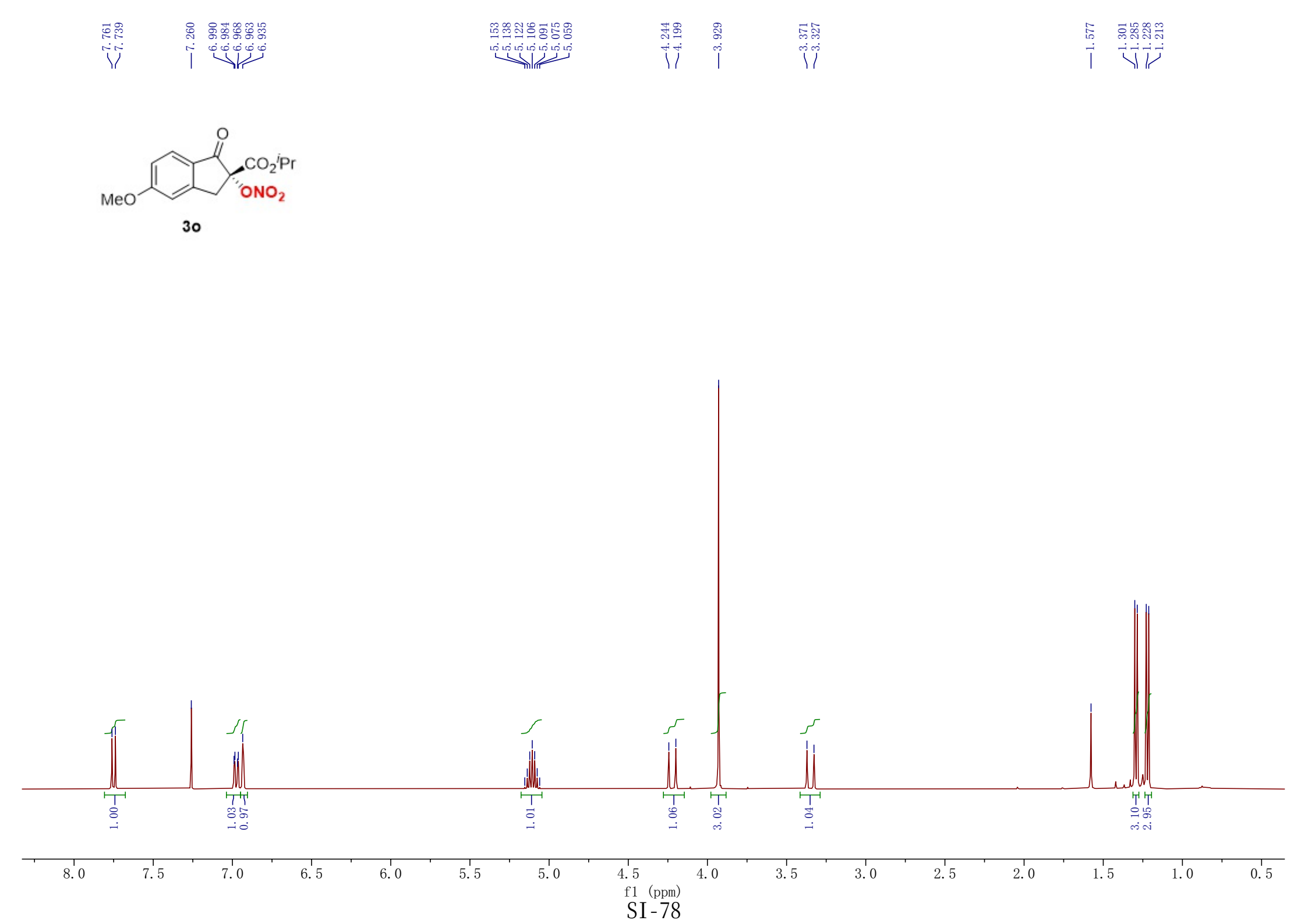
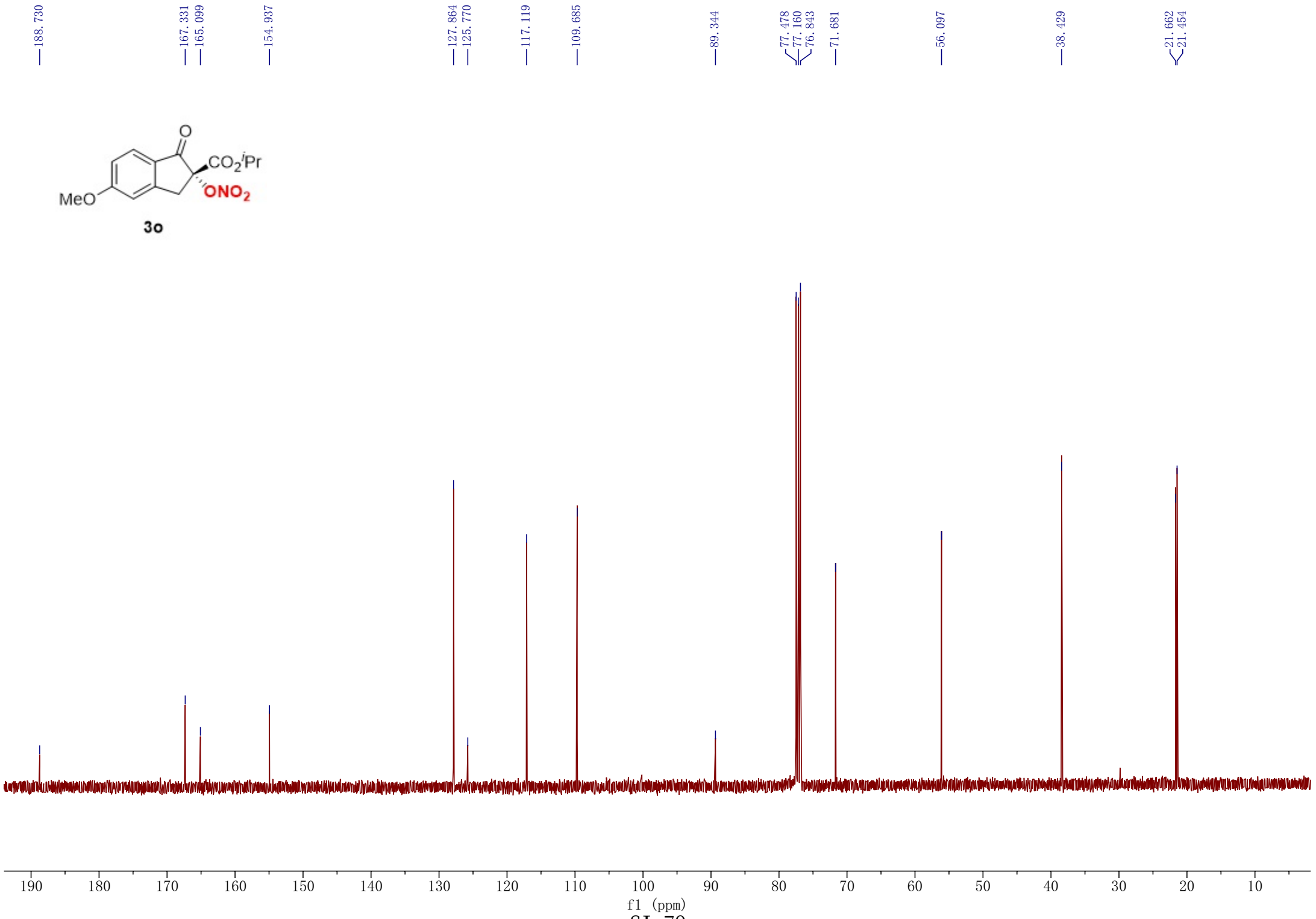
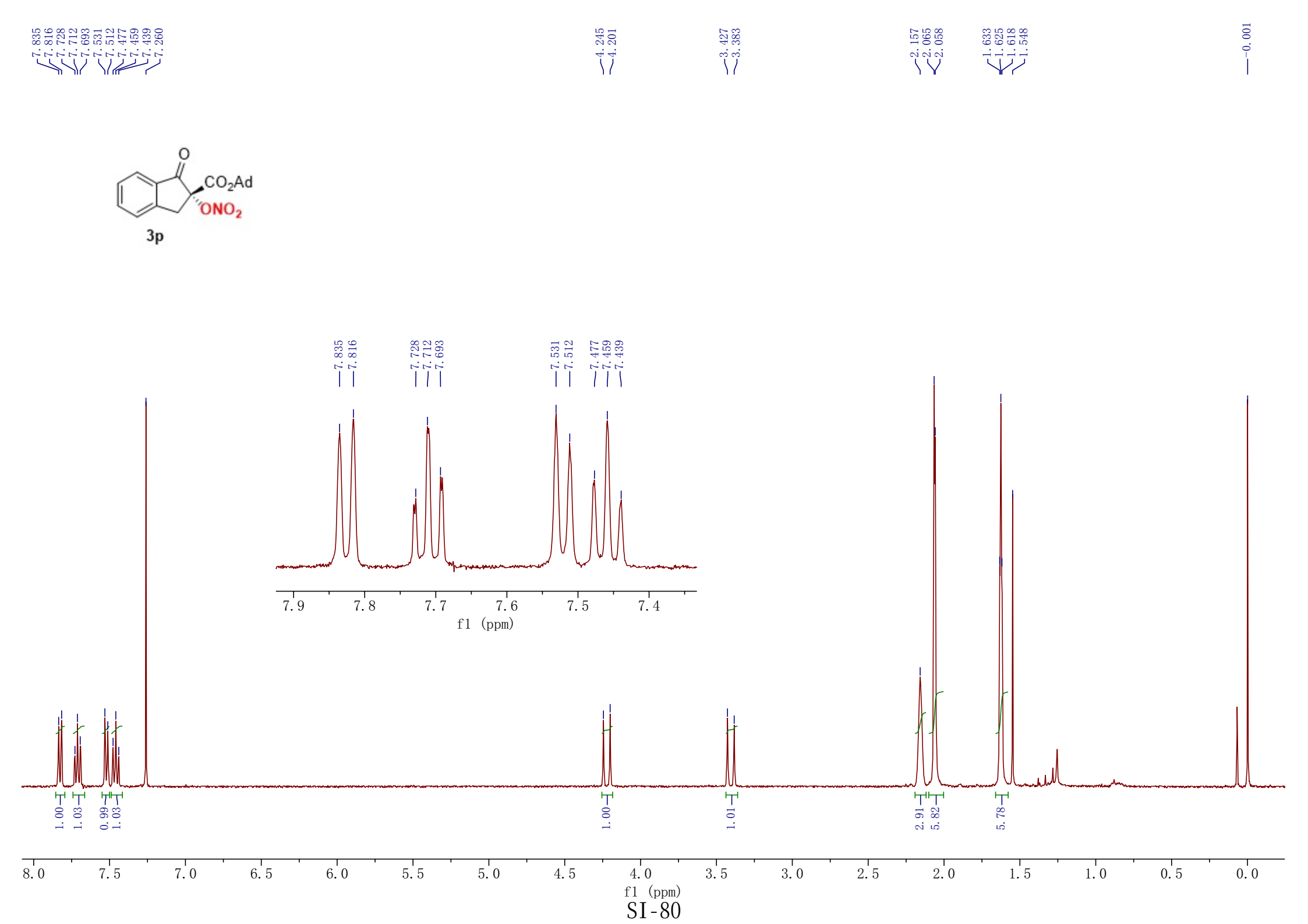
167.442
166.050
154.805
127.907
125.596
117.232
109.728
89.313
77.479
77.160
76.843
56.108
54.001
38.410
O
CO2Me
ONO2
MeO
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

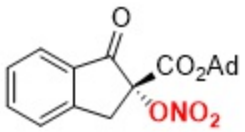

7.756
7.735
7.260
6.989
6.983
6.967
6.962
6.936
5.292
4.312
4.306
4.294
4.288
4.276
4.271
4.258
4.253
4.246
4.202
3.926
3.382
3.338
1.279
1.261
1.243
0.009
O
CO2Et
ONO2
MeO
3n
f1 (ppm)
0.97
1.00
0.98
1.89
1.05
3.00
0.99
3.35


188.626
167.386
165.541
154.871
127.877
125.693
117.168
109.709
89.328
77.478
77.160
76.842
63.429
56.098
38.416
14.070
O
CO2Et
ONO2
MeO
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.761
7.739
7.260
6.990
6.984
6.968
6.963
6.935
5.153
5.138
5.122
5.106
5.091
5.075
5.059
4.244
4.199
3.929
3.371
3.327
1.577
1.301
1.285
1.228
1.213
O
CO2iPr
ONO2
MeO
3o
1.00
1.03
0.97
1.01
1.06
3.02
1.04
3.10
2.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


188.730
167.331
165.099
154.937
127.864
125.770
117.119
109.685
89.344
77.478
77.160
76.843
71.681
56.097
38.429
21.662
21.454
O
CO2iPr
ONO2
MeO
3o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.835
7.816
7.728
7.712
7.693
7.531
7.512
7.477
7.459
7.439
7.260
4.245
4.201
3.427
3.383
2.157
2.065
2.058
1.633
1.625
1.618
1.548
0.001
O
CO2Ad
ONO2
3p
f1 (ppm)
1.00
1.03
0.99
1.03
1.00
1.01
2.91
5.82
5.78

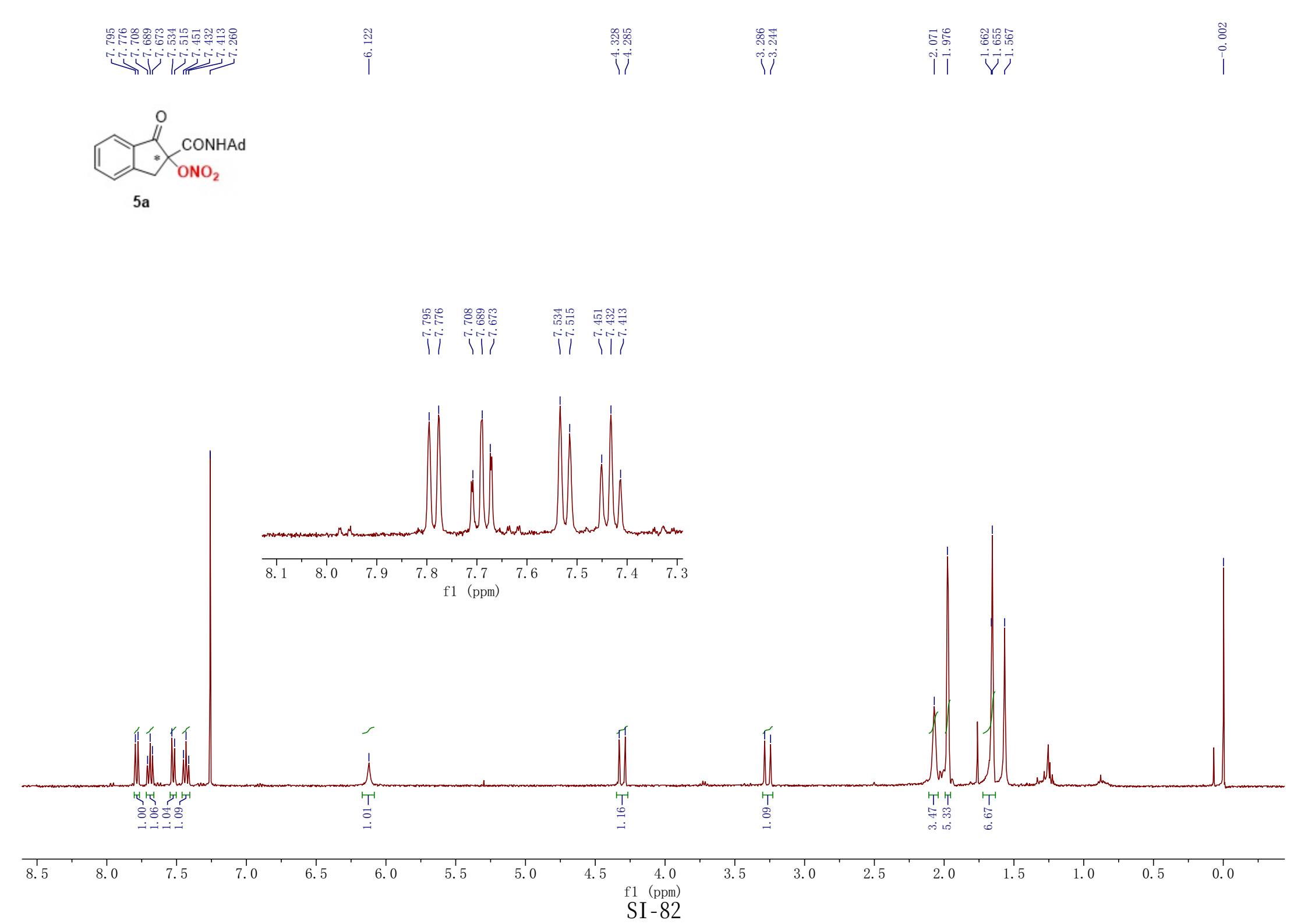


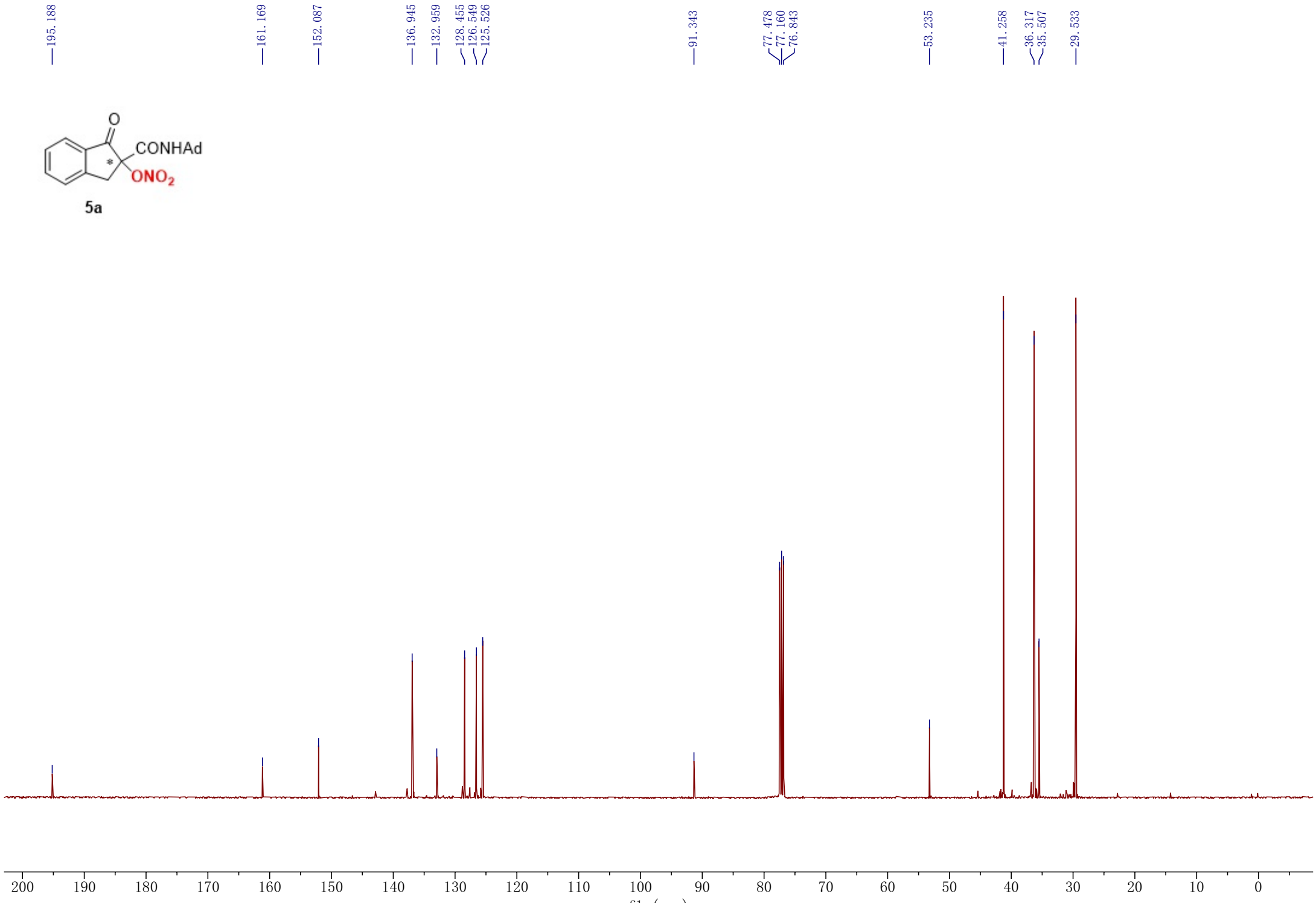
3p

191.488
163.605
151.817
136.980
132.937
128.703
126.470
125.868
89.205
85.179
77.477
77.160
76.842
41.062
38.525
36.045
31.078

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

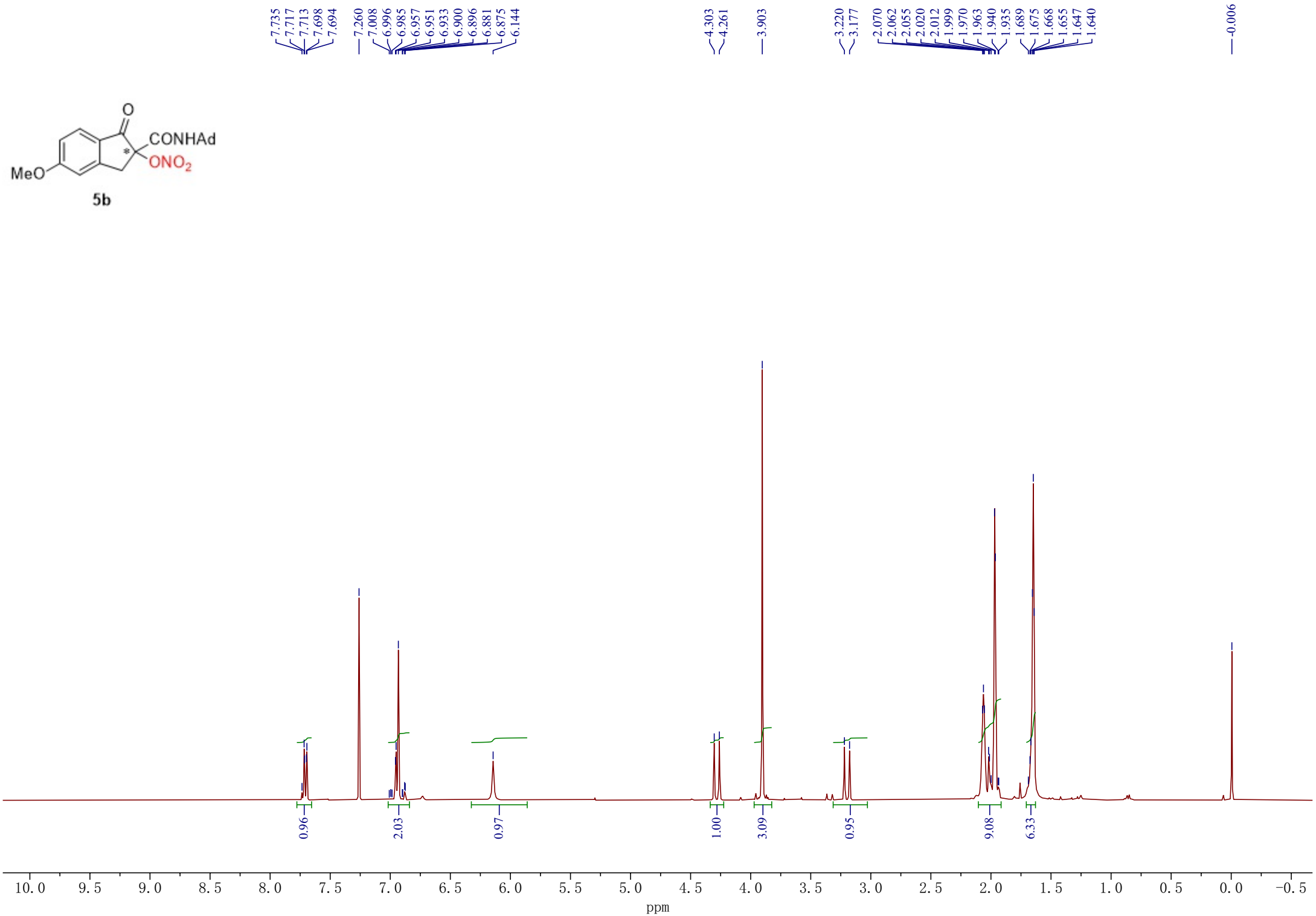
f1 (ppm)

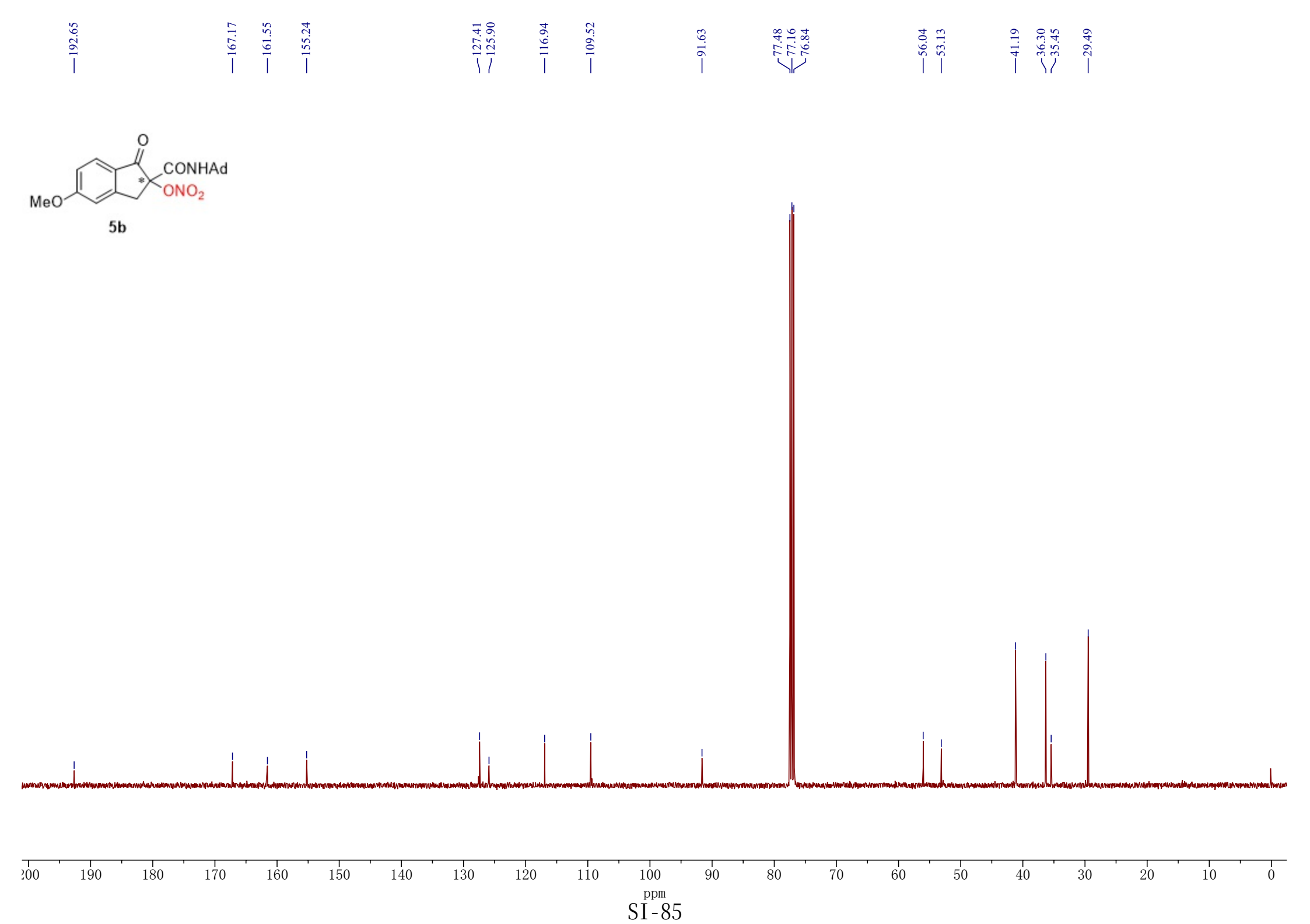

7.795
7.776
7.708
7.689
7.673
7.534
7.515
7.451
7.432
7.413
7.260
6.122
4.328
4.285
3.286
3.244
2.071
1.976
1.662
1.655
1.567
0.002
O
CONHAd
ONO2
5a
f1 (ppm)
1.00
1.06
1.04
1.09
1.01
1.16
1.09
3.47
5.33
6.67


195.188
161.169
152.087
136.945
132.959
128.455
126.549
125.526
91.343
77.478
77.160
76.843
53.235
41.258
36.317
35.507
29.533
O
CONHAd
ONO2
5a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

O
CONHAd
ONO2
MeO

5b


7.735
7.717
7.713
7.698
7.694
7.260
7.008
6.996
6.985
6.957
6.951
6.933
6.900
6.896
6.881
6.875
6.144
4.303
4.261
3.903
3.220
3.177
2.070
2.062
2.055
2.020
2.012
1.999
1.970
1.963
1.940
1.935
1.689
1.675
1.668
1.655
1.647
1.640
-0.006
0.96
2.03
0.97
1.00
3.09
0.95
9.08
6.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm


192.65
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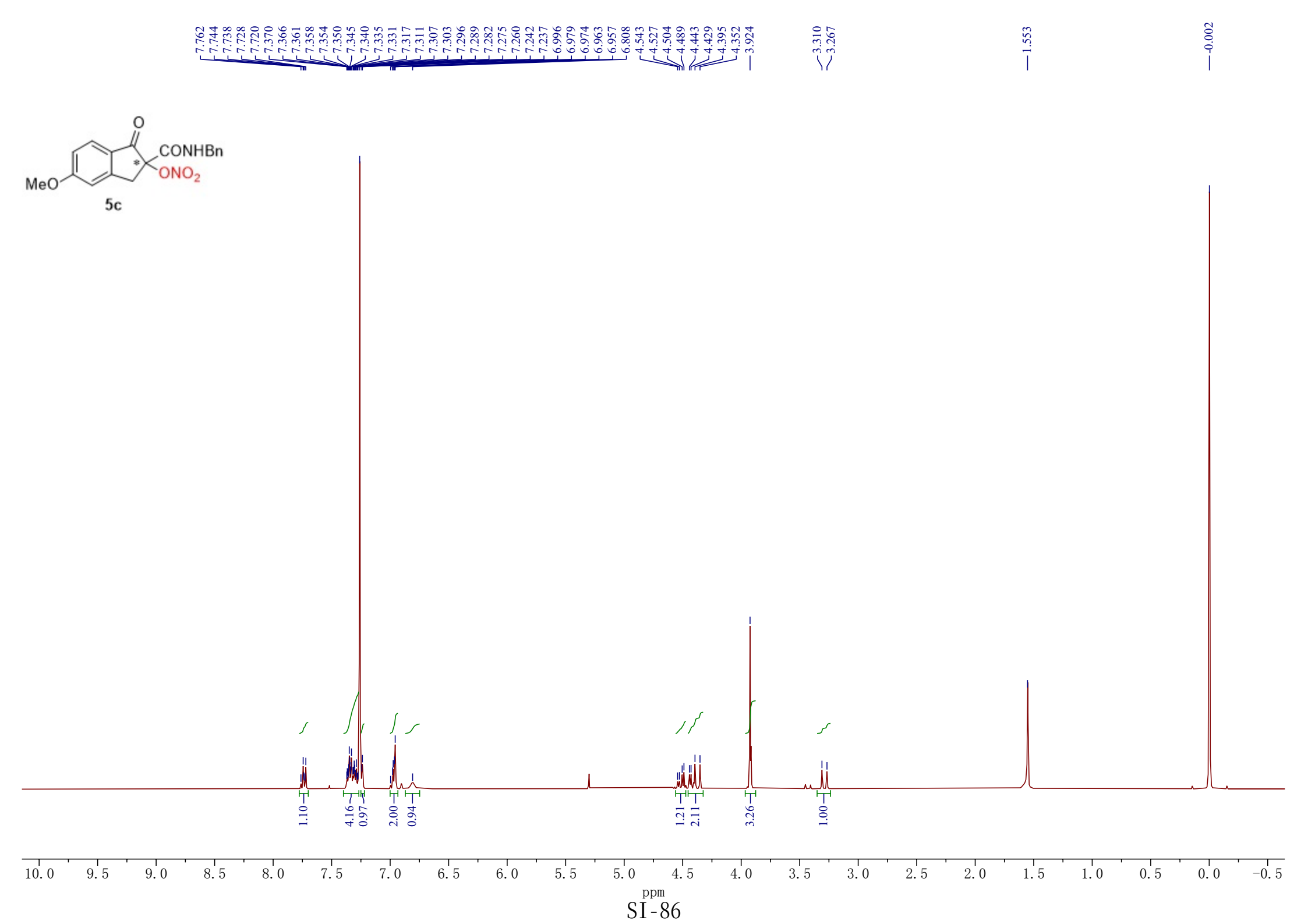
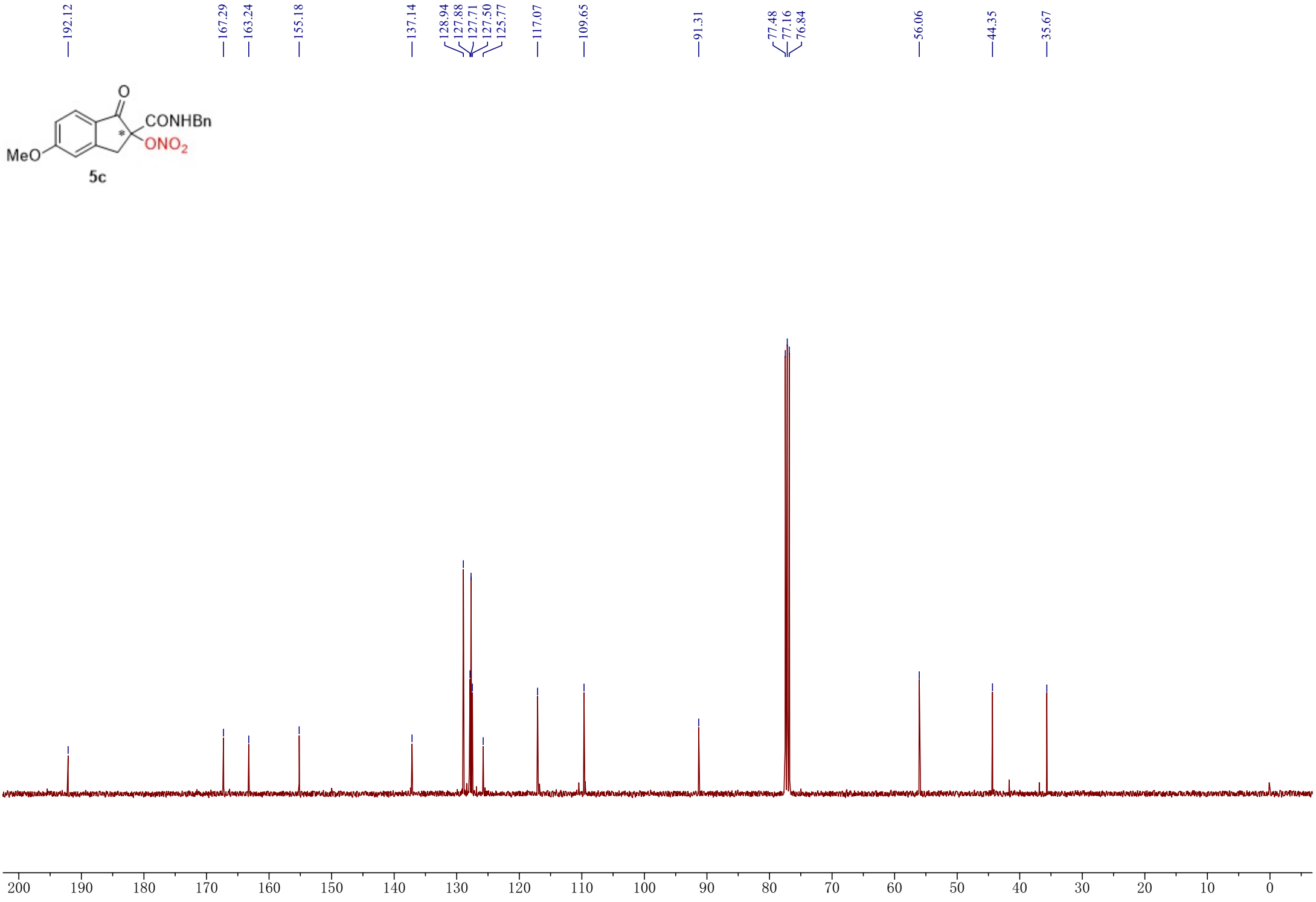
161.55
155.24
127.41
125.90
116.94
109.52
91.63
77.48
77.16
76.84
56.04
53.13
41.19
36.30
35.45
29.49
O
CONHAd
ONO2
MeO
5b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.762
7.744
7.738
7.728
7.720
7.370
7.366
7.361
7.358
7.354
7.350
7.345
7.340
7.335
7.331
7.317
7.311
7.307
7.303
7.296
7.289
7.282
7.275
7.260
7.242
7.237
6.996
6.979
6.974
6.963
6.957
6.808
4.543
4.527
4.504
4.489
4.443
4.429
4.395
4.352
3.924
3.310
3.267
1.553
-0.002
O
CONHBn
ONO2
MeO
5c
1.10
4.16
0.97
2.00
0.94
1.21
2.11
3.26
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm


192.12
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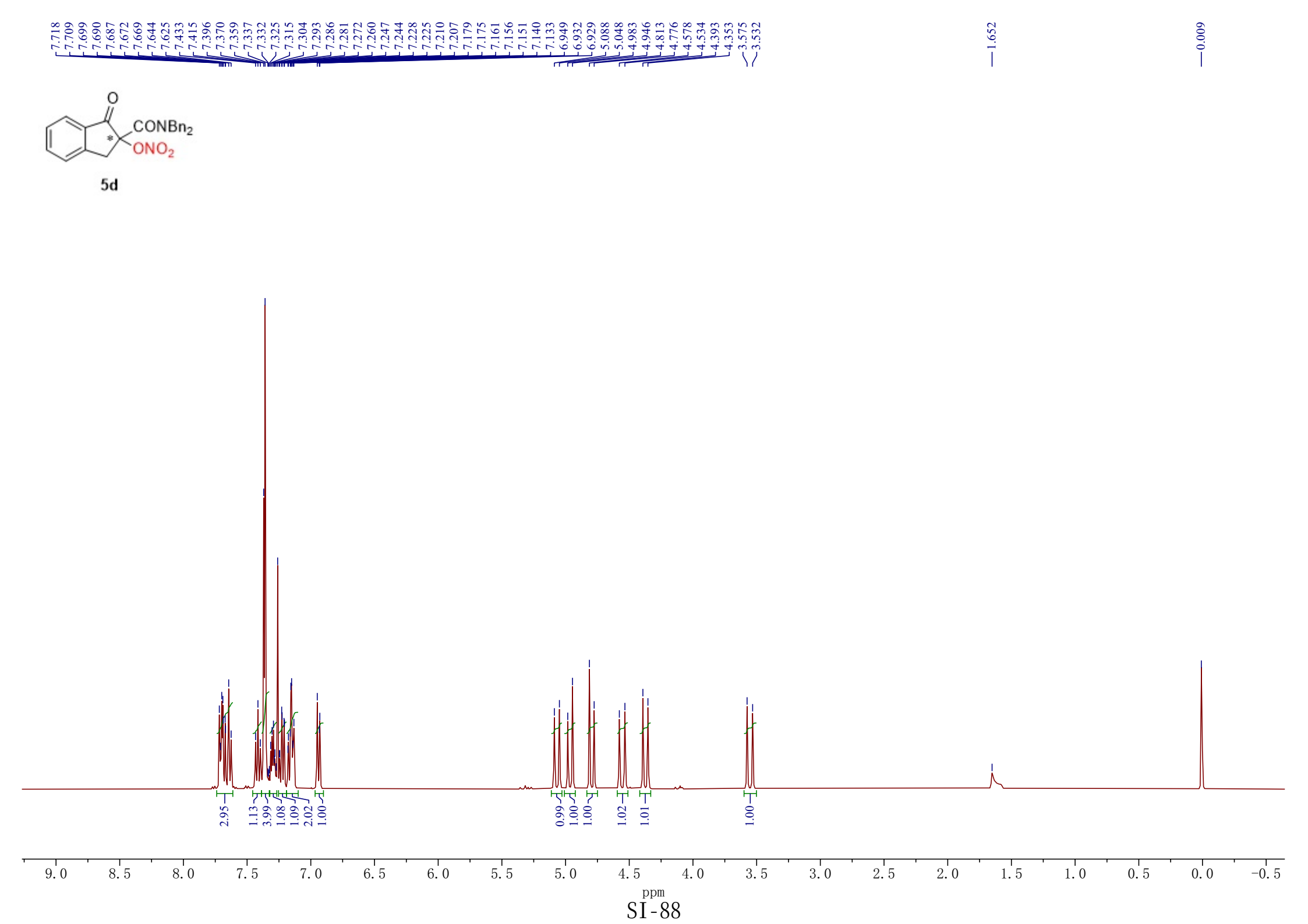
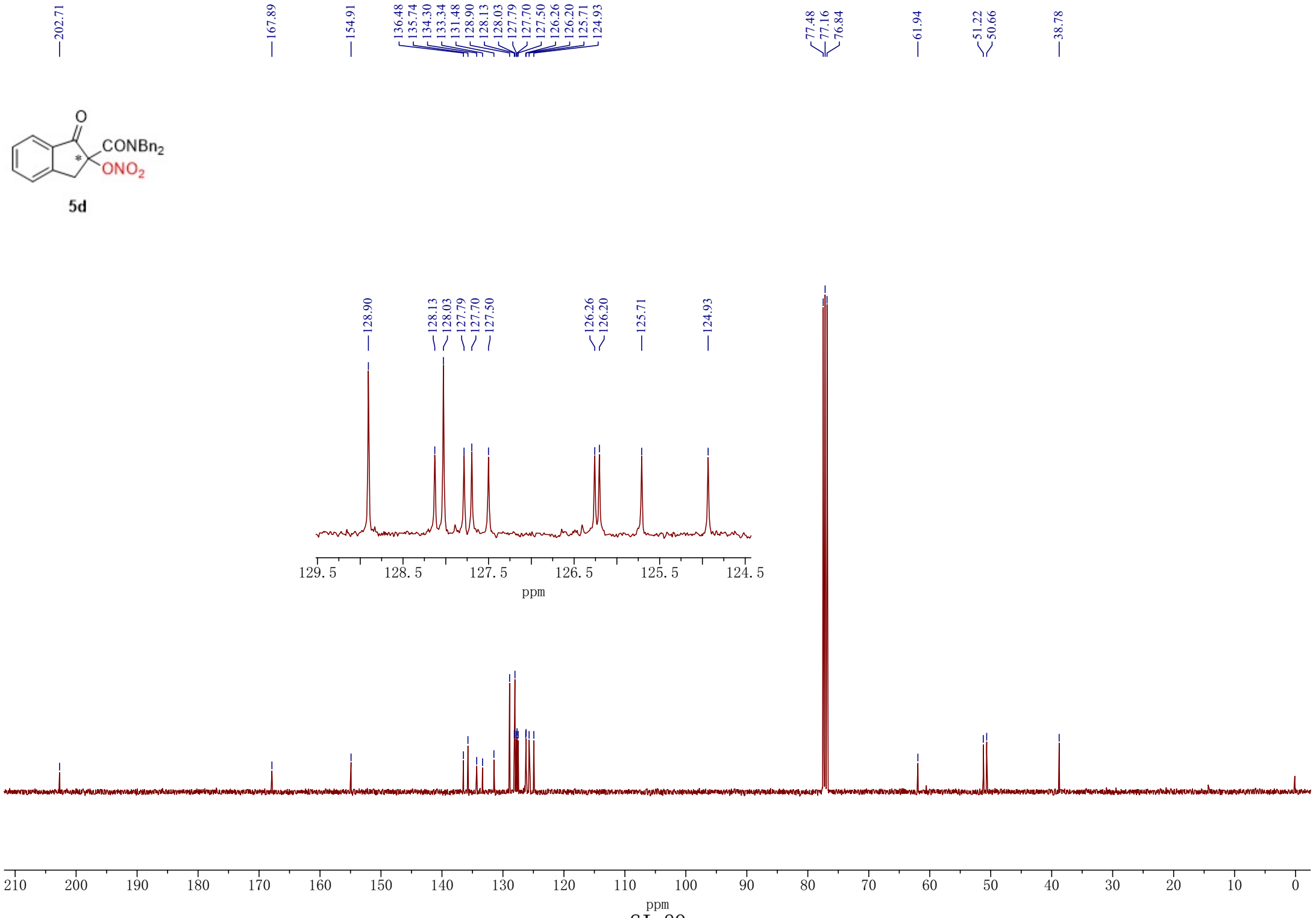
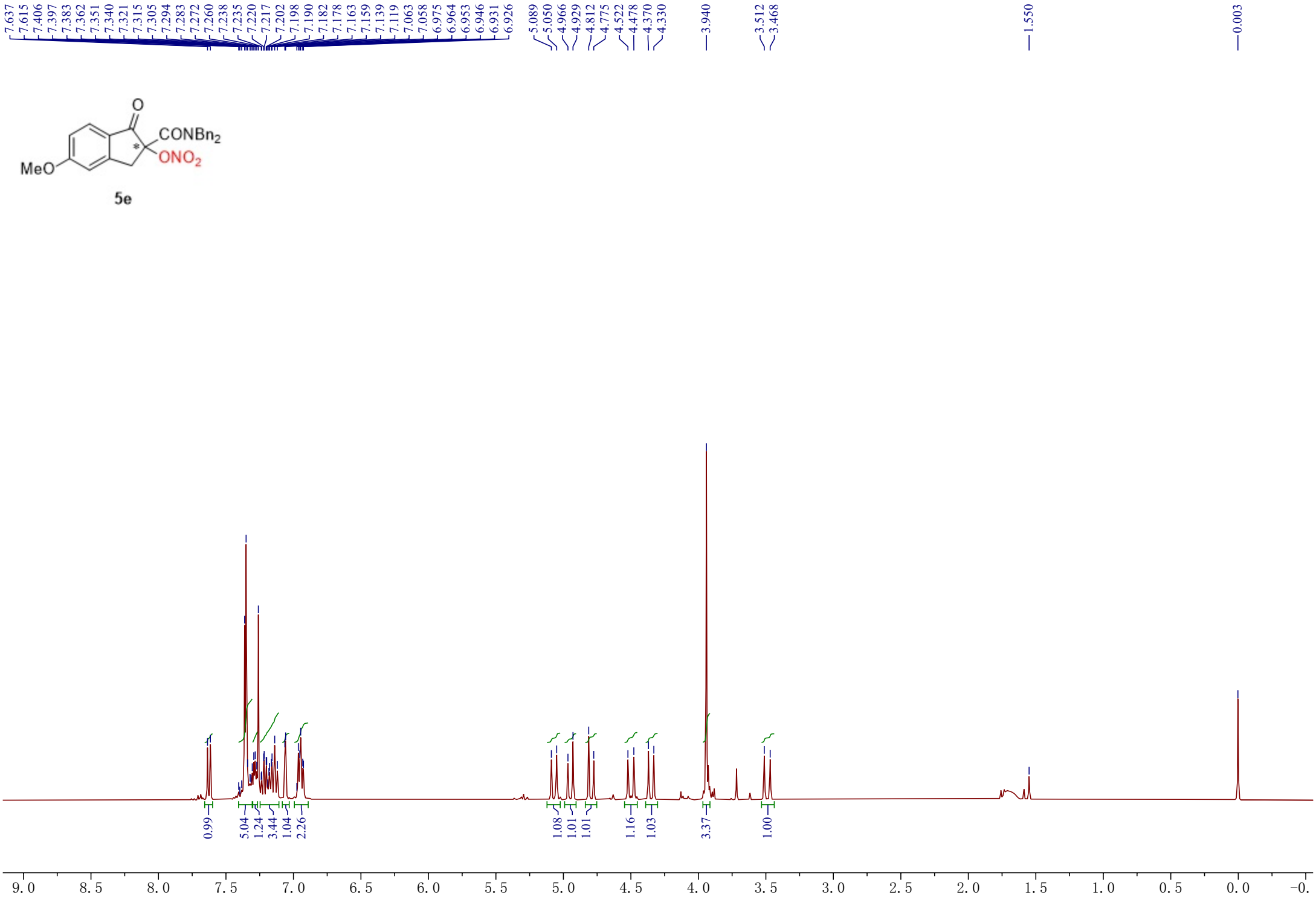
163.24
155.18
137.14
128.94
127.88
127.71
127.50
125.77
117.07
109.65
91.31
77.48
77.16
76.84
56.06
44.35
35.67
O
CONHBn
ONO2
MeO
5c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.718
7.709
7.699
7.690
7.687
7.672
7.669
7.644
7.625
7.433
7.415
7.396
7.370
7.359
7.337
7.332
7.325
7.315
7.304
7.293
7.286
7.281
7.272
7.260
7.247
7.244
7.228
7.225
7.210
7.207
7.179
7.175
7.161
7.156
7.151
7.140
7.133
6.949
6.932
6.929
5.088
5.048
4.983
4.946
4.813
4.776
4.578
4.534
4.393
4.353
3.575
3.532
1.652
0.009
O
CONBn2
ONO2
*
5d
2.95
1.13
3.99
1.08
1.09
2.02
1.00
0.99
1.00
1.00
1.02
1.01
1.00
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
-0.5
ppm


202.71
167.89
154.91
136.48
135.74
134.30
133.34
131.48
128.90
128.13
128.03
127.79
127.70
127.50
126.26
126.20
125.71
124.93
77.48
77.16
76.84
61.94
51.22
50.66
38.78
O
CONBn2
ONO2
5d
ppm
ppm


7.637
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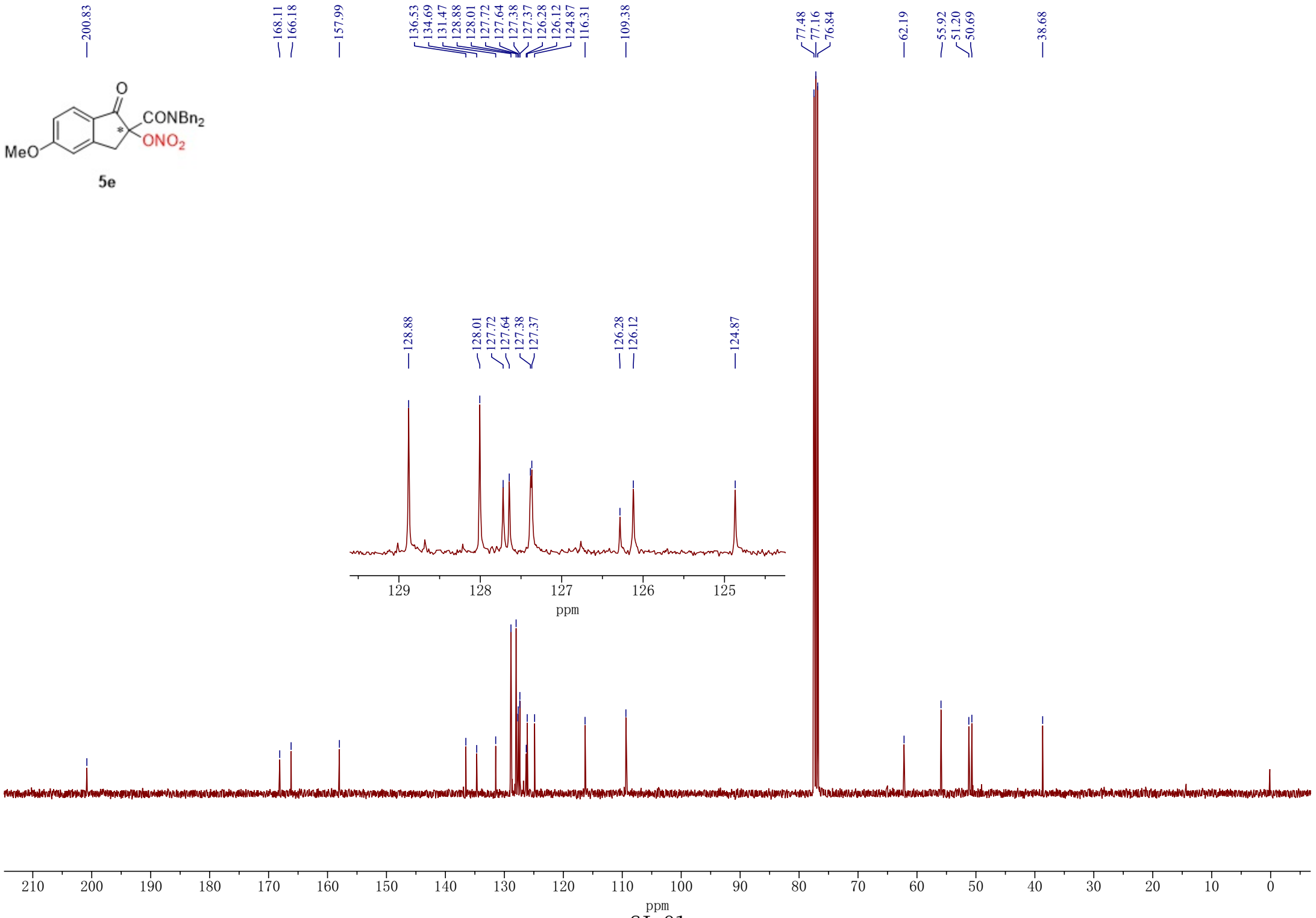
7.406
7.397
7.383
7.362
7.351
7.340
7.321
7.315
7.305
7.294
7.283
7.272
7.260
7.238
7.235
7.220
7.217
7.202
7.198
7.190
7.182
7.178
7.163
7.159
7.139
7.119
7.063
7.058
6.975
6.964
6.953
6.946
6.931
6.926
5.089
5.050
4.966
4.929
4.812
4.775
4.522
4.478
4.370
4.330
3.940
3.512
3.468
1.550
0.003
O
CONBn2
ONO2
MeO
5e
0.99
5.04
1.24
3.44
1.04
2.26
1.08
1.01
1.01
1.16
1.03
3.37
1.00
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.
ppm


200.83
168.11
166.18
157.99
136.53
134.69
131.47
128.88
128.01
127.72
127.64
127.38
127.37
126.28
126.12
124.87
116.31
109.38
77.48
77.16
76.84
62.19
55.92
51.20
50.69
38.68
O
CONBn2
ONO2
MeO
5e
ppm
ppm