Supporting Information

Iron-Catalyzed Remote Arylation of Aliphatic C–H Bond via 1,5-Hydrogen Shift

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Table of Contents

1. General Information

Unless otherwise noted, all reactions were carried out in a flame-dried Schlenk tube under a positive pressure of nitrogen. The reported reaction temperature was the recorded temperature of the oil bath. Thin-layer chromtography (TLC) was performed on glass plates with pre-coated silica gel (0.25 mm thick) and visualized with UV light. Flash chromatography was performed as described by Still et al[1] by using Kanto Silica gel 60 (spherical, 140-325 mesh).

Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and used without further purification. $Fe(acac)_3$ (> 99.9%) and (*Z*)-1,2-bis(diphenylphosphino)ethane (dppen) were purchased from Aldrich Inc. and used as received. $ZnBr_2 \cdot$TMEDA was prepared from $ZnBr_2$ and tetramethylethylenediamine (TMEDA).[2] Anhydrous ethereal solvents (stabilizer-free) were purchased from WAKO Pure Chemical and purified by a solvent purification system (GlassContour) equipped with columns of activated alumina and supported copper catalyst (Q-5) prior to use. The water content was determined with a Karl-Fischer moisture titrator (MKC-210, Kyoto Electronics Company) to be less than 30 ppm. Anhydrous solvents were purified and dried by standard procedures or a solvent purification system (Glass Contour). Moisture content of solvents was measured by a Karl-Fischer moisture titrator (MKC-210, Kyoto Electronics Company).

The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a JEOL ECA-400 spectrometer. Chemical shifts for protons are quoted in parts per million downfield from tetramethylsilane and are referenced to tetramethylsilane (^{1}H NMR: 0 ppm). Chemical shifts for carbons are referenced to the residual solvent (for $CDCl_3$, ^{13}C NMR: 77.16 ppm). Chemical shifts for fluorines are referenced to perfluorobenzene (^{19}F NMR: –164 ppm). Abbreviations are used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling stantant (*J*, Hz). Cyclic preprative chromatography was performed on a LC-92XXII NEXT SERIES, Japan Analytical Industry Co., Ltd. Gas chromatography was performed on a Shimadzu GC-14B and Mass spectra (GC-MS) was performed on a SHIMADZU Paarvum 2 gas chromatography mass spectrometer. High resolution mass spectra was performed on a Bruker microTOF II (APCI)

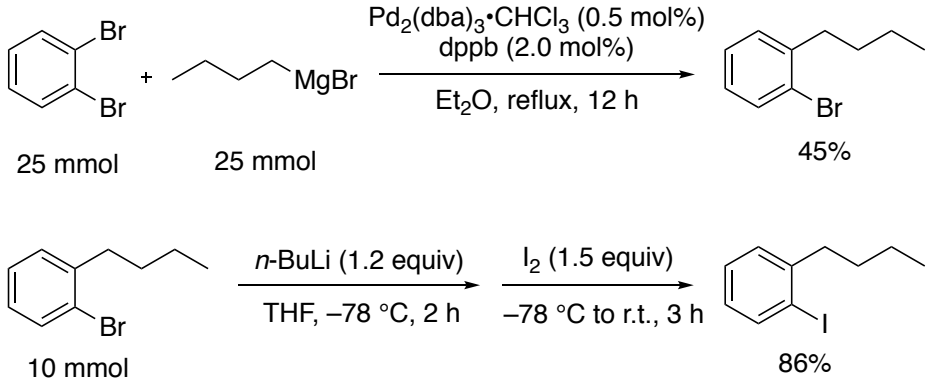
Spectrometer.

2. Preparation of Starting Materials

2.1. General procedure for the synthesis of 2-iodo-1-alkylbenzenes

The synthesis of 2-iodo-1-alkylbenzenes consists of two steps: 1) Kumada cross-coupling of 1,2-dibromobenzene with alkylmagnesium bromide to prepare 2-bromo-1-alkylbenzenes;[3] and 2) synthesis of the aryl iodide by lithiation of the aryl bromide, followed by reaction with iodine.[4] The following known compounds were prepared according to this procedure and the spectral data were in agreement with the literature data: 1-iodo-2-isobuytylbenzene (**1f**),[5] 1-(but-3-en-1-yl)-2-iodobenzene (**5**).[6]

1-Butyl-2-iodobenzene (1a)[7]

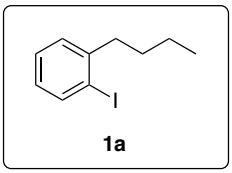


Scheme S1

Butylmagnesium bromide was prepared from 1-bromobutane (25 mmol, 3.75 g) and Mg (30 mmol, 0.72 g) in Et_2O (25 ml), and it was added to a stirred solution of $Pd_2(dba)_3$•($CHCl_3$) (0.5 mol%, 129 mg), 1,4-bis(diphenylphosphino)butane (2 mol%, 213 mg), 1,2-bromobenzene (25 mmol, 5.90 g) and Et_2O (15 ml). The reaction mixture was stired for 12 h under reflux. After completion, saturated aqueous NH_4Cl was added slowly and the mixture was extracted with Et_2O. The combined organic layer was washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and 1-bromo-2-butylbenzene (**1b**) was isolated in 45% yield by silica gel column chromatography (eluent: hexane).

To a stired solution of **1b** (10 mol, 2.13 g) in THF (30 ml) was added dropwise a solution of BuLi in hexane (12 mmol, 8.0 ml, 1.5 M) at –78 °C, and the resulting

solution was stirred for 1 h at that temperature. Iodine (15 mmol, 3.82 g) was added in portions and then the reaction mixture was allowed to warm to room temperature. The reaction was quenched with a saturated aqueous solution of $Na_2S_2O_3$ and extracted with ethyl ether. The combined organic layer was dried over magnesium sulfate and the pure product was isolated by cyclic preparative chromatography in 86% yield.



1a

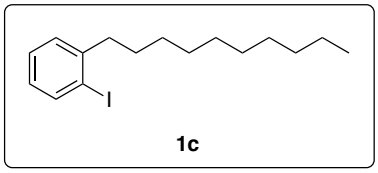
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (dd, *J* = 8.0 Hz, 1H), 7.27-7.16 (m, 2H), 6.87-6.82 (m, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.61-1.52 (m, 2H), 1.46-1.37 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (CDCl3, 100 MHz) δ 145.5, 139.5, 129.4, 128.3, 127.6, 100.8, 40.7, 32.5, 22.6, 14.1;

HRMS (APCI): calculated $C_{10}H_{13}I$ (M+H): 261.0135, found: 261.0123.

1-Decyl-2-iodobenzene (1c)

Following the same procedure with **1a**, 1-bromo-2-decylbenzene was isolated in 44% yield from the coupling reaction of 1,2-dibromobenzene (20 mmol, 4.7 g) with decylmagnesium bromide. After iodination, 1-iodo-2-propylbenzene was isolated by cyclic preprative chromatography in 81% yield as a colorless oil.



1c

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.25-7.22 (m, 1H), 7.20 (dd, *J* = 8.0 Hz, 1H), 6.89-6.82 (m, 1H), 2.69 (d, *J* = 7.6 Hz, 2H), 1.60-1.53 (m, 2H), 1.38-1.26 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H);

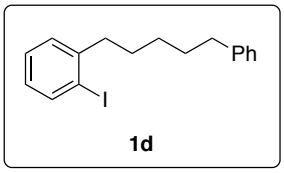
^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.5, 139.5, 129.4, 128.3, 127.6, 100.8, 41.0, 32.1, 30.4, 29.8, 29.7, 29.6, 29.5, 22.9, 14.3 (one carbon signal is overlapped);

HRMS (APCI): calculated $C_{16}H_{25}I$ (M-H): 343.0917, found: 343.0943.

1-Iodo-2-(5-phenylpentyl)benzene (1d)

Following the same procedure with **1a**, 1-bromo-2-(5-phenylpentyl)benzene was isolated in 38% yield from the coupling reaction of 1,2-dibromobenzene (20 mmol, 4.7 g) with (5-phenylpentyl)magnesium bromide. After iodination, 1-iodo-2-(5-phenylpentyl)benzene was isolated by cyclic preprative chromatography in

73% yield as a colorless oil.



1d

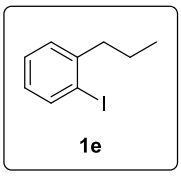
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (dd, *J* = 8.0 Hz, 1H), 7.30-7.22 (m, 3H), 7.20-7.15 (m, 4H), 6.88-6.83 (m, 1H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 1.72-1.57 (m, 4H), 1.48-1.41 (m, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.4, 142.8, 139.5, 129.4, 128.6, 128.4, 127.7, 125.7, 100.7, 40.9, 36.0, 31.4, 30.2, 29.1 (one carbon signal is overlapped);

HRMS (APCI): calculated $C_{17}H_{19}I$ (M-H): 349.0448, found: 349.0475.

1-Iodo-2-propylbenzene (1e)[7]

Following the same procedure with **1a**, 1-bromo-2-propylbenzene was isolated in 54% yield from the coupling reaction of 1,2-dibromobenzene (20 mmol, 4.7 g) with propylmagnesium bromide. After iodination, 1-iodo-2-propylbenzene was isolated by cyclic preprative chromatography in 85% yield as a light red oil.



1e

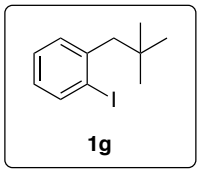
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 6.20 (d, *J* = 7.8 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 2.69 (t, *J* = 6.8 Hz, 2H), 1.68-1.58 (m, 2H), 1.03 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.2, 139.5, 129.5, 128.3, 127.7, 100.8, 42.9, 23.6, 14.0;

HRMS (APCI): calculated $C_9H_{11}I$ (M-H): 244.9822, found: 244.9802.

1-Iodo-2-neopentylbenzene (1g)

Following the same procedure with **1a**, 1-bromo-2-neopentylbenzene was isolated in 48% yield from the coupling reaction of 1,2-dibromobenzene (20 mmol, 4.7 g) with isobutylmagnesium bromide. After iodination, 1-iodo-2-neopentylbenzene was isolated by cyclic preprative chromatography in 76% yield as a colorless oil.



1g

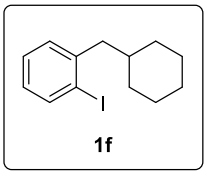
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.24-7.18 (m, 2H), 6.86-6.83 (m, 1H), 2.74 (s, 2H), 0.97 (s, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.9, 139.9, 131.1, 127.7, 127.5, 103.2, 52.4, 33.6, 29.9;

HRMS (APCI): calculated $C_{11}H_{15}I$ (M+H): 275.0291, found: 275.0299.

1-(Cyclohexylmethyl)2-iodobenzene (1i)

Following the same procedure with **1a**, 1-bromo-2-(cyclohexylmethyl)benzene was isolated in 32% yield from the coupling reaction of 1,2-dibromobenzene (10 mmol, 2.4 g) with (cyclohexylmethyl)magnesium bromide. After iodination, 1-(cyclohexylmethyl)2-iodobenzene was isolated by cyclic preprative chromatography in 75% yield as a colorless oil.

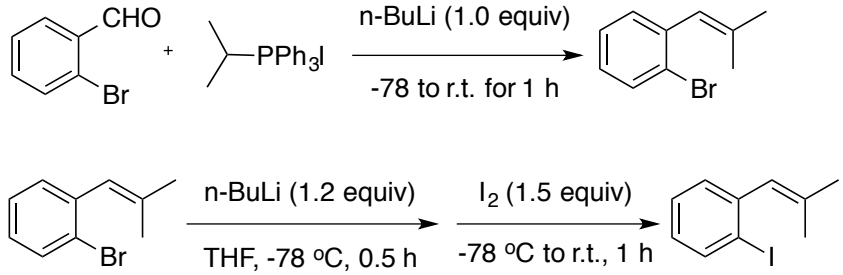


^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.25-7.20 (m, 1H), 7.12 (dd, *J* = 7.2 Hz, 1H), 6.88-6.83 (m, 1H), 2.58 (d, *J* = 7.2 Hz, 2H), 1.70-1.60 (m, 6H), 1.21-1.15 (m, 3H), 1.05-0.99 (m, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.0, 139.6, 130.6, 127.9, 127.6, 101.4, 48.4, 38.4, 33.1, 26.6, 26.4;

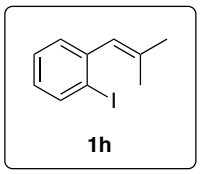
HRMS (APCI): calculated $C_{13}H_{17}I$ (M+H): 301.0448, found: 301.0450.

2.2. Synthesis of 1-iodo-2-(2-methylprop-1-en-1-yl)benzene (1h)



Scheme S2

A solution of BuLi in hexane (5 mmol, 1.5 M) was added to a stirred solution of isopropytriphenylphosphonium iodine in THF at –78 °C. The resulting red mixture was stirred for 0.5 h at –78 °C, then 2-bromobenzaldehyde was added and the resulted mixture was allowed to warm to room temperature and stirred for 1 h. Saturated NH_4Cl was added and the mixture was extracted with diethyl ether. 1-Bromo-2-(2-methylprop-1-en-1-yl)benzene was isolated in 76% yield as an oil. The iodination was performed according to the procedure described for the synthesis of with **1a**. 1-Iodo-2-(2-methylprop-1-en-1-yl)benzene was isolated in 85% yield as colorless oil. The compound data was in aggreement with the literature. [8,9]



1h

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.29 (dd, *J* = 7.6 Hz, 1H), 7.20 (dd, *J* = 8.0 Hz, 1H), 6.91-6.86 (m, 1H), 6.13 (s, 1H), 1.93 (s, 3H), 1.70 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.3, 138.9, 136.5, 130.3, 129.3, 127.9, 127.8, 100.9, 26.1, 19.4;

HRMS (APCI): calculated $C_{10}H_{11}I$ (M+H): 258.9978, found: 259.0000.

2.3. General procedure for the synthesis of Grignard reagents

Grinard reagents were freshly prepared from the corresponding aryl bromide and Mg turnings, and the concentration was determined by titration piror to use. (3-Methoxyphenyl)magnesium bromide was pruchased from Aldrich and titrated prior to use.[10]

Phenylmagnesium bromide

To a dried two-neck 200 ml flask equipped with a cooling condenser and a 20 ml dropping funnel was added Mg turnings (72 mmol, 1.73g) and THF (40 ml) under nitrogen. A solution of bromobenzene (60 mmol, 9.42g) in THF (5 ml) was added to the funnel and then added dropwise. The mixture was heated to initiate the reaction, and then it was stirred for a further 0.5 h at room temperature. The mixture was passed over a pad of Celite under nitrogen to obtained a clear pale brown solution. The concentration was determined as 1.09 mol/L.

(4-Methylphenyl)magnesium bromide

Following the same procedure with 1-bromo-4-methylbenzene (20 mmol, 3.42 g), Mg (22 mmol, 0.53 g) in THF (20 ml), a clear solution of (4-methoxyphenyl)magnesium bromide was obtained. The concentration was determined as 0.91 mol/L.

(4-Methoxyphenyl)magnesium bromide

Following the same procedure with 1-bromo-4-methoxybenzene (20 mmol, 3.74 g), Mg (22 mmol, 0.53 g) in THF (20 ml), a clear solution of (4-methoxyphenyl)magnesium bromide was obtained. The concentration was determined as 0.84 mol/L.

(4-*N,N*-Dimethylphenyl)magnesium bromide

Following the same procedure with 4-bromo-*N,N*-dimethylaniline (20 mmol, 4.0

g), Mg (22 mmol, 0.53 g) in THF (20 ml). The concentration was determined as 0.88 mol/L.

Naphthalen-2-ylmagnesium bromide

Following the same procedure with 2-bromonaphthalene (10 mmol, 2.07 g), Mg (12 mmol, 0.29 g) in THF (10 ml). The concentration was determined as 0.53 mol/L.

(4-Fluorophenyl)magnesium bromide

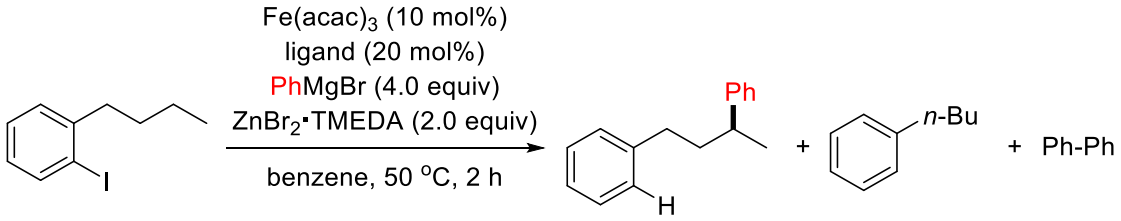
Following the same procedure with 1-bromo-4-fluorobenzene (20 mmol, 3.5 g), Mg (22 mmol, 0.53 g) in THF (20 ml). The concentration was determined as 0.82 mol/L.

3. Iron-Catalyzed Arylation of 1-Iodo-2-Alkylbenzenes

3.1. Survey of the reaction parameters

In order to optimize the reaction conditions, we investigated a variety of reaction parameters (Table S1). Initially, we conducted the reaction in benzene with $Fe(acac)_3$ as a catalyst, dppen as a ligand and *in situ* generated Ph_2Zn as arylation reagent. The desired product was detected by GC in 30% yield, together with a dehalogenated product (butylbenzene) and biphenyl in 33% and 67% respectively (entry 1). We then investigated the role of the ligand. Interestingly, the reaction proceeded well in the absence of a ligand (entry 2), suggesting that the reaction itself does not require a ligand, but an appropriate ligand may stabilize the organoiron species and improve the catalyst turnover. A monodentated phosphine ligand such as Cy_3P or Bu_3P increased the yield slightly (entries 3-4). Next, we investigated several NHC ligands and 1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride (**4**) was found to perform well (entry 7).

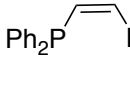
Table S1. Investigation of ligands[a]



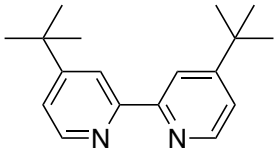
1a **2a** **3a** **6a**

Entry	Ligand	2a/%	3a/%	6a/%	1a/%
1	dppen	30	33	67	trace
2	-[b]	46	25	36	trace
3	Cy_3P	53	24	36	trace
4	Bu_3P	53	24	45	trace
5	dtbpy	50	31	51	ND
6	**L1**	53	22	32	trace
7	***4***	*59*	*19*	*36*	*trace*
8	**L3**	54	2	44	ND
9	**L4**	41	29	47	ND

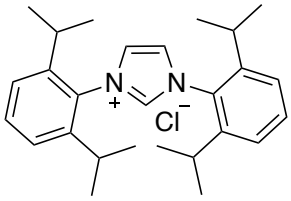
[a]Reaction conditions: **1a** (0.1 mmol), PhMgBr (0.4 mmol, 1.09 M), $Fe(acac)_3$ (10 mol%), ligand (20 mol%), $ZnBr_2$ • TMEDA (0.2 mmol), benzene (1 ml), at 50 °C for 2 h. Yields were estimated by GC analysis using tridecane as an internal standard. [b]No ligand.



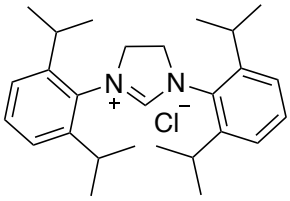
dppen



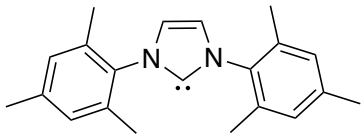
dtbpy



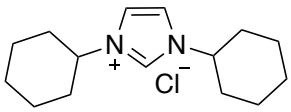
1,3-Bis(2,6-diisopropylphenyl) imidazolium chloride (**L1**)



1,3-Bis(2,6-diisopropylphenyl) imidazolinium chloride (**4**)



1,3-Dimesityl-1H-imidazol-3-ium-2-ide (**L3**)

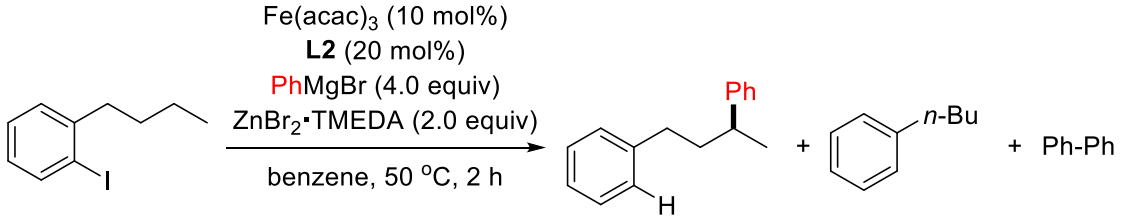


1,3-Dicyclohexylimidazolium chloride (**L4**)

Next, we exmained several zinc reagents generated *in situ* from a zinc salt and

phenylmagnesium bromide (Table S2). The reaction did not proceed when $ZnBr_2$ was used instead of $ZnBr_2 \cdot TMEDA$ (entry 1). The reaction did not proceed when a zinc reagent in Et_2O was used (entry 2), and a large amount of dehalogenated product and biphenyl was formed. A monorganozinc reagent was unreactive (entry 3). Reducing the amount of diphenylzinc resulted in a decreased yield (entry 4); an excess amount of PhMgBr did not negatively affect the reaction (entry 5). The reaction took place in 52% yield by using of $ZnCl_2 \cdot TMEDA$ (entry 6). Other organmetallic reagents such as Me_2Zn and Me_3Al did not react (entries 7 and 8).

Table S2. Investigation of the organometallic reagent[a]



1a **2a** **3a** **6a**

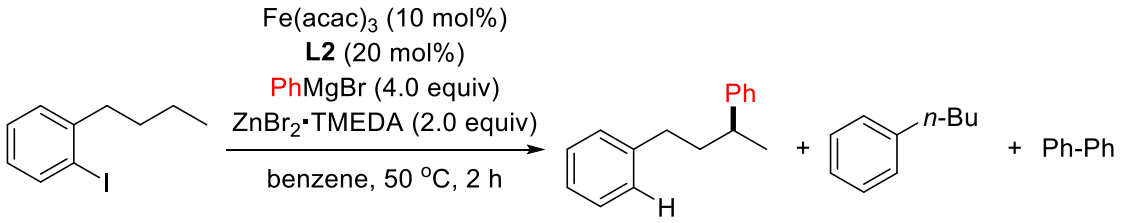
Entry	Variation	2a/%	3a/%	6a/%	1a/%
1	$ZnBr_2$	5	14	36	76
2	Et_2O[b]	6	52	82	24
3	0.2 : 0.2[c]	trace	trace	48	92
4	0.1 : 0.2[c]	33	11	24	40
5	0.2 : 0.8[c]	50	30	72	ND
6	$ZnCl_2 \cdot TMEDA$	52	23	52	ND
7	$AlMe_3$	ND	ND	ND	94
8	$ZnMe_2$	ND	ND	ND	90

[a]Reaction conditions: **1a** (0.1 mmol), PhMgBr (0.4 mmol, 1.09 M), $Fe(acac)_3$ (10 mol%), **L2** (20 mol%), $ZnBr_2 \cdot TMEDA$ (0.2 mmol), benzene (1 ml), at 50 °C for 2 h. Yields were estimated by GC analysis using tridecane as an internal standard. [b]Zinc reagent was prepared in Et_2O; [c]Mole ratio of $ZnBr_2 \cdot TMEDA$ to PhMgBr; $AlMe_3$ (2.0 M in hexane), $ZnMe_2$ (1.2 M in toluene), ND = Not Detected.

With the optimized ligand and zinc reagent in hand, we next examined the iron

catalyst (Table S3). The reaction did not proceed at all in the absence of $Fe(acac)_3$ (entry 1). $Fe(acac)_2$ gave the product in a lower yield (entry 2), and FeF_3 or $CpFe(CO)_2I$ were completely unreactive (entries 3 and 4).

Table S3. Investigation of the iron catalyst[a]



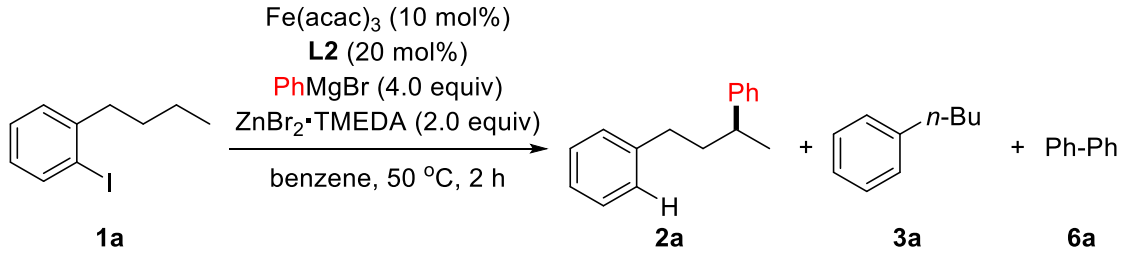
1a **2a** **3a** **6a**

Entry	Variation	2a/%	3a/%	6a/%	1a/%
1	-[b]	ND	ND	41	57
2	$Fe(acac)_2$	37	23	52	ND
3	FeF_3	trace	ND	trace	90
4	$CpFe(CO)_2I$	trace	ND	28	97

[a]Reaction conditions: **1a** (0.1 mmol), PhMgBr (0.4 mmol, 1.09 M), $Fe(acac)_3$ (10 mol%), **L2** (20 mol%), $ZnBr_2$ · TMEDA (0.2 mmol), benzene (1 ml), at 50 °C for 2 h. Yields were estimated by GC analysis using tridecane as an internal standard. [b]No catalyst. ND = Not Detected

The effect of the reaction solvent was also investigated (Table S4). The reaction proceeded in a comparable yield when fluorobenzene was used as a solvent (entry 3) instead of the toxic benzene. Other aromatic solvent gave lower yields, and ether solvents performed poorly.

Table S4. Investigation of solvents[a]

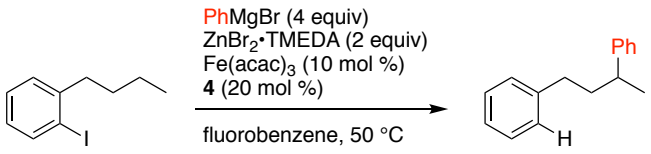


1a **2a** **3a** **6a**

Entry	Variation	2a/%	3a/%	6a/%	1a/%
1	*t*-BuPh	30	28	37	17
2	anisole	27	36	52	trace
3	PhF	57	21	36	trace
4	$PhCF_3$	48	24	36	7
5	DME	14	61	34	20
6	toluene	27	44	57	6
7	THF	10	83	31	ND

[a]Reaction conditions: **1a** (0.1 mmol), PhMgBr (0.4 mmol, 1.09 M), $Fe(acac)_3$ (10 mol%), **L2** (20 mol%), $ZnBr_2$ · TMEDA (0.2 mmol), benzene (1 ml), at 50 °C for 2 h. Yields were estimated by GC analysis using tridecane as an internal standard. [b]No catalyst. DME = 1,2-Dimethoxyethane. THF = Tetrahydrofuran. ND = Not Detected.

3.2. Typical procedure for iron-catalyzed arylation



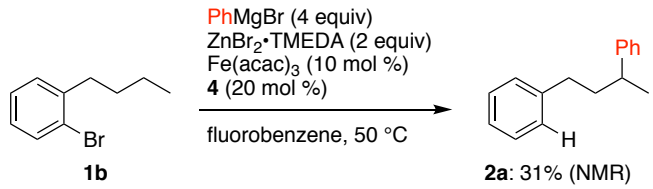
1a **2a**: 57%

First, a solution of Ph_2Zn in fluorobenzene was prepared: To a flame-dired Schlenk tube was added $ZnBr_2$ · TMEDA (0.4 mmol, 135 mg) and THF (1 ml). PhMgBr (0.8 mmol, 1.09 M in THF) was then added under nitrogen and stirred for 20 min. THF was removed carefully under vacumn and fluorobenzene (2 ml) was added. The resulting mixture was used for arylation in the next step.

To a flame-dired Schlenk tube equipped with a magnetic stir bar was added

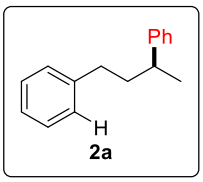
$Fe(acac)_3$ (10 mol%, 7 mg), **4** (20 mol%, 17 mg), fluorobenzene (2 ml) and 1-butyl-2-iodobenzene (0.20 mmol, 52 mg) under nitrogen. The mixture was warmed to 50 °C and a freshly prepared solution of Ph_2Zn in fluorobenzene was added dropwise over 10 min by a gas tight syringe under nitrogen. The resulting mixture was stirred for further 2 h. The reaction was quenched with saturated aqueous NH_4Cl (0.5 ml), the organic layer was passed over a pad of silca gel. The solution was pre-absorbed on silica gel and concentrated by rotary evaporation. The crude product was purified by silica gel column chromatography (hexane) to afford the product **2** in 57% yield.

In addition, the reactivity of 1-bromo-2-butylbenzene was examined under the same reaction conditions. Product **2** was detected in 31% yield by ^{1}H NMR analysis of the crude reaction mixture.



1b **2a**: 31% (NMR)

1,3-Diphenylbutane (Table 2, entry 1-3)[11]



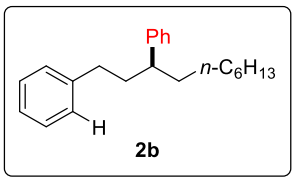
2a

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26-7.04 (m, 10 H), 2.71-2.60 (m, 1H), 2.46-2.41 (m, 2H), 1.89-1.80 (m, 2H), 1.20 (d, J = 6.8 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.4, 142.7, 128.6, 128.5, 128.4, 127.2, 126.1, 125.8, 40.1, 39.6, 34.1, 22.7.

GC-MS (EI) *m/z* (relative intensity): 210 (M^+, 50), 167 (100), 165 (60), 152 (40).

1,3-Diphenyldecane (Table 2, entry 4)



2b

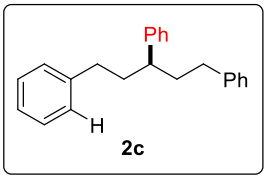
Following the general procedure, the title compound was isolated in 50% yield as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29- 7.04 (m, 10 H), 2.51-2.37 (m, 3H), 1.95-1.80 (m, 2H), 1.62-1.49 (m, 2H), 1.21-1.04 (m, 10H), 0.79 (t, J = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.9, 142.8, 128.5, 128.4, 128.3, 127.9, 126.1, 125.7, 45.7, 38.7, 37.2, 34.0, 32.0, 29.9, 29.4, 27.7, 22.8, 14.3;

HRMS (APCI): calculated $C_{22}H_{30}$ (M+H): 295.2420, found: 295.0497.

1,3,5-Triyltriphenylpentane (Table 2, entry 5)



2c

Following the general procedure, the title compound was isolated in 50% yield as a colorless oil.

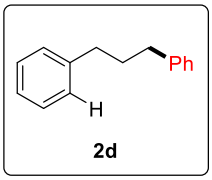
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.33 (m, 2H), 7.27-7.16 (m, 9H), 7.09 (d, *J* = 7.6 Hz, 4H), 2.61-2.50 (m, 1H), 2.49-2.42 (m, 4H), 1.99-1.92 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.3, 142.7, 128.6, 128.5, 128.4, 128.0, 126.3, 125.8, 45.3, 38.9, 33.9.

GC-MS (EI) *m/z* (relative intensity): 300 (M^+, 40), 196 (25), 117 (30), 105 (30), 91 (100).

1,3-Diphenylpropane (Table 2, entry 6)[12]

Following the general procedure, the title compound was isolated in 28% yield as a colorless oil.



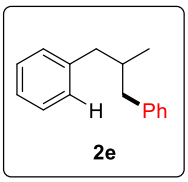
2d

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.10 (m, 10 H), 2.66 (t, *J* = 7.5 Hz, 4 H), 1.88-2.00 (m, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.6, 128.6, 128.5, 125.8, 35.7, 33.1.

GC-MS (EI) *m/z* (relative intensity): 196 (M^+, 45), 167 (100), 165 (60), 152 (40).

1,3-Diphenyl-2-methylpropane (Table 2, entry 7)[13]



2e

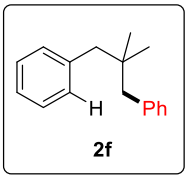
Following the general procedure, the title compound was isolated in 38% yield as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30-7.24 (m, 5H), 7.21-7.12 (m, 5H), 2.69 (dd, *J* = 5.5 Hz, 2H), 2.41 (dd, *J* = 8.0 Hz, 2H), 2.09-1.99 (m, 1H), 0.83 (d, *J* = 6.4 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.4, 129.3, 128.3, 125.9, 43.5, 37.3, 19.3.

GC-MS (EI) *m/z* (relative intensity): 210 (M^+, 50), 119 (60), 91 (100).

2,2-Dimethyl-1,3-diphenylpropane (Table 2, entry 8)[14]



2f

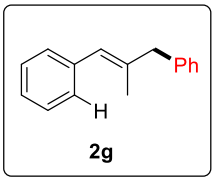
Following the general procedure, the title compound was isolated in 54% yield as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28-7.25 (m, 4H), 7.22 (d, *J* = 6.8 Hz, 2H), 7.15-7.12 (m, 4H), 2.58 (s, 4H), 0.83 (s, 6H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.2, 130.9, 127.8, 126.0, 49.5, 35.6, 26.2.

GC-MS (EI) *m/z* (relative intensity): 224 (M^+, 5), 133 (30), 117 (15), 105 (10), 91 (100).

(2-Methylprop-1-ene-1,3-diyl)dibenzene (Table 2, entry 9)[15]



2g

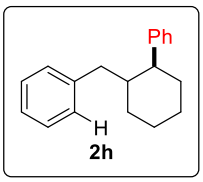
Following the general procedure, a *E*/*Z* mixture was isolated in 35% yield as a colorless oil. The ratio (*E*:*Z* = 3.5:1) was deterimined by crude NMR analysis. A small amount of *E*-isomer could be isolated after performing flash chromatography twice.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.24 (m, 10H), 6.43 (s, 1H), 3.53 (s, 2H), 2.93 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.0, 138.4, 138.2, 129.1, 129.0, 128.5, 128.2, 126.9, 126.3, 126.2, 47.2, 17.8.

GC-MS (EI) *m/z* (relative intensity): 208 (M^+, 55), 193 (50), 178 (30), 130 (35), 115 (100), 91 (55).

1-Benzyl-2-phenylcyclohexane (Table 2, entry 10)



2h

Following the general procedure, a mixture of stereoisomers was isolated in 55% yield which was inseparable by silica gel chromatography. The *dr* value of 3.6 was determined by crude ^{1}H NMR.

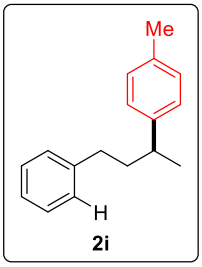
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.28 (m, 2.78H), 7.28-7.10 (m, 8.83 H), 6.99 (d, *J* = 7.3 Hz, 2H), 6.93 (d, *J* = 7.3 Hz, 0.82H), 3.00-2.58 (m, 0.40H), 2.60-2.53 (dd, *J* = 13.2 Hz, 1H), 2.49 (t, *J* = 13.2 Hz, 0.45H), 2.31-2.16 (m, 1.84H), 2.05-1.66 (m, 7.49H), 1.65-1.15 (m, 5.52H), 1.02-0.80 (m, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.8, 142.3, 141.5, 129.3, 129.1, 128.6, 128.3, 128.2,

128.1, 127.8, 126.1, 125.9, 125.6, 125.5, 51.3, 46.6, 44.6, 42.8, 41.1, 36.4, 31.9, 31.8, 28.4, 27.0, 26.7, 26.5, 25.4, 20.5;

HRMS (APCI): calculated $C_{19}H_{22}$ (M-H): 249.1638, found: 249.1615.

1-Methyl-4-(4-phenylbutan-2-yl)benzene (Table 2, entry 11)



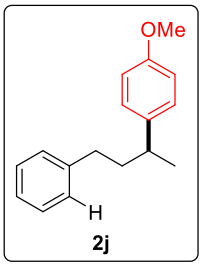
Following the general procedure, the title compound was isolated in 55% yield as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20-7.15 (m, 2H), 7.10-7.01 (m, 7H), 2.66-2.56 (m, 1H), 2.43 (t, *J* = 8.1 Hz, 2H), 2.26 (s, 3H), 1.89-1.74 (m, 2H), 1.18 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.4, 142.8, 135.5, 129.2, 128.5, 128.4, 127.1, 125.7, 40.1, 39.2, 34.1, 22.8, 21.2;

HRMS (APCI): calculated $C_{17}H_{20}$ (M-H): 223.1481, found: 223.1490.

1-Methoxy-4-(4-phenylbutan-2-yl)benzene (Table 2, entry 12)[16]



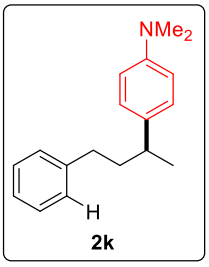
Following the general procedure, the title compound was isolated by GPC in 60% yield as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21-7.16 (m, 2H), 7.11-7.02 (m, 5H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 2.62-2.57 (m, 1H), 2.42 (t, *J* = 7.3 Hz, 2H), 1,83-1.76 (m, 2H), 1.16 (d, *J* = 6.9 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.9, 142.8, 139.5, 128.5, 128.4, 128.0, 125.7, 113.9, 55.4, 40.3, 38.8, 34.1, 22.9.

GC-MS (EI) *m/z* (relative intensity): 240 (M^+, 40), 214 (50), 199 (45), 171 (25), 135 (100), 91 (30).

***N,N*-Dimethyl-4-(4-phenylbutan-2-yl)aniline (Table 2, entry 13)**



Following the general procedure, the title compound was isolated in 31% yield as a light brown oil.

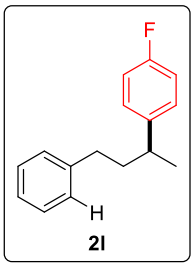
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28-7.23 (m, 2H), 7.18-7.08 (m, 5H), 6.76 (d, *J* = 8.0 Hz, 2H), 2.94 (s, 6H), 2.67-2.61 (m, 1H), 2.51 (t, *J* = 8.0 Hz, 2H), 1.91-1.83 (m, 2H), 1.24 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.0 (two signals overlapping), 128.5, 128.3 (two

signals overlapping), 127.8, 125.7, 113.3, 41.3, 40.4, 38.7, 34.1, 22.9;

MS (APCI): calculated $C_{18}H_{23}N$ (M+H): 254.1903, found: 254.1888.

1-Fluoro-4-(4-phenylbutan-2-yl)benzene (Table 2, entry 14)



Following the general procedure, the title compound was isolated in 38% yield as a colorless oil.

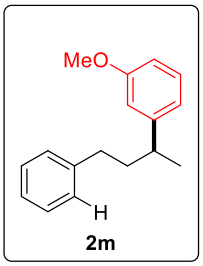
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28-7.25 (m, 2H), 7.20-7.09 (m, 5H), 6.99 (t, J = 8.7 Hz, 2H), 2.75-2.66 (m, 1H), 2.54-2.46 (m, 2H), 1.88 (dt, J = 6.8 Hz, 2H), 1.25 (d, J = 7.3 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.3 ($^1J_{C\text{-}F}$ = 243 Hz), 143.0, 142.5, 128.5, 128.5, 128.4, 125.8, 115.2 ($^2J_{C\text{-}F}$ =15.3 Hz), 40.2, 38.9, 34.0, 22.8;

^{19}F NMR ($CDCl_3$, 376 MHz) δ -120.0;

HRMS (APCI): calculated $C_{16}H_{17}$ (M-H): 227.1231, found: 227.1216.

1-Methoxy-3-(4-phenylbutan-2-yl)benzene (Table 2, entry 15)



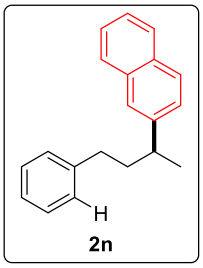
Following the general procedure, the title compound was isolated in 58% yield as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21-7.13 (m, 3H), 7.12-7.05 (m, 3H), 6.73 (d, J = 7.6 Hz, 1H), 6.69-6.66 (m, 2H), 3.74 (s, 3H), 2.67-2.57 (m, 1H), 2.44 (t, J = 6.8 Hz, 2H), 1.91-1.75(m, 2H), 1.19 (d, J = 7.3 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.8, 149.2, 142.7, 129.5, 128.5, 128.4, 125.8, 119.7, 113.2, 111.0, 55.3, 40.0, 39.7, 34.0, 22.6;

HRMS (APCI): calculated $C_{17}H_{20}$ (M-H): 239.1430, found: 239.1412.

2-(4-Phenylbutan-2-yl)naphthalene (Table 2, entry 16)



Following the general procedure, the title compound was isolated in 55% yield as a colorless oil.

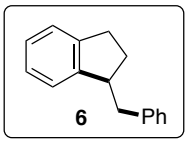
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83-7.79 (m, 3H), 7.63 (s, 1H), 7.49-7.40 (m, 2H), 7.37 (dd, J = 8,0 Hz, 1H), 7.28-7.24 (m, 2H), 7.19-7.12 (m, 3H), 2.93-2.87 (m, 1H), 2.57-2.50 (m, 2H), 2.06-1.96

(m, 2H), 1.36 (d, J = 7.6 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.8, 142.6, 133.8, 132.3, 128.5, 128.4, 128.2, 127.7, 127.6, 126.0, 125.9, 125.8, 125.5, 125.3, 40.0, 39.8, 34.1, 22.7;

HRMS (APCI): calculated $C_{20}H_{20}$ (M-H): 259.1481, found: 259.1498.

1-Benzyl-2,3-dihydro-1*H*-indene (eq. 1)[17]



Following the general procedure, the title compound was isolated in 64% yield as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26-7.21 (m, 2 H), 7.19-7.20 (m, 4H), 7.11-7.03 (m, 3H), 3.43-3.32 (m, 1H), 3.11-3.05 (m, 1H), 2.87-2.66 (m, 2H), 2.66-2.57 (m, 1H), 2.10-2.02 (m, 1H), 1.74-1.66 (m, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.0, 144.3, 141.0, 129.2, 128.4, 126.6, 126.1, 126.0, 124.7, 123.9, 46.6, 41.5, 32.1, 31.3.

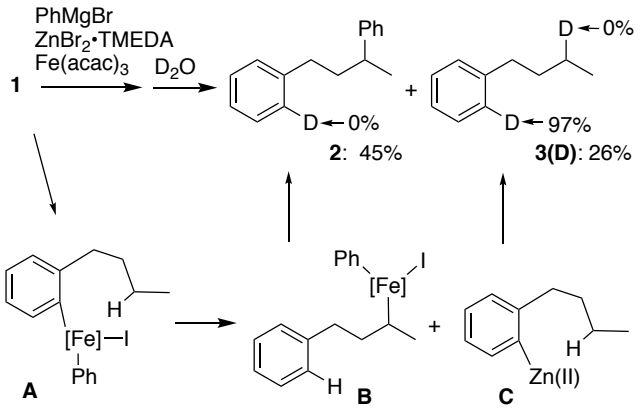
GC-MS (EI) *m/z* (relative intensity): 208 (M^+, 2), 117 (100), 91 (35).

3.3. Reaction on 2 mmol scale (Table 2, entry 2)

The reaction was performed according to the general procedure: to a flame-dired Schlenk tube was added $ZnBr_2 \cdot$TMEDA (4 mmol, 1.35 g) and THF (10 ml). PhMgBr (8 mmol, 1.09 M in THF) was then added under nitrogen and stirred for 1 h. THF was removed thoroughly by gentle heating under vacumn and fluorobenzene (20 ml) was added resulting in a milky solution, which became clear upon heating.

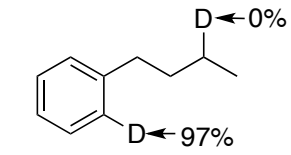
To a 100 ml flame-dired Schlenk tube equipped with a magnetic stir bar was added $Fe(acac)_3$ (10 mol%, 71 mg), **4** (20 mol%, 171 mg), fluorobenzene (20 ml) and 1-butyl-2-iodobenzene (2 mmol, 520 mg) under nitrogen. The reaction mixture was warmed to 50 °C and a warm solution of Ph_2Zn was added dropwise over 20 min by gas-tight syringe under nitrogen. The resulting mixture was vigorously stirred for further 12 h. After completion, the reaction was quenched with saturated aqueous NH_4Cl (10 ml), and the organic layer was passed over a short pad of silca gel. The solution was pre-absorbed on silica gel and concetrated by rotary evaporation. The crude product was purified by silica gel column chromatography (hexane) to afford the product **2** in 47% yield.

3.4. Deuterium-labeling experiment (Scheme 2)



The reaction was performed according to the general procedure: to a flame-dired Schlenk tube was added $ZnBr_2 \cdot TMEDA$ (2 mmol, 676 mg) and THF (5 ml). PhMgBr (8 mmol, 1.09 M in THF) was then added under nitrogen and stirred for 0.5 h. THF was removed thoroughly by gentle heating under vacumn and fluorobenzene (10 ml) was added resulting in a milky solution, which became clear upon heating.

To a flame-dired Schlenk tube equipped with a magnetic stir bar was added $Fe(acac)_3$ (10 mol%, 35 mg), **4** (20 mol%, 86 mg), fluorobenzene (10 ml) and 1-butyl-2-iodobenzene (1 mmol, 260 mg) under nitrogen. The reaction mixture was warmed to 50 °C and a solution of Ph_2Zn was added dropwise over 10 min by gas-tight syringe under nitrogen. The resulting mixture was stirred for further 10 h. After completion, the reaction was quenched with D_2O (1 ml). The products **2** and **3(D)** were isolated in 45% and 26% yield respectively. Note that **3(D)** is volatile and difficult to quantitatively recover.


D
0%
D
97%

4a

2.093
2.080
2.000
2.367
2.073
3.222
PPM
10
8
6
4
2
0
7.18795
7.17192
7.15588
7.15244
7.09746
7.09173
7.08142
7.06310
5.23604
5.23375
5.23146
2.53153
2.51206
2.49259
2.53381
1.51892
1.51548
1.51090
1.50059
1.49601
1.48914
1.47997
1.47654
1.47310
1.45821
1.30700
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1.27035
1.25202
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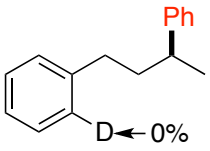
0.88432
0.87401
0.86714
0.85339
0.83506
0.81673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D
0%

3a

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2.000
2.033
3.083
PPM
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8
6
4
2
0
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7.23607
7.23263
7.23046
7.22117
7.20743
7.20285
7.19826
7.18452
7.17994
7.17077
7.16619
7.16130
7.14788
7.13984
7.13412
7.12610
7.12268
7.11923
7.11350
7.11006
7.10548
7.09973
7.09859
7.08715
7.08371
7.08028
7.06539
7.06080
7.05050
7.04019
5.23718
5.23375
5.23146
2.66327
2.64494
2.62776
2.60943
2.46624
2.46051
2.44219
2.43188
2.42615
2.40782
2.39980
2.38491
1.86486
1.85684
1.84768
1.84195
1.83508
1.83164
1.82706
1.82477
1.81789
1.81102
1.80758
1.80529
1.79957
1.79498
1.78811
1.77666
1.19131
1.17413

4. References

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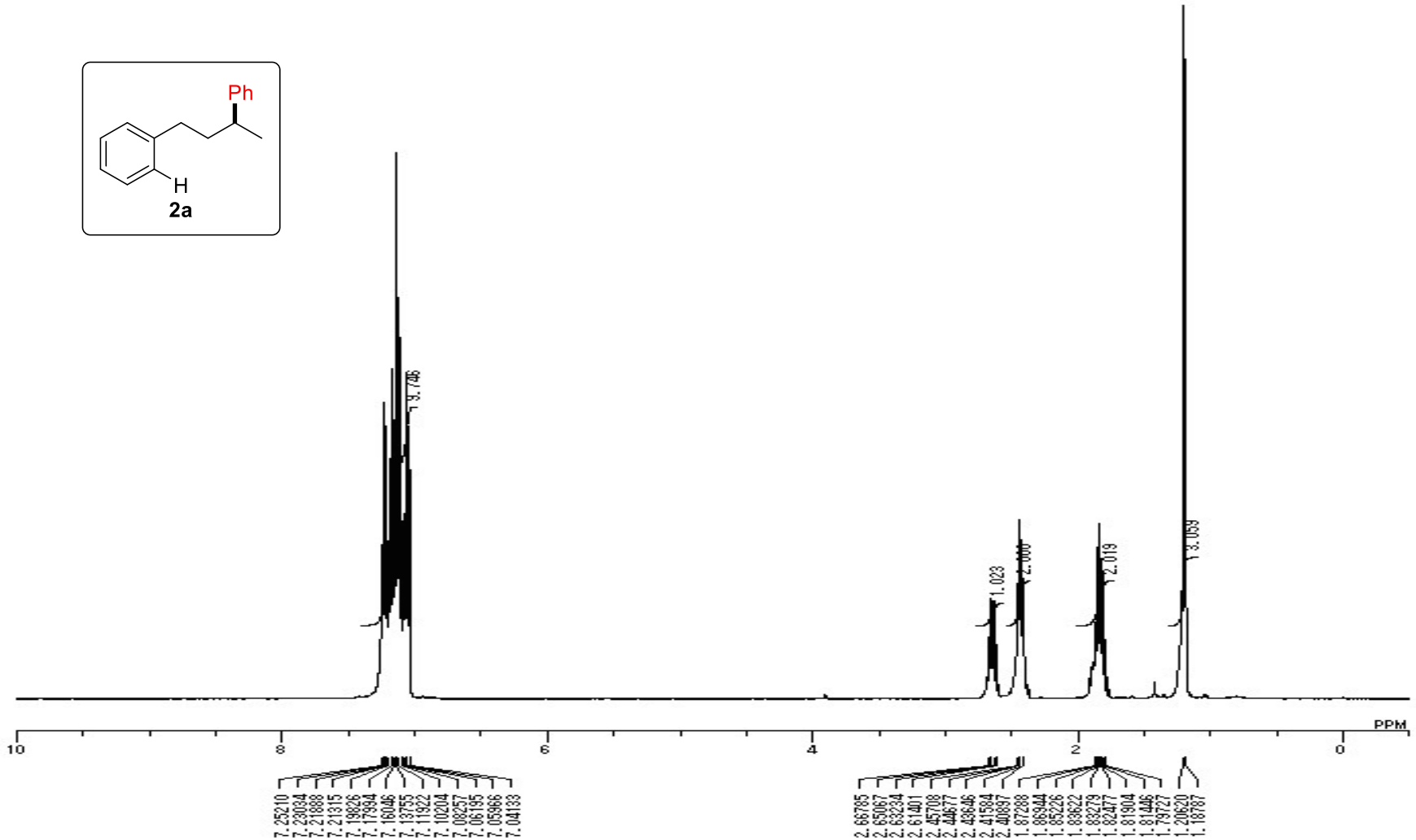
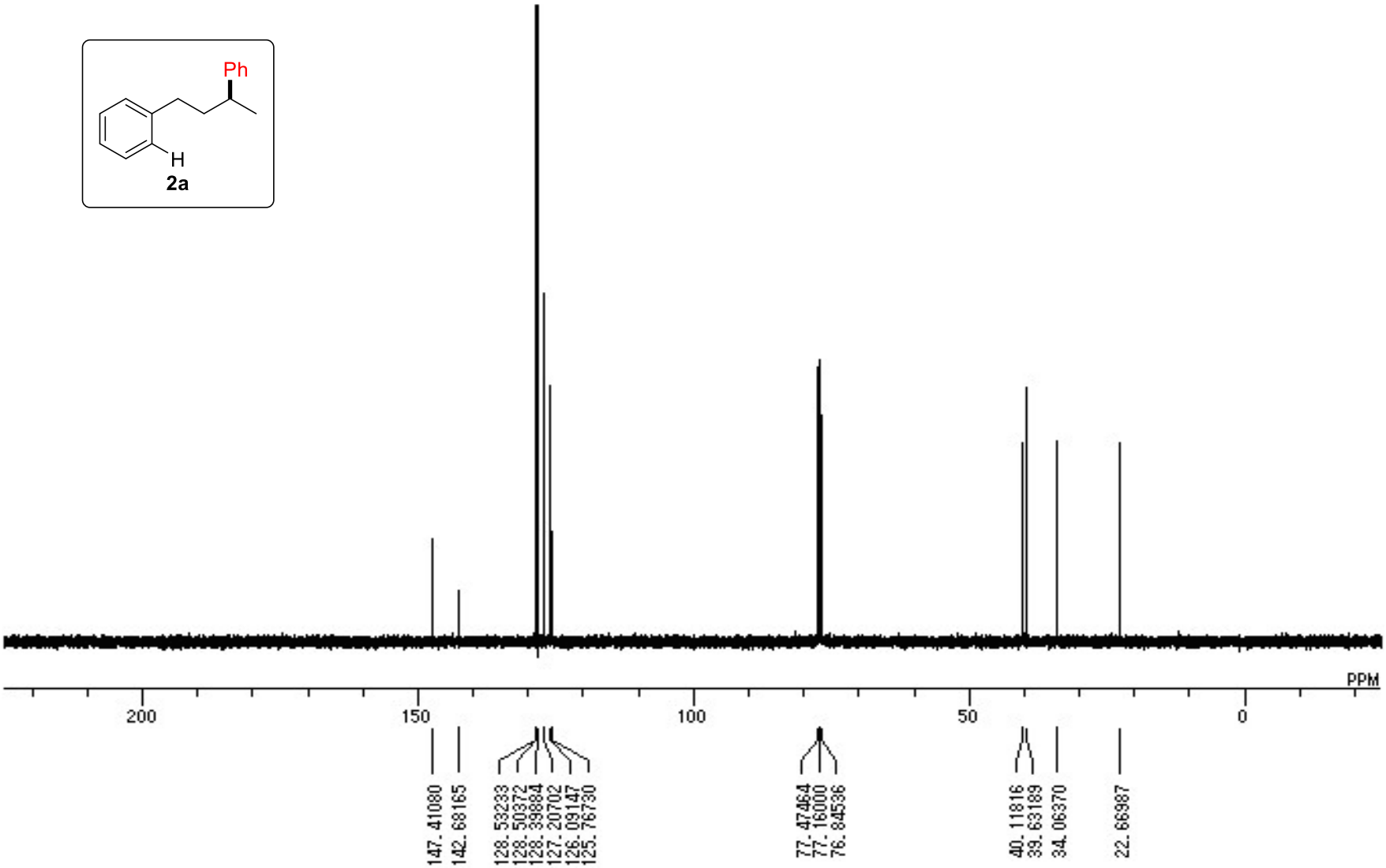
5. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

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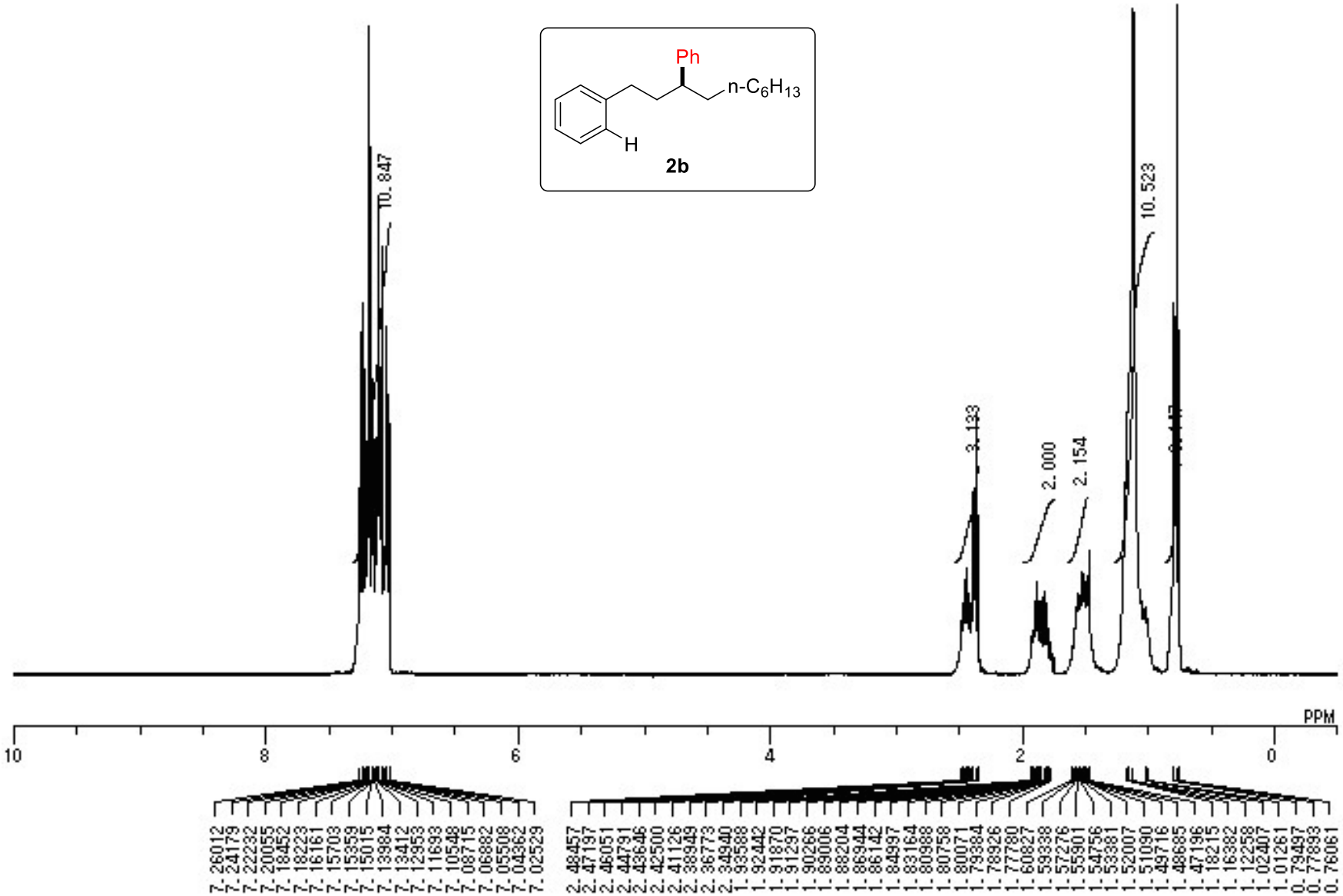
77.16000
76.84536
40.11816
39.63189
34.06370
22.66987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H
2b
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3.133
2.000
2.154
10.523
PPM
10
8
6
4
2
0
7.26012
7.24179
7.22232
7.20055
7.18452
7.18223
7.16161
7.15703
7.15359
7.15015
7.13984
7.13412
7.12953
7.11693
7.10548
7.08715
7.06882
7.05508
7.04362
7.02529
2.48457
2.47197
2.46051
2.44791
2.43646
2.42500
2.41126
2.38949
2.36773
2.34940
1.93588
1.92442
1.91870
1.91297
1.90266
1.89006
1.88204
1.86944
1.86142
1.84997
1.83164
1.80988
1.80758
1.80071
1.79384
1.78926
1.77780
1.60827
1.59338
1.57276
1.55901
1.54756
1.53381
1.52007
1.51090
1.49716
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1.01261
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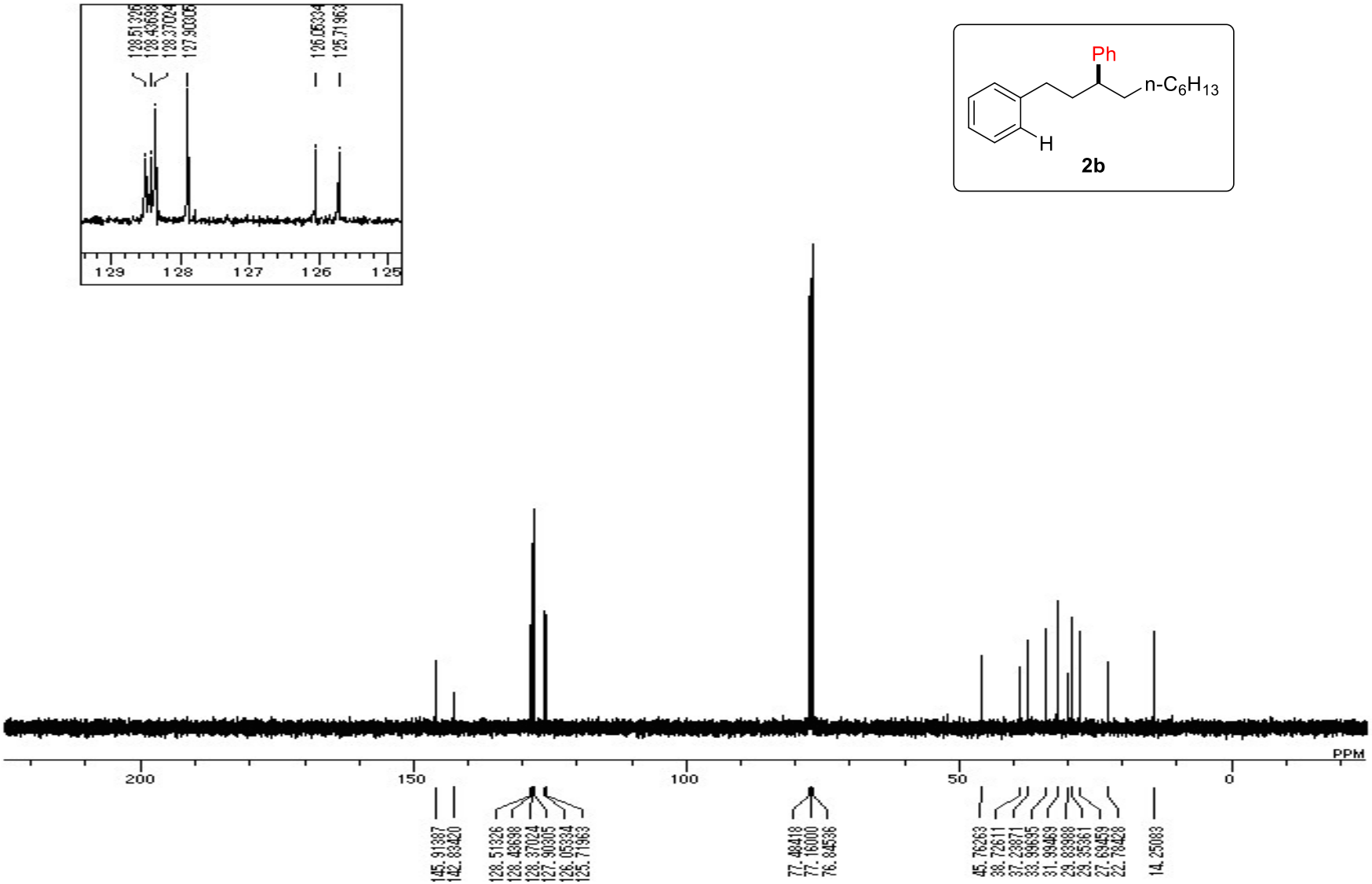
0.76061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H
2b
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100
50
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128.37024
127.90305
126.05334
125.71963
77.48418
77.16000
76.84536
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38.72611
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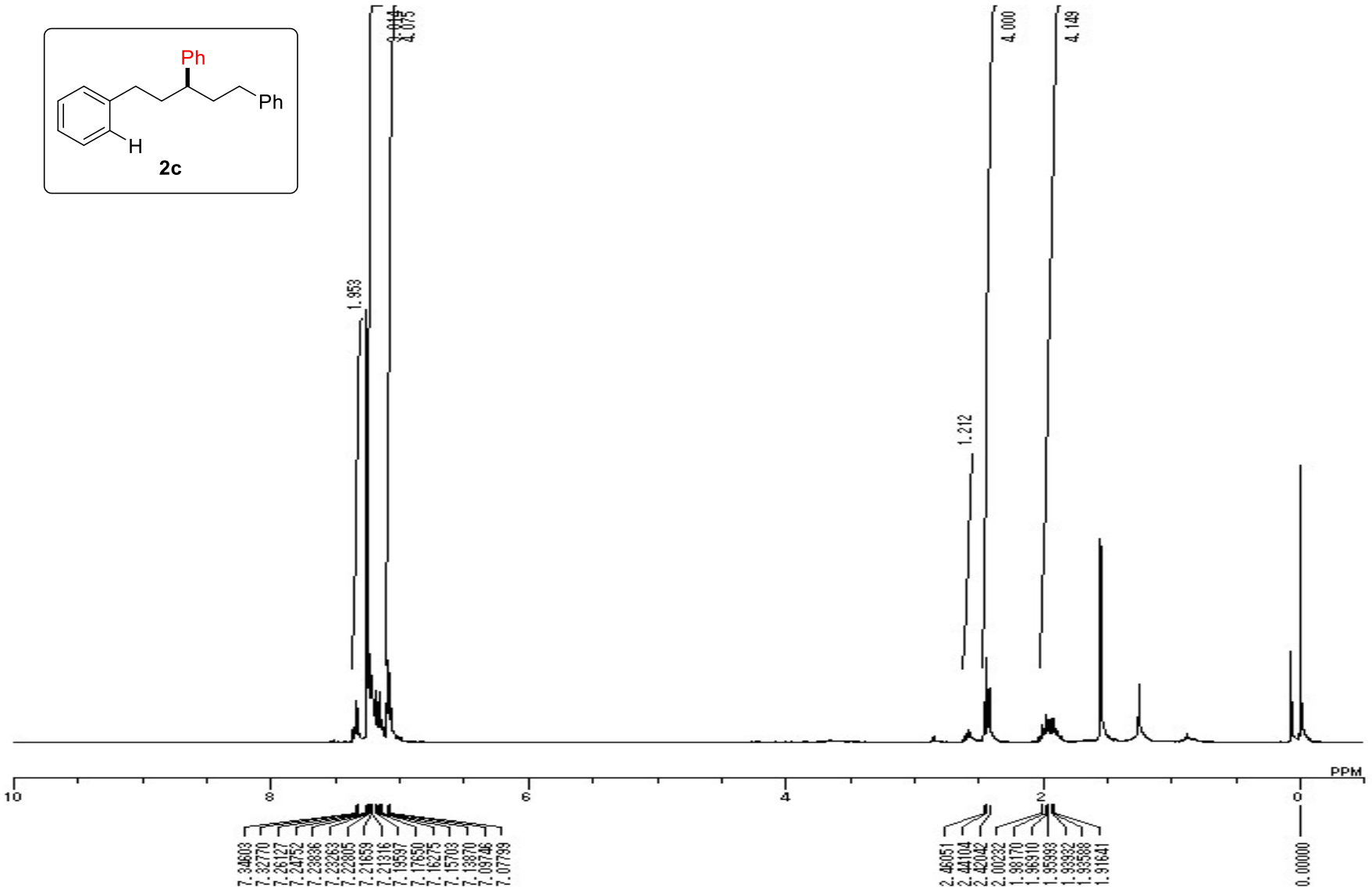
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4.149
1.212
PPM
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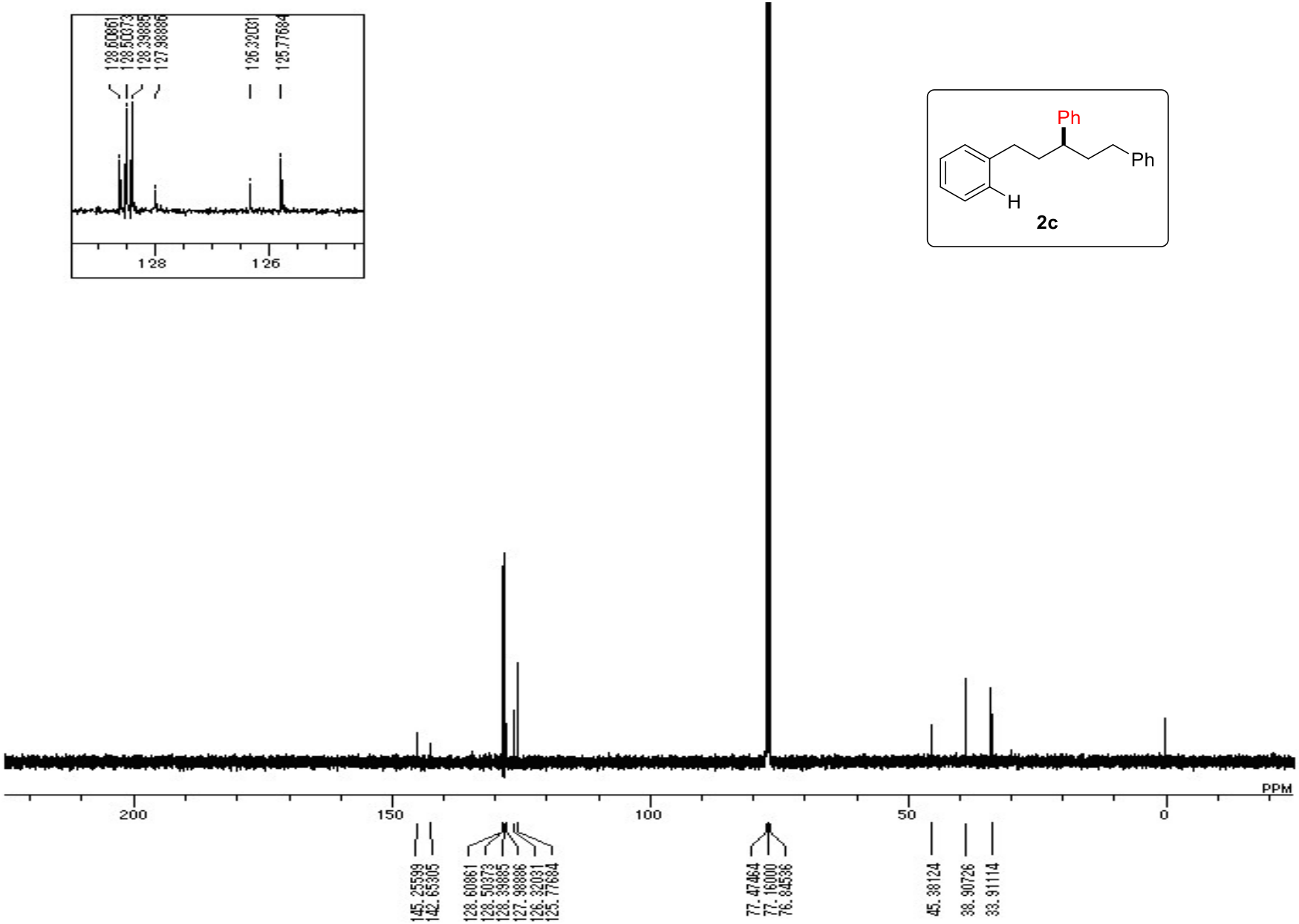
8
6
4
2
0
0.00000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128.50373
128.39885
127.98886
126.32031
125.77684
128
126
Ph
Ph
H
2c
PPM
200
150
100
50
0
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77.16000
76.84536
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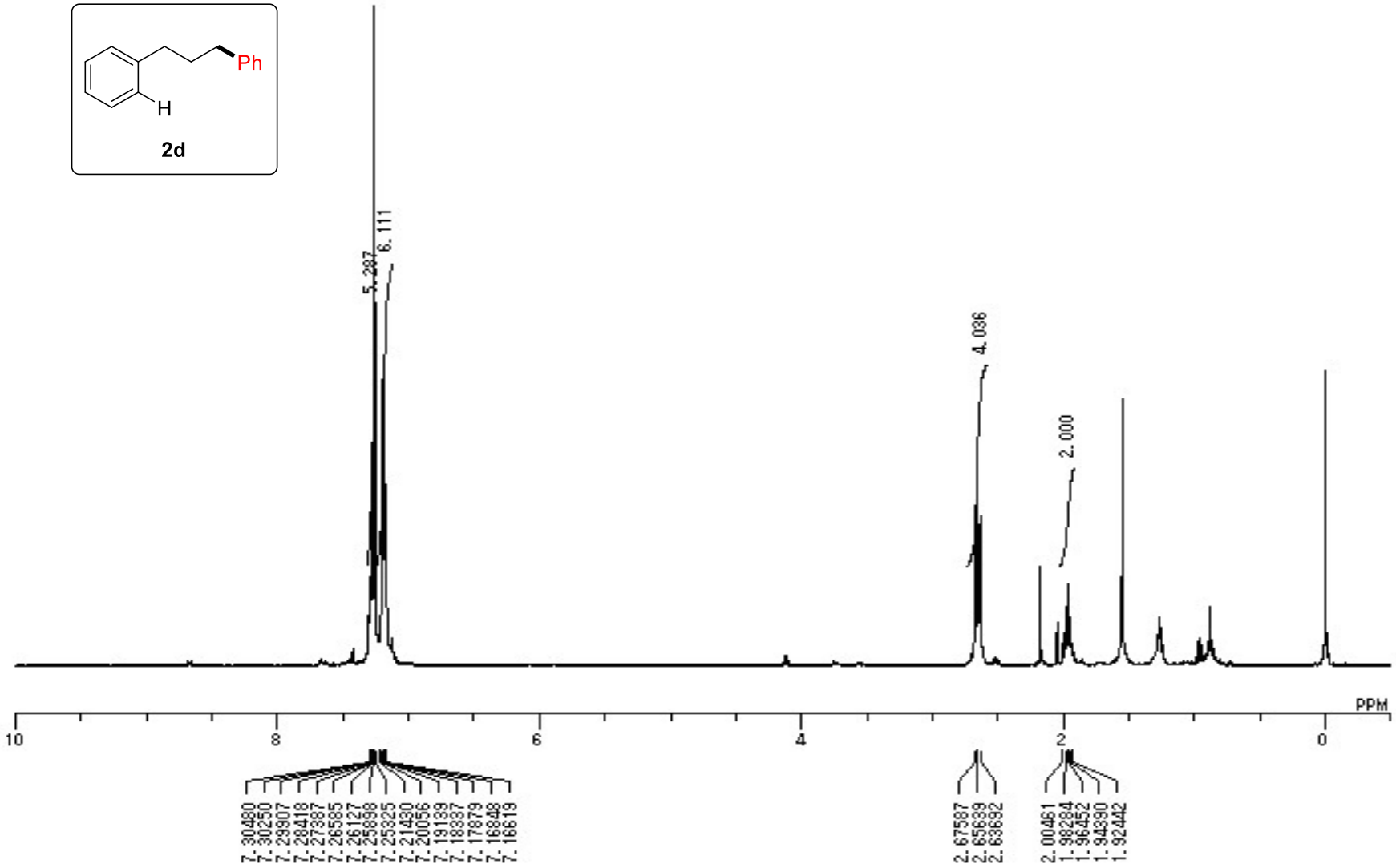
38.90726
33.91114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PPM
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6
4
2
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7.25325
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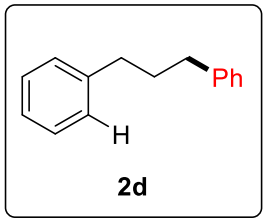
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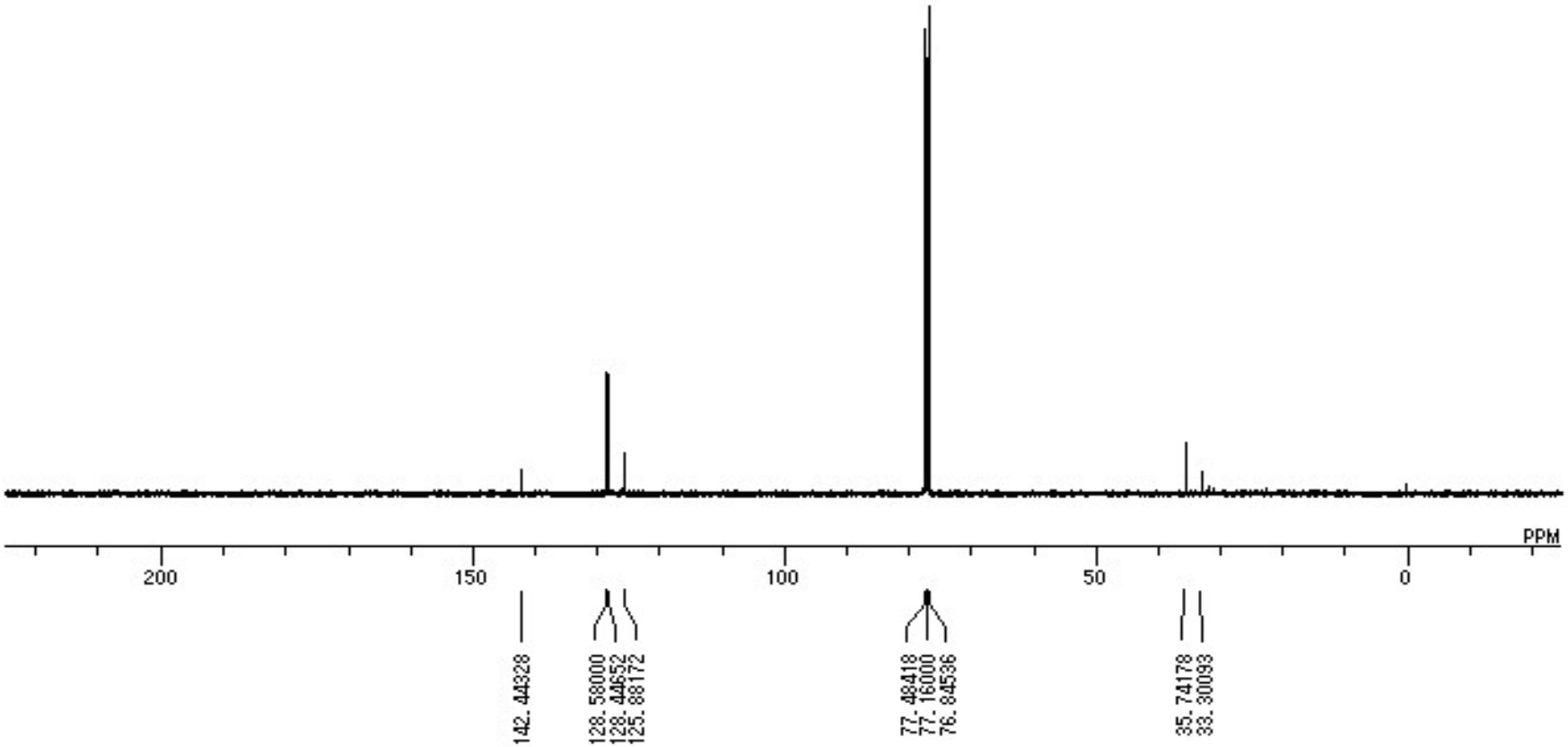
H

2d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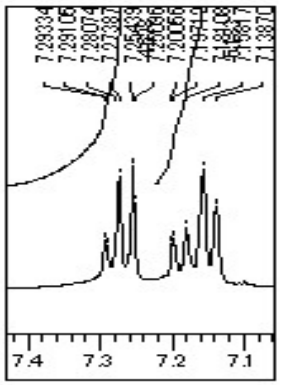
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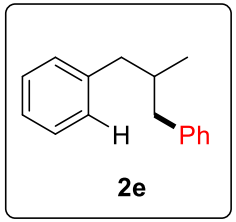
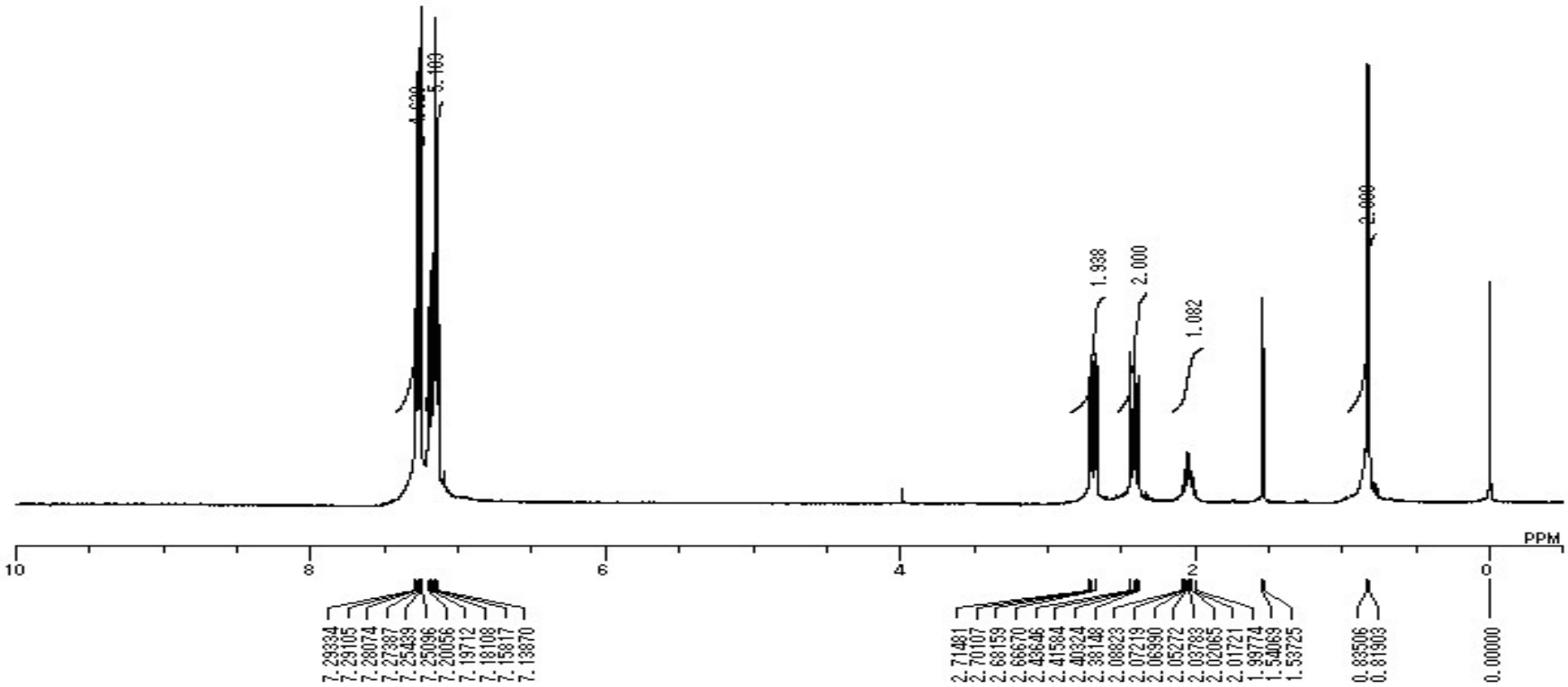
7.13870
7.4
7.3
7.2
7.1


H
Ph

2e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2.000
1.082
2.000
PPM
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8
6
4
2
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7.28074
7.27387
7.25439
7.25096
7.20056
7.19712
7.18108
7.15817
7.13870
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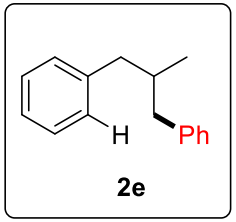
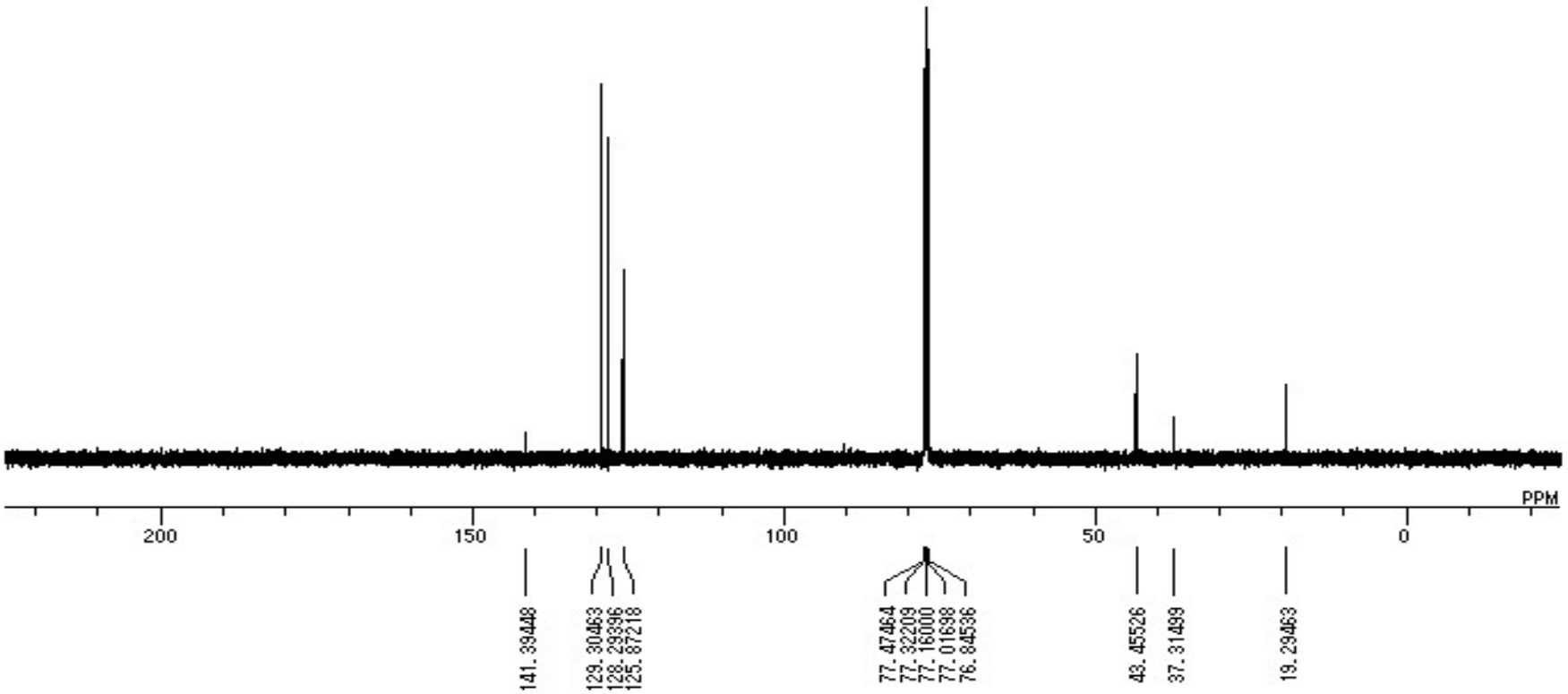

H
Ph

2e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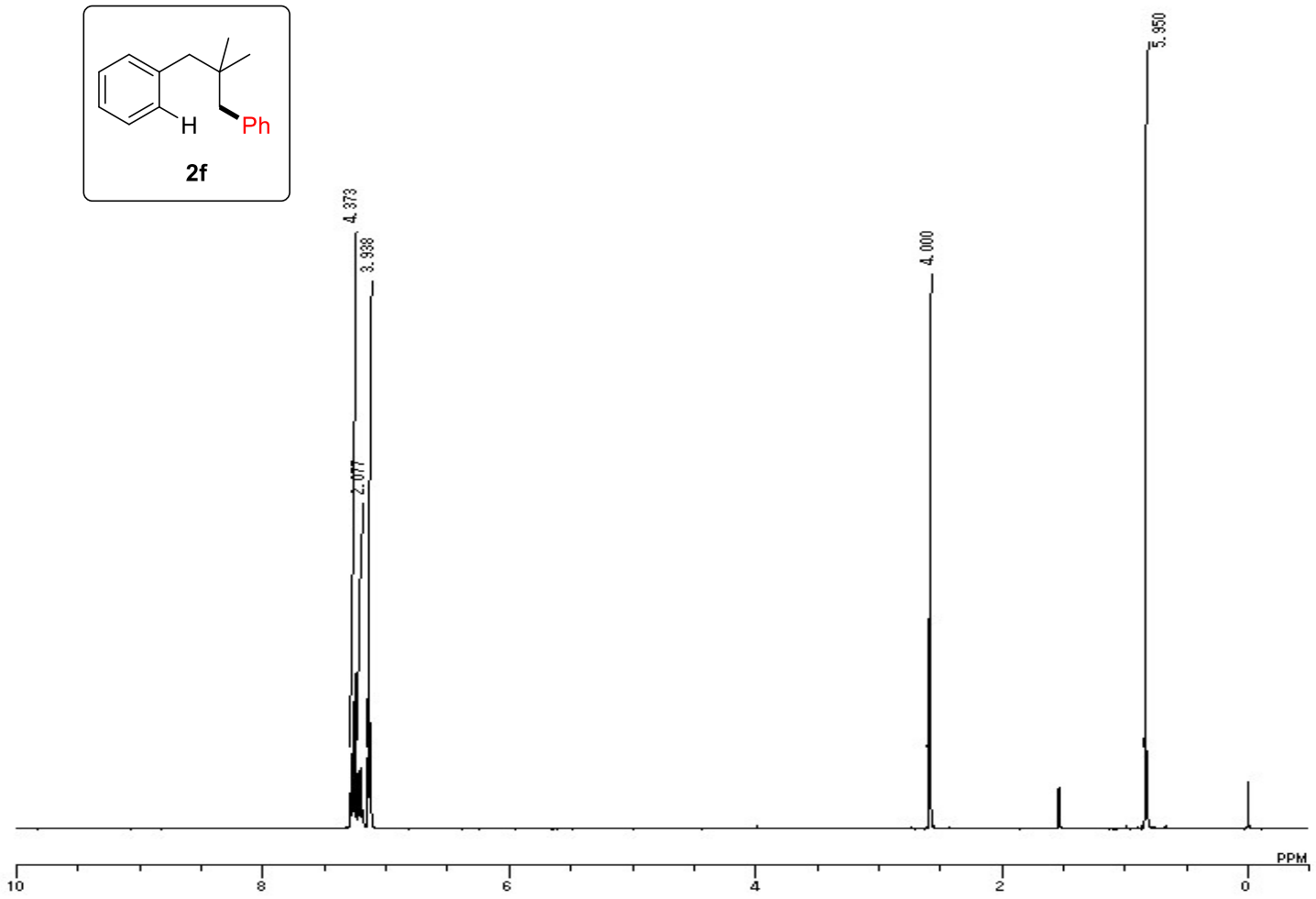
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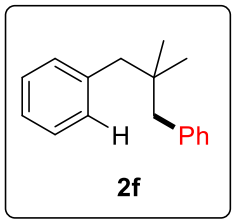
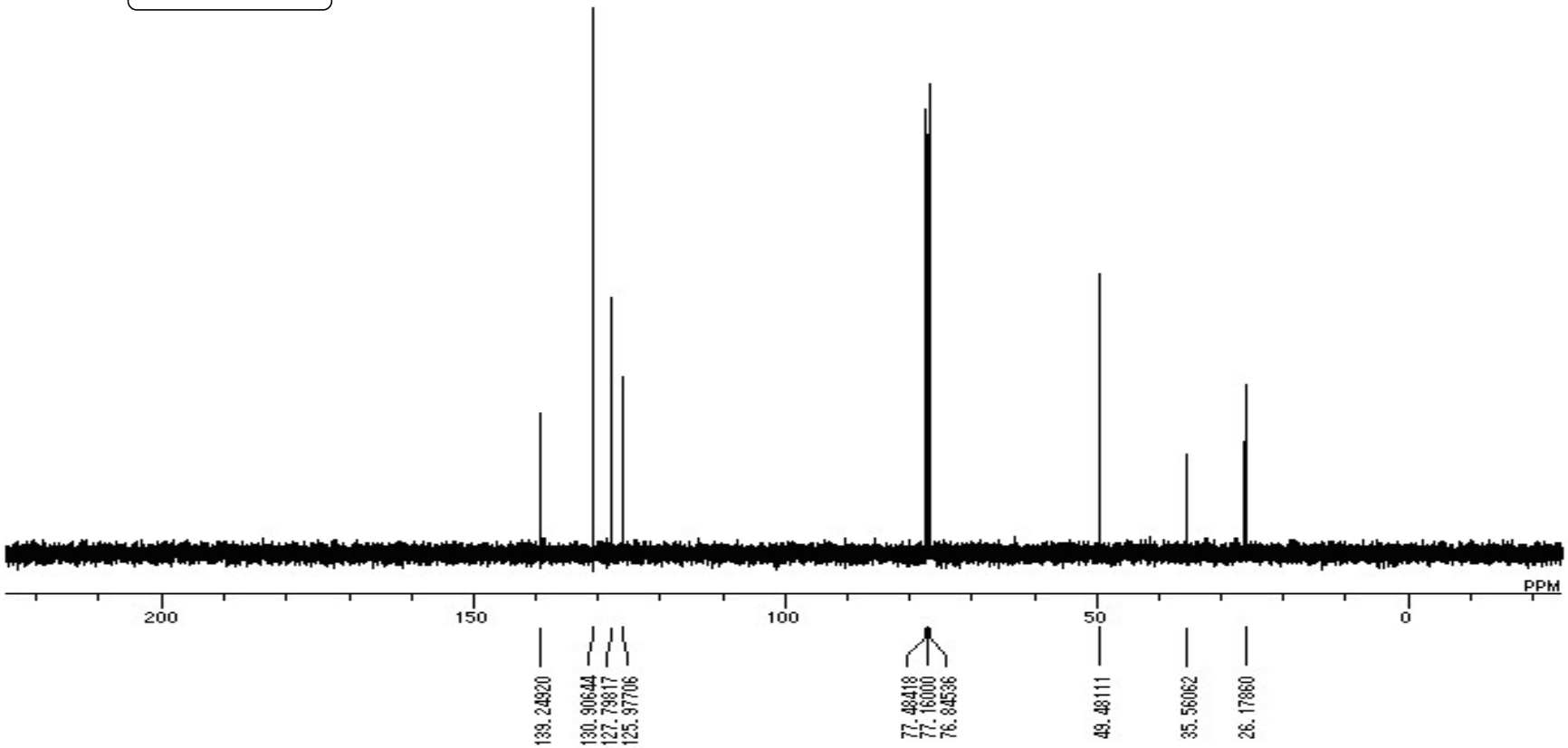
6
4
2
0
PPM


H
Ph

2f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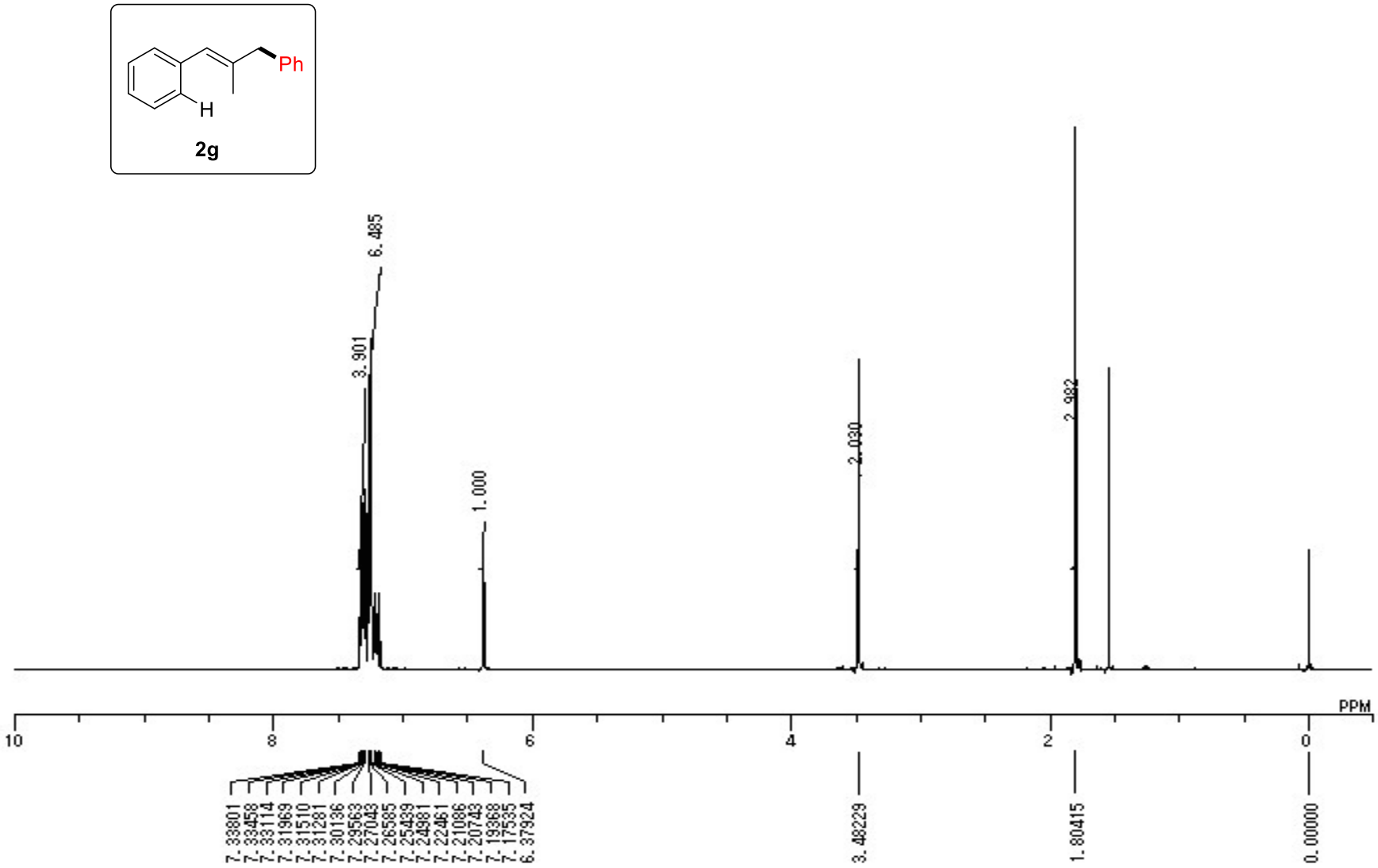
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6
4
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7.31281
7.30136
7.29563
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7.26585
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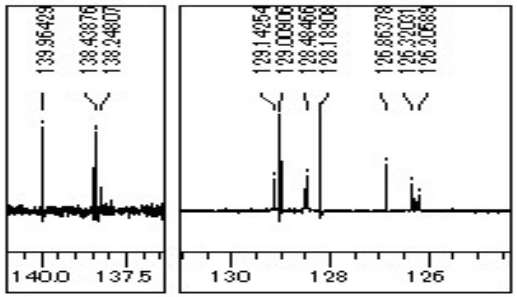
0.00000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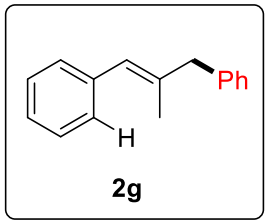
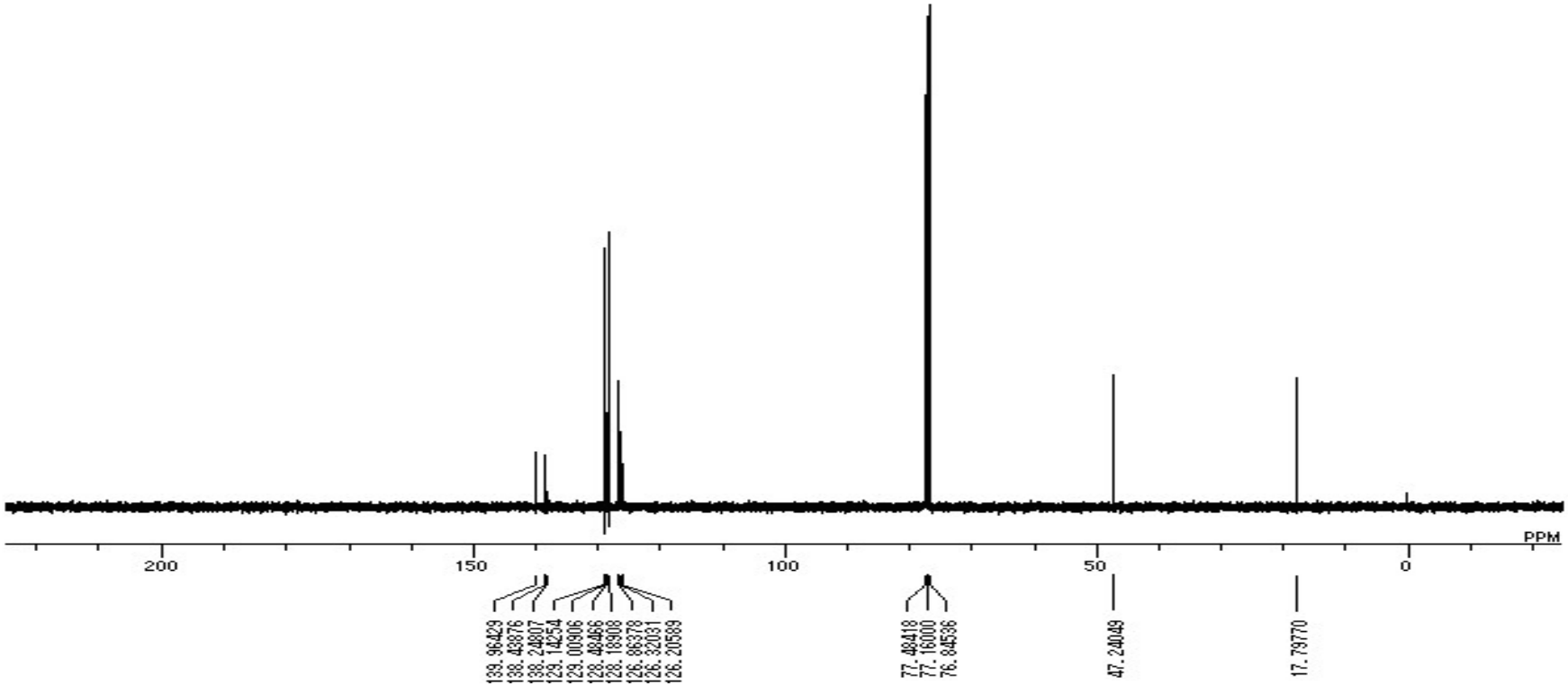
128
126


Ph
H
2g


PPM
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150
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50
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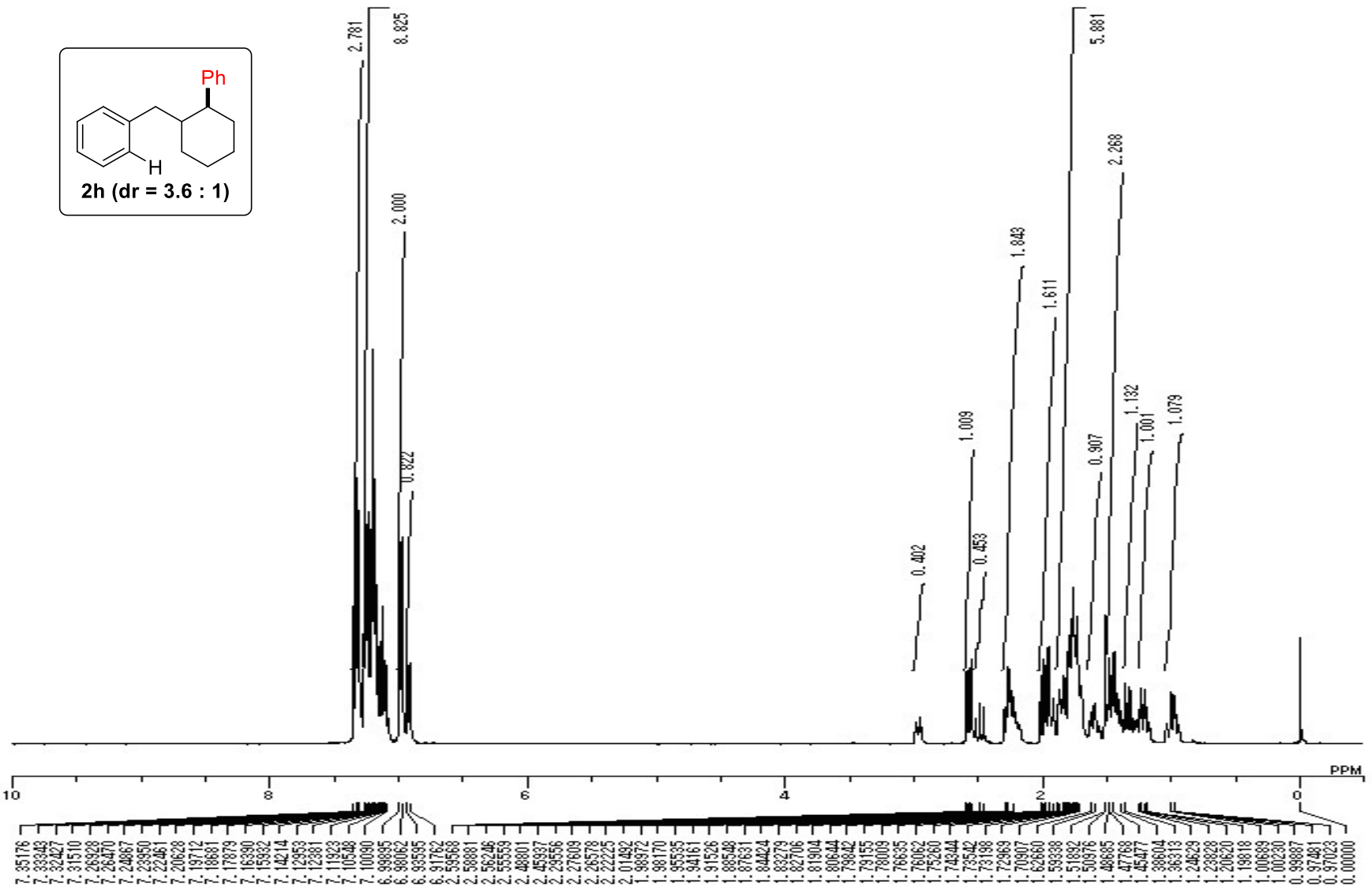
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8.825
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0.402
1.009
0.453
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1.611
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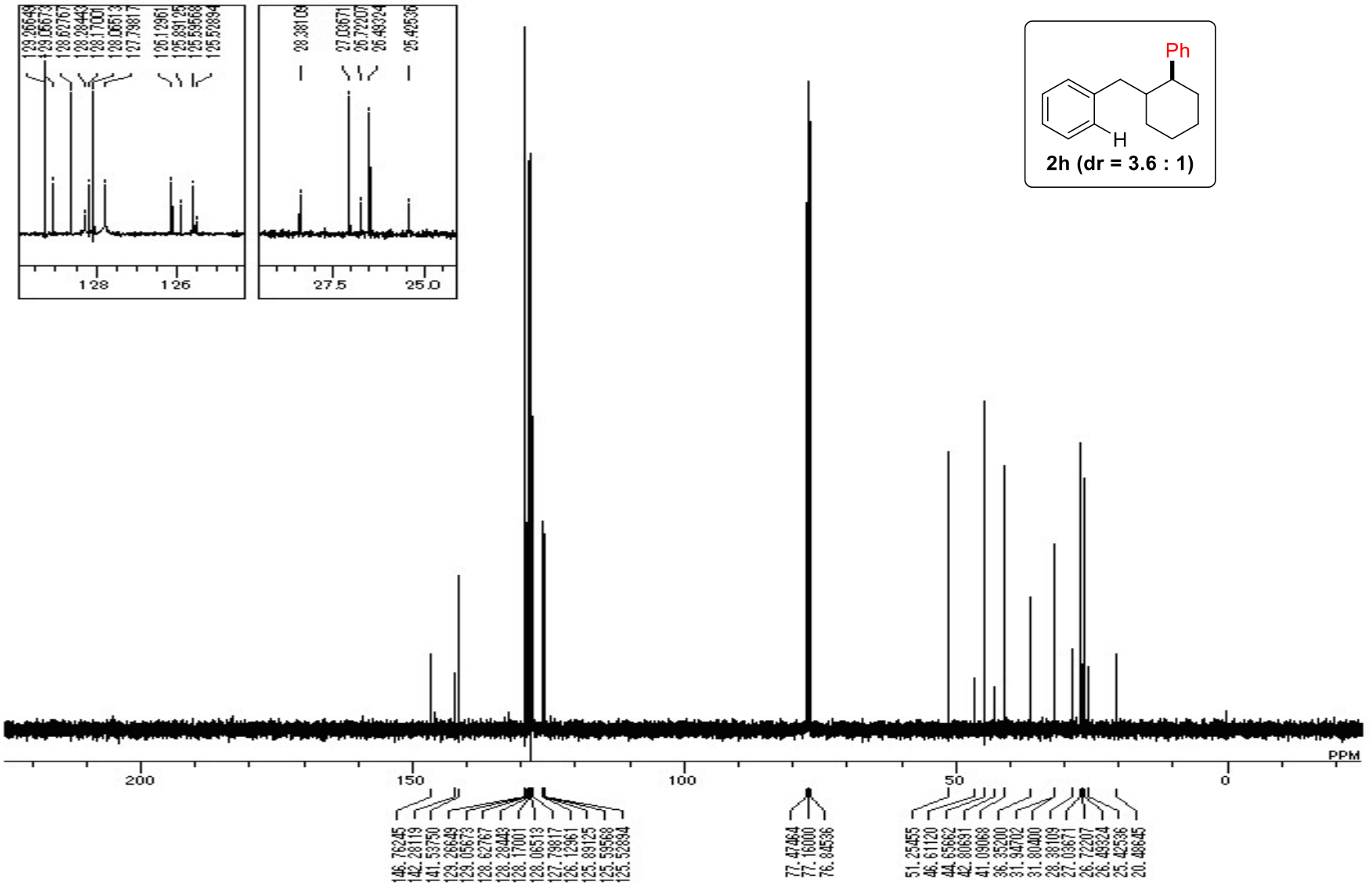
2.268
0.907
1.132
1.001
1.079
PPM
10
8
6
4
2
0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100
50
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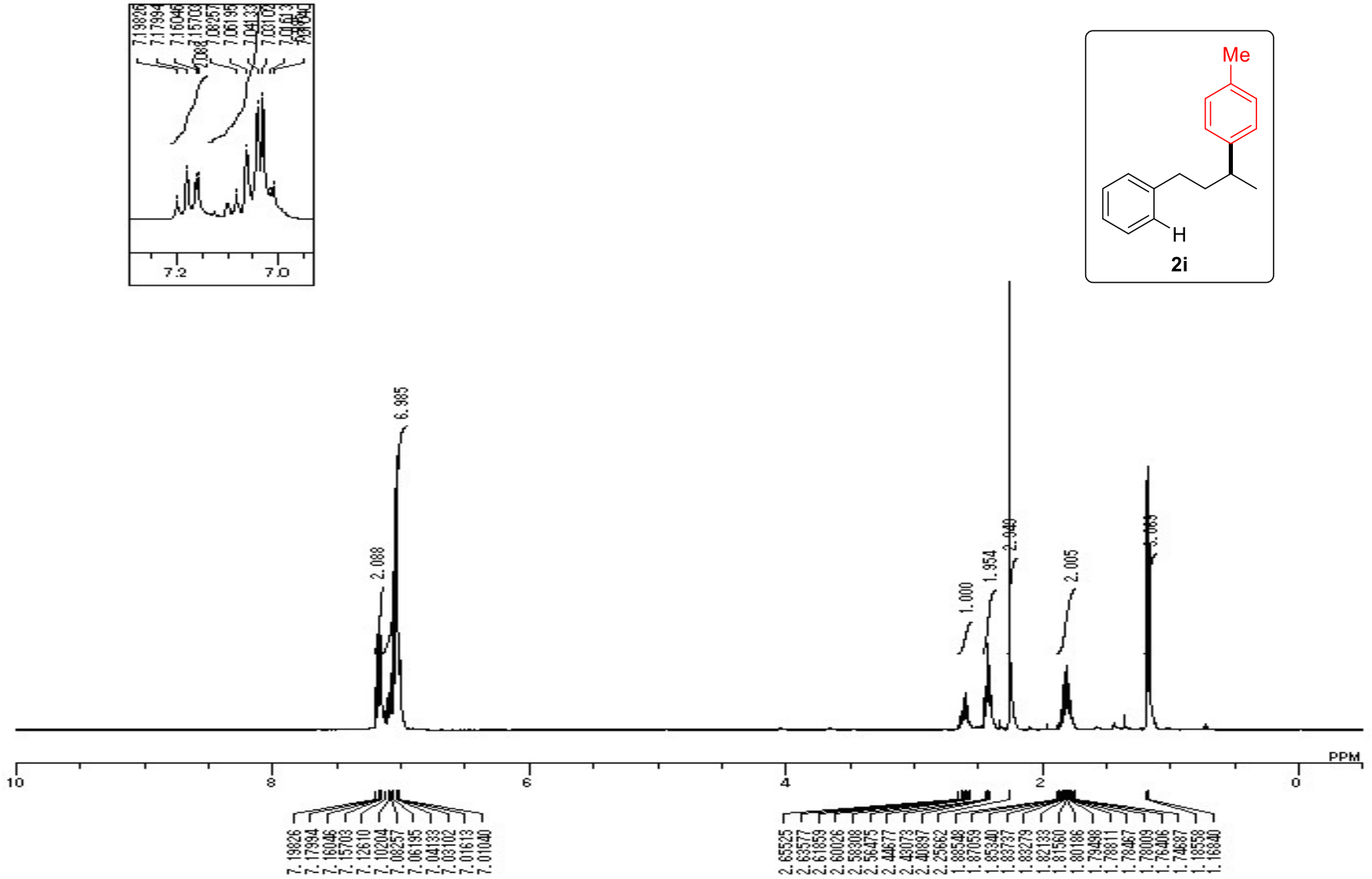
128
126
27.5
25.0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2i
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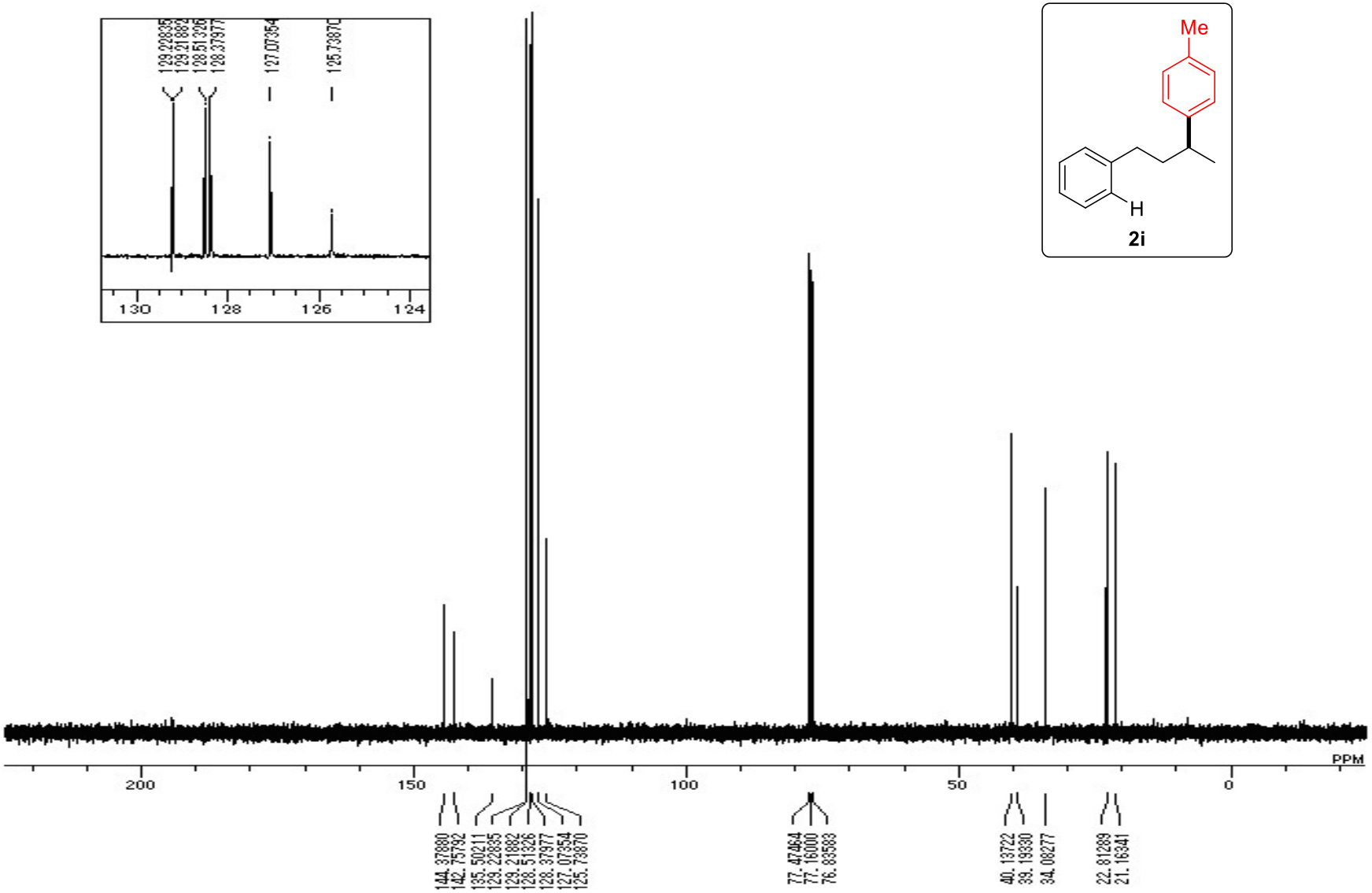
2.940
2.005
PPM
10
8
6
4
2
0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127.07354
125.73870
130
128
126
124
200
150
100
50
0
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135.50211
129.22835
129.21682
128.51326
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127.07354
125.73870
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76.83583
40.13722
39.19330
34.08277
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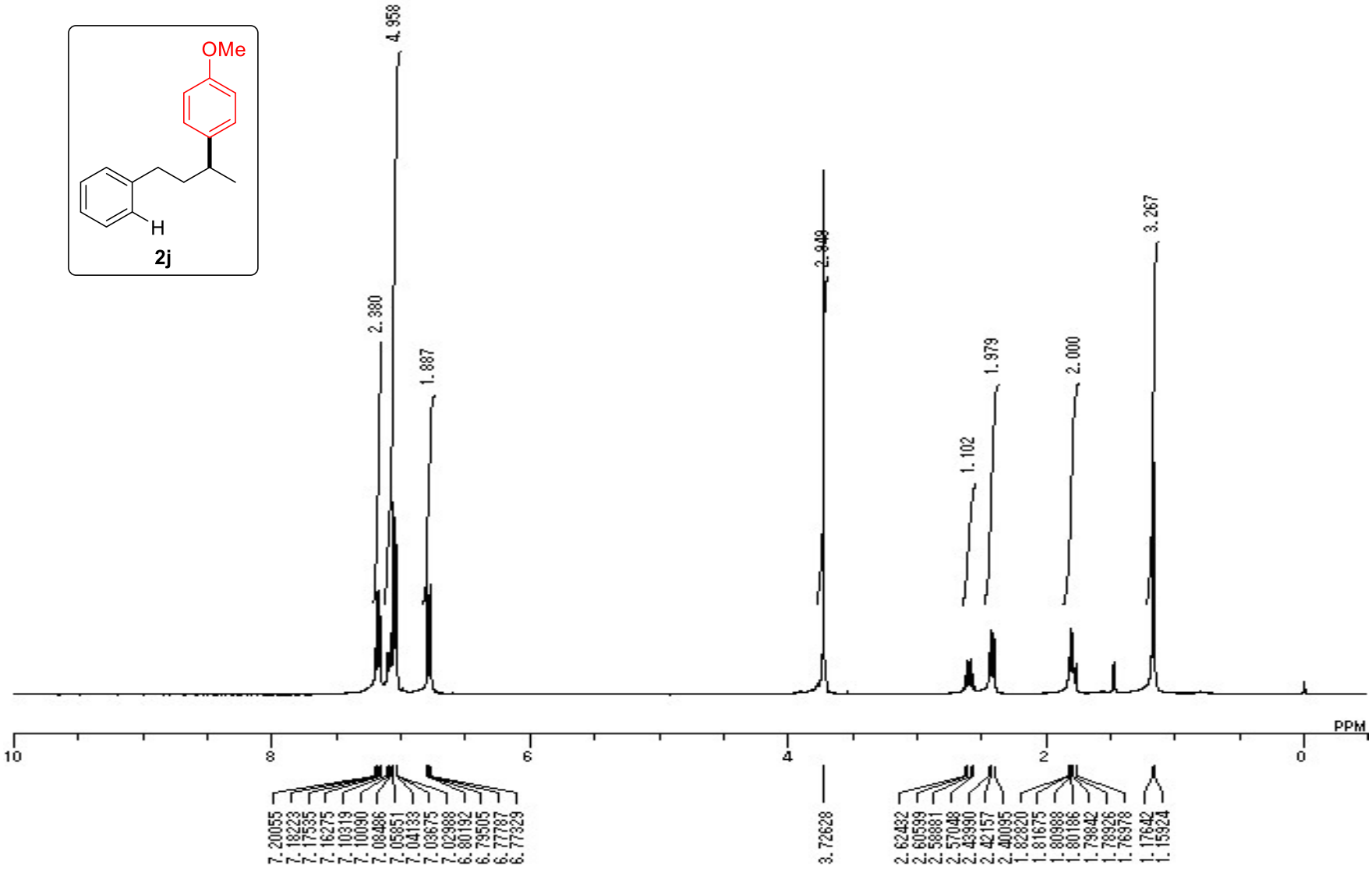
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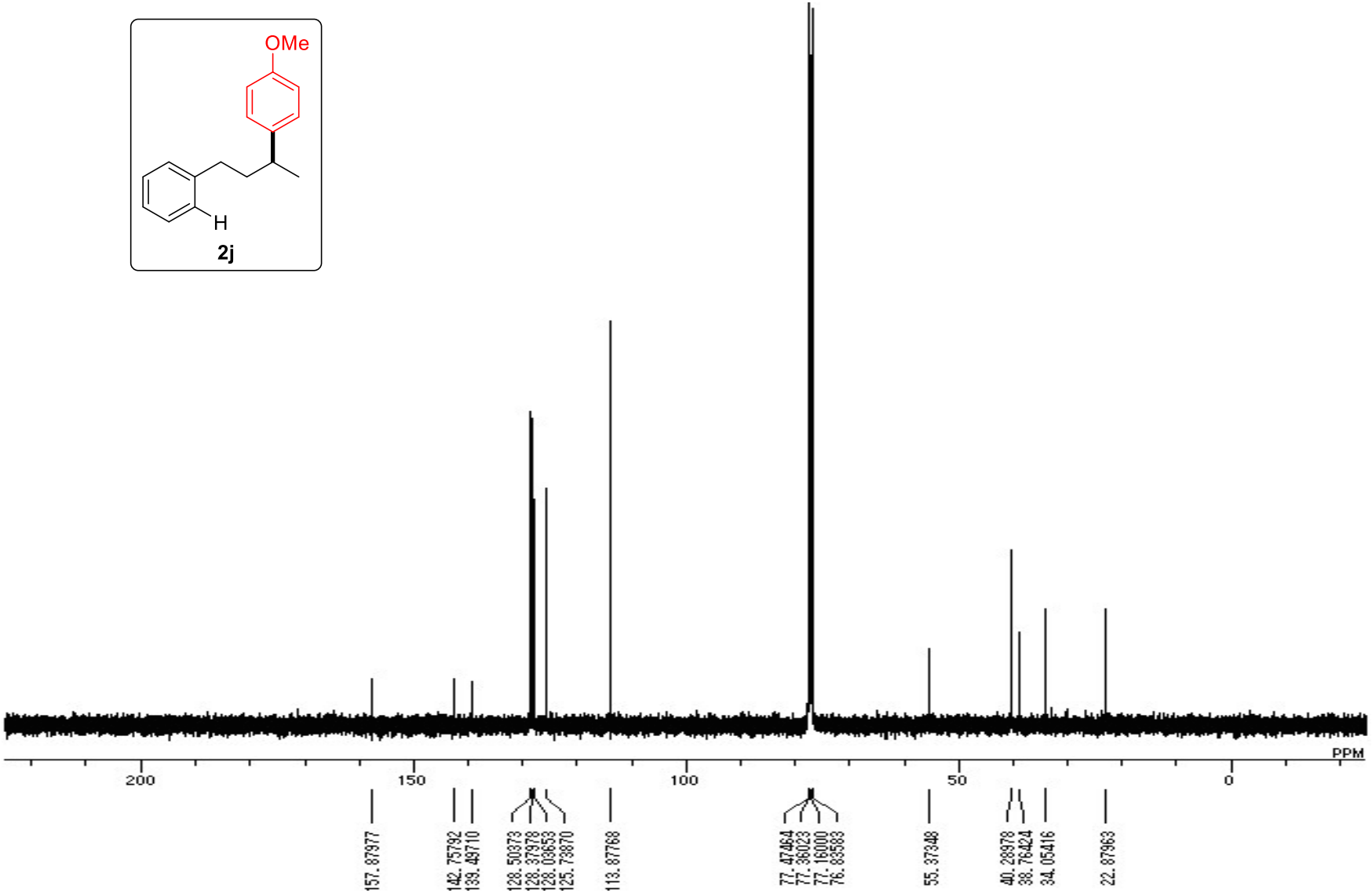
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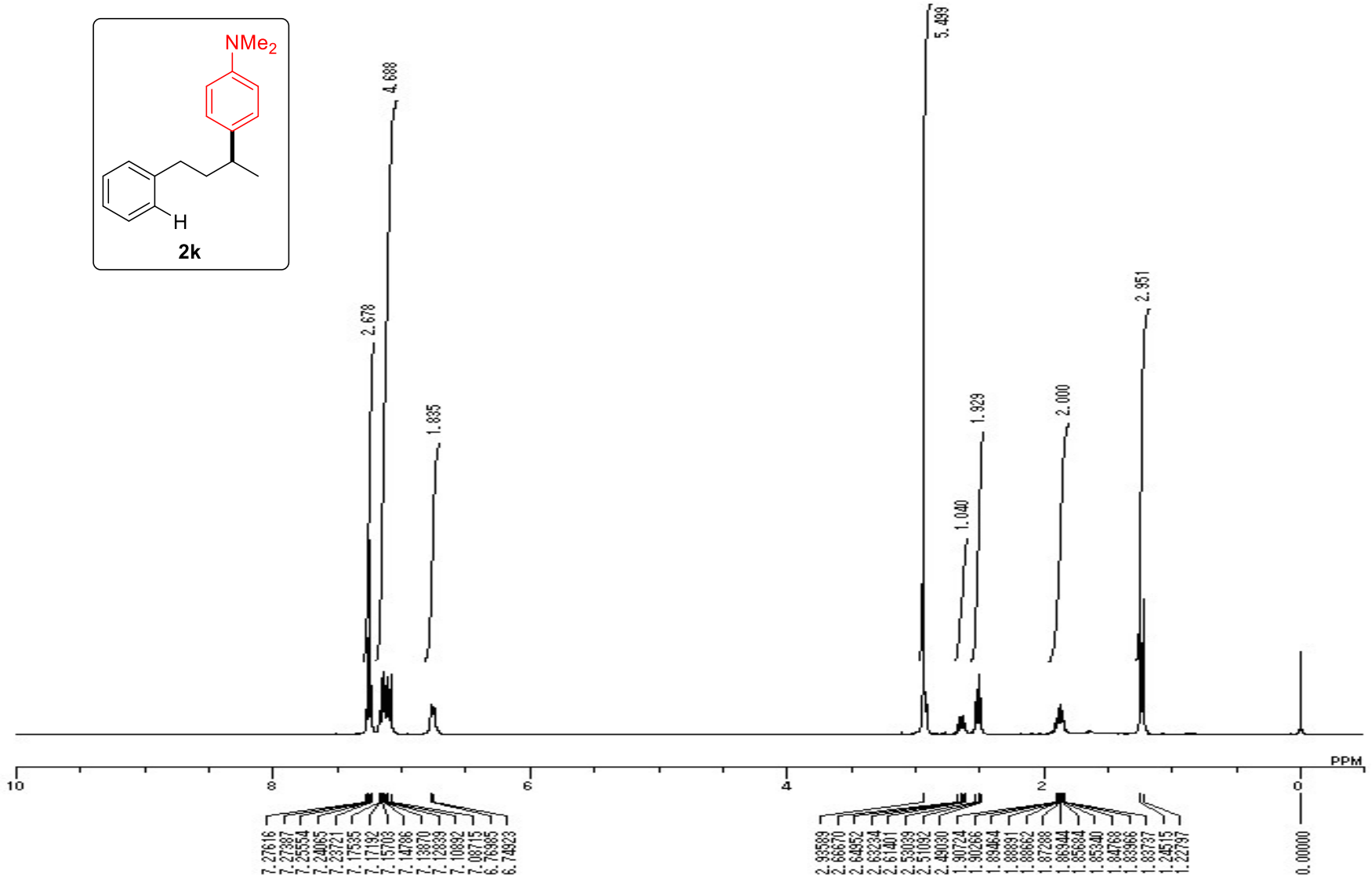
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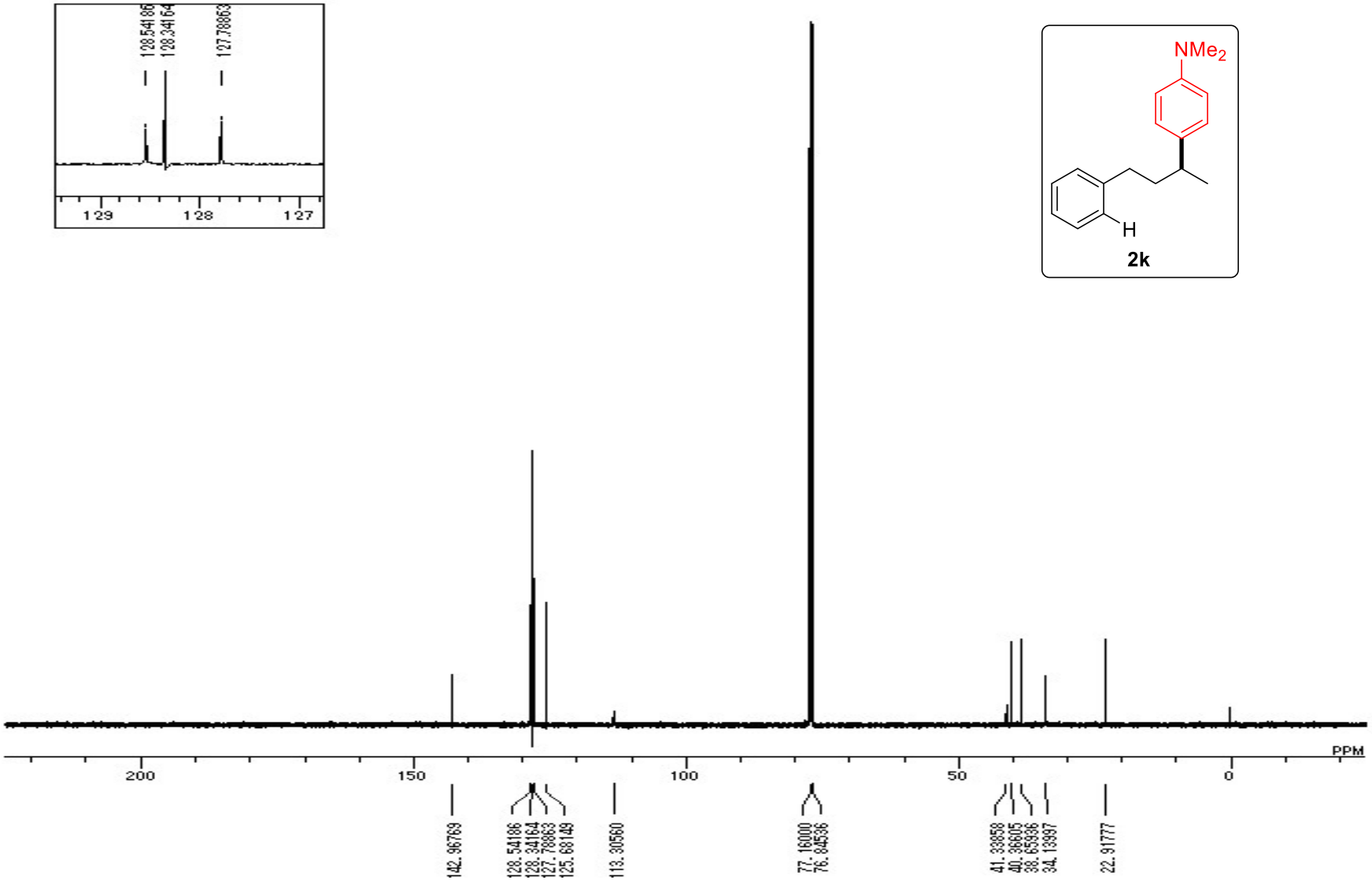
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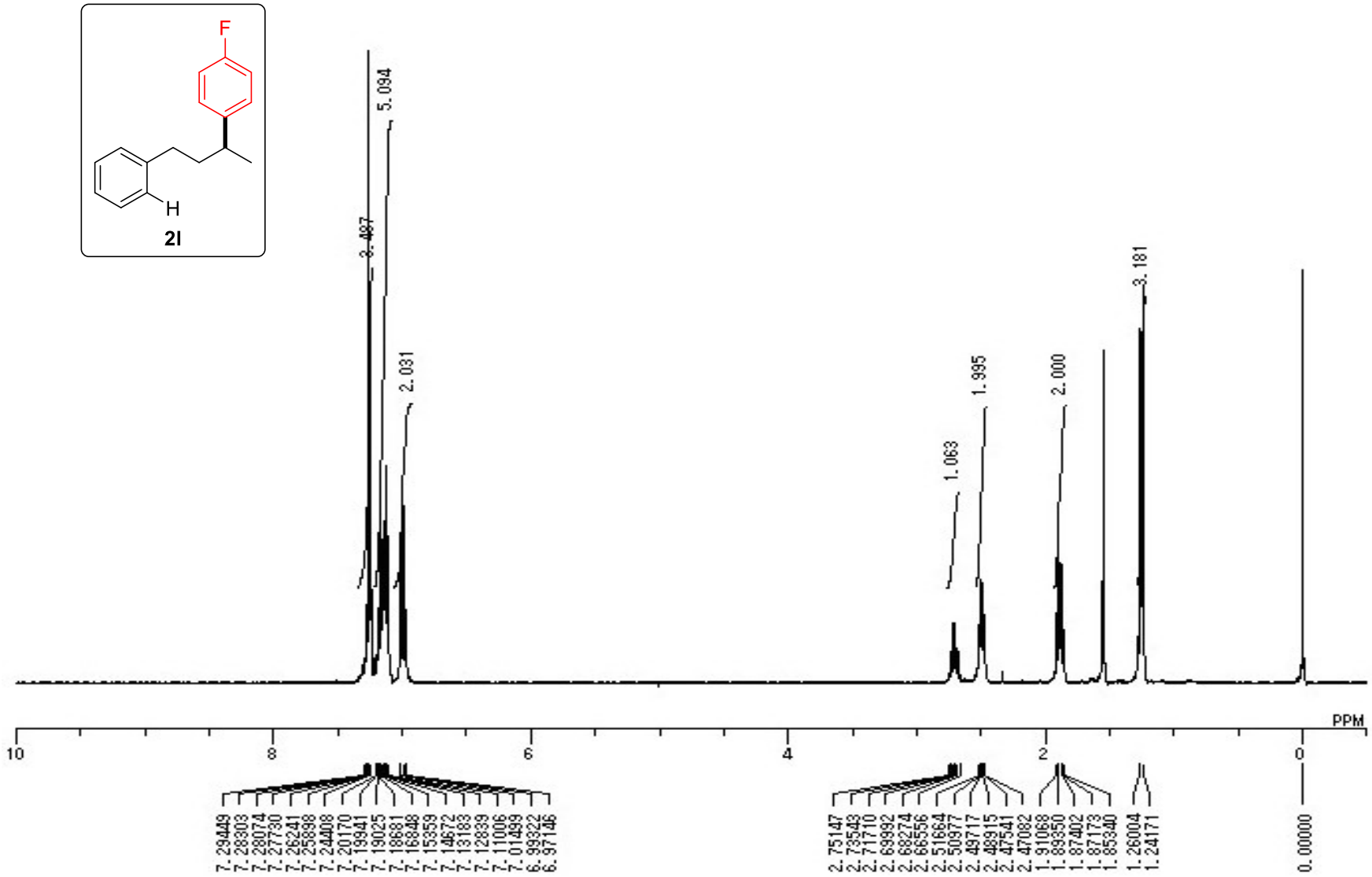
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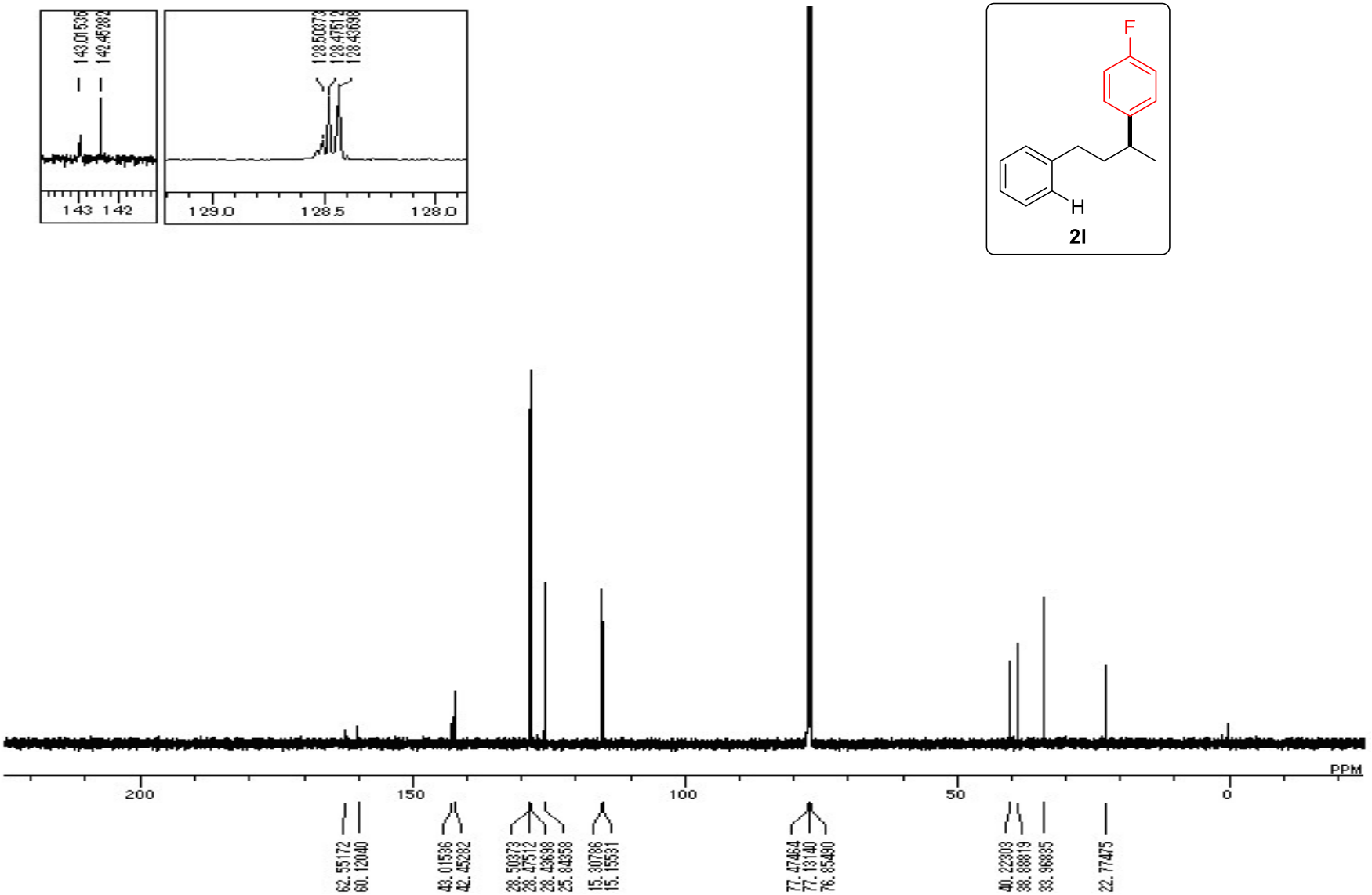
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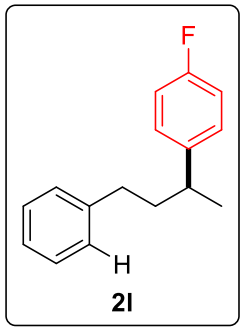

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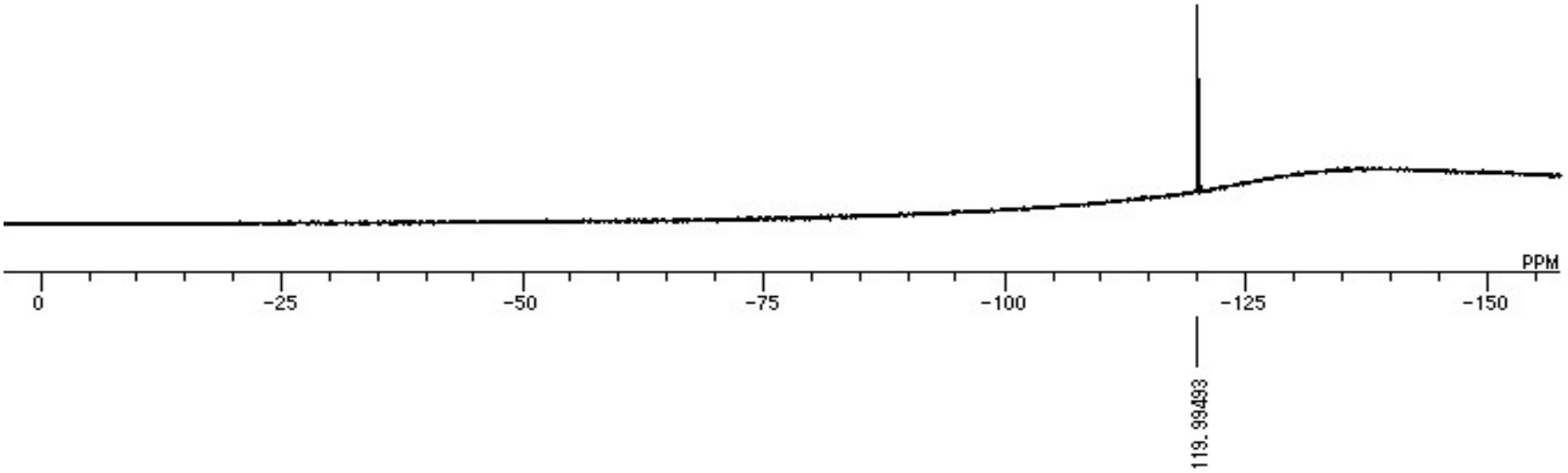

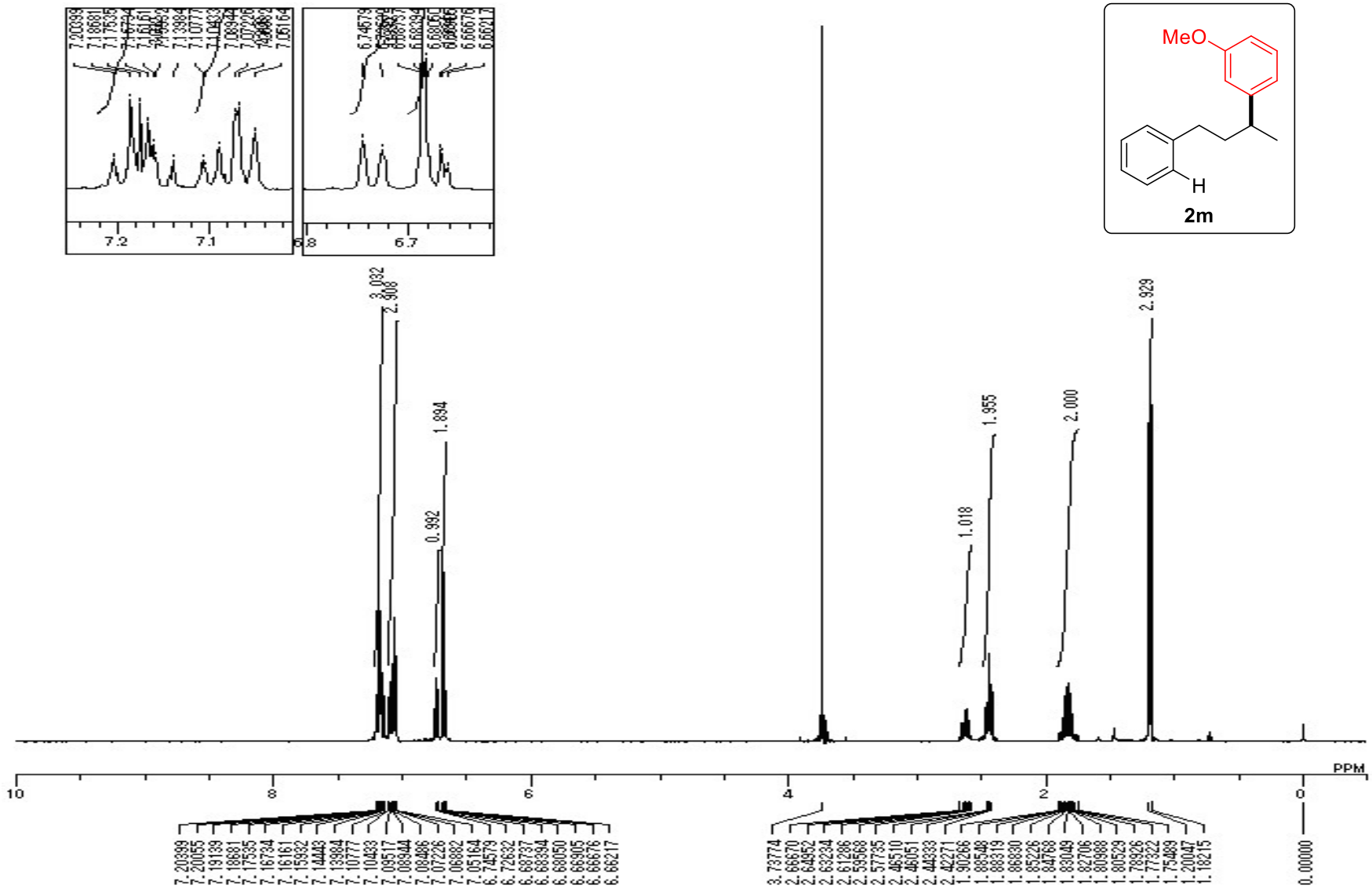
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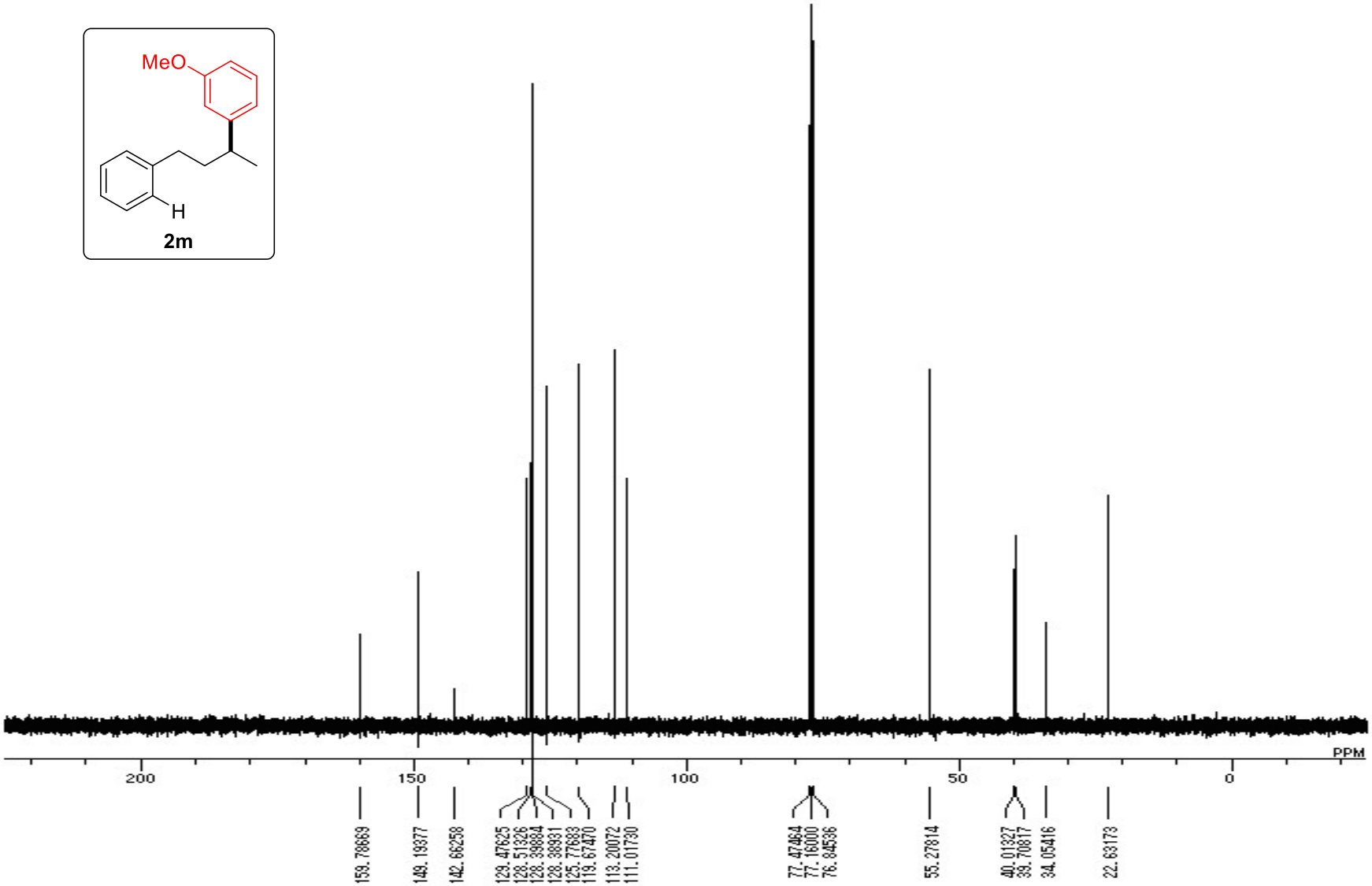
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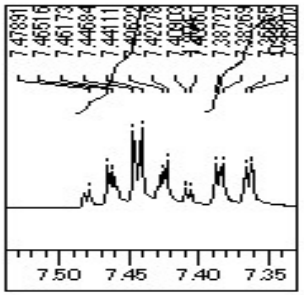
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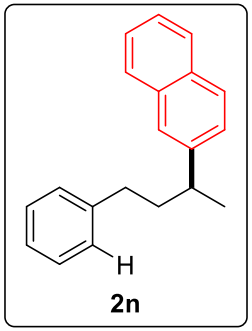
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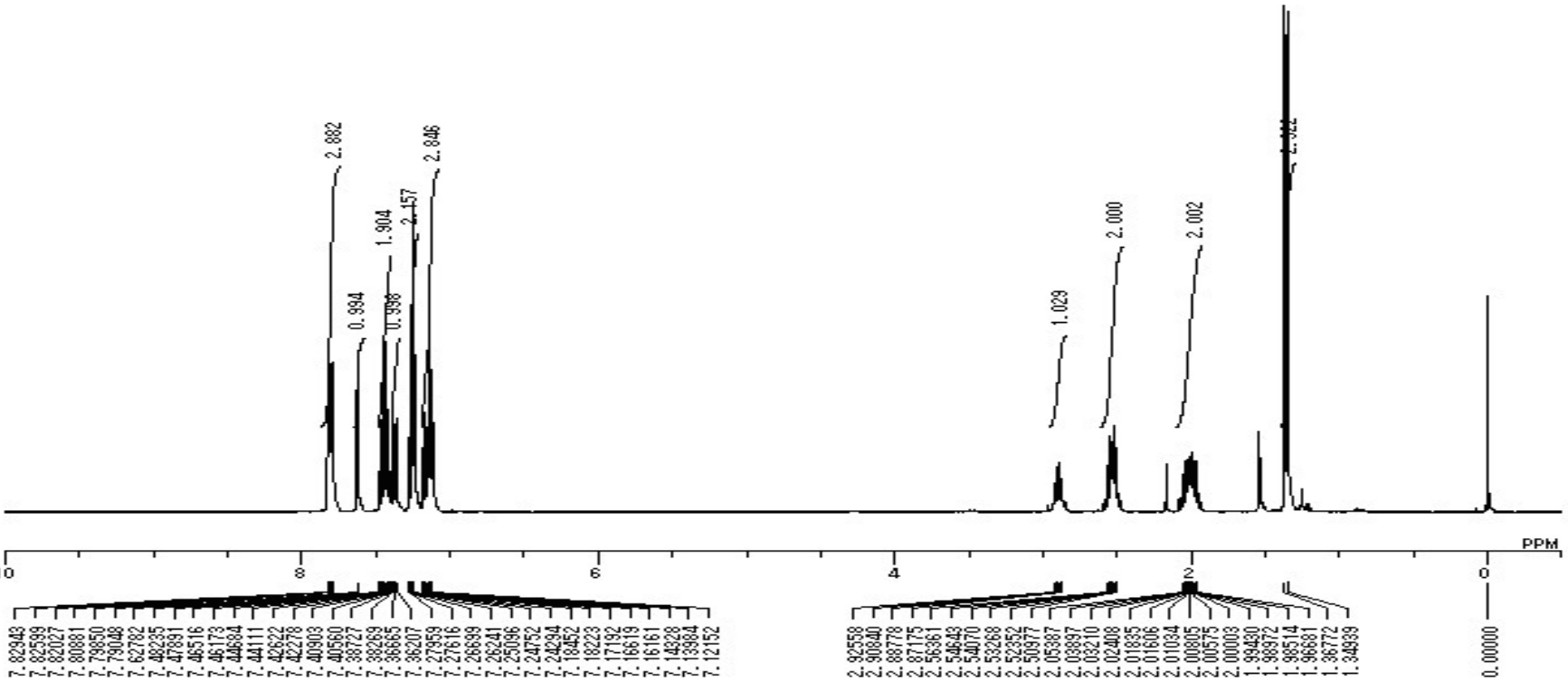
2n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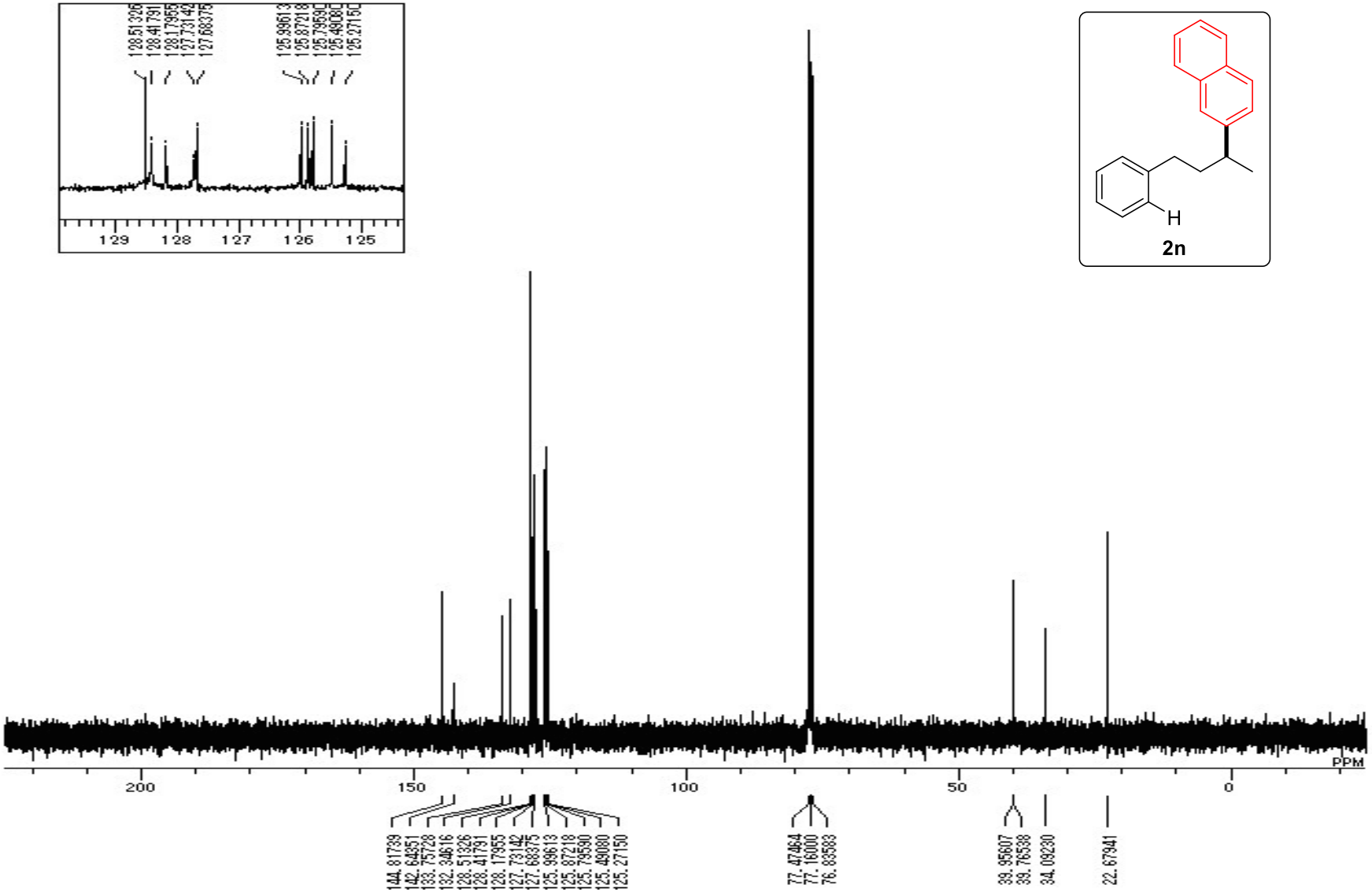
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PPM
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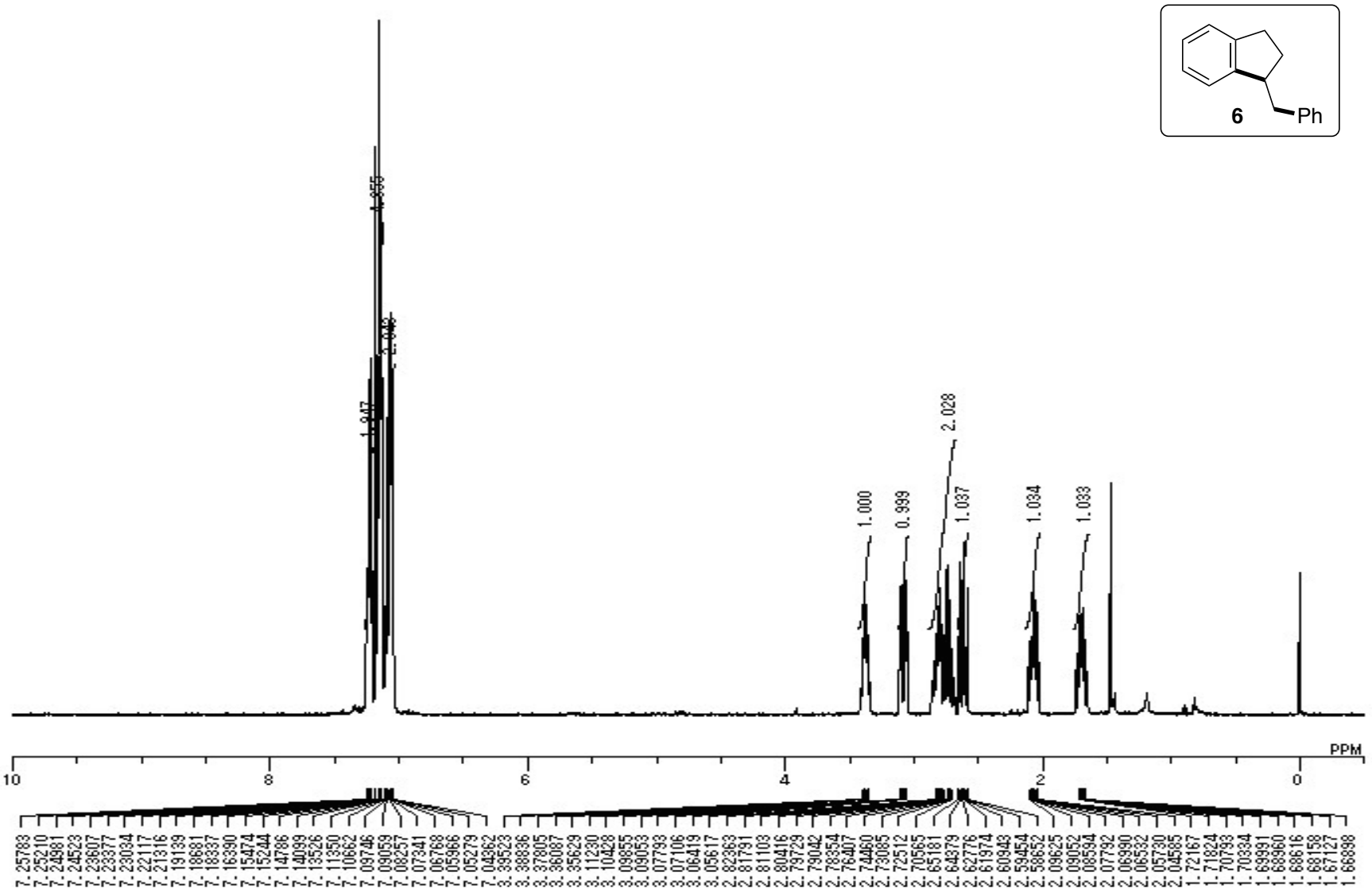
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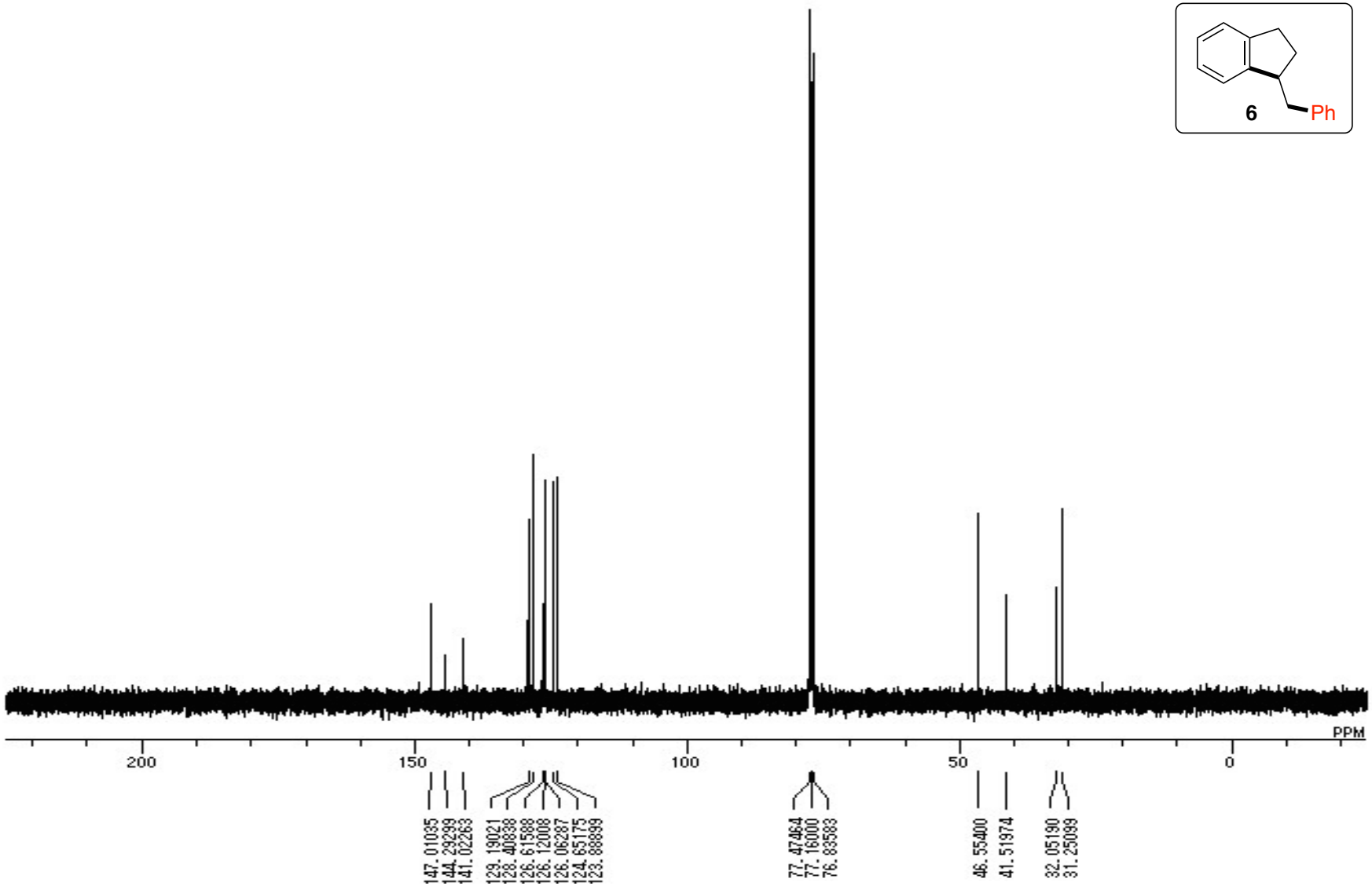
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