Supporting Information for:

Base mediated cascade amidination/alkylation of amines by alcohols

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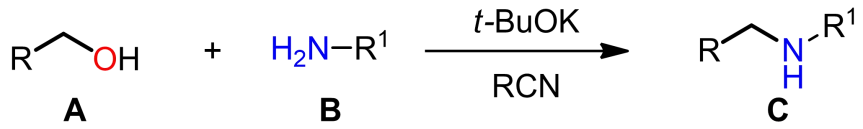
1. General

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 MicroTOF-QII mass (ESI). MN silica gel 60 (0.040 – 0.063 mm particle size) was used for flash column chromatography.

2. Screening of reaction parameters

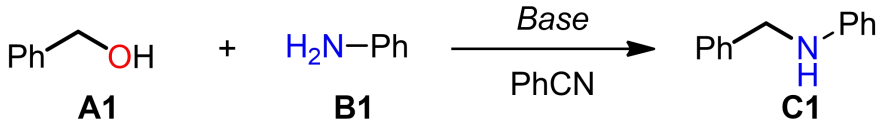
Closed system:



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, base, alcohol (**A1)**, amine (**B1)**, nitrile, and solvent. 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 **C1** (pentane/ethyl ether = 15/1 – 5/1) in the reported yield.

Entry	Parameter
Table S1	The difference of base screening
Table S2	The difference of solvent screening
Table S3	Screening the loading of *t*-BuOK
Table S4	Reaction temperature screening
Table S5	The ratio of **A1** and **B1** screening
Table S6	Reaction system screening

Table S1: The difference of base screening [a]

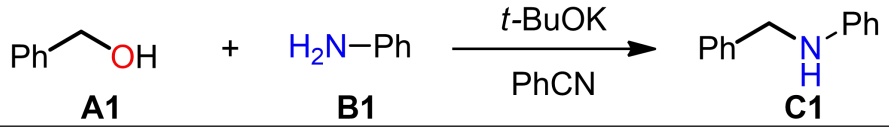


A1 **B1** **C1**

Entry	Base (1.6 equiv)	**C1** (%)
1	Li_2CO_3	0
2	LiOH	0
3	*t*-BuOLi	0
4	LiHMDS	0
5	LDA	0
6	Na_2CO_3	0
7	NaOH	0
8	*t*-BuONa	15
9	NaHMDS	0
10	$NaHCO_3$	0
11	NaH	<5
12	$NaNH_2$	<5
13	NaOAc	0
14	K_2CO_3	0
15	$KHCO_3$	0
16	K_3PO_4	0
17	K_2HPO_4	0
18	KOH	0
19	*t*-BuOK	95
20	KHMDS	86
21	KH	73
22	Cs_2CO_3	0
23	CsOH	0
24	*t*-BuOCs	<5
25	Et_3N	0
26	Pyridine	0
27	DBU	0
28	TMEDA	0
29	DABCO	0
30	DMAP	0
31	-	0

[a] Reaction conditions: *base* (0.8 mmol), **A1** (1.0 mmol, 104 μL), **B1** (0.6 mmol, 55 μL), PhCN (0.5 mmol, 51 μL), 1,4-dioxane (2.0 mL), 120 °C (extern temperature), N_2, 15 h. Yield of **C1** determined by GC-analysis using *n*-dodecane (50 μL) as internal standard.

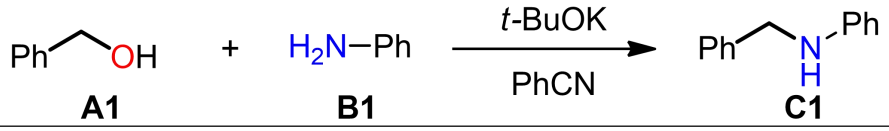
Table S2: The difference of solvent screening [a]



Entry	Solvent (2 mL)	**C1** (%)
1	xylene	49
2	toluene	64
3	benzene	56
4	anisole	82
5	1,4-dioxane	95
6	THF	36
7	2-THF	74
8	diglyme	58
9	CH_3OH	0
10	CH_3CH_2OH	0
11	*i*-PrOH	0
12	*t*-BuOH	<5
13	*t*-AmOH	7
14	DCM	0
15	DCE	0
16	$CHCl_3$	0
17	CH_3NO_2	0
18	NMP	32
19	DMSO	33
20	DMF	7
21	DMAc	6
22	$CH_3CO_2CH_2CH_3$	16

[a] Reaction conditions: *t*-BuOK (0.8 mmol), **A1** (1.0 mmol, 104 μL), **B1** (0.6 mmol, 55 μL), PhCN (0.5 mmol, 51 μL), solvent (2.0 mL), 120 °C (extern temperature), N_2, 15 h. Yield of **C1** determined by GC-analysis using *n*-dodecane (50 μL) as internal standard.

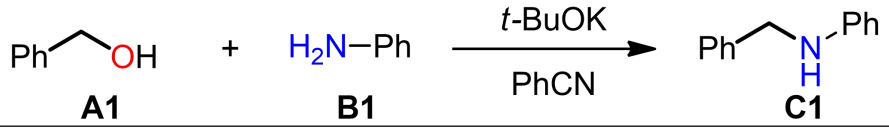
Table S3: Screening the loading of *t*-BuOK [a]



Entry	*t*-BuOK (mmol)	**C1** (%)
1	0	0
2	0.1	0
3	0.2	<5
4	0.4	34
5	0.5	59
6	0.6	72
7	0.7	91
8	0.8	95
9	0.9	94
10	1.0	95
11	1.2	94
12	1.4	95
13	1.6	91
14	1.8	89
15	2.0	85

[a] Reaction conditions: *t*-BuOK (x mmol), **A1** (1.0 mmol, 104 μL), **B1** (0.6 mmol, 55 μL), PhCN (0.5 mmol, 51 μL), 1,4-dioxane (2.0 mL), 120 °C (extern temperature), N_2, 15 h. Yield of **C1** determined by GC-analysis using *n*-dodecane (50 μL) as internal standard.

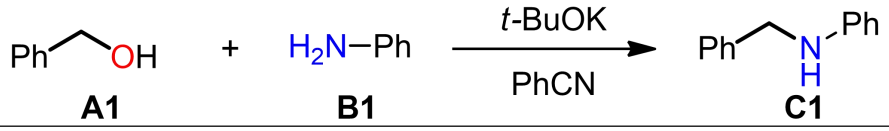
Table S4: Reaction temperature screening [a]



Entry	T [°C]	**C1** (%)
1	RT	0
2	40	0
3	60	0
4	80	21
5	100	52
6	120	95
7	130	94
8[b]	140	88
9[b]	150	62
10[b]	160	41
11[b]	180	<5

[a] Reaction conditions: *t*-BuOK (0.8 mmol), **A1** (1.0 mmol, 104 µL), **B1** (0.6 mmol, 55 µL), PhCN (0.5 mmol, 51 µL), 1,4-dioxane (2.0 mL), T (extern temperature), N_2, 15 h. Yield of **C1** determined by GC-analysis using *n*-dodecane (50 µL) as internal standard.
[b] Reactions carried out in the autoclave.

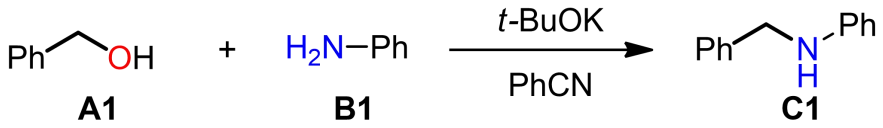
Table S5: The ratio of **A1** and **B1** screening [a]



Entry	**A1** (mmol)	**B1** (mmol)	**PhCN** (mmol)	**C1** (%)
1	0.5	0.6	0.5	76
2	0.6	0.6	0.5	88
3	0.7	0.6	0.5	90
4	0.8	0.6	0.5	90
5	0.9	0.6	0.5	91
6	1.0	0.6	0.5	95
7	1.0	0.5	0.5	69
8	1.0	0.55	0.5	90
9	1.0	0.75	0.5	95
10	1.0	0.5	0	0
11	1.0	0.5	0.1	10
12	1.0	0.5	0.25	39
13	1.0	0.5	0.75	90
14	**1.0**	**0.5**	**0.8**	**96**
15	1.0	0.5	0.85	95
16	1.0	0.5	0.9	96
17	1.0	0.5	1.0	96
18	0.5	1.0	0.5	71
19	0.5	1.0	0.75	71
20	0.5	1.0	1.0	73

[a] Reaction conditions: *t*-BuOK (0.8 mmol), **A1** (x mmol), **B1** (x mmol), PhCN (x mmol), 1,4-dioxane (2.0 mL), 120 °C (extern temperature), N_2, 15 h. Yield of **C1** determined by GC-analysis using *n*-dodecane (50 μL) as internal standard.

Table S6: Reaction system screening [a]

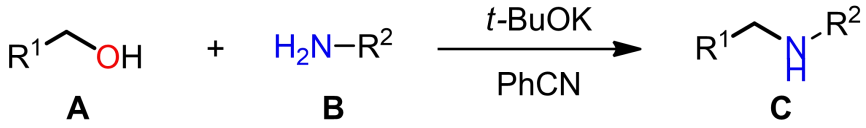


Entry	System		**C1** (%)
1	Seal tube	N_2	96
2	Seal tube	Ar	95
3	Seal tube	air	83
4	Seal tube	O_2	<5
5	Open-reflux	N_2	91
6	Open-reflux	Ar	90
7	Open-reflux	air	81
8	Open-reflux	O_2	<5

[a] Reaction conditions: *t*-BuOK (0.8 mmol), **A1** (1.0 mmol), **B1** (0.5 mmol), PhCN (0.8 mmol), 1,4-dioxane (2.0 mL), 120 °C (extern temperature), N_2, 15 h. Yield of **C1** determined by GC-analysis using *n*-dodecane (50 μL) as internal standard.

3. General procedure for the *N*-alkylation reaction

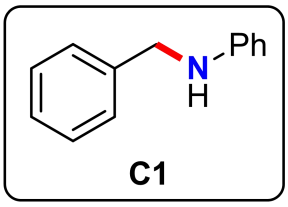
Closed system:



Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (0.8 mmol, 90 mg), alcohols **A** (1.0 mmol**)**, amines **B** (0.5 mmol**)**, nitriles **D** (0.8 mmol), toluene (2.0 mL). The seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (120 °C). After 15 hours the r`eaction 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 **C** (pentane/ethyl ether = 15/1 – 5/1) in the reported yield, respectively.

4. Characterization data

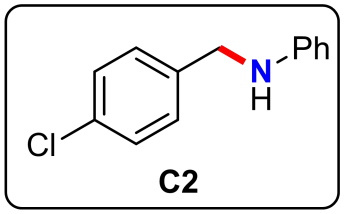
***N*-benzylaniline (C1) :**The title compound was prepared according to the general procedure and purified by column chromatography to give the light yellow oil 83 mg, 91% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.40 – 7.31 (m, 5H), 7.21 (t, *J* = 7.6 Hz, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 2H), 4.36 (s, 2H), 4.06 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 148.1, 139.4, 129.2, 128.6, 127.5, 127.2, 117.5, 112.8, 48.3 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{14}N$ [M+H]: 184.1126, found: 184.1129.



C1

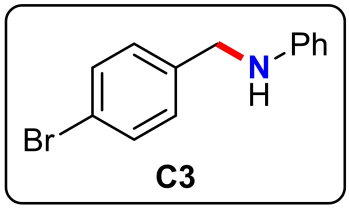
***N*-(4-chlorobenzyl)aniline (C2):** The title compound was prepared according to the general procedure and purified by column chromatography to give as the light yellow oil 89 mg, 82% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.35 (d, *J* = 3.8 Hz, 4H), 7.27 – 7.21 (m, 2H), 6.82 – 6.77 (m, 1H), 6.68 – 6.65 (m, 2H), 4.35 (s, 2H), 4.09 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 147.7, 137.9, 132.7, 129.2, 128.7, 128.6, 117.7, 112.8, 47.5 ppm.

HRMS (ESI) calcd. for $C_{13}H_{13}ClN$ [M+H]: 218.0737, found: 218.0738.



C2

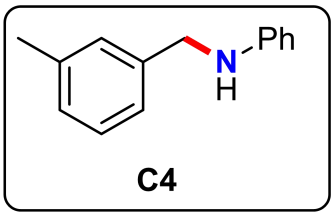
***N*-(4-bromobenzyl)aniline (C3):** The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil 92 mg, 70% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.58-7.55 (m, 2H), 7.36 – 7.29 (m, 4H), 6.87-6.82 (m, 1H), 6.71 (d, *J* = 7.1 Hz, 2H), 4.39 (s, 2H), 4.15 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 147.7, 138.5, 131.6, 129.3, 129.0, 120.9, 117.8, 112.8, 47.6 ppm. **HRMS**



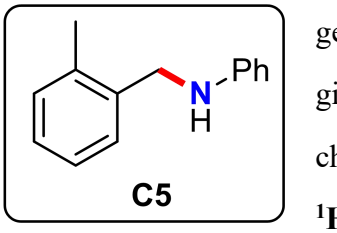
C3

(ESI) calcd. for $C_{13}H_{13}BrN$ [M+H]: 262.0231, found: 262.0235.

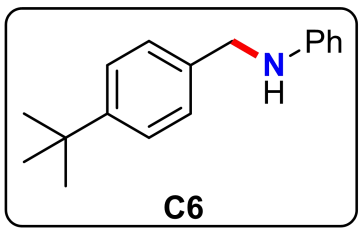
***N*-(3-methylbenzyl)aniline (C4):** The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil 83 mg, 84% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.23-7.18 (m, 5H), 7.15 (d, *J* = 7.2 Hz, 1H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 2H), 4.27 (s, 2H), 3.95 (bs, 1H), 2.38 (s, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 148.1, 139.3, 138.2, 129.1, 128.4, 128.2, 127.9, 124.5, 117.4, 112.7, 48.2, 21.3 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{16}N$ [M+H]: 198.1283, found: 198.1278.



***N*-(2-methylbenzyl)aniline (C5):** The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil 67 mg, 68% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.43 (d, *J* = 6.1 Hz, 1H), 7.31 – 7.26 (m, 5H), 6.85 – 6.68 (m, 1H), 6.74 – 6.71 (m, 2H), 4.35 (s, 2H), 3.90 (bs, 1H), 2.47 (d, *J* = 1.7 Hz, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 148.2, 136.9, 136.3, 130.3, 129.2, 128.2, 127.3, 126.1, 117.4, 112.6, 46.3, 18.9 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{16}N$ [M+H]: 198.1283, found: 198.1281.

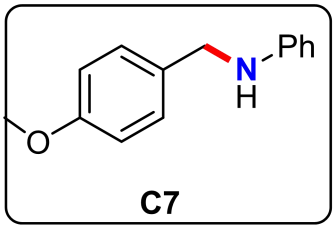


***N*-(4-(tert-butyl)benzyl)aniline (C6):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 108 mg, 90% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, CD_2Cl_2): δ = 7.36 (dd, *J* = 19.9, 8.3 Hz, 4H), 7.17 (t, *J* = 6.2 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 2H), 4.30 (s, 2H), 4.00 (bs, 1H), 1.33 (s, 9H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, CD_2Cl_2): δ = 150.2, 148.5, 136.7, 129.2, 127.3, 125.5,

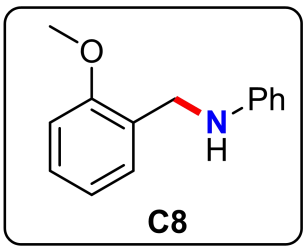


117.3, 112.8, 47.8, 34.5, 31.2 ppm. **HRMS** (ESI) calcd. for $C_{17}H_{22}N$ [M+H]: 240.1752, found: 240.1753.

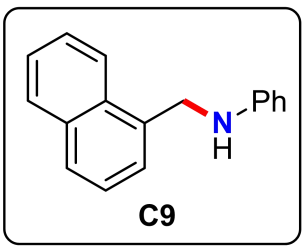
***N*-(4-methoxybenzyl)aniline (C7):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 98 mg, 92% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.31 (d, *J* = 8.3 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 2H), 4.27 (s, 2H), 3.96 (bs, 1H), 3.82 (s, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 158.8, 148.2, 131.3, 129.2, 128.8, 117.4, 114.0, 112.8, 55.3, 47.7 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{16}NO$ [M+H]: 214.1232, found: 214.1234.



***N*-(2-methoxybenzyl)aniline (C8):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 73 mg, 69% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.33 (d, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 8.1 Hz, 1H), 7.19 (dd, *J* = 11.3, 4.3 Hz, 2H), 6.92 (dd, *J* = 16.1, 7.9 Hz, 2H), 6.74 – 6.67 (m, 3H), 4.36 (s, 2H), 4.15 (bs, 1H), 3.88 (s, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 157.3, 148.4, 129.1, 128.8, 128.2, 127.3, 120.5, 117.3, 113.0, 110.2, 55.2, 43.4 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{16}NO$ [M+H]: 214.1232, found: 214.1233.

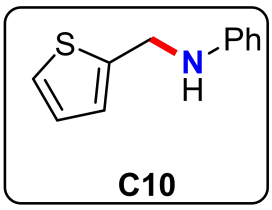


***N*-(naphthalen-1-ylmethyl)aniline (C9):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 81 mg, 70% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 1%). **^{1}H NMR** (299.86

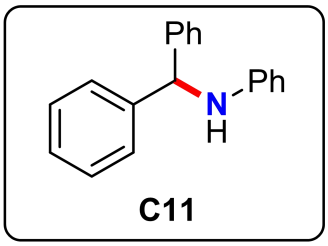


MHz, 23.0 °C, $CDCl_3$): δ = 8.22-8.19 (m, 1H), 8.06-8.03 (m, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.64 (m, 3H), 7.59– 7.54 (m, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 2H), 4.81 (s, 2H), 4.04 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 148.2, 134.3, 133.8, 131.5, 129.3, 128.7, 128.1, 126.3, 126.0, 125.8, 125.5, 123.5, 117.5, 112.7, 46.4 ppm. **HRMS** (ESI) calcd. for $C_{17}H_{16}N$ [M+H]: 234.1283, found: 234.1284.

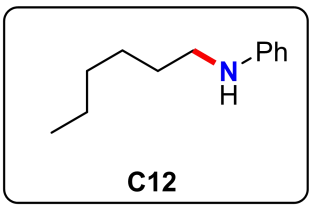
***N*-(naphthalen-1-ylmethyl)aniline (C10):** The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil 76 mg, 80% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, CD_2Cl_2): δ = 7.33 – 7.25 (m, 3H), 7.13 – 7.06 (m, 2H), 6.84 – 6.76 (m, 3H), 4.61 (s, 2H), 4.26 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, CD_2Cl_2): δ = 147.8, 143.4, 129.2, 126.8, 125.0, 124.5, 117.9, 113.1, 43.3. **HRMS** (ESI) calcd. for $C_{11}H_{12}NS$ [M+H]: 190.0690, found: 190.0692.



***N*-benzhydrylaniline (C11):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 46 mg, 36% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 3%). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.45-7.37 (m, 8H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.21 – 7.17 (m, 2H), 6.79-6.75 (m, 1H), 6.62 – 6.60 (m, 2H), 5.58 (s, 1H), 4.29 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 147.4, 142.9, 129.1, 128.8, 127.5, 127.4, 117.7, 113.5, 63.1 ppm. **HRMS** (ESI) calcd. for $C_{19}H_{18}N$ [M+H]: 260.1439, found: 260.1437.

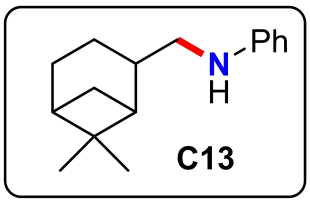


***N*-heptylaniline (C12):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 36 mg, 41%



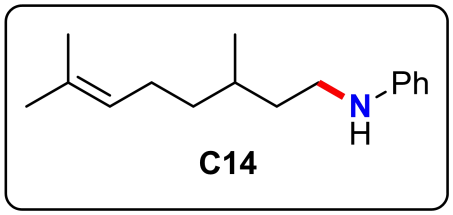
yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, CD_2Cl_2): δ = 7.22-7.17 (m, 2H), 6.73-6.68 (m, 1H), 6.66-6.63 (m, 2H), 3.70 (bs, 1H), 3.14 (t, *J* = 7.2 Hz, 2H), 1.68-1.64 (m, 2H), 1.46-1.38 (m, 6H), 1.00-0.96 (m, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, CD_2Cl_2): δ = 148.8, 129.1, 116.8, 112.5, 43.9, 31.7, 29.5, 26.9, 22.7, 13.9 ppm. **HRMS** (ESI) calcd. for $C_{12}H_{20}N$ [M+H]: 178.1595, found: 178.15956.

***N*-(2-(6,6-dimethylbicyclo[3.1.1]heptan-2-yl)ethyl)aniline (C13):** The title



compound was prepared according to the general procedure and purified by column chromatography to give a white solid 61 mg, 53% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 1%). **^{1}H NMR** (299.86 MHz, 23.0 °C, CD_2Cl_2): δ = 7.19 – 7.14 (m, 2H), 6.70-6.65 (m, 1H), 6.65 – 6.58 (m, 2H), 5.40 – 5.13 (m, 1H), 3.83 – 3.58 (m, 3H), 2.48 – 2.35 (m, 4H), 2.04-2.01 (m, 1H), 1.99 – 1.83 (m, 2H), 1.40 (d, J = 9.3 Hz, 1H), 1.38 (s, 1H), 1.31 (s, 2H), 0.79 (d, J = 4.5 Hz, 3H). **^{13}C NMR** (75.41 MHz, 23.0 °C, CD_2Cl_2): δ = 148.6, 145.8, 129.0, 118.6, 118.2, 116.9, 116.8, 112.7, 45.3, 41.2, 40.9, 40.8, 40.7, 40.5, 27.5, 26.0, 25.9, 25.7, 24.8, 23.7, 23.6, 21.7, 21.5, 19.7. **HRMS** (ESI) calcd. for $C_{16}H_{24}N$ [M+H]: 230.1909, found: 230.190.

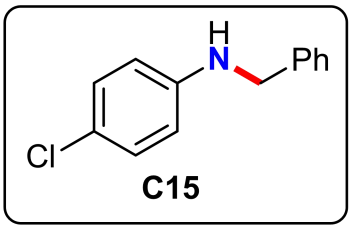
***N*-(3,7-dimethyloct-6-en-1-yl)aniline (C14):** The title compound was prepared



according to the general procedure and purified by column chromatography to give a white solid 46 mg, 40% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 1%). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.22 (t, *J* = 7.9 Hz, 2H), 6.74 (td, *J* = 7.3, 0.8 Hz, 1H), 6.65 (d, *J* = 8.5 Hz, 2H), 5.16 (t, *J* = 7.1 Hz, 1H), 3.58 (bs, 1H), 3.29 – 3.01 (m, 2H), 2.06 (dt, *J* = 15.5, 7.8 Hz, 2H), 1.74 (d, *J* = 7.7 Hz, 3H), 1.72 – 1.56 (m, 5H), 1.46 (tdd, *J* = 11.9, 11.0, 7.0 Hz, 2H), 1.36 – 1.17 (m, 1H), 1.00 (d, *J* = 6.4 Hz, 3H); **^{13}C**

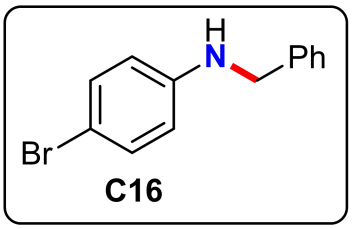
NMR (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 148.6, 131.3, 129.2, 124.7, 117.1, 112.71, 42.0, 37.1, 36.7, 30.5, 25.8, 25.5, 19.6, 17.7. **HRMS** (ESI) calcd. for $C_{16}H_{26}N$ [M+H]: 232.2065, found: 232.2066.

***N*-benzyl-4-chloroaniline (C15):** The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil 91 mg, 84% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.42 – 7.33 (m, 5H), 7.20 – 7.15 (m, 2H), 6.61 – 6.56 (m, 2H), 4.34 (s, 2H), 4.09 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 146.5, 138.8, 128.9, 128.6, 127.3, 127.2, 121.9, 113.8, 48.2 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{13}ClN$ [M+H]: 218.0737, found: 218.0738.



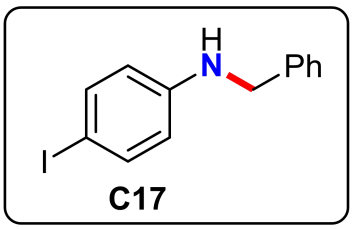
C15

***N*-benzyl-4-bromoaniline (C16):** The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil 89 mg, 68% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.40 – 7.33 (m, 5H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 4.33 (s, 2H), 4.11 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 147.0, 138.8, 131.8, 128.6, 127.3, 114.3, 109.0, 48.1 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{13}BrN$ [M+H]: 262.0231, found: 262.0233.



C16

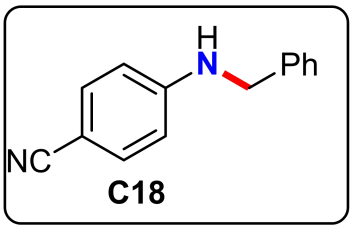
***N*-benzyl-4-iodoaniline (C17):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 66 mg, 43% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.47 – 7.46 (m, 2H), 7.40 – 7.31 (m,



C17

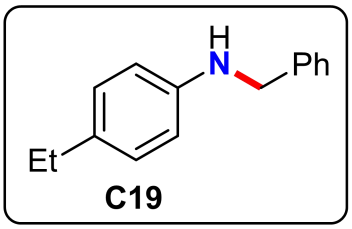
5H), 6.47 – 6.42 (m, 2H), 4.33 (d, *J* = 4.6 Hz, 2H), 4.13 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 147.5, 138.2, 137.7, 128.2, 127.2, 127.3, 115.0, 78.0, 47.9 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{13}IN$ [M+H]: 310.0093, found: 310.0094.

4-(benzylamino)benzonitrile (C18): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 27 mg, 26% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.41 – 7.40 (m, 2H), 7.38-7.31 m, 5H), 6.59 (d, *J* = 8.8 Hz, 2H), 4.66 (bs, 1H), 4.38 (d, *J* = 5.5 Hz, 2H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 151.1, 137.8, 133.8, 128.9, 127.7, 127.3, 120.2, 112.4, 98.5, 47.5 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{13}N_2$ [M+H]: 209.1079, found: 209.1077.



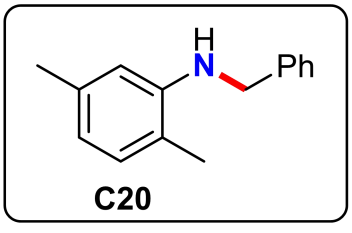
C18

***N*-benzyl-4-ethylaniline (C19):** The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil 95 mg, 90% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.44 – 7.26 (m, 5H), 7.09-7.06 (m, 2H), 6.66-6.62 (m, 2H), 4.35 (s, 2H), 3.95 (bs, 1H), 2.60 (q, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 146.1, 139.6, 133.3, 128.5, 128.5, 127.5, 127.1, 112.9, 48.6, 27.9, 15.9 ppm. **HRMS** (ESI) calcd. for $C_{15}H_{18}N$ [M+H]: 212.1439, found: 212.1438.



C19

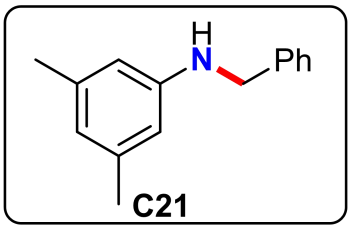
***N*-benzyl-2,5-dimethylaniline (C20):** The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil 106 mg, 71% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1). **^{1}H NMR** (299.86 MHz,



C20

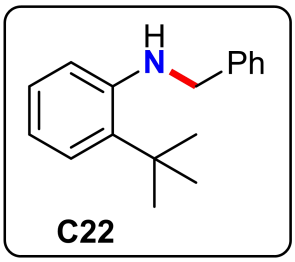
23.0 °C, $CDCl_3$): δ = 7.48 – 7.43 (m, 4H), 7.39-7.36 (m, 1H), 6.51 (s, 1H), 6.38 (s, 2H), 4.39 (s, 2H), 3.97 (bs, 1H), 2.34(s, 6H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 148.3, 139.6, 138.8, 128.5, 127.5, 127.1, 119.5, 110.87, 48.3, 21.4 ppm. **HRMS** (ESI) calcd. for $C_{15}H_{18}N$ [M+H]: 212.1439, found: 212.1440.

***N*-benzyl-3,5-dimethylaniline (C21):** The title compound was prepared according to



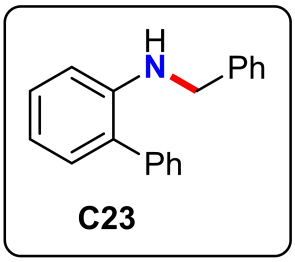
the general procedure and purified by column chromatography to give the yellow oil 87 mg, 83% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.48 – 7.38 (m, 5H), 6.51 (d, *J* = 3.7 Hz, 1H), 6.39(d, *J* = 4.2 Hz, 2H), 4.39 (d, *J* = 4.2 Hz, 2H), 3.97 (bs, 1H), 2.35 (d, *J* = 4.0 Hz, 6H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 148.2, 139.6, 138.8, 128.5, 127.4, 127.1, 119.5, 110.7, 48.3, 21.4 ppm. **HRMS** (ESI) calcd. for $C_{15}H_{18}N$ [M+H]: 212.1439, found: 212.1437.

***N*-benzyl-2-(*tert*-butyl)aniline (C22):** The title compound was prepared according to



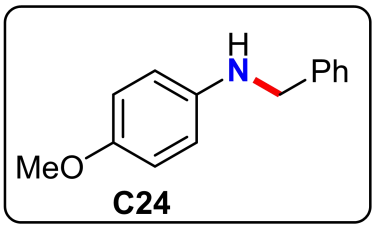
the general procedure and purified by column chromatography to give a white solid 69 mg, 58% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 1%). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.60 – 7.28 (m, 6H), 7.17 (d, *J* = 6.4 Hz, 1H), 6.77 (dt, *J* = 14.4, 7.7 Hz, 2H), 4.47 (d, *J* = 6.3 Hz, 2H), 4.35 (s, 1H), 1.51 (d, *J* = 6.4 Hz, 9H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 146.1, 139.6, 133.2, 128.7, 127.4, 127.2, 126.2, 117.2, 111.9, 109.9, 109.9, 48.8, 34.5, 29.9 ppm. **HRMS** (ESI) calcd. for $C_{17}H_{22}N$ [M+H]: 240.1752, found: 240.1753.

***N*-benzyl-[1,1'-biphenyl]-2-amine (C23):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 91 mg, 70% yield. Purification by column chromatography on silica gel (pentane/ethyl

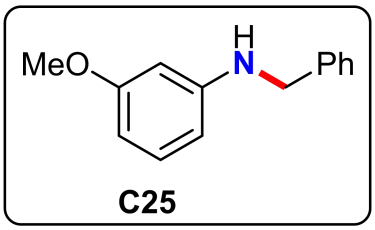


ether = 6 : 1, DCM 10%). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.78 – 7.67 (m, 4H), 7.61 – 7.40 (m, 8H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 4.69 (bs, 1H), 4.55 (s, 2H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 145.2, 139.8, 130.5, 129.7, 129.2, 129.0, 128.9, 127.9, 127.6, 127.3, 117.5, 111.1, 48.3 ppm. **HRMS** (ESI) calcd. for $C_{19}H_{18}N$ [M+H]: 260.1439, found: 260.1440.

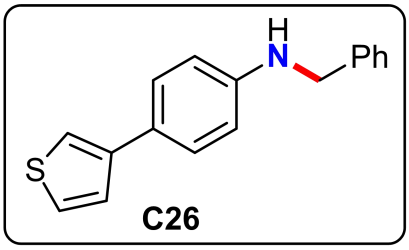
***N*-benzyl-4-methoxyaniline (C24):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 96 mg, 90% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 1%). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.41 – 7.34 (m, 4H), 7.31 – 7.29 (m, 1H), 6.81 – 6.79 (m, 2H), 6.64 – 6.62 (m, 2H), 4.30 (s, 2H), 3.76 (s, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 152.3, 142.3, 139.6, 128.6, 127.6, 127.2, 114.9, 114.2, 55.8, 49.3 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{16}NO$ [M+H]: 214.1232, found: 214.1232.



***N*-benzyl-3-methoxyaniline (C25):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 81 mg, 76% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 1%). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.43 – 7.33 (m, 5H), 7.14 (t, *J* = 8.1 Hz, 1H), 6.36 – 6.25 (m, 2H), 6.24 (t, *J* = 2.3 Hz, 1H), 4.35 (s, 2H), 4.14 (bs, 1H), 3.80 (s, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 160.9, 149.6, 139.4, 130.1, 128.7, 127.6, 127.3, 106.1, 102.8, 99.0, 55.1, 48.4 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{16}NO$ [M+H]: 214.1232, found: 214.1235.



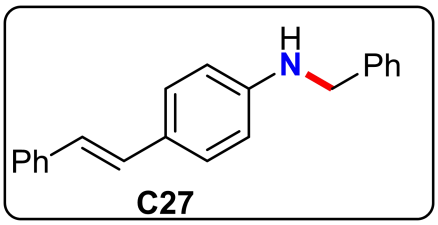
***N*-benzyl-4-(thiophen-2-yl)aniline (C26):** The title compound was prepared according to the general procedure and purified by column chromatography to give a



C26

white solid 110 mg, 83% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1, DCM 10%). **^{1}H NMR** (299.86 MHz, 23.0 °C, CD_2Cl_2): δ = 7.46 – 7.28 (m, 10H), 6.69 (d, *J* = 8.0 Hz, 2H), 4.39 (s, 2H), 4.20 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, CD_2Cl_2): δ = 147.3, 142.5, 139.2, 128.6, 127.4, 127.4, 127.2, 126.1, 125.7, 125.56, 117.7, 113.0, 109.9, 109.9, 48.2 ppm. **HRMS** (ESI) calcd. for $C_{17}H_{16}NS$ [M+H]: 266.1003, found: 266.1005.

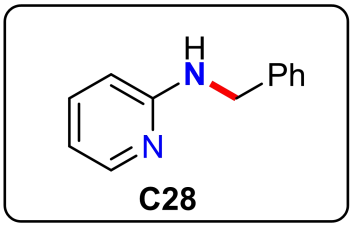
(*E*)-*N*-benzyl-4-styrylaniline (C27): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 94 mg, 66% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 20 : 1, DCM 10%).



C27

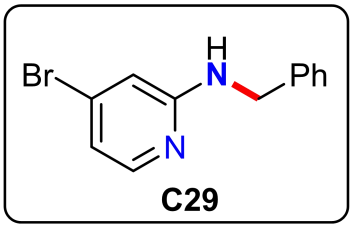
^{1}H NMR (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.50 (d, *J* = 7.7 Hz, 2H), 7.43 – 7.20 (m, 10H), 7.00 (dd, *J* = 39.8, 16.2 Hz, 2H), 6.66 (d, *J* = 8.3 Hz, 2H), 4.39 (s, 2H), 4.24 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 147.8, 139.1, 138.1, 128.8, 128.7, 128.6, 127.8, 127.5, 127.3, 127.1, 126.8, 126.6, 124.6, 113.0, 48.2 ppm. **HRMS** (ESI) calcd. for $C_{21}H_{20}N$ [M+H]: 286.1596, found: 286.1597.

***N*-benzyl-5-bromopyridin-2-amine (C28):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 69 mg, 75% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 5 : 1, DCM 10%). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 8.08 (d, *J* = 4.4 Hz, 1H), 7.48 – 7.28 (m, 5H), 7.27 – 7.17 (m, 1H), 6.63 – 6.50 (m, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 4.92 (s, 1H), 4.48 (d, *J* = 5.7 Hz, 2H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 158.5, 148.2, 139.0, 137.4, 128.6, 127.4, 113.1, 106.8, 46.3. ppm. **HRMS** (ESI) calcd. for $C_{12}H_{13}N_2$ [M+H]: 185.1079, found: 185.1080.



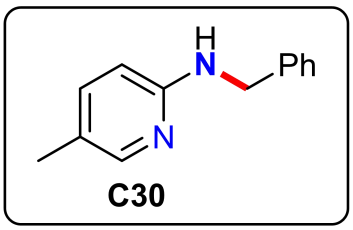
C28

***N*-benzyl-5-bromopyridin-2-amine (C29):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 78 mg, 60% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 5 : 1, DCM 10%).**^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 8.01 (d, *J* = 2.3 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.29 – 7.03 (m, 5H), 6.20 (d, *J* = 8.9 Hz, 1H), 4.99 (s, 1H), 4.39 (d, *J* = 5.8 Hz, 2H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 157.1, 148.7, 139.7, 138.6, 128.7, 127.4, 127.3, 108.2, 107.2, 46.3 ppm. **HRMS** (ESI) calcd. for $C_{12}H_{12}BrN_2$ [M+H]: 263.0184, found: 263.0185.



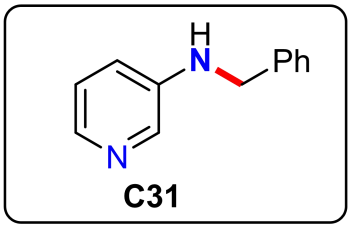
C29

***N*-benzylpyridin-2-amine (C30):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 72 mg, 73% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 5 : 1, DCM 10%). **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.84 (d, *J* = 5.2 Hz, 1H), 7.40 – 7.02 (m, 5H), 6.49 – 6.27 (m, 1H), 6.09 (s, 1H), 4.95 (bs, 1H), 4.38 (d, *J* = 5.7 Hz, 2H), 2.10 (s, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 158.8, 148.3, 147.7, 139.3, 128.5, 127.3, 127.0, 114.6, 114.6, 106.9, 106.8, 46.2, 21.1 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{15}N_2$ [M+H]: 199.1235, found: 199.1238.



C30

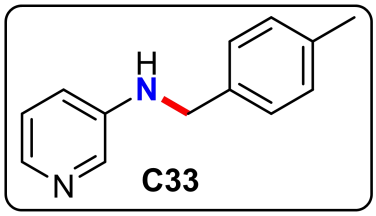
***N*-benzylpyridin-3-amine (C31):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 75 mg, 81% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 5 : 1, DCM 10%). **^{1}H NMR** (299.86 MHz, 23.0 °C, CD_2Cl_2): δ = 8.07 (d, *J* = 2.9 Hz, 1H), 7.94 (dd, *J* = 4.6, 1.3 Hz, 1H), 7.48 – 7.20 (m, 5H), 7.08 (dd, *J* = 8.3, 4.6 Hz, 1H), 6.93-6.89 (m, 1H), 4.40 (br,



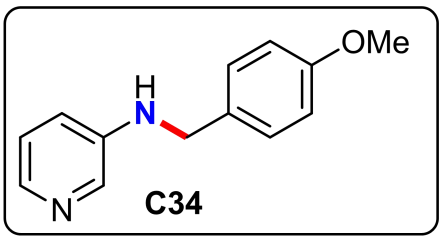
C31

3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, CD_2Cl_2): δ = 143.7, 138.5, 138.2, 135.7, 128.2, 126.9, 126.86, 123.1, 117.9, 47.2 ppm. **HRMS** (ESI) calcd. for $C_{12}H_{13}N_2$ [M+H]: 185.1079, found: 185.1078.

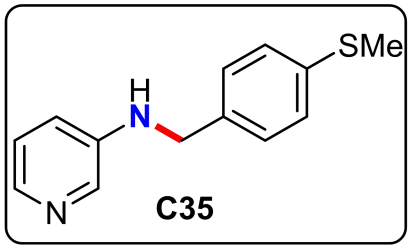
***N*-(4-methylbenzyl)pyridin-3-amine (C33):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 80 mg, 81% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 1%). **^{1}H NMR** (299.86 MHz, 23.0 °C, CD_2Cl_2): δ = 8.05 (dd, *J* = 2.9, 0.5 Hz, 1H), 7.93 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.41 – 7.23 (m, 2H), 7.19 (dd, *J* = 7.0, 1.4 Hz, 2H), 7.07 (ddd, *J* = 8.3, 4.7, 0.7 Hz, 1H), 6.92-6.88 (m, 1H), 4.32 (s, 3H), 2.36 (s, 3H). ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, CD_2Cl_2): δ = 144.2, 138.5, 137.1, 136.1, 135.7, 129.3, 127.3, 123.5, 118.3, 47.4, 20.8 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{15}N_2$ [M+H]: 199.1235, found: 199.1238.



***N*-(4-methoxybenzyl)pyridin-3-amine (C34):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 88 mg, 82% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 1%). **^{1}H NMR** (299.86 MHz, 23.0 °C, CD_2Cl_2): δ = 8.05 (d, *J* = 2.0 Hz, 1H), 7.93 (d, *J* = 4.3 Hz, 1H), 7.43 – 7.23 (m, 2H), 7.08 (dd, *J* = 8.2, 4.6 Hz, 1H), 6.98 – 6.80 (m, 3H), 4.29 (s, 3H), 3.81 (s, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, CD_2Cl_2): δ = 159.0, 138.5, 136.1, 130.7, 128.6, 123.5, 118.3, 114.0, 47.1 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{15}N_2O$ [M+H]: 215.1184, found: 215.1184.

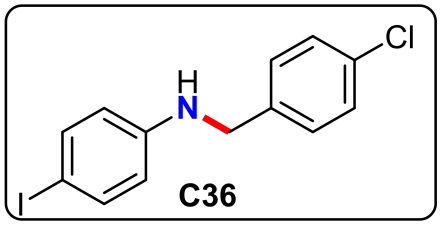


***N*-(4-(methylthio)benzyl)pyridin-3-amine (C35):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 91 mg, 79% yield. Purification by column chromatography on silica gel



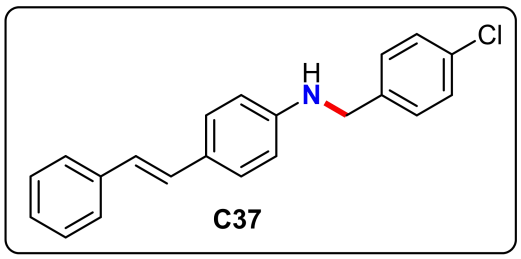
(pentane/ethyl ether = 30 : 1, DCM 1%). **^{1}H NMR** (299.86 MHz, 23.0 °C, CD_2Cl_2): δ = 8.05 (s, 1H), 7.93 (d, *J* = 4.4 Hz, 1H), 7.45 – 7.17 (m, 4H), 7.07 (dd, *J* = 8.2, 4.6 Hz, 1H), 6.97 – 6.70 (m, 1H), 4.37-4.33 (m, 3H), 2.49 (d, *J* = 1.1 Hz, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, CD_2Cl_2): δ = 138.7, 137.6, 136.1, 135.6, 127.9, 126.7, 123.5, 118.3, 47.2, 15.6 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{15}N_2S$ [M+H]: 231.0956, found: 231.0956.

***N*-(4-chlorobenzyl)-4-iodoaniline (C36):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 68 mg, 40% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 1%).



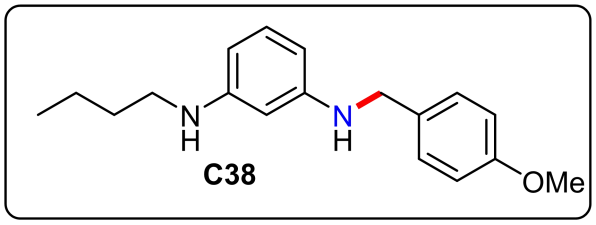
^{1}H NMR (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.46 – 7.43 (m, 2H), 7.39 – 7.33 (m, 4H), 6.47 – 6.44 (m, 2H), 4.34 (s, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 147.9, 138.1, 132.9, 129.4, 128.8, 128.7, 117.8, 112.9, 47.6 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{12}ClIN$ [M+H]: 343.9703, found: 343.9704.

(*E*)-*N*-(4-chlorobenzyl)-4-styrylaniline (C37): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 113 mg, 71% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 1%).



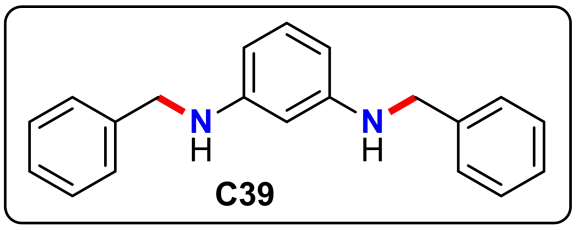
^{1}H NMR (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.53 – 7.52 (m, 2H), 7.41 – 7.28 (m, 8H), 7.25-7.10 (m, 1H), 7.01 (dd, *J* = 38.0, 16.3 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 4.38 (s, 2H), 4.21 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): δ = 147.4, 138.0, 137.7, 132.9, 128.8, 128.6, 128.6, 127.7, 126.8, 126.0, 124.7, 112.9, 47.4 ppm. **HRMS** (ESI) calcd. for $C_{21}H_{19}ClN$ [M+H]: 320.1206, found: 320.1203.

***N*¹-hexyl-*N*³-(4-methoxybenzyl)benzene-1,3-diamine (C38):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 104 mg, 73% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 1%). **¹H NMR** (299.86 MHz, 23.0 °C, CD_2Cl_2): δ = 7.34 – 7.31 (m, 2H), 6.97 – 6.90 (m, 3H), 6.03 – 5.99 (m, 2H), 5.90 (t, *J* = 2.2 Hz, 1H), 4.25 (s, 2H), 3.82 (s, 3H), 3.08 (t, *J* = 7.0 Hz, 2H), 1.62 – 1.57 (m, 2H), 1.48 – 1.40 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H) ppm; **¹³C NMR** (75.41 MHz, 23.0 °C, CD_2Cl_2): δ = 158.8, 149.9, 149.5, 131.9, 129.7, 128.6, 113.8, 102.7, 102.4, 96.9, 55.2, 47.6, 43.6, 31.7, 20.3, 13.7 ppm. **HRMS** (ESI) calcd. for $C_{18}H_{25}N_2O$ [M+H]: 285.1967, found: 285.1966.



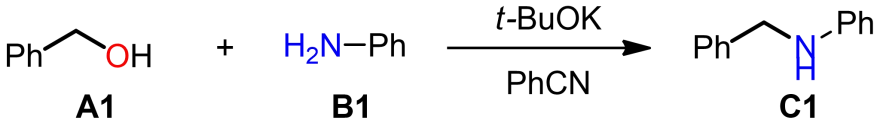
C38

***N*¹,*N*³-dibenzylbenzene-1,3-diamine (C39):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 95 mg, 66% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 1%). **¹H NMR** (299.86 MHz, 23.0 °C, CD_2Cl_2): δ = 7.40-7.27 (m, 10H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.05 (dd, *J* = 8.0, 2.1 Hz, 2H), 5.94 (t, *J* = 2.1 Hz, 1H), 4.30 (d, *J* = 3.5 Hz, 4H), 4.07 (bs, 2H) ppm; **¹³C NMR** (75.41 MHz, 23.0 °C, CD_2Cl_2): δ = 149.4, 140.0, 129.8, 128.5, 127.4, 127.0, 102.9, 97.2, 48.1 ppm. **HRMS** (ESI) calcd. for $C_{20}H_{21}N_2$ [M+H]: 289.1705, found: 289.1707.



C39

5. Gram scale experiments



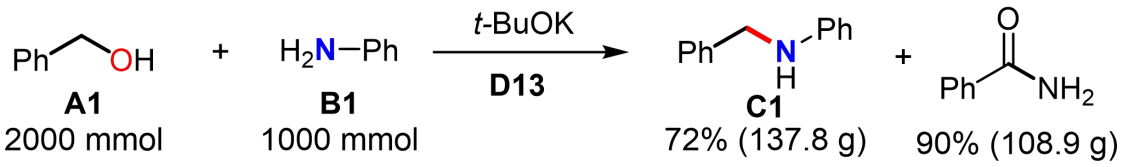
Open system:

10 mmol Scale: Using a nitrogen-filled glove box, an oven-dried Schlenk tube (250 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (16 mmol, 1.79 g), benzyl alcohol **A1** (20 mmol), aniline **B1** (10 mmol), benzonitrile (16 mmol) and 1,4-dioxane (80 mL). 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 24 hours under inert atmosphere in an open system at 120 °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. Then the corresponding reaction mixture was purified by flash column chromatography on a silica gel column (pentane/ethyl ether = 10/1) to give the desired product **C1** in 80.0 % yield (1.47 g).

100 mmol Scale:

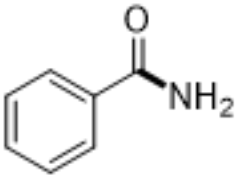
Using a nitrogen-filled glove box, an oven-dried flask (2.5 L volume) was charged with a magnetic stirring bar, *t*-BuOK (160 mol, 17.9 g), benzyl alcohol **A1** (200 mmol), aniline **B1** (100 mmol), benzonitrile (160 mmol) and 1,4-dioxane (0.5 L). The flask was sealed, taken out of the glove box and a reflux condenser was attached under argon stream. The mixture was heated to a gentle reflux for 48 hours under inert atmosphere in an open system at 120 °C (oil bath). After cooling, quenched with half-saturated brine and extracted with dichloromethane (4 x 1 L). The combined organic phase was dried over Na_2SO_4 and concentrated. Then the corresponding reaction mixture was purified by recrystallized to give the desired product **C1** (pentane/diethyl ether at the -10 ºC) in 70.99 % yield (13.01 g).

1000 mmol Scale:



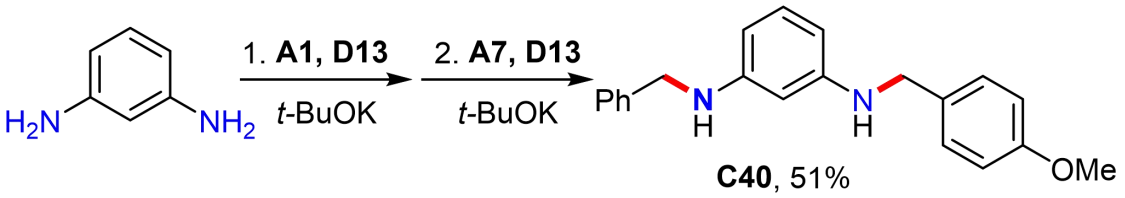
Under nitrogen, an oven-dried flask (25 L volume) was charged with a magnetic stirring bar, *t*-BuOK (1600 mol, 179 g), benzyl alcohol **A1** (2000 mmol), aniline **B1** (1000 mmol), benzonitrile (1600 mmol) and 1,4-dioxane (5 L). The flask was sealed and was put into the autoclave under argon stream. Then the mixture was stirred at 120 °C for 72 hours under inert atmosphere. After cooling, quenched with half-saturated brine and extracted with dichloromethane (4 x 1 L). The combined organic phase was dried over Na_2SO_4 and concentrated. Then the corresponding reaction mixture was purified by recrystallized three times to give the desired benzamide product (DCM/diethyl ether at 0 ºC) in 90 % yield (108.9 g).

Hereafter, the combined organic phase concentrated and was purified by recrystallized three times to give the desired amine product **C1** (diethyl ether/hexane at -30 ºC) in 72 % yield (137.8 g).



Benzamide (CAS: 55-21-0): a white solid 108.9 mg, 90% yield. **Melting Point** (°C): 127–128 °C. **^{1}H NMR** (500 MHz,, $CDCl_3$): δ = 7.82 (d, *J* = 7.3 Hz, 2H), 7.51 (d, *J* = 6.8 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 2H), 6.33 (bs, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.7, 133.4, 131.9, 128.6, 127.3, 81.6 ppm. **HRMS** (ESI) calcd. for C_7H_8NO [M+H]: 122.0606, found: 122.0608.

6. Synthesis of C40

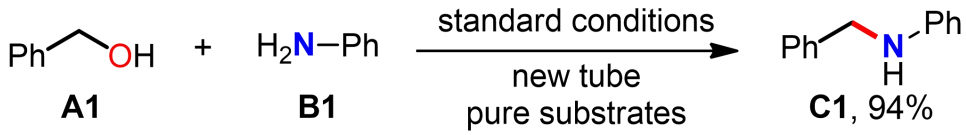


Using a nitrogen-filled glove box, an oven-dried pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (0.8 mmol), **A1** (1.0 mmol), benzene-1,3-diamine (0.6 mmol), **D13** (0.8 mmol) and 1,4-dioxane (2.0 mL). Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (120 °C). After 15 hours the reaction was cooled, **A7** (1.0 mmol), **D13** (0.8 mmol) and 1,4-dioxane (2.0 mL) were added into the reaction mixture. Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (120 °C). After another 15 hours 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 products formation. Purification of the remainder by column chromatography on silica gel gave the corresponding products **C40** (pentane/ethyl ether = 15/1 – 5/1) in the reported yield.

***N*^{1}-benzyl-*N*^{3}-(4-methoxybenzyl)benzene-1,3-diamine (C40):** The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid 83 mg, 51% yield. Purification by column chromatography on silica gel (pentane/ethyl ether = 30 : 1, DCM 3%). **^{1}H NMR** (299.86 MHz, 23.0 °C, CD_2Cl_2): δ = 7.39 (dd, *J* = 7.2, 4.1 Hz, 4H), 7.30 (d, *J* = 8.4 Hz, 3H), 7.11 – 6.79 (m, 3H), 6.05 (dd, *J* = 8.0, 2.2 Hz, 2H), 5.94 (t, *J* = 1.8 Hz, 1H), 4.31 (s, 2H), 4.23 (s, 2H), 4.04 (s, 2H), 3.82 (s, 3H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, CD_2Cl_2): δ = 158.8, 149.5, 149.4, 140.0, 131.9, 129.8, 128.7, 128.5, 128.4, 127.4 127.0, 113.8, 102.9, 102.8, 97.2, 55.2, 48.1, 47.5 ppm. **HRMS** (ESI) calcd. for $C_{21}H_{23}N_2O$ [M+H]: 319.1810, found: 319.1812.

7. Mechanistic investigations

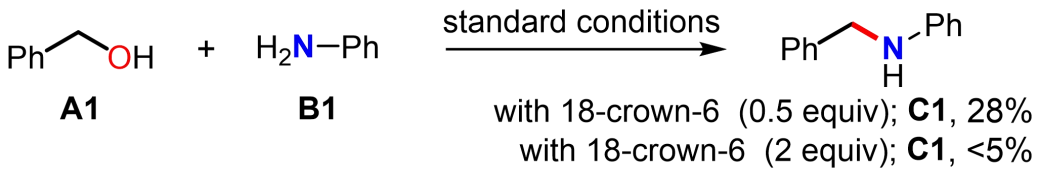
7.1 Control experiments



Entry	Reaction condition		**C1** (%)
1	New seal tube, 99.99% *t*-BuOK	-	94
2	New seal tube, 99.99% *t*-BuOK	Pure substrates	93
3	New seal tube	-	0
4	New seal tube	H_2O (0.8 mmol)	<5

Using a nitrogen-filled glove box, an oven-dried new pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (0.8 mmol), **A1** (1.0 mmol), **B1** (0.5 mmol), **D13** (0.8 mmol) and 1,4-dioxane (2.0 mL). Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (120 °C). After 15 hours 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 products formation.

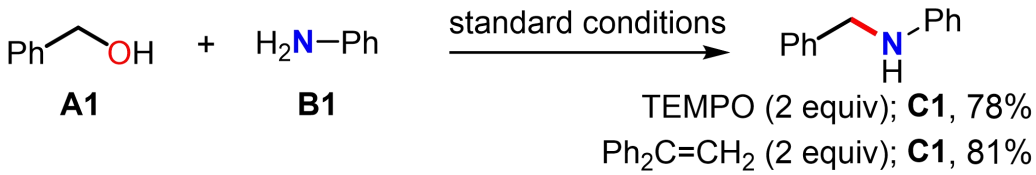
7.2 Control experiments with 18-crown-6 additive



Using a nitrogen-filled glove box, an oven-dried new pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (0.8 mmol), **A1** (1.0 mmol), **B1** (0.5 mmol), **D13** (0.8 mmol), 18-crown-6 and 1,4-dioxane (2.0 mL). Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (120 °C). After 15 hours the reaction was cooled, quenched with half-saturated brine and extracted with dichloromethane (4 x 15 mL). The combined

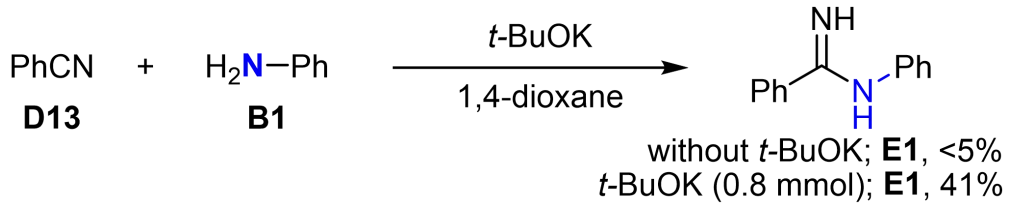
organic phase was dried over Na_2SO_4 and concentrated. A small aliquot of the organic phase was analyzed by GC or GC-MS to monitor products formation.

7.3 Control experiments with radical scavenger



Using a nitrogen-filled glove box, an oven-dried new pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (0.8 mmol), **A1** (1.0 mmol), **B1** (0.5 mmol), **D13** (0.8 mmol), additives (1.0 mmol) and 1,4-dioxane (2.0 mL). Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (120 °C). After 15 hours 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 products formation.

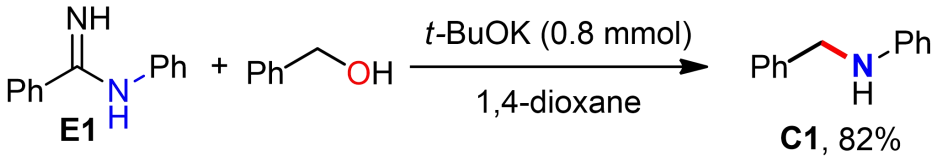
7.4 Isolated the intermediate E1



Using a nitrogen-filled glove box, an oven-dried new pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (0.8 mmol), **B1** (0.6 mmol), **D13** (0.5 mmol) and 1,4-dioxane (2.0 mL). Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (120 °C). After 15 hours 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 products formation. Purification of the remainder by column

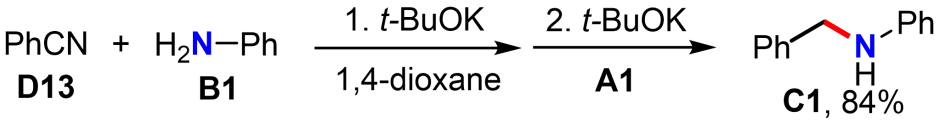
chromatography on silica gel gave the corresponding products **E1** (pentane/ethyl ether = 5/1) in the reported yield.

7.5 The reaction of E1 with alcohols



Using a nitrogen-filled glove box, an oven-dried new pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (0.8 mmol), **A1** (1.0 mmol), **E1** (0.5 mmol) and 1,4-dioxane (2.0 mL). Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (120 °C). After 15 hours 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 products formation.

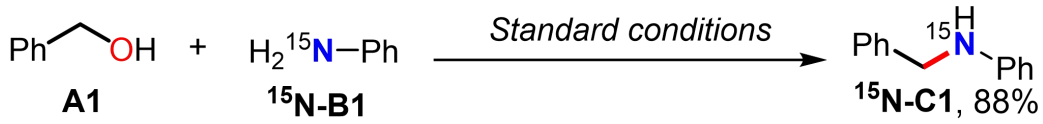
7.6 The cascade reaction



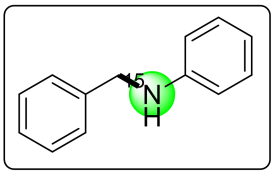
Using a nitrogen-filled glove box, an oven-dried new pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (0.8 mmol), **A1** (1.0 mmol), **B1** (0.5 mmol), **D13** (0.8 mmol) and 1,4-dioxane (2.0 mL). Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (120 °C). After 15 hours the reaction was cooled, **A1** (1.0 mmol) was added into the reaction mixture under the glove box. Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (120 °C). After 15 hours 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 products formation.

7.7 ^{15}N labeled experiment



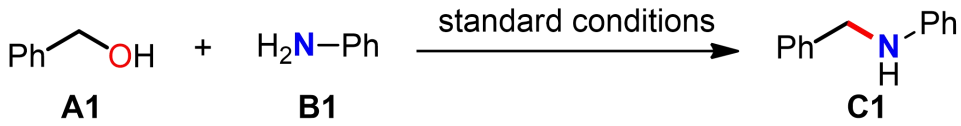
Using a nitrogen-filled glove box, an oven-dried new pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (0.4 mmol), **A1** (0.5 mmol), **^{15}N-B1** (0.25 mmol), **D13** (0.4 mmol) and 1,4-dioxane (1.0 mL). Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (120 °C). After 15 hours 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 products formation. Purification of the remainder by column chromatography on silica gel gave the corresponding products **^{15}N-C1** (pentane/ethyl ether = 15/1 – 5/1) in the reported yield.

***N*-benzylaniline (

^{15}N-C1): the light yellow oil 41.6 mg, 90% yield. **^{1}H NMR** (299.86 MHz, 23.0 °C, $CDCl_3$): δ = 7.40 – 7.14 (m, 5H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 8.1 Hz, 2H), 4.23 (s, 2H), 3.94 (bs, 1H) ppm; **^{13}C NMR** (75.41 MHz, 23.0 °C, $CDCl_3$): *δ* 148.2, 139.4, 129.2, 128.6, 127.5, 127.2, 117.5, 112.8 (d, $^{2}J_{C\text{-}15N}$ = 2.3 Hz), 48.2 (d, $^{1}J_{C\text{-}15N}$ = 2.6 Hz) ppm. **HRMS** (ESI) calcd. for [M+H]: 185.1097, found: 185.1098.

Fig S1 The HRMS of the ***N*-benzylaniline (^{15}N-C1)**

7.8 Time-conversion-plot reaction



Using a nitrogen-filled glove box, an oven-dried new pressure tube (38 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (0.8 mmol), **A1** (1.0 mmol), **B1** (0.5 mmol), **D13** (0.8 mmol) and 1,4-dioxane (2.0 mL). Then the seal tube was closed tightly with a teflon cap, removed from the glove box and immersed into a pre-heated oil bath (120 °C). After desired time the reaction was cooled, quenched with half-saturated brine and a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation. Composition of **A1**, **B1**, **D13, C1**, **E1** and benzamide determined by GC-analysis using *n*-dodecane as internal standard.

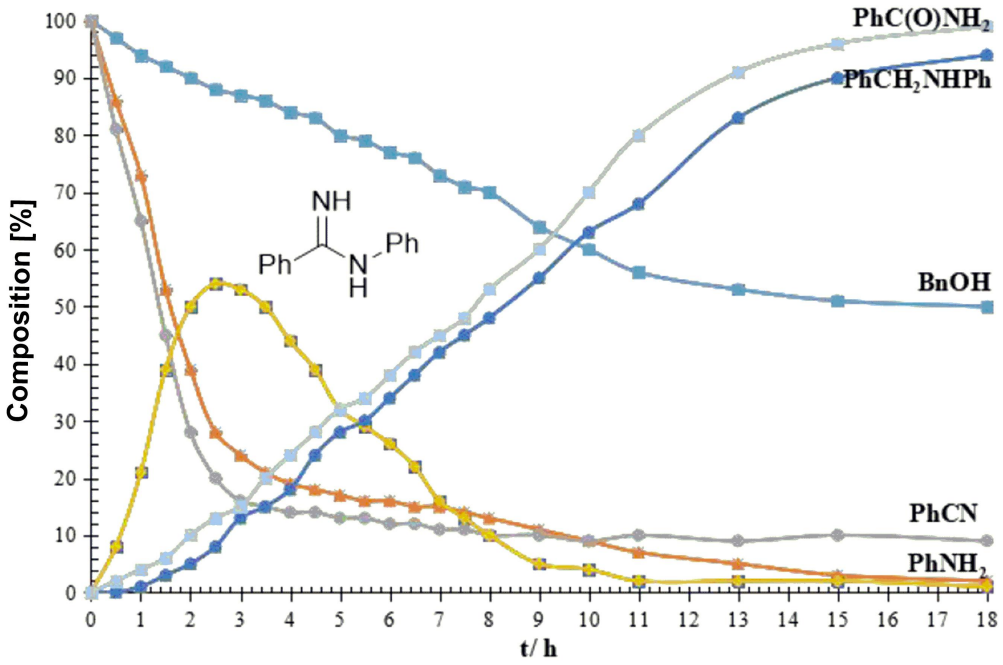
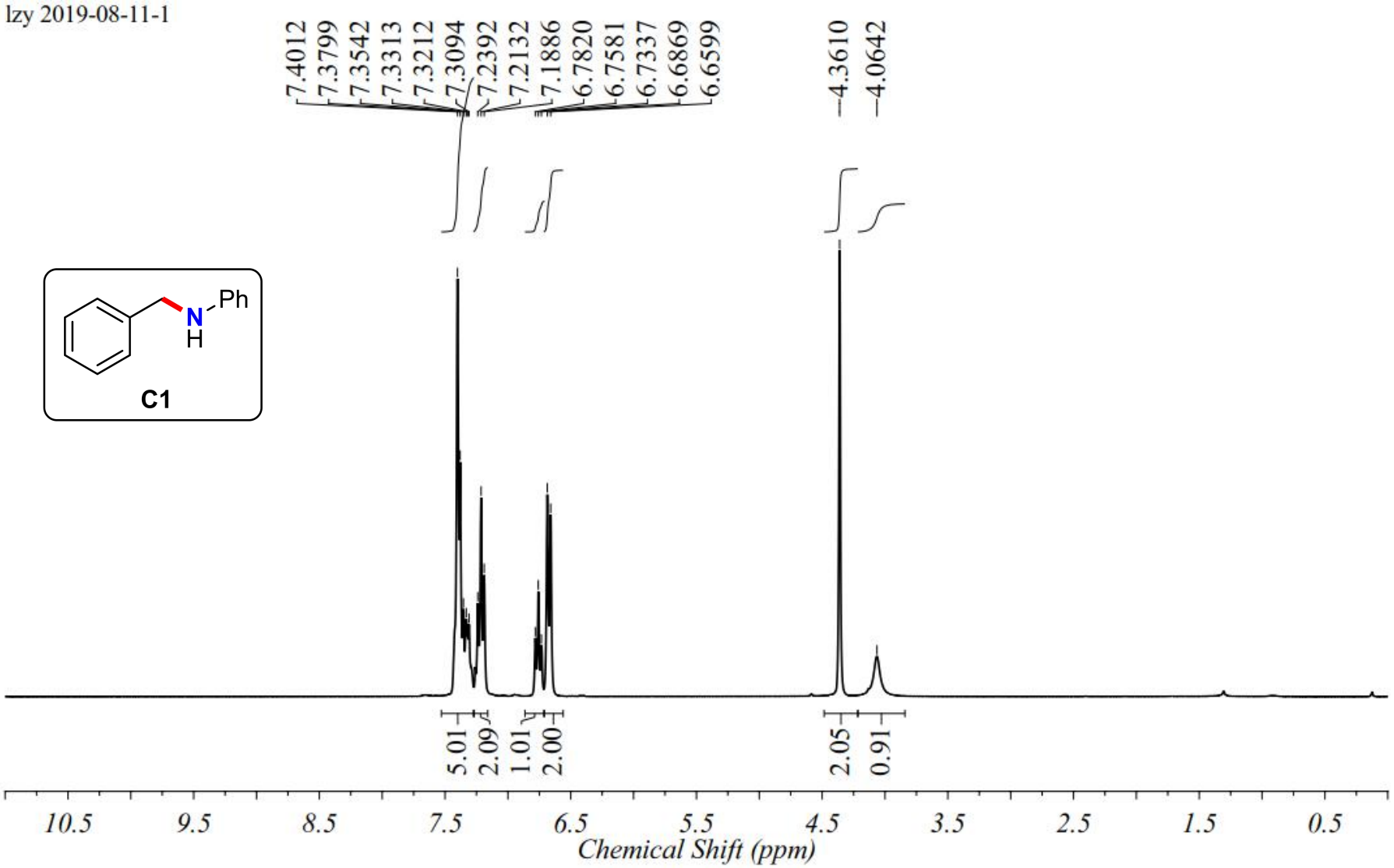


Fig S2 Time-conversion-plot for the reaction

8. References

1. (*a*) R. Fertig, T. Irrgang, F. Freitag, J. Zander and R. Kempe, *ACS Catalysis.,* 2018, **8**, 8525; (*b*) F. Freitag, T. Irrgang, R. Kempe, *J. Am. Chem. Soc.,* 2019, **141**, 11677; (*c*) M. Huang, Y. Li, Y. Li, J. Liu, S. Shu, Y. Liu and Z. Ke, *Chem. Commun.,* 2019, **55**, 6213.
2. (*a*) P. J. Wagner and L. Wang, *Org. Lett.,* 2006, **8**, 645; (*b*) Y. Wang, H. Kobayashi, K. Yamaguchi and N. Mizuno, *Chem. Commun.,* 2012, **48**, 2642; (*c*) D. Wang, H. Liu, D. Yang, P. Wang, Y. Lu and Y. Liu, *ChemCatChem.,* 2017, **9**, 4206.
3. G. Brasche and S. L. Buchwald, *Angew. Chem. Int. Ed.,* 2008, **47**, 1932.
4. U. D. Patil and P. P. Mahulikar, *ISRN Org. Chem.,* 2012, **2012**, 6.

9. NMR Spectra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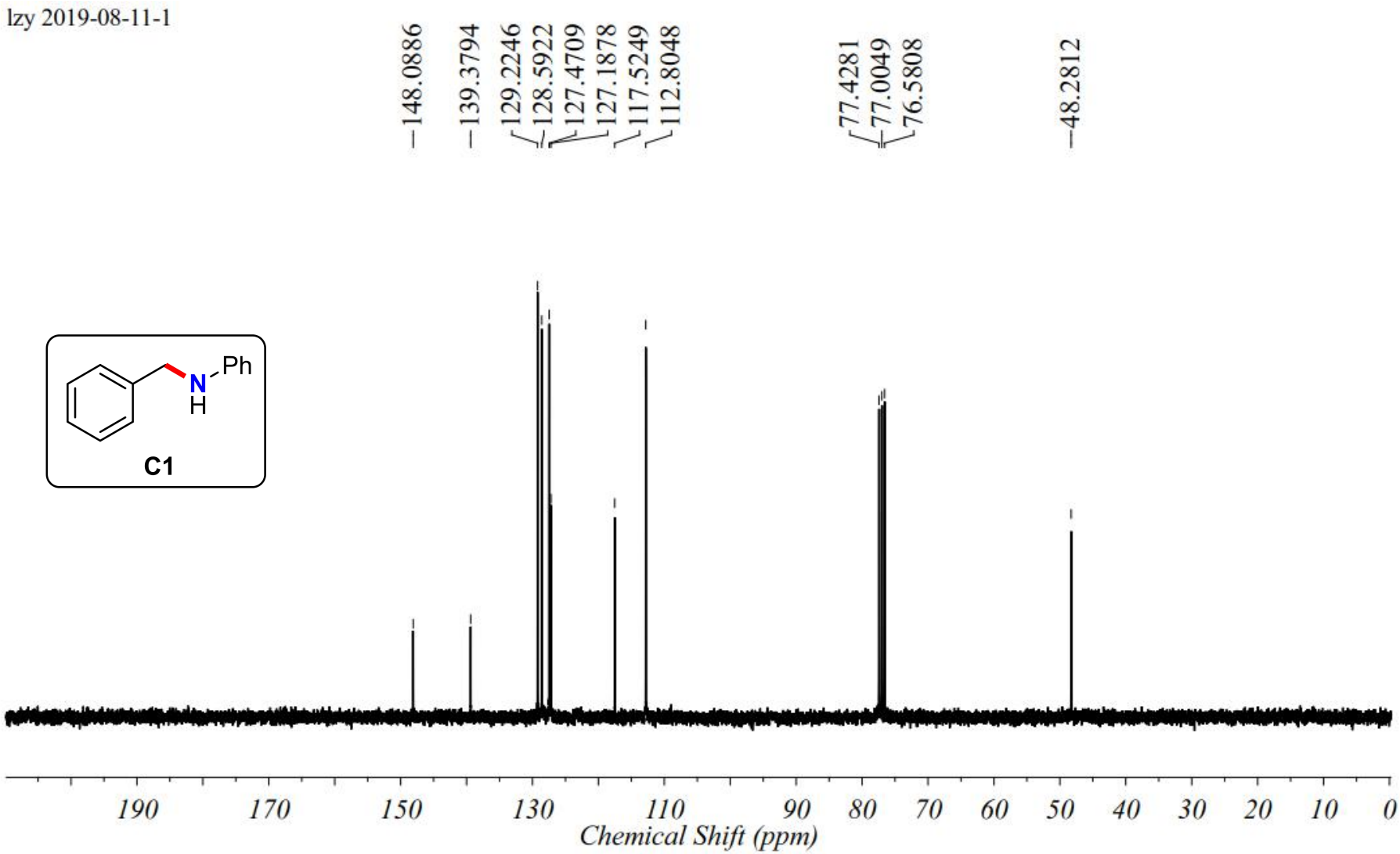
7.3799
7.3542
7.3313
7.3212
7.3094
7.2392
7.2132
7.1886
6.7820
6.7581
6.7337
6.6869
6.6599
4.3610
4.0642
N
H
Ph
C1
5.01
2.09
1.01
2.00
2.05
0.91
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)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127.1878
117.5249
112.8048
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77.0049
76.5808
48.2812
Ph
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H
C1
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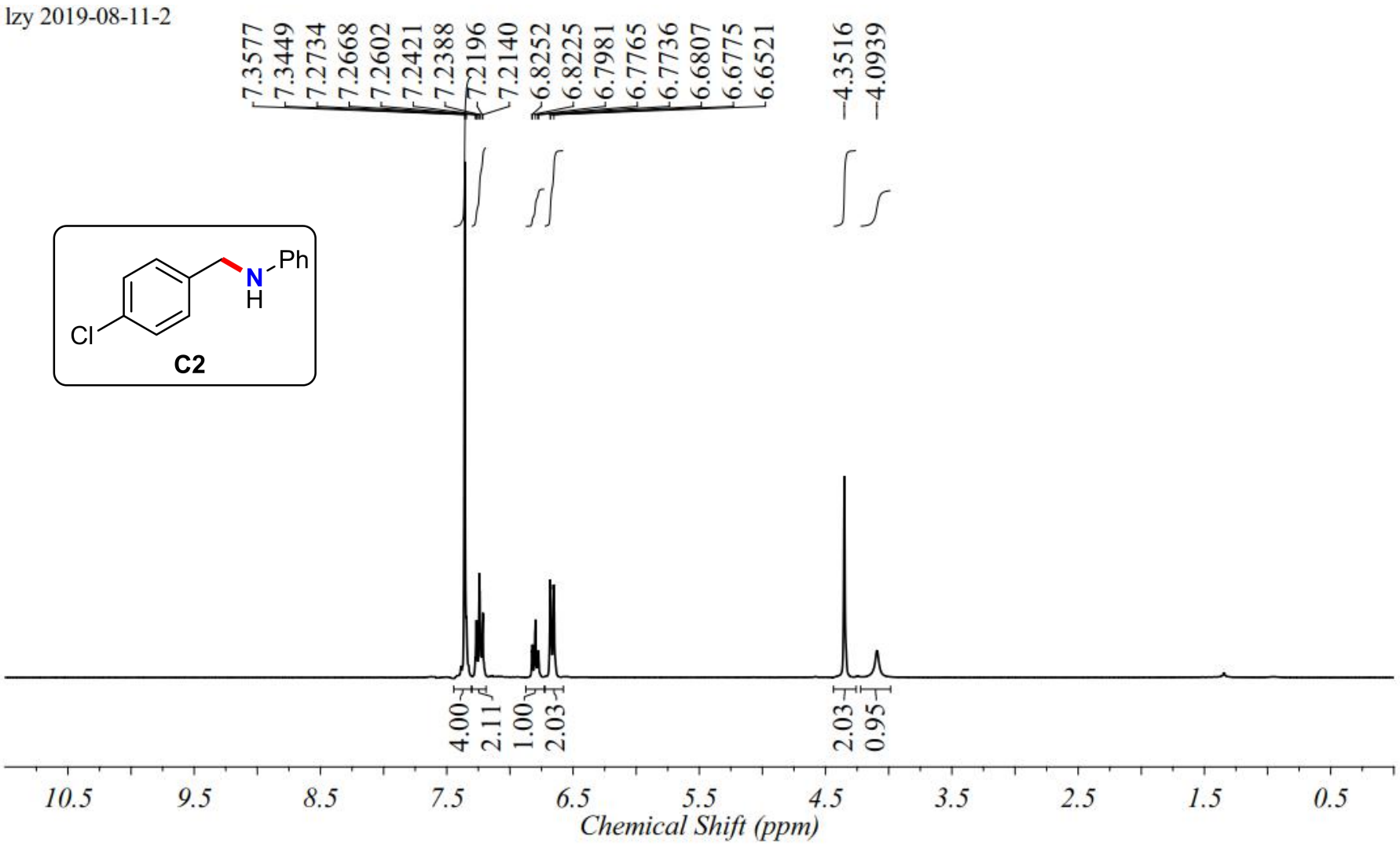
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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7.2388
7.2196
7.2140
6.8252
6.8225
6.7981
6.7765
6.7736
6.6807
6.6775
6.6521
4.3516
4.0939
Ph
N
H
Cl
C2
4.00
2.11
1.00
2.03
2.03
0.95
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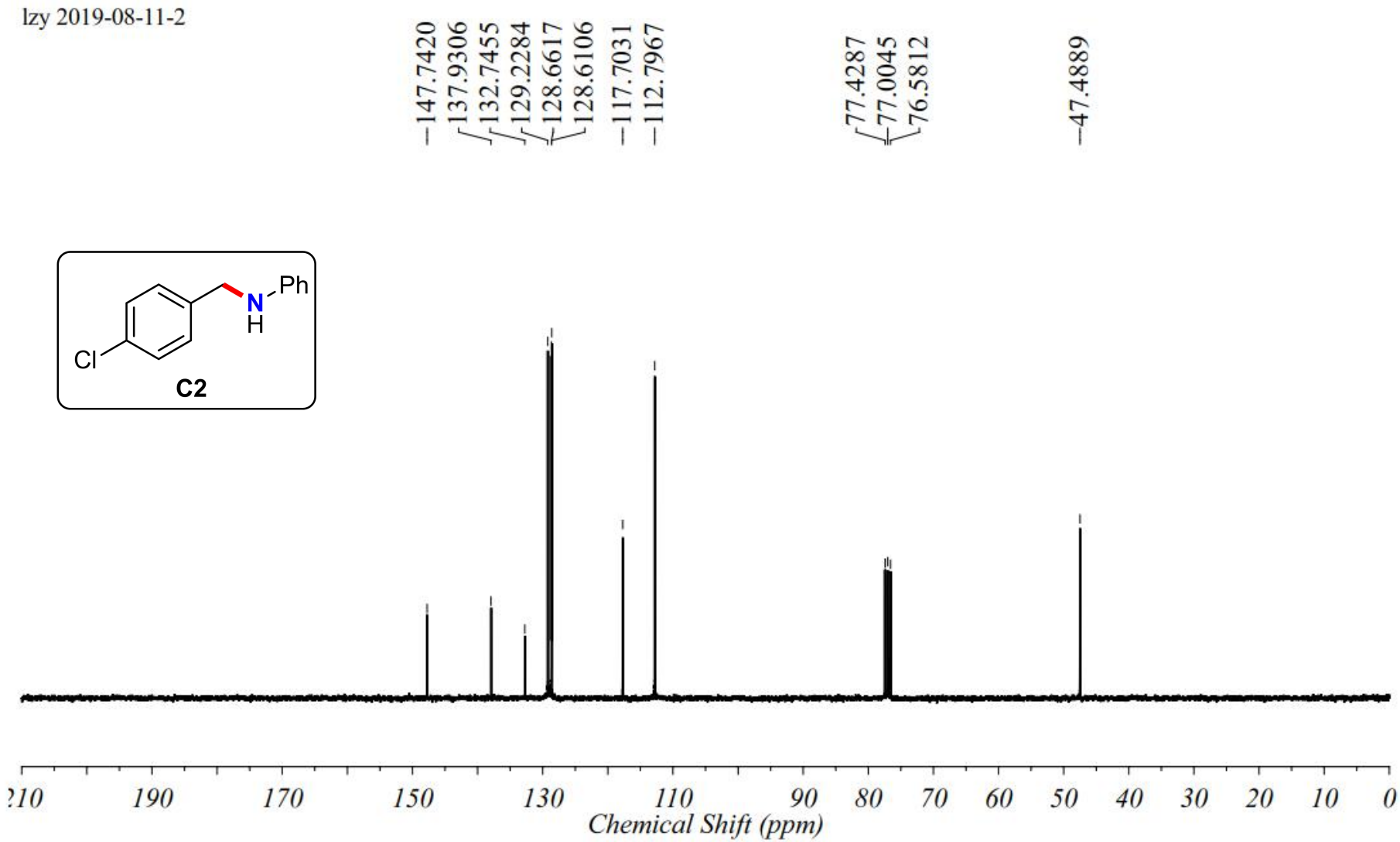
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)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128.6106
117.7031
112.7967
77.4287
77.0045
76.5812
47.4889
Ph
N
H
Cl
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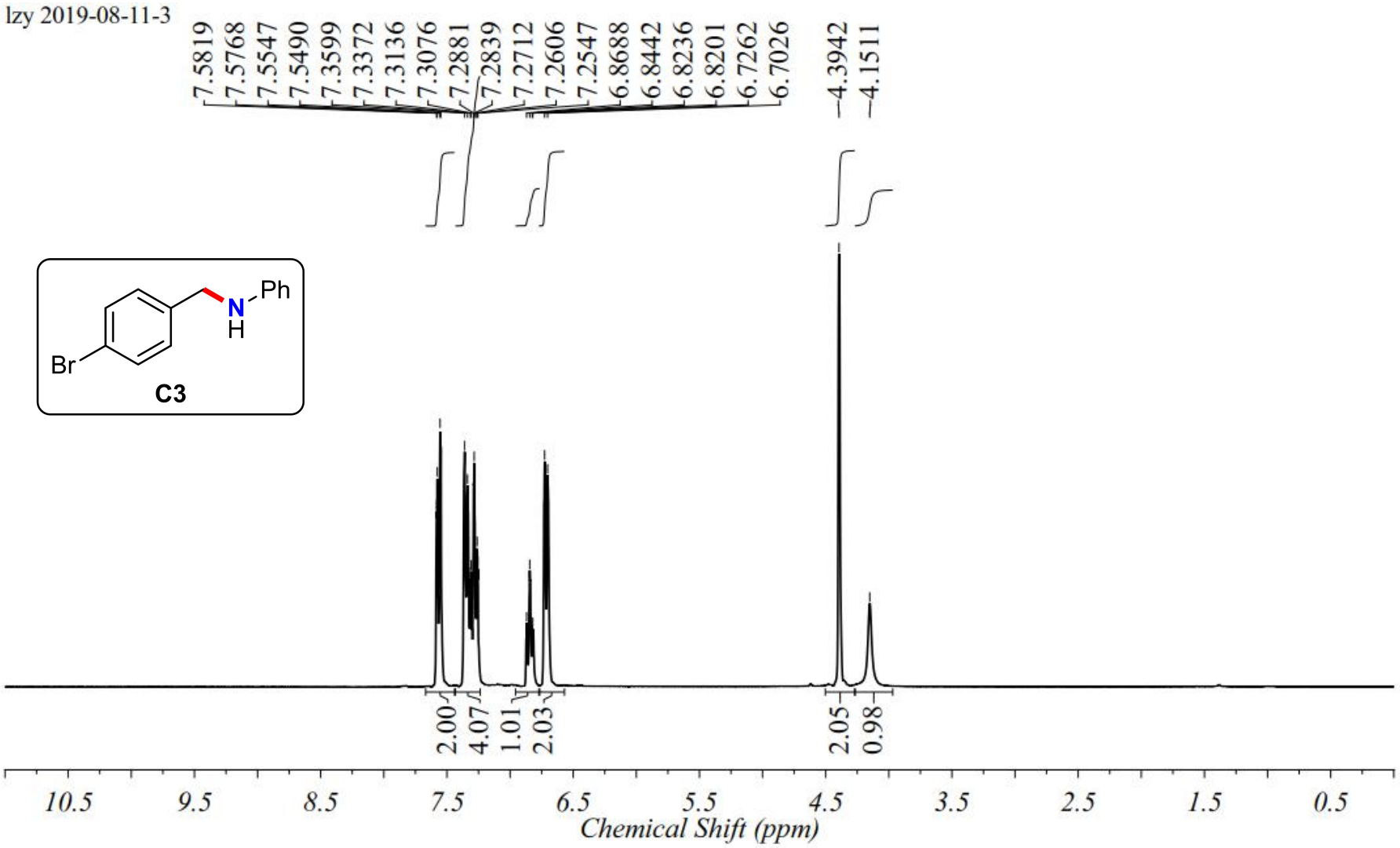
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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7.5768
7.5547
7.5490
7.3599
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7.3136
7.3076
7.2881
7.2839
7.2712
7.2606
7.2547
6.8688
6.8442
6.8236
6.8201
6.7262
6.7026
4.3942
4.1511
Ph
N
H
Br
C3
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4.07
1.01
2.03
2.05
0.98
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

lzy 2019-08-11-3

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138.5030
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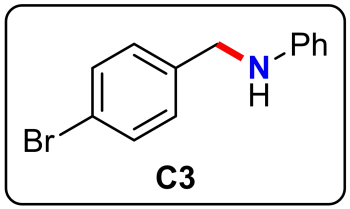
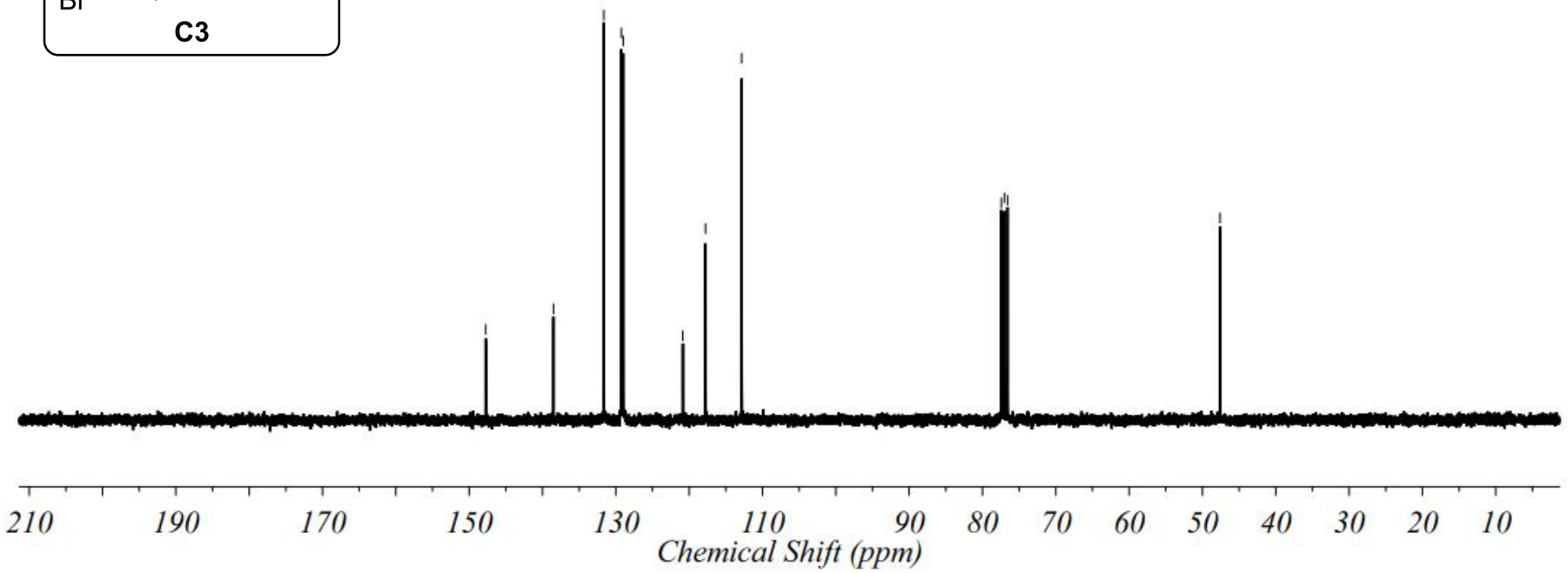
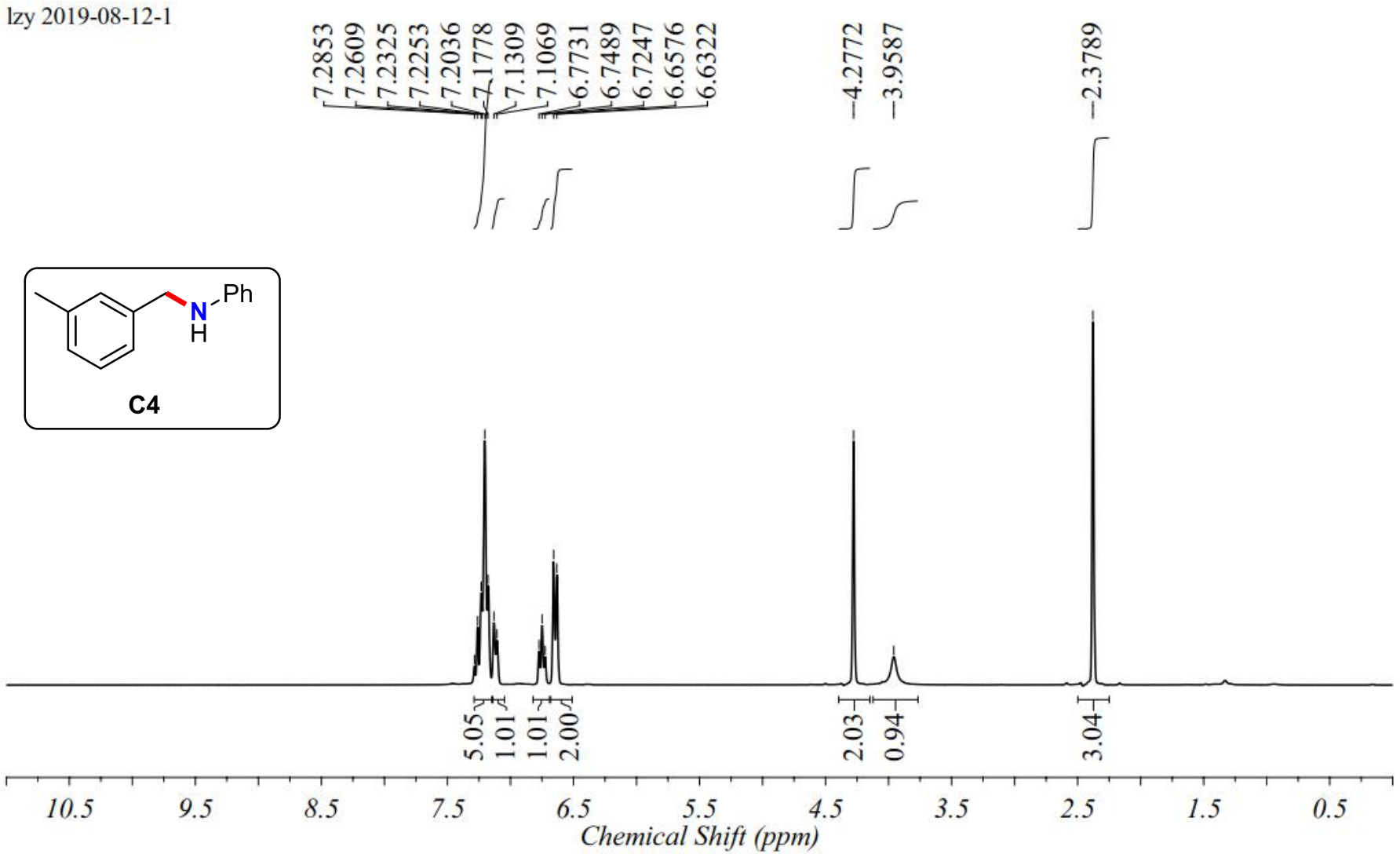
76.5805
47.5985



C3

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6.7731
6.7489
6.7247
6.6576
6.6322
4.2772
3.9587
2.3789
Ph
N
H
C4
5.05
1.01
1.01
2.00
2.03
0.94
3.04
10.5
9.5
8.5
7.5
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4.5
3.5
2.5
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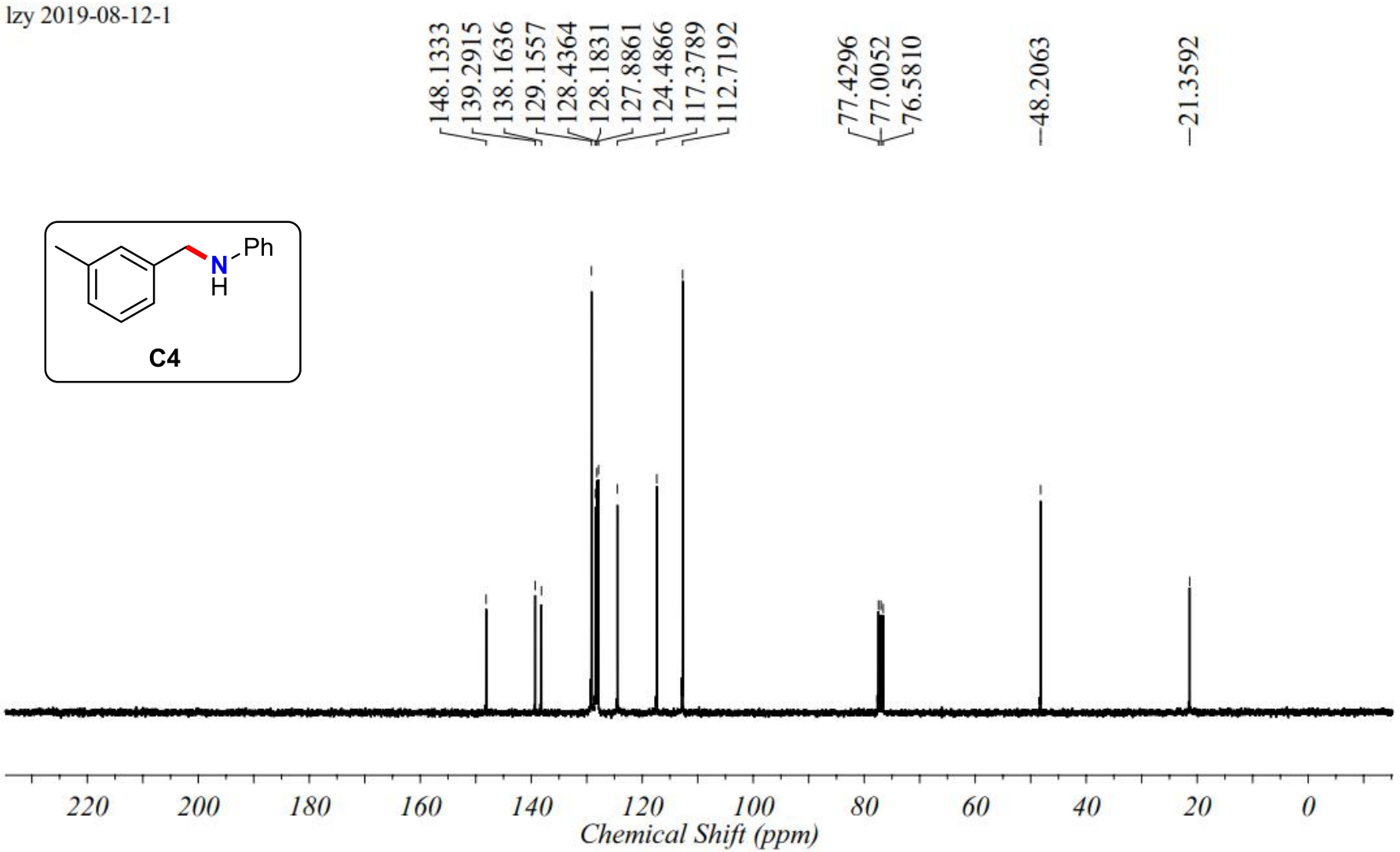
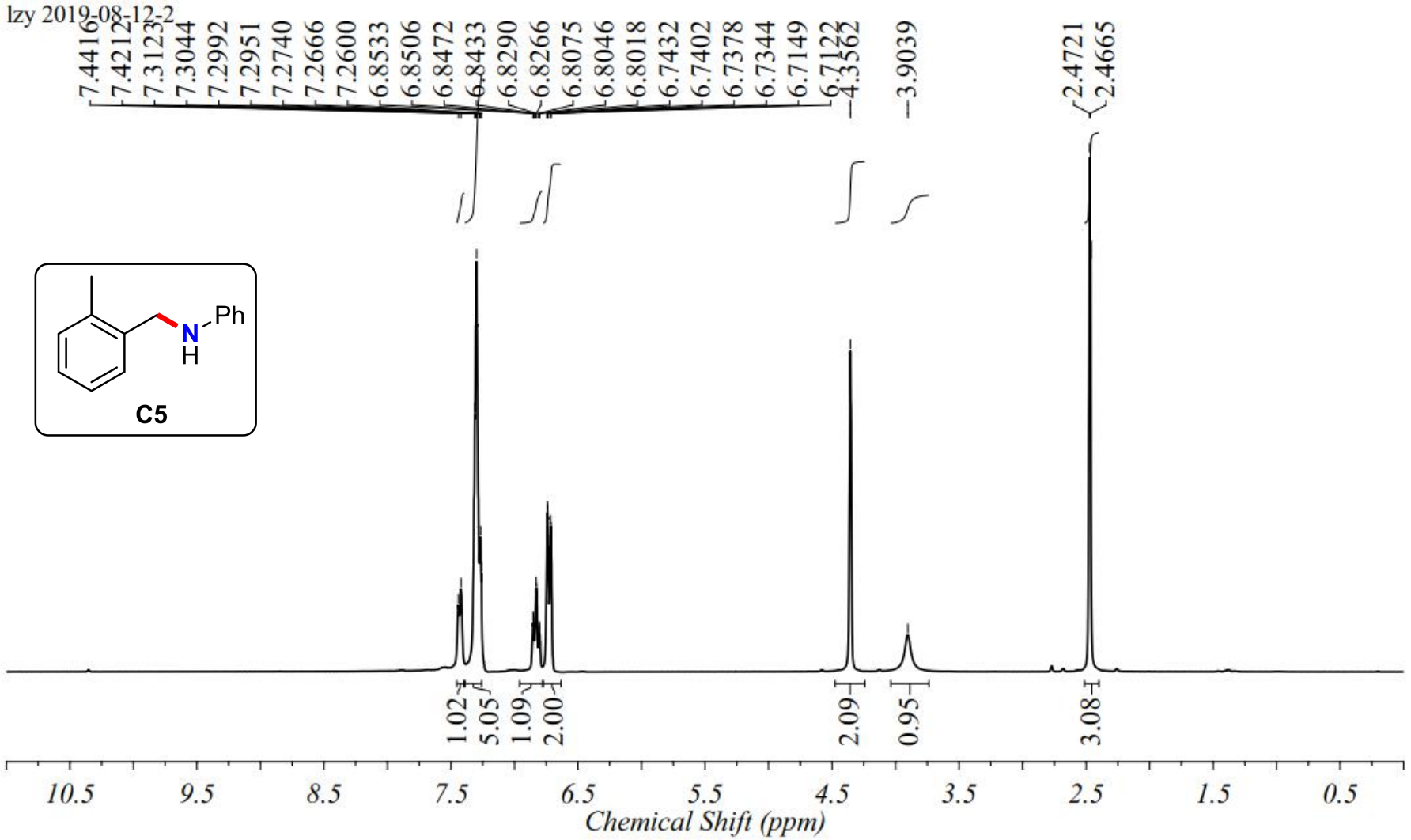
Chemical Shift (ppm)

lzy 2019-08-12-1

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6.8506
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6.7402
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6.7149
6.7122
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Ph
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H
C5
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9.5
8.5
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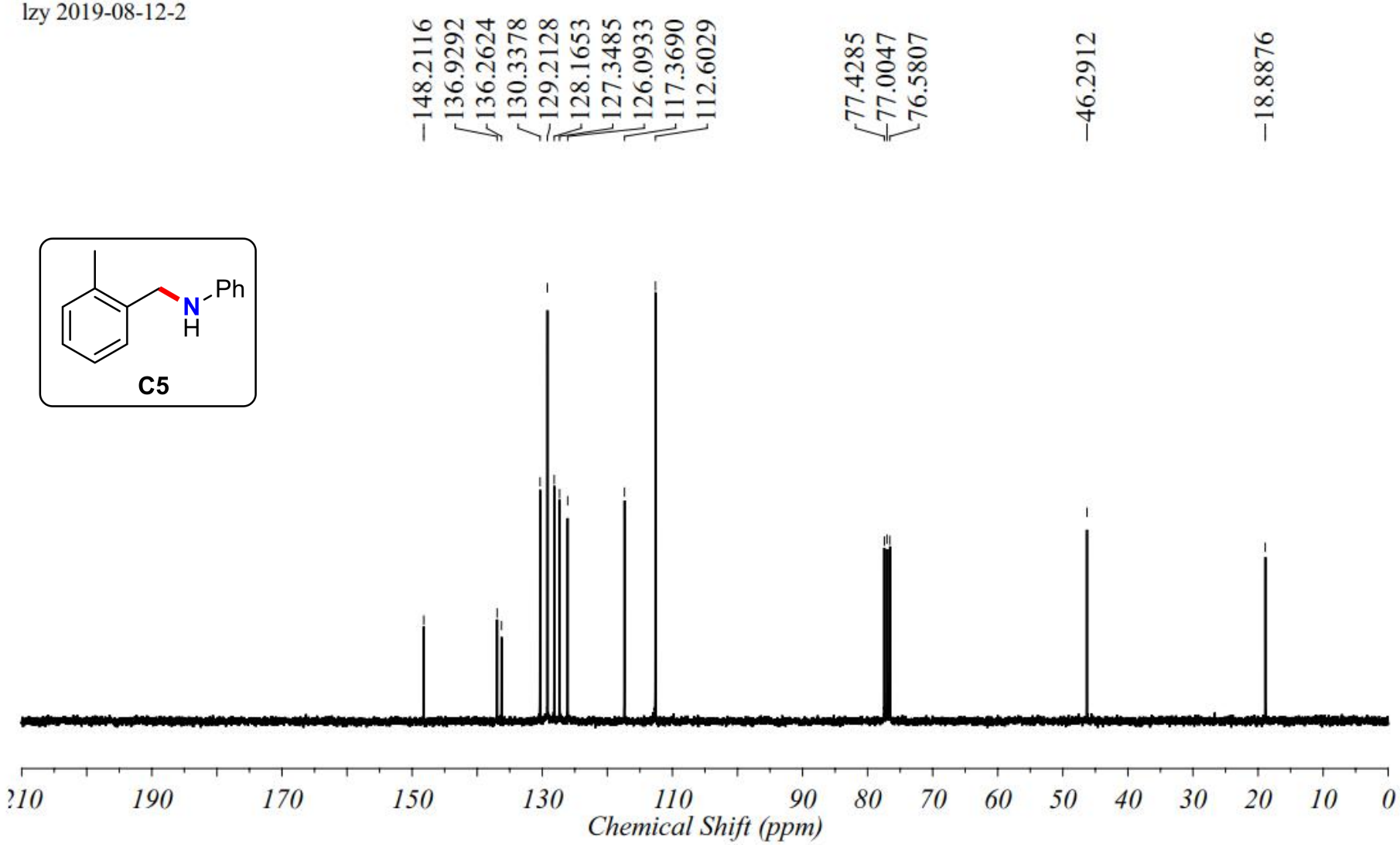
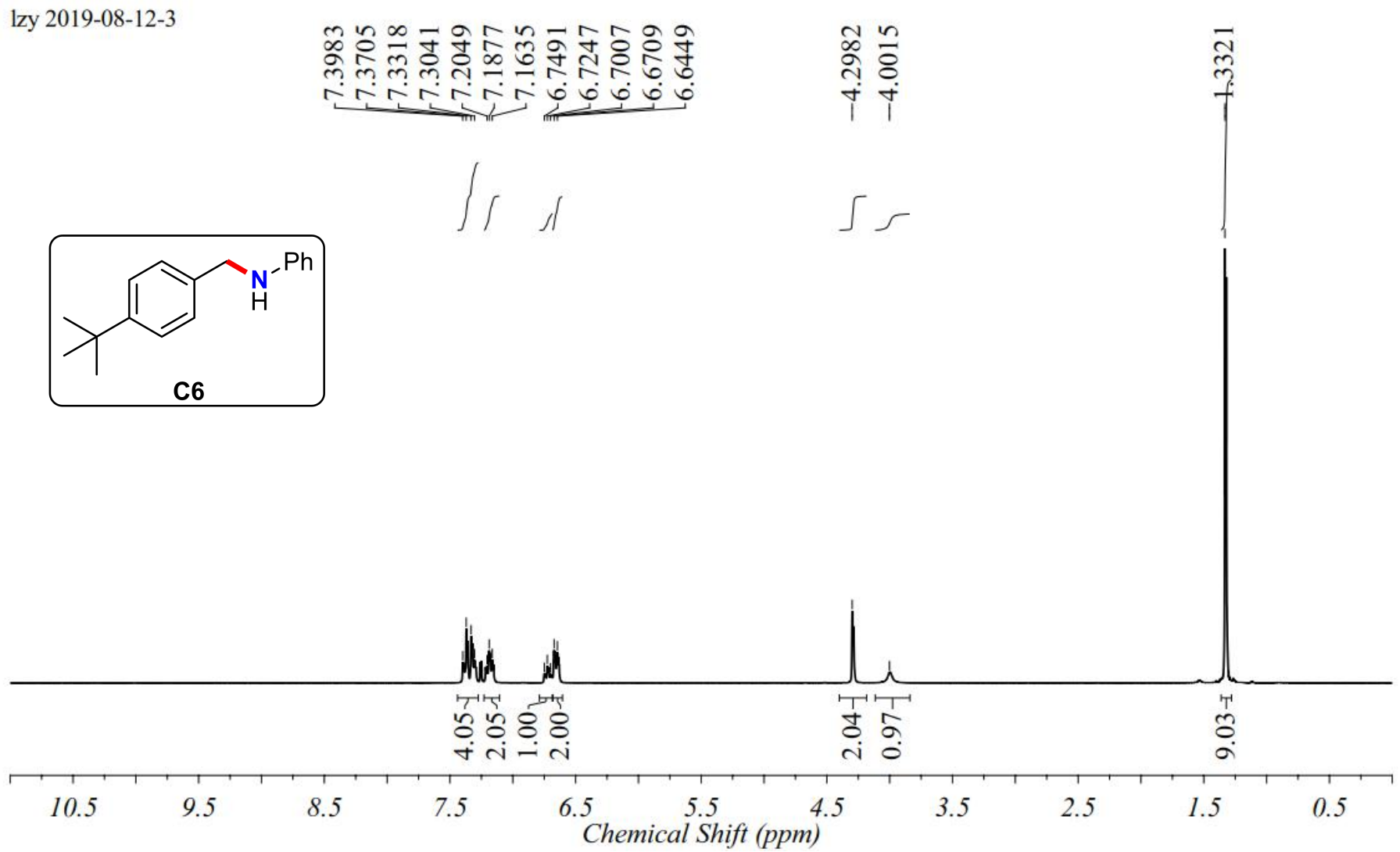
0.5
Chemical Shift (ppm)

lzy 2019-08-12-2

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6.7007
6.6709
6.6449
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4.0015
1.3321
Ph
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H
C6
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1.00
2.00
2.04
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9.03
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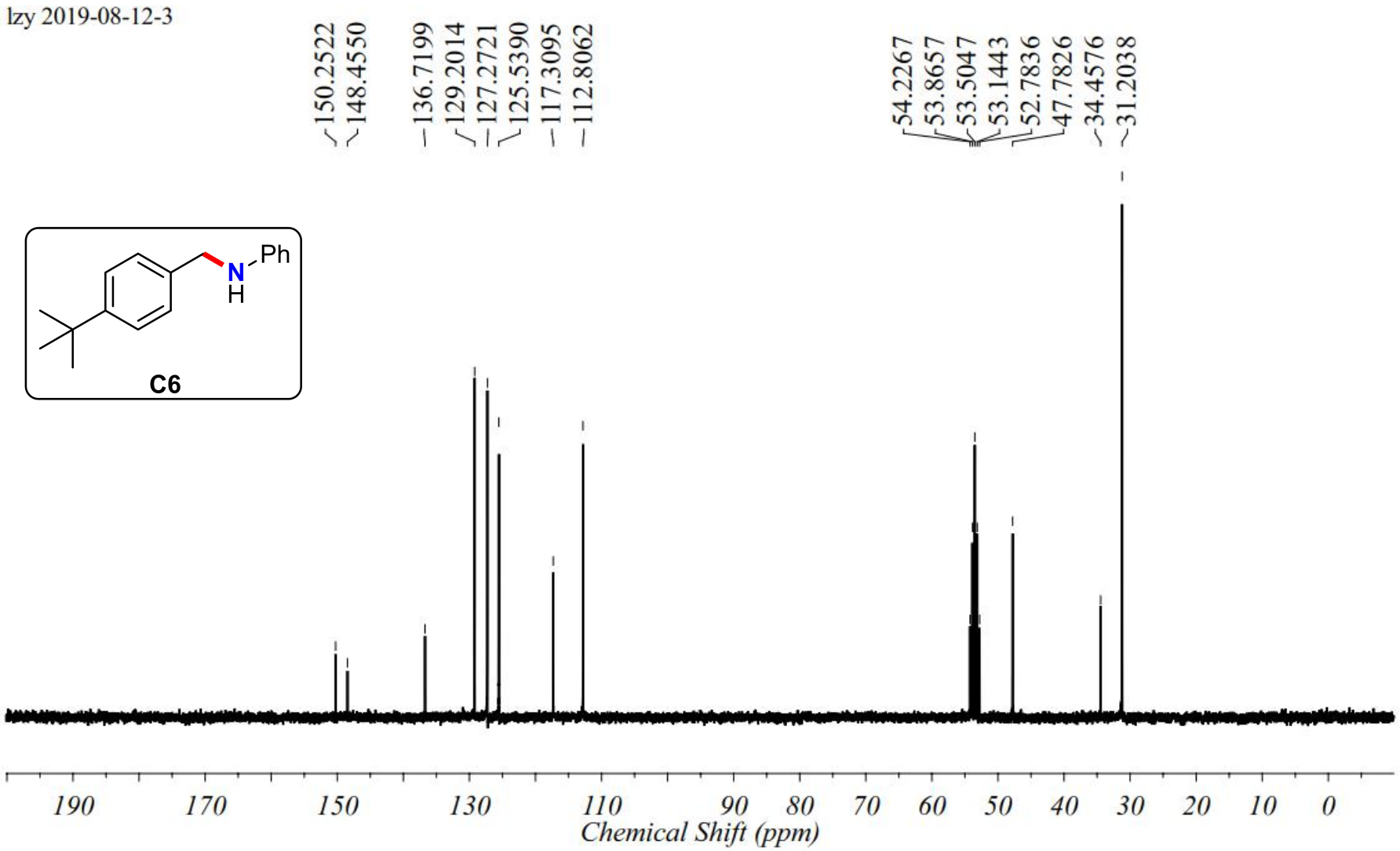
2.5
1.5
0.5
Chemical Shift (ppm)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53.8657
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31.2038
Ph
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C6
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130
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90
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70
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50
40
30
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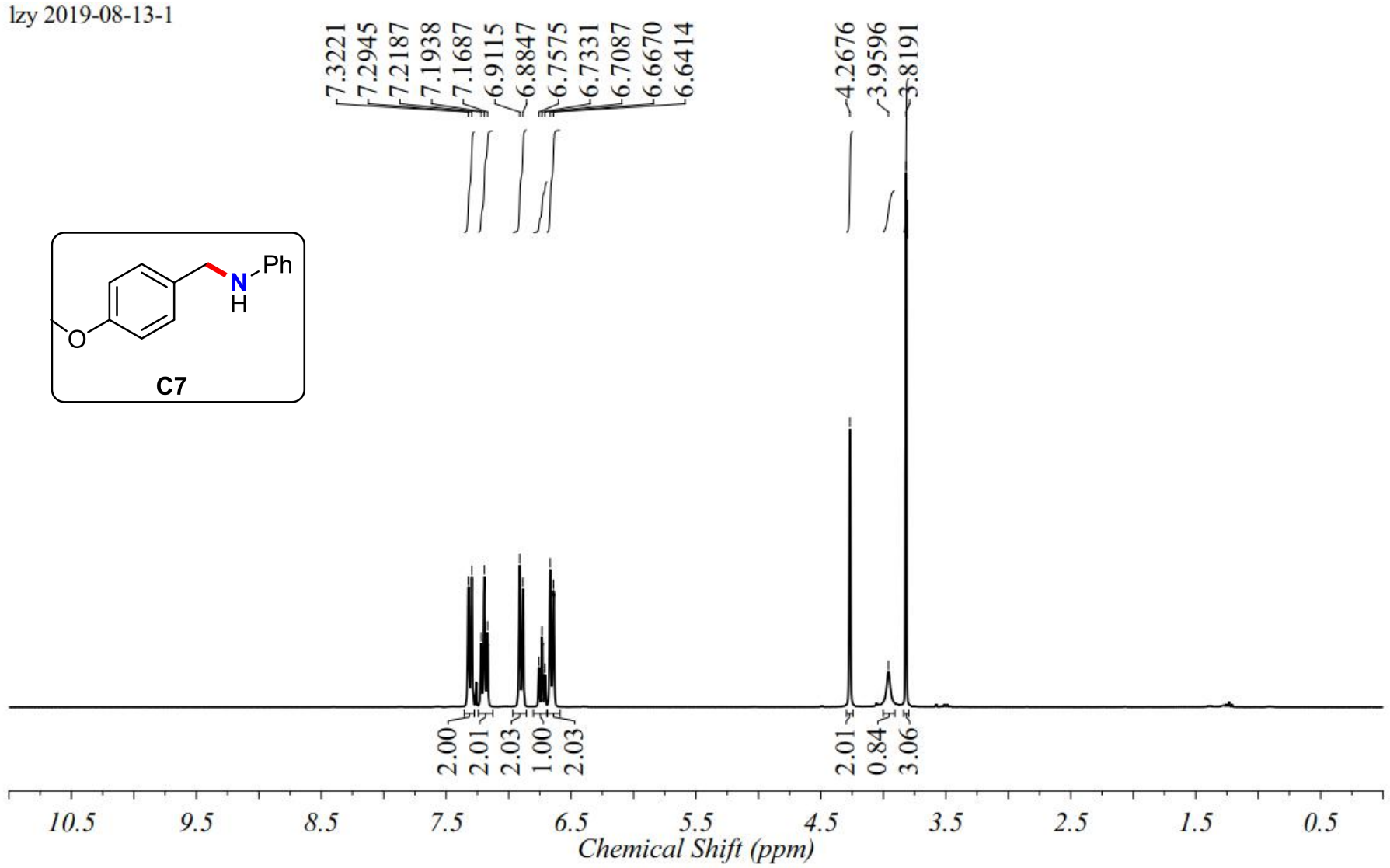
0
Chemical Shift (ppm)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3.9596
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Ph
O
C7
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1.00
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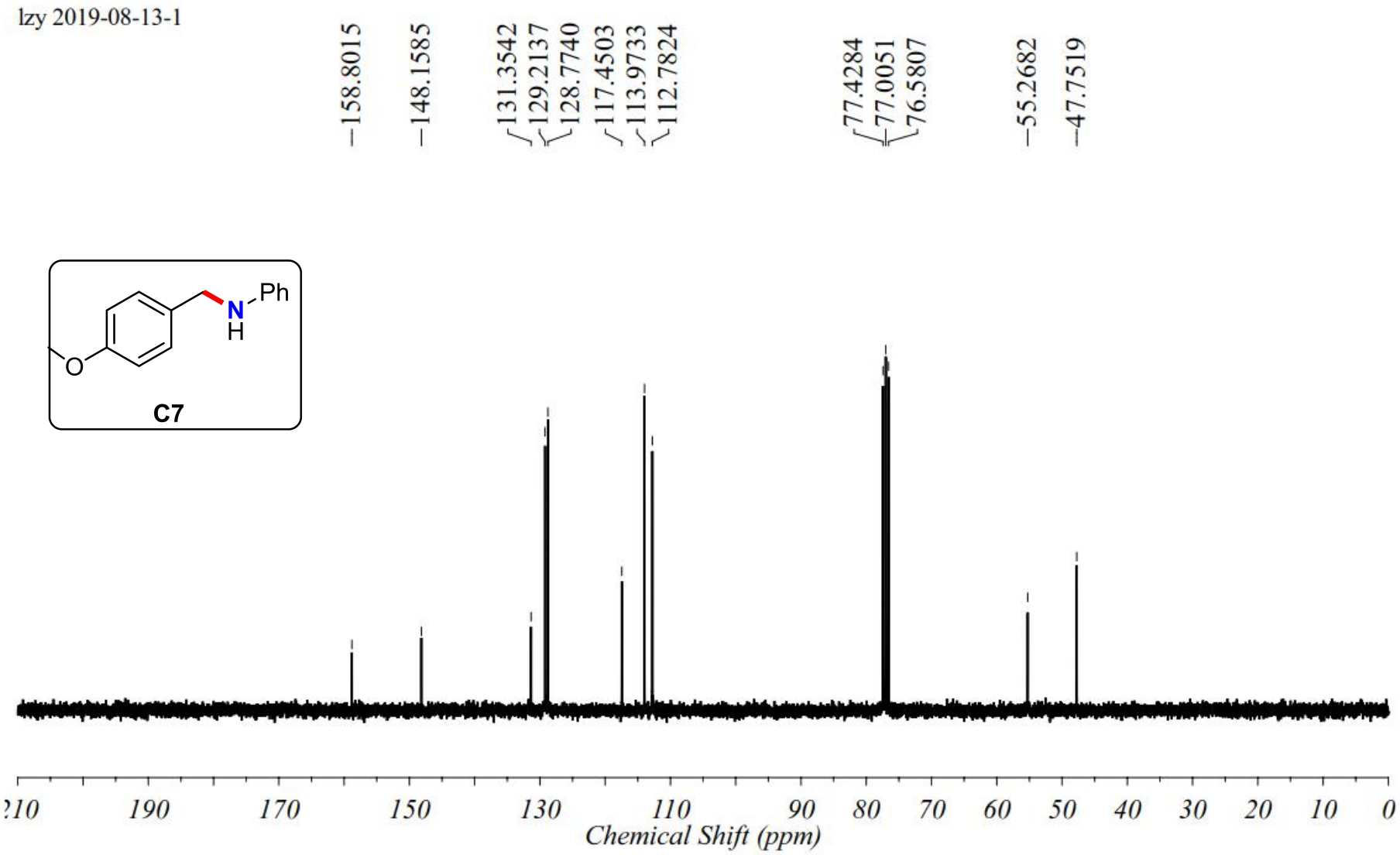
Chemical Shift (ppm)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Ph
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H
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40
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10
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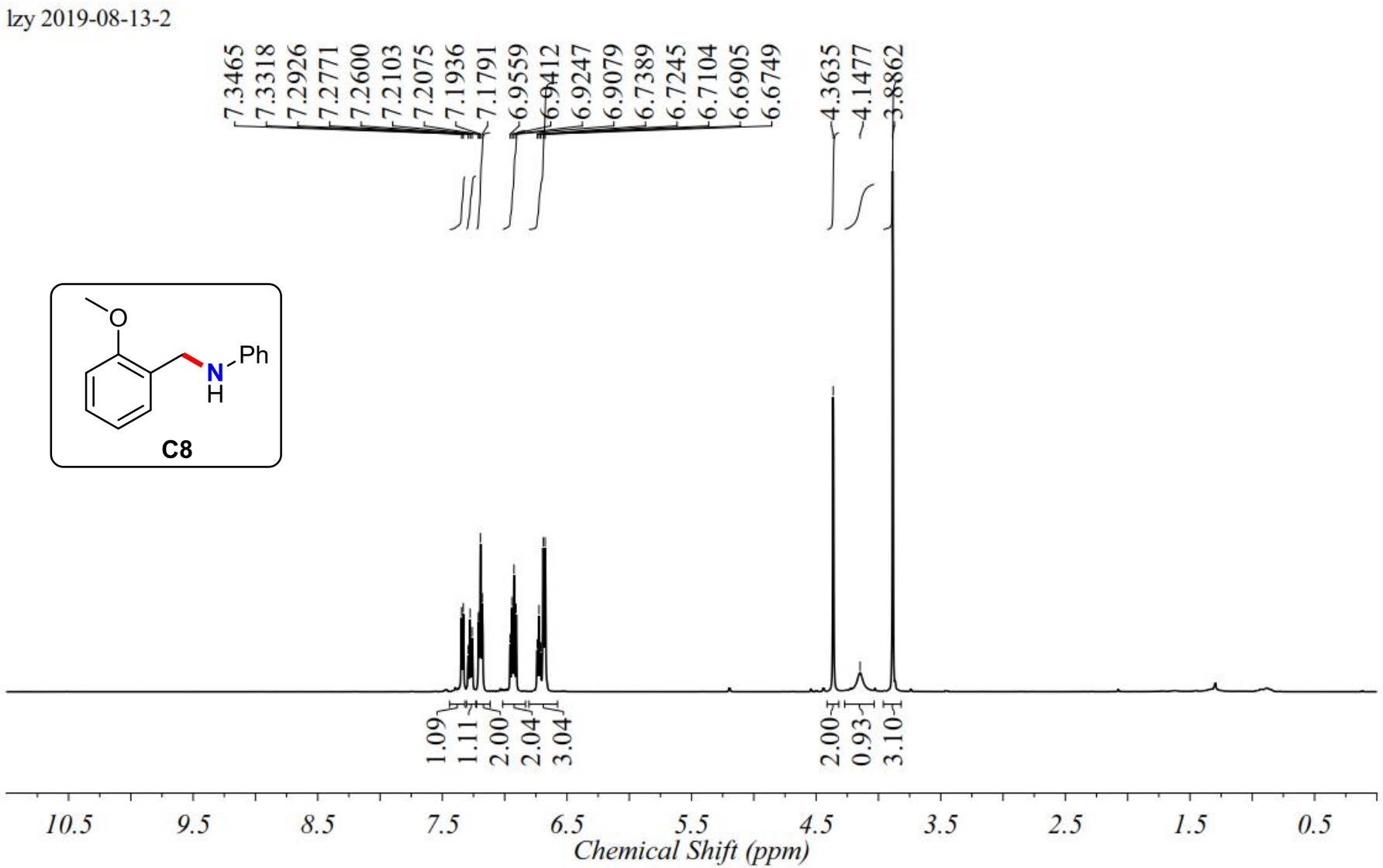
Chemical Shift (ppm)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H
Ph
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3.04
2.00
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3.10
10.5
9.5
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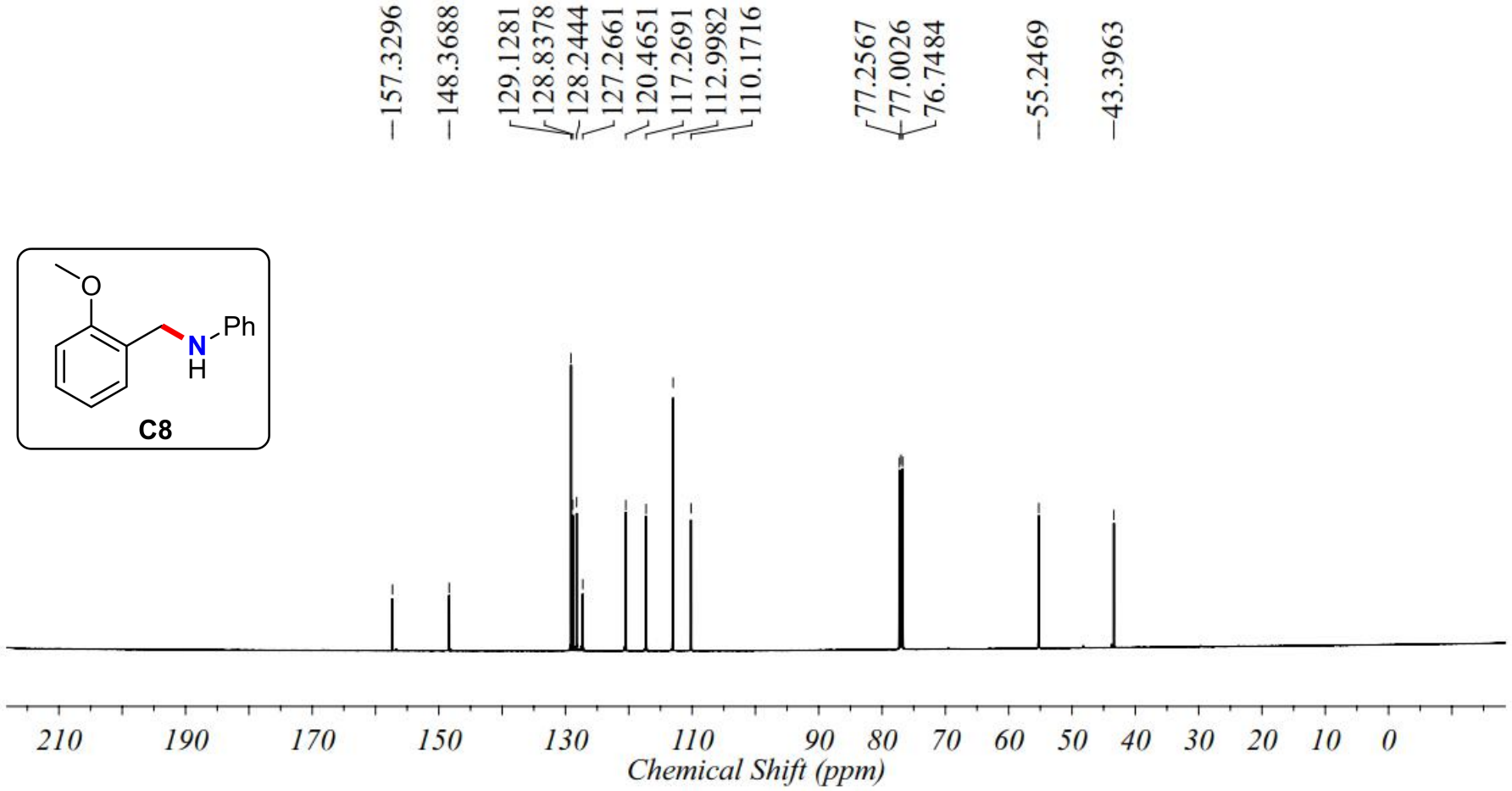
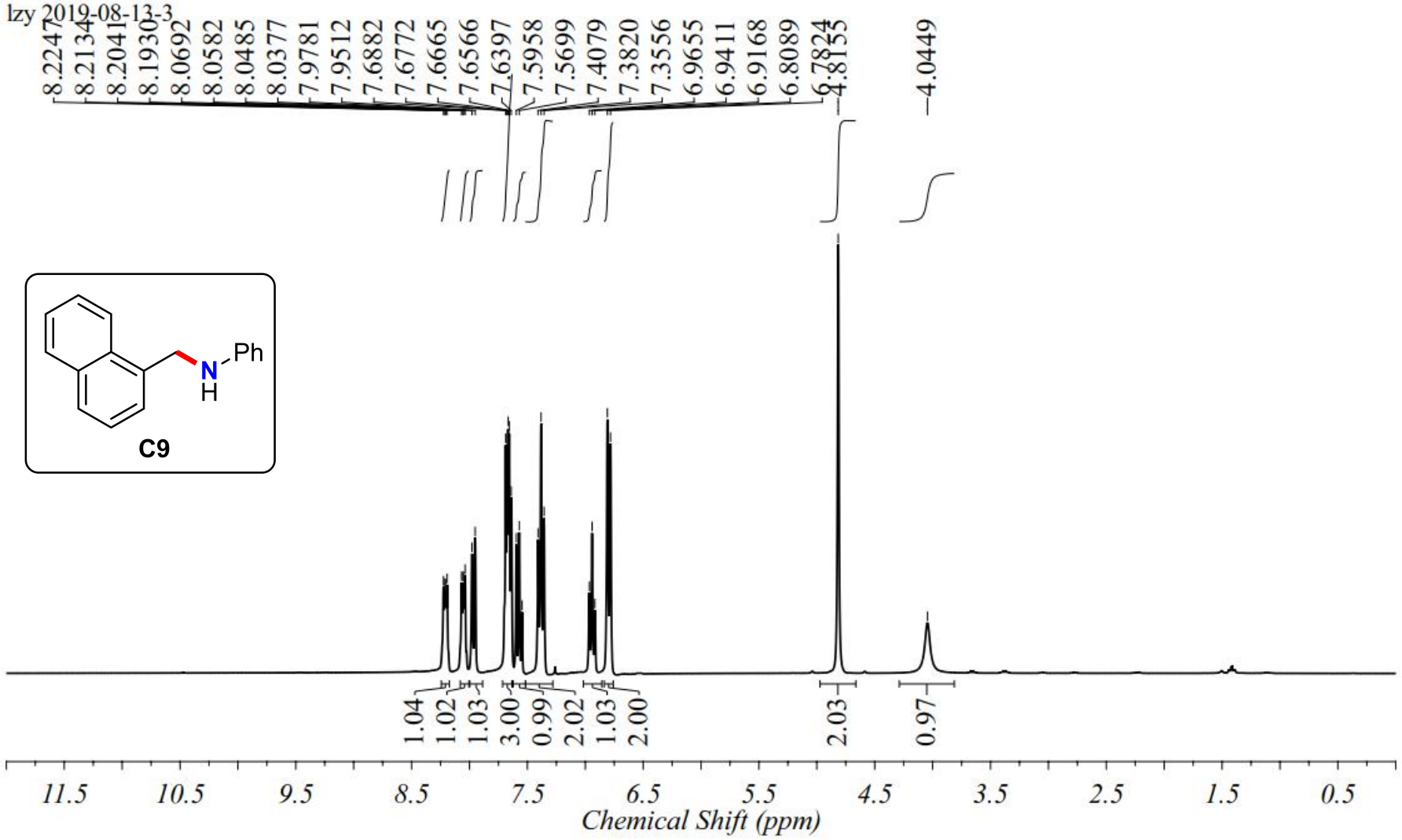
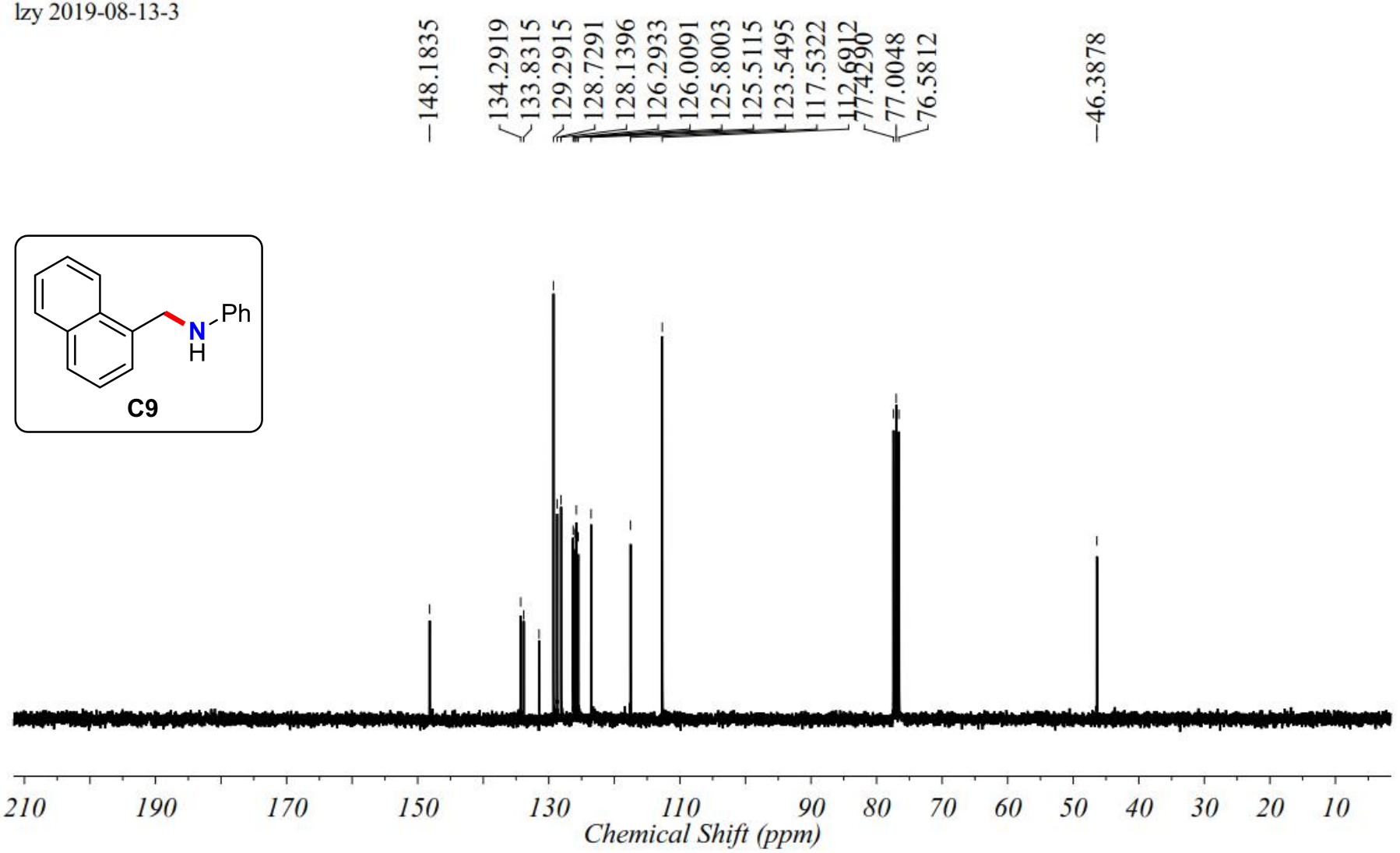
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

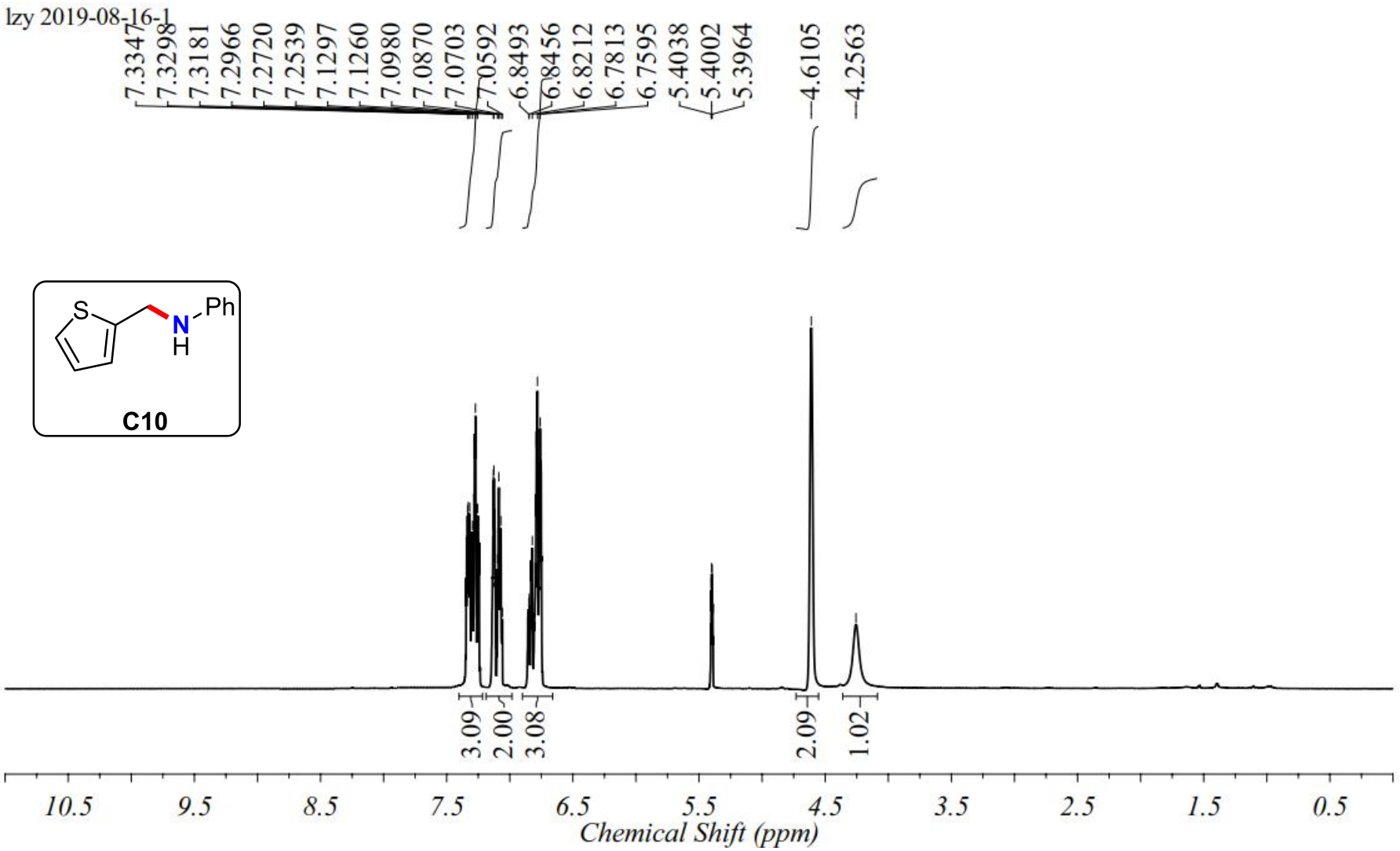
lzy 2019-08-13-2

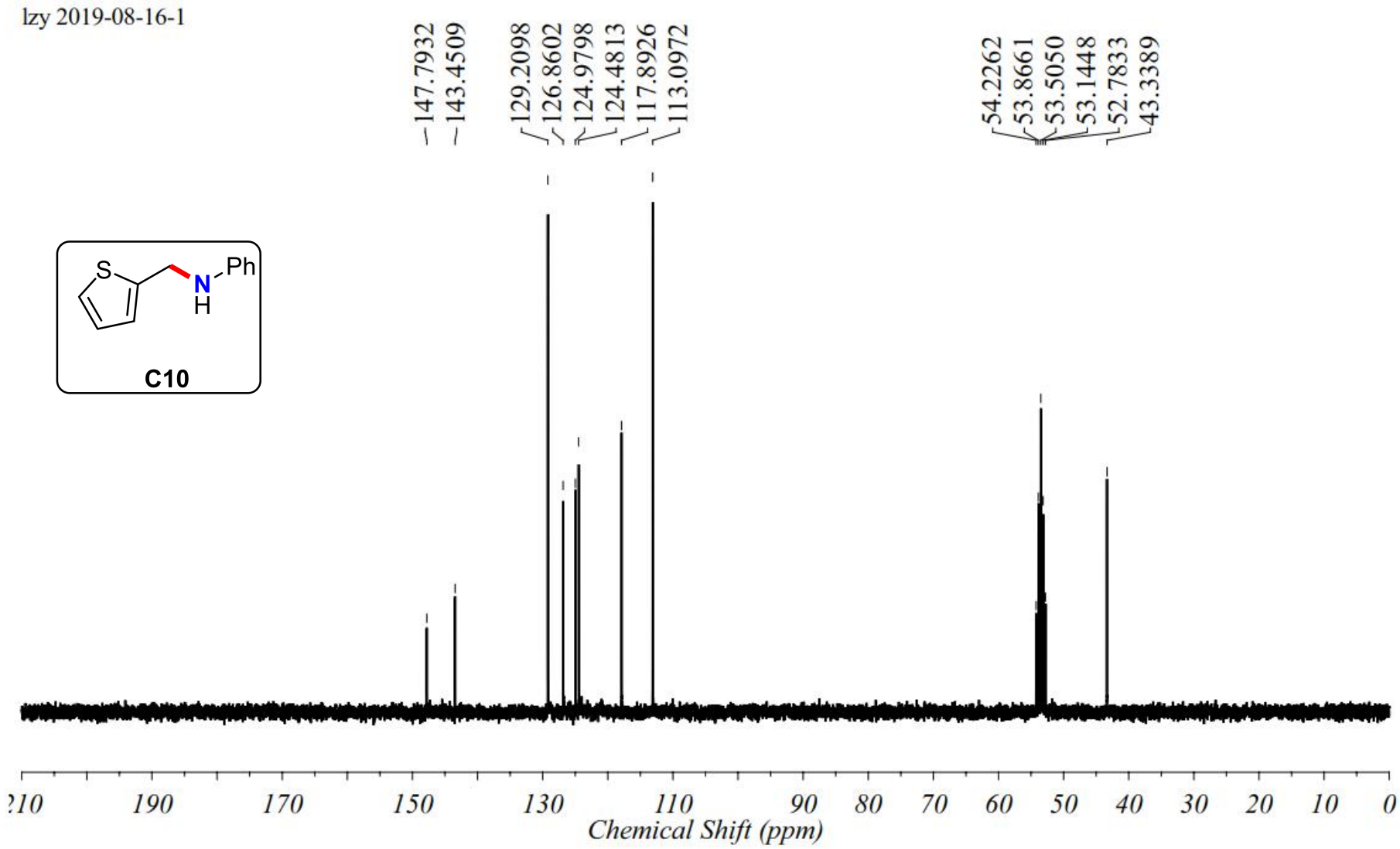


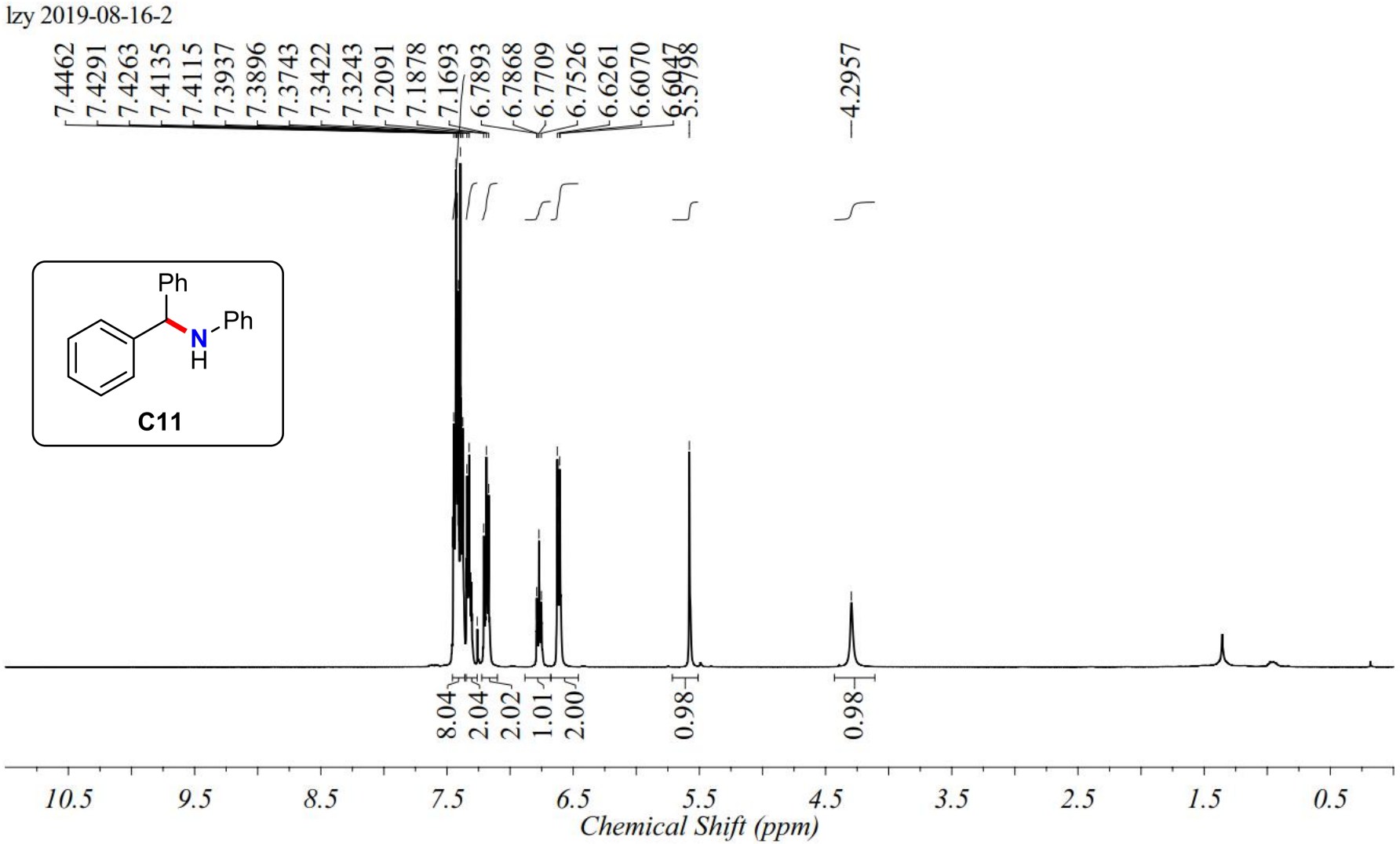

lzy 2019-08-13-3
8.2247
8.2134
8.2041
8.1930
8.0692
8.0582
8.0485
8.0377
7.9781
7.9512
7.6882
7.6772
7.6665
7.6566
7.6397
7.5958
7.5699
7.4079
7.3820
7.3556
6.9655
6.9411
6.9168
6.8089
6.7824
4.8155
4.0449
Ph
N
H
C9
1.04
1.02
1.03
3.00
0.99
2.02
1.03
2.00
2.03
0.97
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

lzy 2019-08-13-3

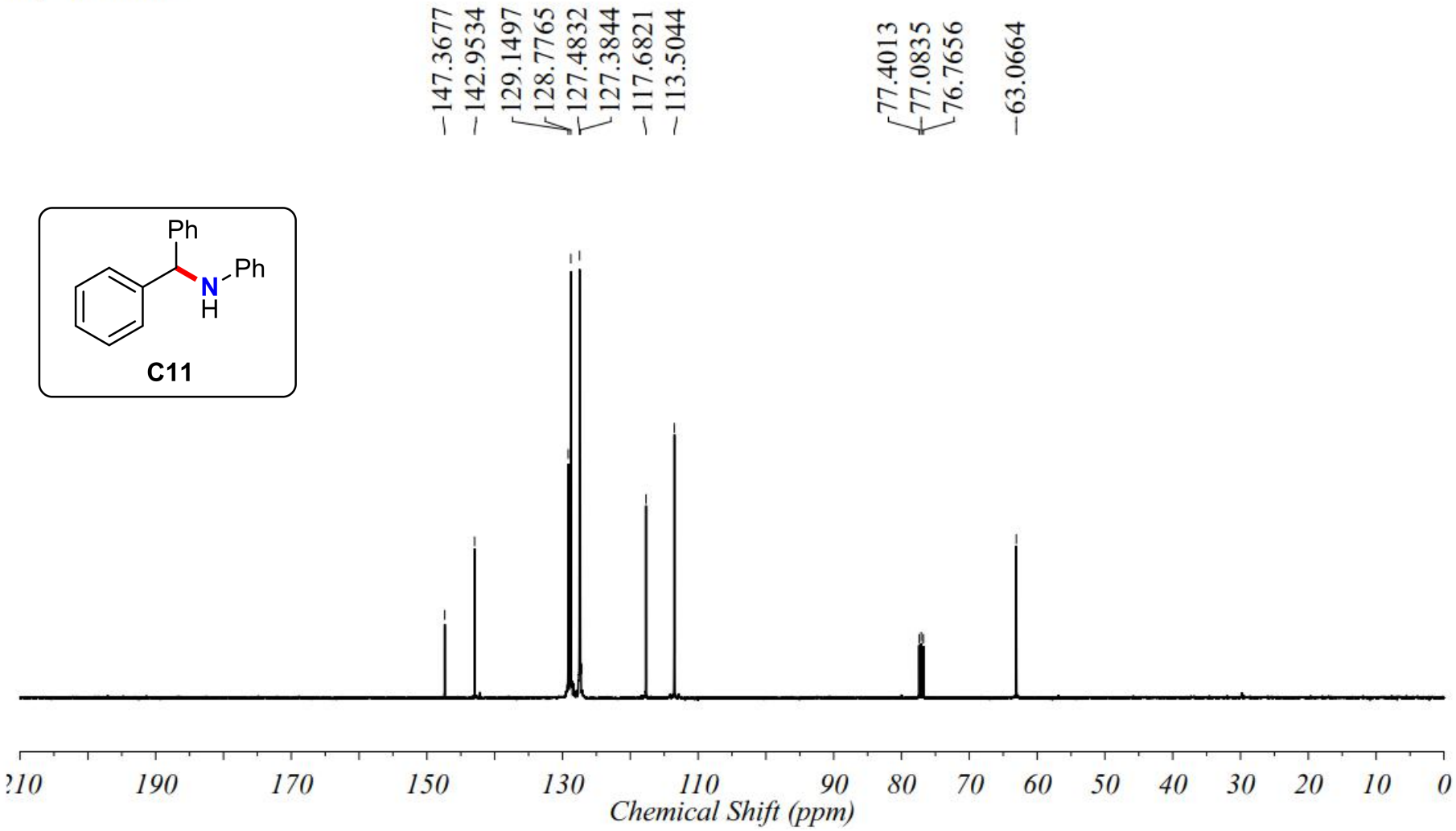


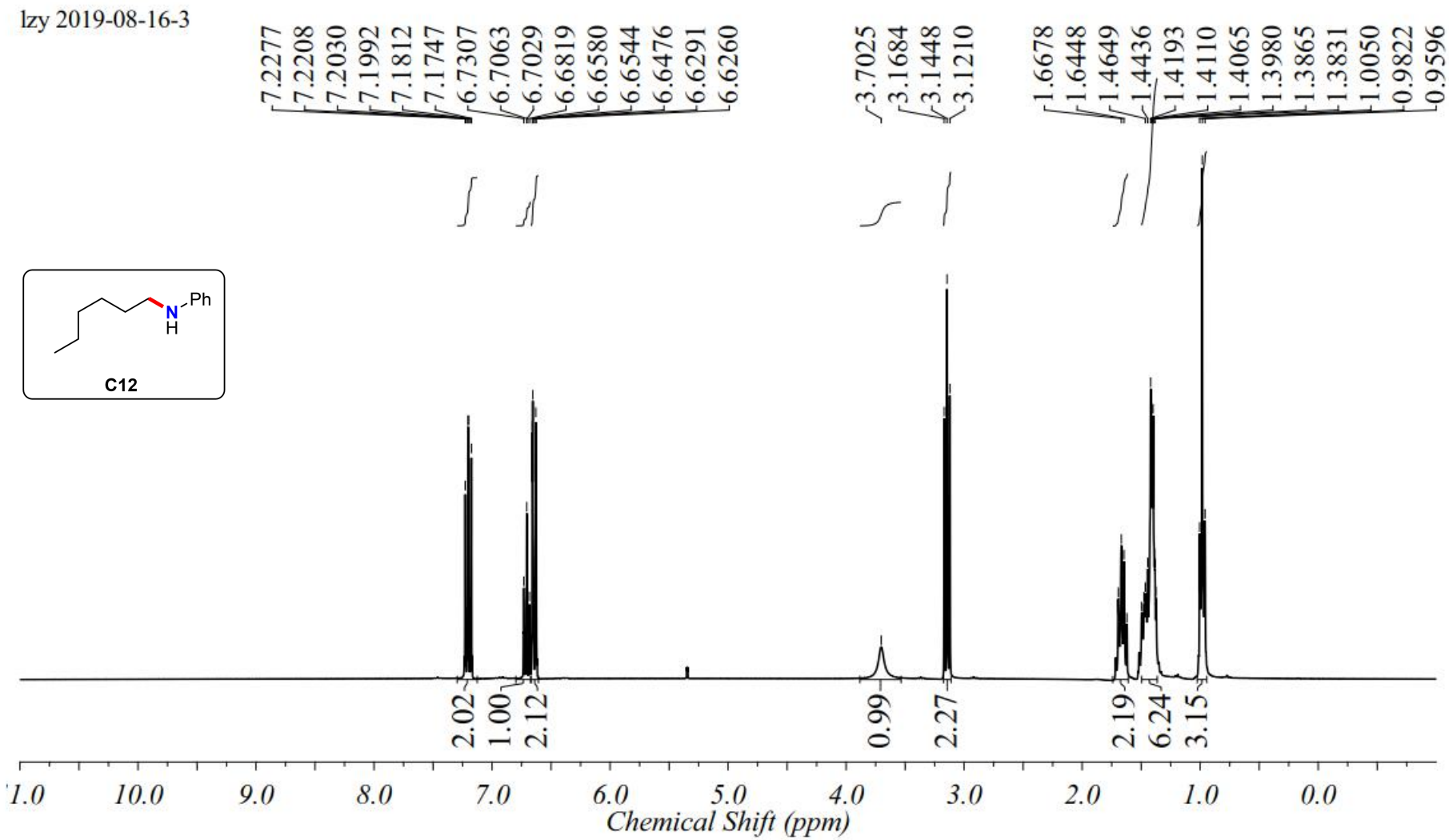

lzy 2019-08-16-1
7.3347
7.3298
7.3181
7.2966
7.2720
7.2539
7.1297
7.1260
7.0980
7.0870
7.0703
7.0592
6.8493
6.8456
6.8212
6.7813
6.7595
5.4038
5.4002
5.3964
4.6105
4.2563
S
N
H
Ph
C10
3.09
2.00
3.08
2.09
1.02
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

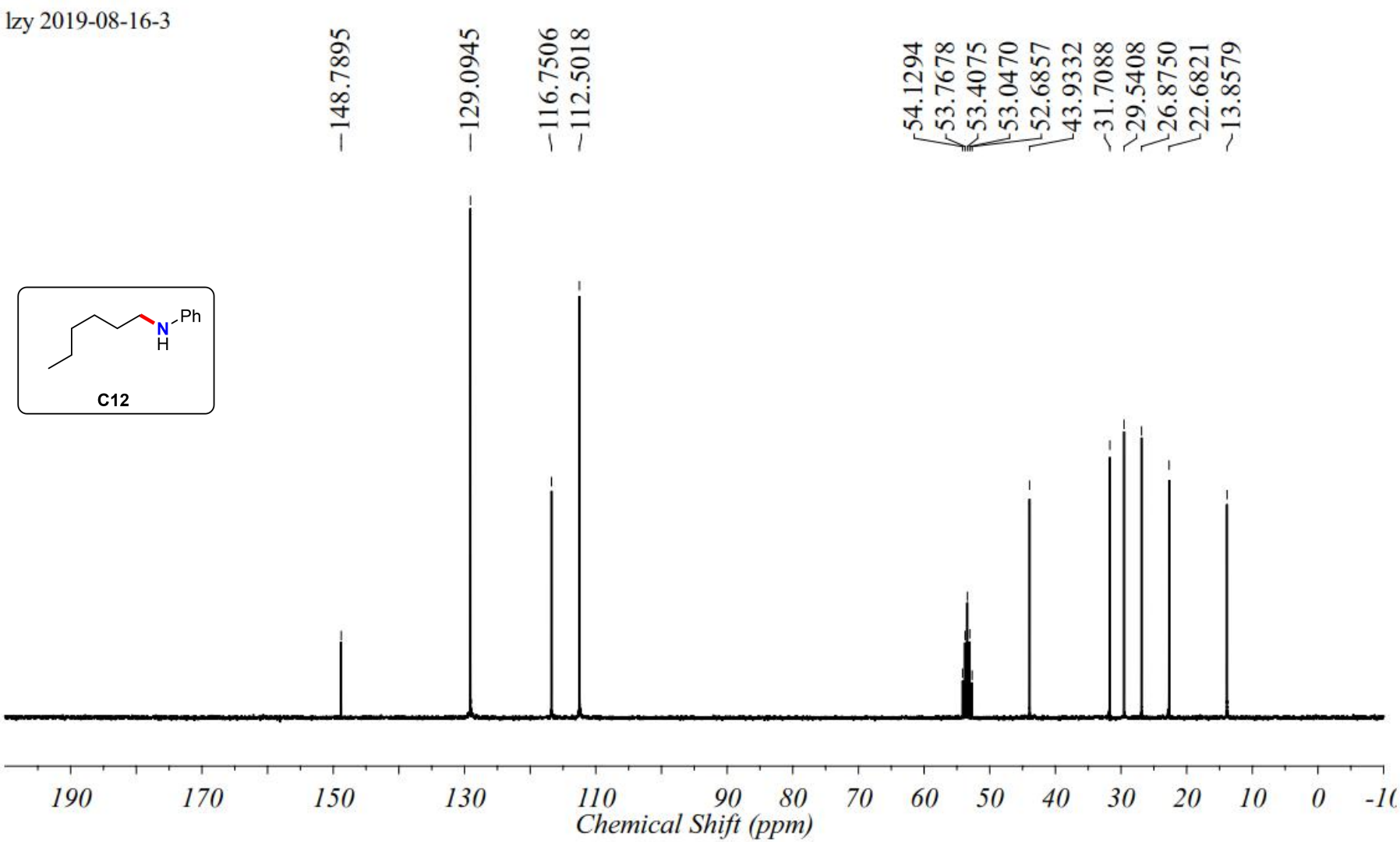

lzy 2019-08-16-1
147.7932
143.4509
129.2098
126.8602
124.9798
124.4813
117.8926
113.0972
54.2262
53.8661
53.5050
53.1448
52.7833
43.3389
S
N
H
Ph
C10
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

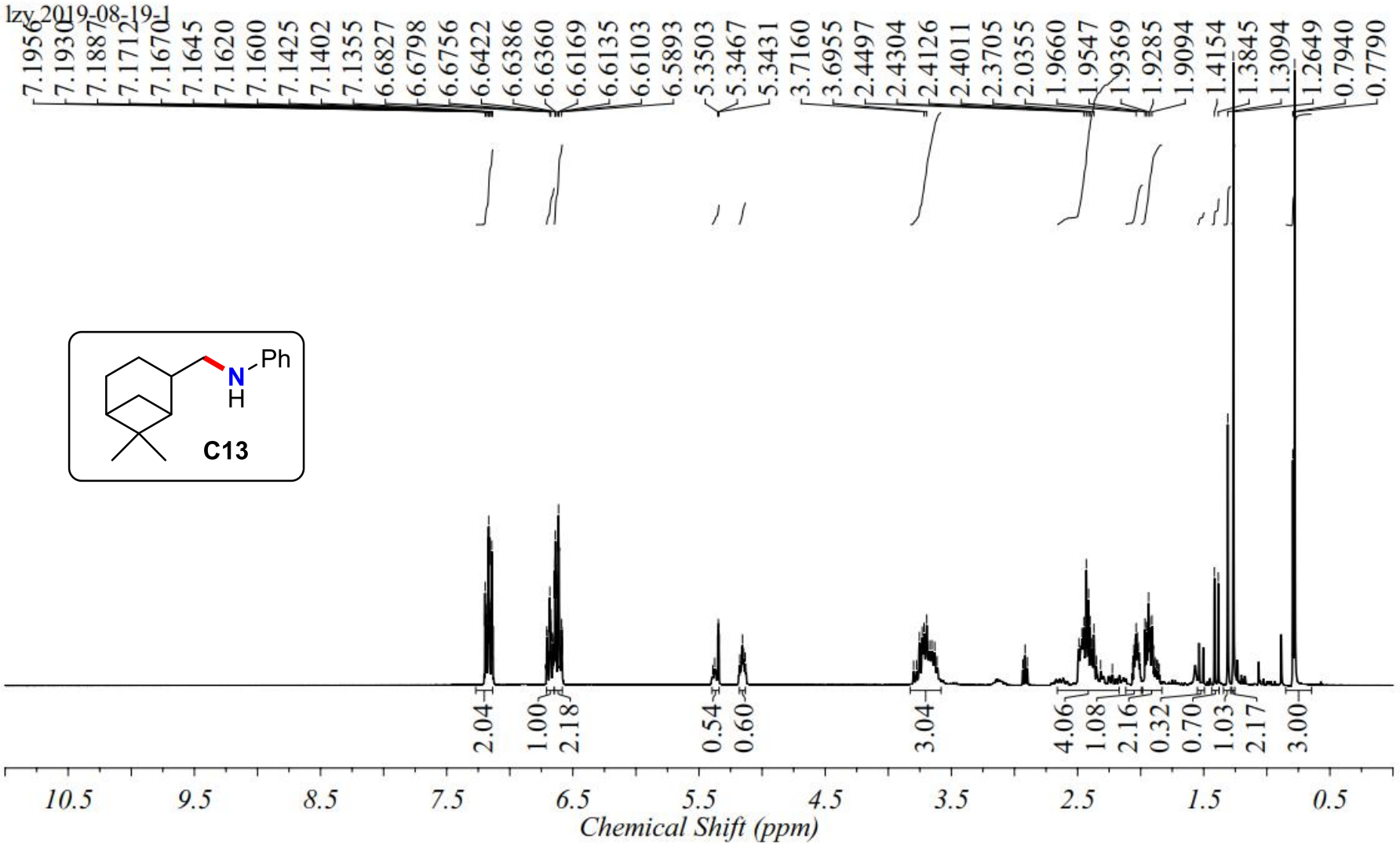

lzy 2019-08-16-2
7.4462
7.4291
7.4263
7.4135
7.4115
7.3937
7.3896
7.3743
7.3422
7.3243
7.2091
7.1878
7.1693
6.7893
6.7868
6.7709
6.7526
6.6261
6.6070
6.6047
5.3798
4.2957
Ph
Ph
N
H
C11
8.04
2.04
2.02
1.01
2.00
0.98
0.98
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

lzy 2019-08-16-2

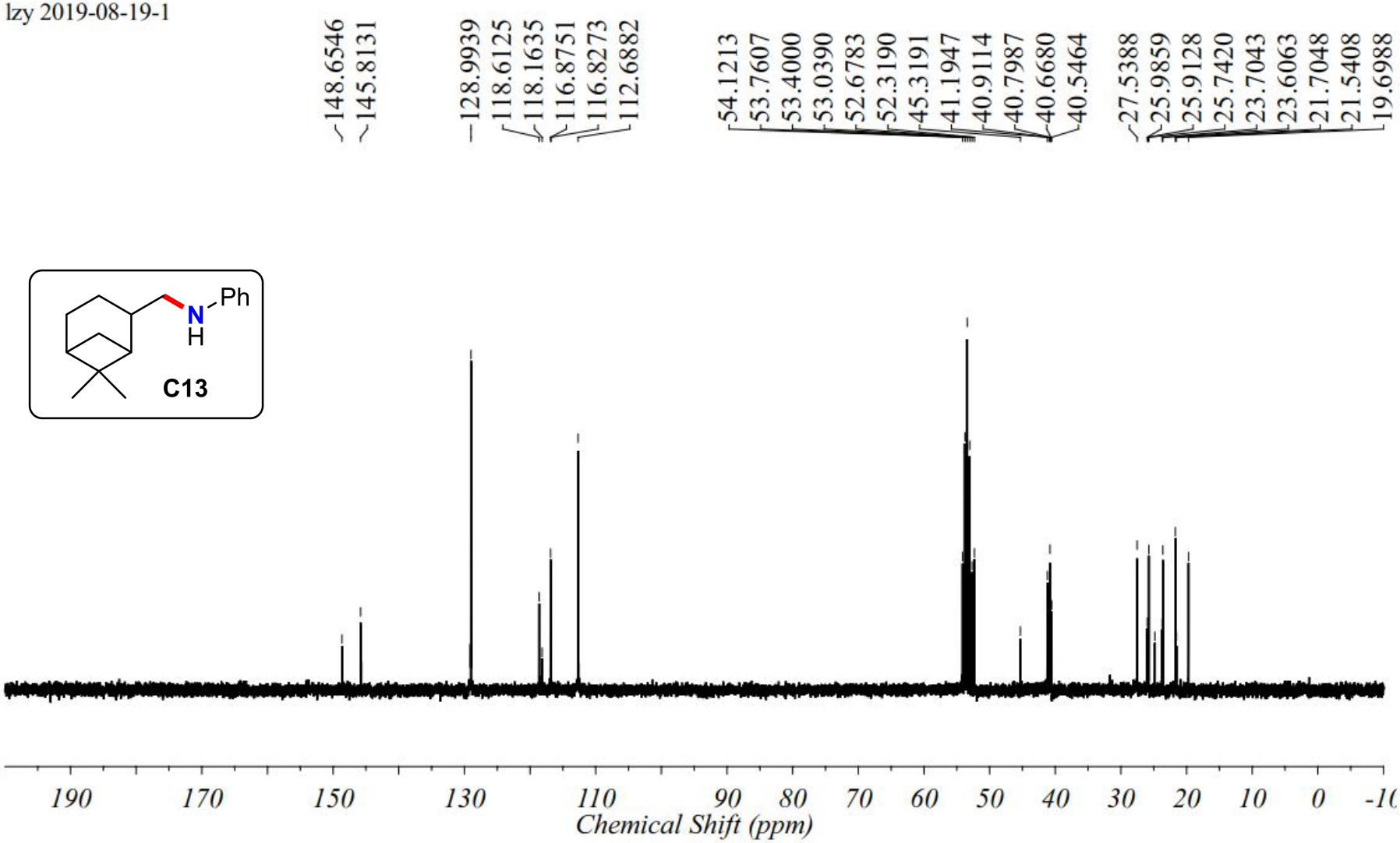


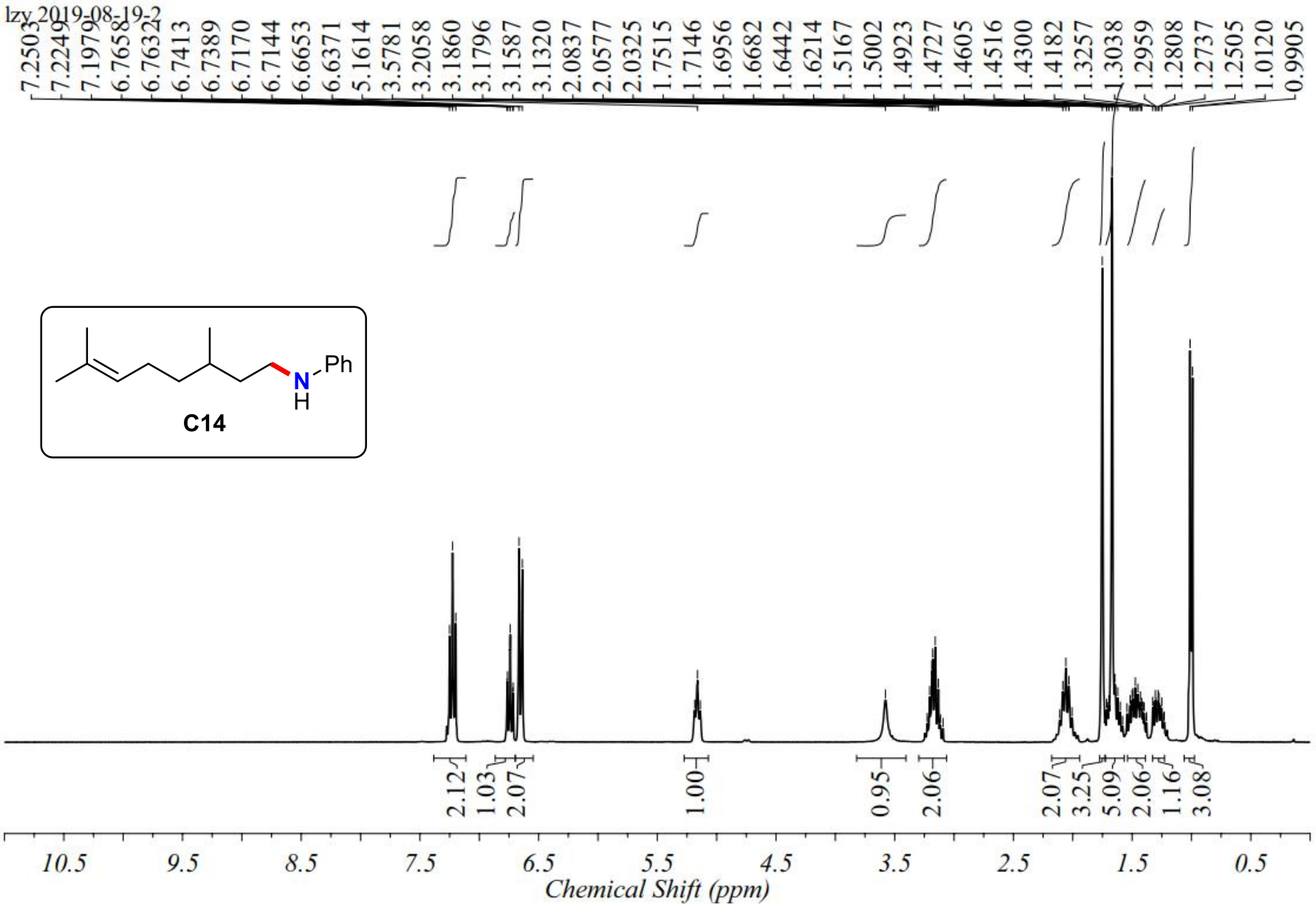

lzy 2019-08-16-3
7.2277
7.2208
7.2030
7.1992
7.1812
7.1747
6.7307
6.7063
6.7029
6.6819
6.6580
6.6544
6.6476
6.6291
6.6260
3.7025
3.1684
3.1448
3.1210
1.6678
1.6448
1.4649
1.4436
1.4193
1.4110
1.4065
1.3980
1.3865
1.3831
1.0050
0.9822
0.9596
Ph
N
H
C12
2.02
1.00
2.12
0.99
2.27
2.19
6.24
3.15
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical Shift (ppm)

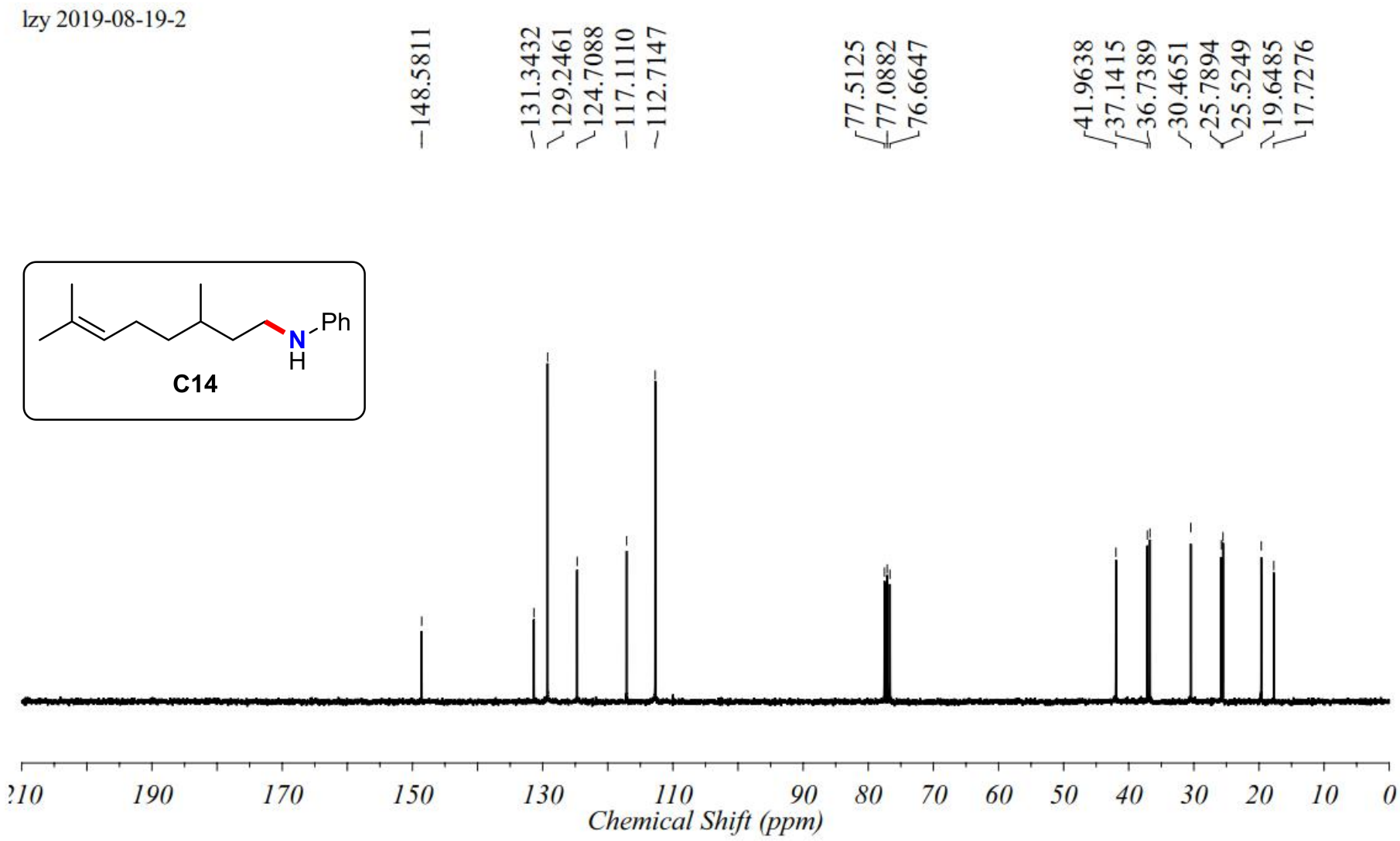

lzy 2019-08-16-3
148.7895
129.0945
116.7506
112.5018
54.1294
53.7678
53.4075
53.0470
52.6857
43.9332
31.7088
29.5408
26.8750
22.6821
13.8579
Ph
N
H
C12
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

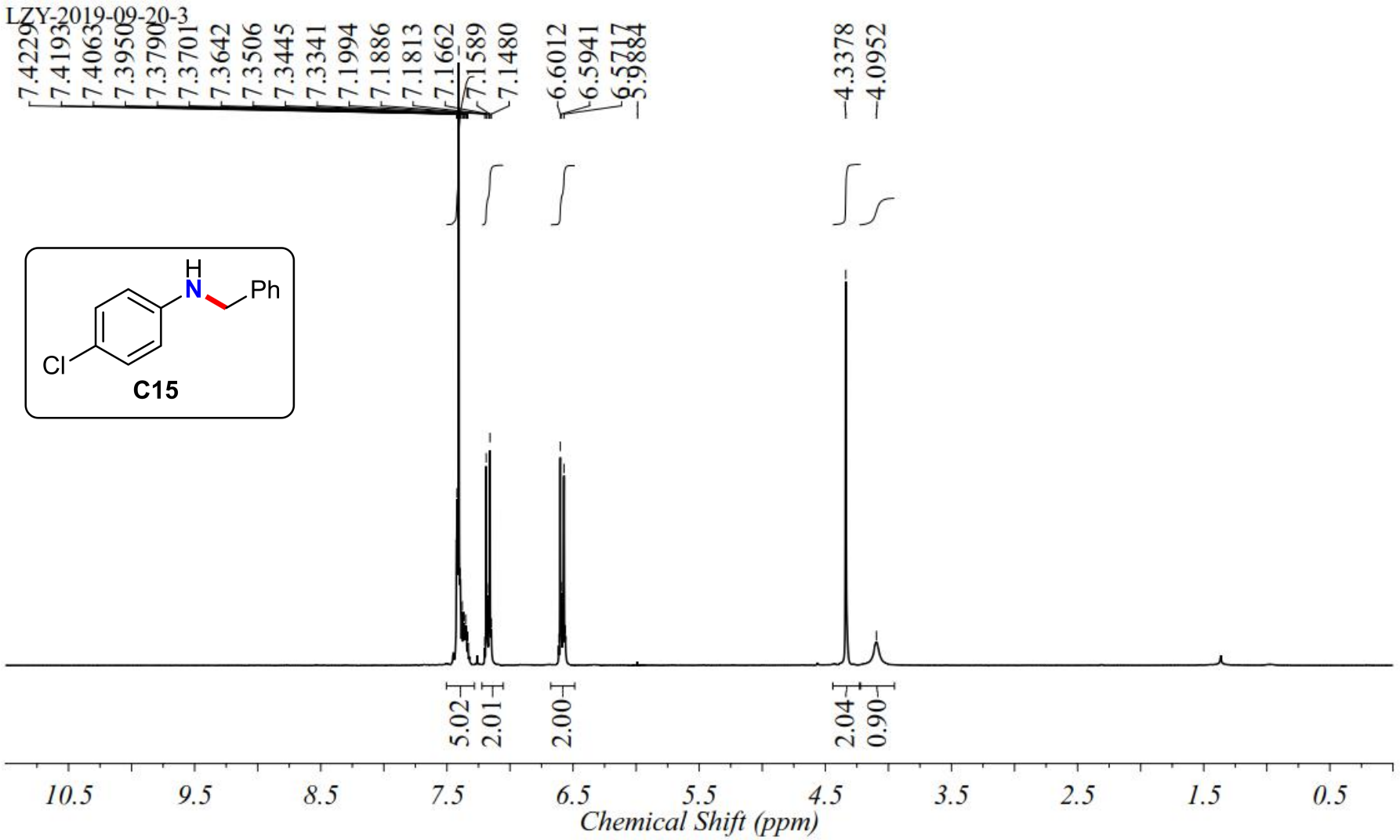

lzy-2019-08-19-1
7.1956
7.1930
7.1887
7.1712
7.1670
7.1645
7.1620
7.1600
7.1425
7.1402
7.1355
6.6827
6.6798
6.6756
6.6422
6.6386
6.6360
6.6169
6.6135
6.6103
6.5893
5.3503
5.3467
5.3431
3.7160
3.6955
2.4497
2.4304
2.4126
2.4011
2.3705
2.0355
1.9660
1.9547
1.9369
1.9285
1.9094
1.4154
1.3845
1.3094
1.2649
0.7940
0.7790
N
H
Ph
C13
2.04
1.00
2.18
0.54
0.60
3.04
4.06
1.08
2.16
0.32
0.70
1.03
2.17
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

lzy 2019-08-19-1

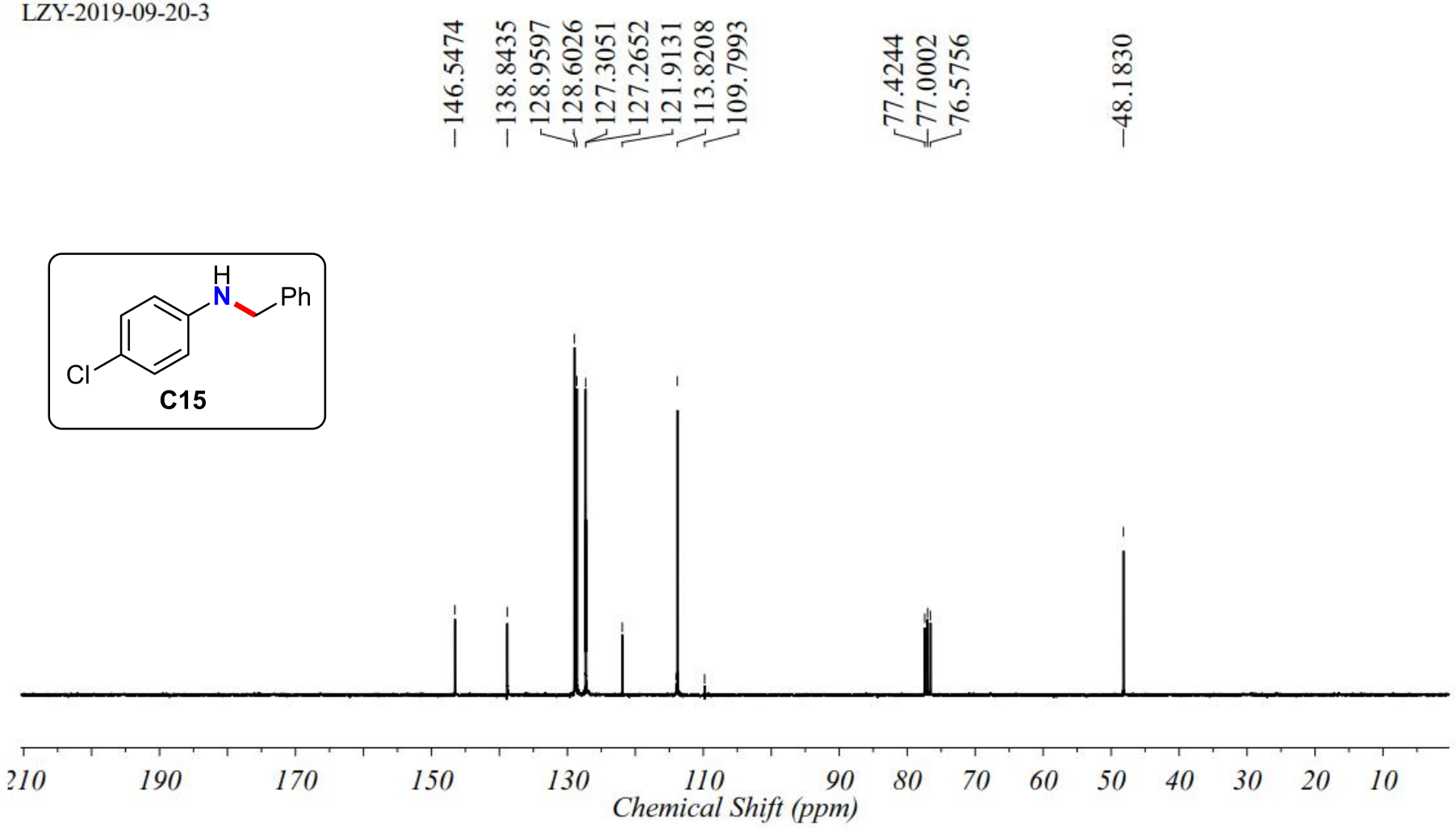


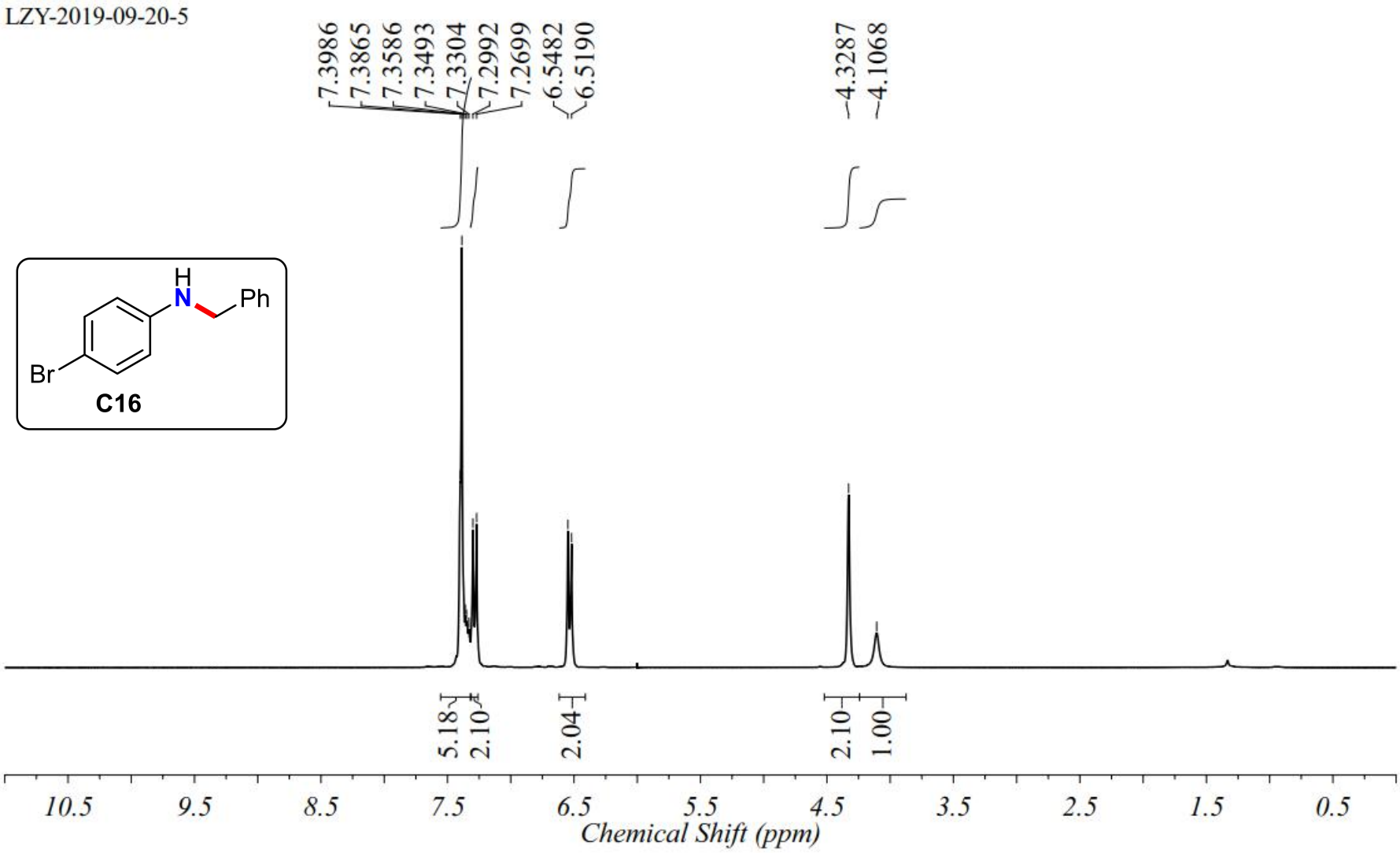

lzy 2019-08-19-2
7.2503
7.2249
7.1979
6.7658
6.7632
6.7413
6.7389
6.7170
6.7144
6.6653
6.6371
5.1614
3.5781
3.2058
3.1860
3.1796
3.1587
3.1320
2.0837
2.0577
2.0325
1.7515
1.7146
1.6956
1.6682
1.6442
1.6214
1.5167
1.5002
1.4923
1.4727
1.4605
1.4516
1.4300
1.4182
1.3257
1.3038
1.2959
1.2808
1.2737
1.2505
1.0120
0.9905
Ph
N
H
C14
2.12
1.03
2.07
1.00
0.95
2.06
2.07
3.25
5.09
2.06
1.16
3.08
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)


lzy 2019-08-19-2
148.5811
131.3432
129.2461
124.7088
117.1110
112.7147
77.5125
77.0882
76.6647
41.9638
37.1415
36.7389
30.4651
25.7894
25.5249
19.6485
17.7276
N
H
Ph
C14
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

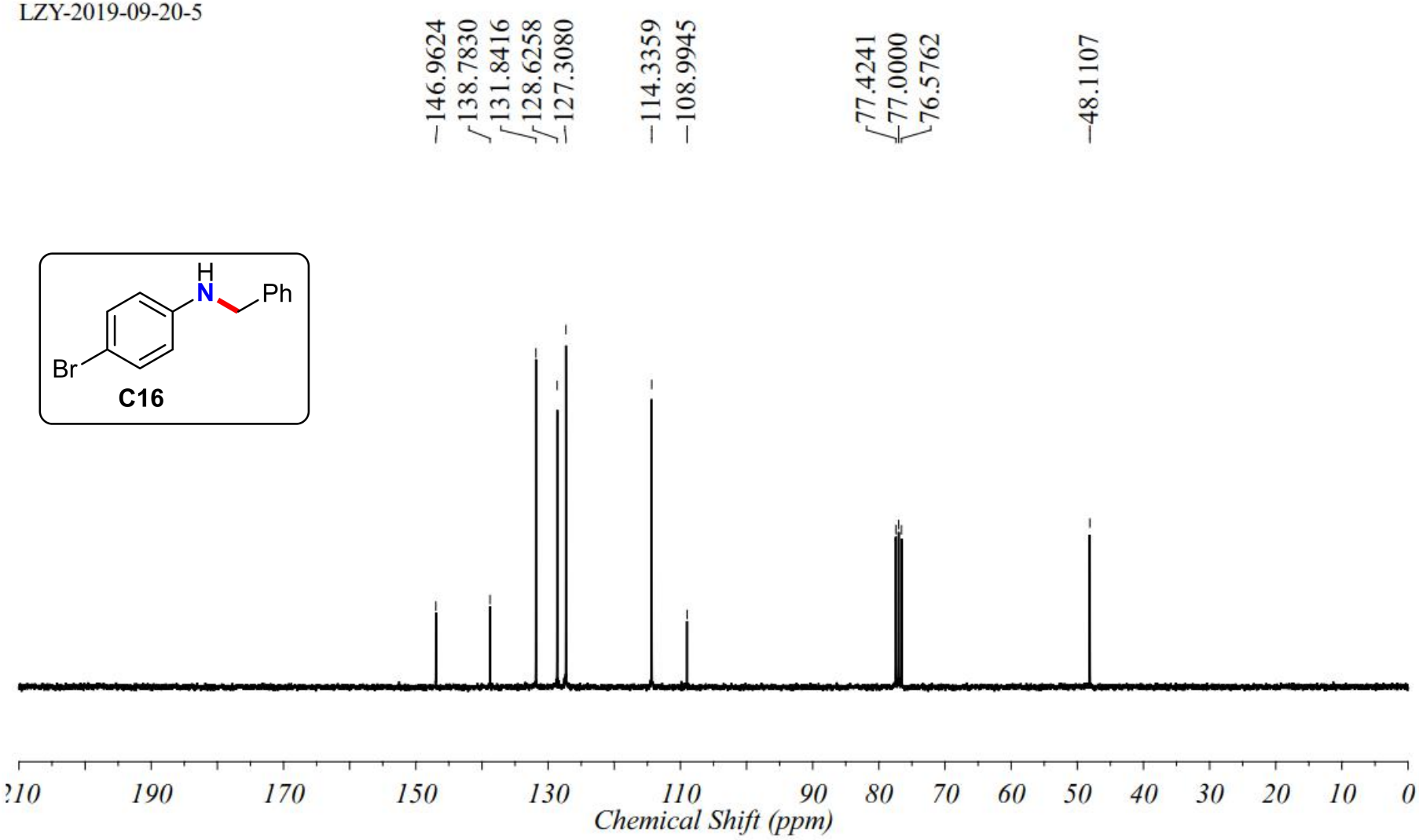

LZY-2019-09-20-3
7.4229
7.4193
7.4063
7.3950
7.3790
7.3701
7.3642
7.3506
7.3445
7.3341
7.1994
7.1886
7.1813
7.1662
7.1589
7.1480
6.6012
6.5941
6.5717
5.9884
4.3378
4.0952
H
N
Ph
Cl
C15
5.02
2.01
2.00
2.04
0.90
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

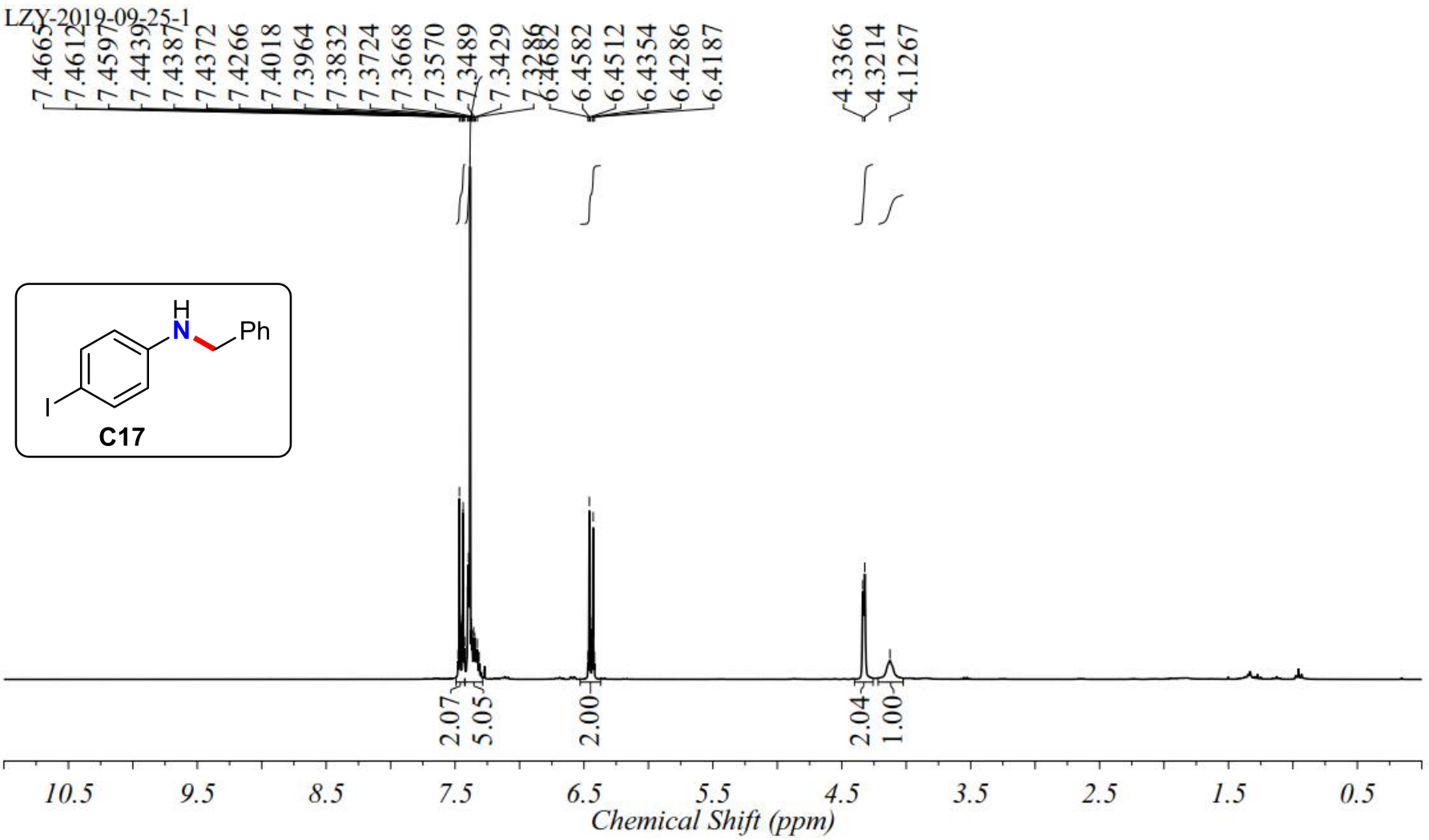
LZY-2019-09-20-3



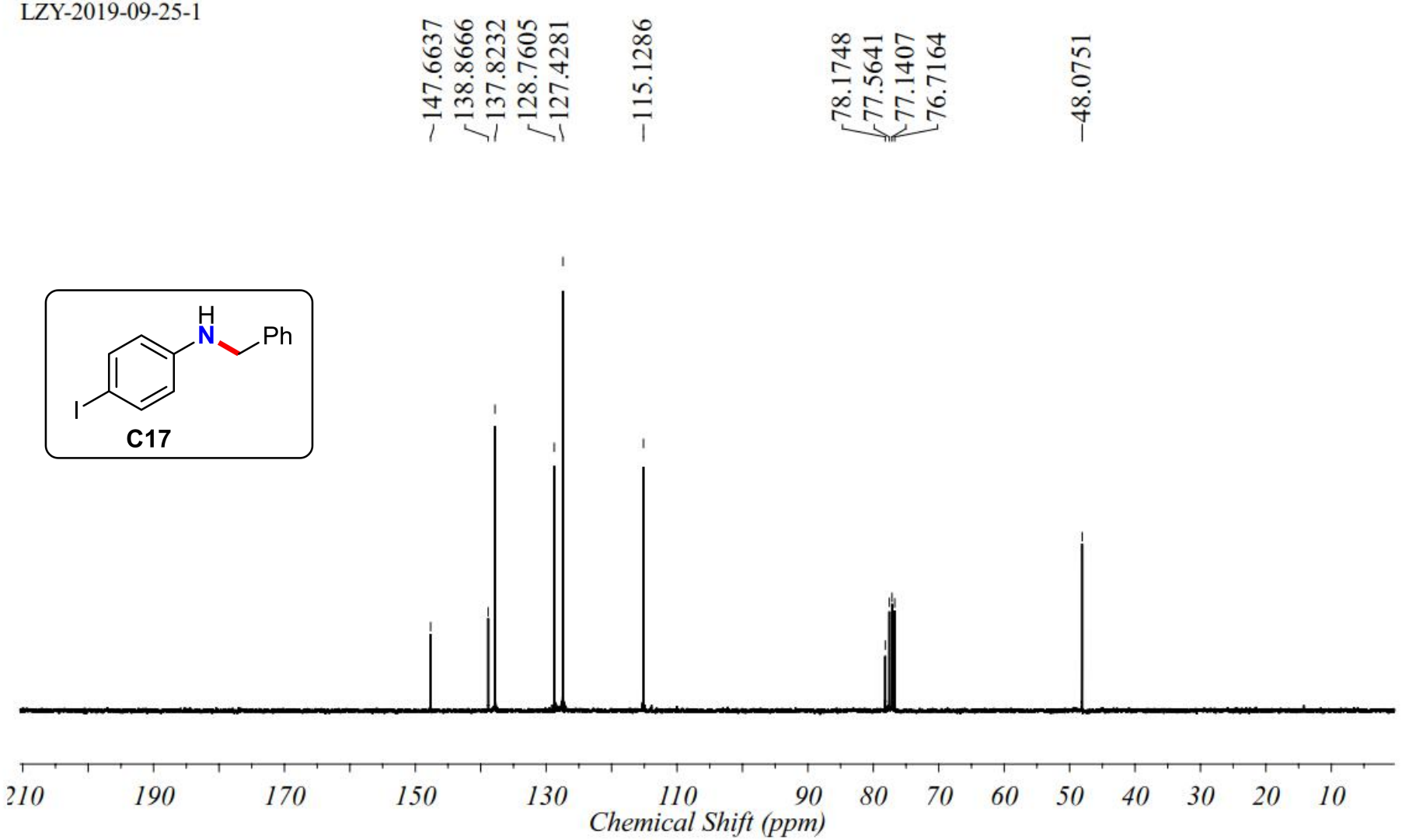

LZY-2019-09-20-5
7.3986
7.3865
7.3586
7.3493
7.3304
7.2992
7.2699
6.5482
6.5190
4.3287
4.1068
H
N
Ph
Br
C16
5.18
2.10
2.04
2.10
1.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

LZY-2019-09-20-5

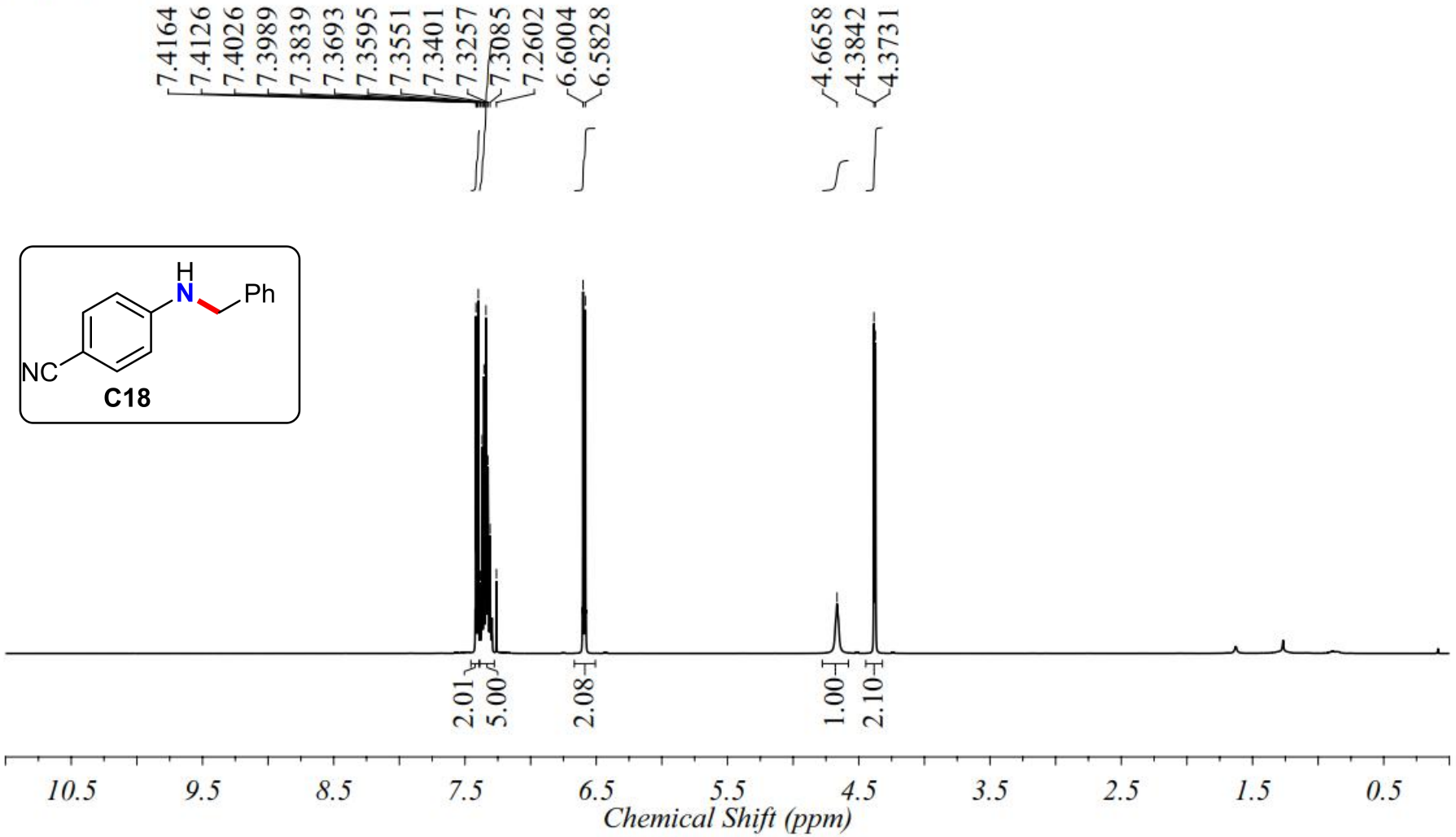



LZY-2019-09-25-1
7.4665
7.4612
7.4597
7.4439
7.4387
7.4372
7.4266
7.4018
7.3964
7.3832
7.3724
7.3668
7.3570
7.3489
7.3429
7.3286
7.3282
6.4582
6.4512
6.4354
6.4286
6.4187
4.3366
4.3214
4.1267
H
N
Ph
I
C17
2.07
5.05
2.00
2.04
1.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

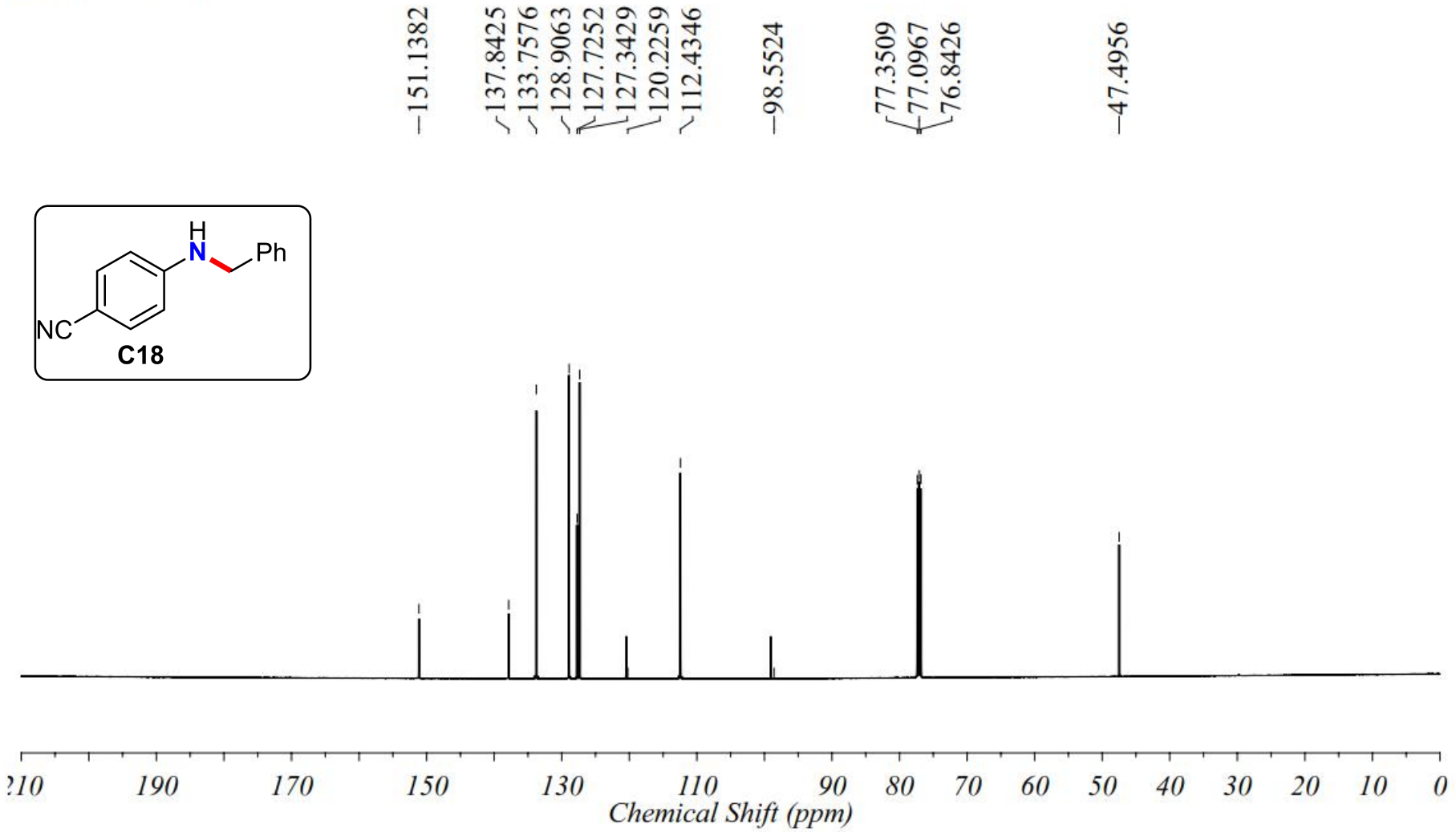
LZY-2019-09-25-1

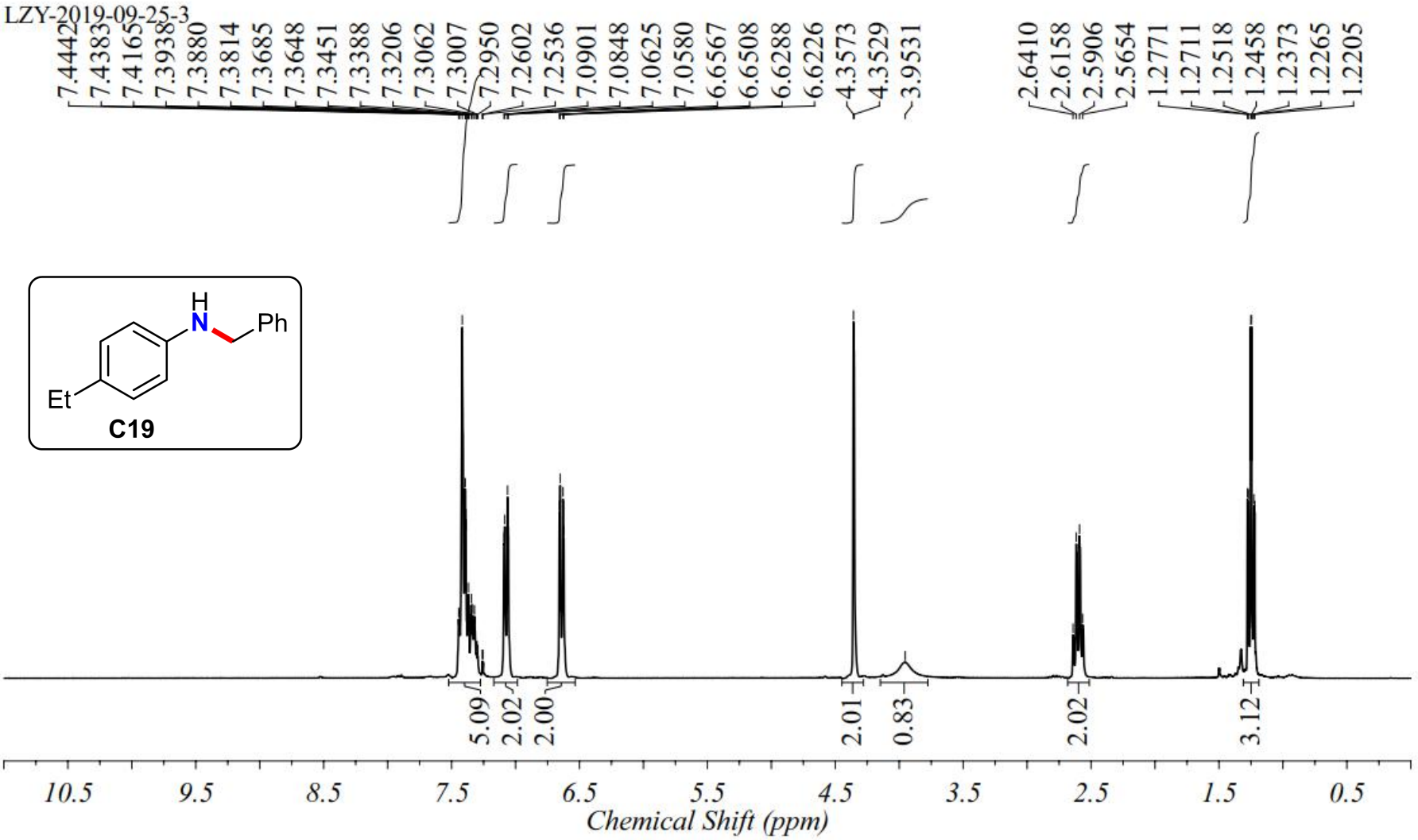


LZY-2019-09-25-2

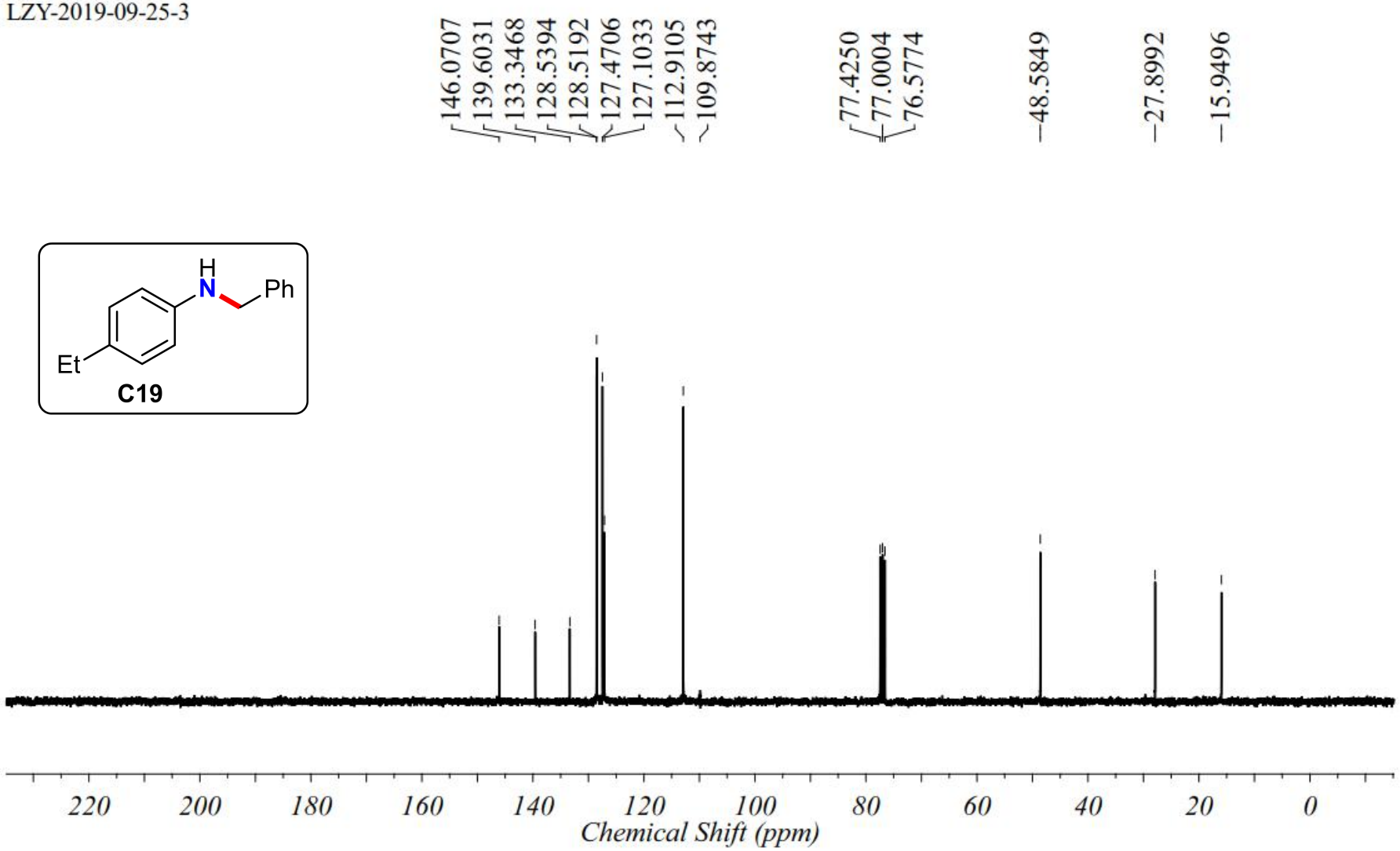


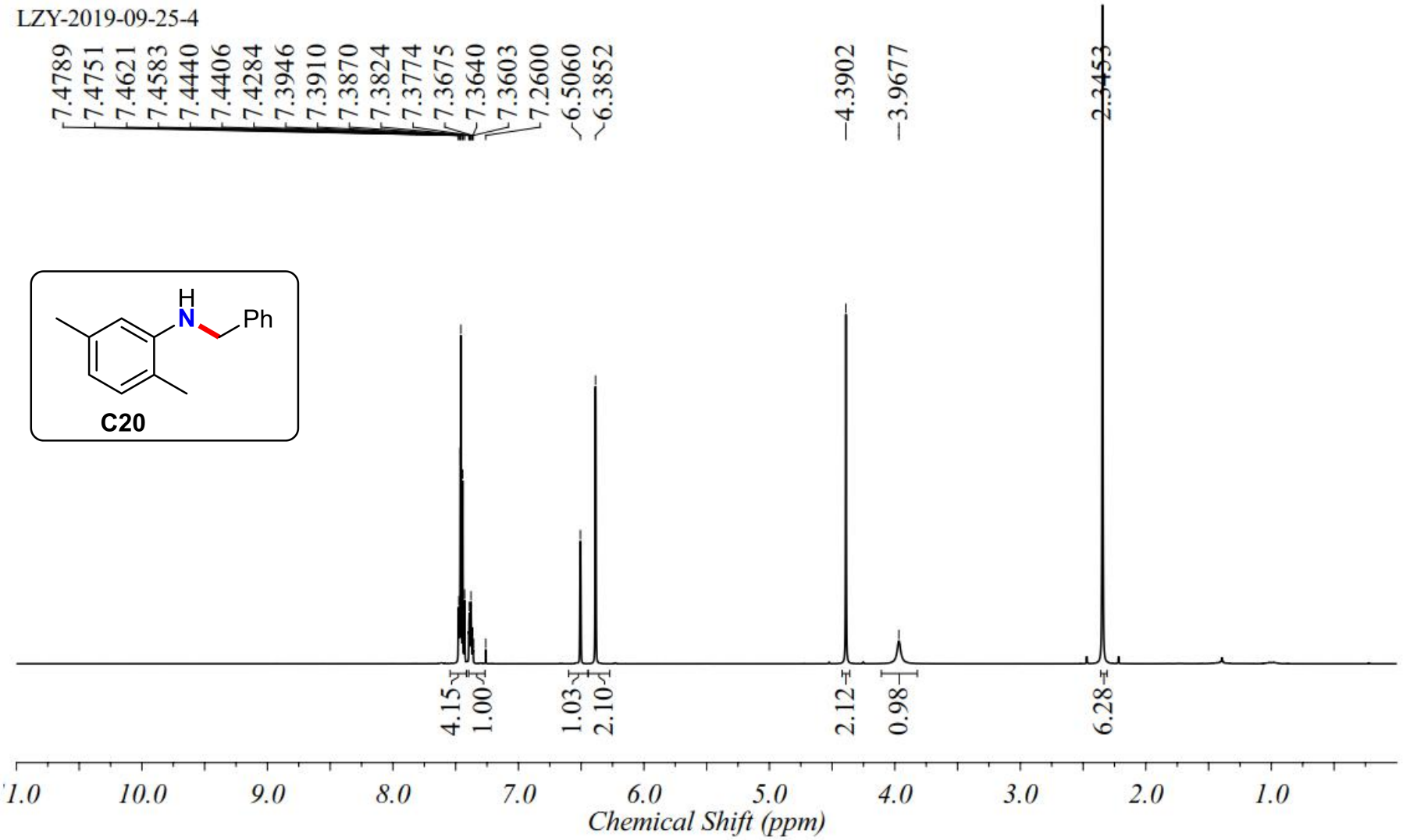
LZY-2019-09-25-2



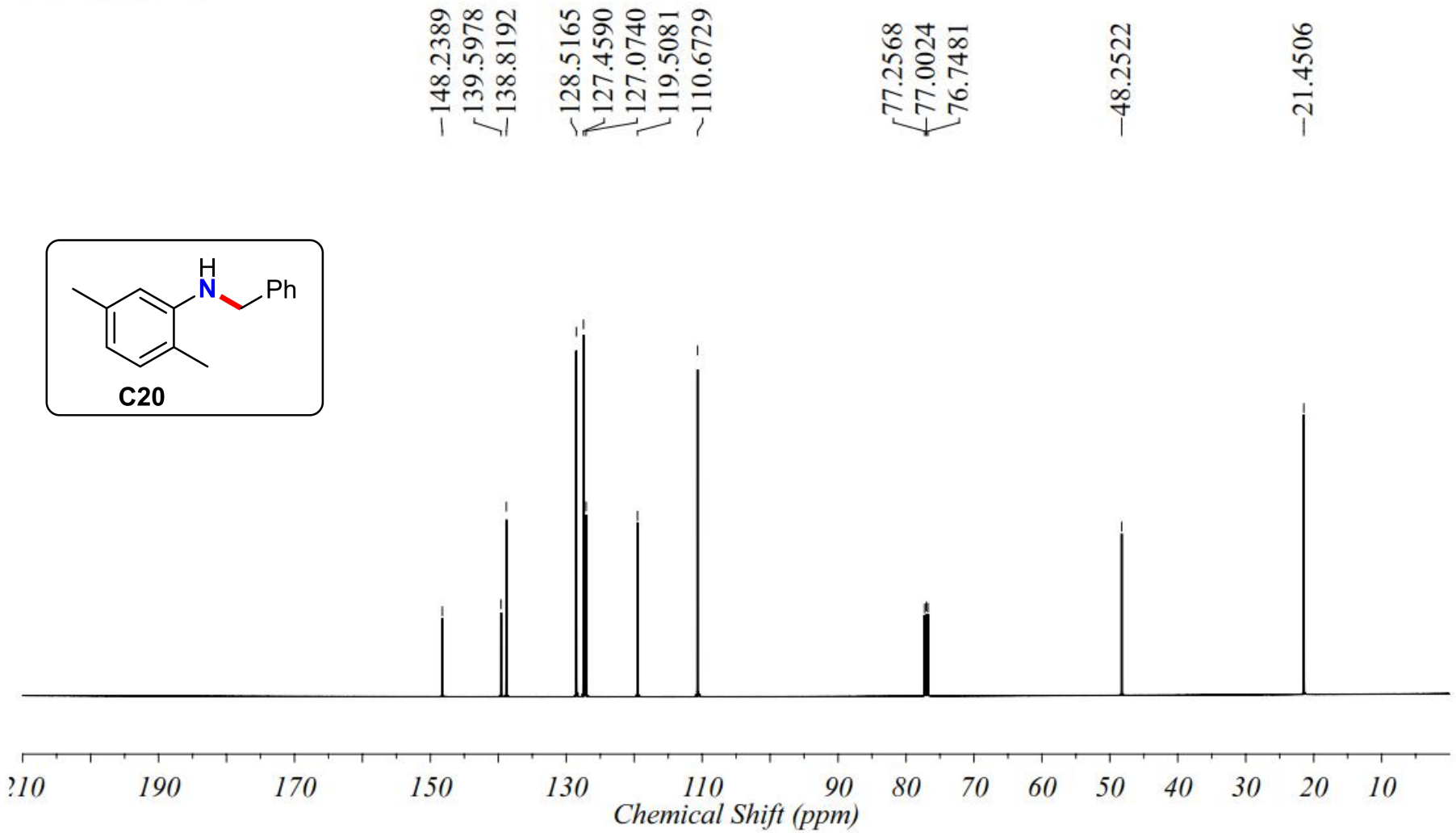

LZY-2019-09-25-3
7.4442
7.4383
7.4165
7.3938
7.3880
7.3814
7.3685
7.3648
7.3451
7.3388
7.3206
7.3062
7.3007
7.2950
7.2602
7.2536
7.0901
7.0848
7.0625
7.0580
6.6567
6.6508
6.6288
6.6226
4.3573
4.3529
3.9531
2.6410
2.6158
2.5906
2.5654
1.2771
1.2711
1.2518
1.2458
1.2373
1.2265
1.2205
H
N
Ph
Et
C19
5.09
2.02
2.00
2.01
0.83
2.02
3.12
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

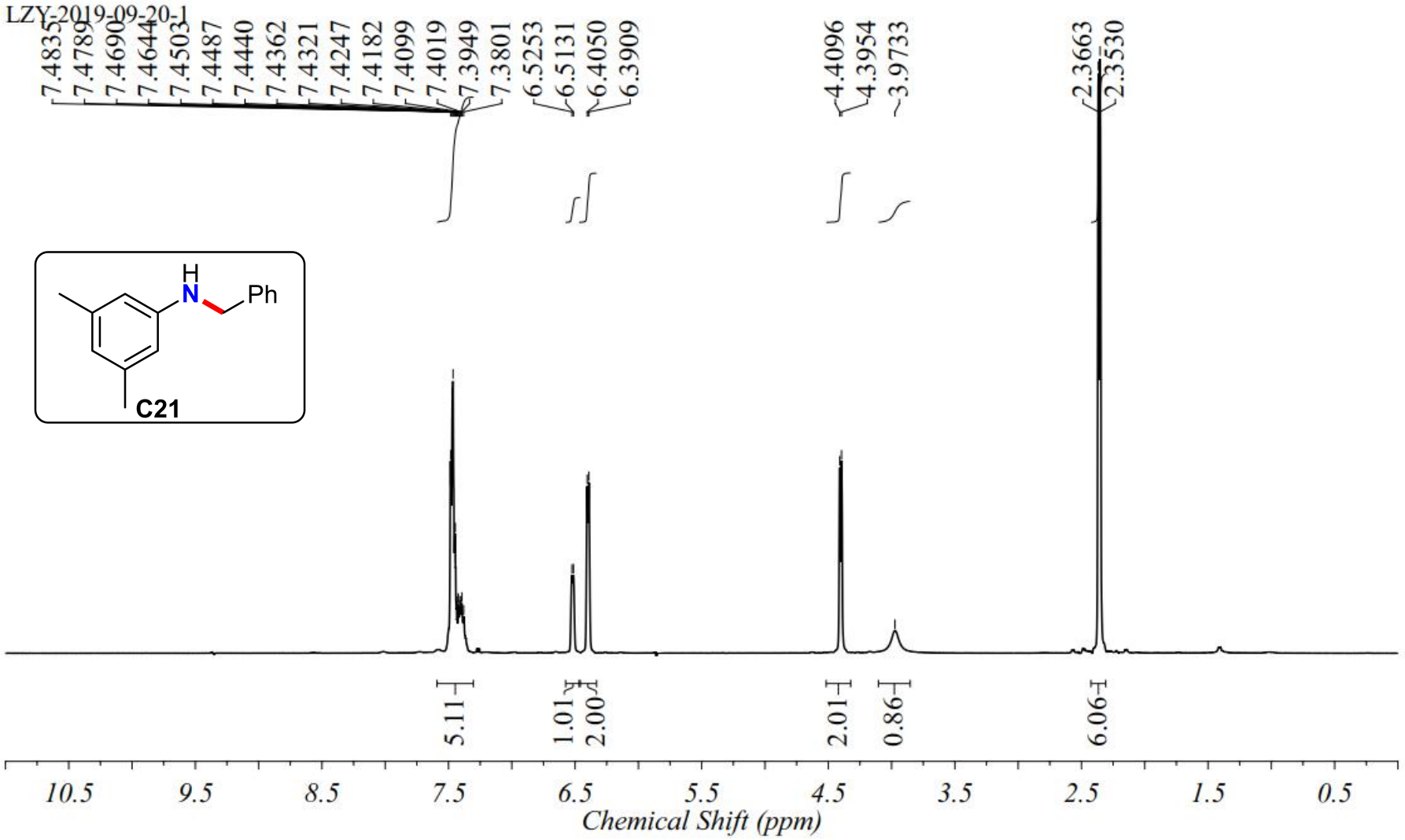
LZY-2019-09-25-3

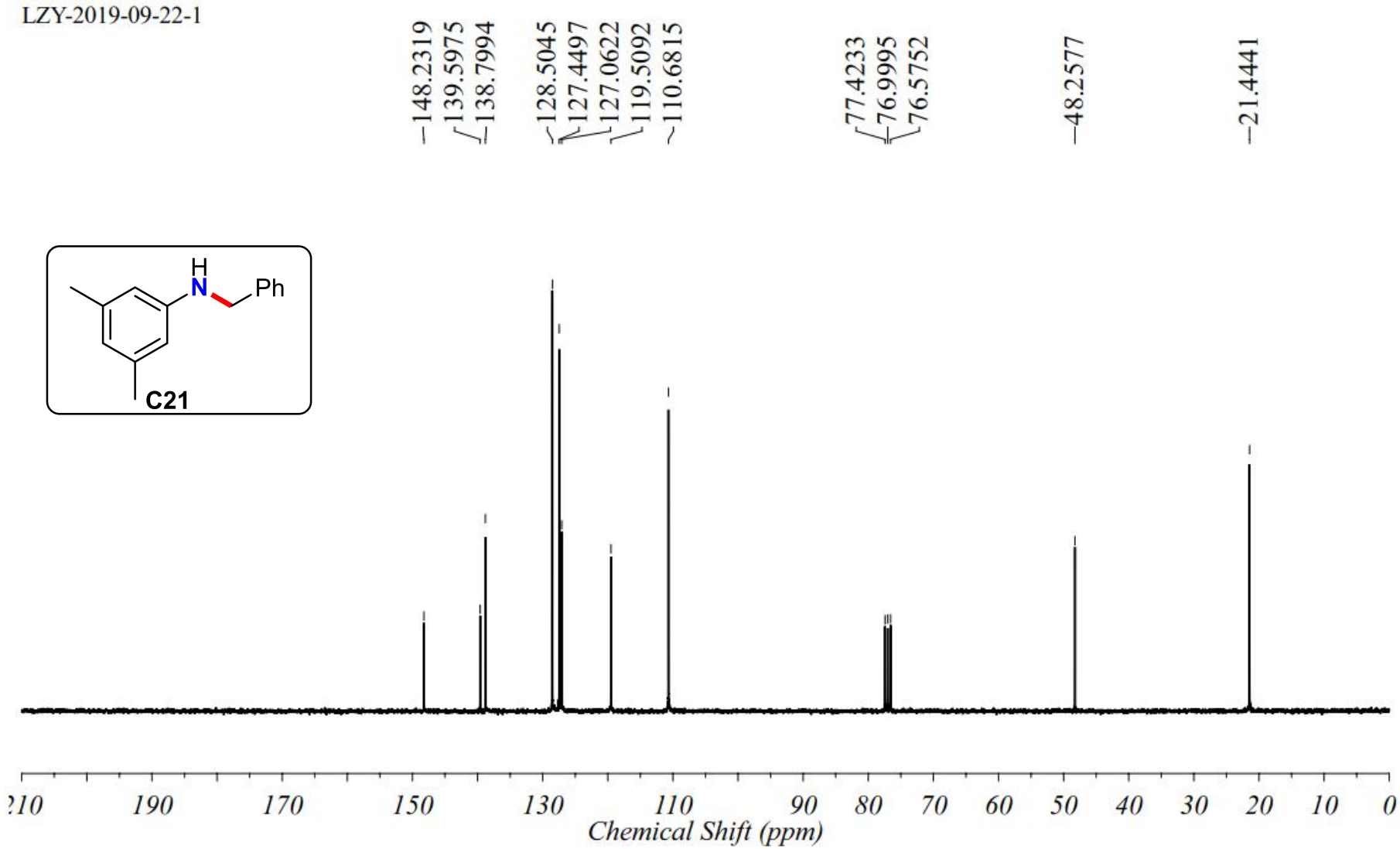


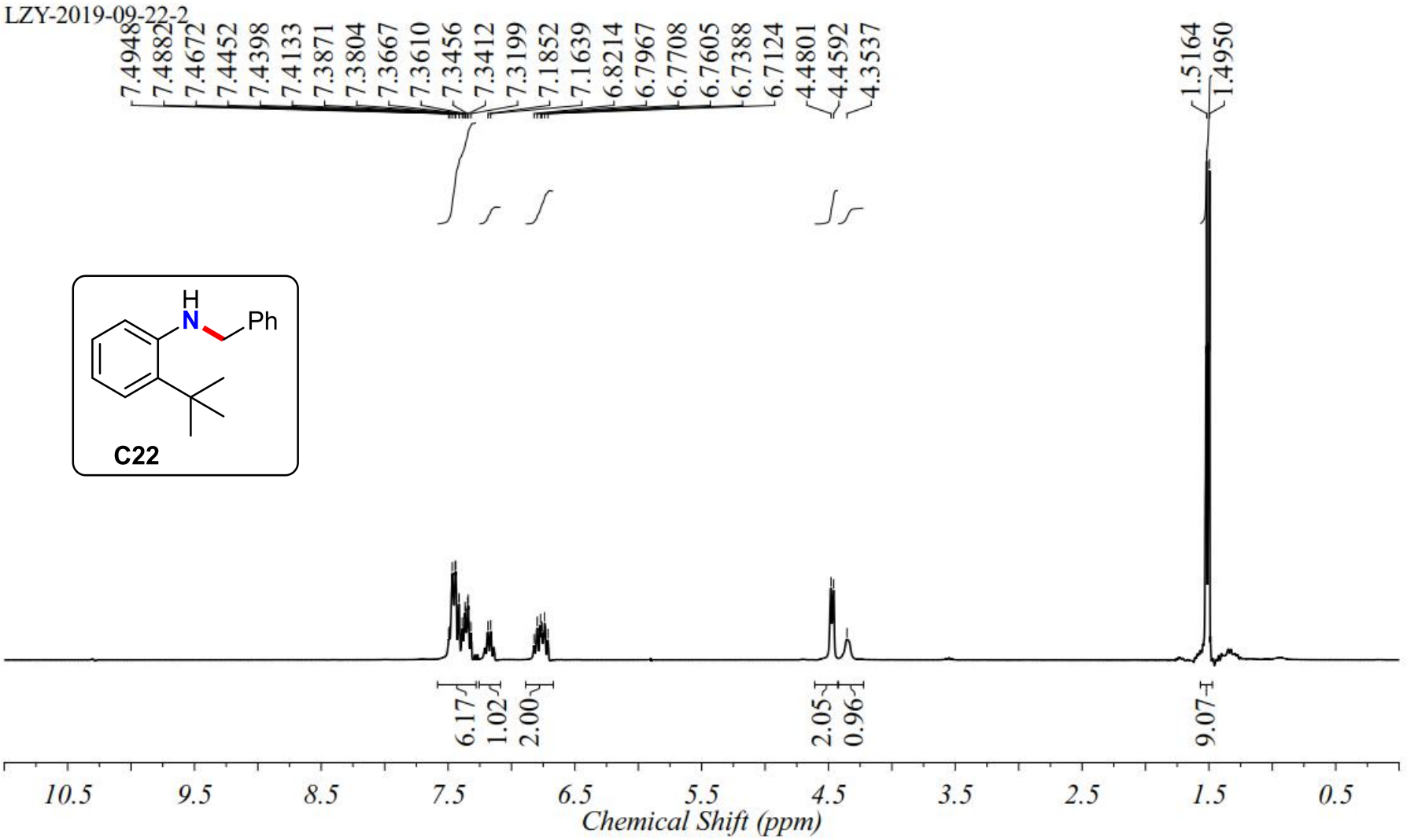

LZY-2019-09-25-4
7.4789
7.4751
7.4621
7.4583
7.4440
7.4406
7.4284
7.3946
7.3910
7.3870
7.3824
7.3774
7.3675
7.3640
7.3603
7.2600
6.5060
6.3852
4.3902
3.9677
2.3453
H
N
Ph
C20
4.15
1.00
1.03
2.10
2.12
0.98
6.28
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

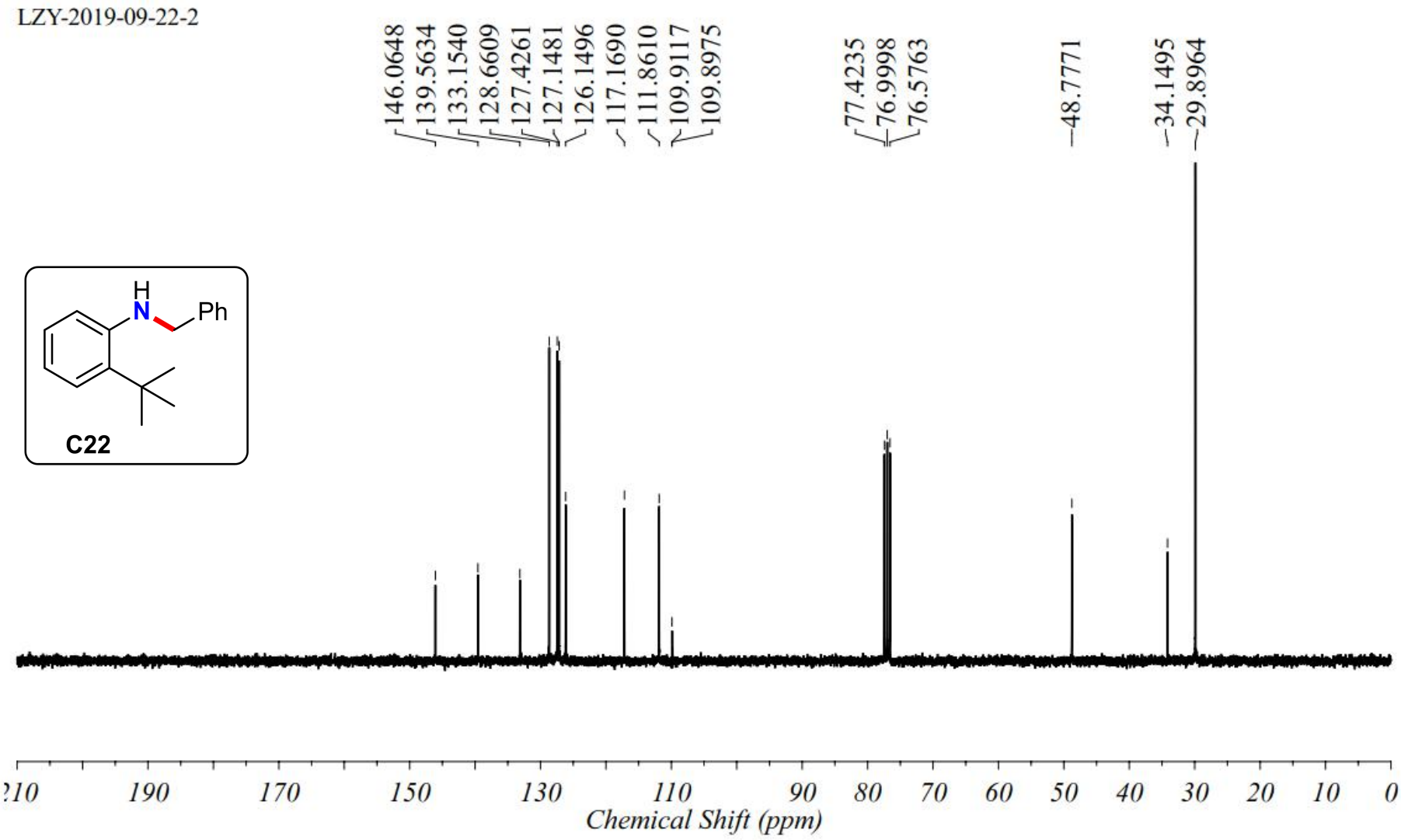
LZY-2019-09-25-4

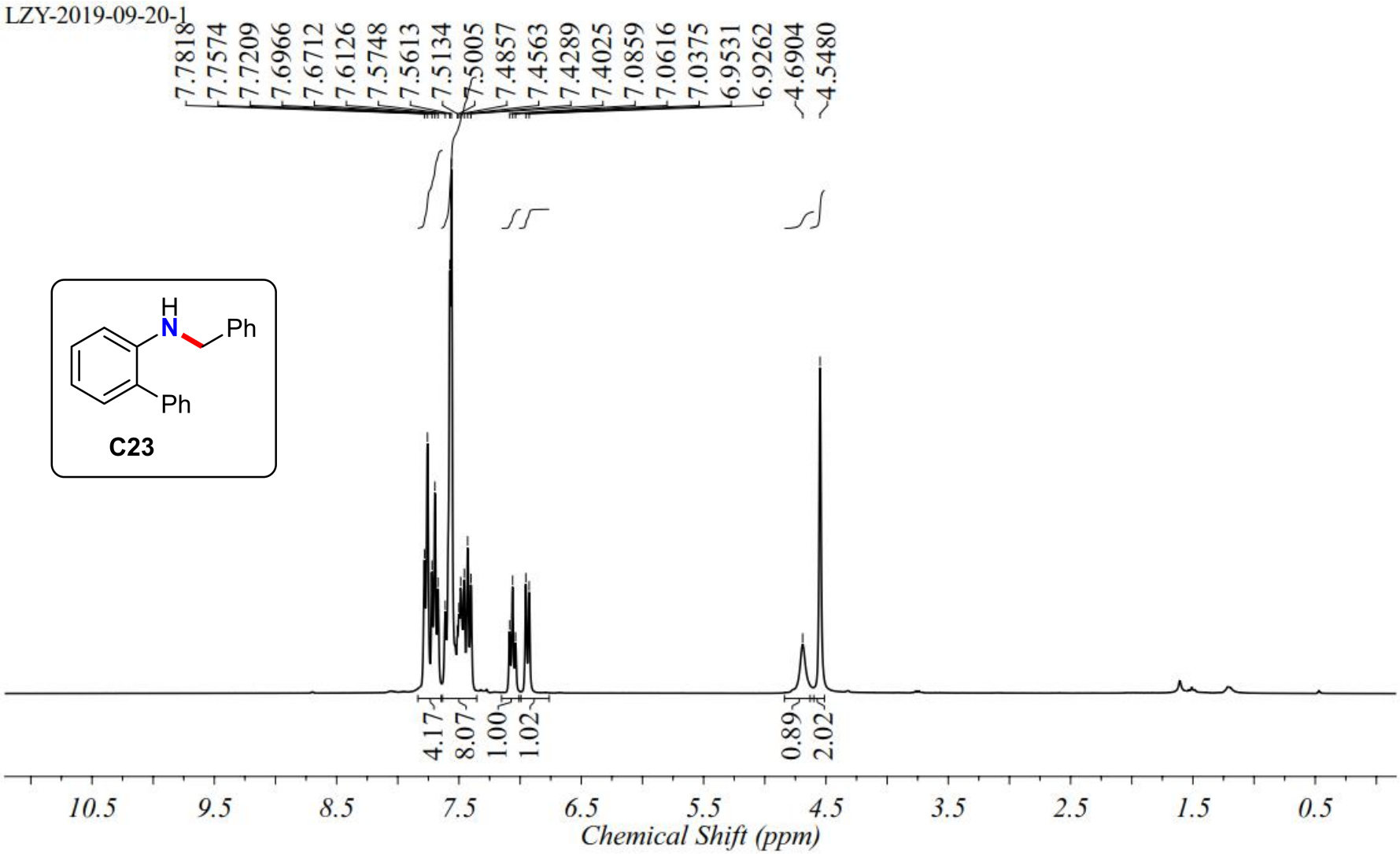



LZY-2019-09-20-1
7.4835
7.4789
7.4690
7.4644
7.4503
7.4487
7.4440
7.4362
7.4321
7.4247
7.4182
7.4099
7.4019
7.3949
7.3801
6.5253
6.5131
6.4050
6.3909
4.4096
4.3954
3.9733
2.3663
2.3530
H
N
Ph
C21
5.11
1.01
2.00
2.01
0.86
6.06
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

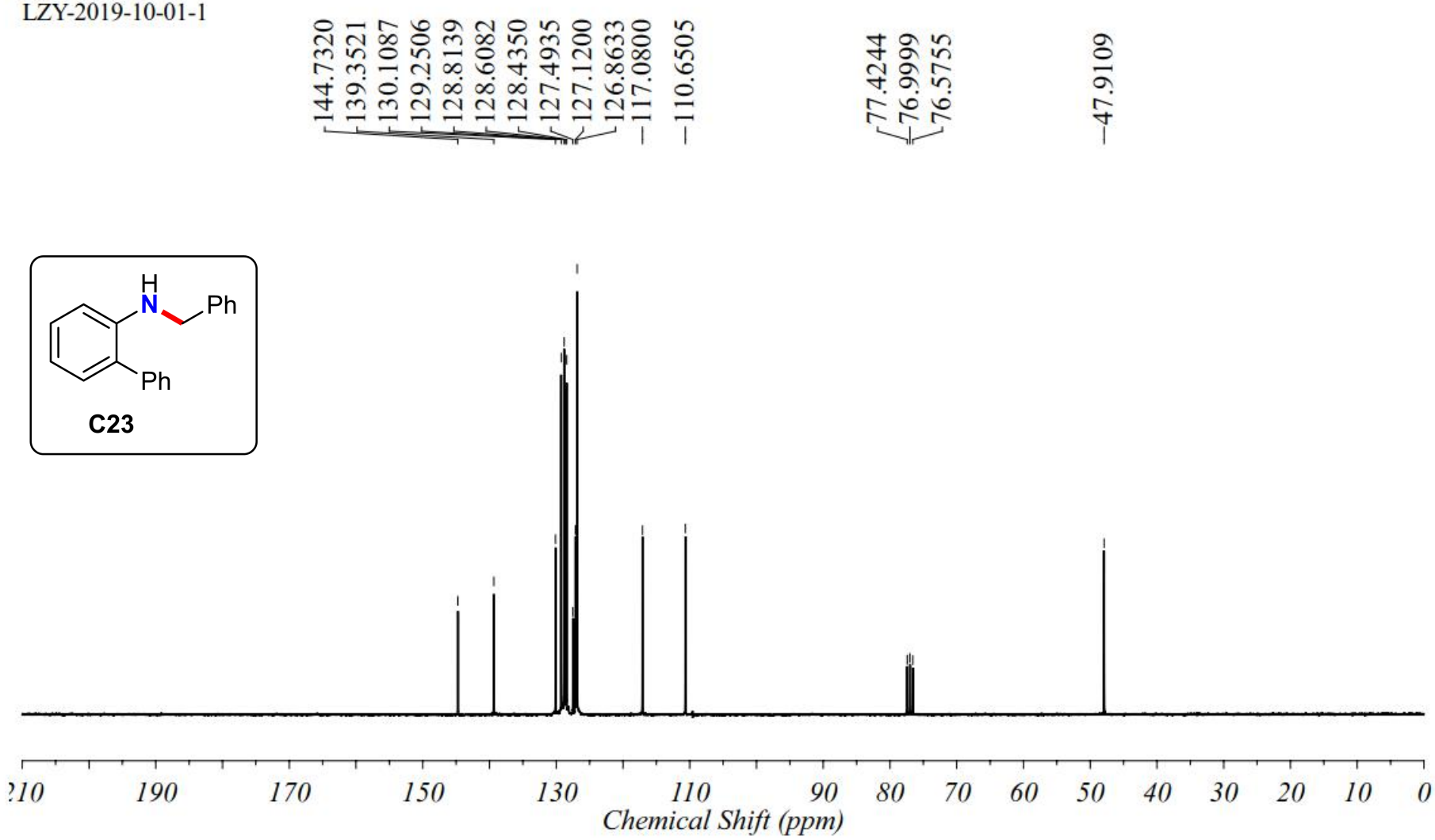

LZY-2019-09-22-1
148.2319
139.5975
138.7994
128.5045
127.4497
127.0622
119.5092
110.6815
77.4233
76.9995
76.5752
48.2577
21.4441
H
N
Ph
C21
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

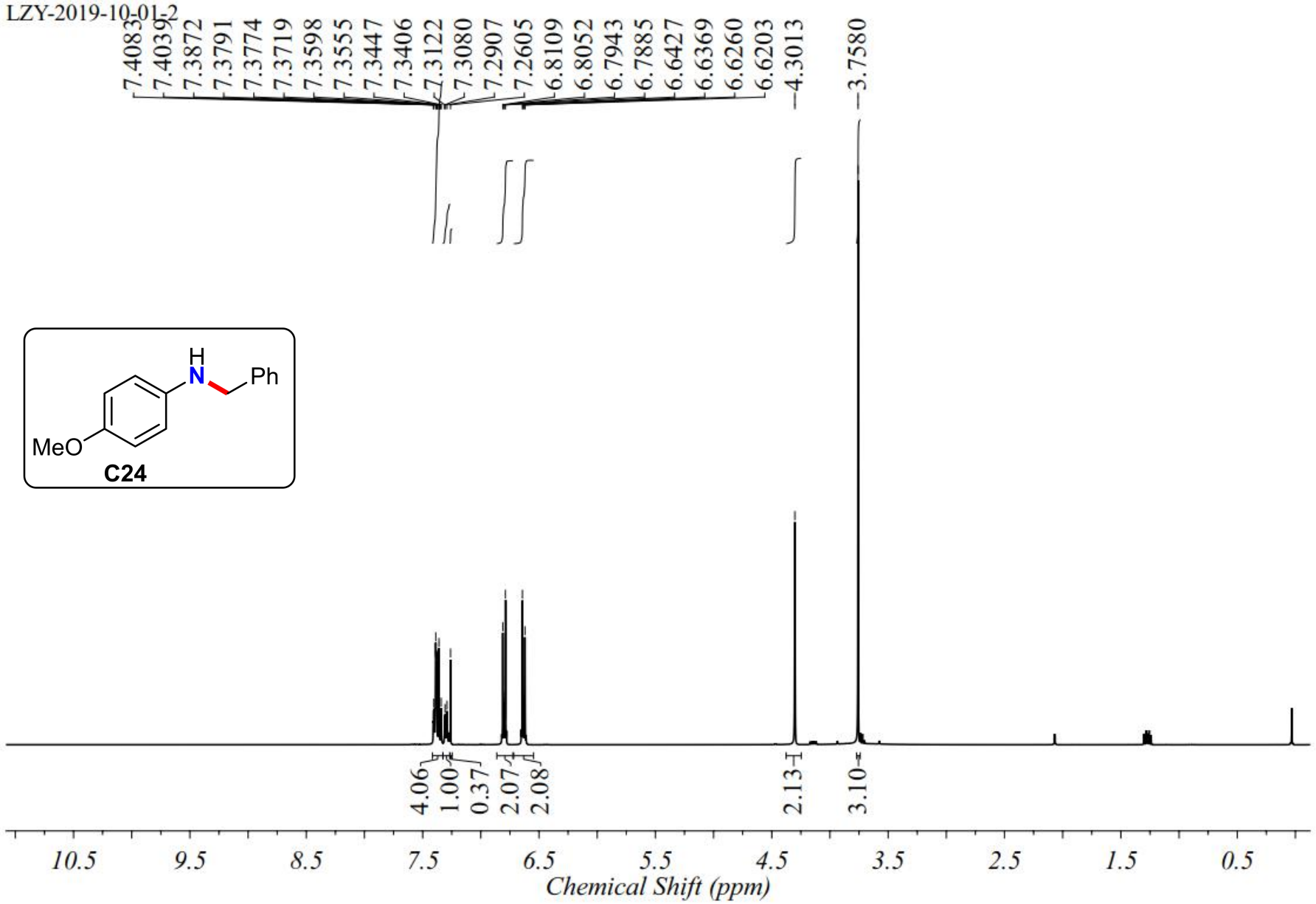

LZY-2019-09-22-2
7.4948
7.4882
7.4672
7.4452
7.4398
7.4133
7.3871
7.3804
7.3667
7.3610
7.3456
7.3412
7.3199
7.1852
7.1639
6.8214
6.7967
6.7708
6.7605
6.7388
6.7124
4.4801
4.4592
4.3537
1.5164
1.4950
H
N
Ph
C22
6.17
1.02
2.00
2.05
0.96
9.07
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)


LZY-2019-09-22-2
146.0648
139.5634
133.1540
128.6609
127.4261
127.1481
126.1496
117.1690
111.8610
109.9117
109.8975
77.4235
76.9998
76.5763
48.7771
34.1495
29.8964
H
N
Ph
C22
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

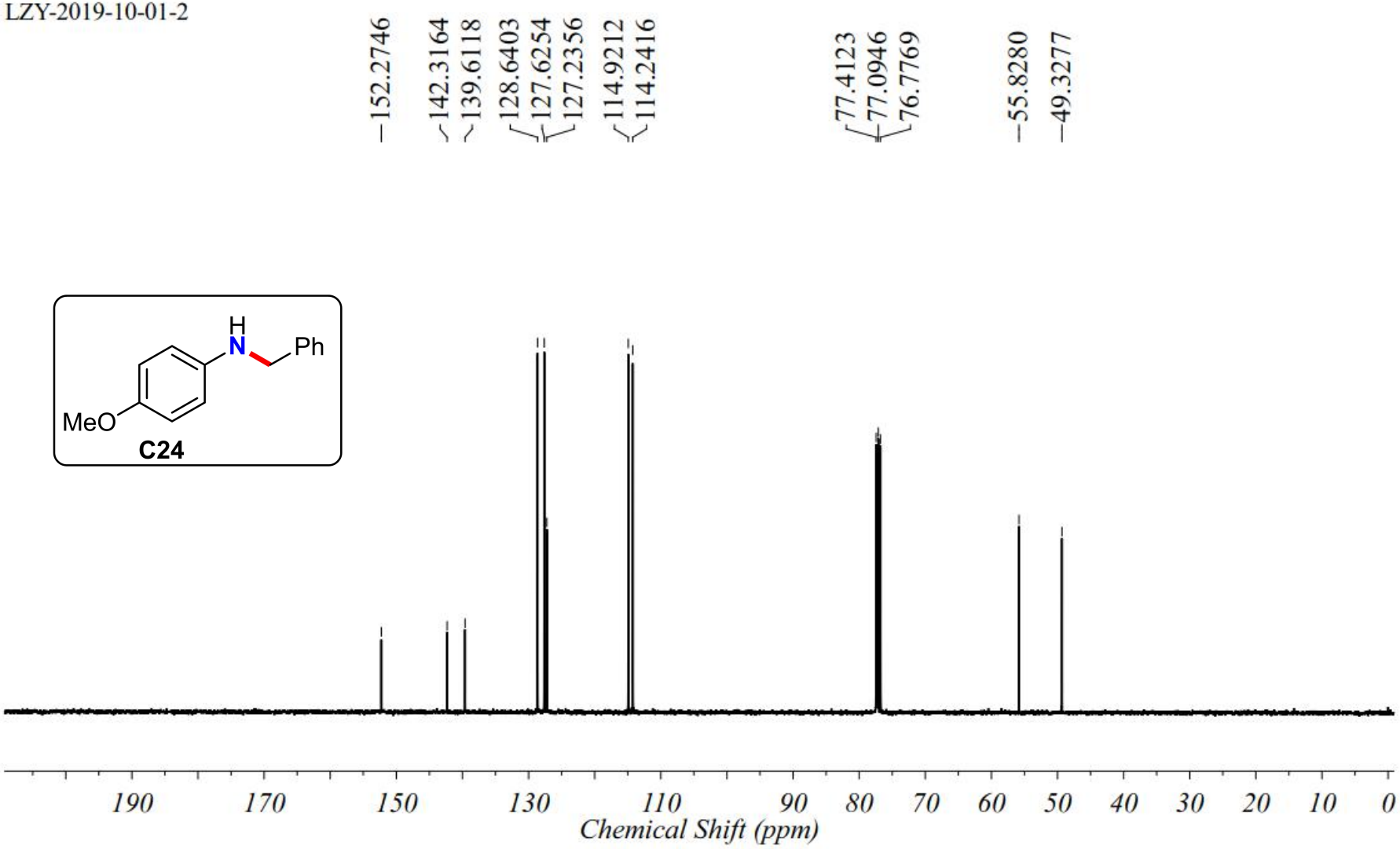

LZY-2019-09-20-1
7.7818
7.7574
7.7209
7.6966
7.6712
7.6126
7.5748
7.5613
7.5134
7.5005
7.4857
7.4563
7.4289
7.4025
7.0859
7.0616
7.0375
6.9531
6.9262
4.6904
4.5480
H
N
Ph
Ph
C23
4.17
8.07
1.00
1.02
0.89
2.02
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

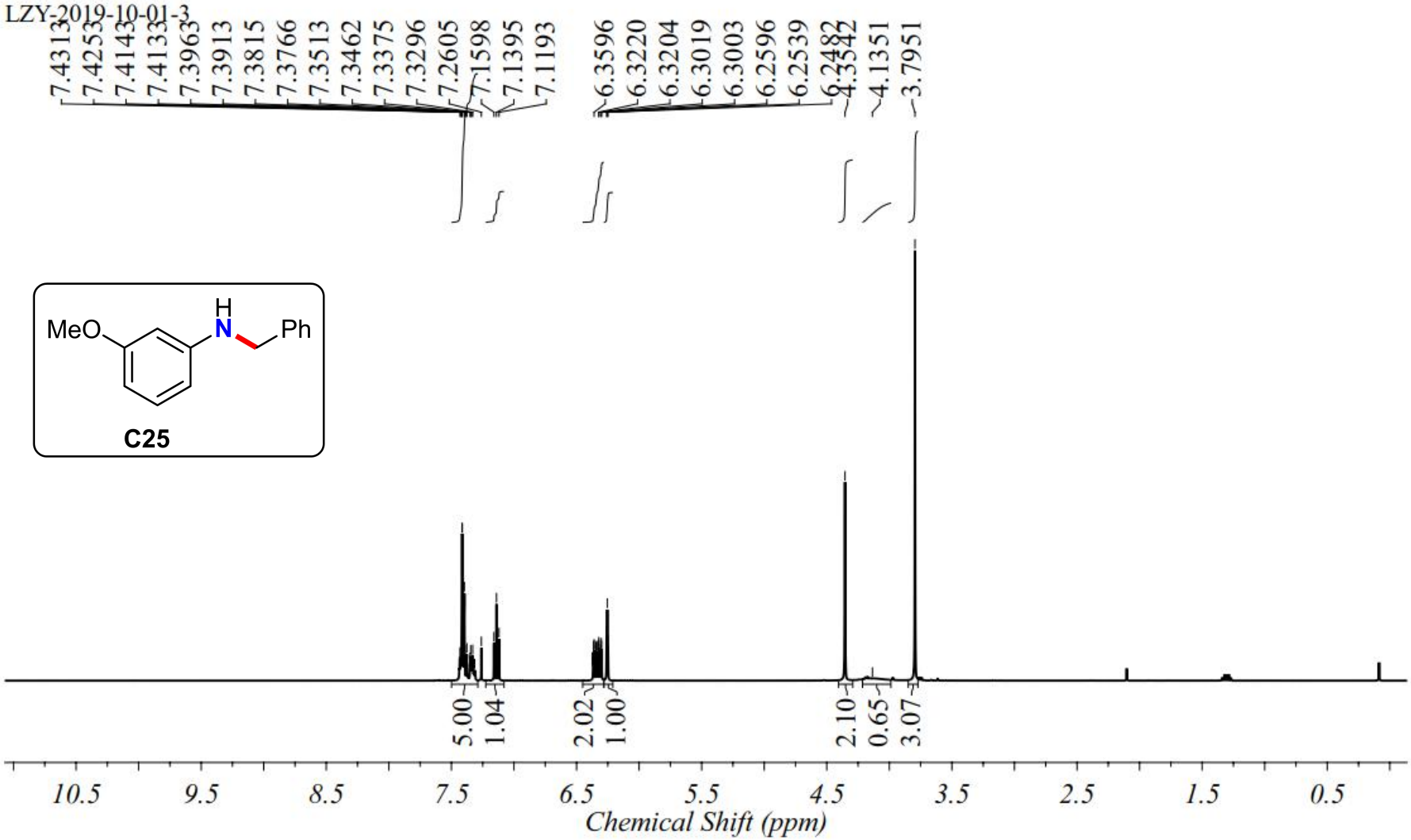
LZY-2019-10-01-1




LZY-2019-10-01-2
7.4083
7.4039
7.3872
7.3791
7.3774
7.3719
7.3598
7.3555
7.3447
7.3406
7.3122
7.3080
7.2907
7.2605
6.8109
6.8052
6.7943
6.7885
6.6427
6.6369
6.6260
6.6203
4.3013
3.7580
H
N
Ph
MeO
C24
4.06
1.00
0.37
2.07
2.08
2.13
3.10
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

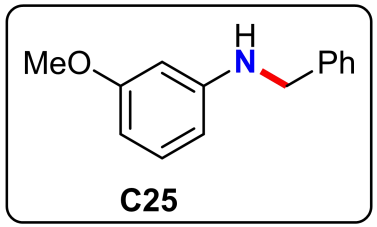
LZY-2019-10-01-2



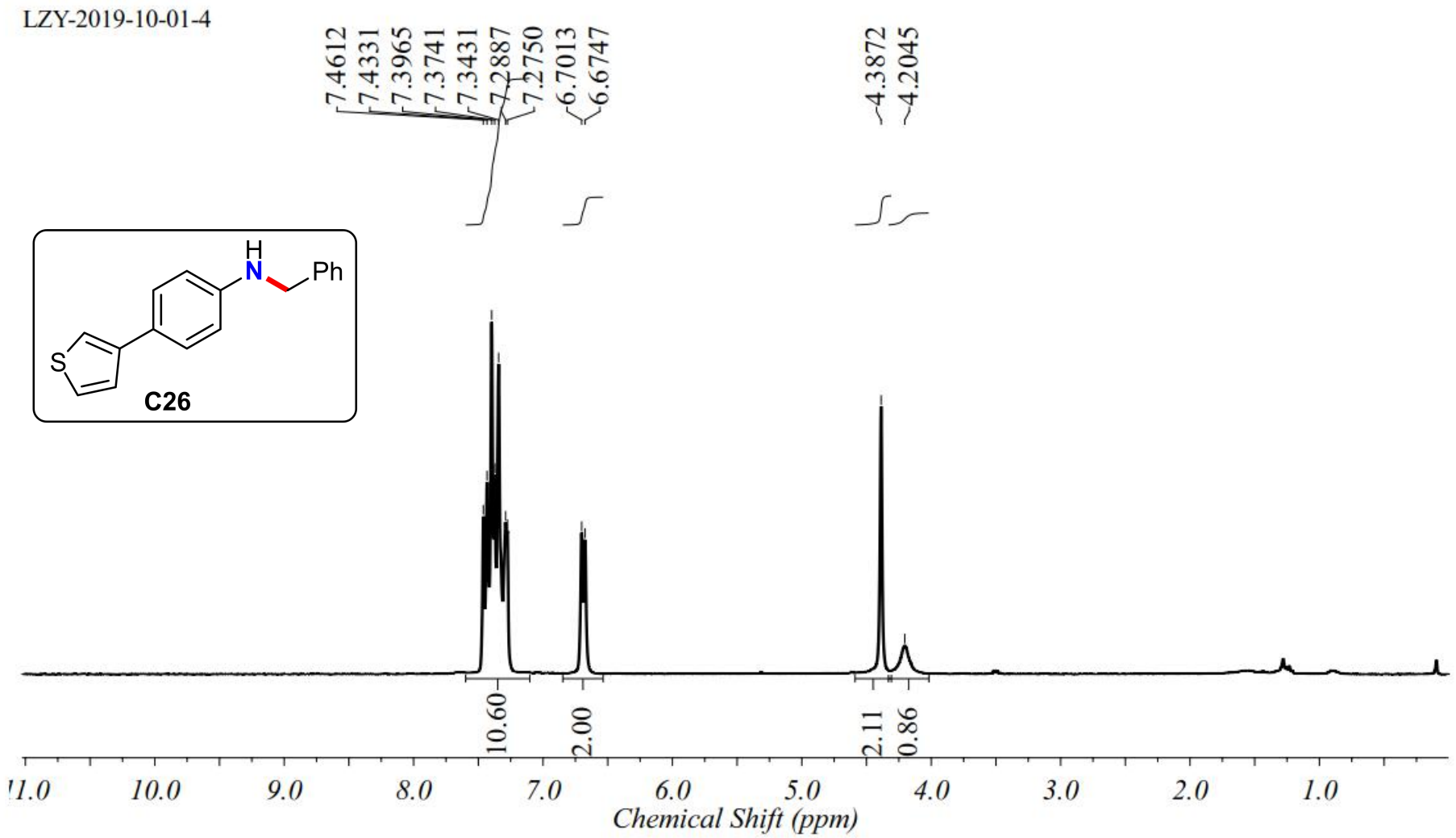

LZY-2019-10-01-3
7.4313
7.4253
7.4143
7.4133
7.3963
7.3913
7.3815
7.3766
7.3513
7.3462
7.3375
7.3296
7.2605
7.1598
7.1395
7.1193
6.3596
6.3220
6.3204
6.3019
6.3003
6.2596
6.2539
6.2482
4.3542
4.1351
3.7951
MeO
H
N
Ph
C25
5.00
1.04
2.02
1.00
2.10
0.65
3.07
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

LZY-2019-10-01-3

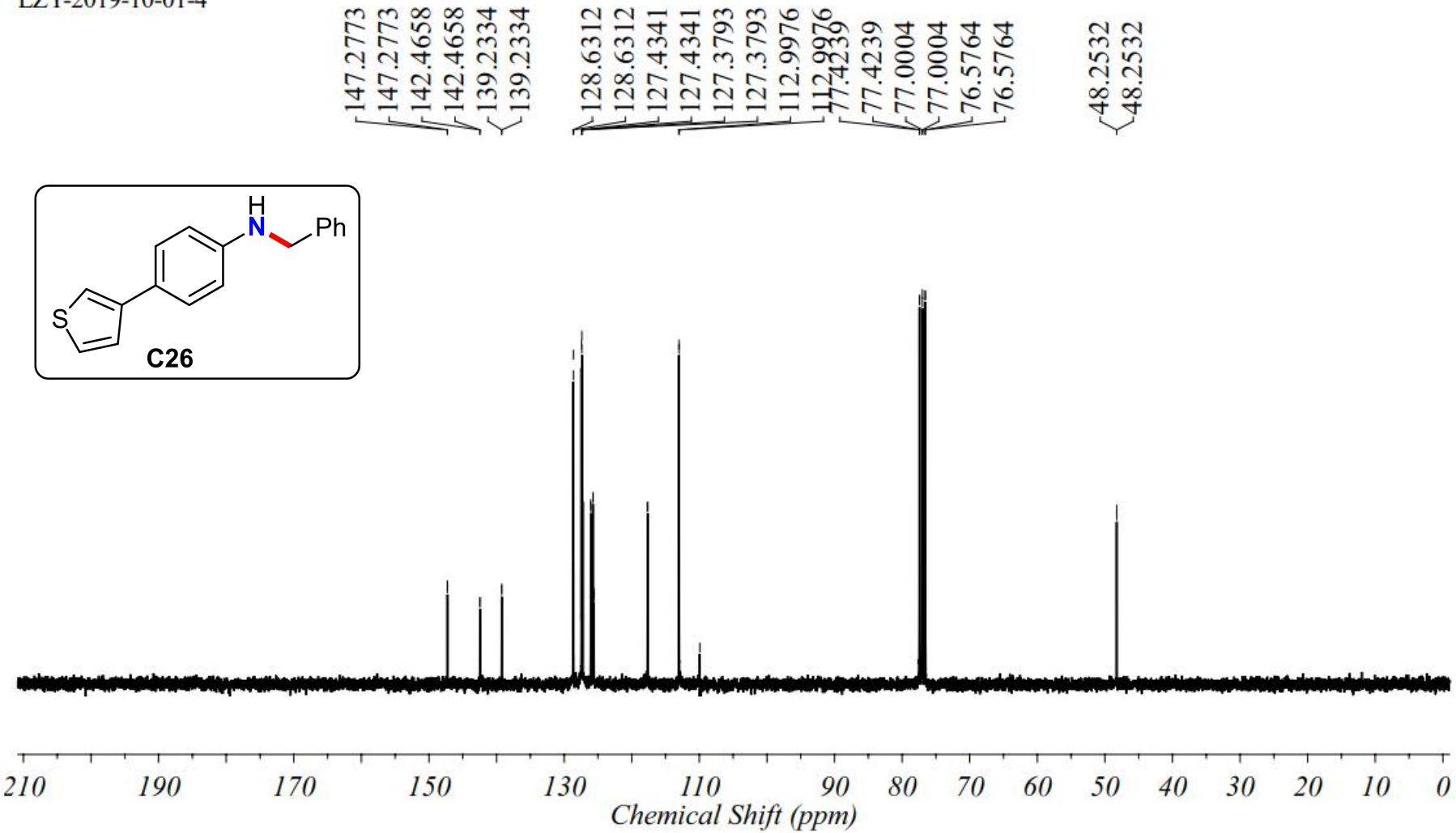
160.8951
149.5849
139.3961
130.0944
128.7230
127.6154
127.3332
106.0959
102.7730
98.9741
77.5047
77.1868
76.8688
55.1297
48.3832

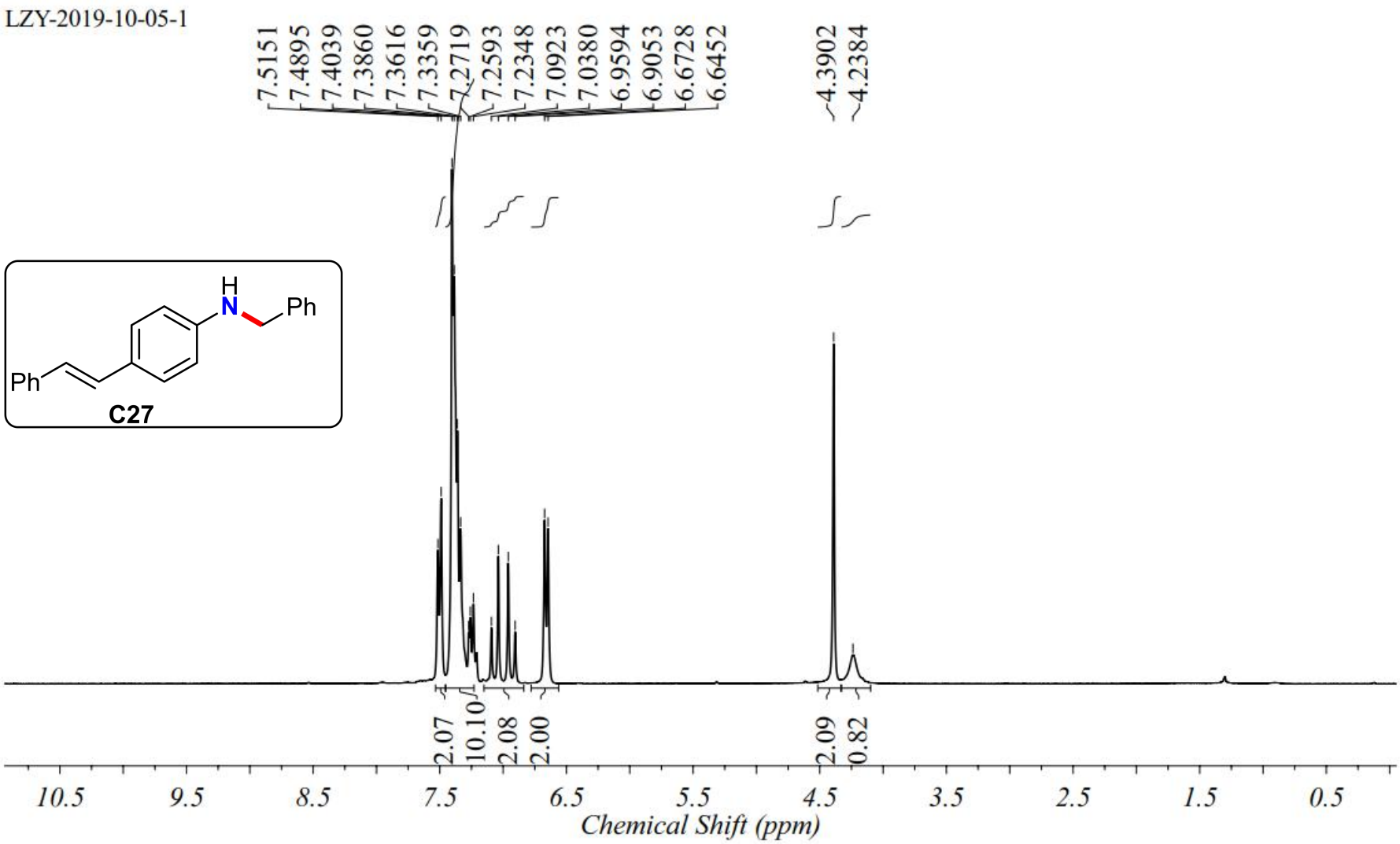


C25

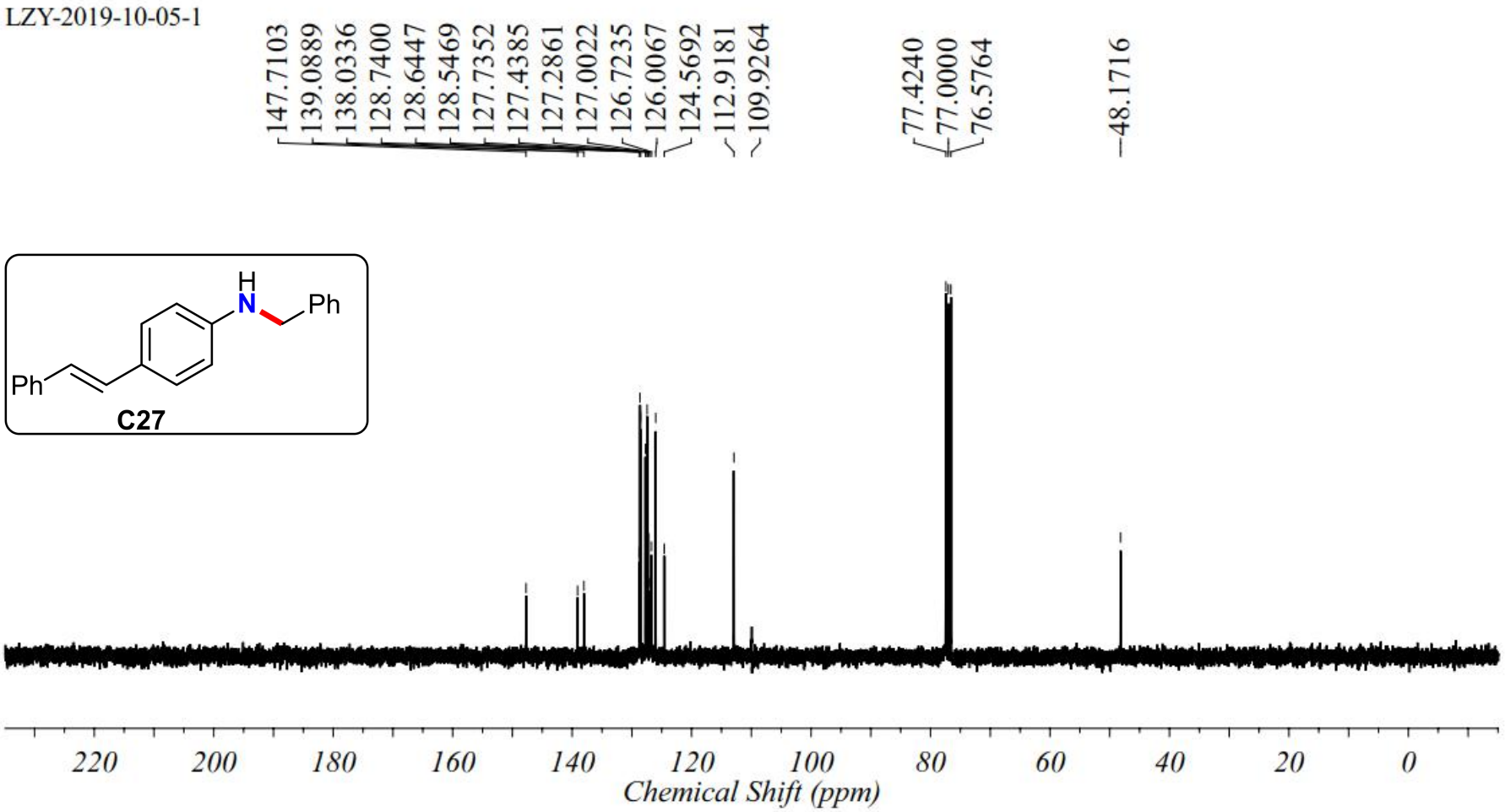

LZY-2019-10-01-4
7.4612
7.4331
7.3965
7.3741
7.3431
7.2887
7.2750
6.7013
6.6747
4.3872
4.2045
H
N
Ph
S
C26
10.60
2.00
2.11
0.86
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

LZY-2019-10-01-4

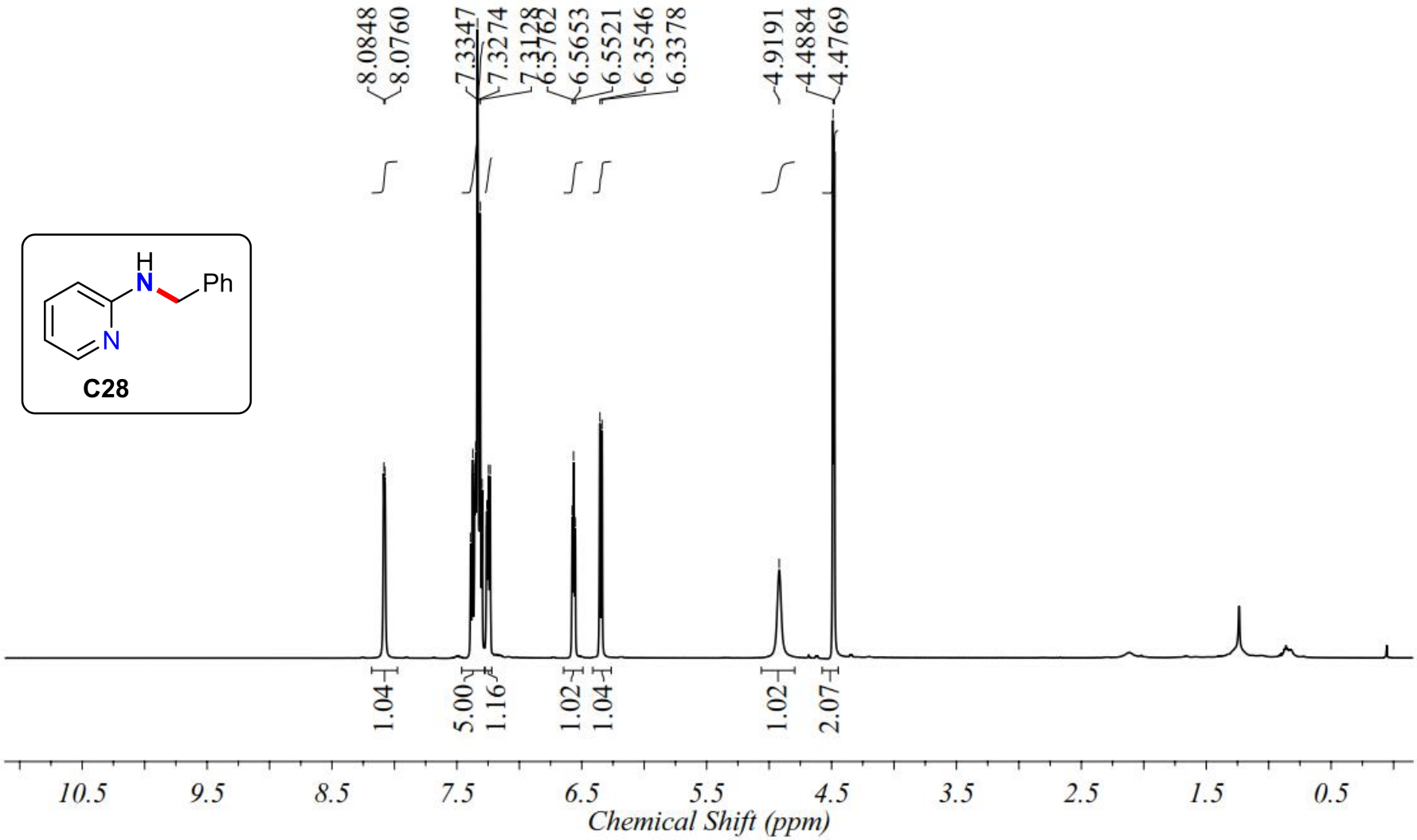



LZY-2019-10-05-1
7.5151
7.4895
7.4039
7.3860
7.3616
7.3359
7.2719
7.2593
7.2348
7.0923
7.0380
6.9594
6.9053
6.6728
6.6452
4.3902
4.2384
H
N
Ph
Ph
C27
2.07
10.10
2.08
2.00
2.09
0.82
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

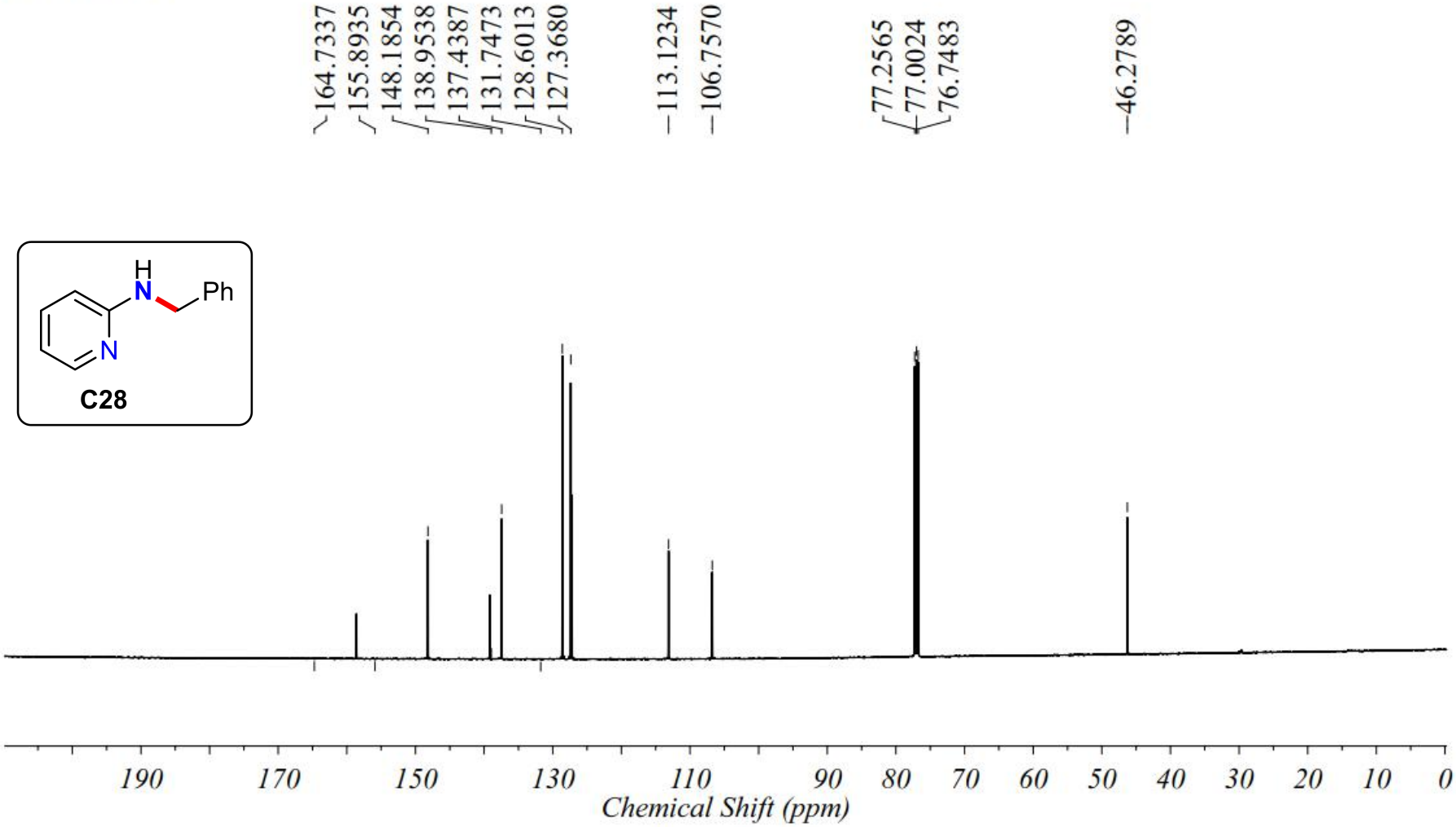
LZY-2019-10-05-1



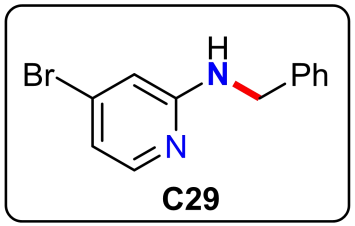
LZY-2019-10-05-3



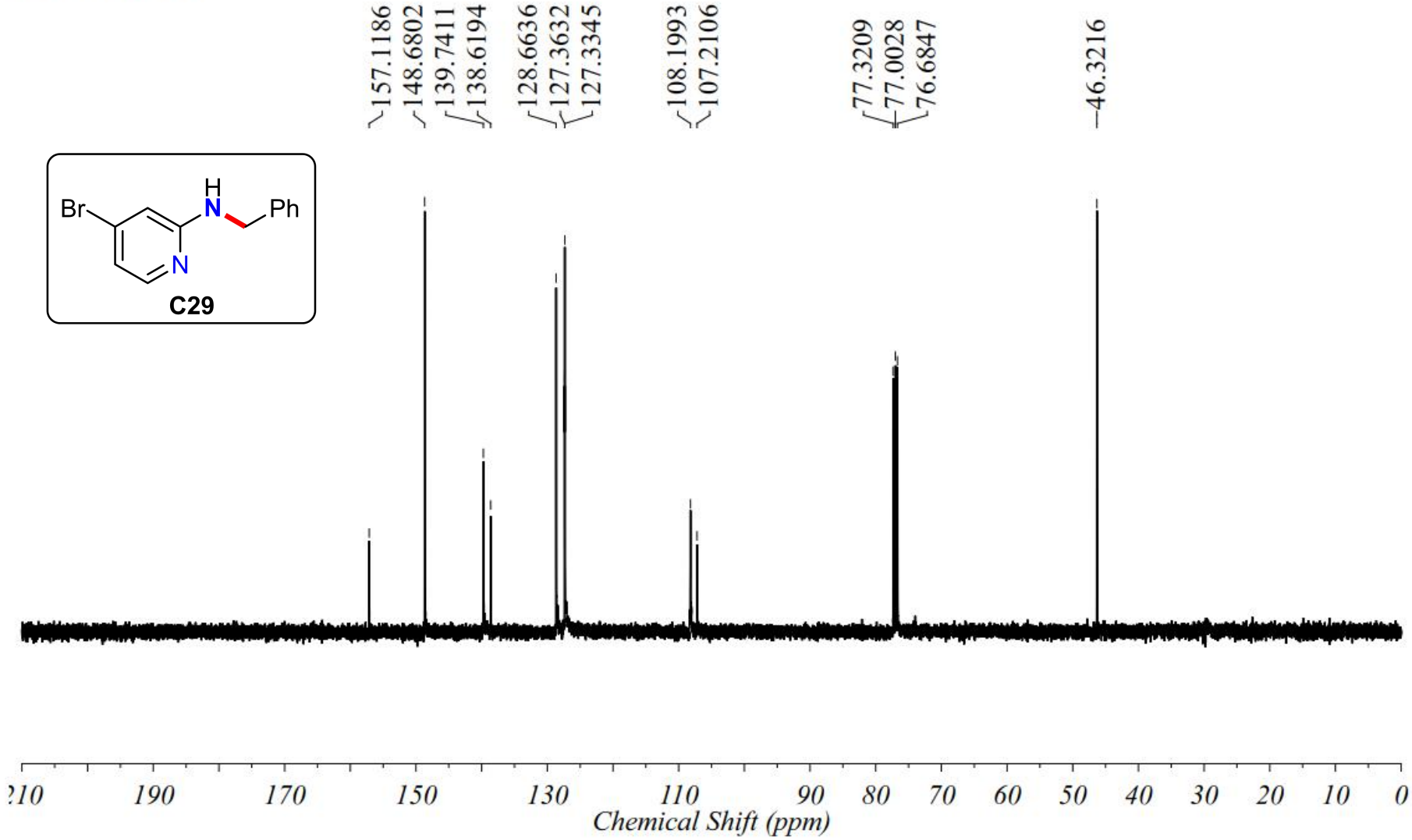
LZY-2019-10-05-3

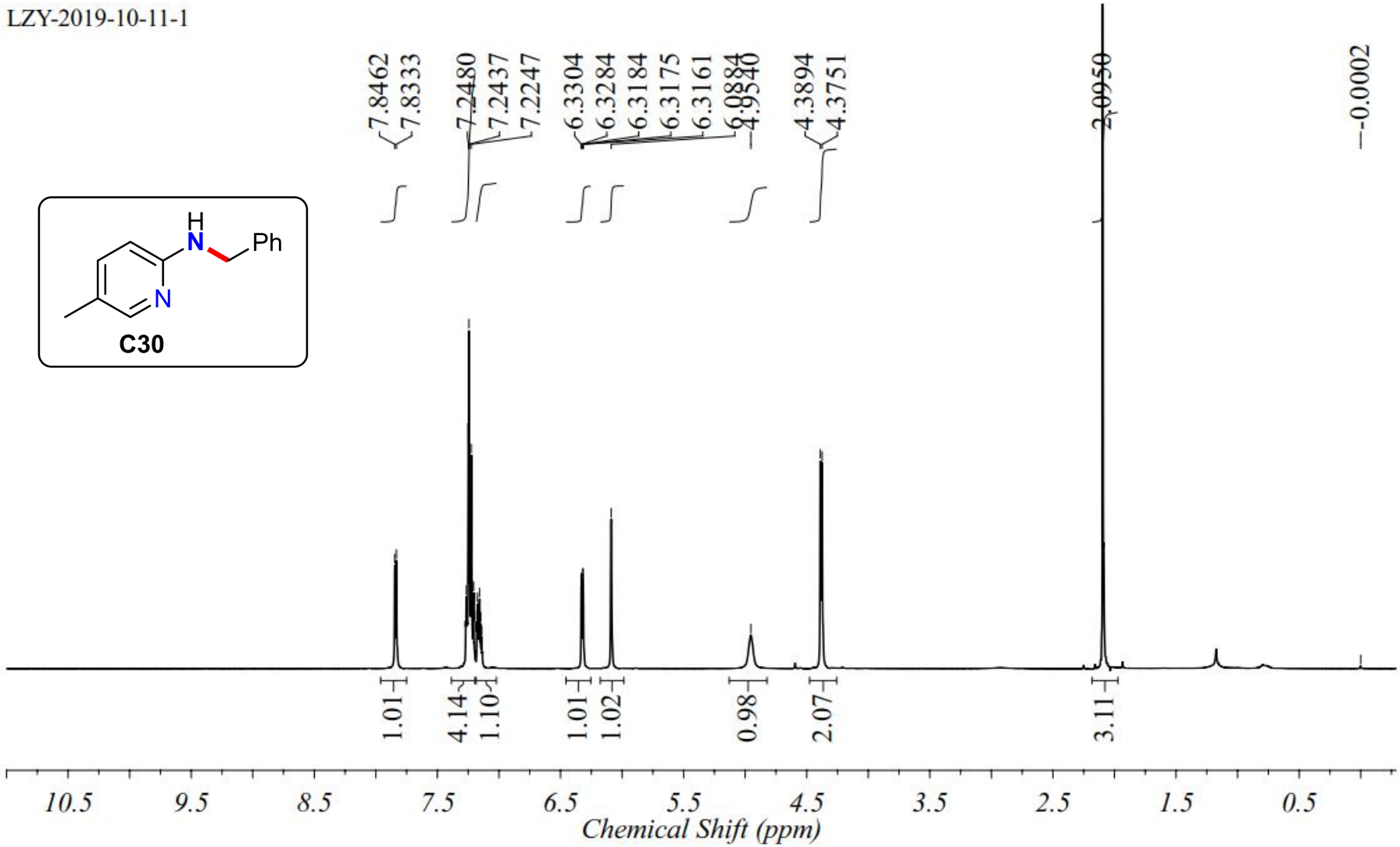


LZY-2019-10-05-4

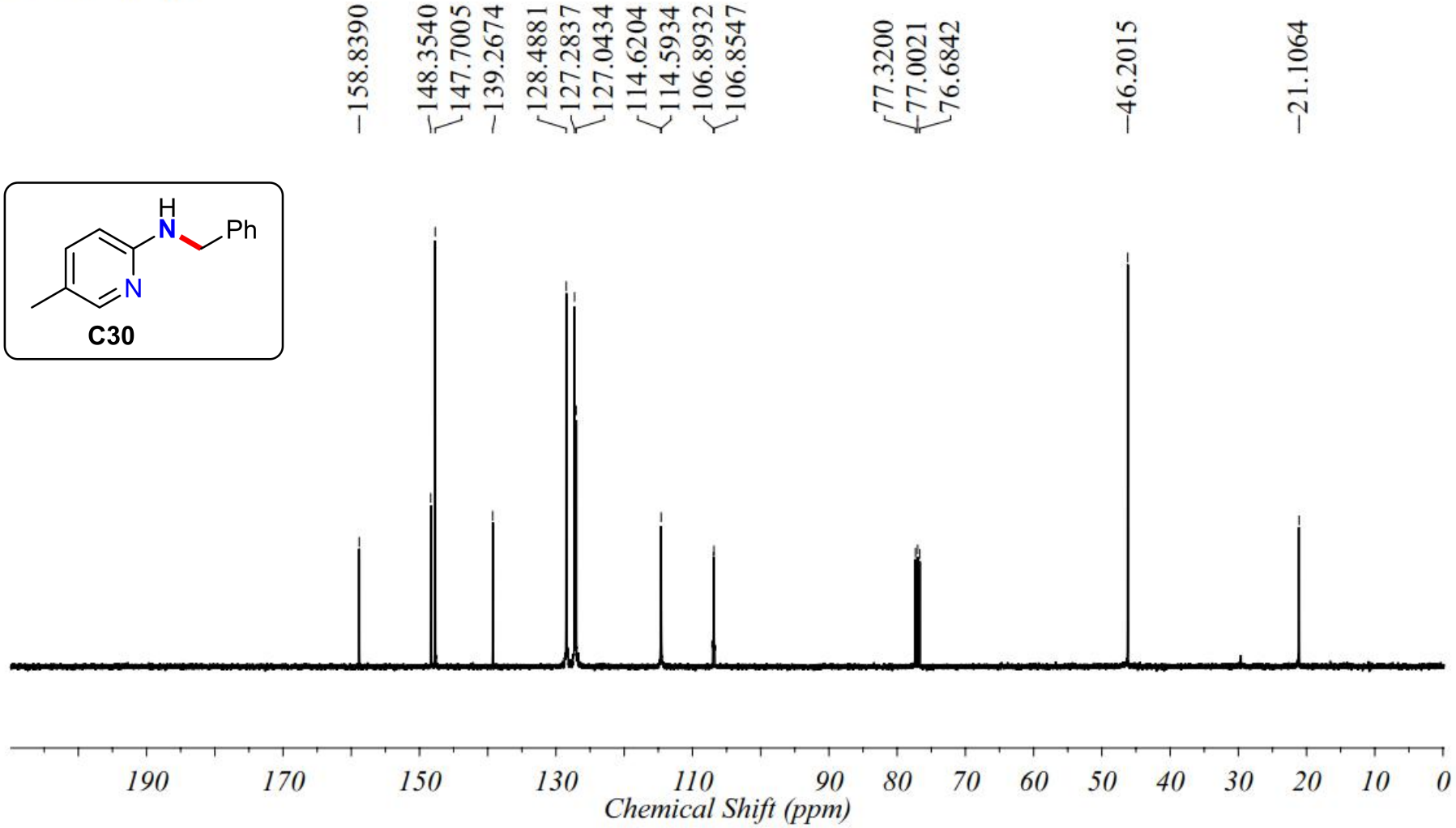


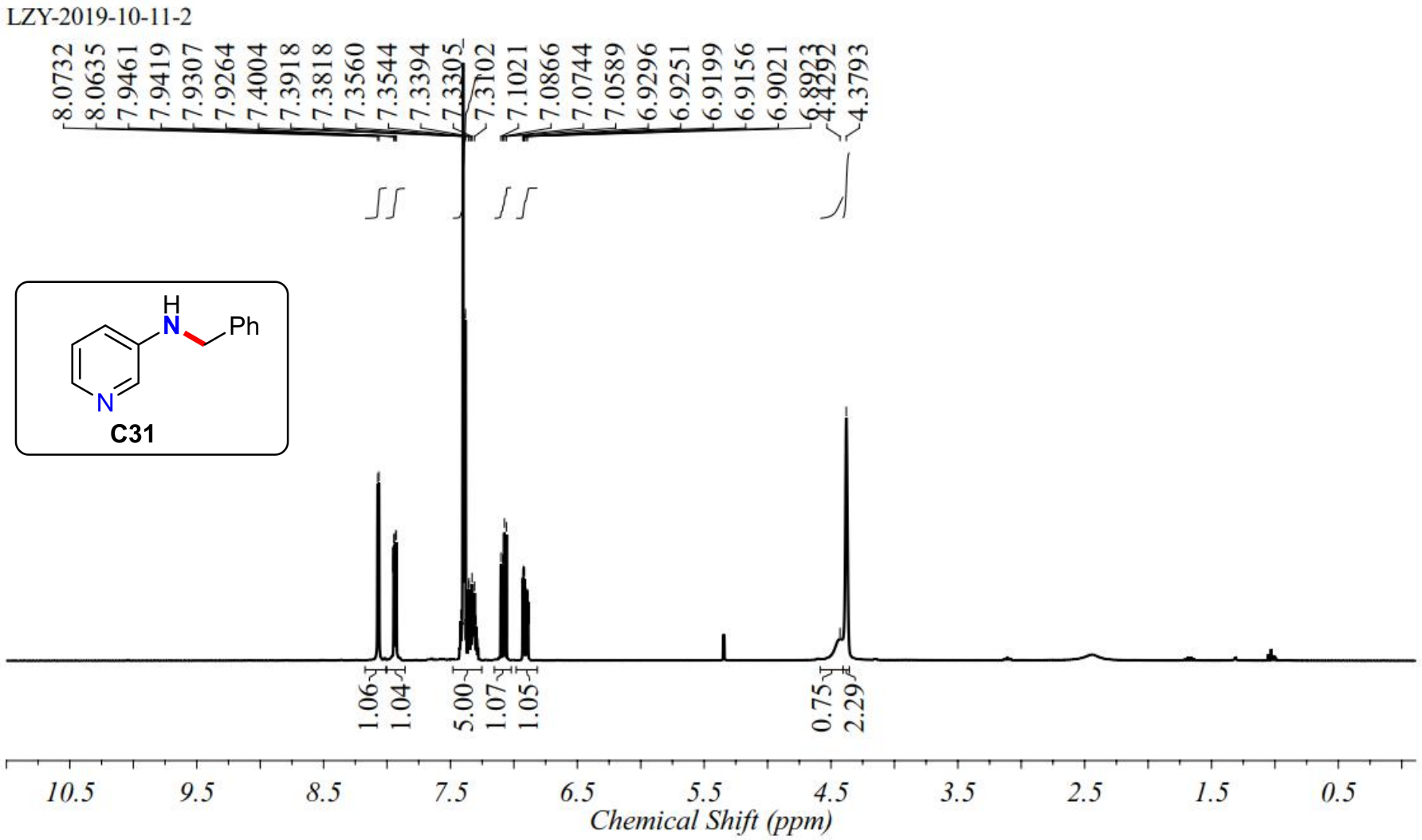
LZY-2019-10-05-4



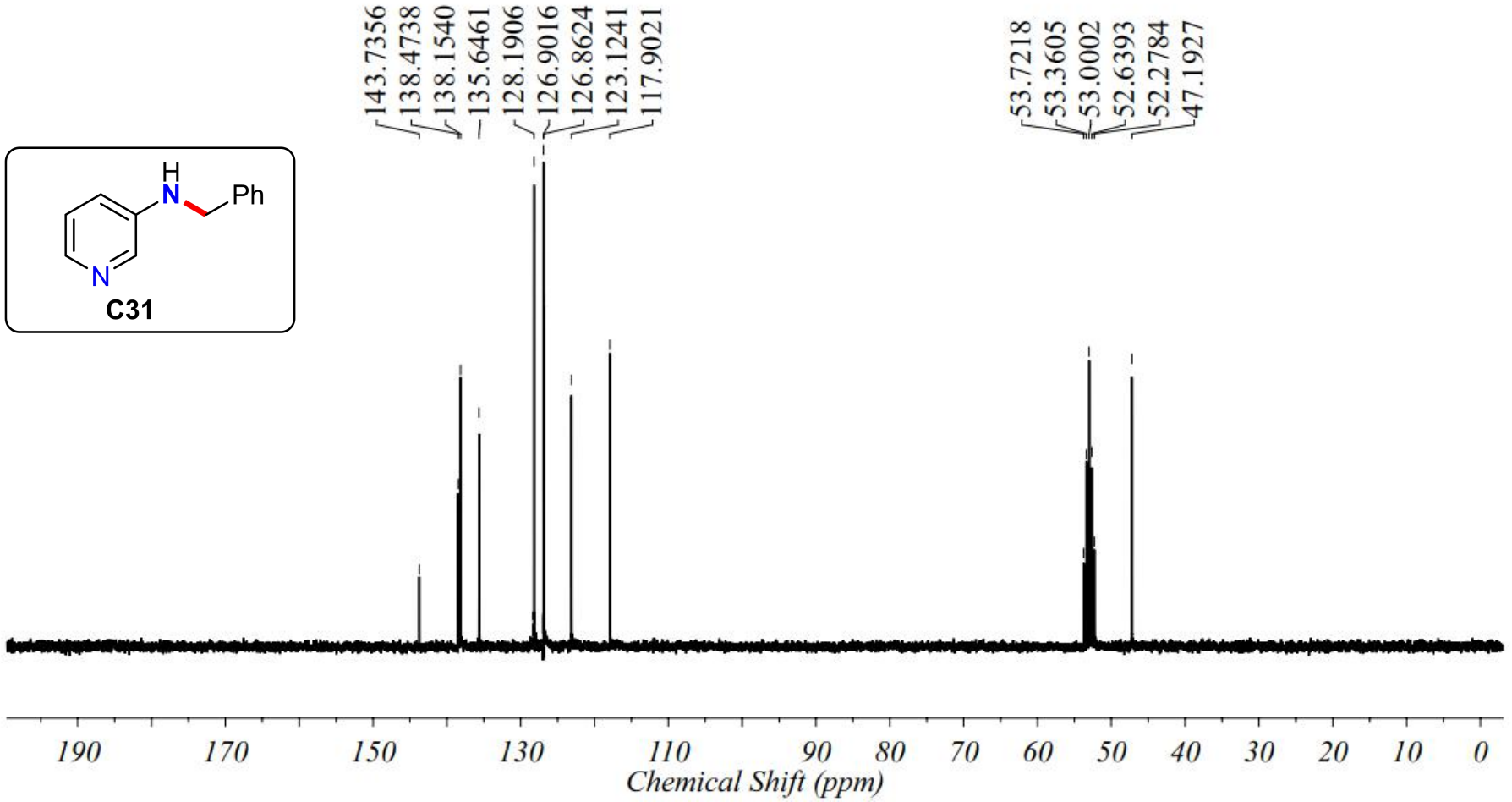

LZY-2019-10-11-1
7.8462
7.8333
7.2480
7.2437
7.2247
6.3304
6.3284
6.3184
6.3175
6.3161
4.3894
4.3751
2.0950
-0.0002
H
N
Ph
N
C30
1.01
4.14
1.10
1.01
1.02
0.98
2.07
3.11
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

LZY-2019-10-11-1

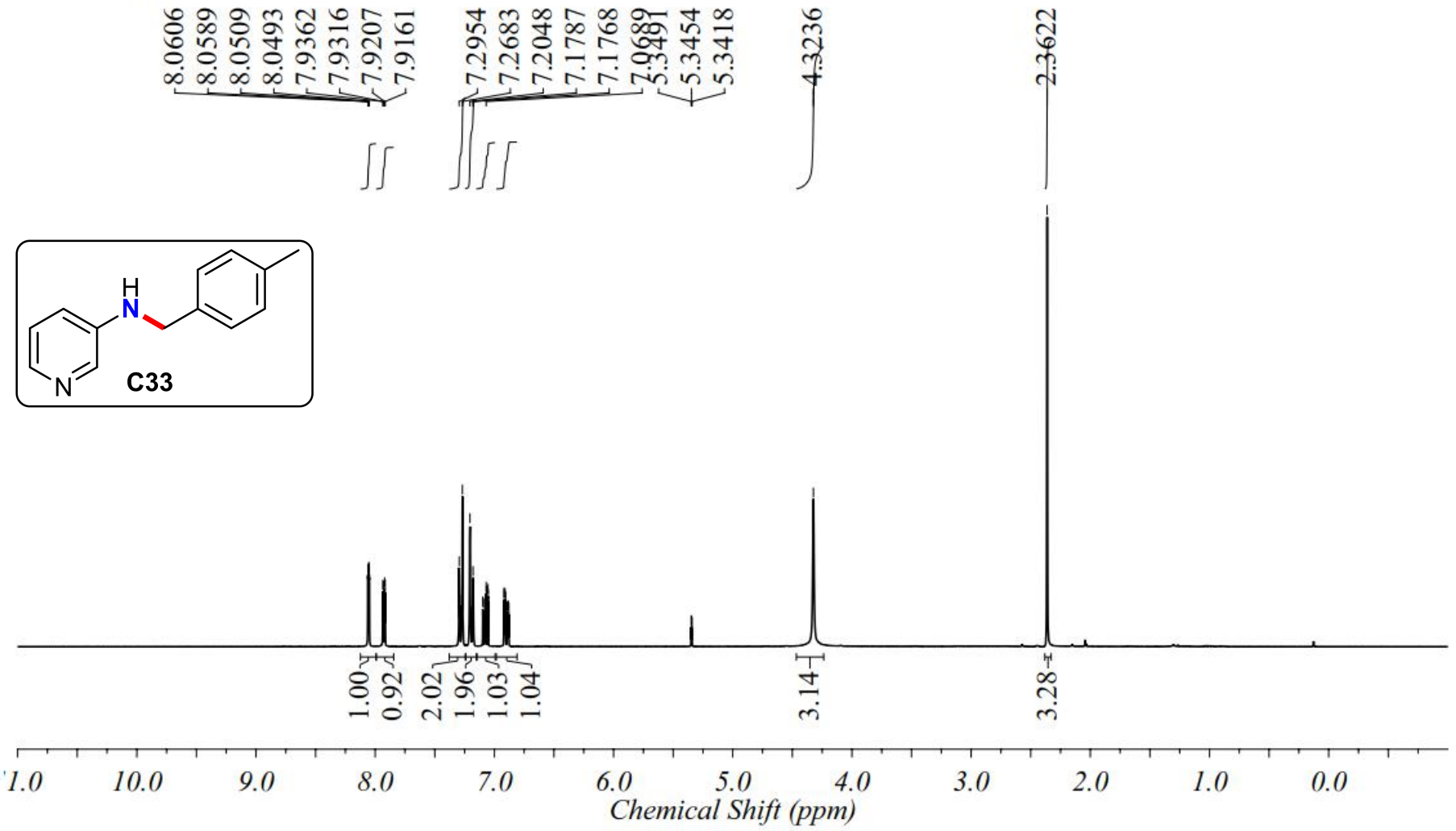



LZY-2019-10-11-2
8.0732
8.0635
7.9461
7.9419
7.9307
7.9264
7.4004
7.3918
7.3818
7.3560
7.3544
7.3394
7.3305
7.3102
7.1021
7.0866
7.0744
7.0589
6.9296
6.9251
6.9199
6.9156
6.9021
4.4292
4.3793
H
N
Ph
N
C31
1.06
1.04
5.00
1.07
1.05
0.75
2.29
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

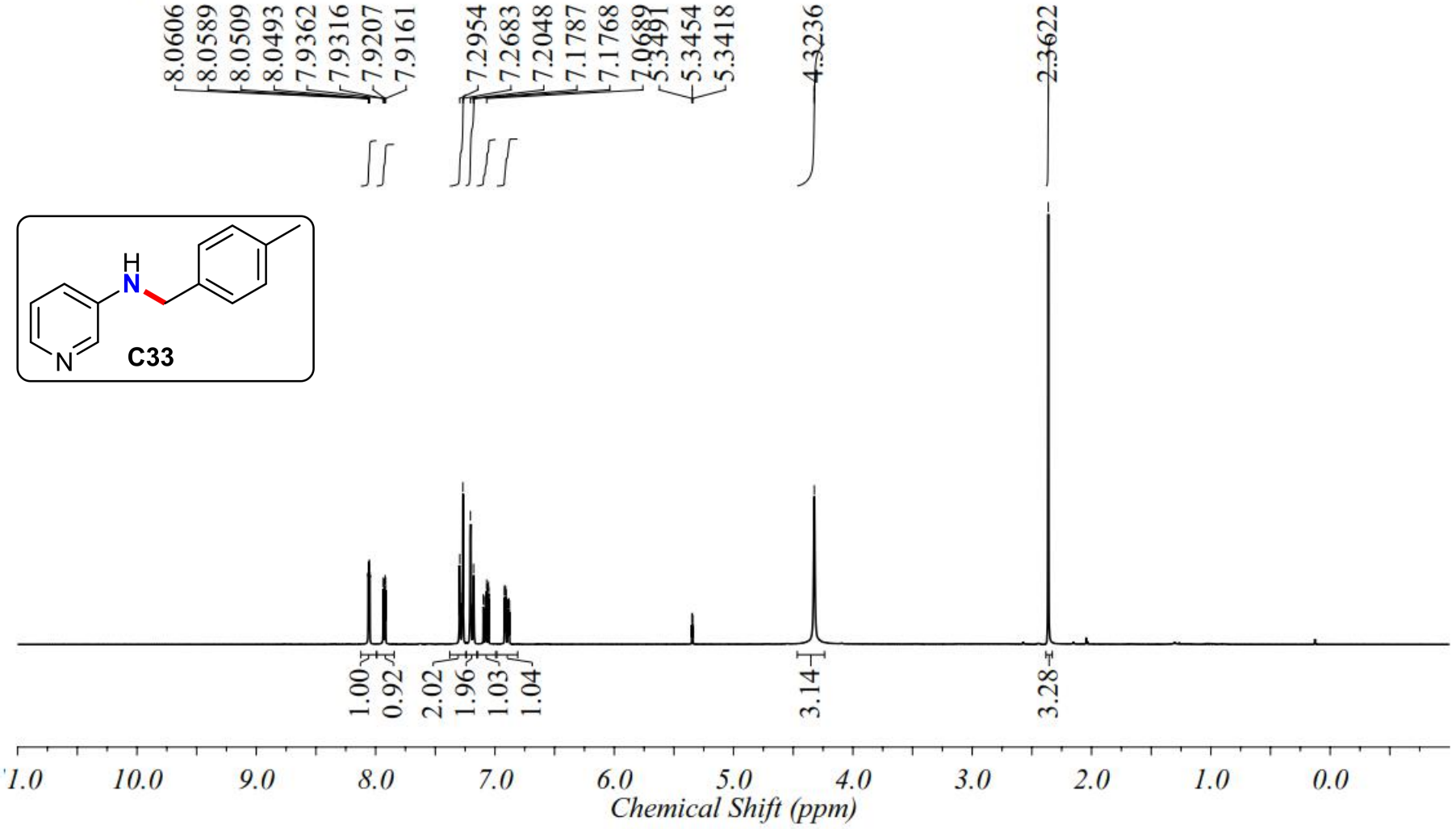
LZY-2019-10-11-2



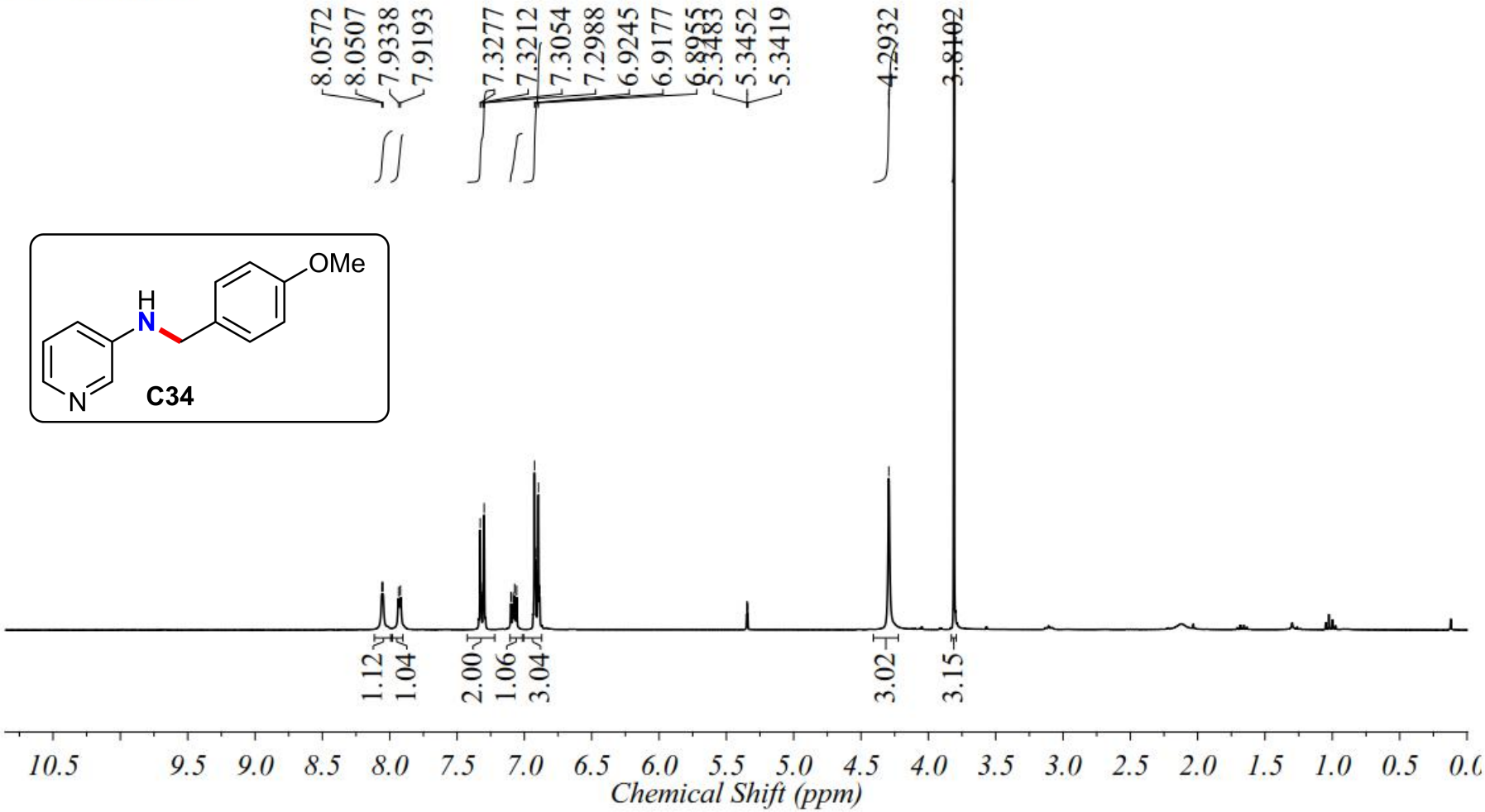
LZY-2019-10-11-3



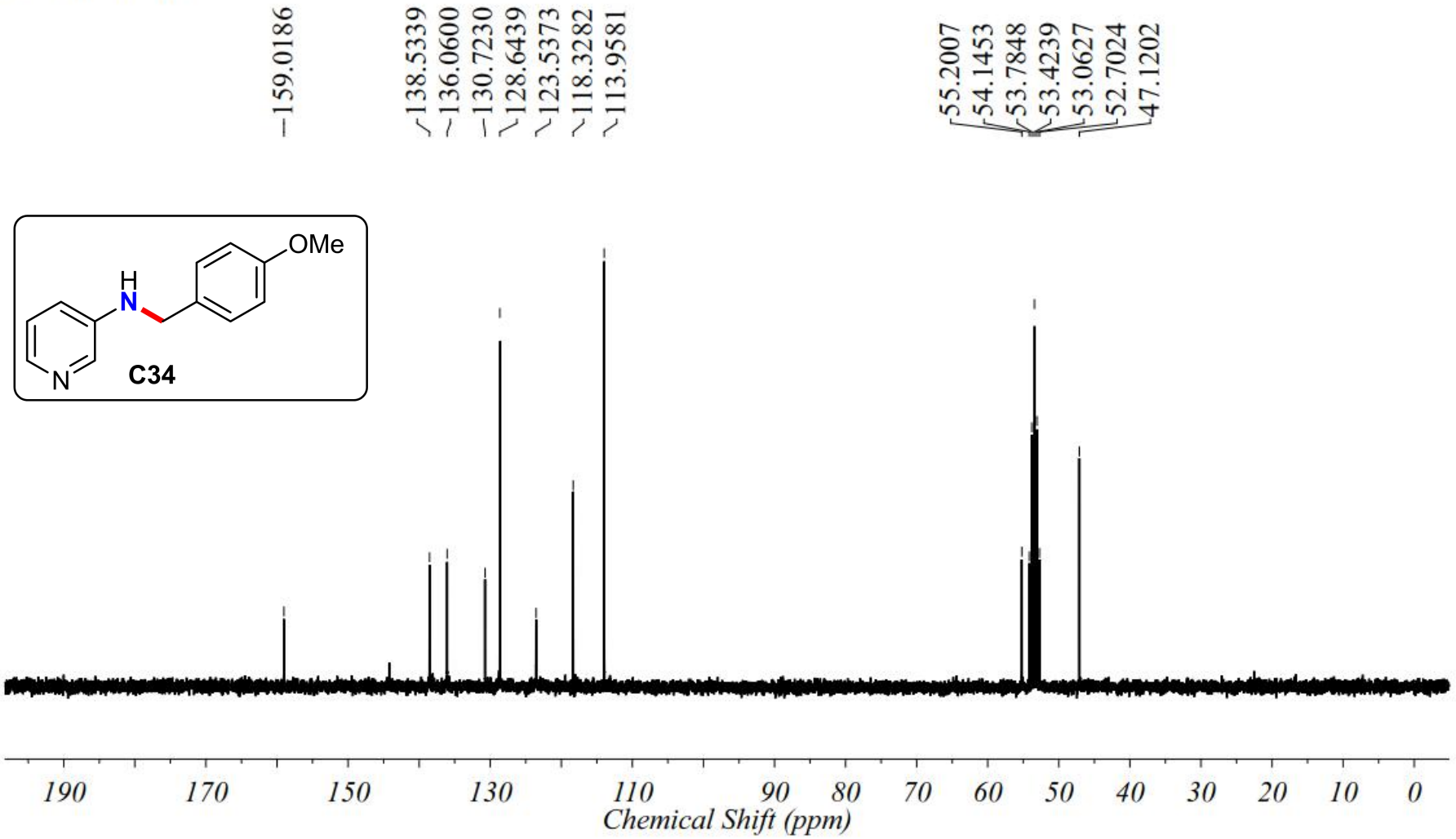
LZY-2019-10-11-3



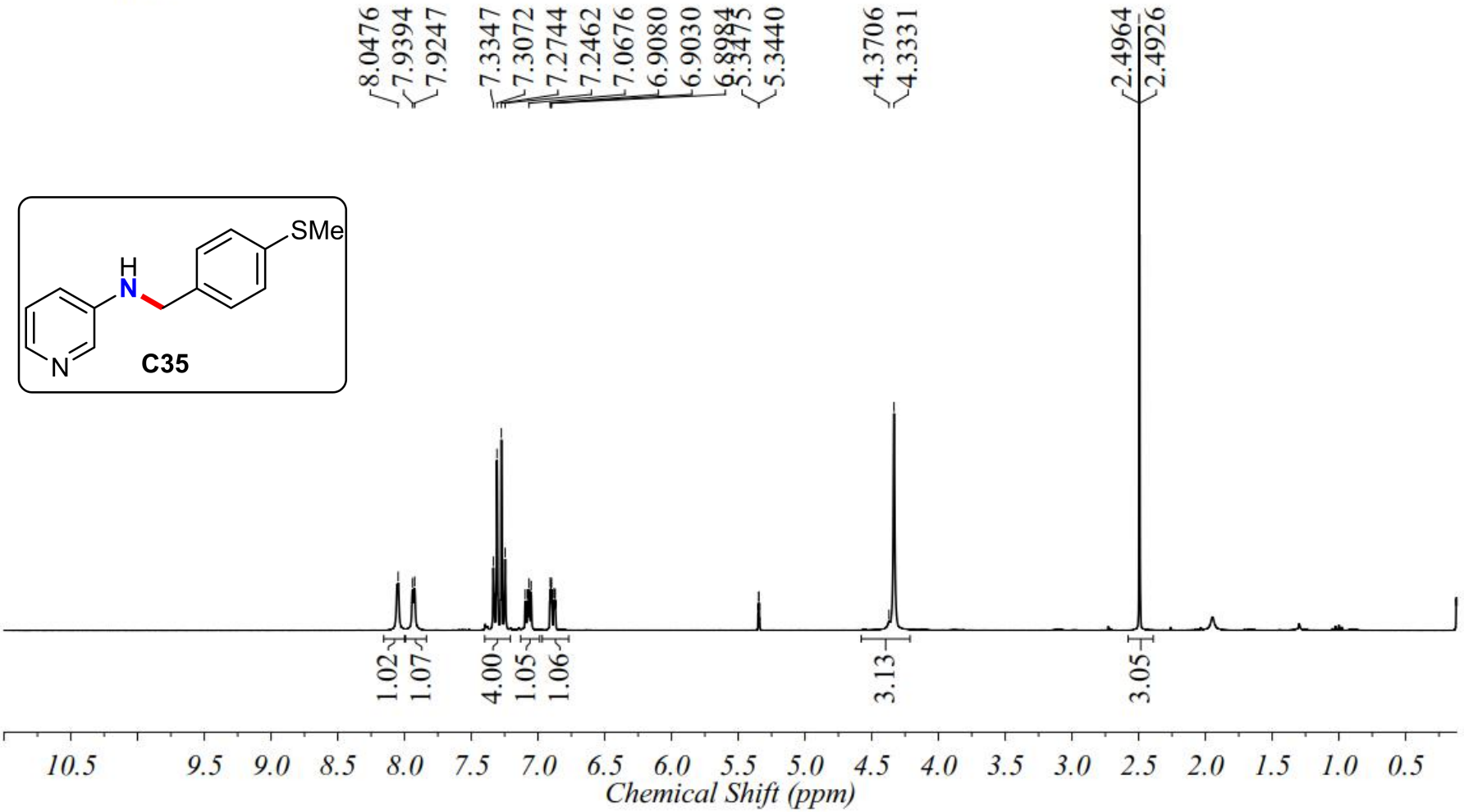
LZY-2019-10-11-4



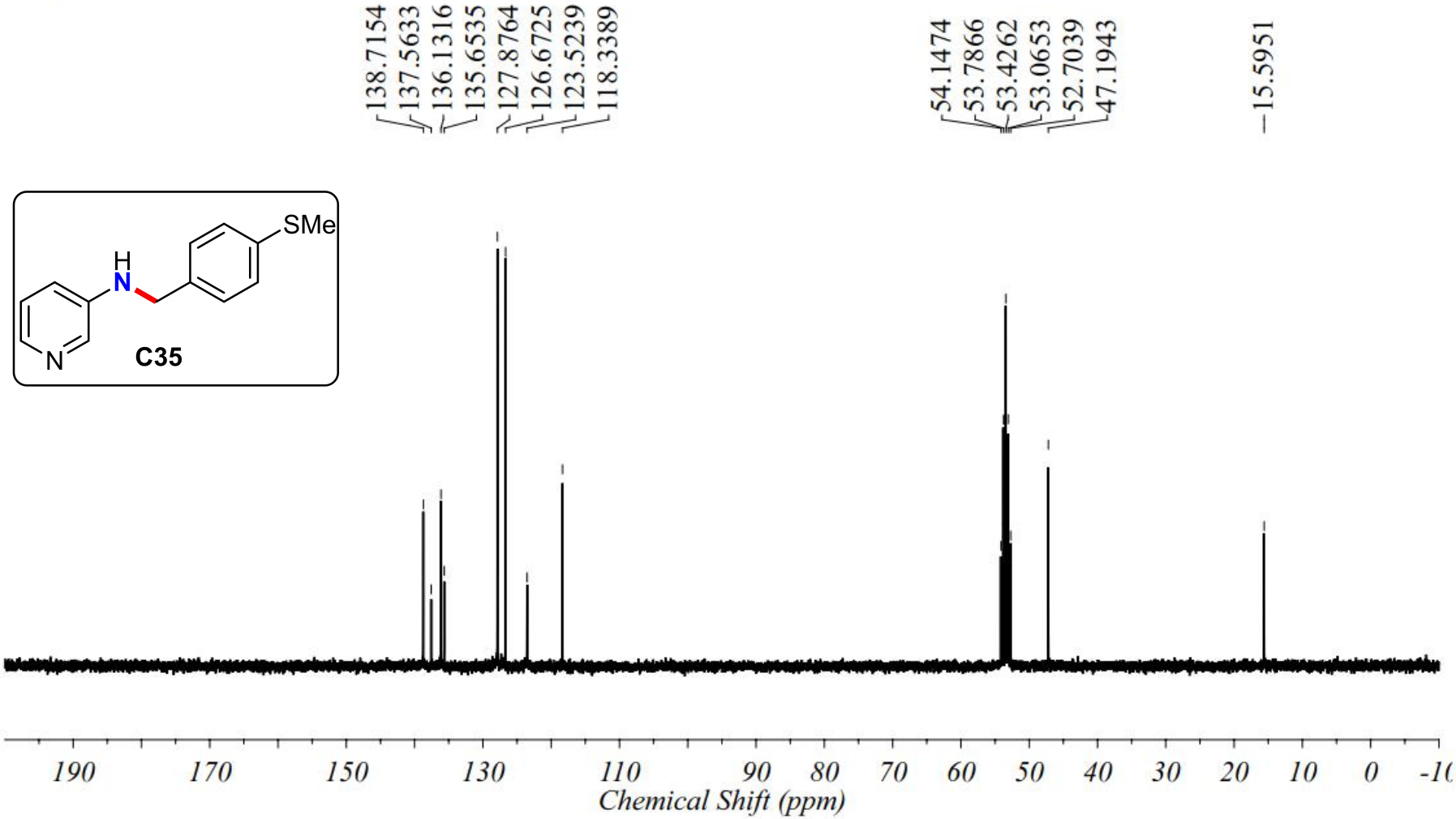
LZY-2019-10-11-4

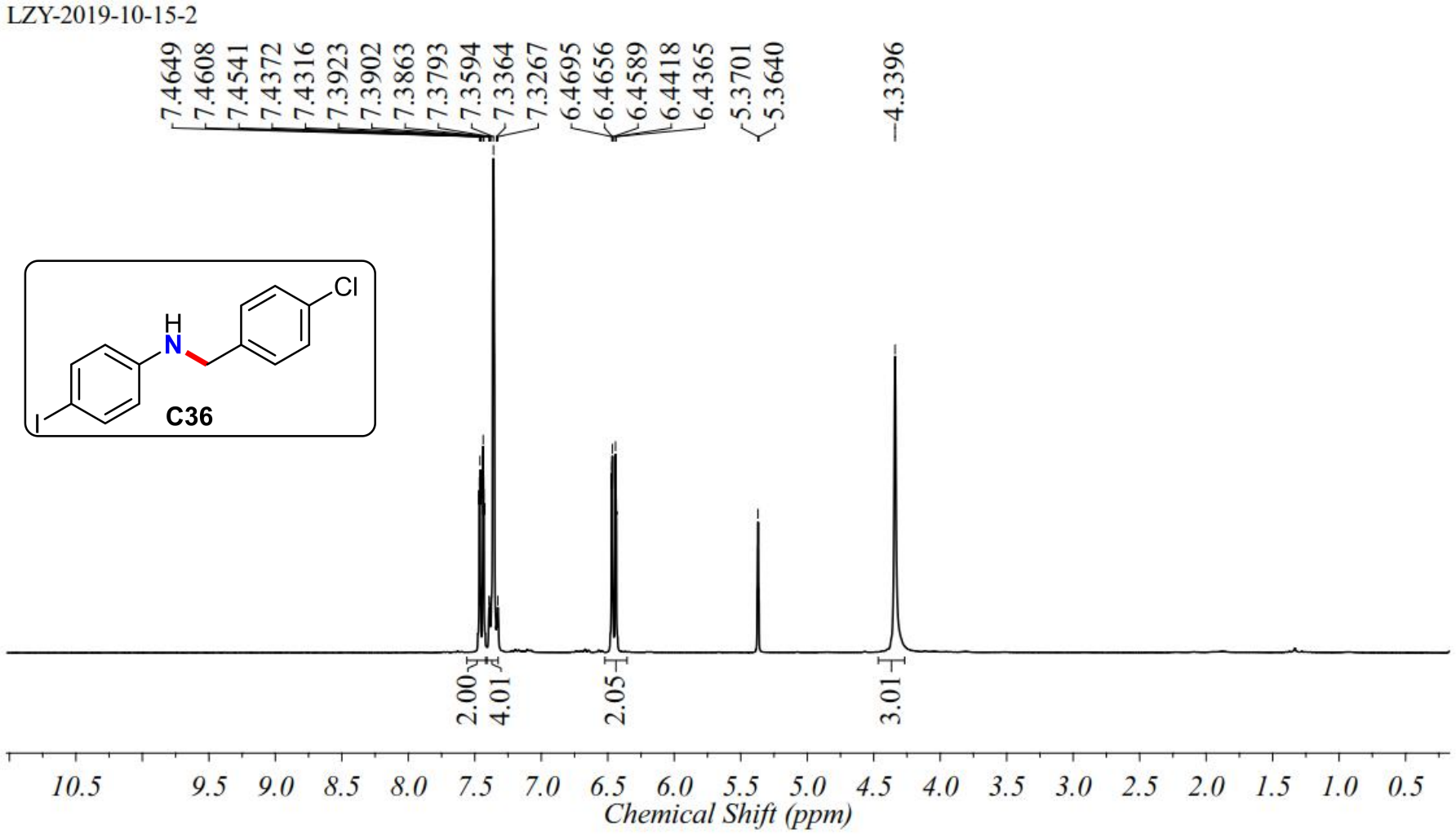


LZY-2019-10-15-1

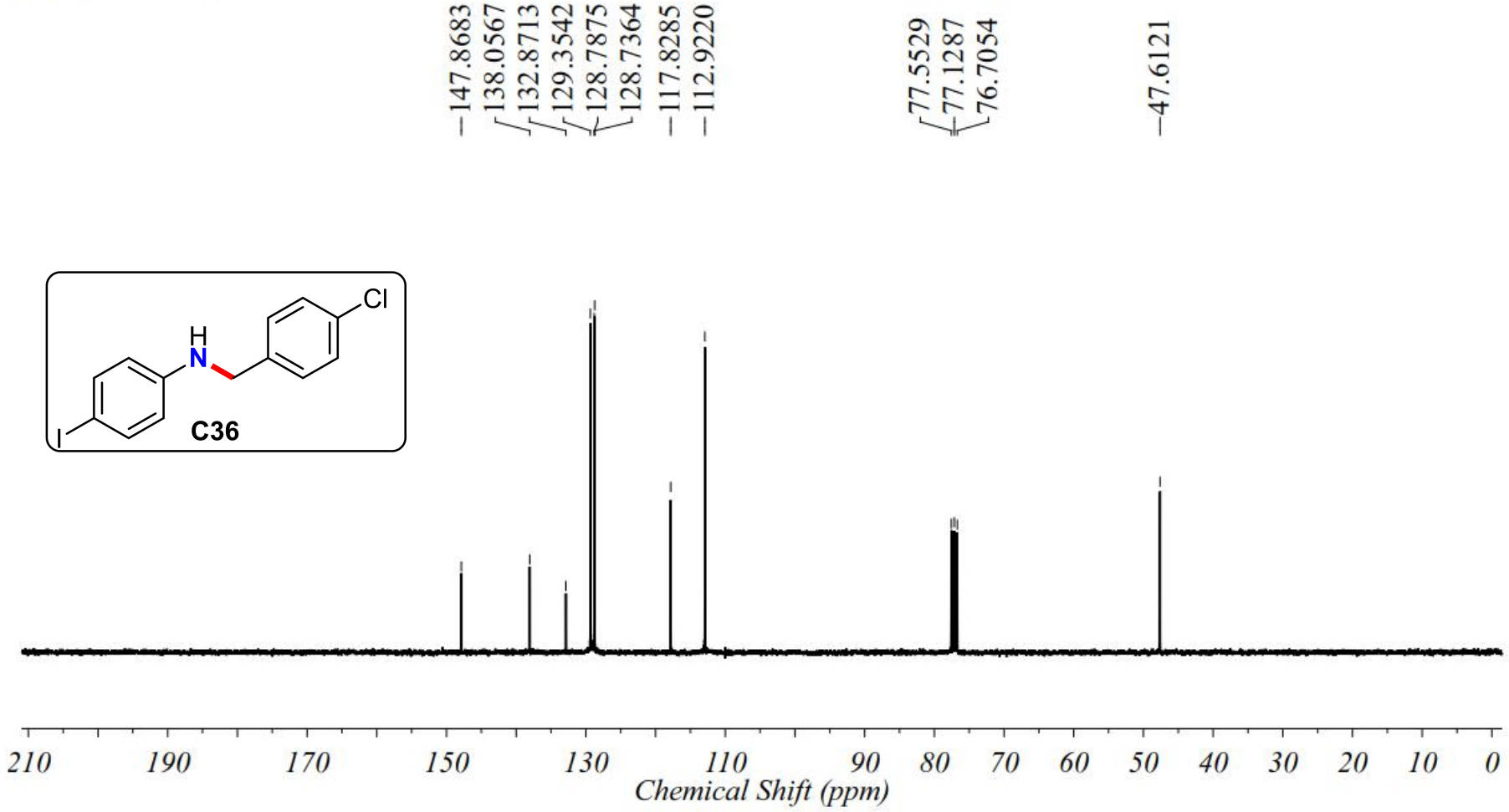


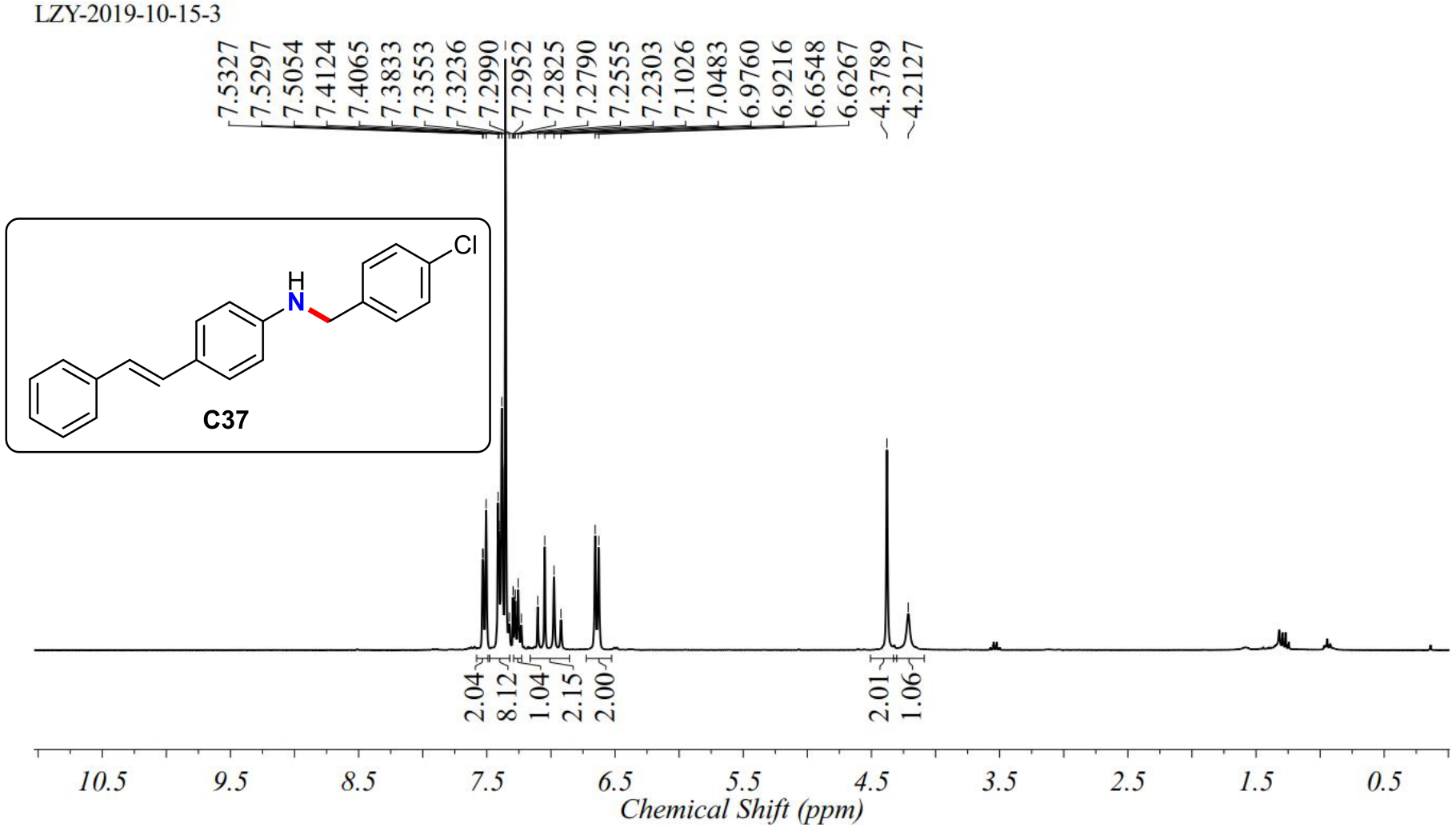
LZY-2019-10-15-1



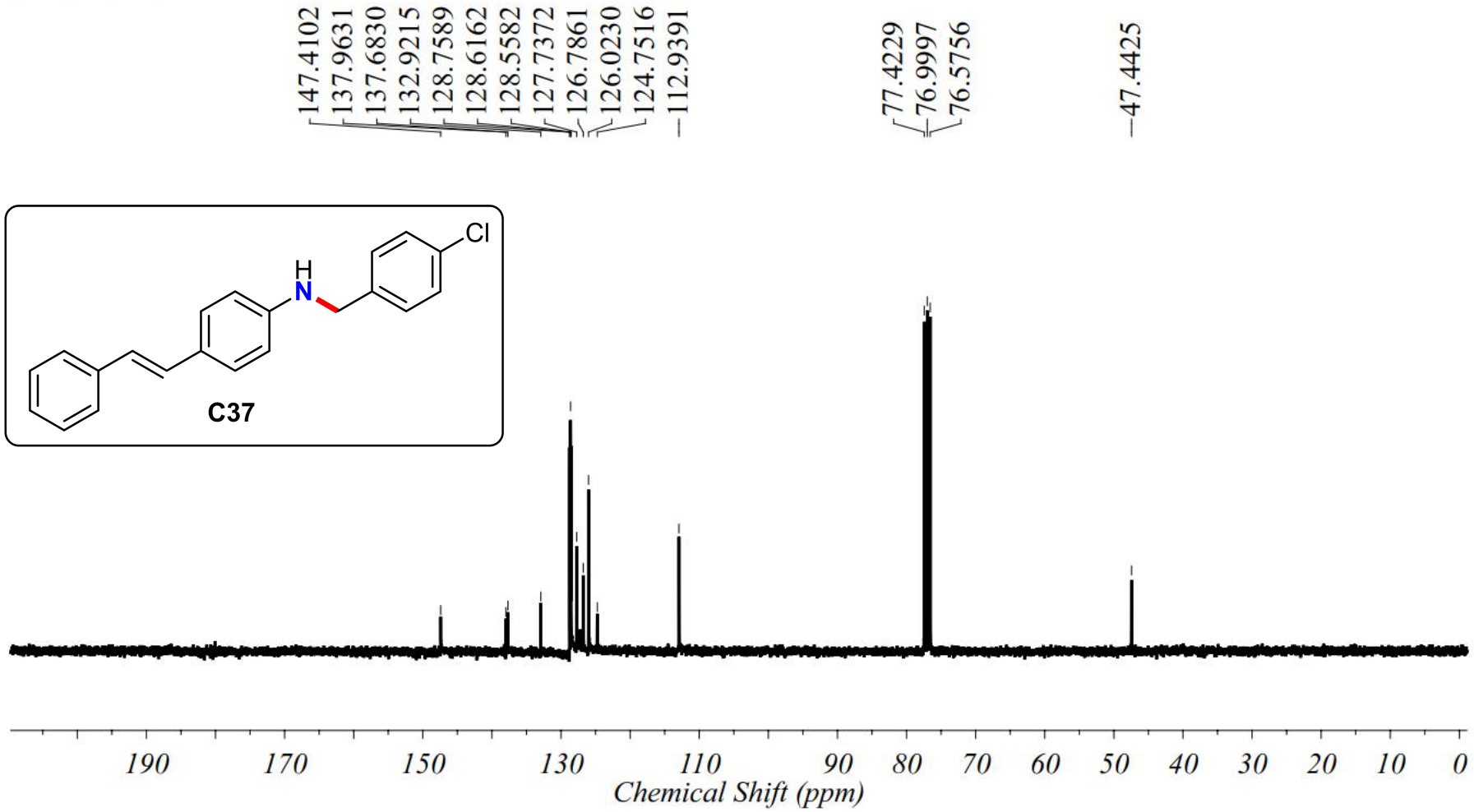

LZY-2019-10-15-2
7.4649
7.4608
7.4541
7.4372
7.4316
7.3923
7.3902
7.3863
7.3793
7.3594
7.3364
7.3267
6.4695
6.4656
6.4589
6.4418
6.4365
5.3701
5.3640
4.3396
Cl
H
N
C36
2.00
4.01
2.05
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

LZY-2019-10-15-2

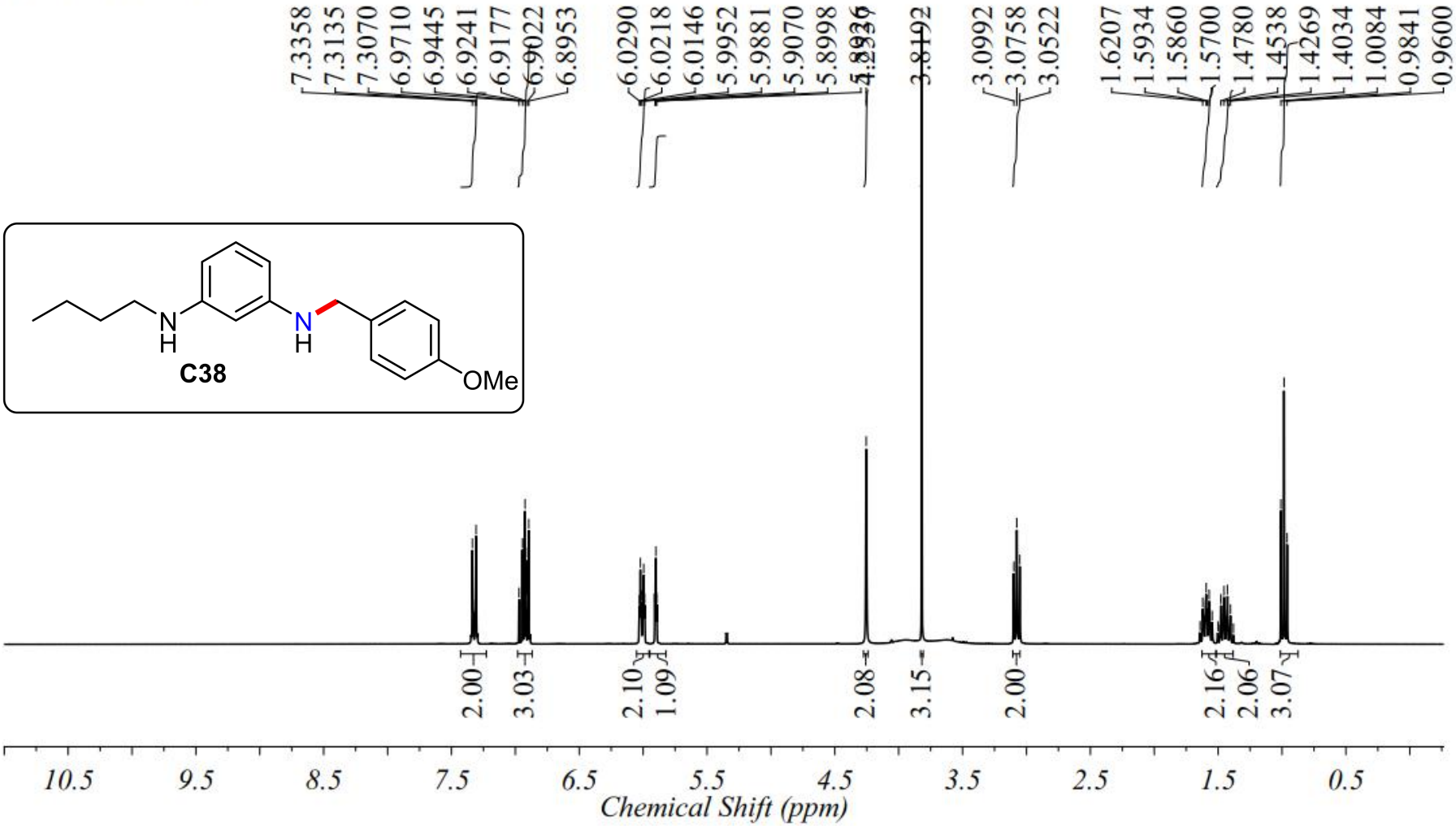



LZY-2019-10-15-3
7.5327
7.5297
7.5054
7.4124
7.4065
7.3833
7.3553
7.3236
7.2990
7.2952
7.2825
7.2790
7.2555
7.2303
7.1026
7.0483
6.9760
6.9216
6.6548
6.6267
4.3789
4.2127
Cl
H
N
C37
2.04
8.12
1.04
2.15
2.00
2.01
1.06
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)

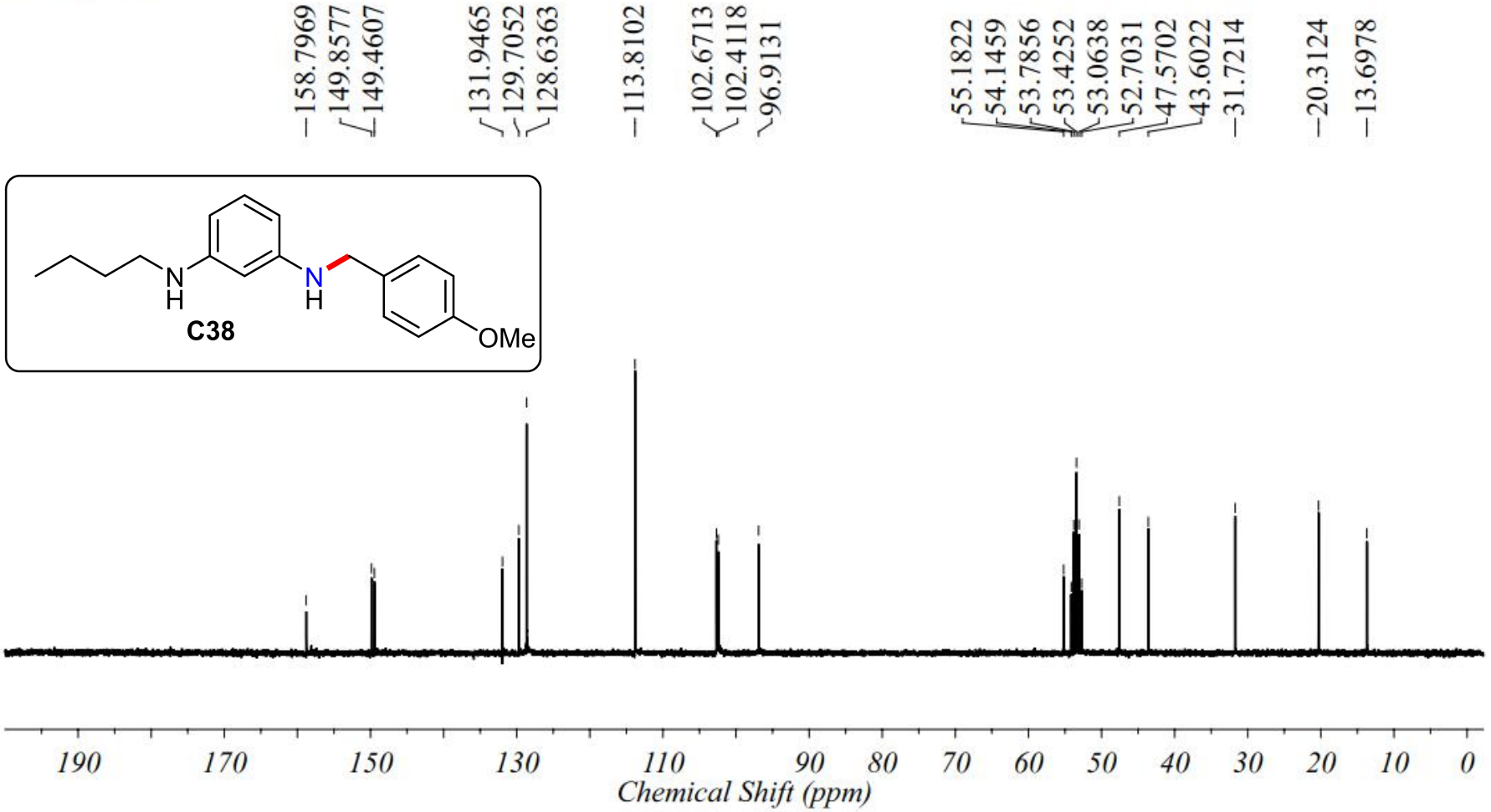
LZY-2019-10-15-3

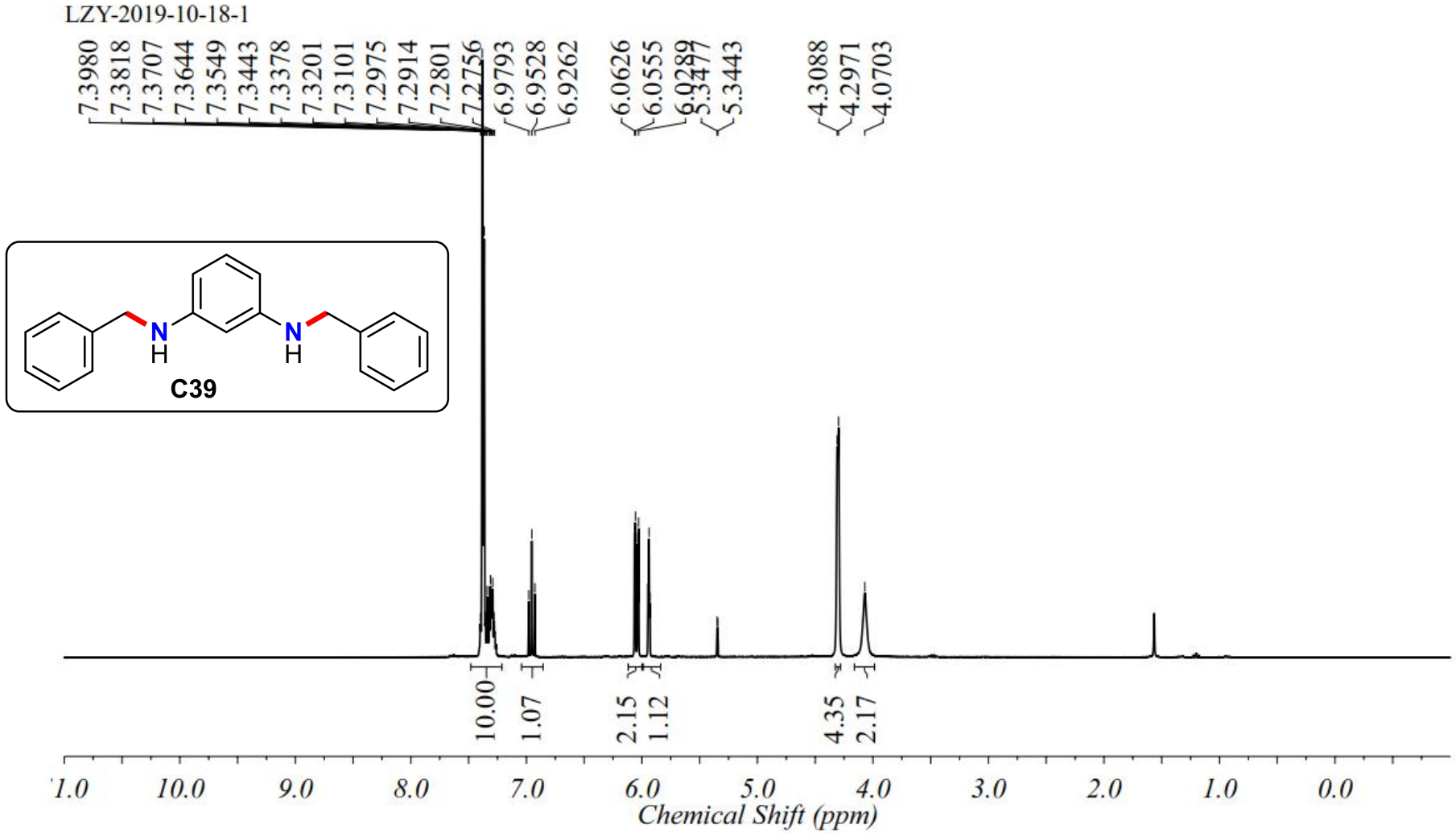


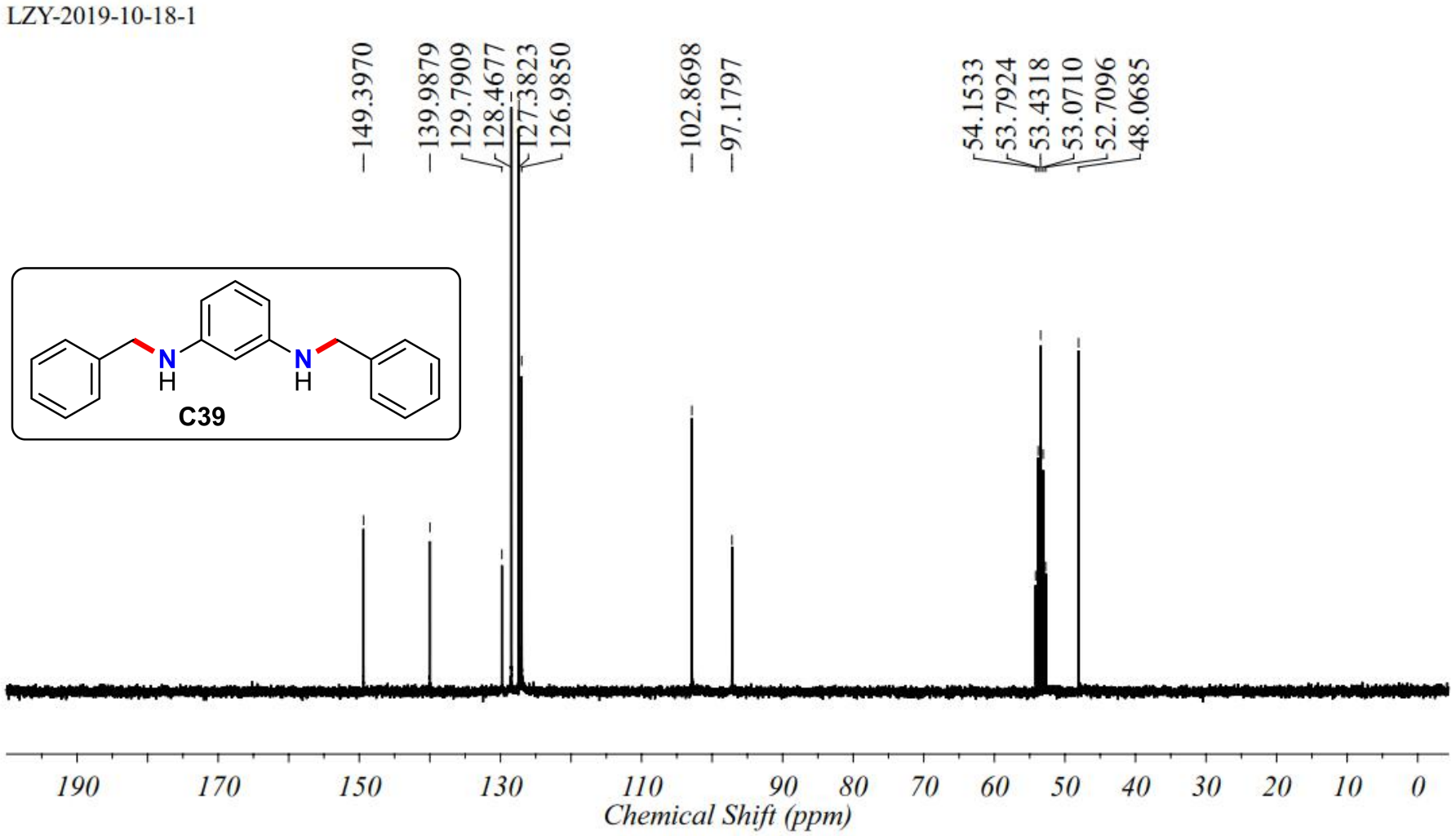
LZY-2019-10-15-4



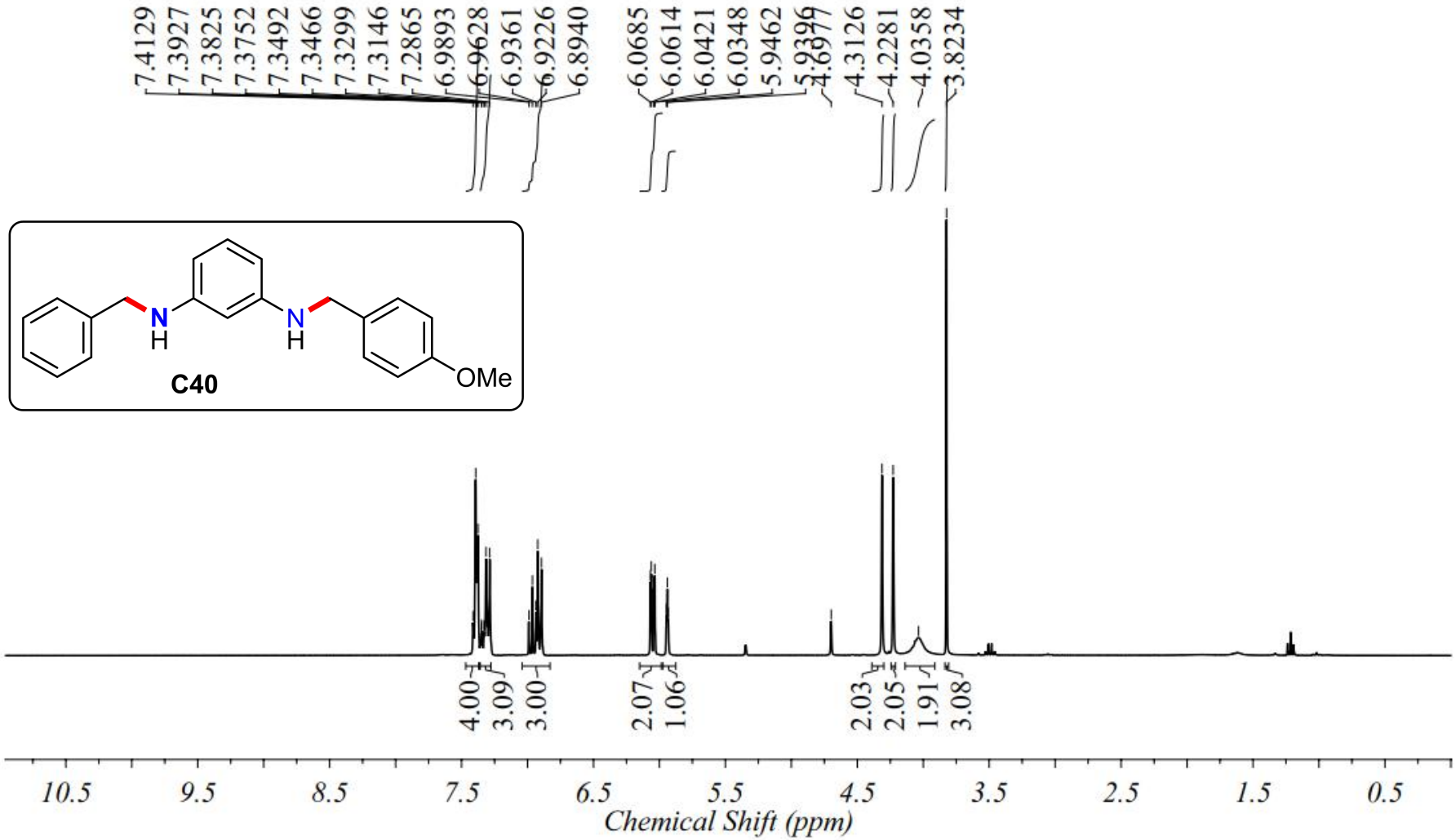
LZY-2019-10-15-4




LZY-2019-10-18-1
7.3980
7.3818
7.3707
7.3644
7.3549
7.3443
7.3378
7.3201
7.3101
7.2975
7.2914
7.2801
7.2756
6.9793
6.9528
6.9262
6.0626
6.0555
5.3443
4.3088
4.2971
4.0703
C39
10.00
1.07
2.15
1.12
4.35
2.17
1.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical Shift (ppm)


LZY-2019-10-18-1
149.3970
139.9879
129.7909
128.4677
127.3823
126.9850
102.8698
97.1797
54.1533
53.7924
53.4318
53.0710
52.7096
48.0685
N
H
N
H
C39
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

LZY-2019-10-18-2



LZY-2019-10-18-2