Supporting Information

Palladium-catalyzed oxidative C-H bond acylation of *N*-nitrosoanilines with toluene derivatives: a traceless approach to *N*-alkyl-2-aminobenzophenones

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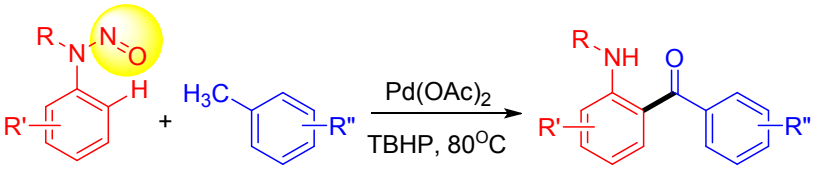

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1. General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliersand used without purification. All the reactions were performed in Rotaflo®(England) resealable screw-cap Schlenk flask (approx. 20 mL volume) in the presence of Teflon coated magnetic stirrer bar (4 mm × 10 mm). 1,2-Dichloroethane (DCE) was distilled under calcium hydride under reduced pressure. Dioxane and toluene were distilled from sodium under nitrogen. The concentration of *tert*-butyl hydroperoxide (TBHP) was determined by means of iodometric method.[1] Thin layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography. ^{1}HNMR spectra were recorded on a Bruker (400 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ)were reported as part per million (ppm) in δ scale downfield from TMS.^{13}C NMR spectra were referenced to $CDCl_3$(δ 77.0 ppm, the middle peak). Coupling constants (J) were reported in Hertz (Hz). High-resolution mass spectra (HRMS)were obtained on a Shimadzu LCMS-IT-TOF. GC-MS analysis was conducted on a HP 5973 GCD system using a HP5MS column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from HP 6890 GC-FID system. Compounds described in the literatures were characterized by comparison of their ^{1}H, and/or ^{13}C NMR spectra to the previously reported data.

2. Preparation of substituted N-nitrosoaniline substrates

All the substituted *N*-nitrosoanilides in Table 2 were prepared from their corresponding precursors with $NaNO_2$ in CH_3CN/H_2O according to the literature method without modifications.[2]

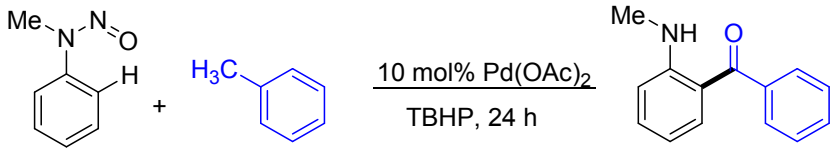
3. General procedures for reaction condition screenings and coupling reactions

General procedures for screening the acylation: The *N*-methyl-*N*-nitrosoaniline (0.137 g, 1.0 mmol) and the metal complex (10 mol% or as indicated in Table 1) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar under air atmosphere. The toluene (2.0 mL) was added into the tube. The solution was stirred for about 1 to 2 minutes until the solid had been dissolved. TBHP (12.0 mmol or as indicated in Table 1) were loaded into the tube. The tube was stirred at room temperature for ~5 minutes and then placed into a preheated oil bath (40-120 ^oC) for 24 hours. After completion of reaction, the reaction tube was allowed to cool to room temperature. Ethyl acetate (~10 mL), dodecane (227 μL, internal standard) and water (~3 ml) were added. The organic layer was subjected to GC analysis. The GC yield obtained was previously calibrated by authentic sample/dodecane calibration curve.

General procedure for C-H bond coupling of steered N-nitrosoaniline and substituted toluene: Substituted *N*-nitrosoanilide (1.0 mmol) and the $Pd(OAc)_2$ (22.4 mg, 0.10 mmol) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. Substituted Toluene (2.0 mL) was added into the tube (The solid substituted toluene was added to 30 equiv.). TBHP (12.0 mmol) were loaded into the tube. The tube was stirred at room temperature for ~5 minutes and then placed into a preheated

oil bath at 80 ^{o}C for 24 hours. After completion of reaction as judged by GC analysis, the reaction tube was allowed to cool to room temperature and quenched with saturated K_2CO_3 and diluted with EtOAc. The organic layer was separated and the aqueous layer was washed with EtOAc. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230-400 mesh) to afford the desired oxidatively coupled product.

Table 1: Screening of reaction conditions[a]



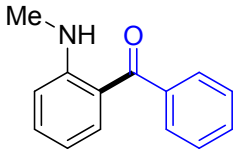
entry	catalyst	oxidant (equiv.)	temp. /°C	%yield[b]
1	$Pd(OAc)_2$	TBHP (6)	100	58
2	$PdCl_2$	TBHP (6)	100	10
3	$Pd(MeCN)_2Cl_2$	TBHP (6)	100	13
4	$Pd(TFA)_2$	TBHP (6)	100	45
5	$Ni(acac)_2$	TBHP (6)	100	0
6	$Rh(PPh_3)_3Cl$	TBHP (6)	100	0
7	$Pd(OAc)_2$	air	100	0
8	$Pd(OAc)_2$	$K_2S_2O_8$ (6)	100	24
9	$Pd(OAc)_2$	$PhI(OAc)_2$ (6)	100	0
10	$Pd(OAc)_2$	(*t*-BuO)$_2$ (6)	100	15
11	$Pd(OAc)_2$	TBHP (8)	100	69
12	$Pd(OAc)_2$	TBHP (10)	100	75
13	$Pd(OAc)_2$	TBHP (12)	100	76
14	$Pd(OAc)_2$	TBHP (16)	100	69
15	**$Pd(OAc)_2$**	**TBHP (12)**	**80**	**85(81)**
16	$Pd(OAc)_2$	TBHP (12)	60	53
17	$Pd(OAc)_2$	TBHP (12)	40	36
18[c]	$Pd(OAc)_2$	TBHP (12)	80	57
19[d]	$Pd(OAc)_2$	TBHP (12)	80	33
20[e]	$Pd(OAc)_2$	TBHP (12)	80	72

[a] Reaction conditions: *N*-nitrosoaniline **1a** (1.0 mmol), catalyst (10 mol%), oxidant (as indicated), toluene (2 mL) were stirred at indicated reaction temperature for 24 h under air. [b]Calibrated GC yields were reported using dodecane as the internal standard. Isolated yield in parenthesis. [c]DCE as solvent (toluene, 10 equiv.). [d]Dioxane as solvent (toluene,

10 equiv.). [e]trifluoromethylbenzene as solvent (toluene, 10 equiv.).

4. Characterization data of coupling products

(2-(methylamino)phenyl)(phenyl)methanone (3ab)



Hexane: EtOAc (50:1); R_f= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (brs, 1H), 7.63-7.60 (m, 2H), 7.53-7.48 (m, 3H), 7.46 (t, *J* = 4.2 Hz, 2H), 7.43 (s, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.60 – 6.52 (m, 1H), 3.00 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 199.39, 152.74, 140.60, 135.54, 134.95, 130.74, 129.07, 128.02, 117.27, 113.61, 111.10, 29.53.

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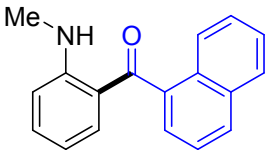
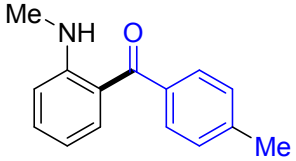
(2-(methylamino)phenyl)(naphthalen-1-yl)methanone（3ac）



Hexane: EtOAc (50:1); R_f= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (brs, 1H), 7.90 (dd, *J* = 14.0, 7.8 Hz, 2H), 7.84-7.79 (m, 1H), 7.51-7.46 (m, 2H), 7.45-7.38 (m, 3H), 7.27-7.22 (m, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.39 (s, 1H), 3.04 (d, *J* = 5.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 200.42, 152.96, 138.77, 136.05, 135.69, 133.56, 129.45, 128.26, 126.71, 126.21, 125.73, 125.31, 124.67, 118.16, 113.84, 111.09, 29.41.

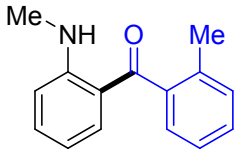
(2-(methylamino)phenyl)(p-tolyl)methanone（3ad）



Hexane: EtOAc (50:1); R_f= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (brs, 1H), 7.51 (d, *J* = 8.2 Hz, 3H), 7.39 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 1H), 6.56-6.50 (m, 1H), 2.95 (d, *J* = 4.8 Hz, 3H), 2.42 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 199.14, 152.56, 141.20, 137.78, 135.32, 134.78, 129.27, 128.67,

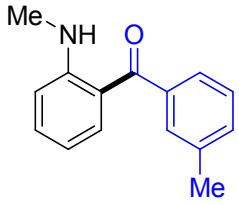
117.32, 113.57, 111.02, 29.42, 21.36.

(2-(methylamino)phenyl)(o-tolyl)methanone（3ae）



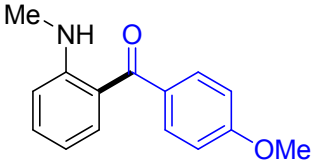
Hexane: EtOAc (50:1); R_f= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (brs, 1H), 7.45 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.45-7.30 (m, 3H), 7.26-7.30 (m, 1H),7.16-7.12 (m, 1H),7.03 (t, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.44 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 2.91 (d, *J* = 5.5 Hz, 3H), 2.42 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 199.99, 152.51, 140.72, 137.93, 135.49, 134.46, 129.34, 127.85, 125.64, 117.15, 113.55, 110.96, 29.37, 20.39.

(2-(methylamino)phenyl)(m-tolyl)methanone（3af）



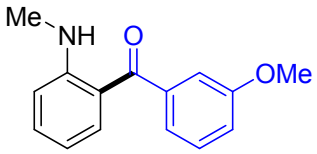
Hexane: EtOAc (50:1); R_f= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (brs, 1H), 7.52 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.45-7.39 (m, 3H), 7.34 (ddd, *J* = 5.5, 3.5, 1.1 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.57 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 3.00 (d, *J* = 5.1 Hz, 3H), 2.44 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 199.61, 152.70, 140.67, 137.84, 135.53, 134.97, 131.39, 129.40, 127.85, 126.14, 117.39, 113.61, 111.05, 29.45, 21.38.

(4-methoxyphenyl)(2-(methylamino)phenyl)methanone（3ag）



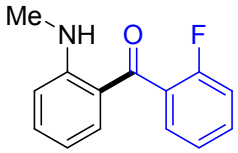
Hexane: EtOAc (10:1); R_f= 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (brs, 1H), 7.66-7.59 (m, 2H), 7.49 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.39 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 6.97-6.91 (m, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.58-6.52 (m, 1H), 3.87 (s, 3H), 2.94 (d, *J* = 4.7 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 198.14, 162.03, 152.31, 134.91, 134.50, 132.89, 131.55, 117.91, 113.60, 113.32, 111.01, 55.41, 29.50.

(3-methoxyphenyl)(2-(methylamino)phenyl)methanone（3ah）



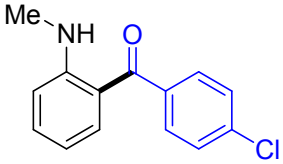
Hexane: EtOAc (10:1); R_f= 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (brs, 1H), 7.56-7.30 (m, 3H), 7.20-6.99 (m, 3H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 7.0 Hz, 1H), 3.86 (s, 3H), 2.99 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 199.04, 159.34, 152.75, 141.95, 135.49, 135.11, 129.02, 121.45, 117.18, 116.77, 113.77, 113.66, 111.09, 55.40, 29.45.

(2-fluorophenyl)(2-(methylamino)phenyl)methanone（3ai）



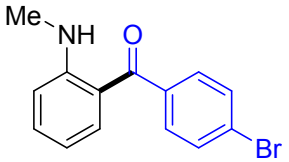
Hexane: EtOAc (50:1); R_f= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (brs, 1H), 7.47 (ddd, *J* = 7.4, 2.5, 1.5 Hz, 1H), 7.45- 7.39 (m, 2H), 7.39-7.34 (m, 1H), 7.25 (td, *J* = 7.5, 1.0 Hz, 1H), 7.20-7.14 (m, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.55 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 3.02 (d, *J* = 5.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 195.25, 152.82, 135.80, 135.38, 131.40 (d, *J* = 8.0 Hz, 18H), 129.60 (d, *J* = 3.5 Hz, 16H), 124.06 (d, *J* = 3.5 Hz, 13H), 117.38, 116.08, 115.87, 114.01, 111.14, 29.35.

(4-chlorophenyl)(2-(methylamino)phenyl)methanone（3aj）



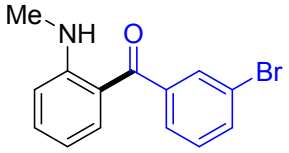
Hexane: EtOAc (50:1); R_f= 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (brs, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.44-7.37 (m, 4H), 6.75 (d, *J* = 9.0 Hz, 1H), 6.53 (t, *J* = 7.5 Hz, 1H), 2.96 (d, *J* = 5.0 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.87, 152.76, 138.89, 136.93, 135.26, 135.12, 130.43, 128.33, 116.93, 113.74, 111.25, 29.45.

(4-bromophenyl)(2-(methylamino)phenyl)methanone（3ak）



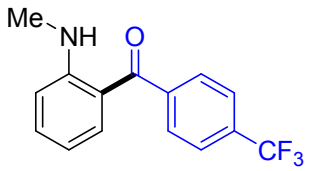
Hexane: EtOAc (50:1); R_f= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (brs, 1H), 7.60-7.55 (m, 2H), 7.48-7.44 (m, 2H), 7.44-7.39 (m, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.53 (dd, *J* = 8.0, 7.1 Hz, 1H), 2.96 (dd, *J* = 5.1, 2.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.94, 152.74, 139.35, 135.30, 135.04, 131.30, 130.55, 125.33, 116.87, 113.76, 111.27, 29.45.

(3-bromophenyl)(2-(methylamino)phenyl)methanone（3al）



Hexane: EtOAc (50:1); R*f*= 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (brs, 1H), 7.72 (t, *J* = 1.7 Hz, 1H), 7.62 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.48 (dd, *J* = 5.0, 3.6 Hz, 1H), 7.43-7.39 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 8.9 Hz, 1H), 6.57-6.52 (m, 1H), 2.97 (d, *J* = 5.0 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.34, 152.87, 142.52, 135.44, 135.24, 133.48, 131.67, 129.61, 127.39, 122.27, 116.63, 113.82, 111.26, 29.43.

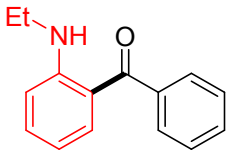
(2-(methylamino)phenyl)(4-(trifluoromethyl)phenyl)methanone（3am）



Hexane: EtOAc (50:1); R_f= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (brs, 1H), 7.72 (dd, *J* = 16.9, 7.8 Hz, 3H), 7.51-7.35 (m, 2H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.57 (t, *J* = 7.1 Hz, 1H), 3.06-2.69 (d, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 197.78, 153.01, 143.94, 135.64, 135.28, 129.98, 128.97, 125.11 (d, *J* = 3.7 Hz, 10H), 116.52, 113.85, 111.37,

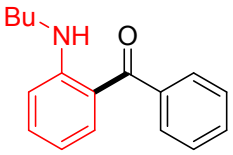
29.41.

(2-(ethylamino)phenyl)(phenyl)methanone（3bb）



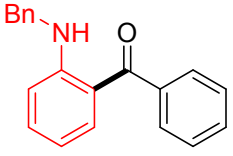
Hexane: EtOAc (50:1); R_f= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (brs, 1H), 7.65-7.61 (m, 2H), 7.52 (dd, *J* = 2.2, 1.6 Hz, 1H), 7.51-7.44 (m, 3H), 7.41 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 6.55 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 3.33 (dd, *J* = 7.1, 4.6 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 199.31, 151.84, 140.65, 135.55, 135.00, 130.66, 128.98, 128.02, 117.03, 113.54, 111.52, 37.36, 14.49.

(2-(butylamino)phenyl)(phenyl)methanone（3cb）



Hexane: EtOAc (50:1); R_f= 0.4; ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.63 (brs, 1H), 7.70–7.56 (m, 2H), 7.55–7.48 (m, 3H), 7.45–7.28 (m,2H), 6.78 (d, *J* = 8.4Hz, 1H), 6.51 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 3.27 (td, *J* = 7.0, 5.2 Hz, 2H), 1.79–1.66 (m, 2H), 1.58–1.44 (m, 2H,), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.67, 152.24, 140.79, 135.79, 135.17, 130.80, 129.11, 128.11, 117.09, 113.56, 111.64, 42.59, 31.37, 20.52, 13.95.

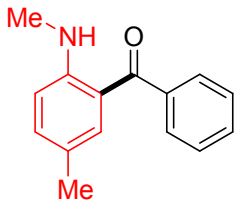
(2-(benzylamino)phenyl)(phenyl)methanone (3db)



Hexane: EtOAc (50:1); R_f= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.00 (brs, 1H), 7.63-7.60 (m, 2H), 7.53 -7.25 (m, 11H), 6.72 (d, *J* = 9.0 Hz, 1H), 6.57- 6.53 (m,1H), 4.50 (d, *J* = 5.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ199.51, 151.27, 140.04, 138.67, 135.65, 135.02, 130.94, 129.20, 128.93, 128.24, 127.38, 127.21, 117.61, 114.22,

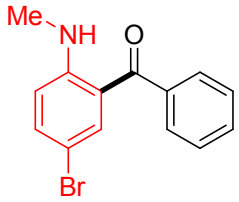
112.71,47.21.

(5-methyl-2-(methylamino)phenyl)(phenyl)methanone（3eb）



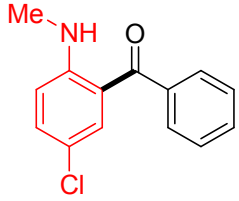
Hexane: EtOAc (50:1); R*f*= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (brs, 1H), 7.65 – 7.59 (m, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.27 (dd, *J* = 11.2, 2.5 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 1H), 2.98 (d, *J* = 3.3 Hz, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.20, 150.91, 140.76, 136.20, 135.02, 130.57, 128.94, 128.01, 122.48, 117.18, 111.22, 29.58, 20.20.

(5-bromo-2-(methylamino)phenyl)(phenyl)methanone（3fb）



Hexane: EtOAc (50:1); R*f*= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.47 (brs, 1H), 7.58-7.55 (m, 3H), 7.54 -7.49 (m, 1H), 7.47 -7.42 (m, 3H), 6.62 (d, *J* = 9.0 Hz, 1H), 2.94(d, *J* = 4.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.20, 151.16, 139.72, 137.53, 137.07, 131.01, 129.02, 128.34, 118.78, 113.24, 105.06, 29.44.

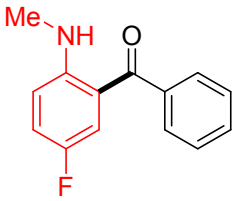
(5-chloro-2-(methylamino)phenyl)(phenyl)methanone（3gb）



Hexane: EtOAc (50:1); R*f*= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (brs, 1H), 7.57 (t, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.34 (dd, *J* = 9.0, 2.3 Hz, 1H), 6.70 (d, *J* = 9.0 Hz, 1H), 2.95(d, *J* = 4.9 Hz, 3H).^{13}C NMR (101 MHz,

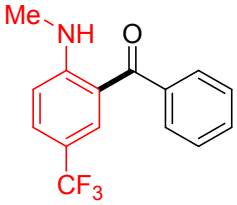
$CDCl_3$) δ 198.31, 151.19, 139.83, 134.86, 134.04, 131.12, 128.93, 128.25, 118.27, 117.93, 112.72, 29.59.

(5-fluoro-2-(methylamino)phenyl)(phenyl)methanone（3hb）



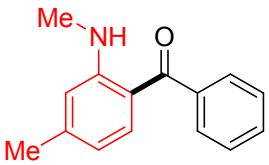
Hexane: EtOAc (50:1); R*f*= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (brs, 1H), 7.64 – 7.56 (m, 2H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.22 – 7.14 (m, 2H), 6.70 (dd, *J* = 10.0, 4.3 Hz, 1H), 2.95 (d, *J* = 4.9 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) 198.24, 153.33, 151.01, 149.55, 139.93, 131.05, 122.81 (d, *J* = 23.0 Hz), 122.93, 122.70, 119.87 (d, *J* = 22.5 Hz), 112.24 (d, *J* = 6.9 Hz), 29.78.

(2-(methylamino)-5-(trifluoromethyl)phenyl)(phenyl)methanone（3ib）



Hexane: EtOAc (50:1); R*f*= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (brs, 1H), 7.78 (d, *J* = 1.1 Hz, 1H), 7.65 – 7.59 (m, 3H), 7.57 (dd, *J* = 5.2, 3.7 Hz, 1H), 7.50 (ddd, *J* = 6.6, 4.4, 1.3 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 1H), 3.03 (d, *J* = 5.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.74, 154.30, 139.57, 132.65 (d, *J* = 4.0 Hz), 131.38, 130.19(d, *J* = 4.0 Hz), 129.00, 128.33, 118.40, 116.21, 111.38, 29.49.

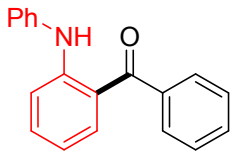
(4-methyl-2-(methylamino)phenyl)(phenyl)methanone(3jb)



Hexane: EtOAc (50:1); R*f*= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (brs, 1H), 7.56 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.43 (dd, *J* = 5.9, 1.4 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 1H), 6.55 (s, 1H), 6.35 (dd, *J* = 8.2, 1.1 Hz, 1H), 2.96 (d, *J* = 4.2 Hz,

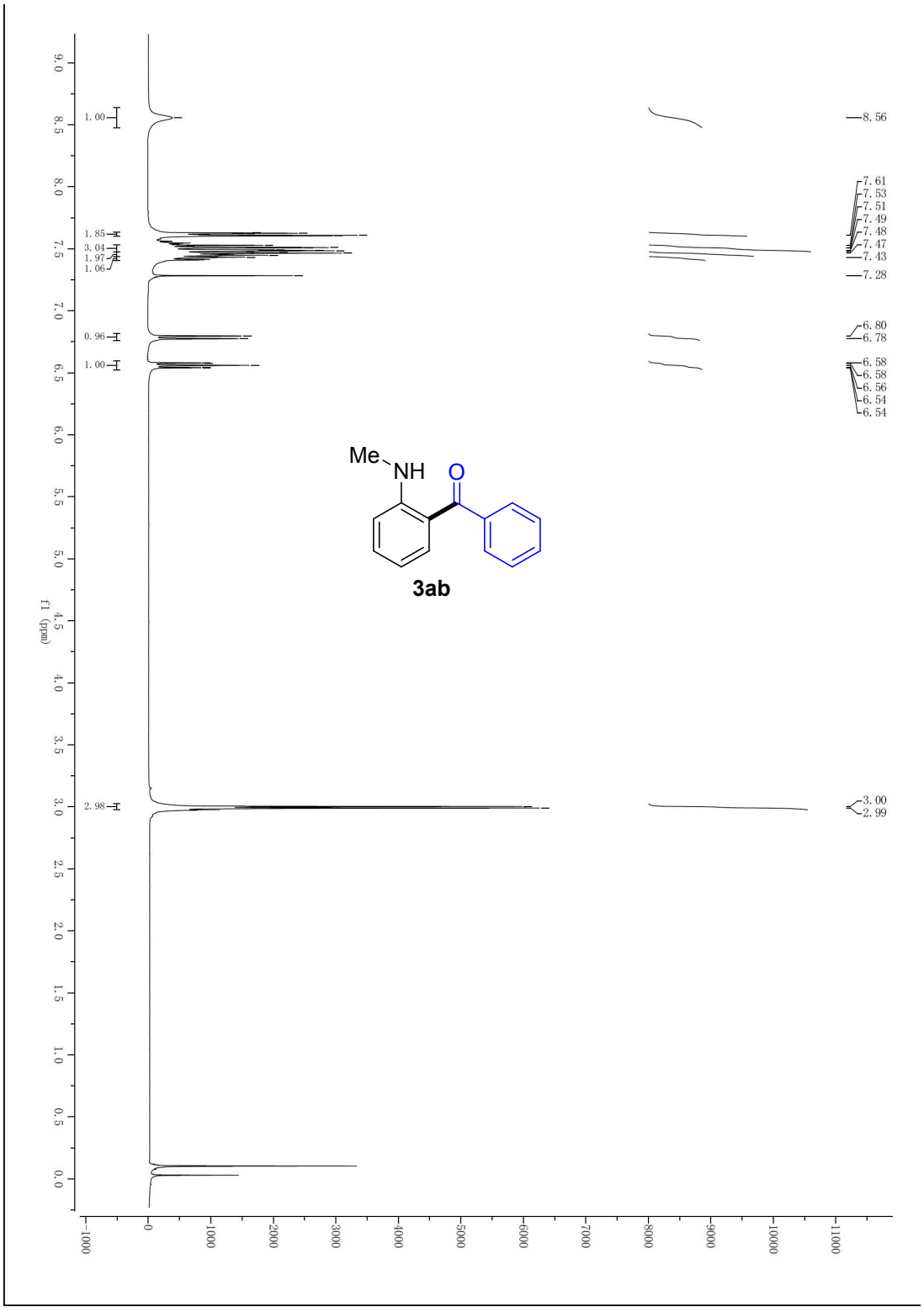
3H), 2.34 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 198.81, 152.98, 146.17, 140.90, 135.63, 130.39, 128.80, 127.97, 115.15, 111.20, 29.40, 22.29.

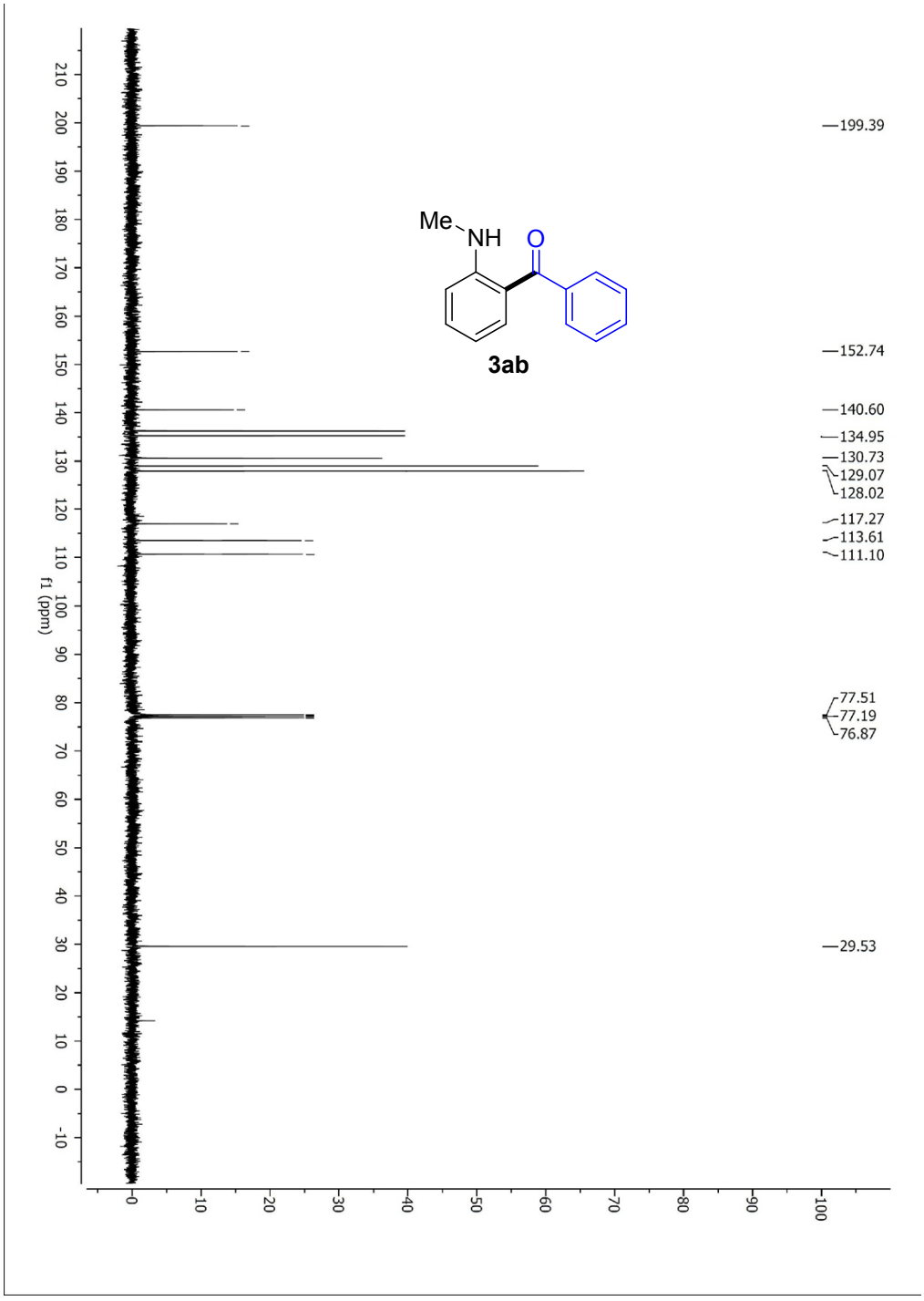
phenyl(2-(phenylamino)phenyl)methanone（3lb）

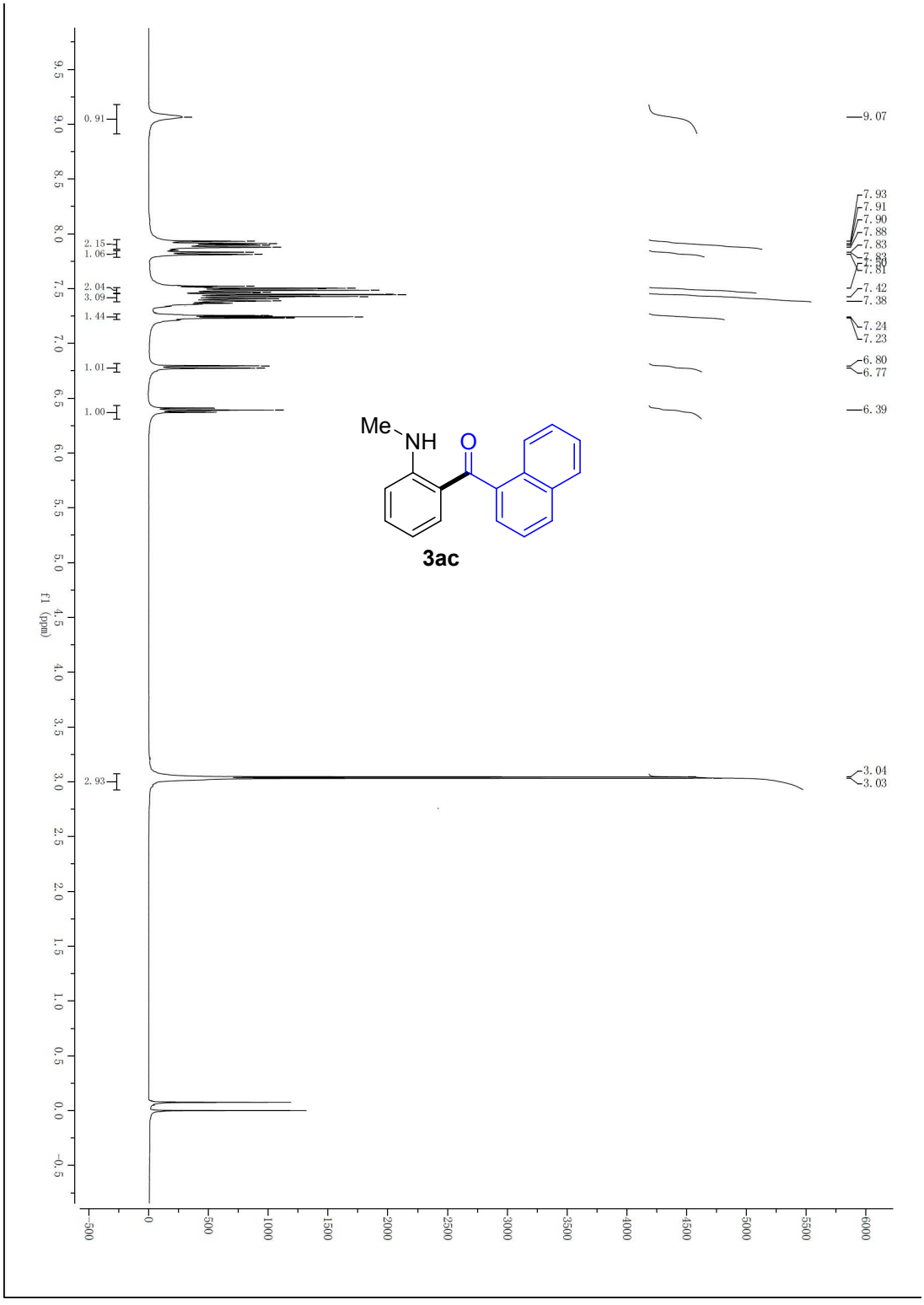


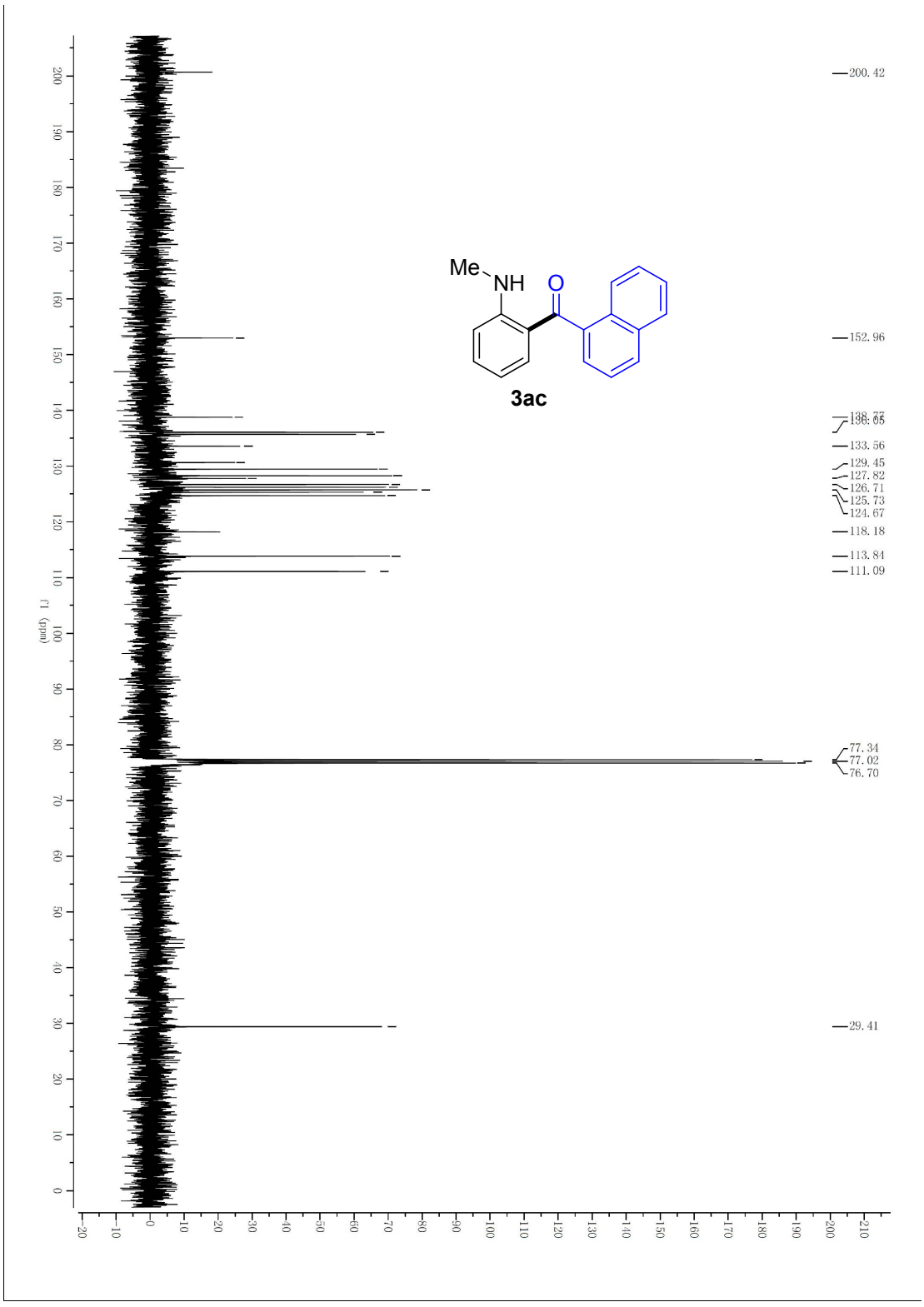
Hexane: EtOAc (50:1); R*f*= 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.12 (brs, 1H), 7.72-7.71 (m, 2H), 7.57-7.55 (m, 2H,), 7.49-7.46 (m, 2H), 7.39-7.38 (m, 2H), 7.36-7.33 (m, 2H), 7.32-7.29 (m, 2H), 7.10 (ddt, J = 7.4, 7.1, 1.3 Hz, 1H), 6.71 (ddd, J = 8.1, 6.6, 1.5 Hz, 1H). (101 MHz, $CDCl_3$) δ 199.17, 148.02, 140.52, 139.78, 134.99,134.21, 131.37, 129.41, 129.38, 128.13, 123.51, 122.18, 119.71, 116.54, 114.61.

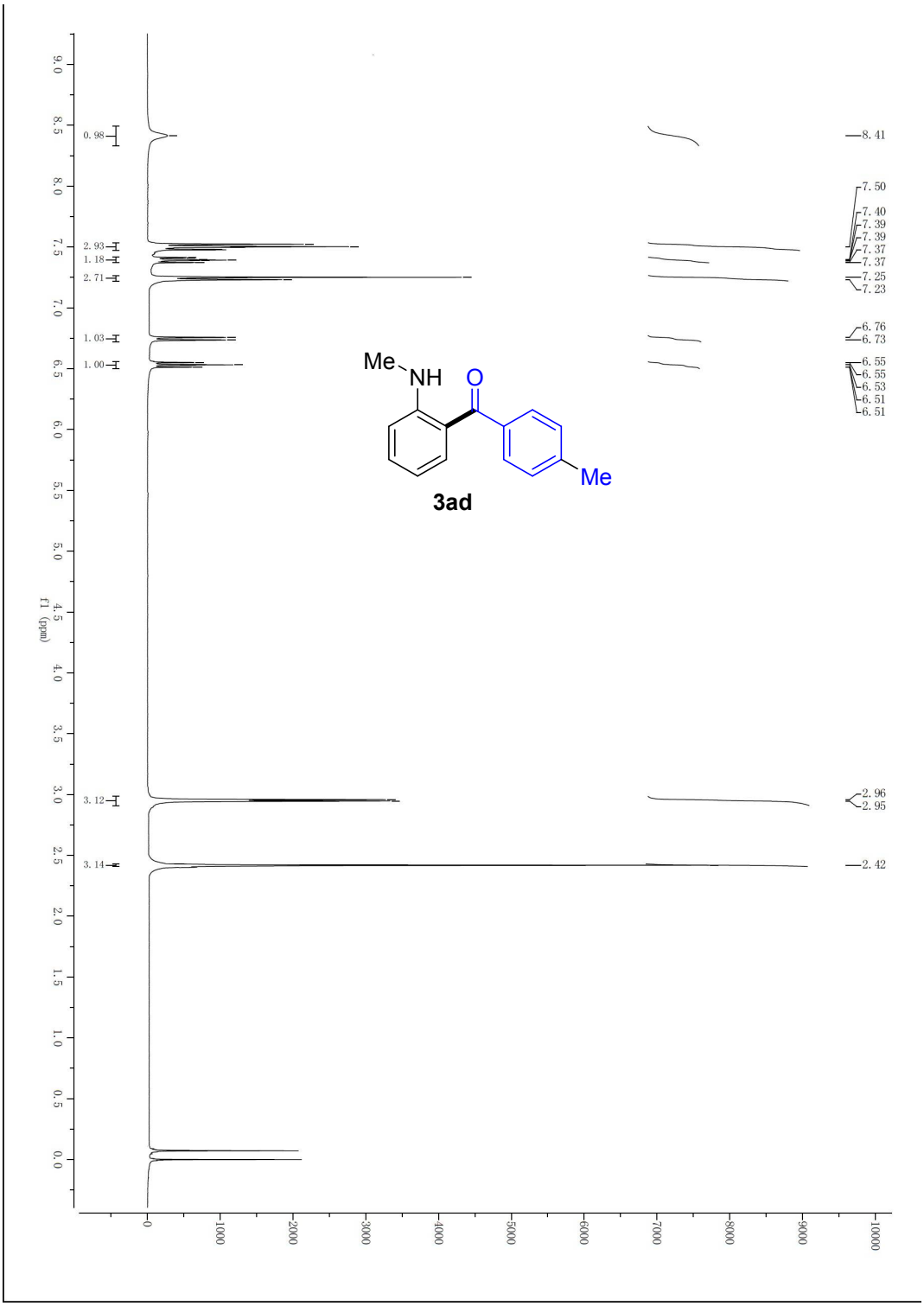
5. ^{1}H and ^{13}C NMR

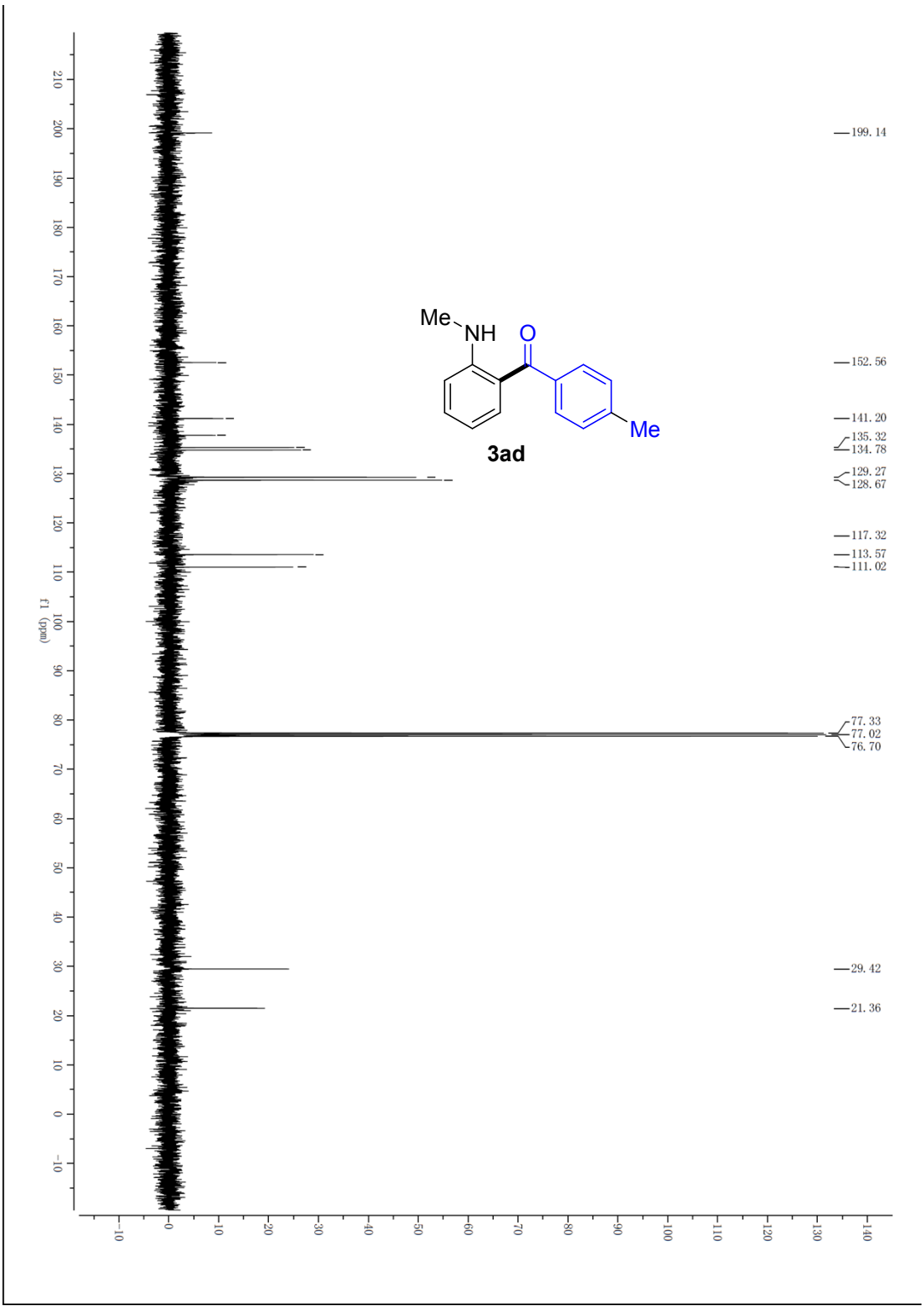



Me
NH
O
3ab
199.39
152.74
140.60
134.95
130.73
129.07
128.02
117.27
113.61
111.10
77.51
77.19
76.87
29.53
f1 (ppm)


9.07
7.93
7.91
7.90
7.88
7.83
7.42
7.38
7.24
7.23
6.80
6.77
6.39
3.04
3.03
0.91
2.15
1.06
2.04
3.09
1.44
1.01
1.00
2.93
Me
NH
O
3ac
f1 (ppm)


Me
NH
O
3ac
200.42
152.96
138.77
136.05
133.56
129.45
127.82
126.71
125.73
124.67
118.18
113.84
111.09
77.34
77.02
76.70
29.41
f1 (ppm)


0.98
2.93
1.18
2.71
1.03
1.00
3.12
3.14
8.41
7.50
7.40
7.39
7.39
7.37
7.37
7.25
7.23
6.76
6.73
6.55
6.55
6.53
6.51
6.51
2.96
2.95
2.42
Me
NH
O
Me
3ad
f1 (ppm)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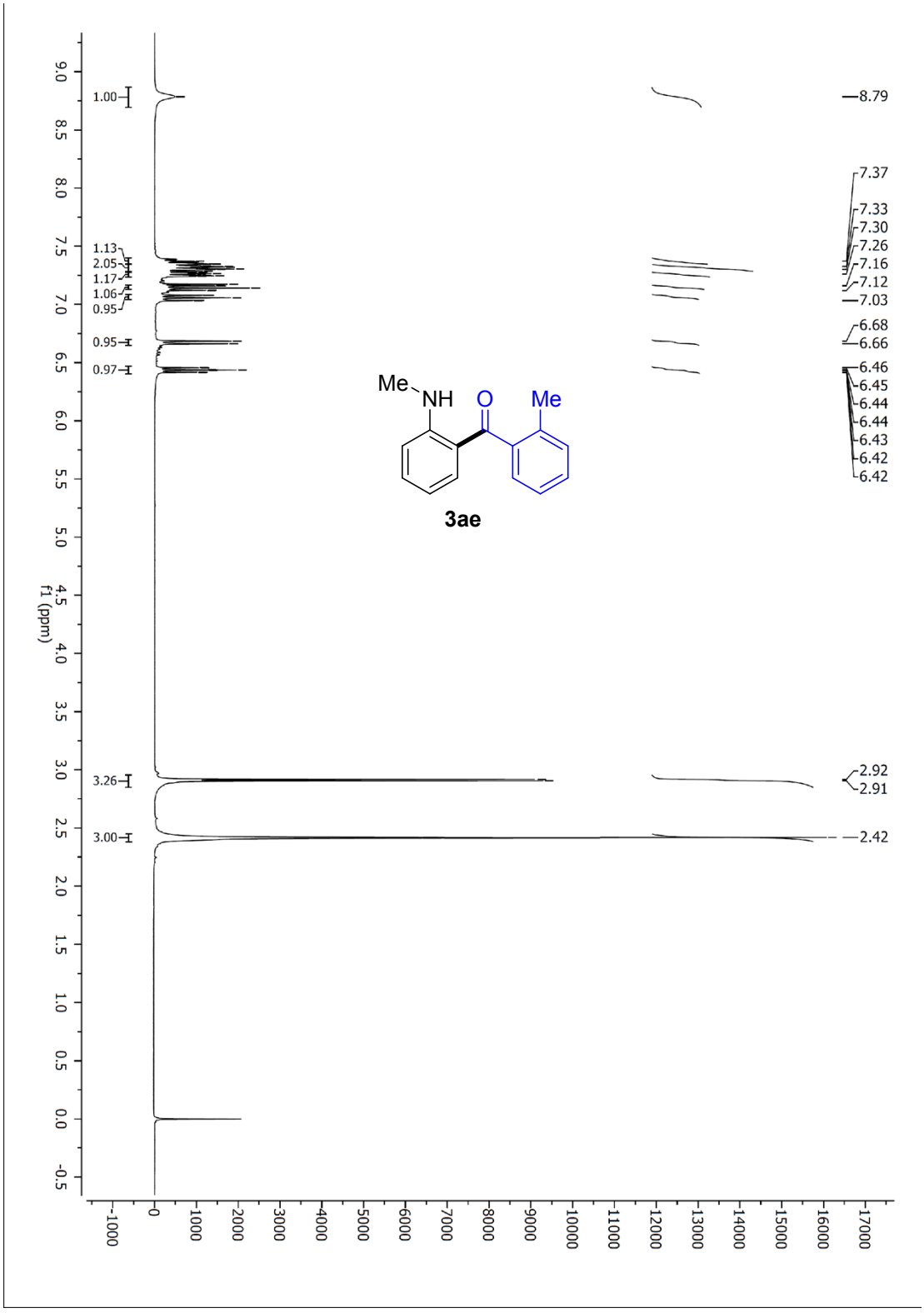
152.56
141.20
135.32
134.78
129.27
128.67
117.32
113.57
111.02
77.33
77.02
76.70
29.42
21.36
Me
NH
O
Me
3ad
f1 (ppm)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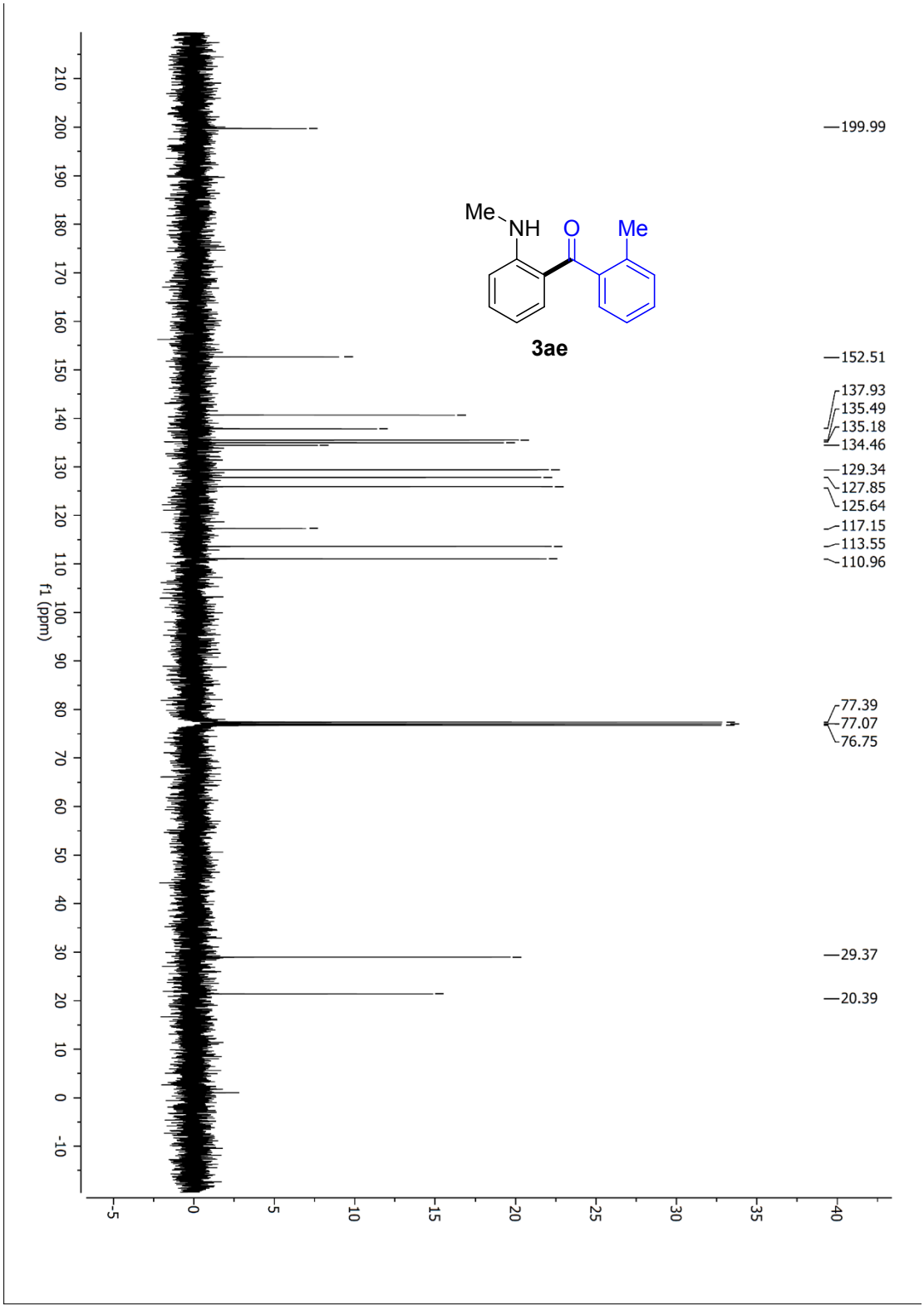
7.37
7.33
7.30
7.26
7.16
7.12
7.03
6.68
6.66
6.46
6.45
6.44
6.44
6.43
6.42
6.42
2.92
2.91
2.42
1.00
1.13
2.05
1.17
1.06
0.95
0.95
0.97
3.26
3.00
Me
NH
O
Me
3ae
f1 (ppm)


Me
NH
O
Me
3ae
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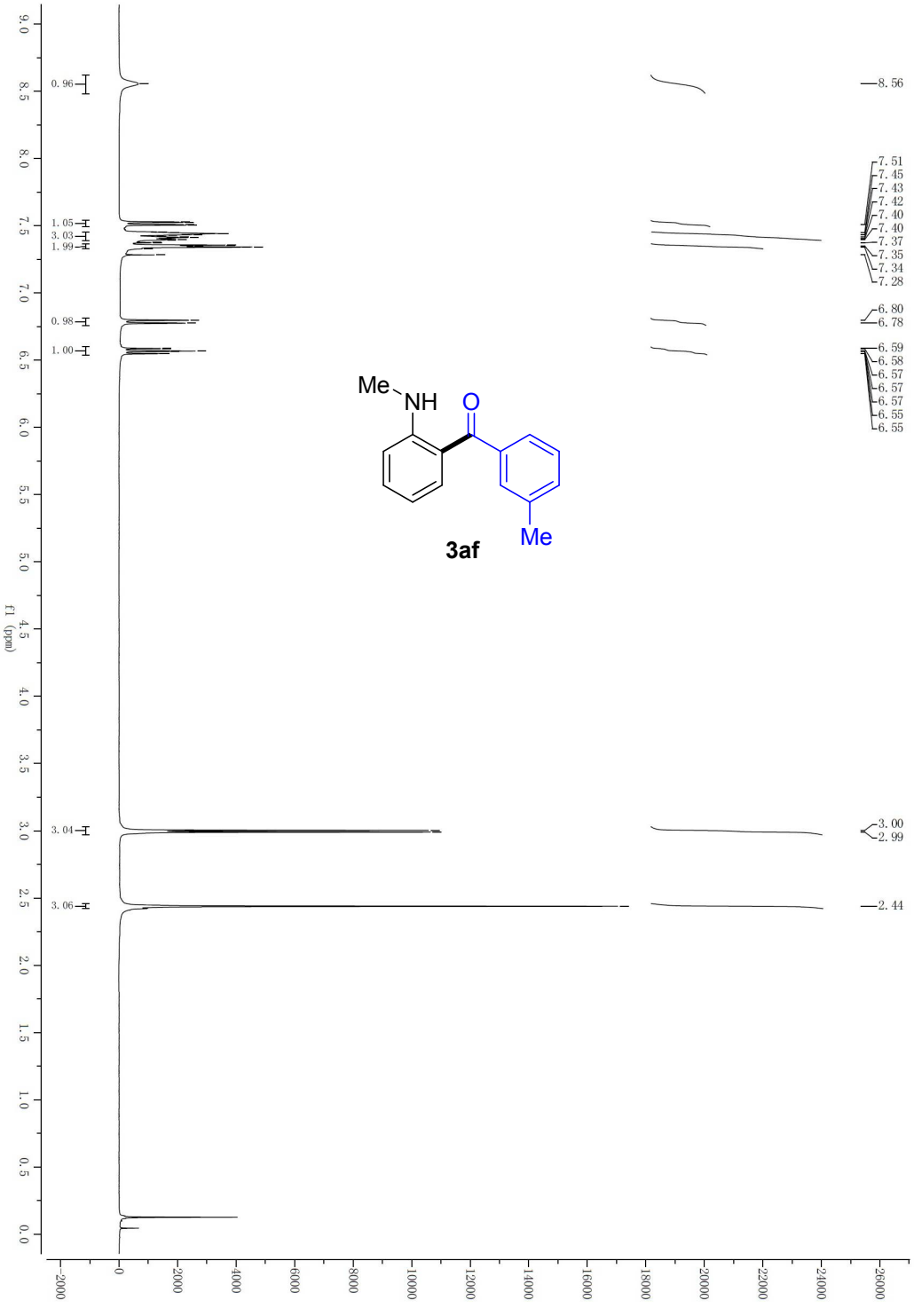
152.51
137.93
135.49
135.18
134.46
129.34
127.85
125.64
117.15
113.55
110.96
77.39
77.07
76.75
29.37
20.39
f1 (ppm)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7.43
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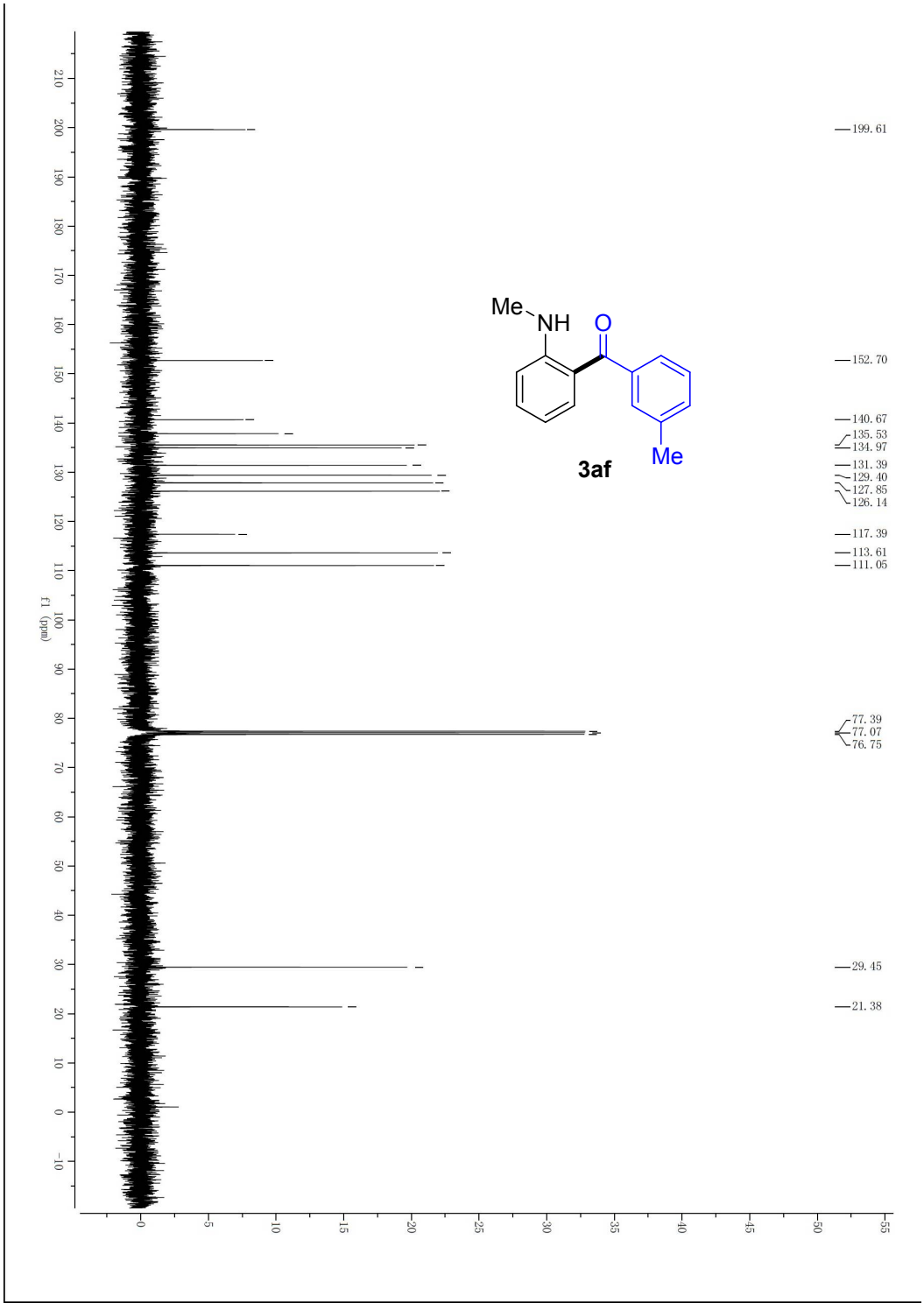
7.40
7.40
7.37
7.35
7.34
7.28
6.80
6.78
6.59
6.58
6.57
6.57
6.57
6.55
6.55
3.00
2.99
2.44
0.96
1.05
3.03
1.99
0.98
1.00
3.04
3.06
Me
NH
O
Me
3af
f1 (ppm)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135.53
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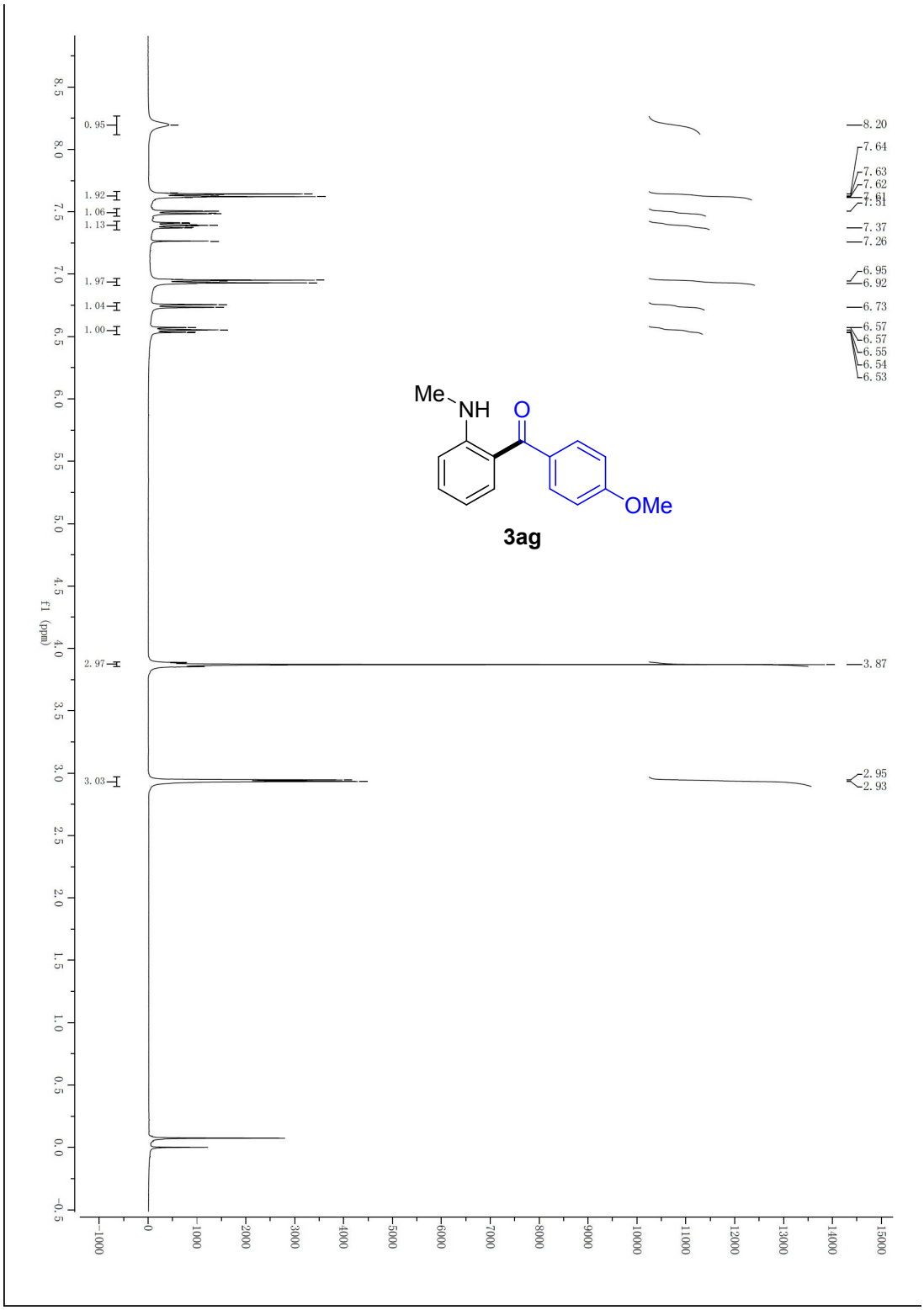
131.39
129.40
127.85
126.14
117.39
113.61
111.05
77.39
77.07
76.75
29.45
21.38
Me
NH
O
Me
3af
f1 (ppm)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NH
O
OMe
3ag
f1 (ppm)
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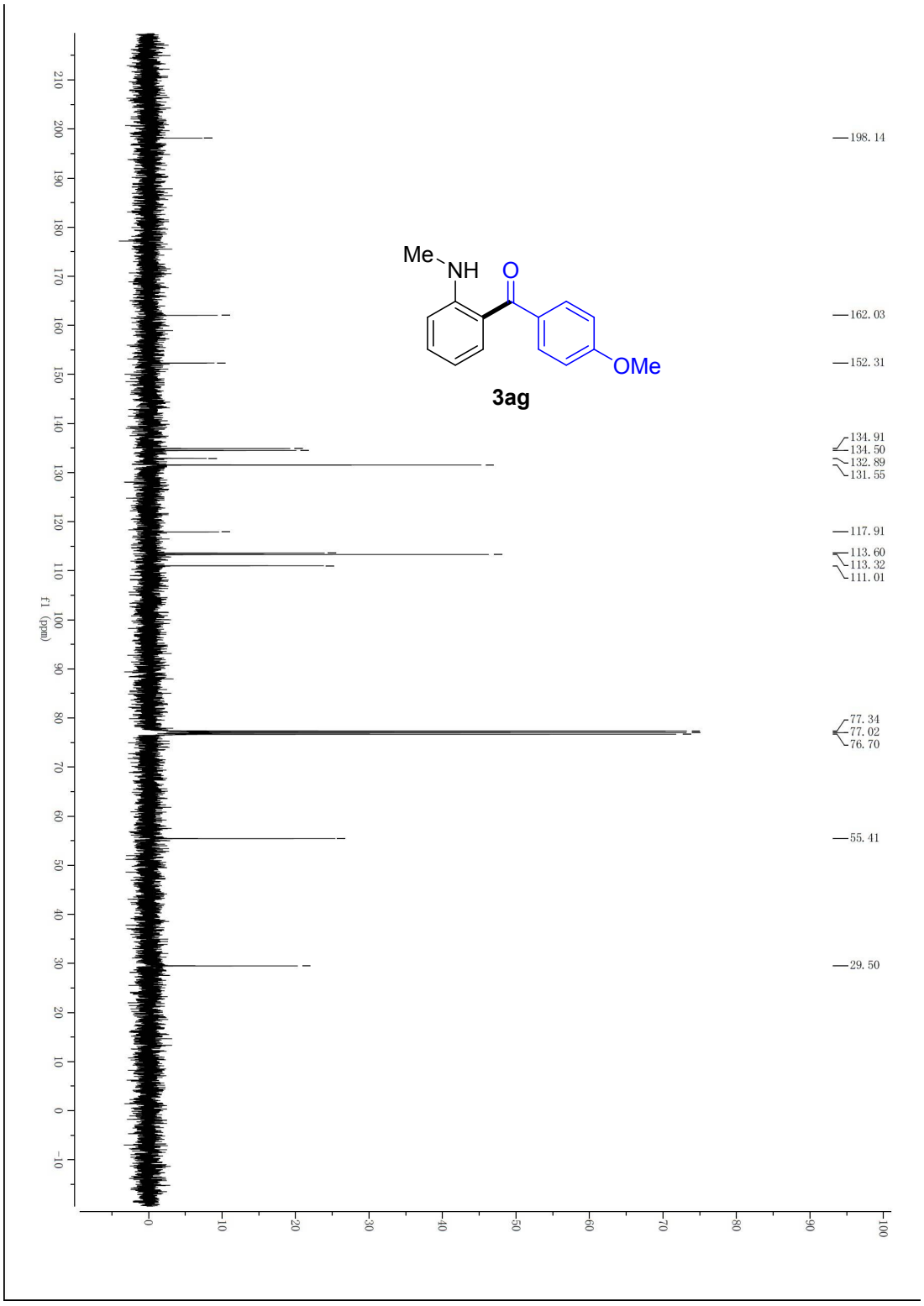
1.92
1.06
1.13
1.97
1.04
1.00
2.97
3.03
8.20
7.64
7.63
7.62
7.61
7.51
7.37
7.26
6.95
6.92
6.73
6.57
6.57
6.55
6.54
6.53
3.87
2.95
2.93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134.50
132.89
131.55
117.91
113.60
113.32
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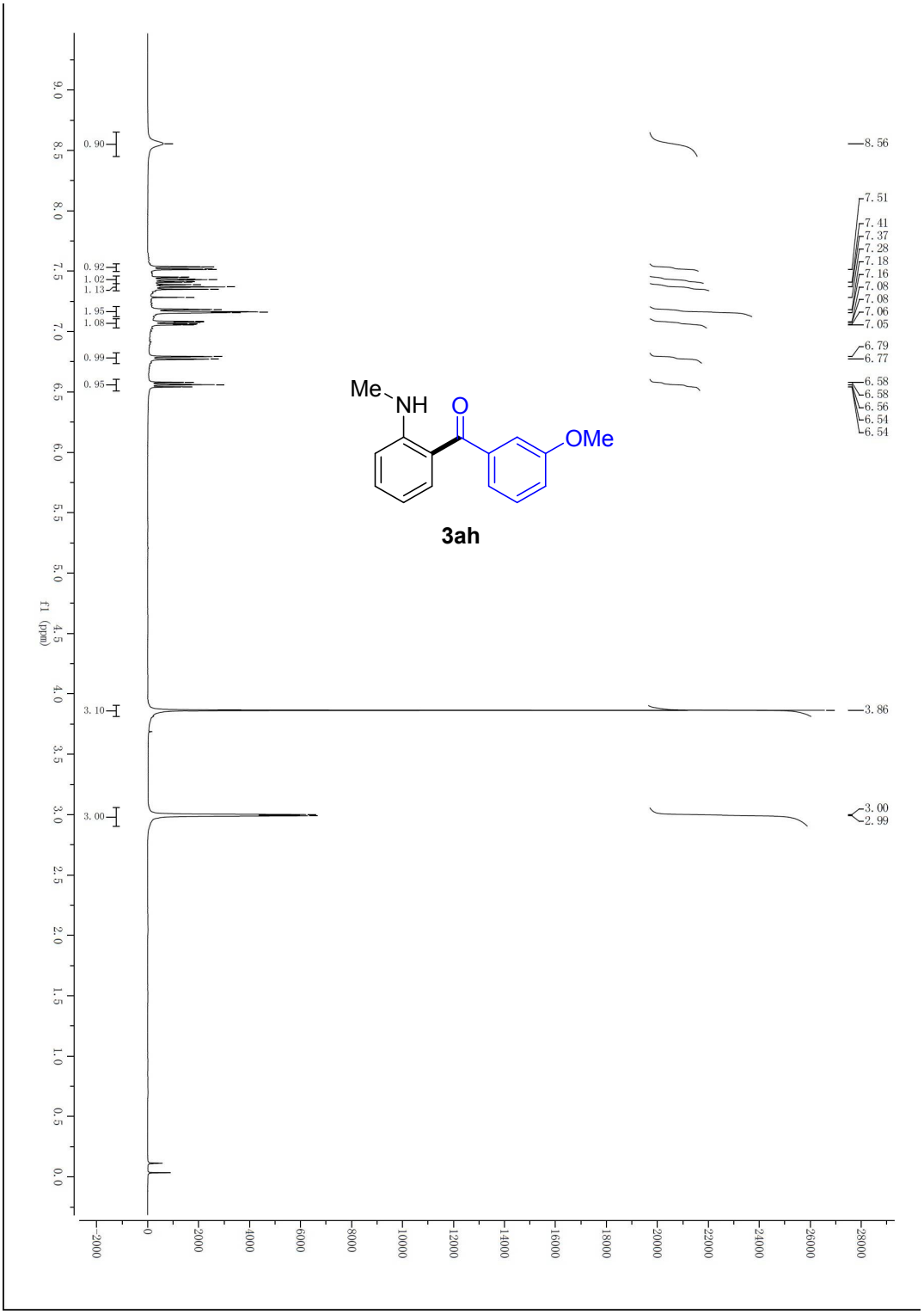
77.02
76.70
55.41
29.50
Me
NH
O
OMe
3ag
f1 (ppm)


Me
NH
O
OMe
3ah
f1 (ppm)
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1.13
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1.08
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0.95
3.10
3.00
8.56
7.51
7.41
7.37
7.28
7.18
7.16
7.08
7.08
7.06
7.05
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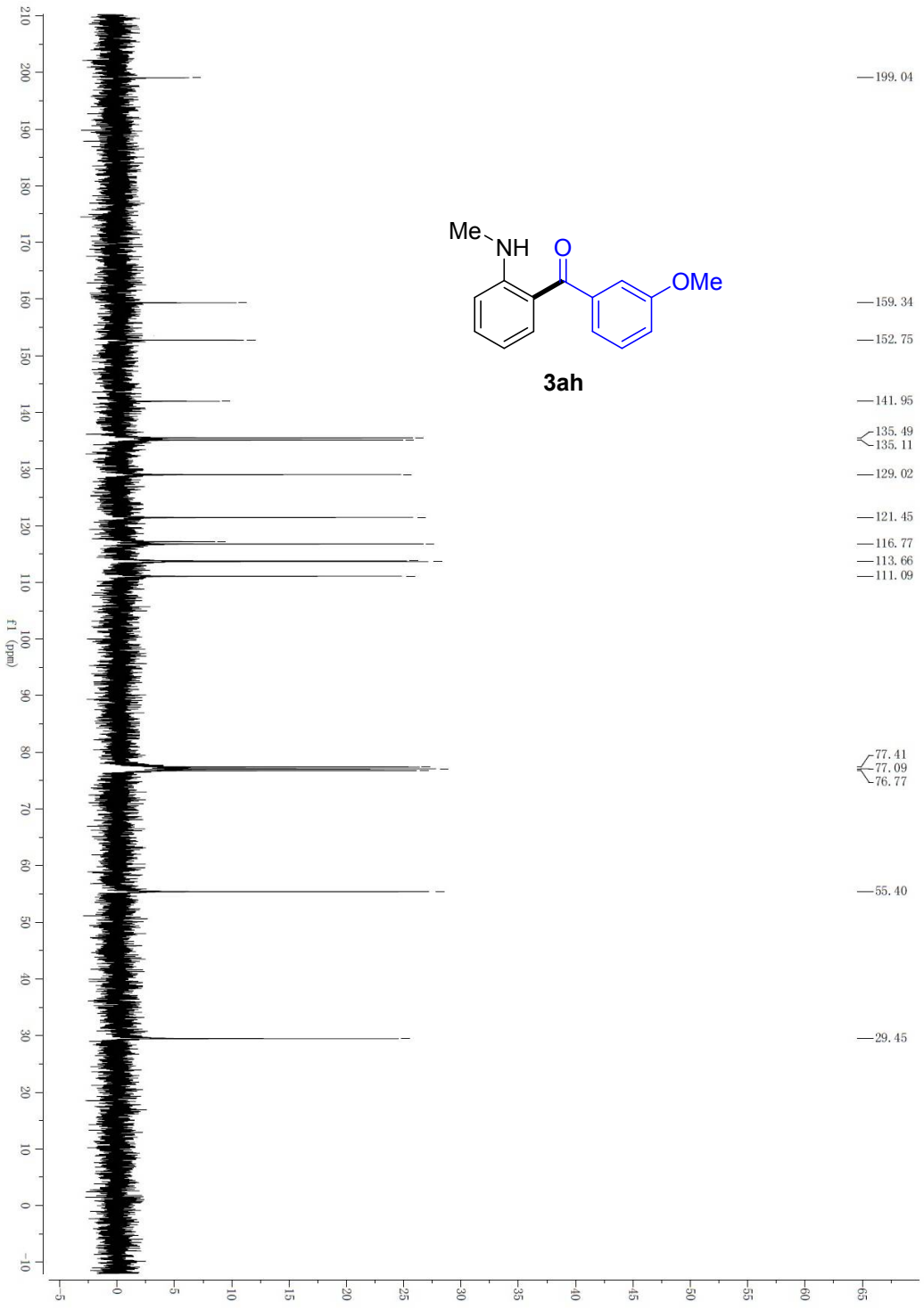
6.56
6.54
6.54
3.86
3.00
2.99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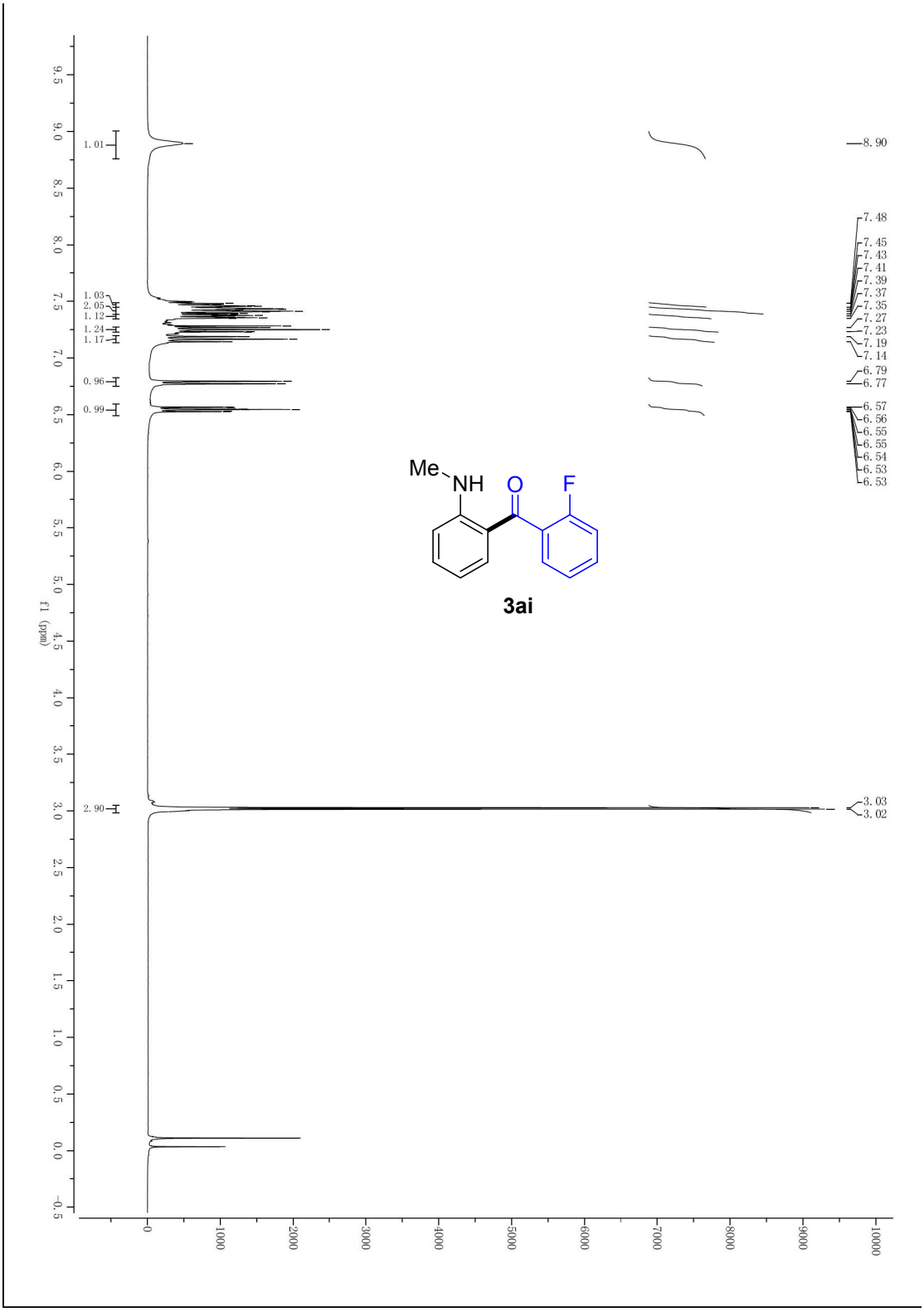
135.49
135.11
129.02
121.45
116.77
113.66
111.09
77.41
77.09
76.77
55.40
29.45
f1 (ppm)
Me
NH
O
OMe

3ah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7.43
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7.35
7.27
7.23
7.19
7.14
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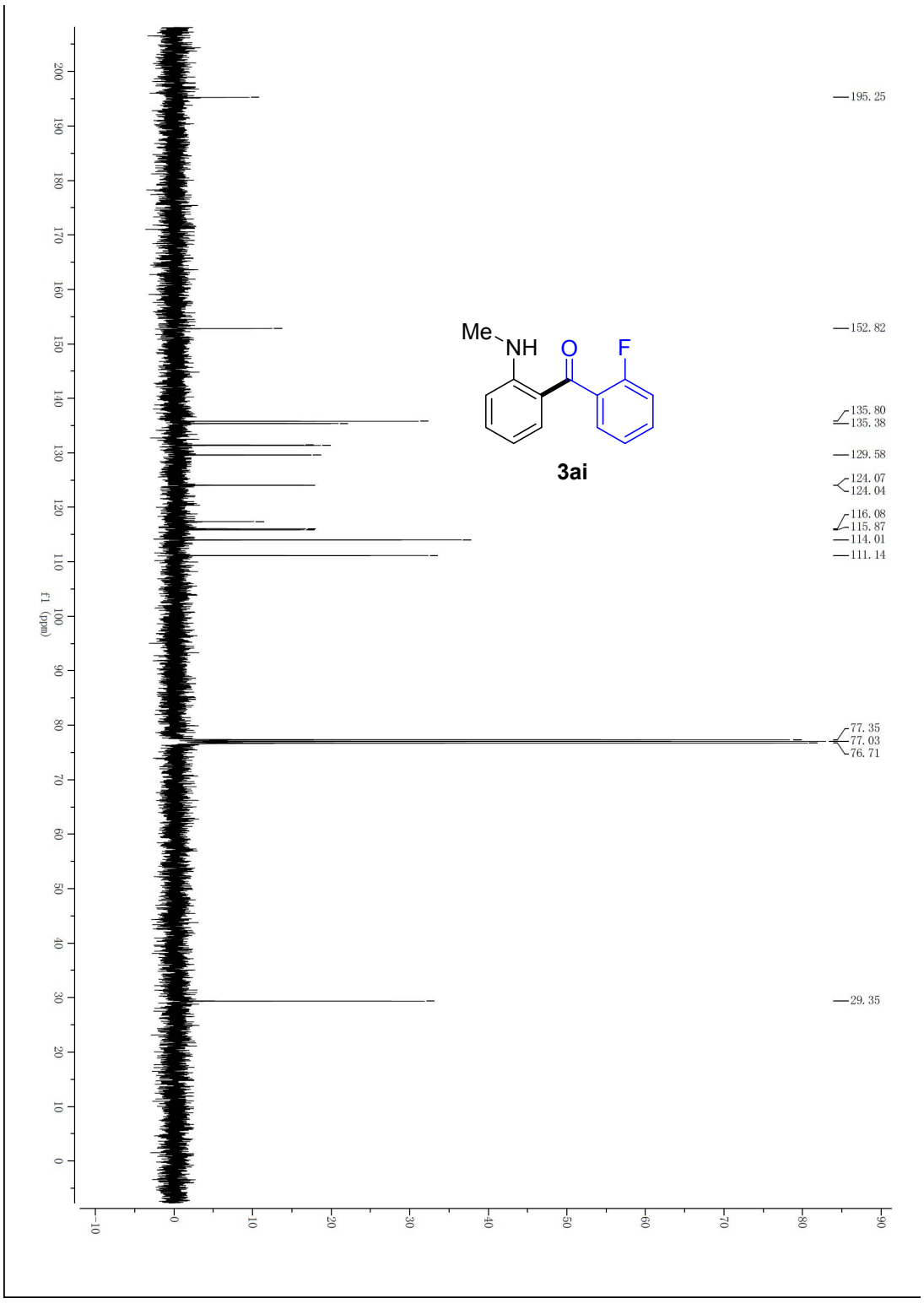
6.77
6.57
6.56
6.55
6.55
6.54
6.53
6.53
3.03
3.02
1.01
1.03
2.05
1.12
1.24
1.17
0.96
0.99
2.90
Me
NH
O
F
3ai
f1 (ppm)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124.07
124.04
116.08
115.87
114.01
111.14
77.35
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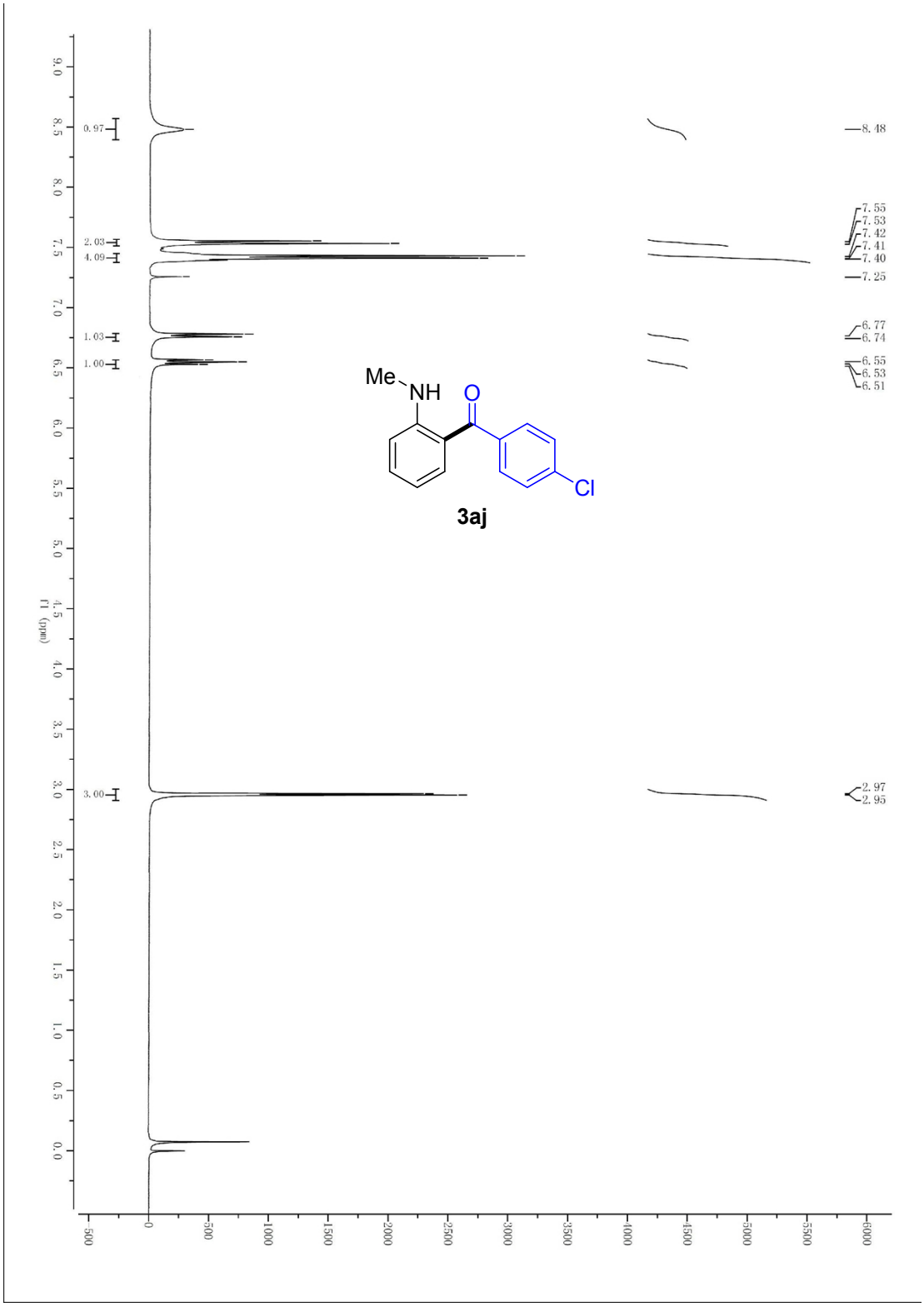
29.35
Me
NH
O
F
3ai
f1 (ppm)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6.74
6.55
6.53
6.51
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2.95
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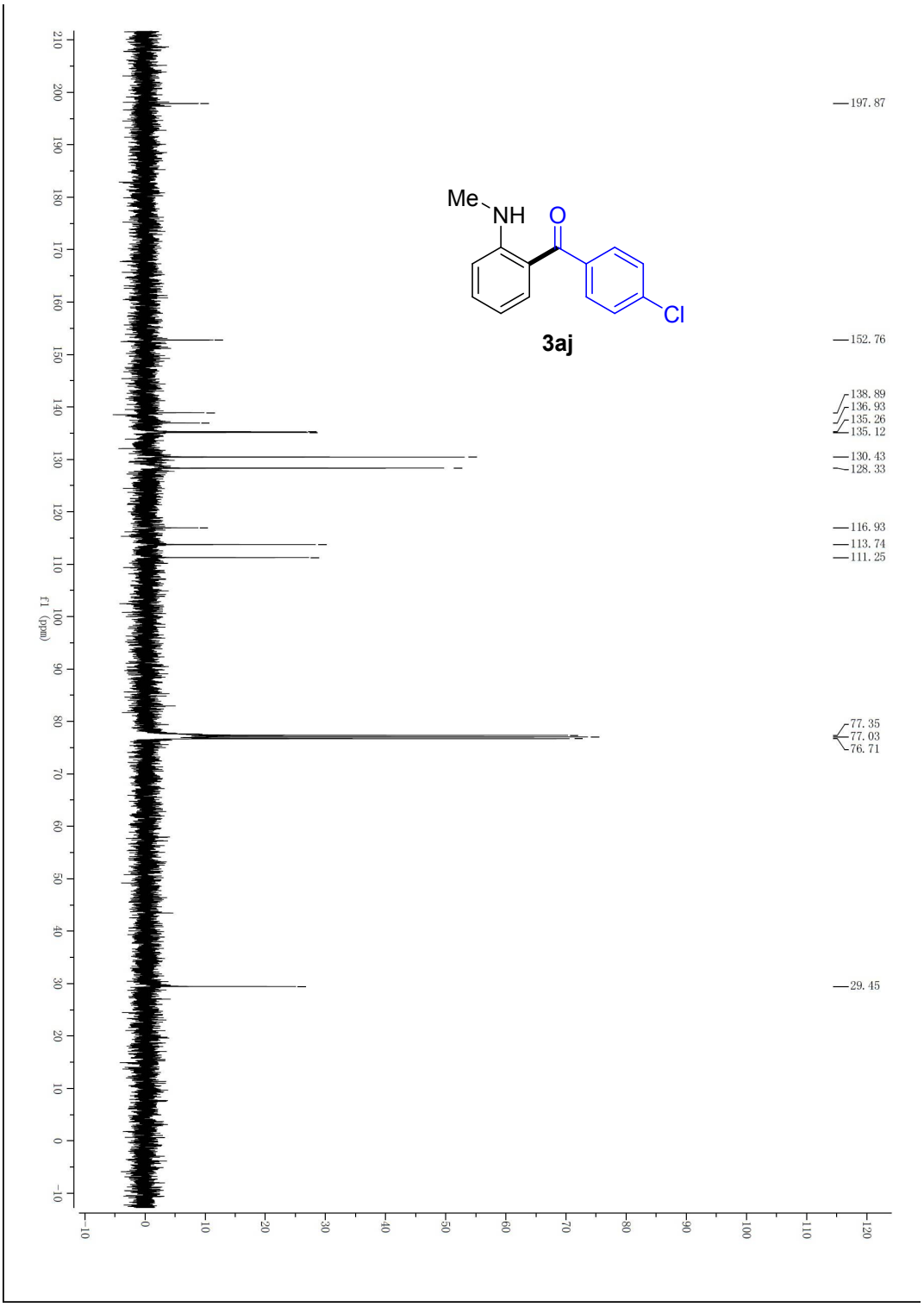
2.03
4.09
1.03
1.00
3.00
Me
NH
O
Cl
3aj
f1 (ppm)


Me
NH
O
Cl
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138.89
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135.26
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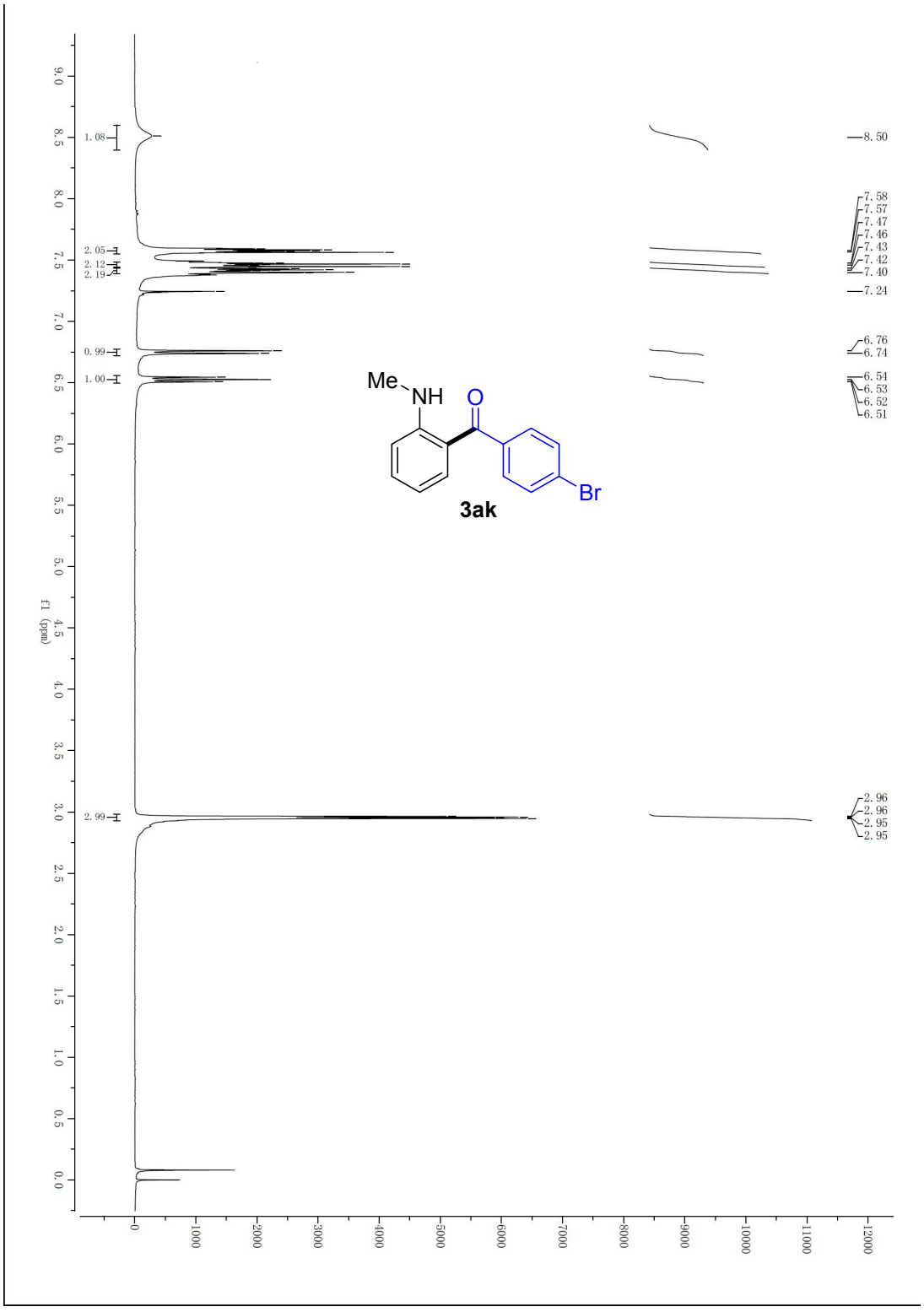
77.35
77.03
76.71
29.45
f1 (ppm)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2.19
0.99
1.00
2.99
8.50
7.58
7.57
7.47
7.46
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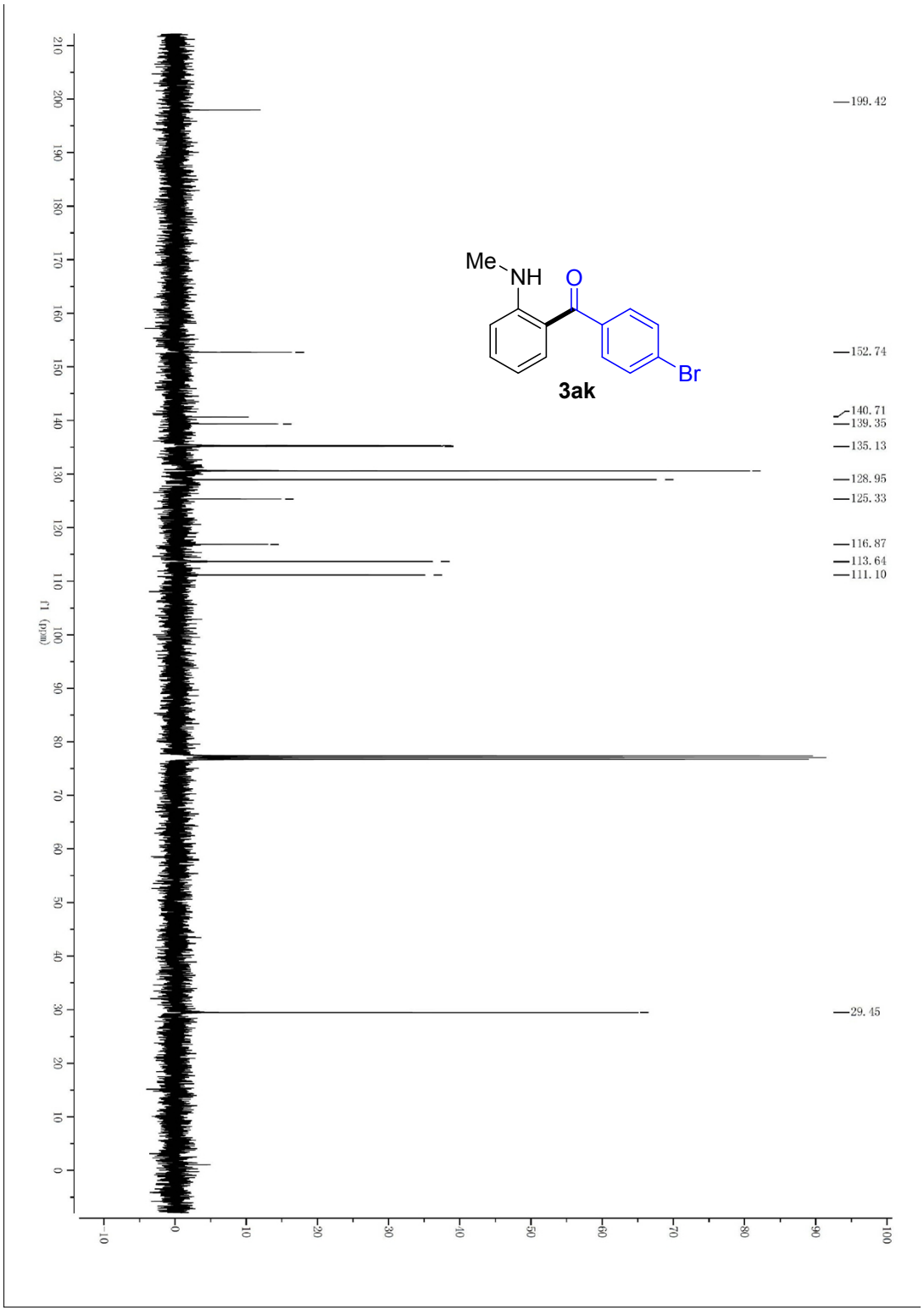
7.42
7.40
7.24
6.76
6.74
6.54
6.53
6.52
6.51
2.96
2.96
2.95
2.95
Me
NH
O
Br
3ak
f1 (ppm)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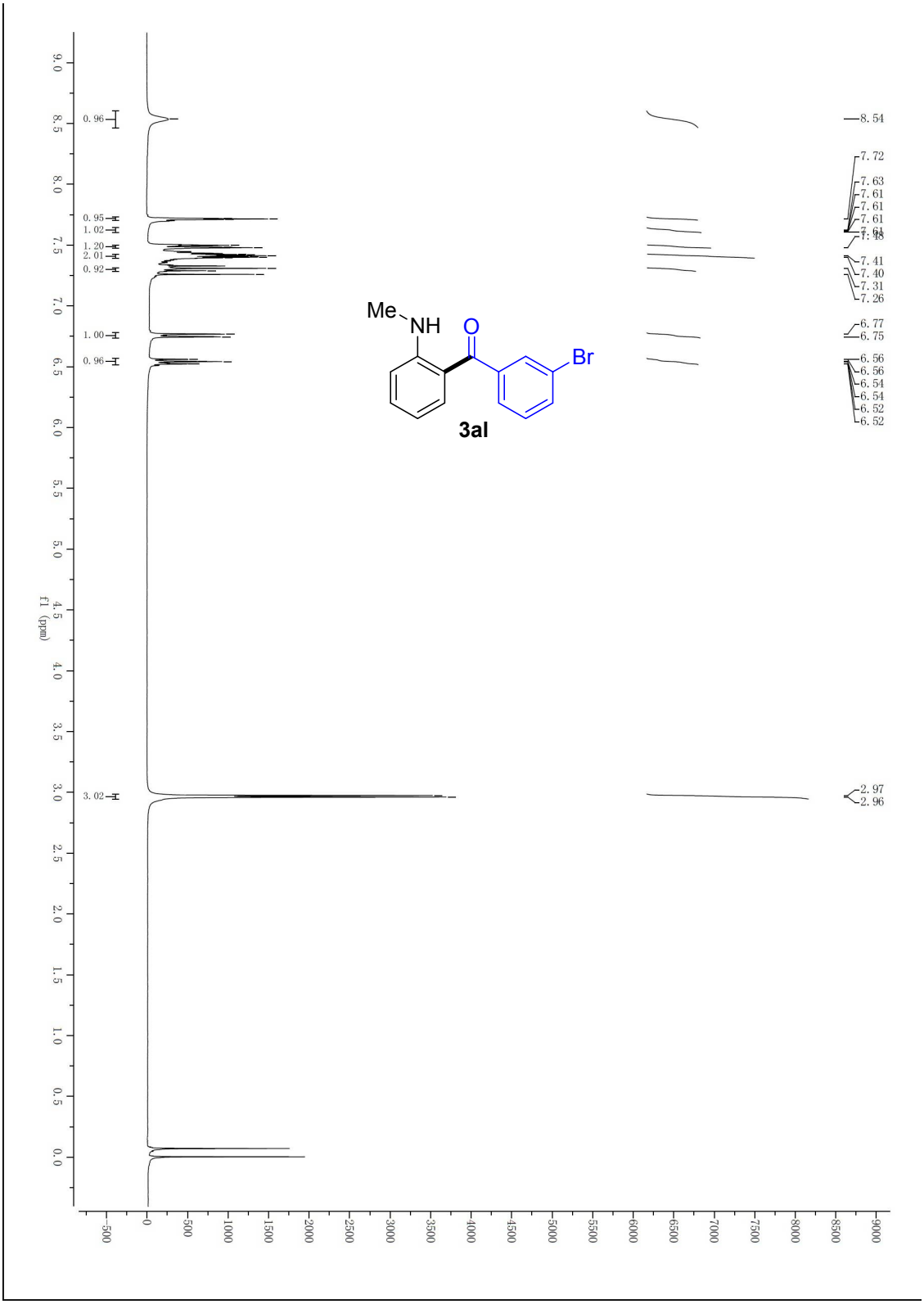
125.33
116.87
113.64
111.10
29.45
f1 (ppm)


Me
NH
O
Br
3al
f1 (ppm)
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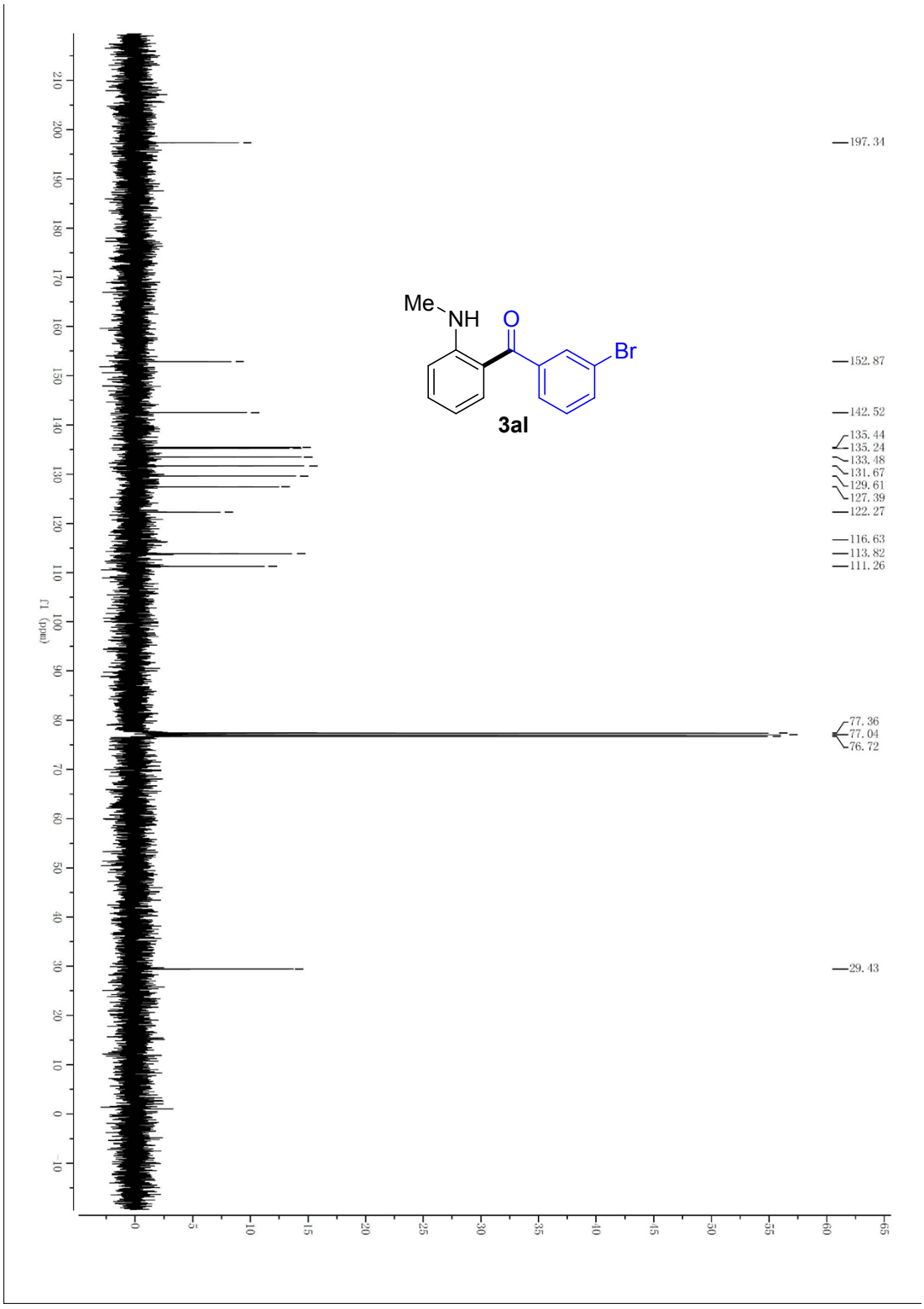
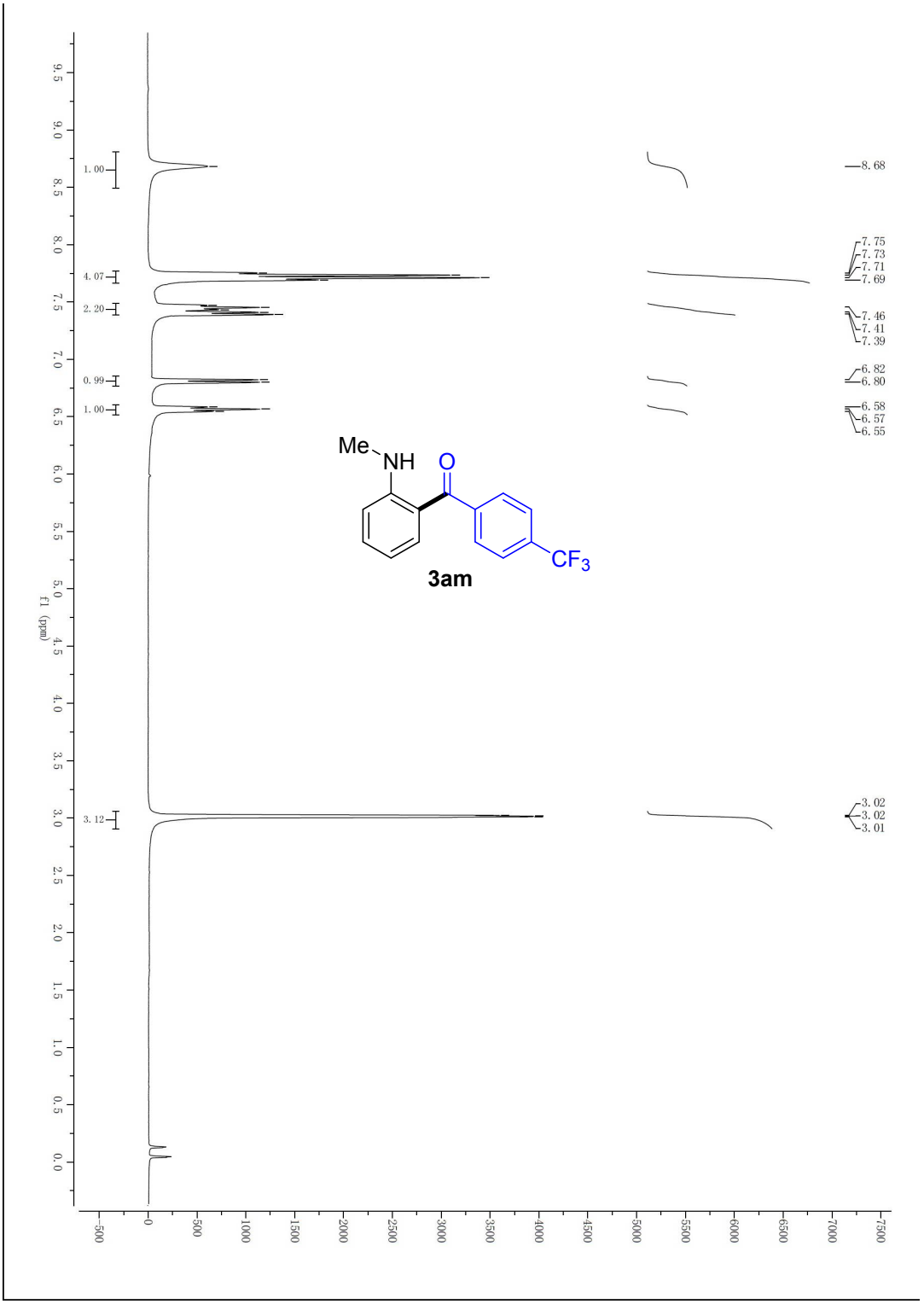
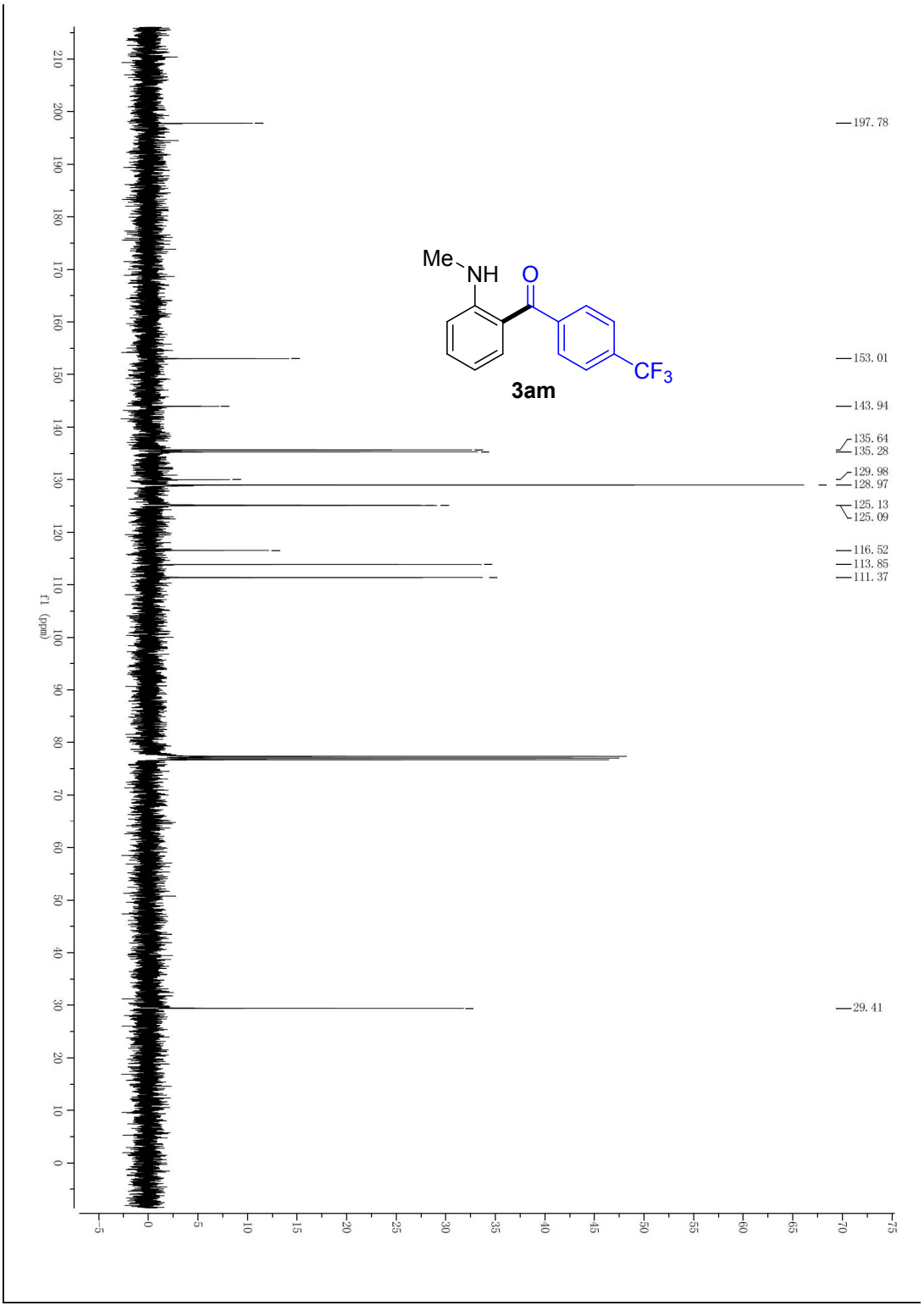
0.95
1.02
1.20
2.01
0.92
1.00
0.96
3.02
8.54
7.72
7.63
7.61
7.61
7.61
7.61
7.41
7.40
7.31
7.26
6.77
6.75
6.56
6.56
6.54
6.54
6.52
6.52
2.97
2.96


Me
NH
O
Br
3aI
197.34
152.87
142.52
135.44
135.24
133.48
131.67
129.61
127.39
122.27
116.63
113.82
111.26
77.36
77.04
76.72
29.43
f1 (ppm)


Me
NH
O
CF3
3am
f1 (ppm)
1.00
4.07
2.20
0.99
1.00
3.12
8.68
7.75
7.73
7.71
7.69
7.46
7.41
7.39
6.82
6.80
6.58
6.57
6.55
3.02
3.02
3.01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NH
O
CF3
3am
197.78
153.01
143.94
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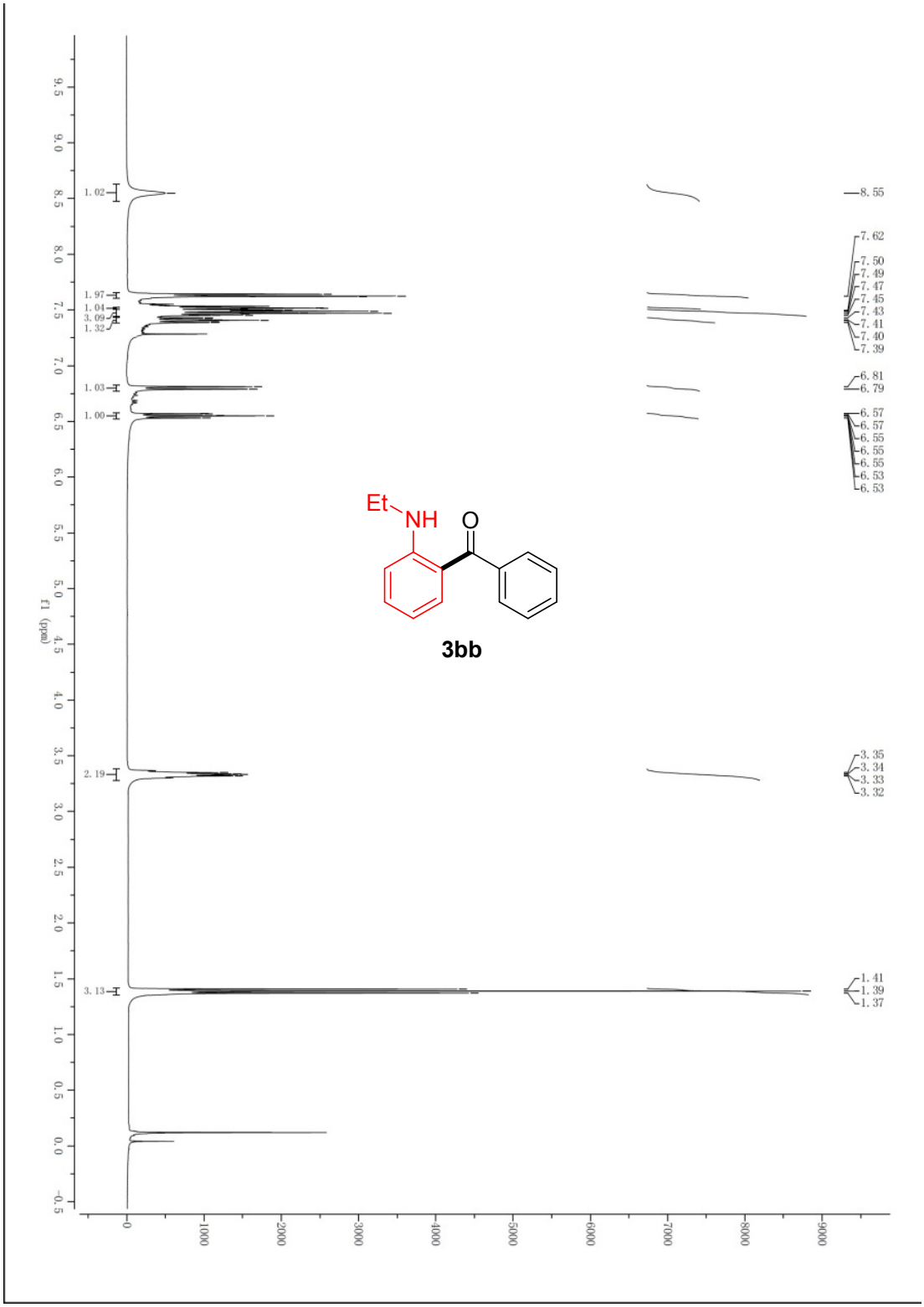
135.28
129.98
128.97
125.13
125.09
116.52
113.85
111.37
29.41
f1 (ppm)


Et
NH
O
3bb
f1 (ppm)
1.02
1.97
1.04
3.09
1.32
1.03
1.00
2.19
3.13
8.55
7.62
7.50
7.49
7.47
7.45
7.43
7.41
7.40
7.39
6.81
6.79
6.57
6.57
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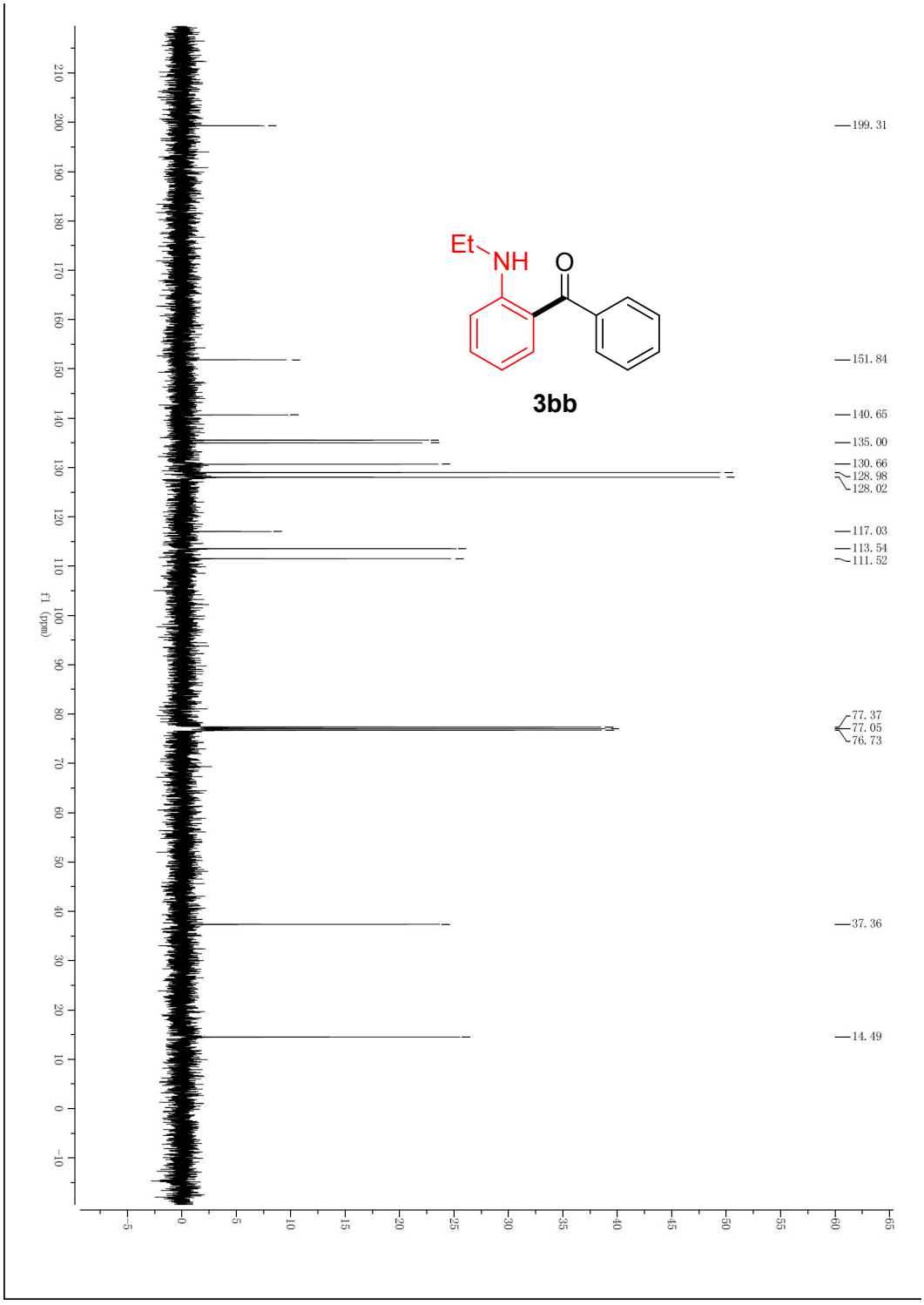
3.34
3.33
3.32
1.41
1.39
1.37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NH
O
3bb
199.31
151.84
140.65
135.00
130.66
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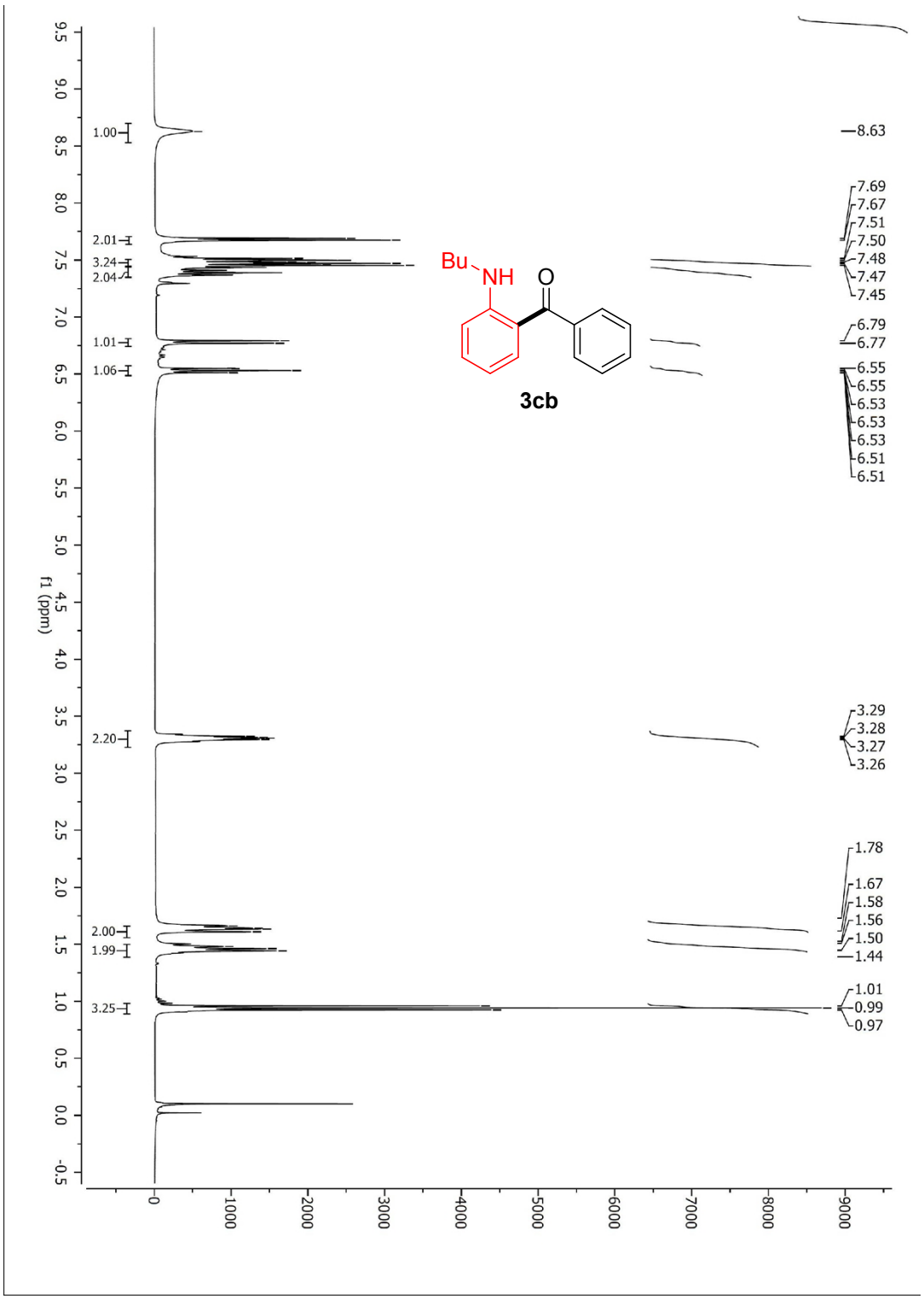
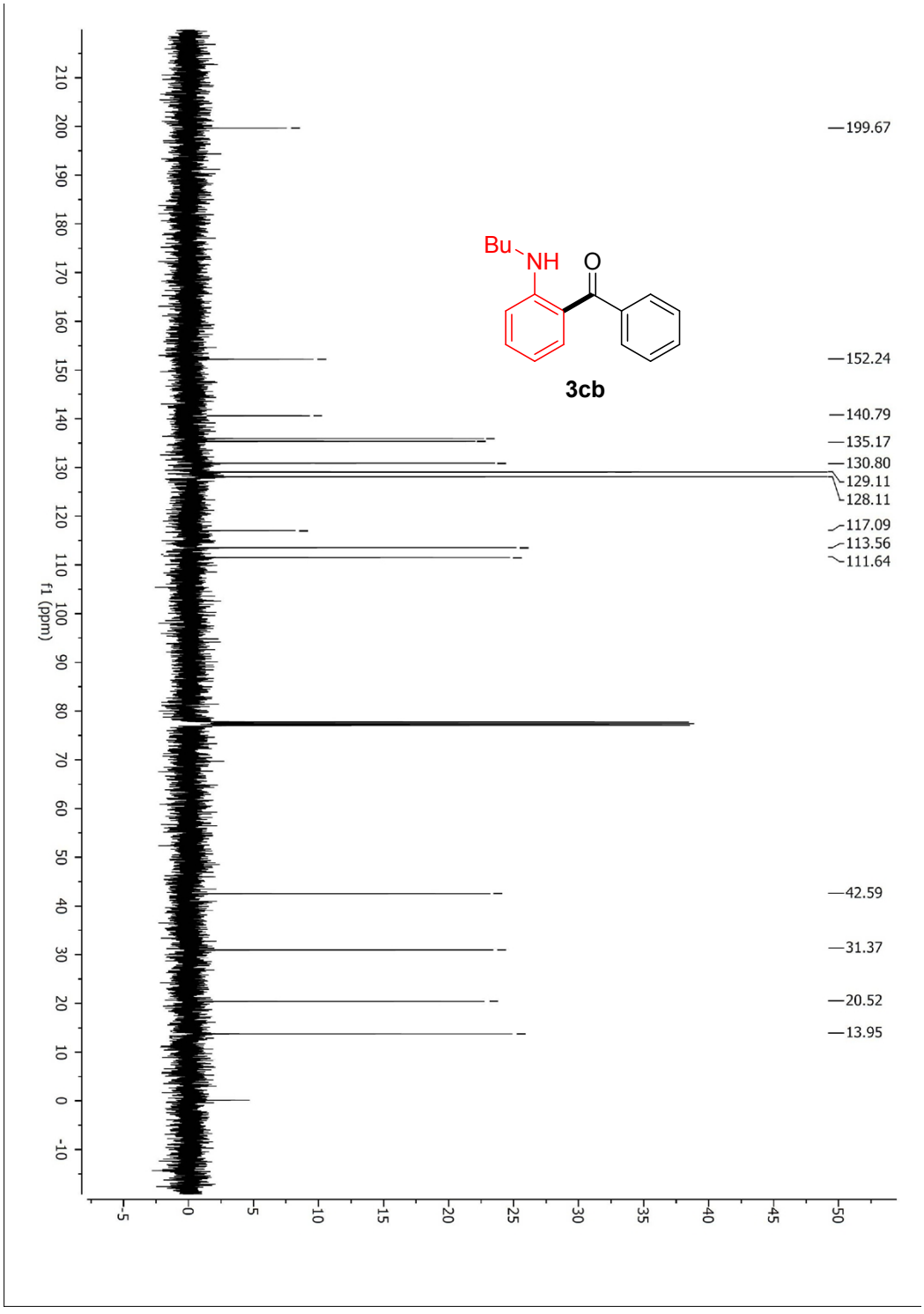
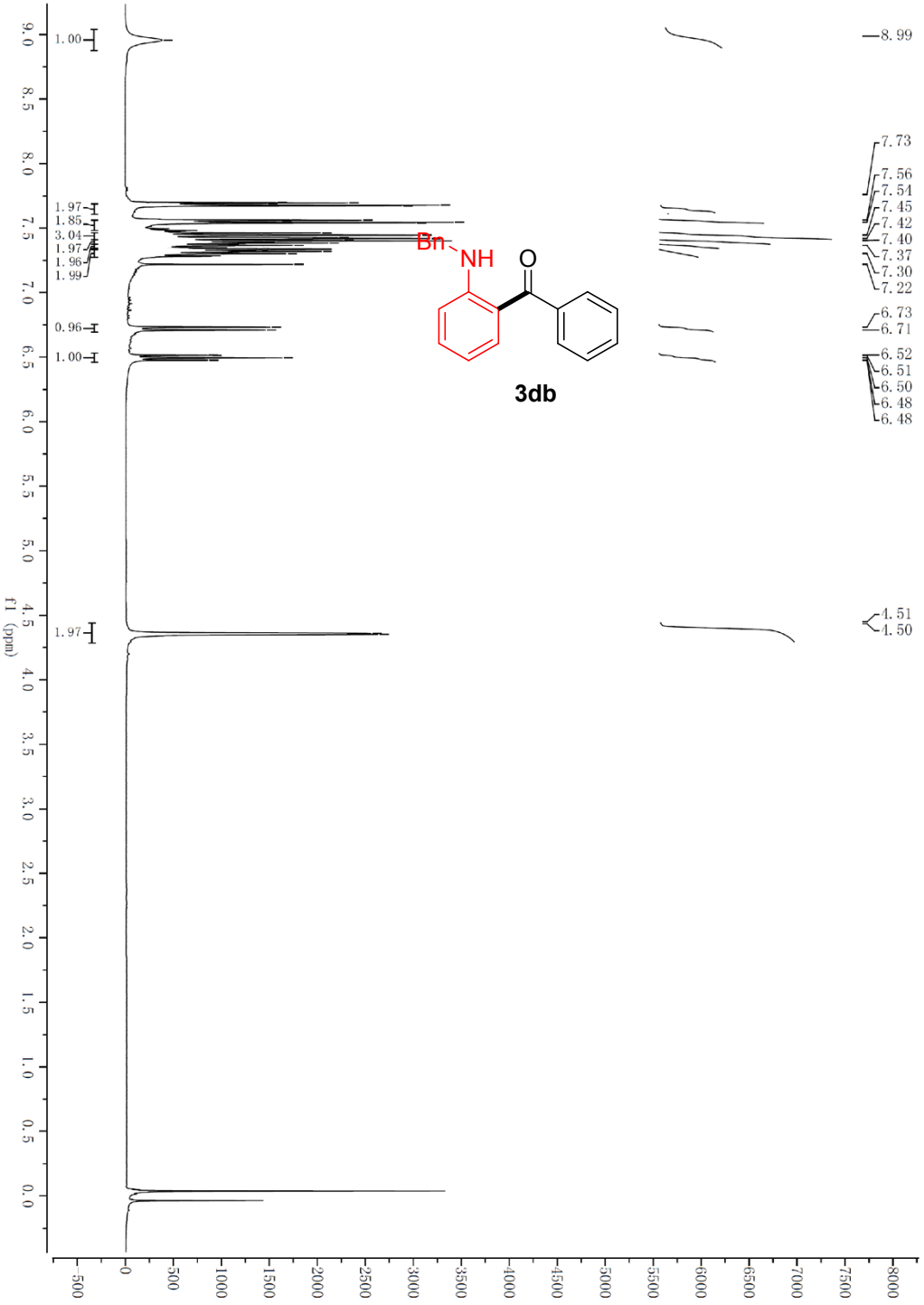
128.02
117.03
113.54
111.52
77.37
77.05
76.73
37.36
14.49
f1 (ppm)


Bu
NH
O
3cb
f1 (ppm)
1.00
2.01
3.24
2.04
1.01
1.06
2.20
2.00
1.99
3.25
8.63
7.69
7.67
7.51
7.50
7.48
7.47
7.45
6.79
6.77
6.55
6.55
6.53
6.53
6.53
6.51
6.51
3.29
3.28
3.27
3.26
1.78
1.67
1.58
1.56
1.50
1.44
1.01
0.99
0.97


Bu
NH
O
3cb
199.67
152.24
140.79
135.17
130.80
129.11
128.11
117.09
113.56
111.64
42.59
31.37
20.52
13.95
f1 (ppm)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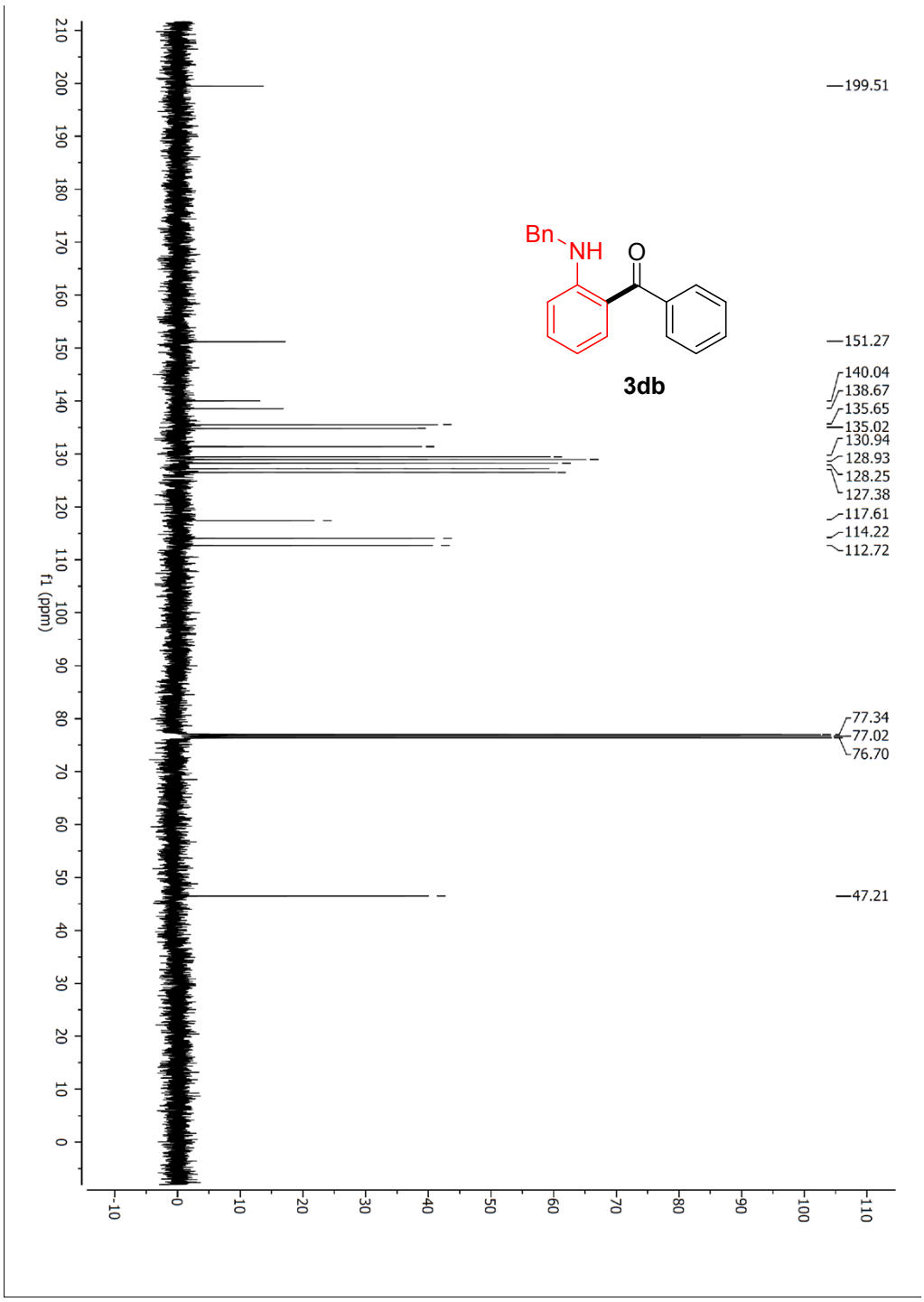
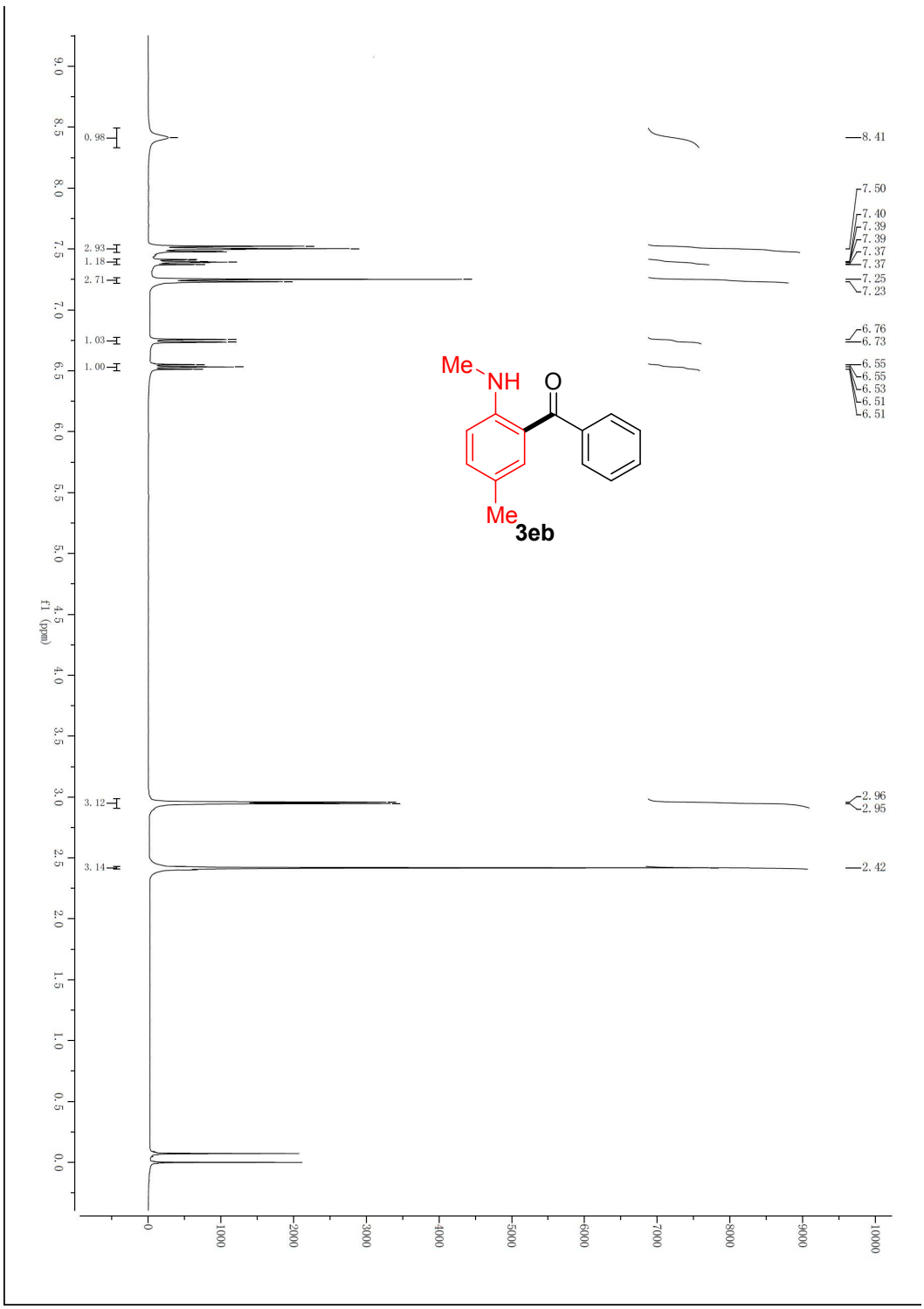
1.97
1.85
3.04
1.97
1.96
1.99
0.96
1.00
1.97
8.99
7.73
7.56
7.54
7.45
7.42
7.40
7.37
7.30
7.22
6.73
6.71
6.52
6.51
6.50
6.48
6.48
4.51
4.50
Bn
NH
O
3db
f1 (ppm)


Bn
NH
O
3db
199.51
151.27
140.04
138.67
135.65
135.02
130.94
128.93
128.25
127.38
117.61
114.22
112.72
77.34
77.02
76.70
47.21
f1 (ppm)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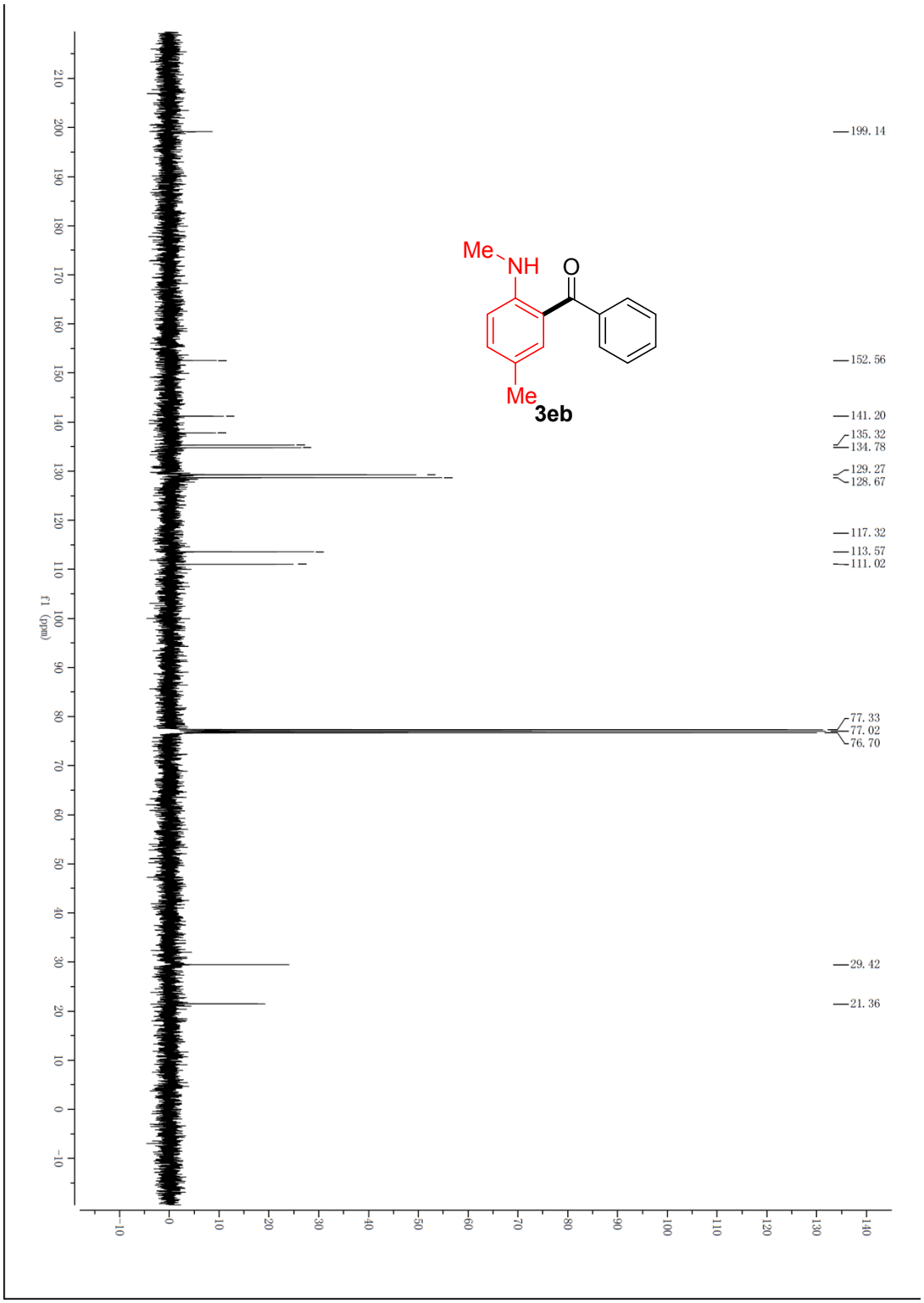
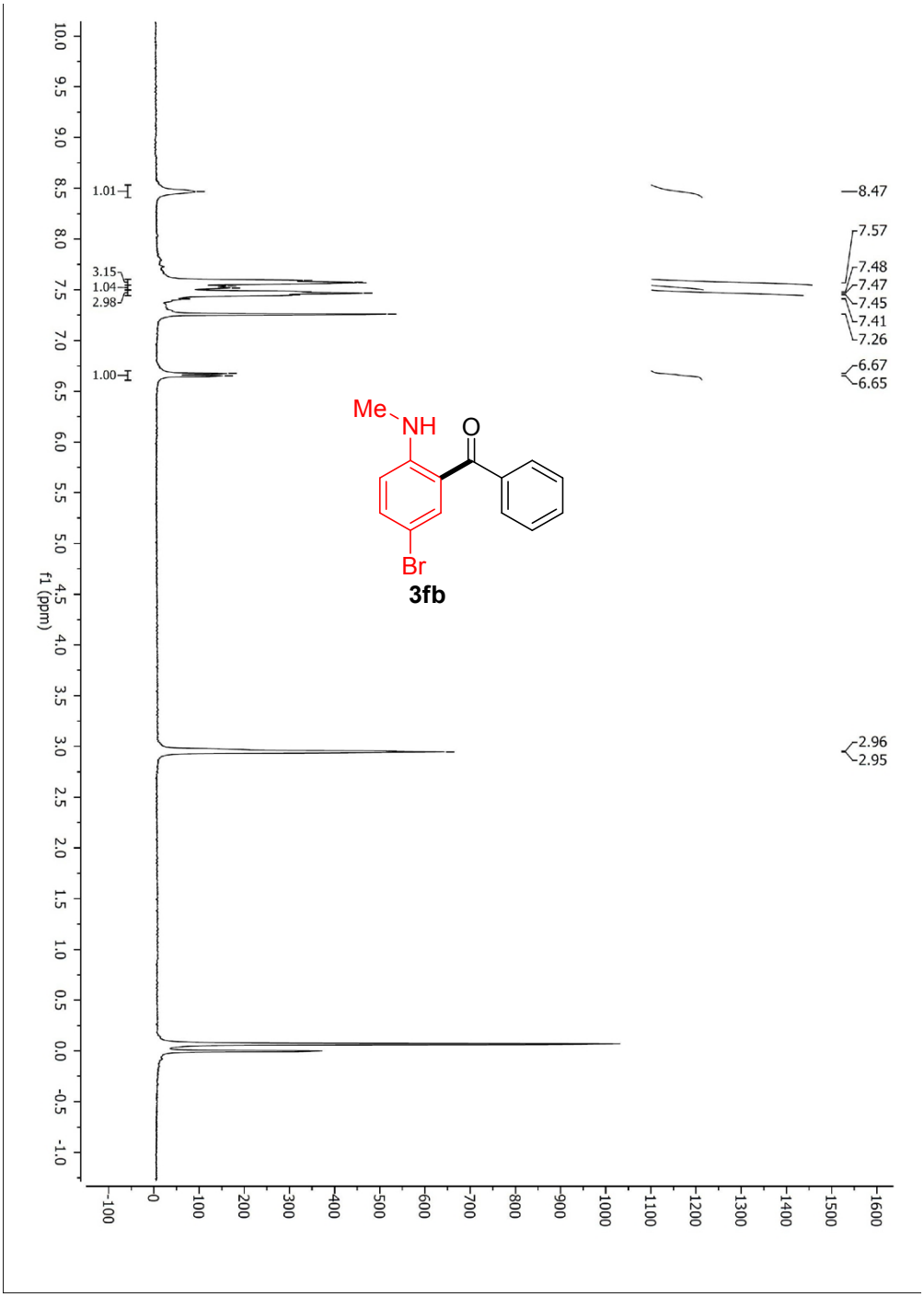
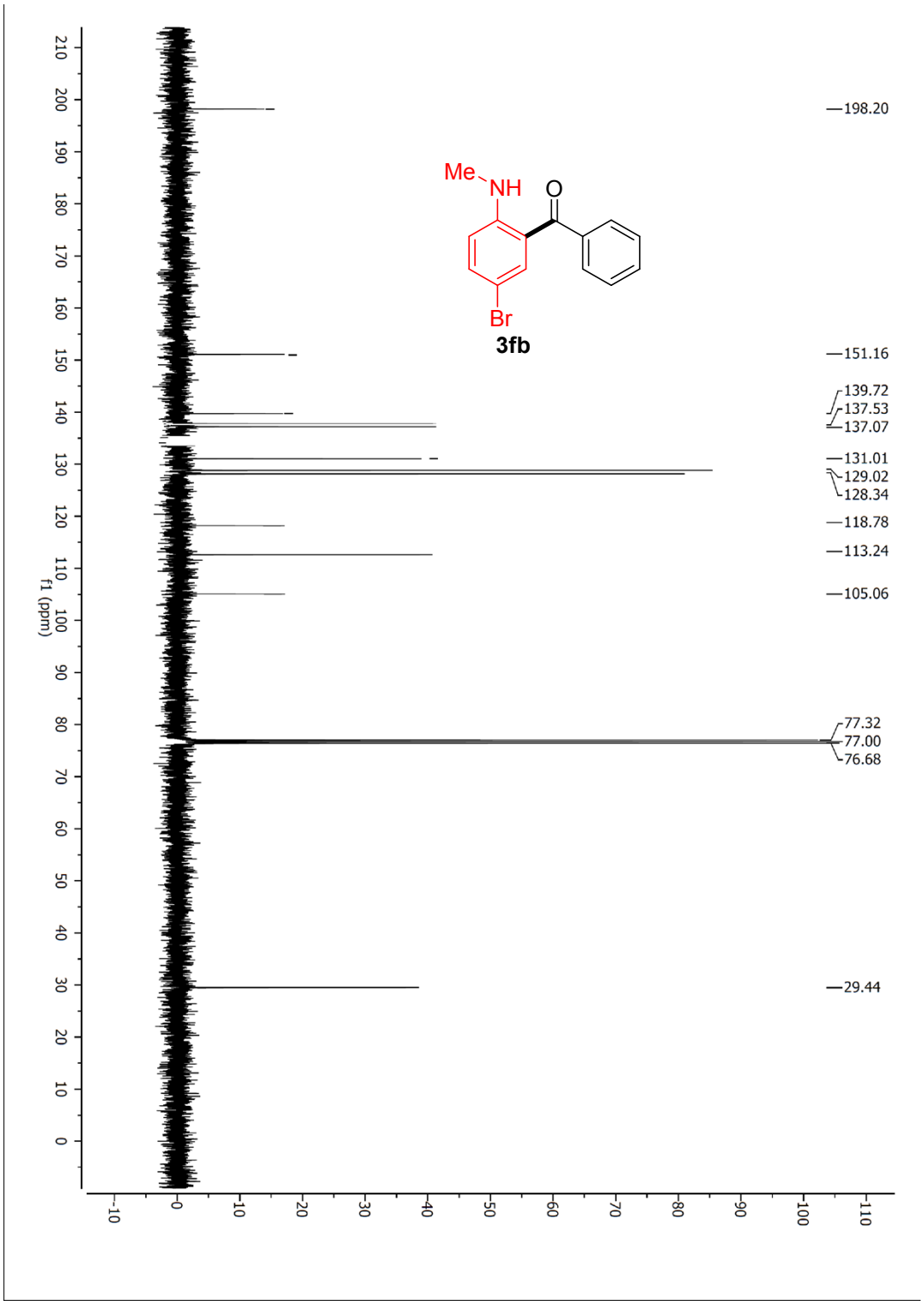
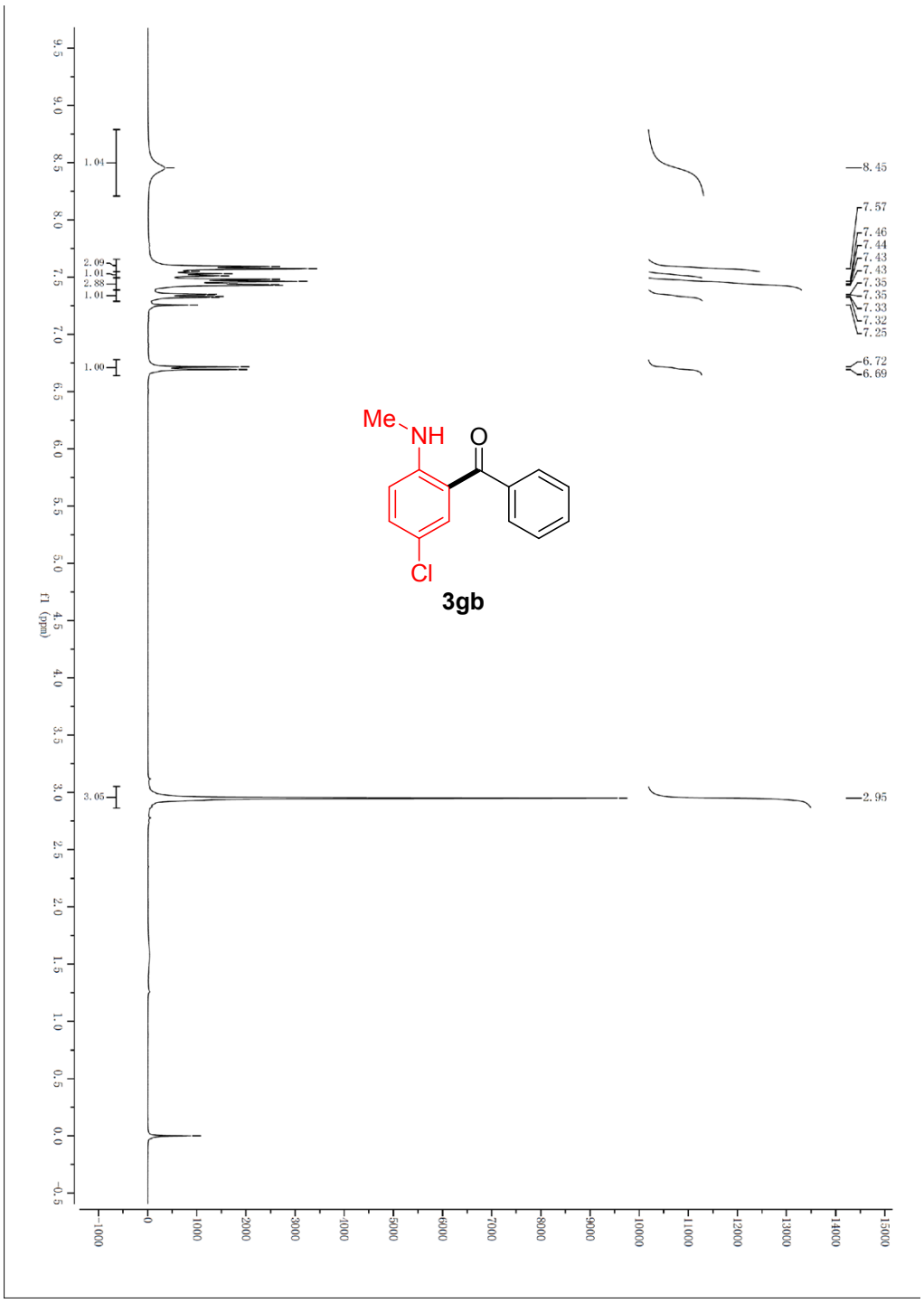
2.93
1.18
2.71
1.03
1.00
3.12
3.14
8.41
7.50
7.40
7.39
7.39
7.37
7.37
7.25
7.23
6.76
6.73
6.55
6.55
6.53
6.51
6.51
2.96
2.95
2.42
Me
NH
O
Me
3eb
f1 (ppm)


199.14
152.56
141.20
135.32
134.78
129.27
128.67
117.32
113.57
111.02
77.33
77.02
76.70
29.42
21.36
Me
NH
O
Me
3eb
f1 (ppm)


1.01
3.15
1.04
2.98
1.00
8.47
7.57
7.48
7.47
7.45
7.41
7.26
6.67
6.65
2.96
2.95
Me
NH
O
Br
3fb
f1 (ppm)


Me
NH
O
Br
3fb
198.20
151.16
139.72
137.53
137.07
131.01
129.02
128.34
118.78
113.24
105.06
77.32
77.00
76.68
29.44
f1 (ppm)


Me
NH
O
Cl
3gb
f1 (ppm)
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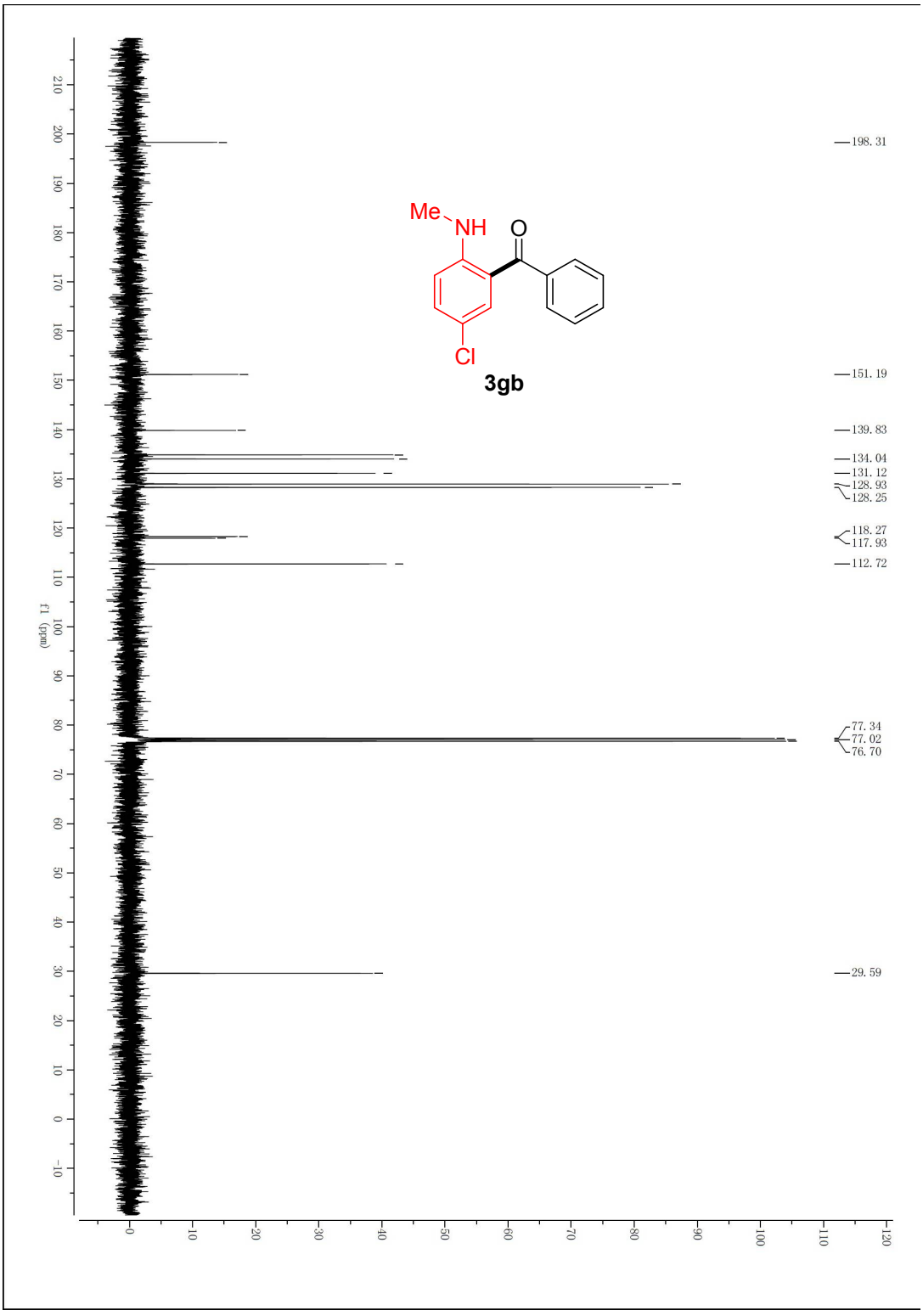
2.09
1.01
2.88
1.01
1.00
3.05
8.45
7.57
7.46
7.44
7.43
7.43
7.35
7.35
7.33
7.32
7.25
6.72
6.69
2.95


Me
NH
O
Cl
3gb
198.31
151.19
139.83
134.04
131.12
128.93
128.25
118.27
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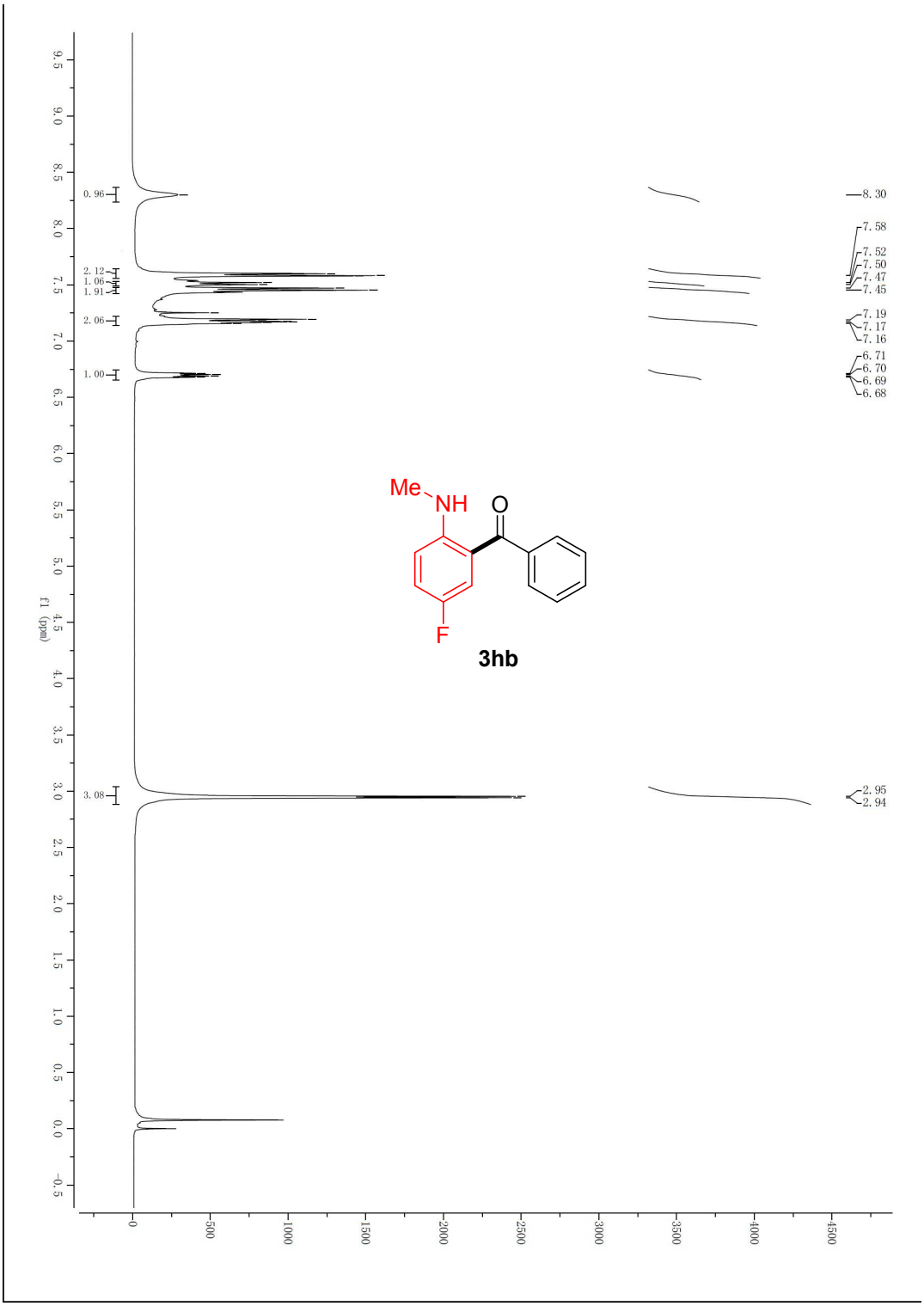
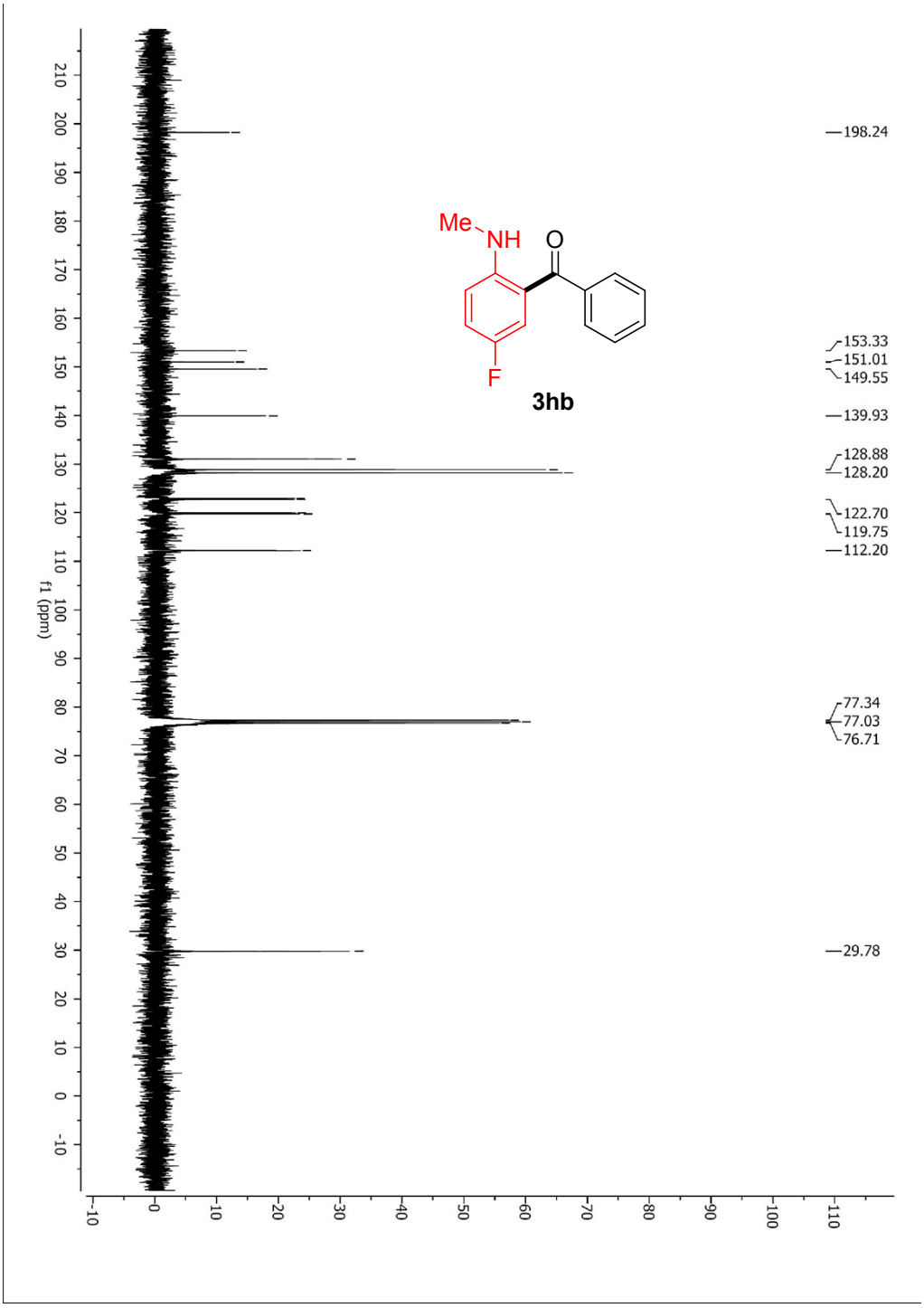
77.34
77.02
76.70
29.59
f1 (ppm)


0.96
2.12
1.06
1.91
2.06
1.00
3.08
8.30
7.58
7.52
7.50
7.47
7.45
7.19
7.17
7.16
6.71
6.70
6.69
6.68
2.95
2.94
Me
NH
O
F
3hb
f1 (ppm)


Me
NH
O
F
3hb
198.24
153.33
151.01
149.55
139.93
128.88
128.20
122.70
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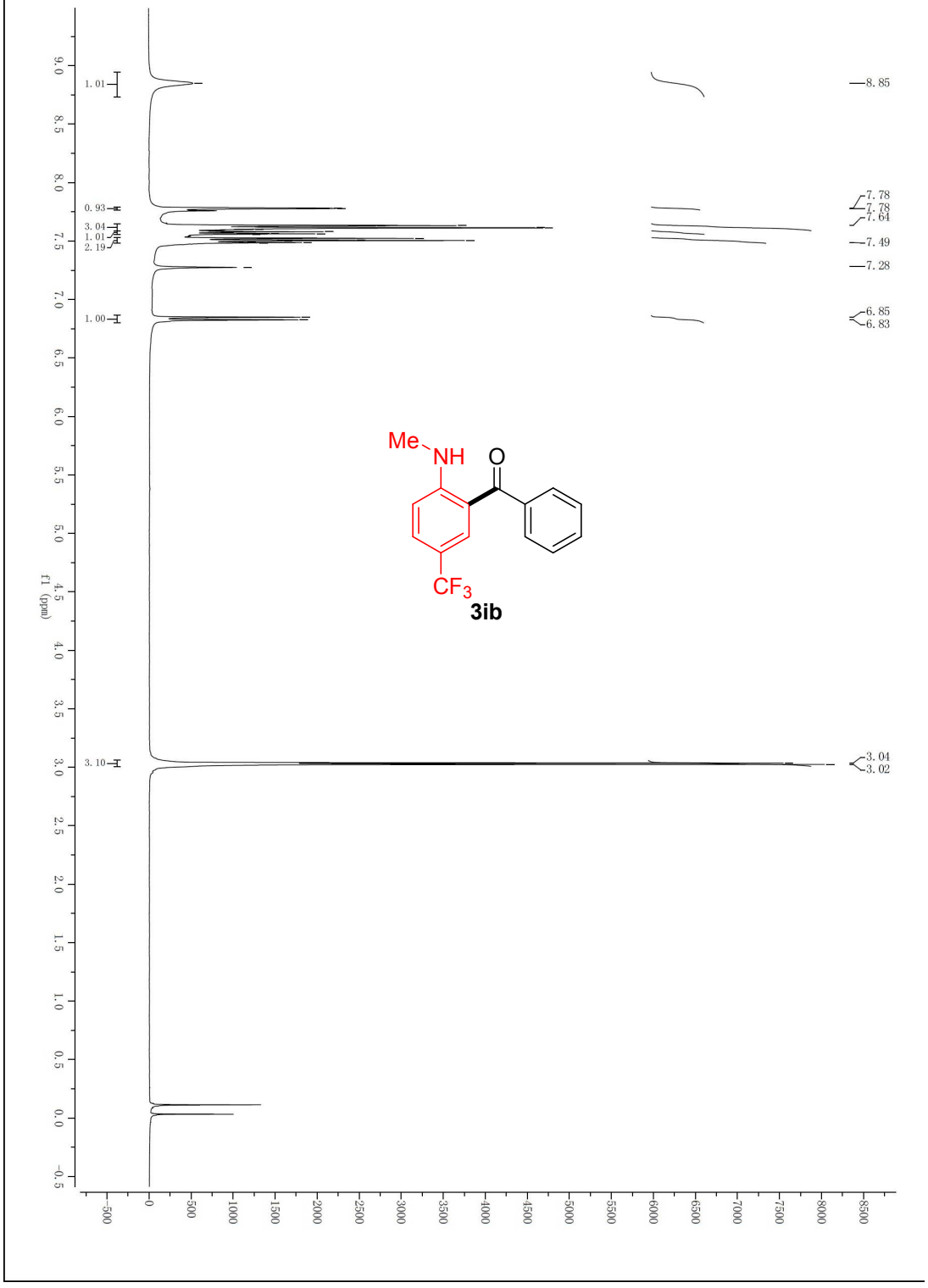
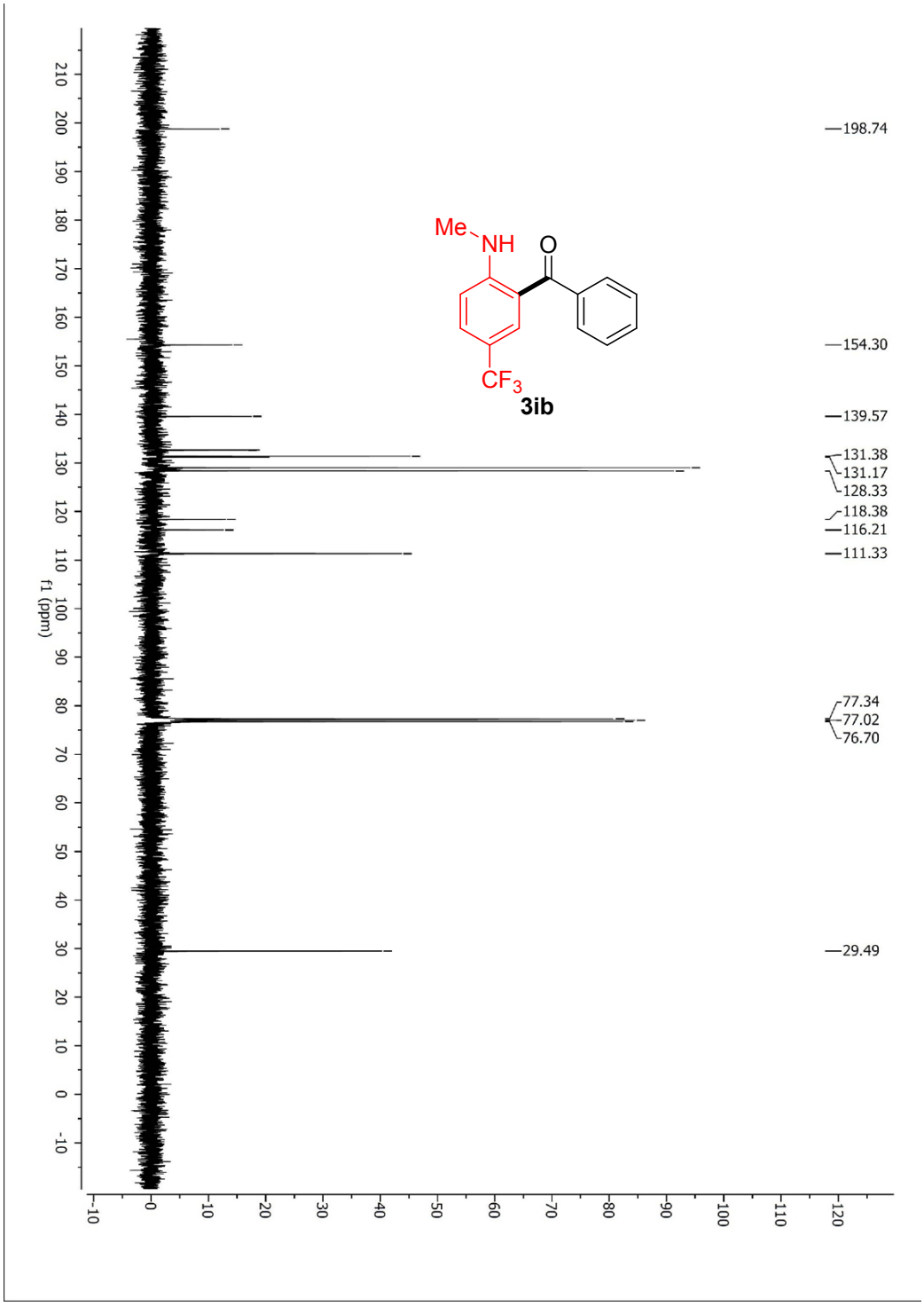
77.34
77.03
76.71
29.78
f1 (ppm)


8.85
7.78
7.78
7.64
7.49
7.28
6.85
6.83
3.04
3.02
1.01
0.93
3.04
1.01
2.19
1.00
3.10
Me
NH
O
CF3
3ib
f1 (ppm)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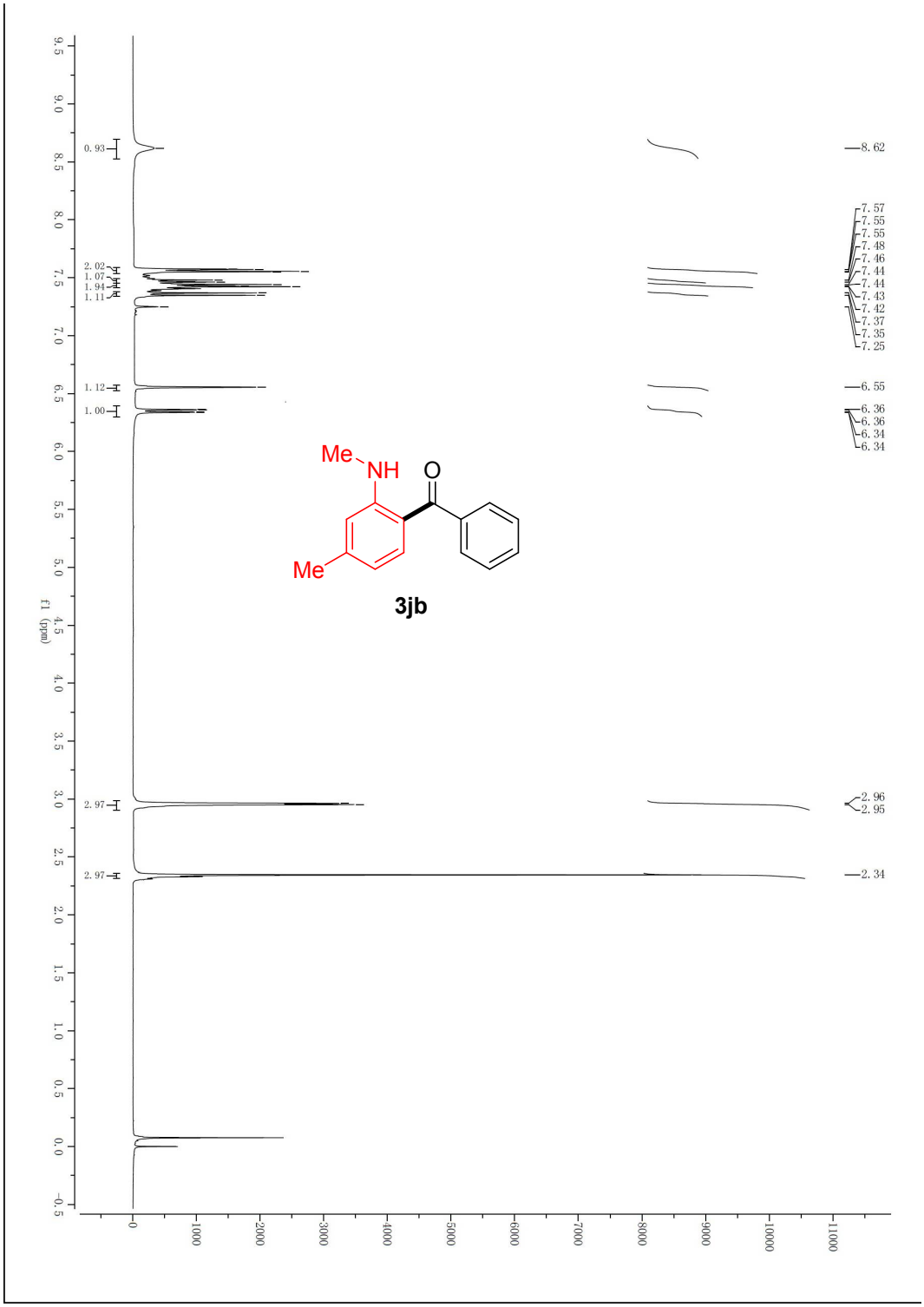
154.30
139.57
131.38
131.17
128.33
118.38
116.21
111.33
77.34
77.02
76.70
29.49
Me
NH
O
CF3
3ib
f1 (ppm)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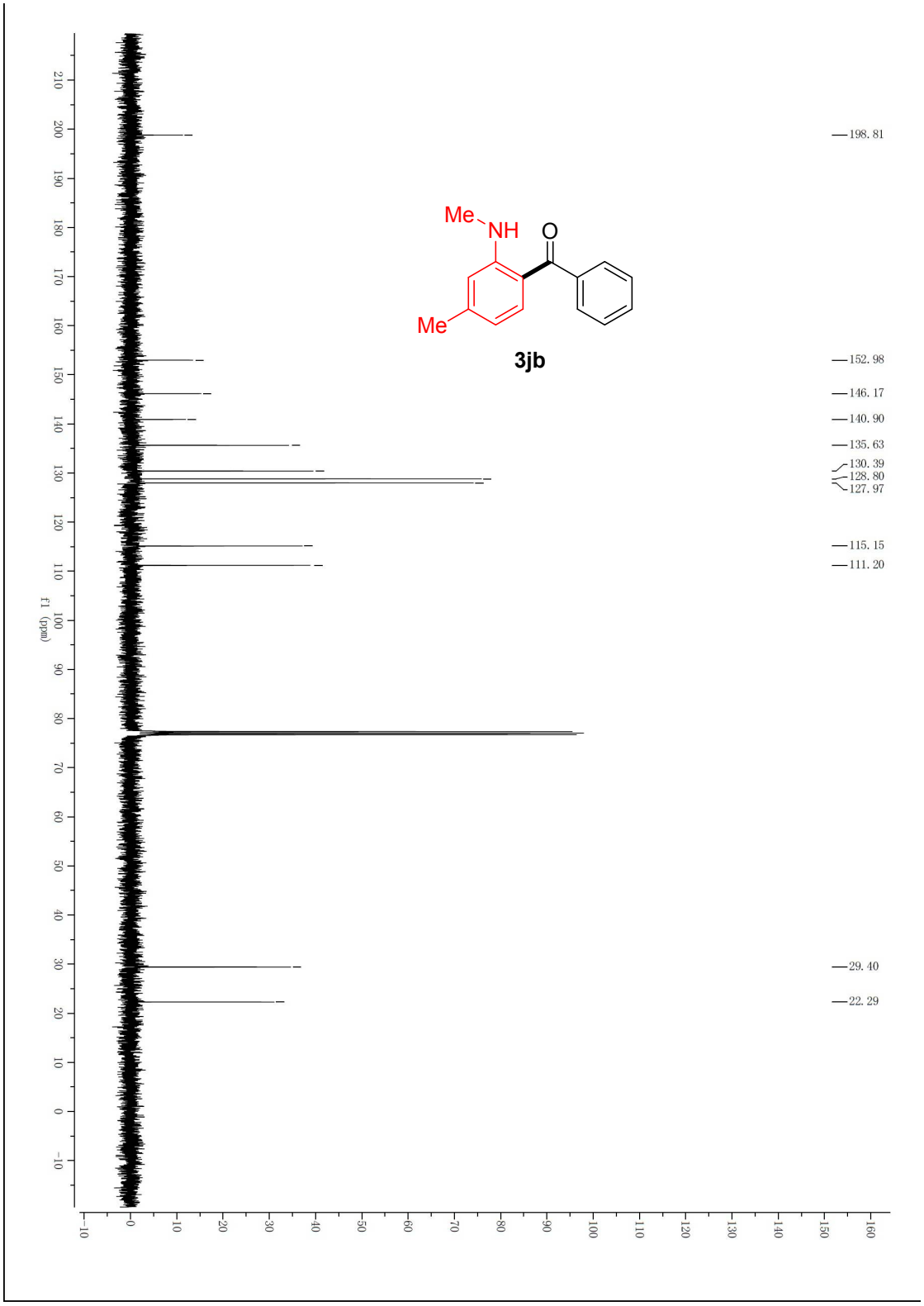
1.07
1.94
1.11
1.12
1.00
2.97
2.97
8.62
7.57
7.55
7.55
7.48
7.46
7.44
7.44
7.43
7.42
7.37
7.35
7.25
6.55
6.36
6.36
6.34
6.34
2.96
2.95
2.34
Me
NH
O
Me
f1 (ppm)

3jb


Me
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O
Me
3jb
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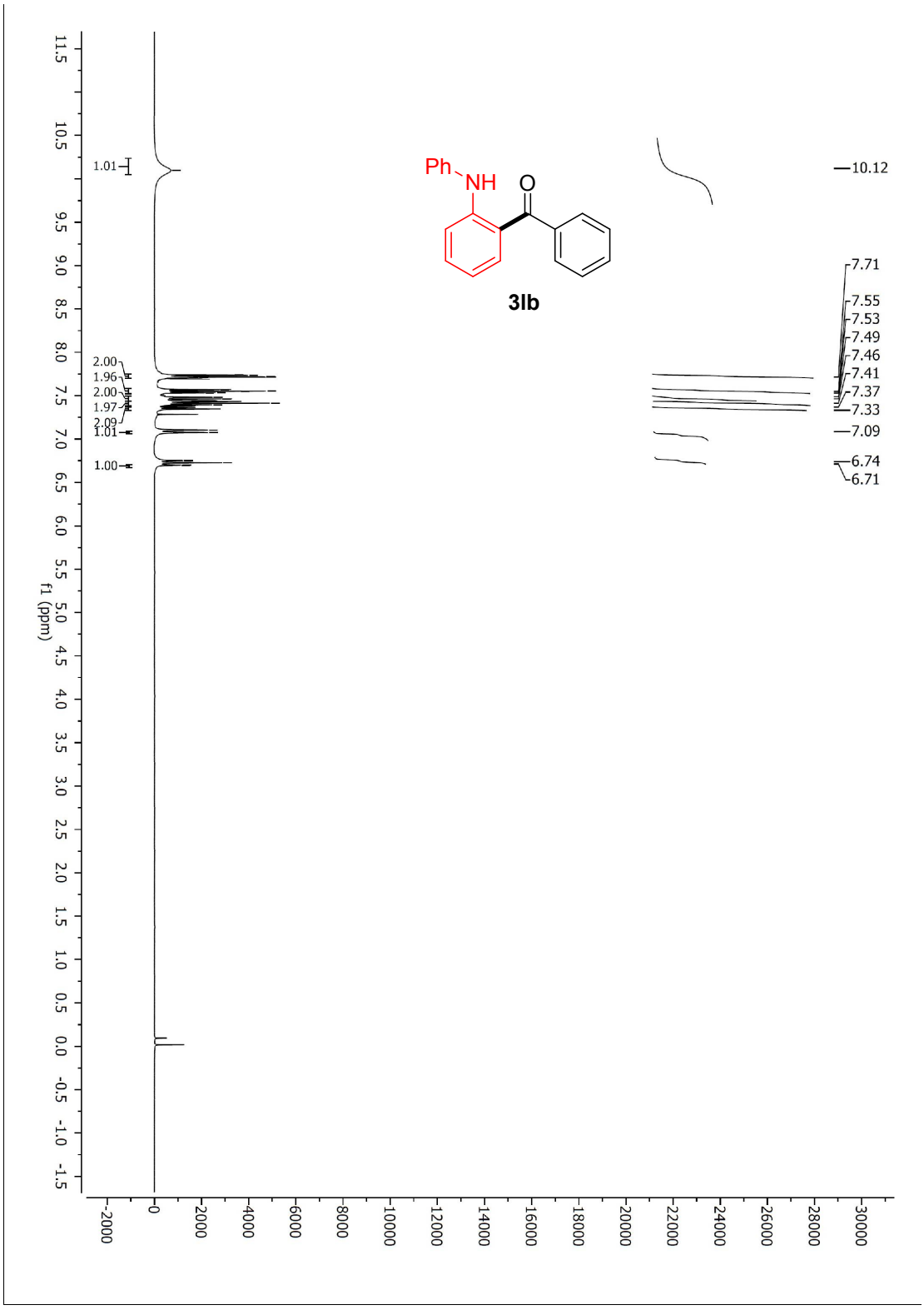
130.39
128.80
127.97
115.15
111.20
29.40
22.29
f1 (ppm)


Ph
NH
O
3Ib
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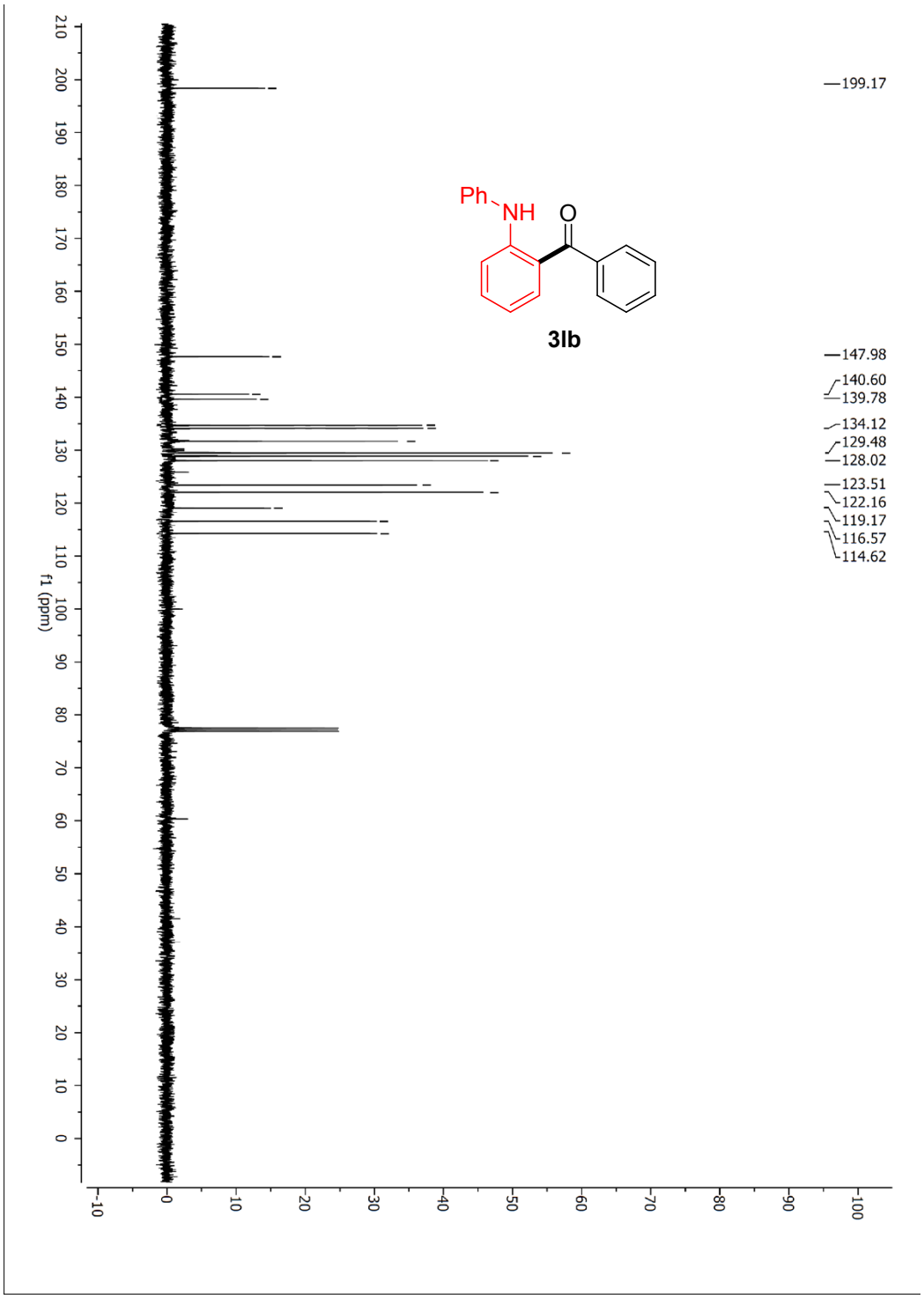
7.71
7.55
7.53
7.49
7.46
7.41
7.37
7.33
7.09
6.74
6.71
1.01
2.00
1.96
2.00
1.97
2.09
1.01
1.00
f1 (ppm)


199.17
147.98
140.60
139.78
134.12
129.48
128.02
123.51
122.16
119.17
116.57
114.62
Ph
NH
O
3lb
f1 (ppm)

6.Reference

[1] W. L. F. Armarego and D. D. Perrin, *In Purification of Laboratory Chemicals*, 4th Ed., Butterworth-Heinemann: Oxford UK: 1996.
[2] C. Wang and Y. Huang, *Org. Lett.*, 2013, **15**, 5294.