Supporting Information

Palladium-Catalyzed Cascade Decarboxylative Amination/6-*endo-dig* Benzannulation of *o*-Alkynylarylketones with *N*-Hydroxyamides to Access Diverse 1-Naphthylamine Derivatives

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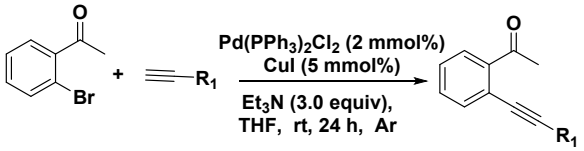
1. General Information

Unless otherwise specified, all reagents and starting materials were purchased from commercial sources and used as received, and the solvents were purified and dried using standard procedures. The chromatography solvents were technical grade and distilled prior to use. The melting points were measured using SGWX-4 melting point apparatus. The NMR spectra were recorded with a Bruker Avance 500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) with $CDCl_3$ as solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. HRMS spectra were obtained with an Agilent 6200 using a quadrupole time-of-flight mass spectrometer equipped with an ESI source.

2. Experimental Section

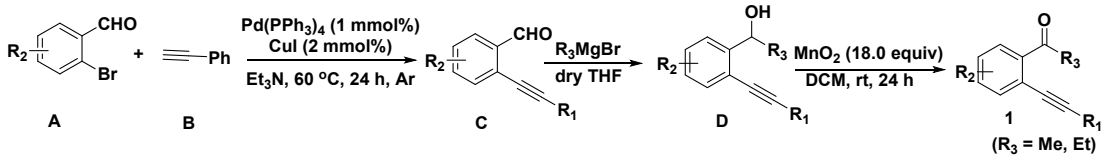
2.1 General procedure for the synthesis of *o*-alkynylarylketones **1**

Method A[1]:



Typical procedure: To a mixture of dichlorobis-(triphenylphosphine)palladium (2 mol %) and *o*-bromoacetophenone (1 equiv) in THF (5.0 mL) was added triethyl amine (3.0 equiv). After being stirred for 10 min at room temperature, terminal acetylene (1.1 equiv) and copper iodide (5 mol %) were added to the mixture. The resulting mixture was stirred at room temperature for 24 h. After the reaction completed, the reaction mixture was quenched with saturated NH_4Cl (aq.), extracted with EtOAc three times, and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude mixture was purified by silica-gel column chromatography and delivered the corresponding products.

Method B[2]:



Typical procedure:

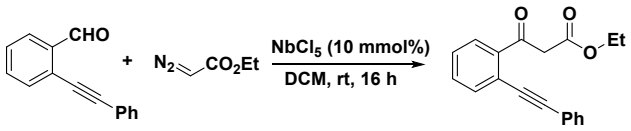
Step 1: To a mixture of $Pd(PPh_3)_4$ (1 mol %) and 2-bromobenzaldehyde **A** (1.0 equiv) in triethyl amine (3 mL). After being stirred for 10 min at room temperature, terminal acetylene **B** (1.1 equiv) and copper iodide (2 mol %) were added to the mixture. The resulting mixture was stirred at 60 °C for 24 h under Ar. The reaction mixture was quenched with saturated aq. NH_4Cl, extracted with EtOAc three times, and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude mixture was purified by silica-gel column chromatography and delivers the corresponding products **C** with excellent yield.

Step 2: Add a solution of substituted benzaldehyde **C** (1.0 equiv) in THF before addition of ethynylmagnesium bromide (1.0 mol/L in THF, 1.5 equiv) at 0 °C. Allow the reaction mixture to warm up to room temperature and stirred for 30 min, then, saturated aq. NH_4Cl (3 mL) was added and stirred for other 10 min, extracted with EtOAc three times, and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration.

The crude product **D** was used directly without further purification.

Step 3: To a solution of **D** (190 mg, 0.61 mmol) in CH_2Cl_2 (5 mL) was added small portions of activated MnO_2 (18.0 equiv) until disappearance of the starting material (TLC monitoring). The crude mixture needs to be filtered and further concentrated and purified by silica-gel column chromatography and gived the corresponding (*o*-alkynyl)arylketones with excellent yield.

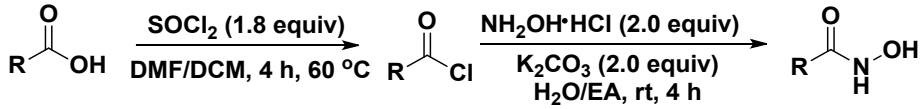
Method C[3]:



To a solution of CH_2Cl_2 (10.0 mL), $NbCl_5$ (10.0 mol %) and orthoalkynyl aldehydes (1 mmol), ethyl 2-diazoacetate (1.2 mmol) was added and the reaction mixture was allowed to stir at 25 ^oC for 16 h. The reaction mixture was filtered and diluted with EtOAc and washed with brine solution. The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography on silica gel.

2.2 General procedure for the synthesis of *N*-hydroxyamides **2**

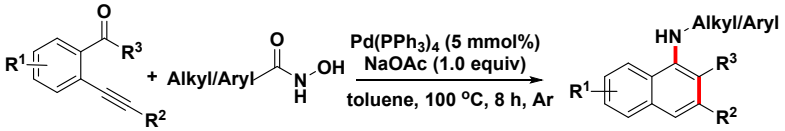
All *N*-hydroxyamides were prepared from the corresponding acid chloride and hydroxylamine hydrochloride according to the known literatures[4].



Step 1: $SOCl_2$ (2.0 equiv.) were added into a round bottom flask charged with a magnetic stir bar. Acid (1.0 equiv.) was dissolved in CH_2Cl_2 (0.5 M) with addition of a few drops of DMF. The solution of acid was dropped into the round bottom flask with $SOCl_2$ at room temperature. Then, the reaction mixture was refluxed in an oil bath preheated to 60 °C for 3 h. The mixture was concentrated in vacuo and the crude product was directly used in the next step.

Step 2: Hydroxylamine hydrochloride (2.0 equiv) was added to a biphasic mixture of K_2CO_3 (2.0 equiv) in a 2:1 mixture of EtOAc (24 mL) and H_2O (12 mL). The resulting solution was cooled to 0°C followed by dropwise addition of the unpurified acid chloride dissolved in a minimum amount of EtOAc. The flask containing the acid chloride was then rinsed with additional EtOAc. The reaction was allowed to stir for 2 h while reaching room temperature. Afterwards, the phases were separated and the aqueous phase was extracted twice with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The pure products were obtained without any further purification.

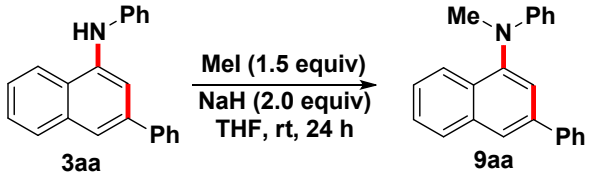
2.3 General procedure for the synthesis of the 1-naphthaleneamines derivatives **3**



The mixture of *o*-alkynylarylketones **1** (0.25 mmol), *N*-hydroxyamide **2** (0.3 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (5 mol%), NaOAc (1.0 equiv.) and toluene (3 mL) were successively added to a

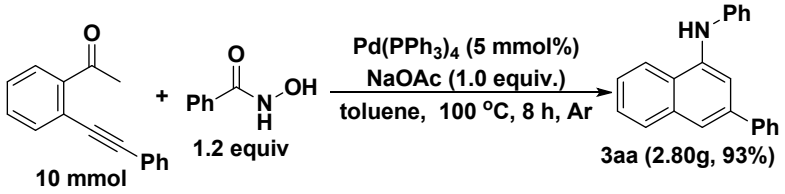
Schlenk reaction tube. The reaction mixture was stirred vigorously in an oil bath preheated to 100 °C under argon atmosphere for 8 hours. After the reaction mixture was cooled to room temperature, extracted with CH_2Cl_2 (3 × 10 mL), and washed with brine. The organic layers were combined, dried over Na_2SO_4, filtered, and then evaporated under vacuum. The residue was purified using flash column chromatography with a silica gel (200-300 mesh), using ethyl acetate and petroleum ether as the elution solvent to give desired product **3**.

2.4 General procedure for the synthesis of **9aa**



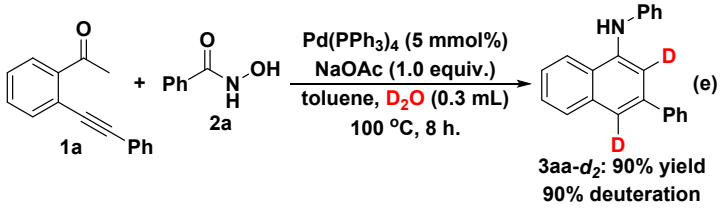
NaH (60% in mineral oil, 0.5 mmol, 2.0 equiv) was added to a solution of the **3aa** (0.25 mmol) in THF (5.0 mL) at 0 °C in portions. After stirring for 20 min at 0 °C, MeI (0.375 mmol, 1.5 equiv) was added drop-wise and the reaction mixture was allowed to warm to room temperature and stirred for another 24 h. After quenching with water, the residue was extracted with ethyl acetate twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtrated and concentrated, and purified by column chromatography to afford **9aa**.

2.5 Gram-scale synthesis of compound **3aa**



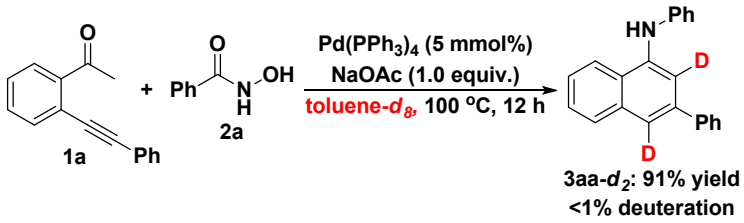
The mixture of 1-(2-(phenylethynyl)phenyl)ethanone **1a** (2.20 g, 10 mmol), *N*-hydroxybenzamide **2a** (1.644 g, 12 mmol), $Pd(PPh_3)_4$ (0.577 g, 0.5 mmol), NaOAc (0.82 g, 10 mmol) and toluene (20 mL) were successively added to a Schlenk reaction tube. The reaction mixture was stirred vigorously in an oil bath preheated to 100 °C under argon atmosphere for 8 hours. After the reaction mixture was cooled to room temperature, extracted with CH_2Cl_2 (3 × 100 mL), and washed with brine. The organic layers were combined, dried over Na_2SO_4, filtered, and then evaporated under vacuum. The residue was purified using flash column chromatography with a silica gel (200-300 mesh), using ethyl acetate and petroleum ether (v:v 1:20) as the elution solvent to give the desired product **3aa** in 93% yield.

2.6 The procedure of deuteration experiments.



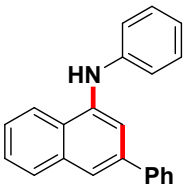
A Schlenk tube of 25 mL equipped with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (5

mol%), NaOAc (1.0 equiv.) in toluene (3 mL)/D_2O (0.3 mL); then, *o*-alkynylarylketones **1** (0.25 mmol), *N*-hydroxyamide **2** (0.3 mmol, 1.2 equiv), were added. The reaction mixture was stirred in an oil bath preheated to 100 °C under argon atmosphere for 8 hours. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude product was extracted with CH_2Cl_2 (3 × 10 mL), and the organic layer was dried over anhydrous Na_2SO_4 and then evaporated under vacuum. The residue was purified using flash column chromatography with a silica gel (200-300 mesh), using ethyl acetate and petroleum ether as the elution solvent to give desired product **3aa-*d*$_2$** in 90% yield.

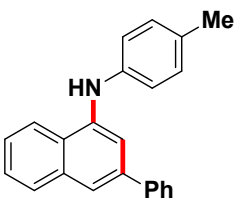


A Schlenk tube of 25 mL equipped with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (5 mol%), NaOAc (1.0 equiv.) in toluene-d_8 (3 mL); then, *o*-alkynylarylketones **1** (0.25 mmol), *N*-hydroxyamide **2** (0.3 mmol, 1.2 equiv), were added. The reaction mixture was heated at 100 °C for 8 h under Ar. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude product was extracted with CH_2Cl_2 (3 × 10 mL), and the organic layer was dried over anhydrous Na_2SO_4 and then evaporated under vacuum. The residue was purified using flash column chromatography with a silica gel (200-300 mesh), using ethyl acetate and petroleum ether as the elution solvent to give desired product **3aa-*d*$_2$** in 91% yield.

3. Analytical data for all products

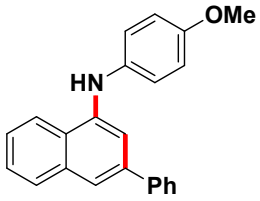


N,3-Diphenylnaphthalen-1-amine (**3aa**).[5] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 94% yield (70 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.78 (s, 1H), 7.69-7.68 (m, 3H), 7.54 (t, J = 7.5 Hz, 1H), 7.50-7.45 (m, 3H), 7.37 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 8.0 Hz, 2H), 7.08 (d, J = 7.5 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.03 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 141.4, 139.6, 139.3, 135.4, 129.9, 129.3, 129.2, 127.8, 127.7, 127.2, 127.0, 126.1, 122.0, 121.2, 121.1, 117.9, 115.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}N$ 296.1434; Found 296.1434.

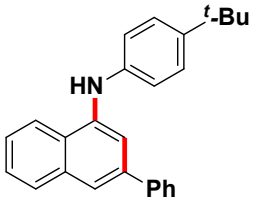


3-Phenyl-*N*-(*p-tolyl*)naphthalen-1-amine (**3ab**).[5] This compound was purified by column

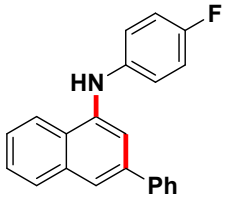
chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 91% yield (70 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.60 (s, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.50-7.45 (m, 3H), 7.37 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 5.99 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 141.6, 140.4, 139.3, 135.3, 131.0, 130.4, 129.3, 129.1, 127.7, 126.9, 126.4, 125.9, 121.7, 120.2, 119.0, 113.6; HRMS (ESI-TOF) m/z: [M + H] $^+$ Calcd for $C_{23}H_{20}N$ 310.1590; Found 310.1589.



N-(4-Methoxyphenyl)-3-phenylnaphthalen-1-amine (**3ac**).[5] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:10) to afford a yellow oil in 84% yield (68 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.65-7.63 (m, 3H), 7.54-7.43 (m, 4H), 7.40 (s, 1H), 7.37-7.33 (m, 1H), 7.14-7.12 (m, 2H), 6.92-6.89 (m, 2H), 3.82 (s,3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.6, 141.7, 139.4, 136.9, 135.3, 129.3, 129.1, 127.7, 127.7, 126.8, 125.8, 125.4, 122.4, 121.3, 119.2, 115.2, 111.3, 56.0; HRMS (ESI-TOF) m/z: [M + H] $^+$ Calcd for $C_{23}H_{20}NO$ 326.1542; Found 326.1539.

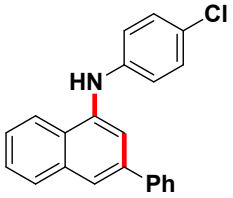


N-(4-(*tert*-Butyl)phenyl)-3-phenylnaphthalen-1-amine (**3ad**).[5] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 86% yield (75 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.73 (s, 1H), 7.70-7.68 (m, 2H), 7.65 (s, 1H), 7.55-7.51 (m, 1H), 7.50-7.45 (m, 3H), 7.38-7.35 (m, 1H), 7.34-7.32 (m, 2H), 7.08-7.05 (m, 2H), 6.01 (s, 1H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 141.9, 141.6, 140.1, 139.3, 135.3, 129.3, 129.1, 127.8, 127.7, 126.9, 126.6, 126.6, 125.9, 121.7, 120.4, 118.1, 114.1, 34.6, 31.9; HRMS (ESI-TOF) m/z: [M + H] $^+$ Calcd for $C_{26}H_{26}N$ 352.2060; Found 352.2063.

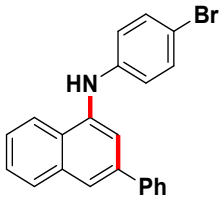


N-(4-Fluorophenyl)-3-phenylnaphthalen-1-amine (**3ae**).[5] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 88% yield (69 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.74 (s, 1H), 7.67 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 8.0 Hz, 1H), 7.50-7.45 (m, 4H), 7.37 (t, J = 7.5 Hz, 1H), 7.06-6.99 (m, 4H), 5.95 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3 (d, $J_{C\text{-}F}$ = 238.4 Hz), 141.4, 140.6, 140.5, 139.3, 135.3, 129.3, 129.2, 127.8, 127.7, 127.0, 126.4, 126.1, 121.7, 120.6 (d, $J_{C\text{-}F}$ = 2.6 Hz), 120.5, 116.5 (d, $J_{C\text{-}F}$ = 22.4 Hz), 113.8; HRMS (ESI-TOF) m/z: [M + H] $^+$ Calcd for

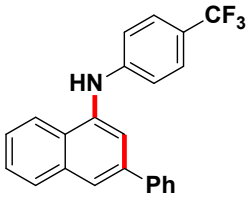
$C_{22}H_{17}FN$ 314.1340; Found 314.1340.



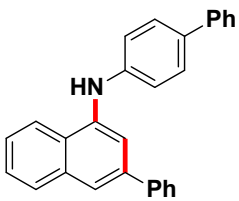
N-(4-Chlorophenyl)-3-phenylnaphthalen-1-amine (**3af**).[5] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 91% yield (75 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.61 (s, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.49-7.45 (m, 3H), 7.37 (t, J = 7.5 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 5.98 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 141.2, 139.2, 139.1, 135.3, 129.7, 129.3, 129.2, 127.9, 127.7, 127.2, 127.1, 126.3, 125.6, 122.0, 121.8, 118.9, 116.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}ClN$ 330.1044; Found 330.1048.



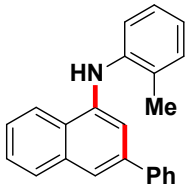
N-(4-Bromophenyl)-3-phenylnaphthalen-1-amine (**3ag**).[5] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 93% yield (87 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.81 (s, 1H), 7.68-7.66 (m, 2H), 7.63 (s, 1H), 7.55-7.52 (m, 1H), 7.49-7.45 (m, 3H), 7.39-7.34 (m, 3H), 6.91-6.89 (m, 2H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 141.9, 139.2, 138.9, 135.3, 132.6, 129.3, 129.2, 127.9, 127.7, 127.4, 127.1, 126.3, 122.1, 121.9, 119.0, 116.6, 112.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}BrN$ 374.0539; Found 374.0532.



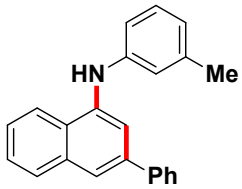
3-Phenyl-*N*-(4-(trifluoromethyl)phenyl)naphthalen-1-amine (**3ah**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 68% yield (62 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99-7.95 (m, 2H), 7.91 (s, 1H), 7.73 (s, 1H), 7.57-7.56 (m, 1H), 7.51-7.46 (m, 5H), 7.40 (t, J = 7.5 Hz, 1H), 6.96 (d, J = 8.5 Hz, 2H), 6.13 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 140.9, 139.2, 137.6, 135.4, 129.3, 128.4, 128.0, 127.7, 127.2, 127.1 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.6, 125.1 (q, $J_{C\text{-}F}$ = 269.1 Hz), 123.3, 122.4, 121.6 (q, $J_{C\text{-}F}$ = 32.4 Hz), 119.5, 115.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{17}F_3N$ 364.1453; Found 364.1450.



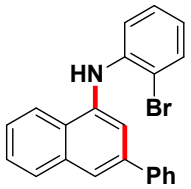
N-([1,1'-Biphenyl]-4-yl)-3-phenylnaphthalen-1-amine (**3ai**) This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 79% yield (73 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.73 (s, 1H), 7.71-7.69 (m, 2H), 7.60-7.58 (m, 2H), 7.56-7.45 (m, 6H), 7.43 (t, J = 7.0 Hz, 2H), 7.38 (t, J = 7.0 Hz, 1H), 7.31 (t, J = 7.0 Hz, 1H), 7.14 (d, J = 8.5 Hz, 2H), 6.10 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 141.3, 141.2, 139.3, 139.2, 135.3, 133.8, 129.3, 129.2, 129.1, 128.5, 127.8, 127.7, 127.2, 127.0, 126.9, 126.9, 126.2, 122.0, 121.4, 117.9, 115.9, 30.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{22}N$ 372.1747; Found 372.1748.



3-Phenyl-*N*-(*o-tolyl*)naphthalen-1-amine (**3aj**).[5] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 88% yield (68 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.67 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.48-7.44 (m, 2H), 7.37-7.35 (m, 2H), 7.27 (d, J = 7.0 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 5.85 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 141.5, 140.3, 139.3, 135.3, 131.3, 129.3, 129.1, 128.0, 127.7, 127.7, 127.4, 126.9, 126.5, 126.0, 122.1, 121.9, 120.4, 119.2, 114.5, 18.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N$ 310.1590; Found 310.1592.

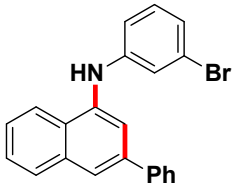


3-Phenyl-*N*-(*m-tolyl*)naphthalen-1-amine (**3ak**).[5] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 90% yield (70 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.78 (s, 1H), 7.71 (s, 1H), 7.68-7.68 (m, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.50-7.46 (m, 3H), 7.38 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 6.91-6.90 (m, 2H), 6.79 (d, J = 7.5 Hz, 1H), 5.98 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 141.4, 139.7, 139.2, 135.3, 129.7, 129.3, 129.2, 127.8, 127.7, 127.2, 126.9, 126.1, 122.0, 121.9, 121.0, 118.7, 115.5, 115.0, 22.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N$ 310.1590; Found 310.1591.

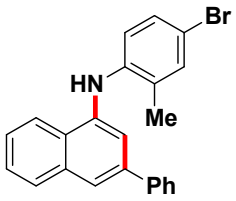


N-(2-Bromophenyl)-3-phenylnaphthalen-1-amine (**3al**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 85% yield (79 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.89 (s, 1H), 7.73-7.69 (m, 3H), 7.59-7.53 (m, 2H), 7.52-7.46 (m, 3H), 7.40-7.36 (m, 1H), 7.10 (t, J = 8.5 Hz,

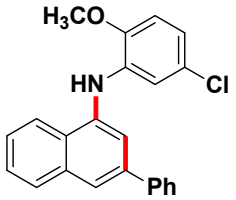
1H), 6.95 (d, J = 8.0 Hz, 1H), 6.73 (t, J = 8.0 Hz, 1H), 6.46 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 141.8, 139.2, 138.1, 135.4, 133.2, 129.3, 129.2, 128.6, 128.5, 127.9, 127.7, 127.1, 126.6, 123.0, 122.5, 120.7, 119.4, 115.9, 111.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}BrN$ 374.0539; Found 374.0531.



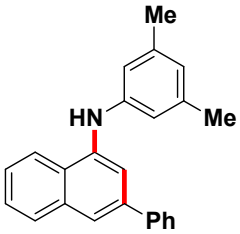
N-(3-Bromophenyl)-3-phenylnaphthalen-1-amine (**3am**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 89% yield (83 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.73-7.70 (m, 3H), 7.57 (t, J = 7.5 Hz, 1H), 7.53-7.50 (m, 3H), 7.41 (t, J = 7.5 Hz, 1H), 7.16-7.11 (m, 2H), 7.04 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 6.00 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 141.1, 139.2, 138.4, 135.3, 131.0, 129.3, 127.9, 127.9, 127.7, 127.1, 126.4, 123.6, 123.3, 122.6, 122.2, 119.6, 118.0, 115.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}BrN$ 374.0539; Found 374.0534.



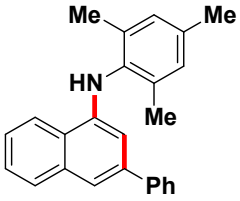
N-(4-Bromo-2-methylphenyl)-3-phenylnaphthalen-1-amine (**3an**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 81% yield (79 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.78 (s, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.55-7.52 (m, 1H), 7.50-7.44 (m, 3H), 7.38-7.35 (m, 3H), 7.20 (dd, J = 8.5, 2.5 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 5.75 (br, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 141.2, 139.7, 139.3, 135.3, 133.8, 130.1, 129.6, 129.3, 129.2, 127.9, 127.7, 127.0, 126.8, 126.2, 121.9, 121.2, 120.1, 115.7, 113.8, 18.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}BrN$ 388.0695; Found 388.0703.



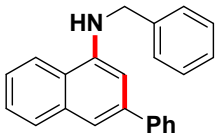
N-(5-Chloro-2-methoxyphenyl)-3-phenylnaphthalen-1-amine (**3ao**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:10) to afford a yellow oil in 75% yield (67 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.86 (s, 1H), 7.74 (s, 1H), 7.72-7.70 (m, 2H), 7.55-7.52 (m, 1H), 7.50-7.46 (m, 1H), 7.40-7.36 (m, 1H), 6.93 (s, 1H), 6.83 (d, J = 8.5 Hz, 1H), 6.77-6.75 (m, 1H), 6.49 (br, 1H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 141.2, 139.2, 138.1, 136.6, 135.4, 129.2, 129.2, 128.3, 127.9, 127.7, 127.1, 126.5, 126.4, 122.6, 122.4, 118.6, 118.5, 113.8, 111.3, 56.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}ClNO$ 360.1150; Found 360.1152.



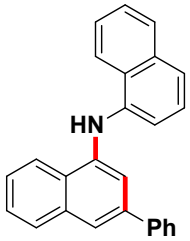
N-(3,5-Dimethylphenyl)-3-phenylnaphthalen-1-amine (**3ap**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 81% yield (65 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.76 (s, 1H), 7.71-7.66 (m, 3H), 7.52 (t, J = 8.0 Hz, 1H), 7.48-7.44 (m, 3H), 7.36 (t, J = 8.0 Hz, 1H), 6.71 (s, 2H), 6.60 (s, 1H), 5.93 (br, 1H), 2.27 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 141.5, 139.8, 139.5, 139.2, 135.3, 129.2, 129.1, 127.2, 126.9, 126.0, 123.0, 122.0, 121.0, 115.7, 115.7, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}N$ 324.5149; Found 324.5153.



N-Mesityl-3-phenylnaphthalen-1-amine (**3aq**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 86% yield (72 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.55-7.50 (m, 5H), 7.39 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.00 (s, 2H), 6.46 (s, 1H), 5.75 (br, 1H), 2.34 (s, 3H), 2.22 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 142.1, 139.7, 135.9, 135.6, 135.5, 135.2, 129.8, 129.4, 128.9, 127.8, 127.5, 126.6, 125.4, 123.4, 120.6, 117.0, 106.5, 21.3, 18.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}N$ 338.1903; Found 338.1907.

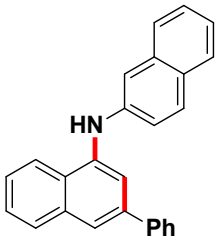


N-Benzyl-3-phenylnaphthalen-1-amine (**3ar**).[6] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 71% yield (55 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.0, 1.0 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.68-7.66 (m, 2H), 7.51-7.32 (m, 11H), 6.90 (s, 1H), 4.76 (br, 1H), 4.57 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 142.4, 139.7, 139.3, 134.9, 129.4, 129.2, 129.1, 128.3, 127.9, 127.8, 127.6, 127.6, 126.6, 125.2, 123.0, 120.2, 116.3, 104.8, 49.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N$ 310.1590; Found 310.1591.

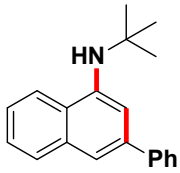


N-(Naphthalen-1-yl)-3-phenylnaphthalen-1-amine (**3as**).[6] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 89% yield

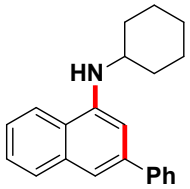
(76 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.78 (s, 1H), 7.62-7.59 (m, 3H), 7.57-7.47 (m, 4H), 7.42 (t, J = 7.5 Hz, 1H), 7.39-7.32 (m, 3H), 7.13 (d, J = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 141.1, 140.5, 139.4, 135.3, 135.1, 129.4, 129.1, 129.1, 127.7, 127.7, 127.3, 127.0, 126.6, 126.6, 126.4, 126.1, 126.1, 122.9, 122.1, 122.1, 120.7, 115.9, 115.2; HRMS (ESI-TOF) m/z: [M + H] $^+$ Calcd for $C_{26}H_{20}N$ 346.1590; Found 346.1593.



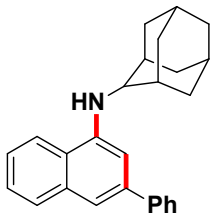
N-(Naphthalen-2-yl)-3-phenylnaphthalen-1-amine (**3at**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 87% yield (75 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.81-7.77 (m, 3H), 7.73 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.52-7.48 (m, 3H), 7.45-7.39 (m, 2H), 7.36-7.32 (m, 3H), 6.16 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 141.3, 139.6, 139.3, 135.4, 135.1, 129.7, 129.5, 129.3, 129.3, 128.1, 127.9, 127.7, 127.4, 127.1, 126.9, 126.2, 123.8, 122.2, 121.6, 120.2, 116.2, 112.1; HRMS (ESI-TOF) m/z: [M + H] $^+$ Calcd for $C_{26}H_{20}N$ 346.1590; Found 346.1592.



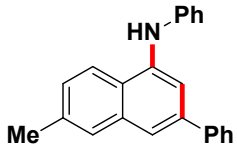
N-(*tert*-Butyl)-3-phenylnaphthalen-1-amine (**3au**).[6] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 85% yield (58 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84-7.80 (m, 2H), 7.73-7.71 (m, 2H), 7.49-7.41 (m, 5H), 7.39-7.36 (m, 1H), 7.19 (s, 1H), 1.53 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 139.3, 135.2, 129.5, 129.1, 127.8, 127.5, 126.3, 125.1, 124.9, 120.6, 116.4, 109.8, 52.1, 30.4; HRMS (ESI-TOF) m/z: [M + H] $^+$ Calcd for $C_{20}H_{22}N$ 276.1747; Found 276.1746.



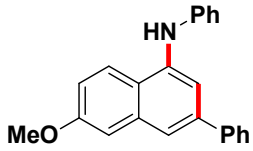
N-Cyclohexyl-3-phenylnaphthalen-1-amine (**3av**).[6] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 89% yield (67 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 8.0, 1.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.74-7.71 (m, 2H), 7.51-7.45 (m, 3H), 7.44-7.42 (m, 1H), 7.41-7.37 (m, 2H), 6.87 (s, 1H), 4.36 (br, 1H), 3.61-3.56 (m, 1H), 2.25-2.22 (m, 2H), 1.86-1.82 (m, 2H), 1.74-1.70 (m, 1H), 1.52-1.43 (m, 2H), 1.40-1.28 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 142.7, 139.9, 135.2, 129.4, 129.0, 127.9, 127.5, 126.4, 124.9, 123.0, 120.1, 115.4, 104.7, 52.1, 33.6, 26.4, 25.4; HRMS (ESI-TOF) m/z: [M + H] $^+$ Calcd for $C_{22}H_{24}N$ 302.1903; Found 302.1908.



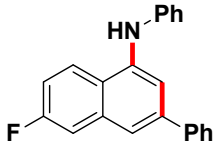
N-(3-Phenylnaphthalen-1-yl)adamantan-2-amine (**3aw**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 76% yield (67 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 9.0 Hz, 1H), 7.85-7.83 (m, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.53-7.48 (m, 3H), 7.46-7.42 (m, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.32 (s, 1H), 2.16 (s, 2H), 2.08 (s, 6H), 1.72 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 141.9, 139.0, 135.2, 129.4, 135.2, 129.4, 129.1, 127.8, 127.5, 126.2, 125.2, 121.2, 117.6, 113.3, 53.3, 43.8, 36.9, 30.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{28}N$ 354.2216; Found 354.2213.



6-Methyl-*N*,3-diphenylnaphthalen-1-amine (**3ba**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 92% yield (71 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.5 Hz, 1H), 7.73-7.70 (m, 4H), 7.63 (s, 1H), 7.49 (t, J = 8.0 Hz, 2H), 7.40 (t, J = 7.5 Hz, 1H), 7.34-7.30 (m, 3H), 7.09-7.07 (m, 2H), 6.97 (t, J = 7.5 Hz, 1H), 5.99 (br, 1H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 141.6, 139.5, 139.3, 136.7, 135.7, 129.8, 129.2, 128.4, 128.3, 127.7, 125.5, 122.0, 120.9, 120.7, 117.8, 114.9, 22.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N$ 310.1590; Found 310.1994.

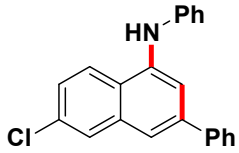


6-Methoxy-*N*,3-diphenylnaphthalen-1-amine (**3ca**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow oil in 90% yield (73 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 9.5 Hz, 1H), 7.70-7.69 (m, 3H), 7.53 (s, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.40-7.37 (m, 1H), 7.31-7.28 (m, 2H), 7.25-7.26 (m, 1H), 7.16-7.14 (m, 1H), 7.06-7.04 (m, 2H), 6.95 (t, J = 7.5 Hz, 1H), 5.97 (br, 1H), 3.96 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 145.1, 141.5, 140.0, 139.7, 136.8, 129.8, 129.2, 127.8, 127.7, 123.9, 122.6, 120.9, 120.3, 118.6, 117.8, 113.9, 107.2, 55.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}NO$ 326.1542; Found 326.1545.

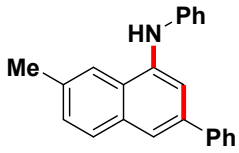


6-Fluoro-*N*,3-diphenylnaphthalen-1-amine (**3da**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 86% yield (67 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 9.0, 6.0 Hz, 1H), 7.71-7.68 (m, 3H), 7.63 (s, 1H), 7.55-7.48 (m, 3H), 7.43-7.40 (m, 1H), 7.35-7.31 (m, 2H), 7.26-7.23 (m, 1H), 7.07-7.05 (m, 2H),

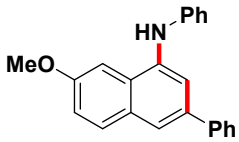
7.00 (t, J = 7.5 Hz, 1H), 5.96 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6 (d, $J_{C\text{-}F}$ = 245.1 Hz), 144.8, 141.1, 140.7, 140.0, 136.5 (d, $J_{C\text{-}F}$ = 9.2 Hz), 129.9, 129.3, 128.1, 127.8, 124.9 (d, $J_{C\text{-}F}$ = 9.0 Hz), 124.3, 121.3, 120.5 (d, $J_{C\text{-}F}$ = 4.8 Hz), 118.1, 116.1 (d, $J_{C\text{-}F}$ = 25.0 Hz), 115.0, 112.3, 112.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}FN$ 314.1340; Found 314.1344.



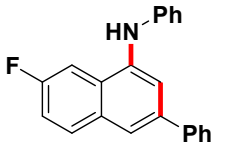
6-Chloro-N,3-diphenylnaphthalen-1-amine (**3ea**).[6] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 88% yield (73 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 9.0 Hz, 1H), 7.88 (s, 1H), 7.68-7.64 (m, 4H), 7.48 (t, J = 7.5 Hz, 2H), 7.42-7.38 (m, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.06-7.04 (m, 2H), 6.99 (t, J = 7.5 Hz, 1H), 5.94 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 141.0, 140.6, 139.9, 136.1, 132.8, 129.9, 129.3, 128.1, 127.8, 127.7, 126.7, 125.4, 124.0, 121.4, 120.2, 118.1, 115.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}ClN$ 330.1044; Found 330.1047.



7-Methyl-*N*,3-diphenylnaphthalen-1-amine (**3fa**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 93% yield (72 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 8.5 Hz, 1H), 7.85 (s, 1H), 7.80 (s, 1H), 7.74-7.72 (m, 3H), 7.51 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 6.99 (t, J = 7.5 Hz, 1H), 5.97 (br, 1H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 141.5, 139.0, 138.3, 136.0, 133.6, 129.9, 129.2, 127.7, 127.5, 121.1, 121.1, 120.9, 117.8, 115.9, 22.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N$ 310.1590; Found 310.1989.

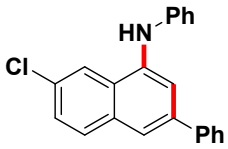


7-Methoxy-*N*,3-diphenylnaphthalen-1-amine (**3ga**).[6] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow oil in 88% yield (72 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5 Hz, 1H), 7.80 (s, 1H), 7.71-7.69 (m, 3H), 7.49 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 1H), 7.33-7.29 (m, 3H), 7.26-7.23 (m, 1H), 7.04 (d, J = 8.5 Hz, 2H), 6.95 (t, J = 7.5 Hz, 1H), 5.82 (br, 1H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3, 145.5, 141.4, 138.6, 136.9, 130.8, 129.8, 129.2, 129.0, 127.6, 121.7, 120.6, 119.6, 117.7, 117.3, 101.2, 55.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}NO$ 326.1542; Found 326.1539.

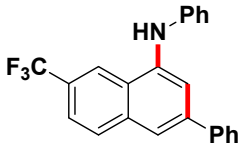


7-Fuoro-*N*,3-diphenylnaphthalen-1-amine (**3ha**).[6] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 82% yield (64 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.90 (m, 1H), 7.79 (s, 1H), 7.72 (s, 1H), 7.69-7.65 (m, 3H),

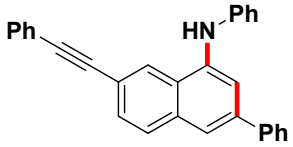
7.49 (t, J = 7.5 Hz, 1H), 7.42-7.38 (m, 1H), 7.34-7.30 (m, 3H), 7.05-7.02 (m, 2H), 6.98 (t, J = 7.5 Hz, 1H), 5.83 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2 (d, $J_{C\text{-}F}$ = 244.5 Hz), 144.9, 141.1, 139.3 (d, $J_{C\text{-}F}$ = 5.4 Hz), 138.6 (d, $J_{C\text{-}F}$ = 2.3 Hz), 132.3, 131.7 (d, $J_{C\text{-}F}$ = 8.9 Hz), 129.9, 129.3, 128.5, 128.4, 127.9, 127.7, 121.3, 121.1, 117.7, 117.4, 117.2, 117.2, 106.3 (d, $J_{C\text{-}F}$ = 22.0 Hz); HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{22}H_{17}FN$ 314.1340; Found 314.1339.



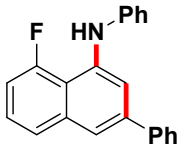
7-Chloro-*N*,3-diphenylnaphthalen-1-amine (**3ia**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 84% yield (70 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.73 (s, 1H), 7.70-7.69 (m, 1H), 7.67-7.65 (m, 2H), 7.49-7.45 (m, 3H), 7.41-7.37 (m, 1H), 7.33-7.29 (m, 2H), 7.07-7.04 (m, 2H), 6.98 (t, = 7.5 Hz, 1H), 5.88 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 141.0, 139.6, 139.1, 133.6, 132.0, 130.8, 129.9, 129.3, 128.0, 127.8, 127.7, 121.3, 121.3, 120.9, 118.0, 116.5; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{22}H_{17}ClN$ 330.1044; Found 330.1039.



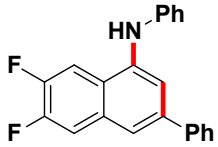
N,3-Diphenyl-7-(trifluoromethyl)naphthalen-1-amine (**3ja**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 72% yield (65 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.77 (s, 1H), 7.76-7.74 (m, 1H), 7.72-7.67 (m, 3H), 7.51-7.48 (m, 2H), 7.44-7.41 (m, 1H), 7.37-7.34 (m, 2H), 7.15-7.13 (m, 2H), 7.05-7.02 (m, 1H), 6.03 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 141.6, 141.0, 140.8, 136.6, 130.2, 130.0, 129.3, 128.3, 127.8 127.6 (q, $J_{C\text{-}F}$ = 32.0 Hz), 125.7 124.9 (q, $J_{C\text{-}F}$ = 270.4 Hz), 122.6, 122.5, 121.9, 120.3, 119.8 (q, $J_{C\text{-}F}$ = 4.3 Hz), 118.7, 115.6; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{23}H_{17}F_3N$ 364.1453; Found 364.1458.



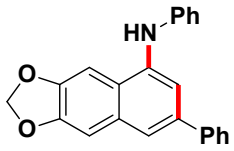
N,3-Diphenyl-7-(phenylethynyl)naphthalen-1-amine (**3ka**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 86% yield (84 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.72-7.60 (m, 7H), 7.47 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.0 Hz, 4H), 7.33 (t, J = 7.5 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.00 (t, J = 7.5 Hz, 1H), 6.03 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 141.2, 140.1, 139.7, 134.7, 132.0, 129.9, 129.5, 129.3, 129.2, 128.8, 128.7, 128.0, 127.7, 126.6, 125.5, 123.6, 121.4, 120.6, 120.5, 118.3, 115.3, 90.5; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{30}H_{22}N$ 396.0571; Found 396.0568.



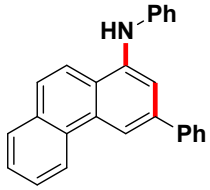
8-Fluoro-*N*,3-diphenylnaphthalen-1-amine (**3la**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 92% yield (72 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.64 (m, 3H), 7.61-7.60 (m, 1H), 7.56-7.55 (m, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.40-7.32 (m, 7H), 7.10-7.06 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6 (d, $J_{C\text{-}F}$ = 245.8 Hz), 142.7, 141.2, 140.6, 140.3, 138.2, 129.9, 129.2, 128.0, 127.7, 126.5 (d, $J_{C\text{-}F}$ = 10.0 Hz), 125.5, 122.9, 121.1, 117.6, 114.5 (d, $J_{C\text{-}F}$ = 8.4 Hz), 110.5 (d, $J_{C\text{-}F}$ = 24.4 Hz), 110.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}FN$ 314.1340; Found 314.1345.



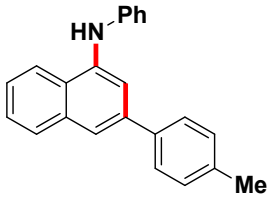
6,7-Difluoro-*N*,3-diphenylnaphthalen-1-amine (**3ma**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 82% yield (68 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.78-7.74 (m, 1H), 7.68 (s, 1H), 7.65-7.60 (m, 4H), 7.48-7.45 (m, 2H), 7.40-7.37 (m, 1H), 7.31-7.27 (m, 2H), 7.00-6.95 (m, 3H), 5.80 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8 (dd, $J_{C\text{-}F}$ = 248.9, 15.1 Hz), 150.3 (dd, $J_{C\text{-}F}$ = 247.2, 14.4 Hz), 144.7, 140.8, 140.3 (d, $J_{C\text{-}F}$ = 2.1 Hz), 139.5 (d, $J_{C\text{-}F}$ = 4.2 Hz), 132.3 (d, $J_{C\text{-}F}$ = 7.1 Hz), 129.9, 129.3, 128.1, 127.6, 124.5 (d, $J_{C\text{-}F}$ = 6.1 Hz), 117.7, 116.8, 114.8, 114.7, 109.3, 109.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{16}F_2N$ 331.9572; Found 396.9576.



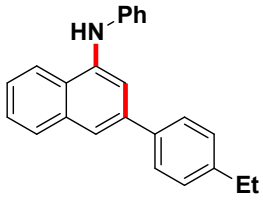
N,7-Diphenylnaphtho[2,3-*d*][1,3]dioxol-5-amine (**3na**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:8) to afford a yellow oil in 94% yield (80 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.65 (m, 2H), 7.55 (s, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.37-7.34 (m, 1H), 7.33 (s, 1H), 7.25-7.23 (m, 2H), 7.20 (s, 1H), 6.93-6.88 (m, 3H), 6.03 (s, 2H), 5.73 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 148.3, 145.8, 141.3, 138.7, 137.9, 132.5, 129.8, 129.2, 127.6, 127.5, 125.2, 121.6, 120.3, 117.1, 116.8, 105.1, 101.6, 99.5, HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{18}NO_2$ 340.4837; Found 340.4840.



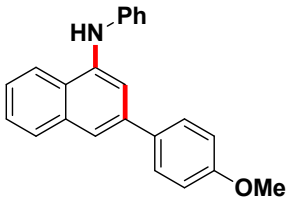
N,3-Diphenylphenanthren-1-amine (**3oa**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 92% yield (80 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, J = 8.0 Hz, 1H), 8.68 (s, 1H), 7.97 (d, J = 9.5 Hz, 1H), 7.92 (dd, J = 8.0, 1.0 Hz, 1H), 7.79-7.77 (m, 3H), 7.74-7.69 (m, 2H), 7.66-7.63 (m, 1H), 7.54-7.49 (m, 2H), 7.44 (t, J = 7.5 Hz, 1H), 7.32-7.29 (m, 2H), 7.03-7.01 (m, 2H), 6.96 (t, J = 7.5 Hz, 1H), 5.97 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 141.8, 140.1, 140.0, 132.6, 132.4, 131.0, 129.8, 129.3, 129.1, 127.9, 127.2, 127.2, 125.7, 123.5, 121.0, 120.7, 118.2, 117.3, 116.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{20}N$ 346.0972; Found 346.0968.



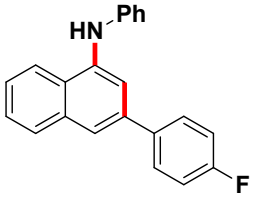
N-Phenyl-3-(*p*-tolyl)naphthalen-1-amine (**3pa**).[5] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 90% yield (70 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.76 (s, 1H), 7.67 (s, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.30-7.27 (m, 4H), 7.07 (d, J = 8.0 Hz, 2H), 6.96-6.92 (m, 1H), 6.01 (br, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 139.5, 139.2, 138.5, 137.6, 135.4, 129.9, 129.8, 129.2, 127.5, 127.1, 126.9, 125.9, 122.0, 120.9, 120.9, 117.8, 115.6, 21.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N$ 310.1590; Found 310.1994.



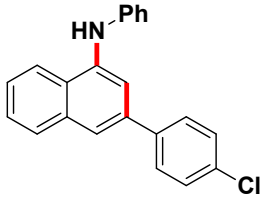
3-(4-Ethylphenyl)-*N*-phenylnaphthalen-1-amine (**3qa**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 91% yield (73 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.77 (s, 1H), 7.68 (s, 1H), 7.62-7.60 (m, 2H), 7.54-7.51 (m, 1H), 7.48-7.45 (m, 1H), 7.31-7.27 (m, 4H), 7.08-7.06 (m, 2H), 6.94 (t, J = 7.5 Hz, 1H), 6.01 (br, 1H), 2.72 (q, J = 7.5 Hz, 2H), 1.29 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 144.0, 139.5, 139.2, 138.7, 135.4, 129.8, 129.2, 128.7, 127.6, 127.0, 126.9, 125.9, 122.0, 121.0, 120.9, 117.9, 115.6, 28.9, 16.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N$ 324.1747; Found 324.1750.



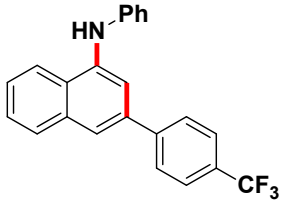
3-(4-Methoxyphenyl)-*N*-phenylnaphthalen-1-amine (**3ra**).[5] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:10) to afford a yellow oil in 92% yield (75 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.74 (s, 1H), 7.66-7.62 (m, 3H), 7.54-7.51 (m, 1H), 7.48-7.45 (m, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.08-7.06 (m, 2H), 7.01 (d, J = 8.0 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.01 (br, 1H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 145.0, 139.5, 138.8, 135.4, 133.9, 129.8, 129.1, 128.7, 126.9, 125.8, 122.0, 120.9, 120.5, 117.8, 115.5, 114.6, 55.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}NO$ 326.1539; Found 326.1542.



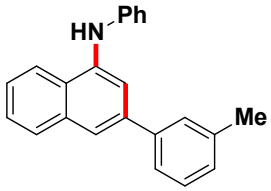
3-(4-Fluorophenyl)-*N*-phenylnaphthalen-1-amine (**3sa**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 91% yield (71 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 7.5 Hz, 1H), 7.91 (d, J = 7.5 Hz, 1H), 7.71 (s, 1H), 7.65-7.60 (m, 3H), 7.56-7.52 (m, 1H), 7.50-7.47 (m, 1H), 7.32-7.28 (m, 2H), 7.14-7.12 (m, 2H), 7.09-7.06 (m, 2H), 6.98-6.95 (m, 1H), 6.02 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{-}F}$ = 245 Hz), 144.8, 139.8, 138.2, 137.5, 135.3, 129.9, 129.3, 127.1, 127.0, 126.1, 122.0, 121.2, 120.8, 118.1, 116.1, 116.0, 115.0; HRMS (ESI-TOF) m/z: [M + H] $^+$ Calcd for $C_{22}H_{17}FN$ 314.1340; Found 314.1343.



3-(4-Chlorophenyl)-*N*-phenylnaphthalen-1-amine (**3ta**).[5] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 89% yield (73 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.71 (s, 1H), 7.60-7.57 (m, 3H), 7.55-7.47 (m, 2H), 7.42-7.41 (m, 2H), 7.30 (t, J = 8.0 Hz, 2H), 7.07 (d, J = 7.5 Hz, 2H), 6.96 (t, J = 7.5 Hz, 1H), 6.03 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 139.8, 138.0, 135.3, 133.8, 129.9, 129.3, 129.3, 128.9, 127.1, 127.1, 126.3, 121.9, 121.3, 120.9, 118.1, 114.7; HRMS (ESI-TOF) m/z: [M + H] $^+$ Calcd for $C_{22}H_{17}ClN$ 330.1044; Found 330.1046.

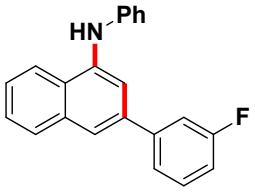


N-Phenyl-3-(4-(trifluoromethyl)phenyl)naphthalen-1-amine (**3ua**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 74% yield (67 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.77-7.76 (m, 3H), 7.71-7.69 (m, 2H), 7.62 (s, 1H), 7.57-7.50 (m, 2H), 7.32-7.29 (m, 2H), 7.10-7.08 (m, 2H), 6.99-6.96 (m, 1H), 6.04 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 144.5, 140.1, 137.7, 135.2, 129.9, 129.6 (q, $J_{C\text{-}F}$ = 30.8 Hz), 129.4, 127.9, 127.2, 126.6, 126.1, 126.1, 124.6 (q, $J_{C\text{-}F}$ = 270.3 Hz), 121.9, 121.5, 121.3, 118.3, 114.3, 114.3; HRMS (ESI-TOF) m/z: [M + H] $^+$ Calcd for $C_{23}H_{17}F_3N$ 364.1453; Found 364.1450.

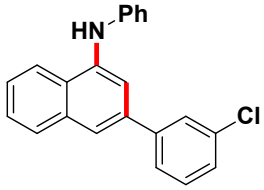


N-Phenyl-3-(m-tolyl)naphthalen-1-amine (**3va**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 87% yield (67 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04(d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.70 (s,1H), 7.56-7.47 (m, 4H), 7.38 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 7.21 (d, J = 7.5 Hz, 1H), 7.08-7.07 (m, 2H), 6.96 (t, J = 7.5 Hz, 1H), 6.02 (br, 1H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 141.4, 139.5, 139.4, 138.8, 135.4, 129.8, 129.3, 129.1, 128.6, 128.5, 127.2, 126.9,

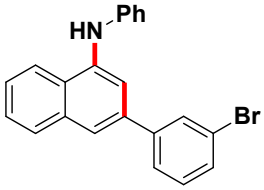
126.0, 124.9, 122.1, 121.3, 120.9, 117.7, 115.9, 22.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N$ 310.1590; Found 310.1986.



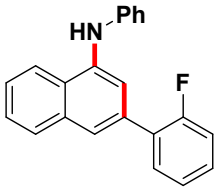
3-(3-Fluorophenyl)-*N*-phenylnaphthalen-1-amine (**3wa**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 86% yield (66 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.74 (s, 1H), 7.62 (s, 1H), 7.56-7.48 (m, 2H), 7.46-7.35 (m, 3H), 7.32-7.28 (m, 2H), 7.09-7.03 (m, 3H), 6.98-6.94 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6 (d, $J_{C\text{-}F}$ = 244.1 Hz), 144.6, 143.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 139.9, 137.9, 137.9, 135.2, 130.6 (d, $J_{C\text{-}F}$ = 8.4 Hz), 129.9, 129.3, 127.2, 127.1, 126.4, 123.3 (d, $J_{C\text{-}F}$ = 2.5 Hz), 121.9, 121.3, 121.1, 118.1, 114.7, 114.6, 114.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}FN$ 314.1340; Found 314.1344.



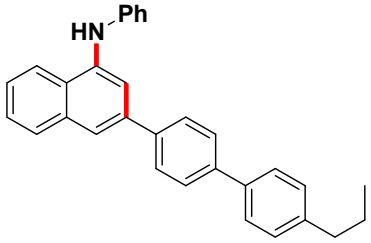
3-(3-Chlorophenyl)-*N*-phenylnaphthalen-1-amine (**3xa**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 91% yield (75 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 9.0 Hz, 1H), 7.73 (s, 1H), 7.66-7.65 (m, 1H), 7.61 (s, 1H), 7.56-7.48 (m, 3H), 7.37 (t, J = 8.0 Hz, 1H), 7.34-7.28 (m, 3H), 7.08-7.06 (m, 2H), 6.95 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 143.3, 139.9, 137.8, 135.2, 135.1, 130.4, 129.9, 129.3, 127.8, 127.3, 127.2, 126.4, 125.9, 122.0, 121.3, 121.2, 118.0, 114.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}ClN$ 330.1044; Found 330.1042.



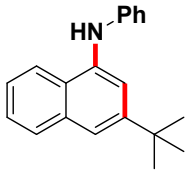
3-(3-Bromophenyl)-*N*-phenylnaphthalen-1-amine (**3ya**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 87% yield (81 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.81-7.80 (m, 1H), 7.72 (s, 1H), 7.59-7.42 (m, 5H), 7.33-7.28 (m, 3H), 7.07-7.06 (m, 2H), 6.95 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 143.6, 139.8, 137.7, 135.2, 130.7, 129.8, 129.3, 127.2, 127.1, 126.4, 126.3, 123.3, 122.0, 121.2, 118.0, 114.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}BrN$ 374.0539; Found 374.0537.



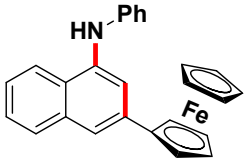
3-(2-Fluorophenyl)-*N*-phenylnaphthalen-1-amine (**3za**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 85% yield (66 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.77 (s, 1H), 7.64 (s, 1H), 7.57-7.50 (m, 3H), 7.38-7.30 (m, 3H), 7.27-7.18 (m, 2H), 7.10 (d, J = 7.5 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 6.03 (br, 1H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4 (d, $J_{C\text{-}F}$ = 246.5 Hz), 144.9, 139.1, 135.1, 134.0, 131.3 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.8, 129.5 129.4, 129.3, 127.2, 126.9, 126.4, 124.8 (d, $J_{C\text{-}F}$ = 3.5 Hz), 123.4 (d, $J_{C\text{-}F}$ = 2.5 Hz), 122.0, 121.0, 117.9, 117.0, 116.6 (d, $J_{C\text{-}F}$ = 22.6 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}FN$ 314.1340; Found 314.1344.



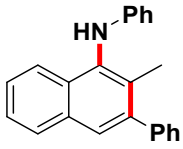
N-Phenyl-3-(4'-propyl-[1,1'-biphenyl]-4-yl)naphthalen-1-amine (**3a'a**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 88% yield (66 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.83 (s, 1H), 7.75 (t, J = 8.0 Hz, 3H), 7.69 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.32-7.29 (m, 4H), 7.09 (d, J = 7.5 Hz, 2H), 6.96 (t, J = 7.5 Hz, 1H), 2.66 (t, J = 7.5 Hz, 2H), 1.75-1.68 (m, 2H), 1.01 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 142.4, 140.6, 139.9, 139.6, 138.8, 138.4, 135.4, 129.8, 129.3, 129.3, 128.0, 127.7, 127.2, 127.2, 127.0, 126.1, 122.0, 121.1, 121.0, 117.9, 115.3, 38.1, 25.0, 14.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{28}NO$ 414.3618; Found 414.3615.



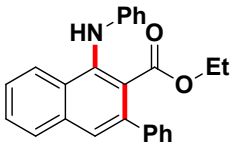
3-(*tert*-Butyl)-*N*-phenylnaphthalen-1-amine (**3b'a**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 68% yield (47 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.58 (s, 1H), 7.58 (s, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.5 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 6.93 (t, J = 7.5 Hz, 1H), 5.96 (br, 1H), 1.43 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 145.7, 138.3, 135.0, 129.8, 129.0, 126.9, 126.5, 125.5, 122.1, 120.3, 119.0, 116.9, 116.5, 35.3, 31.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{22}N$ 276.0894; Found 276.0890.



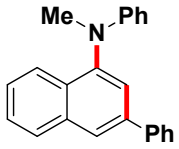
3-(Ferrocenyl)-*N*-phenylnaphthalen-1-amine (**3c'a**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 86% yield (87 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.63 (s, 1H), 7.61 (s, 1H), 7.50 (t, J = 7.0 Hz, 1H), 7.45-7.42 (m, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 7.5 Hz, 2H), 6.97 (t, J = 7.5 Hz, 1H), 5.96 (br, 1H), 4.72 (t, J = 2.0 Hz, 2H), 4.36 (t, J = 2.0 Hz, 2H), 4.08 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 138.9, 137.6, 135.3, 129.8, 128.6, 127.0, 126.9, 125.4, 122.1, 120.9, 119.4, 117.7, 115.9, 85.7, 70.0, 69.9, 69.5, 69.1, 67.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}FeN$ 403.6472; Found 403.6467.



2-Methyl-*N*,3-diphenylnaphthalen-1-amine (**3d'a**).[6] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 88% yield (68 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 7.0 Hz, 1H), 7.70 (s, 1H), 7.48-7.38 (m, 7H), 7.18 (t, J = 7.5 Hz, 2H), 6.77 (t, J = 7.5 Hz, 1H), 6.61 (d, J = 8.0 Hz, 2H), 5.64 (br, 1H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 142.3, 142.2, 135.3, 133.0, 131.8, 131.0, 129.8, 129.7, 128.5, 127.4, 127.2, 126.6, 126.1, 123.8, 118.7, 114.1, 16.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N$ 310.1590; Found 310.1592.



1-(3-Phenyl-1-(phenylamino)naphthalen-2-yl)propan-1-one (**3e'a**). This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 86% yield (75 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 9.0 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.67 (s, 1H), 7.55-7.52 (m, 1H), 7.46-7.34 (m, 6H), 7.16-7.12 (m, 2H), 6.83 (t, J = 7.5 Hz, 1H), 6.70-6.69 (m, 2H), 3.91 (q, J = 7.0 Hz, 2H), 0.72 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 146.6, 142.2, 139.0, 138.7, 135.1, 129.3, 128.8, 128.6, 128.5, 128.2, 127.5, 126.5, 126.3, 126.1, 120.3, 116.9, 61.6, 13.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}NO_2$ 368.1856; Found 368.1854.



N-Methyl-*N*,3-diphenylnaphthalen-1-amine (**9aa**).[7] This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:20) to afford a yellow oil in 92% yield (72 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.73-7.69 (m, 3H), 7.53 (t, J = 7.5 Hz, 1H), 7.50-7.43 (m, 3H), 7.39 (t, J = 7.5 Hz, 1H), 7.20 (t, J = 7.5 Hz, 2H), 6.77 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 9.0 Hz, 2H), 3.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 146.3, 140.9, 139.7, 135.8, 130.8, 129.4, 129.3, 129.2, 127.9, 127.7, 127.0, 126.7, 125.3, 124.7, 124.1, 117.7, 114.0, 40.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N$ 310.1590; Found 310.1586.

4. References

1. (a) Mandal, M.; Balamurugan, R. *Adv. Synth. Catal.* **2018**, *360*, 1453-1465; (b) Chen, X.; Martini, S.; Michelet, V. *Adv. Synth. Catal.* **2019**, *361*, 3612-3618; (c) Miao, T.; Tian, Z.; He, Y.; Chen, F.; Chen, Y.; Yu, Z.; Fan, Q.-H. *Angew. Chem. Int. Ed*. **2017**, *56*, 4135-4139; (d) Guo, B.; Zhang, L.; Yang, L.; Hua, R. *J. Org. Chem.* **2014**, *79*, 4352-4357.

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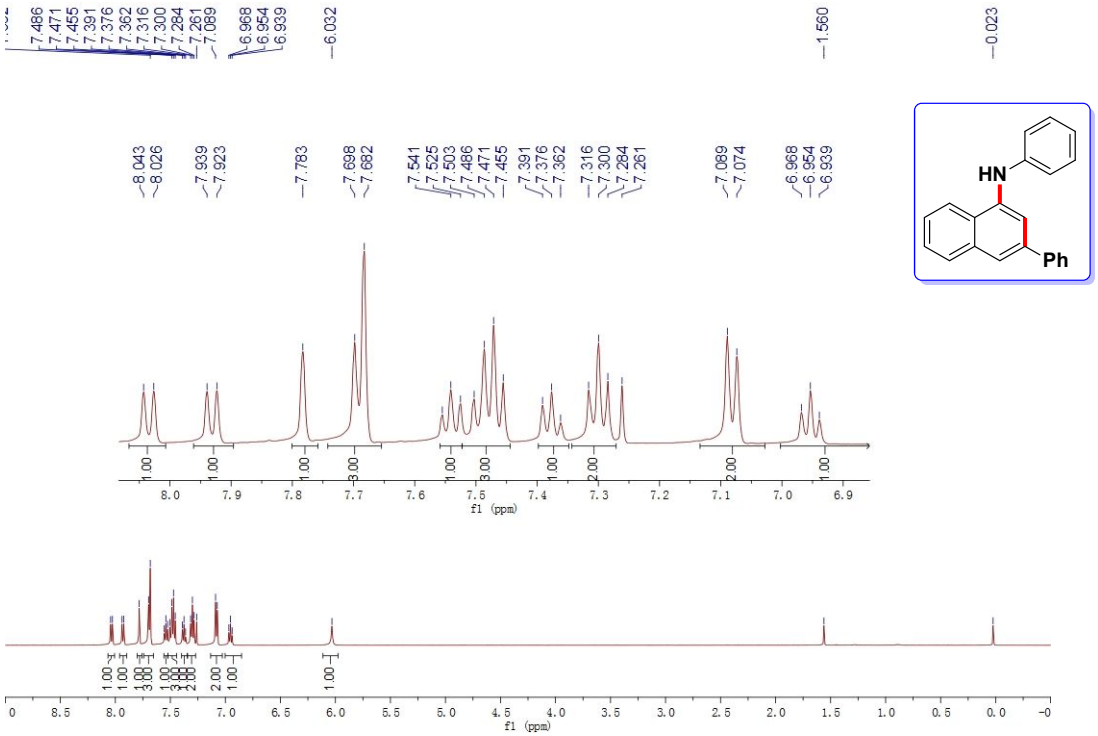
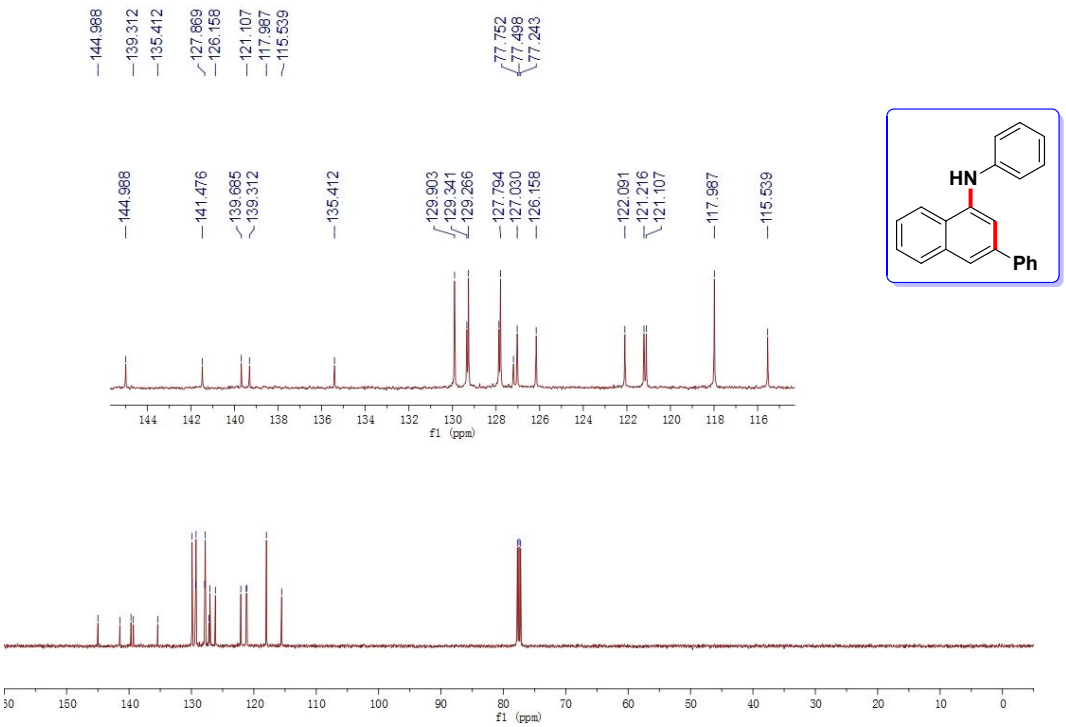
5. Copies of ^{1}H and ^{13}C NMR Spectra for all Compounds

^{1}H NMR and ^{13}C NMR Spectra of Compound 3aa

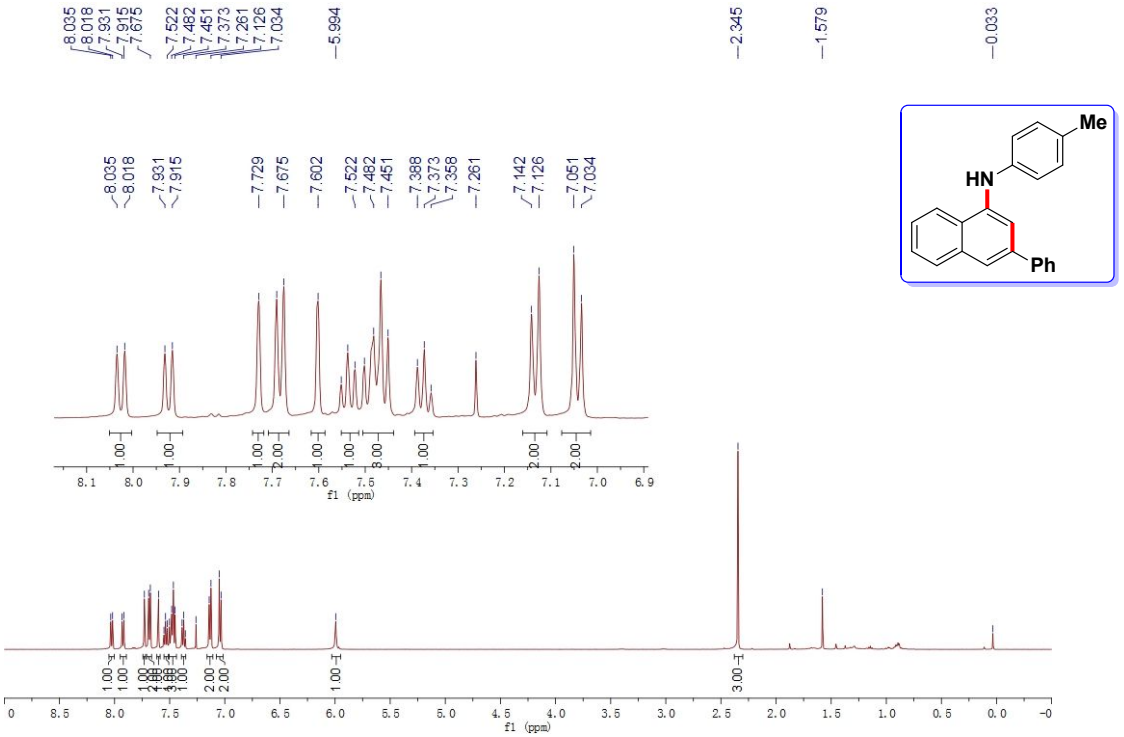


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

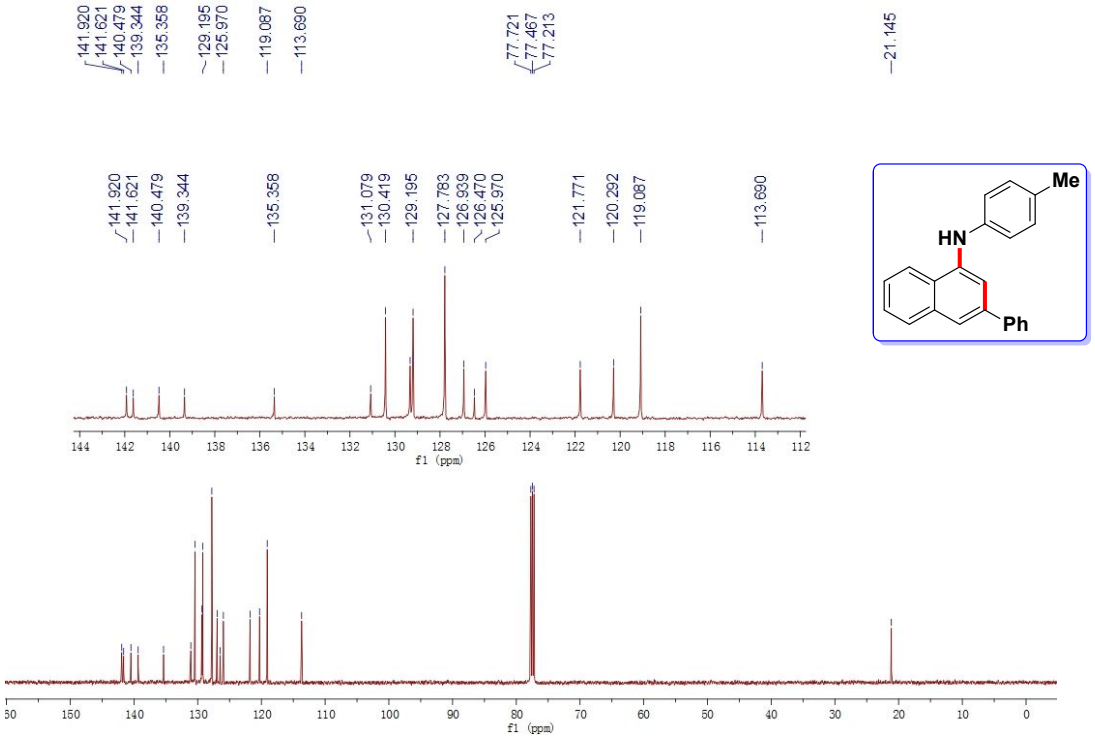


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ab

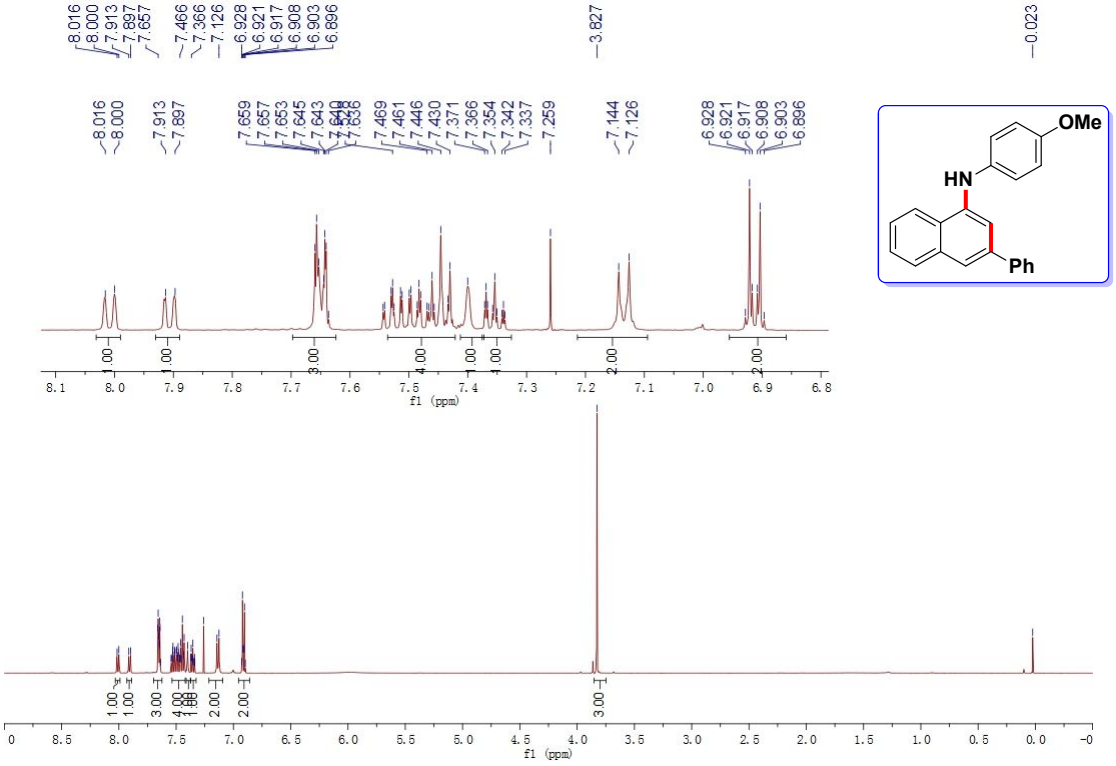


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

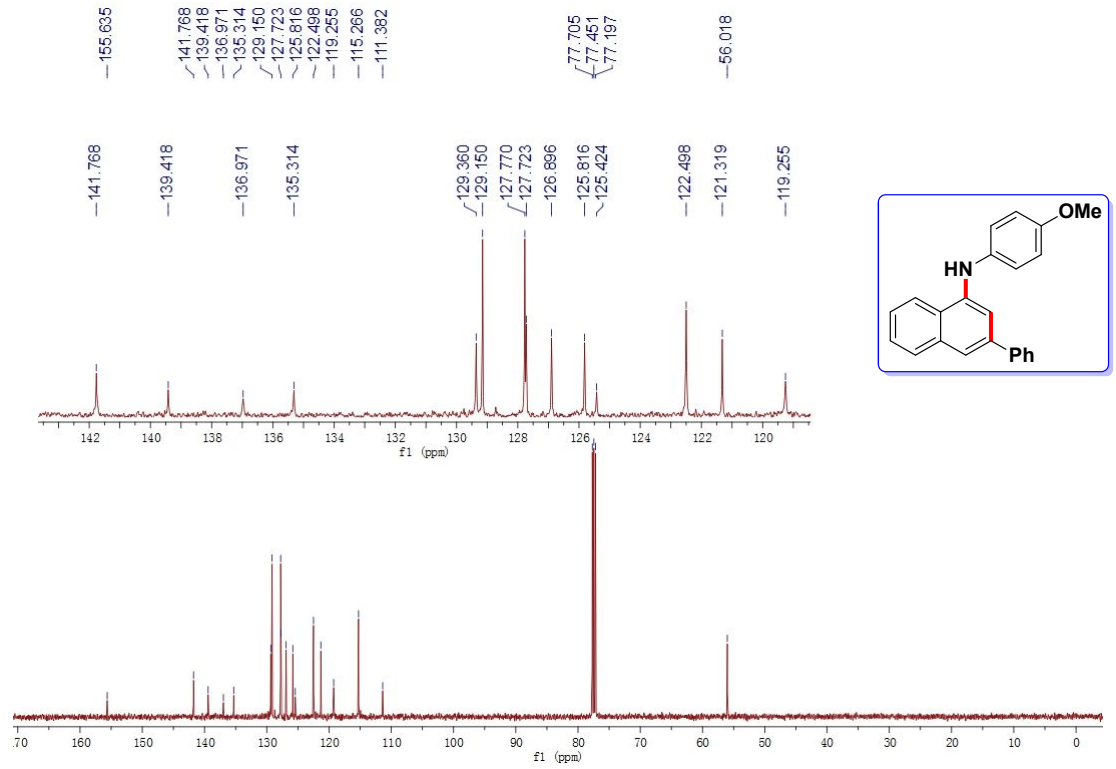


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ac

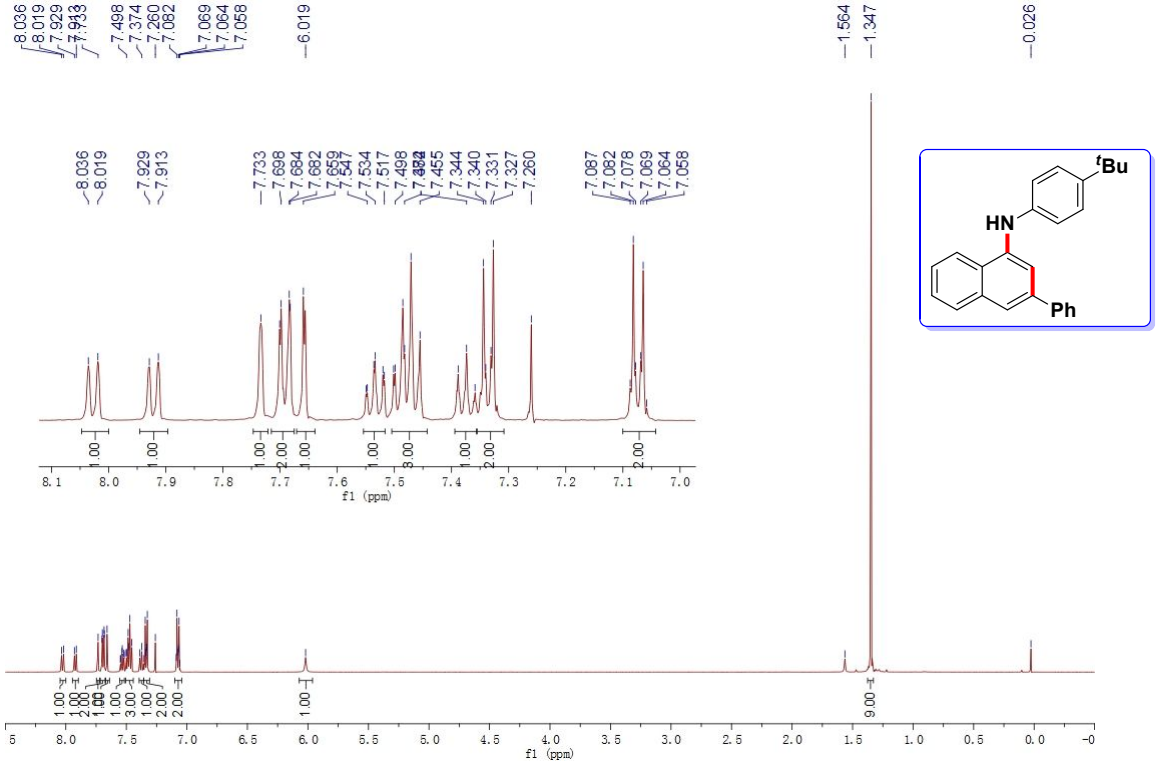


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

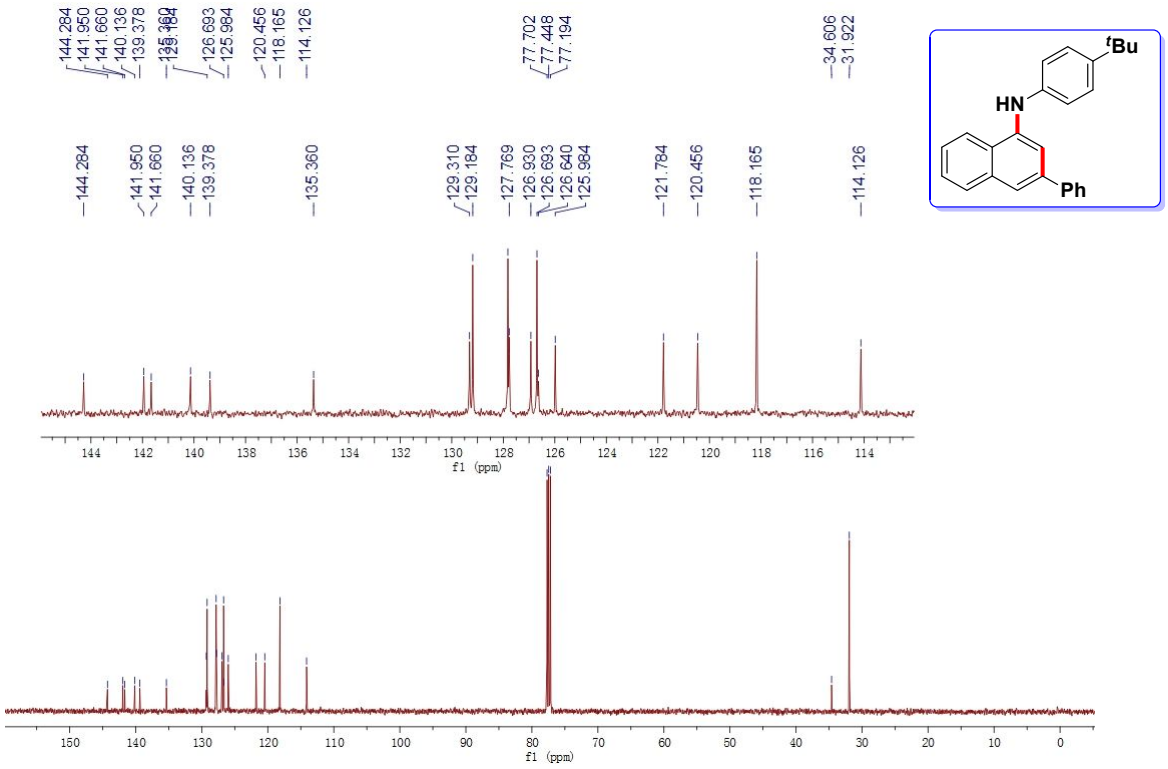


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ad

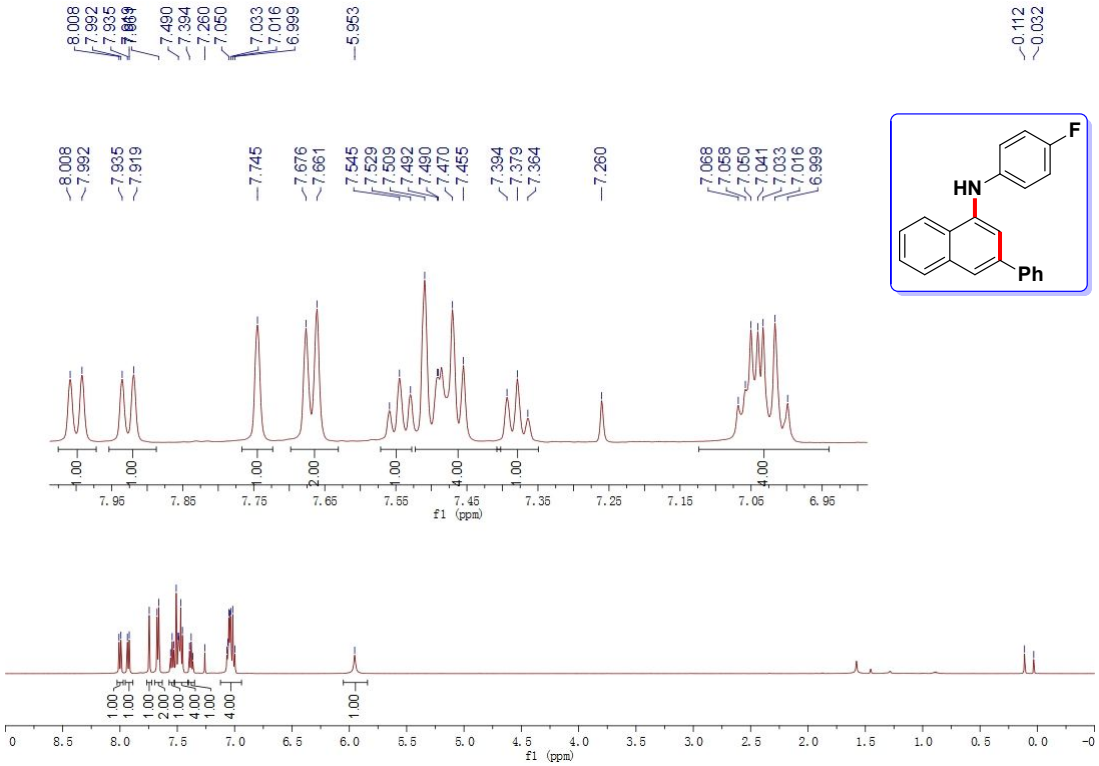


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

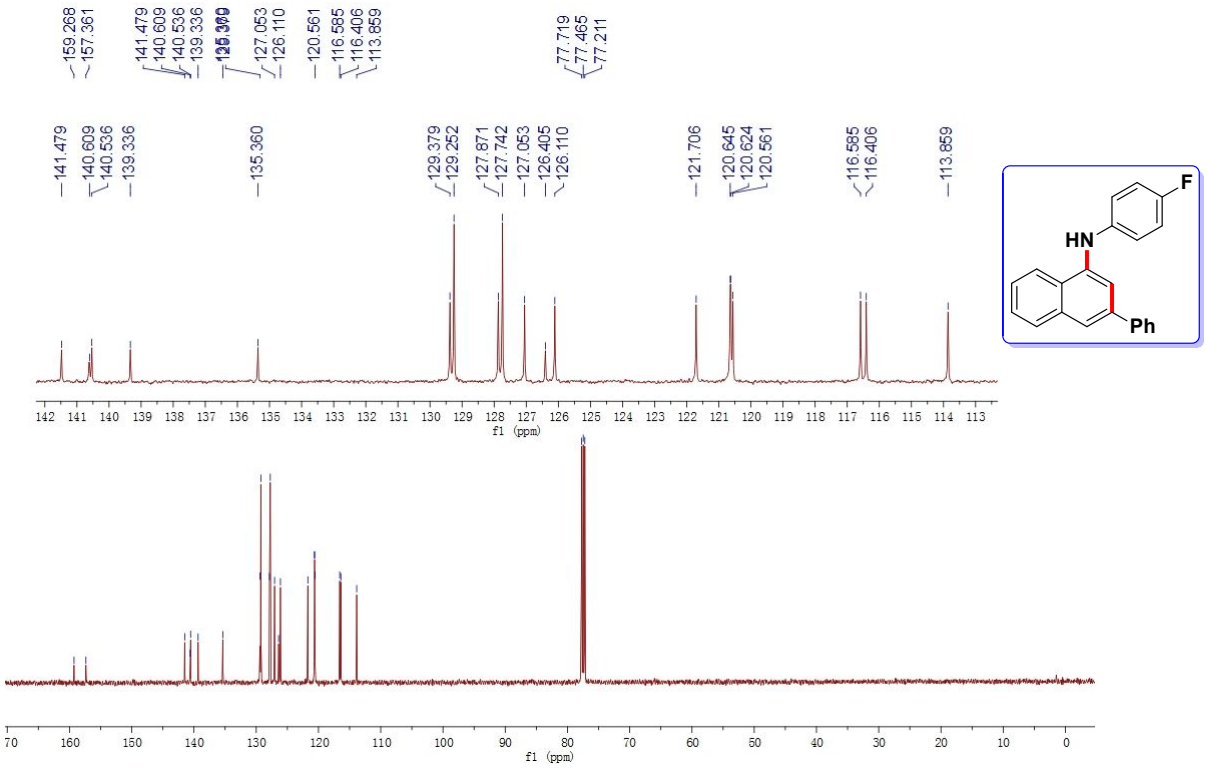


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ae

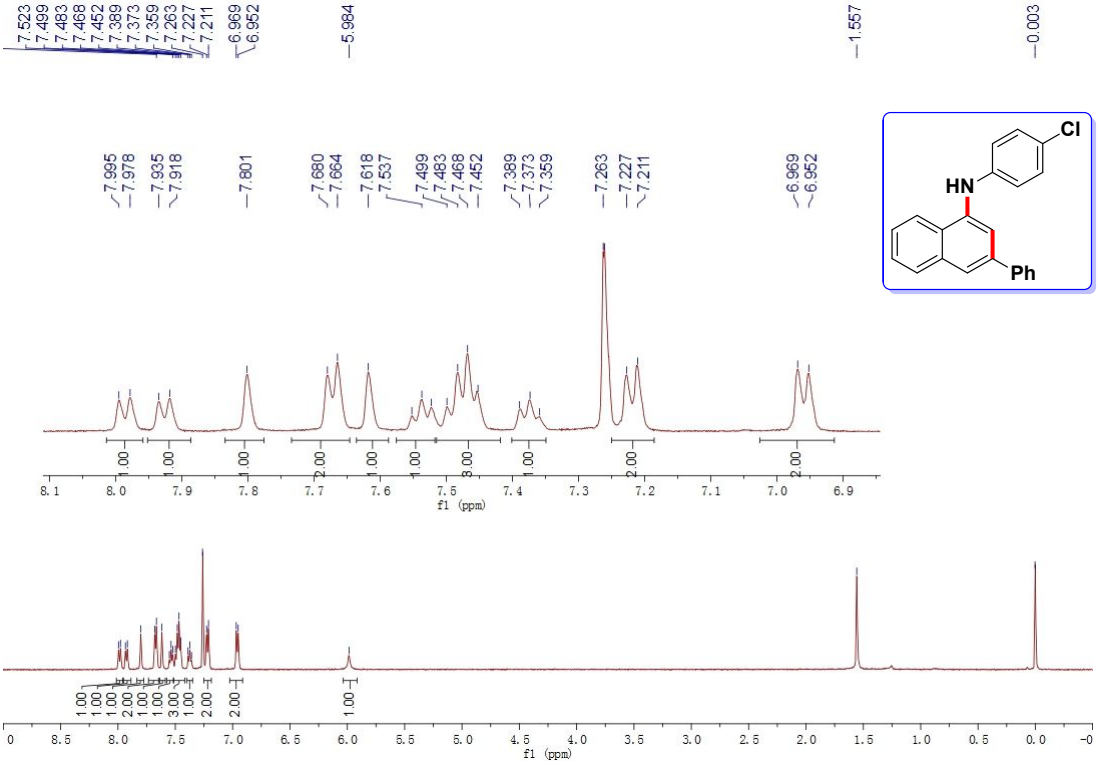


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

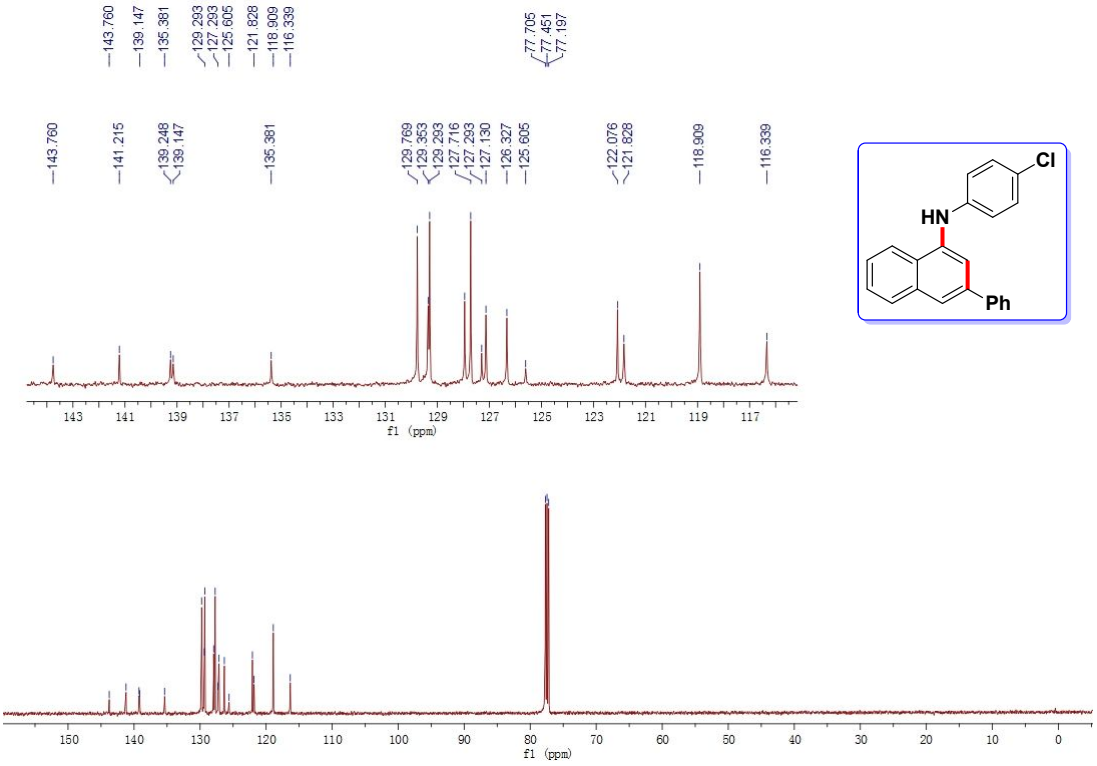


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3af

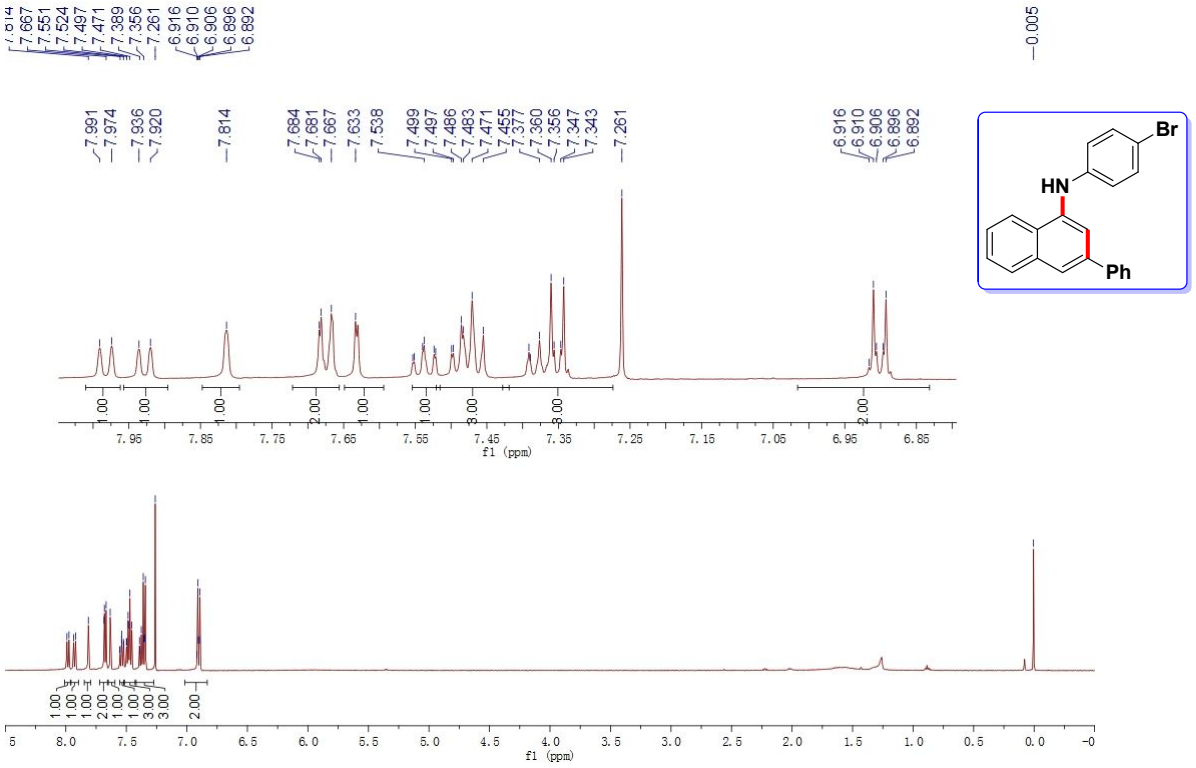


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

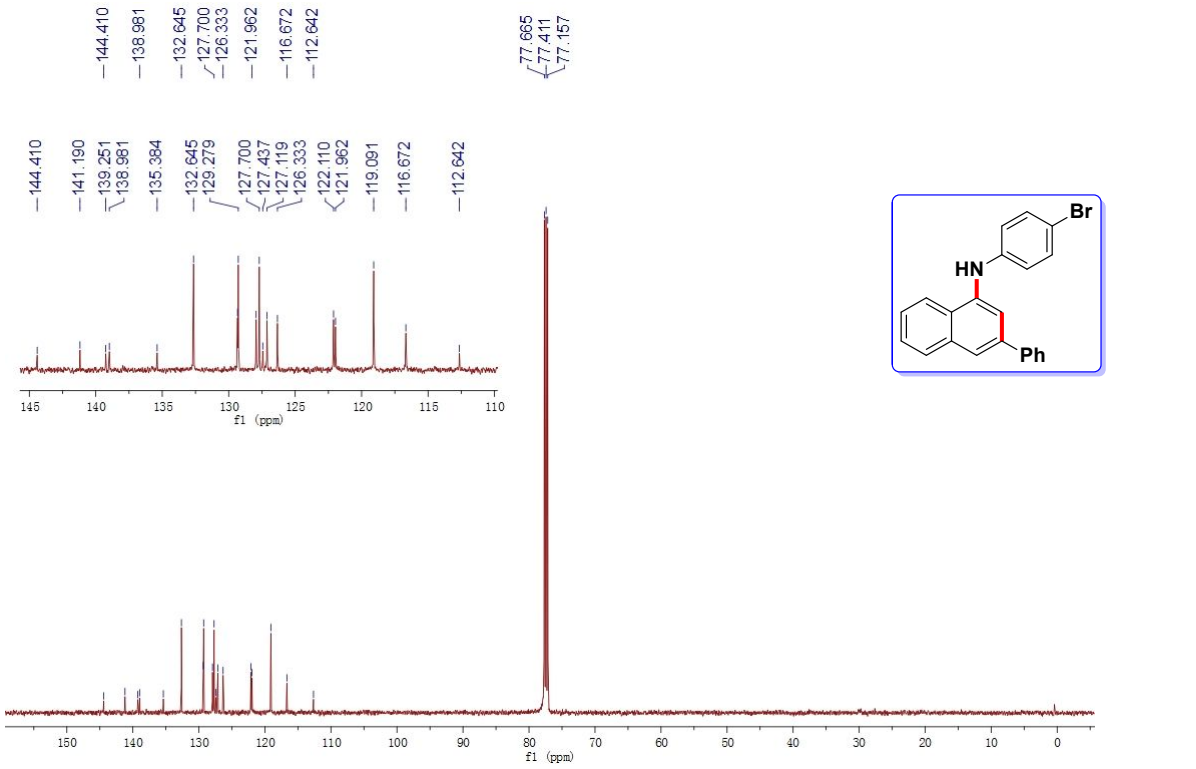


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ag

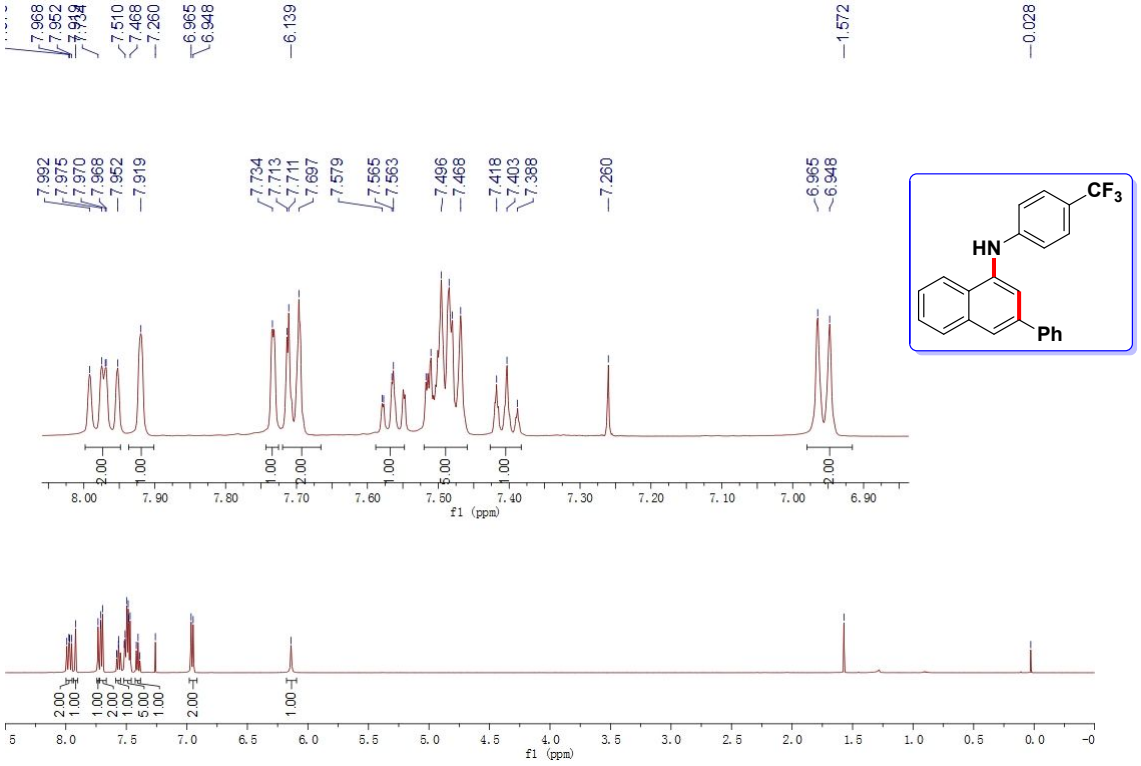


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

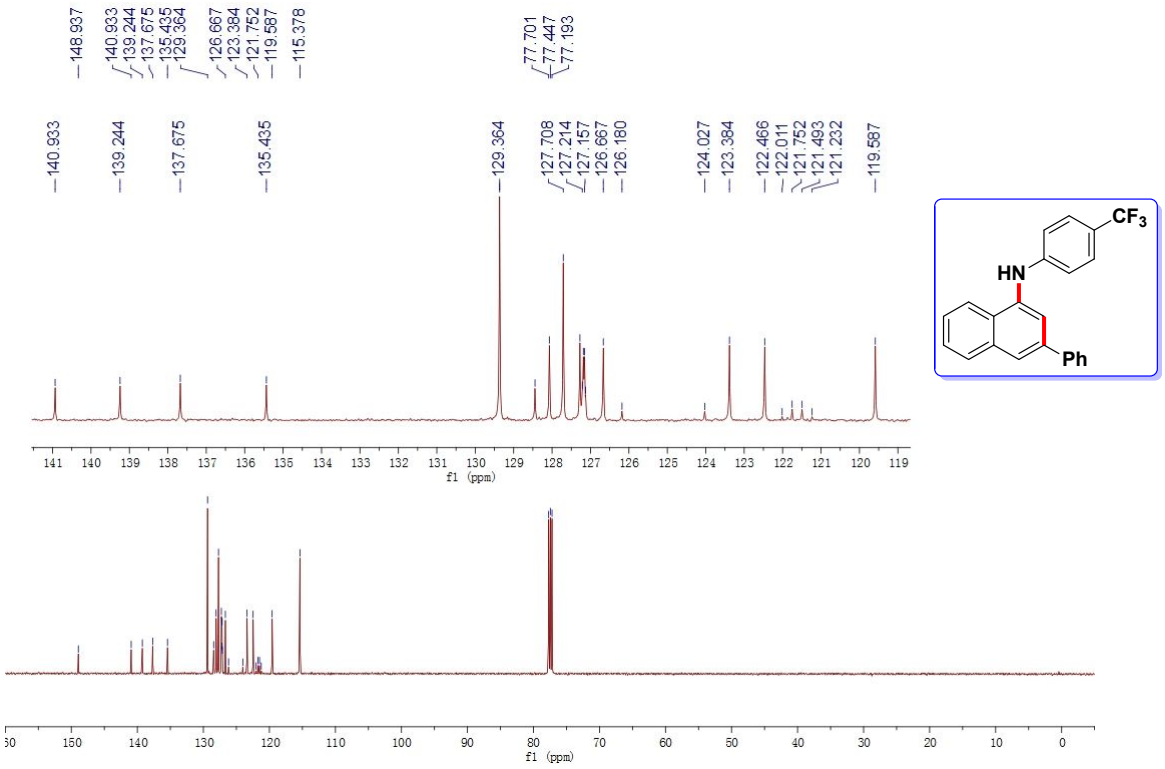


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ah

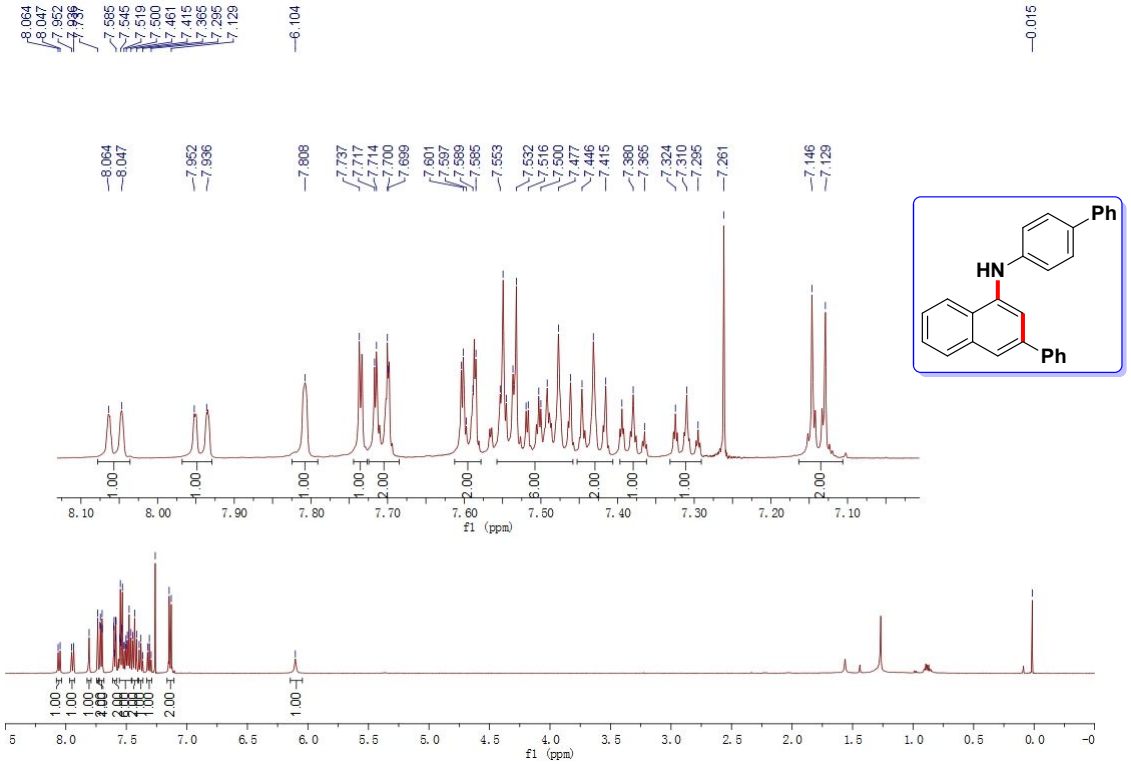


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

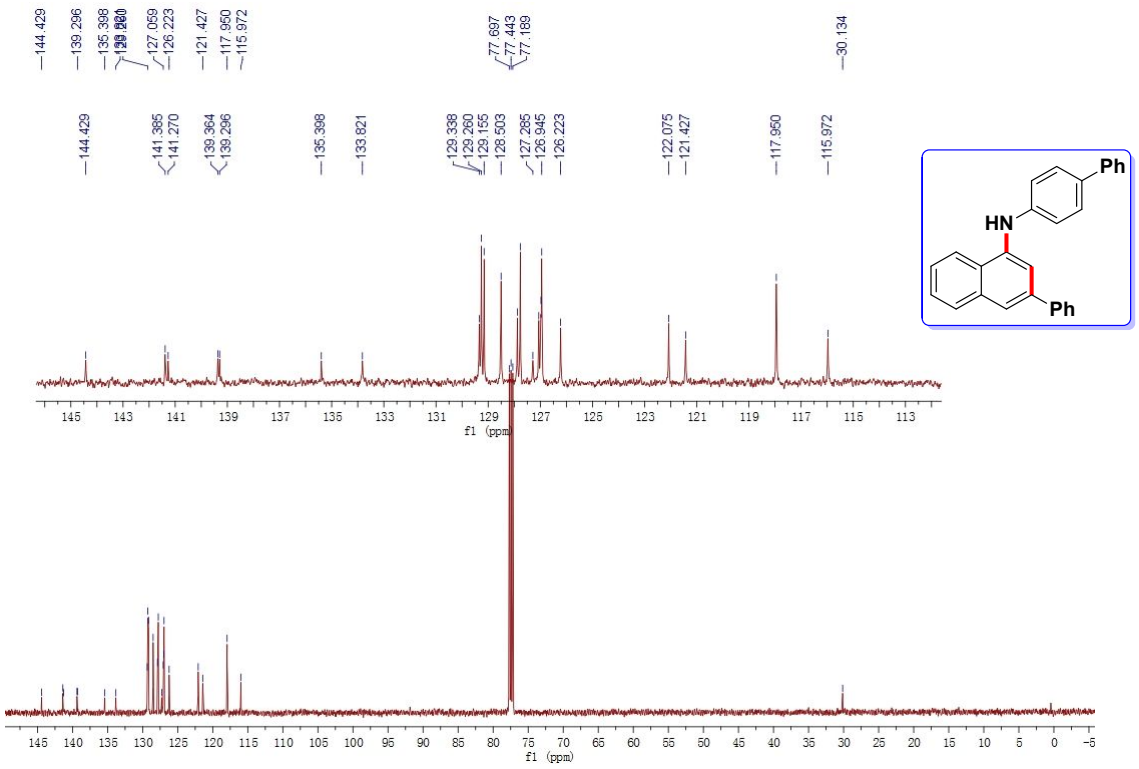


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ai

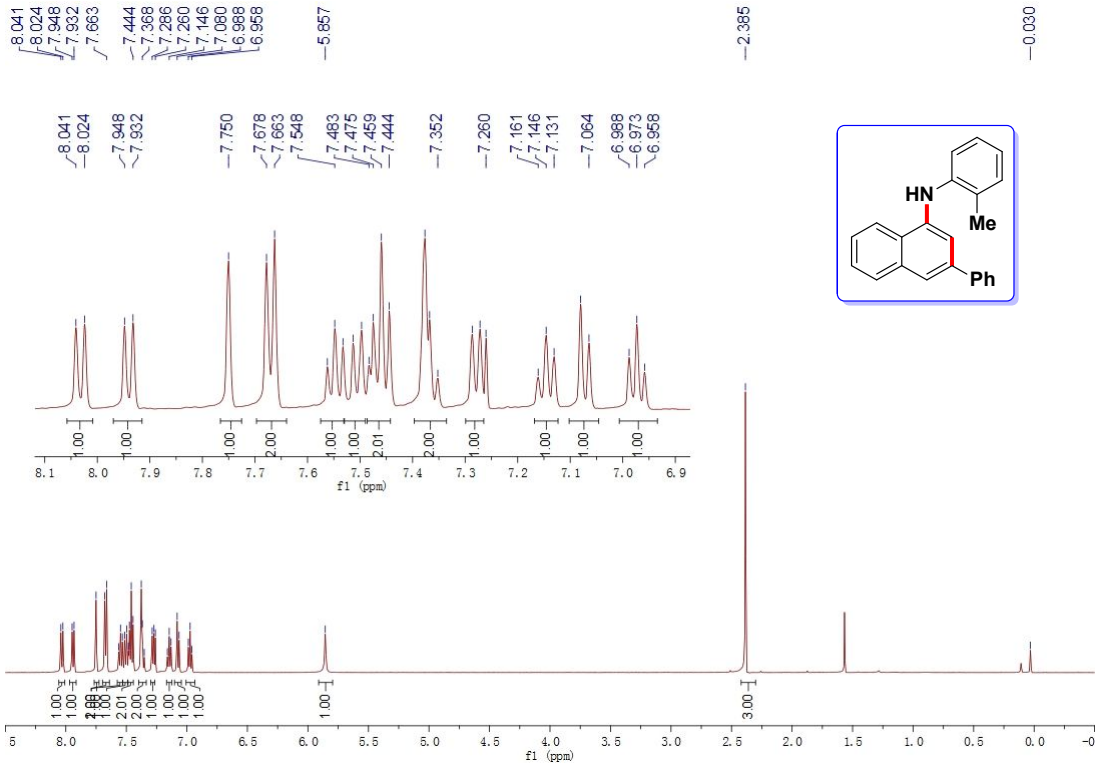


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

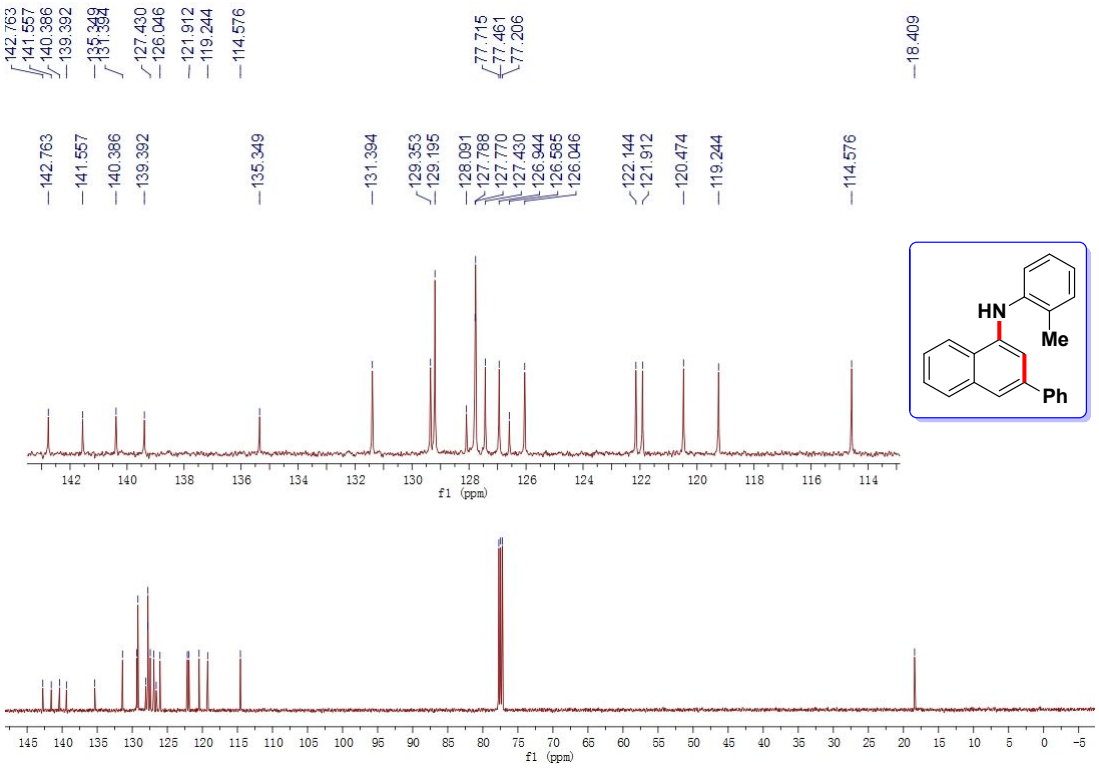


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3aj

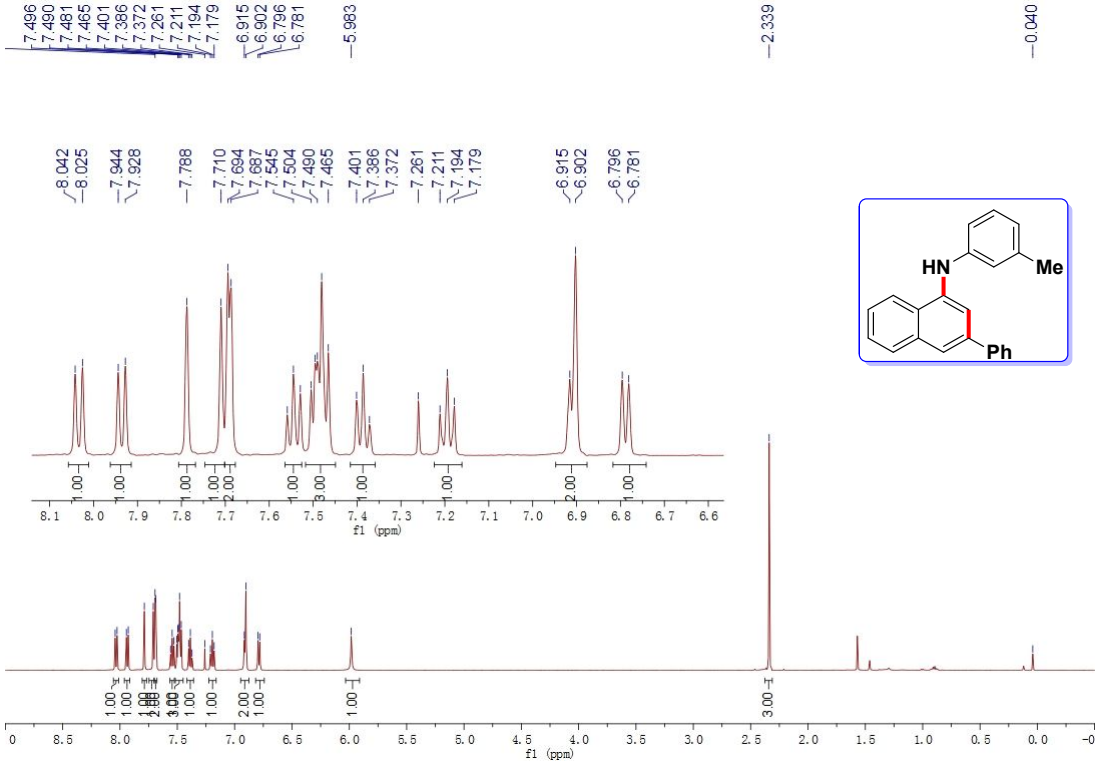


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

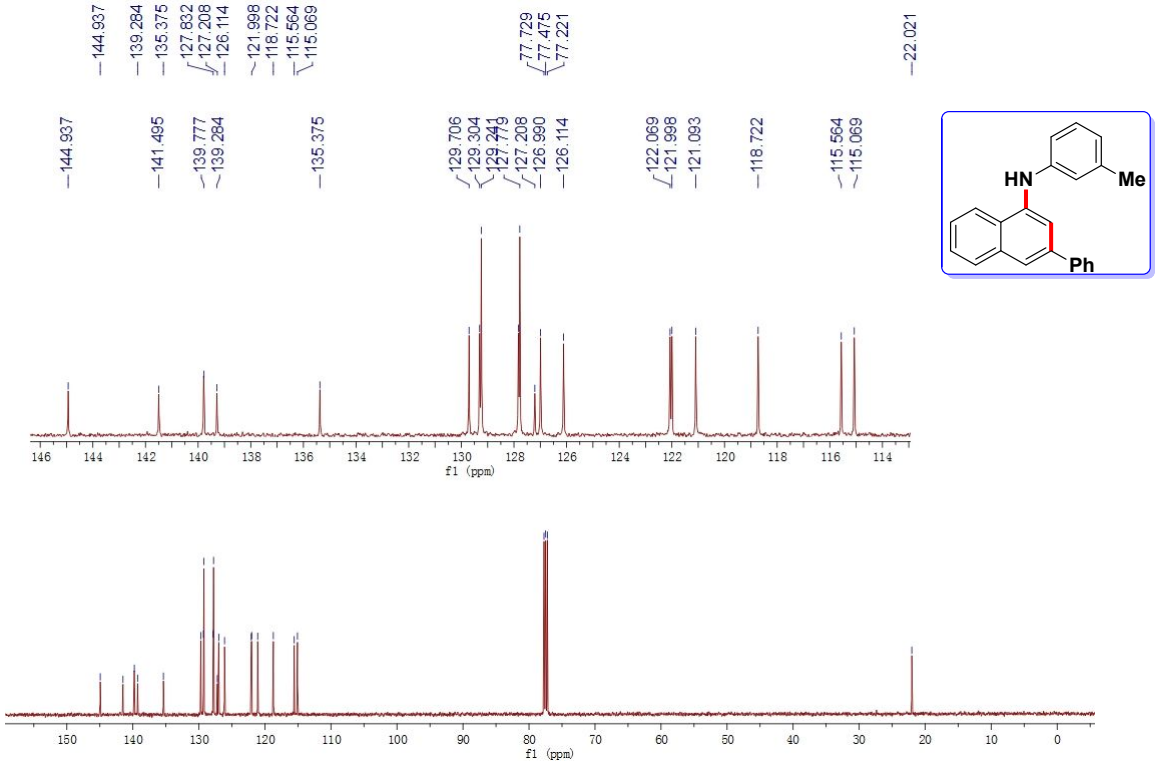


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ak

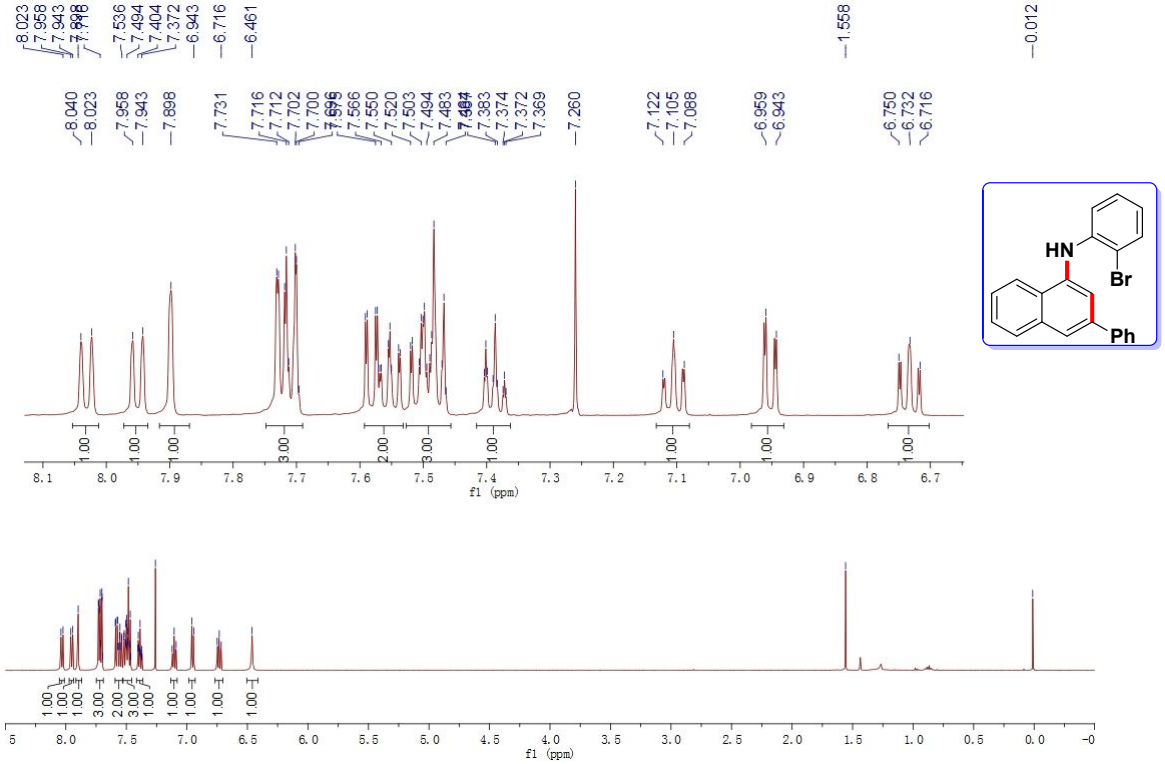


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

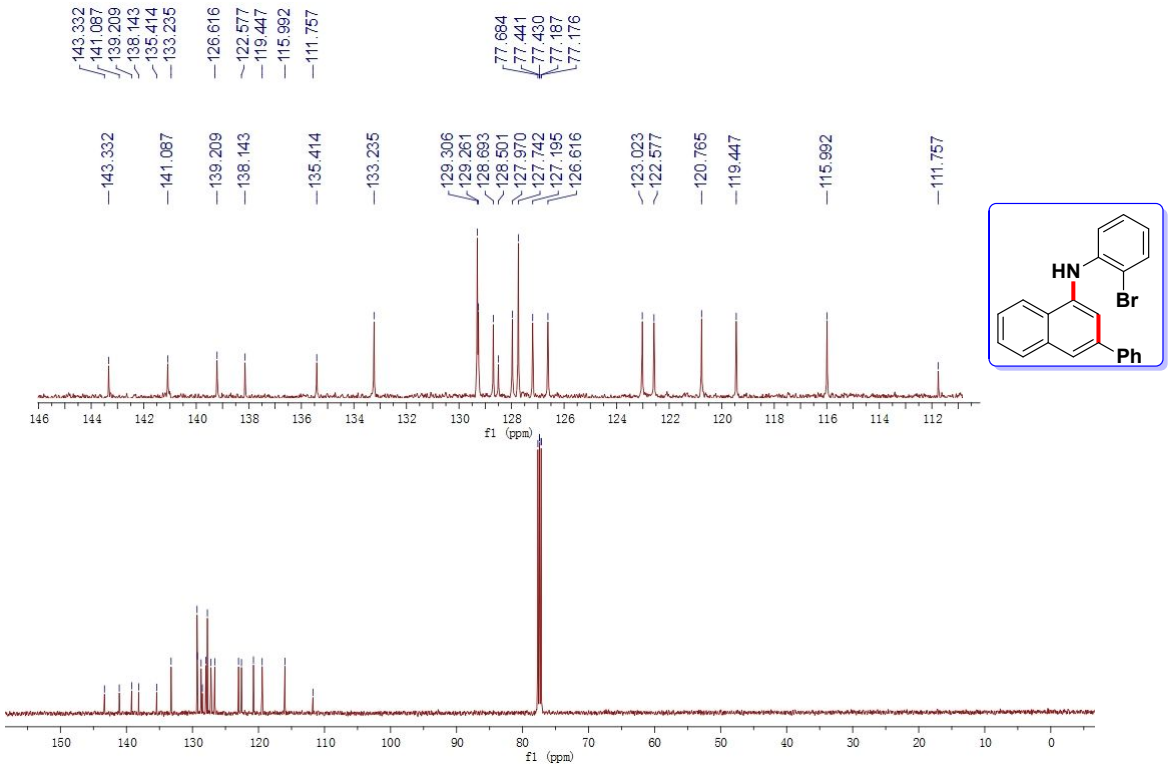


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3al

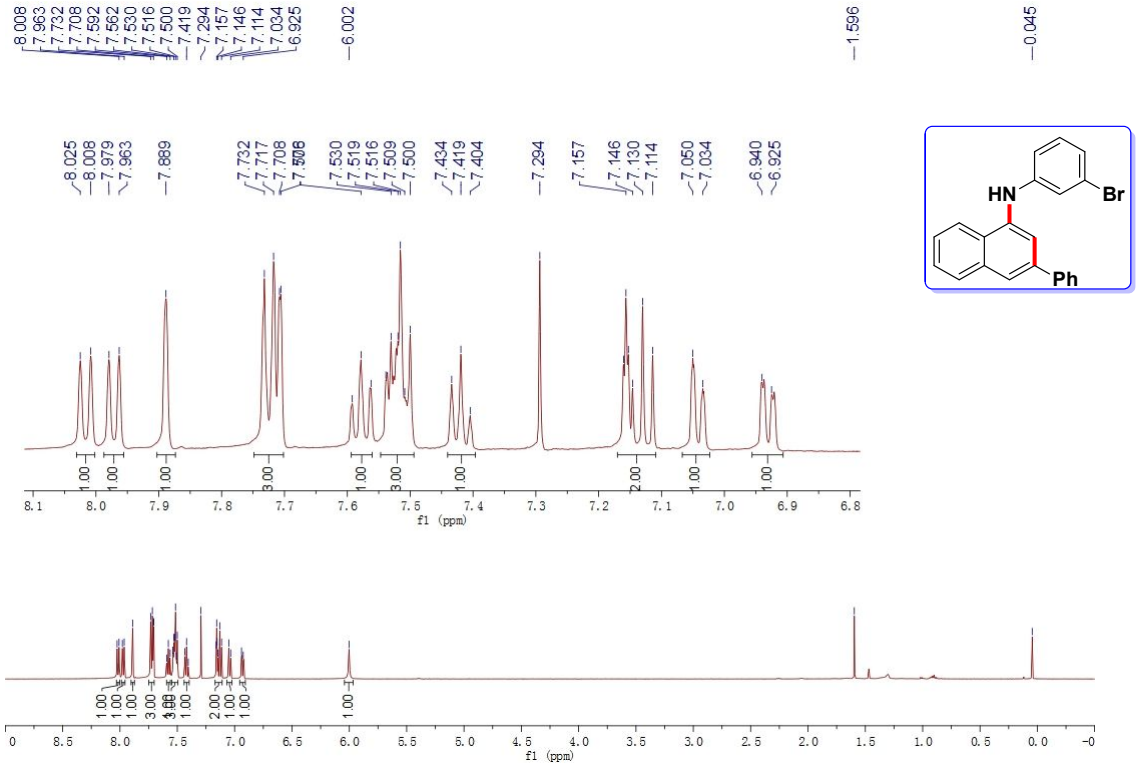


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

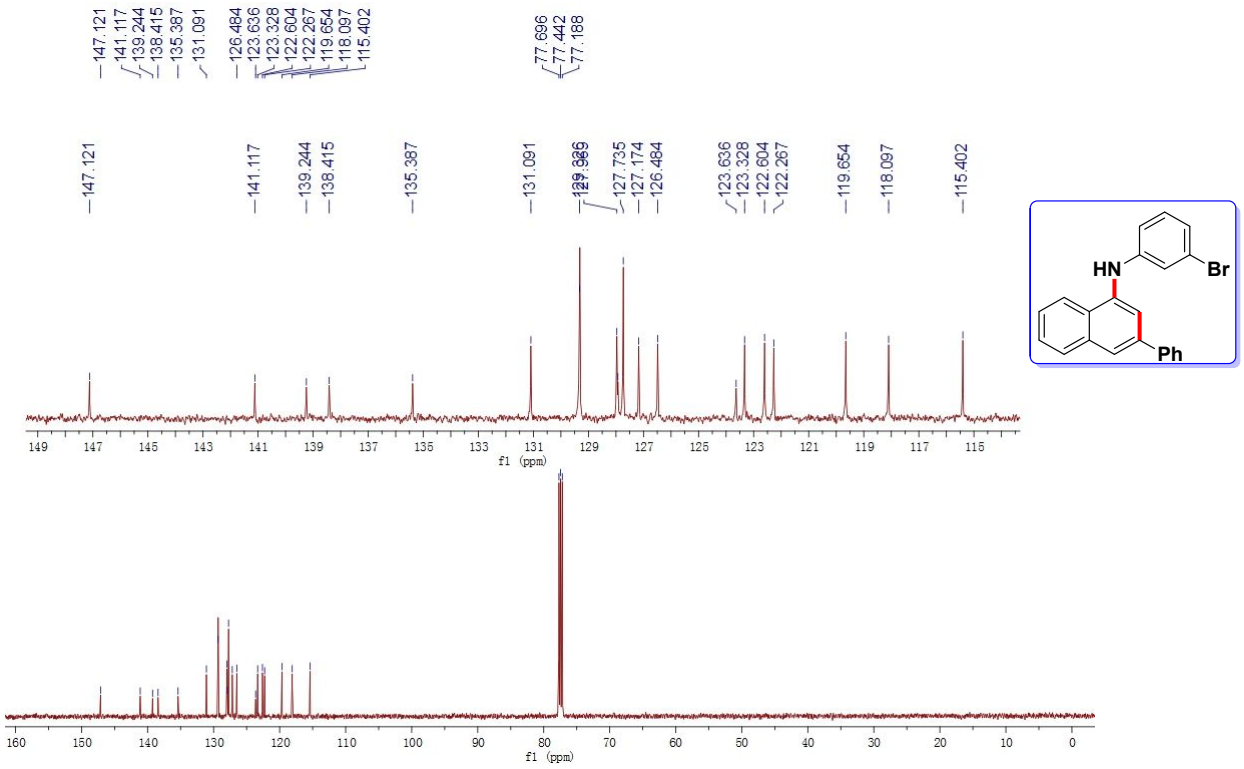


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3am

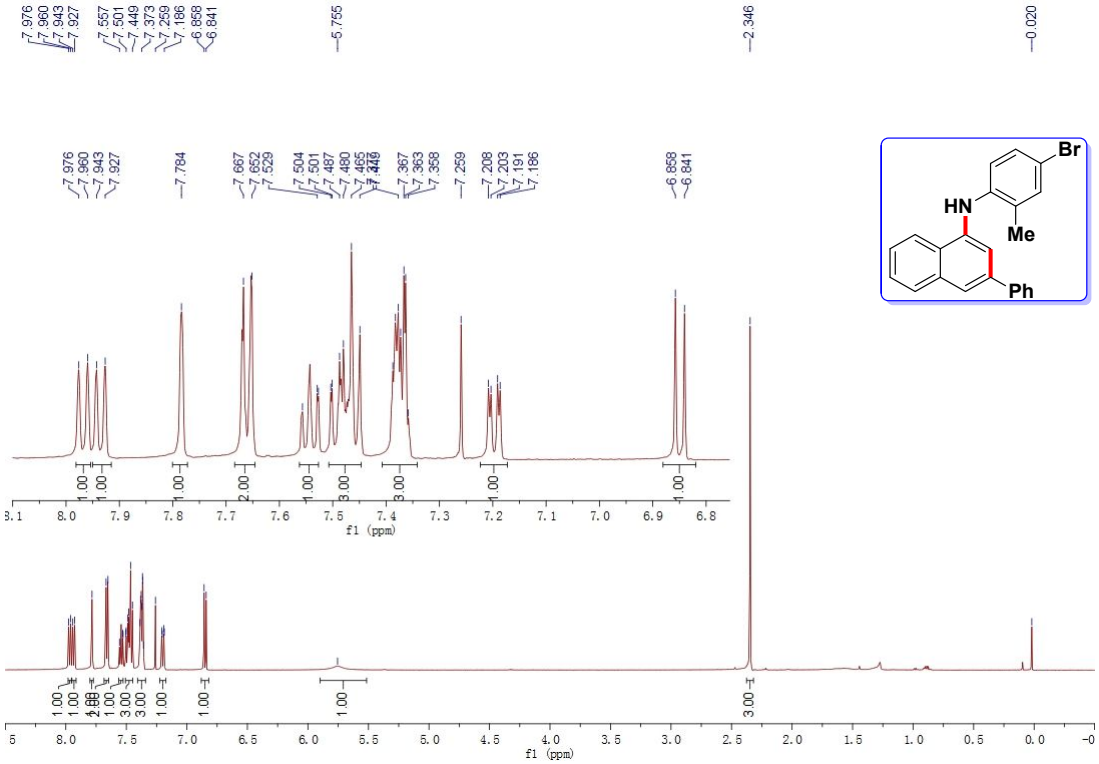


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

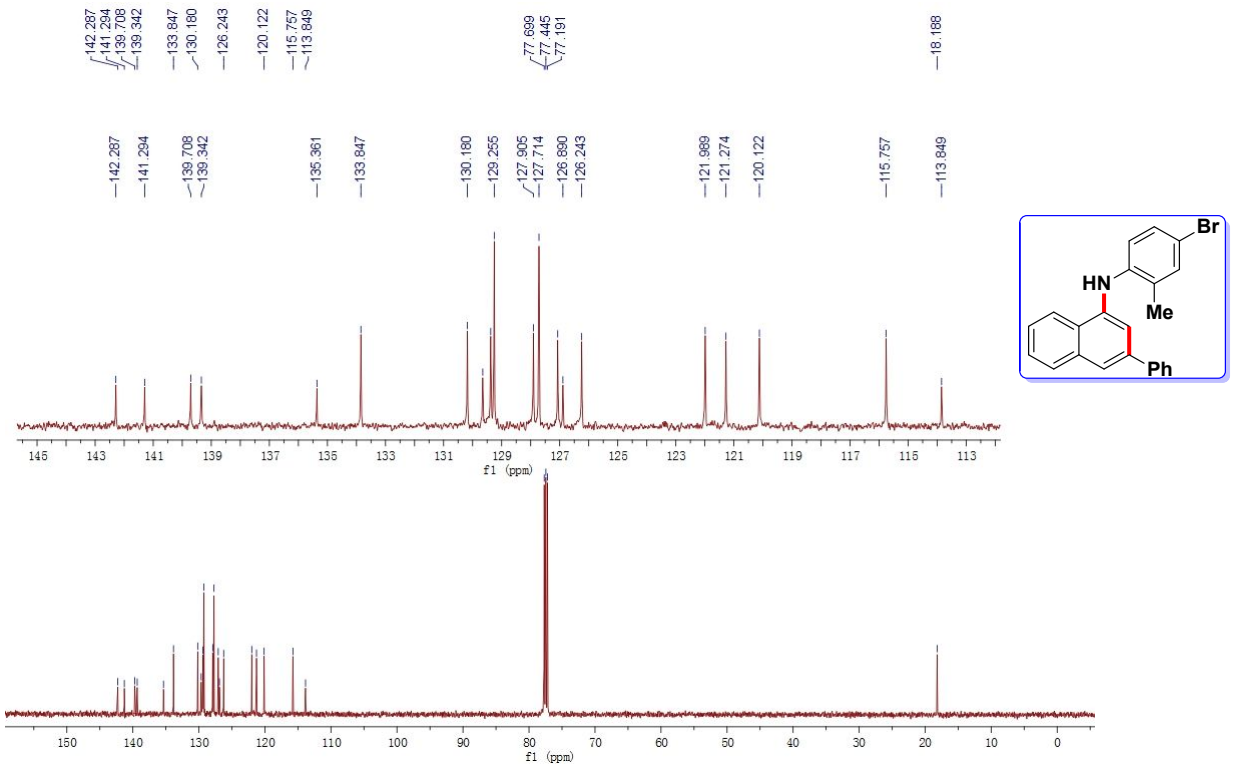


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3an

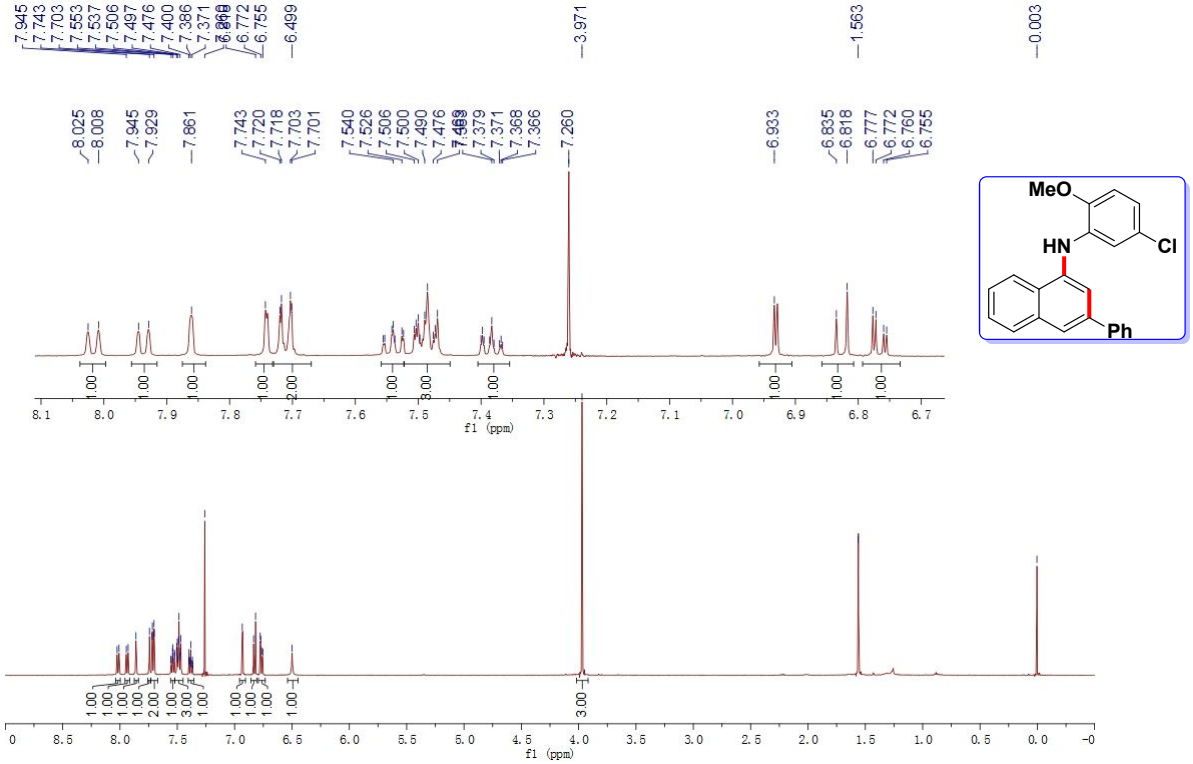


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

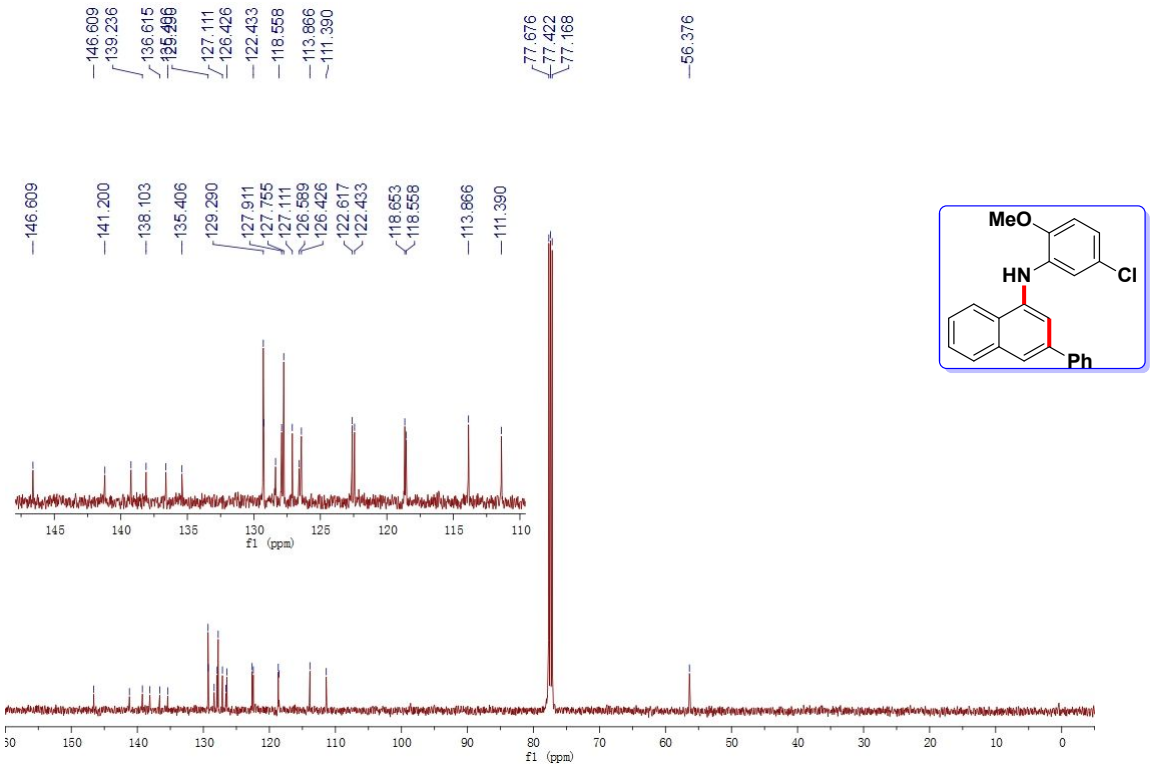


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ao

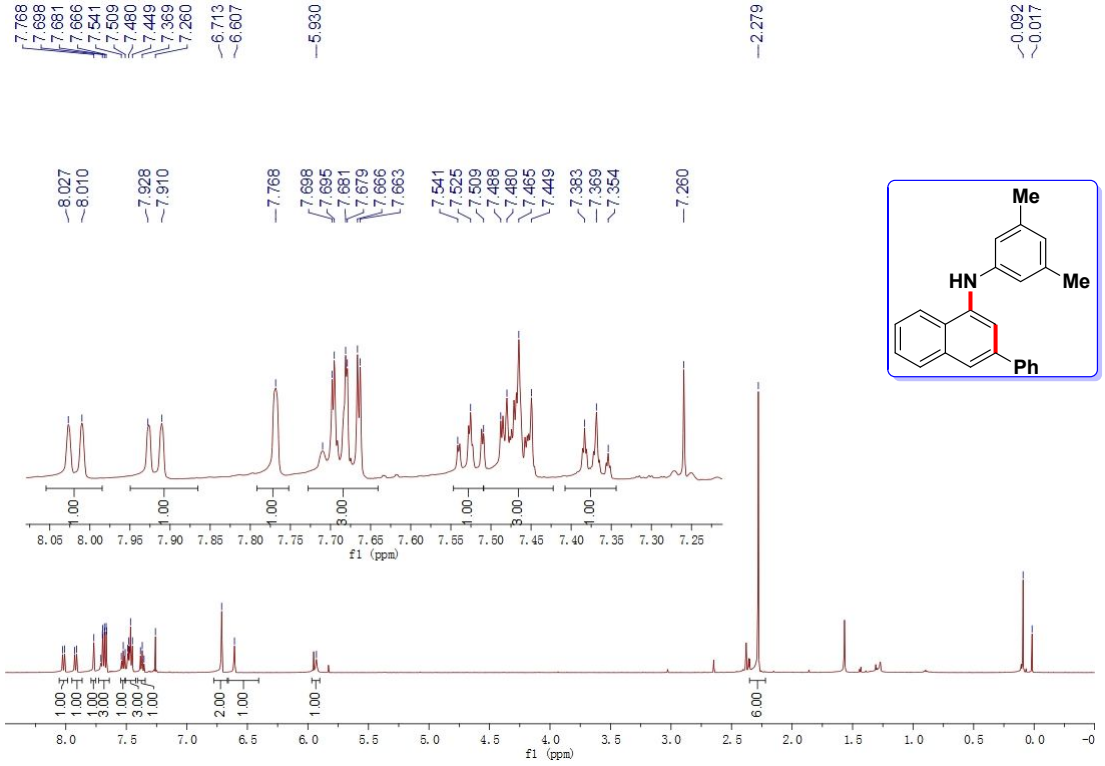


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

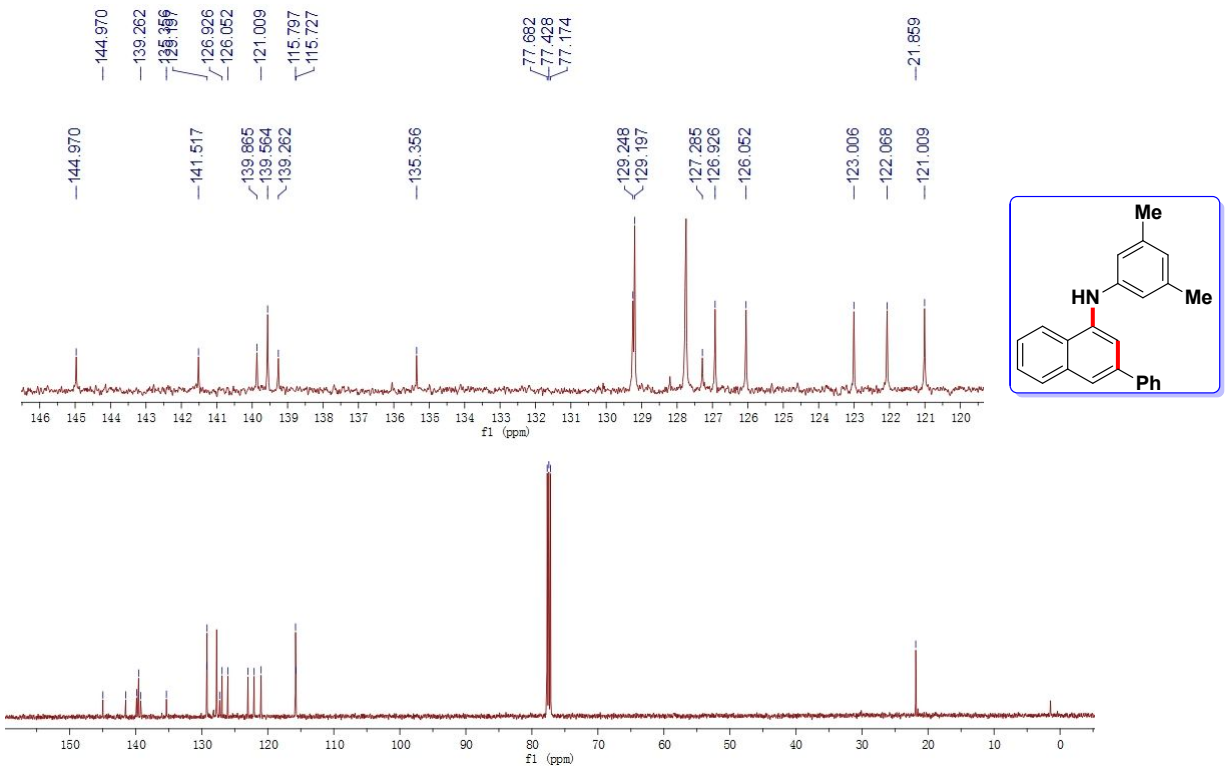


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ap

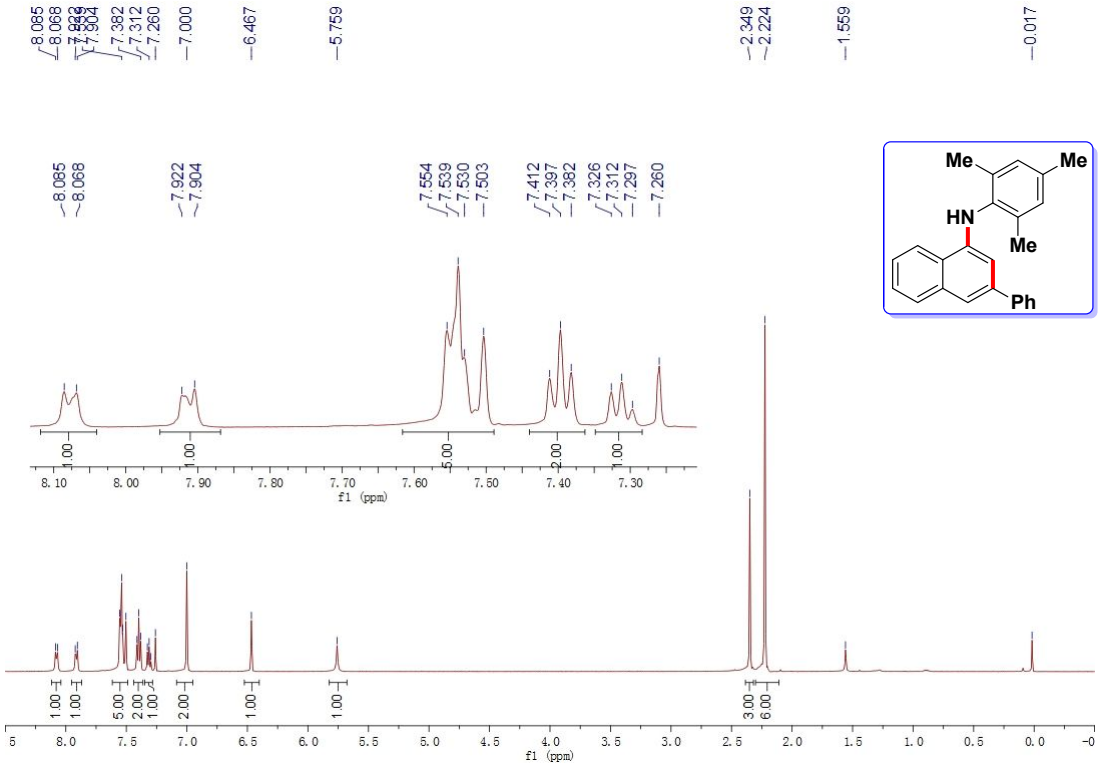


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

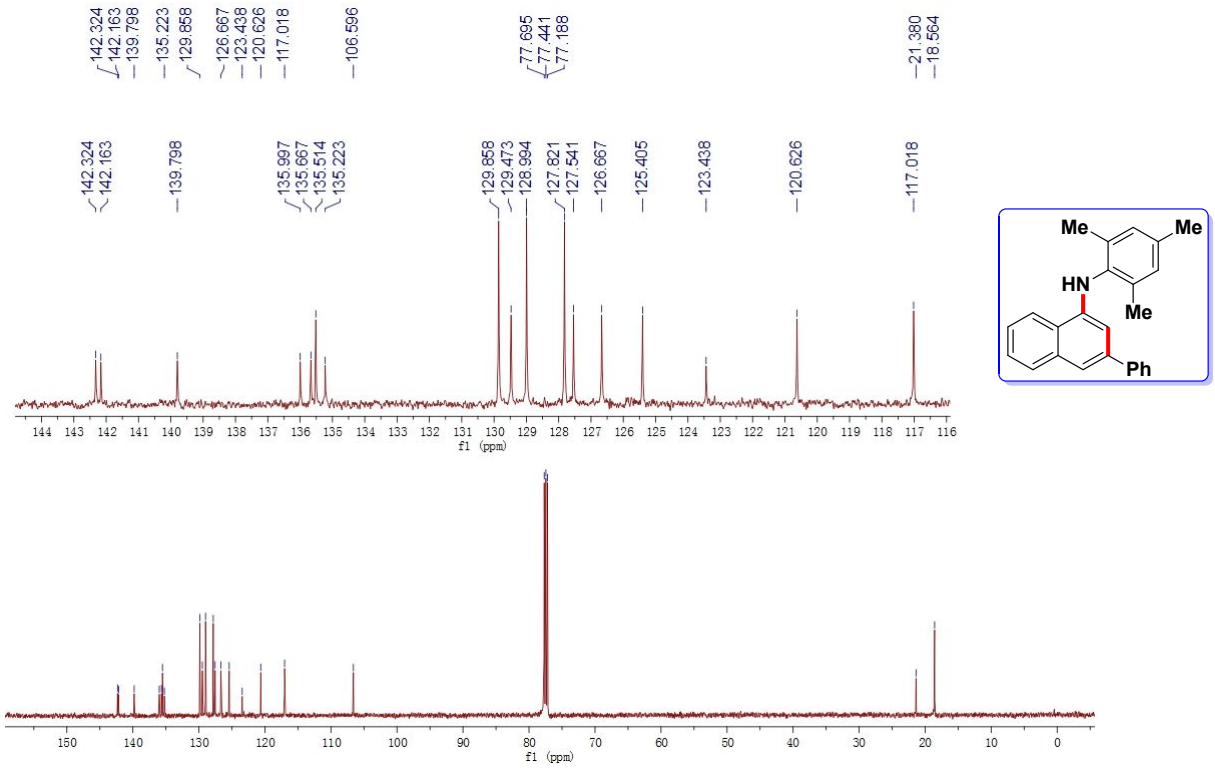


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3aq

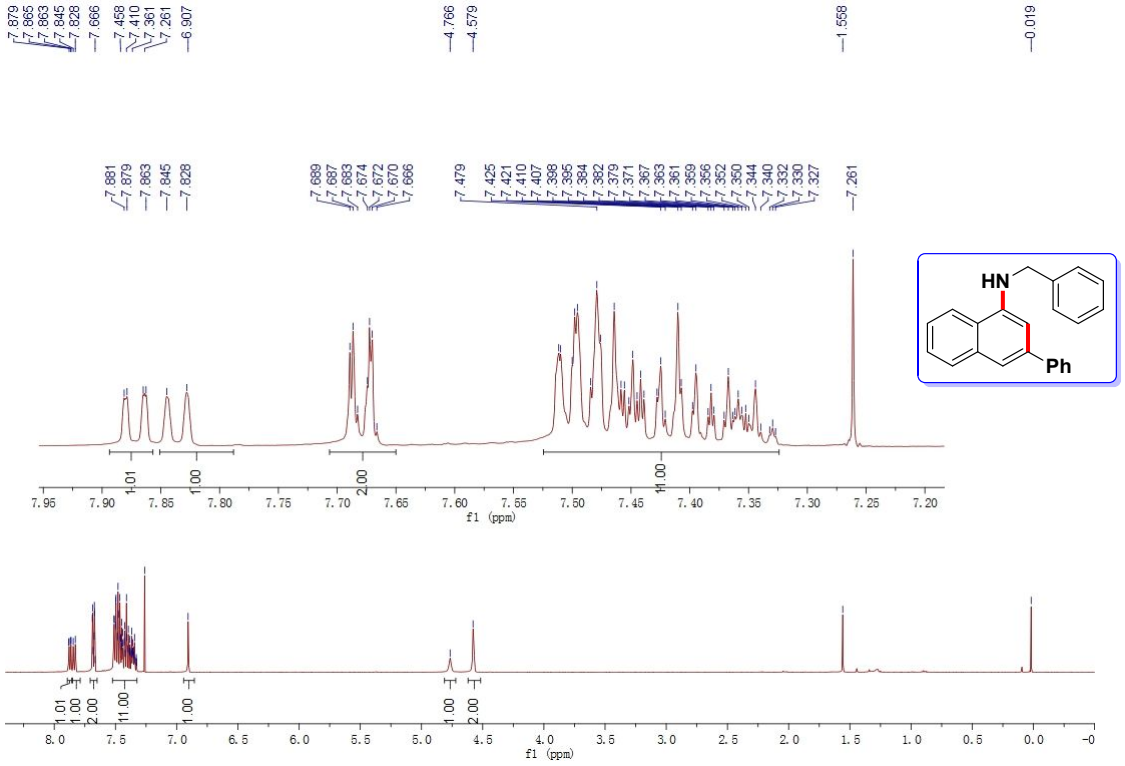


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

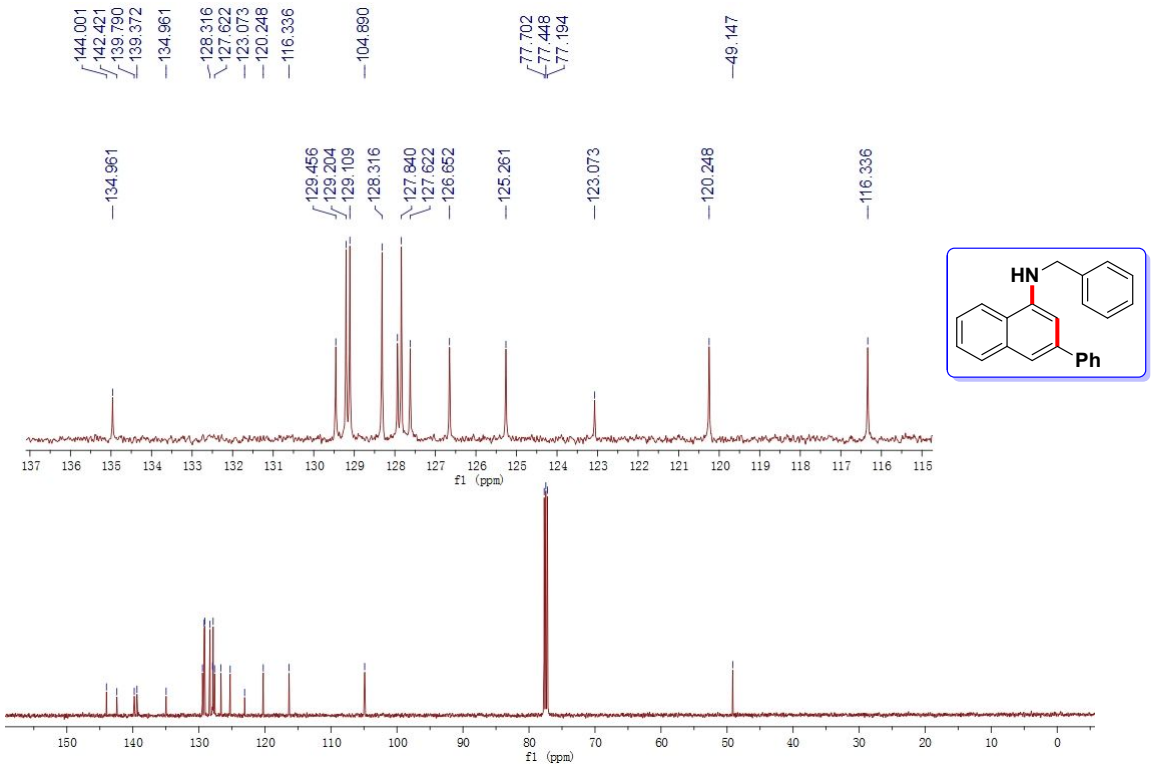


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ar

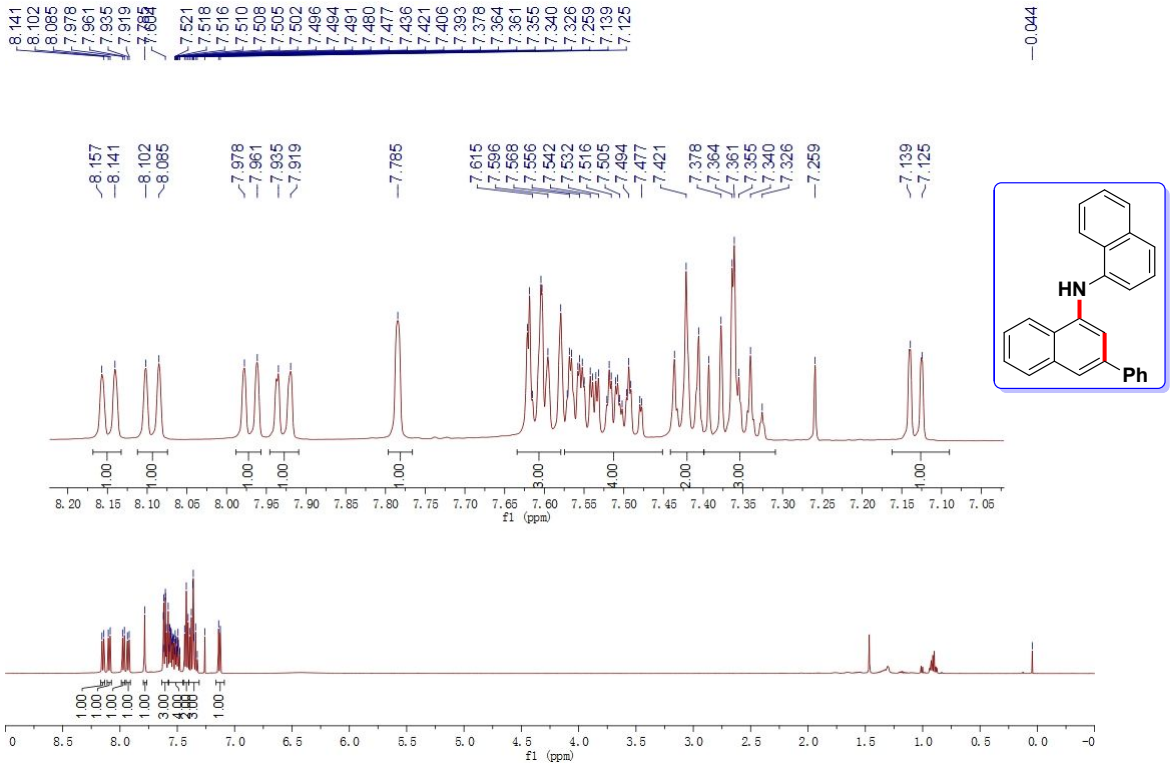


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

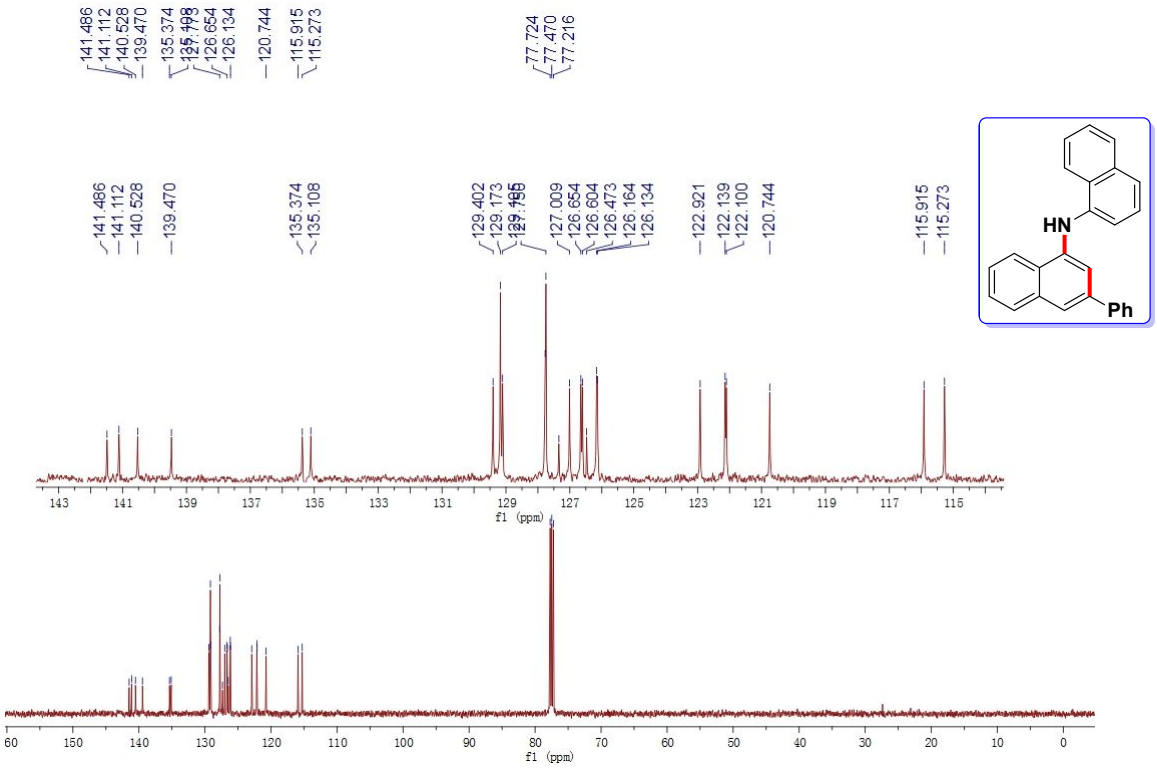


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3as

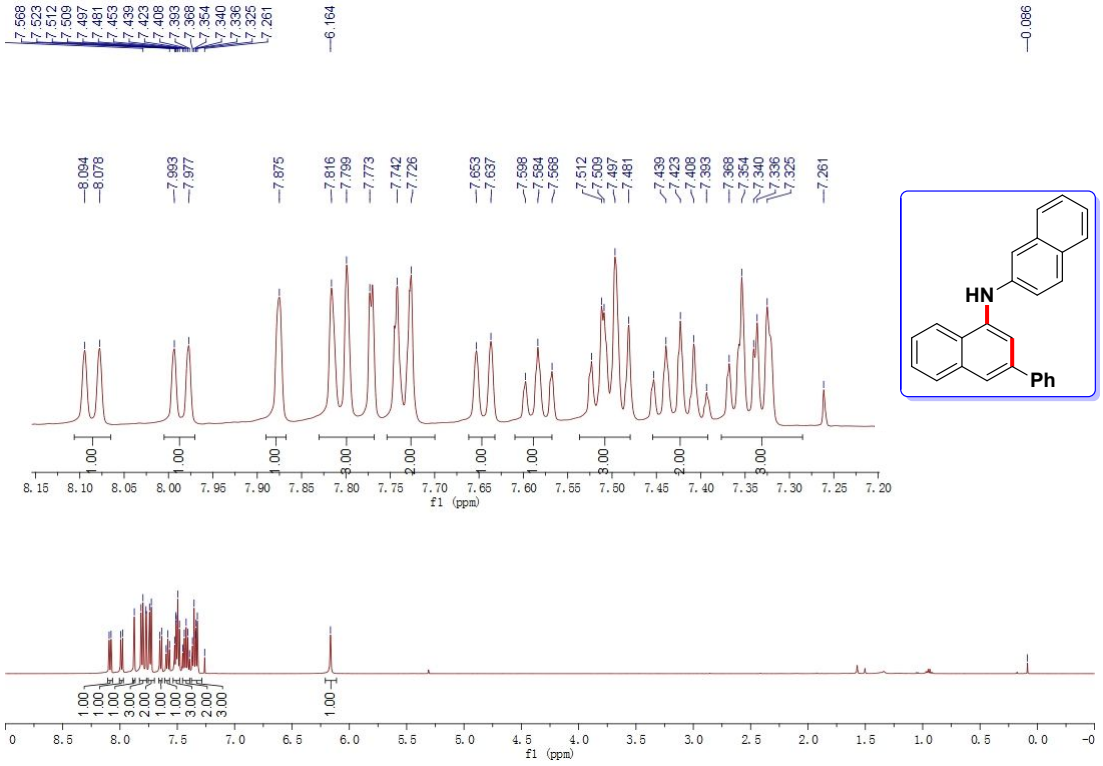


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

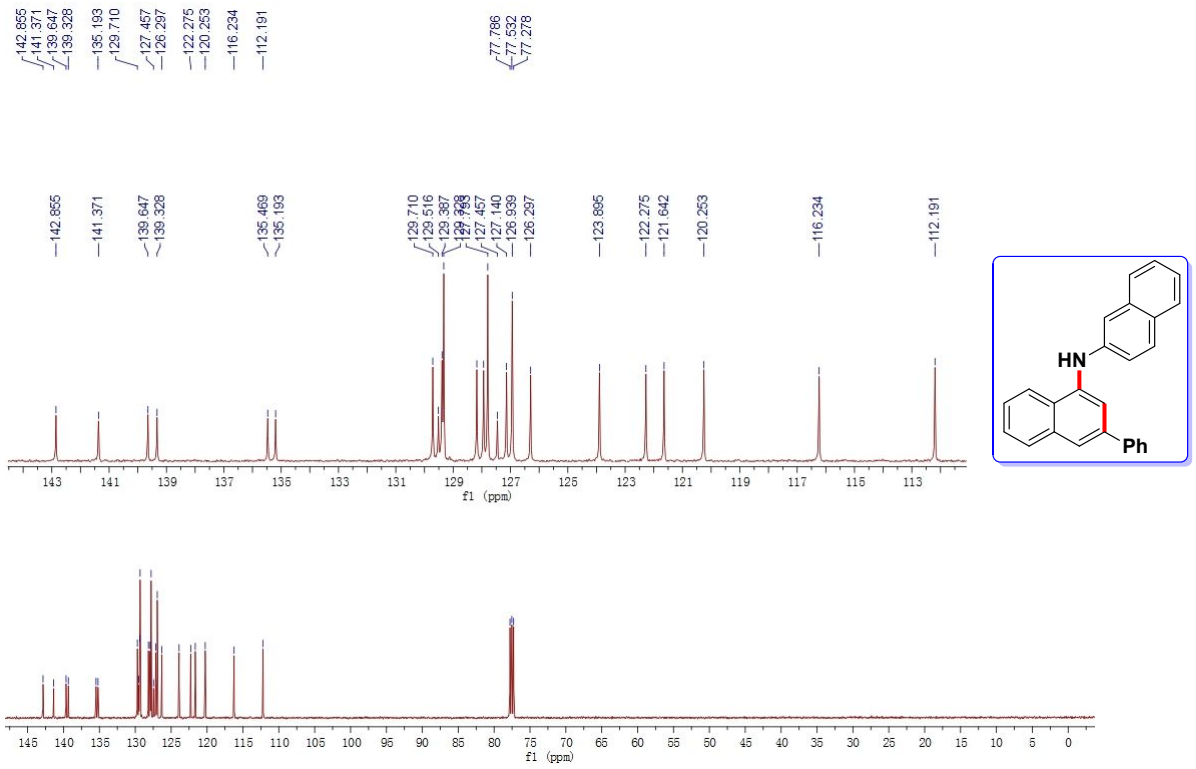


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3at

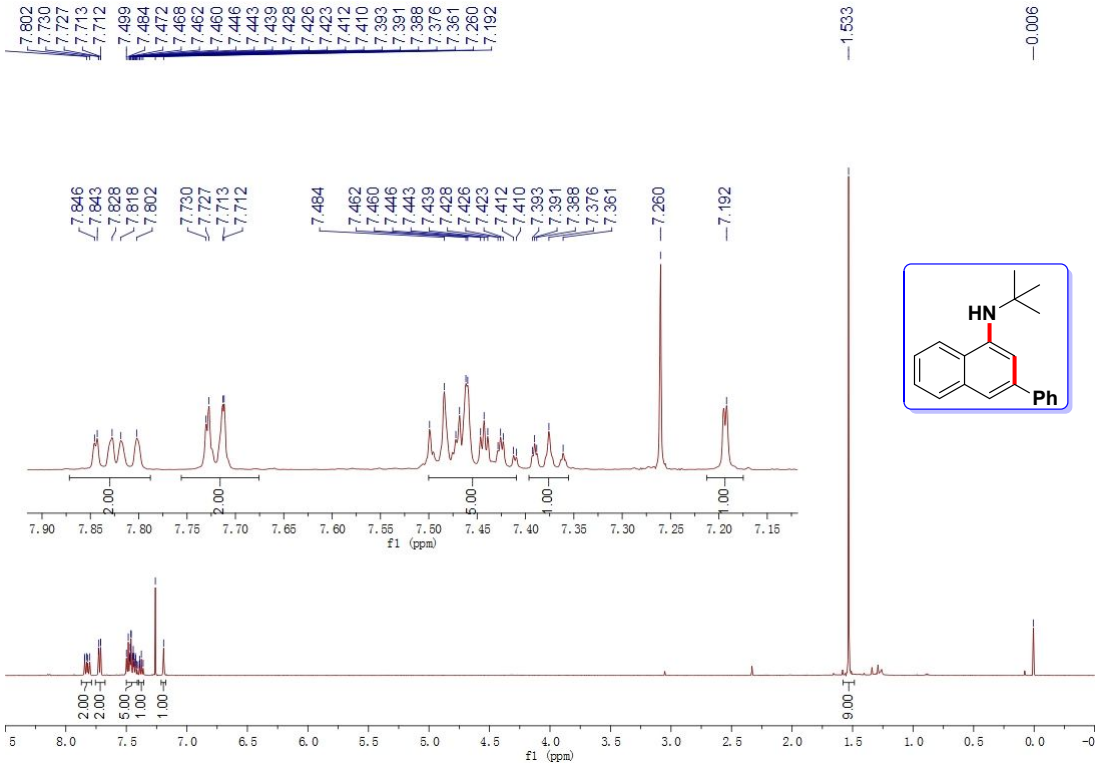


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

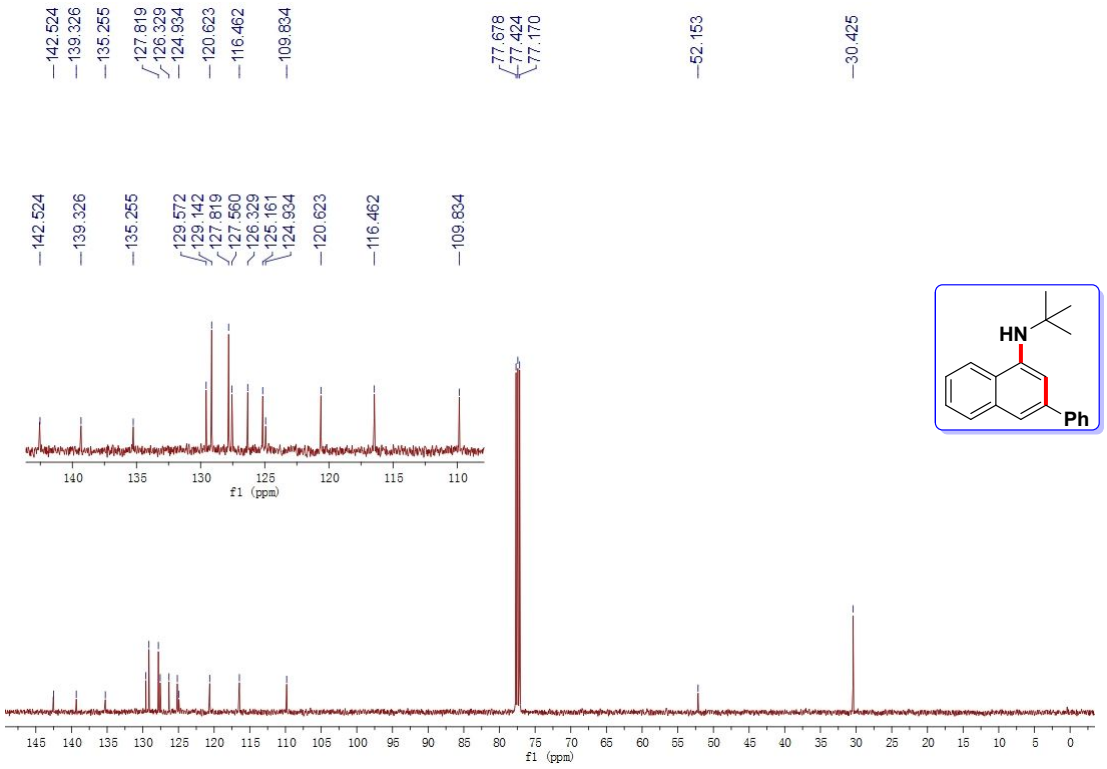


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3au

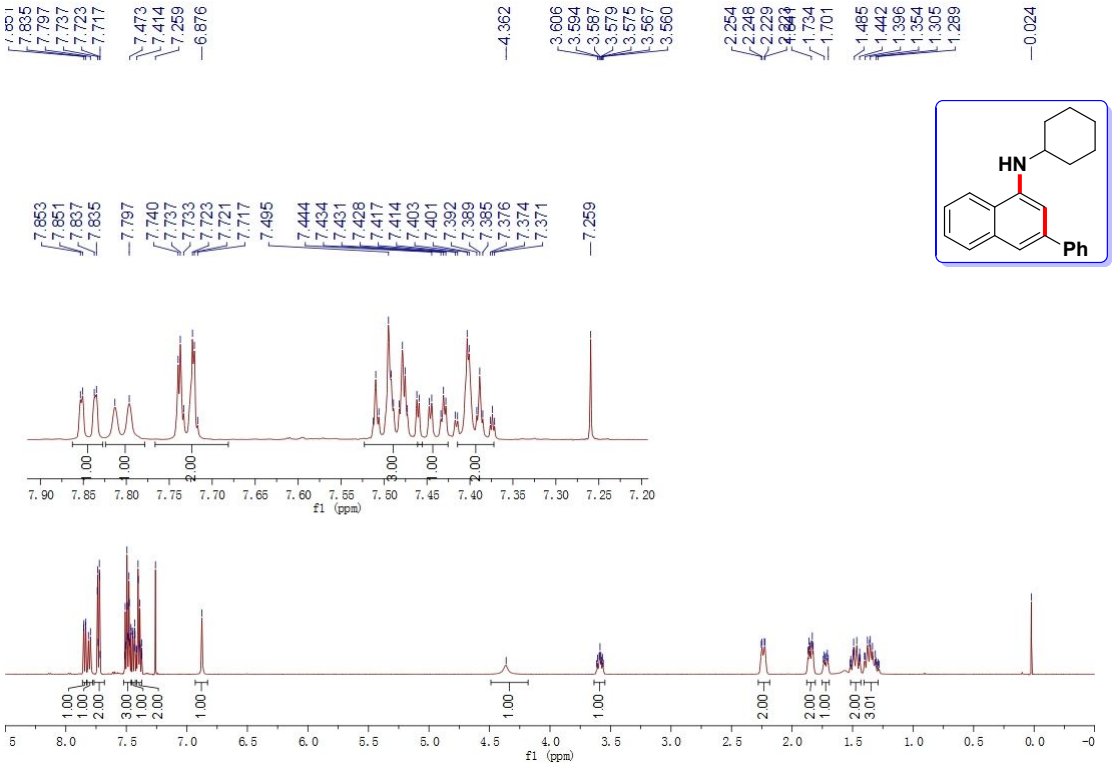


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

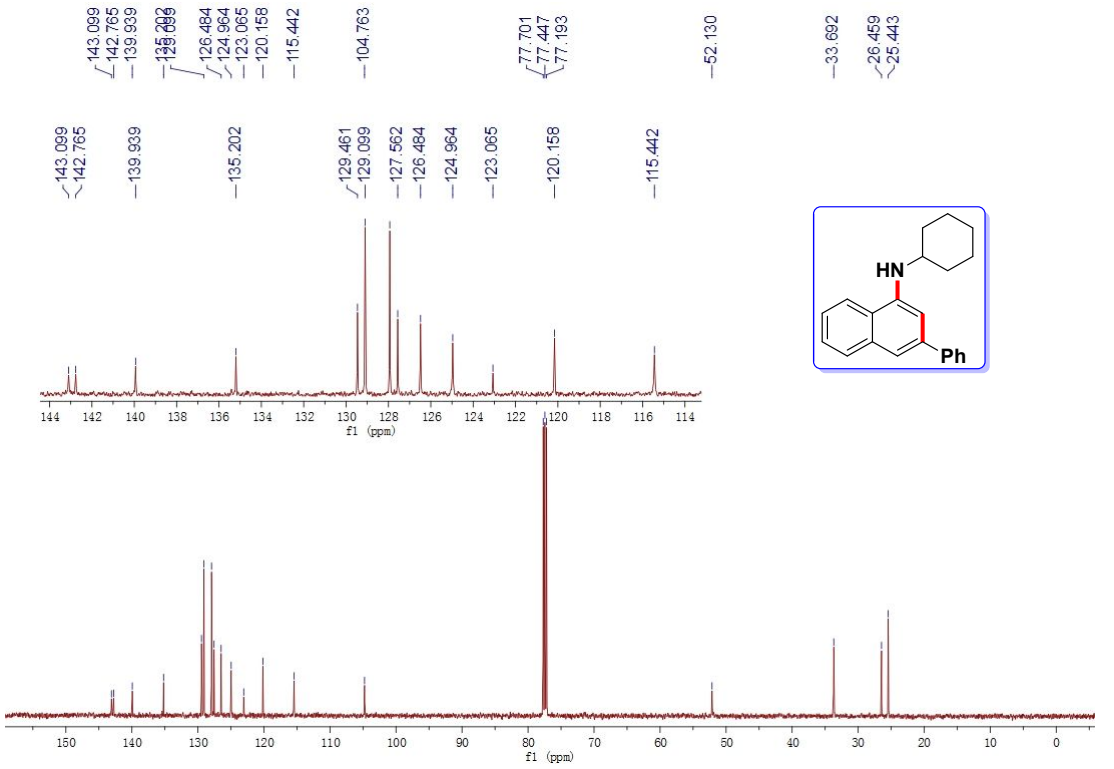


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3av

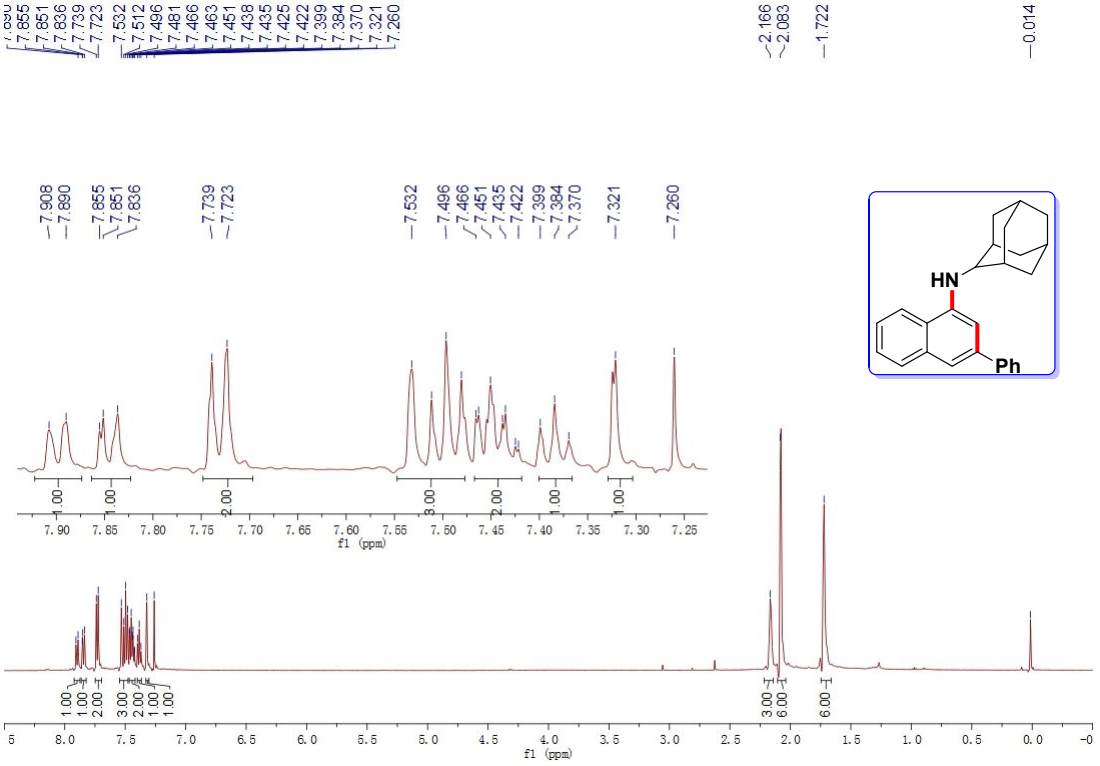


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

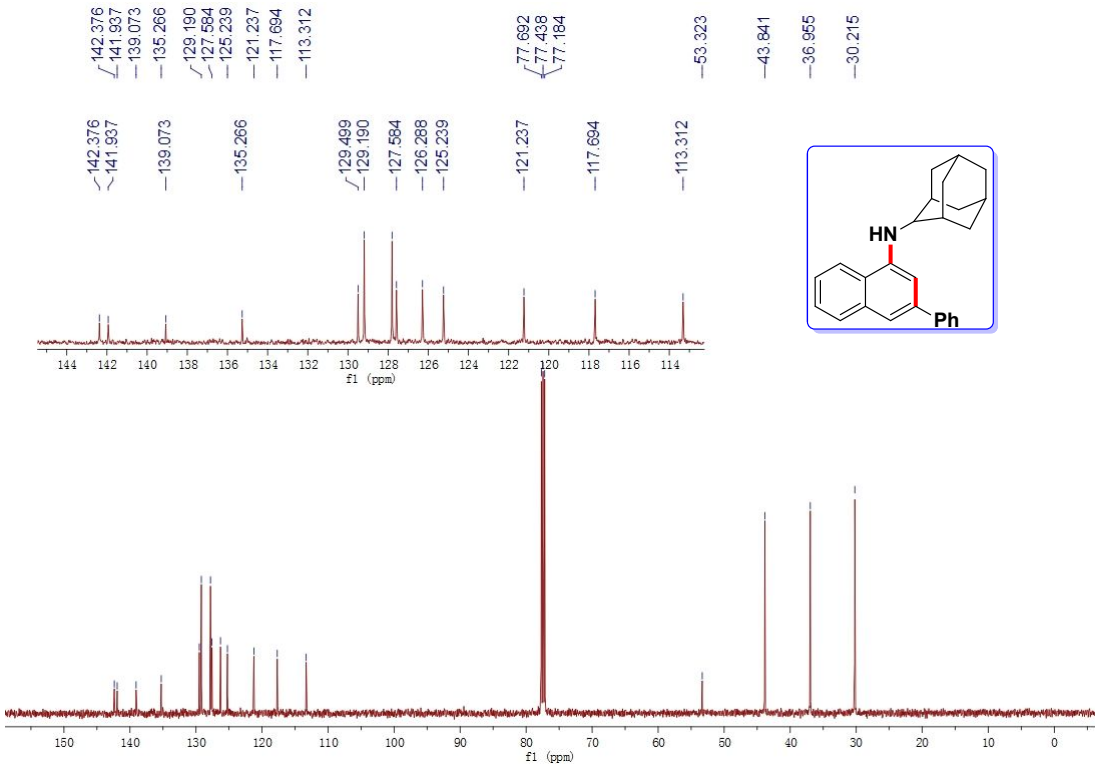


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3aw

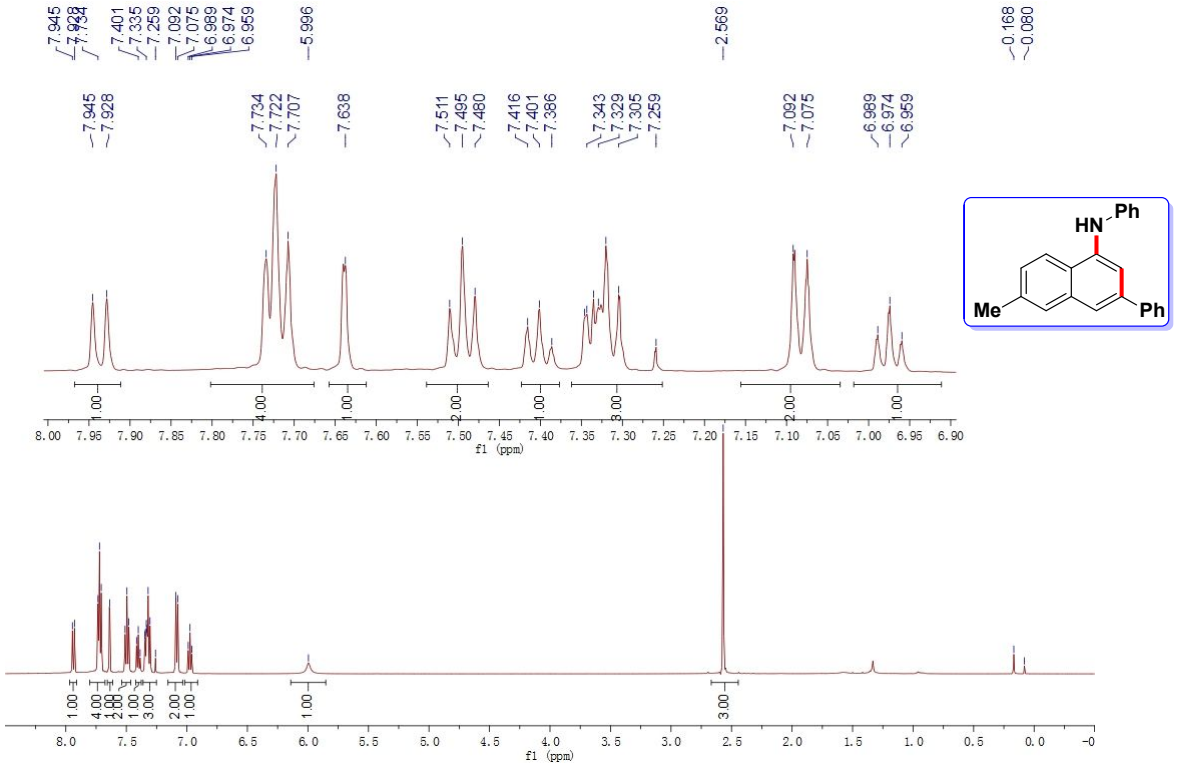


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

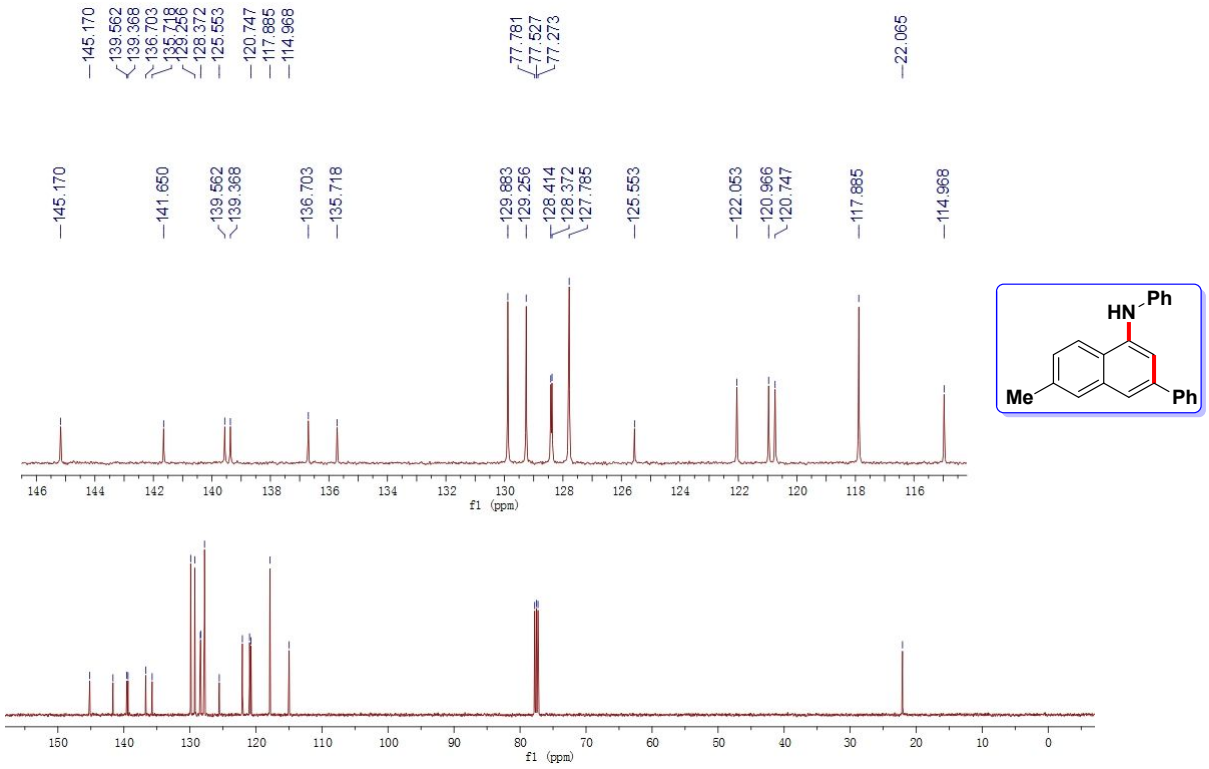


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ba

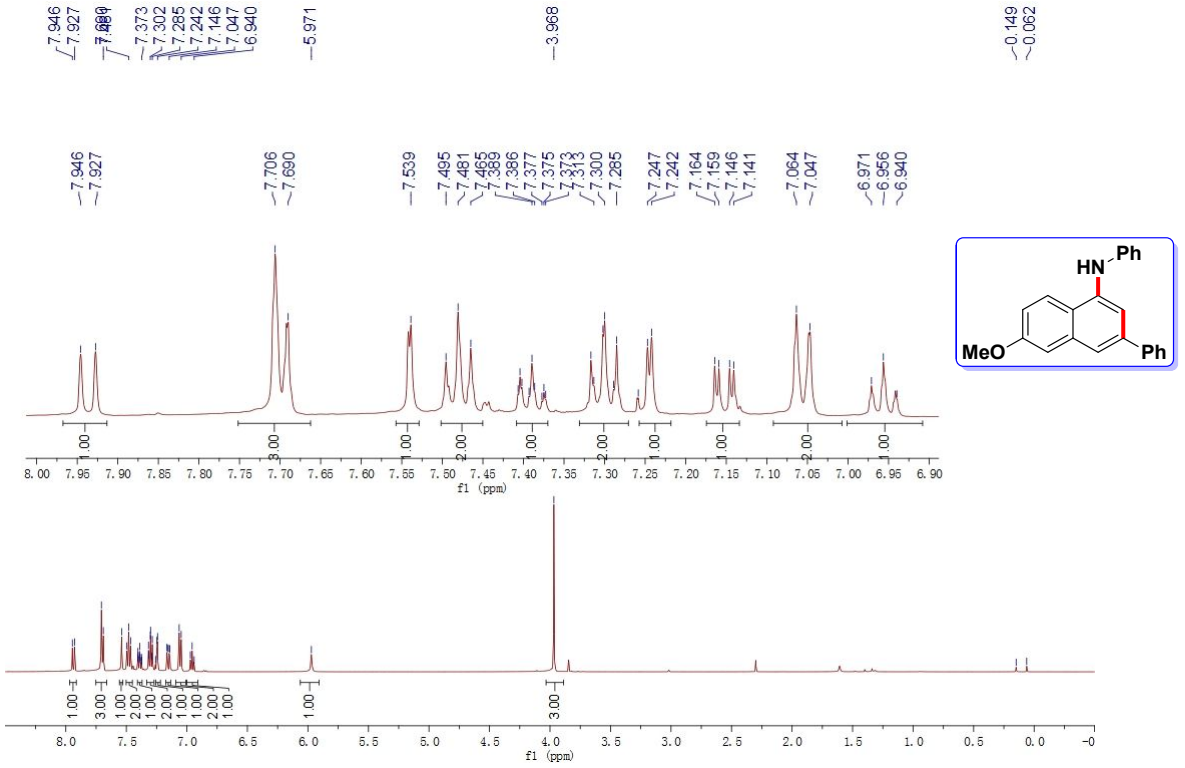


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

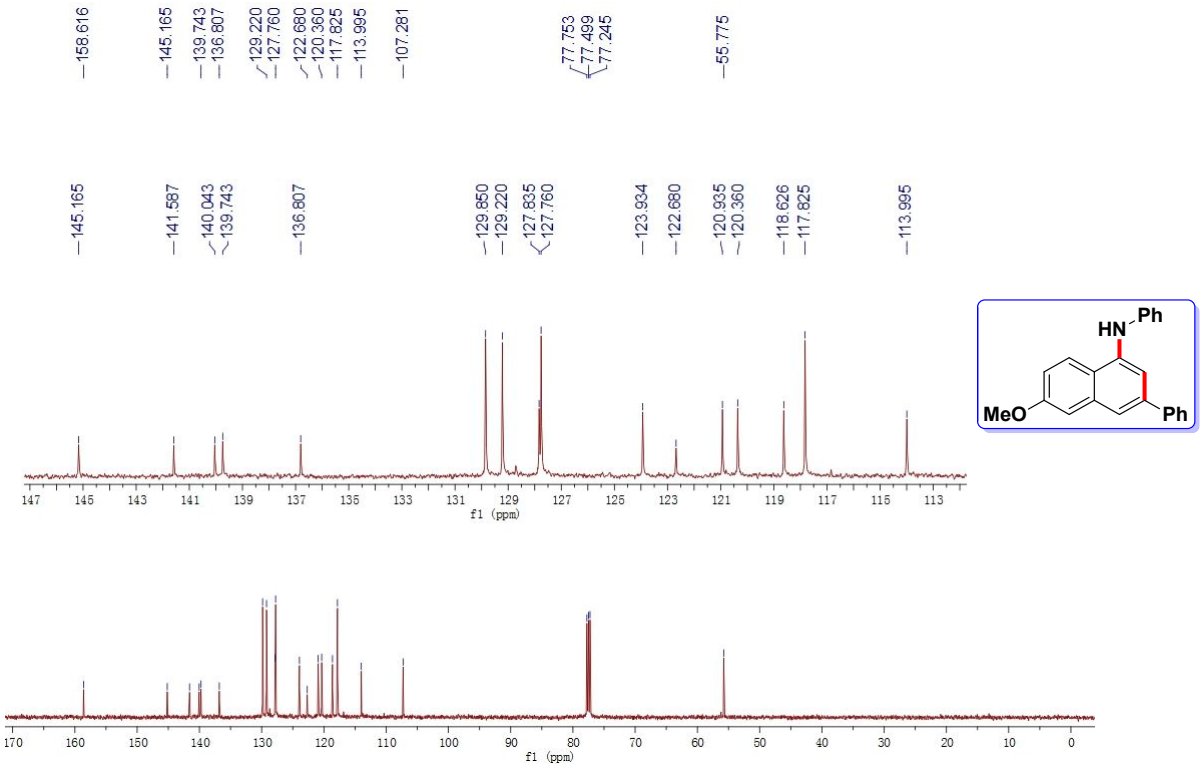


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ca

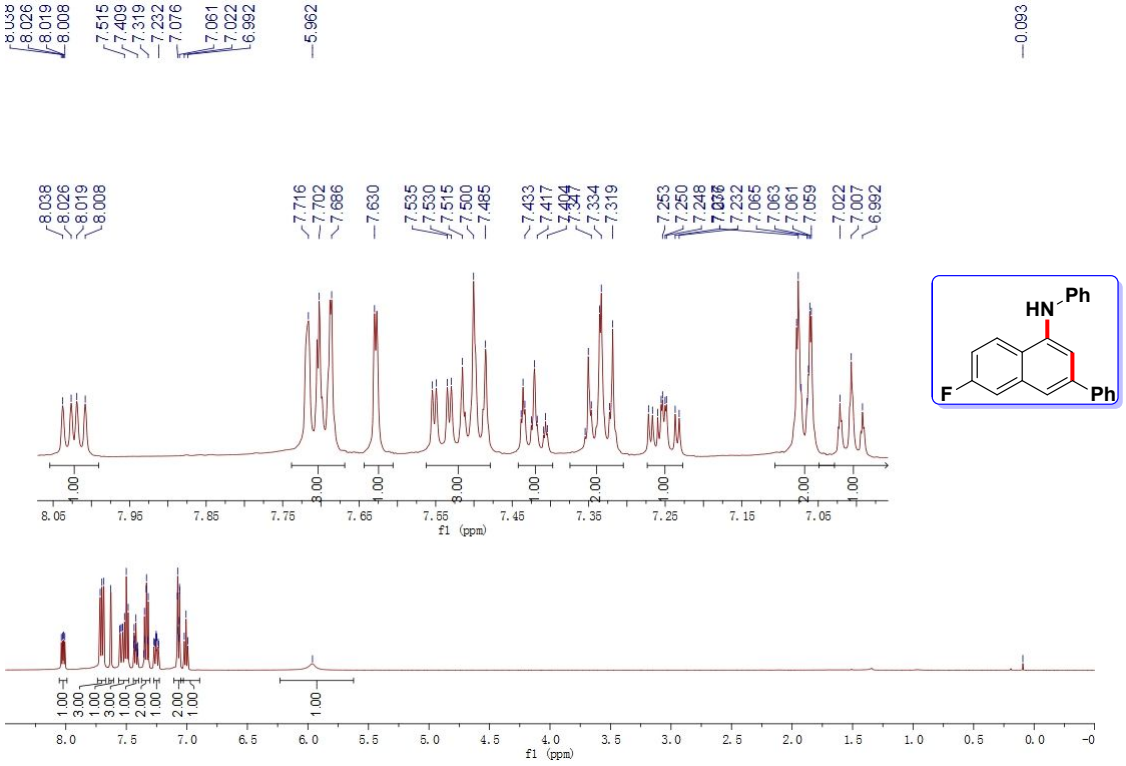


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

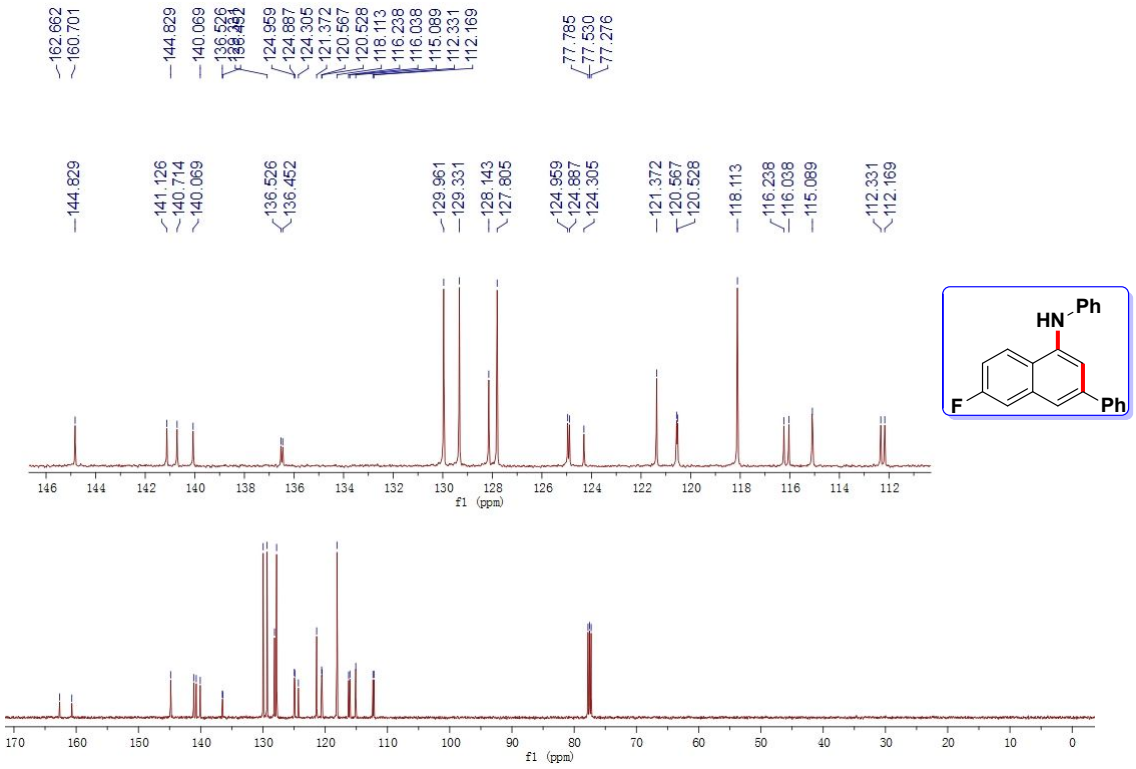


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3da

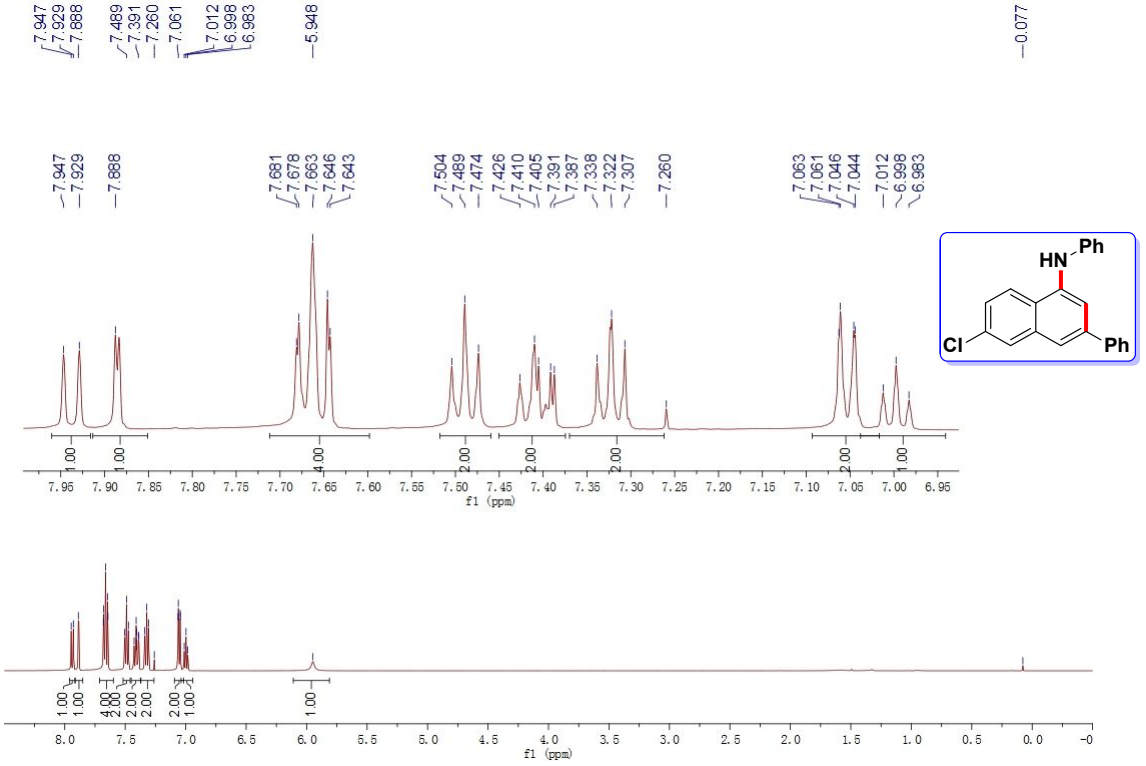


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

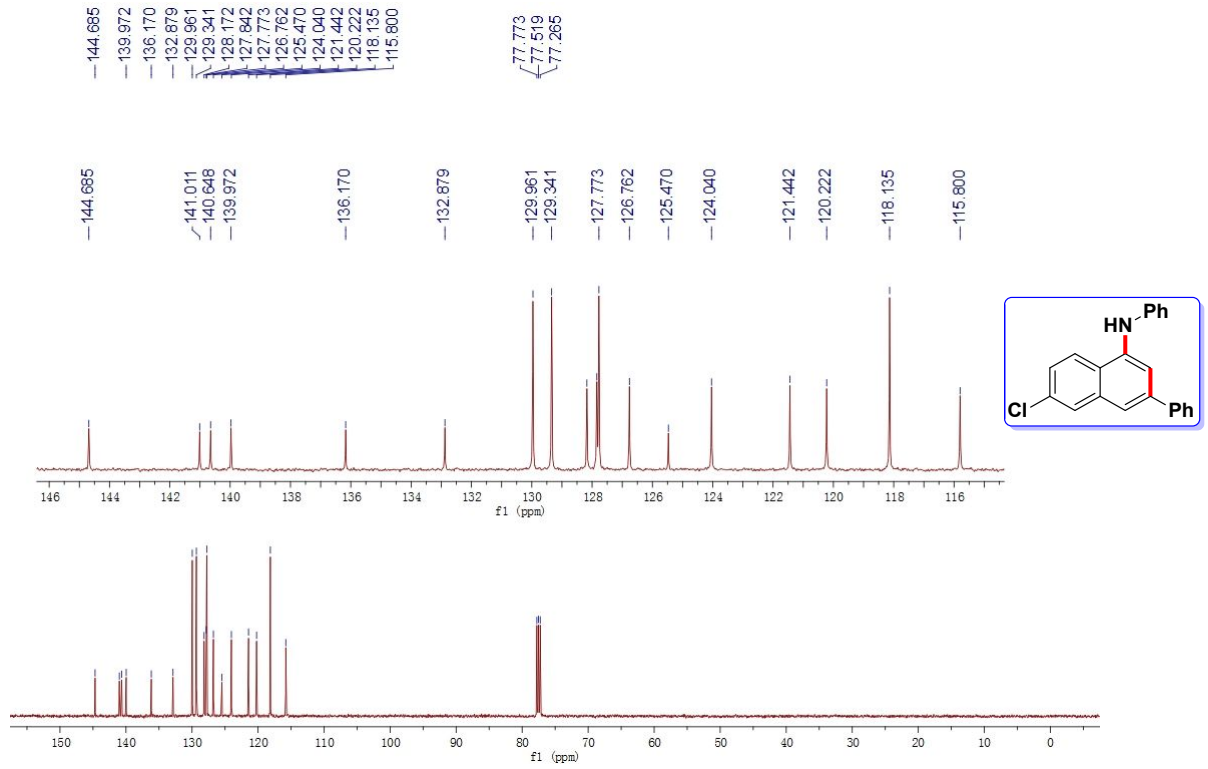


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ea

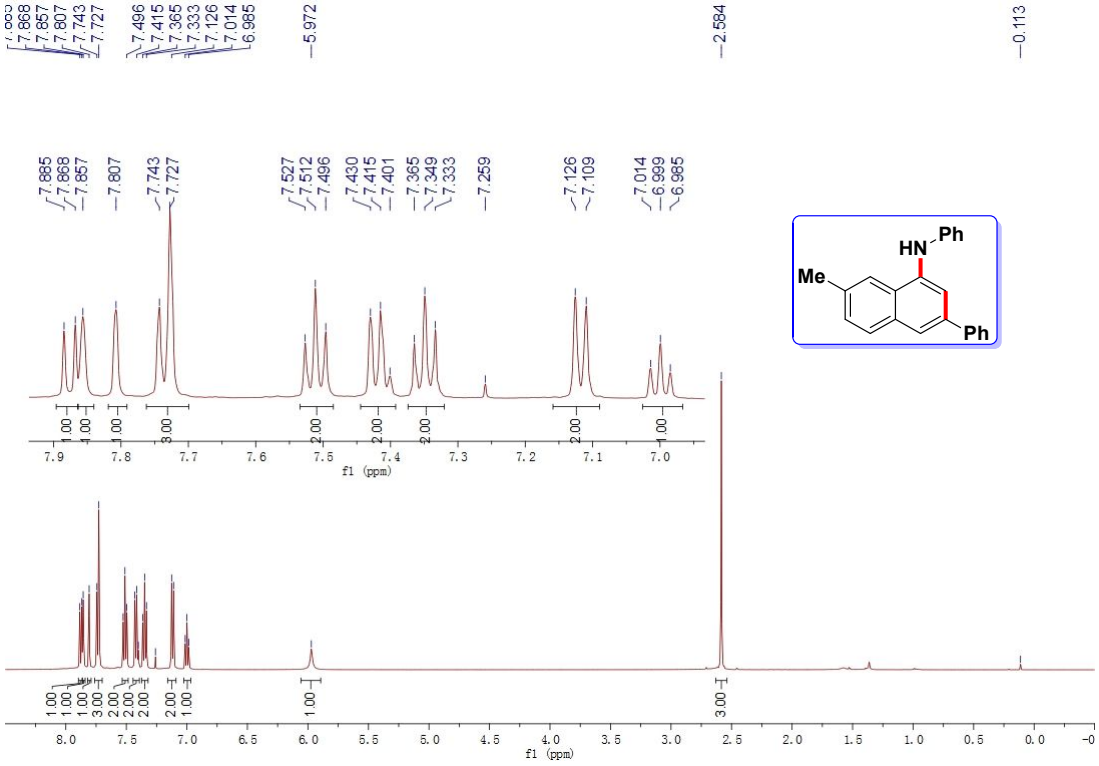


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

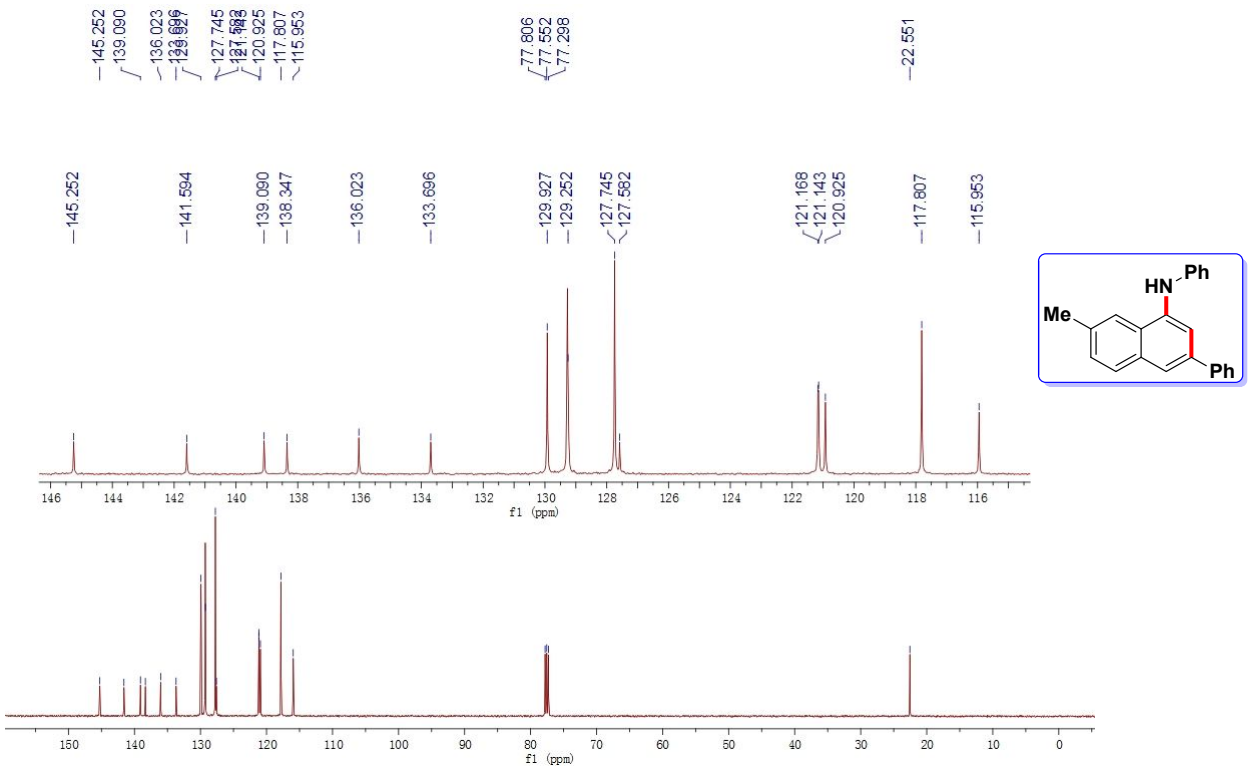


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3fa

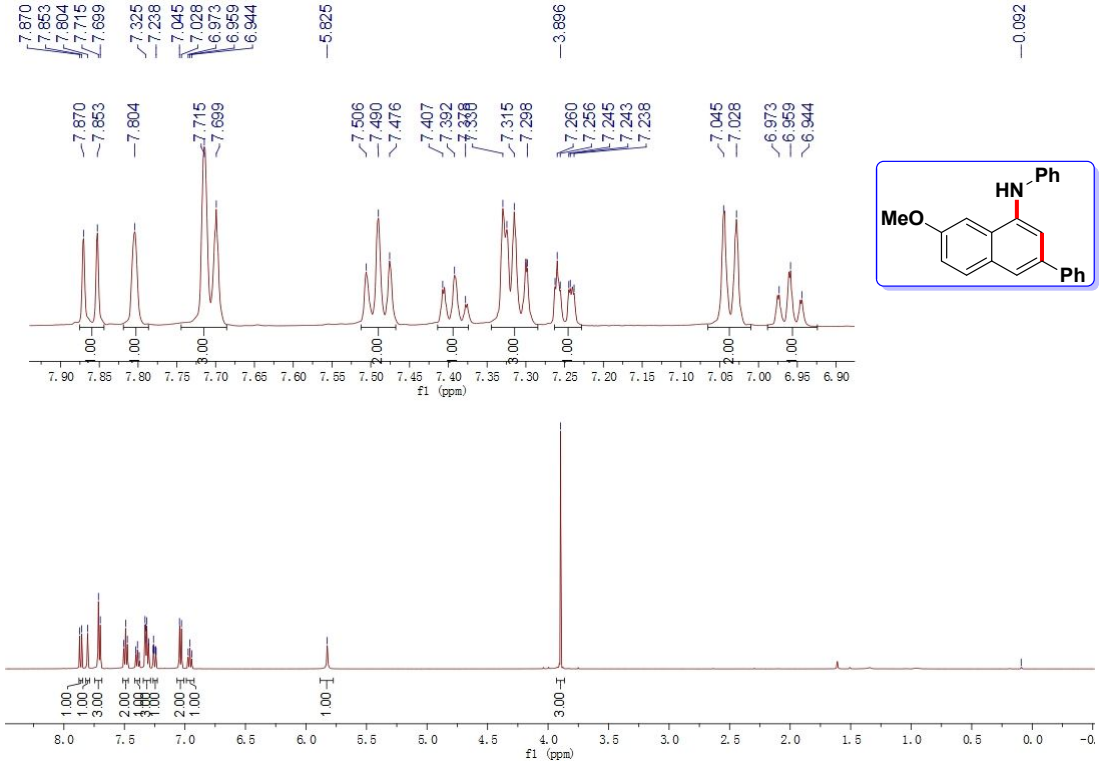


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

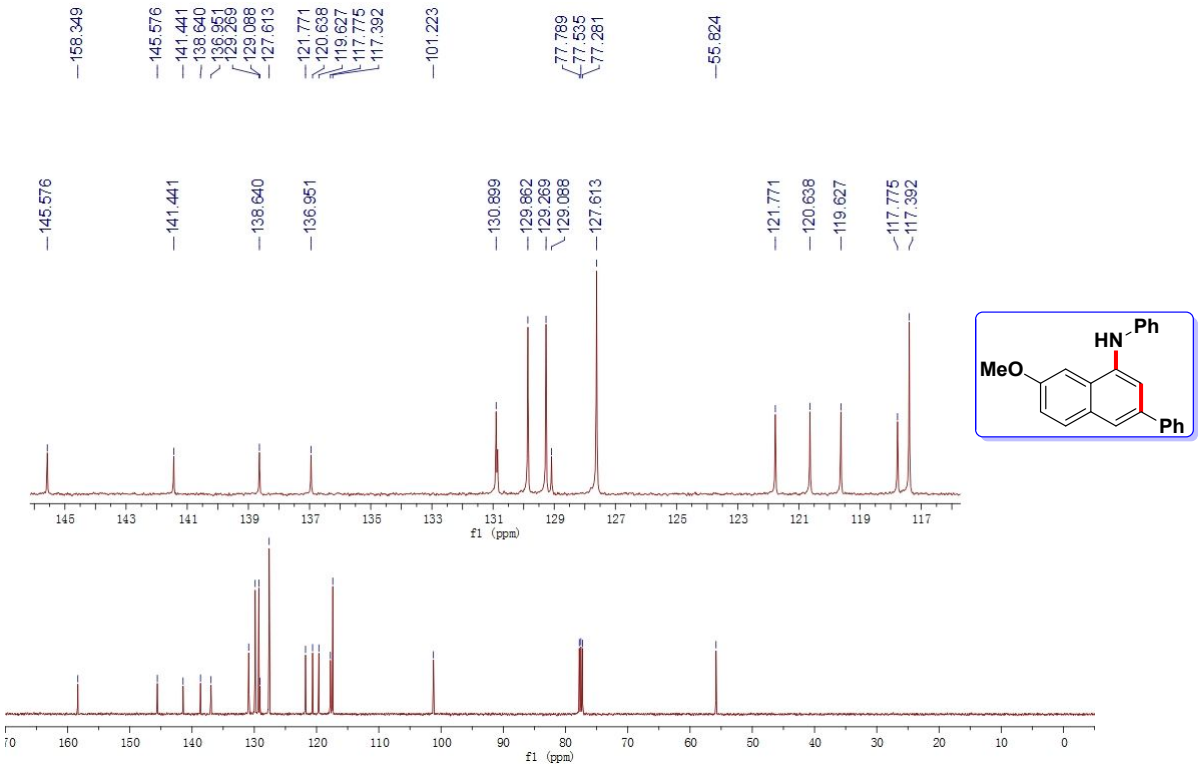


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ga

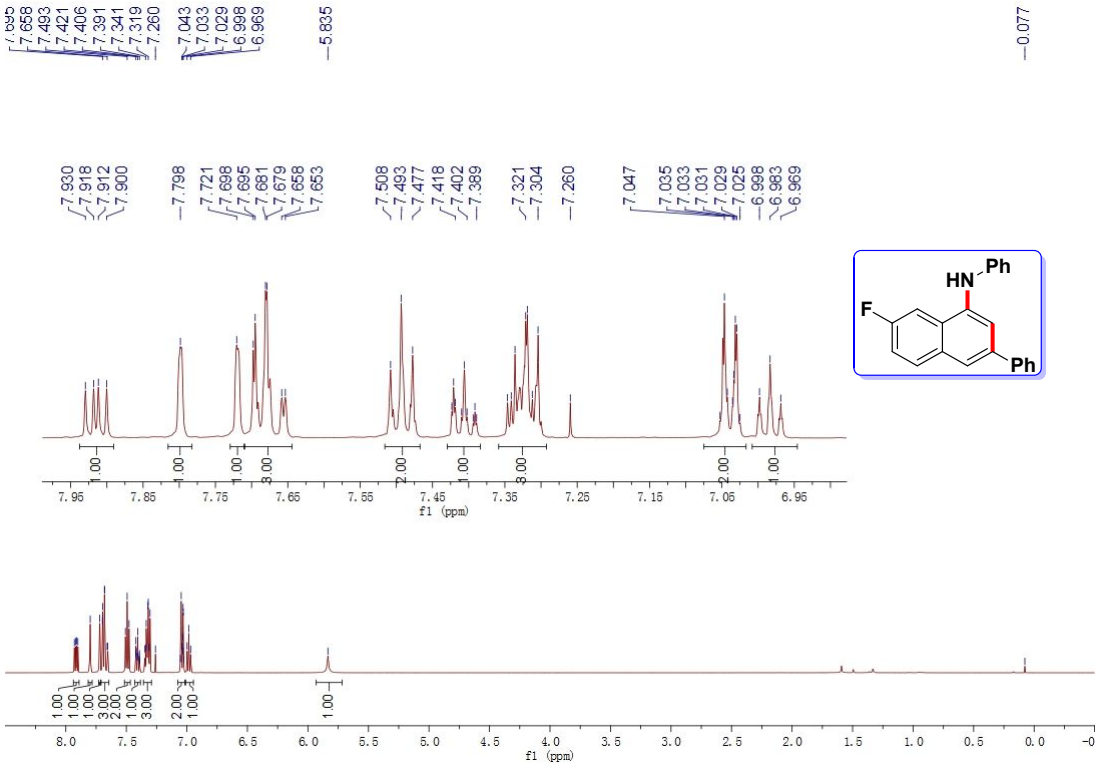


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

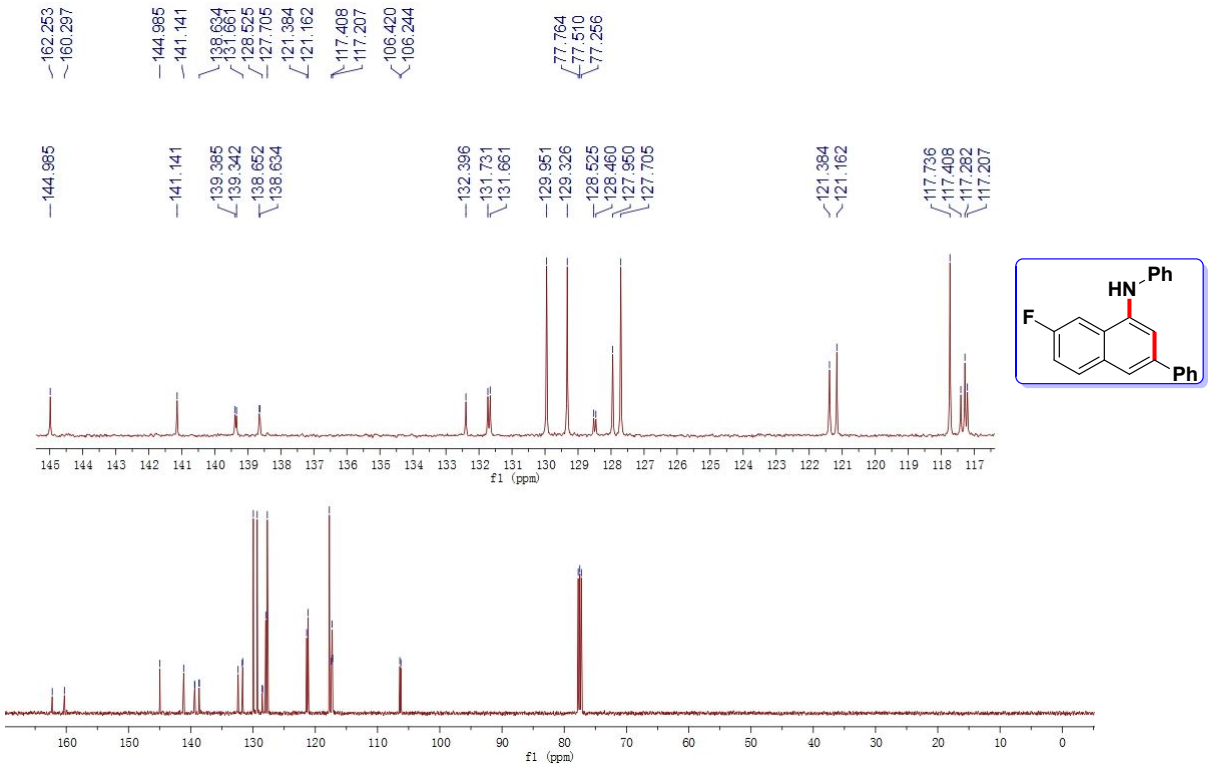


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ha

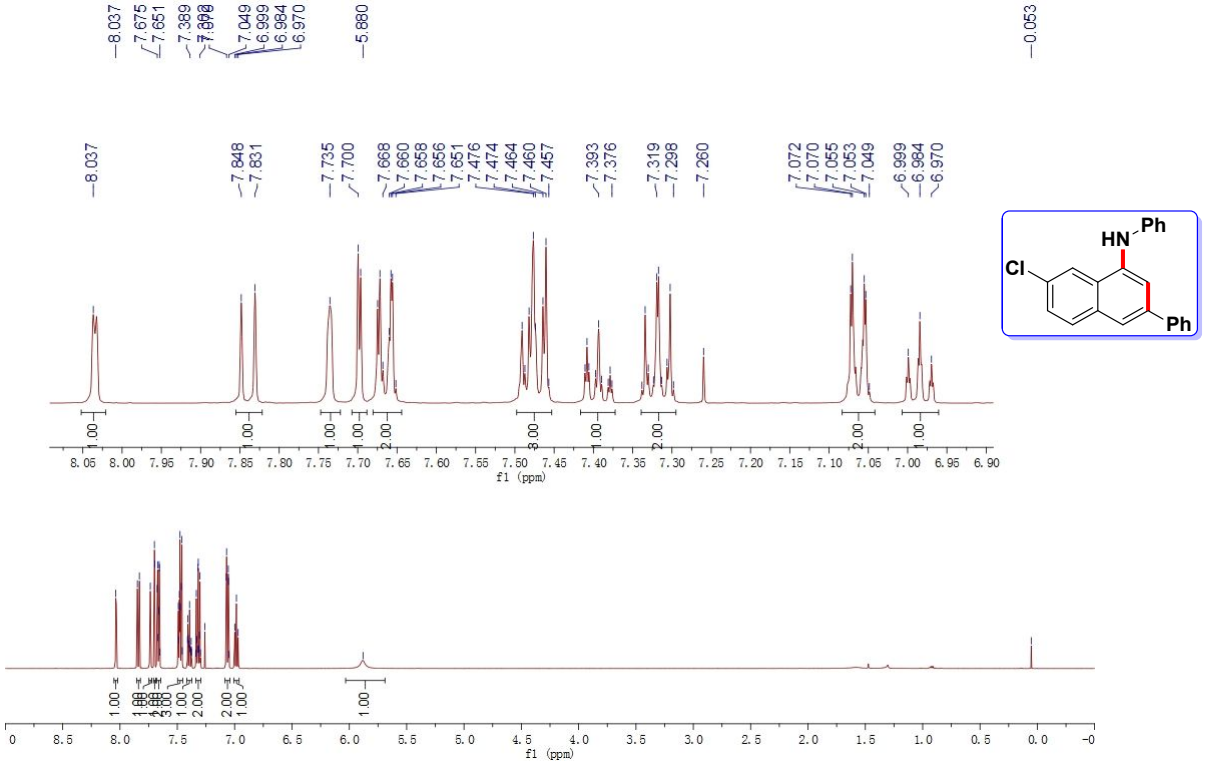


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

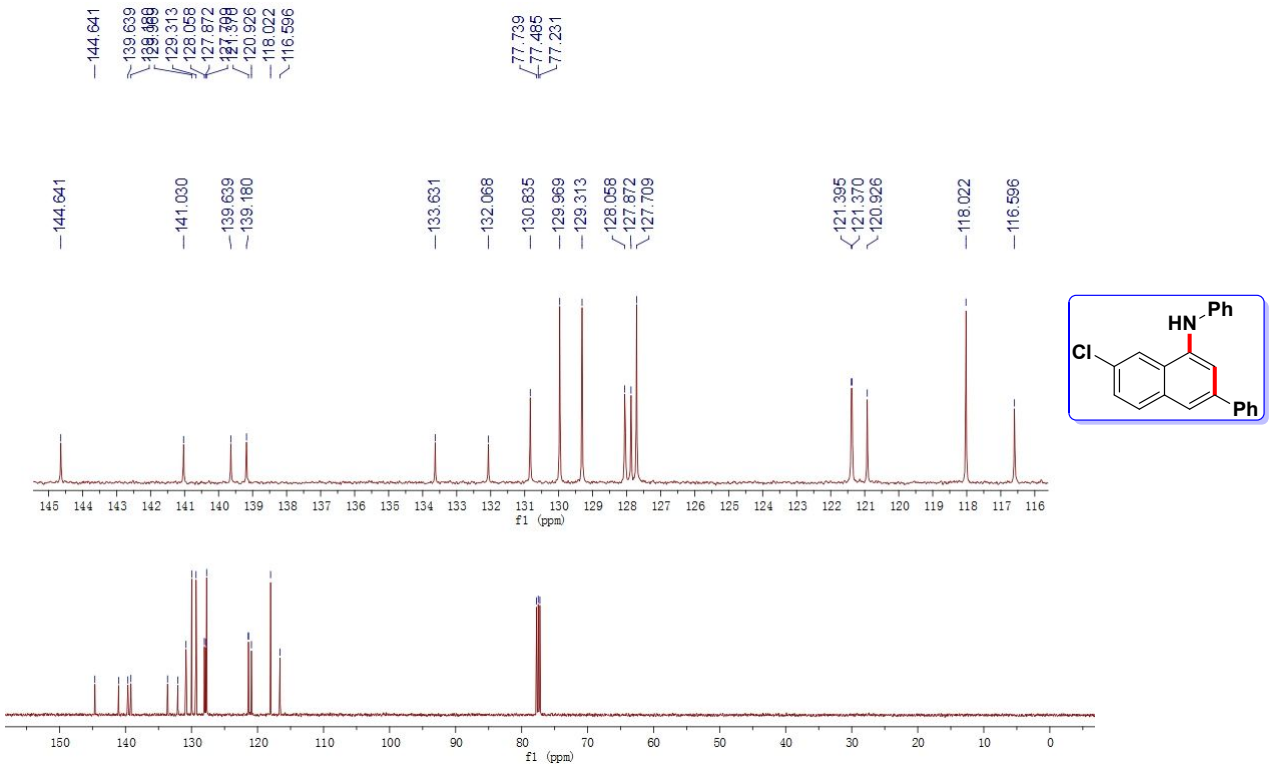


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ia

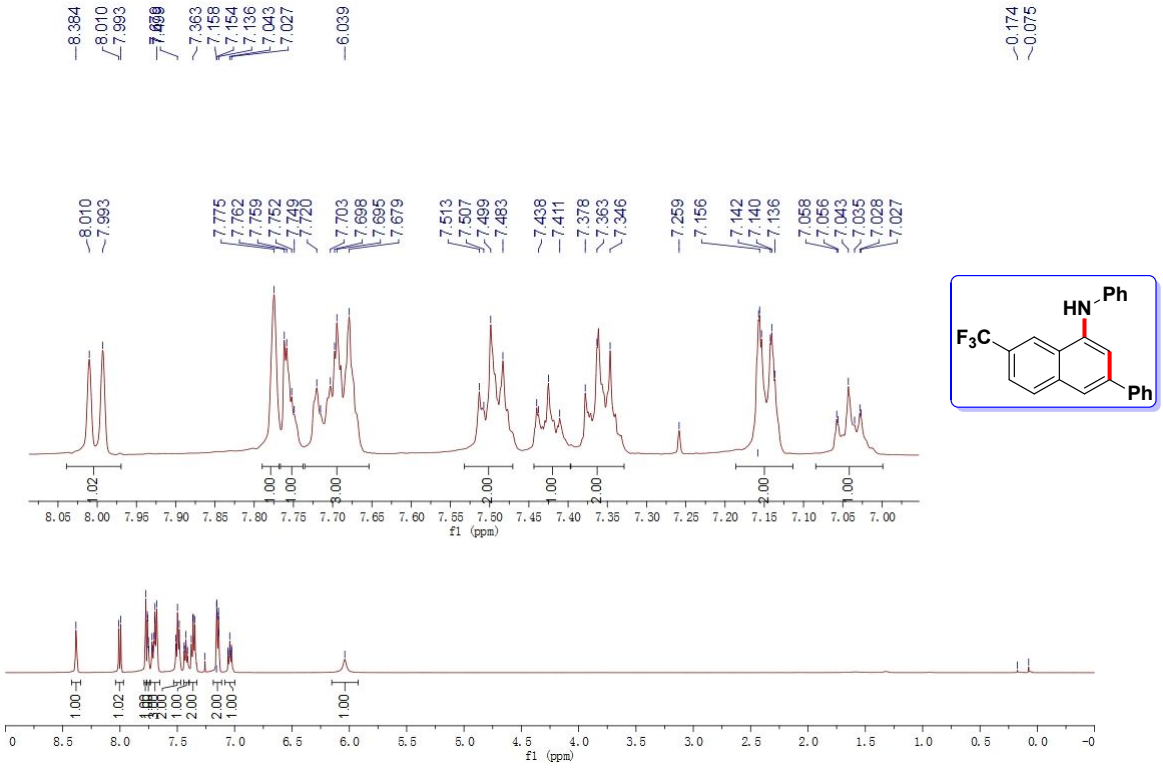


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

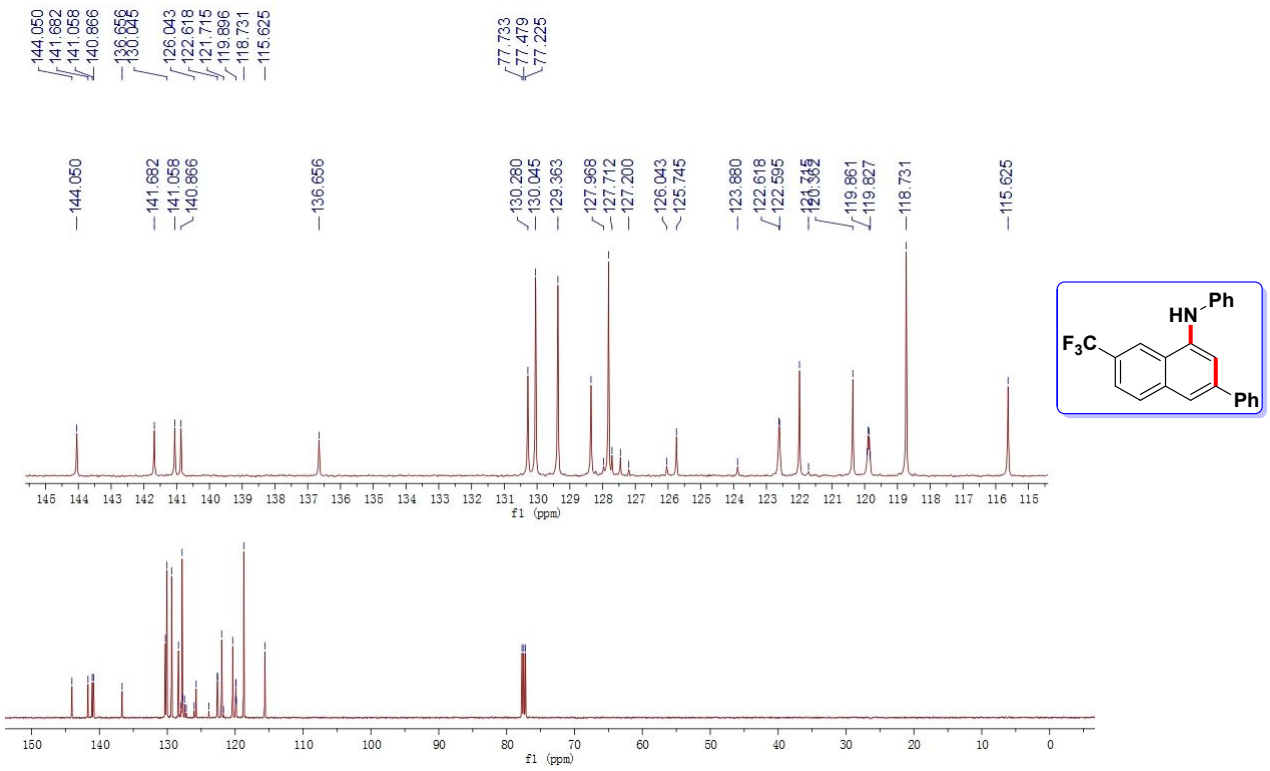


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ja

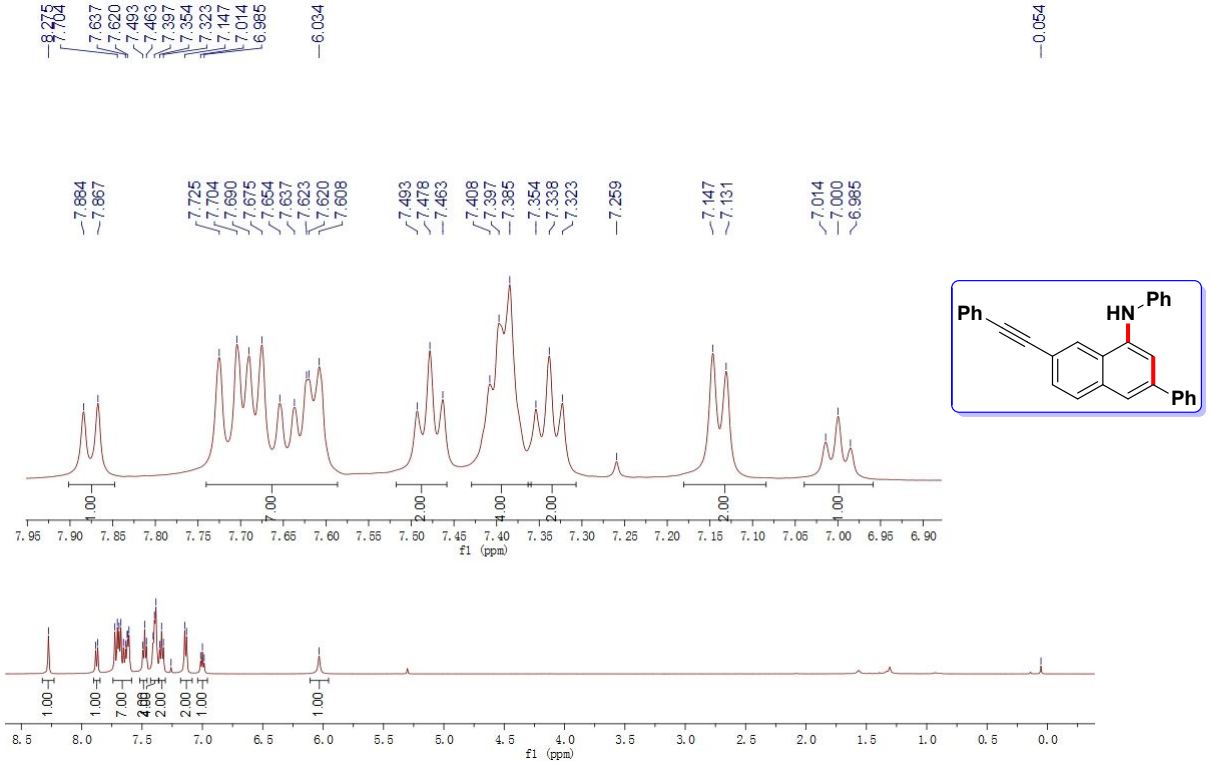


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

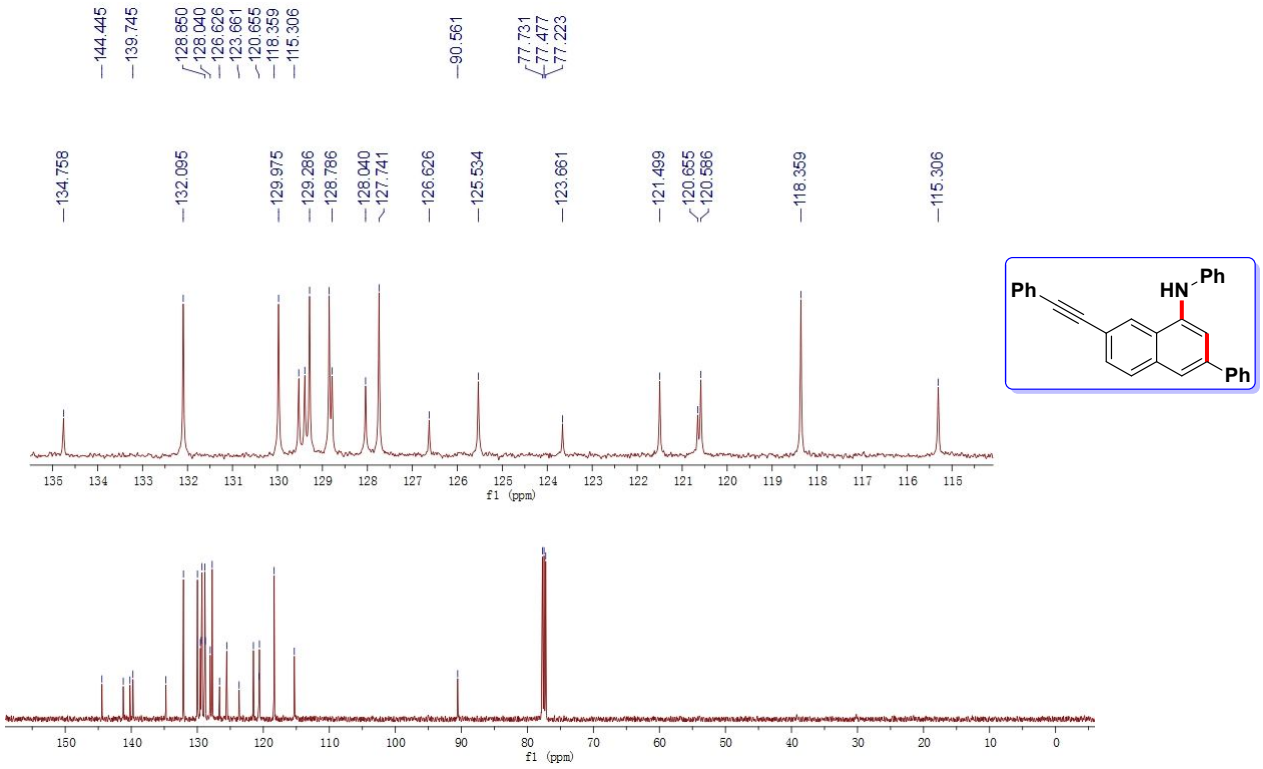


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ka

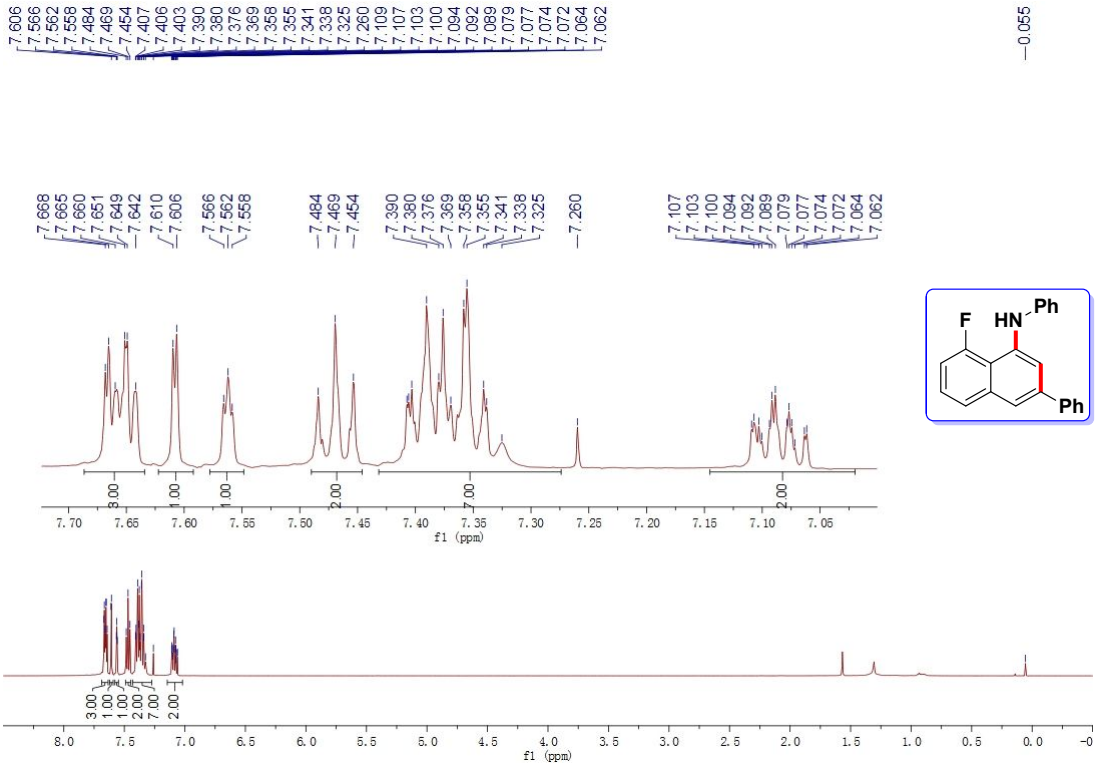


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

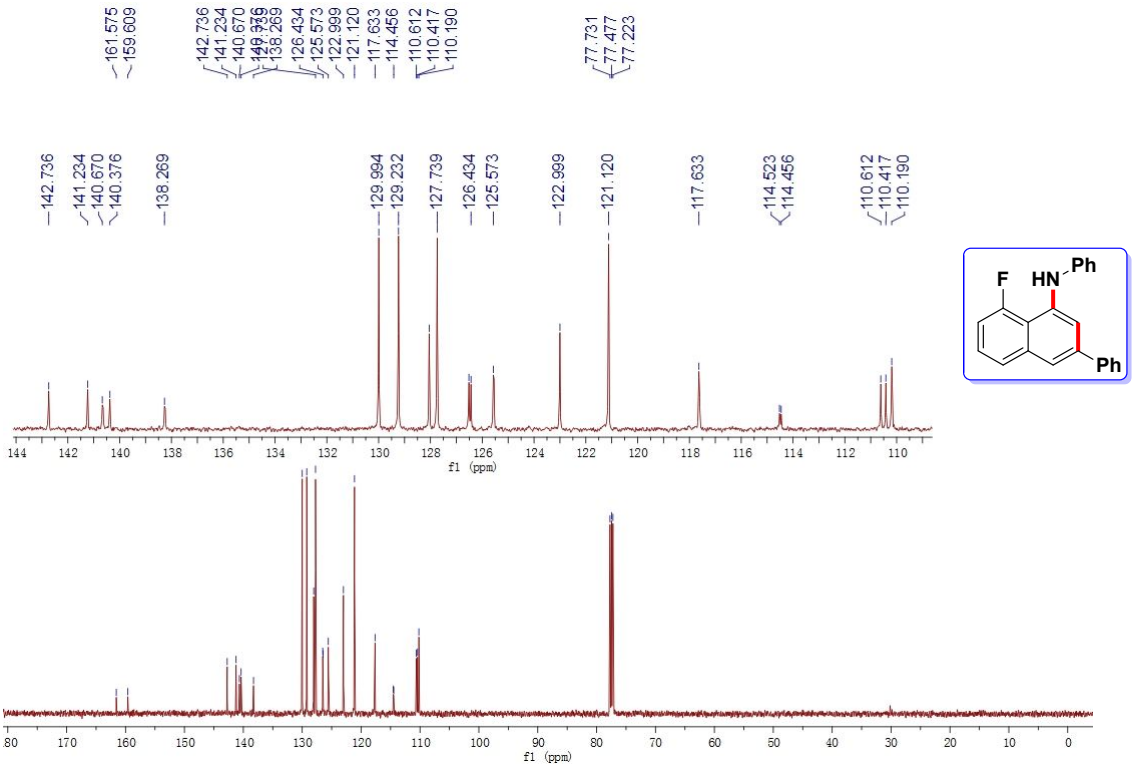


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3la

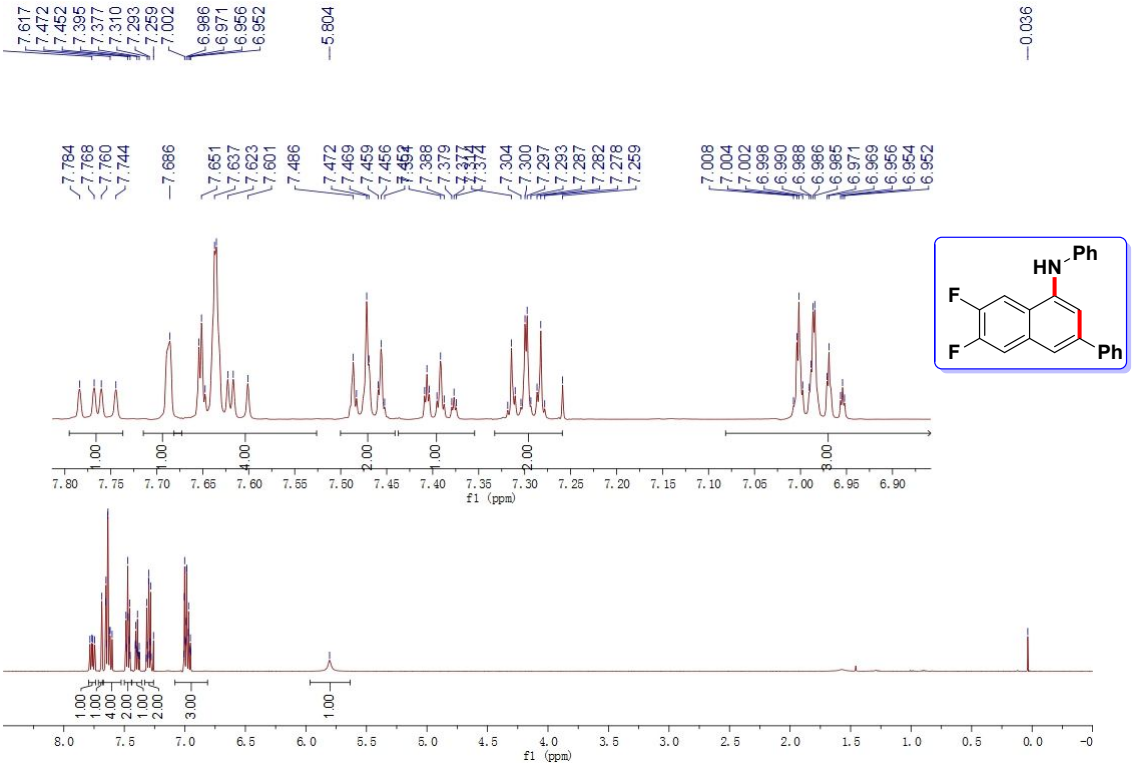


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

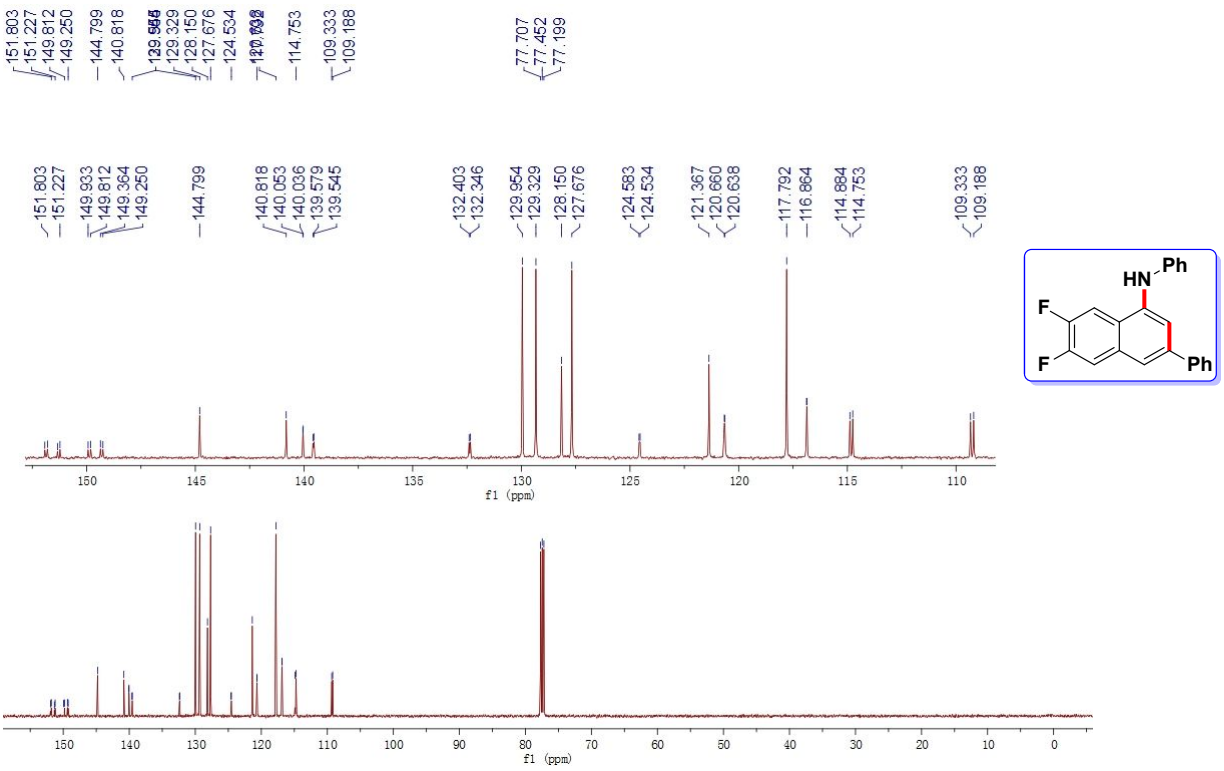


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ma

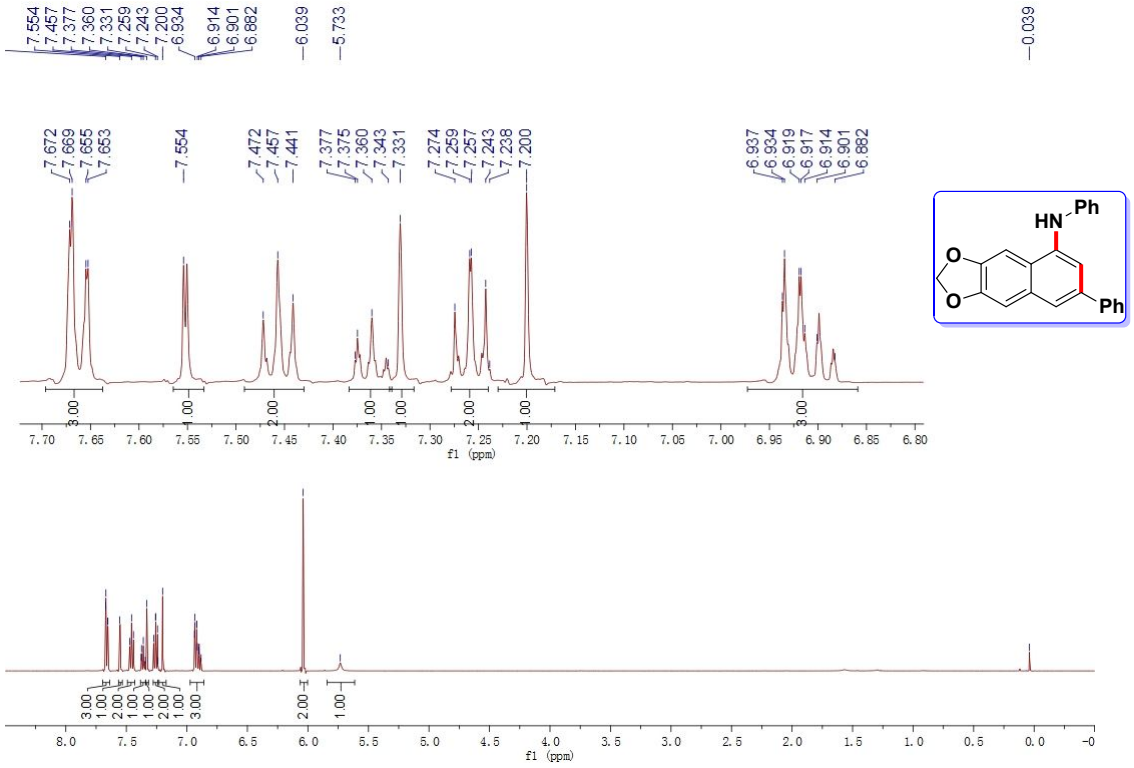


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

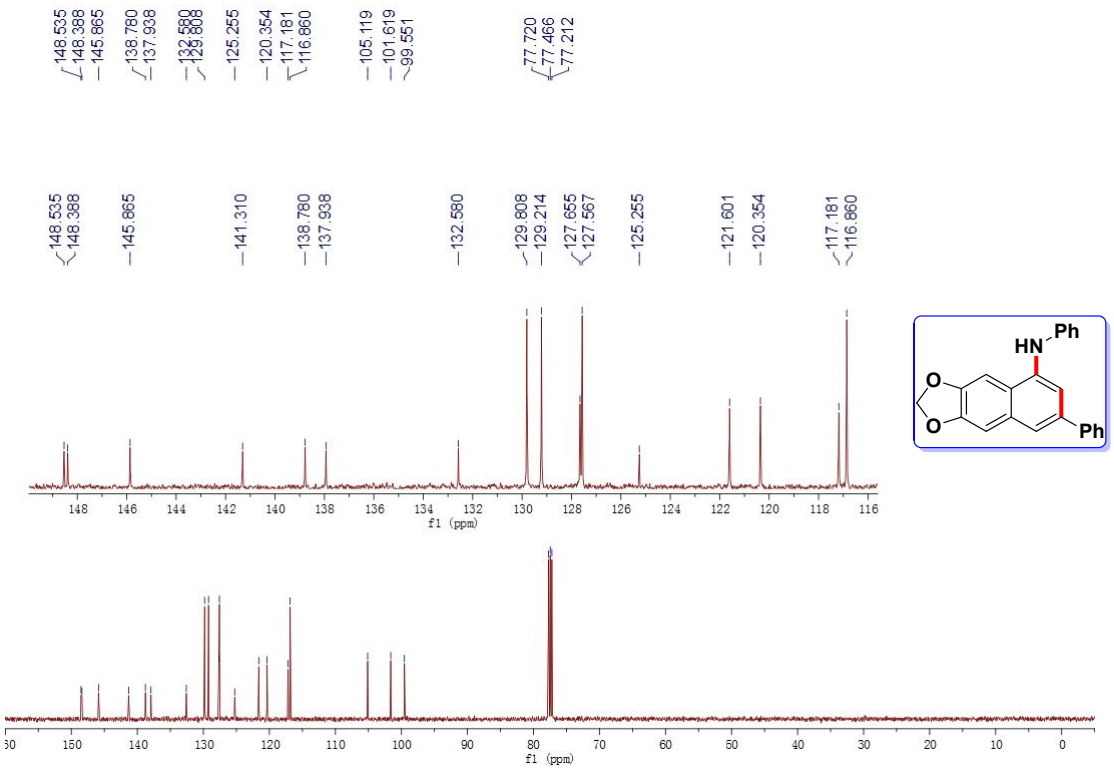


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3na

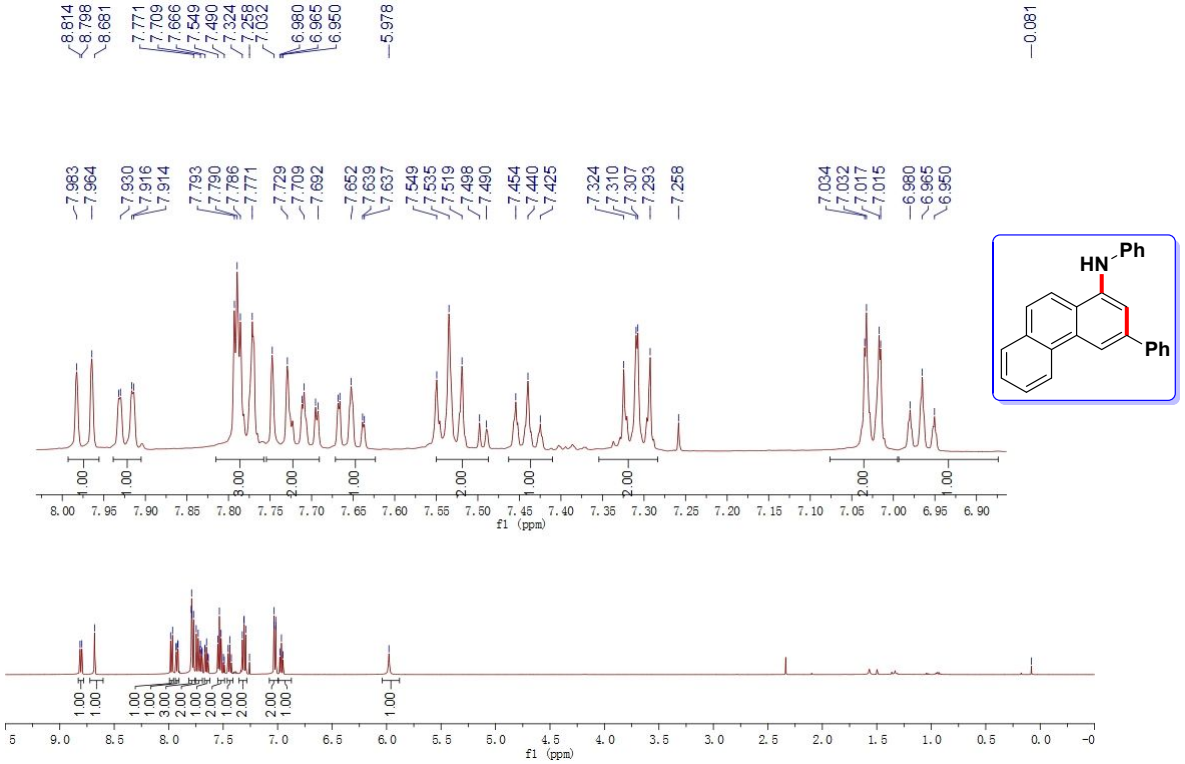


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

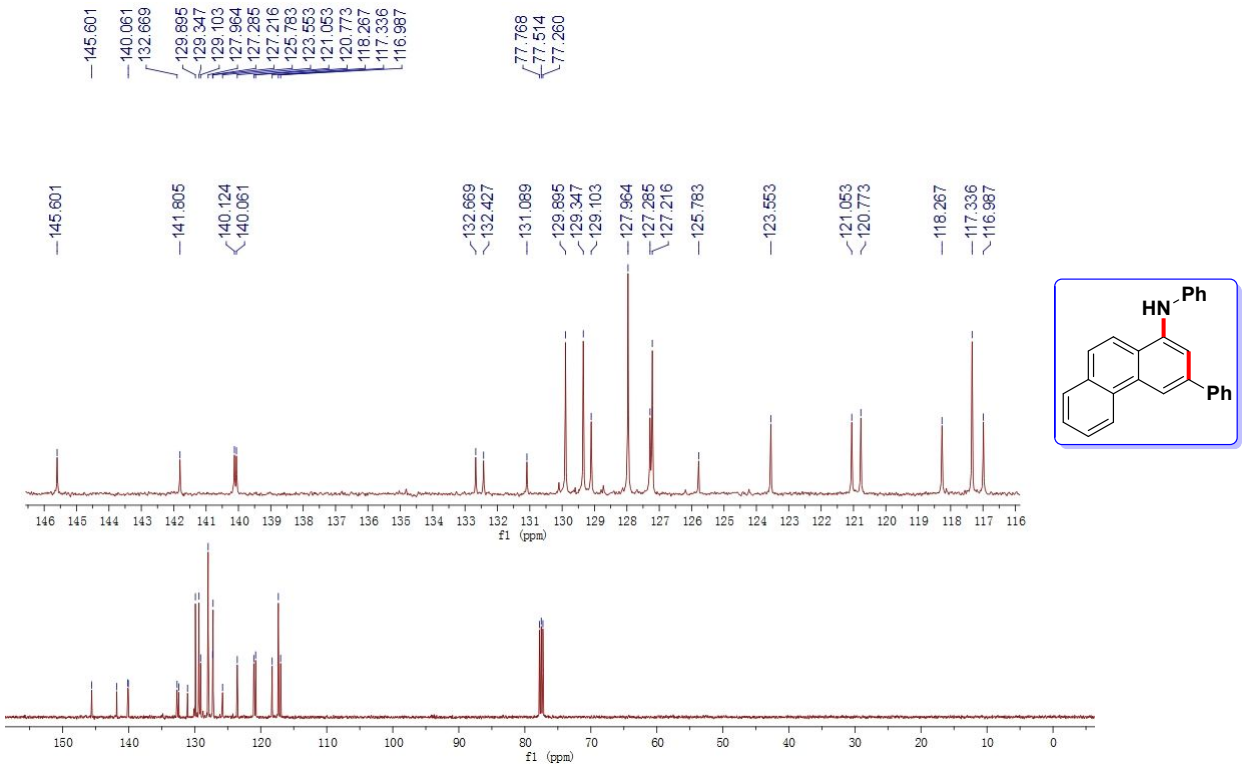


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3oa

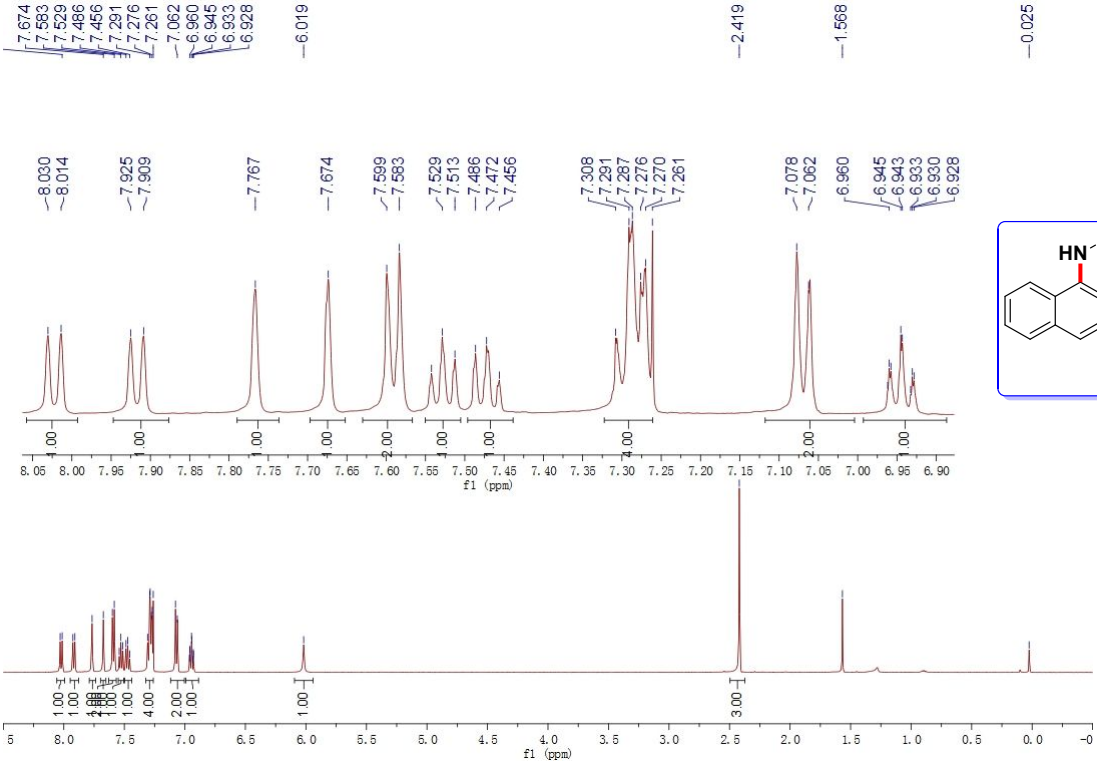


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

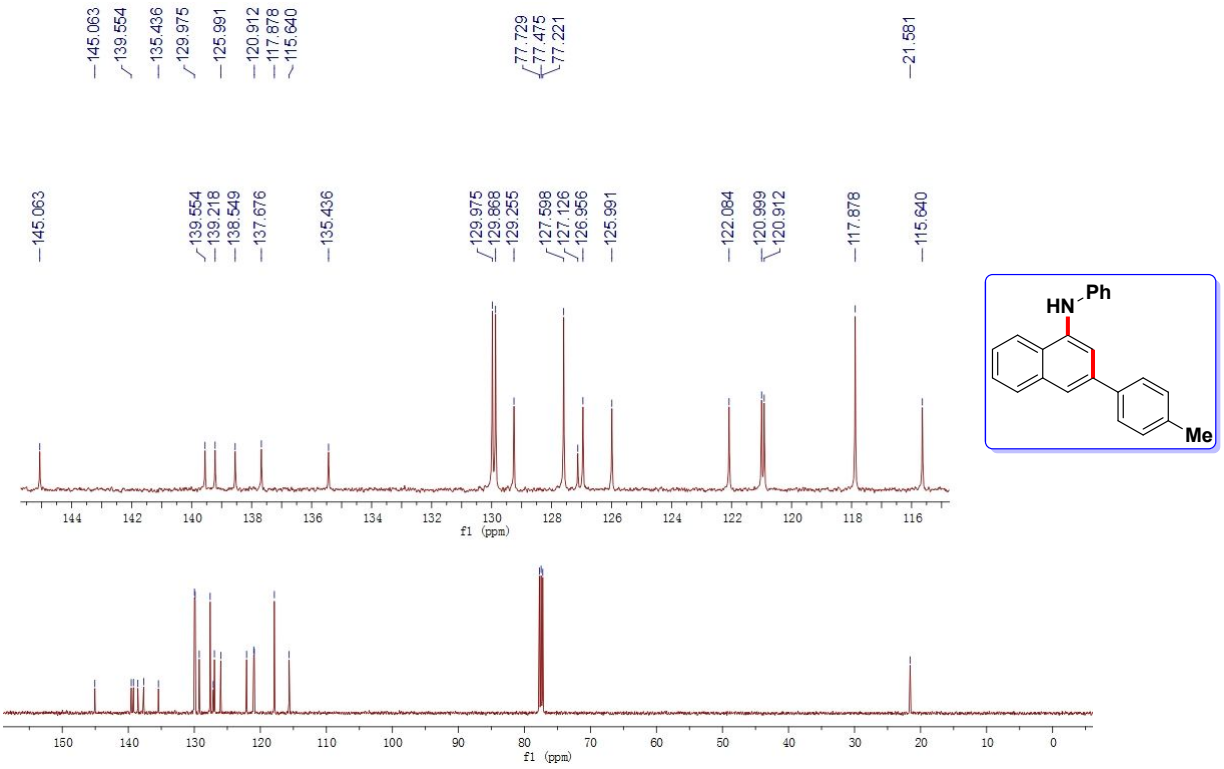


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3pa

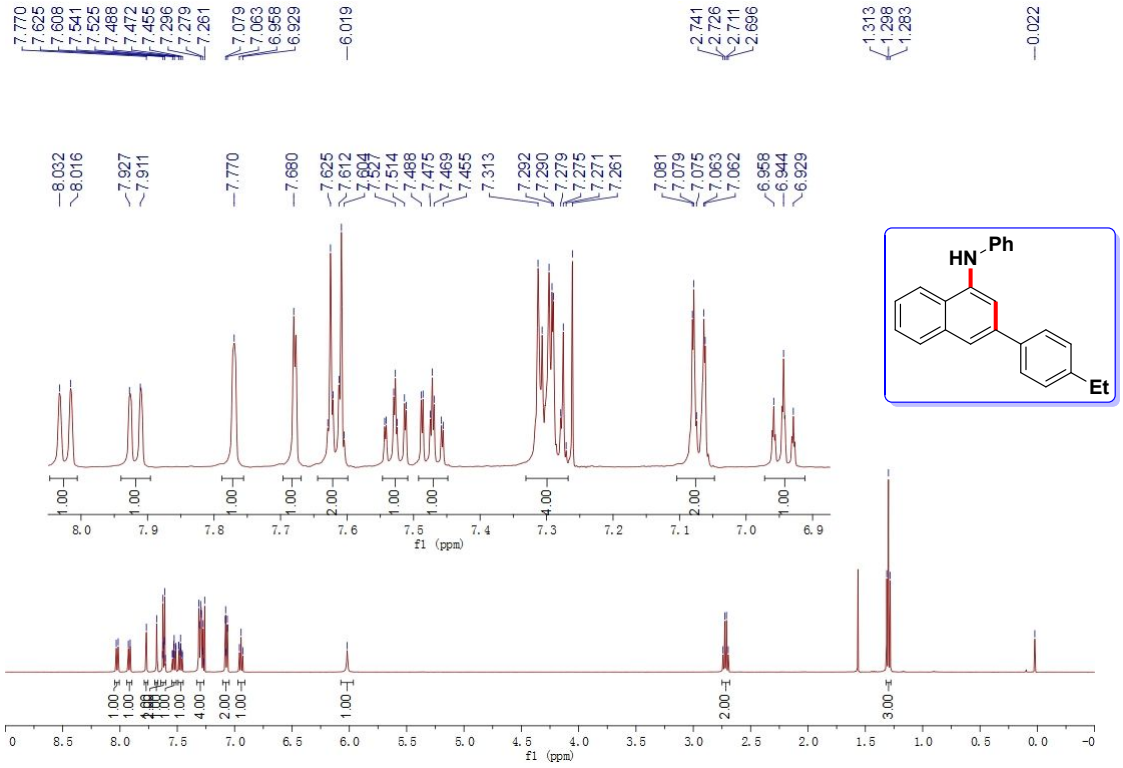


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

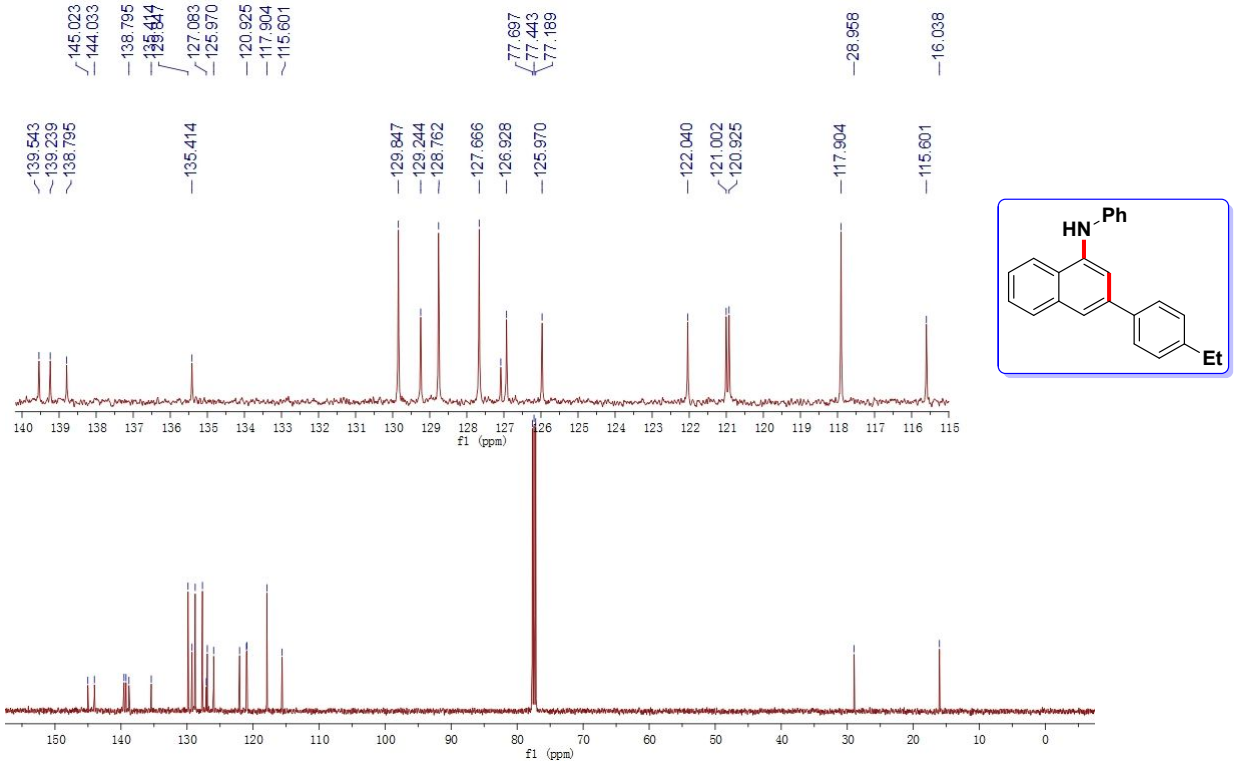


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3qa

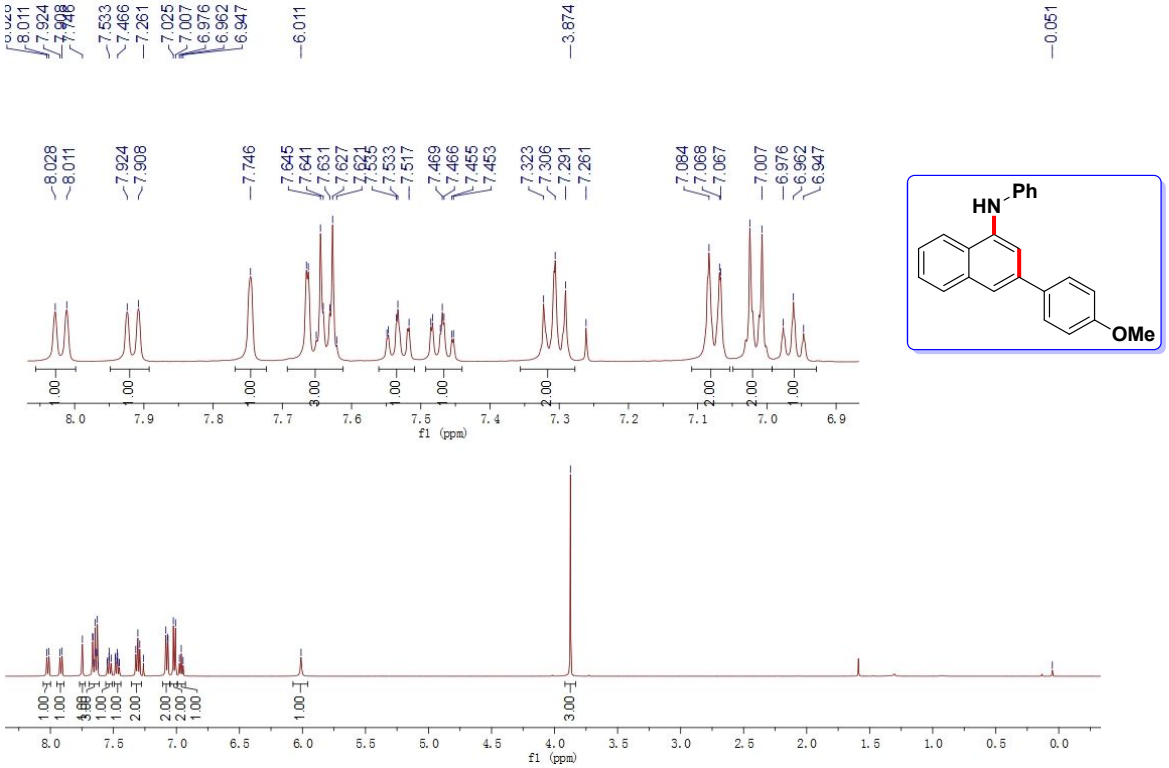


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

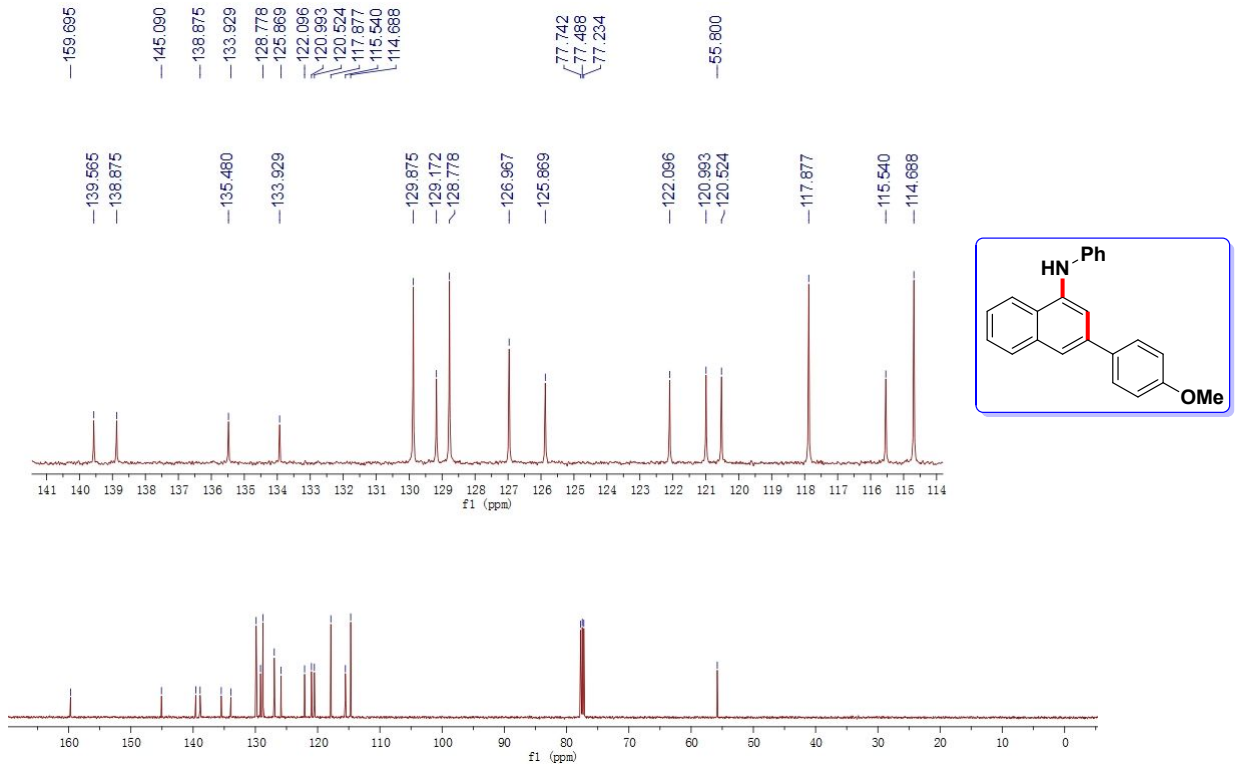


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ra

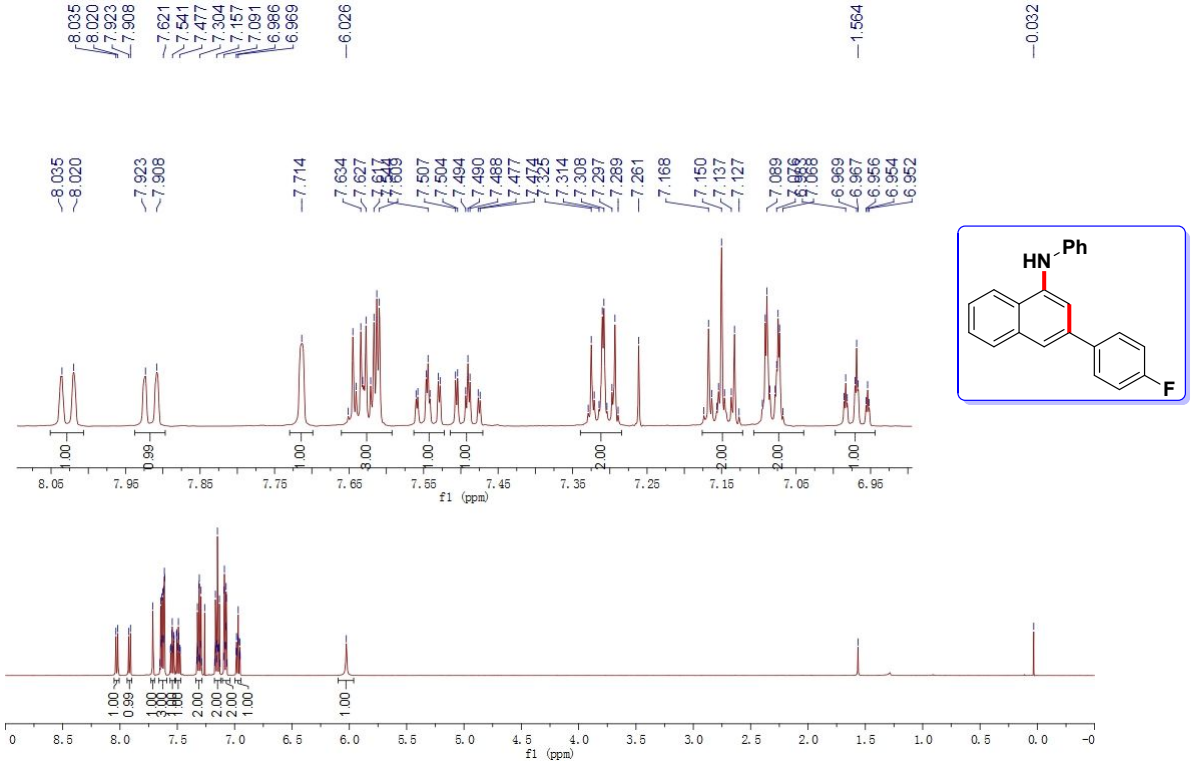


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

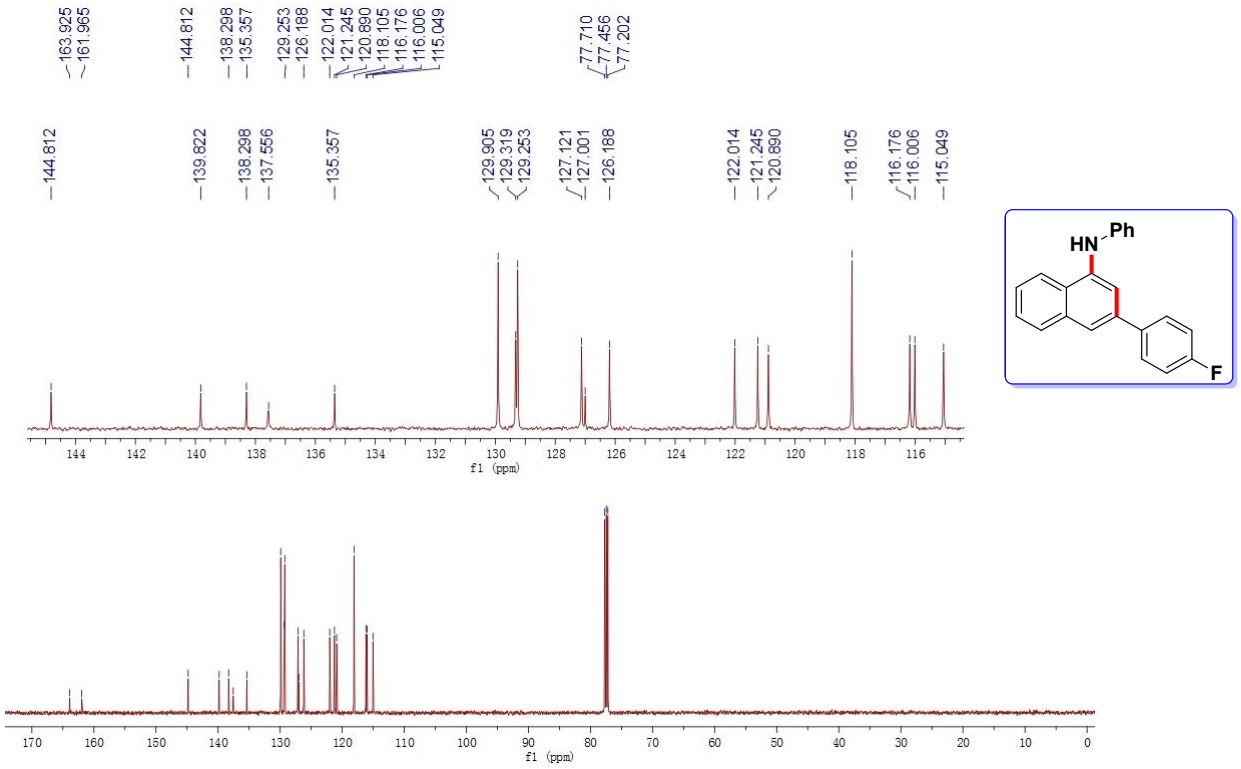


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3sa

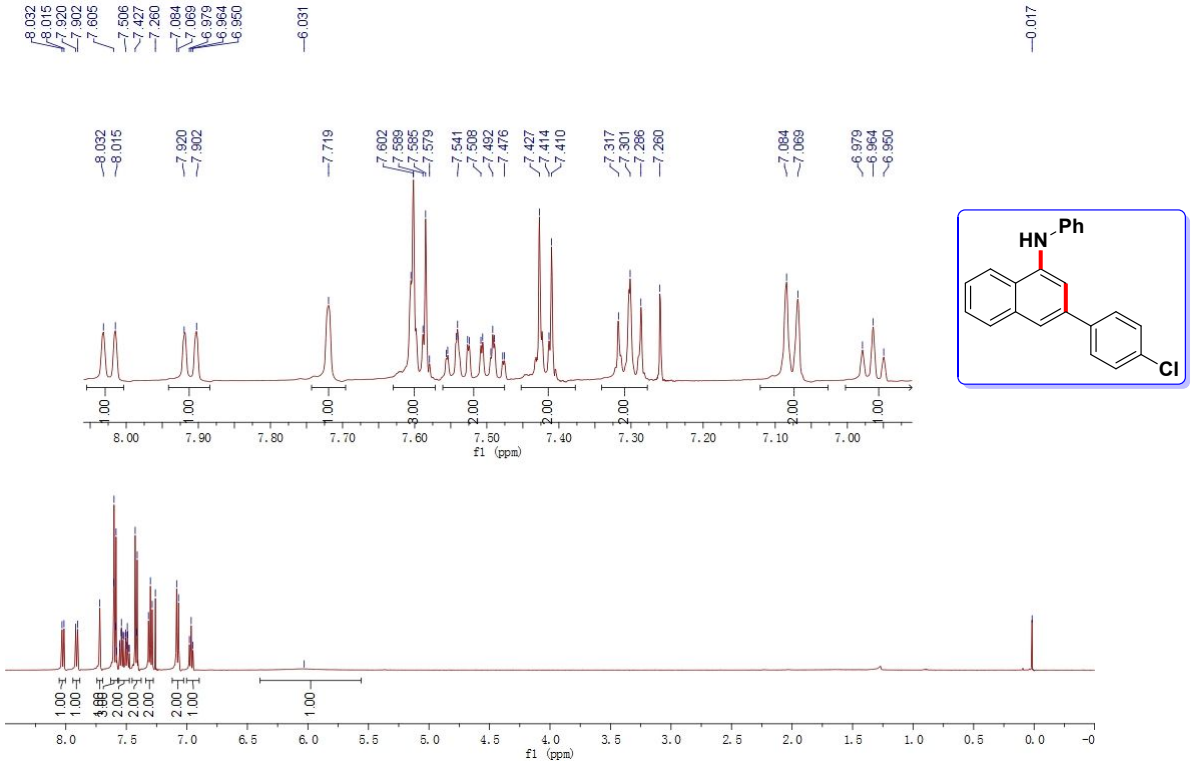


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

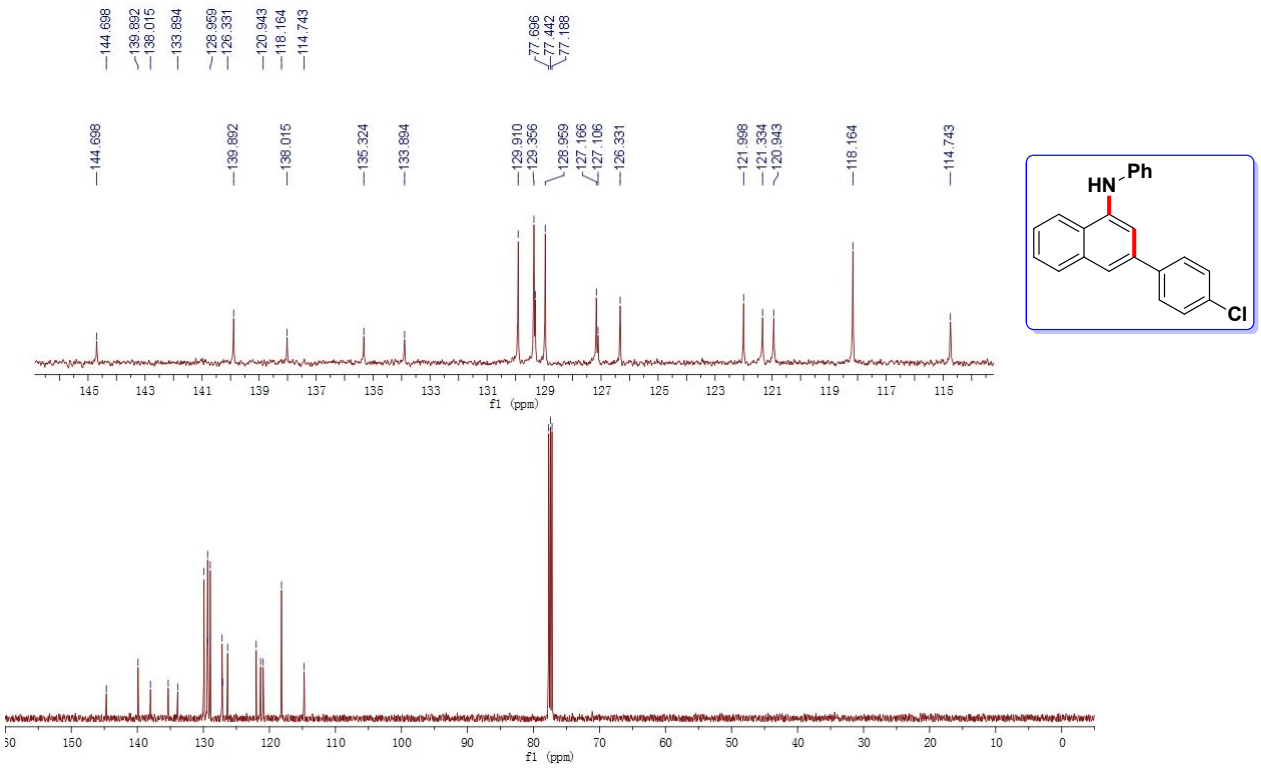


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ta

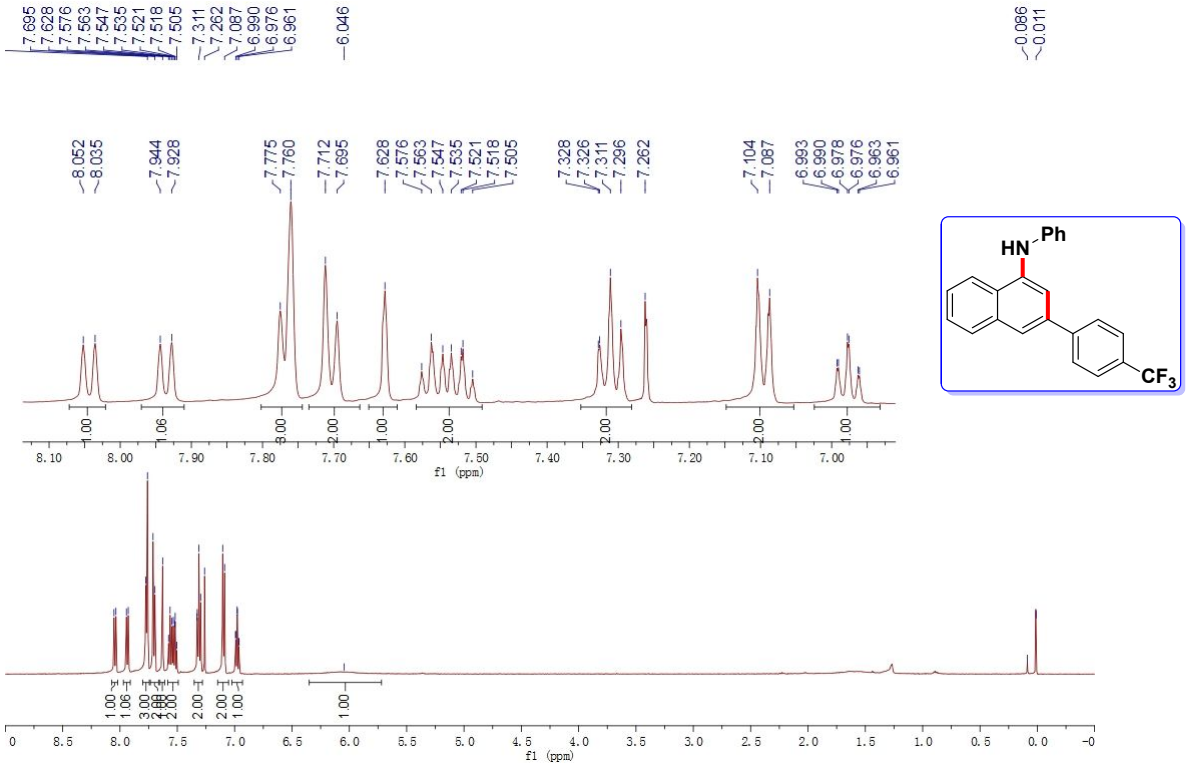


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

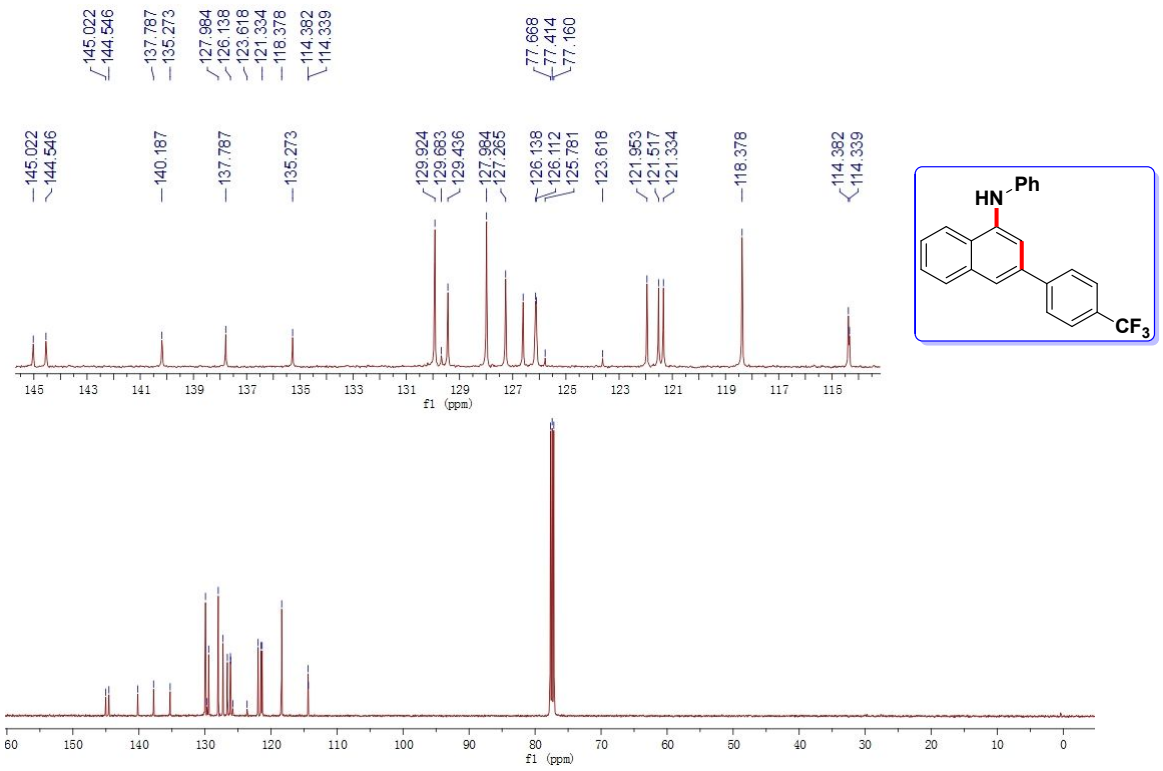


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ua

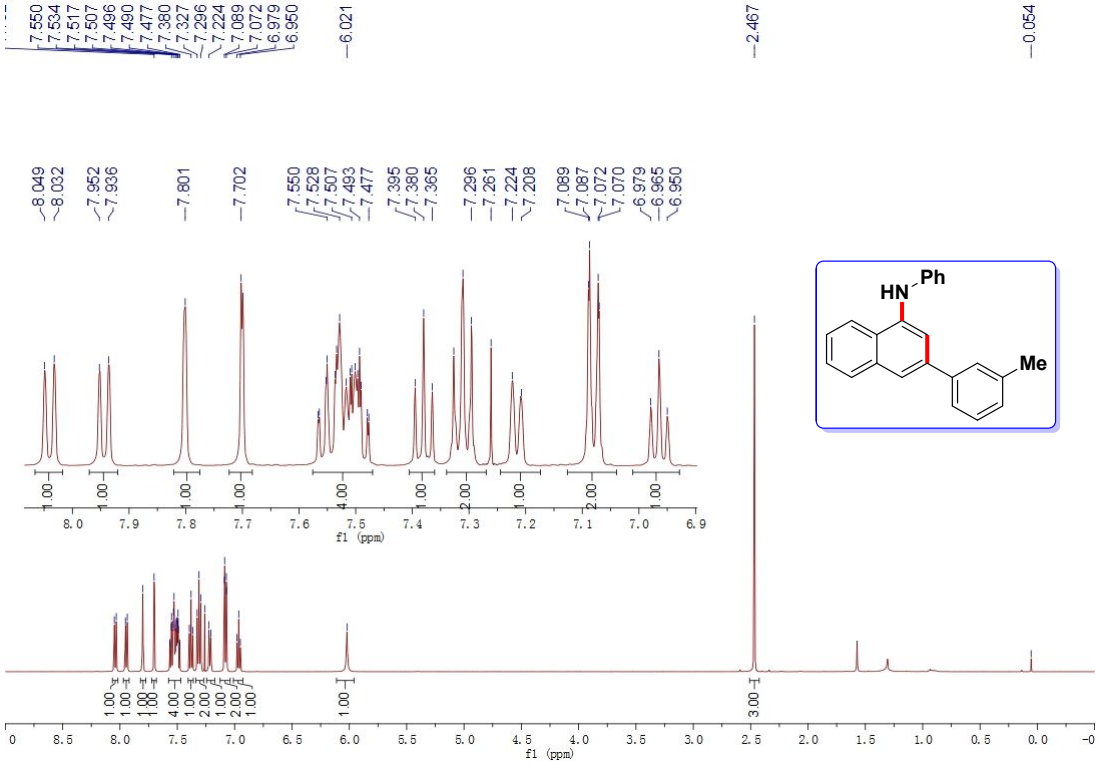


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

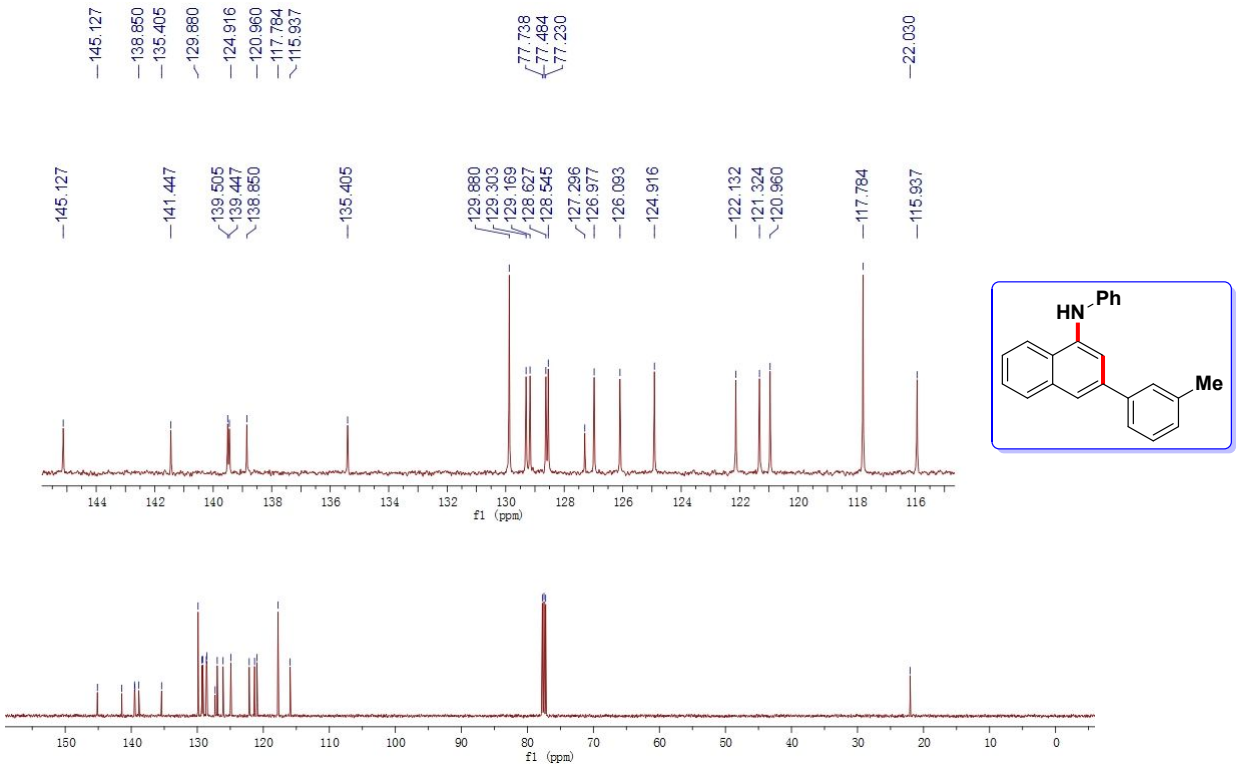


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3va

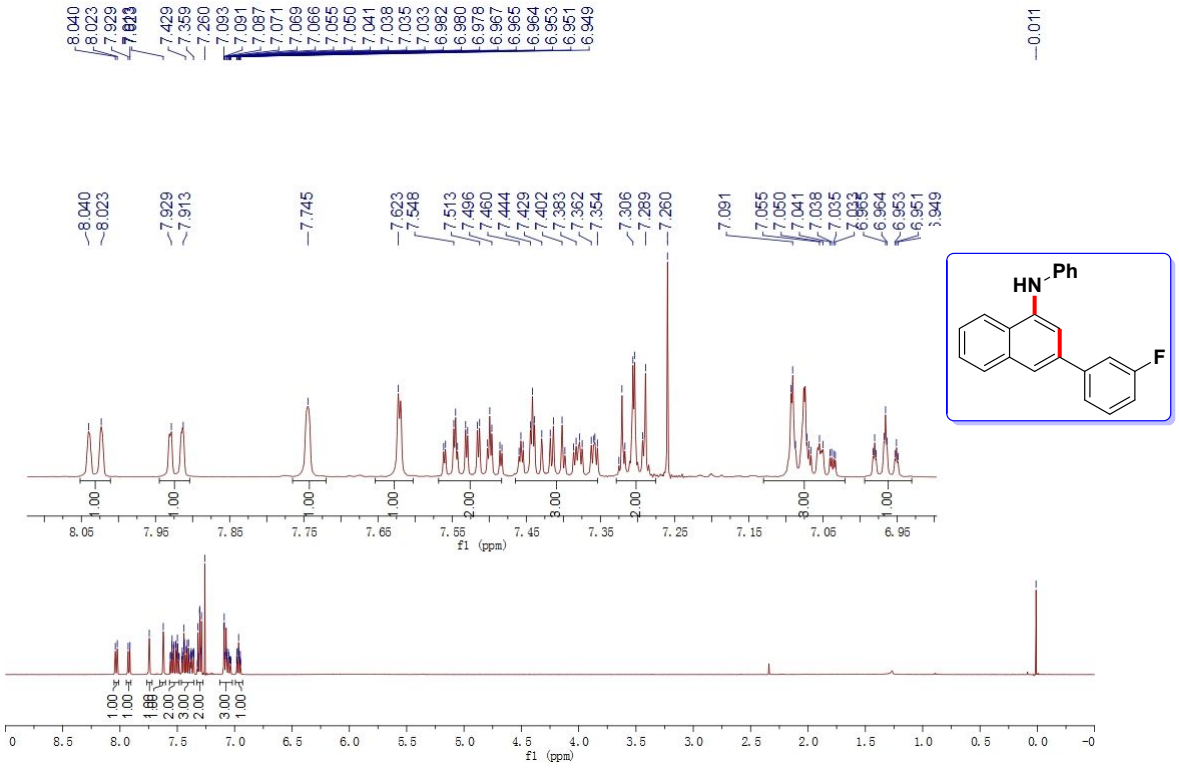


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

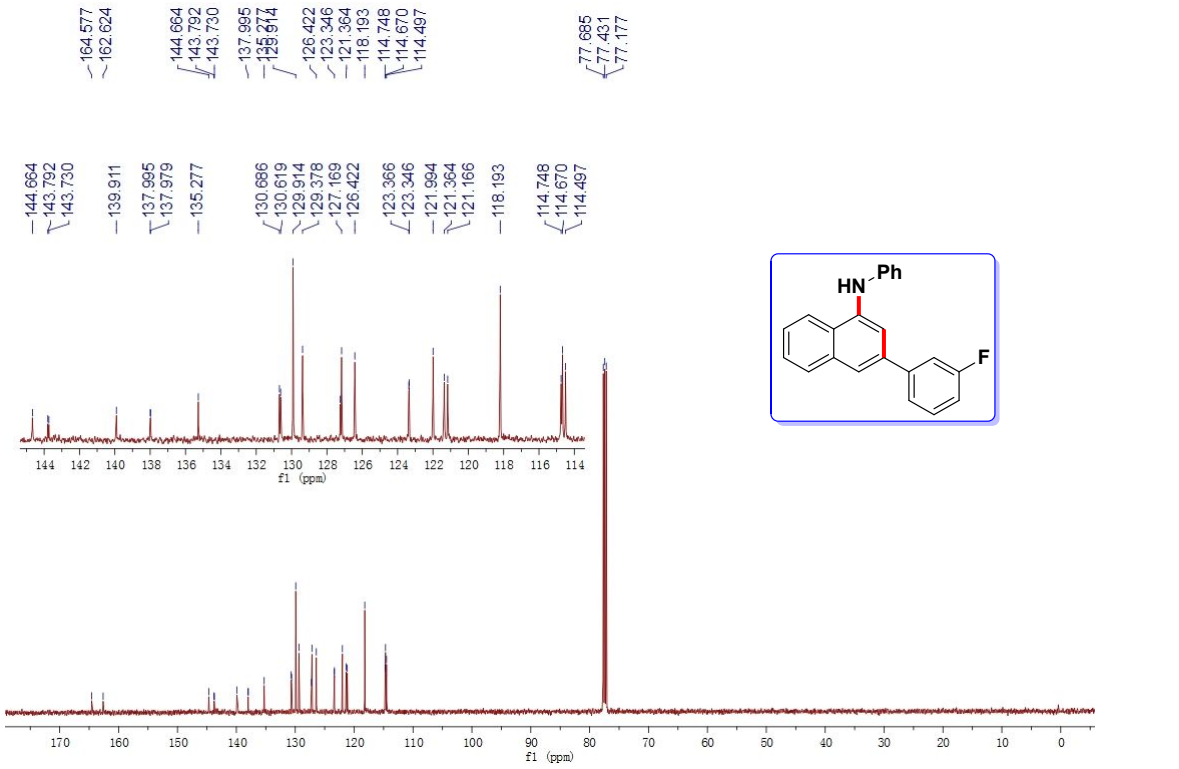


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3wa

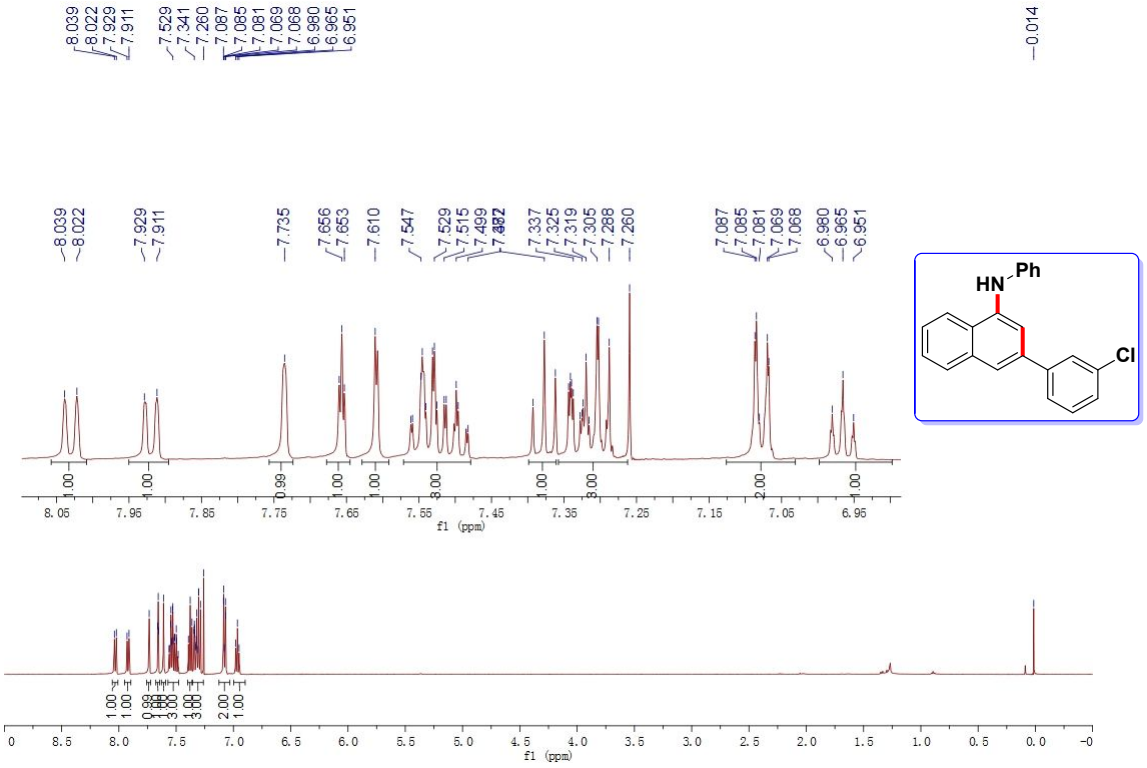


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

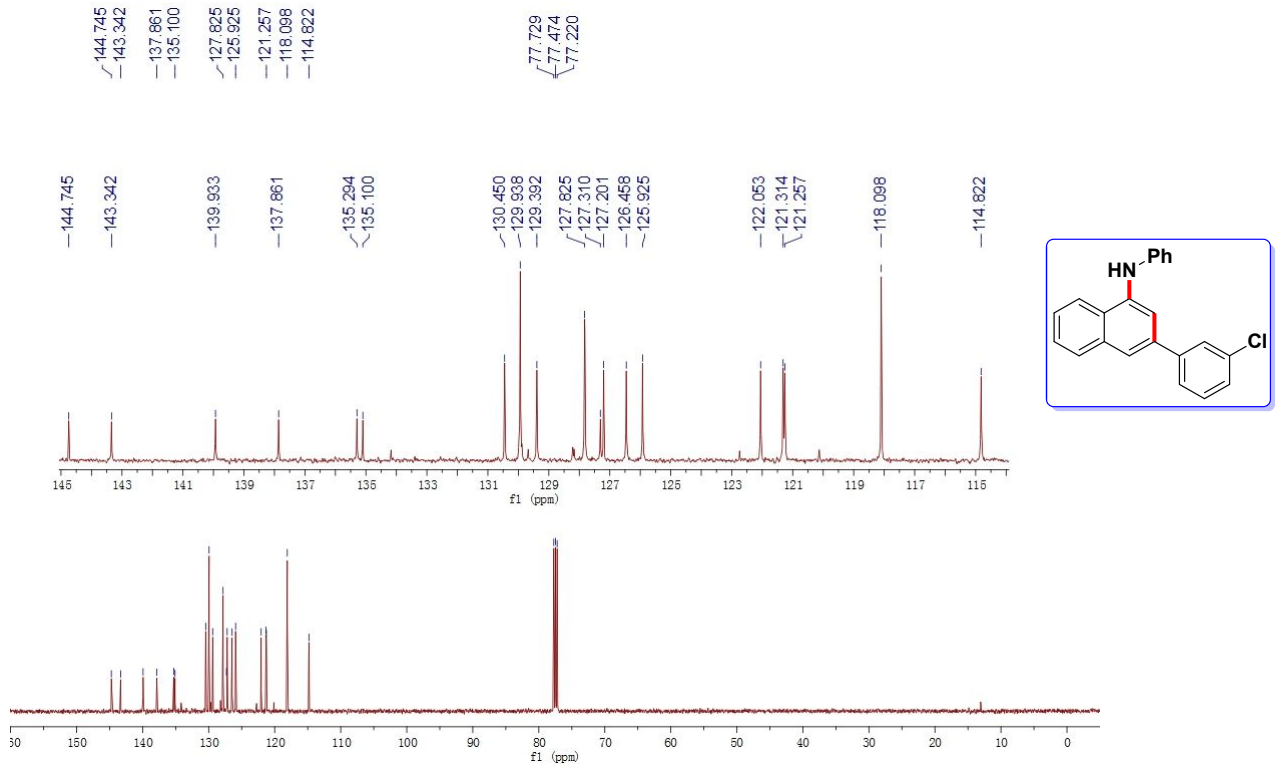


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3xa

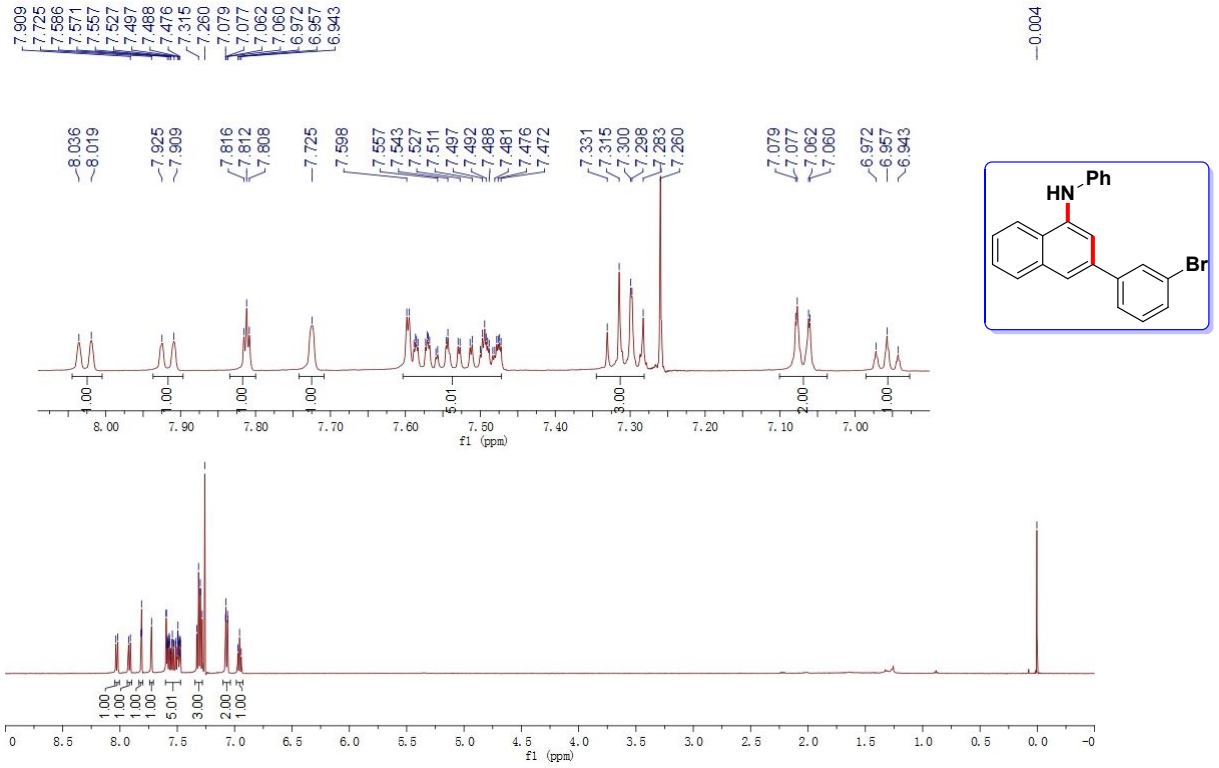


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

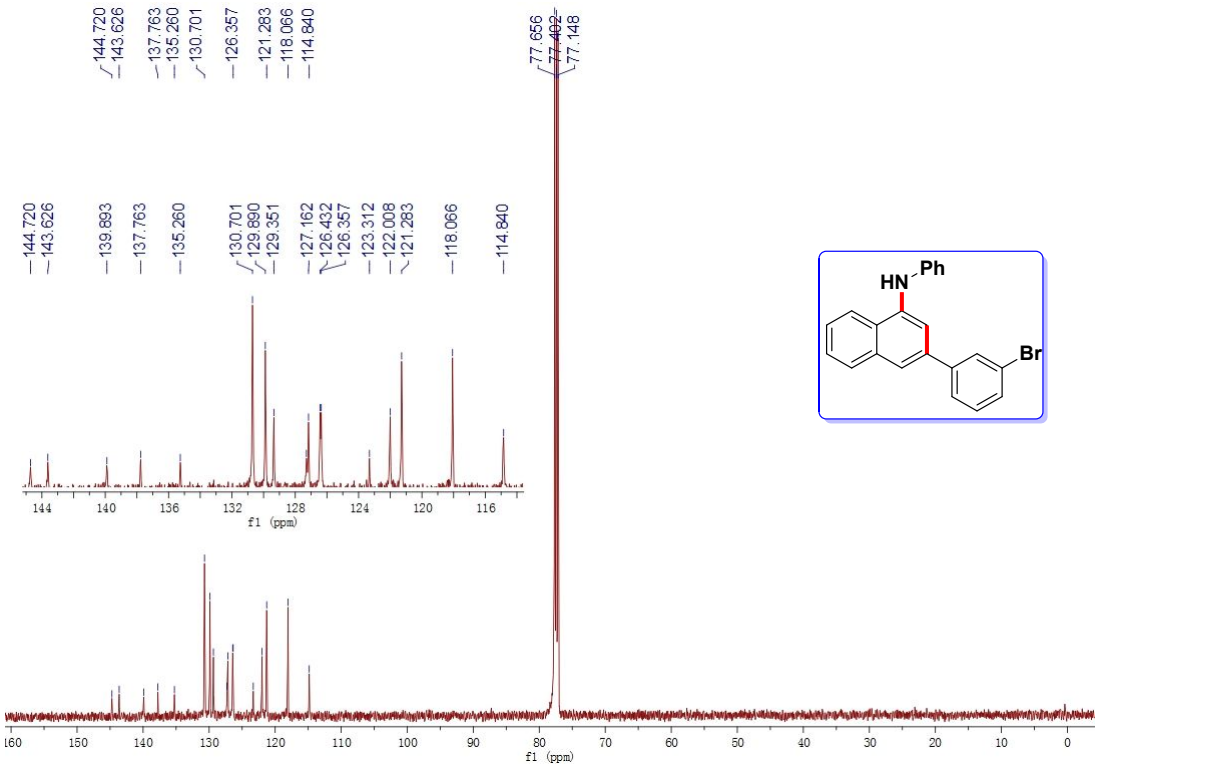


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3ya

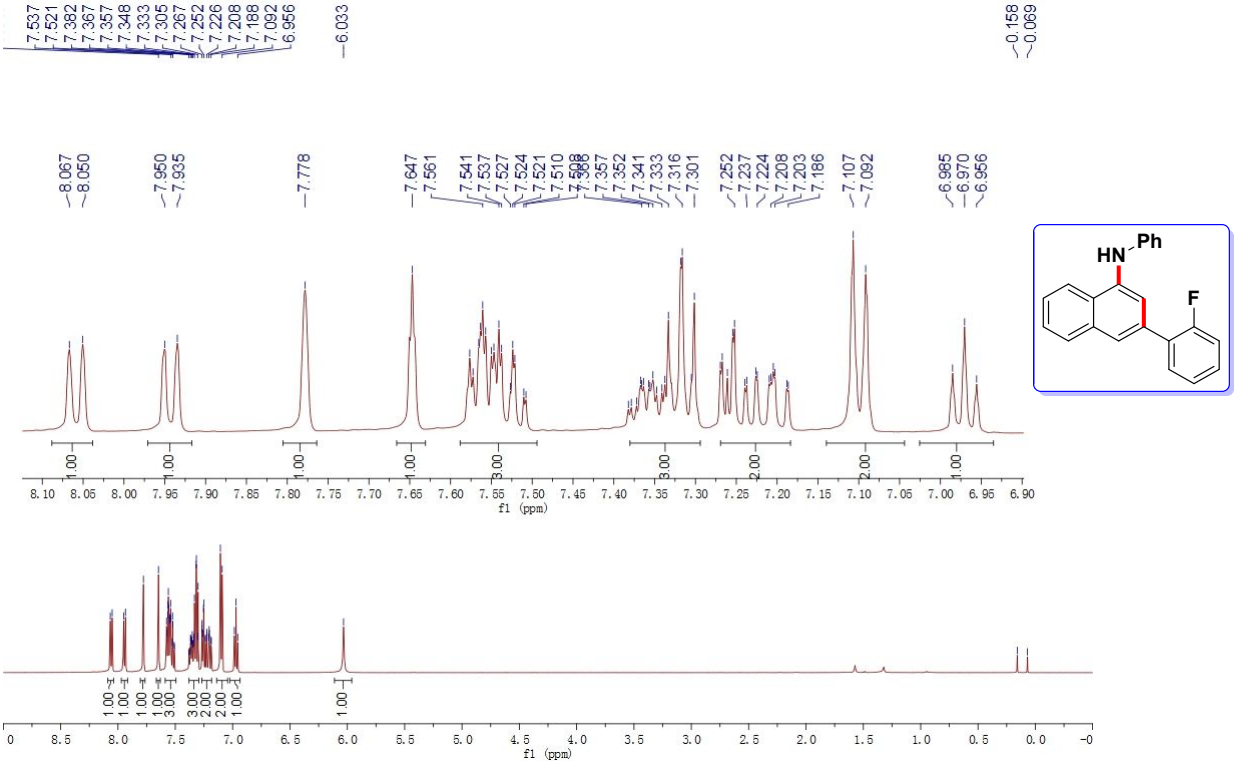


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

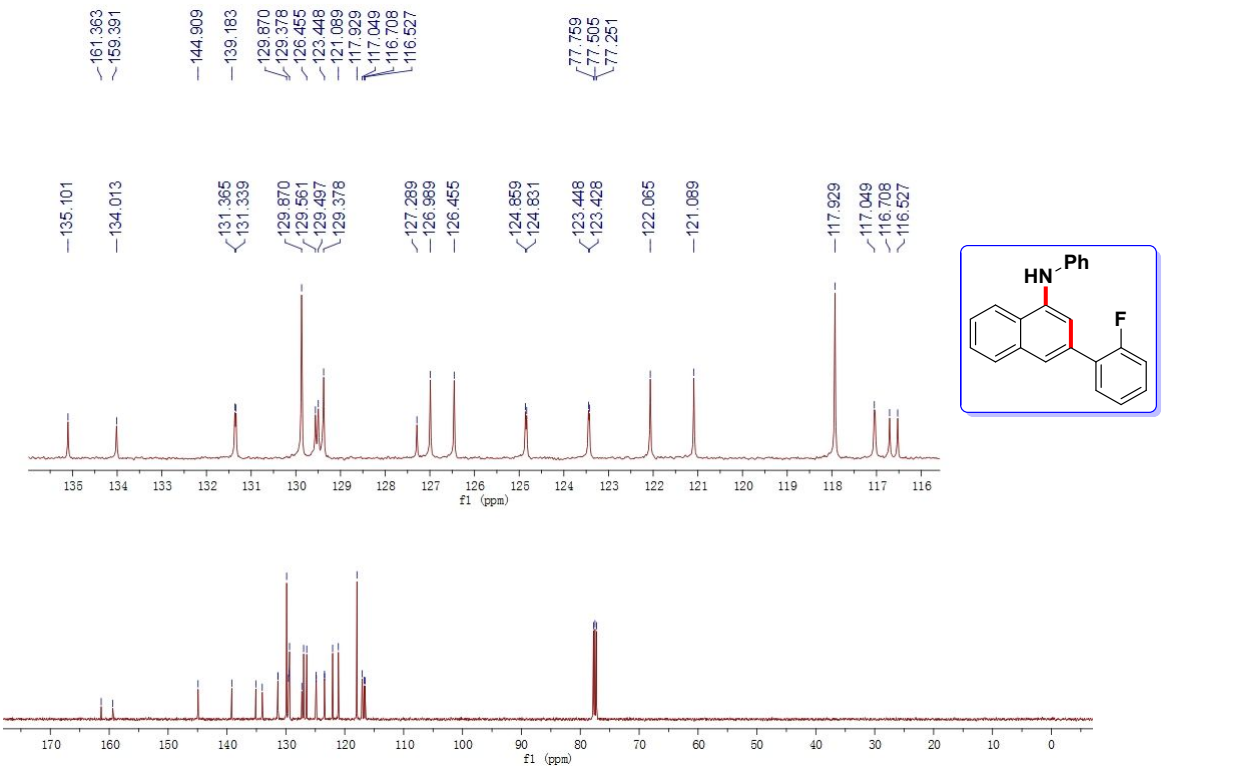


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3za

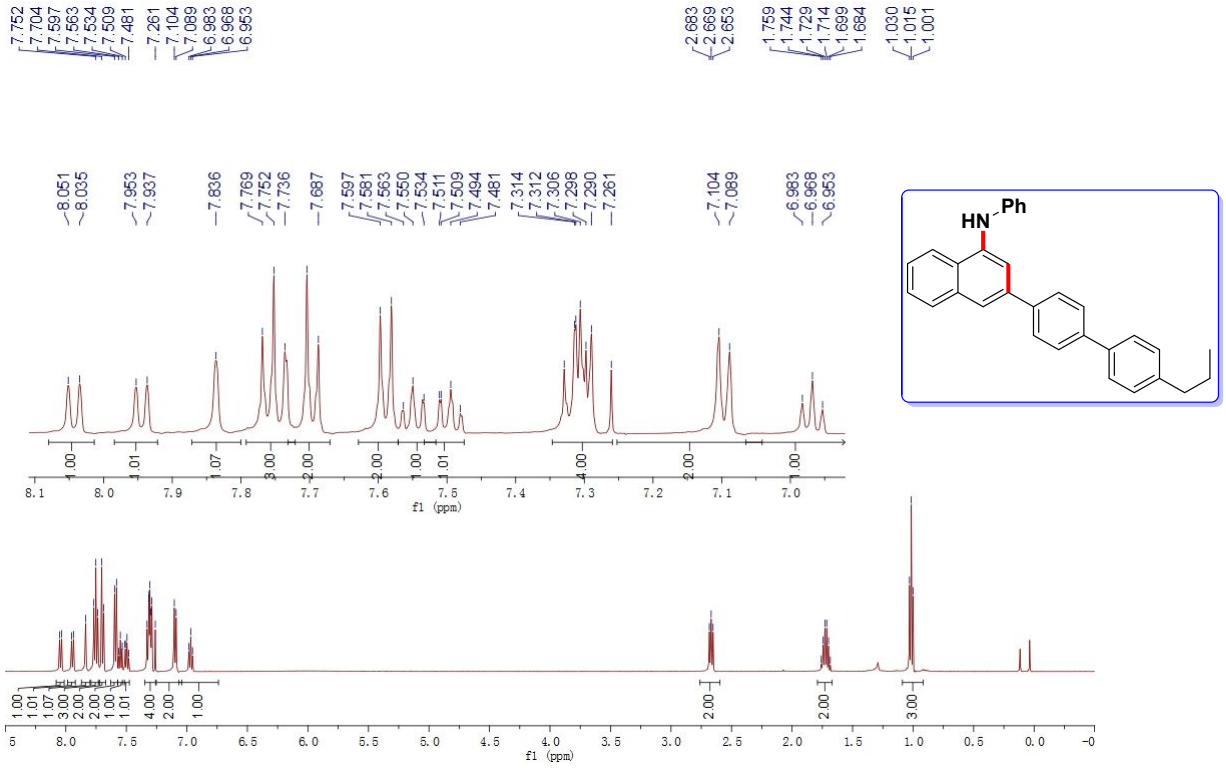


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

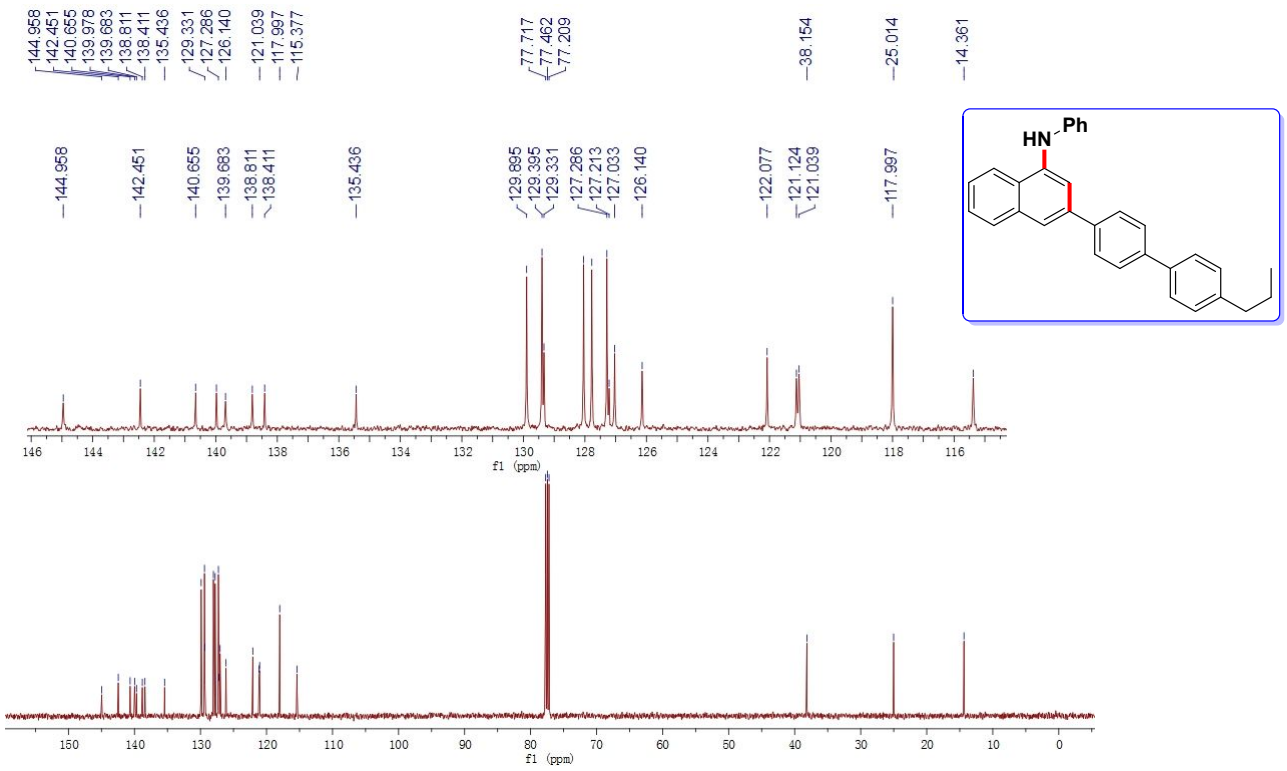


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3a′a

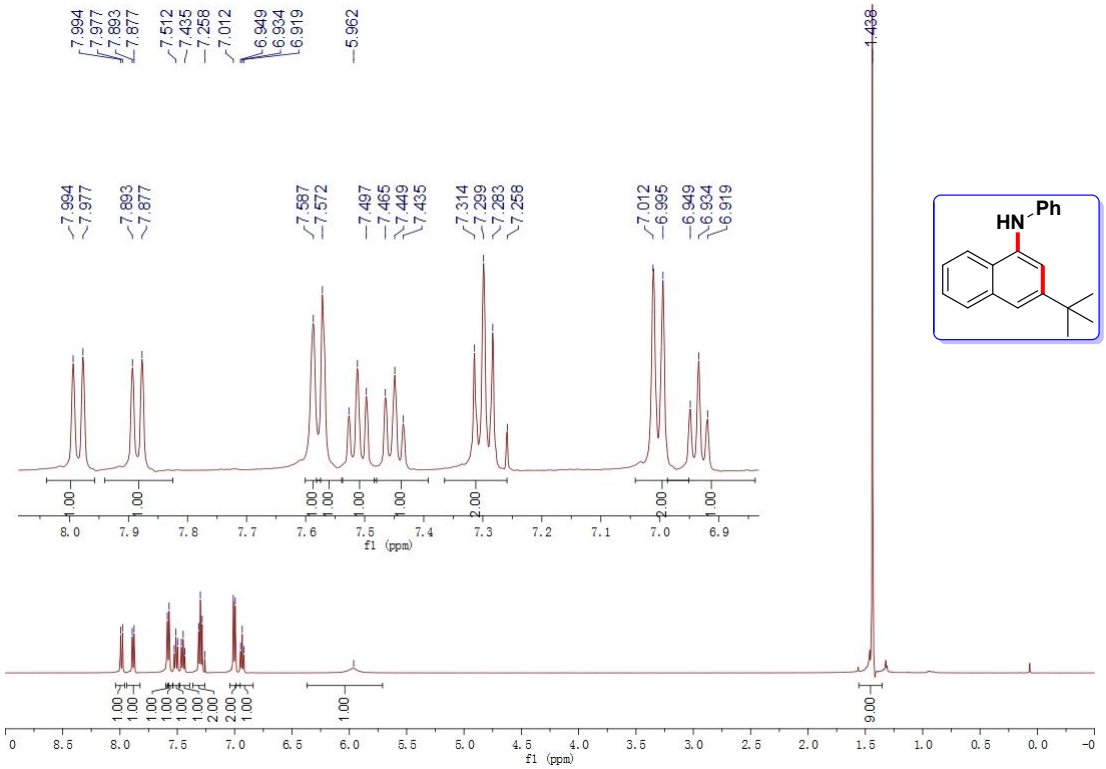


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

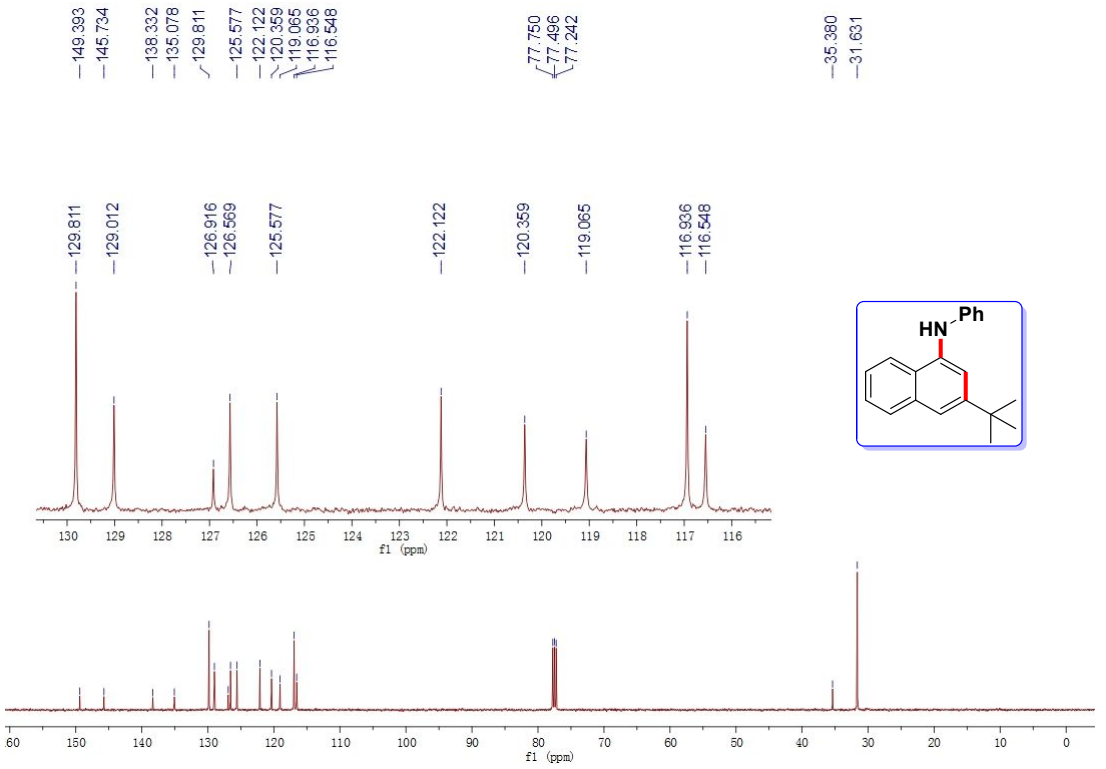


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3b′a

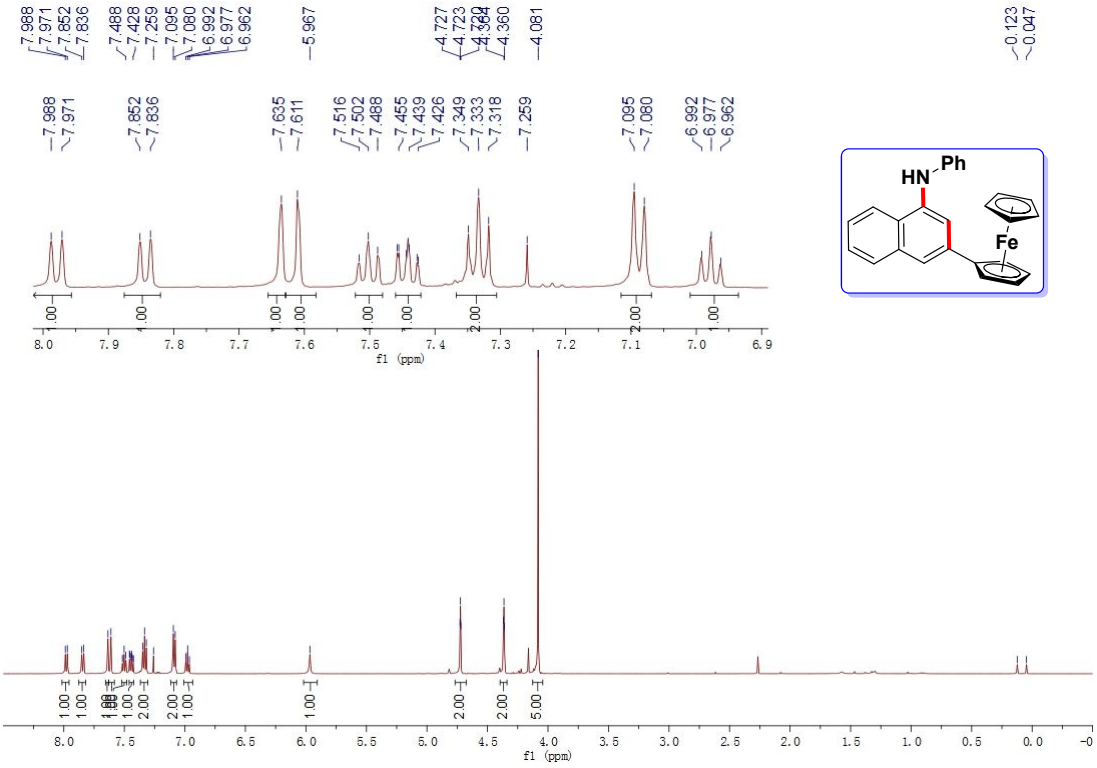


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

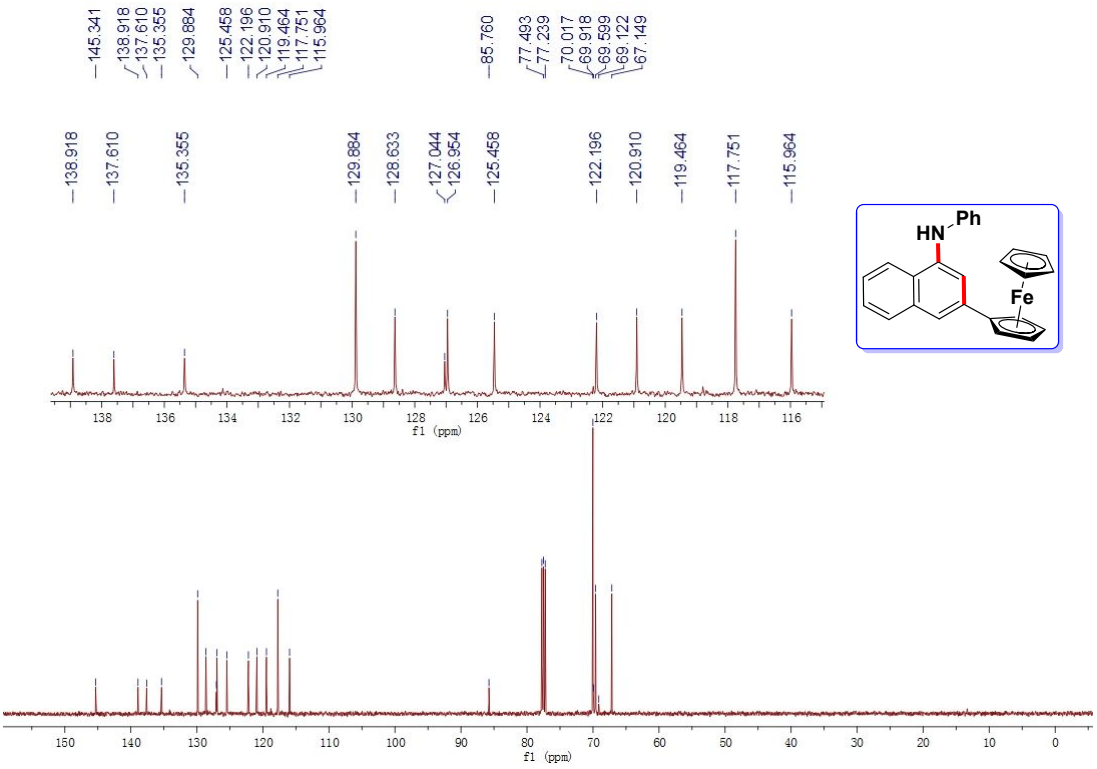


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3c′a

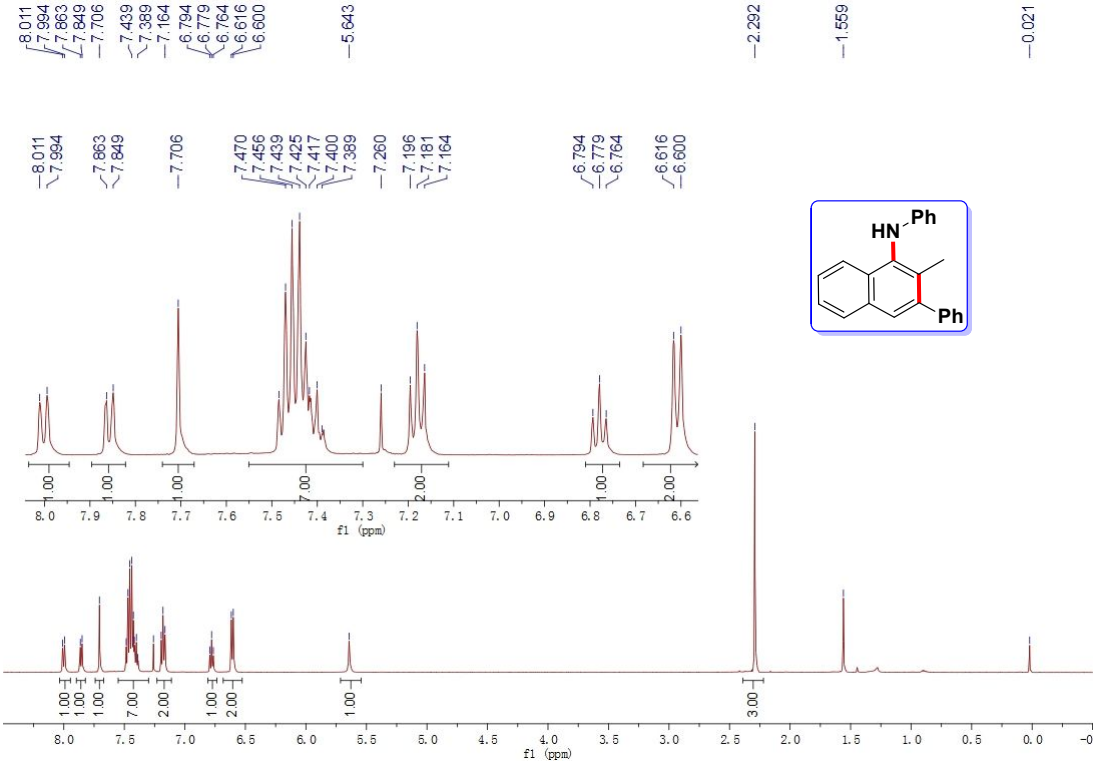


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

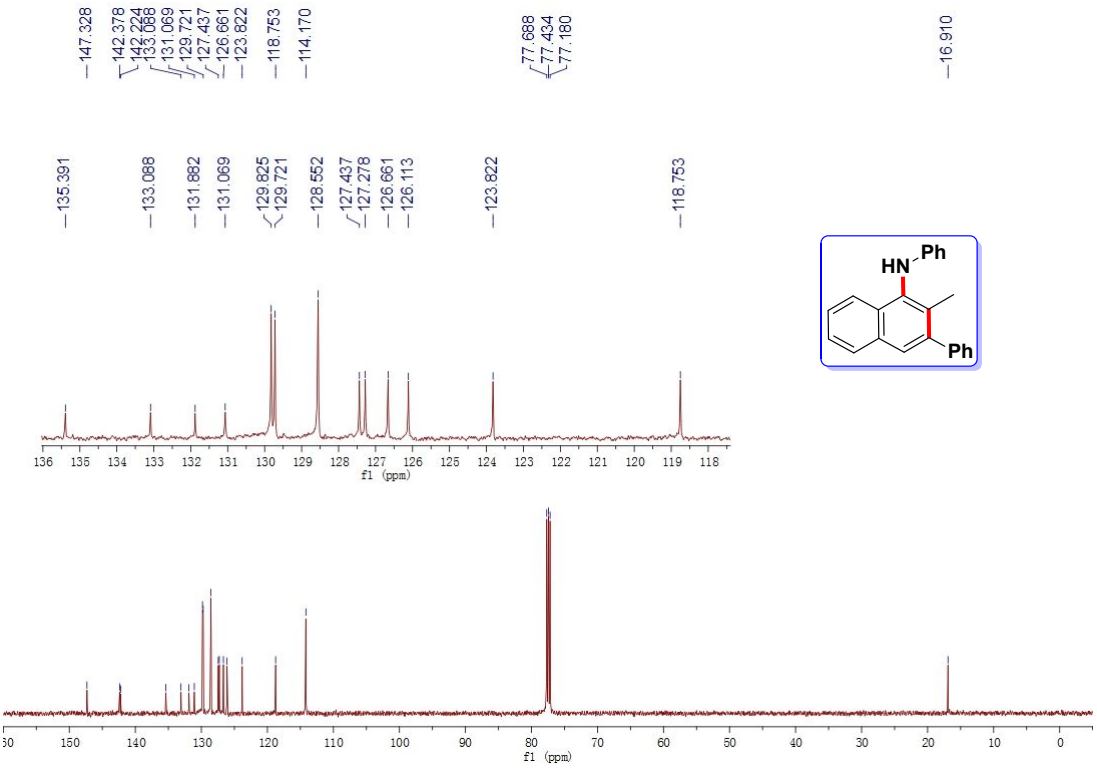


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3d′a

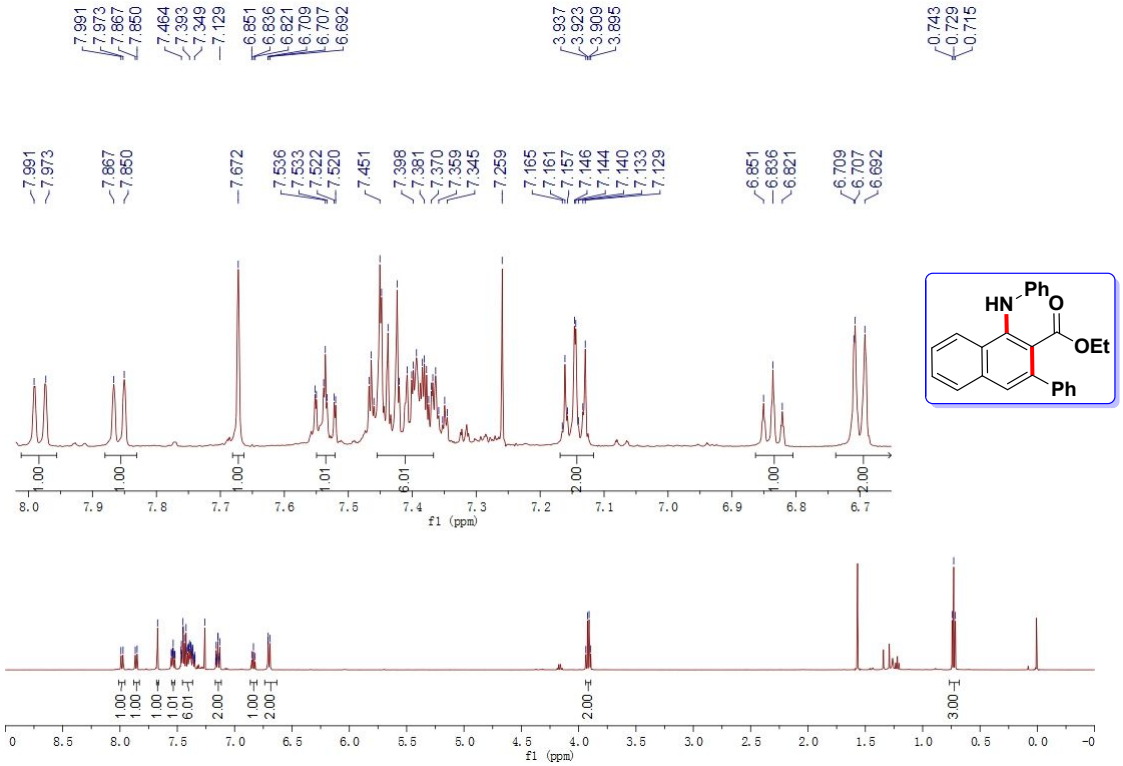


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

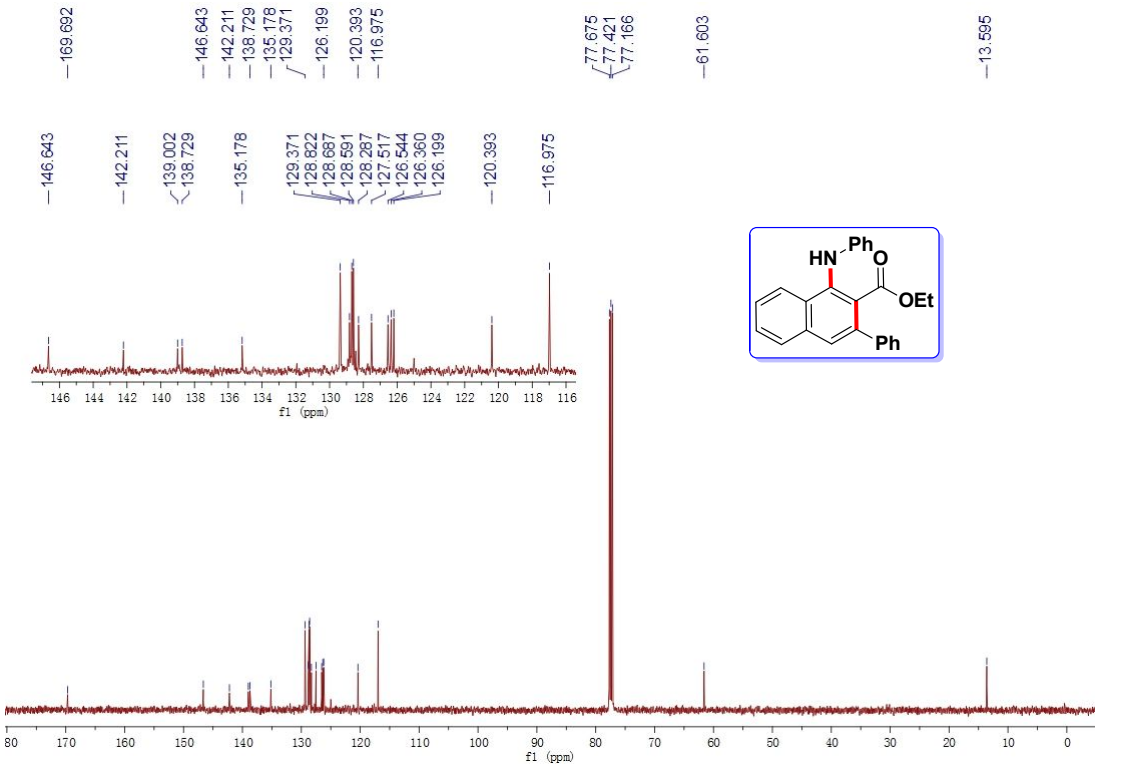


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3e′a

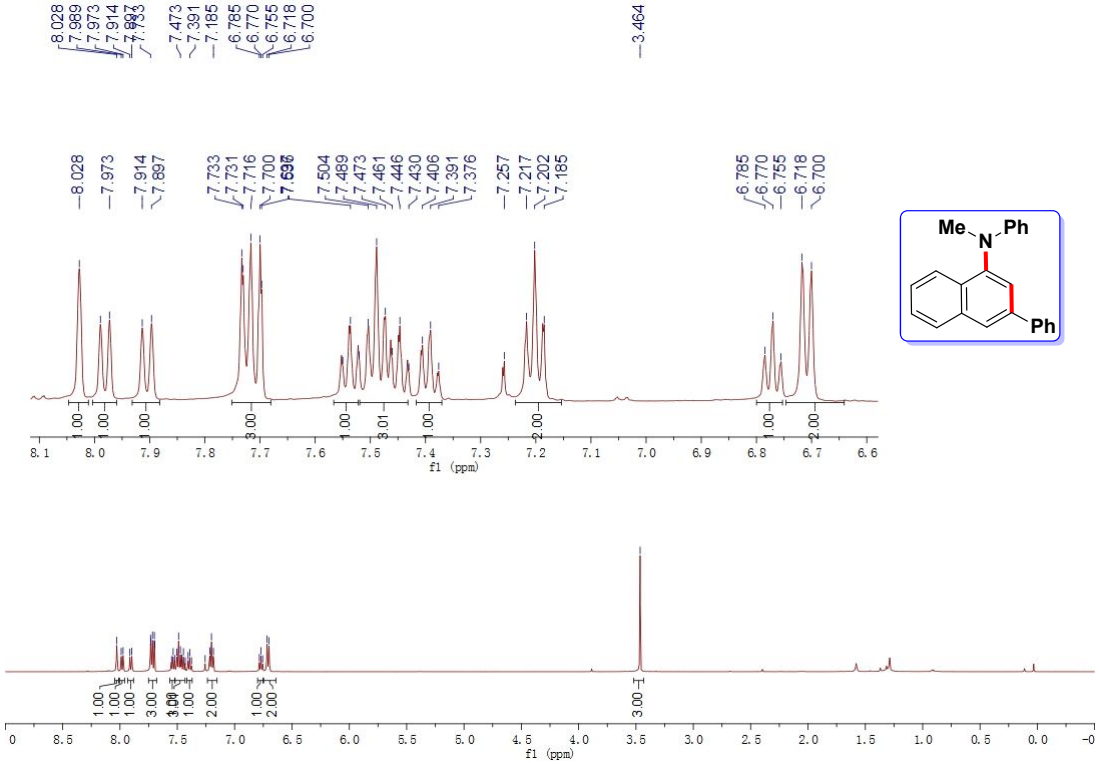


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

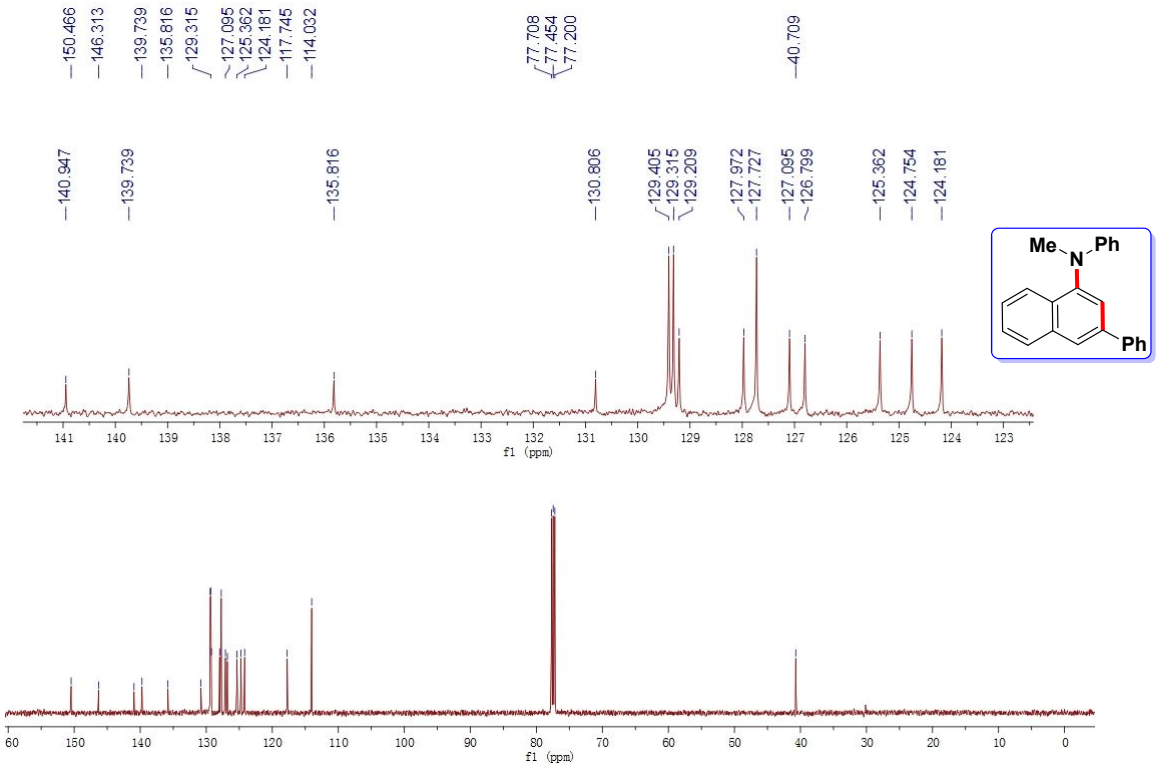


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 9aa

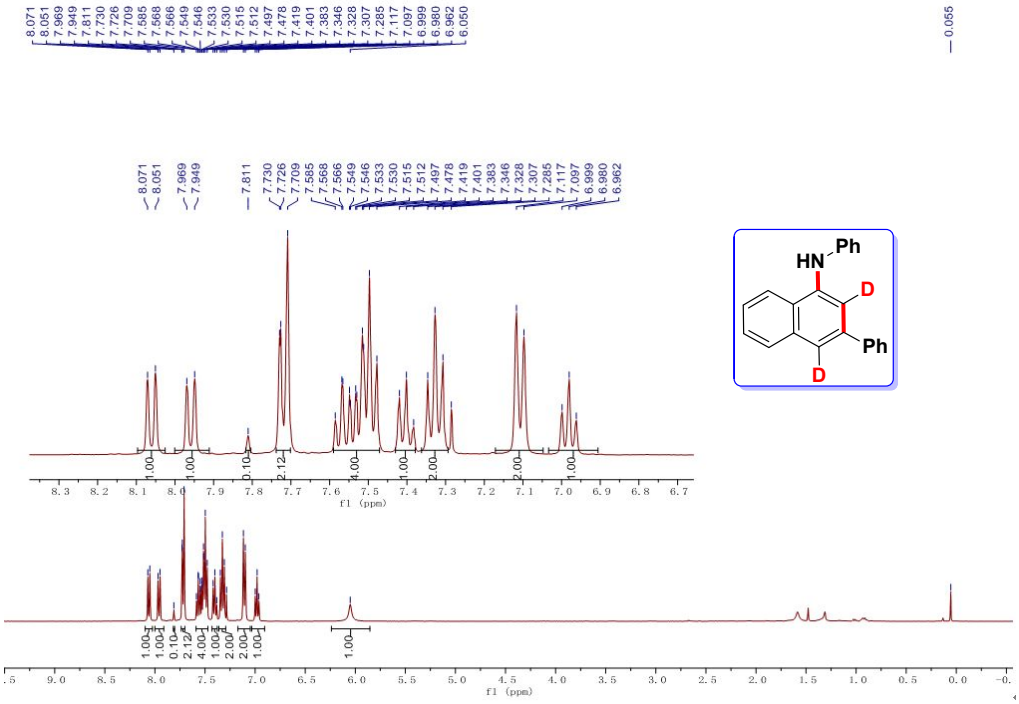


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)



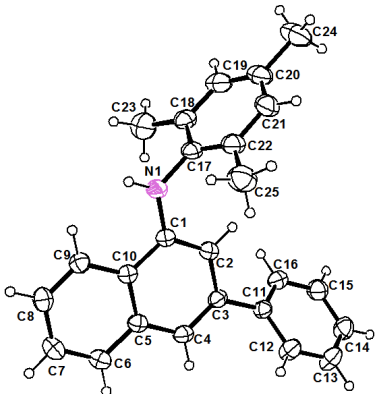
(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H NMR and ^{13}C NMR Spectra of Compound 3aa-d_2



(400 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

6. X-ray Crystallographic Structure of Compound 3aq



The purified compound **3aq** is dissolved in *n*-hexane, and placed in a dark cabinet to slowly evaporate. After several days, a colorless bulk crystal is obtained. The X-ray crystal-structure determinations were obtained on a Bruker Smart CCDC APEX-2 diffractometer (graphite-monochromated Mo *Kα* radiation, *λ*=0.71073 nm) at 293(2) K.

Figure S1. ORTEP drawing of compound **3aq**.
(The ellipsoid contour probability level in the caption of 30 %).

Table S1. Crystal data and structure refinement for **3aq**

Identification code	3aq	
Empirical formula	C25 H23 N	
Formula weight	337.44	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.3366(6) Å	α= 89.050(2)°.
	b = 11.7886(7) Å	β= 78.435(3)°.
	c = 17.7408(12) Å	γ = 83.961(2)°.
Volume	1902.4(2) $Å^3$	
Z	4	
Density (calculated)	1.178 Mg/m^3	
Absorption coefficient	0.068 mm^{-1}	
F(000)	720	
Crystal size	0.230 x 0.210 x 0.200 mm^3	
Theta range for data collection	2.911 to 27.556°.	
Index ranges	-12<=h<=12, -15<=k<=15, -23<=l<=23	
Reflections collected	73192	
Independent reflections	8692 [R(int) = 0.0271]	
Completeness to theta = 25.242°	99.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8692 / 0 / 475	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0573, wR2 = 0.1443	
R indices (all data)	R1 = 0.0743, wR2 = 0.1626	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.346 and -0.327 $e.Å^{-3}$	