Supporting Information

Radical Borylation of Vinyl Azides with NHC–Boranes:

Divergent Synthesis of α-Boryl Ketones and Borylated Triazoles

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1. General information

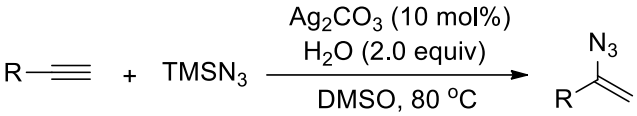
Solvents were purchased from commercial suppliers and used without further purification unless otherwise noted. Commercially available chemicals were obtained from commercial suppliers and used as received without further purification unless otherwise stated.

All reactions were monitored by thin-layer chromatography (TLC) with Huanghai GF254 silica gel coated plates. TLC plates were visualized by exposure to ultraviolet light, and/or staining with the mixture of iodine/silica gel or the solvent of potassium permanganate. Purification of reaction products were carried out by flash chromatography using silica gel (Qingdao Haiyang Co. Ltd, 200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on an Agilent DD2 400-MR or Brucker AV-400 spectrometer at ambient temperature. The chemical shifts for ^{1}H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard (7.26 ppm for $CDCl_3$). The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of $CDCl_3$ (77.00 ppm). Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), quarter (q), triplet (t) and broad (br). High-resolution mass spectra (HRMS) were performed on a Thermo Q Exactive Plus mass instrument (ESI). Melting points (°C) are uncorrected and were recorded on a SGW X-4 apparatus.

No attempts were made to optimize yields for substrate synthesis.

2. Synthesis and characterization of vinyl azides and NHC-boranes

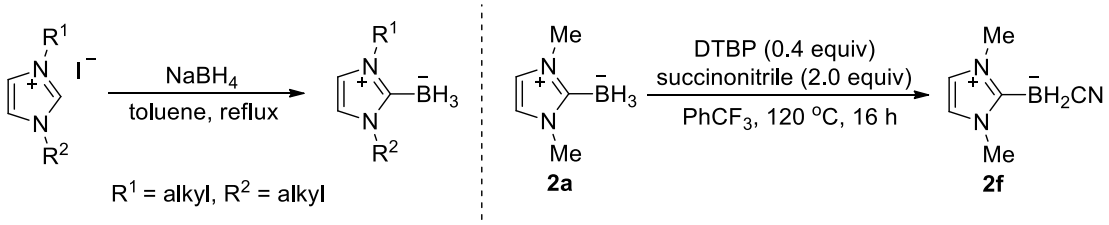
2.1 Typical procedure for the synthesis of vinyl azides[1] (Scheme S1)



The synthesis of vinyl azides **1a**: To a stirred solution of phenylacetylene (0.33 mL, 3.0 mmol), $TMSN_3$ (0.80 mL, 6.0 mmol) and H_2O (0.11 mL, 6.0 mmol) in diemthyl sulfoxide (DMSO) (12 mL) at 80 °C, Ag_2CO_3 (82.7 mg, 0.3 mmol) was added. The mixture was then stirred for 1.0 h (TLC tracking detection). The resulting mixture was cooled to room temperature, diluted with H_2O, and extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude product with flash column chromatography on silica gel (petroleum ether) afforded the desired product as a pale brown oil (296.3 mg, 68% yield).

Other vinyl azides (**1b**-**1ll**) were synthesized according to the procedure described for **1a**. Among them, vinyl azides (**1u** & **1jj**-**1ll**) were new compounds and their spectroscopic data are shown in this supporting information.

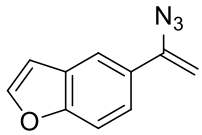
2.2 Synthesis of NHC-boranes (Scheme S2)



NHC-boranes **2a**-**2f** were known compound and prepared according to literature reported procedures.[2]

2.3 The spectroscopic data of new substrates

5-(1-Azidovinyl)benzofuran **(1u)**

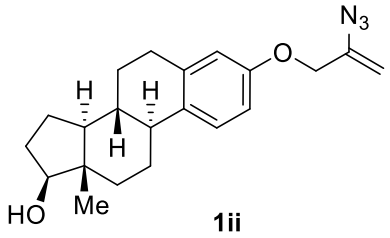


1u

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.51 – 7.44 (m, 2H), 6.76 (dd, *J* = 2.1, 0.8 Hz, 1H), 5.39 (d, *J* = 2.3 Hz, 1H), 4.94 (d, *J* = 2.3 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.3, 145.8, 145.2, 129.4, 127.5,

122.2, 118.7, 111.3, 106.8, 97.4; **HRMS (ESI)** calcd for $C_{10}H_8N_3O^+$ ([M + H]$^+$): 186.0662, found 186.0665.

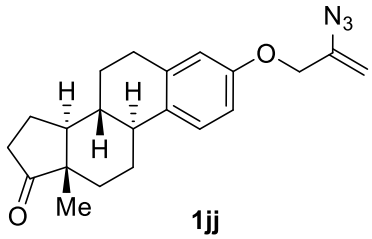
(8*R*,9*S*,13*S*,14*S*,17*S*)-3-((2-Azidoallyl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-17-ol (**1ii**)



1ii

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.7 Hz, 1H), 6.73 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.66 (d, *J* = 2.3 Hz, 1H), 5.03 (d, *J* = 1.7 Hz, 1H), 4.89 (d, *J* = 1.7 Hz, 1H), 4.43 (s, 2H), 3.76 – 3.71 (m, 1H), 2.87 – 2.83 (m, 2H), 2.34 – 2.28 (m, 1H), 2.22 – 2.08 (m, 2H), 1.97 – 1.85 (m, 2H), 1.74 – 1.66 (m, 1H), 1.54 – 1.16 (m, 7H), 0.78 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.7, 142.1, 138.1, 133.5, 126.4, 114.8, 112.2, 100.9, 81.89, 67.69, 50.0, 43.9, 43.2, 38.7, 36.6, 30.5, 29.7, 27.1, 26.2, 23.1, 11.0; **HRMS (ESI)** calcd for $C_{21}H_{28}N_3O_2^+$ ([M + H]$^+$): 354.2176, found 354.2183.

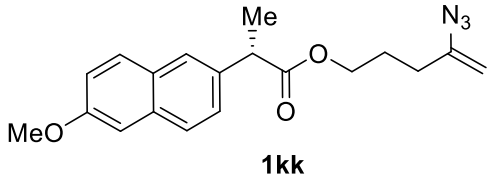
(8*R*,9*S*,13*S*,14*S*)-3-((2-Azidoallyl)oxy)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[a]phenanthren-17(14*H*)-one (**1jj**)



1jj

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 1H), 6.74 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.67 (d, *J* = 2.7 Hz, 1H), 5.03 (d, *J* = 1.5 Hz, 1H), 4.89 (d, *J* = 1.7 Hz, 1H), 4.43 (s, 2H), 2.91 – 2.88 (m, 2H), 2.41 – 2.37 (m, 1H), 2.44 – 2.34 (m, 1H), 2.28 – 2.23 (m, 1H), 2.18 – 2.11 (m, 1H), 2.07 – 1.94 (m, 3H), 1.67 – 1.42 (m, 6H), 0.91 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 220.8, 155.9, 142.1, 137.9, 133.0, 126.4, 115.0, 112.4, 100.9, 67.7, 50.4, 48.0, 44.0, 38.3, 35.8, 31.6, 29.6, 26.5, 25.9, 21.6, 13.8; **HRMS (ESI)** calcd for $C_{21}H_{26}N_3O_2^+$ ([M + H]$^+$): 352.2020, found 352.2025.

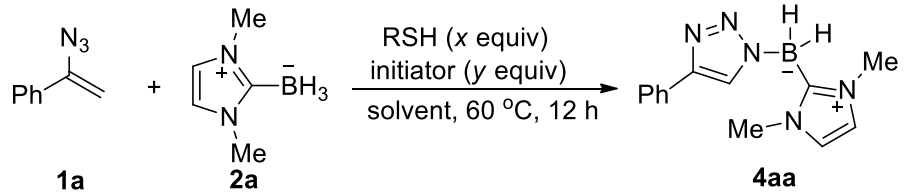
(*S*)-4-Azidopent-4-en-1-yl 2-(6-methoxynaphthalen-2-yl)propanoate (**1kk**)



1kk

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 1.4 Hz, 1H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.15 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 4.57 (d, *J* = 1.6 Hz, 1H), 4.50 (d, *J* = 1.4 Hz, 1H), 4.09 (t, *J* = 6.3 Hz, 2H), 3.91 (s, 3H), 3.86 (q, *J* = 7.2 Hz, 1H), 1.99 (t, *J* = 7.5 Hz, 2H), 1.78 – 1.72 (m, 2H), 1.58 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 174.6, 157.6, 145.5, 135.6, 133.7, 129.2, 128.9, 127.1, 126.2, 125.9, 119.0, 105.6, 98.6, 63.4, 55.3, 45.4, 30.1, 26.2, 18.4; **HRMS (ESI)** calcd for $C_{19}H_{22}N_3O_3^+$ ([M + H]$^+$): 340.1656, found 340.1658.

3. Table S1. Optimization of conditions for the synthesis of 4aa[a]



1a **2a** **4aa**

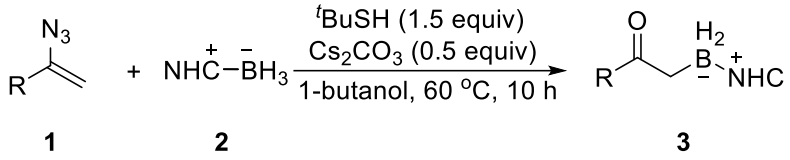
Entry	RSH (*x* equiv)	Initiator (*y* equiv)	Solvent	Yield[b] (%)
1	*tert*-dodecanethiol (1.0)	—	CH_3CN	28
2	TRIP thiol (1.0)	—	CH_3CN	0
3	^{t}BuSH (1.0)	—	CH_3CN	37
4	^{i}Pr$_3$SiSH (1.0)	—	CH_3CN	7
5	^{t}BuSH (1.0)	—	THF	24
6	^{t}BuSH (1.0)	—	CH_3OH	41
7	^{t}BuSH (1.0)	—	DCE	28
8	^{t}BuSH (1.0)	—	toluene	25
9	^{t}BuSH (1.0)	—	DMF	21
10	^{t}BuSH (1.0)	AIBN (1.0)	CH_3OH	50
11	^{t}BuSH (1.0)	DTBP (1.0)	CH_3OH	30
12[c]	^{t}BuSH (1.0)	AIBN (1.0)	CH_3OH	71
13[c]	^{t}BuSH (0.5)	AIBN (1.0)	CH_3OH	35
14[c]	^{t}BuSH (1.2)	AIBN (1.0)	CH_3OH	61
15[c,e]	^{t}BuSH (1.0)	AIBN (1.0)	CH_3OH	31
16[c,f]	^{t}BuSH (1.0)	AIBN (1.0)	CH_3OH	42
17[c]	**^{t}BuSH (1.0)**	**AIBN (1.2)**	**CH_3OH**	**75**
18[c]	^{t}BuSH (1.0)	AIBN (1.5)	CH_3OH	60
19[c]	—	AIBN (1.2)	CH_3OH	9

[a] Reaction conditions: **1a** (1.0 mmol, 2.0 equiv), **2a** (0.5 mmol, 1.0 equiv), RSH (*x* equiv), initiator (*y* equiv), solvent (5 mL), 60 °C, 12 h. [b] Isolated yield. [c] The reaction was carried out under an argon atmosphere. [e] The reaction was carried out at 50 °C. [f] The reaction was carried out at 70 °C. TRIP thiol = 2,4,6-triisopropyl-thiophenol.

4. General procedures for the synthesis of products

4.1 Procedure A: General procedure for the synthesis of α-NHC-boryl ketones 3

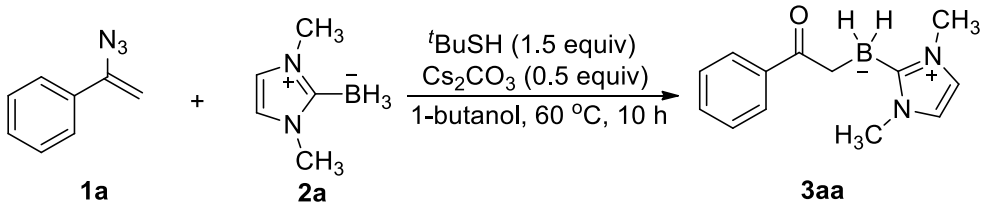
(Scheme S3)



1 **2** **3**

To an oven-dried 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar were added vinyl azide **1** (1.5 mmol, 3.0 equiv), NHC-BH_3 **2** (0.5 mmol, 1.0 equiv), ^{t}BuSH (85 μL, 0.75 mmol, 1.5 equiv), Cs_2CO_3 (81.5 mg, 0.25 mmol, 0.5 equiv), and 1-butanol (5 mL). After stirring at 60 °C for 10 h, the reaction mixture was concentrated under reduced pressure and the crude residue was purified by flash column chromatography (eluent: petroleum ether/EtOAc/Et_3N) on silica gel to afford the desired product **3**.

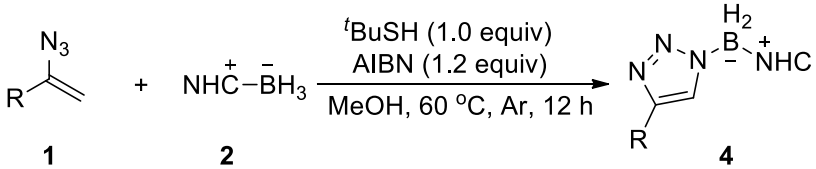
4.2 Procedure B: Gram-scale preparation of 3aa (Scheme S4)



1a **2a** **3aa**

To an oven-dried screw-cap 150 mL sealed tube equipped with a Teflon-coated magnetic stir bar were added vinyl azide **1a** (2.20 g, 15.2 mmol, 3.0 equiv), NHC-BH_3 **2a** (0.55 g, 5.0 mmol, 1.0 equiv), ^{t}BuSH (0.85 mL, 7.50 mmol, 1.5 equiv), Cs_2CO_3 (0.82 g, 2.5 mmol, 0.5 equiv), and 1-butanol (50 mL). After stirring at 60 °C for 10 h, the reaction mixture was concentrated under reduced pressure and the crude residue was purified by flash column chromatography (eluent: 1:1:0.01 petroleum ether/EtOAc/Et_3N) on silica gel to afford **3aa** (0.66 g, 58% yield) as a white solid.

4.3 Procedure C: General procedure for the synthesis of borylated triazoles 4 (Scheme S5)

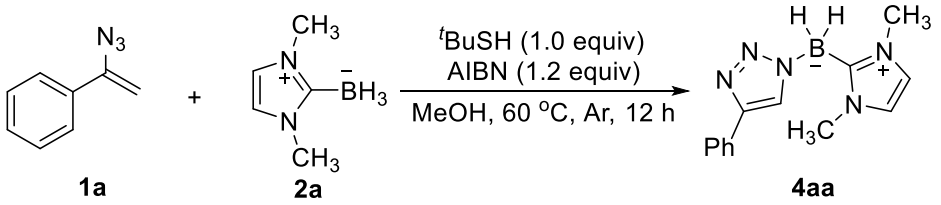


1 **2** **4**

To an oven-dried 25 mL Schlenk tube equipped with a Teflon-coated magnetic stir bar were added vinyl azide **1** (1.0 mmol, 2.0 equiv), NHC-BH_3 **2** (0.5 mmol, 1.0 equiv), AIBN (98.5 mg, 0.6 mmol, 1.2 equiv), and MeOH (5 mL). The tube was sealed with a rubber septum and cooled to -10 °C. Then the tube was evacuated and

backfilled with argon for 3 times. ^{t}BuSH (57 μL, 0.5 mmol, 1.0 equiv) was added via a syringe. After stirring at 60 °C for 12 h, the reaction mixture was concentrated under reduced pressure and the crude residue was purified by flash column chromatography (eluent: CH_2Cl_2/MeOH/Et_3N) on silica gel to afford the desired product **4**.

4.4 Procedure D: Gram-scale preparation of 4aa (Scheme S6)

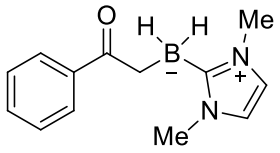


1a 2a 4aa

To an oven-dried screw-cap 150 mL sealed tube equipped with a Teflon-coated magnetic stir bar were added vinyl azide **1a** (1.45 g, 10.0 mmol, 2.0 equiv), NHC-BH_3 **2a** (0.55 g, 5.0 mmol, 1.0 equiv), AIBN (0.98 g, 6.0 mmol, 1.0 equiv), and methanol (50 mL). The tube was sealed with a rubber septum and cooled to -10 °C. Then the tube was evacuated and backfilled with argon for 3 times. ^{t}BuSH (0.56 mL, 5.0 mmol, 1.0 equiv) was added via a syringe. After stirring at 60 °C for 12 h, the reaction mixture was concentrated under reduced pressure and the crude residue was purified by flash column chromatography (eluent: 40:1:0.01 CH_2Cl_2/MeOH/Et_3N) on silica gel to afford **4aa** (0.70 g, 55% yield) as a white solid.

5. Characterization data of products

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-*oxo*-2-phenylethyl)dihydroborate (**3aa**)



3aa

Following the general procedure A, **1a** and **2a** were used. The crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3aa** as a white solid (76.6 mg, 67% yield). R_f = 0.55 (eluent: EtOAc). m.p. 91.1-91.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 6.77 (s, 2H), 3.61 (s, 6H), 2.46 (s, 2H).

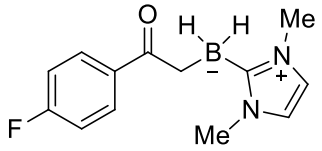
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.3, 138.0, 131.4, 128.4, 128.0, 120.4, 35.9.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.5 (t, *J* = 90.1 Hz).

HRMS (ESI) calcd for $C_{13}H_{17}BN_2NaO^+$ ([M + Na]$^+$): 251.13261, found 251.13184.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(4-fluorophenyl)-2-oxoethyl)dihydroborate

(**3ba**)



3ba

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3ba** as a colorless oil (72.1 mg, 59% yield). R_f = 0.53 (eluent: EtOAc).

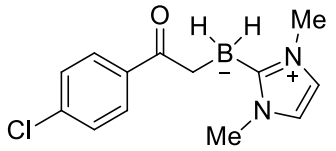
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.8, 5.7 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 6.78 (s, 2H), 3.61 (s, 6H), 2.41 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.7, 164.8 (d, *J* = 251.4 Hz), 134.2 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 9.0 Hz), 120.4, 114.8 (d, *J* = 21.4 Hz), 35.9.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.5 (t, *J* = 90.3 Hz).

HRMS (ESI) calcd for $C_{13}H_{16}BFN_2NaO^+$ ($[M + Na]^+$): 269.1232, found 269.1242.

(2-(4-Chlorophenyl)-2-oxoethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborat e (**3ca**)



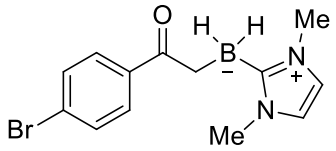
3ca

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3ca** as a white solid (62.7 mg, 48% yield). R_f = 0.59 (eluent: EtOAc). m.p. 96.2-98.1 °C. α-NHC-boryl ketone **3ca** is a known compound. Its characterization data is consistent with the reported data in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.79 (s, 2H), 3.61 (s, 6H), 2.41 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.8, 137.5, 136.2, 129.9, 128.2, 120.4, 35.9.

(2-(4-Bromophenyl)-2-oxoethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborat e (**3da**)



3da

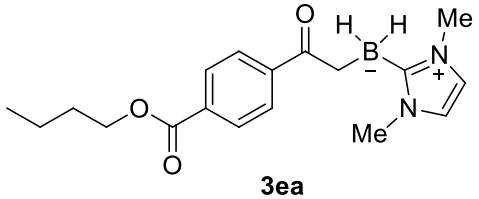
Following the general procedure A, the crude product was purified by flash column

chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3da** as a white solid (93.7 mg, 61% yield). R_f = 0.59 (eluent: EtOAc). m.p. 119.6-121.4 °C. α-NHC-boryl ketone **3da** is a known compound. Its characterization data is consistent with the reported data in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 6.79 (s, 2H), 3.61 (s, 6H), 2.41 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.9, 136.7, 131.1, 130.1, 126.2, 120.4, 35.9.

(2-(4-(Butoxycarbonyl)phenyl)-2-oxoethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**3ea**)



3ea

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3ea** as a white solid (68.6 mg, 42% yield). R_f = 0.66 (eluent: EtOAc). m.p. 72.6-73.5 °C.

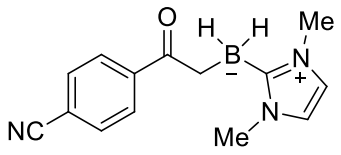
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 4H), 6.78 (s, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.61 (s, 6H), 2.48 (s, 2H), 1.80 – 1.73 (m, 2H), 1.53 – 1.44 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.3, 166.3, 141.4, 132.6, 129.2, 128.2, 120.4, 65.0, 35.9, 30.7, 19.2, 13.7.

^{11}B NMR (160 MHz, $CDCl_3$) δ -28.0 (t, *J* = 90.7 Hz).

HRMS (ESI) calcd for $C_{18}H_{25}BN_2NaO_3^+$ ([M + Na]$^+$): 351.1850, found 351.1861.

(2-(4-Cyanophenyl)-2-oxoethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**3fa**)



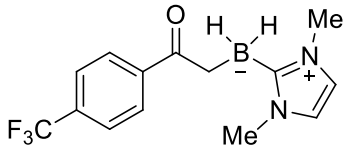
3fa

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3fa** as a white solid (67.4 mg, 54% yield). R_f = 0.58 (eluent: EtOAc). m.p. 113.5-114.8 °C. α-NHC-boryl ketone **3fa** is a known compound. Its characterization data is consistent with the reported data in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 6.81 (s, 2H), 3.63 (s, 6H), 2.44 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.1, 141.2, 131.9, 128.8, 120.5, 118.5, 114.5, 35.8.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)dihydroborate (**3ga**)



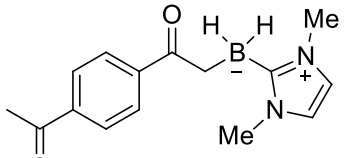
3ga

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3ga** as a white solid (65.8 mg, 45% yield). R_f = 0.66 (eluent: EtOAc). m.p. 86.3-87.7 °C. α-NHC-boryl ketone **3ga** is a known compound. Its characterization data is consistent with the reported data in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 6.80 (s, 2H), 3.62 (s, 6H), 2.46 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.8, 140.8 (q, *J* = 1.2 Hz), 132.7 (q, *J* = 32.3 Hz), 128.7, 125.0 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.3 Hz), 120.5, 35.9.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)dihydroborate (**3ha**)



3ha

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3ha** as a white solid (60.4 mg, 45% yield). R_f = 0.52 (eluent: EtOAc). m.p. 143.3-145.2 °C.

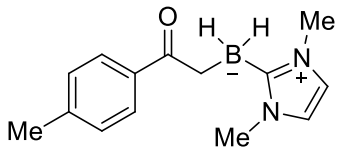
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 6.80 (s, 2H), 3.62 (s, 6H), 2.63 (s, 3H), 2.47 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 198.0, 141.4, 138.8, 128.5, 128.0, 120.4, 35.9, 26.8.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.5 (t, *J* = 90.7 Hz).

HRMS (ESI) calcd for $C_{15}H_{19}BN_2NaO_2^+$ ($[M + Na]^+$): 293.1432, found 293.1443.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-oxo-2-(*p*-tolyl)ethyl)dihydroborate (**3ia**)



3ia

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3ia** as a white solid (71.6 mg, 59% yield). R_f = 0.51 (eluent: EtOAc). m.p. 87.1-87.9 ºC.

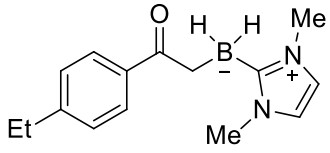
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.76 (s, 2H), 3.61 (s, 6H), 2.42 (s, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0, 141.7, 135.4, 128.6, 128.5, 120.3, 35.8, 21.4.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.4 (t, *J* = 89.9 Hz).

HRMS (ESI) calcd for $C_{14}H_{19}BN_2NaO^+$ ($[M + Na]^+$): 265.1483, found 265.1501.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(4-ethylphenyl)-2-oxoethyl)dihydroborate (**3ja**)



3ja

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3ja** as a white solid (74.3 mg, 58% yield). R_f = 0.55 (eluent: EtOAc). m.p. 74.3-75.9 ºC.

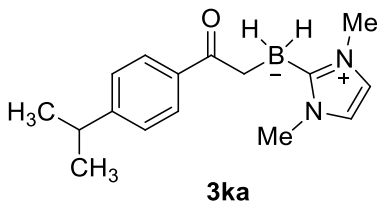
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.76 (s, 2H), 3.61 (s, 6H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.43 (s, 2H), 1.24 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 147.9, 135.7, 128.6, 127.4, 120.3, 35.9, 28.8, 15.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.5 (t, *J* = 90.1 Hz).

HRMS (ESI) calcd for $C_{15}H_{21}BN_2NaO^+$ ($[M + Na]^+$): 279.1639, found 279.1645.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(4-isopropylphenyl)-2-oxoethyl)dihydroborate (**3ka**)



3ka

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3ka** as a colorless oil (65.9 mg, 49% yield). R_f = 0.58 (eluent: EtOAc).

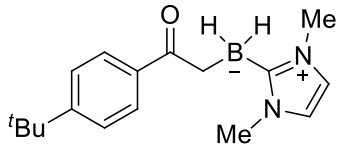
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.77 (s, 2H), 3.62 (s, 6H), 2.99 – 2.88 (m, 1H), 2.43 (s, 2H), 1.26 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 152.5, 135.8, 128.5, 126.0, 120.3, 35.8, 34.0, 23.7.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.5 (t, *J* = 90.1 Hz).

HRMS (ESI) calcd for $C_{16}H_{23}BN_2NaO^+$ ([M + Na]$^+$): 293.1796, found 293.1810.

(2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**3la**)



3la

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3la** as a white solid (95.2 mg, 67% yield). R_f = 0.58 (eluent: EtOAc). m.p. 113.2-114.9 °C.

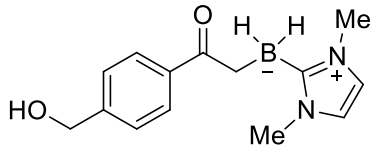
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.77 (s, 2H), 3.62 (s, 6H), 2.43 (s, 2H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 154.7, 135.4, 128.2, 124.8, 120.3, 35.9, 34.8, 31.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.5 (t, *J* = 90.1 Hz).

HRMS (ESI) calcd for $C_{17}H_{25}BN_2NaO^+$ ([M + Na]$^+$): 307.1952, found 307.1955.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(4-(hydroxymethyl)phenyl)-2-oxoethyl)dihydroborate (**3ma**)



3ma

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (15:1:0.01, v/v/v) to afford **3ma** as a white solid (82.6 mg, 64% yield). R_f = 0.59 (eluent: CH_2Cl_2/MeOH = 10:1, v/v). m.p. 128.4-130.2 °C.

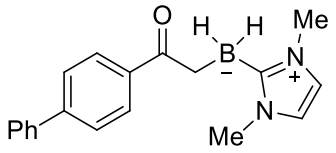
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 6.77 (s, 2H), 4.73 (d, *J* = 5.1 Hz, 2H), 3.61 (s, 6H), 2.44 (s, 2H), 2.10 (t, *J* = 5.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.4, 144.6, 136.9, 128.6, 126.2, 120.4, 64.5, 35.8.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.4 (t, *J* = 90.3 Hz).

HRMS (ESI) calcd for $C_{14}H_{19}BN_2NaO_2^+$ ($[M + Na]^+$): 281.1432, found 281.1442.

(2-([1,1'-Biphenyl]-4-yl)-2-oxoethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydrob orate (**3na**)



3na

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3na** as a white solid (98.6 mg, 65% yield). R_f = 0.56 (eluent: EtOAc). m.p. 156.6-157.3 °C.

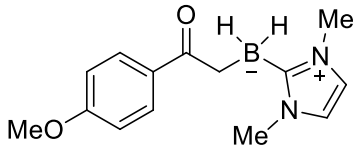
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.61 (m, 4H), 7.47 – 7.43 (m, 2H), 7.39 – 7.35 (m, 1H), 6.78 (d, *J* = 0.7 Hz, 2H), 3.63 (s, 6H), 2.49 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 143.9, 140.4, 136.7, 128.9, 128.8, 127.7, 127.1, 126.6, 120.4, 35.9.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.4 (t, *J* = 90.3 Hz).

HRMS (ESI) calcd for $C_{19}H_{21}BN_2NaO^+$ ($[M + Na]^+$): 327.1639, found 327.1663.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(4-methoxyphenyl)-2-oxoethyl)dihydrobor ate (**3oa**)



3oa

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3oa** as a white solid (79.6 mg, 62% yield). R_f = 0.68 (eluent: EtOAc). m.p. 122.8-124.4 °C.

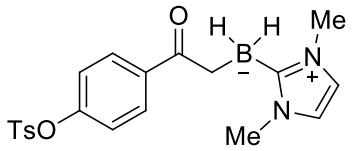
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 6.76 (s, 2H), 3.84 (s, 3H), 3.61 (s, 6H), 2.40 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.0, 162.0, 130.9, 130.3, 120.3, 112.9, 55.2, 35.7.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.4 (t, *J* = 89.9 Hz).

HRMS (ESI) calcd for $C_{14}H_{19}BN_2NaO_2^+$ ([M + Na]$^+$): 281.1432, found 281.1442.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-*oxo*-2-(4-(tosyloxy)phenyl)ethyl)dihydrob orate (**3pa**)



3pa

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3pa** as a colorless oil (106.3 mg, 53% yield). R_f = 0.56 (eluent: EtOAc).

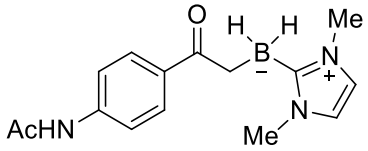
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.78 (s, 2H), 3.60 (s, 6H), 2.45 (s, 3H), 2.39 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 151.7, 145.5, 136.6, 132.2, 130.0, 129.8, 128.4, 121.7, 120.4, 35.8, 21.7.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.5 (t, *J* = 90.4 Hz).

HRMS (ESI) calcd for $C_{20}H_{23}BN_2NaO_4^+$ ([M + Na]$^+$): 421.1364, found 421.1370.

(2-(4-Acetamidophenyl)-2-oxoethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydrob orate (**3qa**)



3qa

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (15:1:0.01, v/v/v) to afford **3qa** as a white solid (68.5 mg, 48% yield). R_f = 0.56 (eluent: CH_2Cl_2/MeOH = 10:1, v/v). m.p. 143.8-146.2 ^{o}C.

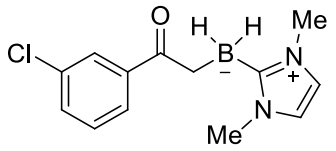
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 6.74 (s, 2H), 3.58 (s, 6H), 2.42 (s, 2H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.7, 169.0, 141.4, 133.3, 129.5, 120.4, 118.6, 35.8, 24.5.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.4 (t, *J* = 90.4 Hz).

HRMS (ESI) calcd for $C_{15}H_{20}BN_3NaO_2^+$ ([M + Na]$^+$): 308.1541, found 308.1553.

(2-(3-Chlorophenyl)-2-oxoethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborat e (**3ra**)



3ra

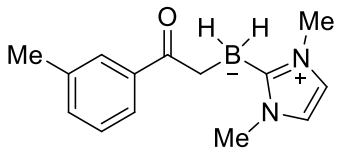
Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3ra** as a white solid (70.5 mg, 54% yield). R_f = 0.64 (eluent: EtOAc). m.p. 90.9-92.4°C. α-NHC-boryl ketone **3ra** is a known compound. Its characterization data is consistent with the reported data in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 6.79 (s, 2H), 3.62 (s, 6H), 2.42 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 139.6, 134.1, 131.2, 129.3, 128.3, 126.6, 120.4, 35.9.

HRMS (ESI) calcd for $C_{13}H_{16}BClN_2NaO^+$ ([M + Na]$^+$): 285.0936, found 285.0945.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-*oxo*-2-(*m*-tolyl)ethyl)dihydroborate (**3sa**)



3sa

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3sa** as a colorless oil (69.3 mg, 58% yield). R_f = 0.57 (eluent: EtOAc).

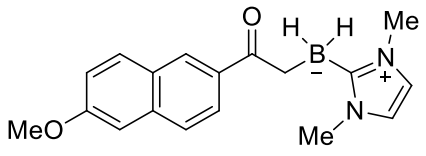
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 2H), 7.28 – 7.26 (m, 2H), 6.77 (s, 2H), 3.61 (s, 6H), 2.44 (s, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.6, 138.0, 137.5, 132.1, 128.8, 127.8, 125.6, 120.3, 35.9, 21.4.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.5 (t, *J* = 90.3 Hz).

HRMS (ESI) calcd for $C_{14}H_{19}BN_2NaO^+$ ([M + Na]$^+$): 265.1483, found 265.1498.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-(6-methoxynaphthalen-2-yl)-2-oxoethyl)di hydroborate (**3ta**)



3ta

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01,

v/v/v) to afford **3ta** as a white solid (77.2 mg, 50% yield). R_f = 0.52 (eluent: EtOAc). m.p. 129.7-131.8 °C.

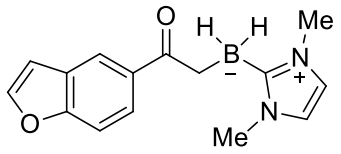
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.06 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.17 – 7.13 (m, 2H), 6.76 (s, 2H), 3.93 (s, 3H), 3.60 (s, 6H), 2.56 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0, 158.9, 136.4, 133.3, 131.0, 129.3, 128.0, 126.2, 125.6, 120.3, 118.9, 105.4, 55.3, 35.9.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.3 (t, *J* = 90.2 Hz).

HRMS (ESI) calcd for $C_{18}H_{21}BN_2NaO_2^+$ ([M + Na]$^+$): 331.1588, found 331.1600.

(2-(Benzofuran-5-yl)-2-oxoethyl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**3ua**)



3ua

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3ua** as a white solid (57.7 mg, 43% yield). R_f = 0.52 (eluent: EtOAc). m.p. 99.7-101.2 °C.

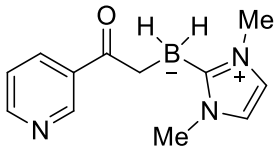
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 1.0 Hz, 1H), 8.03 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.64 (d, *J* = 2.1 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 1H), 6.83 (dd, *J* = 2.2, 1.0 Hz, 1H), 6.77 (s, 2H), 3.61 (s, 6H), 2.51 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 156.7, 145.6, 133.4, 127.0, 125.2, 122.5, 120.3, 110.6, 107.3, 35.9.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.3 (t, *J* = 90.0 Hz).

HRMS (ESI) calcd for $C_{15}H_{17}BN_2NaO_2^+$ ([M + Na]$^+$): 291.1275, found 291.1294.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-oxo-2-(pyridin-3-yl)ethyl)dihydroborate (**3va**)

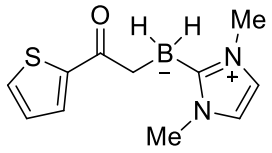


3va

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (30:1:0.01, v/v/v) to afford **3va** as a white solid (45.9 mg, 40% yield). R_f = 0.59 (eluent: CH_2Cl_2/MeOH = 15:1, v/v). m.p. 80.3-81.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 2.2, 1H), 8.66 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.29 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.34 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.79 (s, 2H), 3.62 (s, 6H), 2.43 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 151.8, 150.0, 135.7, 132.7, 123.1, 120.5, 35.8.
^{11}B NMR (160 MHz, $CDCl_3$) δ -27.6 (t, *J* = 90.8 Hz).
HRMS (ESI) calcd for $C_{15}H_{17}BN_2NaO_2^+$ ([M + Na]$^+$): 291.1275, found 291.1294.

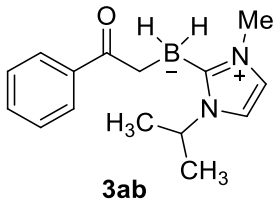
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-*oxo*-2-(thiophen-2-yl)ethyl)dihydroborate (**3wa**)



3wa

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford **3wa** as a colorless oil (57.8 mg, 50% yield). R_f = 0.61 (eluent: AcOEt).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.46 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.05 (dd, *J* = 4.9, 3.7 Hz, 1H), 6.78 (s, 2H), 3.65 (s, 6H), 2.37 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 145.8, 131.03, 130.97, 127.6, 120.4, 35.9.
^{11}B NMR (160 MHz, $CDCl_3$) δ -27.1 (t, *J* = 90.6 Hz).
HRMS (ESI) calcd for $C_{11}H_{15}BN_2NaOS^+$ ([M + Na]$^+$): 257.0890, found 267.0903.

(1-Isopropyl-3-methyl-1*H*-imidazol-3-ium-2-yl)(2-oxo-2-phenylethyl)dihydroborate (**3ab**)



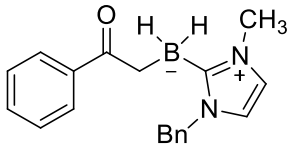
3ab

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (3:1:0.01, v/v/v) to afford **3ab** as a white solid (66.2 mg, 52% yield). R_f = 0.50 (eluent: petroleum ether/AcOEt = 1:1, v/v). m.p. 62.2-64.7 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 2H), 6.88 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 2.0 Hz, 1H), 4.90 – 4.80 (m, 1H), 3.61 (s, 3H), 2.45 (s, 2H), 1.31 (d, *J* = 6.8 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 207.7, 137.9, 131.3, 128.3, 127.9, 120.9, 114.9, 49.4, 35.6, 23.0.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.4 (t, *J* = 90.2 Hz).

HRMS (ESI) calcd for $C_{15}H_{21}BN_2NaO^+$ ([M + Na]$^+$): 279.1639, found 279.1652.

(1-Benzyl-3-methyl-1*H*-imidazol-3-ium-2-yl)(2-oxo-2-phenylethyl)dihydroborate (**3ac**)



3ac

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (3:1:0.01, v/v/v) to afford **3ac** as a colorless oil (75.4 mg, 49% yield). R_f = 0.53 (eluent: petroleum ether/AcOEt = 1:1, v/v).

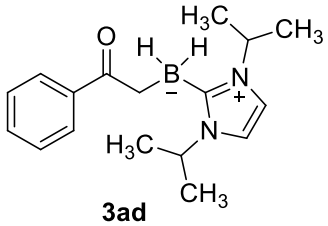
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.1 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.40 – 7.30 (m, 5H), 7.22 (d, *J* = 7.5 Hz, 2H), 6.78 (d, *J* = 1.8 Hz, 1H), 6.65 (d, *J* = 1.9 Hz, 1H), 5.18 (s, 2H), 3.65 (s, 3H), 2.49 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 137.9, 135.5, 131.4, 128.8, 128.3, 128.2, 128.1, 127.9, 120.9, 118.9, 51.9, 35.9.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.3 (t, *J* = 90.5 Hz).

HRMS (ESI) calcd for $C_{19}H_{21}BN_2NaO^+$ ([M + Na]$^+$): 327.1639, found 327.1648.

(1,3-Diisopropyl-1*H*-imidazol-3-ium-2-yl)(2-oxo-2-phenylethyl)dihydroborate (**3ad**)



3ad

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (5:1:0.01, v/v/v) to afford **3ad** as a white solid (64.6 mg, 46% yield). R_f = 0.50 (eluent: petroleum ether/AcOEt = 2:1, v/v). m.p. 77.6-80.2 °C.

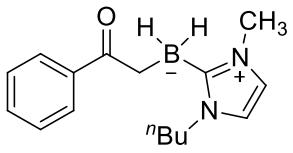
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 2H), 6.92 (s, 2H), 4.96 – 4.86 (m, 2H), 2.45 (s, 2H), 1.32 (d, *J* = 6.8 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.3, 137.9, 131.3, 128.4, 127.8, 115.5, 49.0, 23.1.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.3 (t, *J* = 90.0 Hz).

HRMS (ESI) calcd for $C_{17}H_{25}BN_2NaO^+$ ([M + Na]$^+$): 307.1952, found 307.1967.

(1-Butyl-3-methyl-1*H*-imidazol-3-ium-2-yl)(2-oxo-2-phenylethyl)dihydroborate (**3ae**)



3ae

Following the general procedure A, the crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc/Et_3N (3:1:0.01, v/v/v) to afford **3ae** as a colorless oil (72.8 mg, 54% yield). R_f = 0.50 (eluent: petroleum ether/AcOEt = 1:1, v/v).

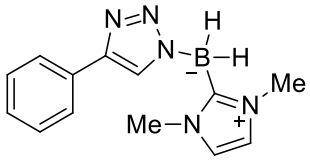
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 2H), 6.80 (d, *J* = 1.8 Hz, 1H), 6.78 (d, *J* = 1.8 Hz, 1H), 3.94 (t, *J* = 7.6 Hz, 2H), 3.63 (s, 3H), 2.45 (s, 2H), 1.69 – 1.61 (m, 2H), 1.29 – 1.20 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 137.9, 131.3, 128.4, 127.9, 120.5, 118.8, 48.2, 35.8, 32.48, 19.68, 13.5.

^{11}B NMR (160 MHz, $CDCl_3$) δ -27.4 (t, *J* = 90.3 Hz).

HRMS (ESI) calcd for $C_{16}H_{23}BN_2NaO^+$ ($[M + Na]^+$): 293.1796, found 193.1815.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-phenyl-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4aa**)



4aa

Following the general procedure C, **1a** and **2a** were used. The crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4aa** as a white solid (95.1 mg, 75% yield). R_f = 0.50 (eluent: CH_2Cl_2/MeOH = 20:1, v/v). m.p. 78.9-80.5 ºC.

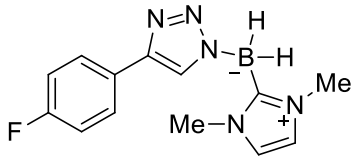
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.78 (s, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.86 (s, 2H), 3.75 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 132.2, 128.5, 126.9, 125.4, 125.1, 121.2, 36.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 91.8 Hz).

HRMS (ESI) calcd for $C_{13}H_{17}BN_5$ ($[M + H]^+$): 254.1572, found 254.1584.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4ba**)



4ba

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4ba** as a colorless oil (84.3 mg, 62% yield). R_f = 0.57 (eluent: CH_2Cl_2/MeOH = 20:1, v/v).

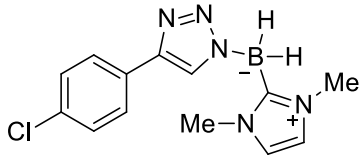
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.0, 5.6 Hz, 2H), 7.73 (s, 1H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.88 (s, 2H), 3.76 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, *J* = 245.0 Hz), 145.4, 128.5 (d, *J* = 3.2 Hz), 126.9 (d, *J* = 7.9 Hz), 124.8, 121.2, 115.3 (d, *J* = 21.4 Hz), 36.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 89.3 Hz).

HRMS (ESI) m/z calcd for $C_{13}H_{16}BFN_5^+$ ($[M + H]^+$): 272.1477, found 272.1483.

(4-(4-Chlorophenyl)-1*H*-1,2,3-triazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**4ca**)



4ca

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4ca** as a white solid (76.1 mg, 53% yield). R_f = 0.53 (eluent: CH_2Cl_2/MeOH = 20:1, v/v). m.p. 121.6-123,4 °C.

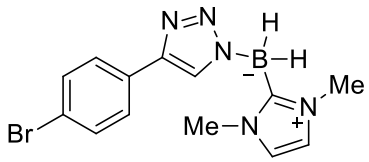
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.0 Hz, 3H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.89 (s, 2H), 3.78 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 132.4, 130.9, 128.7, 126.6, 125.1, 121.2, 36.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 89.1 Hz).

HRMS (ESI) calcd for $C_{13}H_{16}BClN_5^+$ ($[M + H]^+$): 288.1182, found 288.1193.

(4-(4-Bromophenyl)-1*H*-1,2,3-triazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**4da**)



4da

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4da** as a colorless oil (86.5 mg, 52% yield). R_f = 0.53 (eluent: CH_2Cl_2/MeOH = 20:1, v/v).

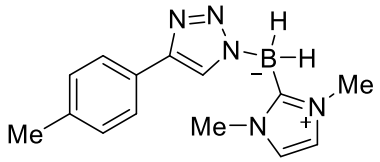
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 6.91 (s, 2H), 3.80 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 131.7, 131.3, 127.0, 125.2, 121.2, 120.6, 36.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.6.

HRMS (ESI) calcd for $C_{13}H_{16}BBrN_5^+$ ($[M + H]^+$): 332.0677, found 332.0679.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-(*p*-tolyl)-1*H*-1,2,3-triazol-1-yl)dihydrobora te (**4ia**)



4ia

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4ia** as a colorless oil (68.1 mg, 51% yield). R_f = 0.53 (eluent: CH_2Cl_2/MeOH = 20:1, v/v).

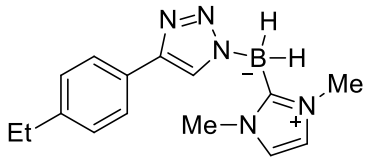
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.90 (s, 2H), 3.79 (s, 6H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 136.5, 129.4, 129.2, 125.3, 124.8, 121.2, 36.2, 22.0.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 90.1 Hz).

HRMS (ESI) m/z calcd for $C_{14}H_{19}BN_5^+$ ($[M + H]^+$): 268.1728, found 268.1730.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-(4-ethylphenyl)-1*H*-1,2,3-triazol-1-yl)dihy droborate (**4ja**)

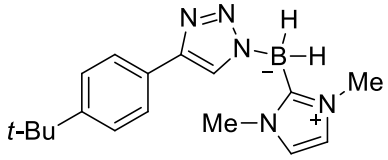


4ja

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4ja** as a colorless oil (88.7 mg, 63% yield). R_f = 0.53 (eluent: CH_2Cl_2/MeOH = 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.7 Hz, 3H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.88 (s, 2H), 3.77 (s, 6H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 143.0, 130.0, 128.0, 125.4, 124.9, 121.2, 36.2, 28.6, 15.5.
^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 88.0 Hz).
HRMS (ESI) calcd for $C_{15}H_{21}BN_5^+$ ($[M + H]^+$): 282.1885, found 282.1886.

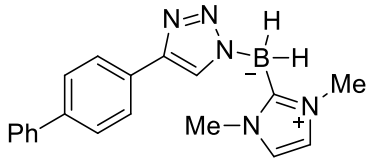
(4-(4-(*tert*-Butyl)phenyl)-1*H*-1,2,3-triazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**4la**)



4la

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4la** as a colorless oil (91.0 mg, 59% yield). R_f = 0.53 (eluent: CH_2Cl_2/MeOH = 20:1, v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 6.89 (s, 2H), 3.77 (s, 6H), 1.33 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 146.3, 129.5, 125.5, 125.2, 124.9, 121.2, 36.2, 34.5, 31.3.
^{11}B NMR (160 MHz, $CDCl_3$) δ -19.6.
HRMS (ESI) calcd for $C_{17}H_{25}BN_5^+$ ($[M + H]^+$): 310.2198, found 310.2202.

(4-([1,1'-Biphenyl]-4-yl)-1*H*-1,2,3-triazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**4na**)



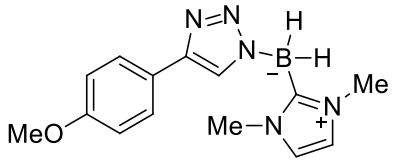
4na

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4na** as a white solid (87.3 mg, 53% yield). R_f = 0.50 (eluent: CH_2Cl_2/MeOH = 20:1, v/v). m.p. 156.8-158.7 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.84 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 4H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 6.89 (s, 2H), 3.80 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 140.9, 139.6, 131.4, 128.8, 127.3, 127.1, 126.9, 125.8, 125.3, 121.3, 36.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.6.

HRMS (ESI) calcd for $C_{19}H_{21}BN_5^+$ ([M + H]$^+$): 330.1885, found 330.1895.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4oa**)



4oa

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4oa** as a colorless oil (76.9 mg, 54% yield). R_f = 0.50 (eluent: CH_2Cl_2/MeOH = 20:1, v/v).

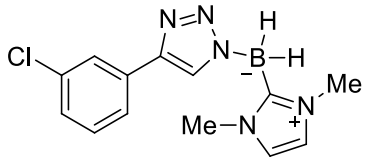
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.71 (s, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.90 (s, 2H), 3.81 (s, 3H), 3.79 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 146.1, 126.7, 125.1, 124.4, 121.2, 114.0, 55.2, 36.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.6 (t, *J* = 87.8 Hz).

HRMS (ESI) calcd for $C_{14}H_{18}BN_5NaO^+$ ([M + Na]$^+$): 306.1497, found 306.1499.

(4-(3-Chlorophenyl)-1*H*-1,2,3-triazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**4ra**)



4ra

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4ra** as a colorless oil (74.5 mg, 52% yield). R_f = 0.53 (eluent: CH_2Cl_2/MeOH = 20:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.79 (s, 1H), 7.71 (d, *J* = 7.1 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 6.91 (s, 2H), 3.80 (s, 6H).

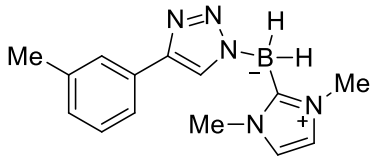
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 134.4, 134.1, 129.8, 126.8, 125.4, 123.5, 121.2, 36.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 84.3 Hz).

HRMS (ESI) calcd for $C_{13}H_{16}BClN_5^+$ ([M + H]$^+$): 288.1182, found 288.1186.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-(*m*-tolyl)-1*H*-1,2,3-triazol-1-yl)dihydrobor

ate (**4sa**)



4sa

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4sa** as a colorless oil (81.7 mg, 61% yield). R_f = 0.53 (eluent: CH_2Cl_2/MeOH = 20:1, v/v).

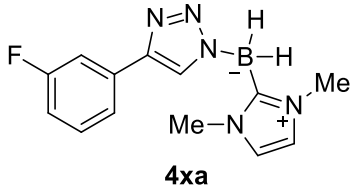
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.67 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.89 (s, 2H), 3.77 (s, 6H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 138.1, 132.1, 128.4, 127.7, 126.1, 125.1, 122.5, 121.2, 36.2, 21.4.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.6 (t, *J* = 88.6 Hz).

HRMS (ESI) m/z calcd for $C_{14}H_{19}BN_5^+$ ([M + H]$^+$): 268.1728, found 268.1733.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-(3-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4xa**)



4xa

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4xa** as a colorless oil (80.2 mg, 59% yield). R_f = 0.57 (eluent: CH_2Cl_2/MeOH = 20:1, v/v).

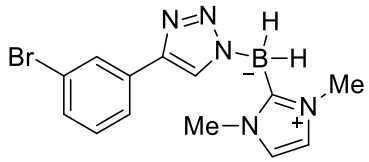
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.59 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.35 – 7.30 (m, 1H), 6.95 – 6.90 (m, 3H), 3.82 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (d, *J* = 244.3 Hz), 145.4 (d, *J* = 2.6 Hz), 134.6 (d, *J* = 8.6 Hz), 130.0 (d, *J* = 8.5 Hz), 125.4, 121.2, 121.0 (d, *J* = 2.8 Hz), 113.6 (d, *J* = 21.3 Hz), 112.2 (d, *J* = 22.7 Hz), 36.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 89.8 Hz).

HRMS (ESI) m/z calcd for $C_{13}H_{16}BFN_5^+$ ([M + H]$^+$): 272.1477, found 272.1484.

(4-(3-Bromophenyl)-1*H*-1,2,3-triazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**4ya**)



4ya

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4ya** as a white solid (79.4 mg, 48% yield). R_f = 0.53 (eluent: CH_2Cl_2/MeOH = 20:1, v/v). m.p. 94.8-96.9 ºC.

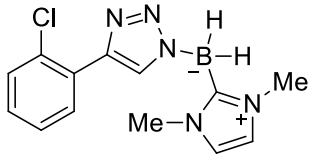
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (t, *J* = 1.7 Hz, 1H), 7.79 (s, 1H), 7.77 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.36 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 6.92 (s, 2H), 3.81 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 134.4, 130.1, 129.7, 128.3, 125.4, 123.9, 122.7, 121.2, 36.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 93.5 Hz).

HRMS (ESI) calcd for $C_{13}H_{16}BBrN_5^+$ ([M + H]$^+$): 332.0677, found 332.0684.

(4-(2-Chlorophenyl)-1*H*-1,2,3-triazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**4za**)



4za

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (35:1:0.01, v/v/v) to afford **4za** as a white solid (72.1 mg, 50% yield). R_f = 0.63 (eluent: CH_2Cl_2/MeOH = 15:1, v/v). m.p. 100.8-102.4 ºC.

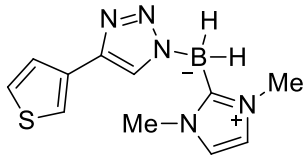
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.18 (s, 1H), 7.40 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.30 (td, *J* = 7.8, 1.3 Hz, 1H), 7.18 (td, *J* = 7.7, 1.8 Hz, 1H), 6.90 (s, 2H), 3.80 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 130.9, 130.9, 130.0, 129.7, 128.7, 127.8, 126.8, 121.2, 36.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 88.5 Hz).

HRMS (ESI) calcd for $C_{13}H_{16}BClN_5^+$ ([M + H]$^+$): 288.1182, found 288.1188.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-(thiophen-3-yl)-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4aaa**)



4aaa

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (35:1:0.01, v/v/v) to afford **4aaa** as a colorless oil (74.3 mg, 57% yield). R_f = 0.66 (eluent: CH_2Cl_2/MeOH = 15:1, v/v).

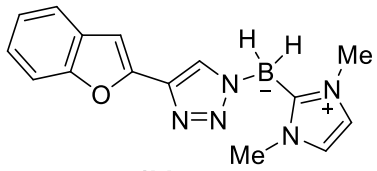
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.58 (d, *J* = 2.9 Hz, 1H), 7.45 (d, *J* = 5.0 Hz, 1H), 7.32 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.89 (s, 2H), 3.77 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 133.5, 126.1, 125.6, 125.0, 121.2, 119.3, 36.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 88.8 Hz).

HRMS (ESI) calcd for $C_{11}H_{15}BN_5S^+$ ($[M + H]^+$): 260.1136, found 260.1140.

(4-(Benzofuran-2-yl)-1*H*-1,2,3-triazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**4bba**)



4bba

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4bba** as a colorless oil (65.8 mg, 45% yield). R_f = 0.57 (eluent: CH_2Cl_2/MeOH = 20:1, v/v).

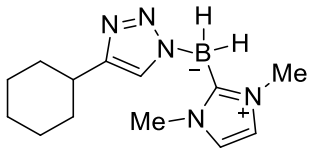
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.57 (d, *J* = 6.9 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.11 (s, 1H), 6.93 (s, 2H), 3.83 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 150.1, 138.7, 129.2, 126.1, 123.6, 122.7, 121.3, 120.8, 110.9, 101.0, 36.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.6 (t, *J* = 89.2 Hz).

HRMS (ESI) calcd for $C_{15}H_{17}BN_5O^+$ ($[M + H]^+$): 294.1521, found 294.1525.

(4-Cyclohexyl-1*H*-1,2,3-triazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**4cca**)



4cca

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4cca** as a colorless oil (72.8 mg, 56% yield). R_f = 0.58 (eluent: CH_2Cl_2/MeOH = 15:1, v/v).

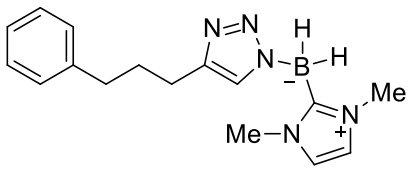
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (s, 1H), 6.88 (s, 2H), 3.73 (s, 6H), 2.75 – 2.69 (m, 1H), 2.04 – 2.01 (m, 2H), 1.78 – 1.75 (m, 2H), 1.70 – 1.67 (m, 1H), 1.39 – 1.34 (m, 4H), 1.26 – 1.21 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 124.5, 121.1, 36.2, 35.3, 33.4, 26.3, 26.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.8 (t, *J* = 92.0 Hz).

HRMS (ESI) calcd for $C_{13}H_{23}BN_5^+$ ($[M + H]^+$): 260.2041, found 260.2050.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-(3-phenylpropyl)-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4dda**)



4dda

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4dda** as a colorless oil (71.7 mg, 49% yield). R_f = 0.58 (eluent: CH_2Cl_2/MeOH = 15:1, v/v).

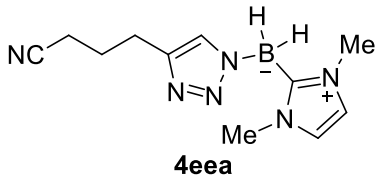
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 3H), 7.20 – 7.14 (m, 3H), 6.89 (s, 1H), 3.75 (s, 6H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.67 (d, *J* = 7.6 Hz, 2H), 2.02 – 1.94 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 142.4, 128.5, 128.2, 126.1, 125.6, 121.1, 36.2, 35.5, 31.6, 25.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 88.4 Hz).

HRMS (ESI) calcd for $C_{16}H_{23}BN_5^+$ ($[M + H]^+$): 296.2041, found 296.2044.

(4-(3-Cyanopropyl)-1*H*-1,2,3-triazol-1-yl)(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (**4eea**)



4eea

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (30:1:0.01, v/v/v) to afford **4eea** as a colorless oil (62.3 mg, 51% yield). R_f = 0.54 (eluent: CH_2Cl_2/MeOH = 15:1, v/v).

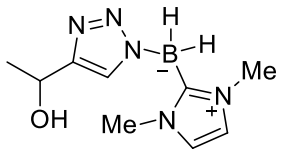
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 6.92 (s, 2H), 3.79 (s, 6H), 2.84 (t, *J* = 7.1 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.08 – 2.01 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 126.5, 121.2, 119.8, 36.3, 25.4, 24.2, 16.4.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.8 (t, *J* = 91.8 Hz).

HRMS (ESI) calcd for $C_{11}H_{18}BN_6^+$ ([M + H]$^+$): 245.1681, found 245.1684.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-(1-hydroxyethyl)-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4ffa**)



4ffa

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (10:1:0.01, v/v/v) to afford **4ffa** as a colorless oil (63.5 mg, 57% yield). R_f = 0.66 (eluent: CH_2Cl_2/MeOH = 5:1, v/v).

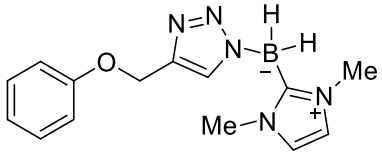
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 6.91 (s, 2H), 5.03 (q, *J* = 6.0 Hz, 1H), 3.75 (s, 6H), 1.53 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 125.0, 121.3, 62.9, 36.2, 23.0.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.6.

HRMS (ESI) calcd for $C_9H_{17}BN_5O^+$ ([M + H]$^+$): 222.1521, found 222.1526.

(1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)(4-(phenoxymethyl)-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4gga**)



4gga

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4gga** as a colorless oil (86.6 mg, 61% yield). R_f = 0.61 (eluent: CH_2Cl_2/MeOH = 15:1, v/v).

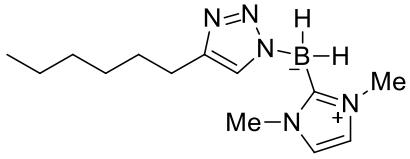
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.24 (t, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.87 (s, 2H), 5.17 (s, 2H), 3.72 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 142.4, 129.3, 128.0, 121.2, 120.7, 114.9, 62.3, 36.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 89.9 Hz).

HRMS (ESI) calcd for $C_{14}H_{19}BN_5O^+$ ([M + H]$^+$): 284.1677, found 284.1683.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-hexyl-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4hha**)



4hha

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4hha** as a colorless oil (71.9 mg, 56% yield). R_f = 0.61 (eluent: CH_2Cl_2/MeOH = 15:1, v/v).

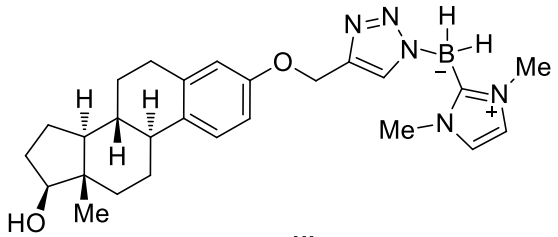
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 6.89 (s, 2H), 3.75 (s, 6H), 2.67 (t, *J* = 7.7 Hz, 2H), 1.66 – 1.59 (m, 2H), 1.38 – 1.27 (m, 6H), 0.86 (t, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 126.0, 121.1, 36.2, 31.7, 29.8, 29.1, 25.7, 22.6, 14.1.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.8 (t, *J* = 90.7 Hz).

HRMS (ESI) calcd for $C_{13}H_{25}BN_5^+$ ([M + H]$^+$): 262.2198, found 262.2212.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-((((8*R*,9*S*,13*S*,14*S*,17*S*)-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4iia**)



4iia

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (30:1:0.01, v/v/v) to afford **4iia** as a white solid (96.6 mg, 42% yield). R_f = 0.50 (eluent: CH_2Cl_2/MeOH = 20:1, v/v). m.p. 212.7-214.1 °C.

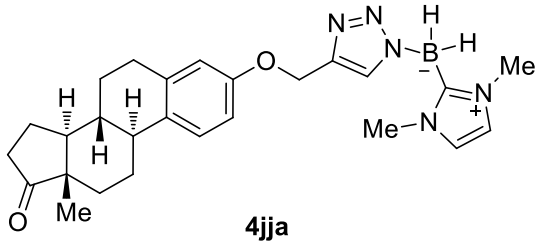
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 6.90 (s, 2H), 6.81 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.74 (d, *J* = 2.7 Hz, 1H), 5.16 (s, 2H), 3.78 (s, 6H), 3.73 (t, *J* = 8.8 Hz, 1H), 2.86 – 2.82 (m, 2H), 2.33 – 2.27 (m, 1H), 2.21 – 2.07 (m, 2H), 1.96 – 1.91 (m, 1H), 1.89 – 1.83 (m, 1H), 1.73 – 1.65 (m, 2H), 1.53 – 1.14 (m, 6H), 0.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 142.6, 137.8, 132.7, 127.9, 126.2, 121.2, 114.8, 112.3, 81.8, 62.4, 50.0, 43.9, 43.2, 38.8, 36.7, 36.3, 30.5, 29.8, 27.2, 26.3, 23.1, 11.0.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.6.

HRMS (ESI) calcd for $C_{26}H_{37}BN_5O_2^+$ ([M + H]$^+$): 462.3035, found 462.3140.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-((((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4jja**)



4jja

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (30:1:0.01, v/v/v) to afford **4jja** as a white solid (77.9 mg, 34% yield). R_f = 0.58 (eluent: CH_2Cl_2/MeOH = 15:1, v/v). m.p. 98.8-100.4 ºC.

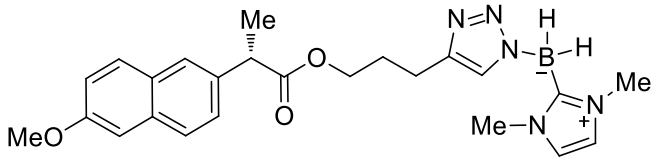
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 6.90 (s, 2H), 6.82 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.75 (d, *J* = 2.3 Hz, 1H), 5.17 (s, 2H), 3.78 (s, 6H), 2.90 – 2.87 (m, 2H), 2.53 – 2.46 (m, 1H), 2.41 – 2.36 (m, 1H), 2.26 – 2.21 (m, 1H), 2.18 – 1.93 (m, 4H), 1.65 – 1.37 (m, 6H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.1, 156.7, 142.6, 137.6, 132.0, 127.9, 126.2, 121.2, 114.8, 112.5, 62.4, 50.4, 48.0, 44.0, 38.3, 36.3, 35.9, 31.5, 29.6, 26.5, 25.9, 21.6, 13.8.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.6.

HRMS (ESI) calcd for $C_{26}H_{35}BN_5O_2^+$ ($[M + H]^+$): 460.2878, found 460.2886.

(*S*)-(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(4-(3-((2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)propyl)-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4kka**)



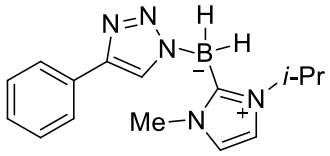
4kka

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (30:1:0.01, v/v/v) to afford **4kka** as a colorless oil (97.5 mg, 44% yield). R_f = 0.57 (eluent: CH_2Cl_2/MeOH = 15:1, v/v). m.p. 98.8-100.4 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.69 (s, 1H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.41 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.14 – 7.11 (m, 3H), 6.86 (s, 2H), 4.12 – 4.05 (m, 2H), 3.90 (s, 3H), 3.85 (q, *J* = 7.4 Hz, 1H), 3.70 (s, 6H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.98 – 1.91 (m, 2H), 1.57 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 157.5, 145.1, 135.8, 133.6, 129.3, 128.9, 127.1, 126.3, 126.3, 125.9, 121.1, 118.9, 105.6, 64.2, 55.3, 45.5, 36.1, 28.6, 21.8, 18.4.
^{11}B NMR (160 MHz, $CDCl_3$) δ -19.8 (t, *J* = 89.2 Hz).
HRMS (ESI) calcd for $C_{24}H_{31}BN_5O_3^+$: ($[M + H]^+$): 448.2514, found 448.2520.

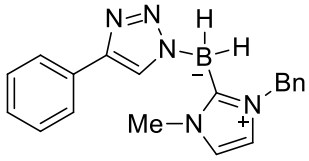
(3-Isopropyl-1-methyl-1*H*-imidazol-3-ium-2-yl)(4-phenyl-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4ab**)



4ab

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4ab** as a colorless oil (89.4 mg, 64% yield). R_f = 0.66 (eluent: CH_2Cl_2/MeOH = 15:1, v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.3 Hz, 2H), 7.77 (s, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 1.9 Hz, 1H), 5.22 – 5.15 (m, 1H), 3.81 (s, 3H), 1.38 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 132.4, 128.5, 126.8, 125.4, 124.9, 121.8, 115.7, 50.4, 36.1, 23.1.
^{11}B NMR (160 MHz, $CDCl_3$) δ -19.8 (t, *J* = 88.8 Hz).
HRMS (ESI) calcd for $C_{15}H_{21}BN_5^+$ ($[M + H]^+$): 282.1885, found 282.1894.

(1-Benzyl-3-methyl-1*H*-imidazol-3-ium-2-yl)(4-phenyl-1*H*-1,2,3-triazol-1-yl)dihydroborate (**4ac**)

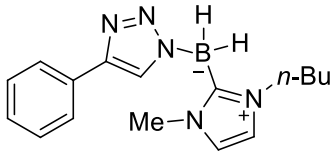


4ac

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4ac** as a colorless oil (75.9 mg, 46% yield). R_f = 0.57 (eluent: CH_2Cl_2/MeOH = 20:1, v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 2H), 7.71 (s, 1H), 7.39 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 7.20 – 7.17 (m, 2H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 2.0 Hz, 1H), 5.41 (s, 2H), 3.84 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 135.0, 132.3, 129.0, 128.5, 128.4, 128.0, 126.8, 125.4, 125.1, 121.8, 119.9, 52.5, 36.3.

^{11}B NMR (160 MHz, $CDCl_3$) δ -19.6 (t, *J* = 88.8 Hz).
HRMS (ESI) calcd for $C_{19}H_{21}BN_5^+$ ([M + H]$^+$): 330.1885, found 330.1893.

(3-Butyl-1-methyl-1*H*-imidazol-3-ium-2-yl)(4-phenyl-1*H*-1,2,3-triazol-1-yl)dihydrob orate (**4ae**)



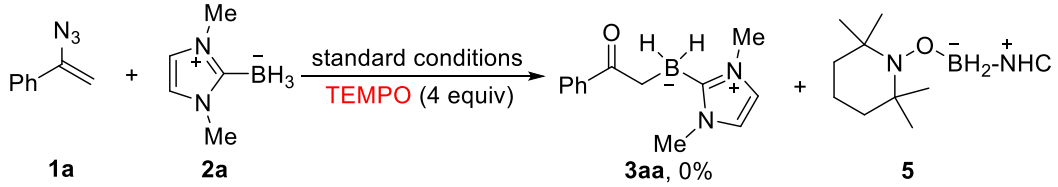
4ae

Following the general procedure C, the crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4ae** as a colorless oil (78.3 mg, 53% yield). R_f = 0.50 (eluent: CH_2Cl_2/MeOH = 20:1, v/v).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.79 (s, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 4.4 Hz, 2H), 4.17 (t, *J* = 7.6 Hz, 2H), 3.79 (s, 3H), 1.73 – 1.66 (m, 2H), 1.36 – 1.25 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 132.4, 128.5, 126.8, 125.4, 125.0, 121.4, 119.8, 49.0, 36.2, 32.6, 19.6, 13.5.
^{11}B NMR (160 MHz, $CDCl_3$) δ -19.7 (t, *J* = 88.5 Hz).
HRMS (ESI) calcd for $C_{16}H_{23}BN_5^+$ ([M + H]$^+$): 296.2041, found 296.2056.

6. Control Experiments

6.1 Radical inhibition experiments (Scheme S7)

equation 1



1a **2a** **3aa**, 0% **5**
detected by HRMS

Followed the general procedure A, to a mixture of vinyl azide **1a** (218.0 mg, 1.5 mmol, 3.0 equiv), NHC-BH_3 **2a** (55.0 mg, 0.5 mmol, 1.0 equiv), ^{t}BuSH (85 μL, 0.75 mmol, 1.5 equiv), and Cs_2CO_3 (81.5 mg, 0.25 mmol, 0.5 equiv) in 1-butanol (5 mL) was added TEMPO (312.5 mg, 2.0 mmol, 4.0 equiv). The reaction mixture was then stirred at 60 °C for 10 h. The NHC-borane-captured TEMPO **5** was detected by HRMS analysis (HRMS (ESI) calcd for $C_{14}H_{29}BN_3O^+$ ([M + H]$^+$): 266.2398, found 266.2405), whereas the desired product **3aa** was not observed according to HRMS analysis. 65% of **1a** (141.2 mg) and 33% of **2a** (18.1 mg) were recovered by column flash chromatography on silica gel.

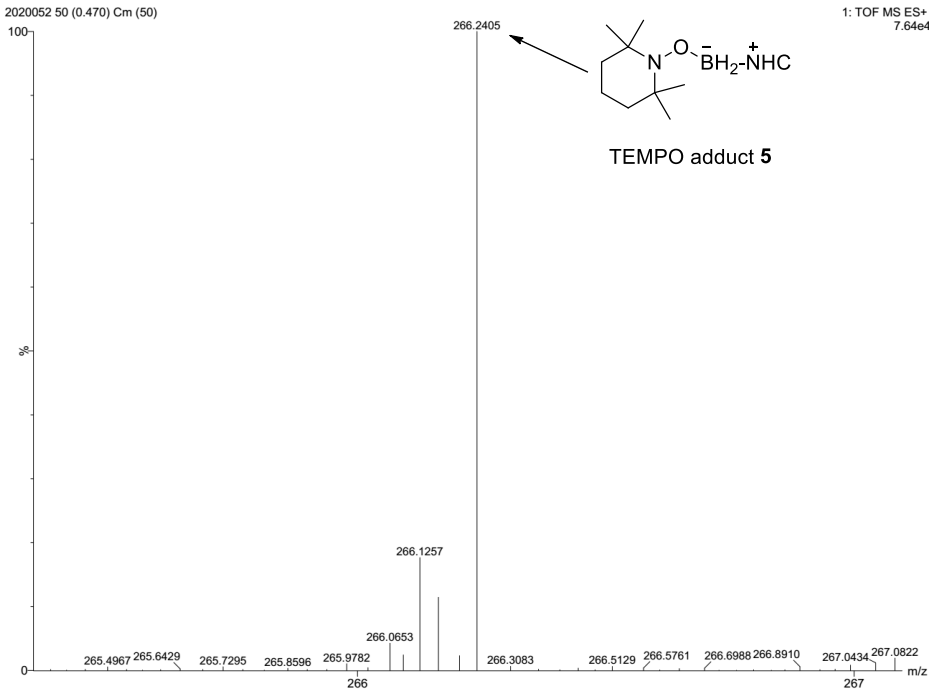
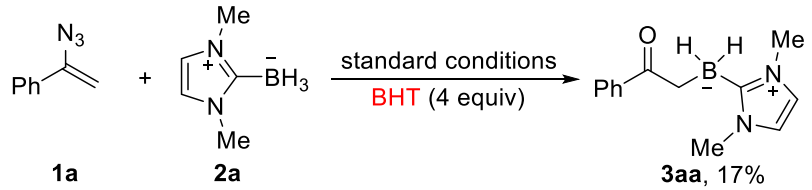


Figure S1. HRMS (ESI) spectrum for product **5**.

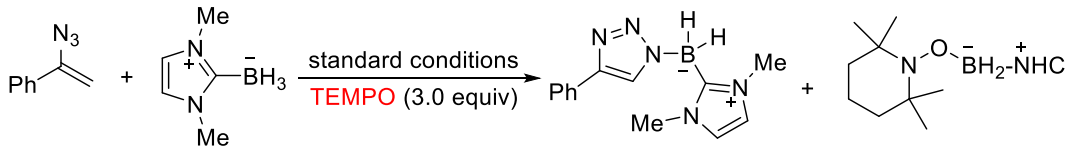
equation 2



1a **2a** **3aa**, 17%

Followed the general procedure A, to a mixture of vinyl azide **1a** (218.0 mg, 1.5 mmol, 3.0 equiv), NHC-BH_3 **2a** (55.0 mg, 0.5 mmol, 1.0 equiv), ^{t}BuSH (85 μL, 0.75 mmol, 1.5 equiv), and Cs_2CO_3 (81.5 mg, 0.25 mmol, 0.5 equiv) in 1-butanol (5 mL) was added BHT (440.8 mg, 2.0 mmol, 4.0 equiv). The reaction mixture was then stirred at 60 °C for 10 h. Product **3aa** was obtained as a white solid (19.2 mg, 17%).

equation 3



1a **2a** **4aa**, 0% **5** detected by HRMS

Followed the general procedure C, to a mixture of vinyl azide **1a** (145.2 mg, 1.0 mmol, 2.0 equiv), NHC-BH_3 **2a** (55.0 mg, 0.5 mmol, 1.0 equiv), ^{t}BuSH (57 μL, 0.5 mmol, 1.0 equiv), and AIBN (98.5 mg, 0.6 mmol, 1.2 equiv) in CH_3OH (5 mL) was added TEMPO (234.3 mg, 1.5 mmol, 3.0 equiv). The reaction mixture was then stirred at 60 °C for 12 h. The NHC-borane-captured TEMPO **5** was detected by HRMS analysis (HRMS (ESI) calcd for $C_{14}H_{29}BN_3O^+$ ([M + H]$^+$): 266.2398, found

266.2412), whereas the desired product **4aa** was not observed according to HRMS analysis. 63% of **1a** (91.8 mg) and 39% of **2a** (21.6 mg) were recovered by column flash chromatography on silica gel.

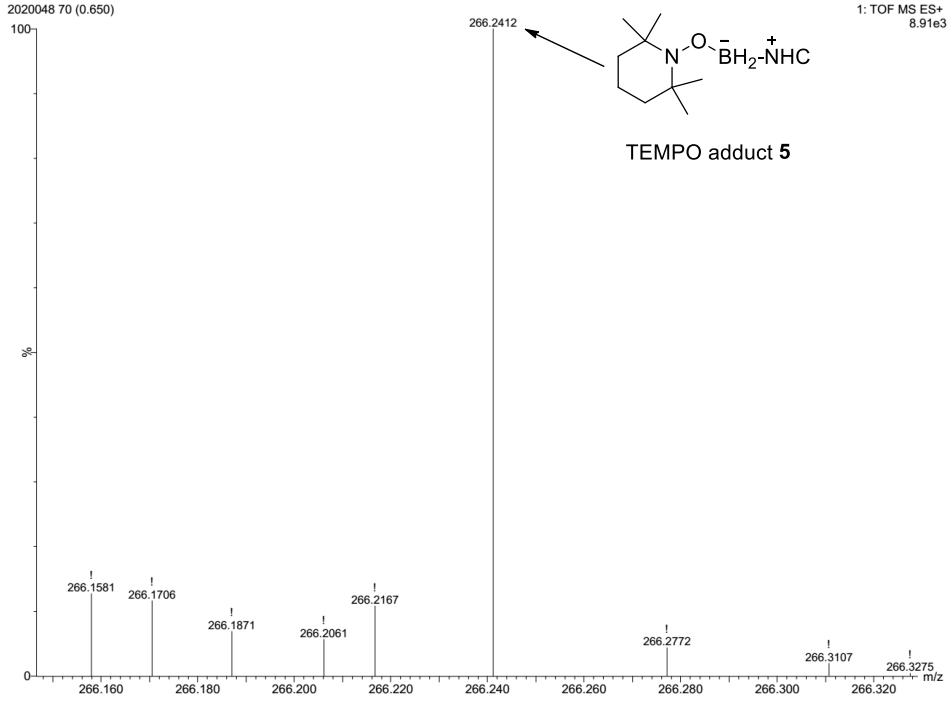
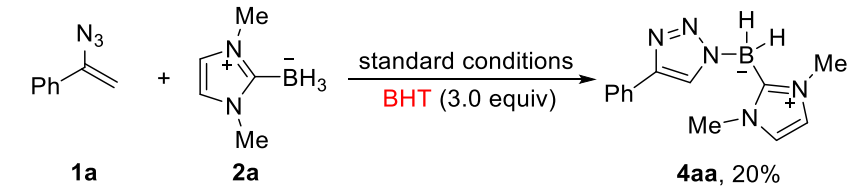


Figure S2. HRMS (ESI) spectrum for product **5**.

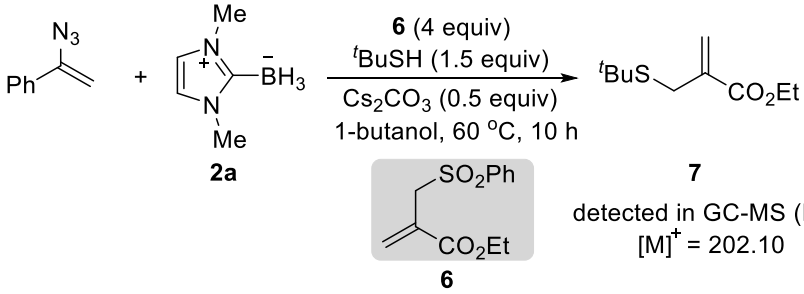
equation 4



1a **2a** **4aa**, 20%

Followed the general procedure C, to a mixture of vinyl azide **1a** (145.2 mg, 1.0 mmol, 2.0 equiv), NHC-BH_3 **2a** (55.0 mg, 0.5 mmol, 1.0 equiv), ^{t}BuSH (57 μL, 0.5 mmol, 1.0 equiv), and AIBN (98.5 mg, 0.6 mmol, 1.2 equiv) in CH_3OH (5 mL) was added BHT (330.6 mg, 1.5 mmol, 3.0 equiv). The reaction mixture was then stirred at 60 ^{o}C for 12 h. Product **4aa** was obtained as a white solid (25.8 mg, 20%).

6.2 Radical trapping experiment (Scheme S8)



2a **6** **7**

detected in GC-MS (EI)
$[M]^+$ = 202.10

Followed the general procedure A, to a mixture of vinyl azide **1a** (87.5 mg, 0.3 mmol, 3.0 equiv), NHC-BH_3 **2a** (22.0 mg, 0.2 mmol, 1.0 equiv), ^{t}BuSH (34 μL, 0.3 mmol, 1.5 equiv), and Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv) in 1-butanol (2 mL) was added ethyl 2-((phenylsulfonyl)methyl)propenoate **6** (203.5 mg, 0.8 mmol, 4.0 equiv). The reaction mixture was then stirred at 60 °C for 10 h. The thiol-captured olefin **7** was detected by GC-MS analysis (GC-MS (EI) calcd for $C_{10}H_{18}O_2S^+$ ($[M]^+$): 202.10, found 202.04), whereas the desired product **3aa** was not observed.

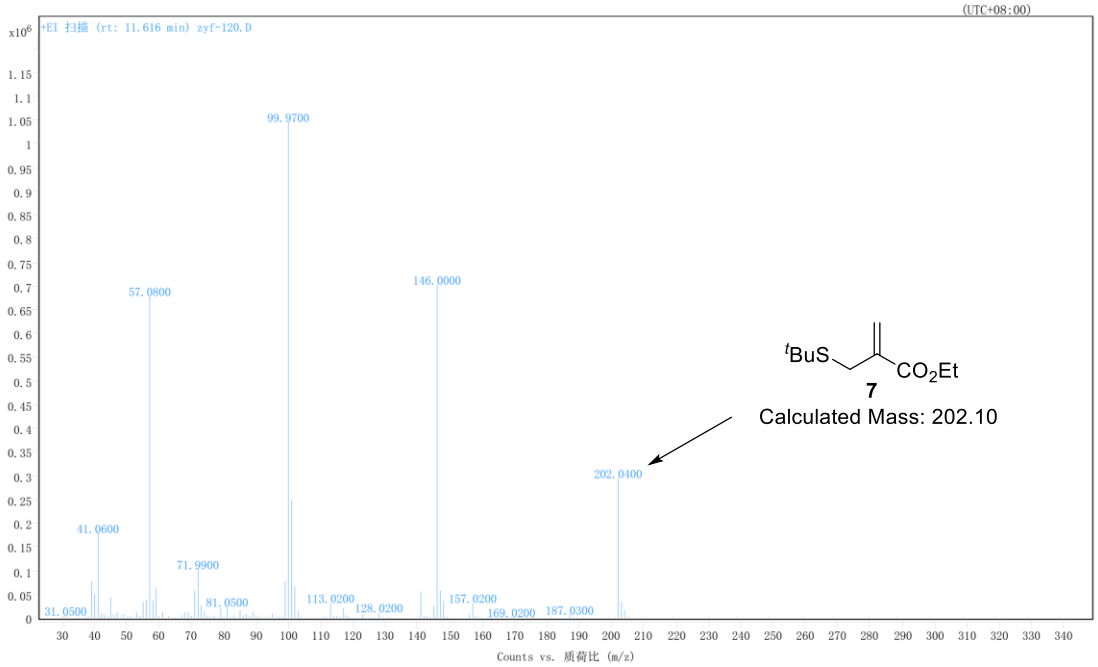
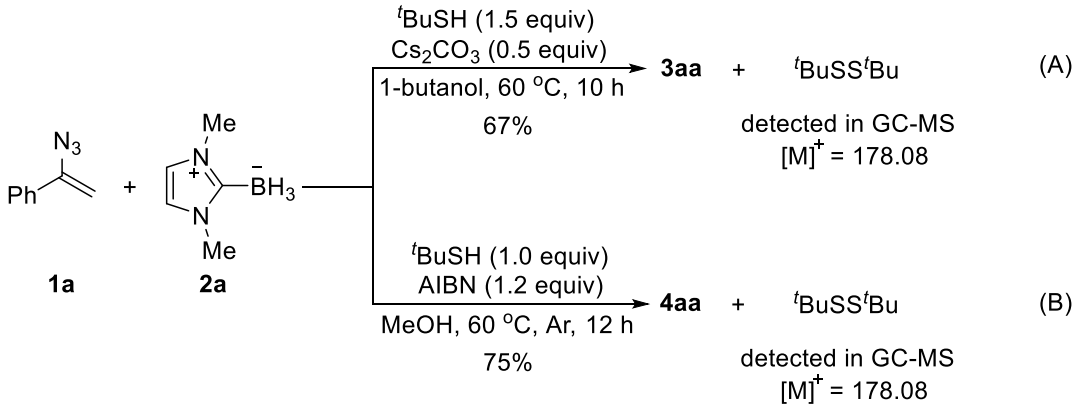


Figure S3. GC-MS (EI) spectrum for product **7**.

6.3 Reaction of 1a with 2a using ^{t}BuSS^{t}Bu instead of ^{t}BuSH (Scheme S8)

equation 1



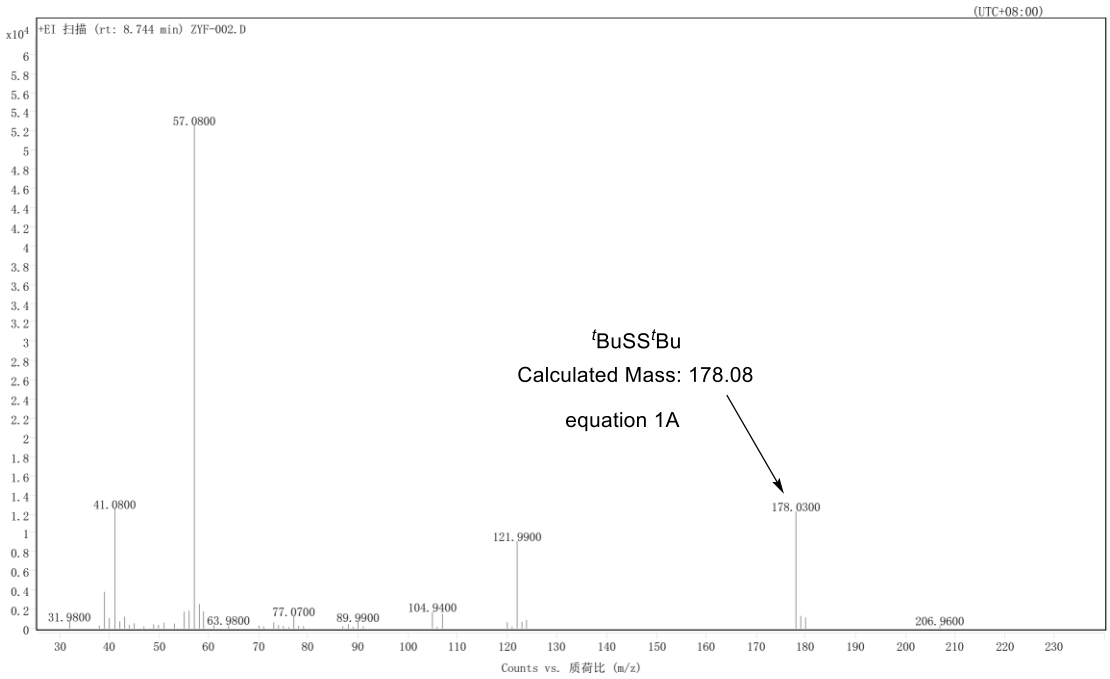


Figure S4. GC-MS (EI) spectra for disulfide.

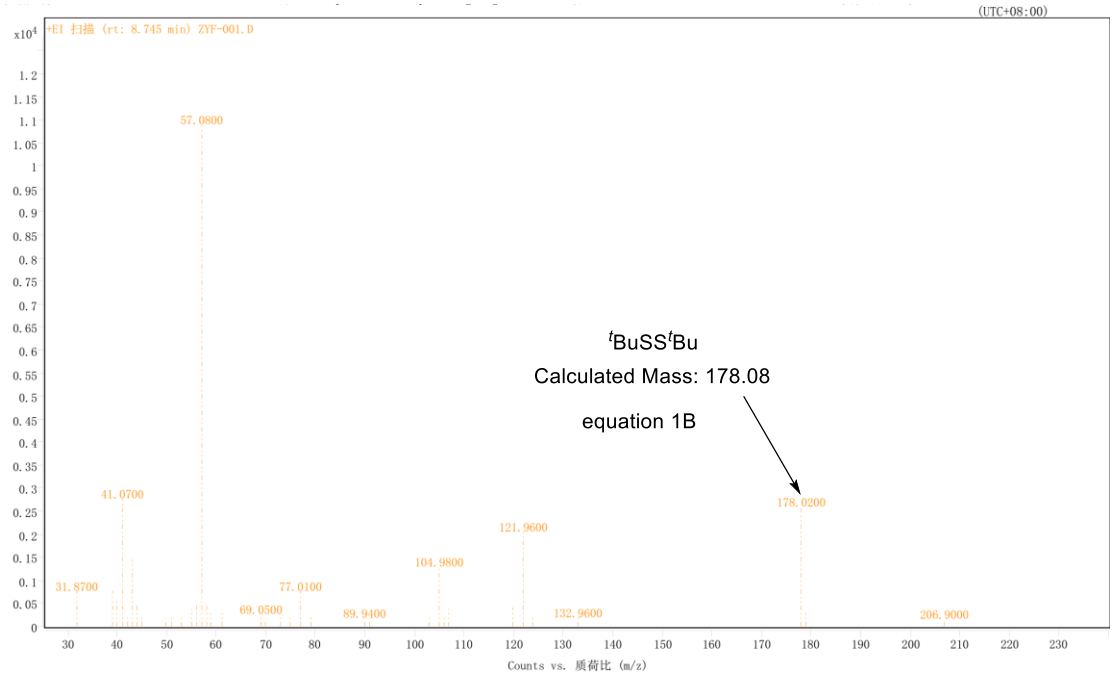
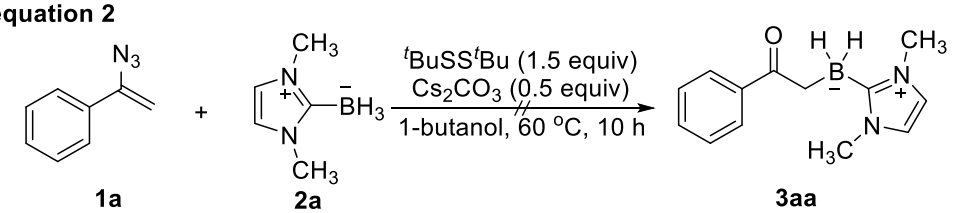


Figure S5. GC-MS (EI) spectrum for disulfide.

equation 2

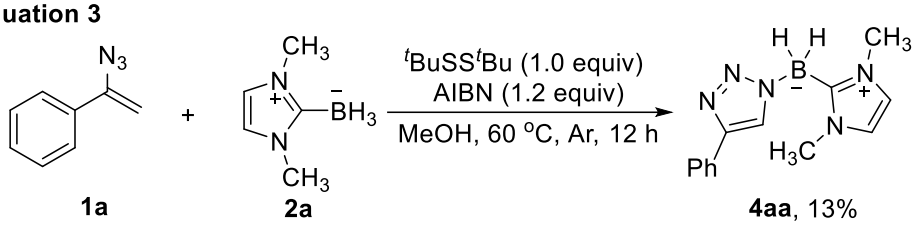


1a **2a** **3aa**

Followed the general procedure A, to a mixture of vinyl azide **1a** (218.0 mg, 1.5

mmol, 3.0 equiv), NHC-BH_3 **2a** (55.0 mg, 0.5 mmol, 1.0 equiv), and Cs_2CO_3 (81.5 mg, 0.25 mmol, 0.5 equiv) in 1-butanol (5 mL) was added ^{t}BuSS^{t}Bu (145 μL, 0.75 mmol, 1.5 equiv). The reaction mixture was then stirred at 60 °C for 10 h. The desired product **3aa** was not detected by TLC and HRMS analyses, and 93% of **2a** was recovered by column flash chromatography on silica gel.

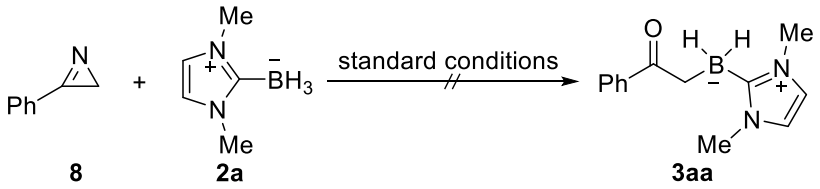
equation 3



1a **2a** **4aa**, 13%

Followed the general procedure C, to a mixture of vinyl azide **1a** (145.2 mg, 1.0 mmol, 2.0 equiv), NHC-BH_3 **2a** (55.0 mg, 0.5 mmol, 1.0 equiv), and AIBN (98.5 mg, 0.6 mmol, 1.2 equiv) in CH_3OH (5 mL) was added ^{t}BuSS^{t}Bu (97 μL, 0.5 mmol, 1.0 equiv). The reaction mixture was then stirred at 60 °C for 12 h. The crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford **4aa** as a white solid (16.7 mg, 13% yield) with the recovery of 53% of **2a**.

6.4 Reaction of 2*H*-azirine 8 with 2a under standard conditions (Scheme S9)

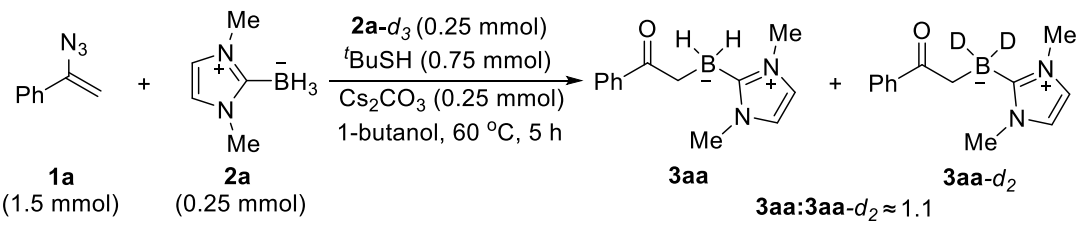


8 **2a** **3aa**

Followed the general procedure A, 2*H*-azirine **6** was used as a substrate instead of vinyl azide **1a**. A mixture of **6** (175.6 mg, 1.5 mmol, 3.0 equiv), NHC-BH_3 **2a** (55.0 mg, 0.5 mmol, 1.0 equiv), ^{t}BuSH (85 μL, 0.75 mmol, 1.5 equiv), and Cs_2CO_3 (81.5 mg, 0.25 mmol, 0.5 equiv) in 1-butanol (5 mL) was stirred at 60 °C for 10 h. The desired product **3aa** was not observed by TLC and HRMS analyses.

6.5 Intermolecular kinetic isotopic effect experiment (Scheme S10)

equation 1

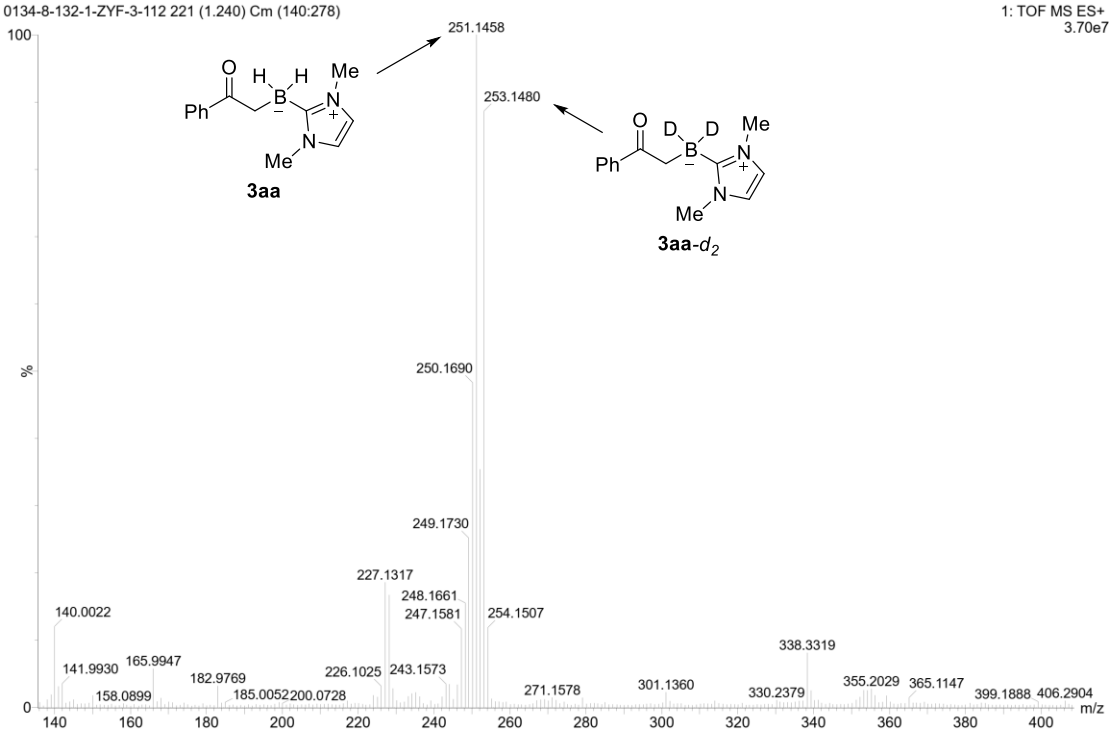


1a (1.5 mmol) **2a** (0.25 mmol) **3aa** **3aa**-d_2

3aa:**3aa**-d_2 ≈ 1.1

Followed the general procedure A, an oven-dried 25 mL Schlenk tube was

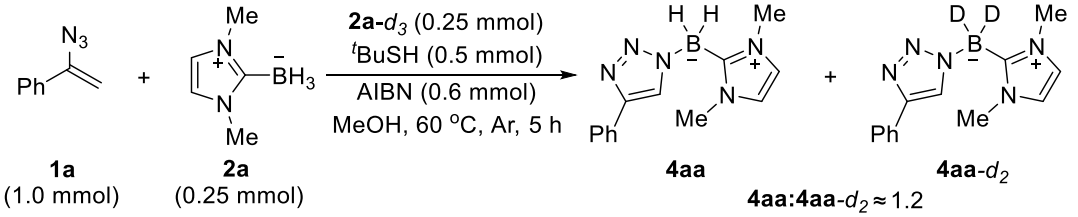
equipped with a magnetic stir bar and charged with vinyl azide **1a** (218.0 mg, 1.5 mmol), NHC-BH_3 **2a** (27.5 mg, 0.25 mmol), NHC-BD_3 **2a**-d_3 (28.3 mg, 0.25 mmol), ^{t}BuSH (85 μL, 0.75 mmol), and Cs_2CO_3 (81.5 mg, 0.25 mmol) in 1-butanol (5 mL). The reaction mixture was then stirred at 60 °C for 5 h. The crude product was purified by flash column chromatography eluting with petroleum ether/EtOAc/Et_3N (1:1:0.01, v/v/v) to afford a mixture of **3aa** and **3aa**-d_2 in a ratio of about 1.1/1 according to LC-MS analysis.



entry	calculated mass	m/z	intensity
3aa	$[M + Na]^+$: 251.1326	251.1458	3.695e7
3aa-d_2	$[M + Na]^+$: 253.1452	253.1480	3.276e7

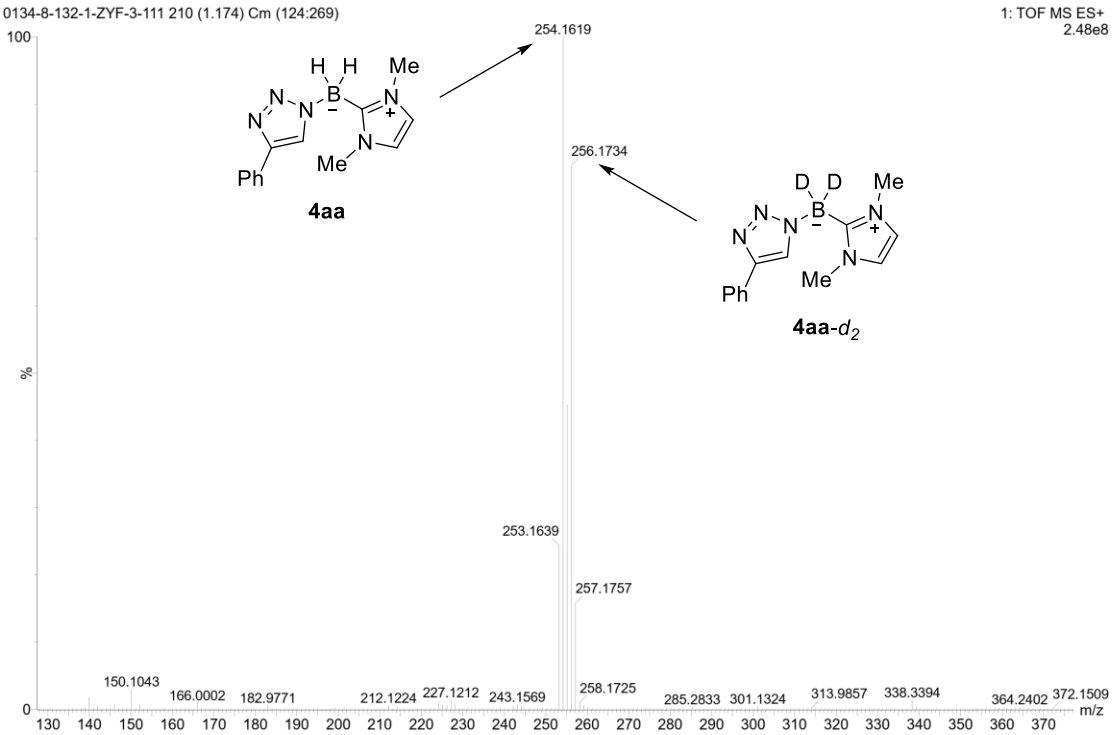
Figure S6. LC-MS (ESI) spectrum for a mixture of **3aa** and **3aa**-d_2.

equation 2



Followed the general procedure C, an oven-dried 25 mL Schlenk tube was equipped with a magnetic stir bar and charged with vinyl azide **1a** (145.2 mg, 1.0 mmol), NHC-BH_3 **2a** (27.5 mg, 0.5 mmol), NHC-BD_3 **2a**-d_3 (28.3 mg, 0.25 mmol),

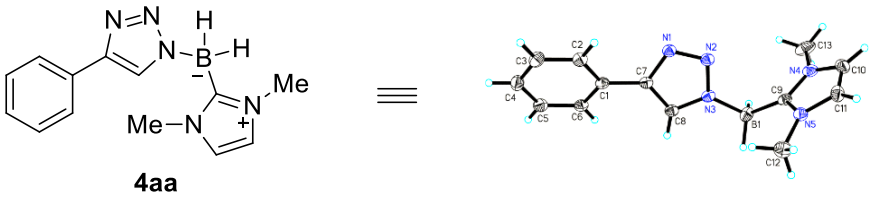
^{t}BuSH (57 μL, 0.5 mmol), and AIBN (98.5 mg, 0.6 mmol) in CH_3OH (5 mL). The reaction mixture was then stirred at 60 °C for 5 h. The crude product was purified by flash column chromatography on silica gel eluting with CH_2Cl_2/MeOH/Et_3N (40:1:0.01, v/v/v) to afford a mixture of **4aa** and **4aa**-d_2 in a ratio of about 1.2/1 according to LC-MS analysis.



entry	calculated mass	m/z	intensity
4aa	$[M + H]^+$: 254.1572	254.1619	2.478e8
4aa-d_2	$[M + H]^+$: 256.1697	256.1734	2.003e8

Figure S7. LC-MS (ESI) spectrum for a mixture of **4aa** and **4aa**-d_2.

7 Single crystal x-ray data



CCDC 2119463

Table S2. Crystal data and structure refinement for 4aa.

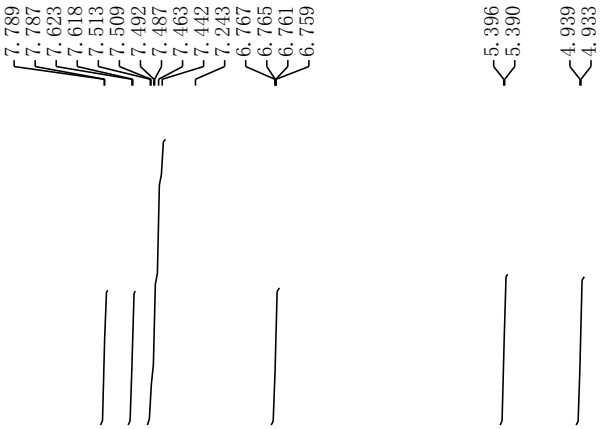
Identification code	**4aa**
Empirical formula	$C_{13}H_{16}BN_5$
Formula weight	253.11

Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	I2/a
a/Å	13.1462(13)
b/Å	8.7576(7)
c/Å	25.691(2)
α/°	90
β/°	102.499(9)
γ/°	90
Volume/Å^3	2887.6(4)
Z	8
ρ_{calc}g/cm^3	1.206
μ/mm^{-1}	0.078
F(000)	1112.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.926 to 49.998
Index ranges	-15 ≤ h ≤ 14, -10 ≤ k ≤ 9, -23 ≤ l ≤ 30
Reflections collected	5648
Independent reflections	2553 [R_{int} = 0.0261, R_{sigma} = 0.0355]
Data/restraints/parameters	2553/0/194
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0466, wR_2 = 0.1073
Final R indexes [all data]	R_1 = 0.0582, wR_2 = 0.1147
Largest diff. peak/hole / e Å^{-3}	0.18/-0.20

8 References

1. Liu, Z.; Liao, P.; Bi, X. General Silver-catalyzed hydroazidation of terminal alkynes by combining TMS-N_3 and H_2O: Synthesis of vinyl azides. *Org. Lett.* **2014**, *16*, 3668−3671.
2. (a) Gardner, S.; Kawamoto, T.; Curran, D. P. Synthesis of 1,3-dialkylimidazol-2-ylidene boranes from 1,3-dialkylimidazolium iodides and sodium borohydride, *J. Org. Chem.* **2015**, *80*, 9794−9797. (b) Kawamoto, T.; Geib, S. J.; Curran, D. P. Radical reactions of *N*-heterocyclic carbene boranes with organic nitriles: Cyanation of NHC-boranes and reductive decyanation of malononitriles, *J. Am. Chem. Soc.* **2015**, *137*, 8617−8622.
3. Dai, W.; Geib, S. J.; Curran, D. P. Facile Synthesis of α-*N*-heterocyclic carbene-boryl ketones from *N*-heterocyclic carbene-boranes and alkenyl triflates. *J. Am. Chem. Soc.* **2019**, *141*, 12355−12361.

9 Copies of ^{1}H, ^{13}C NMR spectra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7.513
7.509
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7.243
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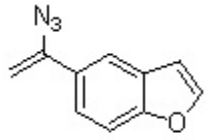
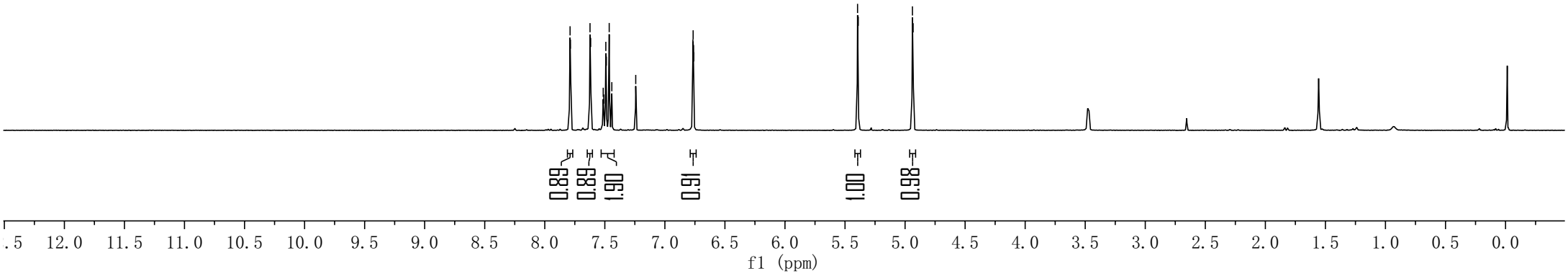
6.759
5.396
5.390
4.939
4.933


N3
O

1u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0.91
1.00
0.98
f1 (ppm)

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145.21
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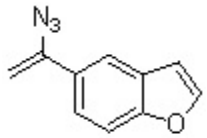
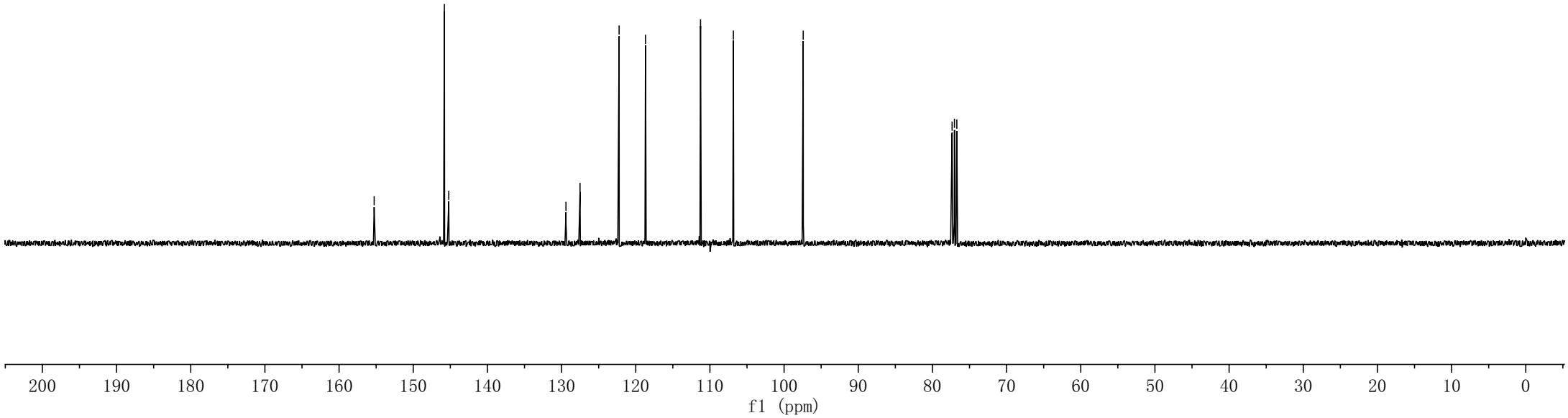
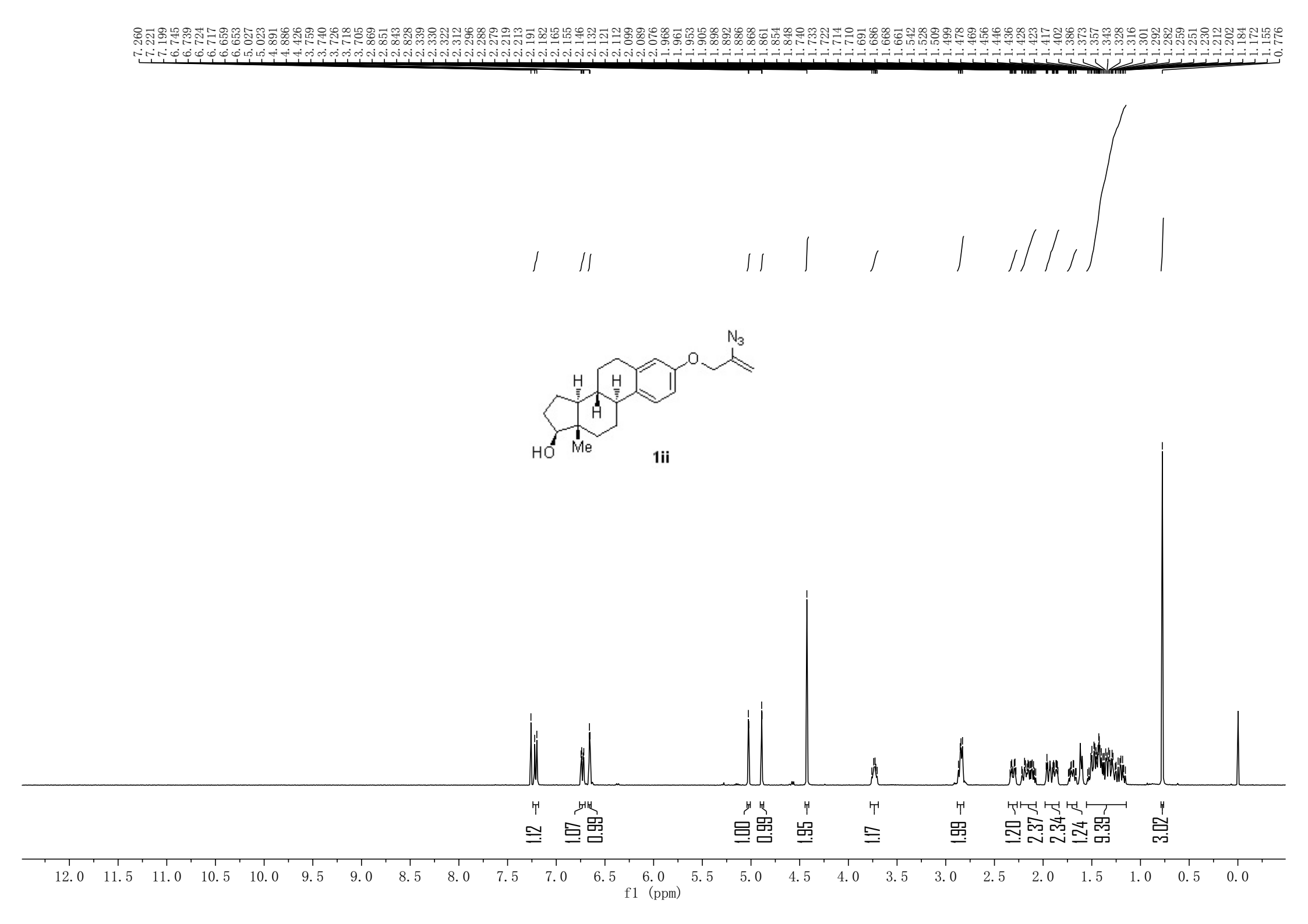
111.26
106.84
97.42
77.35
77.03
76.71



1u

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6.659
6.653
5.027
5.023
4.891
4.886
4.426
3.759
3.740
3.726
3.718
3.705
2.869
2.851
2.843
2.828
2.339
2.330
2.322
2.312
2.296
2.288
2.279
2.219
2.213
2.191
2.182
2.165
2.155
2.146
2.132
2.121
2.112
2.099
2.089
2.076
1.968
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1.953
1.905
1.898
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1.861
1.854
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1.740
1.733
1.722
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1.710
1.691
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1.668
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1.542
1.528
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1.499
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1.469
1.456
1.446
1.436
1.428
1.423
1.417
1.402
1.386
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1.357
1.343
1.328
1.316
1.301
1.292
1.282
1.259
1.251
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1.212
1.202
1.184
1.172
1.155
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H
H
H
HO
Me
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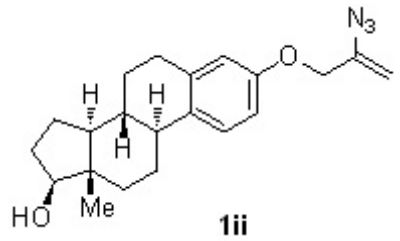
1.00
0.99
1.95
1.17
1.99
1.20
2.37
2.34
1.24
9.39
3.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

155.73
142.09
138.09
133.52
126.35
114.84
112.19
100.85
81.82
77.32
77.00
76.68
67.61
49.95
43.89
43.18
38.70
36.63
30.51
29.72
27.14
26.22
23.07
11.02



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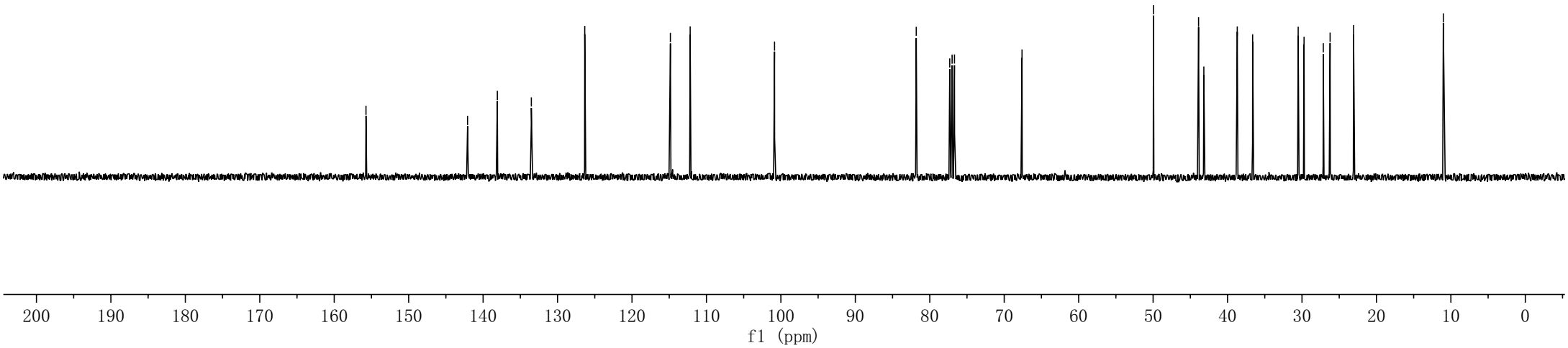

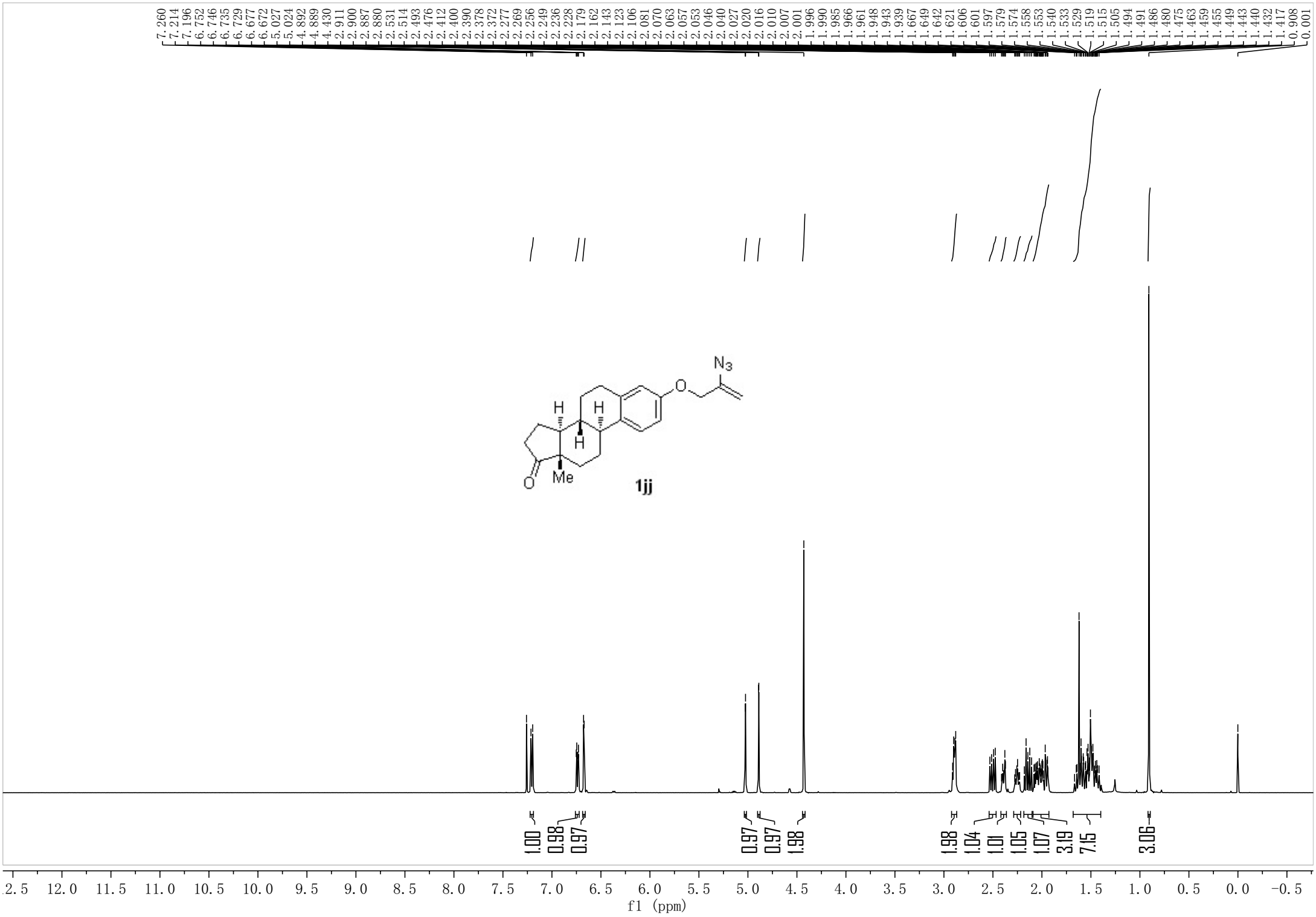
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4.889
4.430
2.911
2.900
2.887
2.880
2.531
2.514
2.493
2.476
2.412
2.400
2.390
2.378
2.372
2.277
2.269
2.256
2.249
2.236
2.228
2.179
2.162
2.143
2.123
2.106
2.081
2.070
2.063
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2.053
2.046
2.040
2.027
2.020
2.016
2.010
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1.621
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1.597
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1.574
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1.553
1.540
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1.529
1.519
1.515
1.505
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1.486
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1.475
1.463
1.459
1.455
1.449
1.443
1.440
1.432
1.417
0.908
0.001
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O
H
H
H
Me
O
1jj
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0.98
0.97
0.97
0.97
1.98
1.98
1.04
1.01
1.05
1.07
3.19
7.15
3.06
2.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
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0.5
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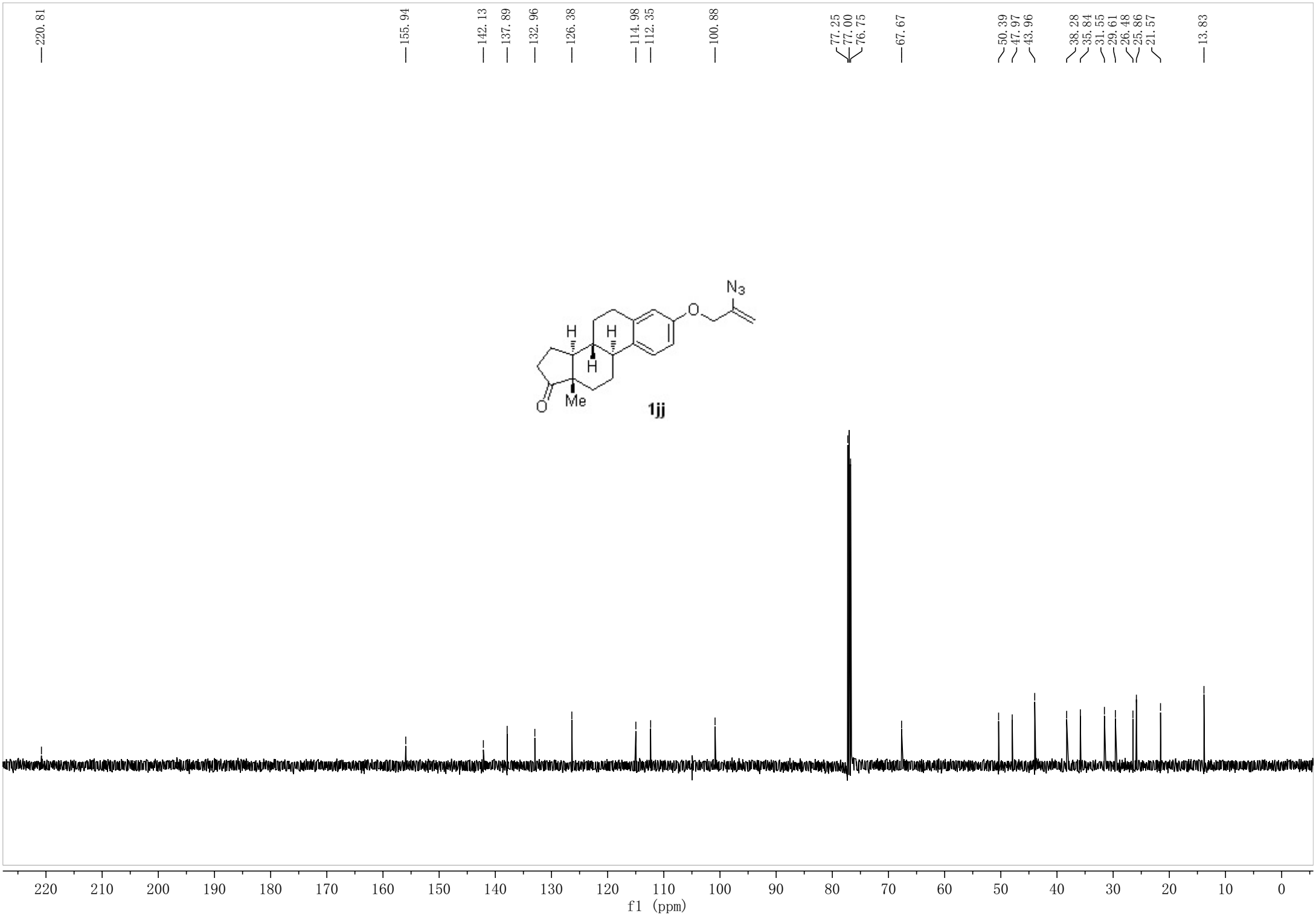
f1 (ppm)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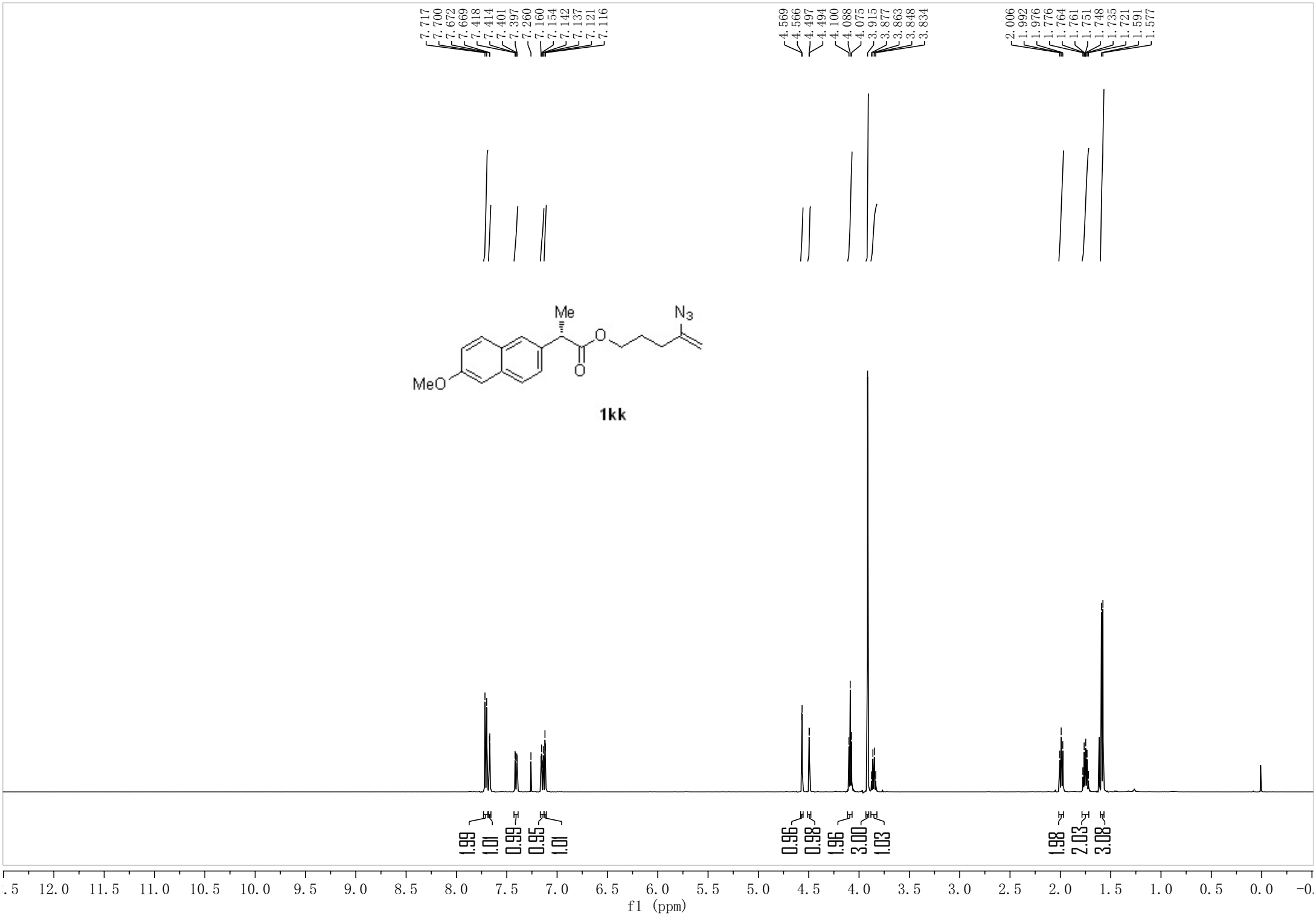
50.39
47.97
43.96
38.28
35.84
31.55
29.61
26.48
25.86
21.57
13.83
N3
O
H
H
H
O
Me
1jj
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.397
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7.154
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7.121
7.116
4.569
4.566
4.497
4.494
4.100
4.088
4.075
3.915
3.877
3.863
3.848
3.834
2.006
1.992
1.976
1.776
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1.761
1.751
1.748
1.735
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1.577
Me
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O
O
MeO
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1.01
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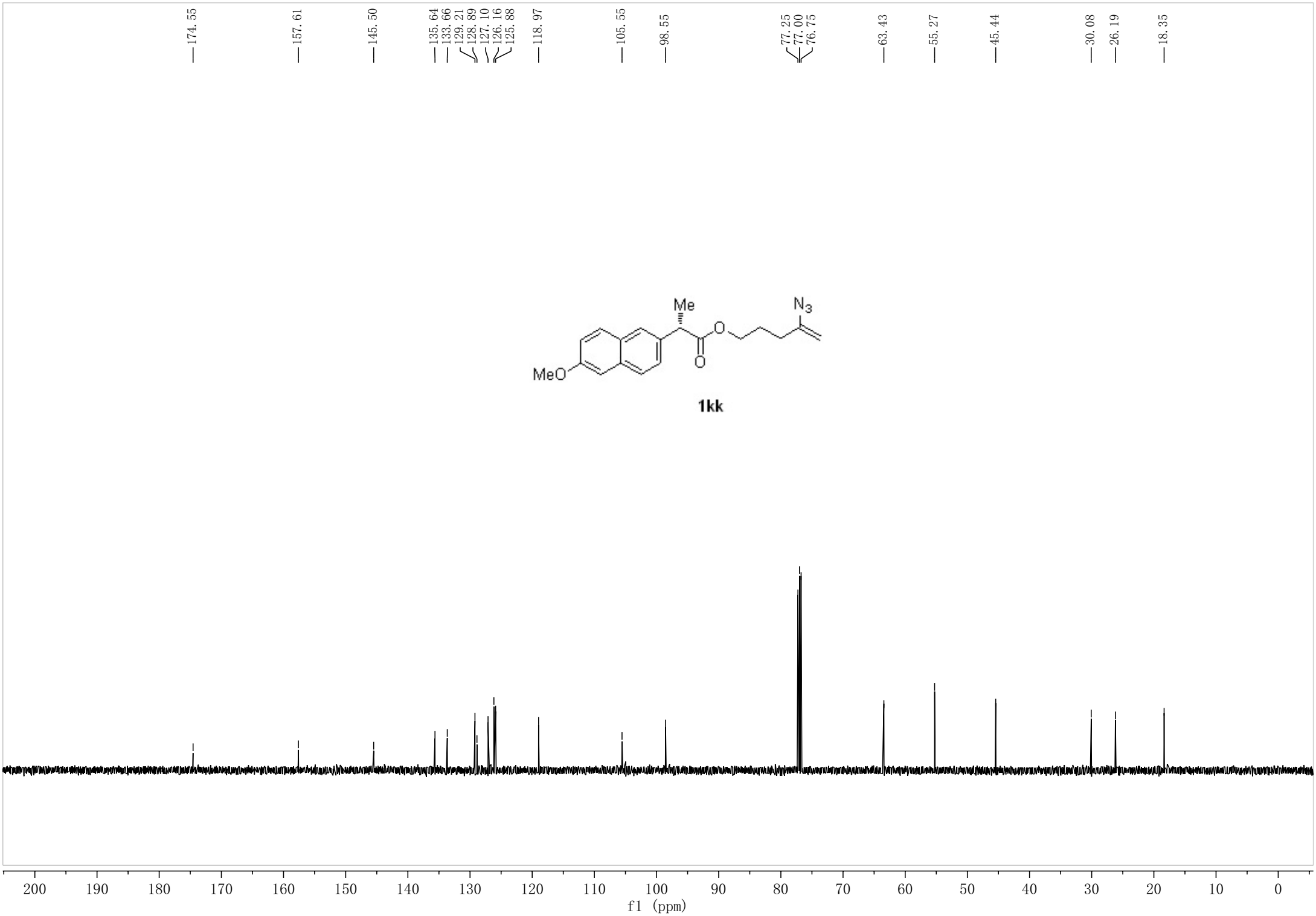
2.03
3.08
f1 (ppm)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77.25
77.00
76.75
63.43
55.27
45.44
30.08
26.19
18.35
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N3
O
O
MeO
1kk
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180
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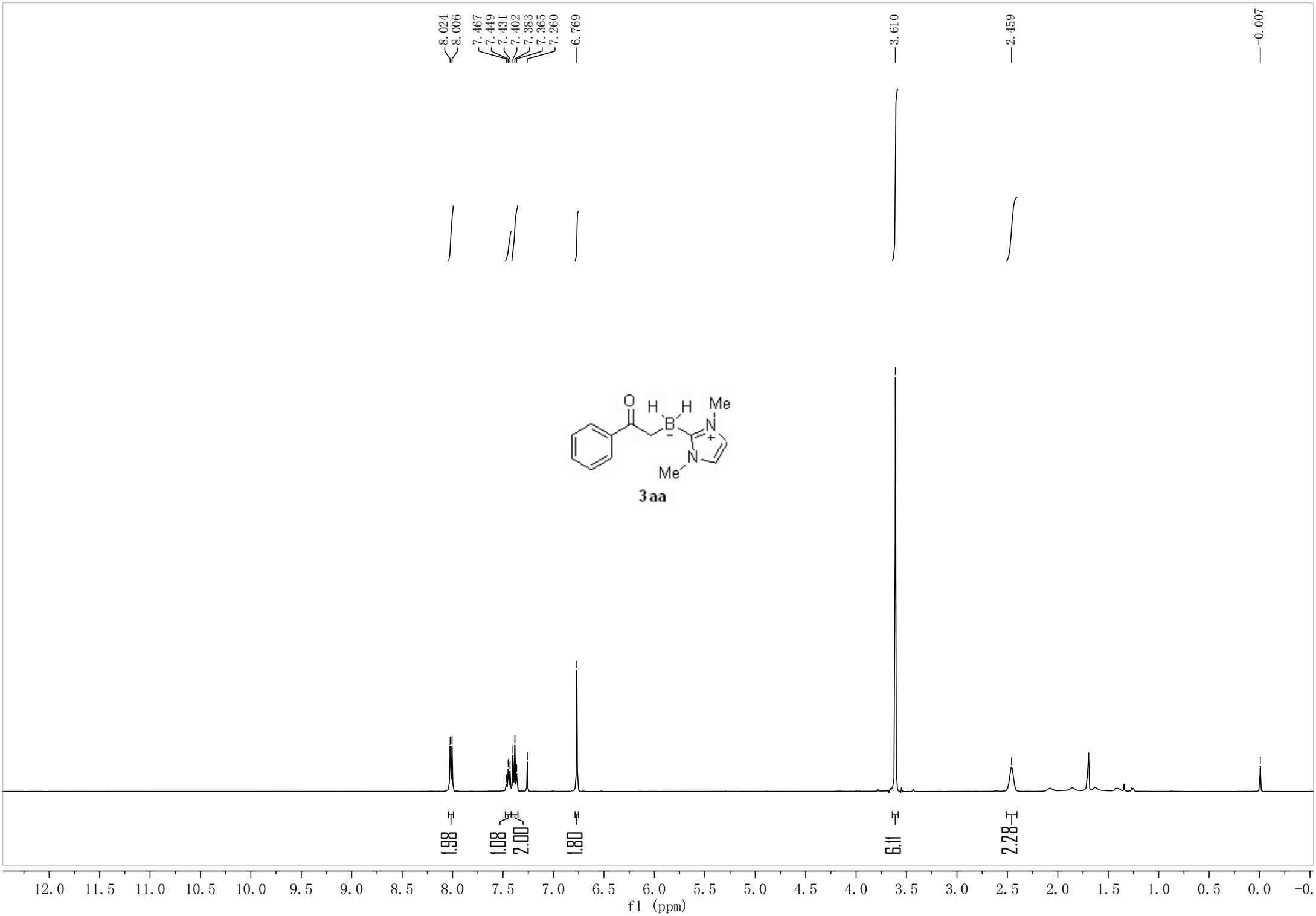
50
40
30
20
10
0
f1 (ppm)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7.402
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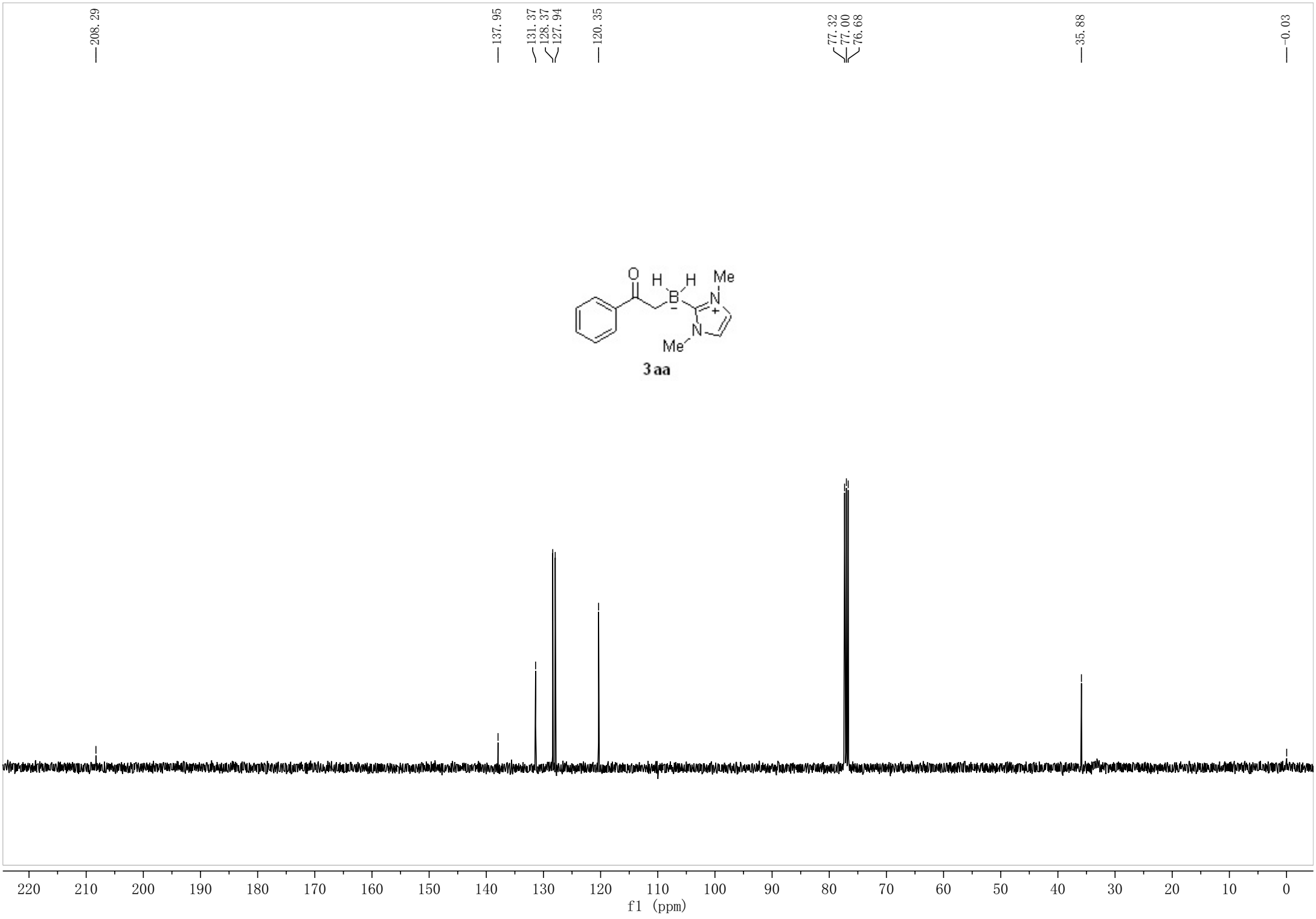
O
H
B
H
Me
N
N
Me
3aa
1.98
1.08
2.00
1.80
6.11
2.28
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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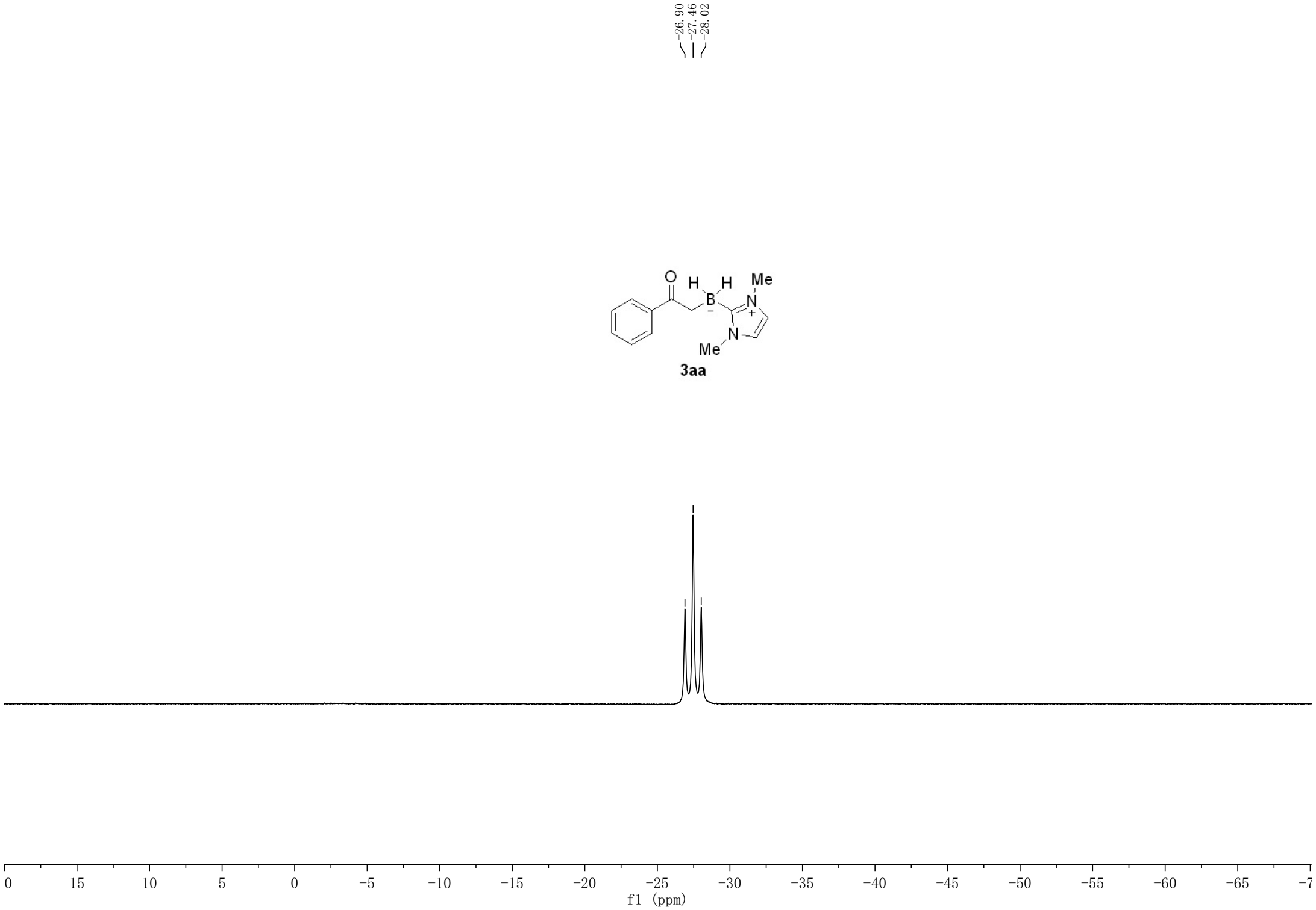
127.94
120.35
77.32
77.00
76.68
35.88
-0.03
O
H
H
B
Me
N
N
Me
3aa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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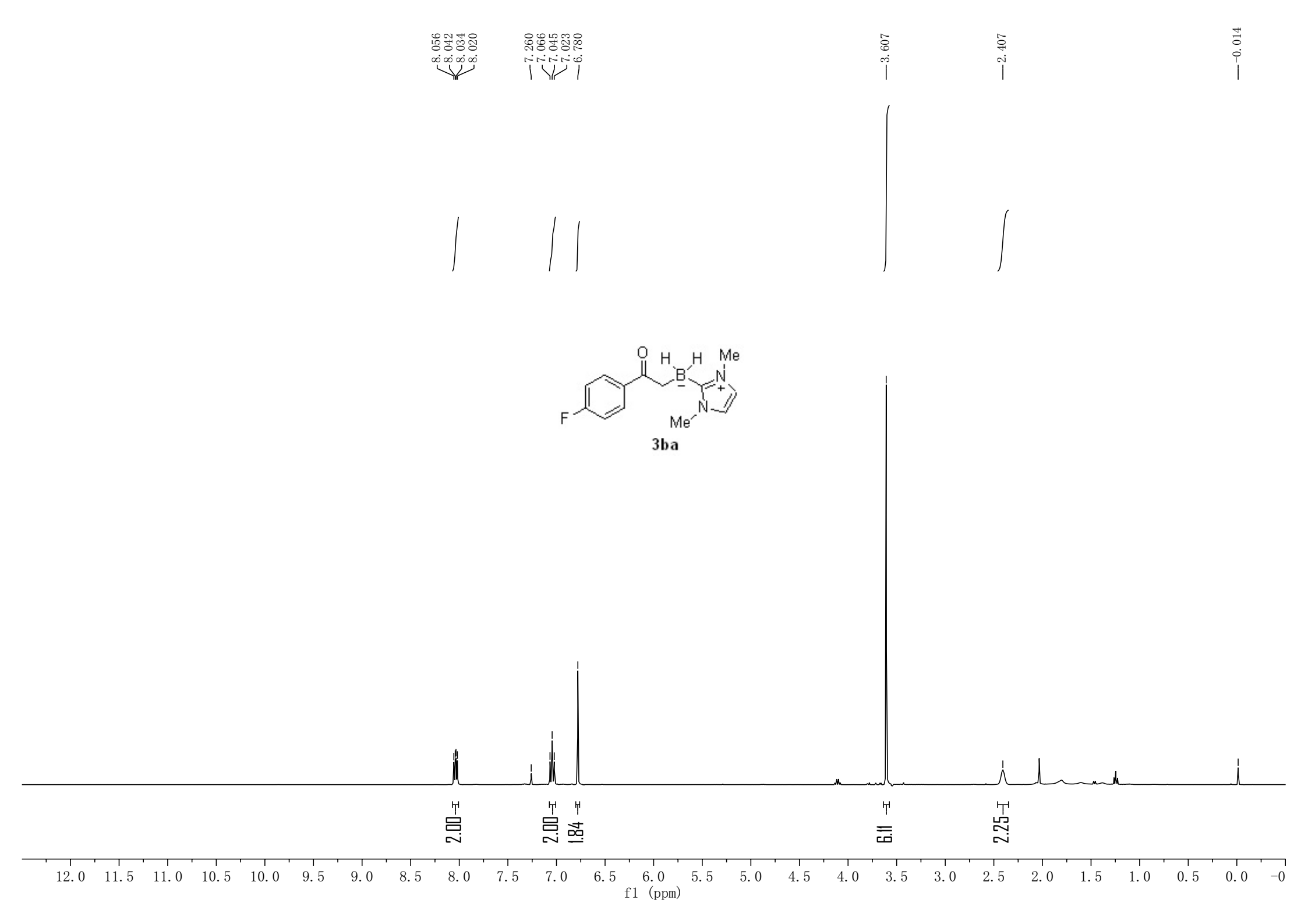
-28.02
O
H
H
B
-
N
+
N
Me
Me
3aa
0
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)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7.045
7.023
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-0.014
O
H
H
B
Me
N
N
Me
F
3ba
2.00
2.00
1.84
6.11
2.25
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

206.68
166.02
163.52
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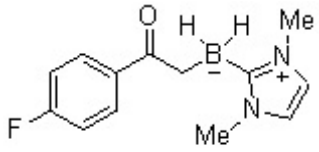
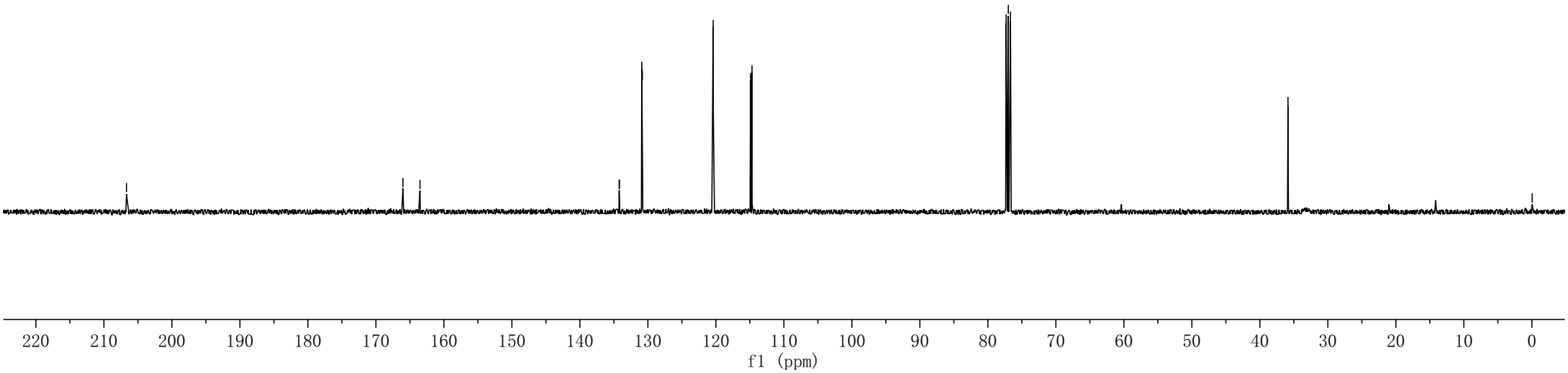
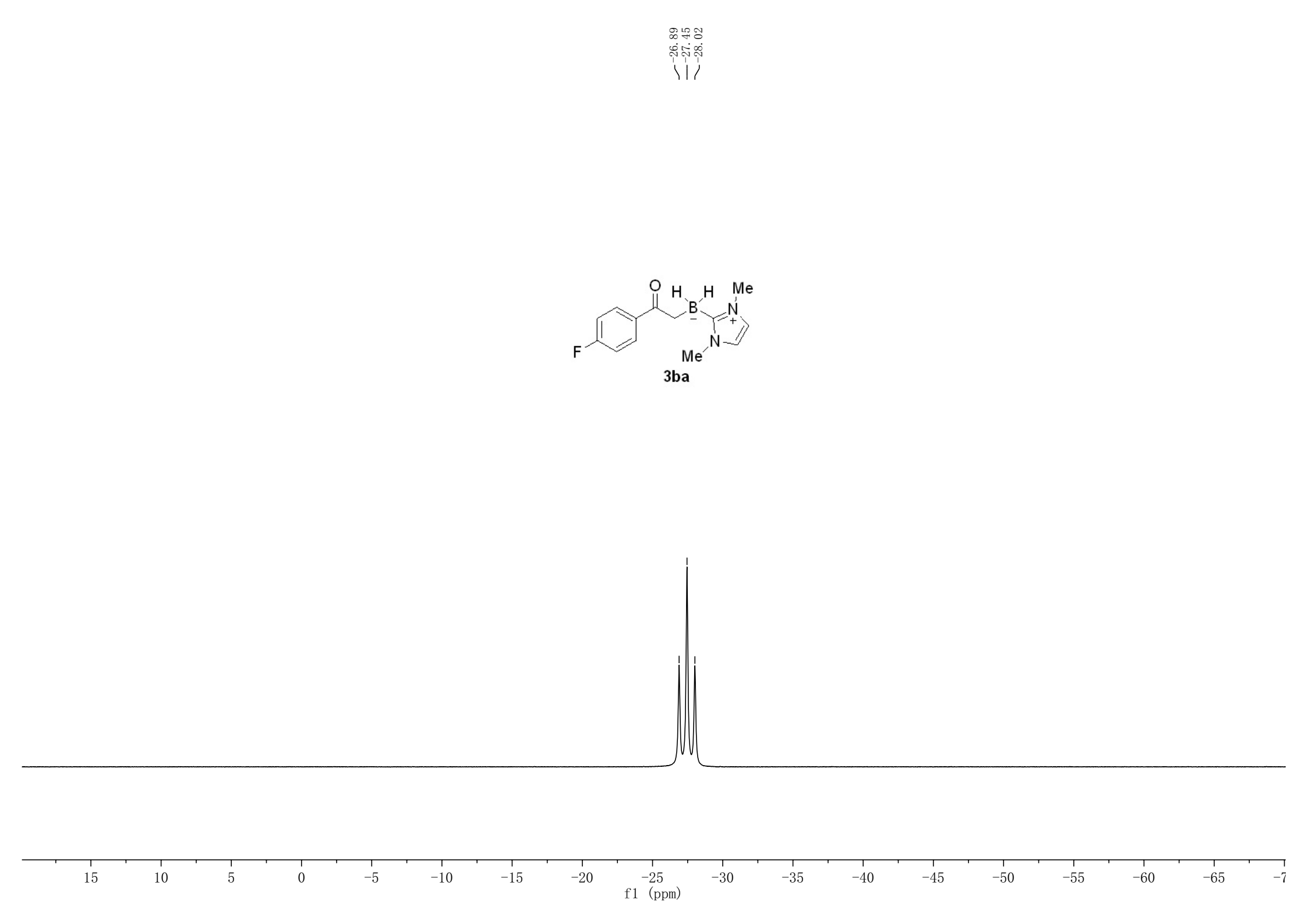


3ba

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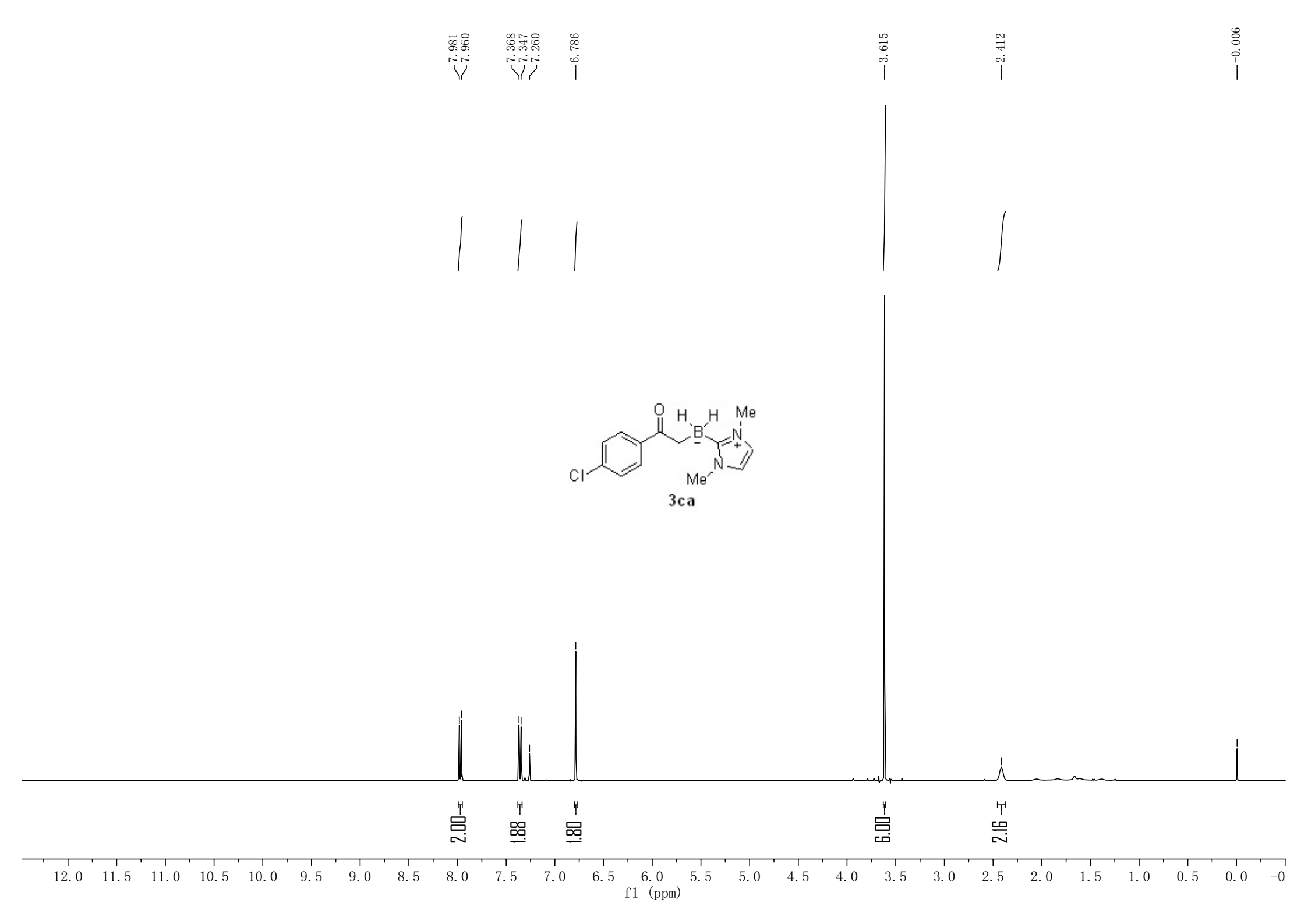
-27.45
-28.02
O
H
H
B
Me
N
N
Me
F
3ba
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)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H
B
H
Me
N
N
Me
Cl
3ca
2.00
1.88
1.80
6.00
2.16
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

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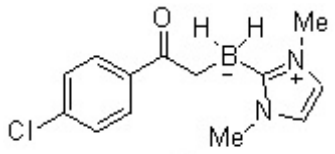
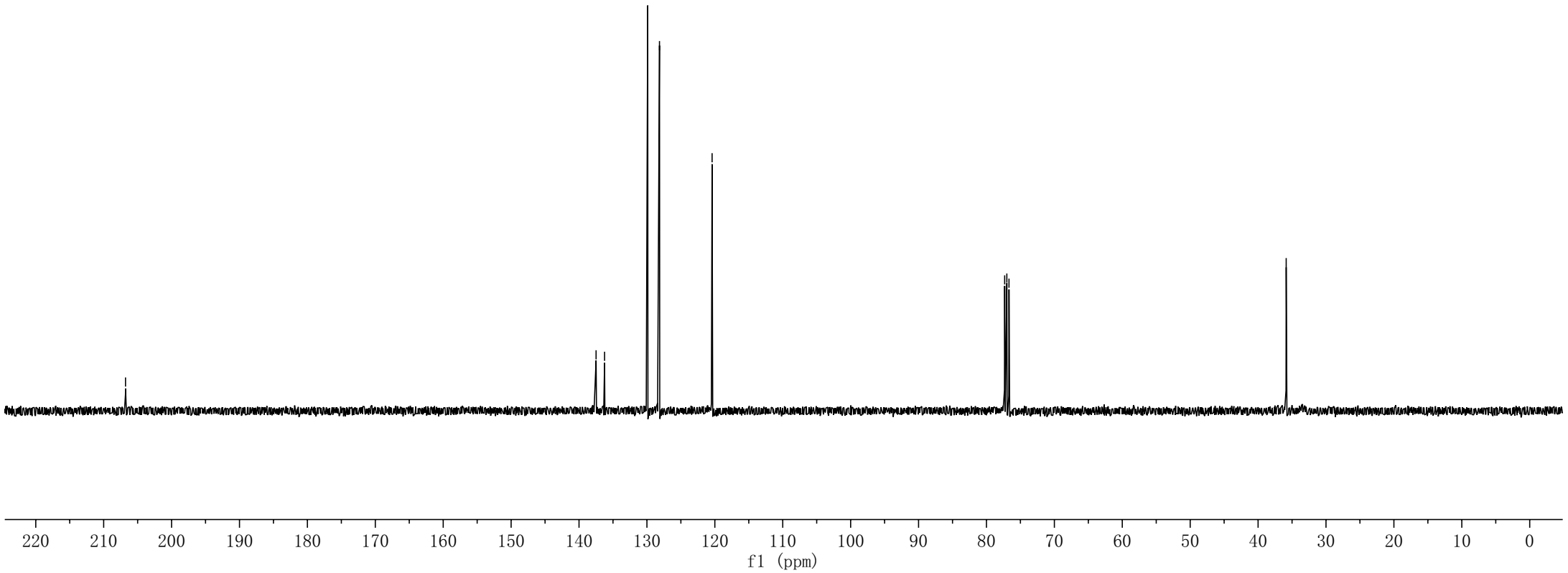
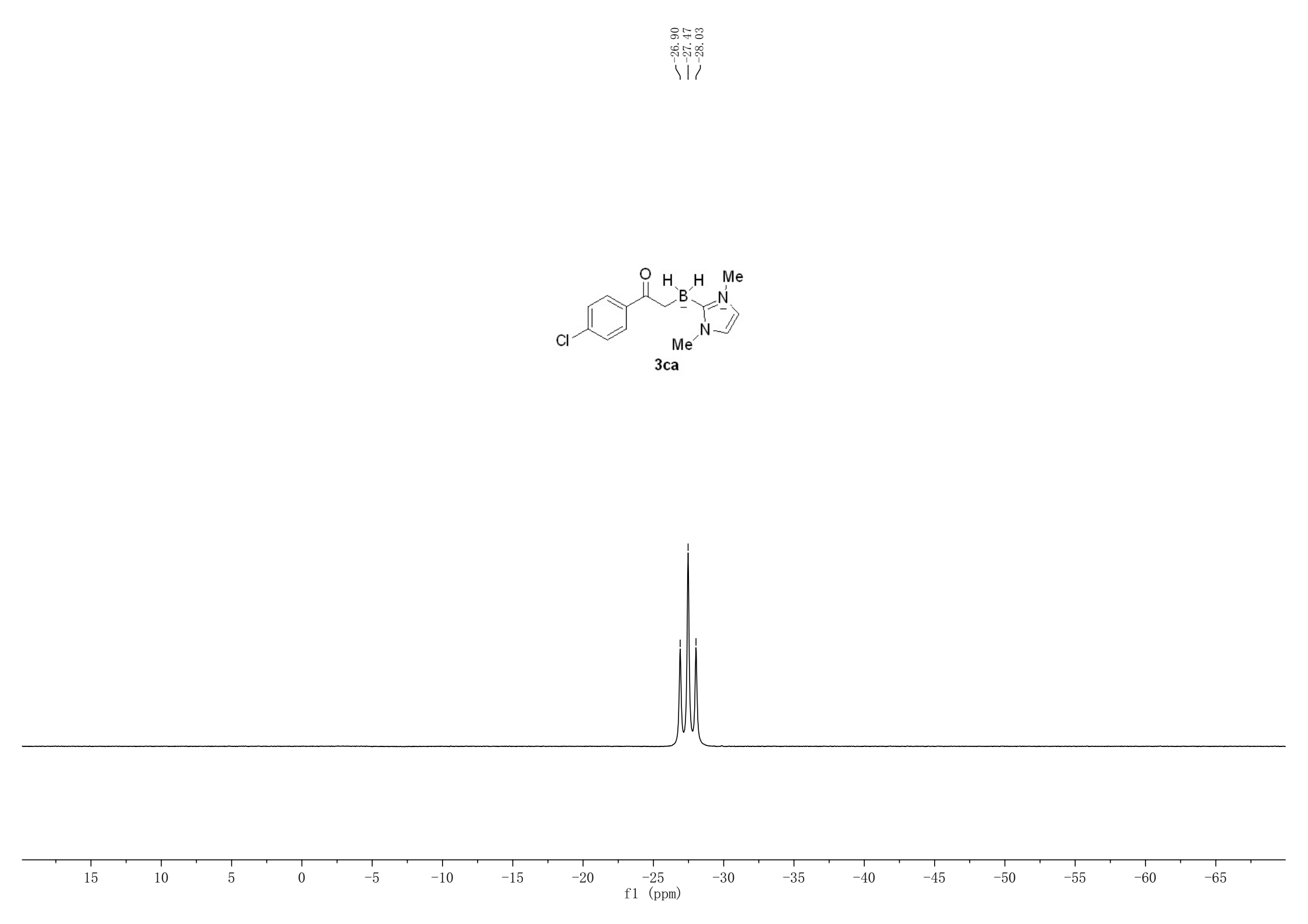
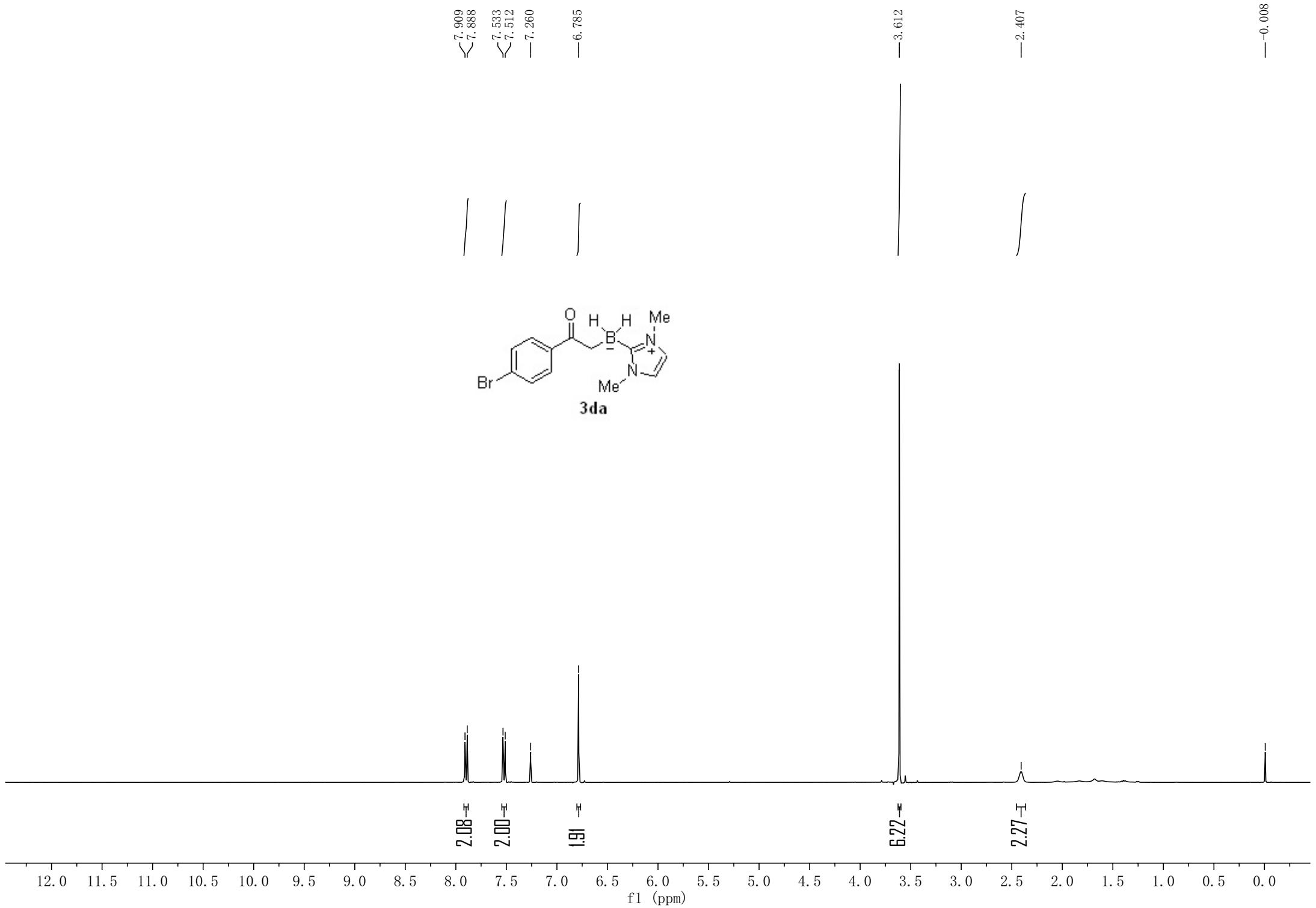
137.49
136.24
129.88
128.15
120.40
77.32
77.00
76.68
35.86

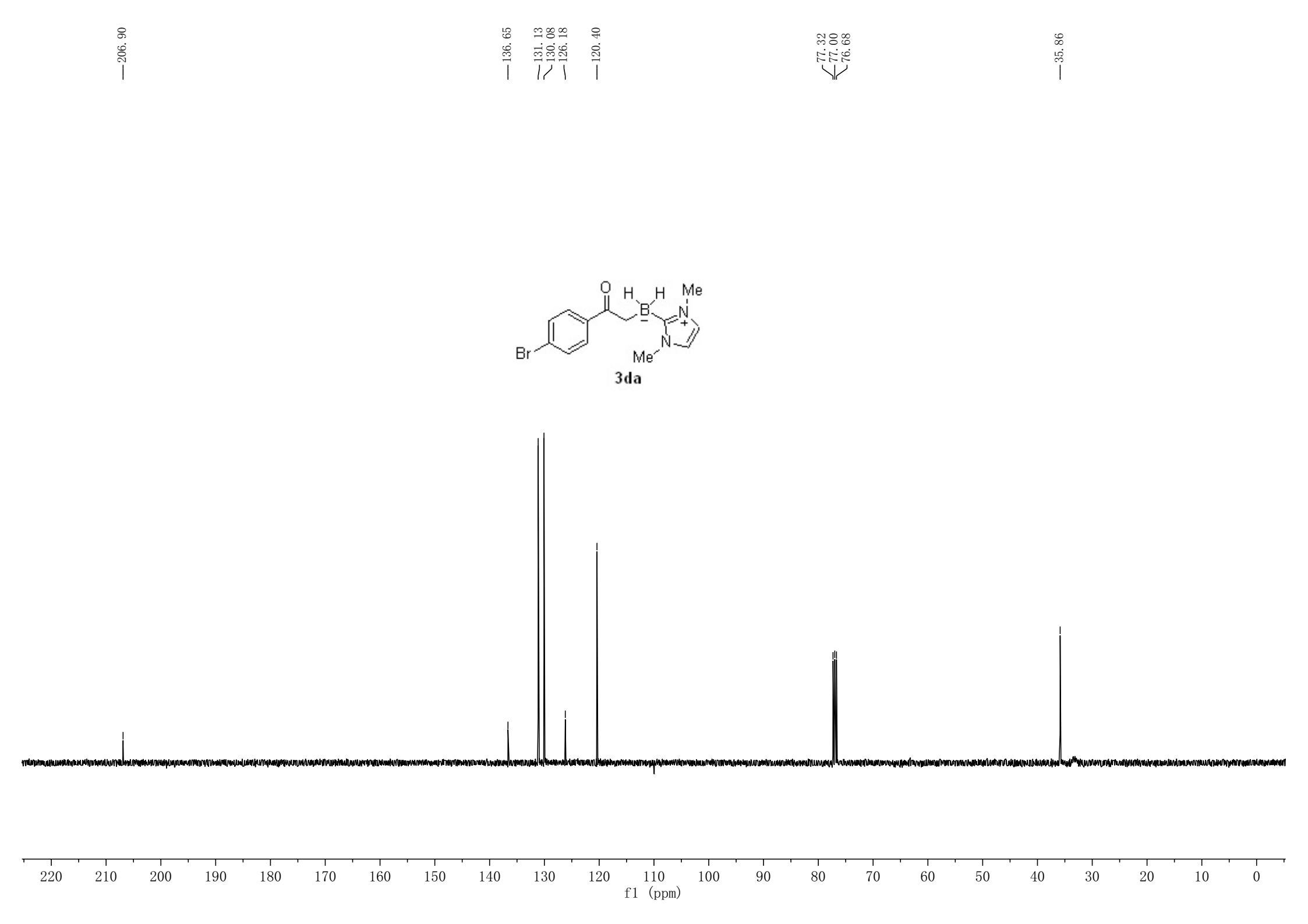


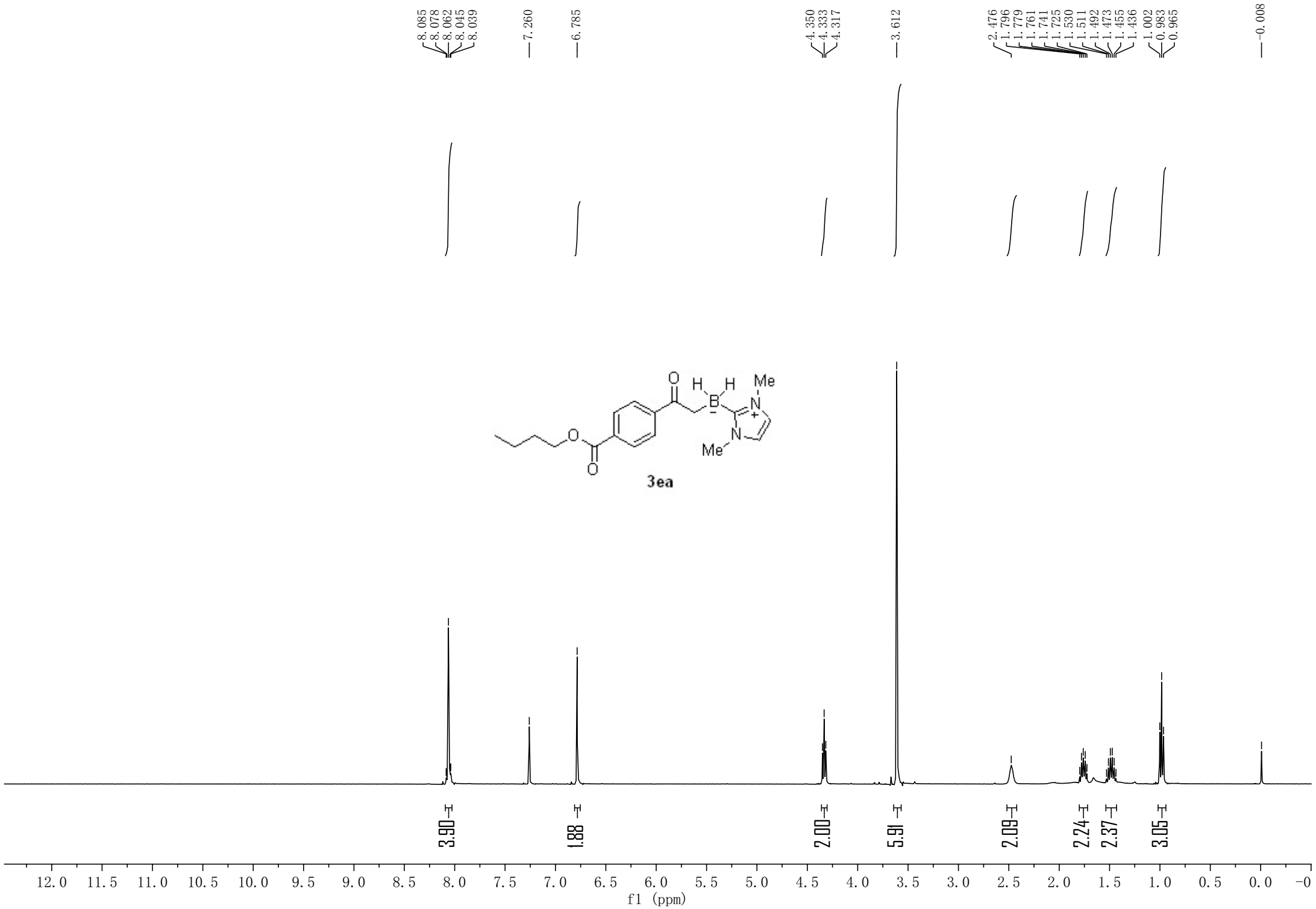
3ca



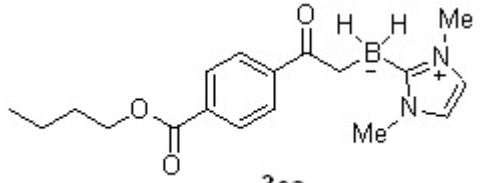

-26.90
-27.47
-28.03
O
H
H
B
Me
N
N
Me
Cl
3ca
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)


7.909
7.888
7.533
7.512
7.260
6.785
3.612
2.407
0.008
O
H
H
B
Me
N
N
Me
Br
3da
2.08
2.00
1.91
6.22
2.27
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

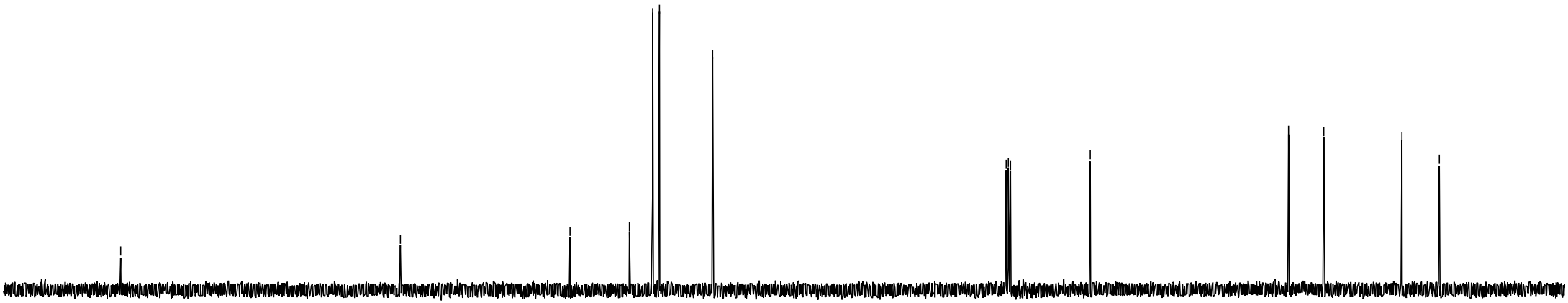

206.90
136.65
131.13
130.08
126.18
120.40
77.32
77.00
76.68
35.86
O
H
H
B
Me
N
N
Me
Br
3da
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

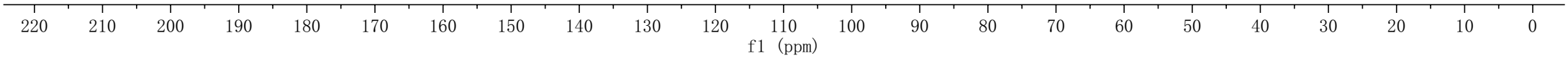

8.085
8.078
8.062
8.045
8.039
7.260
6.785
4.350
4.333
4.317
3.612
2.476
1.796
1.779
1.761
1.741
1.725
1.530
1.511
1.492
1.473
1.455
1.436
1.002
0.983
0.965
-0.008
O
H
H
B
Me
N
N
Me
O
O
3ea
3.90
1.88
2.00
5.91
2.09
2.24
2.37
3.05
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

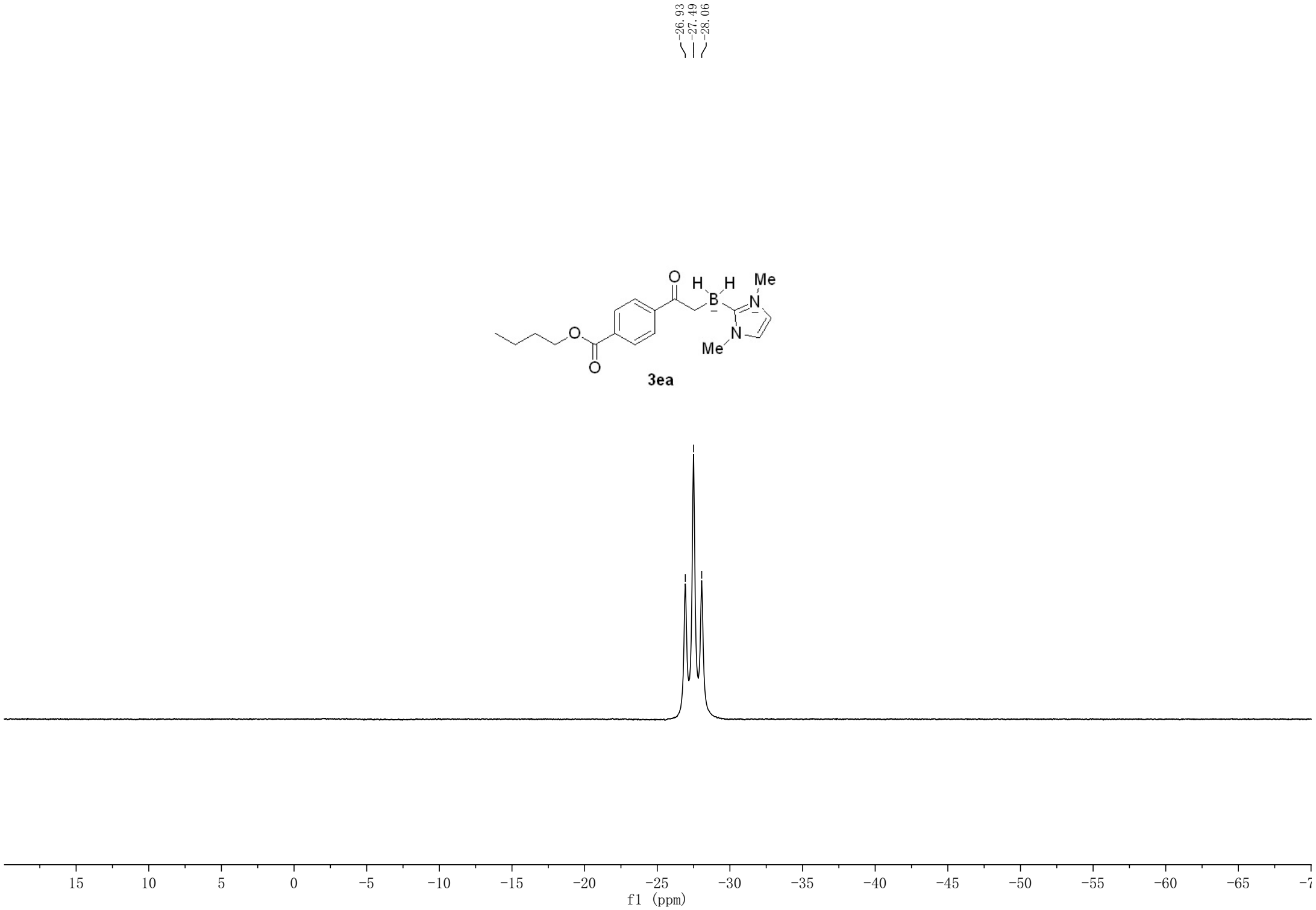
207.33
166.27
141.36
132.64
129.22
128.23
120.42
77.32
77.00
76.68
64.97
35.85
30.68
19.21
13.71

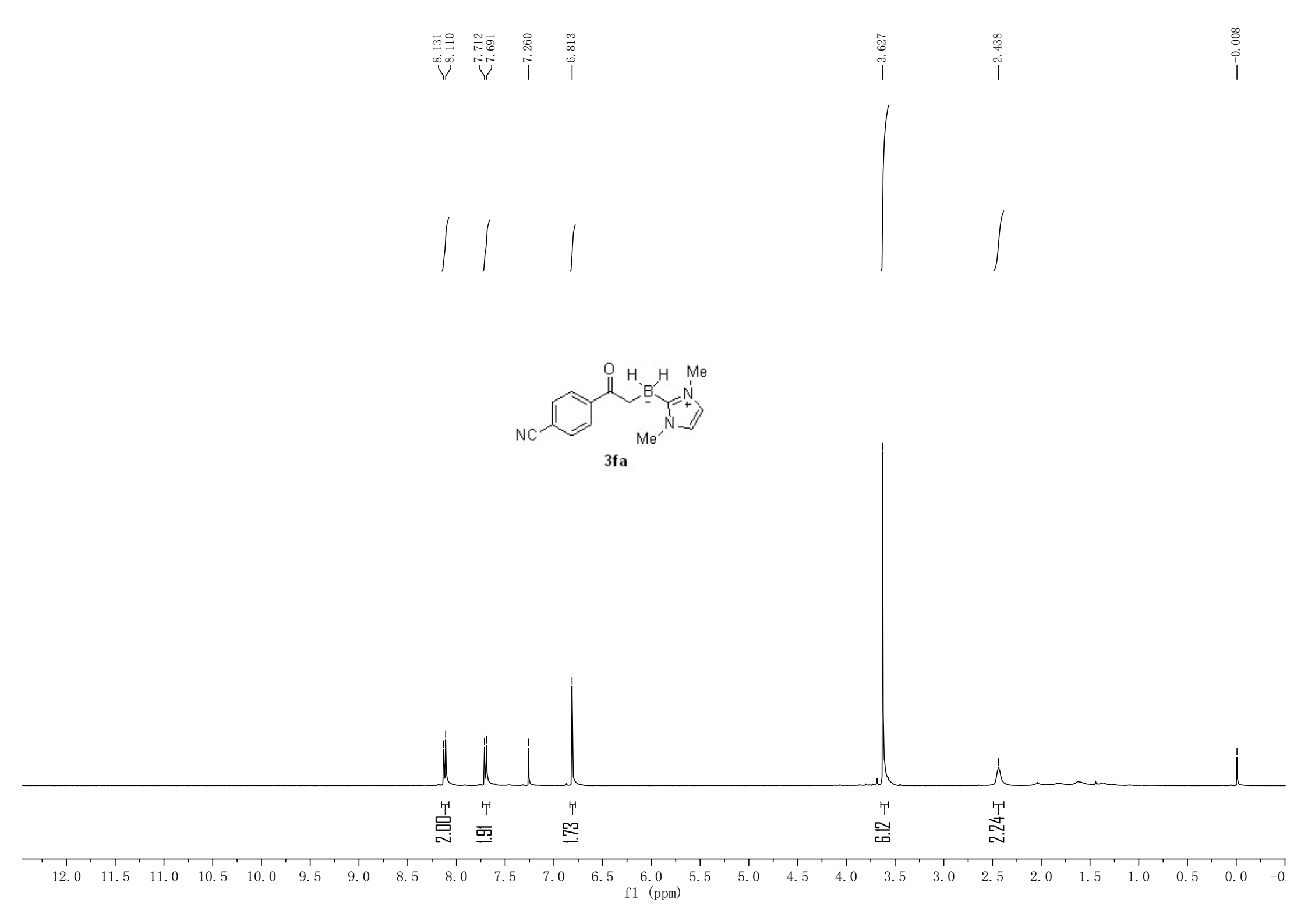


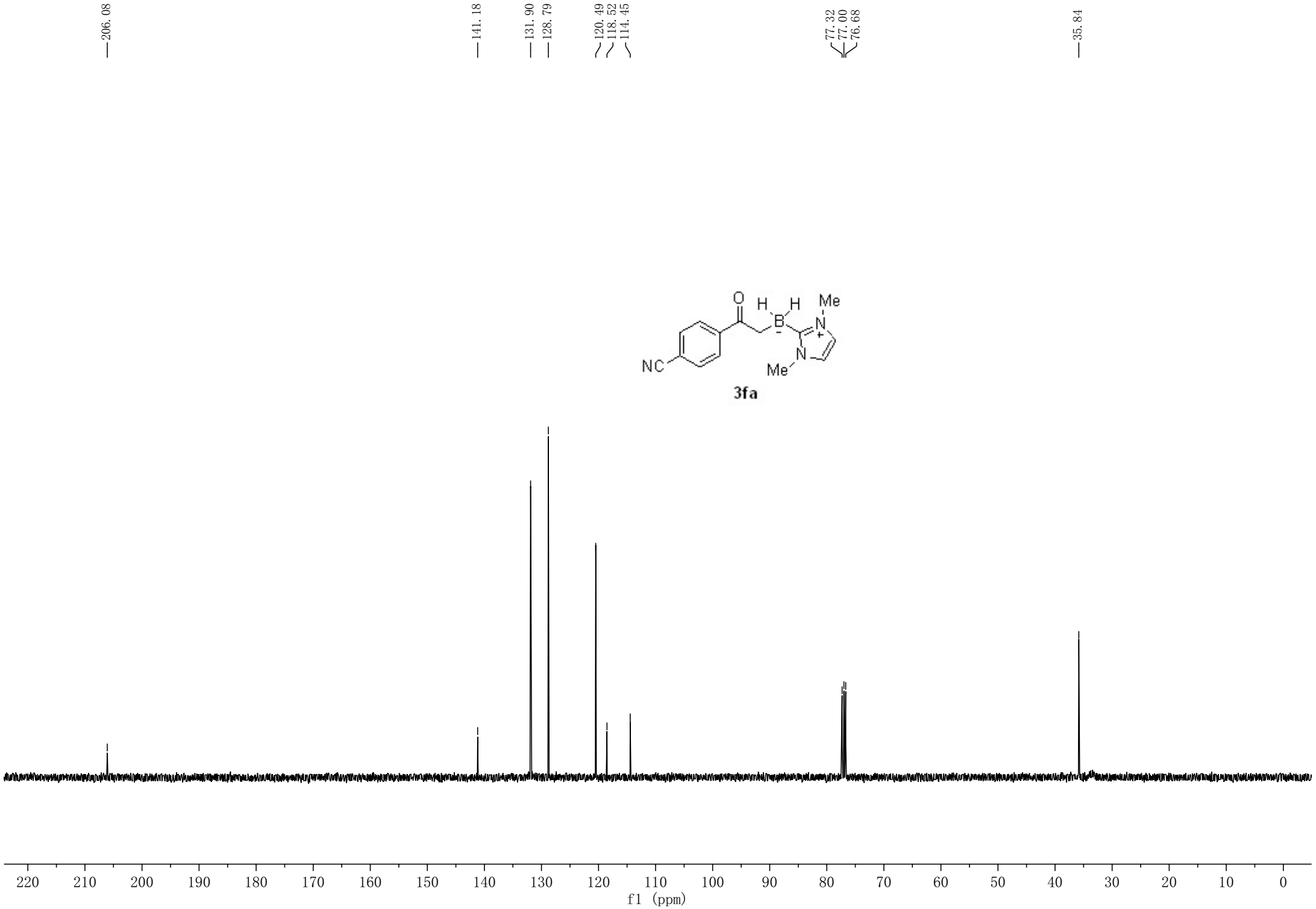
3ea

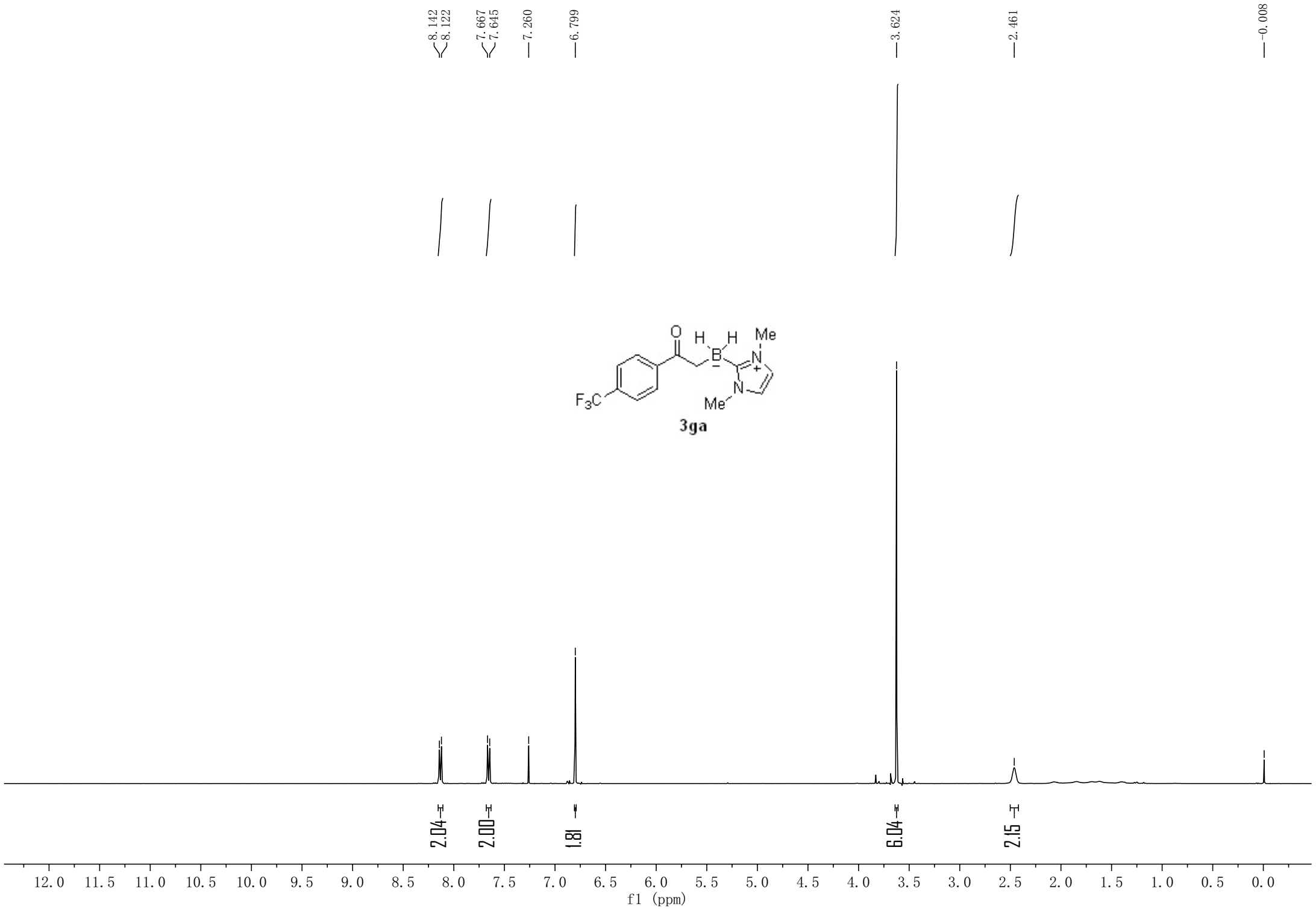


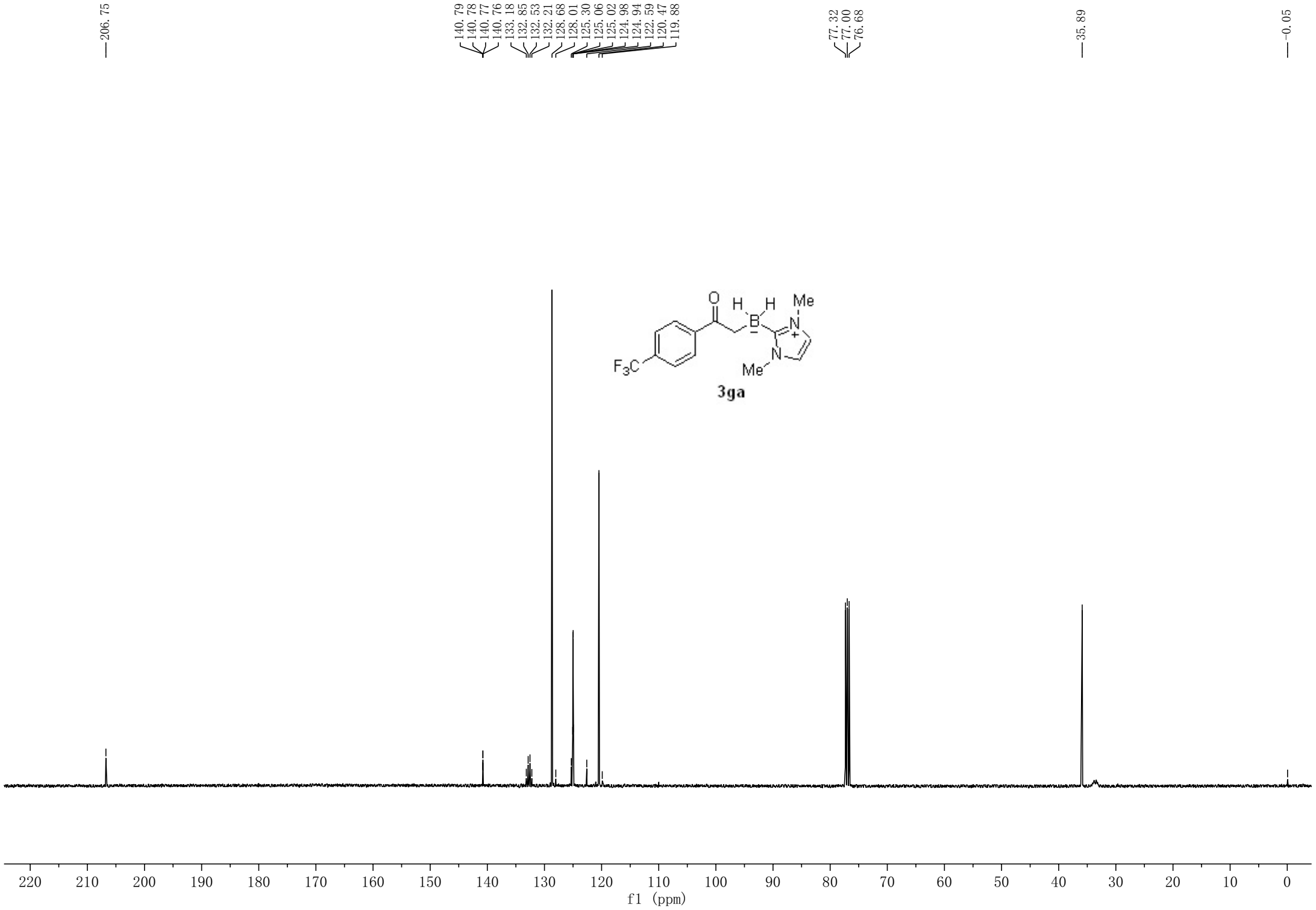


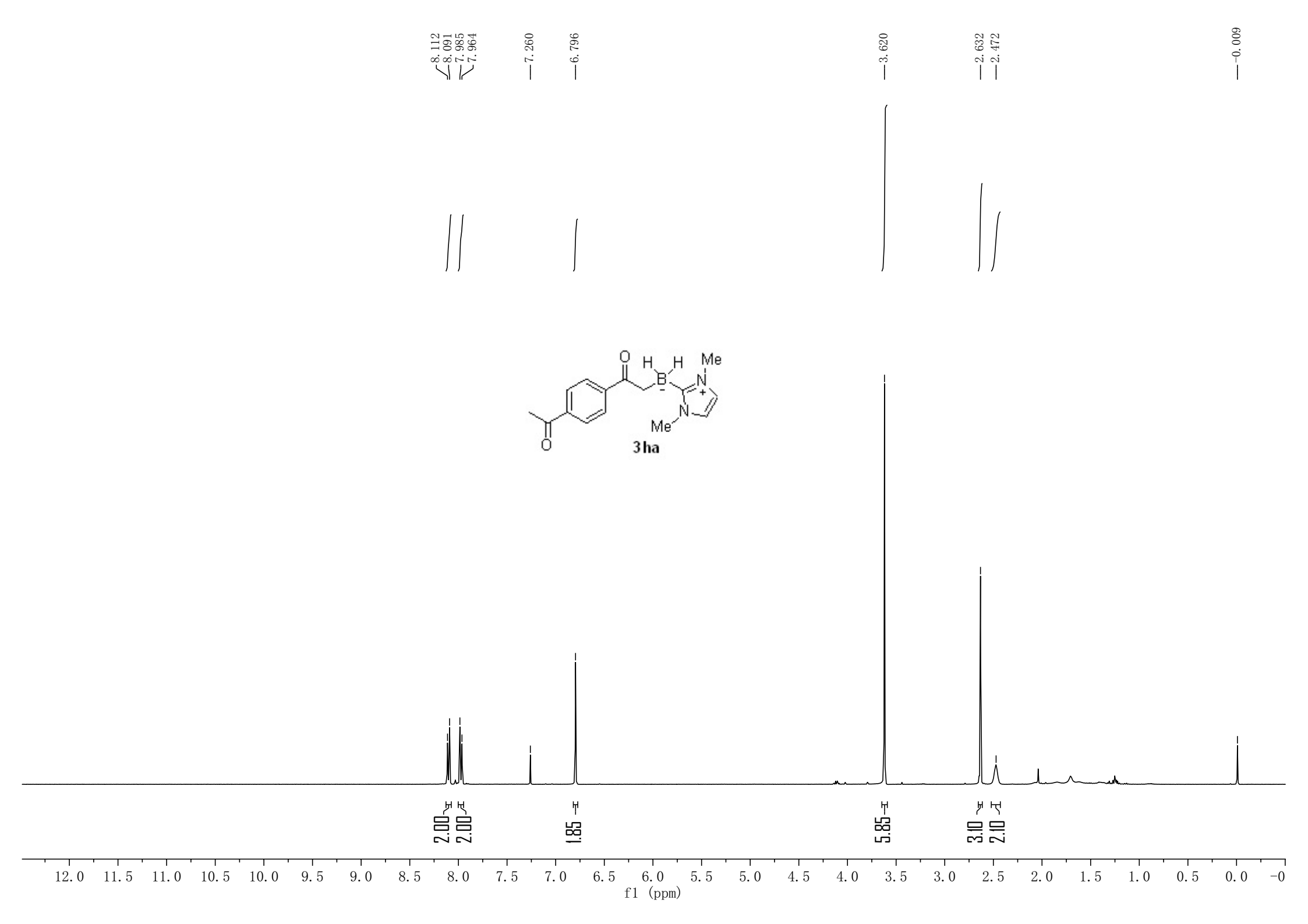

-26.93
-27.49
-28.06
O
H
H
B
Me
N
N
Me
O
O
3ea
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

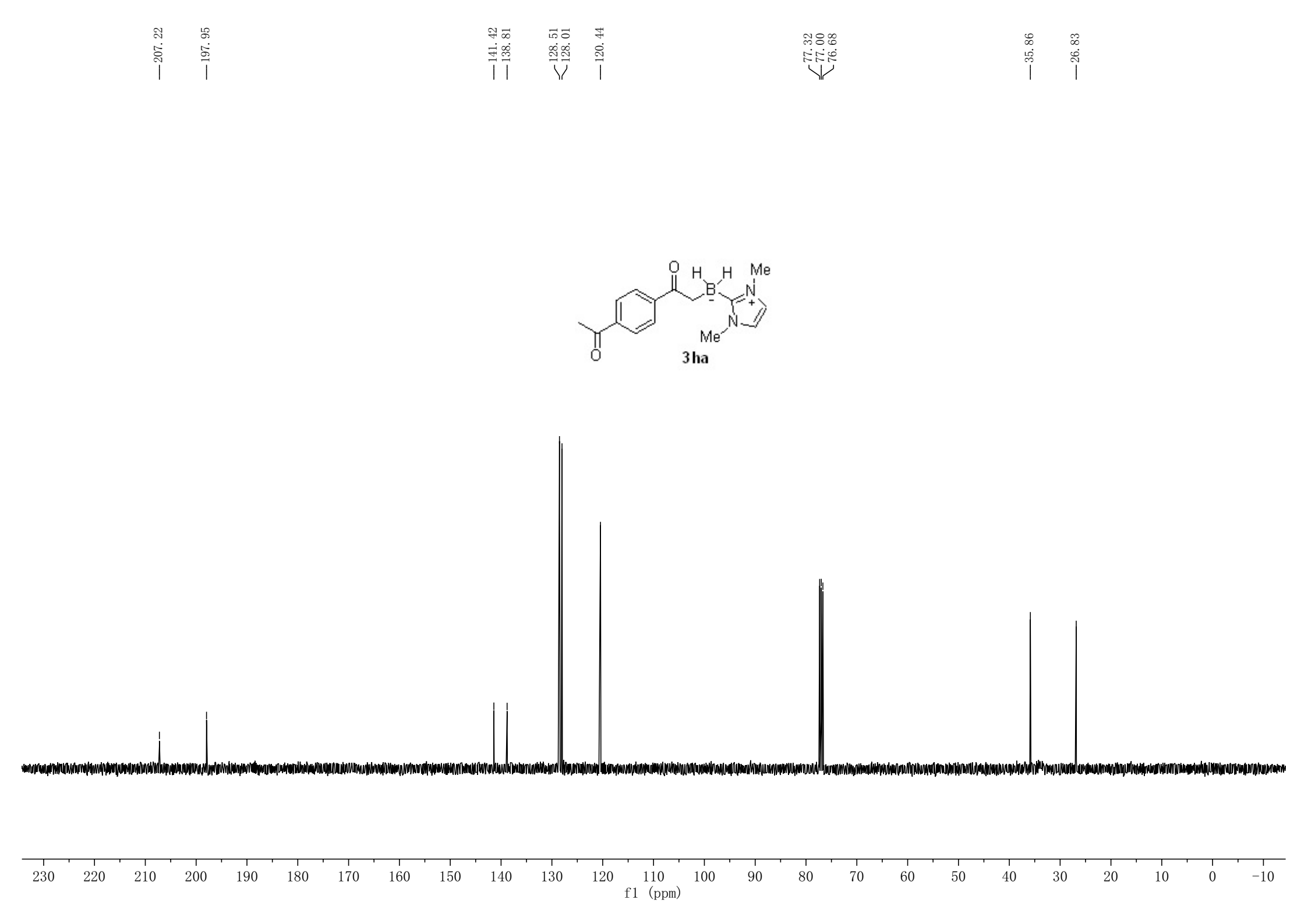

8.131
8.110
7.712
7.691
7.260
6.813
3.627
2.438
0.008
O
H
B
H
Me
N
N
Me
NC
3fa
2.00
1.91
1.73
6.12
2.24
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

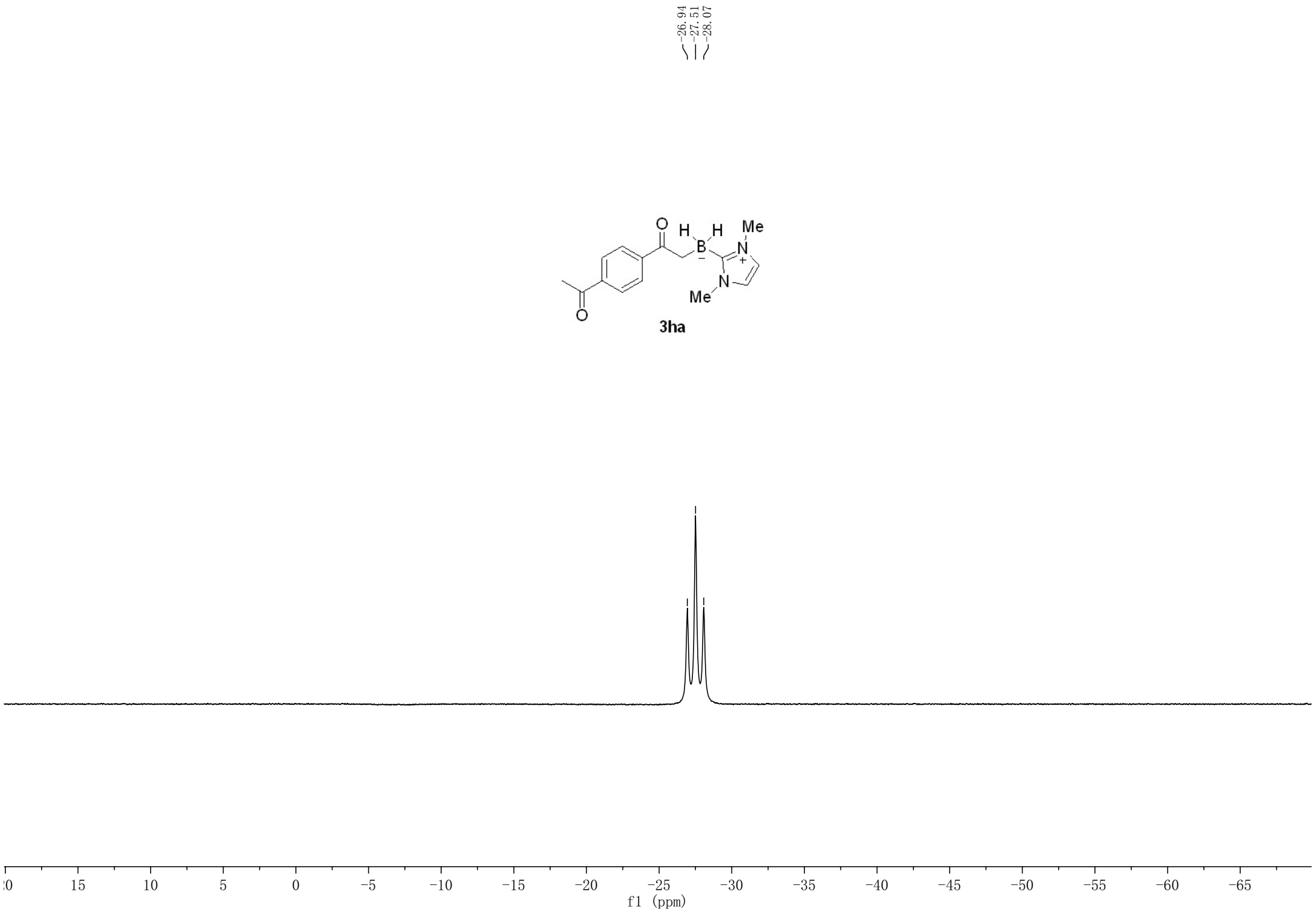

206.08
141.18
131.90
128.79
120.49
118.52
114.45
77.32
77.00
76.68
35.84
O
H
B
H
Me
N
N
Me
NC
3fa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

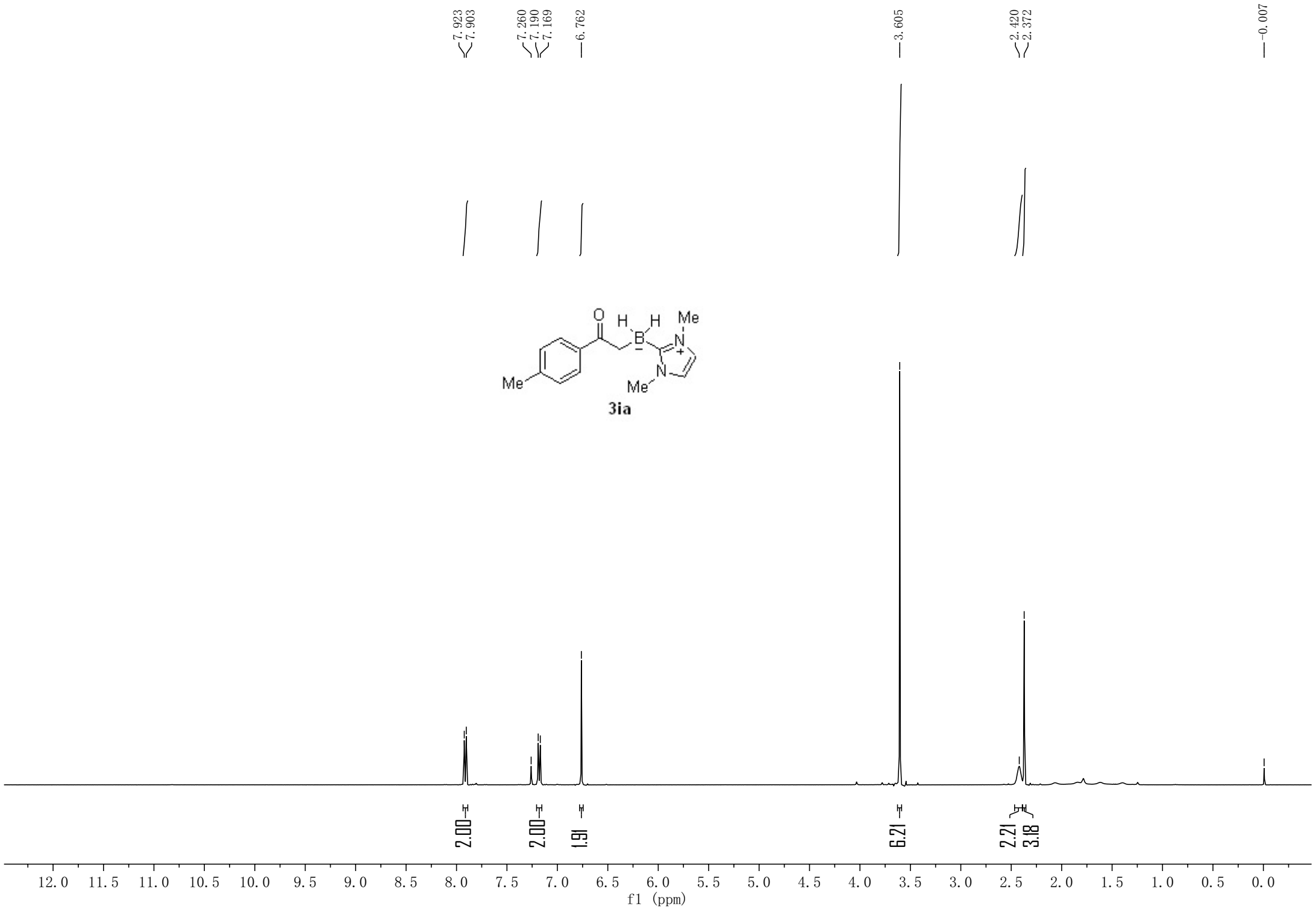

8.142
8.122
7.667
7.645
7.260
6.799
3.624
2.461
-0.008
O
H
H
B
Me
N
N
Me
F3C
3ga
2.04
2.00
1.81
6.04
2.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

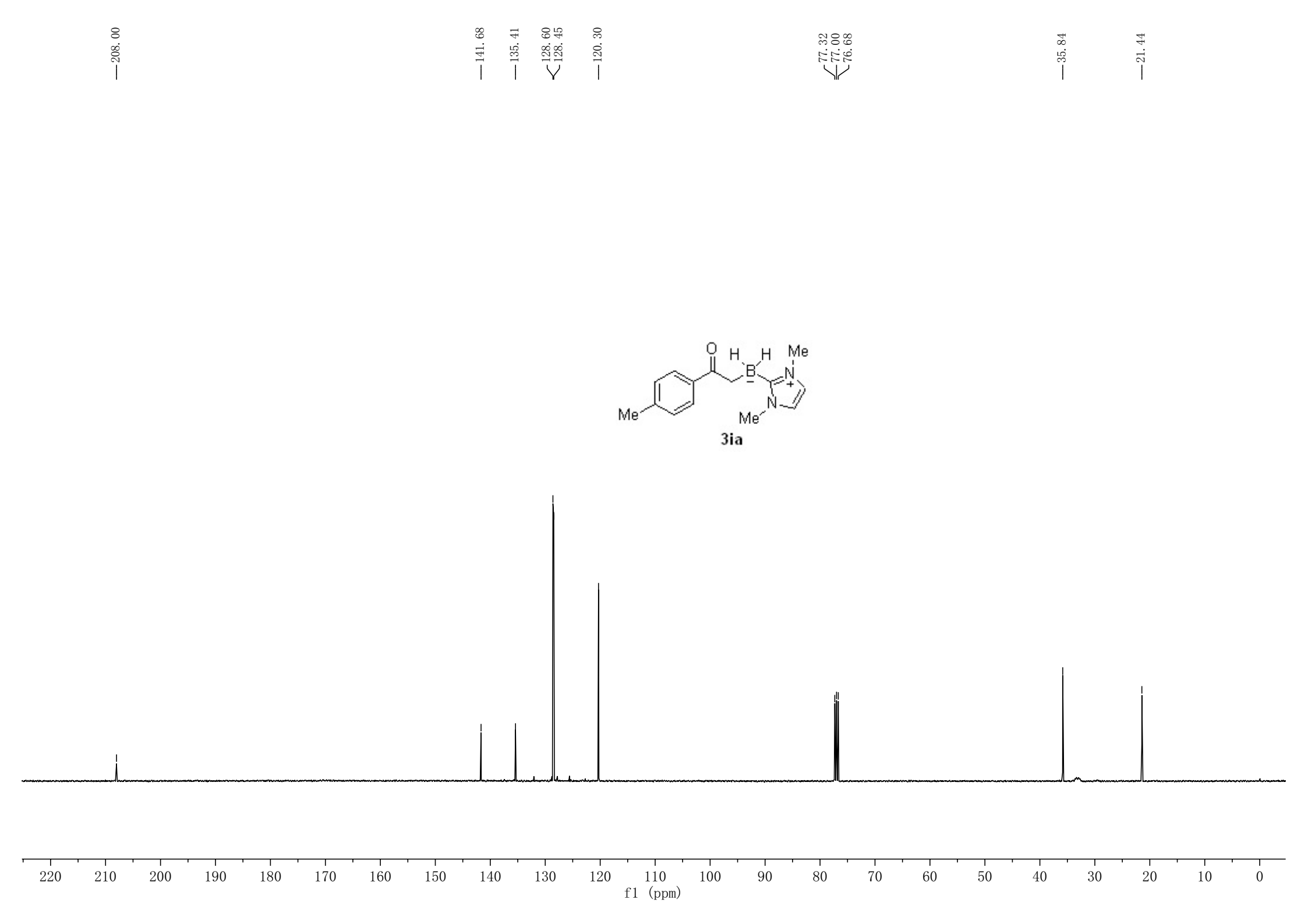

206.75
140.79
140.78
140.77
140.76
133.18
132.85
132.53
132.21
128.68
128.01
125.30
125.06
125.02
124.98
124.94
122.59
120.47
119.88
77.32
77.00
76.68
35.89
-0.05
O
H
H
B
Me
N
N
Me
F3C
3ga
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

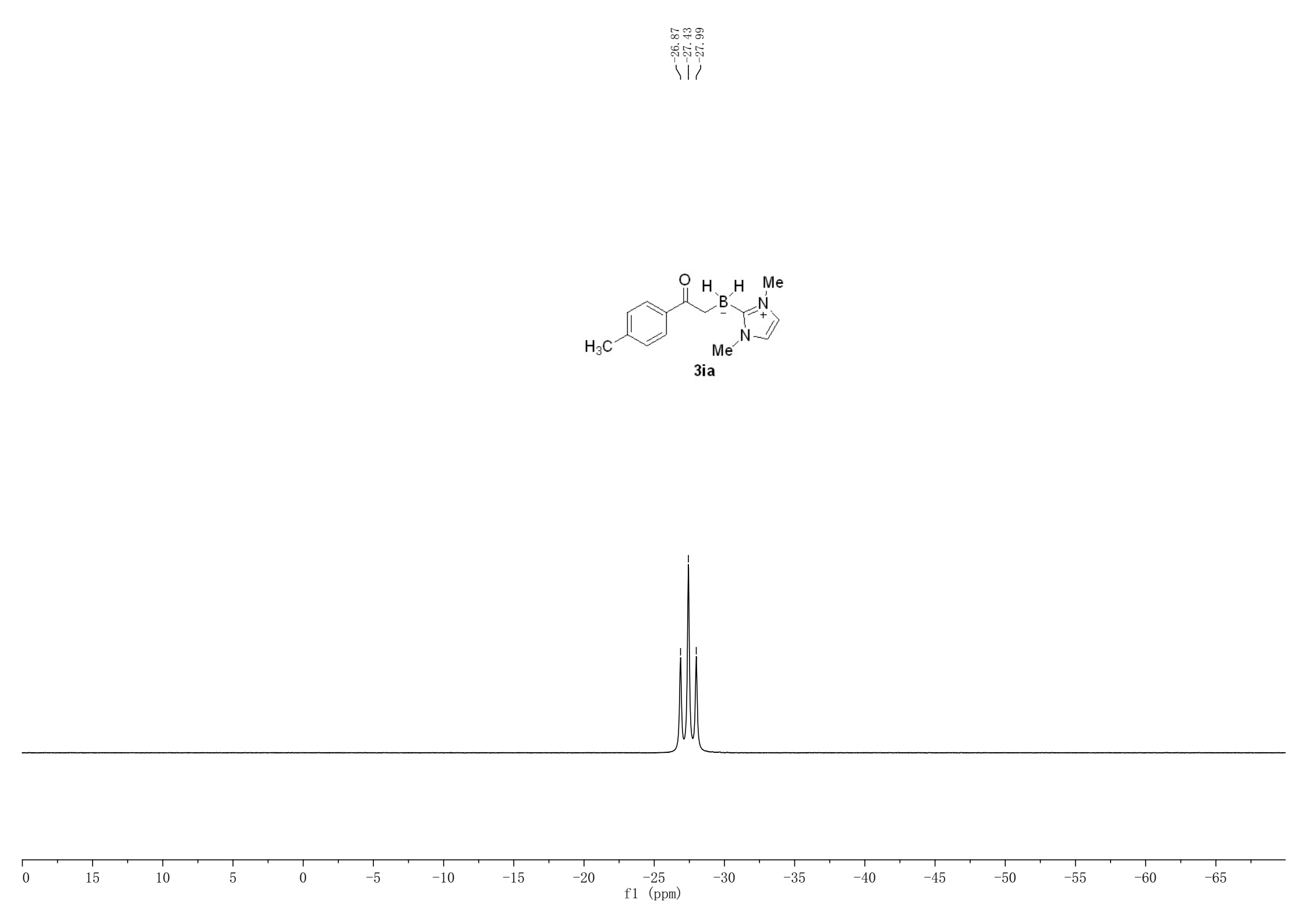

8.112
8.091
7.985
7.964
7.260
6.796
3.620
2.632
2.472
0.009
O
H
H
B
Me
N
N
Me
O
3ha
2.00
2.00
1.85
5.85
3.10
2.10
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

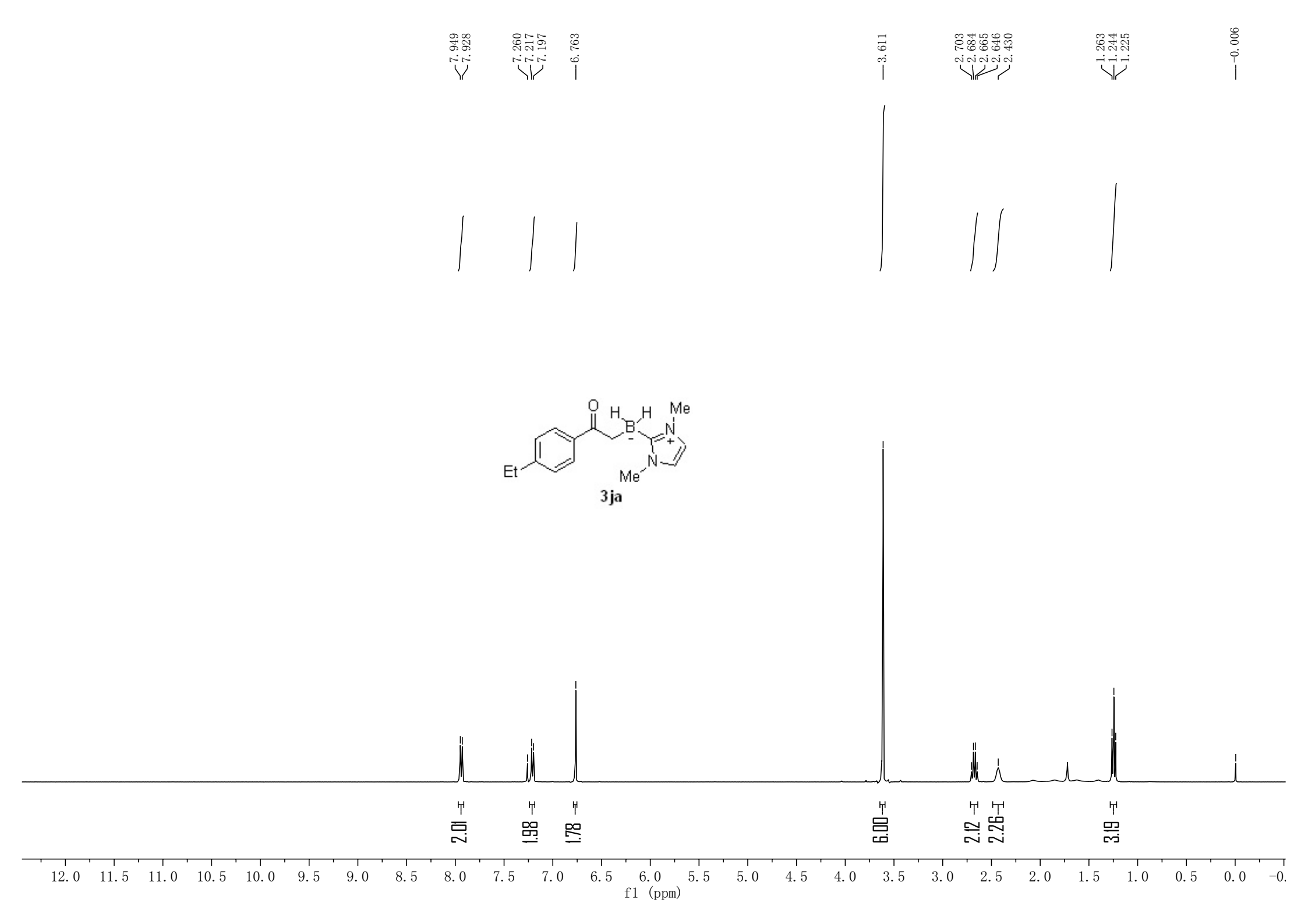

207.22
197.95
141.42
138.81
128.51
128.01
120.44
77.32
77.00
76.68
35.86
26.83
O
H
H
B
Me
N
N
Me
O
3ha
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

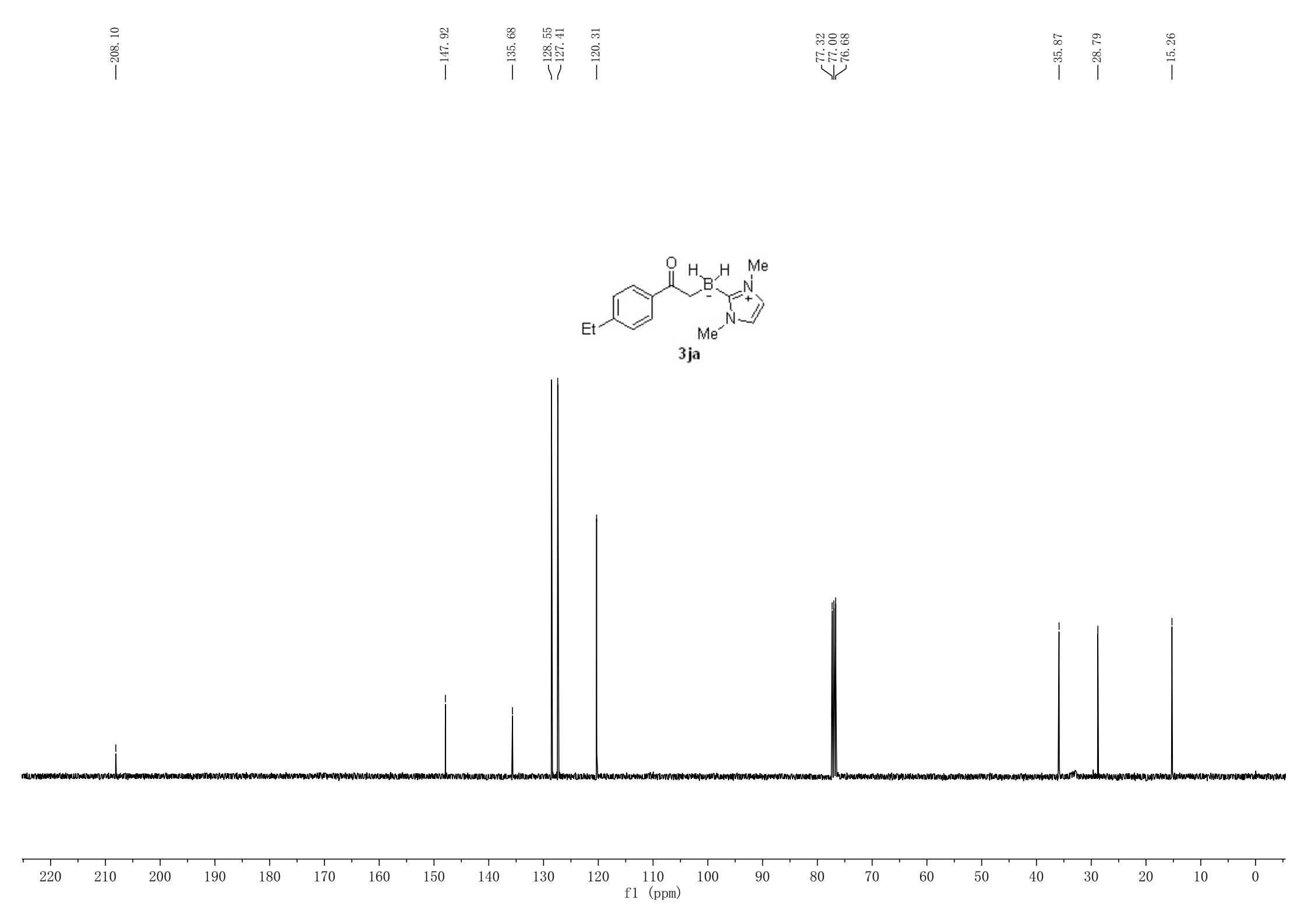

-26.94
-27.51
-28.07
O
H
H
B
Me
N
N
Me
O
3ha
f1 (ppm)

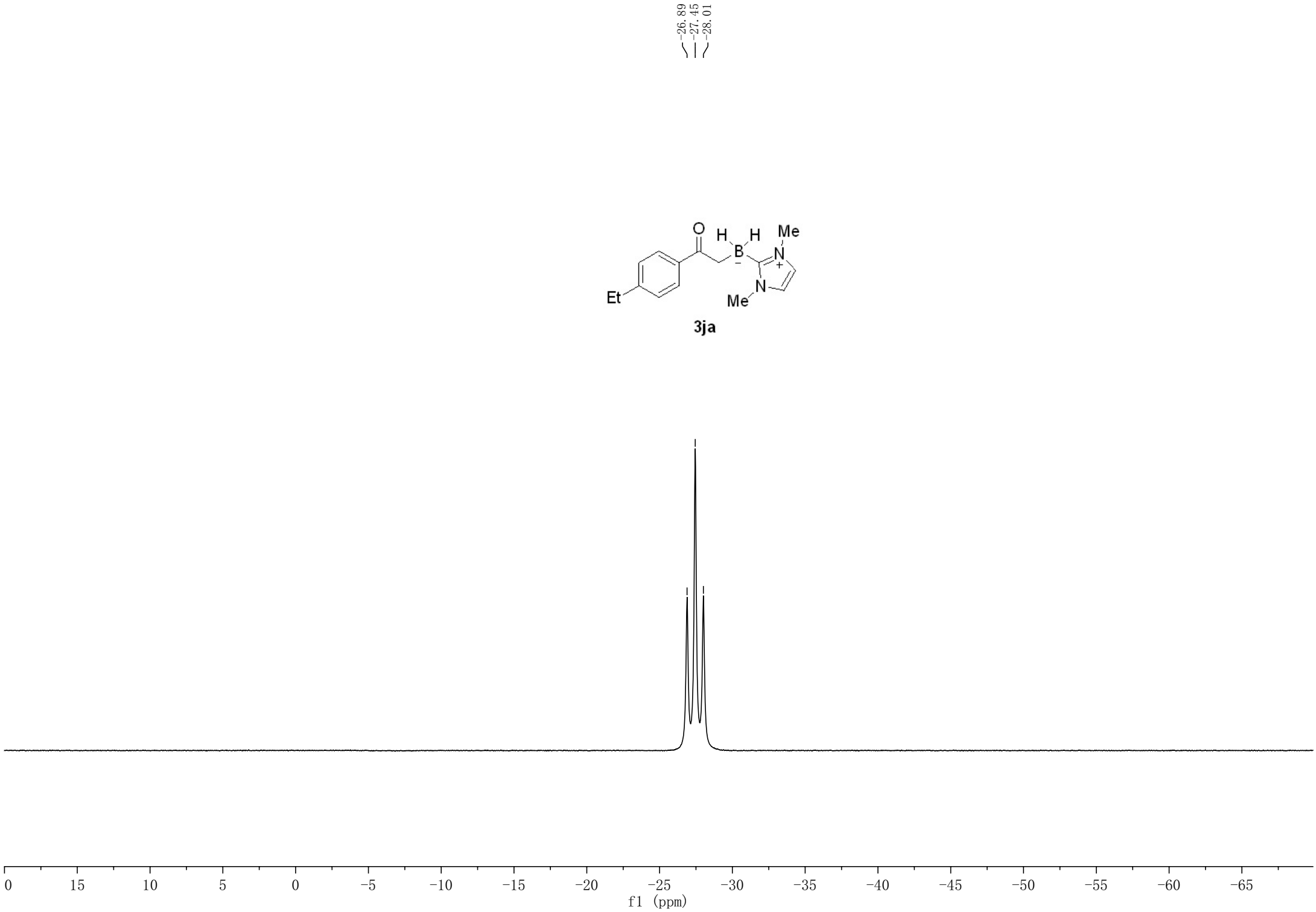

7.923
7.903
7.260
7.190
7.169
6.762
3.605
2.420
2.372
-0.007
O
H
H
B
Me
N
N
Me
Me
3ia
2.00
2.00
1.91
6.21
2.21
3.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

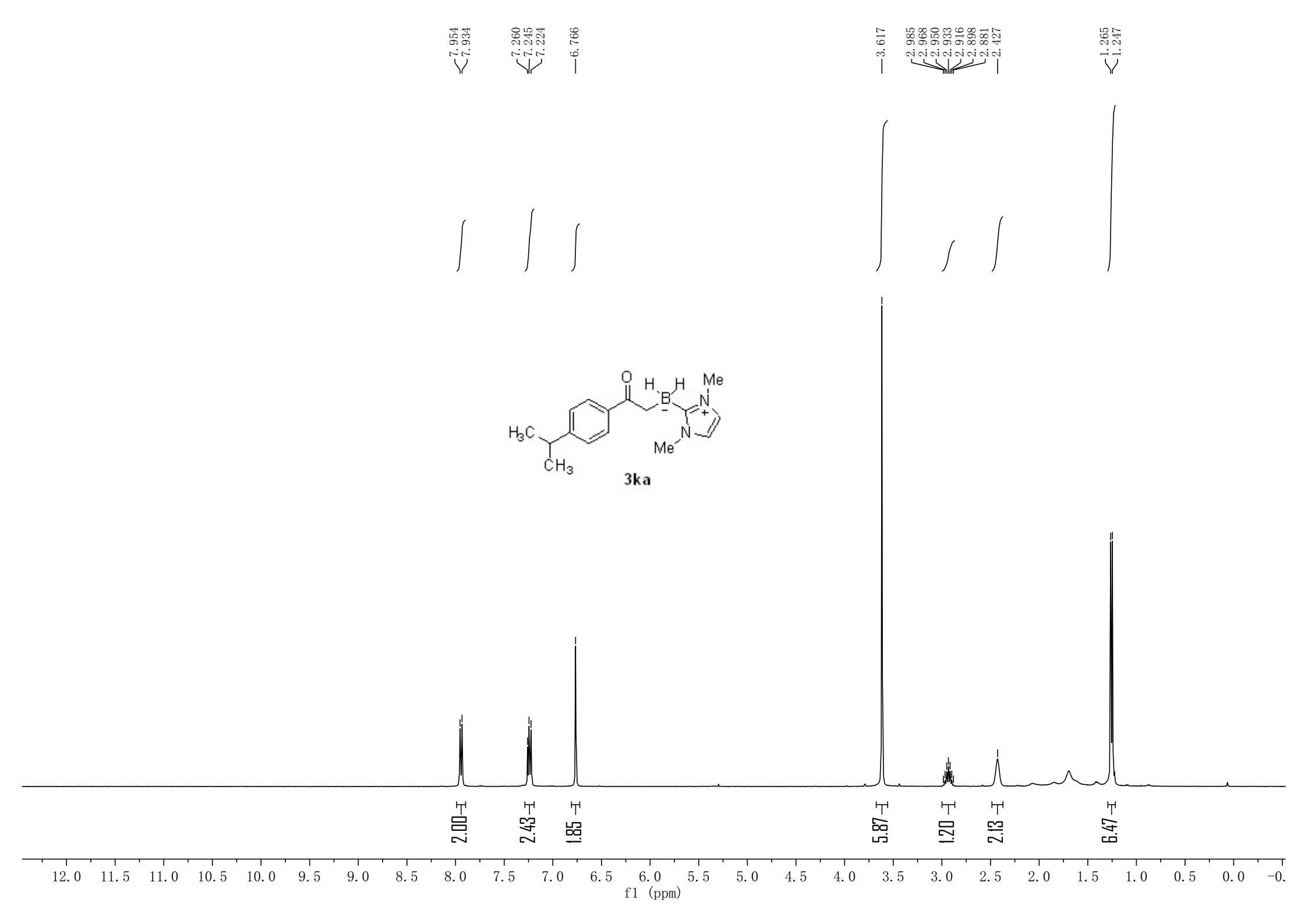

208.00
141.68
135.41
128.60
128.45
120.30
77.32
77.00
76.68
35.84
21.44
O
H
H
B
Me
N
N
Me
Me
3ia
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-26.87
-27.43
-27.99
O
H
H
B
Me
N
N
Me
H3C
3ia
0
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

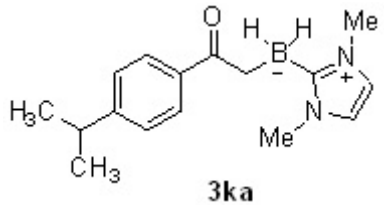

7.949
7.928
7.260
7.217
7.197
6.763
3.611
2.703
2.684
2.665
2.646
2.430
1.263
1.244
1.225
-0.006
O
H
B
H
Me
N
N
Me
Et
3ja
2.01
1.98
1.78
6.00
2.12
2.26
3.19
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


208.10
147.92
135.68
128.55
127.41
120.31
77.32
77.00
76.68
35.87
28.79
15.26
O
H
B
H
Me
N
N
Me
Et
3ja
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

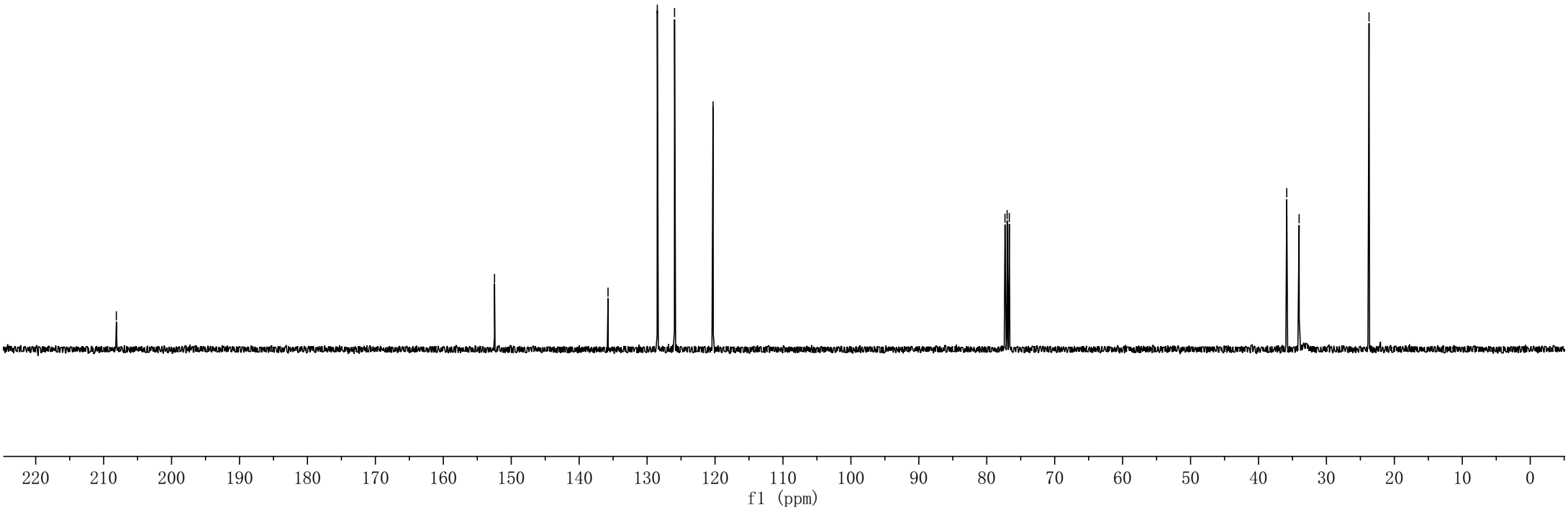

-26.89
-27.45
-28.01
O
H
H
B
Me
N
N
Me
Et
3ja
0
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

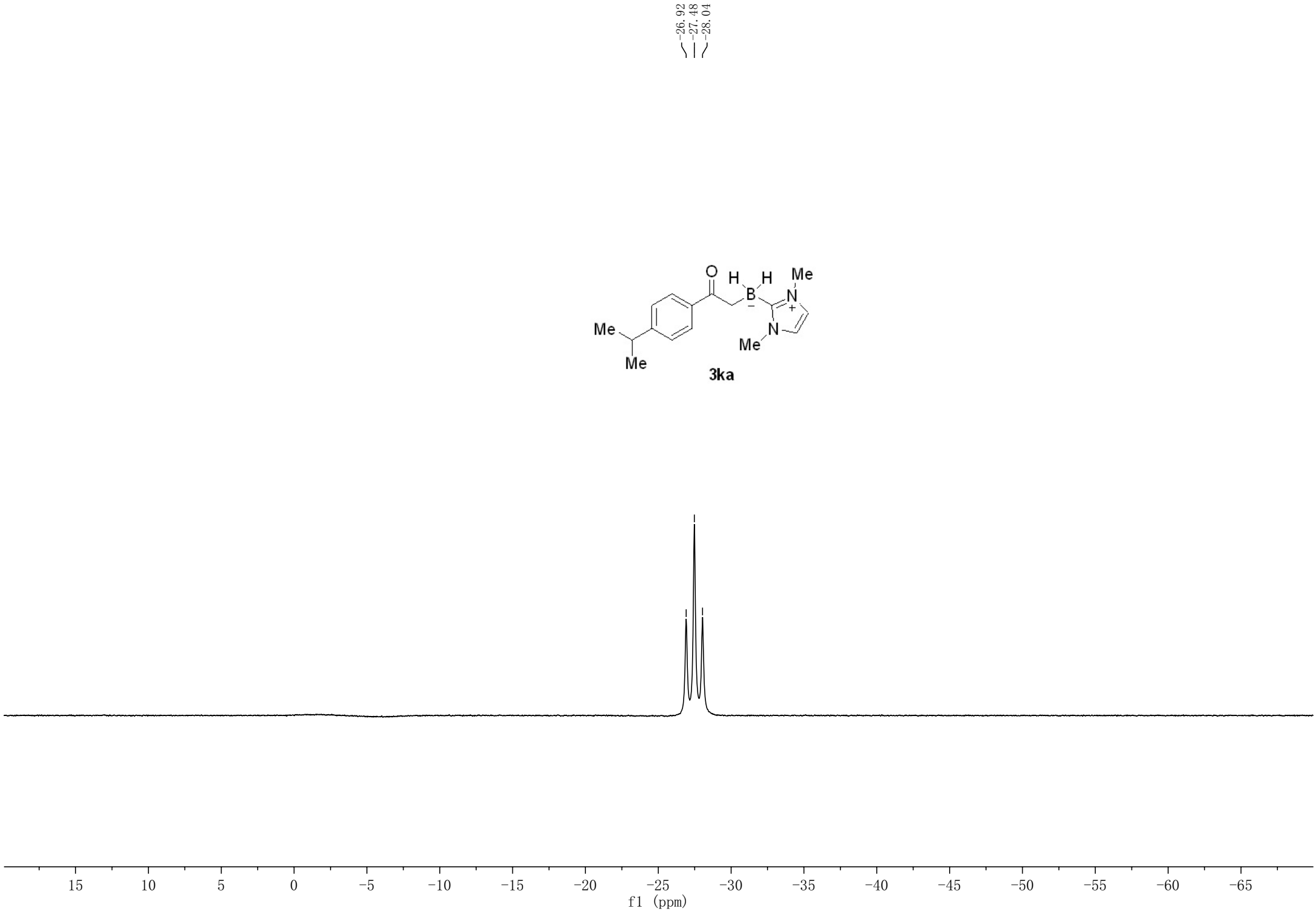

7.954
7.934
7.260
7.245
7.224
6.766
3.617
2.985
2.968
2.950
2.933
2.916
2.898
2.881
2.427
1.265
1.247
O
H
B
H
Me
N
N
Me
H3C
CH3
3ka
2.00
2.43
1.85
5.87
1.20
2.13
6.47
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

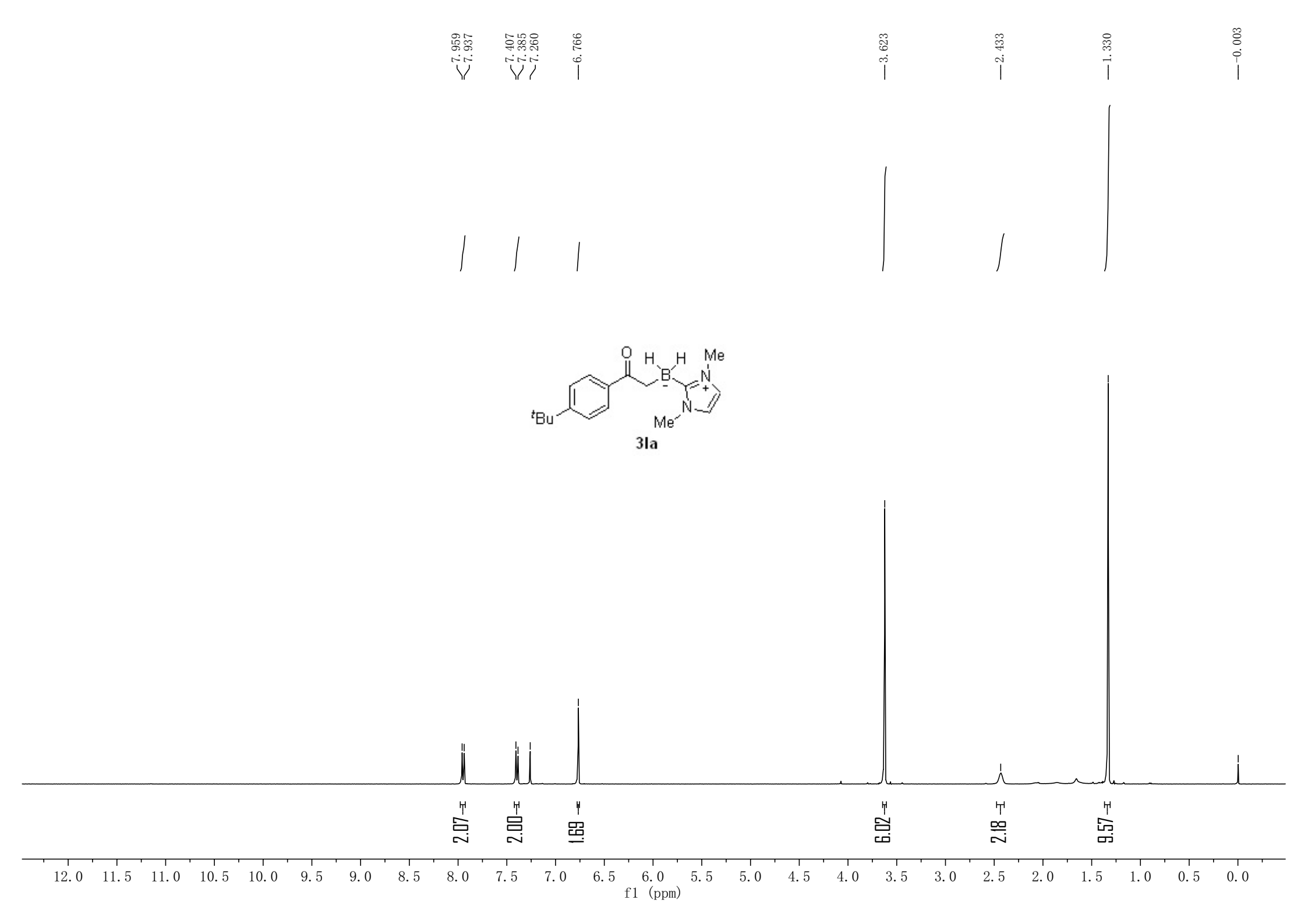
208.132
152.459
135.753
128.498
125.960
120.290
77.318
77.000
76.683
35.843
34.018
23.728



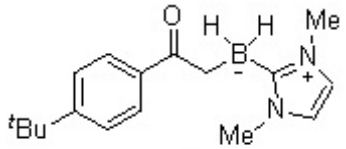
3ka



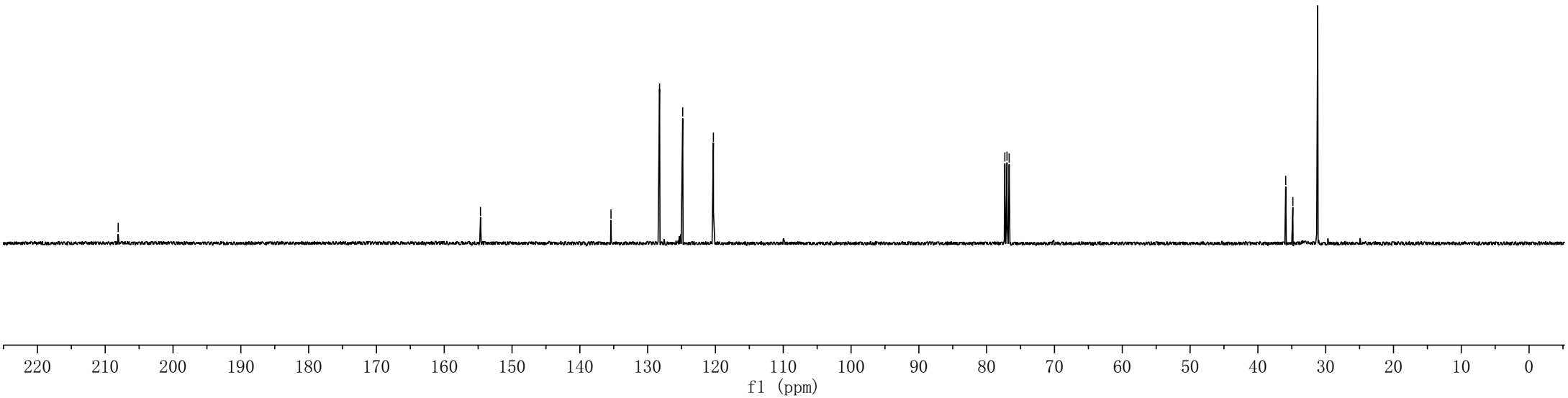

-26.92
-27.48
-28.04
O
H
H
B
Me
N
Me
N
Me
Me
Me
3ka
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

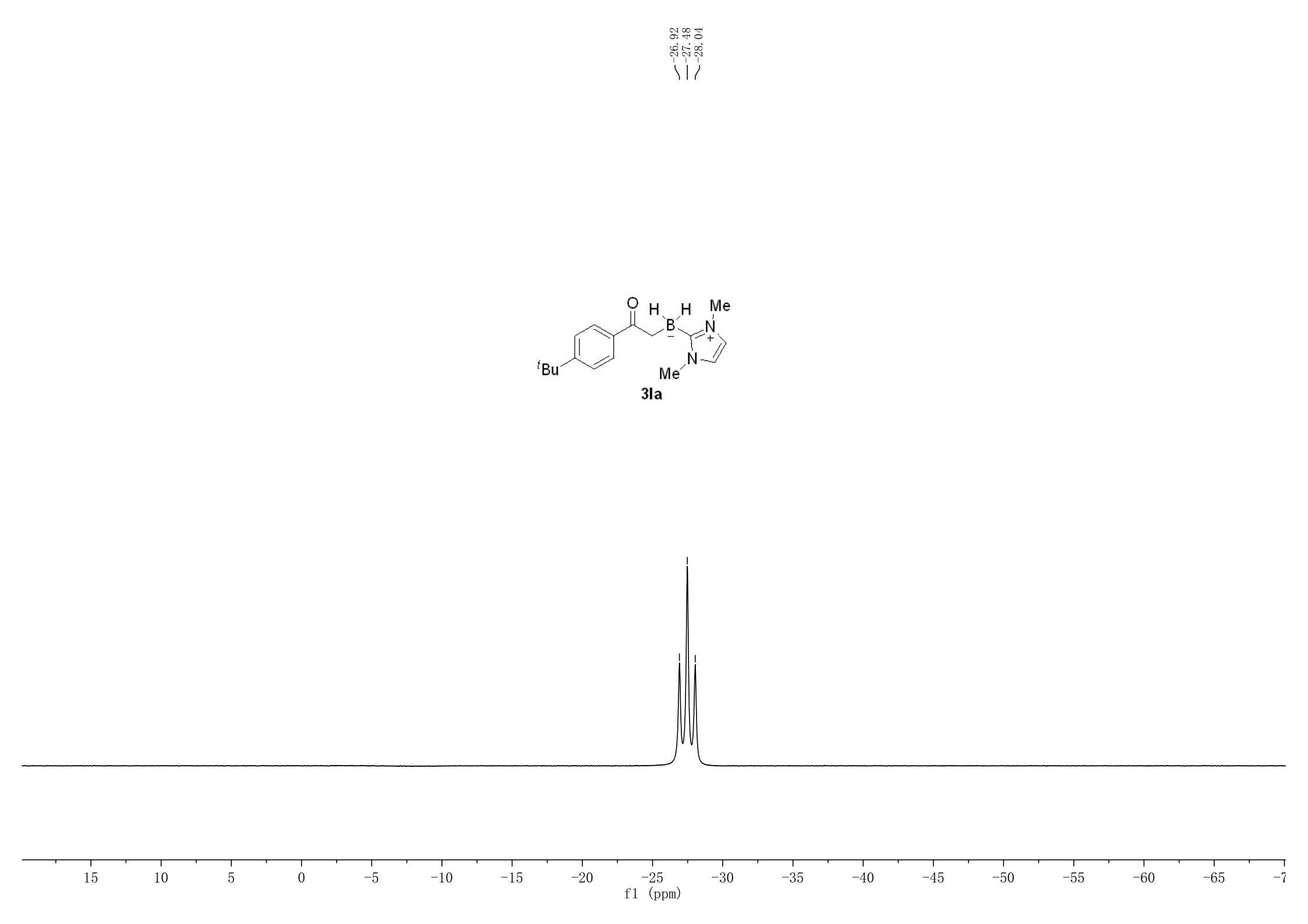

7.959
7.937
7.407
7.385
7.260
6.766
3.623
2.433
1.330
0.003
O
H
H
B
Me
N
N
Me
tBu
3la
2.07
2.00
1.69
6.02
2.18
9.57
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

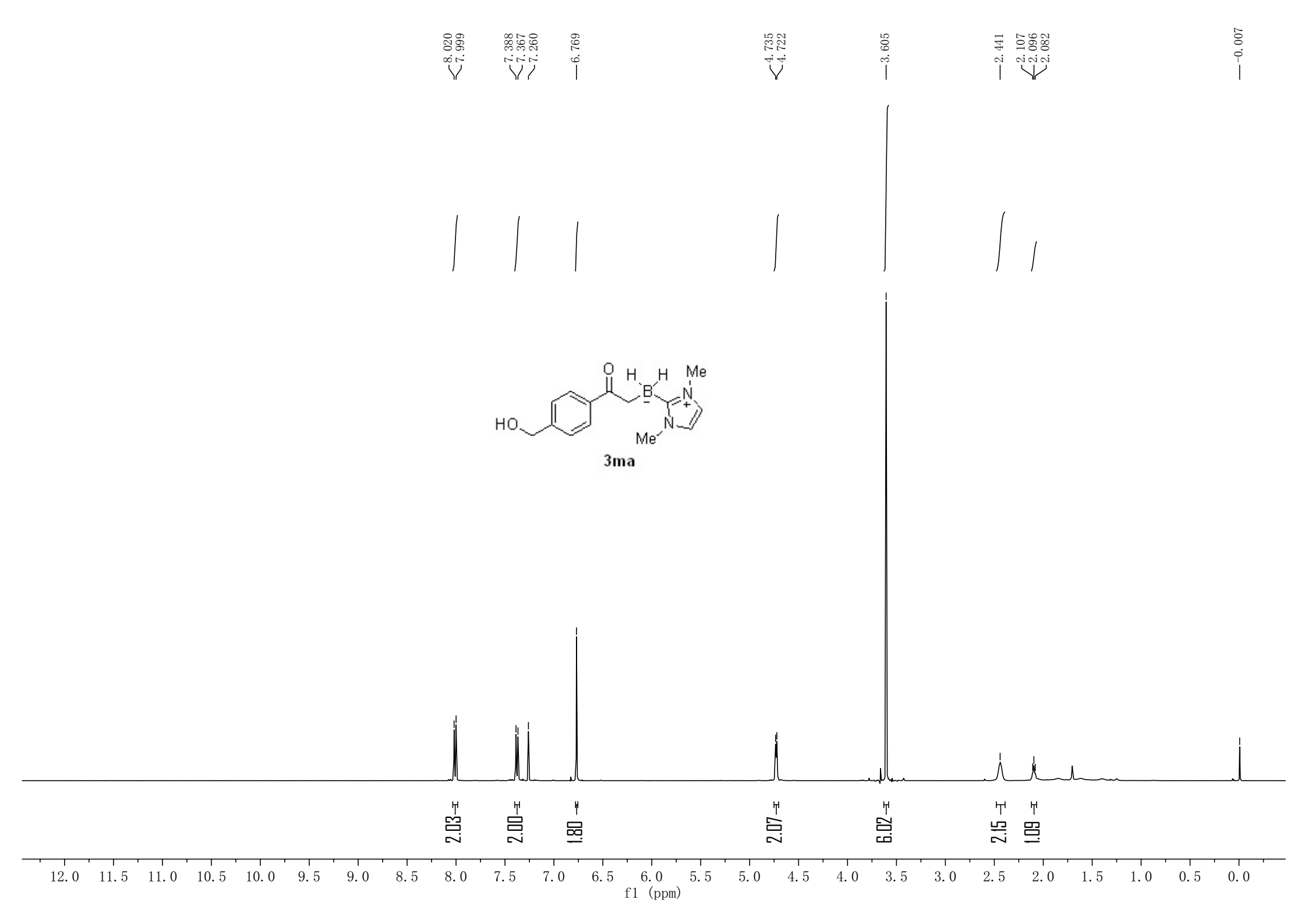
208.09
154.66
135.41
128.24
124.83
120.30
77.32
77.00
76.68
35.89
34.84
31.17



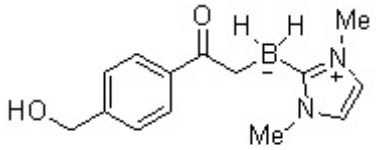
3la




-26.92
-27.48
-28.04
O
H
H
B
Me
N
N
Me
tBu
3la
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)


8.020
7.999
7.388
7.367
7.260
6.769
4.735
4.722
3.605
2.441
2.107
2.096
2.082
-0.007
O
H
H
B
Me
N
N
Me
HO
3ma
2.03
2.00
1.80
2.07
6.02
2.15
1.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

208.35
144.64
136.92
128.56
126.17
120.36
77.32
77.00
76.68
64.52
35.79



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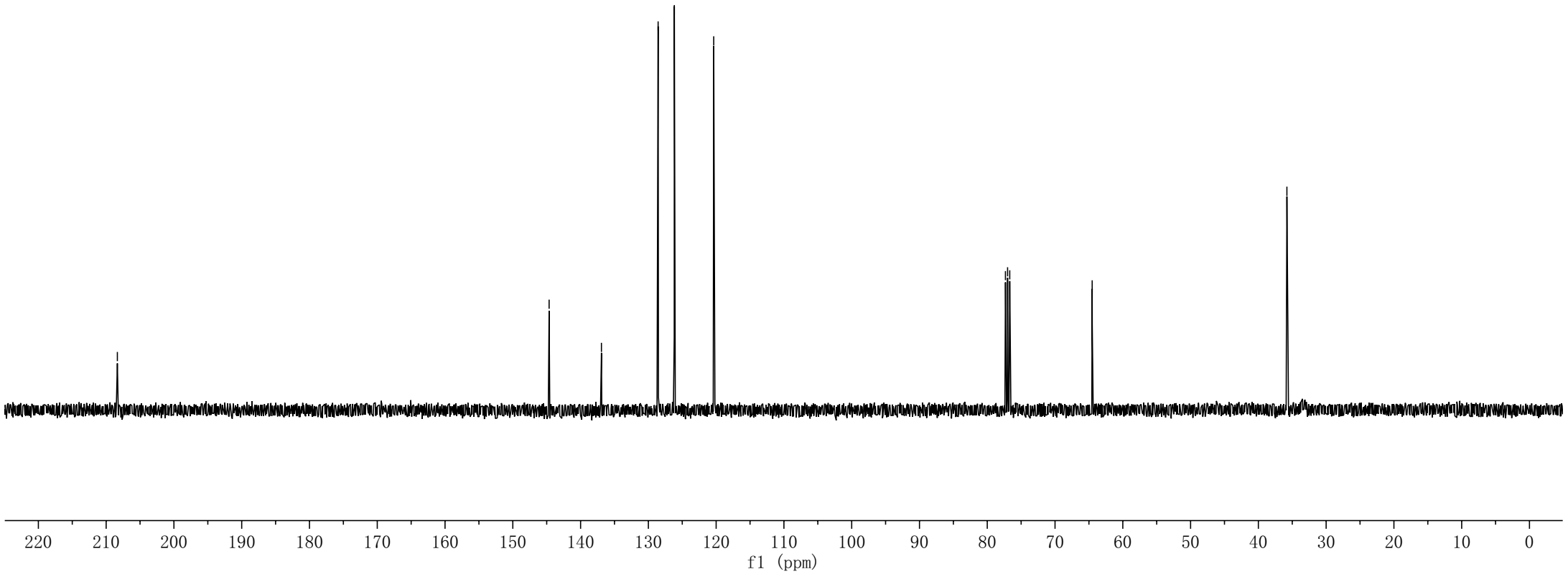
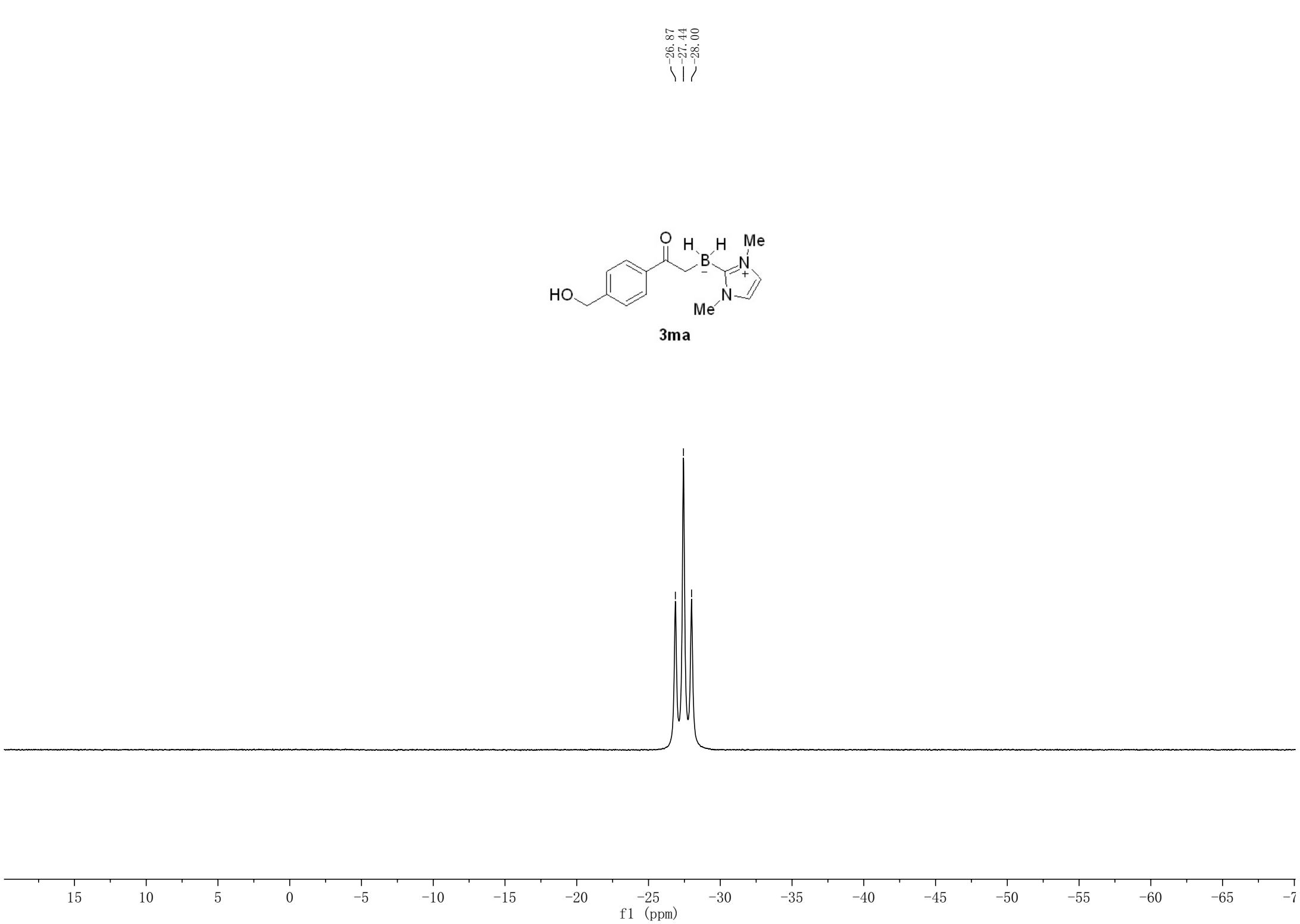
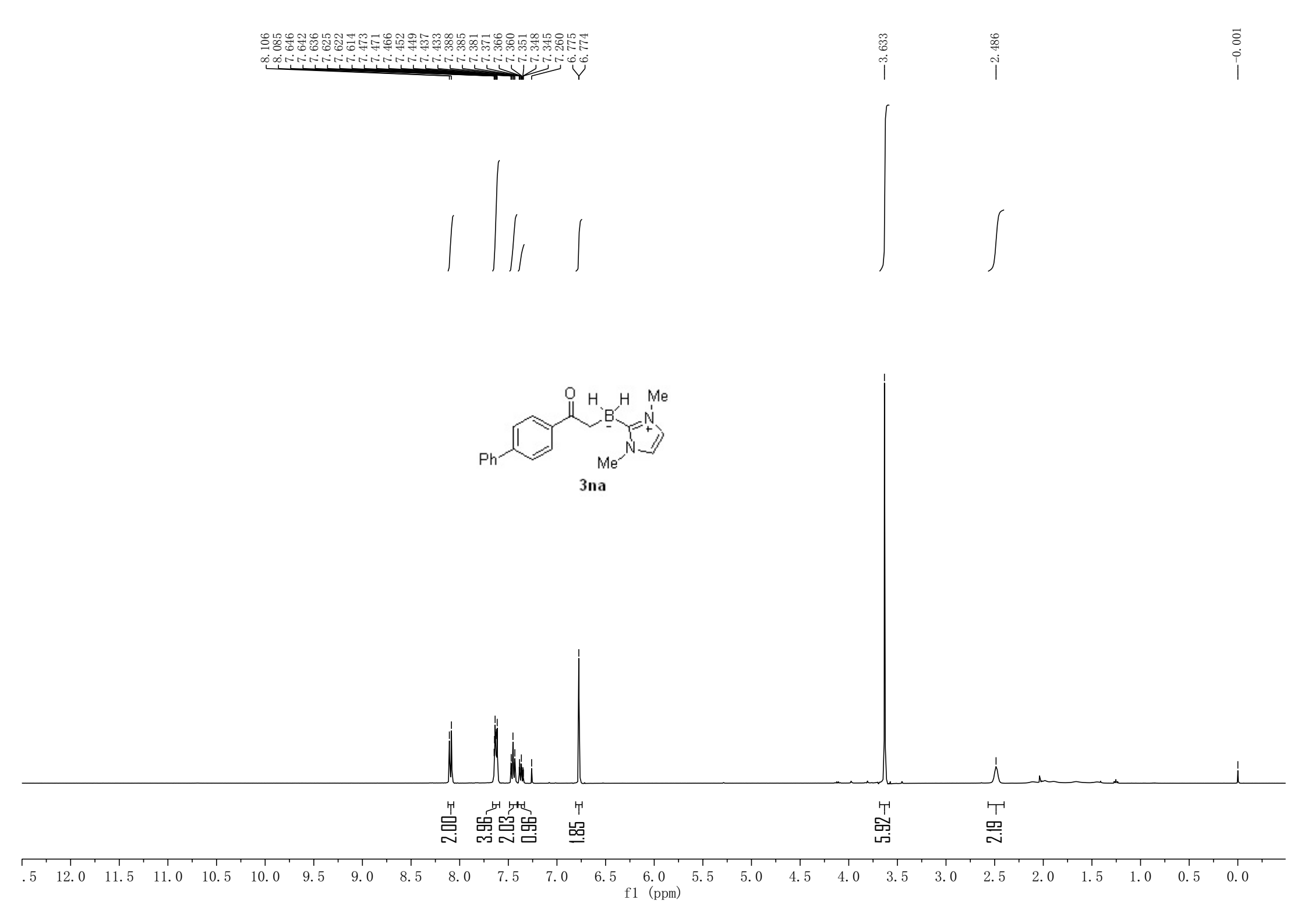
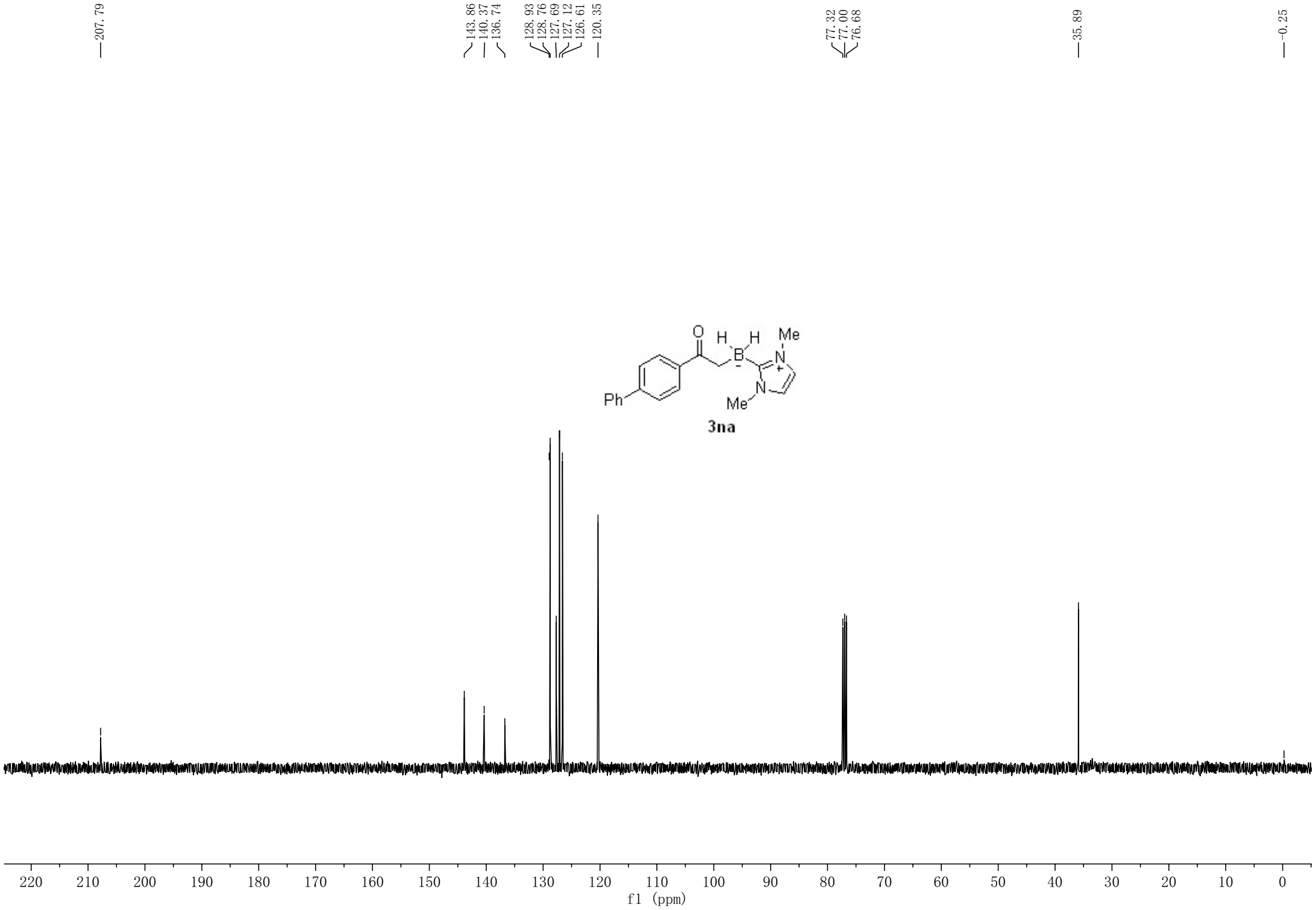
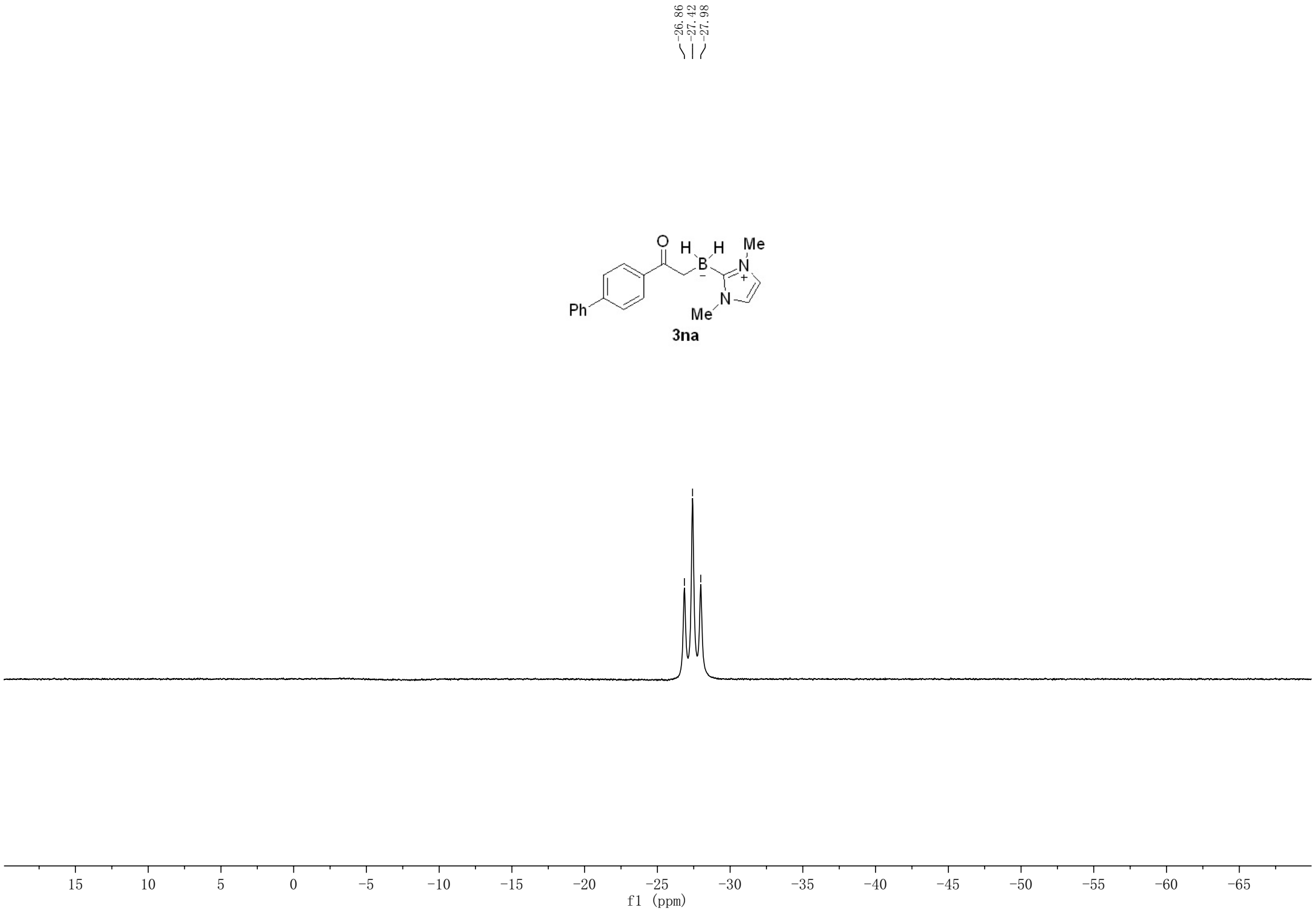


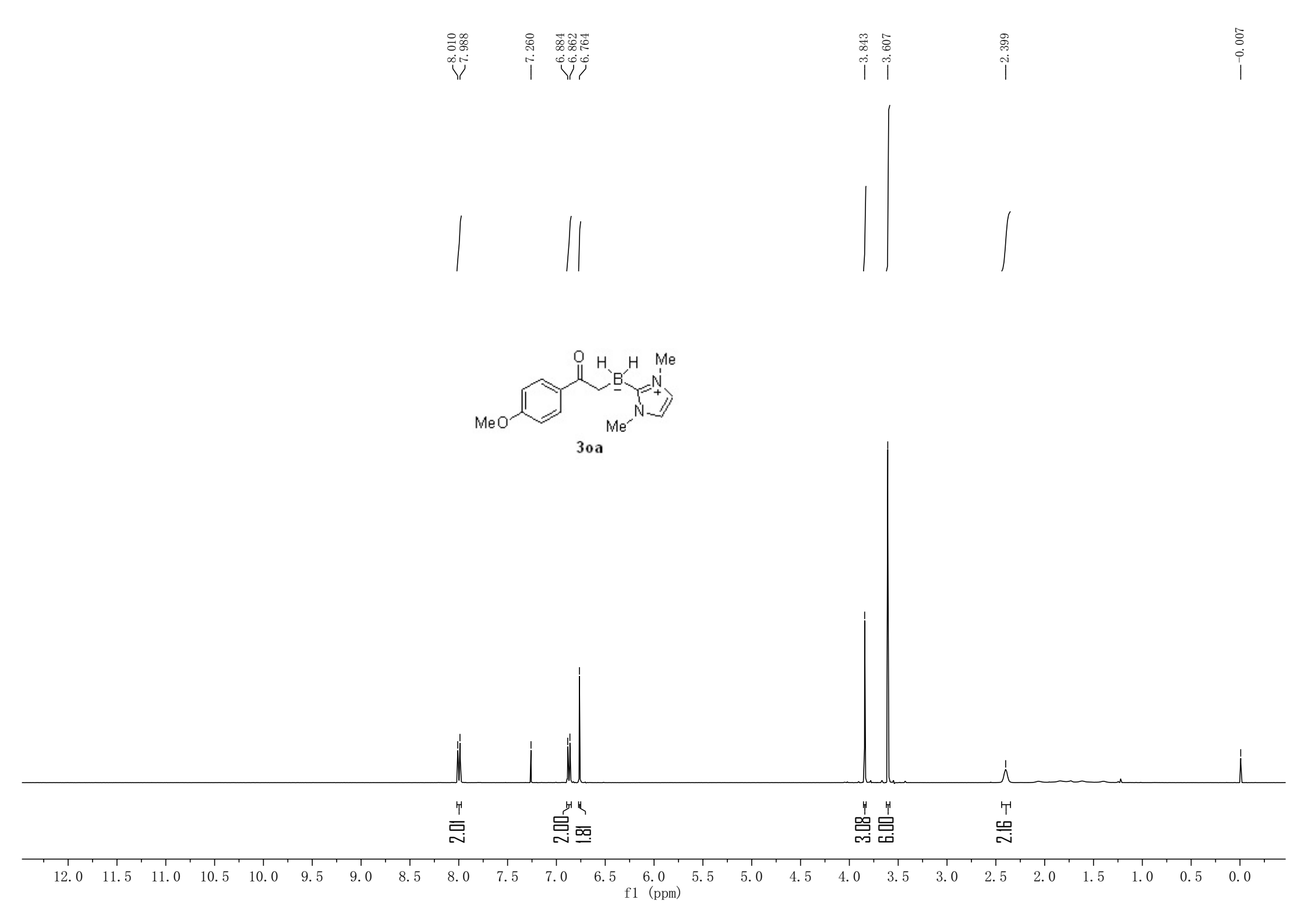

-26.87
-27.44
-28.00
O
H
H
B
Me
N
HO
N
Me
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

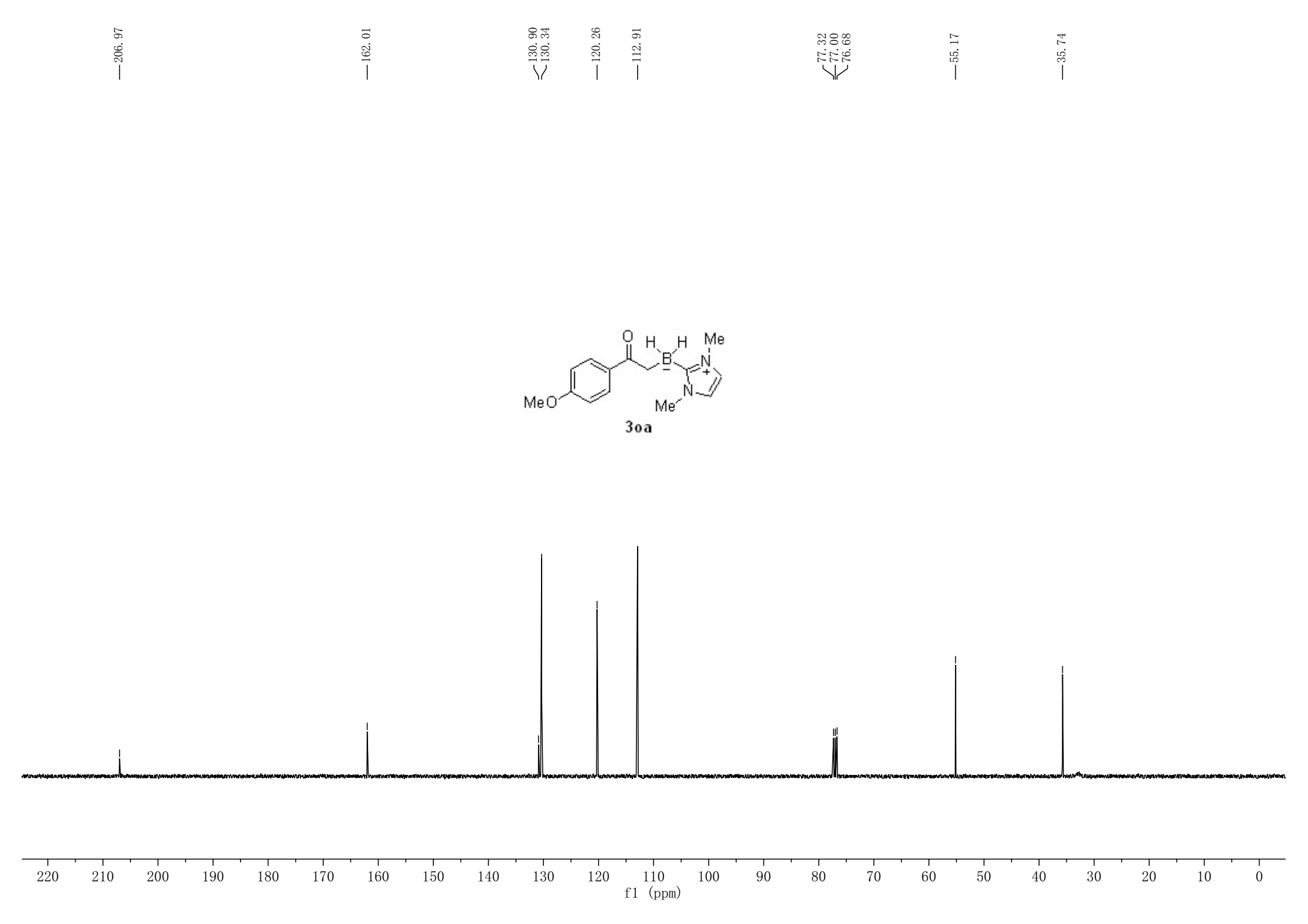
3ma

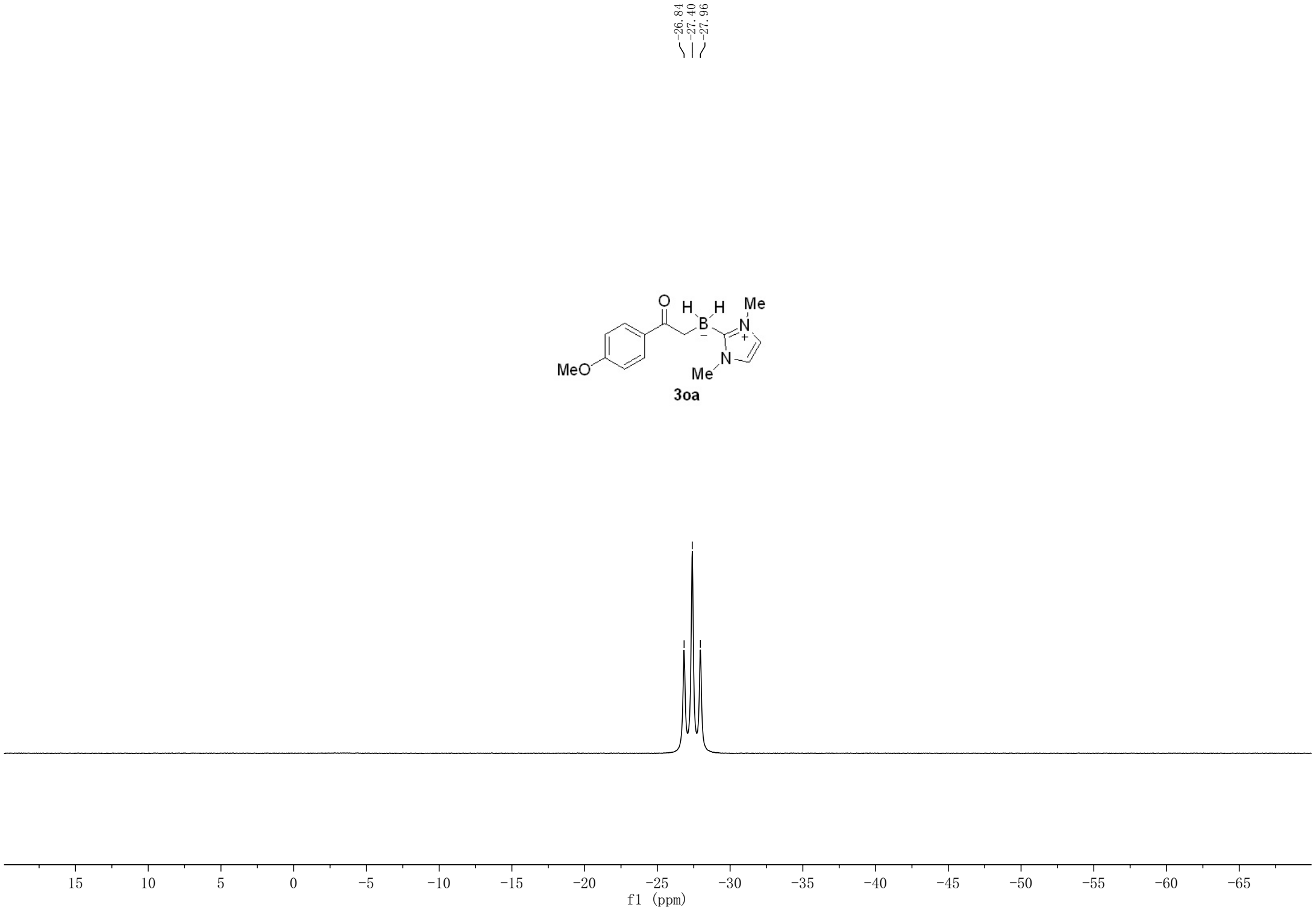

8.106
8.085
7.646
7.642
7.636
7.625
7.622
7.614
7.473
7.471
7.466
7.452
7.449
7.437
7.433
7.388
7.385
7.381
7.371
7.366
7.360
7.351
7.348
7.345
7.260
6.775
6.774
3.633
2.486
0.001
O
H
H
B
Me
N
N
Me
Ph
3na
2.00
3.96
2.03
0.96
1.85
5.92
2.19
f1 (ppm)

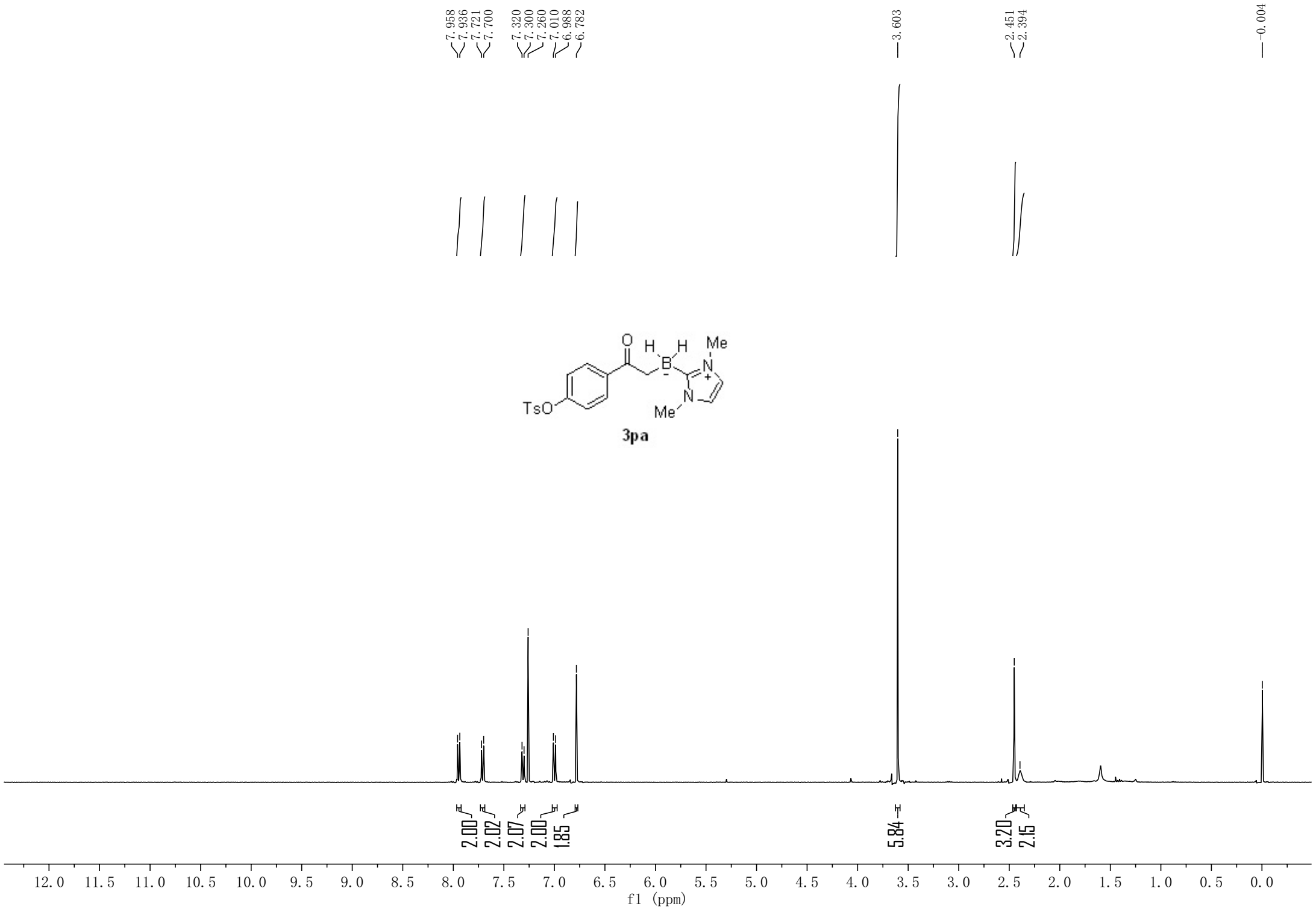

207.79
143.86
140.37
136.74
128.93
128.76
127.69
127.12
126.61
120.35
77.32
77.00
76.68
35.89
-0.25
O
H
B
H
Me
N
N
Me
Ph
3na
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-26.86
-27.42
-27.98
O
H
H
B
Me
N
N
Me
Ph
3na
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

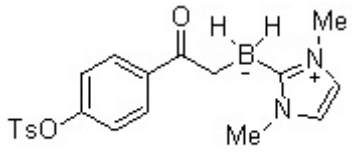

8.010
7.988
7.260
6.884
6.862
6.764
3.843
3.607
2.399
-0.007
O
H
B
H
Me
N
N
Me
MeO
Me
3oa
2.01
2.00
1.81
3.08
6.00
2.16
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


206.97
162.01
130.90
130.34
120.26
112.91
77.32
77.00
76.68
55.17
35.74
O
H
H
B
Me
N
N
Me
MeO
3oa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

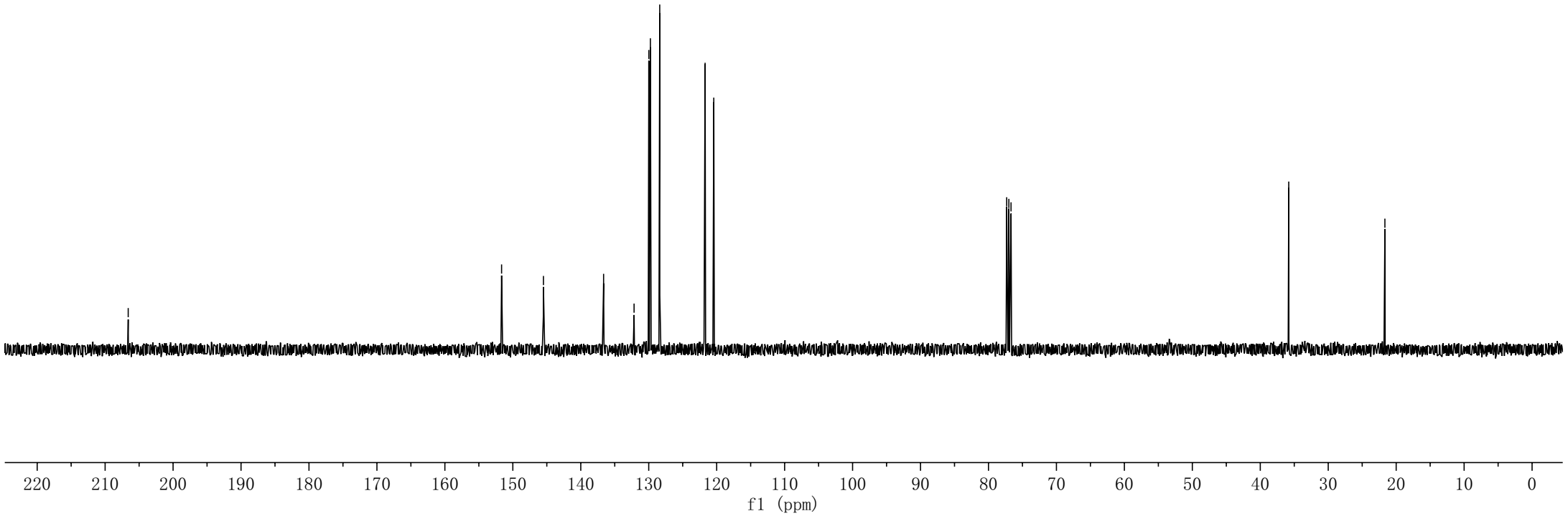

-26.84
-27.40
-27.96
O
H
B
H
Me
N
N
Me
MeO
3oa
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

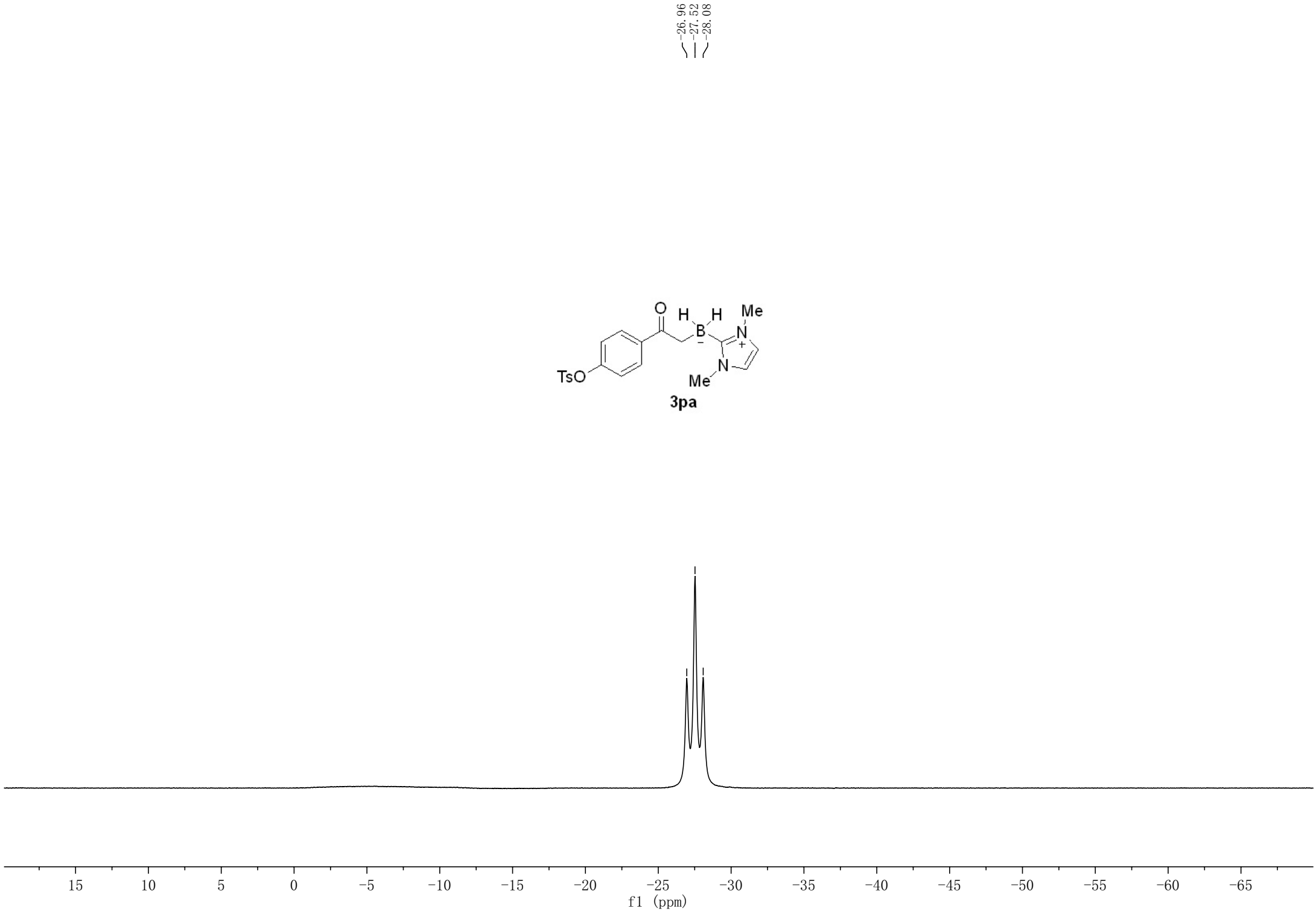

7.958
7.936
7.721
7.700
7.320
7.300
7.260
7.010
6.988
6.782
3.603
2.451
2.394
0.004
O
H
H
B
Me
N
N
Me
TsO
3pa
2.00
2.02
2.07
2.00
1.85
5.84
3.20
2.15
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

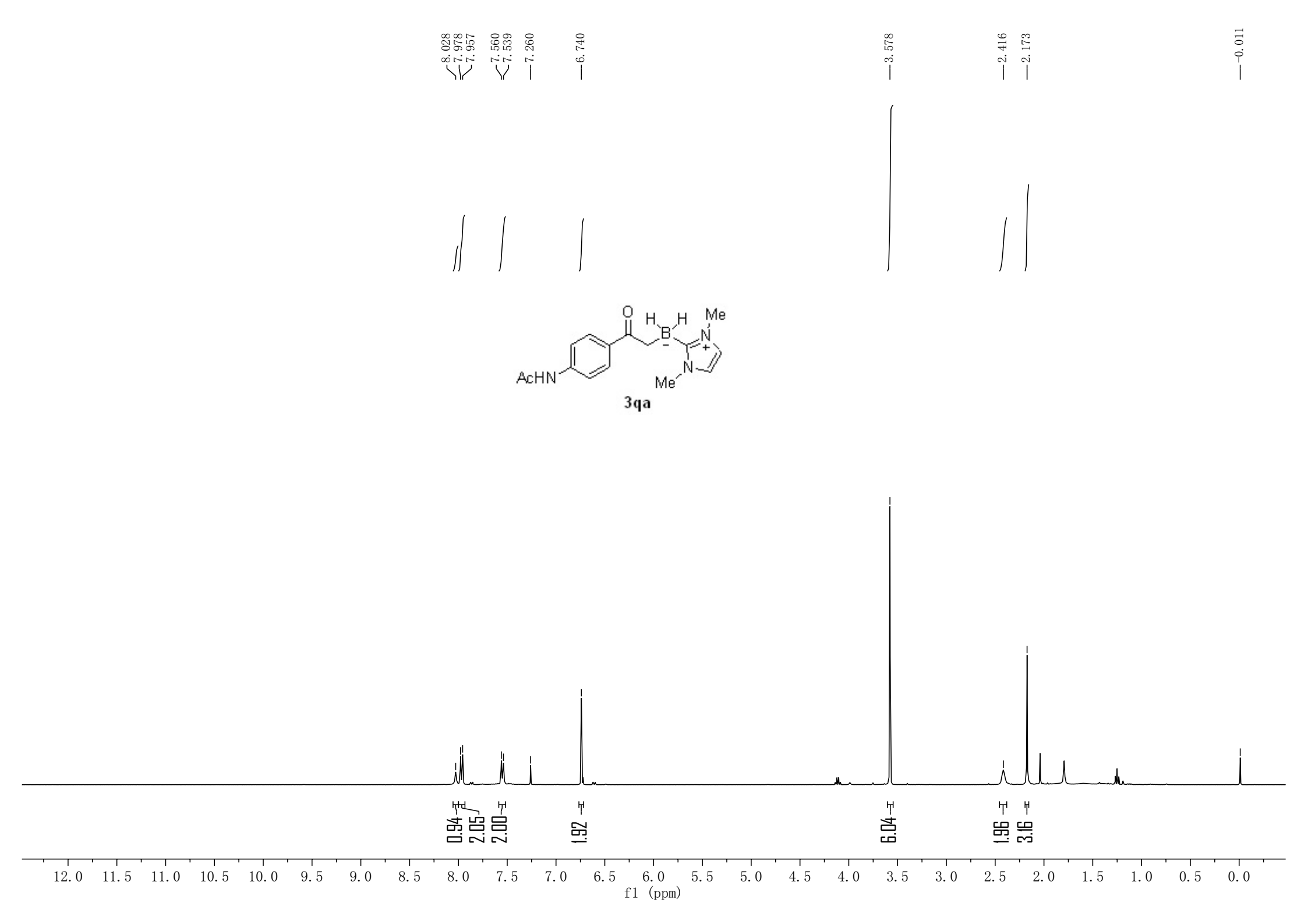
206.60
151.65
145.49
136.64
132.16
129.99
129.75
128.38
121.70
120.42
77.32
77.00
76.68
35.81
21.66

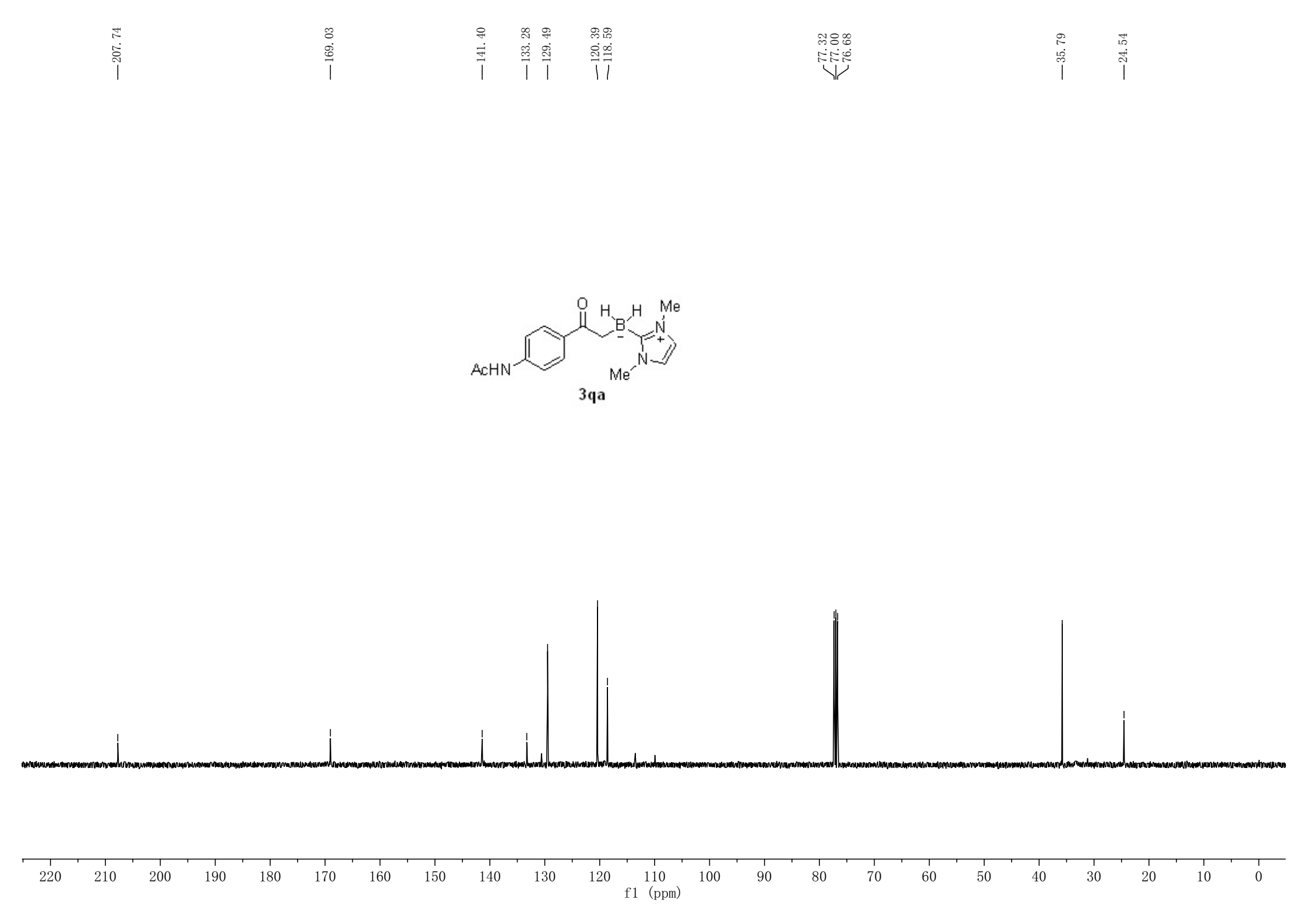


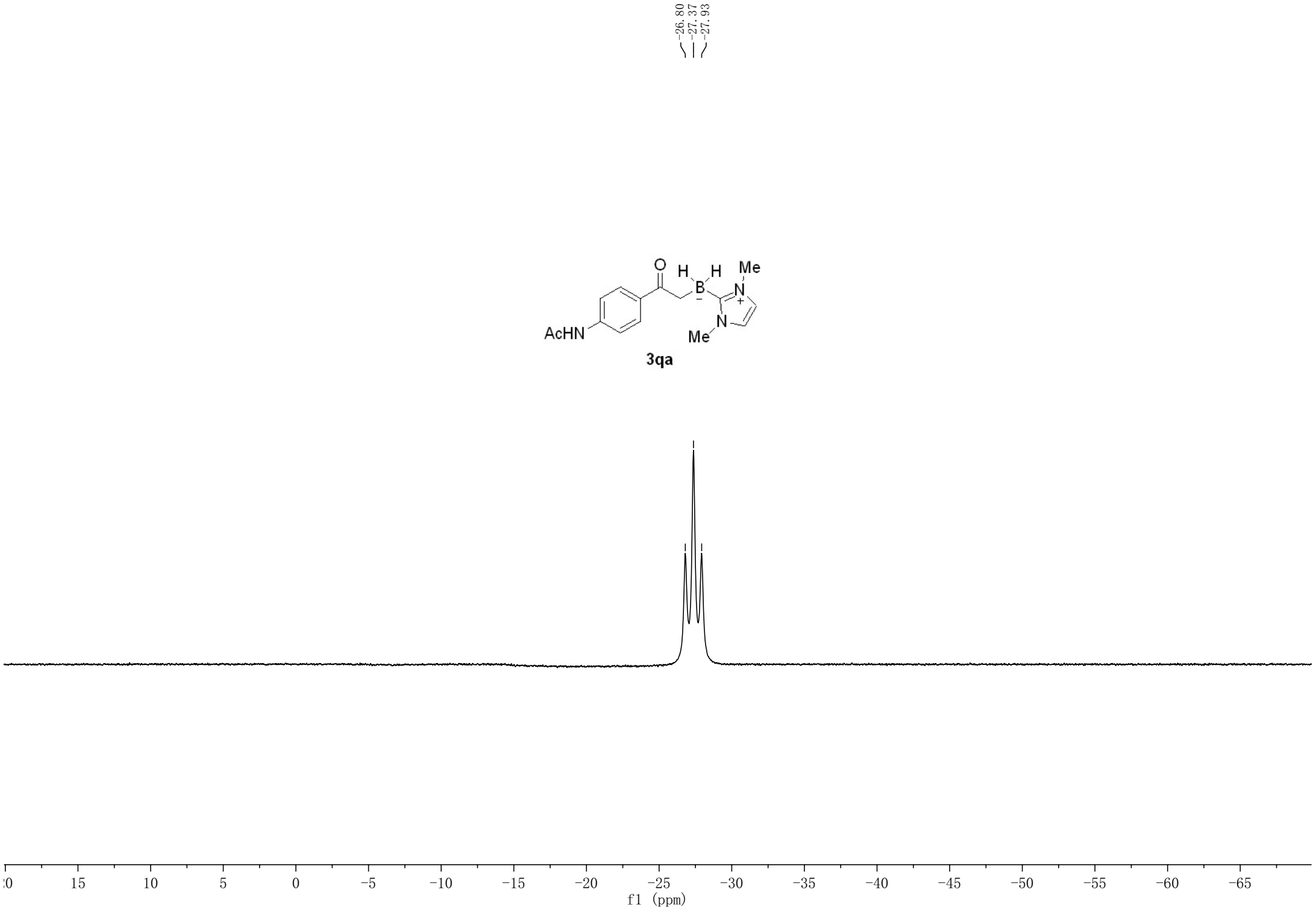
3pa

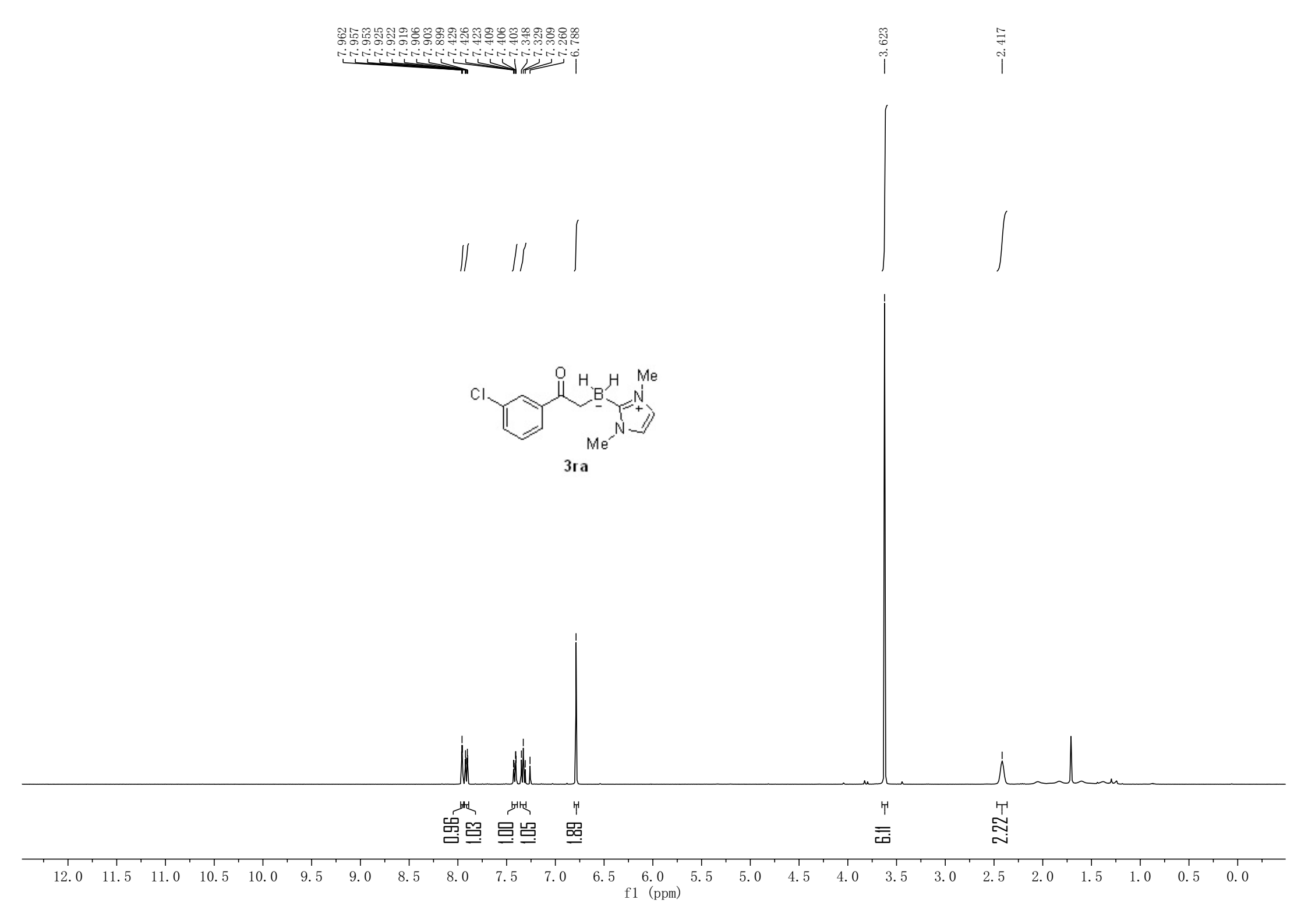



-26.96
-27.52
-28.08
O
H
H
B
Me
N
N
Me
TsO
3pa
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

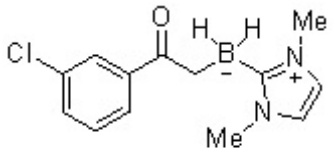

8.028
7.978
7.957
7.560
7.539
7.260
6.740
3.578
2.416
2.173
-0.011
O
H
B
H
Me
N
N
Me
AcHN
3qa
0.94
2.05
2.00
1.92
6.04
1.96
3.16
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


207.74
169.03
141.40
133.28
129.49
120.39
118.59
77.32
77.00
76.68
35.79
24.54
O
H
B
H
Me
N
N
Me
AcHN
3qa
f1 (ppm)

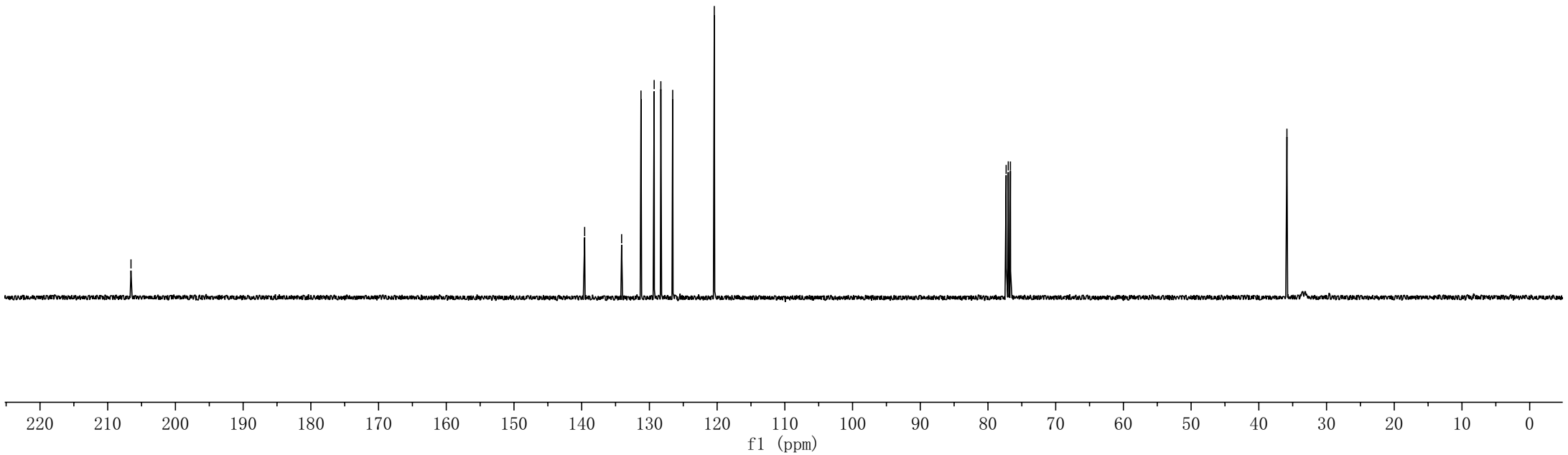

-26.80
-27.37
-27.93
O
H
H
B
Me
N
N
Me
AcHN
3qa
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

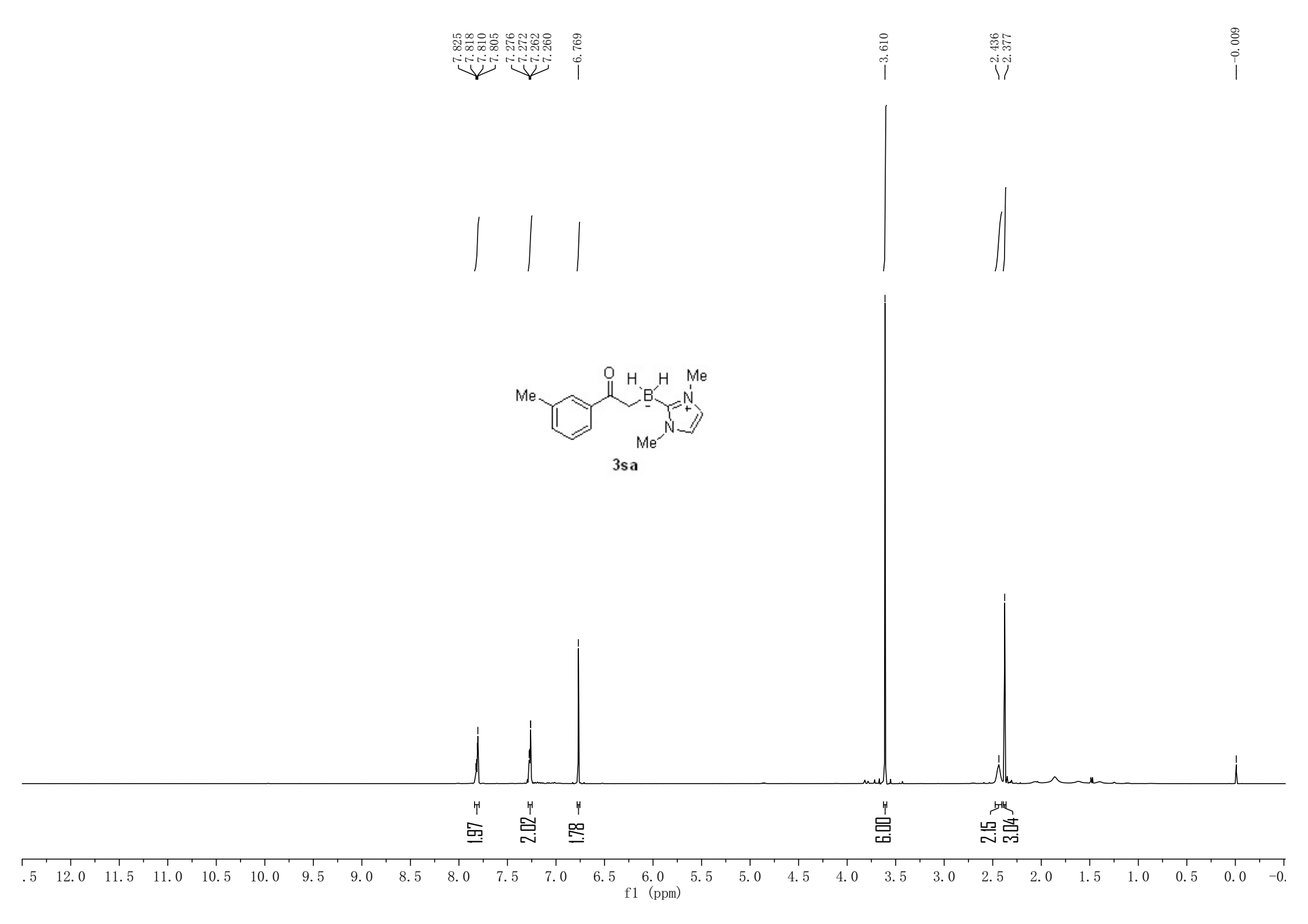

7.962
7.957
7.953
7.925
7.922
7.919
7.906
7.903
7.899
7.429
7.426
7.423
7.409
7.406
7.403
7.348
7.329
7.309
7.260
6.788
3.623
2.417
O
H
B
H
Me
Cl
N
N
Me
3ra
0.96
1.03
1.00
1.05
1.89
6.11
2.22
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

206.56
139.57
134.10
131.24
129.30
128.31
126.56
120.42
77.32
77.00
76.68
35.85

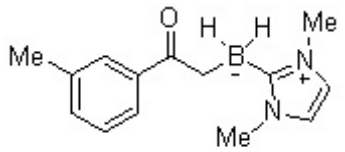


3ra

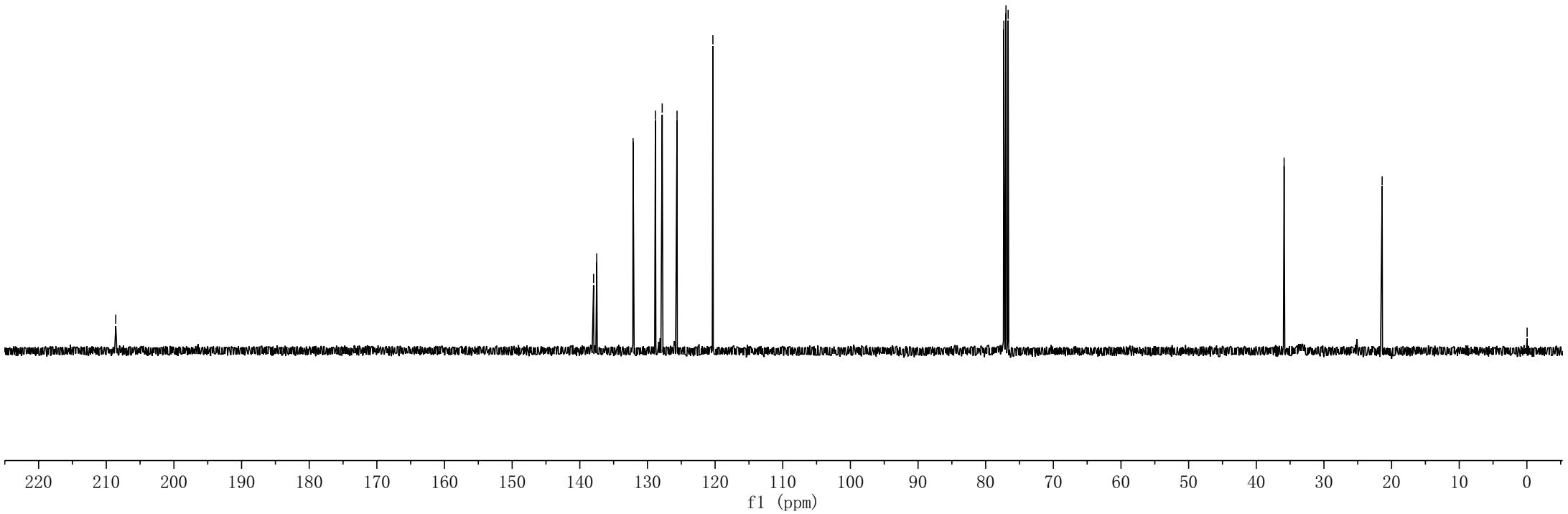


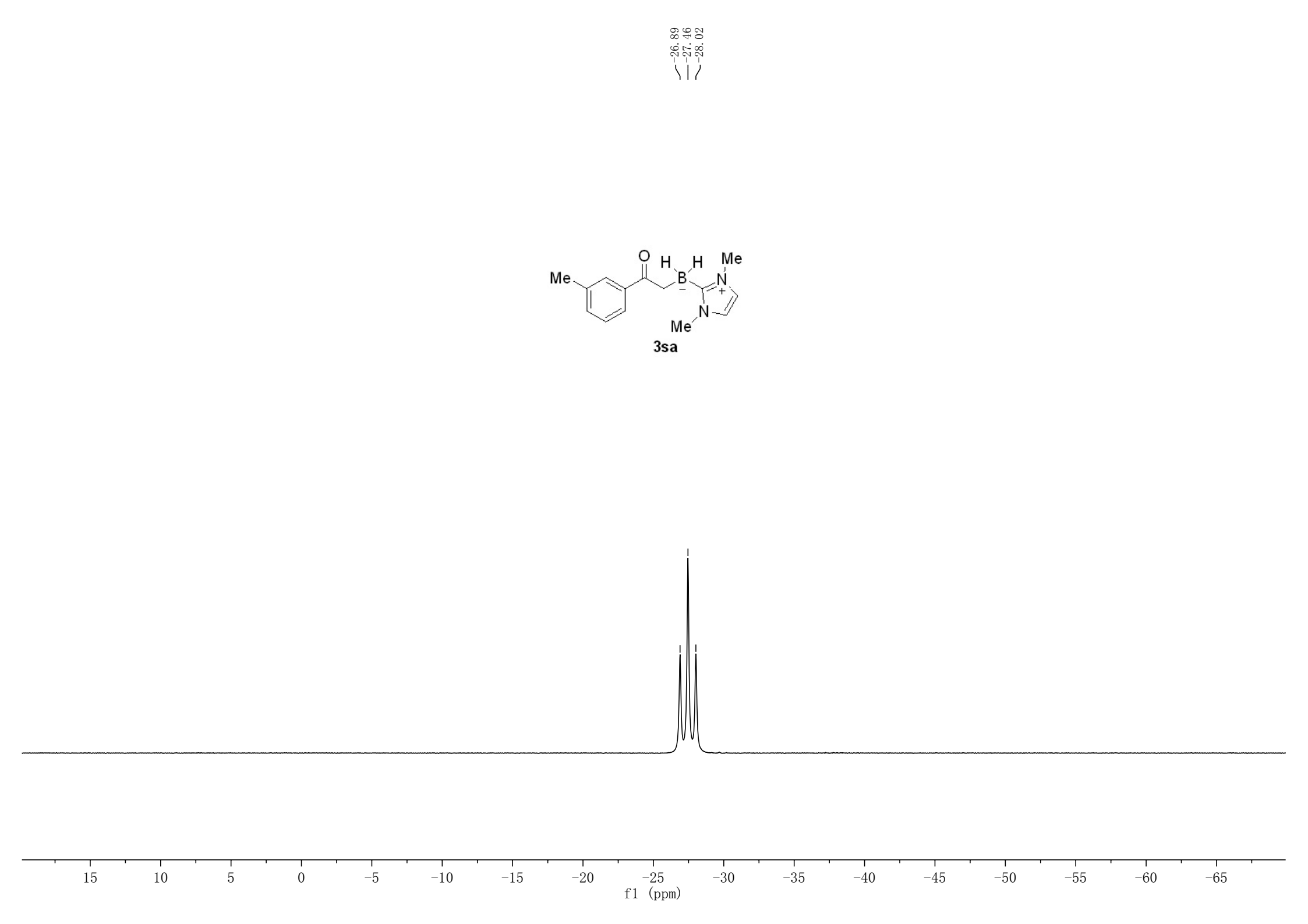

7.825
7.818
7.810
7.805
7.276
7.272
7.262
7.260
6.769
3.610
2.436
2.377
-0.009
Me
O
H
B
H
Me
N
N
Me
3sa
1.97
2.02
1.78
6.00
2.15
3.04
f1 (ppm)

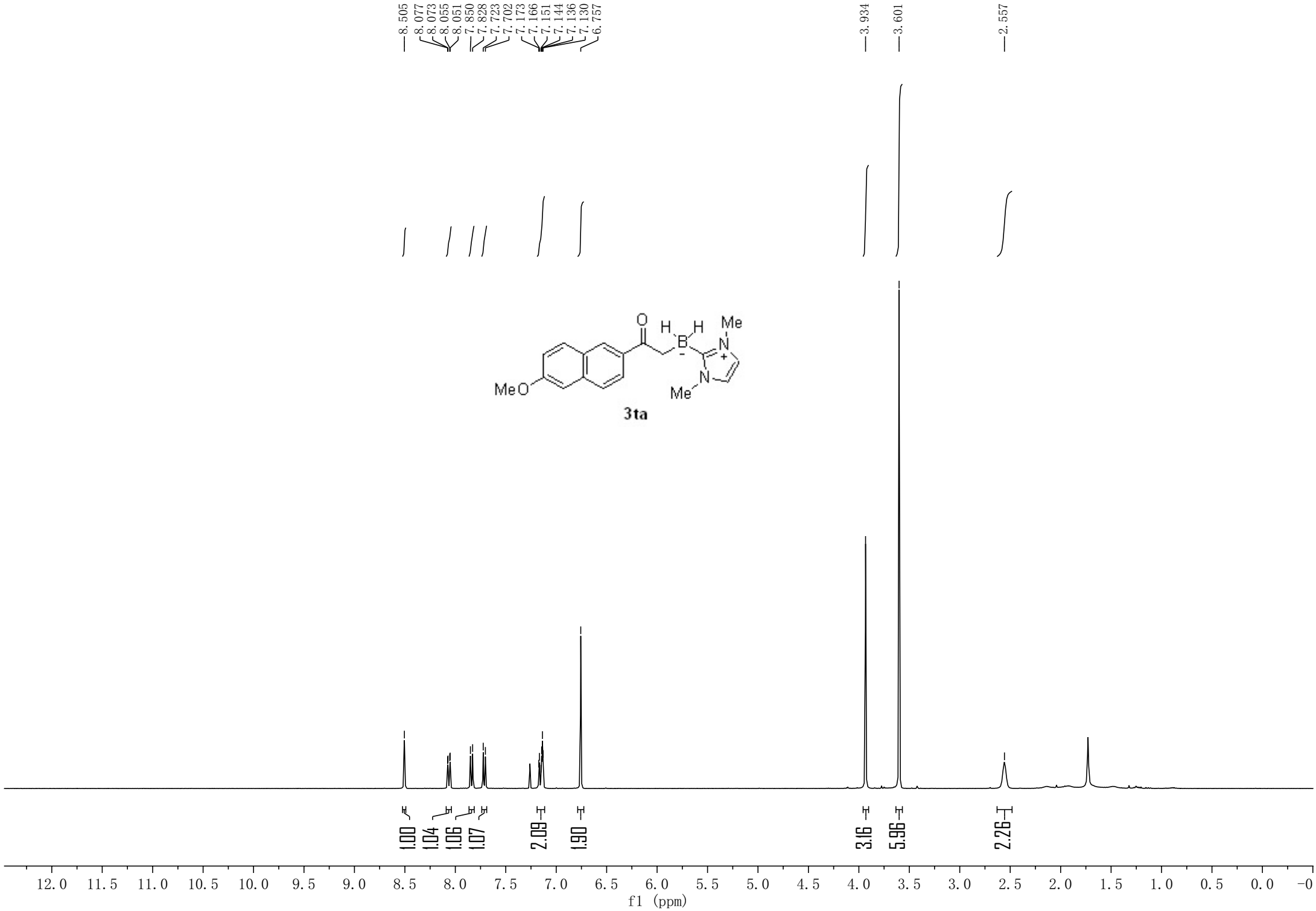
208.60
137.97
137.49
132.12
128.83
127.82
125.63
120.33
77.32
77.00
76.68
35.89
21.40
-0.04



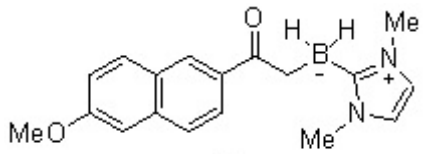
3sa



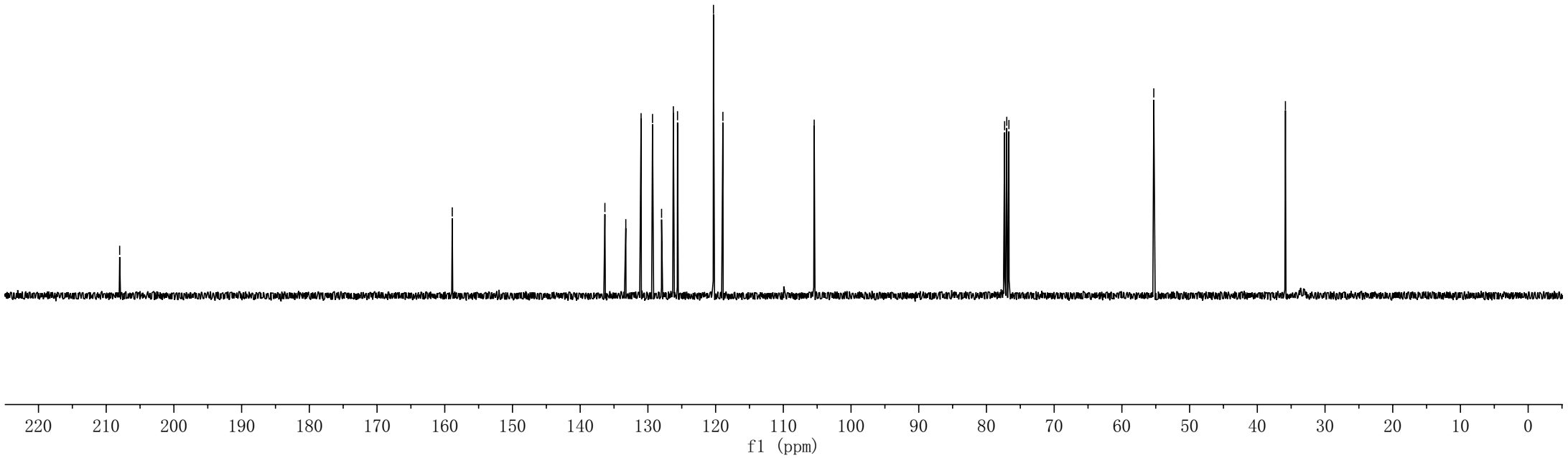

-26.89
-27.46
-28.02
O
H
H
Me
Me
B
N
N
Me
3sa
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

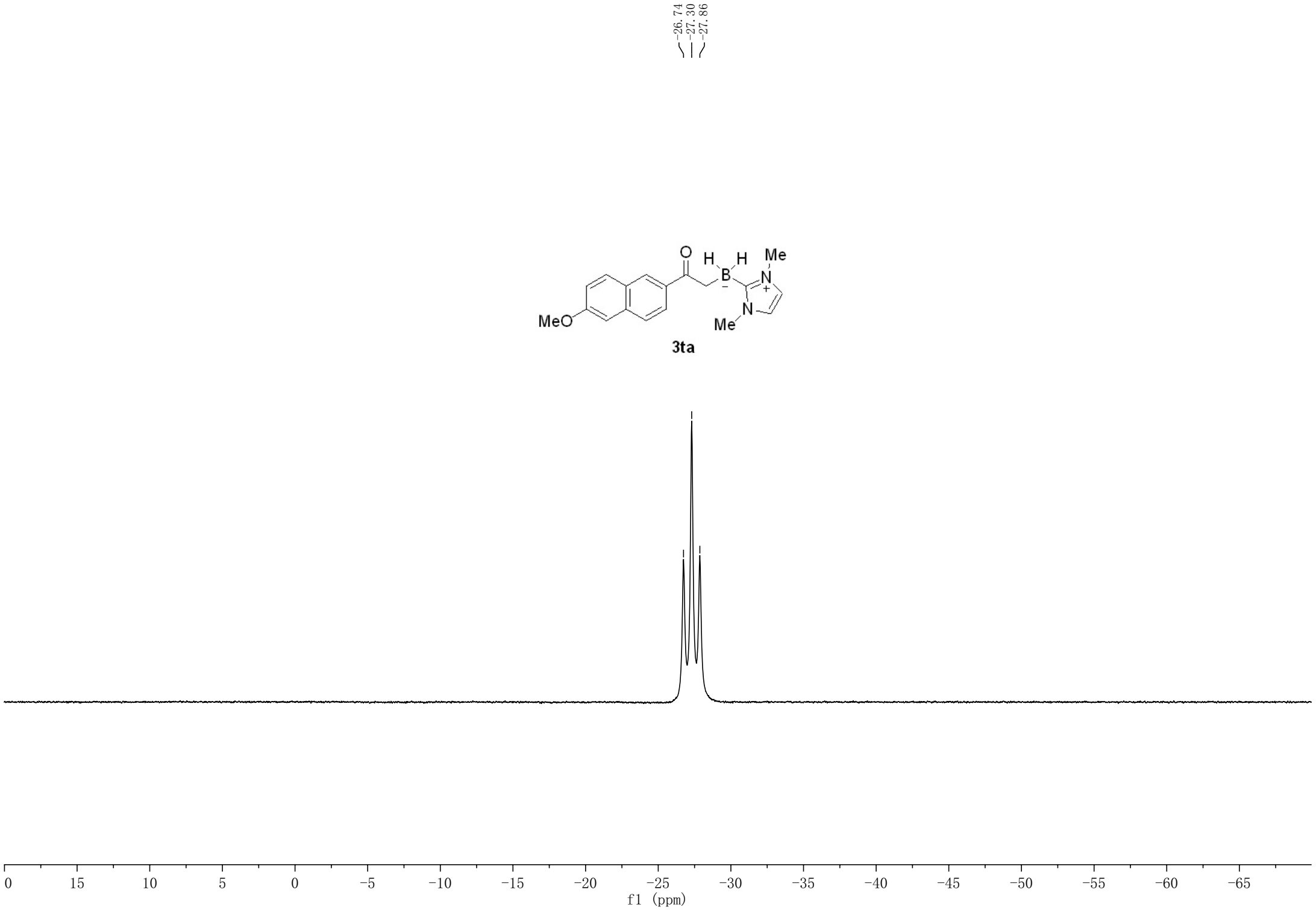

8.505
8.077
8.073
8.055
8.051
7.850
7.828
7.723
7.702
7.173
7.166
7.151
7.144
7.136
7.130
6.757
3.934
3.601
2.557
O
H
B
H
Me
N
N
Me
MeO
3ta
1.00
1.04
1.06
1.07
2.09
1.90
3.16
5.96
2.26
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

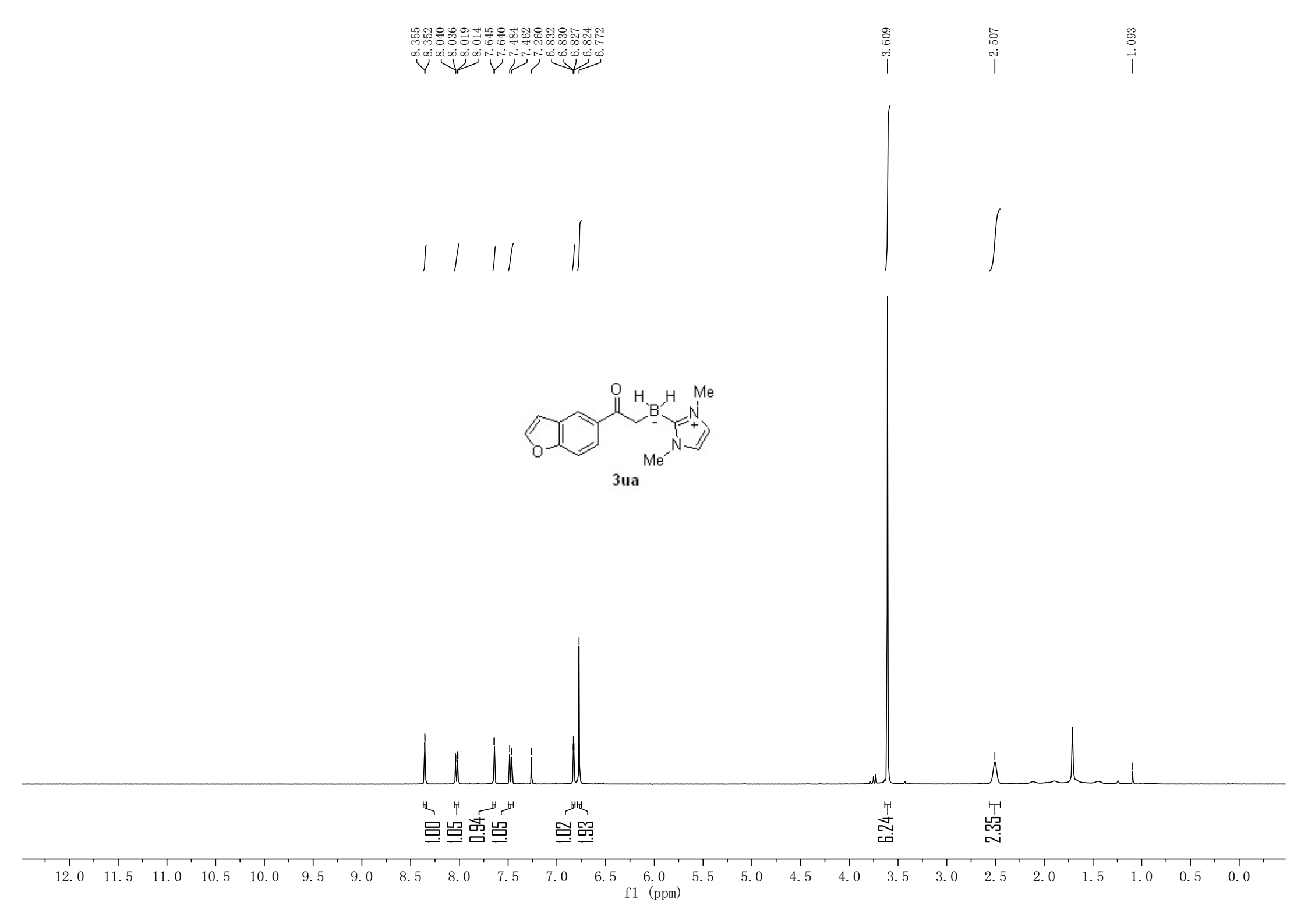
208.01
158.89
136.35
133.26
131.01
129.32
127.98
126.24
125.62
120.32
118.92
105.44
77.32
77.00
76.68
55.29
35.85



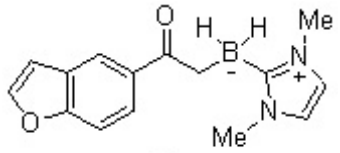
3ta



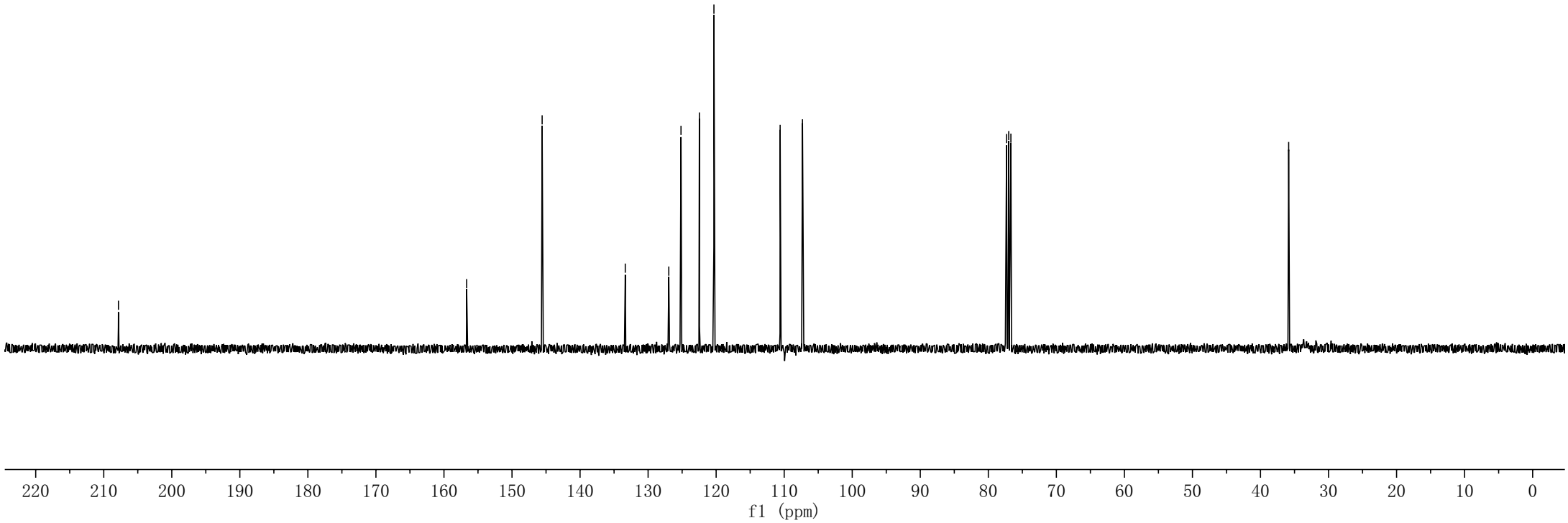

-26.74
-27.30
-27.86
O
H
H
B
Me
N
N
Me
MeO
3ta
0
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

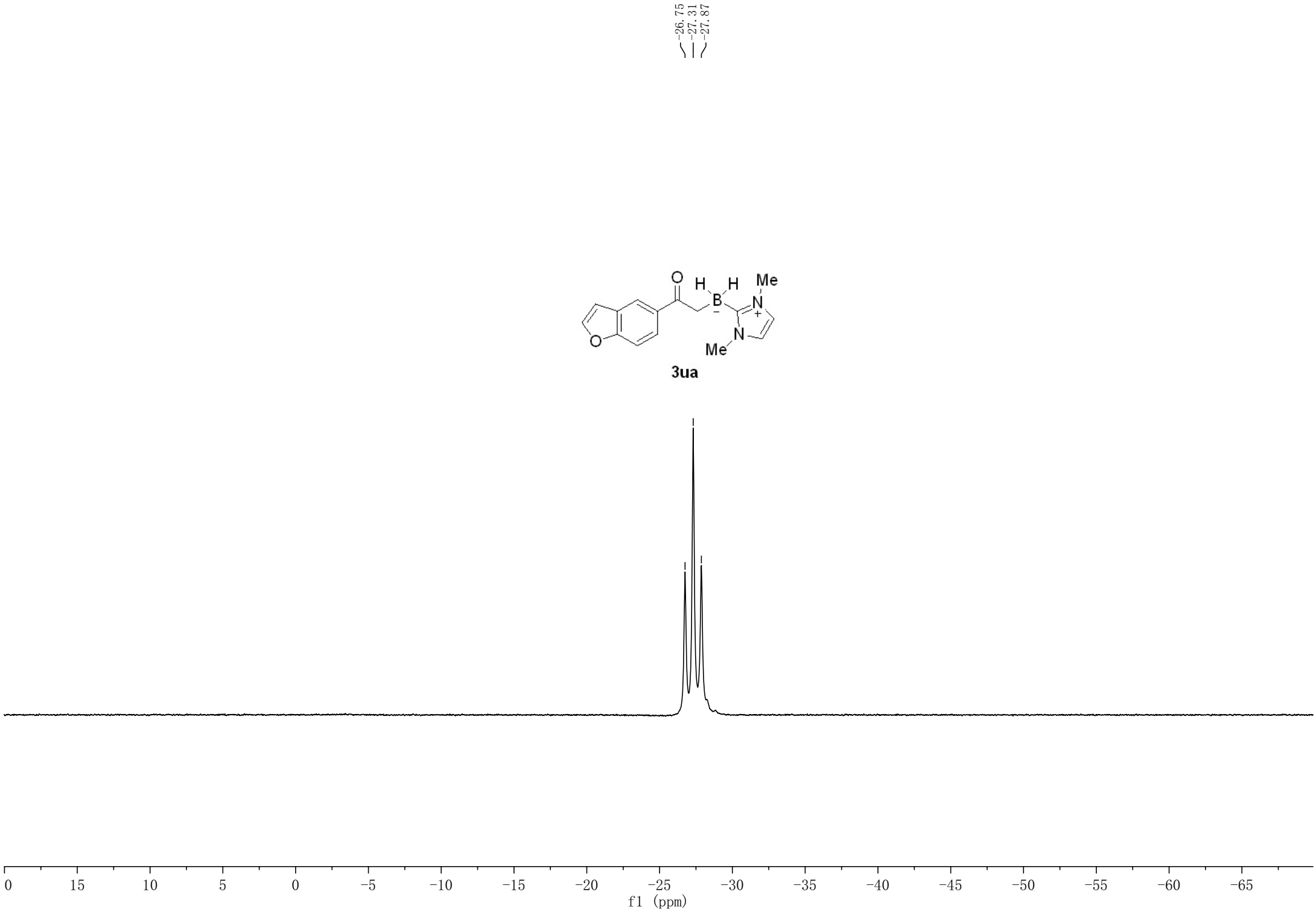

8.355
8.352
8.040
8.036
8.019
8.014
7.645
7.640
7.484
7.462
7.260
6.832
6.830
6.827
6.824
6.772
3.609
2.507
1.093
O
H
B
H
Me
N
N
Me
O
3ua
1.00
1.05
0.94
1.05
1.02
1.93
6.24
2.35
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

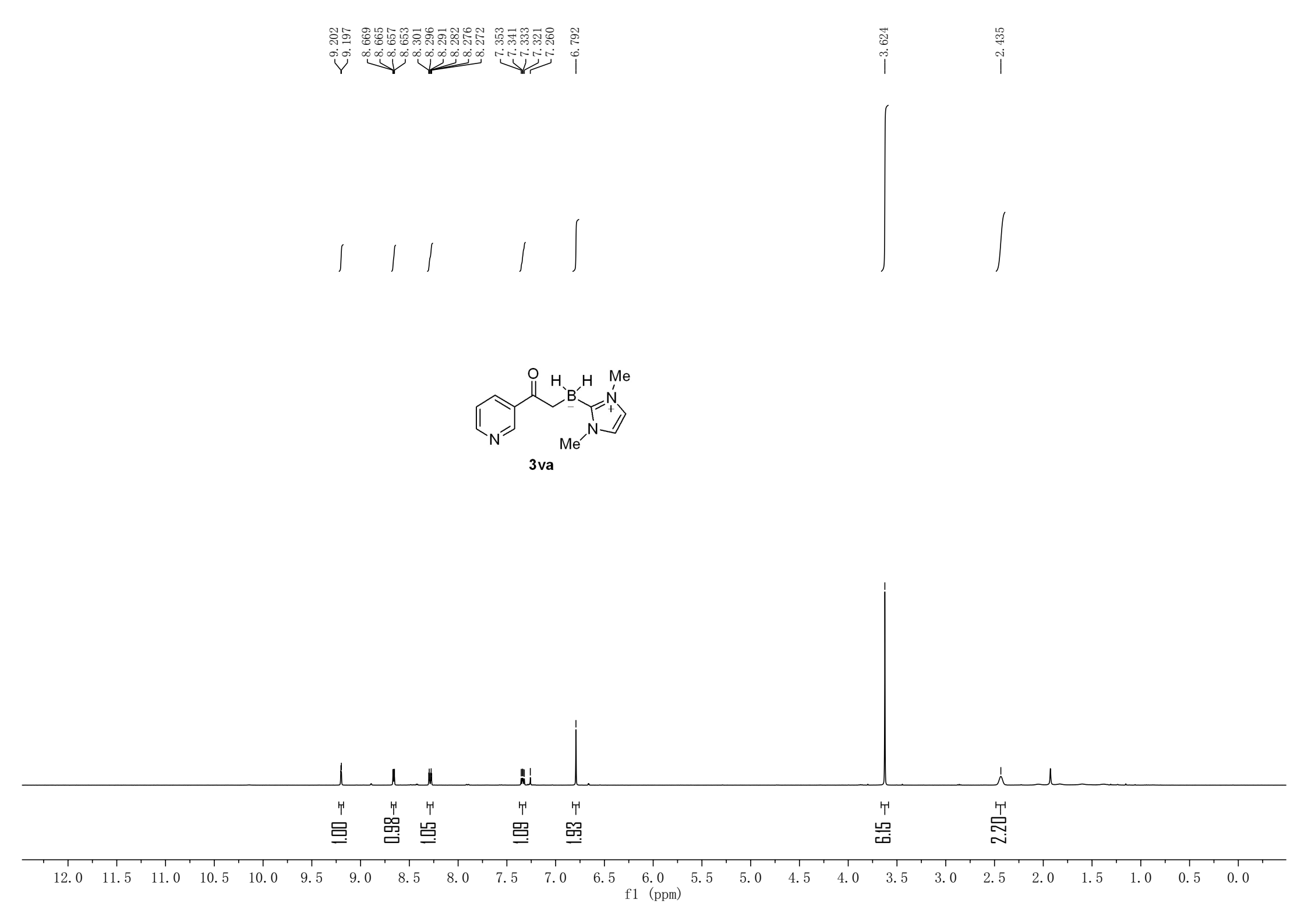
207.84
156.67
145.57
133.35
126.96
125.16
122.47
120.33
110.59
107.31
77.32
77.00
76.68
35.86

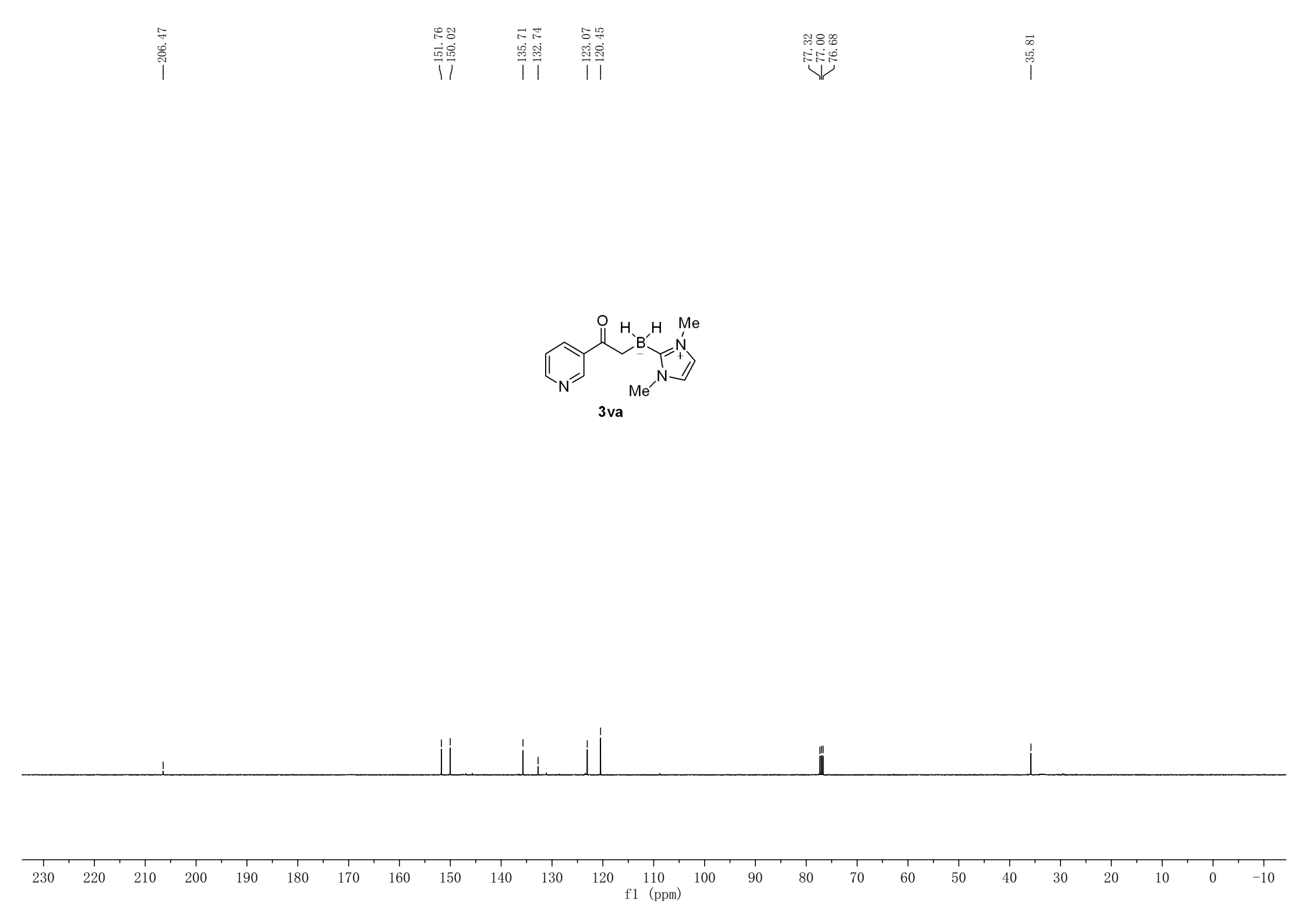


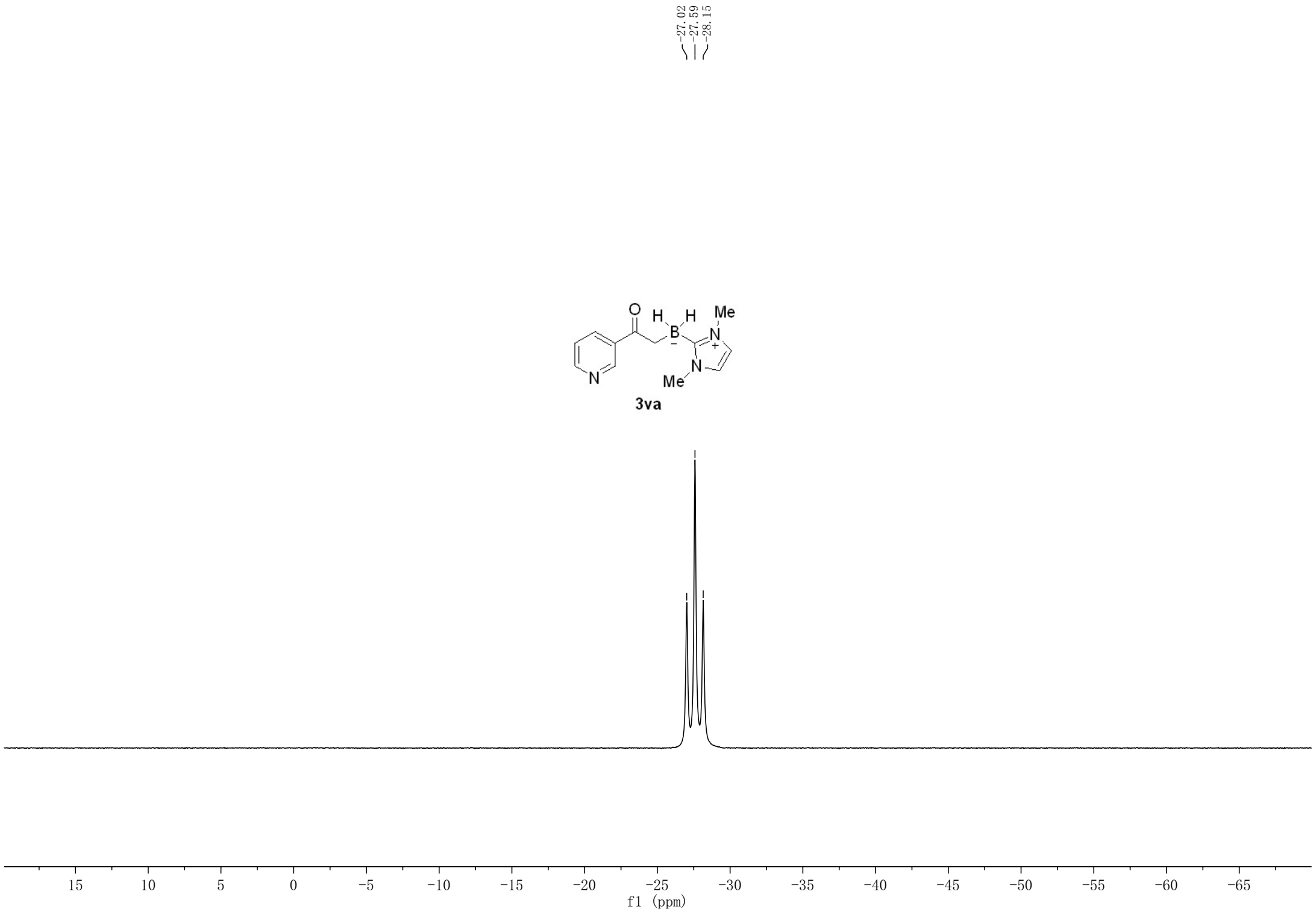
3ua

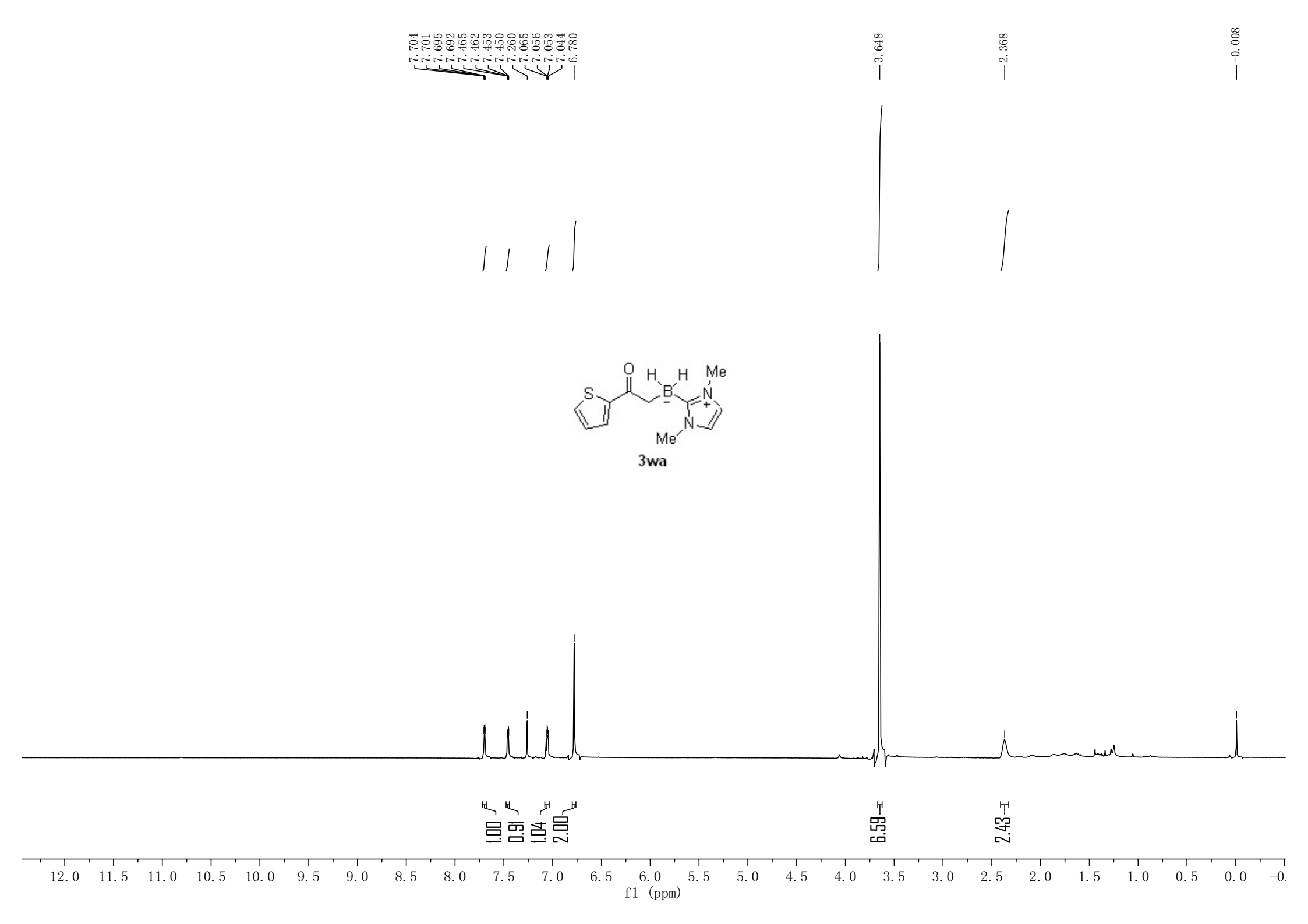


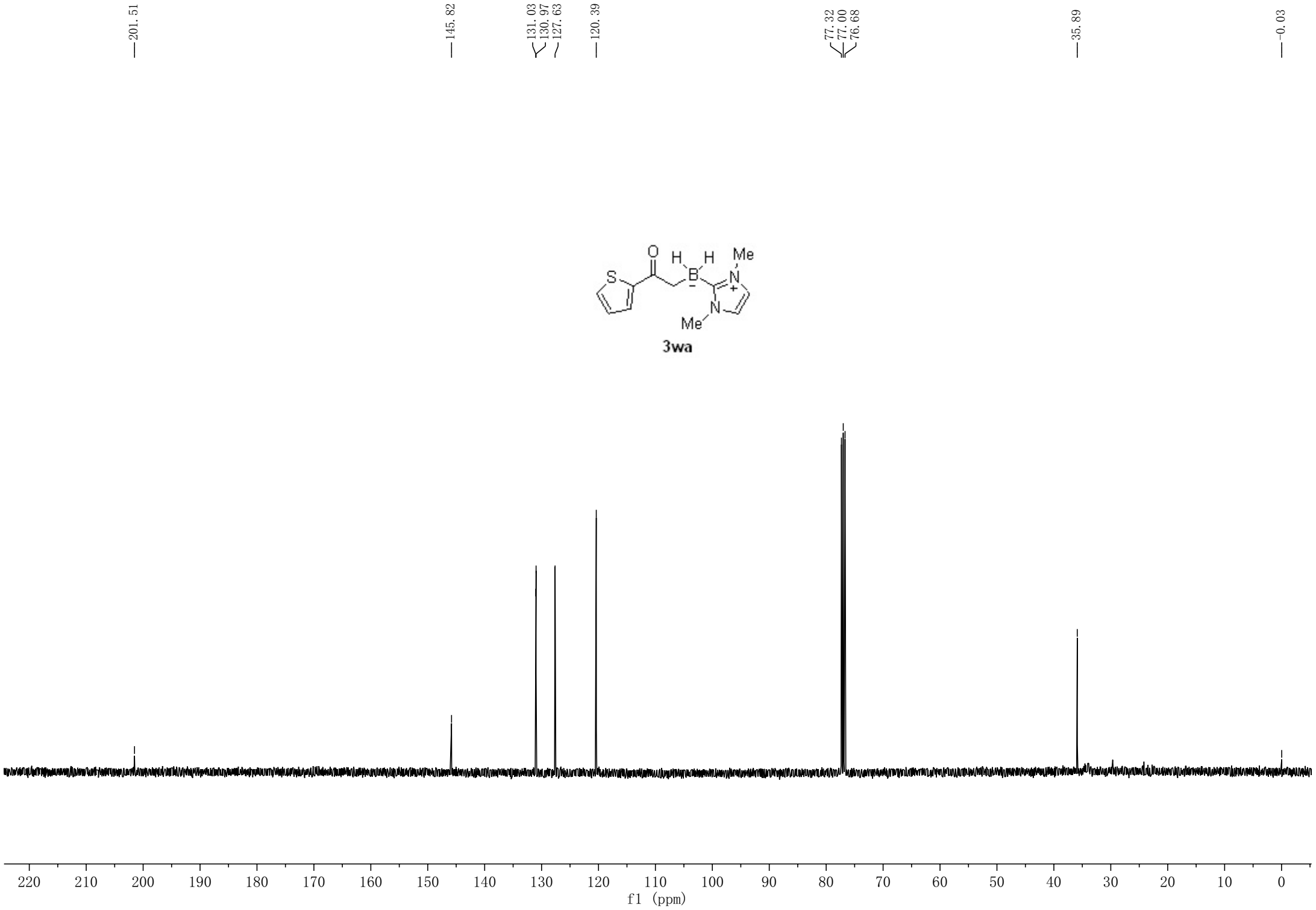

-26.75
-27.31
-27.87
O
H
B
H
Me
N
N
Me
O
3ua
0
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

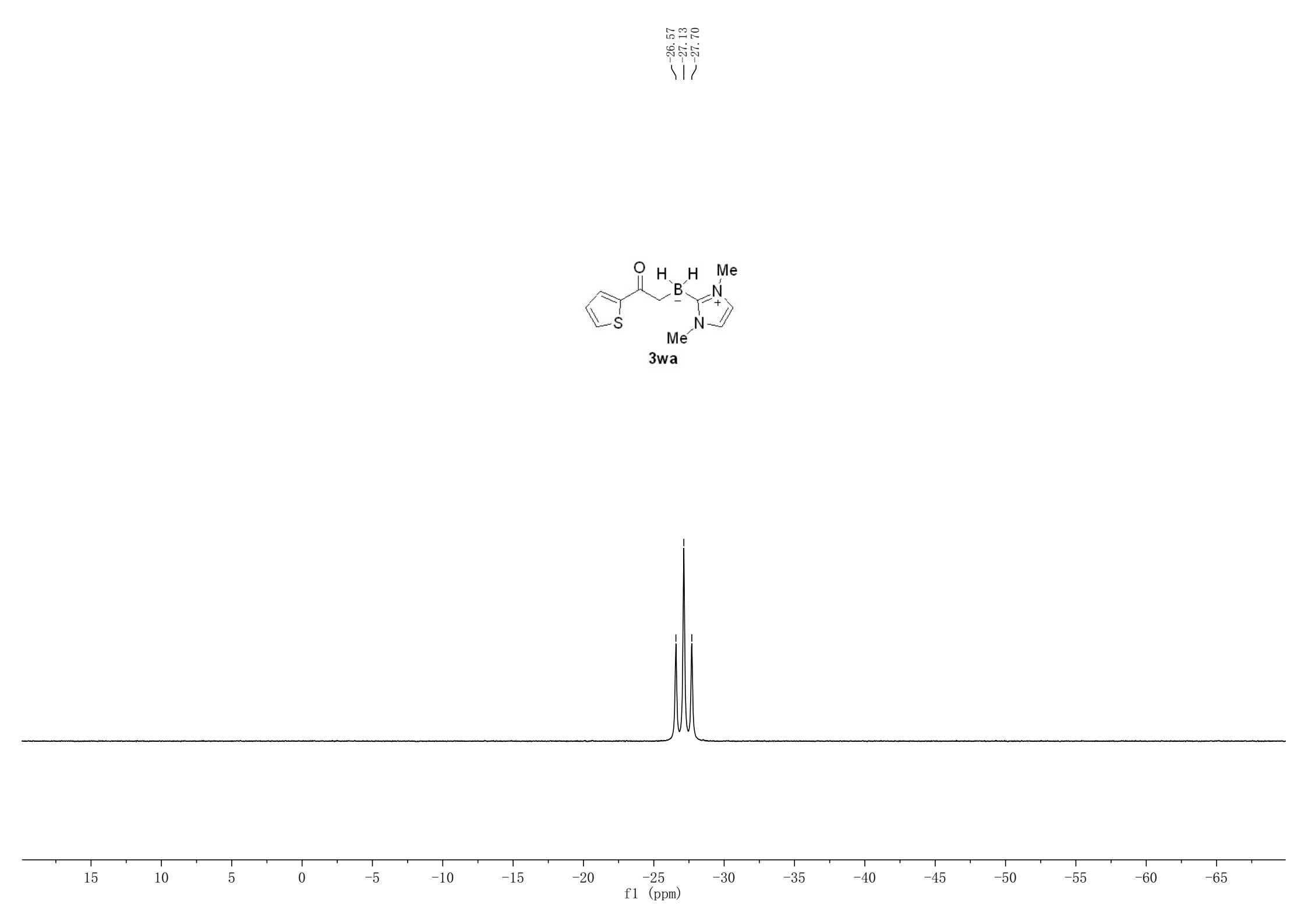

9.202
9.197
8.669
8.665
8.657
8.653
8.301
8.296
8.291
8.282
8.276
8.272
7.353
7.341
7.333
7.321
7.260
6.792
3.624
2.435
O
H
B
H
Me
N
N
Me
3va
1.00
0.98
1.05
1.09
1.93
6.15
2.20
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

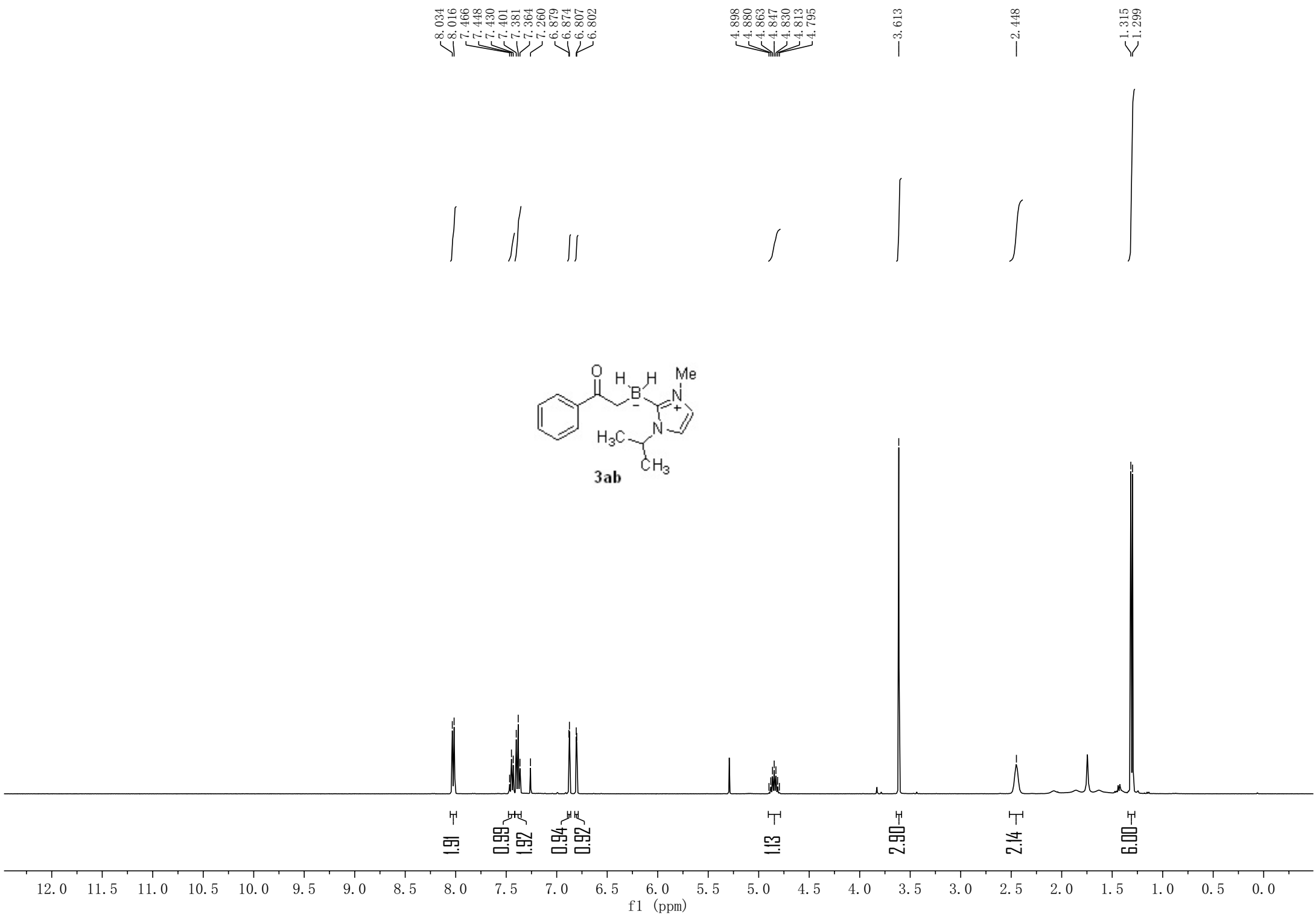

206.47
151.76
150.02
135.71
132.74
123.07
120.45
77.32
77.00
76.68
35.81
O
H
H
B
Me
N
N
Me
3va
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

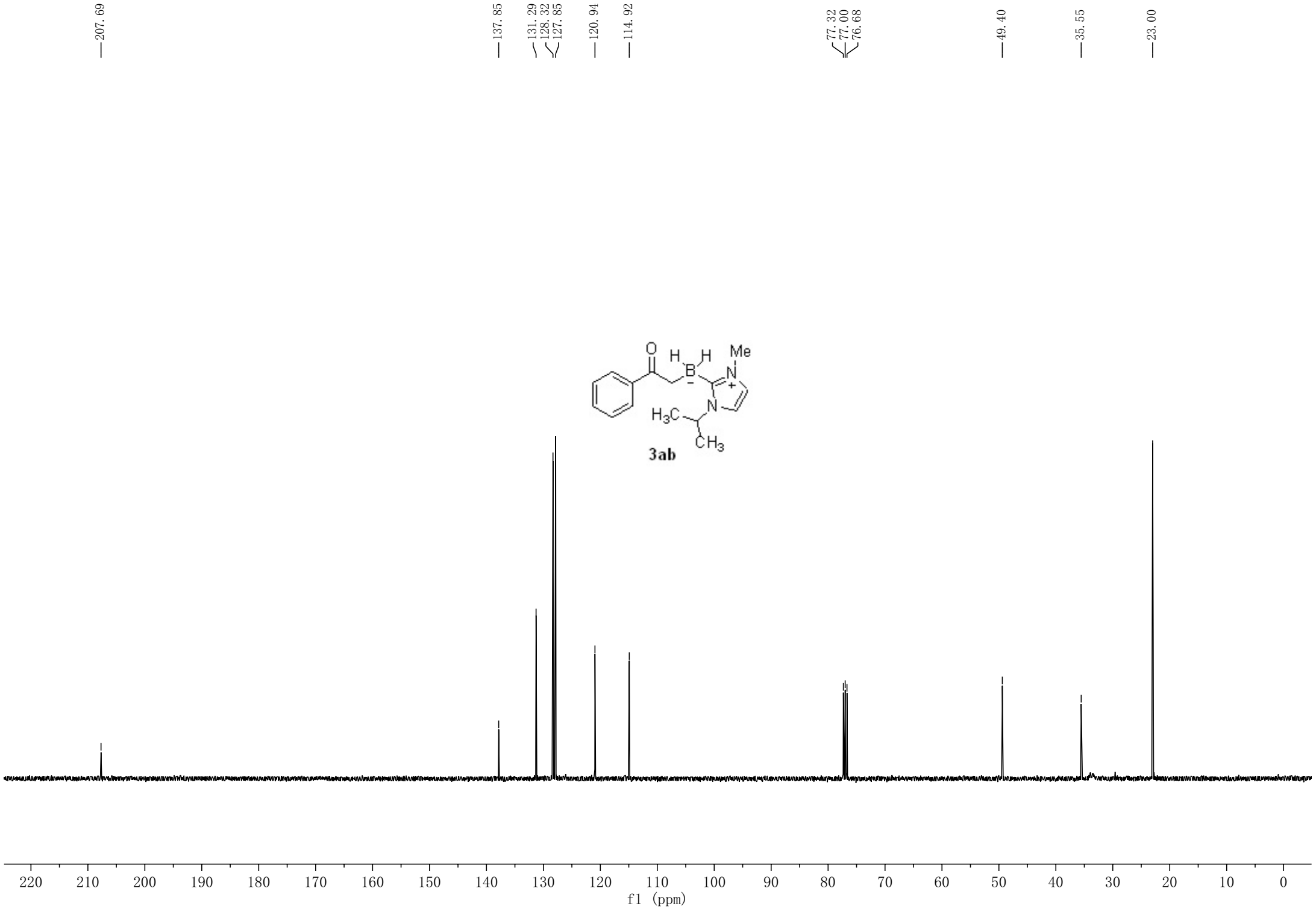

-27.02
-27.59
-28.15
O
H
H
B
Me
N
N
N
Me
3va
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

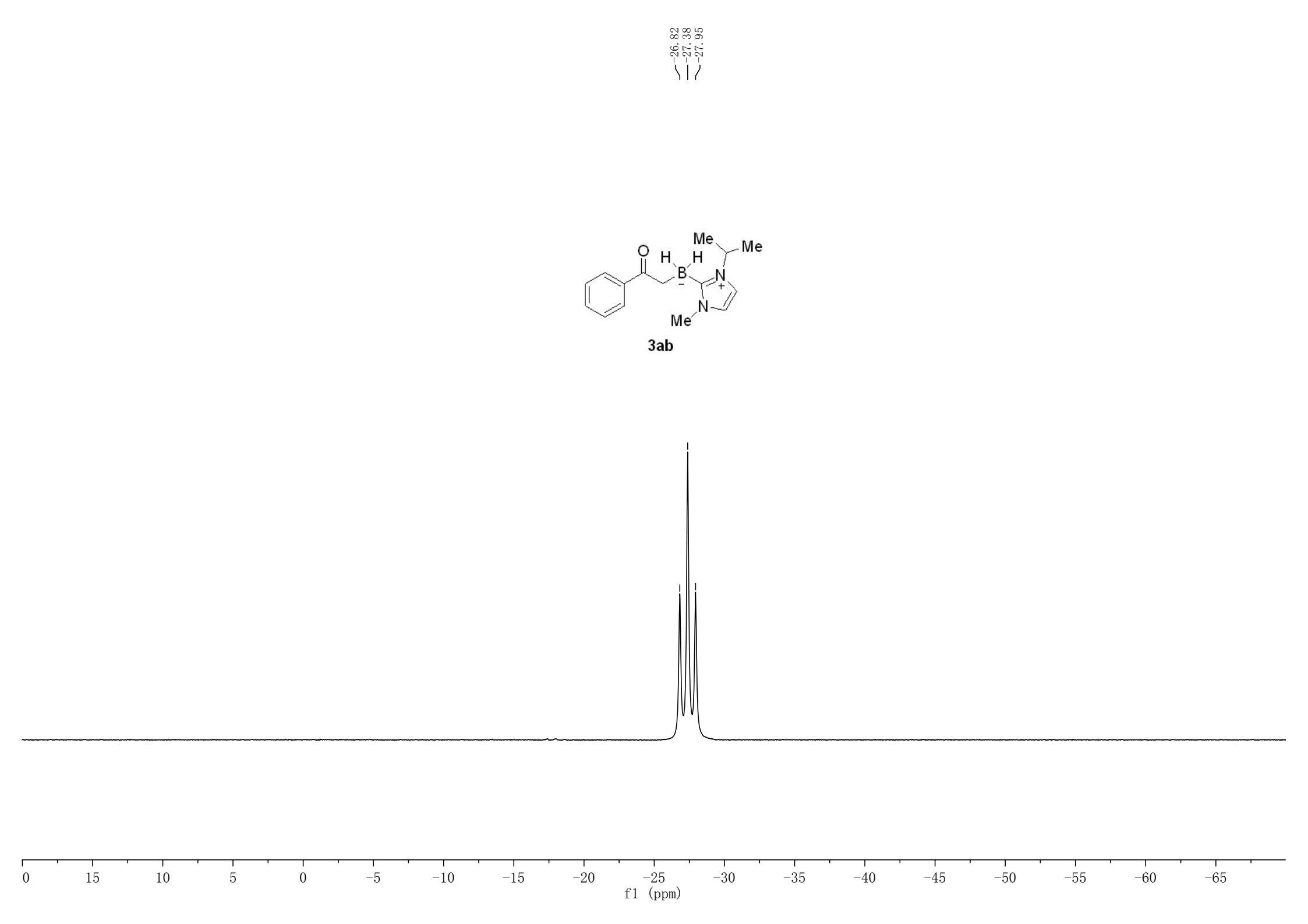

7.704
7.701
7.695
7.692
7.465
7.462
7.453
7.450
7.260
7.065
7.056
7.053
7.044
6.780
3.648
2.368
-0.008
O
H
H
Me
S
B
N
N
Me
3wa
1.00
0.91
1.04
2.00
6.59
2.43
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

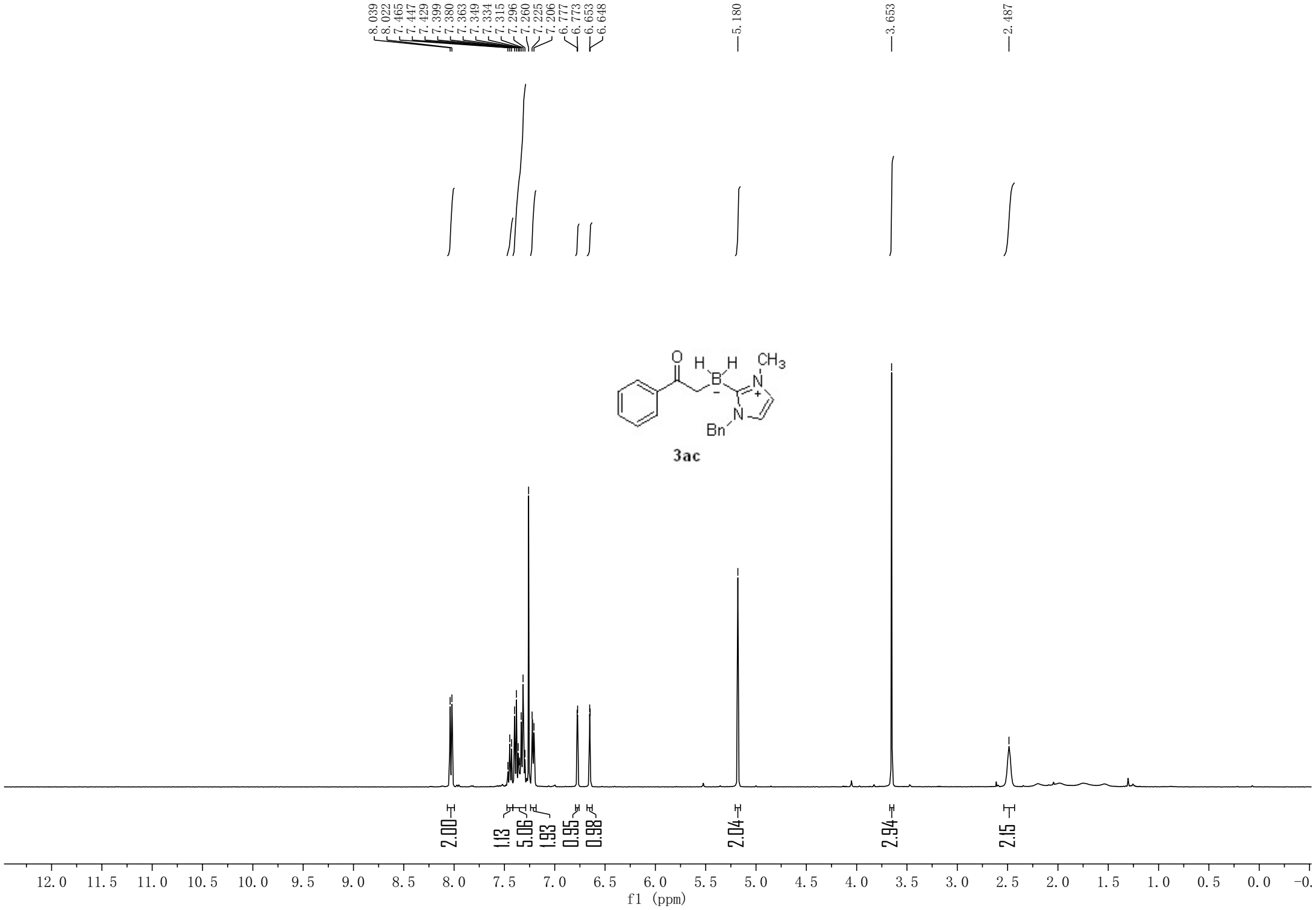

201.51
145.82
131.03
130.97
127.63
120.39
77.32
77.00
76.68
35.89
0.03
O
H
H
Me
S
B
N
N
Me
3wa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

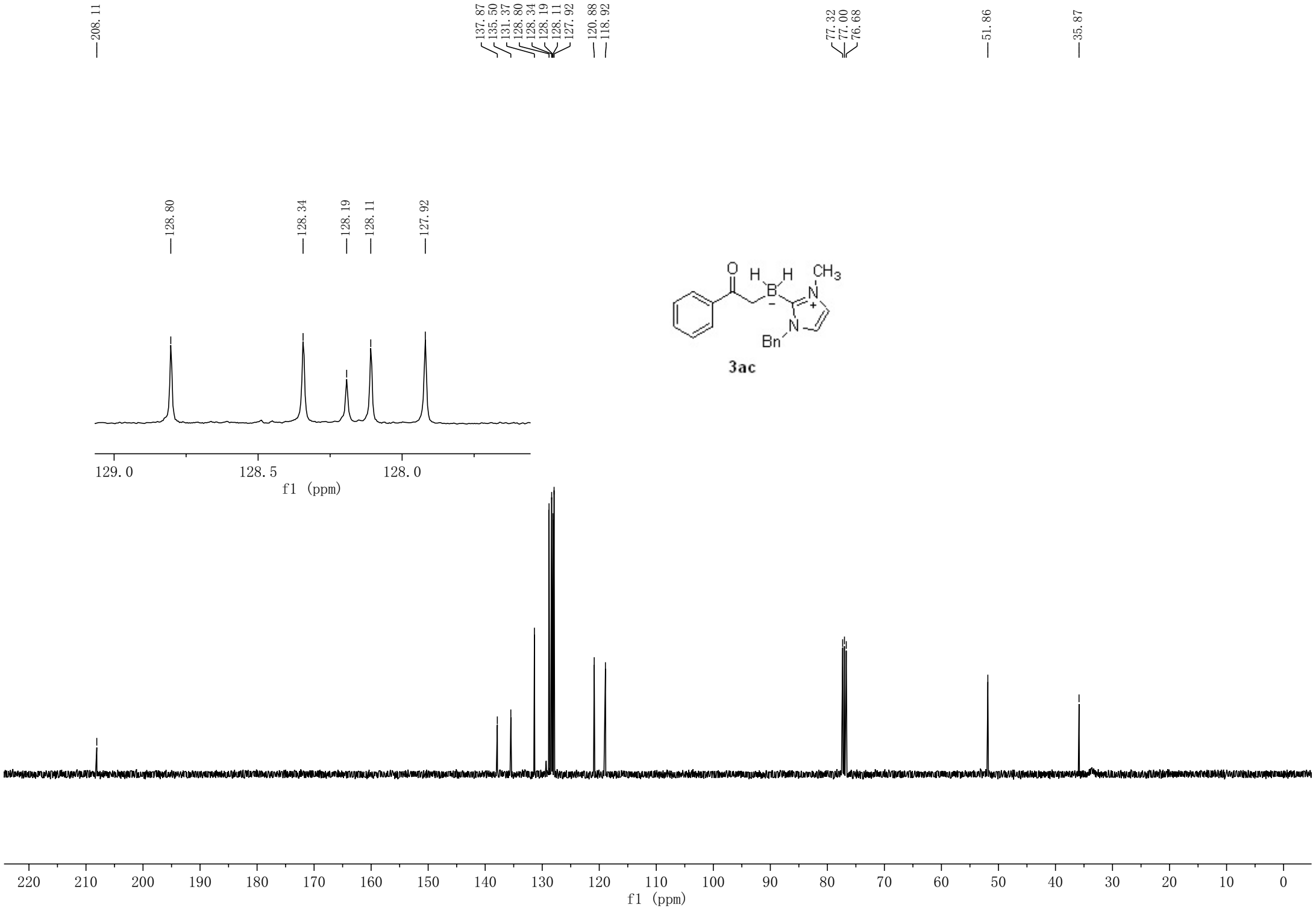

-26.57
-27.13
-27.70
O
H
H
B
Me
N
S
N
Me
3wa
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

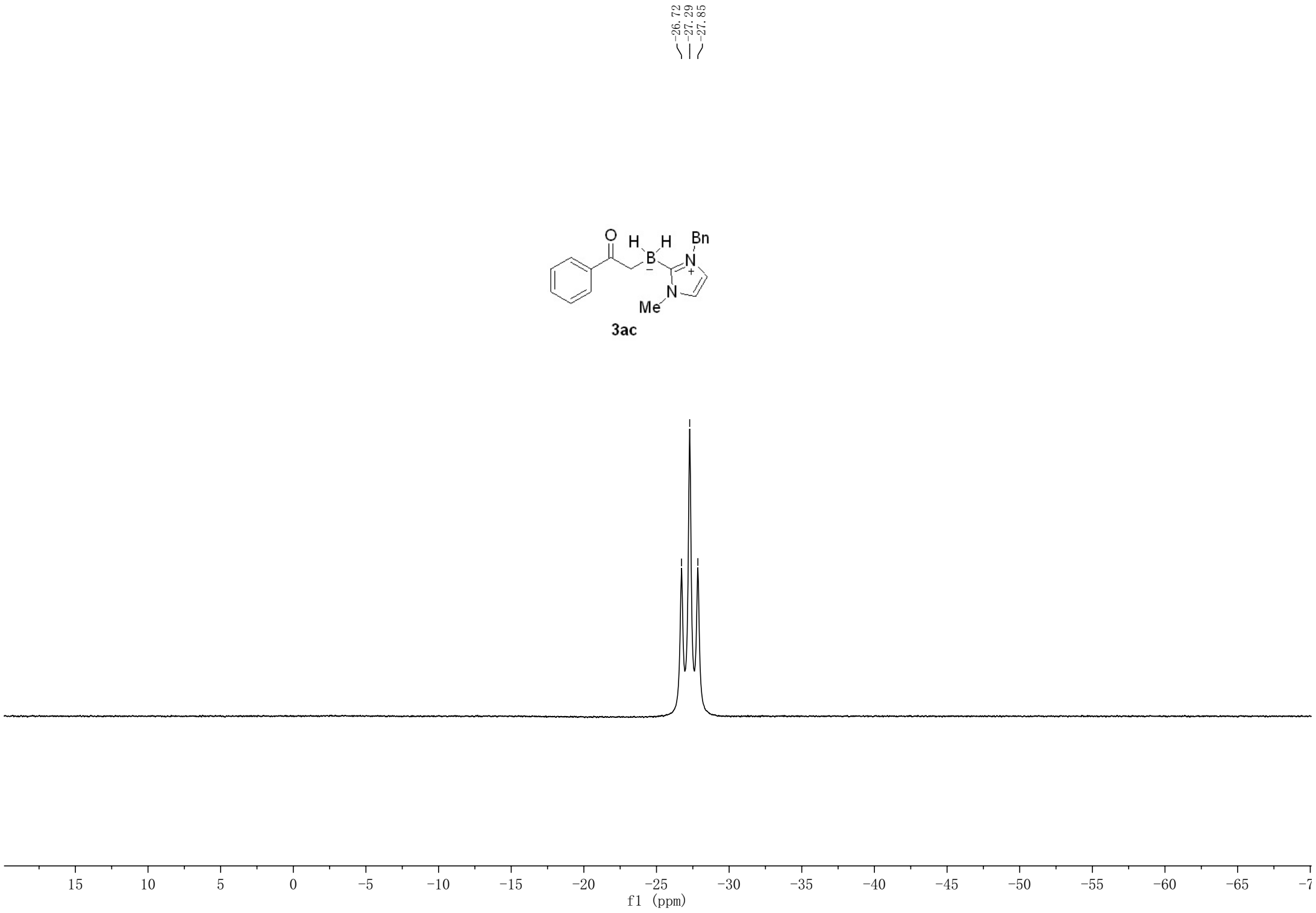

8.034
8.016
7.466
7.448
7.430
7.401
7.381
7.364
7.260
6.879
6.874
6.807
6.802
4.898
4.880
4.863
4.847
4.830
4.813
4.795
3.613
2.448
1.315
1.299
O
H
B
H
Me
N
N
H3C
CH3
3ab
1.91
0.99
1.92
0.94
0.92
1.13
2.90
2.14
6.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

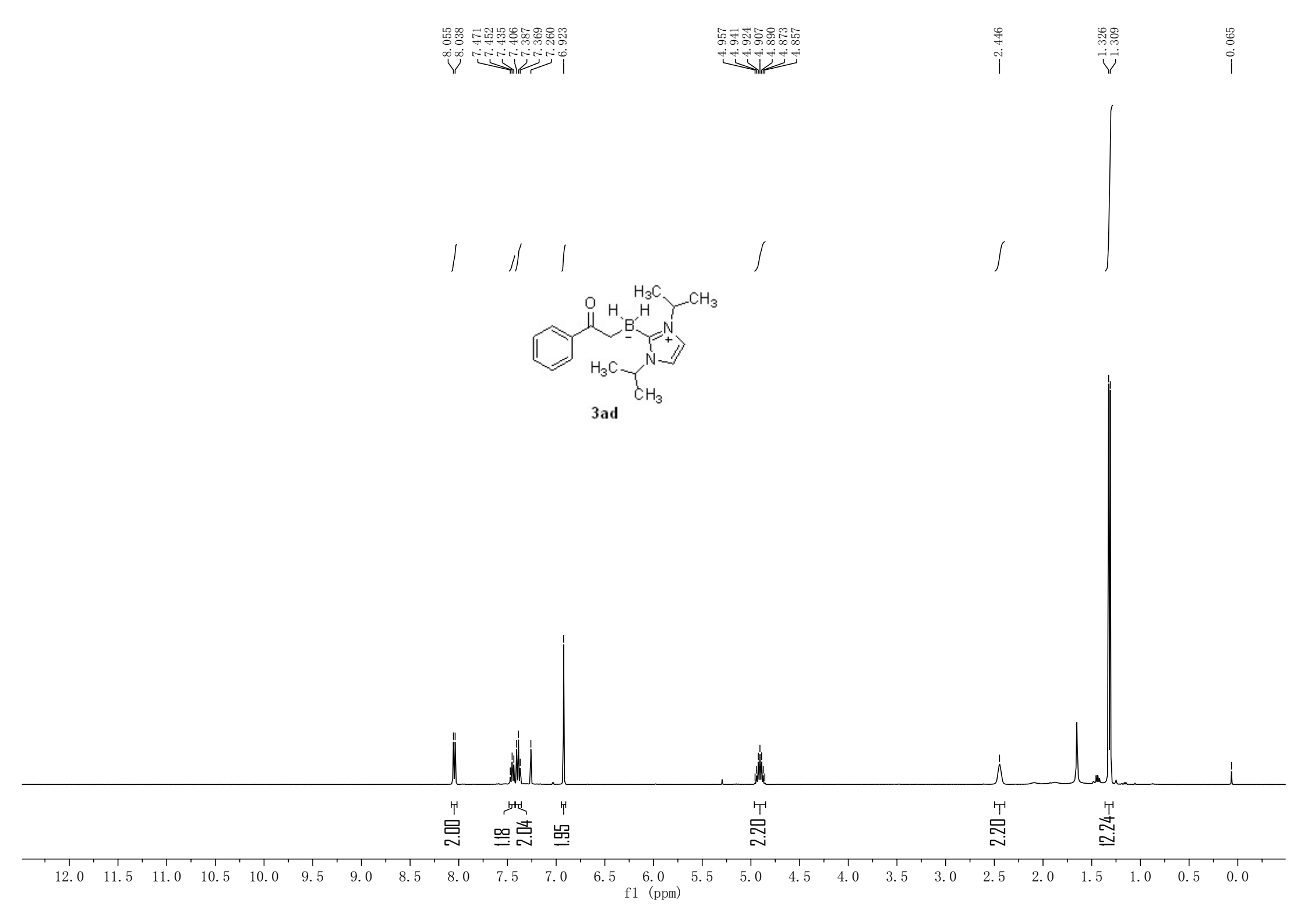

207.69
137.85
131.29
128.32
127.85
120.94
114.92
77.32
77.00
76.68
49.40
35.55
23.00
O
H
B
H
Me
N
N
H3C
CH3
3ab
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

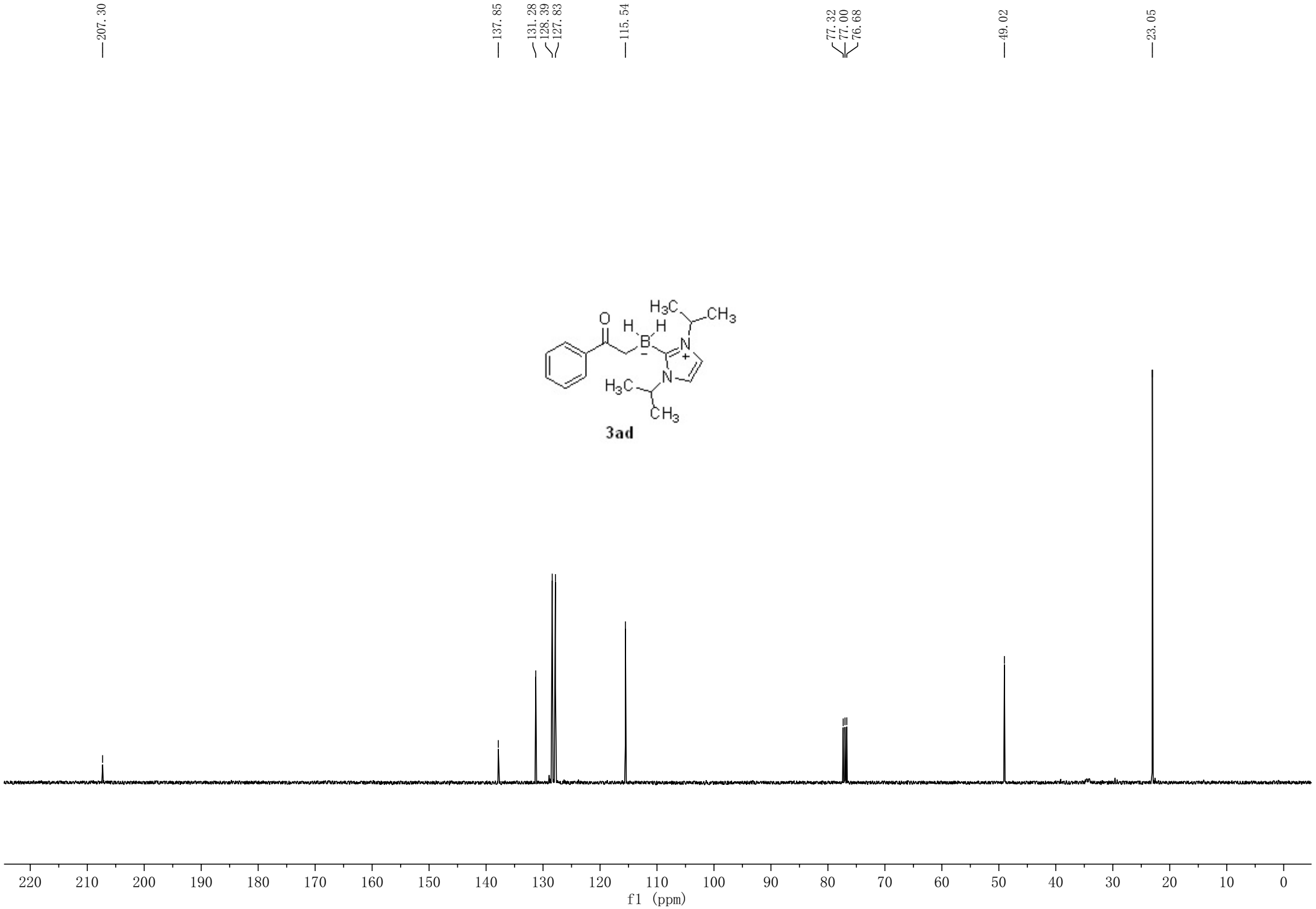

-26.82
-27.38
-27.95
Me
Me
O
H
H
B
N
N
Me
3ab
0
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

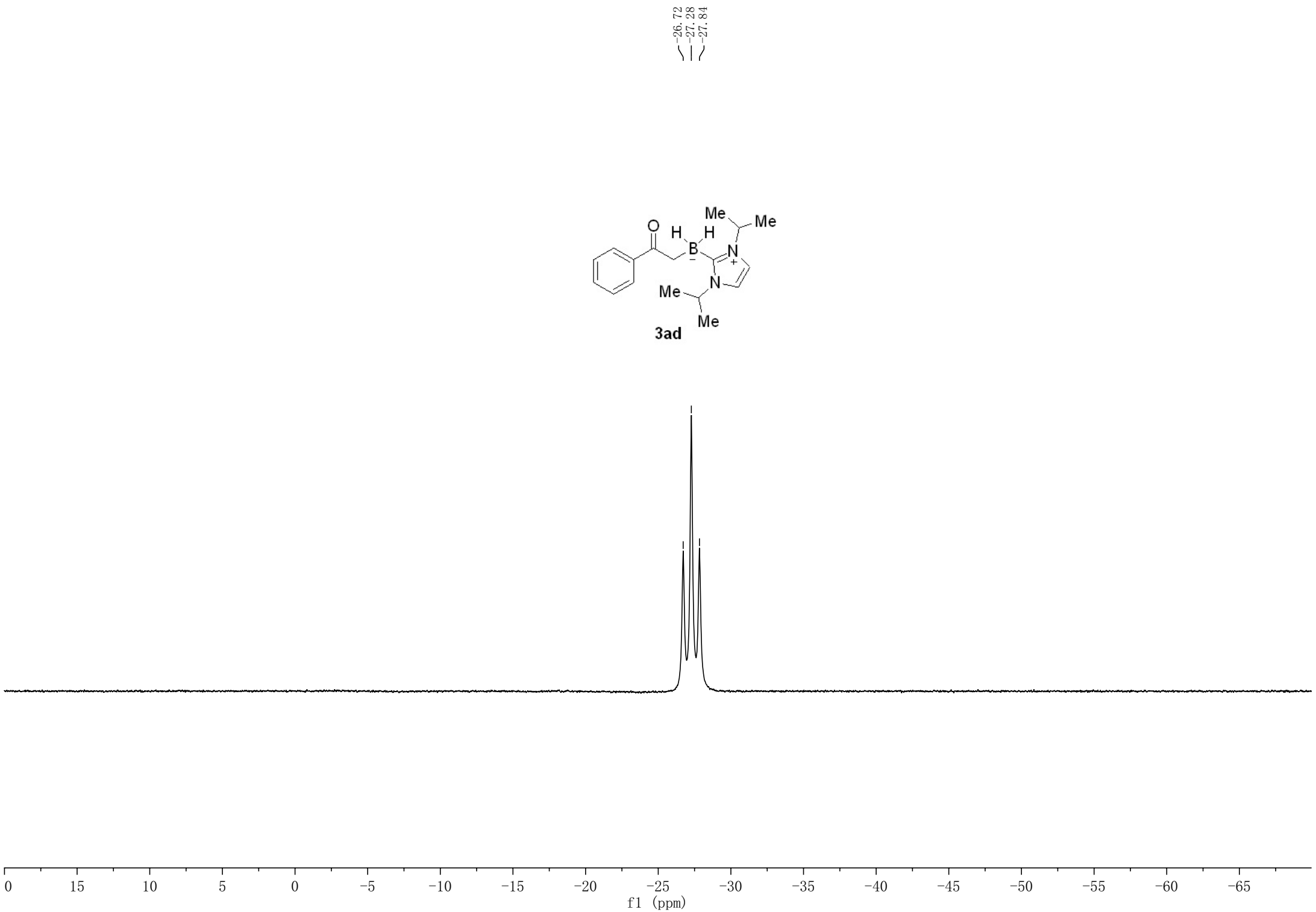

8.039
8.022
7.465
7.447
7.429
7.399
7.380
7.363
7.349
7.334
7.315
7.296
7.260
7.225
7.206
6.777
6.773
6.653
6.648
5.180
3.653
2.487
O
H
B
H
CH3
N
N
Bn
3ac
2.00
1.13
5.06
1.93
0.95
0.98
2.04
2.94
2.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

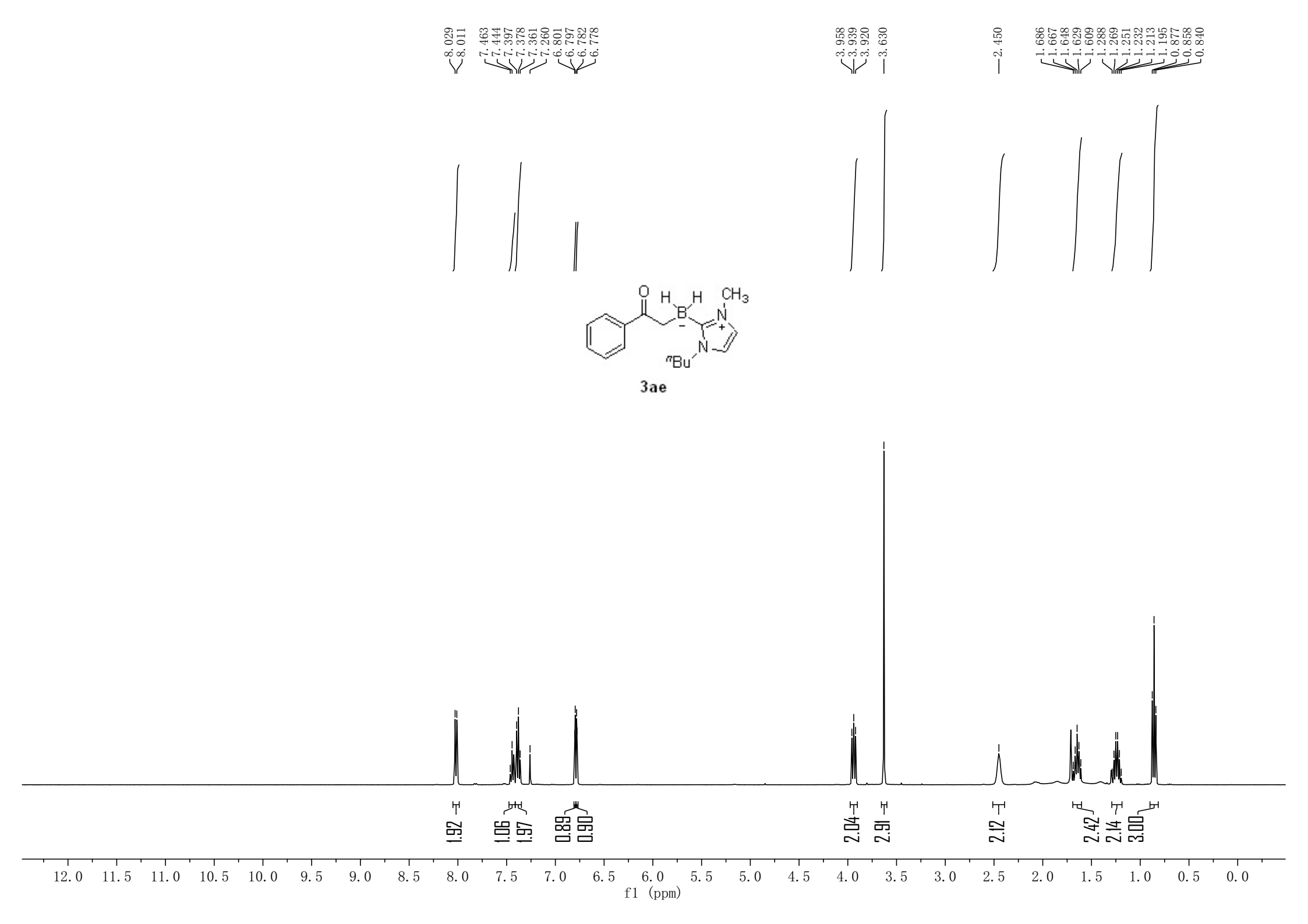

208.11
137.87
135.50
131.37
128.80
128.34
128.19
128.11
127.92
120.88
118.92
77.32
77.00
76.68
51.86
35.87
128.80
128.34
128.19
128.11
127.92
129.0
128.5
128.0
f1 (ppm)
O
H
B
H
CH3
N
N
Bn
3ac
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-26.72
-27.29
-27.85
O
H
H
B
N
Bn
N
Me
3ac
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

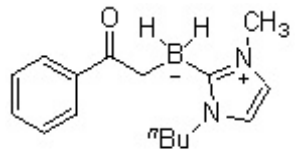

8.055
8.038
7.471
7.452
7.435
7.406
7.387
7.369
7.260
6.923
4.957
4.941
4.924
4.907
4.890
4.873
4.857
2.446
1.326
1.309
0.065
3ad
2.00
1.18
2.04
1.95
2.20
2.20
12.24
f1 (ppm)


207.30
137.85
131.28
128.39
127.83
115.54
77.32
77.00
76.68
49.02
23.05
O
H
H
B
N
N
H3C
CH3
H3C
CH3
3ad
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

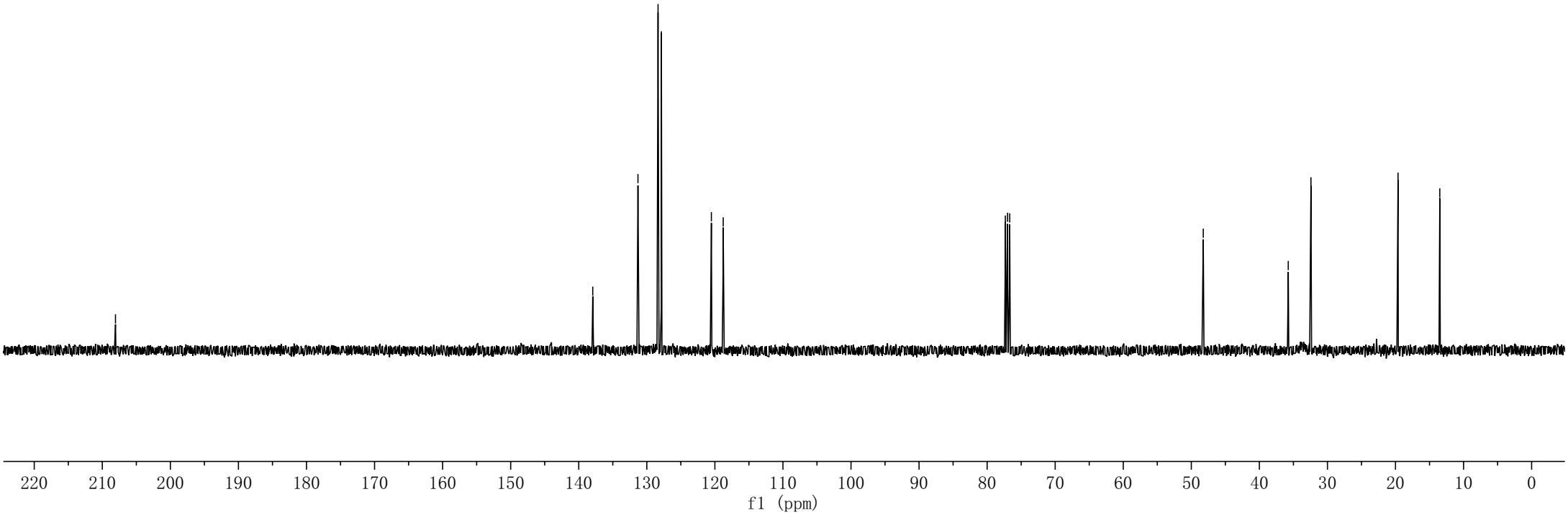

-26.72
-27.28
-27.84
O
H
H
B
N
N
Me
Me
Me
Me
3ad
0
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)

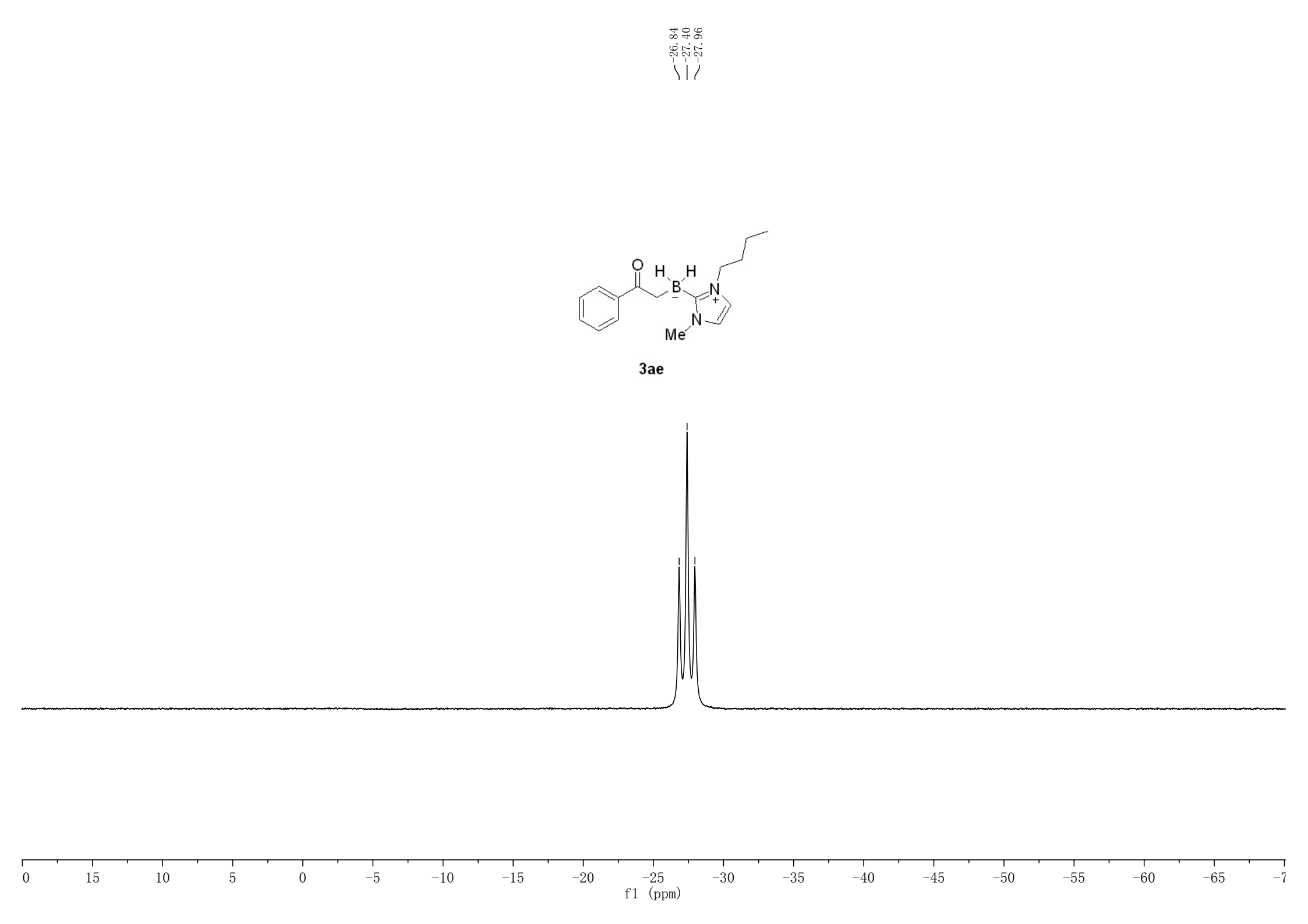

8.029
8.011
7.463
7.444
7.397
7.378
7.361
7.260
6.801
6.797
6.782
6.778
3.958
3.939
3.920
3.630
2.450
1.686
1.667
1.648
1.629
1.609
1.288
1.269
1.251
1.232
1.213
1.195
0.877
0.858
0.840
O
H
B
H
CH3
N
N
nBu
3ae
1.92
1.06
1.97
0.89
0.90
2.04
2.91
2.12
2.42
2.14
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

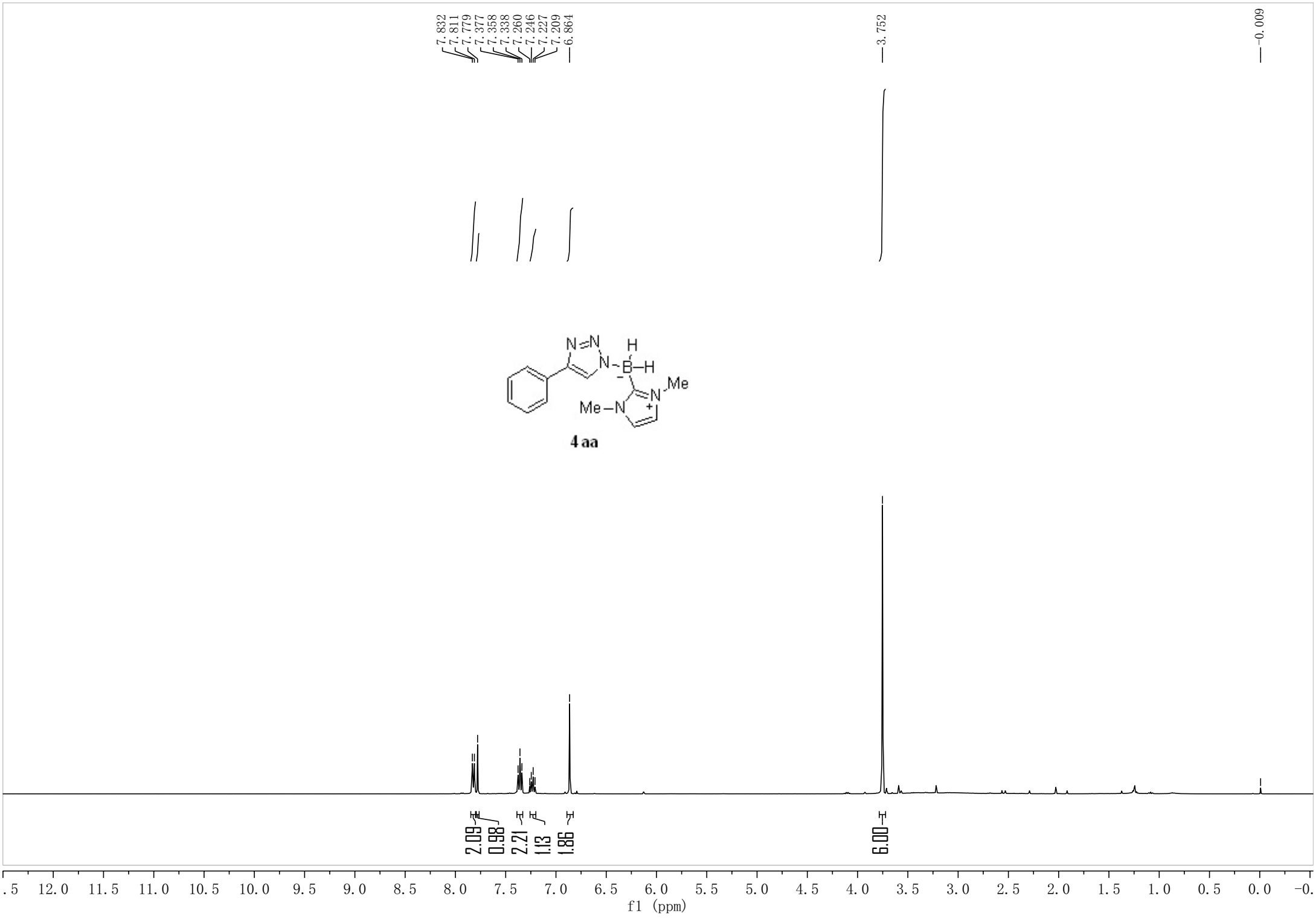
208.06
137.94
131.30
128.35
127.86
120.51
118.77
77.32
77.00
76.68
48.24
35.76
32.42
19.63
13.49



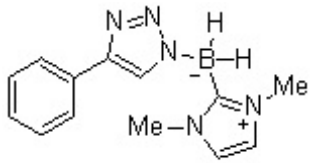
3ae




-26.84
-27.40
-27.96
O
H
H
B
N
N
Me
3ae
0
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
f1 (ppm)


7.832
7.811
7.779
7.377
7.358
7.338
7.260
7.246
7.227
7.209
6.864
3.752
-0.009
N=N
H
N
B–H
Me
N
Me–N
+
4aa
2.09
0.98
2.21
1.13
1.86
6.00
f1 (ppm)

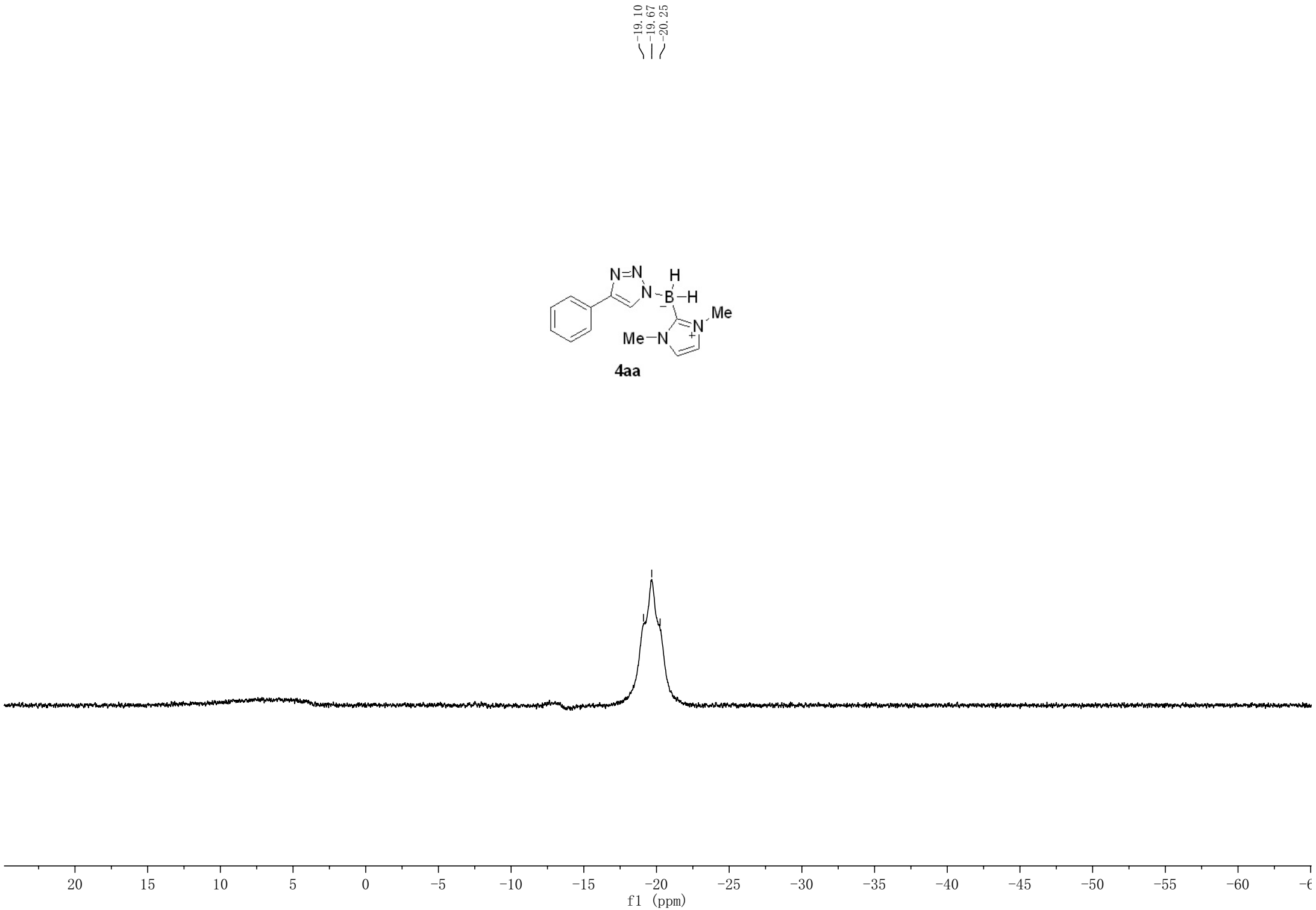
146.25
132.24
128.52
126.86
125.37
125.10
121.19
77.32
77.00
76.68
36.19

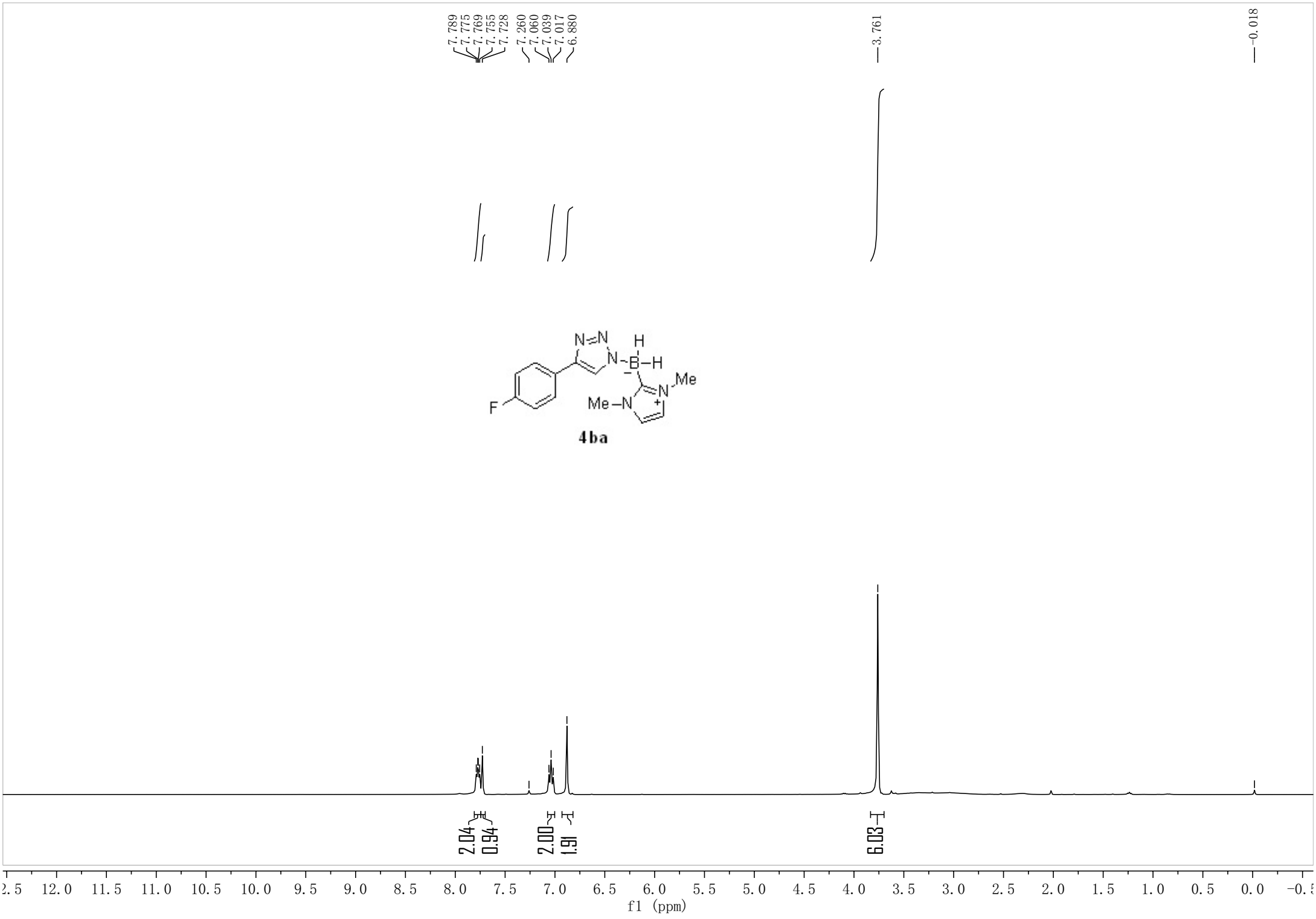


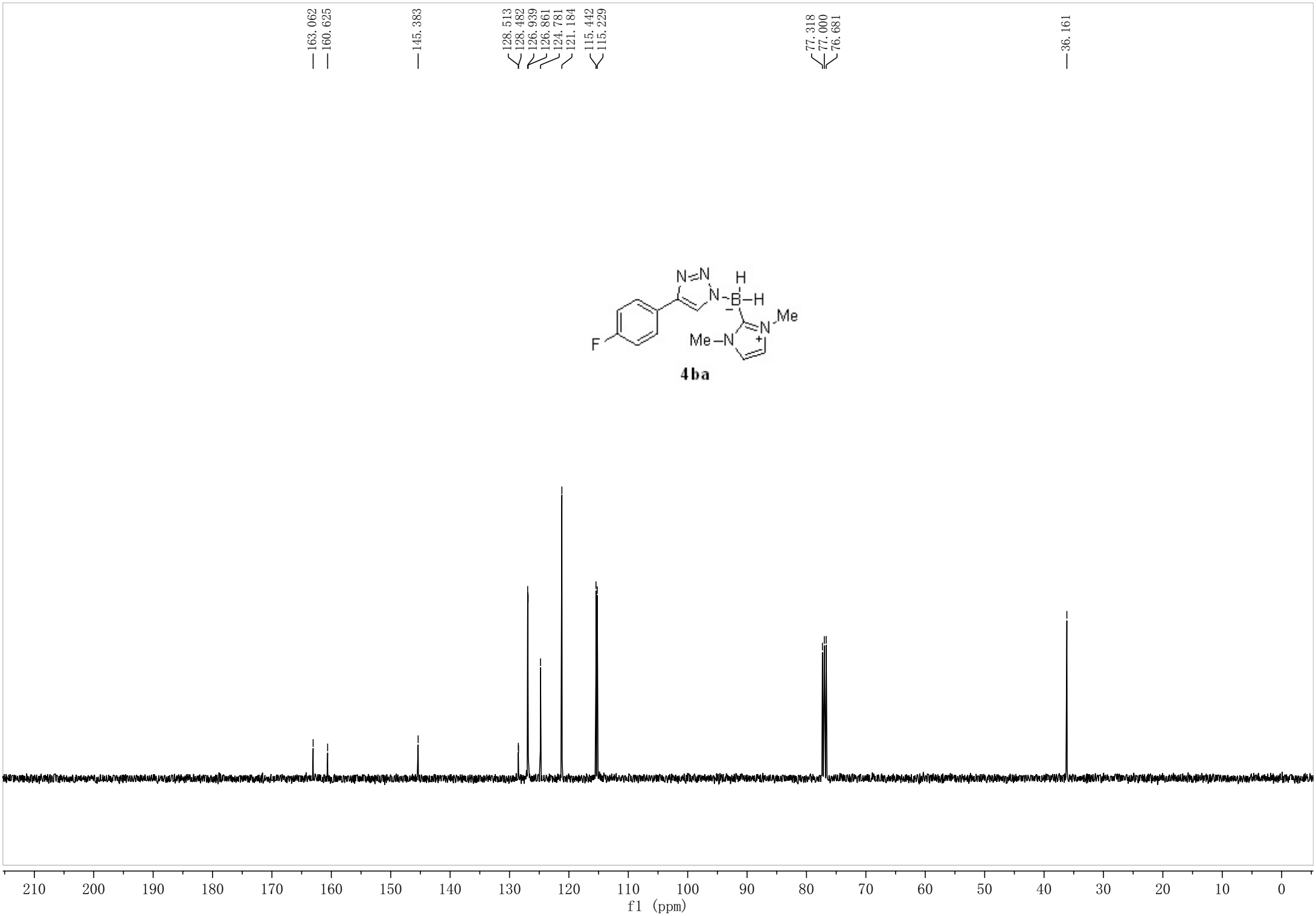
4aa

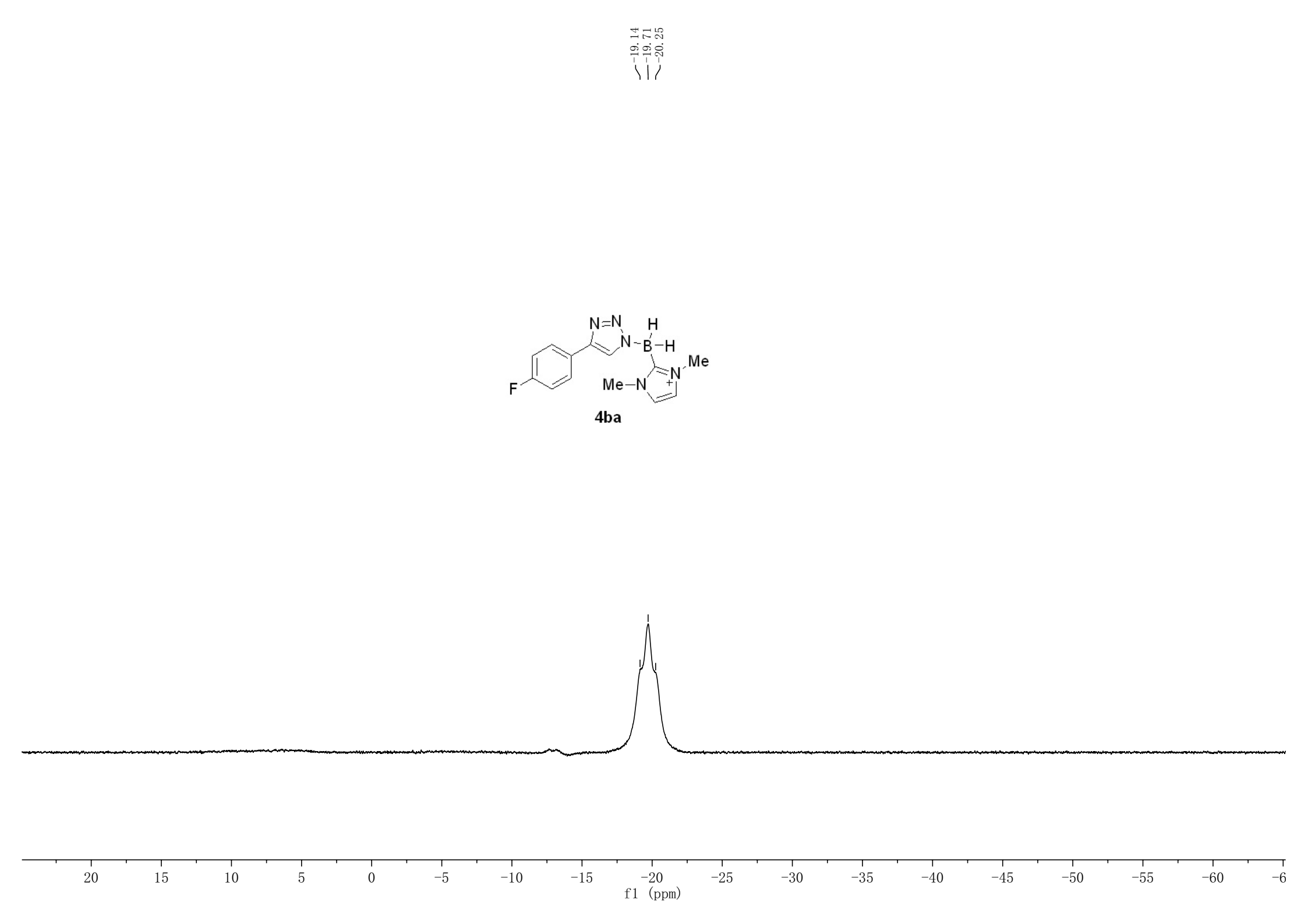
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

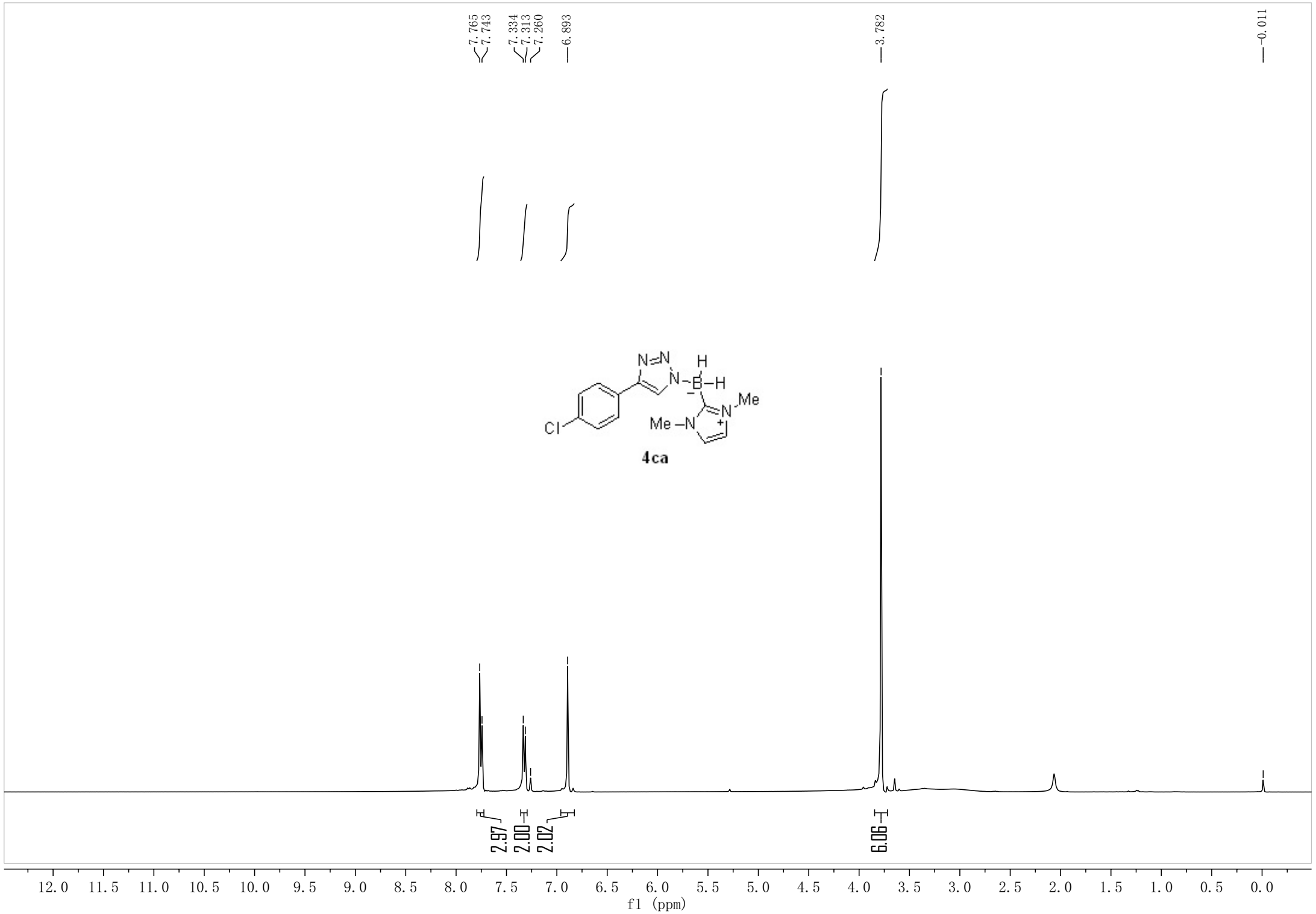
f1 (ppm)

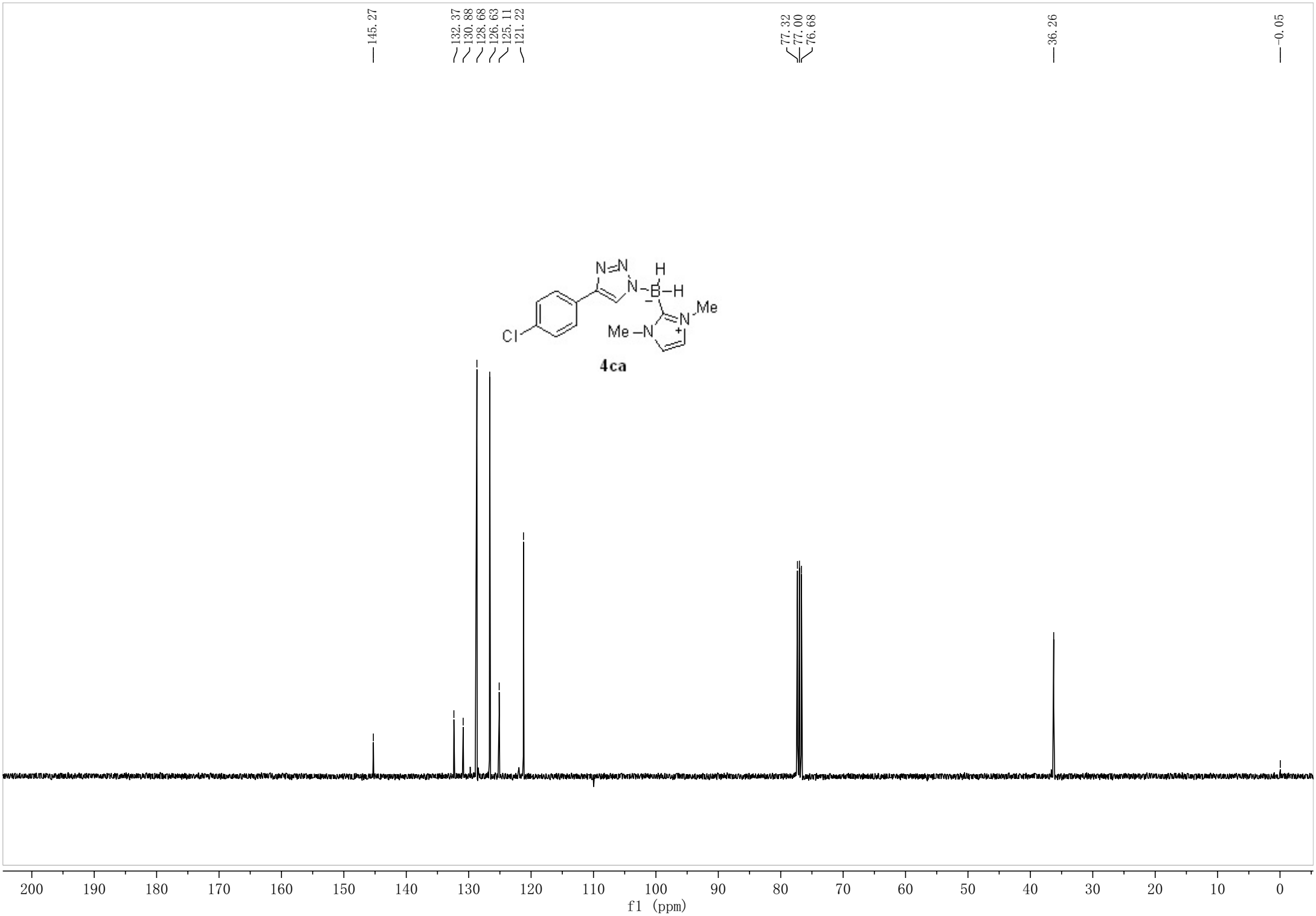

-19.10
-19.67
-20.25
N=N
H
N
B
H
Me
N
Me
N
+
4aa
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

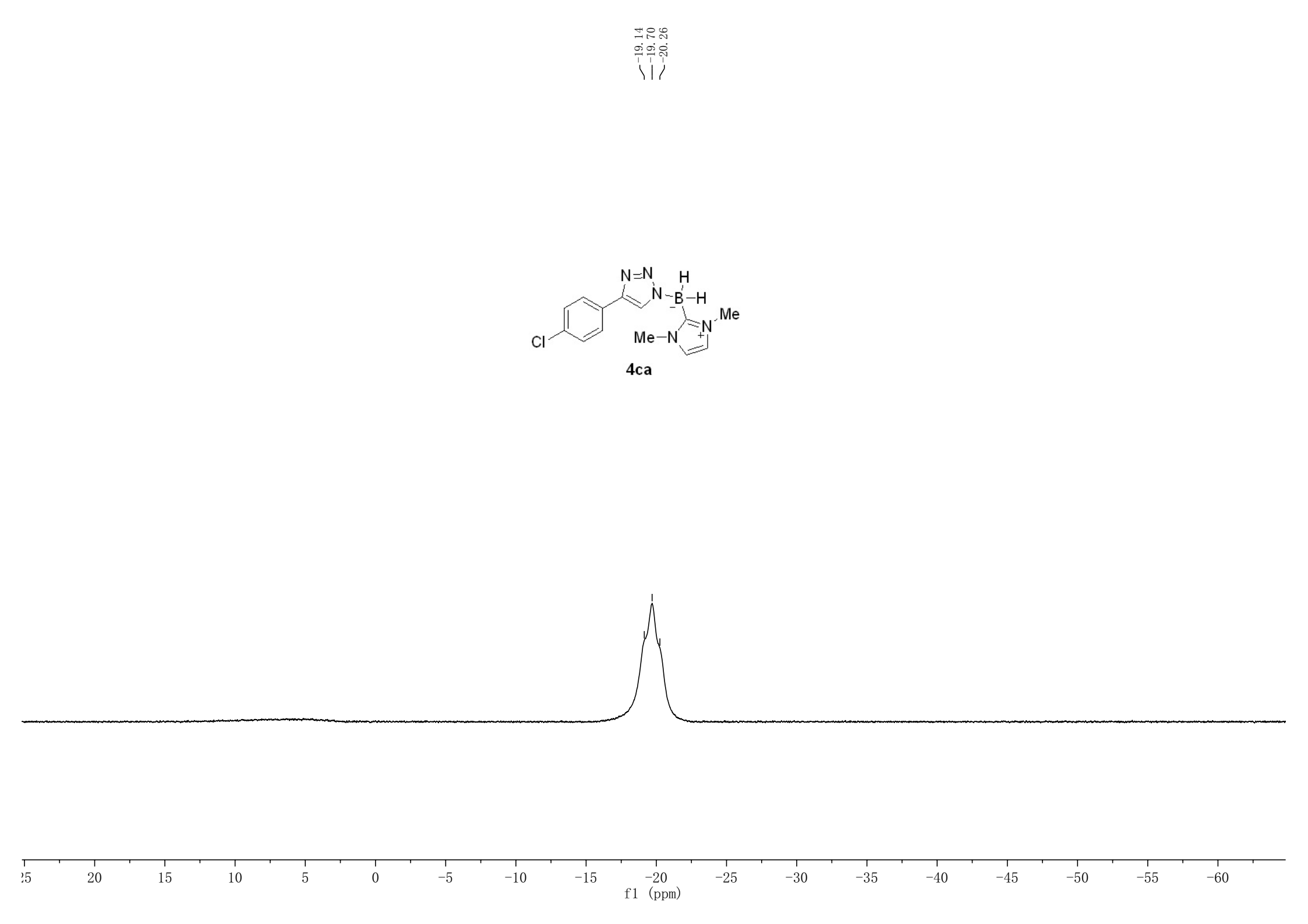

7.789
7.775
7.769
7.755
7.728
7.260
7.060
7.039
7.017
6.880
3.761
-0.018
N=N
H
N
B–H
Me
N
Me–N
F
4ba
2.04
0.94
2.00
1.91
6.03
f1 (ppm)

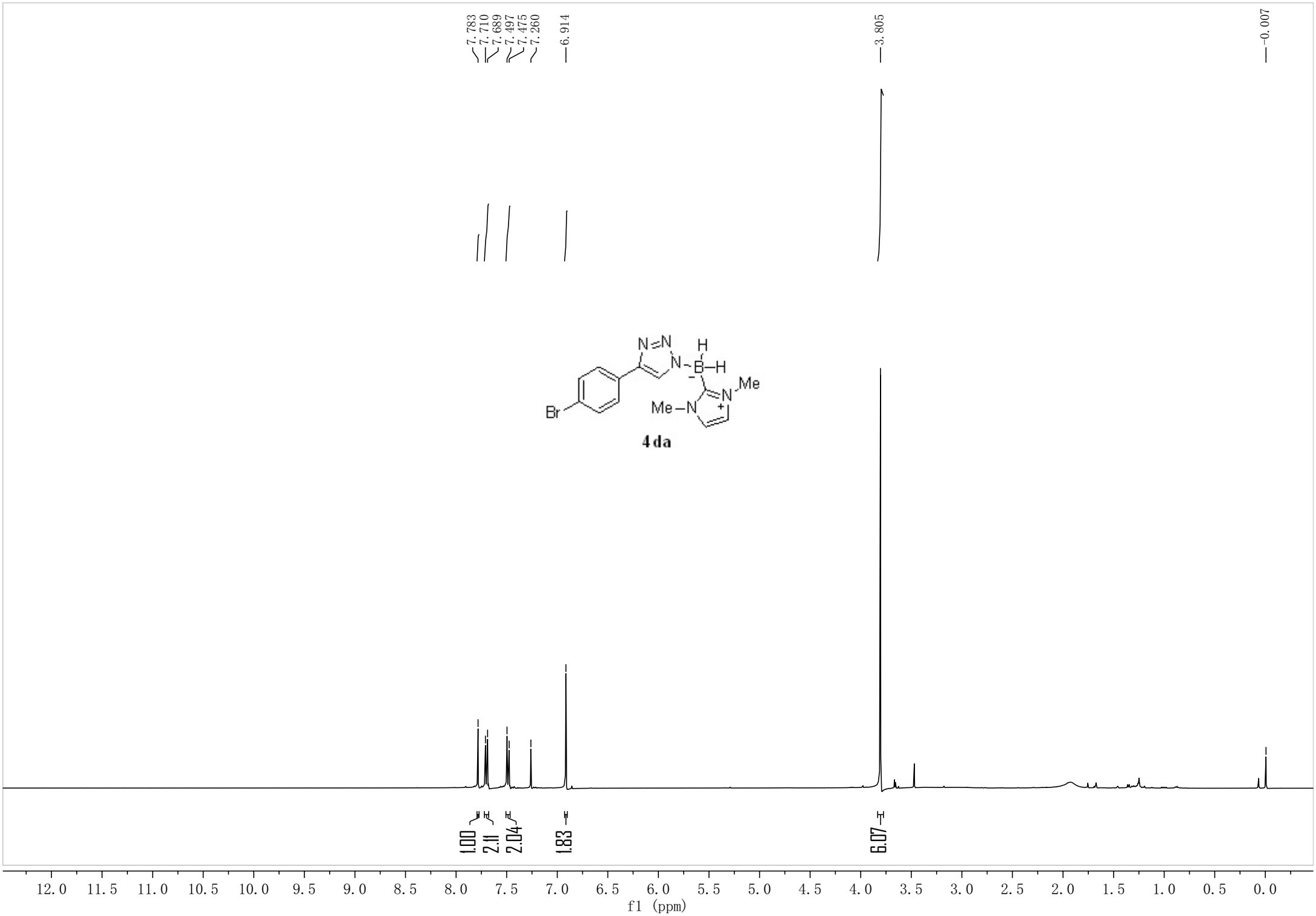

163.062
160.625
145.383
128.513
128.482
126.939
126.861
124.781
121.184
115.442
115.229
77.318
77.000
76.681
36.161
F
Me
Me
4ba
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-19.14
-19.71
-20.25
N=N
H
N
B
H
Me
N
Me
N
+
F
4ba
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-6
f1 (ppm)

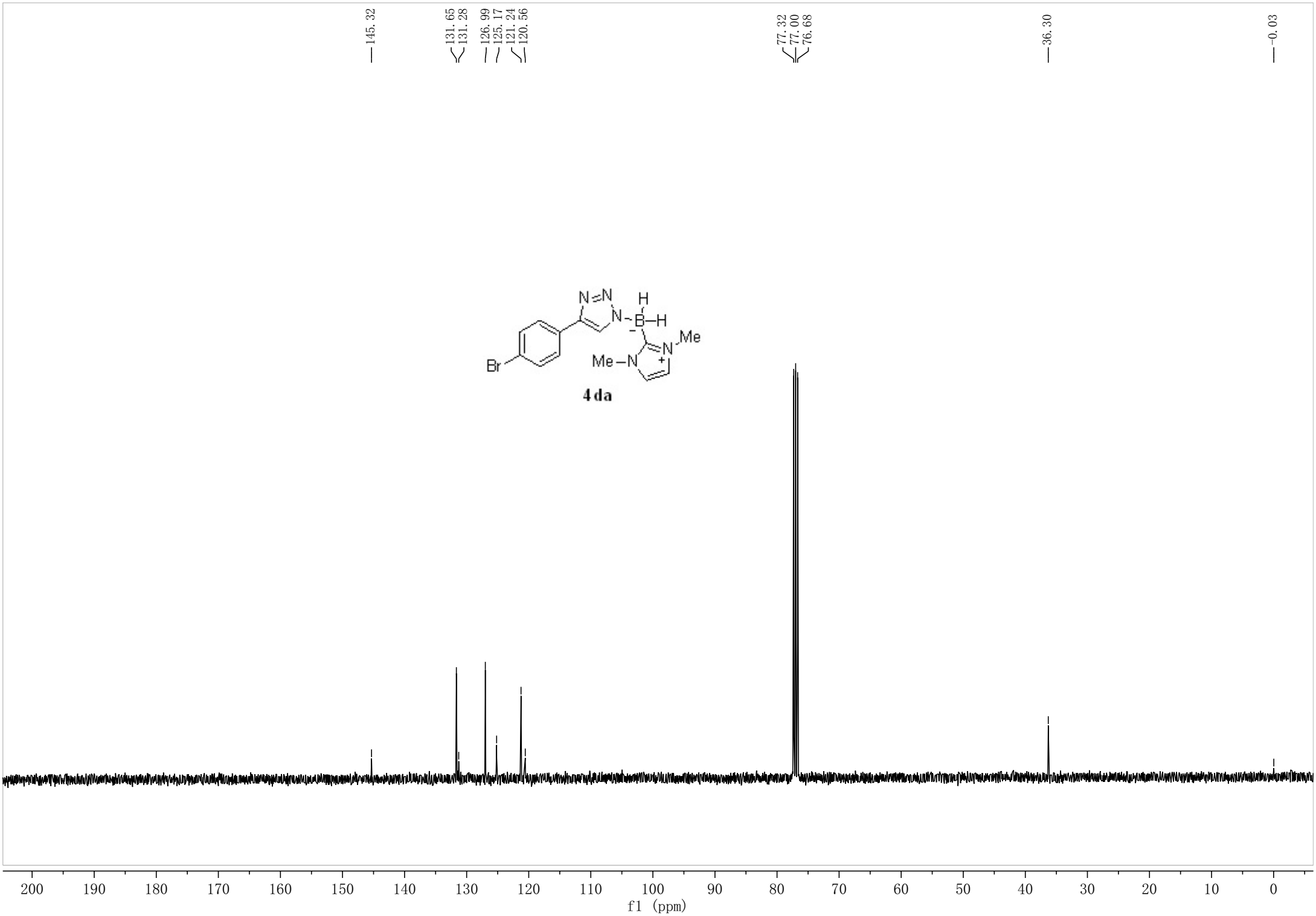

7.765
7.743
7.334
7.313
7.260
6.893
3.782
-0.011
N=N
H
N
B
H
Me
N
Me
N
Cl
4ca
2.97
2.00
2.02
6.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

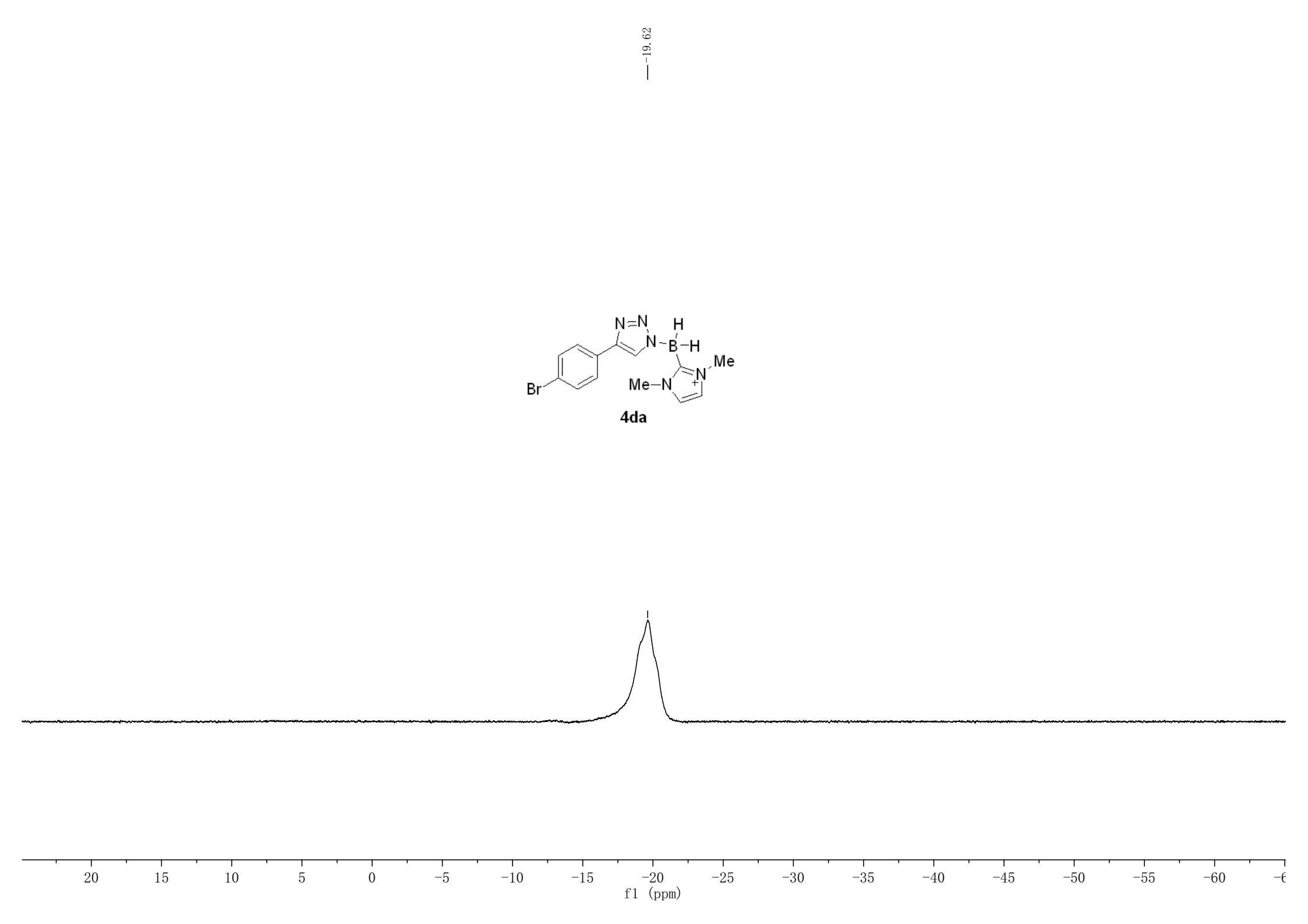

145.27
132.37
130.88
128.68
126.63
125.11
121.22
77.32
77.00
76.68
36.26
-0.05
N=N
H
N
B
H
Me
N
Me
N
Cl
+
4ca
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

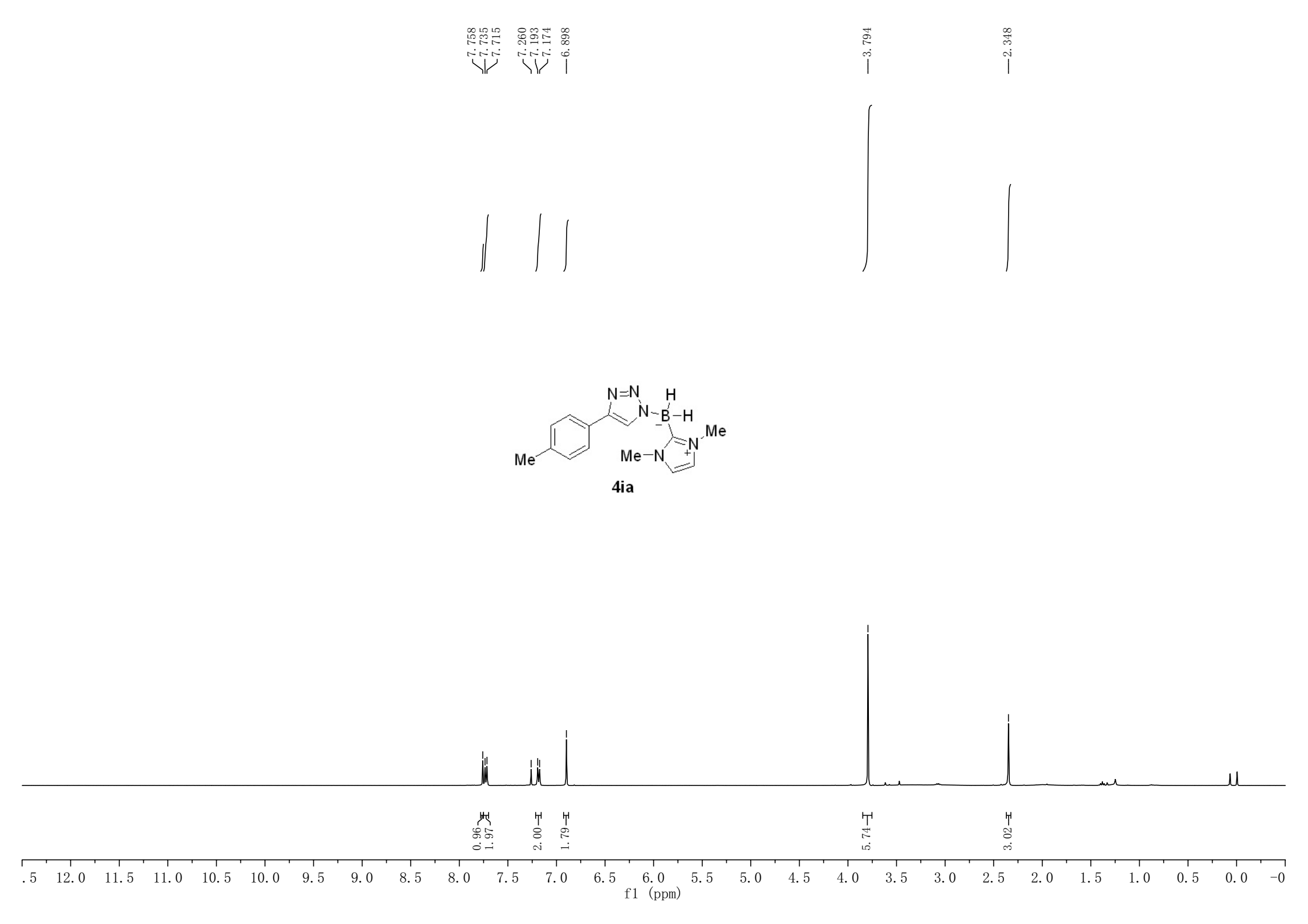

-19.14
-19.70
-20.26
N=N
N
H
B
H
Me
N
Me
N
Cl
+
4ca
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

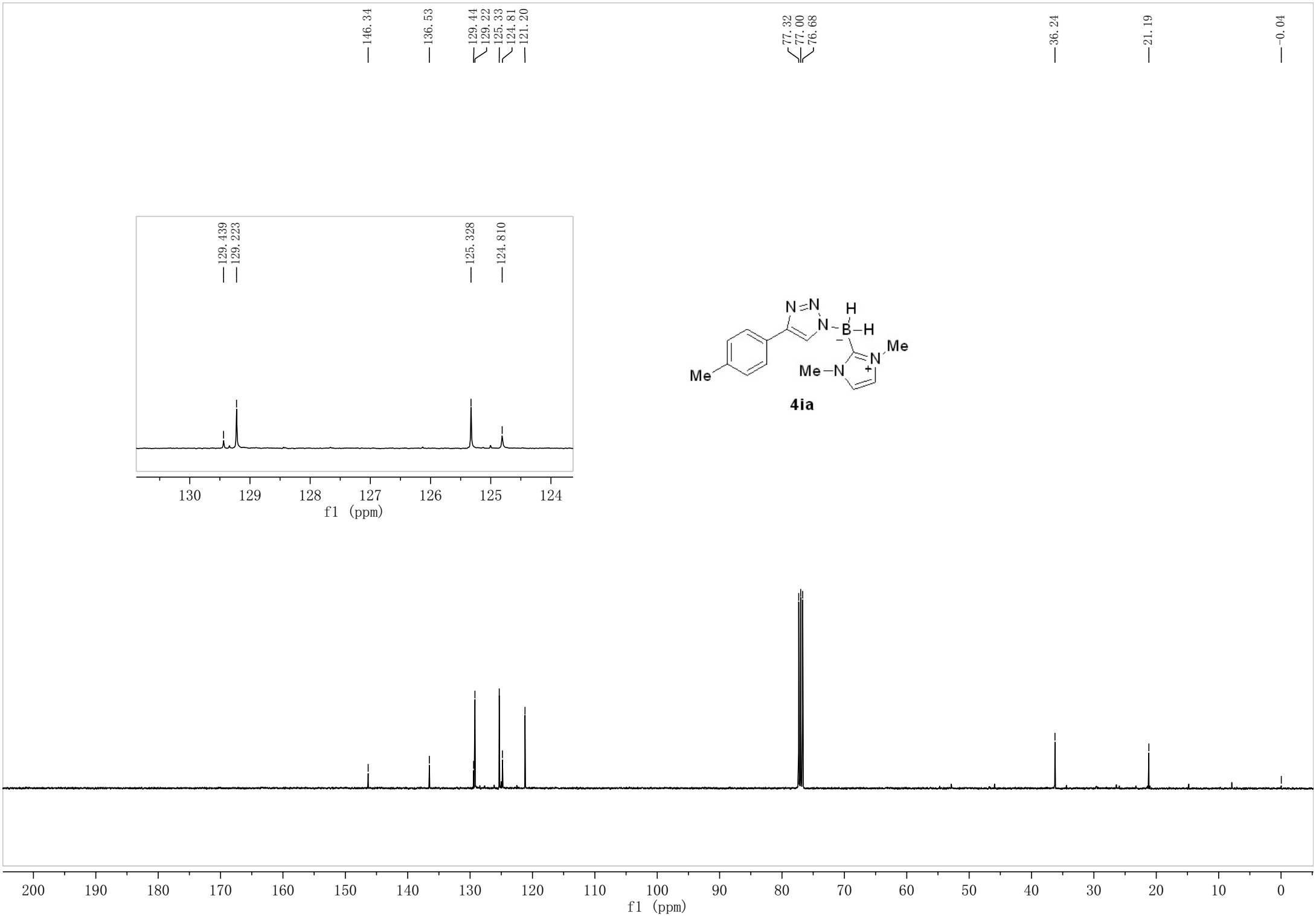

7.783
7.710
7.689
7.497
7.475
7.260
6.914
3.805
-0.007
Br
Me
Me
1.00
2.11
2.04
1.83
6.07
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

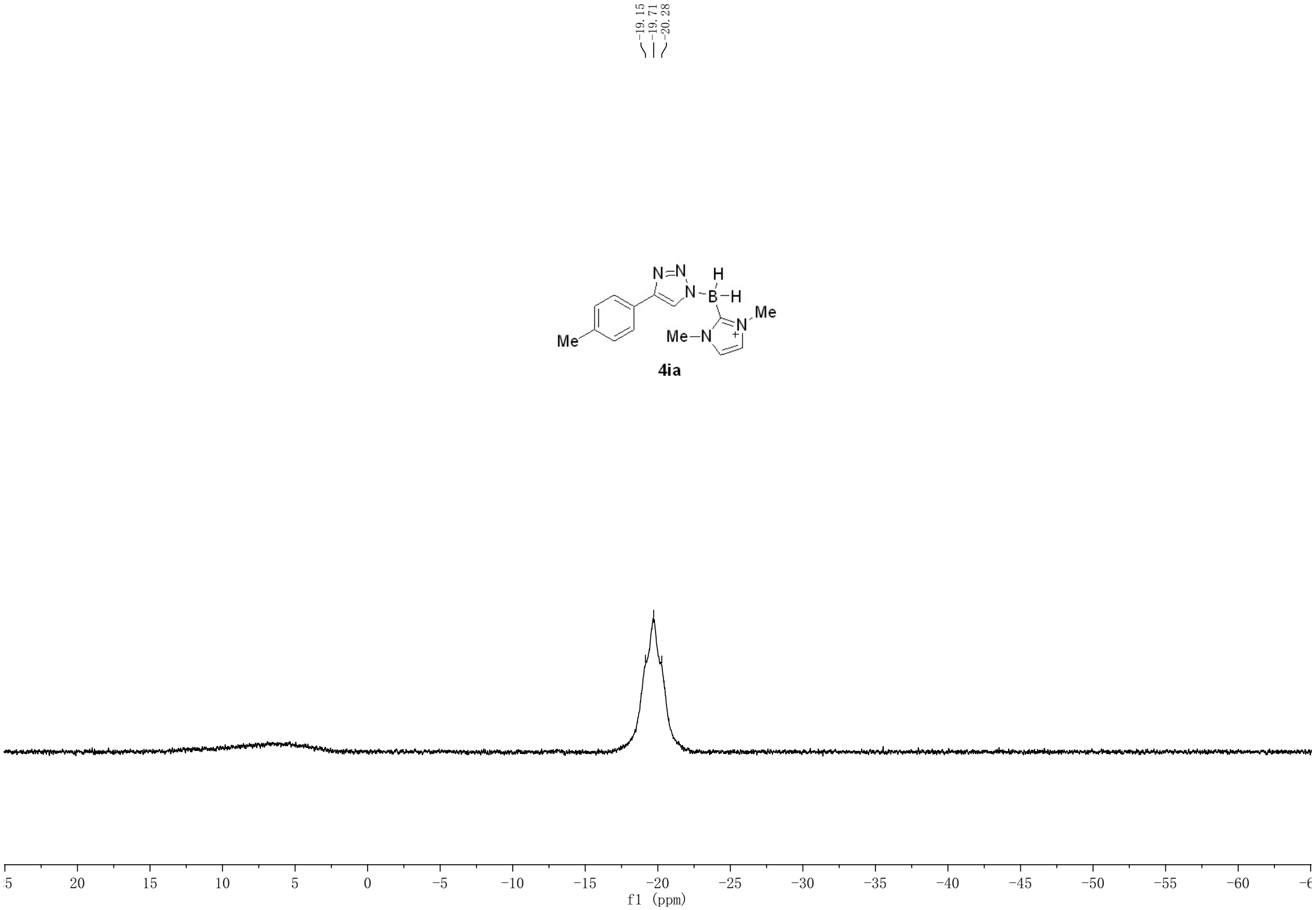
4da

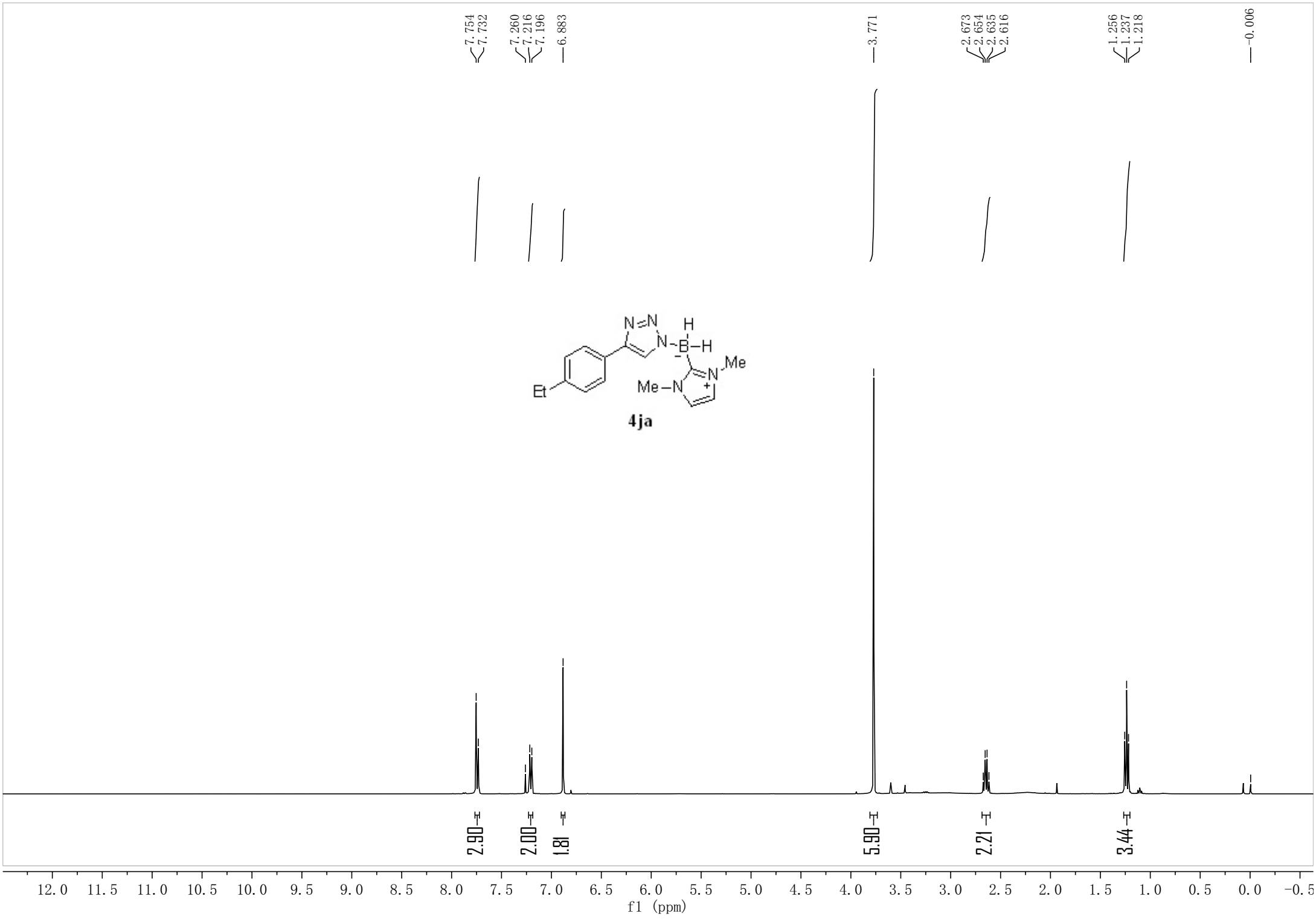

145.32
131.65
131.28
126.99
125.17
121.24
120.56
77.32
77.00
76.68
36.30
-0.03
Br
Me
Me
4da
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

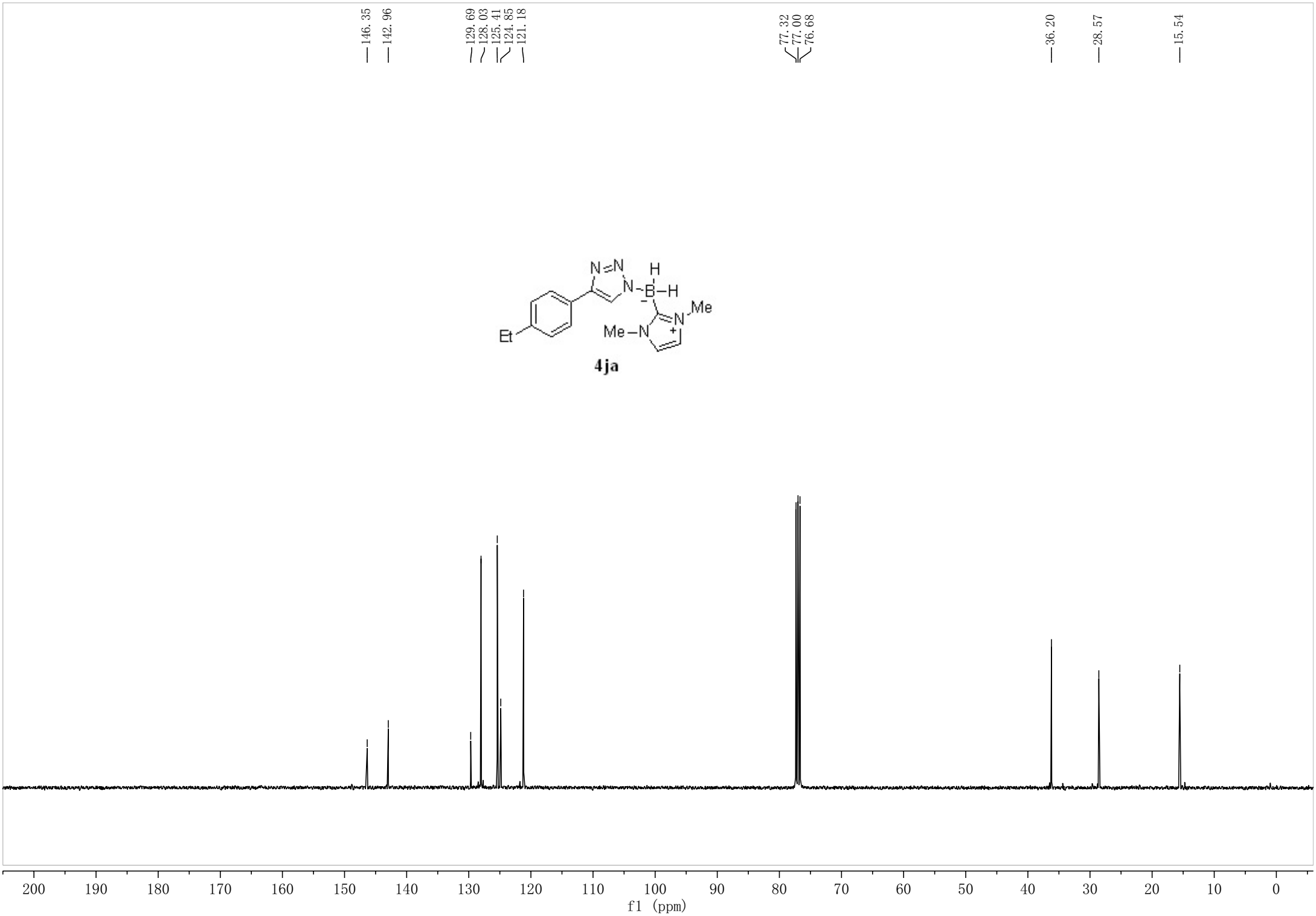

-19.62
N=N
H
N
B
H
Me
N
Me
N
Br
4da
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)


7.758
7.735
7.715
7.260
7.193
7.174
6.898
3.794
2.348
N=N
H
N
B
H
Me
N
Me
Me
N
+
4ia
0.96
1.97
2.00
1.79
5.74
3.02
f1 (ppm)

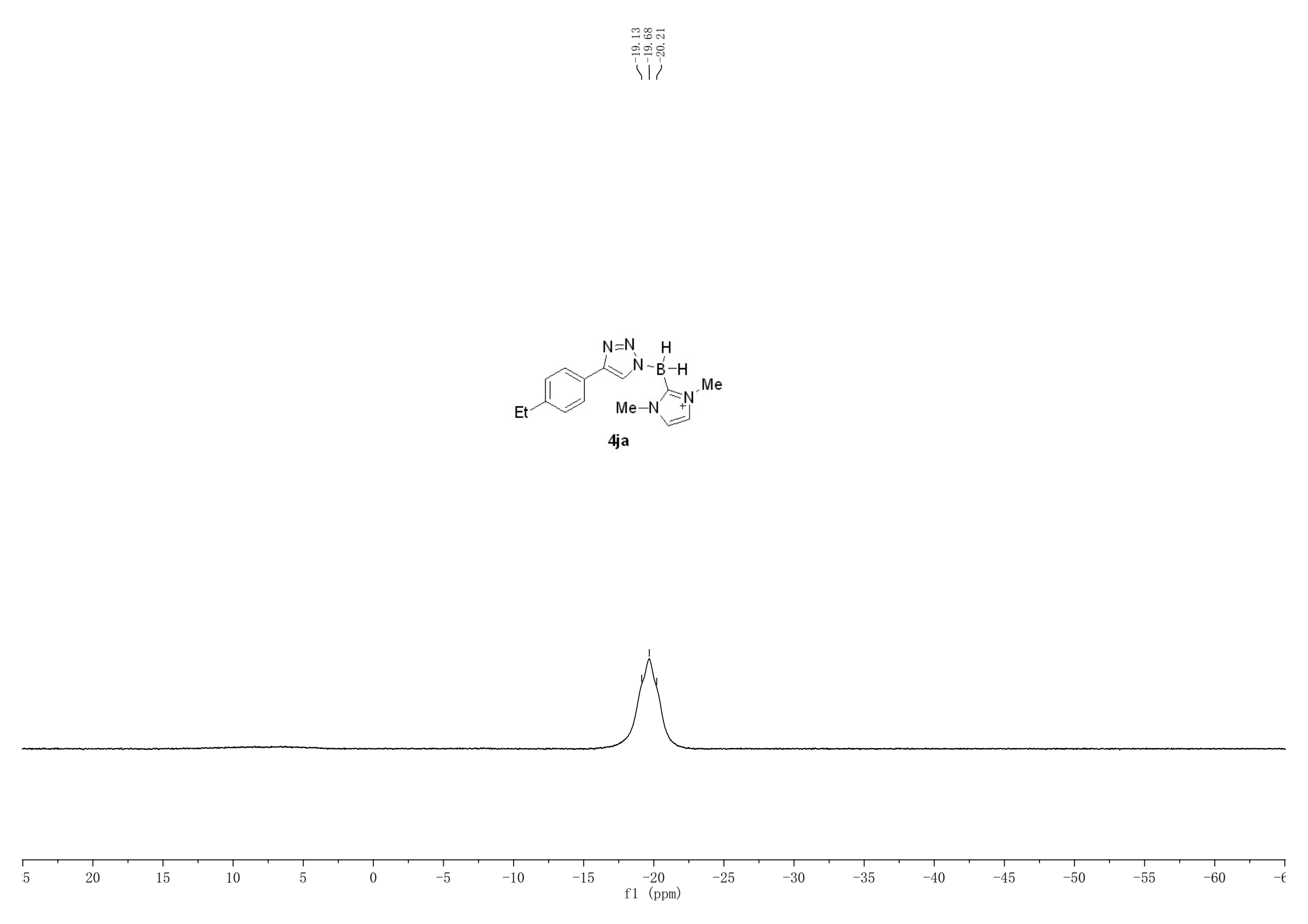

146.34
136.53
129.44
129.22
125.33
124.81
121.20
77.32
77.00
76.68
36.24
21.19
-0.04
129.439
129.223
125.328
124.810
130
129
128
127
126
125
124
f1 (ppm)
Me
Me
Me
4ia
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

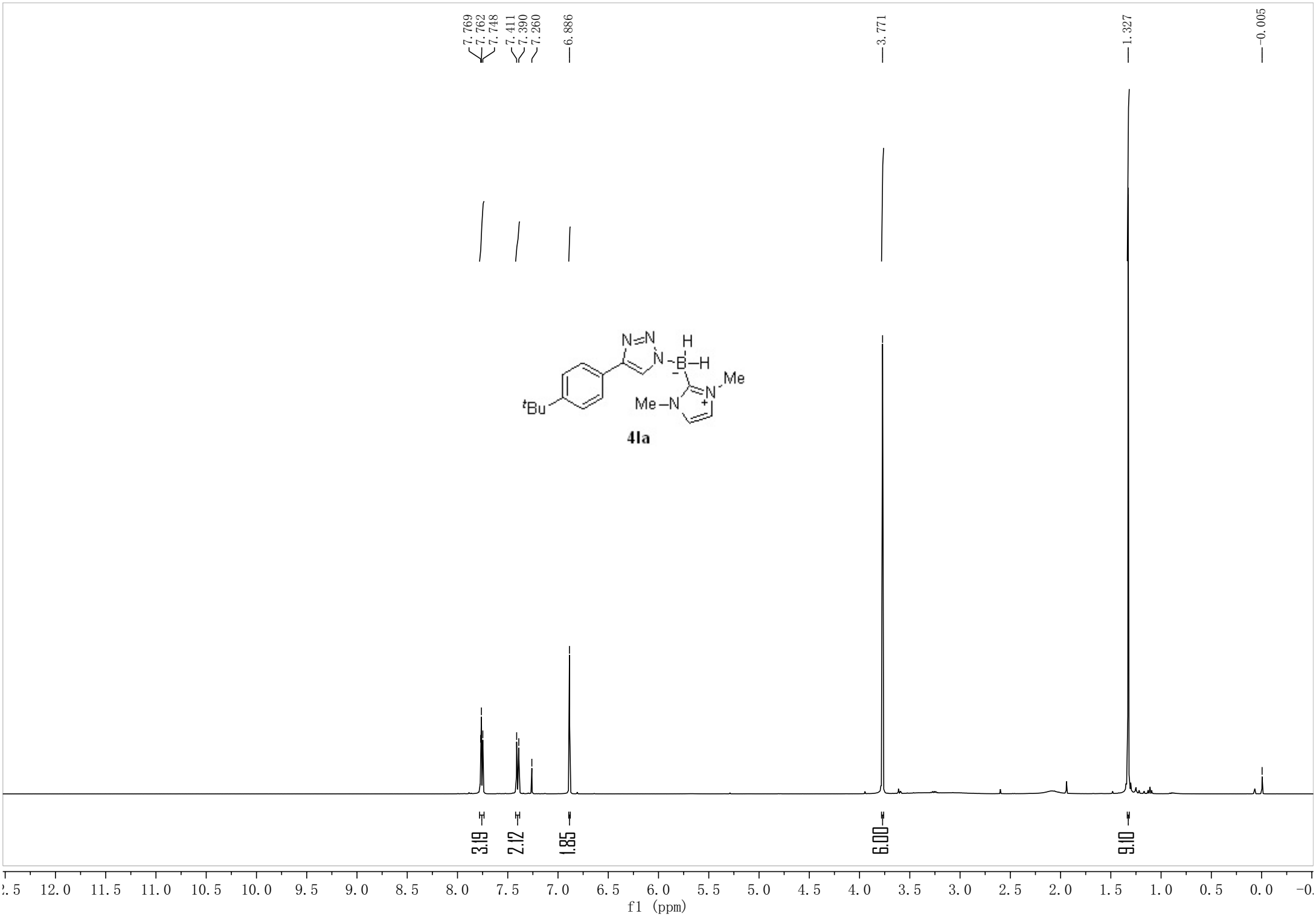

-19.15
-19.71
-20.28
N=N
H
N
B
H
Me
N
Me
Me
N
+
Me
4ia
5
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)


7.754
7.732
7.260
7.216
7.196
6.883
3.771
2.673
2.654
2.635
2.616
1.256
1.237
1.218
-0.006
N=N
H
N-B-H
Me
N
Me-N
Et
4ja
2.90
2.00
1.81
5.90
2.21
3.44
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

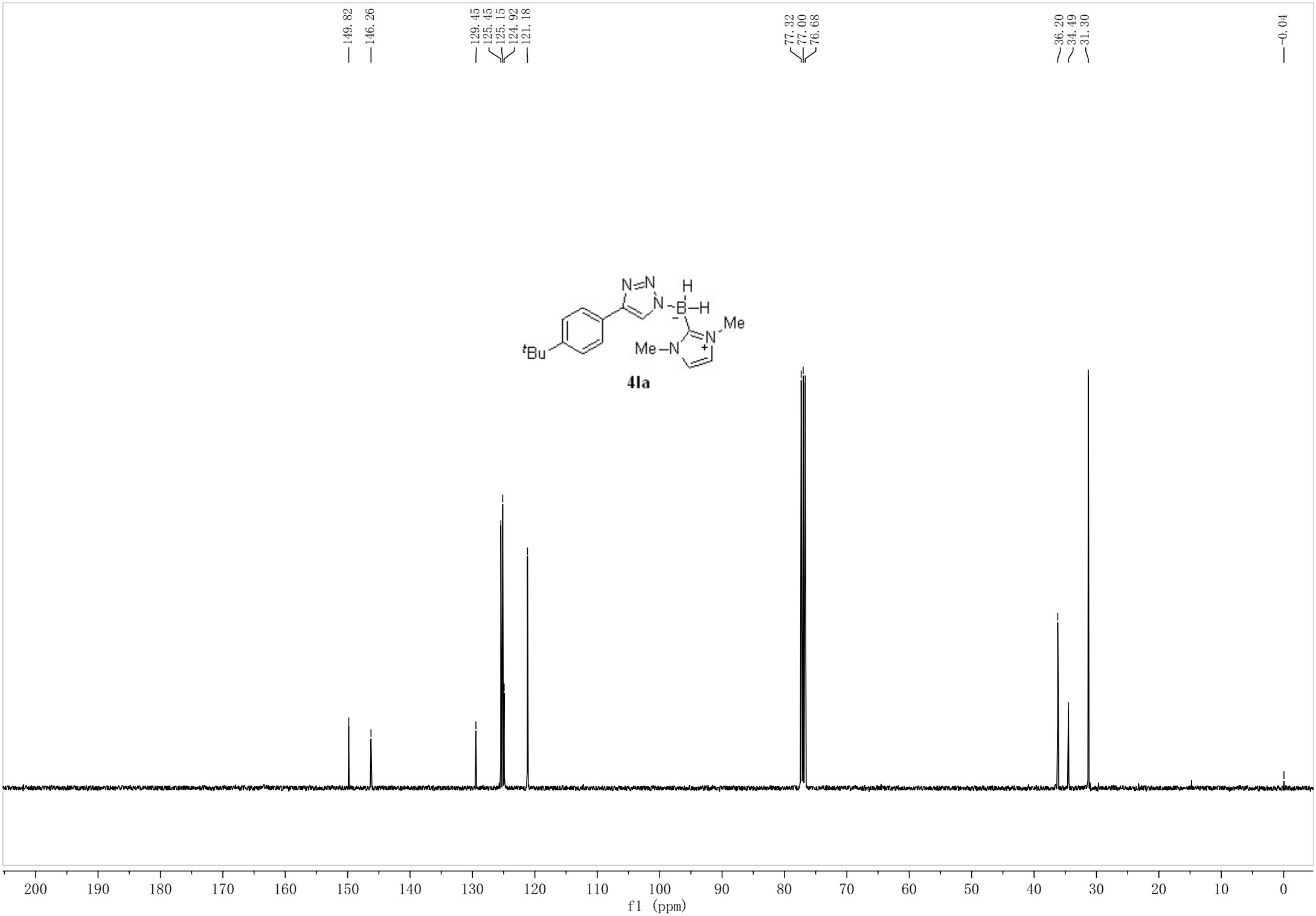

146.35
142.96
129.69
128.03
125.41
124.85
121.18
77.32
77.00
76.68
36.20
28.57
15.54
Et
Me
Me
f1 (ppm)

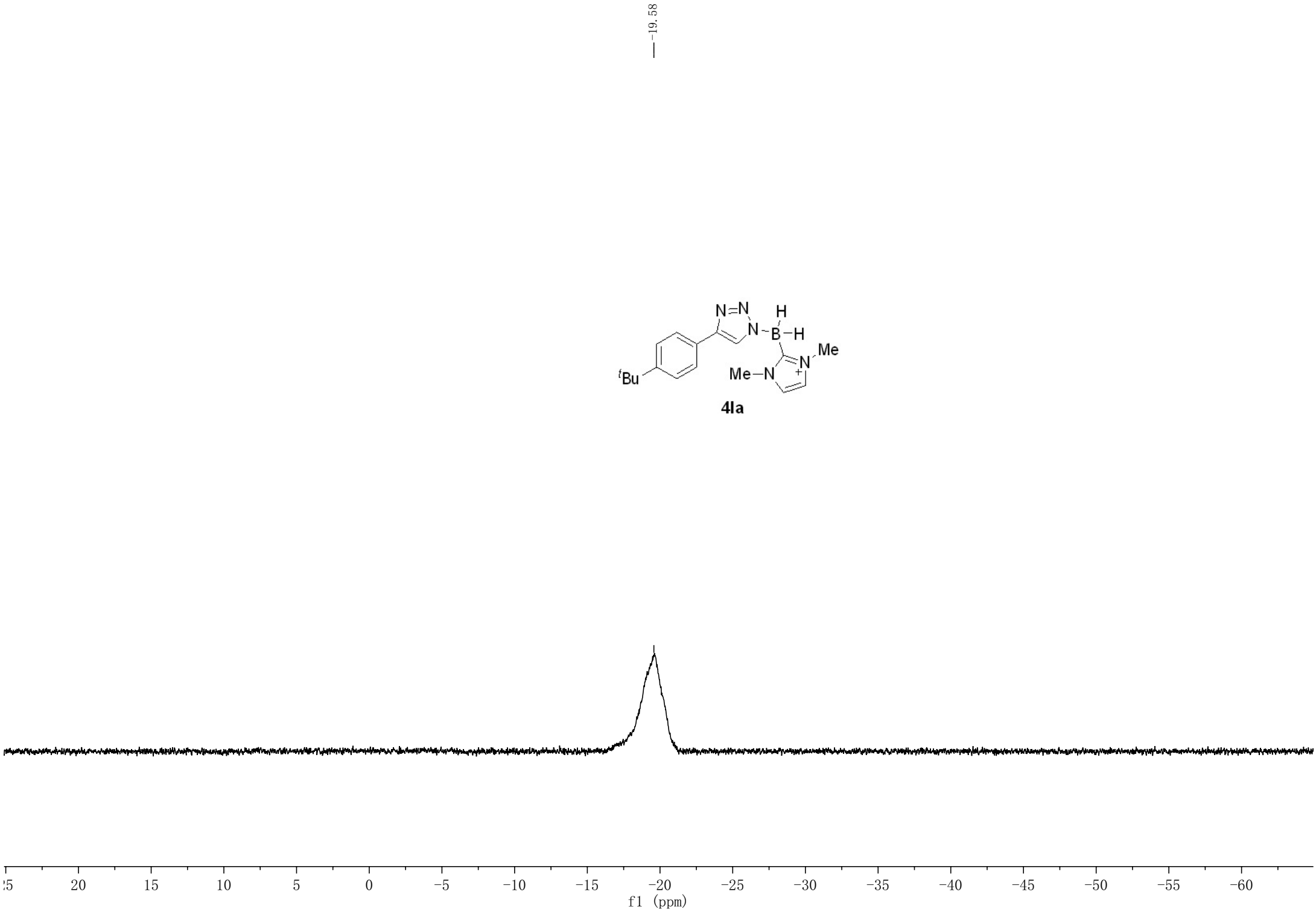
4ja

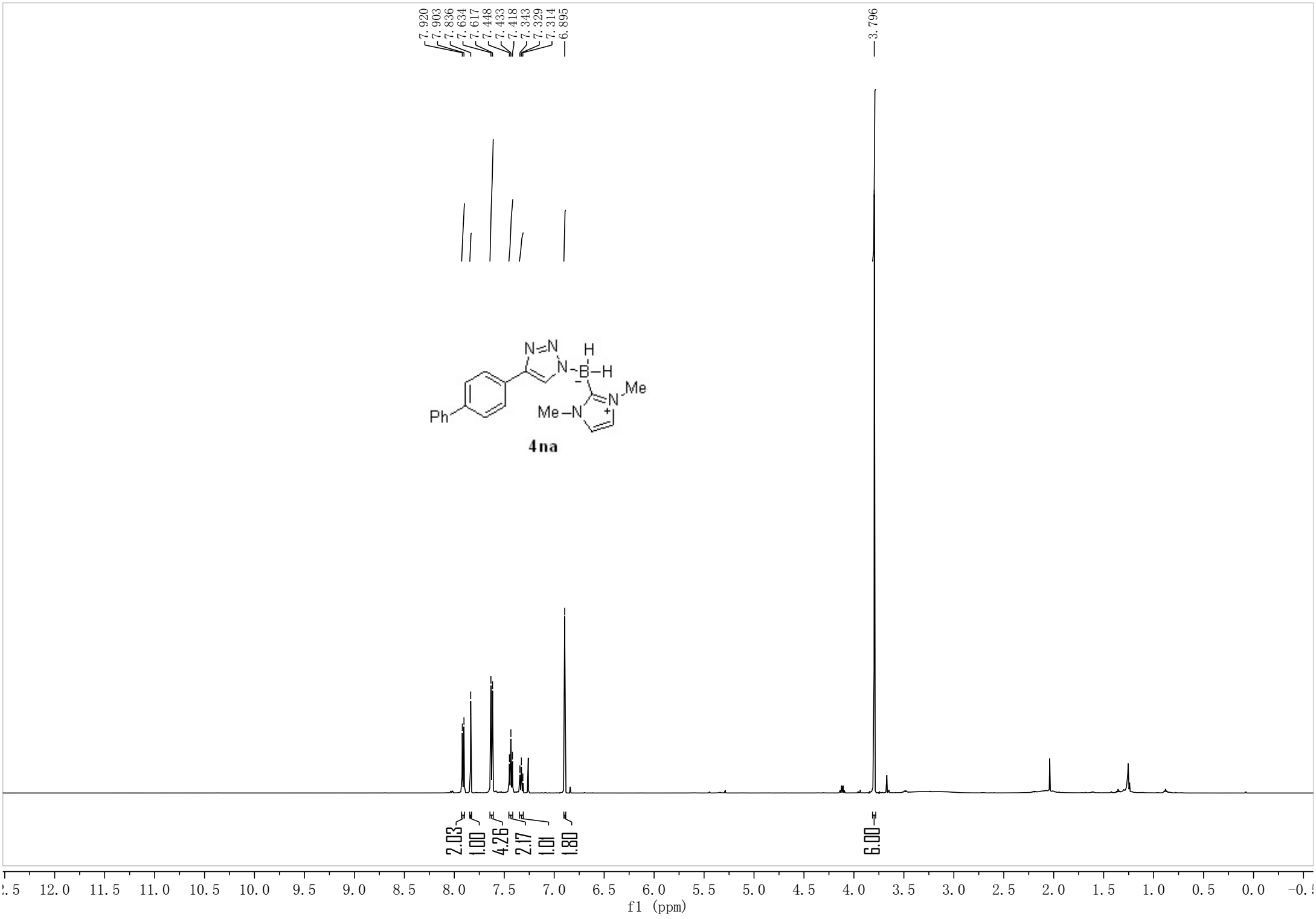

-19.13
-19.68
-20.21
N=N
H
N
B
H
Me
N
Me
N
Et
4ja
5
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

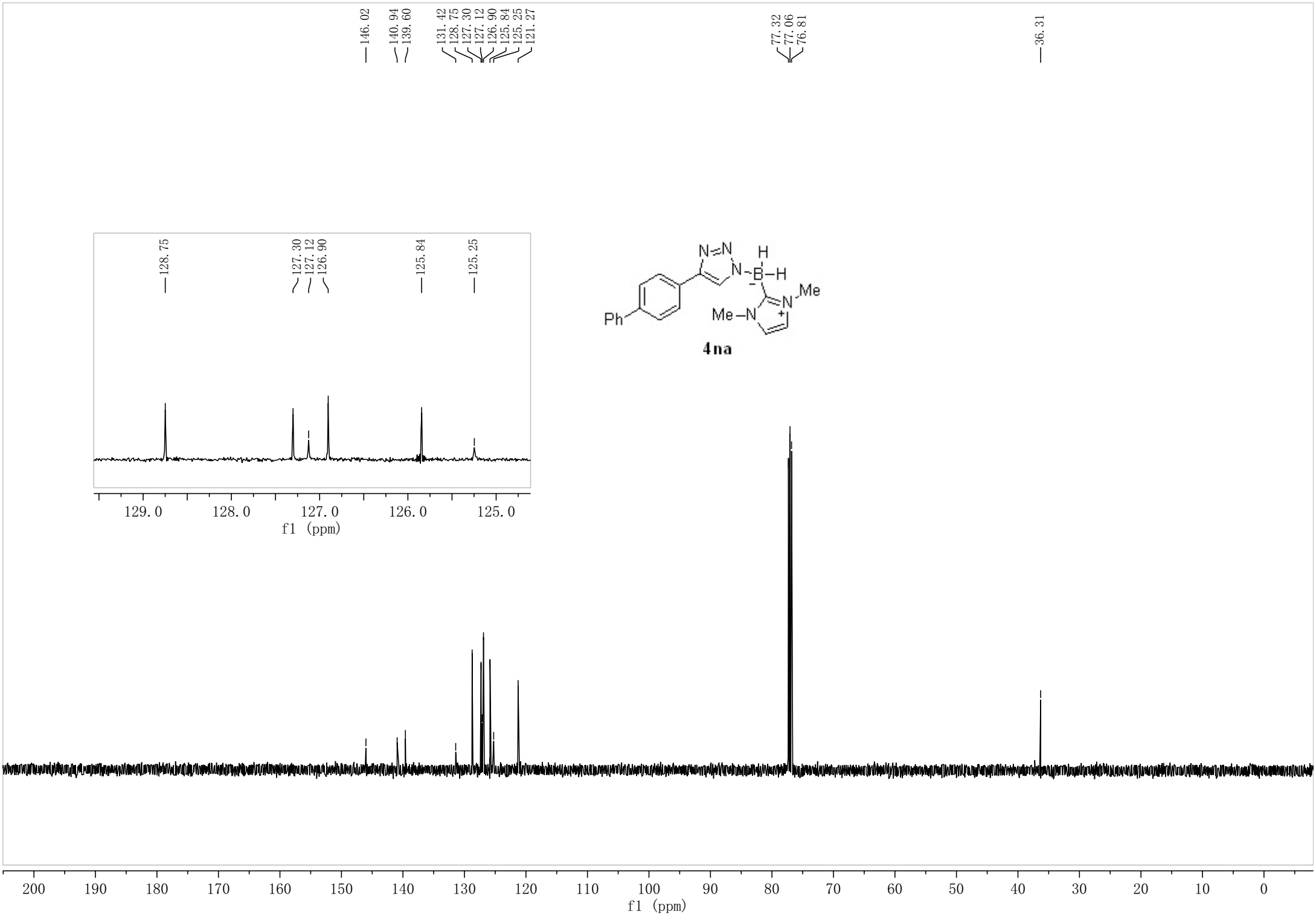

7.769
7.762
7.748
7.411
7.390
7.260
6.886
3.771
1.327
-0.005
3.19
2.12
1.85
6.00
9.10
f1 (ppm)

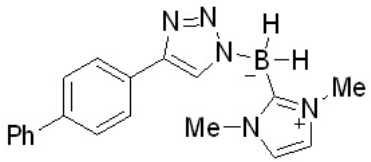
4la


149.82
146.26
129.45
125.45
125.15
124.92
121.18
77.32
77.00
76.68
36.20
34.49
31.30
-0.04
tBu
Me
Me
4la
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-19.58
N=N
H
N
B
H
Me
N
Me
N
+
tBu
4la
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

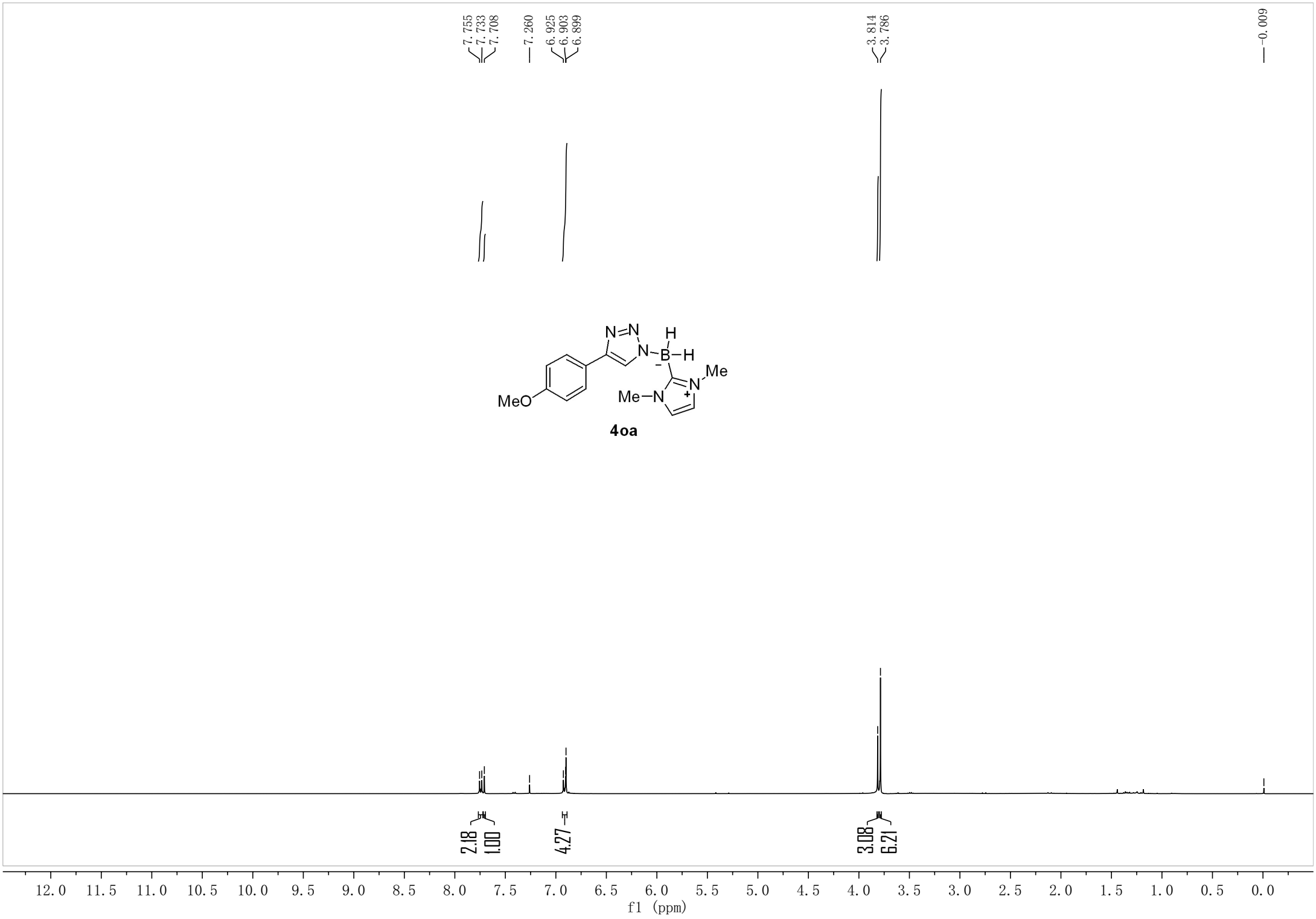

7.920
7.903
7.836
7.634
7.617
7.448
7.433
7.418
7.343
7.329
7.314
6.895
3.796
N=N
H
N
B–H
N
Me
Me–N
Ph
4na
2.03
1.00
4.26
2.17
1.01
1.80
6.00
f1 (ppm)


146.02
140.94
139.60
131.42
128.75
127.30
127.12
126.90
125.84
125.25
121.27
77.32
77.06
76.81
36.31
128.75
127.30
127.12
126.90
125.84
125.25
129.0
128.0
127.0
126.0
125.0
f1 (ppm)
Ph
N=N
N
B
H
Me
Me–N
4na
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N=N
H
N
B
H
Me
N
Me
N
Ph

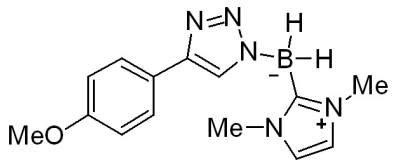
4na

-19.63
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

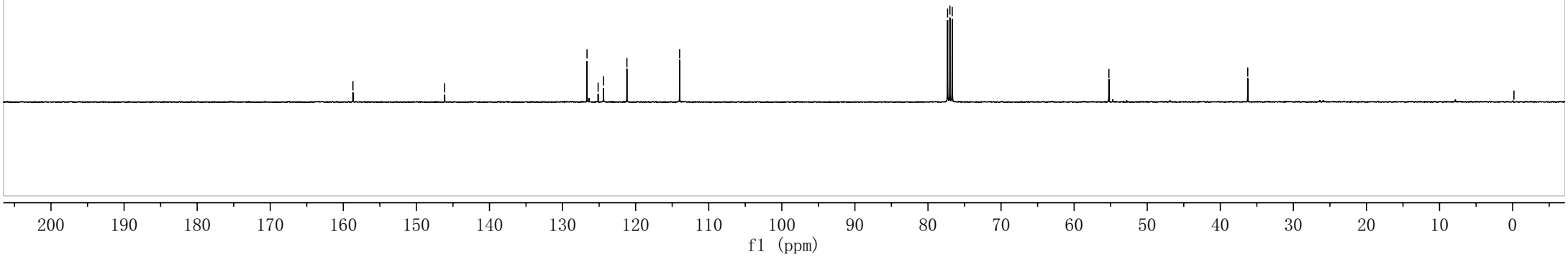

7.755
7.733
7.708
7.260
6.925
6.903
6.899
3.814
3.786
-0.009
MeO
Me
Me
2.18
1.00
4.27
3.08
6.21
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

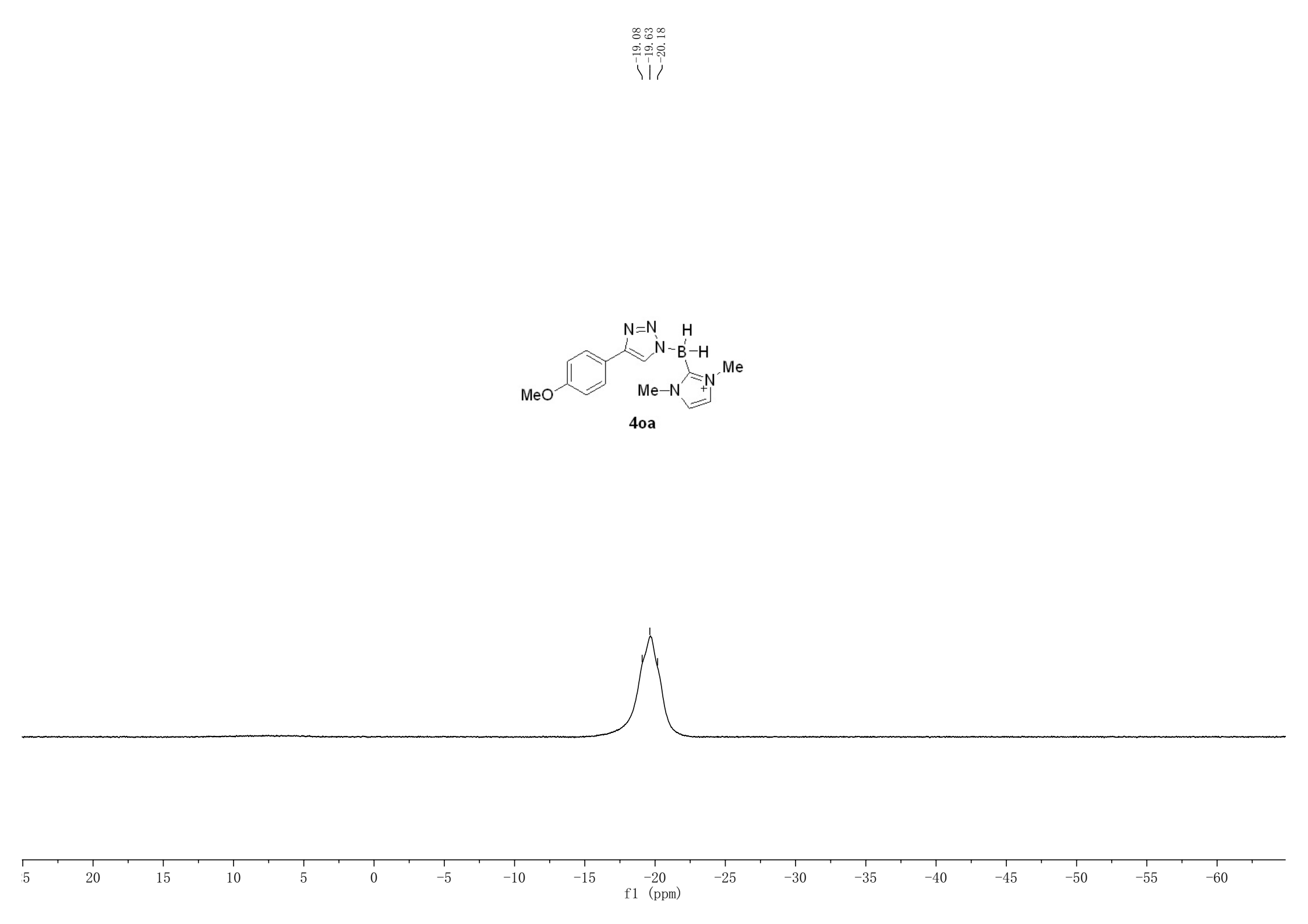
4oa

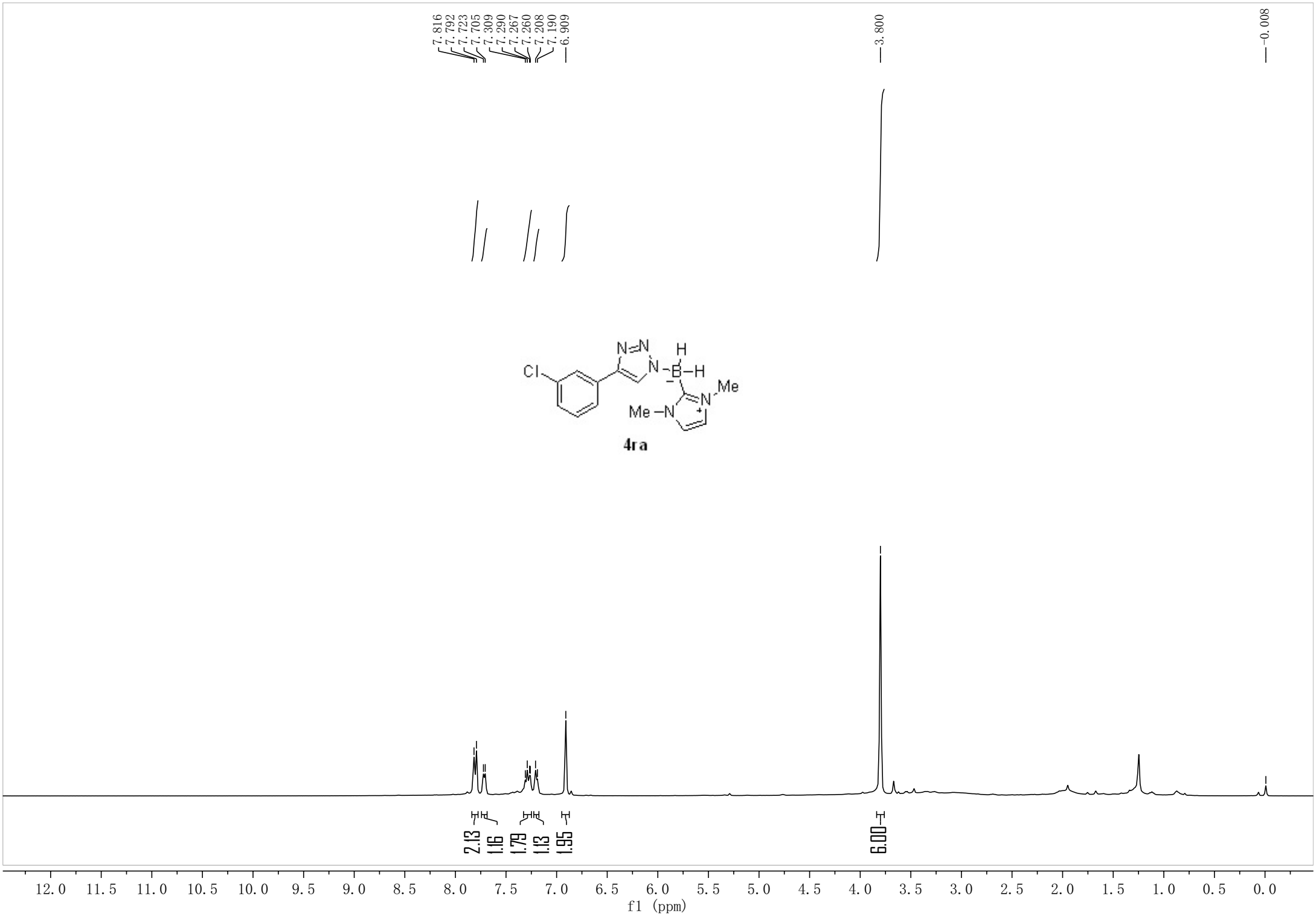
158.68
146.13
126.65
125.13
124.40
121.19
113.98
77.32
77.00
76.68
55.24
36.24
-0.18

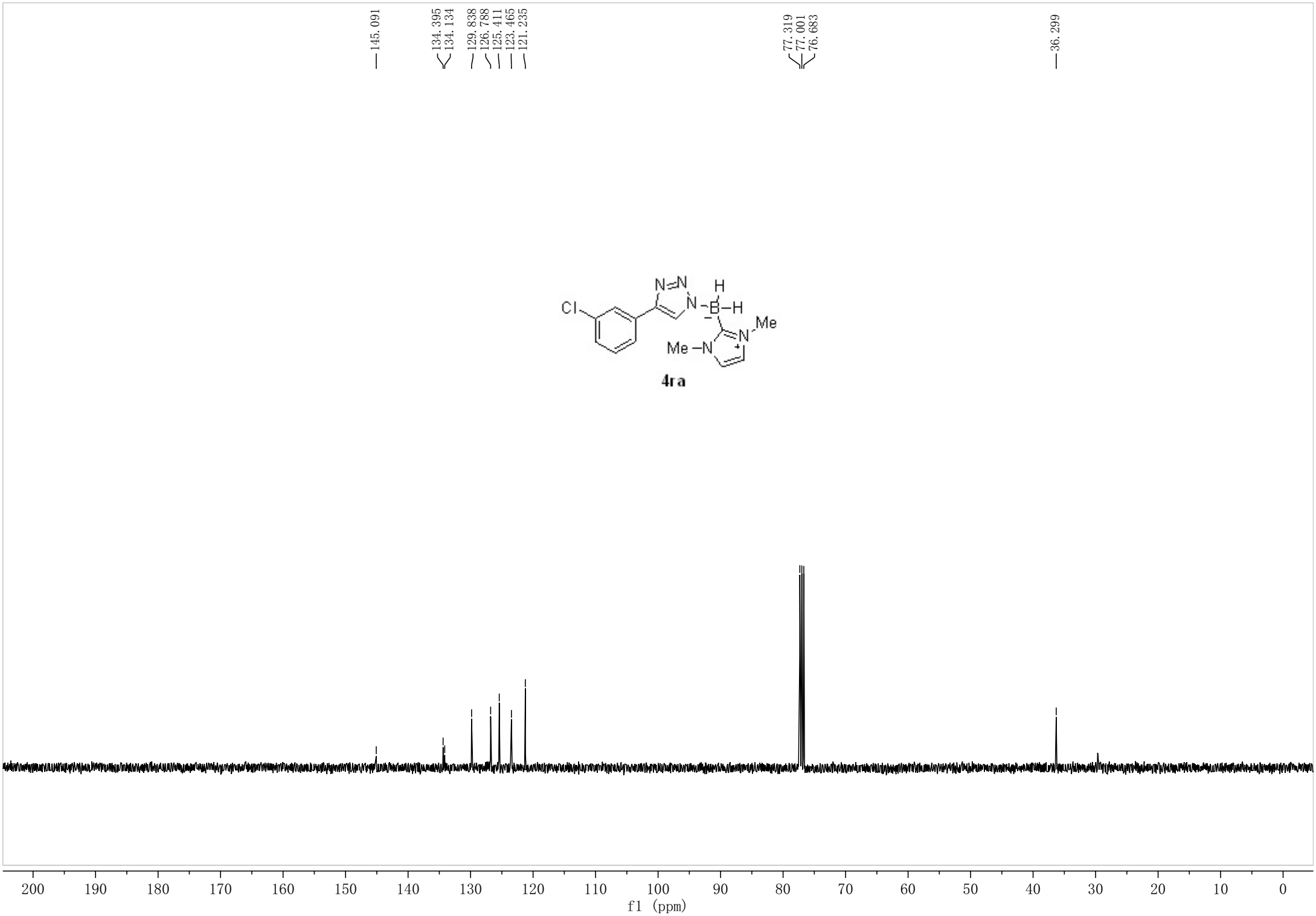


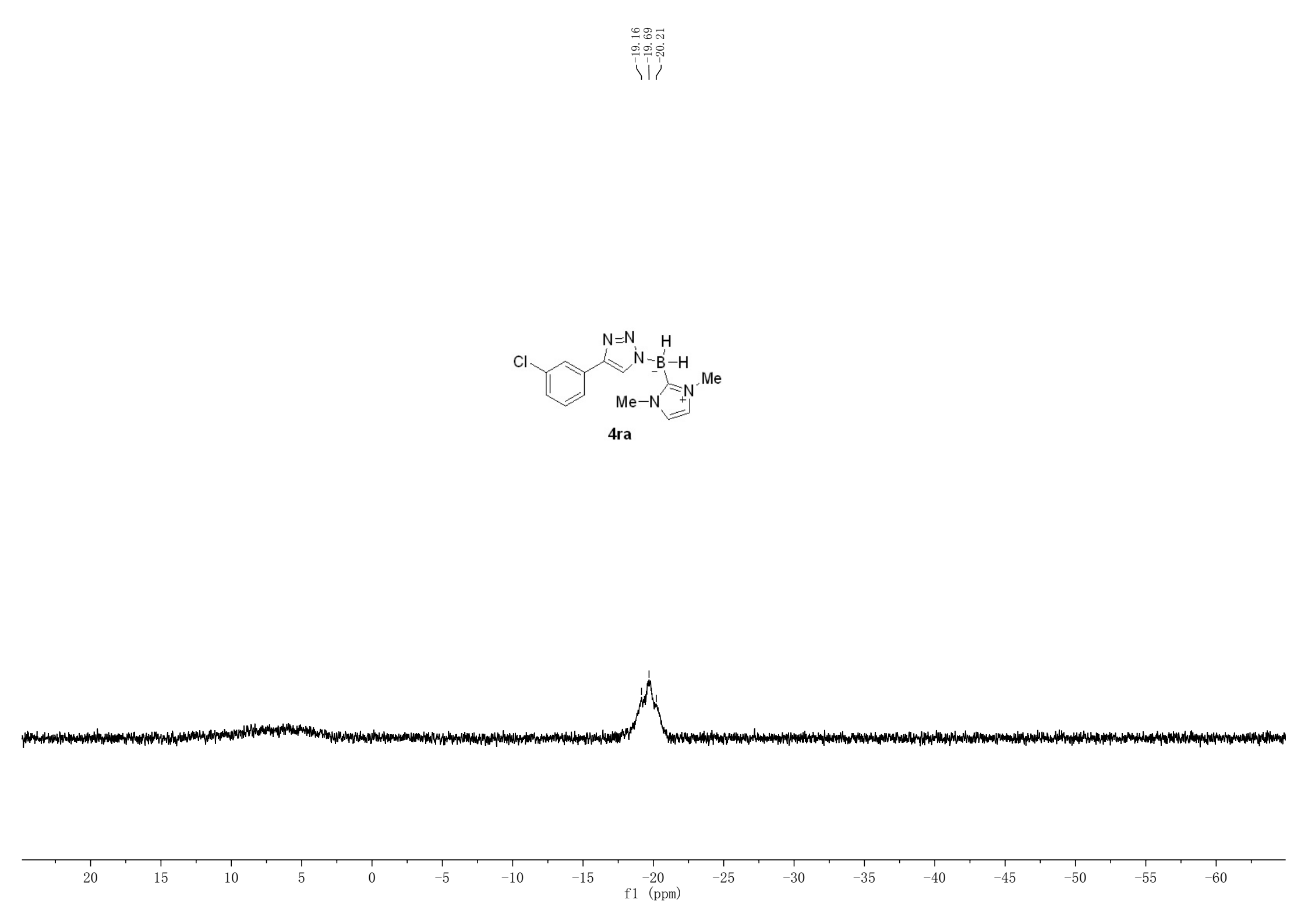
4oa

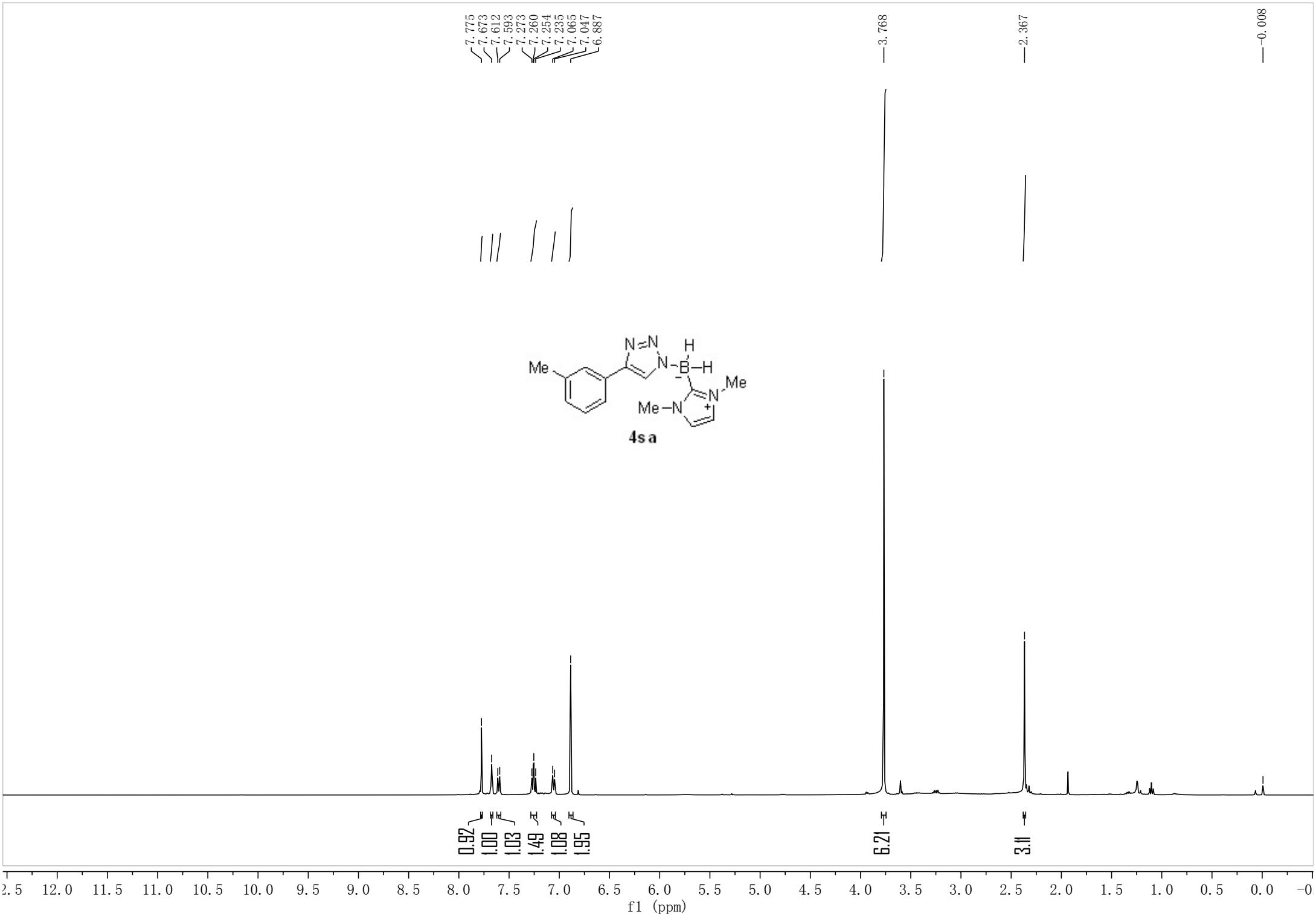


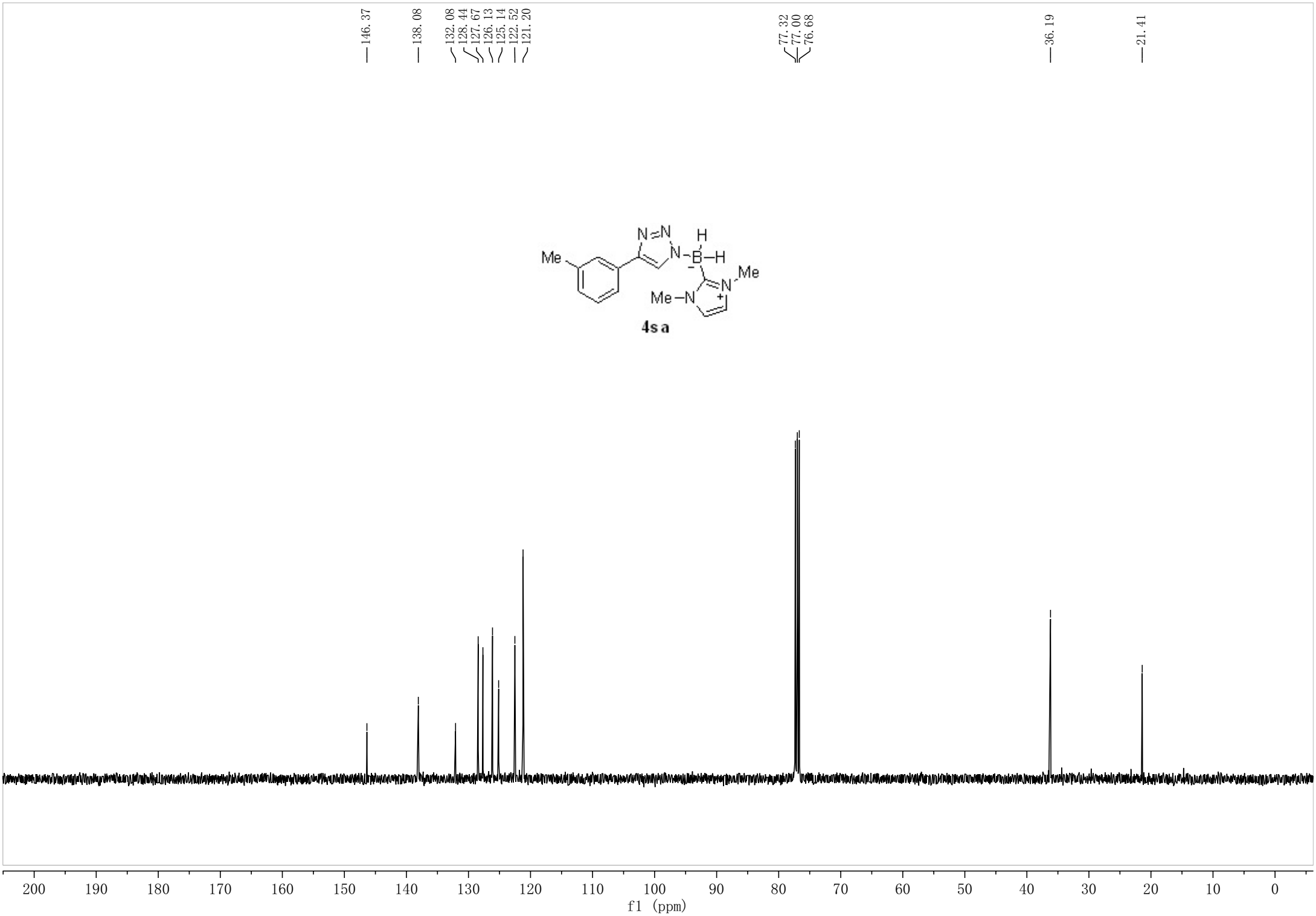

-19.08
-19.63
-20.18
N=N
H
N
B–H
Me
N
Me–N
+
MeO
4oa
5
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

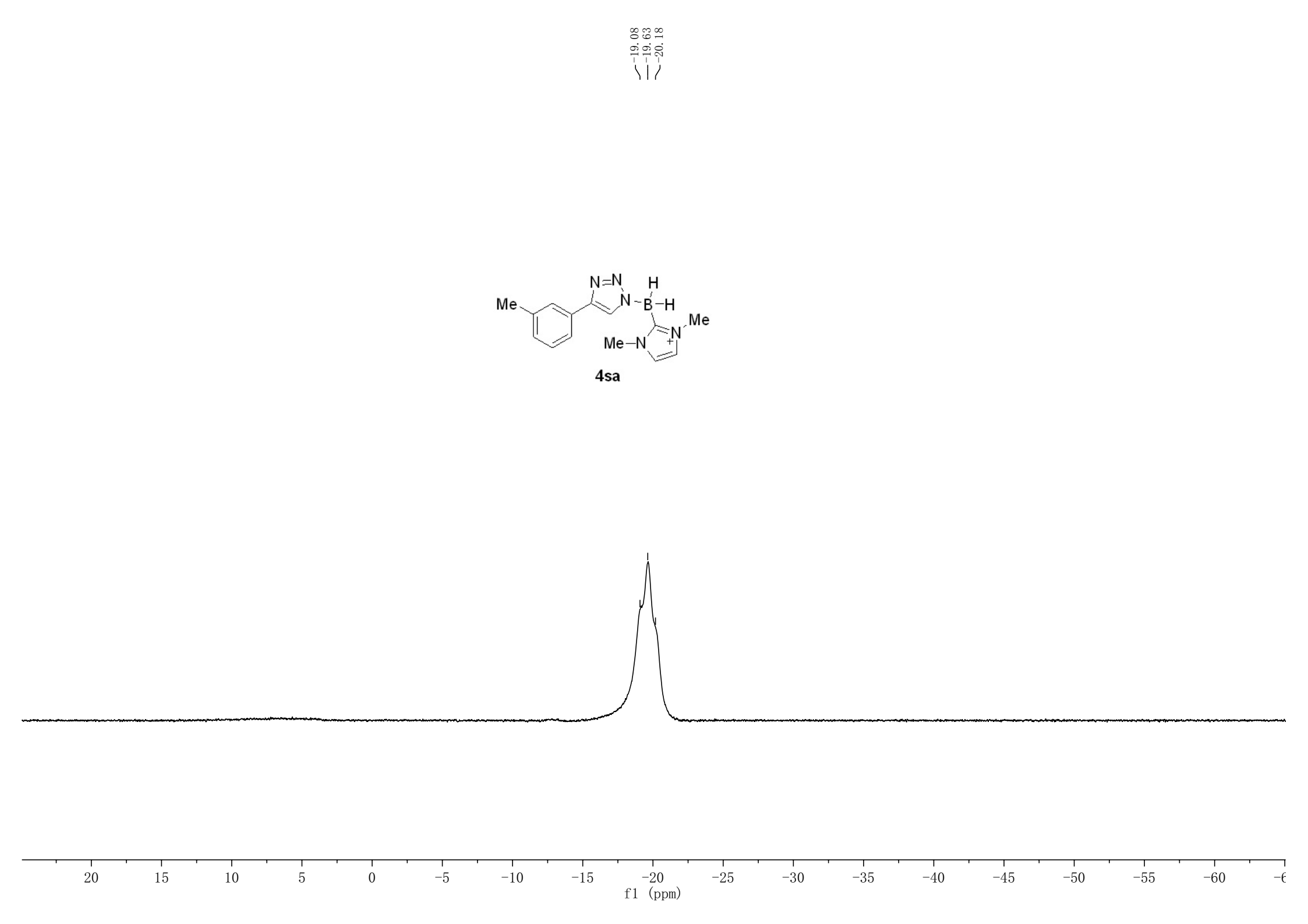

7.816
7.792
7.723
7.705
7.309
7.290
7.267
7.260
7.208
7.190
6.909
3.800
-0.008
Cl
N
N
H
B
H
Me
N
Me
N
4ra
2.13
1.16
1.79
1.13
1.95
6.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

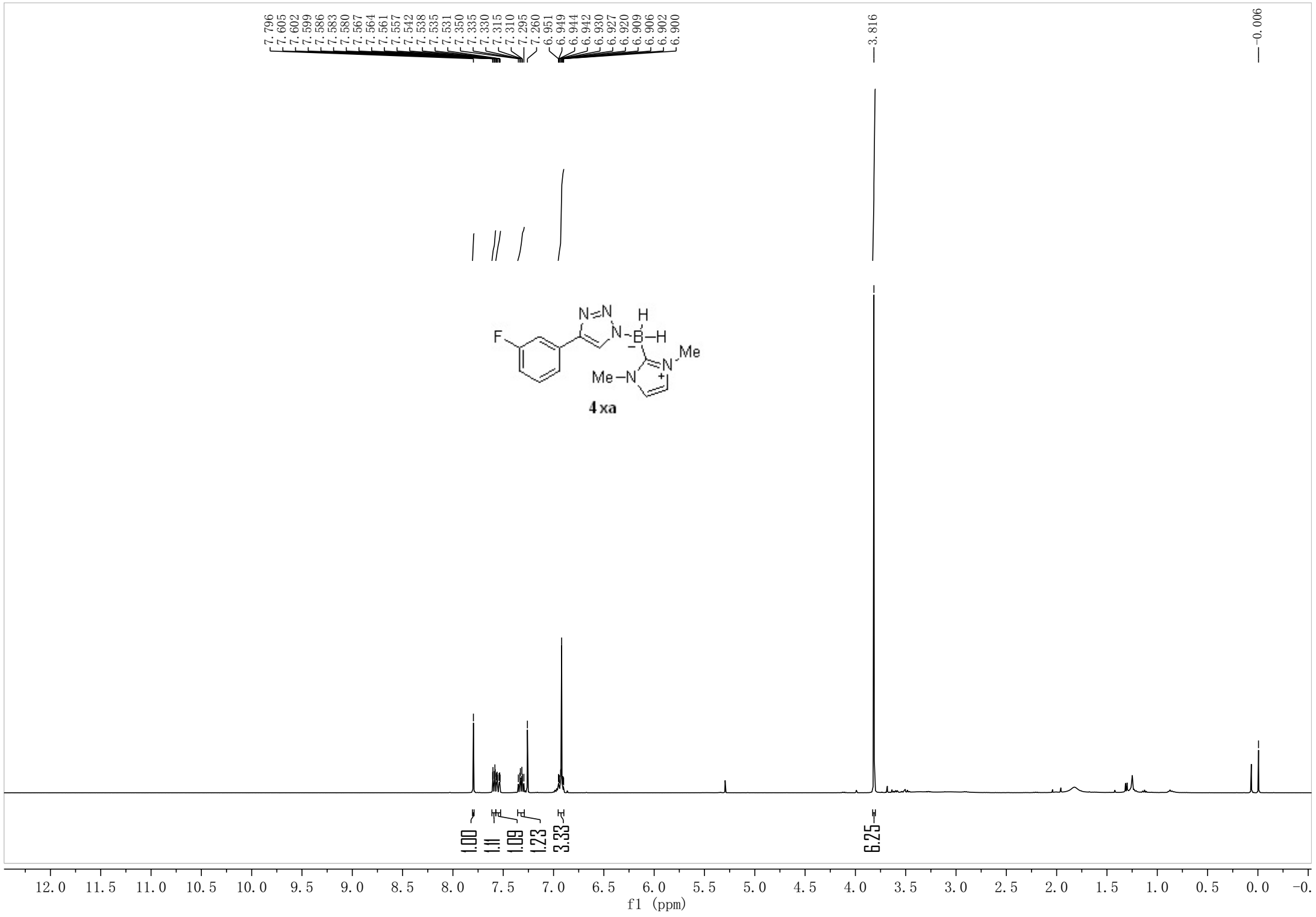

145.091
134.395
134.134
129.838
126.788
125.411
123.465
121.235
77.319
77.001
76.683
36.299
Cl
N=N
N
H
B
H
Me
N
Me
N
+
4ra
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

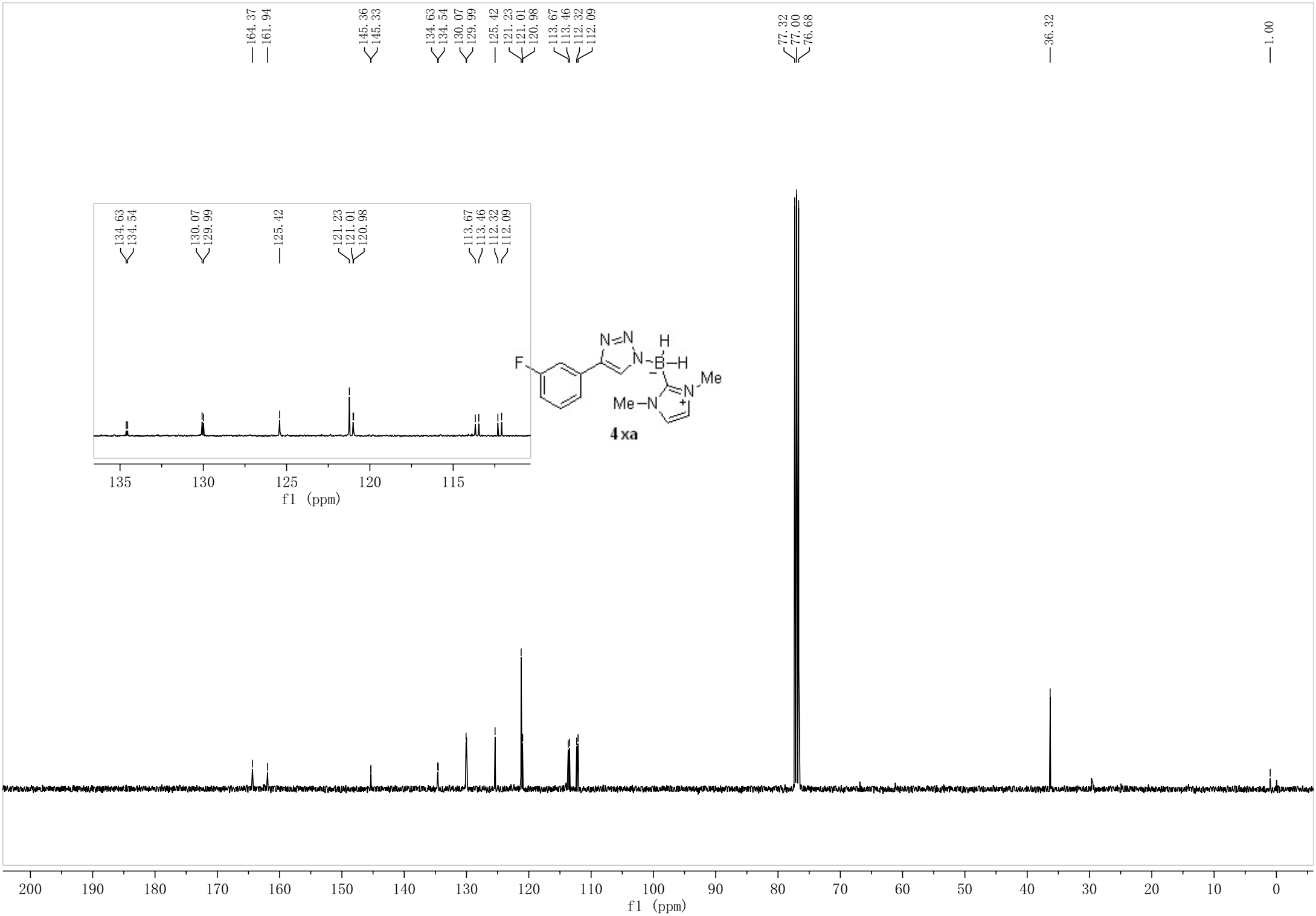

-19.16
-19.69
-20.21
Cl
N=N
N
B
H
H
Me
N
Me
Me—N
+
4ra
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

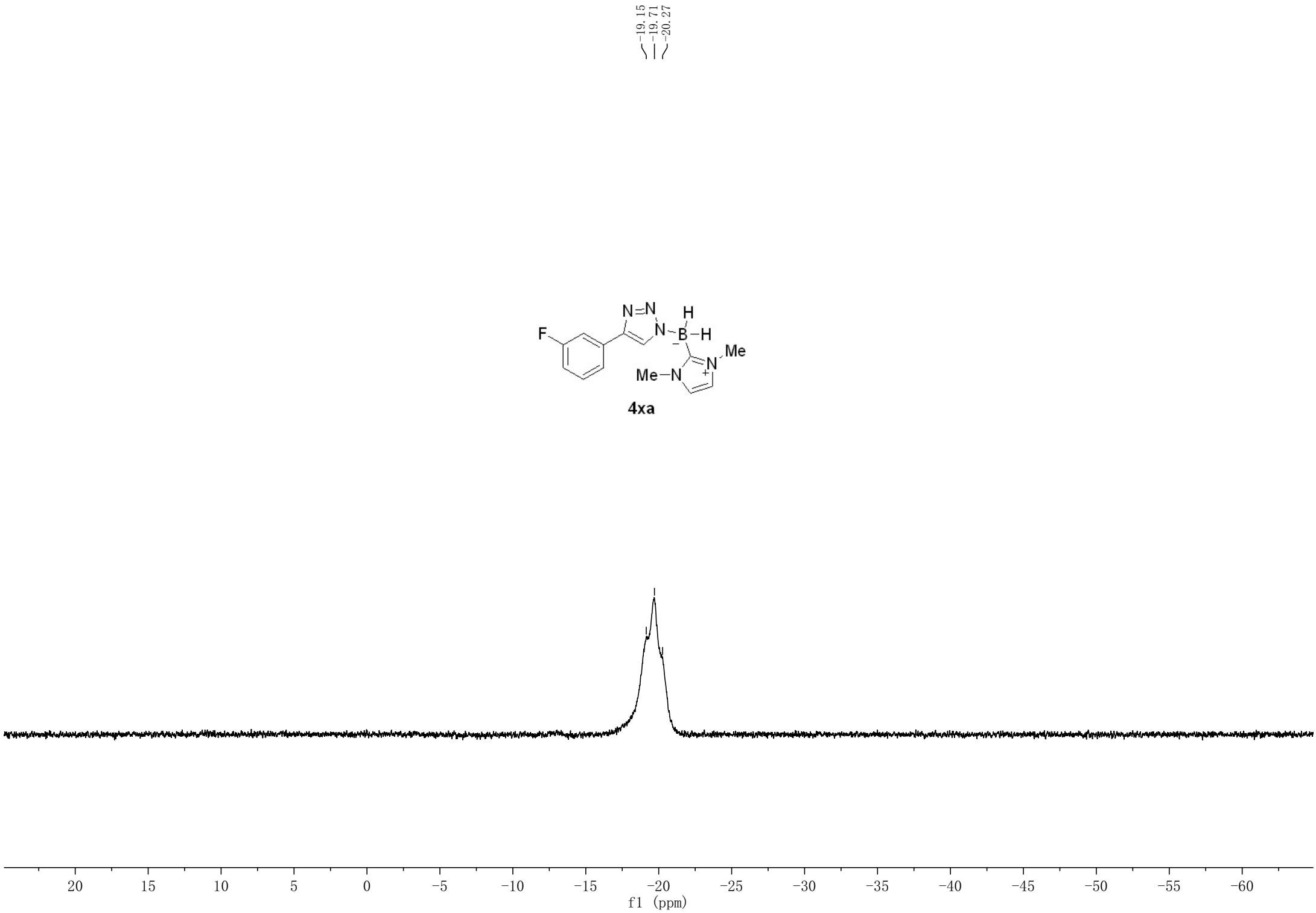

7.775
7.673
7.612
7.593
7.273
7.260
7.254
7.235
7.065
7.047
6.887
3.768
2.367
-0.008
Me
N=N
H
N-B-H
N
Me
Me-N
4sa
0.92
1.00
1.03
1.49
1.08
1.95
6.21
3.11
f1 (ppm)

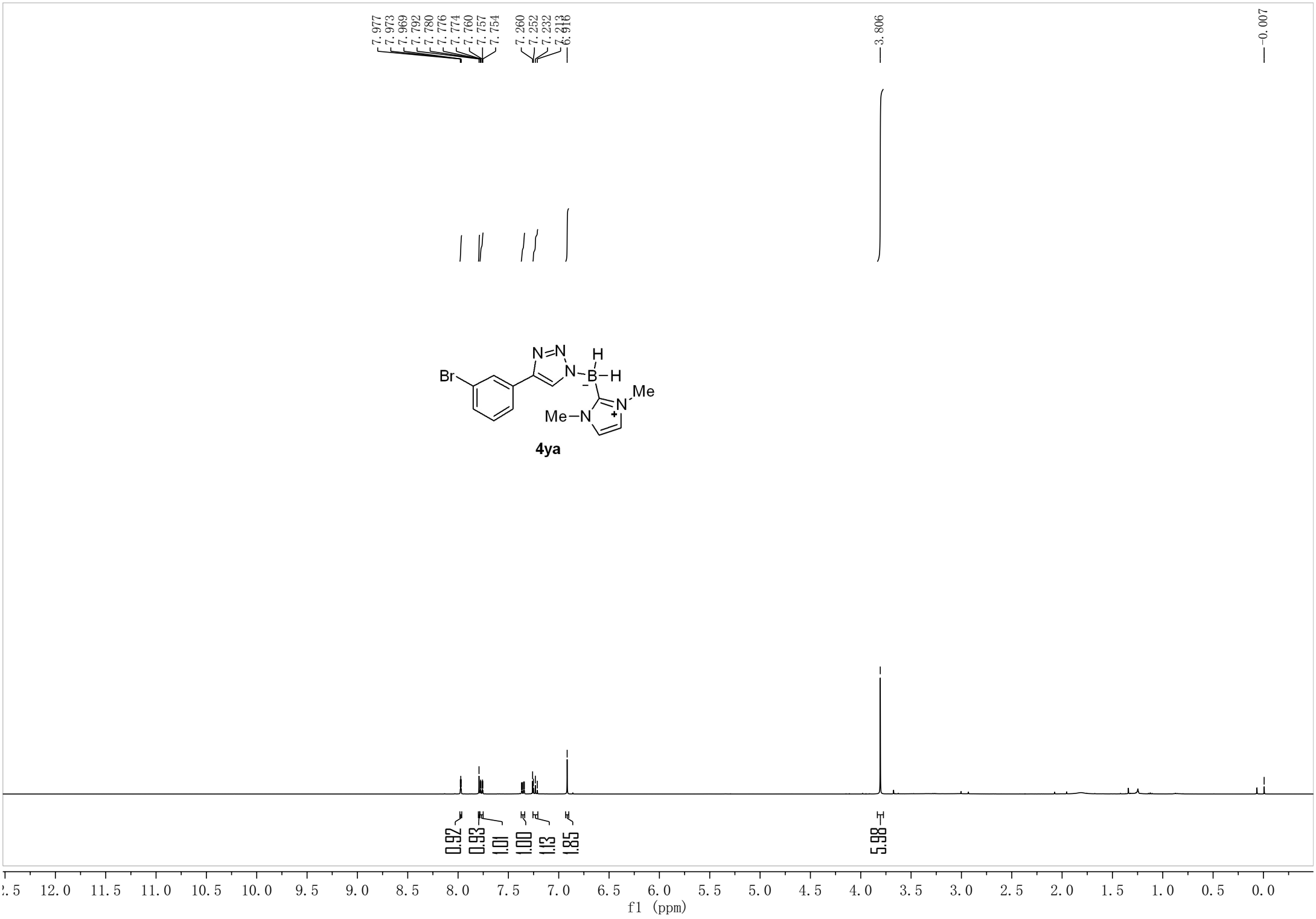

146.37
138.08
132.08
128.44
127.67
126.13
125.14
122.52
121.20
77.32
77.00
76.68
36.19
21.41
Me
N=N
H
N
B
H
Me
N
Me
Me
N
+
4sa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

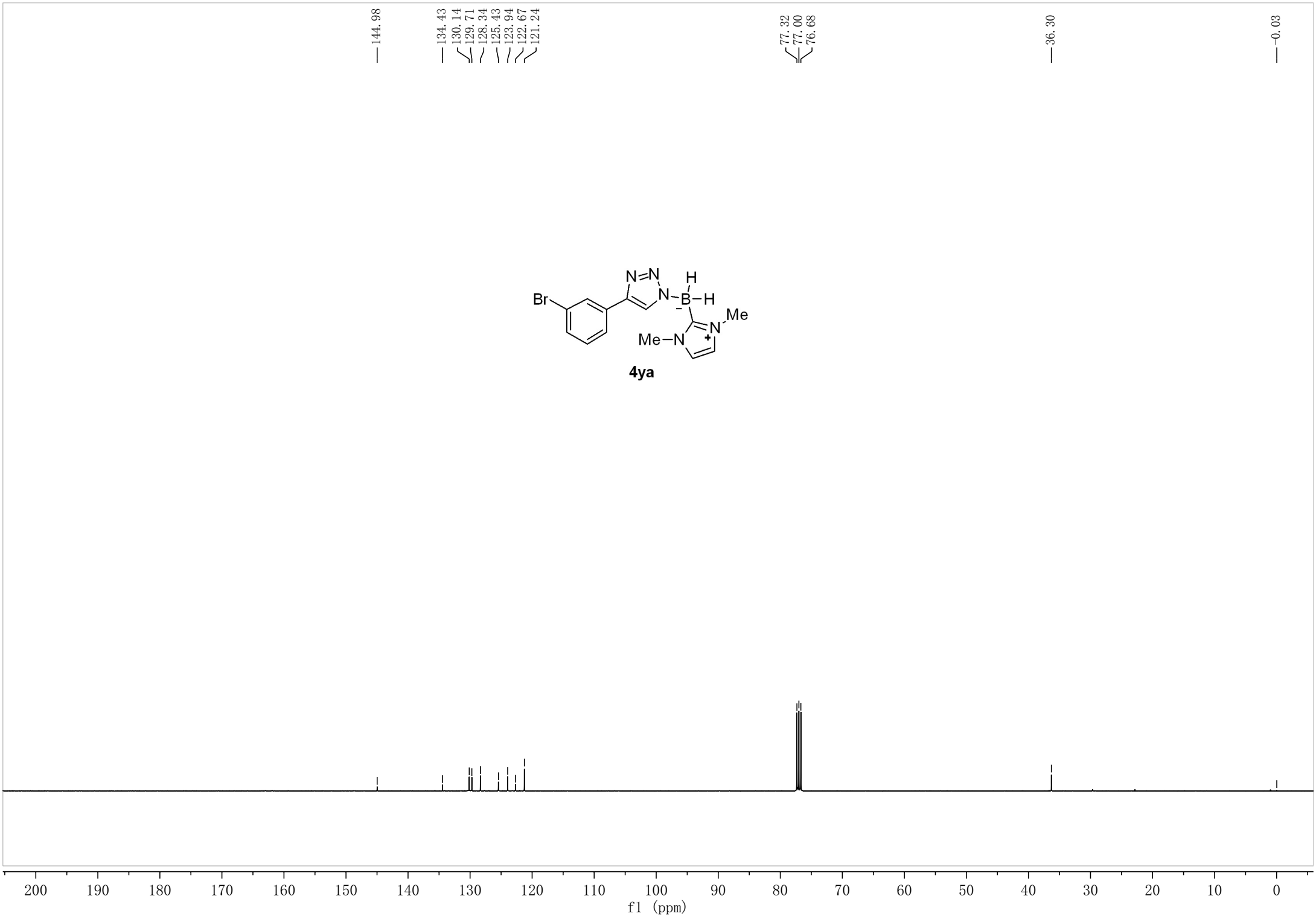

-19.08
-19.63
-20.18
Me
N=N
N
B
H
H
Me
N
Me
Me
N
+
4sa
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

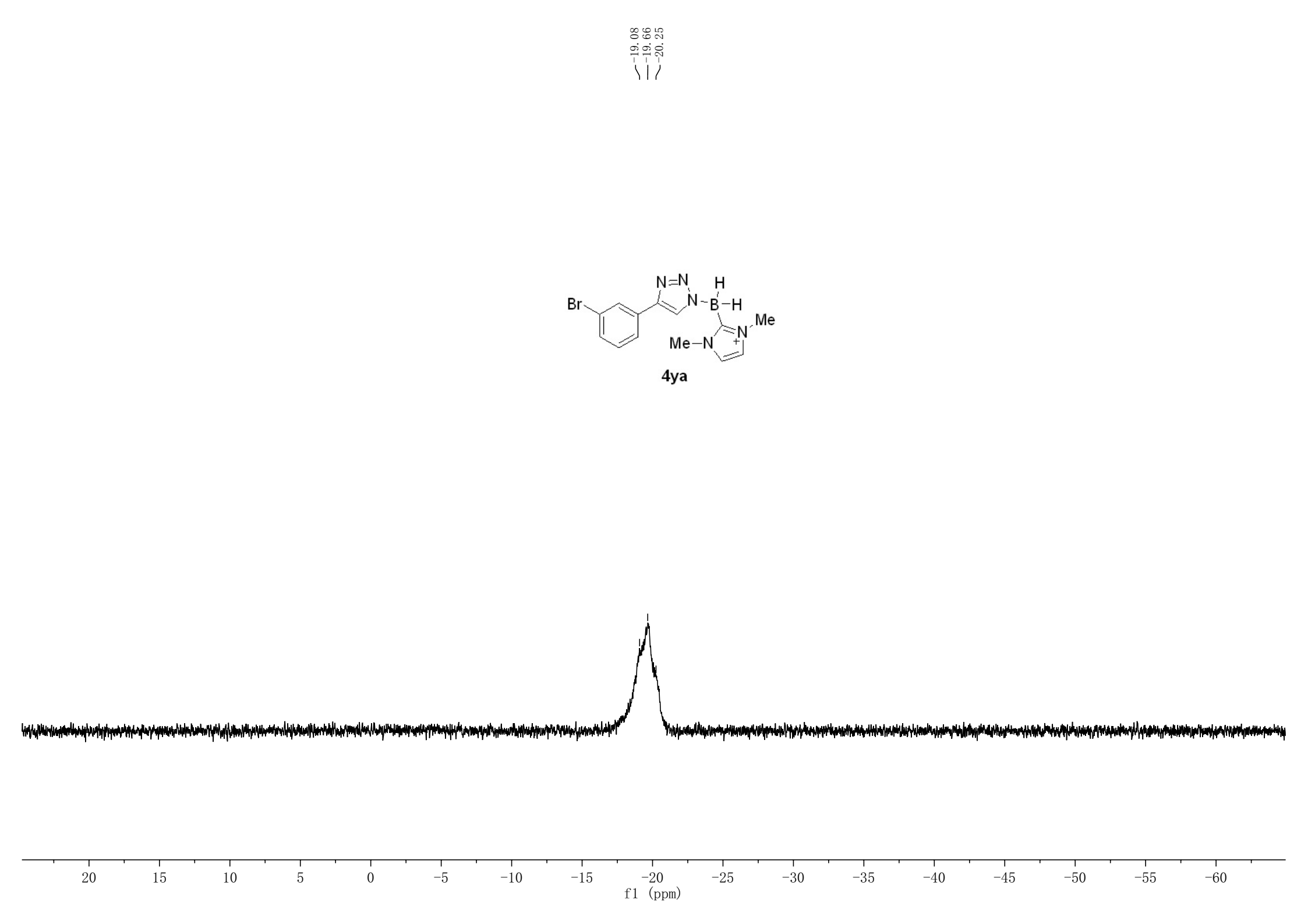

7.796
7.605
7.602
7.599
7.586
7.583
7.580
7.567
7.564
7.561
7.557
7.542
7.538
7.535
7.531
7.350
7.335
7.330
7.315
7.310
7.295
7.260
6.951
6.949
6.944
6.942
6.930
6.927
6.920
6.909
6.906
6.902
6.900
3.816
-0.006
F
N=N
H
N
B
H
Me
N
Me
N
+
4xa
1.00
1.11
1.09
1.23
3.33
6.25
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

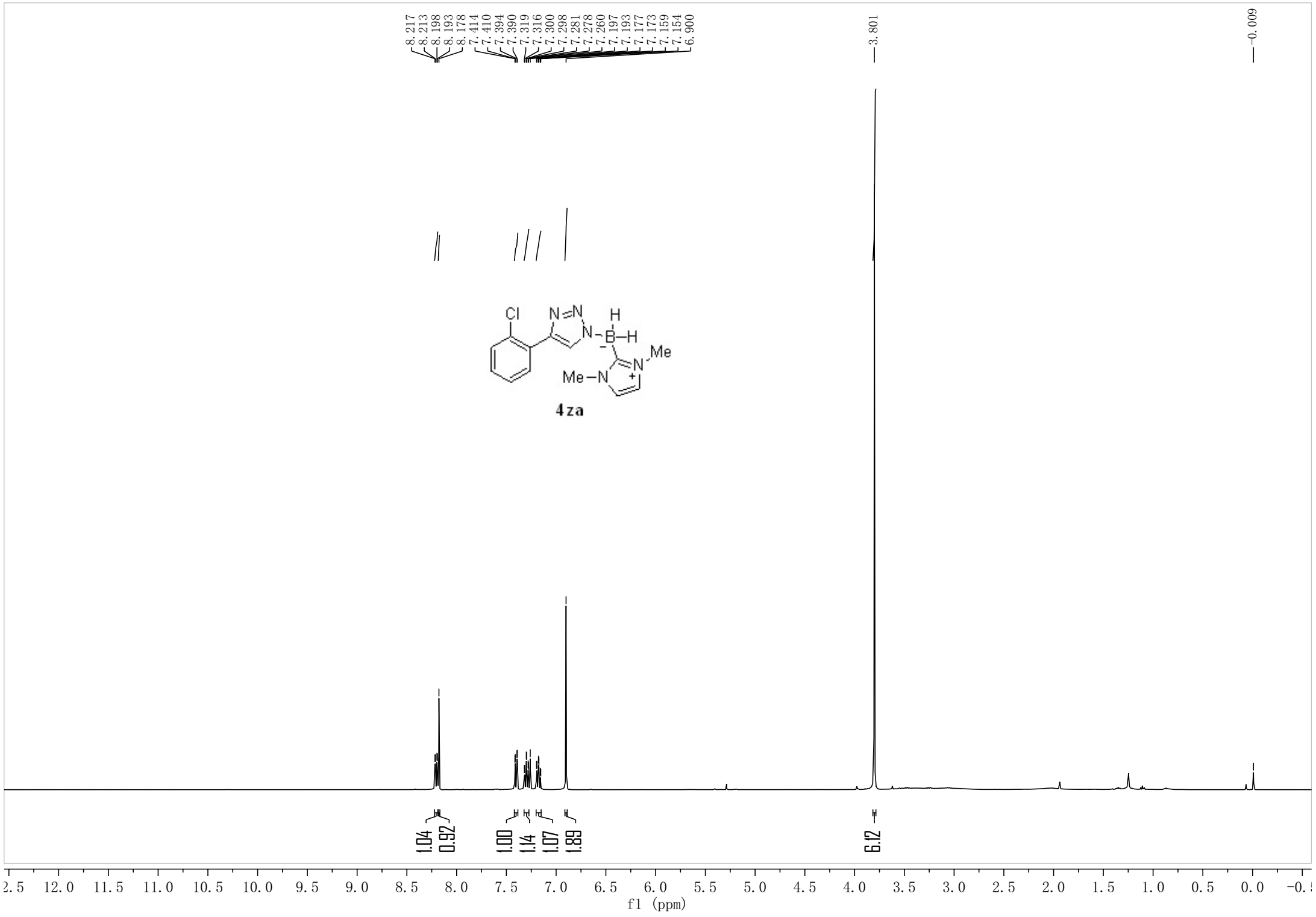

164.37
161.94
145.36
145.33
134.63
134.54
130.07
129.99
125.42
121.23
121.01
120.98
113.67
113.46
112.32
112.09
77.32
77.00
76.68
36.32
1.00
f1 (ppm)
F
N=N
N
B
H
Me
Me
N
4xa


-19.15
-19.71
-20.27
F
N=N
N
B
H
H
Me
N
Me
N
4xa
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

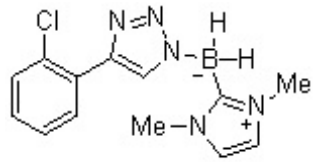

7.977
7.973
7.969
7.792
7.780
7.776
7.774
7.760
7.757
7.754
7.260
7.252
7.232
6.918
3.806
-0.007
Br
N=N
H
N
B
H
Me
N
Me
N
4ya
0.92
0.93
1.01
1.00
1.13
1.85
5.98
f1 (ppm)


144.98
134.43
130.14
129.71
128.34
125.43
123.94
122.67
121.24
77.32
77.00
76.68
36.30
0.03
Br
N=N
N
B
H
H
Me
N
Me
N
4ya
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

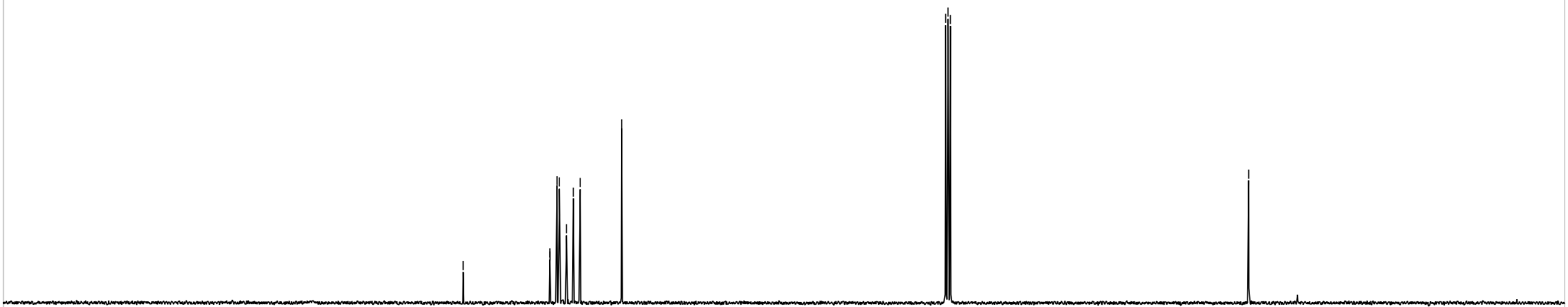

-19.08
-19.66
-20.25
Br
N=N
N
B
H
H
Me
N
Me
N
+
4ya
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)


8.217
8.213
8.198
8.193
8.178
7.414
7.410
7.394
7.390
7.319
7.316
7.300
7.298
7.281
7.278
7.260
7.197
7.193
7.177
7.173
7.159
7.154
6.900
3.801
-0.009
Cl
N=N
H
N
B
H
Me
N
Me
N
+
4za
1.04
0.92
1.00
1.14
1.07
1.89
6.12
f1 (ppm)

142.69
130.94
130.92
129.97
129.66
128.69
127.77
126.83
121.22
77.32
77.00
76.68
36.26

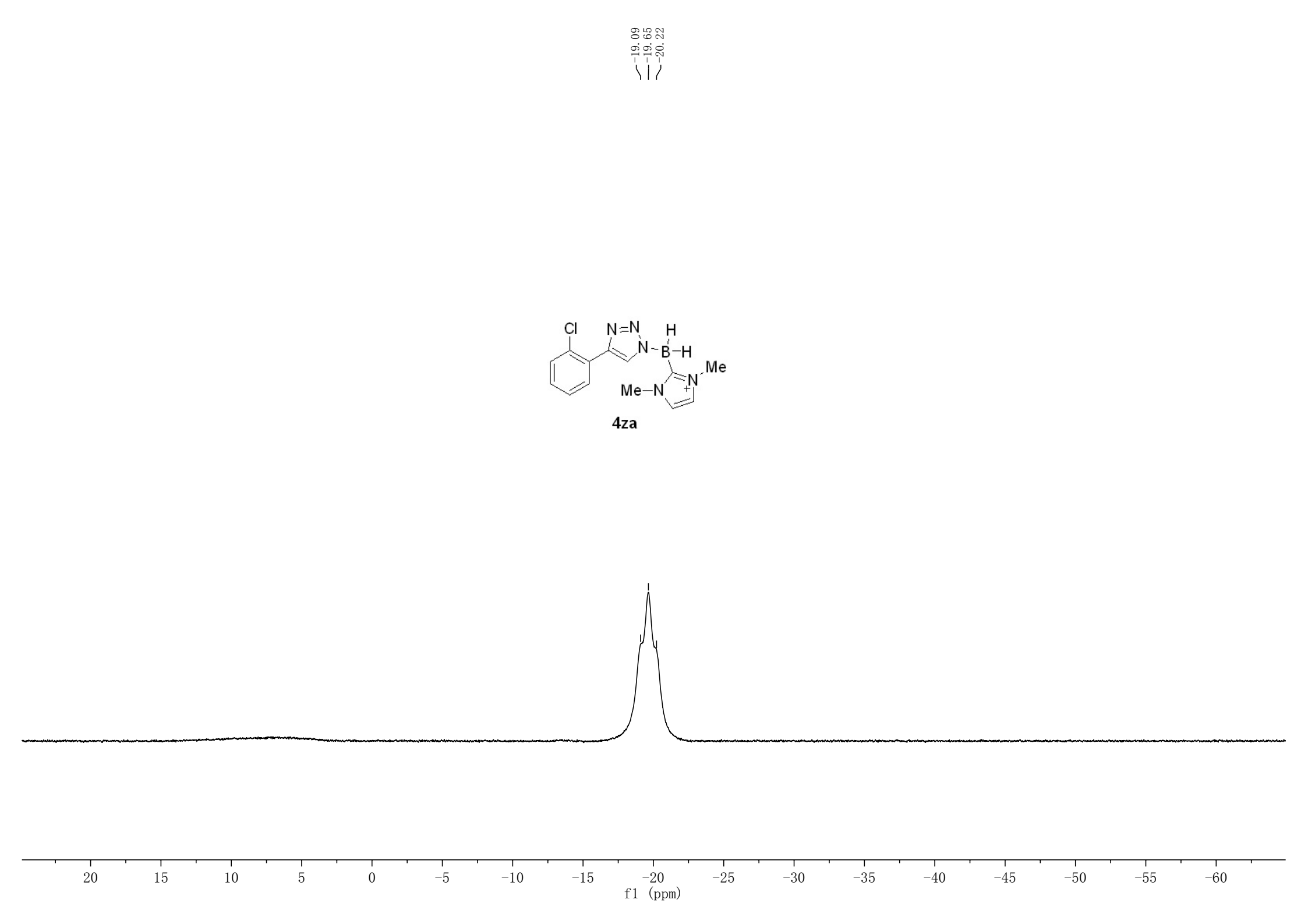


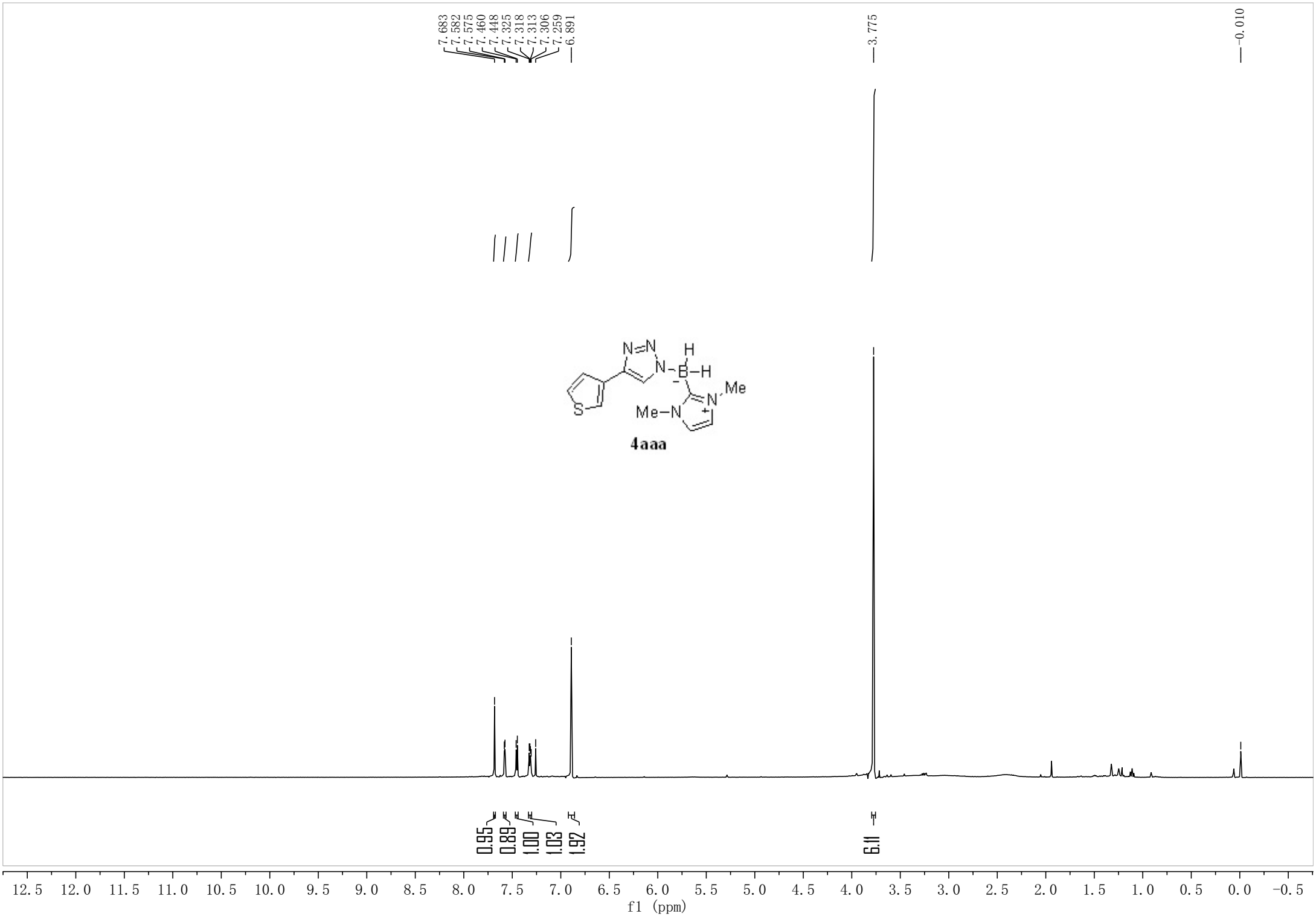
4za

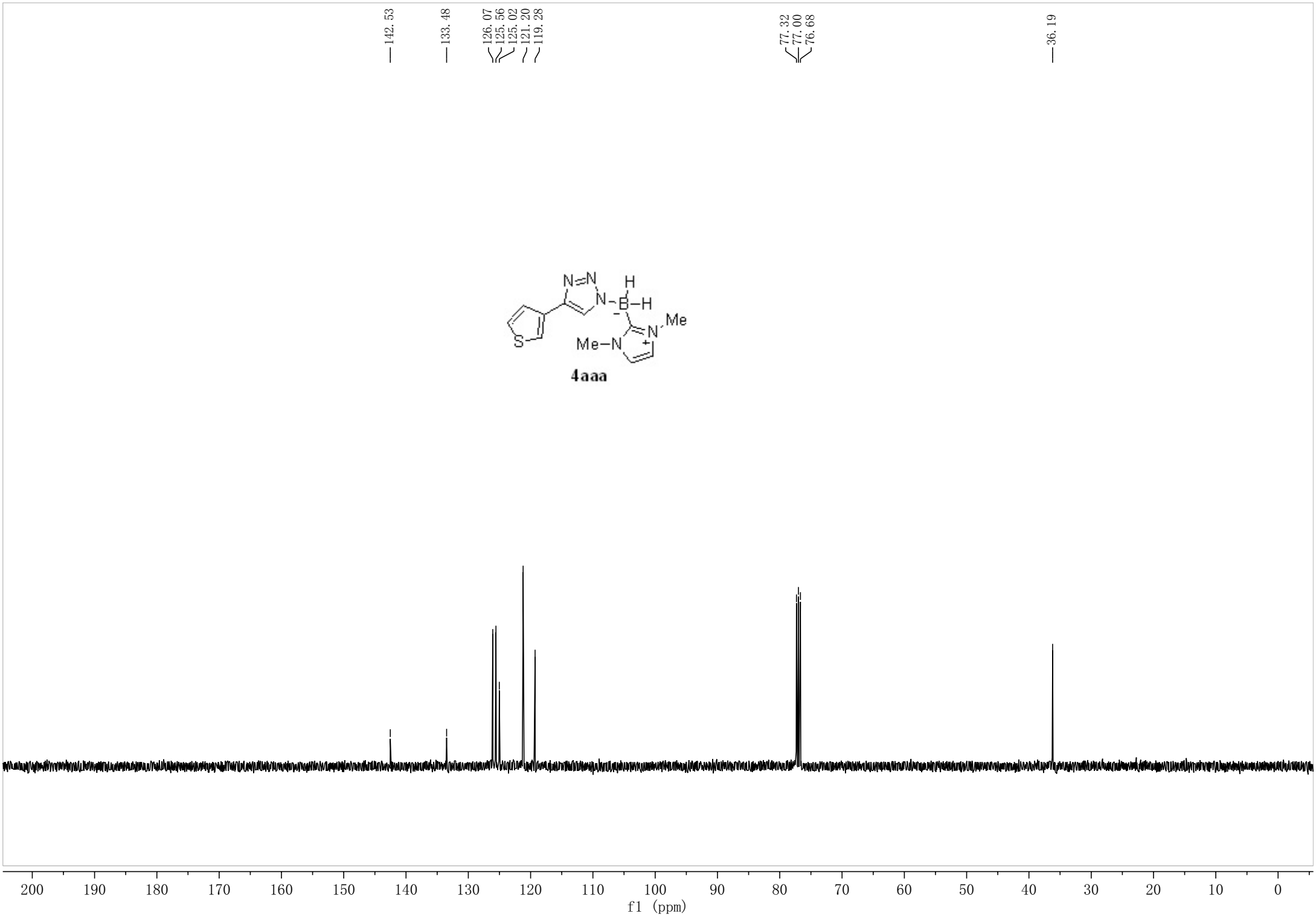


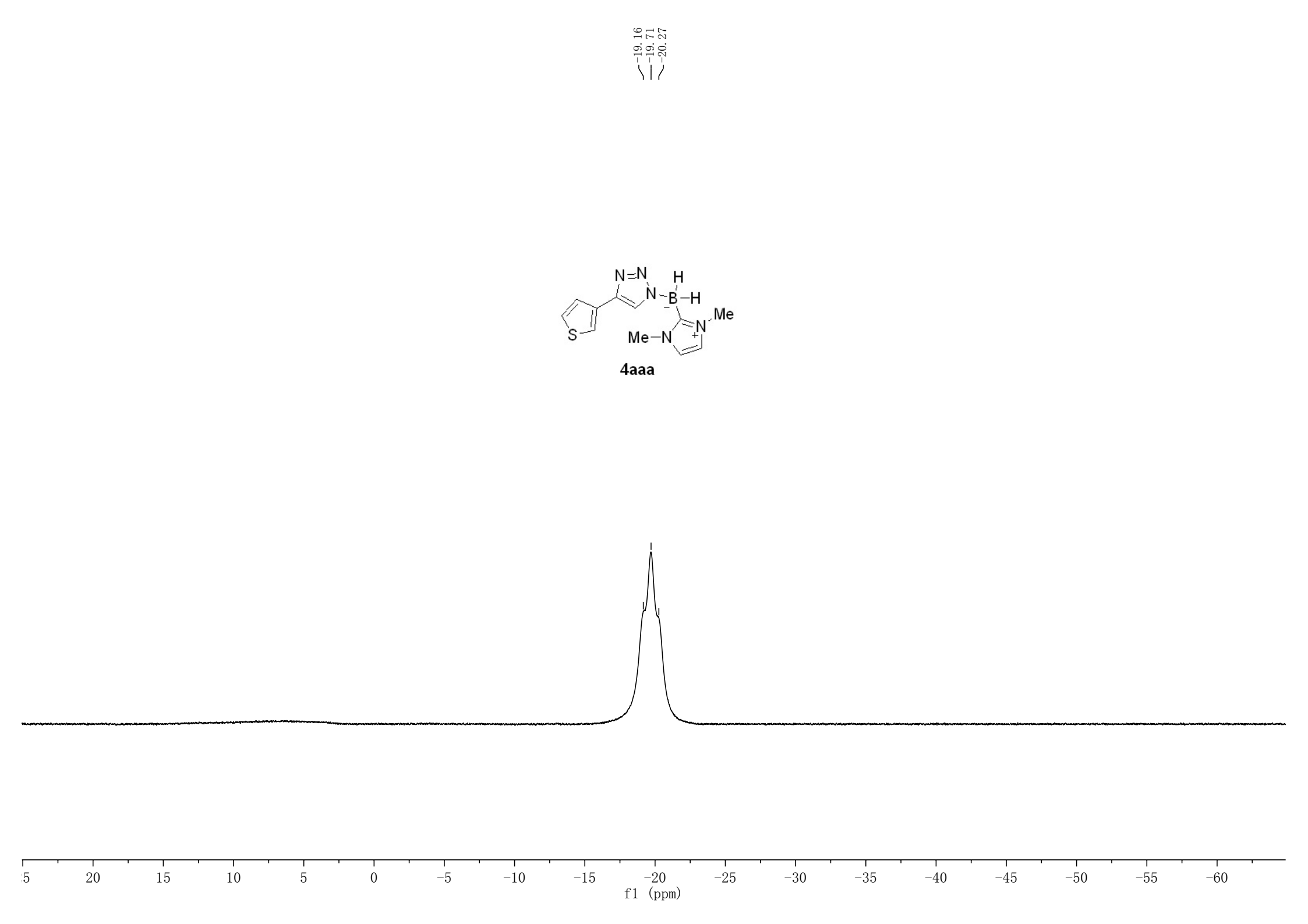
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

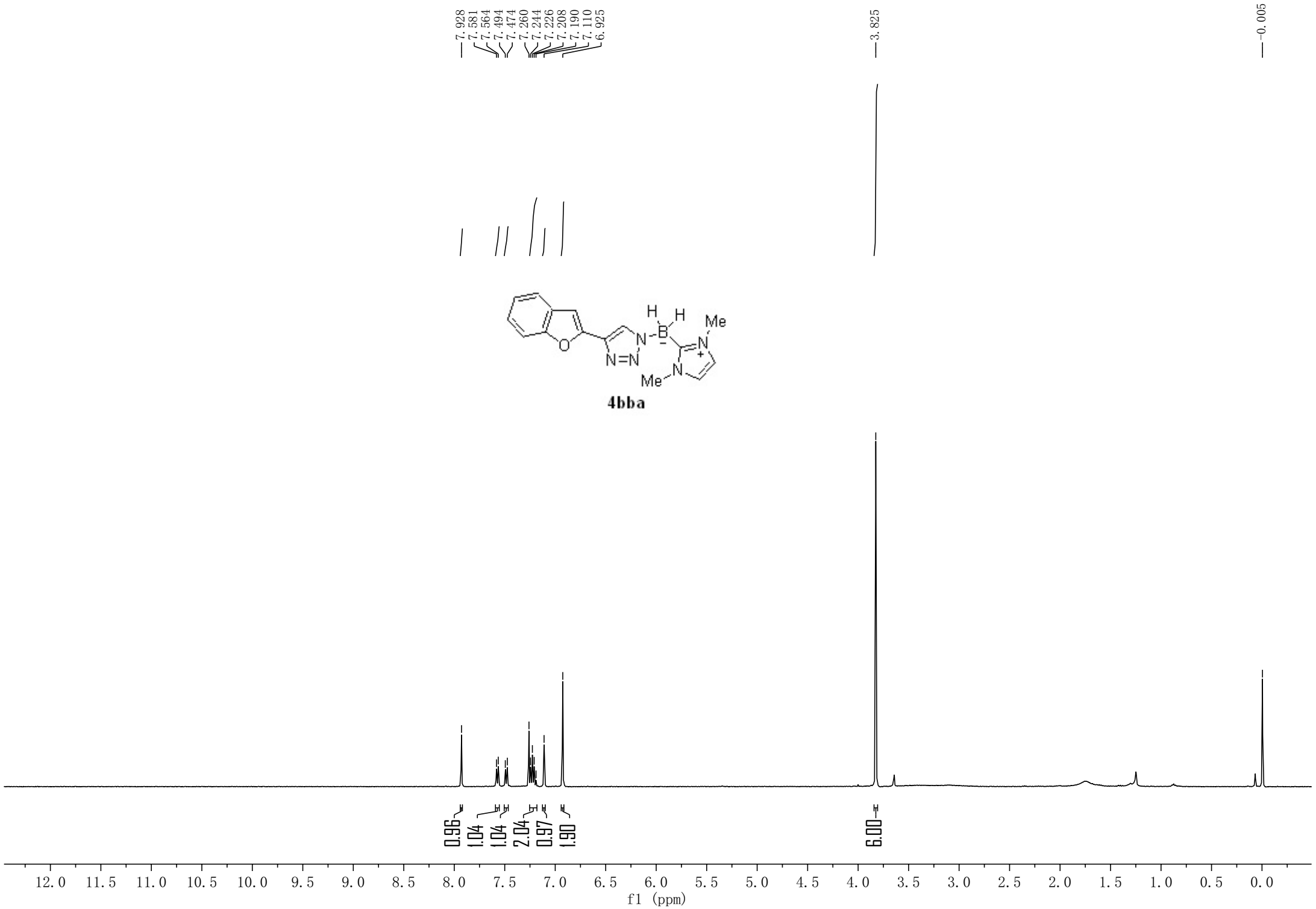
f1 (ppm)

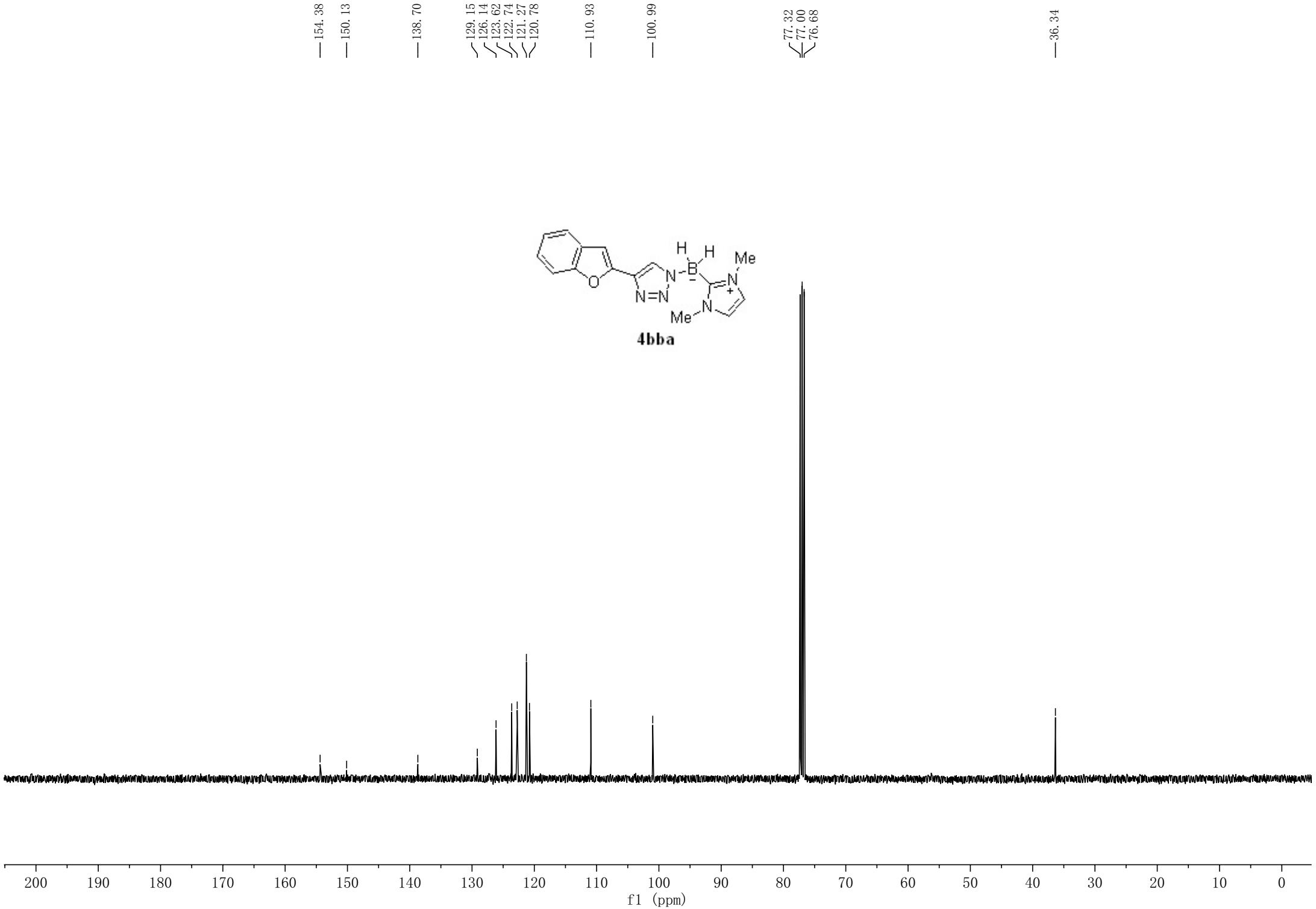

-19.09
-19.65
-20.22
Cl
N=N
H
N
B–H
Me
N
Me–N
+
4za
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)


7.683
7.582
7.575
7.460
7.448
7.325
7.318
7.313
7.306
7.259
6.891
3.775
-0.010
N=N
H
N-B-H
Me
Me-N
S
4aaa
0.95
0.89
1.00
1.03
1.92
6.11
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

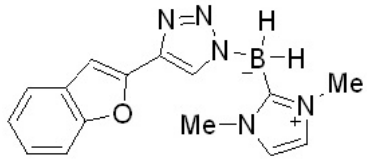

142.53
133.48
126.07
125.56
125.02
121.20
119.28
77.32
77.00
76.68
36.19
N=N
H
N
B
H
Me
N
Me
N
S
4aaa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-19.16
-19.71
-20.27
N=N
H
N
B
H
Me
S
Me
N
N
+
4aaa
5
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

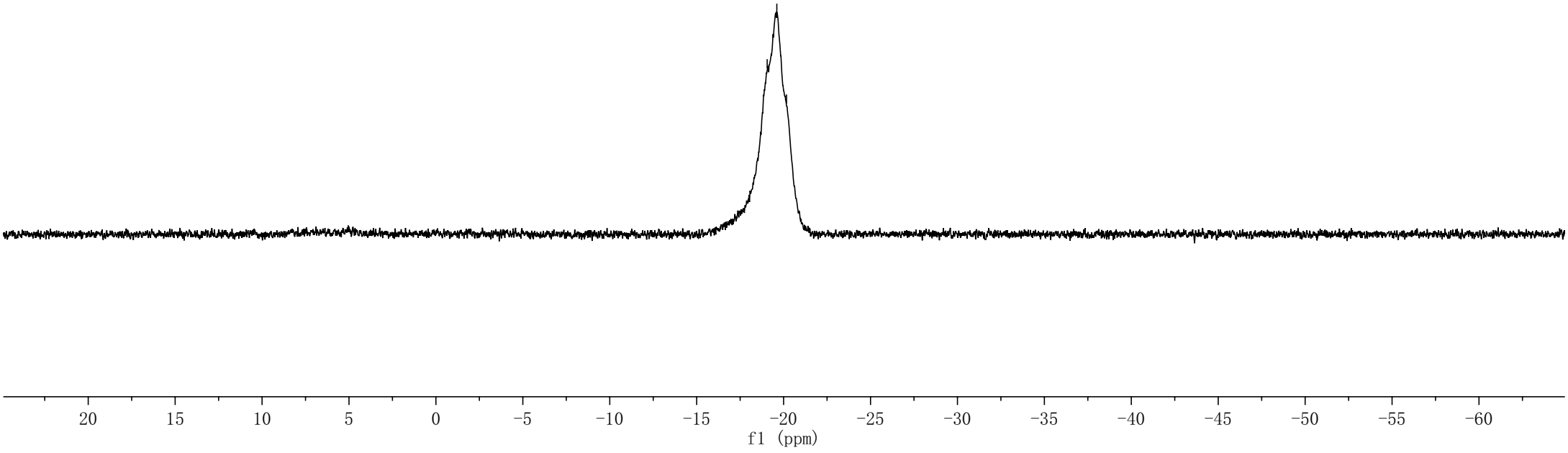

7.928
7.581
7.564
7.494
7.474
7.260
7.244
7.226
7.208
7.190
7.110
6.925
3.825
-0.005
H
H
B
Me
N
N
N=N
Me
O
4bba
0.96
1.04
1.04
2.04
0.97
1.90
6.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

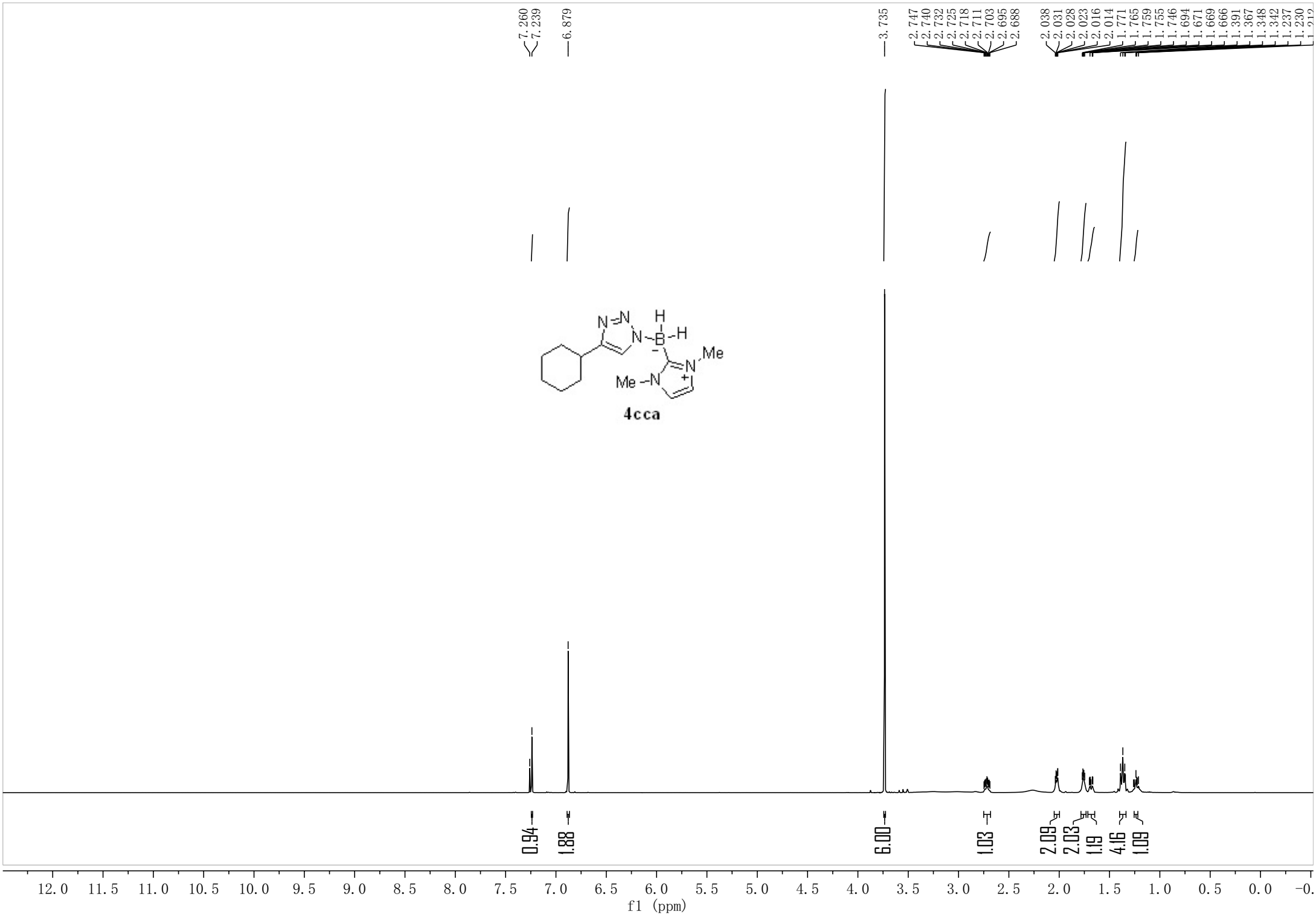

154.38
150.13
138.70
129.15
126.14
123.62
122.74
121.27
120.78
110.93
100.99
77.32
77.00
76.68
36.34
H
H
B
Me
N
N
N=N
O
Me
4bba
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

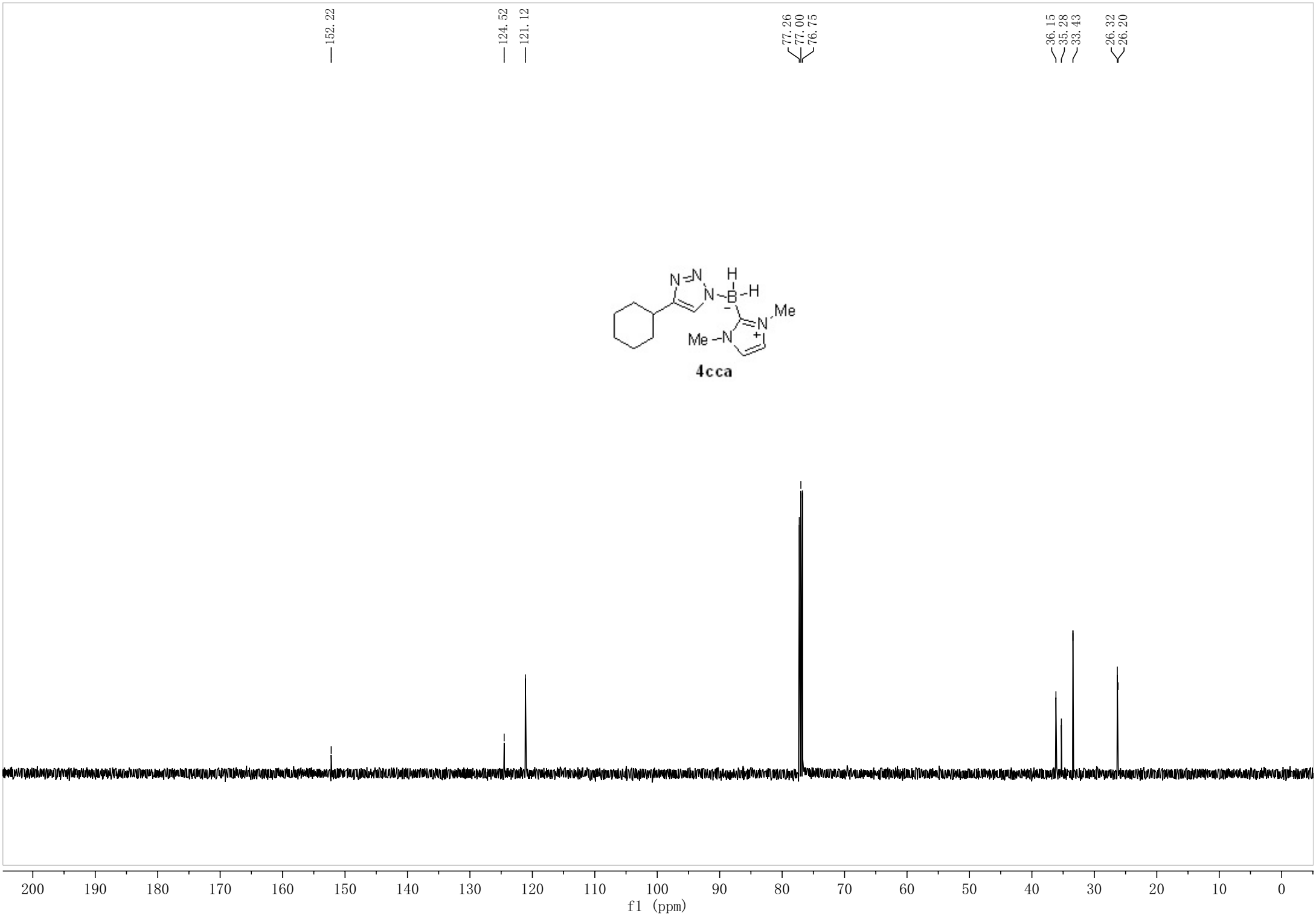
-19.05
-19.61
-20.17

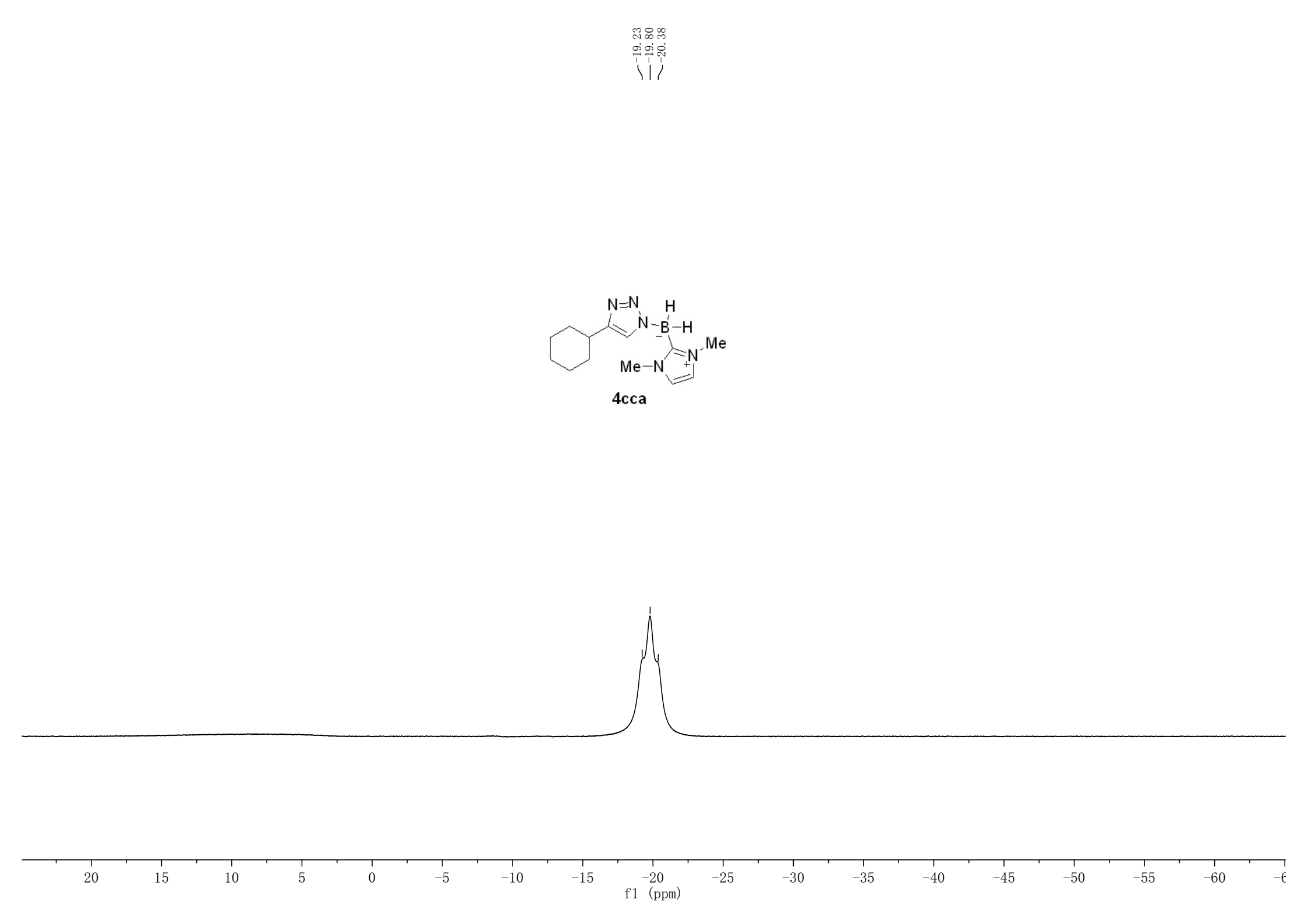


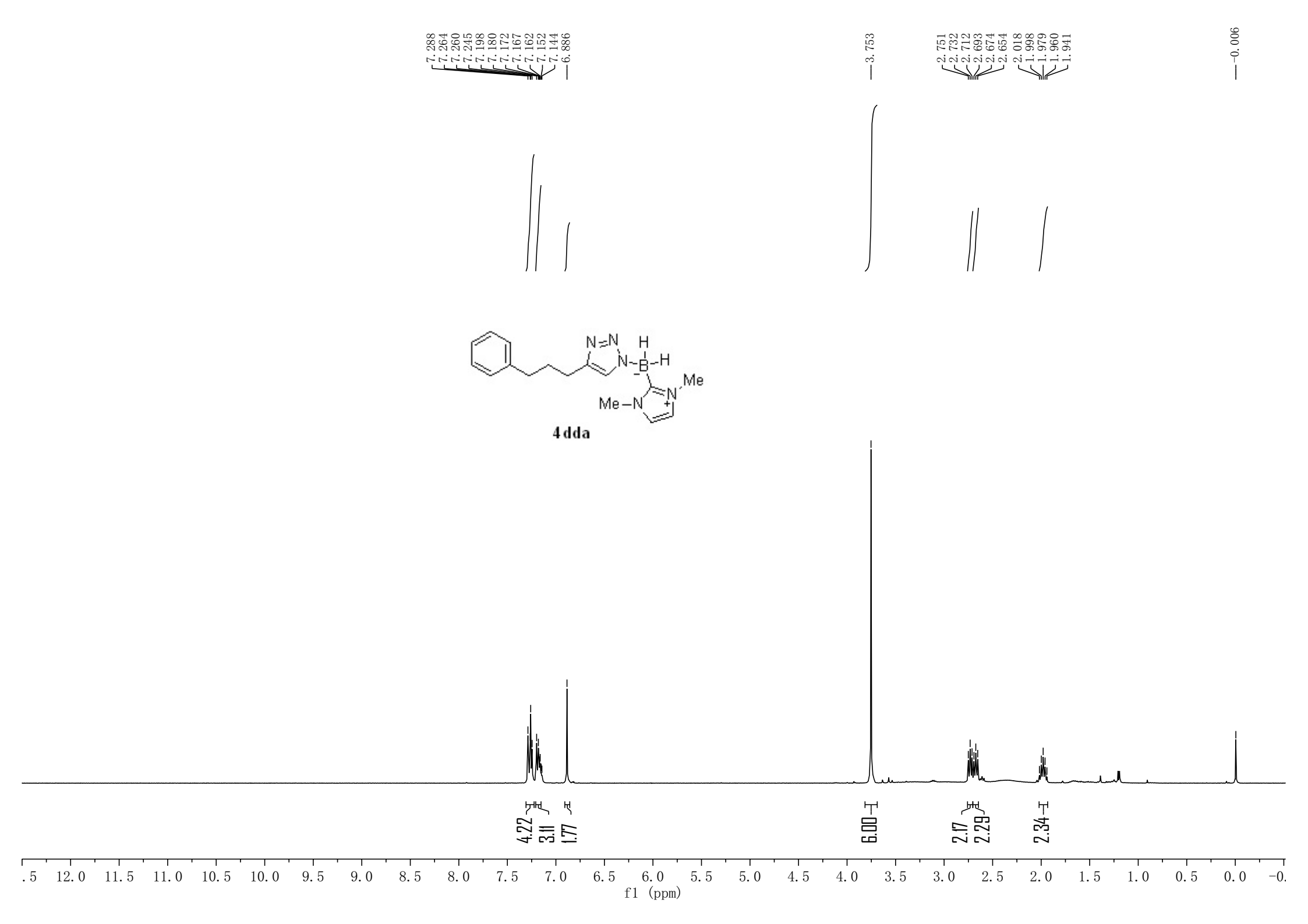
4bba

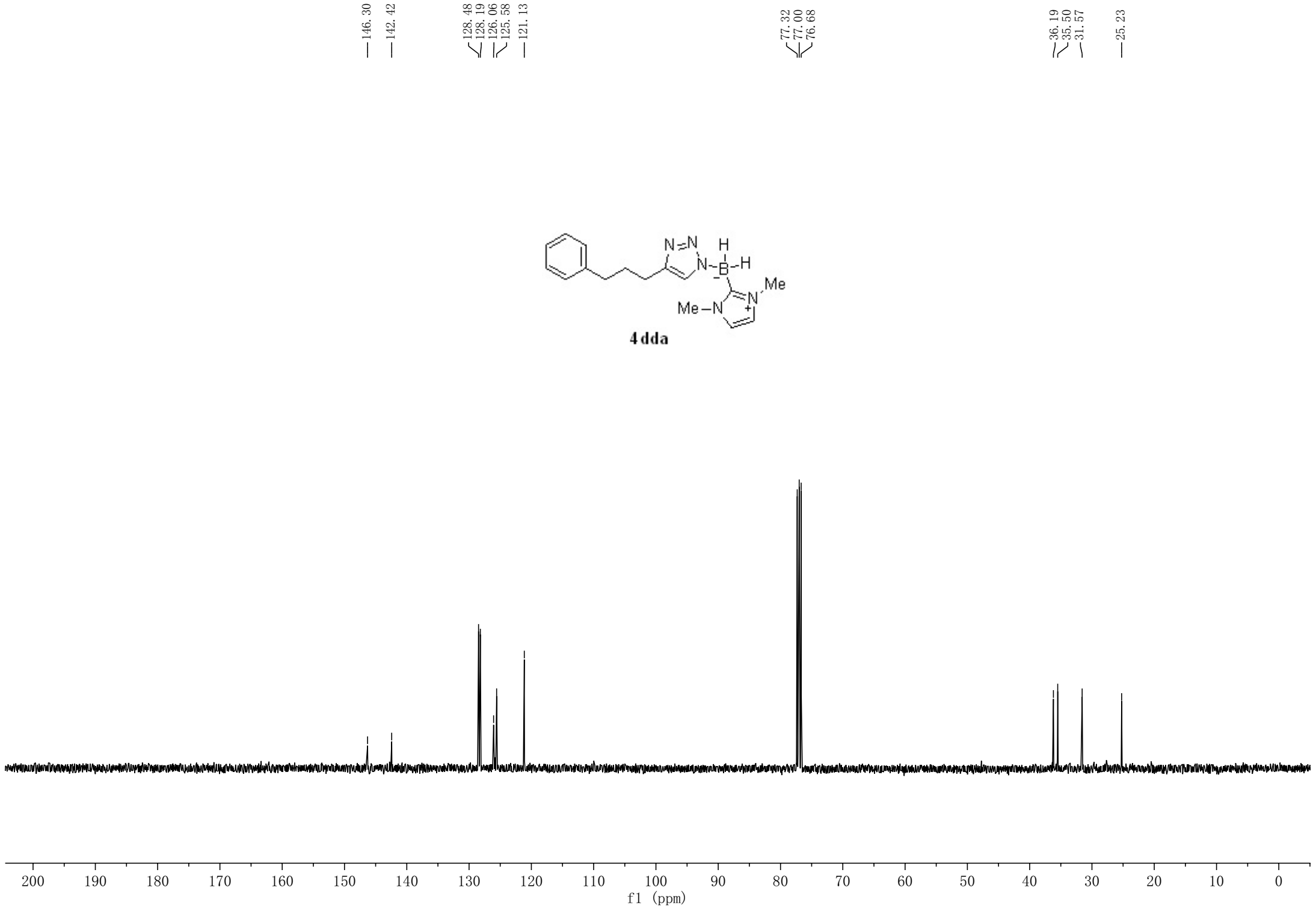


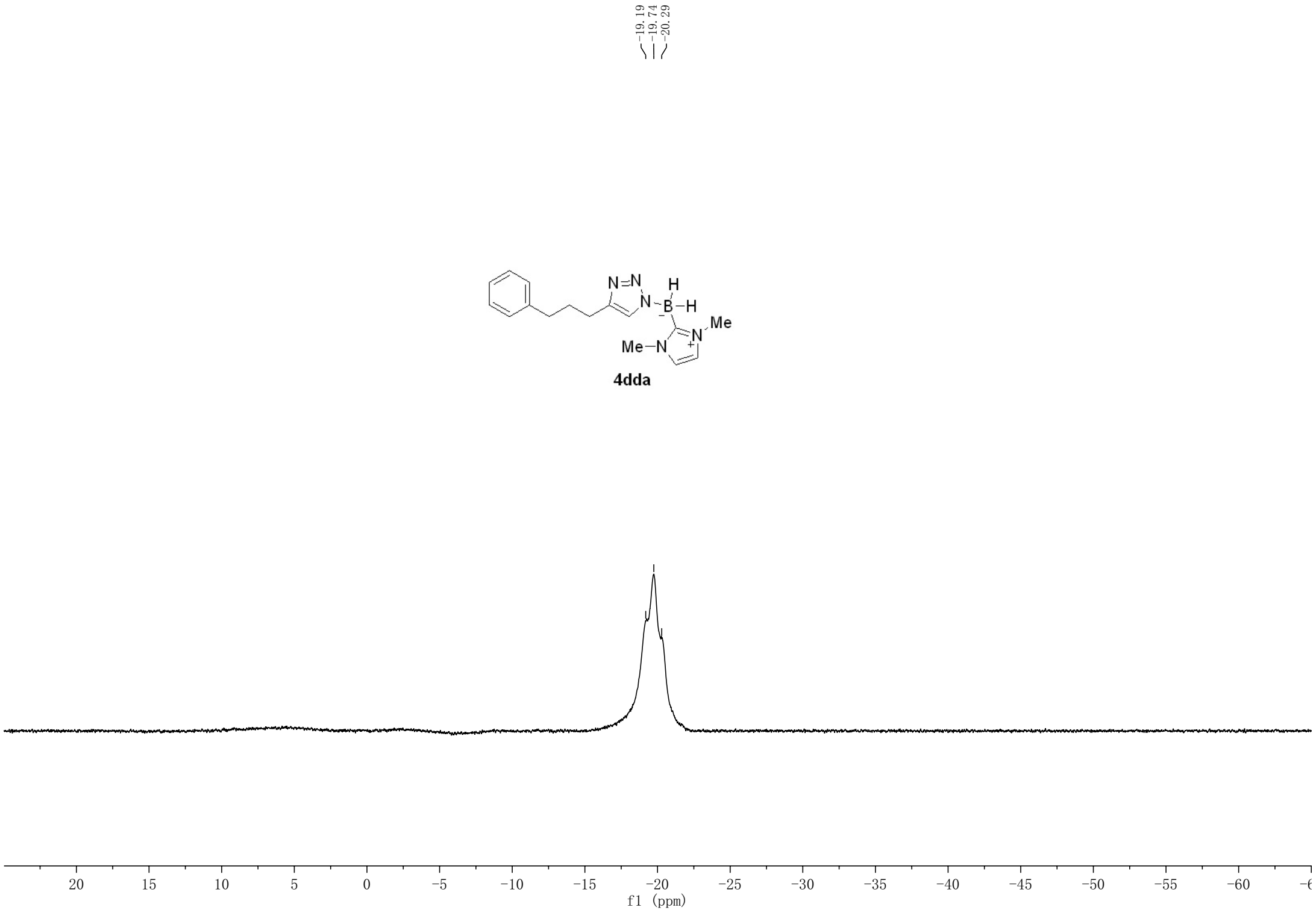

7.260
7.239
6.879
3.735
2.747
2.740
2.732
2.725
2.718
2.711
2.703
2.695
2.688
2.038
2.031
2.028
2.023
2.016
2.014
1.771
1.765
1.759
1.755
1.746
1.694
1.671
1.669
1.666
1.391
1.367
1.348
1.342
1.237
1.230
N
N
H
B
H
Me
Me
N
N
4cca
0.94
1.88
6.00
1.03
2.09
2.03
1.19
4.16
1.09
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

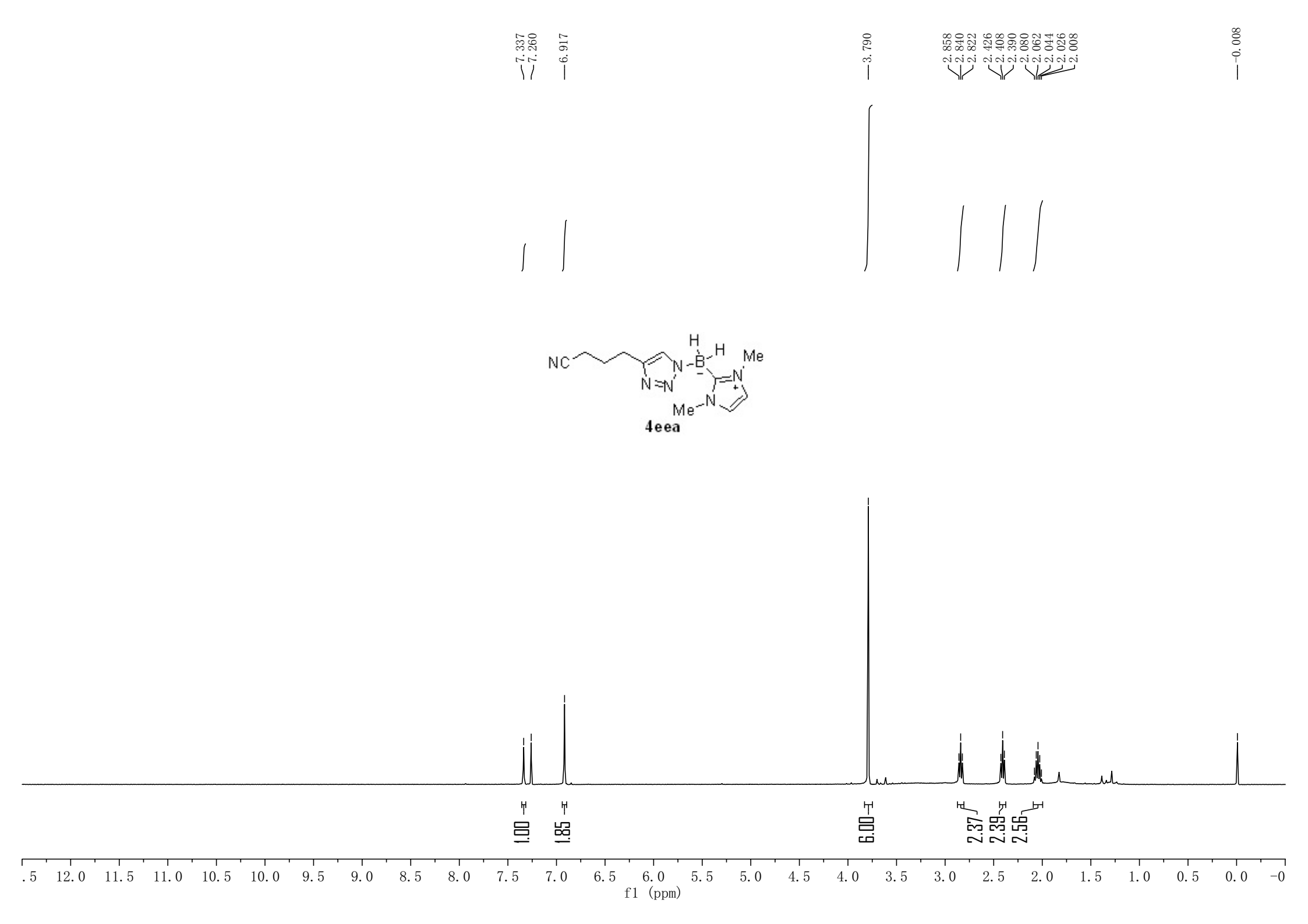

152.22
124.52
121.12
77.26
77.00
76.75
36.15
35.28
33.43
26.32
26.20
Me
Me
4cca
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

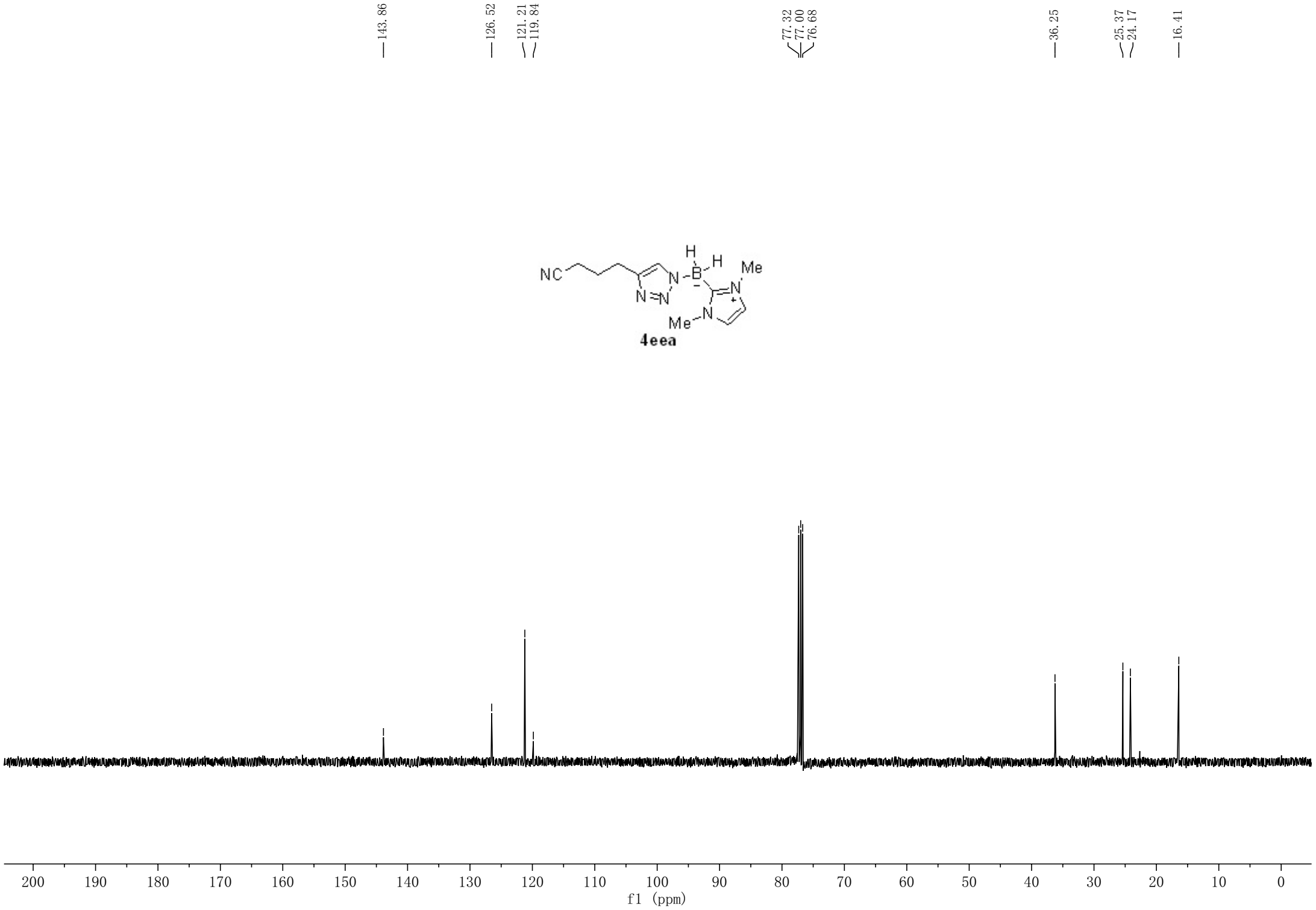

-19.23
-19.80
-20.38
N=N
N
H
B
H
Me
N
Me
N
+
4cca
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

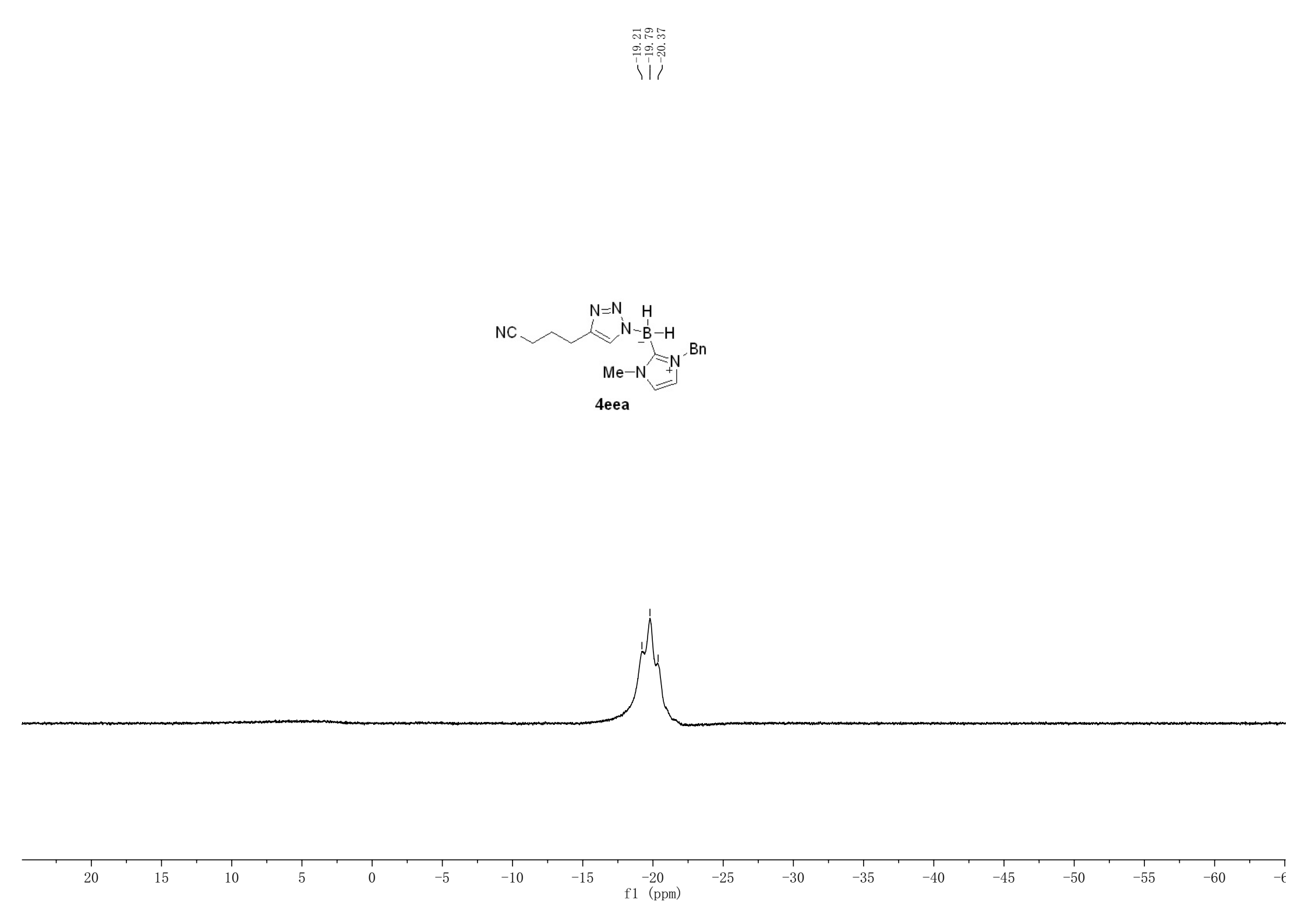

7.288
7.264
7.260
7.245
7.198
7.180
7.172
7.167
7.162
7.152
7.144
6.886
3.753
2.751
2.732
2.712
2.693
2.674
2.654
2.018
1.998
1.979
1.960
1.941
-0.006
4dda
4.22
3.11
1.77
6.00
2.17
2.29
2.34
f1 (ppm)

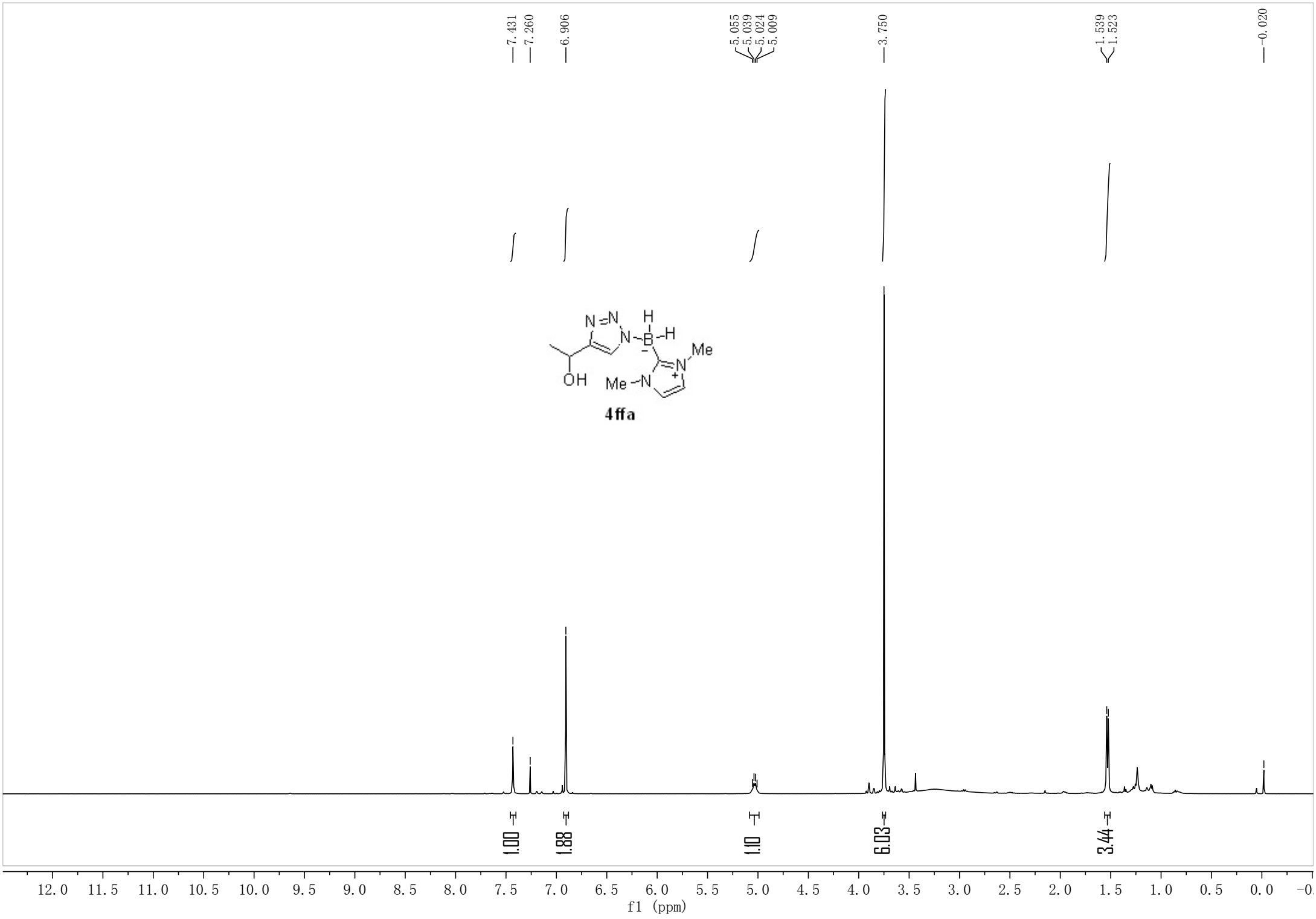

146.30
142.42
128.48
128.19
126.06
125.58
121.13
77.32
77.00
76.68
36.19
35.50
31.57
25.23
N=N
H
N
B
H
Me
N
Me
N
+
4dda
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

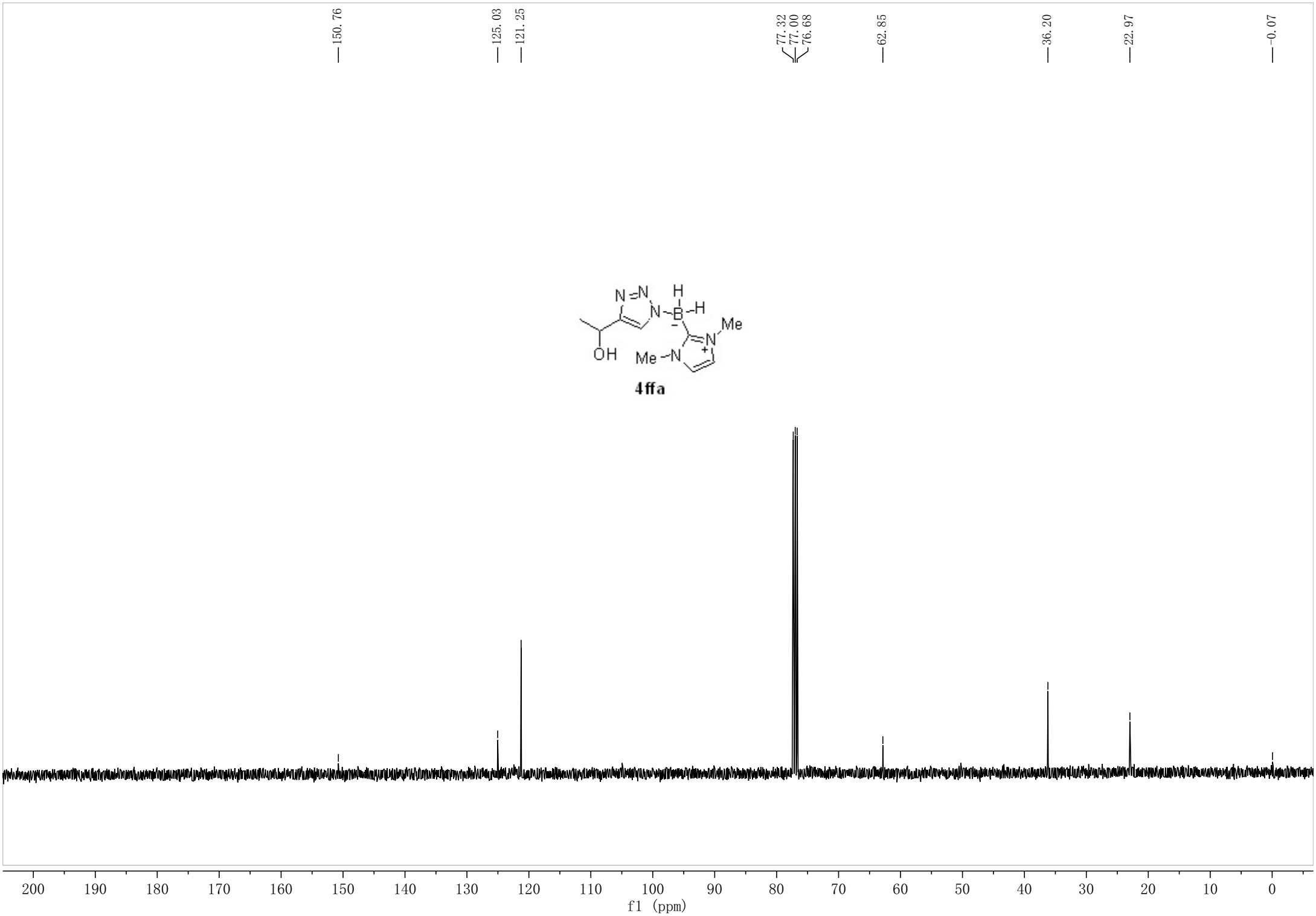

-19.19
-19.74
-20.29
N=N
N
B
H
H
Me
N
Me
N
+
4dda
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

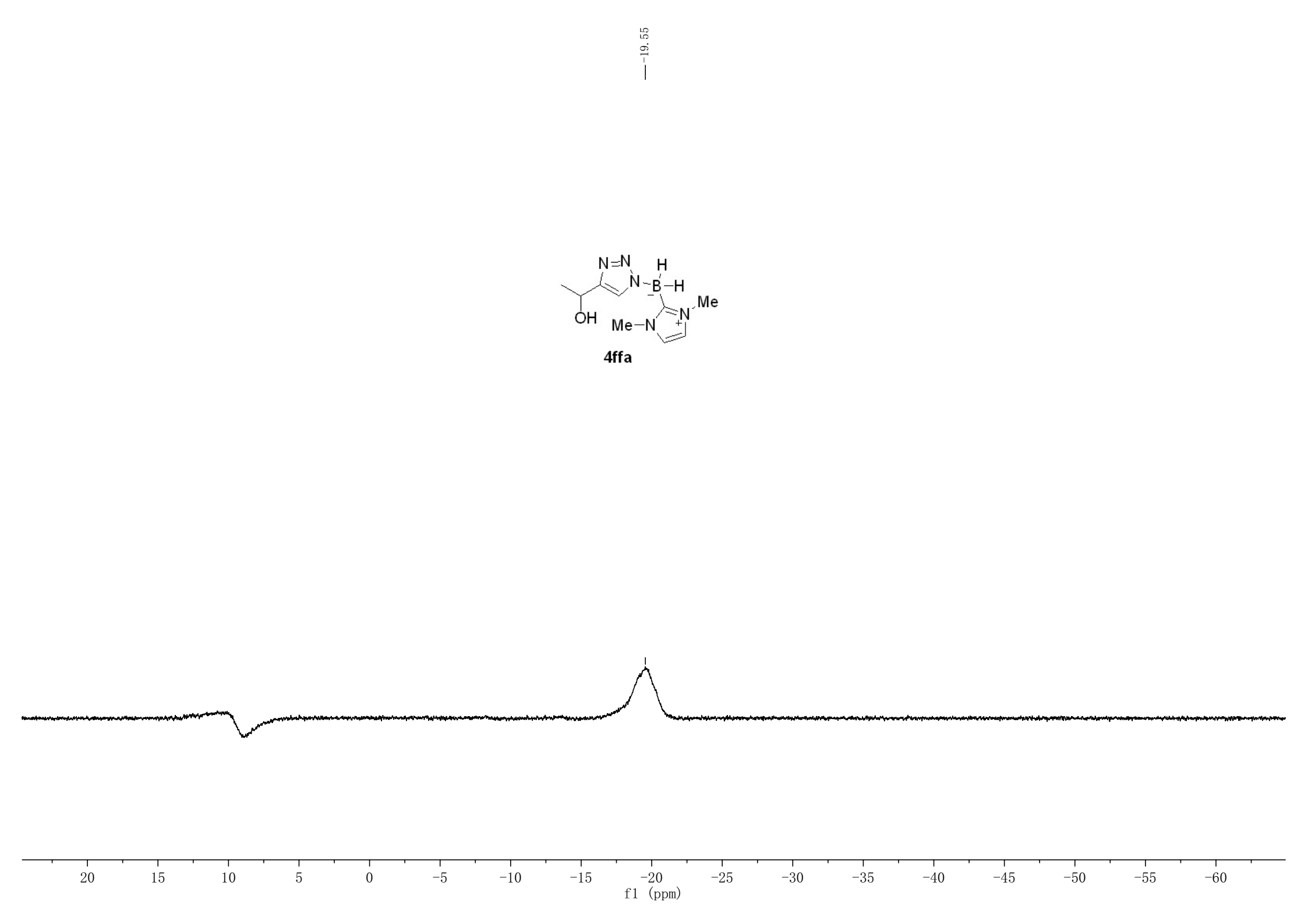

7.337
7.260
6.917
3.790
2.858
2.840
2.822
2.426
2.408
2.390
2.080
2.062
2.044
2.026
2.008
-0.008
NC
N
B
H
H
Me
N
N
N
Me
4eea
1.00
1.85
6.00
2.37
2.39
2.56
f1 (ppm)

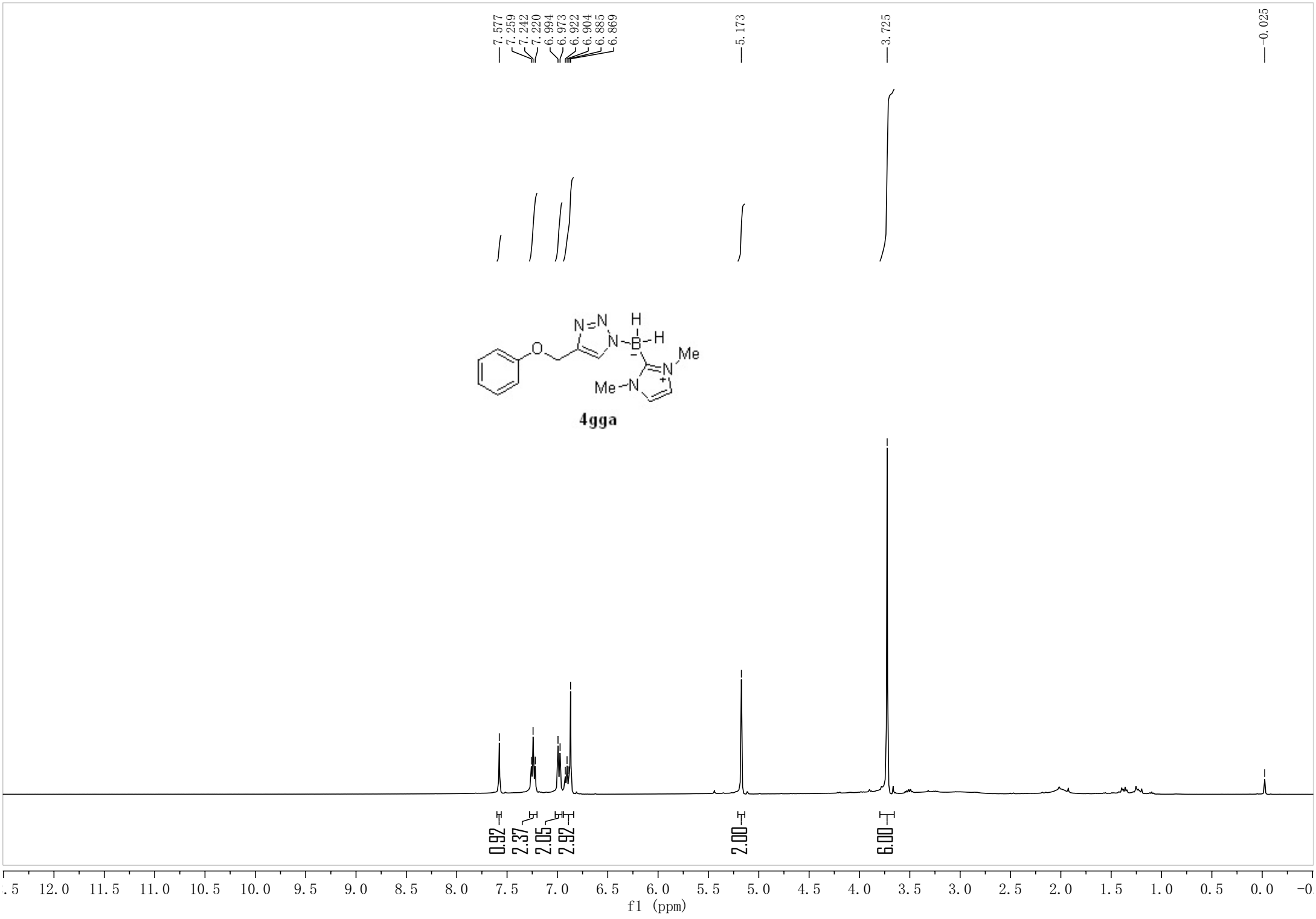

143.86
126.52
121.21
119.84
77.32
77.00
76.68
36.25
25.37
24.17
16.41
NC
H
B
H
Me
N
N
N
N
Me
4eea
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

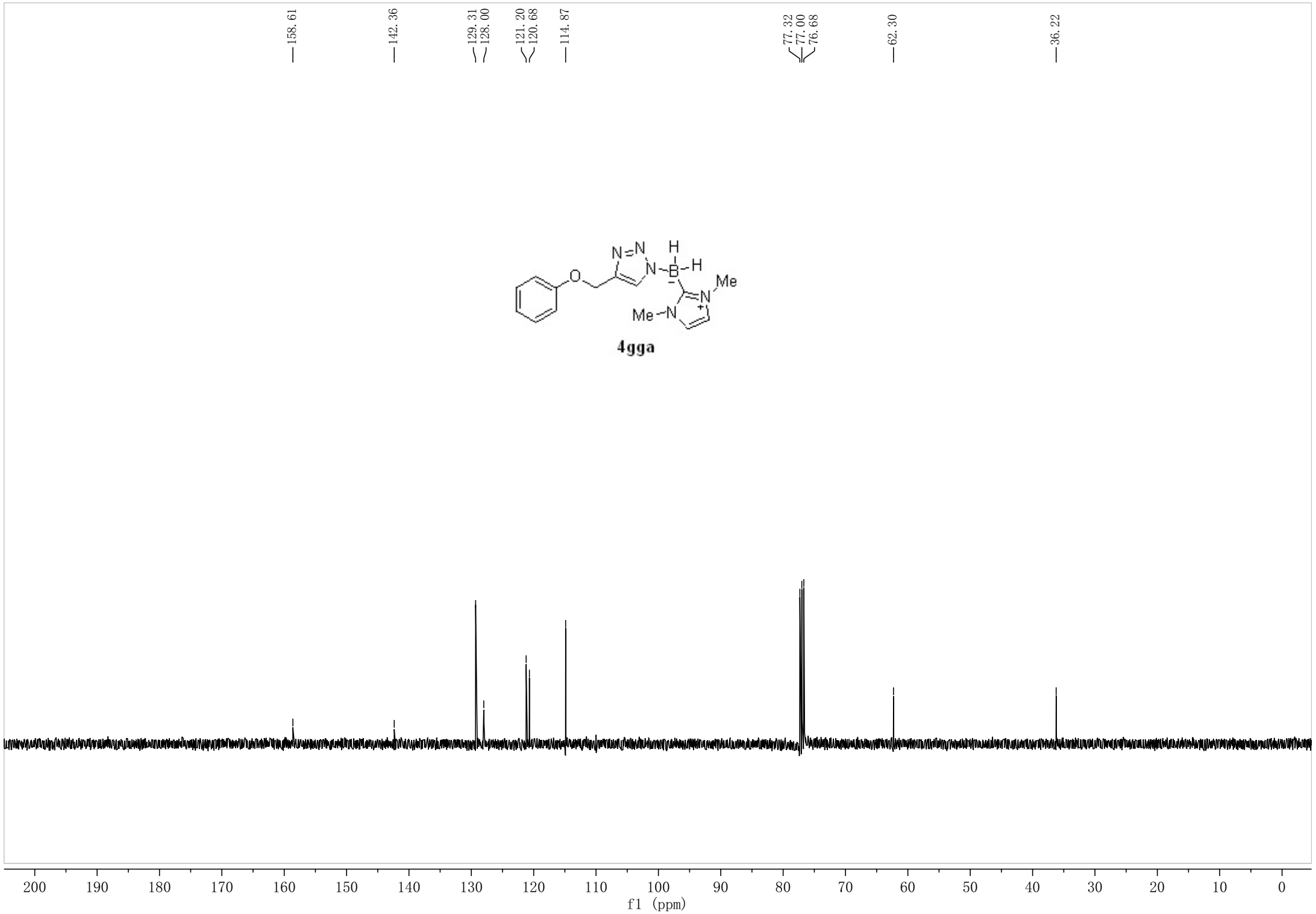

-19.21
-19.79
-20.37
NC
N=N
H
N
B
H
Bn
N
Me
N
4eea
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

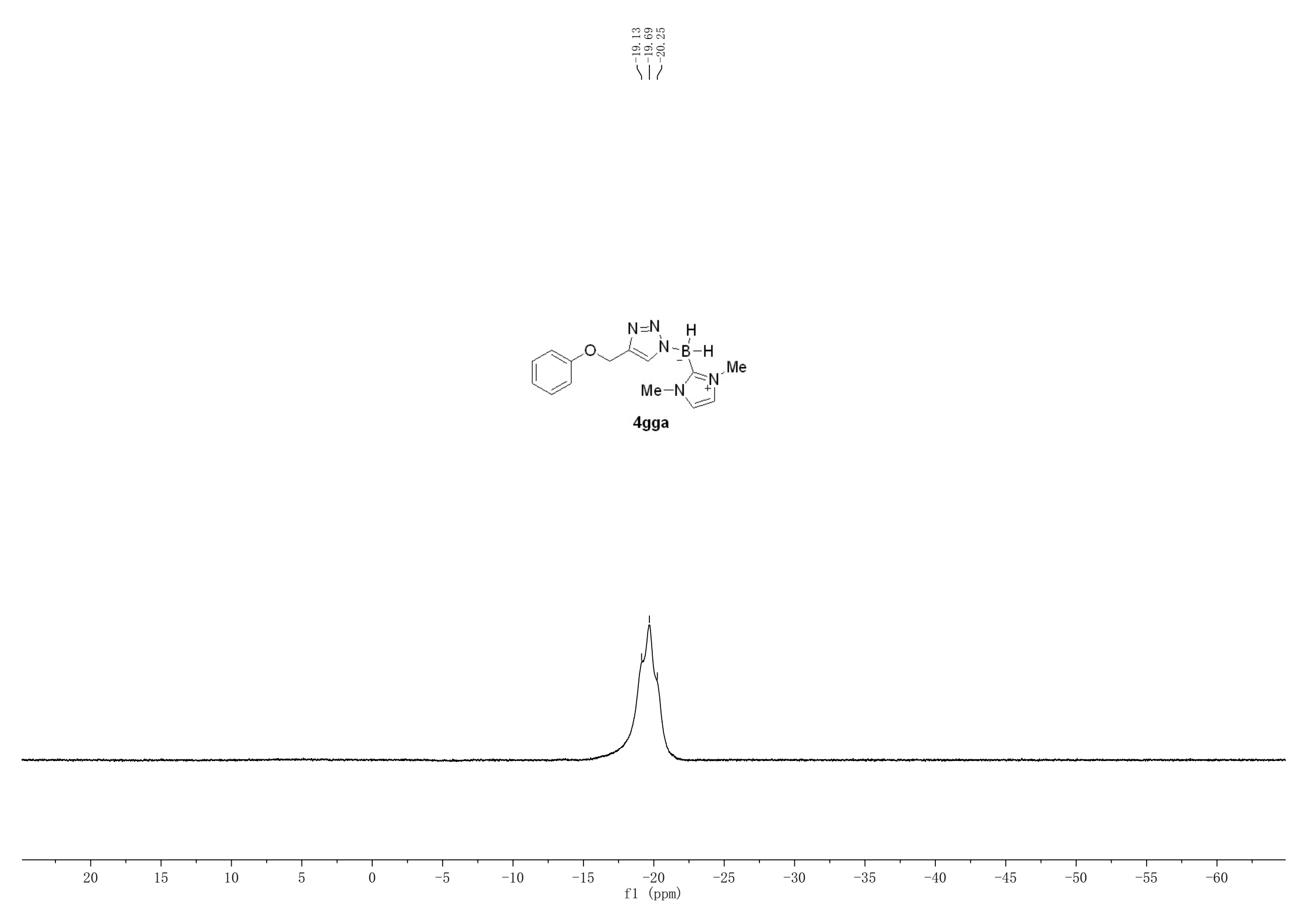

7.431
7.260
6.906
5.055
5.039
5.024
5.009
3.750
1.539
1.523
-0.020
4ffa
1.00
1.88
1.10
6.03
3.44
f1 (ppm)


150.76
125.03
121.25
77.32
77.00
76.68
62.85
36.20
22.97
-0.07
N
N
B
H
H
Me
N
OH
Me
N
4ffa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

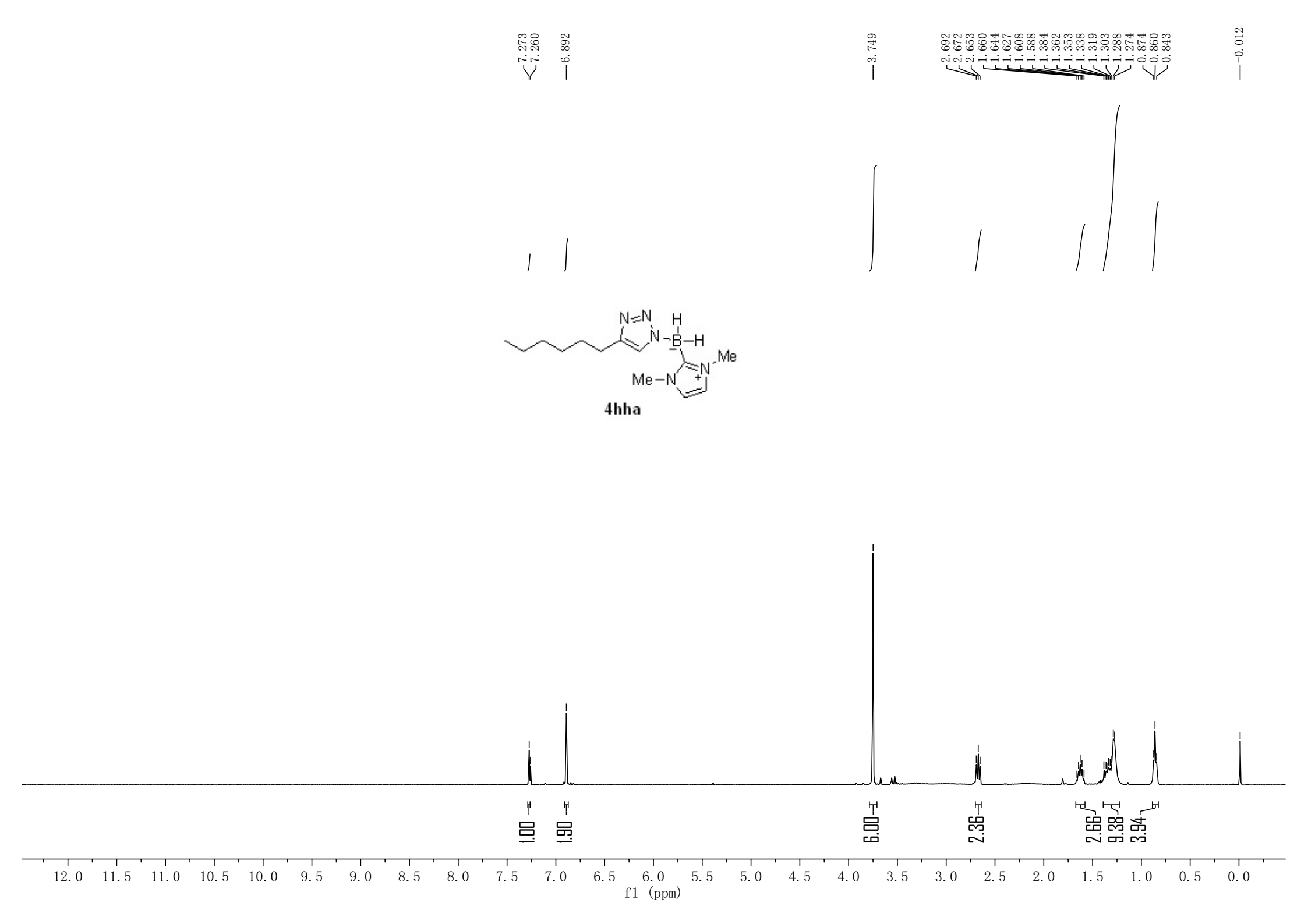

-19.55
N=N
H
N
B
H
Me
OH
Me
N
N
+
4ffa
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

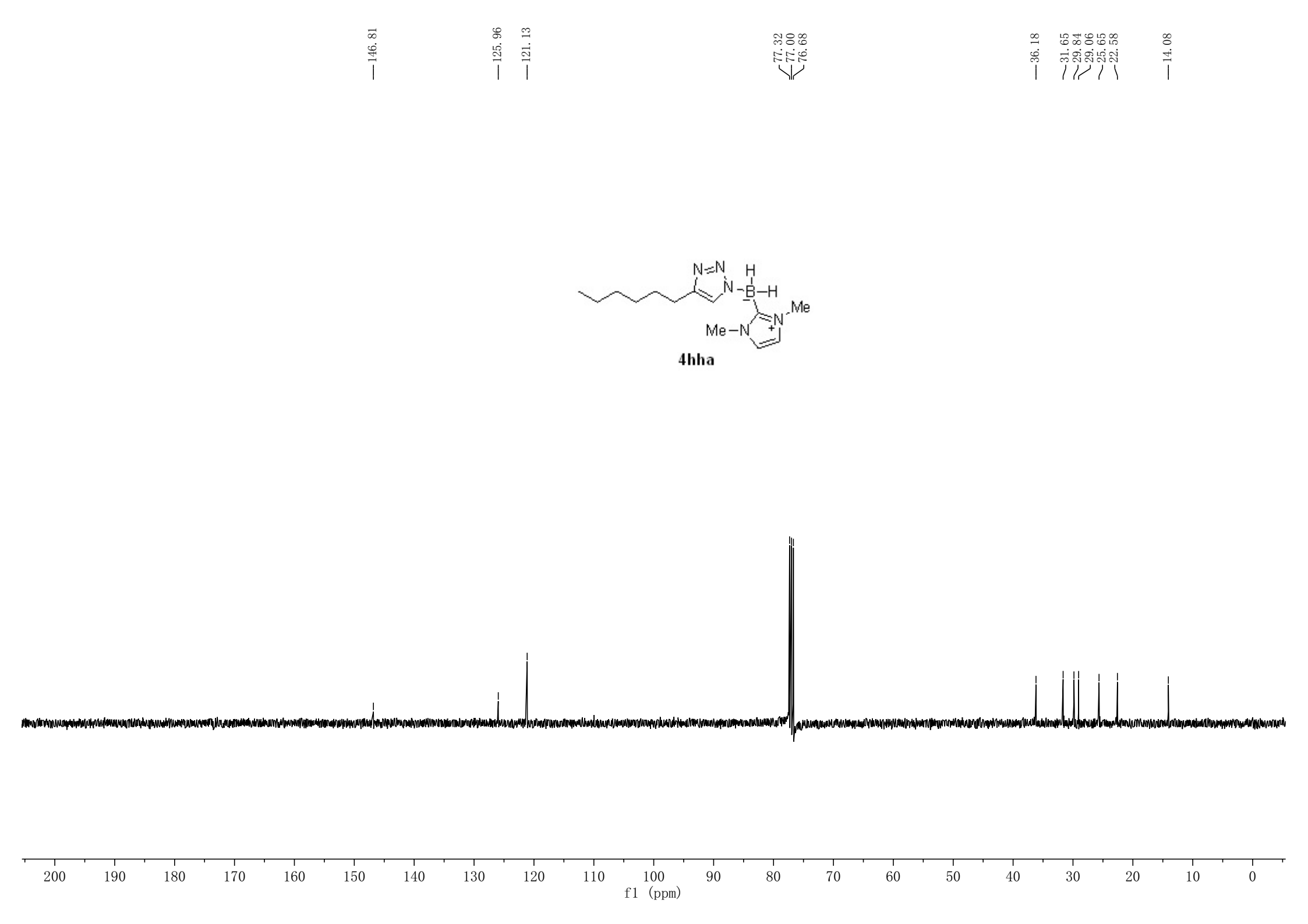

7.577
7.259
7.242
7.220
6.994
6.973
6.922
6.904
6.885
6.869
5.173
3.725
-0.025
4gga
0.92
2.37
2.05
2.92
2.00
6.00
f1 (ppm)


158.61
142.36
129.31
128.00
121.20
120.68
114.87
77.32
77.00
76.68
62.30
36.22
N=N
H
N
B
H
O
Me
N
Me
4gga
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-19.13
-19.69
-20.25
N=N
N
H
B
H
O
Me
N
Me
N
+
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)

4gga


7.273
7.260
6.892
3.749
2.692
2.672
2.653
1.660
1.644
1.627
1.608
1.588
1.384
1.362
1.353
1.338
1.319
1.303
1.288
1.274
0.874
0.860
0.843
-0.012
N=N
H
N
B
H
Me
N
Me
N
4hha
1.00
1.90
6.00
2.36
2.66
9.38
3.94
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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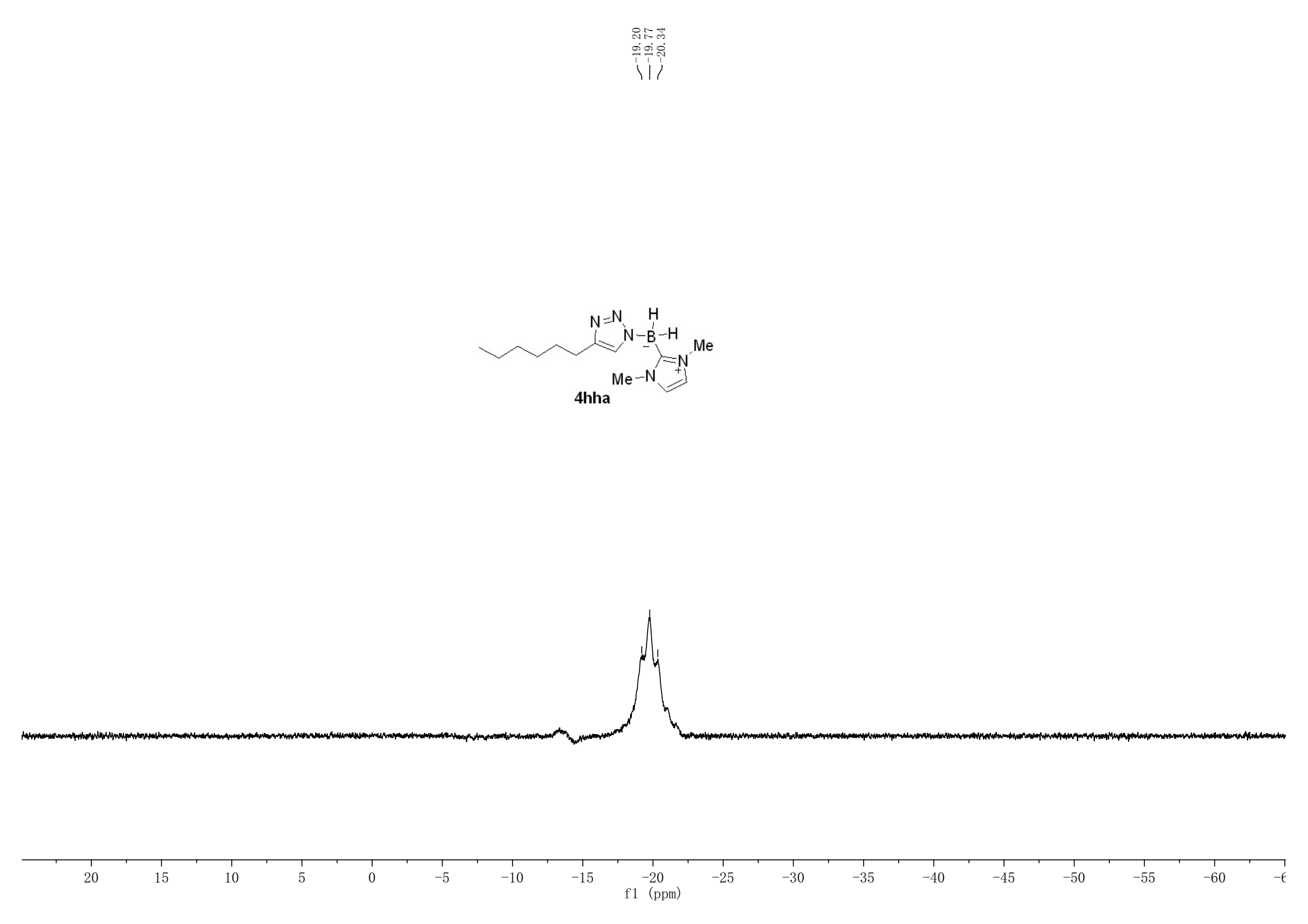
125.96
121.13
77.32
77.00
76.68
36.18
31.65
29.84
29.06
25.65
22.58
14.08
N
N
B
H
H
Me
N
Me
N
+
4hha
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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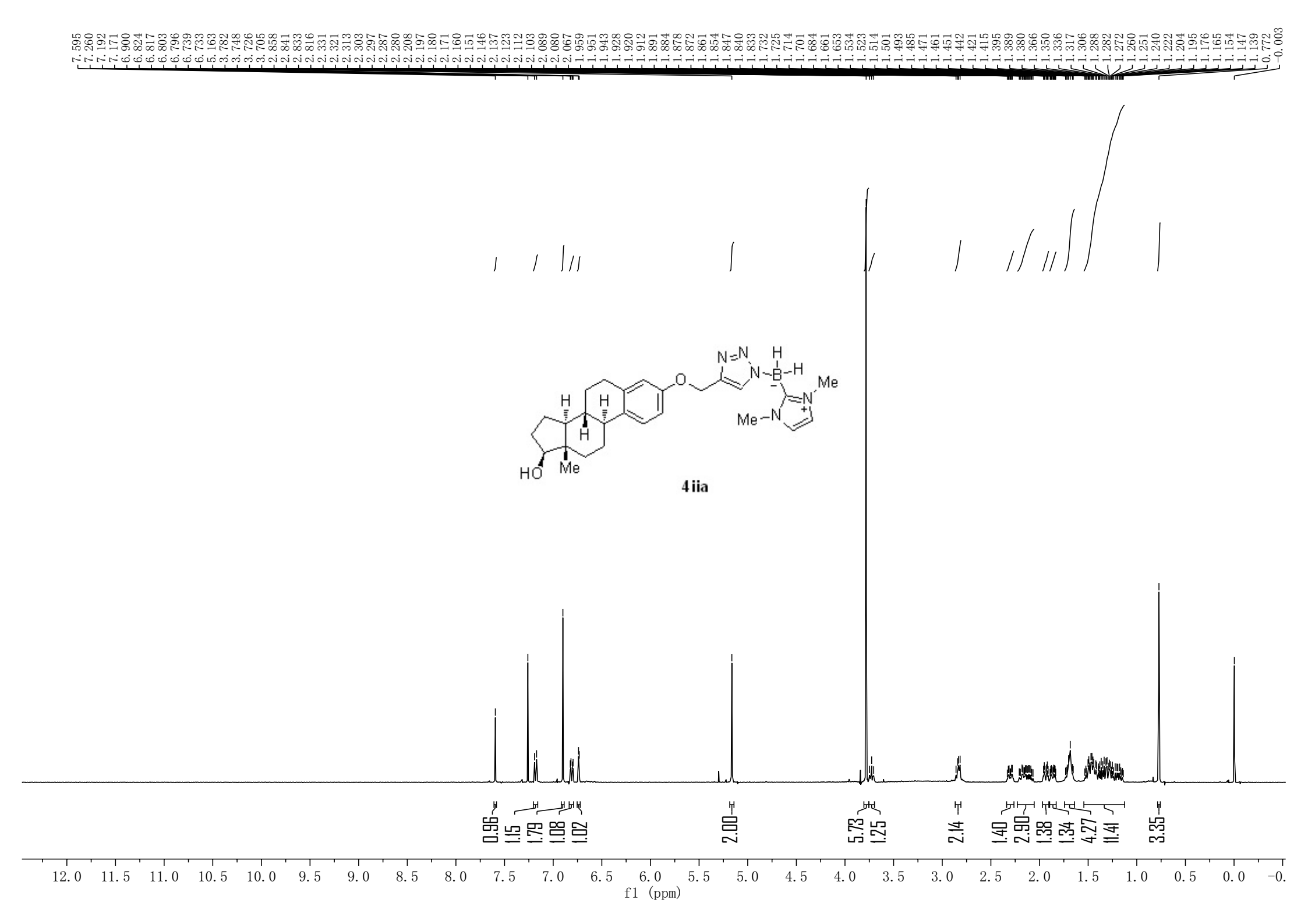
-19.77
-20.34
N
N
H
N
B
H
Me
N
Me
N
4hha
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)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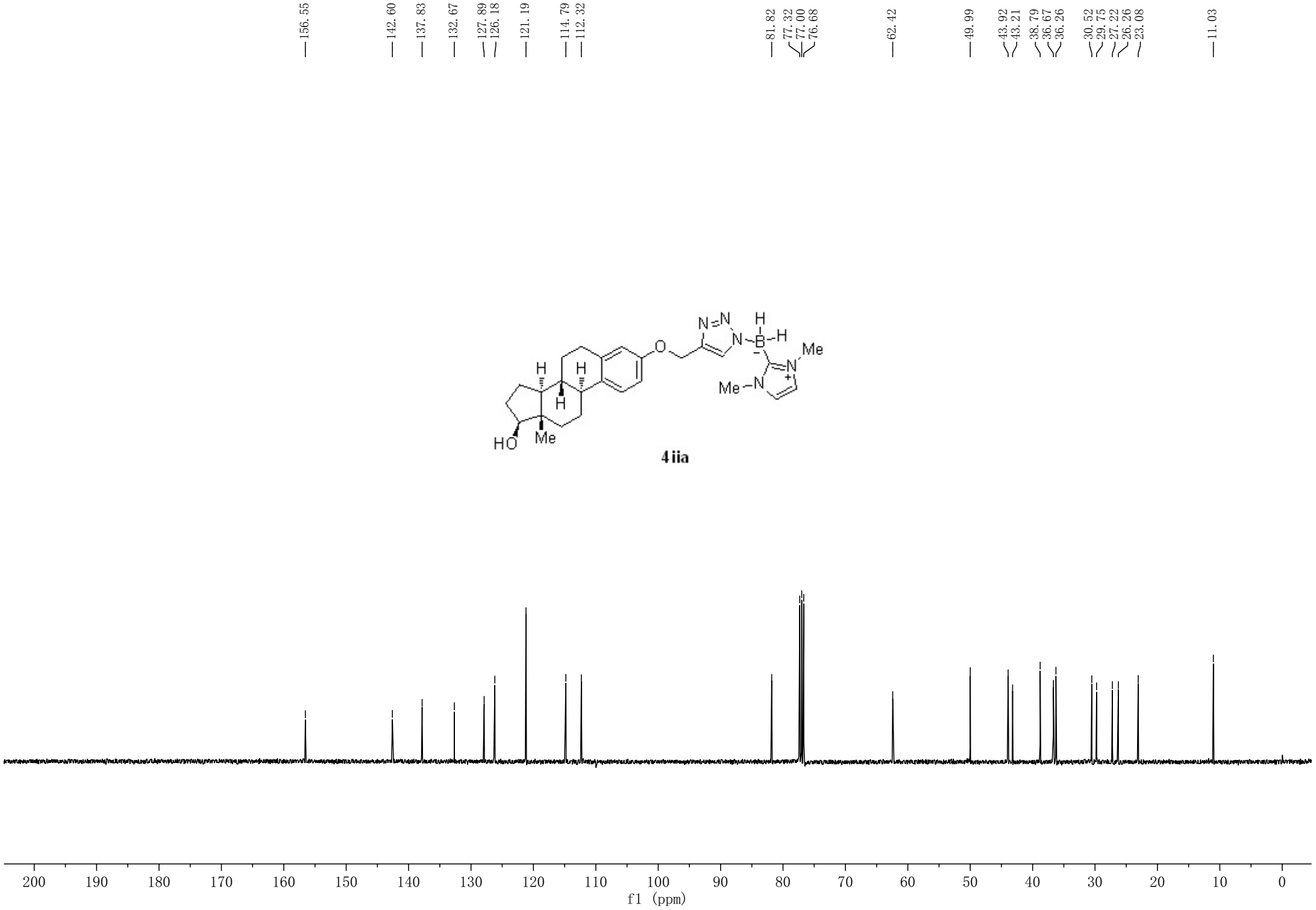
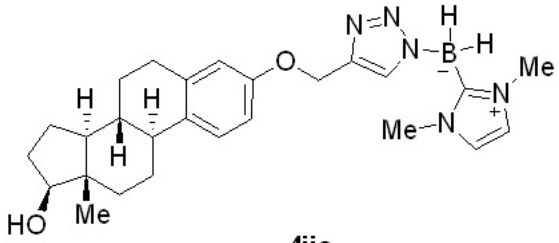
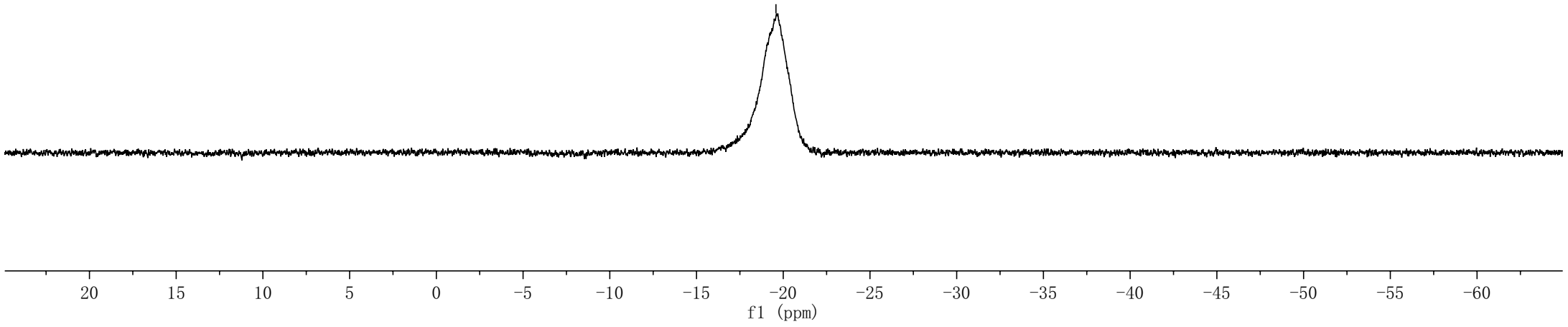
7.260
7.192
7.171
6.900
6.824
6.817
6.803
6.796
6.739
6.733
5.163
3.782
3.748
3.726
3.705
2.858
2.841
2.833
2.816
2.331
2.321
2.313
2.303
2.297
2.287
2.280
2.208
2.197
2.180
2.171
2.160
2.151
2.146
2.137
2.123
2.112
2.103
2.089
2.080
2.067
1.959
1.951
1.943
1.928
1.920
1.912
1.891
1.884
1.878
1.872
1.861
1.854
1.847
1.840
1.833
1.732
1.725
1.714
1.701
1.684
1.661
1.653
1.534
1.523
1.514
1.501
1.493
1.485
1.471
1.461
1.451
1.442
1.421
1.415
1.395
1.389
1.380
1.366
1.350
1.336
1.317
1.306
1.288
1.282
1.272
1.260
1.251
1.240
1.222
1.204
1.195
1.176
1.165
1.154
1.147
1.139
0.772
-0.003
4iia
0.96
1.15
1.79
1.08
1.02
2.00
5.73
1.25
2.14
1.40
2.90
1.38
1.34
4.27
11.41
3.35
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

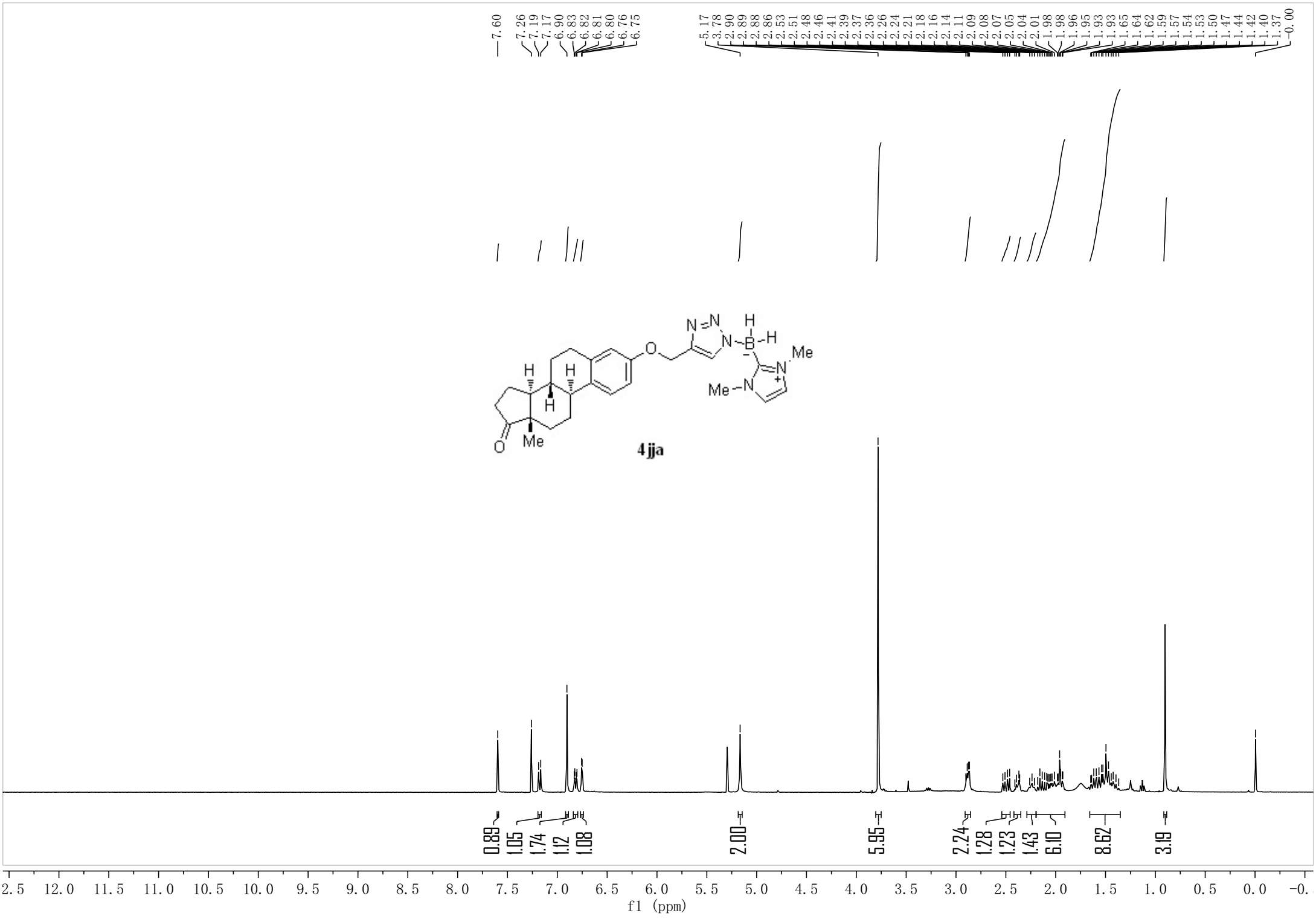

156.55
142.60
137.83
132.67
127.89
126.18
121.19
114.79
112.32
81.82
77.32
77.00
76.68
62.42
49.99
43.92
43.21
38.79
36.67
36.26
30.52
29.75
27.22
26.26
23.08
11.03
N=N
N
B
H
H
Me
N
Me
N
O
H
H
H
HO
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

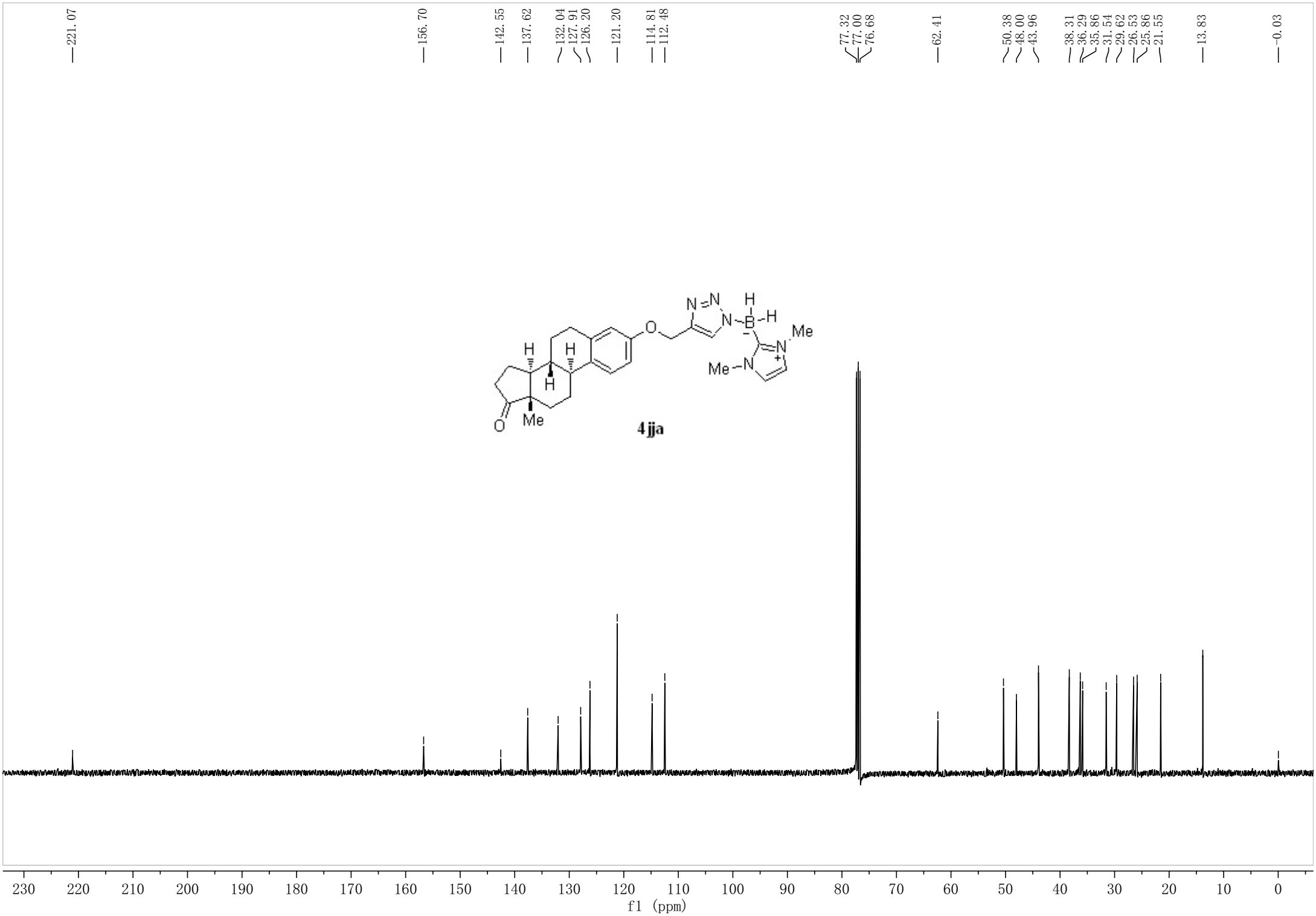
4iia


H
H
H
HO
Me
O
N
N
N
B
H
H
Me
N
Me
N

4iia


-19.58
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)


7.60
7.26
7.19
7.17
6.90
6.83
6.82
6.81
6.80
6.76
6.75
5.17
3.78
2.90
2.89
2.88
2.86
2.53
2.51
2.48
2.46
2.41
2.39
2.37
2.36
2.26
2.24
2.21
2.18
2.16
2.14
2.11
2.09
2.08
2.07
2.05
2.04
2.01
1.98
1.98
1.96
1.95
1.93
1.93
1.65
1.64
1.62
1.59
1.57
1.54
1.53
1.50
1.47
1.44
1.42
1.40
1.37
-0.00
4jja
0.89
1.05
1.74
1.12
1.08
2.00
5.95
2.24
1.28
1.23
1.43
6.10
8.62
3.19
f1 (ppm)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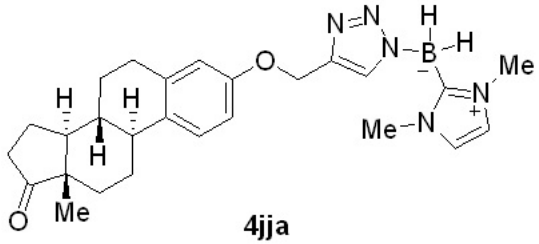
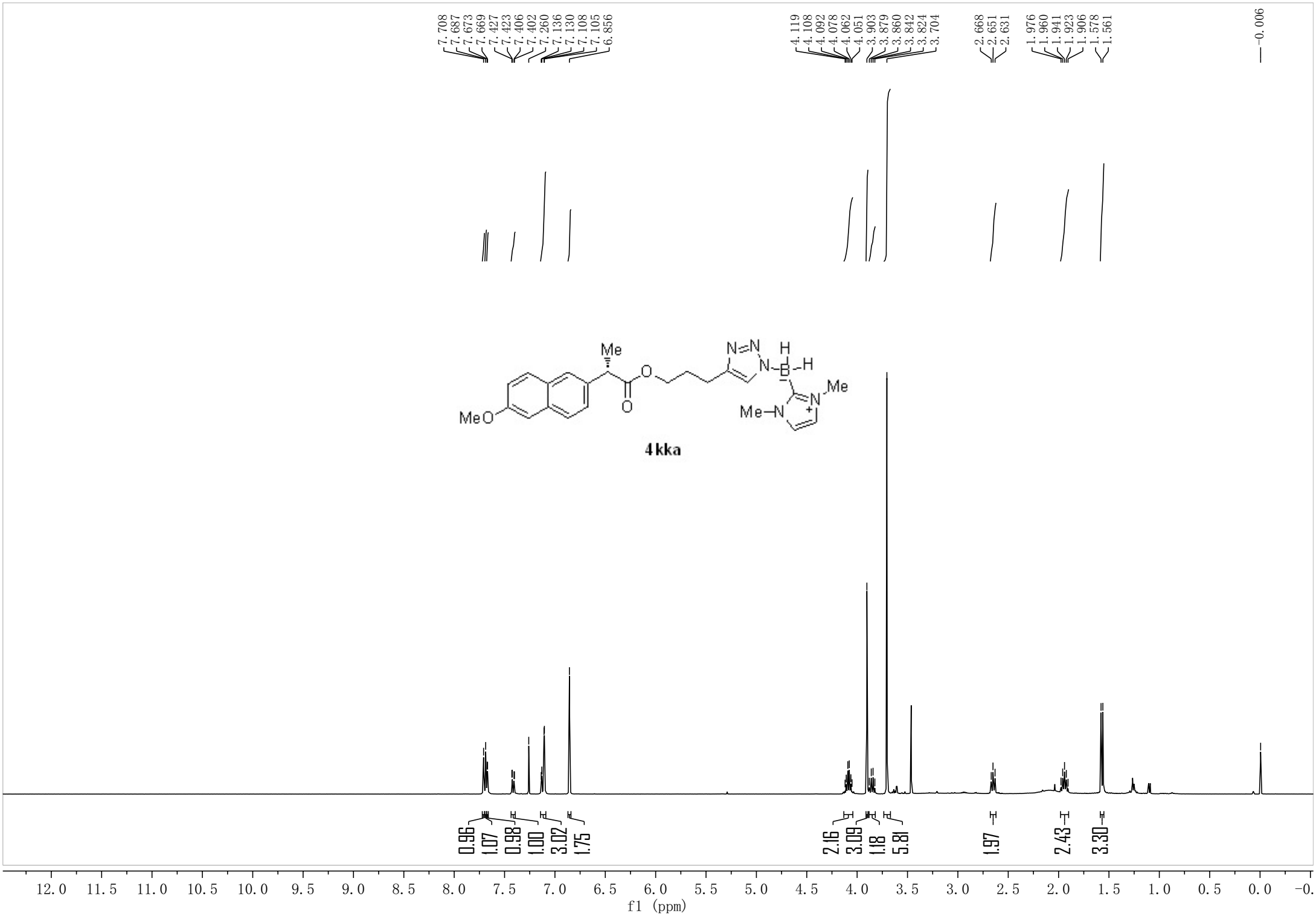
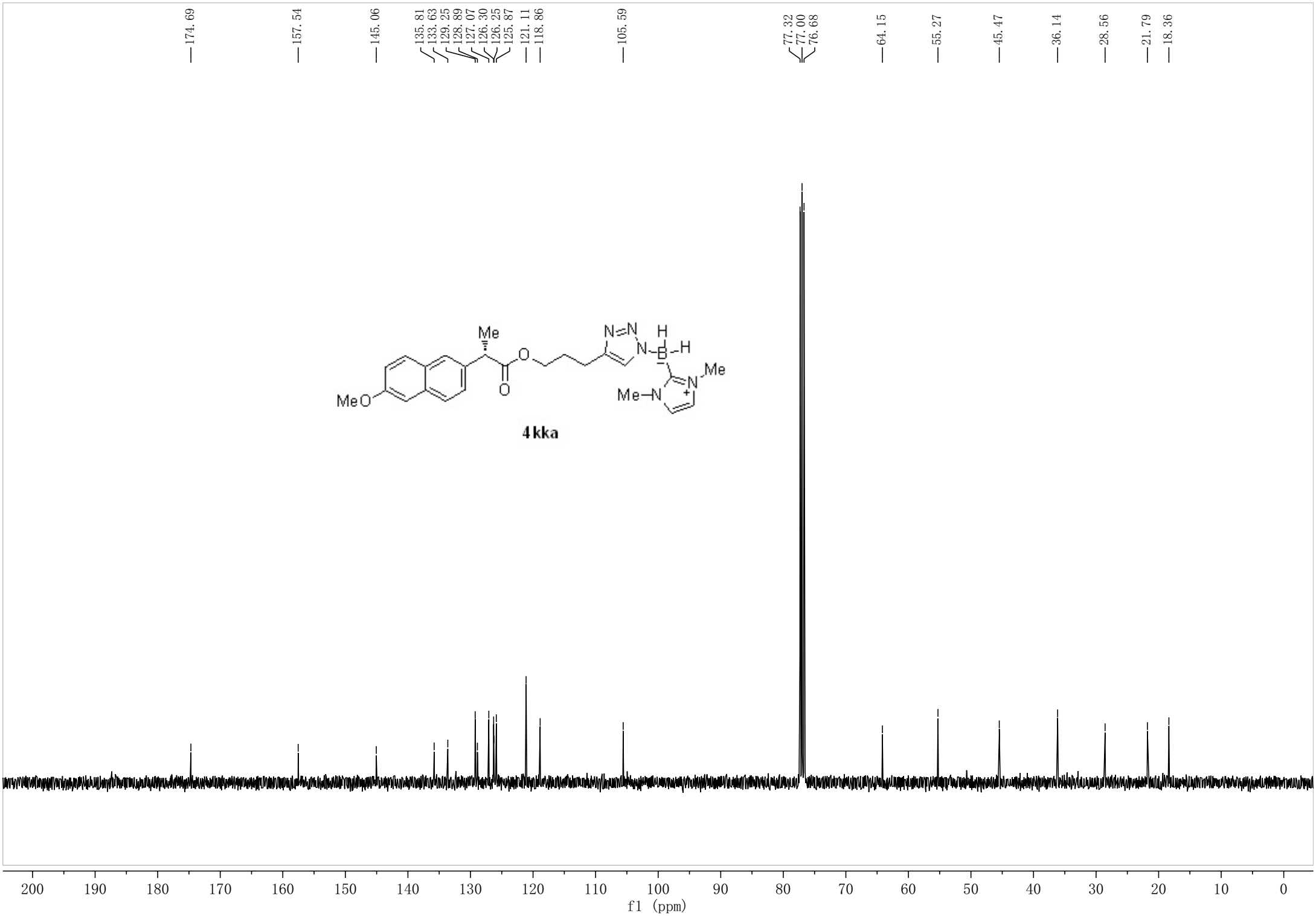
156.70
142.55
137.62
132.04
127.91
126.20
121.20
114.81
112.48
77.32
77.00
76.68
62.41
50.38
48.00
43.96
38.31
36.29
35.86
31.54
29.62
26.53
25.86
21.55
13.83
-0.03
4jja
f1 (ppm)

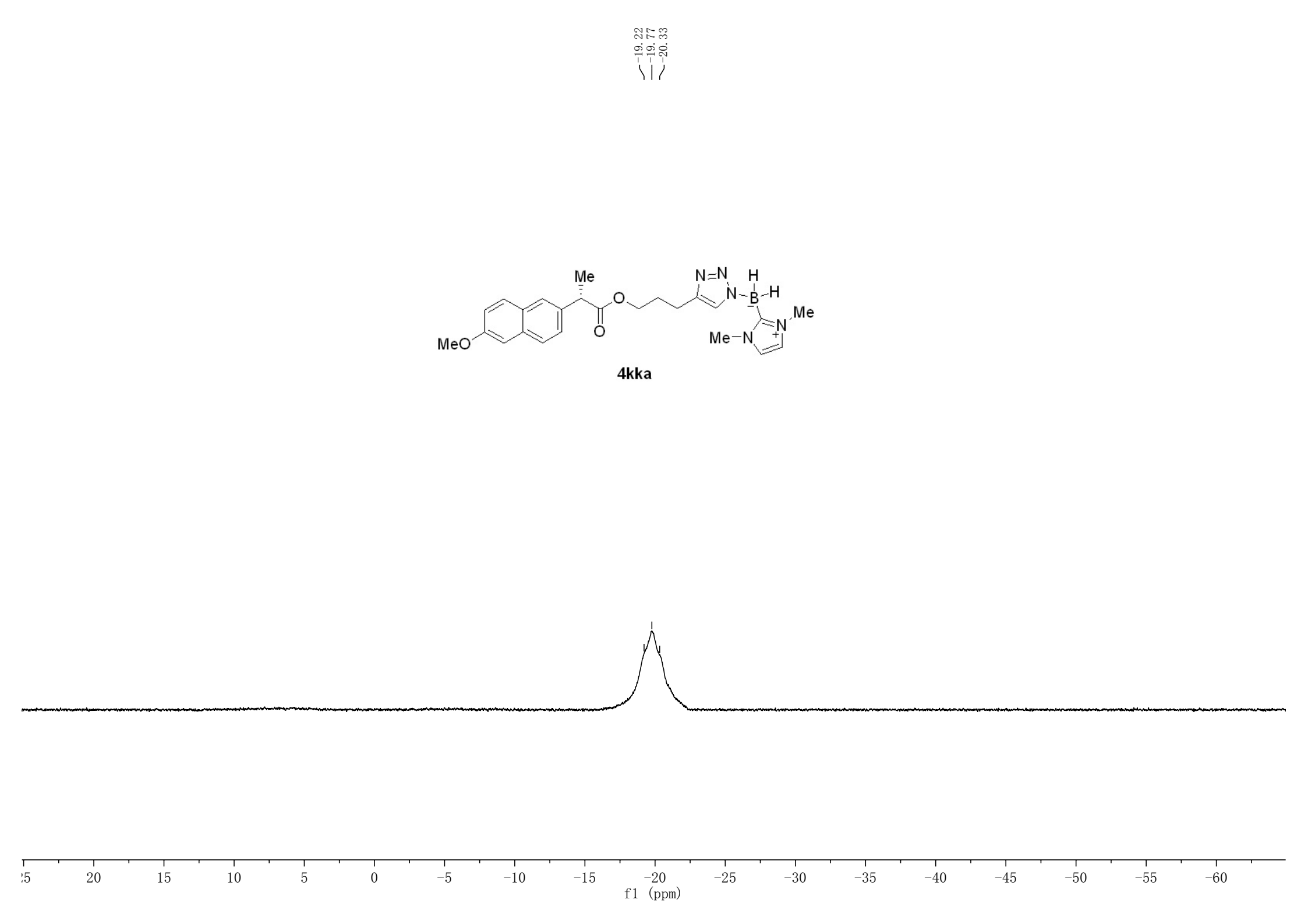

H
H
H
O
Me
O
N
N
N
B
H
H
Me
N
Me
N

4jja

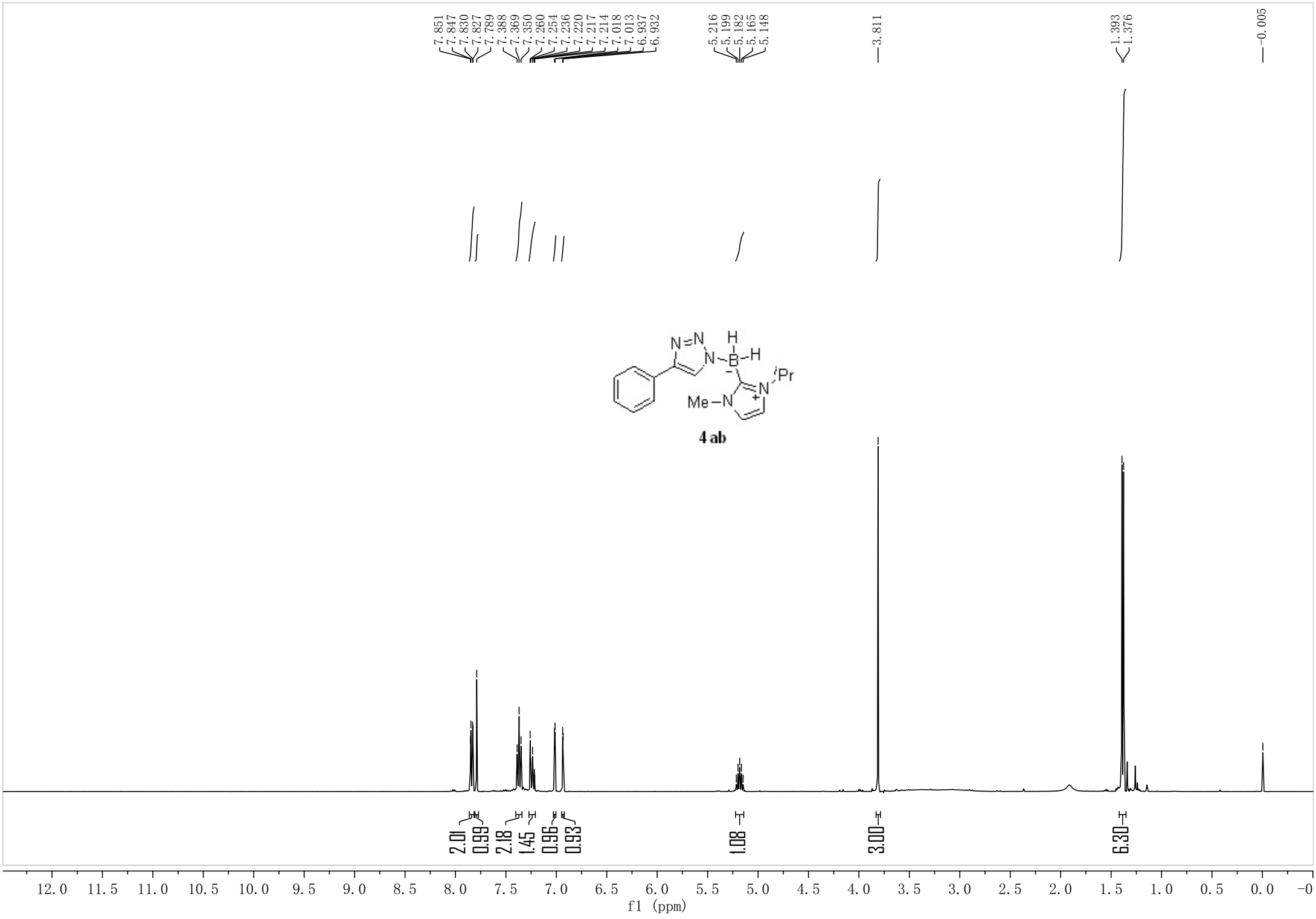
-19.60
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-6
f1 (ppm)


7.708
7.687
7.673
7.669
7.427
7.423
7.406
7.402
7.260
7.136
7.130
7.108
7.105
6.856
4.119
4.108
4.092
4.078
4.062
4.051
3.903
3.879
3.860
3.842
3.824
3.704
2.668
2.651
2.631
1.976
1.960
1.941
1.923
1.906
1.578
1.561
-0.006
Me
O
O
N=N
N
B
H
H
Me
N
Me
Me
N
MeO
4kka
0.96
1.07
0.98
1.00
3.02
1.75
2.16
3.09
1.18
5.81
1.97
2.43
3.30
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

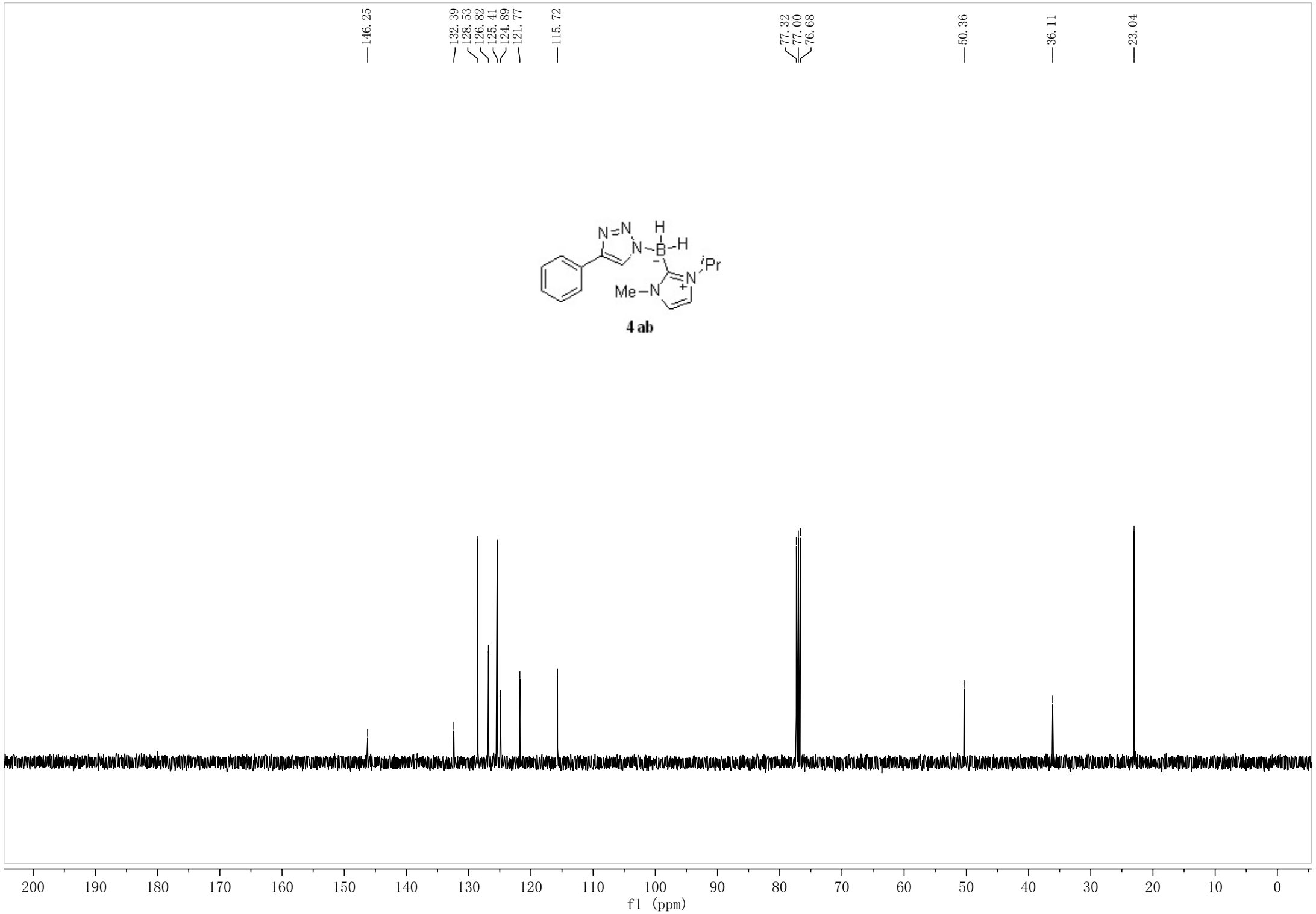

174.69
157.54
145.06
135.81
133.63
129.25
128.89
127.07
126.30
126.25
125.87
121.11
118.86
105.59
77.32
77.00
76.68
64.15
55.27
45.47
36.14
28.56
21.79
18.36
Me
O
O
N=N
H
N
B
H
Me
N
Me
N
+
MeO
4kka
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

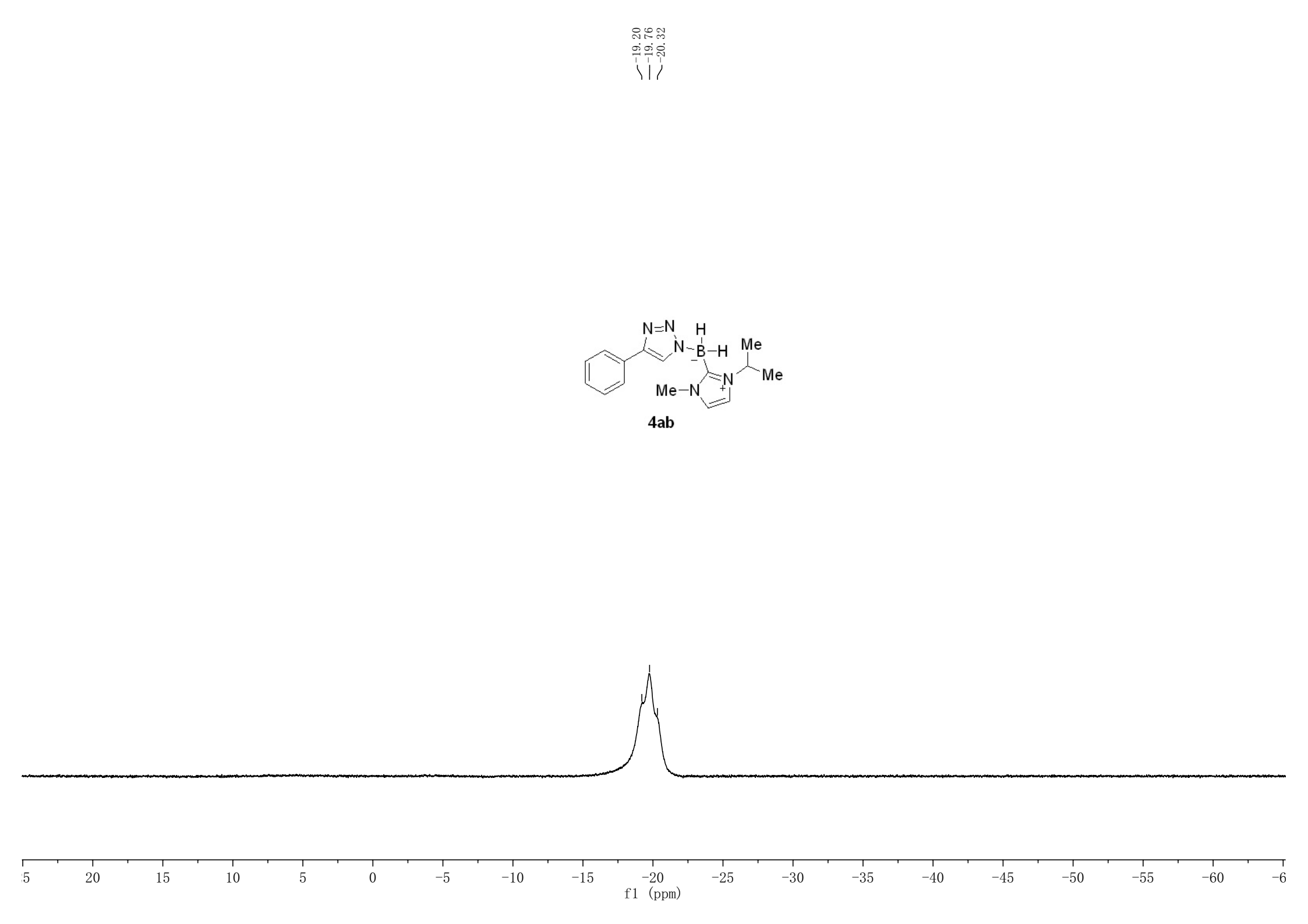


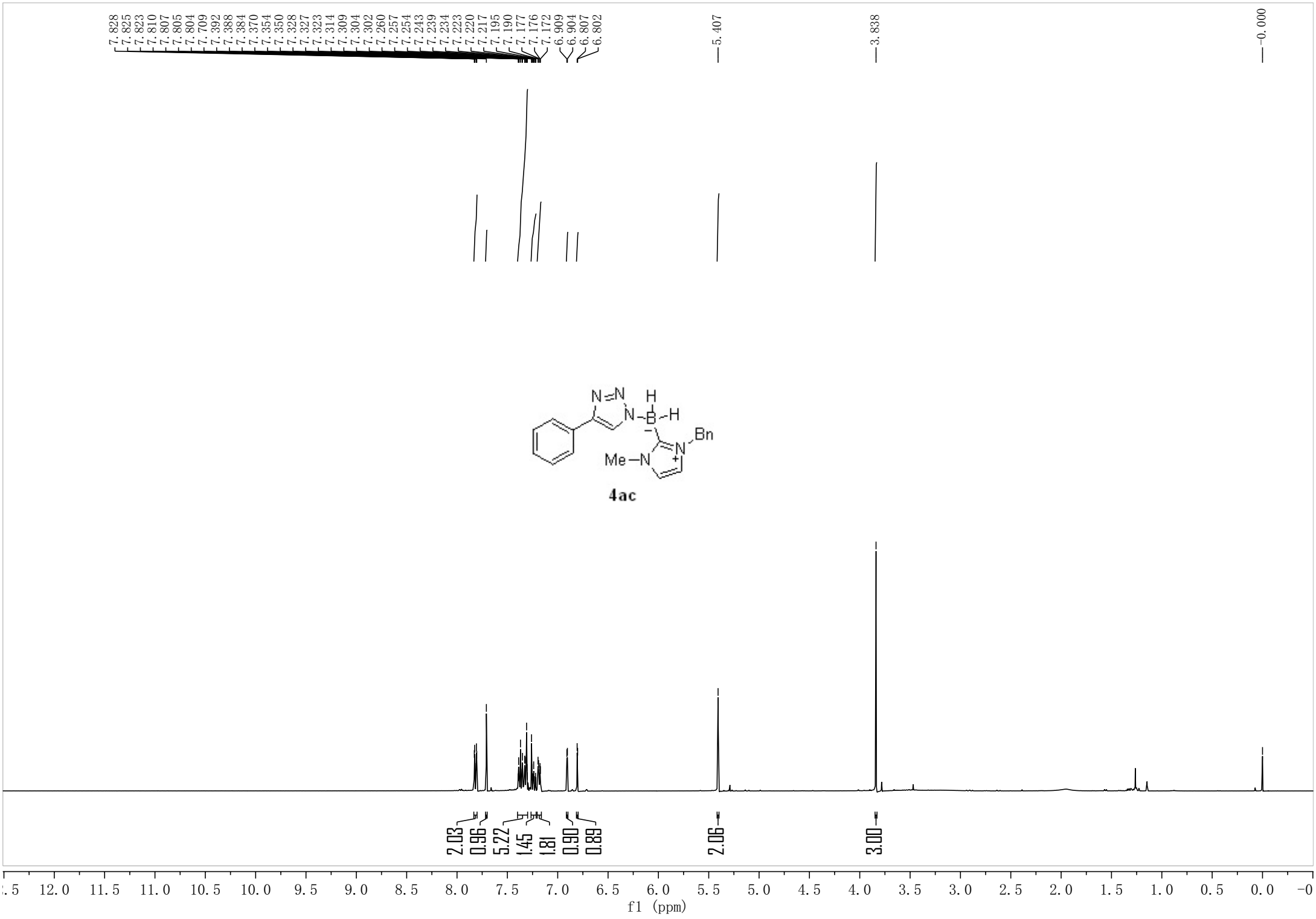
4kka


7.851
7.847
7.830
7.827
7.789
7.388
7.369
7.350
7.260
7.254
7.236
7.220
7.217
7.214
7.018
7.013
6.937
6.932
5.216
5.199
5.182
5.165
5.148
3.811
1.393
1.376
0.005
N=N
H
N
B
H
iPr
Me
N
2.01
0.99
2.18
1.45
0.96
0.93
1.08
3.00
6.30
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

4ab


146.25
132.39
128.53
126.82
125.41
124.89
121.77
115.72
77.32
77.00
76.68
50.36
36.11
23.04
N=N
H
N
B
H
iPr
N
Me
N
+
4 ab
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-19.20
-19.76
-20.32
N=N
N
B
H
H
Me
Me
N
Me
N
4ab
5
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-6
f1 (ppm)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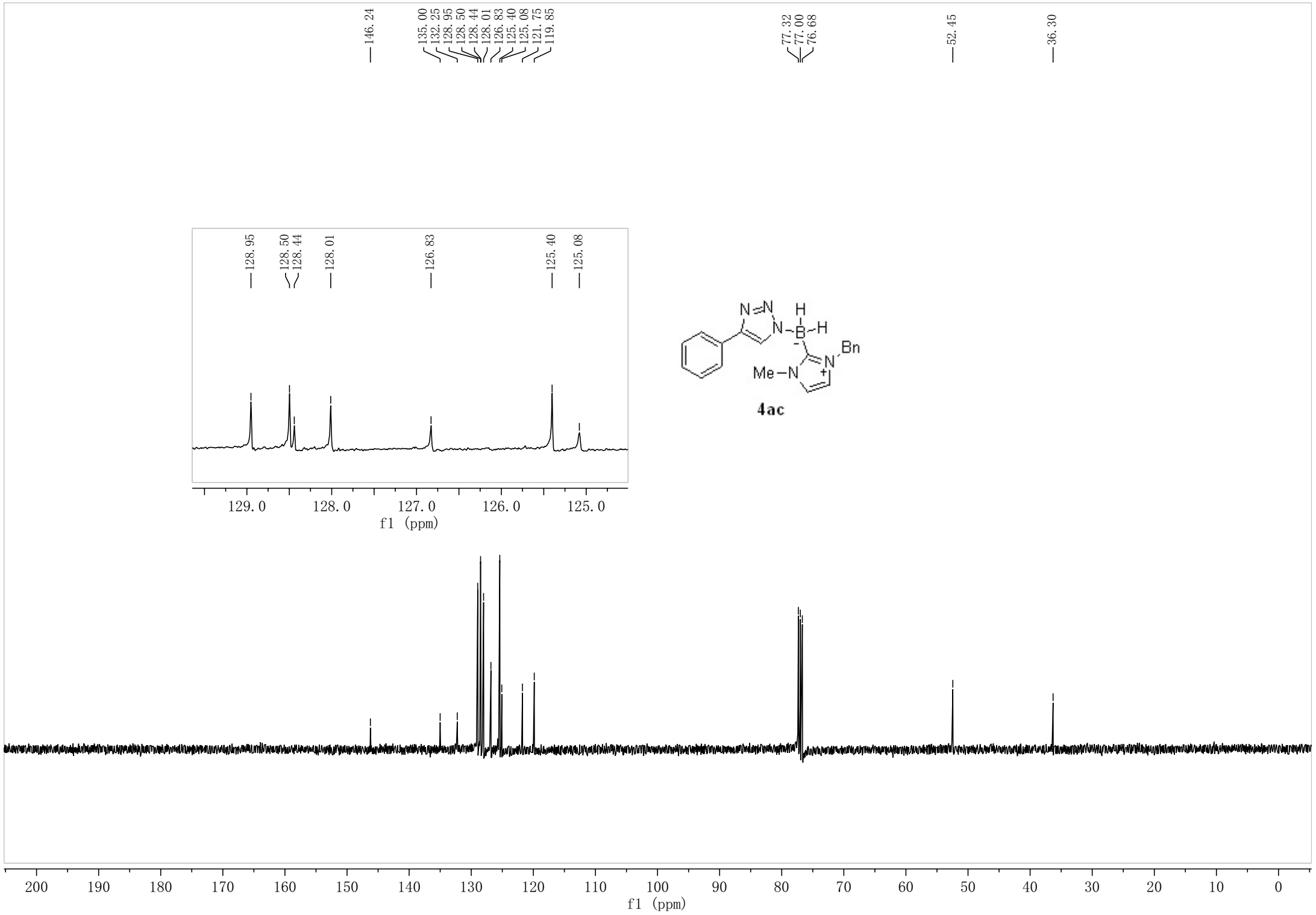
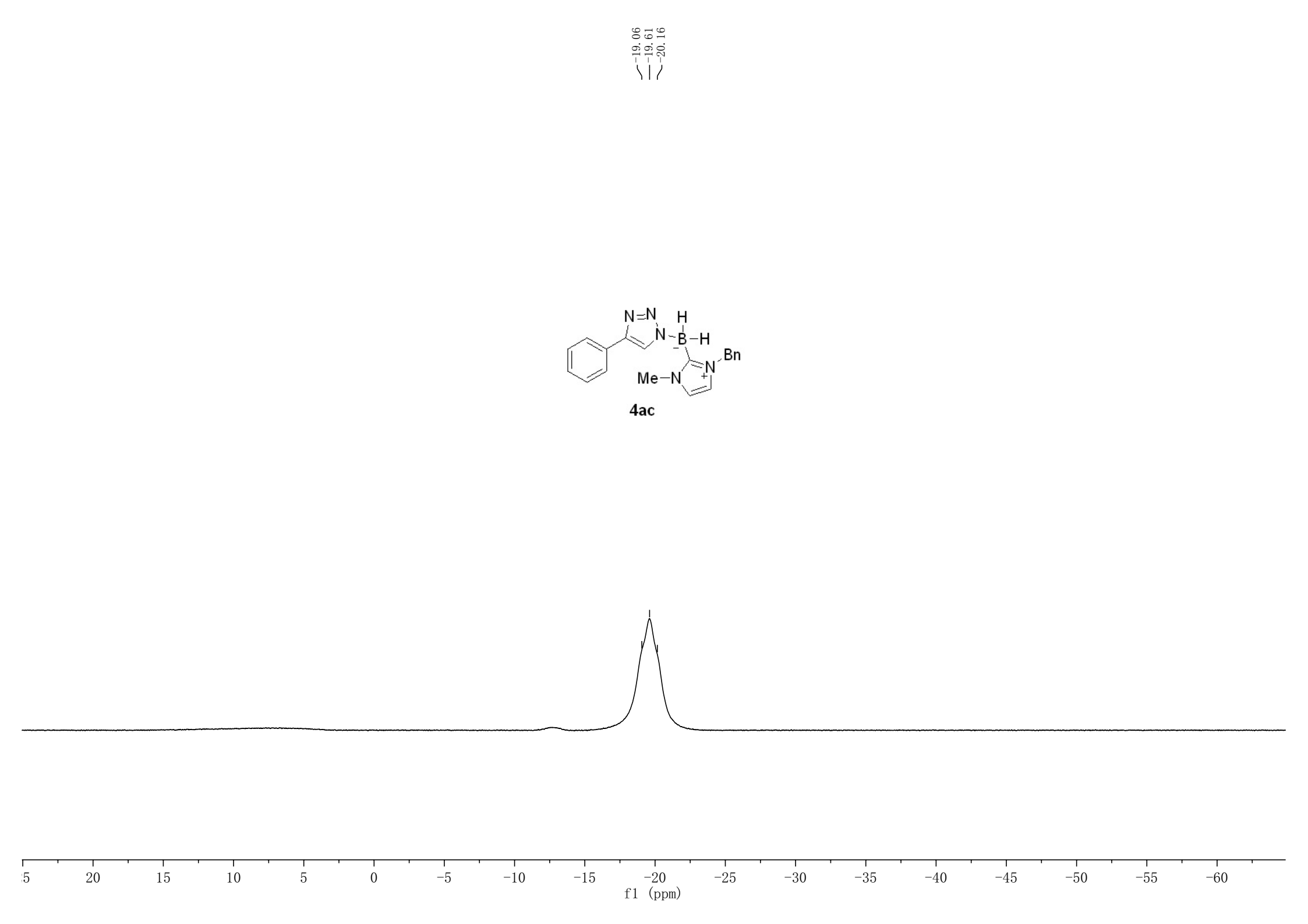
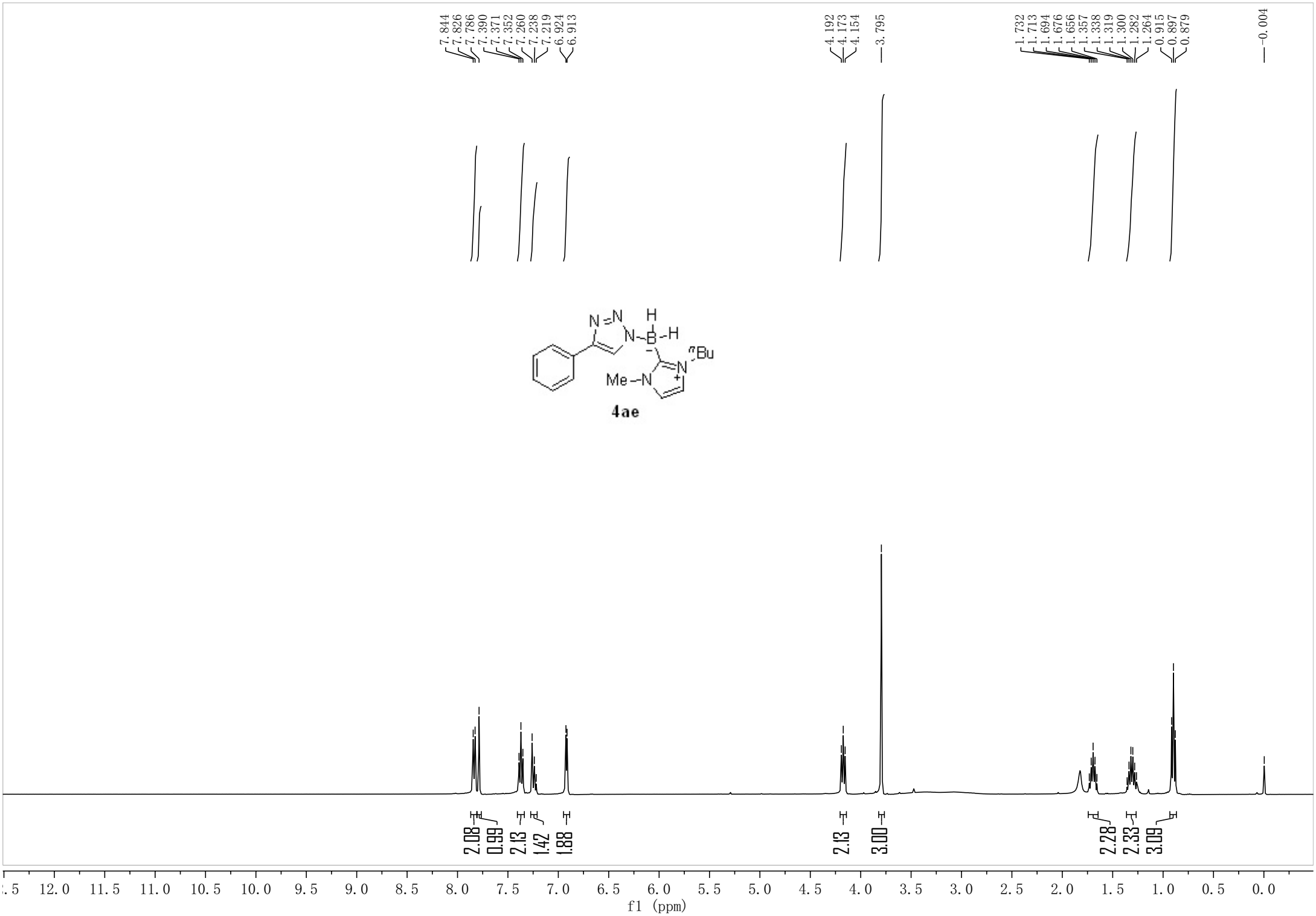
7.825
7.823
7.810
7.807
7.805
7.804
7.709
7.392
7.388
7.384
7.370
7.354
7.350
7.328
7.327
7.323
7.314
7.309
7.304
7.302
7.260
7.257
7.254
7.243
7.239
7.234
7.223
7.220
7.217
7.195
7.190
7.177
7.176
7.172
6.909
6.904
6.807
6.802
5.407
3.838
0.000
N
N
H
B
H
Bn
Me
N
2.03
0.96
5.22
1.45
1.81
0.90
0.89
2.06
3.00
f1 (ppm)

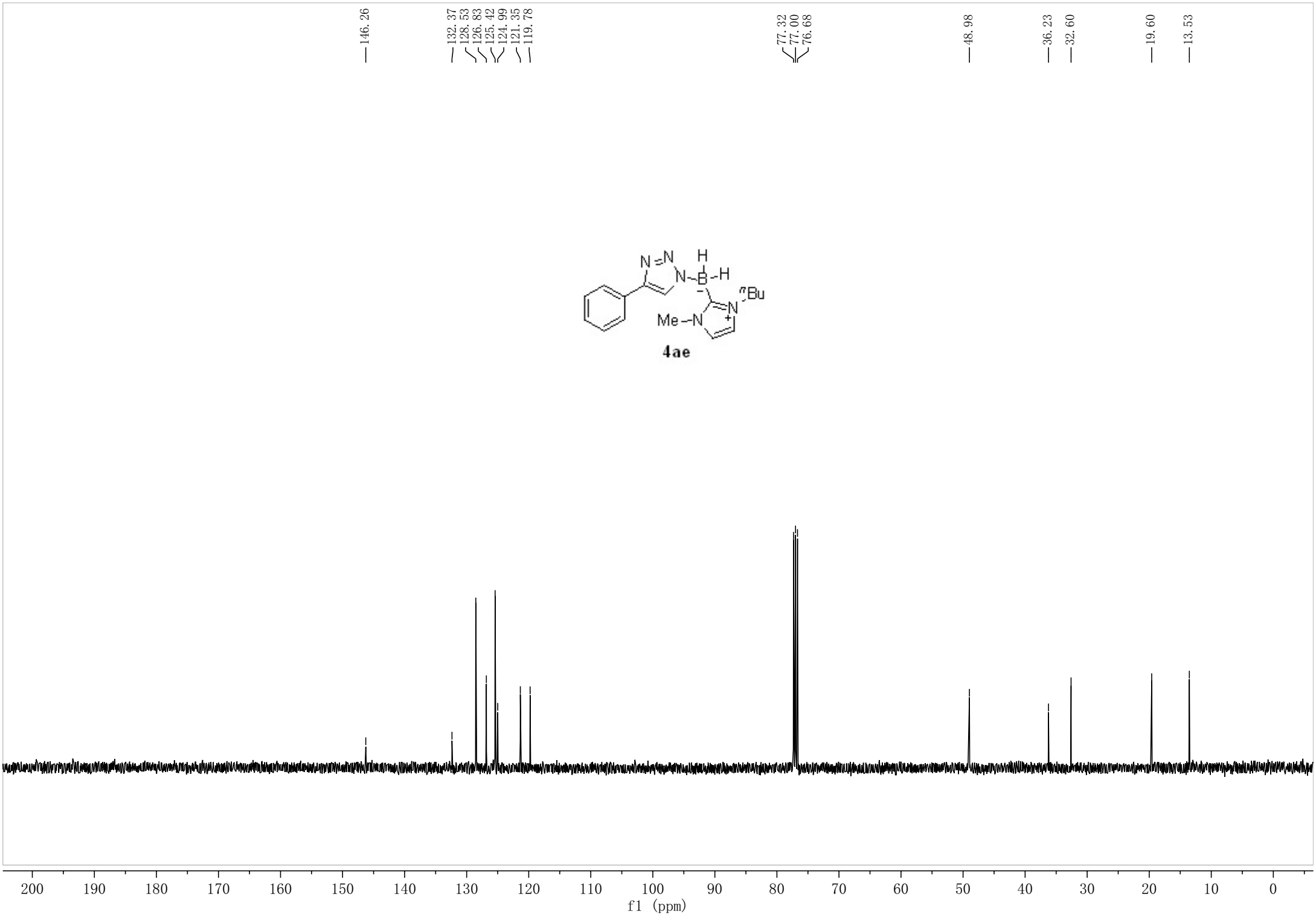
4ac

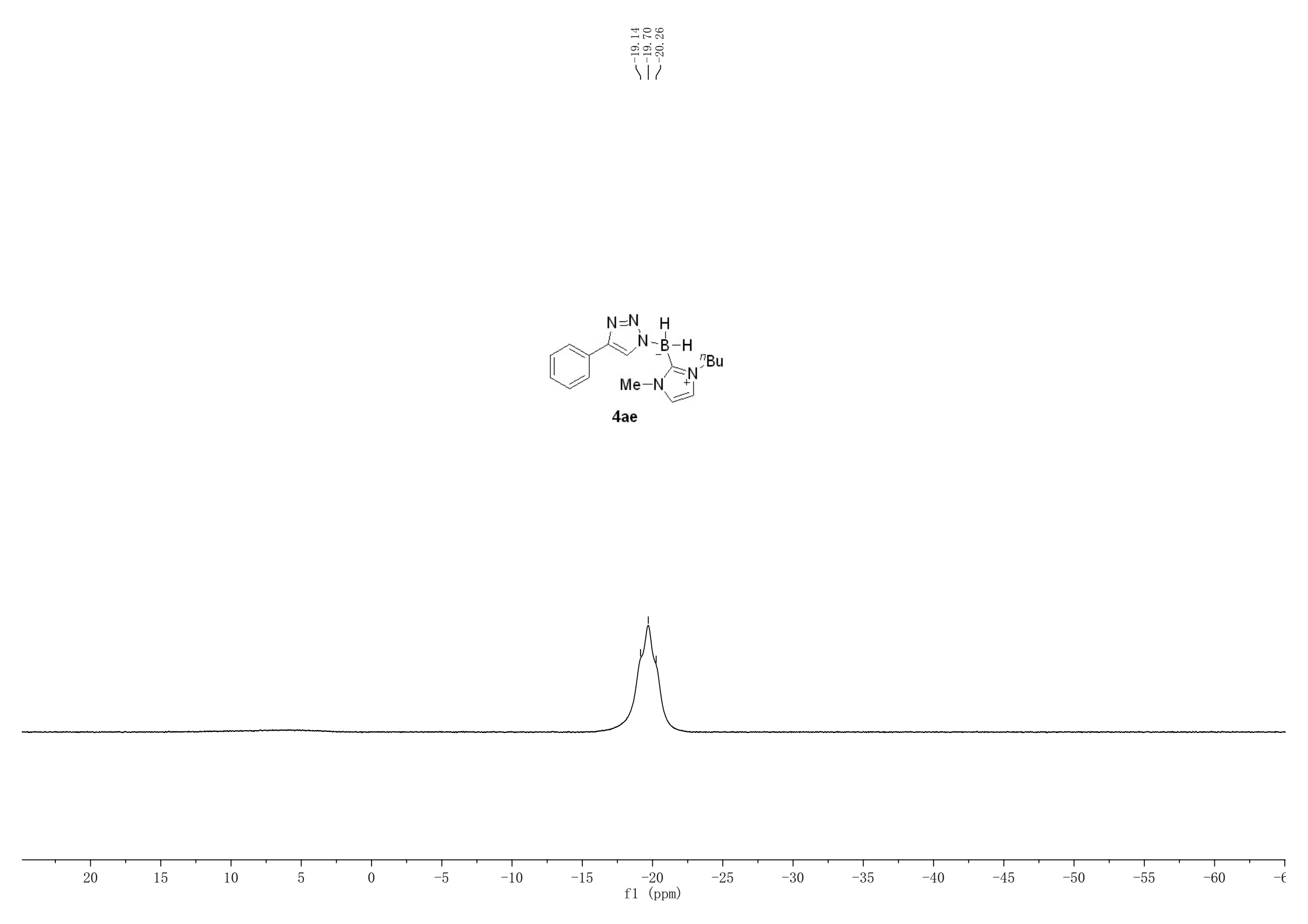

146.24
135.00
132.25
128.95
128.50
128.44
128.01
126.83
125.40
125.08
121.75
119.85
77.32
77.00
76.68
52.45
36.30
128.95
128.50
128.44
128.01
126.83
125.40
125.08
129.0
128.0
127.0
126.0
125.0
f1 (ppm)
N
N
H
B
H
Bn
Me
4ac
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-19.06
-19.61
-20.16
N=N
H
N
B
H
Bn
N
Me
N
4ac
5
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)


7.844
7.826
7.786
7.390
7.371
7.352
7.260
7.238
7.219
6.924
6.913
4.192
4.173
4.154
3.795
1.732
1.713
1.694
1.676
1.656
1.357
1.338
1.319
1.300
1.282
1.264
0.915
0.897
0.879
-0.004
N
N
H
B
H
Bu
Me
N
2.08
0.99
2.13
1.42
1.88
2.13
3.00
2.28
2.33
3.09
f1 (ppm)

4ae


146.26
132.37
128.53
126.83
125.42
124.99
121.35
119.78
77.32
77.00
76.68
48.98
36.23
32.60
19.60
13.53
N=N
H
N-B-H
nBu
N
Me-N
+
4ae
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-19.14
-19.70
-20.26
N=N
H
N
B
H
nBu
N
Me
N
4ae
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)