

Supporting Information

I₂-Catalyzed Synthesis of 3-Aminopyrrole with Homopropargylic Amines and Nitrosoarenes

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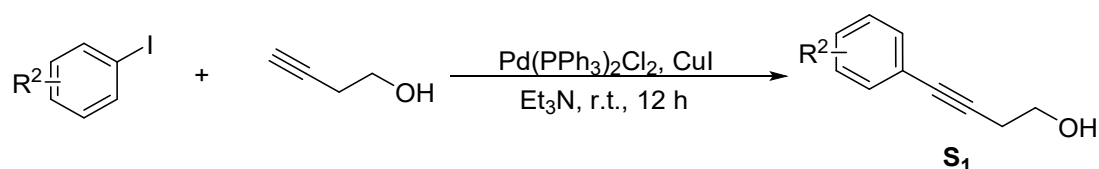
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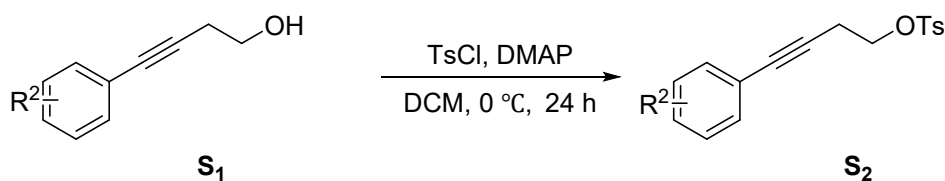
General remark

^1H NMR and ^{13}C NMR spectra were recorded on Bruker 400M and Mercury 300M in CDCl_3 . All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of ^1H NMR and ^{13}C NMR spectra were provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. All reactions were carried out under air in oven-dried glassware, unless otherwise noted. All reagents were purchased commercially and used as received, unless otherwise noted.

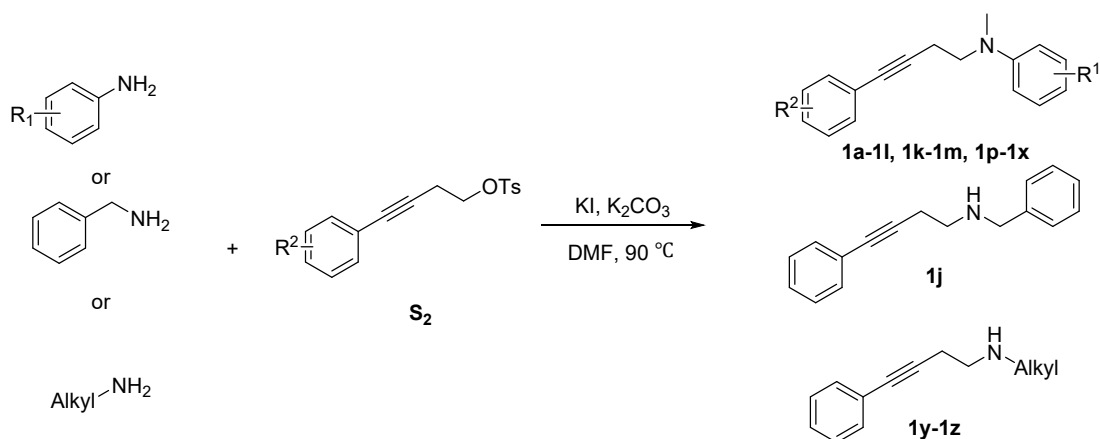
General procedure for the synthesis of aminoalkynes **1a-1ac**^[1-3]:



To a suspension of $\text{Pd(PPh}_3)_2\text{Cl}_2$ (21 mg, 0.03 mmol), CuI (5.7 mg, 0.03 mmol) in Et_3N (1.5 mL) was added a solution of iodobenzene (1.2 eq) and but-3-yn-1-ol (210 mg, 3.0 mmol, 1.0 eq) in Et_3N (15 mL). The mixture was stirred at room temperature for 12 h and then was diluted with EtOAc (20 mL), filtered off and evaporated under reduced pressure. The residue was purified through column chromatography on silica gel (petroleum ether/ EtOAc = 15/1 to 5/1) to afford substituted **S**₁ as yellow oil.

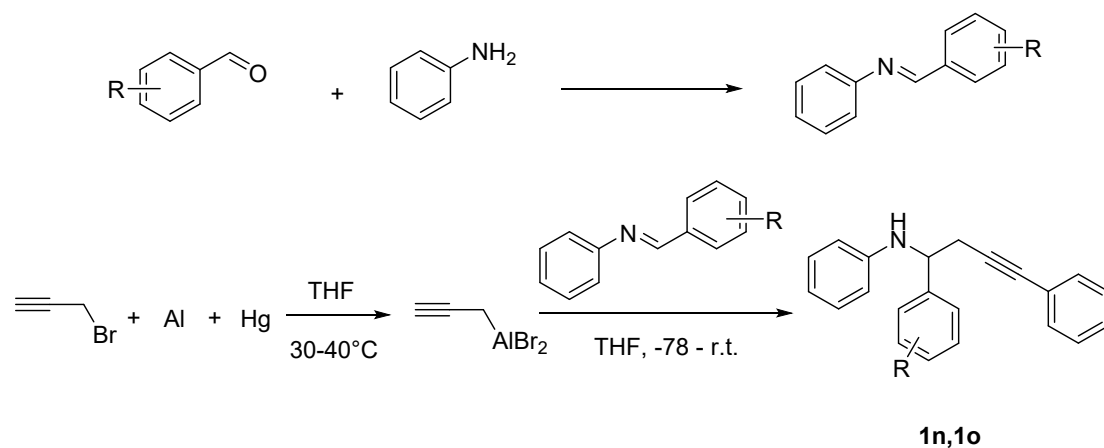


To a solution of **S**₁ (1 equiv.), triethylamine (1.2 eq), and 4-(dimethylamino)pyridine (0.2 eq) in DCM (6 mL/mmol) at 0 °C was added *p*-toluenesulfonyl chloride (1.05 eq) in three portions. The reaction mixture was brought to room temperature and stirred for 15 h. Aq. NaOH (1 N) was added, and the mixture was vigorously stirred for 15 min at rt. The usual workup (DCM , brine) gave *p*-toluenesulfonate derivatives **S**₂ in excellent yields as yellowish oil.



To a solution of aniline (1.5 eq), the above obtained **S₂** (1 eq) and KI (0.1 eq) in DMF (2 mL/mmol) was added K₂CO₃ (3 eq). The mixture was heated to 90 °C. After the complete consumption of **S₂** (TLC), the reaction mixture was cooled to room temperature, quenched with a saturated solution of NH₄Cl, extracted with AcOEt three times (3×20 mL), washed with small amounts of water (100 mL). The combined organic layers were dried with anhydrous Na₂SO₄ and the solvent was removed in vacuo to afford a residue. The residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (40:1) as eluent to provide the desired compounds **1a-1m, 1p-1x** in moderate yields as a yellow oil.

General procedure for the synthesis of *N*-(1-(4-chlorophenyl)-4-phenylbut-3-yn-1-yl)aniline **1u^[3-4]:**

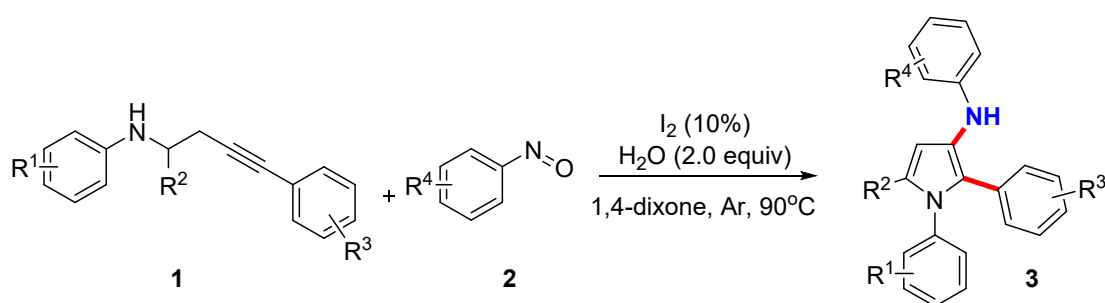


A dried round-bottom flask was charged with benzaldehyde (8.0 mmol), the aniline (8.0 mmol), molecular sieves 4Å (1mg /1.0 mmol aldehyde) and dichloromethane. The reaction mixture was stirred at room temperature and traced by TLC until the reaction finished. Then the mixture was filtered and the filtrate was concentrated

under reduced pressure, gave the pure imines without additional purification.

An aluminum amalgam was prepared from aluminum powder (0.5 g, 18.0 mmol) and a catalytic amount of mercuric chloride (10 mg) in 7.5 mL anhydrous THF by vigorously stirring at room temperature for 1 h under a N₂ atmosphere. A solution of propargyl bromide (18.0 mmol) in 12.5 mL of anhydrous THF was then slowly added to the suspension at such a rate as to maintain the temperature between 30-40°C. After the addition, the reaction mixture was continued to stir until a dark grey solution was obtained. The generated propargyl aluminum sesquibromide solution was added to a solution of imine (6.0 mmol) in 20.0 mL of anhydrous THF at -78°C under N₂ atmosphere. The reaction mixture was stirred at -78°C for about 1 h, then warmed to room temperature and continue to stir for additional 3-4 h (monitored by TLC). The mixture was quenched by adding saturated NH₄Cl (aq), and extracted with EtOAc (3 × 20 mL), and washed with brine, combined organic extracts, dried over MgSO₄, and concentrated in vacuo to give the residue. The residue was purified by flash chromatography over silica gel (gradient elution of EtOAc /petroleum ether, PE : EA = 50 : 1).

General procedure for synthesis of 3-animopyrroles from *N*-(3-butynyl)anilines and nitrosoarenes:



The *N*-(3-butynyl)anilines (**1**, 0.5 mmol), nitrosoarenes (**2**, 1.0 mmol), I₂ (0.05mmol), H₂O (1.0 mmol) were mixed in 1,4-dioxane (2 mL) and this mixture was carried out under argon at 90 °C in sealed tube and the reaction time was monitored by TLC. Then the reaction mixture was cooled to room temperature and the solvent was evaporated in vacuo and the crude product was purified by column chromatography,

eluting with petroleum ether/EtOAc (100:1) to afford the desired 3-animopyrroles (**3**).

X-Ray Crystal Data of Compound **3ta**:

Crystal **3ta** Growth with the Volatilization Method: An amount of 20 mg **3ta** was dissolved in DCE/PE (1:1) on the brown small reagent bottle (5 mL), which acted as good solvent, and a layer of ether was injected on the surface of tetrahydrofuran, and the cap is covered with a thin film, yellow crystals will be presented after seven days. Single crystals of $C_{22}H_{17}FN_2$ (**3ta**) was determinate. A suitable crystal was selected and determinate on a Super Nova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 290.9(4) K during data collection. Using Olex2^[5], the structure was solved with the ShelXS^[6] structure solution program using Direct Methods and refined with the ShelXL^[7] refinement package using Least Squares minimisation.

All hydrogen atoms were placed by geometrical considerations and were added to the structure factor calculations. The crystal structure (excluding structure factor) has been deposited to Cambridge Crystallographic Data Centre and allocated deposition number: **3ta**: CCDC 2290112.

X-Ray Data of Compound 3ta. The ellipsoids are shown at 30% probability.

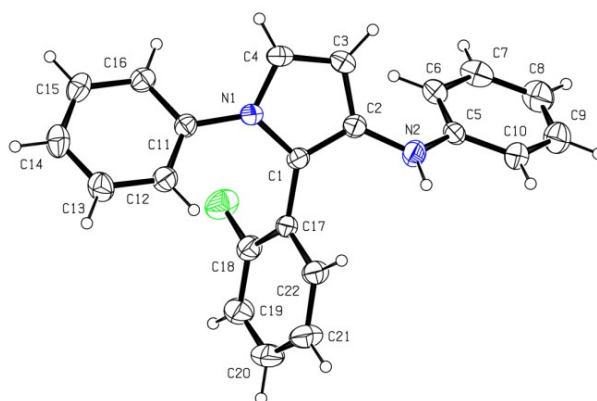


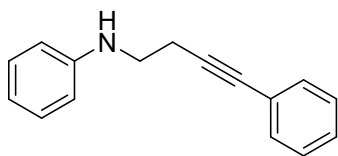
Figure S1 X-Ray Crystal structure of **3ta**

Table S2. Crystal data and structure refinement for **3ta**.

Identification code	3ta
Empirical formula	$C_{22}H_{17}FN_2$
Formula weight	328.38
Temperature/K	290.9(4)
Crystal system	monoclinic
Space group	$P2_1/c$

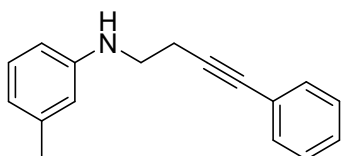
a/Å	6.2418(3)
b/Å	18.1094(7)
c/Å	15.2988(6)
α /°	90.00
β /°	96.701(4)
γ /°	90.00
Volume/Å ³	1717.49(12)
Z	4
ρ_{calc} /cm ³	1.270
μ /mm ⁻¹	0.083
F(000)	688.0
Crystal size/mm ³	0.22 × 0.17 × 0.15
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	6.94 to 52.04
Index ranges	-7 ≤ h ≤ 4, -22 ≤ k ≤ 11, -18 ≤ l ≤ 17
Reflections collected	6256
Independent reflections	3383 [R_{int} = 0.0260, R_{sigma} = 0.0540]
Data/restraints/parameters	3383/0/226
Goodness-of-fit on F ²	1.019
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0524, wR_2 = 0.1131
Final R indexes [all data]	R_1 = 0.0901, wR_2 = 0.1337
Largest diff. peak/hole / e Å ⁻³	0.13/-0.23

The Data of Products:



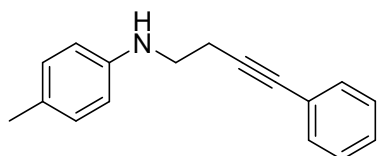
***N*-(3-phenylprop-2-yn-1-yl)aniline (1a)**

Yellow oil (484.0 mg, 73% yield). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.41-7.39 (m, 2 H), 7.30-7.25 (m, 3 H), 7.22-7.18 (m, 2 H), 6.77-6.71 (m, 1 H), 6.70-6.63 (m, 2 H), 3.99 (s, 1 H), 3.40 (t, $J = 6.7$ Hz, 2 H), 2.73 (t, $J = 6.7$ Hz, 2 H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): $\delta = 147.9, 131.8, 129.5, 128.4, 128.1, 123.6, 118.0, 113.3, 87.3, 82.4, 42.9, 20.4$.



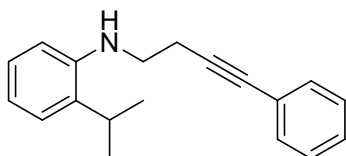
3-methyl-*N*-(4-phenylbut-3-yn-1-yl)aniline (1b)

Yellow oil (486.5mg, 69% yield). ^1H NMR (300 MHz, CDCl_3 , ppm): $\delta = 7.42$ -7.39 (m, 2 H), 7.32-7.28 (m, 3 H), 7.11-7.06 (m, 1 H), 6.58-6.54 (m, 1 H), 6.50-6.47 (m, 2 H), 3.93 (s, 1 H), 3.38 (t, $J = 6.7$ Hz, 2 H), 2.72 (t, $J = 6.7$ Hz, 2 H), 2.29 (d, $J = 2.4$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): $\delta = 147.8, 139.3, 131.8, 129.3, 128.4, 128.0, 123.5, 118.9, 114.1, 110.4, 87.4, 82.3, 42.9, 21.8, 20.3$.



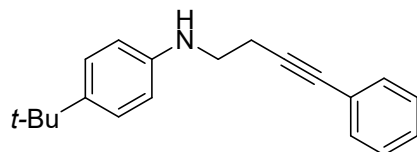
4-methyl-*N*-(4-phenylbut-3-yn-1-yl)aniline (1c)

Yellow oil (465.3mg, 66% yield). ^1H NMR (300 MHz, CDCl_3 , ppm): $\delta = 7.42$ -7.39 (m, 2 H), 7.330-7.26 (m, 3 H), 7.02-6.99 (m, 2 H), 6.60-6.57 (m, 2 H), 3.84 (s, 1H), 3.35 (t, $J = 6.7$ Hz, 2 H), 2.69 (t, $J = 6.7$ Hz, 2H), 2.24 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): $\delta = 145.5, 131.7, 129.9, 128.4, 128.0, 127.1, 123.5, 113.5, 87.4, 82.3, 43.2, 20.5, 20.2$.



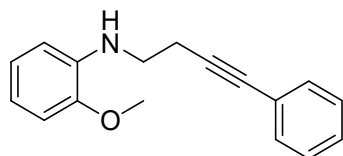
2-isopropyl-*N*-(4-phenylbut-3-yn-1-yl)aniline (1d)

Yellow oil (339.3 mg, 43% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.40-7.37 (m, 2 H), 7.27-7.25 (m, 3 H), 7.16-7.10 (m, 2 H), 6.78-6.73 (m, 1 H), 6.68-6.65 (m, 1 H), 4.11 (s, 1 H), 3.39 (t, *J* = 6.5 Hz, 2 H), 2.92 (p, *J* = 6.7 Hz, 1 H), 2.75 (m, 2 H), 1.25 (d, *J* = 6.8 Hz, 6 H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 144.5, 132.7, 131.7, 128.4, 128.0, 126.9, 125.2, 123.5, 117.8, 110.8, 87.4, 82.6, 42.8, 27.3, 22.4, 20.1.



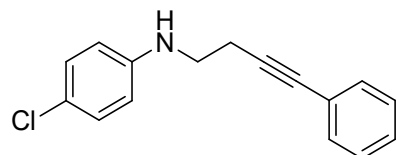
4-(*tert*-butyl)-*N*-(4-phenylbut-3-yn-1-yl)aniline (1e)

Yellow oil (473.7 mg, 57% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.40-7.38 (m, 2 H), 7.28-7.23 (m, 3 H), 7.21-7.20 (m, 2 H), 6.63-6.61 (m, 2 H), 3.85 (s, 1 H), 3.37 (t, *J* = 6.6 Hz, 2 H), 2.70 (t, *J* = 6.6 Hz, 2 H), 1.28 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 145.5, 140.7, 131.7, 128.4, 128.0, 126.2, 123.6, 113.1, 87.5, 82.3, 43.1, 34.0, 31.7, 20.4.



2-methoxy-*N*-(4-phenylbut-3-yn-1-yl)aniline (1f)

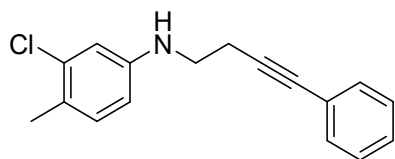
Yellow oil (286.1 mg, 38% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.42-7.39 (m, 2 H), 7.28-7.25 (m, 3 H), 6.90-6.85 (m, 1 H), 6.77-6.75 (m, 1 H), 6.70-6.32 (m, 2 H), 4.57 (s, 1 H), 3.80 (s, 3 H), 3.39 (t, *J* = 6.9 Hz, 2 H), 2.71 (t, *J* = 6.9 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.1, 137.7, 131.7, 128.3, 127.9, 123.6, 121.4, 116.9, 110.1, 109.7, 87.5, 82.2, 55.5, 42.6, 20.2.



4-chloro-*N*-(4-phenylbut-3-yn-1-yl)aniline (1g)

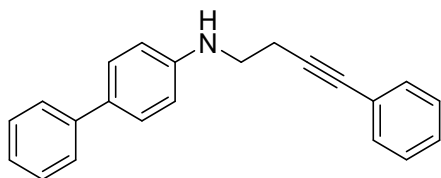
Yellow oil (527.9 mg, 69% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.42-7.38 (m, 2 H), 7.31-7.28 (m, 3 H), 7.15-7.12 (m, 2 H), 6.60-6.56 (m, 2 H), 4.00 (s, 1 H), 3.35 (t, *J* = 6.6 Hz, 2 H), 2.71 (t, *J* = 6.6 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃, ppm):

$\delta = 146.4, 131.8, 129.3, 128.4, 128.2, 128.1, 123.4, 122.5, 114.3, 87.0, 82.5, 42.9, 20.2.$



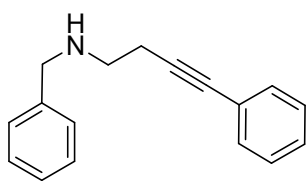
3-chloro-4-methyl-N-(4-phenylbut-3-yn-1-yl)aniline (1h)

Yellow oil (338.9 mg, 42% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.42\text{-}7.39$ (m, 2 H), 7.30-7.28 (m, 3 H), 7.02-7.00 (m, 1 H), 6.68-6.67 (m, 1 H), 6.49-6.46 (m, 1 H), 3.92 (s, 1 H), 3.34 (t, $J = 6.6$ Hz, 2 H), 2.70 (t, $J = 6.6$ Hz, 2 H), 2.25 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 147.0, 135.0, 131.8, 131.5, 128.4, 128.1, 124.8, 123.5, 113.5, 112.1, 87.1, 82.5, 43.0, 20.2, 19.0.$



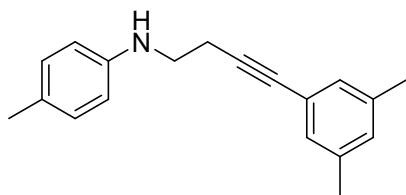
N-(4-phenylbut-3-yn-1-yl)-[1,1'-biphenyl]-4-amine (1i)

Yellow oil (597.0 mg, 67% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.63\text{-}7.61$ (m, 2 H), 7.54-7.46 (m, 6 H), 7.37-7.35 (m, 4 H), 6.79-6.77 (m, 2 H), 4.11 (s, 1 H), 3.47 (t, $J = 6.9$ Hz, 2 H), 2.79 (t, $J = 6.9$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 147.2, 141.3, 131.8, 130.7, 128.8, 128.4, 128.1, 128.0, 126.4, 126.2, 123.5, 113.5, 87.3, 82.4, 42.8, 20.3.$



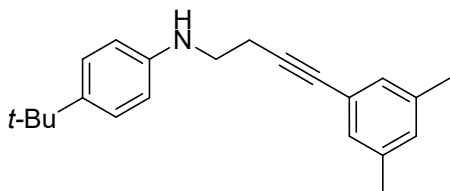
N-benzyl-4-phenylbut-3-yn-1-amine (1j)^[8]

Yellow oil (183.3 mg, 26% yield). ^1H NMR (300 MHz, CDCl_3 , ppm): $\delta = 7.40\text{-}7.38$ (m, 2 H), 7.36-7.31 (m, 4 H), 7.29-7.25 (m, 4 H), 3.86 (s, 2 H), 2.89-2.86 (m, 2 H), 2.66-2.62 (m, 2 H), 2.09 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): $\delta = 140.0, 131.7, 131.4, 128.6, 128.3, 127.9, 127.5, 123.6, 87.8, 81.8, 53.3, 47.5, 20.5.$



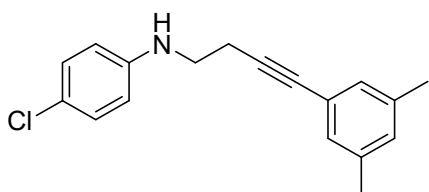
***N*-(4-(3,5-dimethylphenyl)but-3-yn-1-yl)-4-methylaniline (1k)**

Yellow oil (355.1mg, 45% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.03-6.99 (m, 4 H), 6.92 (s, 1 H), 6.60-6.58 (m, 2 H), 3.85 (s, 1 H), 3.35 (t, *J* = 6.6 Hz, 2 H), 2.69 (t, *J* = 6.6 Hz, 2 H), 2.27 (s, 6H), 2.24 (s, 3 H) ; ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 145.6, 138.0, 130.0, 129.9, 129.5, 127.2, 123.2, 113.6, 86.6, 82.6, 43.4, 21.2, 20.5, 20.3.



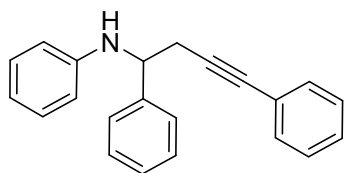
4-(*tert*-butyl)-*N*-(4-(3,5-dimethylphenyl)but-3-yn-1-yl)aniline (1l)

Yellow oil (420.9 mg, 46% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.25-7.23 (m, 2 H), 7.06 (s, 2 H), 6.94 (s, 1 H), 6.65-6.63 (m, 2 H), 3.90 (s, 1 H), 3.38 (t, *J* = 6.6 Hz, 2 H), 2.71 (t, *J* = 6.6 Hz, 2 H), 2.29 (s, 6 H), 1.30 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 145.5, 140.7, 137.9, 129.9, 129.5, 126.2, 123.2, 113.1, 86.7, 82.6, 43.2, 34.0, 31.7, 21.2, 20.4.



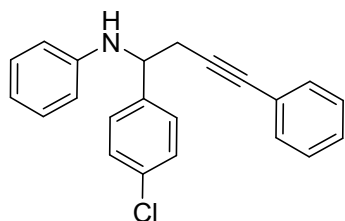
4-Chloro-*N*-(4-(3,5-dimethylphenyl)but-3-yn-1-yl)aniline (1m)^[8]

Yellow oil (297.2 mg, 35% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.13-7.11 (m, 2 H), 7.03 (s, 2 H), 6.92 (s, 1 H), 6.56-6.54 (m, 2 H), 4.52 (s, 1 H), 3.33-3.29 (m, 2 H), 2.69-2.65 (m, 2 H), 2.27 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ 146.3, 137.8, 129.8, 129.3, 129.0, 122.8, 122.1, 114.1, 86.1, 52.6, 42.7, 21.0, 20.0.



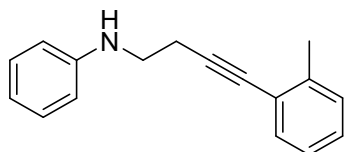
***N*-(1,4-diphenylbut-3-yn-1-yl)aniline (1n)^[8]**

Yellow solid (650.4 mg, 73% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.46-7.44 (m, 2 H), 7.37-7.32 (m, 3 H), 7.29-7.23 (m, 3 H), 7.12-7.07 (m, 2 H), 7.12-7.08 (m, 2 H), 6.69-6.65 (m, 1 H), 6.58-6.55 (m, 2 H), 4.62-4.59 (m, 1 H), 4.48 (s, 1 H), 3.00-2.84 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.2, 142.4, 131.6, 129.1, 128.6, 128.2, 128.0, 127.4, 126.4, 123.2, 117.7, 113.7, 85.8, 83.5, 56.9, 29.2.



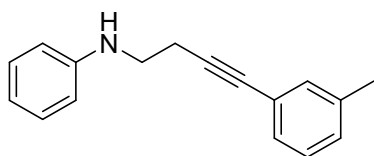
***N*-(1-(4-chlorophenyl)-4-phenylbut-3-yn-1-yl)aniline (1o)^[8]**

Yellow solid (715.0 mg, 72% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.41-7.25 (m, 8 H), 7.14-7.08 (m, 2 H), 6.72-6.67 (m, 2 H), 6.55-6.52 (d, *J* = 12.0 Hz, 2 H), 4.61-4.55 (m, 1 H), 4.48 (s, 1 H), 3.00-2.81 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 146.8, 140.9, 133.1, 131.6, 129.2, 128.8, 128.3, 128.1, 127.8, 123.0, 118.0, 113.7, 85.1, 56.2, 29.2.



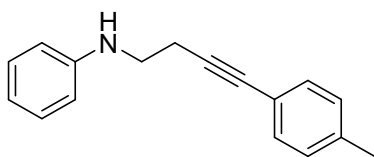
***N*-(4-(*o*-tolyl)but-3-yn-1-yl)aniline (1p)**

Yellow oil (373.7 mg, 53% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.38-7.36 (m, 1 H), 7.20-7.12 (m, 4 H), 7.11-7.08 (m, 1 H), 6.74-6.70 (m, 1 H), 6.65-6.63 (m, 2 H), 3.97 (s, 1 H), 3.37 (t, *J* = 6.6 Hz, 2 H), 2.74 (t, *J* = 6.6 Hz, 2 H), 2.41 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.8, 140.1, 132.0, 129.5, 129.4, 128.0, 125.6, 123.3, 117.9, 113.3, 91.2, 81.3, 43.0, 20.9, 20.4.



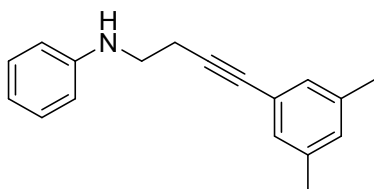
***N*-(4-(*m*-tolyl)but-3-yn-1-yl)aniline (1q)**

Yellow oil (345.5 mg, 49% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.24-7.17 (m, 5 H), 7.11 (s, 1 H), 6.73 (s, 1 H), 6.68-6.66 (m, 2 H), 3.98 (s, 1H), 3.38 (t, *J* = 6.6 Hz, 2 H), 2.71 (t, *J* = 6.6 Hz, 2 H), 2.31 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.9, 138.1, 132.5, 132.3, 129.5, 129.4, 128.9, 123.4, 117.9, 113.3, 86.9, 82.5, 42.9, 21.4, 21.3, 20.3.



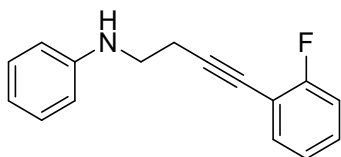
***N*-(4-(*p*-tolyl)but-3-yn-1-yl)aniline (1r)**

Yellow oil (444.2 mg, 63% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.30-7.28 (m, 2 H), 7.18-7.14 (m, 2H), 7.07-7.04 (m, 2 H), 6.73-6.69 (m, 1 H), 6.62-6.60 (m, 2 H), 3.91 (s, 1 H), 3.31 (t, *J* = 6.6 Hz, 2 H), 2.64 (t, *J* = 6.6 Hz, 2 H), 2.29 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 147.8, 138.0, 131.6, 129.4, 129.1, 120.4, 117.7, 113.1, 86.5, 82.3, 42.8, 21.5, 20.2.



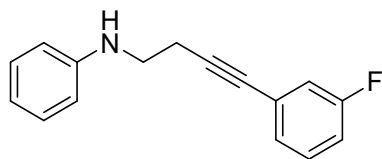
***N*-(4-(3,5-dimethylphenyl)but-3-yn-1-yl)aniline (1s)**

Yellow oil (343.6 mg, 46% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.27-7.23 (m, 2 H), 7.10 (s, 2 H), 6.98 (s, 1 H), 6.81-6.77 (m, 1 H), 6.72-6.70 (m, 2 H), 4.02 (s, 1 H), 3.42 (t, *J* = 6.6 Hz, 2 H), 2.75 (t, *J* = 6.6 Hz, 2 H), 2.33 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.9, 137.9, 129.9, 129.5, 123.1, 117.9, 113.3, 86.5, 82.6, 42.9, 21.2, 20.3.



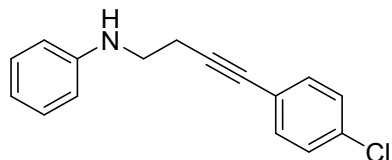
***N*-(4-(2-fluorophenyl)but-3-yn-1-yl)aniline (1t)**

Yellow oil (329.8 mg, 46% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.40-7.36 (m, 1 H), 7.31-7.13 (m, 3 H), 7.10-6.98 (m, 2 H), 6.75-6.71 (m, 1 H), 6.67-6.65 (m, 2 H), 4.01 (s, 1 H), 3.39 (t, *J* = 6.6 Hz, 2 H), 2.74 (t, *J* = 6.6 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 164.1-161.6 (d, *J* = 249.0 Hz, 1 C), 147.6, 133.4, 129.5 (d, *J* = 8.0 Hz, 1 C), 129.3, 123.8 (d, *J* = 4.0 Hz, 1 C), 117.7, 115.4-115.2 (d, *J* = 21.0 Hz, 1 C), 113.1, 111.9-111.8 (d, *J* = 16.0 Hz, 1 C), 92.7, 75.6, 42.5, 20.2.



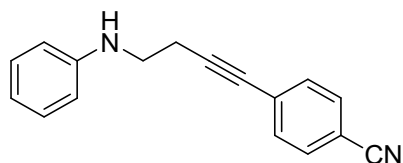
***N*-(4-(3-fluorophenyl)but-3-yn-1-yl)aniline (1u)**

Yellow oil (337.0 mg, 47% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.28-7.14 (m, 4 H), 7.10-7.07 (m, 1 H), 6.99-6.94 (m, 1 H), 6.75-6.72 (m, 1 H), 6.68-6.60 (m, 2 H), 3.94 (s, 1 H), 3.38 (t, *J* = 6.6 Hz, 2 H), 2.69 (t, *J* = 6.6 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 163.5-161.1 (d, *J* = 245.0 Hz, 1 C), 147.5, 129.8, 129.3, 127.5, 125.3-125.2 (d, *J* = 10.0 Hz, 1 C), 118.6-118.3 (d, *J* = 30.0 Hz, 1 C), 117.8, 115.3-115.1 (d, *J* = 22.0 Hz, 1 C), 113.1, 88.4, 81.1, 42.5, 20.1.



***N*-(4-(4-chlorophenyl)but-3-yn-1-yl)aniline (1v)**

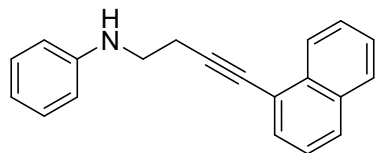
Yellow oil (503.9 mg, 76% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.31-7.29 (m, 2 H), 7.25-7.22 (m, 2 H), 7.20-7.16 (m, 2 H), 6.74-6.70 (m, 1 H), 6.64-6.62 (m, 2 H), 3.91 (s, 1 H), 3.35 (t, *J* = 6.7 Hz, 2 H), 2.67 (t, *J* = 6.7 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.7, 133.9, 133.0, 129.4, 128.7, 122.0, 117.9, 113.2, 88.5, 81.3, 42.7, 20.3.



4-(4-(phenylamino)but-1-yn-1-yl)benzotrile (1w)

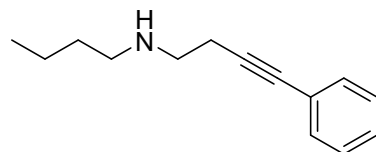
Yellow oil (612.5 mg, 83% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.54-7.52

(m, 2 H), 7.43-7.41 (m, 2 H), 7.21-7.17 (m, 2 H), 6.75-6.73 (m, 1 H), 6.66-6.64 (m, 2 H), 3.96 (s, 1 H), 3.40 (t, $J = 6.6$ Hz, 2 H), 2.72 (t, $J = 6.6$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 147.5, 132.2, 132.0, 129.4, 128.5, 118.6, 117.9, 113.1, 111.2, 92.5, 80.9, 42.5, 20.3$.



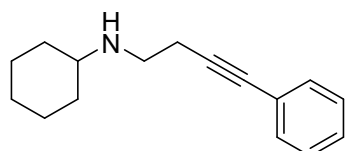
***N*-(4-(naphthalen-1-yl)but-3-yn-1-yl)aniline (1x)**

Yellow oil (430.9 mg, 53% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 8.32$ - 8.29 (m, 1 H), 7.78 - 7.72 (m, 2 H), 7.62 - 7.60 (m, 1 H), 7.53 - 7.48 (m, 2 H), 7.47 - 7.45 (m, 1 H), 7.37 - 7.30 (m, 3 H), 7.19 - 7.15 (m, 2 H), 6.74 - 6.70 (m, 1 H), 6.64 - 6.62 (m, 2 H), 3.97 (s, 1 H), 3.39 (t, $J = 6.7$ Hz, 2 H), 2.78 (t, $J = 6.7$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $147.7, 133.5, 133.2, 131.6, 130.3, 129.4, 129.0, 128.9, 128.5, 128.4, 128.3, 128.2, 126.7, 126.4, 126.2, 125.3, 121.2, 117.8, 113.2, 92.4, 42.9, 22.7, 20.5$.



***N*-butyl-4-phenylbut-3-yn-1-amine (1y) ^[8]**

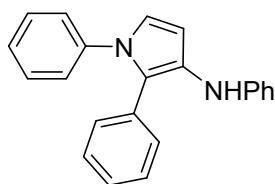
Yellow oil (416.7 mg, 69% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.41$ - 7.39 (m, 2 H), 7.28 - 7.27 (m, 3 H), 2.87 - 2.84 (m, 2 H), 2.66 - 2.60 (m, 4 H), 1.71 (s, 1 H), 1.52 - 1.48 (m, 2 H), 1.39 - 1.35 (m, 2 H), 0.94 - 0.91 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 131.8, 128.5, 127.6, 123.8, 88.1, 81.8, 49.2, 48.7, 47.9, 32.3, 20.6, 14.1$.



***N*-(4-phenylbut-3-yn-1-yl)cyclohexanamine (1z) ^[8]**

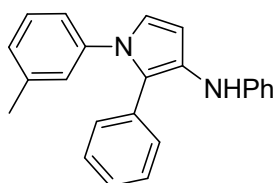
Yellow oil (422.2 mg, 62% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.40$ - 7.38 (m, 2 H), 7.30 - 7.27 (m, 3 H), 2.90 - 2.85 (m, 2 H), 2.62 - 2.58 (m, 2 H), 2.53 - 2.46 (m, 1 H), 1.92 - 1.88 (d, $J = 16.0$ Hz, 2 H), 1.76 - 1.61 (m, 4 H), 1.33 - 1.07 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 131.5, 128.2, 127.6, 123.6, 88.0, 81.7, 56.2, 45.2, 33.6$,

26.1, 25.0, 20.8.



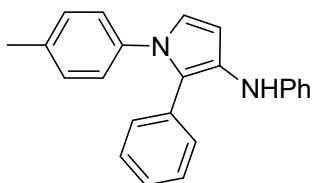
***N*,1,2-triphenyl-1*H*-pyrrol-3-amine (3aa)**

Yellow oil (113.2 mg, 74% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.29-7.25 (m, 2 H), 7.23-7.15 (m, 6 H), 7.12-7.08 (m, 4 H), 6.90-6.89 (m, 3 H), 6.78-6.74 (m, 1 H), 6.42-6.41 (d, *J* = 4.0 Hz, 1 H), 5.23 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.3, 140.4, 131.1, 129.6, 129.2, 128.9, 128.2, 126.5, 126.2, 125.8, 125.3, 125.2, 121.7, 118.1, 114.0, 106.5. HRMS calcd for C₂₂H₁₉N₂ [M+H]⁺ 311.1543; found: 311.1543.



***N*,2-diphenyl-1-(*m*-tolyl)-1*H*-pyrrol-3-amine (3ba)**

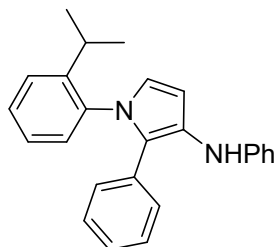
Yellow oil (124.7 mg, 77% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.24-7.15 (m, 6 H), 7.12-7.08 (m, 2 H), 7.05-6.99 (m, 2 H), 6.91-6.87 (m, 4 H), 6.80-6.75 (m, 1 H), 6.42-6.41 (d, *J* = 4.0 Hz, 1 H), 5.25 (s, 1 H), 2.30 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.3, 140.3, 138.9, 131.6, 131.2, 129.6, 129.2, 128.7, 128.2, 127.0, 126.4, 125.8, 125.5, 122.3, 121.7, 118.0, 114.0, 106.4, 21.3. HRMS calcd for C₂₃H₂₁N₂ [M+H]⁺ 325.1699; found: 325.1700.



***N*,2-diphenyl-1-(*p*-tolyl)-1*H*-pyrrol-3-amine (3ca)**

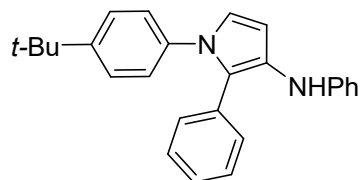
Yellow oil (134.5 mg, 83% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.24-7.17 (m, 5 H), 7.11-7.06 (m, 4 H), 7.01-6.98 (d, *J* = 4.0 Hz, 2 H), 6.89-6.86 (m, 3 H), 6.78-6.6.73 (m, 1 H), 6.40-6.39 (d, *J* = 4.0 Hz, 1 H), 5.23 (s, 1 H), 2.33 (s, 3 H); ¹³C NMR

(100 MHz, CDCl₃, ppm): δ = 147.4, 138.0, 136.0, 131.2, 129.6, 129.5, 129.2, 128.2, 126.4, 125.5, 125.3, 125.1, 121.7, 118.0, 114.0, 106.3, 21.0. HRMS calcd for C₂₃H₂₁N₂ [M+H]⁺ 325.1699; found: 325.1698.



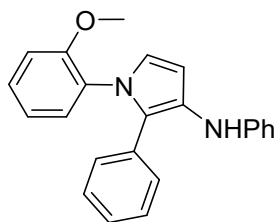
1-(2-isopropylphenyl)-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3da)

Yellow oil (118.0 mg, 67% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.34-7.30 (m, 1 H), 7.27-7.23 (m, 5 H), 7.21-7.11 (m, 2 H), 7.08-7.05 (m, 3 H), 6.90-6.88 (d, *J* = 8.0 Hz, 2 H), 6.79-6.75 (m, 1 H), 6.72-6.71 (d, *J* = 4.0 Hz, 1 H), 6.40-6.39 (d, *J* = 4.0 Hz, 1 H), 5.25 (s, 1 H), 2.74-2.67 (m, 1 H), 1.09-1.08 (d, *J* = 4.0 Hz, 3 H), 0.74-0.72 (d, *J* = 4.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.7, 146.3, 138.4, 131.2, 129.3, 128.7, 128.6, 128.2, 127.3, 126.6, 126.5, 126.4, 126.1, 124.2, 122.6, 118.0, 114.0, 106.1, 27.6, 25.3, 22.4. HRMS calcd for C₂₅H₂₅N₂ [M+H]⁺ 353.2012; found: 353.2010.



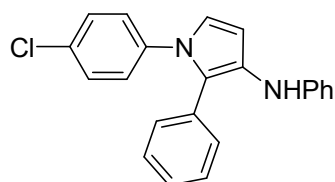
1-(4-(tert-butyl)phenyl)-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3ea)

Yellow oil (155.5 mg, 85% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.30-7.25 (m, 2 H), 7.22-7.15 (m, 5 H), 7.11-7.09 (m, 2 H), 7.05-7.02 (d, *J* = 12.0 Hz, 2 H), 6.89-6.87 (m, 3 H), 6.78-6.74 (m, 1 H), 6.40 (d, *J* = 3.2 Hz, 1 H), 5.23 (s, 1 H), 1.30 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 149.3, 147.5, 137.9, 131.4, 129.7, 129.3, 128.3, 126.5, 125.9, 125.6, 125.3, 124.8, 121.9, 118.1, 114.1, 106.4, 34.6, 31.4. HRMS calcd for C₂₆H₂₇N₂ [M+H]⁺ 367.2169; found: 367.2171.



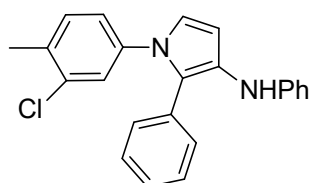
1-(2-methoxyphenyl)-N,2-diphenyl-1H-pyrrol-3-amine (3fa)

Yellow oil (115.9 mg, 68% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.24-7.13 (m, 6 H), 7.08-7.06 (m, 3 H), 6.92-6.85 (m, 4 H), 6.81-6.80 (d, J = 4.0 Hz, 1 H), 6.77-6.72 (m, 1 H), 6.41-6.40 (d, J = 4.0 Hz, 1 H), 5.24 (s, 1 H), 3.52 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 154.3, 147.8, 131.8, 129.6, 129.3, 128.9, 128.7, 128.6, 128.0, 127.0, 126.3, 124.3, 122.2, 120.7, 117.9, 114.0, 112.2, 106.3, 55.5. HRMS calcd for $\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 341.1649; found: 341.1649.



1-(4-chlorophenyl)-N,2-diphenyl-1H-pyrrol-3-amine (3ga)

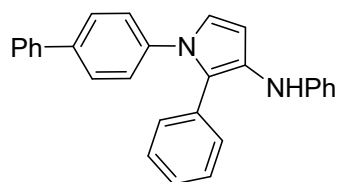
Yellow oil (141.0 mg, 82% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.25-7.17 (m, 7 H), 7.09-7.02 (m, 4 H), 6.88-6.85 (m, 3 H), 6.78-6.75 (m, 1 H), 6.43-6.42 (d, J = 4.0 Hz, 1 H), 5.23 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 147.1, 139.0, 131.9, 130.8, 129.7, 129.2, 129.1, 128.5, 126.8, 126.3, 126.2, 125.0, 121.6, 118.3, 114.1, 106.9. HRMS calcd for $\text{C}_{22}\text{H}_{18}\text{ClN}_2$ $[\text{M}+\text{H}]^+$ 345.1153; found: 345.1152.



1-(3-chloro-4-methylphenyl)-N,2-diphenyl-1H-pyrrol-3-amine (3ha)

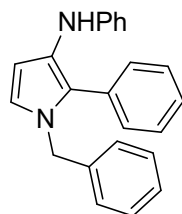
Yellow oil (111.0 mg, 62% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.25-7.18 (m, 6 H), 7.11-7.07 (m, 3 H), 6.89-6.79 (m, 3 H), 6.77-6.74 (m, 2 H), 6.42-6.41 (m, 1 H), 5.23 (s, 1 H), 2.34 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 147.9, 139.9, 135.1, 134.8, 131.7, 131.6, 130.4, 130.0, 129.2, 127.5, 126.7, 126.2, 125.8, 124.4, 122.4, 119.0, 114.8, 107.5, 20.4. HRMS calcd for $\text{C}_{23}\text{H}_{20}\text{ClN}_2$ $[\text{M}+\text{H}]^+$ 359.1310;

found: 359.1310.



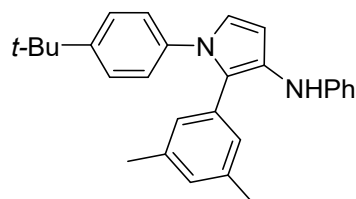
1-([1,1'-biphenyl]-4-yl)-N,2-diphenyl-1H-pyrrol-3-amine (3ia)

Yellow oil (140.8 mg, 73% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.58-7.50 (m, 4 H), 7.46-7.41 (m, 2 H), 7.36-7.34 (m, 1 H), 7.25-7.13 (m, 9 H), 6.95-6.89 (m, 3 H), 6.80-6.75 (m, 1 H), 6.45-6.44 (d, *J* = 4.0 Hz, 1 H), 5.27 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 148.6, 141.4, 141.0, 140.3, 131.0, 130.6, 130.2, 129.7, 128.9, 128.8, 128.3, 128.0, 126.7, 123.1, 119.5, 115.4, 108.0. HRMS calcd for C₂₈H₂₃N₂ [M+H]⁺ 387.1856; found: 387.1856.



1-benzyl-N,2-diphenyl-1H-pyrrol-3-amine (3ja)

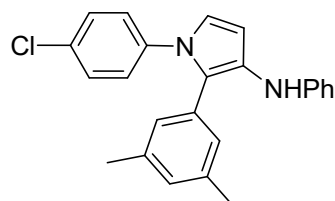
Yellow oil (60.1 mg, 37% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.33-7.29 (m, 3 H), 7.27-7.26 (m, 2 H), 7.25-7.22 (m, 3 H), 7.18-7.14 (m, 3 H), 7.01-6.99 (d, *J* = 8.0 Hz, 2 H), 6.82-6.80 (d, *J* = 8.0 Hz, 2 H), 6.74-6.69 (m, 2 H), 6.30 (d, *J* = 3.2 Hz, 1 H), 5.13 (s, 1 H), 5.05 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.8, 138.6, 131.0, 129.9, 129.1, 128.6, 128.5, 127.3, 127.2, 127.1, 126.5, 123.8, 120.5, 117.7, 113.7, 105.9, 51.0. HRMS calcd for C₂₃H₂₁N₂ [M+H]⁺ 325.1699; found: 325.1698.



1-(4-(tert-butyl)phenyl)-2-(3,5-dimethylphenyl)-N-phenyl-1H-pyrrol-3-amine (3la)

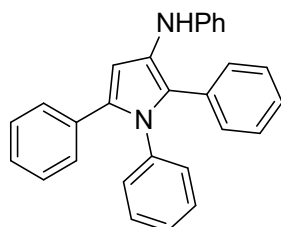
Yellow oil (147.8 mg, 75% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.30-7.25

(m, 2 H), 7.22-7.18 (m, 2 H), 7.04-7.02 (m, 2 H), 6.91-6.89 (m, 2 H), 6.86 (d, $J = 3.2$ Hz, 1 H), 6.79-6.74 (m, 2 H), 6.68 (s, 2 H), 6.41-6.40 (d, $J = 4.0$ Hz, 1 H), 5.27 (s, 1 H), 2.14 (s, 6 H), 1.30 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 149.2, 147.4, 138.0, 137.5, 133.9, 131.1, 130.6, 129.1, 128.1, 127.4, 125.6, 124.9, 121.3, 118.0, 114.2, 105.8, 34.5, 31.3, 21.2$. HRMS calcd for $\text{C}_{28}\text{H}_{31}\text{N}_2$ $[\text{M}+\text{H}]^+$ 395.2482; found: 395.2482.



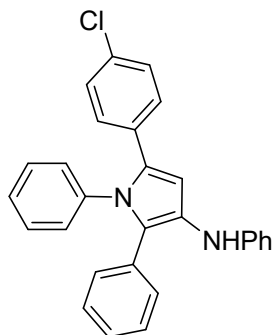
1-(4-chlorophenyl)-2-(3,5-dimethylphenyl)-*N*-phenyl-1*H*-pyrrol-3-amine (3ma)

Yellow oil (145.0 mg, 78% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.25-7.18$ (m, 4 H), 7.06-7.02 (m, 2 H), 6.90-6.88 (m, 2 H), 6.83 (d, $J = 3.2$ Hz, 2 H), 6.79 -6.75 (m, 1 H), 6.69 (s, 2 H), 6.43-6.42 (d, $J = 4.0$ Hz, 1 H), 5.27 (s, 1 H), 2.17 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 147.0, 139.1, 137.9, 131.6, 130.7, 129.2, 129.0, 128.6, 127.5, 126.3, 126.2, 124.6, 121.2, 118.3, 114.3, 106.3, 21.3$. HRMS calcd for $\text{C}_{24}\text{H}_{22}\text{ClN}_2$ $[\text{M}+\text{H}]^+$ 373.1466; found: 373.1468.



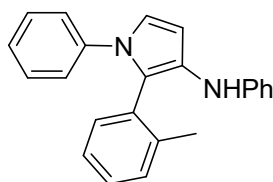
N,1,2,5-tetraphenyl-1*H*-pyrrol-3-amine (3na)

Yellow solid (131.2 mg, 68% yield), melting point: 176-178 °C. ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.22-7.16$ (m, 7 H), 7.15-7.12 (m, 4 H), 7.08-7.06 (m, 2 H), 7.02-6.98 (m, 4 H), 6.94-6.92 (d, $J = 8.0$ Hz, 2 H), 6.78-6.75 (m, 1 H), 6.58 (s, 1 H), 5.26 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 147.0, 138.6, 133.1, 132.8, 131.1, 130.1, 129.2, 128.8, 128.6, 128.5, 128.0, 127.9, 127.0, 126.5, 126.4, 126.3, 125.1, 118.1, 114.1, 106.4$. HRMS calcd for $\text{C}_{28}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]^+$ 387.1856; found: 387.1856.



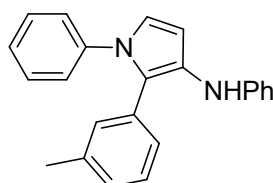
5-(4-chlorophenyl)-N,1,2-triphenyl-1H-pyrrol-3-amine (30a)

Yellow solid (132.3 mg, 63% yield), melting point: 185-187 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.24-7.13 (m, 10 H), 7.04-6.98 (m, 6 H), 6.93-6.91 (d, *J* = 8.0 Hz, 2 H), 6.79-6.75 (m, 1 H), 6.56 (s, 1 H), 5.24 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.0, 138.5, 132.2, 131.9, 131.4, 131.0, 130.1, 129.7, 129.2, 128.8, 128.2, 128.1, 127.4, 127.2, 126.7, 125.3, 118.3, 114.2, 106.5. HRMS calcd for C₂₈H₂₂ClN₂ [M+H]⁺ 421.1466; found: 421.1467.



N,1-diphenyl-2-(*o*-tolyl)-1H-pyrrol-3-amine (3pa)

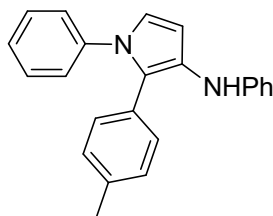
Yellow oil (119.5 mg, 73% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.24-7.15 (m, 6 H), 7.13-7.09 (m, 2 H), 7.03-6.98 (m, 2 H), 6.89-6.85 (m, 4 H), 6.78-6.74 (m, 1 H), 6.41-6.40 (d, *J* = 4.0 Hz, 1 H), 5.23 (s, 1 H), 2.28 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.4, 140.4, 138.9, 131.2, 129.6, 129.2, 128.7, 128.2, 127.0, 126.5, 125.7, 125.6, 125.2, 122.5, 121.7, 118.0, 114.0, 106.4, 21.3. HRMS calcd for C₂₃H₂₁N₂ [M+H]⁺ 325.1699; found: 325.1699.



N,1-diphenyl-2-(*m*-tolyl)-1H-pyrrol-3-amine (3qa)

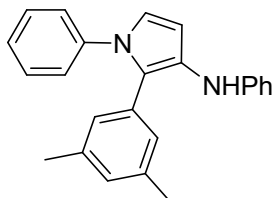
Yellow oil (119.8 mg, 74% yield). ¹H NMR (400 MHz, CDCl₃, ppm): 7.31-7.26 (m, 3 H), 7.23-7.18 (m, 3 H), 7.13-7.07 (m, 3 H), 6.99-7.96 (m, 1 H), 6.92-6.85 (m, 4 H),

6.79-6.74 (m, 1 H), 6.43-6.42 (d, $J = 4.0$ Hz, 1 H), 5.26 (s, 1 H), 2.19 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 147.3, 140.5, 137.8, 131.1, 130.3, 129.2, 128.9, 128.1, 127.3, 126.8, 126.1, 125.2, 125.0, 121.5, 118.1, 114.1, 106.3, 100.0, 21.4$. HRMS calcd for $\text{C}_{23}\text{H}_{21}\text{N}_2$ $[\text{M}+\text{H}]^+$ 325.1699; found: 325.1698.



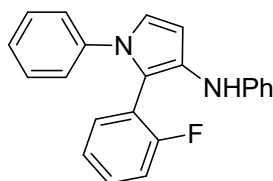
***N*,1-diphenyl-2-(*p*-tolyl)-1*H*-pyrrol-3-amine (3ra)**

Yellow oil (134.5 mg, 83% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.31-7.27$ (m, 2 H), 7.25-7.19 (m, 3 H), 7.14-7.12 (d, $J = 8.0$ Hz, 2 H), 7.04-6.97 (m, 4 H), 6.90-6.88 (m, 3 H), 6.79-6.75 (m, 1 H), 6.42 (d, $J = 3.2$ Hz, 1 H), 5.22 (s, 1 H), 2.29 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 147.4, 140.5, 136.3, 129.5, 129.2, 129.0, 128.9, 128.1, 126.1, 126.0, 125.4, 125.3, 121.4, 118.0, 114.0, 106.5, 21.2$. HRMS calcd for $\text{C}_{23}\text{H}_{21}\text{N}_2$ $[\text{M}+\text{H}]^+$ 325.1699; found: 325.1700.



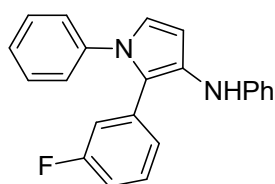
2-(3,5-dimethylphenyl)-*N*,1-diphenyl-1*H*-pyrrol-3-amine (3sa)

Yellow oil (125.0 mg, 74% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): $\delta = 7.30-7.25$ (m, 2 H), 7.22-7.18 (m, 3 H), 7.12-7.10 (m, 2 H), 6.91-6.87 (m, 3 H), 6.80 (s, 1 H), 6.78-6.74 (m, 1 H), 6.69 (s, 2 H), 6.42 (d, $J = 2.8$ Hz, 1 H), 5.28 (s, 1 H), 2.15 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 147.2, 140.5, 137.6, 130.9, 129.2, 128.8, 128.3, 127.4, 126.0, 125.8, 125.1, 124.7, 121.3, 118.1, 114.2, 106.0, 21.3$. HRMS calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]^+$ 339.1856; found: 339.1854.



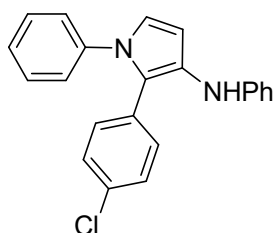
2-(2-fluorophenyl)-*N*,1-diphenyl-1*H*-pyrrol-3-amine (3ta)

Yellow solid (102.4 mg, 78% yield), melting point: 140-142 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.28-7.16 (m, 8 H), 7.14-7.02 (m, 1 H), 6.99-6. 6.87 (m, 3 H), 6.85-6.84 (d, *J* = 4.0 Hz, 2 H), 6.75-6.70 (m, 1 H), 6.45-6.44 (d, *J* = 4.0 Hz, 1 H), 5.33 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 161.5-158.2 (*J* = 326.0 Hz, 1 C), 146.8, 140.5, 132.3 (*J* = 4.0 Hz, 1 C), 129.2, 129.1-129.0 (*J* = 7.0 Hz, 1 C), 127.5, 126.2, 124.1, 124.0, 122.2, 119.4, 119.0, 118.1, 116.0, 115.7, 114.1, 106.2. HRMS calcd for C₂₂H₁₈FN₂ [M+H]⁺ 329.1449; found: 329.1449.



2-(3-fluorophenyl)-*N*,1-diphenyl-1*H*-pyrrol-3-amine (3ua)

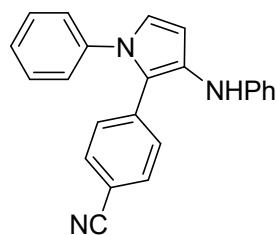
Yellow solid (121.4 mg, 74% yield), melting point: 142-144 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.33-7.20 (m, 6 H), 7.18-7.10 (m, 3 H), 6.91-6.88 (m, 3 H), 6.86 (m, 1 H), 6.81-6.80 (m, 1 H), 6.78-6.75 (m, 1 H), 6.41-6.40 (d, *J* = 4.0 Hz, 1 H), 5.22 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 164.2-160.9 (*J* = 325.0 Hz, 1 C), 147.0, 140.1, 133.3-133.2 (*J* = 12.0 Hz, 1 C), 129.7, 129.6, 129.2-129.1 (*J* = 15.0 Hz, 1 C), 126.5-126.4 (*J* = 10.0 Hz, 1 C), 125.2 (*J* = 8.0 Hz, 1 C), 124.0, 122.4, 118.3, 116.3, 116.0, 114.1, 113.5, 113.2, 106.6. HRMS calcd for C₂₂H₁₈FN₂ [M+H]⁺ 329.1449; found: 329.1450.



2-(4-chlorophenyl)-*N*,1-diphenyl-1*H*-pyrrol-3-amine (3va)

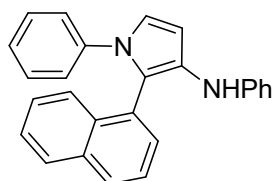
Yellow oil (126.8 mg, 82% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.32-7.29 (m, 2 H), 7.26-7.24 (m, 1 H), 7.22-7.15 (m, 4 H), 7.11-7.10 (d, *J* = 4.0 Hz, 2 H), 7.02-7.00 (d, *J* = 8.0 Hz, 2 H), 6.90 (d, *J* = 2.8 Hz, 1 H), 6.86-6.84 (m, 2 H), 6.79-6.75 (m, 1 H), 6.40 (d, *J* = 2.8 Hz, 1 H), 5.14 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 147.3, 140.3, 132.5, 130.8, 129.7, 129.3, 129.2, 128.6, 126.6, 126.2, 125.4, 124.5,

122.3, 118.4, 114.1, 106.9. HRMS calcd for C₂₂H₁₈ClN₂ [M+H]⁺ 345.1153; found: 345.1153.



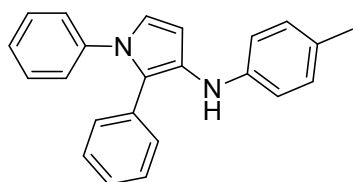
4-(1-phenyl-3-(phenylamino)-1H-pyrrol-2-yl)benzonitrile (3wa)

Yellow solid (142.3 mg, 85% yield), melting point: 142-144 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.45-7.43 (d, *J* = 8.0 Hz, 2 H), 7.35-7.28 (m, 3 H), 7.24-7.16 (m, 4 H), 7.12-7.10 (d, *J* = 8.0 Hz, 2 H), 6.94-6.93 (d, *J* = 4.0 Hz, 1 H), 6.85-6.83 (d, *J* = 8.0 Hz, 2 H), 6.81-6.77 (m, 1 H), 6.41-6.40 (d, *J* = 4.0 Hz, 1 H), 5.19 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 146.7, 139.9, 135.8, 131.9, 129.4, 129.3, 127.7, 126.9, 125.3, 123.9, 123.7, 118.9, 118.7, 114.2, 109.3, 107.1. HRMS calcd for C₂₃H₁₈N₃ [M+H]⁺ 336.1495; found: 336.1496.



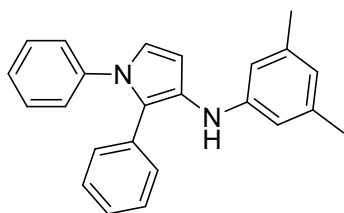
2-(naphthalen-1-yl)-N,1-diphenyl-1H-pyrrol-3-amine (3xa)

Yellow oil (139.9 mg, 80% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.82-7.74 (m, 3 H), 7.41-7.30 (m, 3 H), 7.23-7.20 (m, 1 H), 7.15-6.99 (m, 8 H), 6.85-6.81 (m, 2 H), 6.73-6.71 (m, 1 H), 6.57-6.55 (m, 1 H), 5.06 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 146.4, 140.4, 133.7, 132.6, 129.8, 129.0, 128.9, 128.7, 128.3, 128.1, 127.4, 126.4, 126.0, 125.9, 125.8, 125.3, 124.2, 121.8, 121.2, 118.1, 114.2, 105.3. HRMS calcd for C₂₆H₂₁N₂ [M+H]⁺ 361.1699; found: 361.1700.



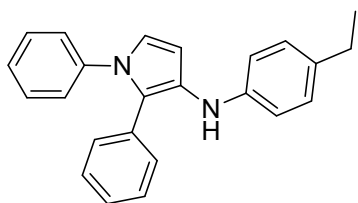
1,2-diphenyl-N-(p-tolyl)-1H-pyrrol-3-amine (3ab)

Yellow oil (141.0 mg, 87% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.30-7.25 (m, 2 H), 7.23-7.19 (m, 3 H), 7.17-7.15 (m, 1 H), 7.12-7.08 (m, 4 H), 7.03-7.01 (d, J = 8.0 Hz, 2 H), 6.89-6.88 (d, J = 4.0 Hz, 1 H), 6.82-6.80 (d, J = 8.0 Hz, 2 H), 6.40 (d, J = 2.8 Hz, 1 H), 5.16 (s, 1 H), 2.27 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 145.0, 140.6, 131.3, 129.8, 129.7, 129.0, 128.3, 127.5, 126.6, 126.5, 126.3, 125.3, 124.8, 121.8, 114.4, 106.3, 20.5. HRMS calcd for $\text{C}_{23}\text{H}_{21}\text{N}_2$ $[\text{M}+\text{H}]^+$ 325.1699; found: 325.1698.



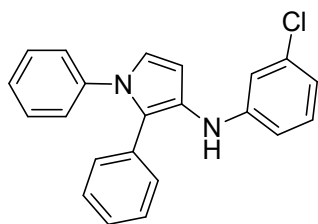
***N*-(3,5-dimethylphenyl)-1,2-diphenyl-1*H*-pyrrol-3-amine (3ac)**

Yellow oil (113.2 mg, 67% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.32-7.18 (m, 6 H), 7.16-7.08 (m, 4 H), 6.91-6.90 (d, J = 4.0 Hz, 1 H), 6.55 (s, 2 H), 6.44-6.43 (d, J = 4.0 Hz, 2 H), 5.18 (s, 1 H), 2.26 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 147.2, 140.5, 138.9, 131.2, 129.7, 128.9, 128.3, 126.5, 126.2, 126.0, 125.3, 124.8, 121.7, 120.1, 111.9, 106.5, 21.5. HRMS calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]^+$ 339.1856; found: 339.1858.



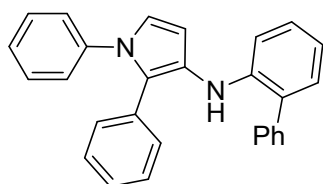
***N*-(4-ethylphenyl)-1,2-diphenyl-1*H*-pyrrol-3-amine (3ad)**

Yellow oil (144.1 mg, 85% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 7.29-7.24 (m, 2 H), 7.22-7.19 (m, 3 H), 7.16-7.15 (m, 1 H), 7.12-7.10 (m, 4 H), 7.08-7.03 (m, 2 H), 6.89-6.88 (d, J = 2.8 Hz, 1 H), 6.85-6.83 (d, J = 8.0 Hz, 2 H), 6.41 (d, J = 3.2 Hz, 1 H), 5.19 (s, 1 H), 2.60-2.54 (m, 2 H), 1.23-1.19 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 145.0, 140.5, 134.1, 131.3, 129.6, 128.9, 128.5, 128.2, 126.5, 126.4, 126.1, 125.2, 124.6, 121.7, 114.3, 106.2, 28.0, 15.9. HRMS calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]^+$ 339.1856; found: 339.1857.



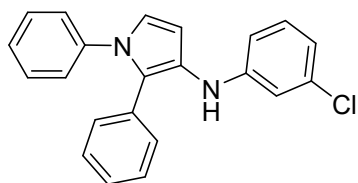
***N*-(3-chlorophenyl)-1,2-diphenyl-1*H*-pyrrol-3-amine (3ae)**

Yellow oil (142.8 mg, 83% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.30-7.26 (m, 2 H), 7.23-7.15 (m, 4 H), 7.12-7.05 (m, 5 H), 6.90-6.89 (d, *J* = 4.0 Hz, 1 H), 6.86-6.85 (m, 1 H), 6.71-6.68 (m, 2 H), 6.38-6.37 (d, *J* = 4.0 Hz, 1 H), 5.24 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 148.7, 140.3, 135.0, 130.9, 130.1, 129.6, 129.0, 128.3, 126.7, 126.4, 126.0, 125.3, 124.6, 121.9, 117.9, 113.5, 112.1, 106.8. HRMS calcd for C₂₂H₁₈ClN₂ [M+H]⁺ 345.1153; found: 345.1153.



***N*-([1,1'-biphenyl]-4-yl)-1,2-diphenyl-1*H*-pyrrol-3-amine (3af)**

Yellow oil (150.5 mg, 78% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.40-7.34 (m, 4 H), 7.28-7.24 (m, 3 H), 7.22-7.18 (m, 2 H), 7.15-7.08 (m, 7 H), 7.00-6.98 (m, 2 H), 6.89-6.88 (d, *J* = 4.0 Hz, 1 H), 6.82-6.78 (m, 1 H), 6.41-6.40 (d, *J* = 4.0 Hz, 1 H), 5.54 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 144.3, 140.5, 139.3, 131.1, 130.2, 129.5, 129.4, 128.9, 128.8, 128.5, 128.1, 127.9, 127.2, 126.4, 126.2, 125.9, 125.6, 125.2, 121.7, 117.7, 112.7, 107.0. HRMS calcd for C₂₈H₂₃N₂ [M+H]⁺ 387.1856; found: 387.1857.



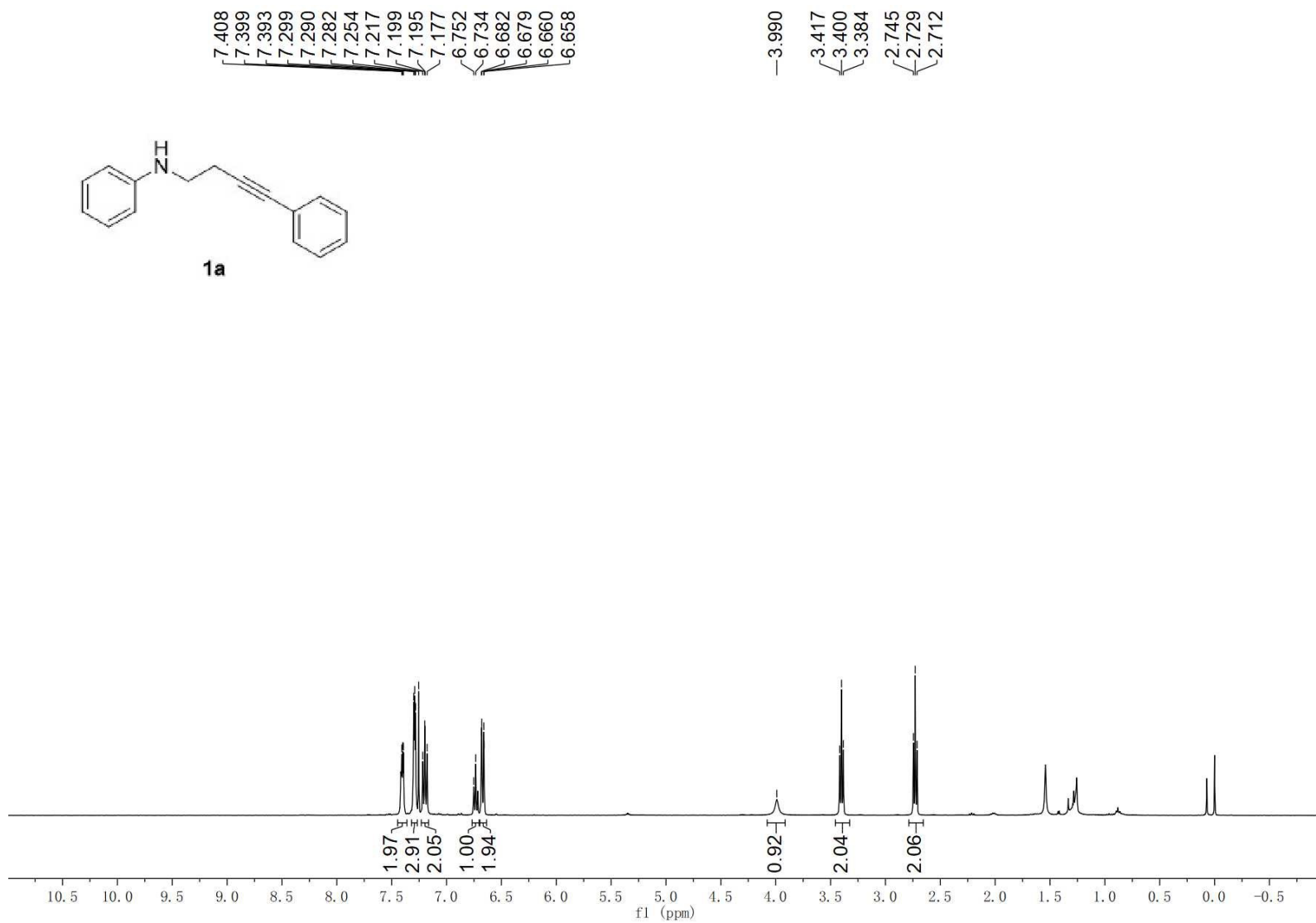
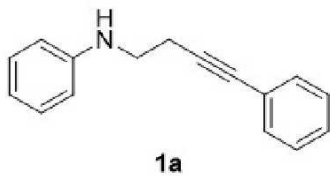
***N*-(4-chlorophenyl)-2-(3,5-dimethylphenyl)-1-(*p*-tolyl)-1*H*-pyrrol-3-amine (3ke)**

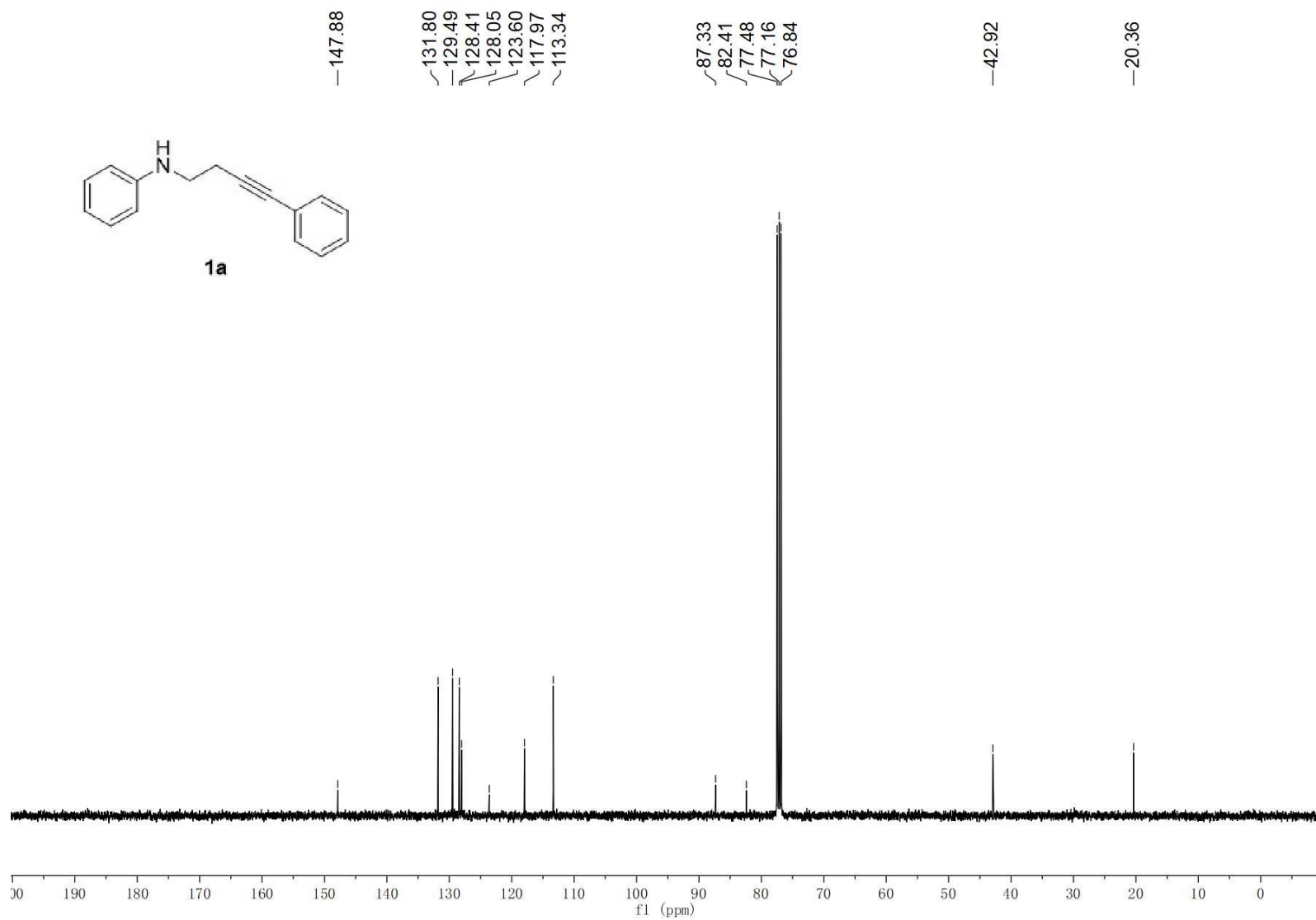
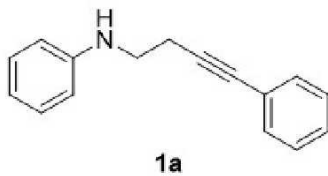
Yellow oil (129.3 mg, 67% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.24-7.23 (m, 1 H), 7.10-7.07 (m, 4 H), 7.02-7.00 (d, *J* = 8.0 Hz, 2 H), 6.86-6.85 (d, *J* = 4.0 Hz,

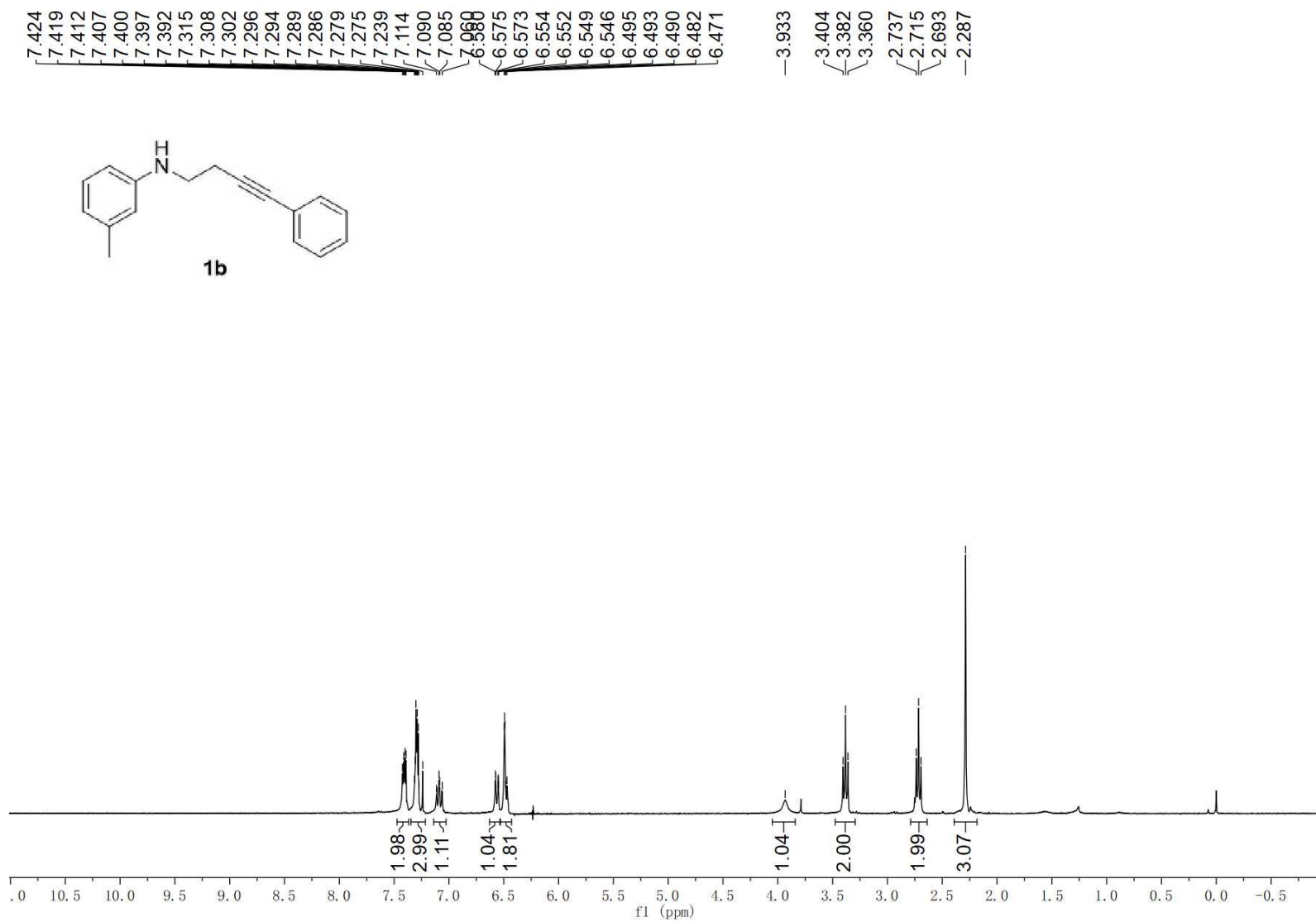
1 H), 6.78 (s, 1 H), 6.68 (s, 2 H), 6.66-6.62 (m, 1 H), 6.38 (d, $J = 3.2$ Hz, 1 H), 5.90 (s, 1 H), 2.33 (s, 3 H), 2.14 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3 , ppm): $\delta = 143.5, 138.1, 137.5, 136.0, 130.7, 129.4, 129.1, 128.3, 127.5, 127.2, 126.1, 125.1, 124.2, 121.5, 119.1, 117.9, 113.4, 106.6, 29.7, 21.2, 20.9$. HRMS calcd for $\text{C}_{25}\text{H}_{24}\text{ClN}_2$ $[\text{M}+\text{H}]^+$ 387.1623; found: 387.1623.

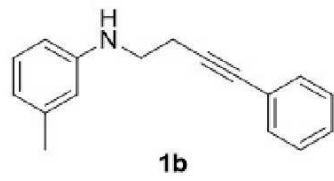
Reference:

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- (2) C. Gronnier, Y. Odabachian, F. Gagosz, *Chem. Commun.* **2011**, 47, 218.
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- (6) Sheldrick, G.M. A Short History of SHELX. *Acta Cryst. A.* **2008**, 64, 112-122.
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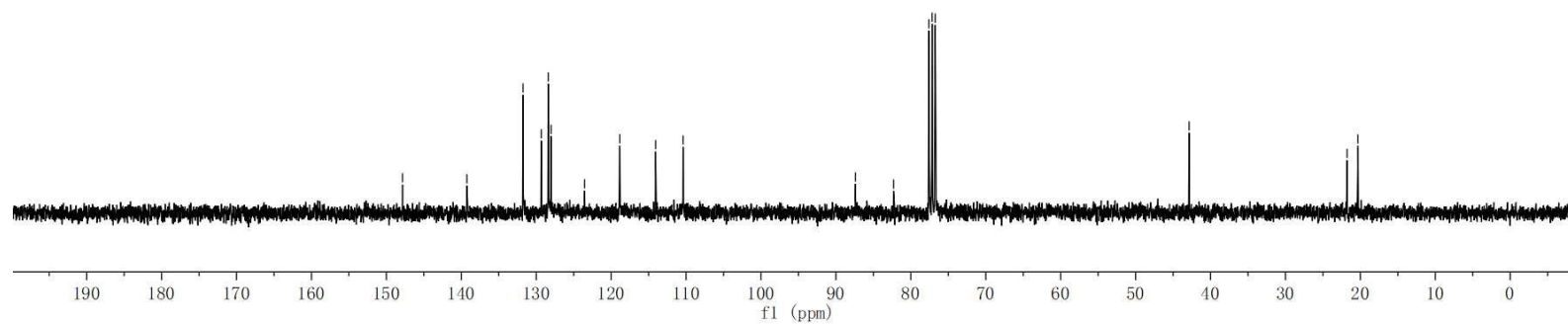


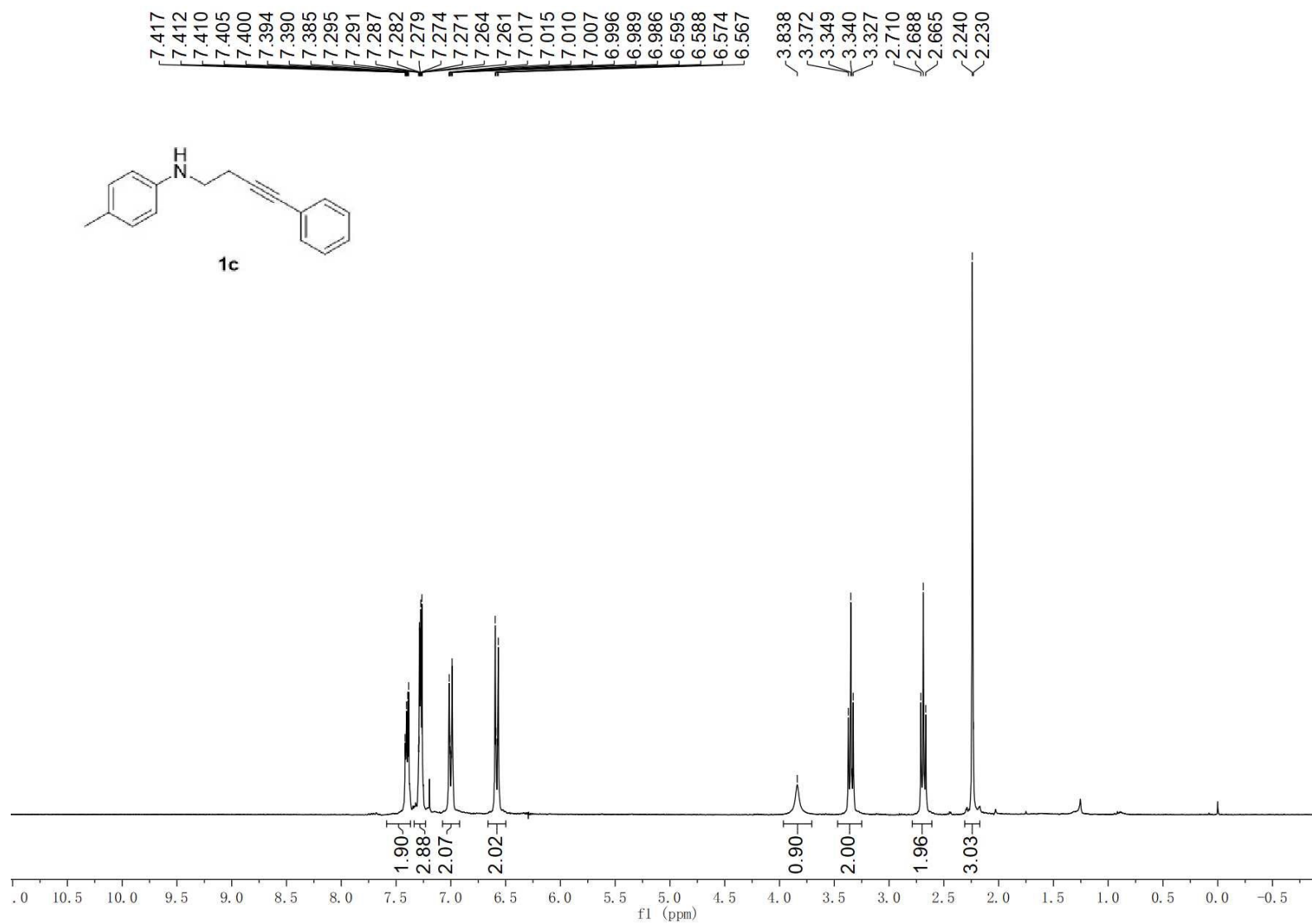
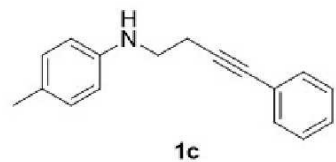


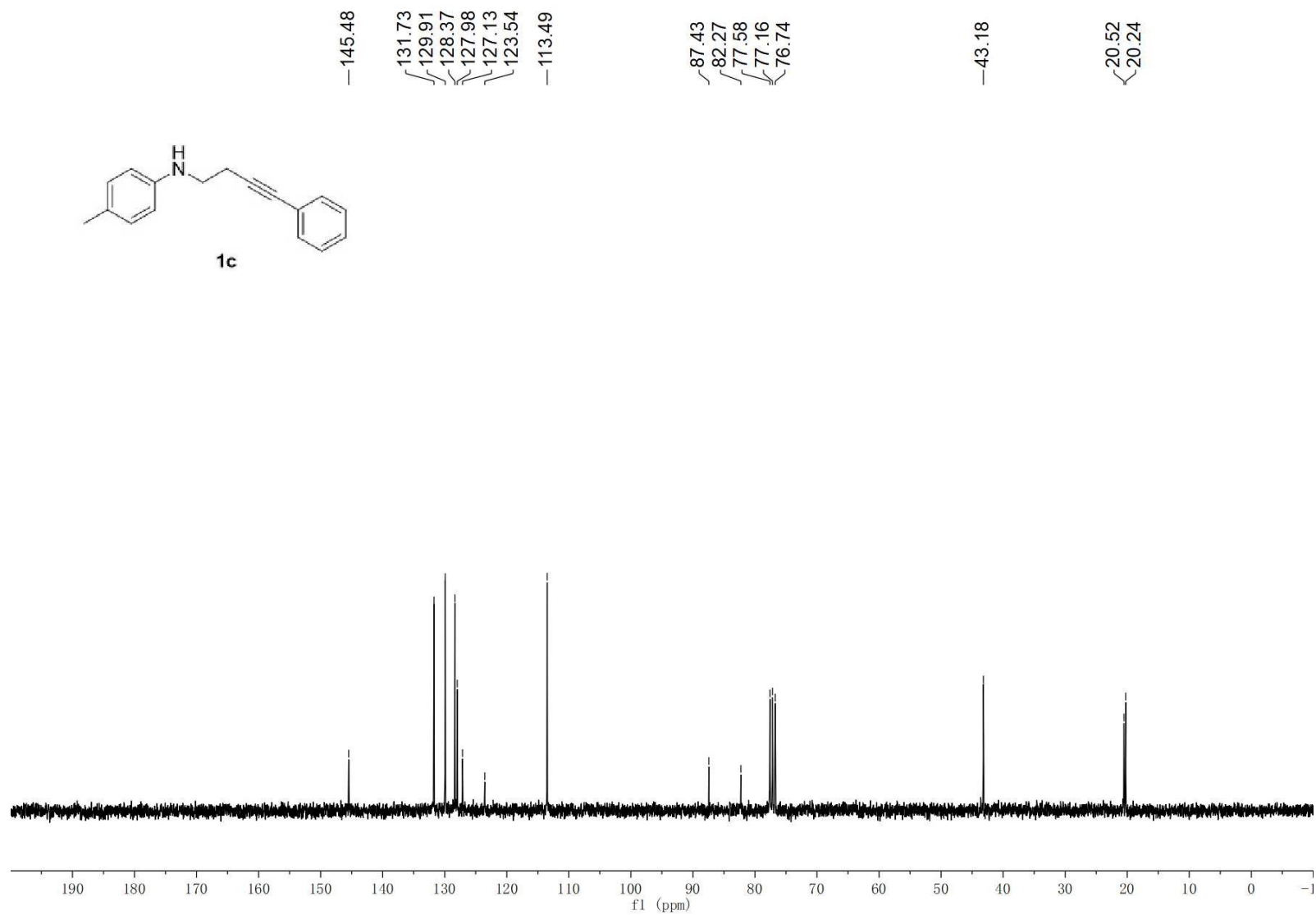
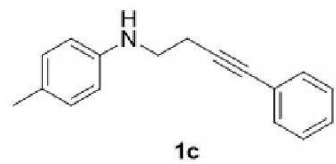


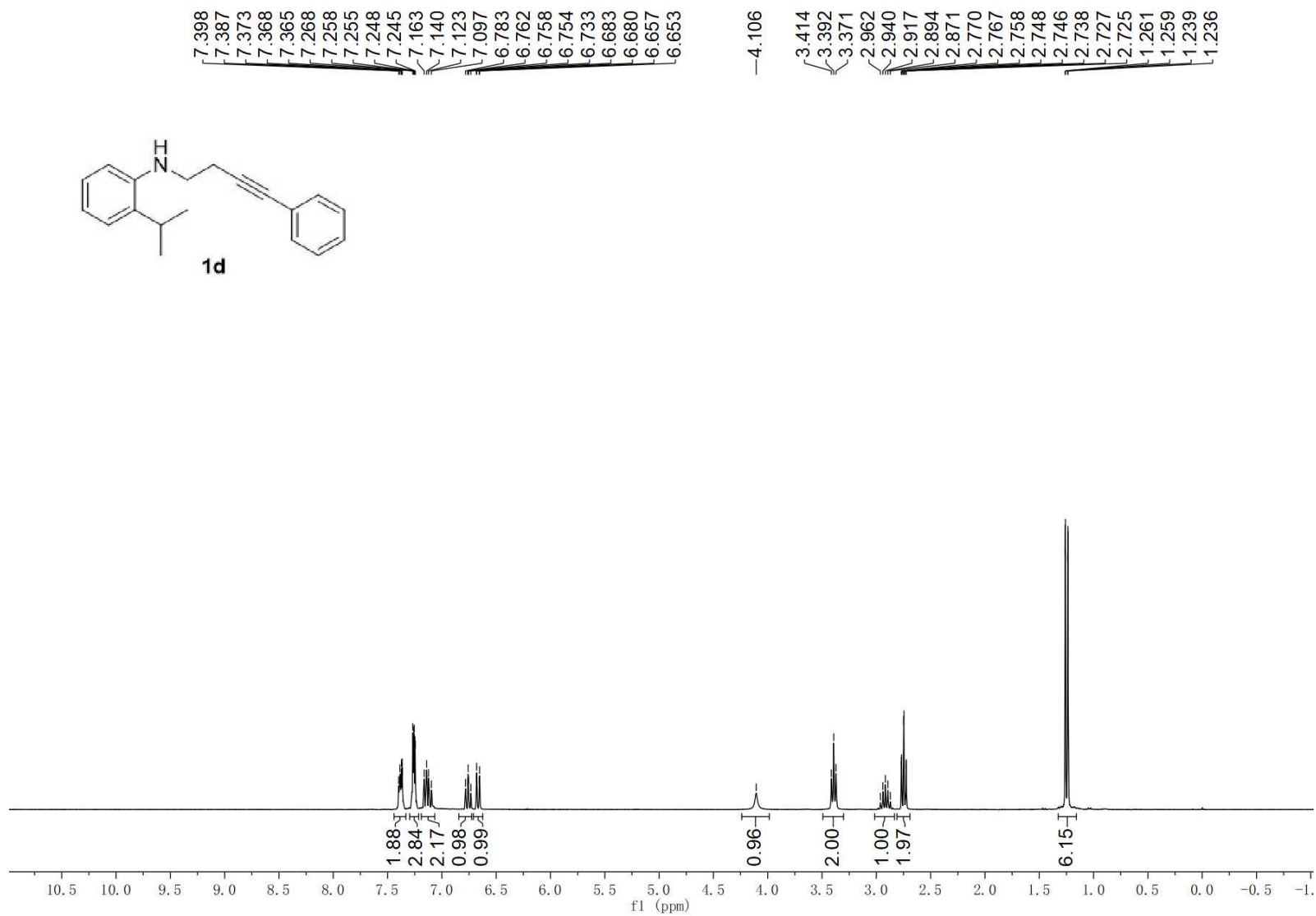
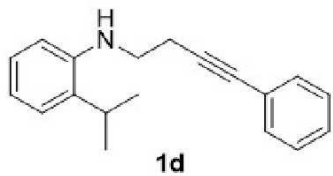


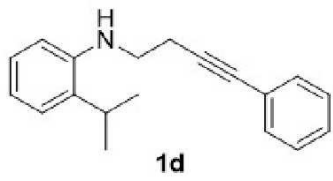
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20.32









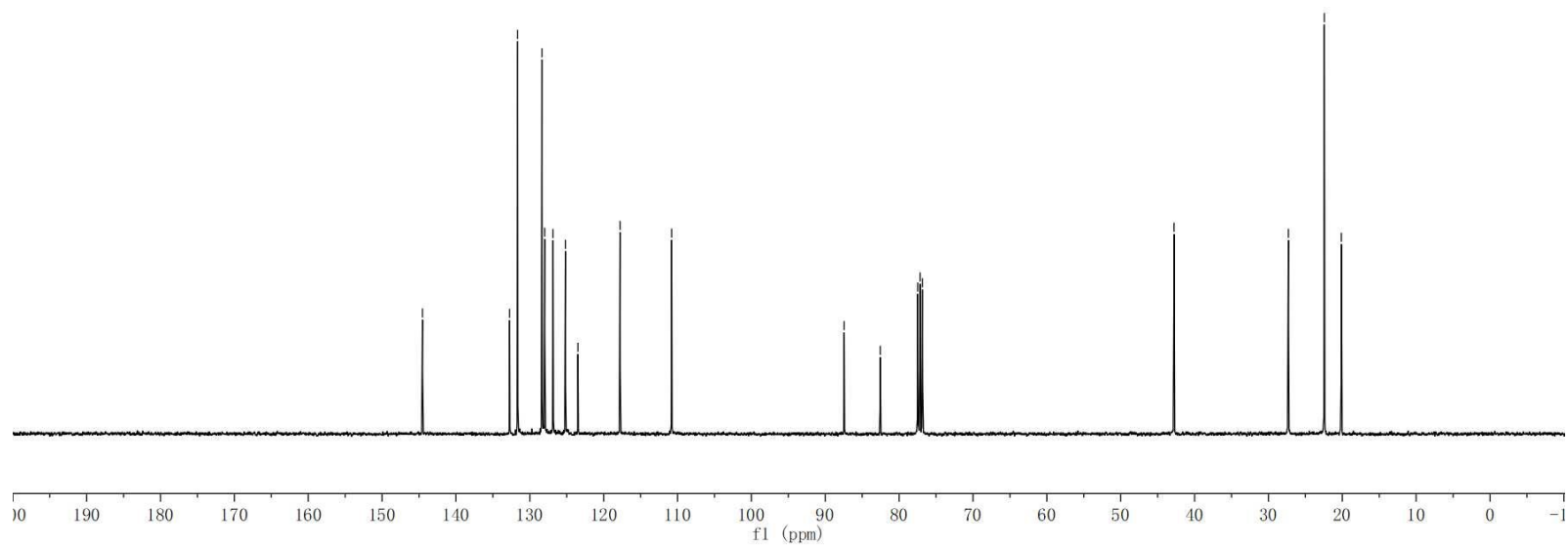


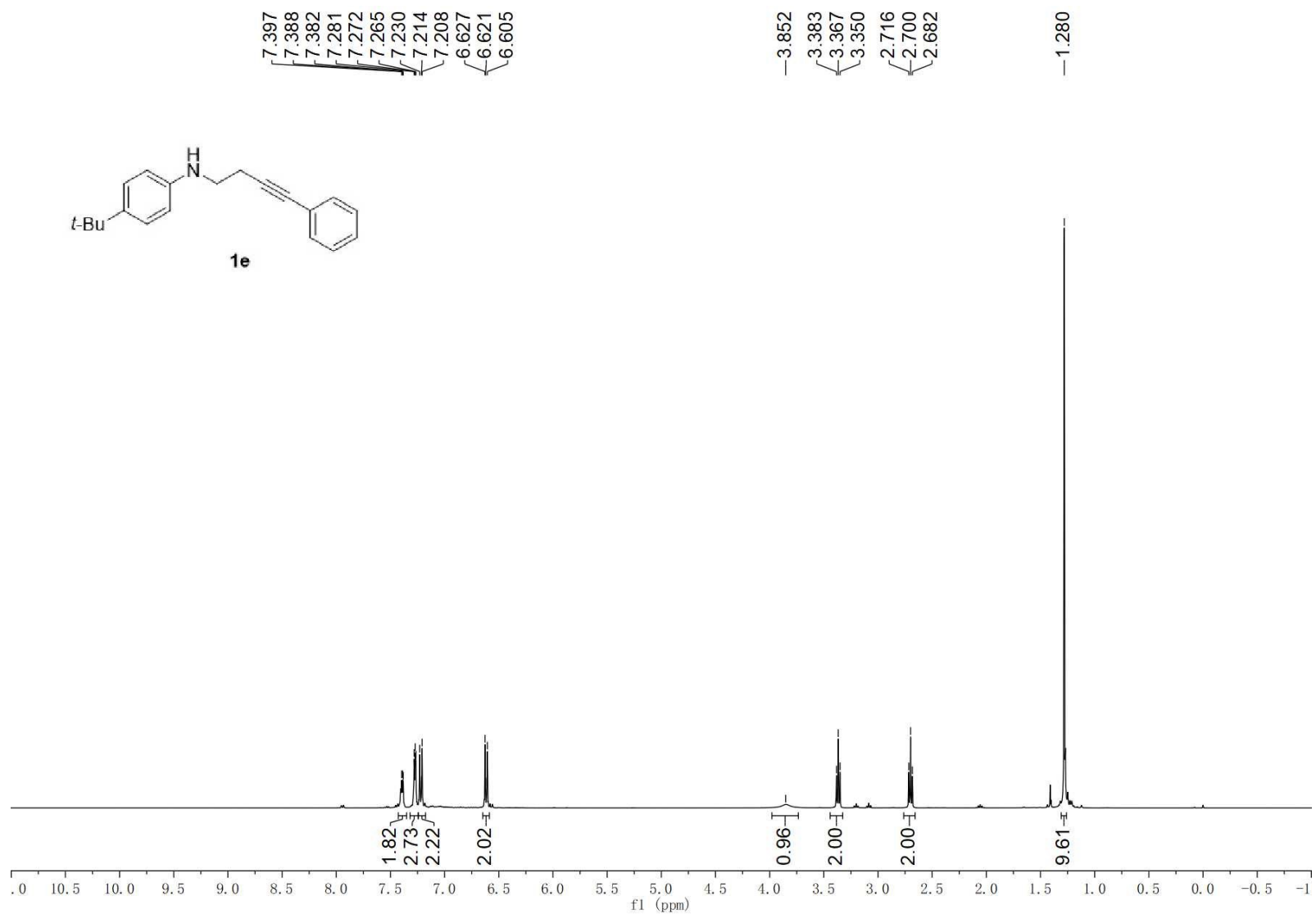
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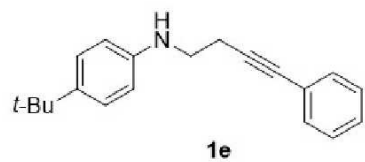
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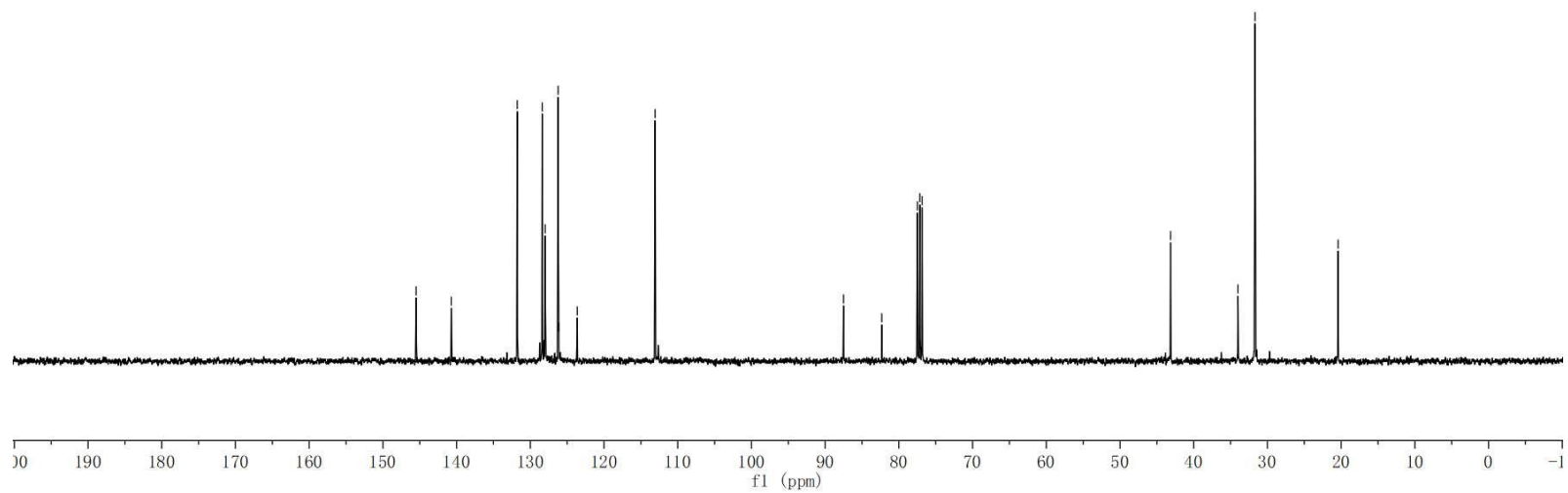


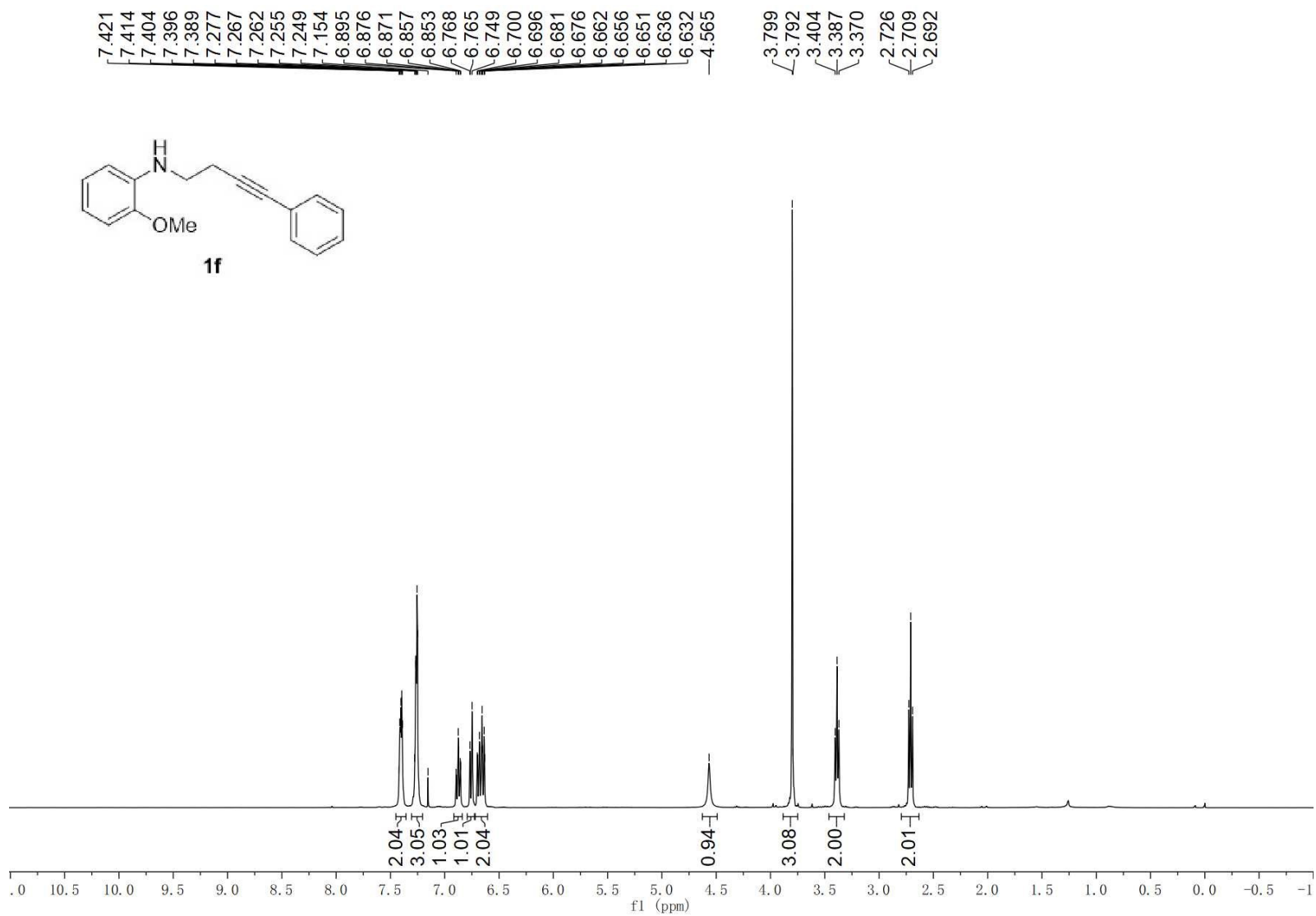
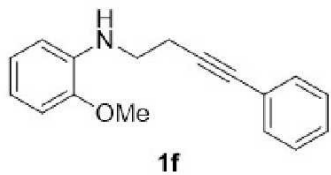
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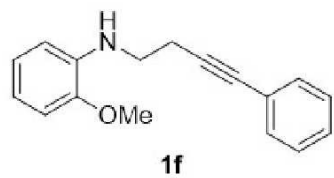
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— 43.14
 ~ 34.00
 ~ 31.68

— 20.41







—147.08

—137.70

—131.66

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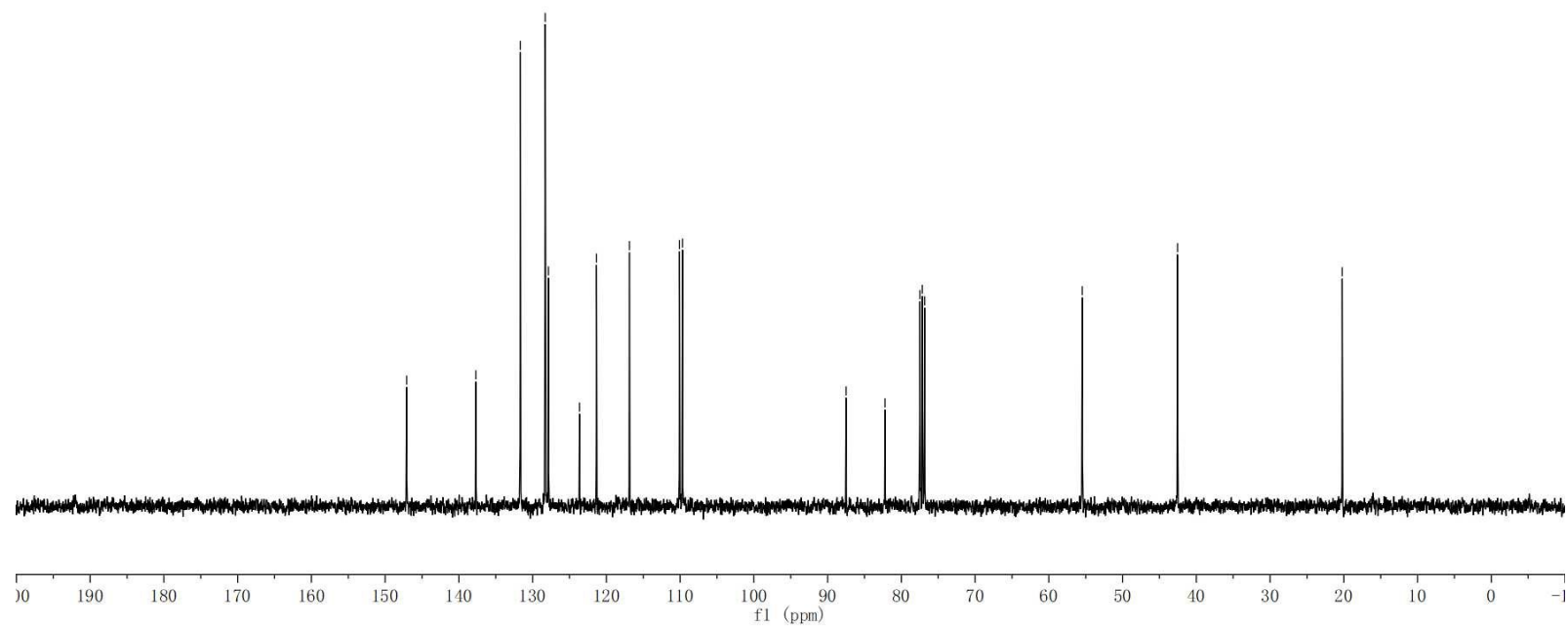
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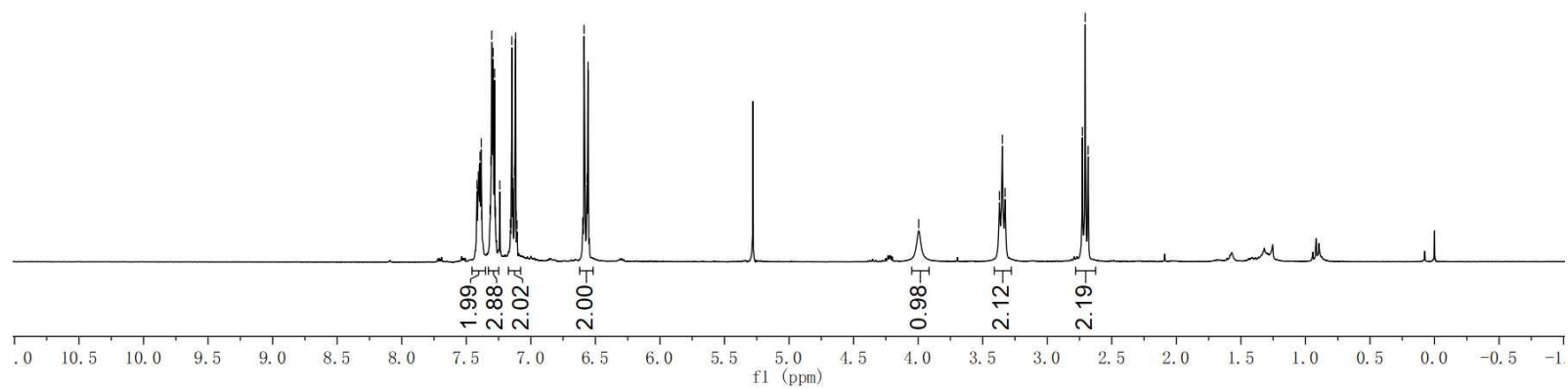
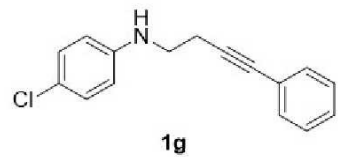
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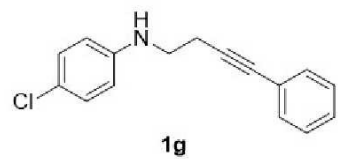
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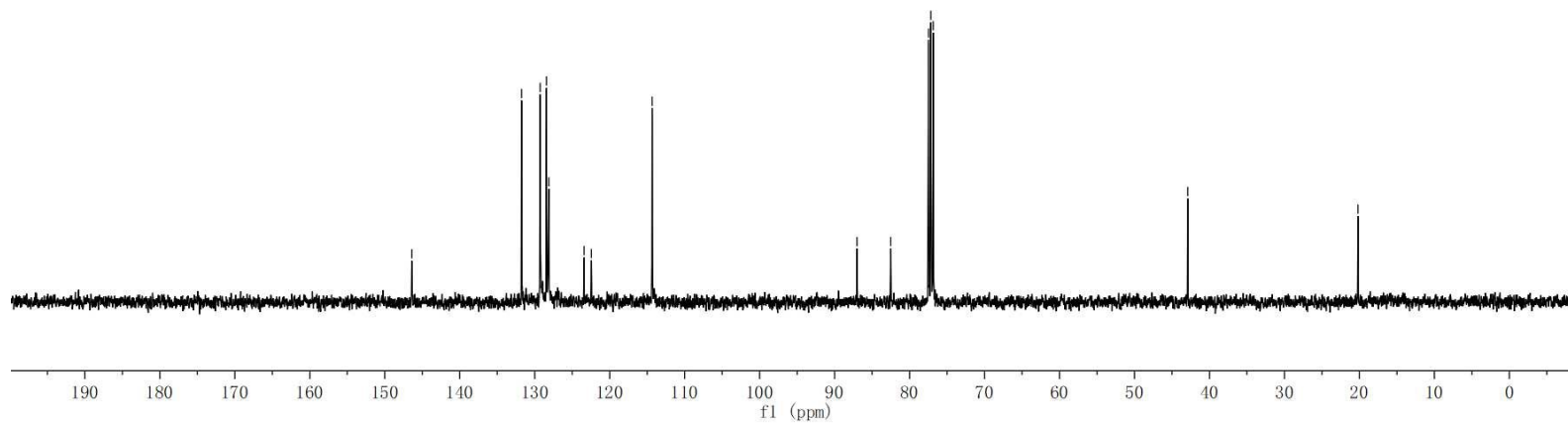


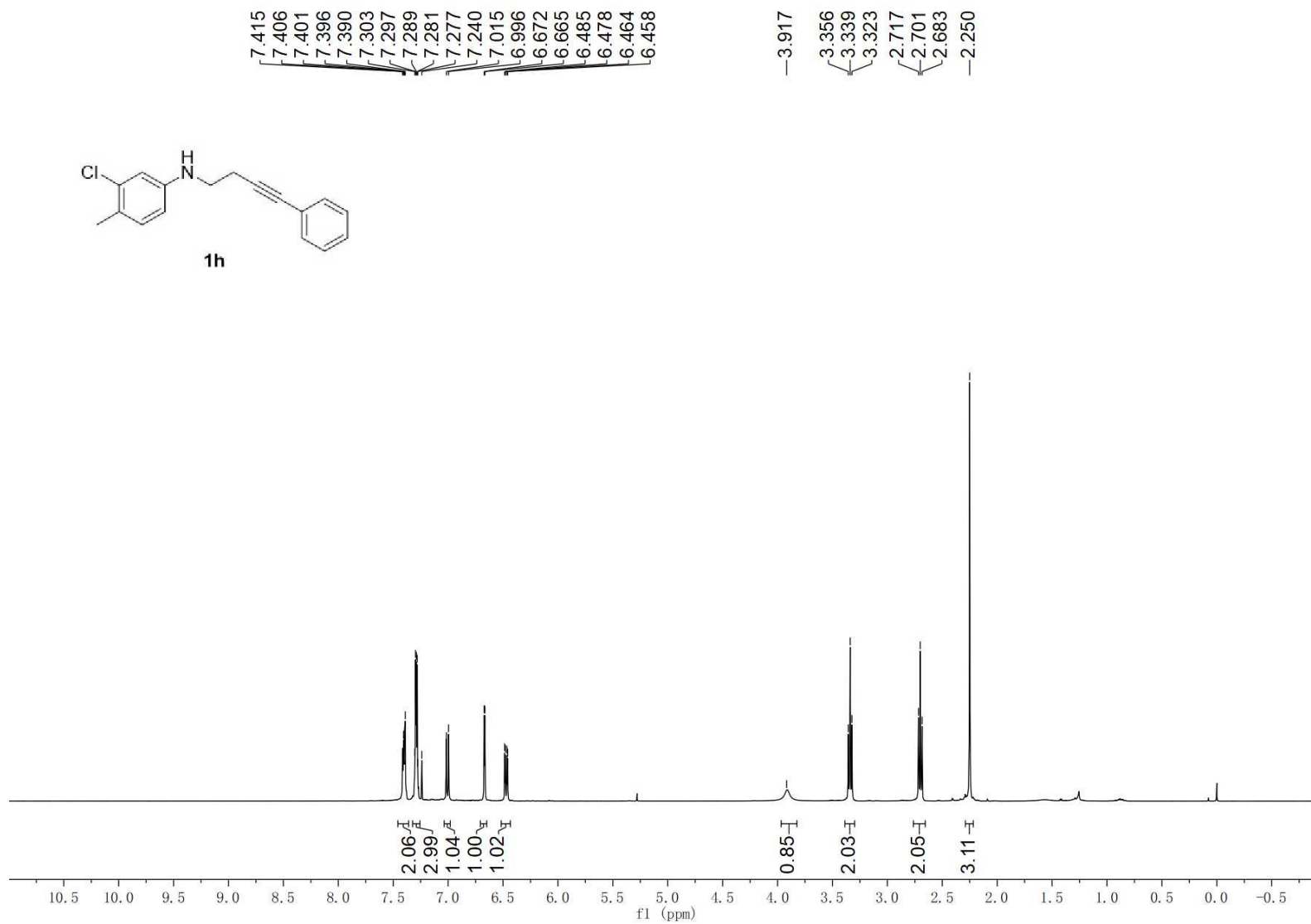
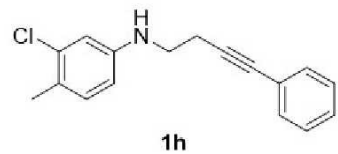
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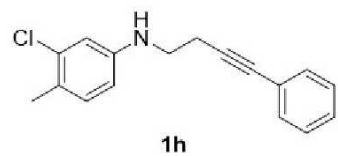
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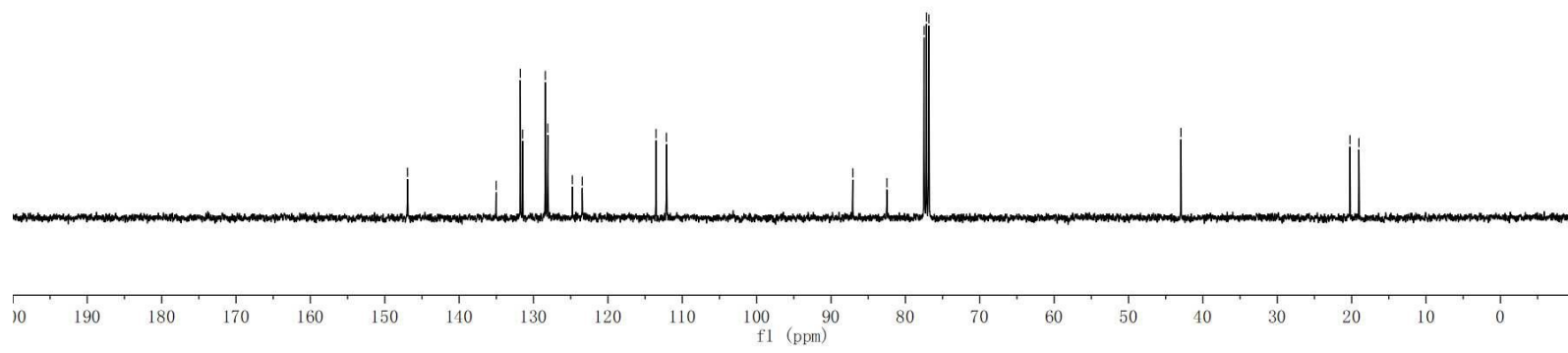
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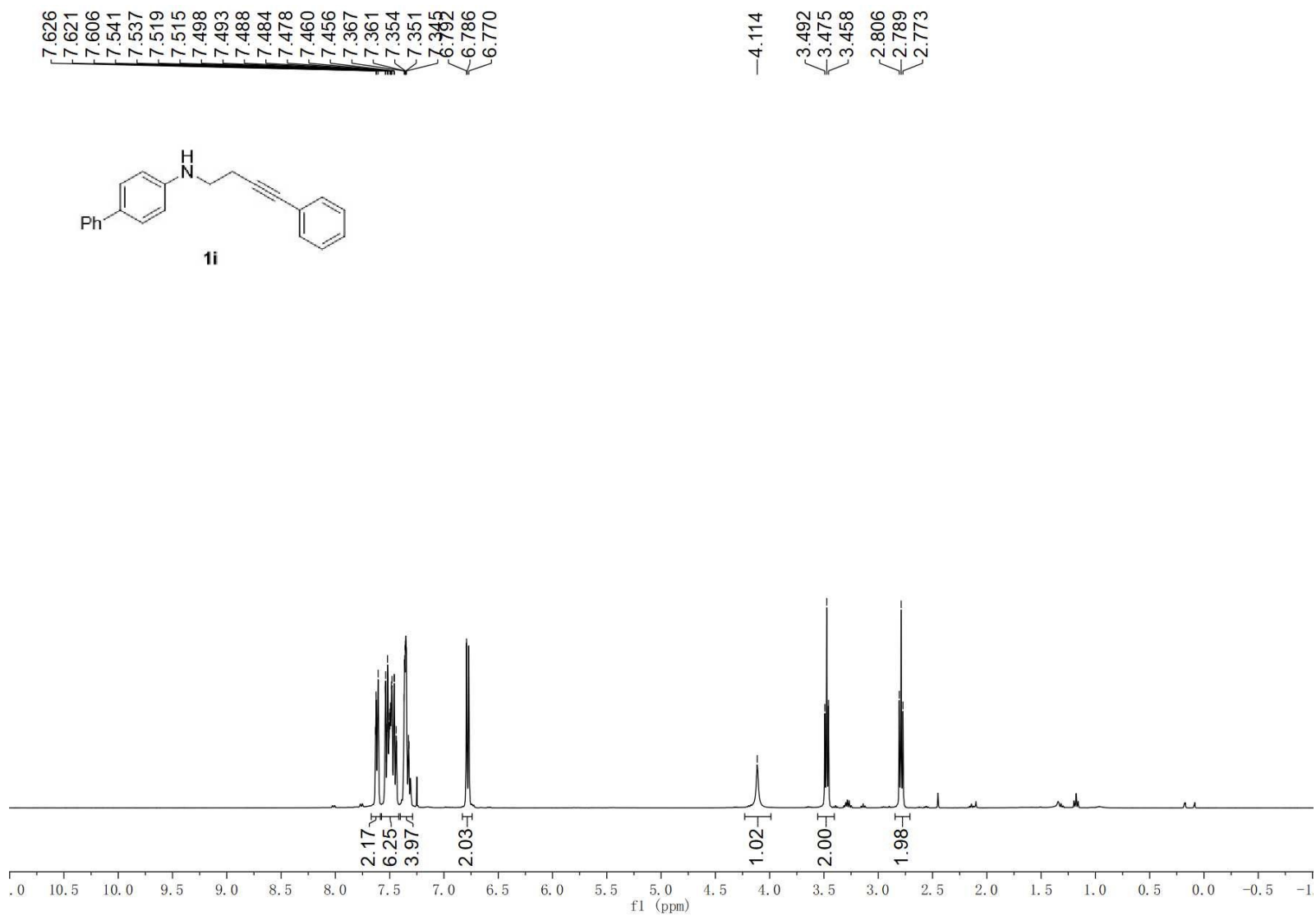
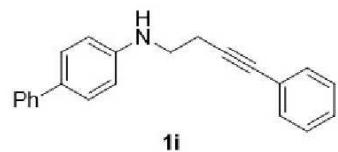


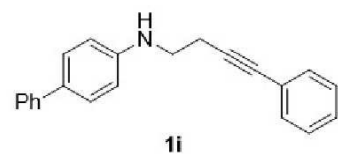




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20.22
19.03





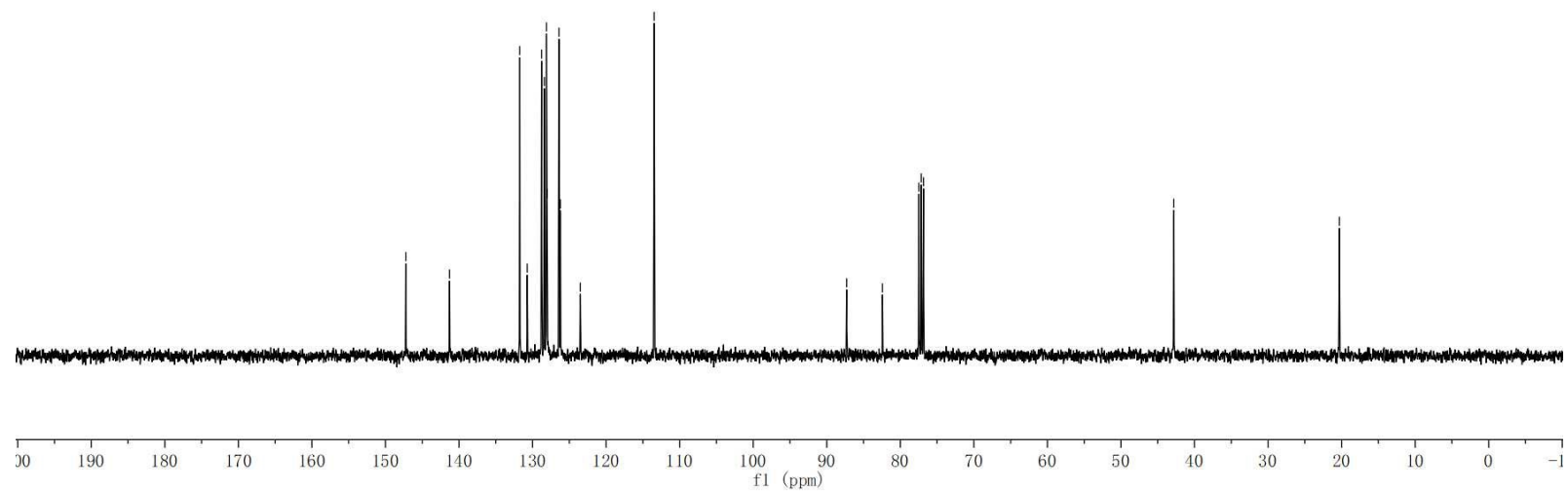


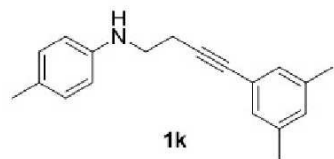
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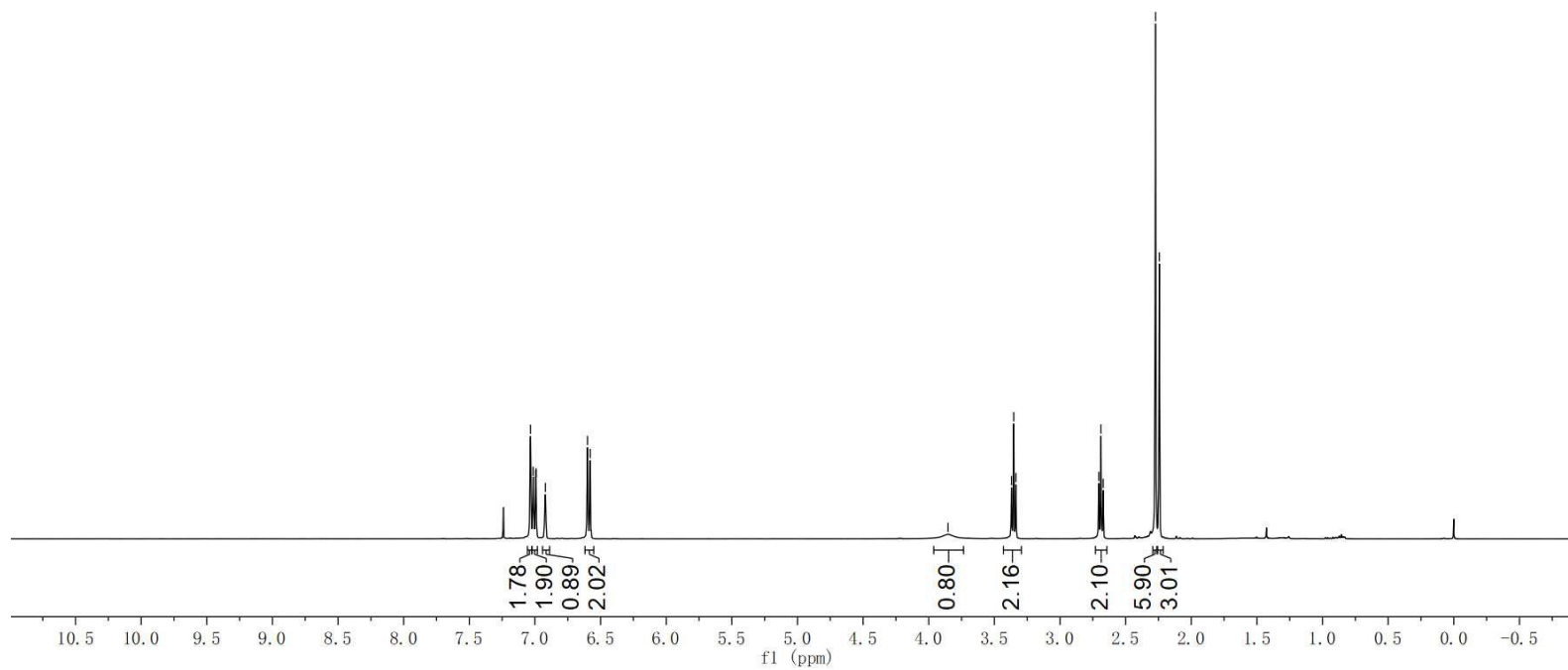
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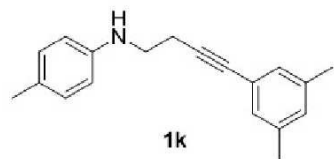




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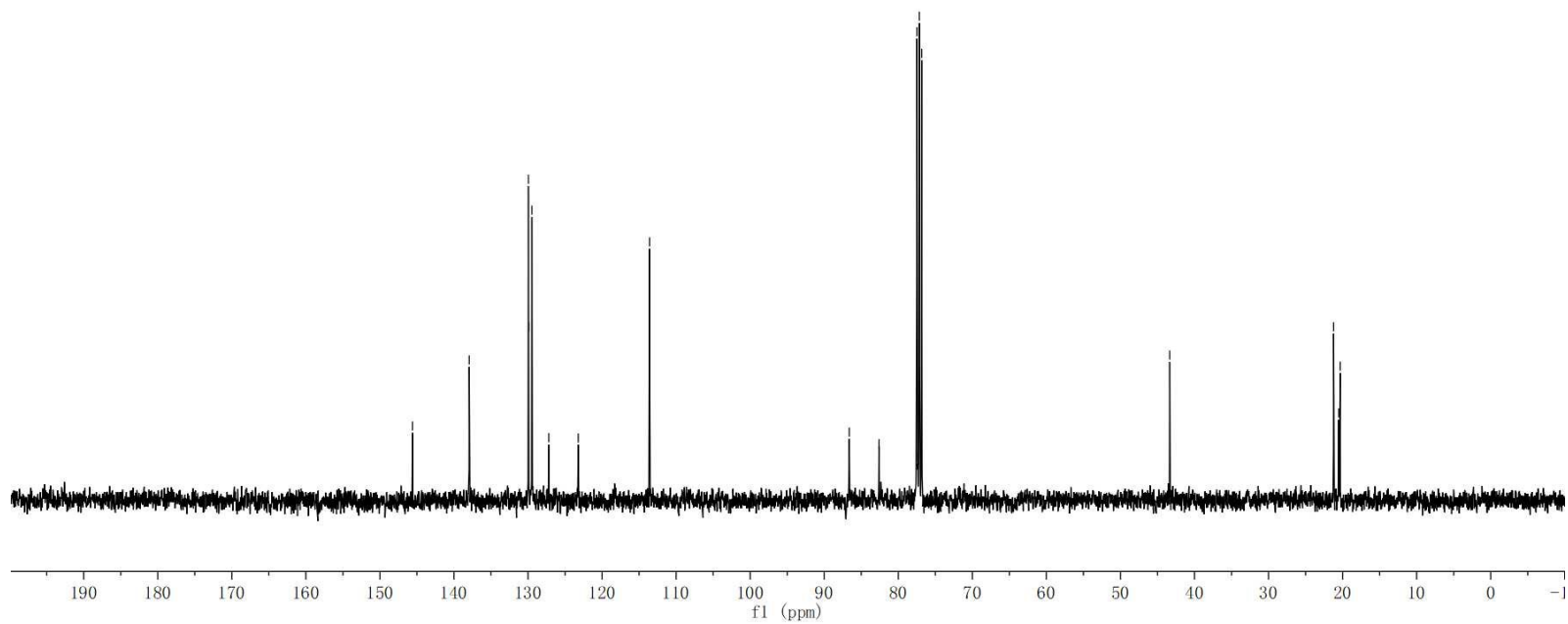


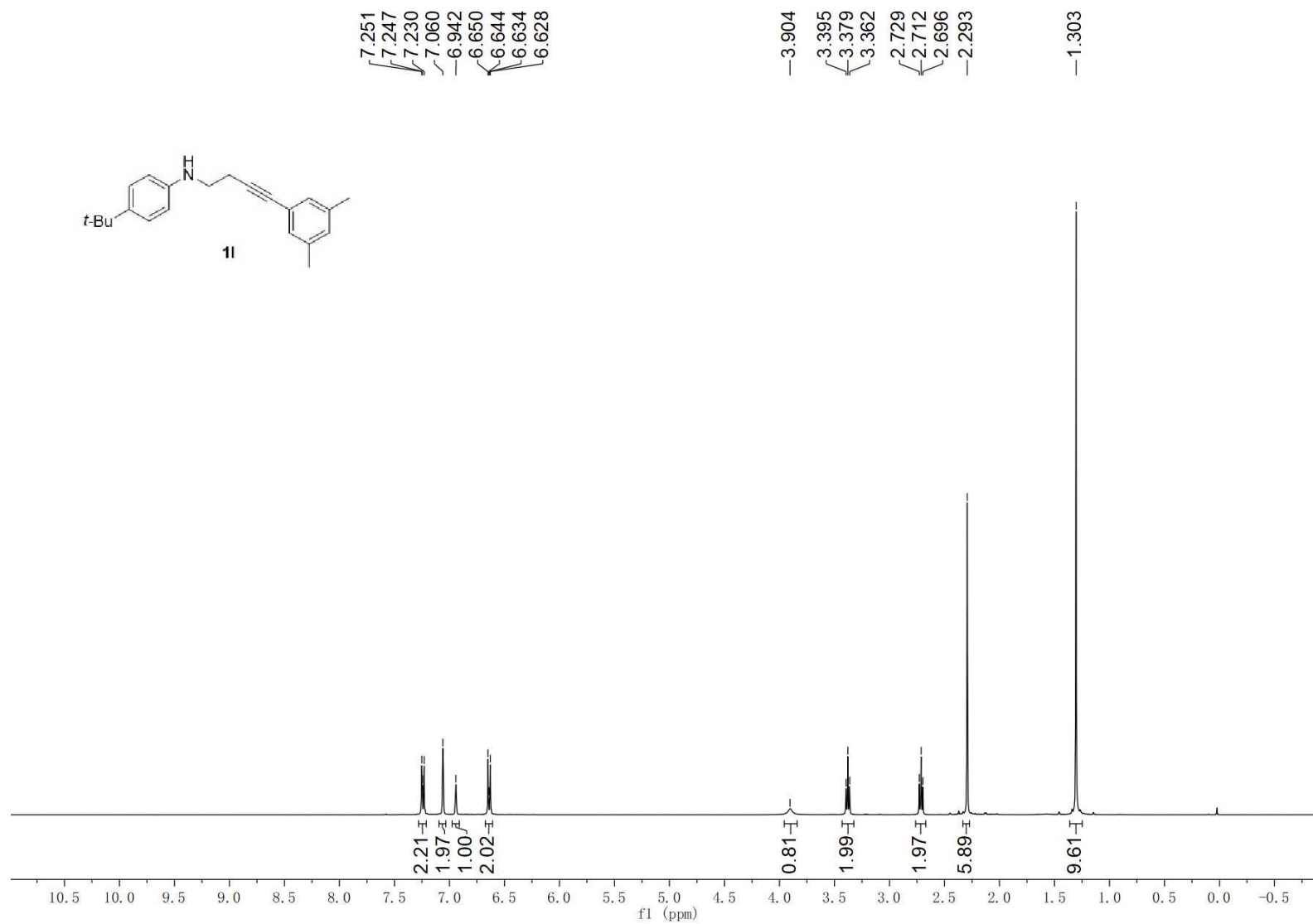
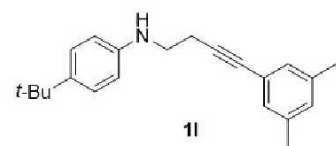
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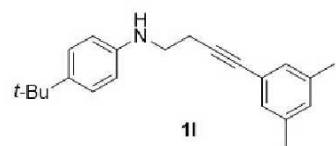
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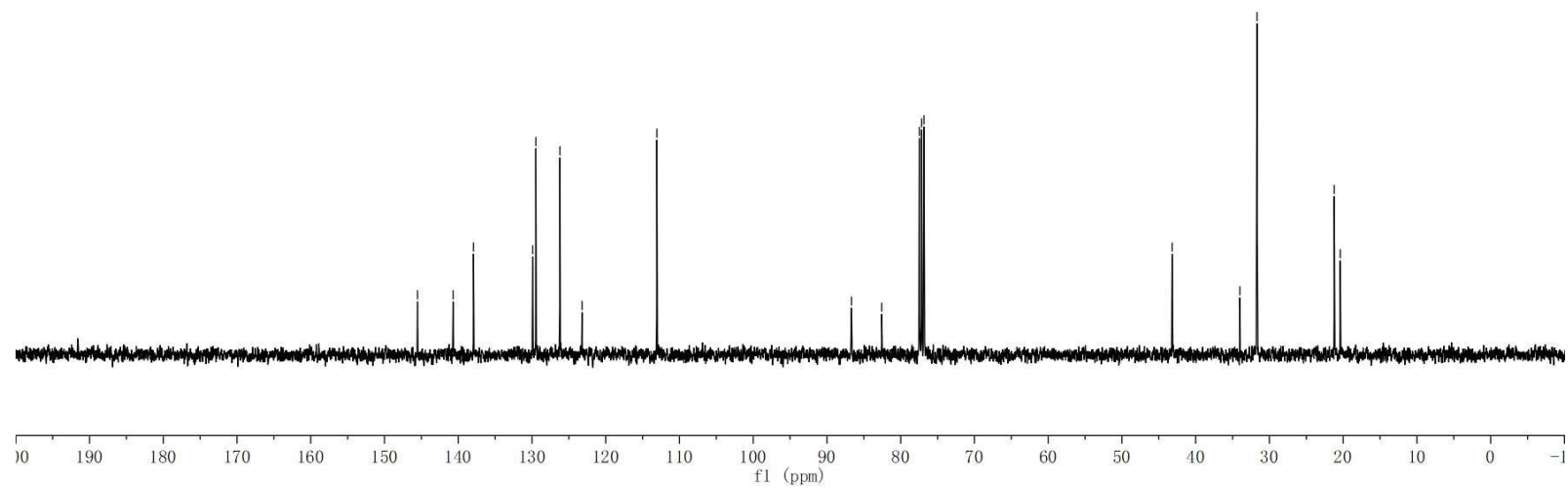
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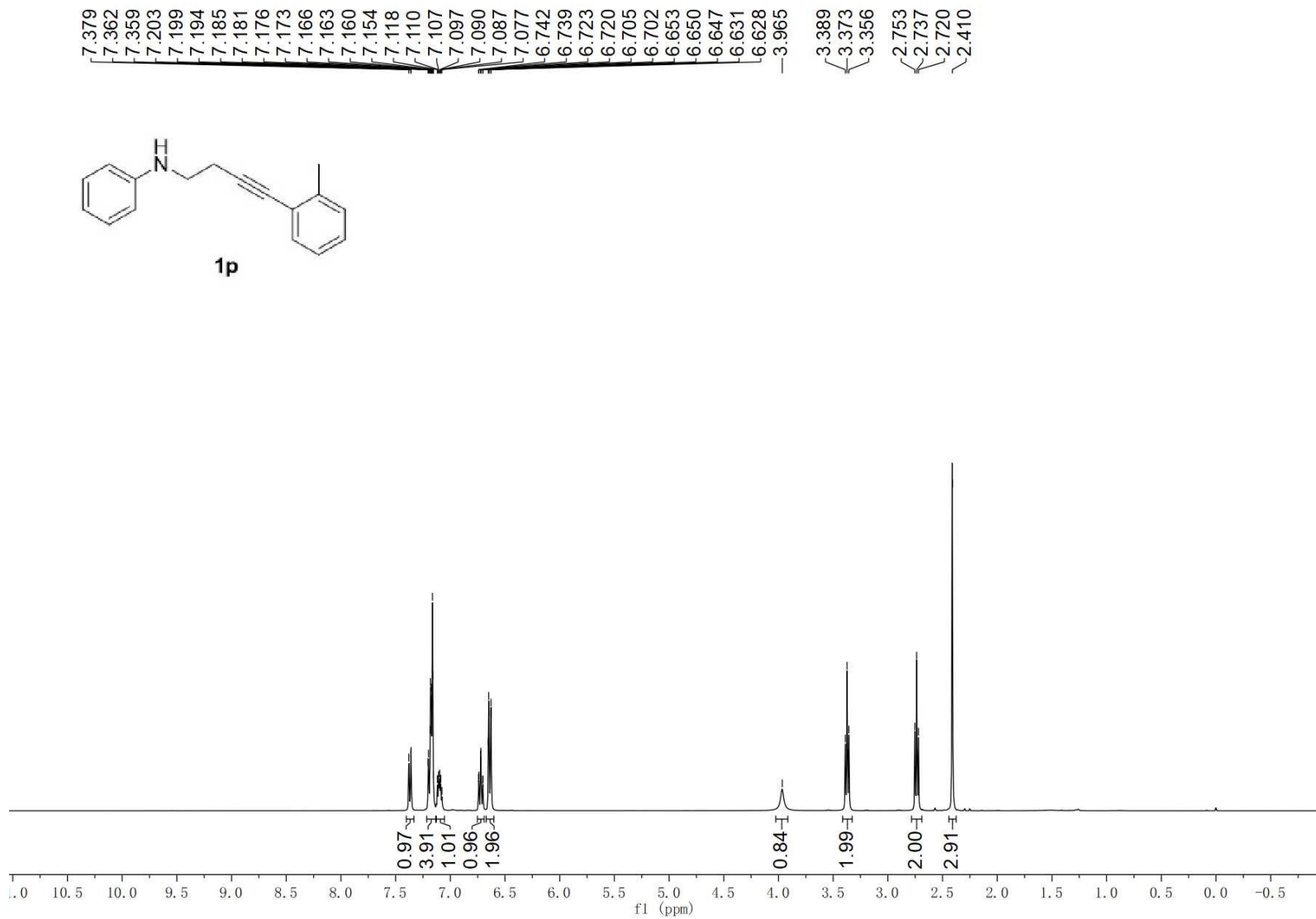
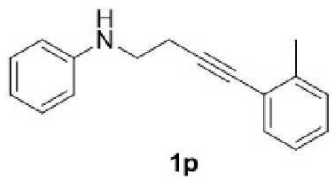
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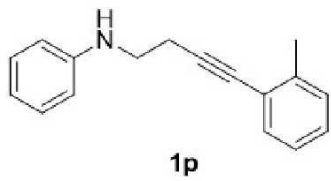
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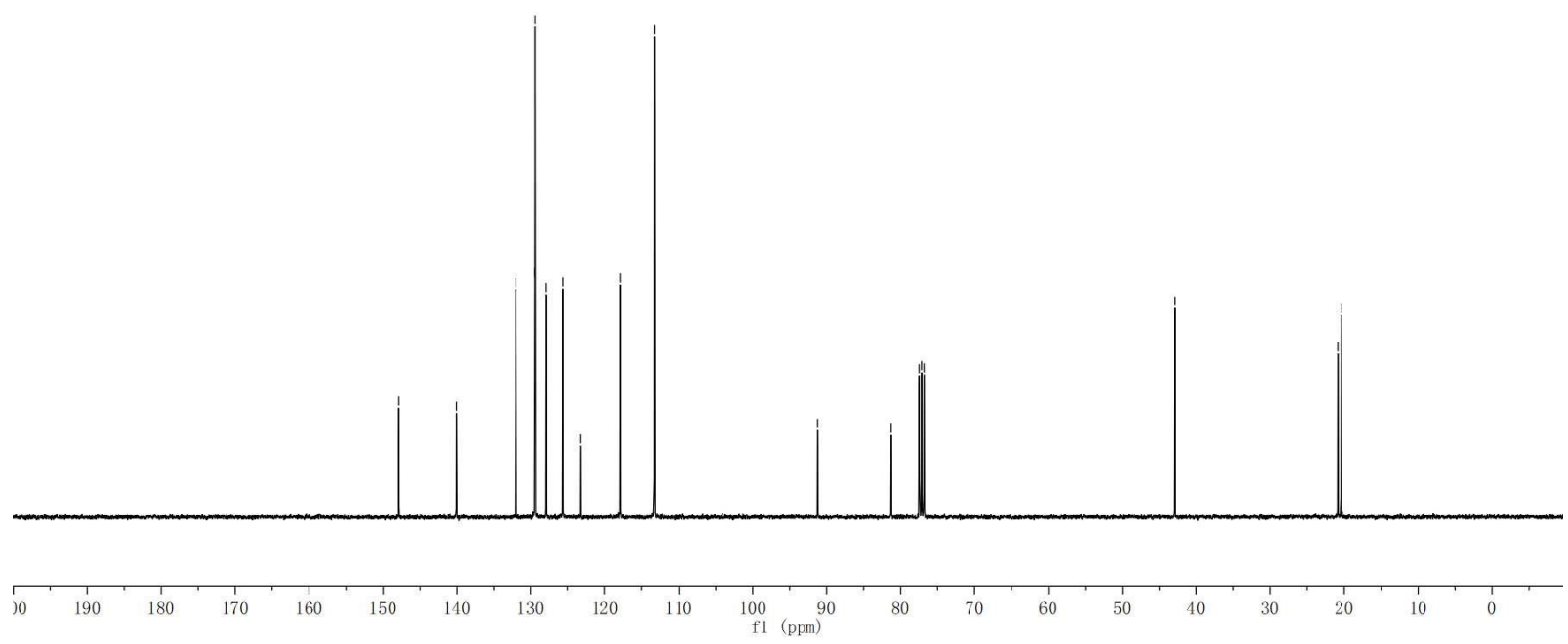


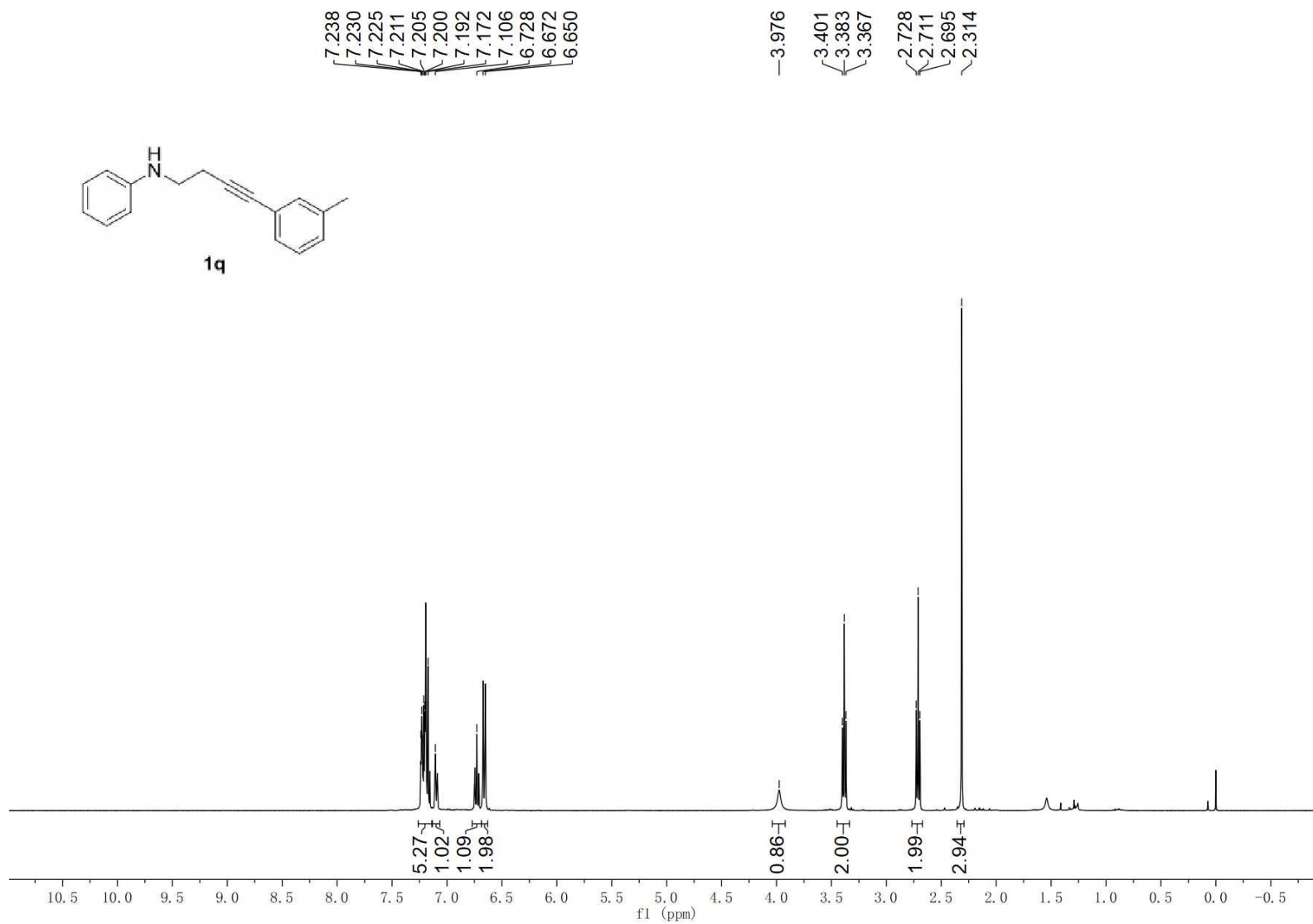
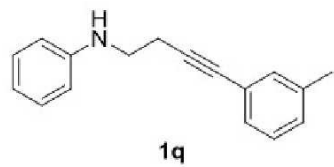
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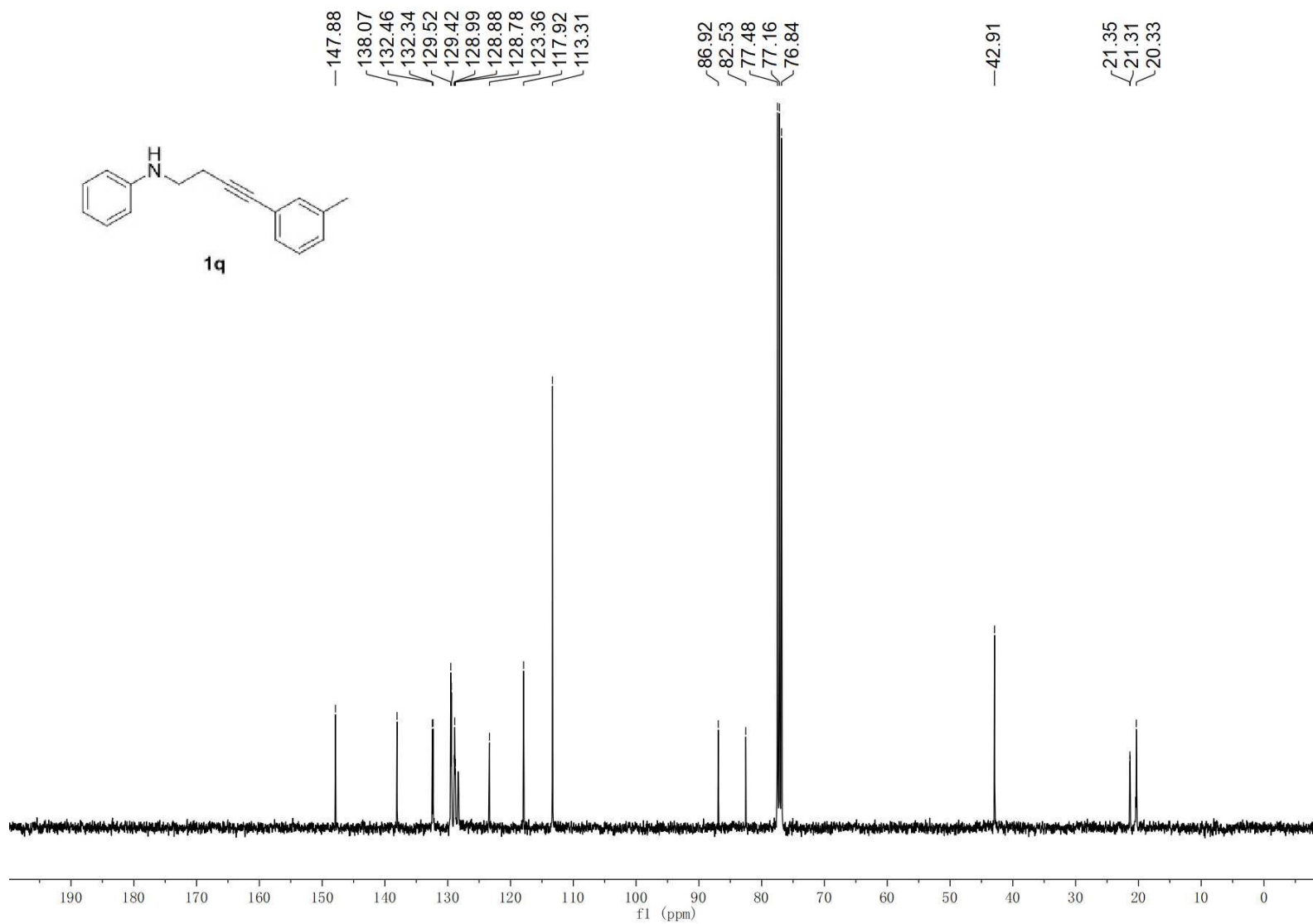
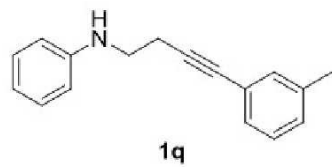
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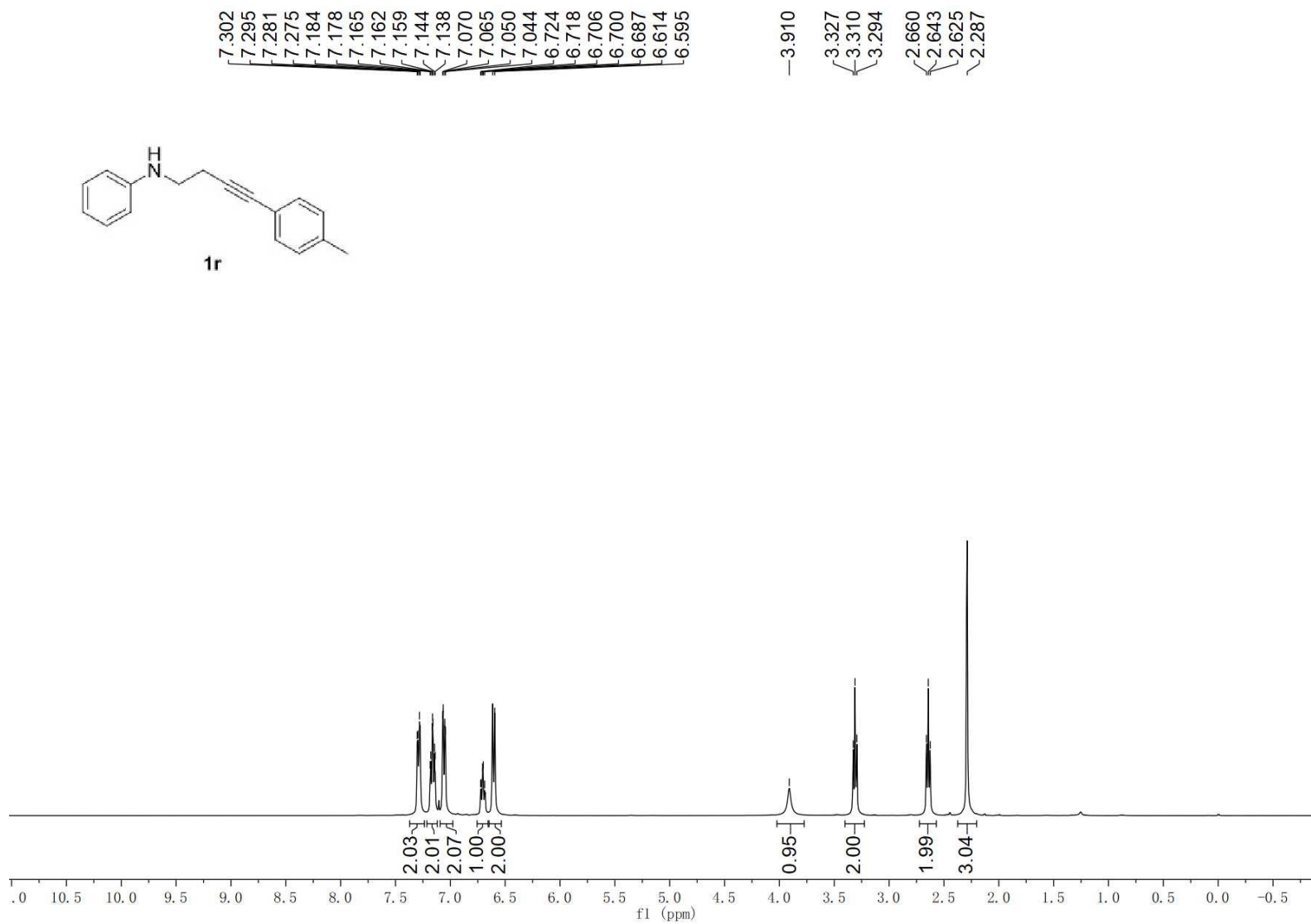
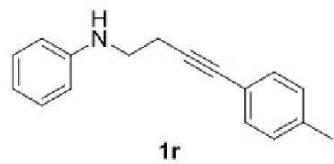
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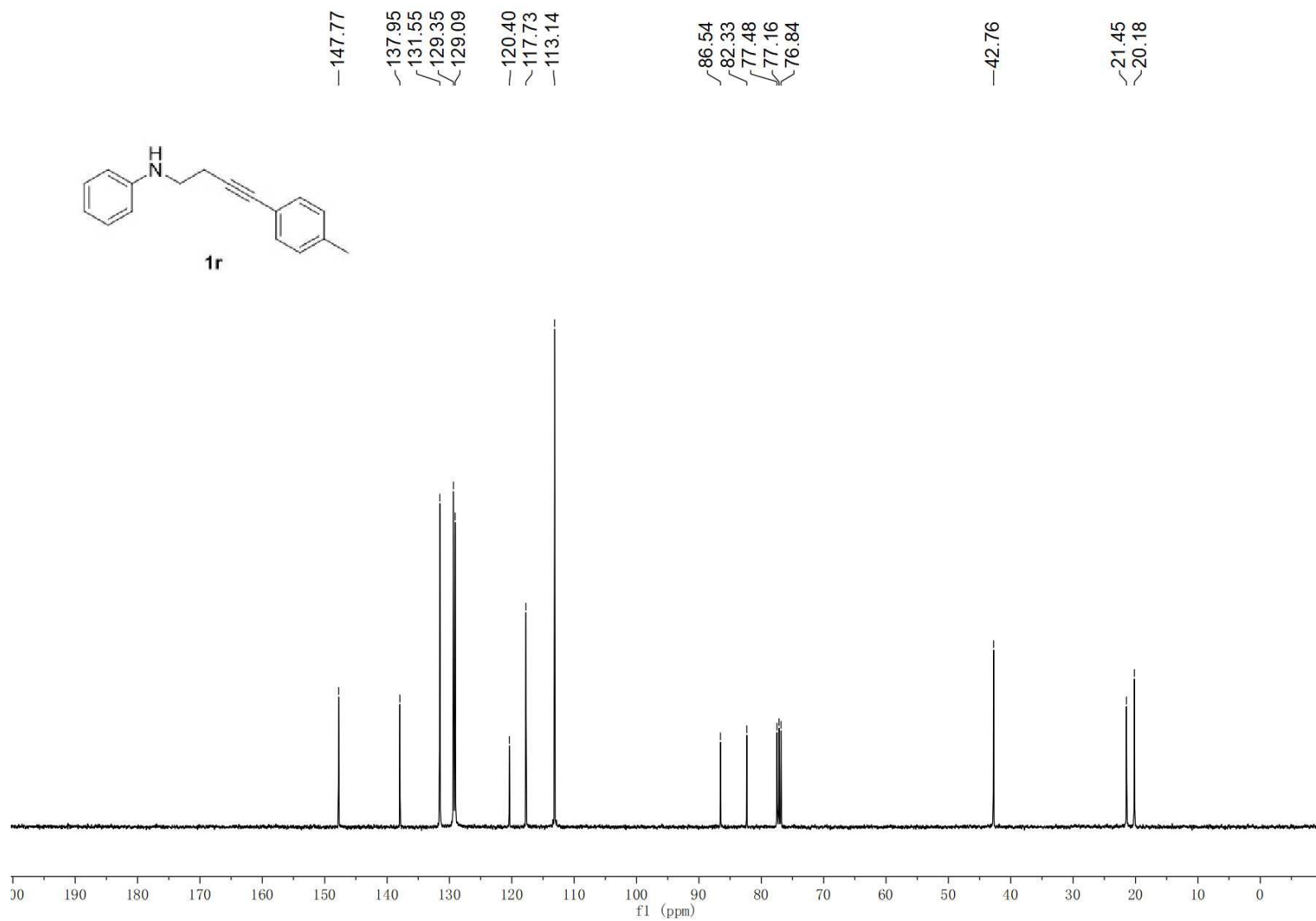
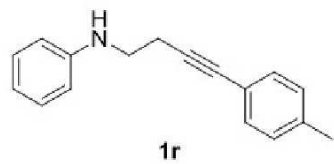
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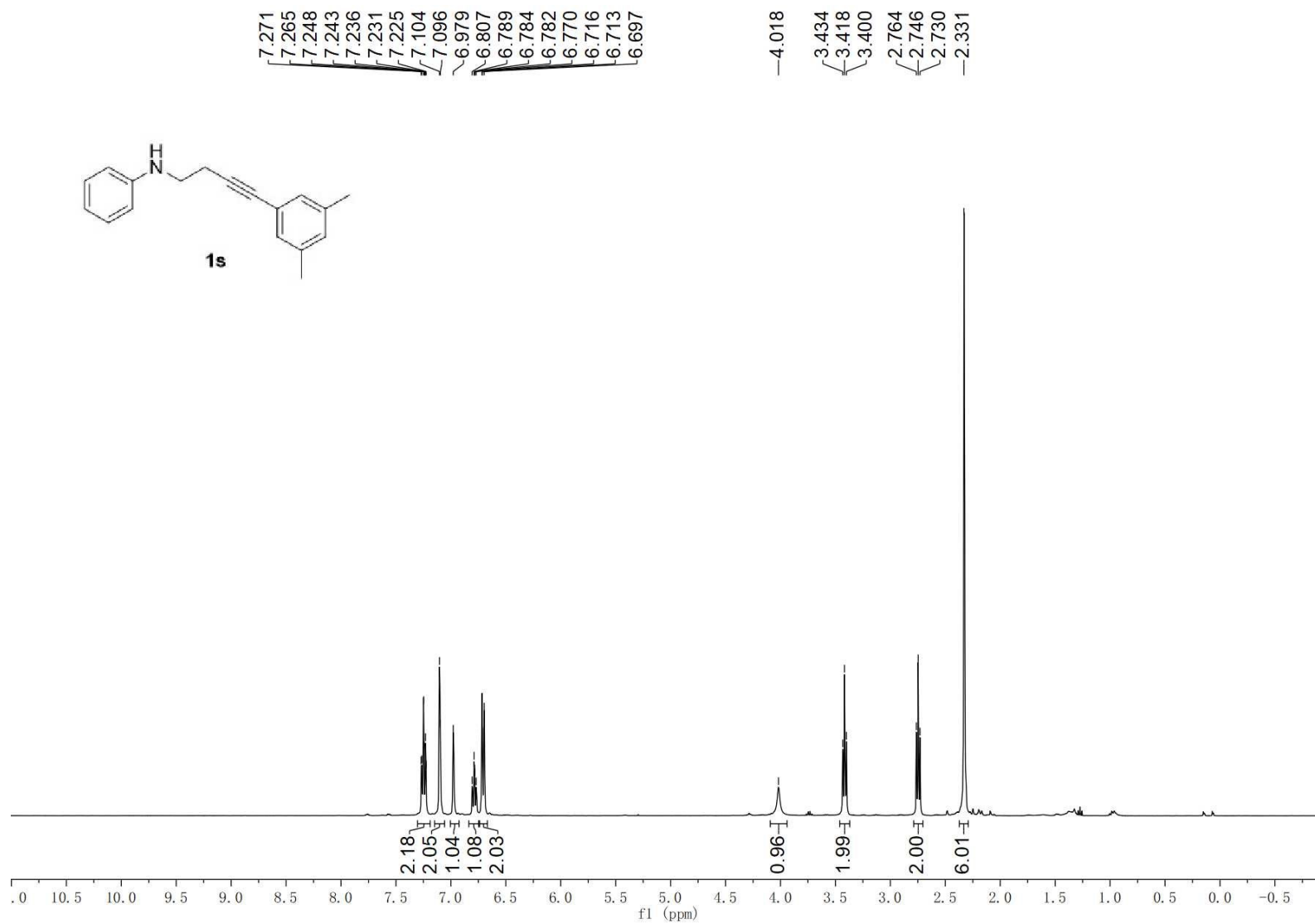
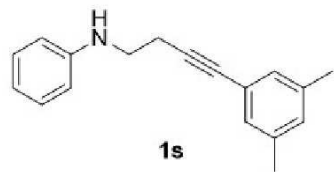


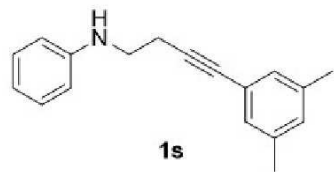












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123.12

-117.87

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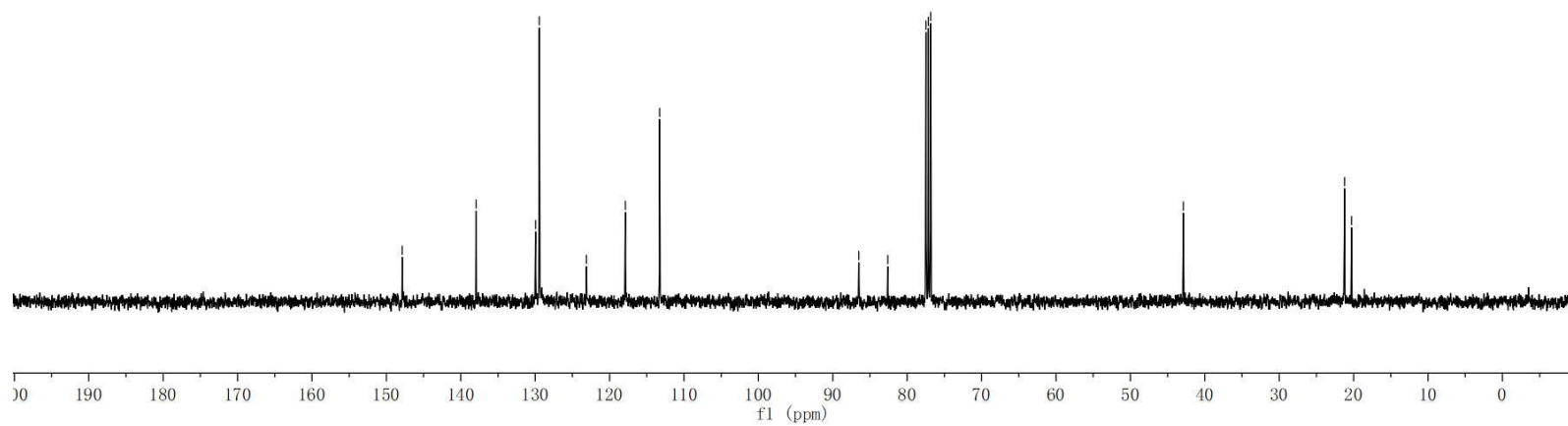
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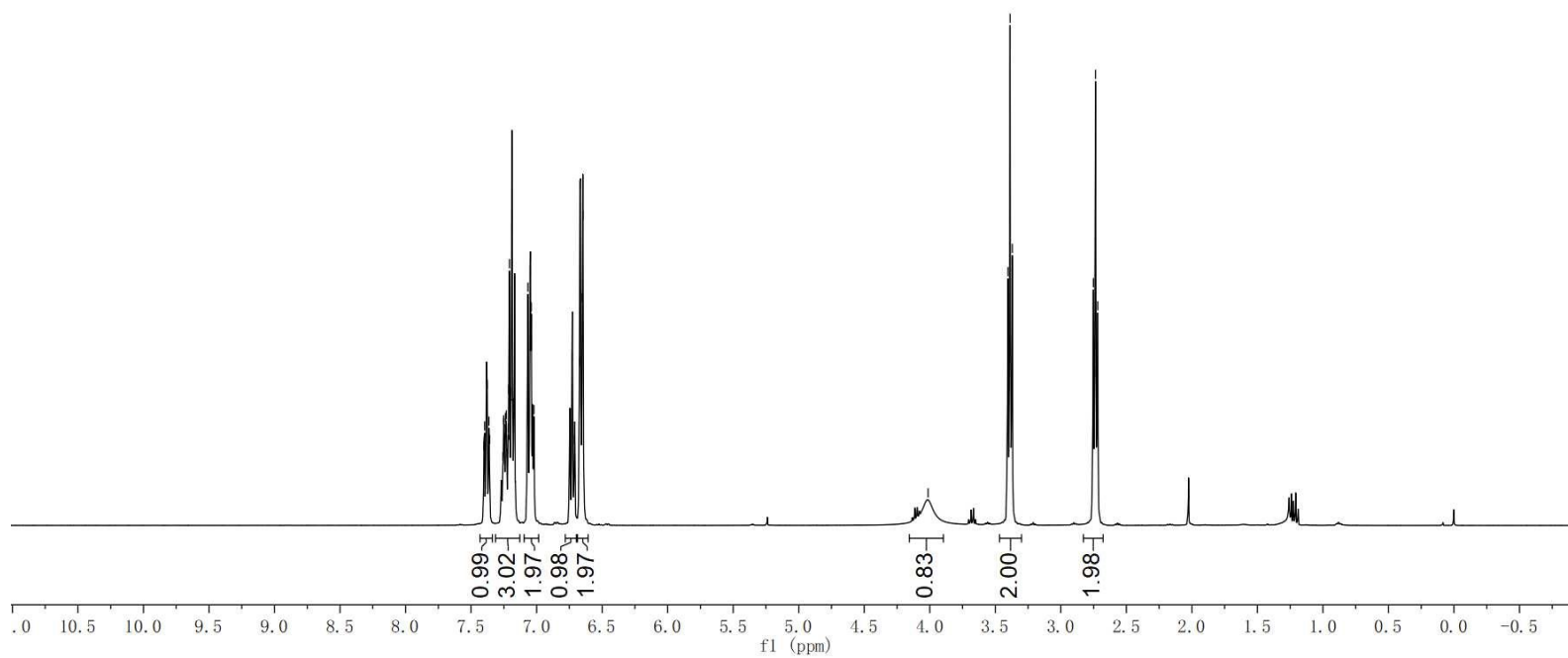
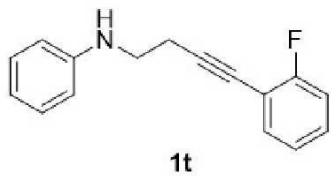
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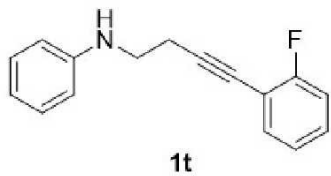
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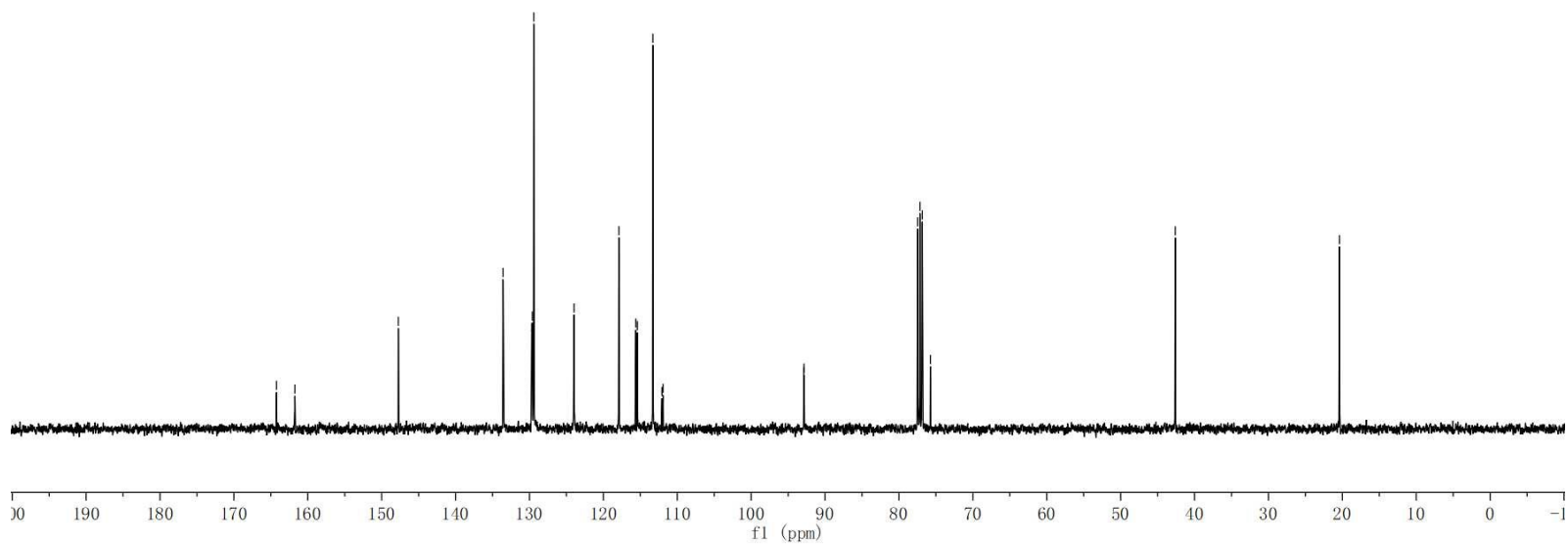
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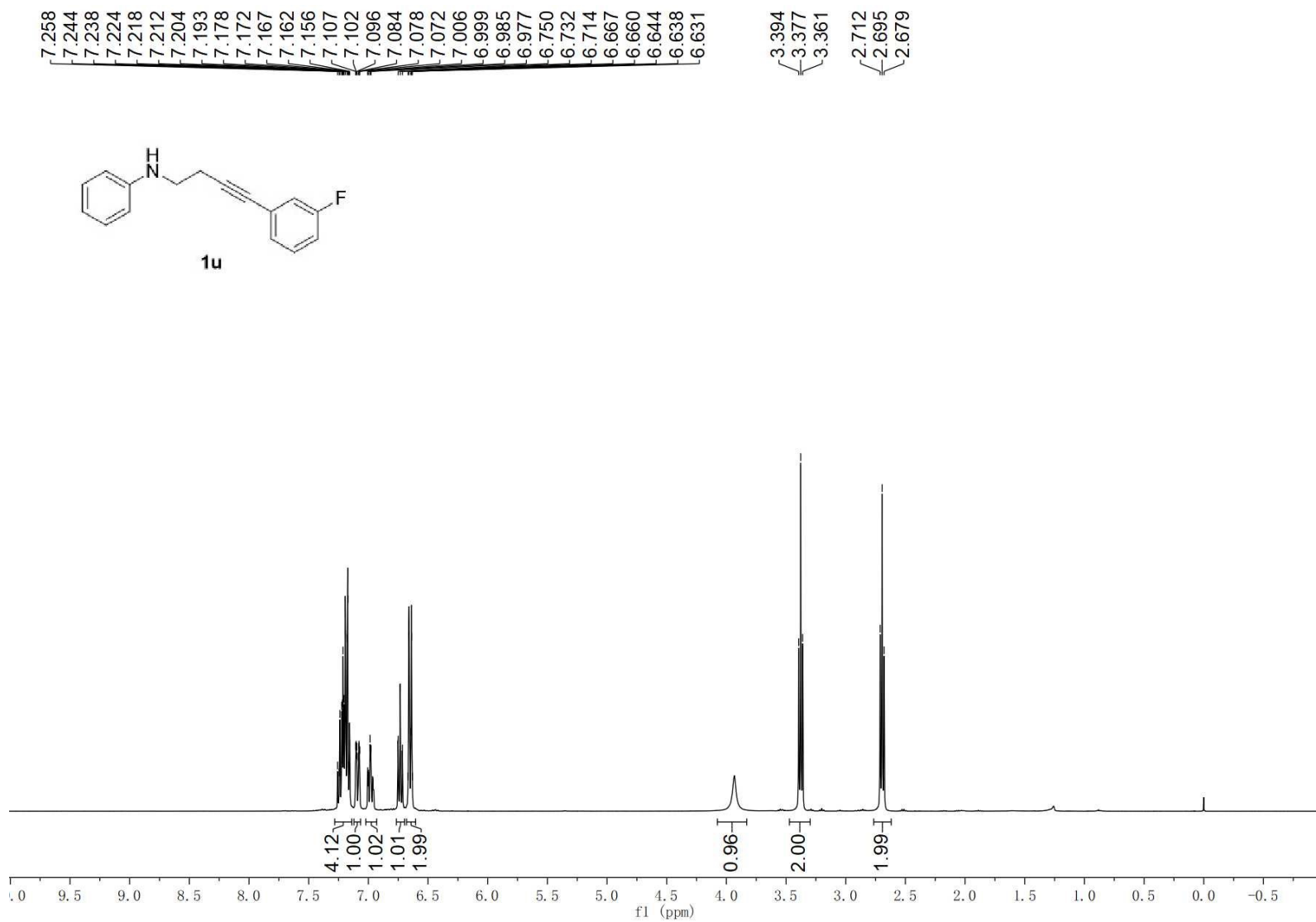
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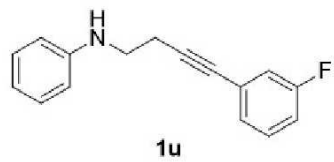
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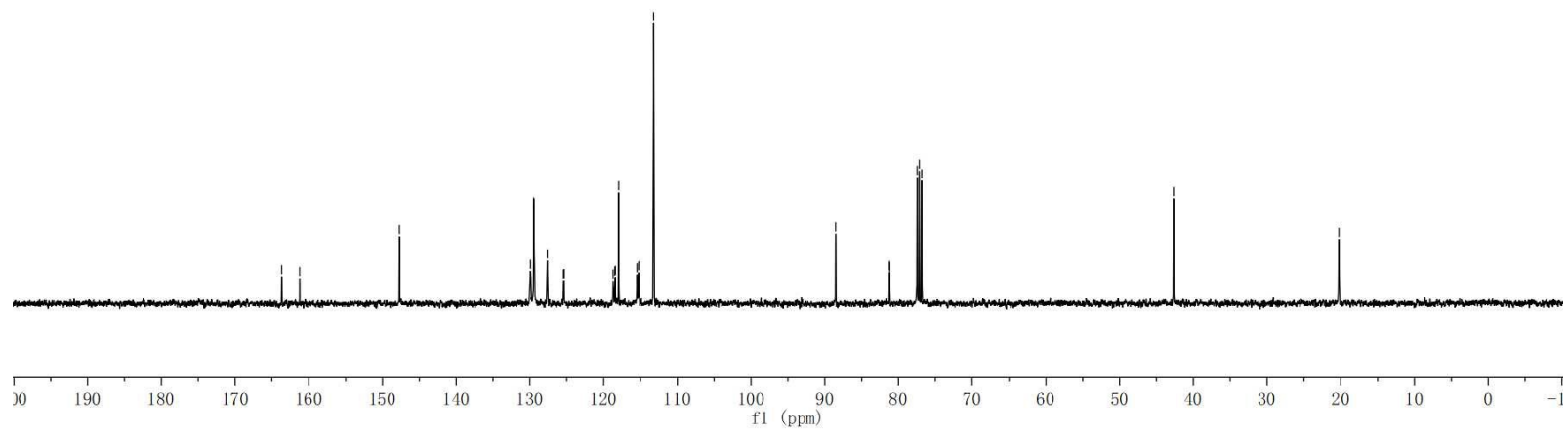
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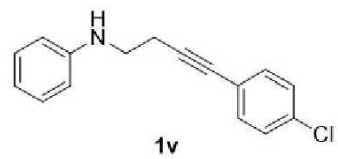
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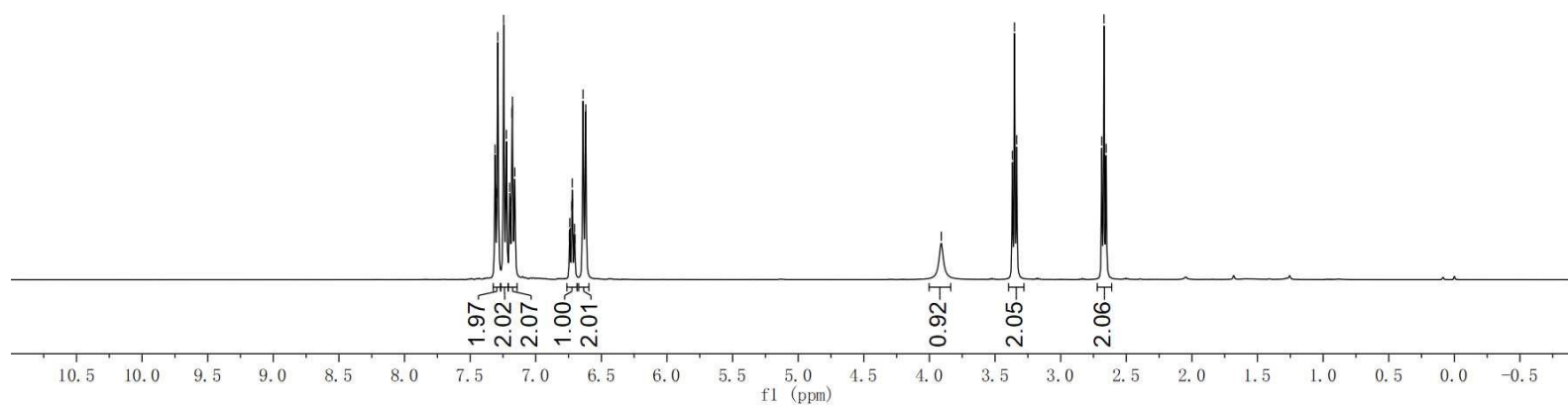
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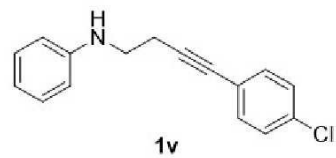




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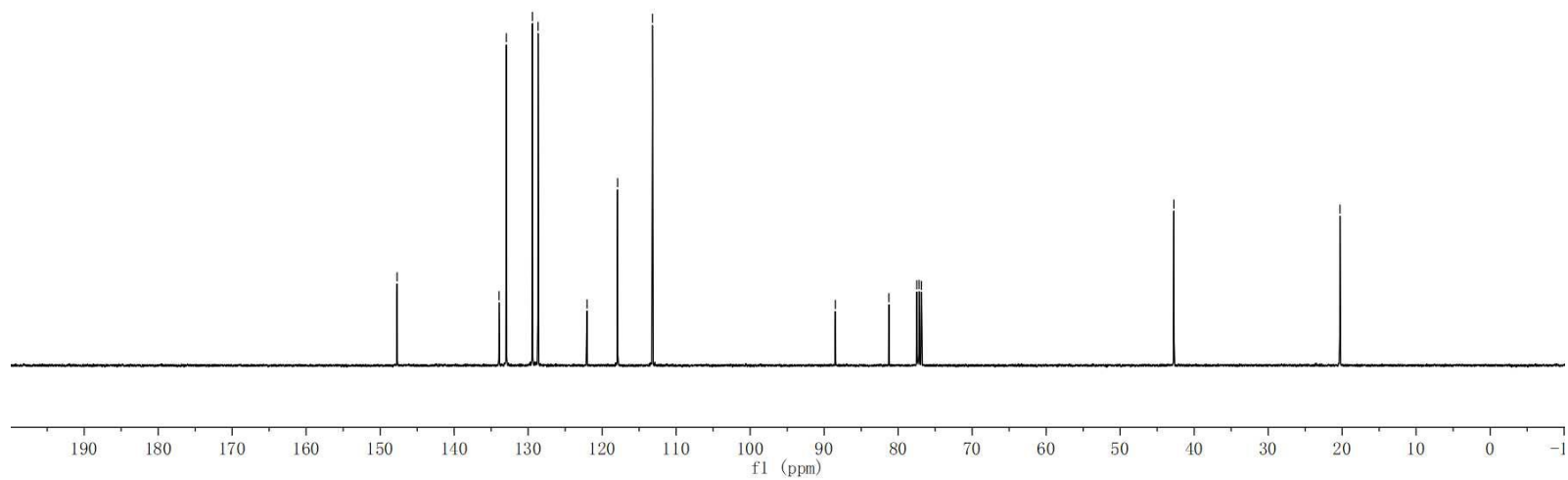
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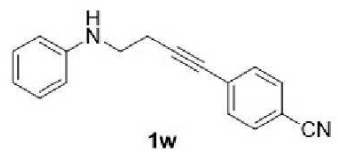
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—76.84

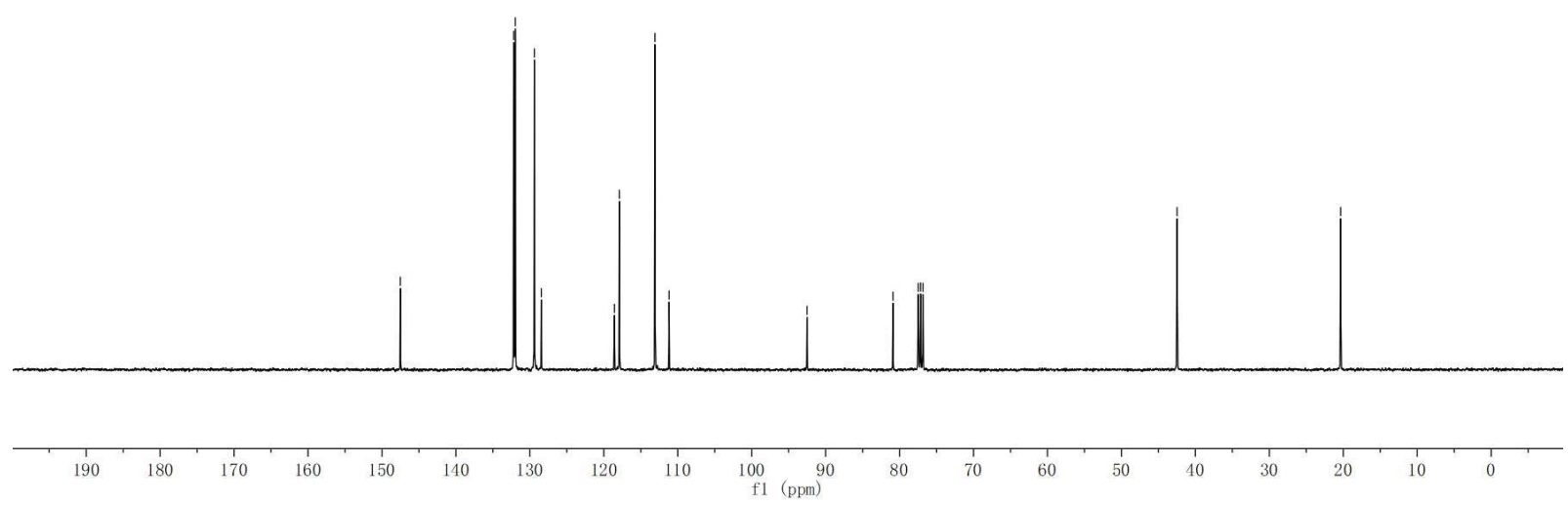
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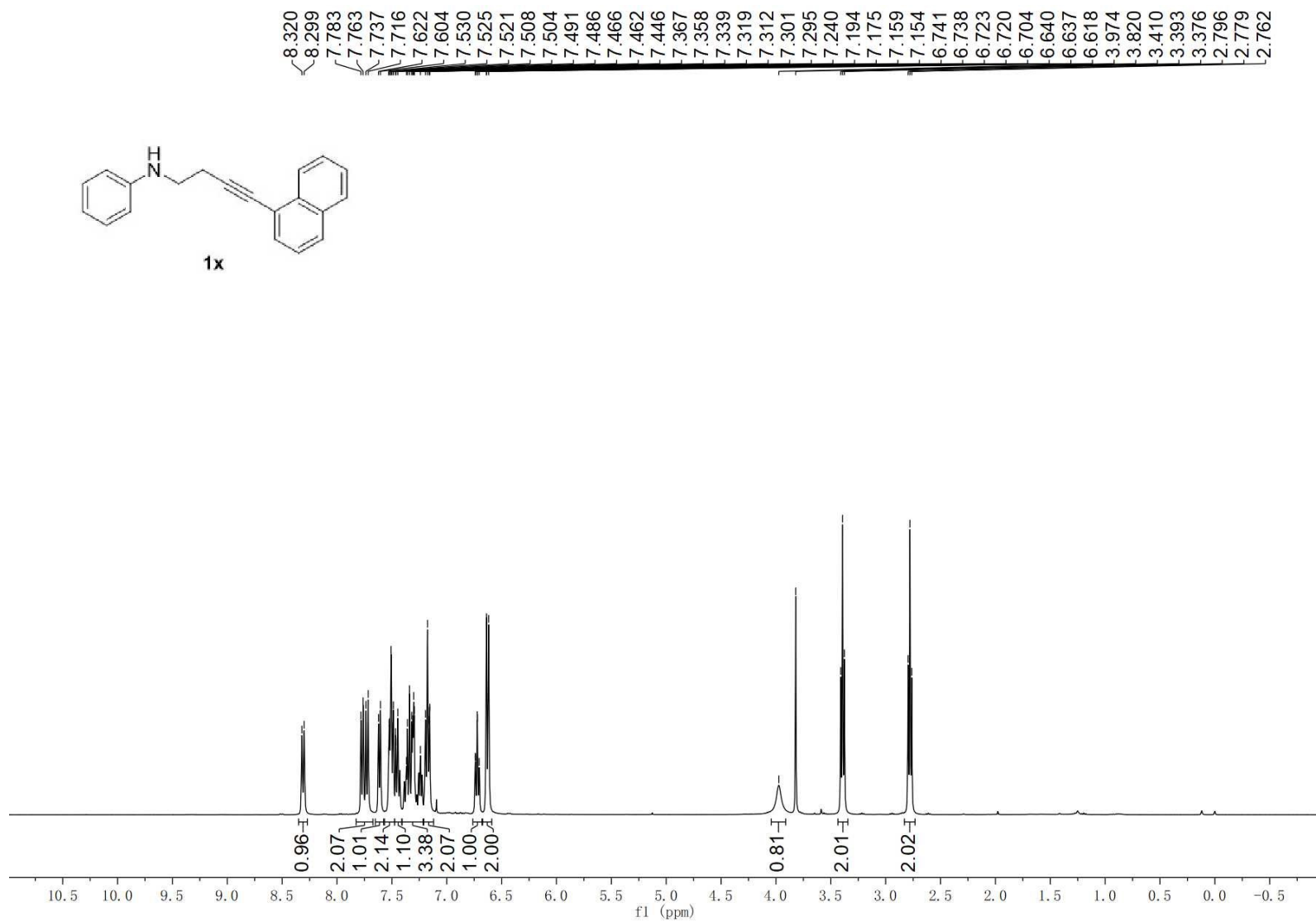
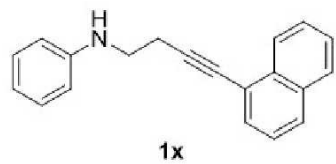
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131.97
129.39
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113.08
111.18
92.51
80.89
77.48
77.16
76.84
42.47
20.34

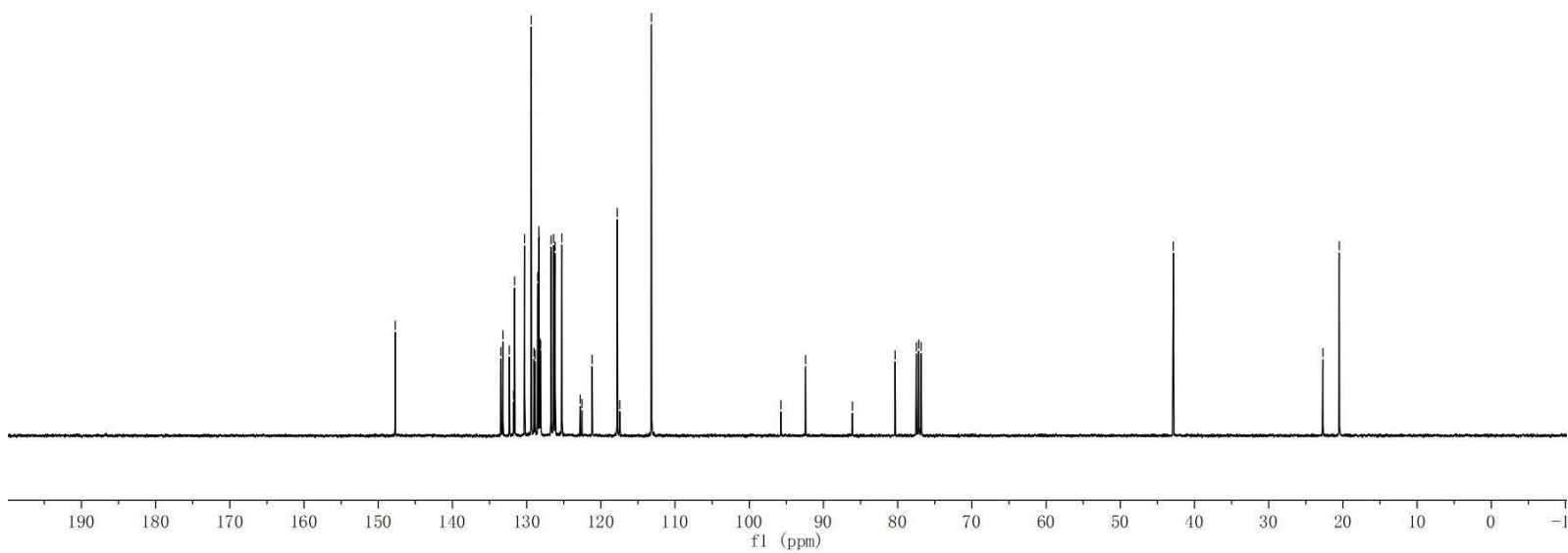
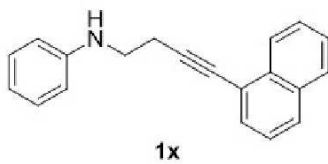


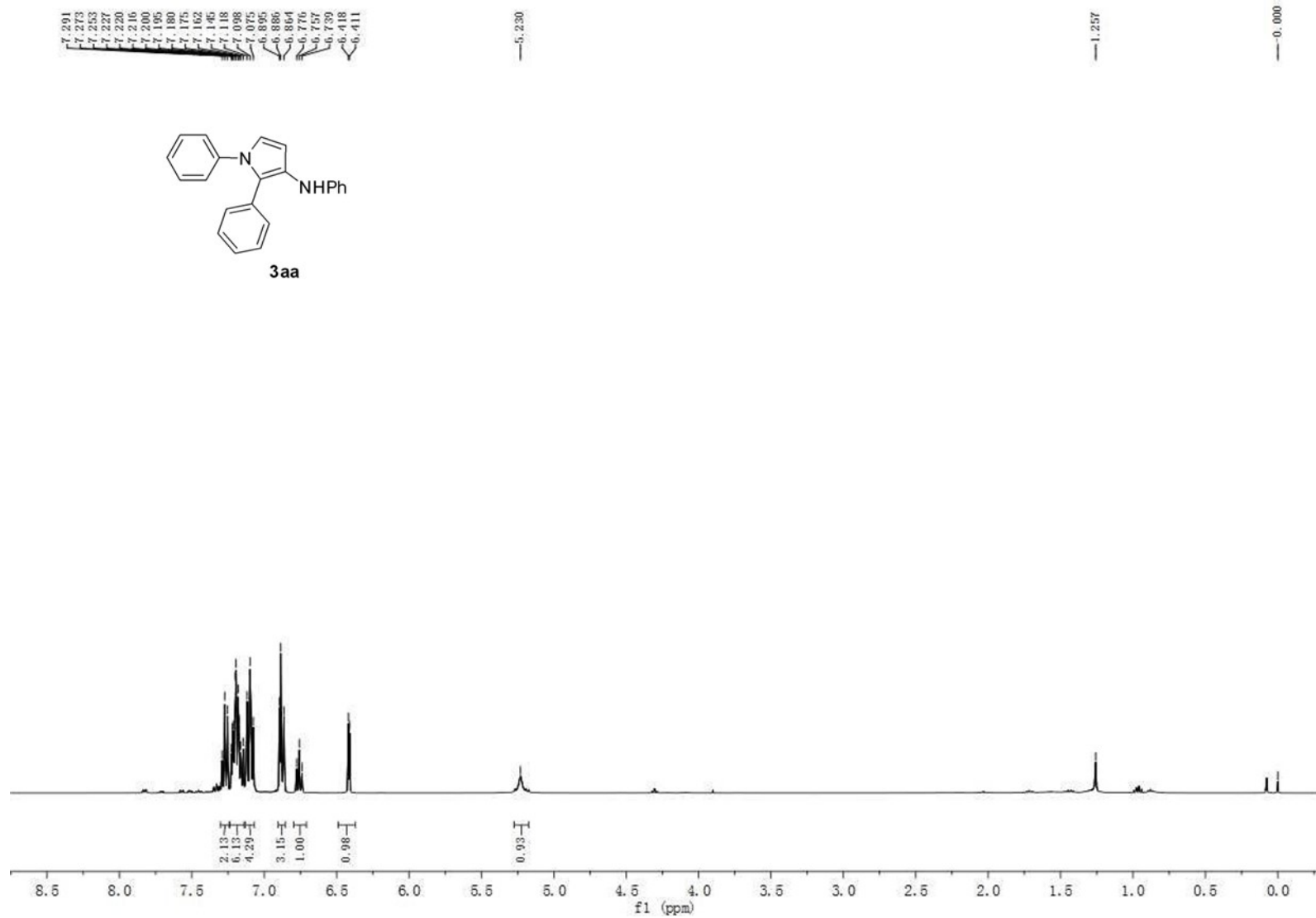


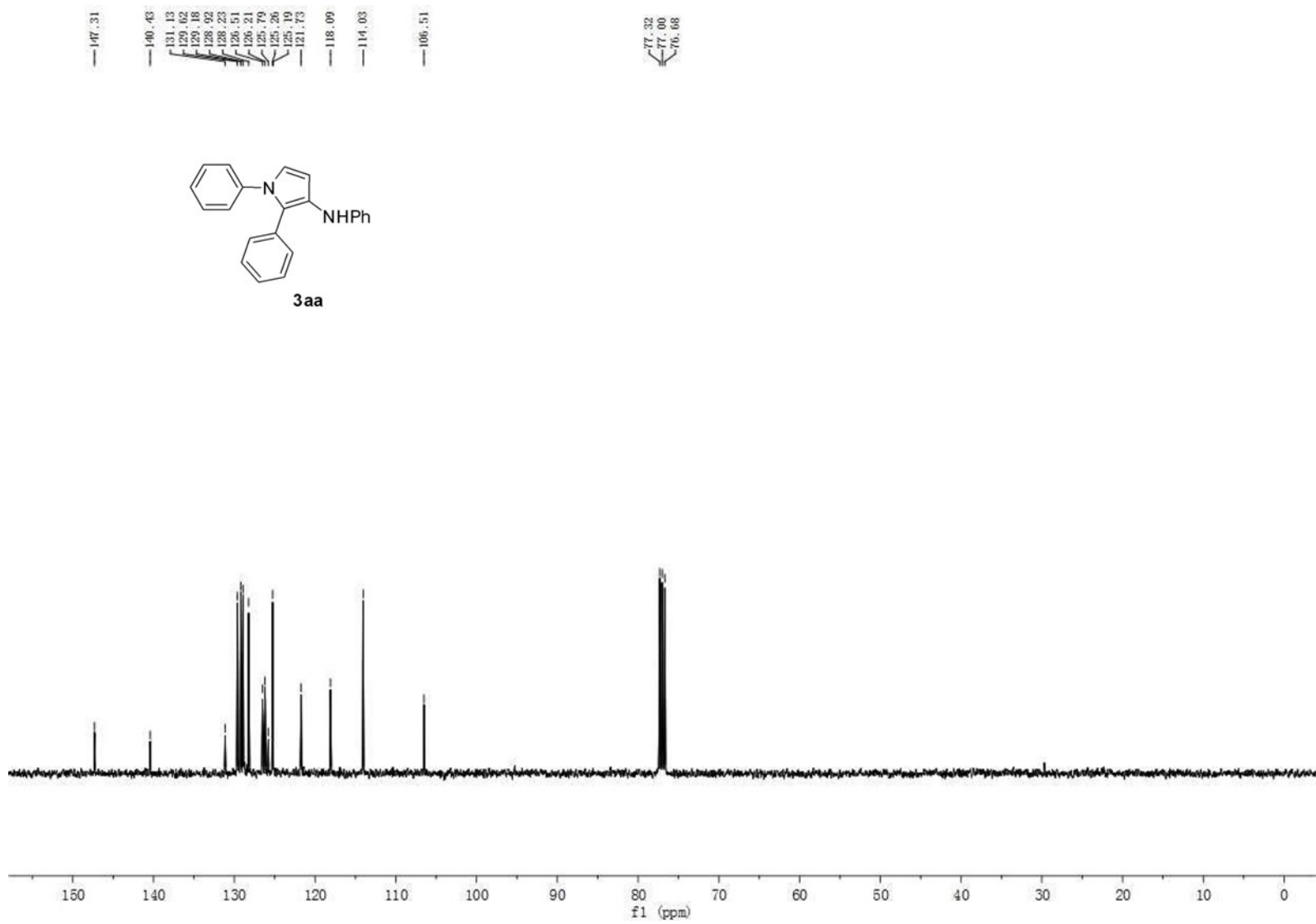
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128.25
128.16
128.13
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126.36
126.17
125.25
122.78
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113.18
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77.48
77.16
76.84

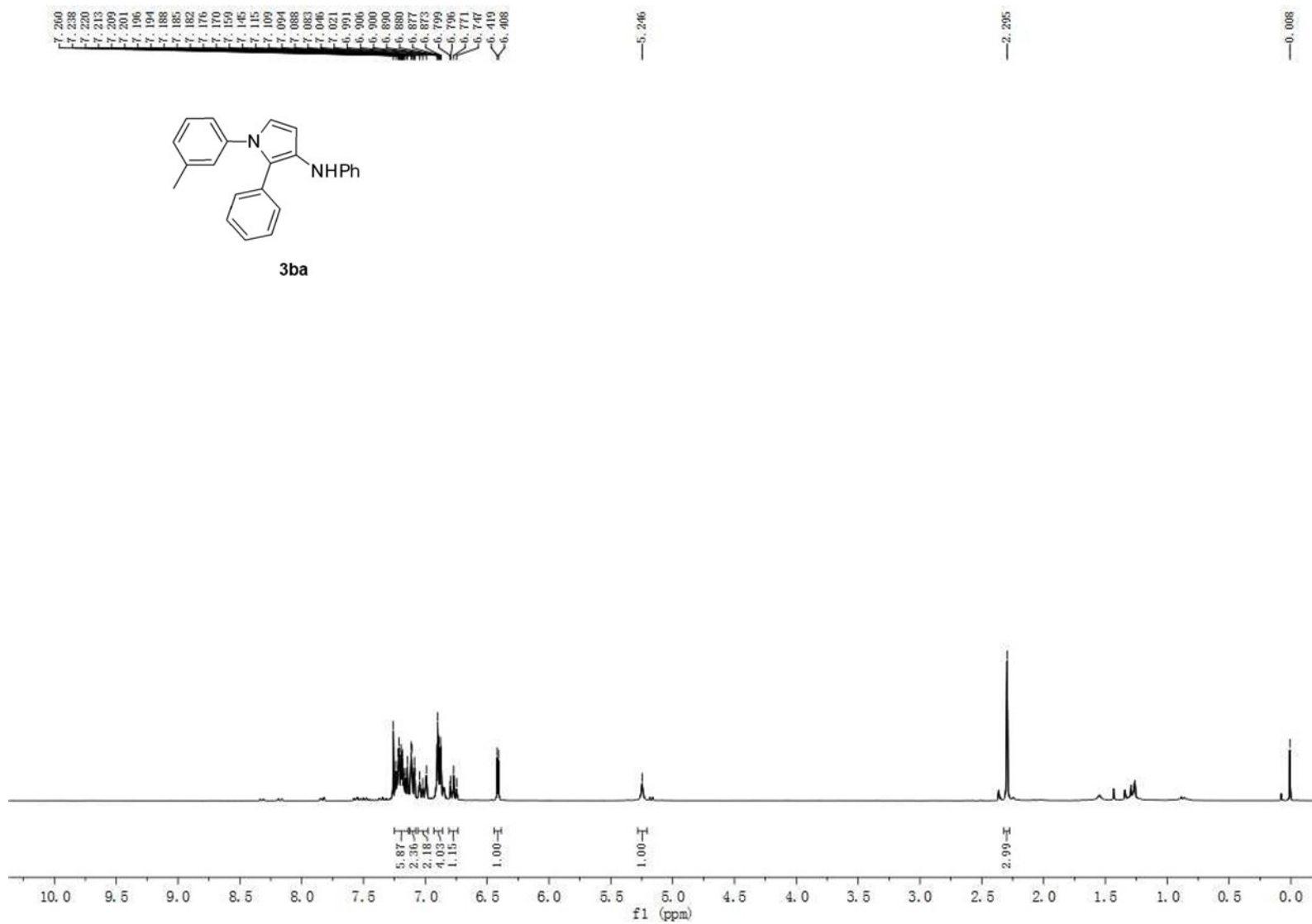
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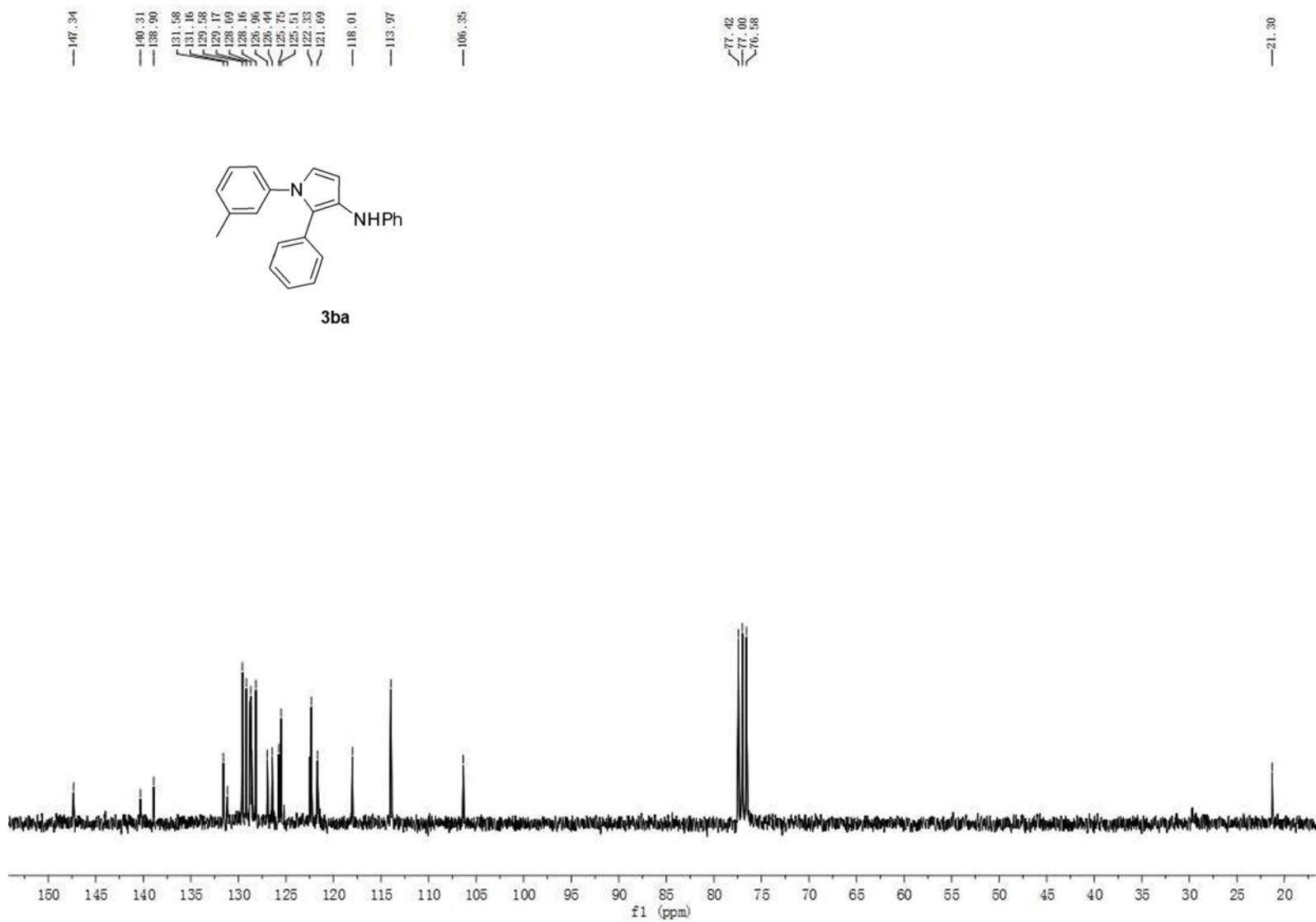
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~20.49

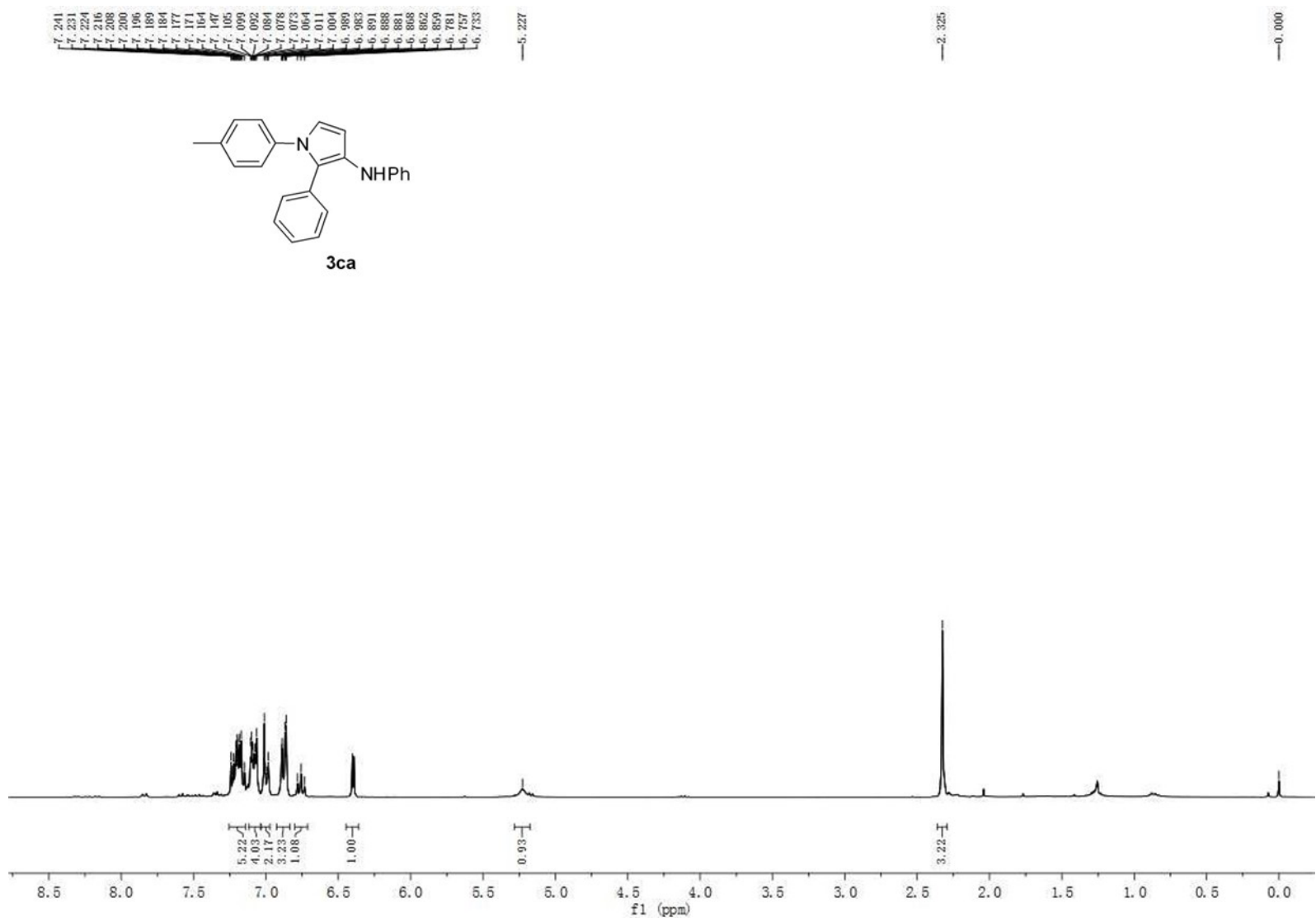


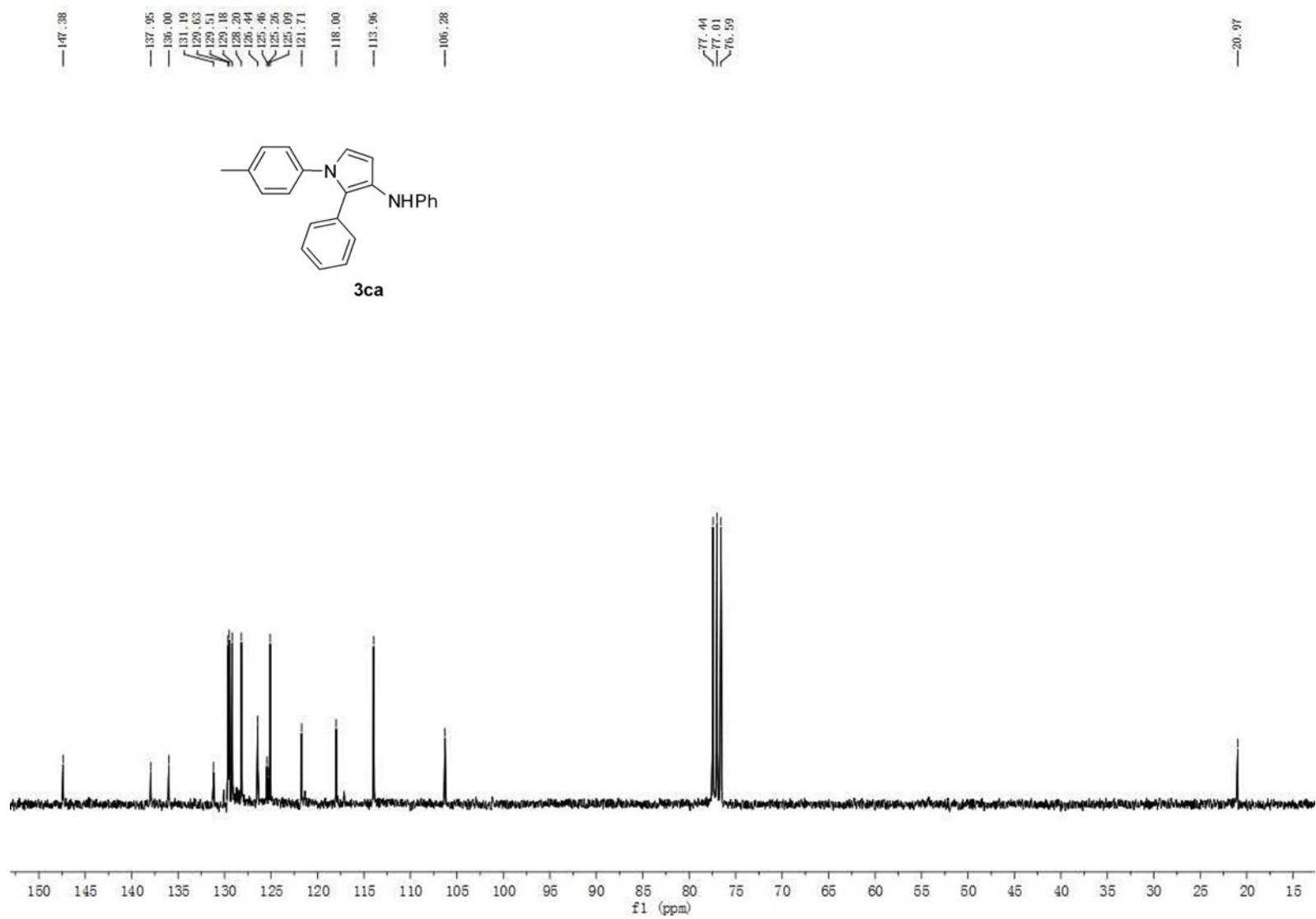


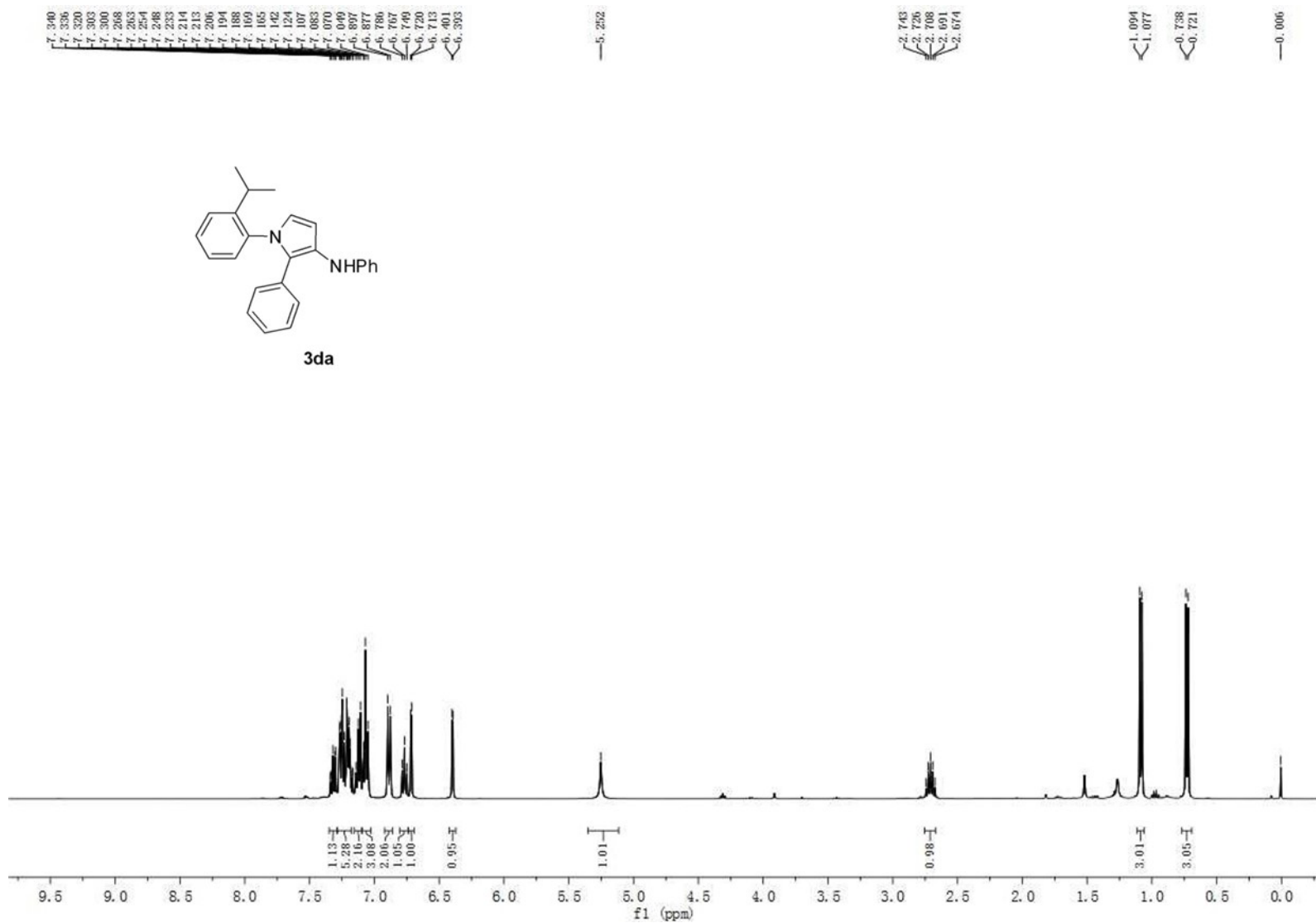


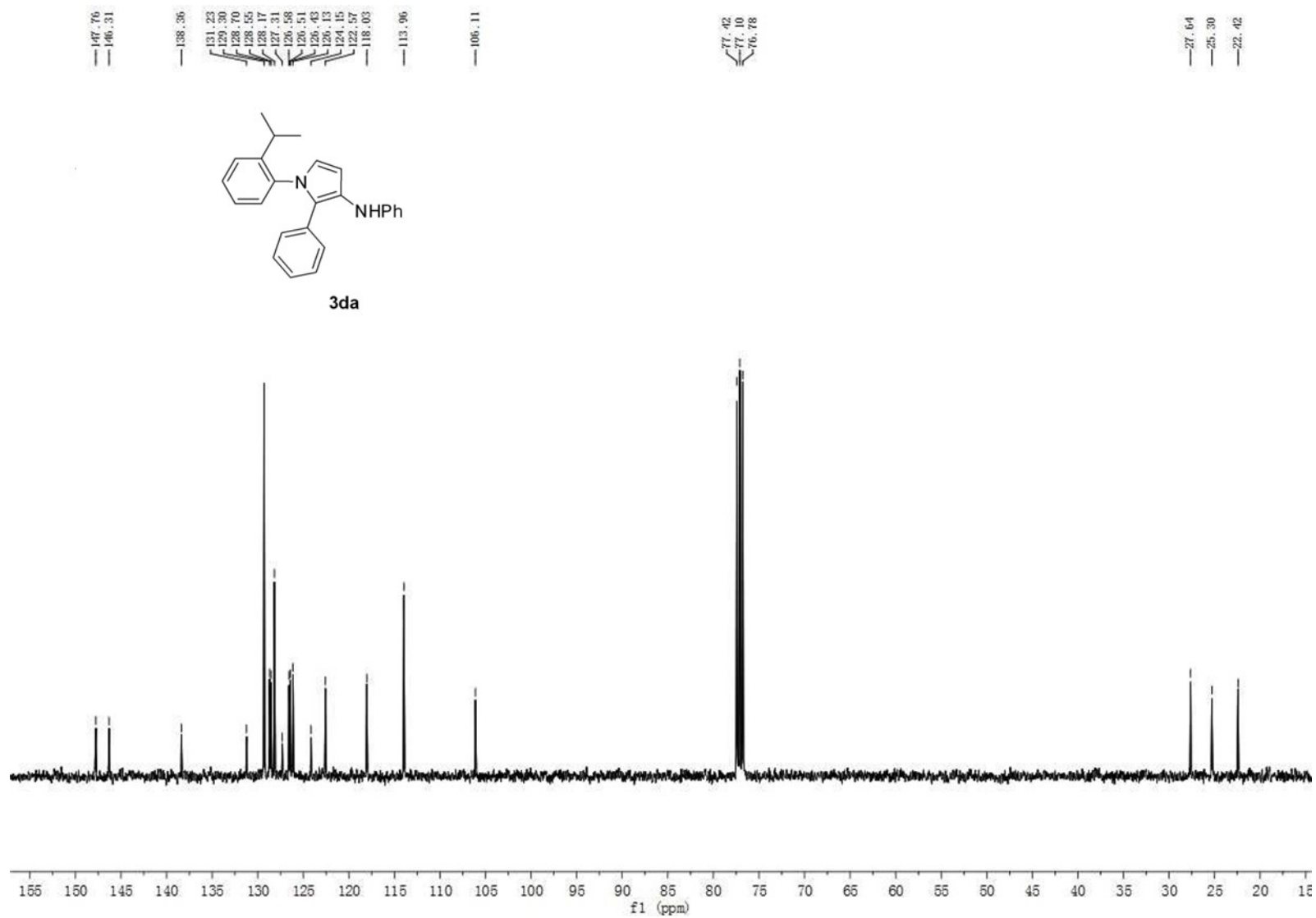


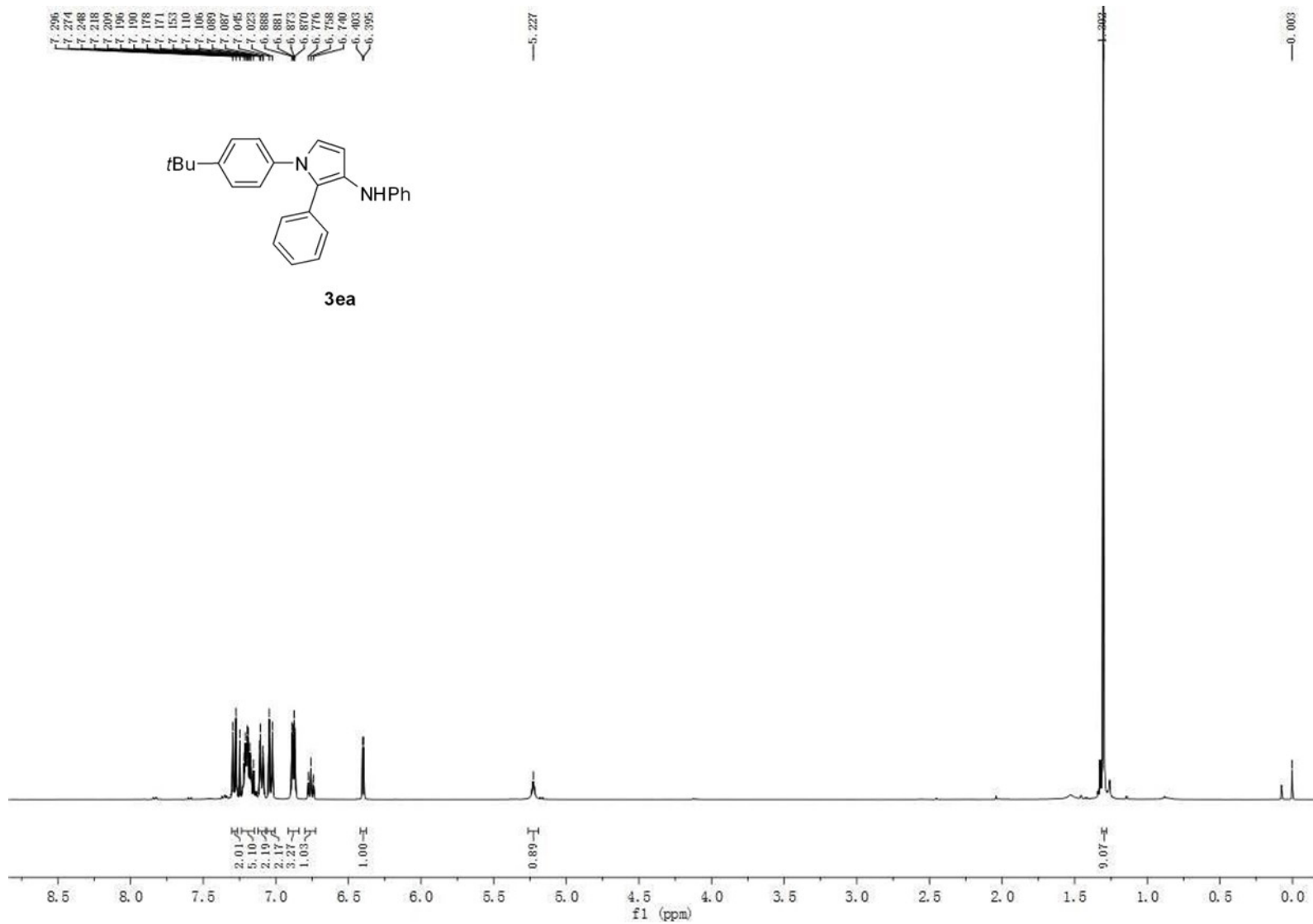


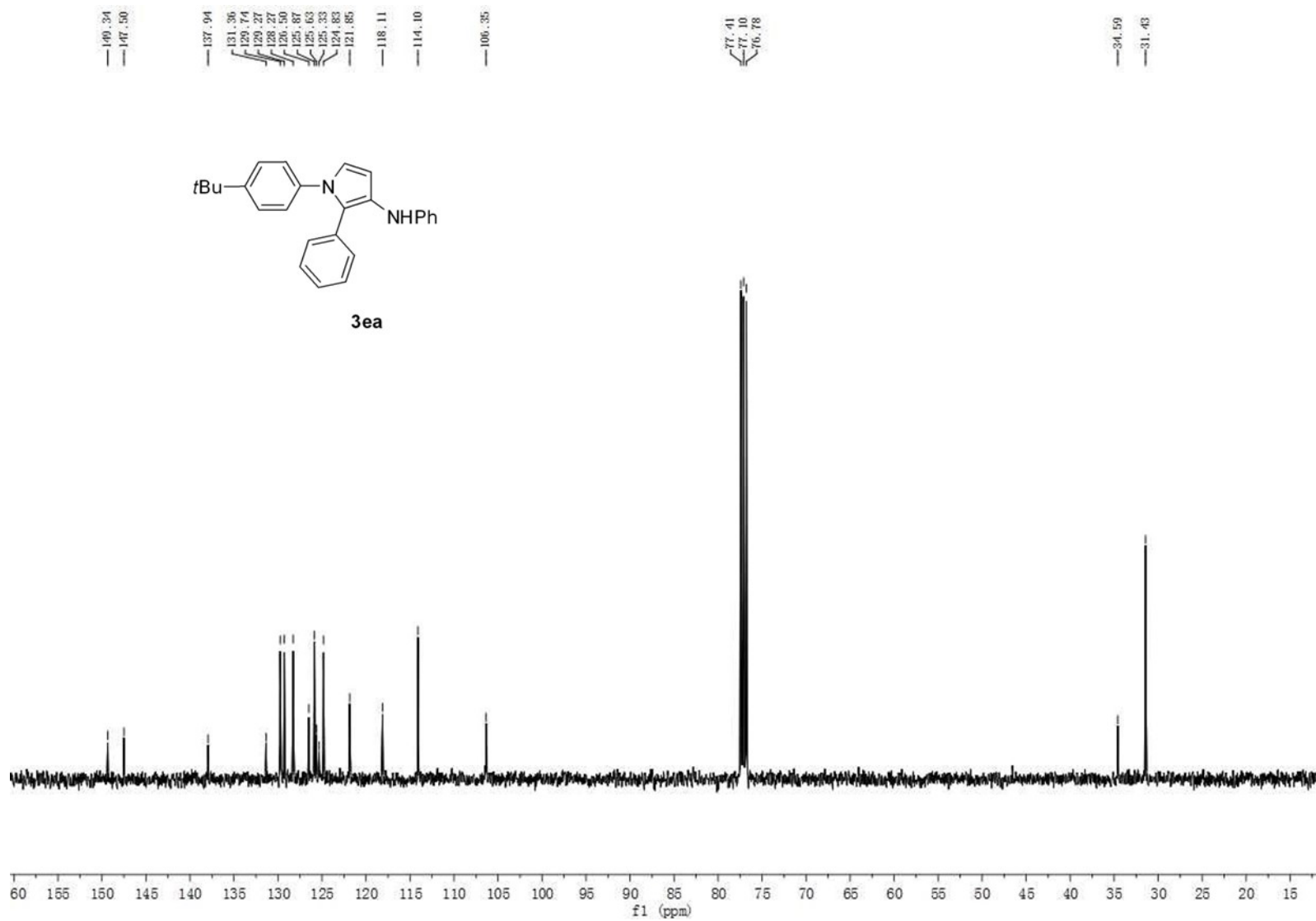


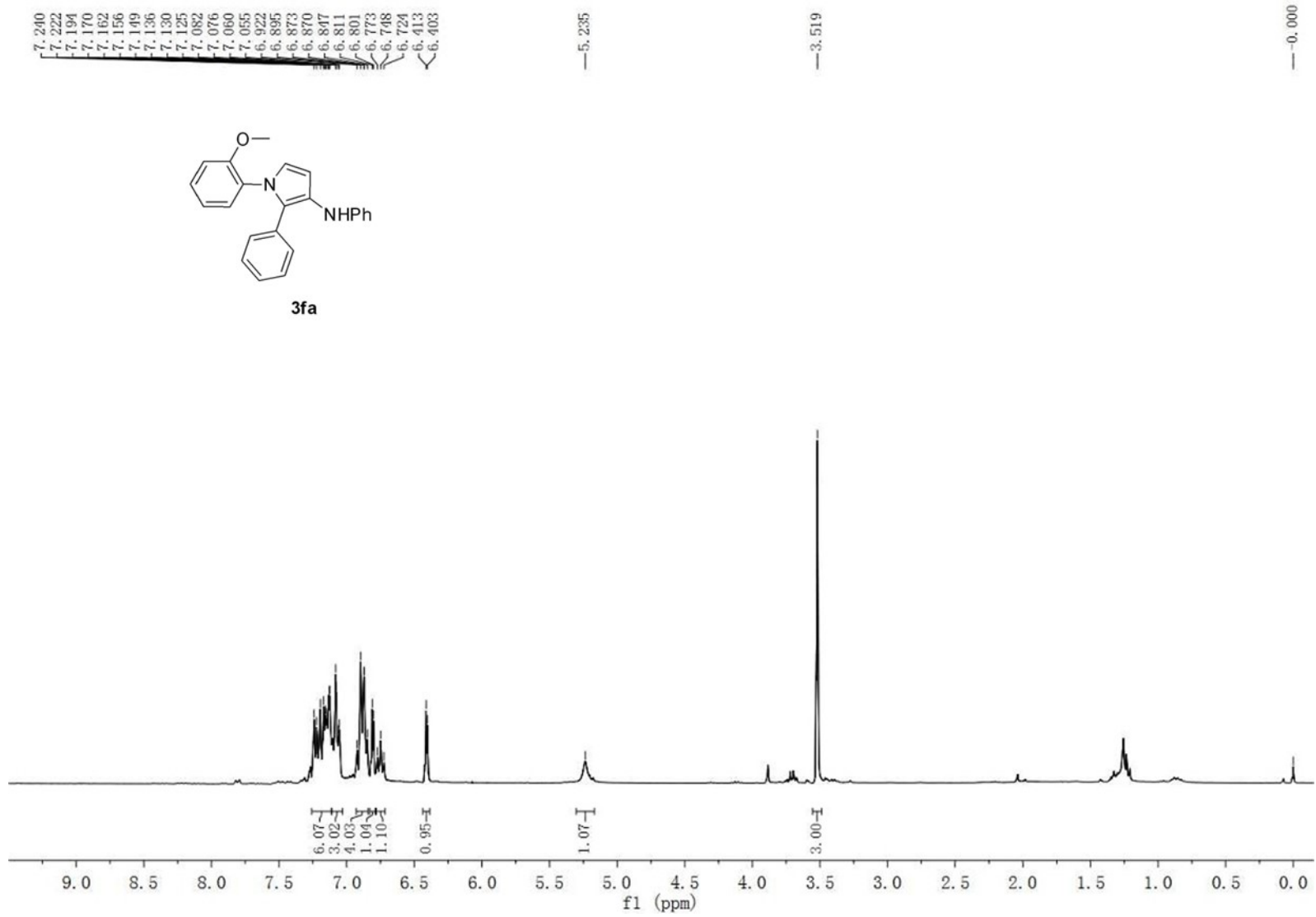


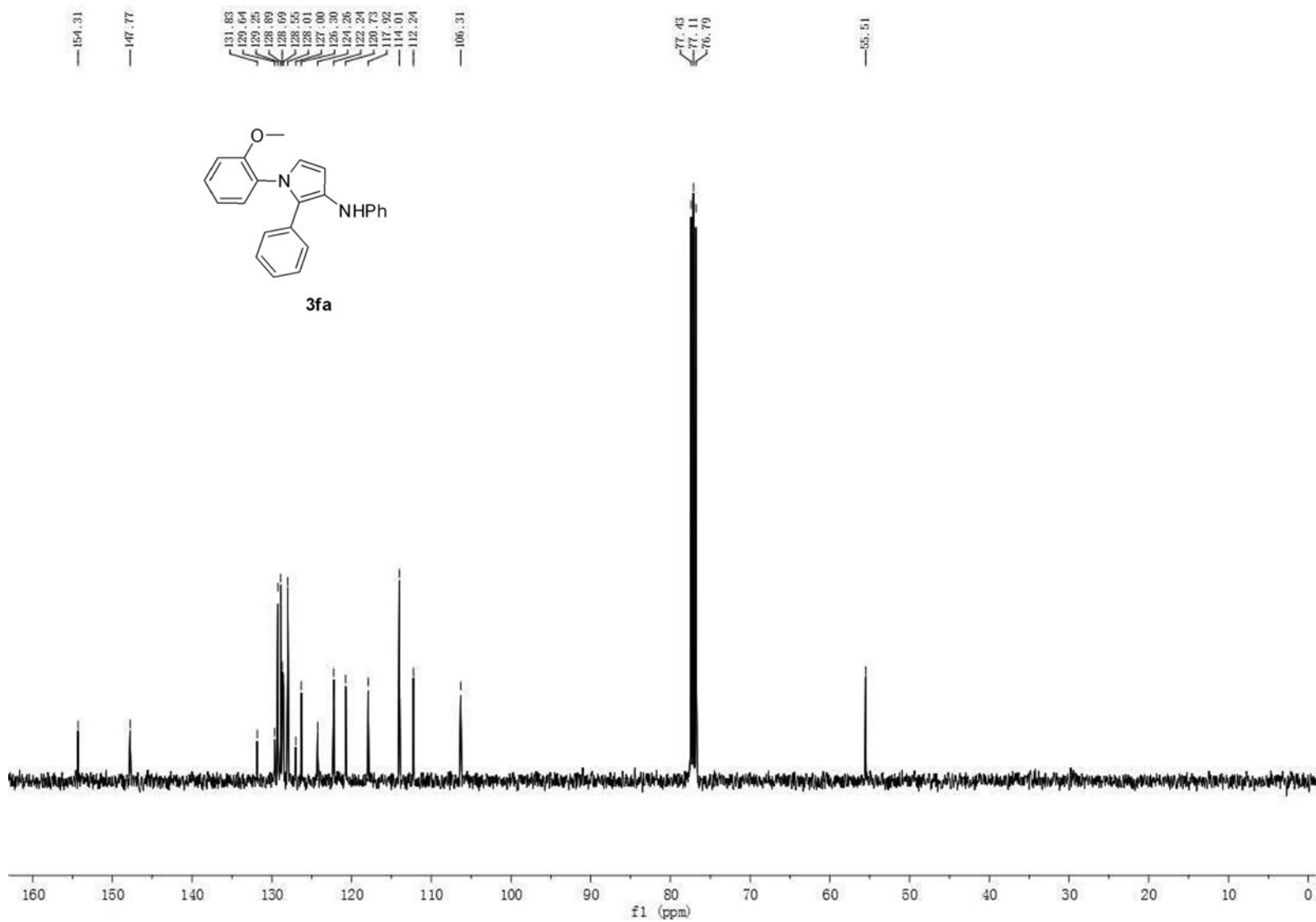








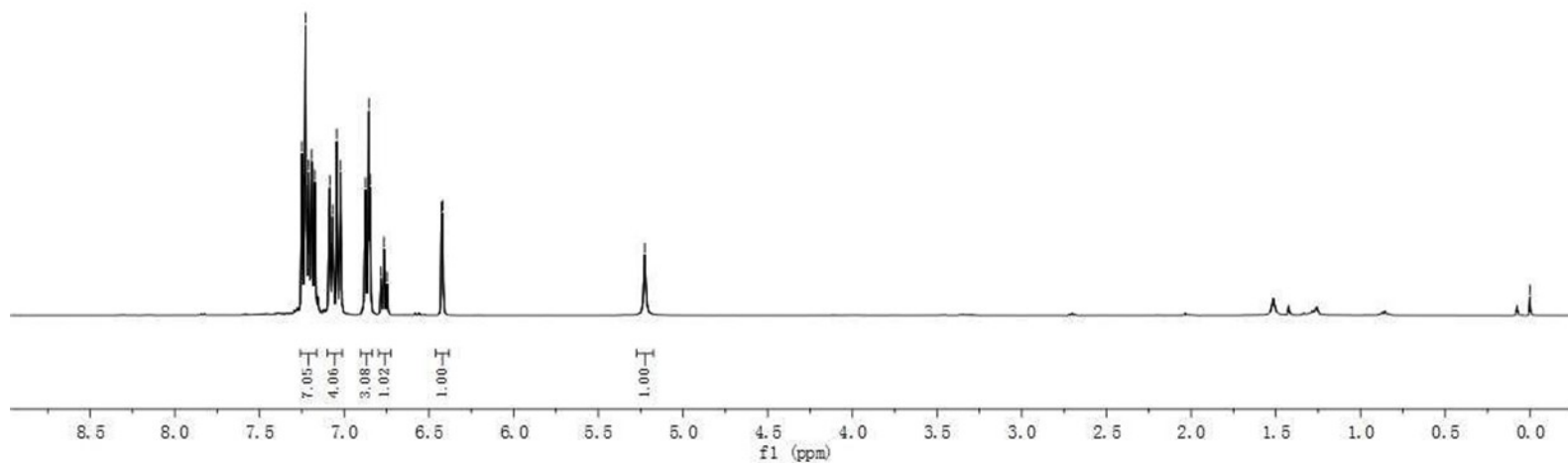
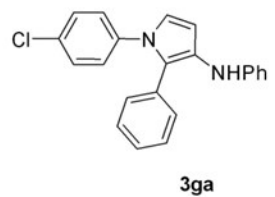


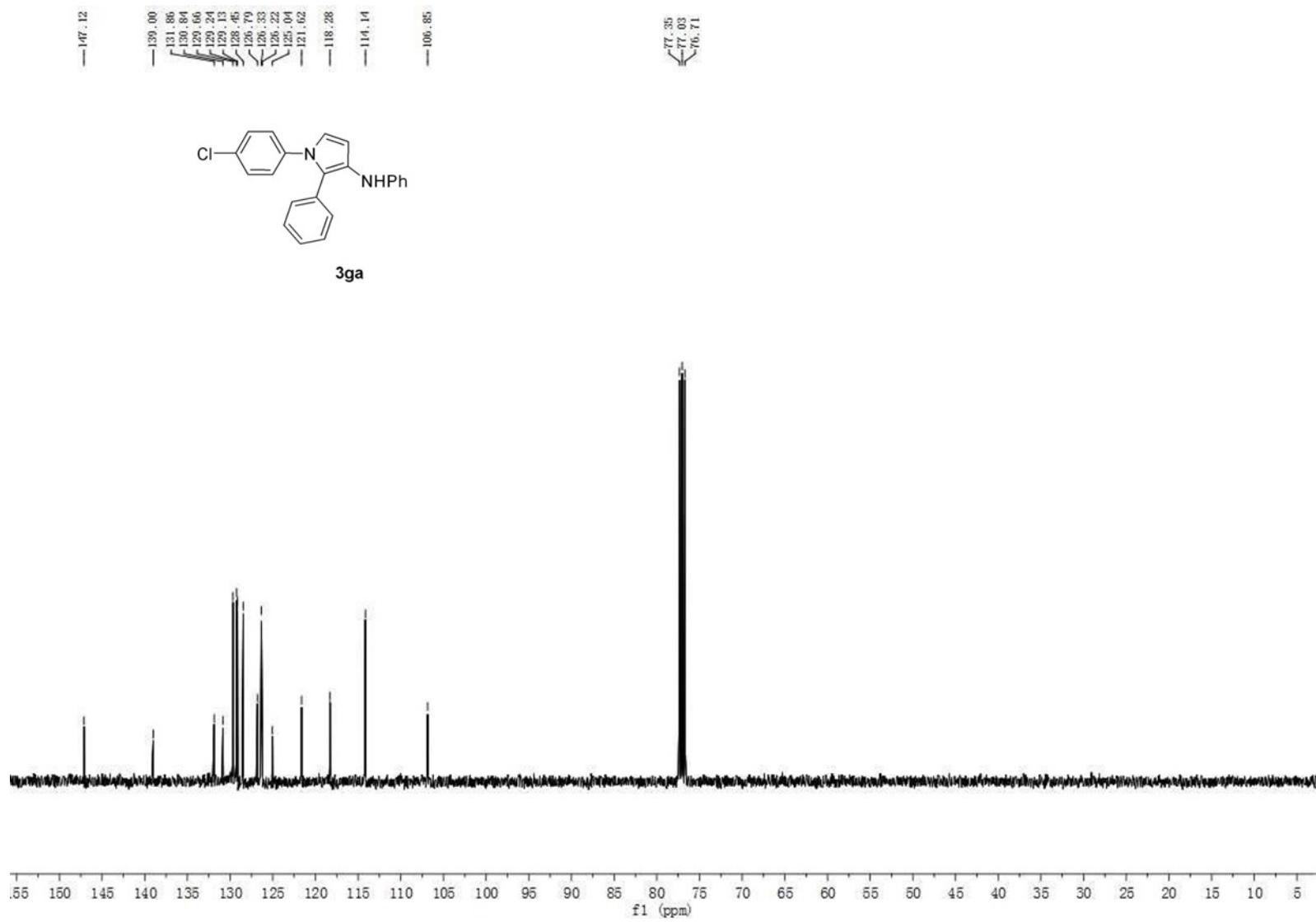


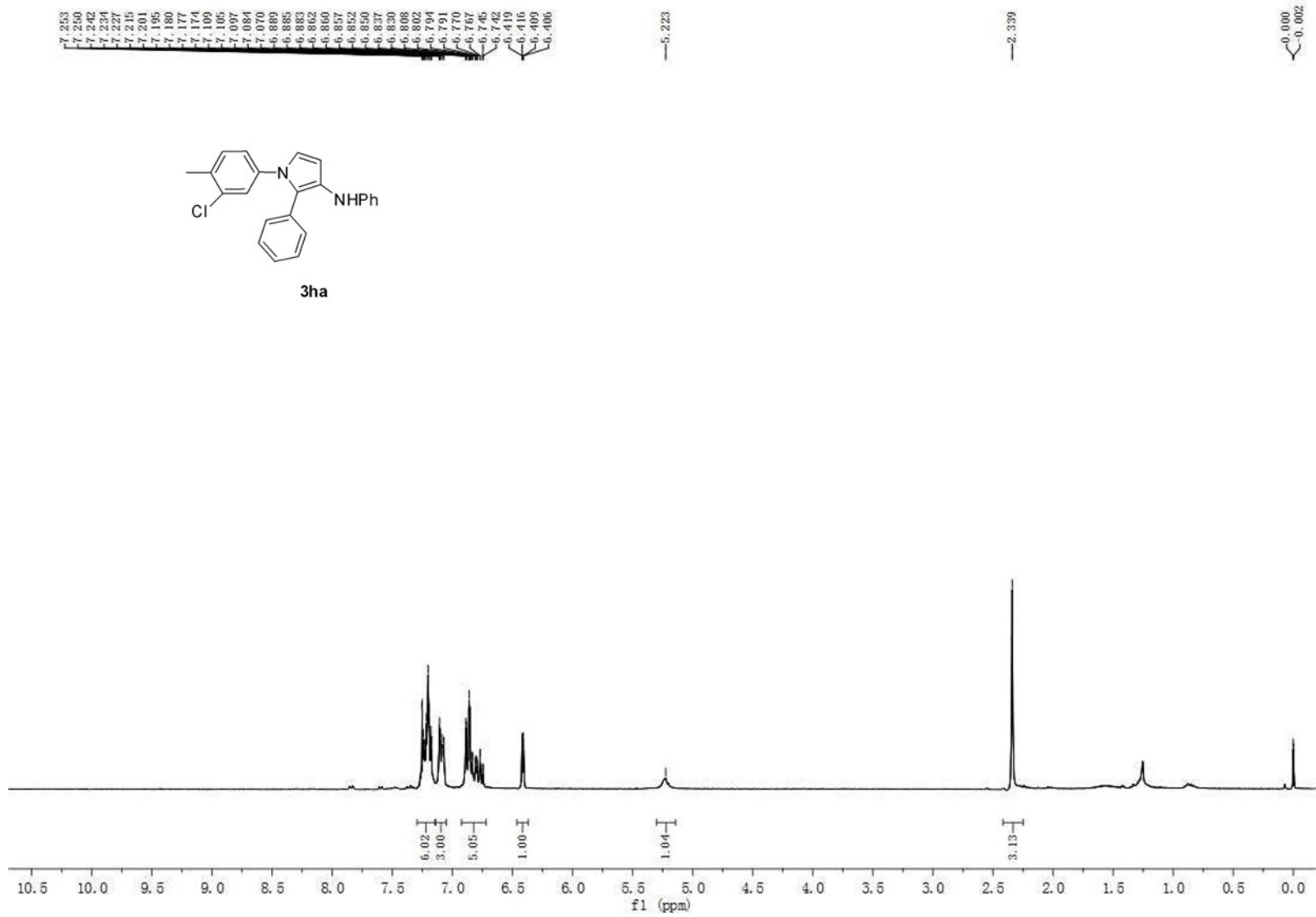
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7.229
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7.210
7.192
7.179
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7.089
7.085
7.068
7.044
7.039
7.027
7.022
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6.853
6.847
6.783
6.765
6.747
6.726
6.718

5.226

0.000





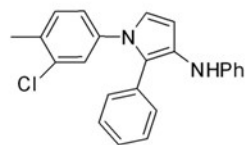


147.90
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122.39
118.83

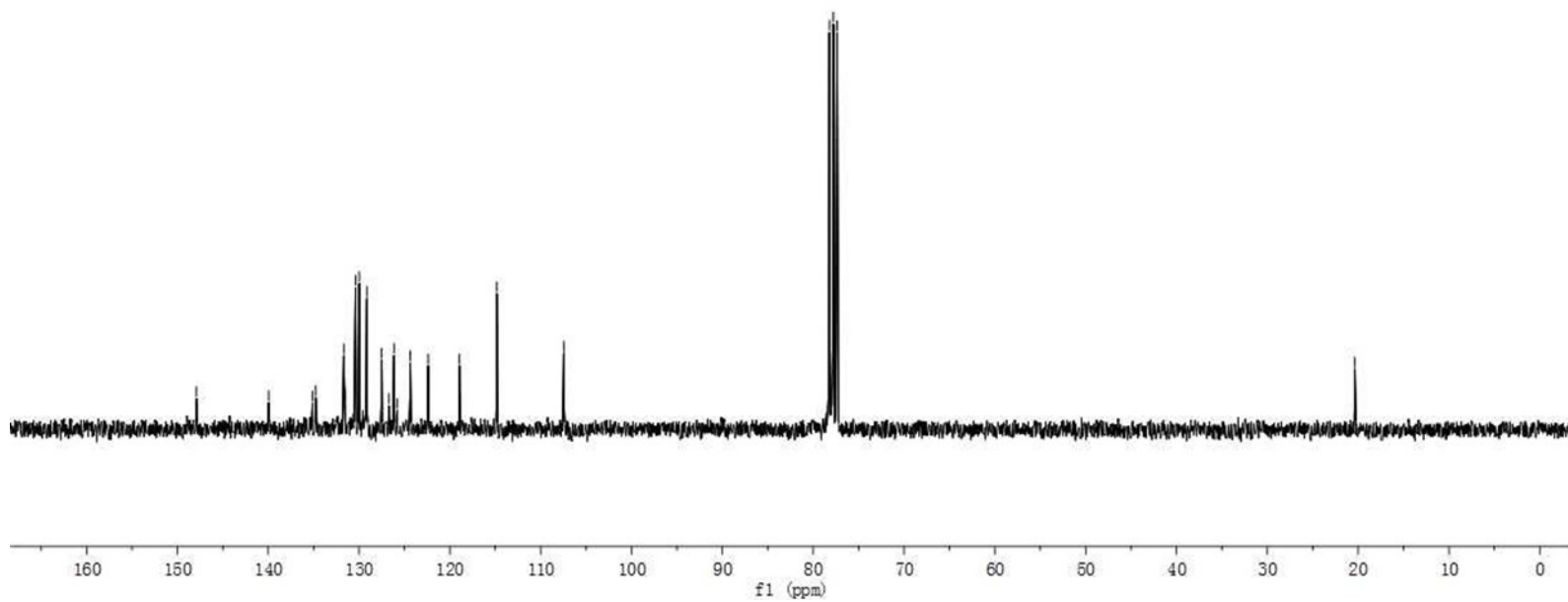
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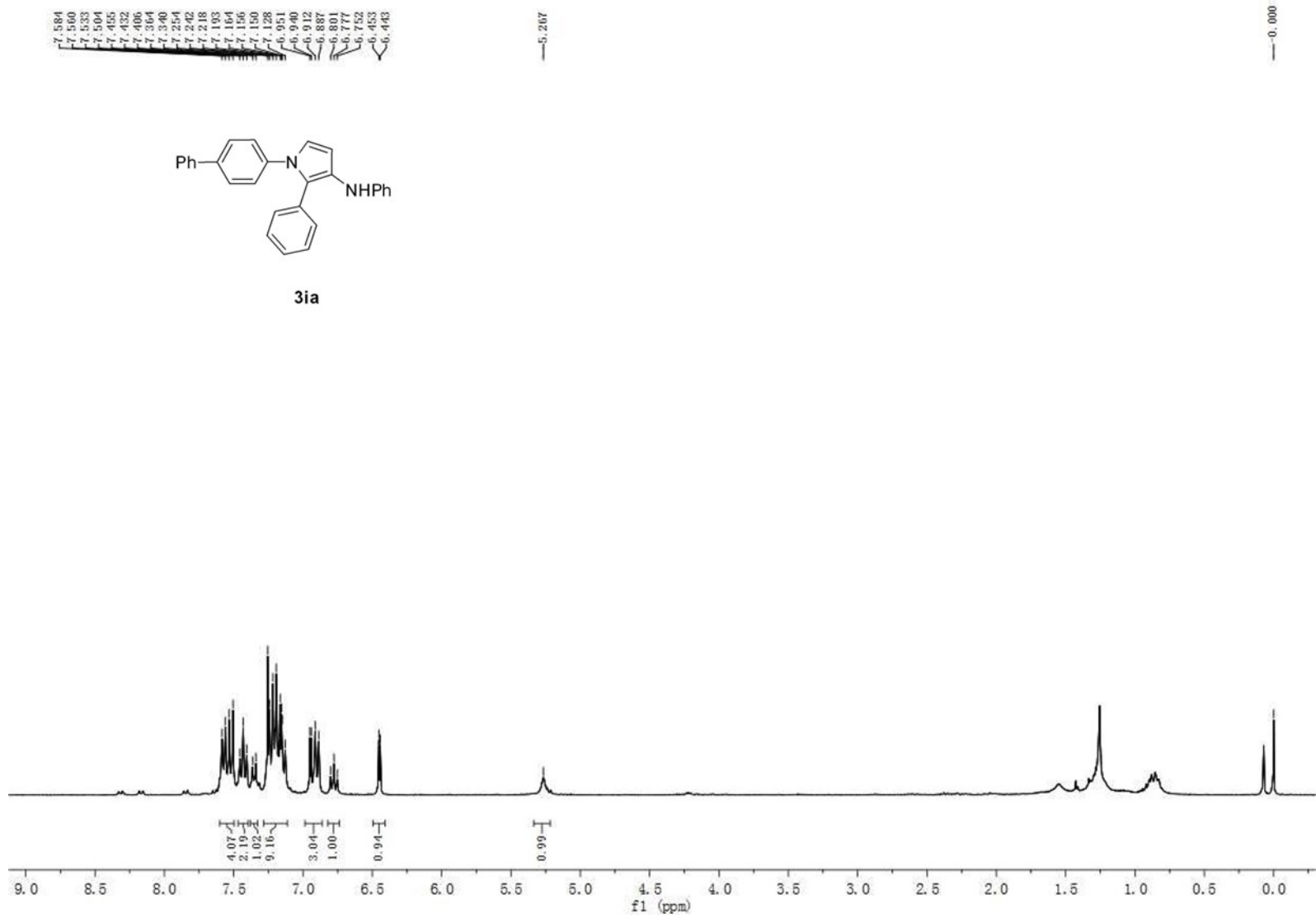
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77.78
77.35

20.36



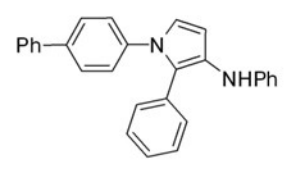
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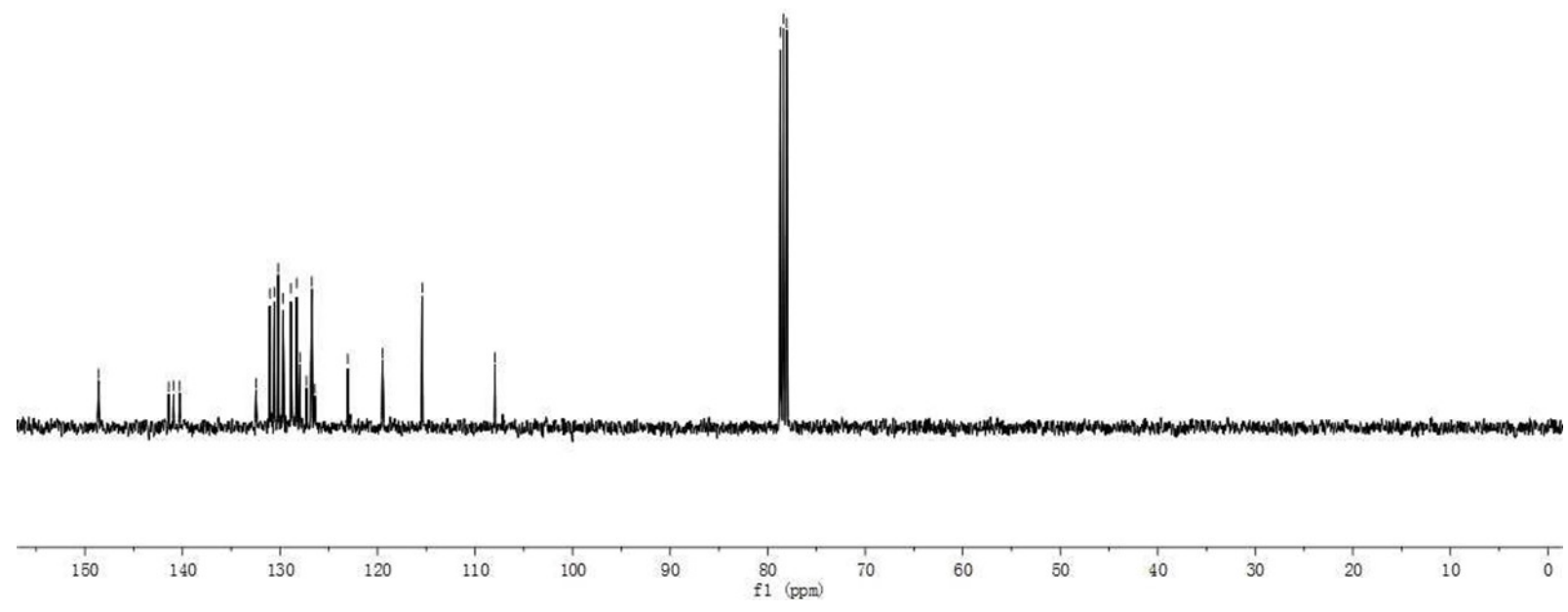


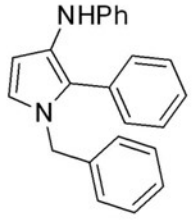
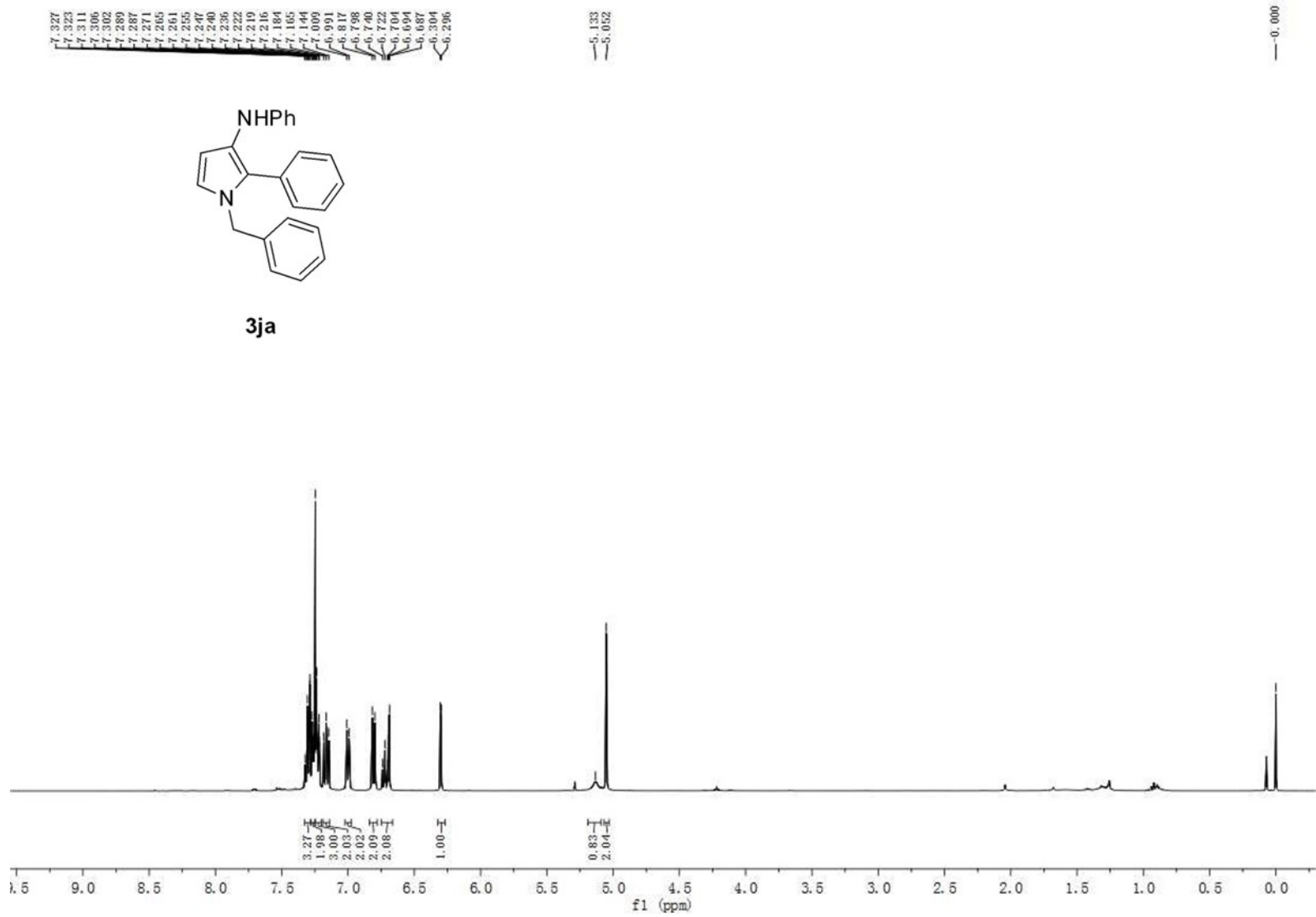
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140.93
140.28
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130.58
130.19
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128.28
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126.63
119.49
115.41
107.96

78.69
78.37
78.05

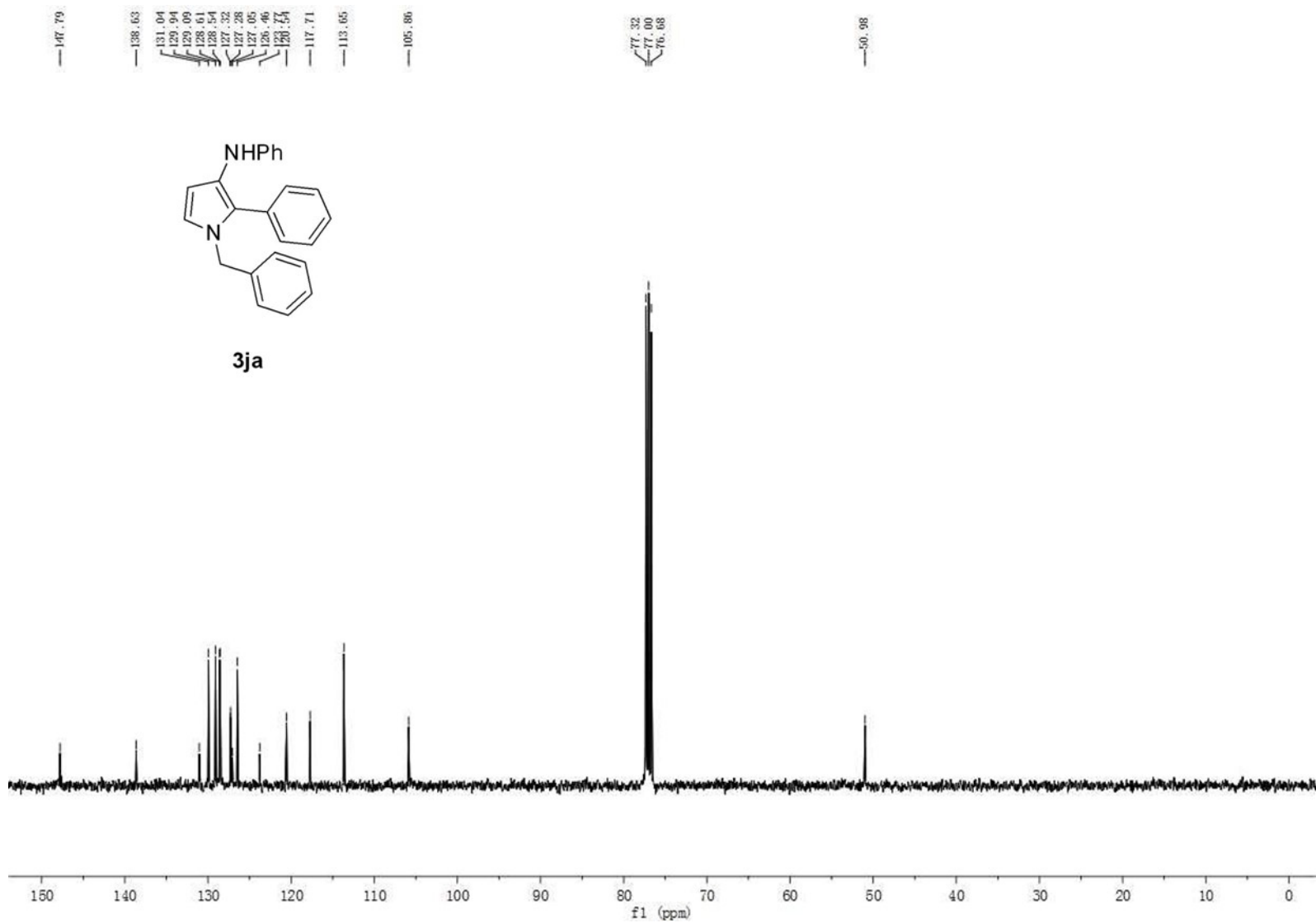


3ia





3ja



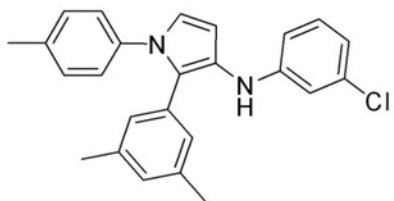
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7.028
7.008
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6.854
6.788
6.679
6.386
6.378

5.898

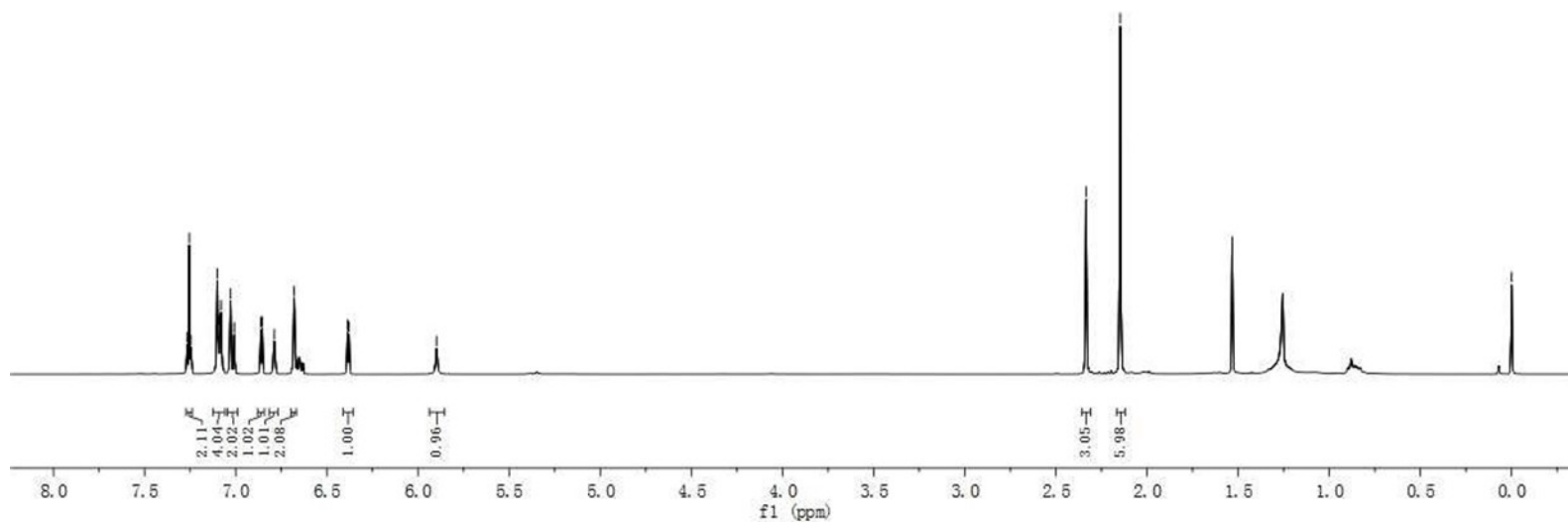
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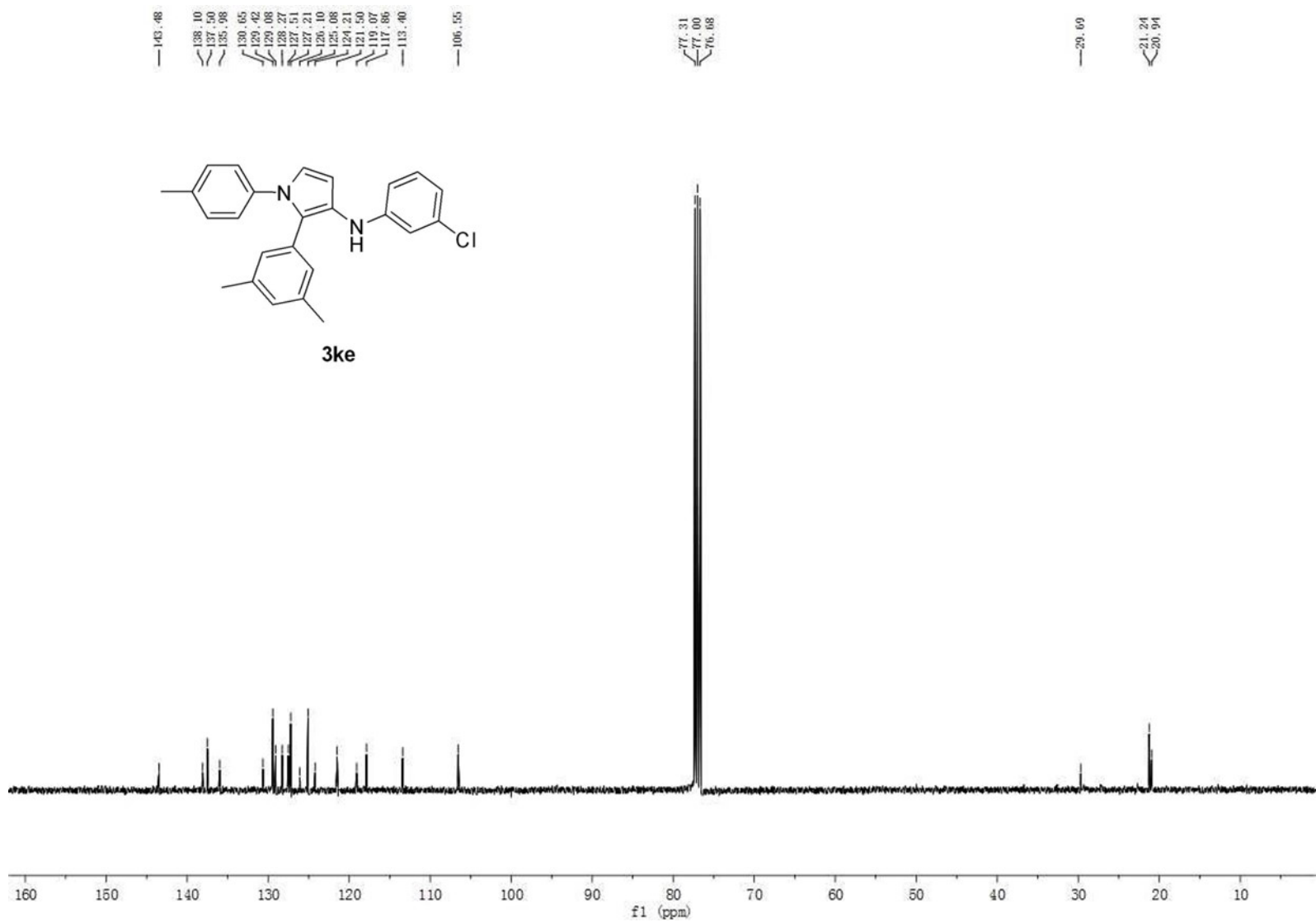
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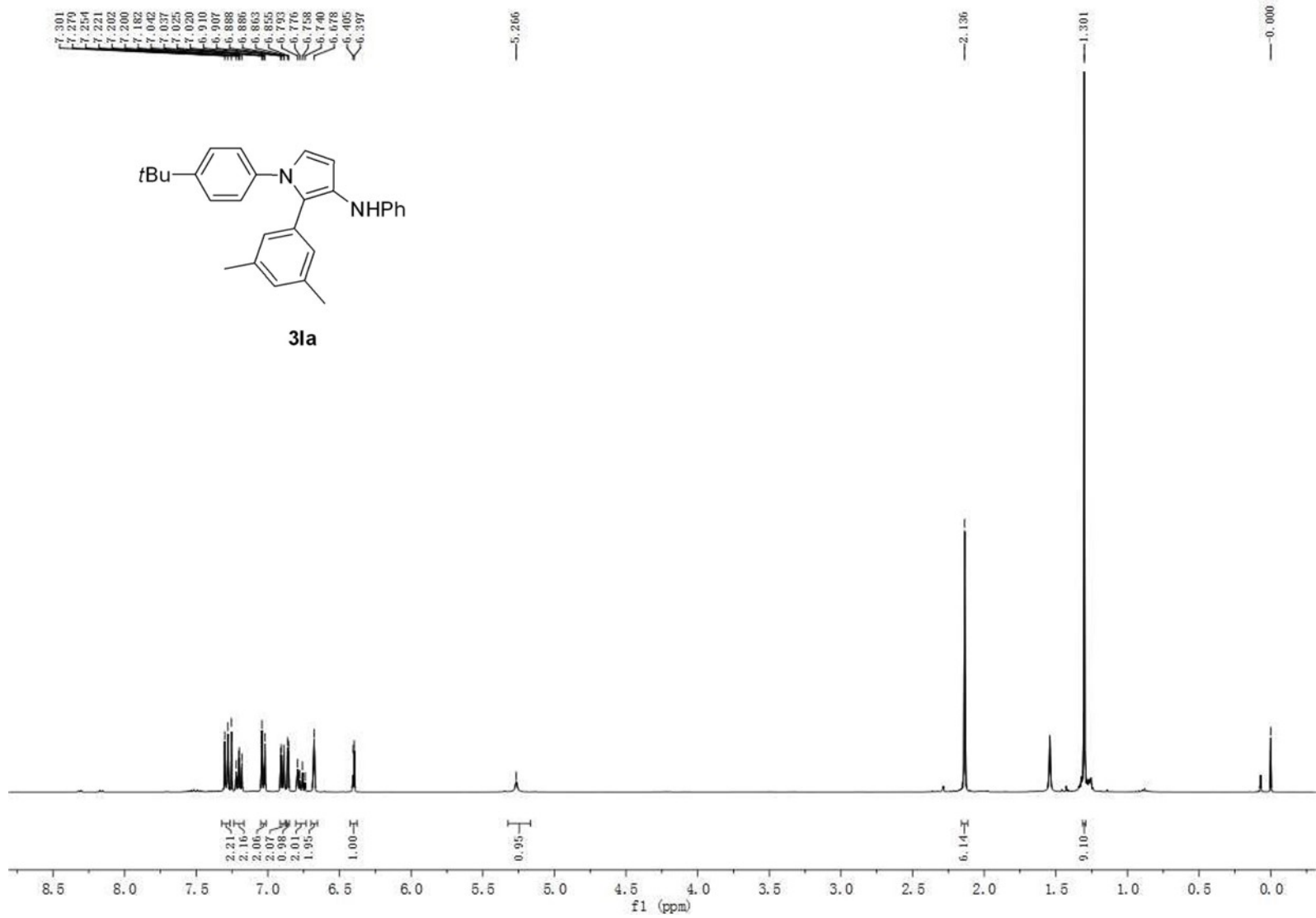
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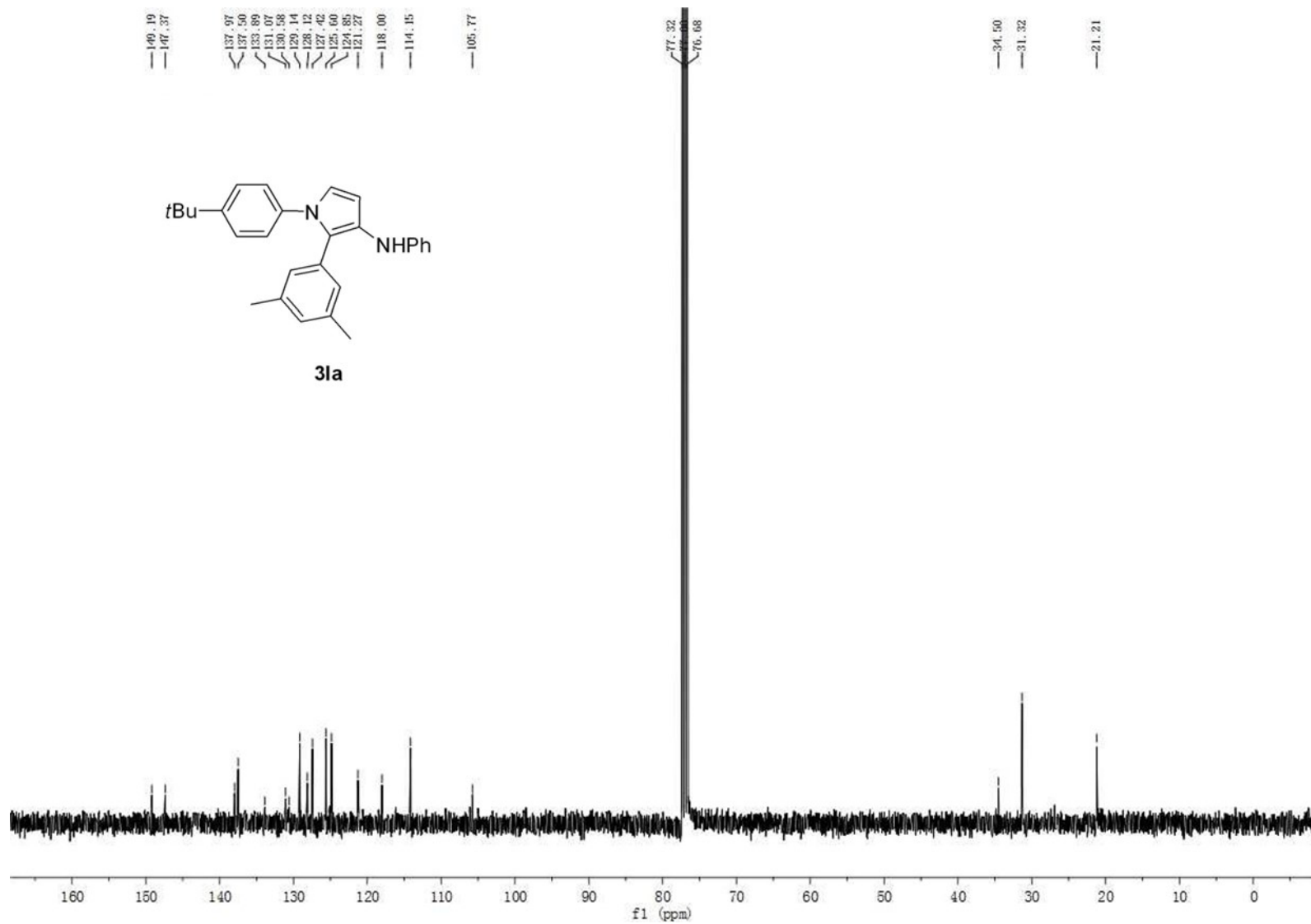


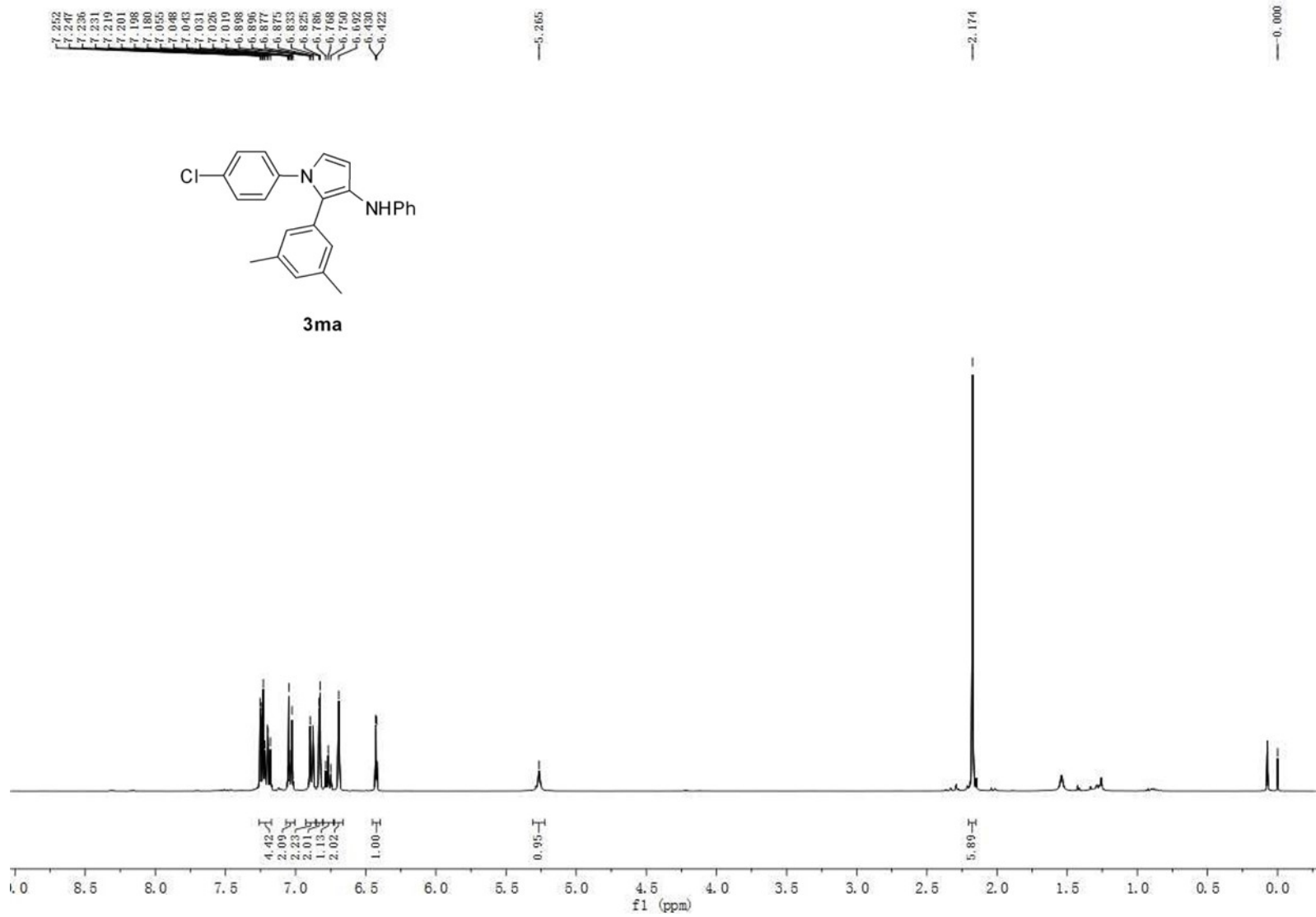
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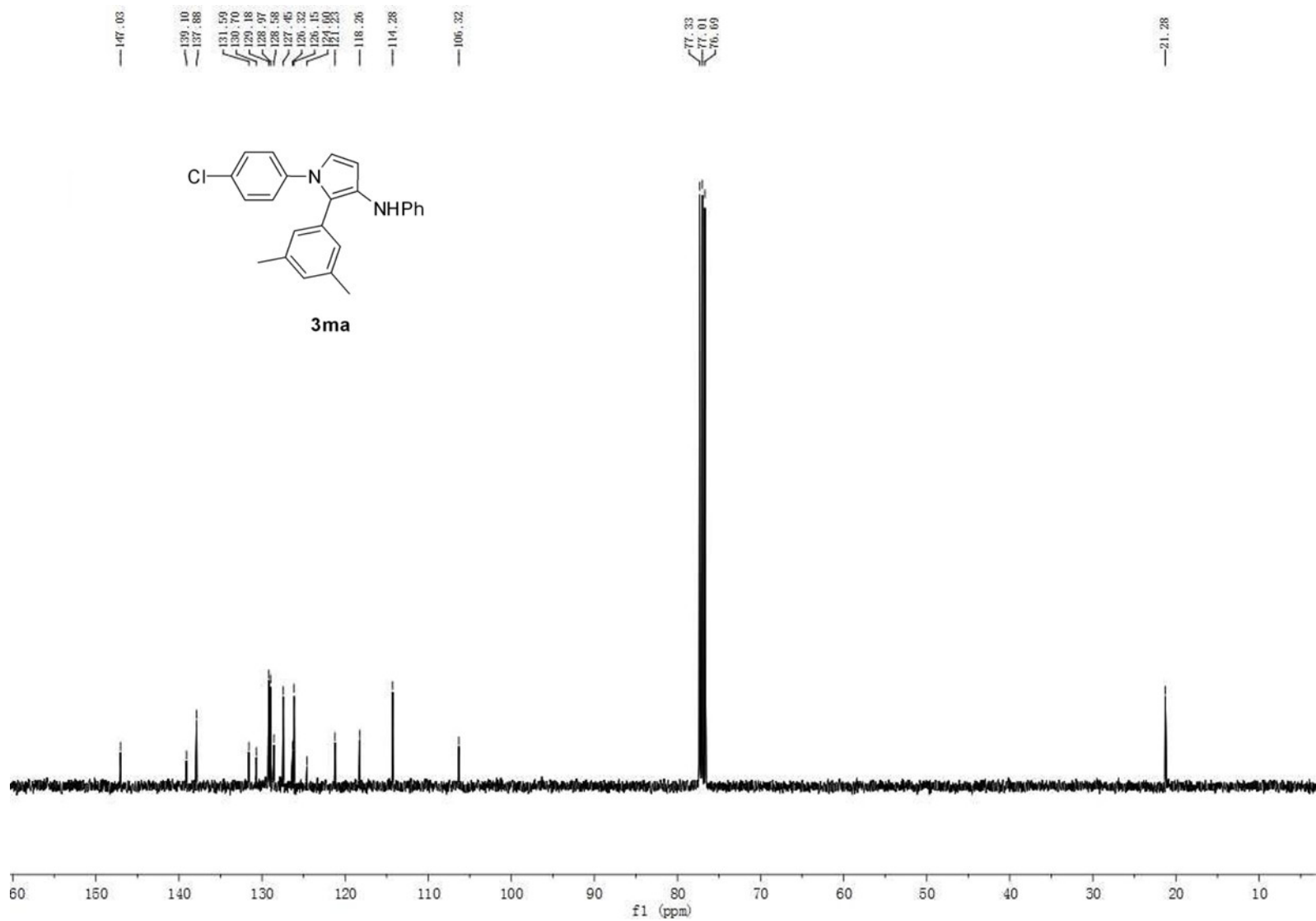


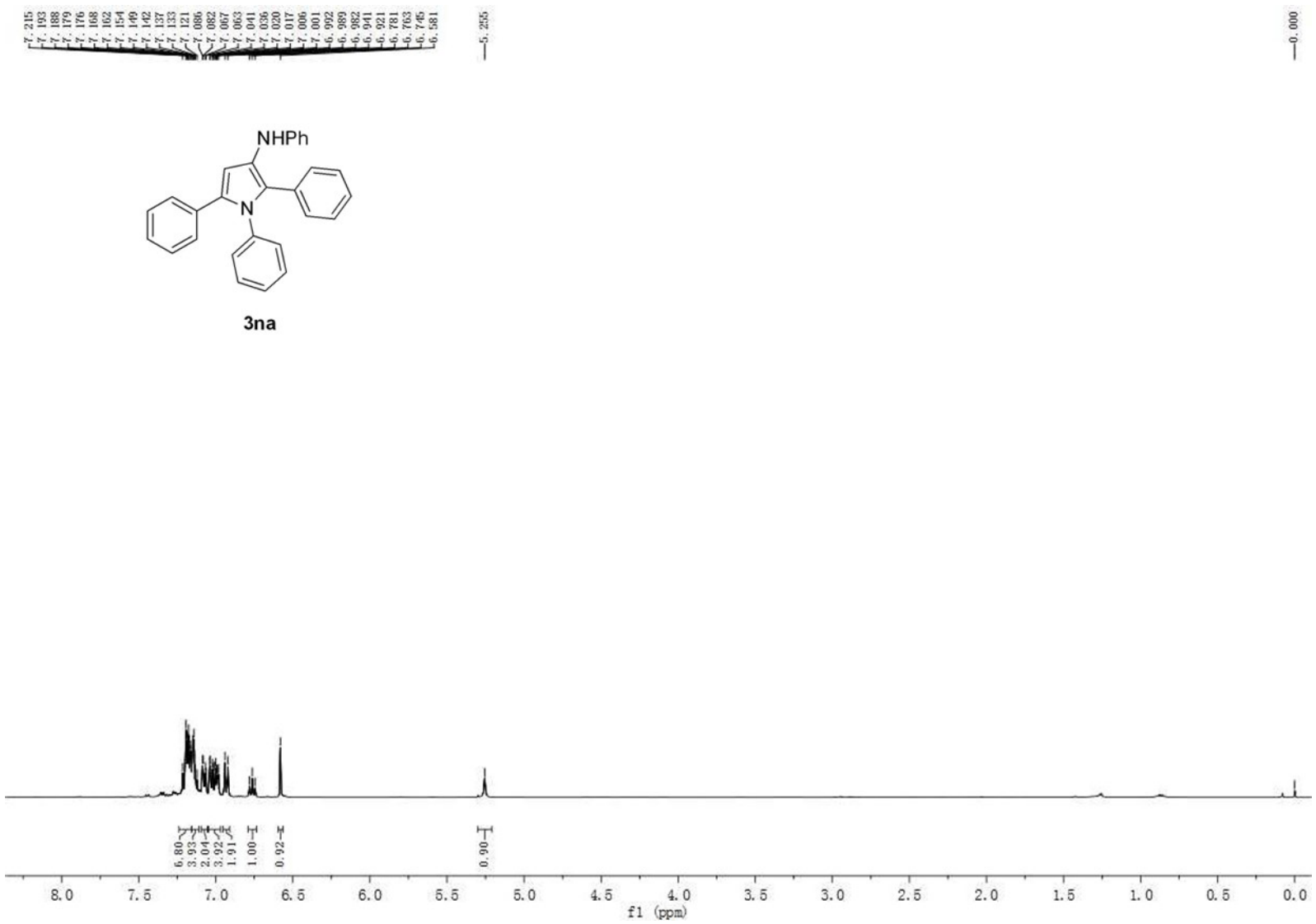


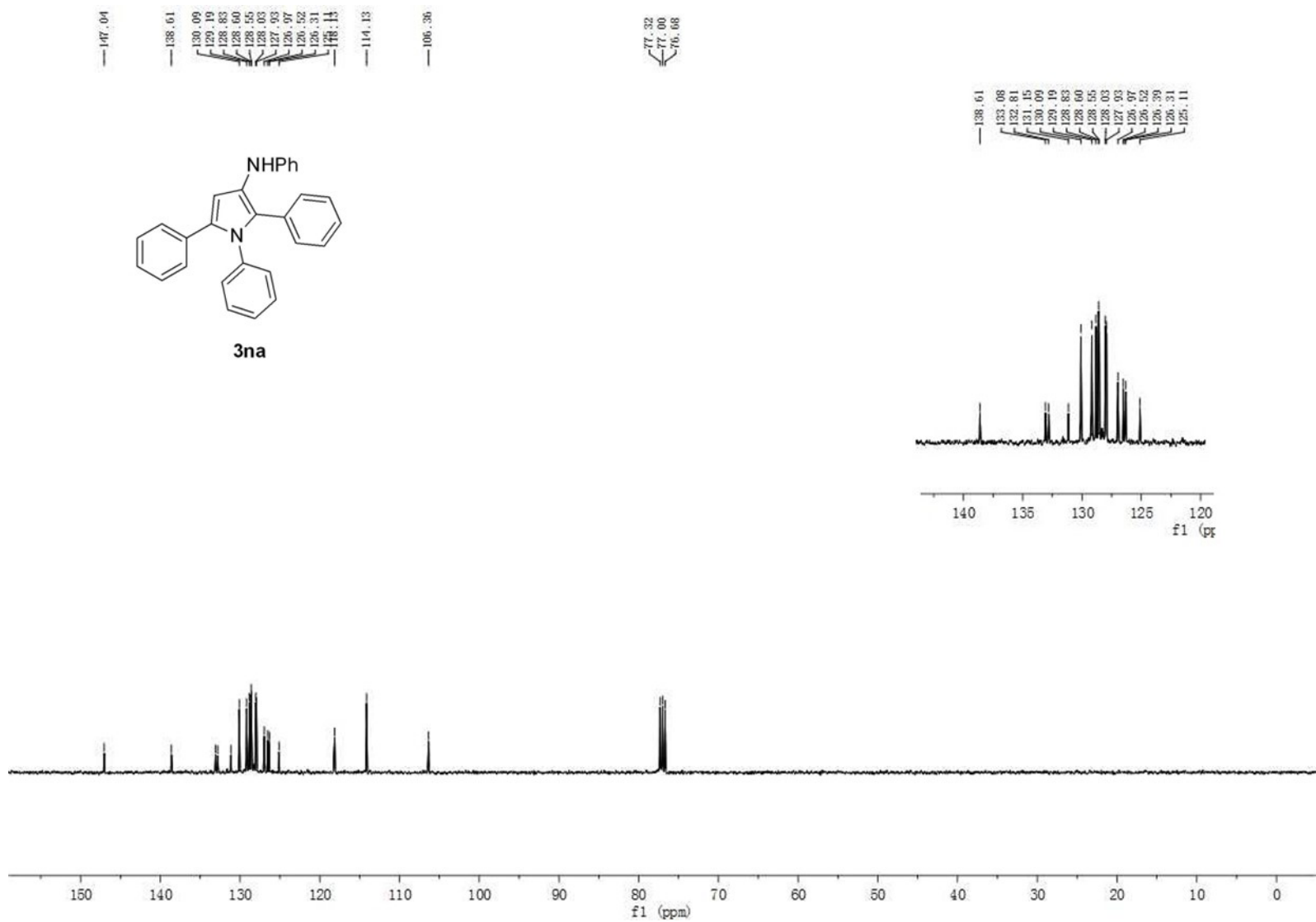








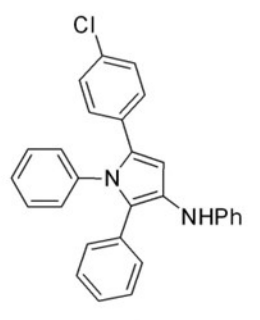




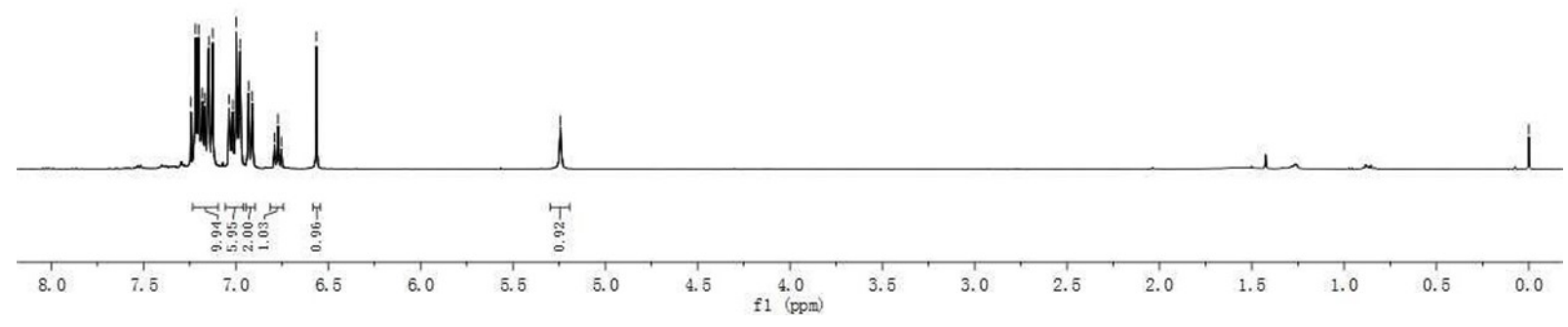
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7.170
7.147
7.125
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7.017
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6.977
6.931
6.912
6.790
6.772
6.754
6.564

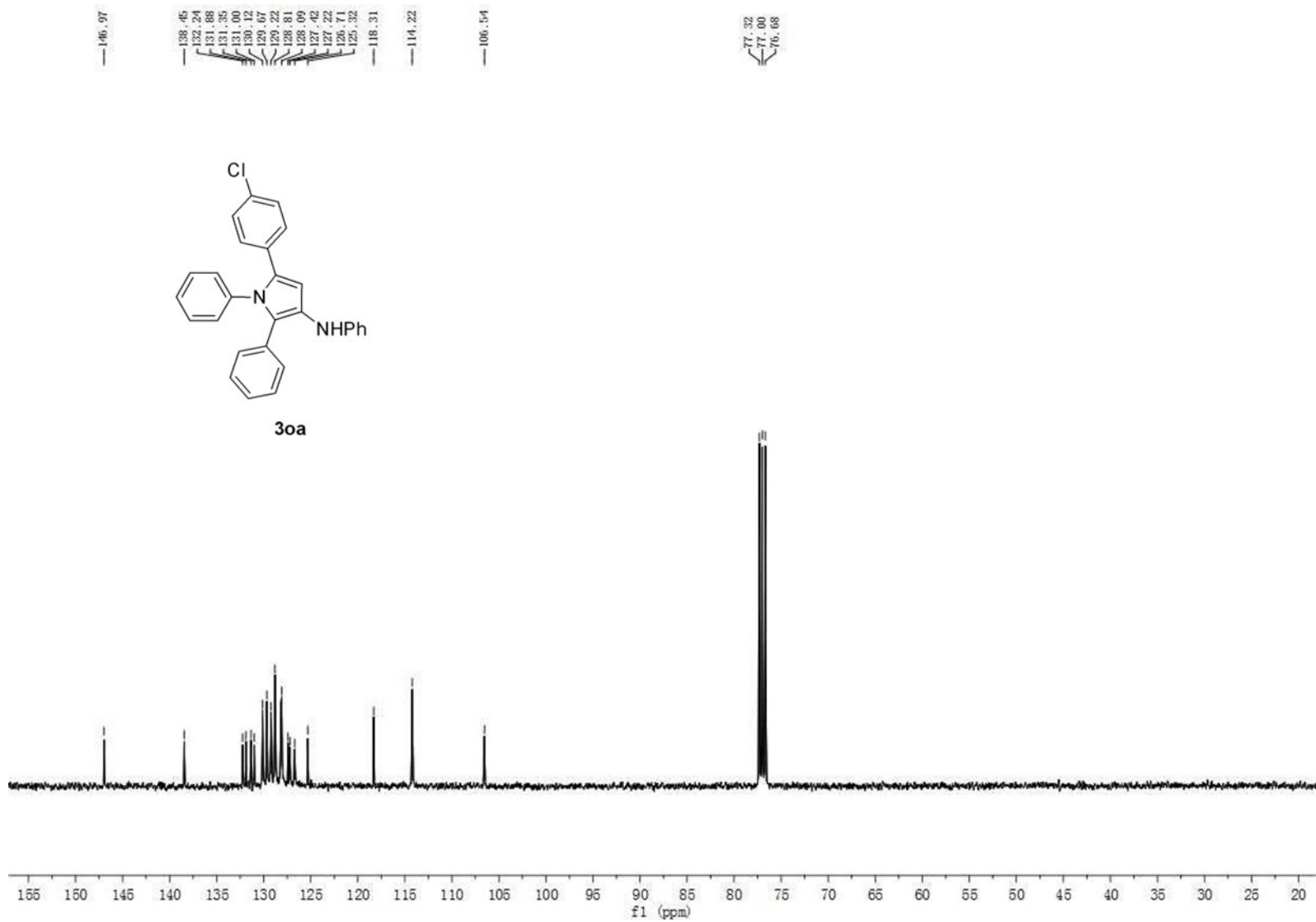
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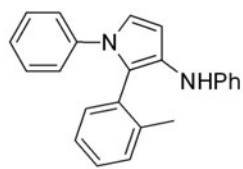


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7.149
7.133
7.114
7.102
7.085
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6.949
6.949
6.779
6.760
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6.408
6.400

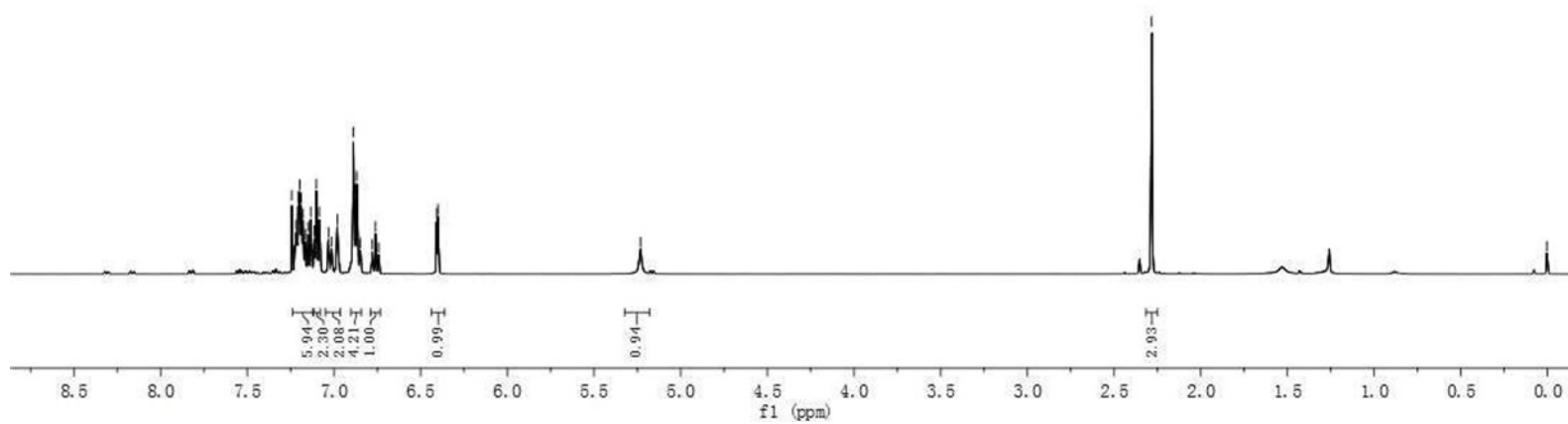
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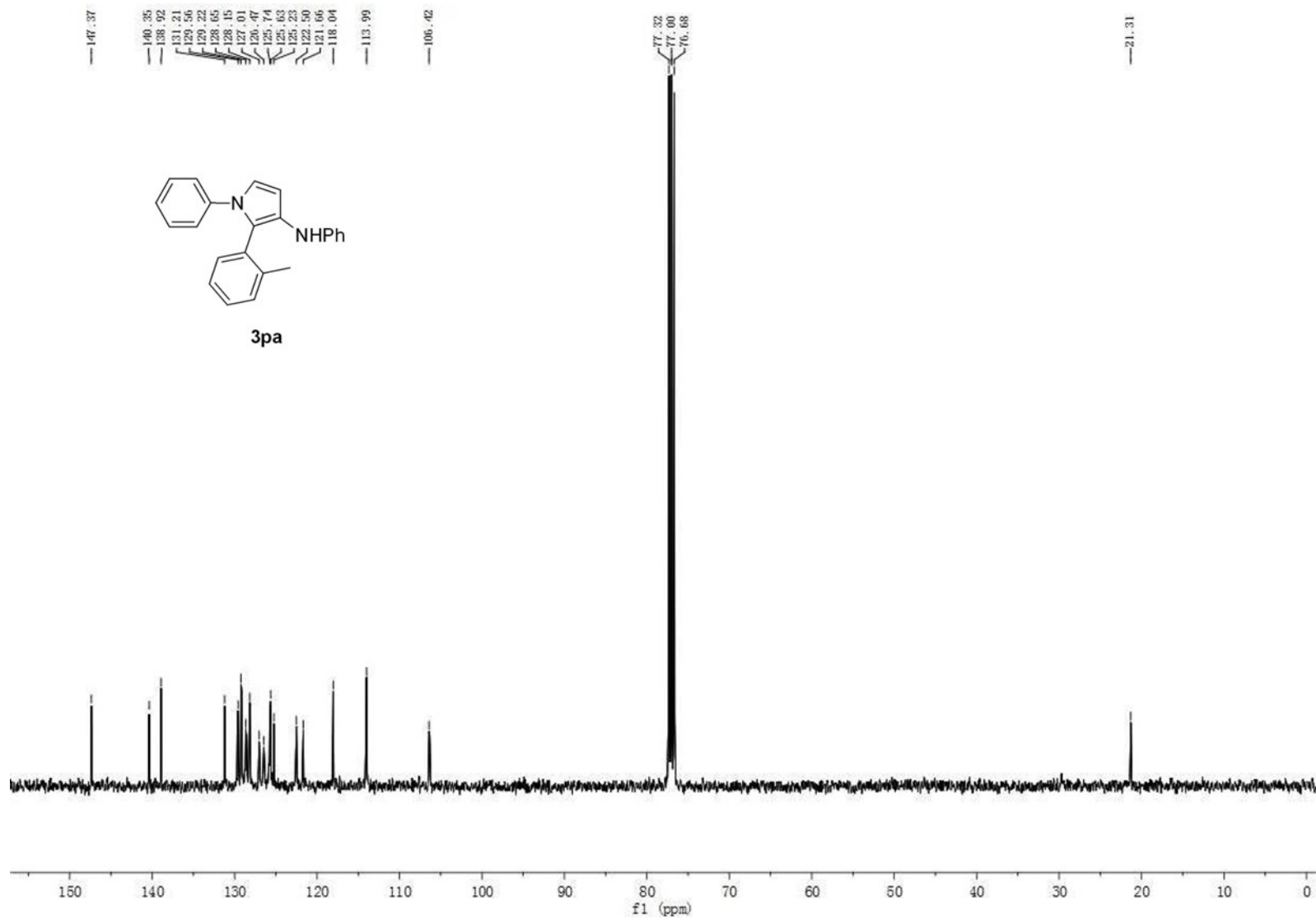
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—0.004

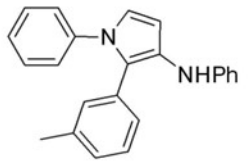
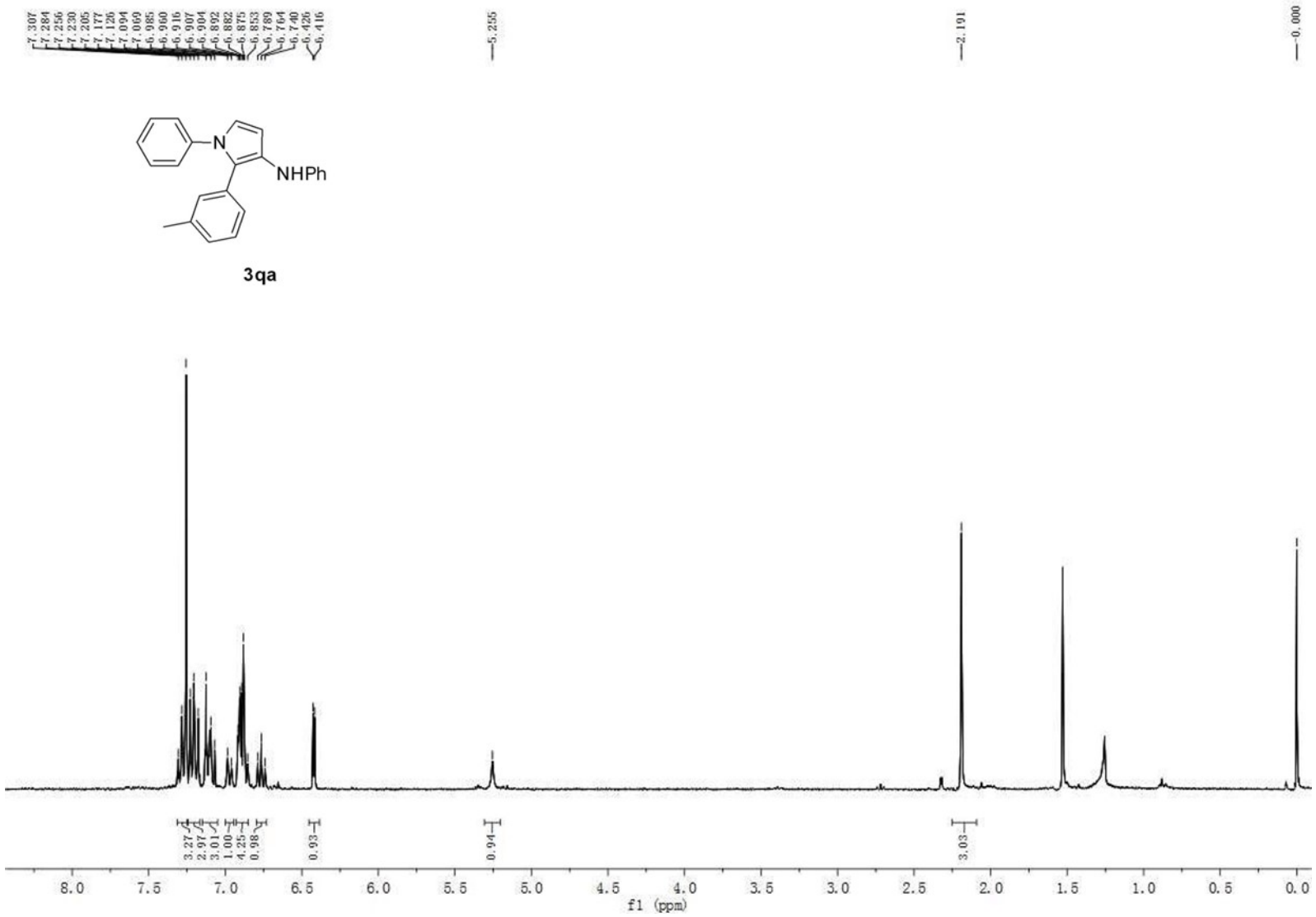


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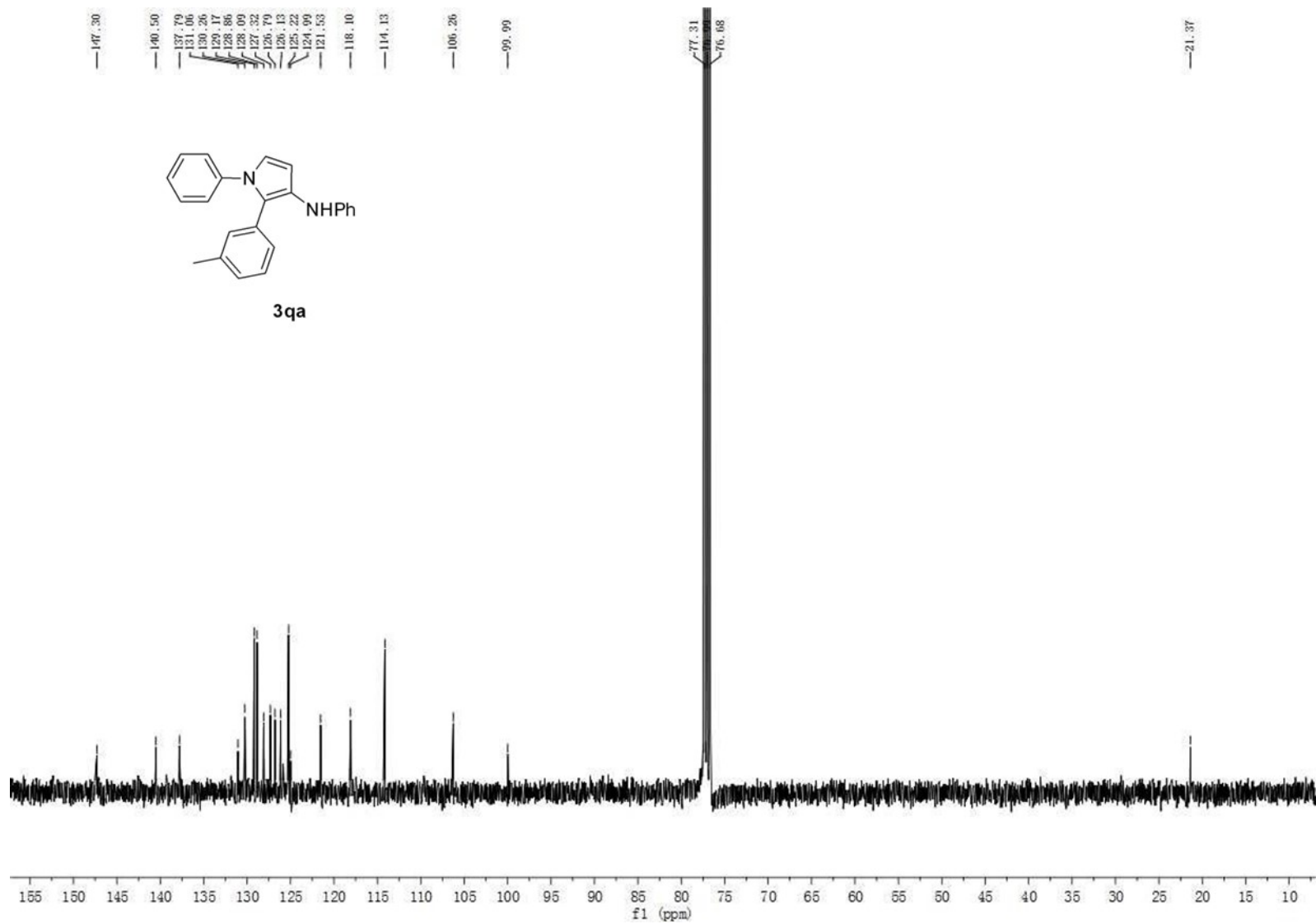


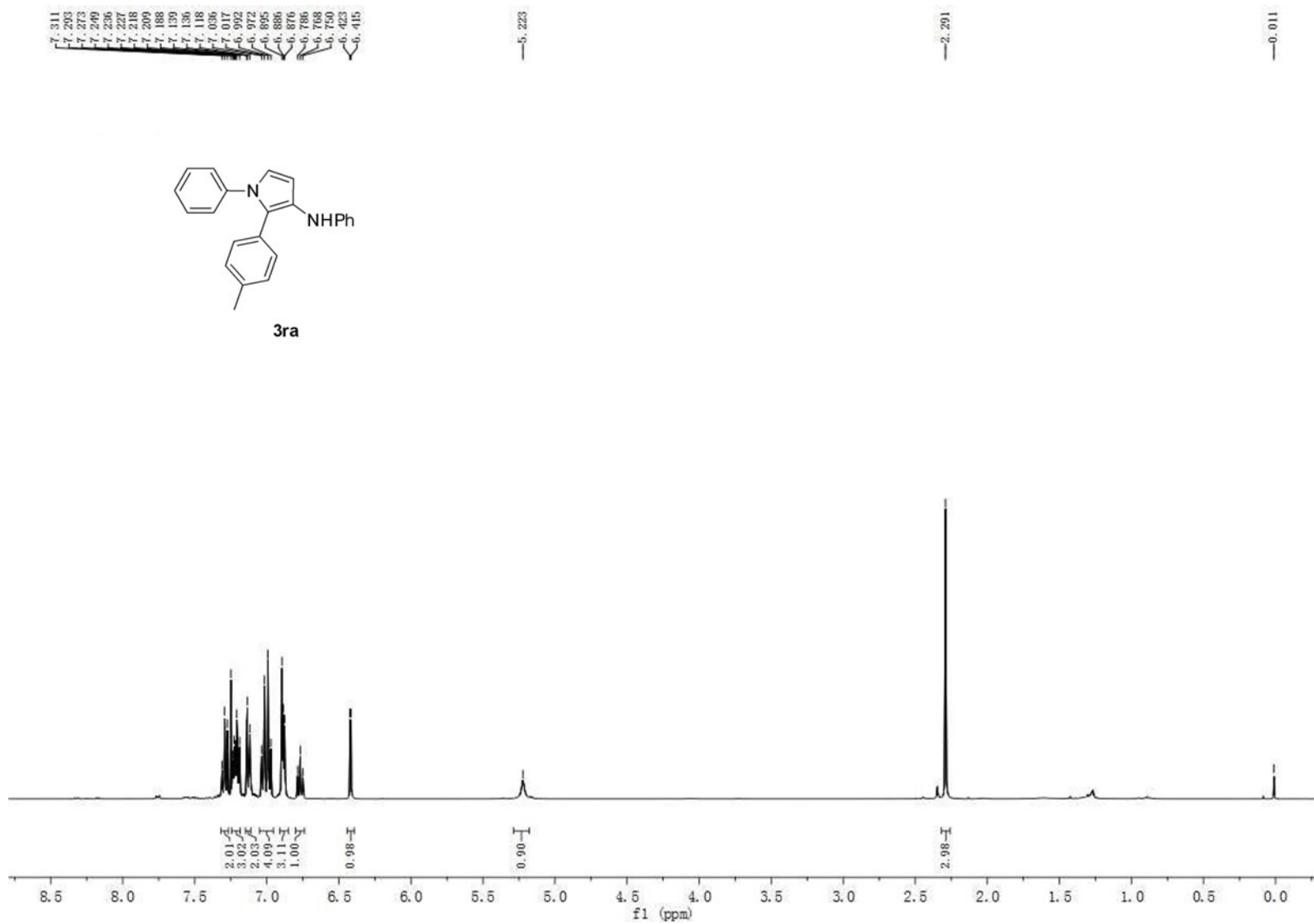


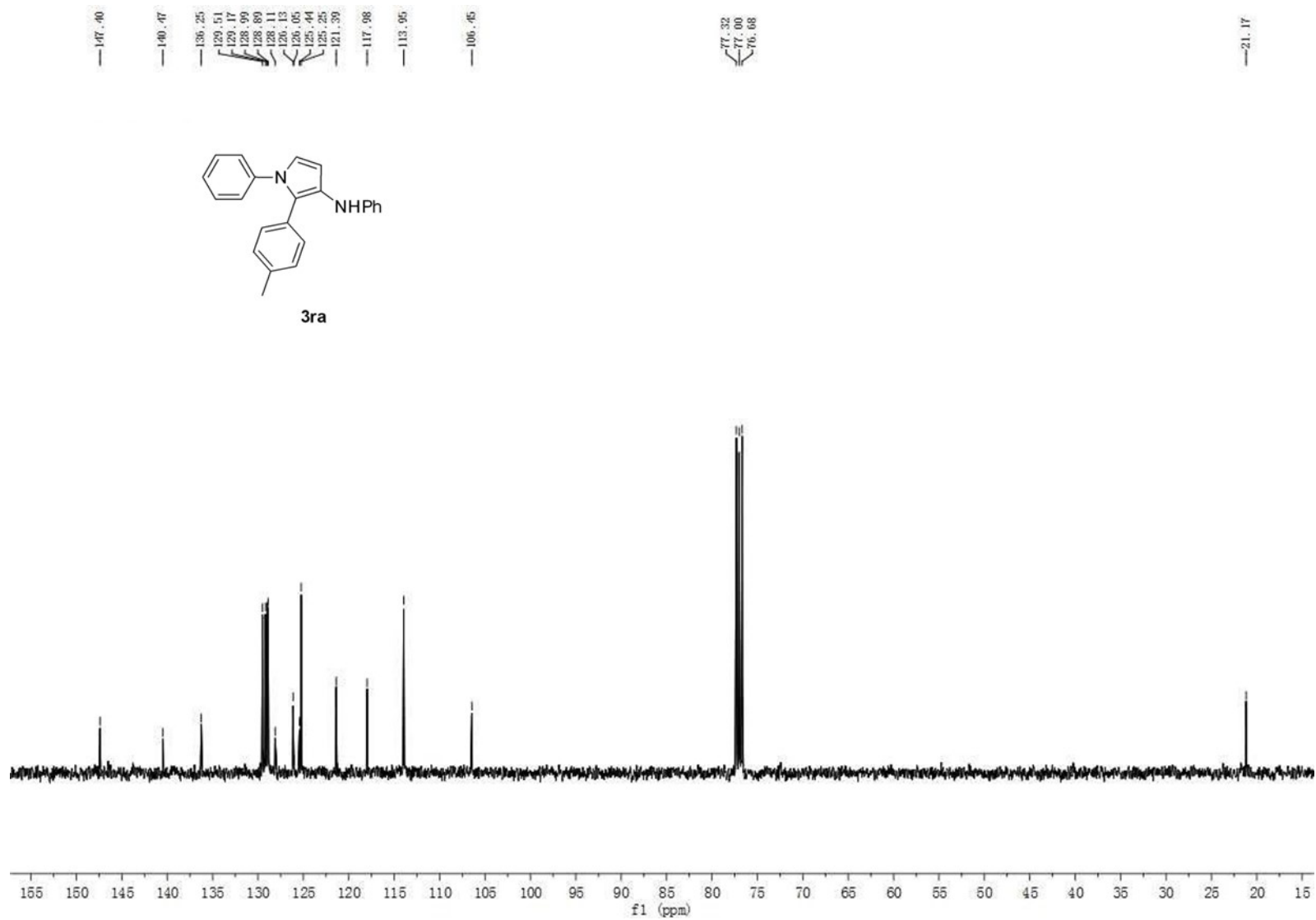
S100

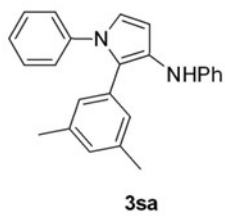
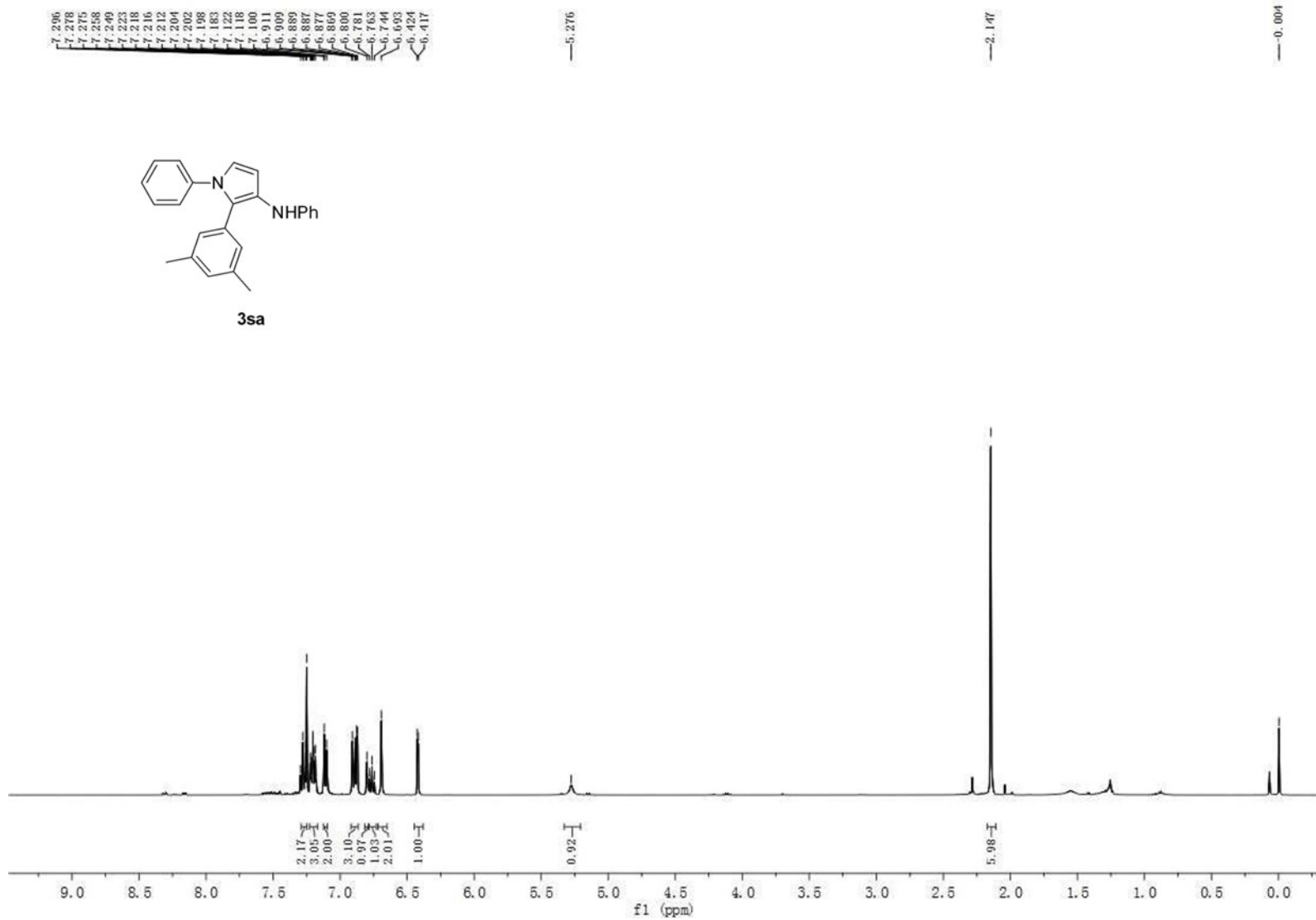


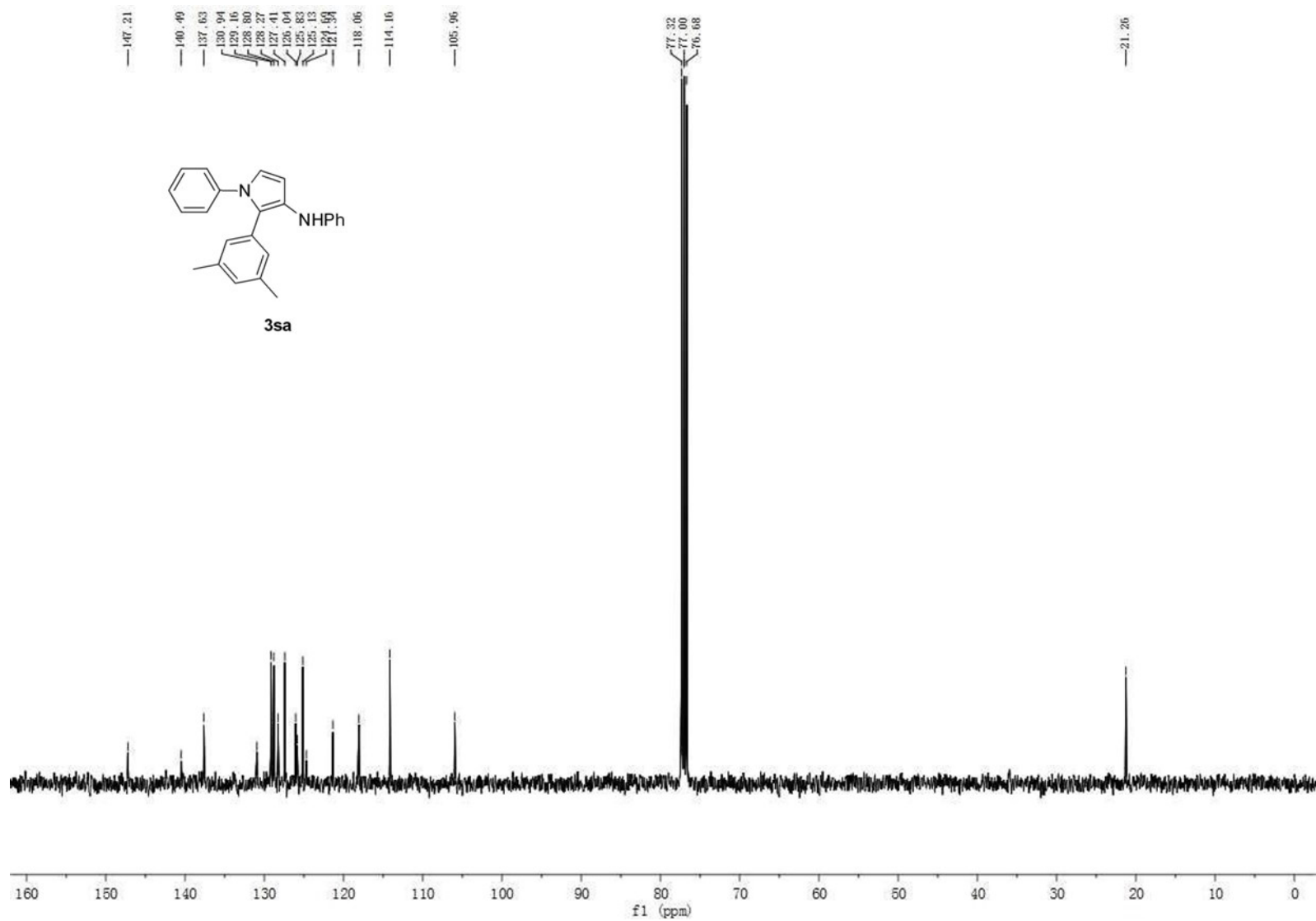
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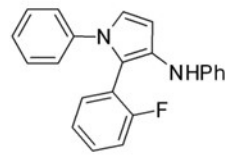
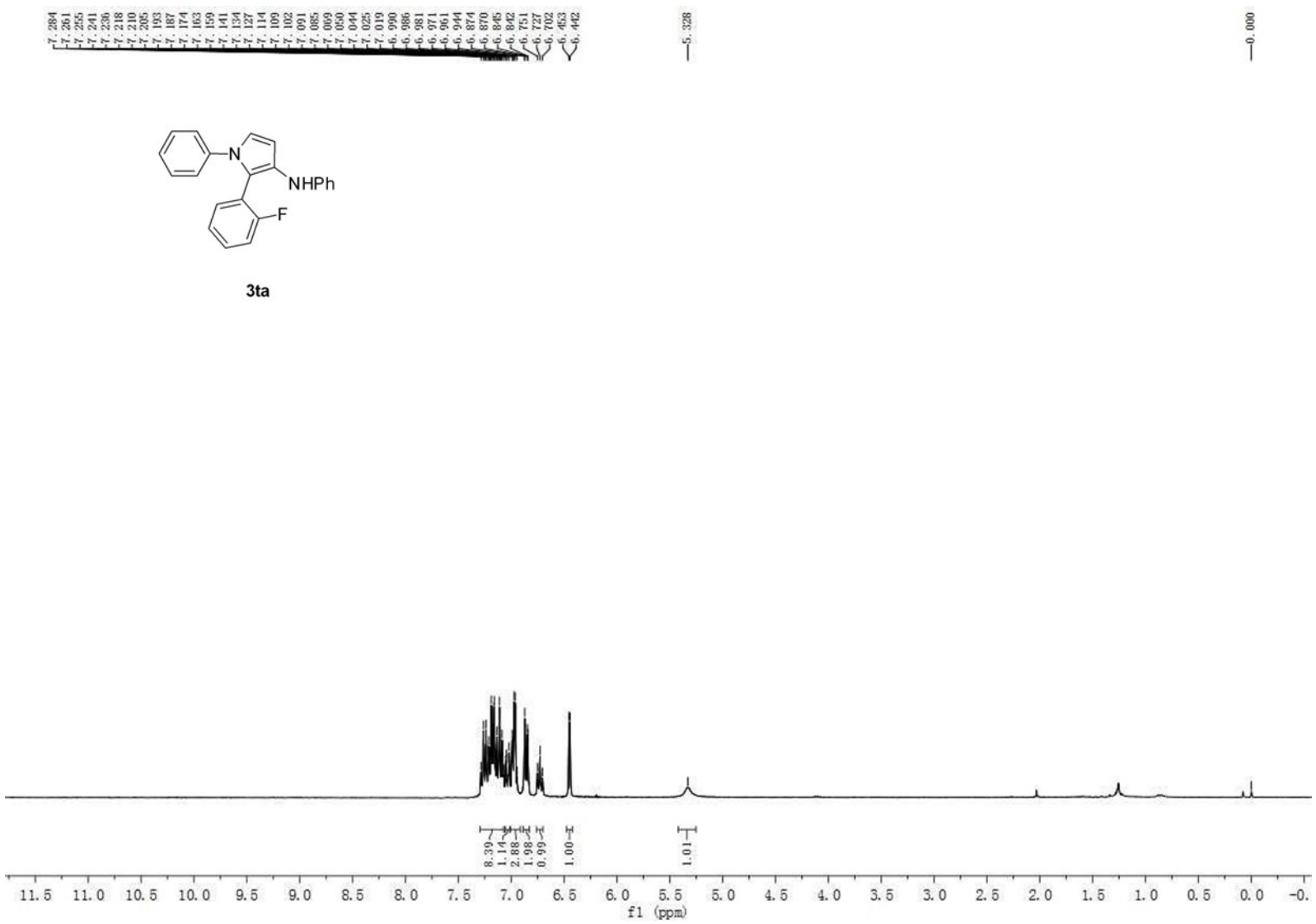




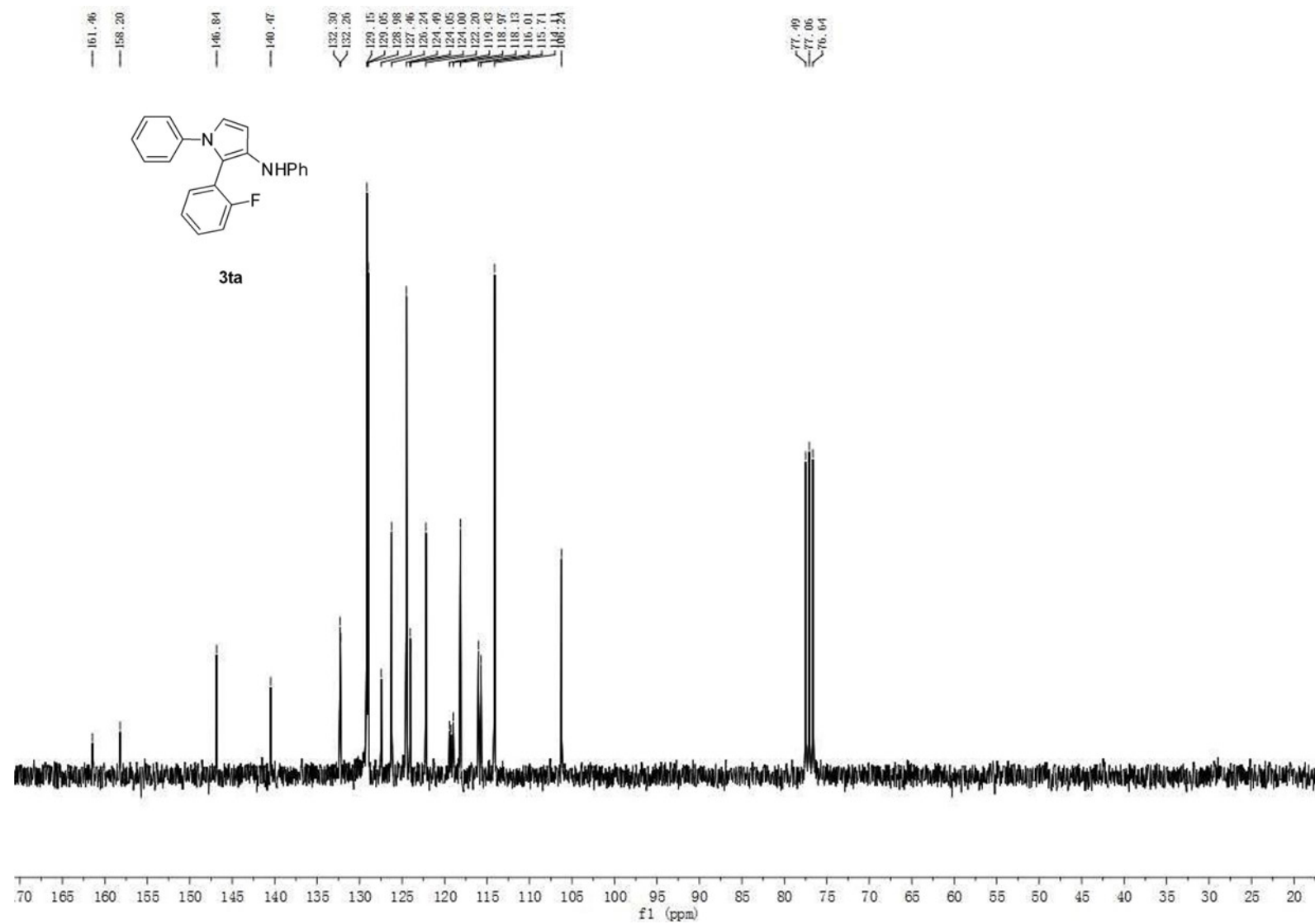




S106



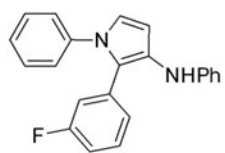
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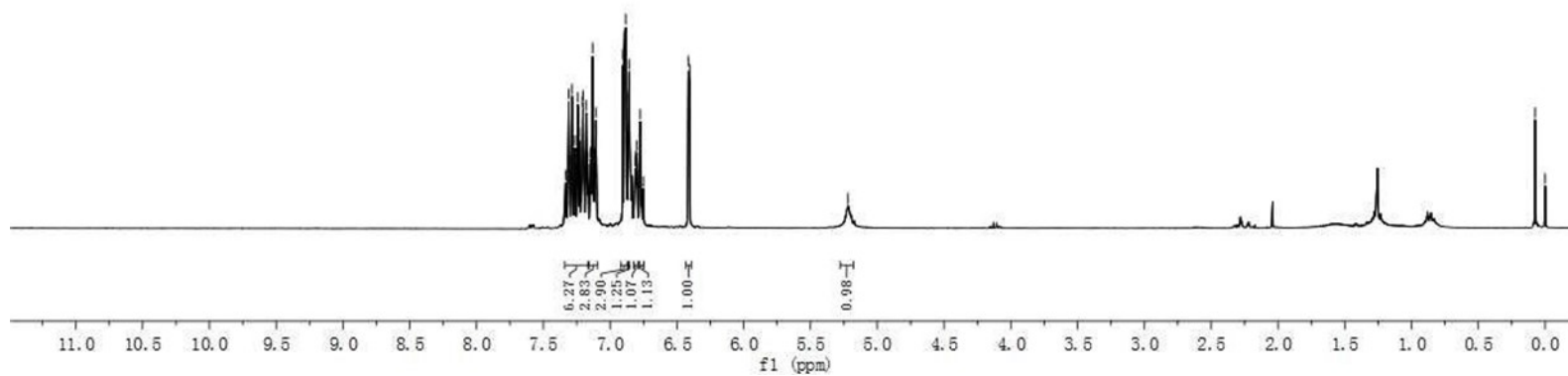
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7.157
7.147
7.139
7.130
7.120
7.120
7.113
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7.104
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6.887
6.883
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6.704

5.219

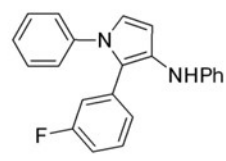
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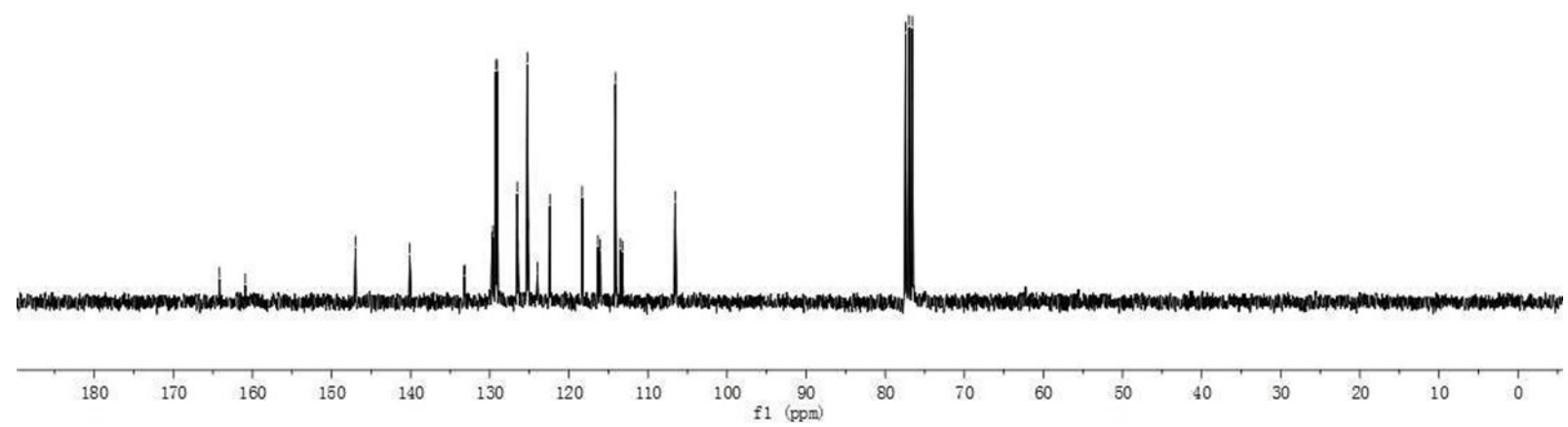
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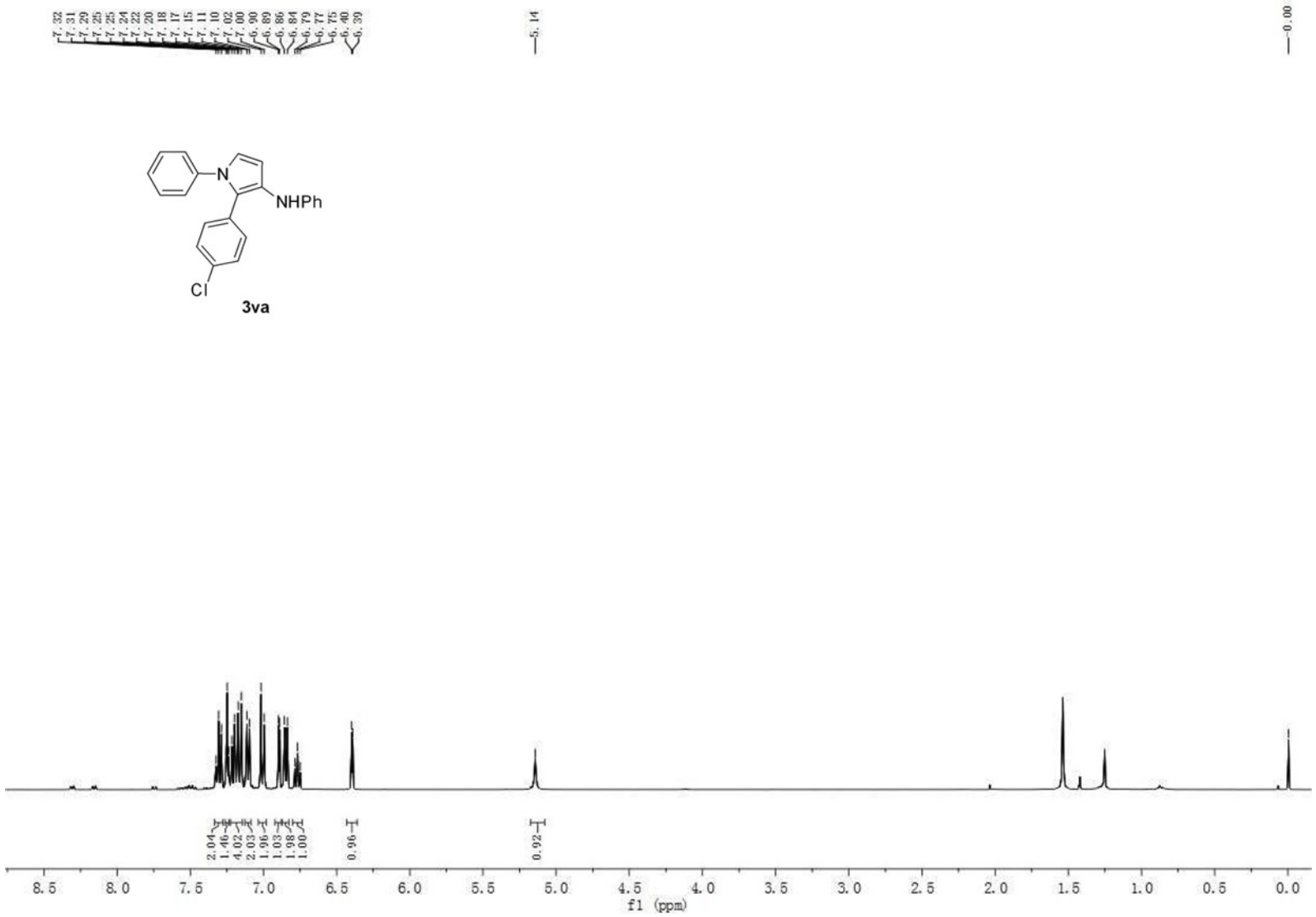


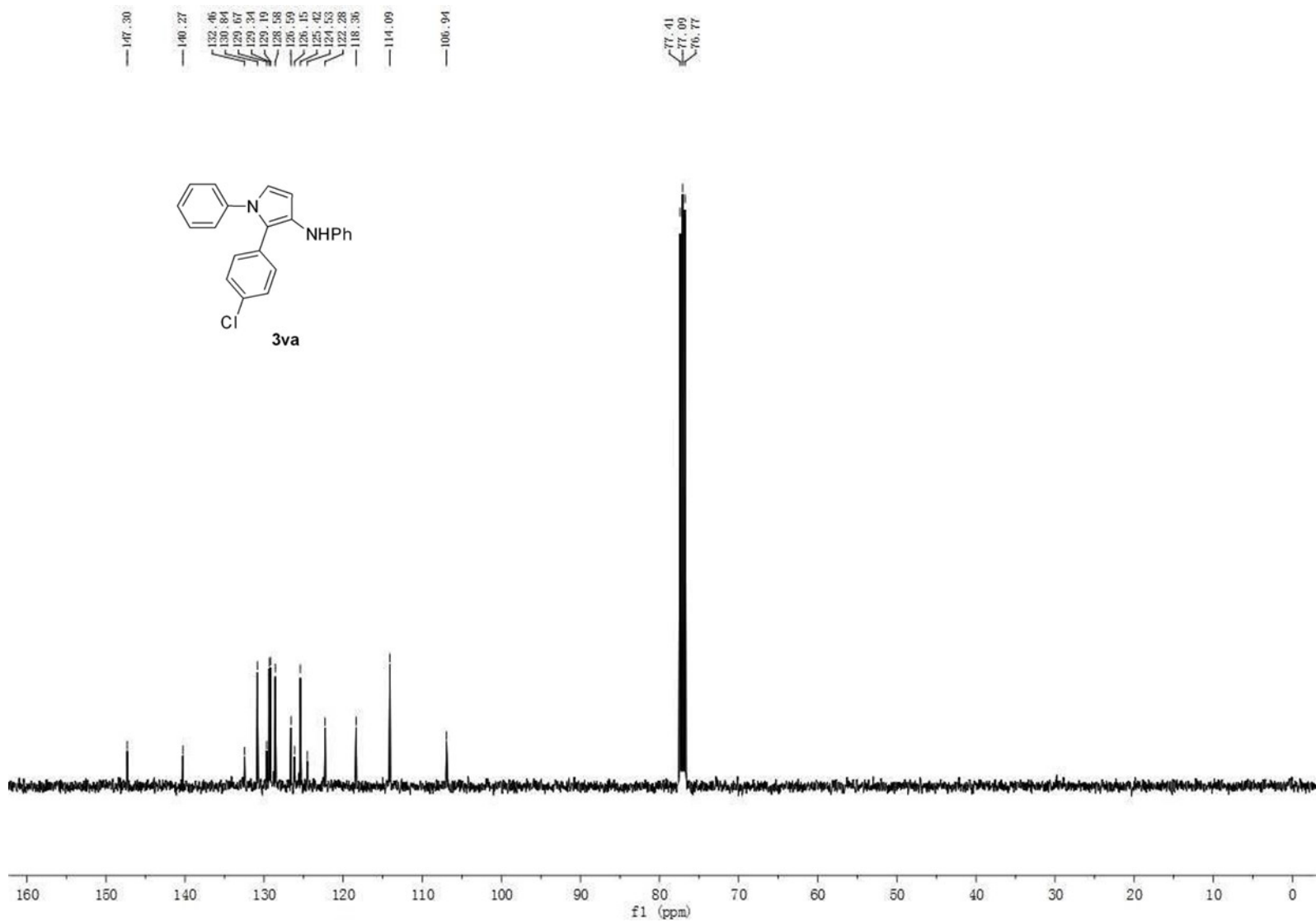
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126.43
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114.12
113.99
113.21
106.55
77.42
77.00
76.58

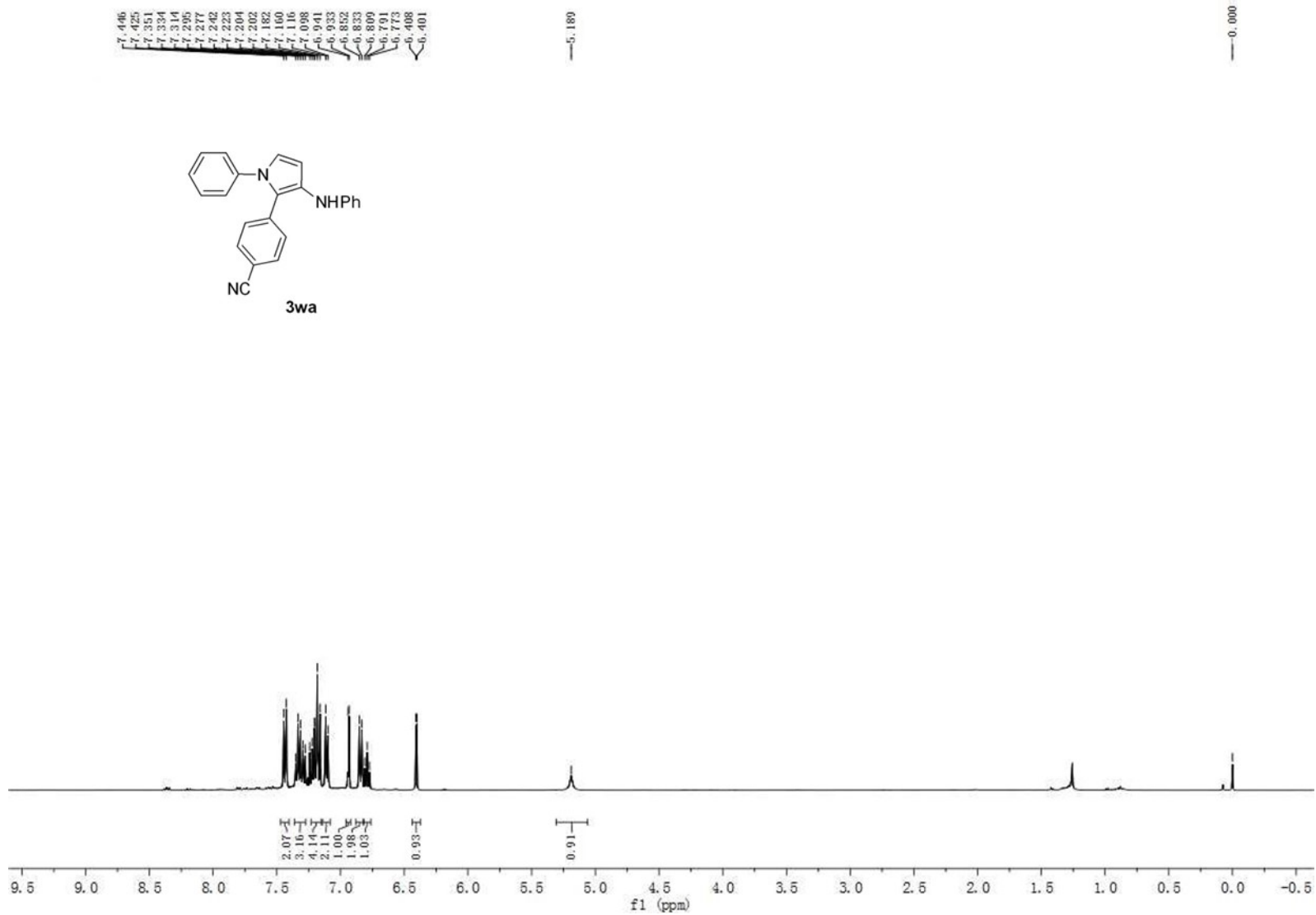


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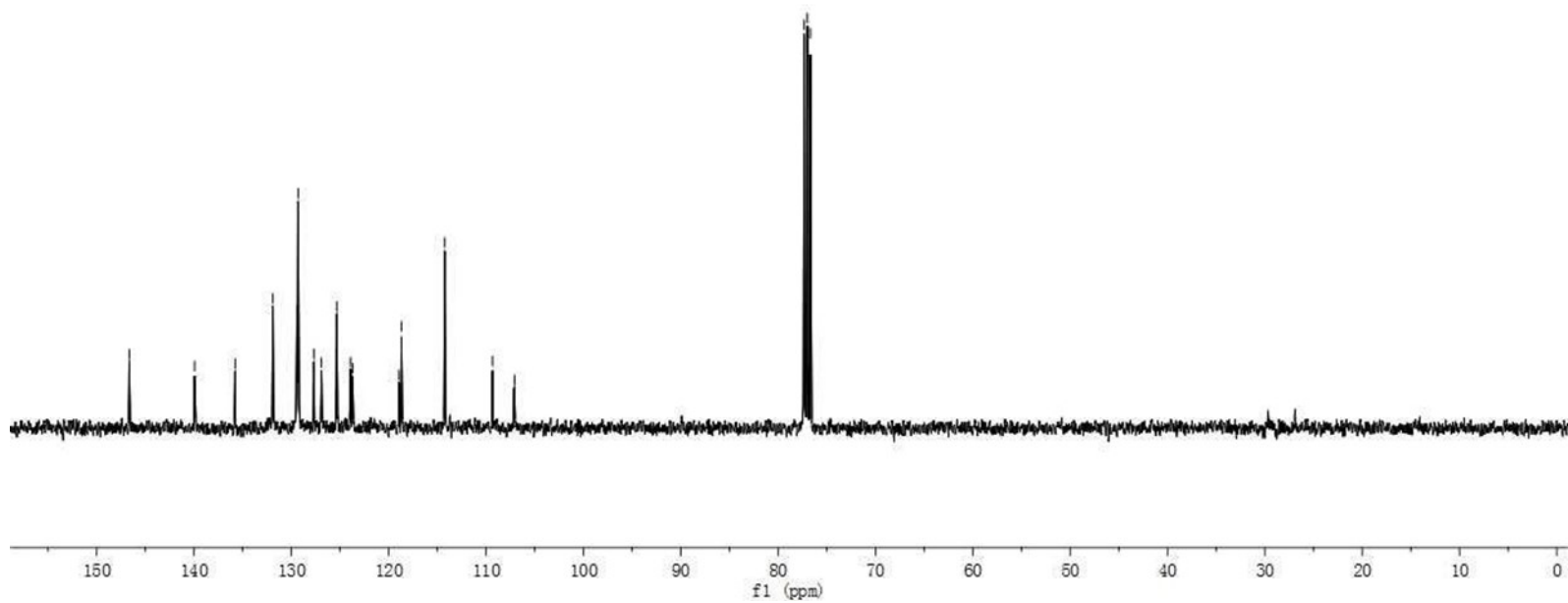
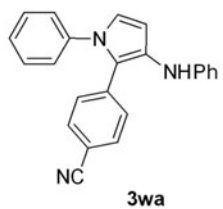






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131.91
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123.92
123.71
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118.09
114.24
109.34
107.08

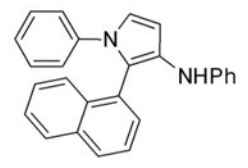
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76.08



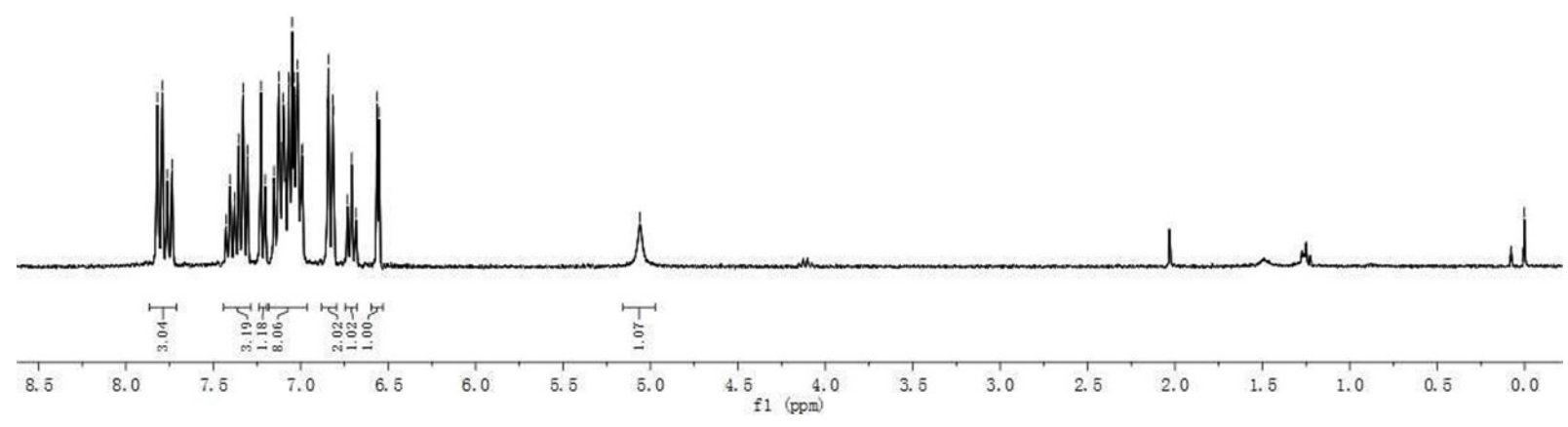
S114

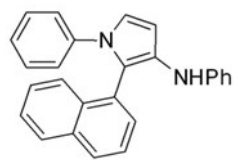
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7.125
7.100
7.037
7.009
7.066
7.049
7.022
7.038
7.018
6.993
6.991
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6.568

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0.000

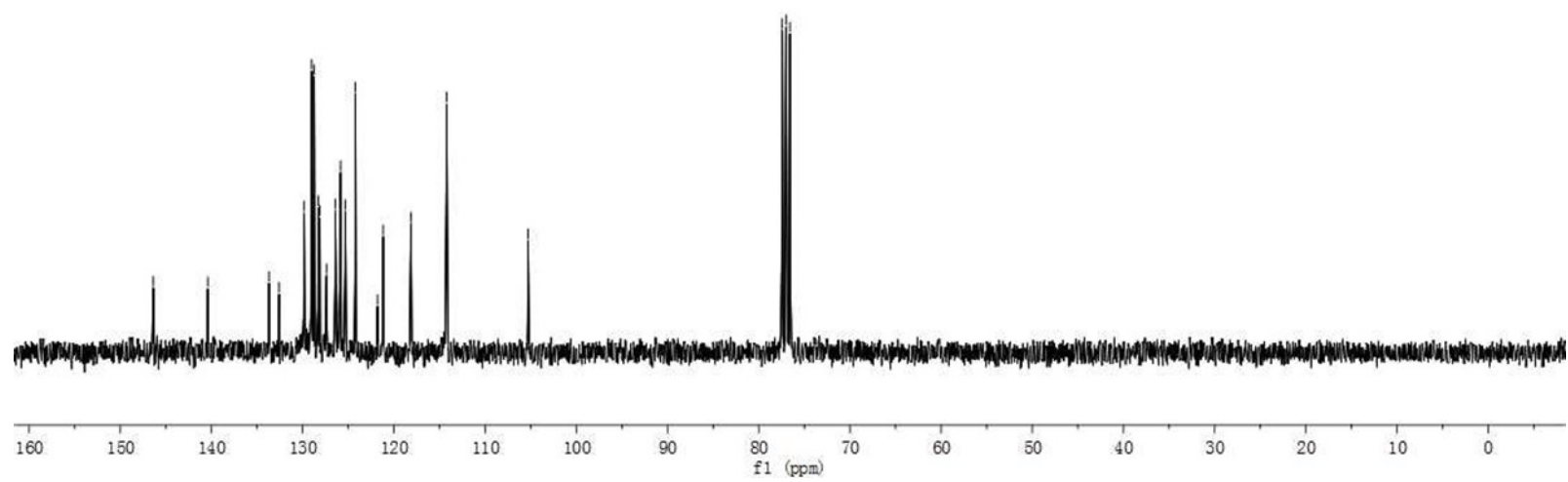


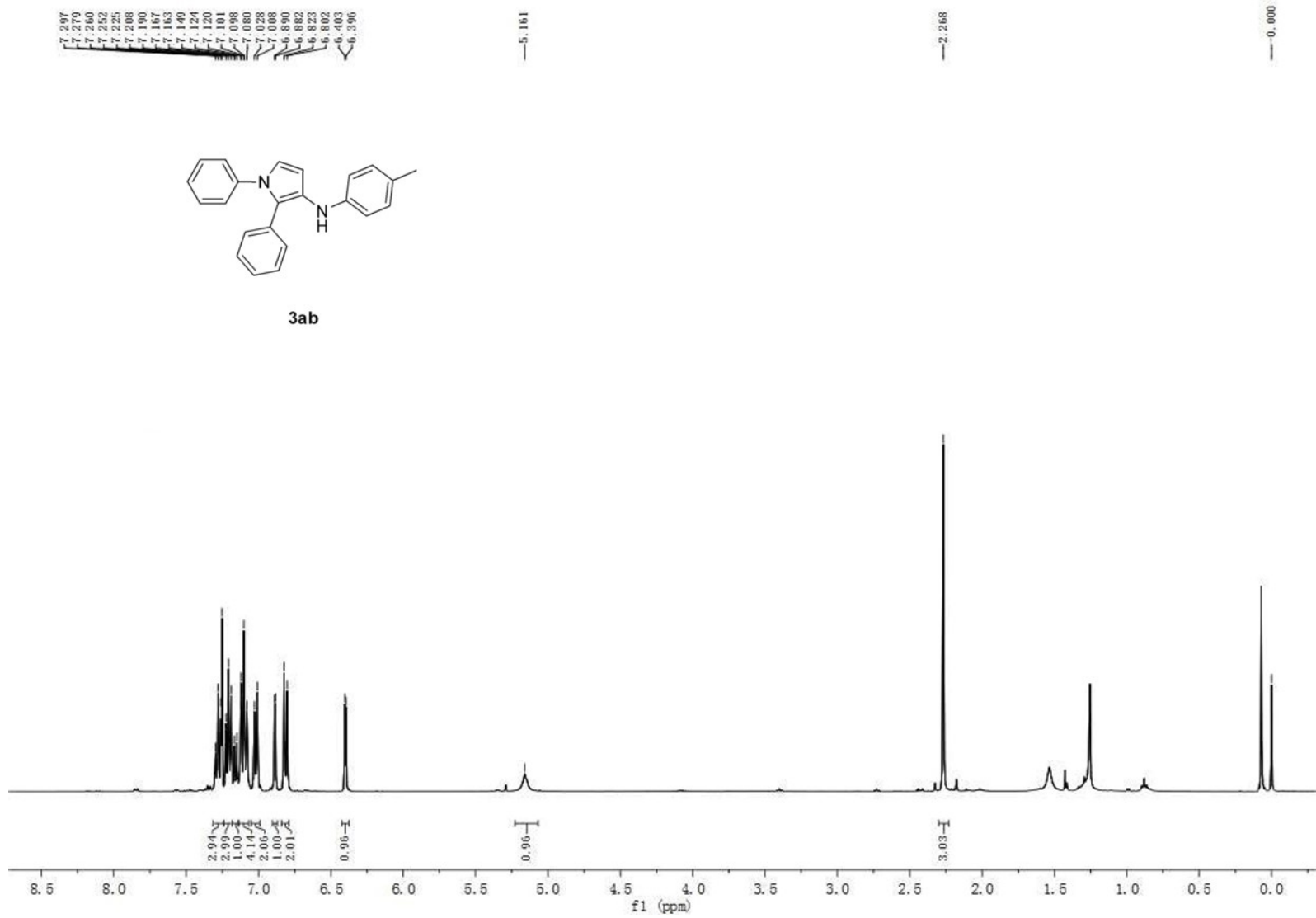
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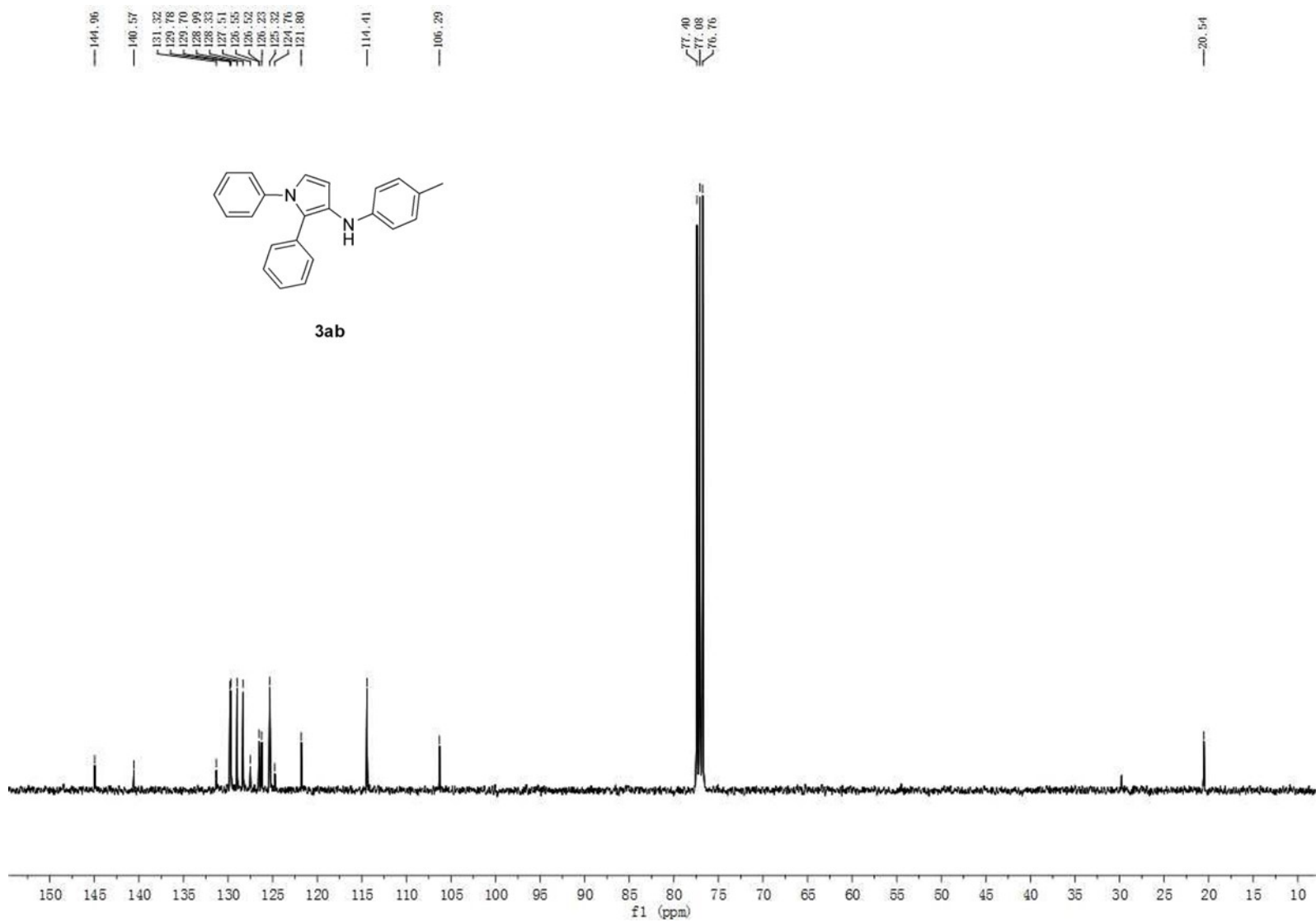


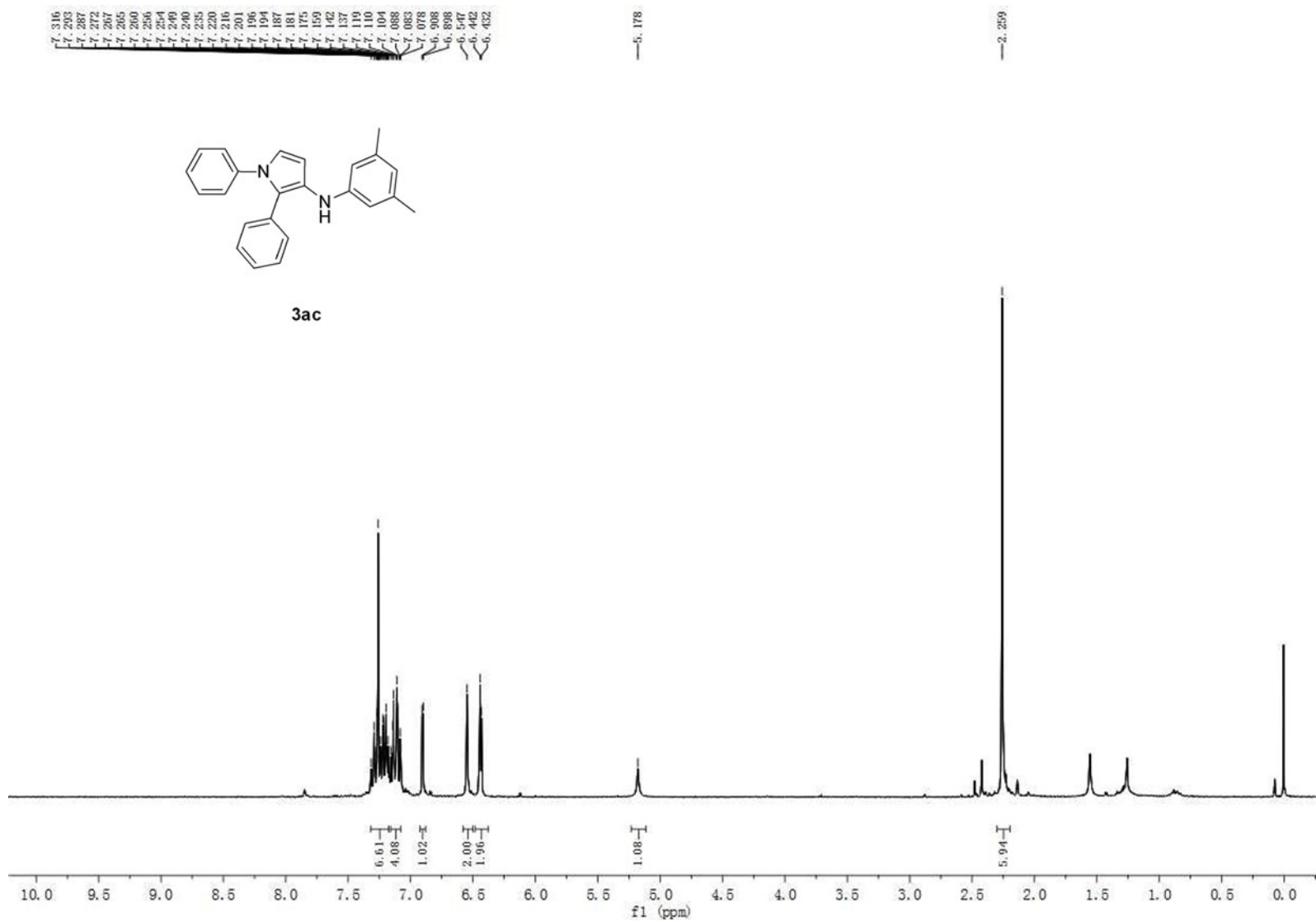


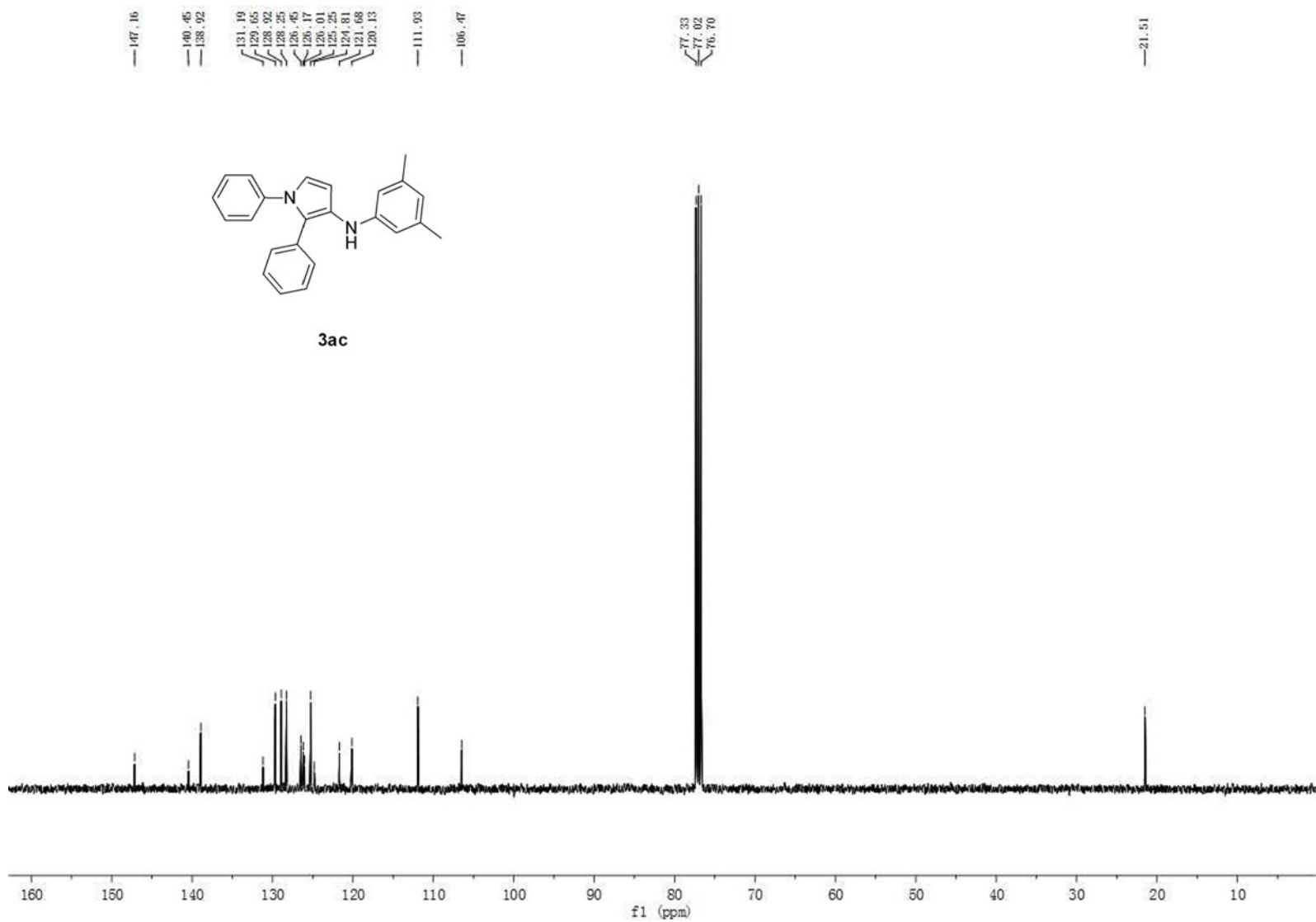
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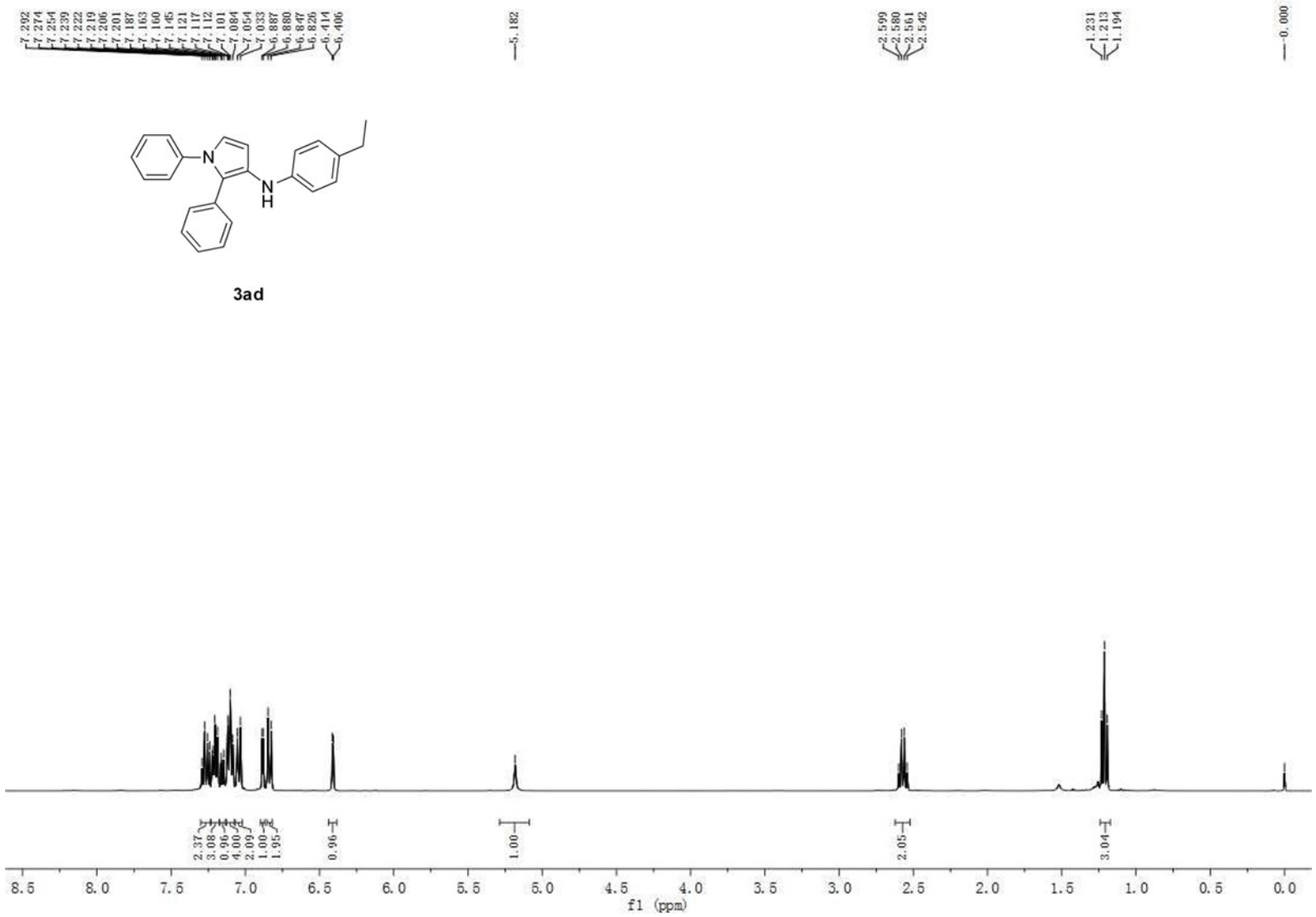










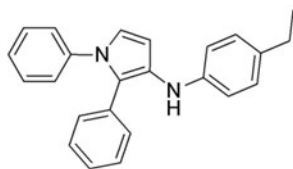


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140.48
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131.25
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128.24
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114.32
106.15

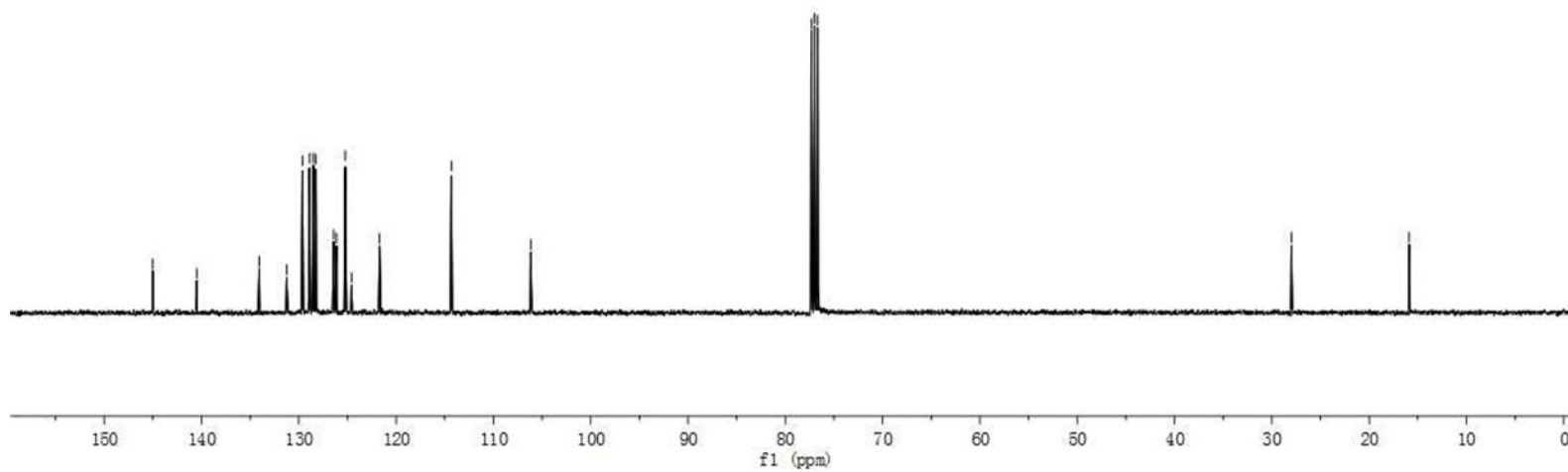
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77.00
76.08

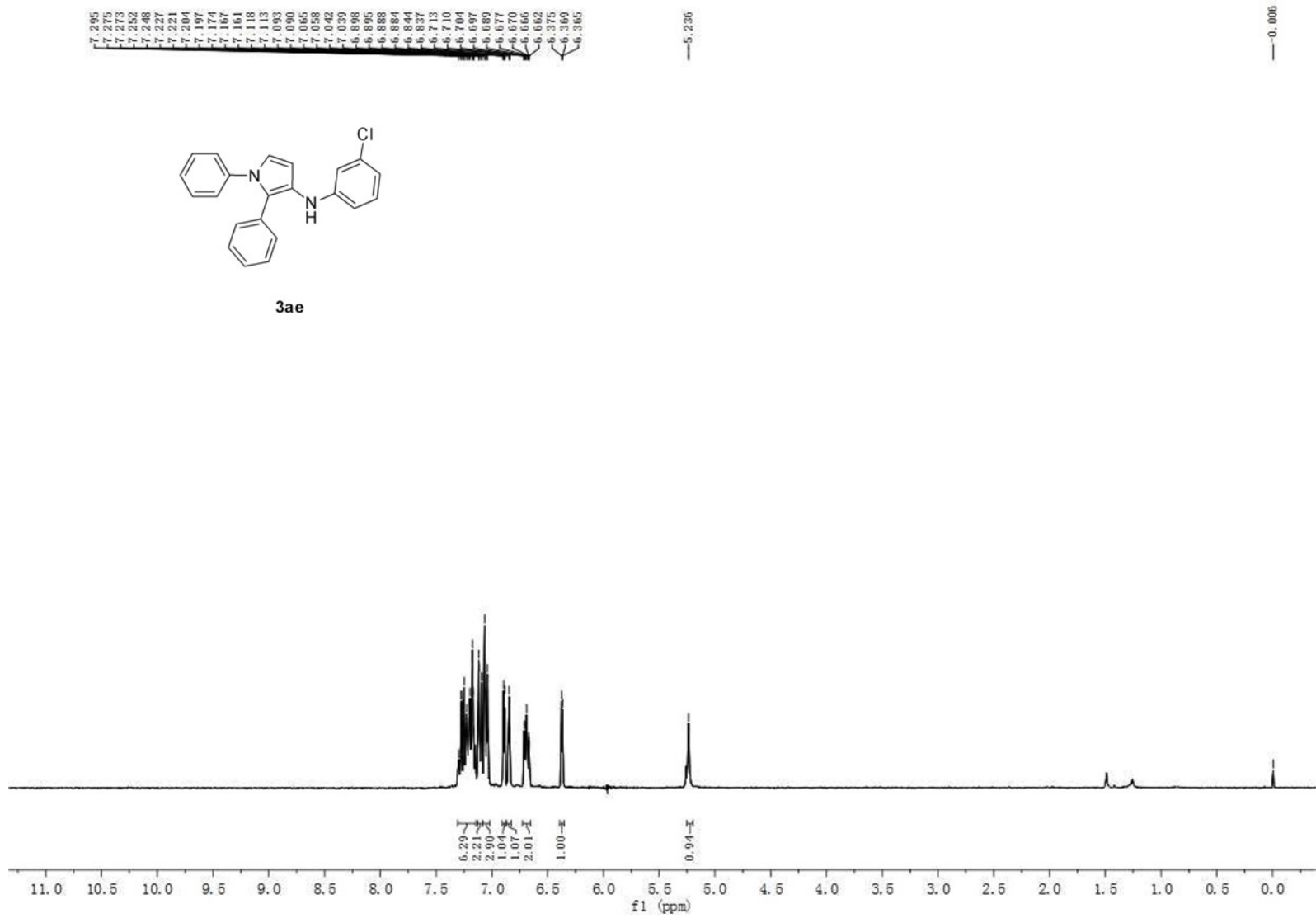
27.99

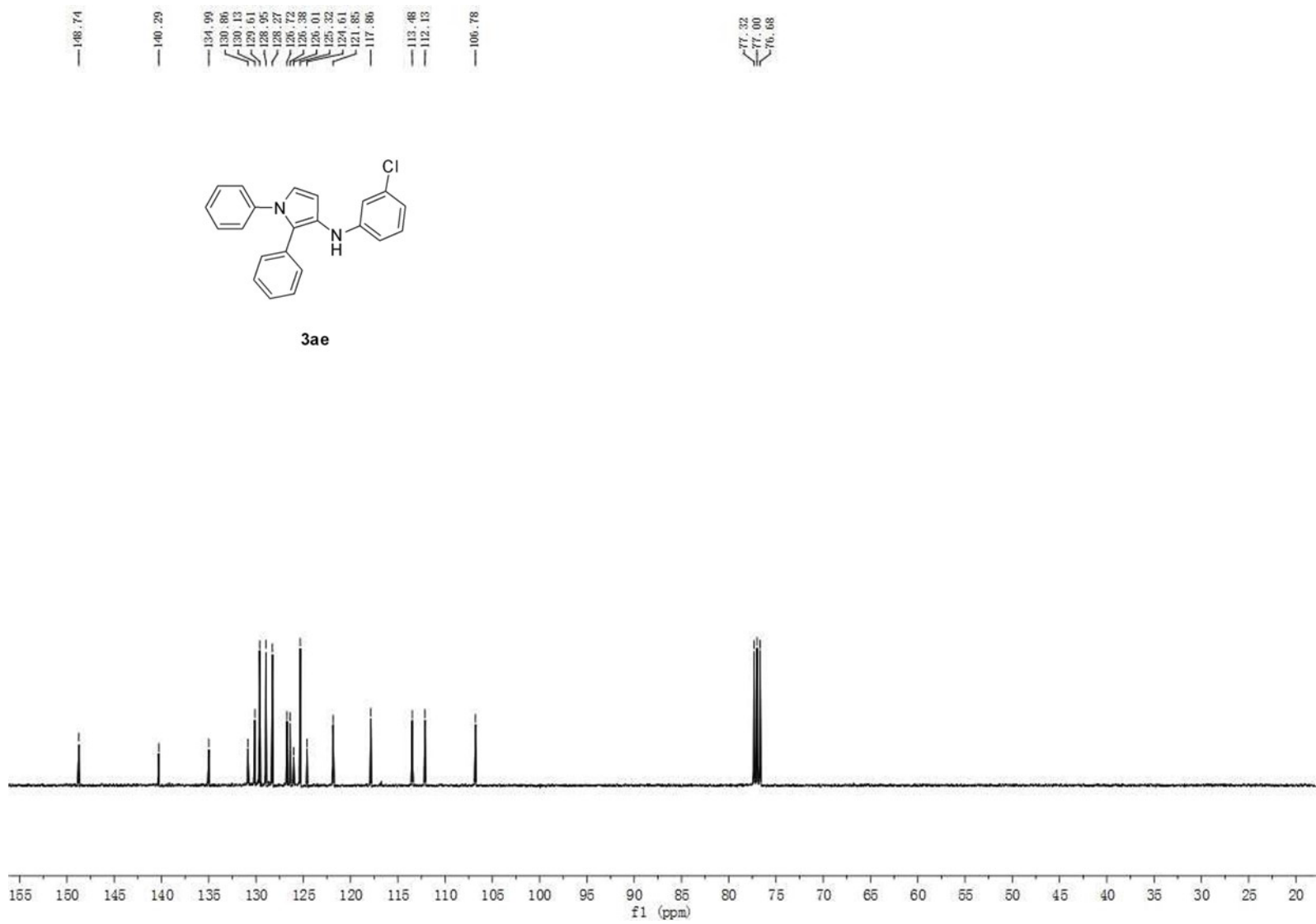
15.89

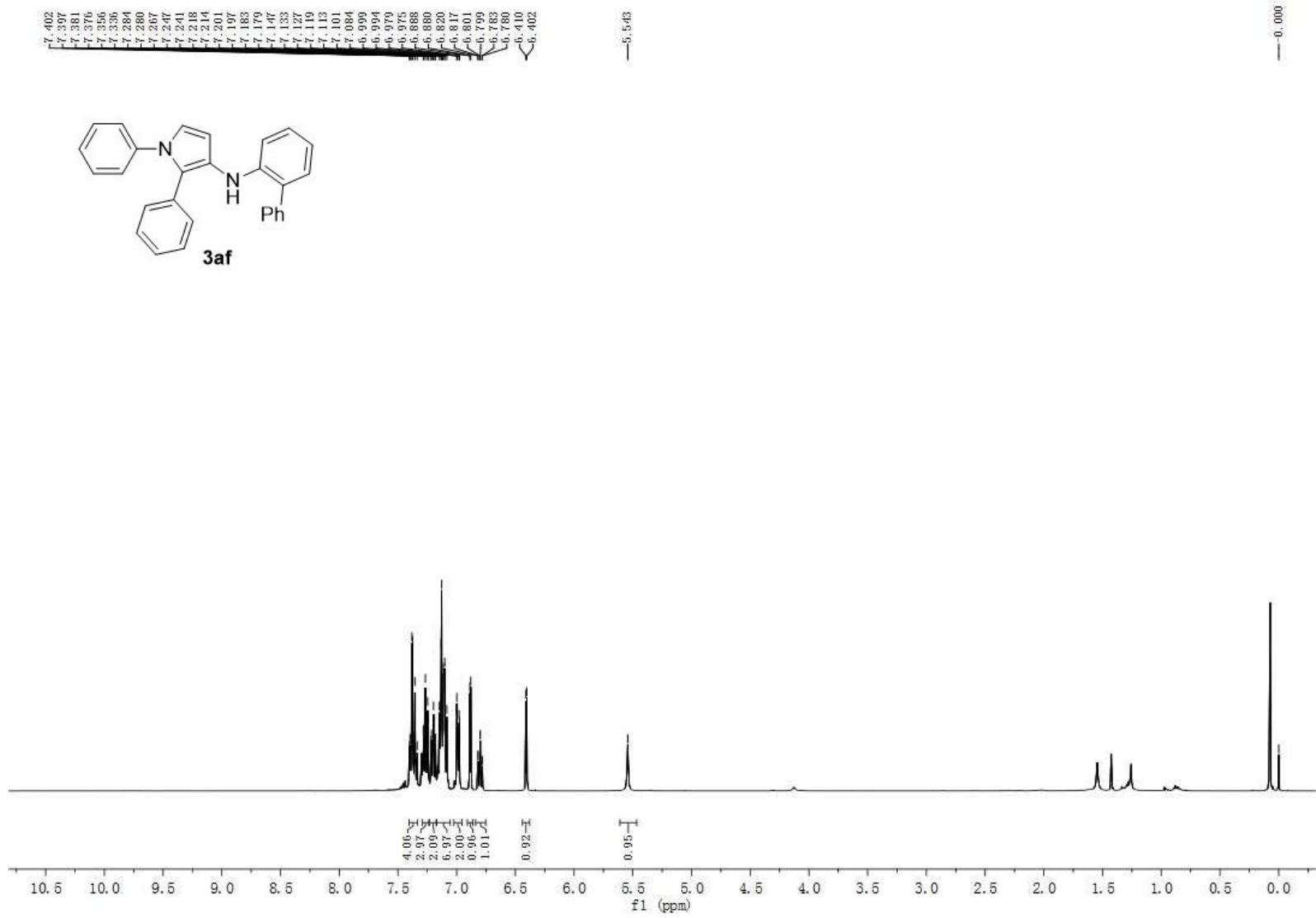


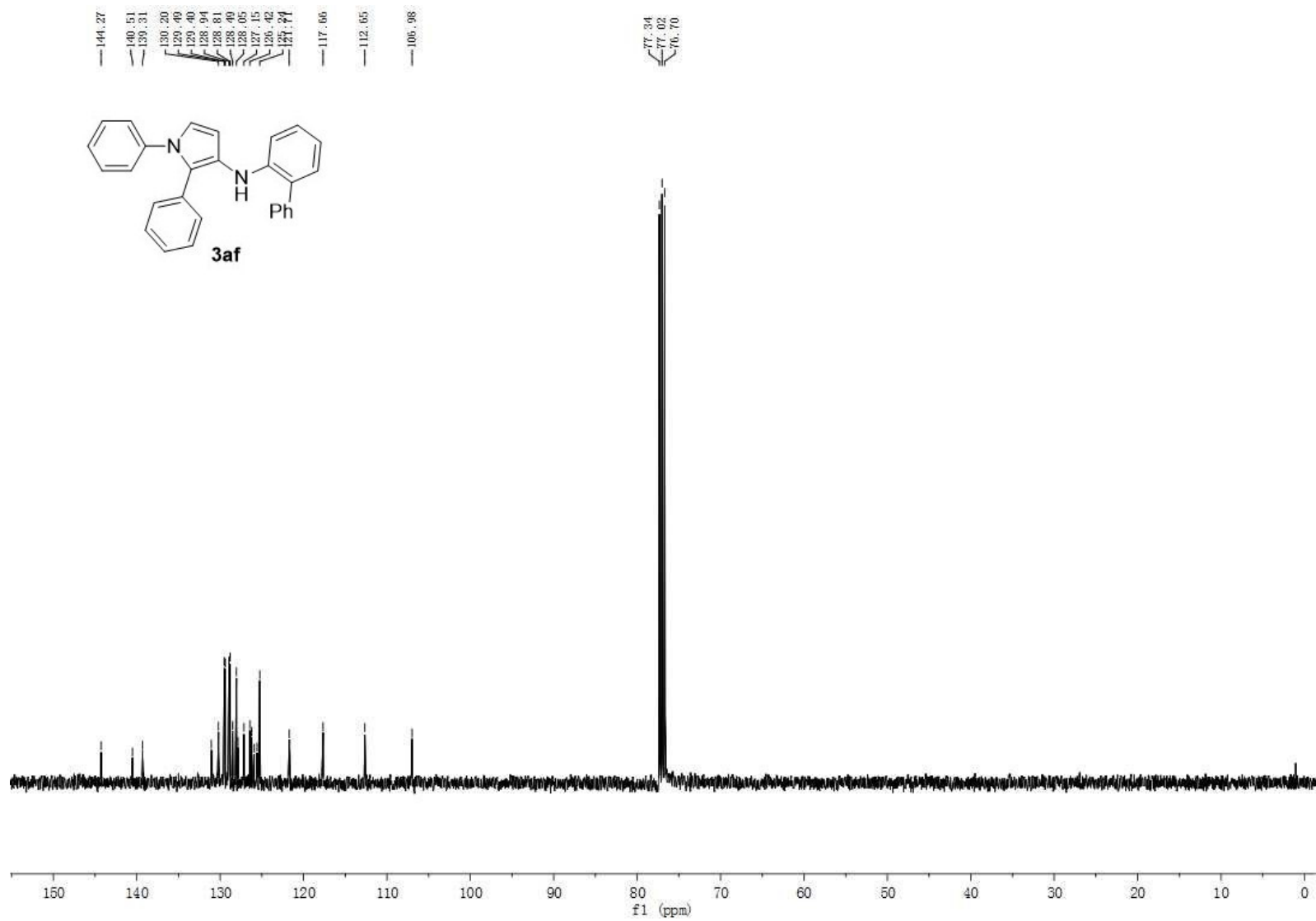
3ad











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