Supporting Information for:

Rapid Access to 3-Aminoindazoles from Nitriles with Hydrazines: A Strategy to Overcome the Basicity Barrier Imparted by Hydrazines

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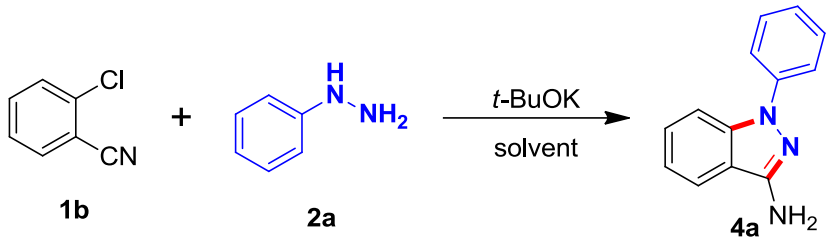
1. General experiment details and materials

Experimental: All reactions and manipulations with air sensitive compounds being present were performed under dry argon (Ar 5.0) or nitrogen (N_2 5.0), using Schlenk and glove box techniques. Non-halogenated solvents were dried over sodium benzophenone, 2-methyltetrahydrofuran (2-Me-THF) was dried over calcium hydride, and halogenated solvents were dried over P_2O_5. Deuterated solvents were bought from Cambridge Isotope Laboratories, distilled accordingly, and stored over molecular sieves (3 Å). Other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were collected on a Varian INOVA 300 and 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvent signal. Coupling constants (J) are given in Hz (coupling patterns: s: singlet, s_br: broad singlet, d: doublet, t: triplet, q: quartet, m: multiplet). GC analyses were carried out using an Agilent Technologies 6890N system equipped with a Machinery-Nagel (MN) Optima 5 HT column (30 m, 320 µm, 0.25 µm) or an Agilent Technologies 6850 system equipped with a MN Optima 17 column (30 m, 320 µm, 0.25 µm). GC/MS analyses were carried out on an Agilent 7890A/MSD 5975C system equipped with a HP-5MS column (30 m, 320 µm, 0.25 µm). High resolution mass spectra (HRMS) were recorded on Bruker Micro TOF-QII mass (ESI). MN silica gel 60 (0.040 – 0.063 mm particle size) was used for flash column chromatography.

2. Optimization of the reaction conditions

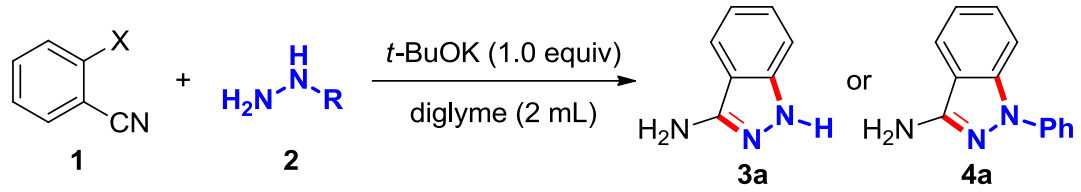
Closed system:

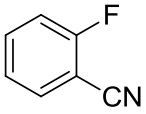
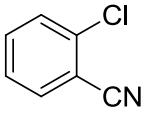
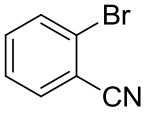
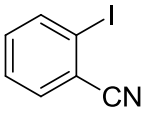
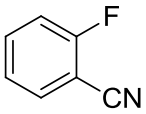
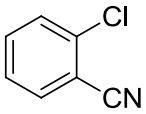
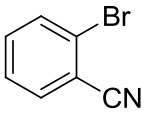
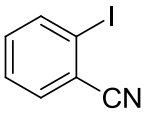
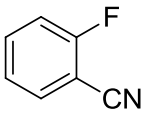
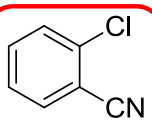
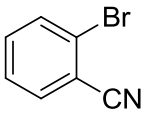
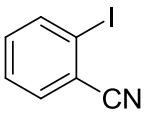


Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, base, phenyl hydrazine (**2a)** and solvent. After stirring of 5 minutes, 2-chlorobenzonitrile（**1b**）was added the mixture reaction. Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (design temperature). After design time the reaction was cooled, quenched with half-saturated brine and extracted with dichloromethane (4 x 15 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. A small aliquot of the organic phase was analyzed by GC or GC-MS to monitor product formation. Purification of the remainder by column chromatography on silica gel gave the corresponding products **4a** (pentane/ethyl ether = 15/1 – 5/1) in the reported yield.

Entry	Parameter
Table S1	Investigated nitriles and hydrazines.
Table S2	Screening the loading of *t*-BuOK
Table S3	The difference of base screening
Table S4	The difference of solvent screening
Table S5	The ratio of **1b** and **2a** screening
Table S6	Reaction temperature screening
Table S7	The reaction time screening
Table S8	Reaction system screening

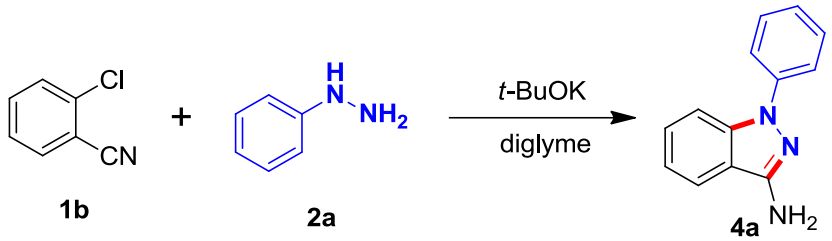
Table S1. Investigated nitriles and hydrazines. [a]



$NH_2NH_2 \cdot nH_2O$ **2a** as partner	 **1a**	 **1b**	 **1c**	 **1d**
	3a, <5%	**3a**, <5%	**3a**, <5%	**3a**, 0%
$NH_2NH_2 \cdot 2HCl$ **2b** as partner	 **1a**	 **1b**	 **1c**	 **1d**
	3a, <5%	**3a**, 7%	**3a**, <5%	**3a**, 0%
$Ph\text{-}NHNH_2$ **2c** as partner	 **1a**	 **1b**	 **1c**	 **1d**
	4a, 78%	**4a**, 83%	**4a**, 67%	**4a**, <5%

[a] Reaction condition : **1** (1.0 mmol), **2** (3.0 mmol), *t*-BuOK (1.0 mmol), diglyme (2.0 mL), N_2, 130 °C (extern temperature), 1 h. Yield of **3a** or **4a** was determined by GC analysis using *n*-dodecane as the internal standard.

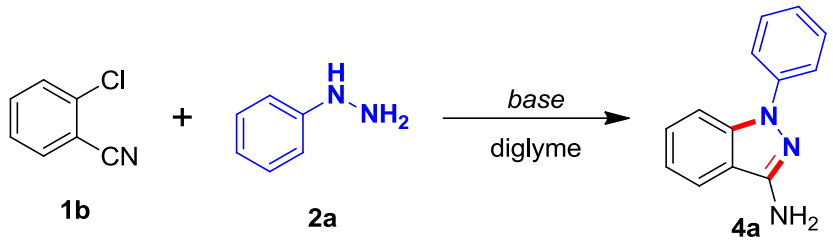
Table S2. Screening the loading of *t*-BuOK [a]



Entry	*t*-BuOK (equiv)	**4a** (%)
1	0.1	<5
2	0.3	21
3	0.5	32
4	0.7	56
5	0.9	61
6	1.0	70
7	1.1	76
8	1.2	85
9	**1.3**	**95**
10	1.4	94
11	1.5	91
12	1.7	88
13	1.8	83
14	1.9	81
15	2.0	78
16	3.0	52

[a] Reaction condition : **1b** (1.0 mmol), **2a** (3.0 mmol), *t*-BuOK (1.3 mmol), diglyme (2.0 mL), N_2, 130 °C (extern temperature), 1 h. Yield of **4a** were determined by GC analysis using *n*-dodecane as the internal standard.

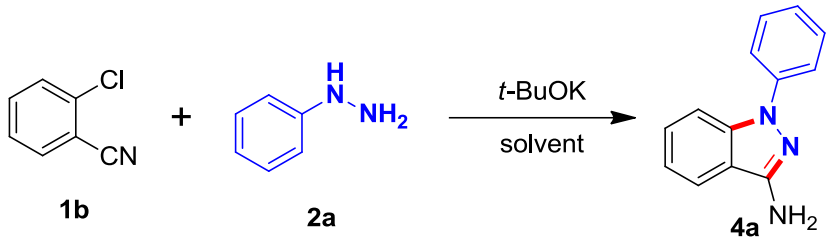
Table S3. The difference of base screening [a]



entry	base	**4a** (%)
1	Cs_2CO_3	0
2	K_2CO_3	0
3	Na_2CO_3	0
4	$KHCO_3$	0
5	K_3PO_4	0
6	K_2HPO_4	0
7	CsOH	<5
8	KOH	9
9	NaOH	<5
10	LiOH	0
11	***t*-BuOK**	**95**
12	*t*-BuONa	60
13	*t*-BuOLi	0
14	KHMDS	68
15	NaHMDS	10
16	LiHMDS	0
17	DBU	0
18	Et_3N	0
19	LEDA	0
20	*n*-BuLi	0
21	-	0

[a] Reaction condition : **1b** (1.0 mmol), **2a** (3.0 mmol), base (1.3 mmol), diglyme (2.0 mL), N_2, 130 ^oC (extern temperature), 1 h. Yield of **4a** were determined by GC analysis using *n*-dodecane as the internal standard.

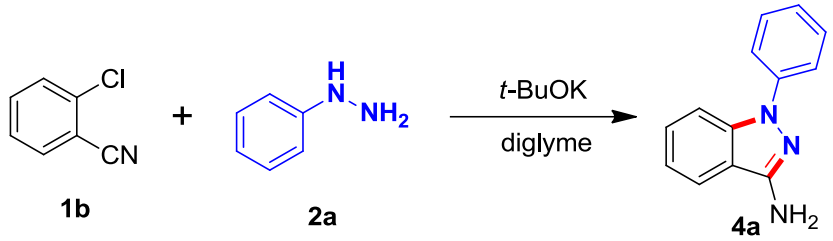
Table S4. The difference of solvent screening [a]



Entry	solvent	**4a** (%)
1	**diglyme**	**95**
2	1,4-dioxane	87
3	1,2-Dimethoxyethane	80
4	Anisole	77
5	THF	82
6	4-MeTHF	78
7	benzene	73
8	xylene	81
9	Toluene	85
10	DMSO	74
11	DMF	52
12	DMAc	53
13	MeOH	0
14	EtOH	0
15	*i*-PrOH	0
16	*t*-BuOH	<5
17	*t*-AmOH	38
18	CH_3CN	0
19	CH_3NO_2	0
20	$CH_3C(O)OCH_2CH_3$	<5

[a] Reaction condition : **1b** (1.0 mmol), **2a** (3.0 mmol), *t*-BuOK (1.3 mmol), solvent (2.0 mL), N_2, 130 °C (extern temperature), 1 h. Yield of **4a** were determined by GC analysis using *n*-dodecane as the internal standard.

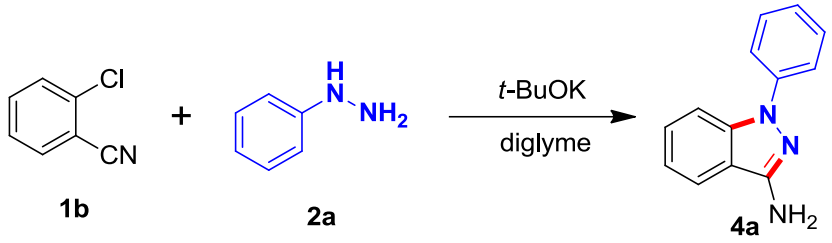
Table S5. The ratio of 1a and 1b screening [a]



Entry	**1b**	**2a**	**4a** (%)
1	2.0	1	24
2	1.8	1	49
3	1.6	1	50
4	1.4	1	54
5	1.2	1	67
6	1	1	70
7	1	1.1	73
8	1	1.2	78
9	1	1.3	82
10	1	1.4	84
11	1	1.5	84
12	1	2	87
13	**1**	**3**	**95**
14	1	4	94
15	1	5	92

[a] Reaction condition : **1b** (x mmol), **2a** (x mmol), *t*-BuOK (1.3 mmol), diglyme (2.0 mL), N_2, 130 °C (extern temperature), 1 h. Yield of **4a** were determined by GC analysis using *n*-dodecane as the internal standard.

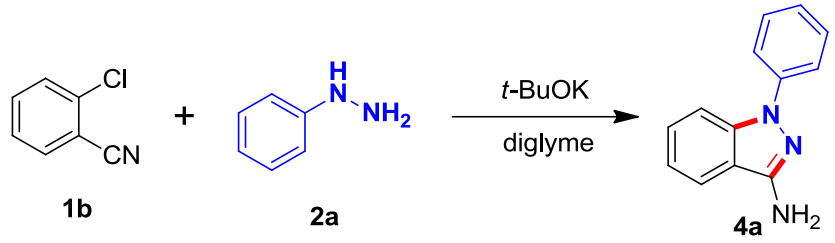
Table S6. **The reaction temperature screening** [a]



Entry	T/°C	**4a** (%)
1	20	<5
2	40	43
3	60	64
4	80	72
5	100	78
6	120	89
7	**130**	**95**
8	140	94

[a] Reaction condition : **1b** (1.0 mmol), **2a** (3.0 mmol), *t*-BuOK (1.3 mmol), diglyme (2.0 mL), N_2, T (extern temperature), 1 h. Yield of **4a** were determined by GC analysis using *n*-dodecane as the internal standard.

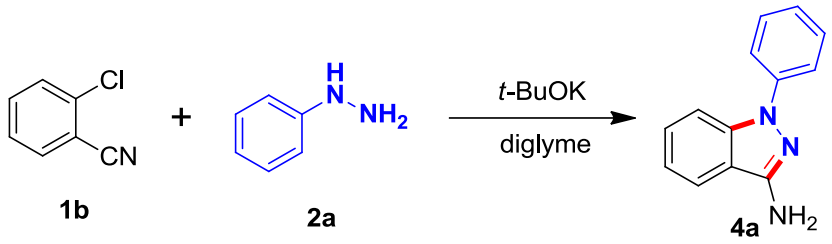
Table S8. The reaction time screening [a]



Entry	t/min	**4a** (%)
1	10	39
2	20	61
3	30	75
4	40	83
5	50	90
6	**60**	**95**
7	120	94
8	180	96

[a] Reaction condition : **1b** (1.0 mmol), **2a** (3.0 mmol), *t*-BuOK (1.3 mmol), diglyme (2.0 mL), N_2, 130 °C (extern temperature), t. Yield of **4a** were determined by GC analysis using *n*-dodecane as the internal standard.

Table S8: Reaction system screening [a]

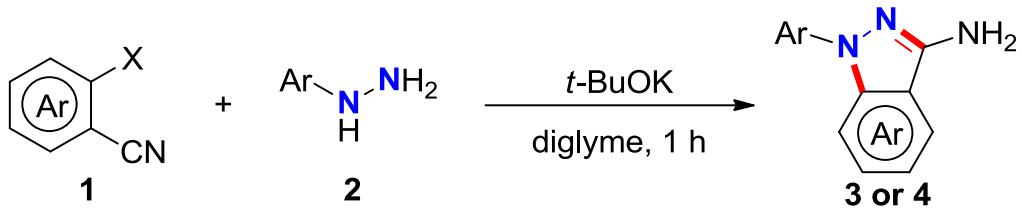


Entry	System		**4a** (%)
1	Seal tube	N_2	95
2	Seal tube	Ar	96
3	Seal tube	air	73
4	Seal tube	O_2	<5
5	Open-reflux	N_2	90
6	Open-reflux	Ar	91
7	Open-reflux	air	62
8	Open-reflux	O_2	<5

[a] Reaction condition : **1b** (1.0 mmol), **2a** (3.0 mmol), *t*-BuOK (1.3 mmol), diglyme (2.0 mL), 130 °C (extern temperature), 1 h. Yield of **4a** were determined by GC analysis using *n*-dodecane as the internal standard.

3. General procedure for the annulation reaction

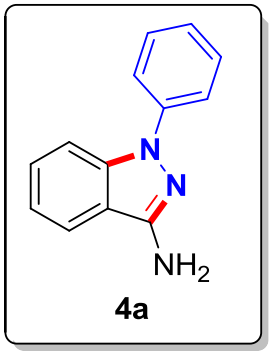
Closed system:



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, base, hydrazines (**2)** and diglyme. After stirring of five minutes, nitriles (1) was added the mixture reaction. Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (design temperature). After design time the reaction was cooled, quenched with half-saturated brine and extracted with dichloromethane (4 x 15 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. A small aliquot of the organic phase was analyzed by GC or GC-MS to monitor product formation. Purification of the remainder by column chromatography on silica gel gave the corresponding products **3a** or **4a** (pentane/ethyl ether = 15/1 – 5/1) in the reported yield.

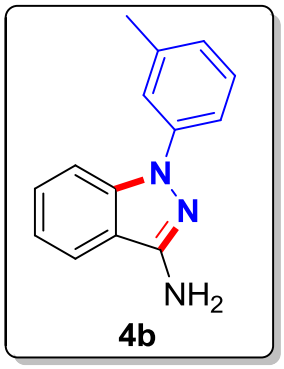
4. Experimental characterization data for products

1-phenyl-1H-indazol-3-amine (4a): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (6/1, v/v) to give the desired product as a white solid (198 mg, 95%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 3H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.48 (m, 2H), 7.41 (m, *J* = 7.5 Hz, 1H), 7.24 (m, 1H), 7.13 (m, 1H), 4.22 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.1, 140.4, 139.5, 129.2, 127.7, 124.9, 121.2, 119.7 ,119.6, 116.5, 110.1. **HRMS** (ESI) calcd. for $C_{13}H_{12}N_3$ [M+H]: 209.0953, found: 209.0958.



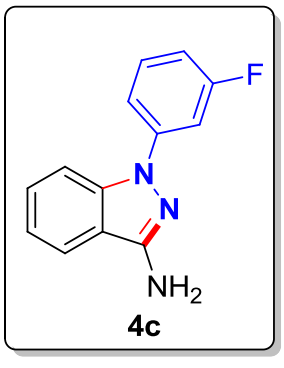
4a

1-(m-tolyl)-1H-indazol-3-amine (4b): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (6/1, v/v) to give the desired product as a white solid (205 mg, 92%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.49 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.36 (m, 1H), 7.12 (m, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 3.39 (s, 2H), 2.43 (s, 3H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.0, 140.1, 139.2, 138.9, 128.7, 127.4, 125.4, 121.6, 119.6, 119.4, 117.9, 116.3, 109.9, 21.1. **HRMS** (ESI) calcd. for $C_{14}H_{14}N_3$ [M+H]: 223.1188, found: 223.1189.



4b

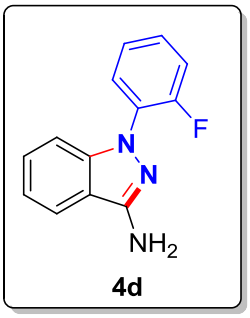
1-(3-fluorophenyl)-1H-indazol-3-amine(4c): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (6/1, v/v) to give the desired product as a white solid (211 mg, 93%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.47 (m, *J* = 13.5, 8.0 Hz, 2H), 7.42 (m, 2H), 7.17 (m, 1H), 6.93 (m, 1H), 3.05 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.3, 161.9, 149.5, 142.0, 142.0, 139.49, 130.0, 130.0, 128.1, 120.2,



4c

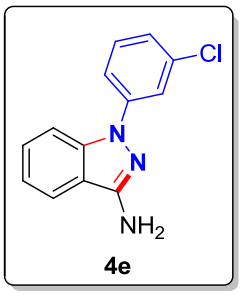
119.8, 117.0, 116.0,116.0, 111.4, 111.2, 110.2, 108.3, 108.0. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -111.28 (s); **HRMS** (ESI) calcd. for $C_{13}H_{11}FN_3$[M+H]: 228.0937, found: 228.0940.

1-(2-fluorophenyl)-1H-indazol-3-amine (4d): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (8/1, v/v) to give the desired product as a white solid (140 mg, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (m, 2H), 7.42 – 7.36 (m, 1H), 7.34 – 7.28 (m, 2H), 7.25 (m, 2H), 7.13 (m, 1H), 4.02 (s, 2H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.7, 154.2, 149.8, 141.1, 127.7 (dd, *J* = 14.8, 9.7 Hz), 127.0 (d, *J* = 1.1 Hz), 124.6 (d, *J* = 3.7 Hz), 119.7, 119.4, 116.6 (d, *J* = 19.8 Hz), 116.1 , 110.36 (d, *J* = 5.9 Hz).;**^{19}F NMR** (377 MHz, $CDCl_3$) δ -120.35 (s). **HRMS** (ESI) calcd. for $C_{13}H_{11}FN_3$[M+H]: 228.0937, found: 228.0939.



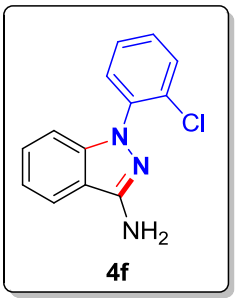
4d

1-(3-chlorophenyl)-1H-indazol-3-amine (4e): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (6/1, v/v) to give the desired product as a white solid (221 mg, 91%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.45 (m, 1H), 7.40 (m, 1H), 7.22 – 7.13 (m, 2H), 2.68 (s, 2H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.5, 141.6, 139.4, 134.8, 130.2 , 128.1, 124.6, 121.0, 120.3, 119.8, 118.7, 117.0, 110.2. **HRMS** (ESI) calcd. for $C_{13}H_{11}ClN_3$ [M+H]: 243.0563, found: 243.0564.



4e

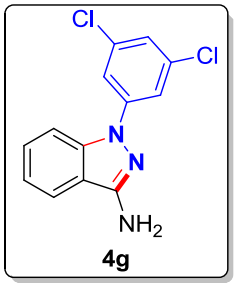
1-(2-chlorophenyl)-1H-indazol-3-amine (4f): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (5/1, v/v) to give the desired product as a white solid (133 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.56 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.48 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.13 (m, 2H), 4.25 (s, 2H)**;^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.5, 141.2, 137.1, 130.3, 128.9, 128.4, 127.2,



4f

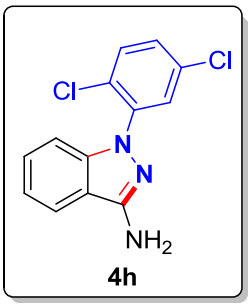
119.4, 115.6, 110.2. **HRMS** (ESI) calcd. for $C_{13}H_{11}ClN_3$ [M+H]: 243.0563, found: 243.0560.

1-(3,5-dichlorophenyl)-1H-indazol-3-amine (4g): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (8/1, v/v) to give the desired product as a white solid (250 mg, 90%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 1H), 7.62 (m, 3H), 7.51 – 7.47 (m, 1H), 7.23 – 7.18 (m, 2H), 2.14 – 2.05 (m, 2H).; **^{13}C NMR** (101 MHz, DMSO) δ 152.3, 143.1, 139.2, 135.3, 129.2, 122.8, 121.8, 121.1, 118.9, 117.6, 111.1.**HRMS** (ESI) calcd. for $C_{13}H_{10}Cl_2N_3$ [M+H]: 278.0252, found: 278.0257.



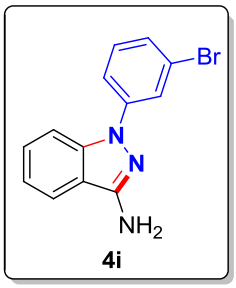
4g

1-(2,5-dichlorophenyl)-1H-indazol-3-amine (4h): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (8/1, v/v) to give the desired product as a white solid (141 mg, 51%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 1H), 7.48 (m, 2H), 7.39 (m, 1H), 7.30 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.18 – 7.09 (m, 2H), 4.34 (s, 2H).;**^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.9, 141.5, 138.5, 133.0, 131.4, 129.1, 128.8, 128.6, 127.7, 120.1, 119.5, 116.2, 110.7; **HRMS** (ESI) calcd. for $C_{13}H10C_{l2}N_3$ [M+H]: 278.0252, found: 278.0258.



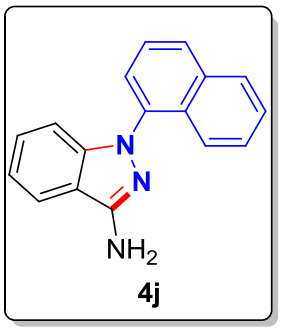
4h

1-(3-bromophenyl)-1H-indazol-3-amine (4i): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (8/1, v/v) to give the desired product as a white solid (253 mg, 88%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.62 (m, 2H), 7.44 (m, 1H), 7.37 – 7.30 (m, 2H), 7.16 (m, *J* = 7.5 Hz, 1H), 3.79 (s, 2H).; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.5, 141.7, 139.5, 130.5, 128.2, 127.6, 124.0, 122.9, 120.4, 119.8, 119.2, 117.0, 110.2;**HRMS** (ESI) calcd. for $C_{13}H_{11}BrN_3$ [M+H]: 288.0136, found: 288.0140.

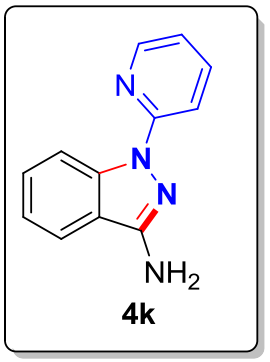


4i

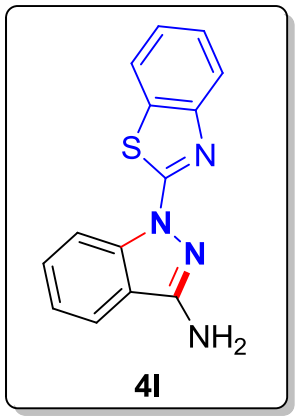
1-(naphthalen-1-yl)-1H-indazol-3-amine (4j): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (6/1, v/v) to give the desired product (150 mg, 58%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 14.5, 8.0 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.56 (m, 3H), 7.46 (m, 1H), 7.34 – 7.29 (m, 1H), 7.17 – 7.11 (m, 2H), 4.28 (s, 2H).;**^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.0, 142.3, 136.1, 134.6, 129.8, 128.07 (d, *J* = 2.6 Hz), 127.4, 126.6, 126.4, 125.3, 123.9 (d, *J* = 10.3 Hz), 119.5 (d, *J* = 4.3 Hz), 115.6, 110.2; **HRMS** (ESI) calcd. for $C_{17}H_{14}N_3$ [M+H]: 260.1188, found: 260.1191.



1-(pyridin-2-yl)-1H-indazol-3-amine (4k): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (5/1, v/v) to give the desired product as a white solid (183 mg, 87%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.5 Hz, 1H), 8.44 (d, *J* = 4.0 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.50 (m, 1H), 7.20 (m, 1H), 7.00 (dd, *J* = 6.5, 5.5 Hz, 1H), 4.32 (s, 2H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.2, 149.8, 147.5, 139.8, 137.8, 128.5, 121.1, 118.8, 118.0, 117.6, 115.3, 111.9; **HRMS** (ESI) calcd. for $C_{12}H_{10}N_4$ [M+H]:211.0984, found: 211.0988.

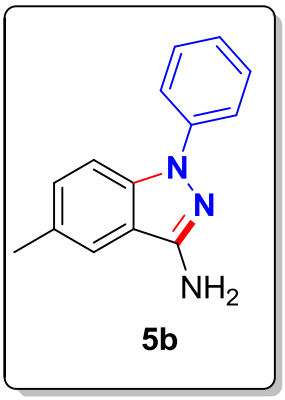


1-(benzo[d]thiazol-2-yl)-1H-indazol-3-amine (4l): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (8/1, v/v) to give the desired product as a white solid (186 mg, 70%). **^{1}H NMR** (500 MHz, DMSO) δ 8.67 (d, *J* = 8.5 Hz, 1H), 8.11 (m, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.81 (m, 1H), 7.60 (m, *J* = 7.5 Hz, 1H), 7.49 (m, *J* = 7.5 Hz, 1H), 7.43 (m, 1H), 6.83 (s, 2H).;**^{13}C NMR** (126 MHz, DMSO) δ 160.9, 153.7, 152.4, 139.2, 131.7, 130.2,

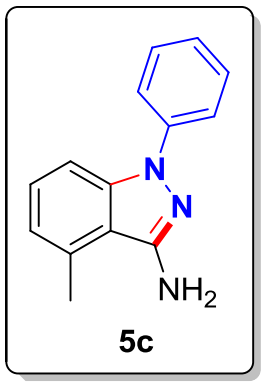


126.8, 123.6 ,123.2, 122.2, 121.8, 121.1, 120.1, 114.1,; **HRMS** (ESI) calcd. for $C_{14}H_{11}N_4S$[M+H]: 267.0704, found: 267.0710.

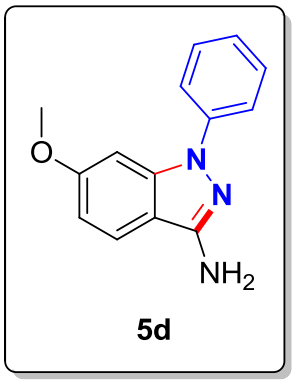
5-methyl-1-phenyl-1H-indazol-3-amine(5b): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (5/1, v/v) to give the desired product as a white solid (209 mg, 94%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.46 (m, 2H), 7.37 (s, 1H), 7.25 – 7.19 (m, 2H), 3.91 (s, 2H), 2.46 (s, 3H).;**^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.6, 140.6, 138.2, 129.6, 129.20 (d, *J* = 12.5 Hz), 124.5, 120.8, 118.8, 116.8, 109.9, 20.99. **HRMS** (ESI) calcd. for $C_{14}H_{14}N_3$ [M+H]: 223.1188, found: 223.1186.



4-methyl-1-phenyl-1H-indazol-3-amine (5c): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (5/1, v/v) to give the desired product as a white solid (205 mg, 92%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.47 (m, 3H), 7.23 (m, 2H), 6.82 (d, *J* = 7.0 Hz, 1H), 3.93 (s, 2H), 2.72 (s, 3H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.8, 140.3 (d, *J* = 19.6 Hz), 132.0, 129.2, 127.9, 125.0, 121.6, 120.9, 115.9, 107.9, 19.1; **HRMS** (ESI) calcd. for $C_{13}H_{13}N_3$ [M+H]: 224.1188, found: 224.1190.

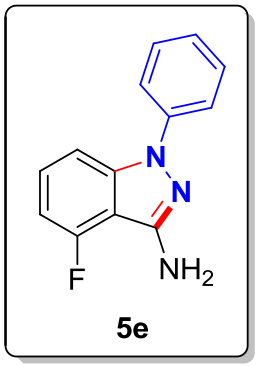


6-methoxy-1-phenyl-1H-indazol-3-amine (5d): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (6/1, v/v) to give the desired product as a white solid (172 mg, 72%).**^{11}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.55 – 7.41 (m, 3H), 7.28 – 7.23 (m, 1H), 7.02 (m, 1H), 6.77 (dd, *J* = 9.0, 2.0 Hz, 1H), 4.02 (s, 2H), 3.85 (s, 3H).;**^{13}C NMR** (101 MHz, DMSO) δ



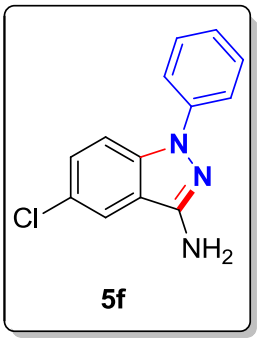
160.7, 151.3, 141.3, 140.6, 129.9, 124.4, 122.4, 120.6, 112.2, 110.7, 92.6, 55.8; **HRMS** (ESI) calcd. For $C_{14}H_{14}N_3O$ [M+H]: 240.1137, found: 240.1142.

4-fluoro-1-phenyl-1H-indazol-3-amine (5e): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (6/1, v/v) to give the desired product as a white solid (127 mg, 56%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.43 (m, 3H), 7.26 (m, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 4.68 (s, 2H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.8, 141.0, 140.0, 129.4, 128.5, 127.0, 125.8, 122.0, 121.7, 120.1, 113.7, 109.0; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -61.63 (s). **HRMS** (ESI) calcd. For $C_{13}H_{11}FN_3$ [M+H]: 228.0937, found: 228.0944.



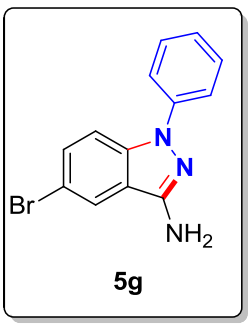
5e

5-chloro-1-phenyl-1H-indazol-3-amine(5f): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (5/1, v/v) to give the desired product as a white solid (207 mg, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.55 (m, 2H), 7.47 (m, 2H), 7.31 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.24 (m, 1H), 4.26 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.26 (s), 140.06 (s), 138.08 (s), 129.37 (s), 128.21 (s), 125.46 (s), 125.14 (s), 121.41 (s), 119.04 (s), 117.37 (s), 111.34 (s), 77.25 (s), 76.87 (d, *J* = 32.0 Hz), 76.65 – 76.41 (m). **HRMS** (ESI) calcd. for $C_{13}H_{11}ClN_3$ [M+H]: 244.0642, found: 244.0645.



5f

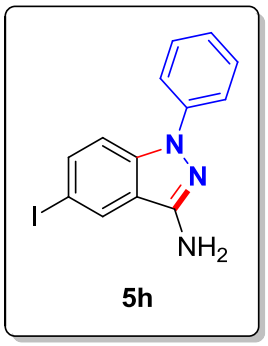
5-bromo-1-phenyl-1H-indazol-3-amine (5g): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (8/1, v/v) to give the desired product as a white solid (216 mg, 75%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.5 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 9.0 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 1H), 3.54 (s, 2H).; **^{13}C NMR** (101 MHz, DMSO) δ 150.6, 140.7, 138.0, 130.8,



5g

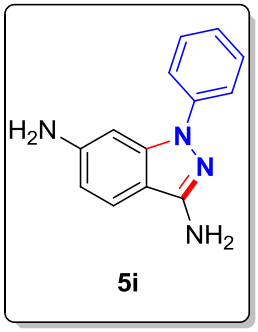
129.9, 124.9, 124.1, 120.6, 119.3, 112.5, 111.4.; **HRMS** (ESI) calcd. for $C_{13}H_{11}BrN_3$ [M+H]: 288.0136, found: 288.0143.

5-iodo-1-phenyl-1H-indazol-3-amine (5h): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (8/1, v/v) to give the desired product as a white solid (17 8mg, 53%).**^{1}H NMR** (500 MHz, DMSO) δ 8.43 (s, 1H), 7.82 – 7.69 (m, 4H), 7.64 (m, 2H), 7.37 (m, 1H), 6.16 (s, 2H).;**^{13}C NMR** (101 MHz, DMSO) δ 150.2, 140.7, 138.2, 136.0, 130.2, 129.9, 124.9, 120.6, 120.1, 112.8, 82.3; **HRMS** (ESI) calcd. for $C_{13}H_{11}IN_3$ [M+H]: 335.9998, found: 336.0000.



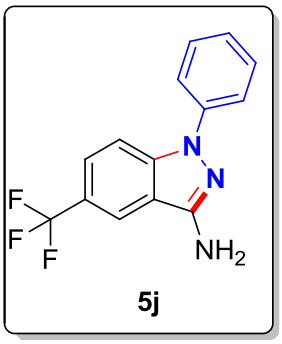
5h

1-phenyl-1H-indazole-3,6-diamine (5i): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (8/1, v/v) to give the desired product as a white solid (213 mg, 95%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.85 (s, 1H), 6.51 (d, *J* = 8.5 Hz, 1H), 4.11 (s, 4H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2, 147.3, 141.1, 140.6, 128.9 , 124.1, 120.7, 120.5, 110.7, 109.8, 93.0; **HRMS** (ESI) calcd. for $C_{13}H_{13}N_4$ [M+H]: 225.1140, found: 225.1143.



5i

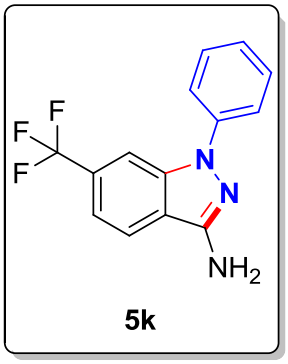
1-phenyl-5-(trifluoromethyl)-1H-indazol-3-amine (5j): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (5/1, v/v) to give the desired product as a white solid (247 mg, 89%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* =8.0 Hz, 2H), 7.58 (d, *J* =9.0 Hz, 1H), 7.50 (m, 2H), 7.30 (m, 1H), 4.28 (s, 2H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.7, 140.4, 139.7, 129.4, 125.9, 124.3 (d, *J* = 3.2 Hz), 121.8 (d,



5j

J = 10.2 Hz), 118.0 (d, *J* = 4.4 Hz), 115.8, 110.6; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -60.76 (s); **HRMS** (ESI) calcd. for $C_{14}H_{11}F3N_3$ [M+H]: 278.0905, found: 278.0910.

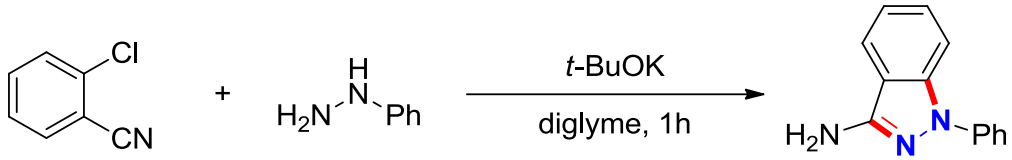
1-phenyl-6-(trifluoromethyl)-1H-indazol-3-amine (5k): Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column petroleum ether/ethyl acetate (5/1, v/v) to give the desired product as a white solid (180 mg, 65%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.52 (m, 2H), 7.33 (m, 2H), 4.30 (s, 2H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.9, 139.7, 138.6, 129.5, 126.0, 121.8, 120.7, 118.1, 116.3 (d, *J* = 3.3 Hz), 107.8 (q, *J* = 4.6 Hz); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -61.63 (s).; **HRMS** (ESI) calcd. for $C_{14}H_{11}F_3N_3$ [M+H]: 278.0905, found: 278.0909.



5k

5. Gram scale experiments

Open system:



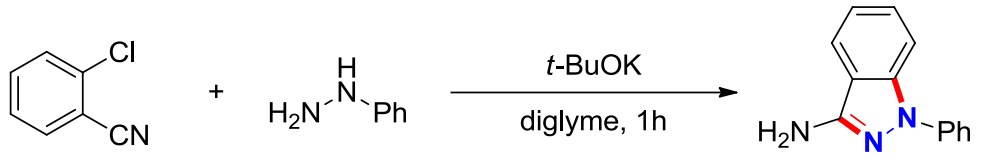
1b 10 mmol

2a 30 mmol

4a 94% (1.96 g)

10 mmol scale:

Using a nitrogen-filled glove box, an oven-dried Schleck tube (250 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (13 mmol, 1.46 g), phenyl hydrazine (30 mmol, 3.244 g) and diglyme (40 mL). After stirring of 5 minutes, 2-chlorobenzonitrile (10 mmol, 1.376 g) was added the mixture reaction, the tube was sealed, taken out of the glove box and a reflux condenser was attached under argon stream. The mixture was heated to a gentle reflux for an hours under inert atmosphere in an open system at 130 °C (oil bath). After cooling, quenched with half-saturated brine and extracted with dichloromethane (4 x 200 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. A small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (pentane/ethyl ether = 5/1) to give the desired products **4a** in 94 % yield (1.96 g).



1b **2a** **4a**

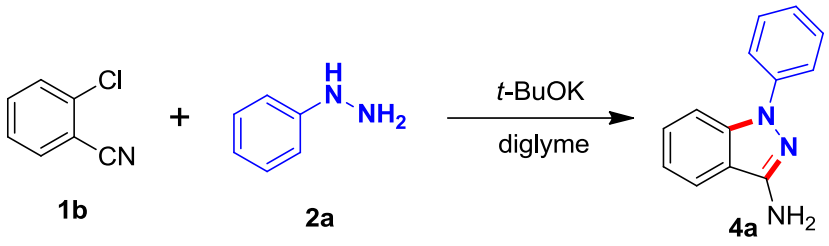
100 mmol 300 mmol 90% (18.81 g)

100 mmol scale:

Using a nitrogen-filled glove box, an oven-dried Schleck tube (2.5 L volume) was charged with a magnetic stirring bar, *t*-BuOK (0.13 mmol, 14.6 g), phenyl hydrazine (0.3 mol, 32.44 g) and diglyme (0.5 L). After stirring of 5 minutes, 2-chlorobenzonitrile (0.1 mol, 13.76 g) was added the mixture reaction, the tube was sealed, taken out of the glove box and a reflux condenser was attached under argon stream. The mixture was heated to a gentle reflux for an hours under inert atmosphere in an open system at 130 °C (oil bath). After cooling, quenched with half-saturated brine and extracted with dichloromethane (4 x 200 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. A small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation. Then the corresponding reaction mixture was purified by recrystallized to give the desired product (diethyl ether/DCM) to give the desired products **4a** in 90 % yield (18.81 g).

6. Mechanistic investigations

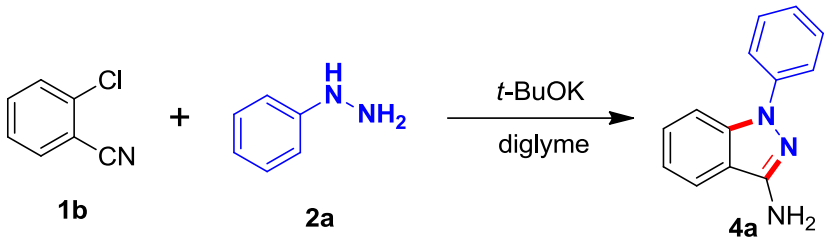
6.1 Control experiments



Entry	Reaction condition		**4a** (%)
1	98% *t*-BuOK	new seal tube	95
2	99.99% *t*-BuOK	new seal tube	96
3	--	new seal tube	0

Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (1.3 mmol), phenyl hydrazine (3.0 mmol) and diglyme (2.0 mL). After stirring of 5 minutes, 2-chlorobenzonitrile (1.0 mmol) was added the mixture reaction. Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (design temperature). After design time the reaction was cooled, quenched with half-saturated brine and extracted with dichloromethane (4 x 15 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. A small aliquot of the organic phase was analyzed by GC to monitor product formation.

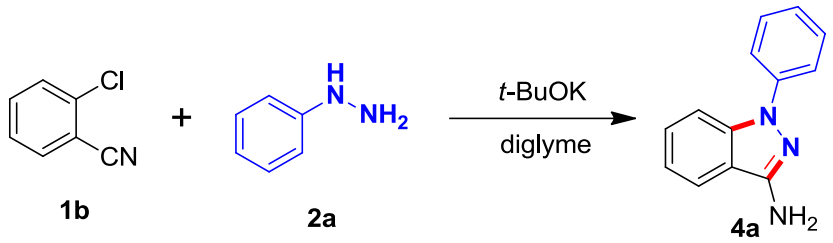
6.2 Control experiments with transition metal additives



Entry	Reaction condition	Additive	**4a** (%)
1	99.99% *t*-BuOK	CuBr (5 mol%)	92
2	99.99% *t*-BuOK	$Pd(OAc)_2$ (5 mol%)	93
3	--	CuBr (5 mol%)	<5
4	--	$Pd(OAc)_2$ (5 mol%)	<5

Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (1.3 mmol), phenyl hydrazine (3.0 mmol), additives (0.05 mmol) and diglyme (2.0 mL). After stirring of 5 minutes, 2-chlorobenzonitrile (1.0 mmol) was added the mixture reaction. Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (design temperature). After design time the reaction was cooled, quenched with half-saturated brine and extracted with dichloromethane (4 x 15 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. A small aliquot of the organic phase was analyzed by GC to monitor product formation.

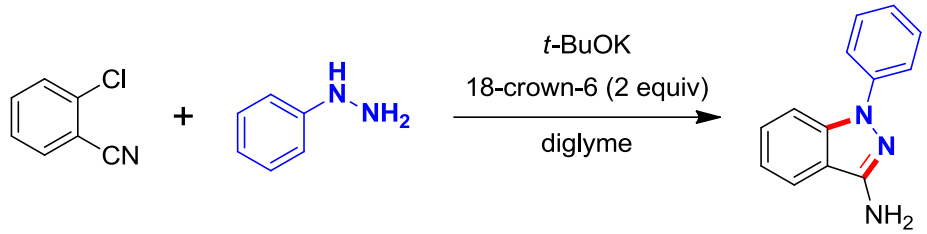
6.3 Control experiments with radical scavenger



Entry	Reaction condition	Radical scavenger	**4a** (%)
1	99.99% *t*-BuOK	TEMPO (1 equiv)	91
2	99.99% *t*-BuOK	$Ph_2C=CH_2$ (1 equiv)	90
3	99.99% t-BuOK	TEMPO (2 equiv)	90
4	99.99% t-BuOK	$Ph_2C=CH_2$ (2 equiv)	89

Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (1.3 mmol), phenyl hydrazine (3.0 mmol), radical scavengers and diglyme (2.0 mL). After stirring of 5 minutes, 2-chlorobenzonitrile (1.0 mmol) was added the mixture reaction. Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (design temperature). After design time the reaction was cooled, quenched with half-saturated brine and extracted with dichloromethane (4 x 15 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. A small aliquot of the organic phase was analyzed by GC to monitor product formation.

6.4 Control experiments with 18-crown-6 additive



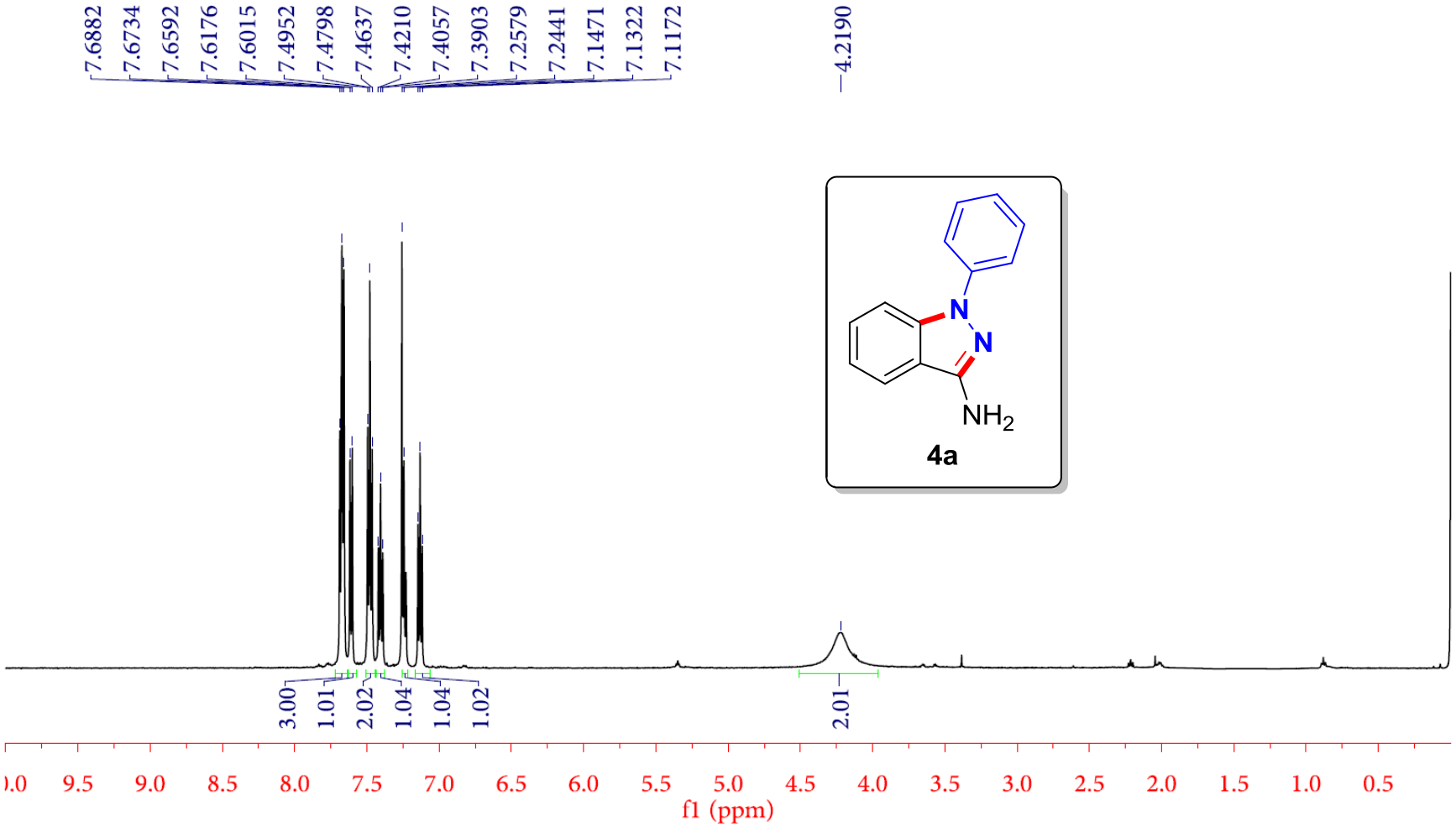
1b **2a** **4a**, 95%

Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (1.3 mmol), phenyl hydrazine (3.0 mmol), 18-crown-6 (2.0 mmol) and diglyme (2.0 mL). After stirring of 5 minutes, 2-chlorobenzonitrile (1.0 mmol) was added the mixture reaction. Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (design temperature). After design time the reaction was cooled, quenched with half-saturated brine and extracted with dichloromethane (4 x 15 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. A small aliquot of the organic phase was analyzed by GC to monitor product formation.

7. References

1. Vasudevan, A.; Souers, A. J.; Freeman, J. C.; Verzal, M. K.; Gao, J.; Mulhern, M. M.; Wodka, D.; Lynch, J. K.; Engstrom, K. M.; Wagaw, S. H.; Brodjian, S.; Dayton, B.; Falls, D. H.; Bush, E.; Brune, M.; Shapiro, R. D.; Marsh, K. C.; Hernandez, L. E.; Collins, C. A.; Kym, P. R. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 5293.
2. Kruger, A. W.; Rozema, M. J.; Chu-Kung, A.; Gandarilla, J.; Haight, A. R.; Kotecki, B. J.; Richter, S. M.; Schwartz, A. M.; Wang, Z. *Org. Process. Res. Dev.* **2009,** *13*, 1419.
3. Antonysamy, S.; Hirst, G.; Park, F.; Sprengeler, P.; Stappenbeck, F.; Steensma, R.; Wilson, M.; Wang, M. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 279.

8. Copies for ^{1}H NMR and ^{13}C NMR of the 3-aminoindazoles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7.2579
7.2441
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7.1322
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2.02
1.04
1.04
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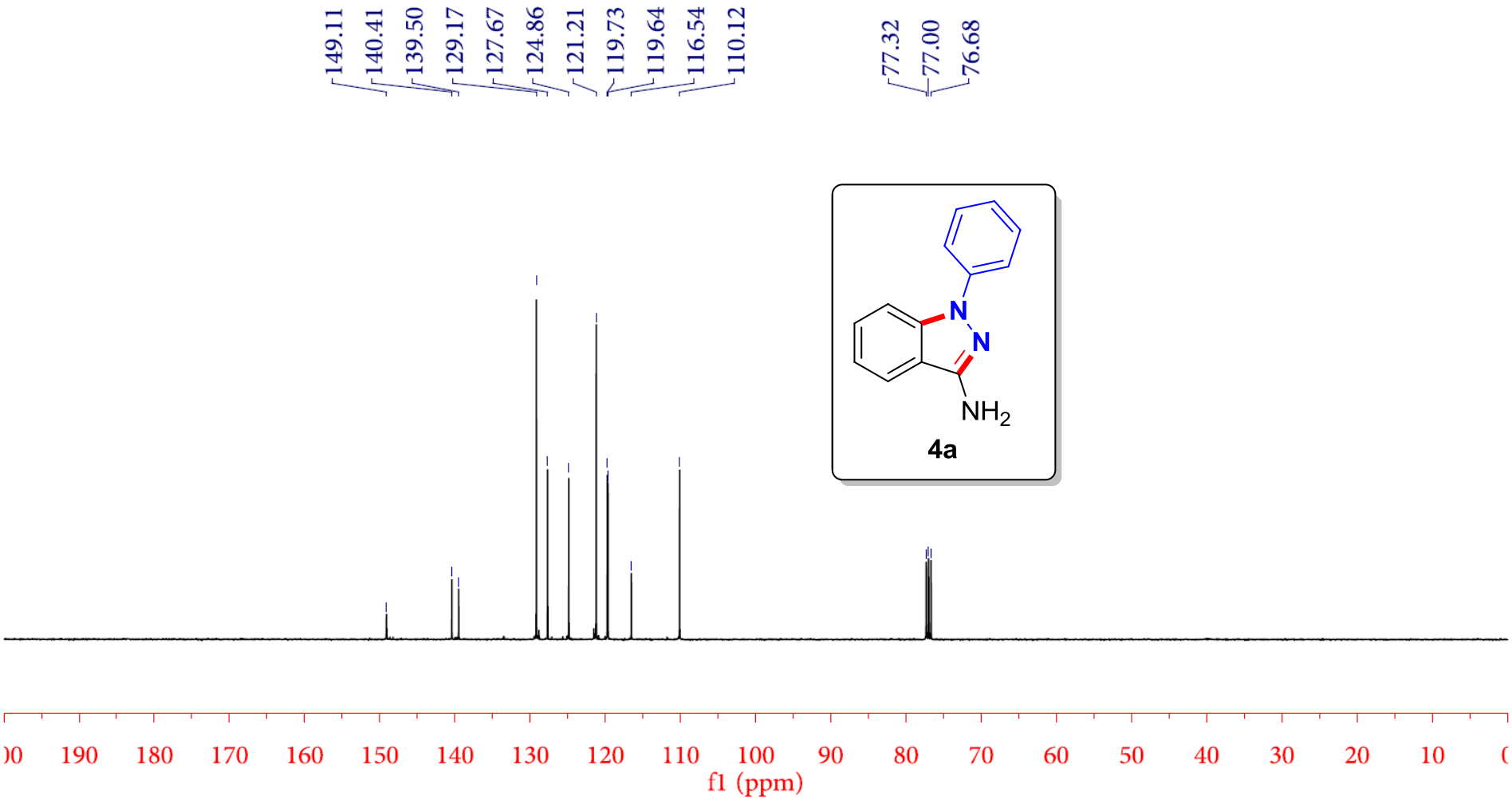
2.01
f1 (ppm)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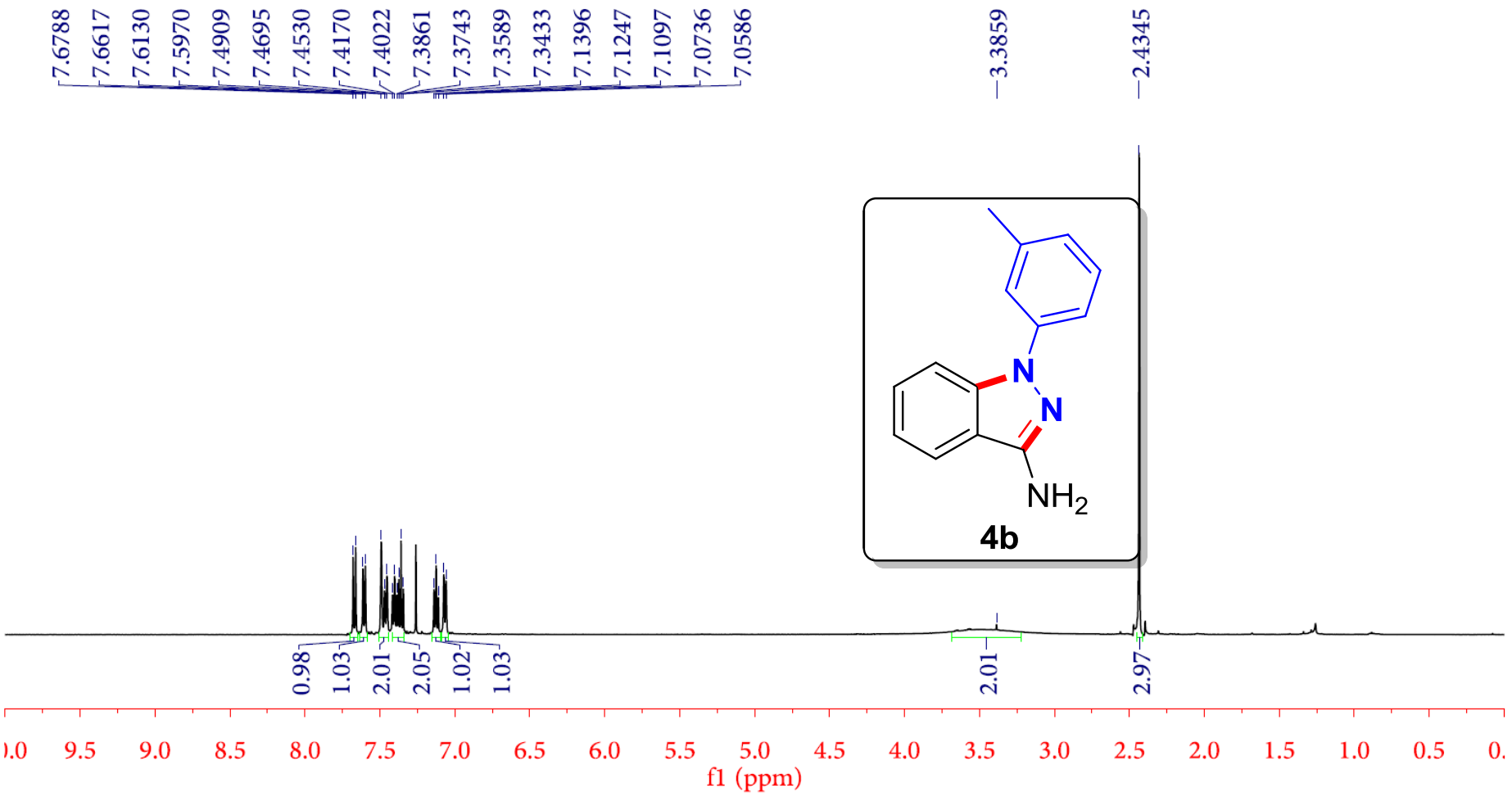
N
NH2
4a
f1 (ppm)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3.3859
2.4345
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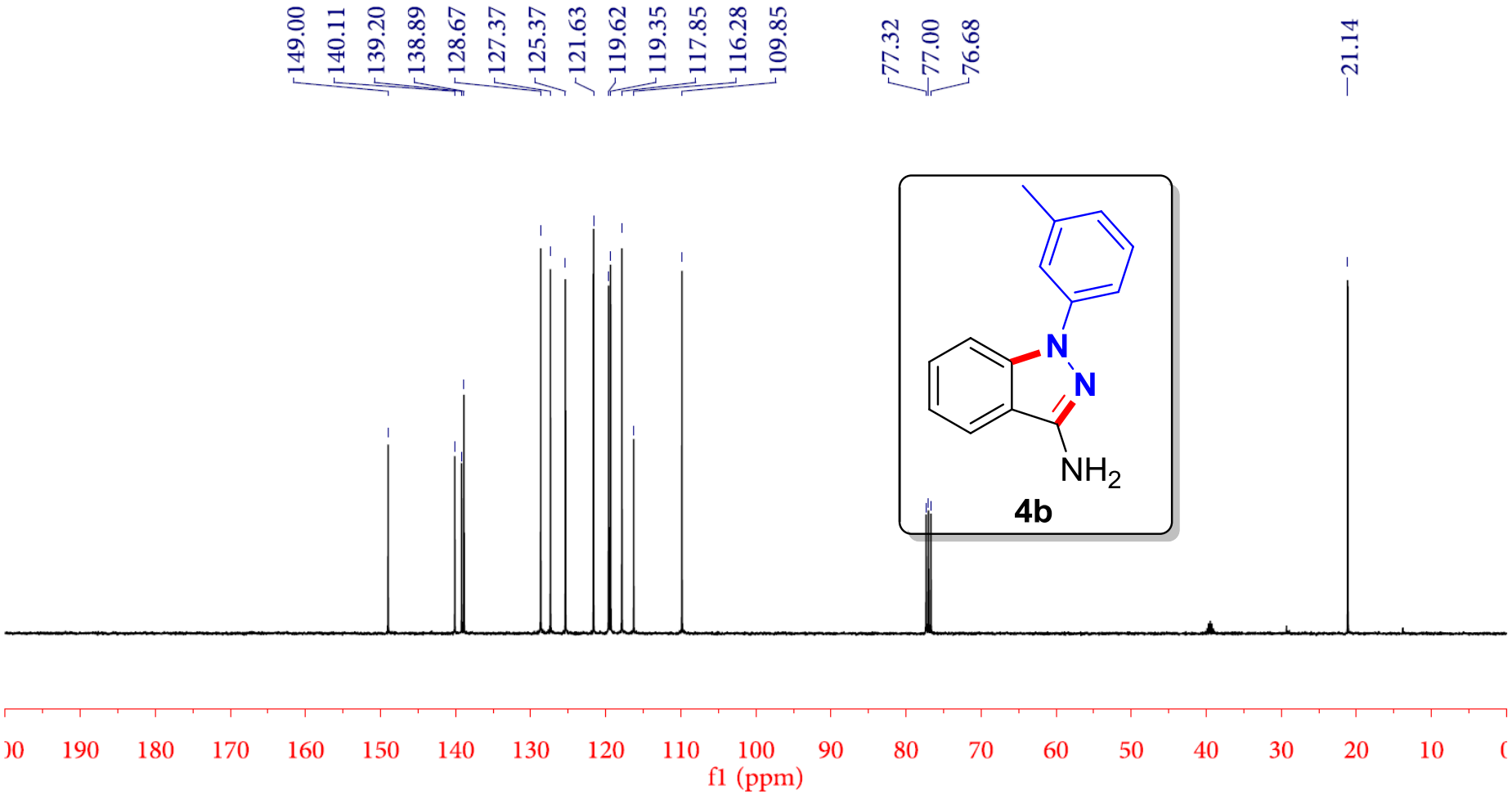
1.03
2.01
2.97
f1 (ppm)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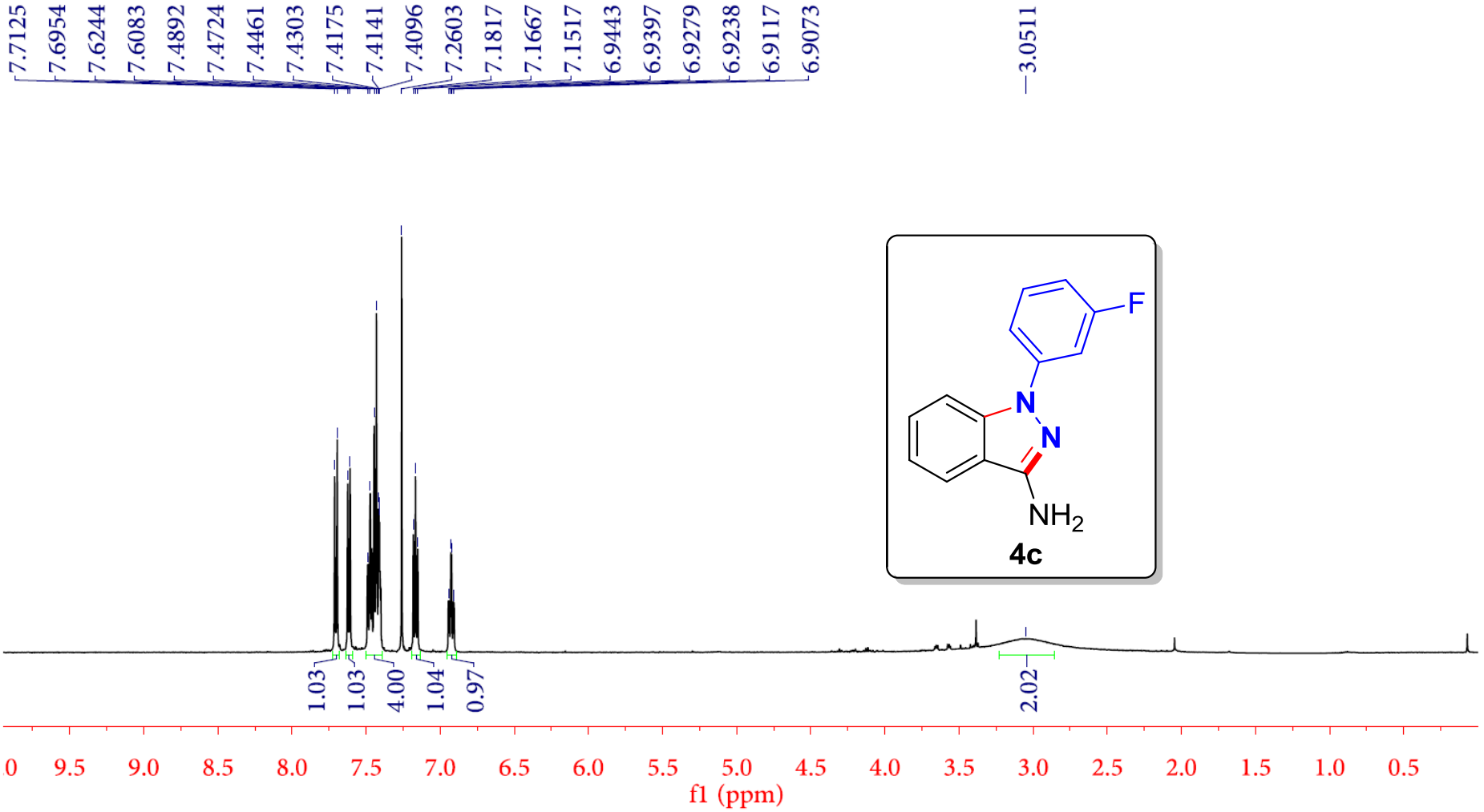
NH2
4b
f1 (ppm)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N
NH2
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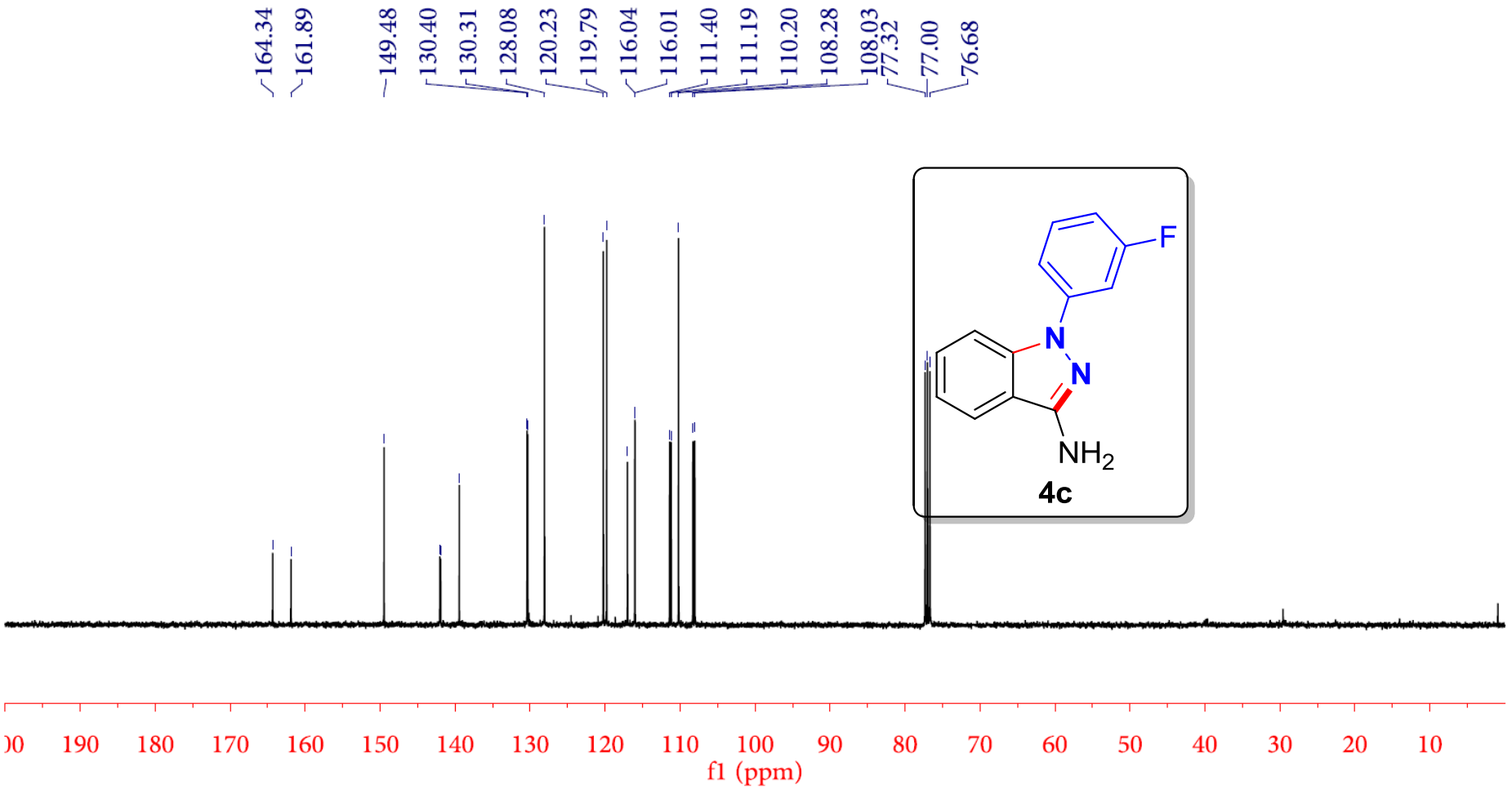
f1 (ppm)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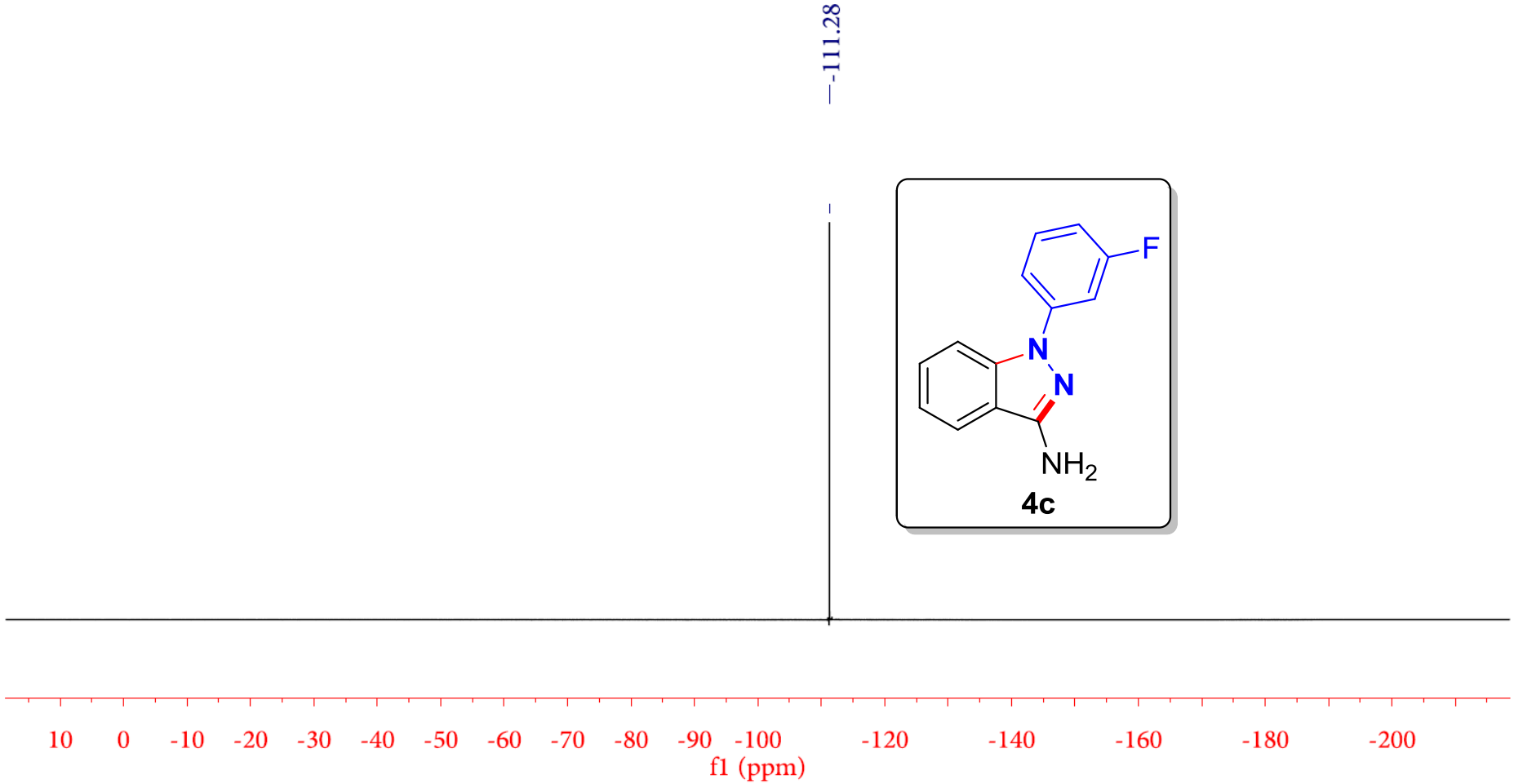
4c
f1 (ppm)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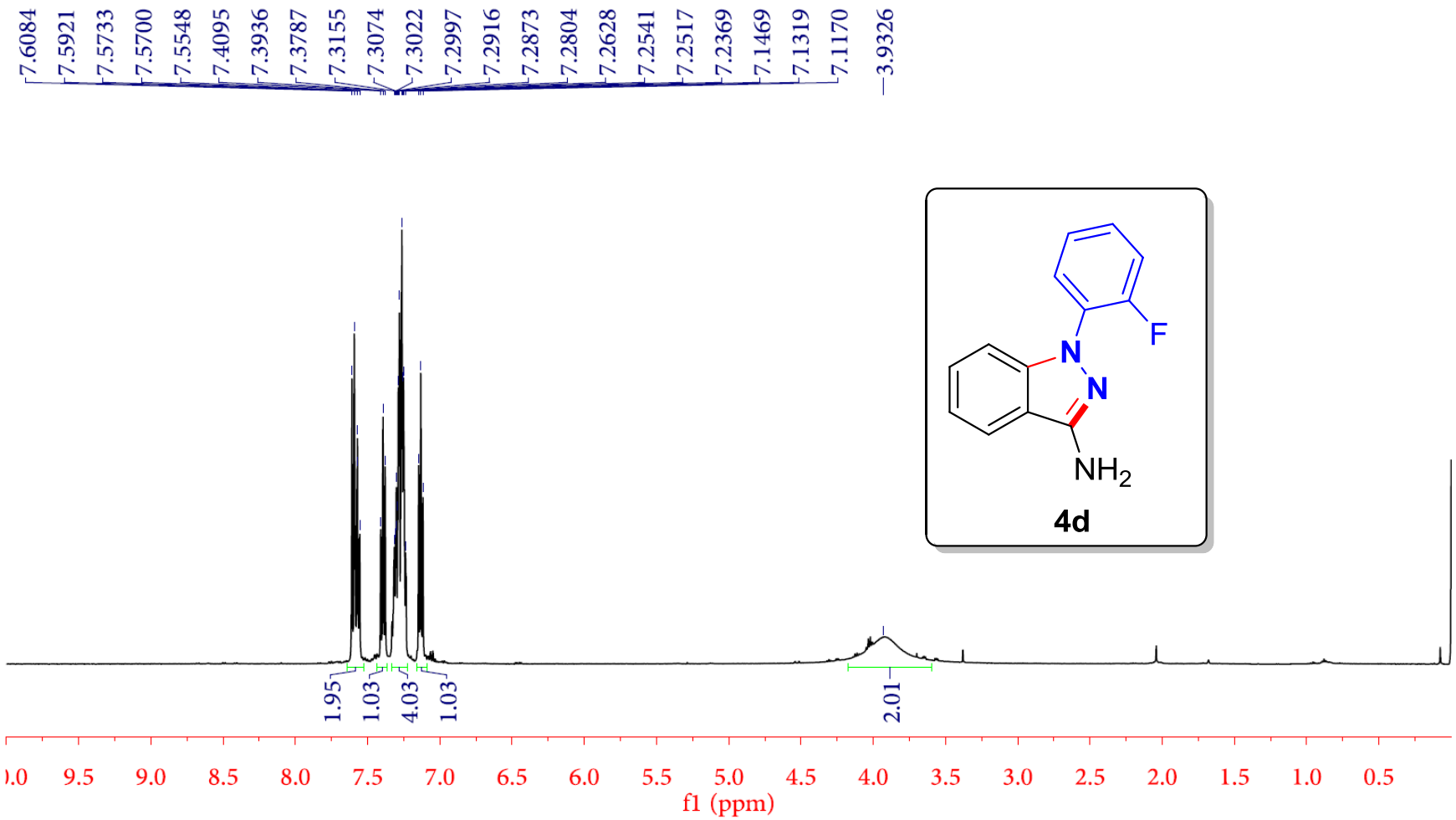
f1 (ppm)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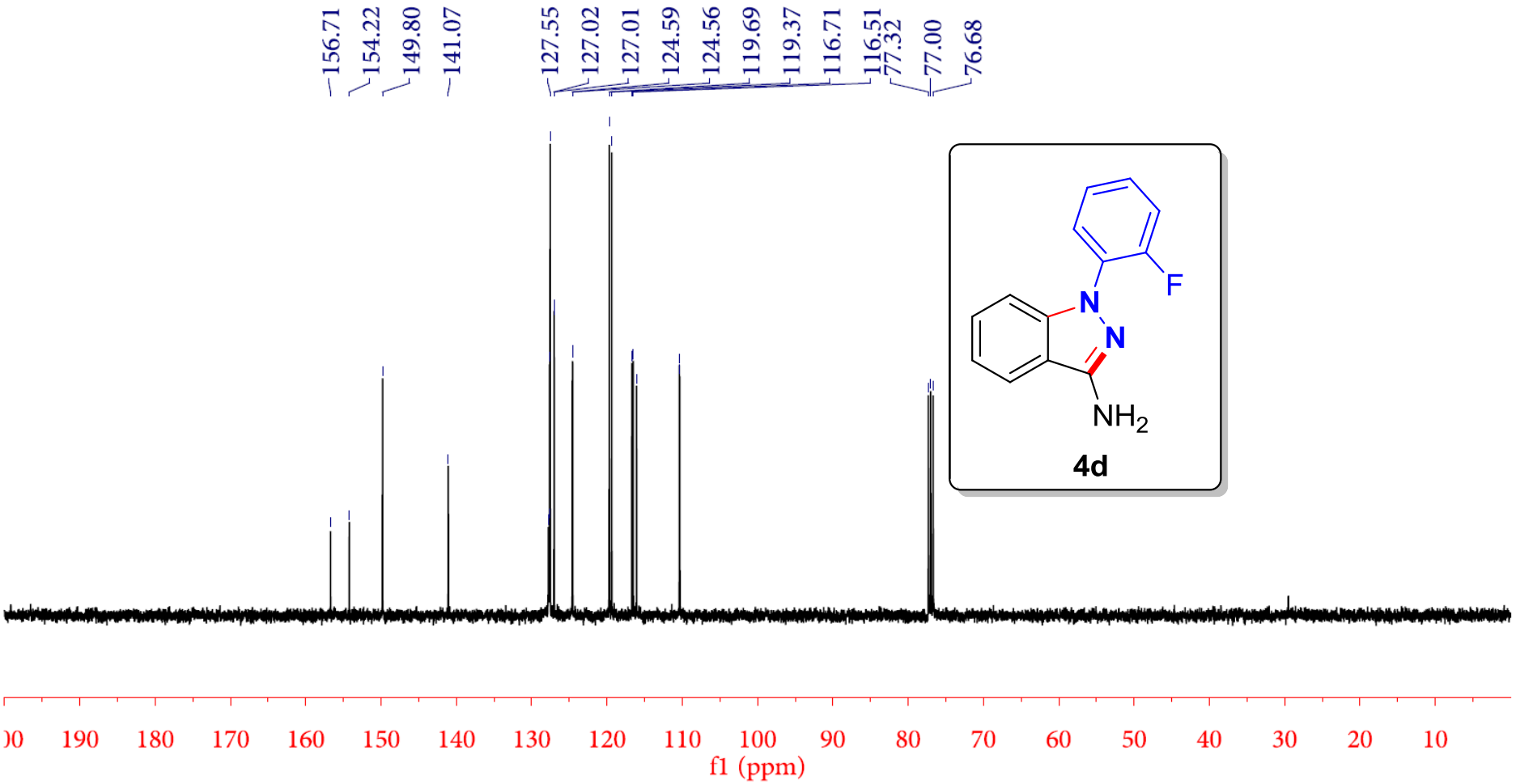
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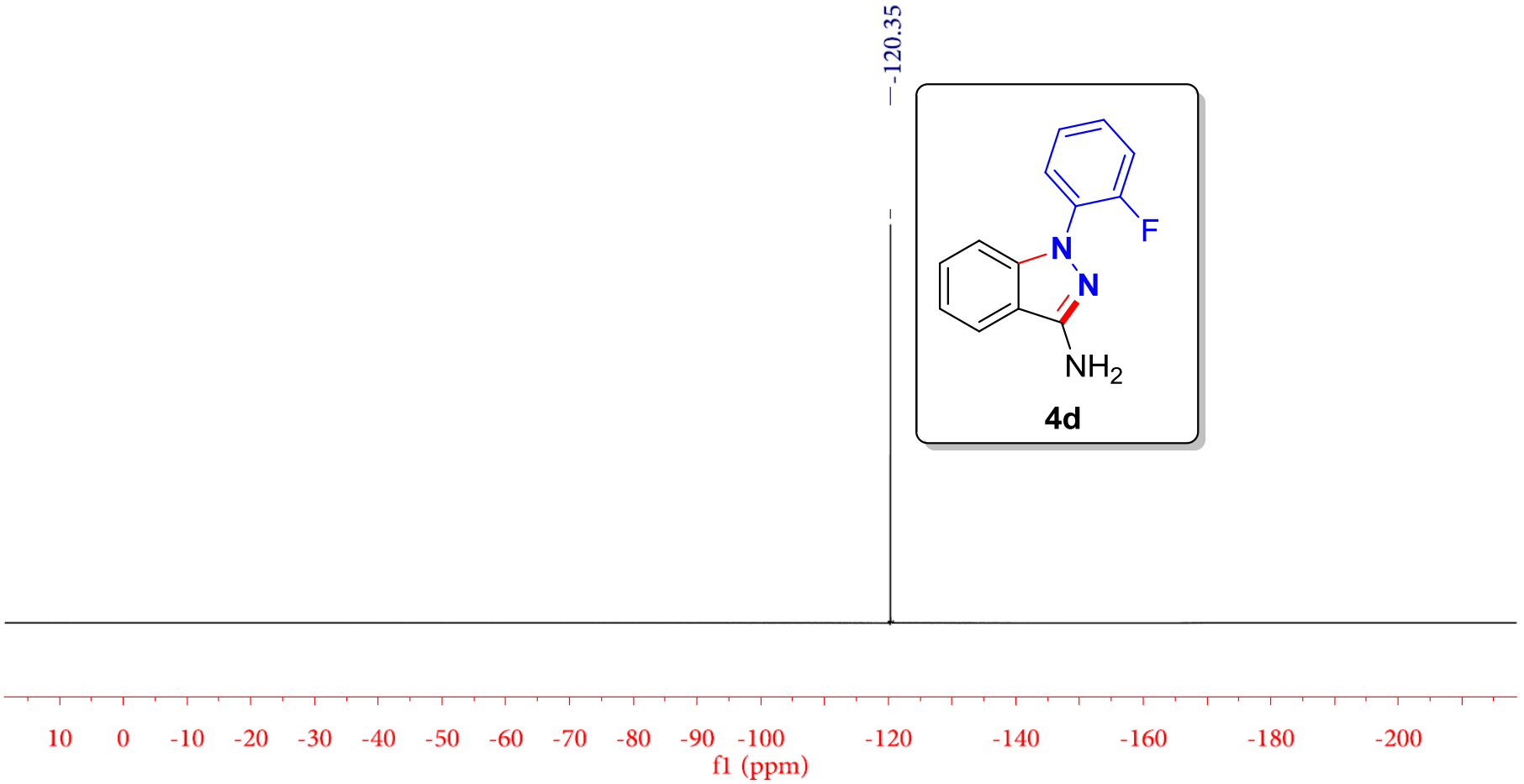
f1 (ppm)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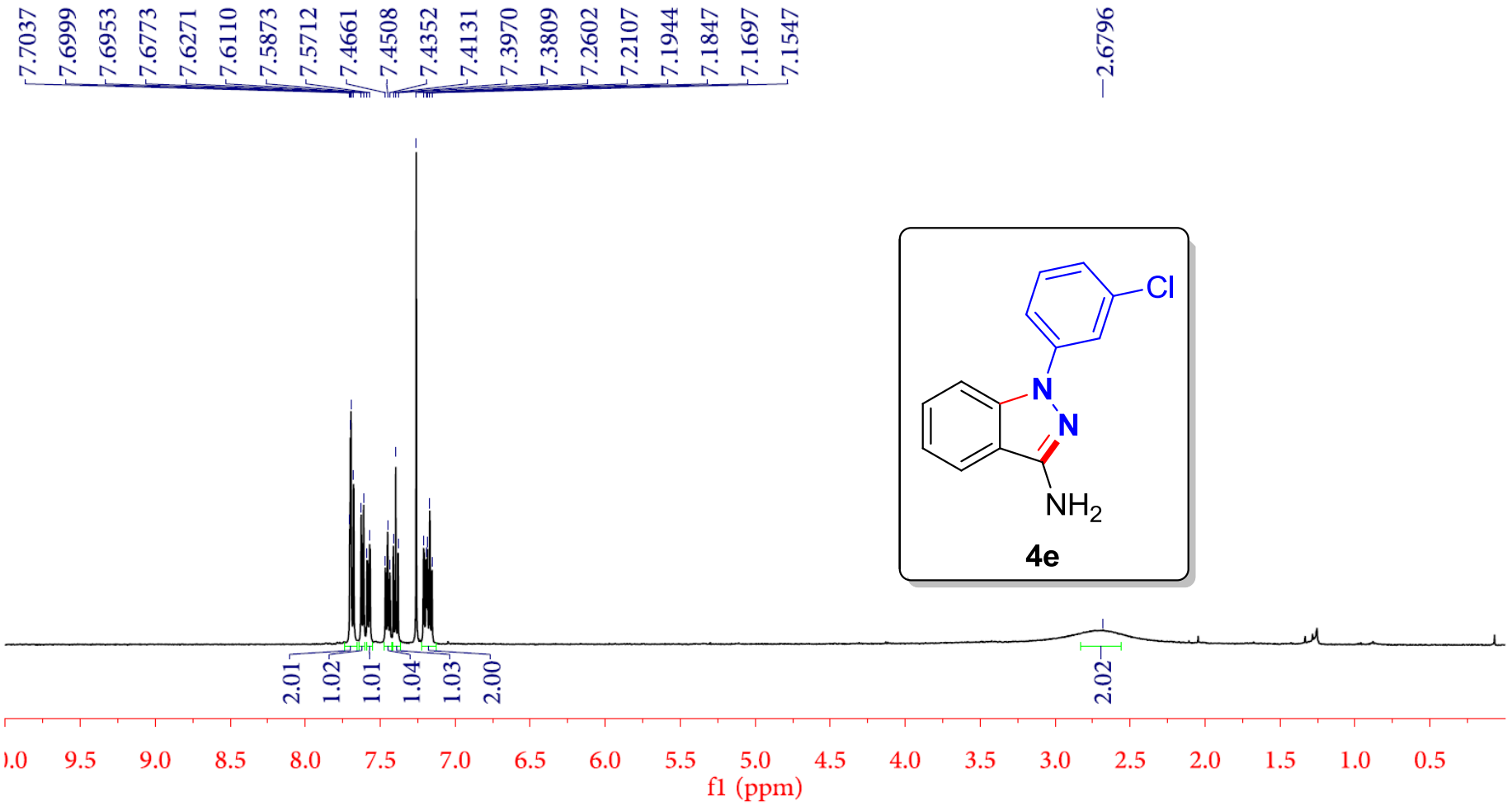
f1 (ppm)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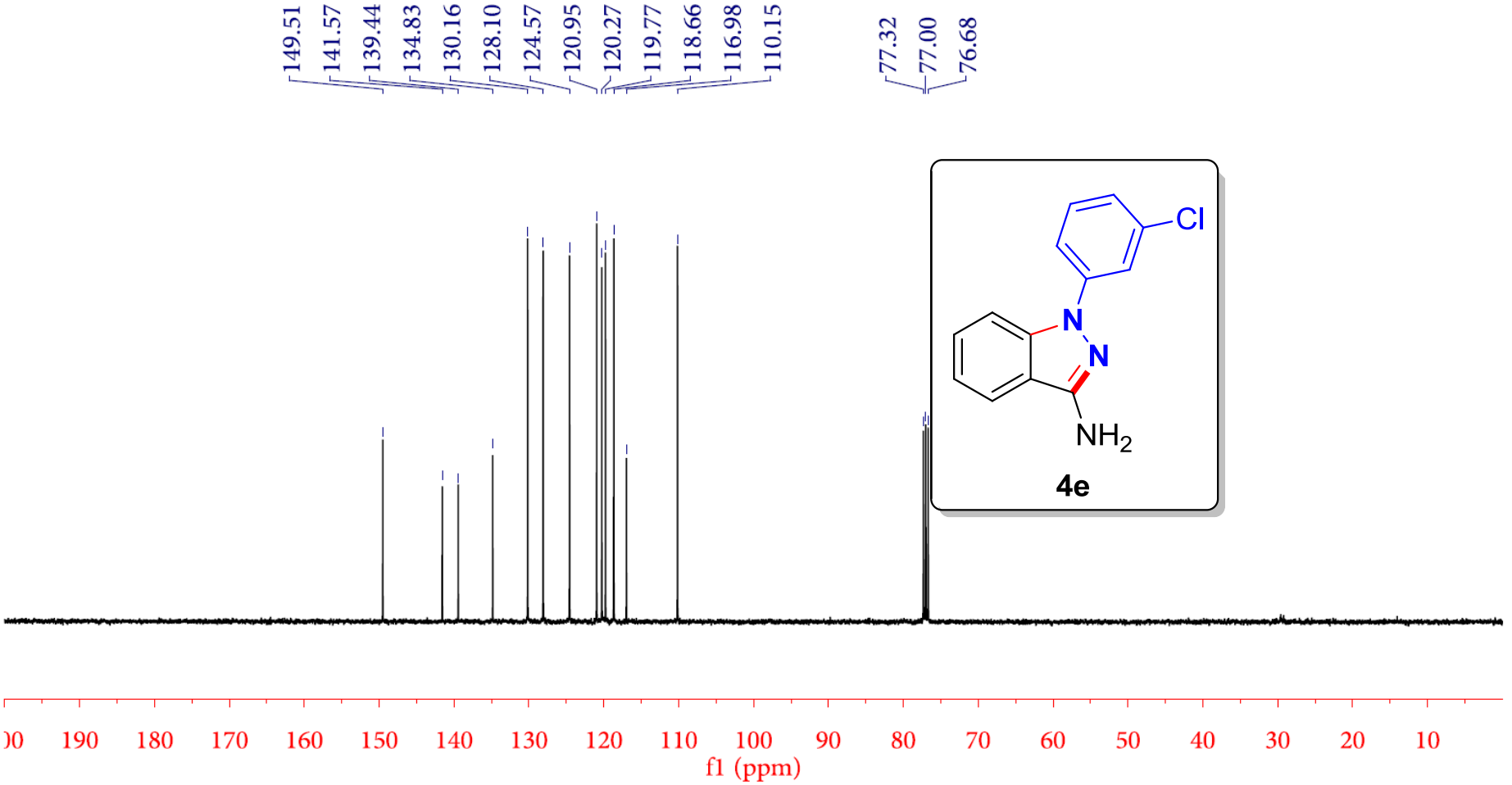
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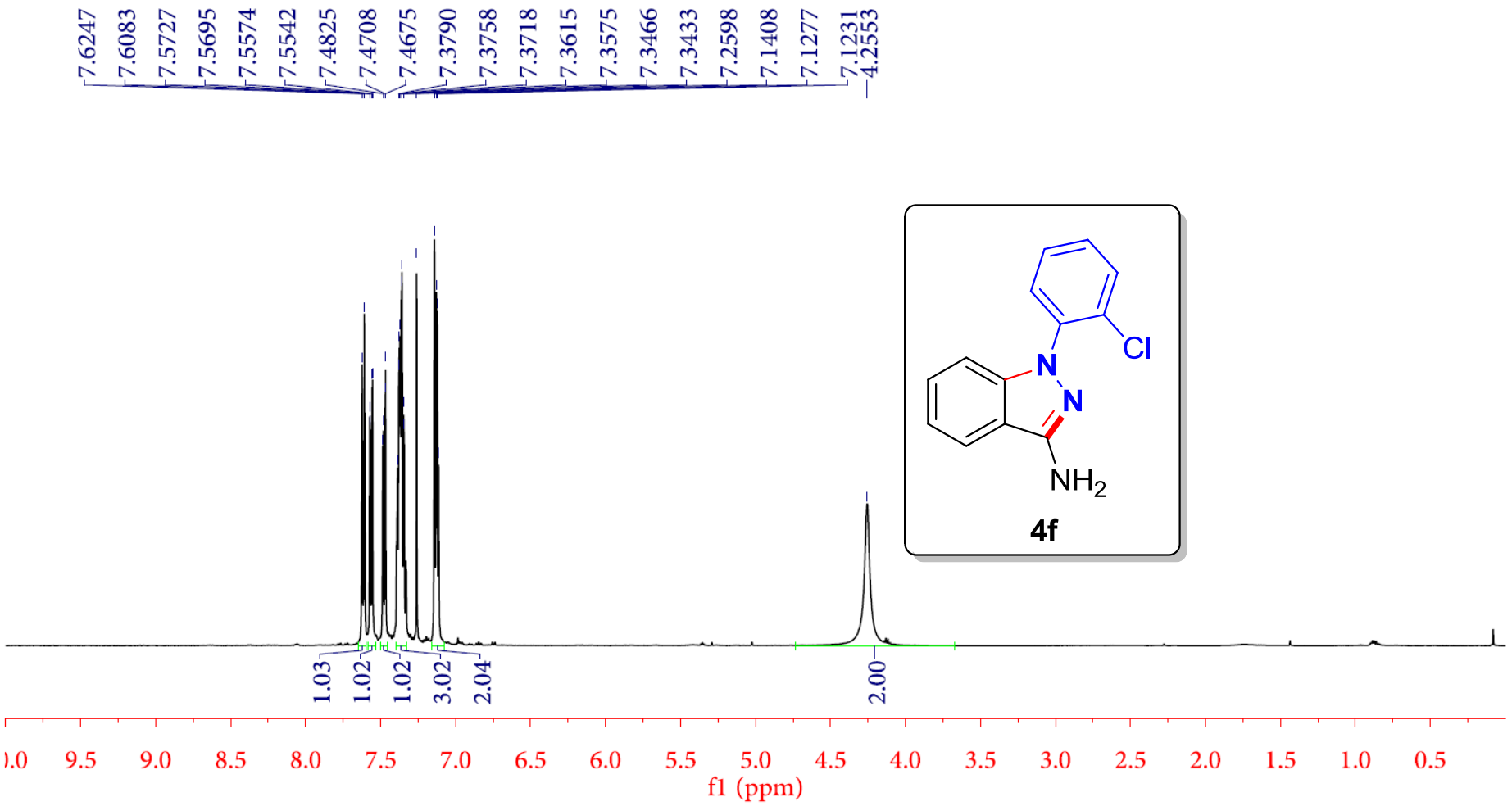
f1 (ppm)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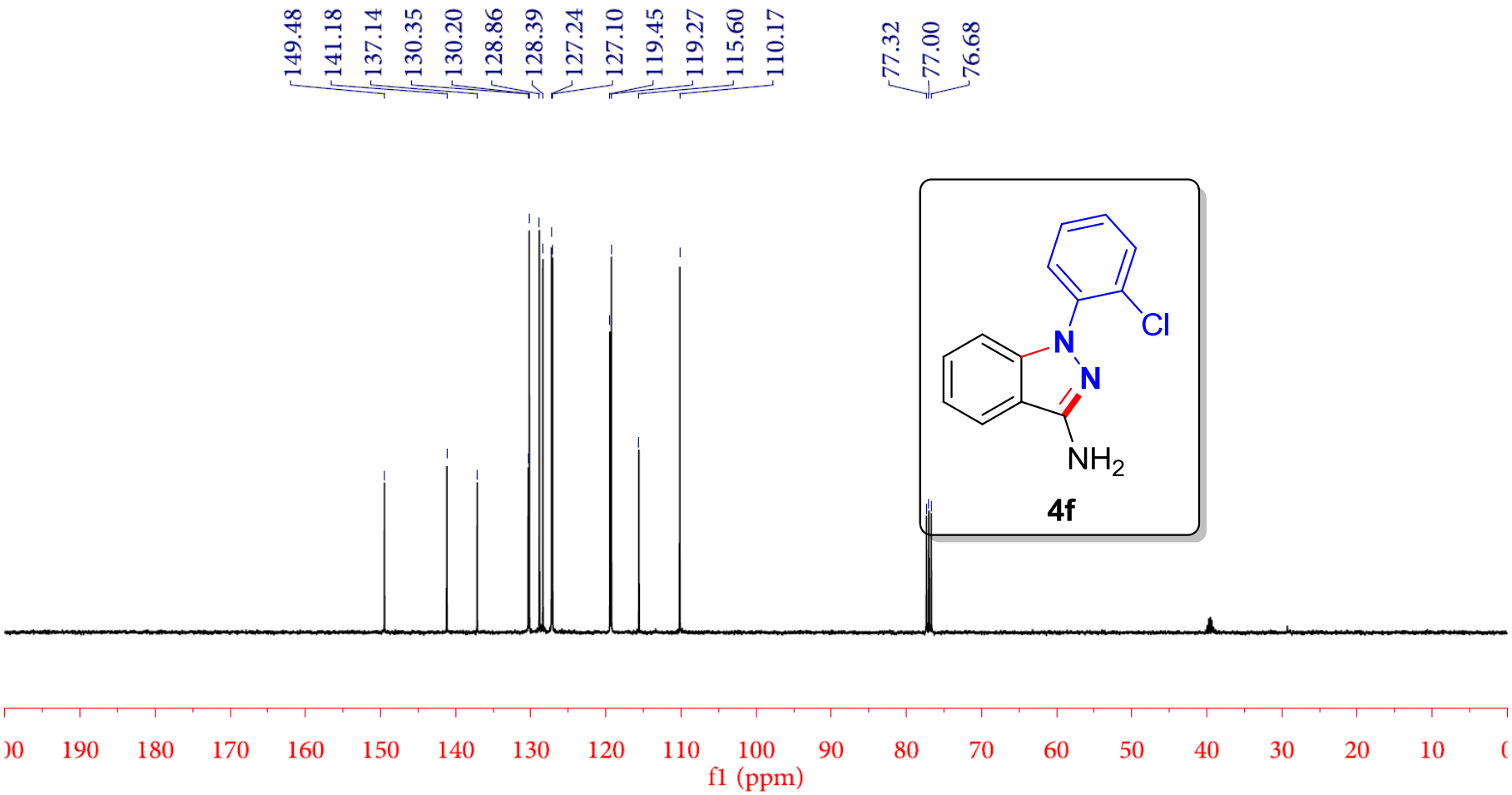
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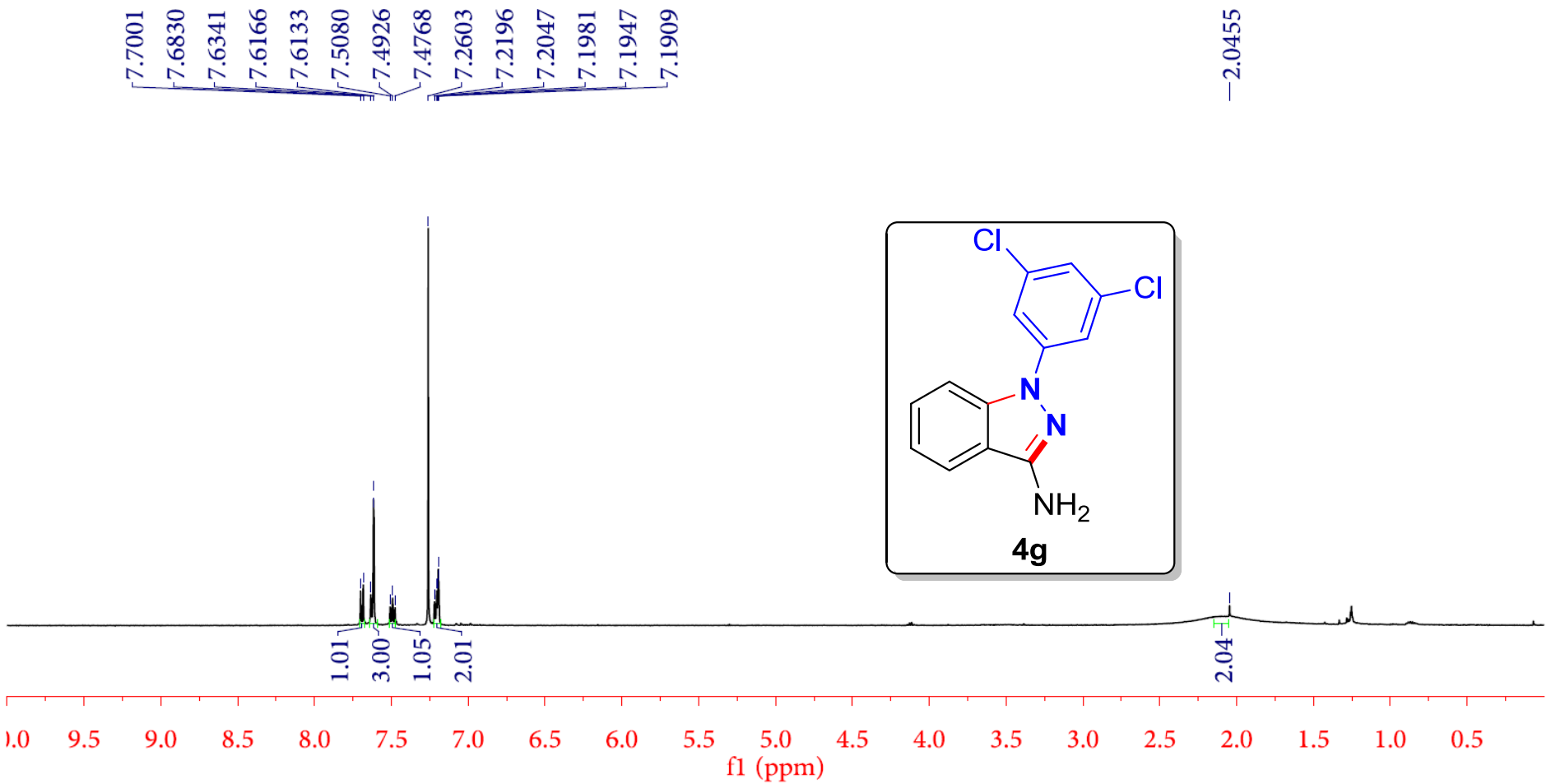
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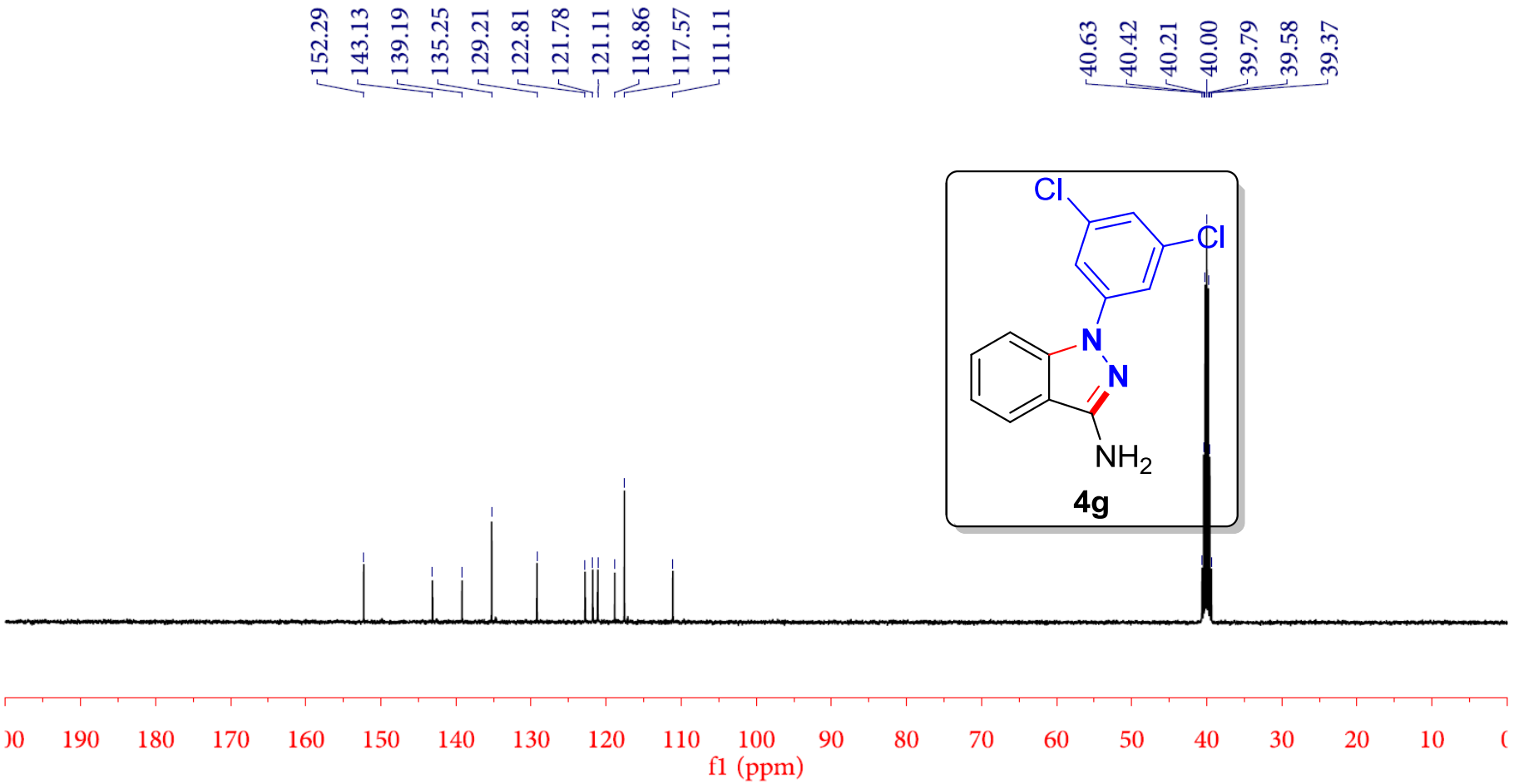
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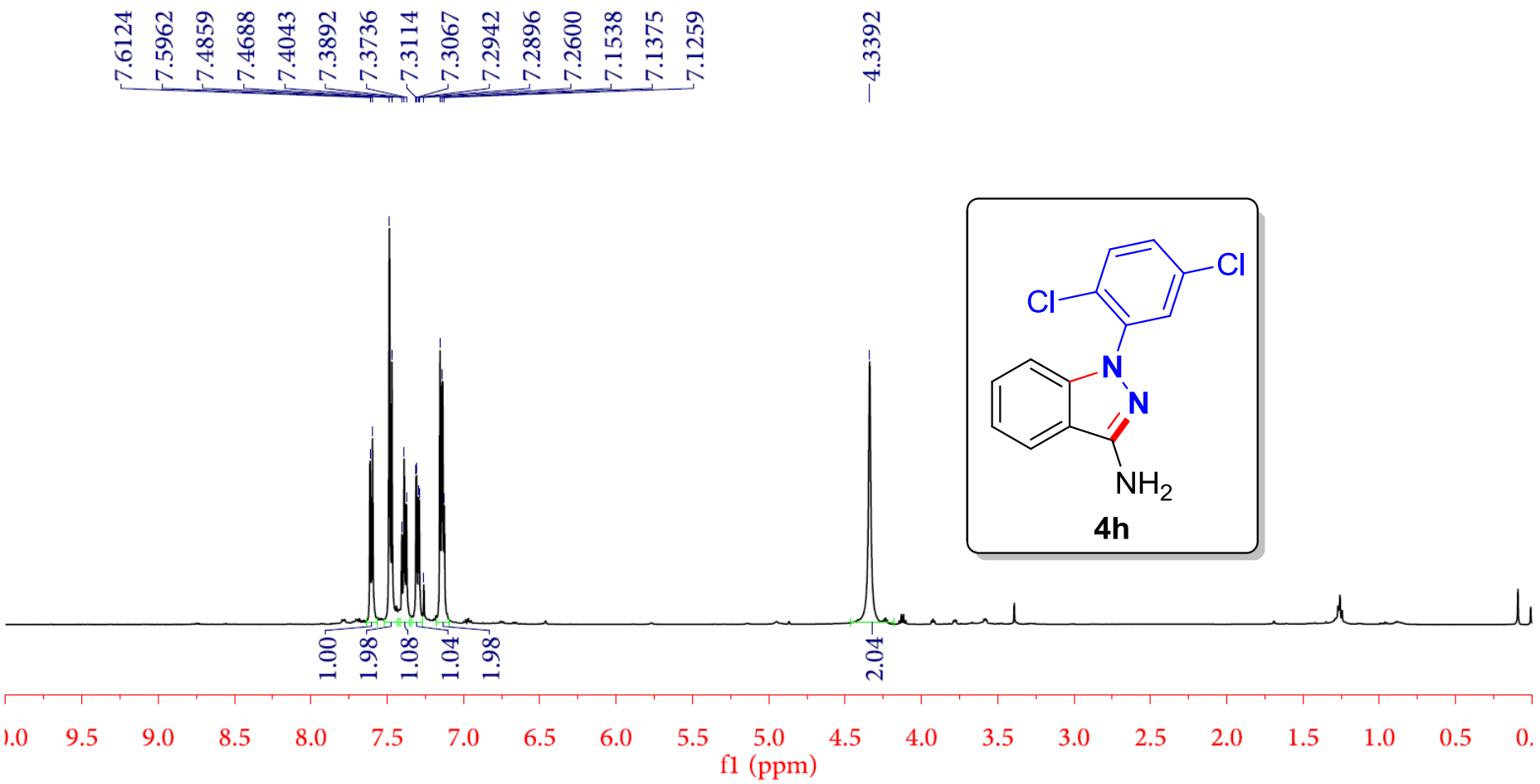
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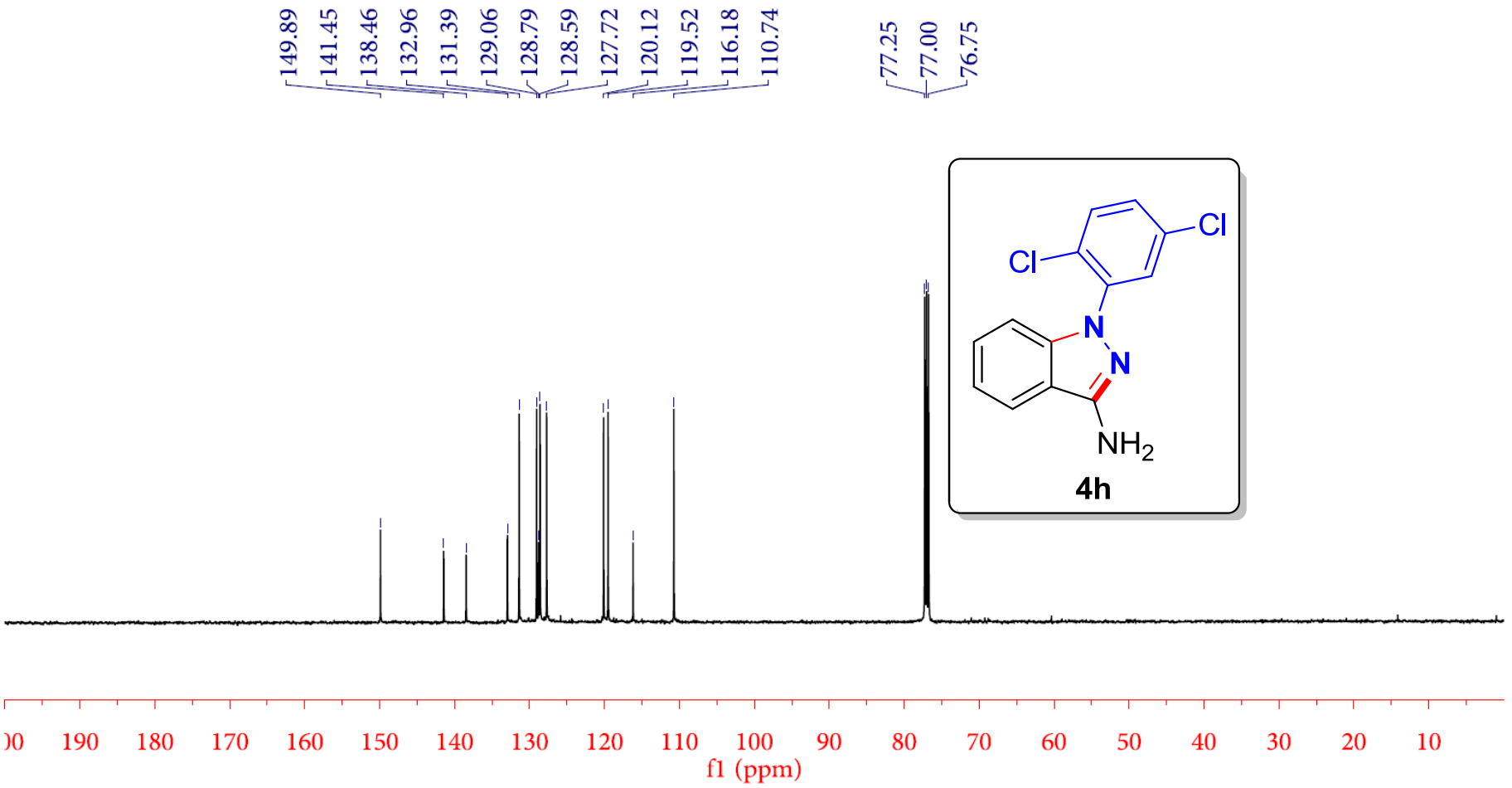
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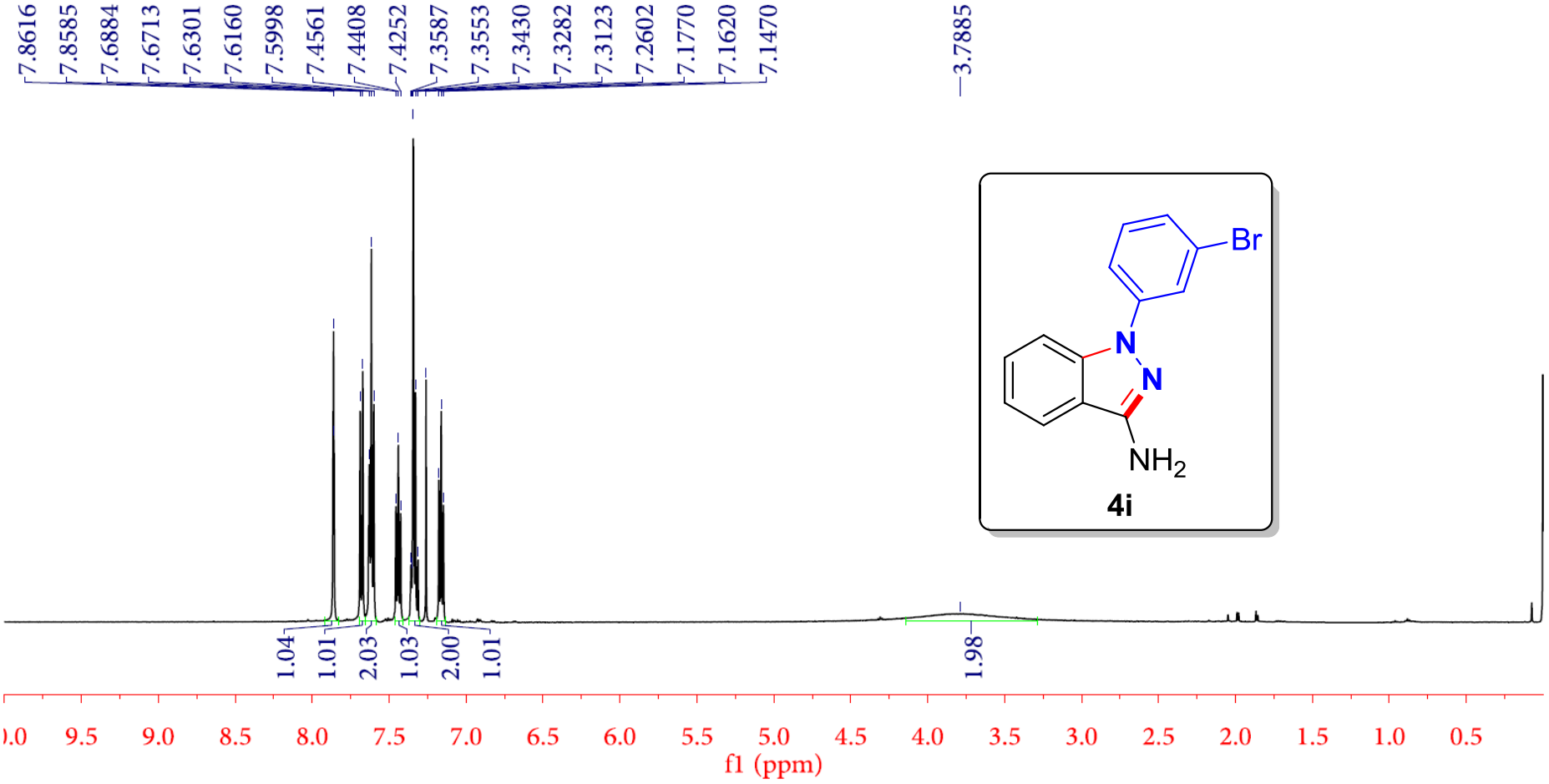
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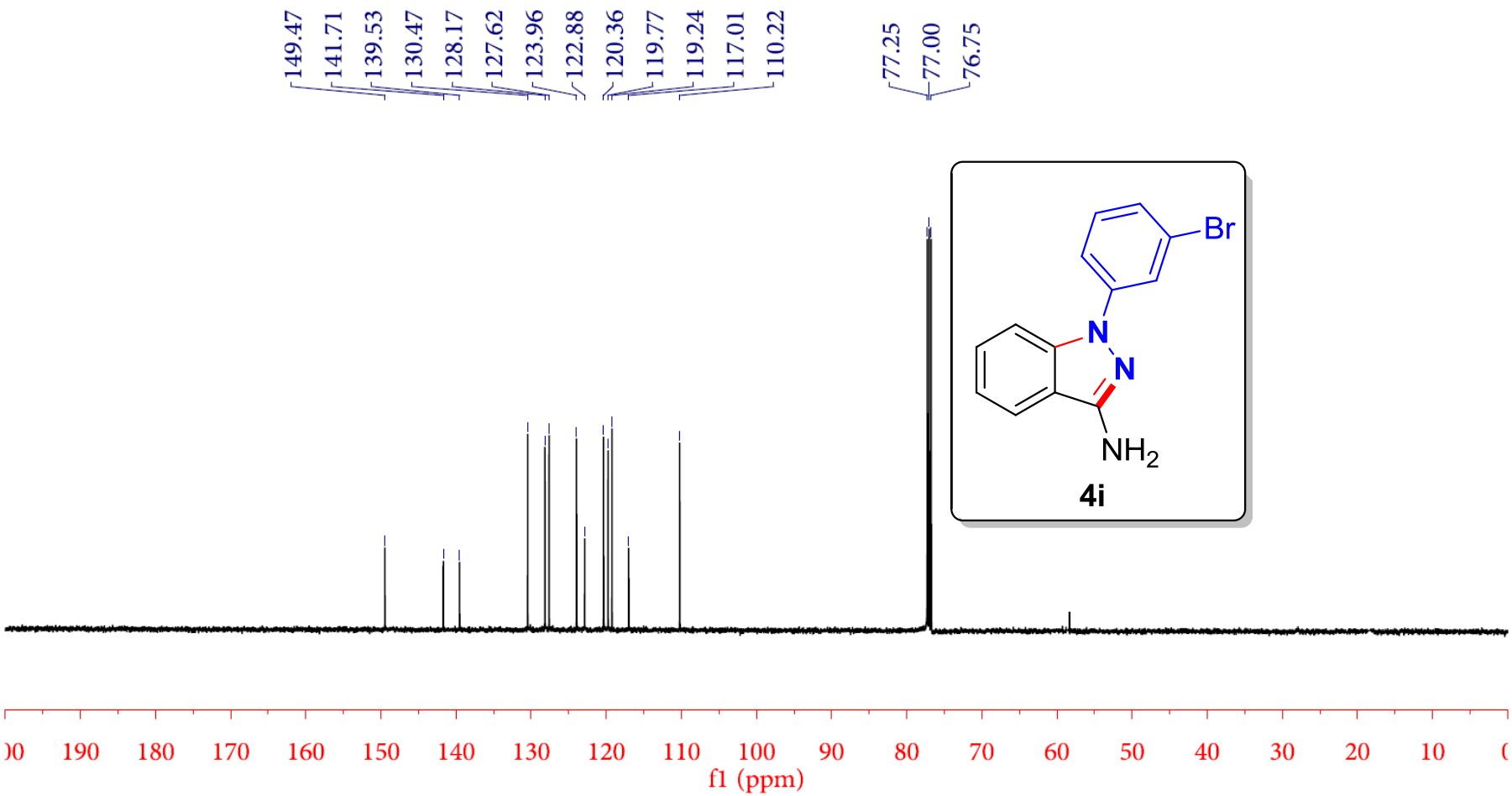
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40
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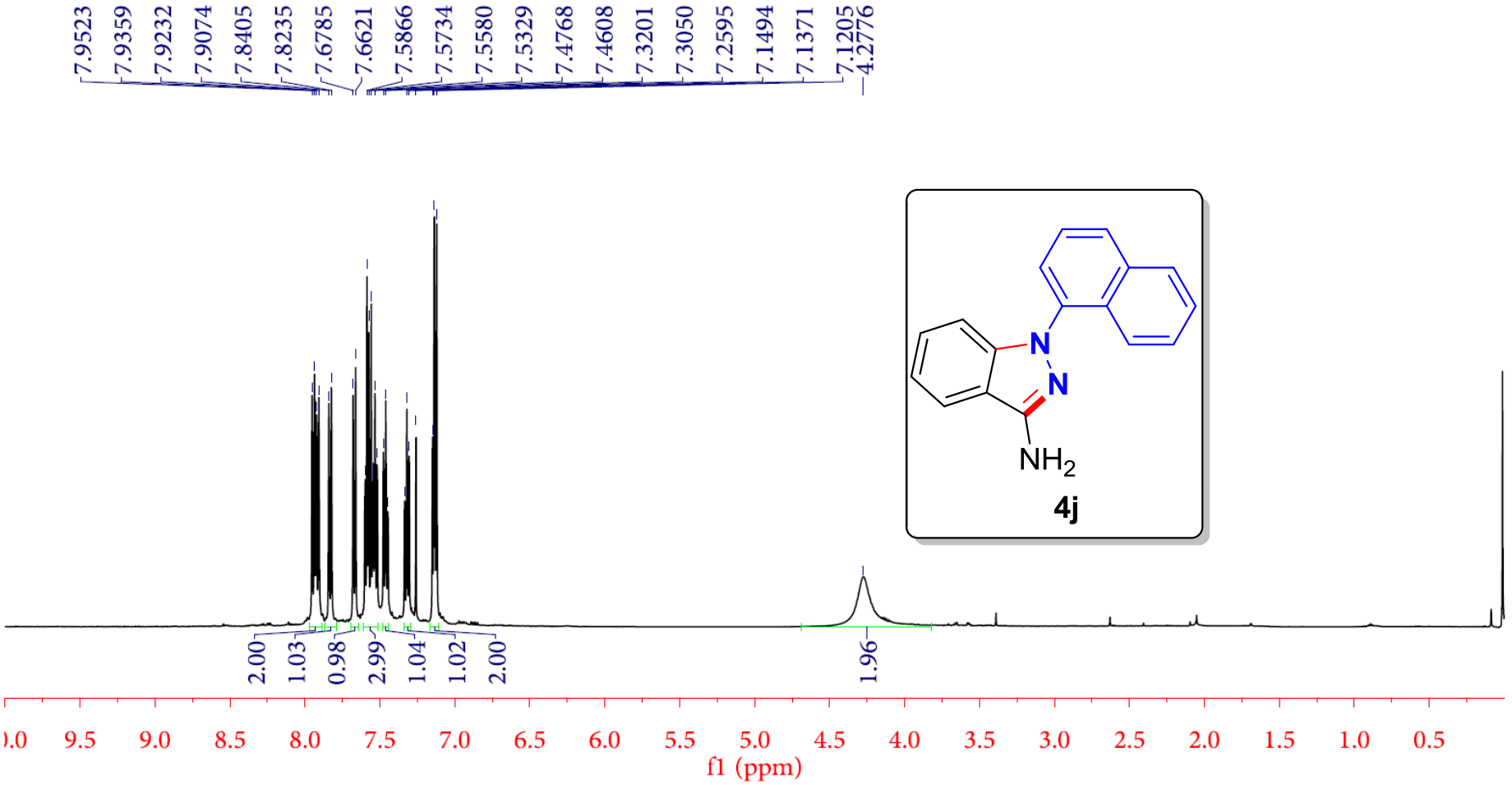
f1 (ppm)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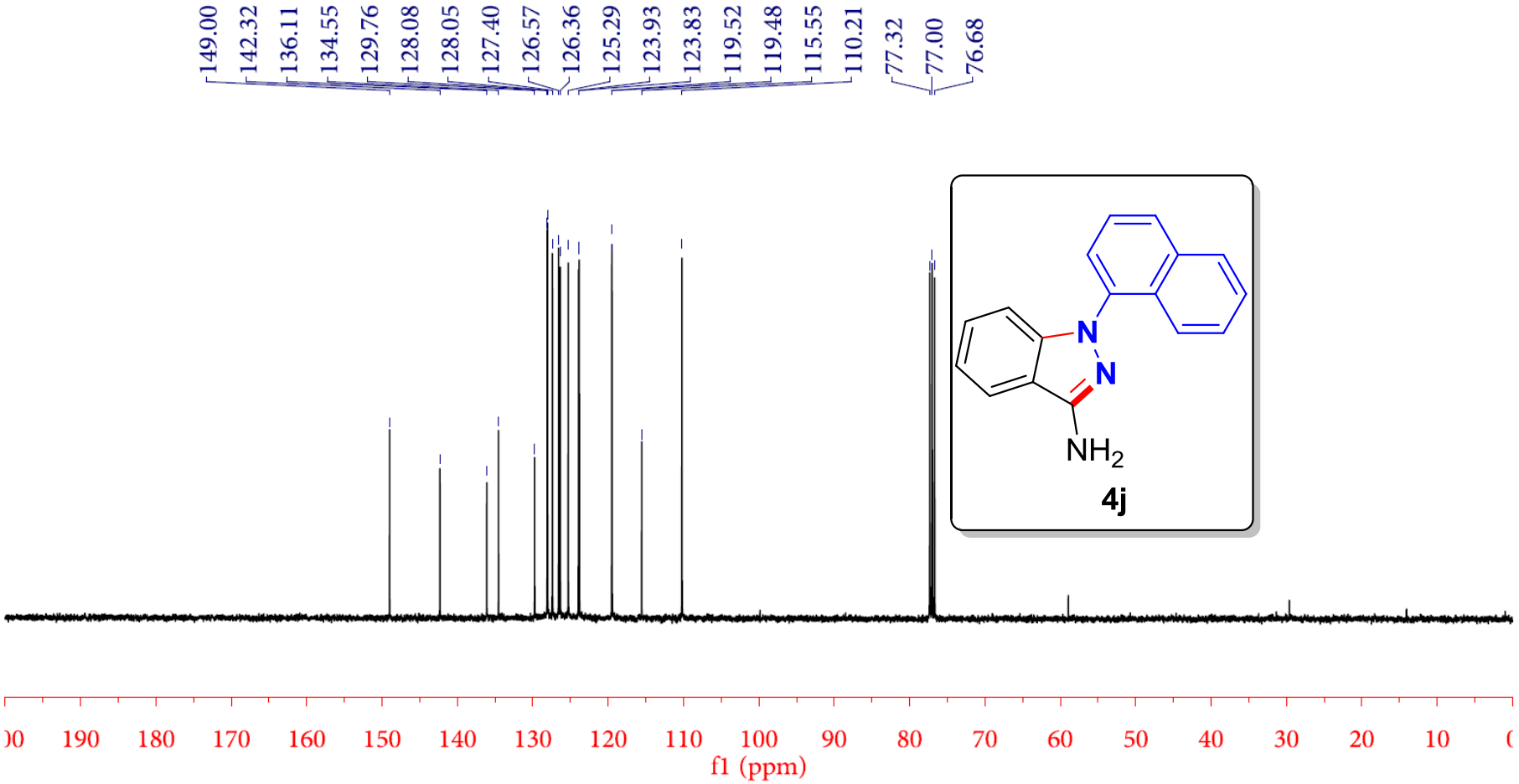
7.9359
7.9232
7.9074
7.8405
7.8235
7.6785
7.6621
7.5866
7.5734
7.5580
7.5329
7.4768
7.4608
7.3201
7.3050
7.2595
7.1494
7.1371
7.1205
4.2776
2.00
1.03
0.98
2.99
1.04
1.02
2.00
1.96
N
N
NH2
4j
f1 (ppm)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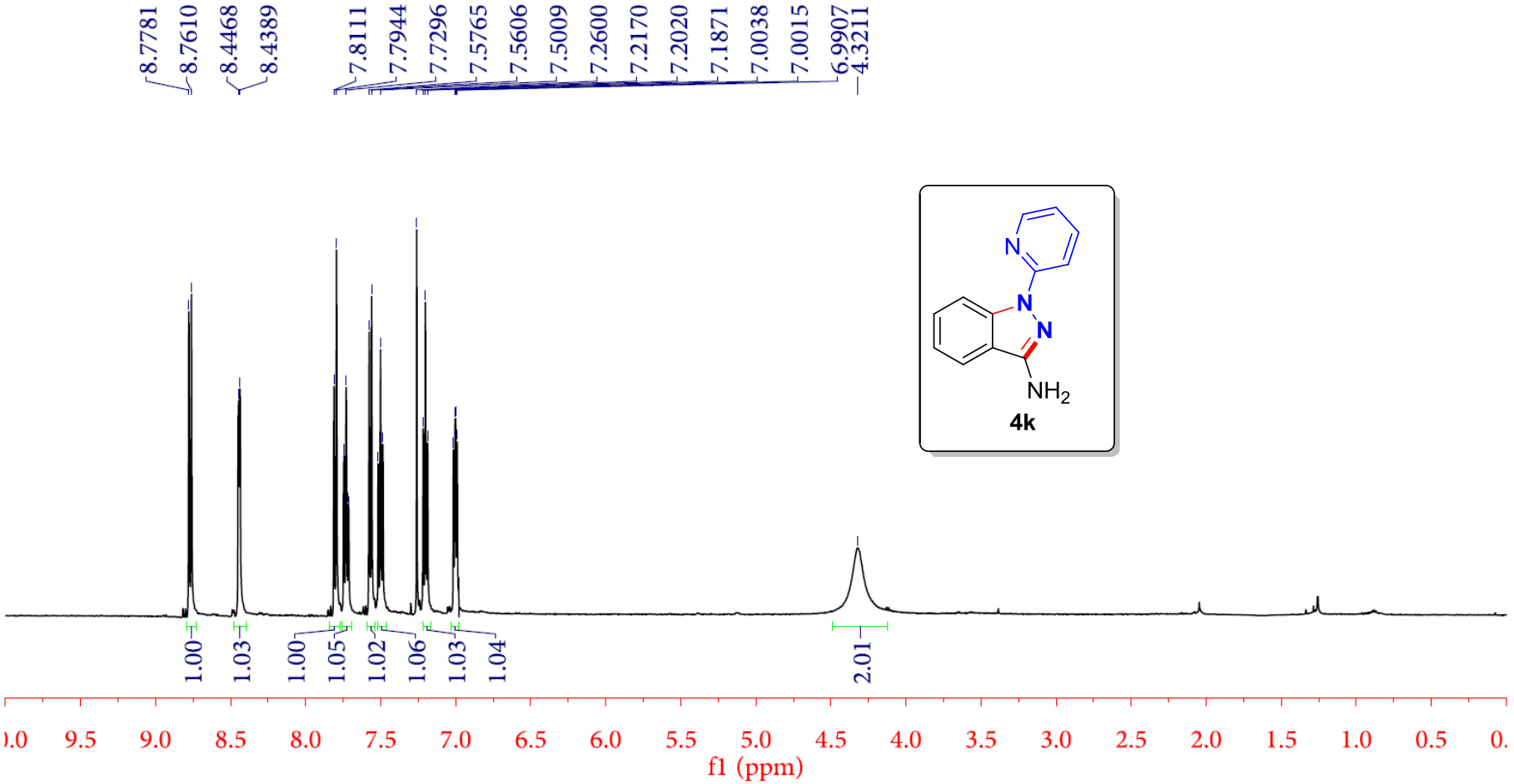
142.32
136.11
134.55
129.76
128.08
128.05
127.40
126.57
126.36
125.29
123.93
123.83
119.52
119.48
115.55
110.21
77.32
77.00
76.68
N
N
NH2
4j
f1 (ppm)


8.7781
8.7610
8.4468
8.4389
7.8111
7.7944
7.7296
7.5765
7.5606
7.5009
7.2600
7.2170
7.2020
7.1871
7.0038
7.0015
6.9907
4.3211
N
N
N
NH2
4k
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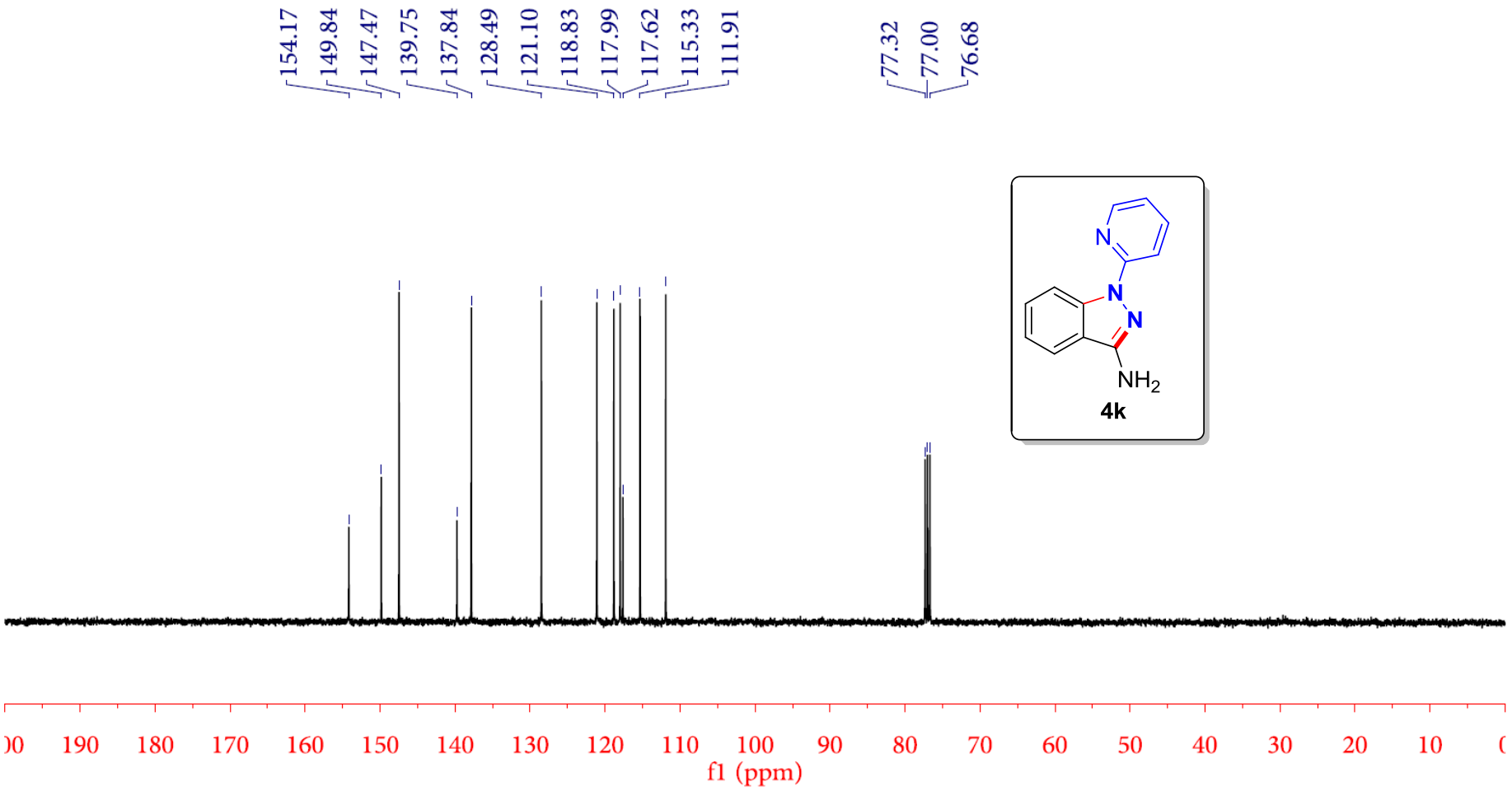
1.03
1.00
1.05
1.02
1.06
1.03
1.04
2.01
f1 (ppm)


154.17
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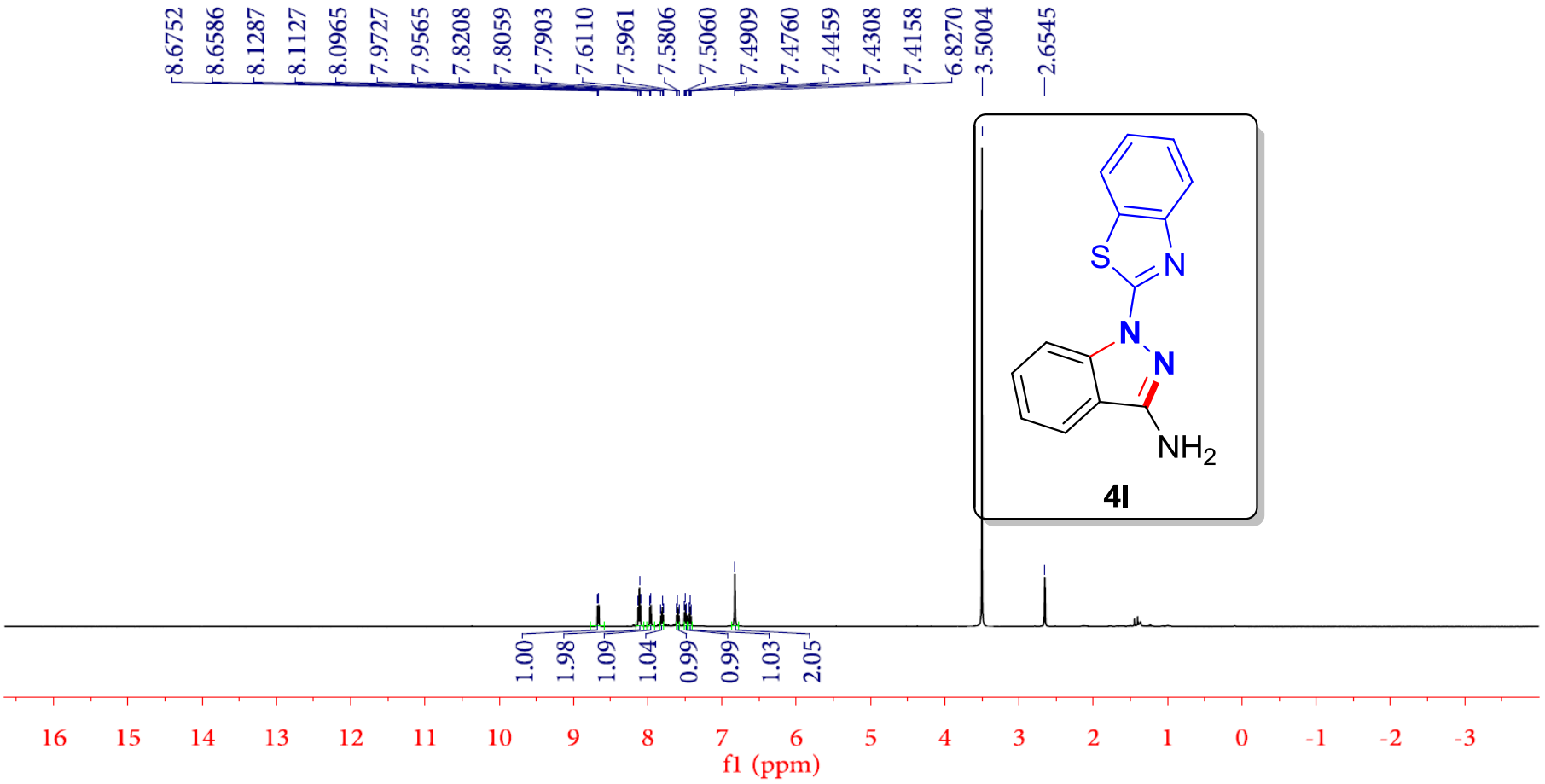
147.47
139.75
137.84
128.49
121.10
118.83
117.99
117.62
115.33
111.91
77.32
77.00
76.68
N
N
N
NH2
4k
f1 (ppm)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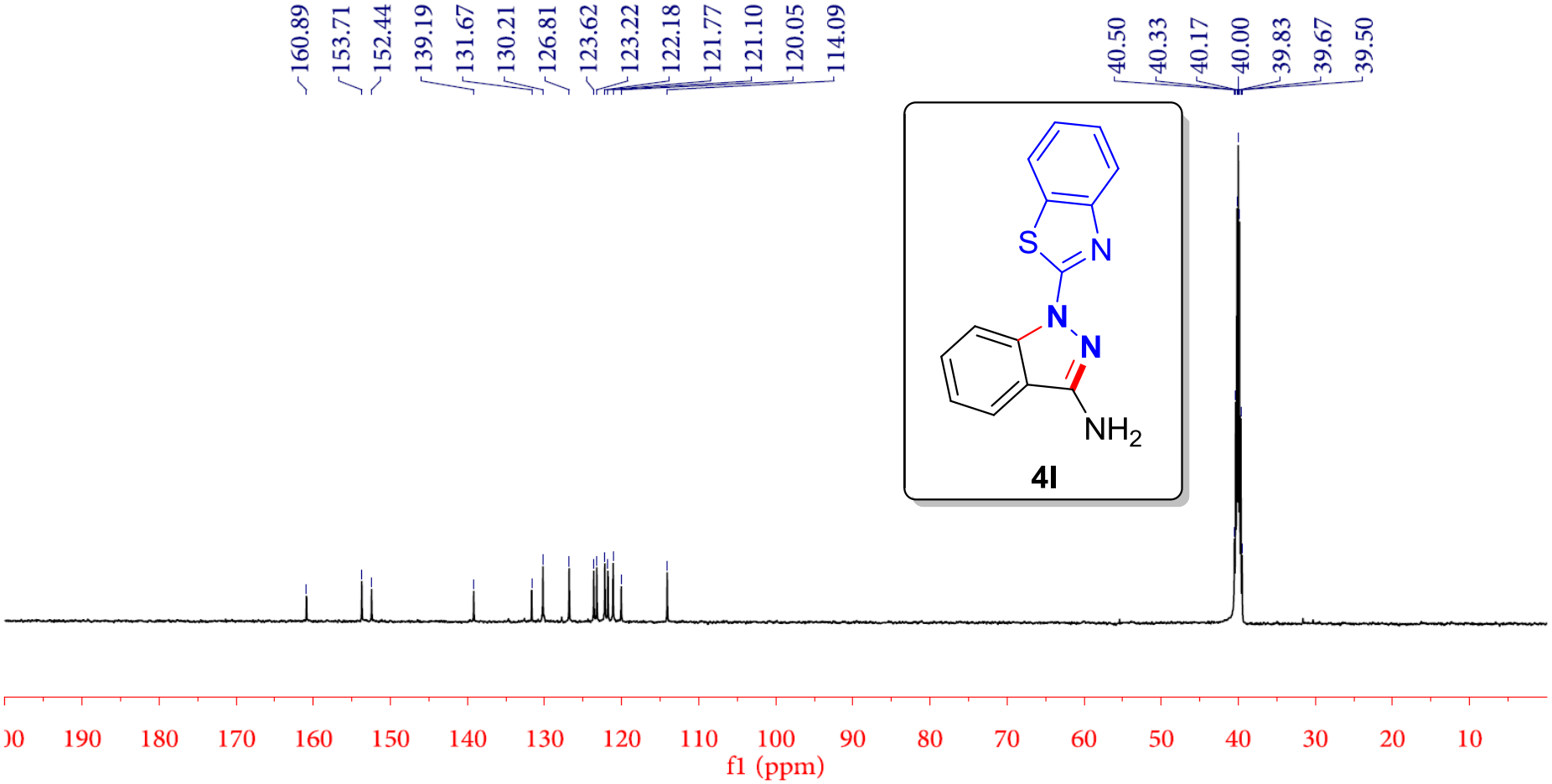
8.1287
8.1127
8.0965
7.9727
7.9565
7.8208
7.8059
7.7903
7.6110
7.5961
7.5806
7.5060
7.4909
7.4760
7.4459
7.4308
7.4158
6.8270
3.5004
2.6545
S
N
N
N
NH2
4l
1.00
1.98
1.09
1.04
0.99
0.99
1.03
2.05
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)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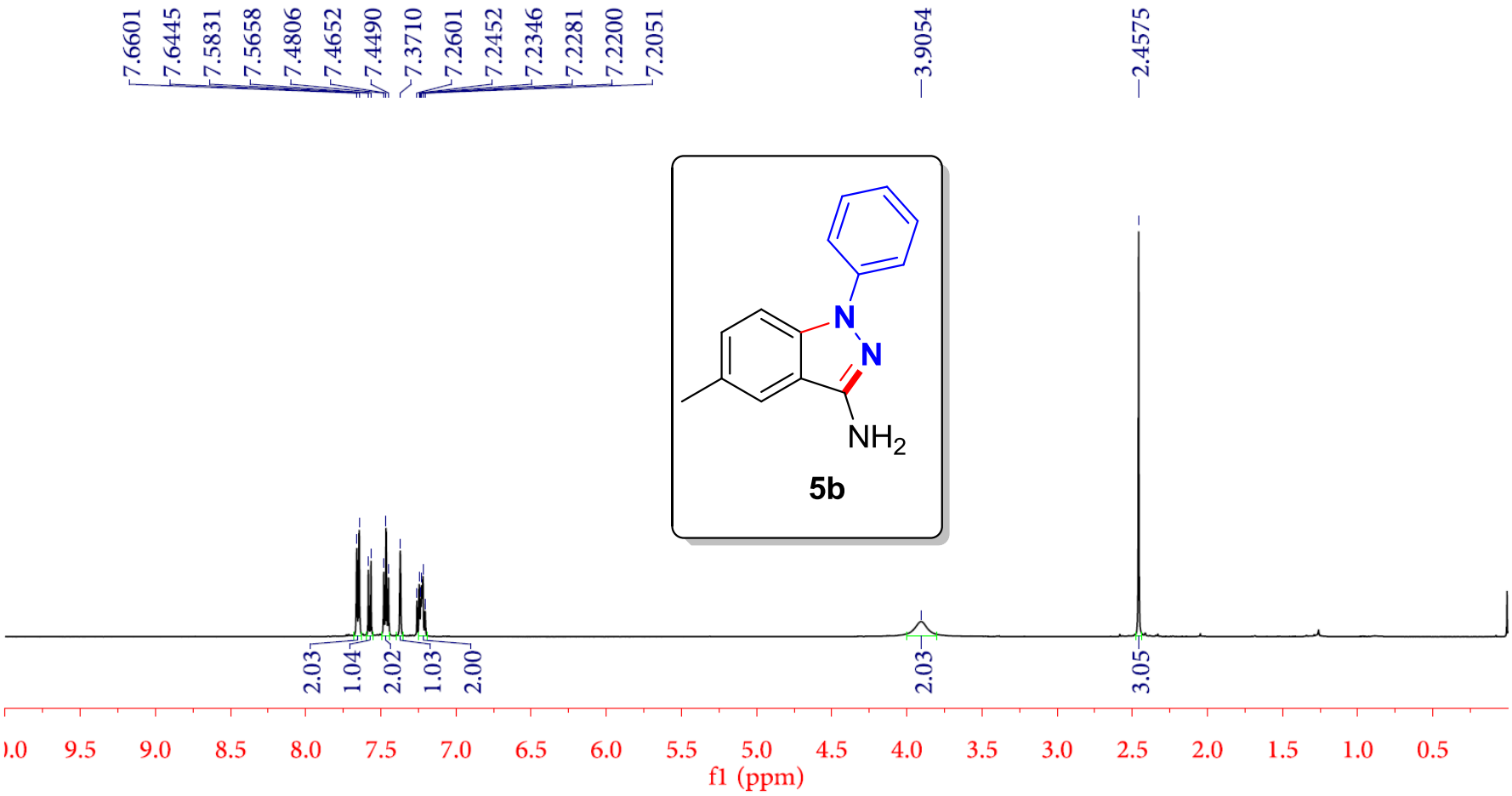
153.71
152.44
139.19
131.67
130.21
126.81
123.62
123.22
122.18
121.77
121.10
120.05
114.09
40.50
40.33
40.17
40.00
39.83
39.67
39.50
S
N
N
N
NH2
4l
f1 (ppm)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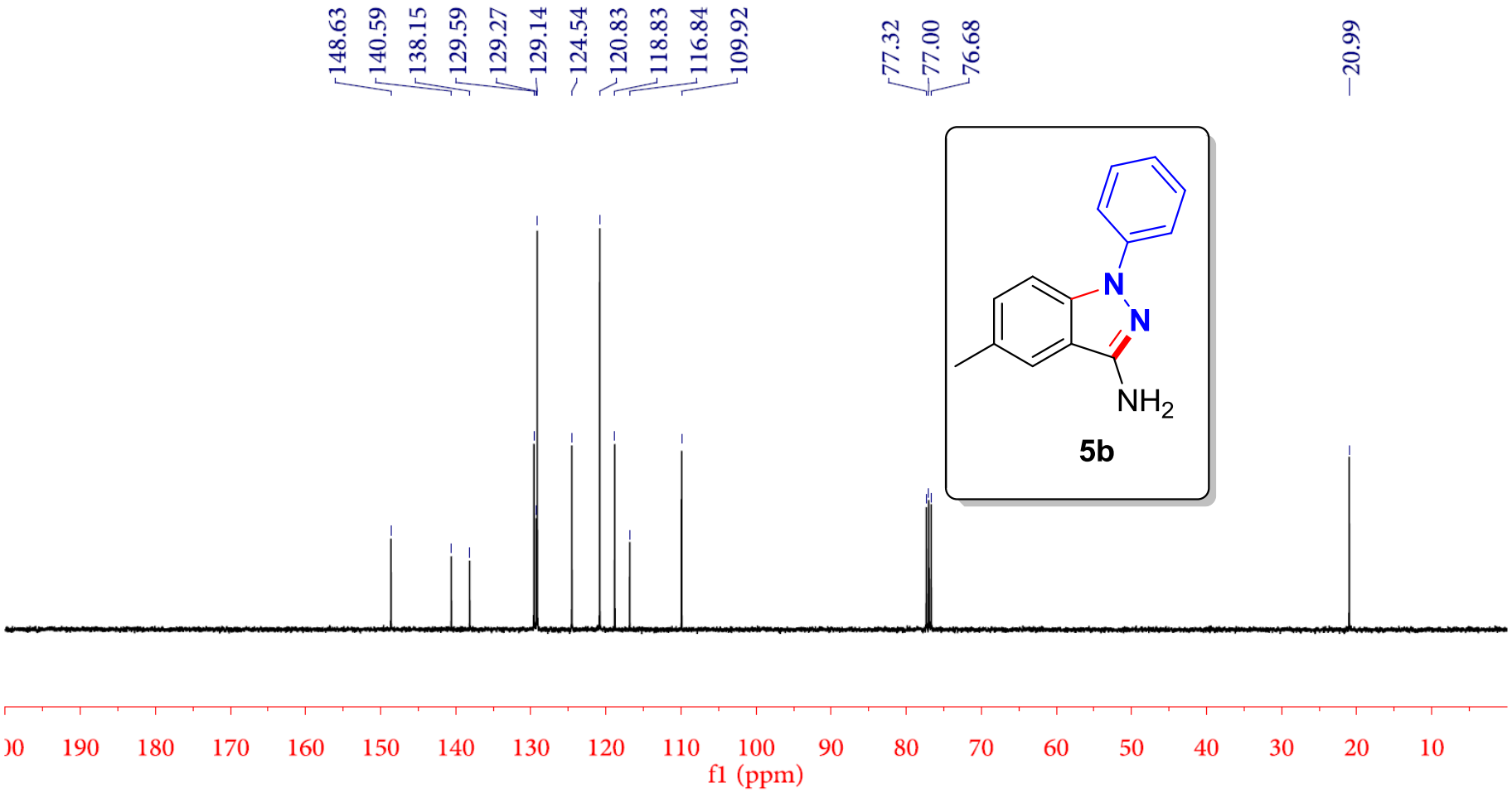
7.6445
7.5831
7.5658
7.4806
7.4652
7.4490
7.3710
7.2601
7.2452
7.2346
7.2281
7.2200
7.2051
3.9054
2.4575
N
N
NH2
5b
2.03
1.04
2.02
1.03
2.00
2.03
3.05
f1 (ppm)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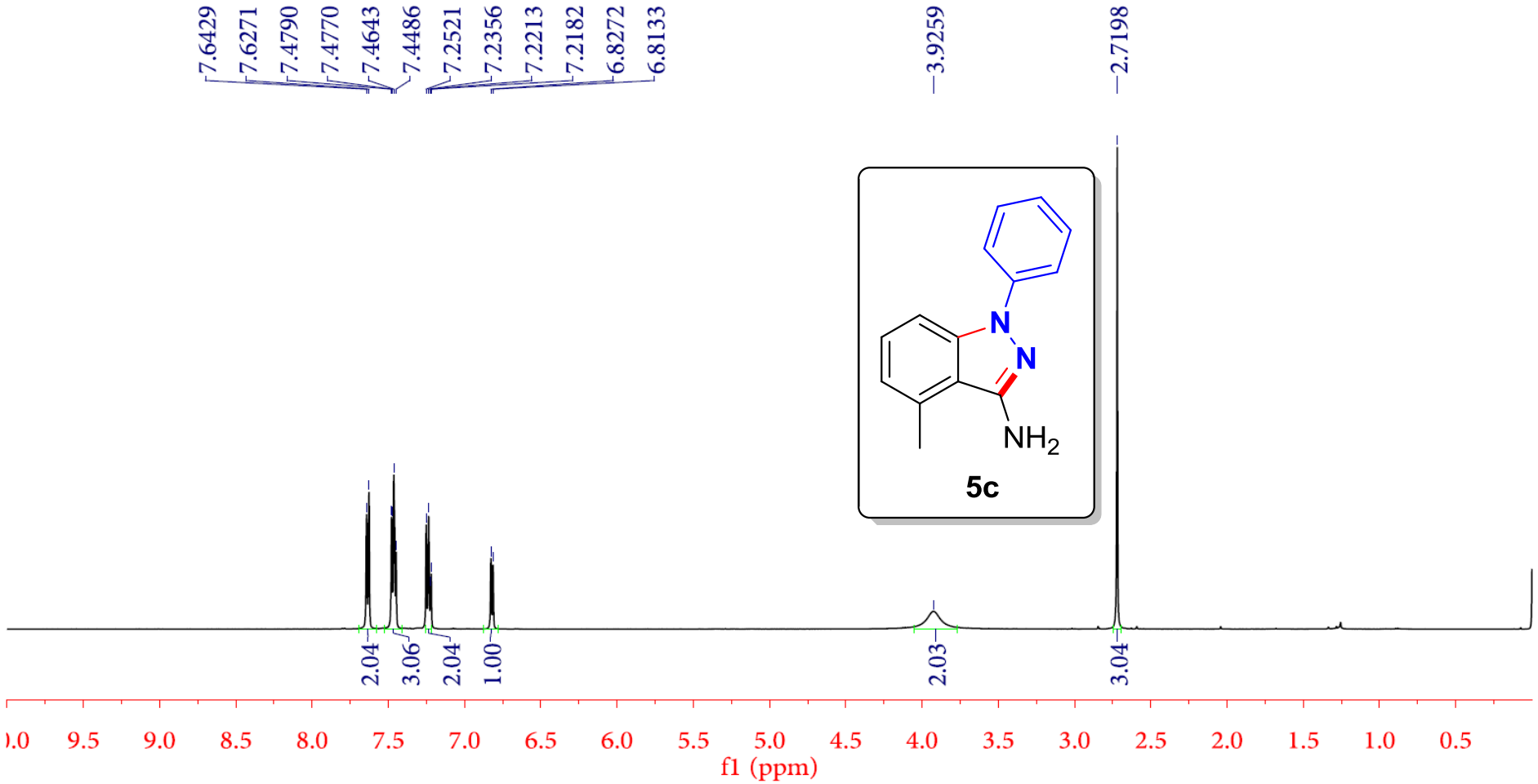
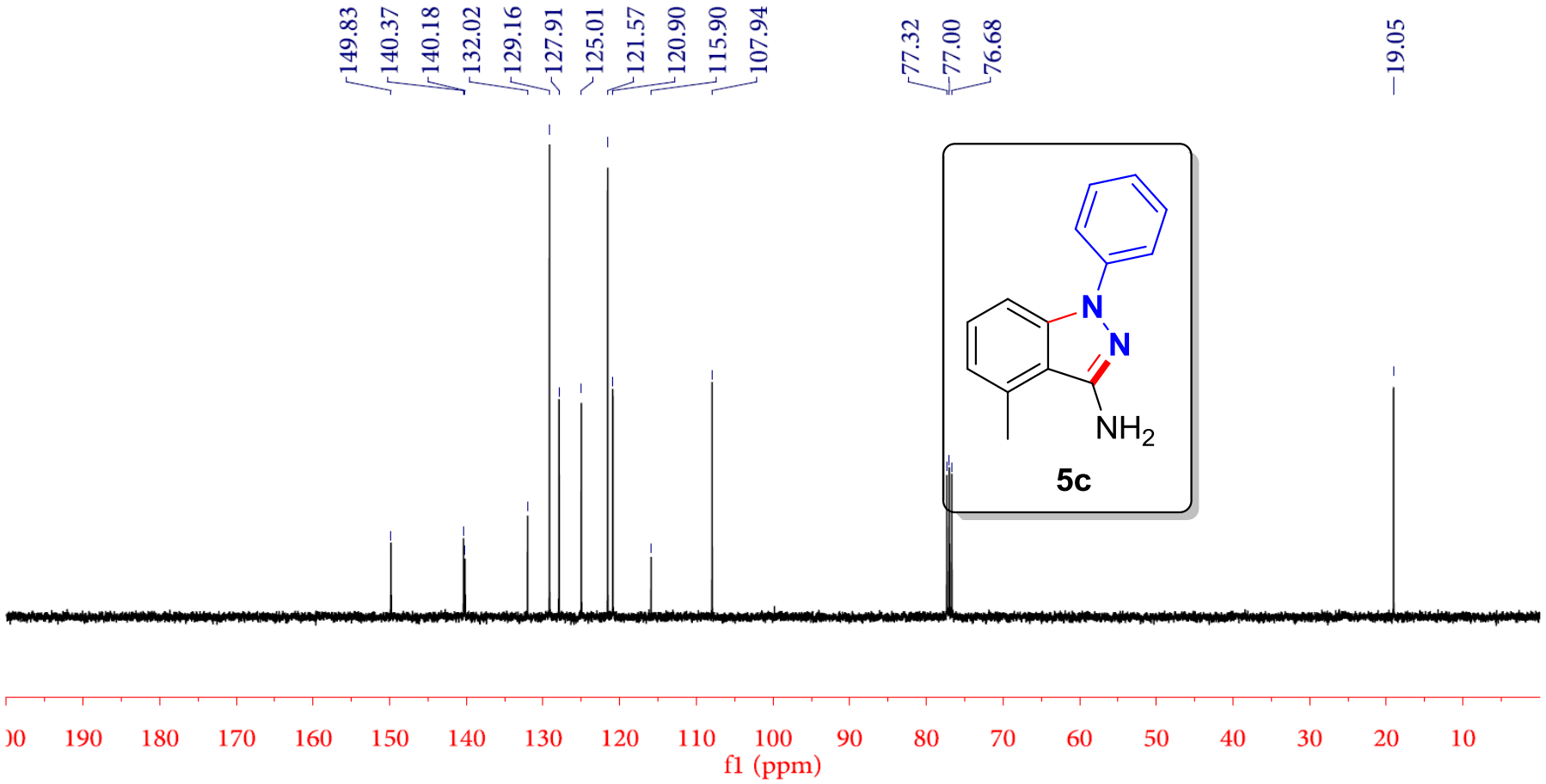
140.59
138.15
129.59
129.27
129.14
124.54
120.83
118.83
116.84
109.92
77.32
77.00
76.68
20.99
N
N
NH2
5b
f1 (ppm)


7.6429
7.6271
7.4790
7.4770
7.4643
7.4486
7.2521
7.2356
7.2213
7.2182
6.8272
6.8133
3.9259
2.7198
N
N
NH2
5c
2.04
3.06
2.04
1.00
2.03
3.04
f1 (ppm)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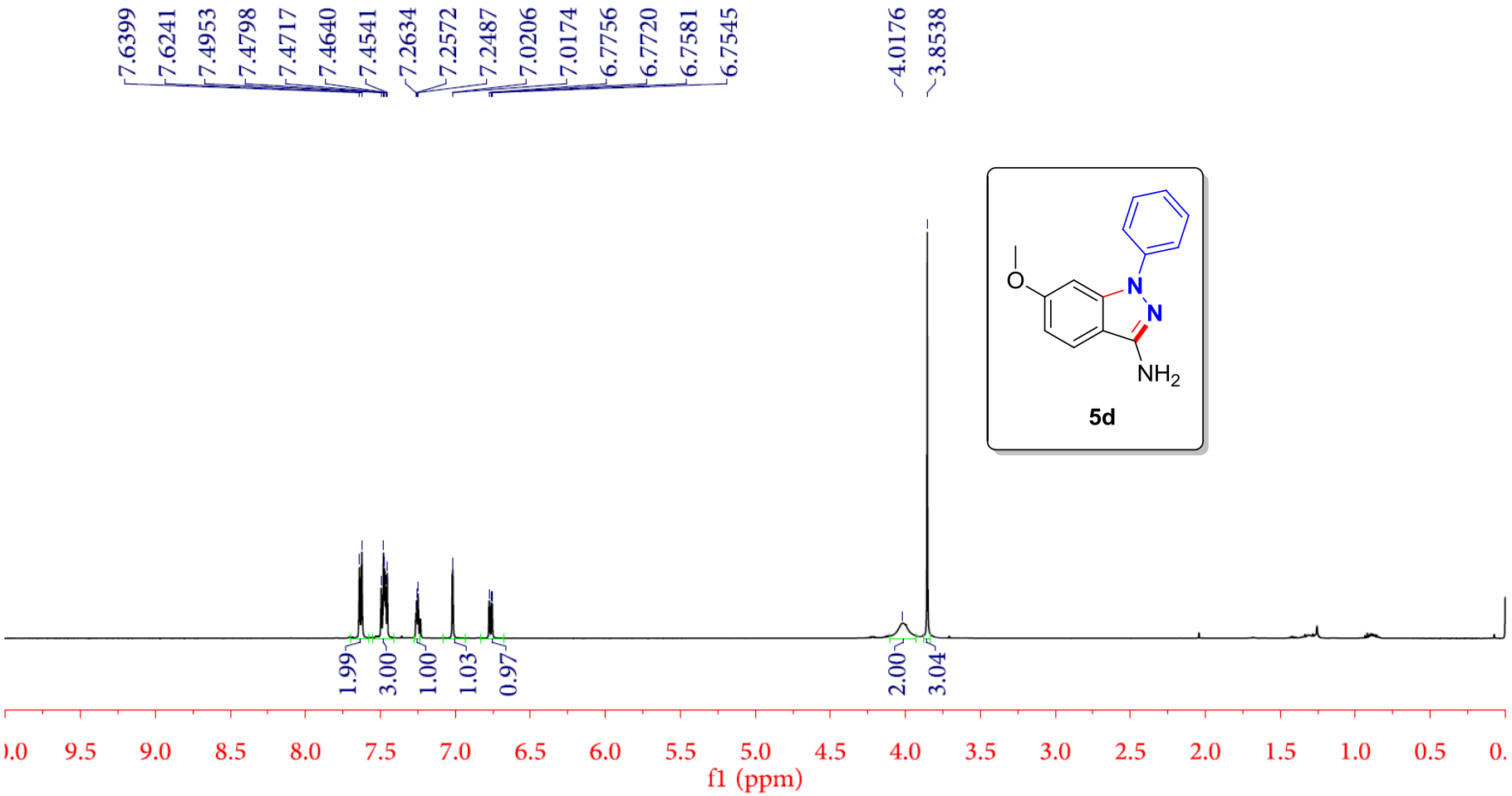
140.37
140.18
132.02
129.16
127.91
125.01
121.57
120.90
115.90
107.94
77.32
77.00
76.68
19.05
N
N
NH2
5c
f1 (ppm)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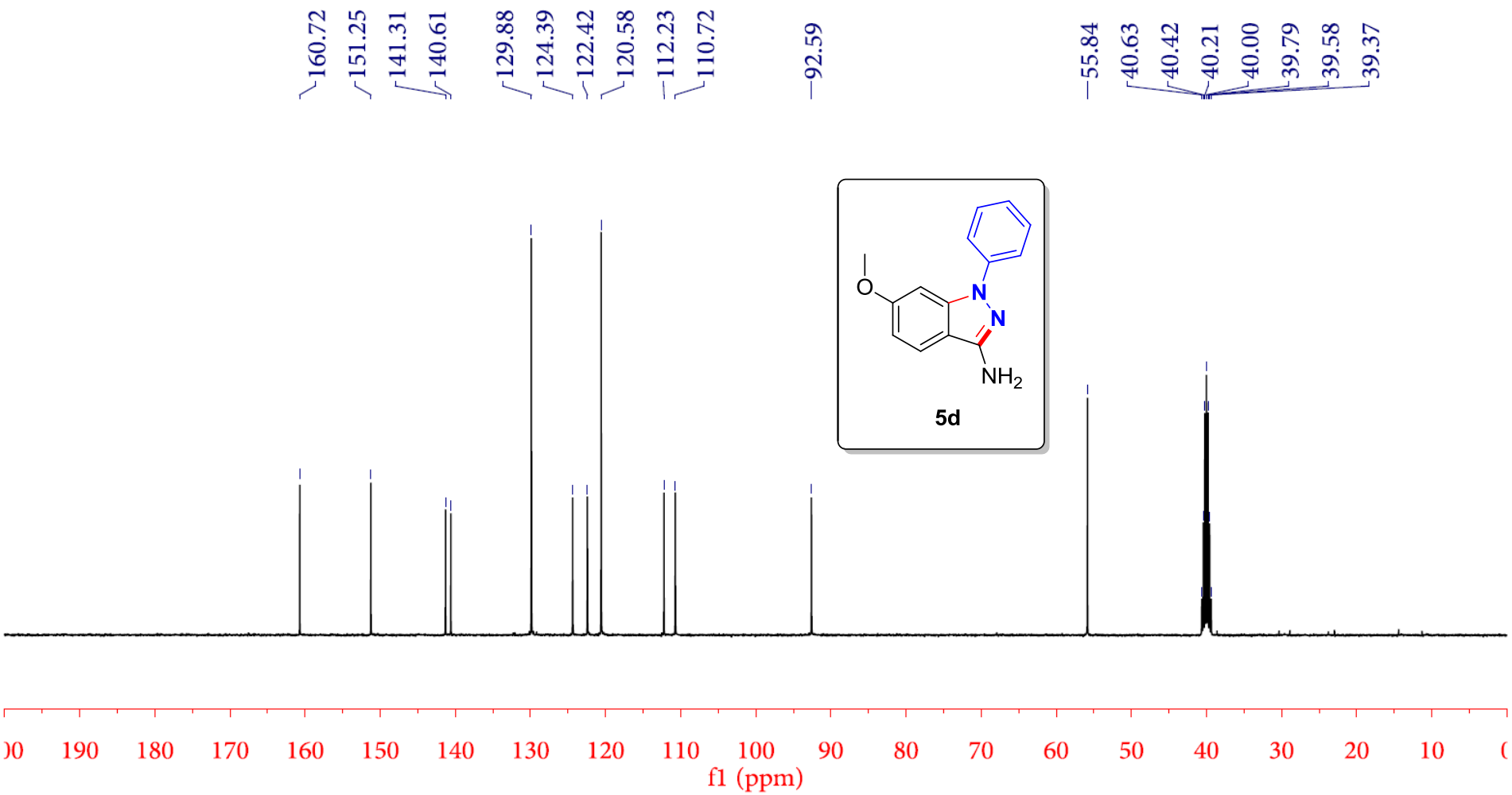
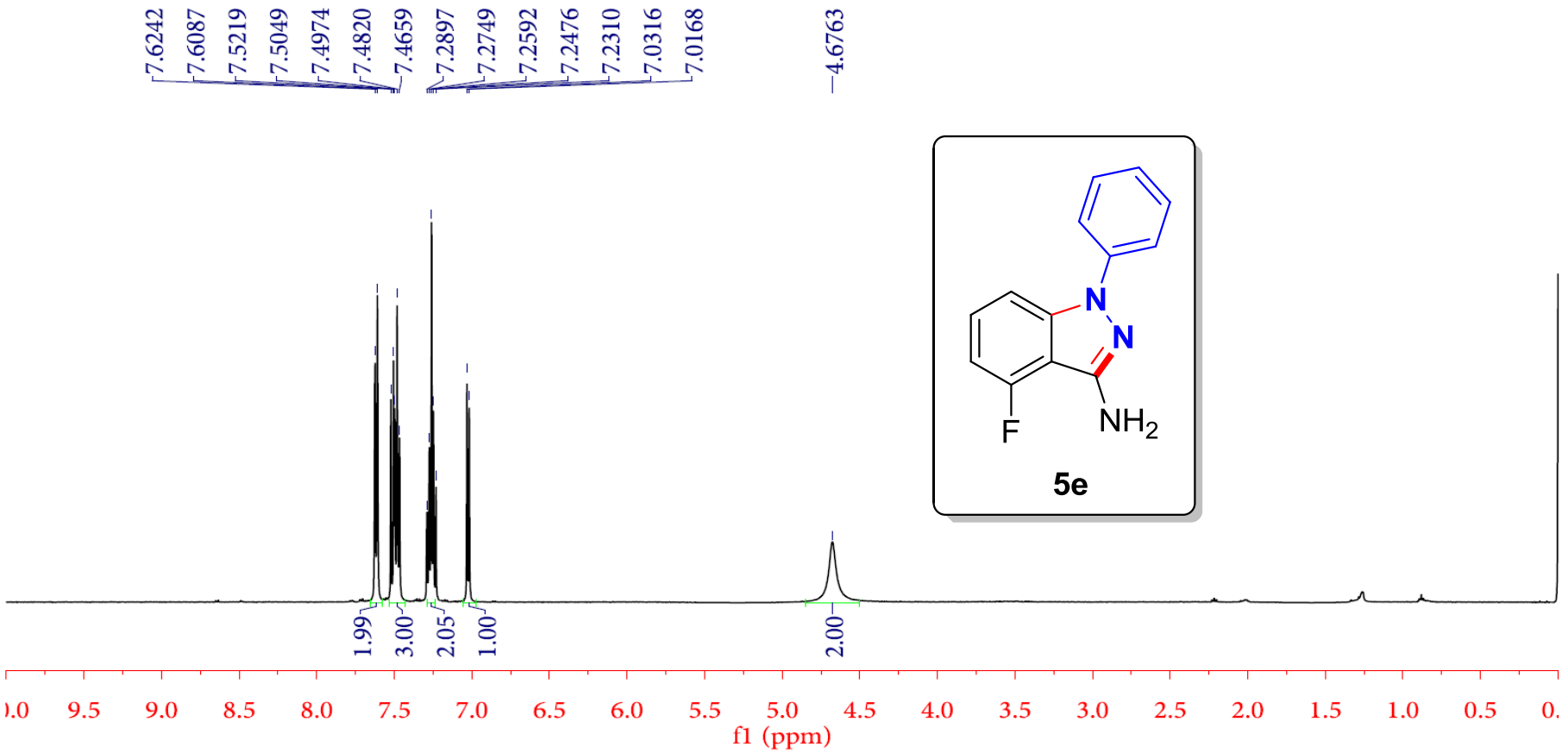
7.4953
7.4798
7.4717
7.4640
7.4541
7.2634
7.2572
7.2487
7.0206
7.0174
6.7756
6.7720
6.7581
6.7545
4.0176
3.8538
O
N
N
NH2
5d
1.99
3.00
1.00
1.03
0.97
2.00
3.04
f1 (ppm)


160.72
151.25
141.31
140.61
129.88
124.39
122.42
120.58
112.23
110.72
92.59
55.84
40.63
40.42
40.21
40.00
39.79
39.58
39.37
O
N
N
NH2
5d
f1 (ppm)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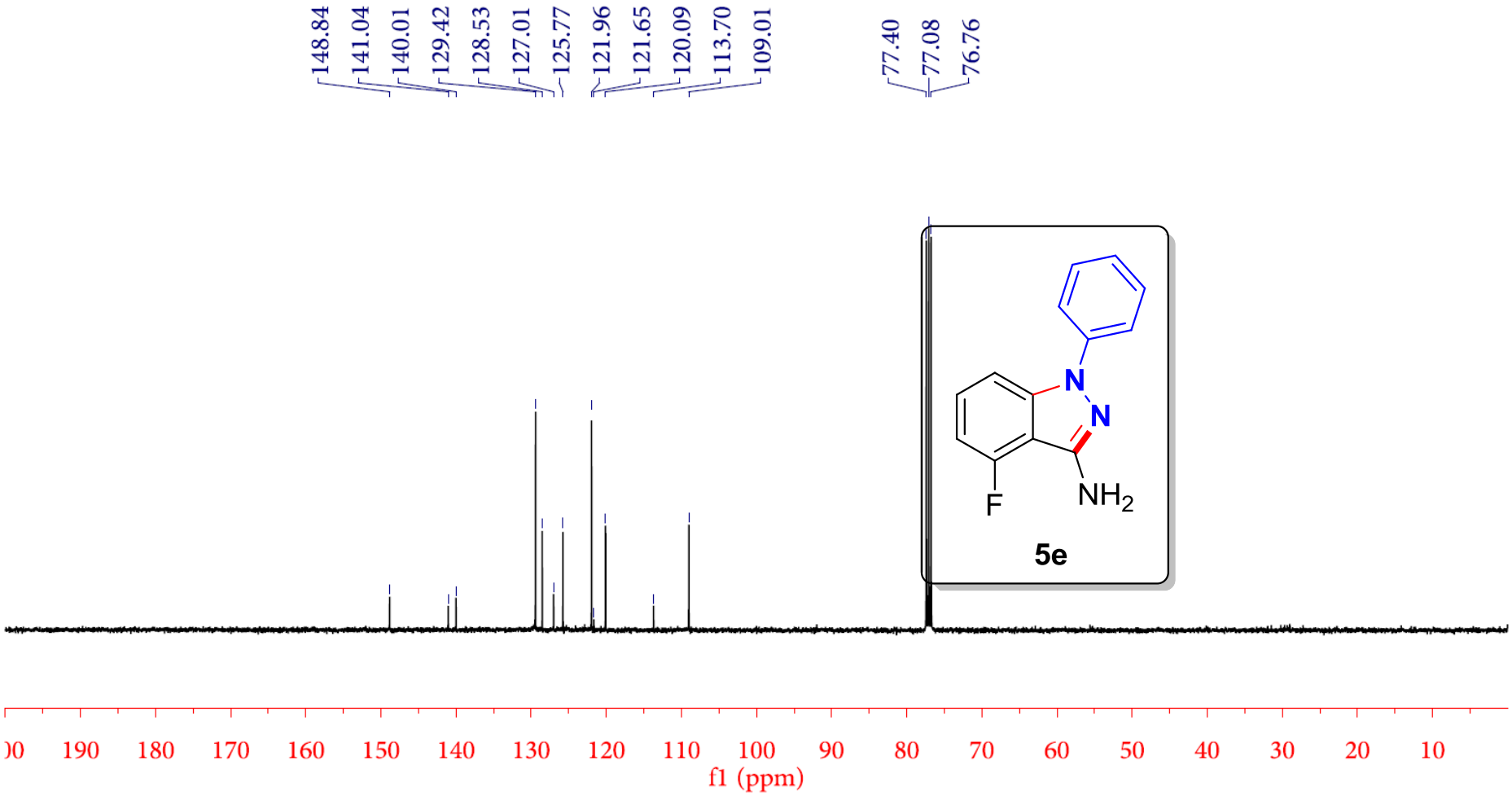
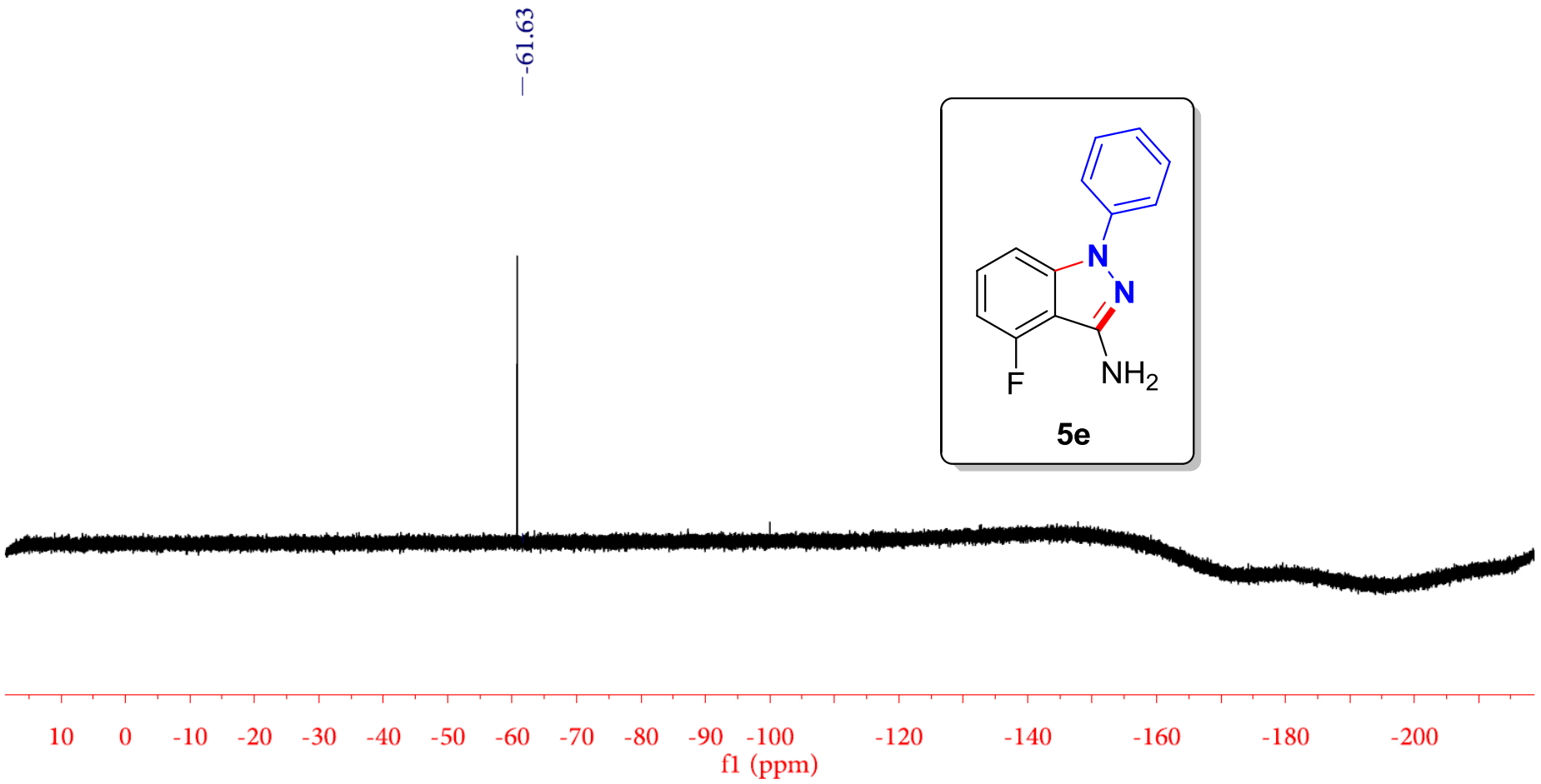
7.6087
7.5219
7.5049
7.4974
7.4820
7.4659
7.2897
7.2749
7.2592
7.2476
7.2310
7.0316
7.0168
4.6763
1.99
3.00
2.05
1.00
2.00
f1 (ppm)
N
N
F
NH2
5e


148.84
141.04
140.01
129.42
128.53
127.01
125.77
121.96
121.65
120.09
113.70
109.01
77.40
77.08
76.76
N
N
F
NH2
5e
f1 (ppm)


-61.63
N
N
F
NH2
5e
10
0
-10
-20
-30
-40
-50
-60
-70
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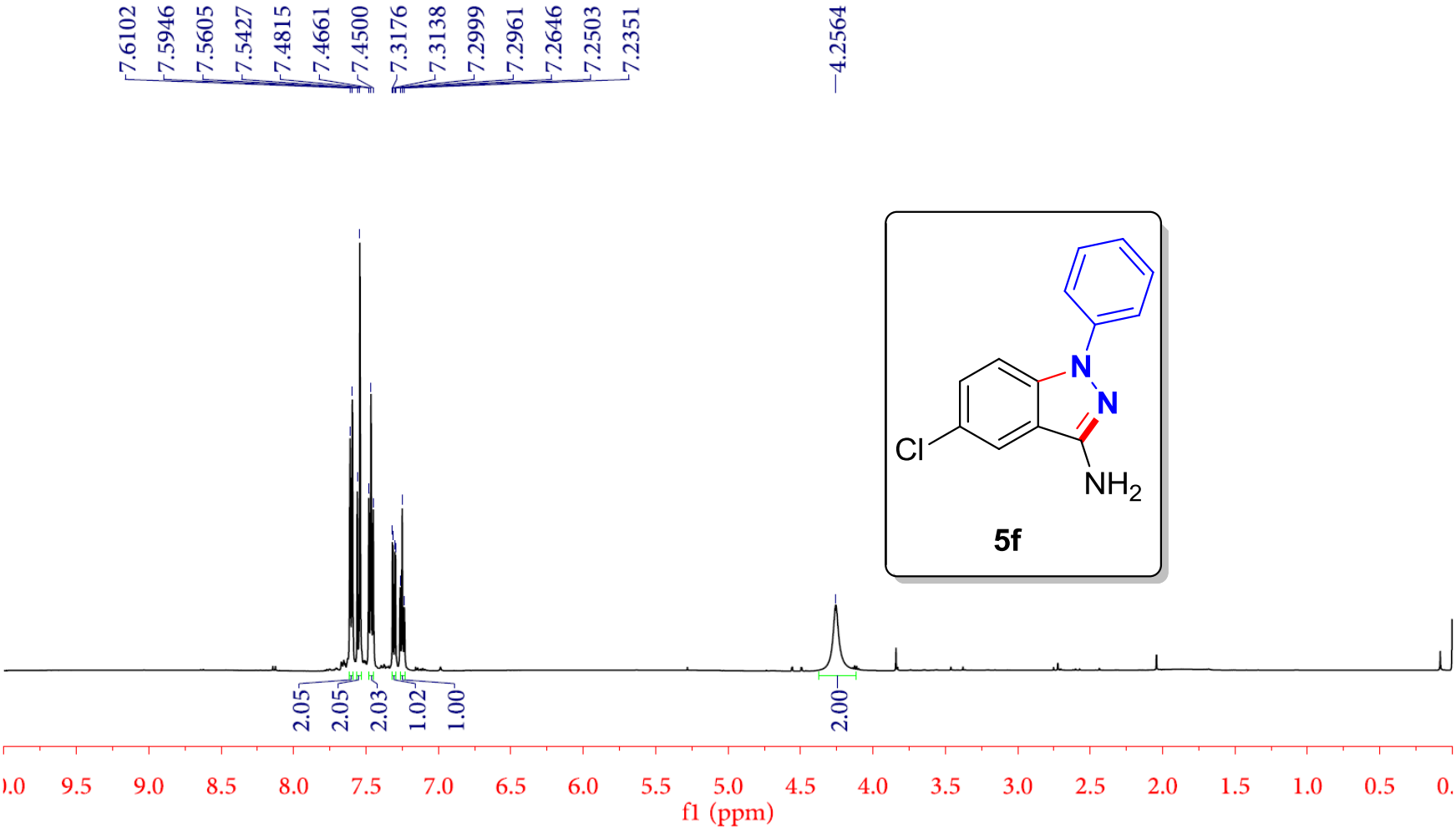
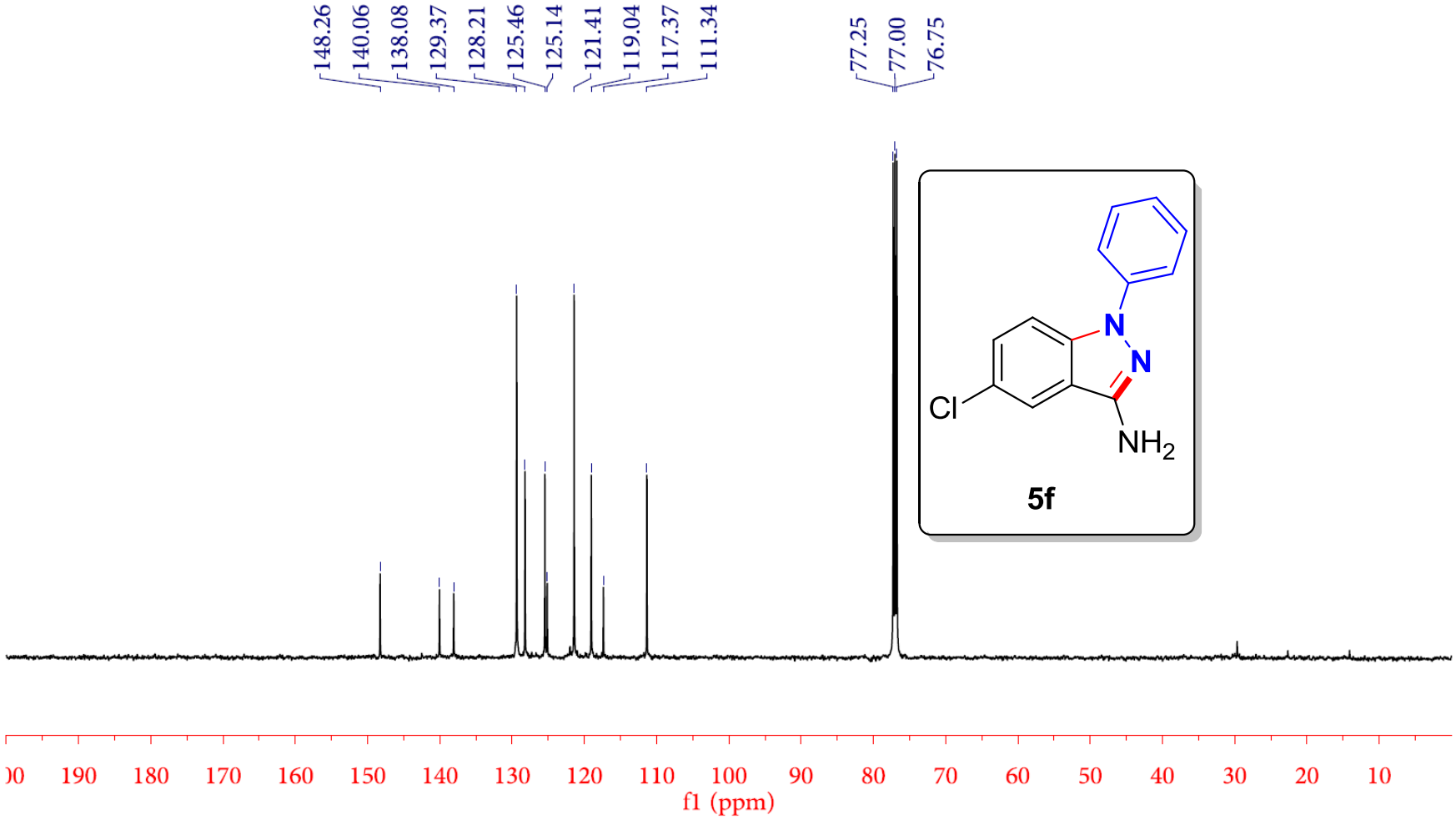
-120
-140
-160
-180
-200
f1 (ppm)


7.6102
7.5946
7.5605
7.5427
7.4815
7.4661
7.4500
7.3176
7.3138
7.2999
7.2961
7.2646
7.2503
7.2351
4.2564
Cl
N
N
NH2
5f
2.05
2.05
2.03
1.02
1.00
2.00
f1 (ppm)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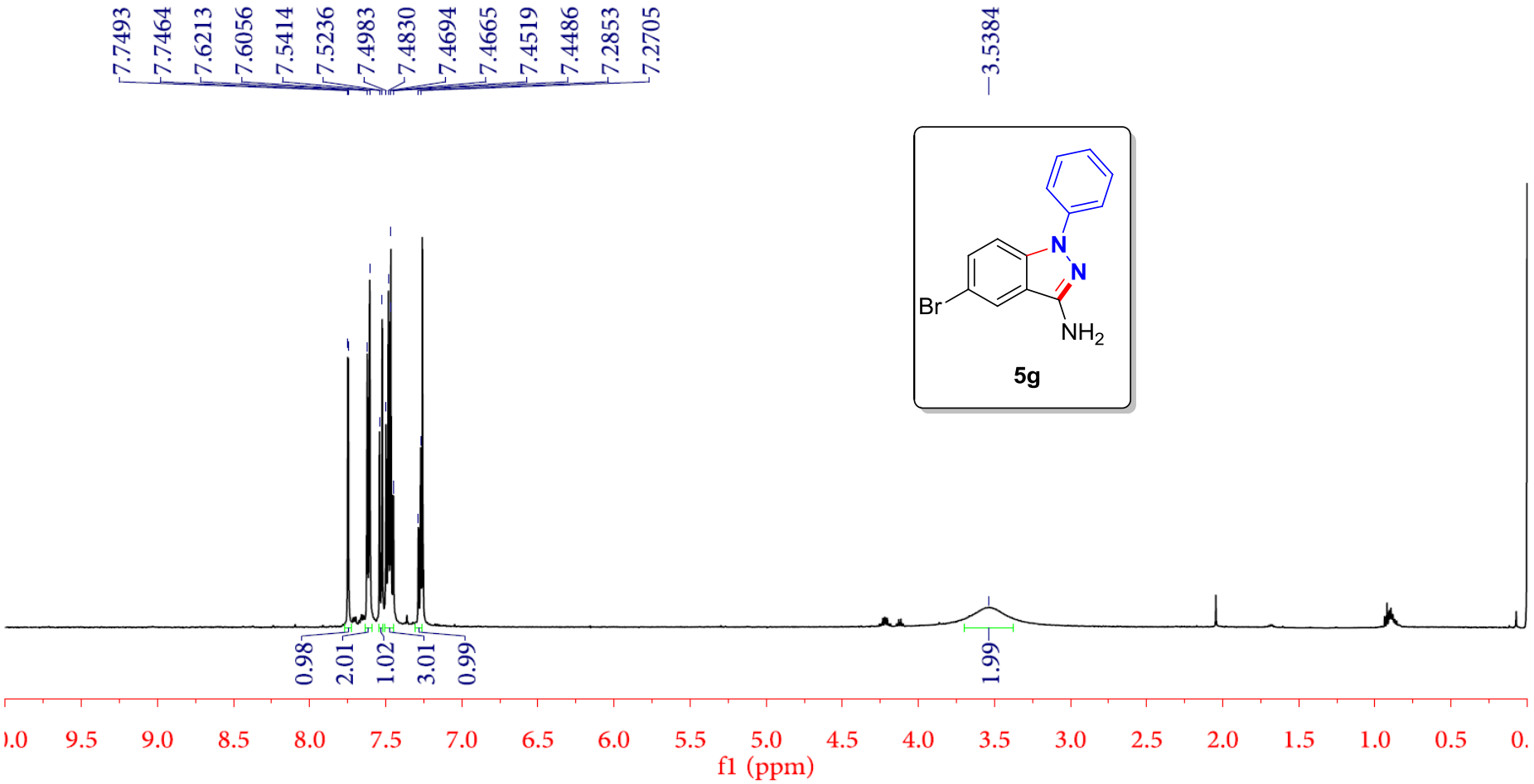
138.08
129.37
128.21
125.46
125.14
121.41
119.04
117.37
111.34
77.25
77.00
76.75
N
N
Cl
NH2
5f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.7493
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7.6213
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7.5414
7.5236
7.4983
7.4830
7.4694
7.4665
7.4519
7.4486
7.2853
7.2705
3.5384
Br
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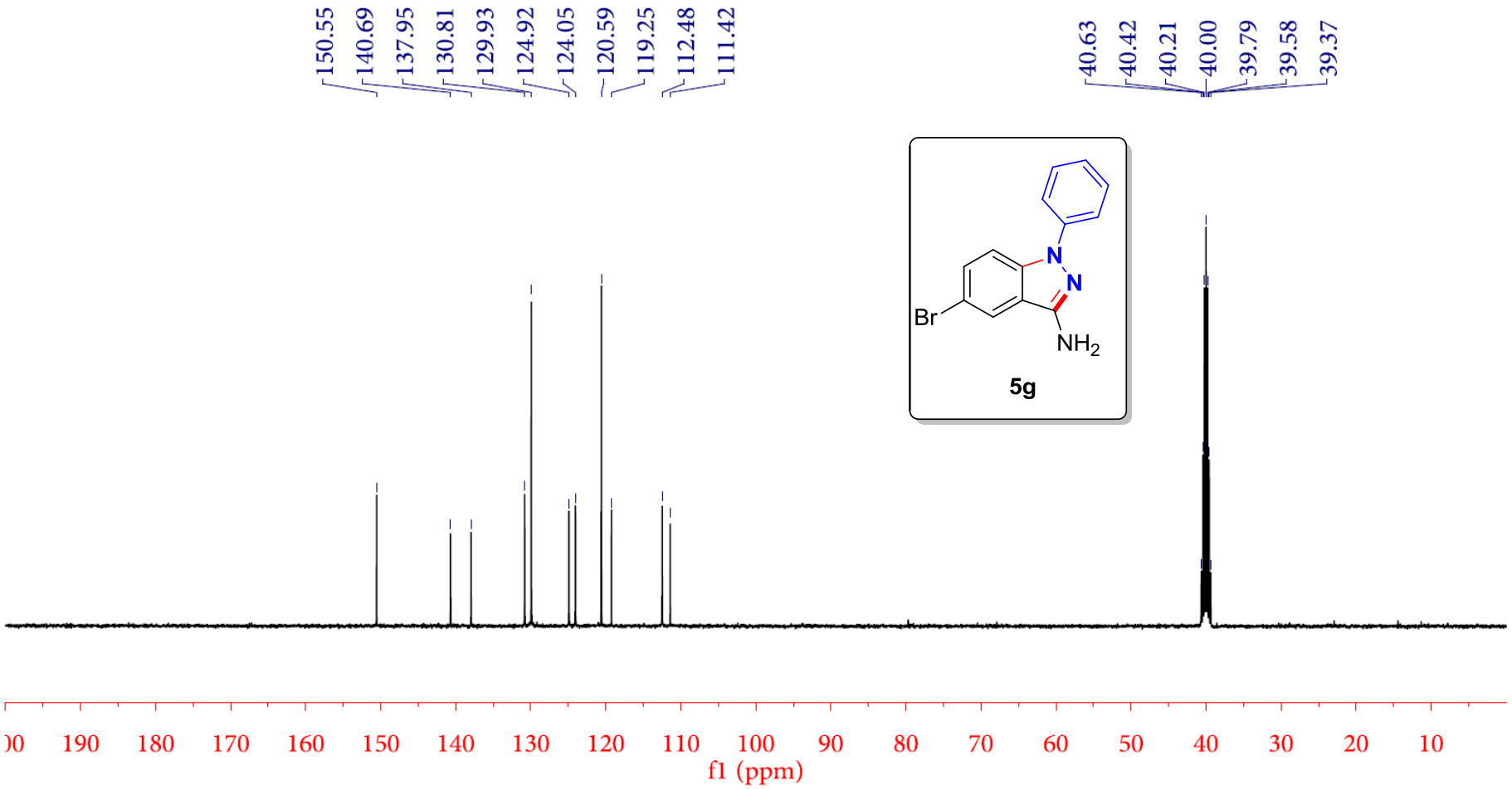
N
NH2
5g
0.98
2.01
1.02
3.01
0.99
1.99
f1 (ppm)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129.93
124.92
124.05
120.59
119.25
112.48
111.42
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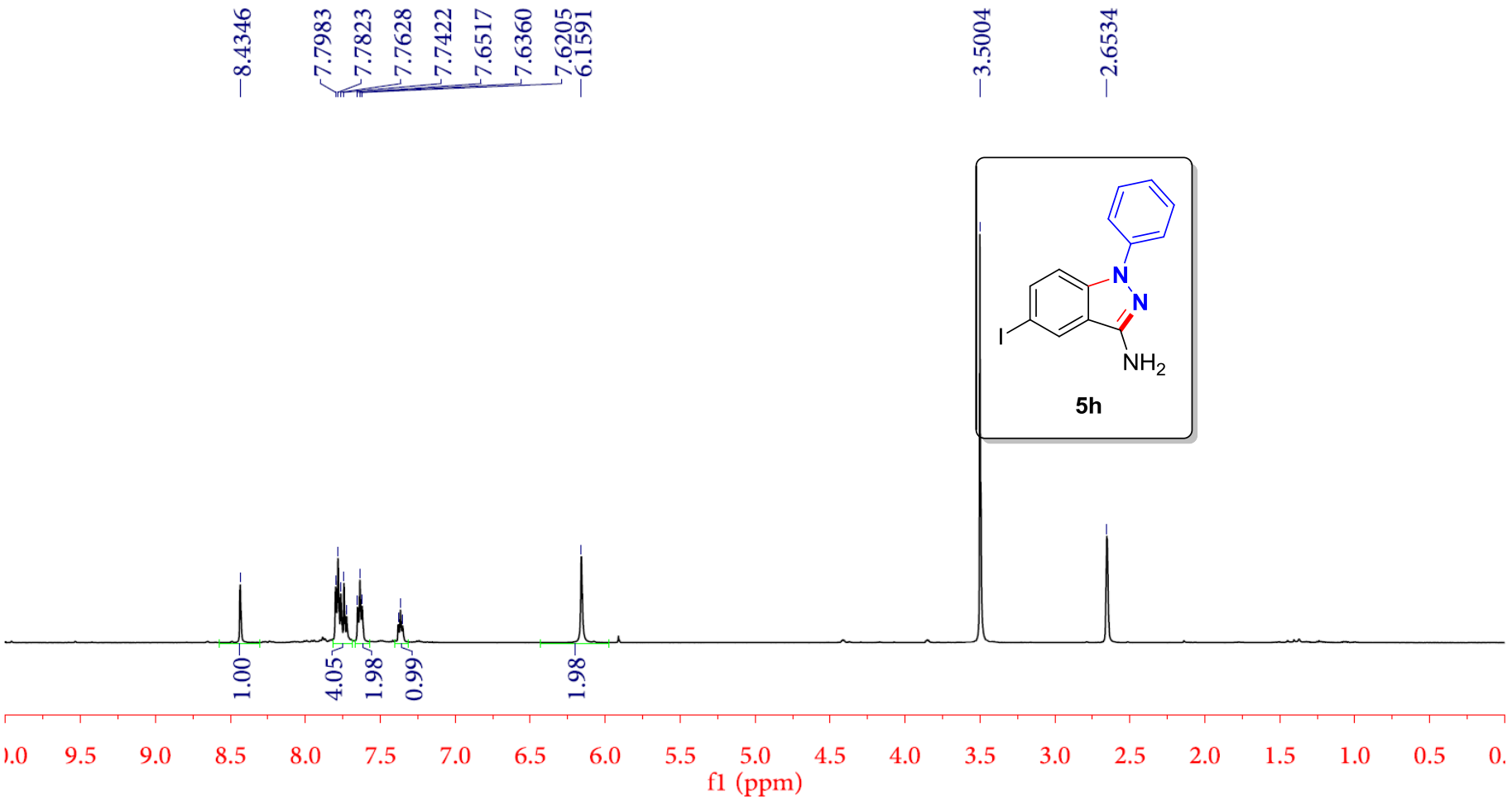
40.42
40.21
40.00
39.79
39.58
39.37
Br
N
N
NH2
5g
f1 (ppm)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7.7983
7.7823
7.7628
7.7422
7.6517
7.6360
7.6205
6.1591
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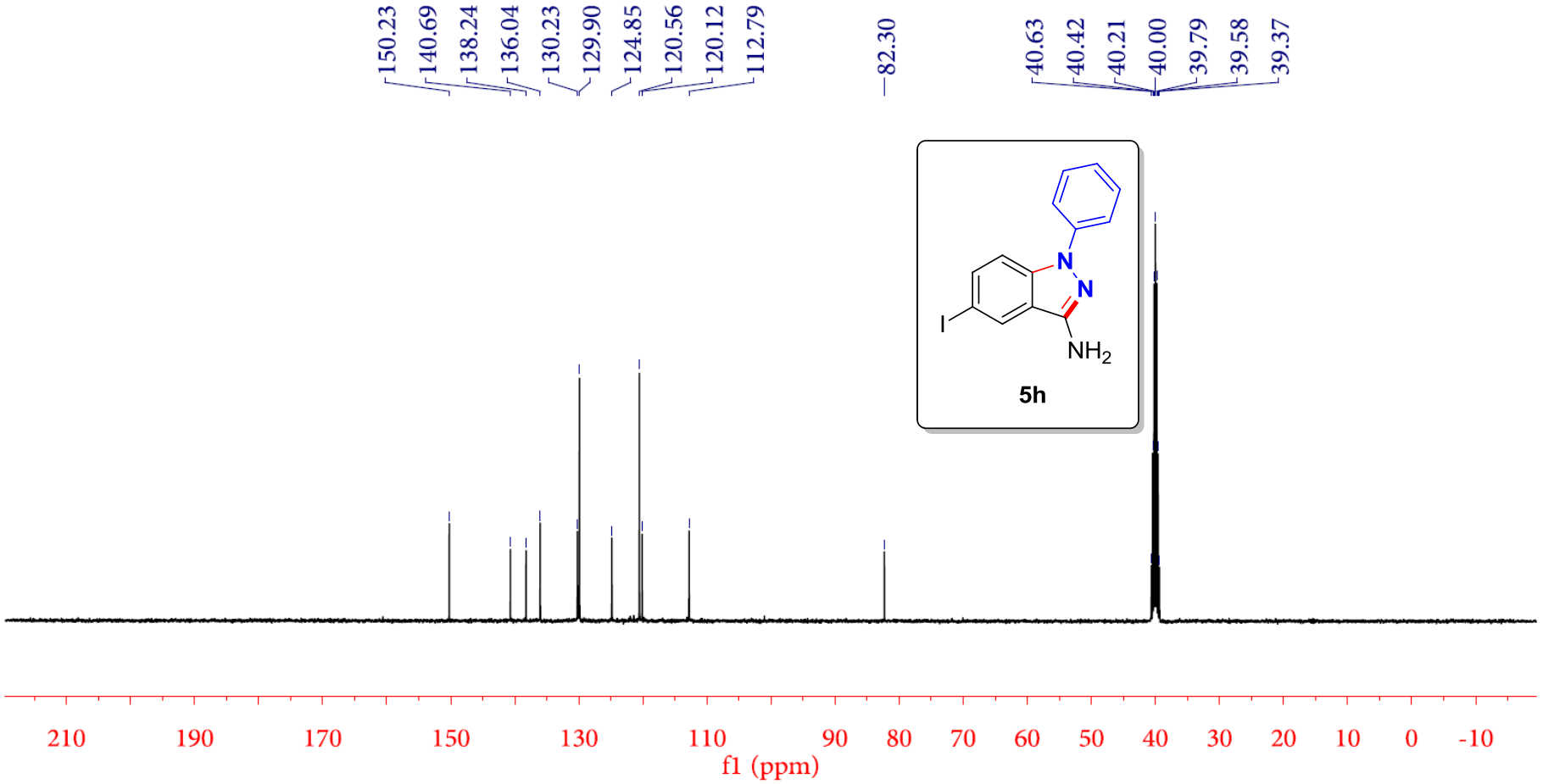
N
N
I
NH2
5h
1.00
4.05
1.98
0.99
1.98
f1 (ppm)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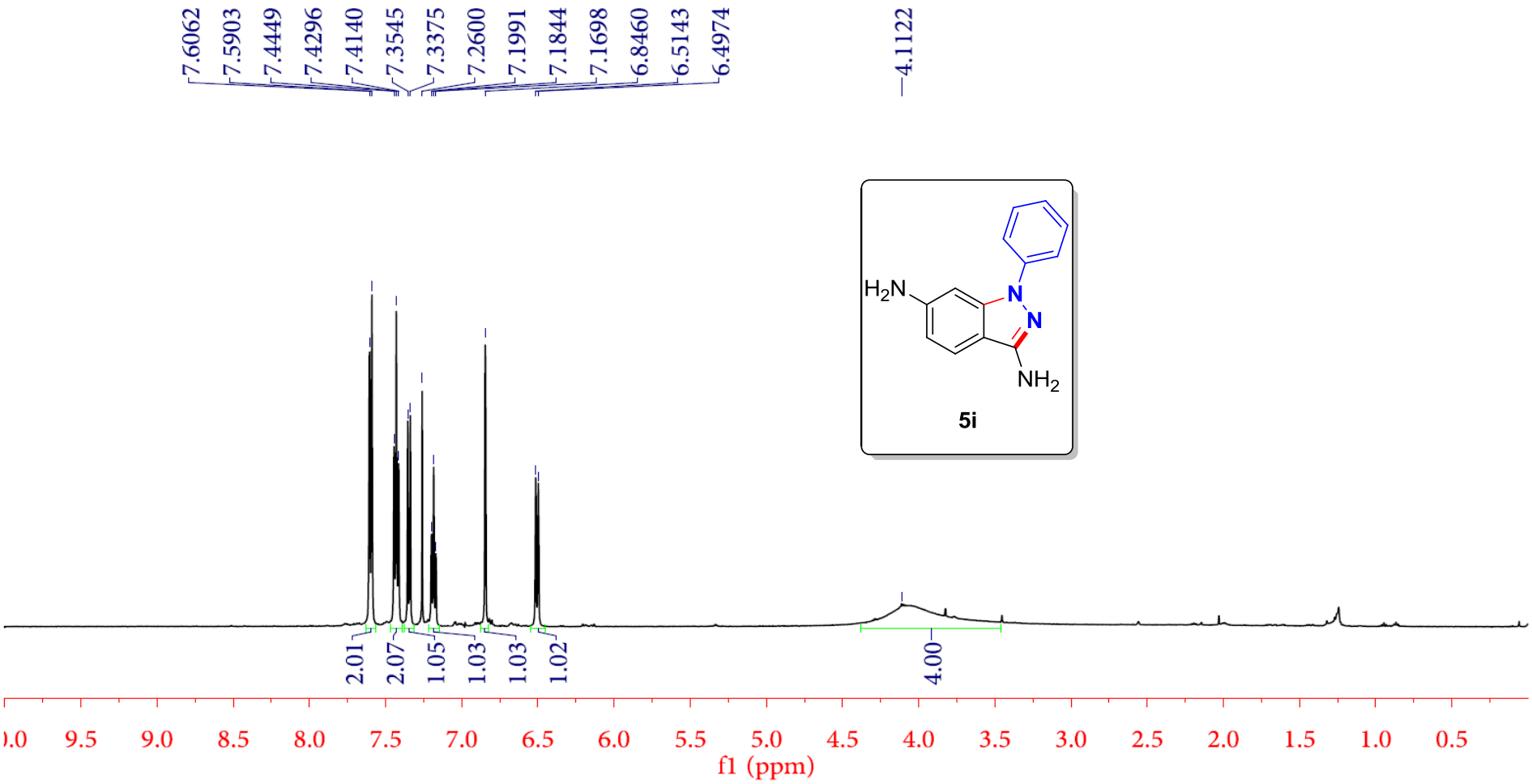
138.24
136.04
130.23
129.90
124.85
120.56
120.12
112.79
82.30
40.63
40.42
40.21
40.00
39.79
39.58
39.37
N
N
I
NH2
5h
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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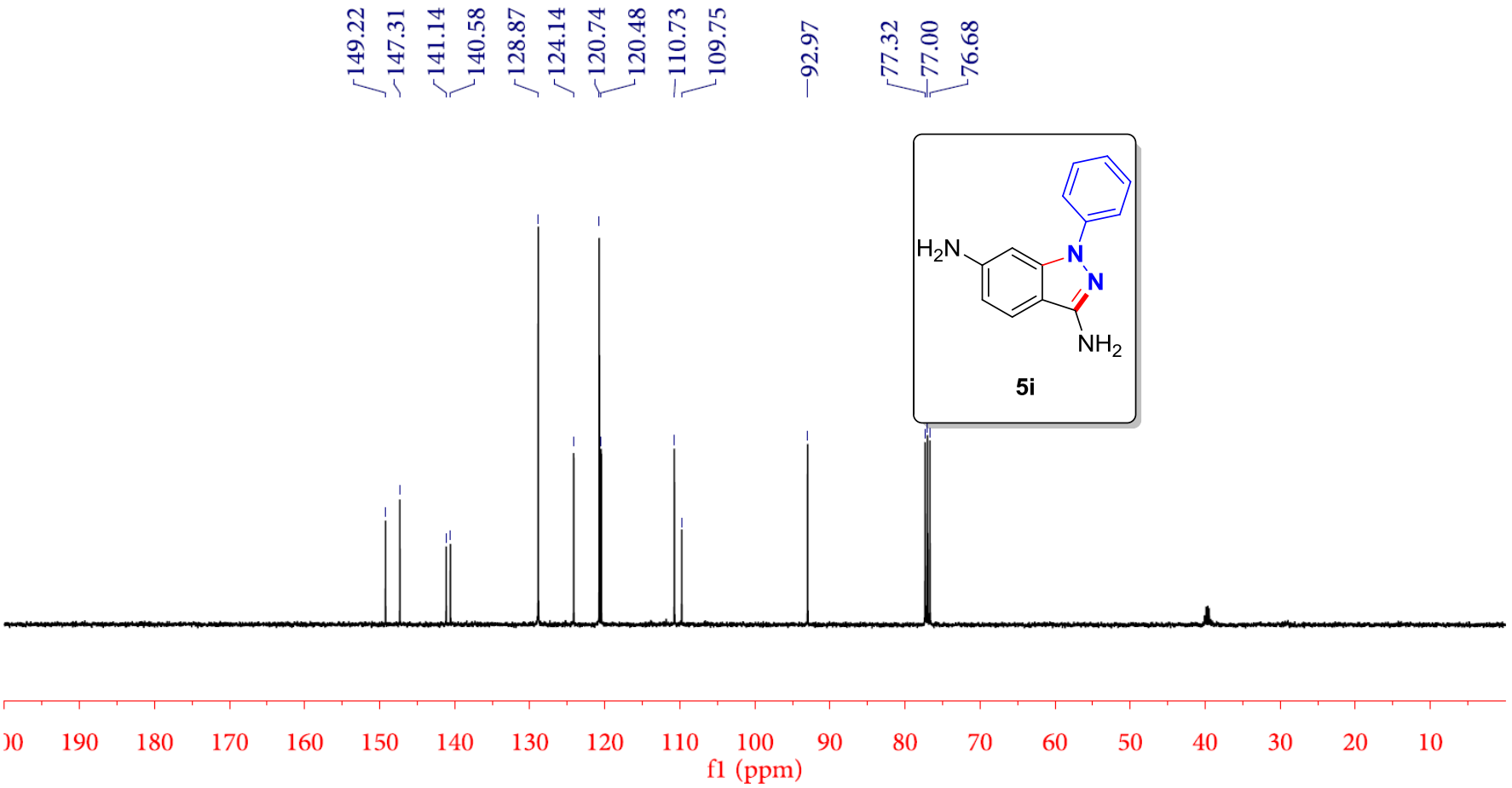
7.3375
7.2600
7.1991
7.1844
7.1698
6.8460
6.5143
6.4974
4.1122
H2N
N
N
NH2
5i
2.01
2.07
1.05
1.03
1.03
1.02
4.00
f1 (ppm)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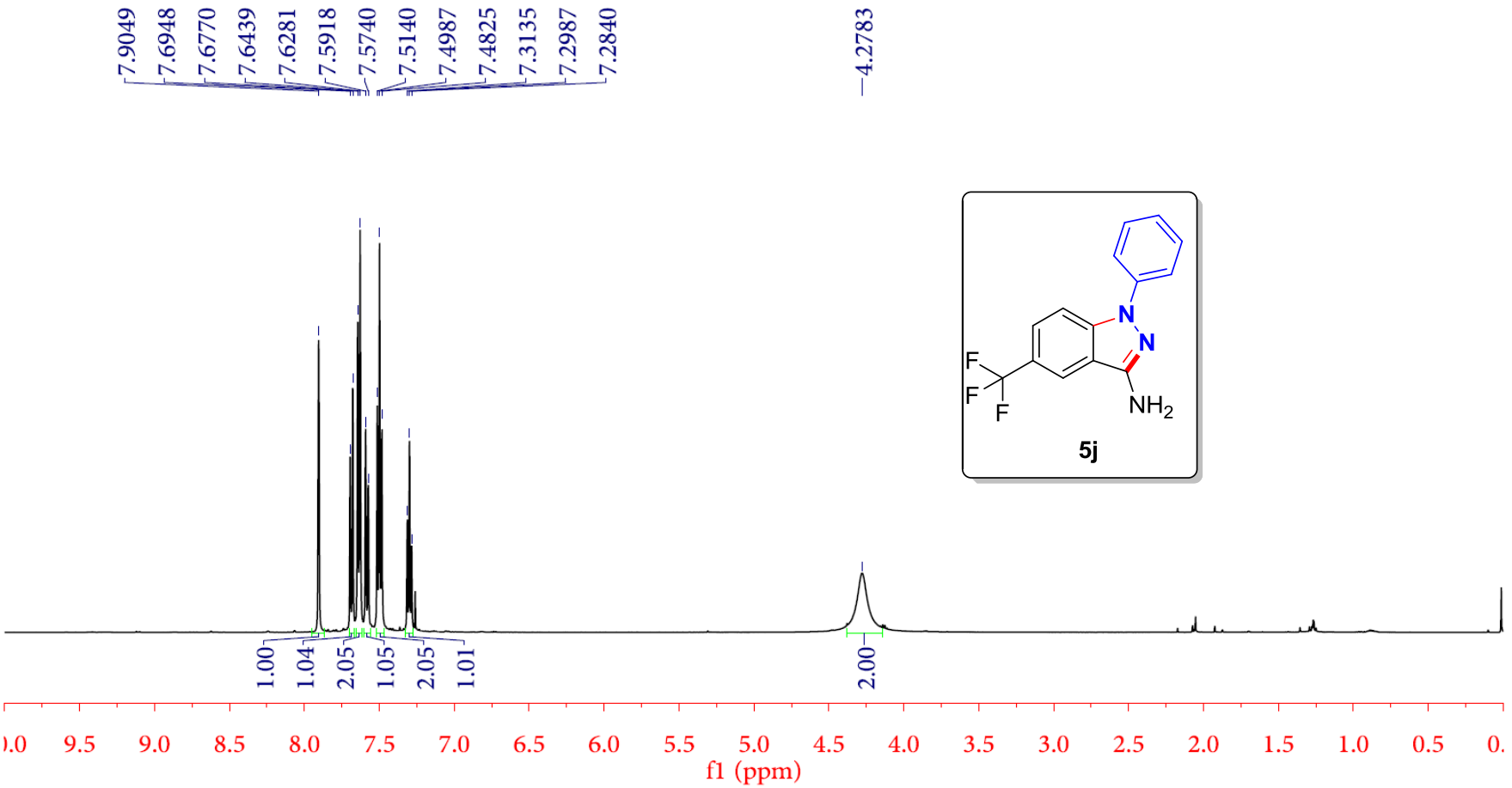
124.14
120.74
120.48
110.73
109.75
92.97
77.32
77.00
76.68
H2N
N
N
NH2
5i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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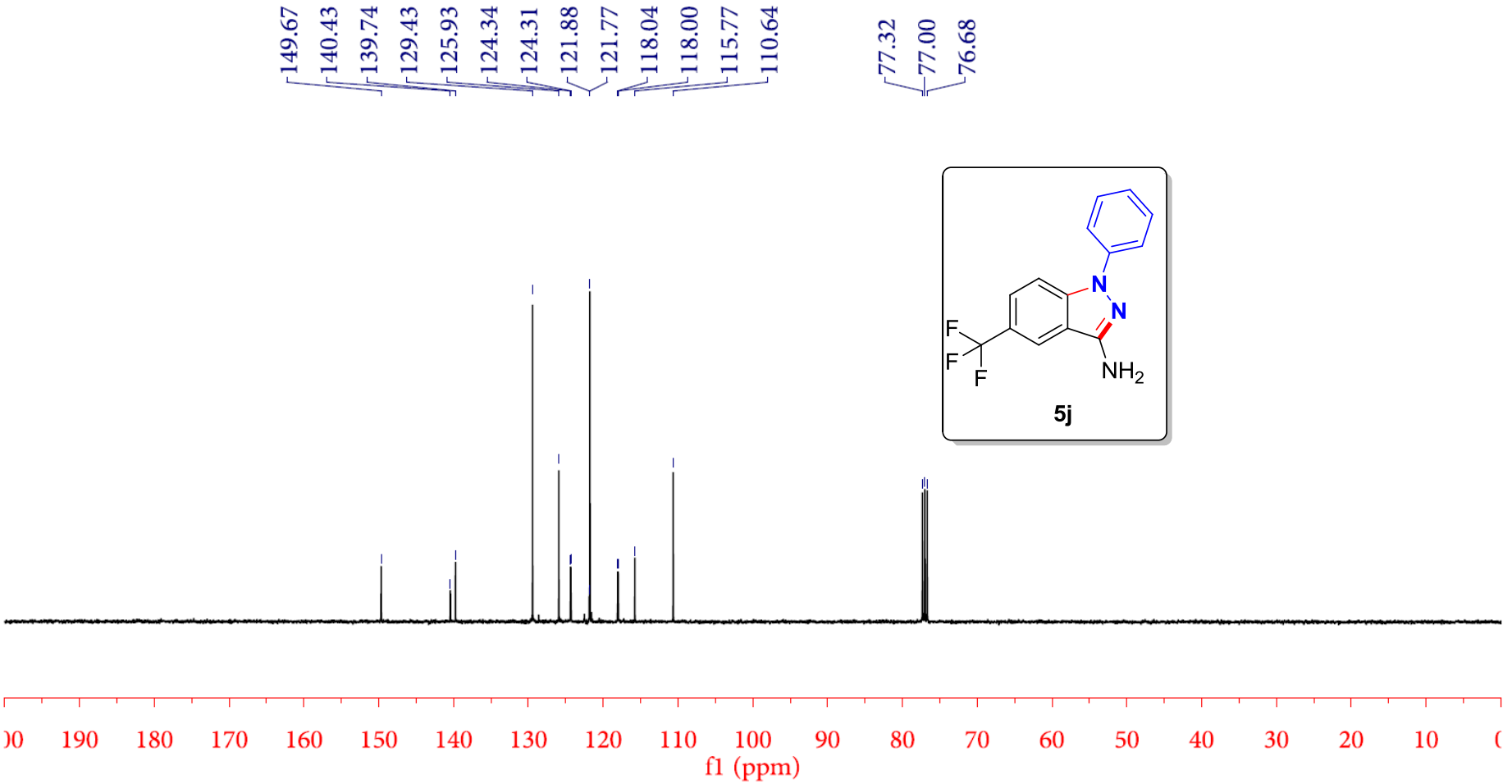
7.6281
7.5918
7.5740
7.5140
7.4987
7.4825
7.3135
7.2987
7.2840
4.2783
1.00
1.04
2.05
1.05
2.05
1.01
2.00
f1 (ppm)
N
N
F
F
F
NH2
5j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124.31
121.88
121.77
118.04
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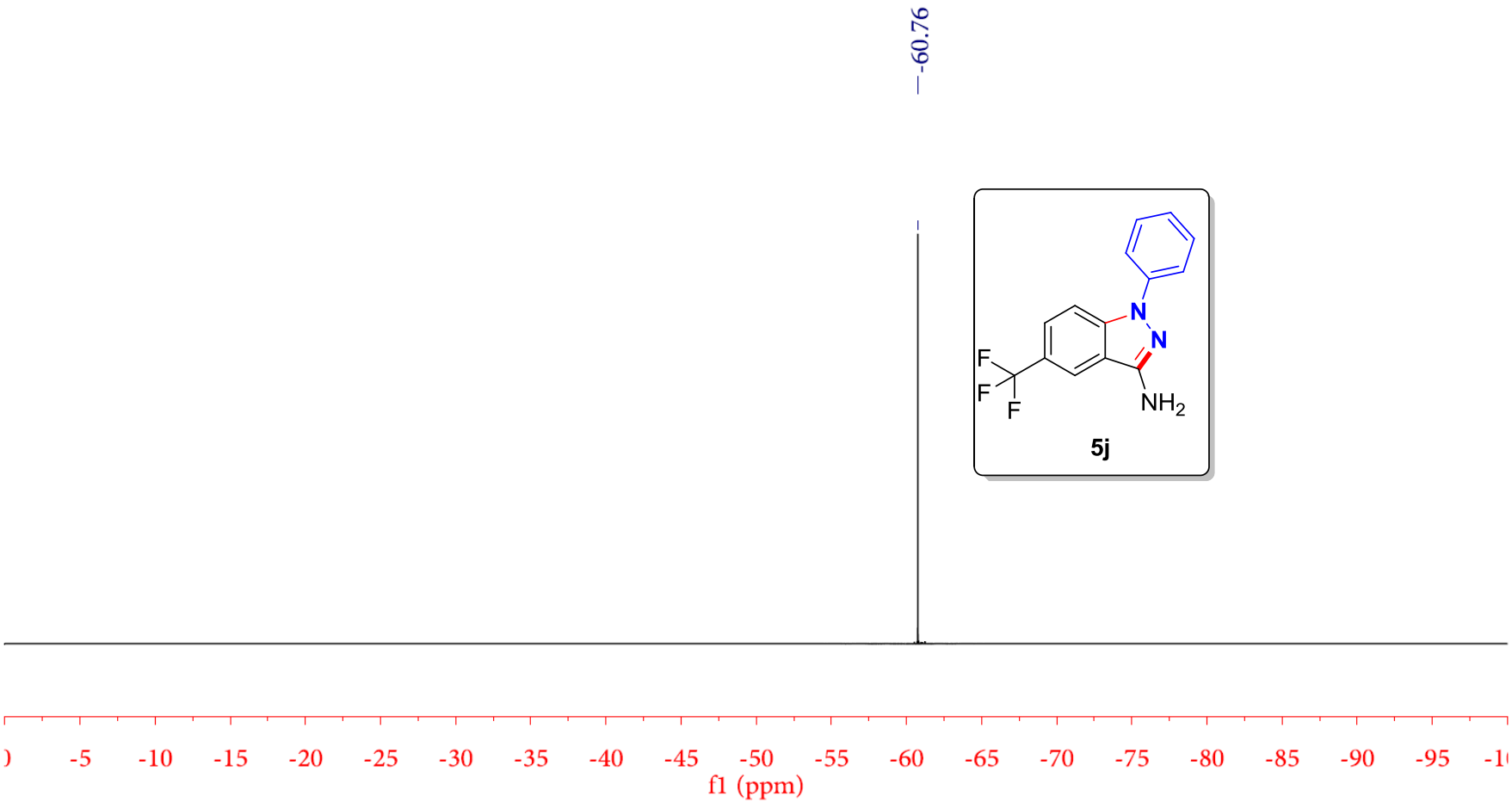
77.32
77.00
76.68
N
N
F
F
F
NH2
5j
f1 (ppm)


-60.76
F
F
F
N
N
NH2
5j
-5
-10
-15
-20
-25
-30
-35
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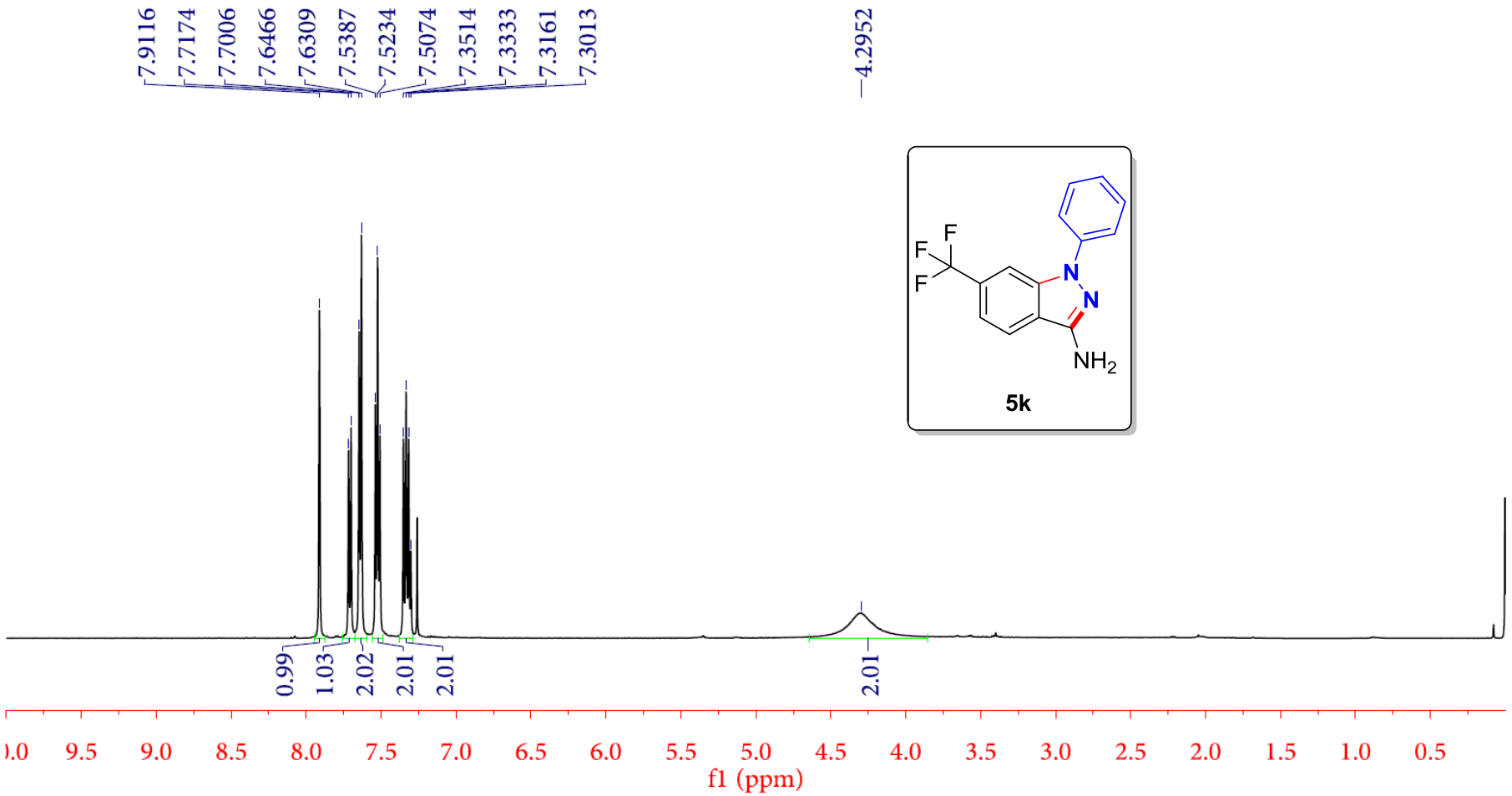
-75
-80
-85
-90
-95
f1 (ppm)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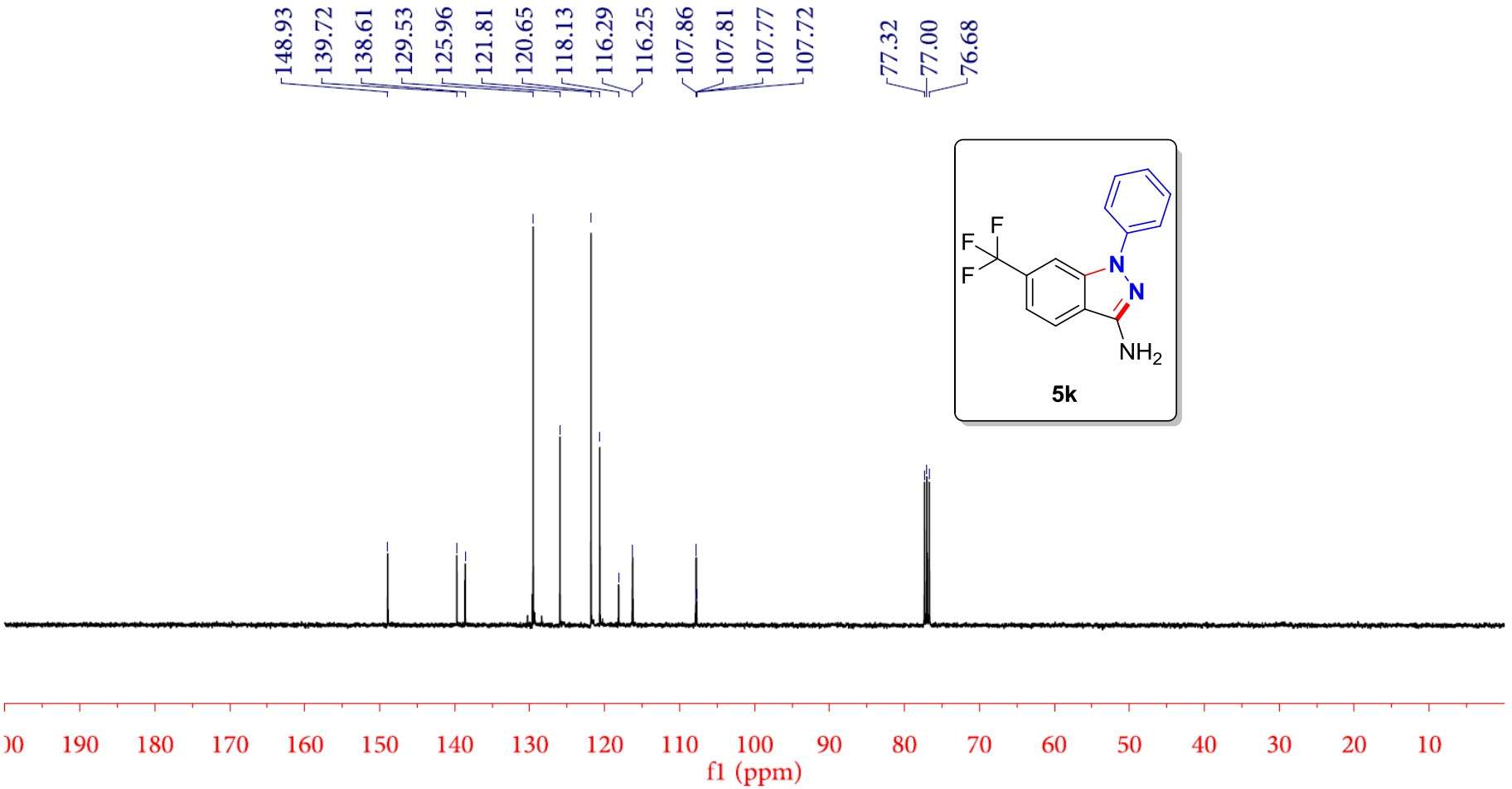
7.6466
7.6309
7.5387
7.5234
7.5074
7.3514
7.3333
7.3161
7.3013
4.2952
F
F
F
N
N
NH2
5k
0.99
1.03
2.02
2.01
2.01
2.01
f1 (ppm)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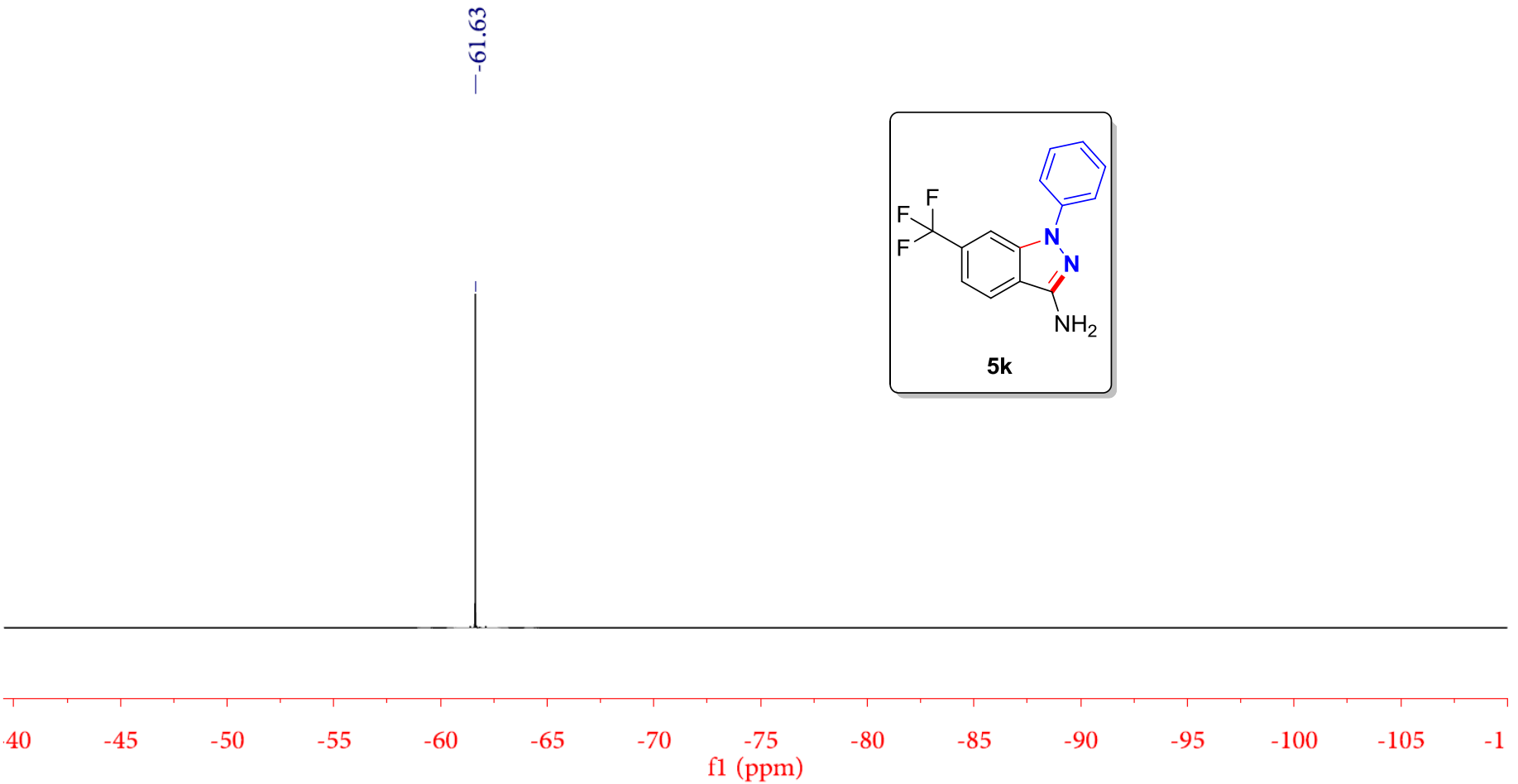
120.65
118.13
116.29
116.25
107.86
107.81
107.77
107.72
77.32
77.00
76.68
F
F
F
N
N
NH2
5k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-61.63
F
F
F
N
N
NH2
5k
40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-1
f1 (ppm)