A New Hypervalent Iodine(III/V) Oxidant and Its Application to the Synthesis of 2*H*-Azirines

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Supporting Information

1. General Information

All reactions were carried out at room temperature under air unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz or 600 MHz spectrometer at 25 ^oC. Chemical shifts values are given in ppm and referred as the internal standard to TMS: 0.00 ppm. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; m, multiplet and dd, doublet of doublets, brs, broad singlet. The coupling constants *J*, are reported in Hertz (Hz). High resolution mass spectrometry (HRMS) was obtained on a Q-TOF micro spectrometer. Melting points were determined with a Micromelting point apparatus without corrections. Organic solutions were concentrated by rotary evaporation below 40 °C in vacuum. TLC plates were visualized by exposure to ultraviolet light.

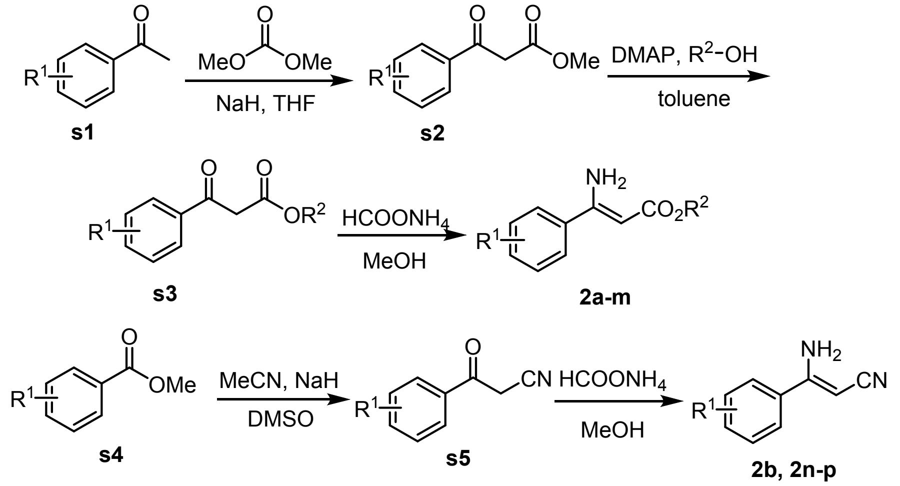
Reagents were purchased as reagent grade and were used without further purification. The solvents were dried by CaH_2 before use. All reactions were performed in standard glassware, heated at 70 ^oC for 3 h before use. Flash column chromatography was performed over silica gel 200-300 m and the eluent was a mixture of ethyl acetate (EA) and petroleum ether (PE).

Before use, *m*CPBA was dissolved in $CHCl_3$, dried over anhydrous sodium sulfate, removed the solid *via* filtration, concentrated to give the anhydrous *m*CPBA.

2. Experimental Section

2.1 Preparation of Substrates 2

General Procedure



Substrates **2a**-**m** were prepared adapted from a previously reported procedure:[1]

To a solution of ketone (20 mmol) in THF (80 mL) was added methyldicarbonate (60 mmol) and NaH (40 mmol, 60%). The reaction mixture was refluxed until TLC indicated complete consumption of the ketone. After cooling, the reaction mixture was poured into ice-water (100 mL), acidified with aqueous HCl (3 M) to pH 2-3 and extracted with EA (100 mL x 3). The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The desired pure product was obtained by silica gel chromatography using a mixture of EA /PE (v/v = 1/9) as eluent.

Methyl benzoylacetate **S2** (5.45 g, 30 mmol) was dissolved in toluene (15 mL). To this solution was added DMAP (183 mg, 1.5 mmol, 5 mol%) and alcohol (36 mmol, 1.2 equiv). The resulting mixture was heated to reflux until TLC indicated complete consumption of **S2**. The reaction mixture was concentrated via rotary evaporation and purified via flash chromatography (mobile phase: either varying concentrations of EA in hexanes or 1% EA in 1:1 CH_2Cl_2:hexanes) on silica gel to isolate the product away from the unreacted starting material.

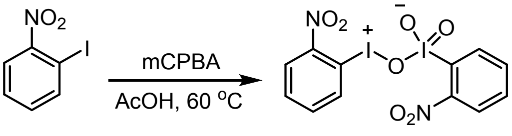
S3 (15 mmol) was dissolved in absolute methanol (60 mL), followed by the addition of ammonium formate (75 mmol). The reaction mixture was stirred under reflux and then was filtered through a short pad of Celite. The filtrate was concentrated *in vacuo*. To the residue was added water (100 mL), then EA (100 mL x 3) was used to extract the mixture and the organic layer was combined, dried over anhydrous Na_2SO_4 and evaporated to dryness. The desired pure product was purified by silica gel chromatography using a mixture of PE and EA as eluent

Substrates **2b**, **2n**-**p** were prepared adapted from a previously reported procedure:[2]

NaH (3.8 g, 95 mmol) was added to an ice cooled solution of acetonitrile (5.6 mL, 1.095 mmol) in DMSO (3.0 mL) and the mixture was stirred at ambient temperature for 20 min. Methyl benzoate **S4** (10.0 g, 73.0 mmol) was added to the reaction mixture and stirring was continued for 2 h. The excess of NaH was quenched by addition of ice-cold water to the reaction mixture. The resulting reaction mixture was treated with diluted HCI (pH ~2) to obtain a white solid which was collected by filtration and dried under vacuum. The solid was recrystallized with a mixture of hexane and diethyl ether (v:v = 1:1) to yield a white solid (10.5 g, 98%).

The obtained β-keto acetonitrile **S5** (15 mmol) was dissolved in absolute MeOH (60 mL), followed by the addition of ammonium formate (75 mmol). The reaction mixture was stirred under reflux until TLC indicated the total consumption of **S5** and filtered through a short pad of Celite. The filtrate was concentrated *in vacuo*. To the residue was added water (100 mL), then EA (100 mL ×3) was used to extract the mixture and the organic layer was combined, dried over Na_2SO_4 and evaporated to dryness. The desired pure product was obtained by silica gel chromatography using a mixture of PE and EA as eluent.

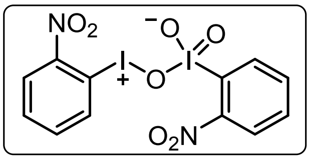
2.2 Preparation of Iodine(III/V) 1



1

To a suspension of *o*-nitro iodobenzene (2.5 g, 10 mmol) in acetic acid (50 mL) was added mCPBA (22.0 mmol) at 60 °C. The resulting mixture was kept at the same temperature for 3 h. TLC indicated that the total consumption of *o*-nitro iodobenzene. Then the solvent was removed and the residue was purified by flash column chromatography on silica gel (MeOH/CH_2Cl_2 = 5/95) to afford the desired iodine(III/V) **1** (1.4 g, Isolated yield = 52%, brsm yield = 66%). At the same time, 22% unreacted starting material was recovered. A re-chromatographic purification result indicated that 8% of product 1 was lost during the silica gel chromatographic purification.

Hypervalent Iodine Reagent(III/V) 1

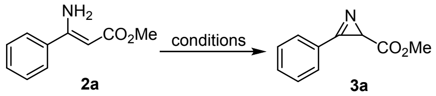


Following the general procedure, **1** was purified by silica gel chromatography (5% MeOH/CH_2Cl_2). Yield: 52% (brsm yield: 66%), an orange solid, decomposed at 110 - 111 ^{o}C. ^{1}H NMR (600 MHz, CD_3OD-d_4) δ 8.54 (d, *J* = 8.2 Hz, 1H), 8.39 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.16 (dd, *J* = 7.6, 1.7 Hz, 1H), 8.10 (t, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.87 – 7.76 (m, 3H). ^{13}C NMR (151 MHz, CD_3OD–d_4) δ 149.1, 145.8, 138.4, 137.9, 135.7, 133.8, 132.3, 128.3, 127.8, 126.7, 117.2, 115.2. HRMS (ESI) calcd for $C_{12}H_8I_2N_2O_7Na^+$ [M + Na^+] 568.8325, found 568.8325.

2.3 Preparation of Compounds 3

2.3.1 Conditions optimization for the synthesis of 2*H*-azirine 3a

Table 1 Optimization of the reaction conditions[a]

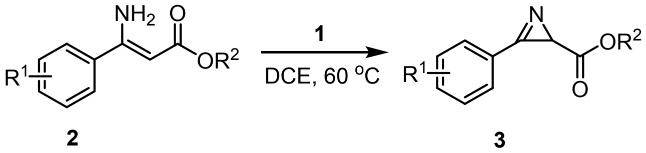


Entry	Oxidant (equiv)	Additive	Solvent	Temp. (^{o}C)	Time [h]	Yield [%][b]
1	**1** (0.5)	none	DCE	rt	5	trace
2	**1** (0.5)	none	DCE	60	3.5	47
3	**1** (0.7)	none	EtOAc	60	4	57
4	**1** (0.7)	none	toluene	60	4	70
5	**1** (0.7)	none	MeCN	60	4	53
6	**1** (0.7)	none	MeOH	60	3.5	19
7	**1** (0.7)	none	PhCl	60	3.5	55
8	**1 (0.7)**	**none**	**DCE**	**60**	**3.5**	**80**
9	**1** (0.7)	none	AcOH	60	3	55
10[e]	**1** (0.7)	BF_3•Et_2O	DCE	60	3	76
11[e]	**1** (0.7)	TBSOTf	DCE	60	3	73
12[c]	**1** (0.7)	none	AcOH	60	2	ND

13[d]	**1** (0.7)	none	AcOH	60	5.5	26
14	**PIDA (2.0)**	none	DCE	rt	5	NR
15	**PIDA (2.0)**	none	DCE	60	2	NR
16	**PIDA (2.0)**	none	AcOH	60	3	NR
17	**PIFA (2.0)**	none	DCE	60	3	NR
18	**PhIO (2.0)**	none	DCE	60	3	NR
19	**IBX (2.0)**	none	DCE	60	3	NR
20	**DMP (2.0)**	none	DCE	60	6	trace
21	**PhIO$_2$ (2.0)**	none	DCE	60	3	NR

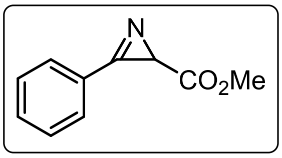
[a] Reaction conditions: **2a** (1.0 mmol), **1** (0.7 mmol), DCE (5 mL), stirred at 60 °C for 3.5 h. [b] Isolated yield. [c] **2a** (1.0 mmol), *o*-nitroiodobenzene (2.0 mmol), *m*CPBA (2.2 mmol), AcOH (5 mL). [d] *o*-Nitroiodobenzene (2.0 mmol), *m*CPBA (2.2 mmol), AcOH (5 mL), stirred at 60 °C for 3 h, then add **2a** (1.0 mmol), stirred at the same temperature for another 2.5 h. [e] 2.0 Equiv of additive was used.

2.3.2 General procedure for the synthesis of 2*H*-Azirines 3



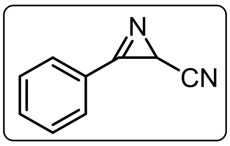
To a suspension of substrates **2** (1 mmol) in DCE (5 mL) was added **1** (0.7 mmol) at 60 °C. The resulting mixture was kept at the same temperature until TLC indicated that the total consumption of substrates **2**. Then H_2O (30 mL) was added and the reaction mixture was extracted with EA (30 mL × 2). The organic phase was washed with brine (30 mL × 1), dried over anhydrous Na_2SO_4. The solvent was removed and the residue was purified by flash column chromatography on silica gel (EA/PE = 5/95) to afford the desired compounds **3**.

Methyl 3-phenyl-2*H*-azirine-2-carboxylate (3a)



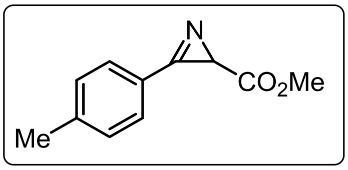
Following the general procedure, **3a** was purified by silica gel chromatography (5% EA/PE). Yield: 80%, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.89 (m, 2H), 7.66 – 7.64 (m, 1H), 7.61 – 7.56 (m, 2H), 3.75 (s, 3H), 2.86 (s, 1H). ^{13}C NMR (151 MHz, CDCl3) δ 172.1, 158.5, 134.0, 130.5, 129.4, 122.2, 77.3, 77.1, 76.8, 52.3, 29.5. HRMS (ESI) calcd for $C_{10}H_9NNaO_2^+$ [M + Na$^+$] 198.0525, found 198.0525.

3-Phenyl-2*H*-azirine-2-carbonitrile (3b)



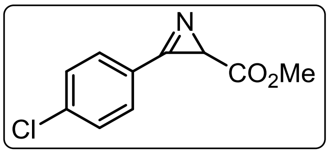
Following the general procedure, **3b** was purified by silica gel chromatography (5% EA/PE). Yield: 79%, yellow oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.94 (m, 2H), 7.75 – 7.72 (m, 1H), 7.66 – 7.63 (m, 2H), 2.62 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 134.9, 130.6, 129.7, 121.0, 119.2, 14.4. HRMS (ESI) calcd for $C_9H_6N_2Na^+$ [M + Na$^+$] 165.0423, found 165.0423.

Methyl 3-(*p*-tolyl)-2*H*-azirine-2-carboxylate (3c)



Following the general procedure, **3b** was purified by silica gel chromatography (5% EA/PE). Yield: 63%, yellow oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 3.74 (s, 3H), 2.83 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 158.0, 145.1, 130.5, 130.1, 119.4, 52.3, 29.3, 22.0. HRMS (ESI) calcd for $C_{11}H_{11}NNaO_2^+$ [M + Na$^+$] 212.0682, found 212.0683.

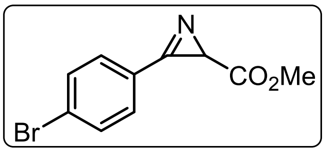
Methyl 3-(4-chlorophenyl)-2*H*-azirine-2-carboxylate (3d)



Following the general procedure, **3d** was purified by silica gel chromatography (5% EA/PE). Yield: 66%, a yellow solid, mp. 37 - 38 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 3.75 (s, 3H), 2.88 (s, 1H). ^{13}C

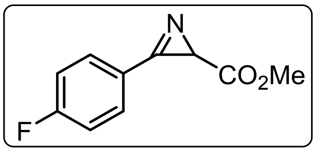
NMR (151 MHz, $CDCl_3$) δ 171.8, 157.9, 140.5, 131.6, 129.9, 120.7, 52.5, 29.7. HRMS (ESI) calcd for $C_{10}H_8{}^{35}ClNNaO_2^+$ [M + Na^+] 232.0136, found 232.0136.

Methyl 3-(4-bromophenyl)-2*H*-azirine-2-carboxylate (3e)



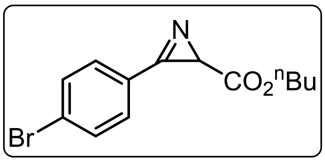
Following the general procedure, **3e** was purified by silica gel chromatography (5% EA/PE). Yield: 62%, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (m, 4H), 3.75 (s, 3H), 2.87 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 158.1, 132.9, 131.7, 129.1, 121.2, 52.4, 29.7. HRMS (ESI) calcd for $C_{10}H_8{}^{79}BrNNaO_2^+$ [M + Na^+] 275.9631, found 275.9631.

Methyl 3-(4-fluorophenyl)-2*H*-azirine-2-carboxylate (3f)



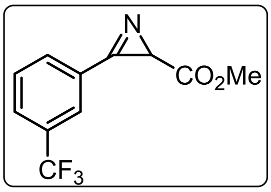
Following the general procedure, **3f** was purified by silica gel chromatography (5% EA/PE). Yield: 73%, a yellow solid, mp. 43 - 44 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.5, 5.4 Hz, 2H), 7.28 (t, J = 8.5 Hz, 2H), 3.75 (s, 3H), 2.87 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 166.0 (d, $^1J_{C\text{-}F}$ = 255.5 Hz), 157.6, 132.9 (d, $^3J_{C\text{-}F}$ = 9.5 Hz), 118.6 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 117.0 (d, $^2J_{C\text{-}F}$ = 22.4 Hz), 52.38, 29.6. HRMS (ESI) calcd for $C_{10}H_8FNNaO_2^+$ [M + Na^+] 216.0431, found 216.0430.

***ⁿ*Butyl 3-(4-bromophenyl)-2*H*-azirine-2-carboxylate (3g)**



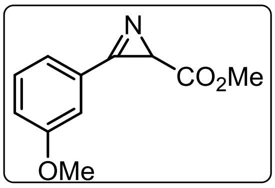
Following the general procedure, **3g** was purified by silica gel chromatography (5% EA/PE). Yield: 64%, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 4H), 4.20 – 4.13 (m, 2H), 2.86 (s, 1H), 1.68 – 1.55 (m, 2H), 1.36 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 171.4, 158.24, 132.8, 131.6, 129.0, 121.3, 65.3, 30.6, 29.9, 19.0, 13.7. HRMS (ESI) calcd for $C_{13}H_{14}{}^{79}BrNNaO_2{}^+$ [M + Na$^+$] 318.0100, found 318.0100.

Methyl 3-(3-(trifluoromethyl)phenyl)-2*H*-azirine-2-carboxylate (3h)



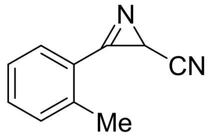
Following the general procedure, **3h** was purified by silica gel chromatography (5% EA/PE). Yield: 59%, yellow oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.20 – 8.07 (m, 2H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 2.95 (s, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 171.6, 158.4, 133.4, 132.2 (d, $^2J_{C\text{-}F}$ = 33.29 Hz), 130.5 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 130.1, 127.2 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.2569 (d, $^1J_{C\text{-}F}$ = 271.0 Hz), 123.2565, 52.6, 29.9. HRMS (ESI) calcd for $C_{11}H_8F_3NNaO_2{}^+$ [M + Na$^+$] 266.0399, found 266.0399.

Methyl 3-(3-methoxyphenyl)-2*H*-azirine-2-carboxylate (3i)



Following the general procedure, **3i** was purified by silica gel chromatography (5% EA/PE). Yield: 46%, yellow oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.50 – 7.44 (m, 2H), 7.41 (d, *J* = 1.2 Hz, 1H), 7.18 (ddd, *J* = 8.0, 2.3, 1.2 Hz, 1H), 3.88 (s, 3H), 3.75 (s, 3H), 2.86 (s, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ172.01, 160.15, 158.67, 130.41, 123.37, 123.11, 120.67, 114.26, 55.59, 52.29, 29.77. HRMS (ESI) calcd for $C_{11}H_{11}NNaO_3{}^+$ [M + Na$^+$] 228.0631, found 228.0631.

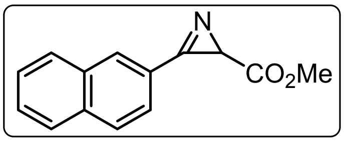
Methyl 3-(3,4-dichlorophenyl)-2*H*-azirine-2-carboxylate (3j)



3p

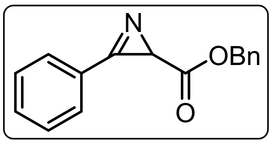
Following the general procedure, **3j** was purified by silica gel chromatography (5% EA/PE). Yield: 63%, a yellow solid, mp. 100 - 101 ^{o}C.. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.9 Hz, 1H), 7.76 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 3.76 (s, 3H), 2.91 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 157.7, 138.7, 134.2, 131.9, 131.6, 129.1, 122.1, 77.3, 77.1, 76.9, 52.6, 30.0. HRMS (ESI) calcd for $C_{10}H_7{}^{35}Cl_2NNaO_2^+$ [M + Na$^+$] 265.9746, found 265.9745.

Methyl 3-(naphthalen-2-yl)-2*H*-azirine-2-carboxylate (3k)



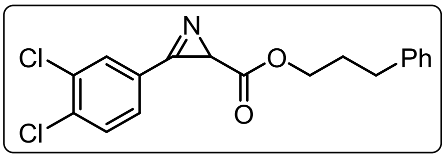
Following the general procedure, **3k** was purified by silica gel chromatography (2% DCM/PE). Yield: 48%, a yellow solid, mp. 69 - 70 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.02 – 7.94 (m, 3H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 9.6, 4.7 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 3.76 (s, 3H), 2.95 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.2, 158.6, 135.9, 132.9, 132.7, 129.5, 129.2, 129.2, 128.1, 127.4, 124.8, 119.5, 52.4, 29.7. HRMS (ESI) calcd for $C_{14}H_{11}NNaO_2^+$ [M + Na$^+$] 248.0682, found 248.0683.

Benzyl 3-phenyl-2*H*-azirine-2-carboxylate (3l)



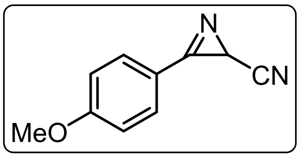
Following the general procedure, **3l** was purified by silica gel chromatography (3% EA/PE). Yield: 60%, a yellow solid, mp. 49 - 50 ^{o}C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.96 – 7.95 (m, 2H), 7.80 – 7.75 (m, 1H), 7.70 – 7.68 (m, 2H), 7.44 – 7.31 (m, 5H), 5.24 – 5.11 (m, 2H), 3.01 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.1, 158.0, 135.8, 134.4, 130.3, 129.8, 128.45, 128.1, 127.9, 121.5, 66.2, 28.8. HRMS (ESI) calcd for $C_{16}H_{13}NNaO_2^+$ [M + Na$^+$] 274.0838, found 274.0838.

3-Phenylpropyl 3-(3,4-dichlorophenyl)-2*H*-azirine-2-carboxylate (3m)



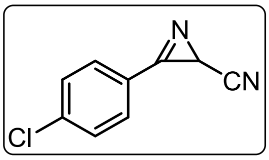
Following the general procedure, **3m** was purified by silica gel chromatography (5% EA/PE). Yield: 28%, a yellow solid, mp. 39 - 40 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.98 (d, *J* = 1.9 Hz, 1H), 7.76 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.20 – 7.18 (m, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 4.21 – 4.13(m, 2H), 2.90 (s, 1H), 2.68 – 2.65 (m, 2H), 2.00 – 1.95 (m, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 171.1, 157.8, 140.9, 138.7, 134.2, 131.9, 131.7, 129.0, 128.5, 128.4, 126.1, 122.2, 64.8, 32.0, 30.2, 30.1. HRMS (ESI) calcd for $C_{18}H_{15}{}^{35}Cl_2NNaO_2^+$ [M + Na$^+$] 370.0372, found 370.0372.

3-(4-Methoxyphenyl)-2*H*-azirine-2-carbonitrile (3n)



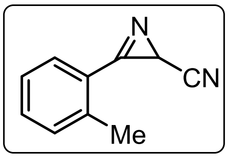
Following the general procedure, **3n** was purified by silica gel chromatography (5% EA/PE). Yield: 78%, yellow oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 3.93 (s, 3H), 2.55 (s, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 164.9, 157.1, 132.9, 119.7, 115.3, 113.0, 55.8, 14.1. HRMS (ESI) calcd for $C_{10}H_8N_2NaO^+$ [M + Na$^+$] 195.0529, found 195.0528.

3-(4-Chlorophenyl)-2*H*-azirine-2-carbonitrile (3o)



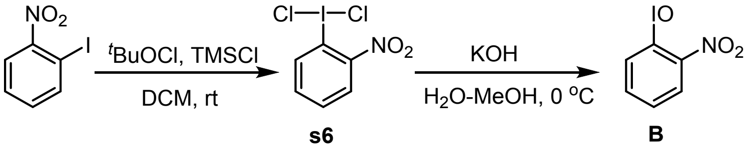
Following the general procedure, **3o** was purified by silica gel chromatography (5% EA/PE). Yield: 68%, a white solid, mp. 78 - 79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.66 – 7.61 (m, 2H), 2.63 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 141.7, 131.7, 130.3, 119.4, 118.9, 14.6. HRMS (ESI) calcd for $C_9H_5{}^{35}ClN_2Na^+$ [M + Na$^+$] 199.0033, found 199.0033.

3-(*o*-Tolyl)-2*H*-azirine-2-carbonitrile (3p)



Following the general procedure, **3p** was purified by silica gel chromatography (5% EA/PE). Yield: 32%, yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.45 (dd, *J* = 16.6, 7.9 Hz, 2H), 2.71 (s, 3H), 2.52 (s, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 157.7, 142.2, 134.5, 132.8, 131.3, 126.8, 119.7, 119.6, 20.0, 12.6. HRMS (ESI) calcd for $C_{10}H_8N_2Na^+$ [M + Na$^+$] 179.0580, found 179.0581.

2.4 Preparation of *o*-nitroiodosylbenzene

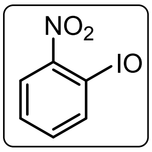


a) To a solution of *o*-nitroiodobenzene (1.25 g, 5.0 mmol) and trimethylsilyl chloride (1.9 mL, 15 mmol) in CH_2Cl_2 (3 mL) was slowly added *tert*-butyl hypochlorite (1.13 mL, 10 mmol) at ambient temperature. After the reaction mixture was stirred at same temperature for 5 h, the yellow precipitate was filtered, washed 3 times with hexane, and then dried in vacuum to give product **S6** (1.30 g, 4.08 mmol, 82%) as a yellow solid.[3]

b) To a solution of potassium hydroxide (800 g, 14.29 mmol) in the mixed solvent of H_2O (4.5 mL) and MeOH (1.5 mL) was slowly added **S6** (1.2 g, 4.53 mmol) at 0

°C. After being stirred at same temperature for 30 min, the reaction mixture was diluted with H_2O (5 mL). The resulting precipitate was filtered, washed 3 times with H_2O and CH_2Cl_2, and then dried *in vacuum* to give *o*-nitroiodosylbenzene (1.05, 3.96 mmol, 80% for two steps) as a yellow solid.[3]

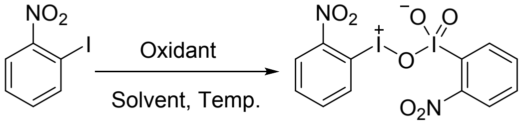
Spectral Data of *o*-nitro iodosylbenzene (B)



Following the general procedure, **B** was purified by filtered. Yield: 80%, an orange solid, decomposed at 100-101 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.46 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.08 – 8.03 (m, 1H), 7.96 – 7.91 (m, 1H), 7.80 – 7.75 (m, 1H). HRMS (ESI) calcd for $C_6H_5INO_3^+$ [M + H$^+$] 265.9309, found 265.9308.

3. Optimization of Iodine(III/V) 1's Synthesis

The initial reactivity assay employed *o*-nitroiodobenzene as the substrate to optimize the reaction parameters. The results are summarized in Table 2. First, when *o*-nitroiodobenzene was treated with H_2O_2 in water at room temperature for 3 h, no product **1** was obtained (Table 1, entry 1). Then we investigated the scope of oxidant and solvent (Table 1, entries 2-7). To our delight, the application of *m*CPBA as oxidant led to the formation of **1** in a yield of 10% (Table 1, entry 6). Solvent screening revealed that AcOH was found to be the desirable solvent for this specific reaction, as the yield of the product could reach 48% (Table 1, entry 8). We also investigated the dosage of the oxidant (Table 1, entries 8-11) and the best result was obtained when 2.2 equivalent of the mCPBA was added, as the yield was increased to 52% (Table 1, entry 10).



1

Table 2 Optimization of Iodine(III/V) 1 [a]

Entry	Oxidant (equiv)	Solvent	Temp. (°C)	Time [h]	Yield [%][b]
1	**H_2O_2** (2.0)	H_2O	rt	3	NR
2	**H_2O_2** (2.0)	H_2O-MeCN (1:1)	40	3	NR
3	**$NaIO_4$** (2.0)	aq. AcOH (30%)	60	3.5	NR
4	**Oxone** (2.0)	H_2O-MeCN (3:1)	rt	4	ND
5	**CH_3CO_3H** (2.0)	none	rt	4	NR
6	***m*CPBA** (2.0)	DCE	60	4	10
7	***m*CPBA** (2.0)	MeOH	60	3.5	ND
8	***m*CPBA** (2.0)	AcOH	60	3	48
9	***m*CPBA** (1.1)	AcOH	60	4	30
10	***m*CPBA** (2.2)	**AcOH**	60	3	52
11	***m*CPBA** (3.0)	AcOH	60	3	51

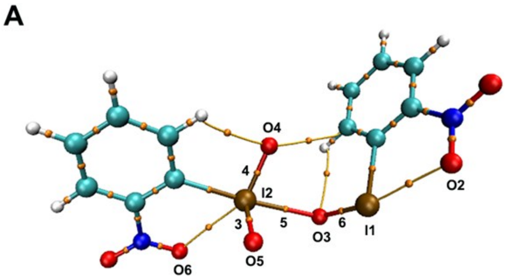
[a] Reaction conditions: *o*-nitroiodobenzene (1.0 mmol), *m*CPBA (2.2 mmol), AcOH (6 mL), stirred at 60 °C for 3 h. [b] Isolated yield.

4. Computational Details

DFT computations were performed using the ORCA 4.1.2 software,[4] all hypervalent iodine molecules were optimized at the B3LYP level of theory[5] with basis set def2-TZVP incorporating Stuttgart–Dresden effective core potentials for iodine atoms.[6] D3 dispersion correction with Becke–Jones damping[7] was used both in structure optimization and in wave function calculation for 'atom in molecule (AIM)' analysis[8] (using Multiwfn program[9]), generation of molecular electrostatic potential surface (using Multiwfn[9] and VMD program[10]), and mayer bond order analyses[11] (using Multiwfn program[9]).

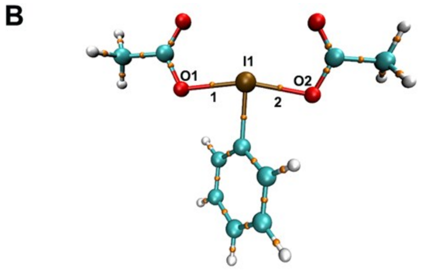
4.1 Comparisons of the strength of I–O bonds in Iodine(III/V) 1 and the existing hypervalent iodine reagents

All the I–O bond-containing hypervalent iodine reagents shown in Figure **1S** were inspected in CSD version 5.40 using ConQuest version 2.0.2. The DFT calculations were performed with ORCA 4.1.2 software.[4] The I–O bond-containing hit molecules from CSD database were optimized at the B3LYP level of theory with basis set def2-TZVP incorporating Stuttgart–Dresden effective core potentials for iodine atoms,[5, 12] and with D3 dispersion correction with Becke–Jones damping[7]. Atoms in molecule (AIM) analyses were used to identify important noncovalent interactions in the form of bond paths and bond critical points (BCPs).[8] Electron densities at such bond critical points (ρ_{bcp}) and Mayer bond order analyses were employed in this study for evaluating the relative strength of the I–O bonds.[11] The values of ρ_{bcp} and Mayer bond order of I–O bonds of hypervalent iodine reagents were summarized below. The Figure 1S shown us that both electron density at BCP (5) in AIM analysis and Mayer bond order of I(2)–O(3) bond in Iodine(III/V) **1** had the lowest value in all hypervalent iodine reagents shown in Figure 1S, a result indicating that I(2)–O(3) bond in iodine(III/V) **1** was a relative weak covalent bond.



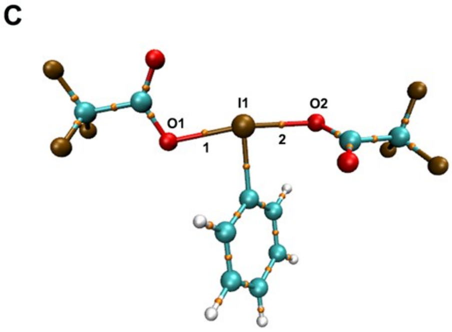
BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(3)	0.202	I(2)-O(5) bond	1.57
(4)	0.198	I(2)-O(4) bond	1.49
(5)	**0.0503**	**I(2)-O(3) bond**	**0.240**
(6)	0.173	I(1)-O(3) bond	1.29

Iodine(III/V) 1



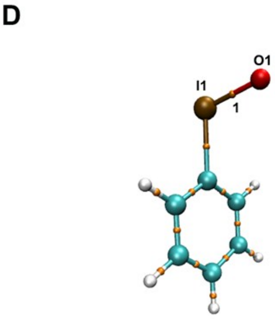
BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(1)	0.0911	I(1)-O(1) bond	0.566
(2)	0.0933	I(1)-O(2) bond	0.572

PIDA



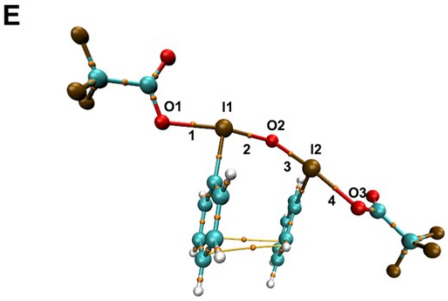
BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(1)	0.0944	I(1)-O(1) bond	0.586
(2)	0.0912	I(1)-O(2) bond	0.585

PIFA



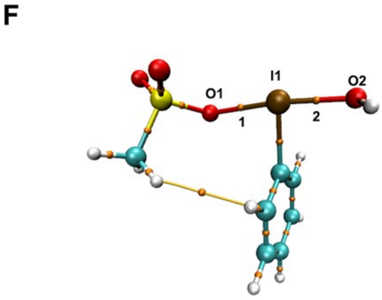
BCP	Electron density at BCP ρ_{BCP}	Bond	Mayer bond order
(1)	0.177	I(1)-O(1) bond	1.47

PhIO



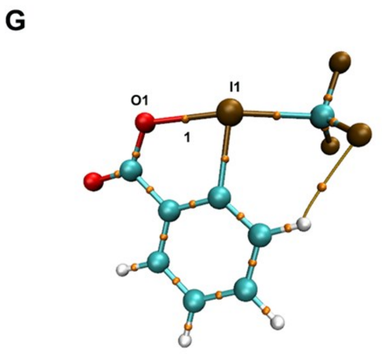
BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(1)	0.0812	I(1)-O(1) bond	0.501
(2)	0.118	I(1)-O(2) bond	0.778
(3)	0.122	I(2)-O(2) bond	0.811
(4)	0.0781	I(2)-O(3) bond	0.494

μ-oxo BTI



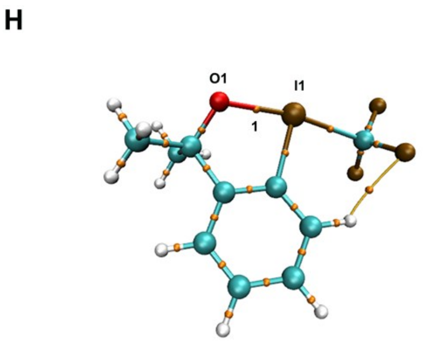
BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(1)	0.0784	I(1)-O(1) bond	0.478
(2)	0.123	I(1)-O(2) bond	0.857

HTIB



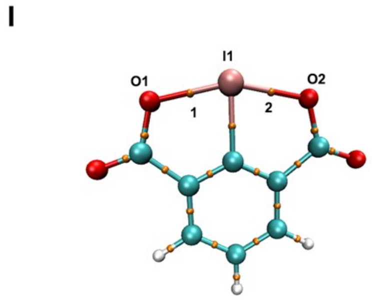
BCP	Electron density at BCP ρ_{BCP}	Bond	Mayer bond order
(1)	0.0865	I(1)-O(1) bond	0.551

Togni’s reagent II



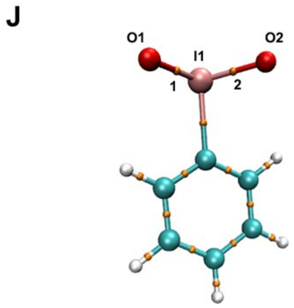
BCP	Electron density at BCP ρ_{BCP}	Bond	Mayer bond order
(1)	0.104	I(1)-O(1) bond	0.687

Togni’s reagent



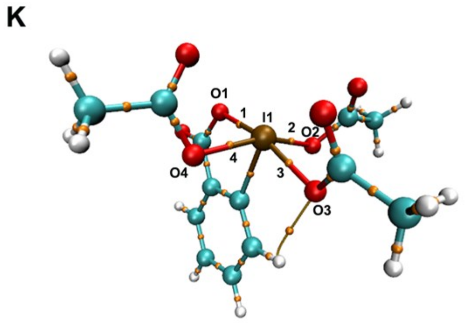
BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(1)	0.101	I(1)-O(1) bond	0.698
(2)	0.101	I(1)-O(2) bond	0.697

Iodosodilactone



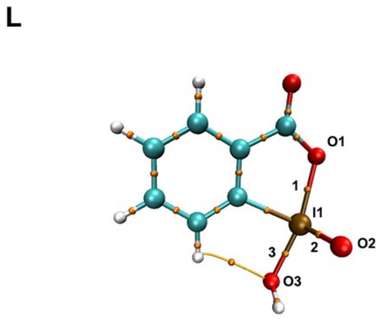
BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(1)	0.200	I(1)-O(1) bond	1.61
(2)	0.200	I(1)-O(2) bond	1.61

$PhIO_2$



BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(1)	0.115	I(1)-O(1) bond	0.745
(2)	0.105	I(1)-O(2) bond	0.677
(3)	0.112	I(1)-O(3) bond	0.725
(4)	0.100	I(1)-O(4) bond	0.651

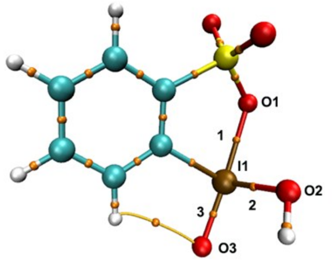
DMP



BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(1)	0.105	I(1)-O(1) bond	0.670
(2)	0.206	I(1)-O(2) bond	1.62
(3)	0.133	I(1)-O(3) bond	0.863

IBX

M



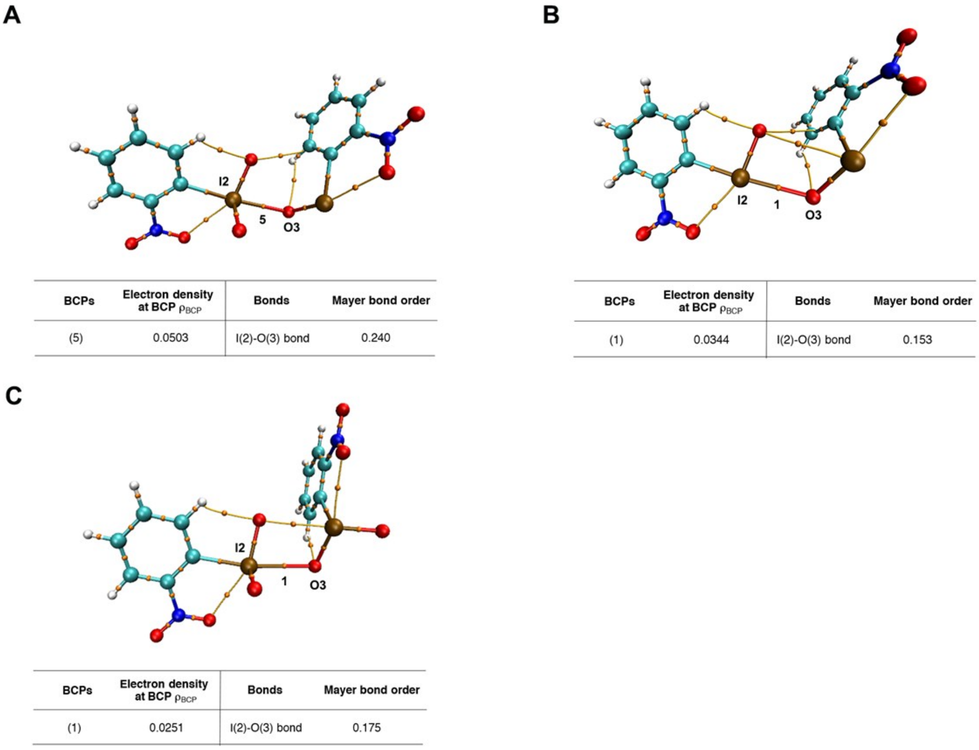
BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(1)	0.0764	I(1)-O(1) bond	0.493
(2)	0.153	I(1)-O(2) bond	0.975
(3)	0.200	I(1)-O(3) bond	1.61

IBS

Figure 1S. The summary of electron density at the BCPs and Mayer bond orders of I–O bonds in some commonly used hypervalent iodine reagents. The BCPs were represented by orange spheres, the bond paths connecting the nuclei with critical points were also represented by yellow lines. (A) Iodine(III/V) **1**. (B) PIDA, CSD refcode: IBZDAC. (C) PIFA, CSD refcode: CEZBE0. (D) PhIO, CSD refcode: OYALOR. (E) μ-oxo BTI, CSD refcode: DAJTUD. (F) HTIB analogues, CSD refcode: BACCOZ. (G) Togni's reagent II, CSD refcode: IXOKAH. (H) Togni's reagent, CSD refcode: KEWNUW02. (I) Iodosodilactone, CSD refcode: GEHYEZ. (J) $PhIO_2$, CSD refcode: IODYBZ. (K) DMP, CSD refcode: ZAZJOB. (L) IBX, CSD refcode: IOBNZA01. (M) IBS, CSD refcode: WIWJUK.

4.2 Comparisons of the strength of I···O bonds in Iodine(III/V) 1 and all-iodine(III) and all-iodine(V) agents.

The all-iodine(III) orall-iodine(V) derivatives of molecule **1** were constructed based on the principal of T-shape molecular geometry about hypervalent iodine centers,[13] both derivatives were optimized at the B3LYP level of theory with basis set def2-TZVP.[5, 12] The values of ρbcp and Mayer bond order of I2···O3 bond of molecule **1** and its derivatives were summarized in **Figure 2S**, a result of which indicates that the I2···O3 bond in all-iodine(III) or all-iodine(V) derivatives of molecule **1** was weaker than the one in molecule **1**. Thus, the presence of two iodine centers in different oxidation states (III and V) represent a stability advantage with respect to other-valent iodine (all-iodine(III) or all-iodine(V)) species.



BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(5)	0.0503	I(2)-O(3) bond	0.240

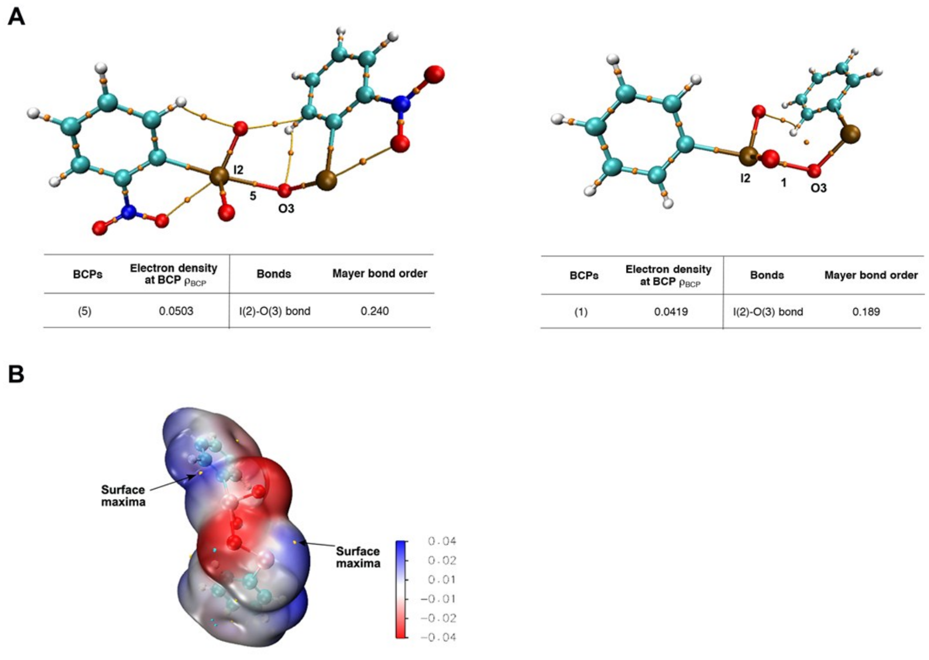
BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(1)	0.0344	I(2)-O(3) bond	0.153

BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(1)	0.0251	I(2)-O(3) bond	0.175

Figure 2S. The summary of electron density at the BCPs and Mayer bond orders of I2–O3 bonds in molecule **1** and its derivatives. The BCPs were represented by orange spheres, the bond paths connecting the nuclei with critical points were also represented by yellow lines. (A) Molecule **1**. (B) All-iodine(III) derivative of molecule **1**. (C) All-iodine(V) derivative of molecule **1**.

4.3 The molecular electrostatic potential surfaces of iodine(III/V) 1 without nitro groups

The iodine(III/V) **1** without two nitro groups was optimized at the B3LYP level of theory with basis set def2-TZVP incorporating Stuttgart–Dresden effective core potentials for iodine atoms,[5, 12] and with D3 dispersion correction with Becke–Jones damping[7]. Multiwfn and VMD program were used to generate molecular electrostatic potential surface.[9-10] The electro-positive regions (surface maxima) around I(III) or I(V) atoms were shown in Figure 3S, leading to the interactions with oxygen atoms of nitro groups.



BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(5)	0.0503	I(2)-O(3) bond	0.240

BCPs	Electron density at BCP ρ_{BCP}	Bonds	Mayer bond order
(1)	0.0419	I(2)-O(3) bond	0.189

Figure 3S. (A) The comparison of the I2–O3 bonds in hypervalent iodine molecule with or without nitro groups. (B) Molecular electrostatic potential surfaces of the hypervalent iodine molecule without nitro groups (unit: a. u.).

4.4 Calculations Support for the Proposed mechanism

4.4.1 Another Possible Reaction Pathway for the Formation of 2*H*-azirine 3

We also proposed another possible reaction pathway, which involves the formation of C-I intermediate, for the formation of the 2*H*-azirine product using this new hypervalent iodine(III/V) oxidant (**Figure 4S**). First, the reaction of the enamine substrate with hypervalent iodine(III/V) **1** afforded imine intermediate **e**, *via* the formation of the C-I bond. Next, the intramolecular azirination occurred within **e** giving 2*H*-azirine product **3**, with the concurrent generation of hypervalent iodine(III/III) **f**. Following the reaction of another molecular enamine substrate with this intermediate **f**, the imine intermediate g was formed via the formation of the C-I bond. Then, the second azirination occurred within g giving rise to the formation of the second molecule of 2*H*-azirine product **3**, after removal of *o*-nitro iodobenzene and *o*-nitro iodosylbenzene.

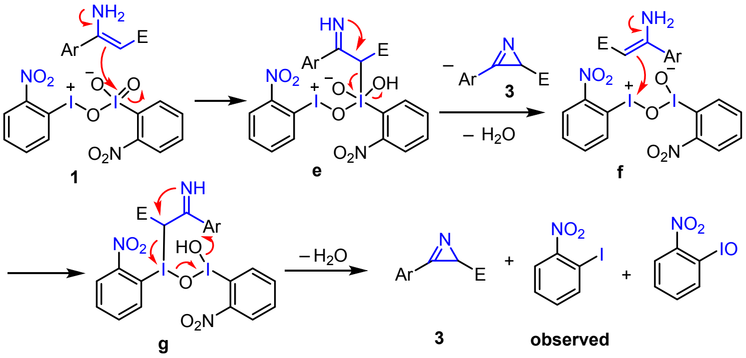


Figure 4S An alternative mechanism for the synthesis of 2*H*-azirine.

4.4.2 Evaluation of the key intermediates E and e

In order to acquire the preliminary support for the suggested mechanisms, DFT calculations were carried out on intermediate **E** and **e**. Firstly, we generated various conformations of intermediate **e** and **E** (Figure 5S-A and Figure 5S-C), then optimized each conformation at the B3LYP level of theory with basis set def2-TZVP using ORCA 4.1.2 software.[4-5, 12] We found that the optimized lowest-energy conformation of intermediate **E** was computed to be 7.35 kcal/mol lower in single point energy than the one of intermediate **e** (Figure 5S-B and Figure 5S-D). An implication of this finding is the propensity that the azirination reaction proceeded through the I-N bond intermediate, rather than the C-I bond intermediate.

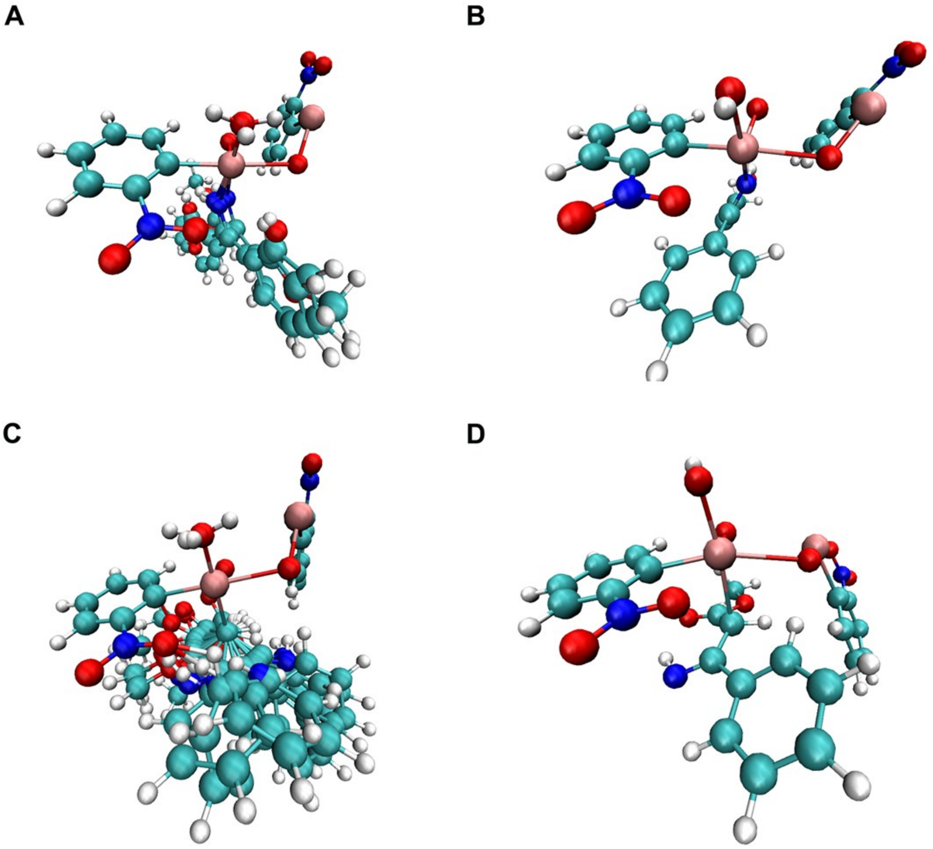


Figure 5S. (A) Generated conformations of intermediate **E** for optimizations. (B) The optimized lowest-energy conformation of intermediate **E**, which was 7.35 kcal/mol lower than the lowest-energy conformation of intermediate **e**. (C) Generated conformations of intermediate **e** for optimizations. (D) The optimized lowest-energy conformation of intermediate **e**.”

5. Notes and References

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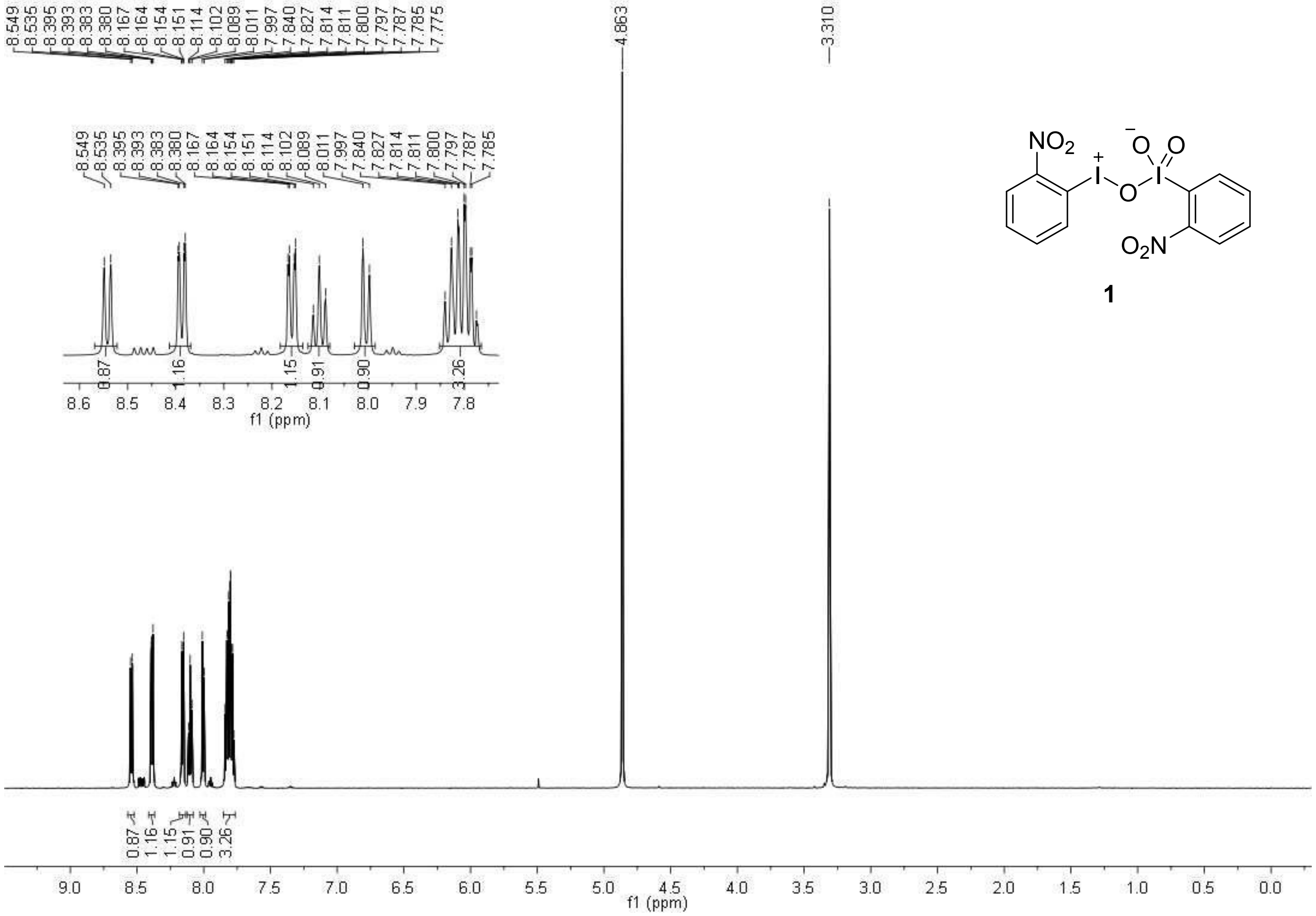
6. ¹H-NMR and ¹³C-NMR Spectra



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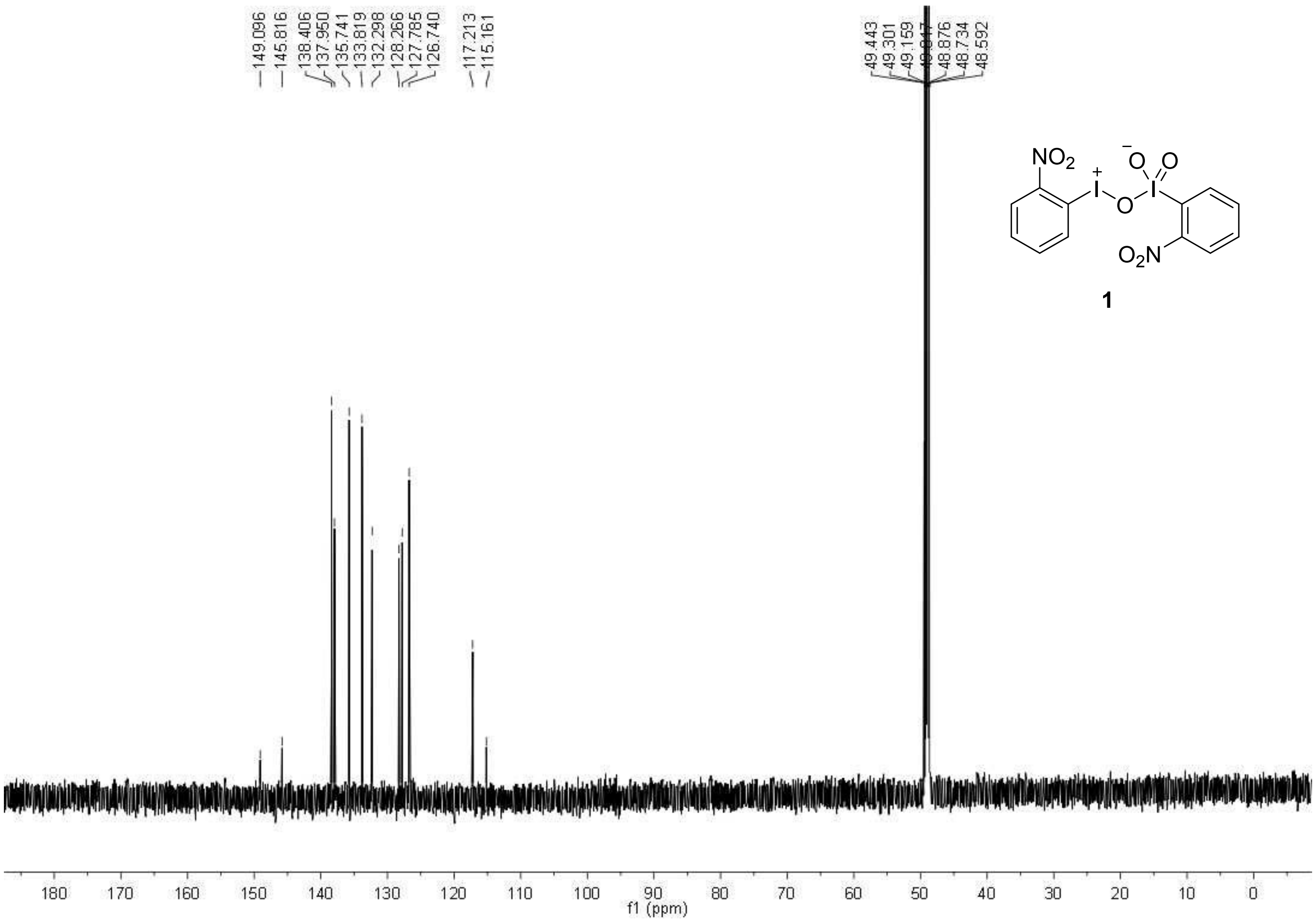
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49.159
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48.876
48.734
48.592
NO_2
O_2N
I
I
O
O
O
1
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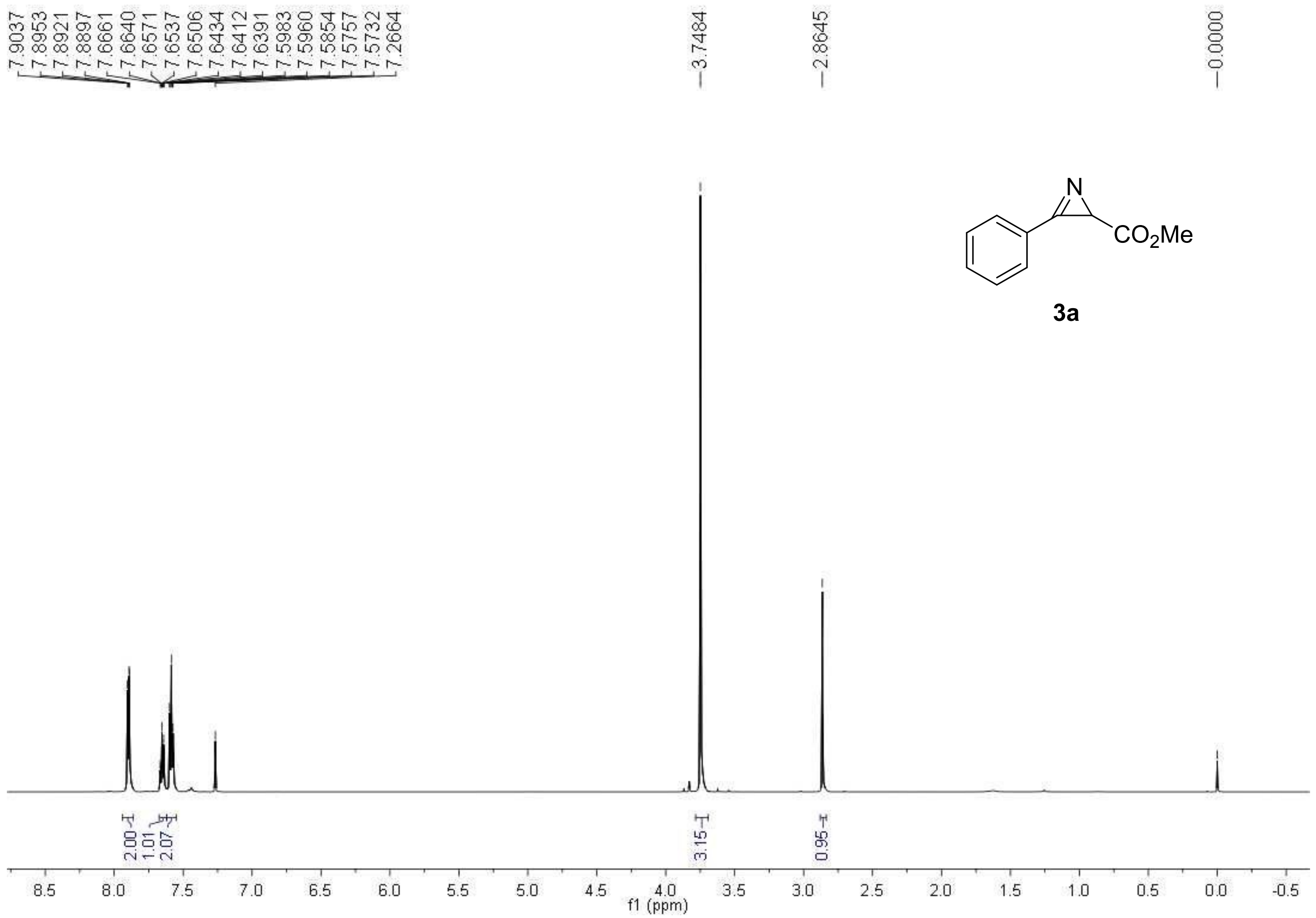
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N
CO$_2$Me
3a
2.00
1.01
2.07
3.15
0.95
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8.0
7.5
7.0
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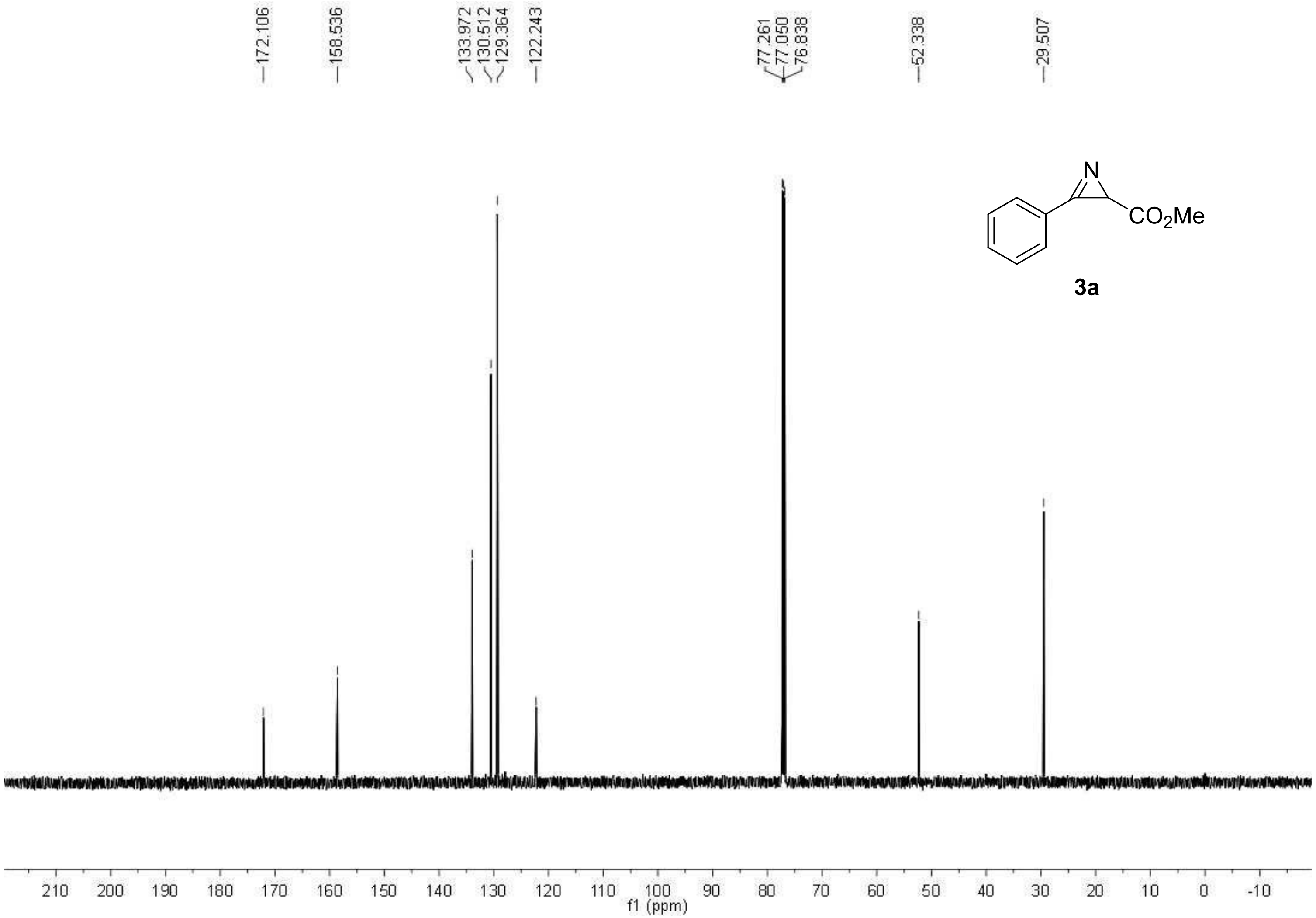
f1 (ppm)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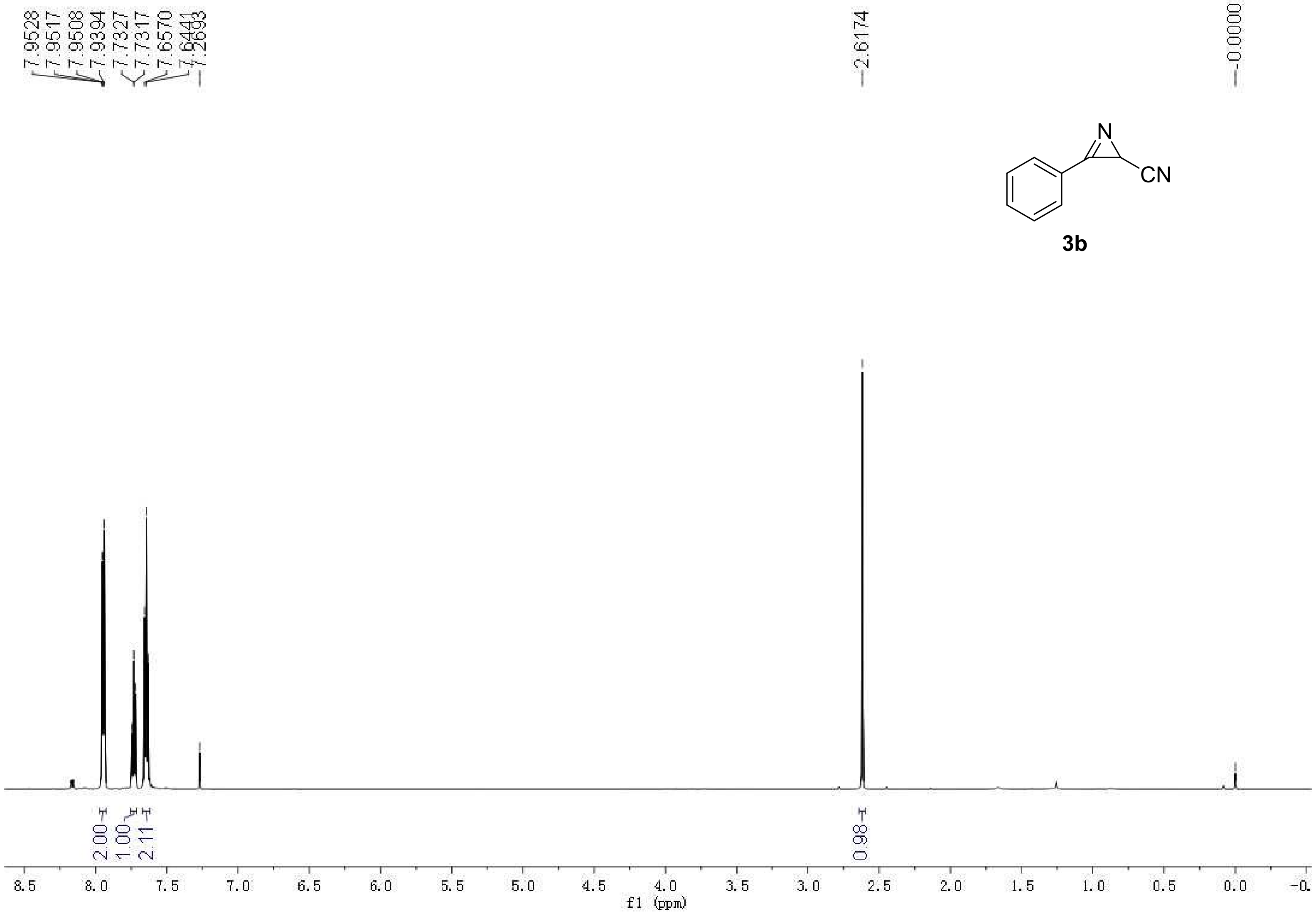
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CN
3b
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1.00
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7.0
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6.0
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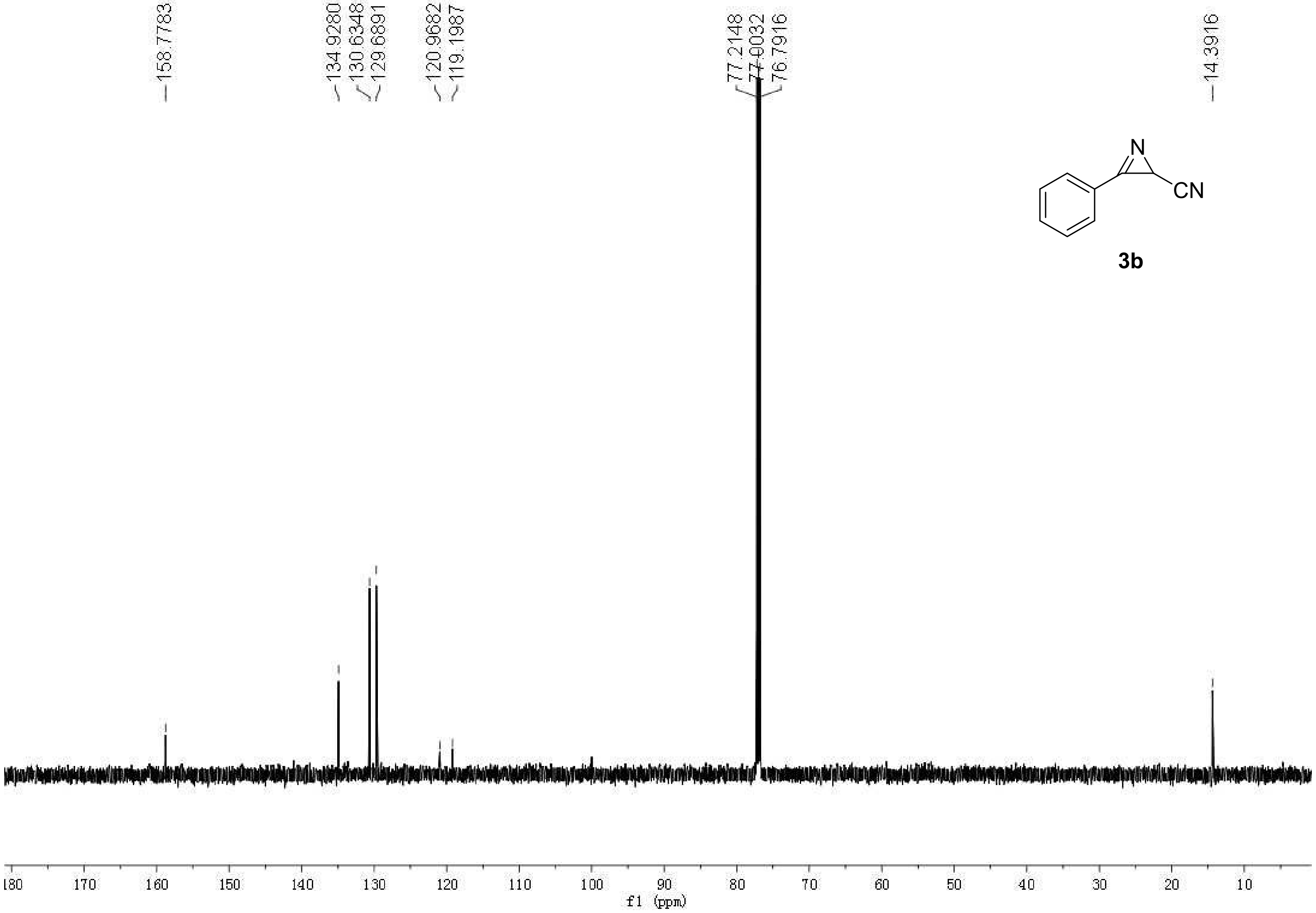
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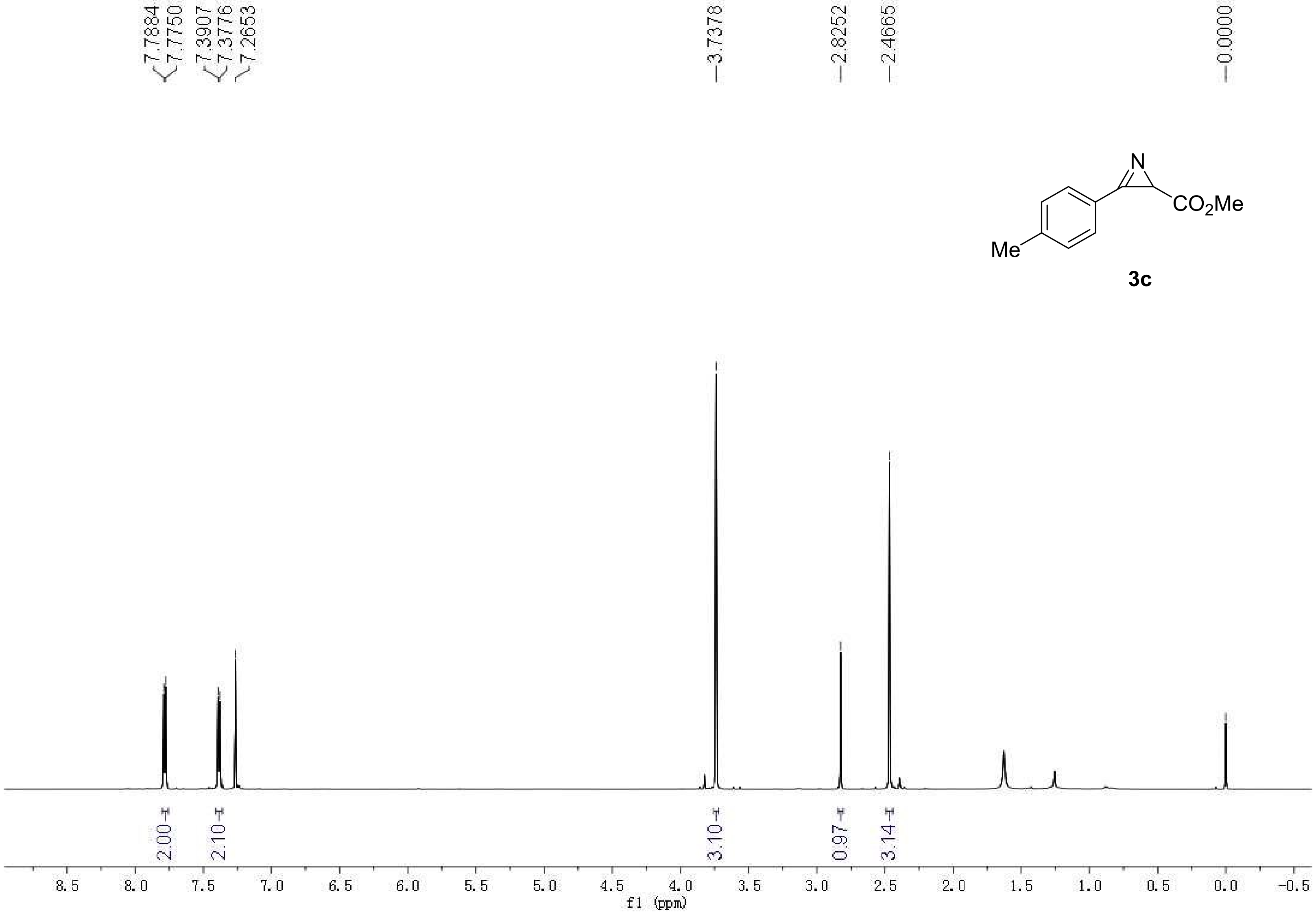
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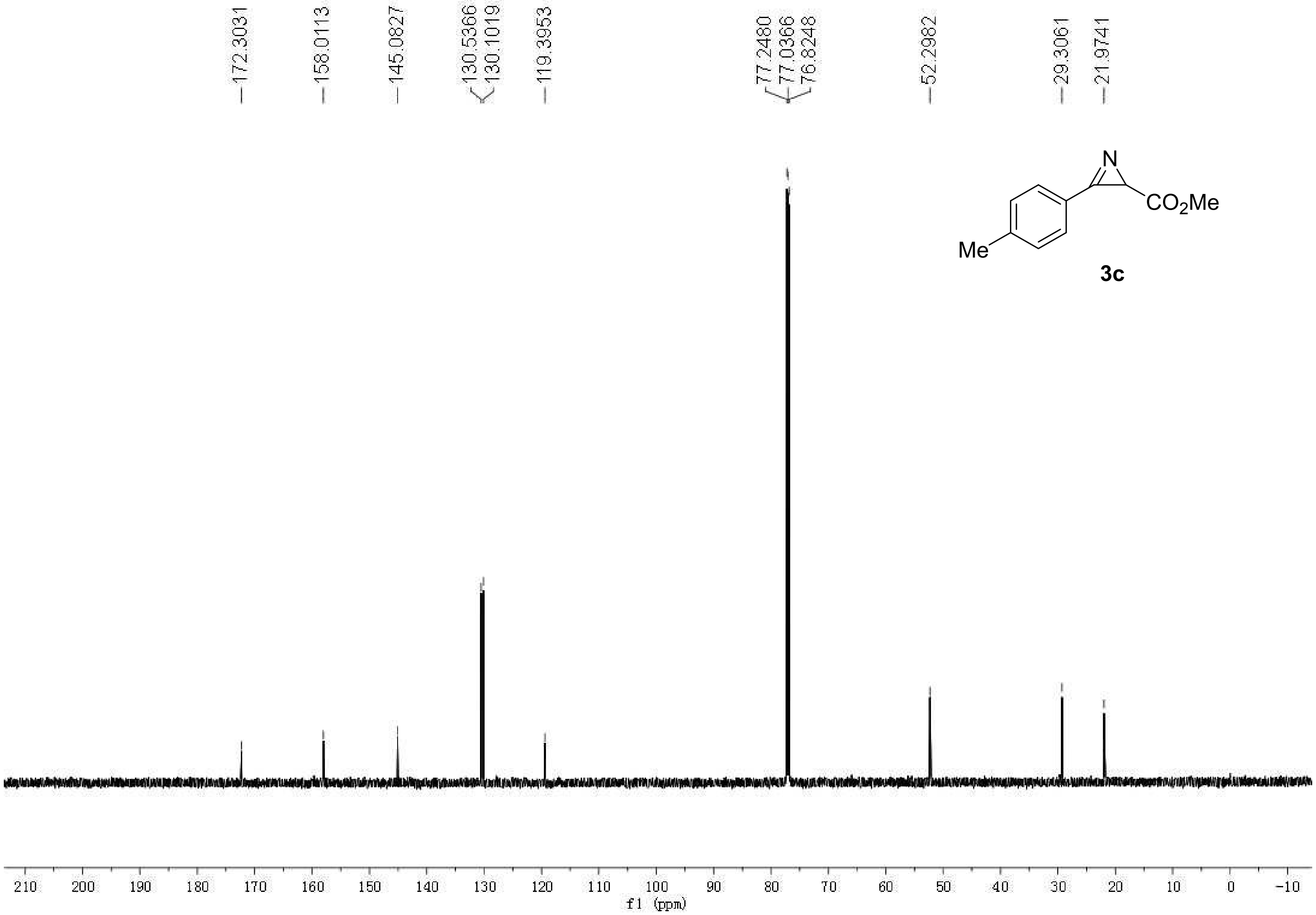
f1 (ppm)

3c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CO2Me
Me
3c
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200
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180
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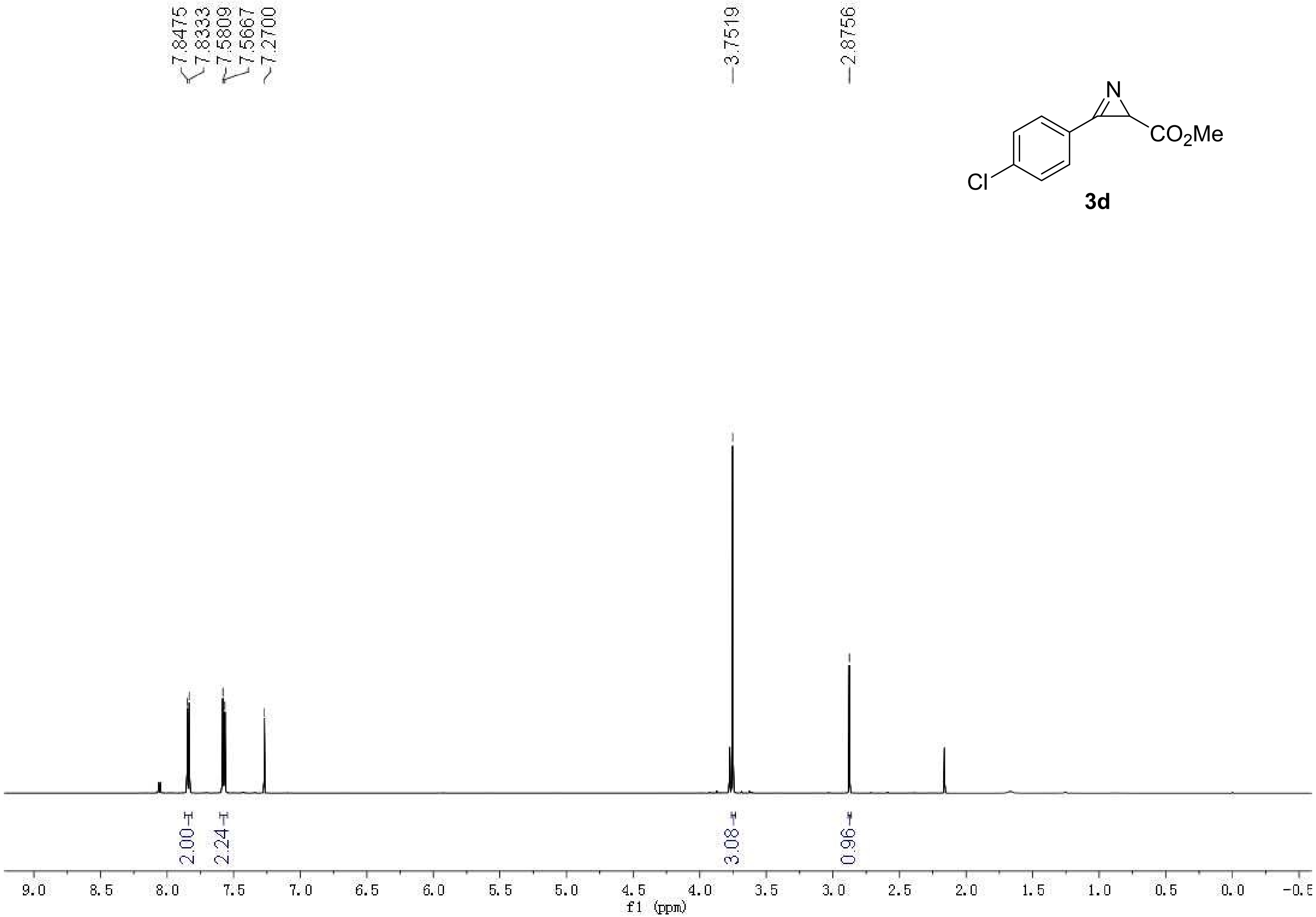
f1 (ppm)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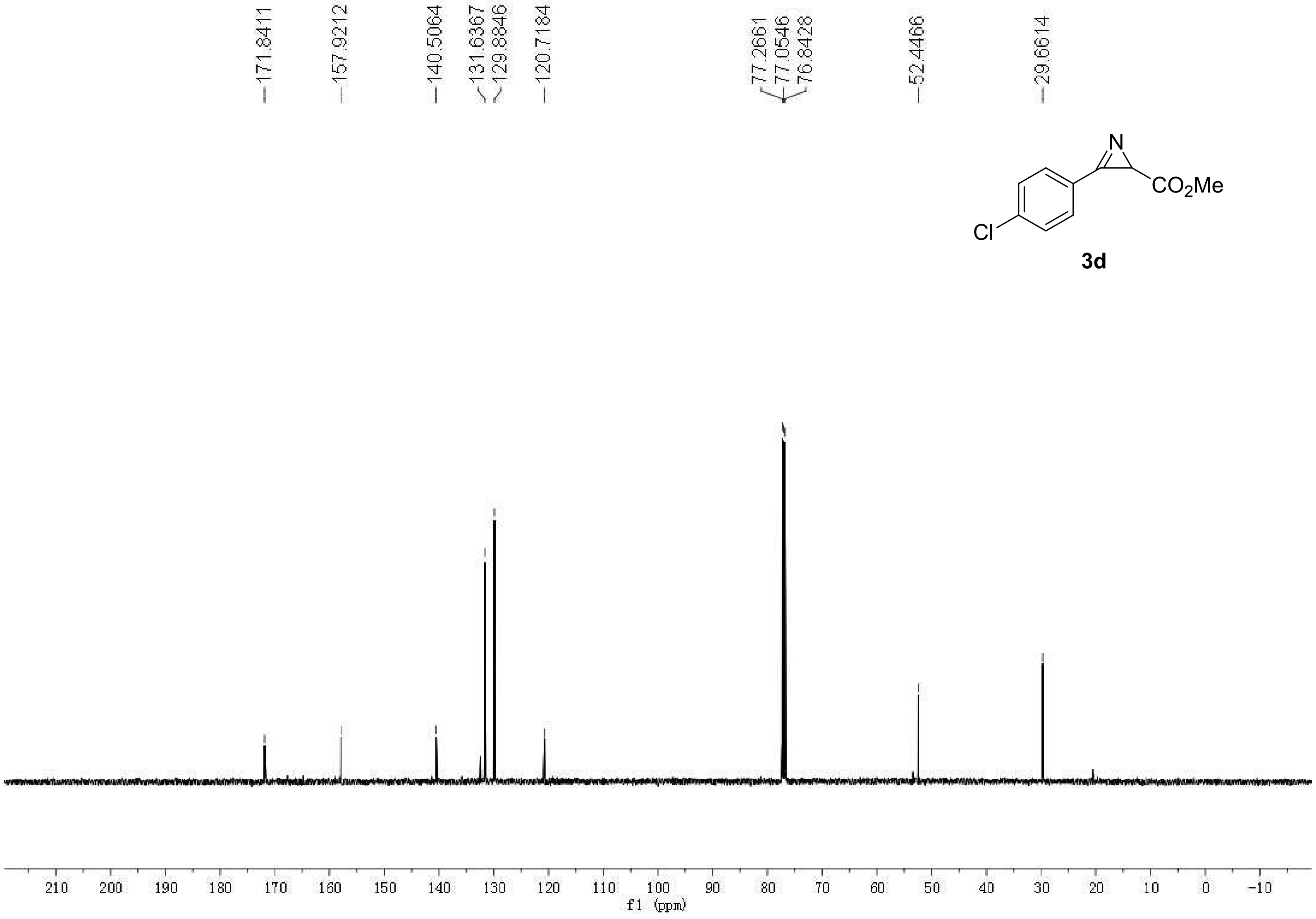
f1 (ppm)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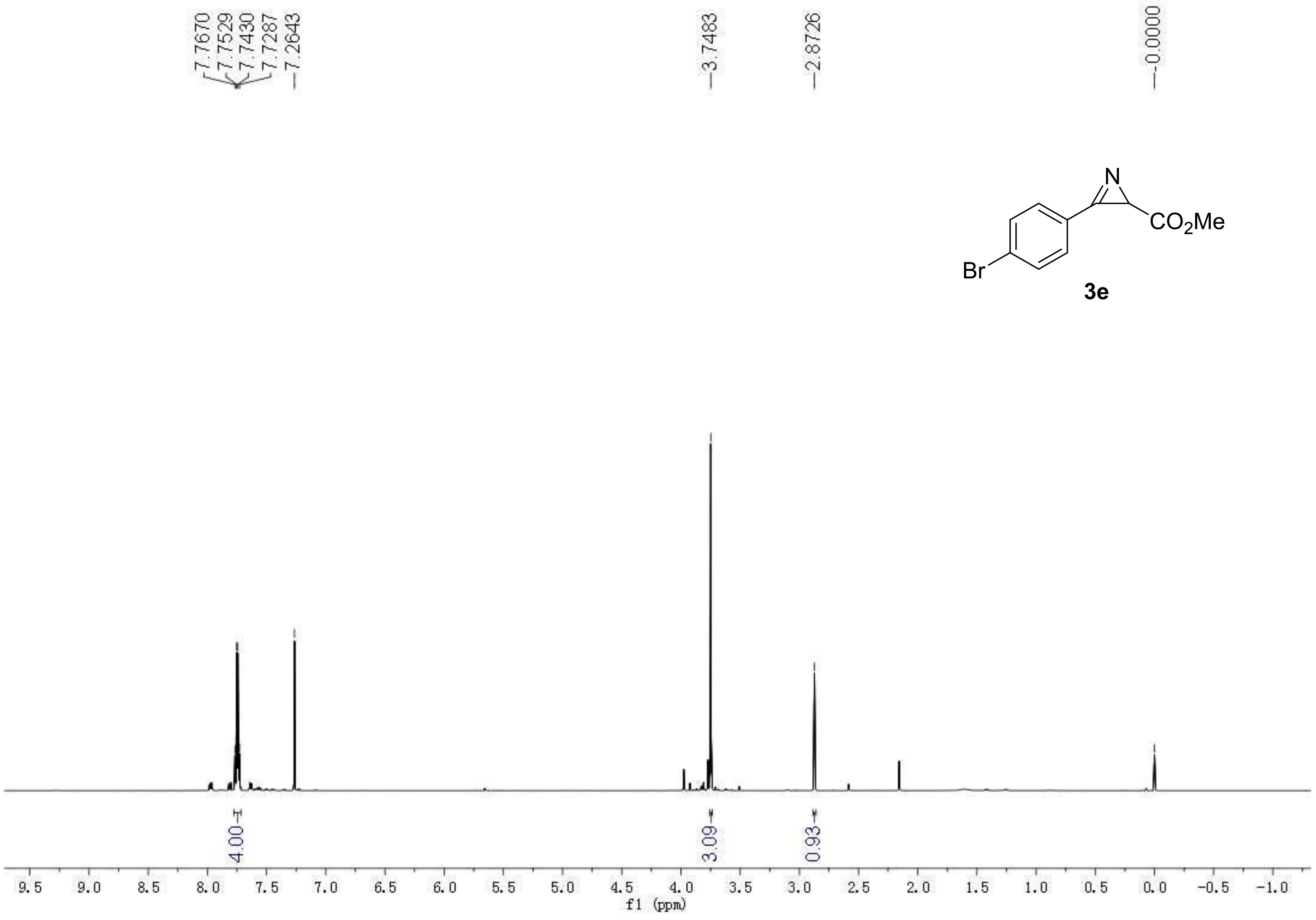
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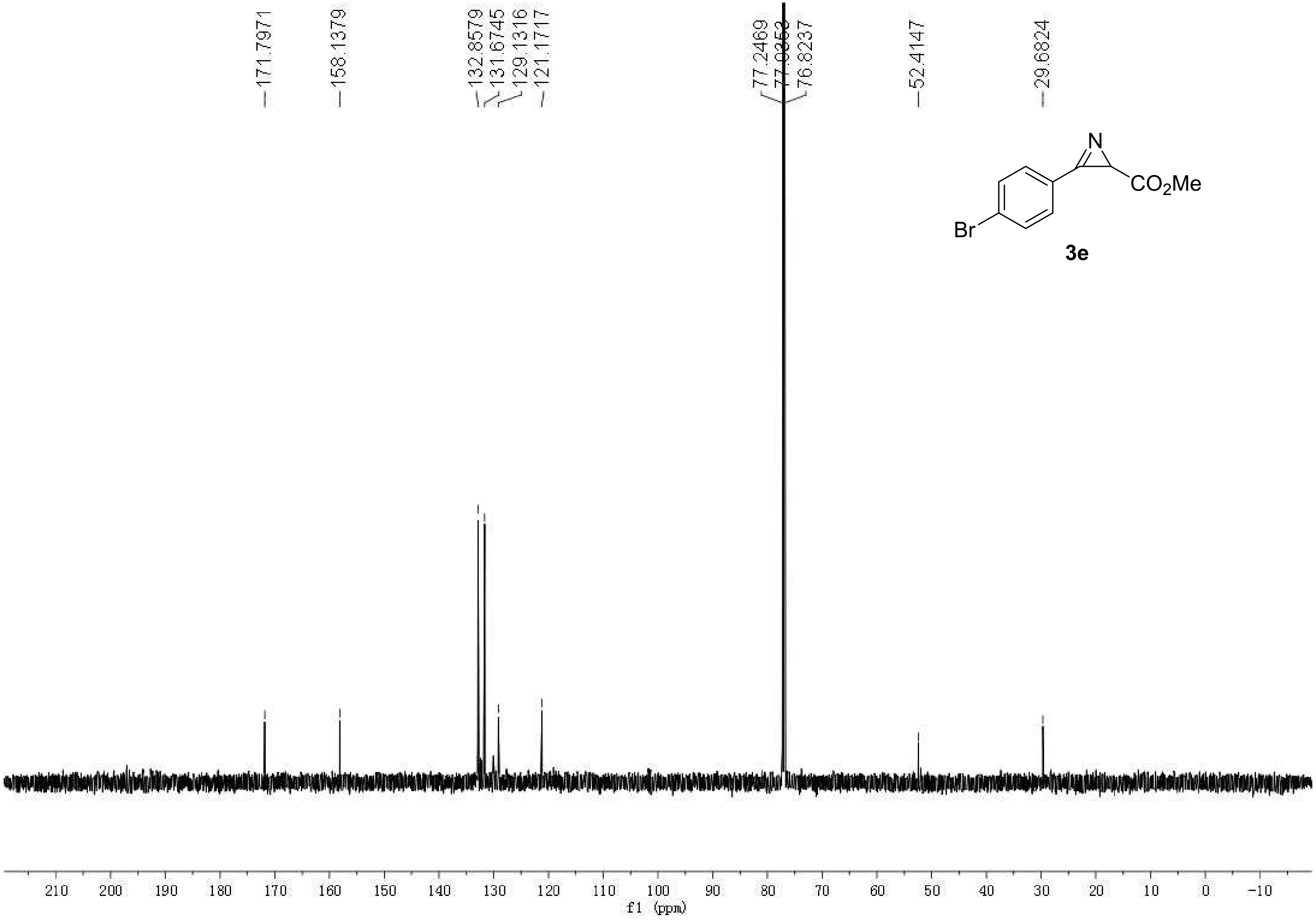
f1 (ppm)

3e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3e
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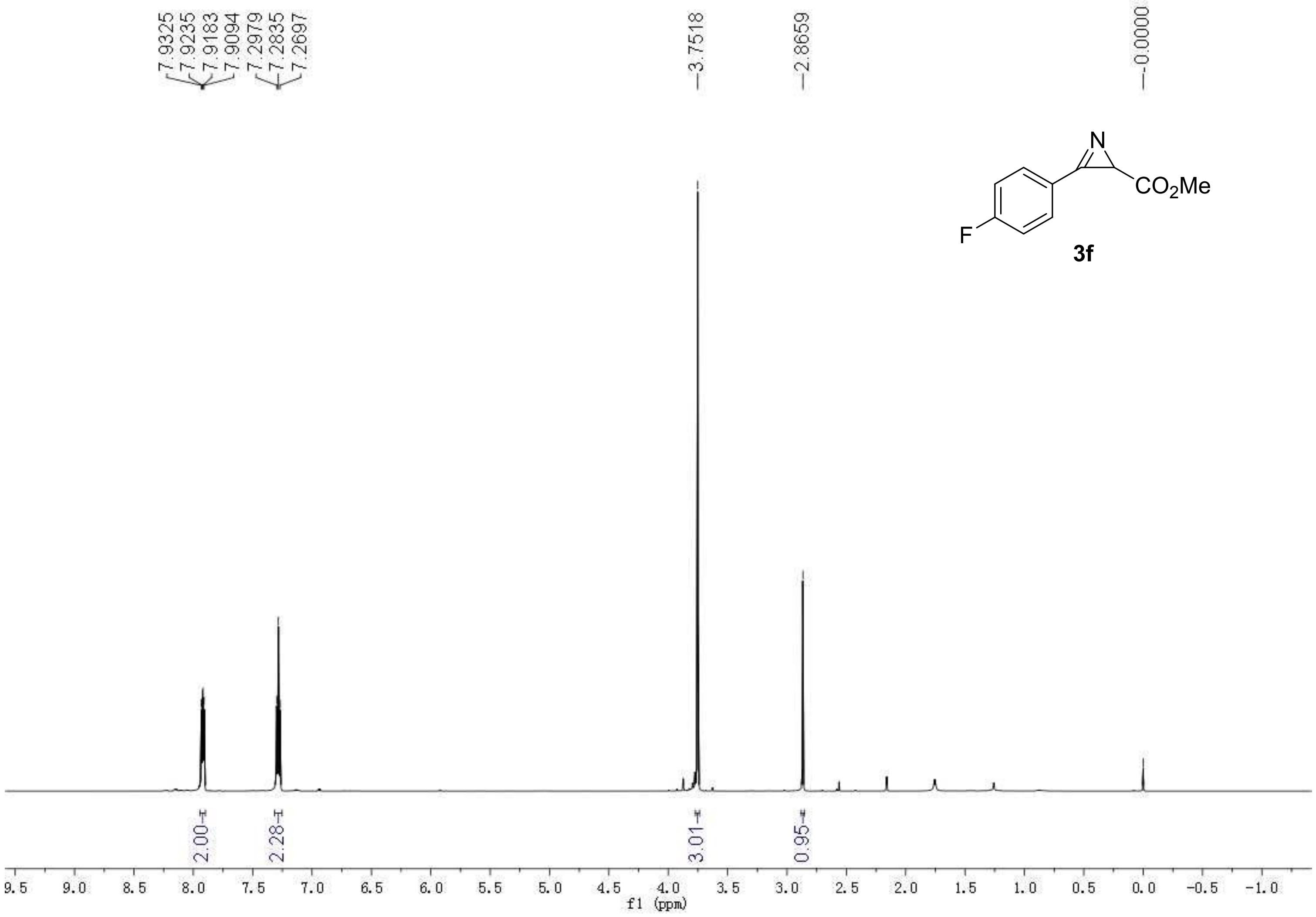

3f

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F
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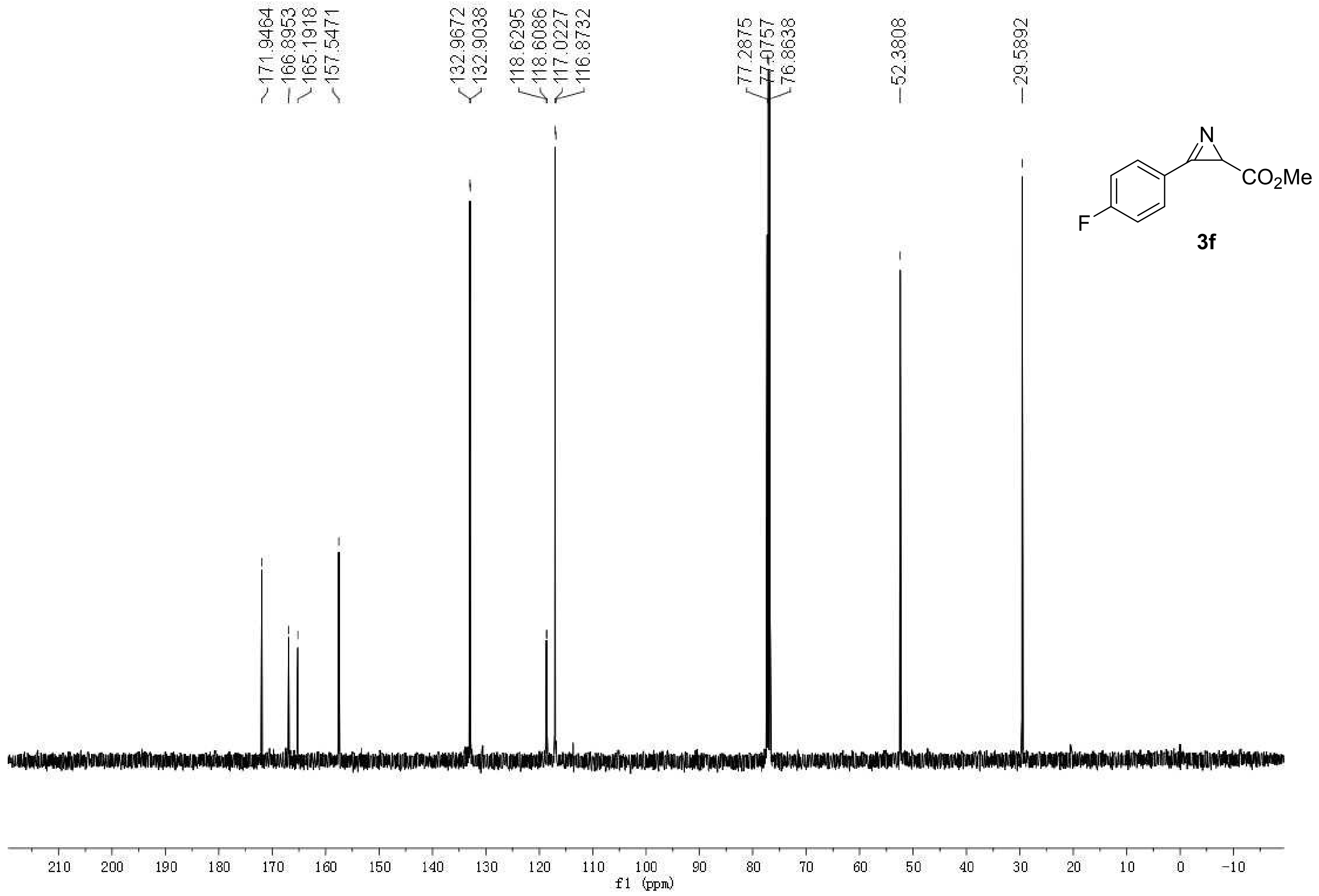
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f1 (ppm)

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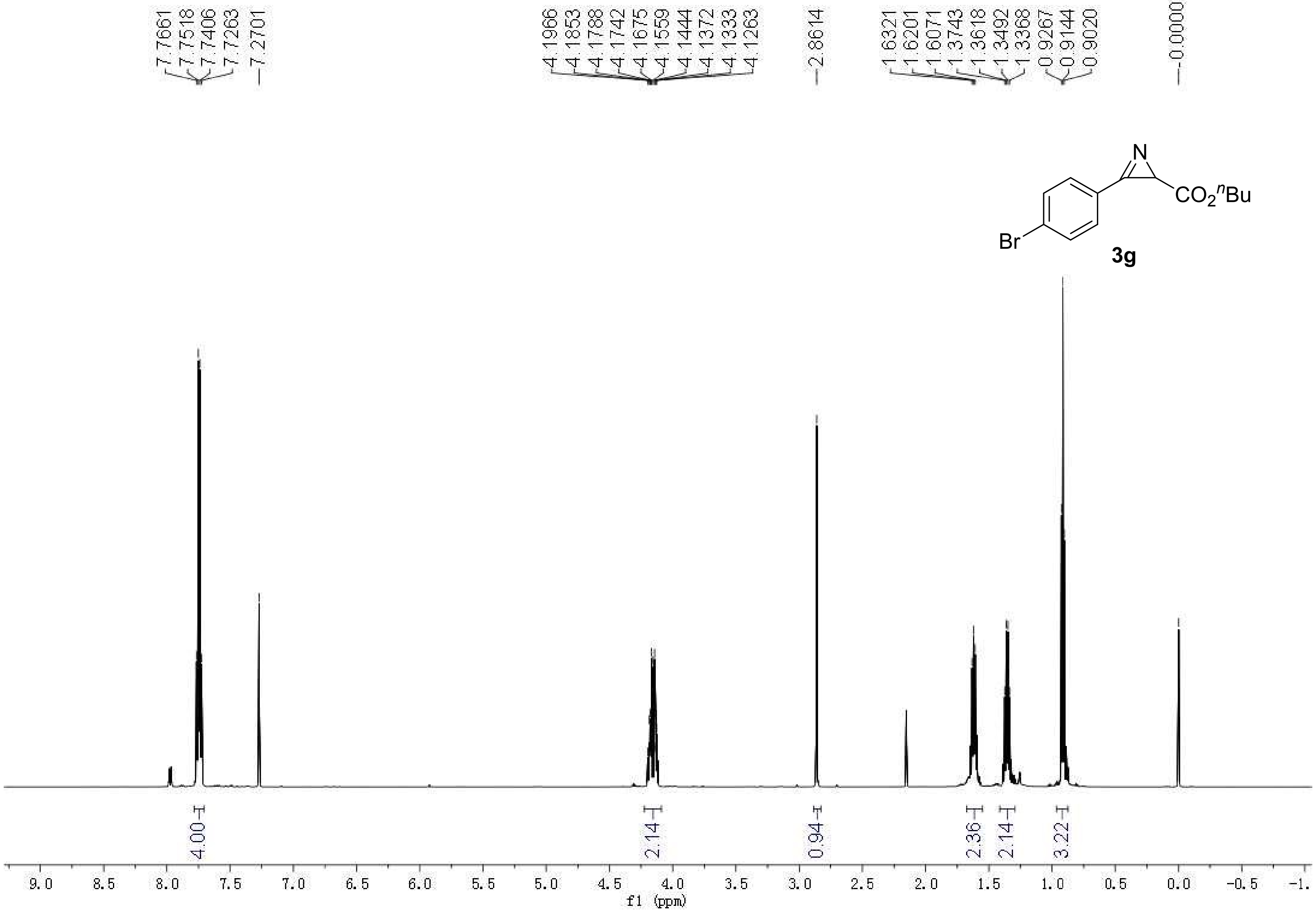
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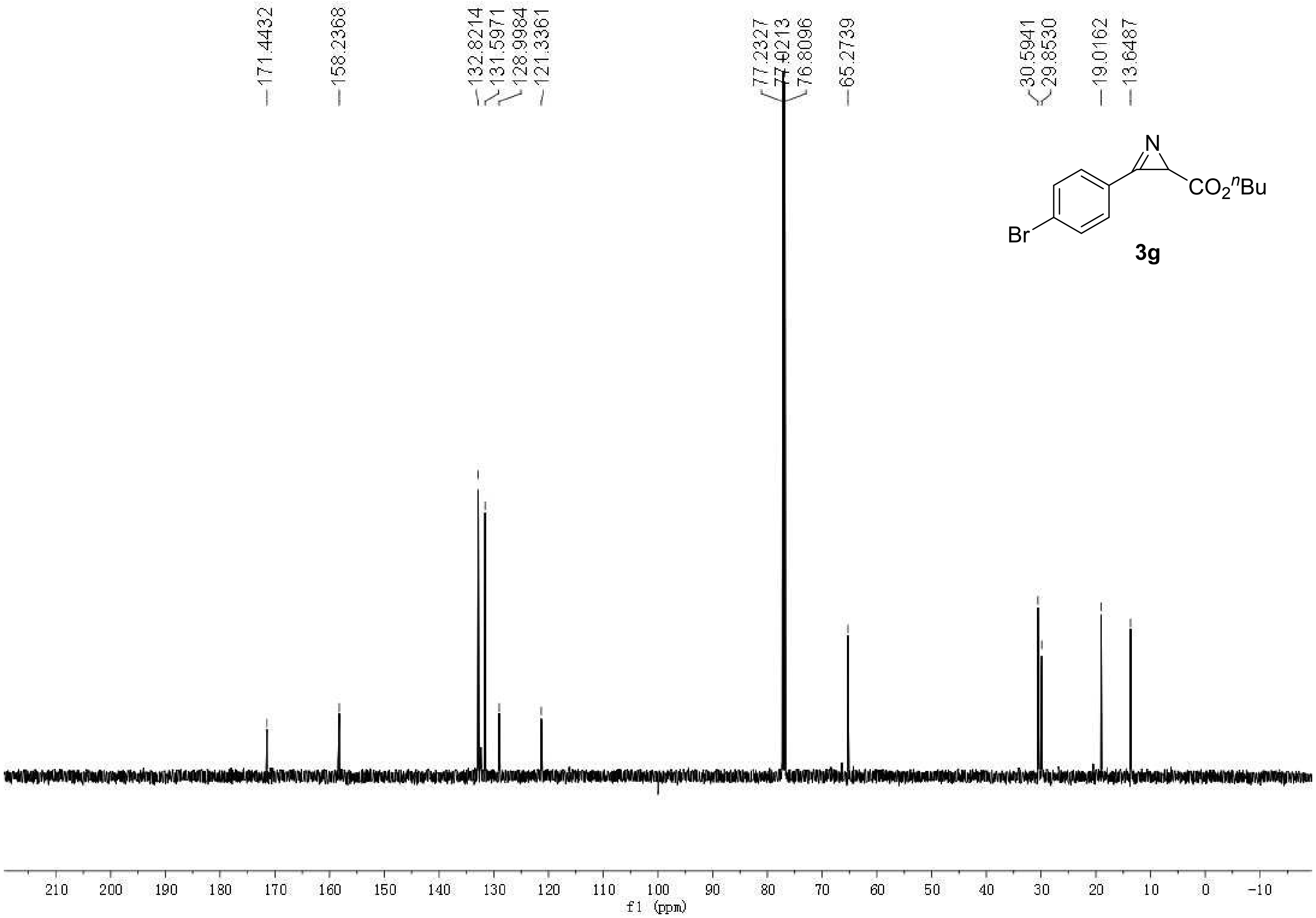
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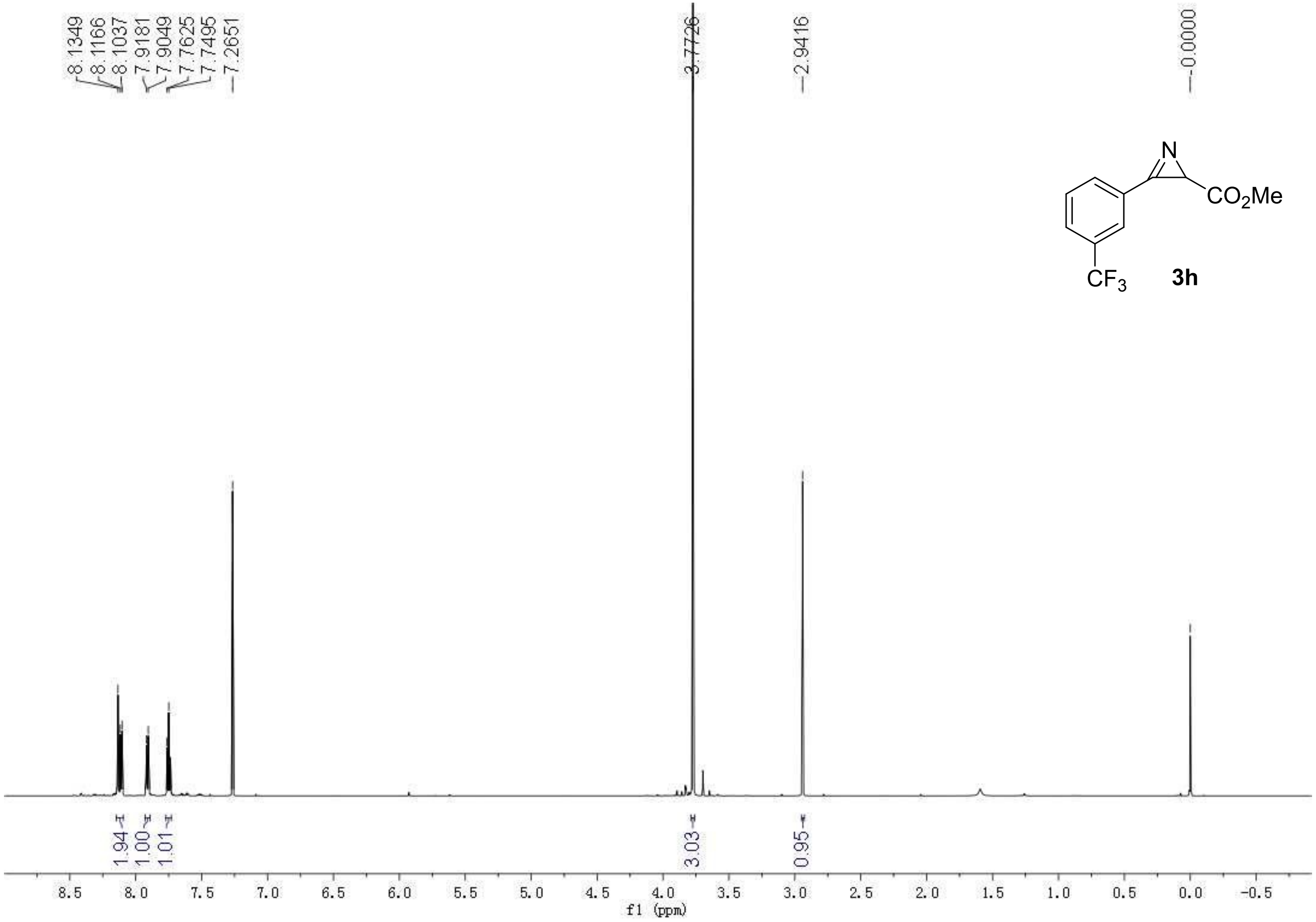
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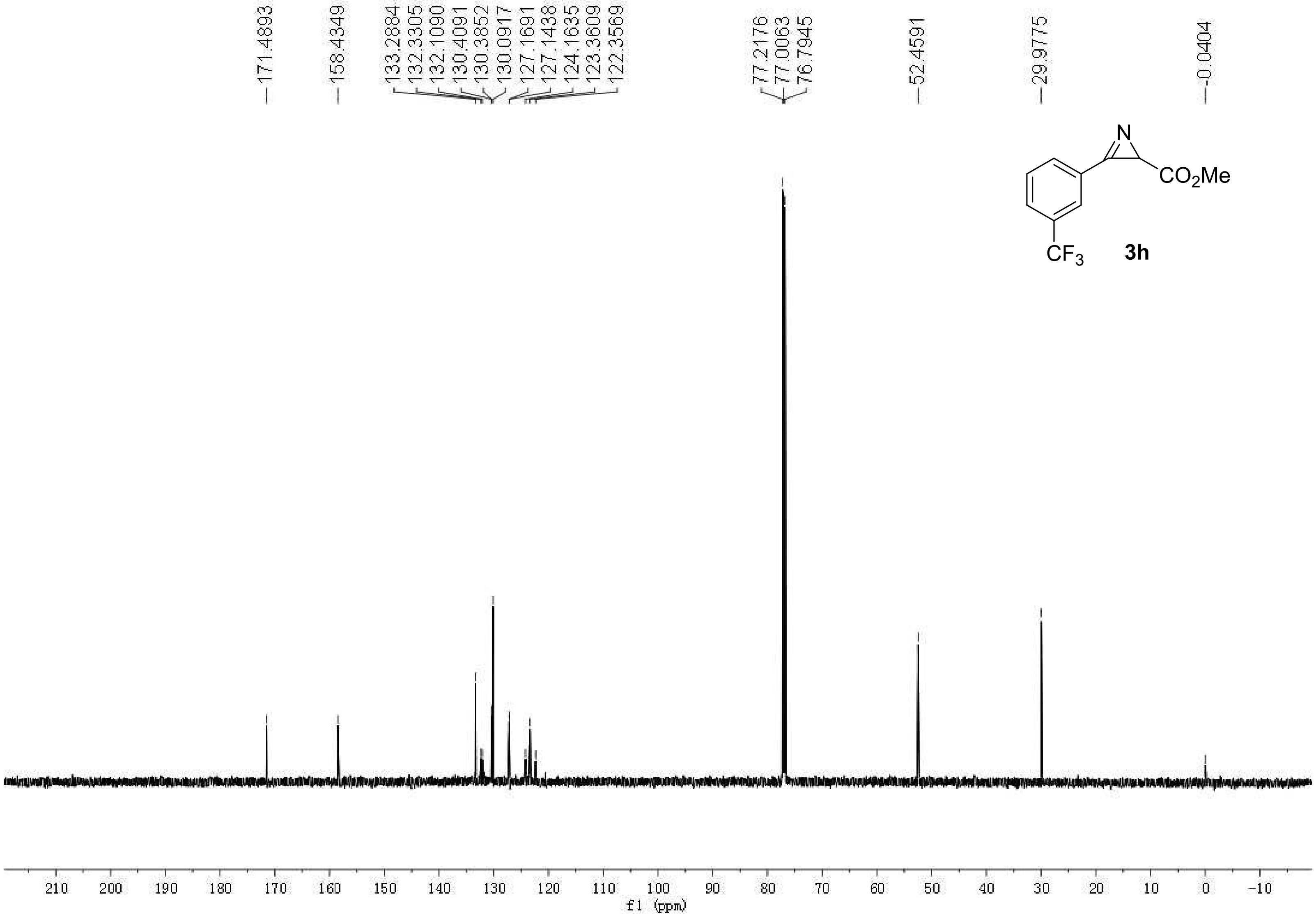
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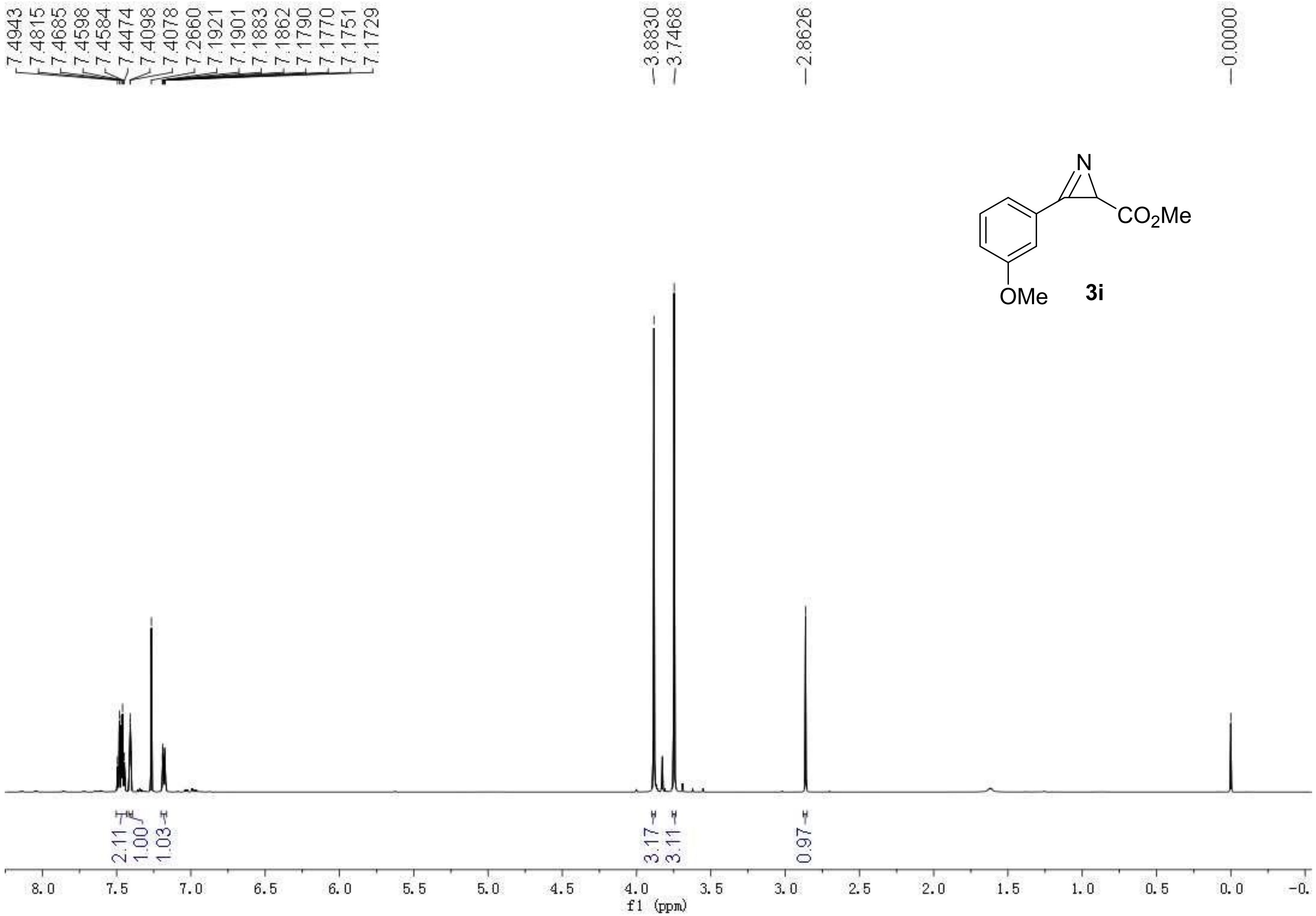
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OMe
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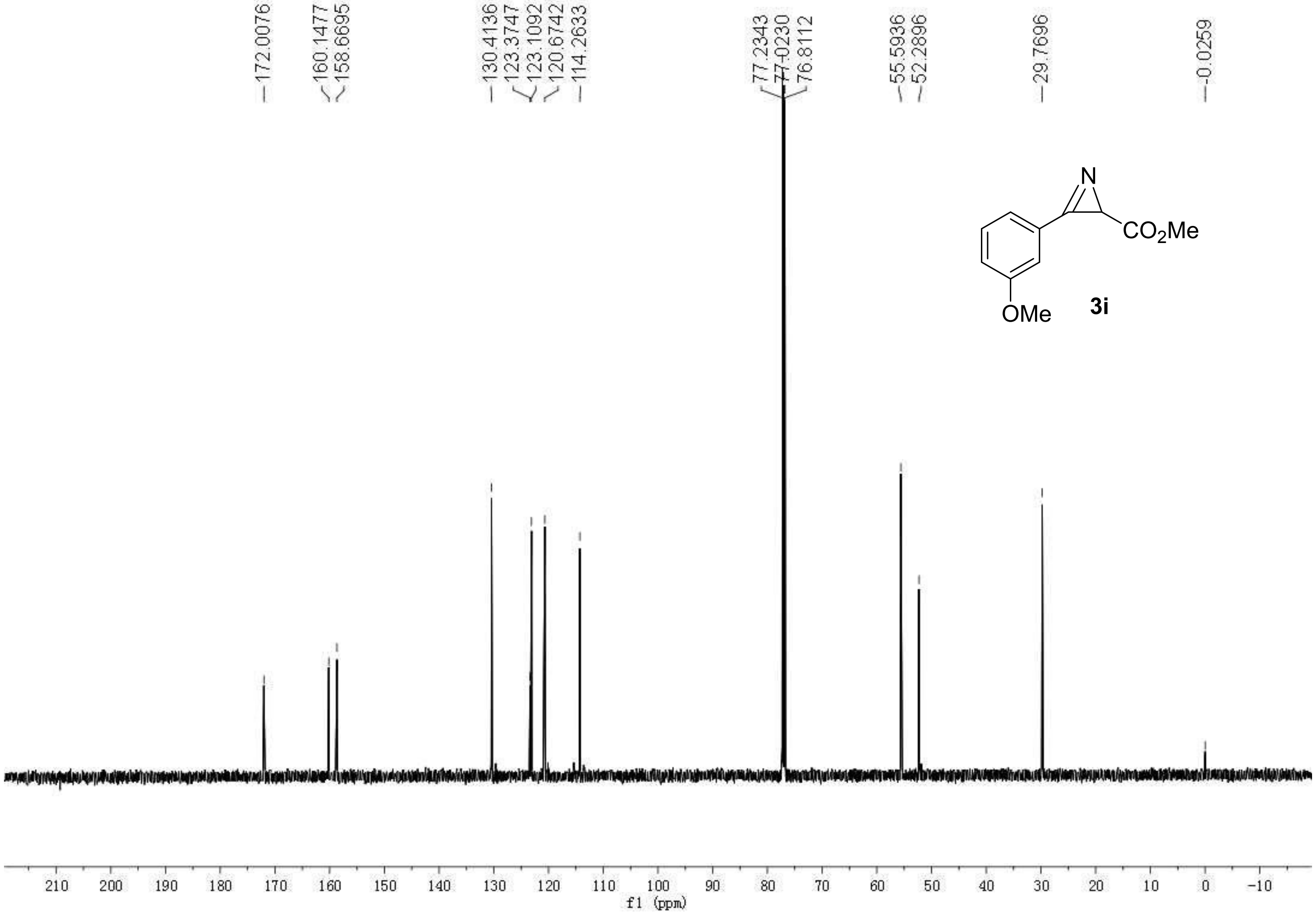
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OMe
3i
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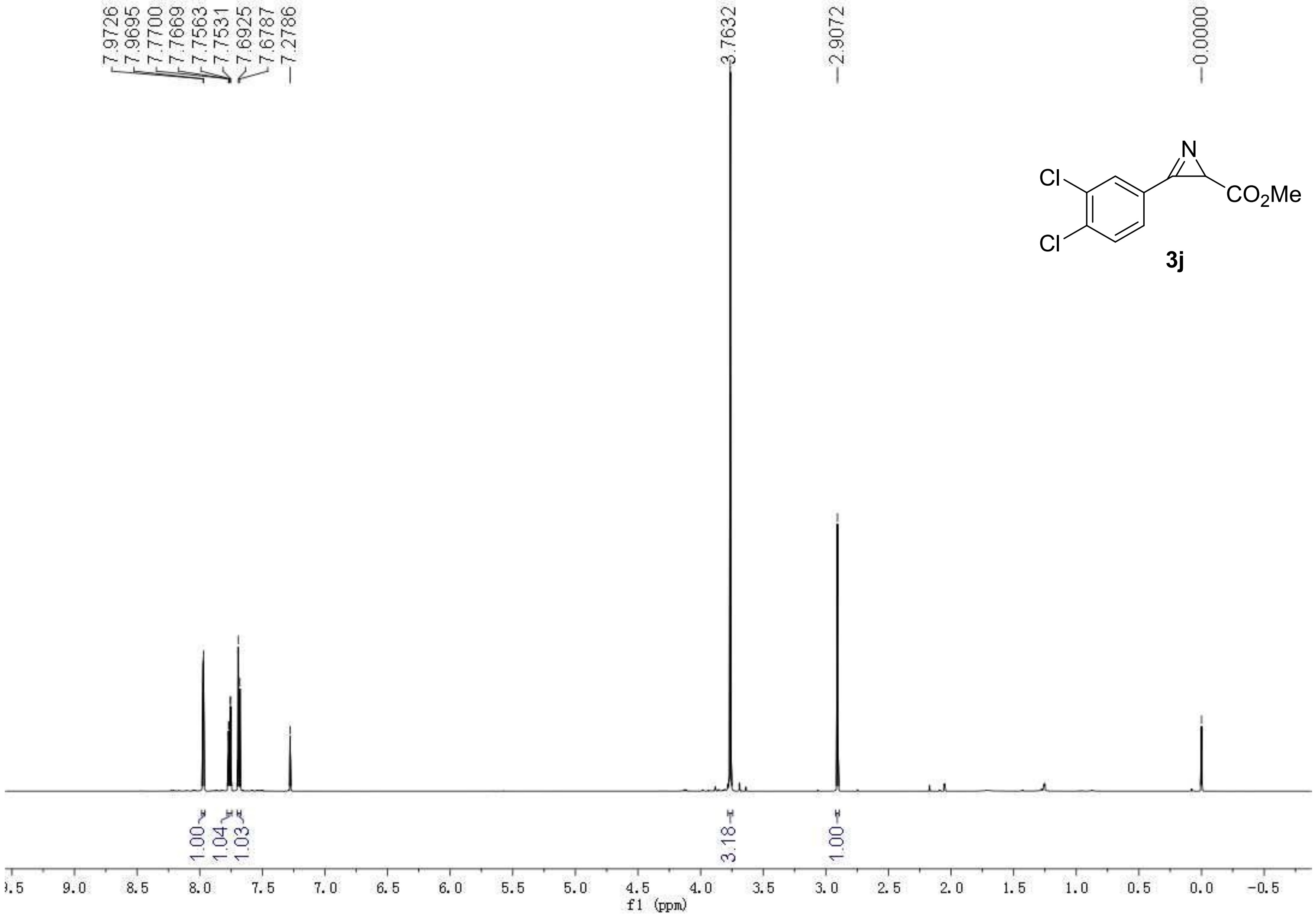
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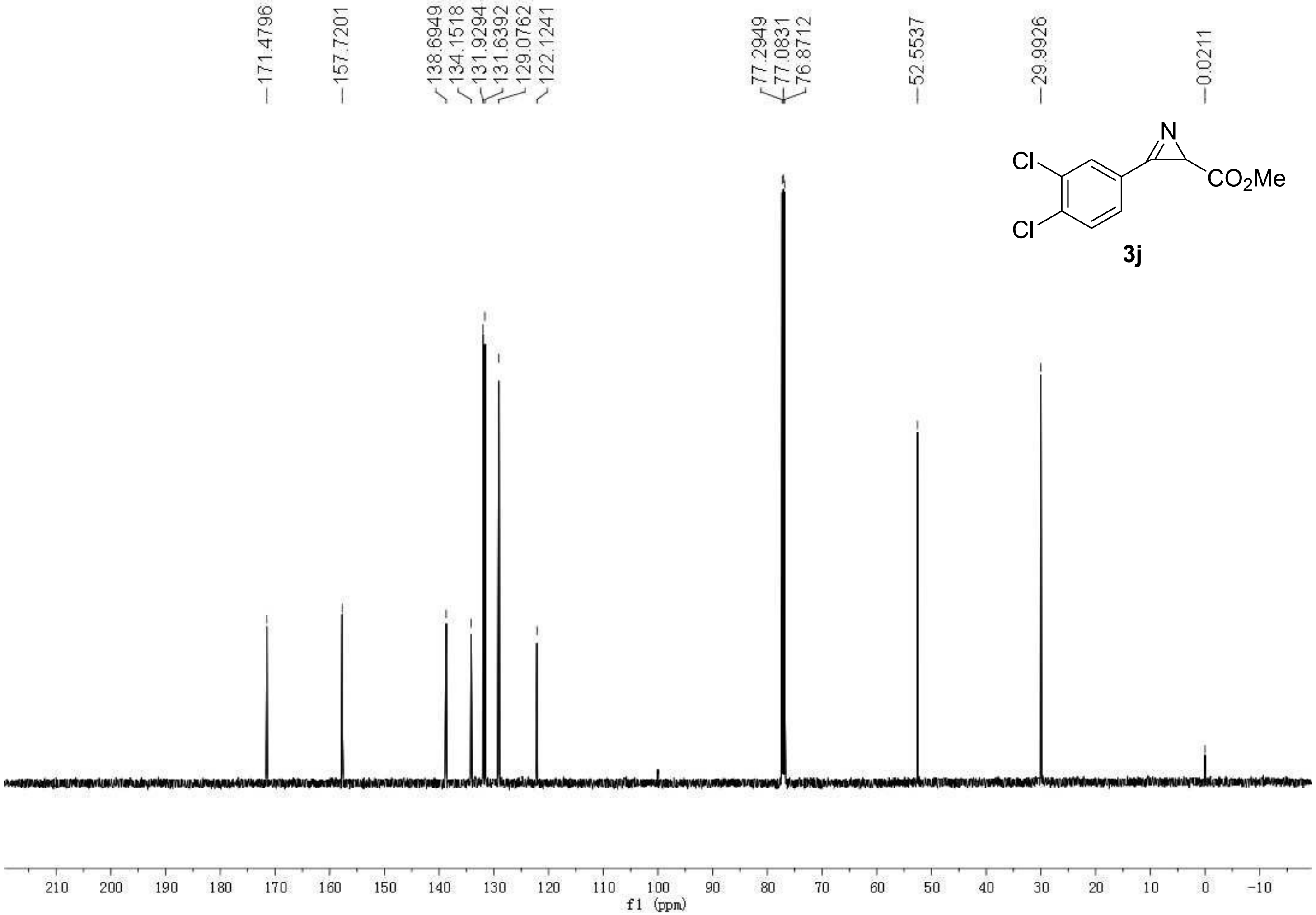
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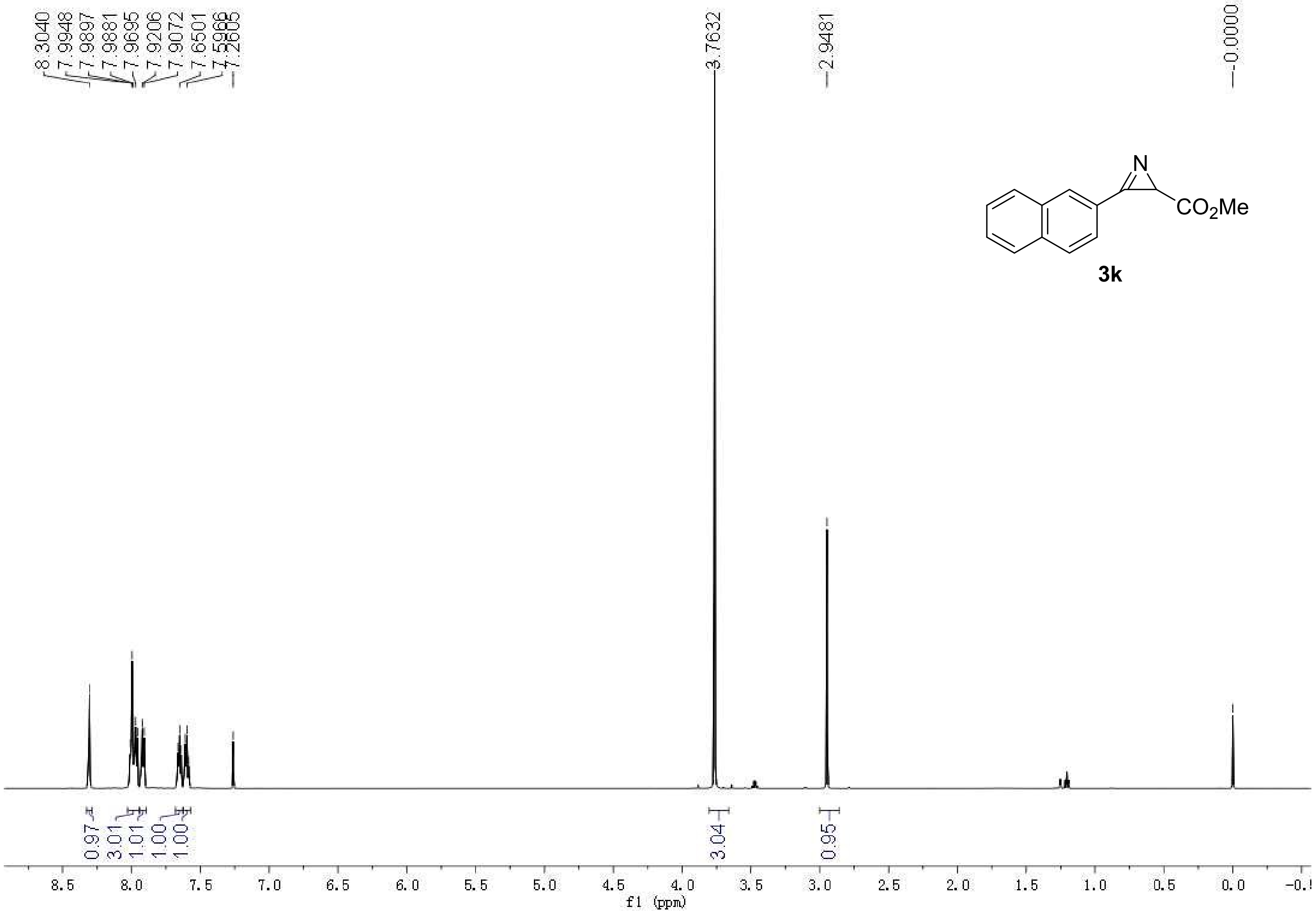
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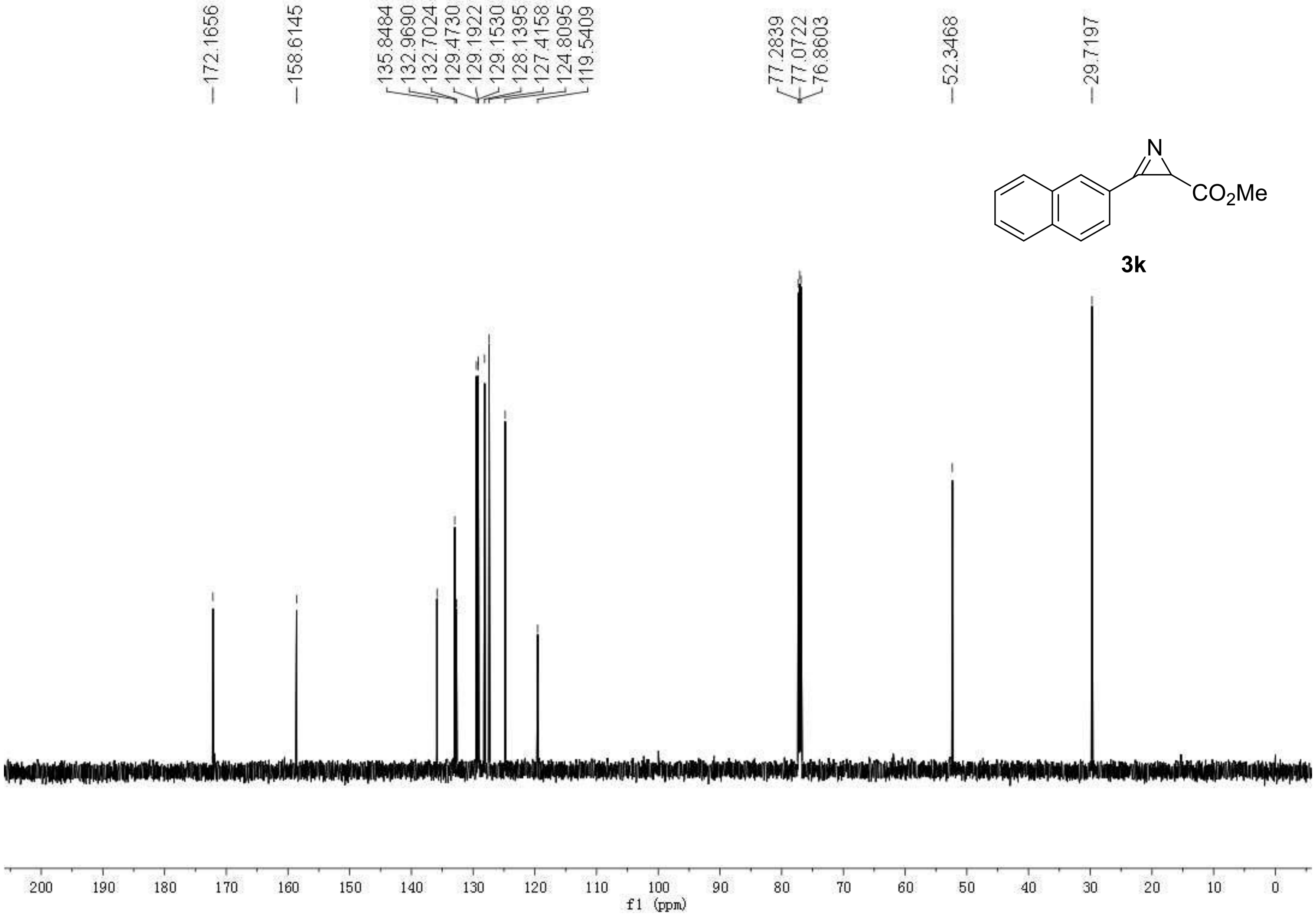
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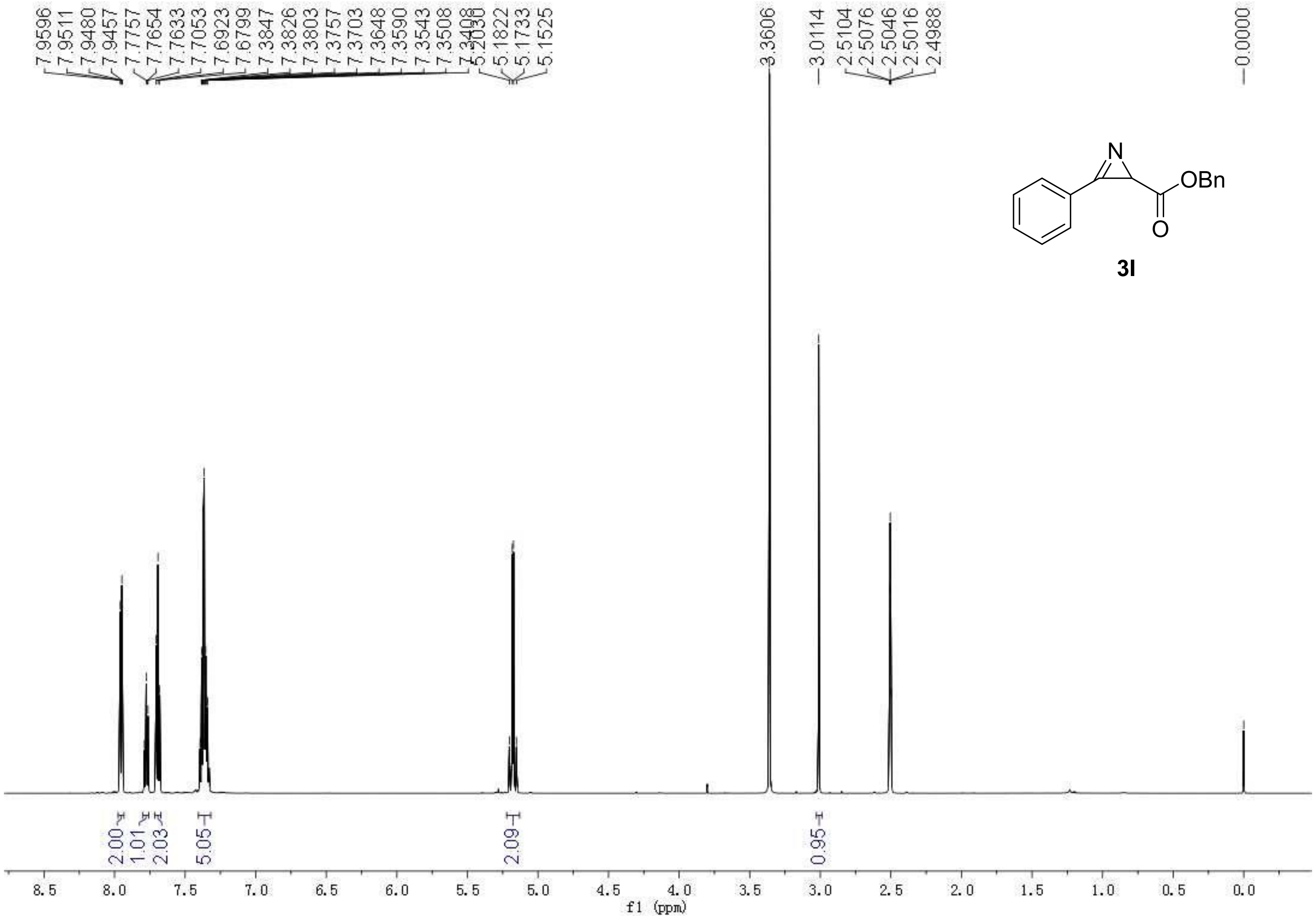
3k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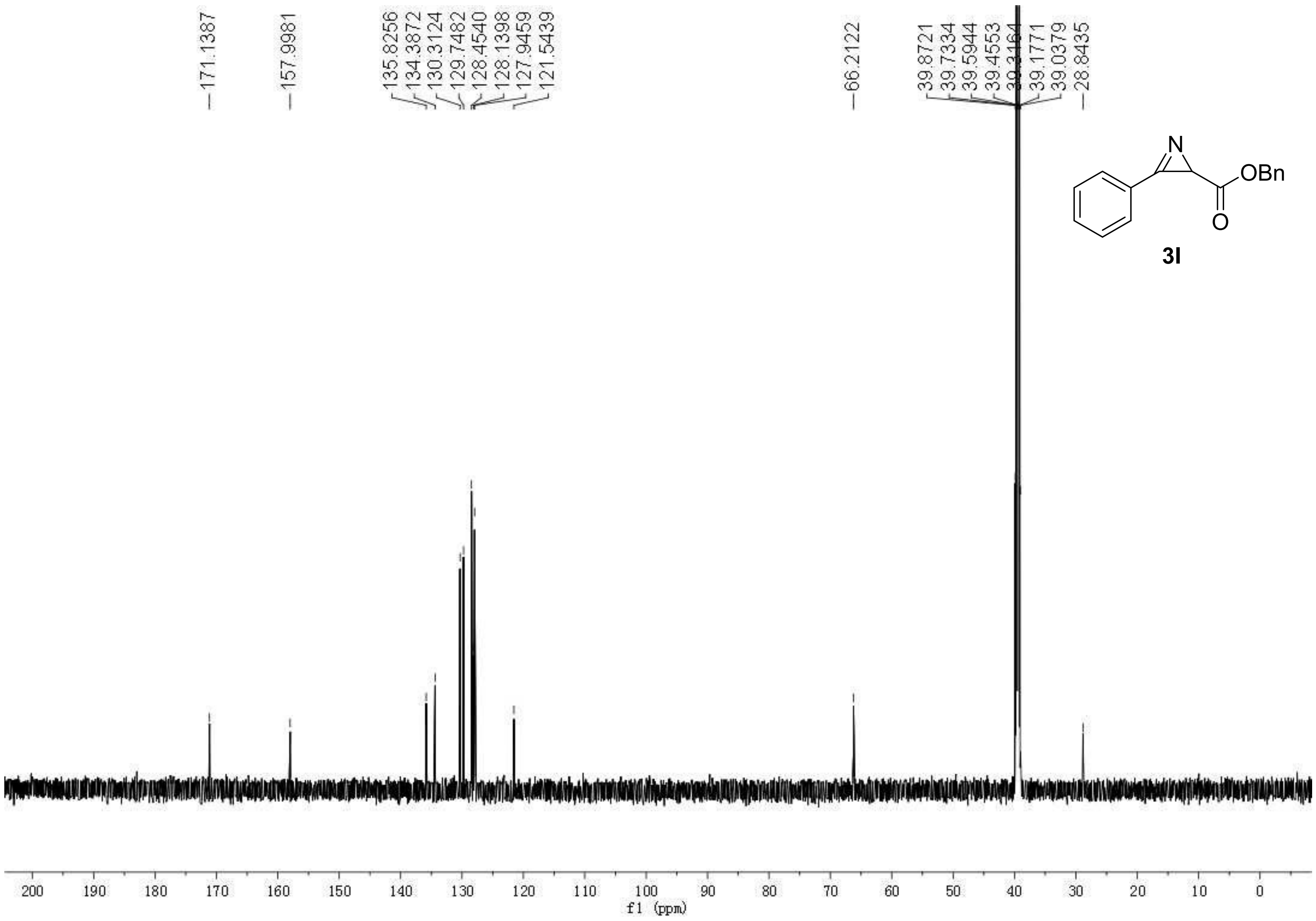
f1 (ppm)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66.2122
39.8721
39.7334
39.5944
39.4553
39.3164
39.1771
39.0379
28.8435
N
OBn
O
3l
200
190
180
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130
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110
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90
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50
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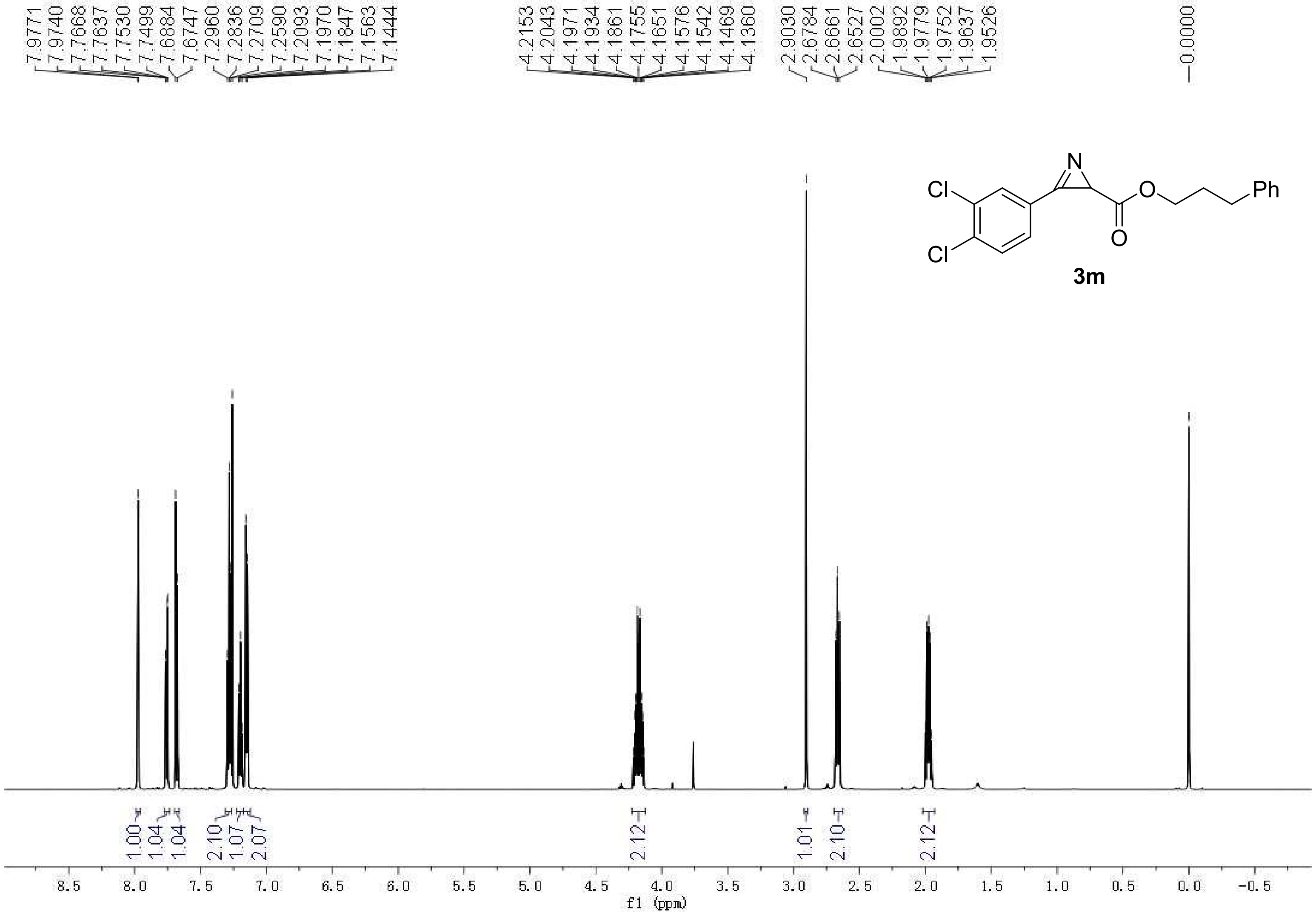
f1 (ppm)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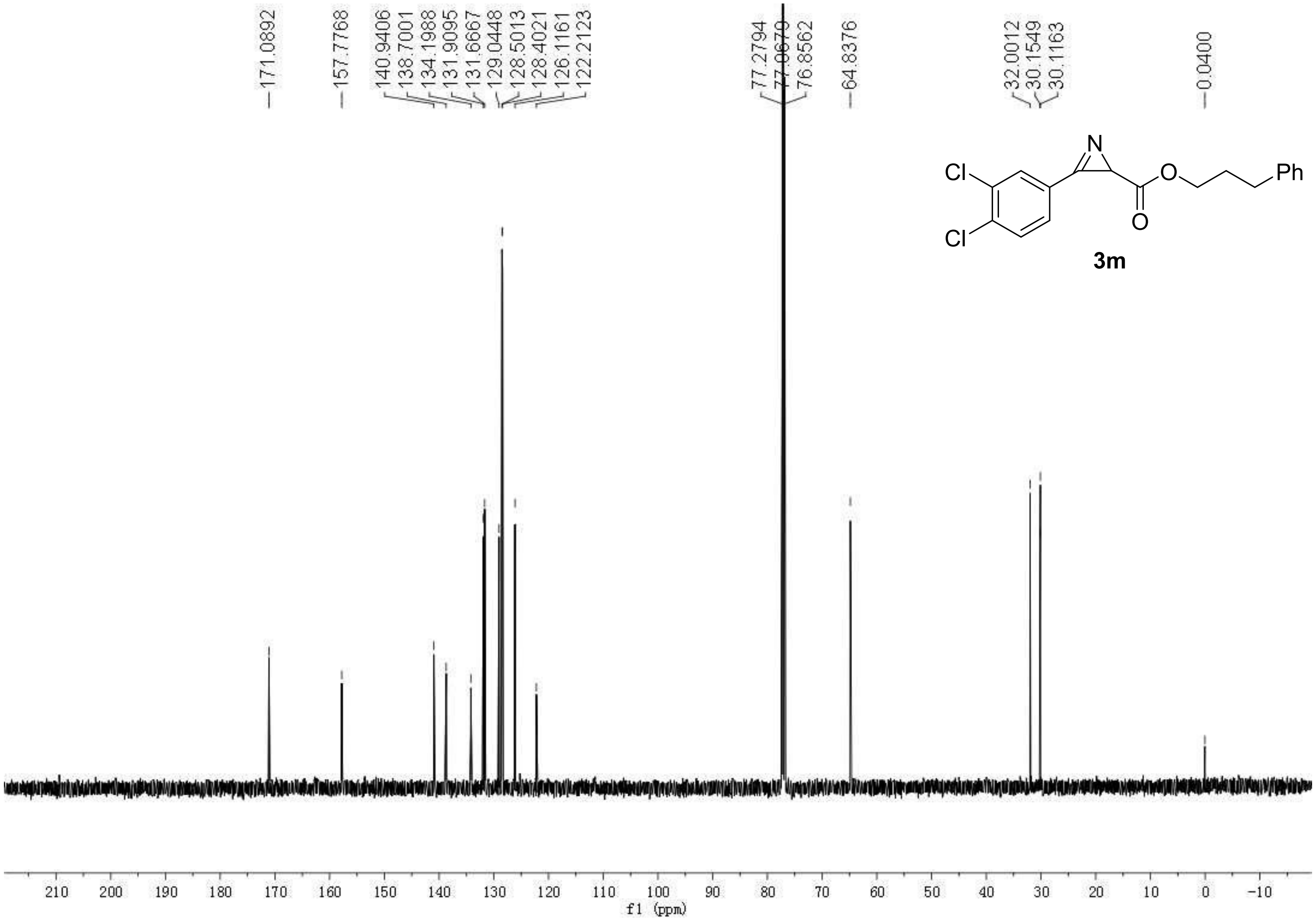
7.2709
7.2590
7.2093
7.1970
7.1847
7.1563
7.1444
4.2153
4.2043
4.1971
4.1934
4.1861
4.1755
4.1651
4.1576
4.1542
4.1469
4.1360
2.9030
2.6784
2.6661
2.6527
2.0002
1.9892
1.9779
1.9752
1.9637
1.9526
0.0000
Cl
Cl
N
O
O
Ph
3m
1.00
1.04
1.04
2.10
1.07
2.07
2.12
1.01
2.10
2.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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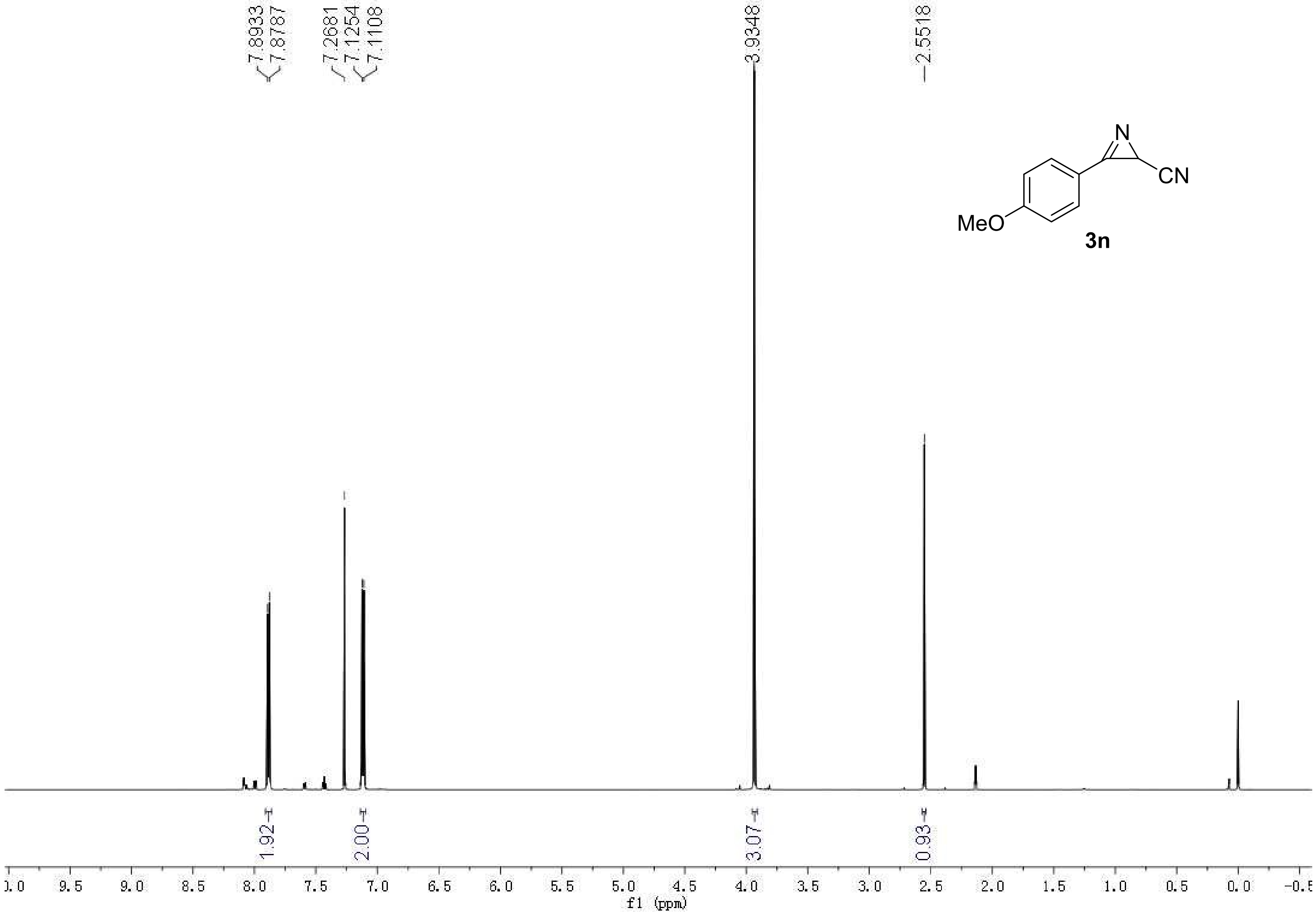
128.4021
126.1161
122.2123
77.2794
77.0679
76.8562
64.8376
32.0012
30.1549
30.1163
0.0400
N
Cl
Cl
O
O
Ph
3m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.2681
7.1254
7.1108
3.9348
2.5518
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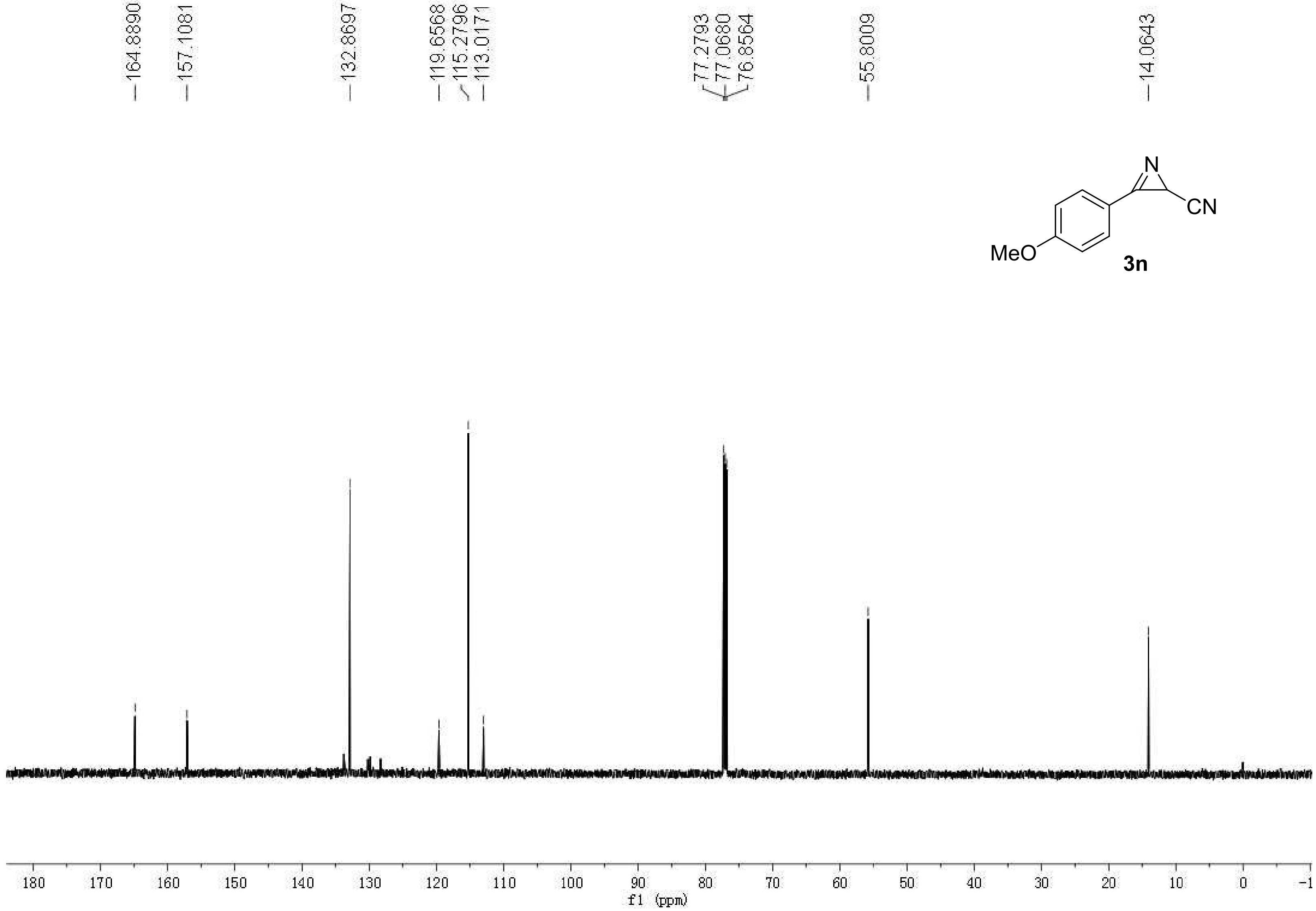
CN
MeO
3n
1.92
2.00
3.07
0.93
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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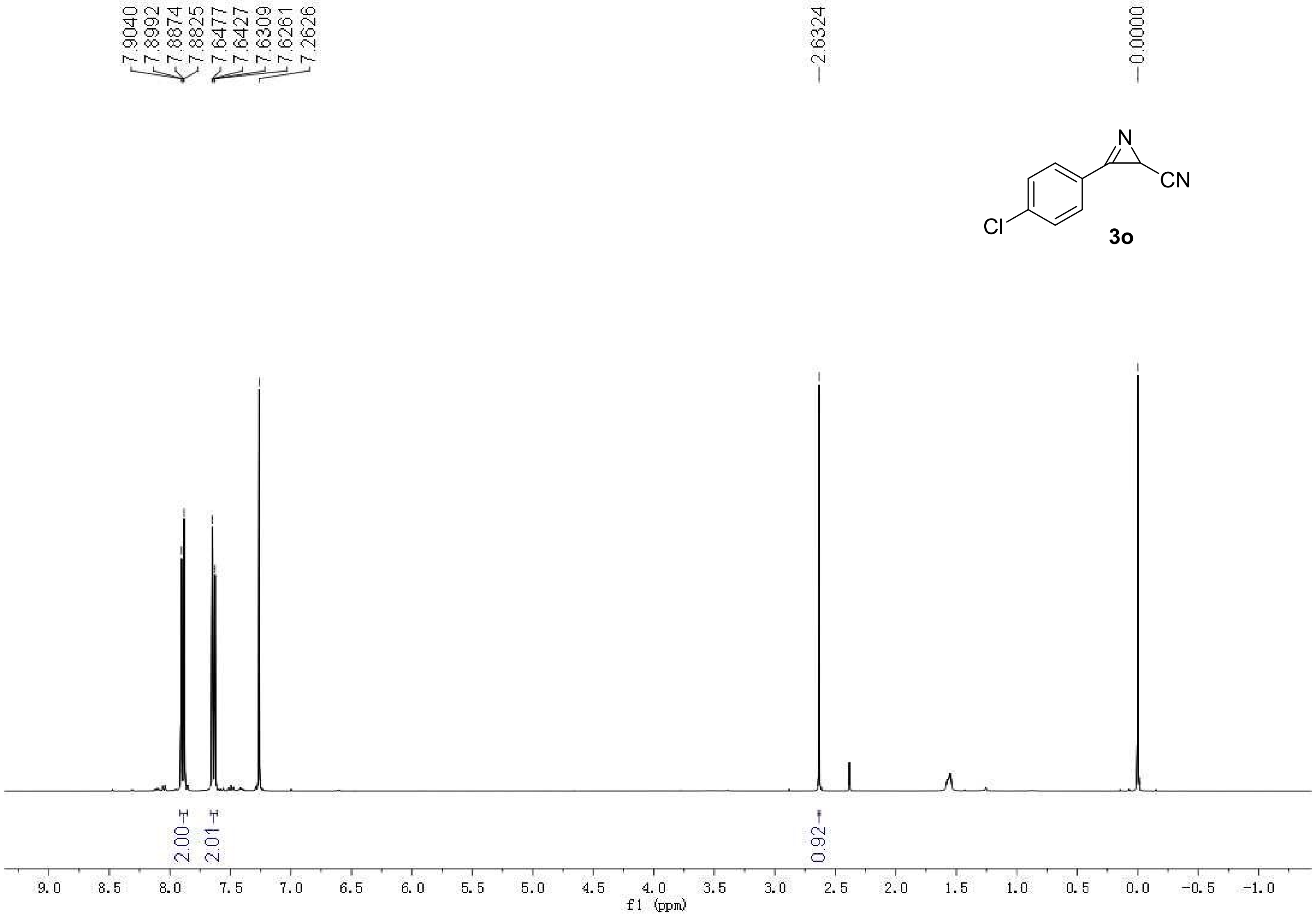
115.2796
113.0171
77.2793
77.0680
76.8564
55.8009
14.0643
N
CN
MeO
3n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)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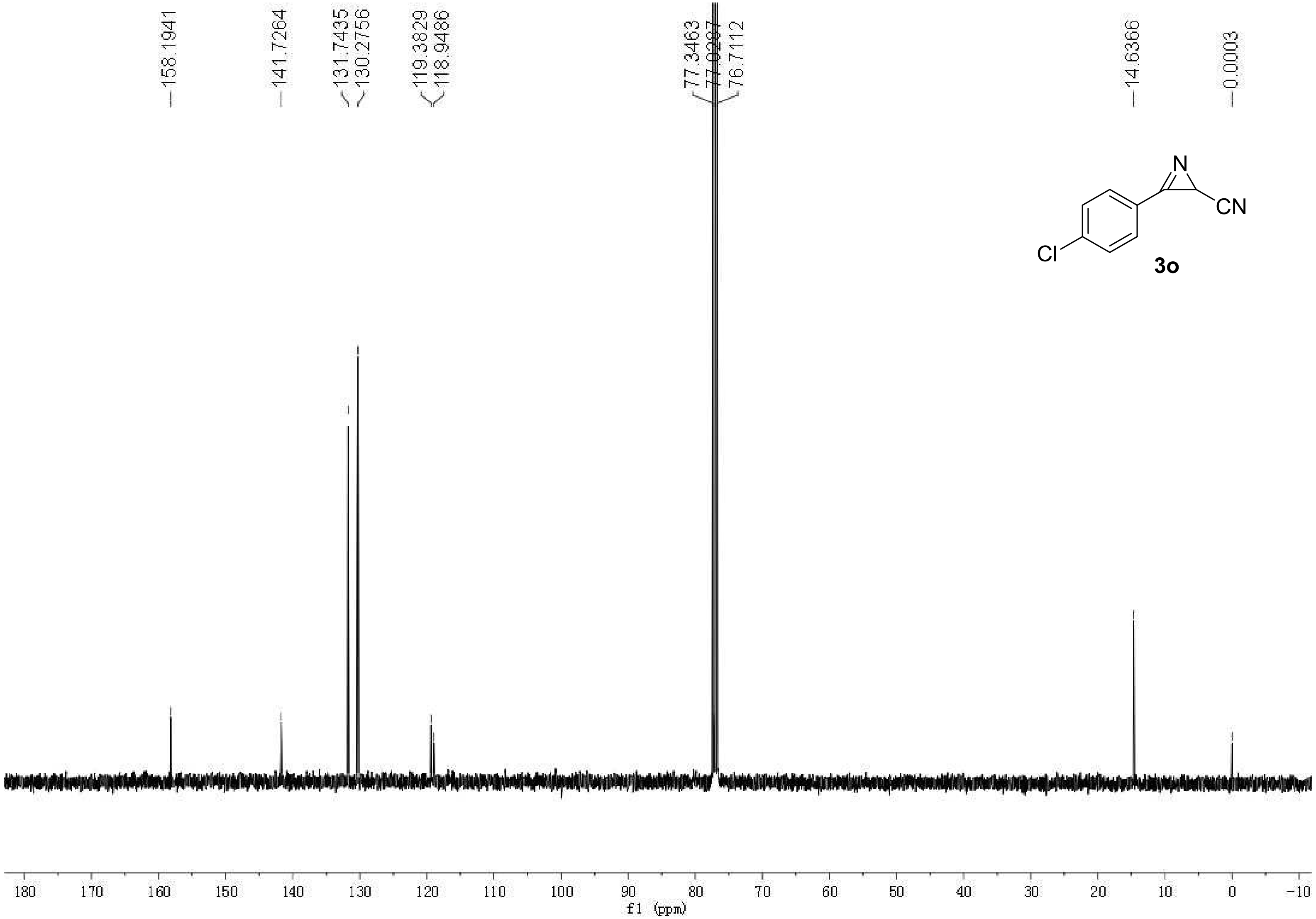
7.8874
7.8825
7.6477
7.6427
7.6309
7.6261
7.2626
2.6324
0.0000
N
CN
Cl
3o
2.00
2.01
0.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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76.7112
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0.0003
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CN
Cl
3o
180
170
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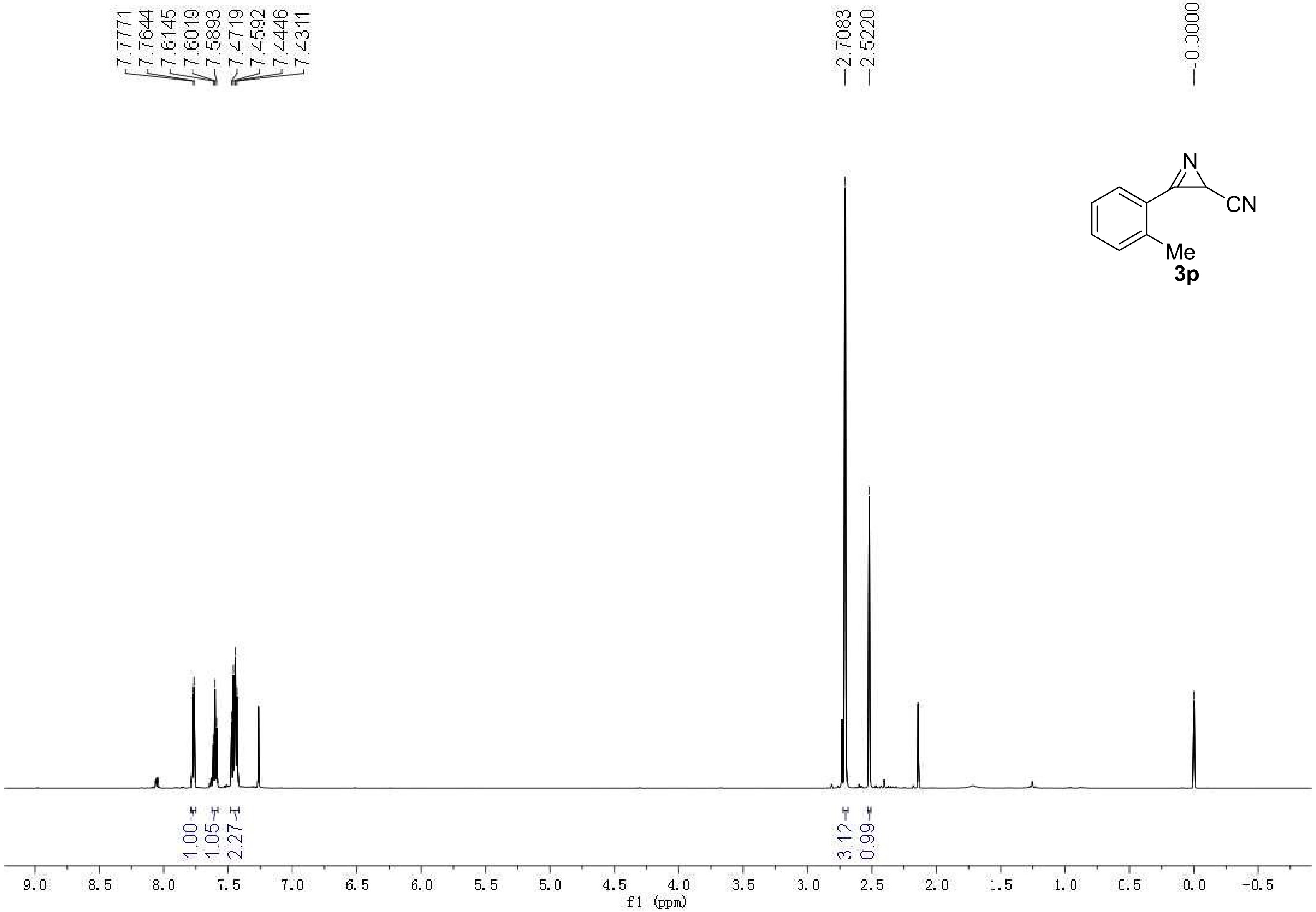
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.5893
7.4719
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7.4311
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2.5220
0.0000
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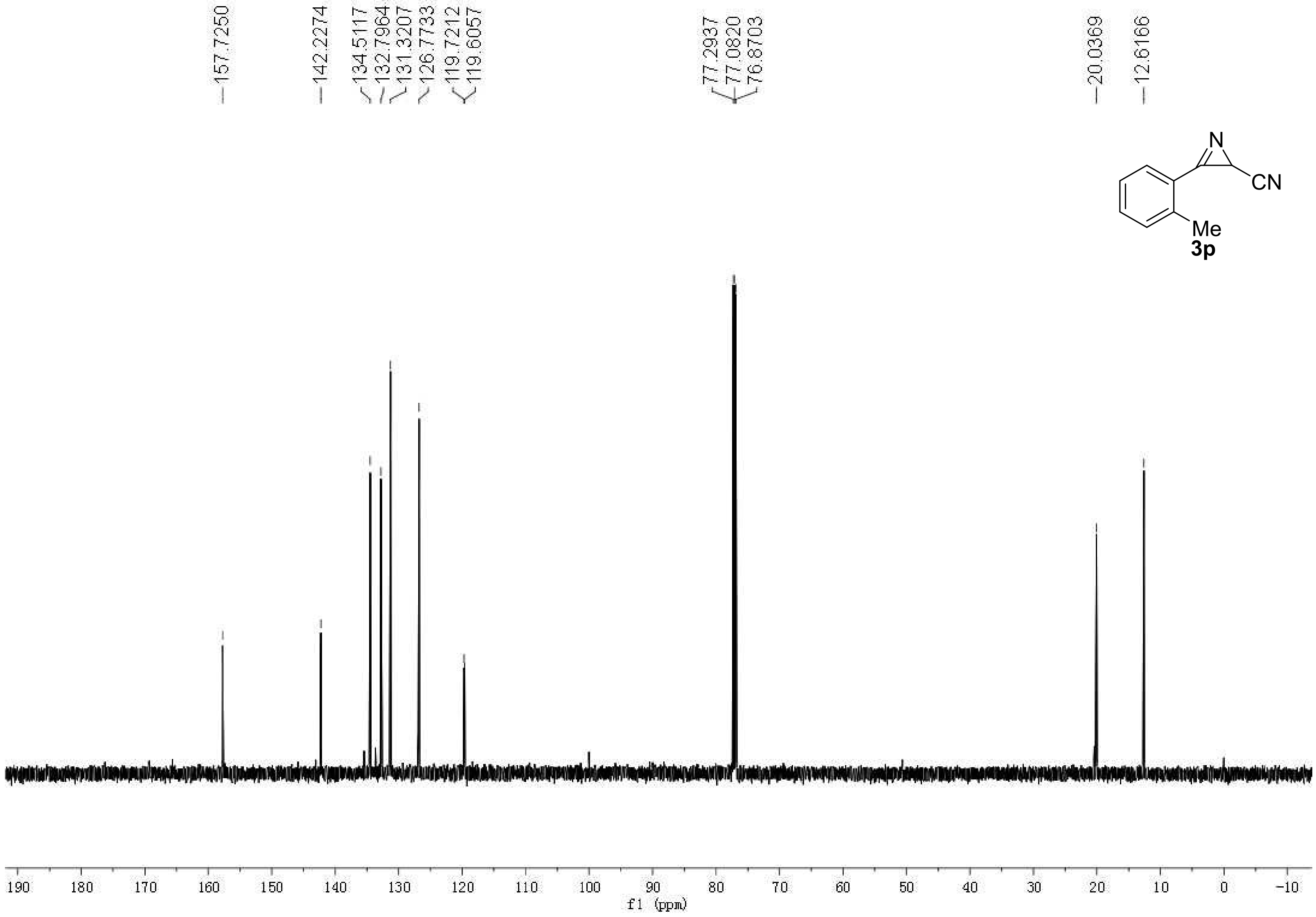
CN
Me
1.00
1.05
2.27
3.12
0.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3p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132.7964
131.3207
126.7733
119.7212
119.6057
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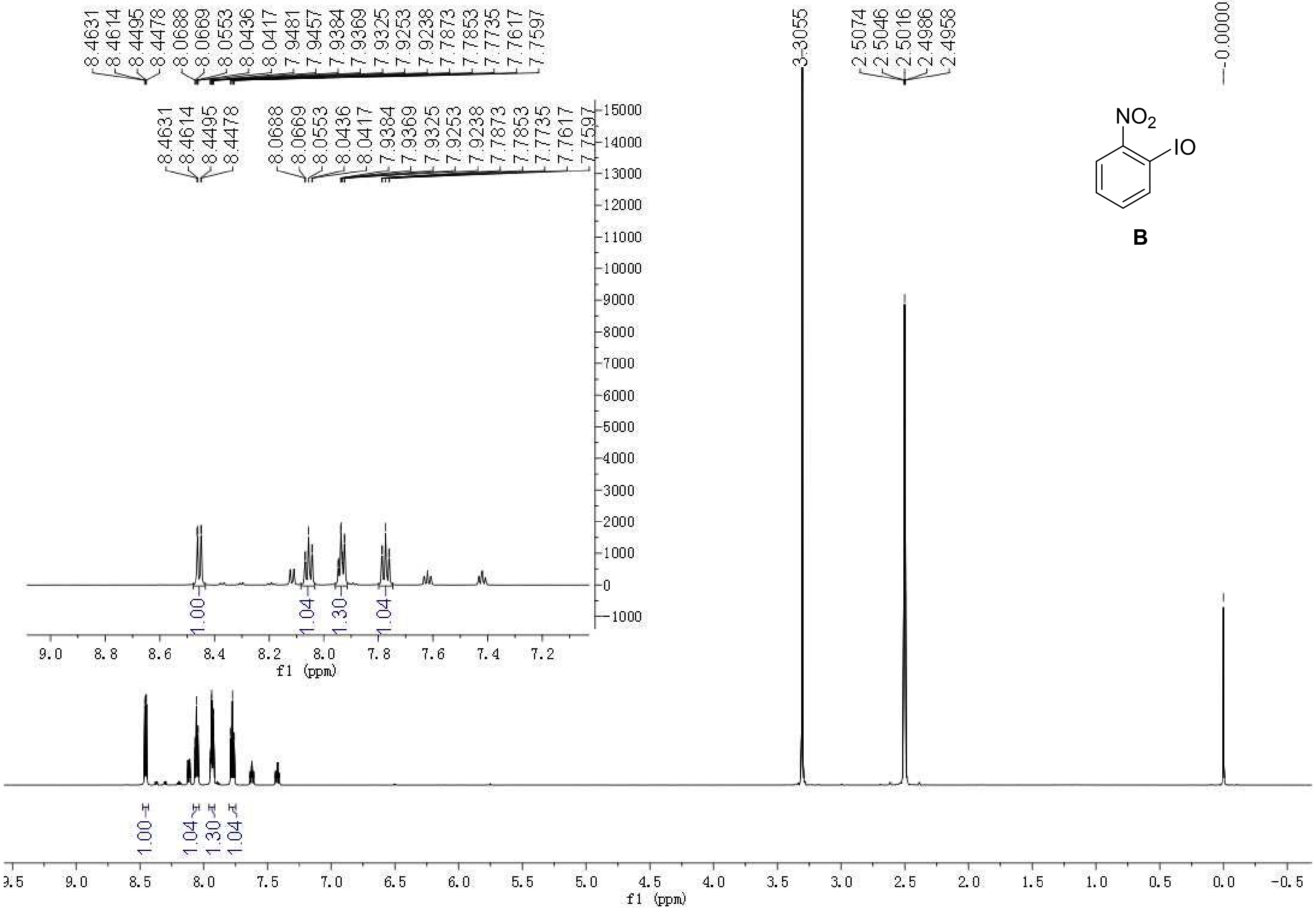
77.0820
76.8703
20.0369
12.6166
N
CN
Me
3p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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8.4478
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8.0553
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8.0417
7.9481
7.9457
7.9384
7.9369
7.9325
7.9253
7.9238
7.7873
7.7853
7.7735
7.7617
7.7597
3.3055
2.5074
2.5046
2.5016
2.4986
2.4958
0.0000
NO2
IO
1.00
1.04
1.30
1.04
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

B

7. X-ray Structure and Data of Iodine(III/V) 1

checkCIF (basic structural check) running

Checking for embedded fcf data in CIF ...
*Found embedded fcf data in CIF. Extracting fcf data from uploaded CIF, please wait***.**

checkCIF/PLATON (basic structural check)

Structure factors have been supplied for datablock(s) Iodine(III/V) **1**

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report
Structure factor report

Datablock: Iodine(III/V) 1

Bond precision: C-C = 0.0203 A Wavelength=1.54184

Cell:	a=8.2007(5)	b=7.7793(5)	c=24.6164(18)
	alpha=90	beta=90	gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1570.42(18)	1570.42(18)
Space group	P n a 21	P n a 21
Hall group	P 2c -2n	P 2c -2n
Moiety formula	C12 H8 I2 N2 O7	C12 H8 I2 N2 O7
Sum formula	C12 H8 I2 N2 O7	C12 H8 I2 N2 O7
Mr	546.00	546.00

Dx,g cm-3	2.309	2.309
Z	4	4
Mu (mm-1)	31.828	31.828
F000	1024.0	1024.0
F000'	1025.33	
h,k,lmax	10,9,30	10,9,30
Nref	3196[1637]	2485
Tmin,Tmax	0.453,0.705	0.116,0.808
Tmin'	0.032	

Correction method= # Reported T Limits: Tmin=0.116 Tmax=0.808 AbsCorr = GAUSSIAN

Data completeness= 1.52/0.78 Theta(max)= 73.913

R(reflections)= 0.0538(2048) wR2(reflections)= 0.1334(2485)

S = 1.100 Npar= 184

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT342_ALERT_3_B Low Bond Precision on C-C Bonds .... 0.02033 Ang.

Author response: Bond precision depends on following factors: 1) data parameter ratio; 2) the inverse of the normal matrix of least square; 3) the residual between observed and calculated intensities; 4) the accuracy of the cell constants.

In this case, the alert is mainly caused by the third factor. The observed intensities might still be affected by both extremely strong absorbers (mu = 31 mm-1) and small needle-shaped sample (0.01 x 0.02 x 0.10 mm^3), though the numerical and empirical absorption correction were applied; crystal structure model affected by high thermal vibration might induce a low precision of C-C bond lengths, for the data was collected at room temperature.

Alert level C

PLAT213_ALERT_2_C Atom O1 has ADP max/min Ratio ..... 3.1 prolat

PLAT234_ALERT_4_C Large Hirshfeld Difference O2 --N2 . 0.22 Ang.

PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N1 Check

Author response: See above response (PLAT342_ALERT_3_B). The abnormal behavior in ADP was caused by both the poor-quality dataset and high thermal motion of the atoms.

PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 7 Report

Author response: Missing data probably due to the skip region of detector.

PLAT915_ALERT_3_C No Flack x Check Done: Low Friedel Pair Coverage 59 %

Author Response: This alert is due to limitations of the data-collection strategy suggested by the CrysAlipro software (version 171.39,45g). A Friedel pair coverage of 59% was obtained; The Flack x parameter was -0.03 (3), indicating that the absolute structure of the system has been correctly determined because of the presence of the heavy atom (Iodine).

PLAT971_ALERT_2_C Check Calcd Resid. Dens. 0.92A From I2 1.51 eA-3

Author response: The alert is caused by Fourier termination error.

PLAT975_ALERT_2_C Check Calcd Resid. Dens. 0.86A From O7 0.61 eA-3
And 2 other PLAT975 Alerts
More ...

Author response: The alert is mainly caused by poor-quality dataset.

PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density. 0 Info

Author response: The alert is due to the poor-quality dataset and inferior structure model. For an accurately determined structure, bond densities on C-C bonds should be observed.

Alert level G

PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 8.70 Why ?

Author response: High WGHT indicates the significant systematic errors in the dataset and crystal structure. This Alert is probably due to both the poor-quality dataset and the presence of large residual densities in the presence of heavy atom (Iodine).

PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K) 293 Check
PLAT200_ALERT_1_G Reported _diffrn_ambient_temperature ..... (K) 293 Check

Author response: Data were processed after some time: when we realized that the data were collected at room temperature. Crystals were no more available.

PLAT431_ALERT_2_G Short Inter HL..A Contact I1 ..O6 . 2.70 Ang.
-1/2+x,3/2-y,z = 3_465 Check
PLAT431_ALERT_2_G Short Inter HL..A Contact I2 ..O7 . 2.53 Ang.
1/2+x,3/2-y,z = 3_565 Check

Author response: The intermolecular iodine --- oxygen bond distance reported is acceptable based on the bond length distribution of iodine --- oxygen bond, which was derived from derived from the Cambridge Structural Database.

PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 71 Note

Author response: This alert results from detector edge cut off. The reflections located on the edge of the detector were removed in order to avoid inaccurate integration of reflection intensities.

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
10 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
10 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

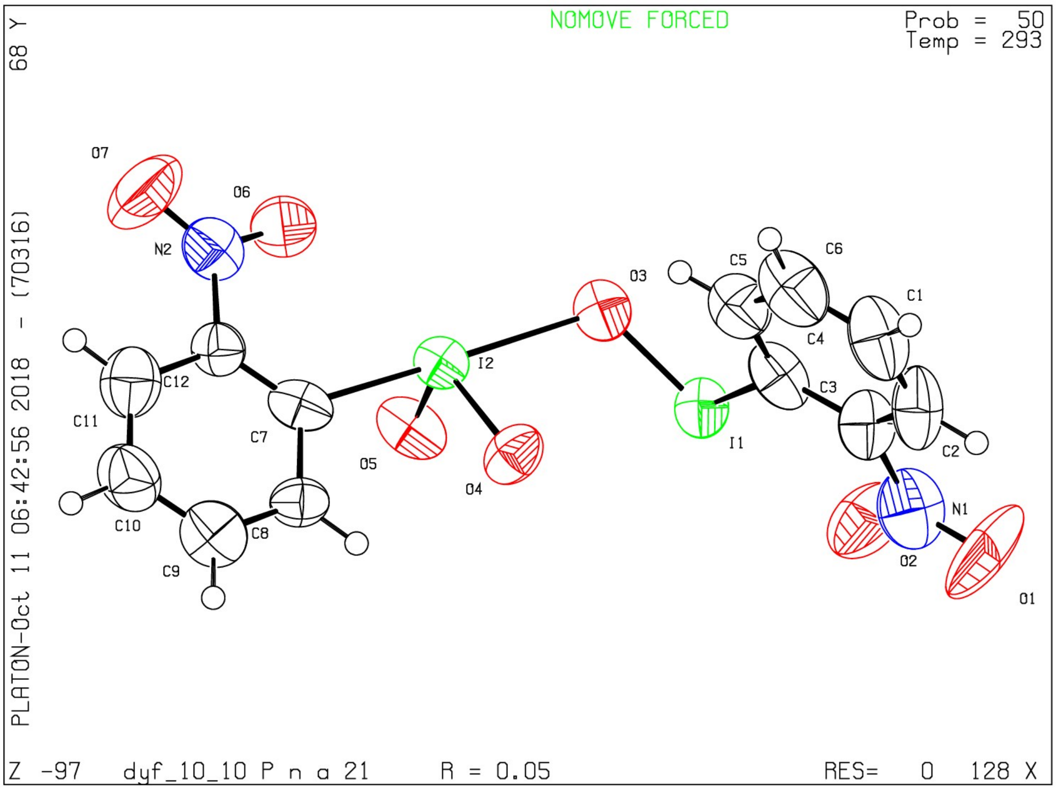
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock Iodine(III/V) 1 - ellipsoid plot



Iodine(III/V) 1

Table 3 Crystal data and structure refinement for Iodine(III/V) 1.

Identification code	Iodine(III/V) 1
Empirical formula	$C_{12}H_8I_2N_2O_7$
Formula weight	546.00
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	8.2007(5)
b/Å	7.7793(5)
c/Å	24.6164(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1570.42(18)
Z	4
ρ_{calc}g/cm^3	2.309

μ/mm^{-1}	31.828
F(000)	1024.0
Crystal size/mm^3	0.107 × 0.022 × 0.011
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.182 to 147.826
Index ranges	$-8 \leq h \leq 10$, $-8 \leq k \leq 9$, $-30 \leq l \leq 28$
Reflections collected	5347
Independent reflections	2485 [R_{int} = 0.0583, R_{sigma} = 0.0734]
Data/restraints/parameters	2485/1/184
Goodness-of-fit on F^2	1.100
Final R indexes [I>=2σ (I)]	R_1 = 0.0538, wR_2 = 0.1263
Final R indexes [all data]	R_1 = 0.0668, wR_2 = 0.1335
Largest diff. peak/hole / e Å^{-3}	1.72/-1.00
Flack parameter	-0.01(3)

Table 4 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Iodine(III/V) 1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
I2	3738.0(14)	7292.8(13)	5622.6(8)	46.0(3)
I1	1876.6(16)	9468.8(17)	4437.7(7)	57.0(4)
O3	4220(30)	7880(20)	6728(8)	79(5)
O7	1654(17)	6694(18)	5726(8)	69(5)
O5	2801(19)	9820(20)	5117(7)	62(4)
N1	5040(30)	6660(30)	6914(9)	65(5)
O6	4124(19)	6370(20)	4976(7)	62(4)
O4	5710(40)	6720(30)	7349(9)	119(9)
O2	1310(30)	9330(30)	3383(10)	105(7)
C6	4053(17)	9930(20)	3996(6)	63(6)
C5	5490(20)	10240(20)	4277(5)	74(8)
C4	6936(17)	10510(20)	3995(8)	88(9)
C3	6941(17)	10470(20)	3430(8)	85(9)
C2	5500(20)	10160(20)	3148(5)	81(9)

C1	4058(17)	9890(20)	3431(6)	65(6)
N2	2580(30)	9500(40)	3106(12)	89(7)
C12	4638(17)	5096(13)	6055(5)	53(5)
C7	5155(19)	5126(16)	6593(5)	52(5)
C8	5740(20)	3630(20)	6836(5)	78(8)
C9	5800(20)	2111(16)	6541(7)	83(8)
C10	5280(20)	2080(14)	6004(7)	73(7)
C11	4701(18)	3573(17)	5760(5)	53(5)
O1	2630(40)	9450(50)	2631(8)	142(12)

Table 5 Anisotropic Displacement Parameters (Å^2×10^3) for Iodine(III/V) 1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I2	29.1(5)	51.3(6)	57.6(6)	0.3(8)	2.3(6)	1.3(4)
I1	48.2(7)	65.2(8)	57.6(7)	7.0(8)	0.5(9)	1.7(6)
O3	112(16)	58(10)	69(11)	-16(9)	13(11)	15(10)
O7	46(8)	54(8)	107(15)	4(9)	8(9)	3(6)
O5	55(10)	65(9)	67(10)	7(8)	1(8)	2(7)
N1	65(13)	61(12)	69(13)	-1(10)	21(11)	0(10)
O6	58(9)	72(9)	56(8)	-6(7)	-11(7)	19(7)
O4	170(20)	123(18)	65(13)	-29(13)	-28(16)	34(17)
O2	78(14)	150(20)	87(16)	-8(14)	-27(12)	-5(14)
C6	49(14)	56(12)	83(17)	12(11)	25(13)	8(10)
C5	66(16)	65(15)	90(20)	10(13)	-9(14)	5(12)
C4	64(17)	77(18)	120(30)	26(18)	2(18)	8(14)
C3	50(15)	92(19)	110(20)	39(18)	26(17)	6(14)
C2	80(20)	91(19)	71(17)	30(15)	11(17)	34(17)
C1	47(14)	80(16)	67(16)	16(12)	18(12)	12(11)

N2	69(15)	107(19)	91(19)	10(15)	24(14)	8(13)
C12	27(10)	49(11)	83(16)	-6(10)	4(10)	-1(8)
C7	47(12)	48(11)	61(13)	-1(9)	1(11)	10(9)
C8	73(18)	86(18)	77(18)	13(15)	-5(15)	8(15)
C9	90(20)	59(15)	100(20)	10(14)	4(17)	15(14)
C10	58(16)	68(15)	92(19)	-1(14)	10(14)	20(12)
C11	51(12)	52(11)	56(13)	-12(9)	4(10)	3(9)
O1	140(20)	260(40)	29(10)	-22(14)	4(11)	-10(20)

Table 6 Bond Lengths for Iodine(III/V) 1.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
I2	O7	1.790(14)		C5	C4	1.3900
I2	O5	2.448(15)		C4	C3	1.3900
I2	O6	1.776(16)		C3	C2	1.3900
I2	C12	2.145(10)		C2	C1	1.3900
I1	O5	1.856(17)		C1	N2	1.49(3)
I1	C6	2.120(12)		N2	O1	1.17(3)
O3	N1	1.25(3)		C12	C7	1.3900
N1	O4	1.21(3)		C12	C11	1.3900
N1	C7	1.44(2)		C7	C8	1.3900
O2	N2	1.25(3)		C8	C9	1.3900
C6	C5	1.3900		C9	C10	1.3900
C6	C1	1.3900		C10	C11	1.3900

Table 7 Bond Angles for Iodine(III/V) 1.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O7	I2	O5	88.9(6)		C1	C2	C3	120.0
O7	I2	C12	92.9(6)		C6	C1	N2	122.7(15)
O6	I2	O7	101.1(8)		C2	C1	C6	120.0
O6	I2	O5	85.8(7)		C2	C1	N2	117.3(15)
O6	I2	C12	93.4(6)		O2	N2	C1	114(2)
C12	I2	O5	178.1(6)		O1	N2	O2	125(3)
O5	I1	C6	95.4(7)		O1	N2	C1	121(3)
I1	O5	I2	118.0(8)		C7	C12	I2	124.3(7)
O3	N1	C7	118(2)		C7	C12	C11	120.0
O4	N1	O3	123(2)		C11	C12	I2	115.7(7)
O4	N1	C7	119(2)		C12	C7	N1	121.2(13)
C5	C6	I1	119.2(9)		C12	C7	C8	120.0
C5	C6	C1	120.0		C8	C7	N1	118.7(13)
C1	C6	I1	120.8(9)		C9	C8	C7	120.0
C6	C5	C4	120.0		C8	C9	C10	120.0
C3	C4	C5	120.0		C11	C10	C9	120.0
C4	C3	C2	120.0		C10	C11	C12	120.0

Table 8 Torsion Angles for Iodine(III/V) 1.

A	B	C	D	Angle/°		A	B	C	D	Angle/°
I2	C12	C7	N1	3.5(17)		C5	C6	C1	N2	177.9(19)
I2	C12	C7	C8	-179.3(11)		C5	C4	C3	C2	0.0
I2	C12	C11	C10	179.4(10)		C4	C3	C2	C1	0.0
I1	C6	C5	C4	178.9(11)		C3	C2	C1	C6	0.0
I1	C6	C1	C2	-178.8(11)		C3	C2	C1	N2	-178.0(18)
I1	C6	C1	N2	-1.0(18)		C2	C1	N2	O2	-178(2)
O3	N1	C7	C12	11(3)		C2	C1	N2	O1	-1(4)
O3	N1	C7	C8	-165.8(17)		C1	C6	C5	C4	0.0
N1	C7	C8	C9	177.2(16)		C12	C7	C8	C9	0.0
O4	N1	C7	C12	-169(2)		C7	C12	C11	C10	0.0

O4	N1	C7	C8	14(3)		C7	C8	C9	C10	0.0
C6	I1	O5	I2	-95.7(8)		C8	C9	C10	C11	0.0
C6	C5	C4	C3	0.0		C9	C10	C11	C12	0.0
C6	C1	N2	O2	4(3)		C11	C12	C7	N1	-177.2(17)
C6	C1	N2	O1	-179(3)		C11	C12	C7	C8	0.0
C5	C6	C1	C2	0.0						

Table 9 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Iodine(III/V) 1.

Atom	*x*	*y*	*z*	U(eq)
H5	5488.27	10263.95	4655.1	88
H4	7898.78	10718.51	4183.17	106
H3	7907.77	10653.41	3240.94	101
H2	5506.24	10133.75	2770.64	97
H8	6082.22	3654.91	7195.37	94
H9	6187.29	1112.95	6703.75	100
H10	5323.26	1061.47	5806.47	87
H11	4354.17	3551.95	5400.8	64