Supporting Information

Ruthenium-Catalyzed Direct C2–H Selenylation of (Benz)imidazole

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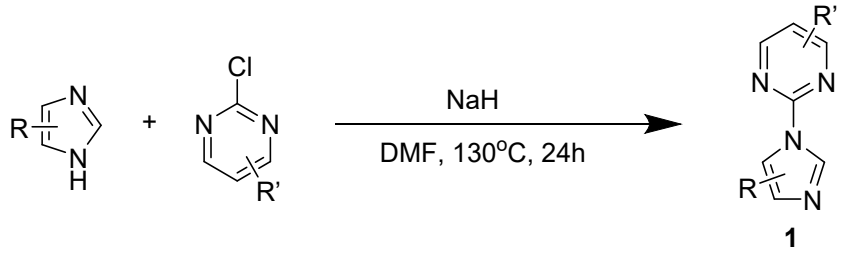
1. General information.

All reagents were obtained from commercial sources and used as supplied. All reactions were carried out in flame-dried glassware under argon atmosphere unless otherwise noted. Catalytic experiments were performed in Schlenk-type flasks under air atmosphere unless otherwise noted. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Thin-layer chromatography (TLC) were carried out on 0.25 mm Merck silica gel (60-F254). Flash column chromatography was performed using silica gel Silica 60 M, 0.04-0.063 mm. Technical grade petroleum ether (40-60), *n*-heptane and ethyl acetate were used for column chromatography. $CDCl_3$ was stored under nitrogen over molecular sieves. NMR spectra were recorded on AV 300, AV 360, AVANCE III 400, JEOL ECZ400 or DRX 400 Bruker spectrometers. ^1H NMR spectra were referenced to residual protiated solvent (δ = 7.26 ppm for $CDCl_3$, δ = 2.50 ppm for DMSO-d_6) and ^{13}C chemical shifts are reported relative to deuterated solvents (δ = 77.0 ppm for $CDCl_3$, δ = 39.5 ppm for DMSO-d_6). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad. HRMS were recorded on a ESI-TOF mass spectrometer. Melting points were measured on micro melting point apparatus and uncorrected.

2. General procedure for synthesis substrates 1 and 2.

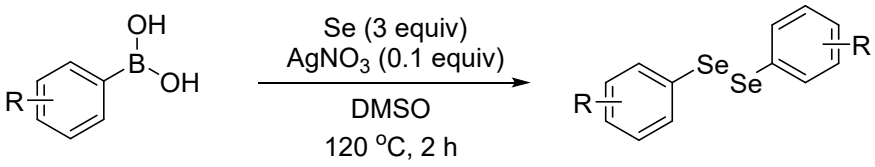
Synthesis of compounds 1 according to the following procedure[1]**:**



1

In an oven-dried round-bottom flask with a stir bar, imidazole (5 mmol, 1.0 equiv) was dissolved in anhydrous DMF (15 mL). The reaction mixture was cooled to 0 °C in an ice bath, and NaH (240 mg (60%), 6 mmol, 1.2 equiv) was added. After the reaction mixture was vigorously stirred at 0 °C for 1 h, 2-chloropyrimidine (0.7g, 6 mmol, 1.2 equiv) was added. After that, the reaction mixture was heated and stirred vigorously at 130 °C in an oil bath for 24 h. The resulting mixture was cooled to room temperature, quenched with water (15 mL) and extracted with EtOAc (3 × 15 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and evaporated in vacuo. The crude residue was purified by flash column chromatography on silica gel using a mixture of hexane and EtOAc to afford the desired compound **1**.

Synthesis of compounds 2 according to the following procedure[2]**:**

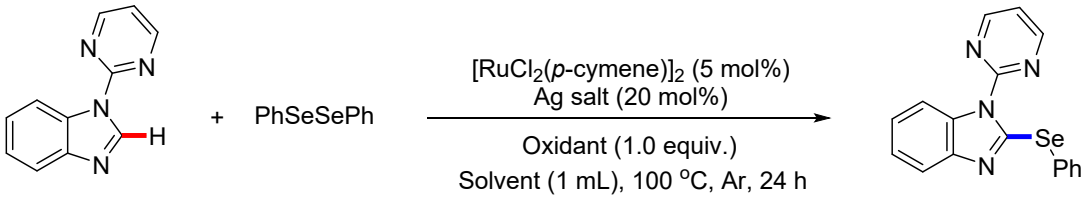


To a Schlenk tube were added arylboronic acid (0.4 mmol), selenium (1.2 mmol), $AgNO_3$ (0.04 mmol), and DMSO (2.0 mL). The mixture was stirred in a heating mantle preheated to 120 °C for 2 h. After cooled to room temperature, the reaction mixture was diluted with H_2O (10 mL), and extracted with EtOAc (3×10 mL). The combined organic phase was washed with water and brine (30 mL), dried over anhydrous Na_2SO_4, and then evaporated under reduced pressure. The residue was purified by column chromatography to give the desired diselenides **2**.

3. Reaction optimization.

3.1. General procedure: A suspension of substrate **1** (0.3 mmol, 1.0 equiv.), diselenide **2** (0.45 mmol, 1.5 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), AgOTf (20 mol%), and $Cu(OAc)_2$ (0.3 mmol, 1.0 equiv.) in DMSO (3.0 mL) was stirred at 100 ^oC for 24 hours under argon atmosphere. Then, the reaction mixture was cooled down to room temperature and diluted with H_2O (15 mL), followed by extraction with EA (3 × 20 mL). The combined organic layers were washed with brine (30 mL) and dried over Na_2SO_4. Then the solvent was evaporated in *vacuo*, and the resulting crude reaction mixture was purified by flash column chromatography to afford the corresponding product **3**-**5** as analytically pure solids.

3.2. Screening of reaction conditions.



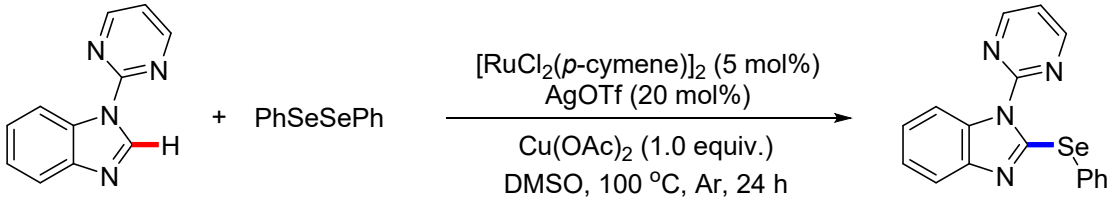
1a **2a** **3aa**

Entry[a]	Oxidant	Ag salt	Solvent	T	Yield[b]
1	AgOAc	$AgSbF_6$	TFE	100°C	15
2	AgOAc	$AgSbF_6$	1,4-dixoane	100°C	traces
3	AgOAc	$AgSbF_6$	CH_3CN	100°C	traces
4	AgOAc	$AgSbF_6$	toluene	100°C	30
5	AgOAc	$AgSbF_6$	HFIP	100°C	traces
6	AgOAc	$AgSbF_6$	DMF	100°C	traces
7	AgOAc	$AgSbF_6$	DMSO	100°C	54
8	AgOAc	$AgSbF_6$	DCE	100°C	29
9	AgOAc	AgOTf	DMSO	100°C	68
10	Ag_2O	AgOTf	DMSO	100°C	traces
11	$K_2S_2O_8$	AgOTf	DMSO	100°C	traces
12	AgTFA	AgOTf	DMSO	100°C	<10
13	$PhI(OAc)_2$	AgOTf	DMSO	100°C	18
14	Ag_3PO_4	AgOTf	DMSO	100°C	traces
15	$Cu(OAc)_2$	AgOTf	DMSO	100°C	83 (81)
16	$Cu(OAc)_2\ H_2O$	AgOTf	DMSO	100°C	44
17	$Cu(OAc)_2$	AgF_6P	DMSO	100°C	59
18	$Cu(OAc)_2$	$AgNTf_2$	DMSO	100°C	36
19	$Cu(OAc)_2$	$AgBF_4$	DMSO	100°C	38
20	$Cu(OAc)_2$ (1.5 eq)	AgOTf	DMSO	100°C	64
21	$Cu(OAc)_2$ (1.2 eq)	AgOTf	DMSO	100°C	63
22	$Cu(OAc)_2$ (0.5 eq)	AgOTf	DMSO	100°C	31
23	$Cu(OAc)_2$ (0.1 eq)	AgOTf	DMSO	100°C	traces
24[c]	$Cu(OAc)_2$	AgOTf	DMSO	100°C	43
25[d]	$Cu(OAc)_2$	AgOTf	DMSO	100°C	42
26[e]	$Cu(OAc)_2$	AgOTf	DMSO	100°C	31
26[f]	$Cu(OAc)_2$	AgOTf	DMSO	100°C	79
27	$Cu(OAc)_2$	AgOTf	DMSO	80°C	<10
28[g]	$Cu(OAc)_2$	AgOTf	DMSO	100°C	31
29	——	AgOTf	DMSO	100°C	<10
30	$Cu(OAc)_2$	——	DMSO	100°C	32

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), AgOTf (20 mol%), $Cu(OAc)_2$ (0.1 mmol, 1.0 equiv.), DMSO (1.0 mL), 100 °C, 24 h, Ar. [b]Determined by ^1H NMR spectroscopy against an internal standard (dibromomethane). The isolated yield is shown in parentheses. [c]With 2.0 eq of **2a**. [d]With 1.0 eq of **2a**. [e]With 0.5 eq of **2a**. [f]13h. [g]Without Ru catalyst.

4. Synthetic applications.

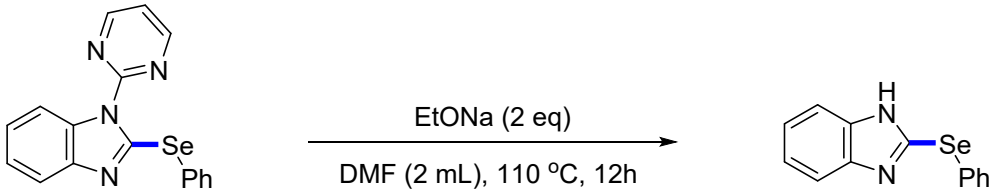
Gram-scale reactions:



1a, (4.0 mmol) **2a**, (6.0 mmol) **3aa**, 80% (1.12g)

A suspension of substrate **1a** (4.0 mmol, 1.0 equiv.), diphenyl diselenide **2a** (6.0 mmol, 1.5 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), AgOTf (20 mol%), and $Cu(OAc)_2$ (4.0 mmol, 1.0 equiv.) in DMSO (40 mL) was stirred at 100 °C for 24 hours under argon atmosphere. Then, the reaction mixture was cooled down to room temperature and diluted with H_2O (150 mL), followed by extraction with EA (3 × 200 mL). The combined organic layers were washed with brine (300 mL) and dried over Na_2SO_4. Then the solvent was evaporated in *vacuo*, and the resulting crude reaction mixture was purified by flash column chromatography to afford the corresponding product **3aa** as analytically pure solids.

Deprotection of 3aa:



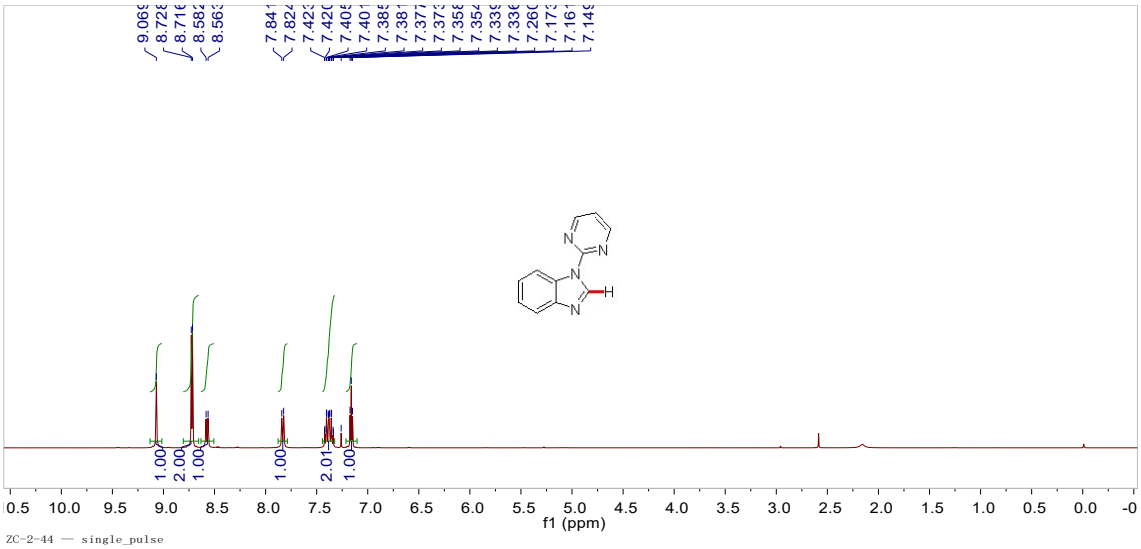
3aa **4**, 82%

To an oven-dried pressure tube with a stir bar was sequentially added **3aa** (70.2 mg, 0.2 mmol), EtONa (27.2 mg, 0.4 mmol) and dry DMF (2.0 mL). After being degassed and refilled with nitrogen three times, the tube was sealed and the reaction mixture was heated and stirred vigorously at 110 °C in an oil bath for 12 h. The resulting mixture was then cooled to room temperature, exposed to air, poured into 20 mL water and extracted with EtOAc (3 × 15 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to give the target product (**4**, white solid, 44.8 mg, 82%).

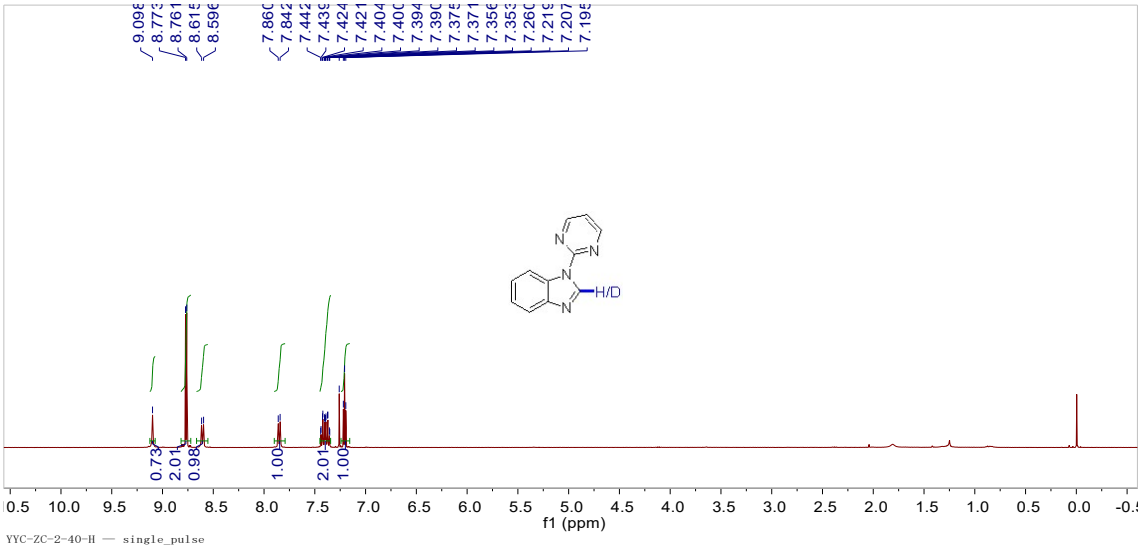
5. Experimental mechanistic studies

Deuteration experiments.

In an oven dried Schlenk tube, to a solution of substrate **1a** (0.1 mmol, 1 equiv.) in DMSO (0.9 mL) and D_2O (0.1 mL) was added the combined reagents under argon: $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), AgOTf (20 mol%), and $Cu(OAc)_2$ (0.1 mmol, 1.0 equiv.). The Schlenk tube was sealed with a Teflon cap and it was heated to 100 °C for 24 h. Then, the reaction mixture was cooled down to room temperature and diluted with H_2O (5 mL), followed by extraction with EA (3 × 10 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. Then the solvent was evaporated *in vacuo*, and the resulting crude reaction mixture was purified by flash column chromatography to afford the deuterated product as a white solid in 27% yield (see spectra below).

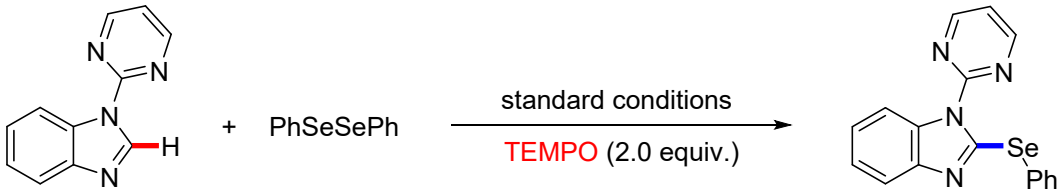


^1H NMR ($CDCl_3$) spectrum of **1a** in a reaction without using D_2O.



^{1}H NMR ($CDCl_3$) spectrum of **1a**-*d* showing low intensity of the peak at 9.09 ppm.

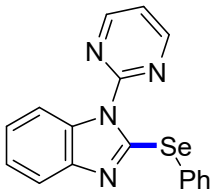
Radical inhibitor experiment



3aa, 61%

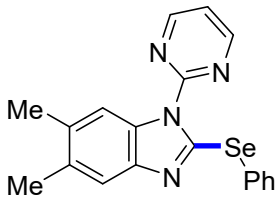
A suspension of substrate **1a** (0.3 mmol, 1.0 equiv.), diselenide **2a** (0.45 mmol, 1.5 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (5 mol%), AgOTf (20 mol%), $Cu(OAc)_2$ (0.3 mmol, 1.0 equiv.), and TEMPO (0.6 mmol, 2.0 equiv.) in DMSO (3.0 mL) was stirred at 100 °C for 24 hours under argon atmosphere. Then, the reaction mixture was cooled down to room temperature and diluted with H_2O (15 mL), followed by extraction with EA (3 × 20 mL). The combined organic layers were washed with brine (30 mL) and dried over Na_2SO_4. Then the solvent was evaporated in *vacuo*, and the resulting crude reaction mixture was purified by flash column chromatography to afford the corresponding product **3aa** in 61% yield.

6. Characterization data of products.



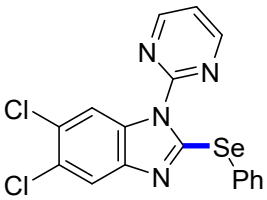
3aa

2-(phenylselanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3aa): White solid, yield = 81%, 85.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (d, J = 4.8 Hz, 2H), 8.58-8.55 (m, 1H), 7.88-7.86 (m, 2H), 7.64-7.62 (m, 1H), 7.48-7.43 (m, 3H), 7.33-7.25 (m, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.0, 156.5, 148.9, 145.1, 136.2, 134.7, 129.8, 129.4, 129.0, 123.6, 123.2, 119.0, 117.7, 115.1 ppm. HRMS (ESI) calcd. for [M + H]$^+$ $C_{17}H_{13}N_4Se$ 353.0300, found 353.0297.



3ba

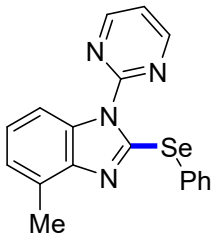
5,6-dimethyl-2-(phenylselanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3ba): White solid, yield = 57%, 65.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J = 5.2 Hz, 2H), 8.29 (s, 1H), 7.85-7.82 (m, 2H), 7.44-7.41 (m, 3H), 7.38 (s, 1H), 7.20 (dd, J = 4.8 , 4.8 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 157.9, 156.5, 147.5, 143.6, 136.1, 133.1, 132.3, 132.0, 130.0, 129.3, 128.9, 119.3, 117.5, 115.3, 20.6, 20.2 ppm. HRMS (ESI) calcd. for [M + H]$^+$ $C_{19}H_{17}N_4Se$ 381.0613, found 381.0615.



3ca

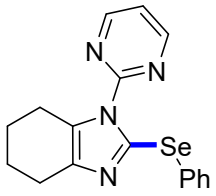
5,6-dichloro-2-(phenylselanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3ca): White solid, yield = 65%, 82.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (d, J = 4.8 Hz, 2H), 8.71 (s, 1H), 7.81 (d, J = 7.6 Hz, 2H), 7.66 (s, 1H), 7.48-7.42 (m, 3H), 7.29 (dd, J = 4.8, 4.8 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.1, 158.0, 151.7, 144.4,

136.3, 133.7, 129.5, 129.3, 129.2, 127.6, 126.9, 119.9, 118.2, 116.7 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{17}H_{11}Cl_2N_4Se$ 420.9521, found 420.9507.



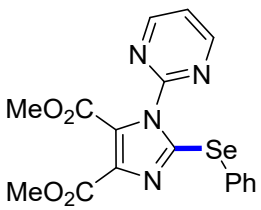
3da

4-methyl-2-(phenylselanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3da): White solid, yield = 50%, 55.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J = 4.8 Hz, 2H), 8.36 (d, J = 8.4 Hz, 1H), 7.90-7.88 (m, 2H), 7.44-7.40 (m, 3H), 7.21-7.17 (m, 2H), 7.08 (d, J = 7.2, 1H), 2.50 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.0, 156.6, 147.3, 144.3, 135.8, 134.4, 130.2, 129.0, 128.6, 124.2, 123.0, 117.6, 112.5, 16.4 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{18}H_{15}N_4Se$ 367.0456, found 367.0454.



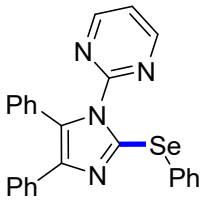
3ea

2-(phenylselanyl)-1-(pyrimidin-2-yl)-4,5,6,7-tetrahydro-1*H*-benzo[d]imidazole (3ea): White solid, yield = 58%, 62.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, J = 4.8 Hz, 2H), 7.70-7.68 (m, 2H), 7.32-7.30 (m, 3H), 7.19 (dd, J = 4.8, 4.8 Hz, 1H), 2.95-2.92 (m, 2H), 2.59-2.56 (m, 2H), 1.83-1.74 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.0, 156.1, 139.7, 136.3, 134.8, 130.4, 129.2, 128.6, 128.2, 118.2, 24.7, 24.6, 23.4, 22.9 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{17}H_{17}N_4Se$ 357.0613, found 357.0608.



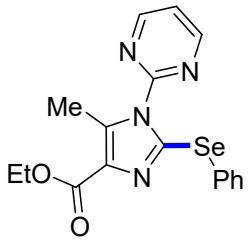
3fa

dimethyl 2-(phenylselanyl)-1-(pyrimidin-2-yl)-1*H*-imidazole-4,5-dicarboxylate (3fa): White solid, yield = 75%, 94.3 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, J = 4.8 Hz, 2H), 7.72-7.69 (m, 2H), 7.35-7.30 (m, 4H), 3.92 (s, 3H), 3.81 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 161.9, 161.7, 158.4, 154.2, 141.3, 135.3, 134.1, 130.1, 129.3, 128.9, 128.2, 119.9, 53.2, 52.2 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{17}H_{15}N_4O_4Se$ 419.0253, found 419.0244.



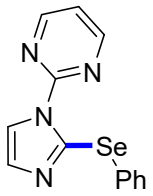
3ga

2-(4,5-diphenyl-2-(phenylselanyl)-1*H*-imidazol-1-yl)pyrimidine (3ga): White solid, yield = 81%, 110.6 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, J = 4.8 Hz, 2H), 7.63 (s, 2H), 7.46 (d, J = 7.2 Hz, 2H), 7.27-7.14 (m, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.3, 156.2, 140.4, 136.6, 133.9, 133.6, 131.1, 130.9, 130.5, 129.7, 129.1, 128.5, 128.1, 127.9, 127.5, 127.0, 119.7 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{25}H_{19}N_4Se$ 455.0769, found 455.0759.



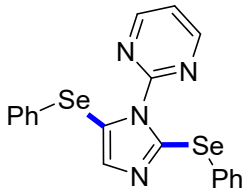
3ha

ethyl 5-methyl-2-(phenylselanyl)-1-(pyrimidin-2-yl)-1H-imidazole-4-carboxylate (3ha): White solid, yield = 53%, 61.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J = 4.8 Hz, 2H), 7.48-7.45 (m, 2H), 7.33 (dd, J = 5.2, 4.8 Hz, 1H), 7.21-7.17 (m, 3H), 4.34 (q, J = 7.2 Hz, 2H), 2.66 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 163.4, 158.6, 155.6, 138.9, 136.2, 133.4, 131.4, 129.4, 129.1, 127.9, 120.3, 60.5, 14.5, 12.1 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{17}H_{17}N_4O_2Se$ 389.0511, found 389.0508.



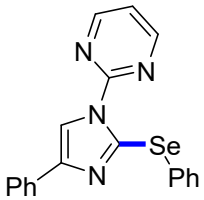
3ia

2-(2-(phenylselanyl)-1*H*-imidazol-1-yl)pyrimidine (3ia): White solid, yield = 32%, 29.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (d, J = 4.8 Hz, 2H), 8.05 (d, J = 1.6 Hz, 1H), 7.82-7.79 (m, 2H), 7.43-7.40 (m, 3H), 7.22 (dd, J = 4.8, 4.8 Hz, 1H), 7.10 (d, J = 1.6 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.4, 155.2, 139.1, 136.4, 131.4, 129.4, 129.1, 128.9, 119.3, 118.3 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{13}H_{11}N_4Se$ 303.0143, found 303.0136.



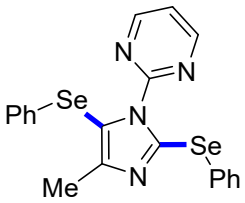
3ia'

2-(2,5-bis(phenylselanyl)-1*H*-imidazol-1-yl)pyrimidine (3ia'): White solid, yield = 40%, 55.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J = 4.8 Hz, 2H), 7.69-7.71 (m, 2H), 7.58-7.59 (m, 2H), 7.32-7.35 (m, 3H), 7.24-7.28 (m, 4H), 6.56 (s, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.0, 155.4, 140.3, 135.9, 134.7, 134.4, 130.3, 129.5, 129.3, 129.0, 128.9, 128.4, 119.6, 118.7 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{19}H_{15}N_4Se$ 458.9622, found 458.9627.



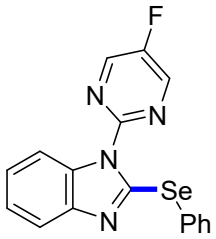
3ja

2-(4-phenyl-2-(phenylselanyl)-1*H*-imidazol-1-yl)pyrimidine (3ja): White solid, yield = 52%, 65.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, J = 4.8 Hz, 2H), 8.35 (s, 1H), 7.91-7.88 (m, 2H), 7.73-7.71 (m, 2H), 7.45-7.41 (m, 3H), 7.33 (dd, J = 7.6, 7.6 Hz, 2H), 7.24-7.18 (m, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.3, 155.0, 143.3, 139.1, 135.9, 133.4, 129.4, 129.0, 128.6, 128.5, 127.3, 125.1, 118.1, 114.3 ppm. HRMS (ESI) calcd. for $[M + K]^+$ $C_{19}H_{14}KN_4Se$ 417.0015, found 417.0005.



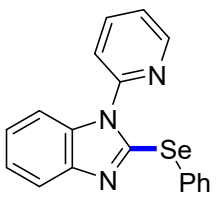
3ka

2-(4-methyl-2,5-bis(phenylselanyl)-1H-imidazol-1-yl)pyrimidine (3ka): White solid, yield = 50%, 70.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, J = 4.8 Hz, 2H), 7.60-7.58 (m, 2H), 7.31-7.26 (m, 4H), 7.19-7.14 (m, 5H), 2.24 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.2, 155.9, 148.6, 139.6, 134.1, 132.9, 129.5, 129.3, 129.2, 128.2, 126.5, 119.7, 114.2, 14.5 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{20}H_{17}N_4Se_2$ 472.9778, found 472.9767.



3la

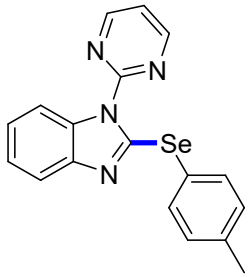
1-(5-fluoropyrimidin-2-yl)-2-(phenylselanyl)-1*H*-benzo[*d*]imidazole (3la): White solid, yield = 75%, 88.5 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (s, 2H), 8.42-8.40 (m, 1H), 7.86-7.84 (m, 2H), 7.63-7.61 (m, 1H), 7.46-7.42 (m, 3H), 7.28-7.26 (m, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 156.3, 153.7, 152.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 148.7, 145.7 (d, $J_{C\text{-}F}$ = 22.4 Hz), 144.9, 136.1, 134.6, 129.4, 129.3, 129.1, 123.4 (d, $J_{C\text{-}F}$ = 42.8 Hz), 119.0, 114.5 ppm. ^{19}F{^{1}H} NMR (235 MHz, $CDCl_3$): δ = -141.8 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{17}H_{12}FN_4Se$ 371.0206, found 371.0204.



3ma

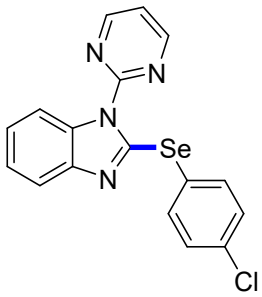
2-(phenylselanyl)-1-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole (3ma): White solid, yield = 75%, 26.3 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (d, J = 3.6 Hz, 1H), 7.93 (ddd, J = 7.6, 7.6, 2.0 Hz, 1H), 7.73-7.66 (m, 3H), 7.61 (d, J = 8.0 Hz, 1H), 7.51-7.49 (m, 1H),

7.39-7.30 (m, 4H), 7.28-7.22 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 149.6, 149.3, 146.6, 144.7, 138.9, 135.4, 135.0, 129.5, 128.7, 128.3, 123.2, 123.0, 122.9, 119.6, 118.5, 110.2 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{17}H_{13}N_4Se$ 352.0347, found 352.0345.



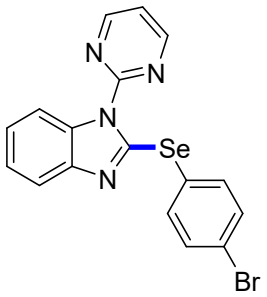
3ab

1-(pyrimidin-2-yl)-2-(*p*-tolylselanyl)-1*H*-benzo[*d*]imidazole (3ab): White solid, yield = 63%, 69.4 mg. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, J = 4.8 Hz, 2H), 8.53-8.51 (m, 1H), 7.71 (dd, J = 6.4, 2.0 Hz, 2H), 7.61-7.59 (m, 1H), 7.28-7.22 (m, 4H), 7.19 (dd, J = 4.8, 4.8 Hz, 1H), 2.40 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 157.9, 156.5, 149.3, 145.1, 139.0, 136.2, 134.8, 130.2, 126.1, 123.5, 123.0, 119.0, 117.7, 115.0, 21.6 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{18}H_{15}N_4Se$ 367.0456, found 367.0454.



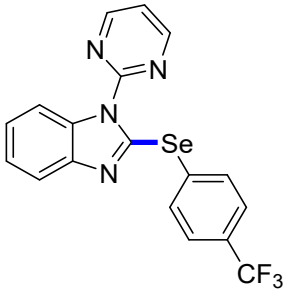
3ac

2-((4-chlorophenyl)selanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3ac): White solid, yield = 71%, 82.4 mg. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, J = 4.8 Hz, 2H), 8.52-8.49 (m, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.58-7.55 (m, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.26-7.18 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.0, 156.4, 148.4, 145.0, 137.5, 135.3, 134.7, 129.6, 128.0, 123.7, 123.3, 119.0, 117.8, 115.2 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{17}H_{12}ClN_4Se$ 386.9910, found 386.9910.



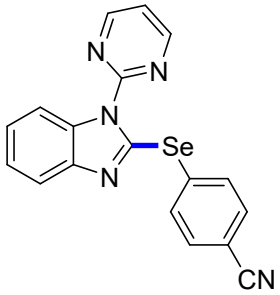
3ad

2-((4-bromophenyl)selanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3ad): White solid, yield = 75%, 96.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J = 4.8 Hz, 2H), 8.51-8.49 (m, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.58-7.55 (m, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.26-7.22 (m, 2H), 7.18 (dd, J = 4.8, 4.8 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.0, 156.4, 148.3, 145.0, 137.7, 134.7, 132.5, 128.7, 123.7, 123.6, 123.3, 119.0, 117.8, 115.2 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{17}H_{12}BrN_4Se$ 430.9405, found 430.9393.



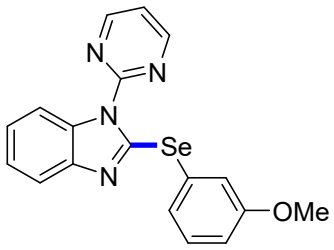
3ae

1-(pyrimidin-2-yl)-2-((4-(trifluoromethyl)phenyl)selanyl)-1*H*-benzo[*d*]imidazole (3ae): White solid, yield = 77%, 97.3 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, J = 4.8 Hz, 2H), 8.57-8.55 (m, 1H), 7.98 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.63-7.61 (m, 1H), 7.33-7.26 (m, 2H), 7.21 (dd, J = 4.8, 4.8 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.0, 156.2, 147.7, 144.9, 135.9, 134.8, 134.5, 130.7 (q, $J_{C\text{-}F}$ = 32.4 Hz), 125.9 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.2 (q, $J_{C\text{-}F}$ = 270.7 Hz), 123.8, 123.4, 118.9, 117.8, 115.2 ppm. ^{19}F{^{1}H} NMR (235 MHz, $CDCl_3$): δ = -63.9 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{18}H_{12}F_3N_4Se$ 421.0174, found 421.0180.



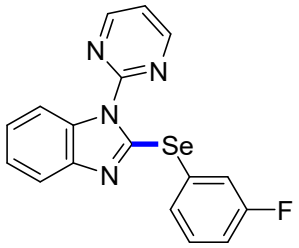
3af

4-((1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazol-2-yl)selanyl)benzonitrile (3af): White solid, yield = 69%, 78.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, J = 4.8 Hz, 2H), 8.51-8.48 (m, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.55-7.52 (m, 1H), 7.26-7.19 (m, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 157.1, 155.3, 146.1, 143.9, 135.8, 135.1, 133.5, 131.5, 122.9, 122.6, 118.0, 117.9, 116.9, 114.3, 111.4 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{18}H_{12}N_5Se$ 378.0252, found 378.0243.



3ag

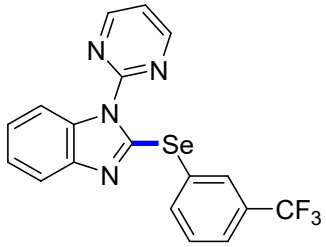
2-((3-methoxyphenyl)selanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3ag): White solid, yield = 49%, 56.3 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, J = 4.8 Hz, 2H), 8.51-8.48 (m, 1H), 7.60-7.58 (m, 1H), 7.40-7.37 (m, 2H), 7.30 (dd, J = 8.4, 8.0 Hz, 1H), 7.25-7.22 (m, 2H), 7.18 (dd, J = 5.2, 4.8Hz, 1H), 6.95-6.92 (m, 1H), 3.79 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 159.8, 158.0, 156.4, 148.8, 145.1, 134.6, 130.6, 130.1, 128.2, 123.6, 123.2, 121.1, 119.0, 117.7, 115.2, 115.0, 55.4 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{18}H_{15}N_4OSe$ 383.0406, found 383.0408.



3ah

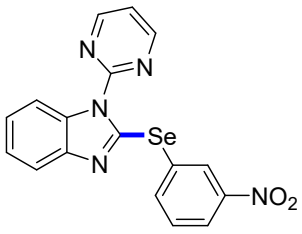
2-((3-fluorophenyl)selanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[d]imidazole (3ah): White

solid, yield = 78%, 86.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, J = 4.8 Hz, 2H), 8.57-8.53 (m, 1H), 7.65-7.60 (m, 3H), 7.42-7.37 (m, 1H), 7.32-7.26 (m, 2H), 7.21 (dd, J = 5.2, 4.8 Hz, 1H), 7.16-7.11 (m, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 163.9, 161.4, 158.0, 156.3, 148.1, 145.0, 134.6, 131.4 (d, $J_{C\text{-}F}$ = 3.6 Hz), 130.4 (d, $J_{C\text{-}F}$ = 7.8 Hz), 123.5 (d, $J_{C\text{-}F}$ = 38.9 Hz), 122.8 (d, $J_{C\text{-}F}$ = 21.7 Hz), 119.0, 117.7, 116.1 (d, $J_{C\text{-}F}$ = 21.0 Hz), 115.2 ppm. ^{19}F{^{1}H} NMR (235 MHz, $CDCl_3$): δ = -111.8 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{17}H_{12}FN_4Se$ 371.0206, found 371.0193.



3ai

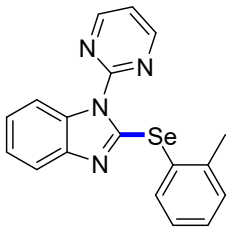
1-(pyrimidin-2-yl)-2-((3-(trifluoromethyl)phenyl)selanyl)-1*H*-benzo[d]imidazole (3ai): White solid, yield = 78%, 98.5 mg. δ = 8.82 (d, J = 4.8 Hz, 2H), 8.57-8.54 (m, 1H), 8.10 (s, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H),7.61-7.58 (m, 1H), 7.53 (dd, J = 7.6, 7.6 Hz, 1H), 7.32-7.27 (m, 2H), 7.22 (dd, J = 4.8, 4.8 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.0, 156.3, 147.8, 145.0, 139.5, 134.6, 132.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 131.3 (q, $J_{C\text{-}F}$ = 32.0 Hz), 131.1, 129.5, 125.7 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.0 (q, $J_{C\text{-}F}$ = 271.3 Hz), 123.8, 123.4, 118.9, 117.8, 115.2 ppm. ^{19}F{^{1}H} NMR (235 MHz, $CDCl_3$): δ = -62.4 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{18}H_{12}F_3N_4Se$ 421.0174, found 421.0161.



3aj

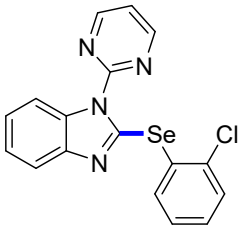
2-((3-nitrophenyl)selanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3aj): White solid, yield = 84%, 100.3 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, J = 4.8 Hz, 2H), 8.65 (s, 1H), 8.52-8.50 (m, 1H), 8.22 (dd, J = 8.4, 2.4 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 7.52 (dd, J = 8.0, 8.0 Hz, 2H), 7.25-7.19 (m, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.1, 156.3, 148.5, 147.4, 144.9, 142.3, 134.6, 132.0, 130.7, 129.8, 123.9, 123.6, 119.0, 117.9, 115.3 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{17}H_{12}N_5O_2Se$ 398.0151,

found 398.0148.



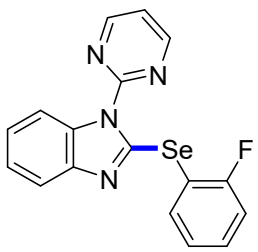
3ak

1-(pyrimidin-2-yl)-2-(o-tolylselanyl)-1*H*-benzo[*d*]imidazole (3ak): White solid, yield = 50%, 55.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (d, J = 4.8 Hz, 2H), 8.56-8.54 (m, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.60-7.58 (m, 1H), 7.40-7.38 (m, 2H), 7.30-7.22 (m, 4H), 2.51 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.0, 156.5, 148.3, 145.2, 143.2, 137.5, 134.7, 130.5, 130.4, 129.9, 126.8, 123.5, 123.1, 119.0, 117.7, 115.1, 23.0 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{18}H_{15}N_4Se$ 367.0456, found 367.0449.



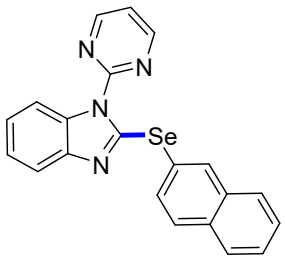
3al

2-((2-chlorophenyl)selanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3al): White solid, yield = 65%, 75.5 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (s, 2H), 8.53 (d, J = 7.6 Hz, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.36 (dd, J = 7.6, 7.6 Hz, 1H), 7.30-7.23 (m, 3H), 7.17 (s, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.0, 156.3, 147.6, 145.1, 139.1, 138.4, 134.5, 130.6, 130.4, 129.9, 127.5, 123.6, 123.3, 119.0, 117.7, 115.1 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{17}H_{12}ClN_4Se$ 386.9910, found 386.9901.



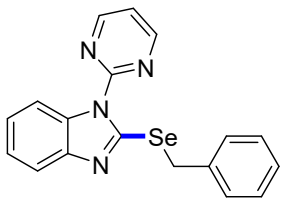
3am

2-((2-fluorophenyl)selanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[d]imidazole (3am): White solid, yield = 66%, 73.5 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, J = 5.2 Hz, 2H), 8.58-8.56 (m, 1H), 7.92-7.88 (m, 1H), 7.62-7.60 (m, 1H), 7.52-7.46 (m, 1H), 7.32-7.27 (m, 2H), 7.26-7.22 (m, 2H), 7.19 (dd, J = 5.2, 4.8 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 164.3, 161.8, 157.9, 156.2, 147.4, 145.1, 138.1 (d, $J_{C\text{-}F}$ = 2.5 Hz), 134.6, 131.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 124.9 (d, $J_{C\text{-}F}$ = 3.8 Hz), 123.4 (d, $J_{C\text{-}F}$ = 41.3 Hz), 119.0, 117.6, 117.1 (d, $J_{C\text{-}F}$ = 22.9 Hz), 115.9 (d, $J_{C\text{-}F}$ = 24.0 Hz), 115.2 ppm. ^{19}F{^{1}H} NMR (235 MHz, $CDCl_3$): δ = -101.1 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{17}H_{12}FN_4Se$ 371.0206, found 371.0190.



3an

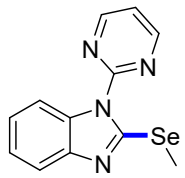
2-(naphthalen-2-ylselanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3an): White solid, yield = 73%, 88.3 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (d, J = 4.8 Hz, 2H), 8.56 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 6.8 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.55-7.41 (m, 4H), 7.28-7.22 (m, 2H), 7.18 (dd, J = 7.6, 7.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 157.1, 155.6, 147.5, 144.2, 135.5, 134.3, 133.6, 133.3, 129.8, 128.0, 127.7, 125.9, 125.25, 125.19, 122.5, 122.1, 118.1, 116.8, 114.0 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{21}H_{15}N_4Se$ 403.0456, found 403.0453.



3ao

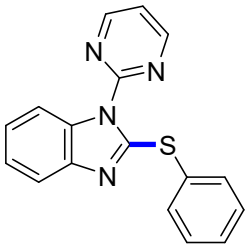
2-(benzylselanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3ao): White solid, yield = 86%, 94.7 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, J = 4.8 Hz, 2H), 8.59-8.56 (m, 1H), 7.78-7.76 (m, 1H), 7.49-7.46 (m, 2H), 7.37-7.29 (m, 4H), 7.25-7.22 (m, 1H), 7.18 (dd, J = 4.8, 4.8 Hz, 1H), 4.61 (s, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ =

157.8, 156.4, 149.3, 145.2, 138.1, 134.6, 129.4, 128.7, 127.0, 123.8, 123.1, 118.2, 117.6, 115.4, 32.3 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{18}H_{15}N_4Se$ 367.0456, found 367.0453.



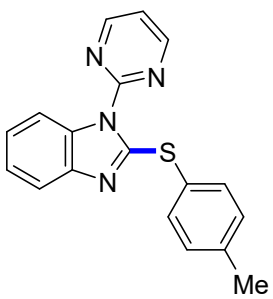
3ap

2-(methylselanyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3ap): White solid, yield = 91%, 79.4 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, J = 4.8 Hz, 2H), 8.56-8.54 (m, 1H), 7.73 (dd, J = 6.8, 2.0 Hz, 1H), 7.33-7.28 (m, 2H), 7.20 (dd, J = 4.8, 4.8 Hz, 1H), 2.57 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 157.9, 156.6 149.1, 145.1, 134.9, 123.7, 123.0, 118.2, 117.7, 115.4, 8.8 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{12}H_{11}N_4Se$ 291.0143, found 291.0135.



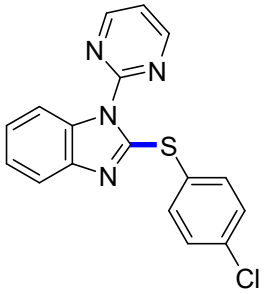
3aq

2-(phenylthio)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3aq): white solid, yield = 91%, 83.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (d, J = 4.8 Hz, 2H), 8.40-8.38 (m, 1H), 7.73-7.71 (m, 2H), 7.59-7.57 (m, 1H), 7.46-7.42 (m, 3H), 7.28-7.22 (m, 2H), 7.18 (dd, J = 4.8, 4.8 Hz, 1H) ppm. ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ = 158.1, 156.4, 153.3, 143.8, 134.9, 134.5, 131.1, 129.3, 129.2, 123.6, 123.2, 118.9, 118.0, 114.6 ppm. HRMS (ESI) calcd. for $[M + Na]^+$ $C_{17}H_{12}N_4SNa$ 327.0675, found 327.0667.



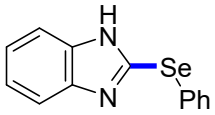
3ar

1-(pyrimidin-2-yl)-2-(p-tolylthio)-1*H*-benzo[*d*]imidazole (3ar): white solid, yield = 85%, 81.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J = 4.8 Hz, 2H), 8.40-8.38 (m, 1H), 7.61-7.58 (m, 3H), 7.28-7.24 (m, 4H), 7.20-7.18 (m, 1H), 2.39 (s, 3H) ppm. ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ = 158.1, 156.4, 153.8, 143.8, 139.5, 135.0, 134.5, 130.2, 127.4, 123.6, 123.1, 118.9, 118.0, 114.5, 21.5 ppm. HRMS (ESI) calcd. for $[M + Na]^+$ $C_{18}H_{14}N_4SNa$ 341.0831, found 341.0831.



3as

2-((4-chlorophenyl)thio)-1-(pyrimidin-2-yl)-1*H*-benzo[*d*]imidazole (3as): white solid, yield = 85%, 86.4 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J = 4.8 Hz, 2H), 8.43-8.40 (m, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.59-7.57 (m, 1H) ppm, 7.40 (d, J = 8.8 Hz, 2H), 7.29-7.23 (m, 2H), 7.22-7.19 (m, 1H) ppm. ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ = 158.1, 156.3, 152.8, 143.7, 136.2, 135.5, 134.4, 129.7, 129.6, 123.8, 123.4, 118.9, 118.0, 114.7 ppm. HRMS (ESI) calcd. for $[M + Na]^+$ $C_{17}H_{11}N_4SClNa$ 361.0285, found 361.0280.



4

2-(phenylselanyl)-1*H*-benzo[*d*]imidazole (4): White solid, yield = 75%, 26.3 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79-6.76 (m, 2H), 6.72-6.67 (m, 2H), 6.54-6.50 (m, 3H), 6.42-6.38 (m, 2H), 4.13 (s, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 133.9, 131.5, 125.2, 121.4, 120.1, 119.3, 114.4, 106.0 ppm. HRMS (ESI) calcd. for $[M + H]^+$ $C_{13}H_{11}N_2Se$ 275.0082, found 275.0093.

7. References.

[1] a) H. Zhao; Z. Luo; J. Yang; B. Li; J. Han; L. Xu; W. Lai; P. J. Walsh, *Chem. Eur. J.* 2022, **28**, e202200441; b) L. Wang; N. Liu; B. Dai, *RSC Adv.* 2015, **5**, 82097-82111.

[2] Y.-T. Ma; C. Lin; X.-B. Huang; M.-C. Liu; Y.-B. Zhou; H.-Y. Wu, *Chem. Commun.*, 2022, **58**, 6550-6553.

8. X-ray crystallographic data for 3ac (CCDC-2378943).

Table 1. Crystal data and structure refinement for **3ac**.

Identification code	A
Empirical formula	C15.75 H11 Cl N4 Se
Formula weight	370.69
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbcn
Unit cell dimensions	a = 9.5939(6) A alpha = 90 deg. b = 18.5686(11) A beta = 90 deg. c = 17.3143(10) A gamma = 90 deg.
Volume	3084.5(3) A^3
Z, Calculated density	8, 1.597 Mg/m^3
Absorption coefficient	2.608 mm^-1
F(000)	1476
Crystal size	0.182 x 0.134 x 0.123 mm
Theta range for data collection	3.170 to 25.006 deg.
Limiting indices	-11<=h<=11, -22<=k<=22, -20<=l<=20
Reflections collected / unique	22884 / 2715 [R(int) = 0.0344]
Completeness to theta = 25.006	99.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2715 / 0 / 208
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0254, wR2 = 0.0623
R indices (all data)	R1 = 0.0306, wR2 = 0.0661

Extinction coefficient	n/a
Largest diff. peak and hole	0.255 and -0.388 e.A^-3

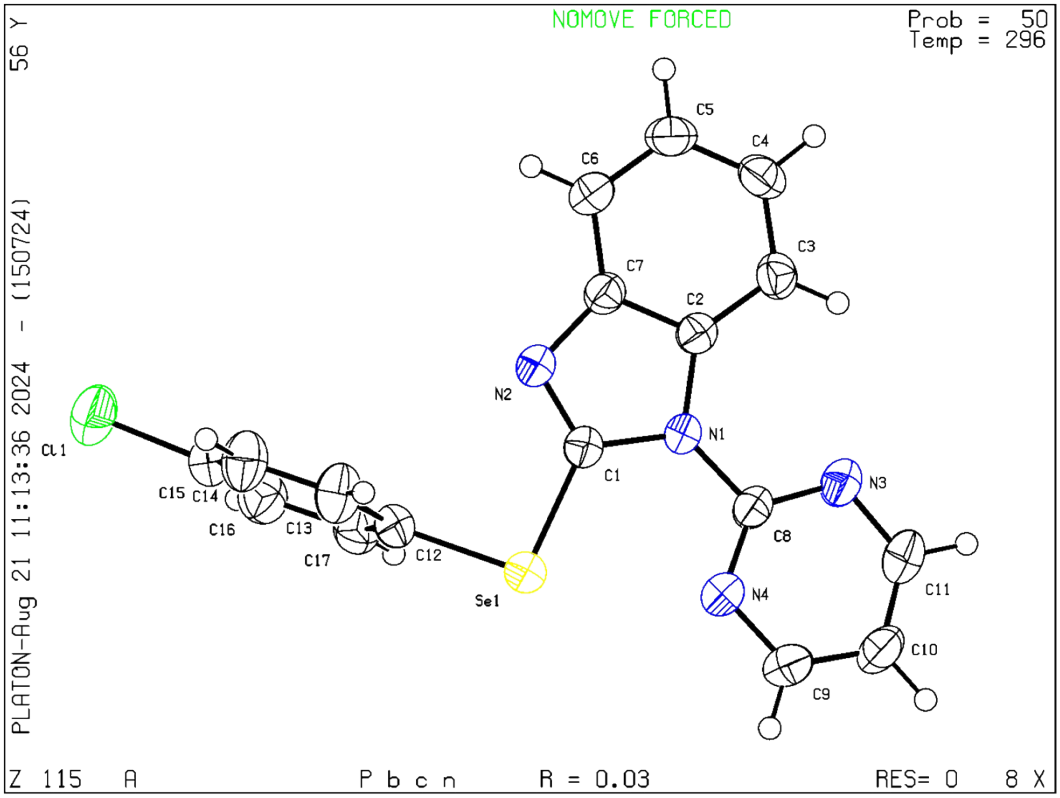


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3ac**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	3720(1)	2043(1)	5063(1)	72(1)
Se(1)	4354(1)	5331(1)	6150(1)	44(1)
N(1)	2570(2)	5810(1)	7402(1)	33(1)
N(2)	2816(2)	4607(1)	7324(1)	39(1)
N(3)	1995(2)	7017(1)	7570(1)	49(1)
N(4)	3883(2)	6663(1)	6773(1)	46(1)
C(1)	3192(2)	5222(1)	7034(1)	35(1)
C(2)	1686(2)	5519(1)	7966(1)	33(1)
C(3)	750(2)	5818(1)	8485(1)	39(1)
C(4)	31(3)	5347(1)	8957(1)	44(1)
C(5)	240(3)	4607(1)	8917(1)	47(1)
C(6)	1160(2)	4312(1)	8396(1)	44(1)
C(7)	1876(2)	4775(1)	7910(1)	36(1)
C(8)	2826(2)	6537(1)	7241(1)	35(1)
C(9)	4105(3)	7352(1)	6595(1)	55(1)
C(10)	3305(3)	7895(1)	6885(1)	53(1)
C(11)	2268(3)	7699(1)	7373(2)	55(1)
C(12)	4187(2)	4340(1)	5819(1)	41(1)
C(13)	5036(3)	3813(1)	6129(1)	53(1)
C(14)	4918(3)	3107(1)	5884(2)	57(1)
C(15)	3941(3)	2941(1)	5331(1)	48(1)
C(16)	3119(3)	3457(1)	5000(1)	52(1)
C(17)	3247(2)	4166(1)	5247(1)	46(1)

Table 3. Bond lengths [A] and angles [deg] for **3ac**.

Cl(1)-C(15)	1.744(2)
Se(1)-C(1)	1.904(2)
Se(1)-C(12)	1.934(2)
N(1)-C(1)	1.397(2)
N(1)-C(8)	1.400(2)
N(1)-C(2)	1.402(2)
N(2)-C(1)	1.299(2)
N(2)-C(7)	1.393(3)
N(3)-C(8)	1.326(3)
N(3)-C(11)	1.338(3)
N(4)-C(8)	1.318(3)
N(4)-C(9)	1.333(3)
C(2)-C(3)	1.386(3)
C(2)-C(7)	1.395(3)
C(3)-C(4)	1.383(3)
C(4)-C(5)	1.389(3)
C(5)-C(6)	1.376(3)
C(6)-C(7)	1.387(3)
C(9)-C(10)	1.364(4)
C(10)-C(11)	1.354(4)
C(12)-C(17)	1.378(3)
C(12)-C(13)	1.382(3)
C(13)-C(14)	1.383(3)
C(14)-C(15)	1.374(4)
C(15)-C(16)	1.367(3)
C(16)-C(17)	1.391(3)
C(1)-Se(1)-C(12)	95.12(8)
C(1)-N(1)-C(8)	125.94(16)
C(1)-N(1)-C(2)	105.92(15)
C(8)-N(1)-C(2)	128.12(16)
C(1)-N(2)-C(7)	105.25(16)
C(8)-N(3)-C(11)	114.2(2)
C(8)-N(4)-C(9)	115.76(19)
N(2)-C(1)-N(1)	113.12(17)
N(2)-C(1)-Se(1)	124.47(14)
N(1)-C(1)-Se(1)	122.24(14)
C(3)-C(2)-C(7)	121.79(19)
C(3)-C(2)-N(1)	133.47(18)
C(7)-C(2)-N(1)	104.71(16)
C(4)-C(3)-C(2)	116.9(2)
C(3)-C(4)-C(5)	121.6(2)
C(6)-C(5)-C(4)	121.3(2)
C(5)-C(6)-C(7)	117.9(2)
C(6)-C(7)-N(2)	128.56(18)
C(6)-C(7)-C(2)	120.47(19)

N(2)-C(7)-C(2)	110.97(17)
N(4)-C(8)-N(3)	127.41(18)
N(4)-C(8)-N(1)	115.38(17)
N(3)-C(8)-N(1)	117.21(17)
N(4)-C(9)-C(10)	122.4(2)
C(11)-C(10)-C(9)	116.3(2)
N(3)-C(11)-C(10)	123.9(2)
C(17)-C(12)-C(13)	119.9(2)
C(17)-C(12)-Se(1)	119.35(17)
C(13)-C(12)-Se(1)	120.67(17)
C(12)-C(13)-C(14)	120.3(2)
C(15)-C(14)-C(13)	118.8(2)
C(16)-C(15)-C(14)	121.9(2)
C(16)-C(15)-Cl(1)	119.21(19)
C(14)-C(15)-Cl(1)	118.89(19)
C(15)-C(16)-C(17)	118.9(2)
C(12)-C(17)-C(16)	120.1(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **3ac**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cl(1)	105(1)	42(1)	71(1)	-12(1)	6(1)	-6(1)
Se(1)	51(1)	35(1)	47(1)	-1(1)	16(1)	-1(1)
N(1)	38(1)	26(1)	35(1)	-1(1)	3(1)	0(1)
N(2)	45(1)	28(1)	43(1)	-1(1)	7(1)	0(1)
N(3)	55(1)	31(1)	62(1)	-1(1)	12(1)	3(1)
N(4)	57(1)	32(1)	50(1)	0(1)	11(1)	-5(1)
C(1)	37(1)	31(1)	38(1)	-1(1)	3(1)	1(1)
C(2)	35(1)	32(1)	31(1)	0(1)	-3(1)	-2(1)
C(3)	45(1)	37(1)	35(1)	-6(1)	-1(1)	1(1)
C(4)	45(1)	53(1)	34(1)	-4(1)	7(1)	-4(1)
C(5)	53(1)	48(1)	40(1)	5(1)	7(1)	-13(1)
C(6)	52(1)	34(1)	45(1)	3(1)	4(1)	-5(1)
C(7)	40(1)	32(1)	36(1)	0(1)	-1(1)	-3(1)
C(8)	41(1)	28(1)	36(1)	0(1)	-3(1)	-2(1)
C(9)	72(2)	41(1)	52(1)	4(1)	13(1)	-13(1)
C(10)	76(2)	29(1)	54(1)	4(1)	1(1)	-8(1)
C(11)	68(2)	32(1)	64(2)	-2(1)	4(1)	6(1)
C(12)	42(1)	36(1)	45(1)	-3(1)	11(1)	2(1)
C(13)	53(1)	45(1)	61(2)	-8(1)	-11(1)	7(1)
C(14)	59(1)	45(1)	66(2)	-4(1)	-7(1)	14(1)
C(15)	59(1)	39(1)	47(1)	-7(1)	11(1)	1(1)
C(16)	57(1)	53(1)	46(1)	-5(1)	-4(1)	-2(1)
C(17)	50(1)	45(1)	44(1)	2(1)	4(1)	8(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3ac**.

	x	y	z	U(eq)
H(3A)	613	6313	8514	47
H(4A)	-609	5529	9310	53
H(5A)	-251	4306	9250	56
H(6A)	1297	3816	8371	52
H(9A)	4832	7466	6262	66
H(10A)	3462	8374	6755	64
H(11A)	1714	8060	7583	66
H(13A)	5689	3934	6504	64
H(14A)	5491	2751	6089	68
H(16A)	2484	3335	4616	62
H(17A)	2697	4524	5026	56

Table 6. Torsion angles [deg] for **3ac**.

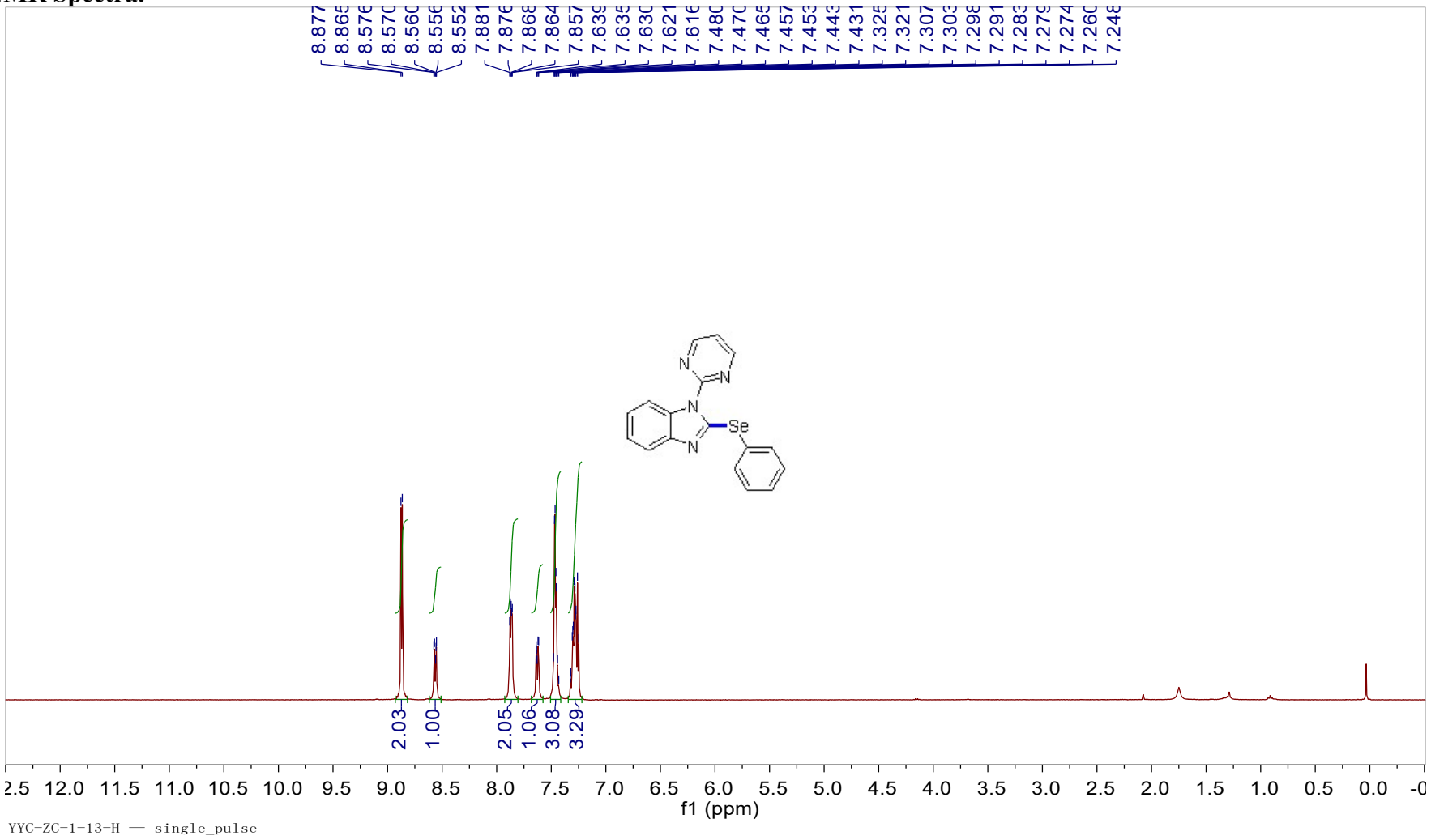
C(7)-N(2)-C(1)-N(1)	0.9(2)
C(7)-N(2)-C(1)-Se(1)	-174.46(15)
C(8)-N(1)-C(1)-N(2)	176.74(18)
C(2)-N(1)-C(1)-N(2)	-1.7(2)
C(8)-N(1)-C(1)-Se(1)	-7.8(3)
C(2)-N(1)-C(1)-Se(1)	173.75(13)
C(1)-N(1)-C(2)-C(3)	-176.3(2)
C(8)-N(1)-C(2)-C(3)	5.2(3)
C(1)-N(1)-C(2)-C(7)	1.8(2)
C(8)-N(1)-C(2)-C(7)	-176.69(18)
C(7)-C(2)-C(3)-C(4)	1.2(3)
N(1)-C(2)-C(3)-C(4)	179.1(2)
C(2)-C(3)-C(4)-C(5)	0.4(3)
C(3)-C(4)-C(5)-C(6)	-1.0(4)
C(4)-C(5)-C(6)-C(7)	0.1(3)
C(5)-C(6)-C(7)-N(2)	-177.6(2)
C(5)-C(6)-C(7)-C(2)	1.5(3)
C(1)-N(2)-C(7)-C(6)	179.5(2)
C(1)-N(2)-C(7)-C(2)	0.3(2)
C(3)-C(2)-C(7)-C(6)	-2.2(3)
N(1)-C(2)-C(7)-C(6)	179.42(19)
C(3)-C(2)-C(7)-N(2)	177.05(18)
N(1)-C(2)-C(7)-N(2)	-1.3(2)
C(9)-N(4)-C(8)-N(3)	-2.2(3)
C(9)-N(4)-C(8)-N(1)	177.8(2)
C(11)-N(3)-C(8)-N(4)	2.1(3)
C(11)-N(3)-C(8)-N(1)	-178.0(2)
C(1)-N(1)-C(8)-N(4)	-9.5(3)
C(2)-N(1)-C(8)-N(4)	168.63(18)
C(1)-N(1)-C(8)-N(3)	170.53(19)
C(2)-N(1)-C(8)-N(3)	-11.3(3)
C(8)-N(4)-C(9)-C(10)	0.8(4)
N(4)-C(9)-C(10)-C(11)	0.6(4)
C(8)-N(3)-C(11)-C(10)	-0.4(4)
C(9)-C(10)-C(11)-N(3)	-0.7(4)
C(17)-C(12)-C(13)-C(14)	-1.9(4)
Se(1)-C(12)-C(13)-C(14)	-179.4(2)
C(12)-C(13)-C(14)-C(15)	-0.3(4)
C(13)-C(14)-C(15)-C(16)	2.3(4)
C(13)-C(14)-C(15)-Cl(1)	-176.2(2)
C(14)-C(15)-C(16)-C(17)	-2.0(4)
Cl(1)-C(15)-C(16)-C(17)	176.48(18)
C(13)-C(12)-C(17)-C(16)	2.2(3)
Se(1)-C(12)-C(17)-C(16)	179.73(17)
C(15)-C(16)-C(17)-C(12)	-0.3(4)

Symmetry transformations used to generate equivalent atoms:

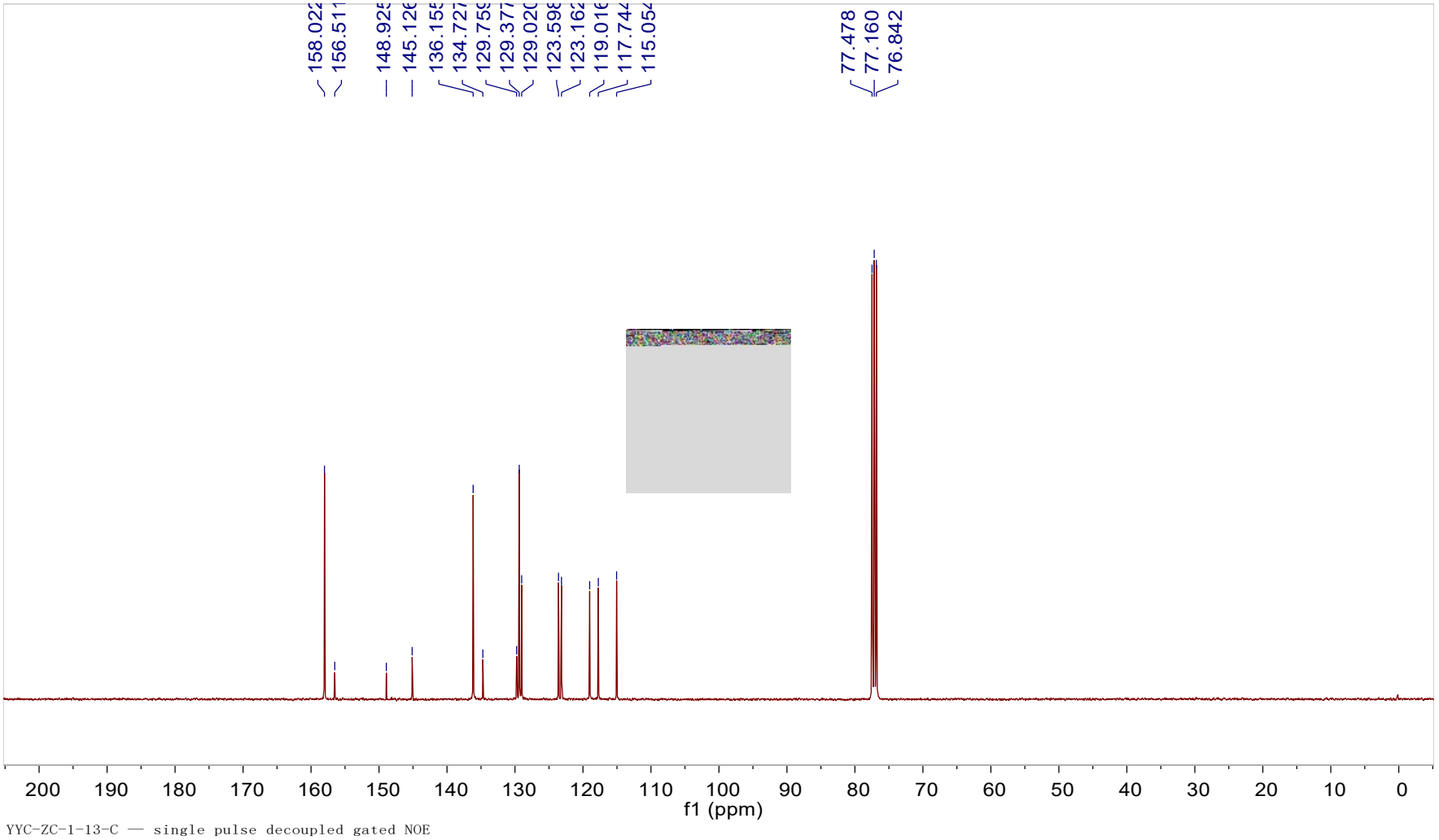
Table 7. Hydrogen bonds for A [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

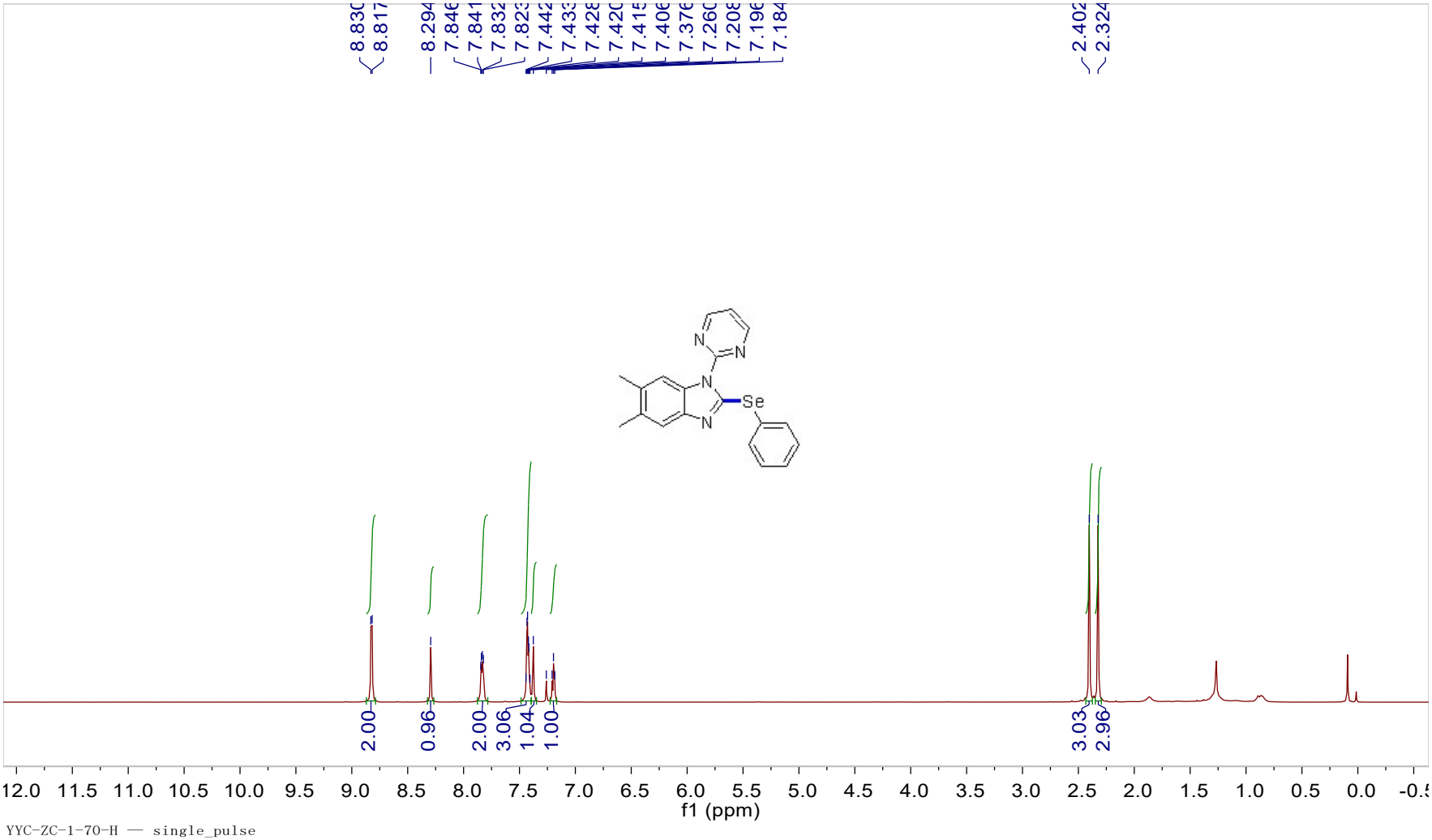
9. NMR Spectra.



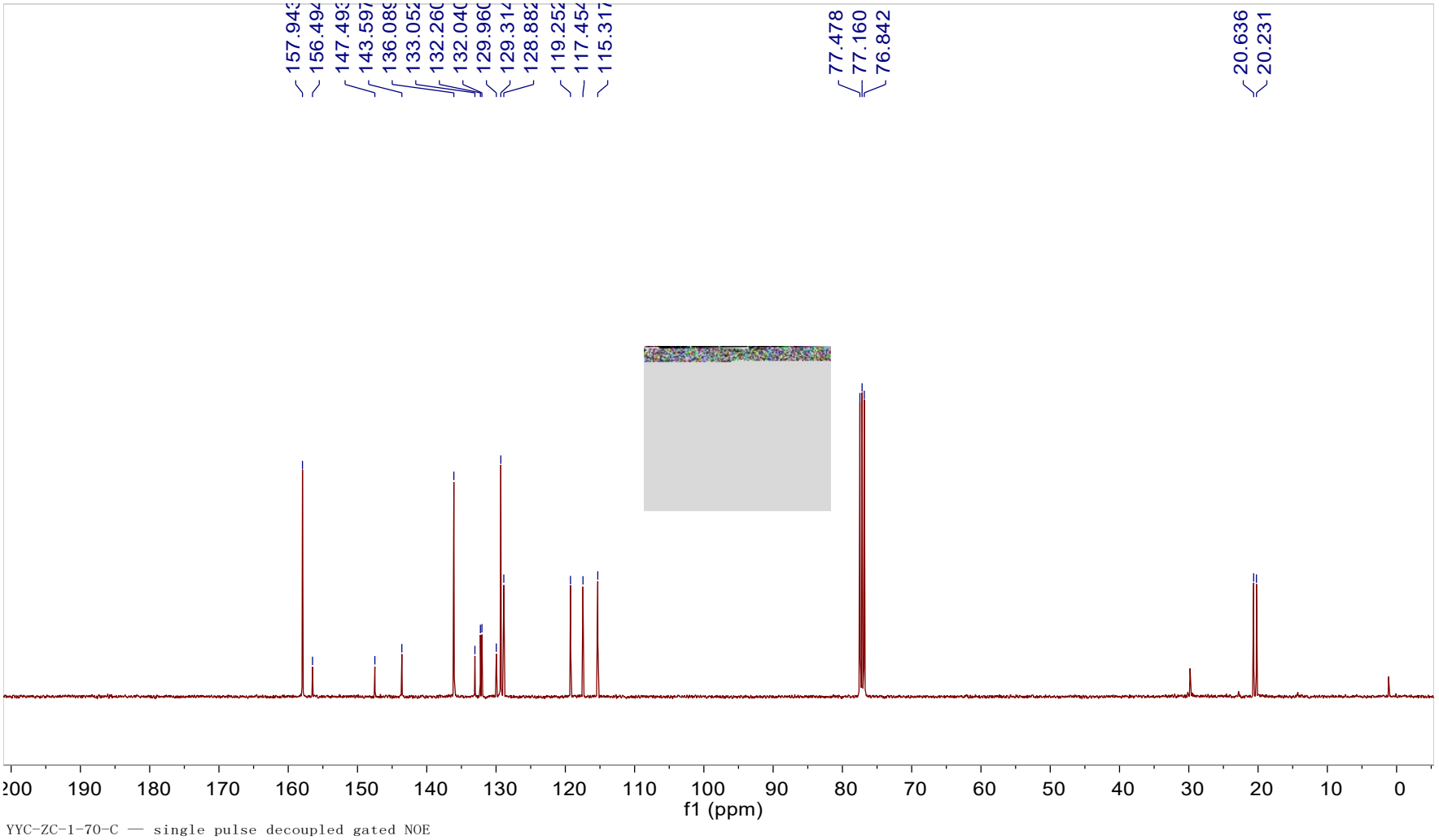
^{1}H NMR spectrum of **3aa**.



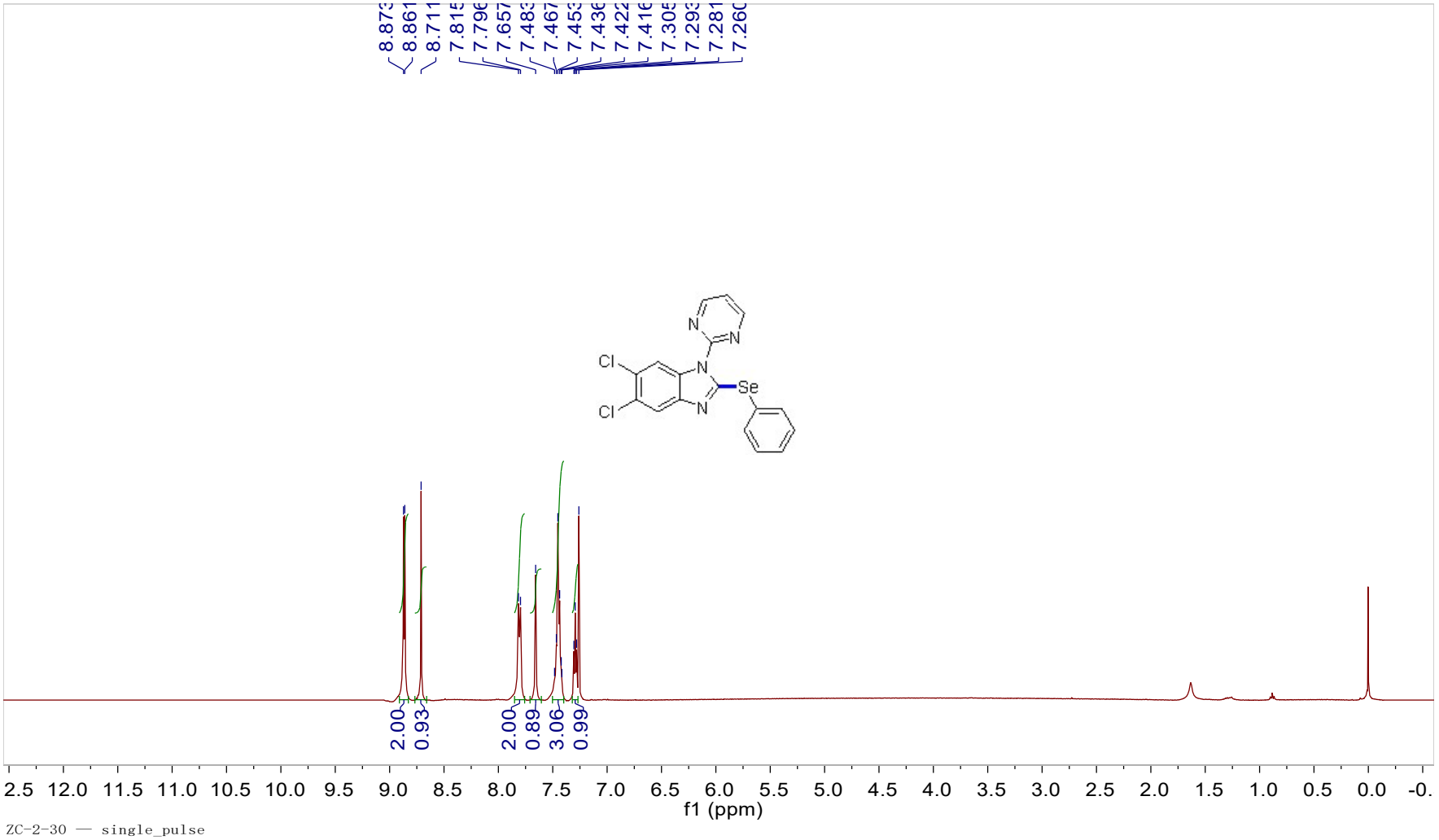
$^{13}C\{^{1}H\}$ NMR spectrum of **3aa**.



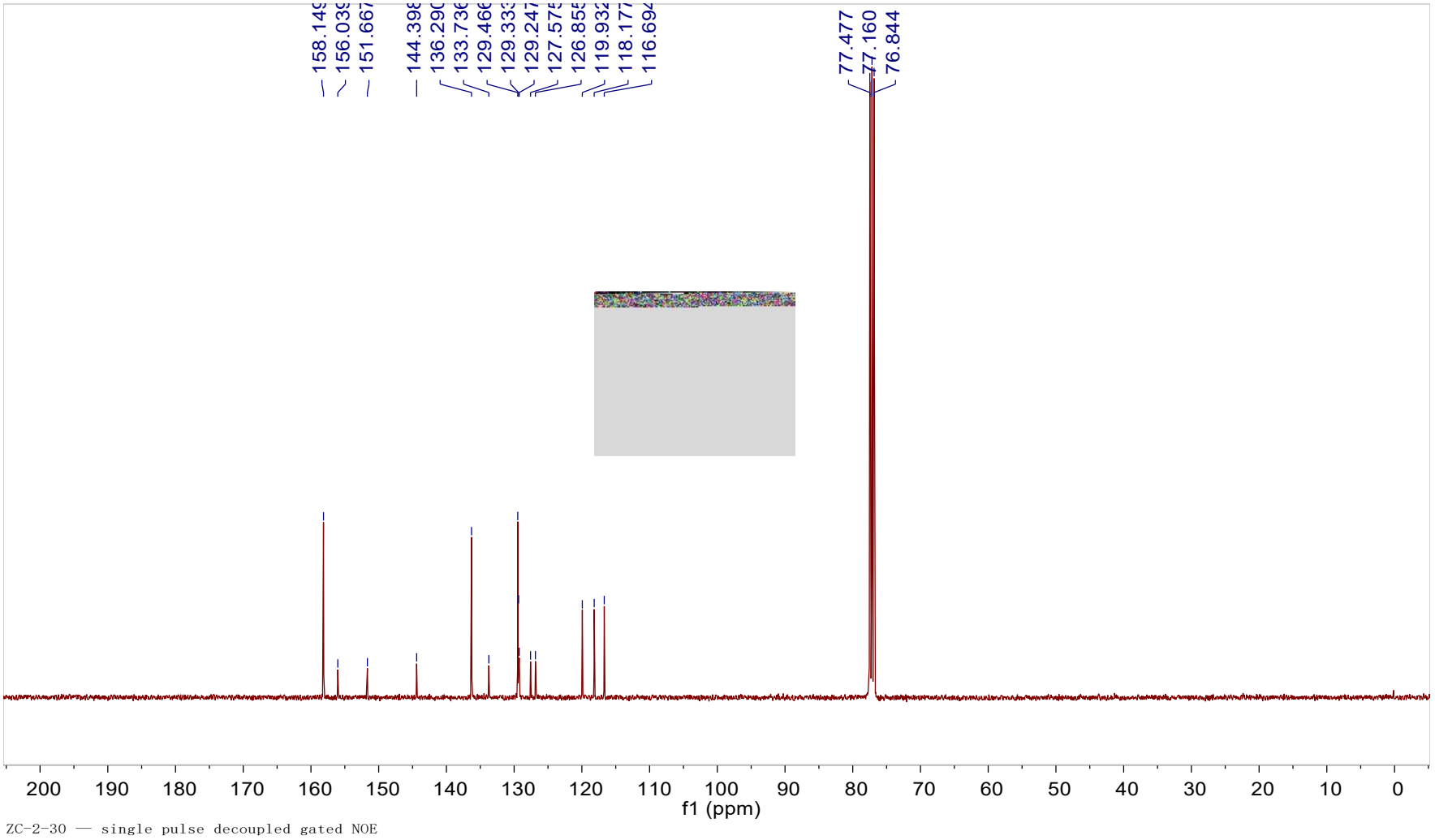
^{1}H NMR spectrum of **3ba**.



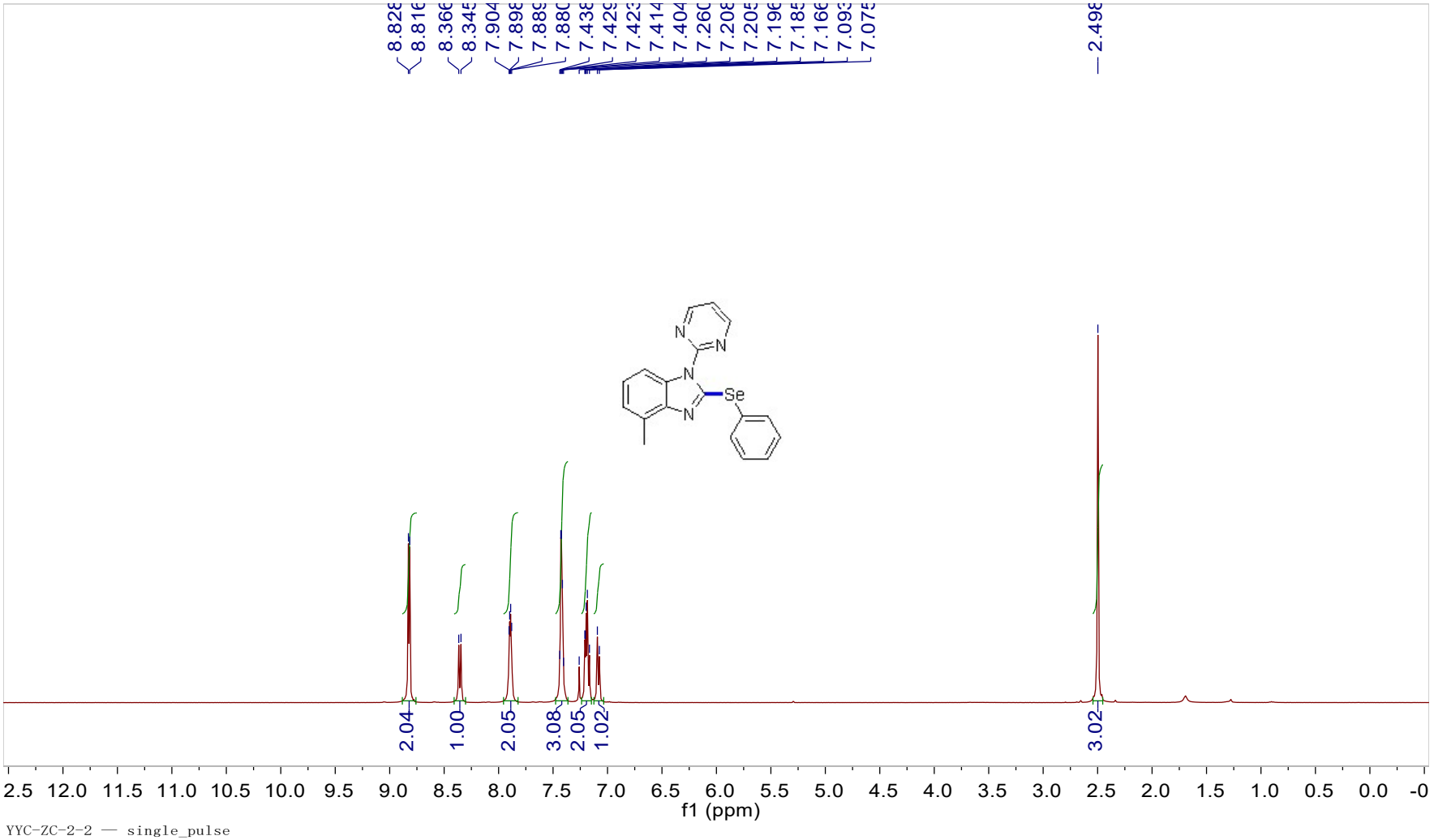
$^{13}C\{^{1}H\}$ NMR spectrum of **3ba**.



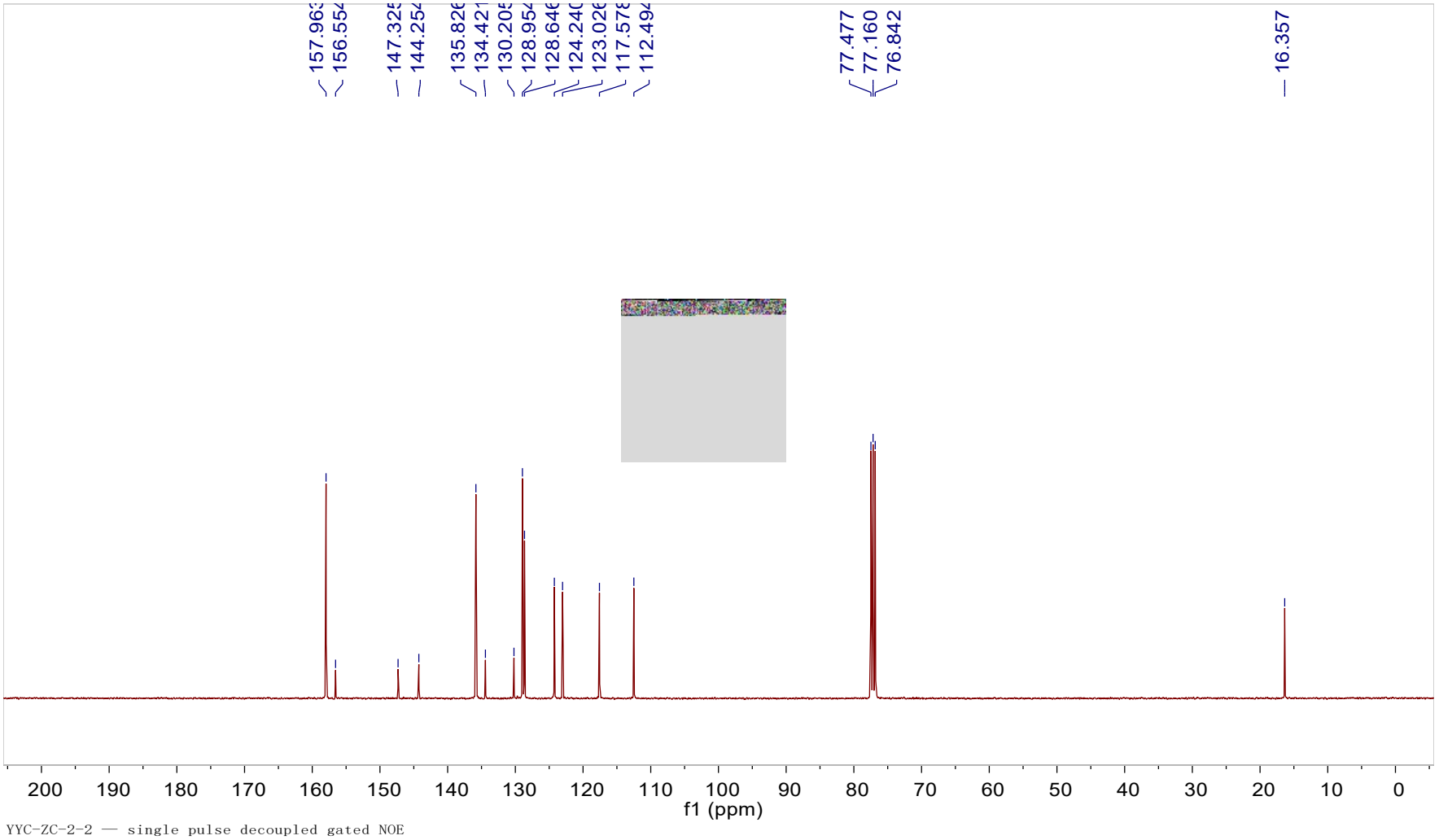
^{1}H NMR spectrum of **3ca**.



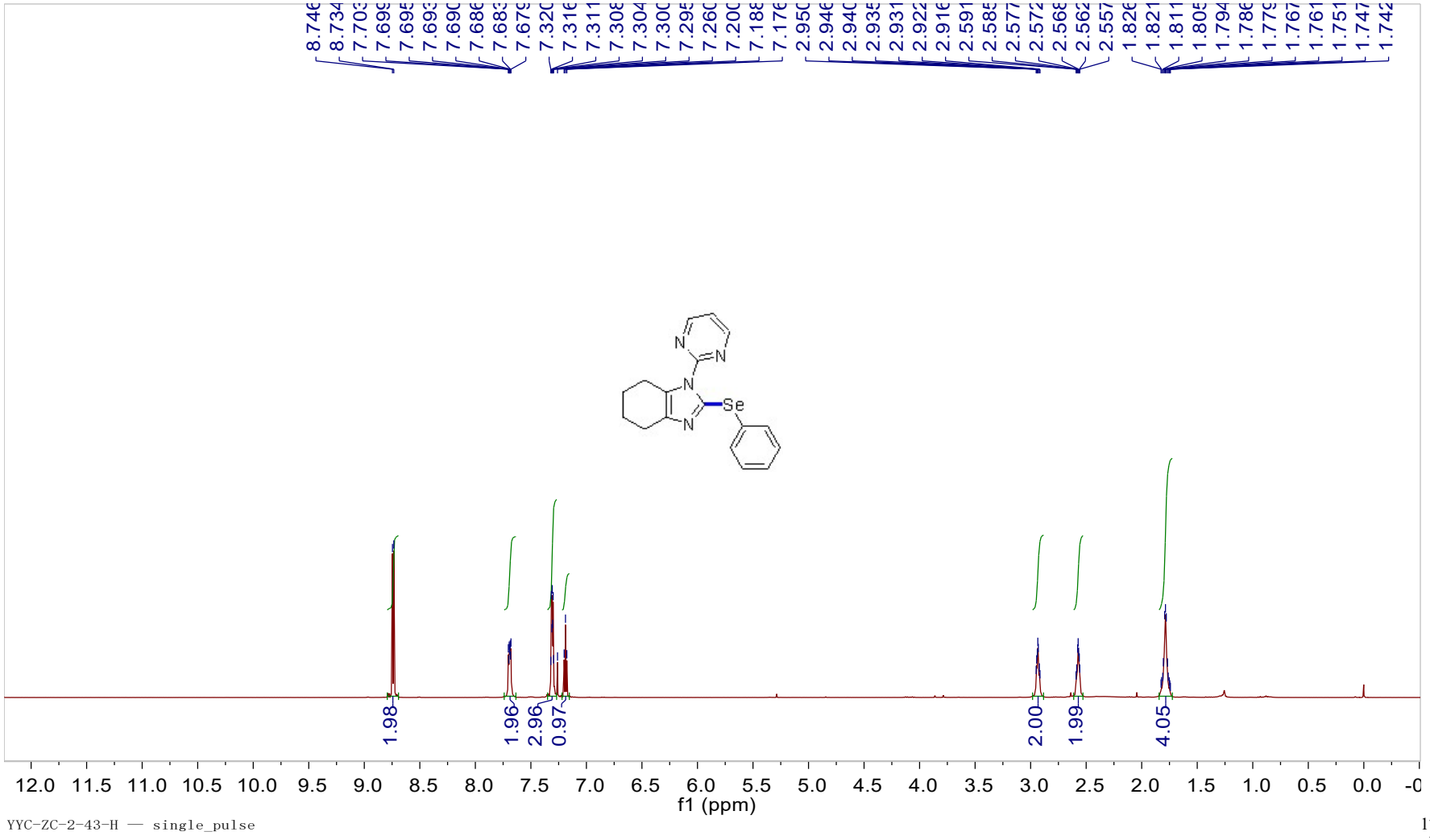
$^{13}C\{^{1}H\}$ NMR spectrum of **3ca**.



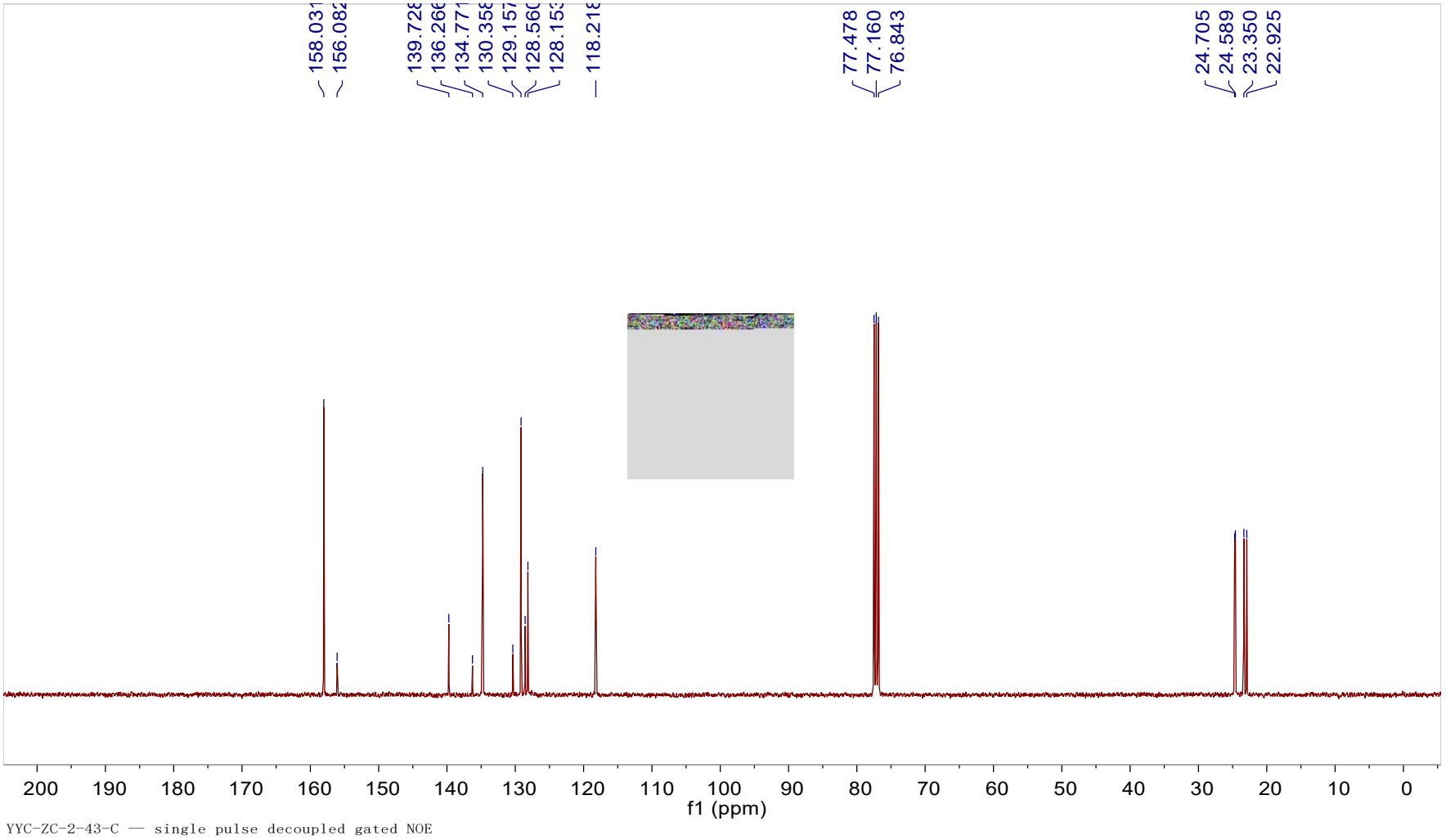
^{1}H NMR spectrum of **3da**.



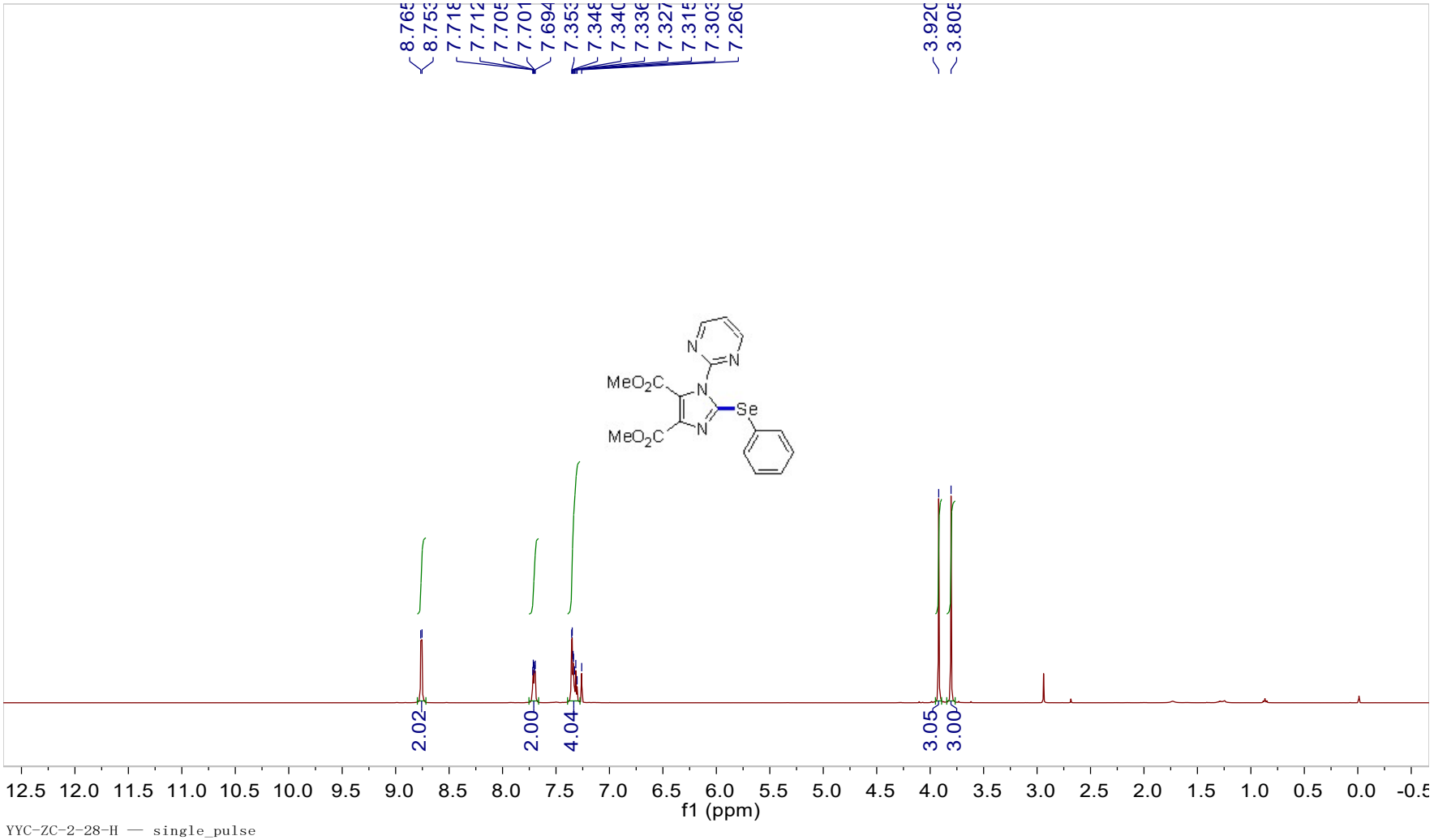
$^{13}C\{^{1}H\}$ NMR spectrum of **3da**.



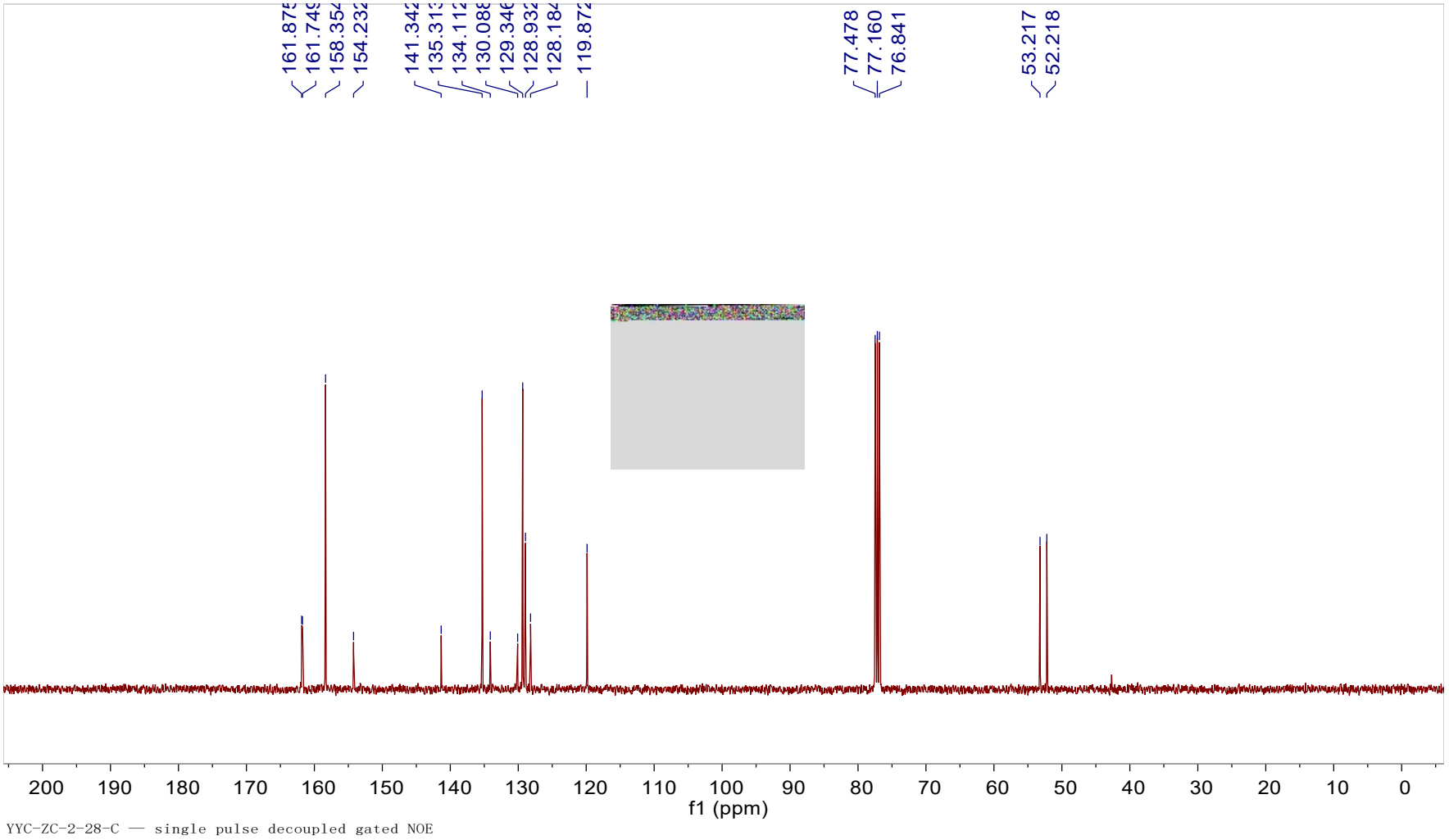
NMR spectrum of **3ea**.



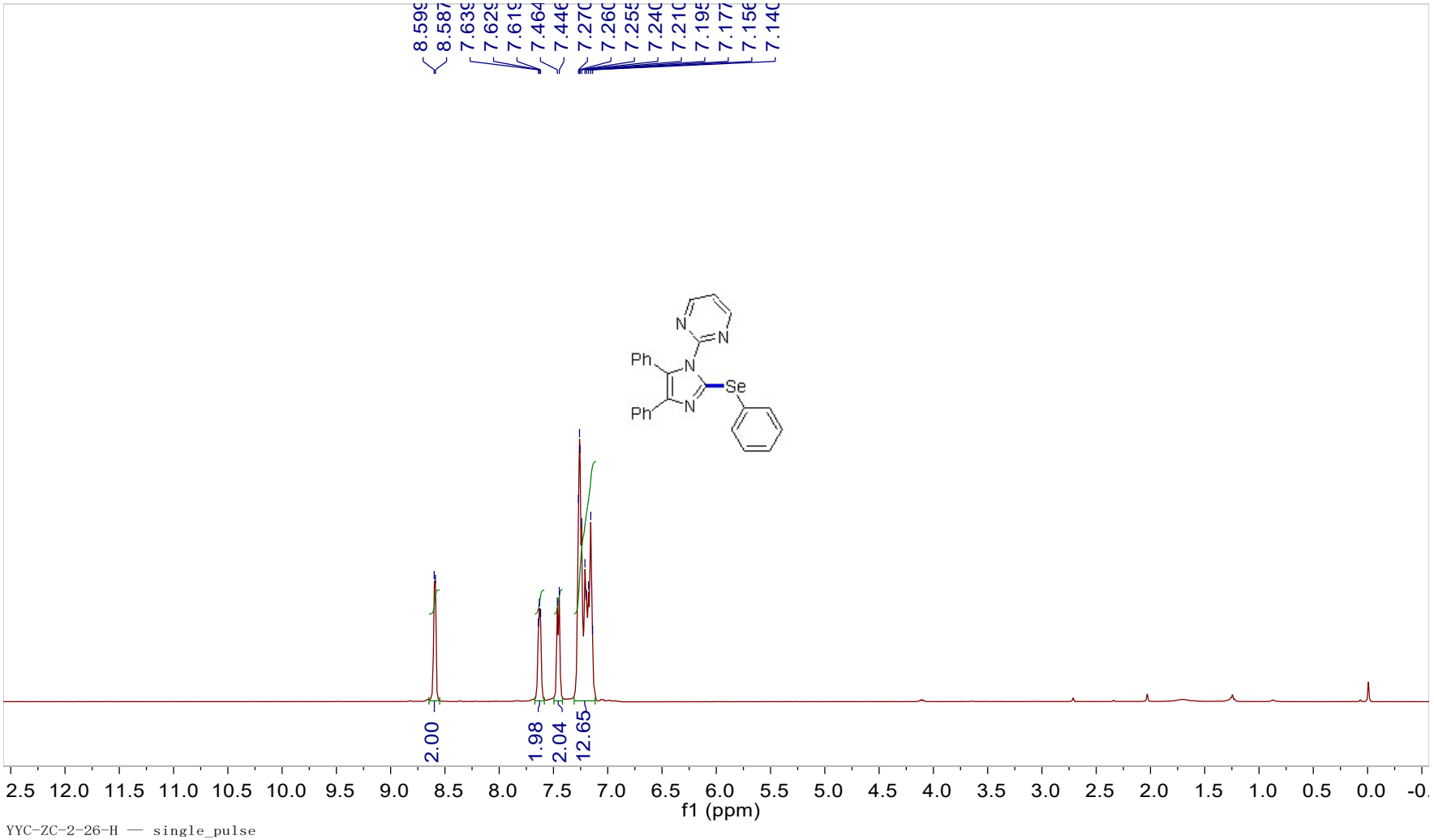
$^{13}C\{^{1}H\}$ NMR spectrum of **3ea**.



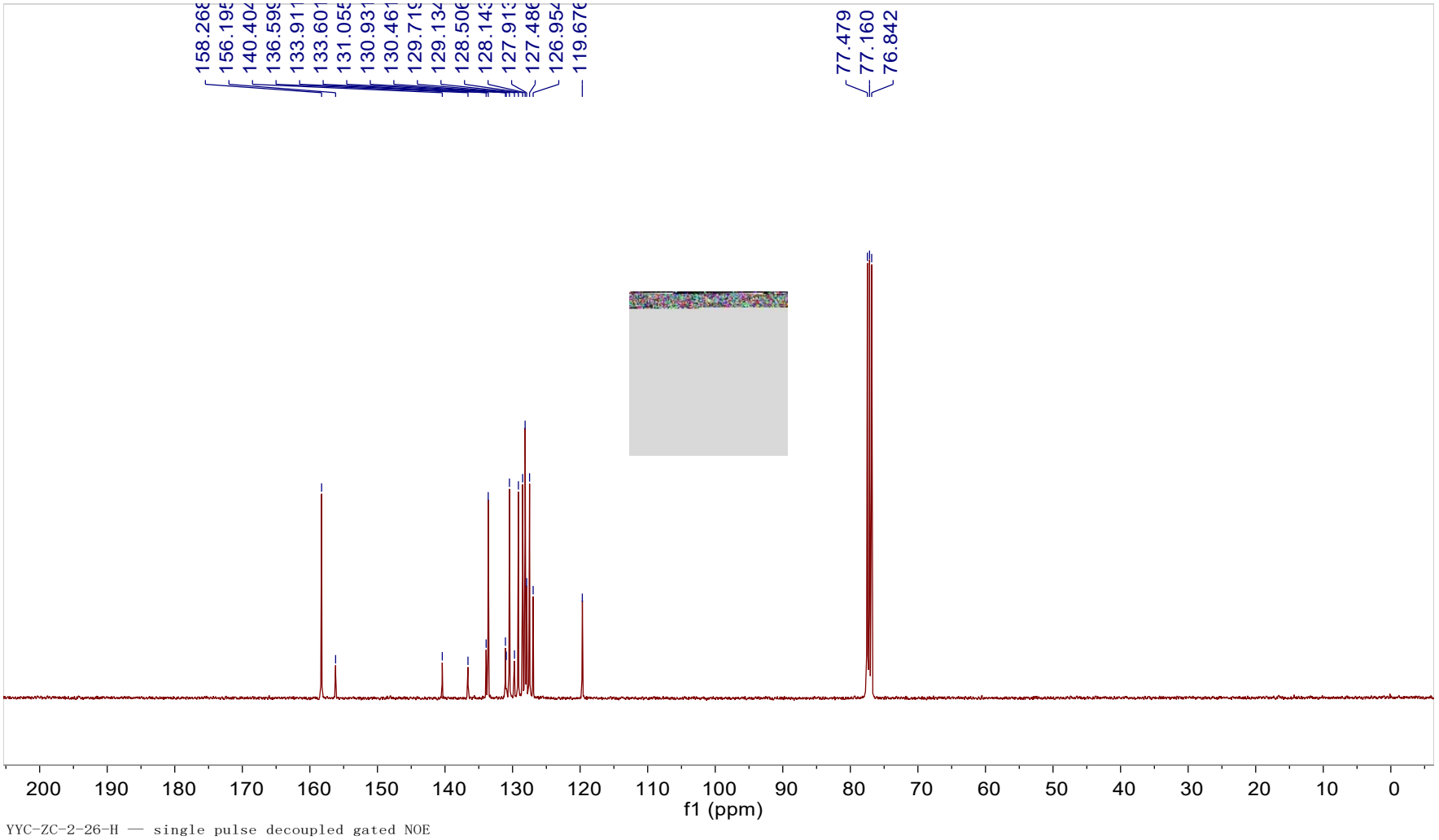
^{1}H NMR spectrum of **3fa**.



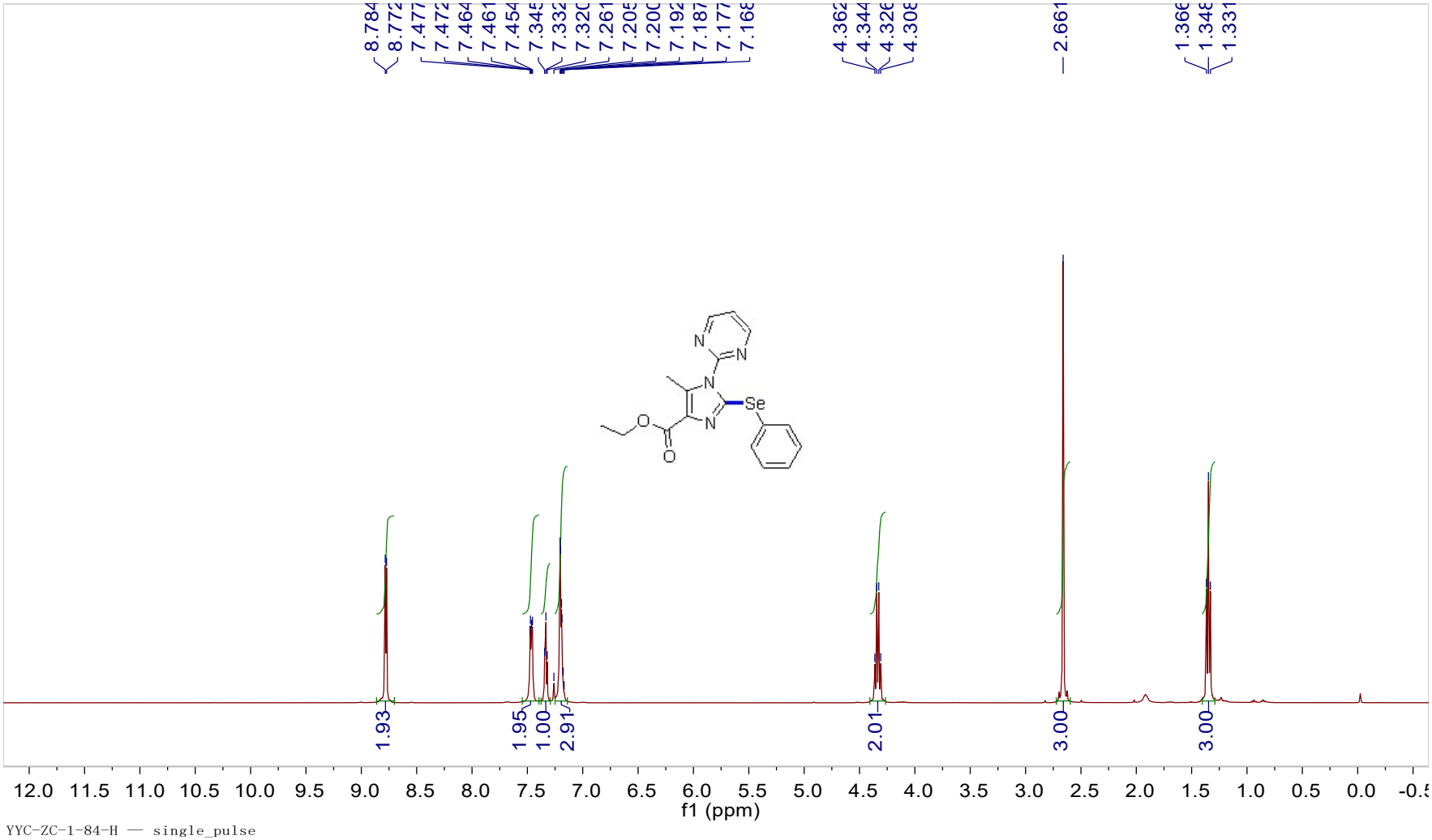
$^{13}C\{^{1}H\}$ NMR spectrum of **3fa**.



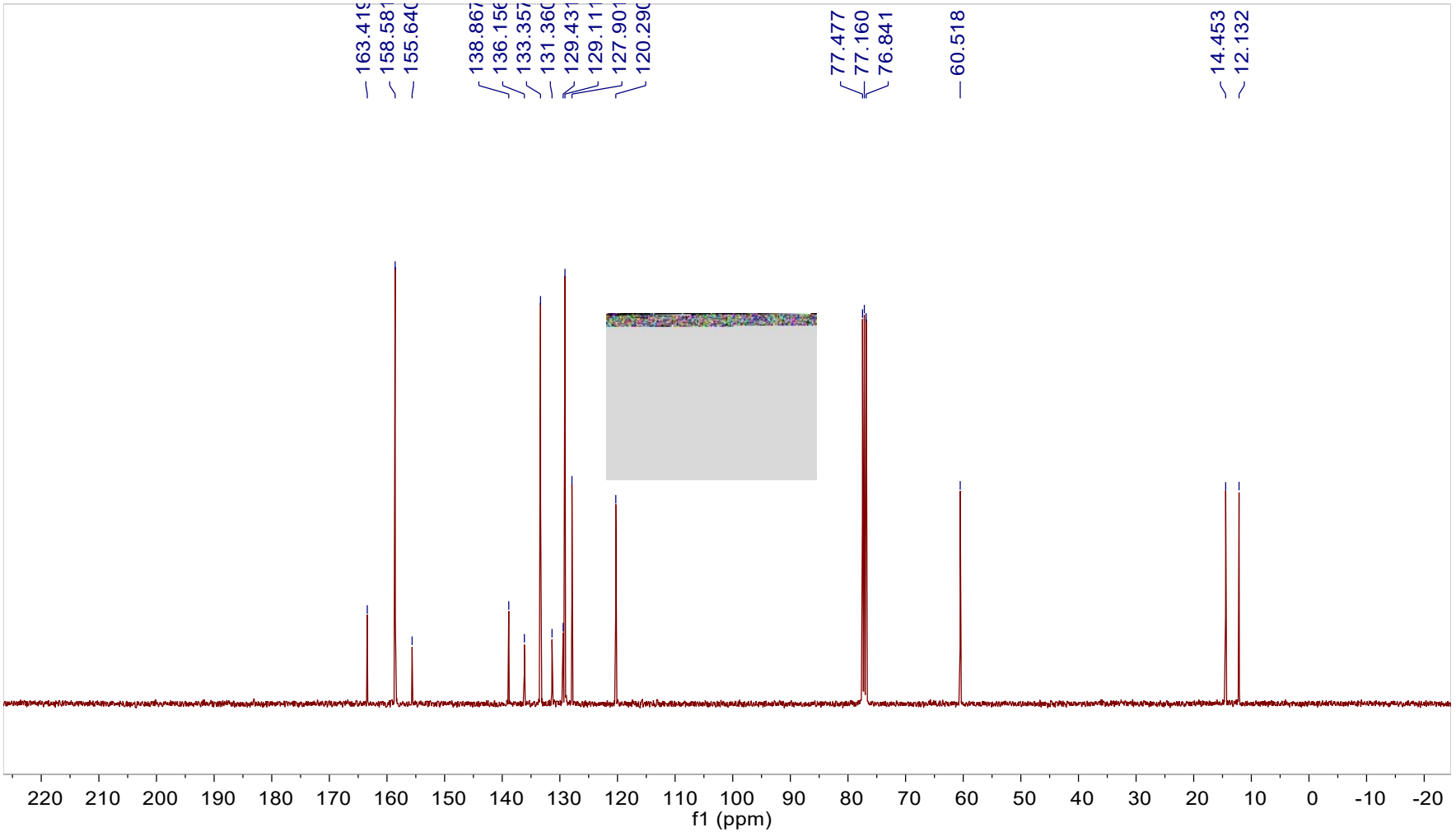
^{1}H NMR spectrum of **3ga**.



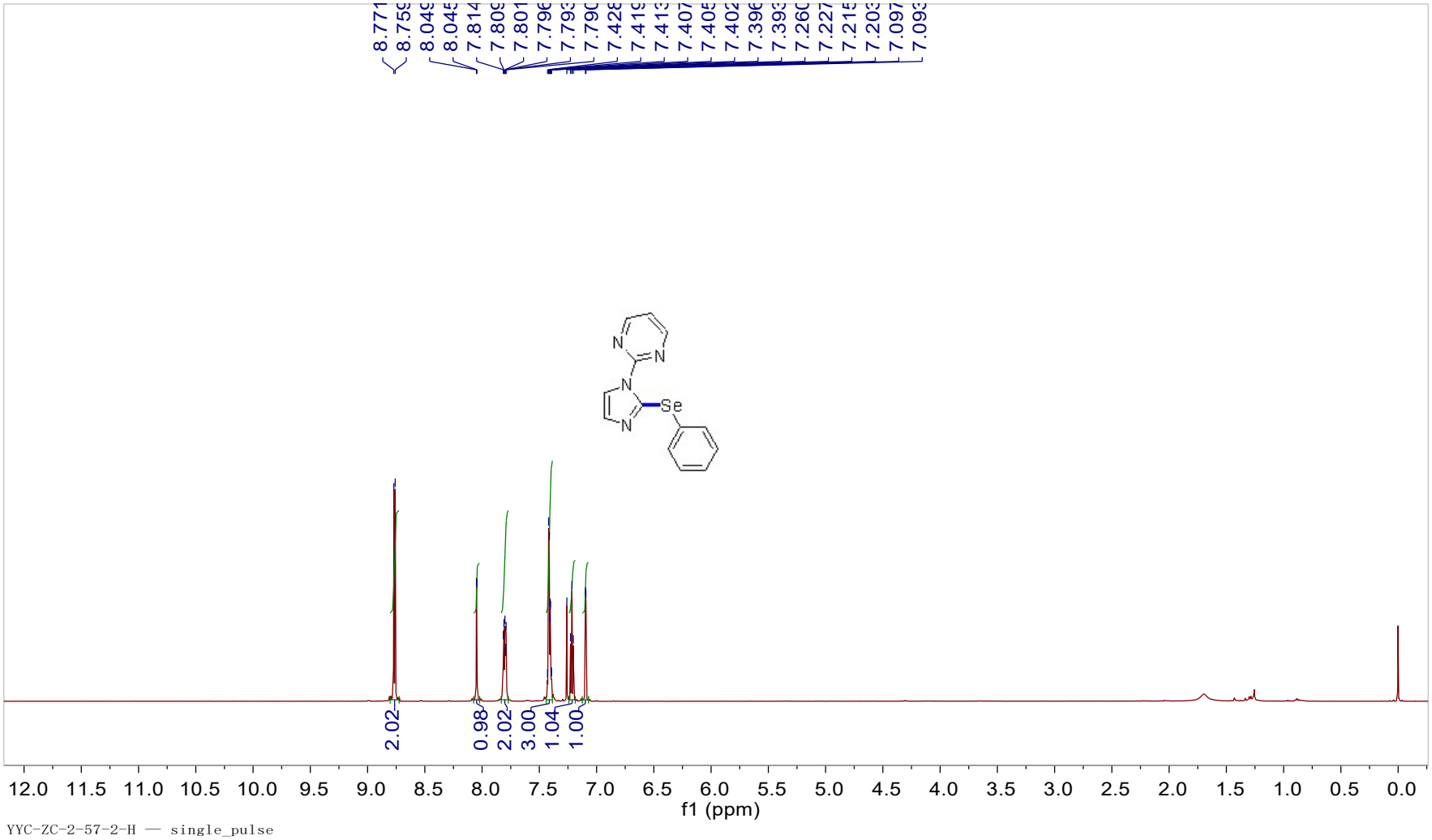
$^{13}C\{^{1}H\}$ NMR spectrum of **3ga**.



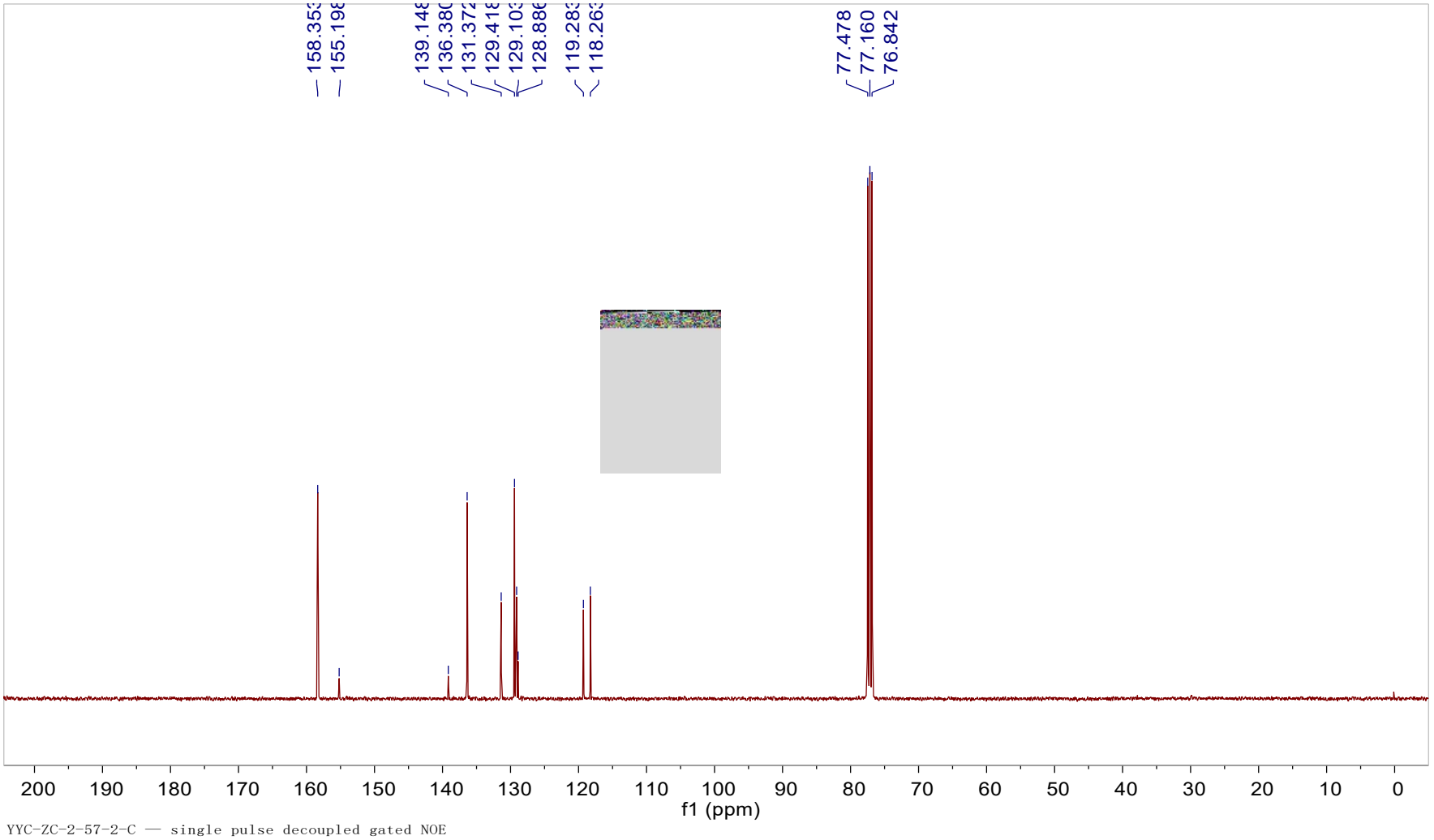
^{1}H NMR spectrum of **3ha**.



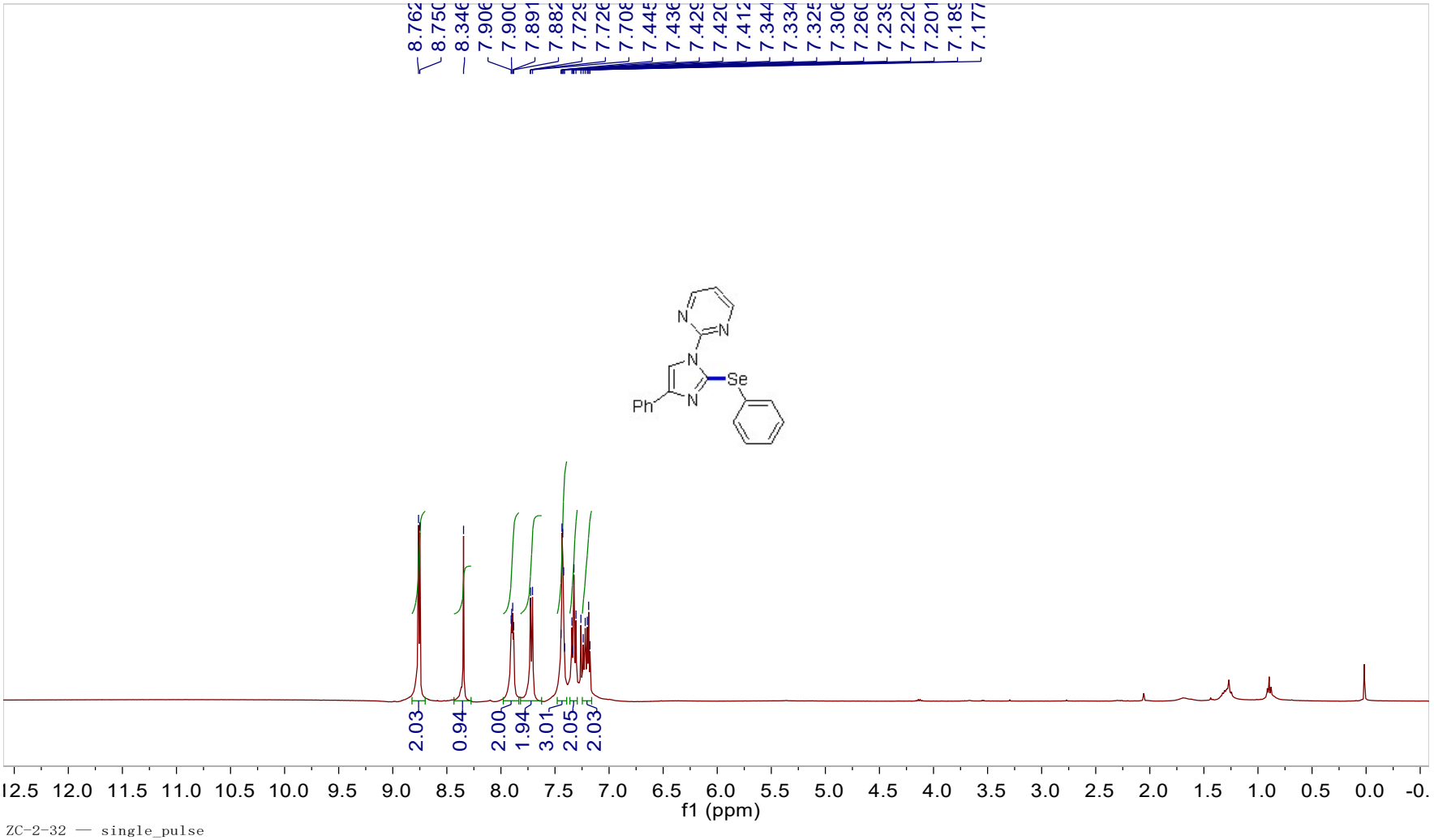
$^{13}C\{^{1}H\}$ NMR spectrum of **3ha**.



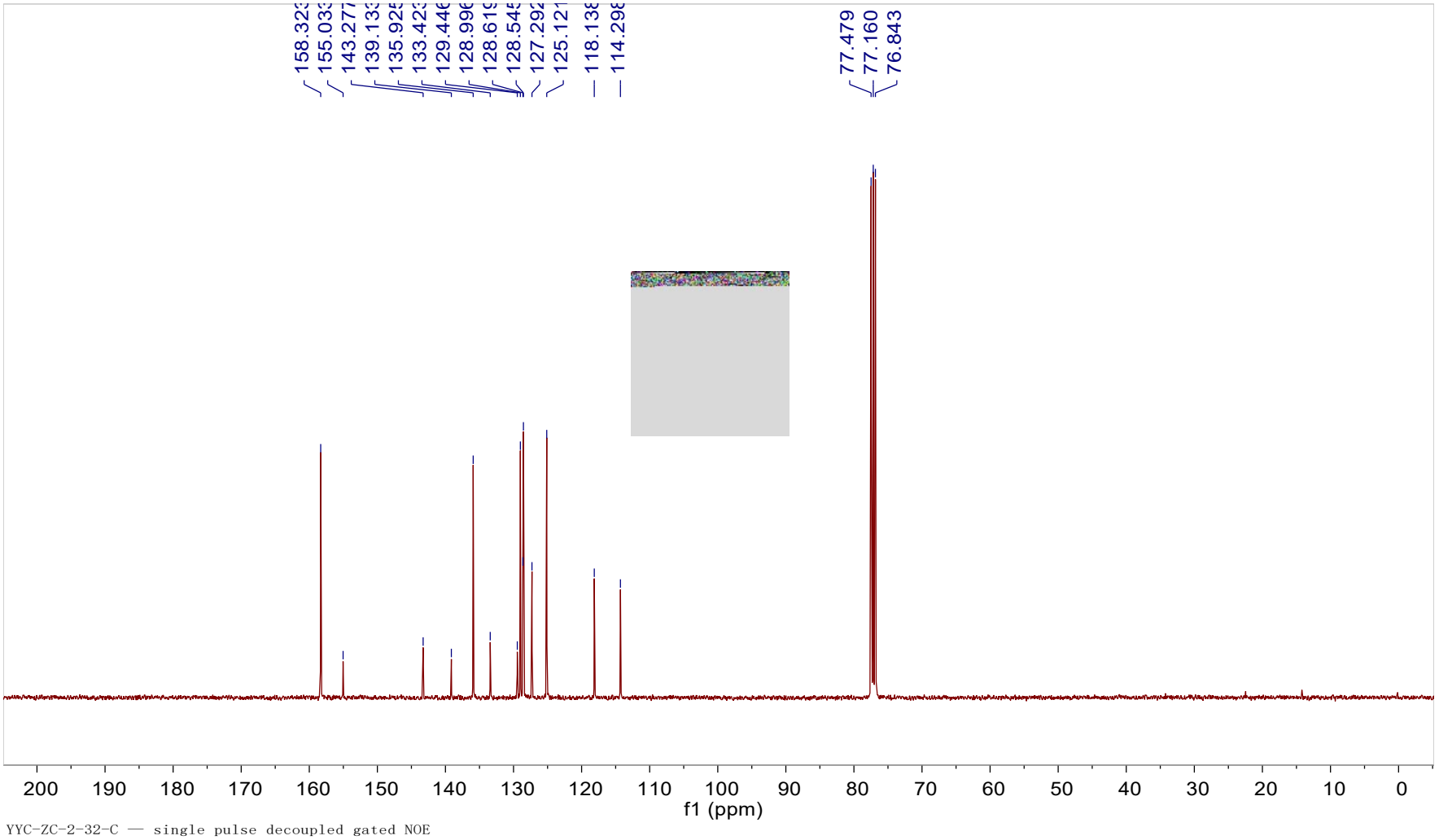
^{1}H NMR spectrum of **3ia**.



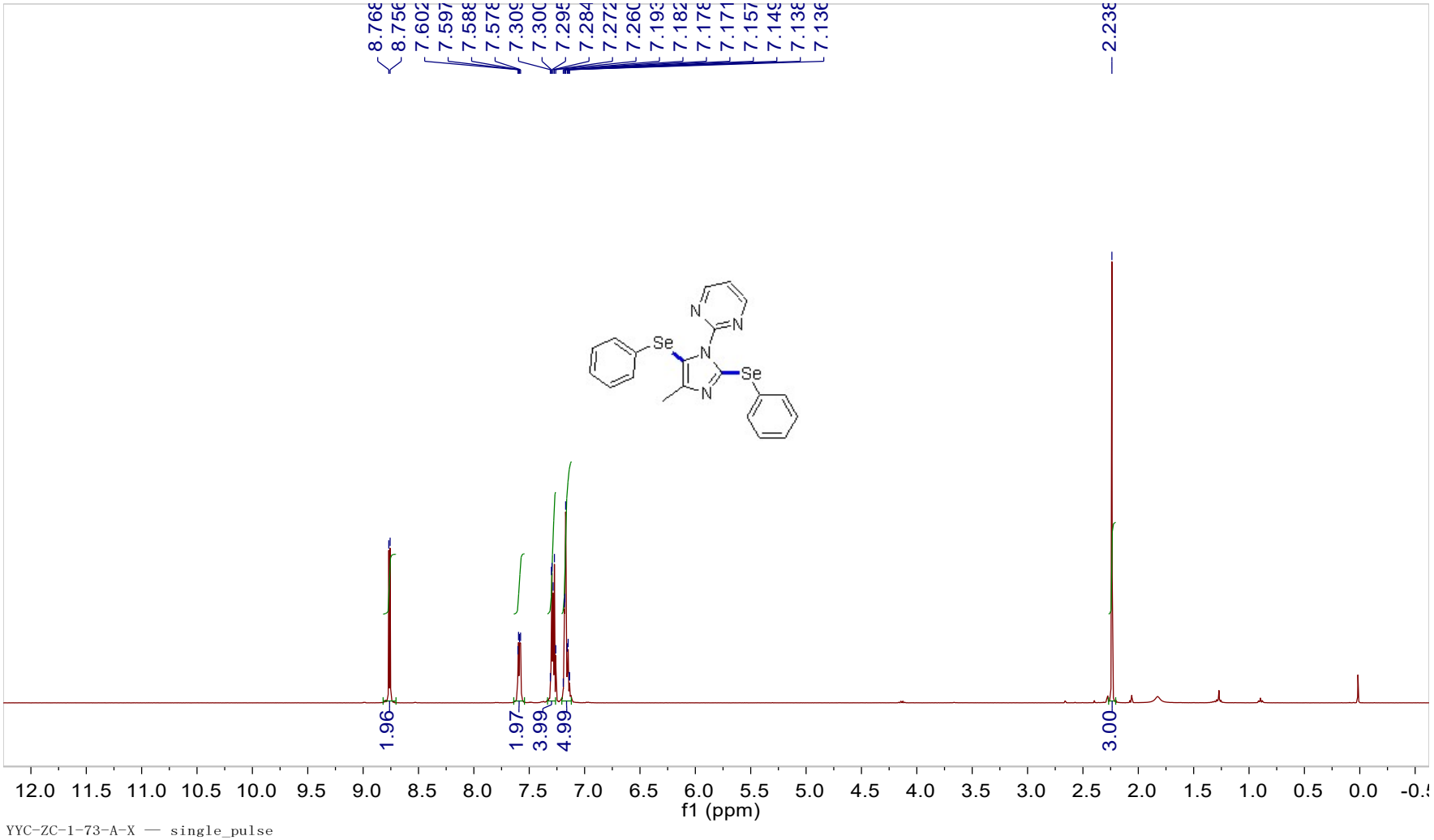
$^{13}C\{^{1}H\}$ NMR spectrum of **3ia**.



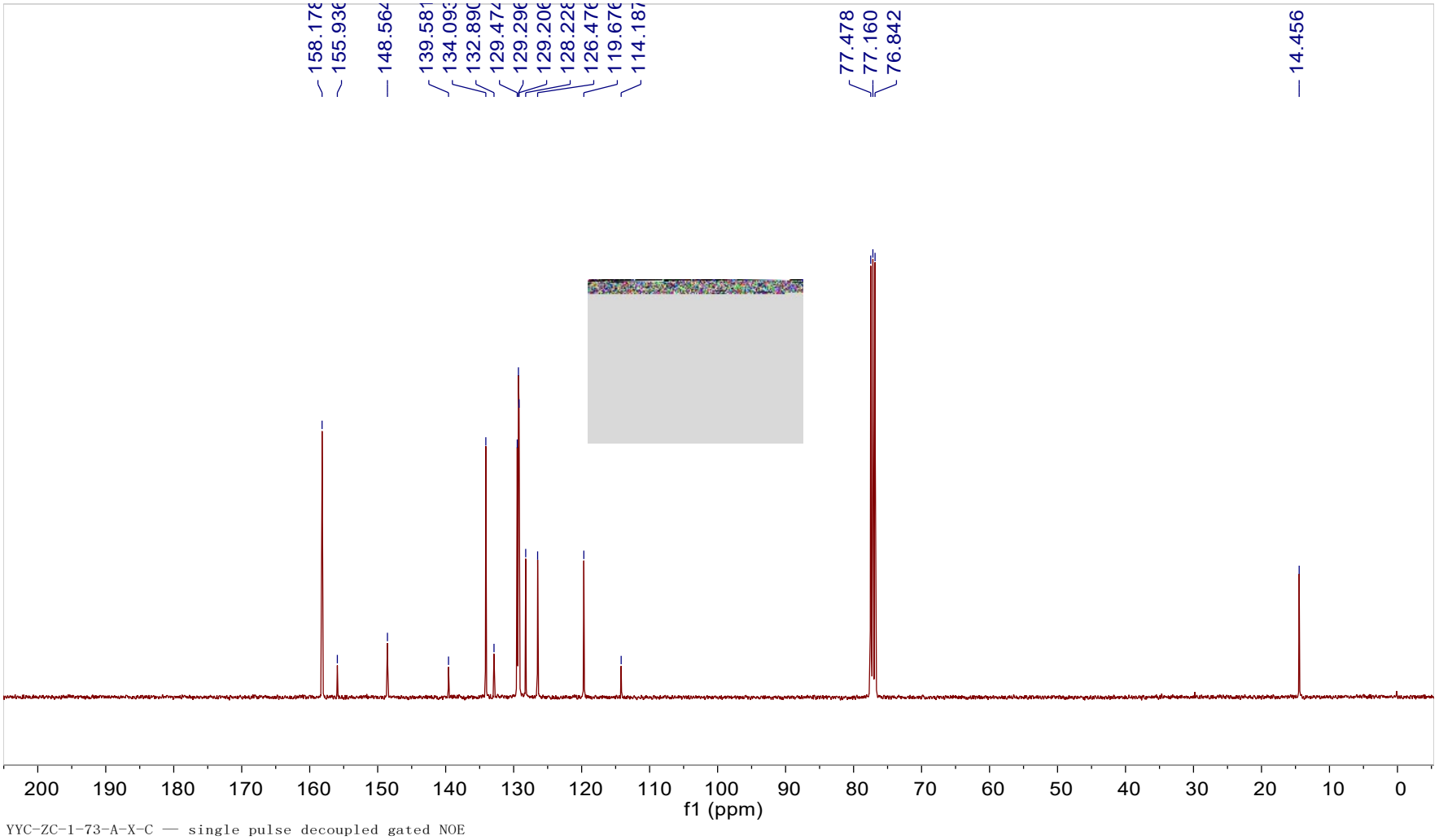
^{1}H NMR spectrum of **3ja**.



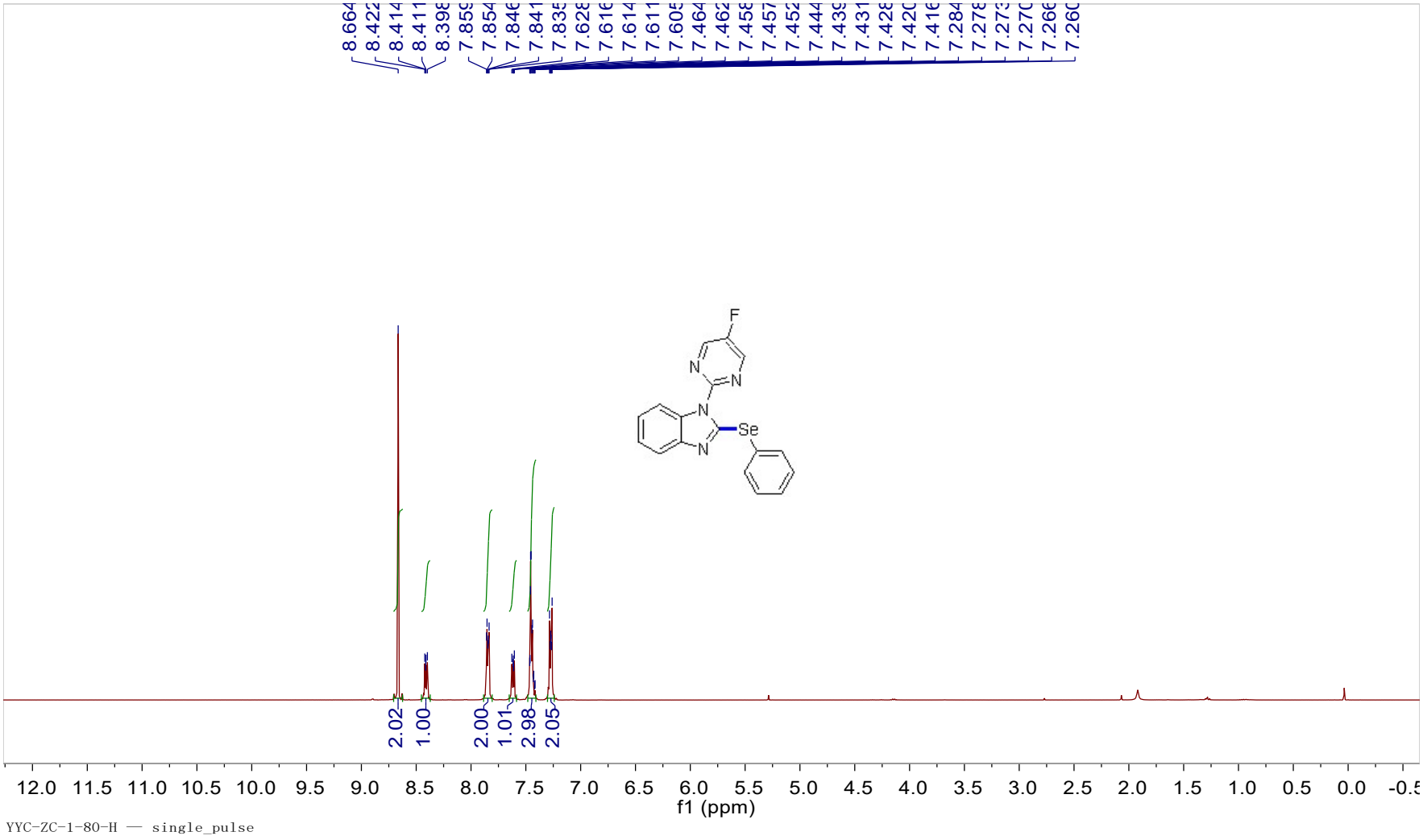
$^{13}C\{^{1}H\}$ NMR spectrum of **3ja**.



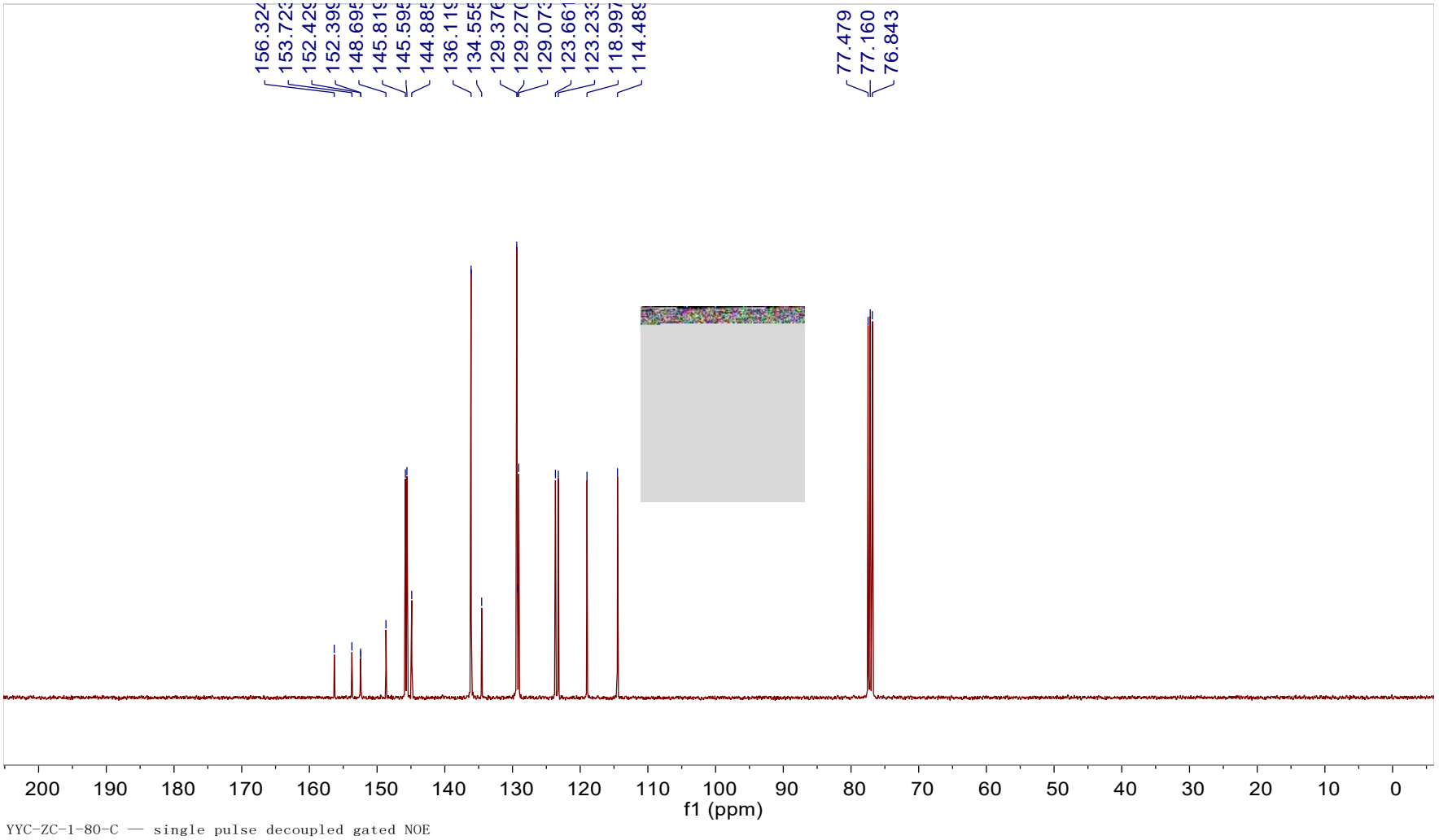
^{1}H NMR spectrum of **3ka**.



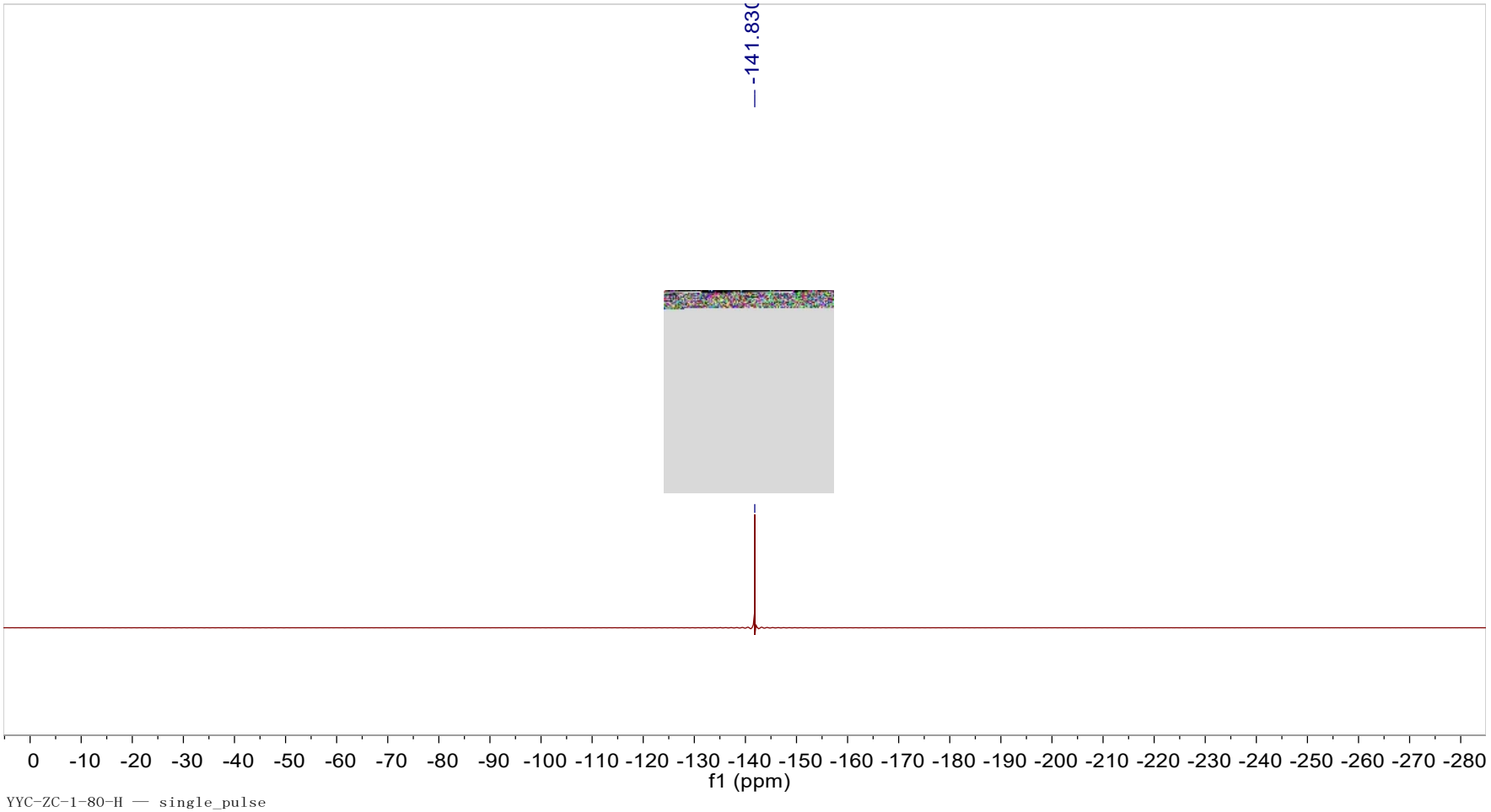
$^{13}C\{^{1}H\}$ NMR spectrum of **3ka**.



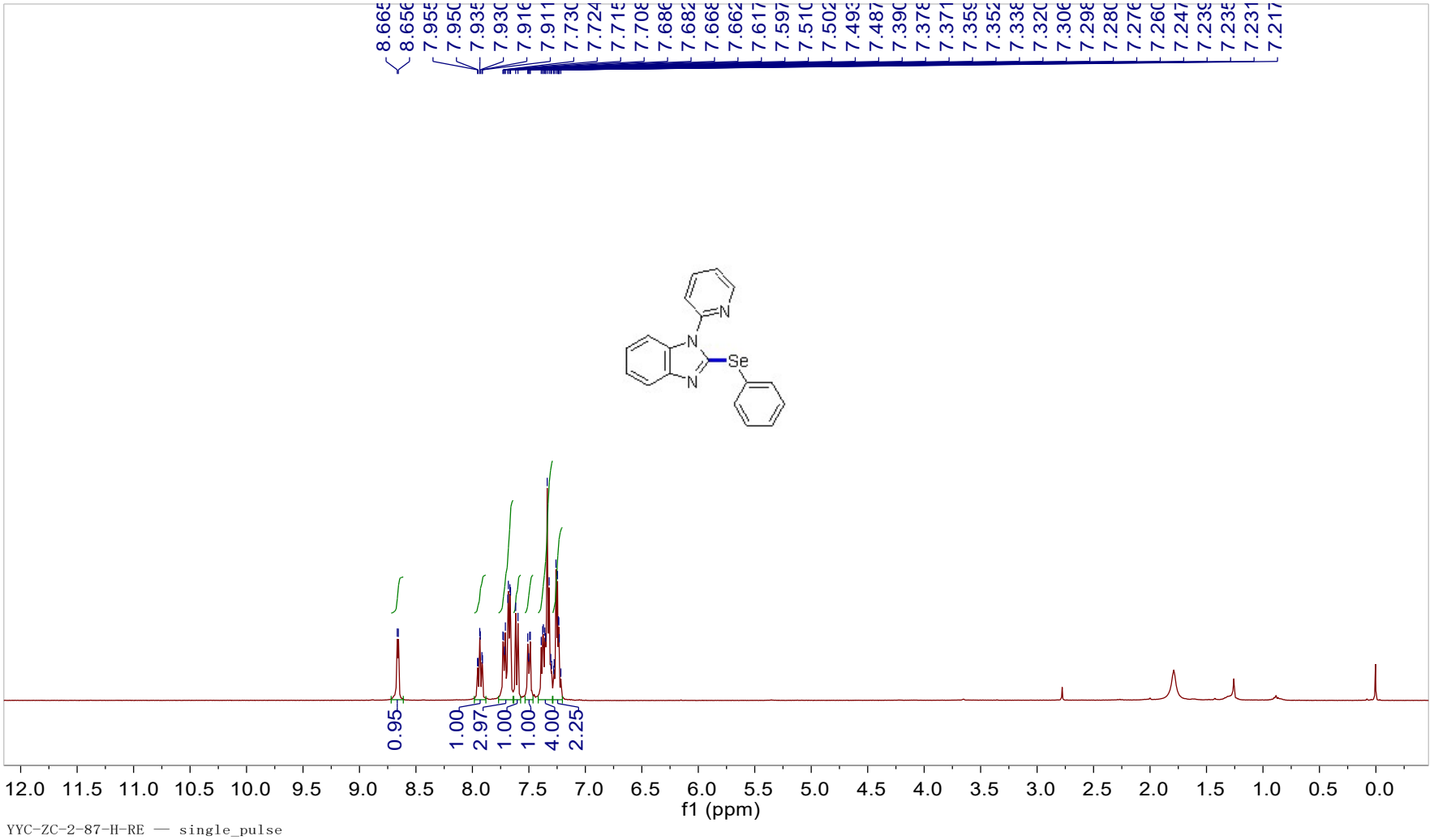
^{1}H NMR spectrum of **3la**.



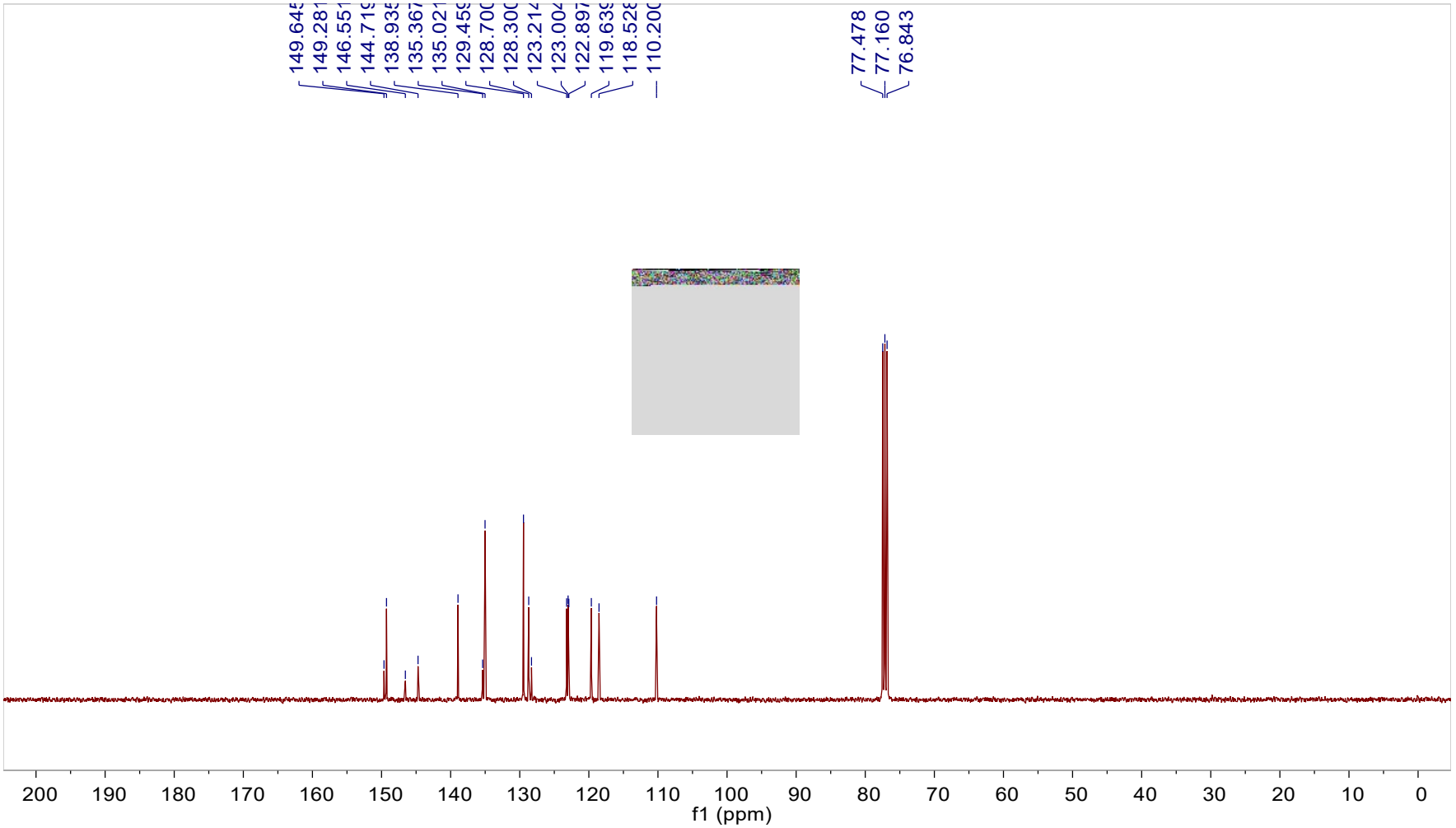
$^{13}C\{^{1}H\}$ NMR spectrum of **3la**.



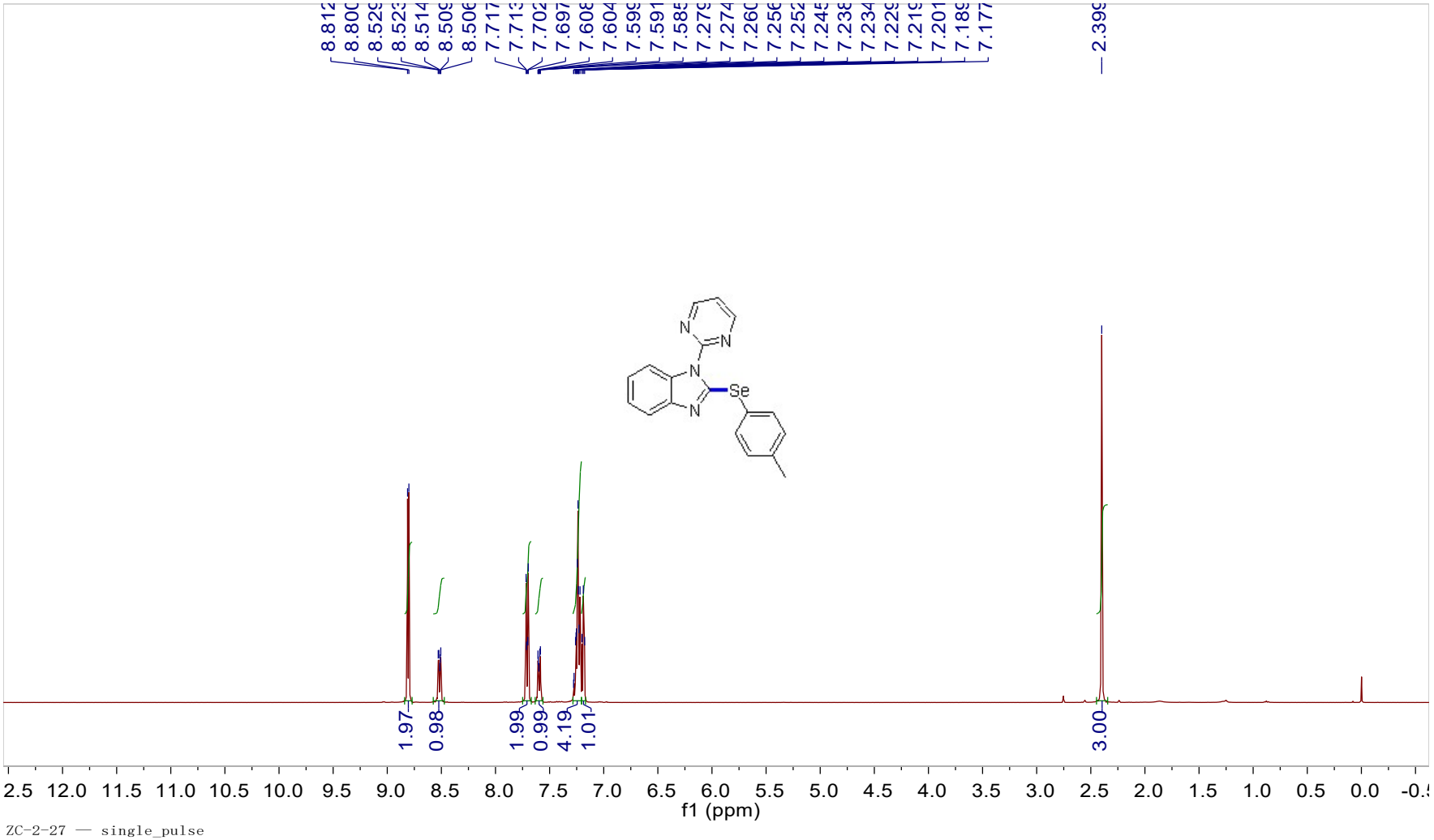
$^{19}F\{^{1}H\}$ NMR spectrum of **3la**.



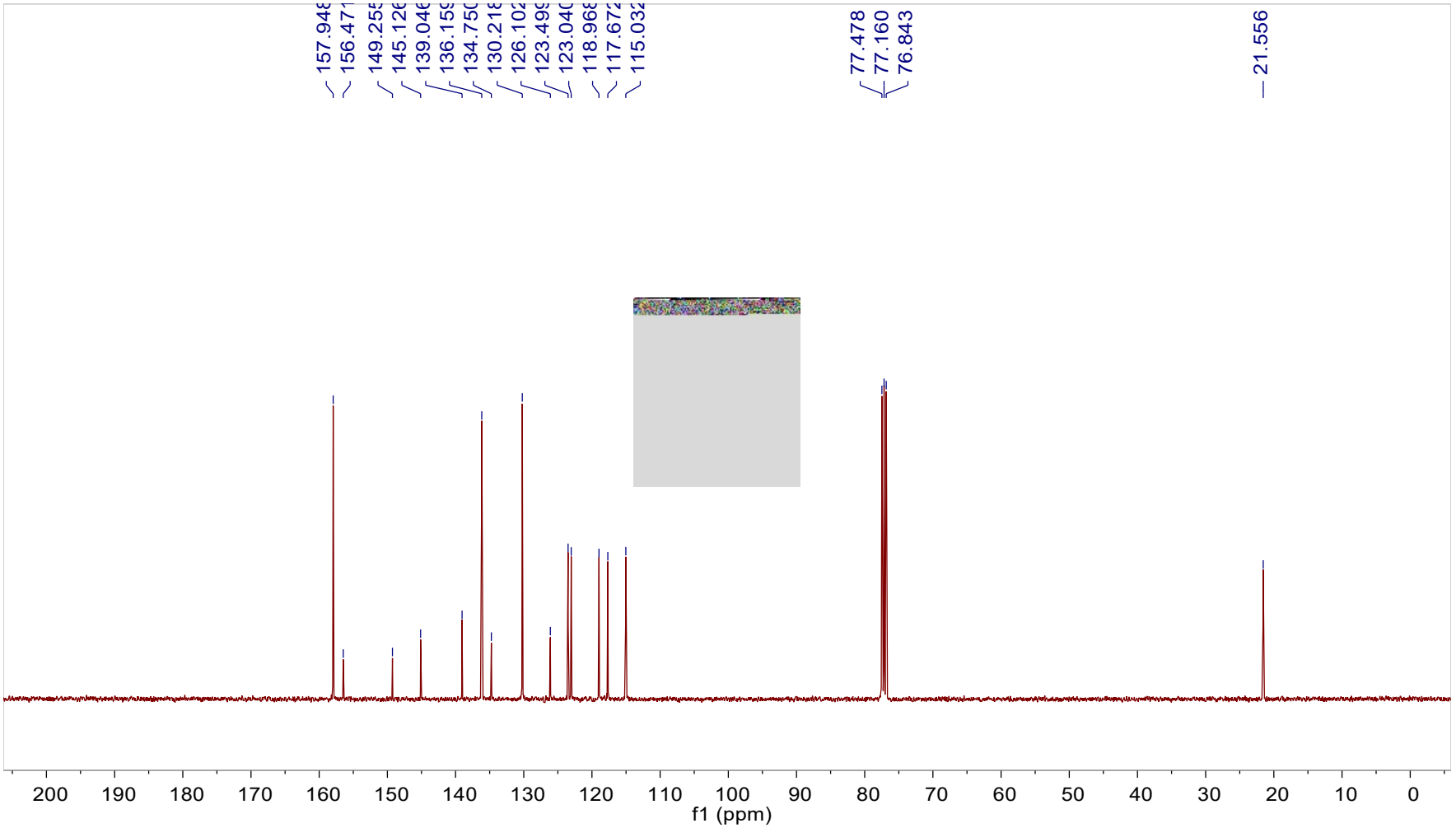
^{1}H NMR spectrum of **3ma**.



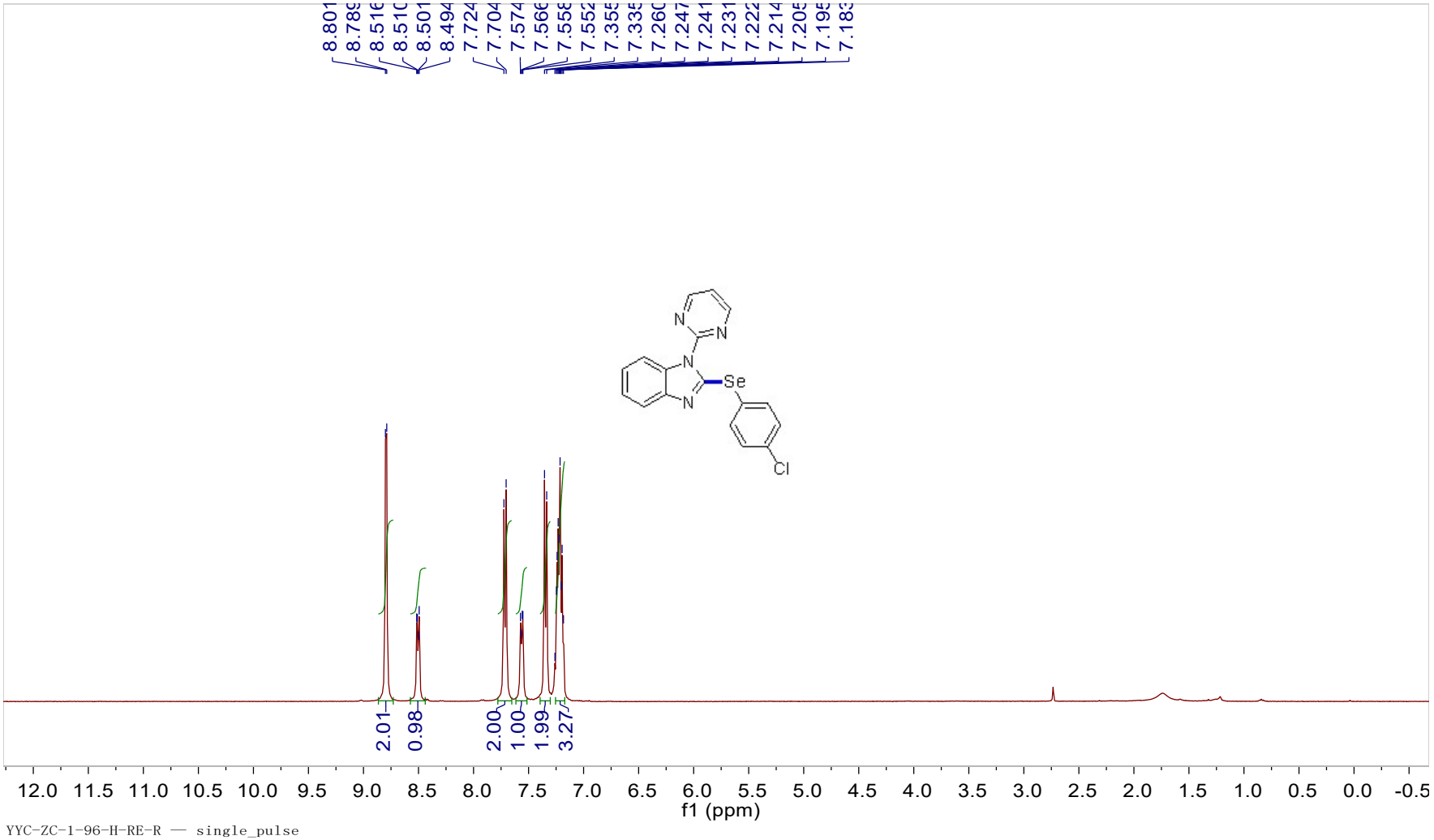
$^{13}C\{^{1}H\}$ NMR spectrum of **3ma**.



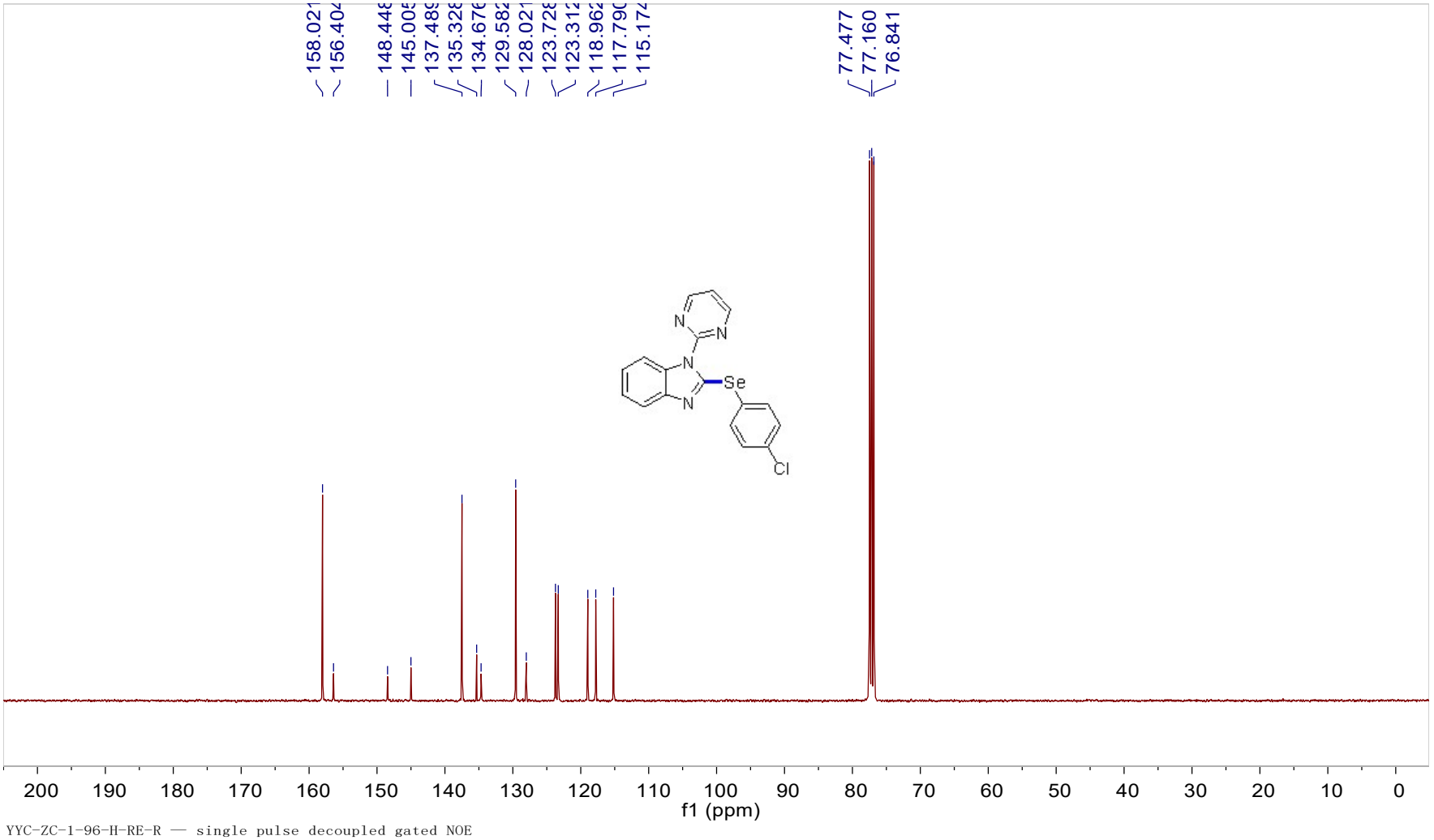
^{1}H NMR spectrum of **3ab**.



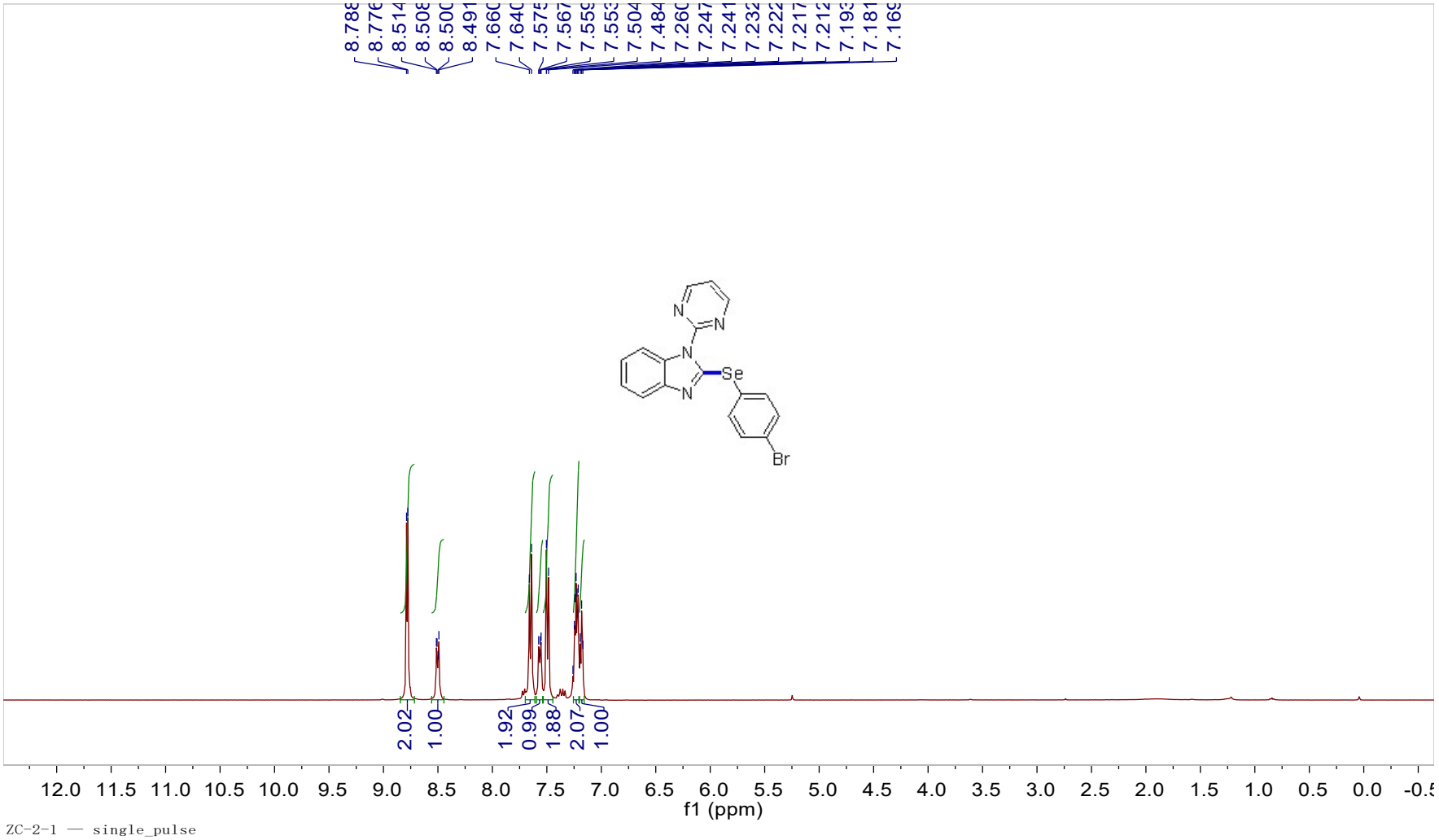
$^{13}C\{^{1}H\}$ NMR spectrum of **3ab**.



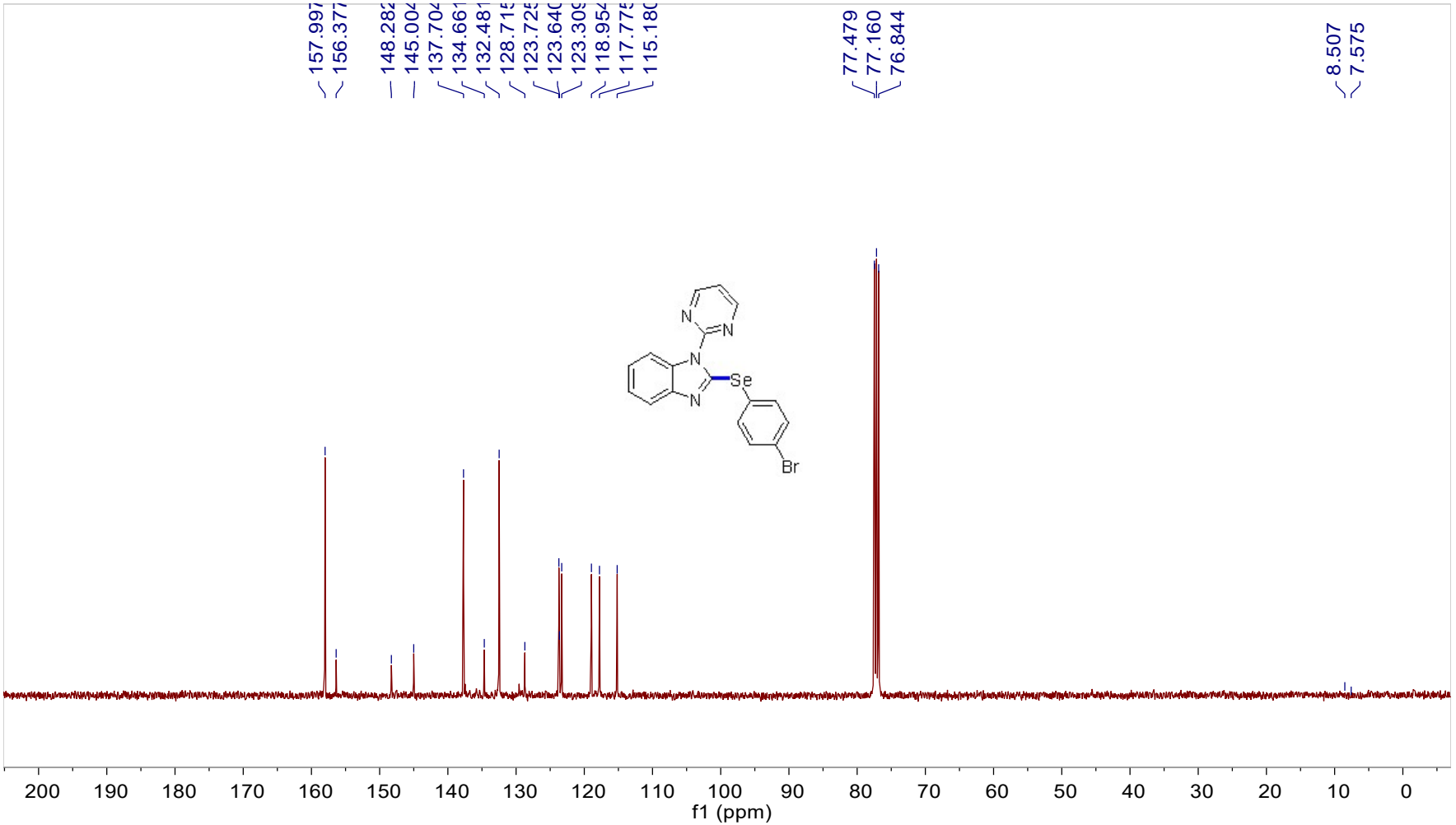
^{1}H NMR spectrum of **3ac**.



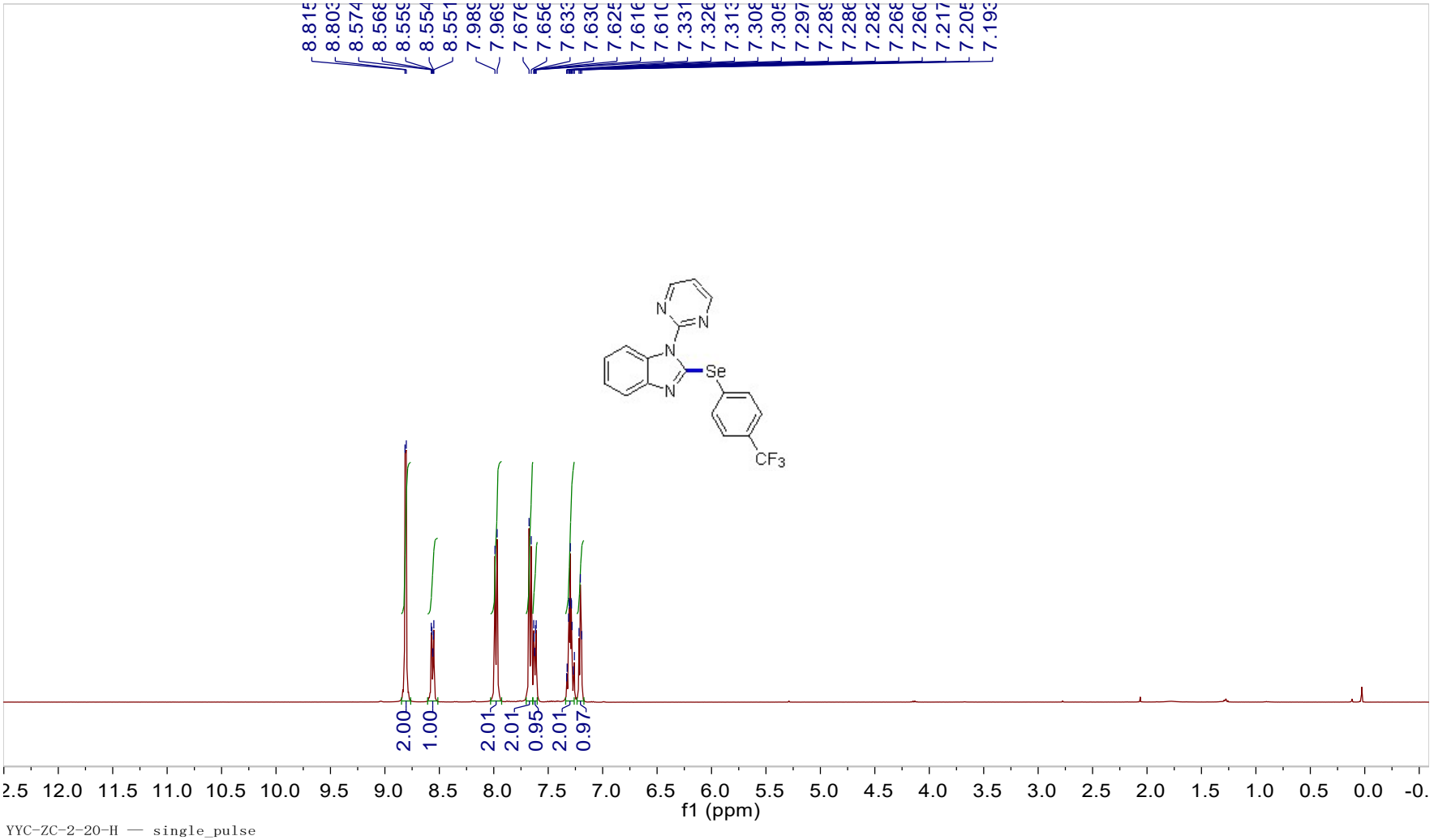
$^{13}C\{^{1}H\}$ NMR spectrum of **3ac**.



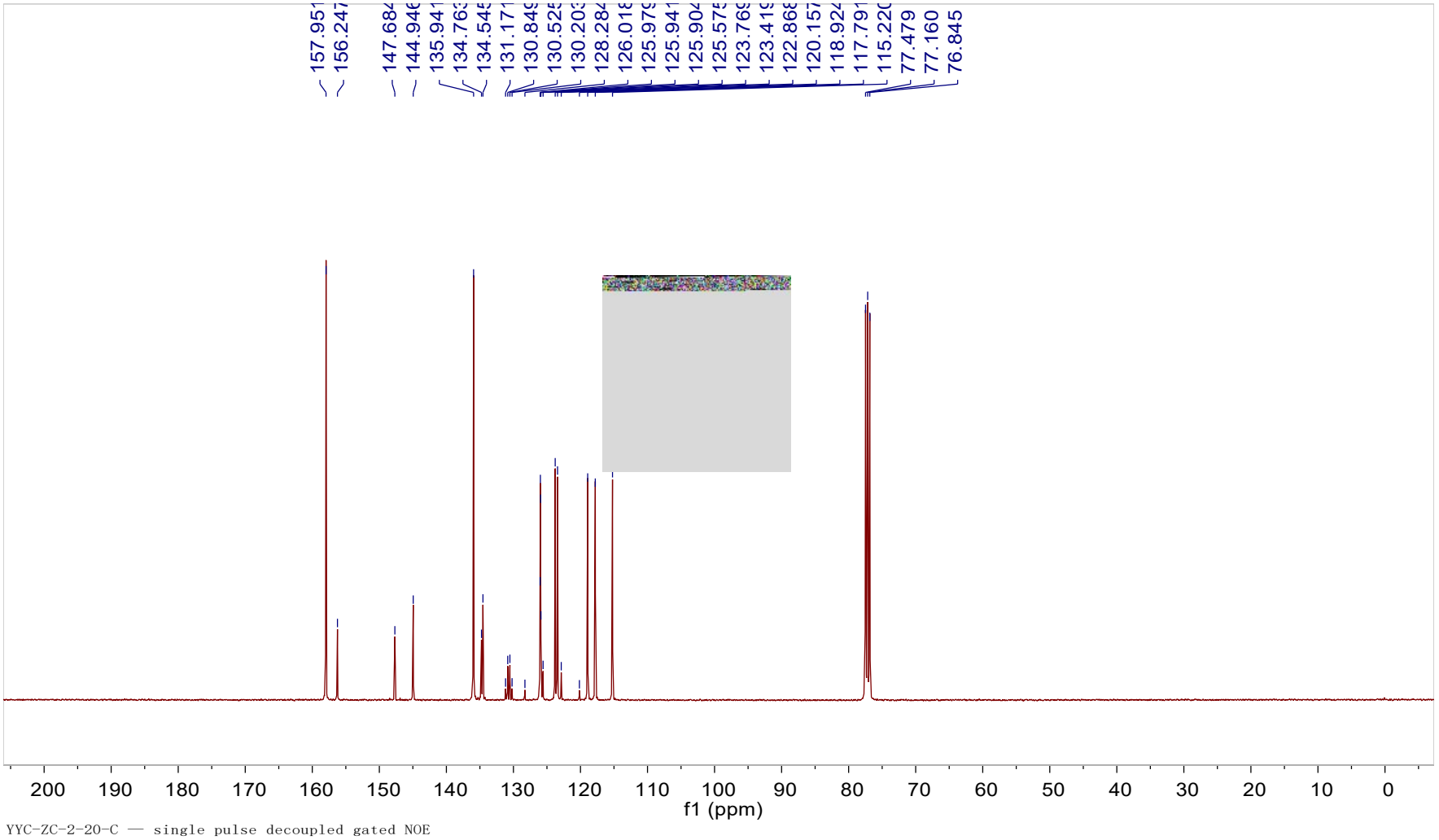
^{1}H NMR spectrum of **3ad**.



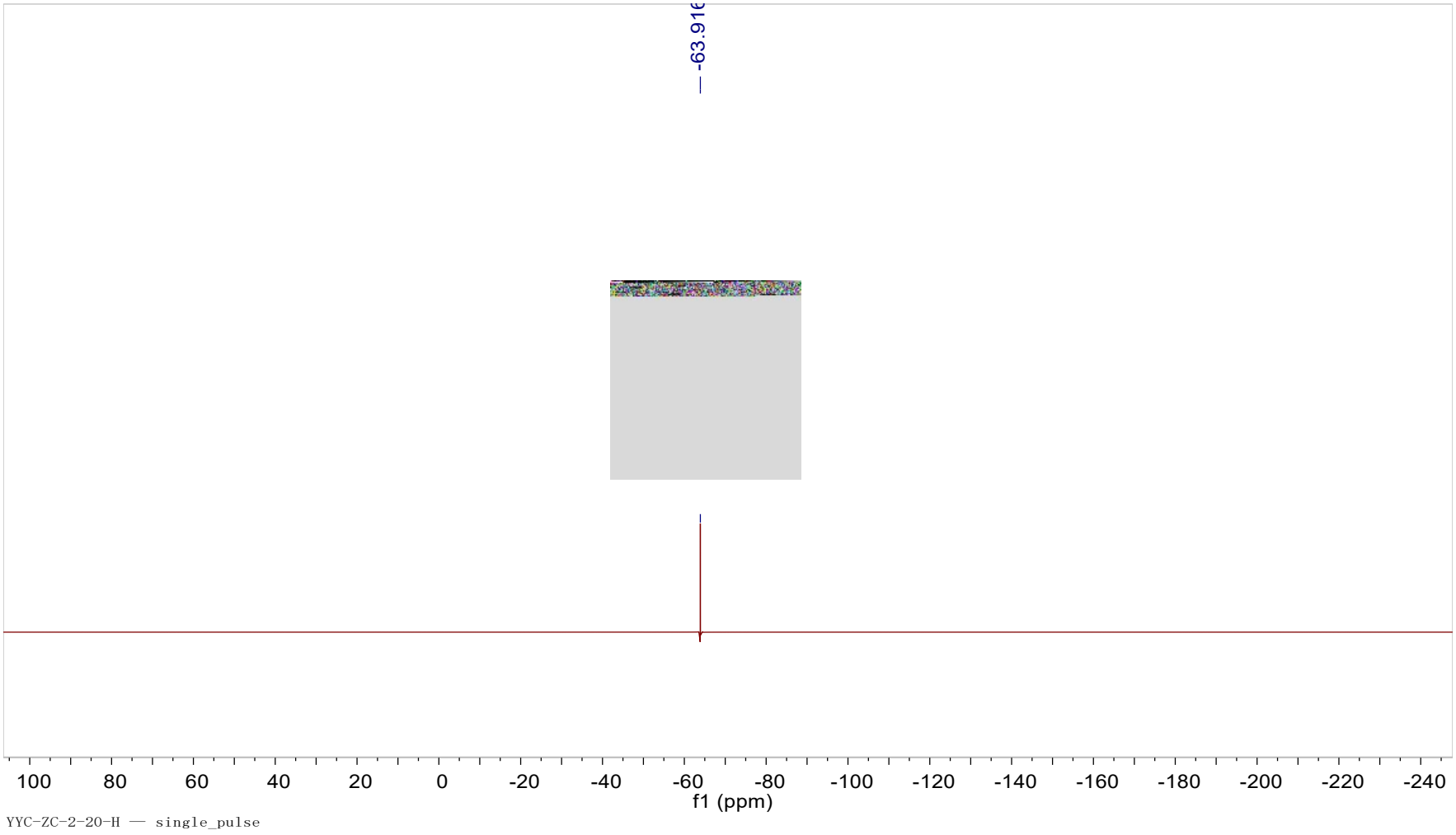
$^{13}C\{^{1}H\}$ NMR spectrum of **3ad**.



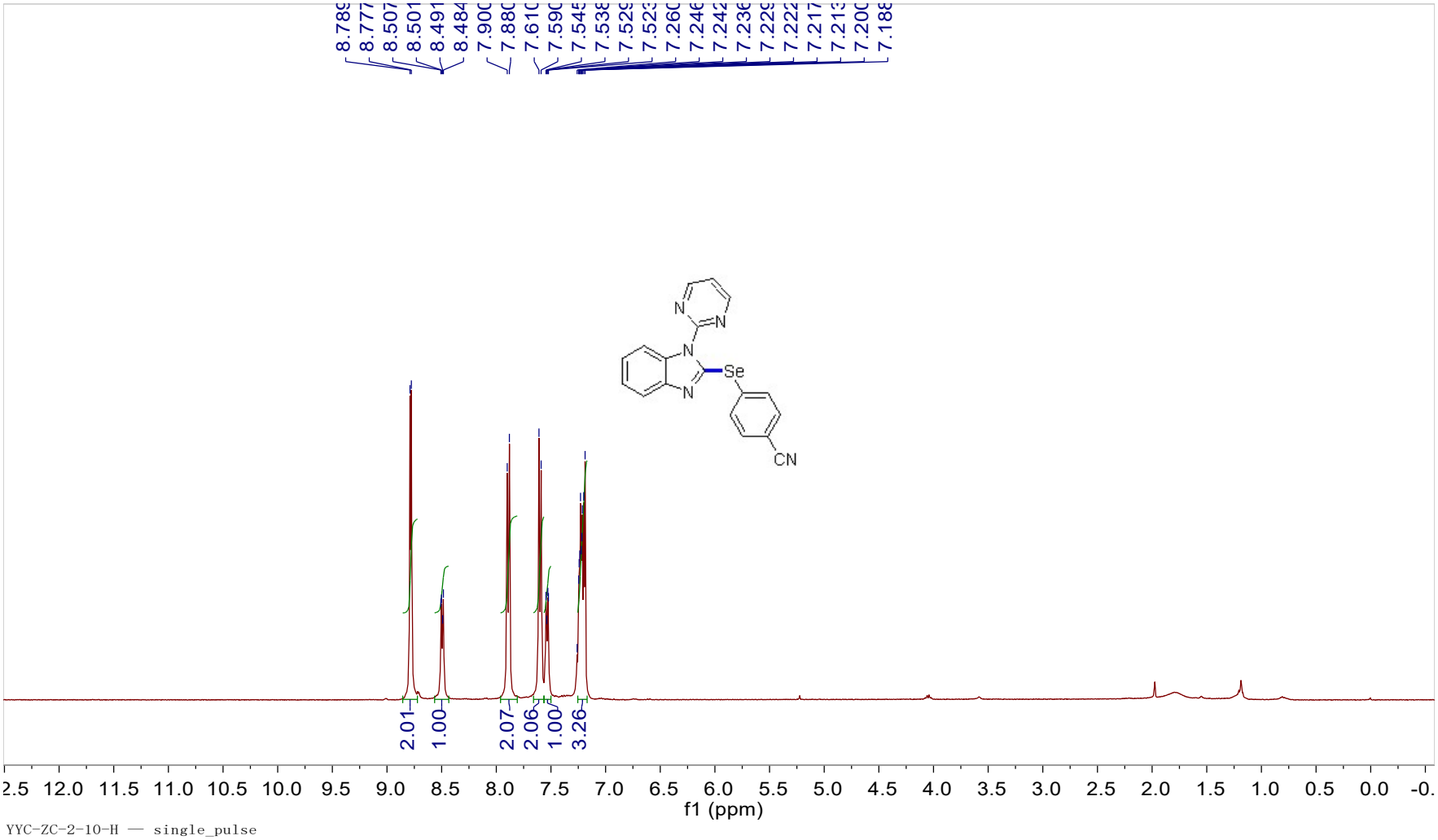
^{1}H NMR spectrum of **3ae**.



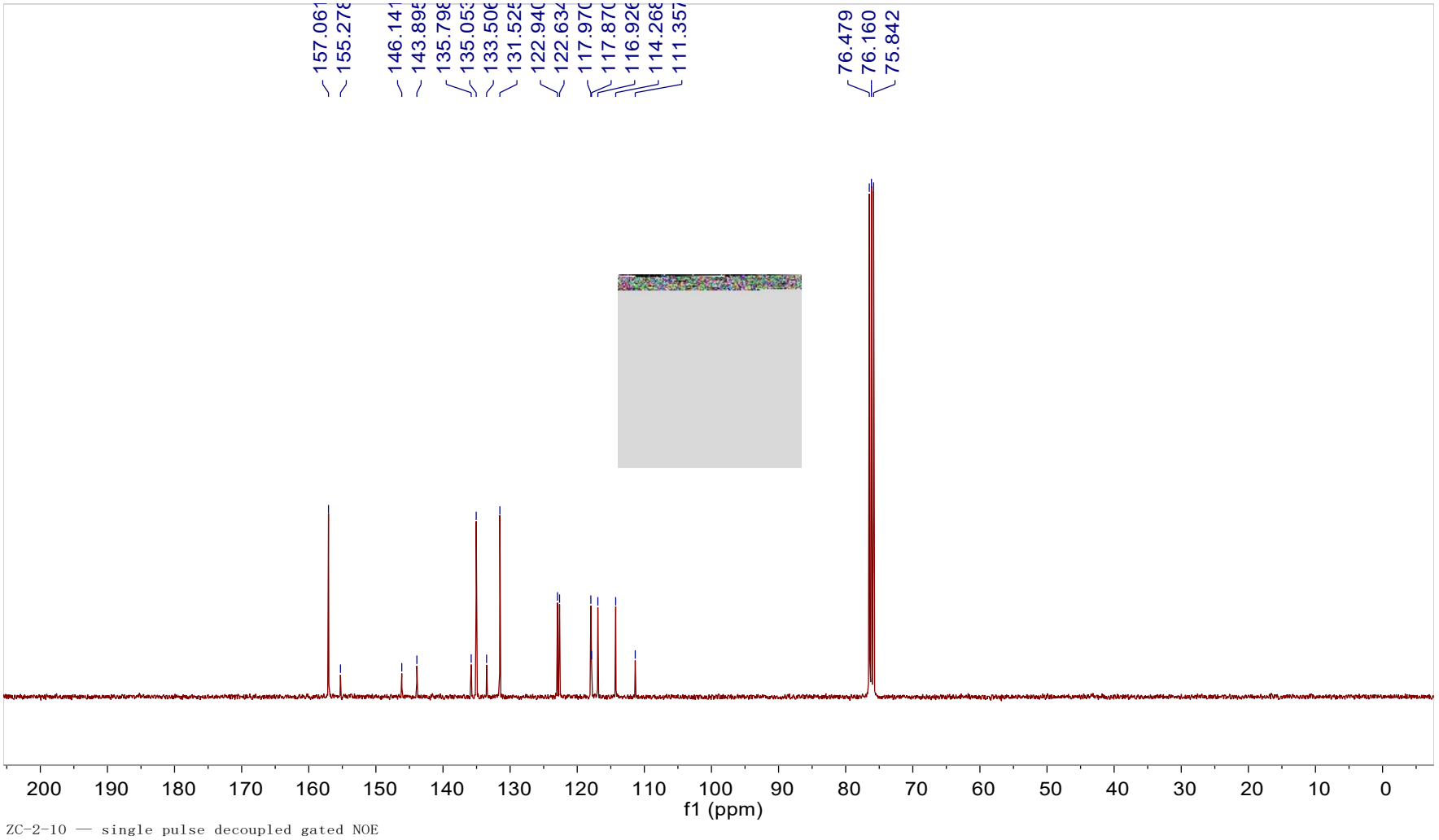
$^{13}C\{^{1}H\}$ NMR spectrum of **3ae**.



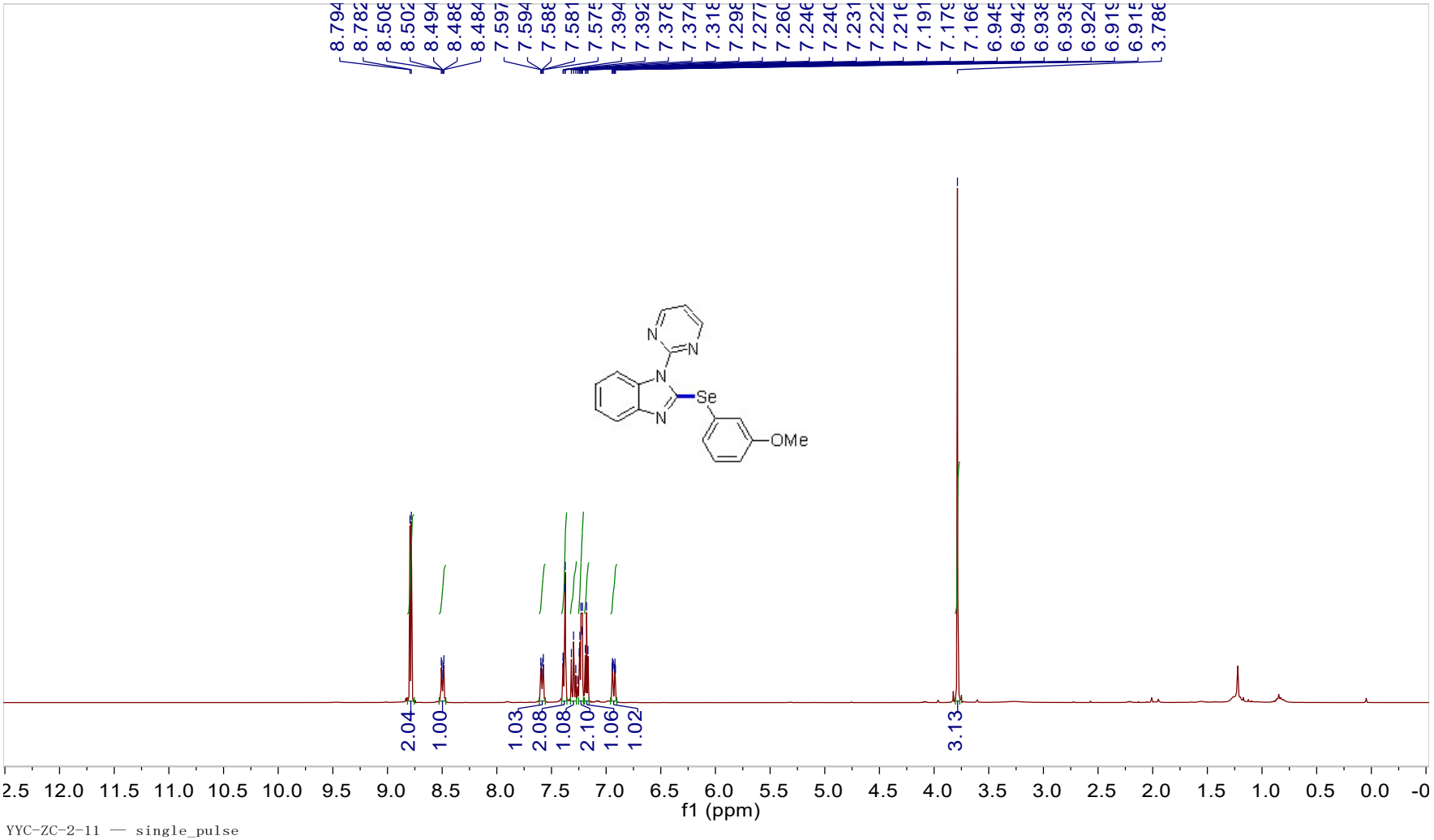
$^{19}F\{^{1}H\}$ NMR spectrum of **3ae**.



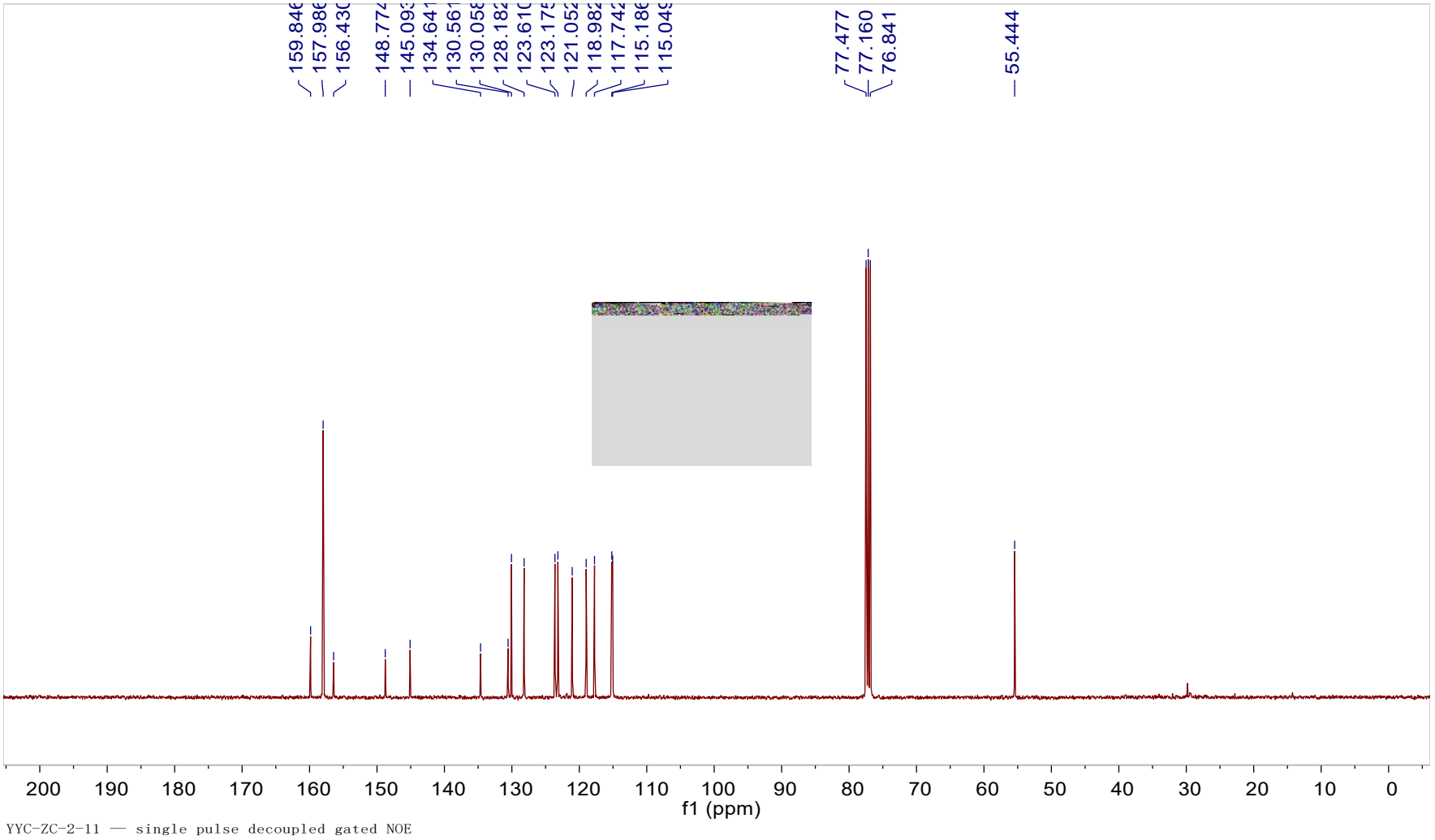
^{1}H NMR spectrum of **3af**.



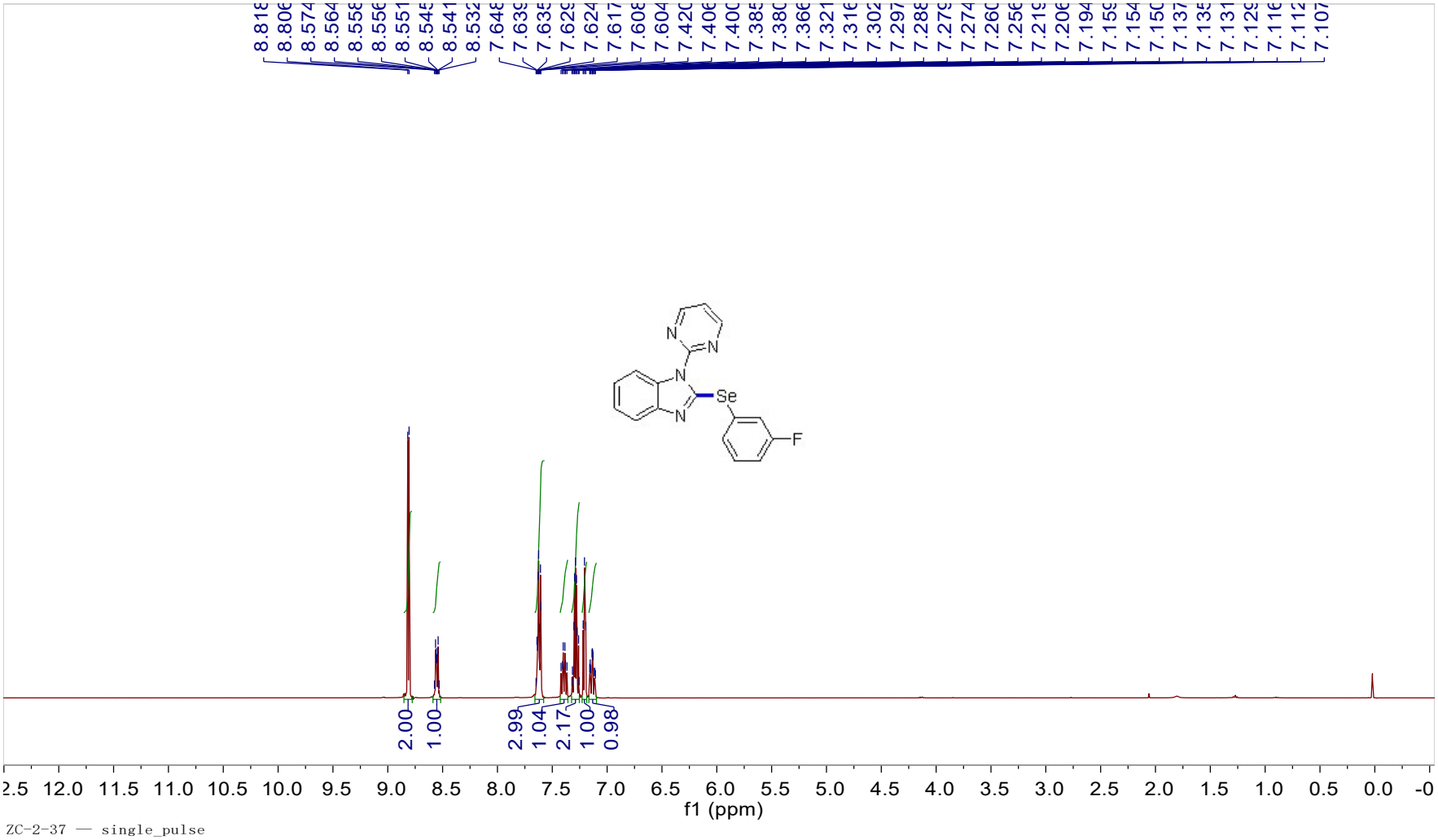
$^{13}C\{^{1}H\}$ NMR spectrum of **3af**.



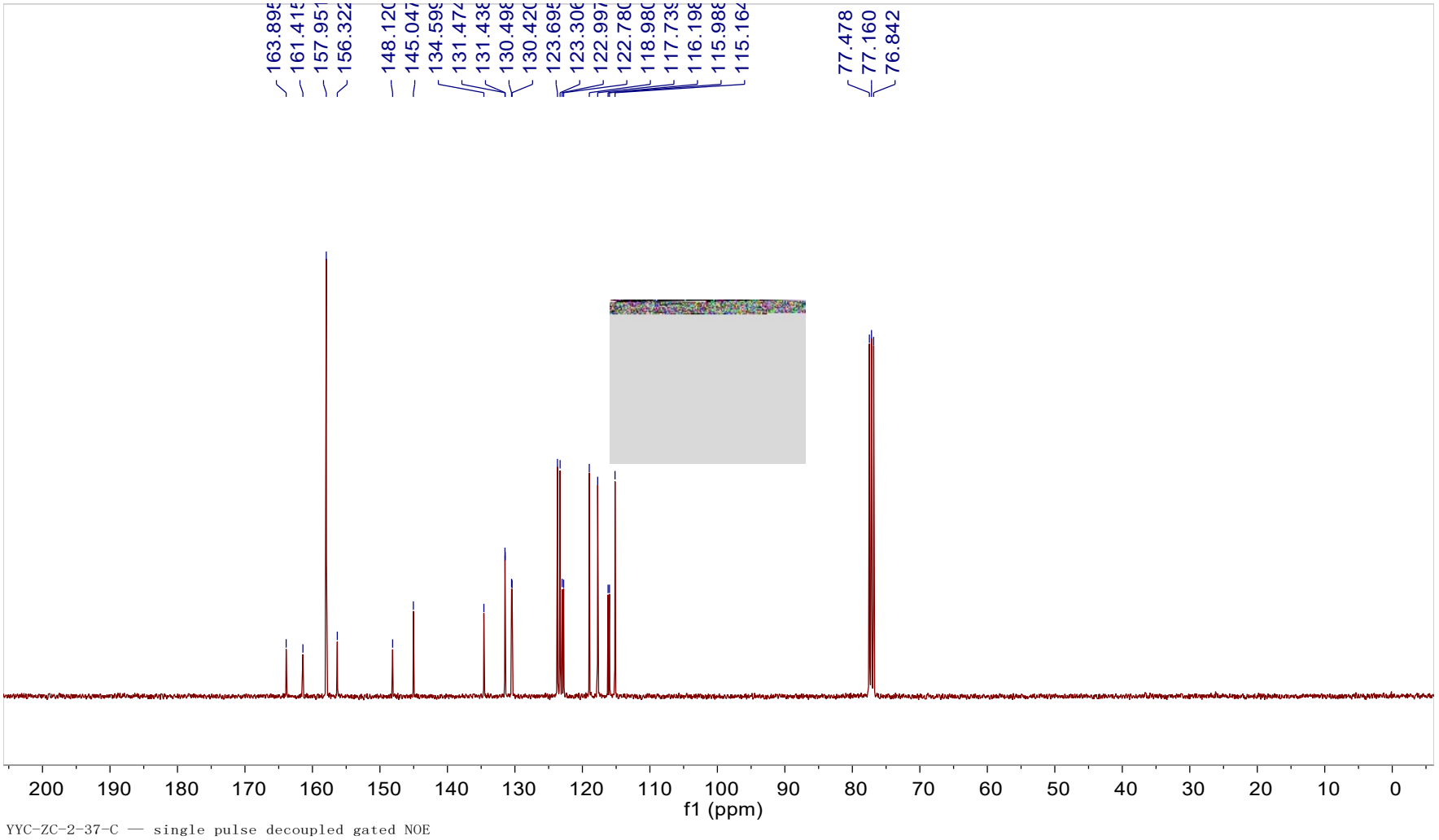
^{1}H NMR spectrum of **3ag**.



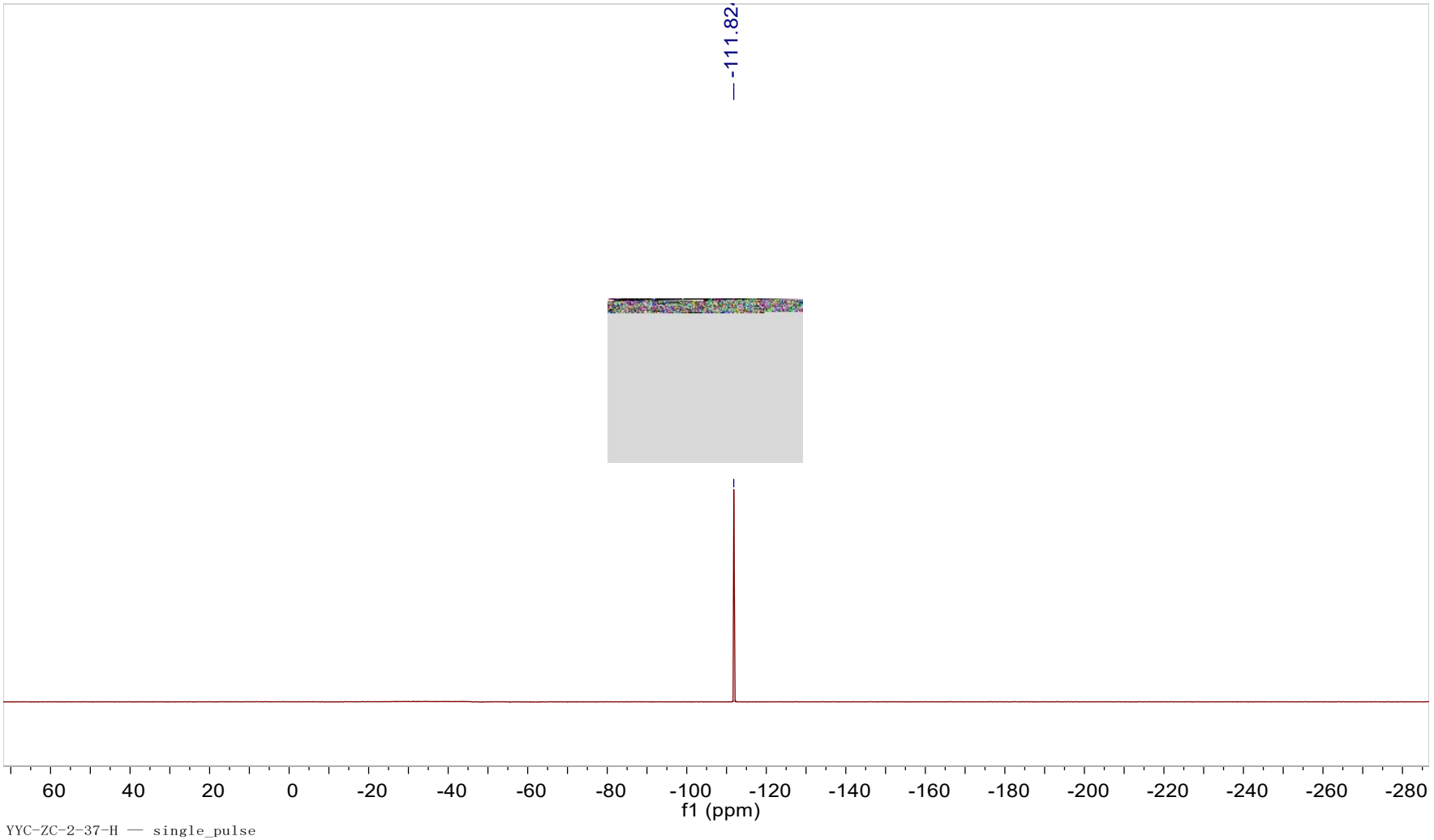
$^{13}C\{^{1}H\}$ NMR spectrum of **3ag**.



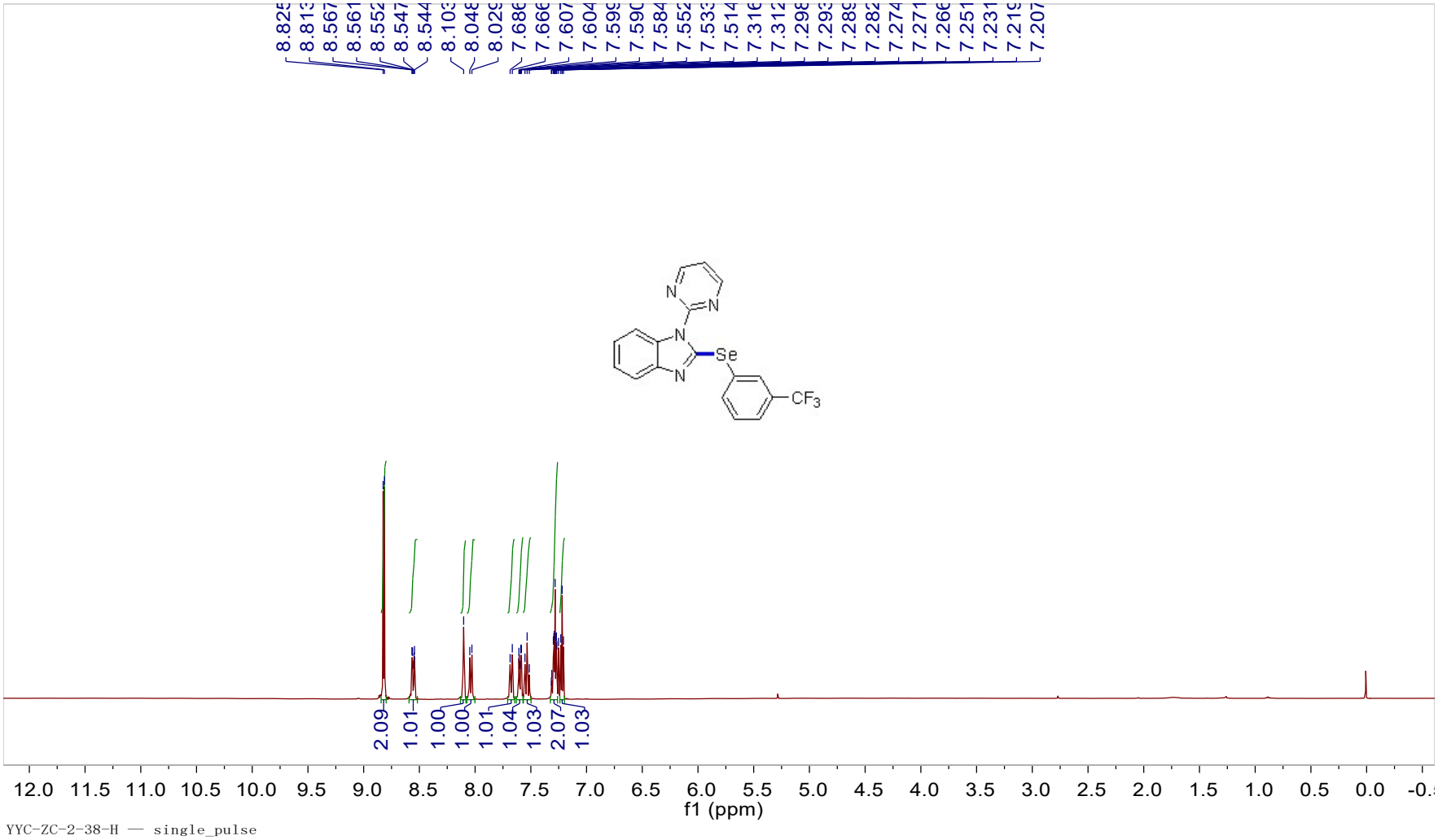
^{1}H NMR spectrum of **3ah**.



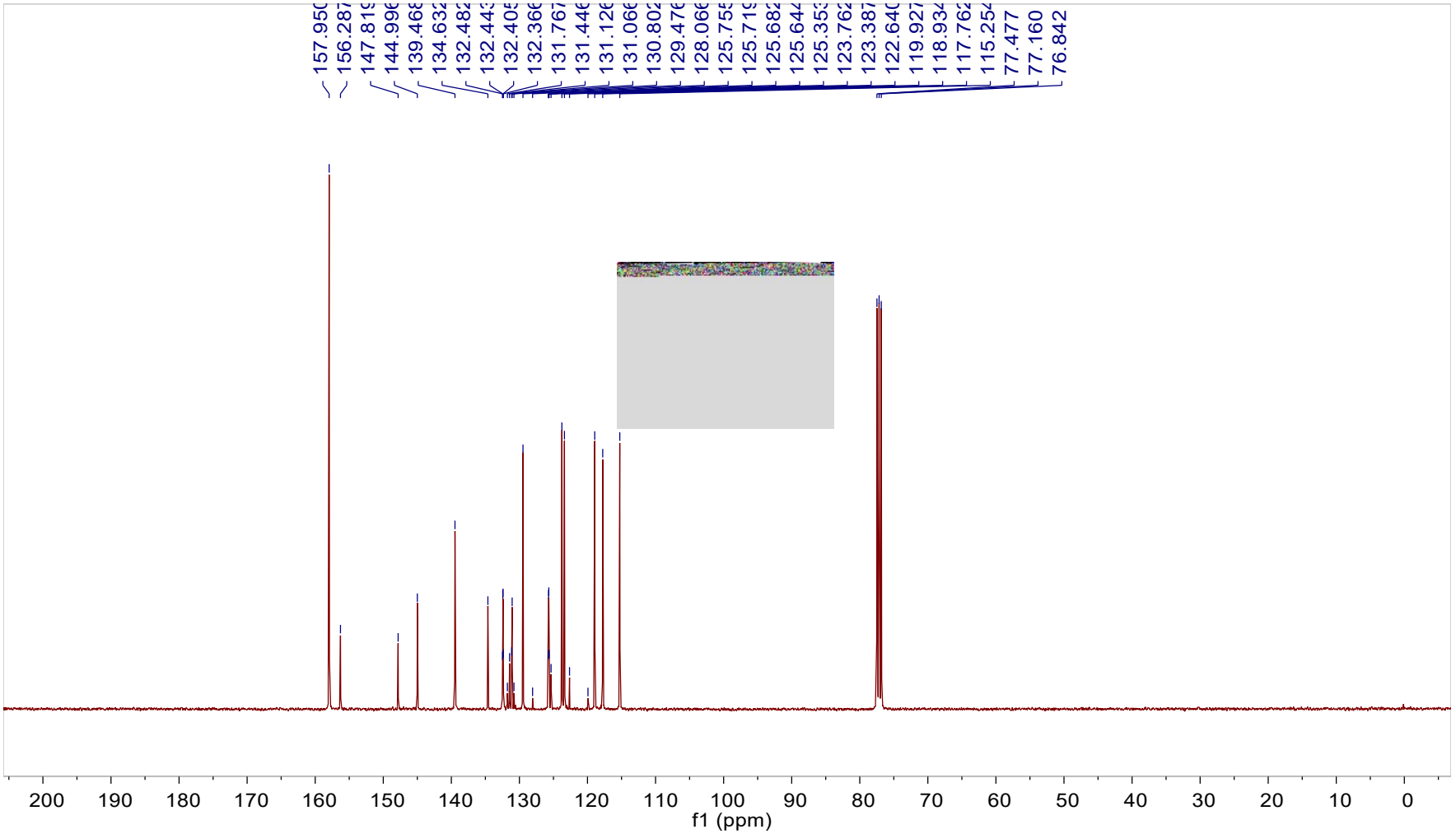
$^{13}C\{^{1}H\}$ NMR spectrum of **3ah**.



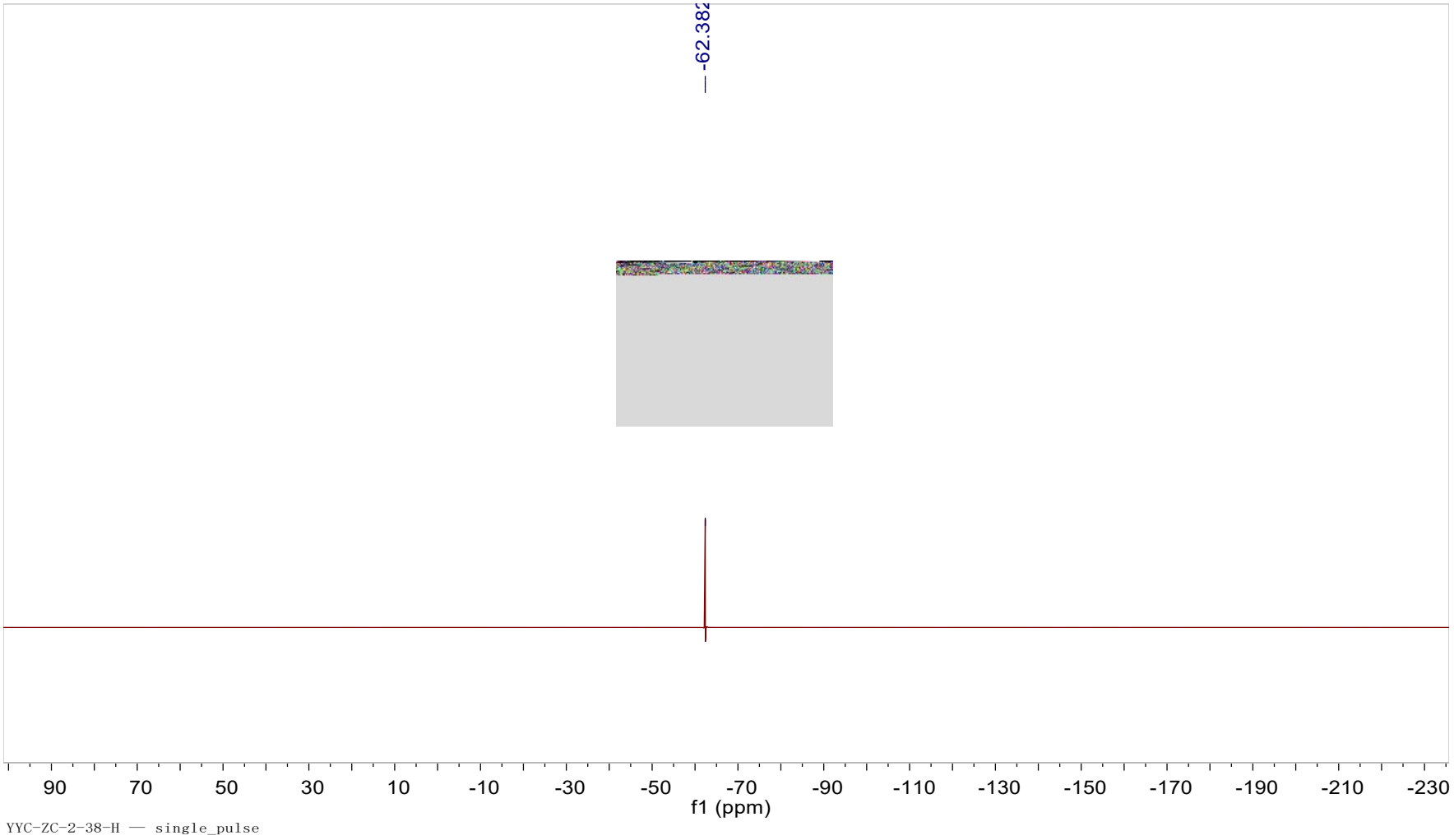
$^{19}F\{^{1}H\}$ NMR spectrum of **3ah**.



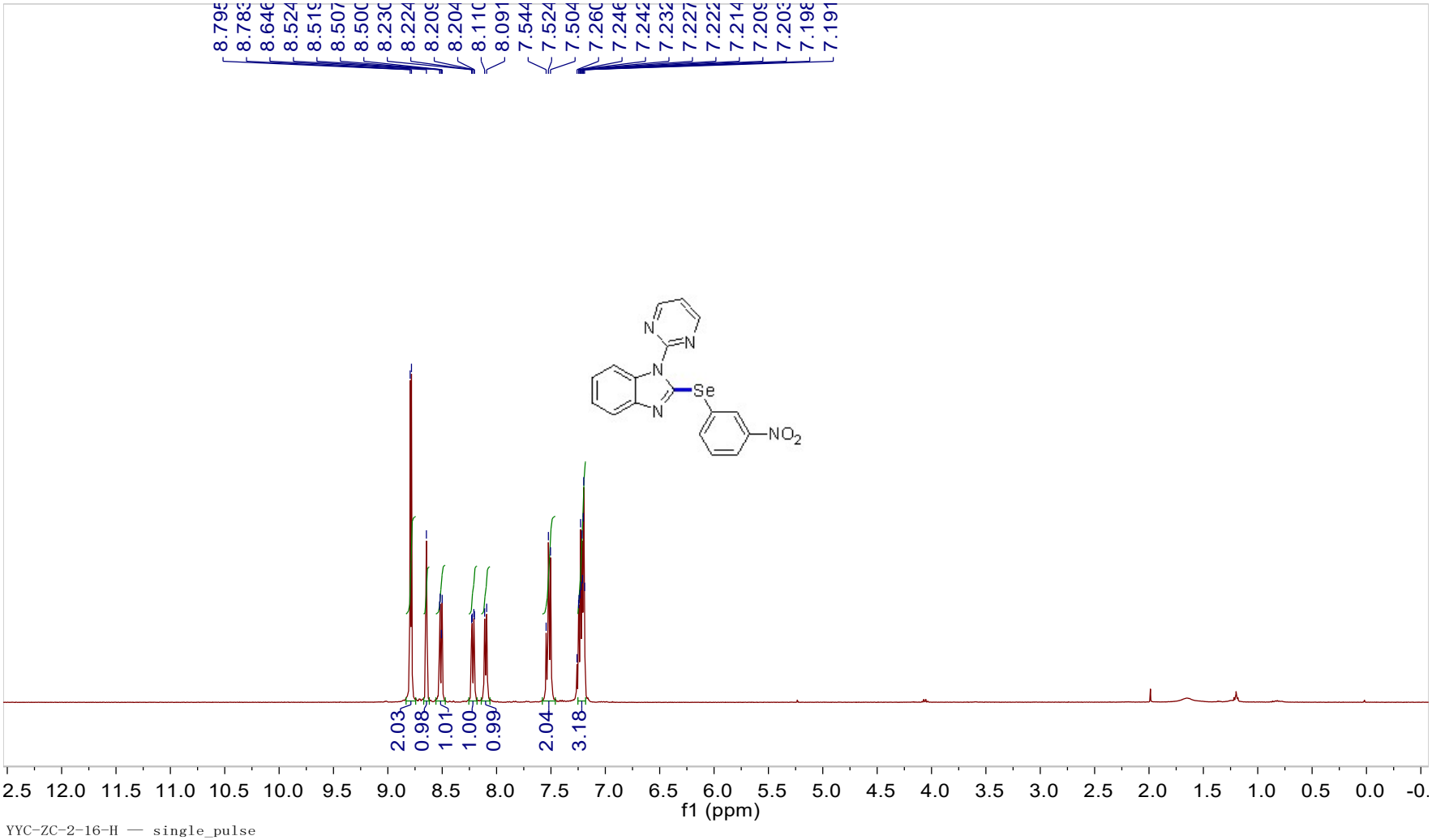
^{1}H NMR spectrum of **3ai**.



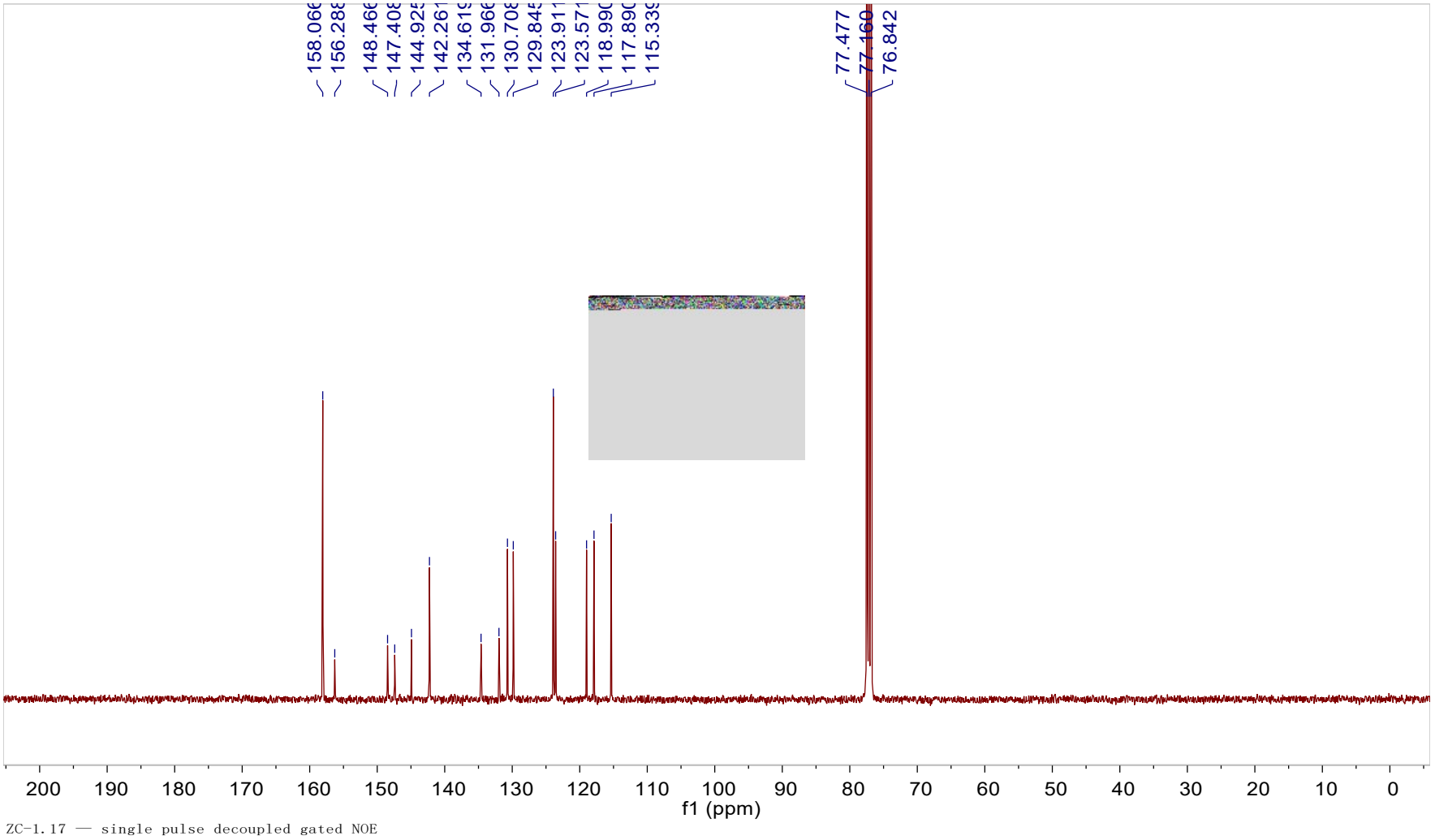
$^{13}C\{^{1}H\}$ NMR spectrum of **3ai**.



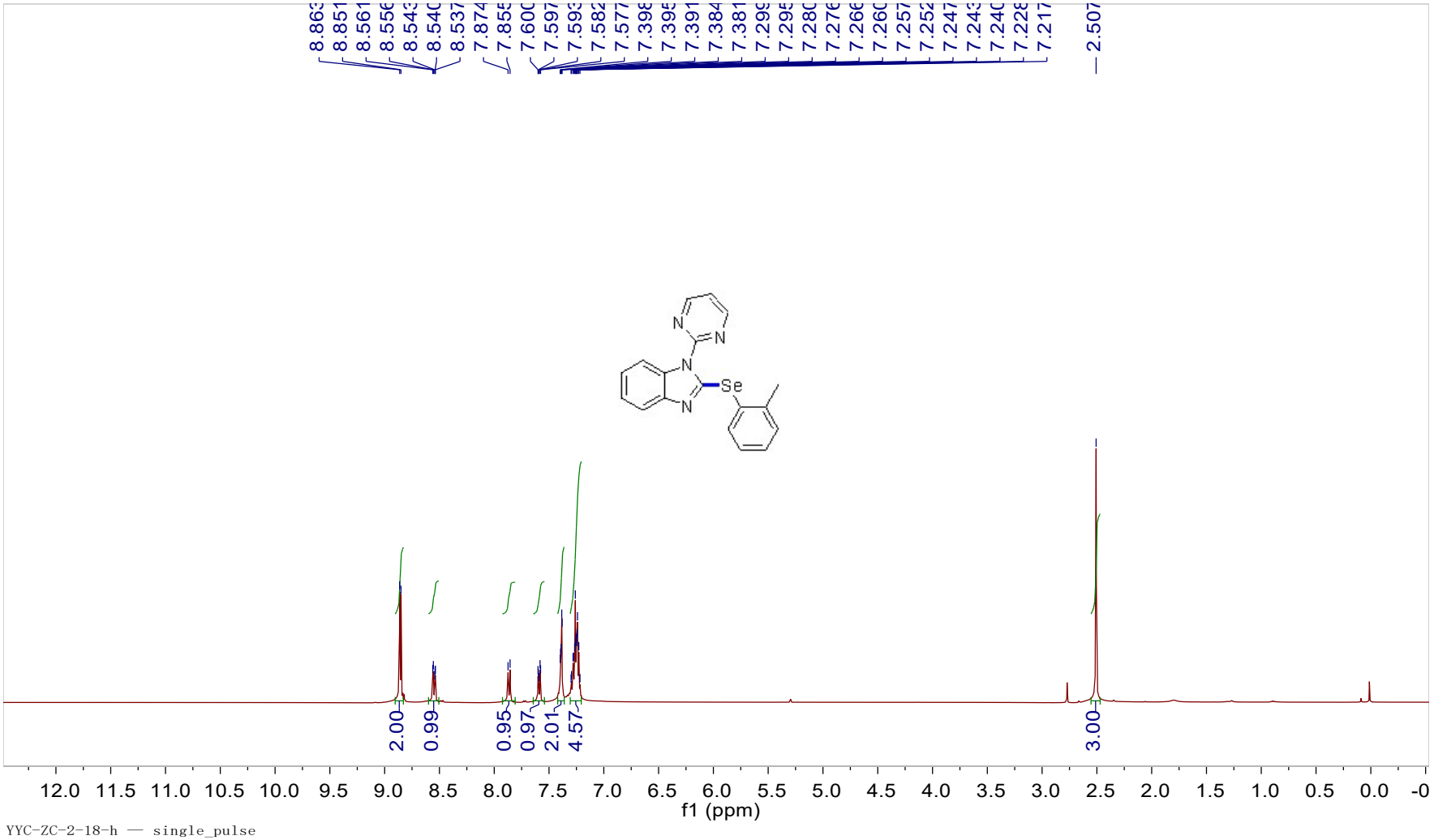
$^{19}F\{^{1}H\}$ NMR spectrum of **3ai**.



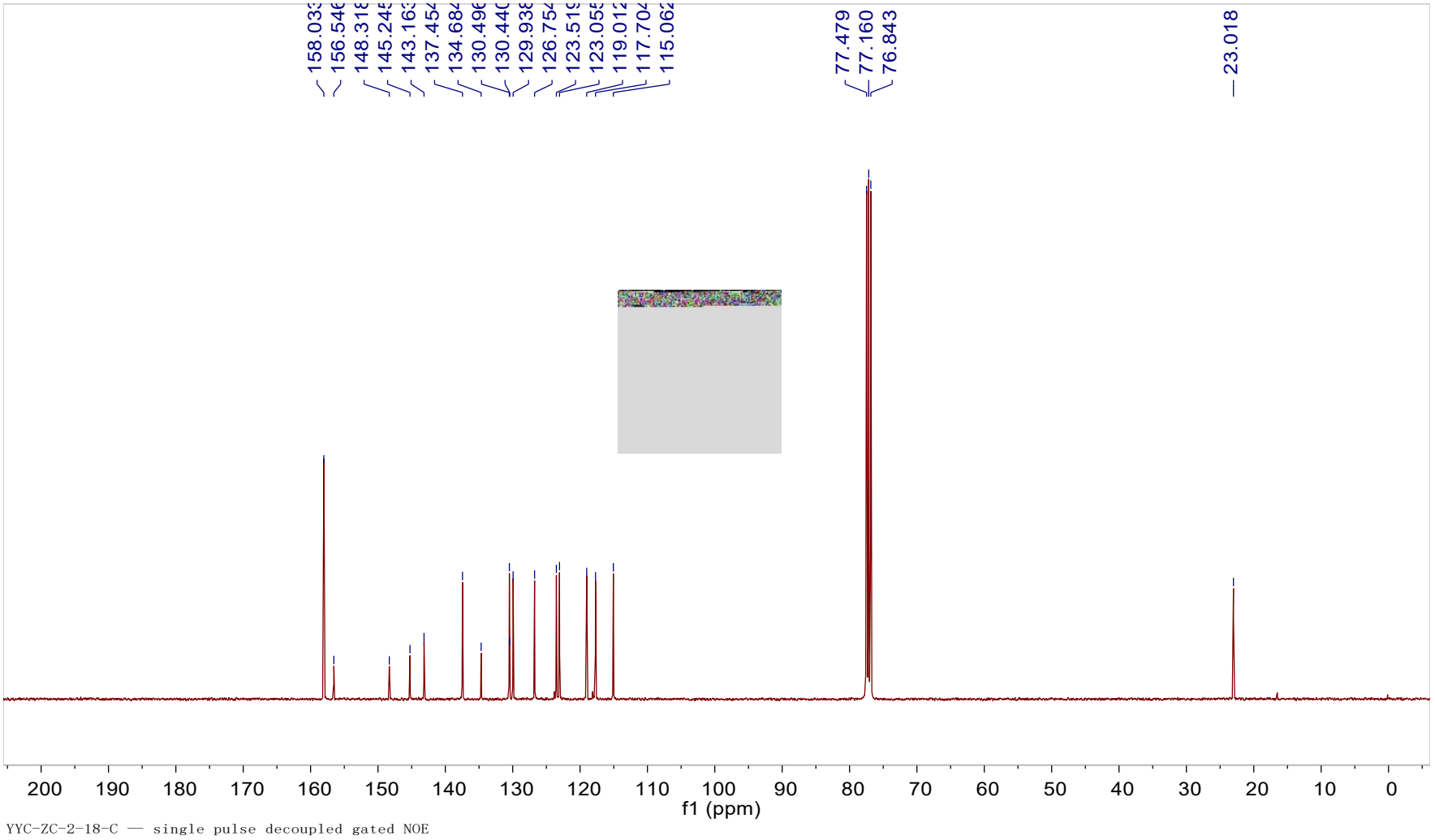
^{1}H NMR spectrum of **3aj**.



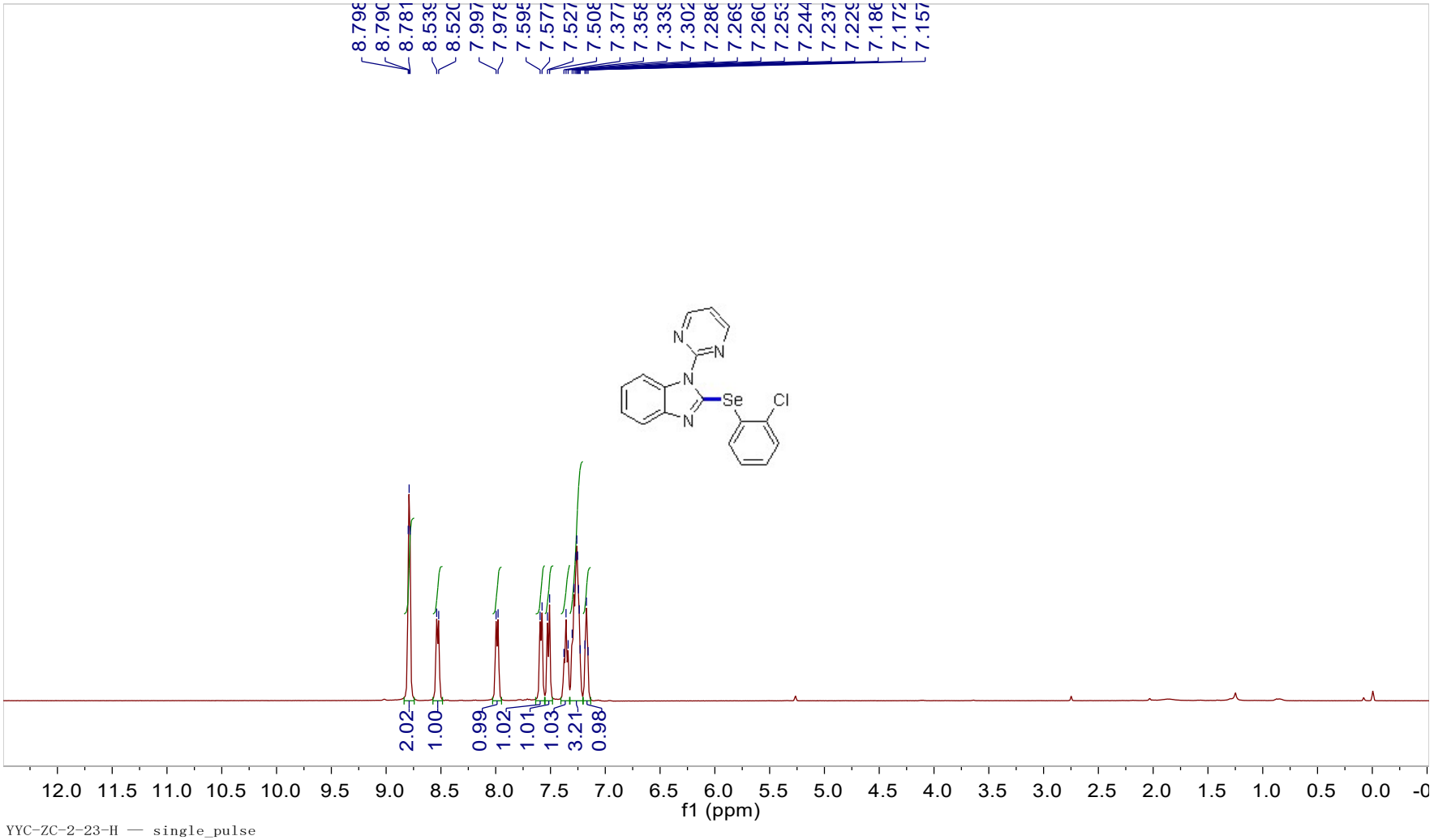
$^{13}C\{^{1}H\}$ NMR spectrum of **3aj**.



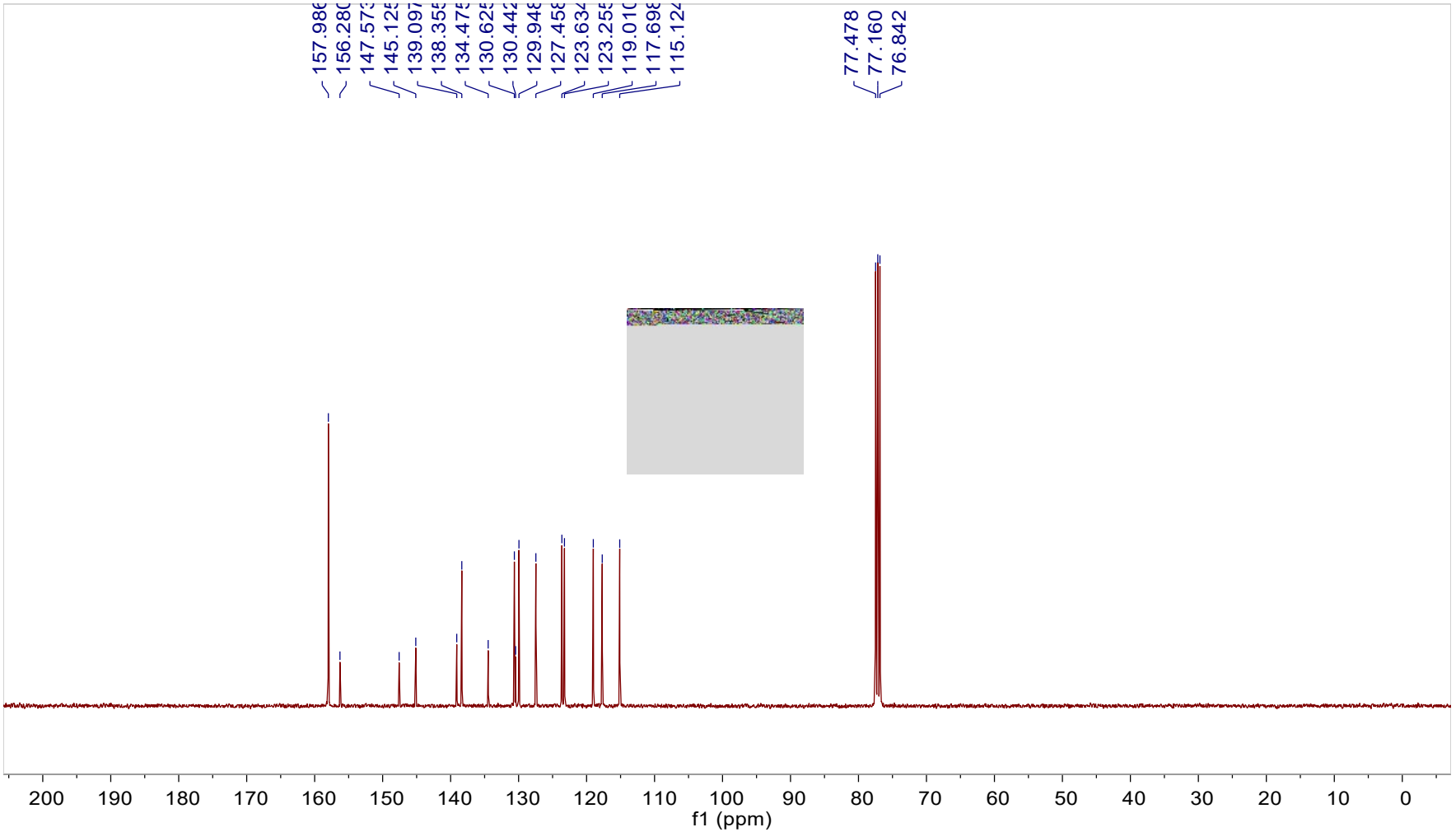
^{1}H NMR spectrum of **3ak**.



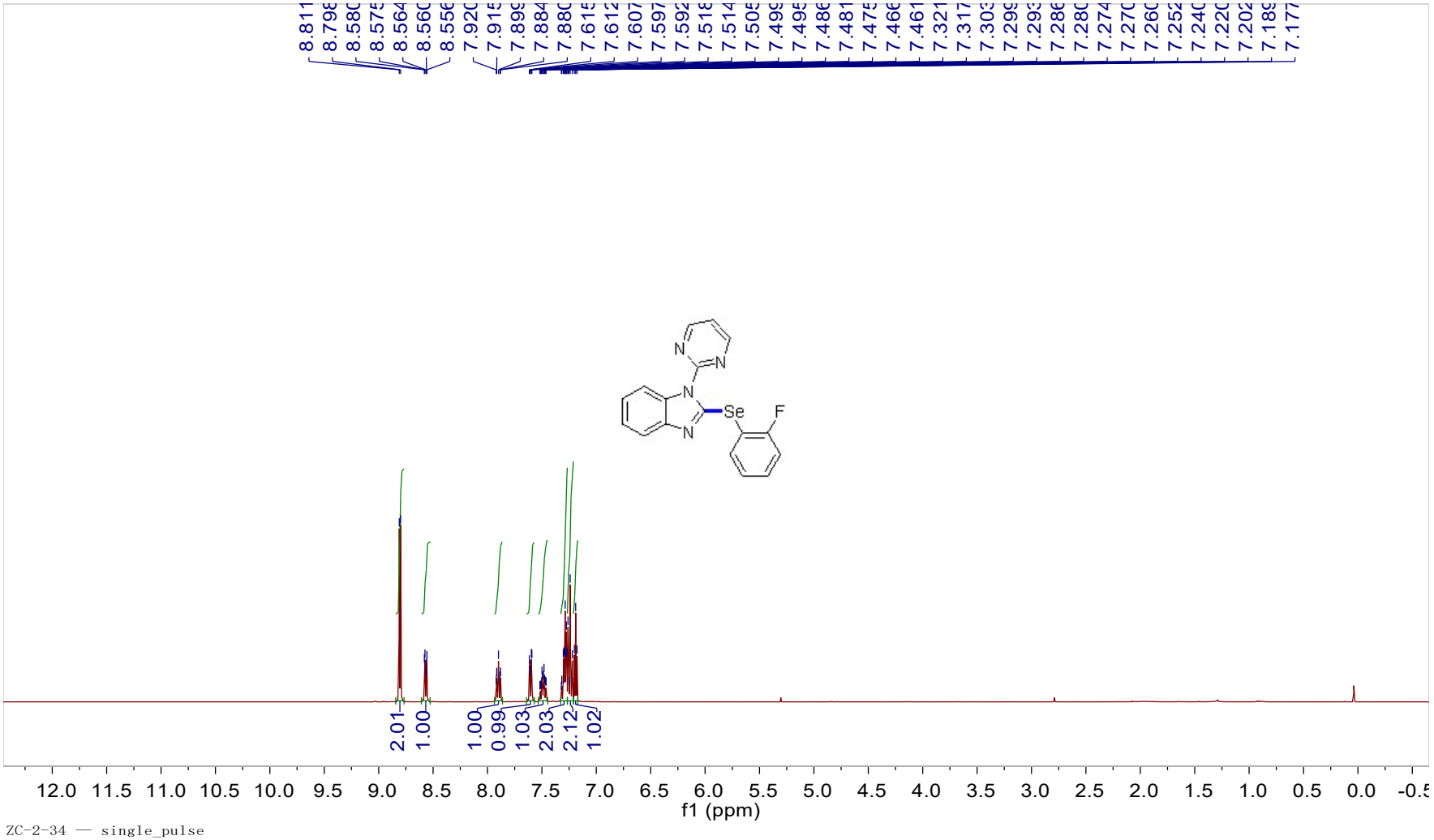
$^{13}C\{^{1}H\}$ NMR spectrum of **3ak**.



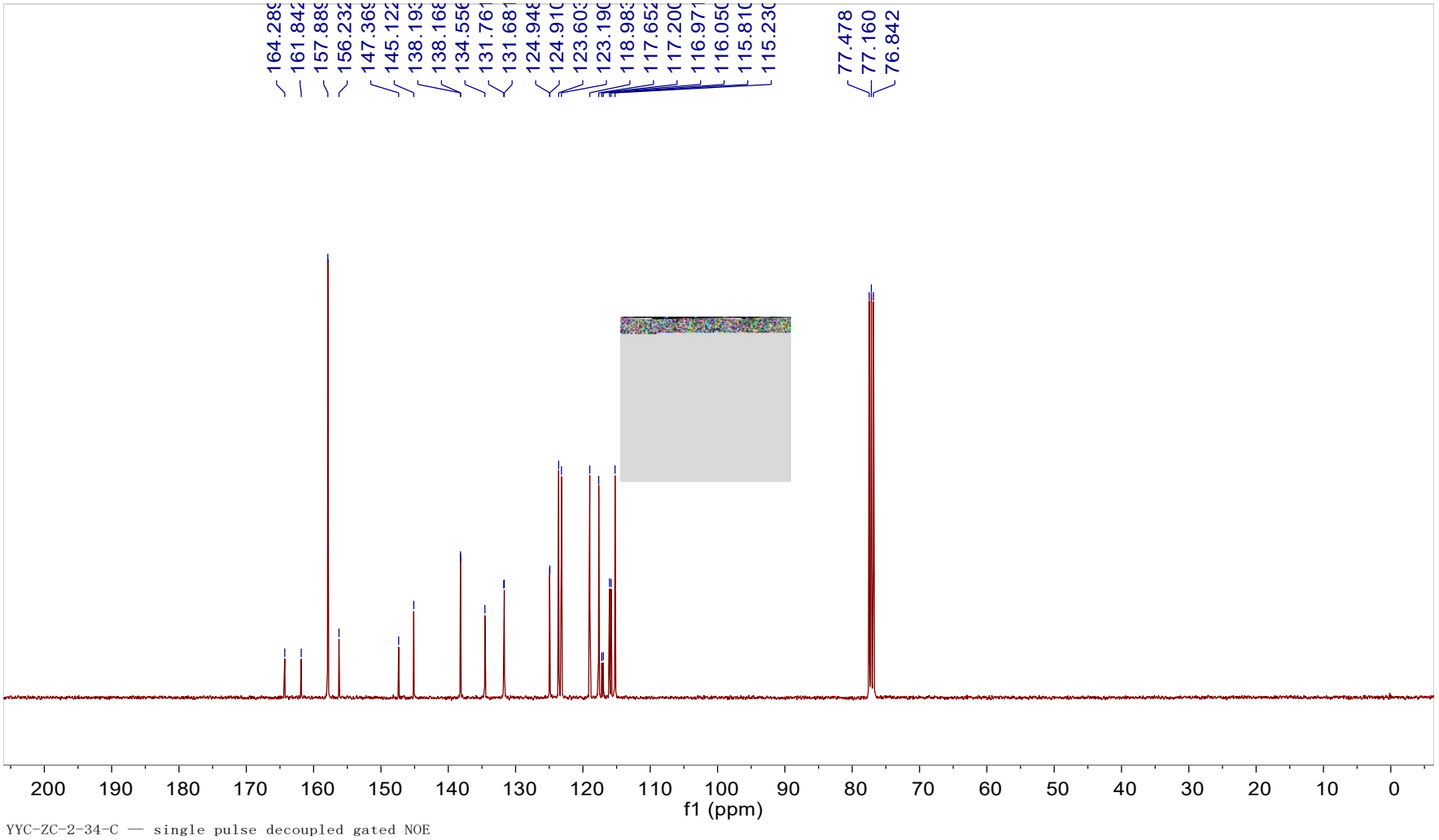
^{1}H NMR spectrum of **3al**.



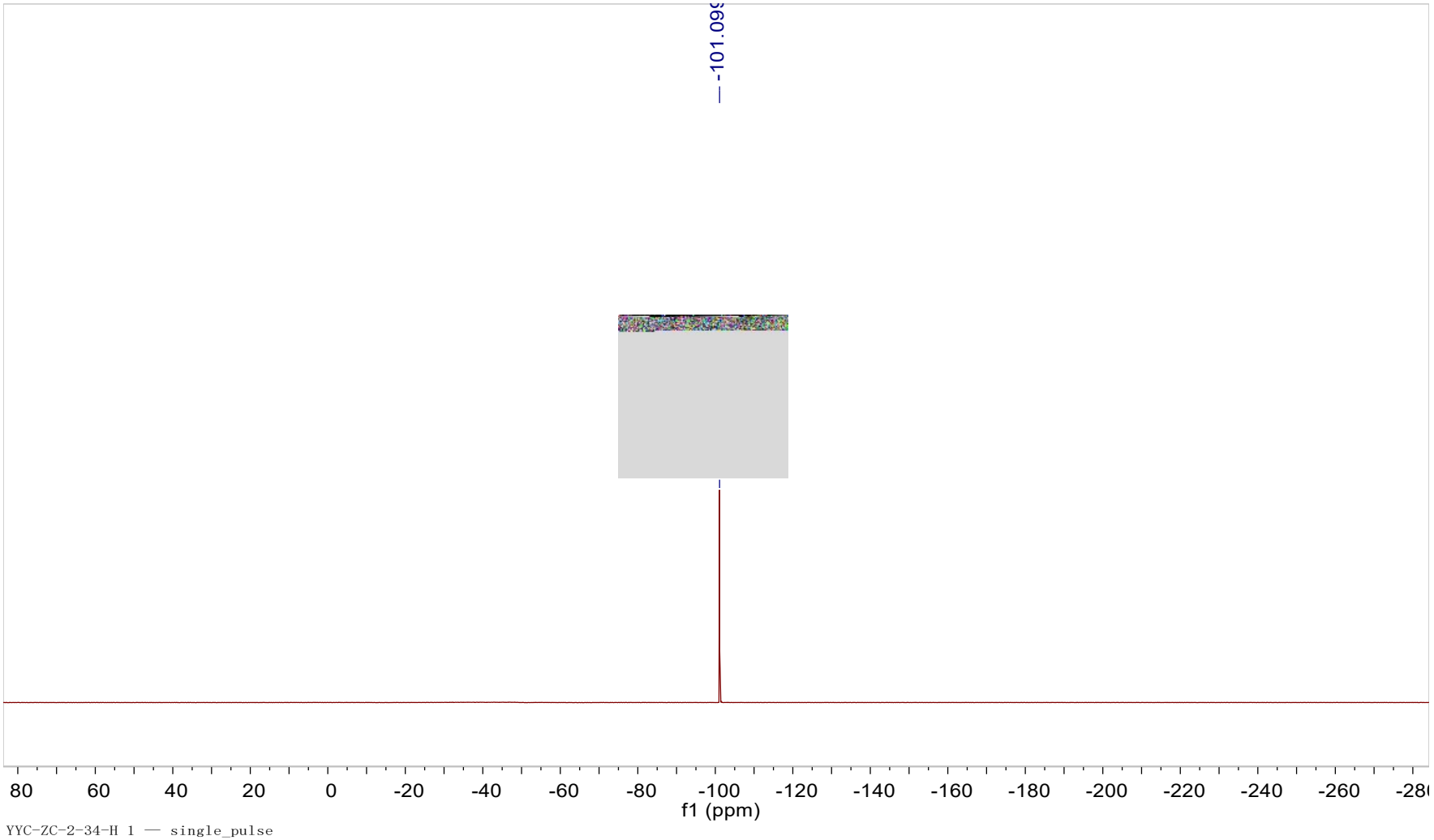
$^{13}C\{^{1}H\}$ NMR spectrum of **3al**.



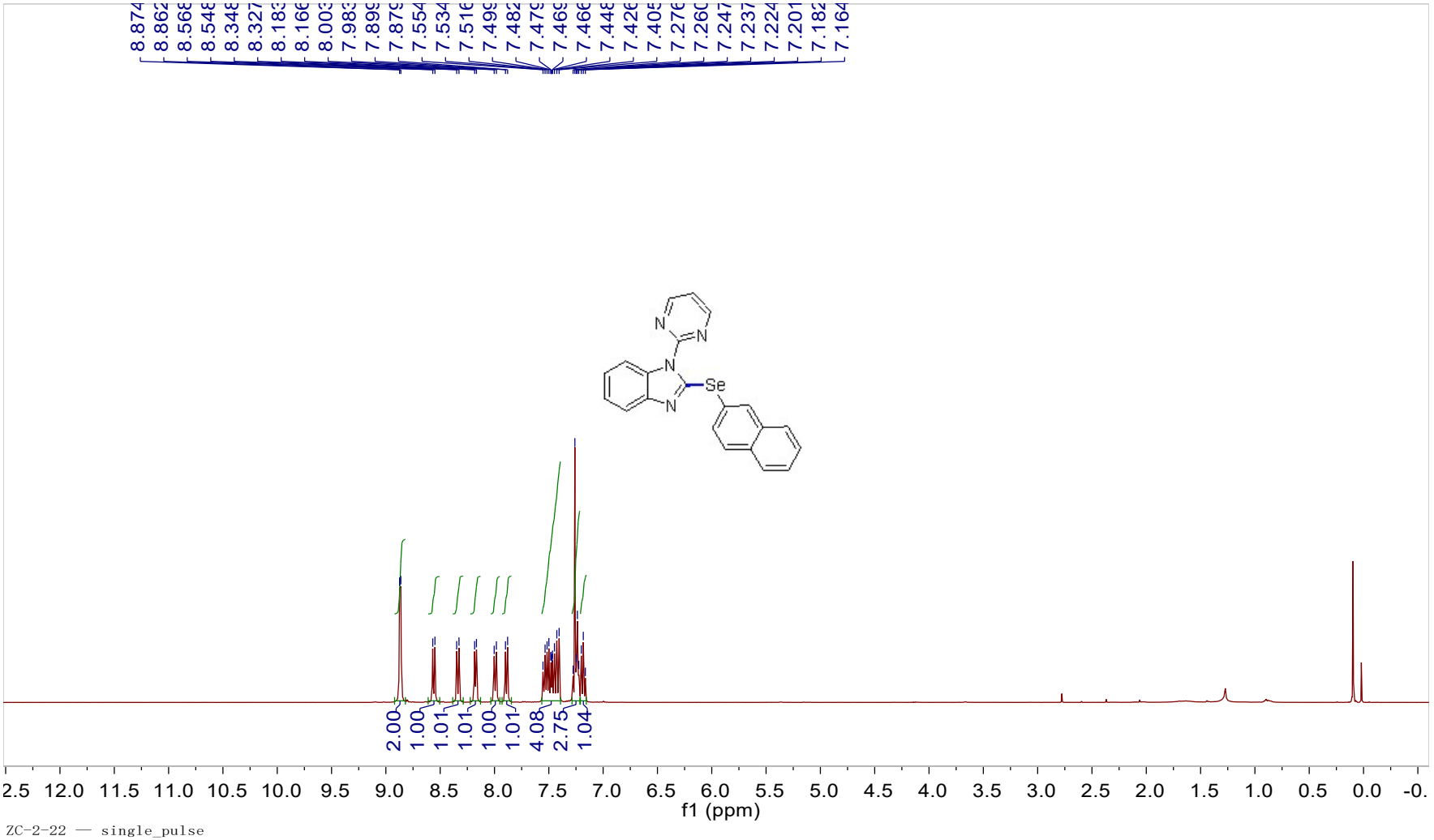
^{1}H NMR spectrum of **3am**.



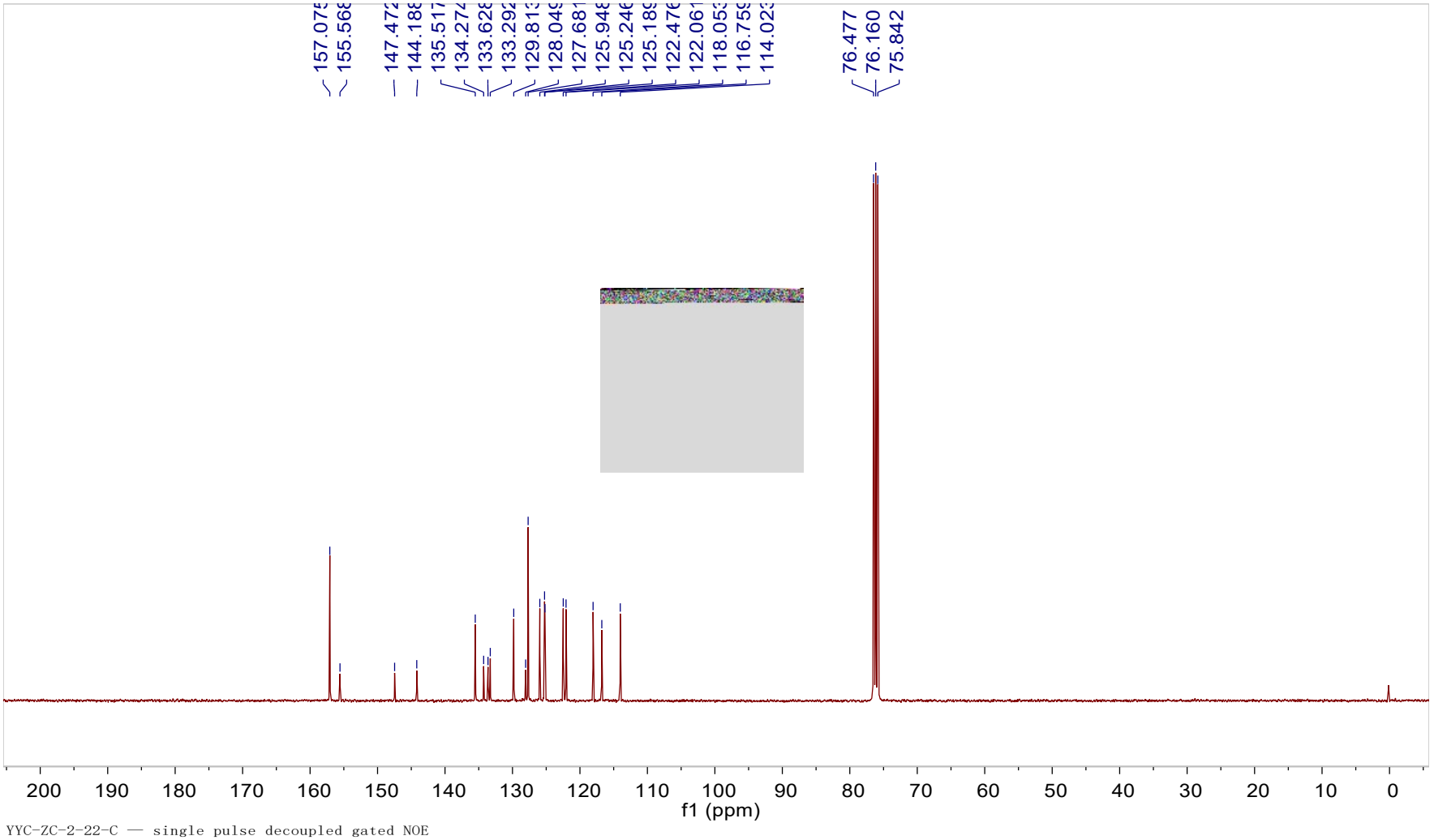
$^{13}C\{^{1}H\}$ NMR spectrum of **3am**.



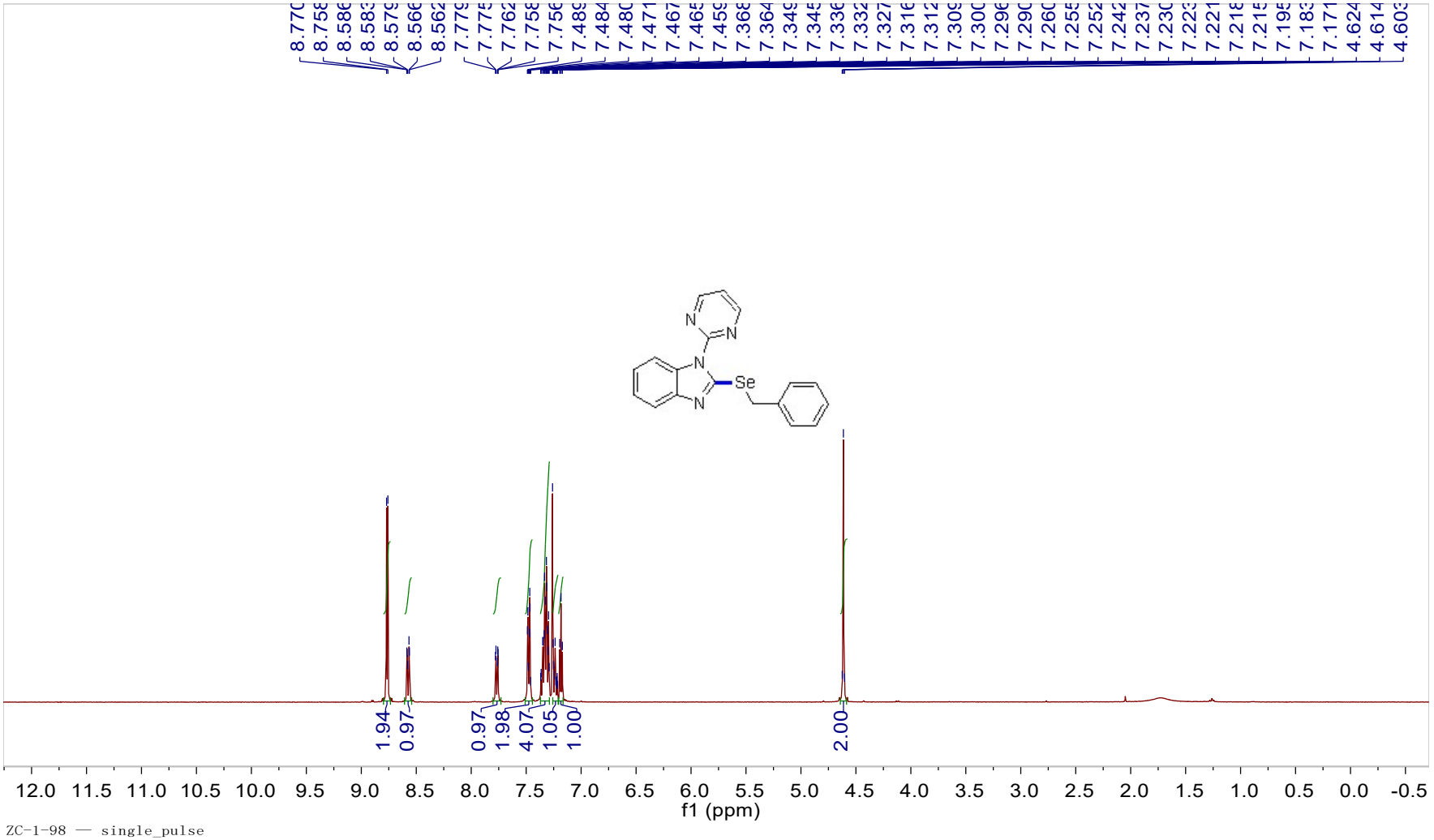
$^{19}F\{^{1}H\}$ NMR spectrum of **3am**.



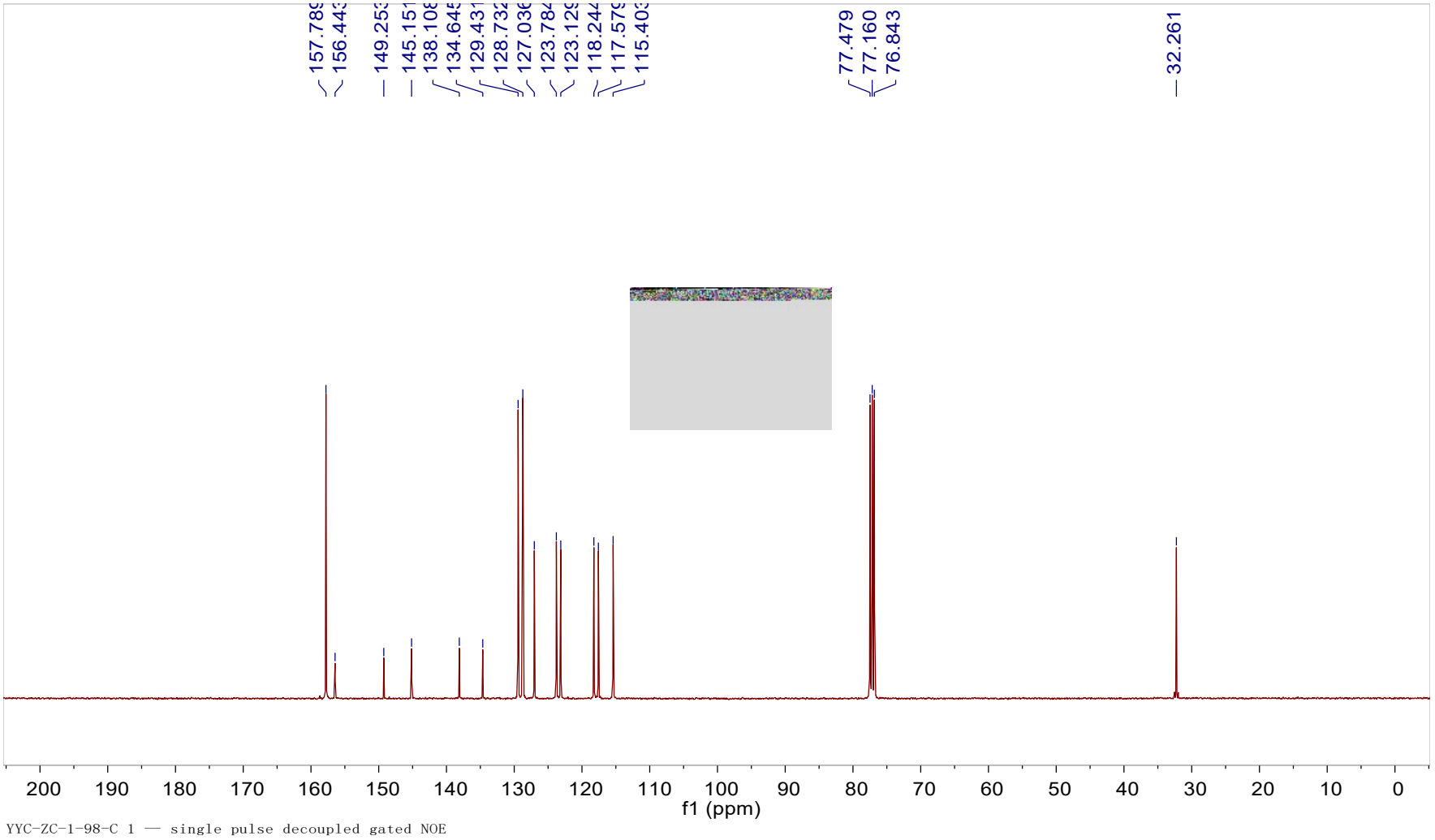
^{1}H NMR spectrum of **3an**.



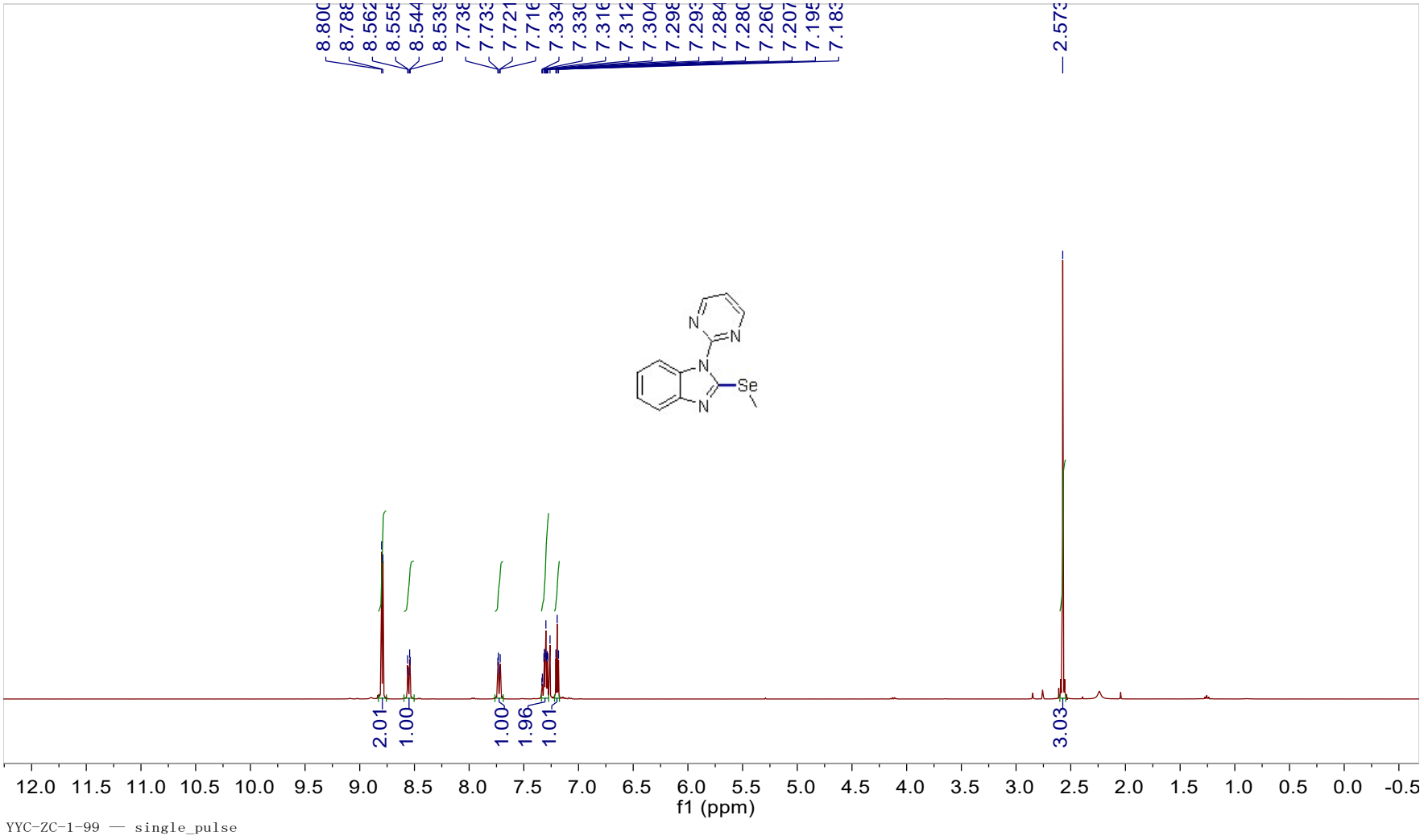
$^{13}C\{^{1}H\}$ NMR spectrum of **3an**.



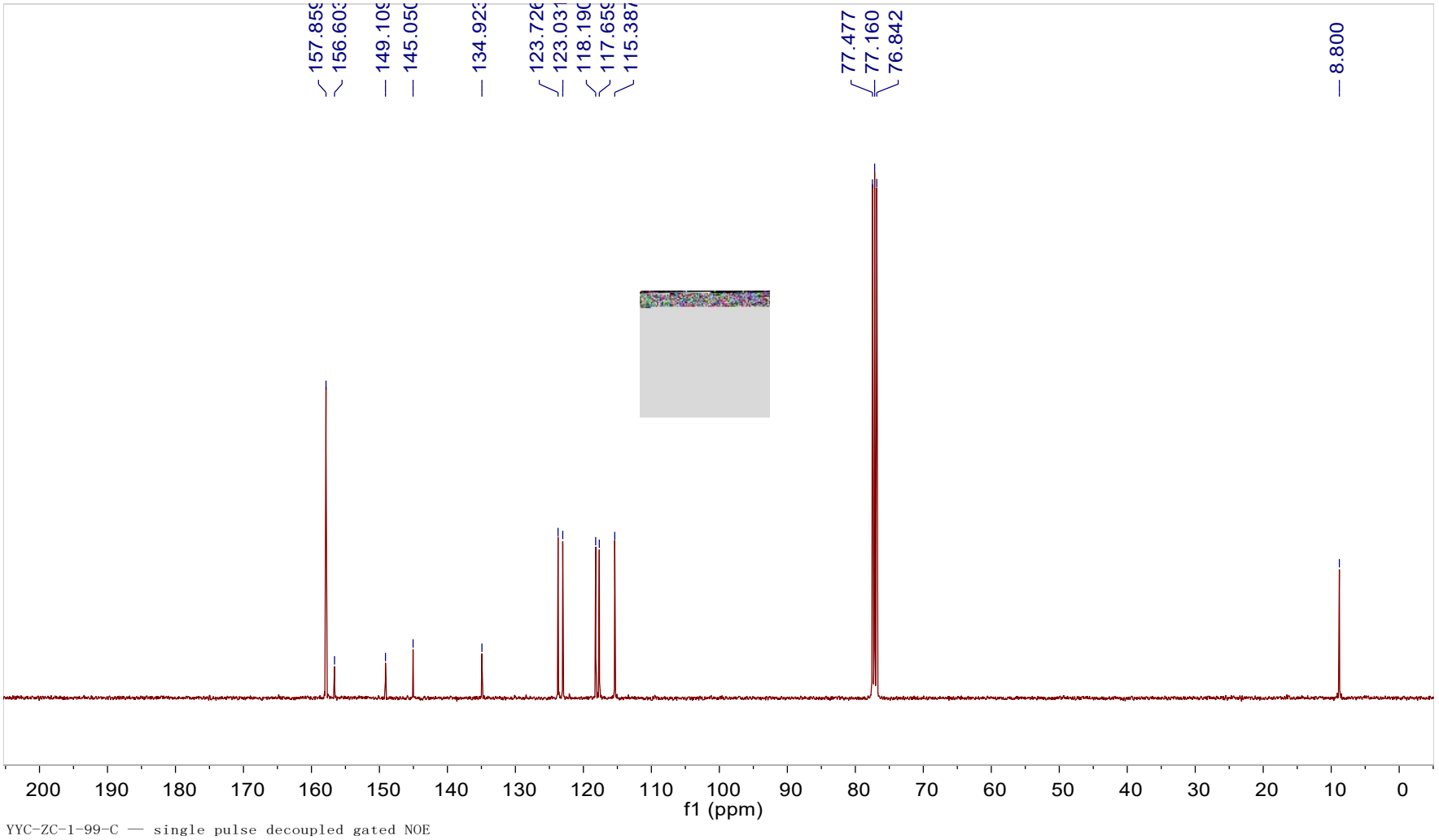
^{1}H NMR spectrum of **3ao**.



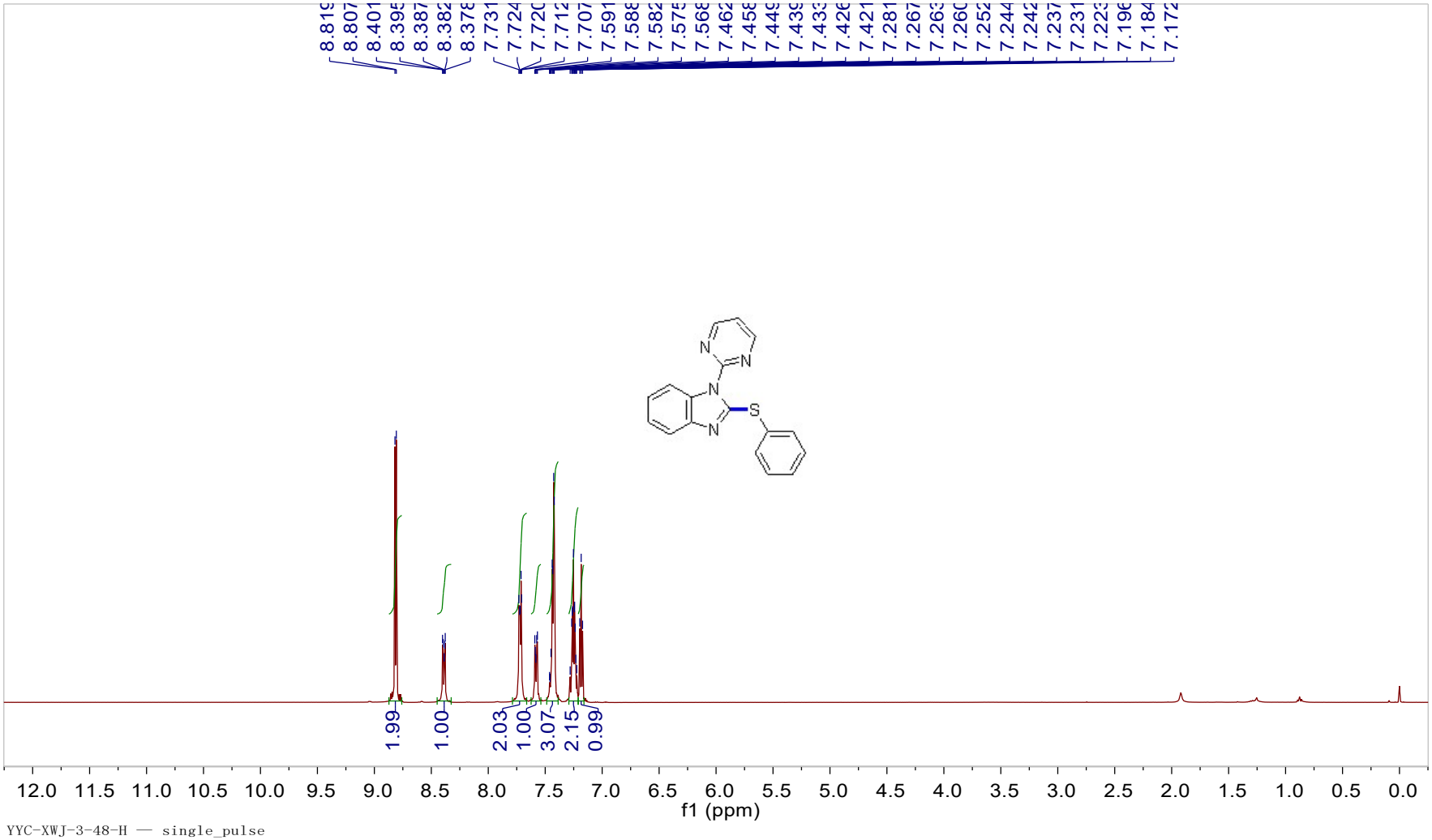
$^{13}C\{^{1}H\}$ NMR spectrum of **3ao**.



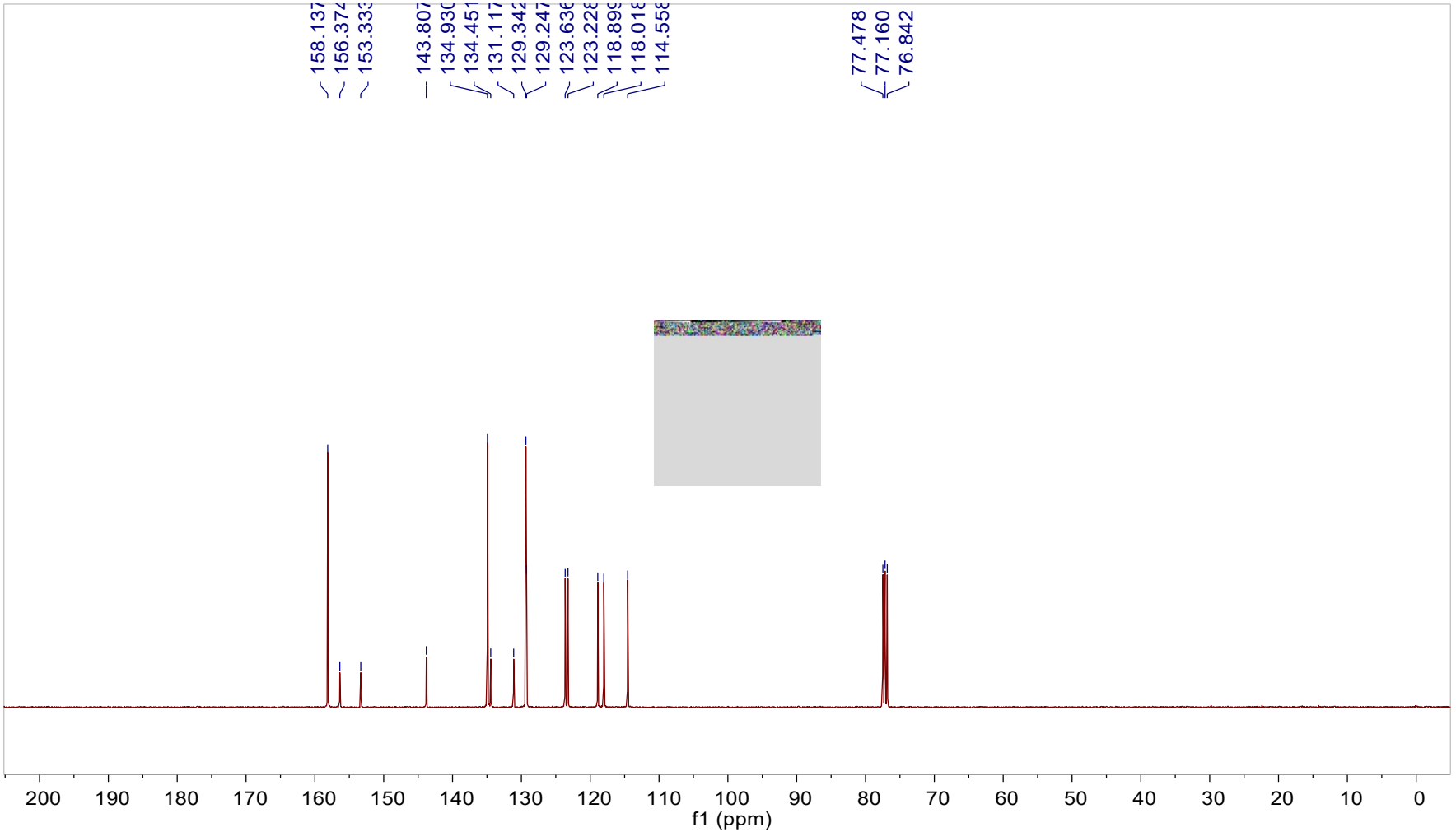
^{1}H NMR spectrum of **3ap**.



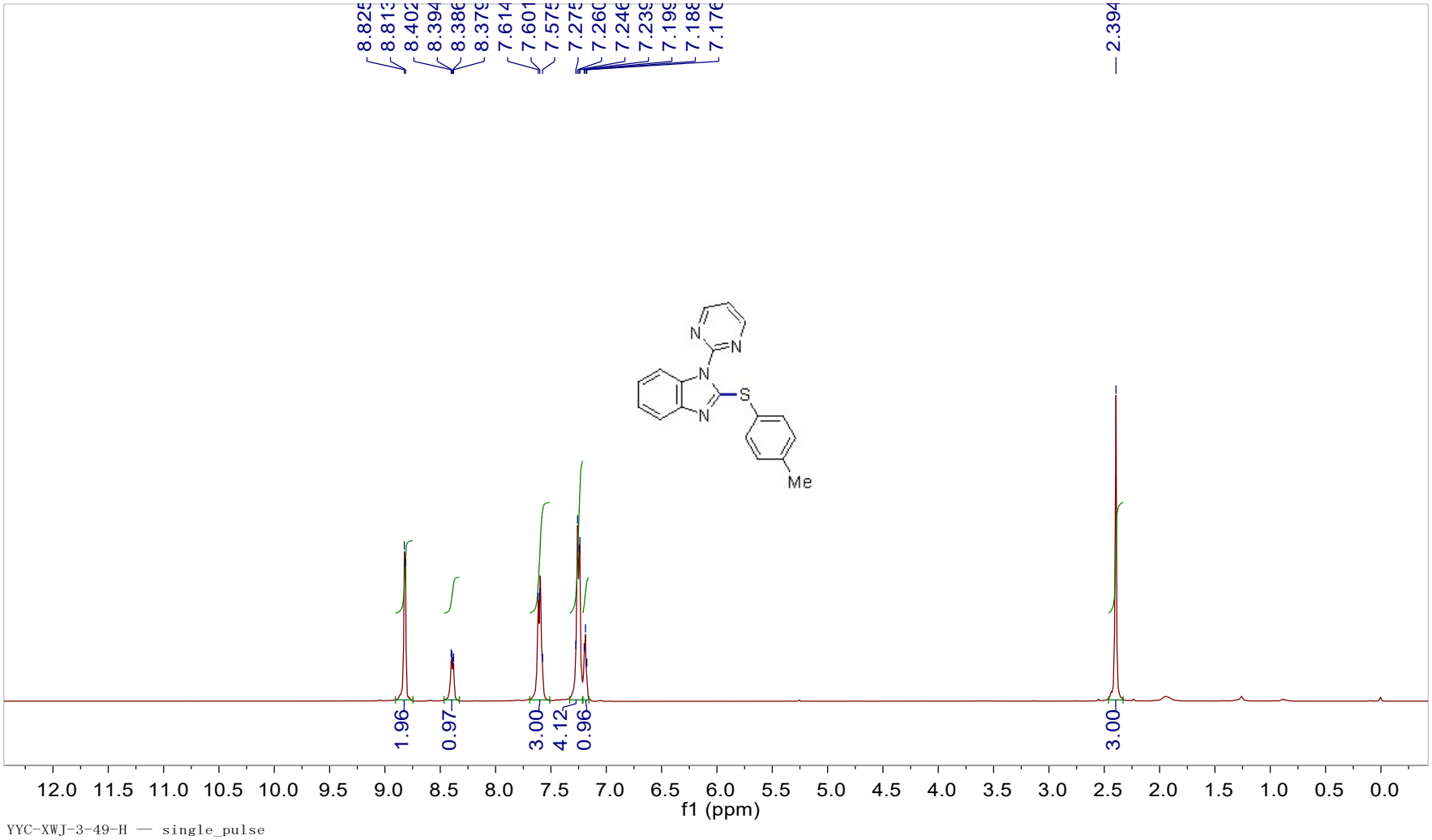
$^{13}C\{^{1}H\}$ NMR spectrum of **3ap**.



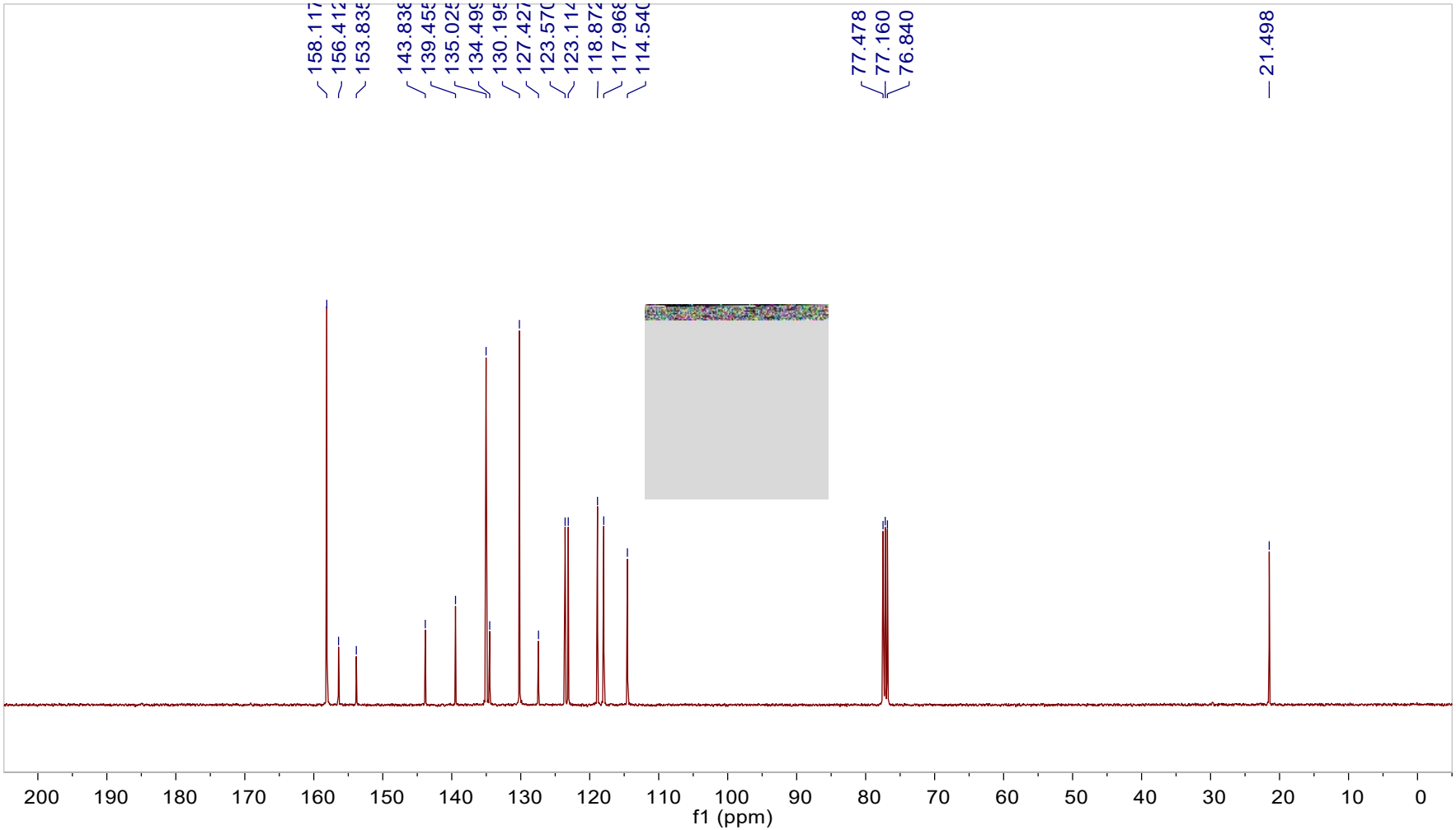
^{1}H NMR spectrum of **3aq**.



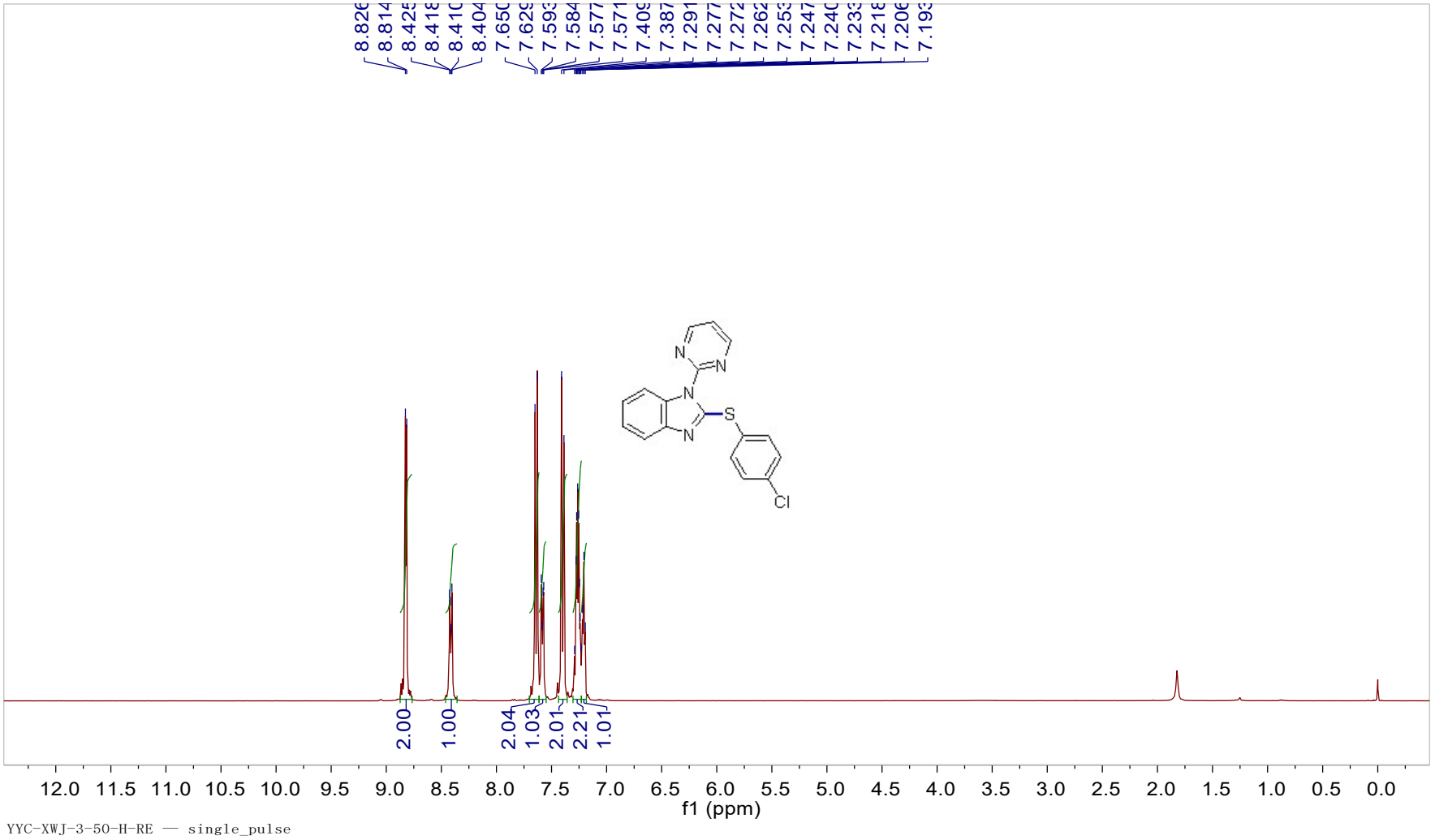
$^{13}C\{^{1}H\}$ NMR spectrum of **3aq**.



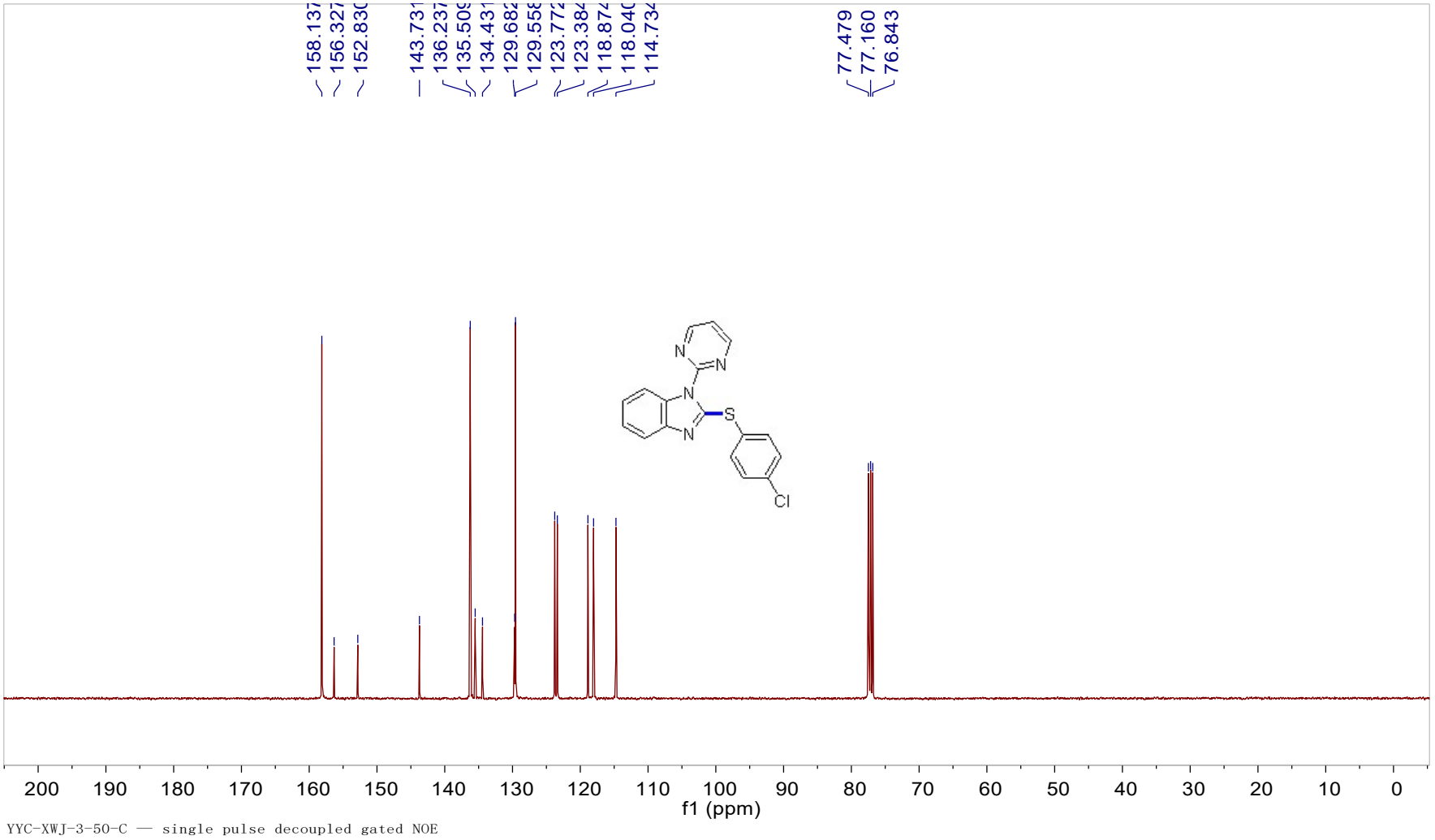
^{1}H NMR spectrum of **3ar**.



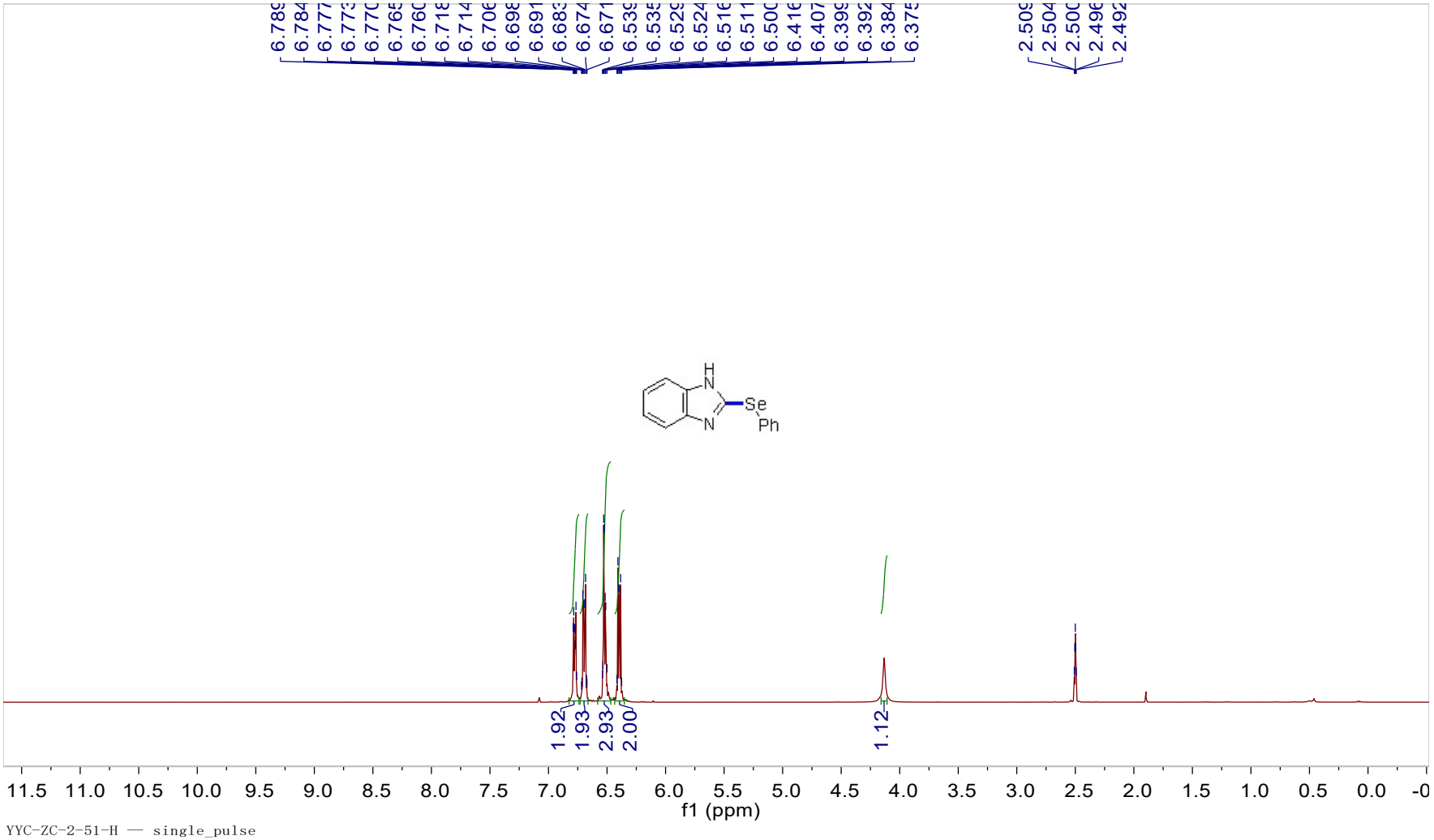
$^{13}C\{^{1}H\}$ NMR spectrum of **3ar**.



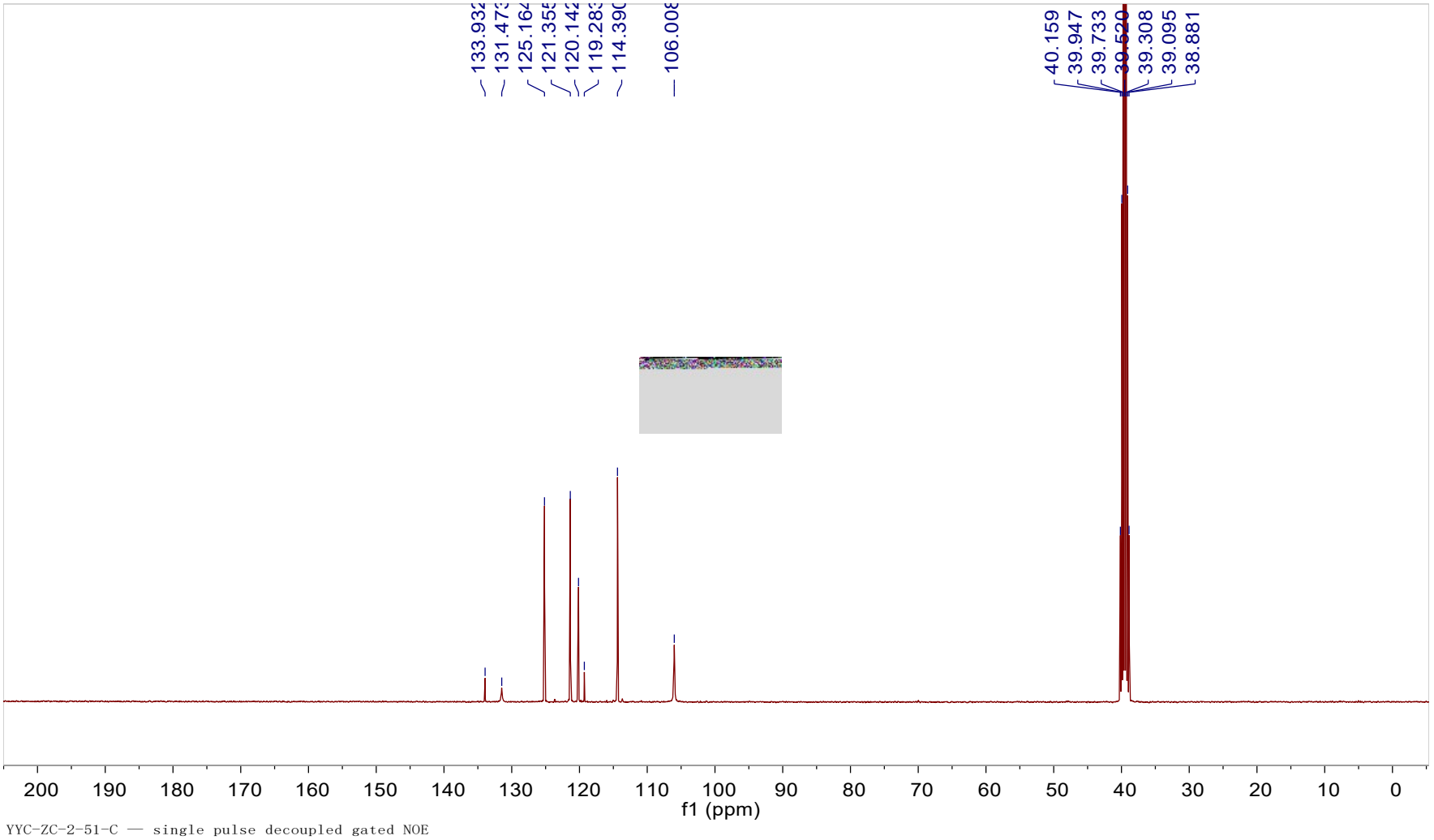
^{1}H NMR spectrum of **3as**.



$^{13}C\{^{1}H\}$ NMR spectrum of **3as**.



^{1}H NMR spectrum of **4**.



$^{13}C\{^{1}H\}$ NMR spectrum of **4**.