Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A facile approach for synthesis of *nido*-carborane fused oxazoles via one pot deboronation/cyclization of 9-amide-*o*-carboranes

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Context

General information

1a-1s were synthesized according to literature methods（The detailed procedure were shown in the experimental section）[1-3]. Other materials were purchased from Acros, J&K and Aladdin, and used as received unless otherwise specified. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petroleum ether was 60-90 ^{o}C. ^{1}H, ^{1}H{^{11}B }, ^{13}C{^{1}H}, ^{11}B{^{1}H} and B^{11} NMR spectra were recorded on the Bruker 600MHz instruments. All ^{1}H NMR and ^{13}C{^{1}H} NMR spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard, and ^{11}B{^{1}H} NMR spectral data was referenced to external BF_3•Et_2O. HRMS data were measured with ESI techniques.

The calculations were performed using the DFT program Dmol3 in Materials Studio (Accelrys, San Diego, CA), in which the physical wave functions were expanded in terms of numerical basis sets. The double numerical basis set with polarisation function (DNP)[4,5], that is comparable to the 6-31G** basis set, was utilised during the calculations[6]. The core electrons were treated with DFT semicore pseudopotentials. The exchange-correlation energy was calculated using the PBE and GGA methods[7]. Special point sampling integration over the Brillouin zone was employed using Monkhorst-Pack schemes with a 5 × 5 × 1 k-point mesh[8]. A Fermi smearing of 0.005 Ha and a global orbital cutoff of 7 Å were employed. The convergence criteria for the geometric optimization and energy calculation were set as follows: (1) self-consistent field tolerance of 1.0×10^{-6} Ha/atom, (2) energy tolerance of 1.0×10^{-5} Ha/atom, (3) maximum force tolerance of 0.002 Ha/Å, and (4) maximum displacement tolerance of 0.005 Å.

Experimental

1. **General procedure for synthesis of 1a-1p (Take 1a as an example)**[1,2]

To a 25 mL dried flask was sequentially added 9-iodo-*o*-carborane (500 mg, 1.85 mmol), 3 equivalents of benzamide (671.5 mg, 5.54 mmol), 5 equivalents of K_3PO_4 (1.96 g, 9.23 mmol), 5 mol % of 2-dicyclohexylphosphino-2’-(*N*, *N*-dimethylamino)biphenyl (DavePhos) (36 mg, 0.09 mmol), 2.5 mol % of $Pd_2(dba)_3$ (42 mg, 0.046 mmol) and 8 mL of toluene under argon atmosphere. After the reaction mixture was stirred at 100 ^{o}C for 2-4 hours until the color was changed from purple to orange, the reaction mixture was cooled to room temperature. Then, the mixture was filtered through a short silica gel column using ethyl acetate as eluent. After evaporation of the solvent, the residue was purified by column chromatography on 200-300 mesh silica gel with petroleum ether/EtOAc=4:1 as eluent, and gave **1a** with 55% yield (267 mg).

9-benzamide-*o*-carborane (1a) ^{1}H NMR(600 MHz, $CDCl_3$, *ppm*): δ 7.75-7.74 (d, 2H, *J*=6Hz), 7.47-7.44 (dd, 1H, *J*=6Hz), 7.41-7.38 (dd, 2H, *J*=6Hz), 5.76 (s, 1H), 3.64(s, 1H), 3.59 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, *ppm*): δ 169.0, 135.5, 131.2, 128.4, 127.0, 51.5, 45.9.

2. **General procedure for synthesis of 1q-1s(Take 1q as an example)** [3]

To a 50 mL dried flask was added 9-iodo-*o*-carborane (1.35 g, 5 mmol) and tetrahydrofuran (20 mL) under an argon atmosphere. Then 6.9 mL *n*-BuLi (1.6 M, 11 mmol) was added at 0^{o}C and stirred for 2 h. After slowly added iodomethane (1.37 mL, 22 mmol) at 0 ^{o}C, the reaction mixture was stirred at 80 ^{o}C for 6 h. After cooled to room temperature, the mixture was quenched with water and extracted with ethyl acetate. The organic phase was washed with water (3x10mL), $NaHCO_3$ (aq.) (3x10mL) and brine (3x10mL) in sequence, then dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was sublimation at 60 ^{o}C and gave 1,2-Me_2-9-I-*o*-carborane with 85% yield (1.27 g).

Then, to a 25 mL dried flask was sequentially added 1,2-Me_2-9-iodo-*o*-carborane (298.2 mg, 1mmol), 3 equivalents of the benzamide (363 mg, 3 mmol), 5 equivalents of K_3PO_4 (1.06 g, 5 mmol), 5 mol % of 2-dicyclohexylphosphino-2'-(*N*, *N*-dimethylamino)biphenyl (DavePhos) (20 mg, 0.05 mmol), 2.5 mol % of $Pd_2(dba)_3$ (23 mg, 0.025 mmol) and 4 mL of toluene under an argon atmosphere, then stirred at 100 ^{o}C for 5 h. After the reaction mixture was cooled to room temperature, the mixture was filtered through a short silica gel column using ethyl acetate as eluent. After evaporation of the solvent, the residue was purified by column chromatography on 200-300 mesh silica gel with petroleum ether/EtOAc=8:1~4:1 as eluent, and gave the 1q with 56% yield (164 mg).

1,2-Me_2-9-benzamide-*o*-carborane (1q) ^1H NMR(600 MHz, $CDCl_3$, *ppm*): δ 7.77-7.75 (d, 2H, *J*=6 Hz), 7.45-7.44 (dd, 1H, *J*=6 Hz), 7.40-7.38 (dd, 2H, *J*=6Hz), 5.67 (s, 1H), 2.08 (brs, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$, *ppm*): δ 169.0, 135.7, 131.1, 128.3, 127.1, 70.3, 64.7, 23.7, 21.8.

3. General procedure for synthesis of *nido*-7,8-carborane fused oxazoles (3a-3s) (Take 3a as an example)

To a 10 mL dried flask was sequentially added 9-benzamide-*o*-carborane (26.3 mg, 0.1 mmol), 1,4-dioxane (1 mL), $Pd(OAc)_2$ (2.3 mg, 0. 01 mmol), AgOAc (33.4 mg, 0. 2 mmol) and K_2CO_3 (13.8 mg, 0. 1 mmol) under an argon atmosphere. After the reaction mixture was stirred at 100 ^oC for 24h until 9-benzamide-*o*-carborane was consumed completely, the mixture was cooled to room temperature and filtered through a short silica gel column using ethyl acetate as eluent. After evaporation of the solvent, the residue was purified by column chromatography on 200-300 mesh silica gel with petroleum ether/EtOAc=10:1 as eluent. The desired product **3a** was obtained with 93% yield (23.5 mg).

4. Procedure for synthesis of 4(Cs^+)

To a 10 mL dried flask was sequentially added 1,2-Me_2-9-benzamide-*o*-carborane (58.2 mg, 0.2 mmol), 1,4-dioxane (2 mL), $Pd(OAc)_2$ (4.6 mg, 0.02 mmol) , and Cs_2CO_3 (65.2 mg, 0.2 mmol) under an argon atmosphere. After the reaction mixture was stirred at 100 ^oC for 12 h, the mixture was cooled to room temperature and filtered through a short silica gel column using ethyl acetate as eluent (60 mL). After evaporation of the solvent, the residue was purified by column chromatography on 200-300 mesh silica gel with petroleum ether/EtOAc=1:1 as eluent to gave the product **4(Cs^+)** (53.9 mg, 65% yield). Its exact structure was confirmed by X-ray crystallographic analysis.

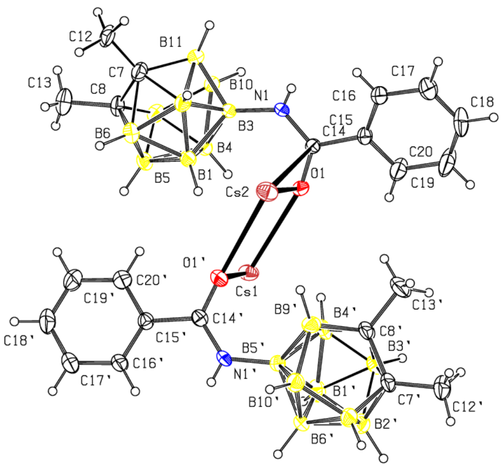
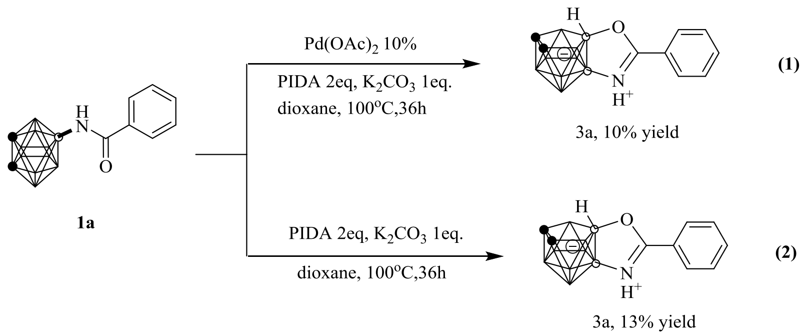
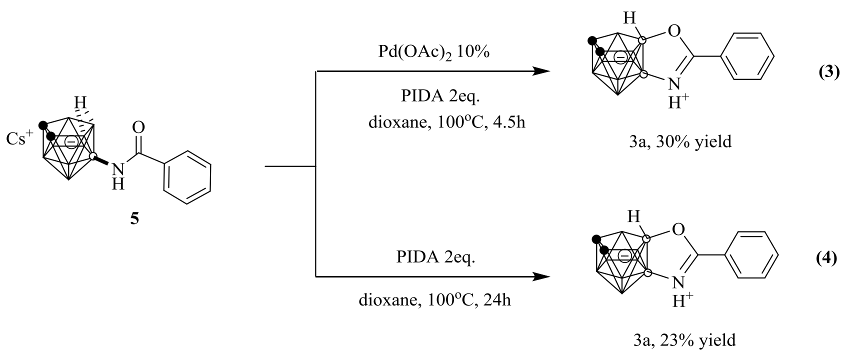


Figure S3. Crystal structure of **4**(Cs^+).

5. Effect of PIDA for synthesis of *nido*-carborane fused oxazole (3a)



Scheme S1. Effect of PIDA for deboronation/cyclization of 9-benzamide-*o*-carborane (1a).



Scheme S2. Effect of PIDA for cyclization of 6-benzamide-*nido*-carborane (5).

Table S1. Calculated Mulliken charge

	9-amide-*o*-caroborane	*o*-carborane
C1	-0.262	-0.254
H1	0.175	0.171
C2	-0.260	-0.252
H2	0.171	0.171
B3	0.087	0.098
H3	0.010	0.008
B4	**-0.010**	**0.024**
H4	**0.023**	**-0.000**
B5	0.004	0.025
H5	0.034	0.001
B6	0.084	0.098
H6	0.010	0.008
B7	0.014	0.027
H7	0.000	-0.000
B8	**-0.072**	**-0.031**
H8	**-0.007**	**-0.012**
B9	0.415	-0.013
N1	-0.427	-0.018
B10	**-0.075**	**-0.030**
H10	**-0.006**	**-0.011**
B11	0.016	0.022
H11	0.001	-0.000
B12	**-0.063**	**-0.012**
H12	**-0.015**	**-0.018**

Table S2. Detailed calculated Mulliken charge

9-benzamide-*o*-carborane:

	charge	spin
N (1)	−0.427	0.000
O (2)	−0.456	0.000
C (3)	−0.262	0.000
C (4)	−0.260	0.000
H (5)	0.171	0.000
H (6)	0.175	0.000
C (7)	0.419	0.000
B (8)	0.084	0.000
H (9)	0.010	0.000
B (10)	0.004	0.000
H (11)	0.034	0.000
B (12)	−0.010	0.000
H (13)	0.023	0.000
B (14)	0.087	0.000
H (15)	0.010	0.000
B (16)	0.016	0.000
H (17)	0.001	0.000
B (18)	−0.075	0.000
H (19)	−0.006	0.000
B (20)	0.415	0.000
B (21)	−0.072	0.000
H (22)	−0.007	0.000
B (23)	0.014	0.000
H (24)	0.000	0.000
B (25)	−0.063	0.000
H (26)	−0.015	0.000
H (27)	0.198	0.000
C (28)	−0.083	0.000
C (29)	−0.079	0.000
C (30)	−0.106	0.000
C (31)	−0.052	0.000
C (32)	−0.061	0.000
C (33)	−0.082	0.000
H (34)	0.085	0.000
H (35)	0.085	0.000
H (36)	0.086	0.000
H (37)	0.114	0.000
H (38)	0.086	0.000

o-carborane:

Mulliken atomic charges:

	charge	spin
H (1)	−0.018	0.000
C (2)	−0.252	0.000
C (3)	−0.254	0.000
H (4)	0.171	0.000
H (5)	0.171	0.000
B (6)	0.098	0.000
H (7)	0.008	0.000
B (8)	0.027	0.000
H (9)	−0.000	0.000
B (10)	0.022	0.000
H (11)	−0.000	0.000
B (12)	0.098	0.000
H (13)	0.008	0.000
B (14)	0.024	0.000
H (15)	−0.000	0.000
B (16)	−0.031	0.000
H (17)	−0.012	0.000
B (18)	−0.012	0.000
B (19)	−0.030	0.000
H (20)	−0.011	0.000
B (21)	0.025	0.000
H (22)	0.001	0.000
B (23)	−0.013	0.000
H (24)	−0.018	0.000

Reference:

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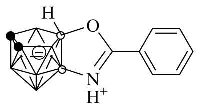
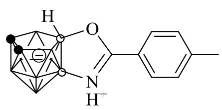
Spectroscopic data for products



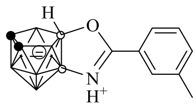
3a

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.86 (brs, 1H, *N-H*), 7.81-7.79 (dd, 2H, *J*=6Hz), 7.71-7.68 (dd, 1H, *J*=6Hz), 7.55-7.52 (m, 2H), 2.05 (s, 1H, *Cage C-H*), 1.81 (s, 1H, *Cage C-H*); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 178.9, 135.2, 129.4, 128.1, 125.4, 38.2, 35.8; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.5 (1B), -3.9 (1B, *B-N*), -8.6 (1B), -14.8 (1B), -16.0 (1B), -21.9 (1B), -24.4 (1B), -25.6 (1B), -39.4 (1B); HRMS: calculated for $C_9B_9H_{15}NO^-$ $(M-H)^-$ 252.1997, found 252.2016. Element analysis calcd (%) for $C_9B_9H_{16}NO$: C 42.98, H 6.41; found: C 43.11, H 6.41.



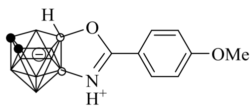
3b

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.77 (brs, 1H, *N-H*), 7.69-7.68 (d, 2H, *J*=6Hz), 7.33-7.32 (d, 2H, *J*=6Hz), 2.45 (s, 3H, *-CH_3*), 2.04 (s, 1H, *Cage C-H*), 1.79 (s, 1H, *Cage C-H*); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 178.9, 146.7, 130.1, 128.2, 122.6, 38.4, 35.8, 21.9; $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.6 (1B), -3.9 (1B, *B-N*), -8.5 (1B), -14.6 (1B), -16.0 (1B), -21.9 (1B), -24.5 (1B), -25.6 (1B), -39.4 (1B); HRMS: calculated for $C_{10}B_9H_{19}NO^+$ $(M+H)^+$ 267.23350, found 267.23270. Element analysis calcd (%) for $C_{10}B_9H_{18}NO$: C 45.23, H 6.83; found: C 45.60, H 6.98.



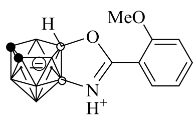
3c

^1H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.82 (brs, 1H, *N-H*), 7.62 (s, 1H), 7.59-7.58 (d, 1H, *J*=6Hz), 7.50-7.49 (d, 1H, *J*=6Hz), 7.42-7.40 (dd, 1H, *J*=6Hz), 2.42 (s, 3H, $-CH_3$), 2.04 (s, 1H, *Cage C-H*), 1.80 (s, 1H, *Cage C-H*); $^{13}C\{^1H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 179.1, 139.6, 135.9, 129.3, 128.7, 125.3, 125.2, 38.3, 35.7, 21.2; $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.5 (1B), -3.9 (1B, *B-N*), -8.5 (1B), -14.6 (1B), -15.9 (1B), -21.8 (1B), -24.4 (1B), -25.5 (1B), -39.3 (1B); HRMS: calculated for $C_{10}B_9H_{19}NO^+$ $(M+H)^+$ 267.23350, found 267.23392.



3d

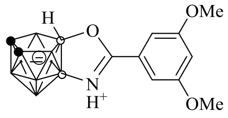
^1H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.75-7.74 (d, 2H, *J*=6Hz), 7.62 (brs, 1H, *N-H*), 6.99-6.97 (d, 2H, *J*=6Hz), 3.89 (s, 3H, $-OCH_3$), 2.03 (s, 1H, *Cage C-H*), 1.79 (s, 1H, *Cage C-H*); $^{13}C\{^1H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 178.3, 165.1, 130.4, 117.5, 114.8, 55.8, 38.1, 35.8; $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.6 (1B), -4.0 (1B, *B-N*), -8.4 (1B), -14.4 (1B), -16.1 (1B), -21.9 (1B), -24.5 (1B), -25.6 (1B), -39.4 (1B); HRMS: calculated for $C_{10}B_9H_{19}NO_2^+$ $(M+H)^+$ 282.23204, found 282.23239.



3e

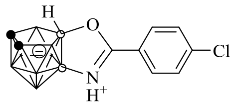
^1H NMR (600MHz, $CDCl_3$, *ppm*): δ 9.34 (brs, 1H, *N-H*), 8.02-8.01 (d, 1H, *J*=6Hz), 7.63-7.61 (dd, 1H, *J*=6Hz), 7.12-7.10 (dd, 1H, *J*=6Hz), 7.07-7.05 (d, 1H, *J*=6Hz), 4.07 (s, 3H, $-OCH_3$), 2.03 (s, 1H, *Cage C-H*), 1.78 (s, 1H, *Cage C-H*); $^{13}C\{^1H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 176.1, 159.2, 136.6, 132.0, 121.7, 113.4, 111.7, 56.5, 38.3, 35.7; $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.7 (1B), -3.9 (1B, *B-N*), -8.7 (1B),

-14.6 (1B), -16.6 (1B), -22.1 (1B), -24.6 (1B), -25.5 (1B), -39.4 (1B); HRMS: calculated for $C_{10}B_9H_{19}NO_2^+$ $(M+H)^+$ 282.23204, found 282.23212.



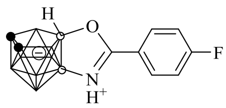
3f

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.85 (brs, 1H, *N-H*), 6.87 (s, 2H), 6.71 (s, 1H), 3.83 (s, 6H, -OCH_3), 2.05 (s, 1H, *Cage C-H*), 1.80 (s, 1H, *Cage C-H*); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 178.8, 161.3, 126.9, 107.3, 105.8, 55.8, 38.4, 35.8; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.5 (1B), -3.9 (1B, *B-N*), -8.6 (1B), -14.8 (1B), -16.0 (1B), -21.8 (1B), -24.5 (1B), -25.5 (1B), -39.4 (1B); HRMS: calculated for $C_{11}B_9H_{19}NO_3^-$ $(M-H)^-$ 312.2208, found 312.2229. Element analysis calcd (%) for $C_{11}B_9H_{20}NO_3$: C 42.40, H 6.47; found: C 42.63, H 6.96.



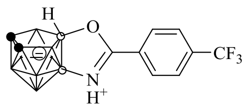
3g

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.89 (brs, 1H, *N-H*), 7.75-7.74 (d, 2H, *J*=6Hz), 7.52-7.51 (d, 2H, *J*=6Hz), 2.05 (s, 1H, *Cage C-H*), 1.81 (s, 1H, *Cage C-H*); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 178.9, 135.2, 129.4, 128.1, 125.4, 38.4, 35.8; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.5 (1B), -3.9 (1B, *B-N*), -8.7 (1B), -14.9 (1B), -16.1 (1B), -21.9 (1B), -24.5 (1B), -25.6 (1B), -39.4 (1B); HRMS: calculated for $C_9B_9H_{14}NOCl^-$ $(M-H)^-$ 286.1607, found 286.1636.



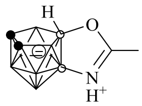
3h

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.88-7.85 (m, 3H), 7.25-7.23 (m, 2H), 2.08 (s, 1H, *Cage C-H*), 1.83 (s, 1H, *Cage C-H*); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 177.7, 166.8 (*J*=258Hz), 130.9 (*J*=9Hz), 121.7, 116.9 (*J*=21Hz), 38.6, 35.8; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.5 (1B), -4.0 (1B, *B-N*), -8.6 (1B), -14.8 (1B), -16.1 (1B), -21.9 (1B), -24.4 (1B), -25.6 (1B), -39.4 (1B); HRMS: calculated for $C_9B_9H_{14}NOF^-$ $(M-H)^-$ 270.1902, found 270.1914.



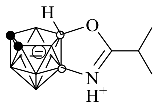
3i

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 8.13 (brs, 1H, *N-H*), 7.96-7.95 (d, 2H, *J*=6Hz), 7.82-7.81 (d, 2H, *J*=6Hz), 2.08 (s, 1H, *Cage C-H*), 1.83 (s, 1H, *Cage C-H*); $^{13}C\{^{1}H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 177.5, 136.5 (*J*=33Hz), 128.7, 128.5, 126.5 (*J*=3Hz), 122.9 (*J*=272Hz), 38.9, 35.9; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.4 (1B), -3.9 (1B, *B-N*), -8.8 (1B), -15.1 (1B), -16.1 (1B), -21.8 (1B), -24.4 (1B), -25.6 (1B), -39.3 (1B); HRMS: calculated for $C_{10}B_9H_{14}NOF_3^-$ $(M-H)^-$ 320.1871, found 320.1872.



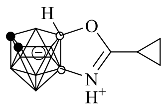
3j

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.43 (brs, 1H, *N-H*), 2.24 (s, 3H, -CH_3), 1.99 (s, 1H, *Cage C-H*), 1.76 (s, 1H, *Cage C-H*); $^{13}C\{^{1}H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 183.5, 38.5, 35.9, 19.3; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.7 (1B), -4.4 (1B, *B-N*), -8.8 (1B), -14.8 (1B), -16.3 (1B), -21.9 (1B), -24.6 (1B), -25.7 (1B), -39.6 (1B); HRMS: calculated for $C_4B_9H_{13}NO^-$$(M-H)^-$ 190.1840, found 190.1841.



3k

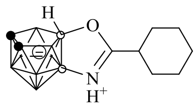
^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.40 (brs, 1H, *N-H*), 2.71-2.65 (m, 1H, *J*=6Hz, -CH-), 1.99 (s, 1H, *Cage C-H*), 1.74 (s, 1H, *Cage C-H*), 1.21-1.20 (d, 6H, *J*=6Hz, -CH_3); $^{13}C\{^{1}H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 190.9, 38.2, 35.6, 32.5, 18.7, 18.6; $^{11}B\{^{1}H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.6 (1B), -4.3 (1B, *B-N*), -8.6 (1B), -14.8 (1B), -16.2 (1B), -21.9 (1B), -24.5 (1B), -25.7 (1B), -39.5 (1B); HRMS: calculated for $C_6B_9H_{17}NO^-$ $(M-H)^-$ 218.2153, found 218.2158.



3l

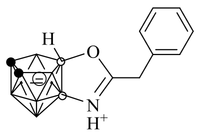
^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.44 (brs, 1H, *N-H*), 1.97 (s, 1H, *Cage C-H*), 1.73 (s, 1H, *Cage C-H*), 1.65-1.59 (m, 1H), 1.27-1.24 (m, 1H), 1.20-1.11 (m, 3H);

$^{13}C\{^1H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 187.1, 37.9, 35.9, 13.2, 10.8, 10.7; $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.8 (1B), -4.4 (1B, *B-N*), -8.4 (1B), -14.2 (1B), -16.4 (1B), -21.9 (1B), -24.6 (1B), -25.6 (1B), -39.5 (1B); HRMS: calculated for $C_6B_9H_{15}NO^-$ $(M-H)^-$ 216.1996, found 216.2006.



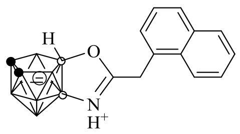
3m

^1H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.31 (brs, 1H, *N-H*), 2.41-2.36 (m, 1H), 1.98 (s, 1H, *Cage C-H*), 1.91-1.89 (m, 2H), 1.81-1.79 (m, 2H), 1.74-1.69 (m, 2H), 1.35-1.26 (m, 4H), 1.22-1.18 (m, 1H); $^{13}C\{^1H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 189.9, 41.3, 38.2, 35.4, 28.9, 28.8, 25.1, 24.9, 24.8; $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.6 (1B), -4.3 (1B, *B-N*), -8.6 (1B), -14.8 (1B), -16.2 (1B), -21.9 (1B), -24.5 (1B), -25.7 (1B), -39.5 (1B); HRMS: calculated for $C_9B_9H_{21}NO^-$ $(M-H)^-$ 258.2466, found 258.2468.



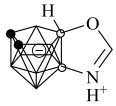
3n

^1H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.45-7.40 (m, 3H), 7.18-7.17 (m, 2H), 3.81-3.73 (m, 2H, -CH_2-), 1.99 (s, 1H, *Cage C-H*), 1.76 (s, 1H, *Cage C-H*); $^{13}C\{^1H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 185.9, 130.3, 129.9, 129.5, 129.0, 38.8, 38.4, 35.7; $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.6 (1B), -4.2 (1B, *B-N*), -8.7 (1B), -14.9 (1B), -16.1 (1B), -21.9 (1B), -24.4 (1B), -25.6 (1B), -39.5 (1B); HRMS: calculated for $C_{10}B_9H_{19}NO^+$ $(M+H)^+$ 266.23713, found 266.23724.



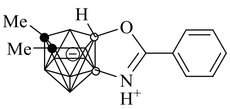
3o

^1H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.94-7.93 (d, 2H, *J*=6Hz), 7.61-7.55 (m, 3H), 7.50-7.48 (dd, 1H, *J*=6Hz), 7.40-7.39 (d, 1H, *J*=6Hz), 7.08 (brs, 1H, *N-H*), 4.18 (s, 2H, -CH_2-), 1.97 (s, 1H, *Cage C-H*), 1.75 (s, 1H, *Cage C-H*); $^{13}C\{^1H\}$ NMR (150MHz, $CDCl_3$, *ppm*): δ 185.7, 134.1, 131.0, 130.2, 129.3, 129.2, 127.8, 126.9, 126.4, 125.6, 122.5, 38.5, 36.6, 35.9; $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.7 (1B), -4.3 (1B, *B-N*), -8.9 (1B), -15.0 (1B), -16.1 (1B), -21.9 (1B), -24.5 (1B), -25.7 (1B), -39.6 (1B); HRMS: calculated for $C_{14}B_9H_{19}NO^-$ (M-H)$^-$ 316.2310, found 316.2325.



3p

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 8.02 (brs, 1H, *N-H*), 7.75 (s, 1H), 2.04 (s, 1H, *Cage C-H*), 1.80 (s, 1H, *Cage C-H*); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 171.3, 39.1, 35.7; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ -2.5 (1B), -4.5 (1B, *B-N*), -9.1 (1B), -15.6 (1B), -16.4 (1B), -21.8 (1B), -24.3 (1B), -25.6 (1B), -39.4 (1B); HRMS: calculated for $C_3B_9H_{11}NO^-$ (M-H)$^-$ 176.1684, found 176.1679.



3q

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.85 (brs, 1H, *N-H*), 7.79-7.77 (m, 2H), 7.69-7.67 (m, 1H), 7.54-7.51 (m, 2H), 1.44 (s, 3H, -*CH_3*), 1.40 (s, 3H, -*CH_3*); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 178.8, 135.1, 129.4, 128.1, 125.5, 54.0, 52.3, 21.3, 20.3; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ -1.0 (1B), -4.8 (1B, *B-N*), -7.4 (1B), -13.7 (1B), -15.8 (1B), -16.8 (1B), -20.8 (1B), -21.8 (1B), -38.2 (1B); HRMS: calculated for $C_{11}H_{21}B_9NO^+$ (M+H)$^+$281.24915, found 281.24954.

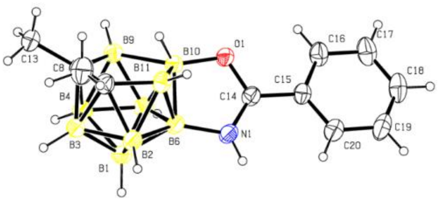
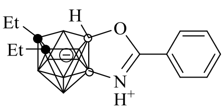


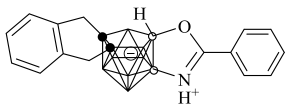
Figure S4. Crystal structure of 3q.



3r

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.89 (brs, 1H, *N-H*), 7.79-7.78 (d, *J*=6Hz, 2H), 7.69-7.67 (dd, *J*=6Hz, 1H), 7.54-7.51 (m, 2H), 1.91-1.80 (m, 2H, -*CH_2*-), 1.71-1.63 (m, 2H, -*CH_2*-), 1.04-0.99 (m, 6H, -*CH_3*); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 178.7, 135.0, 129.4, 128.1, 125.5, 60.6, 59.1, 26.6, 25.9, 14.9, 14.7; ^{11}B{^{1}H} NMR

(192 MHz, $CDCl_3$, *ppm*): δ -2.5 (1B), -4.6 (1B, *B-N*), -8.7 (1B), -15.7 (2B), -16.5 (1B), -21.5 (1B), -22.6 (1B), -38.5 (1B); HRMS: calculated for $C_{13}B_9H_{25}NO^+$ $(M+H)^+$ 309.28045, found 309.28076.



3s-10

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.81 (brs, 1H), 7.75-7.73 (d, *J*=6Hz, 2H), 7.68-7.66 (dd, *J*=6Hz, 1H), 7.52-7.49 (dd, *J*=6Hz, 2H), 7.15-7.13 (m, 2H), 7.10-7.08 (m, 1H), 7.05-7.04 (m, 1H), 3.24-3.20 (m, 2H), 2.98-2.89 (m, 2H); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 178.8, 137.5, 137.1, 135.2, 129.4, 128.1, 127.1, 126.9, 126.3, 126.2, 125.3, 57.2, 55.2, 38.9, 37.9; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ -0.8 (1B), -4.7 (1B), -7.1 (1B), -14.3 (1B), -15.9 (2B), -21.6 (1B), -22.8 (1B), -37.2 (1B); HRMS: calculated for $C_{17}B_9H_{21}NO^-$ $(M-H)^-$ 354.2466, found 354.2493.

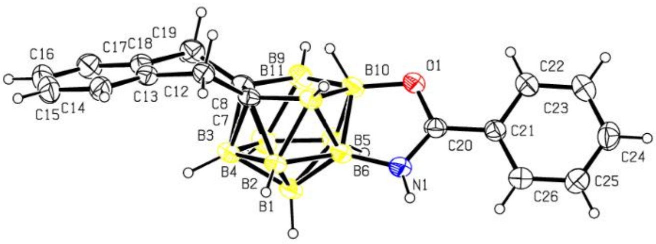
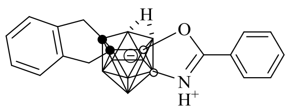


Figure S1. Crystal structures of 3s-10.



3s-11

^{1}H NMR (600MHz, $CDCl_3$, *ppm*): δ 7.83 (brs, 1H), 7.75-7.74 (d, *J*=6Hz, 2H), 7.69-7.66 (dd, *J*=6Hz, 1H), 7.53-7.50 (dd, *J*=6Hz, 2H), 7.15-7.13 (m, 2H), 7.10-7.08 (m, 1H), 7.06-7.05 (m, 1H), 3.24-3.21 (m, 2H), 2.99-2.90 (m, 2H), -2.23 (brs, 1H); ^{13}C{^{1}H} NMR (150MHz, $CDCl_3$, *ppm*): δ 178.8, 137.5, 137.1, 135.1, 129.4, 128.1, 127.1, 126.9, 126.3, 126.2, 125.4, 56.9, 55.2, 38.9, 37.9; ^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, *ppm*): δ -0.9 (1B), -4.8 (1B), -7.2 (1B), -14.3 (1B), -16.0 (2B), -21.7 (1B), -22.9 (1B), -37.3 (1B); HRMS: calculated for $C_{17}B_9H_{21}NO^-$ $(M-H)^-$ 354.2466, found

354.2491.

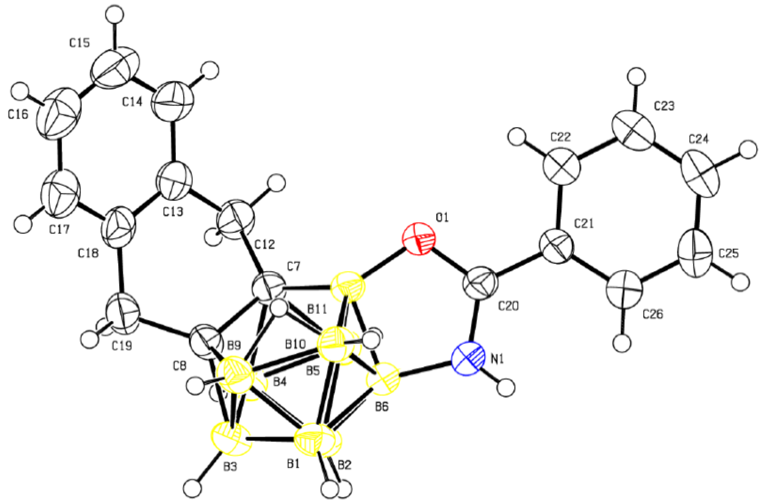
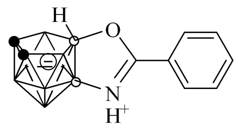


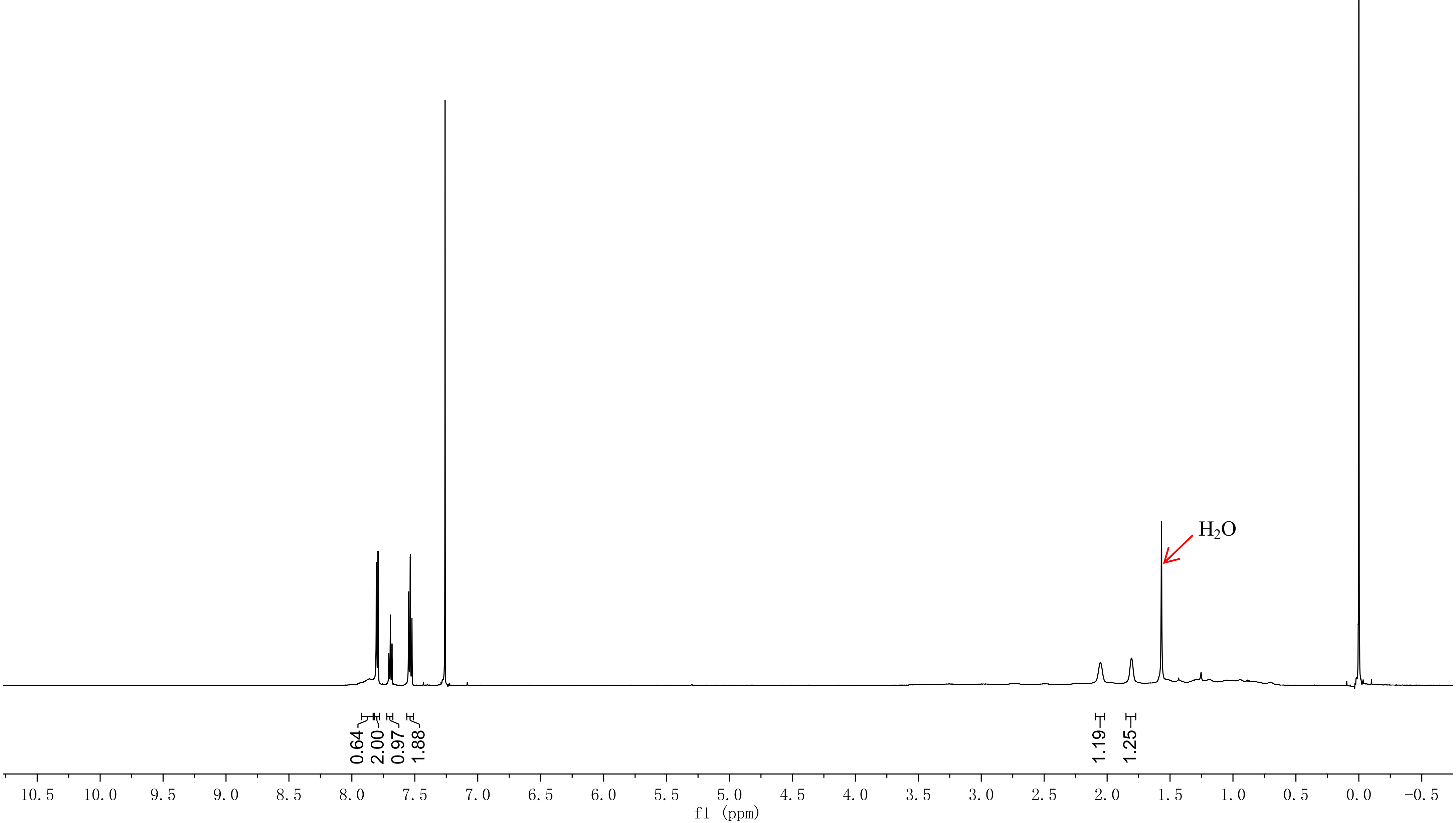
Figure S2. Crystal structures of 3s-11.

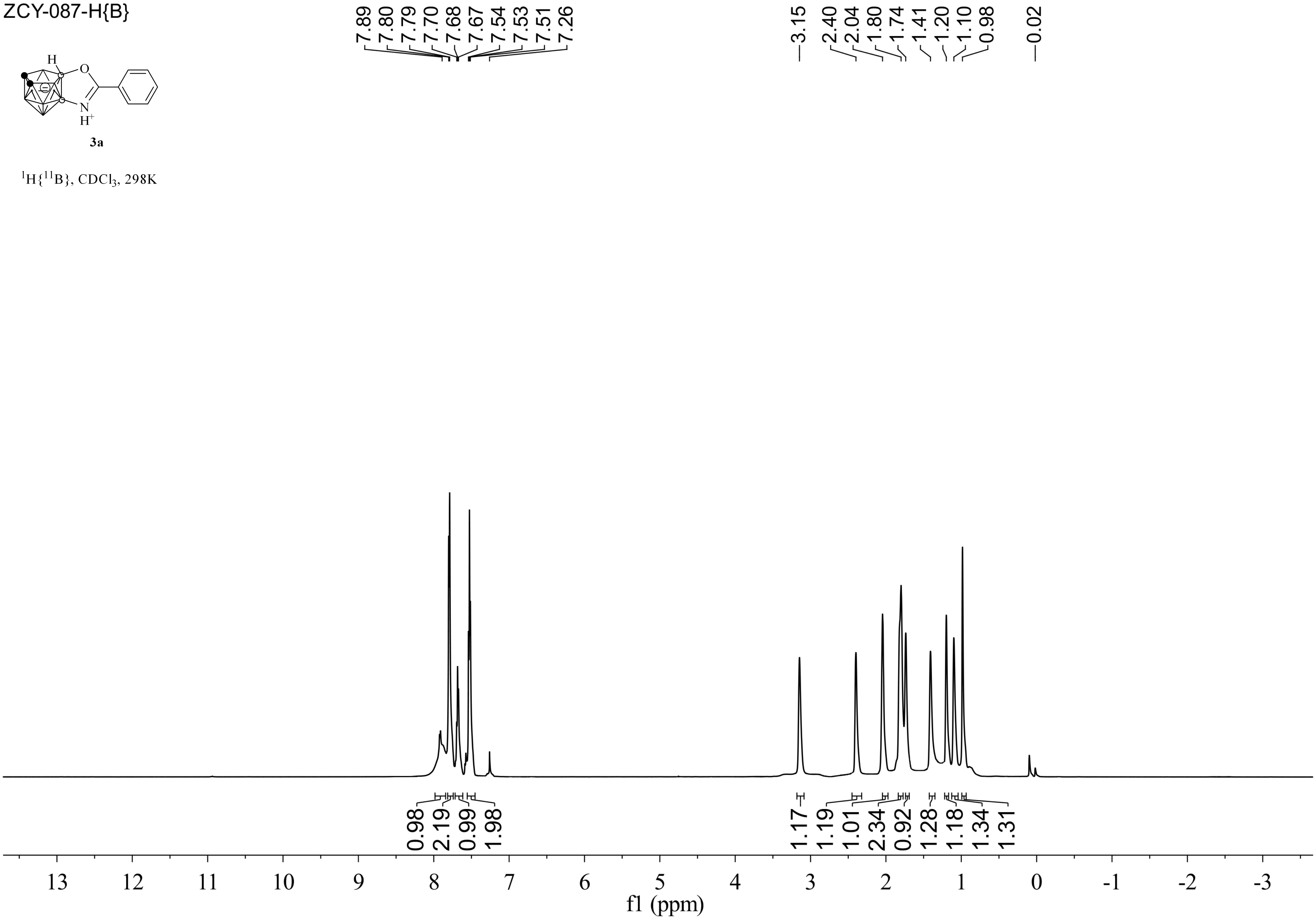
ZCY-087-H



3a

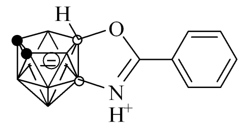
^1H, $CDCl_3$, 298K





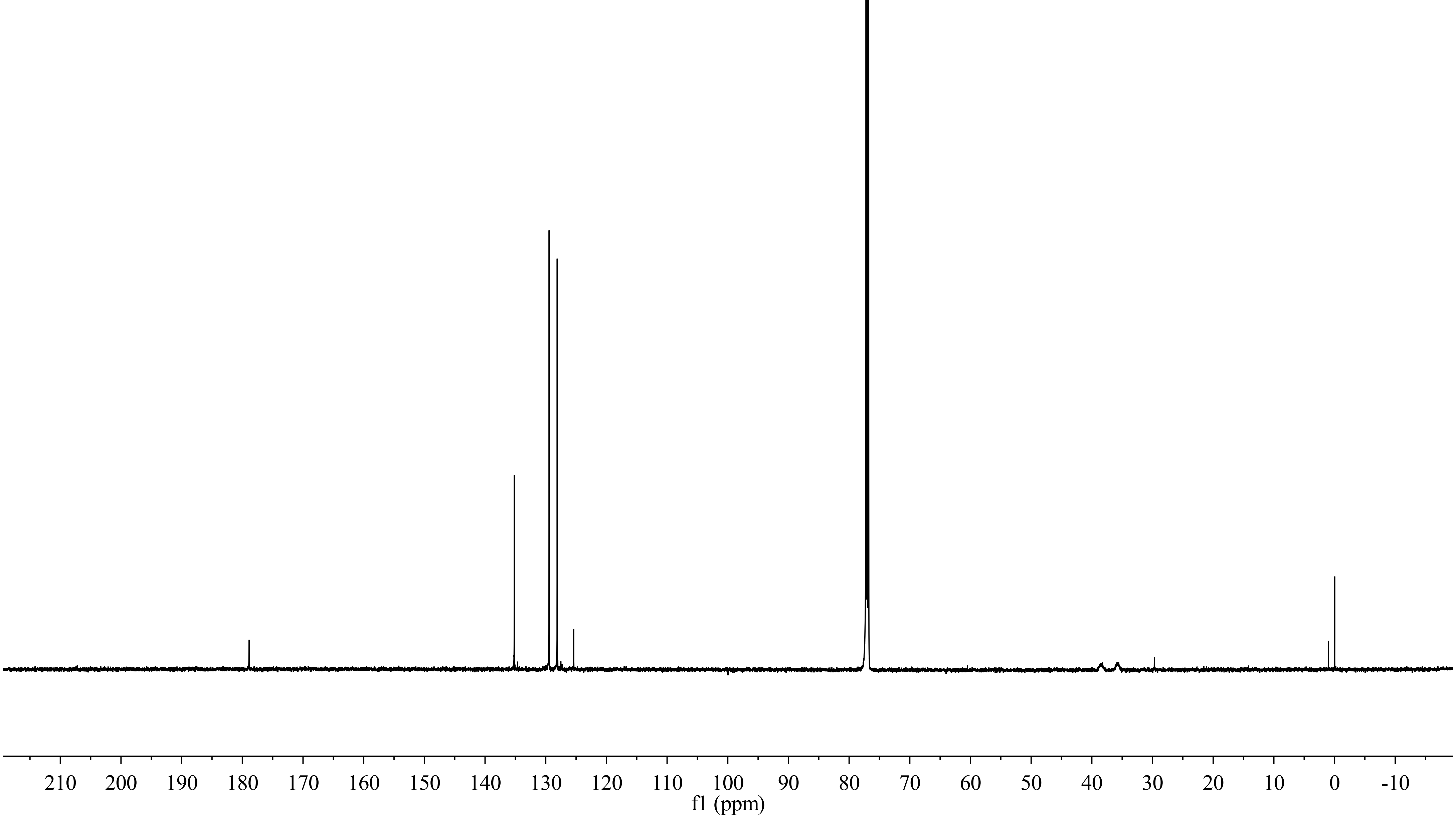
ZCY-087-H{B}
H
O
N
H+
3a
1H{11B}, CDCl3, 298K
7.89
7.80
7.79
7.70
7.68
7.67
7.54
7.53
7.51
7.26
3.15
2.40
2.04
1.80
1.74
1.41
1.20
1.10
0.98
0.02
0.98
2.19
0.99
1.98
1.17
1.19
1.01
2.34
0.92
1.28
1.18
1.34
1.31
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

ZCY-087-C

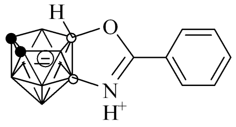


3a

^{13}C, $CDCl_3$, 298K

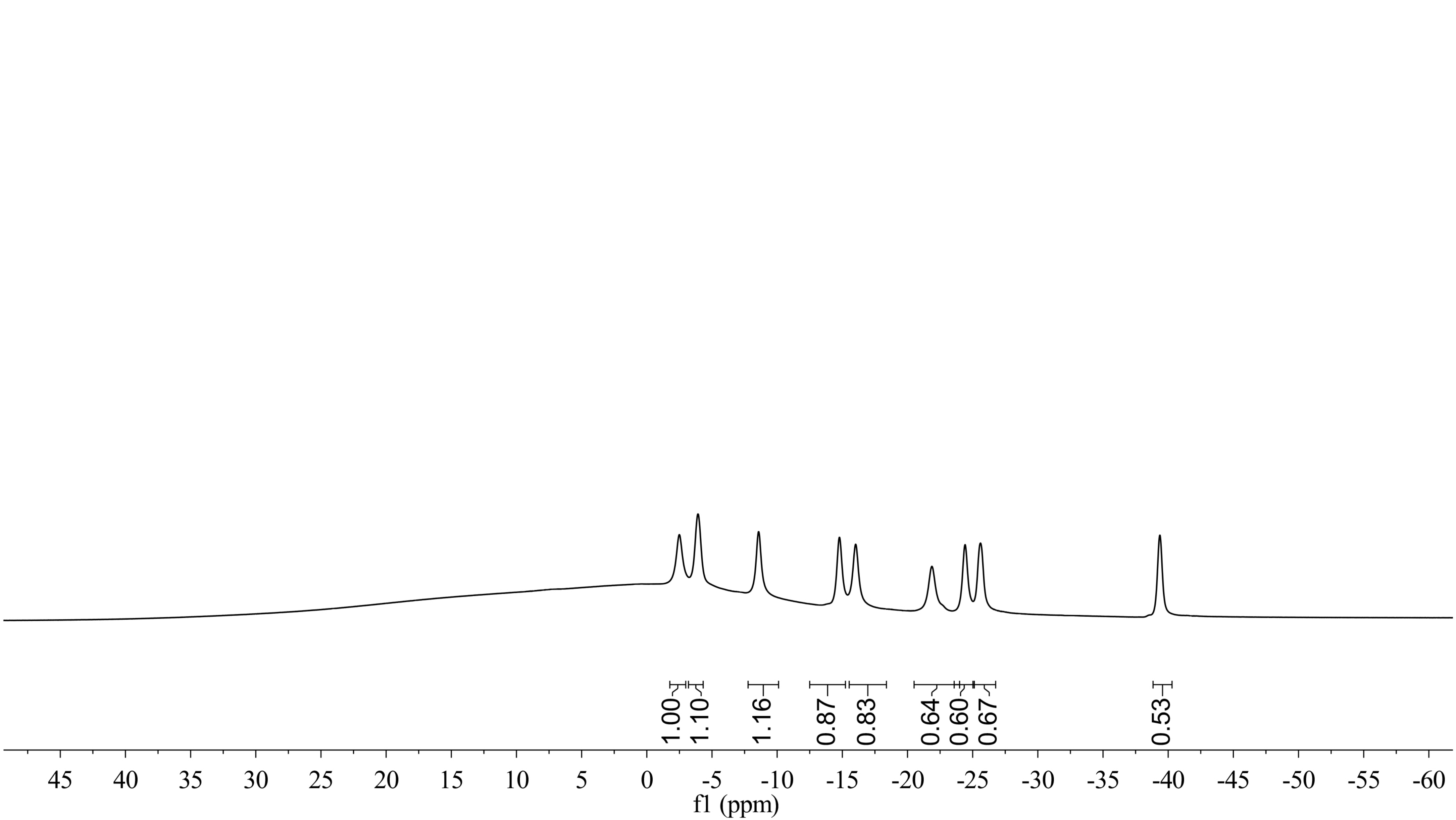


ZCY-087-B{H}

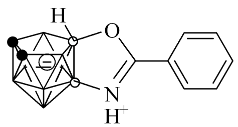


3a

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

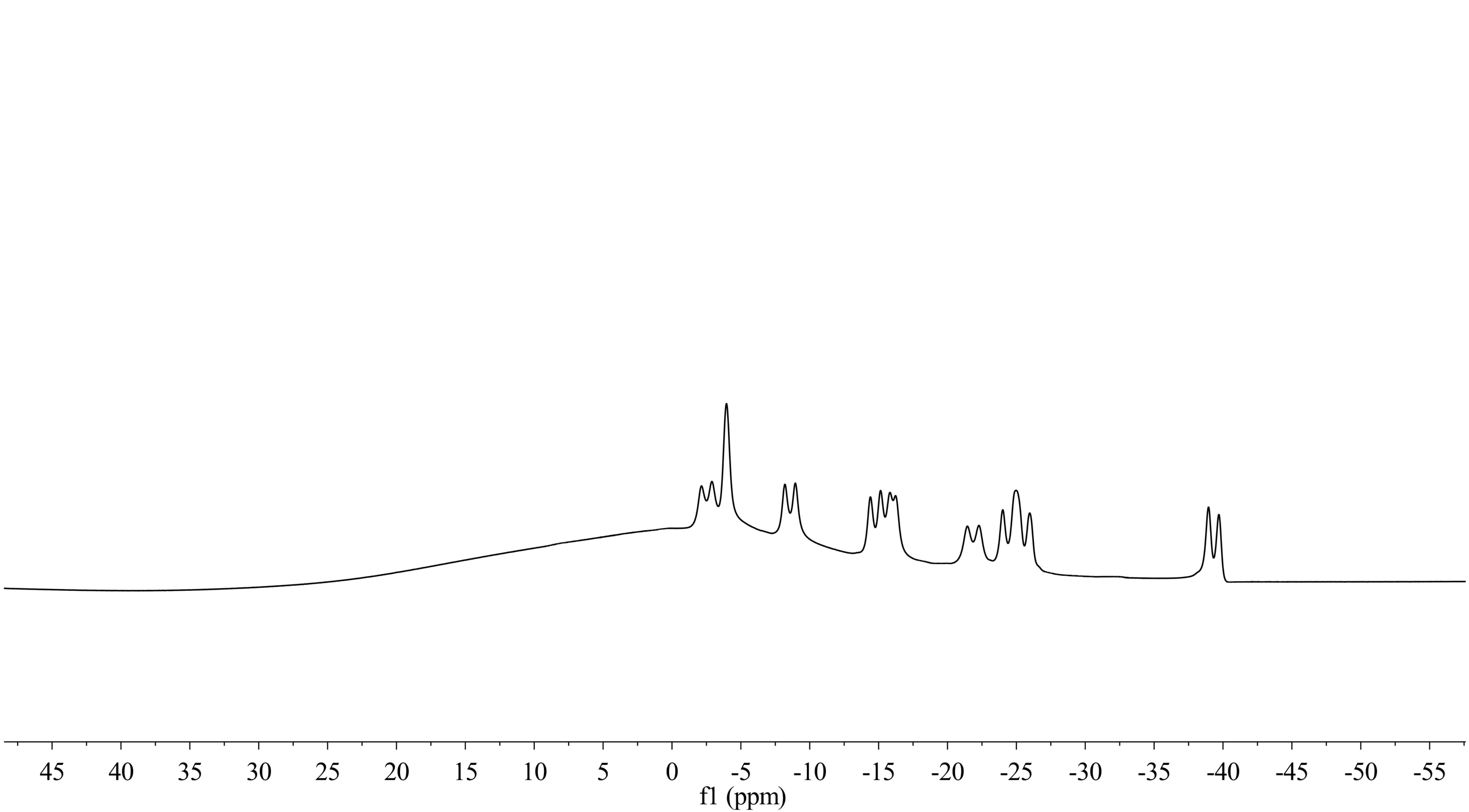


ZCY-087-B

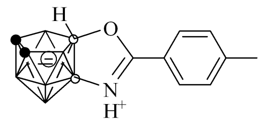


3a

^{11}B, $CDCl_3$, 298K

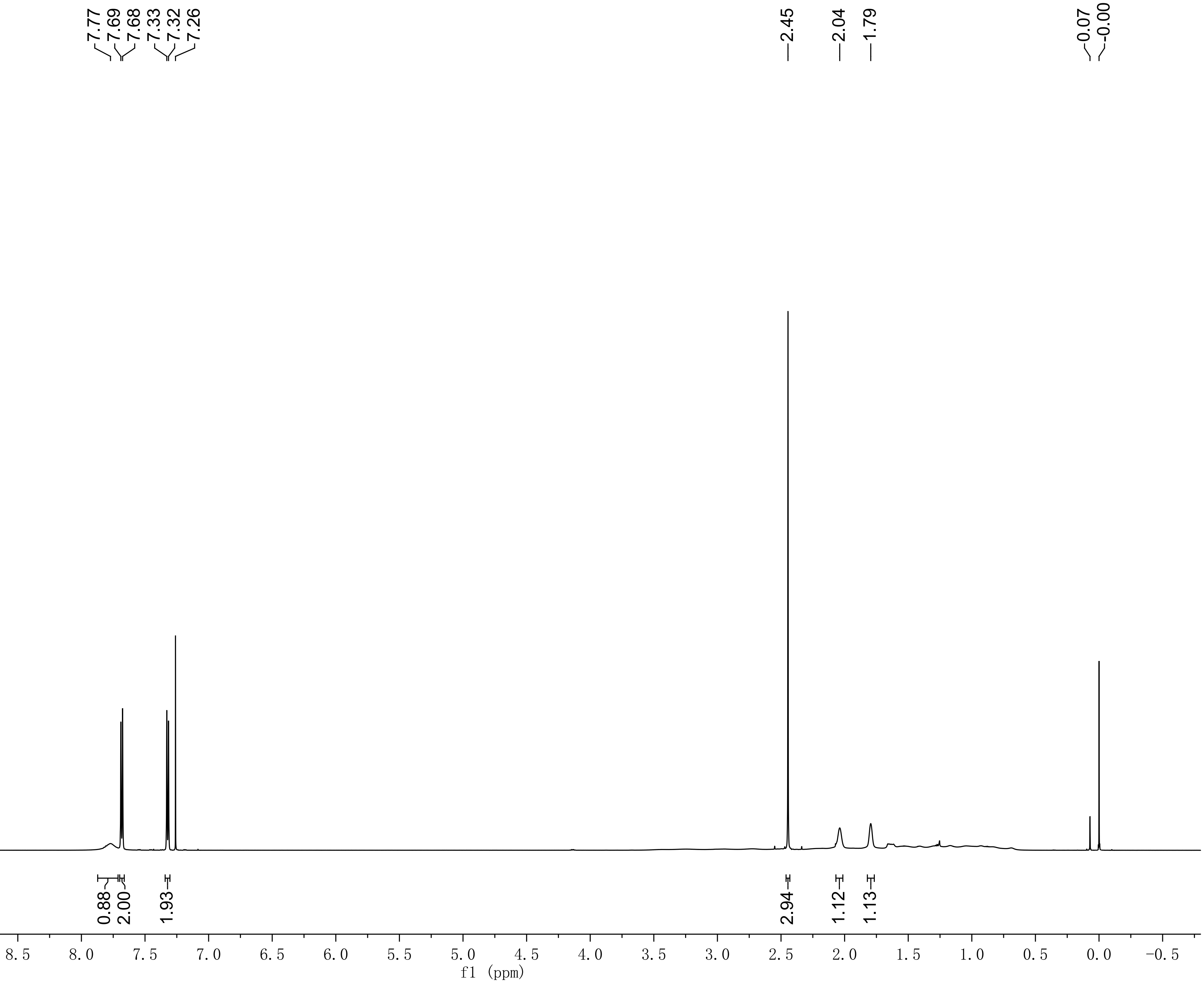


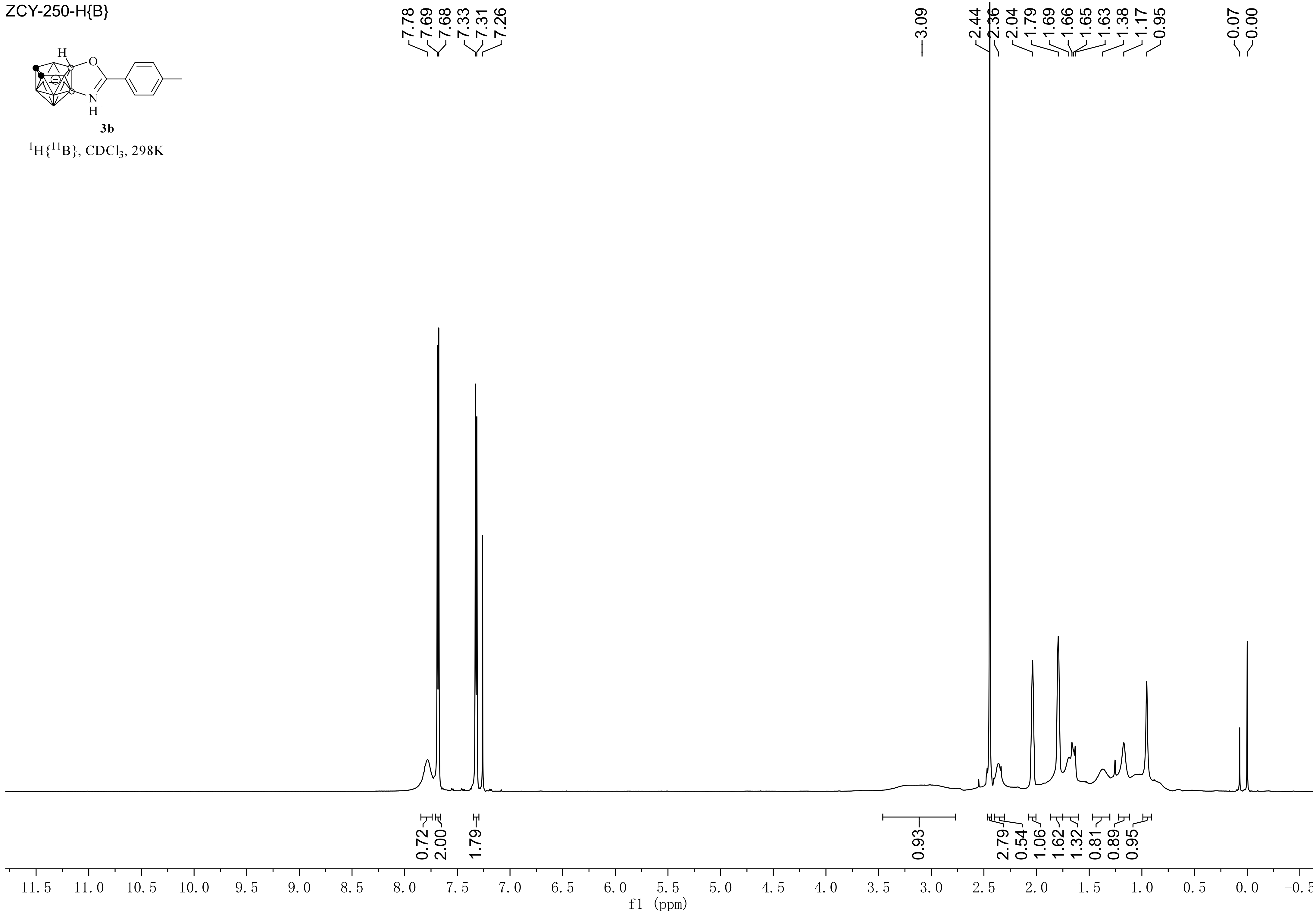
ZCY-250-H



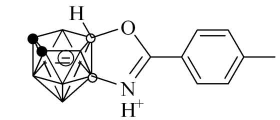
3b

^{1}H, $CDCl_3$, 298K



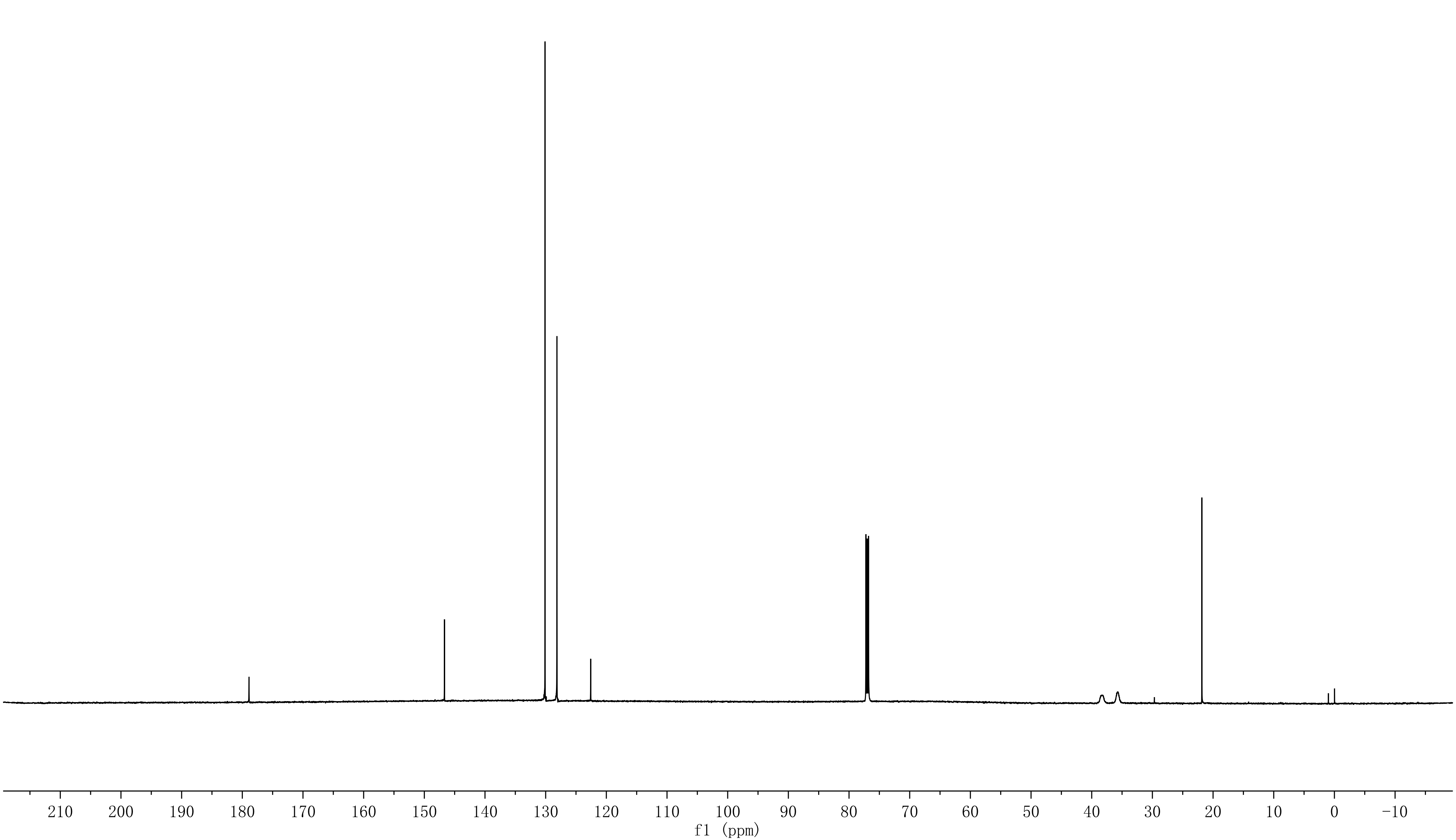

ZCY-250-H{B}
H
O
N
H+
3b
1H{11B}, CDCl3, 298K
7.78
7.69
7.68
7.33
7.31
7.26
3.09
2.44
2.36
2.04
1.79
1.69
1.66
1.65
1.63
1.38
1.17
0.95
0.07
0.00
0.72
2.00
1.79
0.93
2.79
0.54
1.06
1.62
1.32
0.81
0.89
0.95
f1 (ppm)

ZCY-250-C

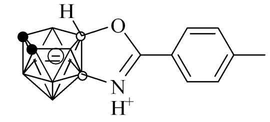


3b

^{13}C, $CDCl_3$, 298K

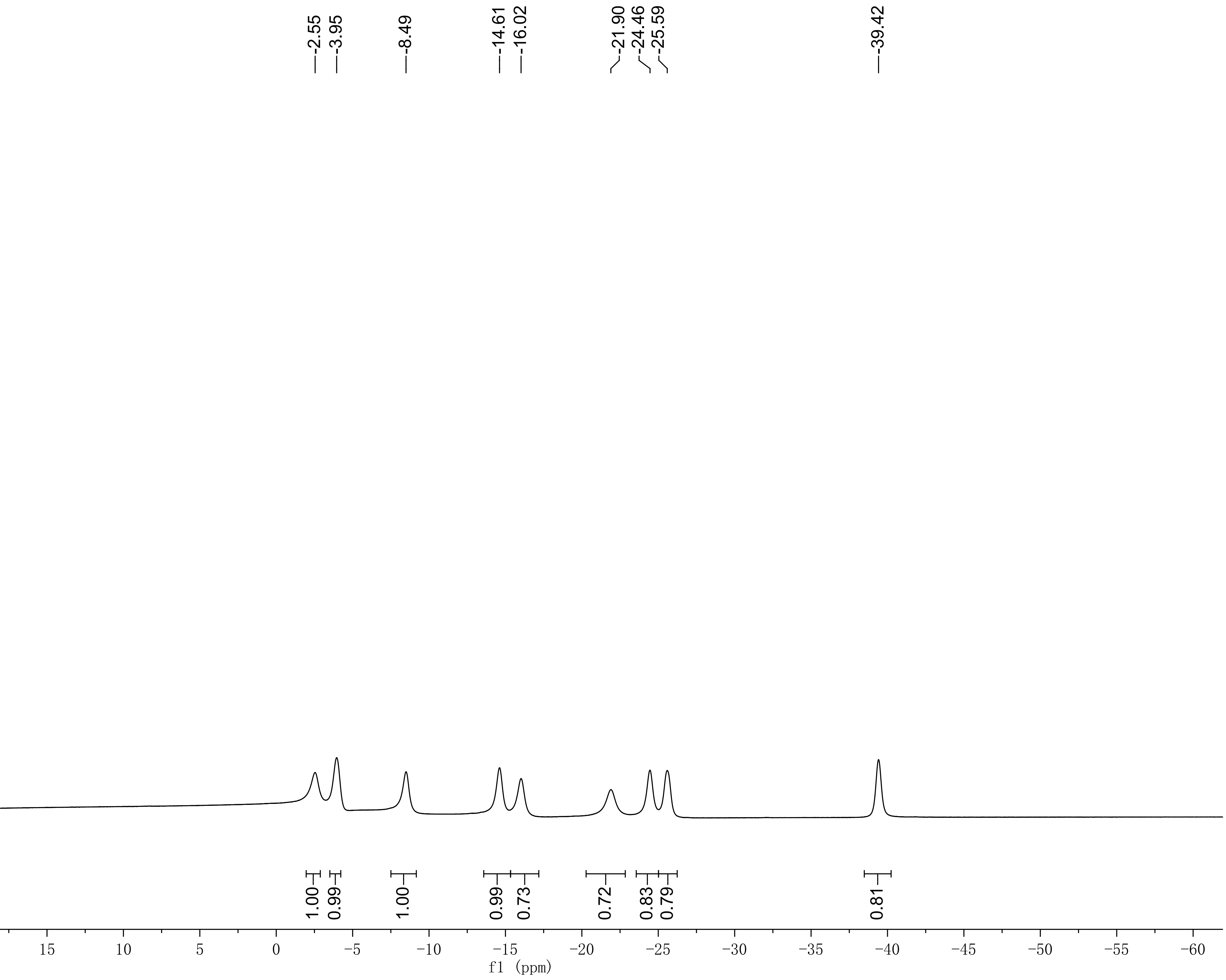


ZCY-250-B{H}

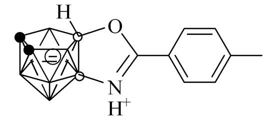


3b

$^{11}B\{^1H\}$, $CDCl_3$, 298K

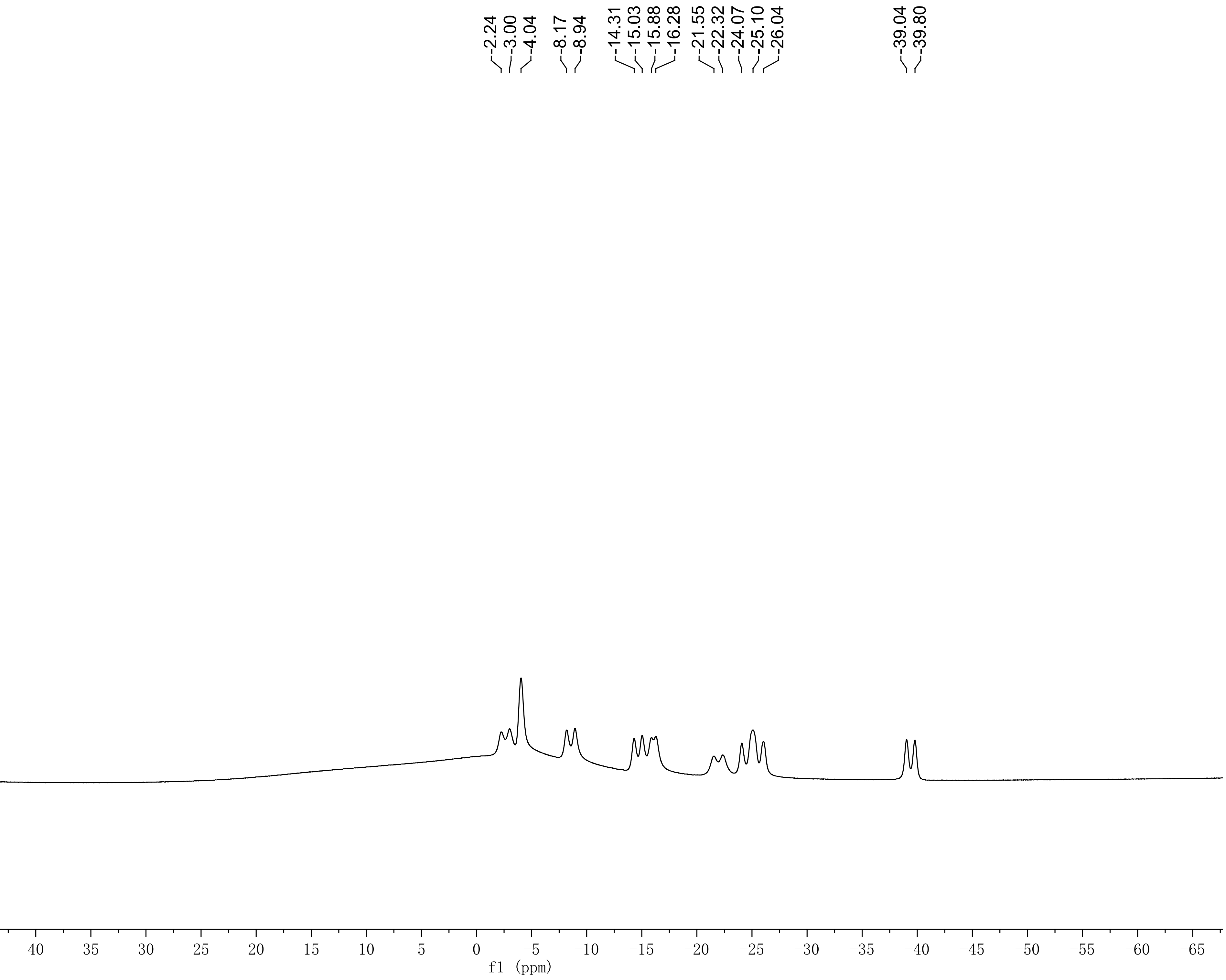


ZCY-250-B

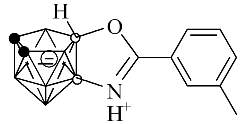


3b

^{11}B, $CDCl_3$, 298K

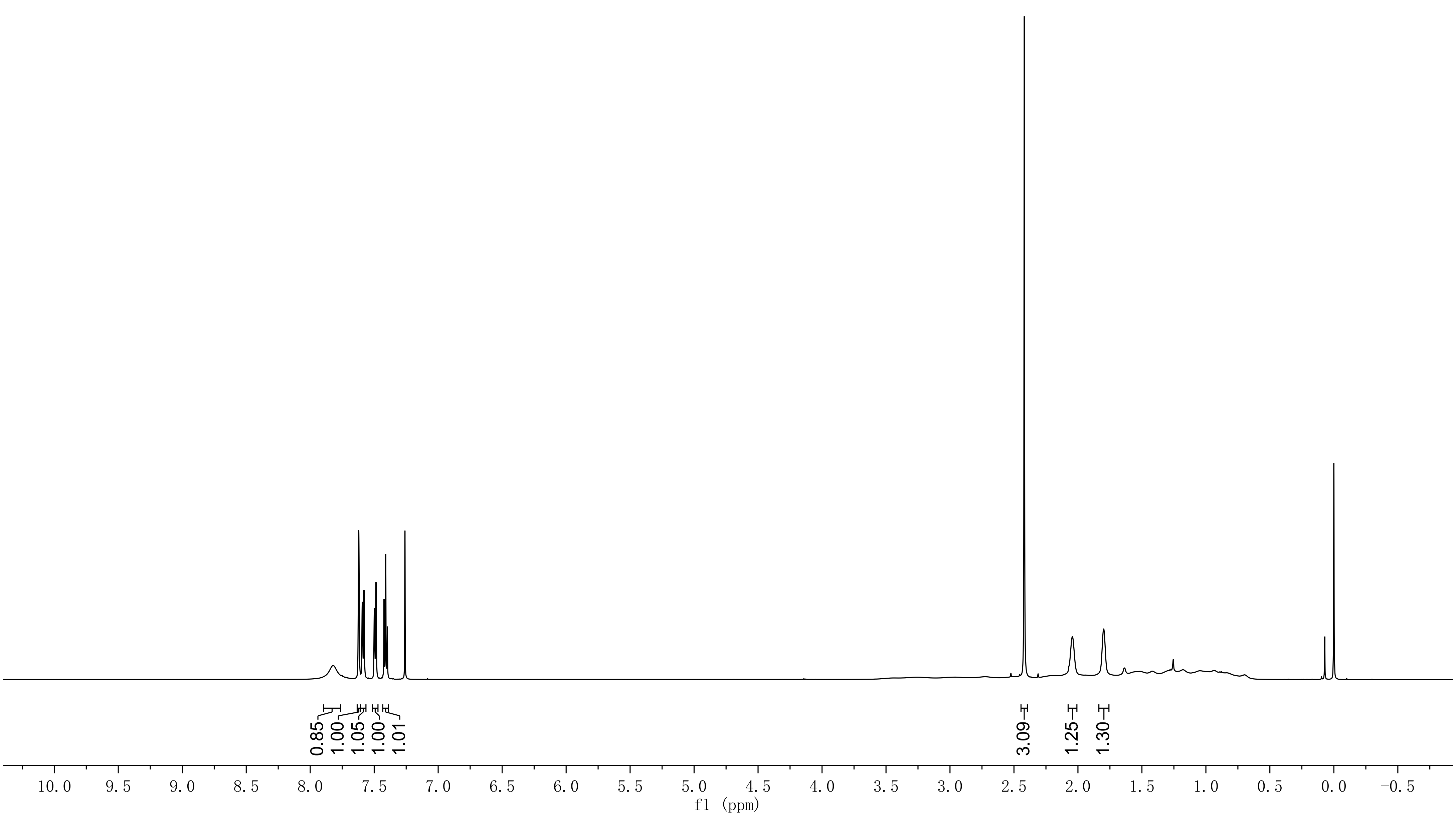


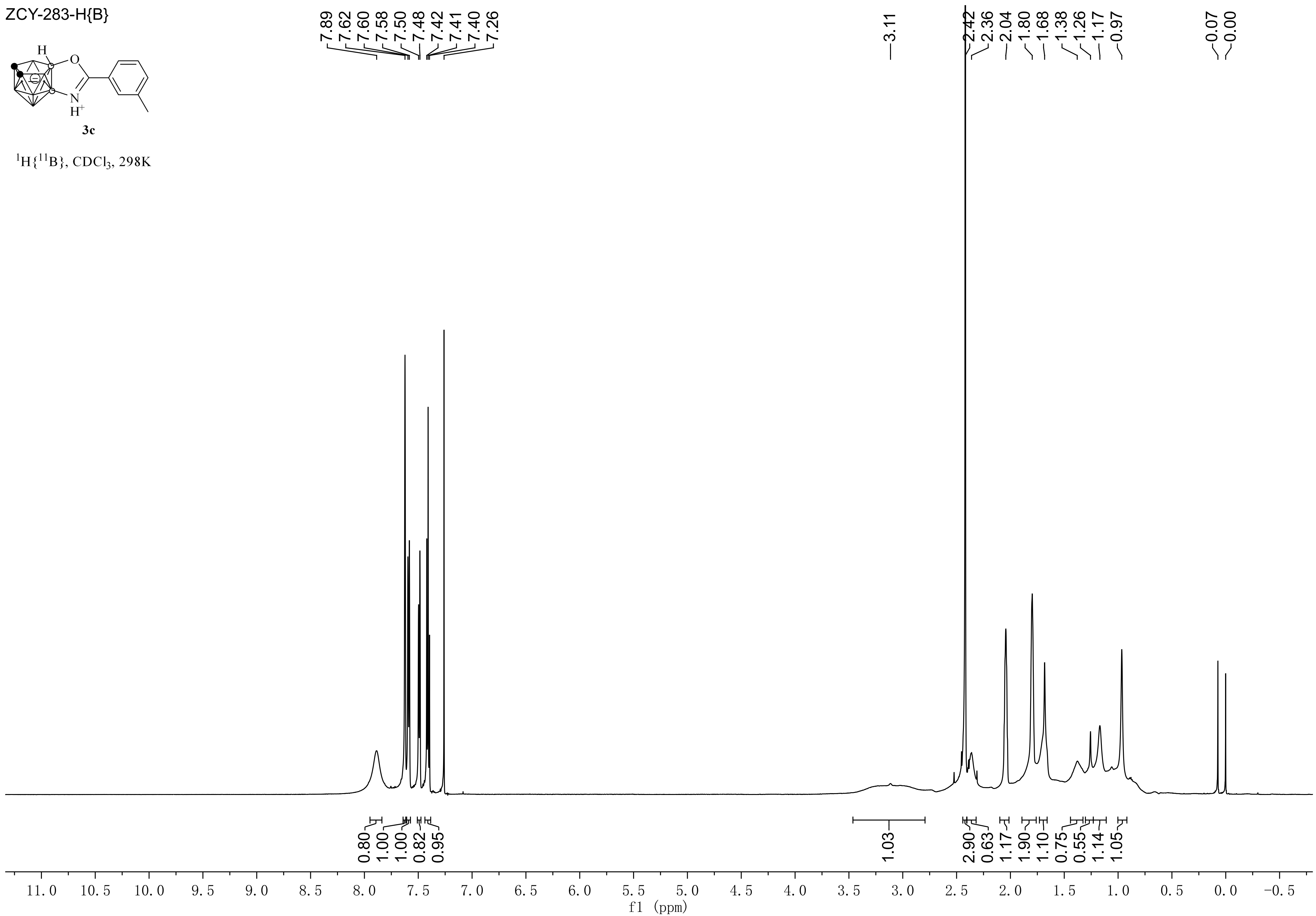
ZCY-283-H



3c

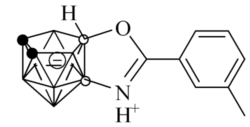
^{1}H, $CDCl_3$, 298K





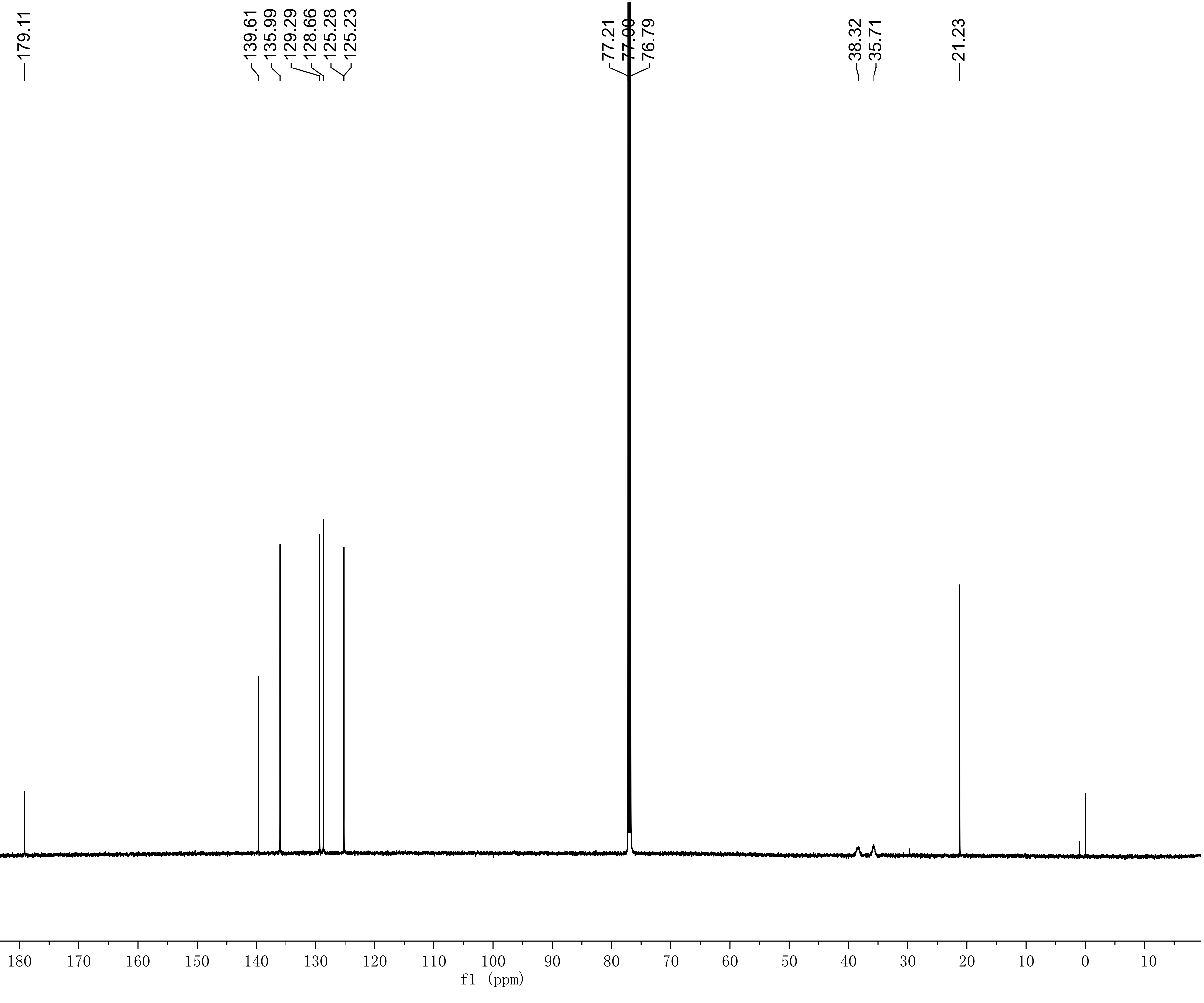
ZCY-283-H{B}
3c
$^{1}H\{^{11}B\}$, $CDCl_3$, 298K
7.89 7.62 7.60 7.58 7.50 7.48 7.42 7.41 7.40 7.26
3.11
2.42 2.36 2.04 1.80 1.68 1.38 1.26 1.17 0.97
0.07 0.00
0.80 1.00 1.00 0.82 0.95
1.03
2.90 0.63 1.17 1.90 1.10 0.75 0.55 1.14 1.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

ZCY-283-C

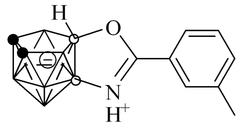


3c

^{13}C, $CDCl_3$, 298K

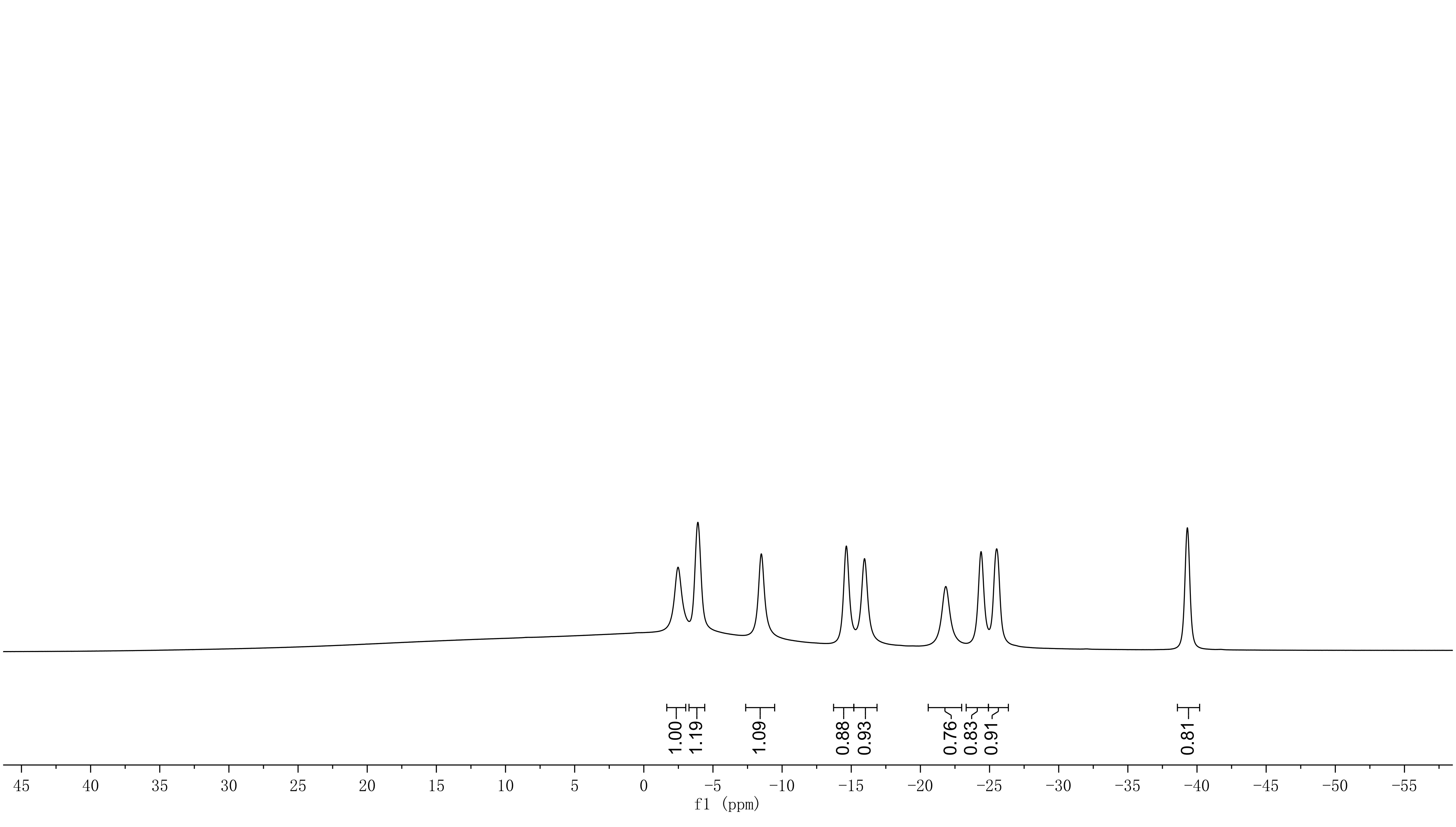


ZCY-283-B{H}

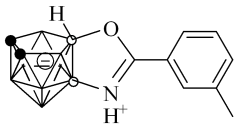


3c

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

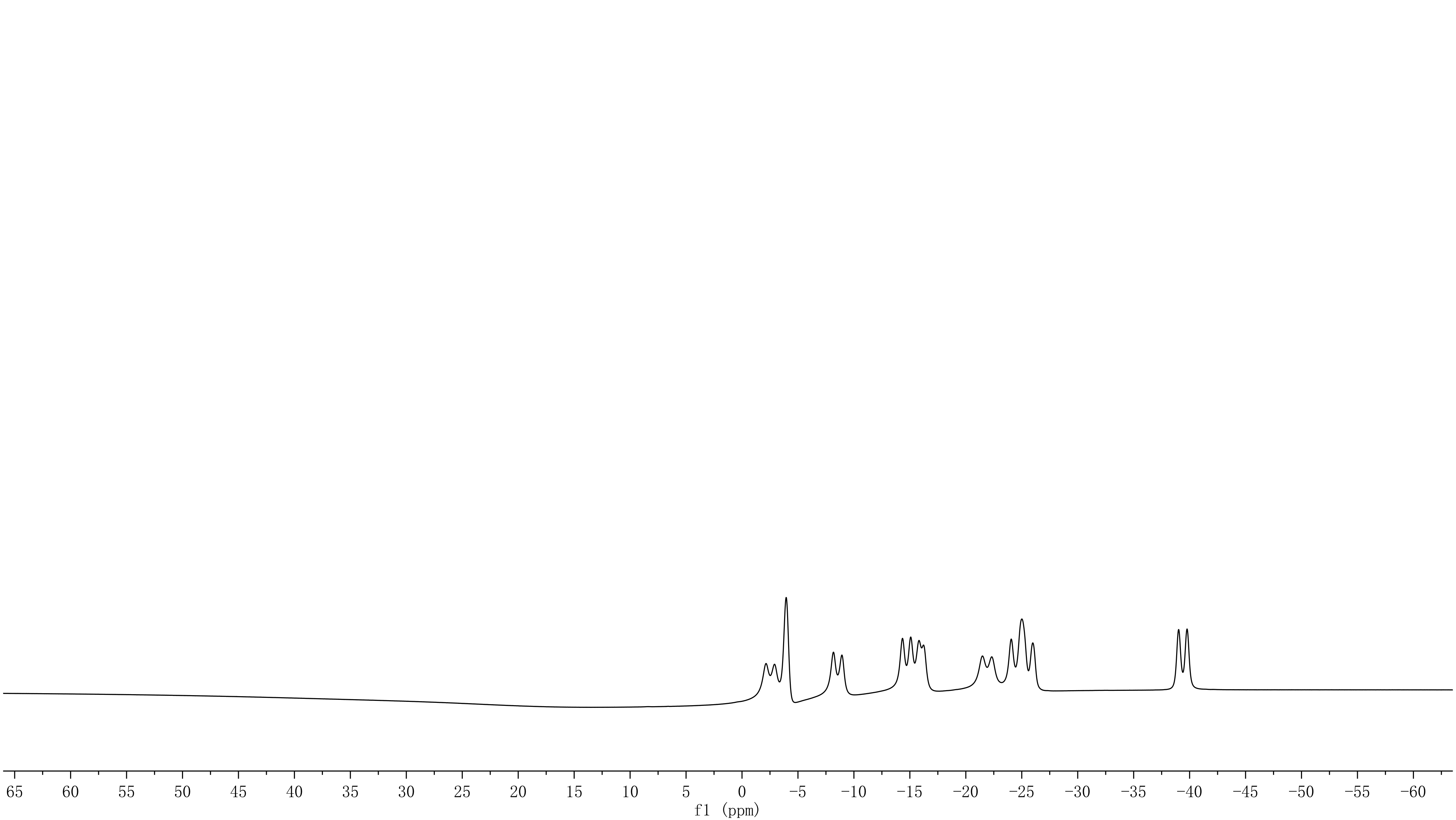


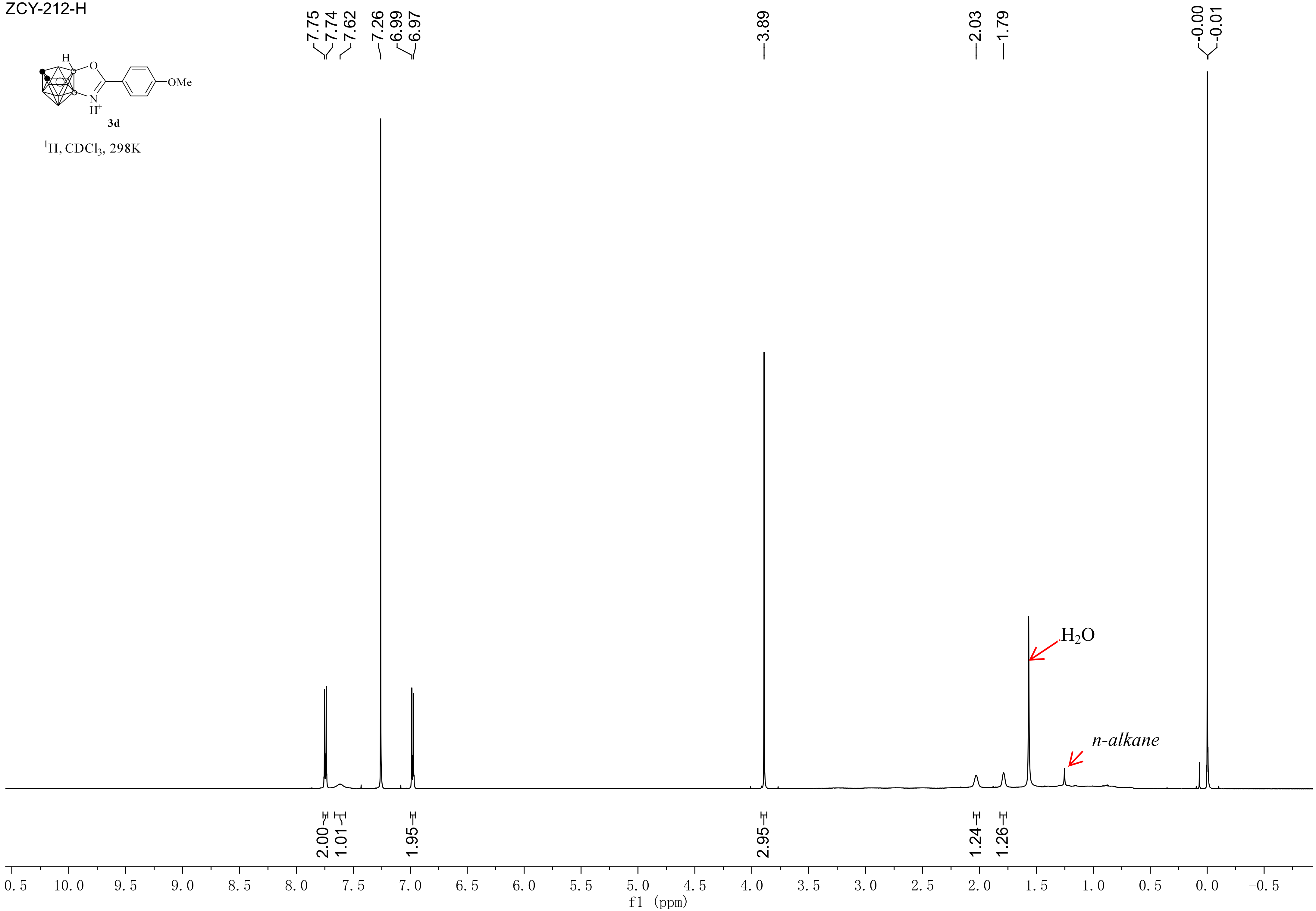
ZCY-283-B



3c

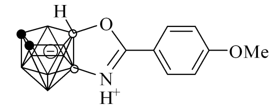
^{11}B, $CDCl_3$, 298K





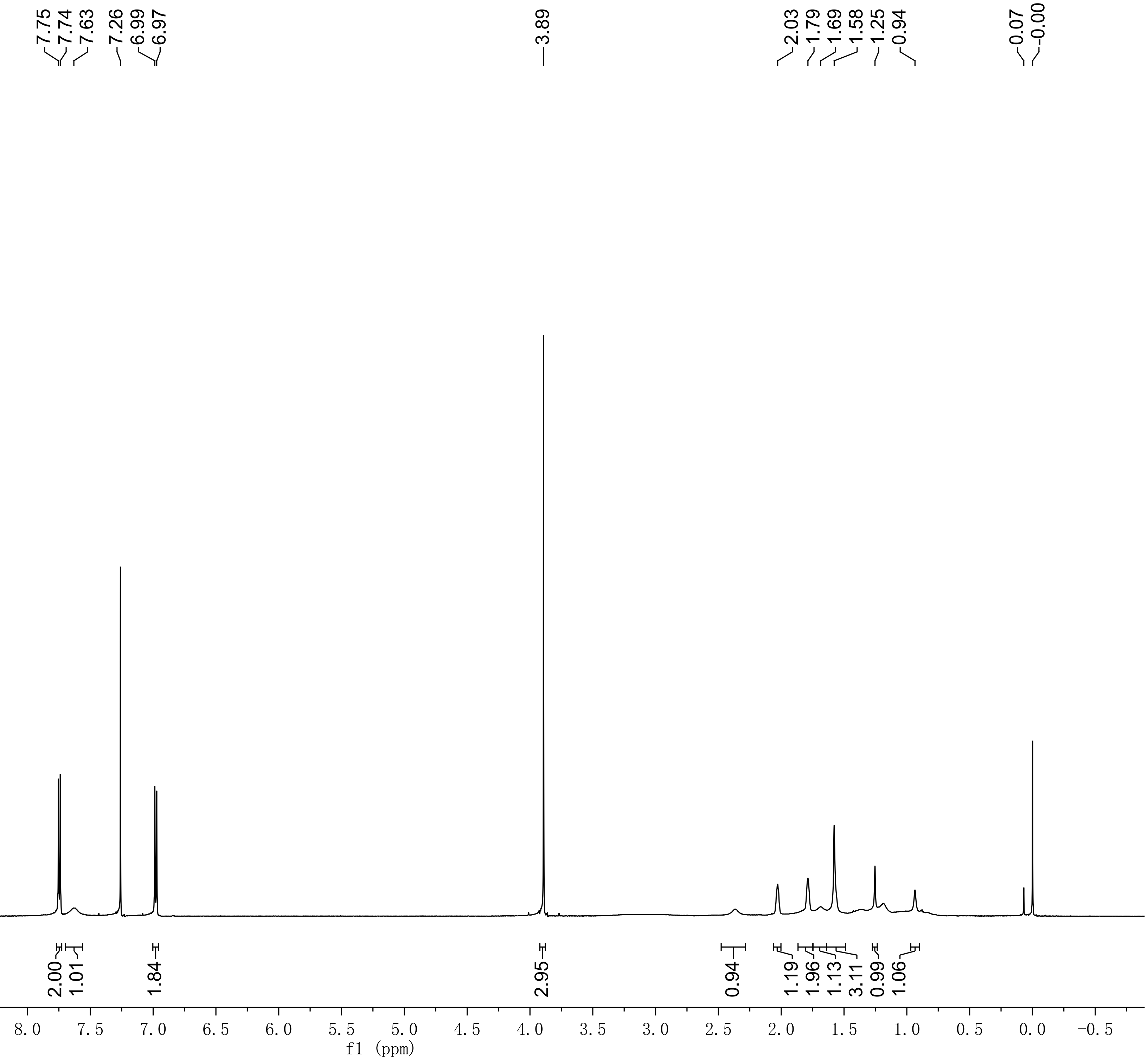
ZCY-212-H
H
O
N
H+
OMe
3d
1H, CDCl3, 298K
7.75
7.74
7.62
7.26
6.99
6.97
3.89
2.03
1.79
-0.00
-0.01
H2O
n-alkane
2.00
1.01
1.95
2.95
1.24
1.26
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

ZCY-212-H{B}

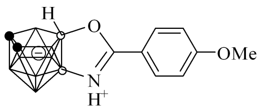


3d

$^{1}H\{^{11}B\}$, $CDCl_3$, 298K

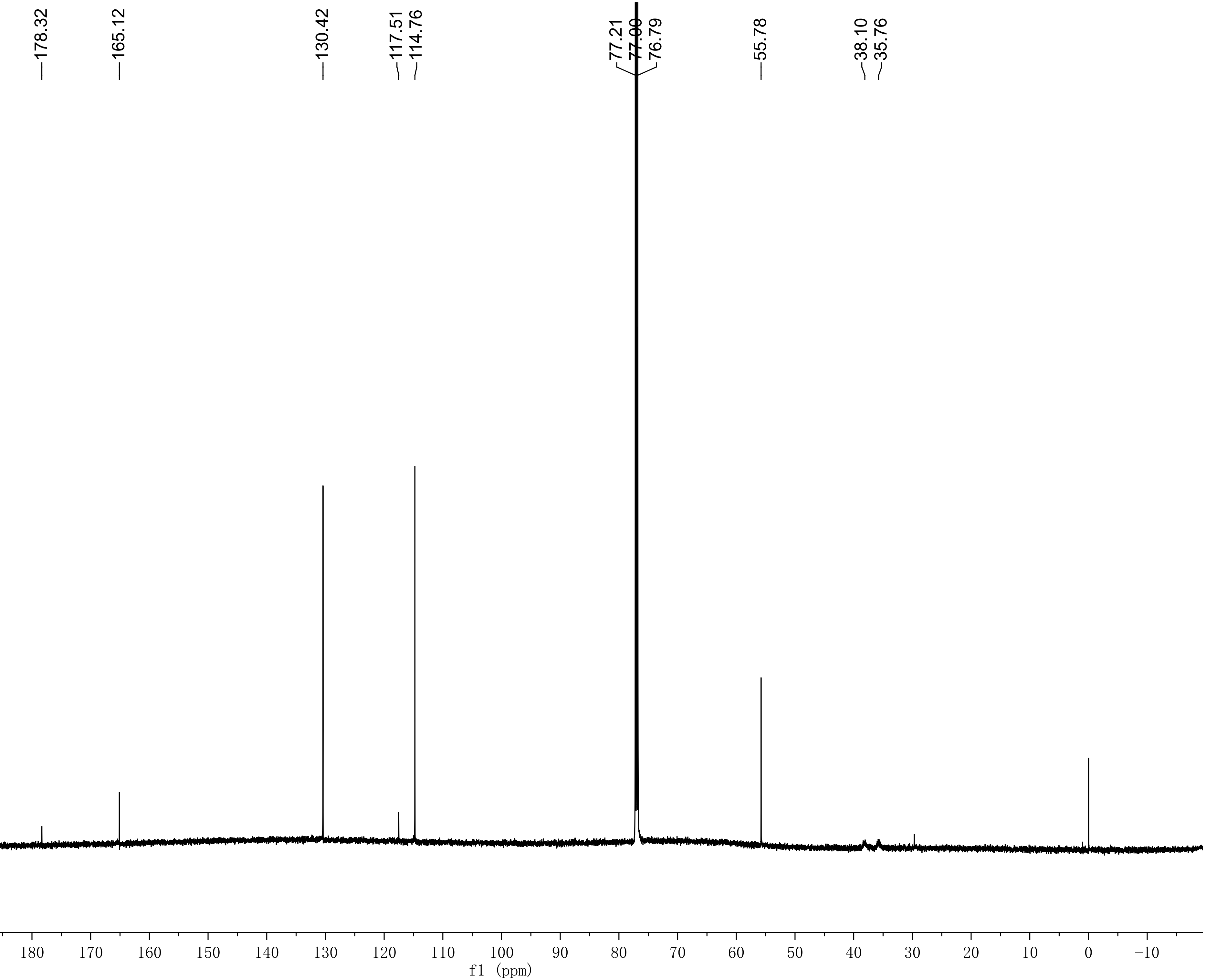


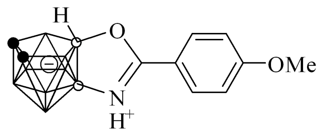
ZCY-212-C



3d

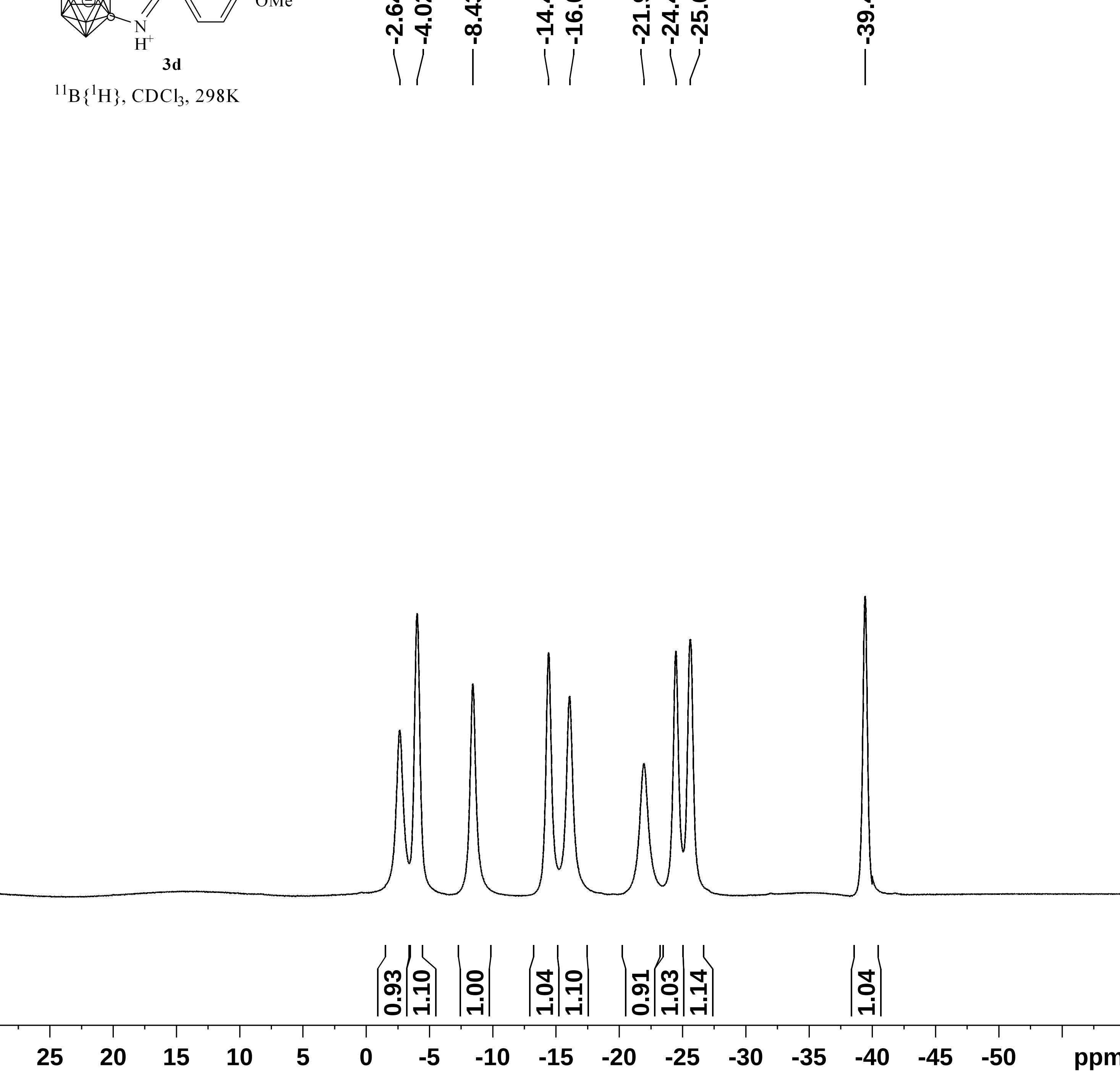
^{13}C, $CDCl_3$, 298K





3d

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

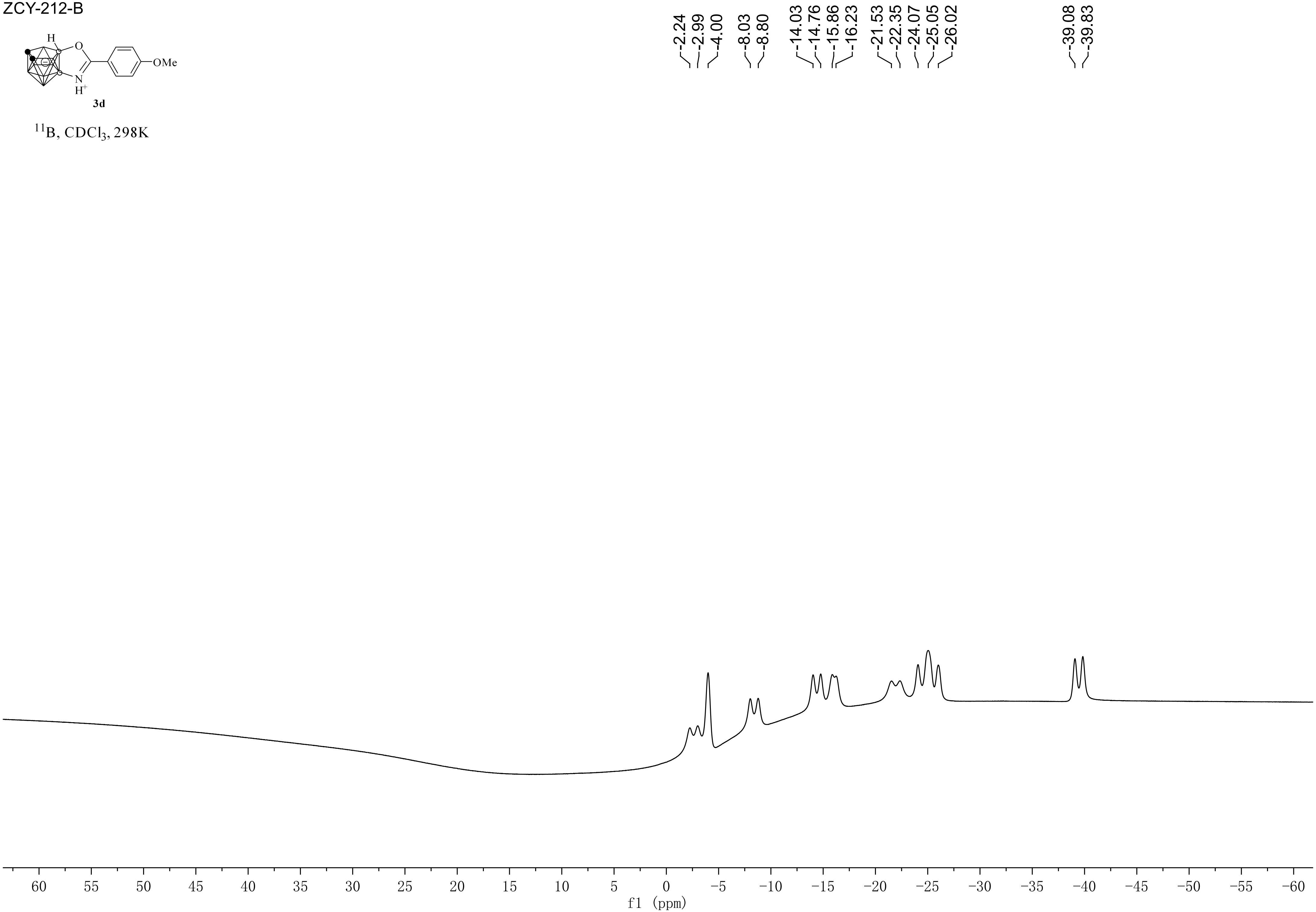


分析测试中心核磁实验室 SWUST

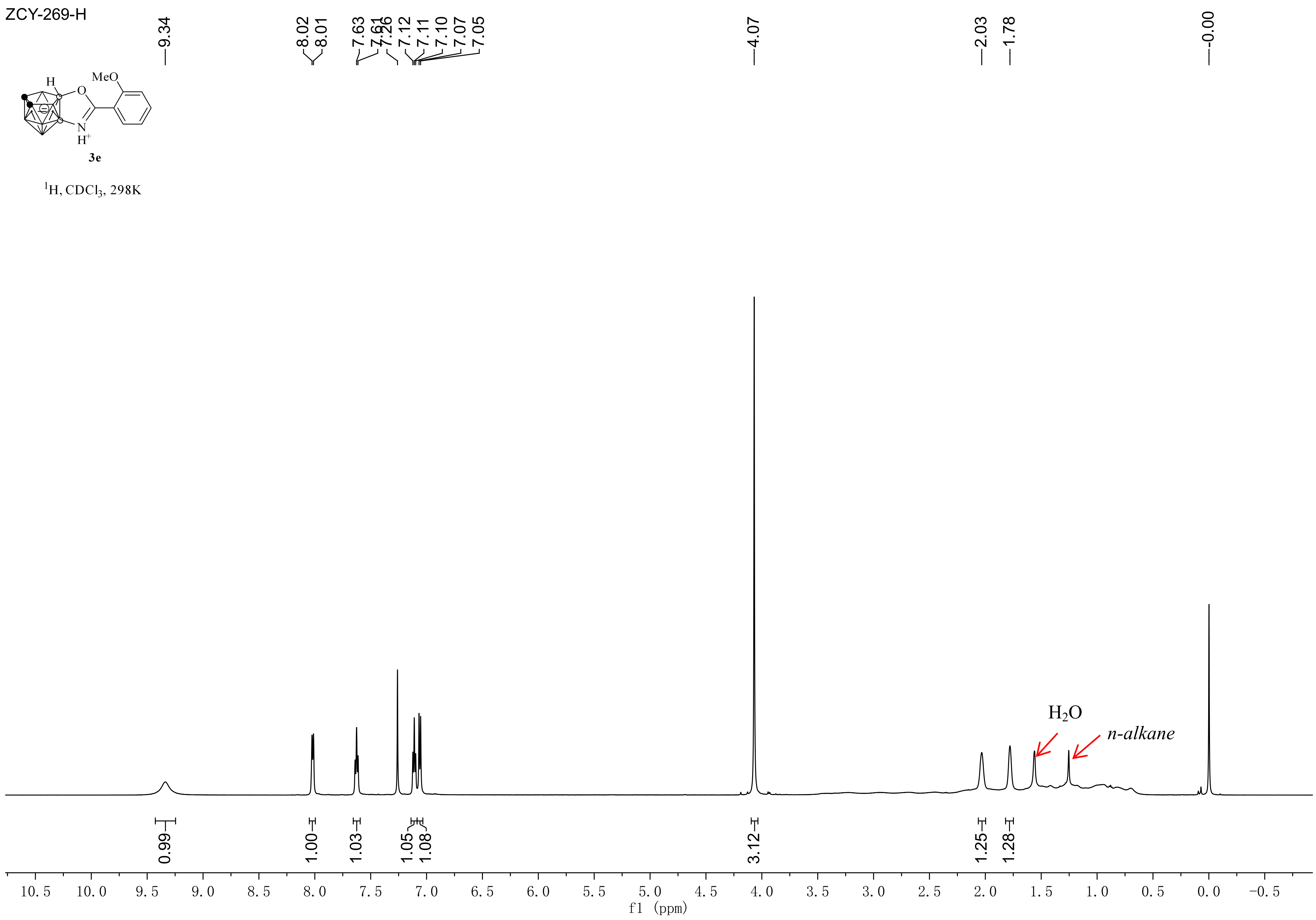
NMR Teacher : Huang

```
Current Data Parameters
NAME              20180327
EXPNO                  112
PROCNO                   1

F2 - Acquisition Parameters
Date_             20180328
Time                  2.02
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   85536
SOLVENT              CDCl3
NS                    5126
DS                       4
SWH             50000.000 Hz
FIDRES           0.584549 Hz
AQ              0.8553600 sec
RG                  172.47
DW                  10.000 usec
DE                    6.50 usec
TE                   298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        192.5526102 MHz
NUC1                   11B
P1                   25.00 usec
PLW1       180.00000000 W

======== CHANNEL f2 ========
SFO2        600.1737063 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2        23.00000000 W
PLW12        0.57832998 W
PLW13        0.28338000 W

F2 - Processing parameters
SI                   32768
SF          192.5583870 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```

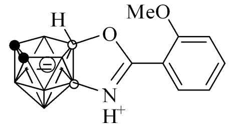
ZCY-212-B



3d
^{11}B, CDCl$_3$, 298K
-2.24
-2.99
-4.00
-8.03
-8.80
-14.03
-14.76
-15.86
-16.23
-21.53
-22.35
-24.07
-25.05
-26.02
-39.08
-39.83
60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 −60
f1 (ppm)

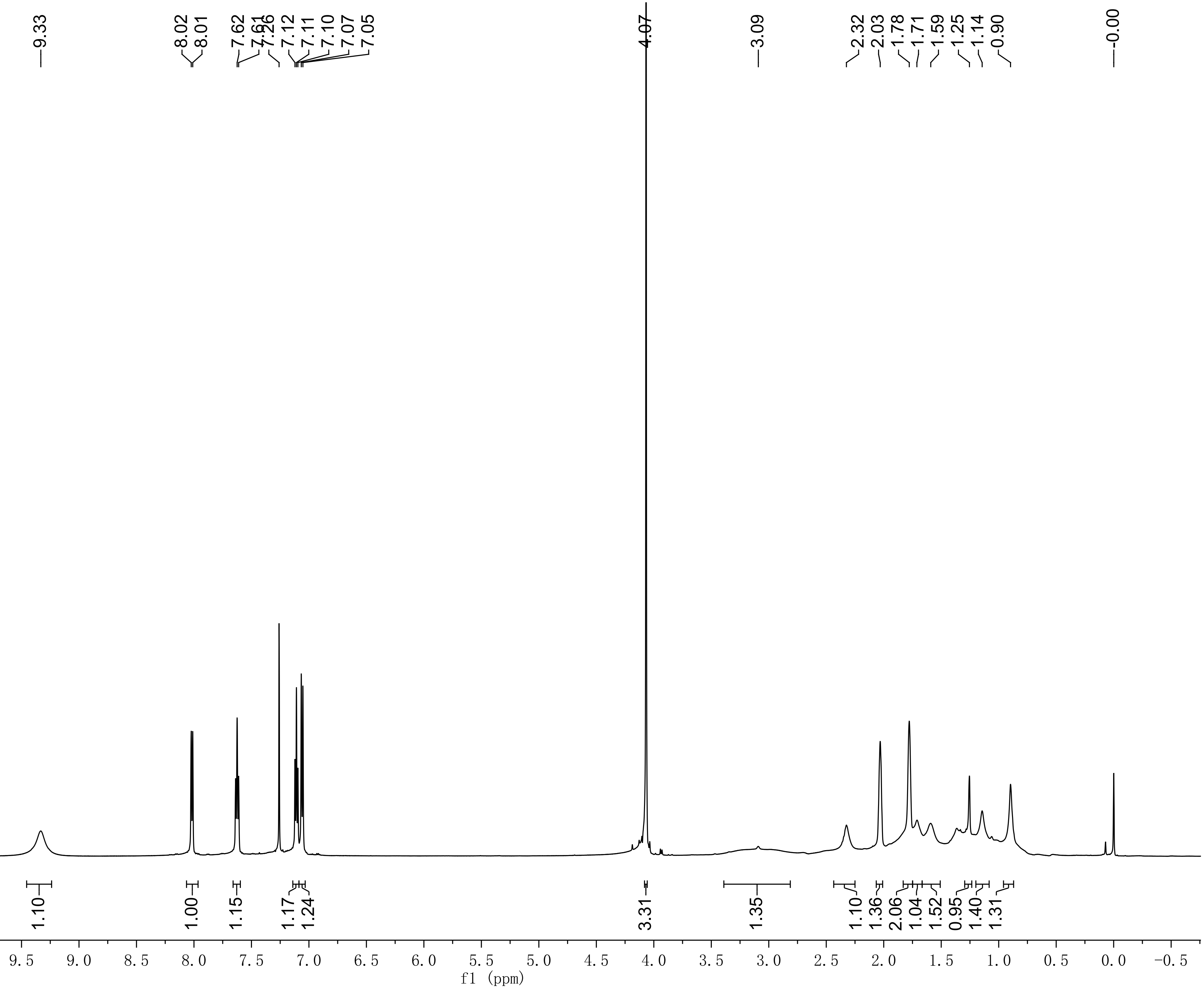

ZCY-269-H
9.34
8.02
8.01
7.63
7.61
7.26
7.12
7.11
7.10
7.07
7.05
4.07
2.03
1.78
-0.00
MeO
H
O
N
H+
3e
1H, CDCl3, 298K
H2O
n-alkane
0.99
1.00
1.03
1.05
1.08
3.12
1.25
1.28
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

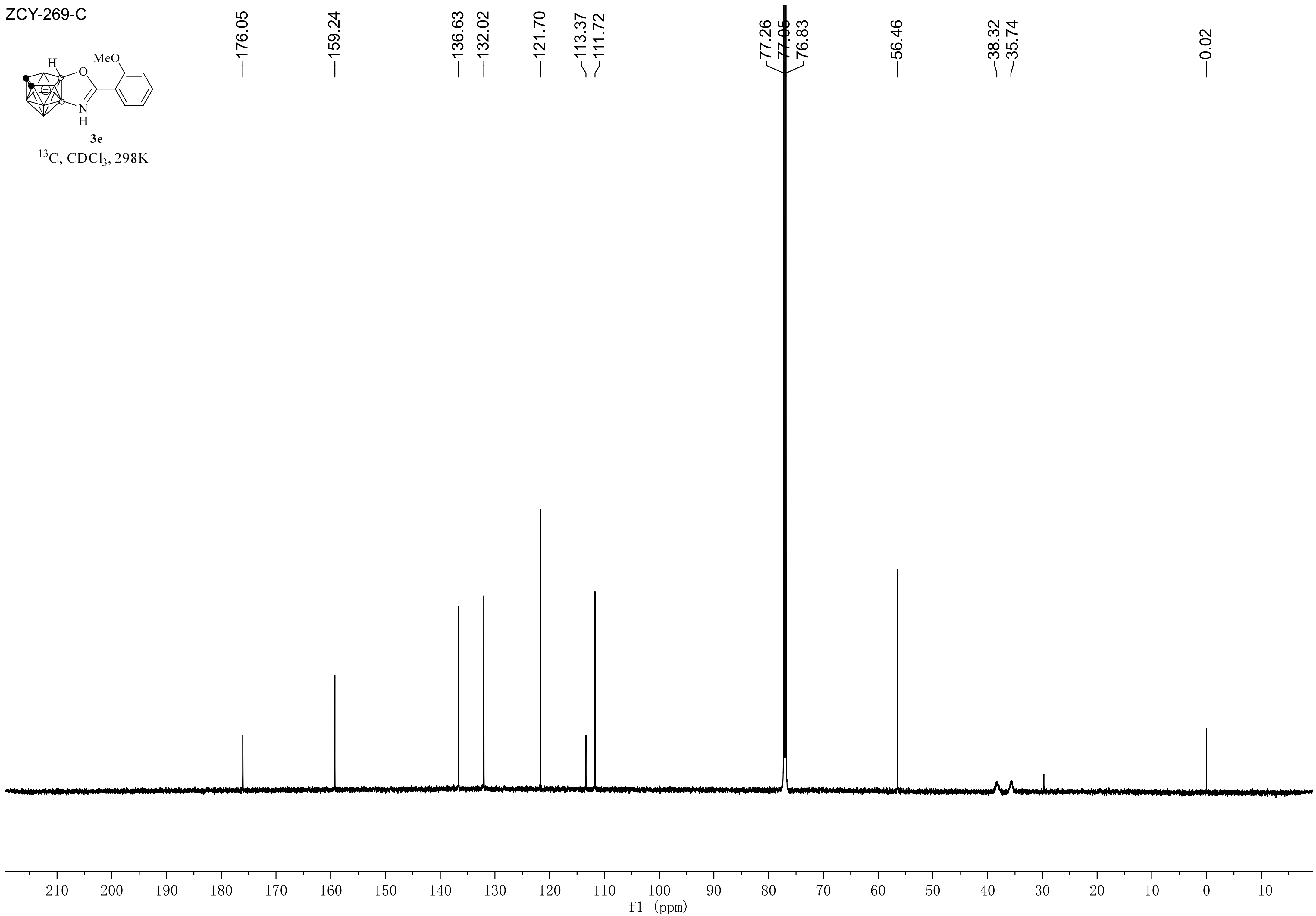
ZCY-269-H{B}



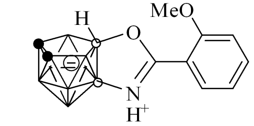
3e

$^{1}H\{^{11}B\}$, $CDCl_3$, 298K



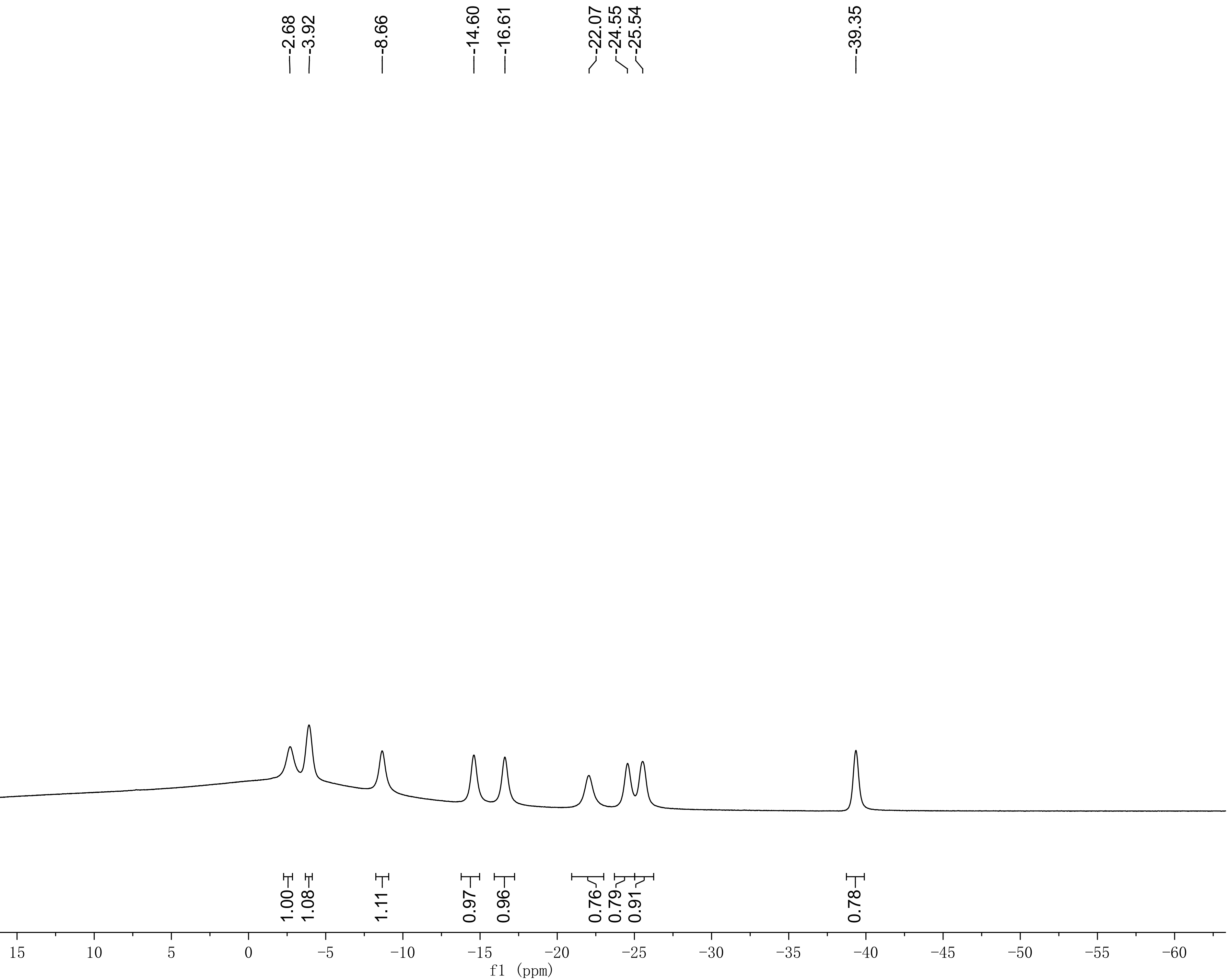

ZCY-269-C
MeO
H
O
N
H+
3e
13C, CDCl3, 298K
176.05
159.24
136.63
132.02
121.70
113.37
111.72
77.26
77.05
76.83
56.46
38.32
35.74
0.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

ZCY-269-B{H}

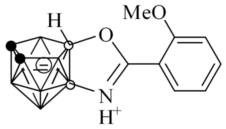


3e

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

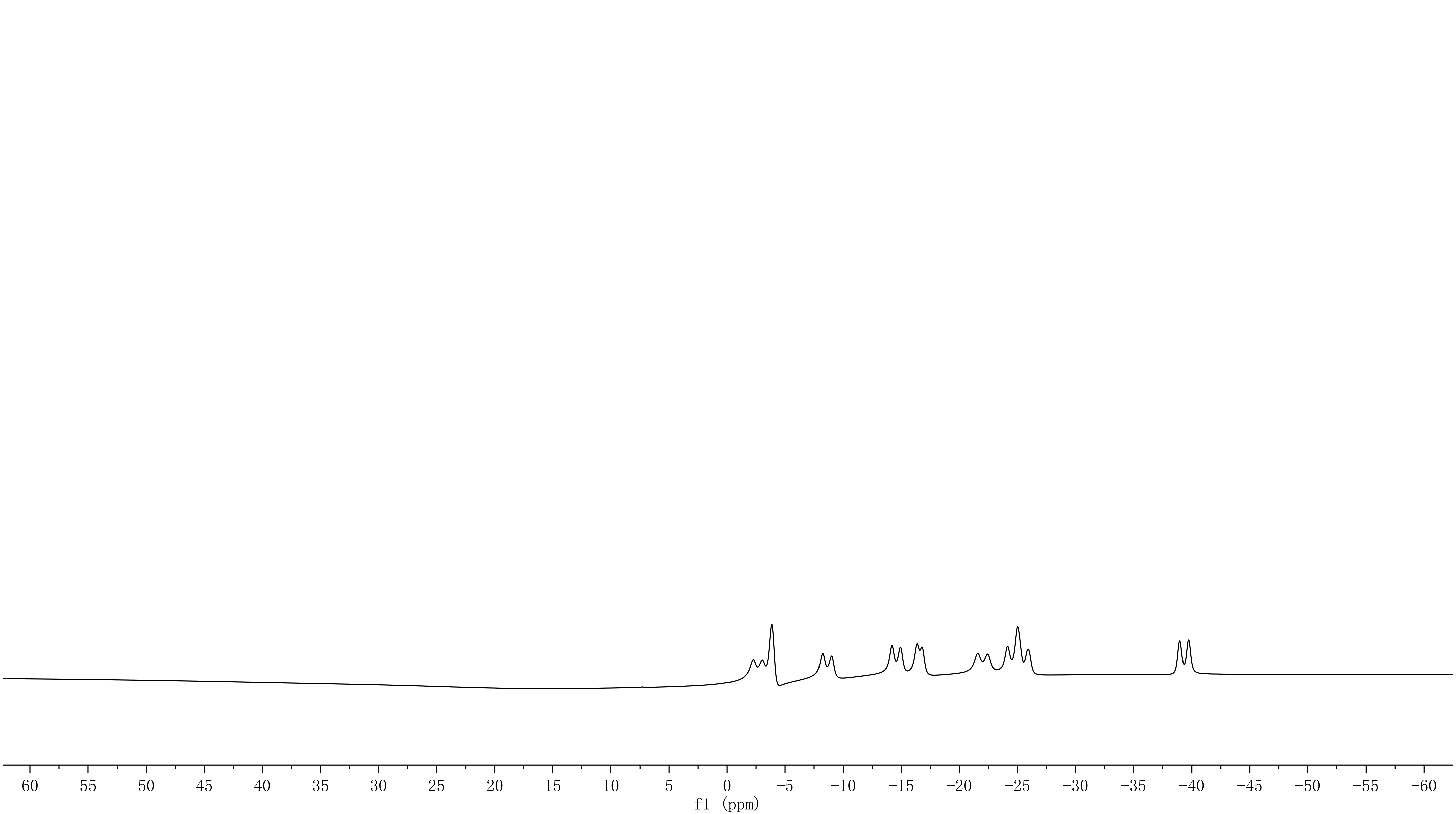


ZCY-269-B

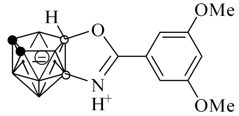


3e

^{11}B, $CDCl_3$, 298K

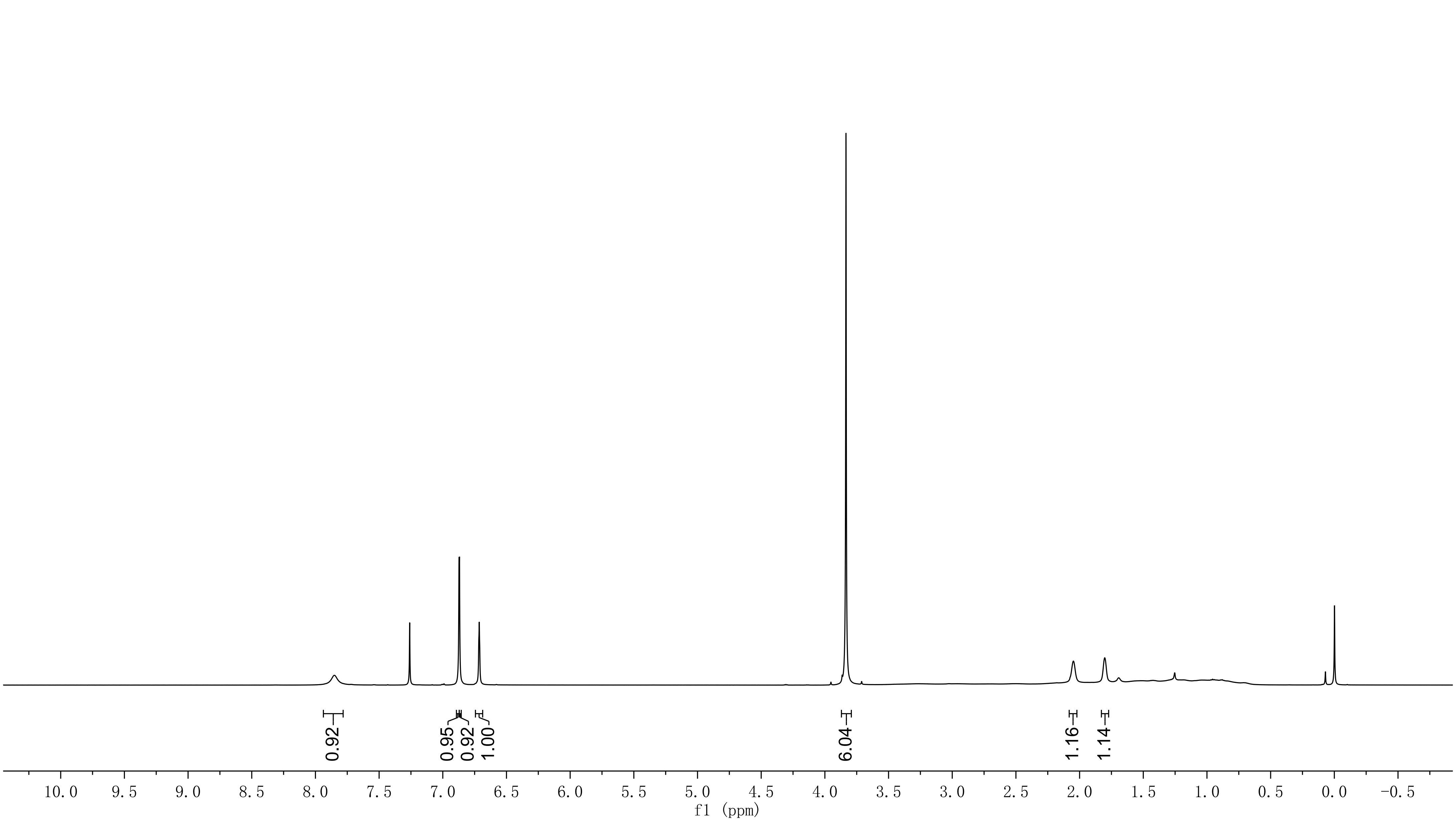


ZCY-260-H

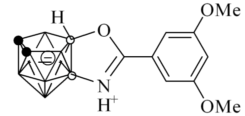


3f

^{1}H, $CDCl_3$, 298K

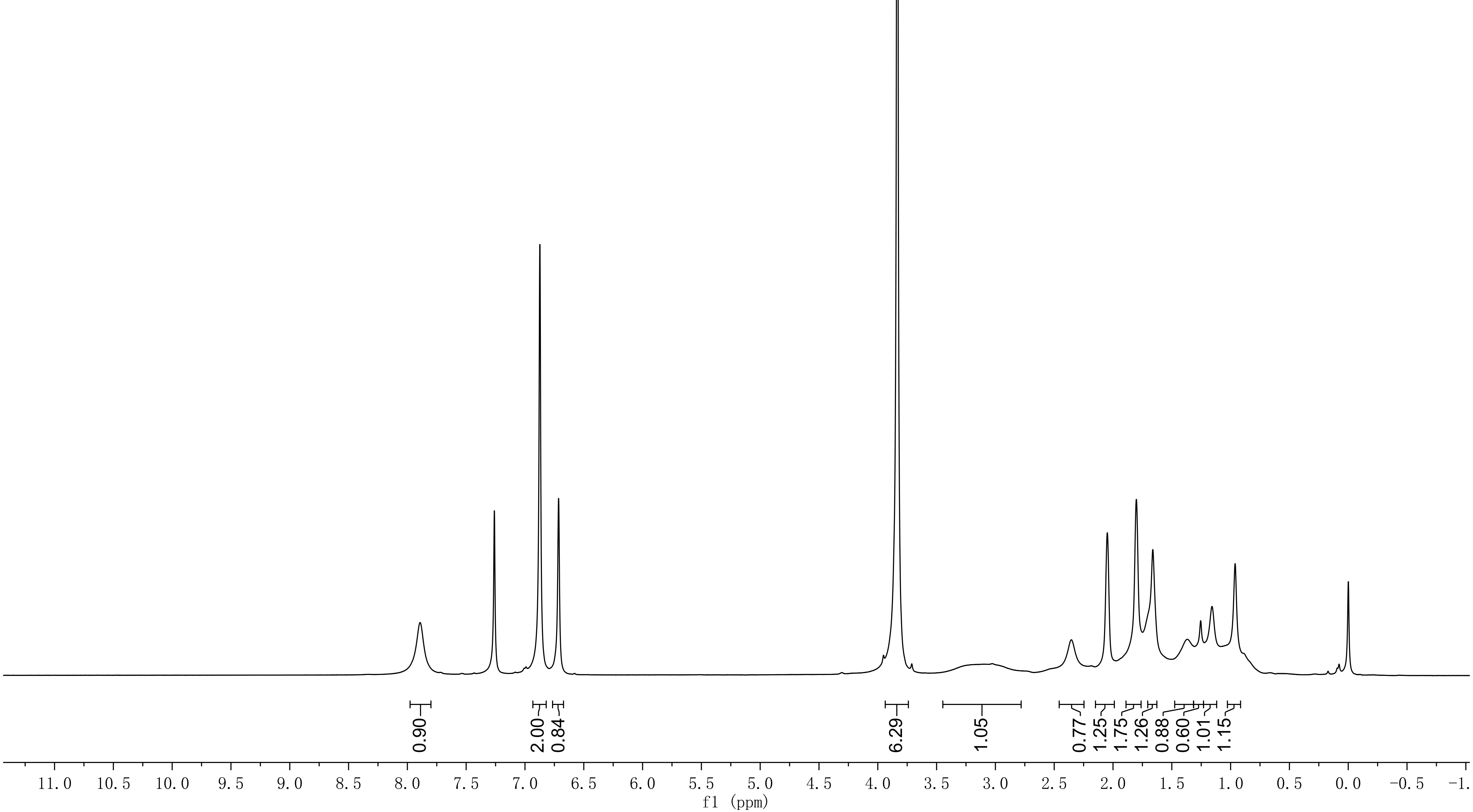


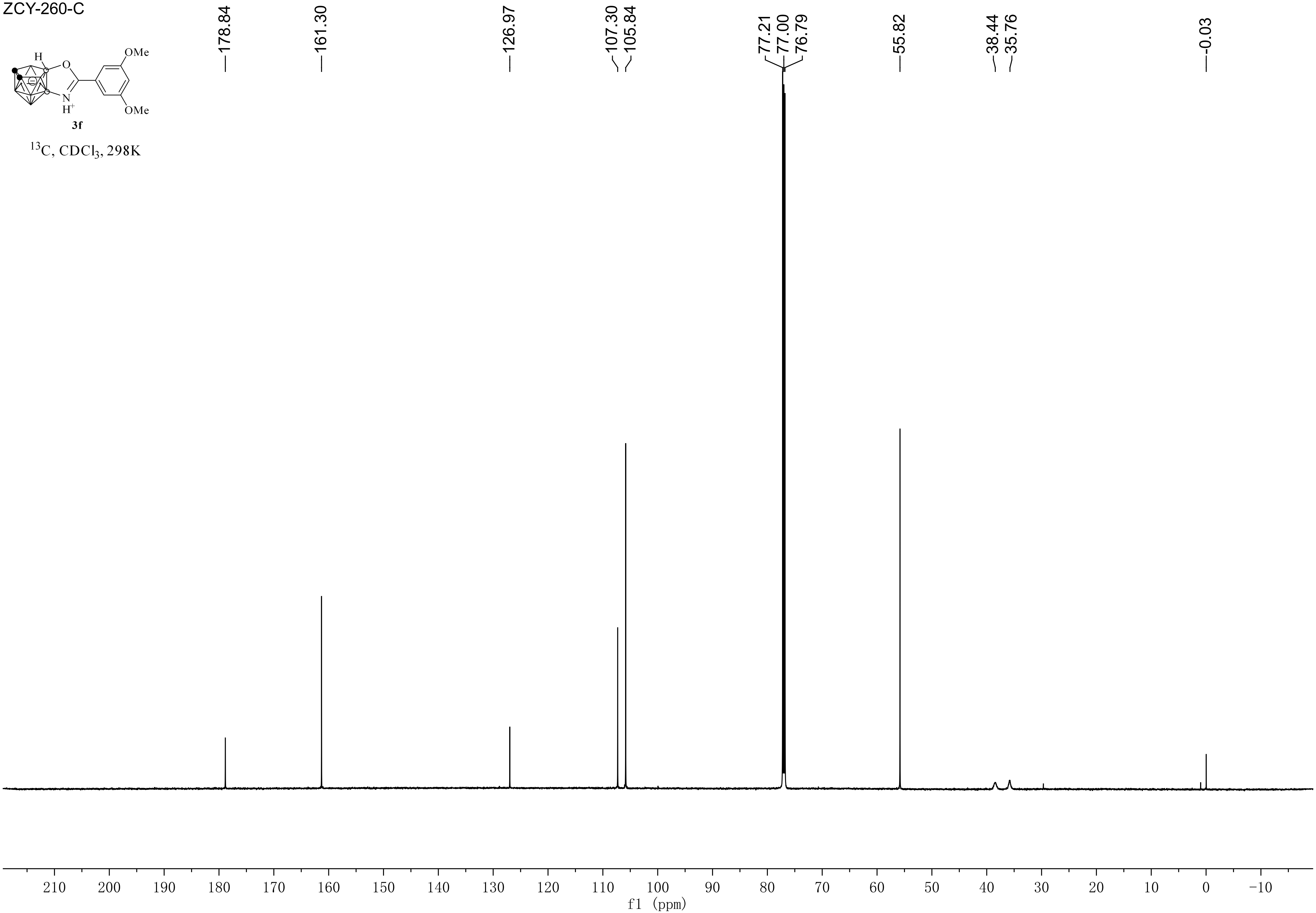
ZCY-260-H{B}



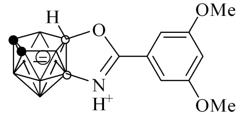
3f

$^{1}H\{^{11}B\}$, $CDCl_3$, 298K



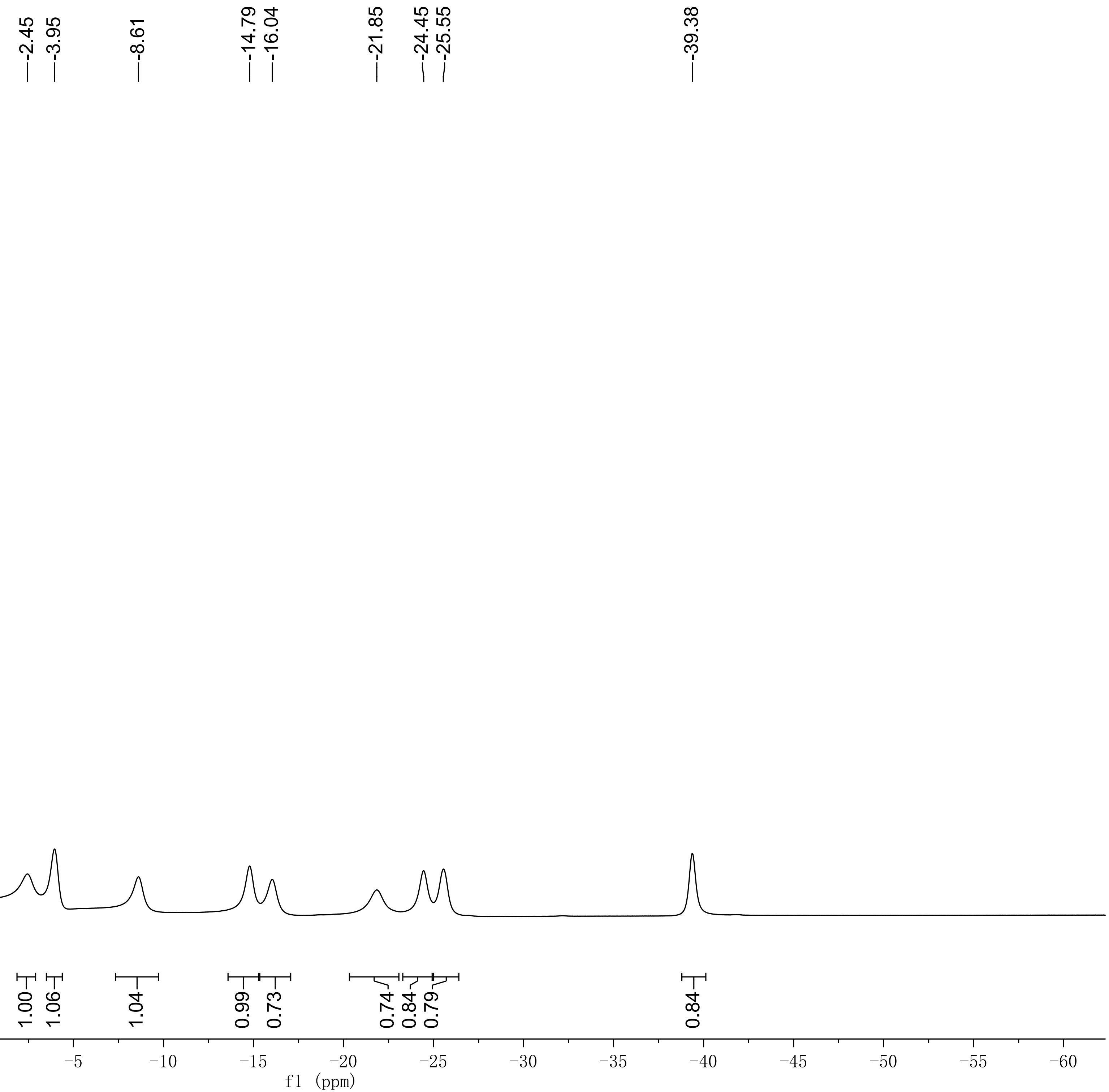

ZCY-260-C
H
O
OMe
N
H+
OMe
3f
13C, CDCl3, 298K
178.84
161.30
126.97
107.30
105.84
77.21
77.00
76.79
55.82
38.44
35.76
-0.03
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

ZCY-260-B{H}

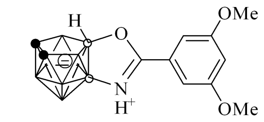


3f

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

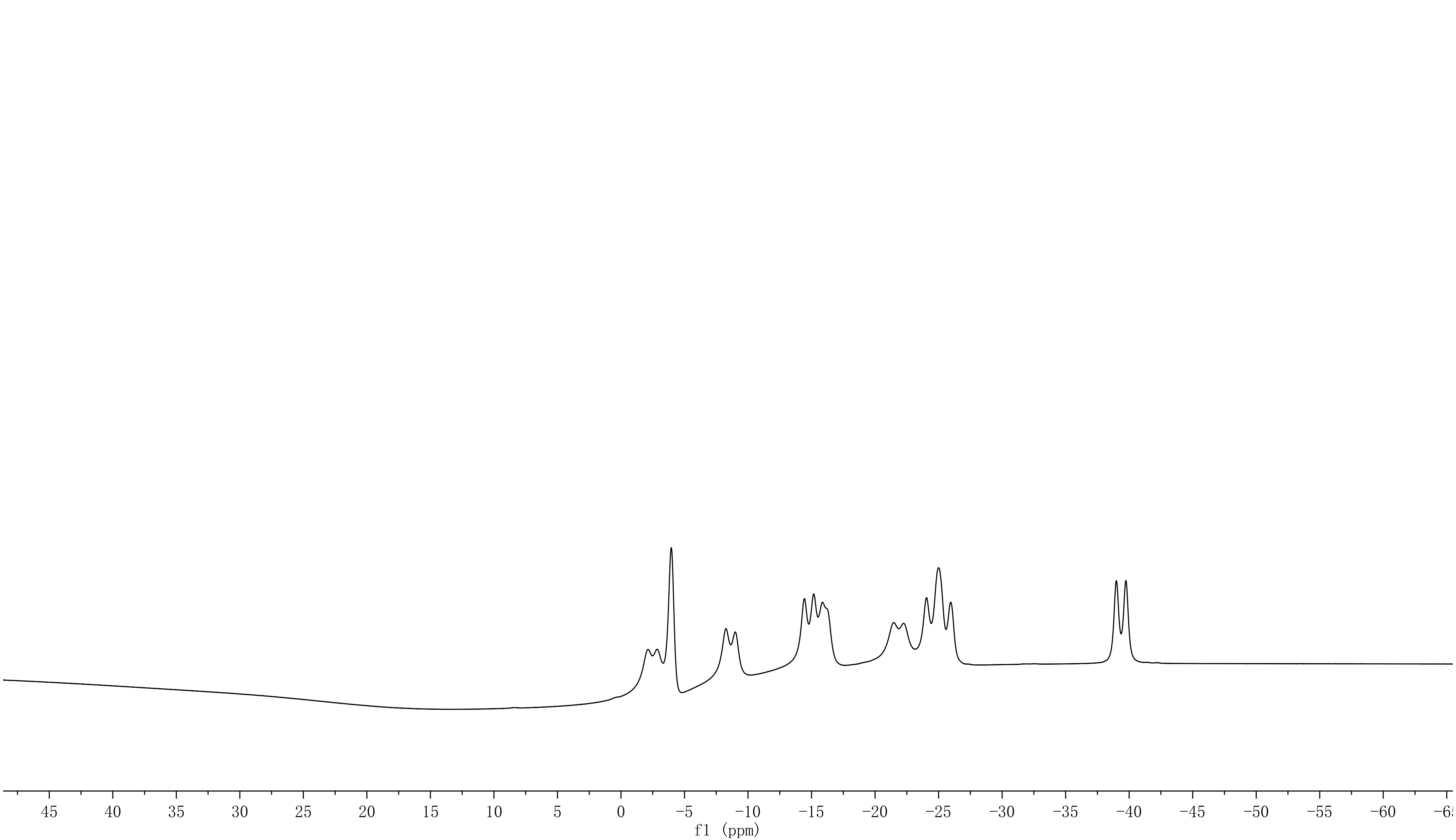


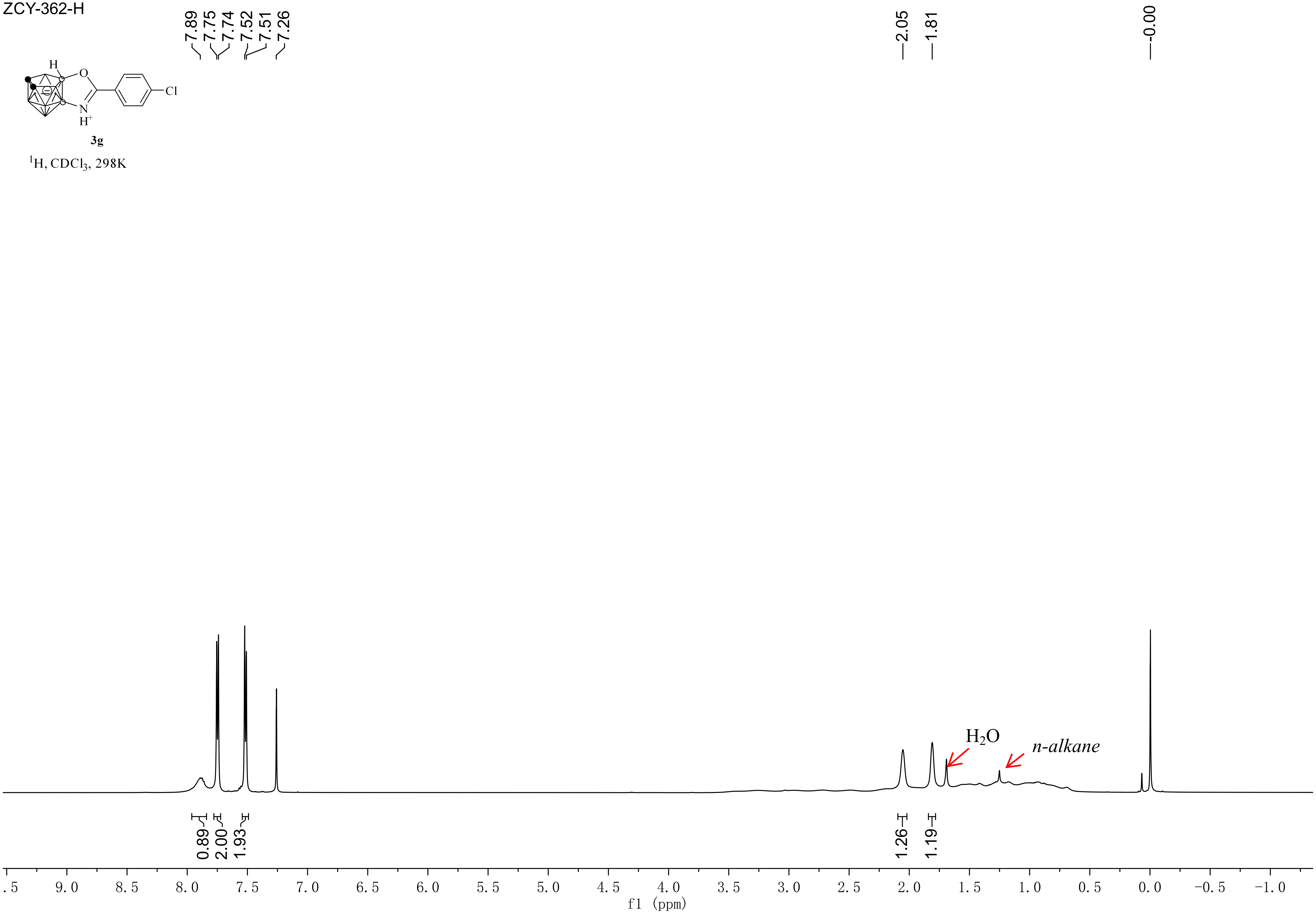
ZCY-260-B



3f

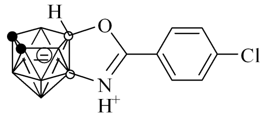
^{11}B, $CDCl_3$, 298K





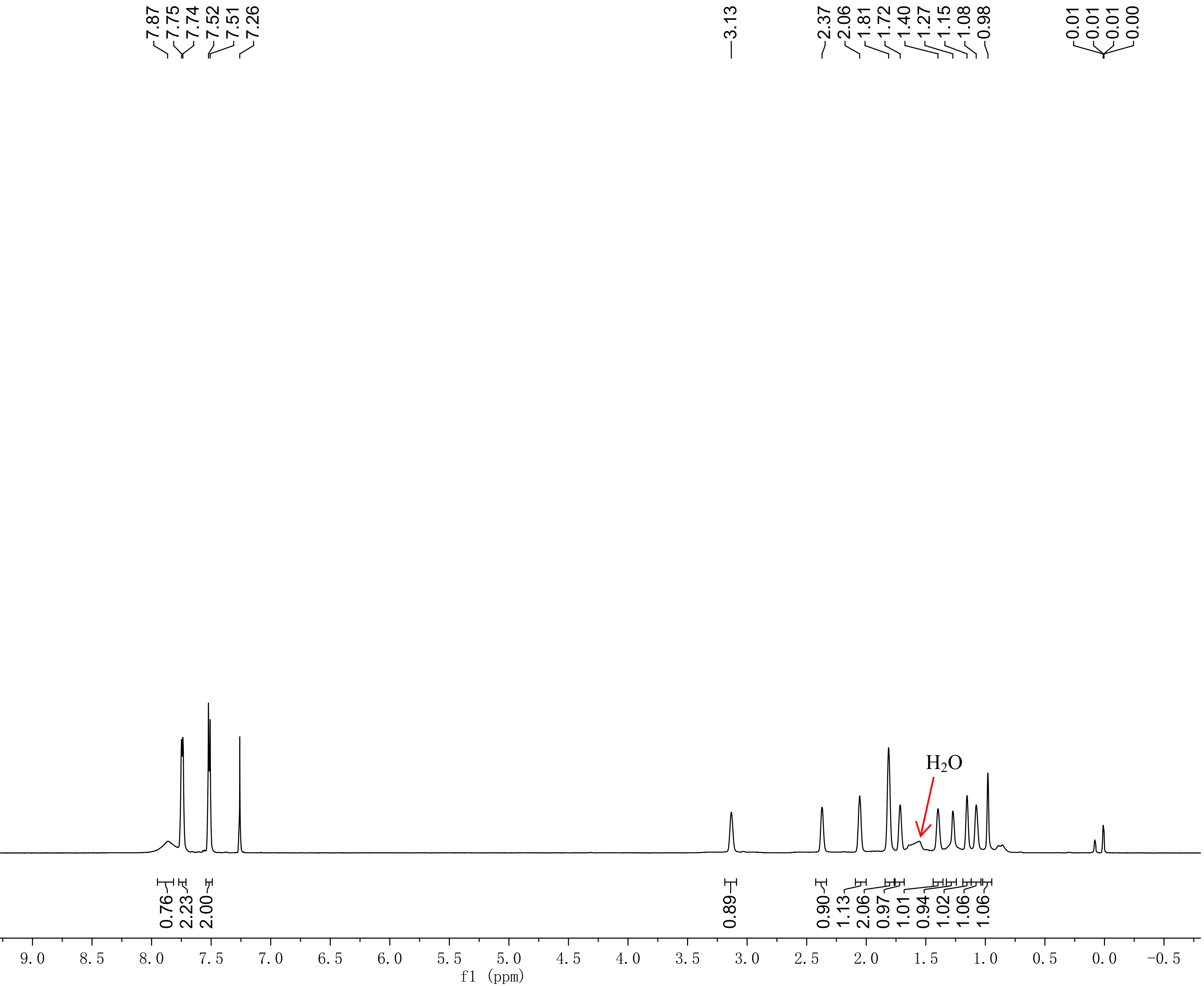
ZCY-362-H
7.89
7.75
7.74
7.52
7.51
7.26
2.05
1.81
-0.00
H
O
N
H+
Cl
3g
1H, CDCl3, 298K
H2O
n-alkane
0.89
2.00
1.93
1.26
1.19
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

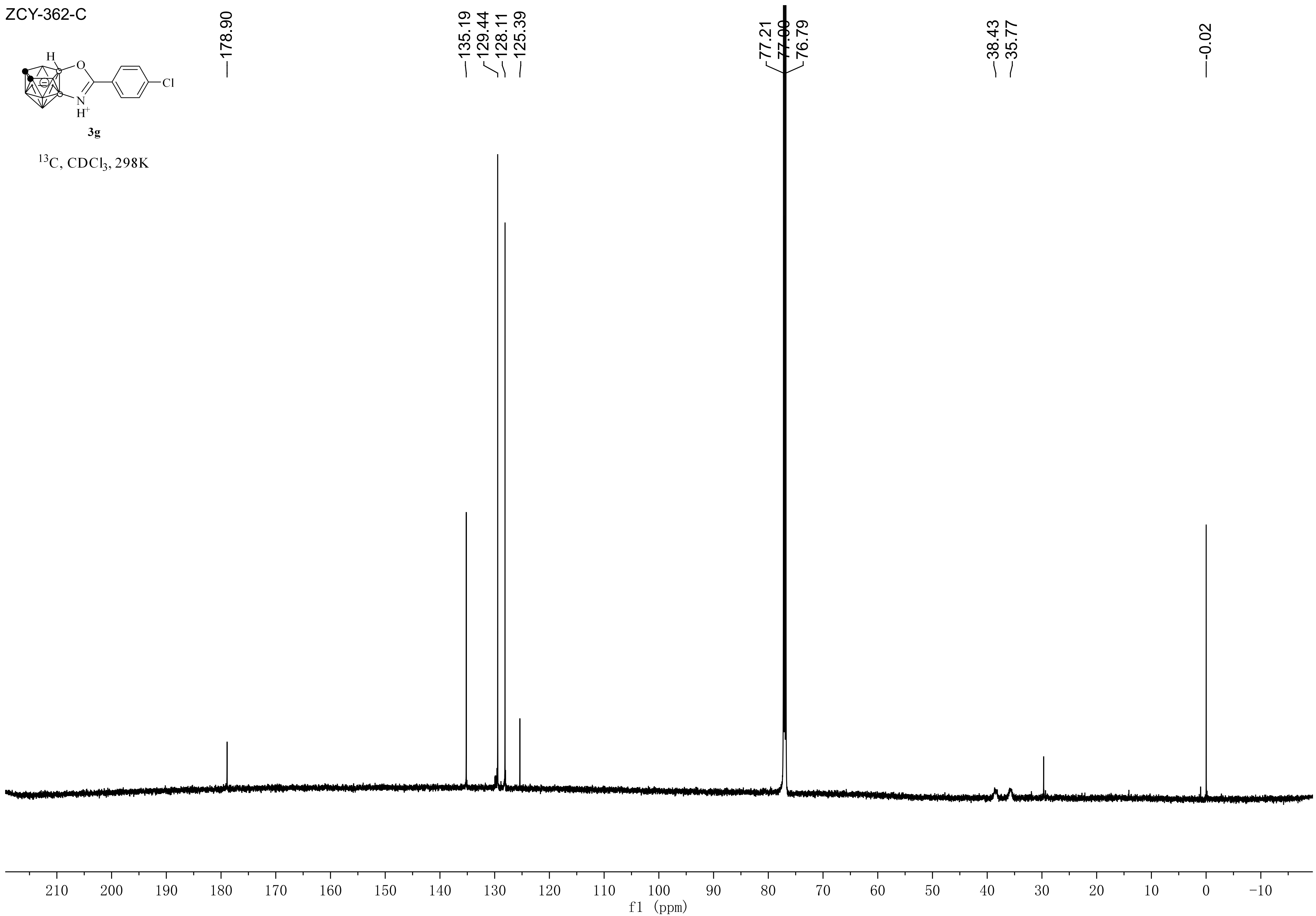
ZCY-362-H{B}

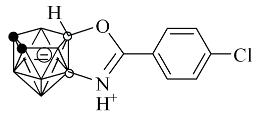


3g

$^1H\{^{11}B\}$, $CDCl_3$, 298K

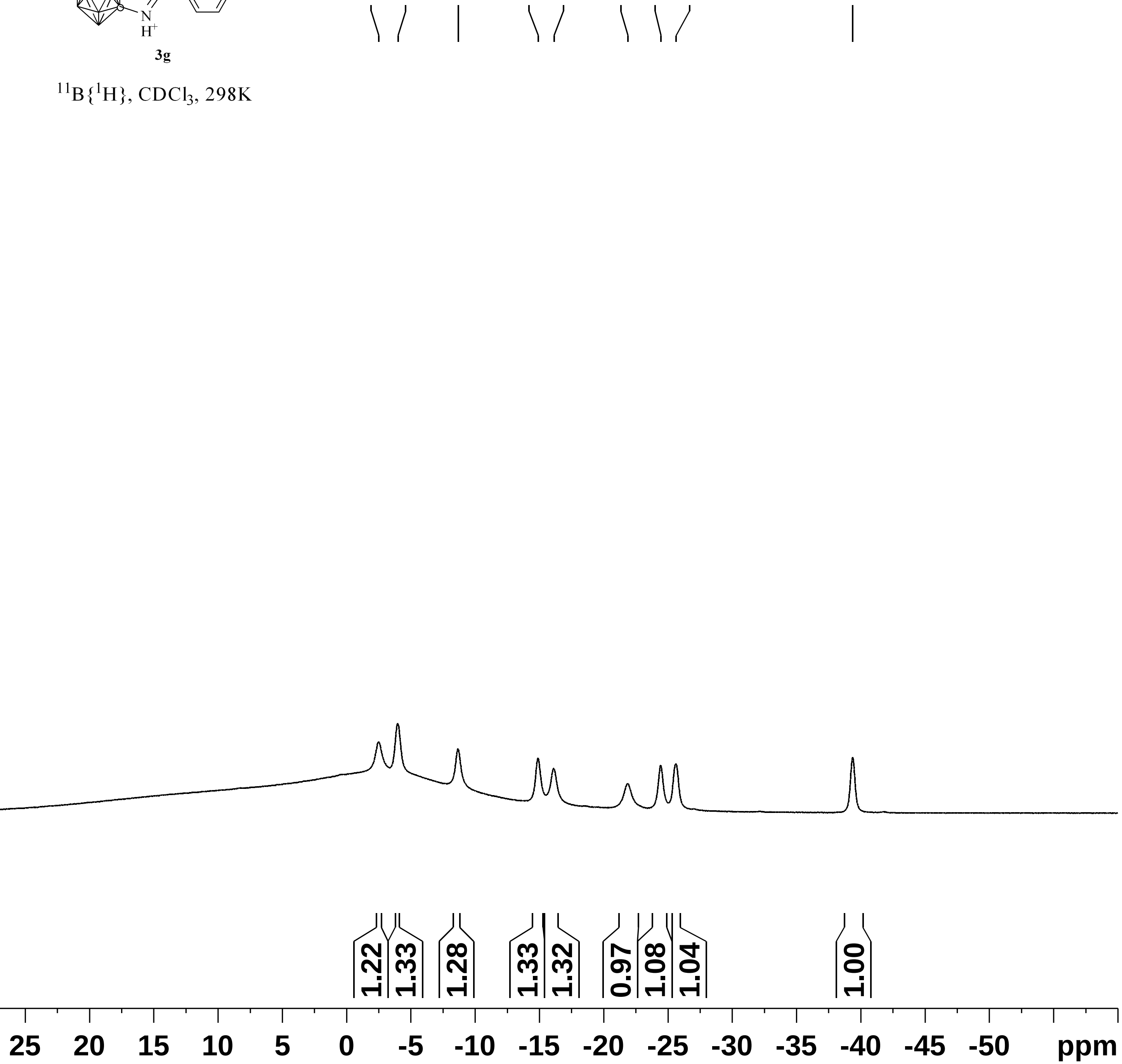



ZCY-362-C
178.90
135.19
129.44
128.11
125.39
77.21
77.00
76.79
38.43
35.77
-0.02
H
O
N
H+
Cl
3g
13C, CDCl3, 298K
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3g

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

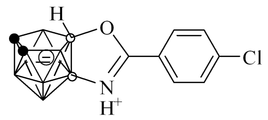


分析测试中心核磁实验室 SWUST

NMR Teacher : Huang

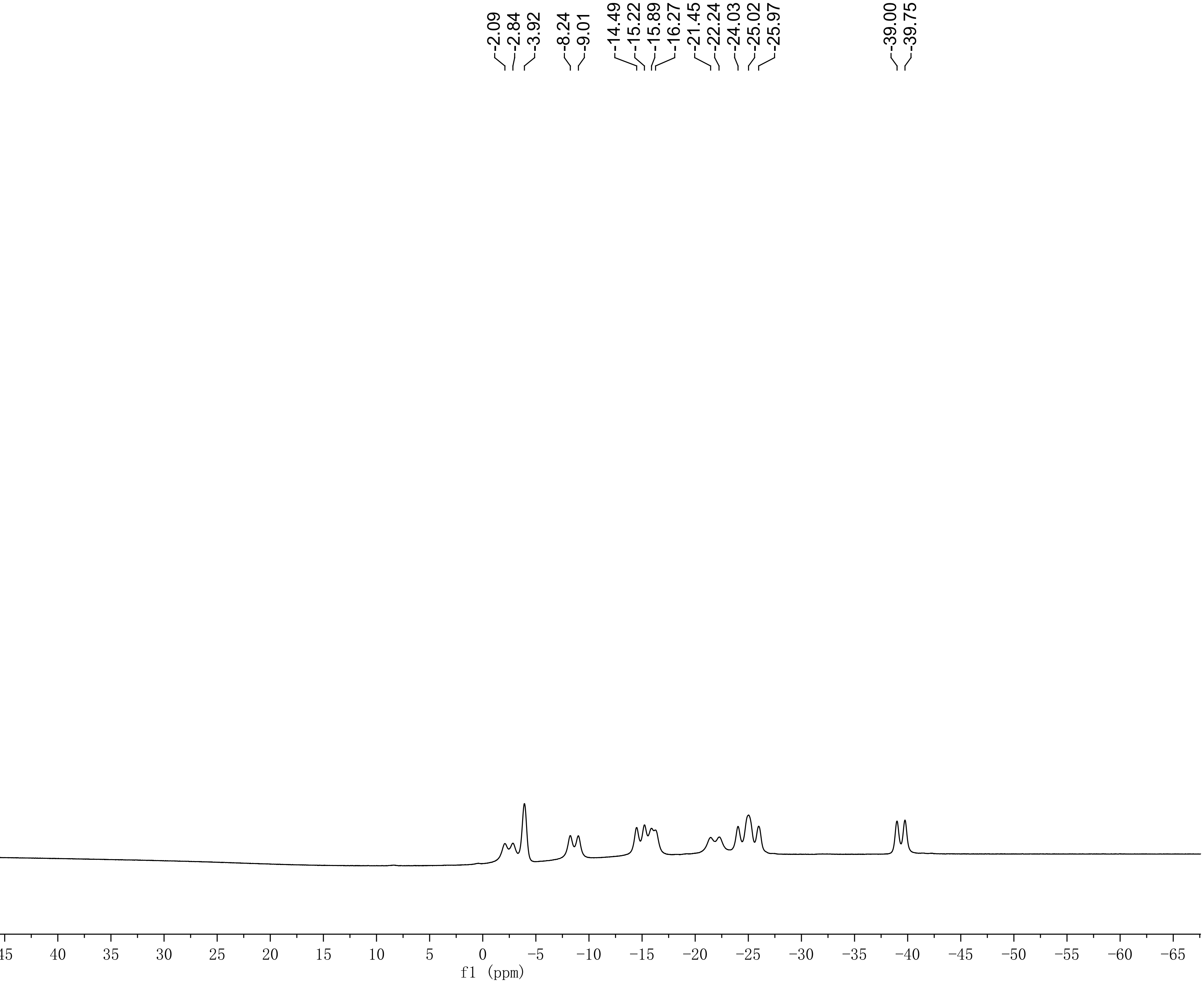
```
Current Data Parameters
NAME             20180528
EXPNO                 202
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180529
Time                 0.35
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  85536
SOLVENT             CDCl3
NS                   5000
DS                      4
SWH             50000.000 Hz
FIDRES           0.584549 Hz
AQ              0.8553600 sec
RG                 172.47
DW                 10.000 usec
DE                   6.50 usec
TE                  298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          192.5526102 MHz
NUC1                  11B
P1                  25.00 usec
PLW1         180.00000000 W

======== CHANNEL f2 ========
SFO2          600.1737063 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               70.00 usec
PLW2          23.00000000 W
PLW12          0.57832998 W
PLW13          0.28338000 W

F2 - Processing parameters
SI                  32768
SF            192.5583870 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

ZCY-362-B

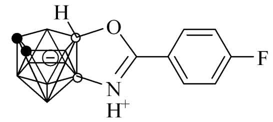


3g

^{11}B, $CDCl_3$, 298K

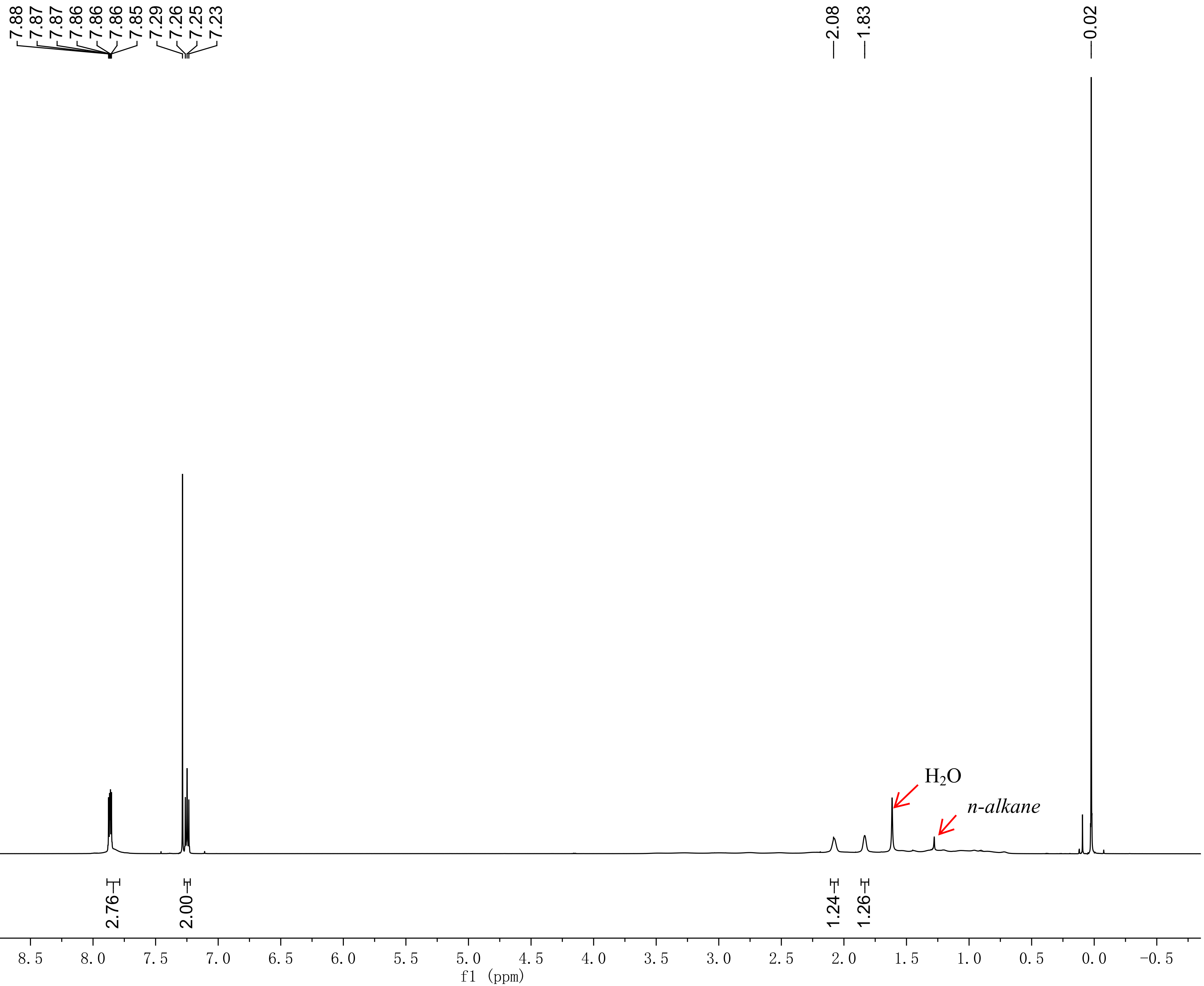


ZCY-213-H

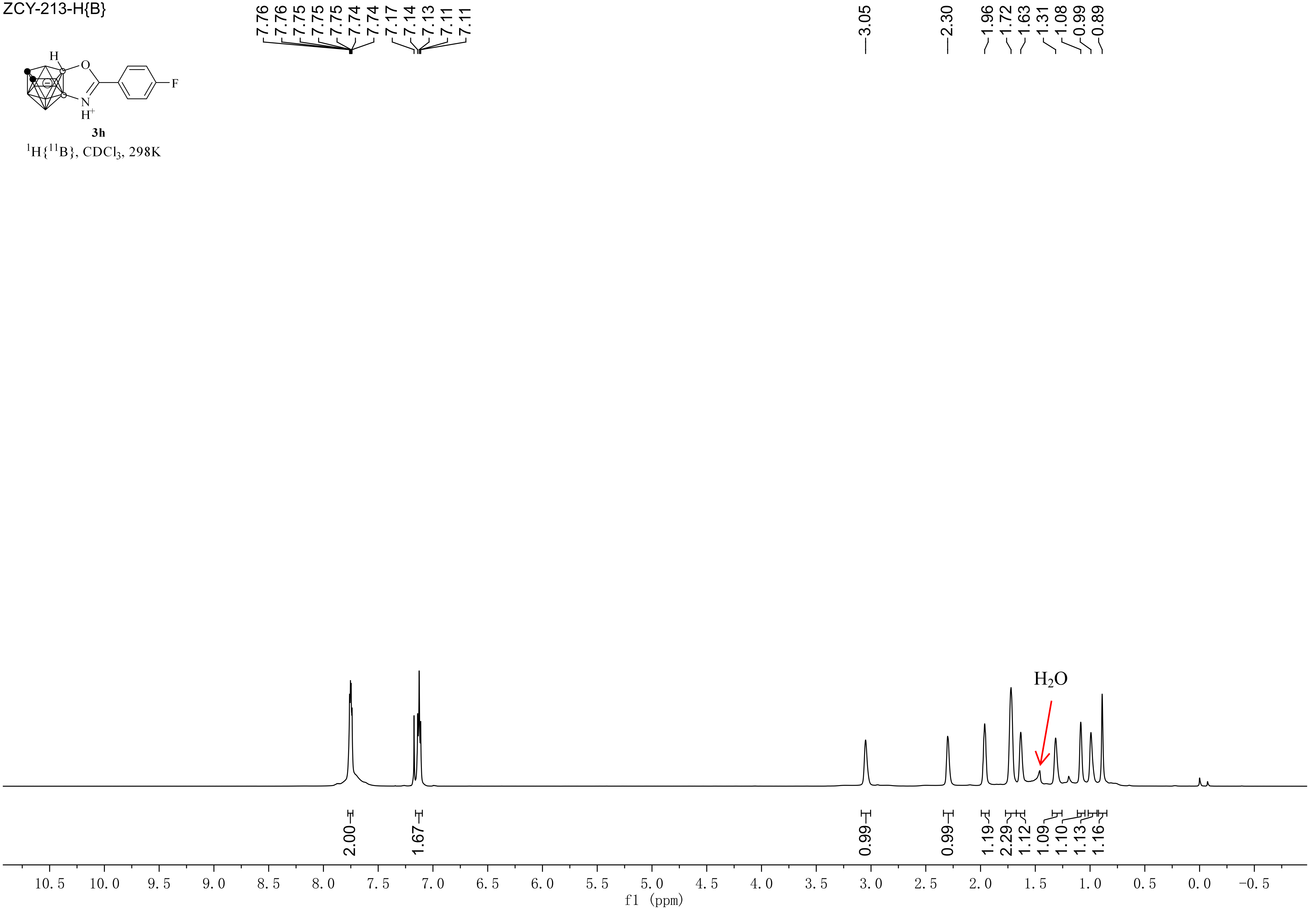


3h

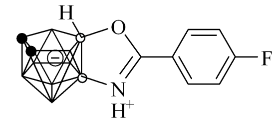
^1H, $CDCl_3$, 298K



ZCY-213-H{B}

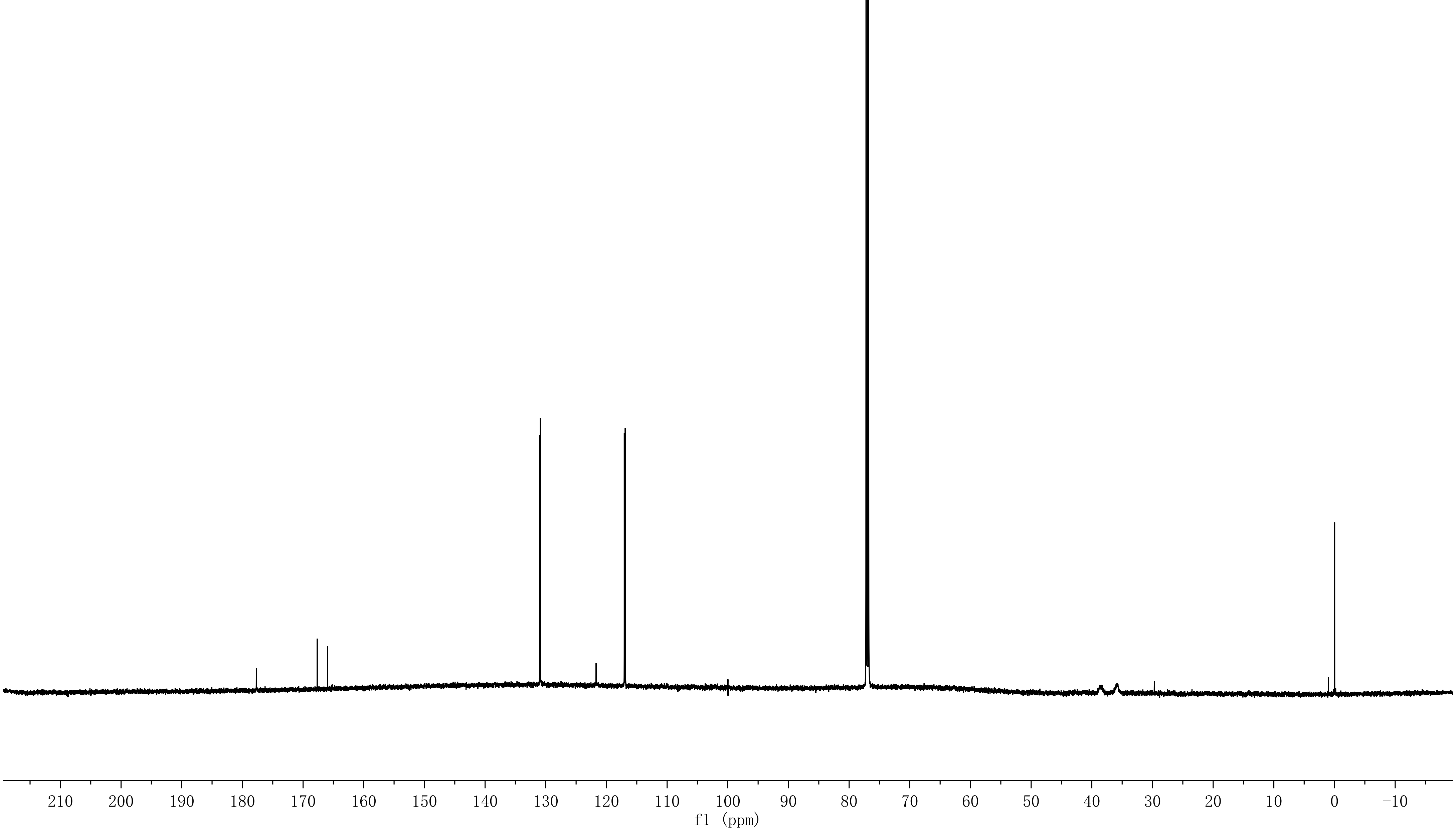

3h
$^{1}H\{^{11}B\}$, $CDCl_3$, 298K
7.76
7.76
7.75
7.75
7.75
7.74
7.74
7.17
7.14
7.13
7.11
7.11
3.05
2.30
1.96
1.72
1.63
1.31
1.08
0.99
0.89
H2O
2.00
1.67
0.99
0.99
1.19
2.29
1.12
1.09
1.10
1.13
1.16
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

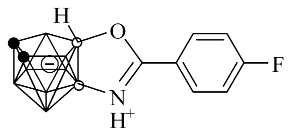
ZCY-213-C



3h

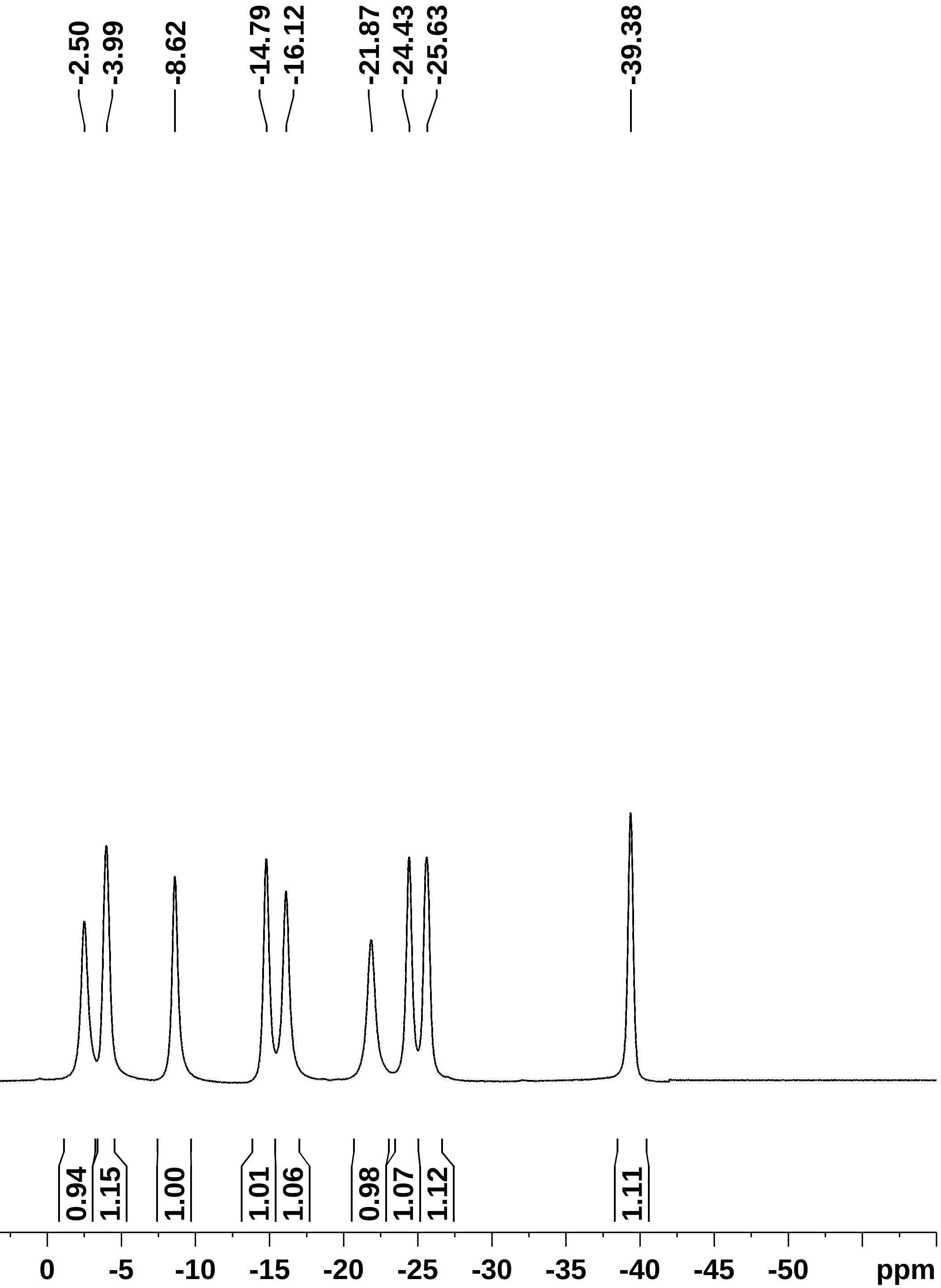
^{13}C, $CDCl_3$, 298K





3h

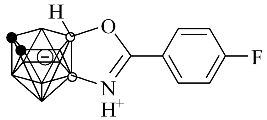
$^{11}B\{^1H\}$, $CDCl_3$, 298K



NMR Teacher : Huang

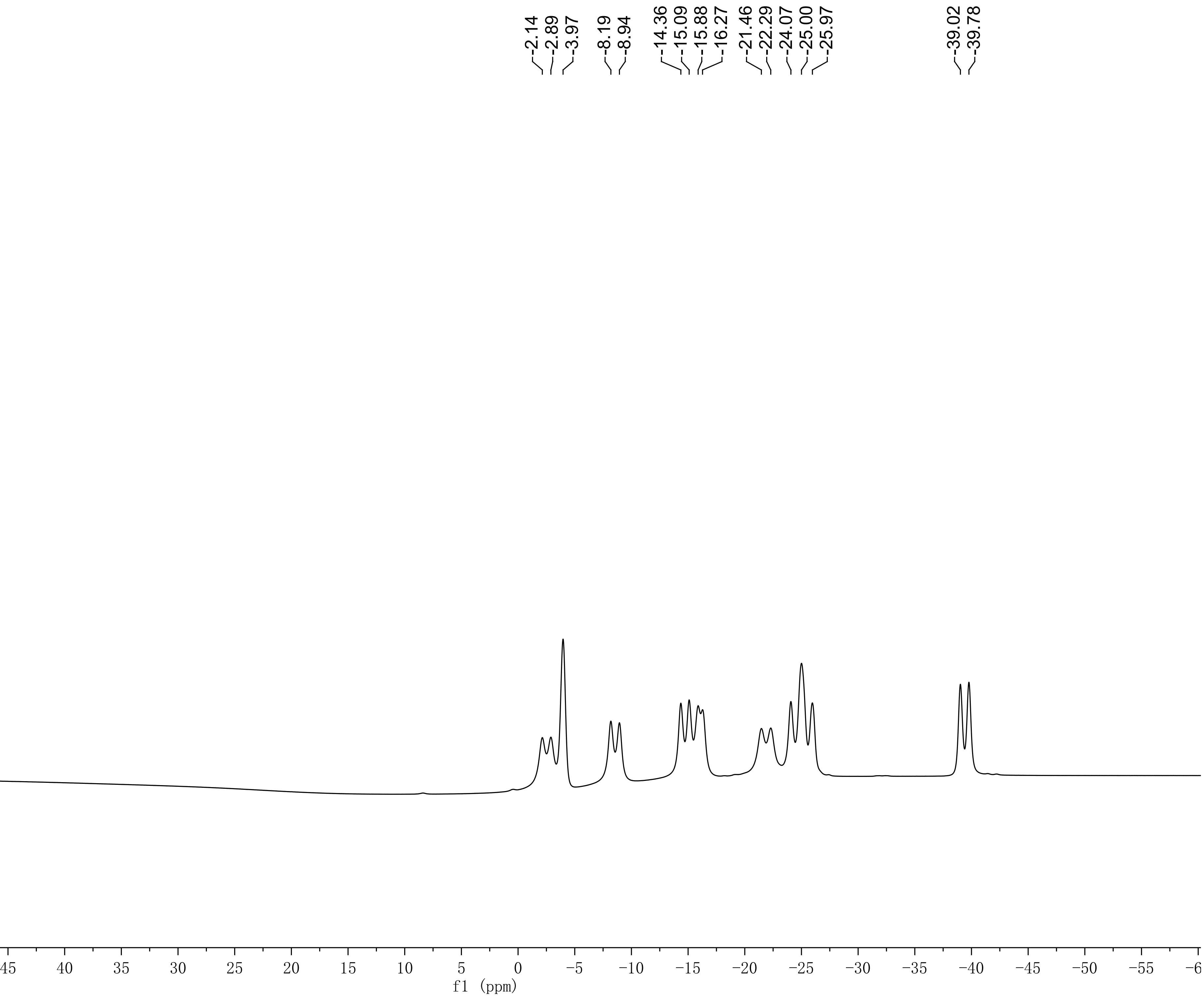
```
Current Data Parameters
NAME            20180327
EXPNO                122
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180328
Time                6.17
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                85536
SOLVENT           CDCl3
NS                 5126
DS                    4
SWH           50000.000 Hz
FIDRES         0.584549 Hz
AQ            0.8553600 sec
RG               172.47
DW               10.000 usec
DE                 6.50 usec
TE                297.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        192.5526102 MHz
NUC1                11B
P1                25.00 usec
PLW1       180.00000000 W

======== CHANNEL f2 ========
SFO2        600.1737063 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             70.00 usec
PLW2        23.00000000 W
PLW12        0.57832998 W
PLW13        0.28338000 W

F2 - Processing parameters
SI                32768
SF          192.5583870 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

ZCY-213-B

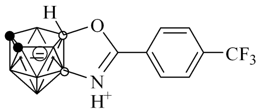


3h

^{11}B, $CDCl_3$, 298K

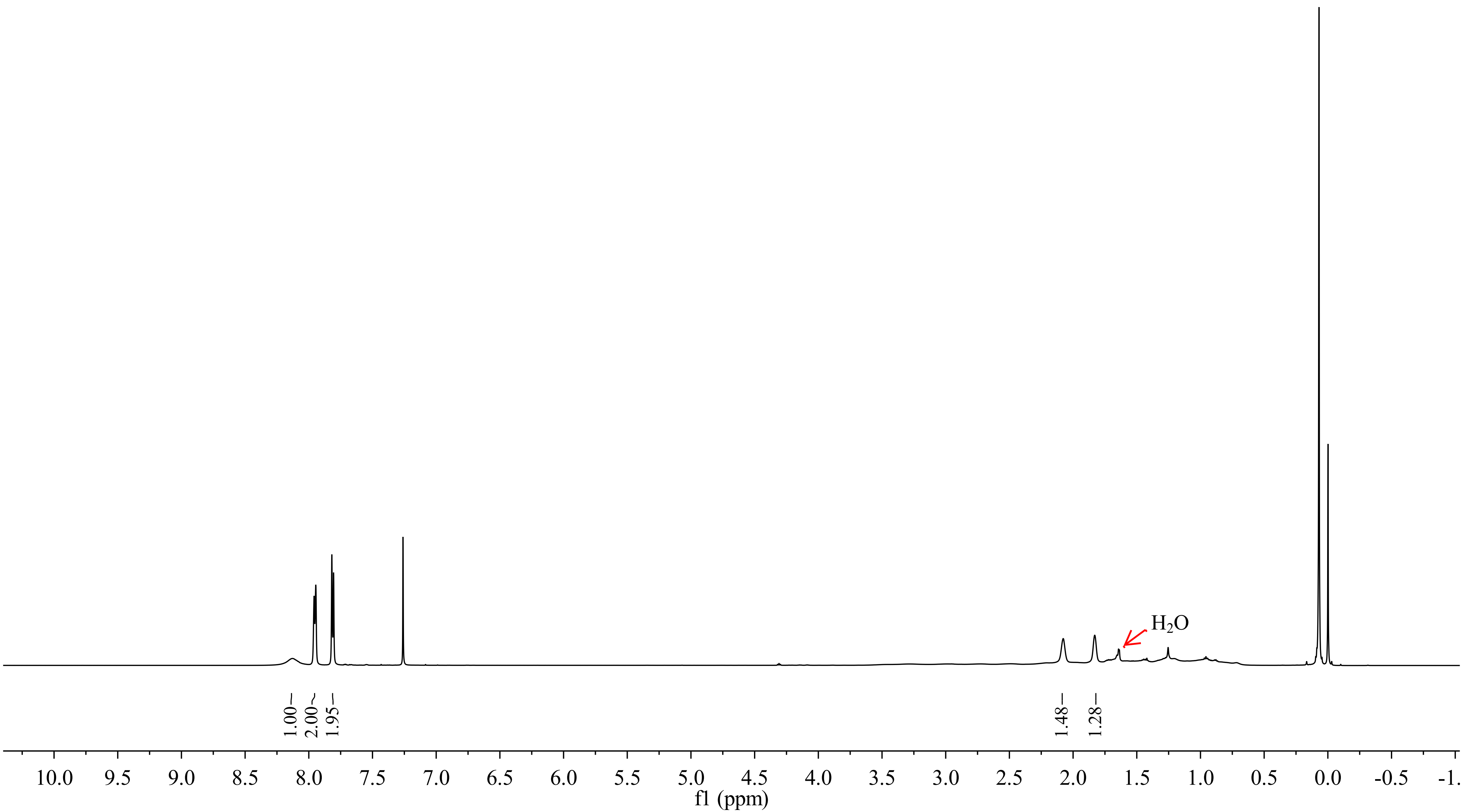


ZCY-265-H

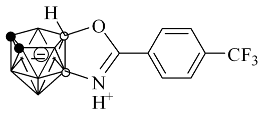


3i

[1]H, $CDCl_3$, 298K

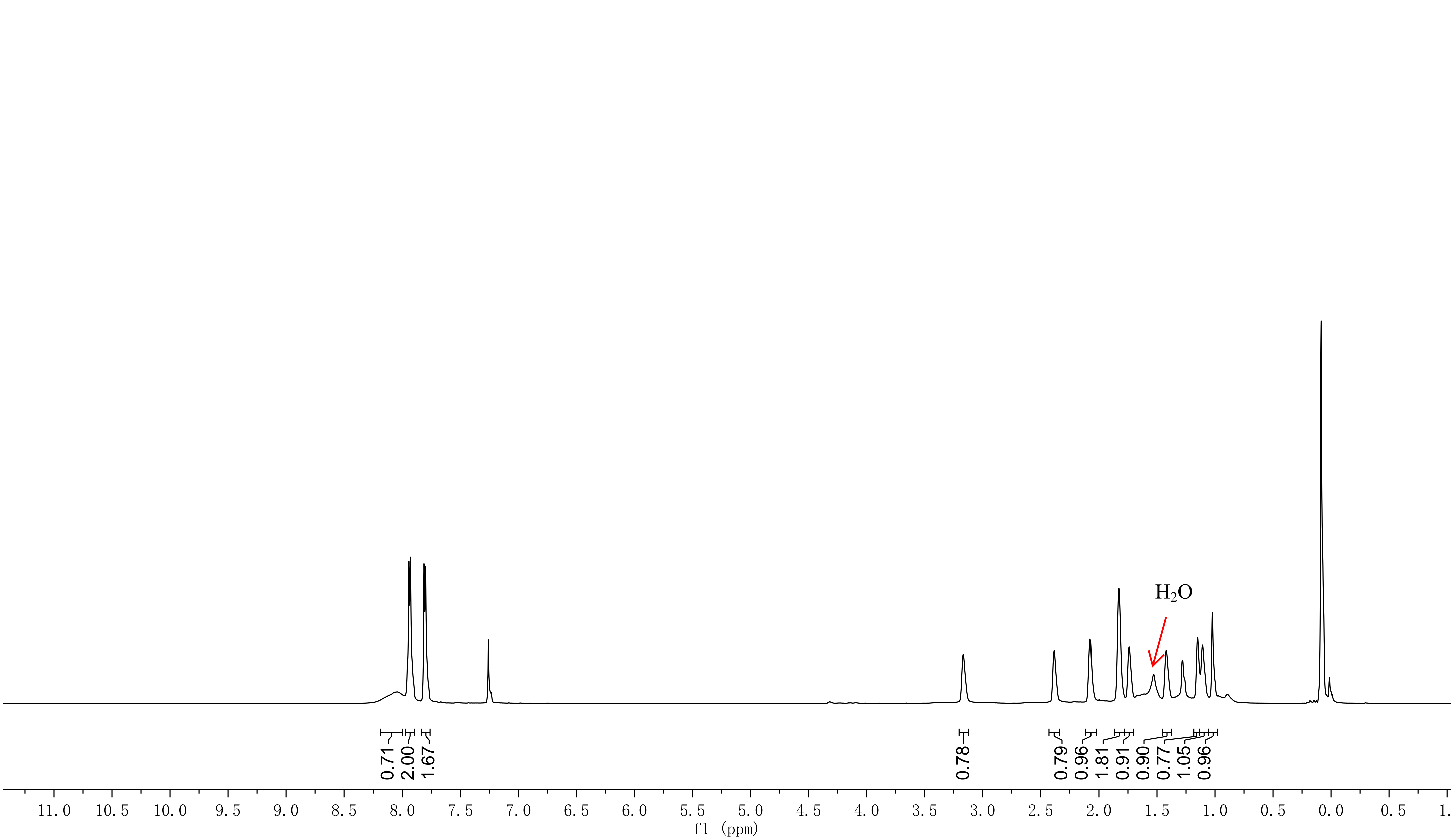


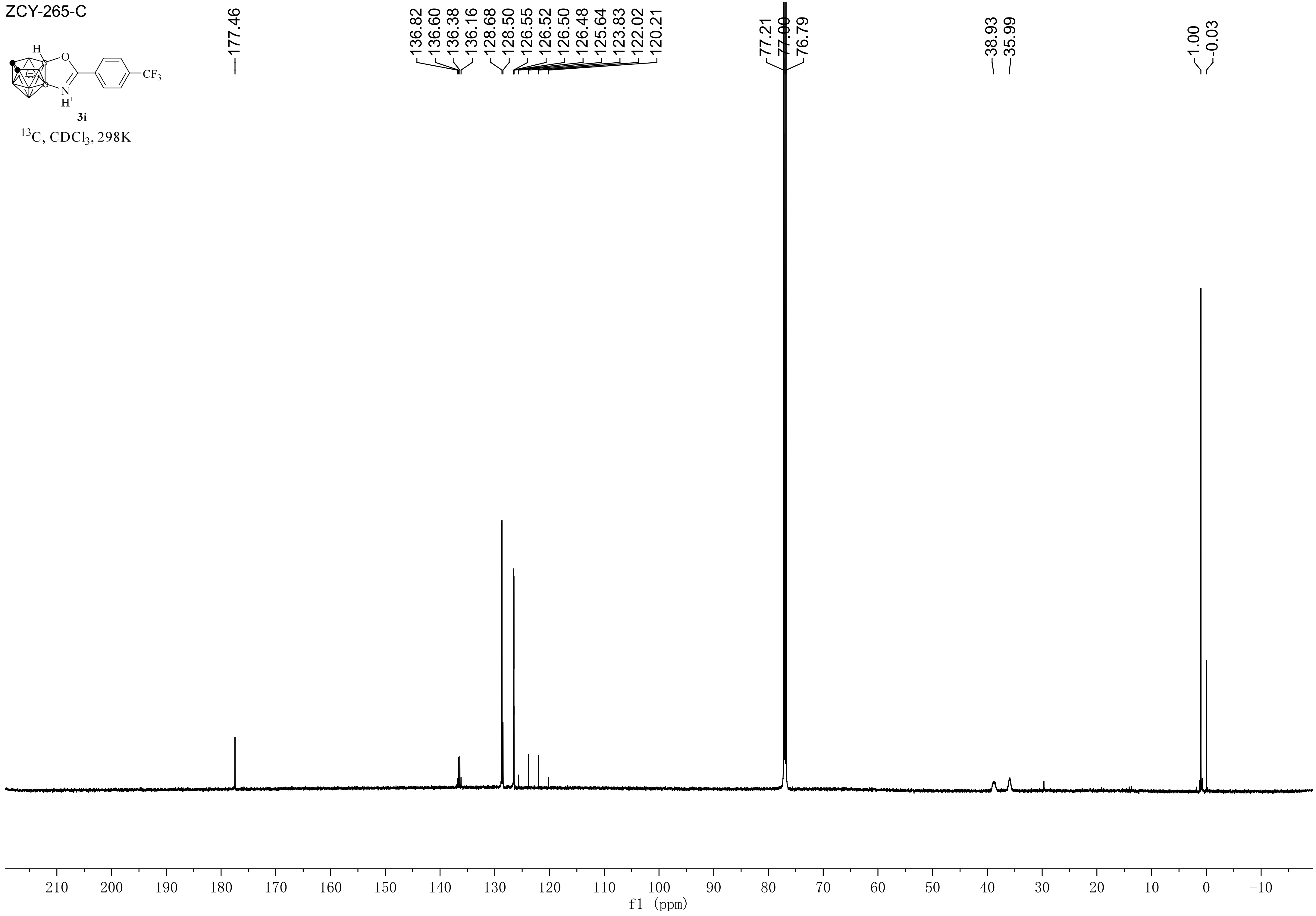
ZCY-265-H{B}



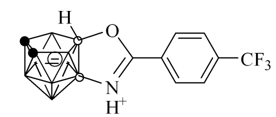
3i

$^{1}H\{^{11}B\}$, $CDCl_3$, 298K



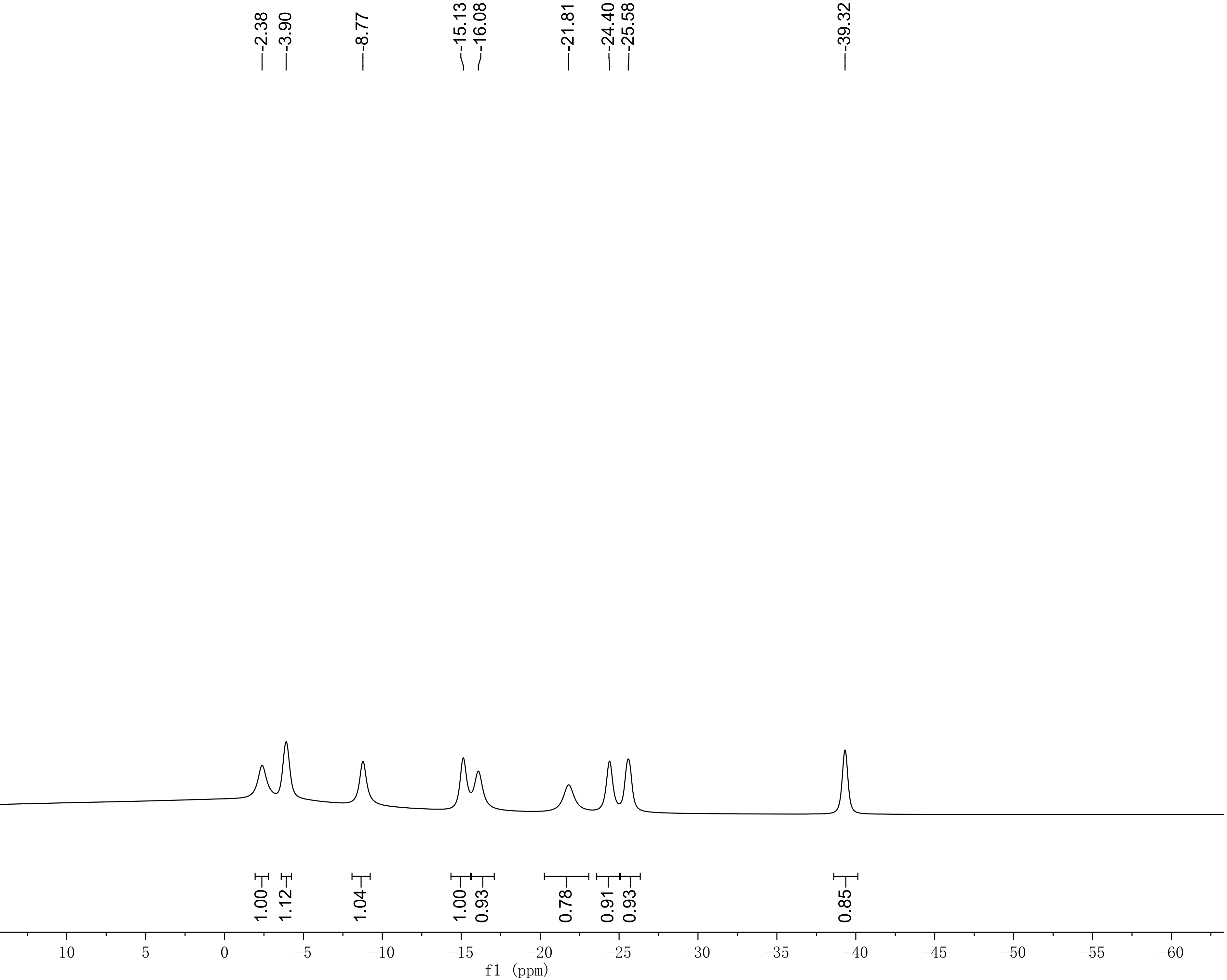

ZCY-265-C
H
O
N
H+
CF3
3i
13C, CDCl3, 298K
177.46
136.82
136.60
136.38
136.16
128.68
128.50
126.55
126.52
126.50
126.48
125.64
123.83
122.02
120.21
77.21
77.00
76.79
38.93
35.99
1.00
-0.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

ZCY-265-B{H}

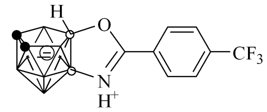


3i

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

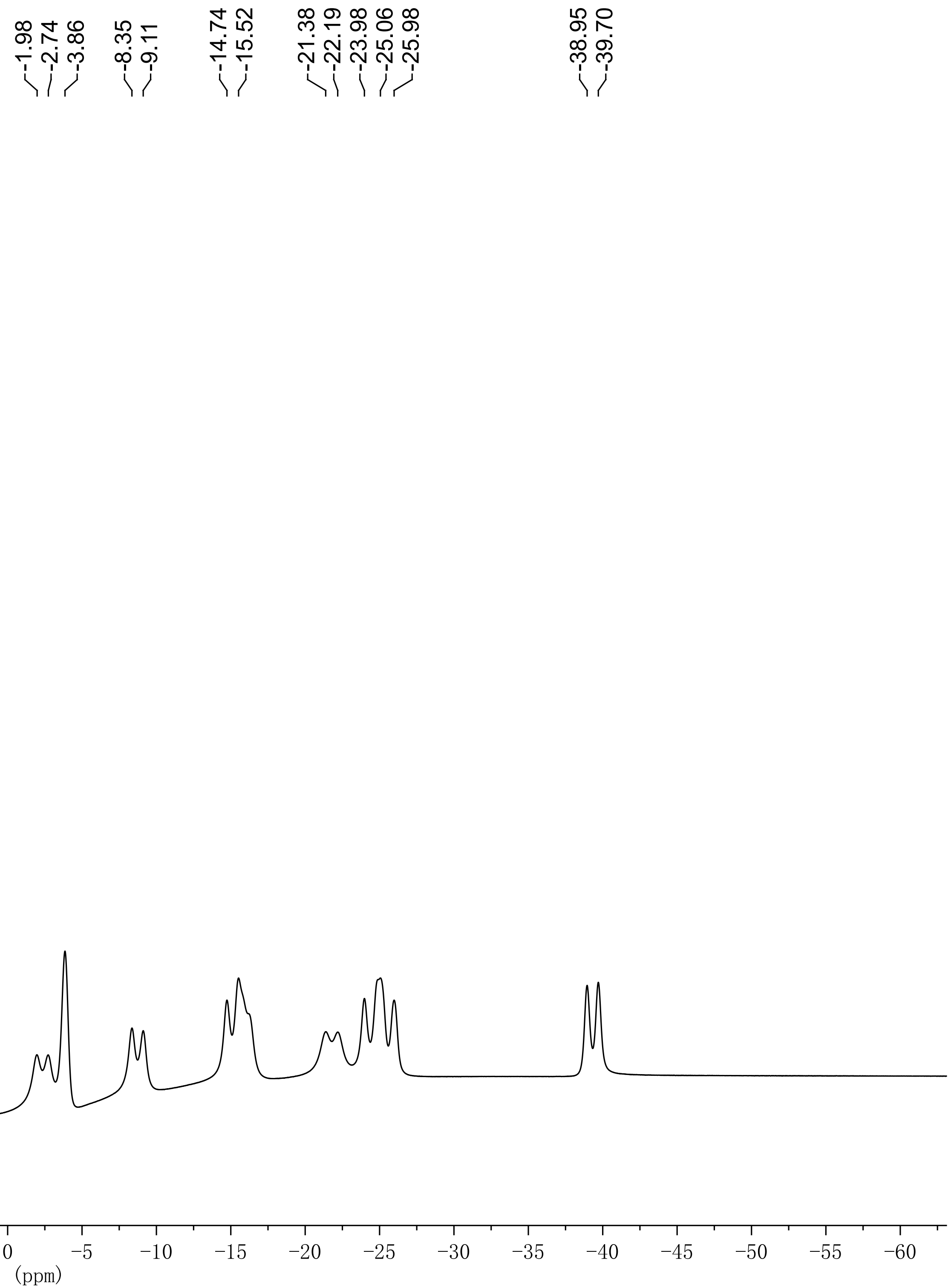


ZCY-265-B

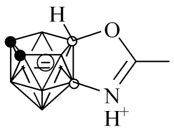


3i

^{11}B, $CDCl_3$, 298K

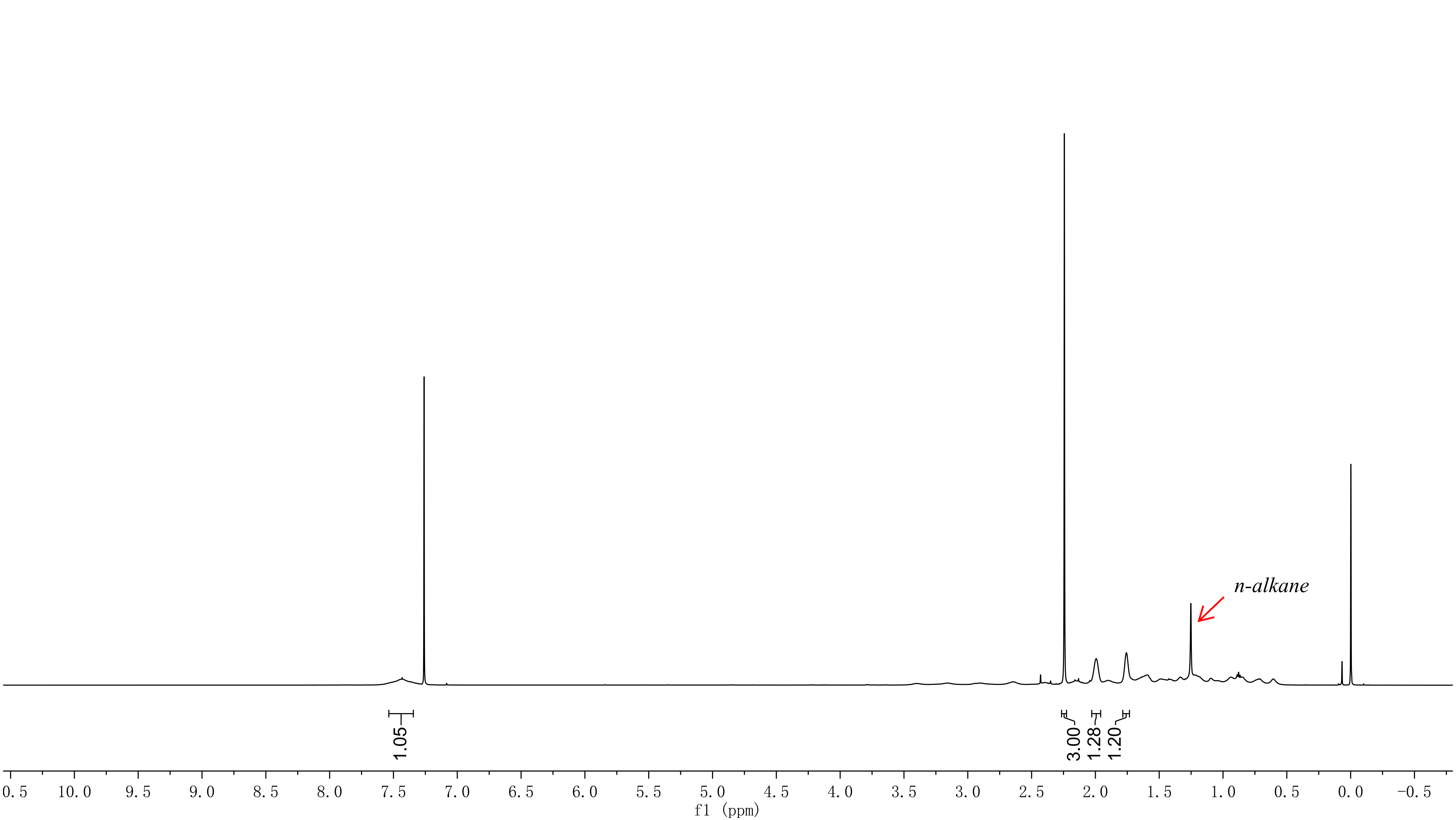


ZCY-206-H

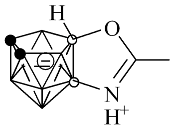


3j

^1H, $CDCl_3$, 298K

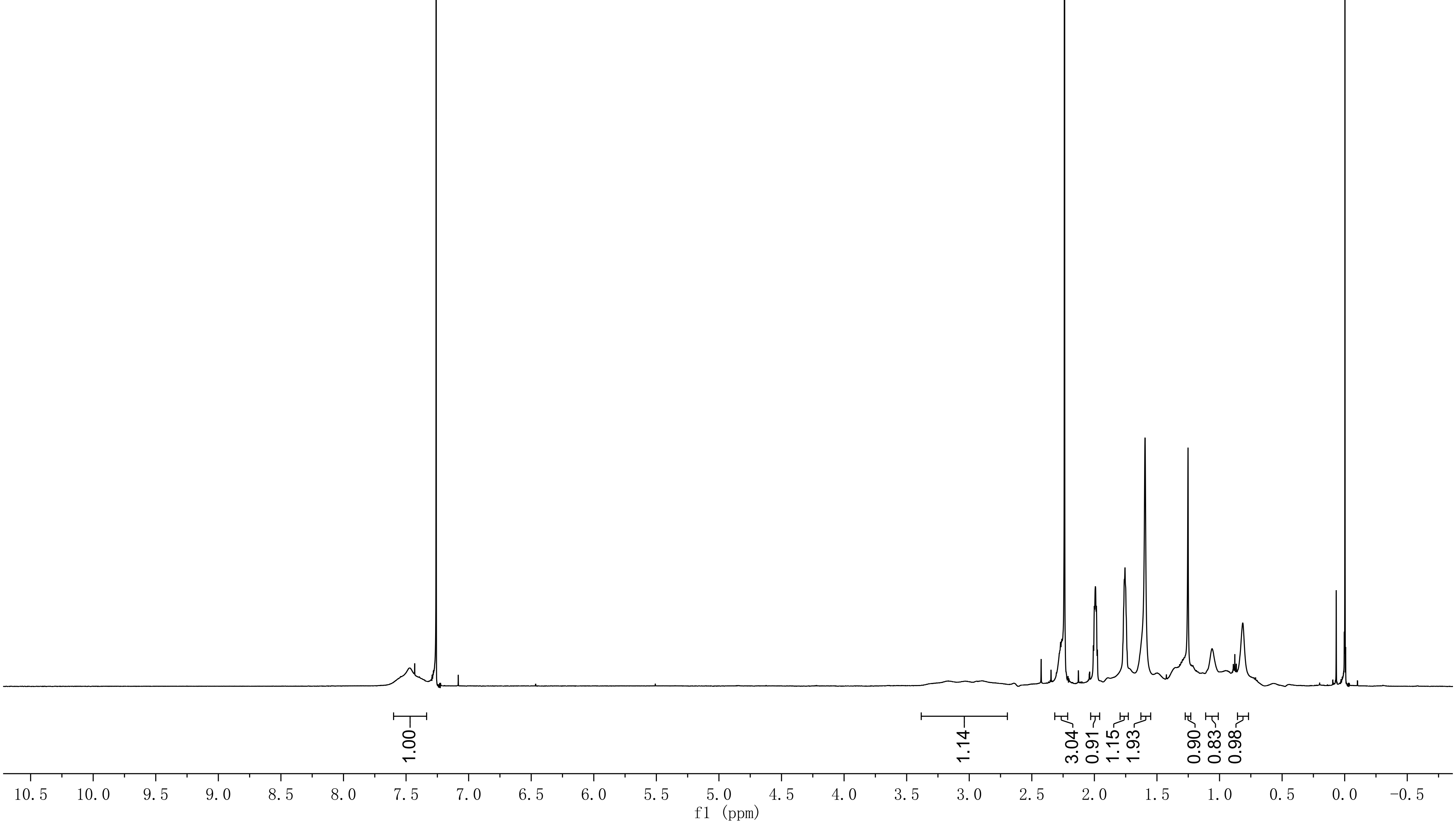


ZCY-206-H{B}

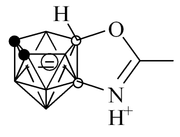


3j

$^{1}H\{^{11}B\}$, $CDCl_3$, 298K

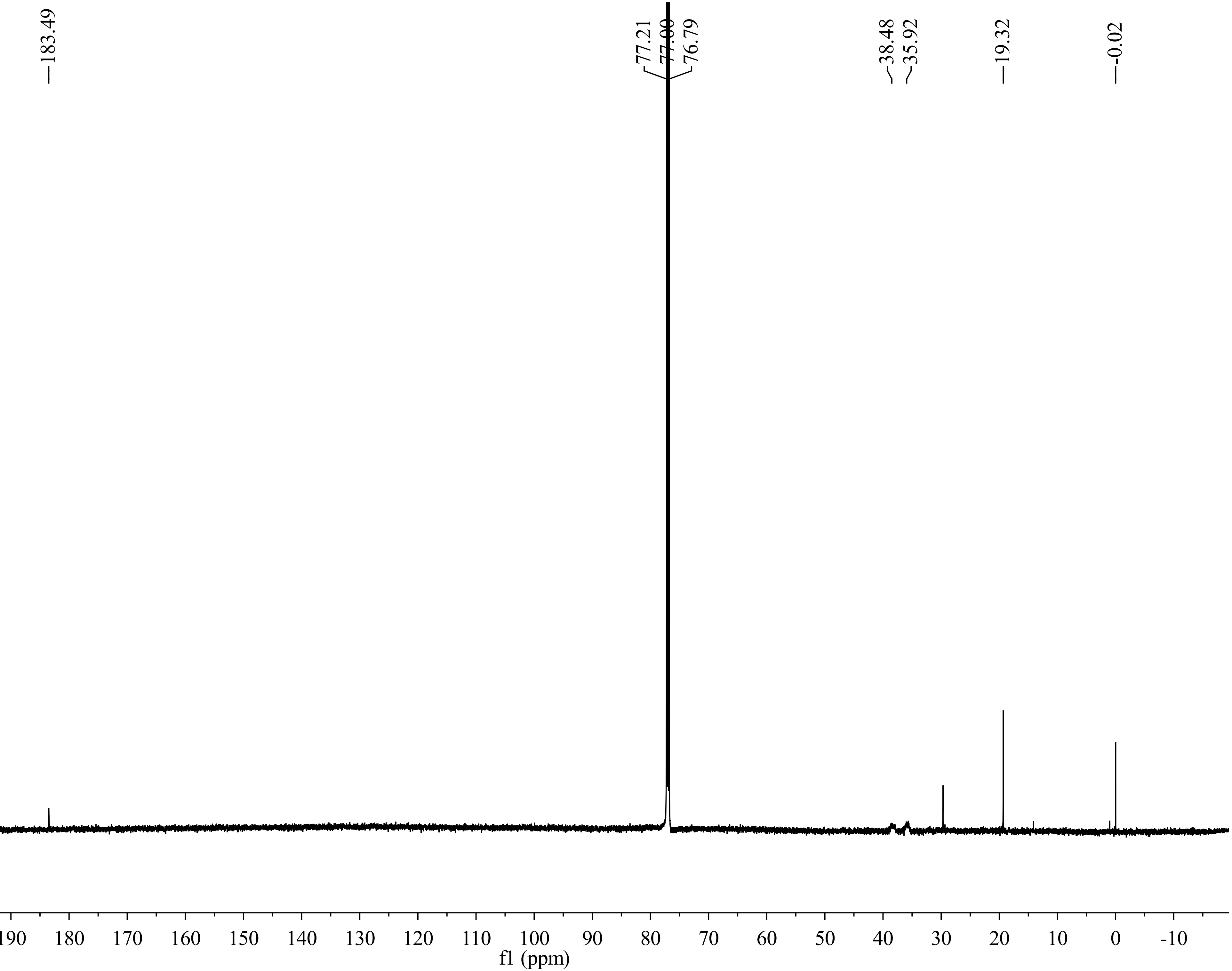


ZCY-206-C

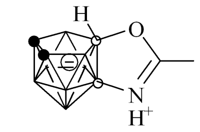


3j

^{13}C, $CDCl_3$, 298K

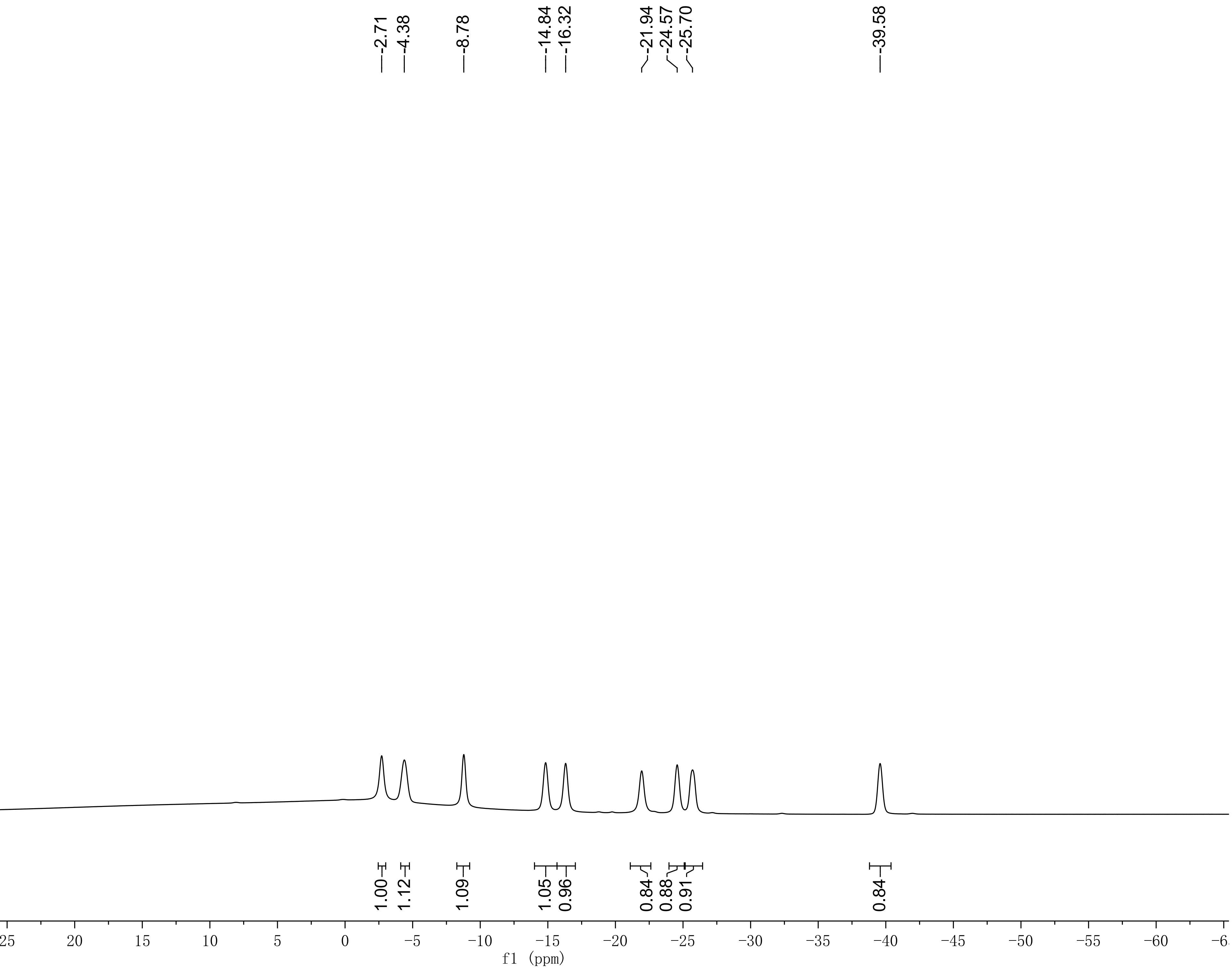


ZCY-206-B{H}

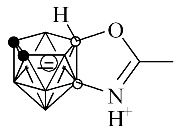


3j

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

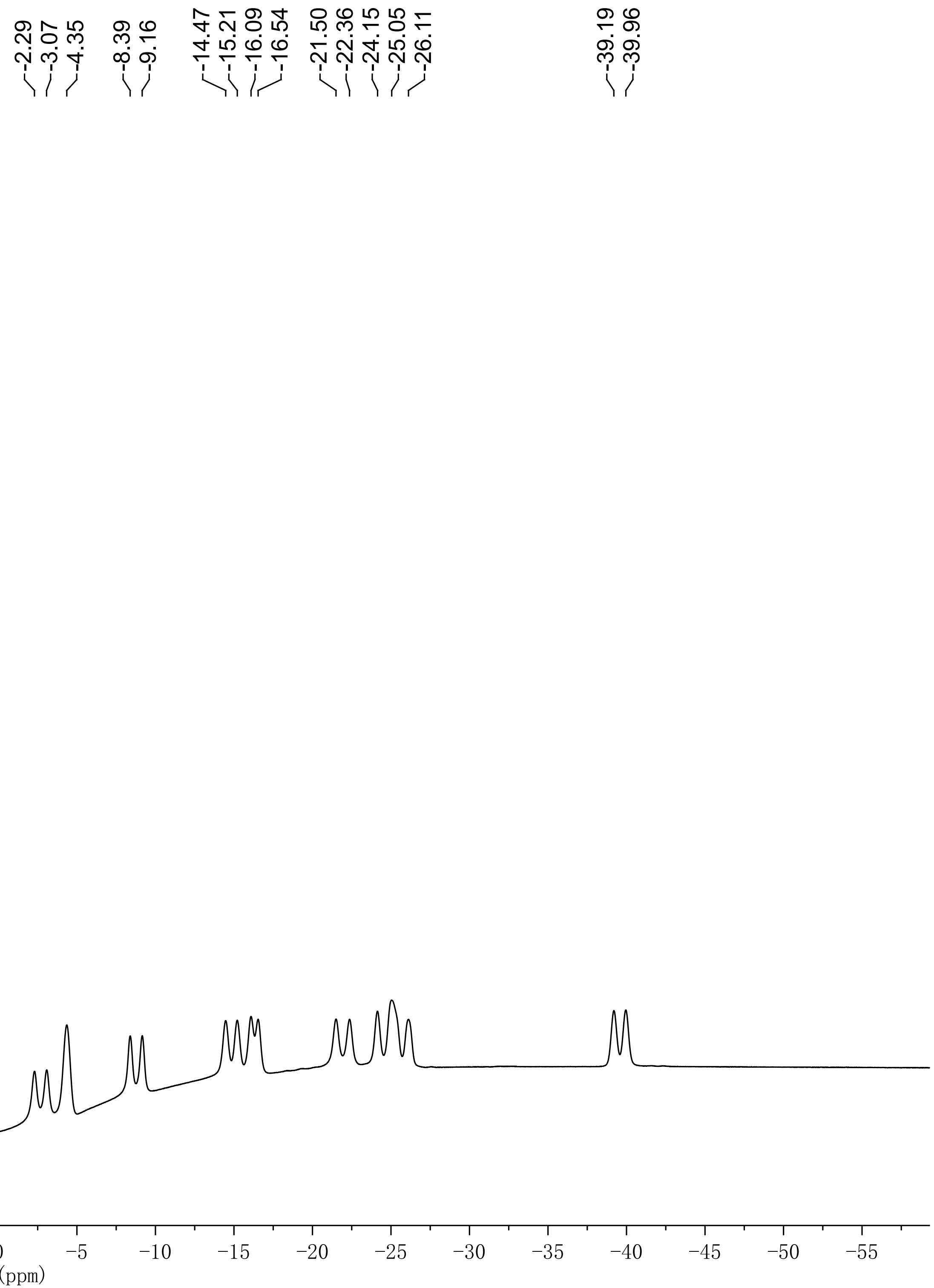


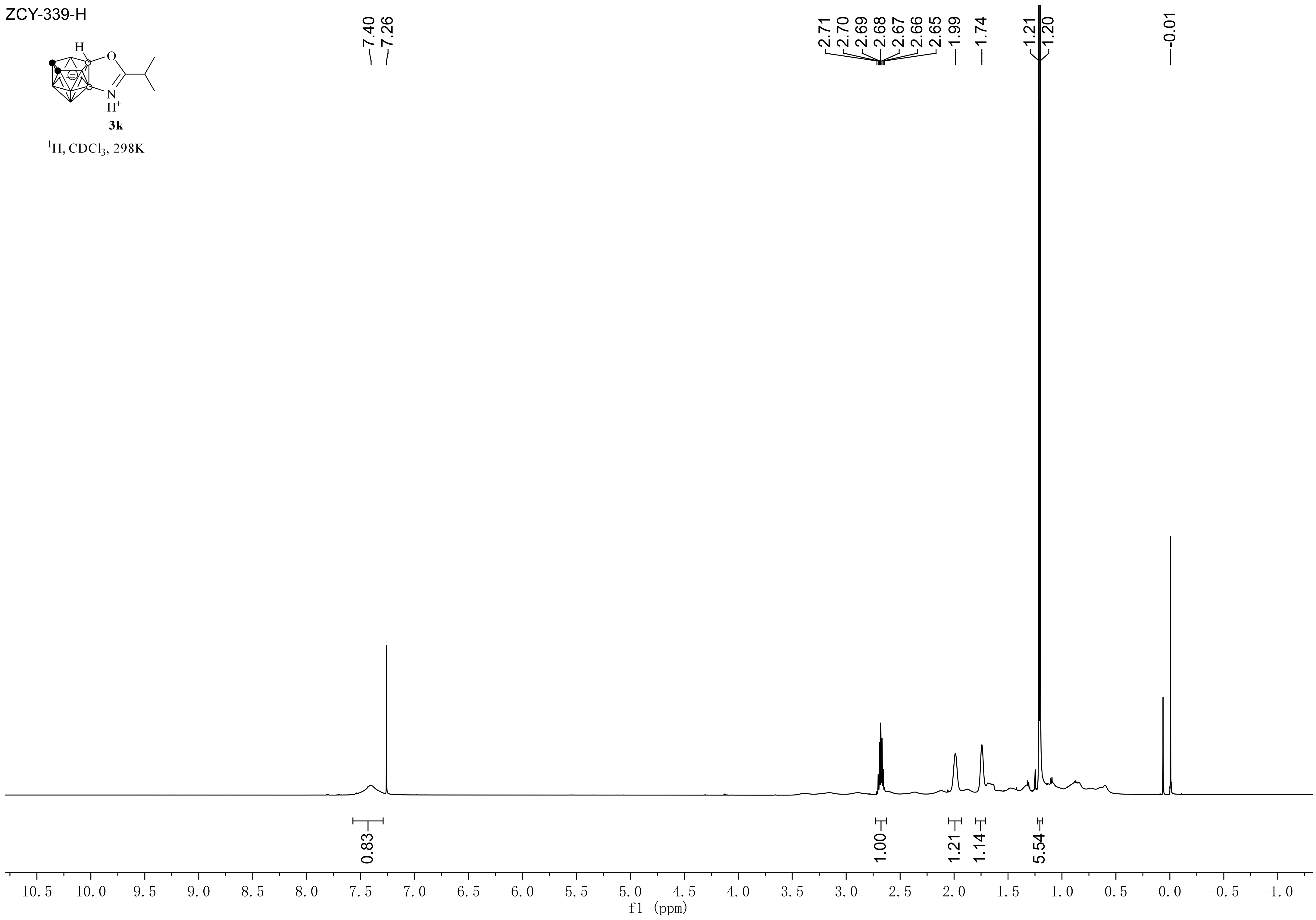
ZCY-206-B

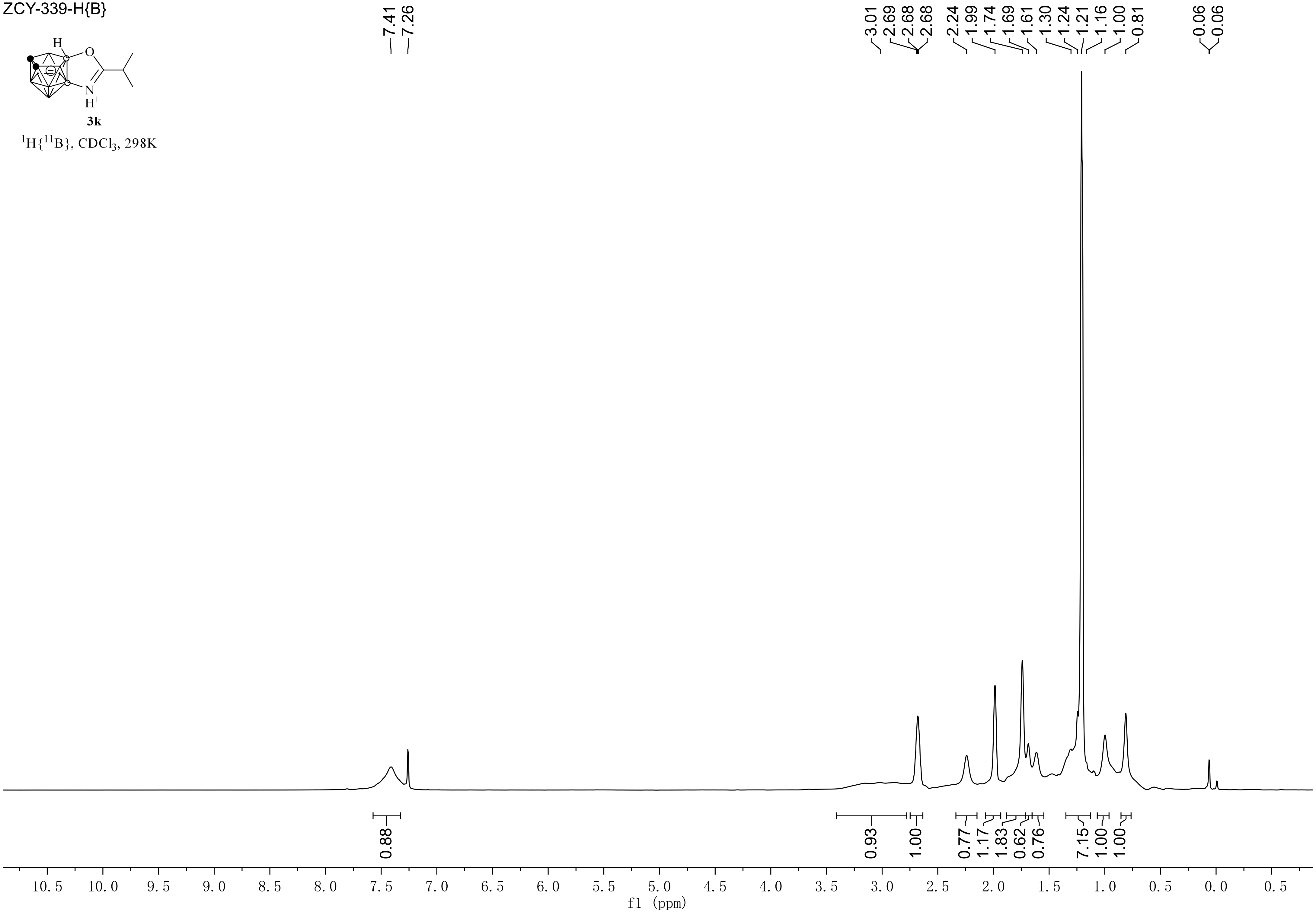


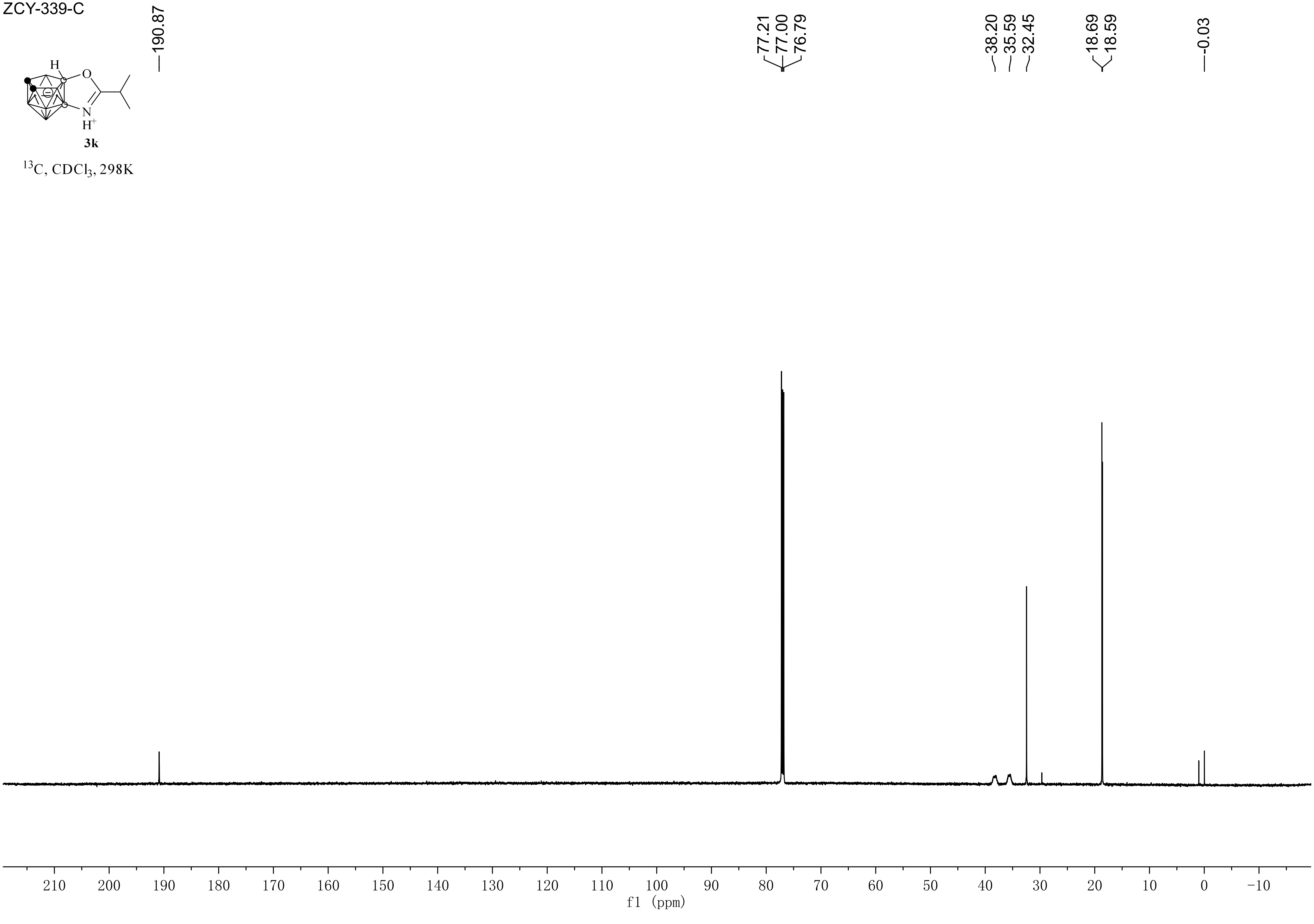
3j

^{11}B, $CDCl_3$, 298K

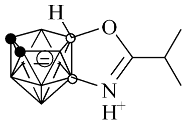



ZCY-339-H
H
O
N
H+
3k
1H, CDCl3, 298K
7.40
7.26
2.71
2.70
2.69
2.68
2.67
2.66
2.65
1.99
1.74
1.21
1.20
-0.01
0.83
1.00
1.21
1.14
5.54
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


ZCY-339-H{B}
H
O
N
H+
3k
$^{1}H\{^{11}B\}$, $CDCl_3$, 298K
7.41
7.26
3.01
2.69
2.68
2.68
2.24
1.99
1.74
1.69
1.61
1.30
1.24
1.21
1.16
1.00
0.81
0.06
0.06
0.88
0.93
1.00
0.77
1.17
1.83
0.62
0.76
7.15
1.00
1.00
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)

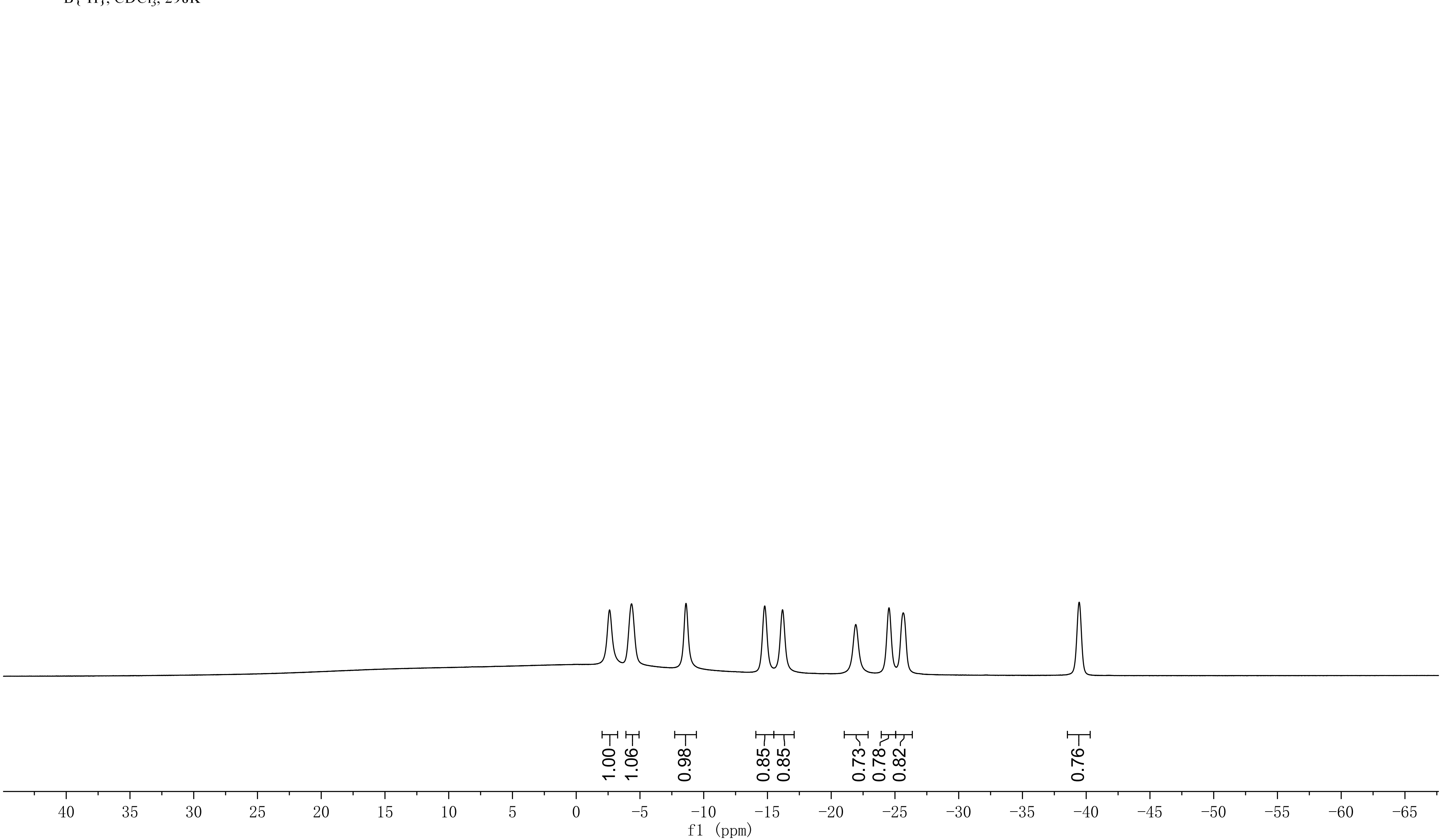

ZCY-339-C
H
O
N
H+
3k
13C, CDCl3, 298K
190.87
77.21
77.00
76.79
38.20
35.59
32.45
18.69
18.59
-0.03
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

ZCY-339-B{H}

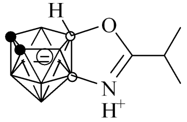


3k

$^{11}B\{^1H\}$, $CDCl_3$, 298K

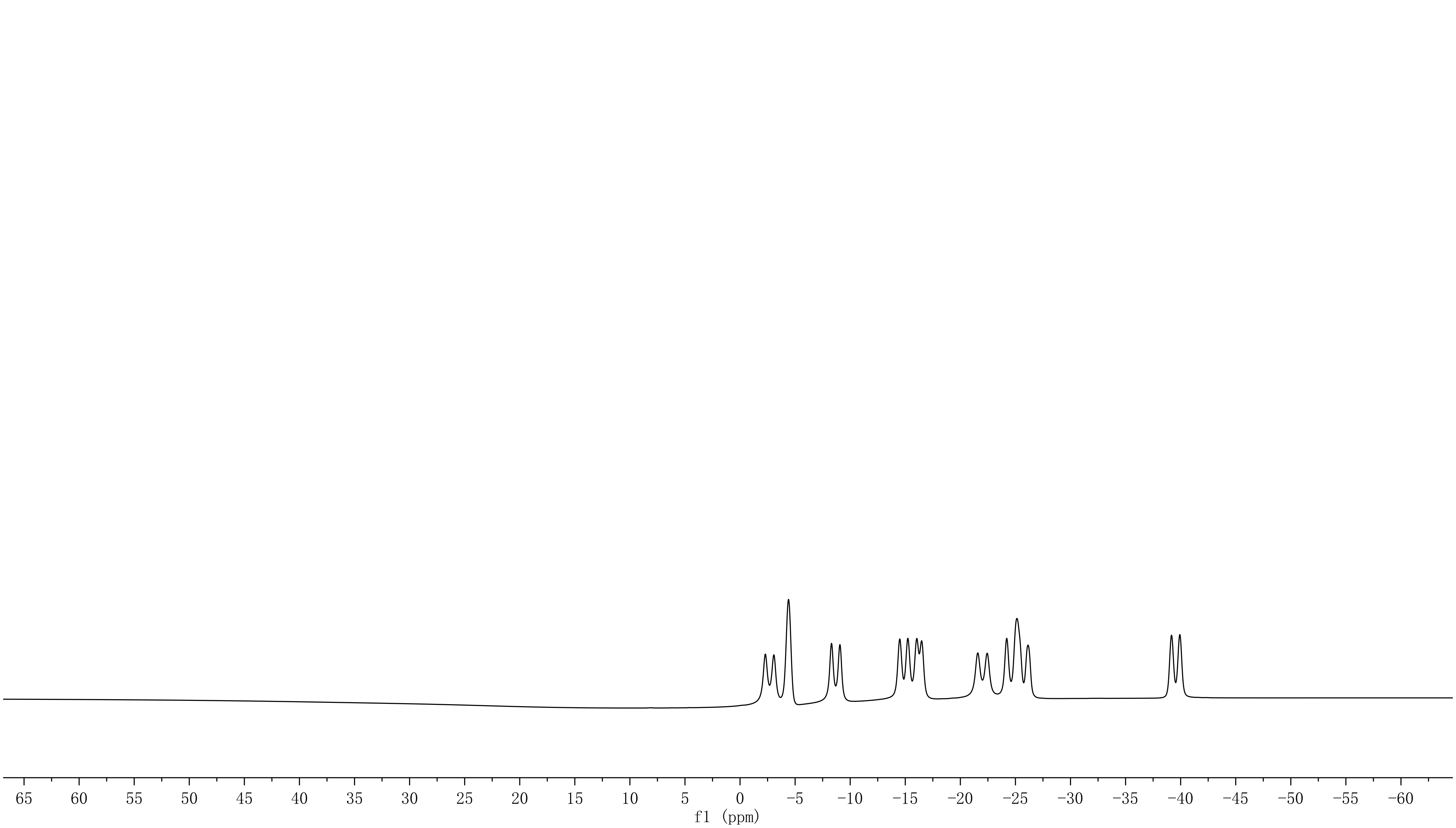


ZCY-339-B

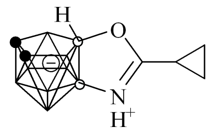


3k

^{11}B, $CDCl_3$, 298K

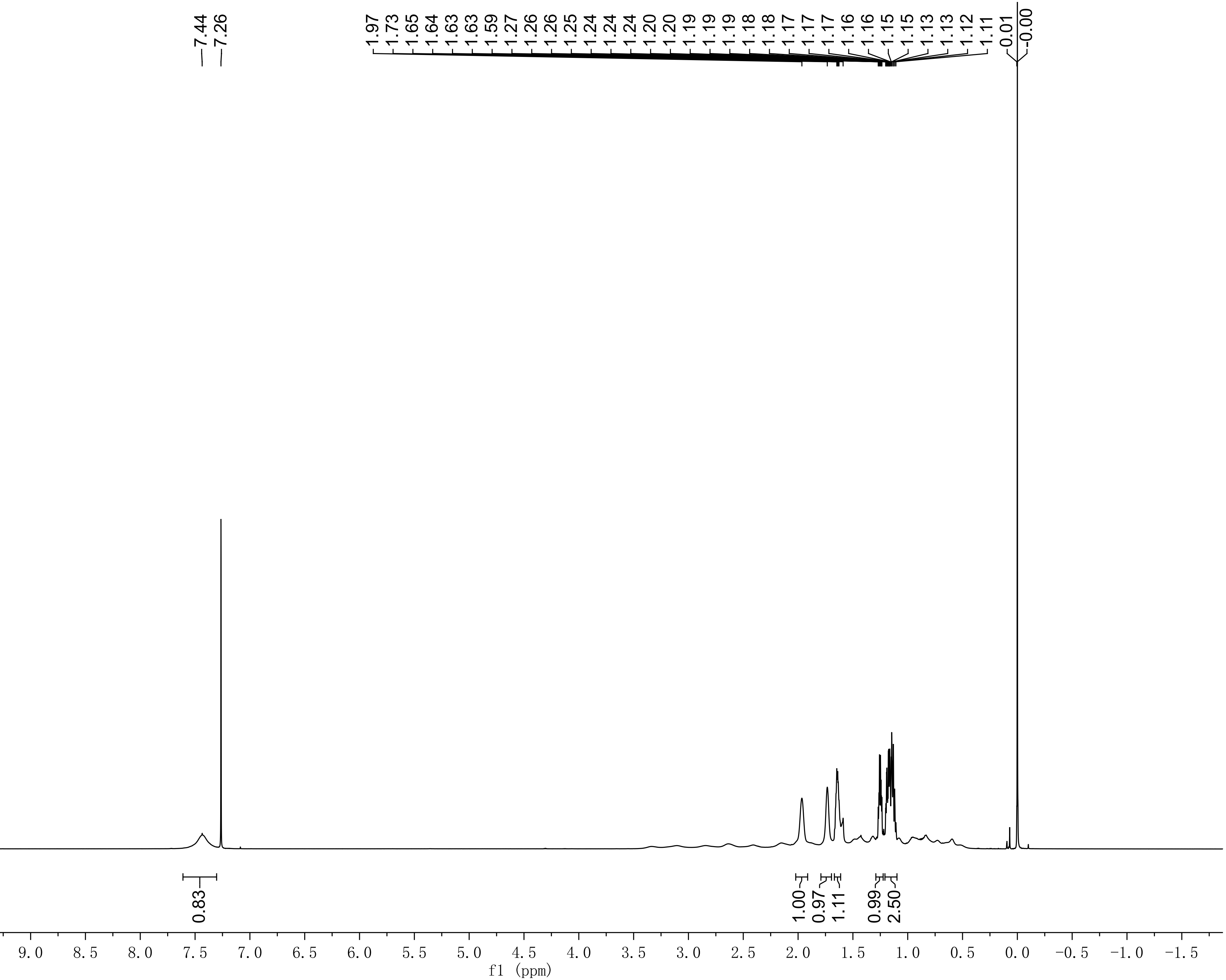


ZCY-325-H

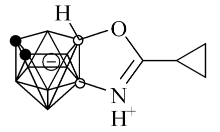


3l

^{1}H, $CDCl_3$, 298K

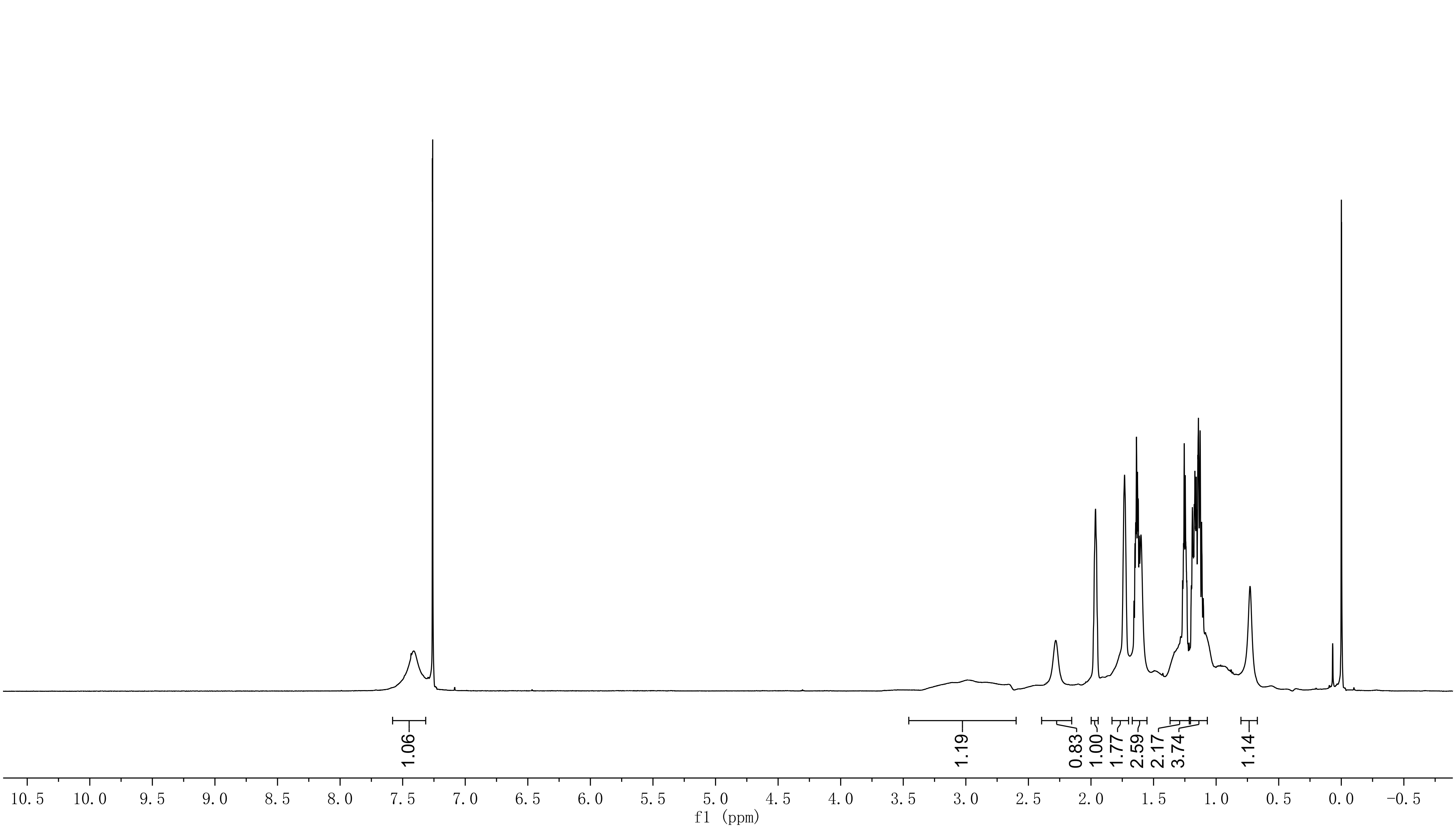


ZCY-325-H{B}

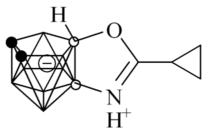


3l

$^{1}H\{^{11}B\}$, $CDCl_3$, 298K

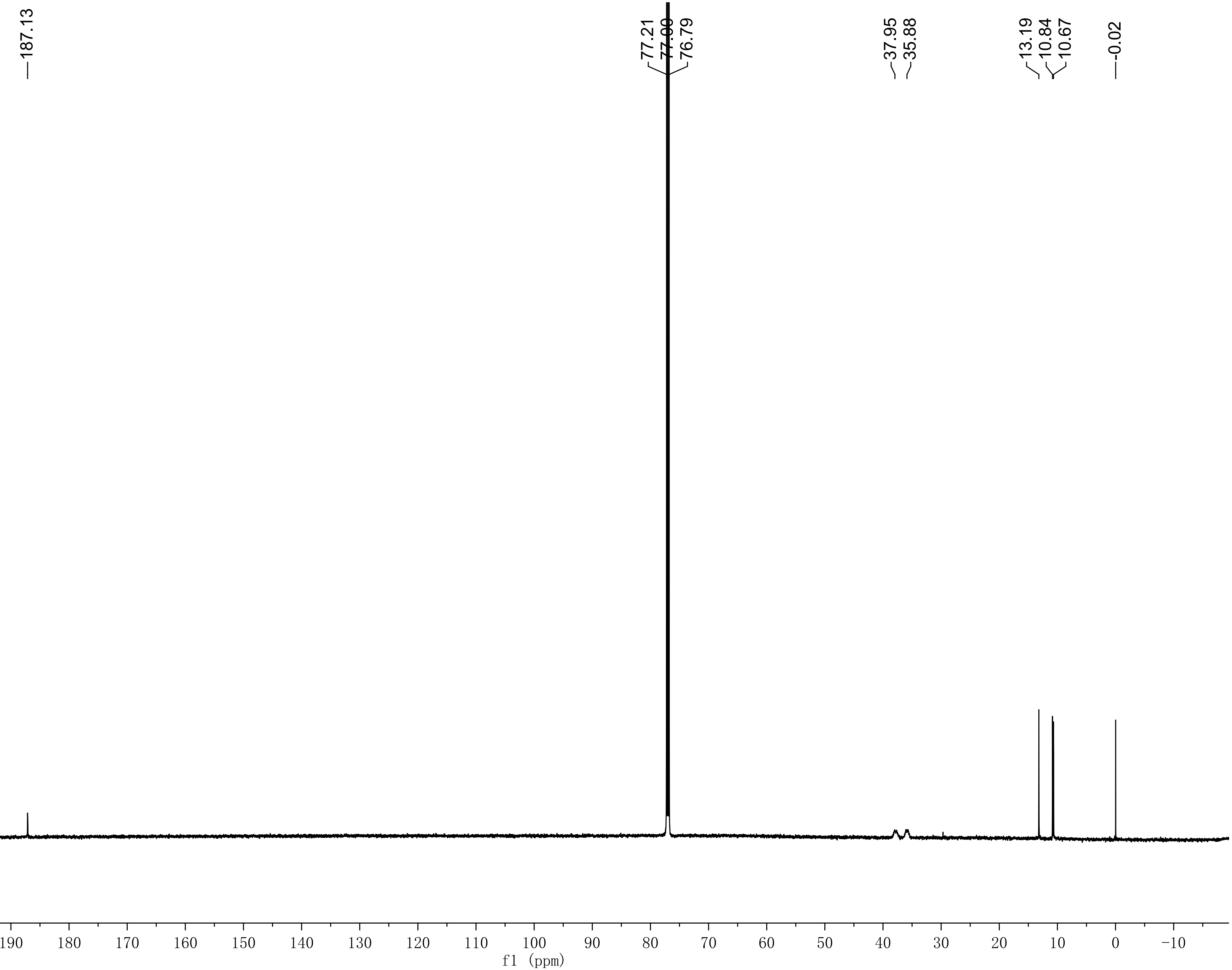


ZCY-325-C

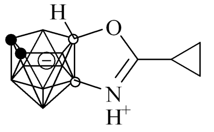


3l

^{13}C, $CDCl_3$, 298K

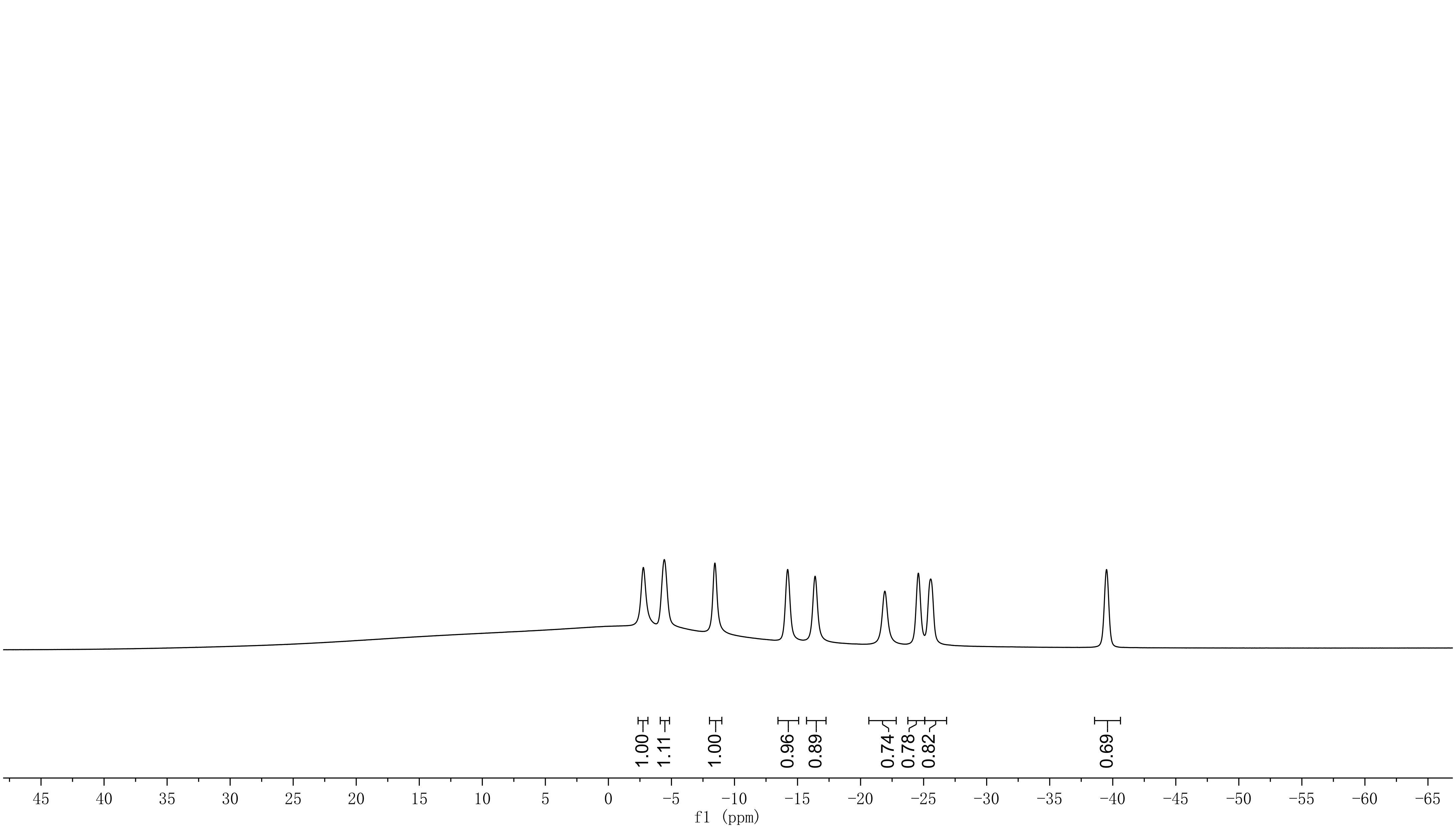


ZCY-325-B{H}

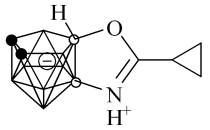


3l

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

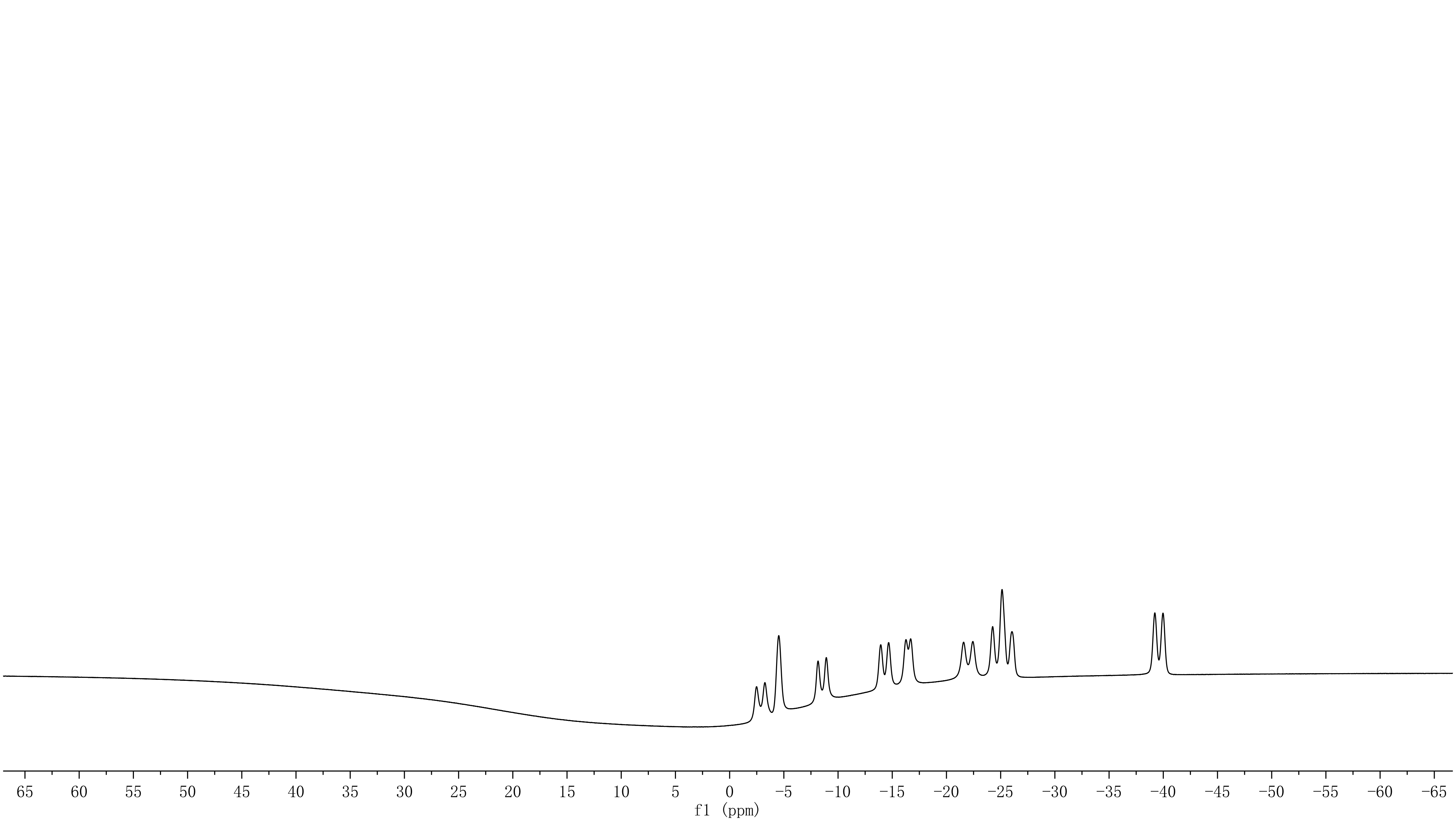


ZCY-325-B

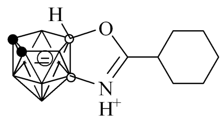


3l

^{11}B, $CDCl_3$, 298K

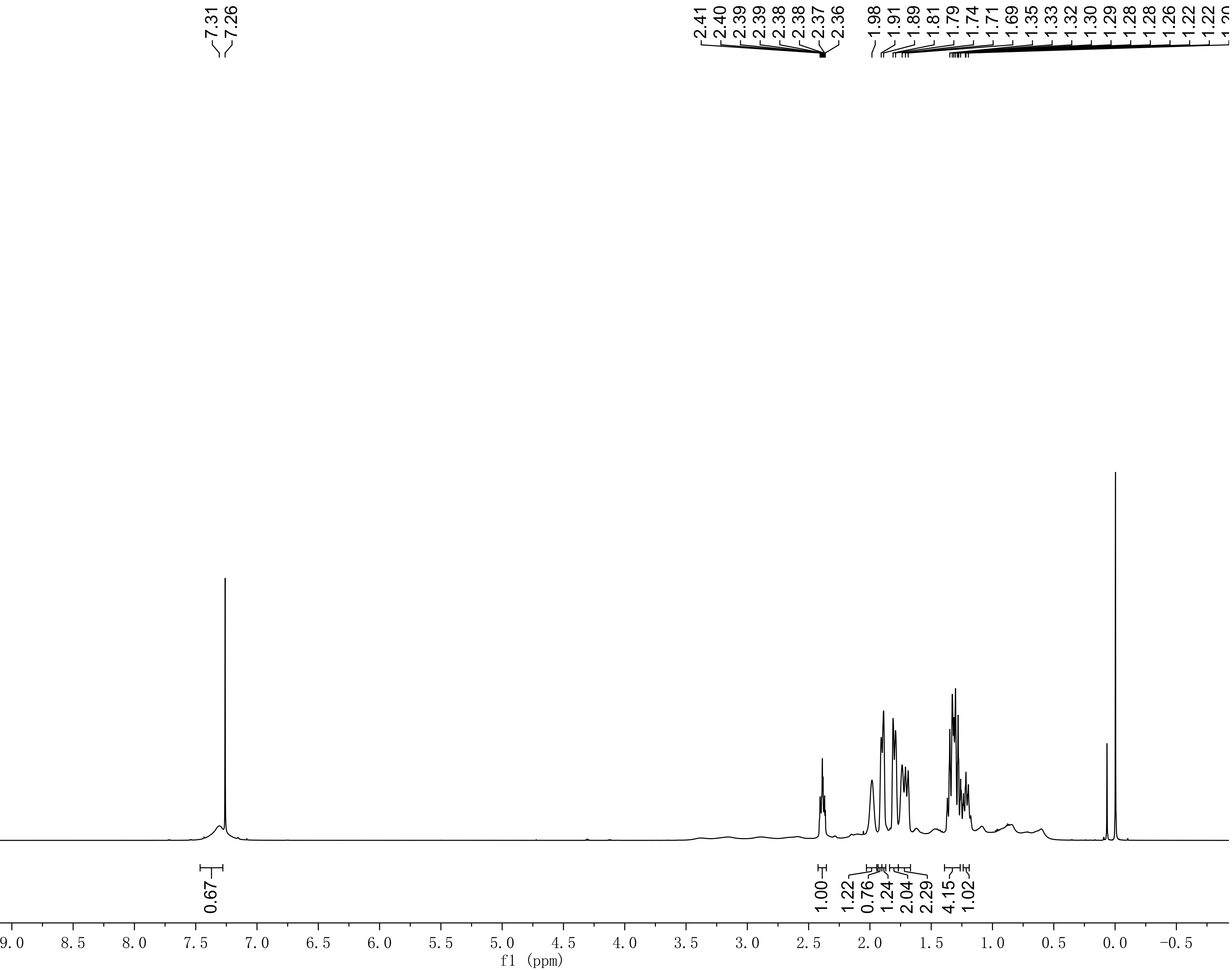


ZCY-301-H

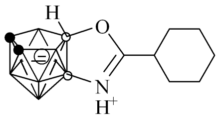


3m

^{1}H, $CDCl_3$, 298K

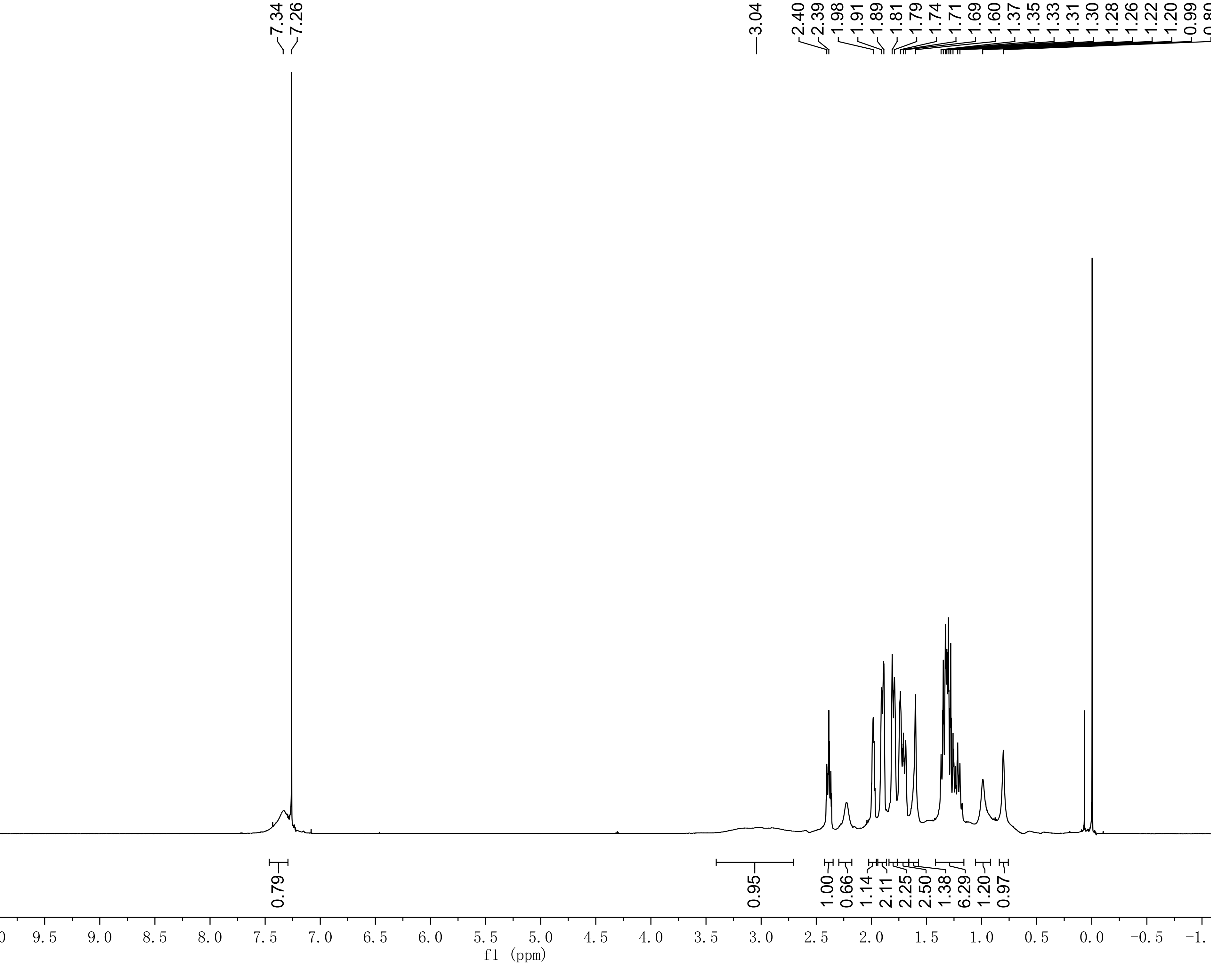


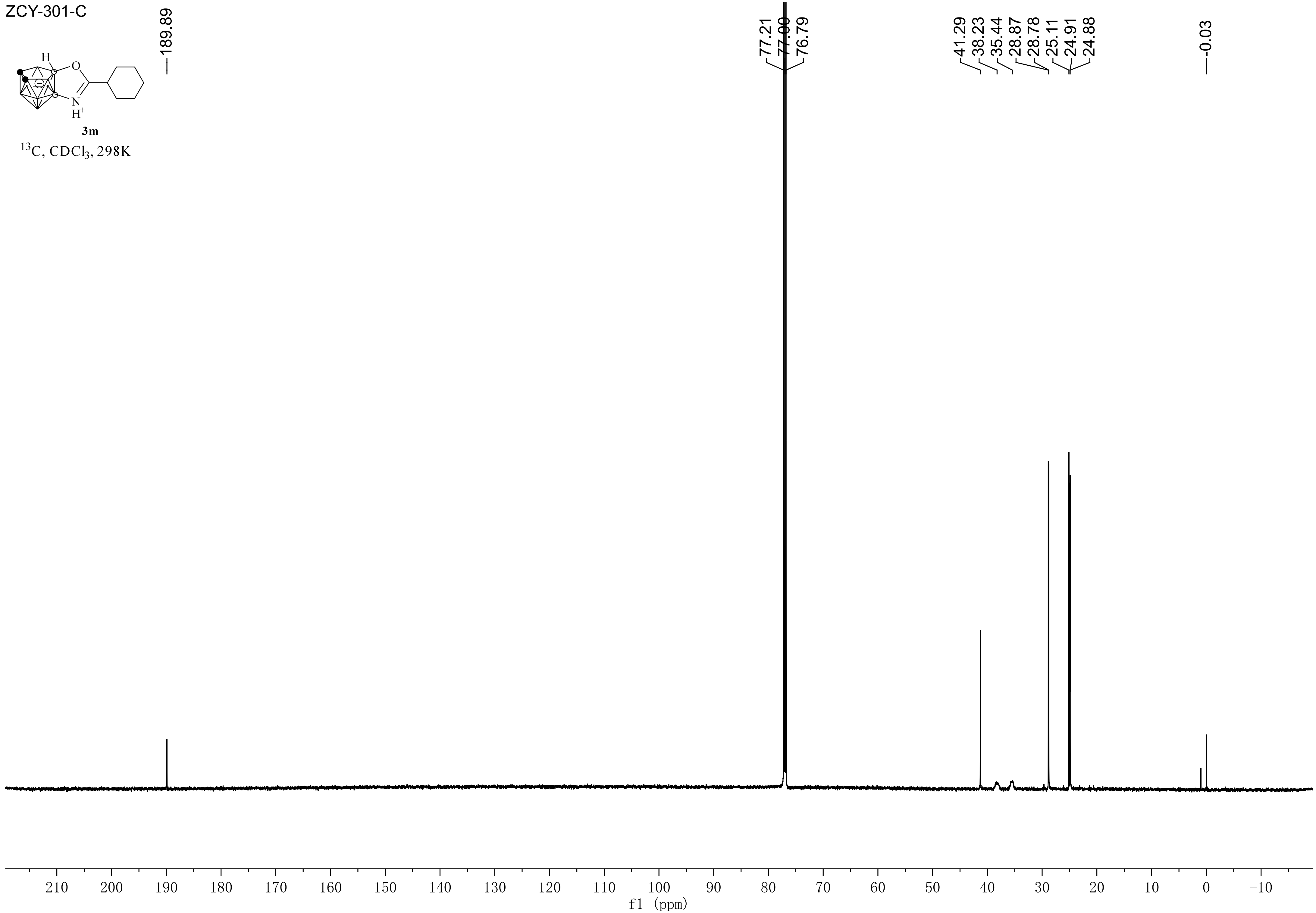
ZCY-301-H{B}



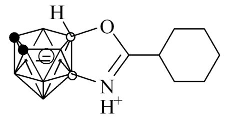
3m

$^{1}H\{^{11}B\}$, $CDCl_3$, 298K



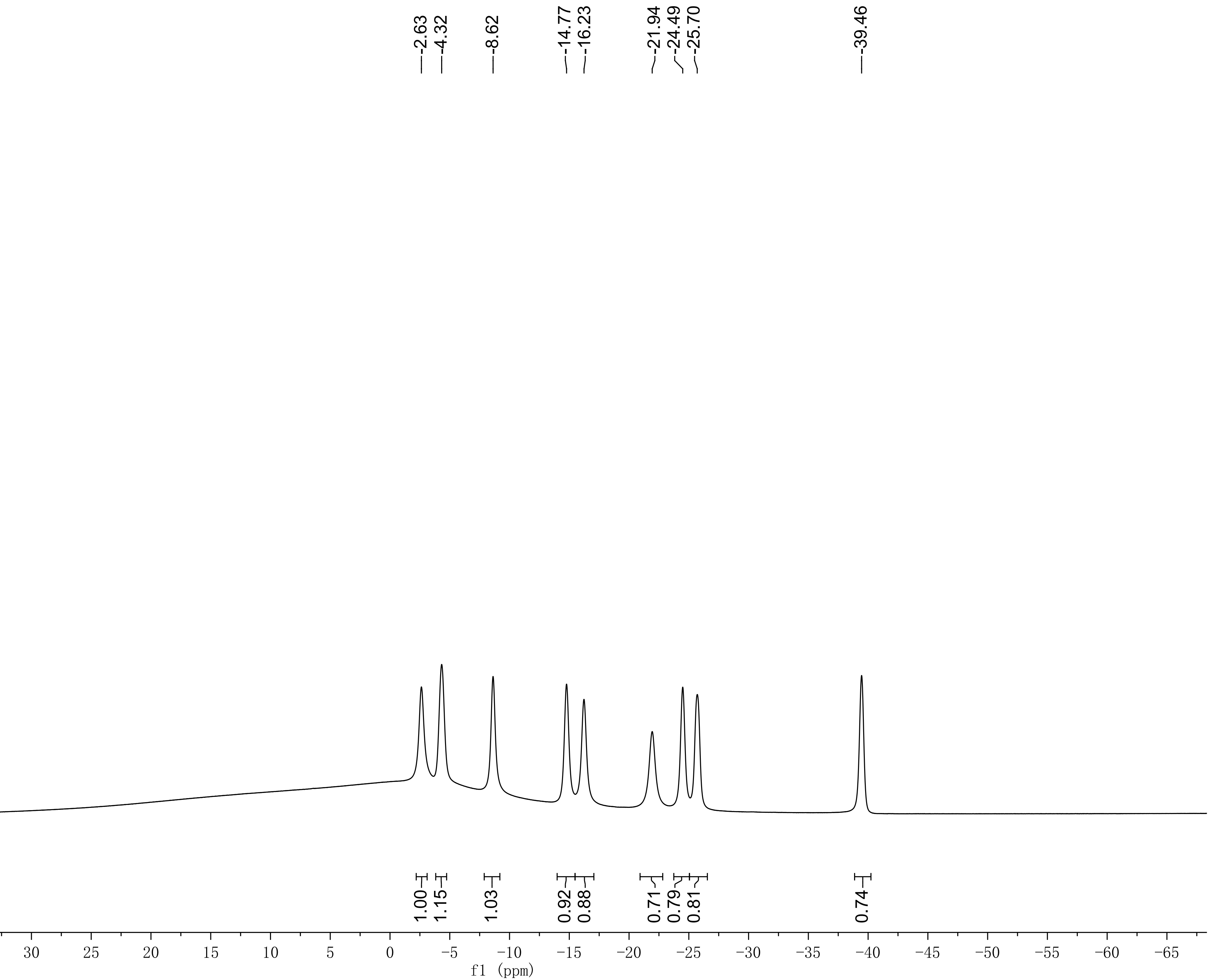

ZCY-301-C
189.89
77.21
77.00
76.79
41.29
38.23
35.44
28.87
28.78
25.11
24.91
24.88
-0.03
H
O
N
H+
3m
13C, CDCl3, 298K
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

ZCY-301-B{H}

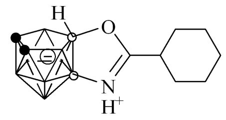


3m

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

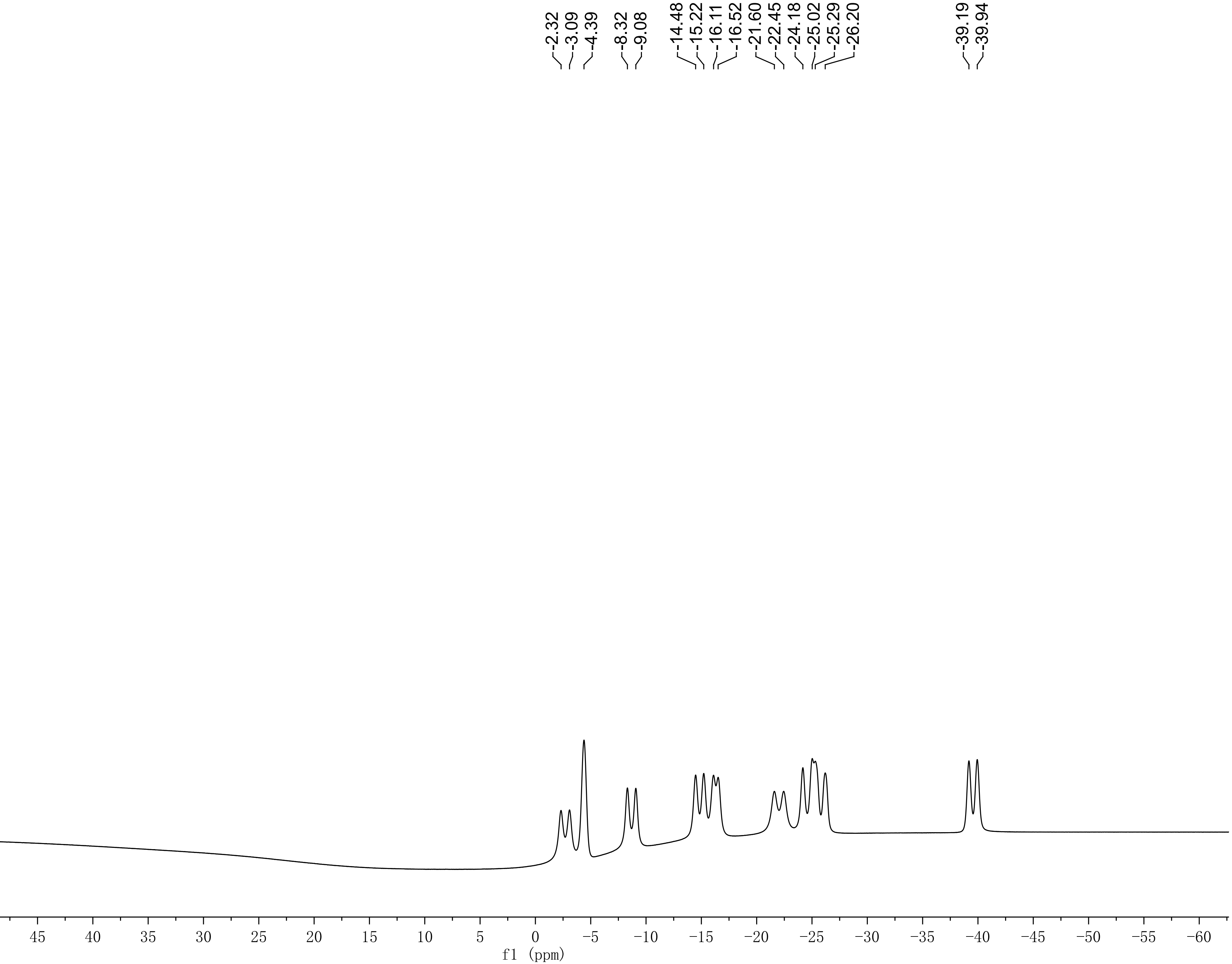


ZCY-301-B

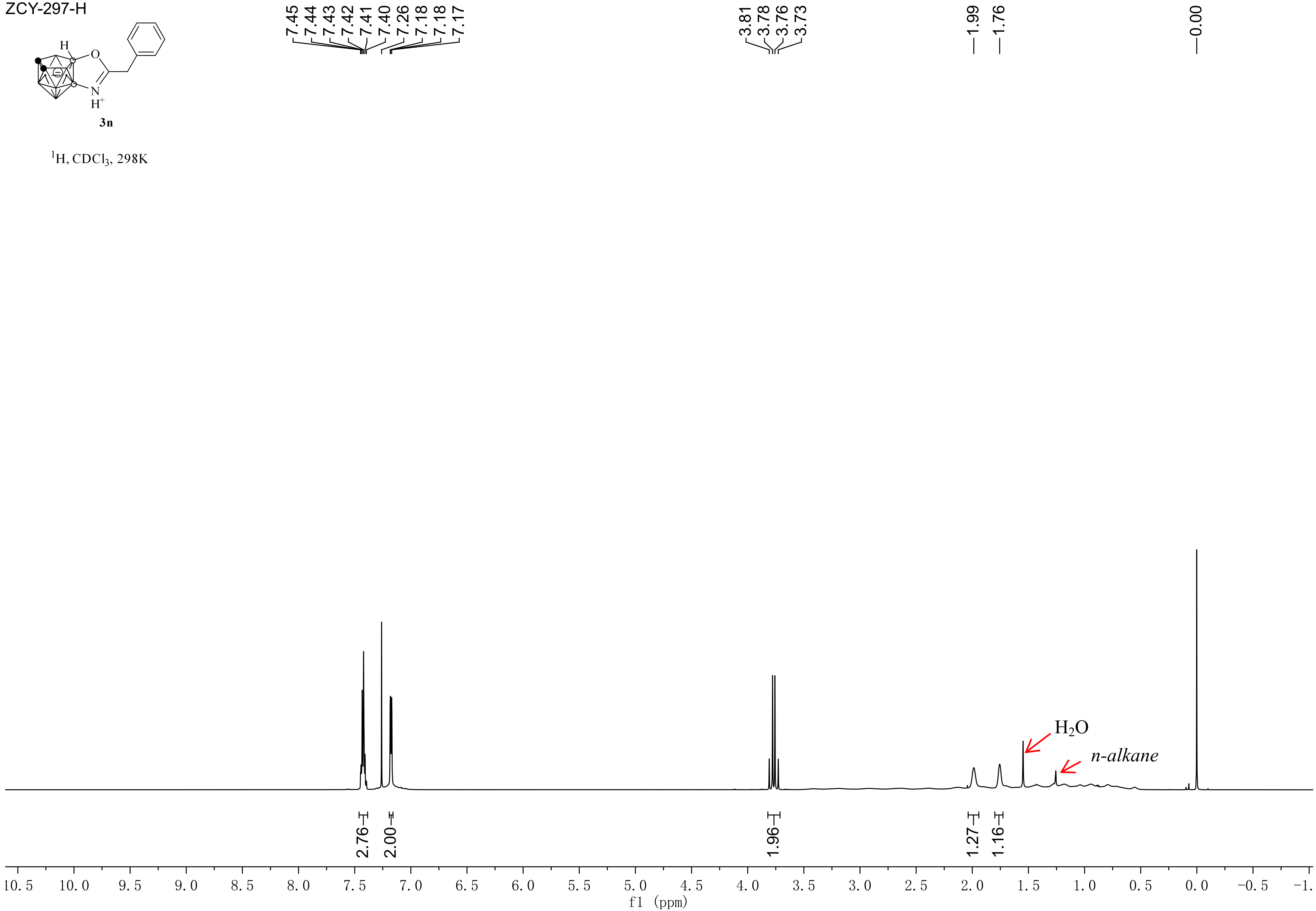


3m

^{11}B, $CDCl_3$, 298K

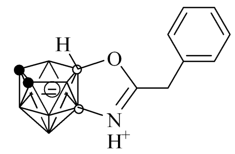


ZCY-297-H



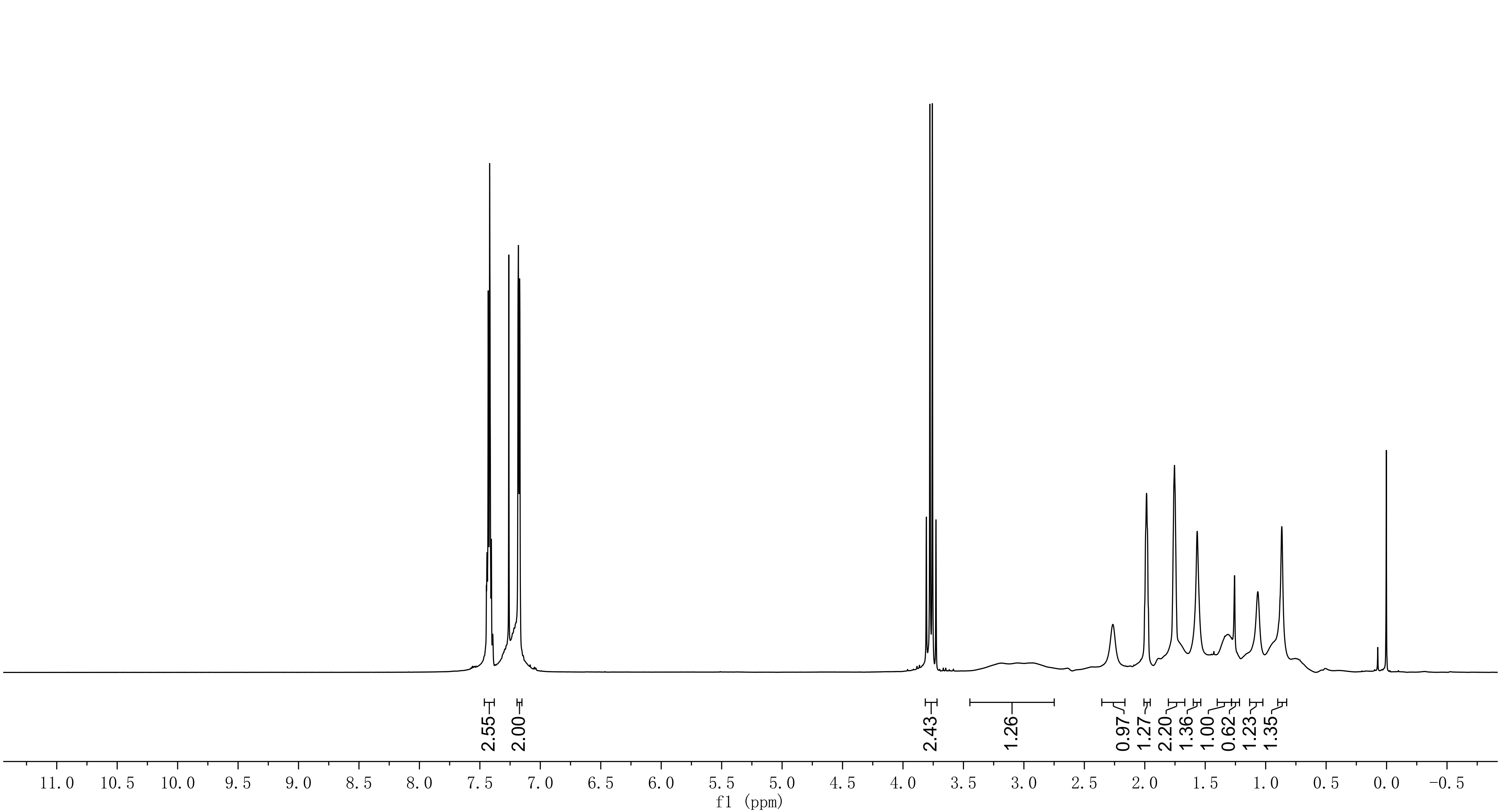
3n
^{1}H, CDCl$_3$, 298K
7.45
7.44
7.43
7.42
7.41
7.40
7.26
7.18
7.18
7.17
3.81
3.78
3.76
3.73
1.99
1.76
0.00
H$_2$O
n-alkane
2.76
2.00
1.96
1.27
1.16
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

ZCY-297-H{B}

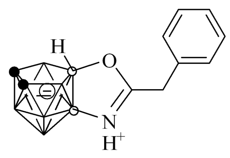


3n

$^{1}H\{^{11}B\}$, $CDCl_3$, 298K

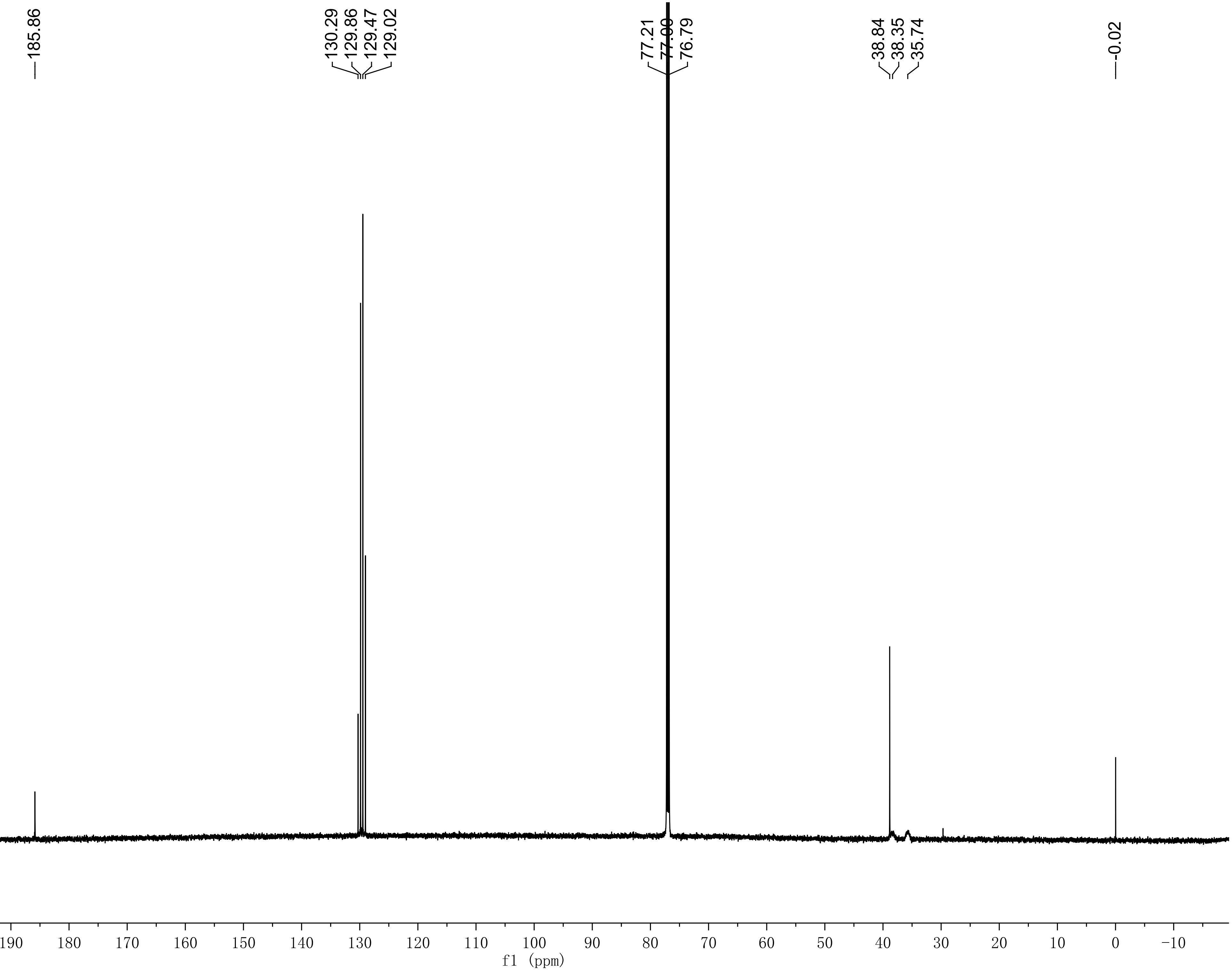


ZCY-297-C

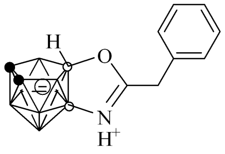


3n

^{13}C, $CDCl_3$, 298K

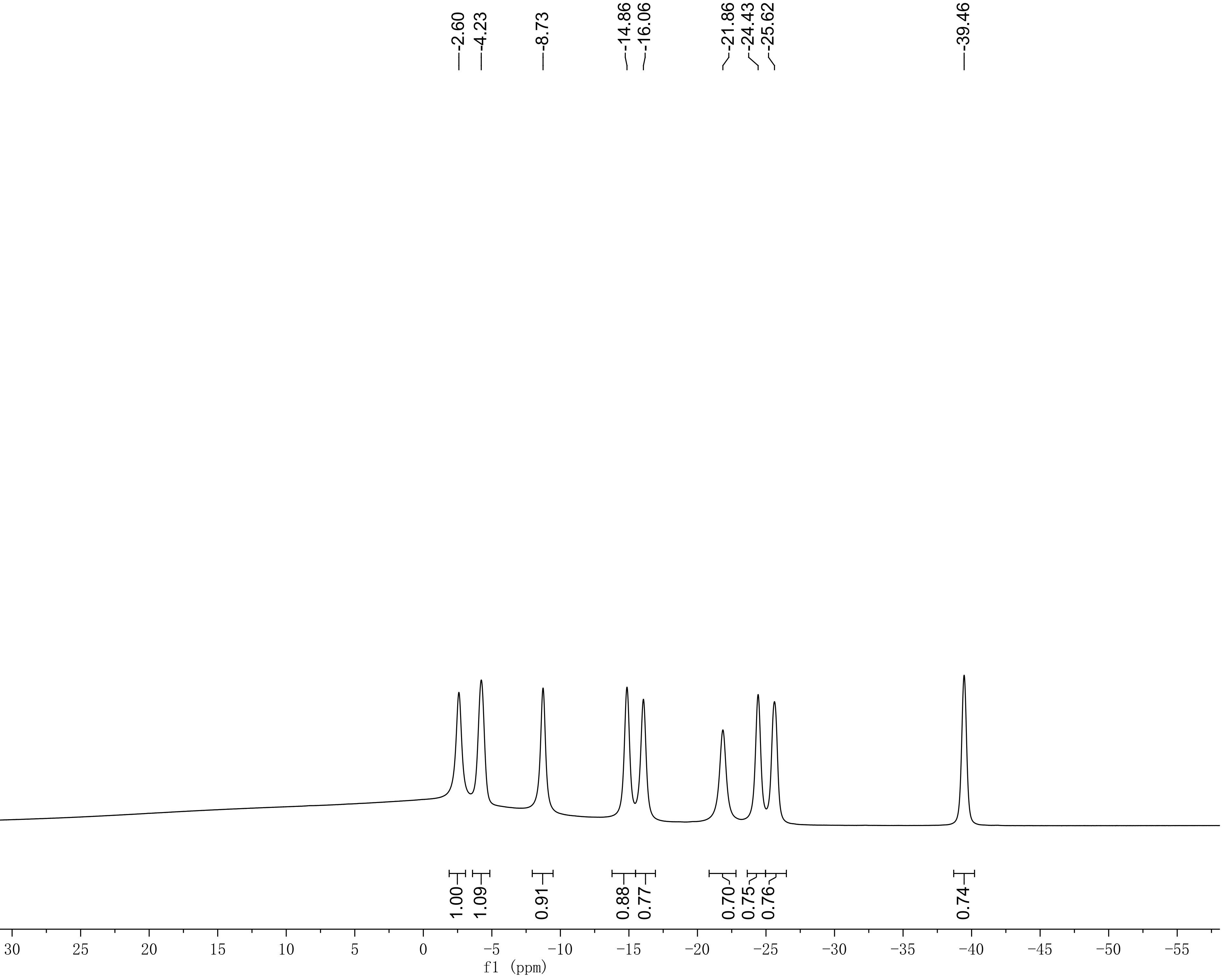


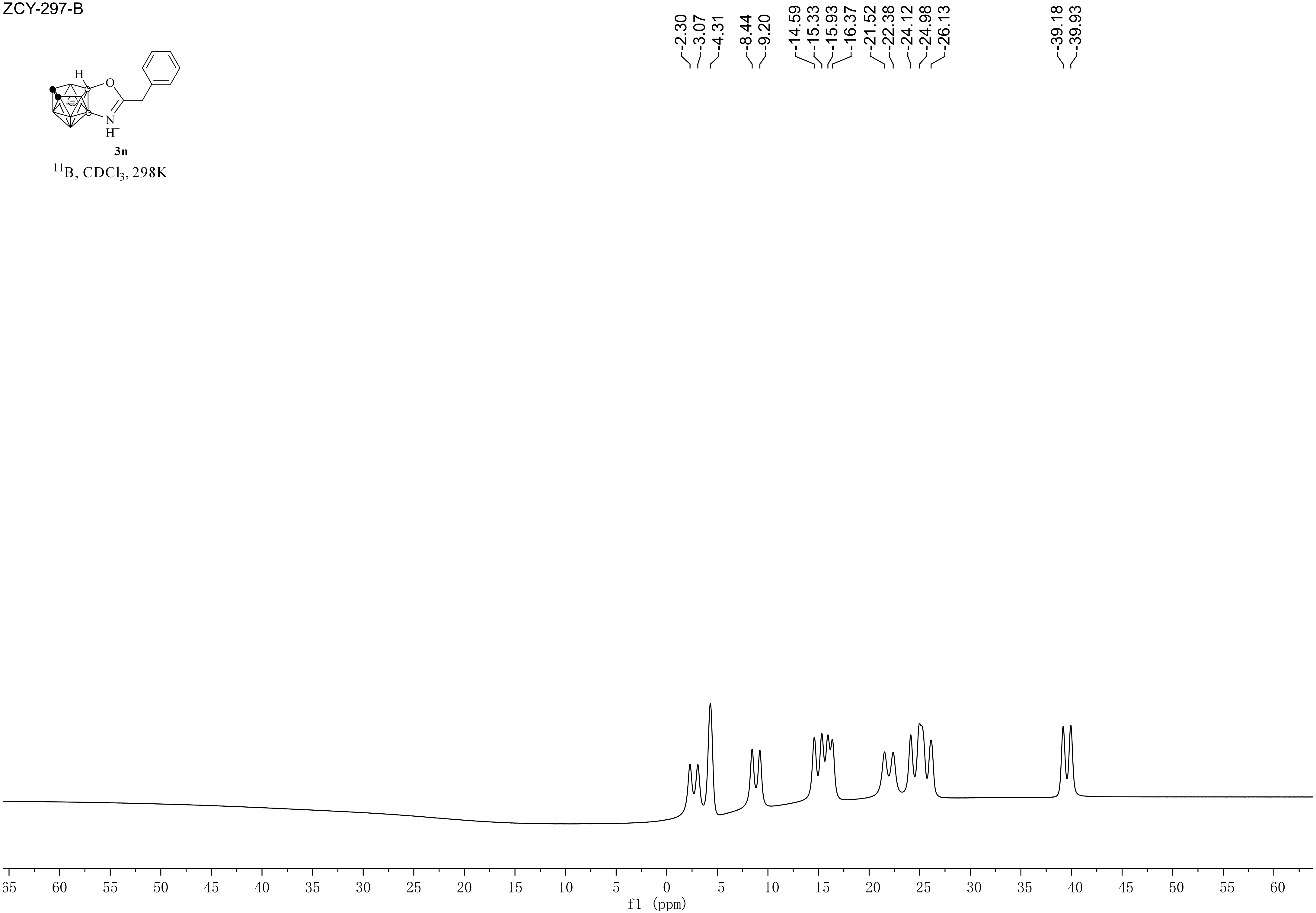
ZCY-297-B{H}



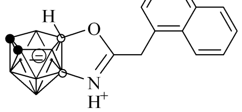
3n

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K



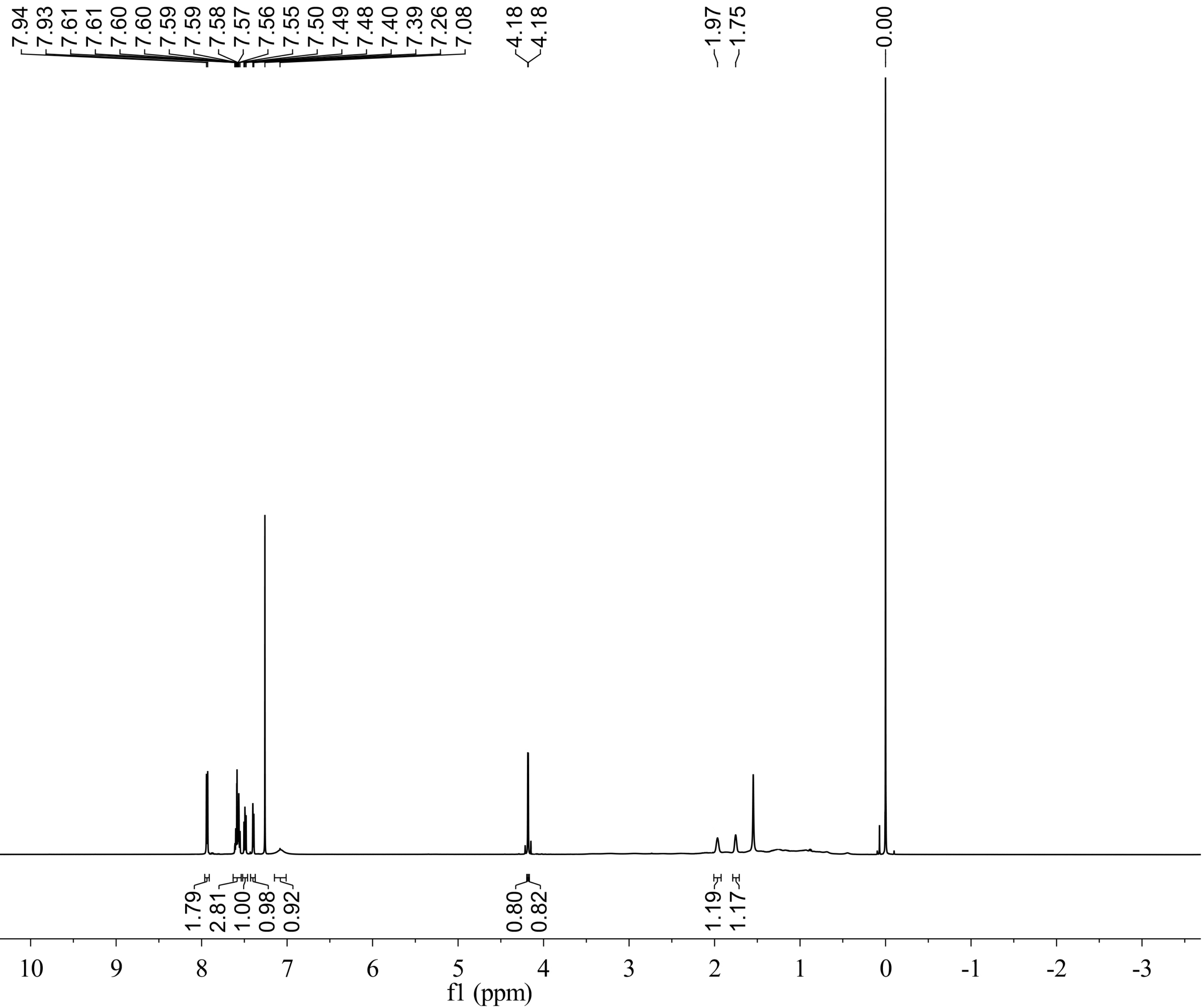

ZCY-297-B
H
O
N
H+
3n
^{11}B, $CDCl_3$, 298K
-2.30
-3.07
-4.31
-8.44
-9.20
-14.59
-15.33
-15.93
-16.37
-21.52
-22.38
-24.12
-24.98
-26.13
-39.18
-39.93
65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55 −60
f1 (ppm)

ZCY-349-H

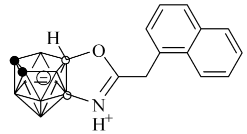


3o

^1H, $CDCl_3$, 298K

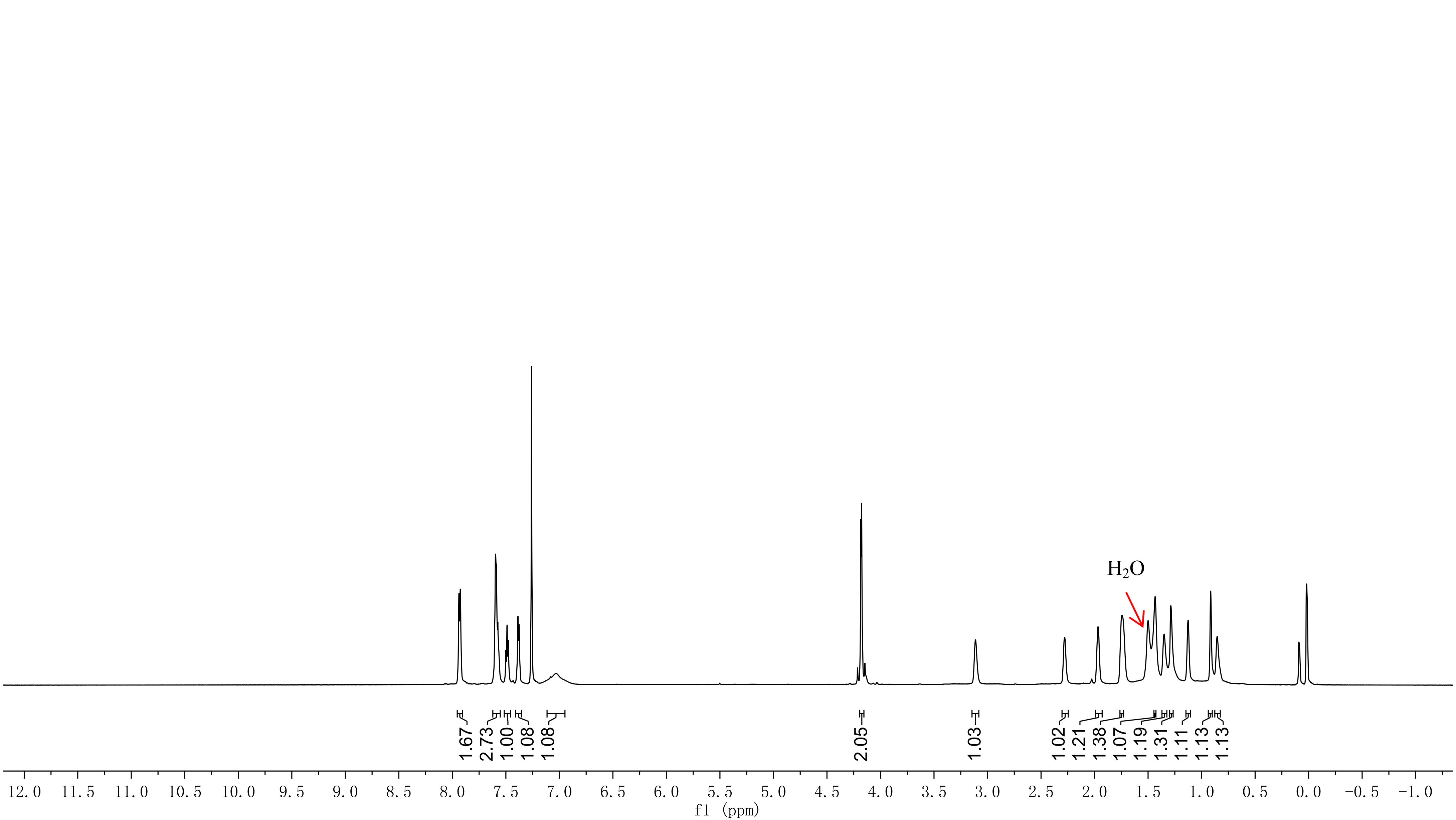


ZCY-349-H{B}

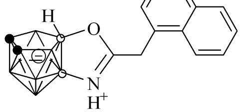


3o

$^{1}H\{^{11}B\}$, $CDCl_3$, 298K

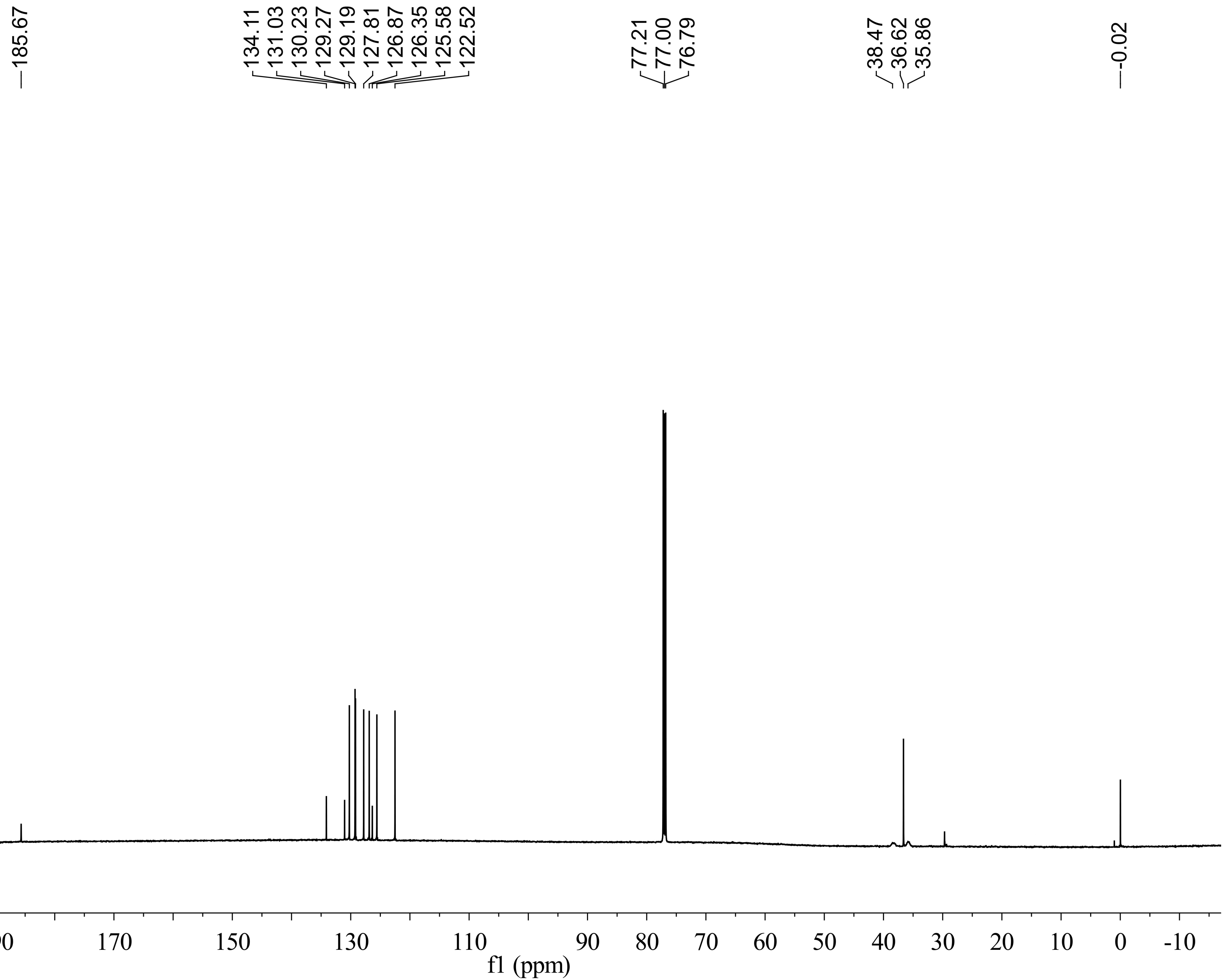


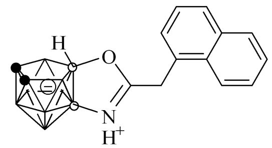
ZCY-349-C



3o

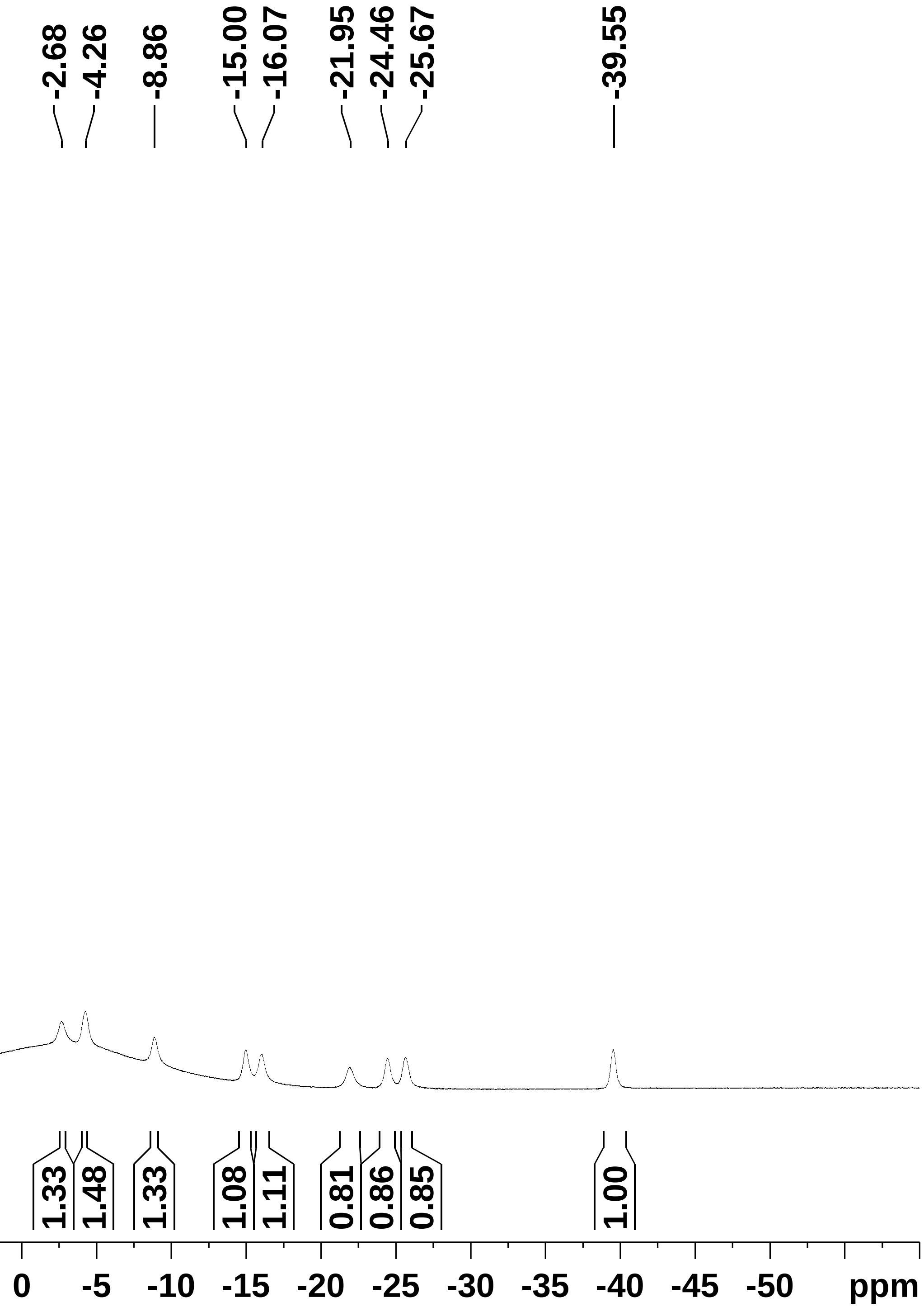
^{13}C, $CDCl_3$, 298K





3o

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

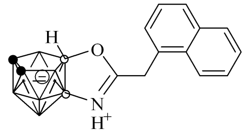


分析测试中心核磁实验室 SWUST

NMR Teacher : Huang

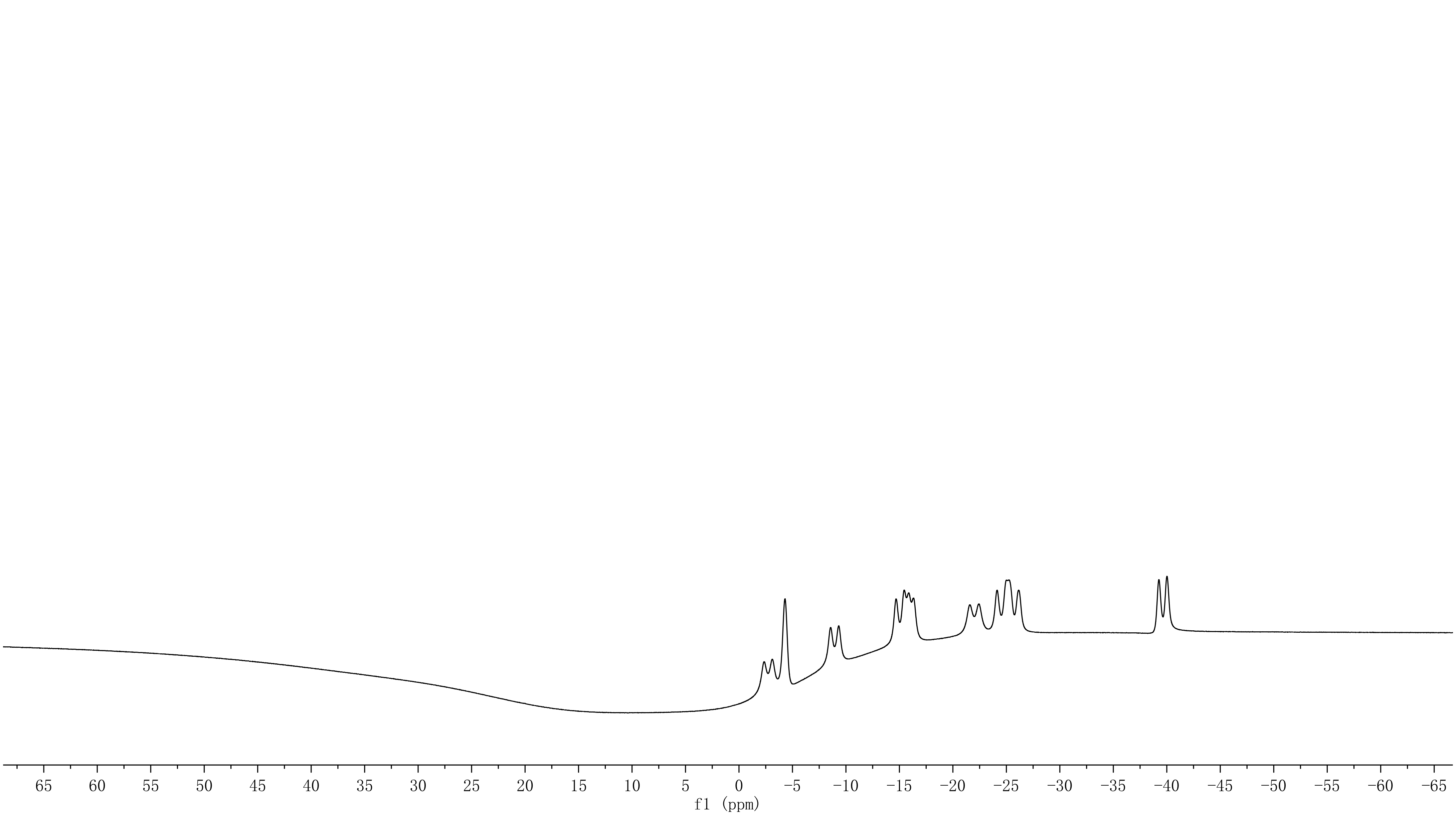
```
Current Data Parameters
NAME              20180531
EXPNO                  532
PROCNO                   1

F2 - Acquisition Parameters
Date_             20180602
Time                  1.03
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  85536
SOLVENT              CDCl3
NS                   5000
DS                      4
SWH            50000.000 Hz
FIDRES          0.584549 Hz
AQ             0.8553600 sec
RG                 172.47
DW                 10.000 usec
DE                   6.50 usec
TE                  298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         192.5526102 MHz
NUC1                  11B
P1                  25.00 usec
PLW1        180.00000000 W

======== CHANNEL f2 ========
SFO2         600.1737063 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               70.00 usec
PLW2         23.00000000 W
PLW12         0.57832998 W
PLW13         0.28338000 W

F2 - Processing parameters
SI                  32768
SF           192.5583691 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

ZCY-349-B

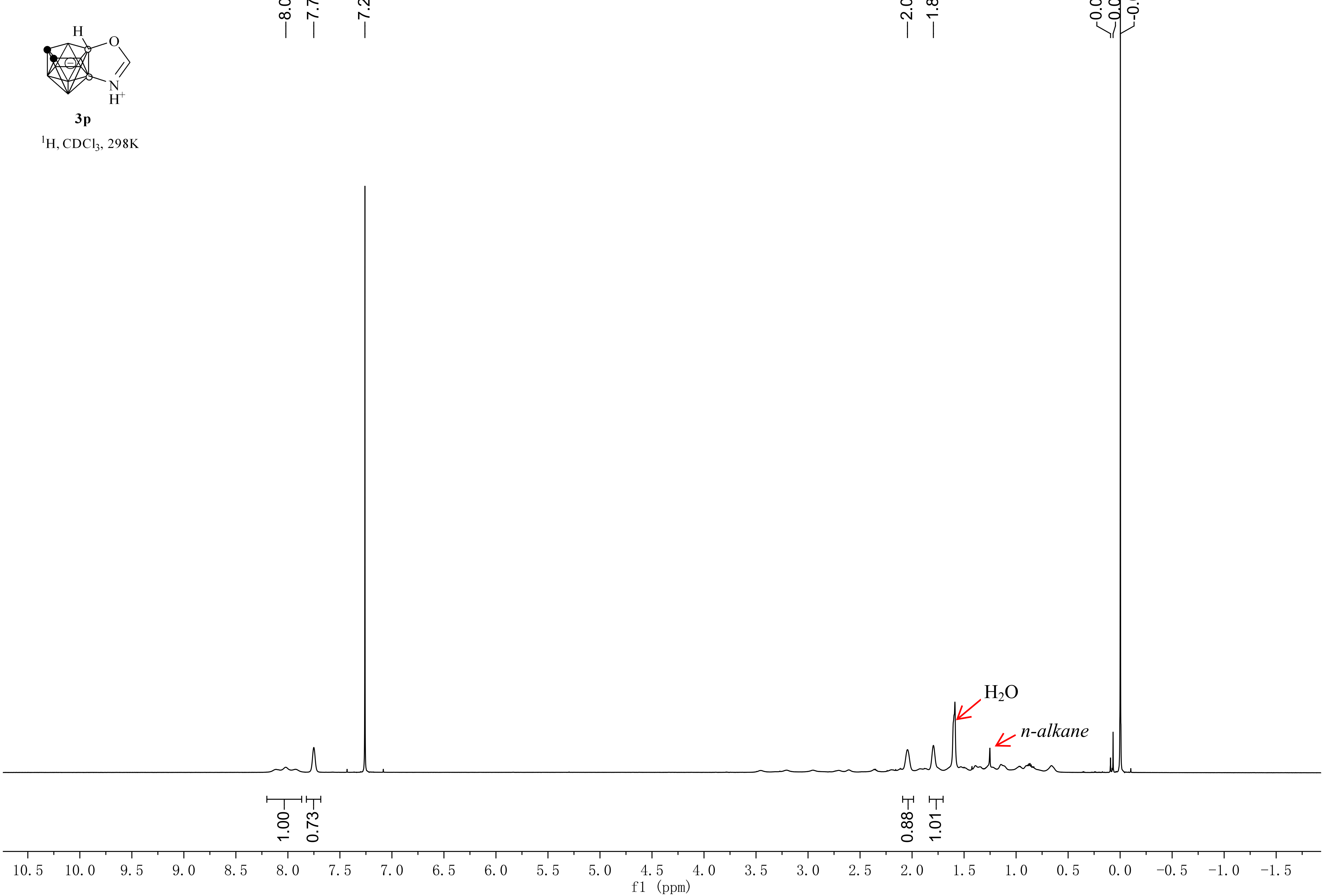


3o

^{11}B, $CDCl_3$, 298K

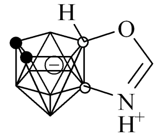


ZCY-318-H



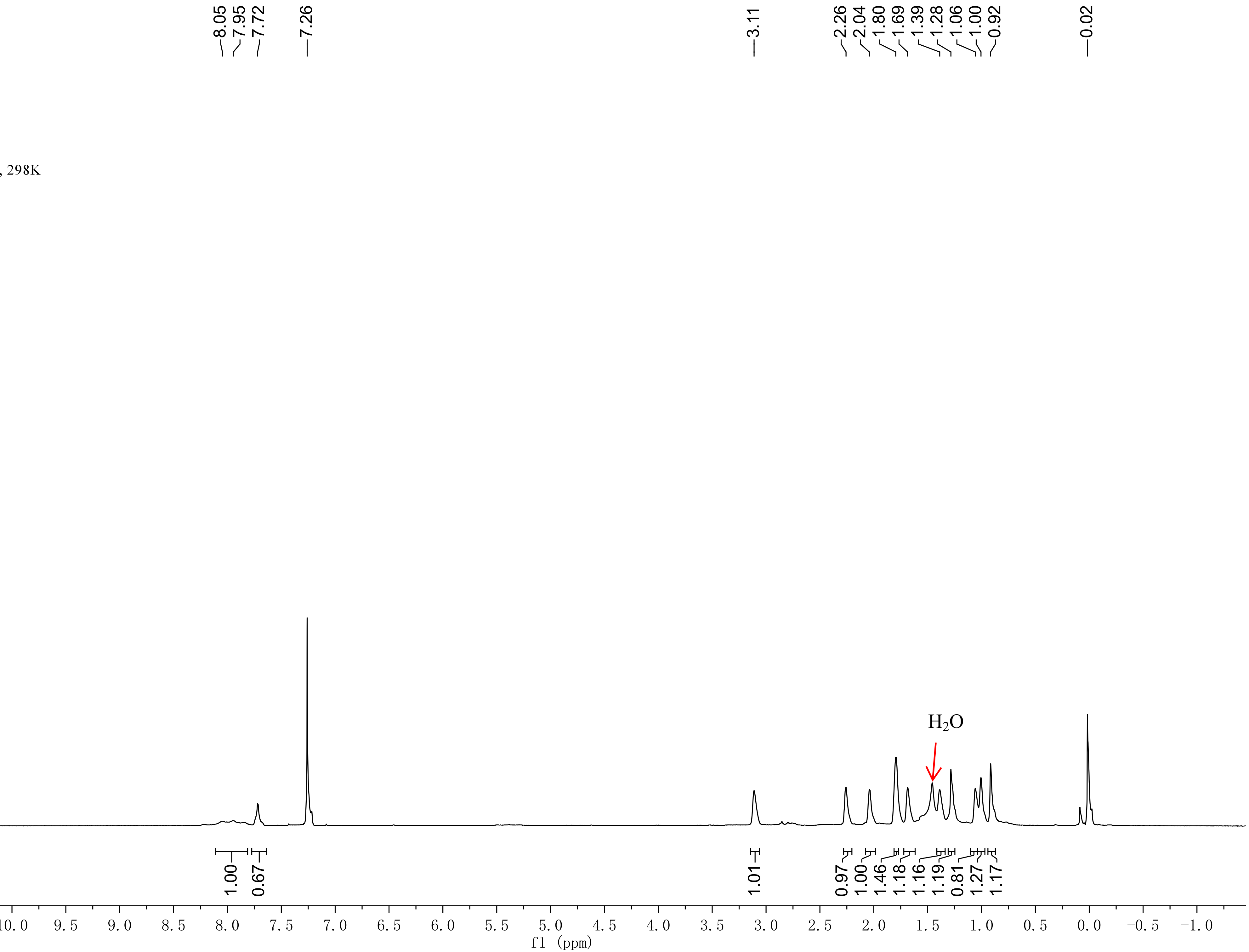
3p
^{1}H, CDCl$_3$, 298K
8.02
7.75
7.26
2.04
1.80
0.09
0.07
-0.00
H_2O
n-alkane
1.00
0.73
0.88
1.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

ZCY-318-H{B}

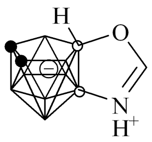


3p

$^1H\{^{11}B\}$, $CDCl_3$, 298K

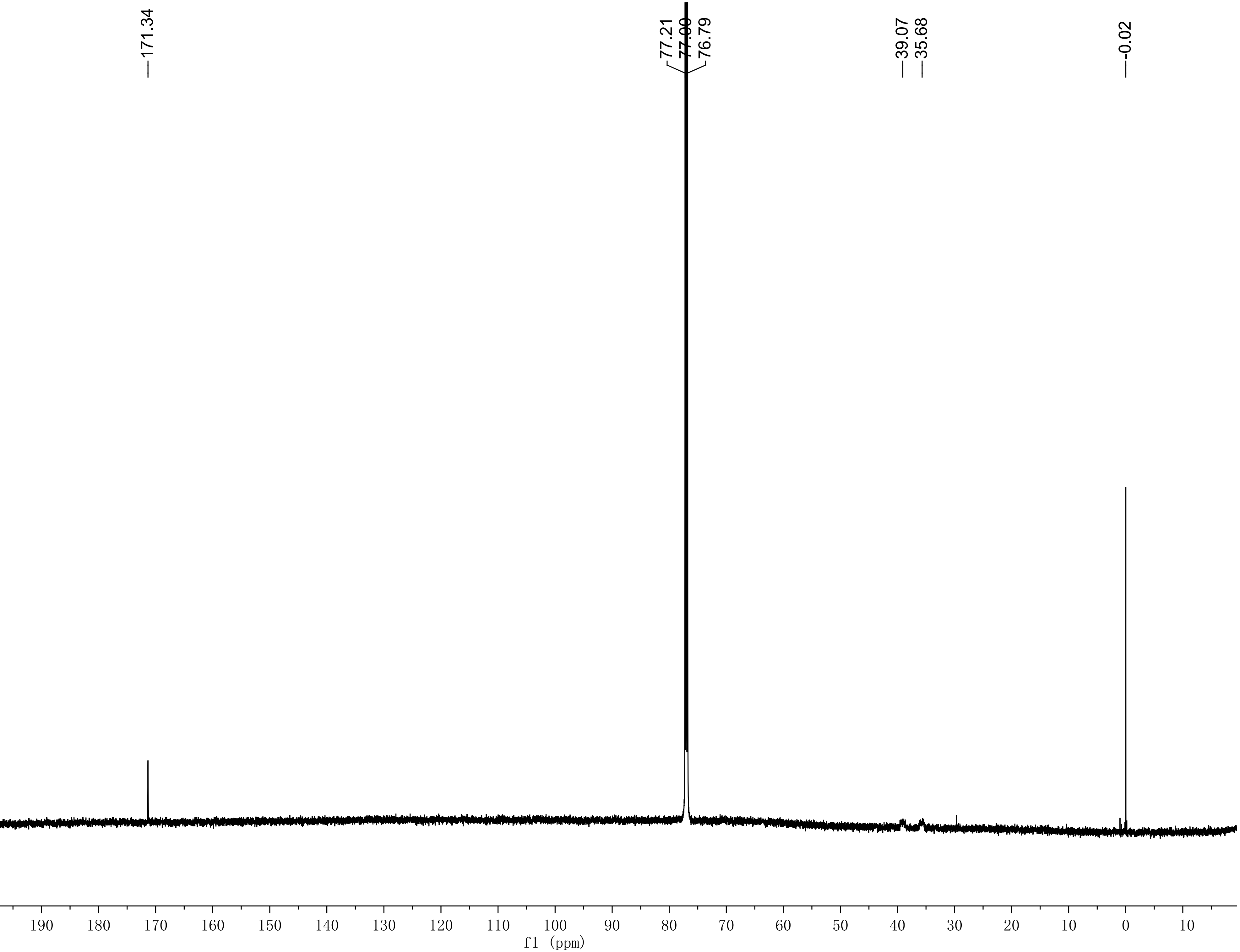


ZCY-318-C

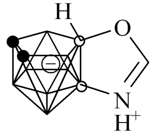


3p

^{13}C, $CDCl_3$, 298K

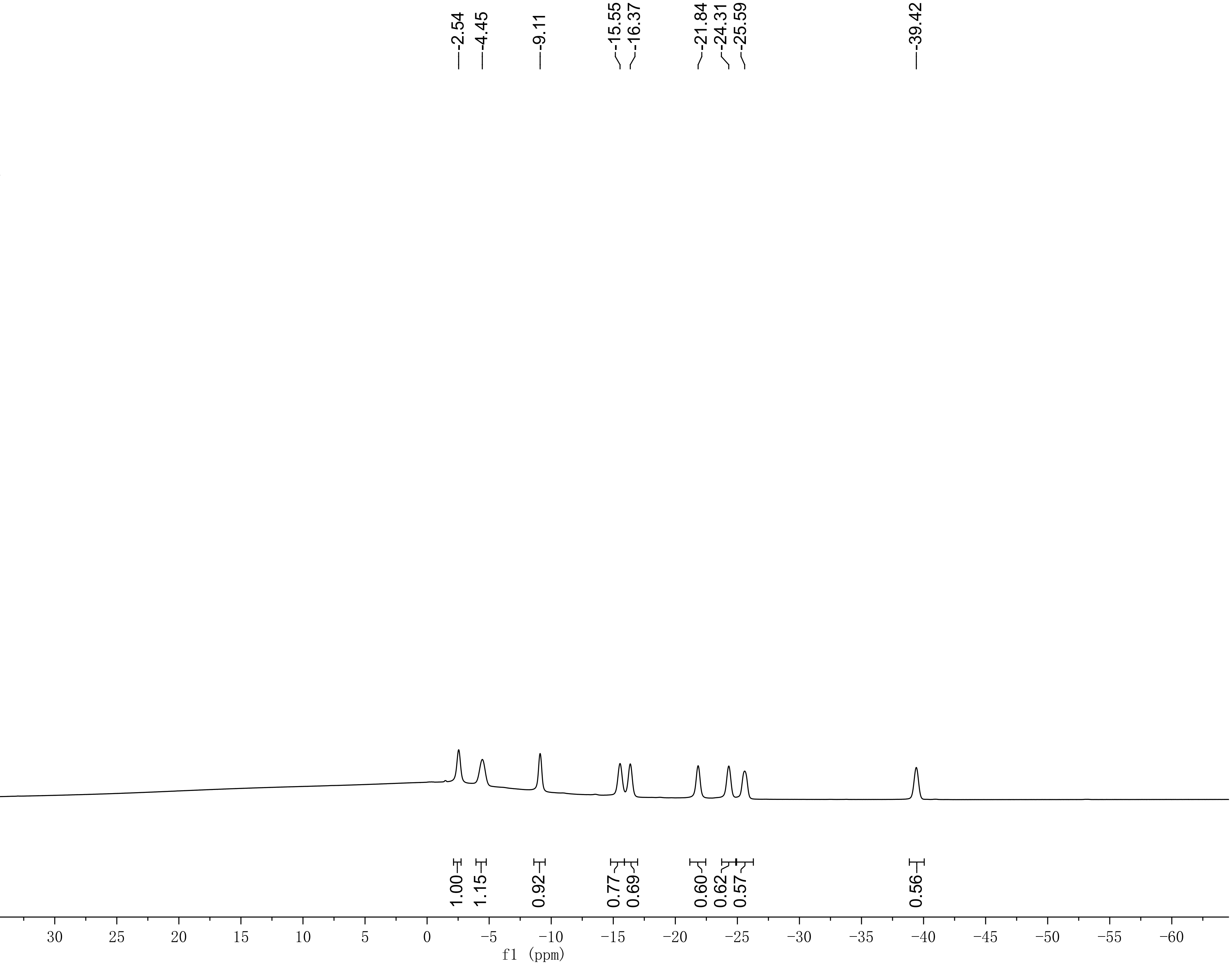


ZCY-318-B{H}

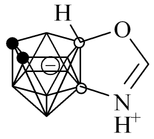


3p

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

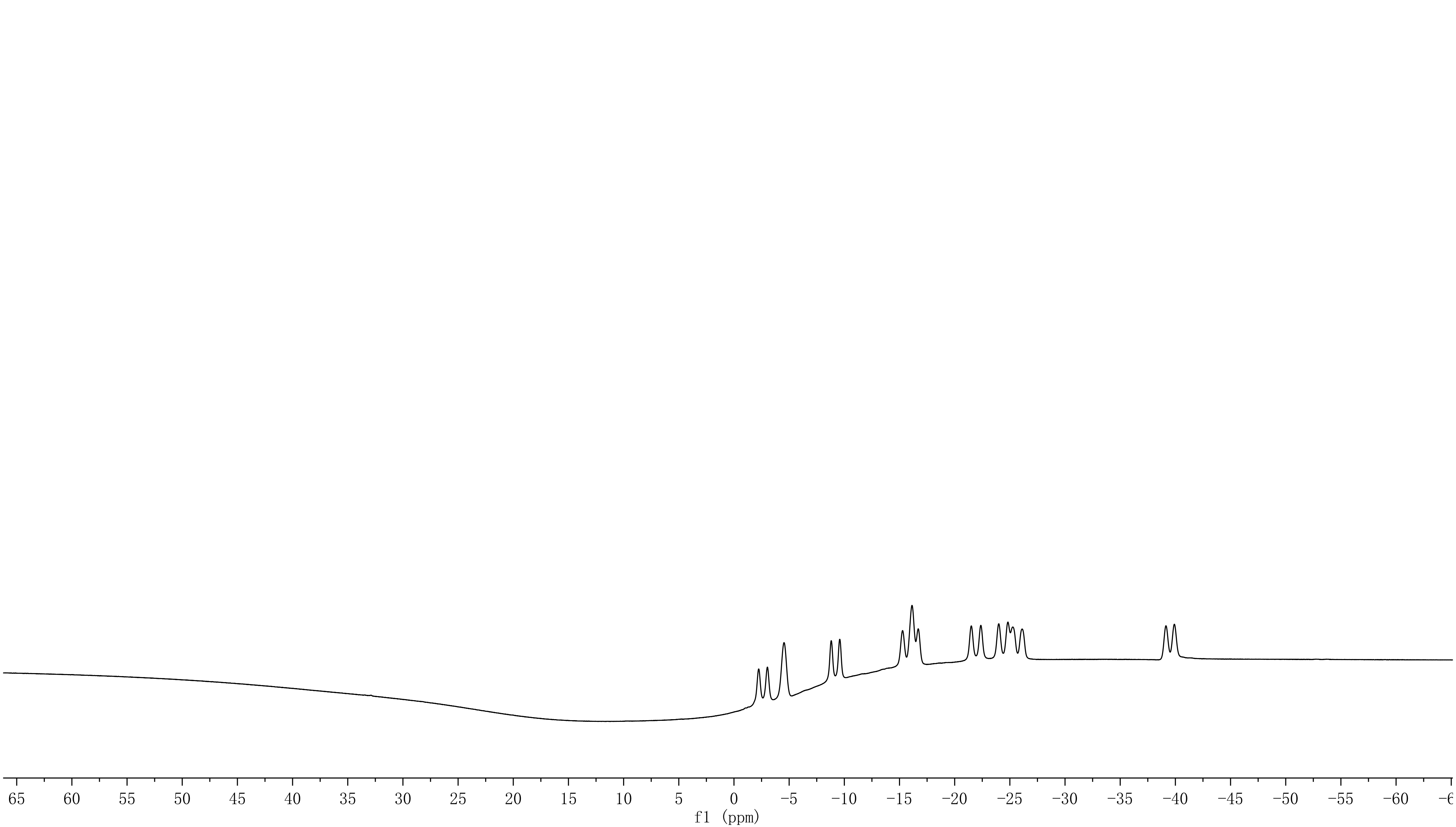


ZCY-318-B

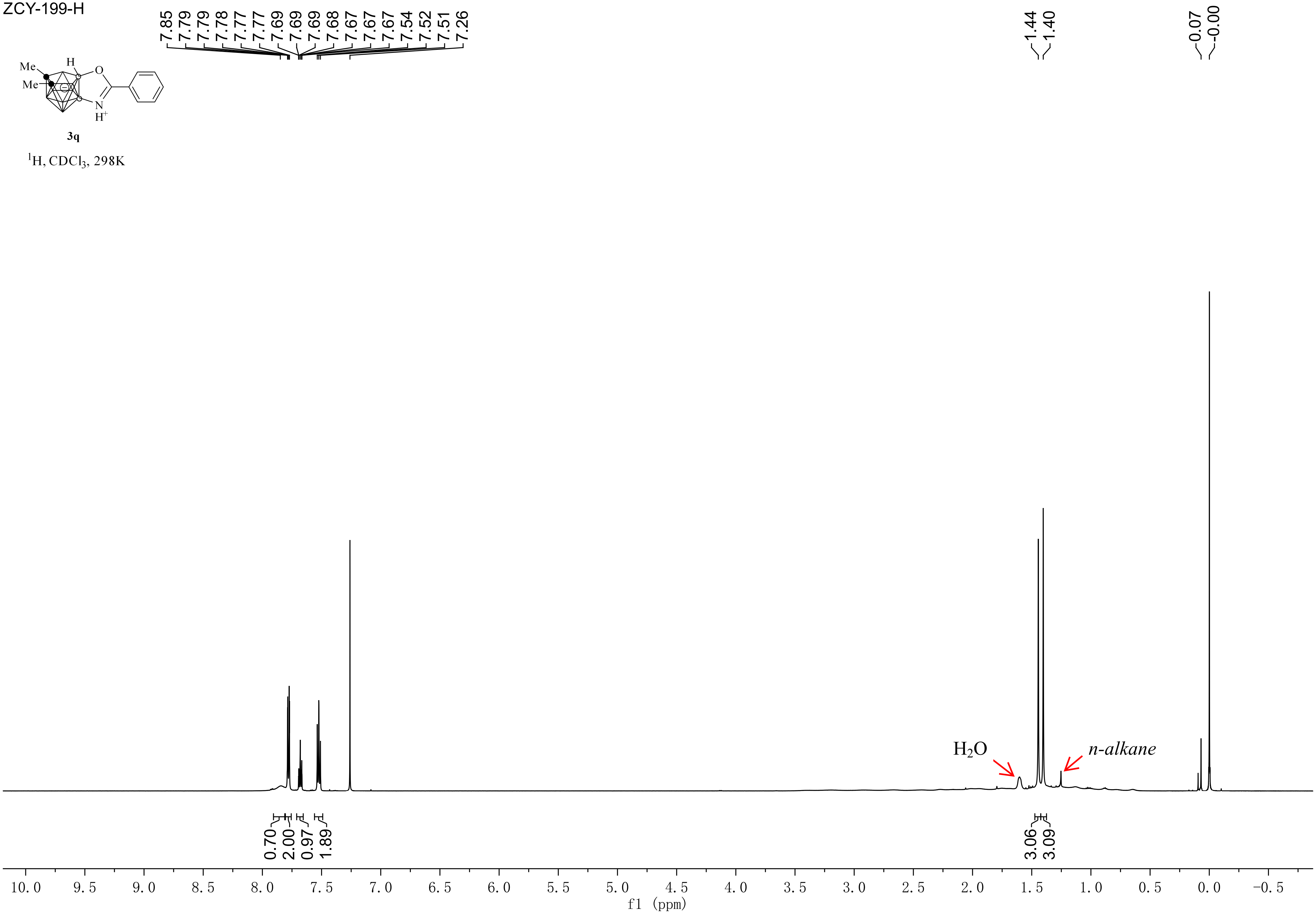


3p

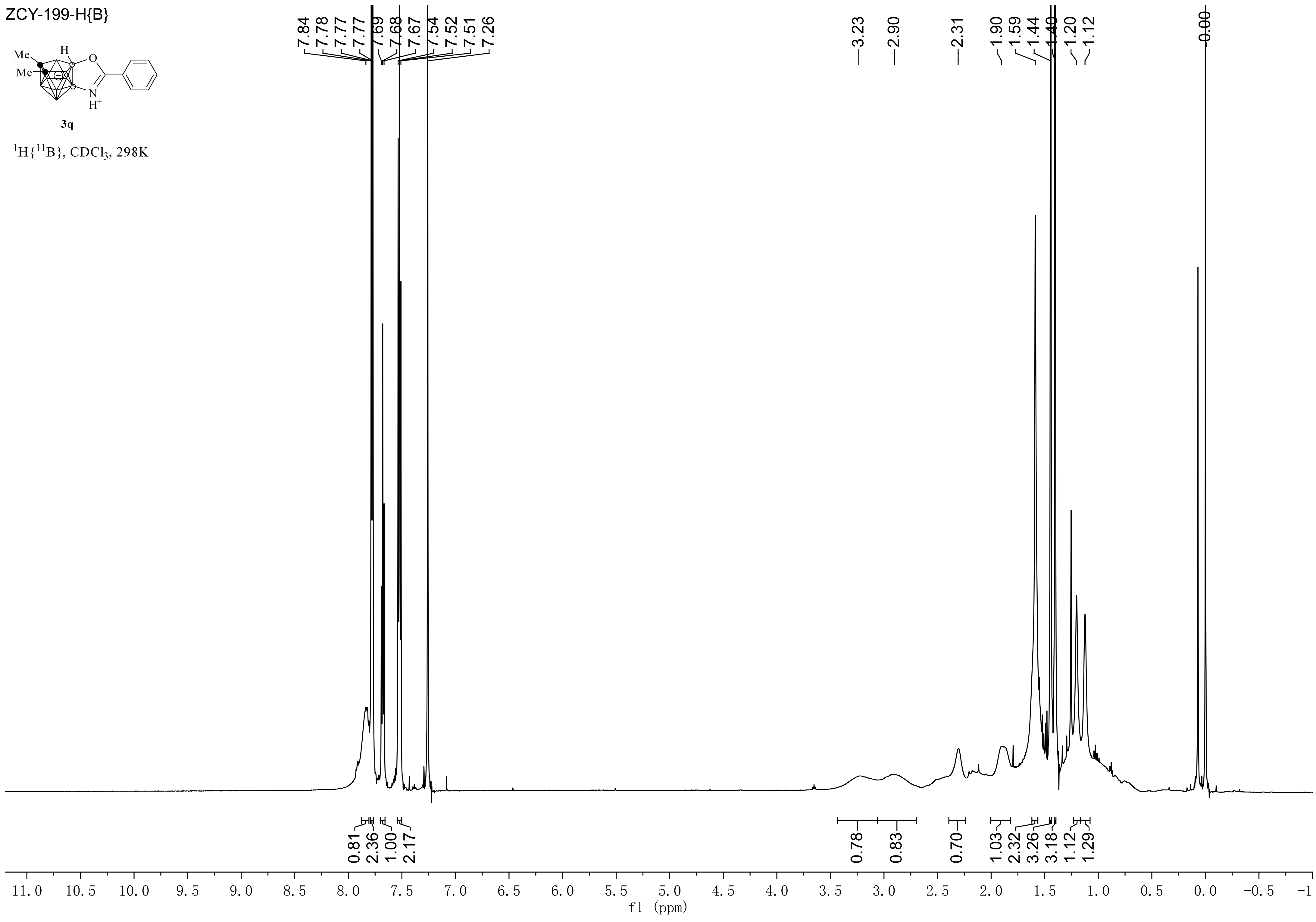
^{11}B, $CDCl_3$, 298K



ZCY-199-H

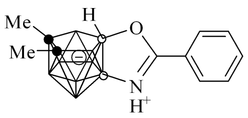


Me
Me
H
O
N
H+
3q
[1]H, CDCl3, 298K
7.85
7.79
7.79
7.78
7.77
7.77
7.69
7.69
7.69
7.68
7.67
7.67
7.67
7.54
7.52
7.51
7.26
1.44
1.40
0.07
-0.00
H2O
n-alkane
0.70
2.00
0.97
1.89
3.06
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



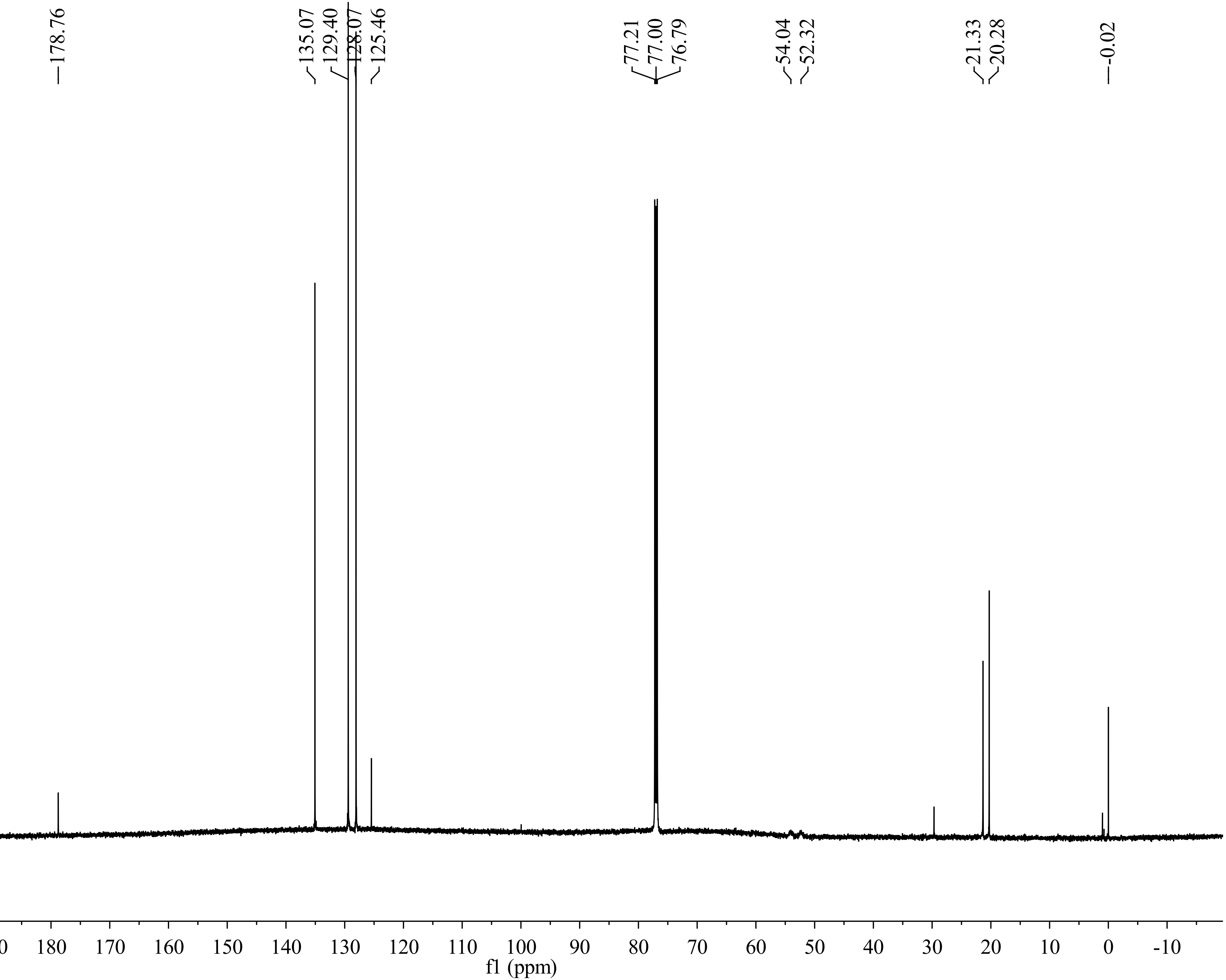
ZCY-199-H{B}
Me
Me
H
O
N
H+
3q
1H{11B}, CDCl3, 298K
7.84
7.78
7.77
7.77
7.69
7.68
7.67
7.54
7.52
7.51
7.26
3.23
2.90
2.31
1.90
1.59
1.44
1.40
1.20
1.12
0.00
0.81
2.36
1.00
2.17
0.78
0.83
0.70
1.03
2.32
3.26
3.18
1.12
1.29
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

ZCY-199-C

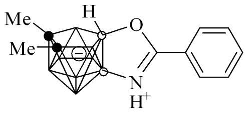


3q

^{13}C, $CDCl_3$, 298K

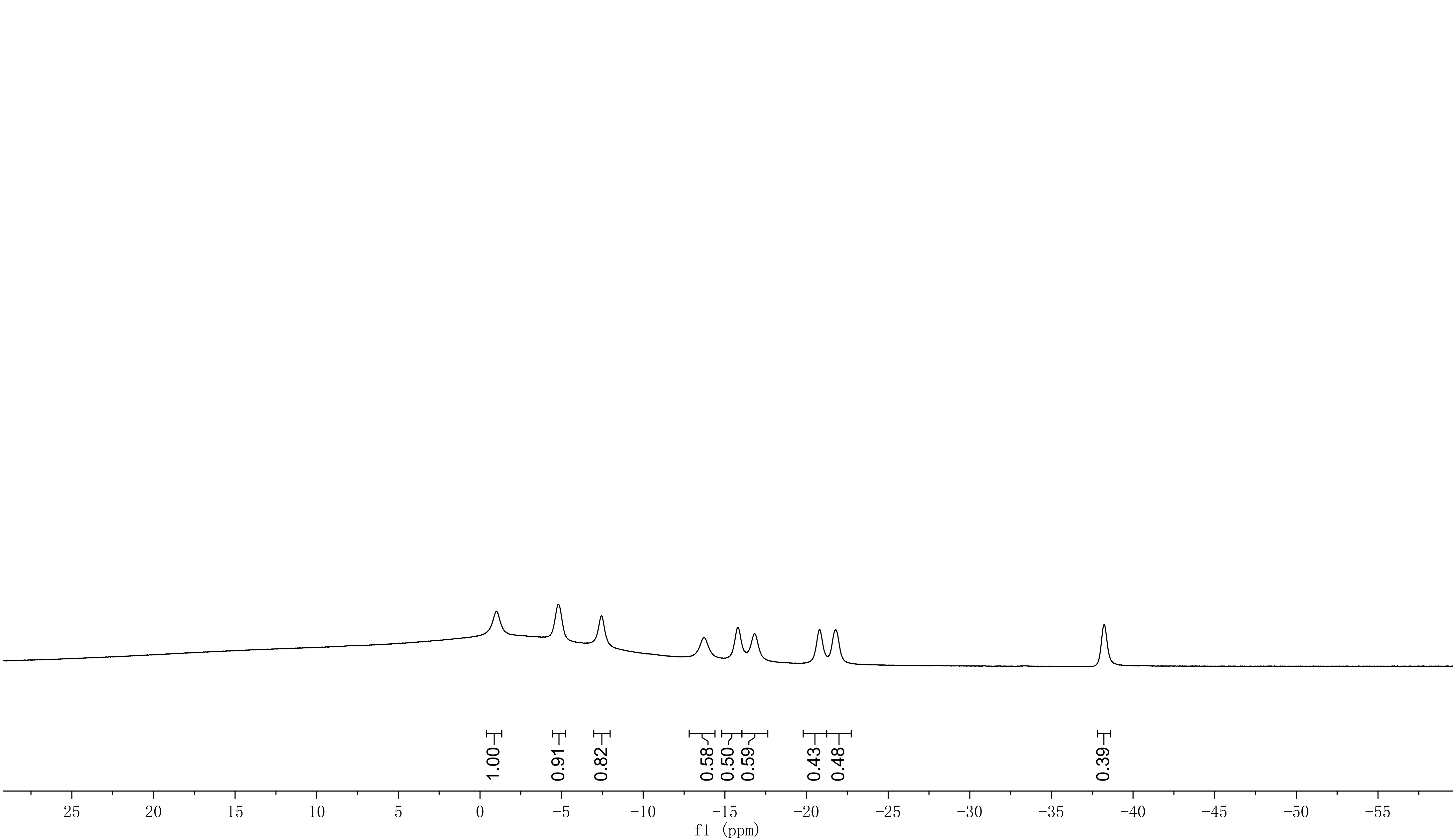


ZCY-199-B{H}

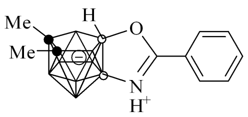


3q

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

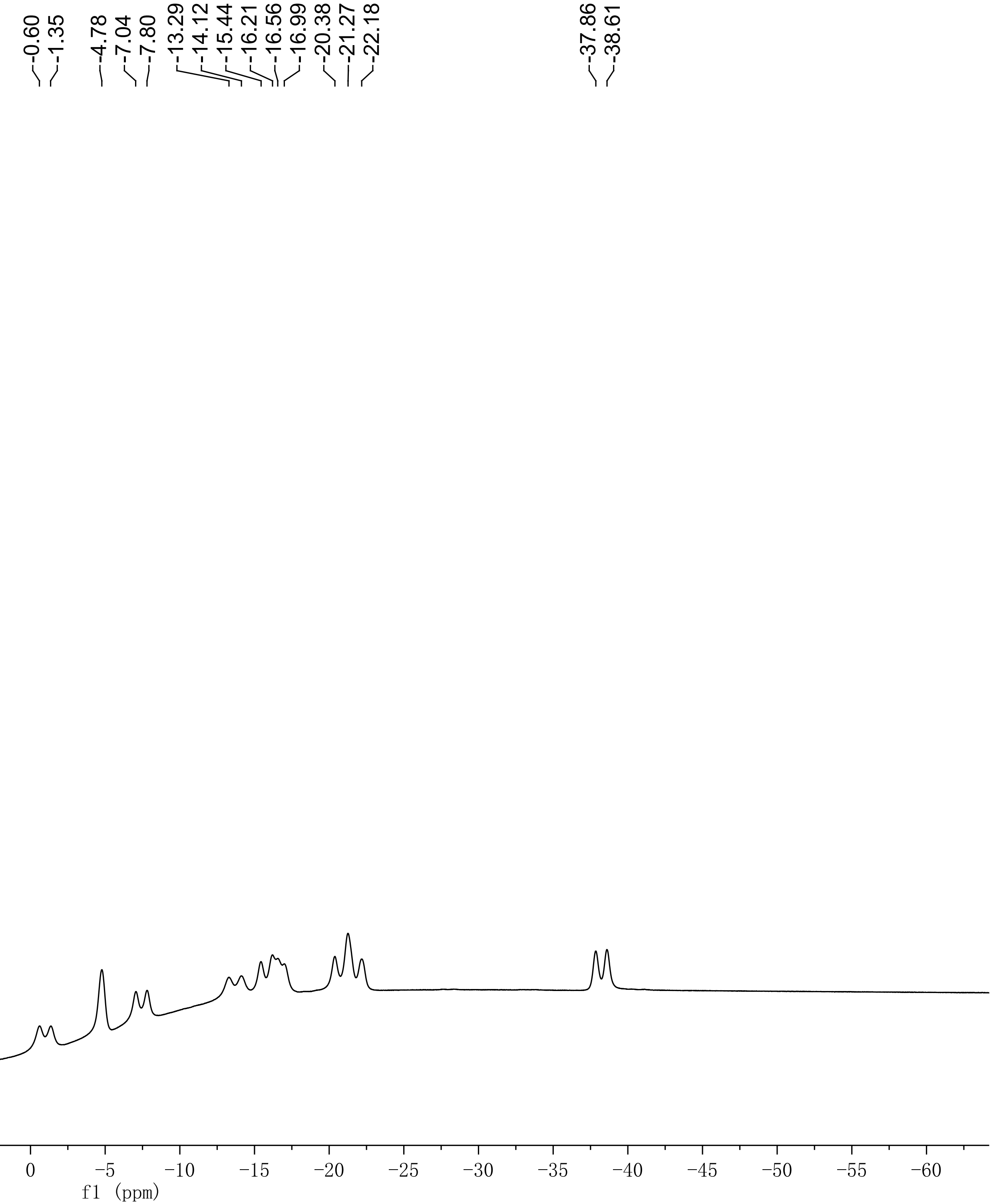


ZCY-199-B

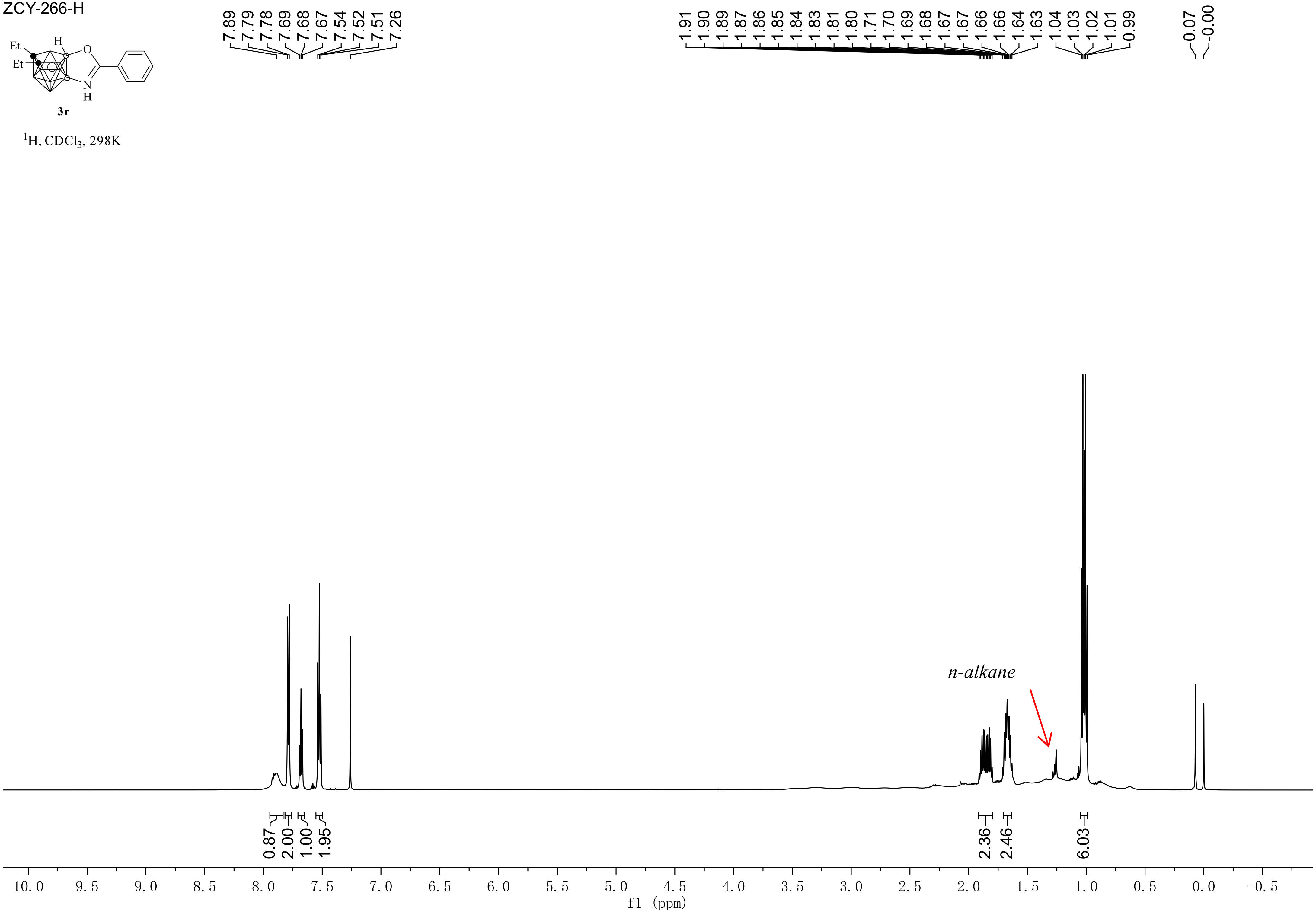


3q

^{11}B, $CDCl_3$, 298K

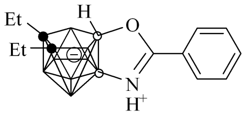


ZCY-266-H



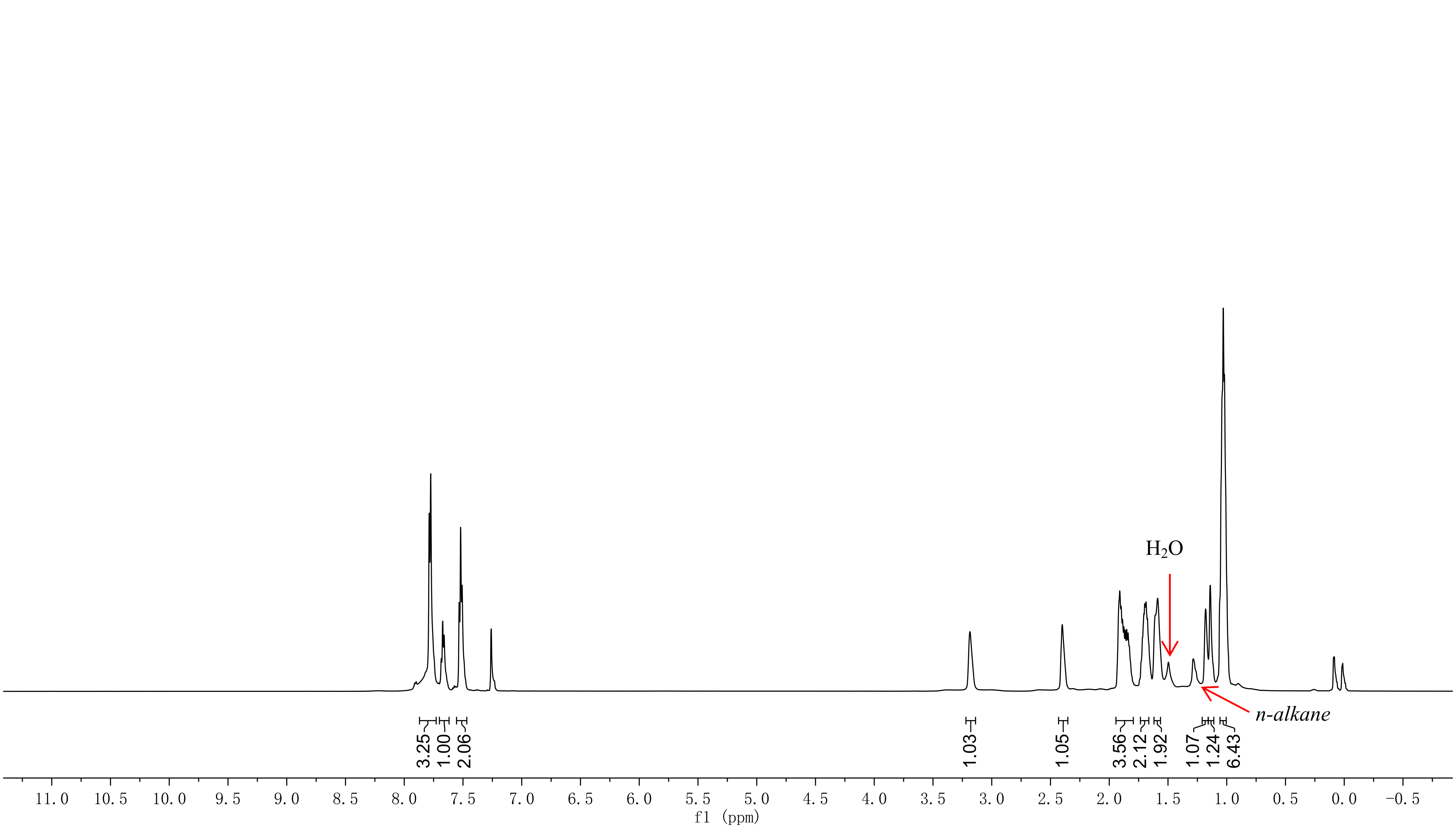
Et
Et
H
O
N
H+
3r
1H, CDCl3, 298K
7.89
7.79
7.78
7.69
7.68
7.67
7.54
7.52
7.51
7.26
1.91
1.90
1.89
1.87
1.86
1.85
1.84
1.83
1.81
1.80
1.71
1.70
1.69
1.68
1.67
1.67
1.66
1.66
1.64
1.63
1.04
1.03
1.02
1.01
0.99
0.07
-0.00
n-alkane
0.87
2.00
1.00
1.95
2.36
2.46
6.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

ZCY-266-H{B}

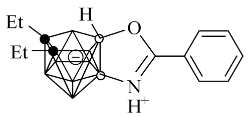


3r

$^1H\{^{11}B\}$, $CDCl_3$, 298K

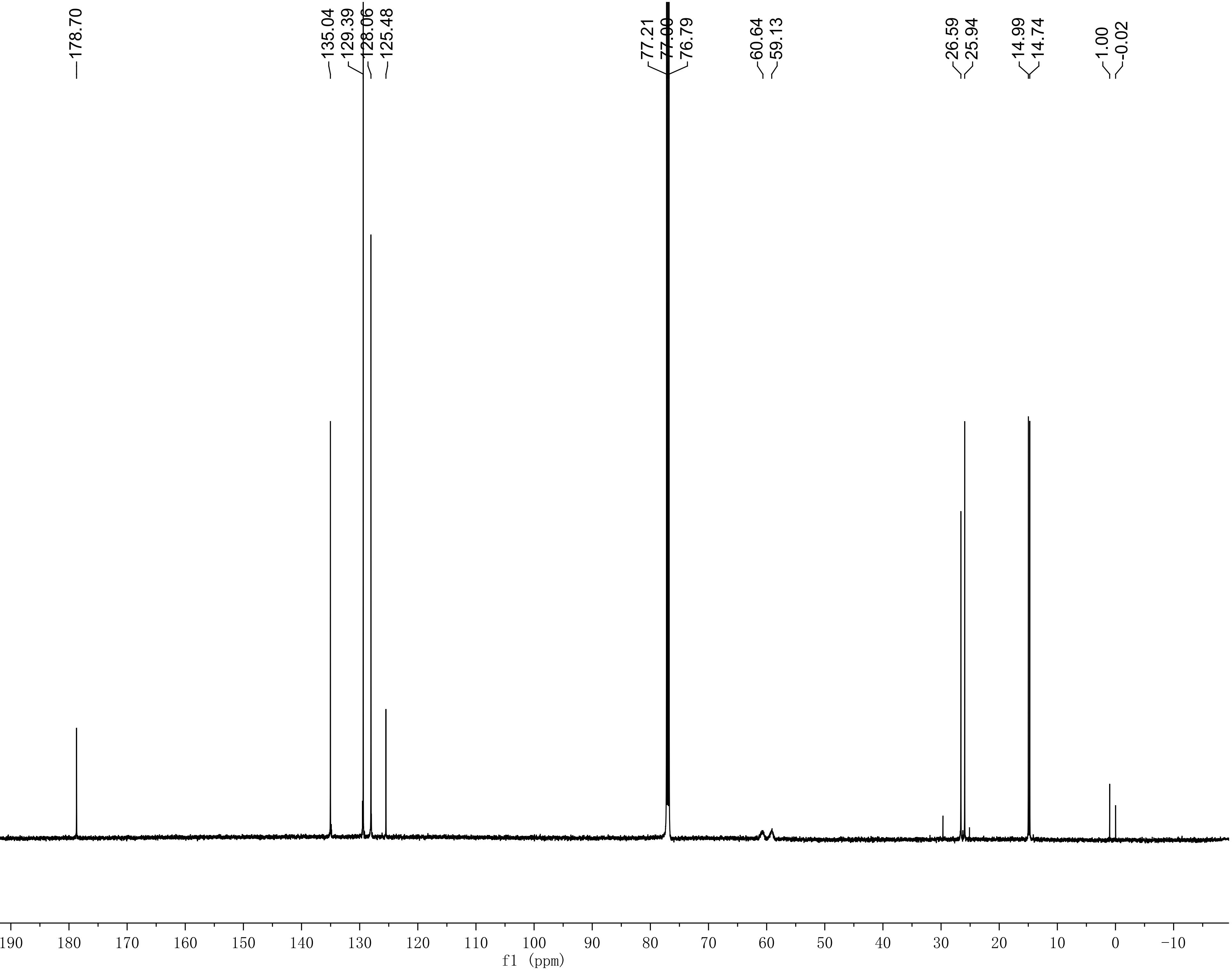


ZCY-266-C

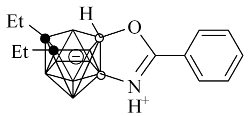


3r

^{13}C, $CDCl_3$, 298K

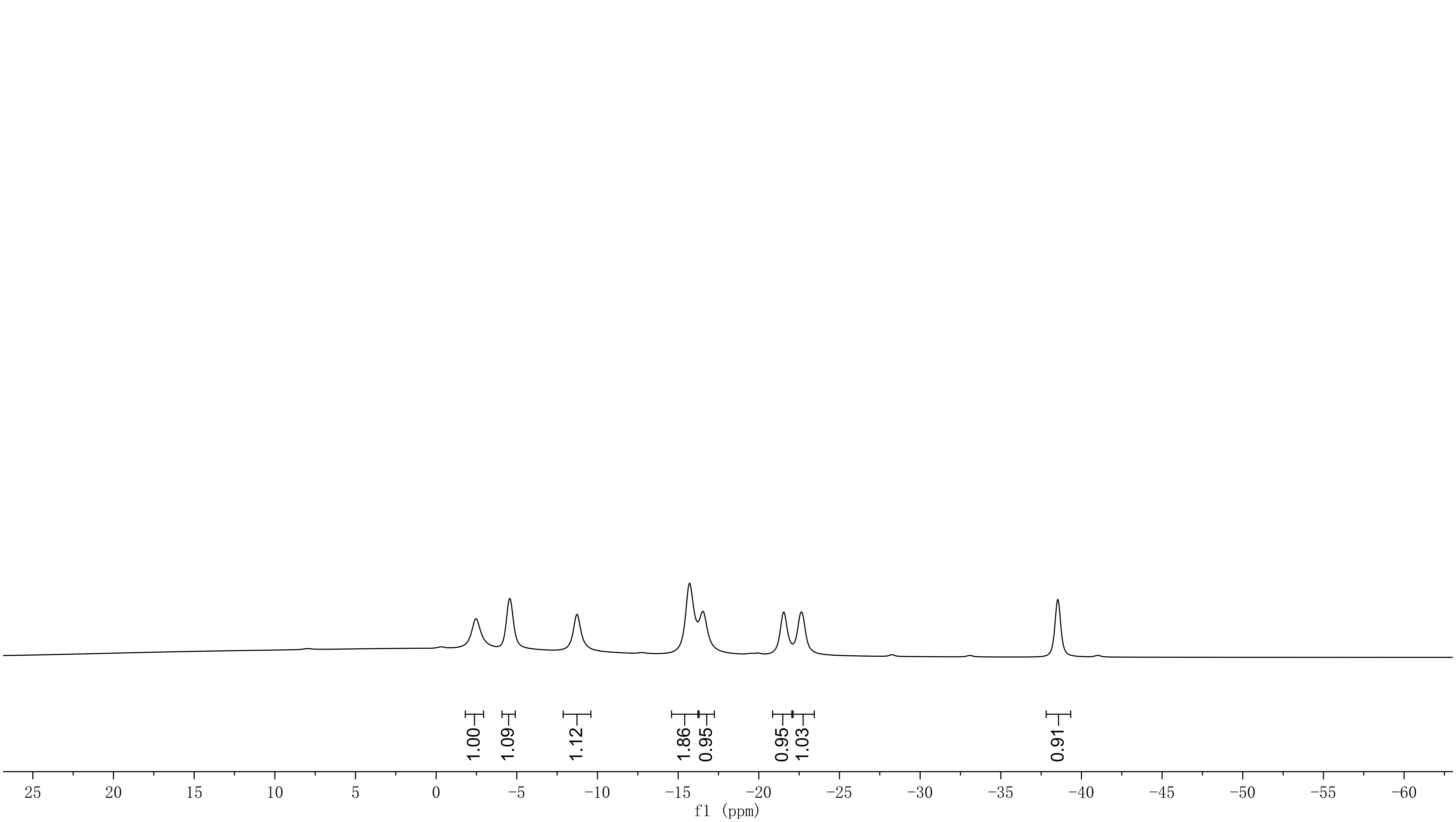


ZCY-266-B{H}

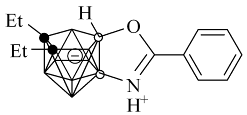


3r

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

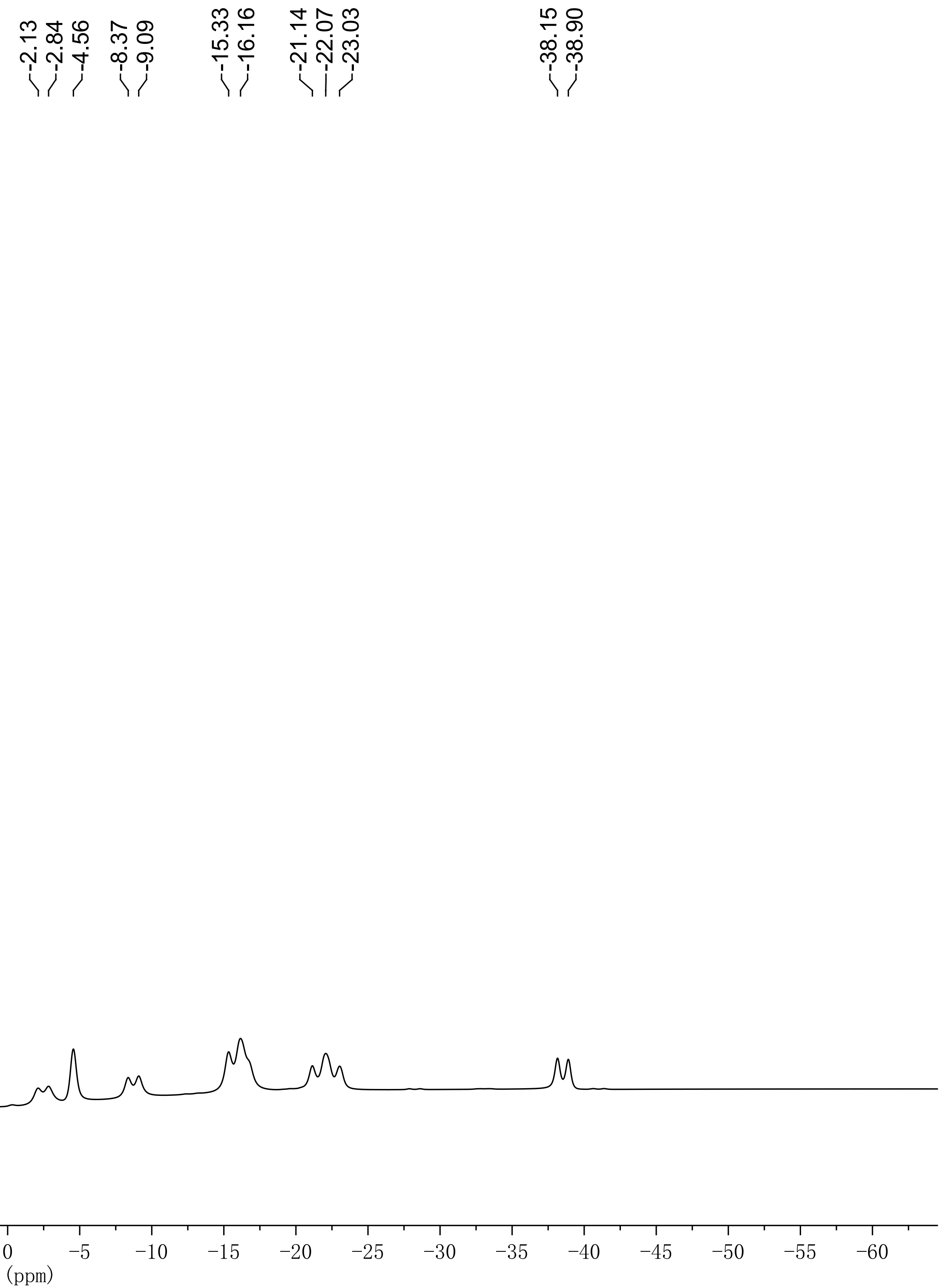


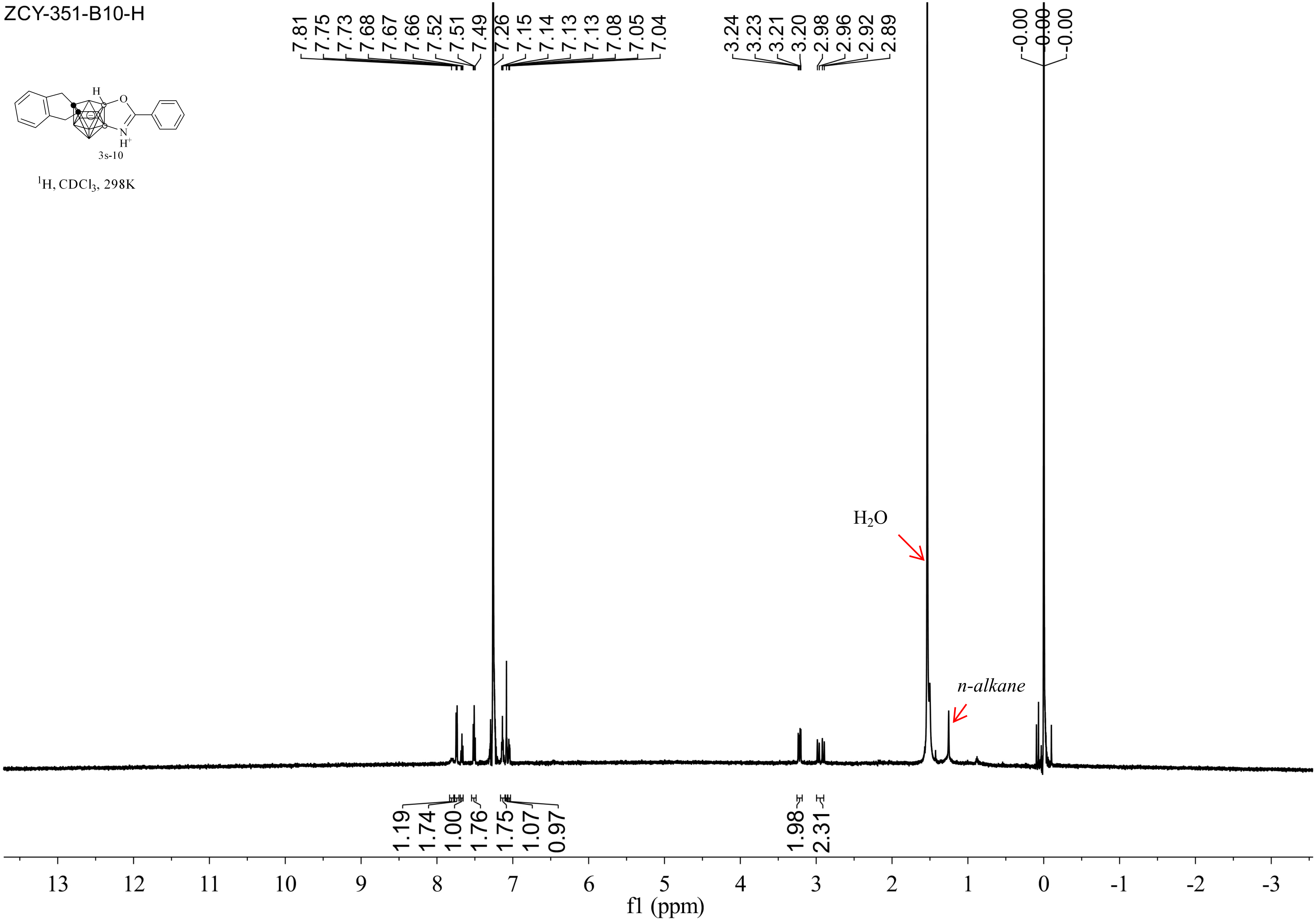
ZCY-266-B



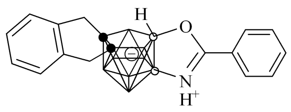
3r

^{11}B, $CDCl_3$, 298K



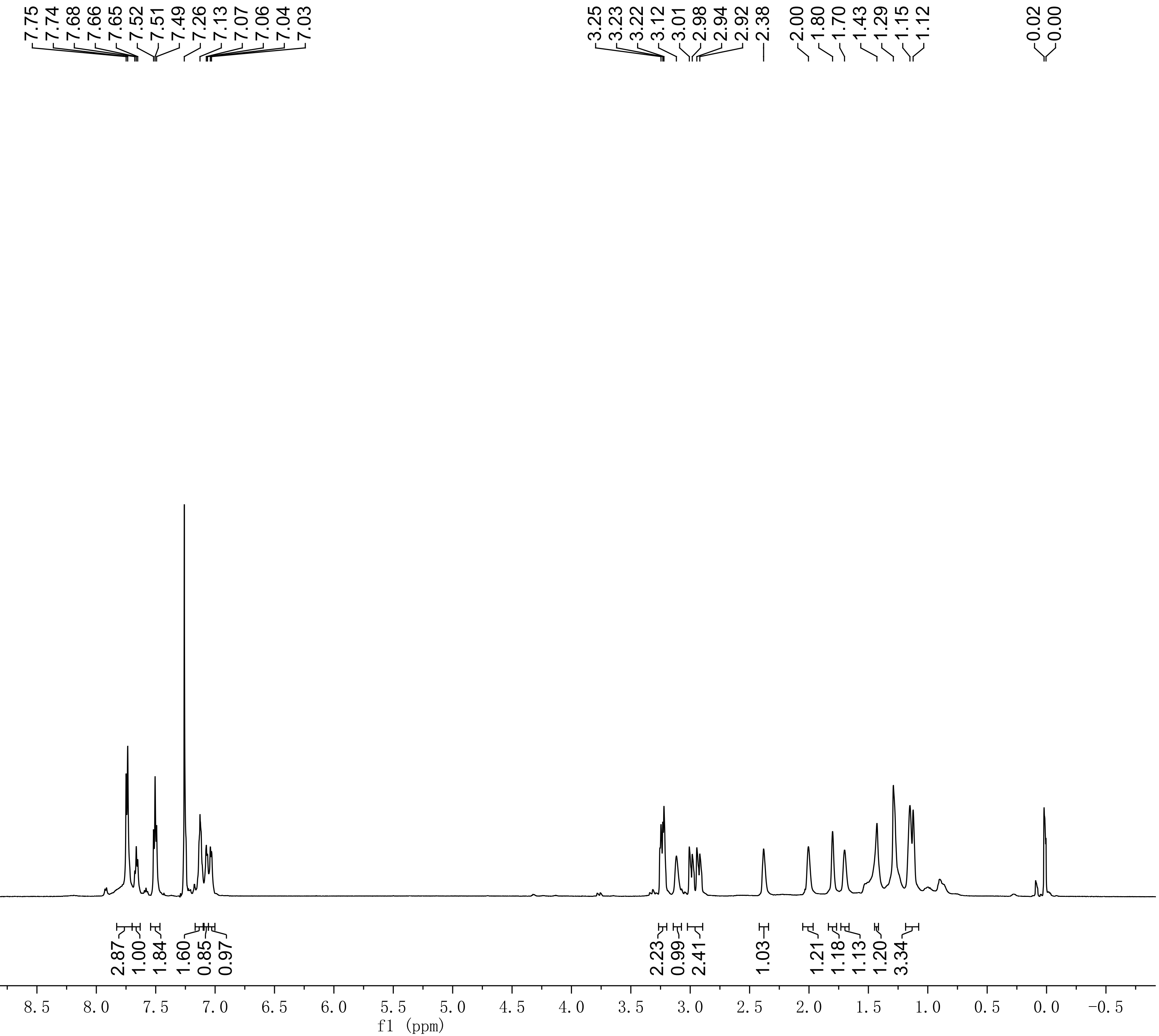

ZCY-351-B10-H
H
O
N
H+
3s-10
1H, CDCl3, 298K
7.81
7.75
7.73
7.68
7.67
7.66
7.52
7.51
7.49
7.26
7.15
7.14
7.13
7.13
7.08
7.05
7.04
3.24
3.23
3.21
3.20
2.98
2.96
2.92
2.89
-0.00
-0.00
-0.00
H2O
n-alkane
1.19
1.74
1.00
1.76
1.75
1.07
0.97
1.98
2.31
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

ZCY-351-B10-H{B}

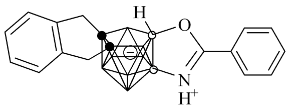


3s-10

$^{1}H\{^{11}B\}$, $CDCl_3$, 298K

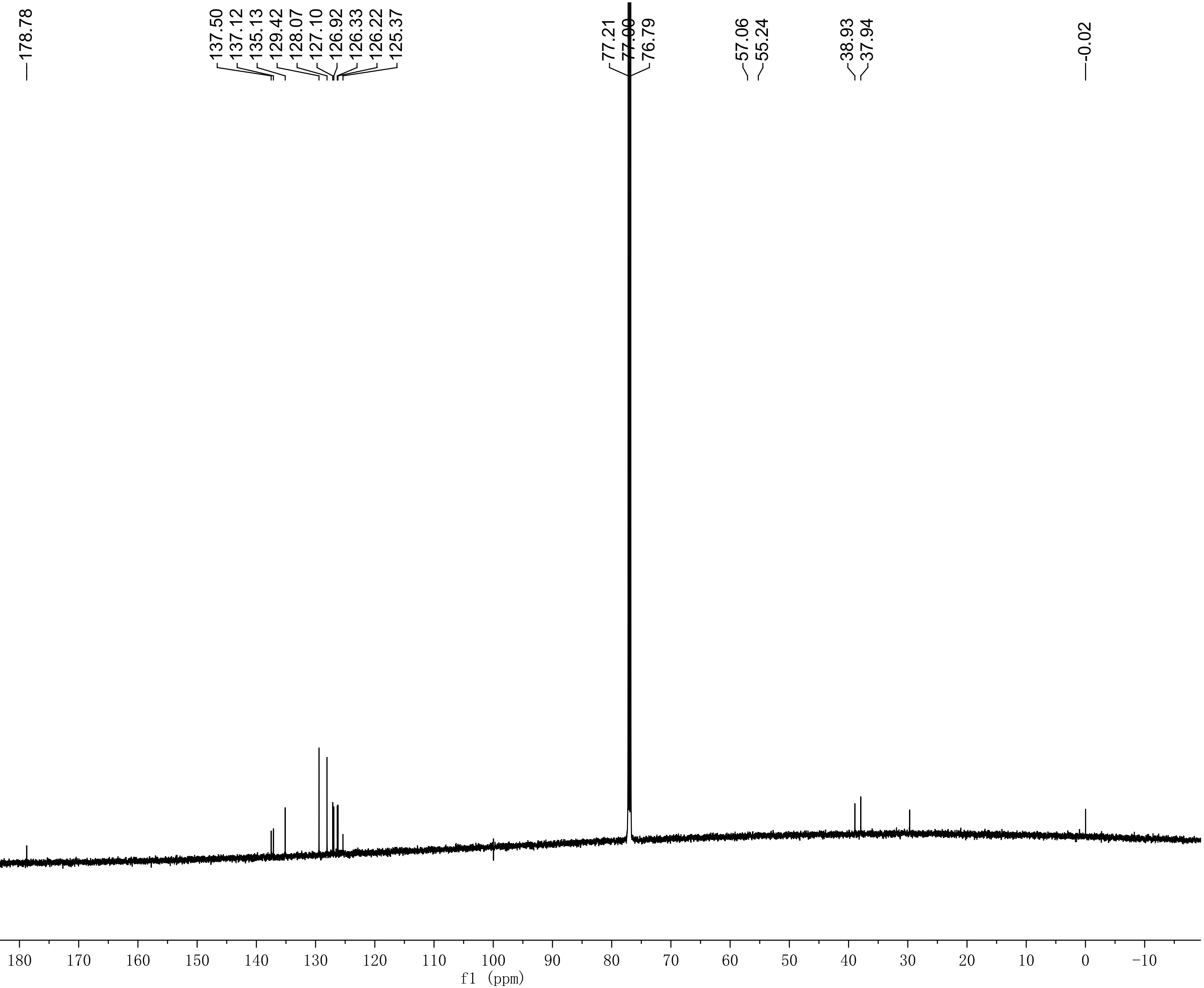


ZCY-351-B10-C

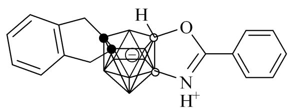


3s-10

^{13}C, $CDCl_3$, 298K

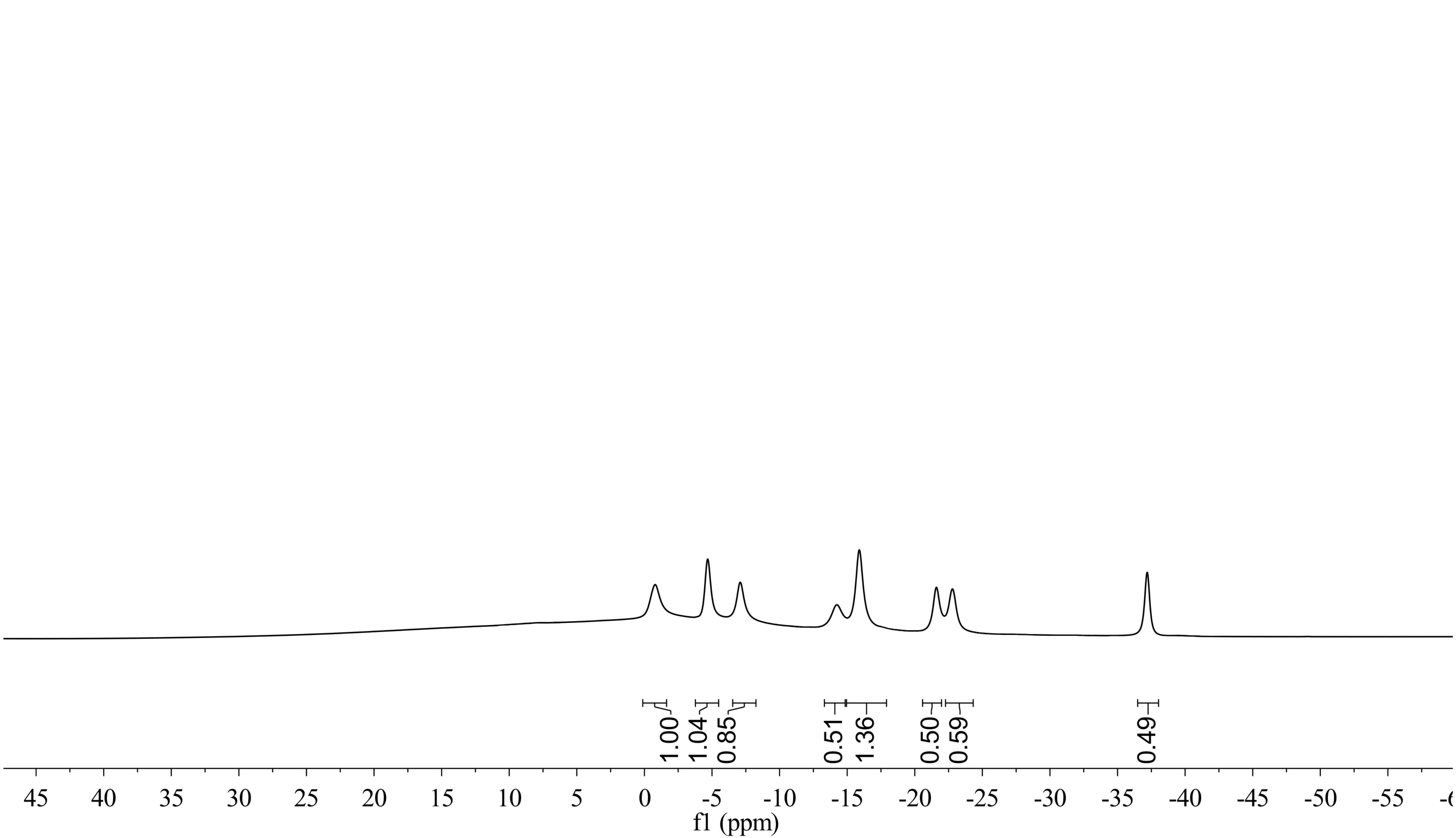


ZCY-351-B10-B{H}

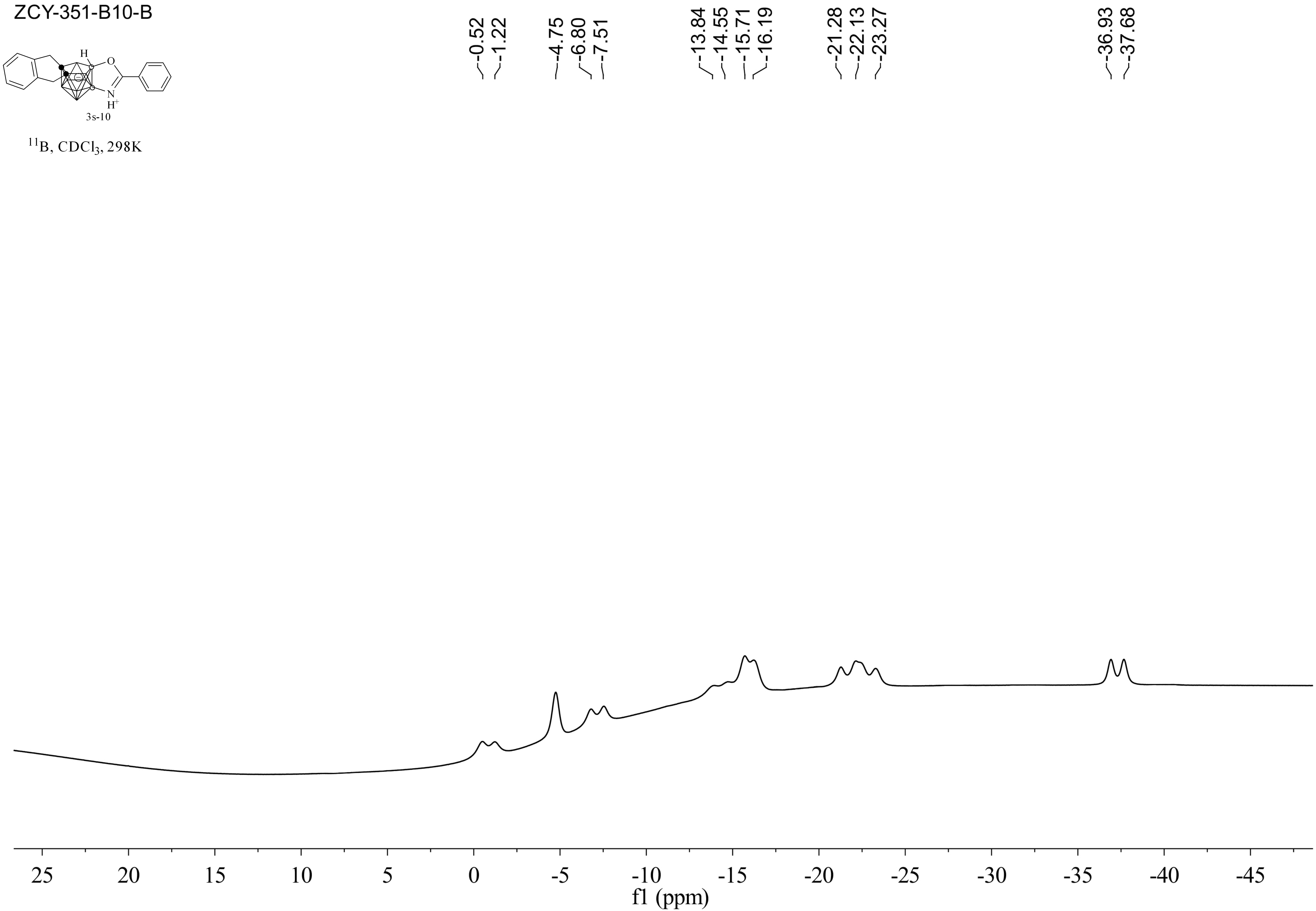


3s-10

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K

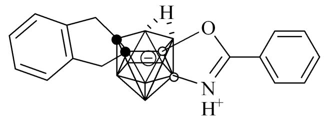


ZCY-351-B10-B



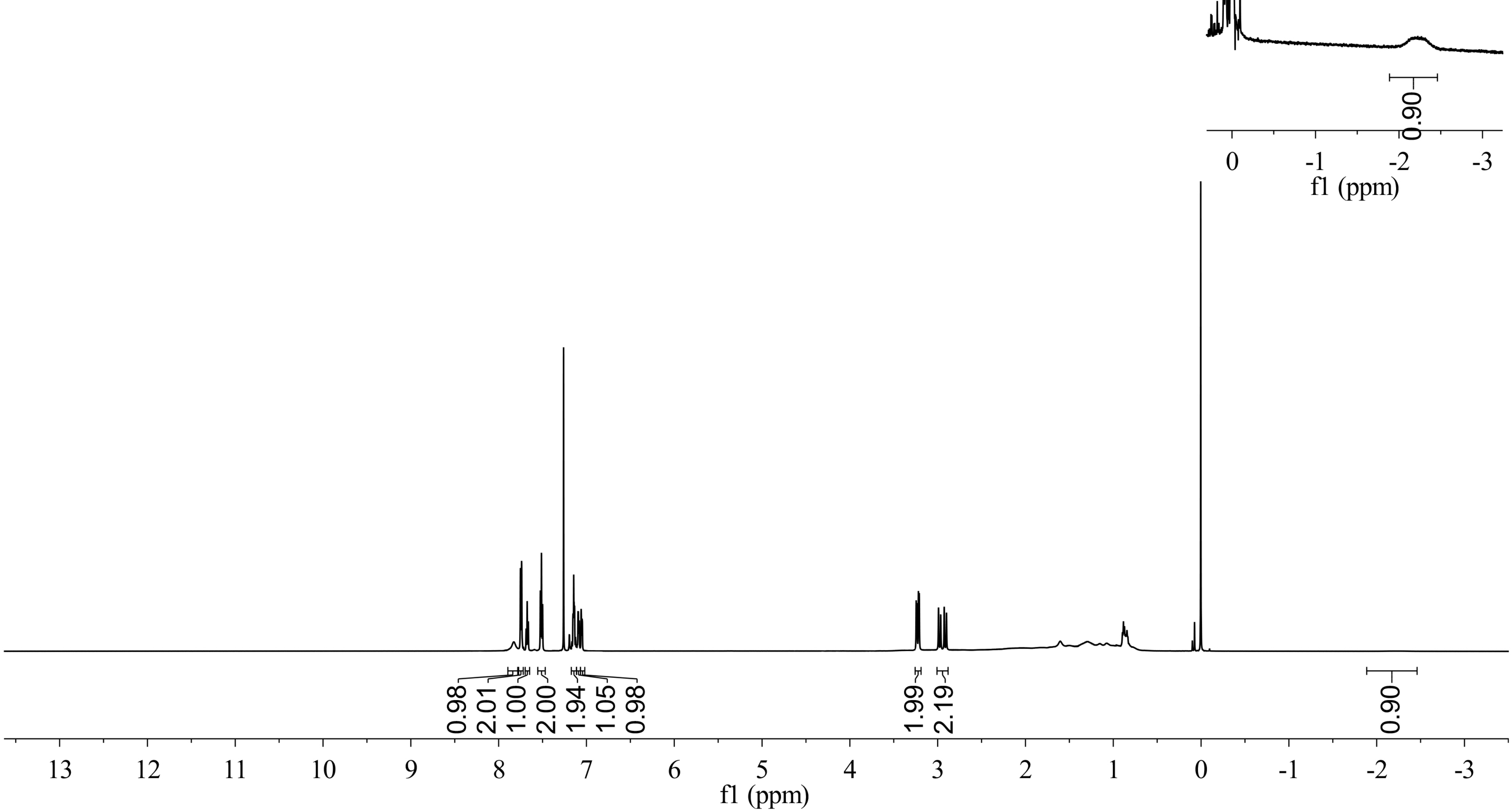
H
O
N
H+
3s-10
11B, CDCl3, 298K
-0.52
-1.22
-4.75
-6.80
-7.51
-13.84
-14.55
-15.71
-16.19
-21.28
-22.13
-23.27
-36.93
-37.68
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

ZCY-351-B11-H

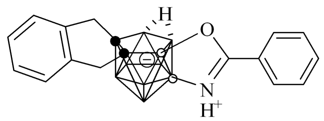


3s-11

^{1}H, $CDCl_3$, 298K

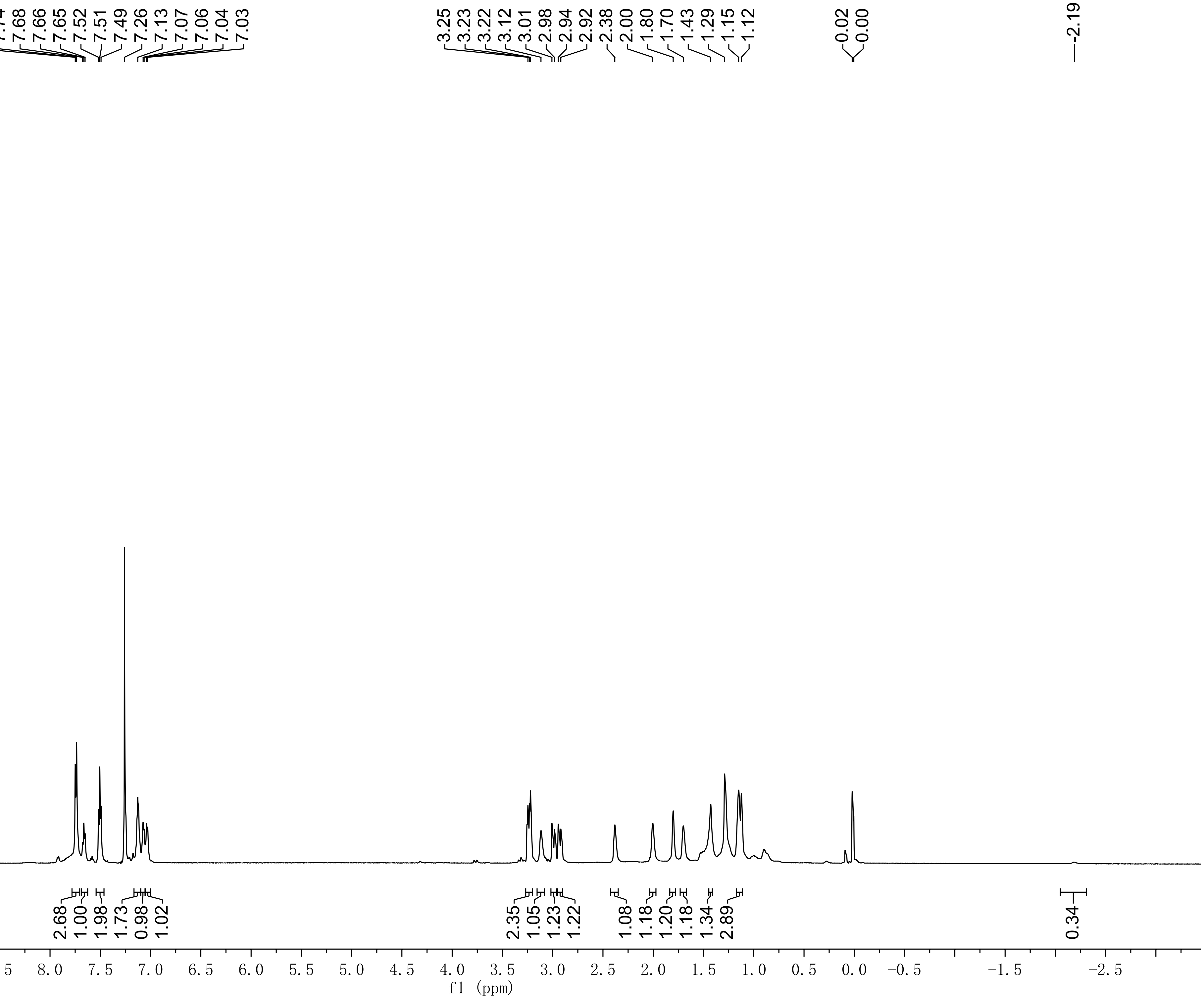


ZCY-351-B11-H{B}



3s-11

$^{1}H\{^{11}B\}$, $CDCl_3$, 298K



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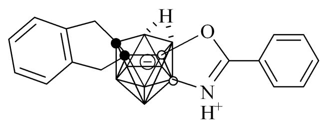
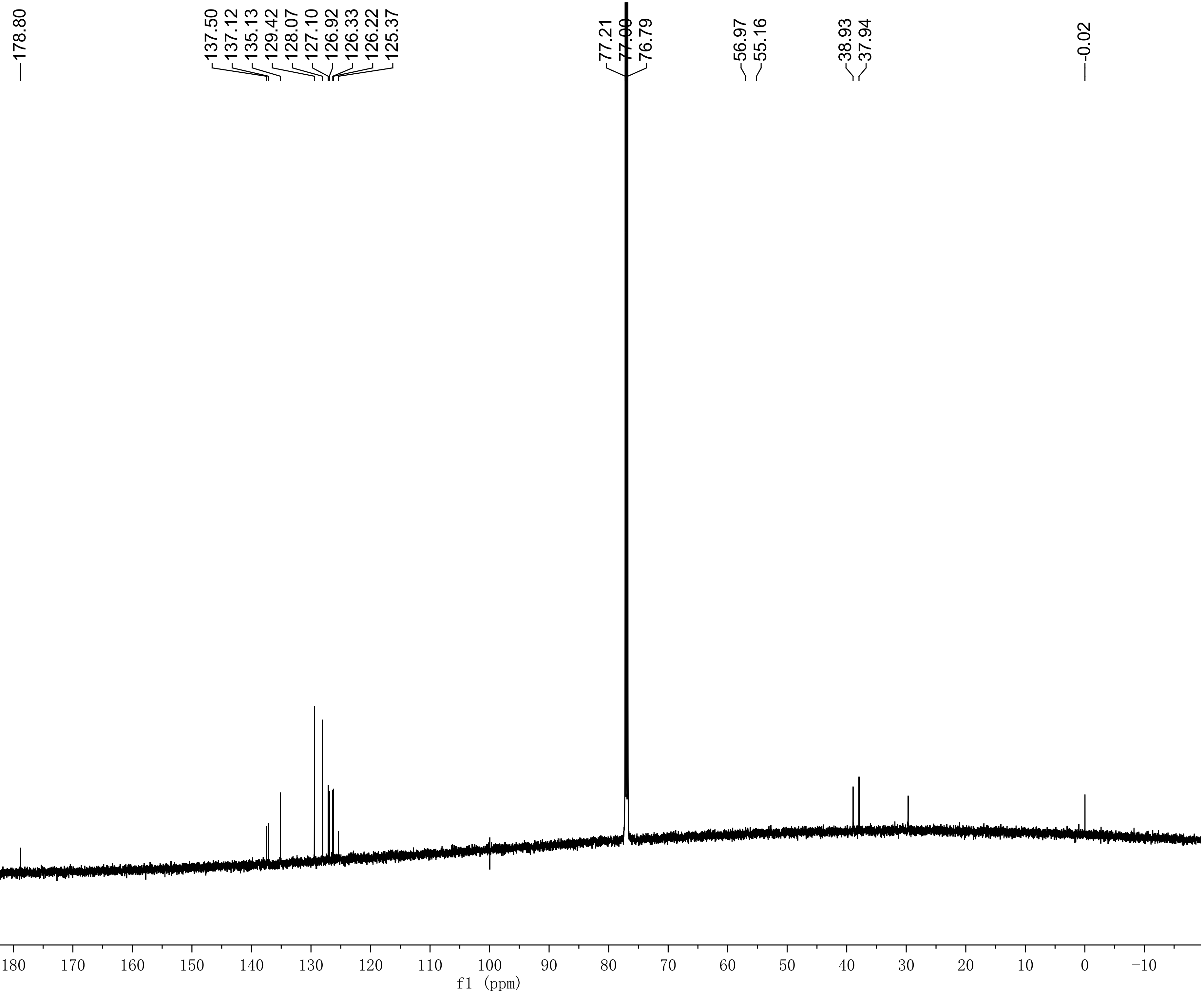


3s-11

^{13}C, $CDCl_3$, 298K



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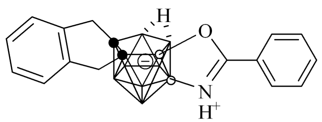
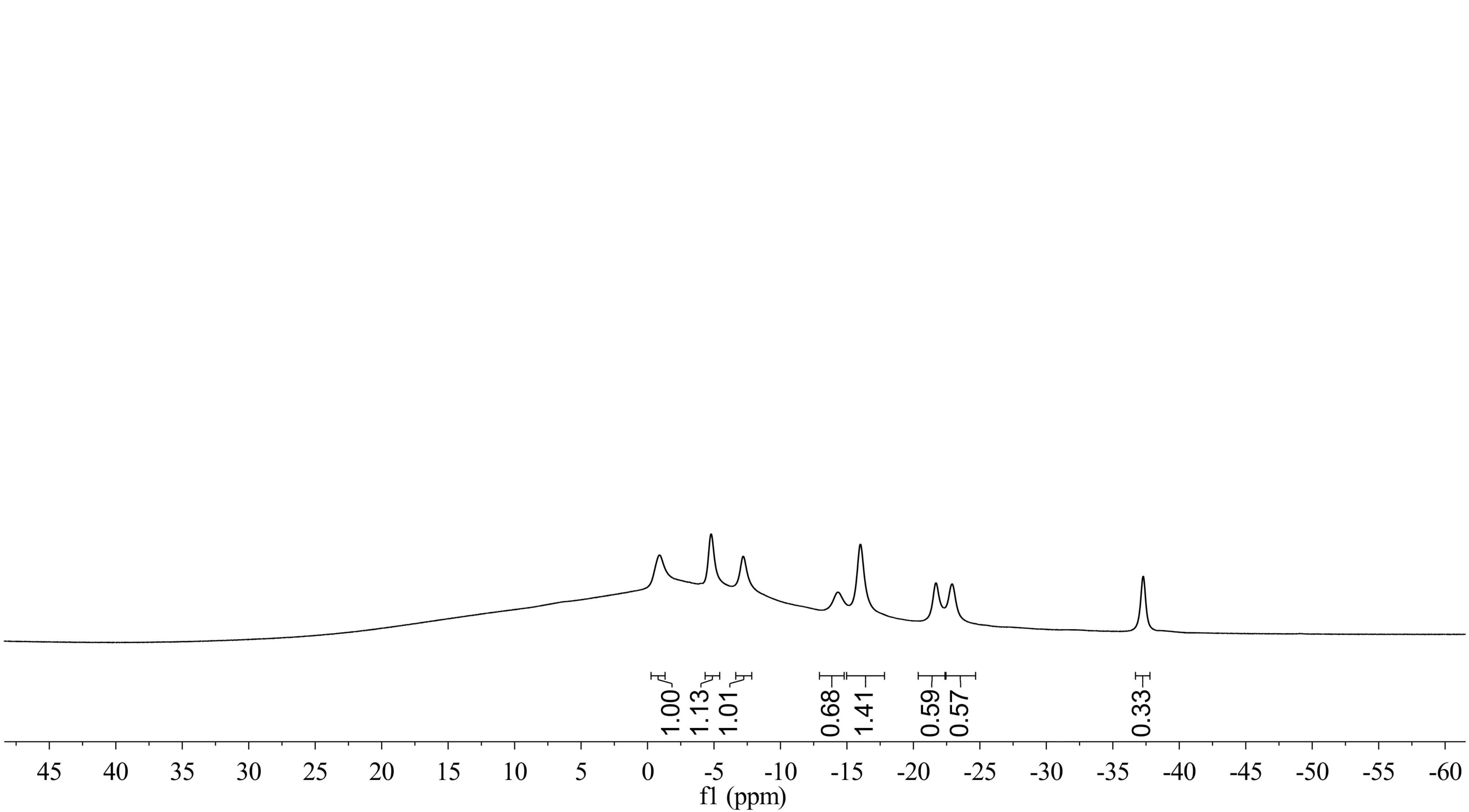


3s-11

$^{11}B\{^{1}H\}$, $CDCl_3$, 298K



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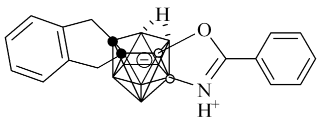

3s-11

^{11}B, $CDCl_3$, 298K