Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Supporting Information

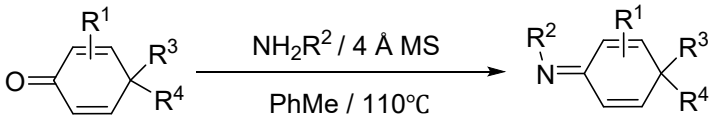
Contents

1. General Information

Unless otherwise stated, all reagents were commercially available and used without further purification. All reactions were performed in a double-necked flask. 400 MHz H-1 NMR and 101 MHz C-13 NMR spectra were measured on Agilent spectrometer, using $CDCl_3$, d6-DMSO as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature and chemical shifts are expressed in δ ppm. HRMS spectra were recorded by Agilent 6545. Flash column chromatographic purification of products was accomplished by forced-flow chromatography on silica gel (200-300 mesh) using petroleum ether/ethyl acetate as eluent.

2. Experimental Section

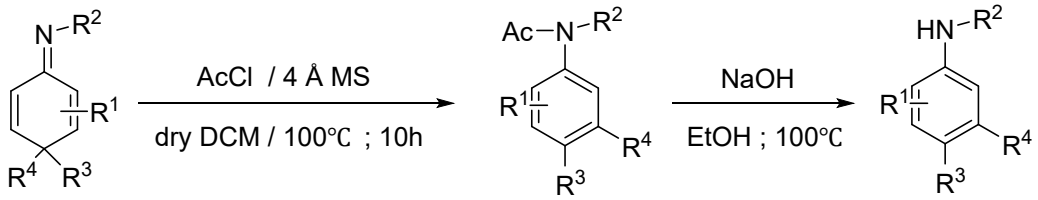
2.1 General procure for the prepration of the staring materials.



1

To a 25 mL-sealed tube was added 200 mg of 4 Å MS, substituted-cyclohexadienones (8.0 mmol), amines (9.6 mmol, 1.2 equiv.), and PhMe (6.0 mL), and the reaction was stirred for 24 h at 110 ℃.[1] After completion of the reaction, the reaction mixture was filtrated and concentrated under vacuum. The crude product was further purified through flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE/EA = 100/1-20/1, v/v) to afford target imines **1**.

2.2 General procedure for acid-promoted rearrangement of 2,5-cyclohexadienone imines and the corresponding hydrolysis.



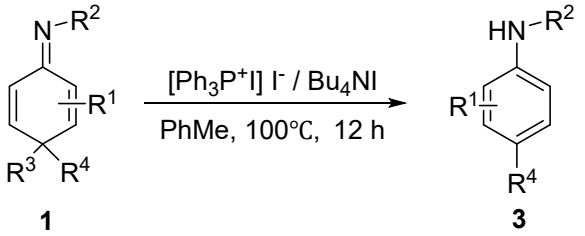
1 **2** **2'**

To a 25 mL-sealed tube was added 4 Å MS, substrate **1** (0.1 mmol), AcCl (8.0 equiv.), and dry DCM (1.0 mL), and the reaction was stirred for 10 h at 100 ℃. After completion of the reaction, the reaction mixture was poured into $NaHCO_3$ aqueous solution (5 mL) and extracted with ethyl acetate (5 mLx3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was further purified through flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE/EA = 25/1-6/1, v/v) to afford target

compounds **2**.

The collected compound **2** is transferred to the sealed tube, into which 2 mL ethanol and NaOH (3 equiv.), and the reaction was stirred for 2 h at 100 ℃.[2] After completion of the reaction, the reaction mixture was washed with water (6 mL) and extracted with ethyl acetate (5 mLx3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was further purified through flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE/EA = 500/1-100/1, v/v) to afford target compounds **2'**.

2.3 General procedure for demethylaromatization of 2,5-cyclohexadienone imines



1 **3**

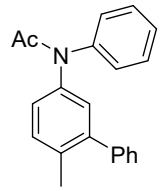
To a 25 mL-sealed tube was added substrate **1** (0.1 mmol), $Ph_3P \cdot I_2$ (0.15 mmol, 1.5 equiv. Was *in-situ* prepared via the reaction of triphenylphosphine with iodine), *n*-Bu_4NI (0.1 mmol, 1.0 equiv), and PhMe (1.0 mL), and the reaction was stirred for 12 h at 100 ℃. After completion of the reaction, the reaction mixture was poured into $Na_2S_2O_3$ aqueous solution (5 mL) and extracted with ethyl acetate (5 mLx3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was further purified through flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE/EA = 100/1-20/1, v/v) to afford target compounds **4**.

2.4 Spectra data of the products 2a~2q.

*It should be noted that, when **R^2** is an aryl group, the peaks of aryl carbon in C-13 NMR spectra of products **2** overlap, thus we did not write down the C-13 NMR*

*spectra data of **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2k**, **2l**, **2m**, **2n**, **2o**, **2p** and **2q**. This might be attributed to the presence of multiple resonance equations. However, when acetyl group of **2** was cleaved through hydrolysis, the peaks of aryl carbon in C-13 NMR spectra of the corresponding free amine products do not overlap again. Therefore, **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2k**, **2l**, **2m**, **2n**, **2o**, **2p** and **2q** were respectively hydrolyzed with NaOH in EtOH/H_2O to give the corresponding free amine products **2'**.*

N-(6-methyl-[1,1'-biphenyl]-3-yl)-N-phenylacetamide (2a)

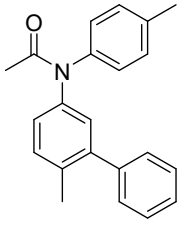


Isolated yield 88%.Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.33 (m, 5H), 7.33 – 7.28 (m, 5H), 7.26 (d, *J* = 6.9 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.16 (s, 1H), 2.27 (s, 3H), 2.11 (s, 3H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 302.1545, found: 302.1540.

N-(6-methyl-[1,1'-biphenyl]-3-yl)-N-(p-tolyl)acetamide (2b)

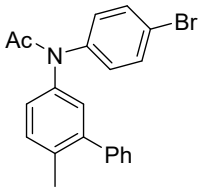


Isolated yield 86%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 19.2 Hz, 3H), 7.30 (t, *J* = 6.0 Hz, 3H), 7.17 (d, *J* = 15.4 Hz, 6H), 2.35 (s, 3H), 2.26 (s, 3H), 2.10 (s, 3H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 316.1701, found: 316.1695.

N-(4-bromophenyl)-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2c)

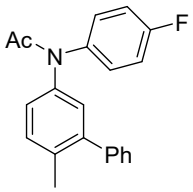


Isolated yeild 85%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.37 (m, 4H), 7.35 (d, *J* = 7.0 Hz, 1H), 7.28 (d, *J* = 6.7 Hz, 3H), 7.22 – 7.07 (m, 4H), 2.26 (d, *J* = 8.8 Hz, 3H), 2.10 (d, *J* = 8.4 Hz, 3H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 380.0650, found:380.0645 .

N-(4-fluorophenyl)-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2d)

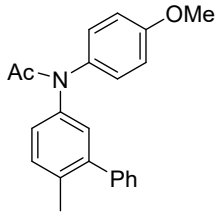


Isolated yield 80%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.34 (m, 3H), 7.26 (d, *J* = 6.9 Hz, 5H), 7.20 – 6.97 (m, 4H), 2.27 (d, *J* = 12.8 Hz, 3H), 2.09 (d, *J* = 17.2 Hz, 3H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 320.1451, found:320.1446 .

N-(4-methoxyphenyl)-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2e)

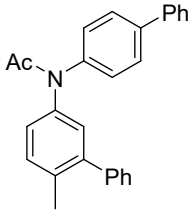


Isolated yield 77%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 19.7 Hz, 2H), 7.33 – 7.17 (m, 6H), 7.14 (s, 2H), 6.94 – 6.84 (m, 2H), 3.79 (s, 3H), 2.24 (s, 3H), 2.07 (s, 3H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 332.1651, found: 332.1645.

N-([1,1'-biphenyl]-4-yl)-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2f)

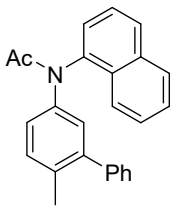


Isolated yield 61%. White solid, mp 143.1-143.3 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.5 Hz, 4H), 7.46 – 7.39 (m, 4H), 7.36 (d, *J* = 8.1 Hz, 4H), 7.31 (d, *J* = 7.6 Hz, 3H), 7.25 – 7.16 (m, 2H), 2.28 (s, 3H), 2.13 (s, 3H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 378.1858, found: 378.1853.

N-(6-methyl-[1,1'-biphenyl]-3-yl)-N-(naphthalen-1-yl)acetamide (2g)

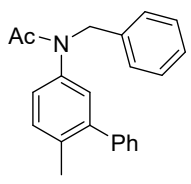


Isolated yield 62%. White solid, mp 57.4-57.2 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.89 (t, *J* = 10.2 Hz, 2H), 7.61 – 7.45 (m, 4H), 7.40 – 7.28 (m, 5H), 7.26 (d, *J* = 7.3 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 1H), 2.21 (s, 3H), 1.93 (s, 3H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 352.1701, found: 352.1695.

N-benzyl-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2h)



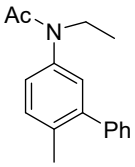
Isolated yield 73%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.30 – 7.14 (m, 8H), 6.94 – 6.81 (m, 2H), 4.91 (s, 2H), 2.26 (s, 3H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.44, 143.07, 140.70, 140.53, 137.67, 135.20, 131.44, 129.39, 129.00, 128.89, 128.36, 128.23, 127.32, 127.23, 126.74, 52.80, 22.77, 20.13.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 316.1701, found: 316.1695.

N-ethyl-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2i)



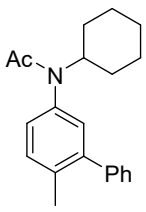
Isolated yield 30%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.03 (d, *J* = 6.6 Hz, 2H), 3.74 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 1.87 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.03, 143.28, 140.75, 140.63, 135.16, 131.48, 129.24, 129.01, 128.27, 127.27, 126.74, 43.85, 22.83, 20.09, 13.13.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 254.1545, found:254.1539 .

N-cyclohexyl-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2j)



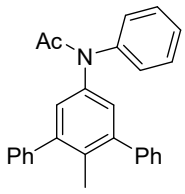
Isolated yield 40%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (td, *J* = 7.2, 1.4 Hz, 2H), 7.37 – 7.32 (m, 1H), 7.31 – 7.28 (m, 2H), 7.26 (d, *J* = 8.5 Hz, 1H), 6.97 – 6.92 (m, 2H), 4.64 – 4.48 (m, 1H), 2.29 (s, 3H), 1.80 (s, 2H), 1.77 (d, *J* = 1.4 Hz, 3H), 1.70 (d, *J* = 13.3 Hz, 2H), 1.54 (d, *J* = 12.2 Hz, 1H), 1.37 (q, *J* = 13.4 Hz, 2H), 1.06 (q, *J* = 11.1 Hz, 2H), 0.97 – 0.83 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.05, 142.75, 140.76, 137.37, 135.44, 131.20, 131.03, 129.08, 128.75, 128.26, 127.24, 53.58, 31.61, 25.74, 25.35, 23.59, 20.17.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 308.2014, found: 308.2009.

N-(2'-methyl-[1,1':3',1''-terphenyl]-5'-yl)-N-phenylacetamide (2k)

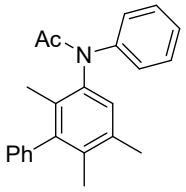


Isolated yield 91%. White solid, mp 136.6-136.9 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 5H), 7.37 (d, *J* = 7.5 Hz, 10H), 7.21 (s, 2H), 2.13 (s, 6H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 378.1858, found: 378.1853.

N-phenyl-N-(2,5,6-trimethyl-[1,1'-biphenyl]-3-yl)acetamide (2l)

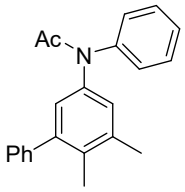


Isolated yield 55%. White solid, mp 171.4-171.6 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 14.5, 7.2 Hz, 2H), 7.34 (q, *J* = 9.3, 7.6 Hz, 5H), 7.19 – 6.97 (m, 4H), 2.28 (s, 3H), 2.04 (s, 3H), 1.92 (d, *J* = 22.0 Hz, 6H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 330.1858, found: 330.1852.

N-(5,6-dimethyl-[1,1'-biphenyl]-3-yl)-N-phenylacetamide (2m)

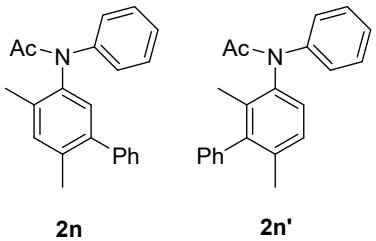


Isolated yield 61%. White solid, mp 125.3-125.7 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 3H), 7.36 – 7.30 (m, 5H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.12 (s, 1H), 7.02 (s, 1H), 2.33 (s, 3H), 2.15 (s, 3H), 2.10 (s, 3H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 316.1701, found: 316.1695.

N-(4,6-dimethyl-[1,1'-biphenyl]-3-yl)-N-phenylacetamide (2n) and N-(2,6-dimethyl-[1,1'-biphenyl]-3-yl)-N-phenylacetamide (2n')

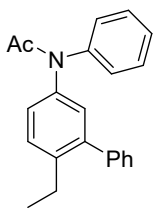


Isolated yield 58%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dt, *J* = 14.3, 7.4 Hz, 2H), 7.32 (d, 7H), 7.20 – 7.05 (m, 3H), 2.25 (d, *J* = 19.6 Hz, 3H), 1.97 (d, *J* = 52.3 Hz, 6H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 316.1701, found: 316.1695.

N-(6-ethyl-[1,1'-biphenyl]-3-yl)-N-phenylacetamide (2o)

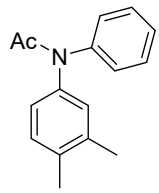


Isolated yield 87%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, *J* = 7.4 Hz, 7H), 7.31 – 7.25 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 10.3 Hz, 1H), 2.58 (q, *J* = 7.6 Hz, 2H), 2.11 (s, 3H), 1.06 (t, *J* = 7.5 Hz, 3H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 316.1701, found: 316.1695.

N-(3,4-dimethylphenyl)-N-phenylacetamide (2p)

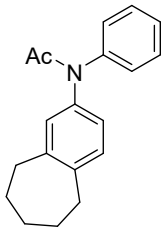


Isolated yield 90%. White solid, mp 96.2-96.5 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 4H), 7.23 – 7.08 (m, 2H), 7.06 (s, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 2.22 (s, 6H), 2.05 (s, 3H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 240.1388, found: 240.1394.

N-phenyl-N-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-2-yl)acetamide (2q)



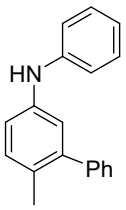
Isolated yield 80%. White solid, mp 104.7-105.0 ℃..

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 2H), 7.27 (dd, *J* = 7.1, 1.5 Hz, 2H), 7.18 (s, 1H), 7.07 (d, *J* = 10.7 Hz, 1H), 7.00 – 6.93 (m, 2H), 2.74 (t, *J* = 10.4 Hz, 4H), 2.04 (s, 3H), 1.81 (t, *J* = 6.0 Hz, 2H), 1.61 (d, *J* = 5.8 Hz, 4H).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 280.1701, found: 280.1722.

2.5 Spectral data of the products 2a'~2q'.

6-methyl-N-phenyl-[1,1'-biphenyl]-3-amine (2a')



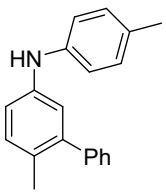
Isolated yield 91%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.4 Hz, 2H), 7.47 (d, *J* = 7.1 Hz, 3H), 7.37 (t, *J* = 7.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.09 (m, 4H), 7.02 (t, *J* = 7.4 Hz, 1H), 5.69 (s, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.76, 142.96, 142.06, 140.87, 131.33, 129.51, 129.26, 128.25, 126.99, 120.68, 120.07, 118.12, 117.52, 117.39, 19.86.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 260.1439, found: 260.1434.

6-methyl-N-(p-tolyl)-[1,1'-biphenyl]-3-amine (2b')



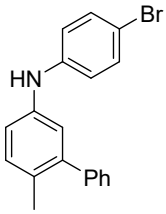
Isolated yield 91%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.10 – 7.00 (m, 4H), 5.46 (s, 1H), 2.38 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.86, 142.12, 141.66, 140.88, 131.23, 130.49, 129.96, 129.21, 128.15, 127.49, 126.88, 119.04, 118.43, 116.51, 20.76, 19.75.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 274.1596, found: 274.1590.

N-(4-bromophenyl)-6-methyl-[1,1'-biphenyl]-3-amine (2c')



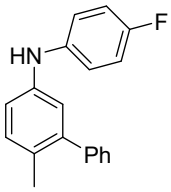
Isolated yield 90%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.3 Hz, 2H), 7.42 – 7.34 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.05 – 6.98 (m, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.60 (s, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.00, 142.95, 141.76, 140.08, 132.21, 131.36, 129.13, 128.96, 128.22, 127.02, 120.45, 118.54, 117.90, 112.15, 19.83.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 338.0544, found: 338.0539.

N-(4-fluorophenyl)-6-methyl-[1,1'-biphenyl]-3-amine (2d')



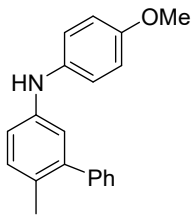
Isolated yield 88%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 6.8 Hz, 3H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.11 – 6.96 (m, 6H), 5.31 (s, 1H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.83 (d, J_{F-C} = 238.0 Hz), 142.97, 141.98, 141.61, 139.54 (d, J_{F-C} = 2.2 Hz), 131.33, 129.16, 128.20, 127.86, 126.96, 119.89 (d, J_{F-C} = 7.7 Hz), 119.02, 116.46, 115.98 (d, J_{F-C} = 22.3 Hz), 19.74.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 278.1345, found: 278.1340.

N-(4-methoxyphenyl)-6-methyl-[1,1'-biphenyl]-3-amine (2e')



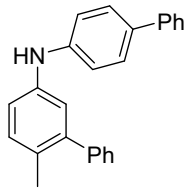
Isolated yield 88%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.37 – 7.32 (m, 3H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 4H), 5.37 (s, 1H), 3.80 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.98, 142.77, 142.13, 136.28, 131.15, 129.46, 129.12, 128.05, 126.77, 126.65, 121.56, 117.67, 115.18, 114.73, 55.60, 19.59.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 290.1545, found: 290.1539.

N-([1,1'-biphenyl]-4-yl)-6-methyl-[1,1'-biphenyl]-3-amine (2f')



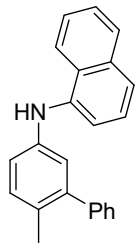
Isolated yield 85%. White solid, mp 85.6-85.9 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.43 (dd, *J* = 6.1 Hz, 4H), 7.37 (t, *J* = 6.6 Hz, 3H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.10 – 7.04 (m, 2H), 4.79 (s, 1H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.00, 142.91, 141.85, 140.90, 140.42, 133.35, 131.25, 129.12, 128.74, 128.52, 128.12, 128.01, 126.89, 126.54, 126.52, 120.17, 117.66, 117.32, 19.75.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 336.1752, found: 336.1747.

N-(6-methyl-[1,1'-biphenyl]-3-yl)naphthalen-1-amine (2g')



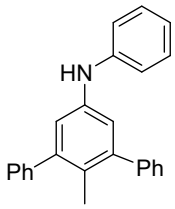
Isolated yield 74%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 7.1 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.52 (t, *J* = 5.0 Hz, 2H), 7.46 – 7.33 (m, 7H), 7.21 (d, *J* = 8.9 Hz, 1H), 6.98 (d, *J* = 6.6 Hz, 2H), 5.89 (s, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.85, 142.21, 141.95, 139.22, 134.71, 131.22, 129.44, 129.13, 128.58, 128.07, 127.76, 127.29, 126.82, 126.10, 125.59, 122.40, 121.62, 119.55, 117.01, 114.78, 19.70.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 310.1596, found: 310.1590.

2'-methyl-N-phenyl-[1,1':3',1''-terphenyl]-5'-amine (2k')



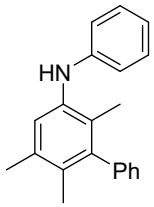
Isolated yield 98%. White solid, mp 105.6-105.9 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 7H), 7.43 – 7.37 (m, 3H), 7.30 (t, *J* = 7.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.06 (s, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 5.74 (s, 1H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.93, 143.29, 142.49, 140.29, 129.44, 129.35, 128.15, 126.92, 125.72, 120.87, 118.72, 117.70, 18.02.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 336.1752, found: 336.1747.

2,5,6-trimethyl-N-phenyl-[1,1'-biphenyl]-3-amine (2l')



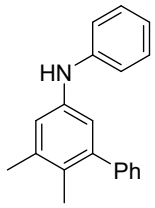
Isolated yield 70%. White solid, mp 118.4-118.7 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.16 (s, 1H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.89 (t, *J* = 7.3 Hz, 1H), 5.35 (s, 1H), 2.31 (s, 3H), 1.96 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.19, 143.29, 142.10, 138.18, 134.63, 129.51, 129.32, 129.01, 128.41, 126.56, 126.03, 121.74, 119.56, 116.33, 20.52, 17.11, 15.55.

HRMS (ESI-TOF) m/z Calcd for C18$H_{15}N$ $[M+H]^+$: 288.1752, found: 288.1747.

5,6-dimethyl-N-phenyl-[1,1'-biphenyl]-3-amine (2m')



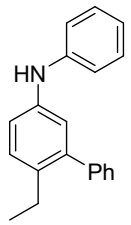
Isolated yield 88%. White solid, mp 117.1-117.5 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 3H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.99 (s, 1H), 6.96 – 6.89 (m, 2H), 5.47 (s, 1H), 2.36 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.69, 143.22, 142.57, 140.09, 138.33, 129.36, 128.04, 127.02, 126.73, 120.51, 119.15, 117.69, 117.35, 117.15, 20.96, 16.35.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 274.1596, found: 274.1590.

6-ethyl-N-phenyl-[1,1'-biphenyl]-3-amine (2o')



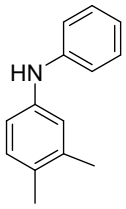
Isolated yield 97%. Colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.4 Hz, 2H), 7.42 – 7.32 (m, 5H), 7.18 (t, *J* = 7.0 Hz, 3H), 7.08 (s, 1H), 7.03 (d, *J* = 5.5 Hz, 1H), 7.00 (t, *J* = 5.5 Hz, 1H), 5.44 (s, 1H), 2.65 (q, *J* = 7.5 Hz, 2H), 1.17 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.27, 142.84, 142.43, 141.90, 134.69, 131.03, 129.53, 129.44, 128.09, 126.53, 120.95, 117.90, 117.87, 115.09, 26.35, 15.70.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 274.1596, found: 274.1590.

3,4-dimethyl-N-phenylaniline (2p')



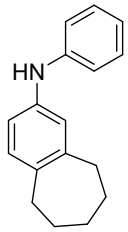
Isolated yield 96%. White solid, mp 54.3-54.6 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.8 Hz, 2H), 7.06 (dd, *J* = 11.6, 8.0 Hz, 3H), 6.96 – 6.88 (m, 3H), 5.60 (s, 1H), 2.27 (d, *J* = 3.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.03, 140.61, 137.57, 130.37, 129.74, 129.32, 120.42, 120.28, 116.97, 116.34, 19.98, 19.02.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 198.1283, found: 198.1277.

N-phenyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-2-amine (2q')



Isolated yield 96%. White solid, mp 101.1-101.3 ℃.

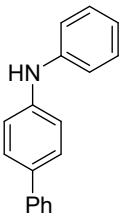
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.6 Hz, 2H), 7.16 – 7.09 (m, 3H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 2H), 5.50 (s, 1H), 2.85 (t, *J* = 10.1 Hz, 4H), 1.95 (p, *J* = 6.0 Hz, 2H), 1.77 (p, *J* = 5.4 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.65, 143.98, 140.83, 136.74, 129.98, 129.41, 120.40, 119.69, 117.25, 115.76, 37.02, 36.14, 32.88, 28.84, 28.57.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 238.1569, found: 238.1590.

2.6 Spectral data of the products 3a~3r.

N-phenyl-[1,1'-biphenyl]-4-amine (3a)



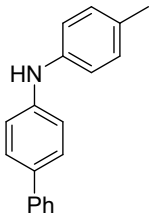
Isolated yield 78%. White solid, mp 110.2-110.4 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.9 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.39 – 7.31 (m, 3H), 7.19 – 7.14 (m, 4H), 7.02 (t, J = 7.3 Hz, 1H), 5.78 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.89, 142.60, 140.88, 133.74, 129.45, 128.80, 128.01, 126.65, 126.57, 121.27, 118.14, 117.84.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 246.1283, found: 246.1270.

N-(p-tolyl)-[1,1'-biphenyl]-4-amine (3b)



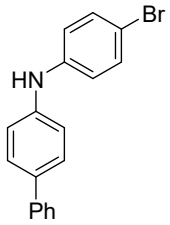
Isolated yield 76%. White solid, mp 125.7-125.9 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 6.8, 1.5 Hz, 2H), 7.50 (dd, J = 8.6, 3.0 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.33 – 7.25 (m, 1H), 7.09 (ddd, J = 17.6, 8.4, 5.7 Hz, 6H), 5.65 (s, 1H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.39, 140.91, 139.99, 133.04, 131.19, 129.90, 128.69, 128.42, 127.93, 126.45, 119.16, 116.85, 20.71.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 260.1439, found: 260.1433.

N-(4-bromophenyl)-[1,1'-biphenyl]-4-amine (3c)



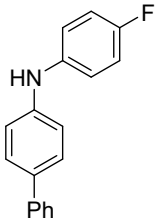
Isolated yield 70%. White solid, mp 121.3-121.6 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.57 – 7.52 (m, 2H), 7.48 – 7.43 (m, 2H), 7.42 – 7.32 (m, 3H), 7.12 (d, J = 6.2 Hz, 2H), 6.98 (d, J = 6.4 Hz, 2H), 5.70 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.15, 141.84, 140.67, 134.37, 132.26, 128.82, 128.08, 126.79, 126.59, 119.30, 118.32, 112.88.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 324.0388, found: 324.0383.

N-(4-fluorophenyl)-[1,1'-biphenyl]-4-amine (3d)[3]



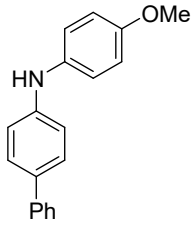
Isolated yield 60%. Red solid, mp 87.4-87.6 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.09 (dd, *J* = 8.6, 4.7 Hz, 2H), 7.06 – 6.98 (m, 4H), 5.65 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.13 (d, J = 240.4 Hz), 143.32, 140.79, 138.62 (d, J = 2.6 Hz), 133.33, 128.76, 128.04, 126.59, 126.50, 120.81 (d, J = 7.8 Hz), 116.79, 116.01 (d, J = 22.5 Hz).

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 264.1189, found: 264.1184.

N-(4-methoxyphenyl)-[1,1'-biphenyl]-4-amine (3e)



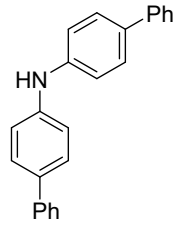
Isolated yield 82%. White solid, mp 119.1-119.3 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.51 (dd, *J* = 9.1, 2.5 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.13 (dd, *J* = 9.0, 3.0 Hz, 2H), 7.00 (dd, *J* = 8.6, 3.0 Hz, 2H), 6.92 (dd, *J* = 9.0, 3.1 Hz, 2H), 5.58 (s, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.44, 144.64, 141.01, 135.49, 132.35, 128.74, 127.97, 126.43, 126.40, 122.43, 115.77, 114.75, 55.60.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 276.1388, found: 276.1383.

di([1,1'-biphenyl]-4-yl)amine (3f)



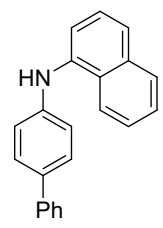
Isolated yield 42%. White solid, mp 208.7-208.9 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.46 (s, 1H), 7.57 (dd, *J* = 14.8, 8.3 Hz, 8H), 7.38 (t, *J* = 7.6 Hz, 4H), 7.25 (t, *J* = 7.3 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 143.12, 140.45, 131.90, 129.27, 127.84, 126.85, 126.23, 117.57.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 322.1596, found: 322.1591.

N-([1,1'-biphenyl]-4-yl)naphthalen-1-amine (3g)



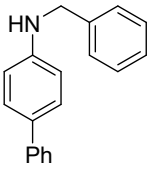
Isolated yield 83%. White solid, mp 141.6-141.8 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.64 (dd, *J* = 11.7, 6.3 Hz, 3H), 7.54 (p, *J* = 6.8 Hz, 4H), 7.49 – 7.43 (m, 4H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.00 (s, 0H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.30, 140.94, 138.49, 134.77, 133.27, 128.77, 128.61, 128.02, 127.96, 126.56, 126.55, 126.22, 126.08, 125.82, 123.34, 121.92, 117.40, 116.50.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 296.1439, found: 296.1433.

N-benzyl-[1,1'-biphenyl]-4-amine (3h)



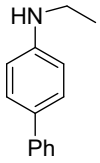
Isolated yield 72%. White solid, mp 86.1-86.4 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.18 (m, 10H), 6.72 (d, *J* = 8.5 Hz, 2H), 4.39 (s, 2H), 4.13 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.54, 141.21, 139.28, 130.47, 128.66, 128.62, 127.94, 127.47, 127.28, 126.28, 126.05, 113.09, 48.32.

HRMS (ESI-TOF) m/z Calcd for $C_{19}H_{17}N$ $[M+H]^+$: 260.1439, found: 260.1430.

N-ethyl-[1,1'-biphenyl]-4-amine (3i)



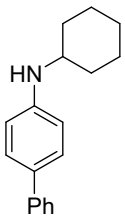
Isolated yield 69%. White solid, mp 61.2-61.5 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.3 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 2H), 3.67 (s, 1H), 3.26 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.99, 141.43, 130.08, 128.77, 128.00, 126.35, 126.11, 113.10, 38.56, 14.99.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 198.1283, found: 198.1277.

N-cyclohexyl-[1,1'-biphenyl]-4-amine (3j)



Isolated yield 70%. White solid, mp 71.4-71.6 ℃.

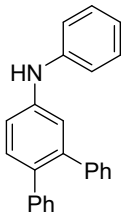
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.4 Hz, 2H), 7.48 – 7.36 (m, 4H), 7.25 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 2H), 3.63 (s, 1H), 3.38

– 3.22 (m, 1H), 2.10 (d, *J* = 12.0 Hz, 2H), 1.85 – 1.74 (m, 2H), 1.68 (dd, *J* = 9.1, 4.2 Hz, 1H), 1.47 – 1.34 (m, 2H), 1.33 – 1.25 (m, 1H), 1.25 – 1.13 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.82, 141.34, 129.68, 128.60, 127.94, 126.21, 125.90, 113.29, 51.70, 33.48, 25.93, 25.02.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 252.1752, found: 252.1747.

N-phenyl-[1,1':2',1''-terphenyl]-4'-amine (3k)



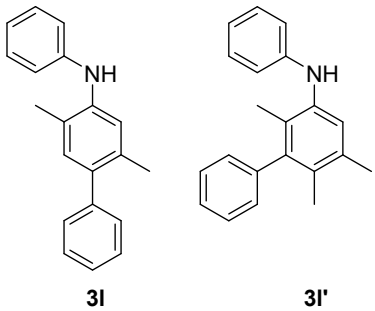
Isolated yield 48%. White solid, mp 97.9-98.1 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (ddd, *J* = 15.7, 8.0, 3.4 Hz, 3H), 7.22 – 7.10 (m, 13H), 6.97 (dd, *J* = 7.0, 2.9 Hz, 1H), 5.81 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.73, 142.56, 141.61, 141.52, 141.31, 133.24, 131.63, 129.86, 129.78, 129.42, 127.85, 127.80, 126.53, 125.99, 121.32, 119.32, 118.27, 116.30.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 322.1596, found: 322.1591.

2,5-dimethyl-N-phenyl-[1,1'-biphenyl]-4-amine (3l) and 2,5,6-trimethyl-N-phenyl-[1,1'-biphenyl]-3-amine (3l')



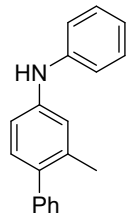
3l **3l'**

3l:Isolated yield 27%. **3l'**:Isolated yield 18%. White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 4H), 7.36 – 7.20 (m, 8H), 7.14 (d, *J* = 7.2 Hz, 3H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.88 (tt, *J* = 14.5, 7.3 Hz, 4H), 5.38 (s, 1H), 5.32 (s, 1H), 2.26 (s, 3H), 2.25 (s, 2H), 2.21 (s, 2H), 1.90 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.12, 143.96, 143.22, 142.04, 141.81, 140.23, 138.12, 135.65, 134.57, 133.67, 132.37, 129.42, 129.32, 129.25, 128.34, 127.99, 126.49, 126.40, 125.92, 125.43, 121.61, 120.47, 120.23, 119.50, 117.59, 116.28, 20.46, 20.22, 17.36, 17.04, 15.48.

2-methyl-N-phenyl-[1,1'-biphenyl]-4-amine (3m)



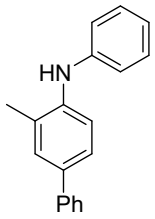
Isolated yield 58%. White solid, mp 66.9-67.1 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.41 – 7.31 (m, 5H), 7.20 (d, *J* = 8.8 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.04 – 6.97 (m, 3H), 5.73 (s, 1H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.14, 142.28, 141.80, 136.51, 134.87, 130.83, 129.43, 129.42, 128.09, 126.48, 121.04, 119.40, 118.02, 115.13, 20.76.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 260.1439, found: 260.1433.

3-methyl-N-phenyl-[1,1'-biphenyl]-4-amine (3n)



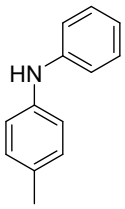
Isolated yield 66%. White solid, mp 75.3-75.5 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.41 (dd, *J* = 20.8, 11.5 Hz, 4H), 7.29 (dd, *J* = 13.4, 8.0 Hz, 4H), 7.02 (d, *J* = 7.1 Hz, 2H), 6.93 (t, *J* = 6.5 Hz, 1H), 5.43 (s, 1H), 2.33 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.64, 140.95, 140.72, 134.56, 129.61, 129.35, 128.68, 128.04, 126.64, 126.60, 125.39, 120.75, 118.45, 117.84, 18.07.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 260.1439, found: 260.1433.

4-methyl-N-phenylaniline (3p)



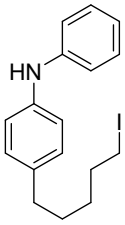
Isolated yield 70%. White solid, mp 80.3-80.5 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.00 (dd, *J* = 8.3, 2.5 Hz, 4H), 6.88 (t, *J* = 7.3 Hz, 1H), 5.60 (s, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.89, 140.22, 130.90, 129.83, 129.29, 120.25, 118.85, 116.80, 20.69.

HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 184.1126, found: 184.1120.

4-(5-iodopentyl)-N-phenylaniline (3q)



Isolated yield 52%. Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.02 (dd, *J* = 8.0, 3.5 Hz, 4H), 6.89 (t, *J* = 7.6 Hz, 1H), 5.63 (s, 1H), 3.19 (t, *J* = 7.0 Hz, 2H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.86 (p, *J* = 7.1 Hz, 2H), 1.63 (p, *J* = 7.6 Hz, 2H), 1.45 (dt, *J* = 15.1, 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.70, 140.67, 135.30, 129.31, 129.19, 120.41, 118.57, 117.03, 34.98, 33.45, 30.56, 30.14, 7.14.

HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{20}IN$ $[M+H]^+$: 366.0719, found: 366.0710.

References

1 (a) Lai P S, Dubland J A, Sarwar M G, et al. Carbon–carbon bond-forming reactions of α-carbonyl carbocations: exploration of a reversed-polarity equivalent of enolate chemistry[J]. Tetrahedron, 2011, 67(39): 7586-7592. (b) Wei Y, Deb I, Yoshikai N. Palladium-catalyzed aerobic oxidative cyclization of N-aryl imines: Indole synthesis from anilines and ketones[J]. Journal of the American Chemical Society, 2012, 134(22): 9098-9101.

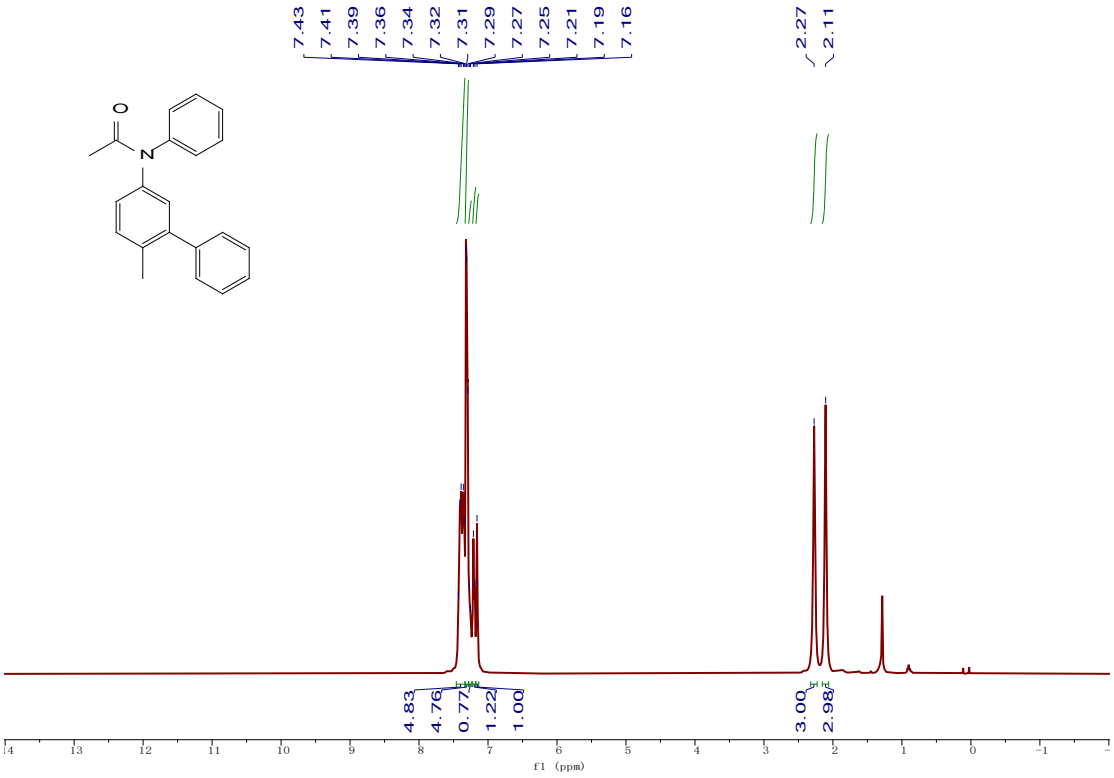
2 Chen Y, Huang Z, Jiang Y, et al. Direct para-Selective C–H Amination of Iodobenzenes: Highly Efficient Approach for the Synthesis of Diarylamines[J]. The Journal of Organic Chemistry, 2021, 86(12): 8226-8235.

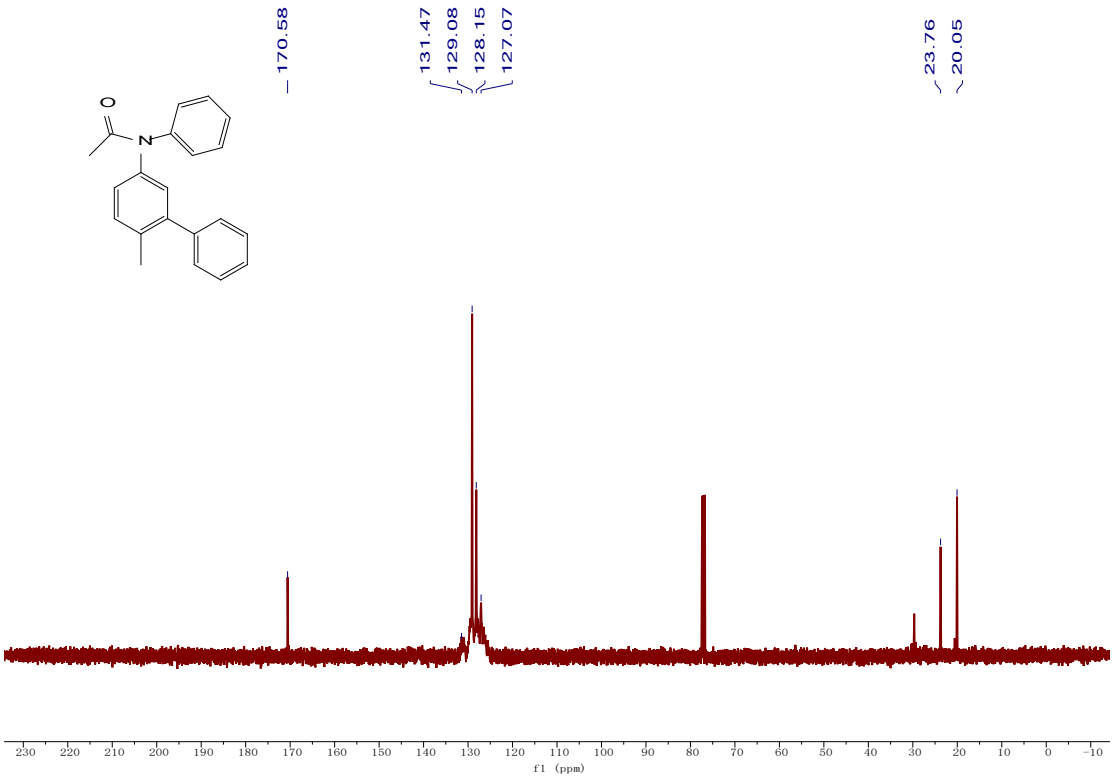
3 Li J, Wang Z X. Nickel-catalyzed amination of aryl 2-pyridyl ethers via cleavage of the carbon–oxygen bond[J]. Organic letters, 2017, 19(14): 3723-3726.

3. ^{1}H NMR and ^{13}C NMR spectra of products.

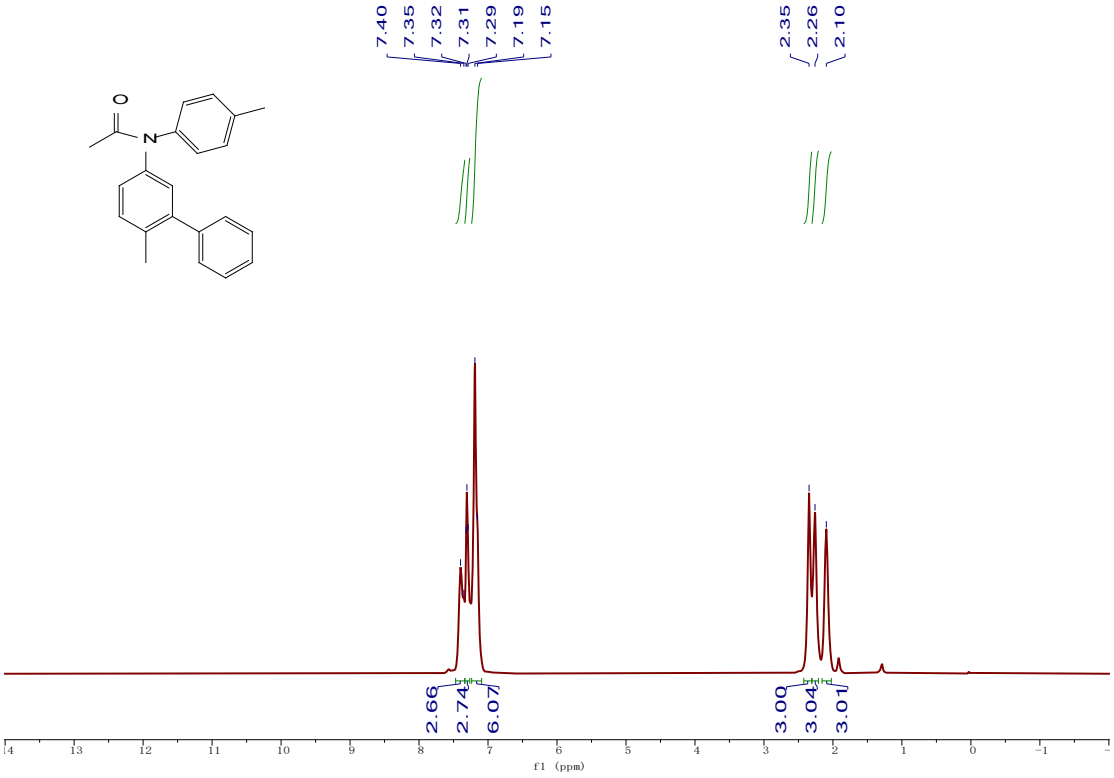
3.1 ^{1}H NMR and ^{13}C NMR spectra of products 2a~2q.

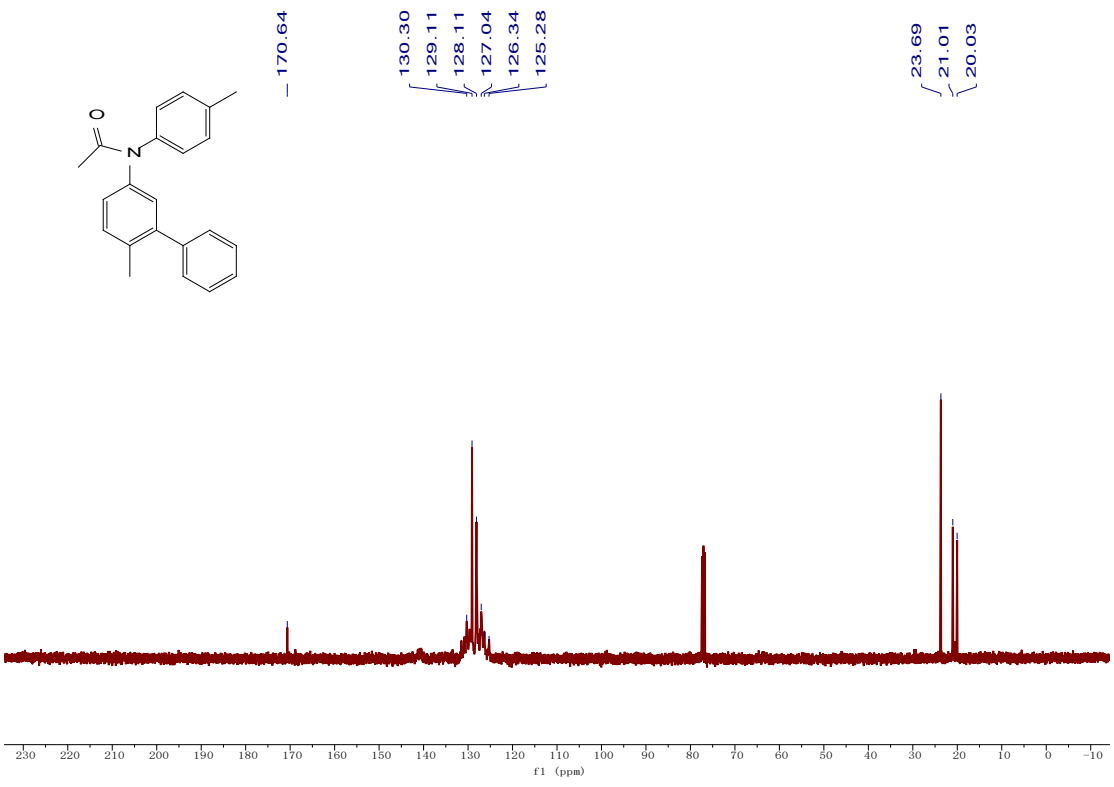
N-(6-methyl-[1,1'-biphenyl]-3-yl)-N-phenylacetamide (2a)



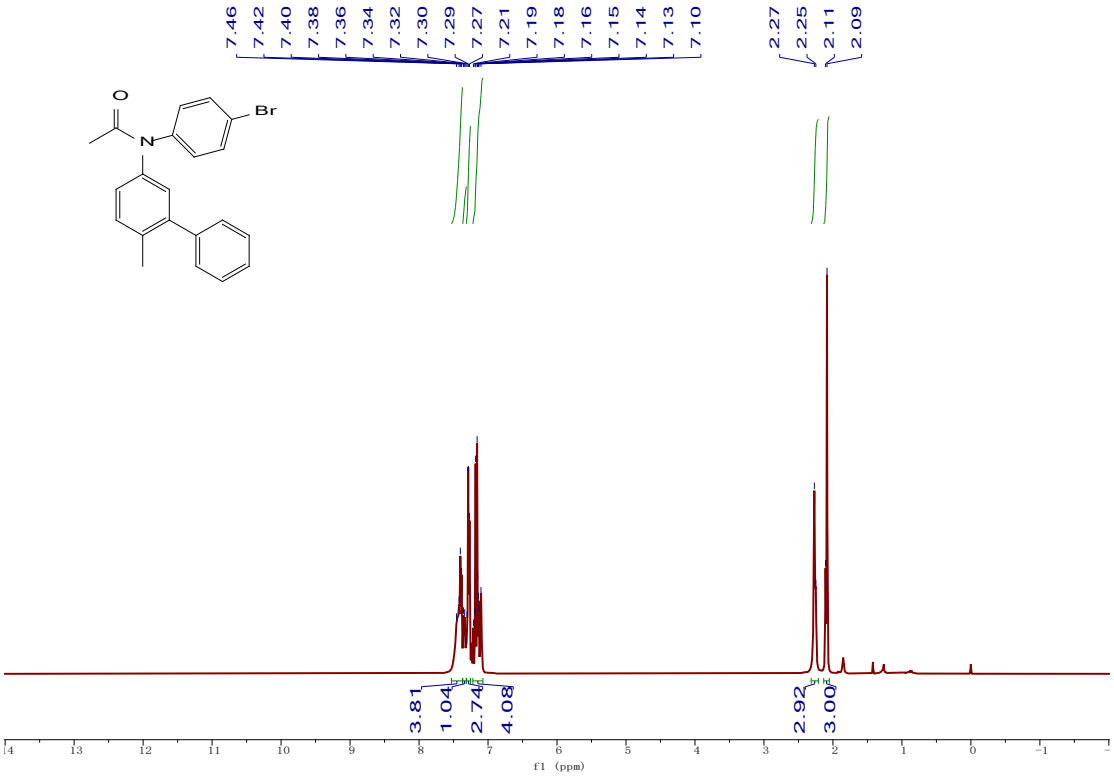


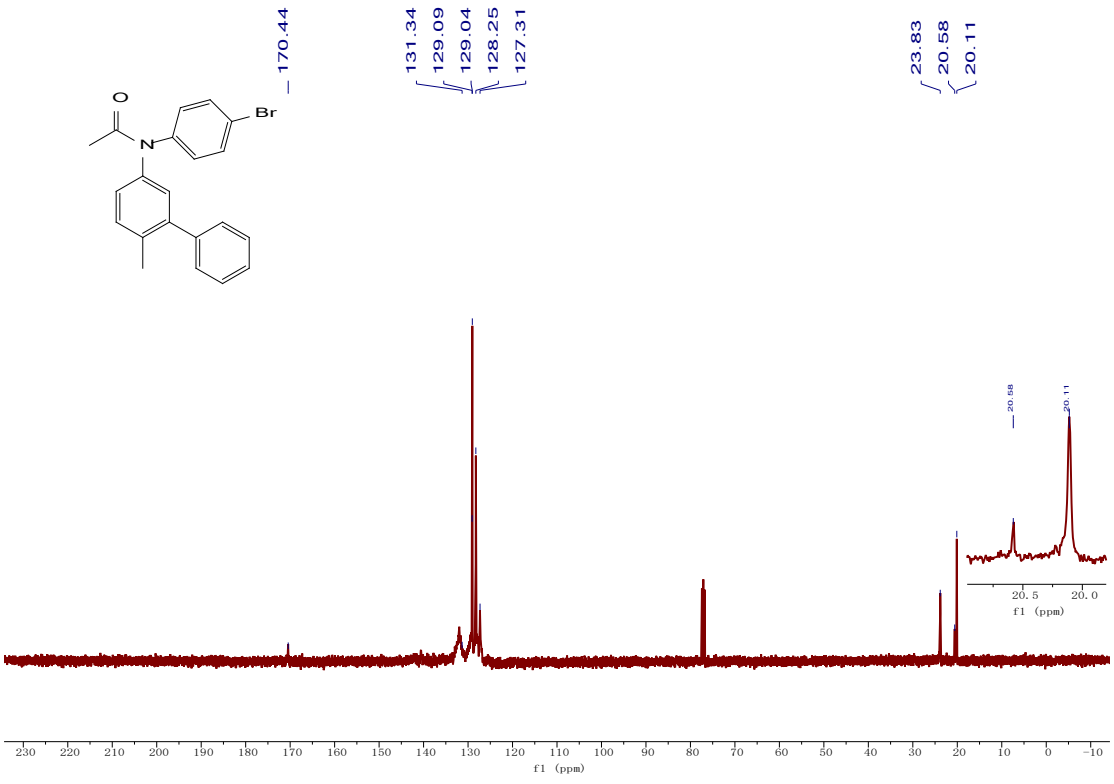
N-(6-methyl-[1,1'-biphenyl]-3-yl)-N-(p-tolyl)acetamide (2b)



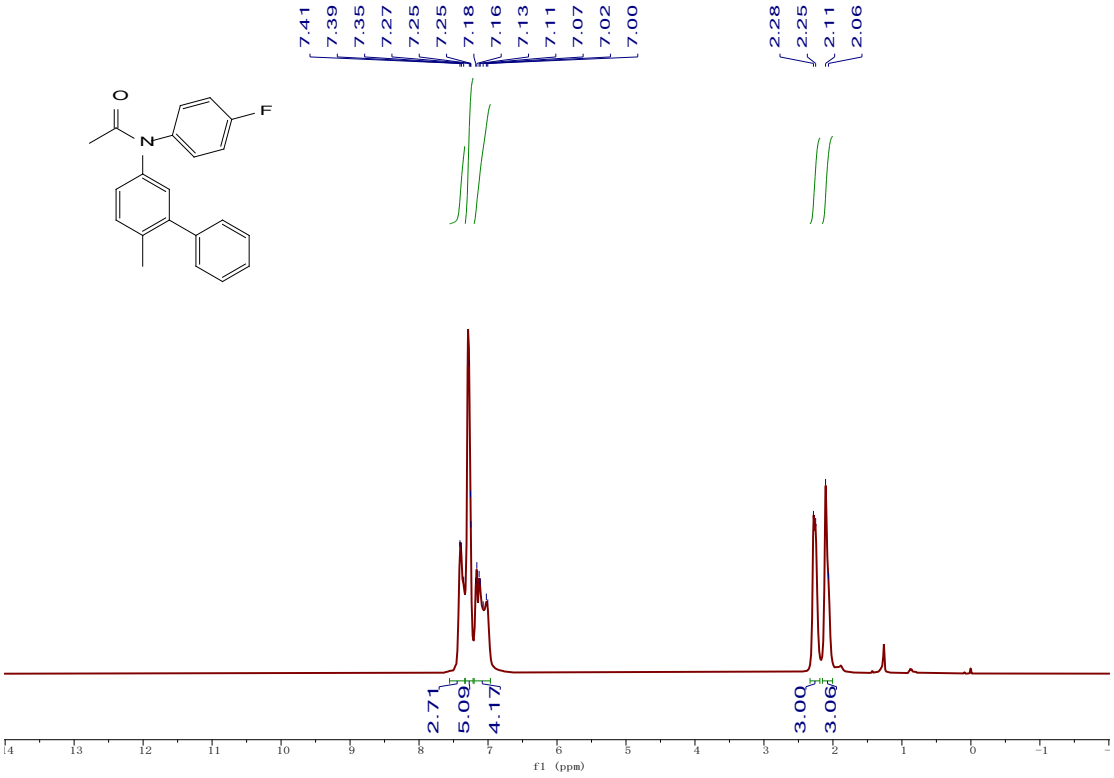


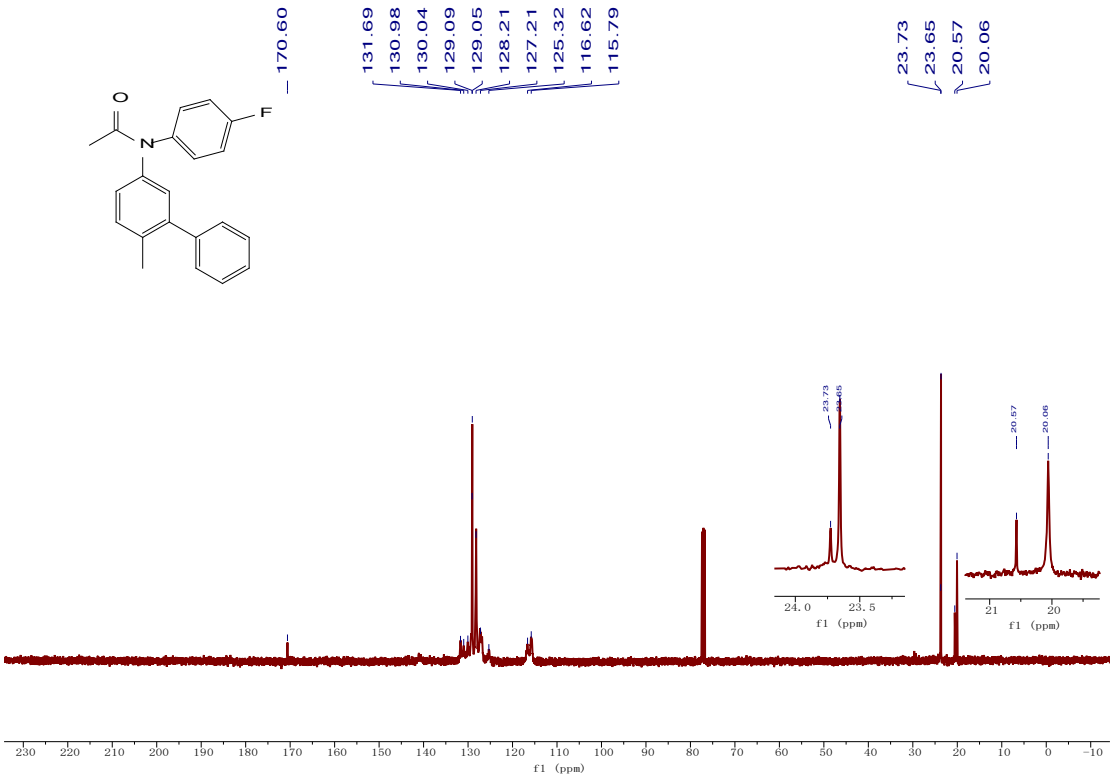
N-(4-bromophenyl)-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2c)



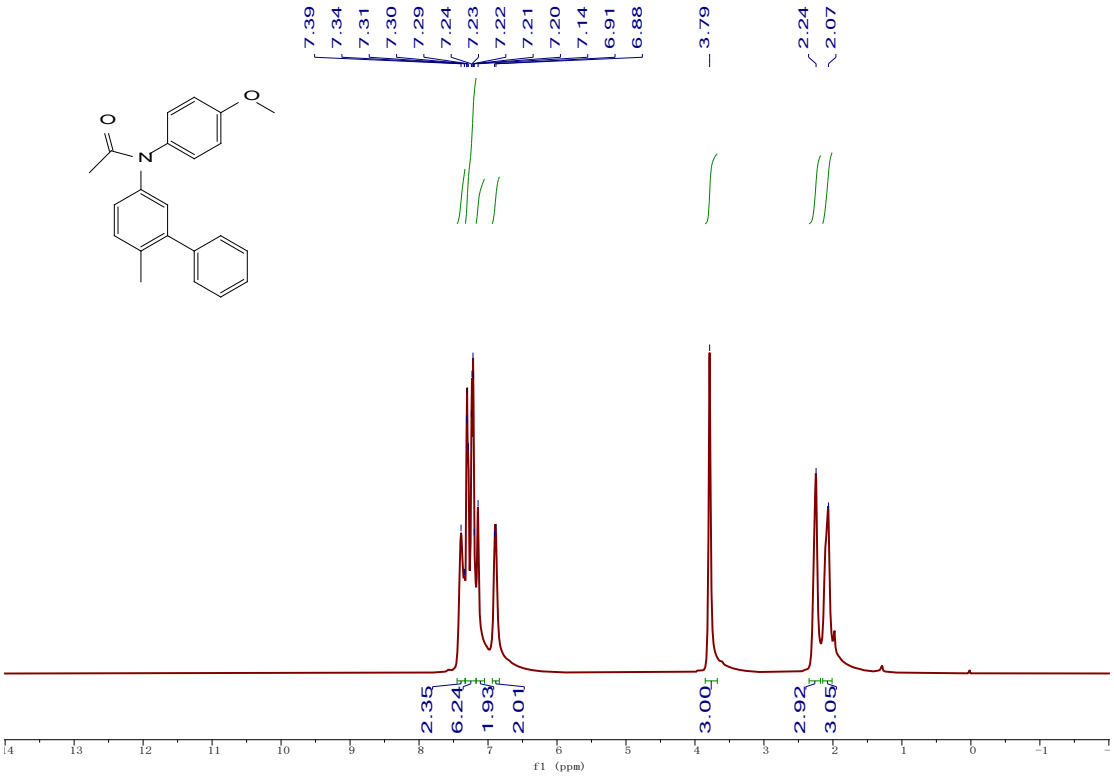


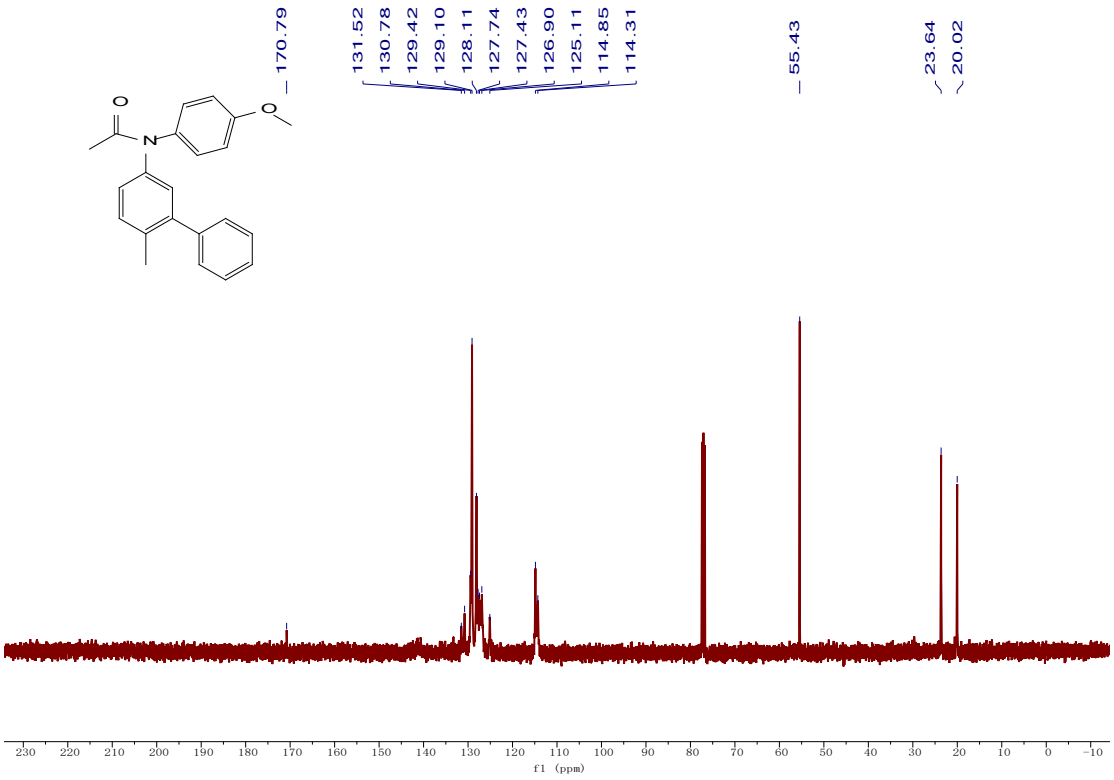
N-(4-fluorophenyl)-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2d)



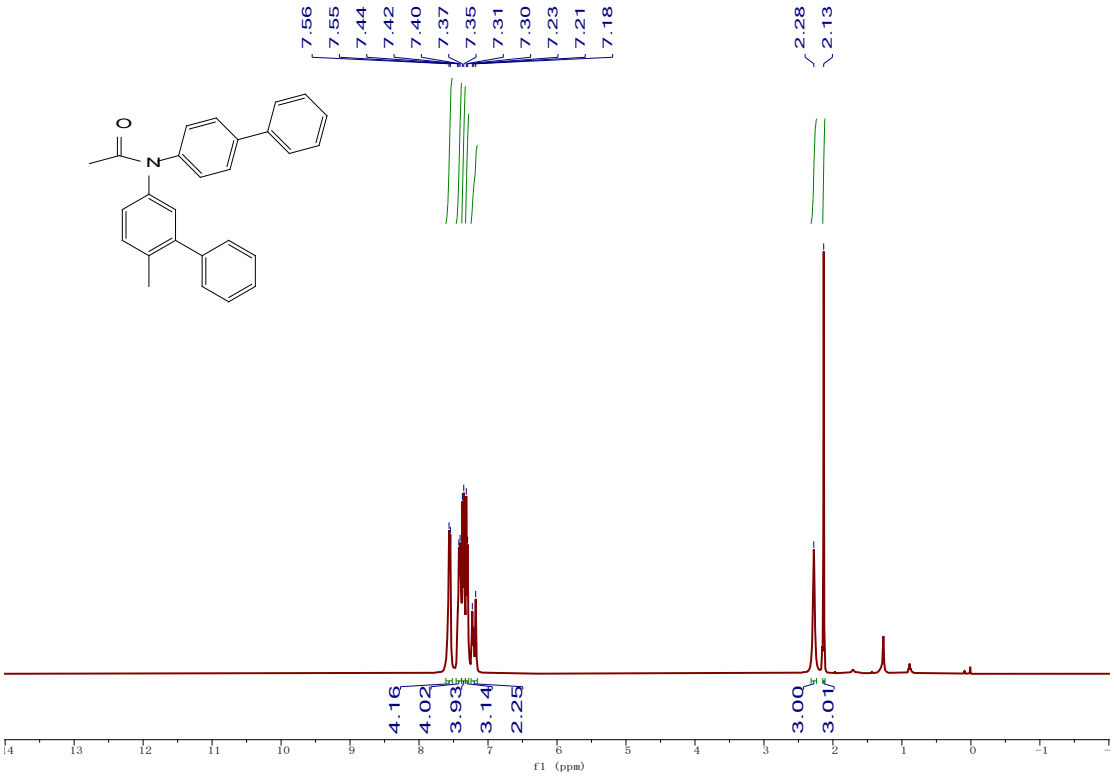


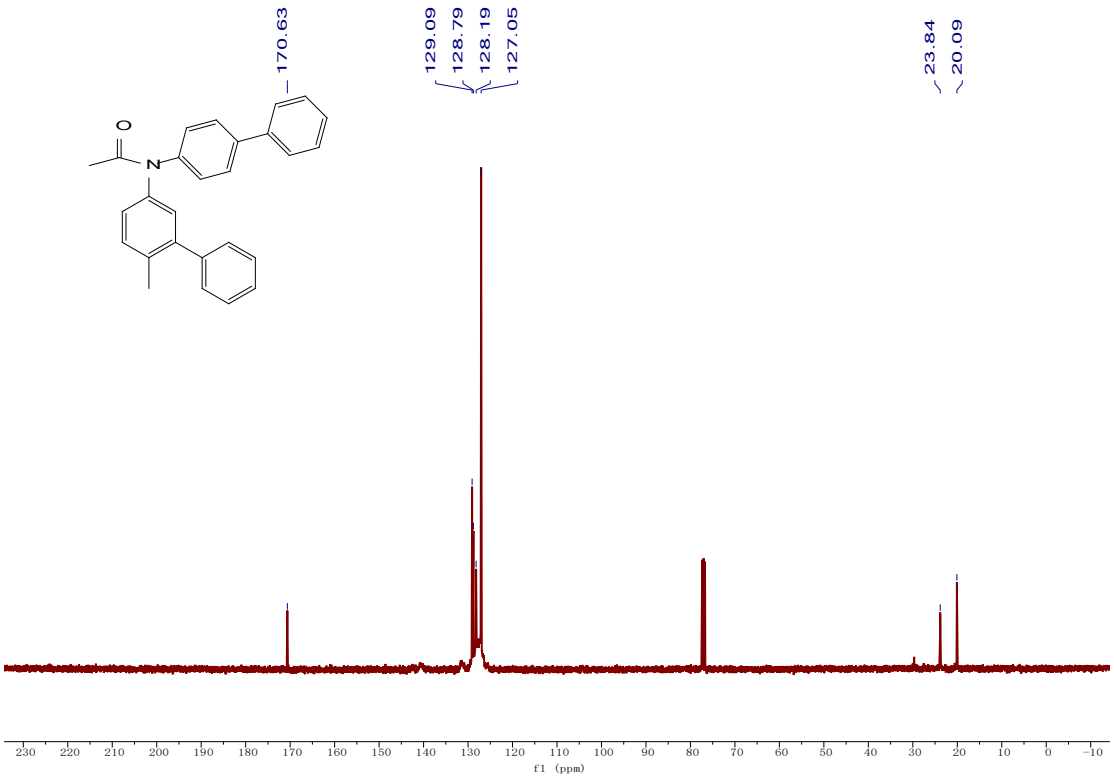
N-(4-methoxyphenyl)-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2e)



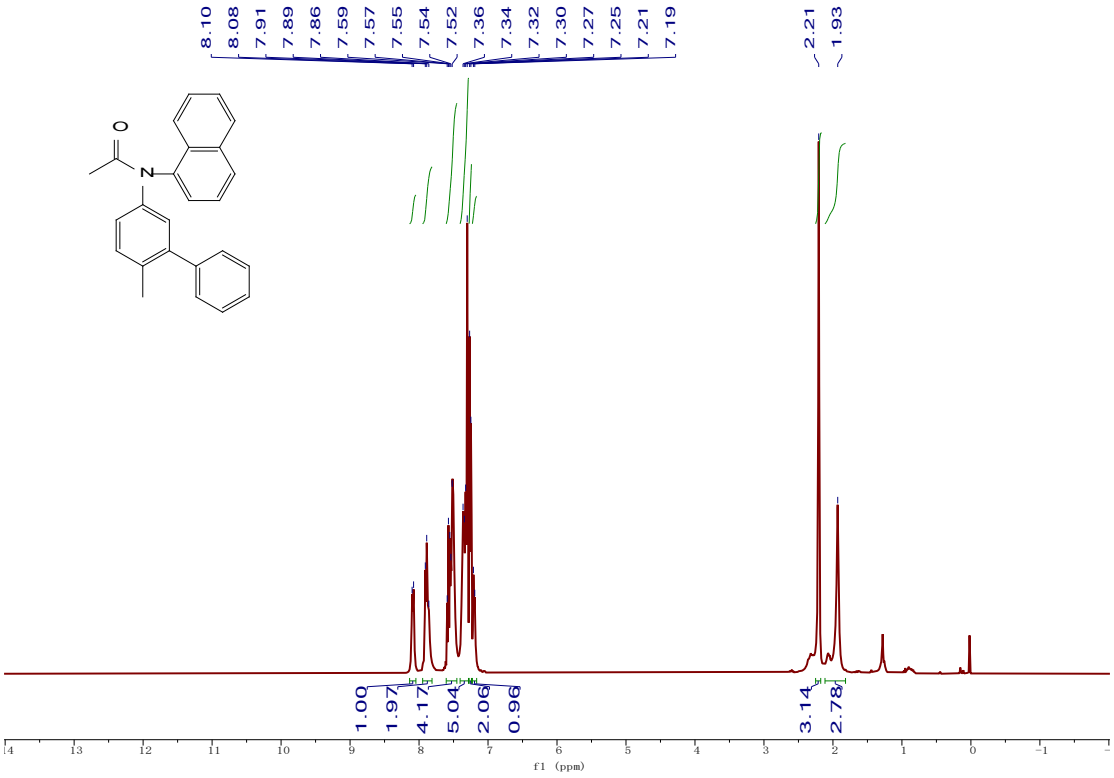


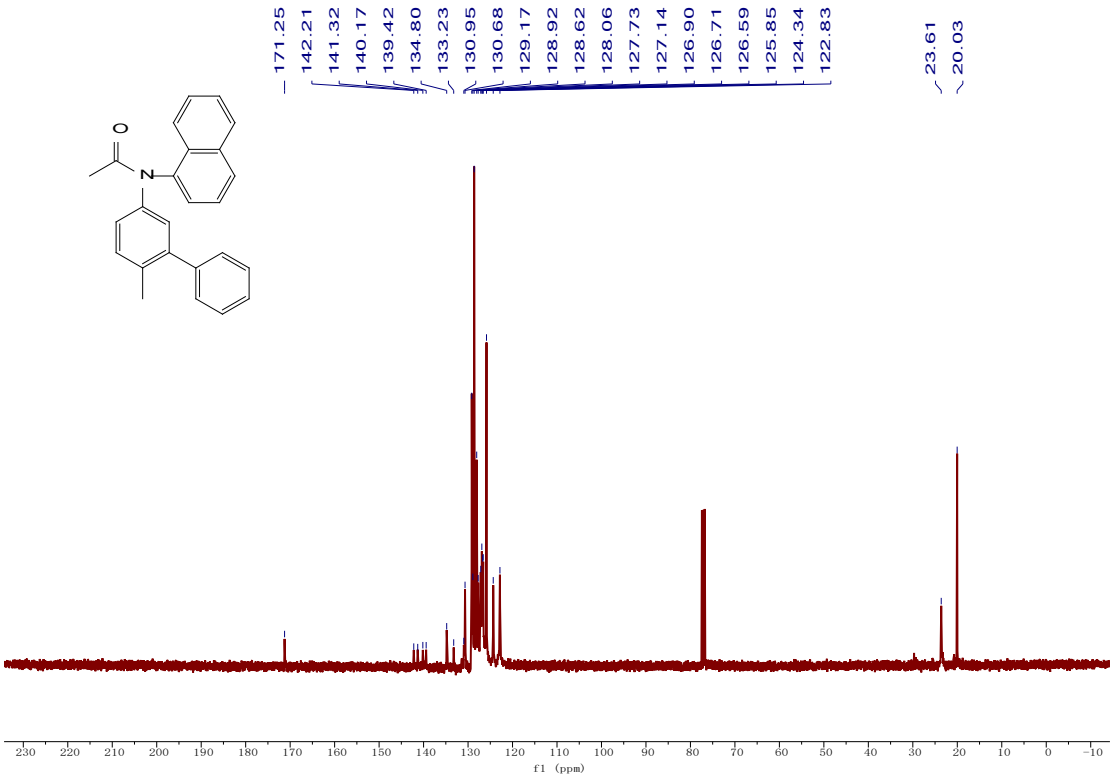
N-([1,1'-biphenyl]-4-yl)-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2f)



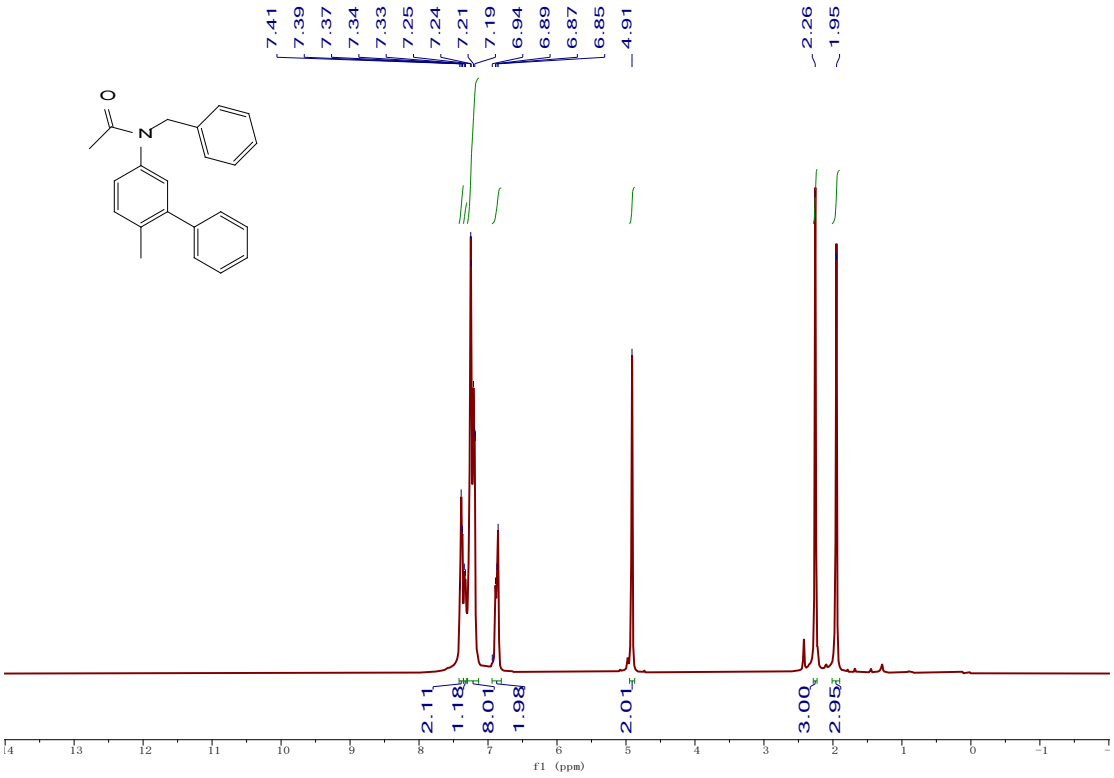


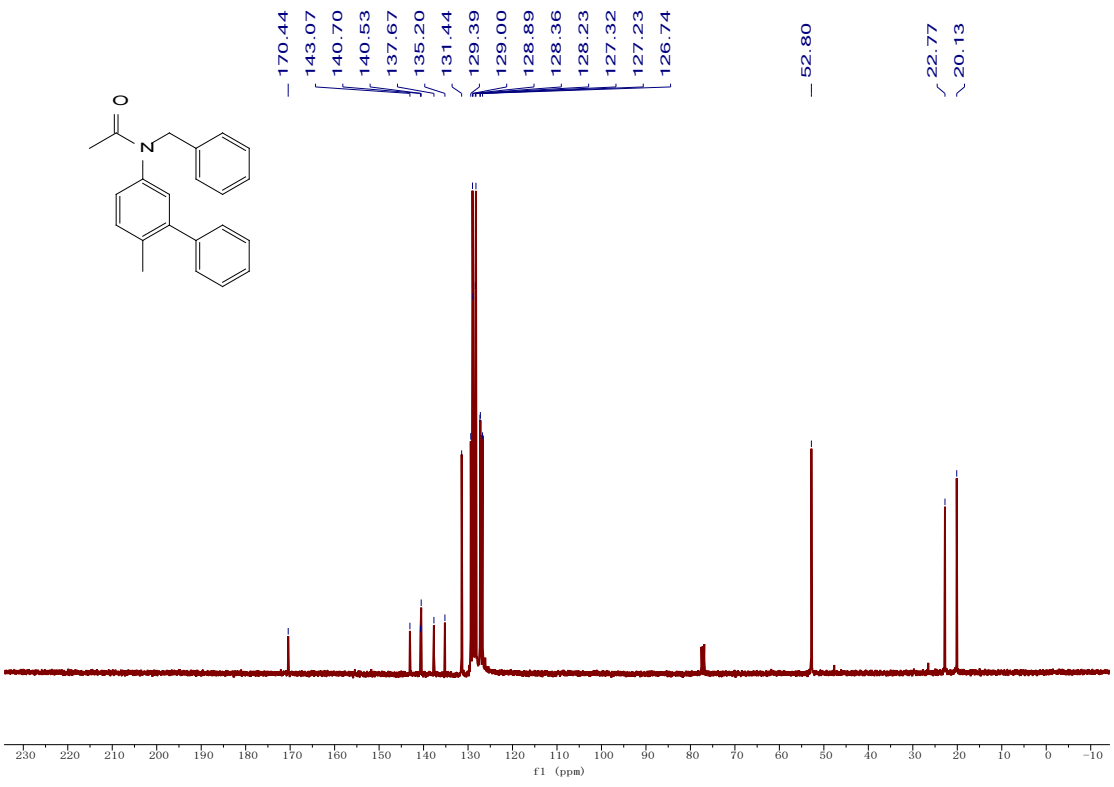
N-(6-methyl-[1,1'-biphenyl]-3-yl)-N-(naphthalen-1-yl)acetamide (2g)



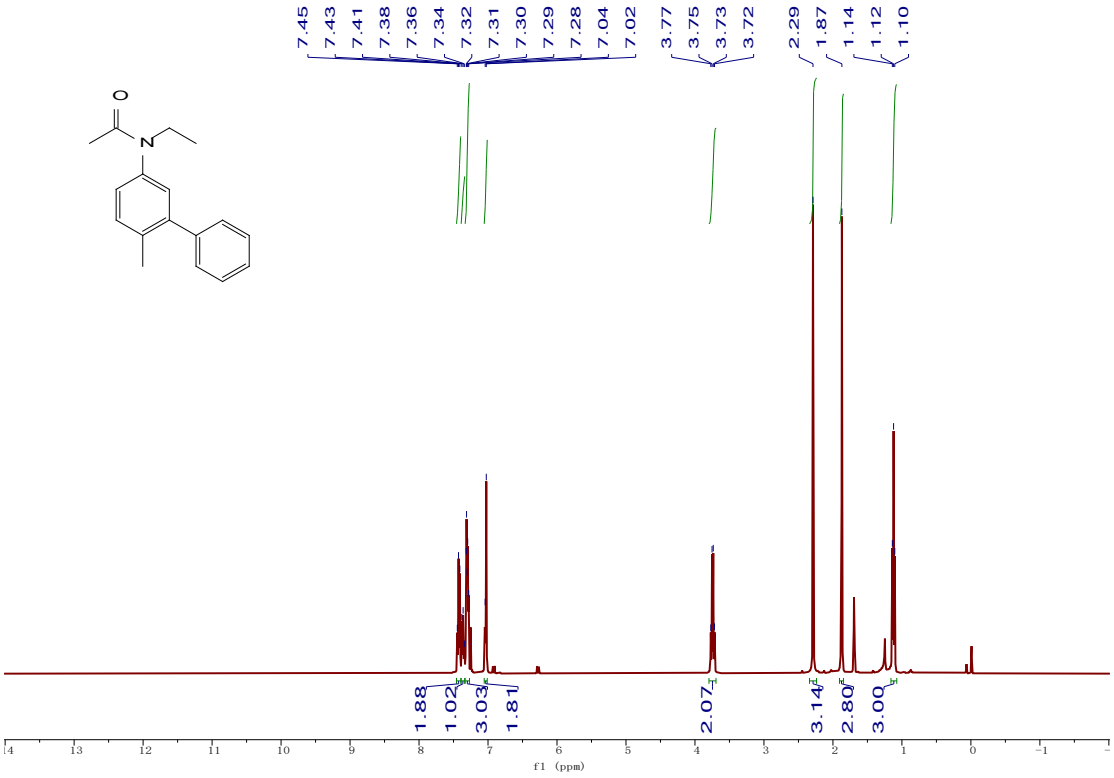


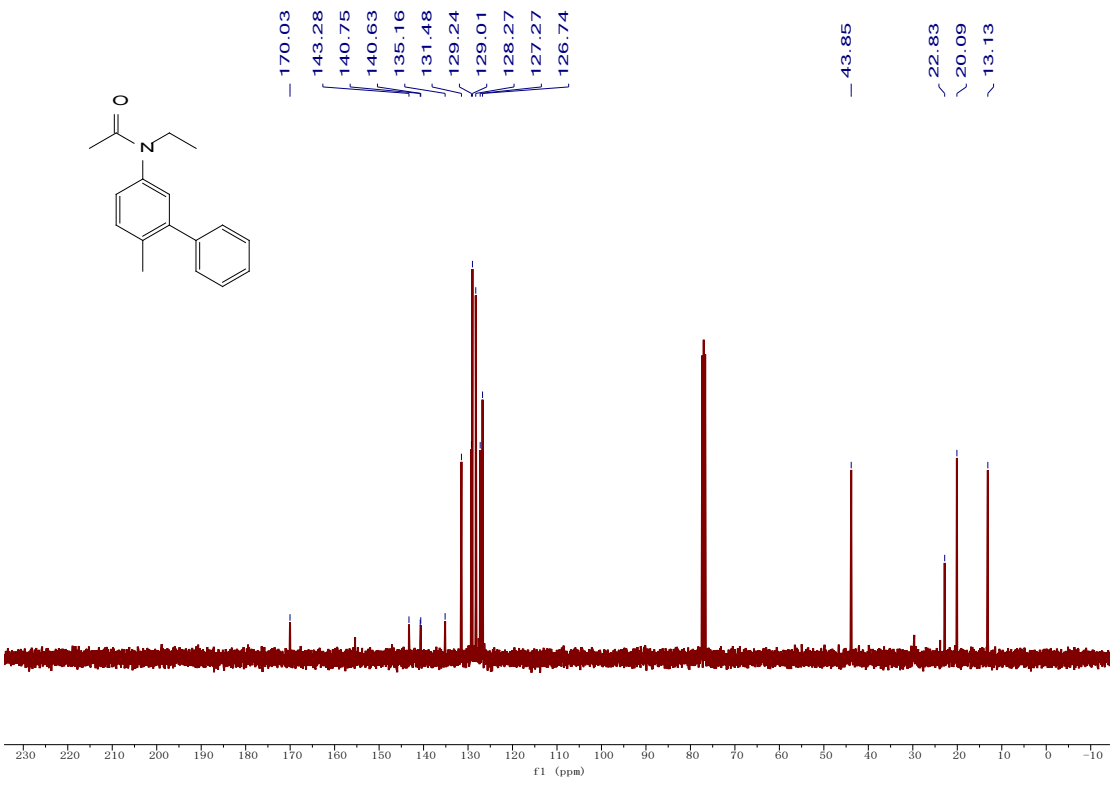
N-benzyl-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2h)



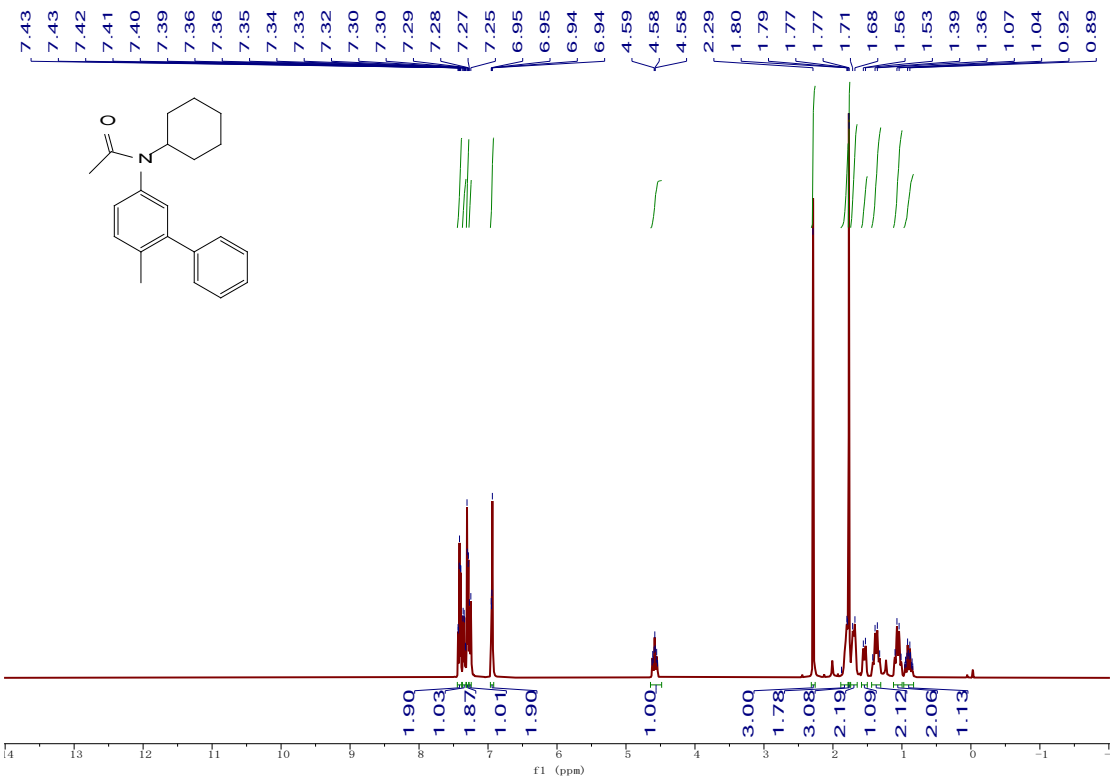


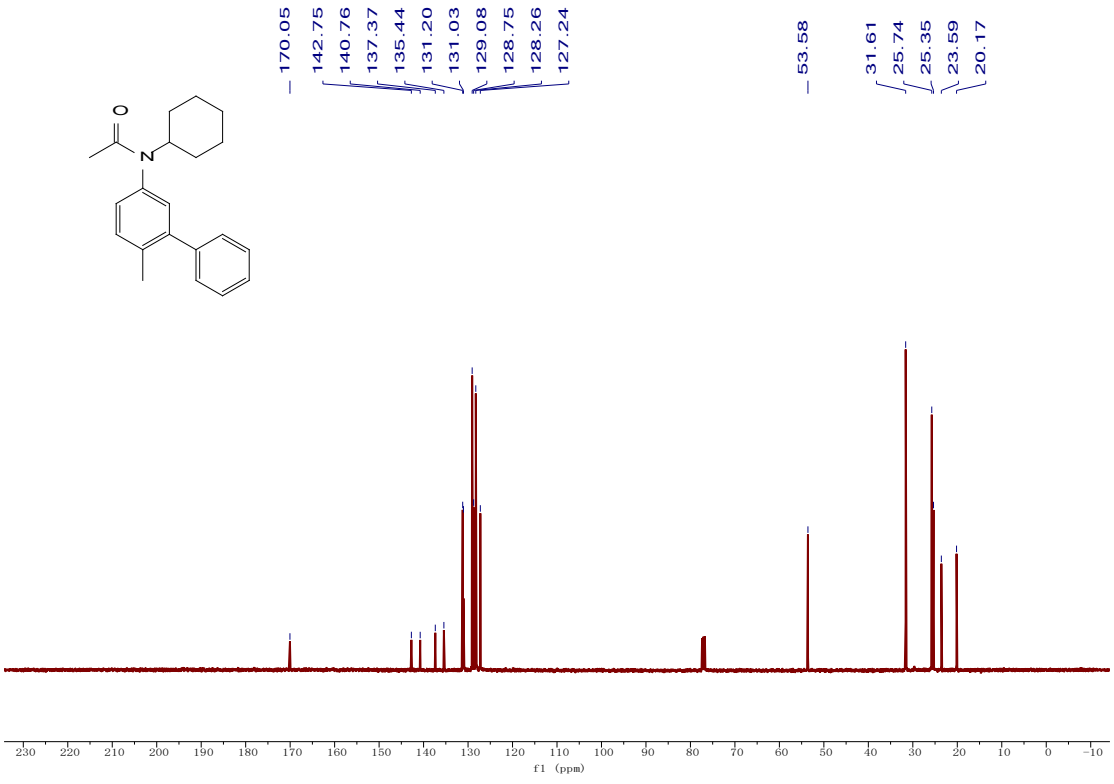
N-ethyl-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2i)



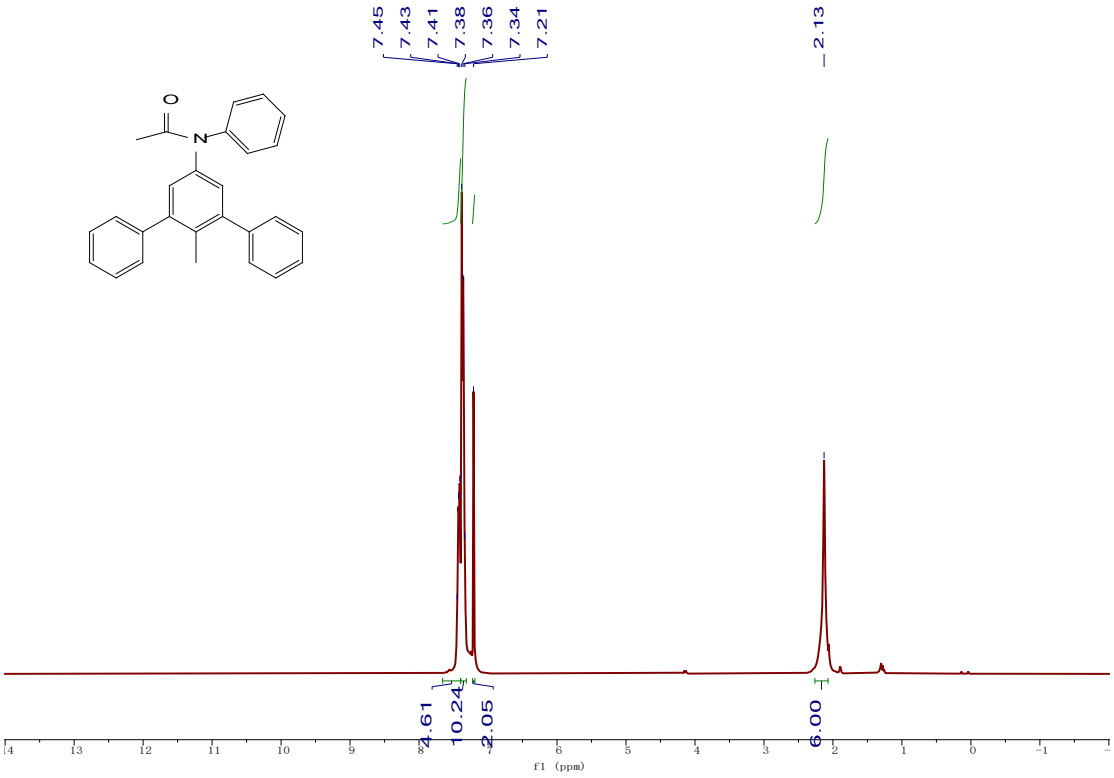


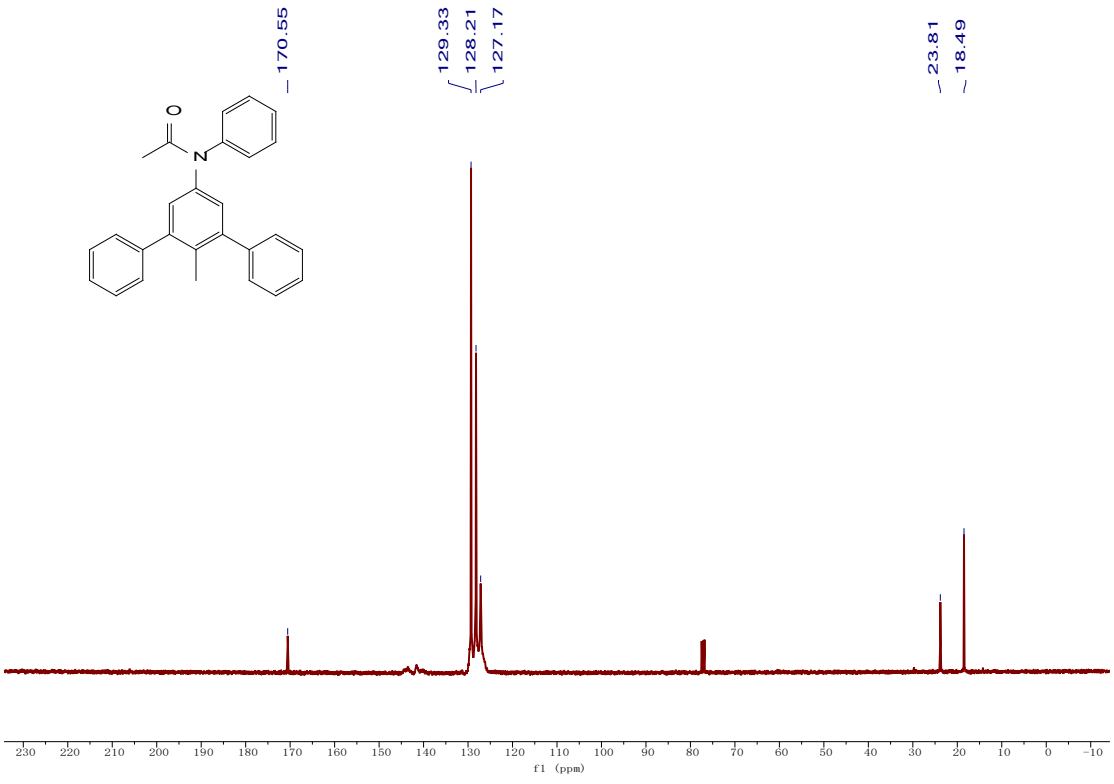
N-cyclohexyl-N-(6-methyl-[1,1'-biphenyl]-3-yl)acetamide (2j)



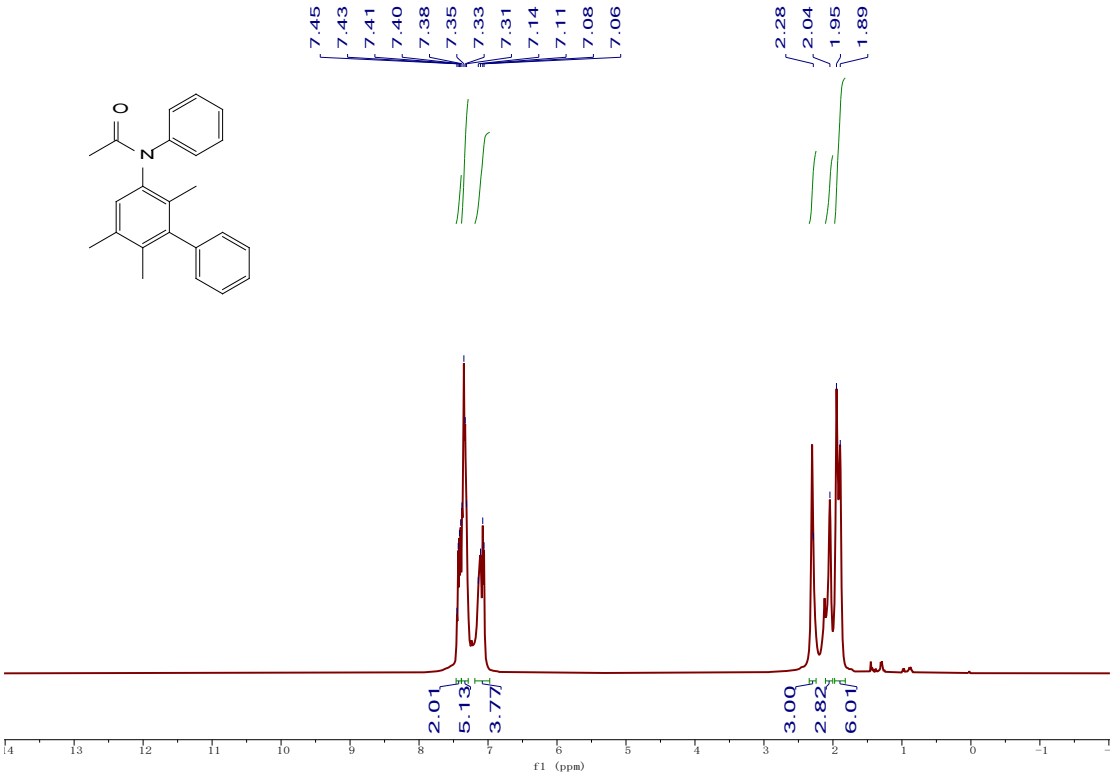


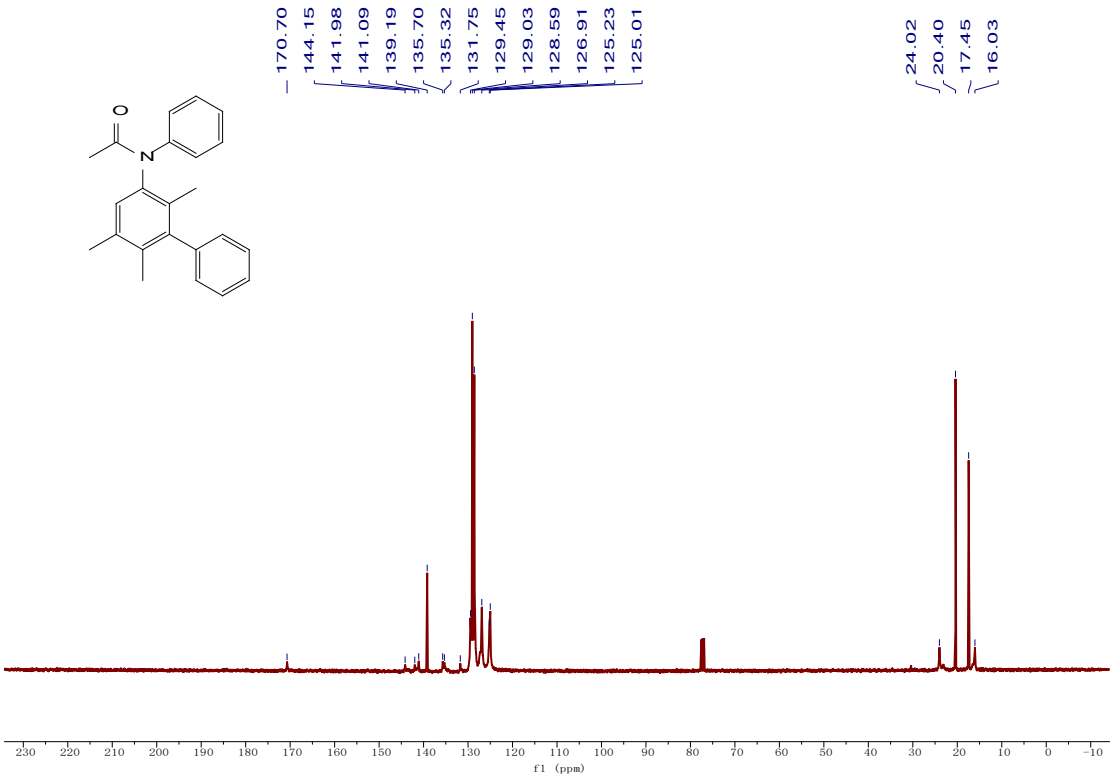
N-(2'-methyl-[1,1':3',1''-terphenyl]-5'-yl)-N-phenylacetamide (2k)



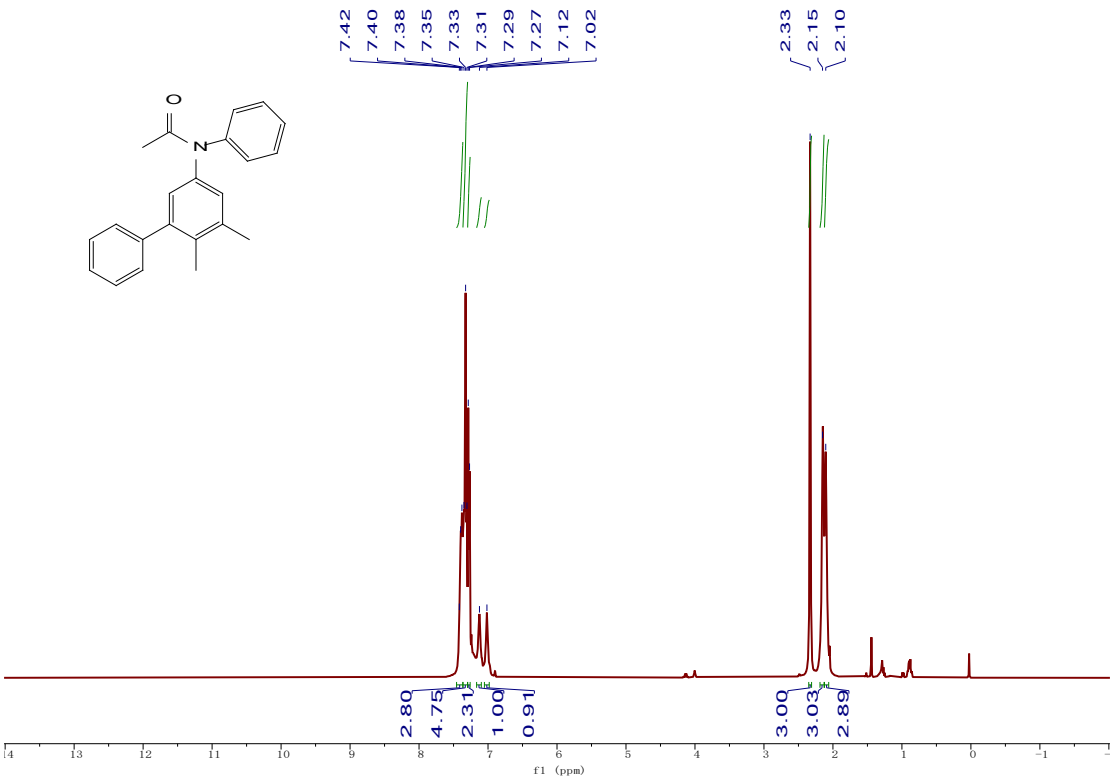


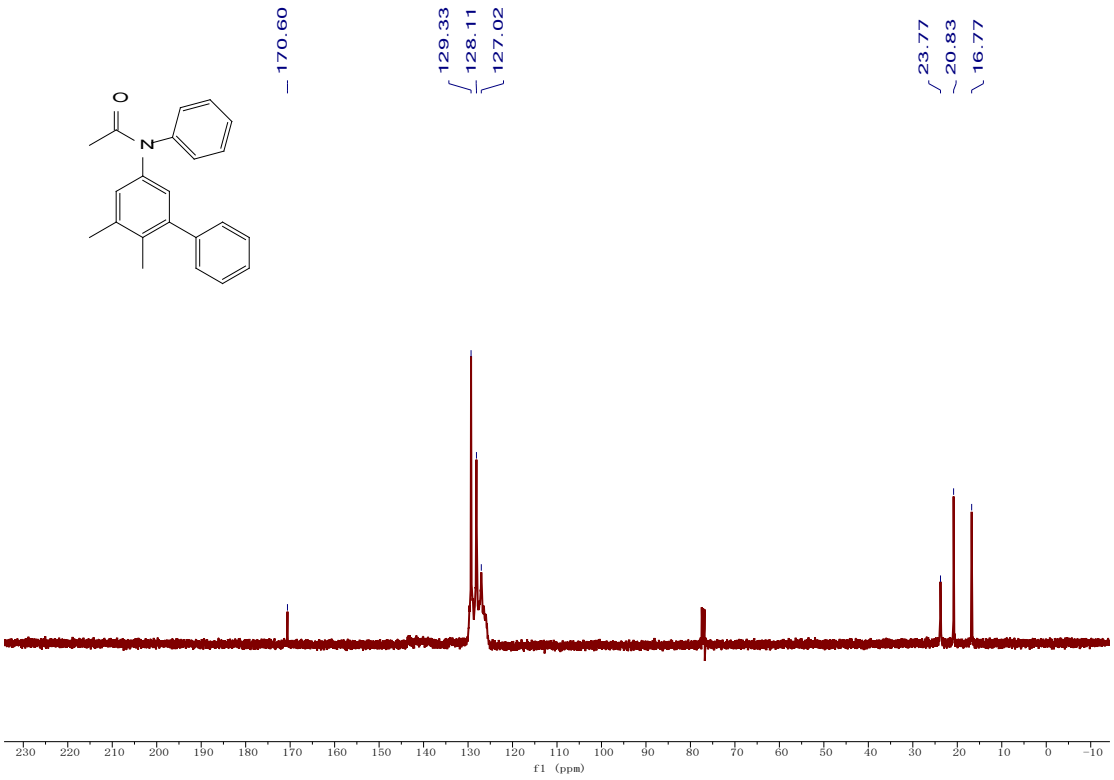
N-phenyl-N-(2,5,6-trimethyl-[1,1'-biphenyl]-3-yl)acetamide (2l)



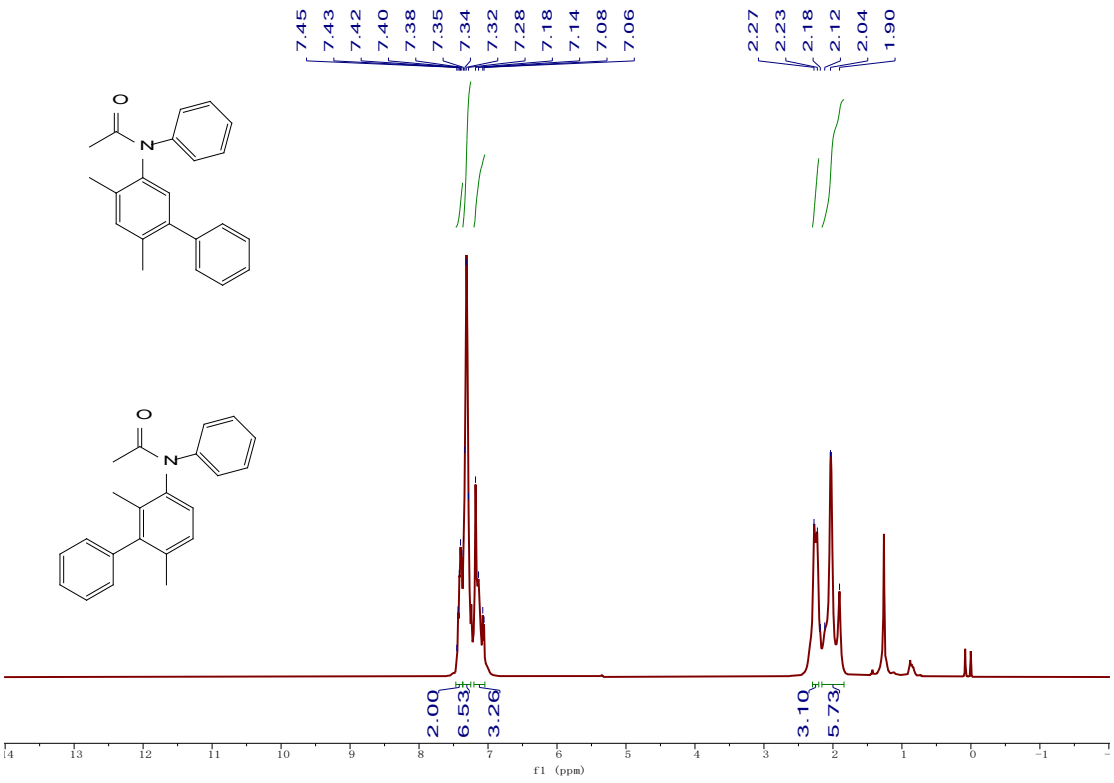


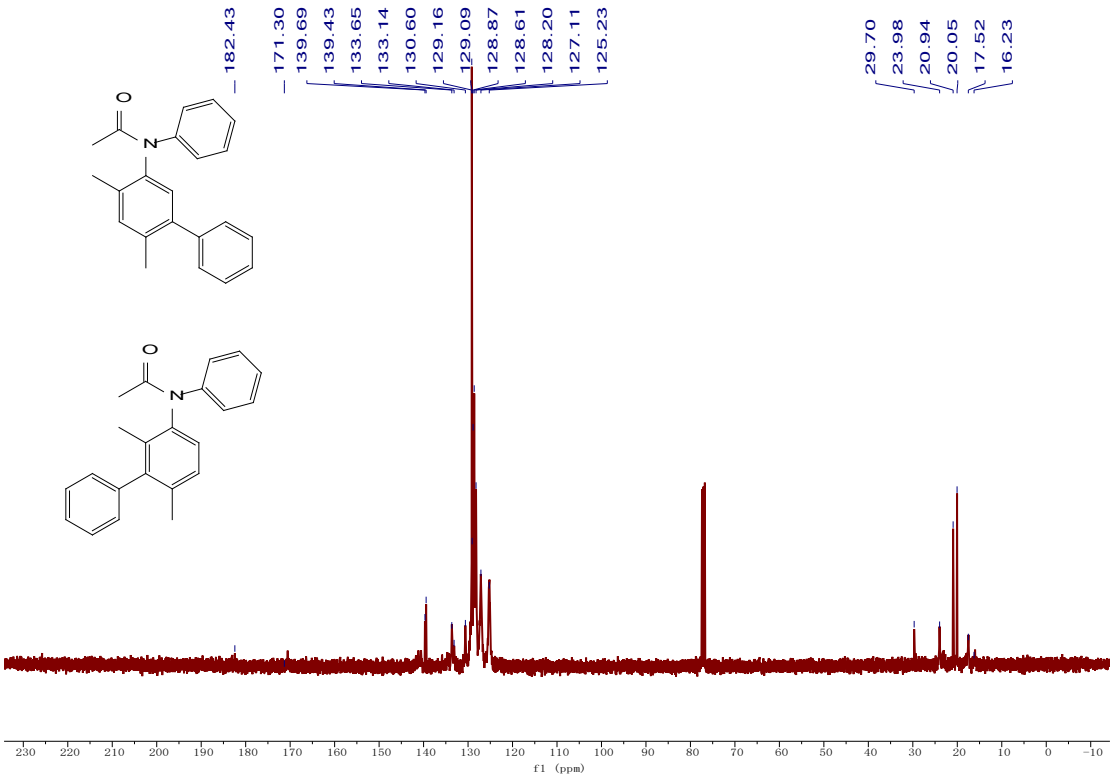
N-(5,6-dimethyl-[1,1'-biphenyl]-3-yl)-N-phenylacetamide (2m)



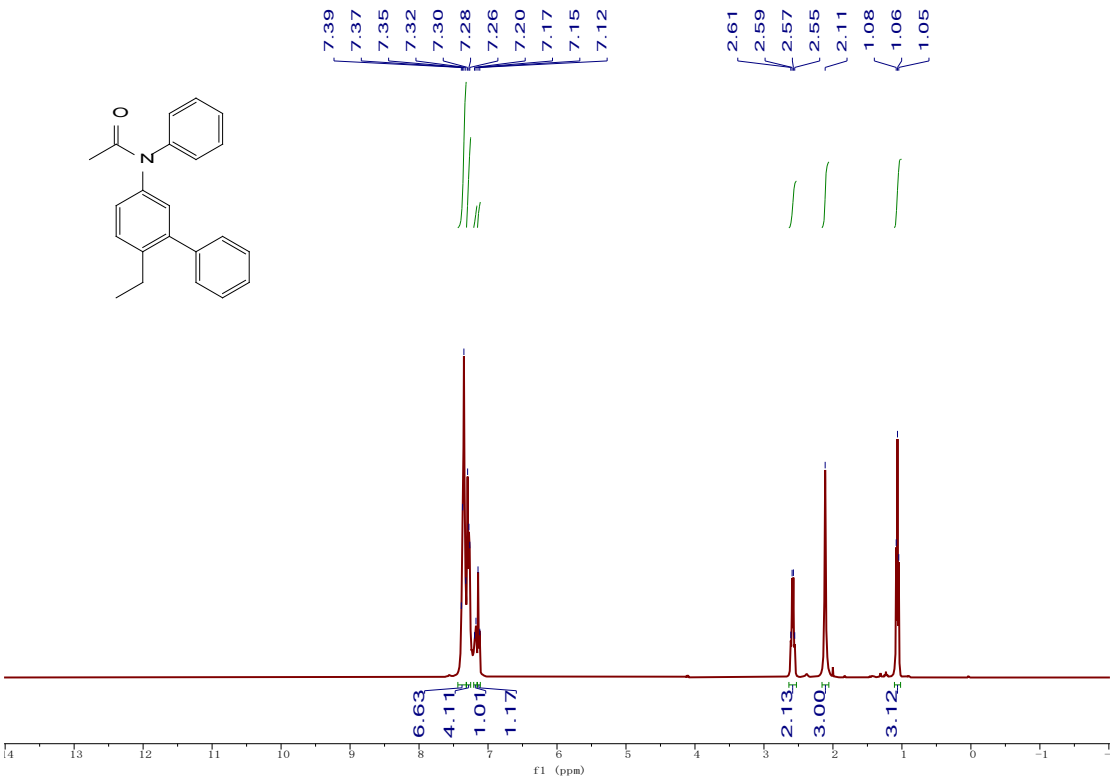


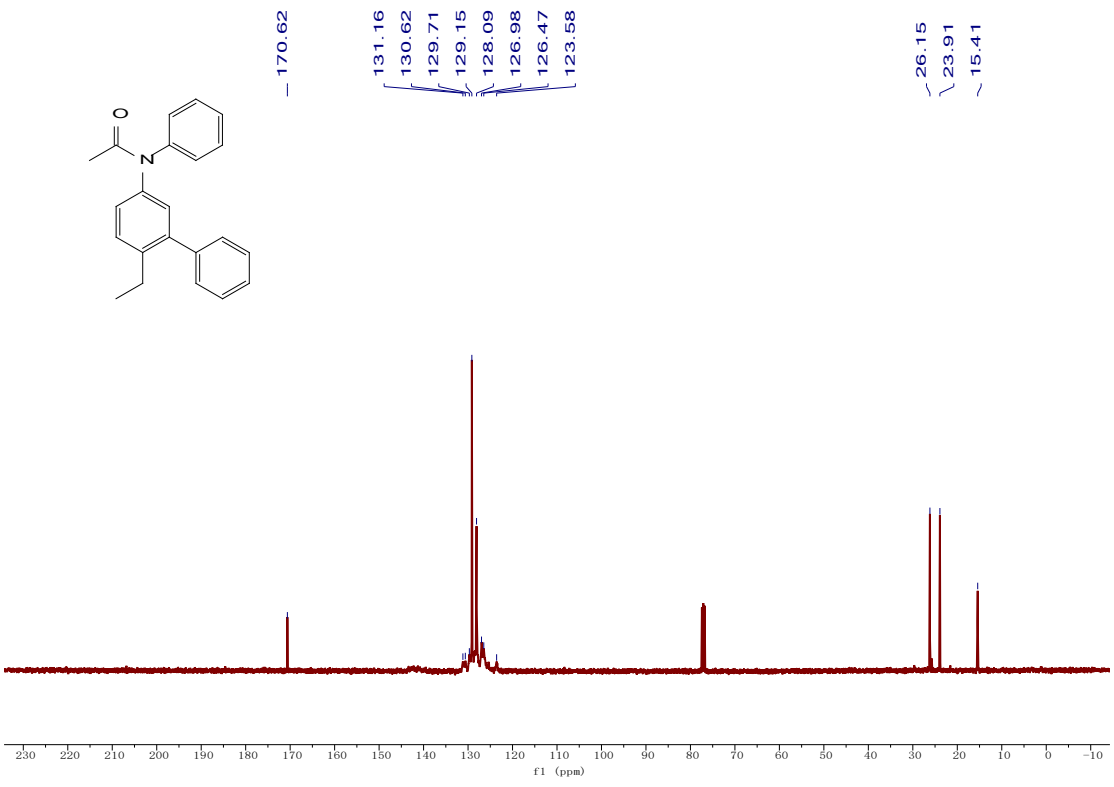
N-(4,6-dimethyl-[1,1'-biphenyl]-3-yl)-N-phenylacetamide (2n) and N-(2,6-dimethyl-[1,1'-biphenyl]-3-yl)-N-phenylacetamide (2n')



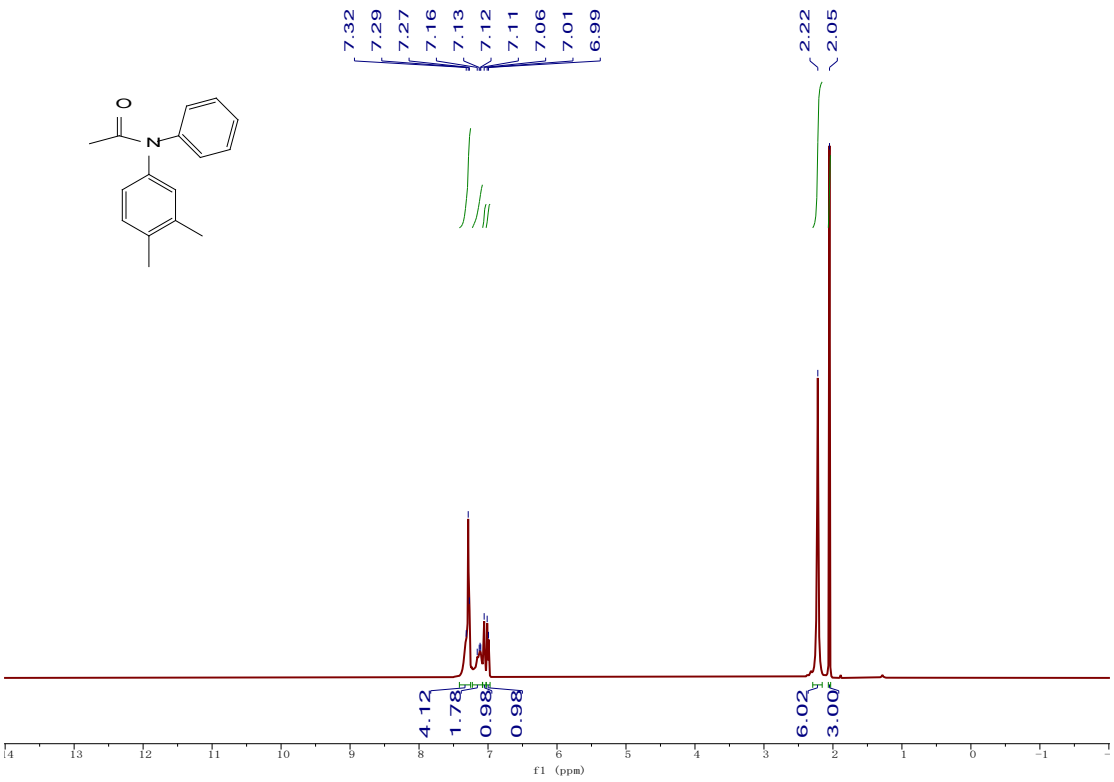


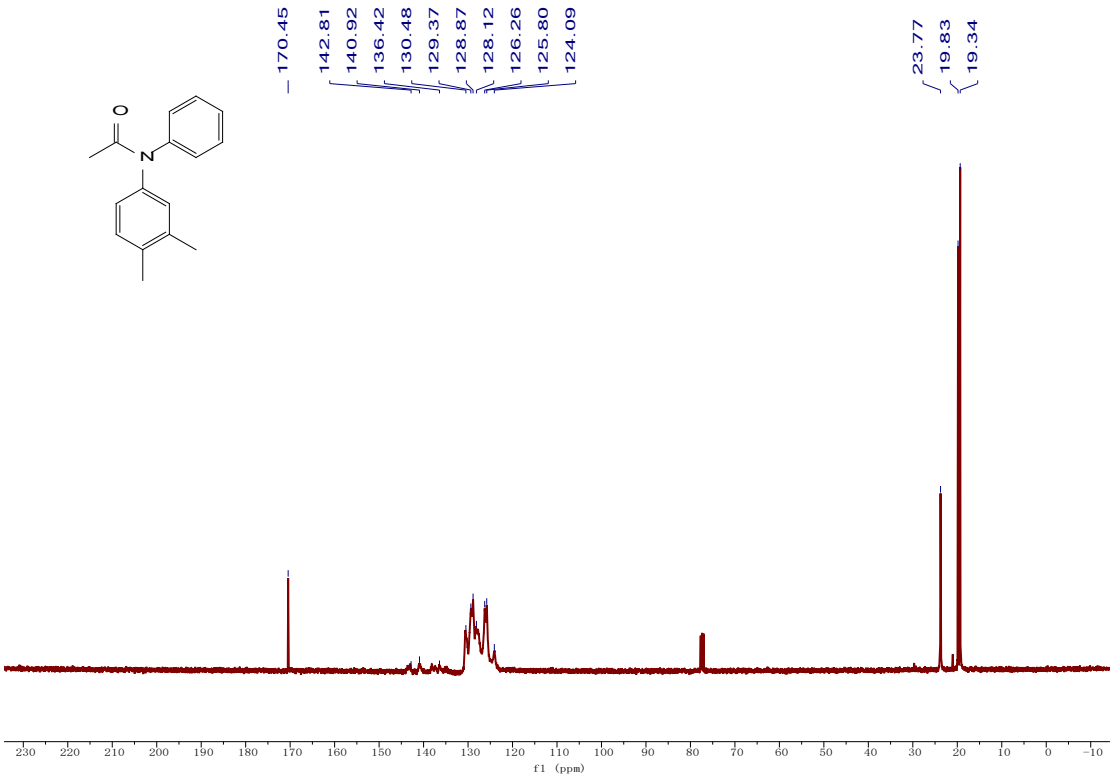
N-(6-ethyl-[1,1'-biphenyl]-3-yl)-N-phenylacetamide (2o)



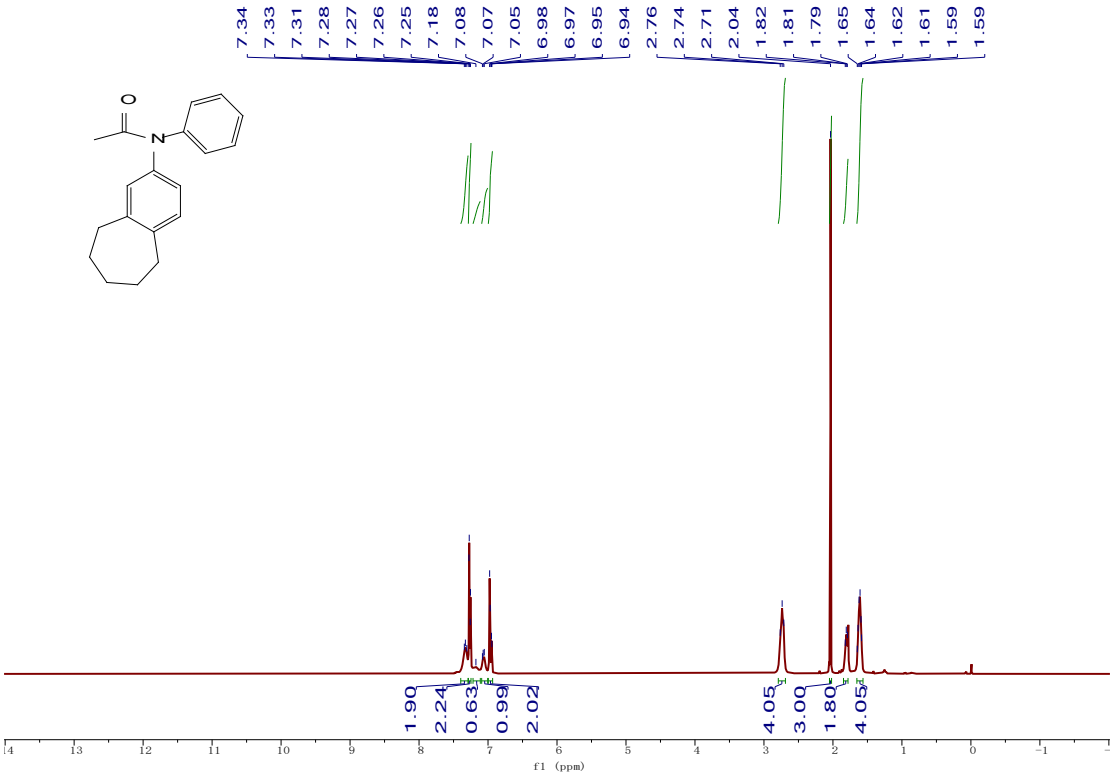


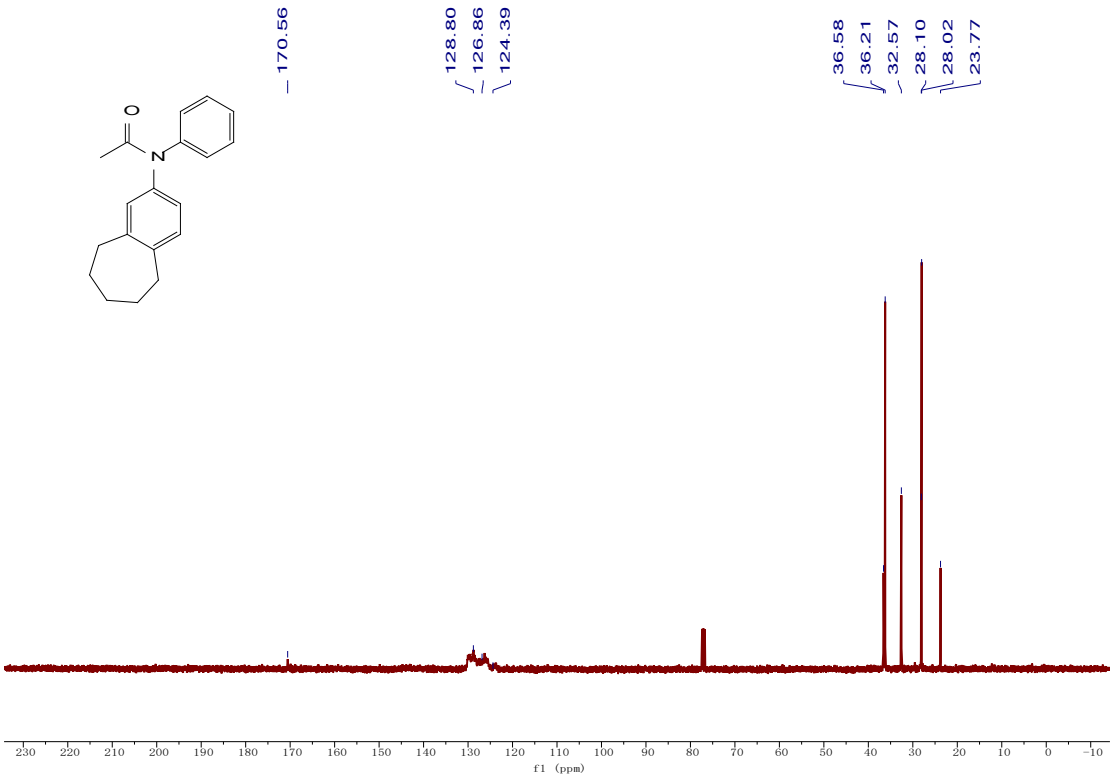
N-(3,4-dimethylphenyl)-N-phenylacetamide (2p)





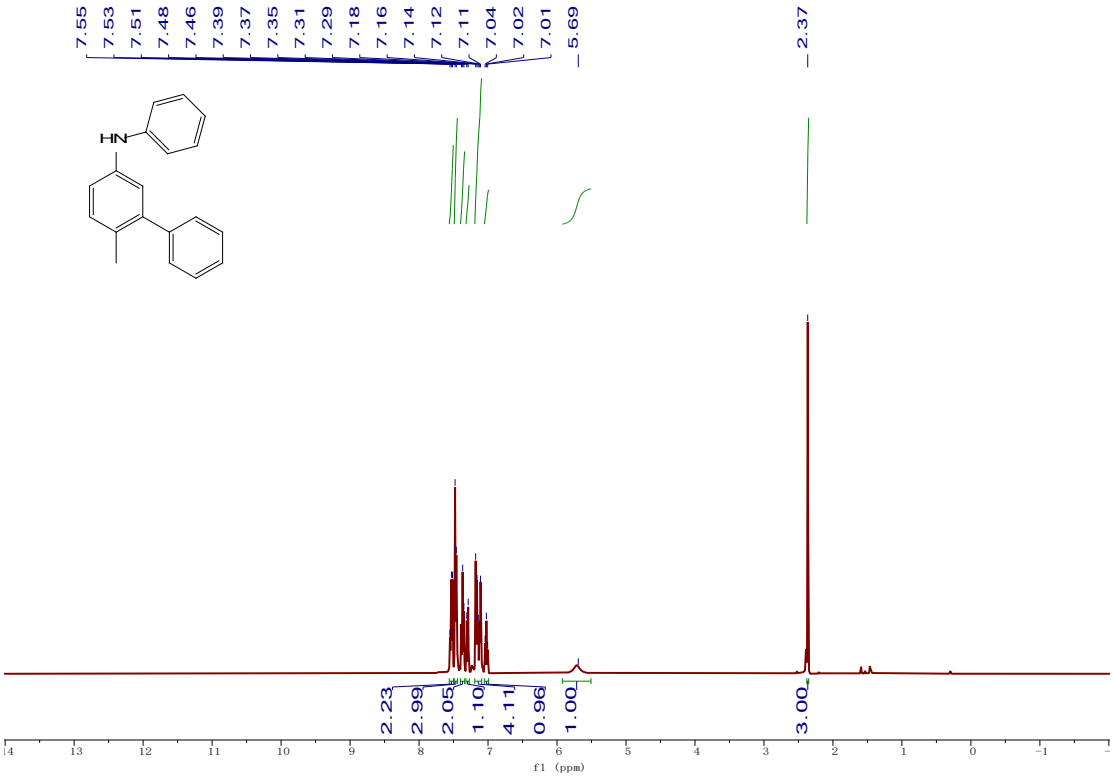
N-phenyl-N-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-2-yl)acetamide (2q)

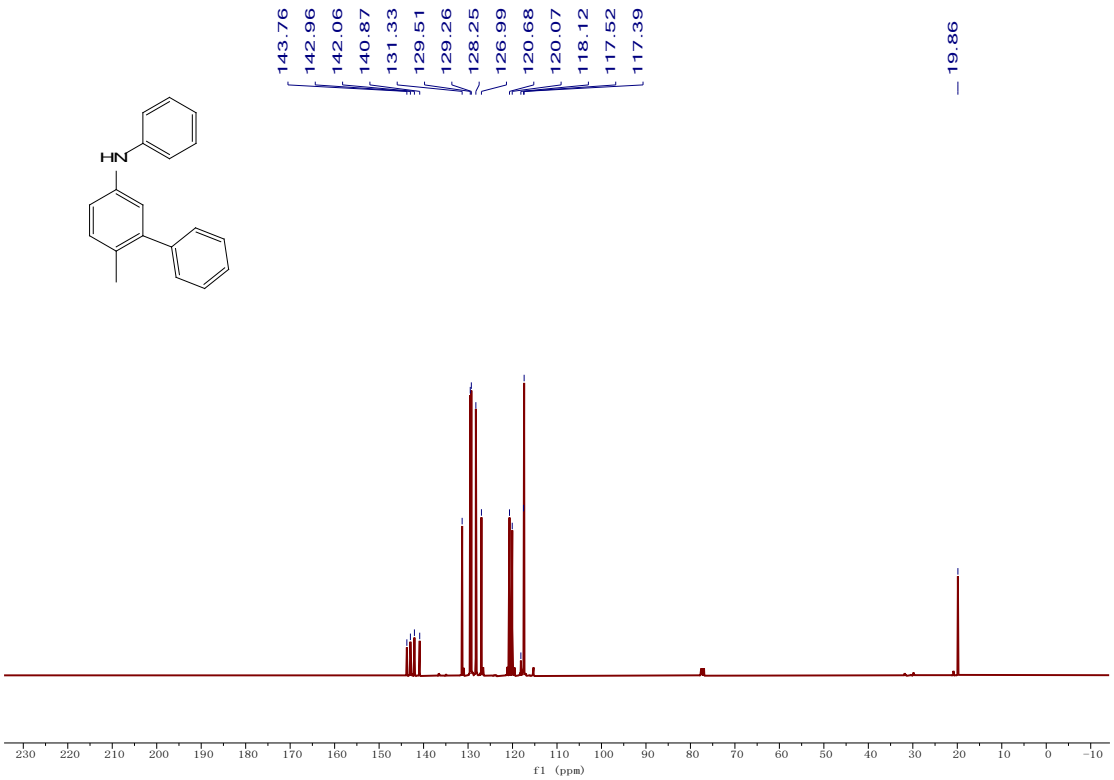




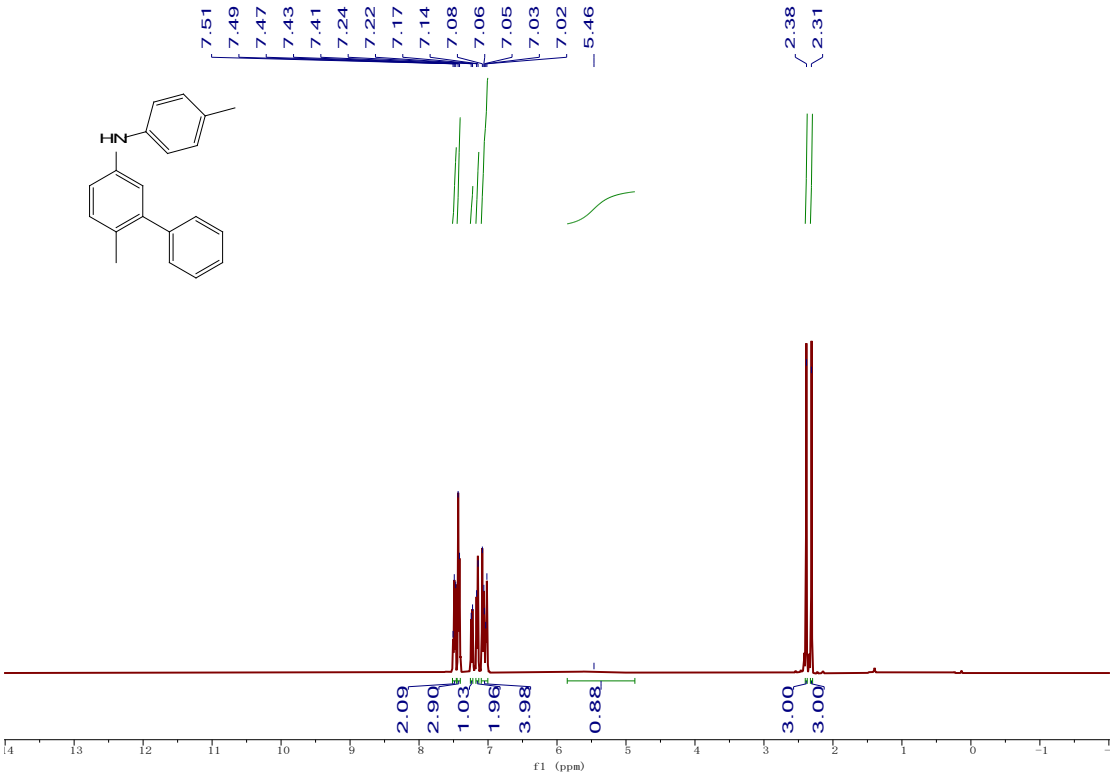
3.2 ^{1}H NMR and ^{13}C NMR spectra of products 2a'~2q'.

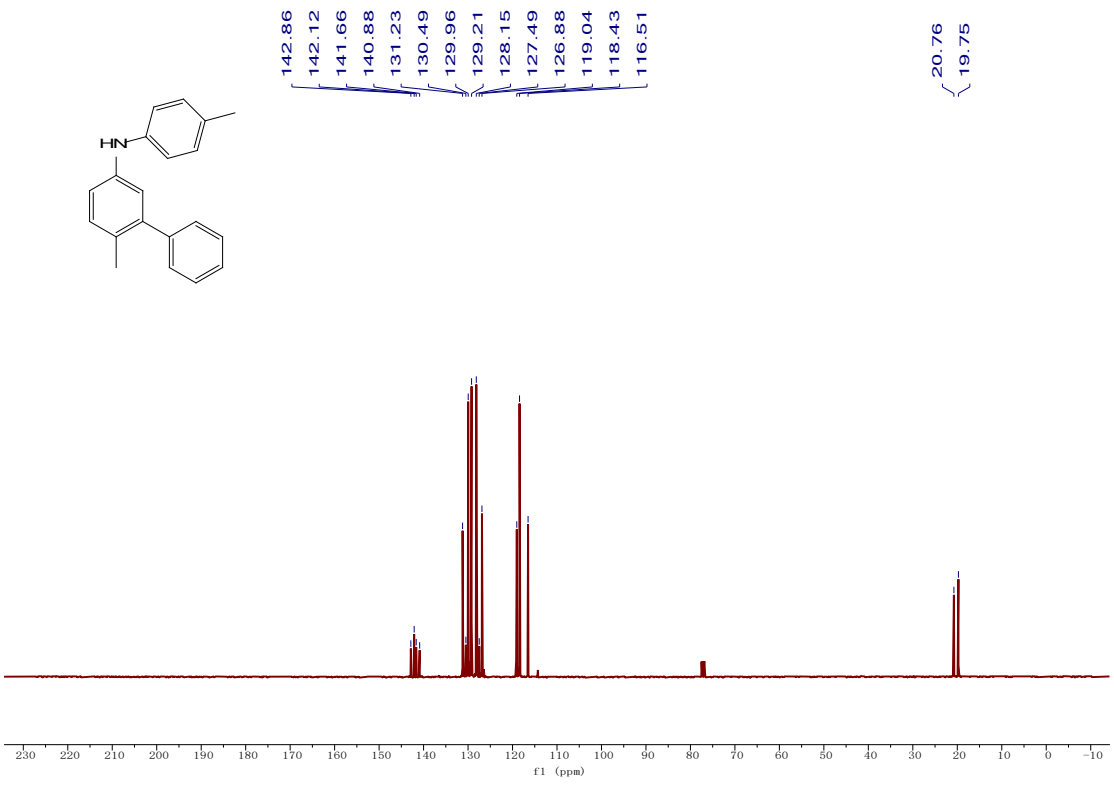
6-methyl-N-phenyl-[1,1'-biphenyl]-3-amine (2a')



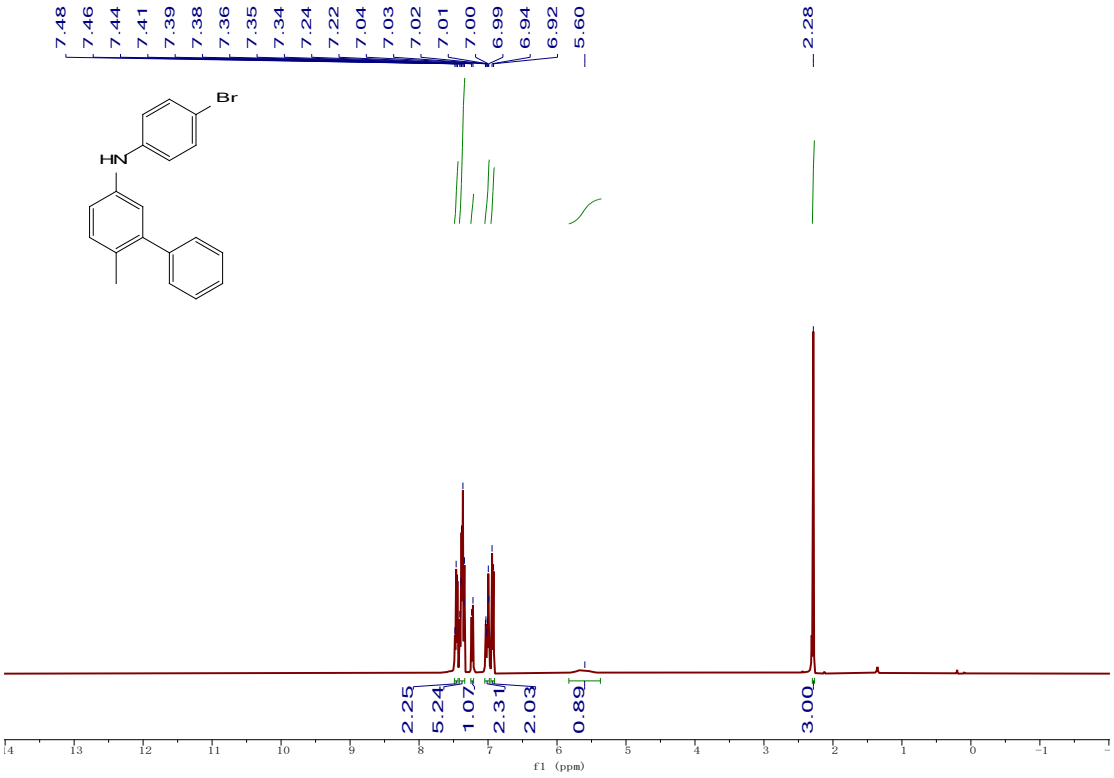


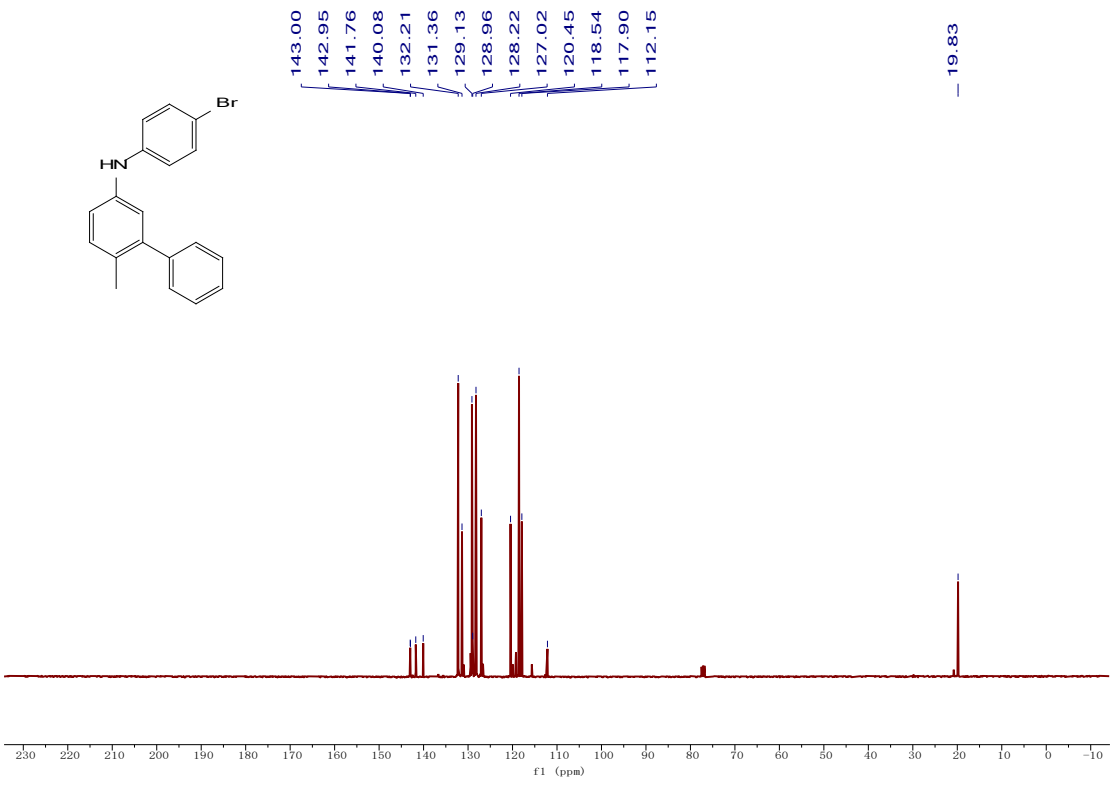
6-methyl-N-(p-tolyl)-[1,1'-biphenyl]-3-amine (2b'）



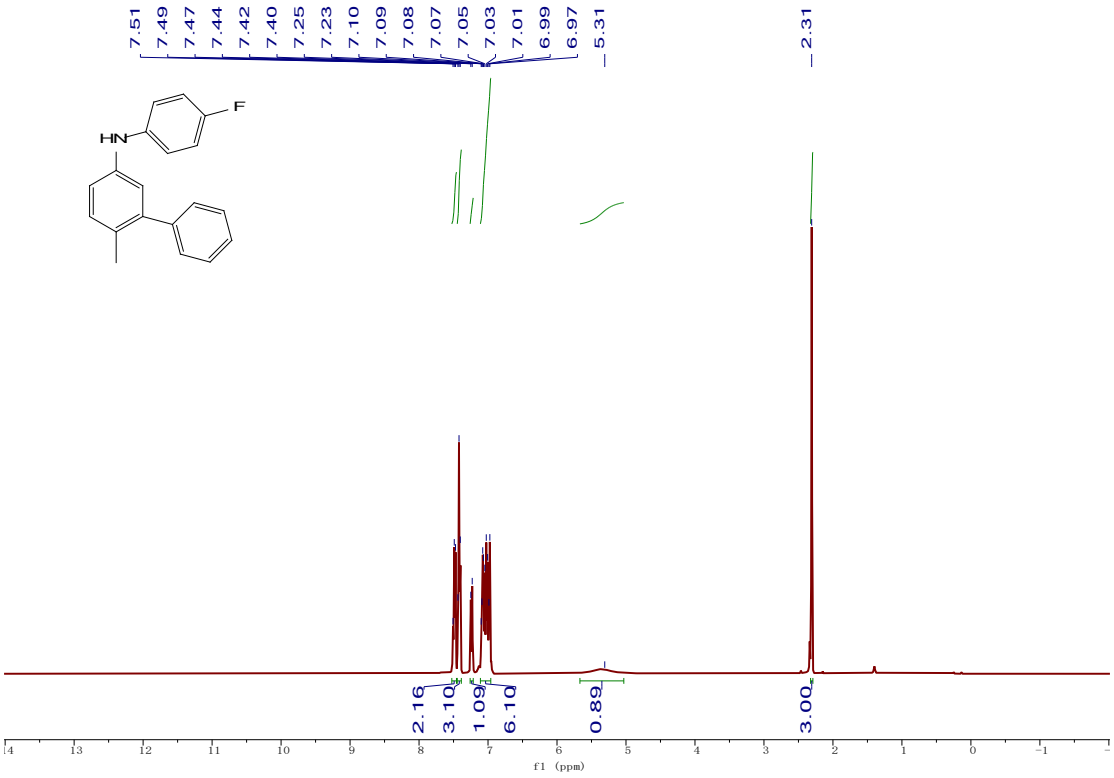


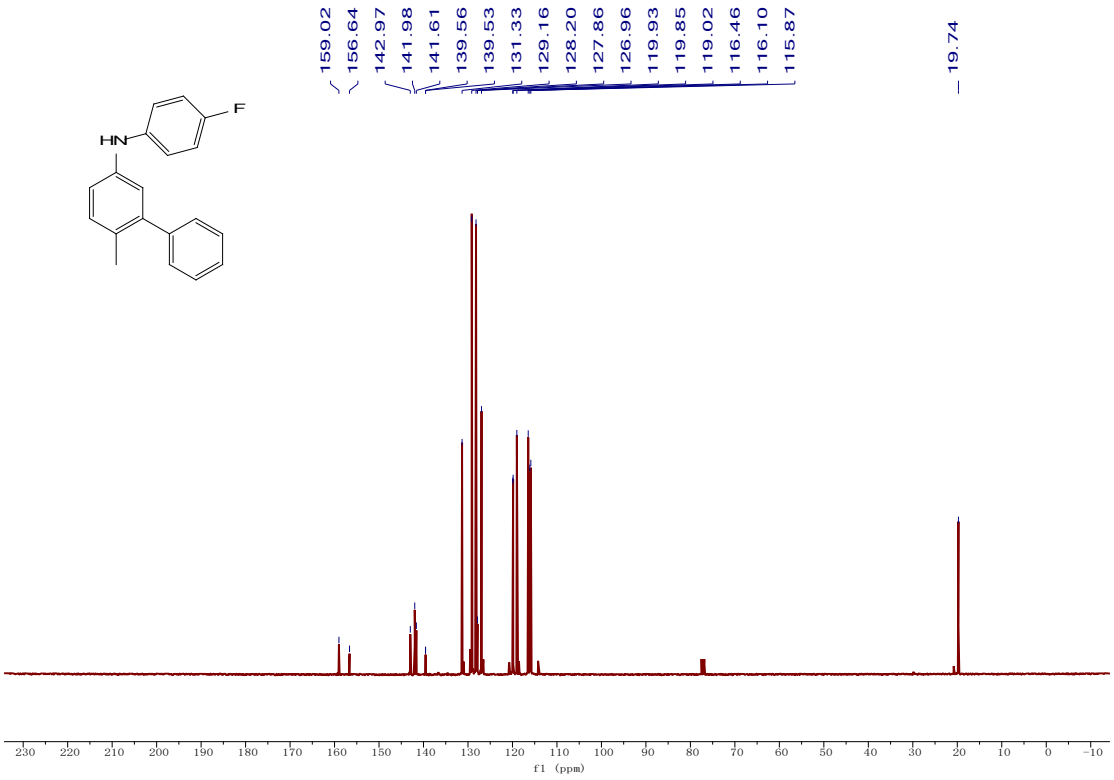
N-(4-bromophenyl)-6-methyl-[1,1'-biphenyl]-3-amine (2c')



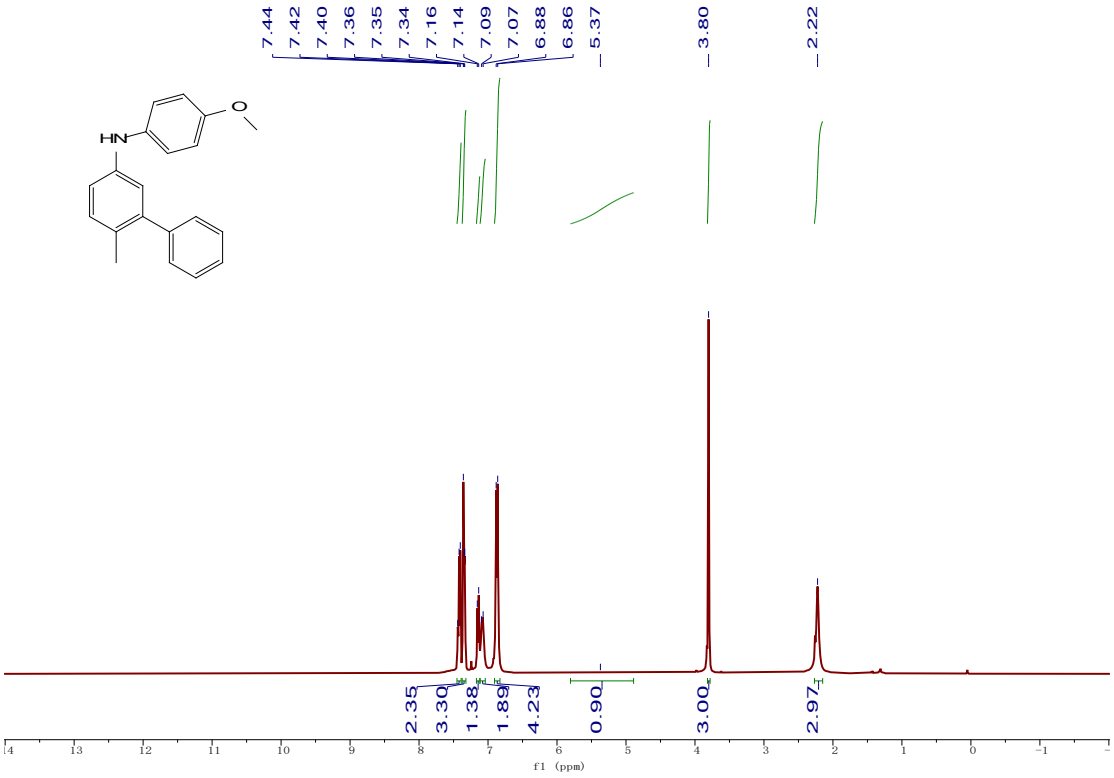


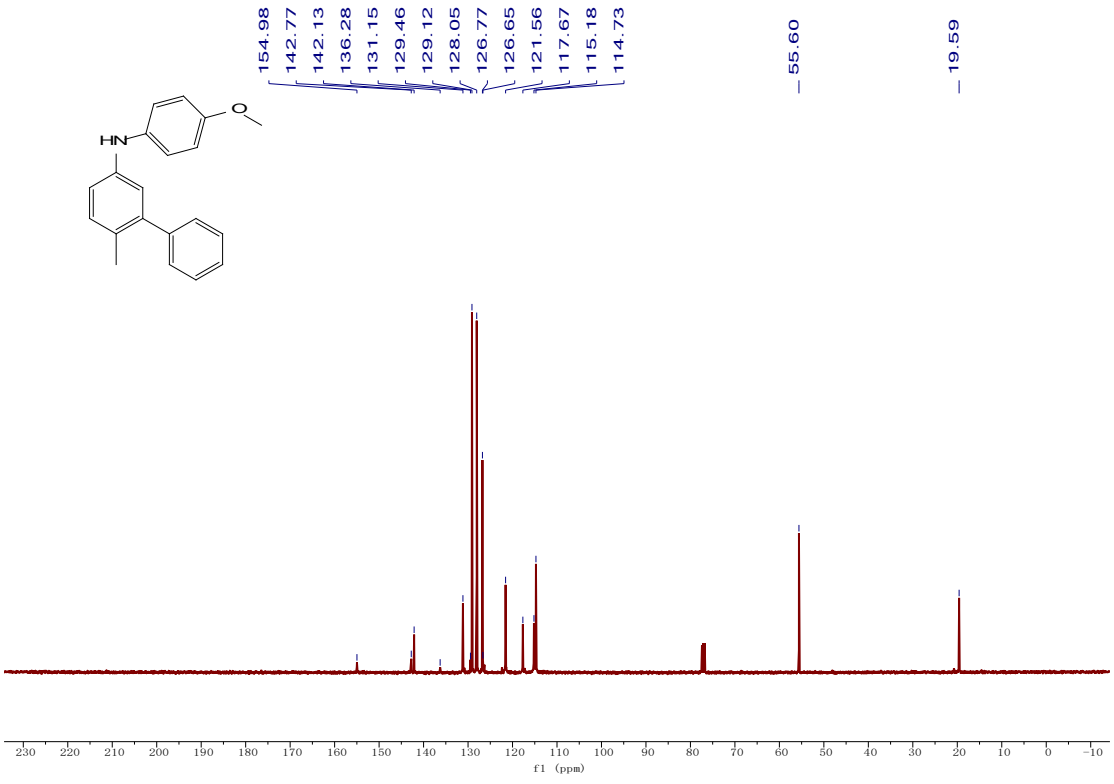
N-(4-fluorophenyl)-6-methyl-[1,1'-biphenyl]-3-amine (2d')



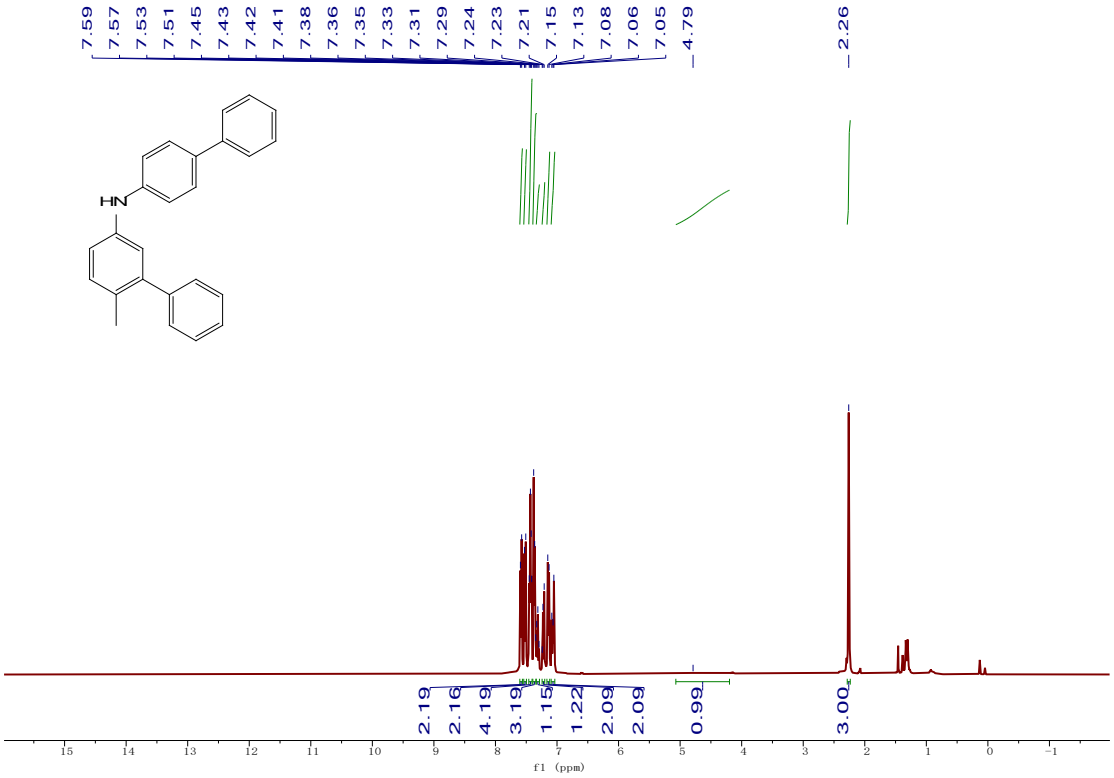


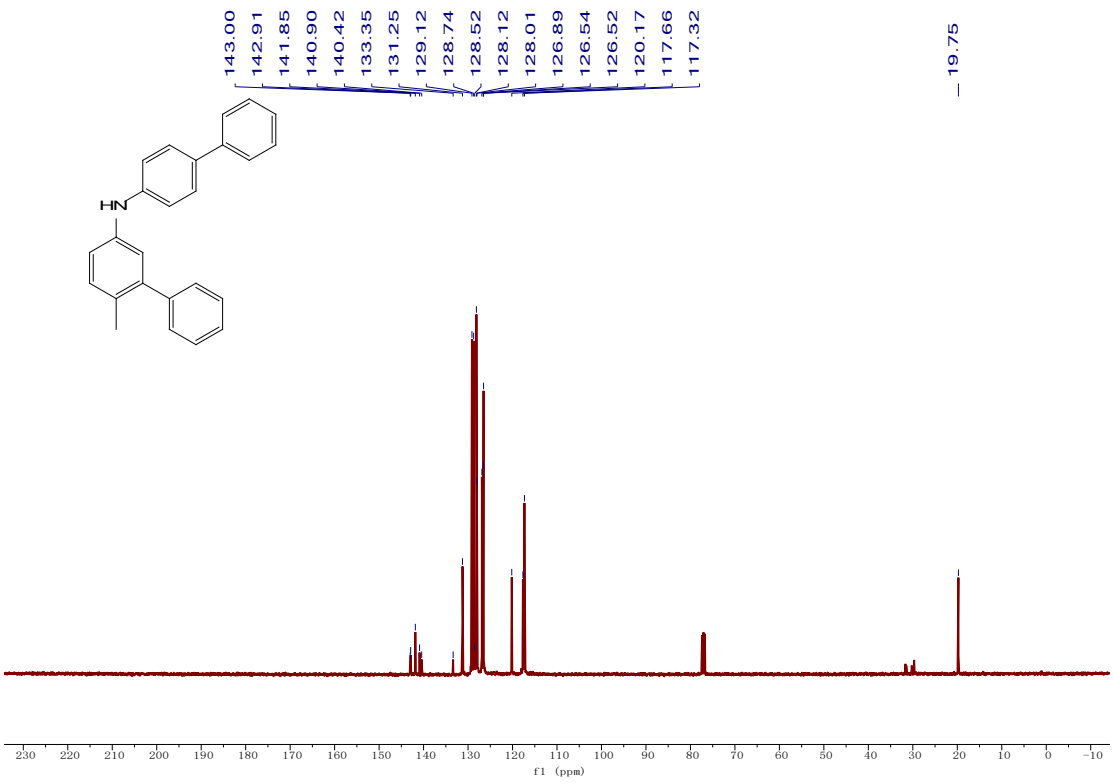
N-(4-methoxyphenyl)-6-methyl-[1,1'-biphenyl]-3-amine (2e')



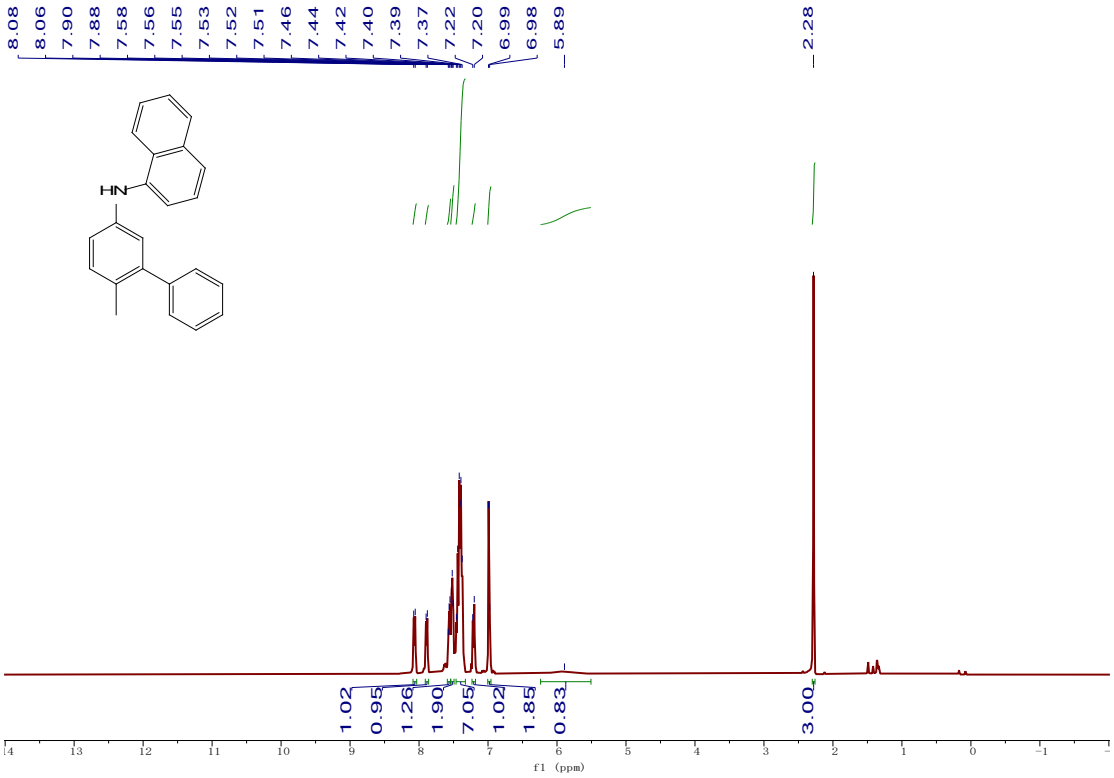


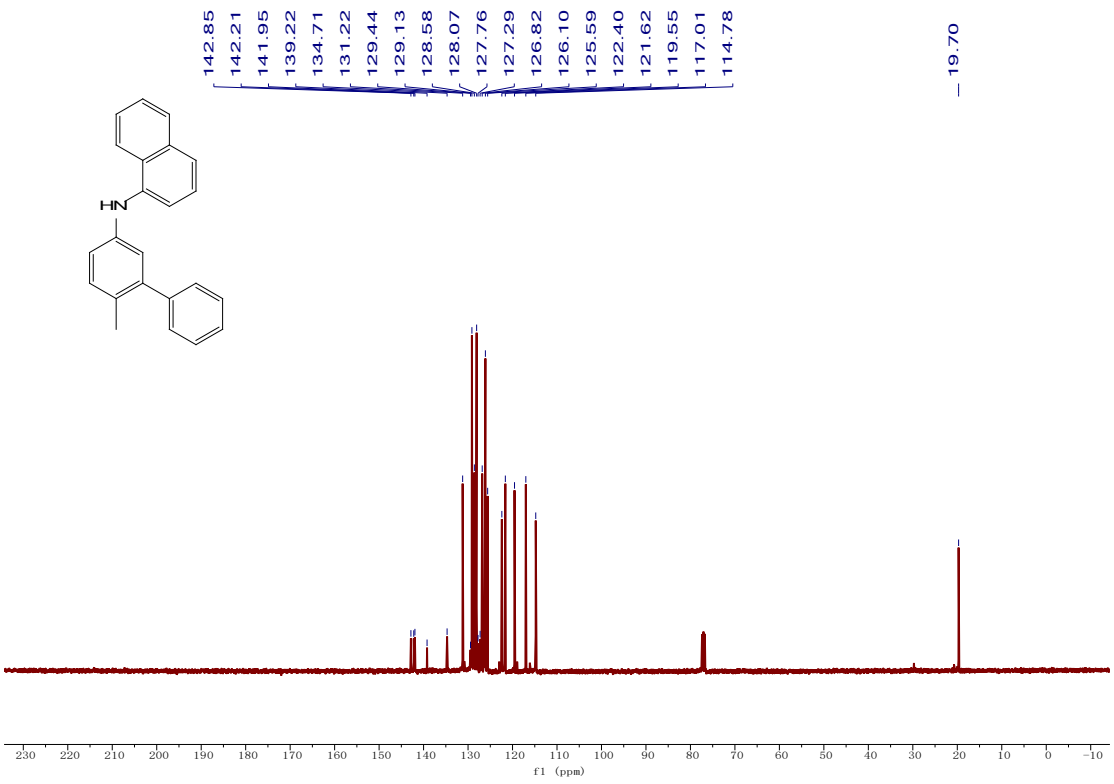
N-([1,1'-biphenyl]-4-yl)-6-methyl-[1,1'-biphenyl]-3-amine (2f')



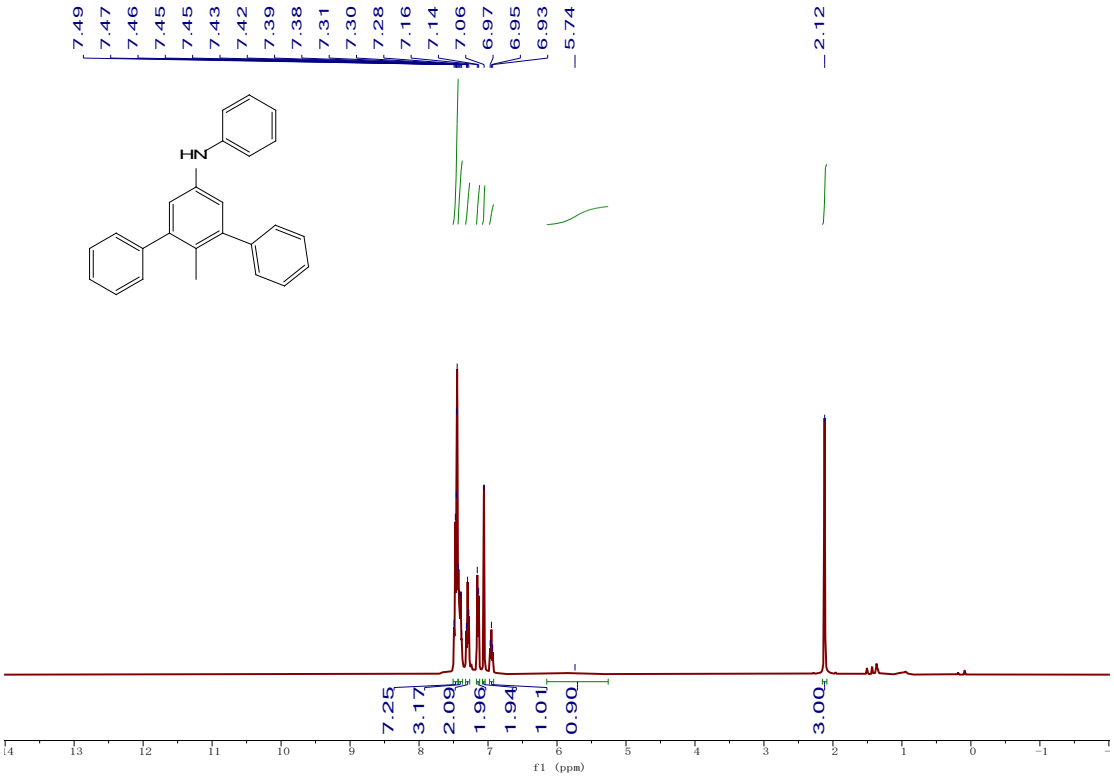


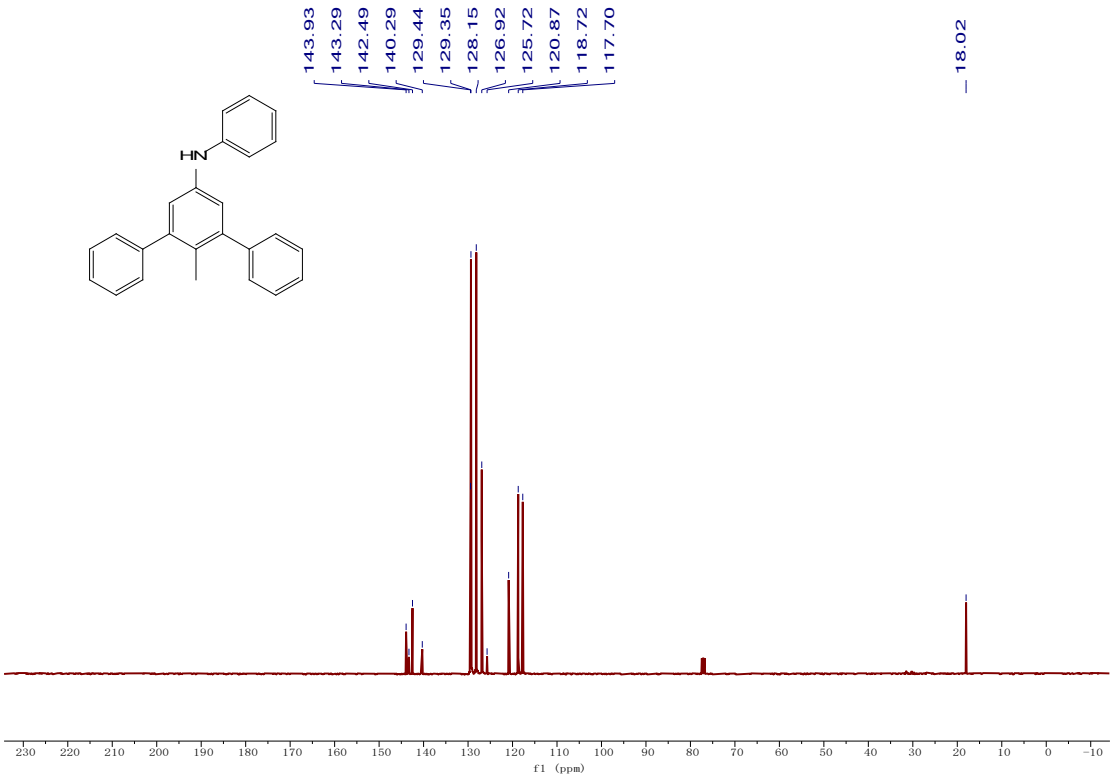
N-(6-methyl-[1,1'-biphenyl]-3-yl)naphthalen-1-amine (2g')



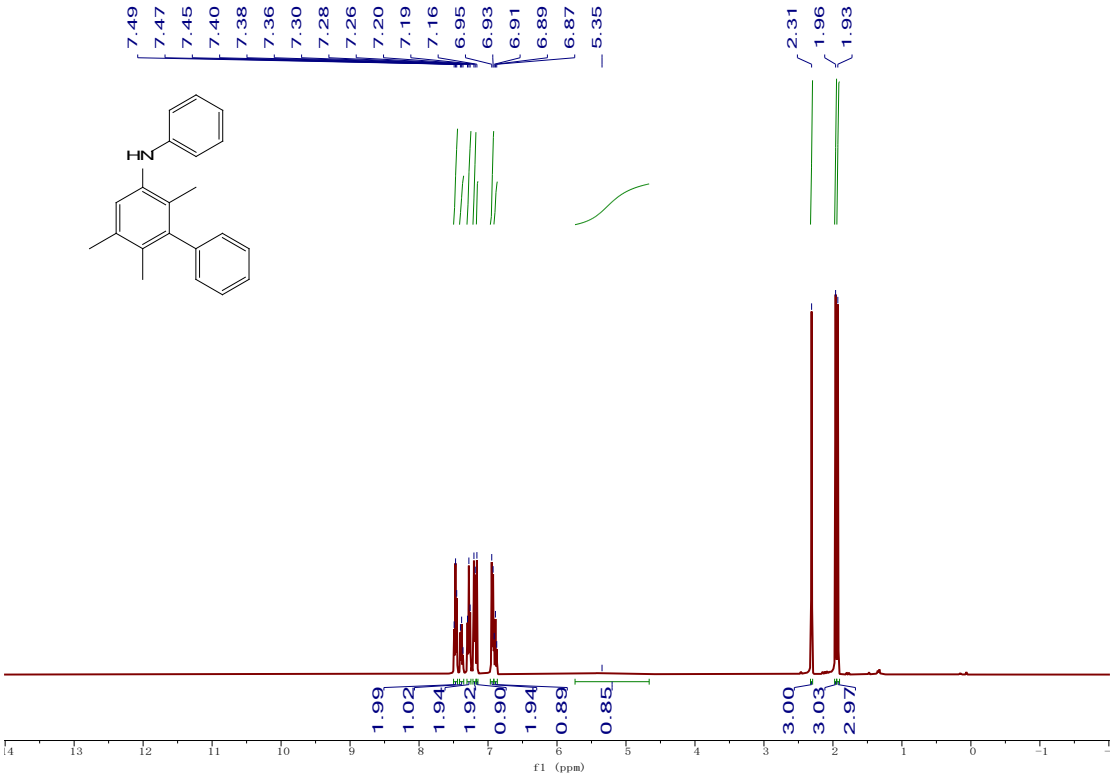


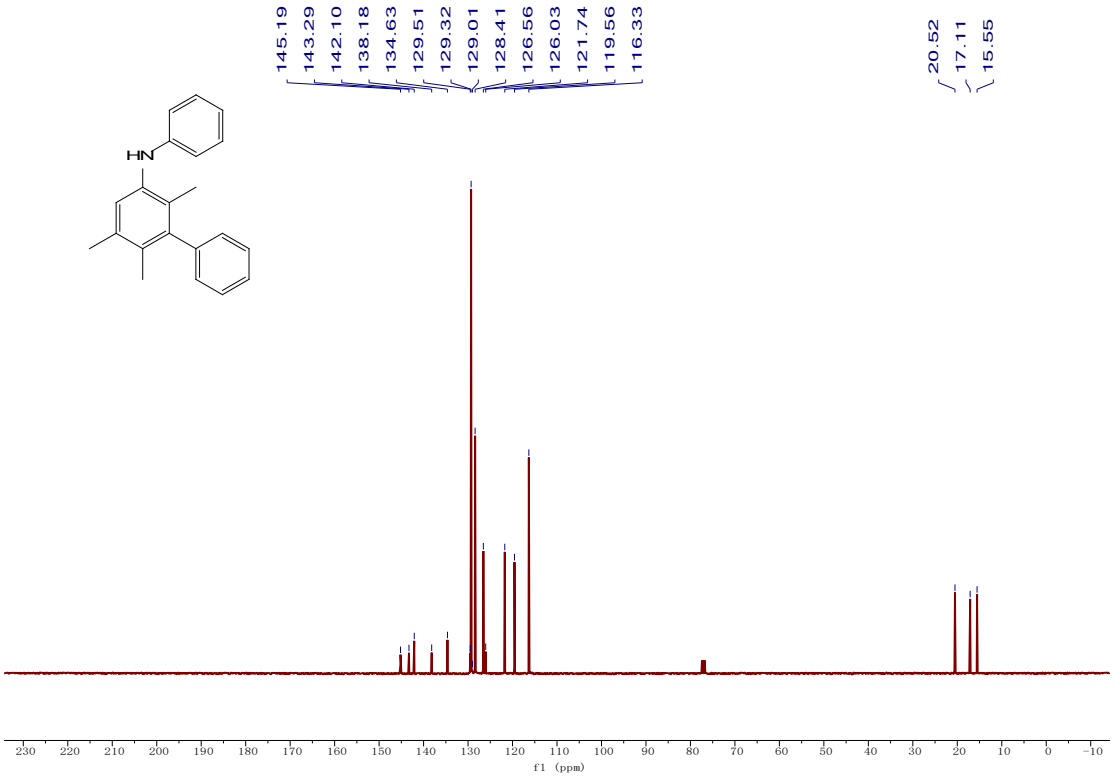
2'-methyl-N-phenyl-[1,1':3',1''-terphenyl]-5'-amine (2k')



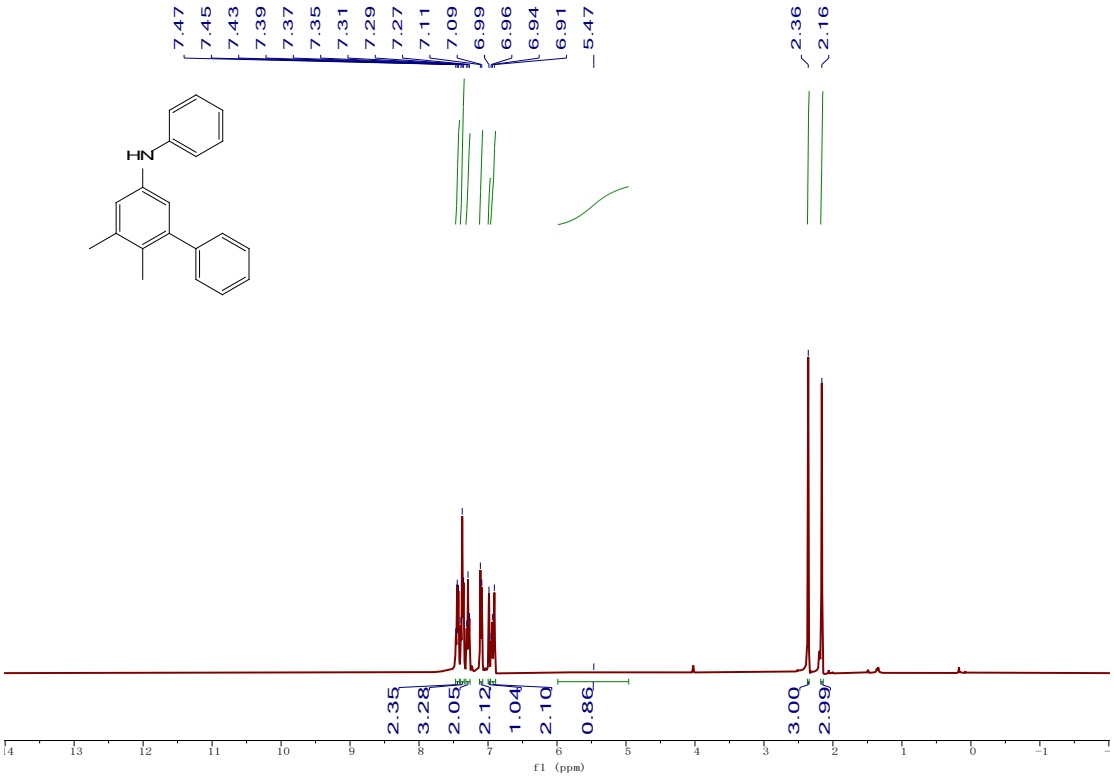


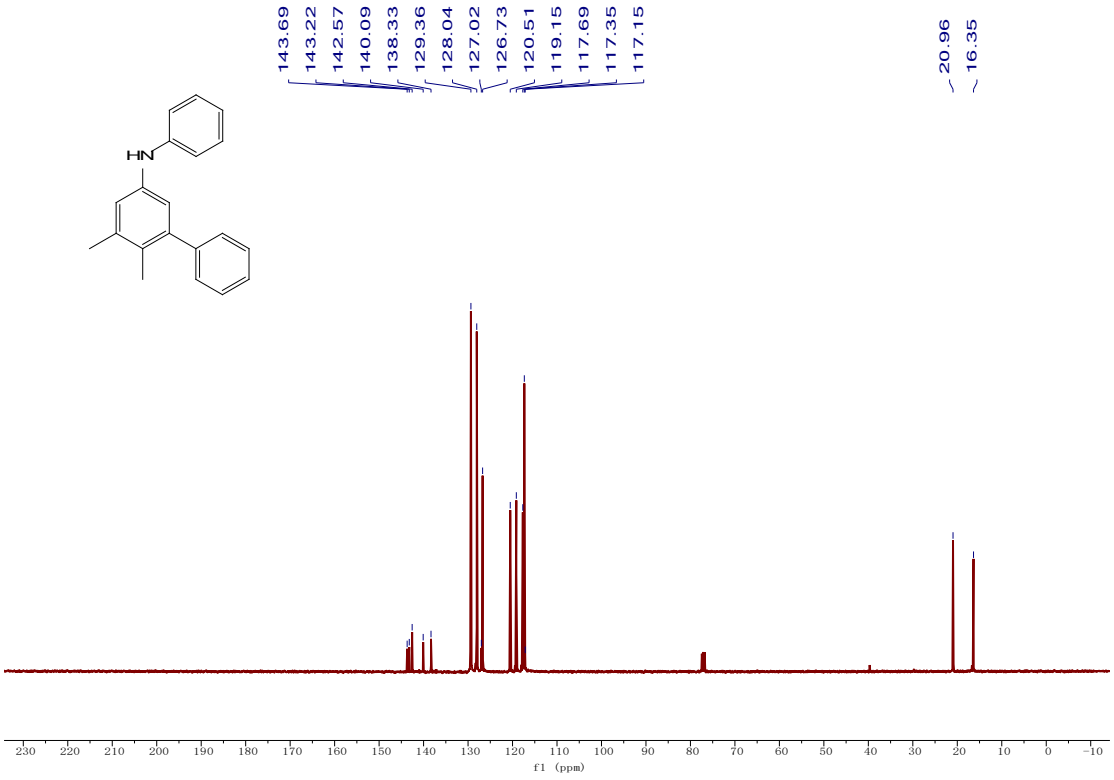
2,5,6-trimethyl-N-phenyl-[1,1'-biphenyl]-3-amine (2l')



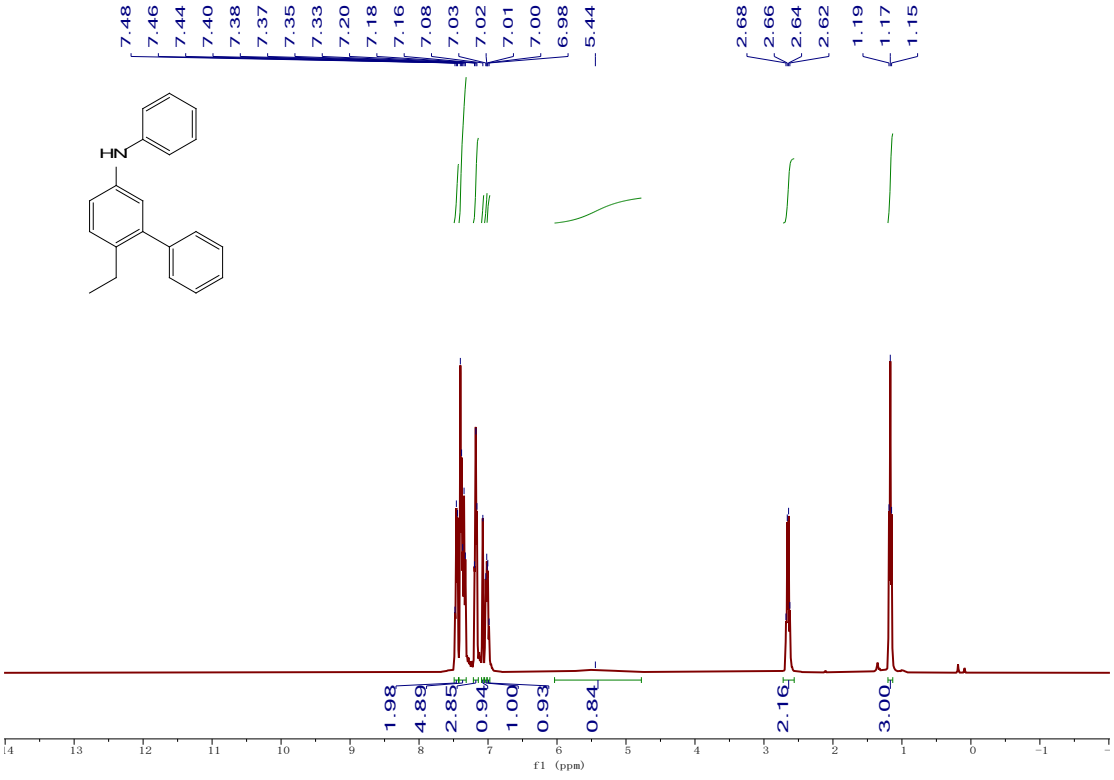


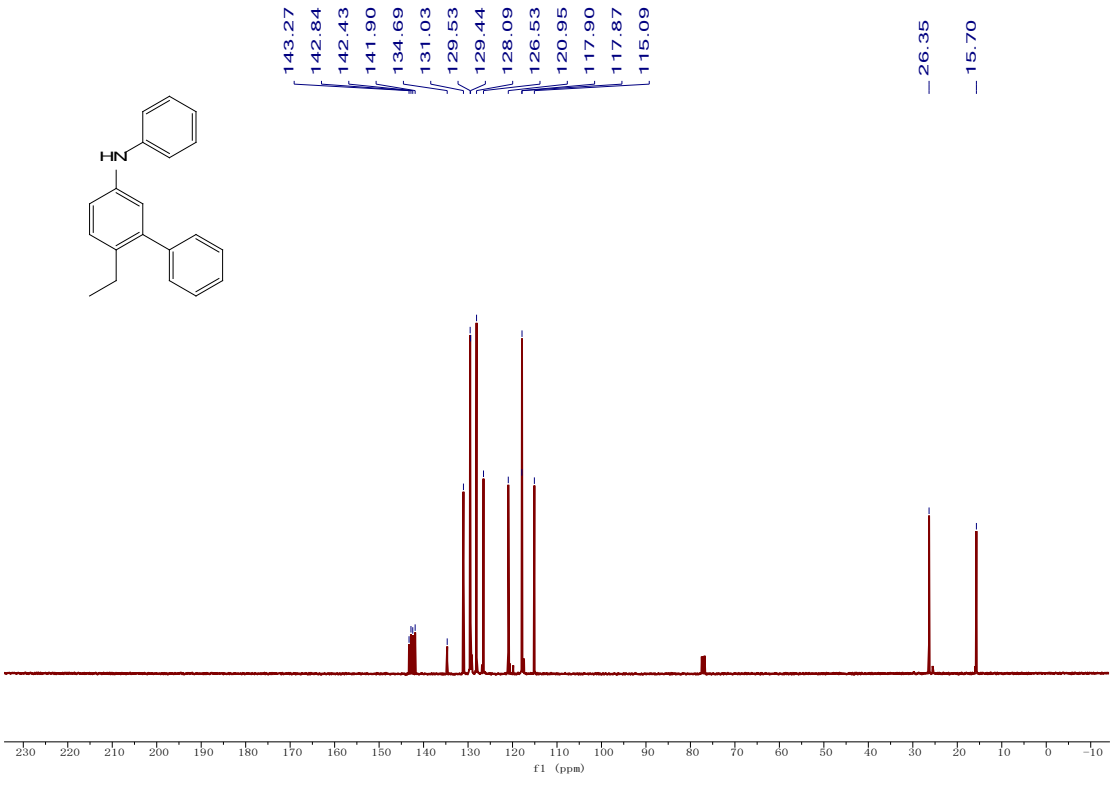
5,6-dimethyl-N-phenyl-[1,1'-biphenyl]-3-amine (2m')



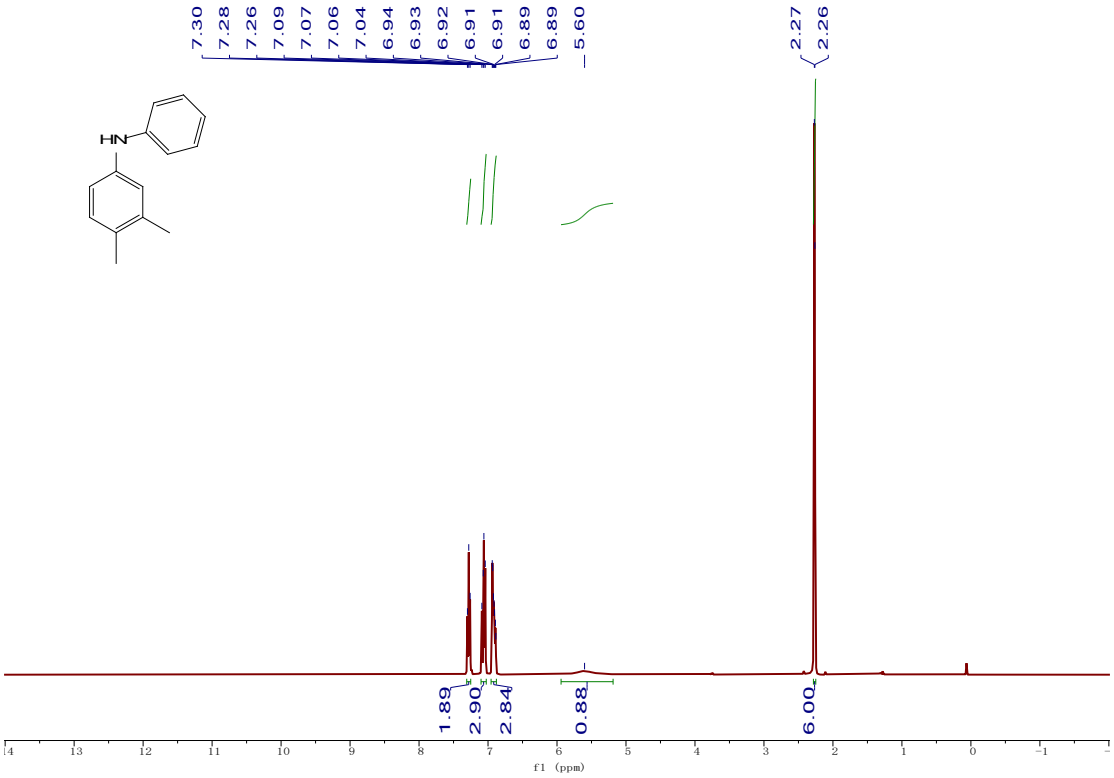


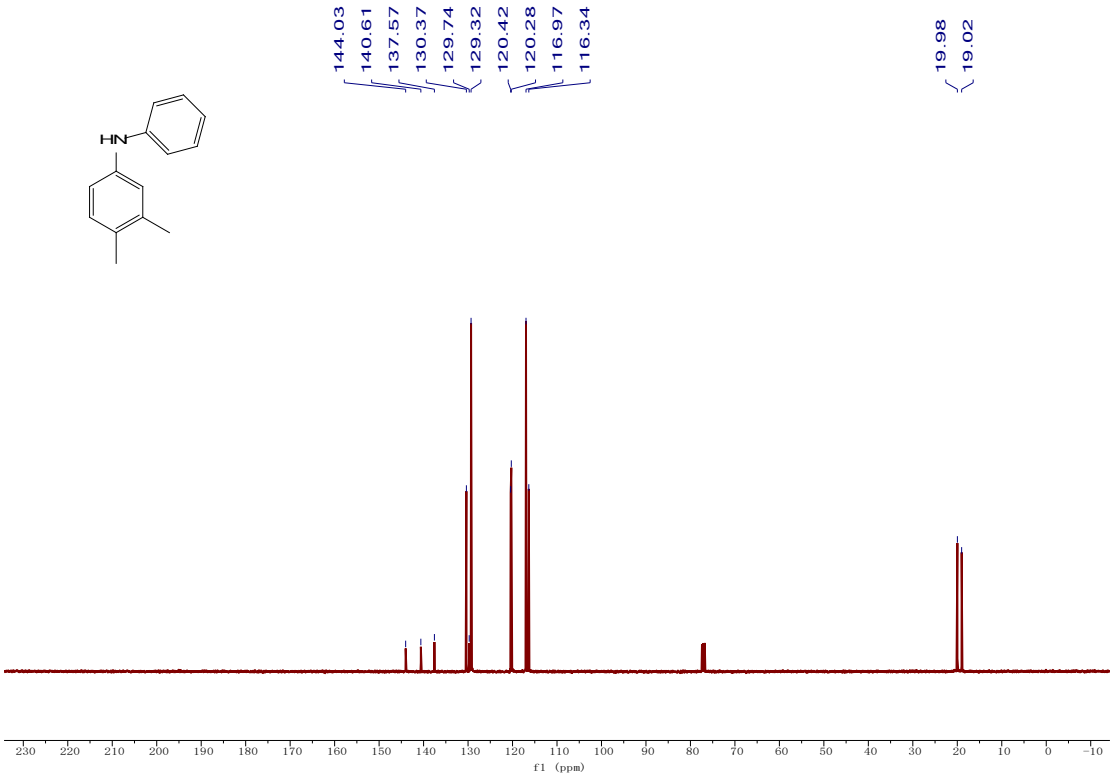
6-ethyl-N-phenyl-[1,1'-biphenyl]-3-amine (2o')



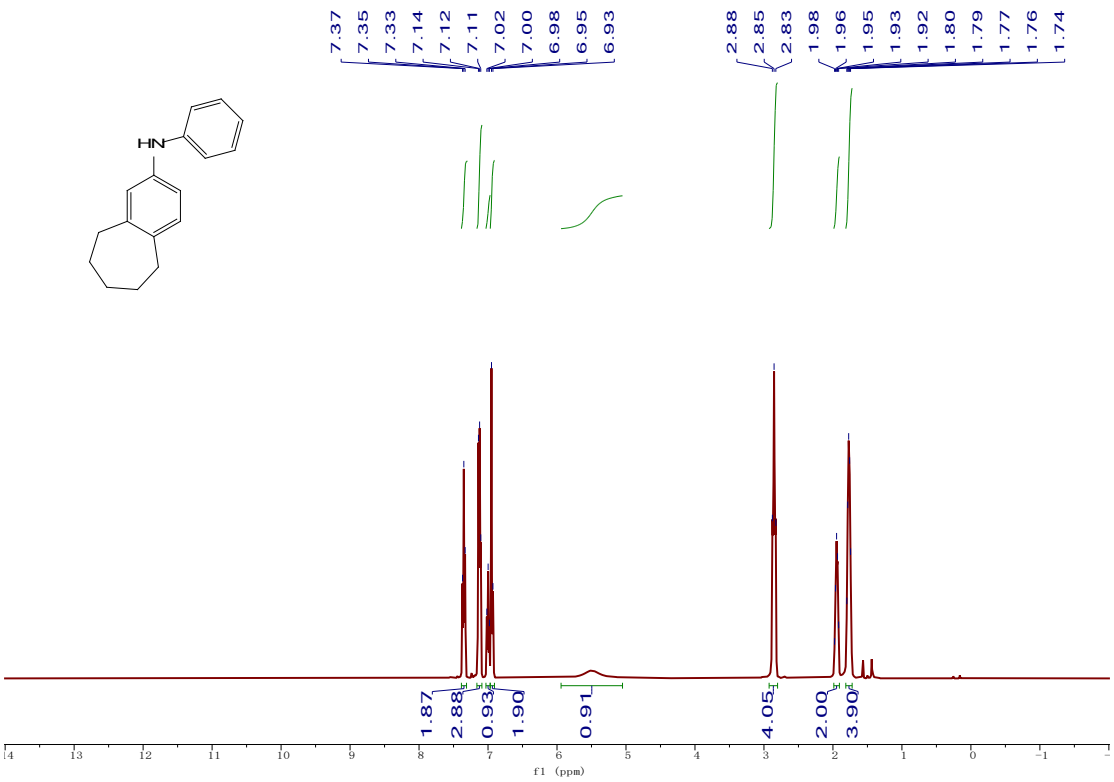


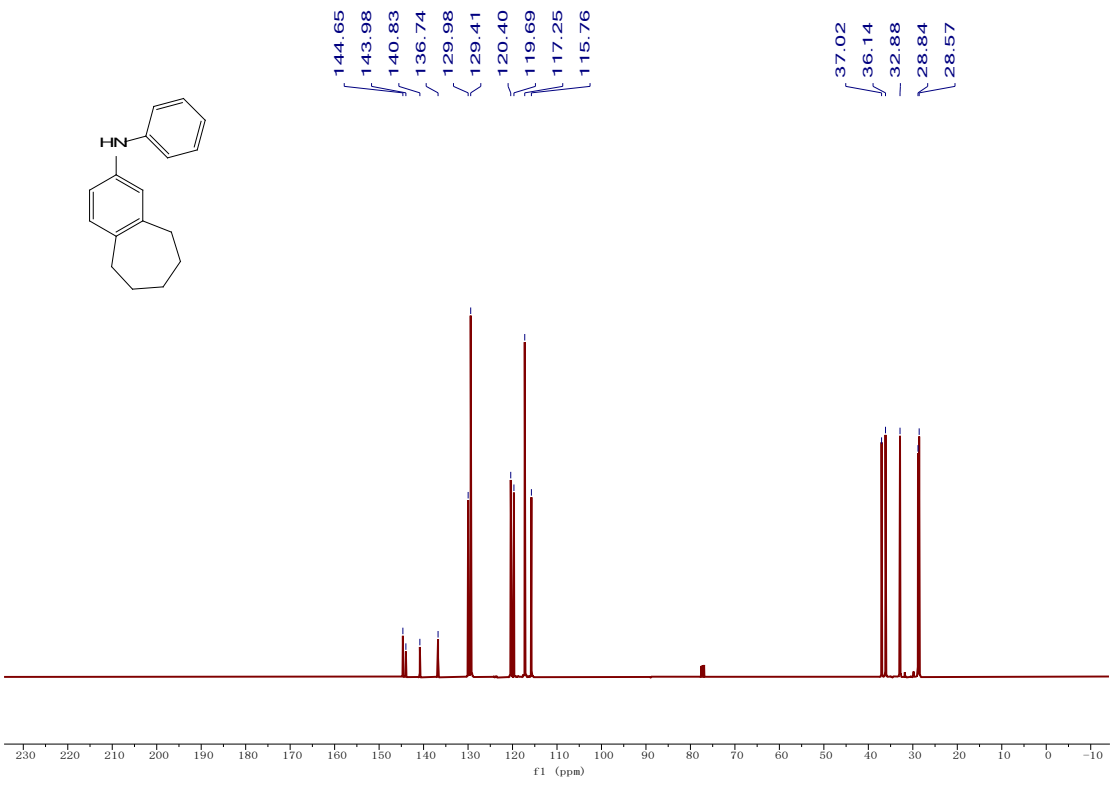
3,4-dimethyl-N-phenylaniline (2p')





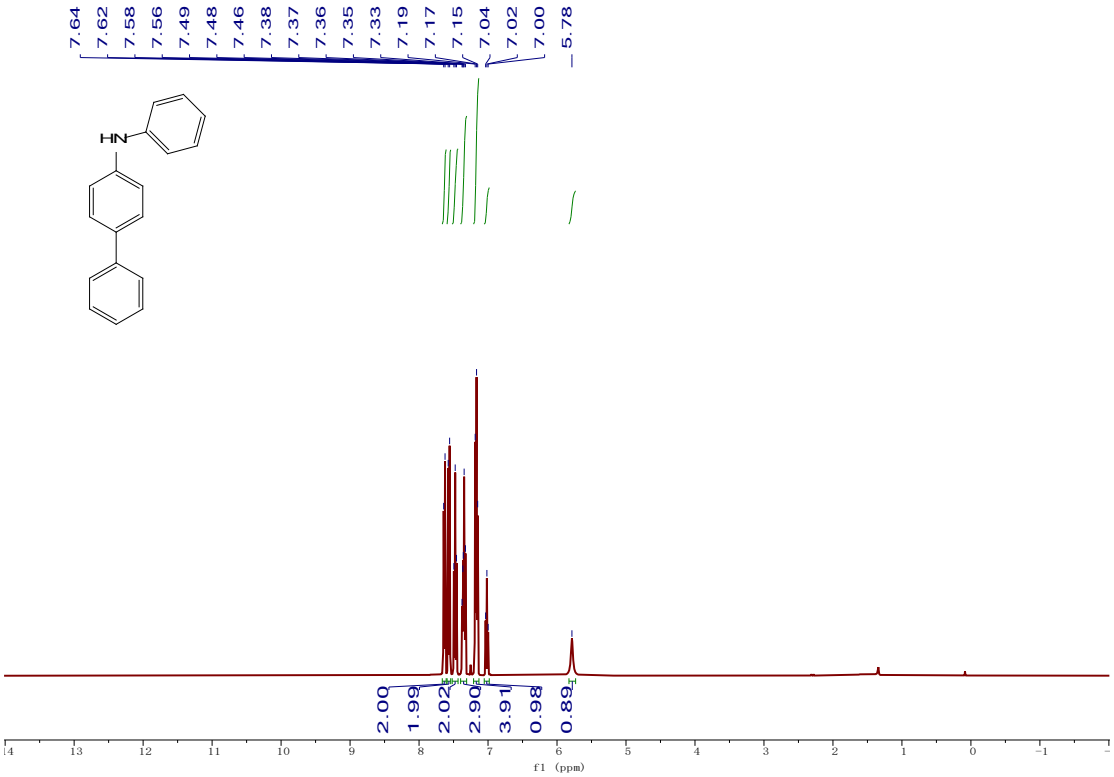
N-phenyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-2-amine (2q')

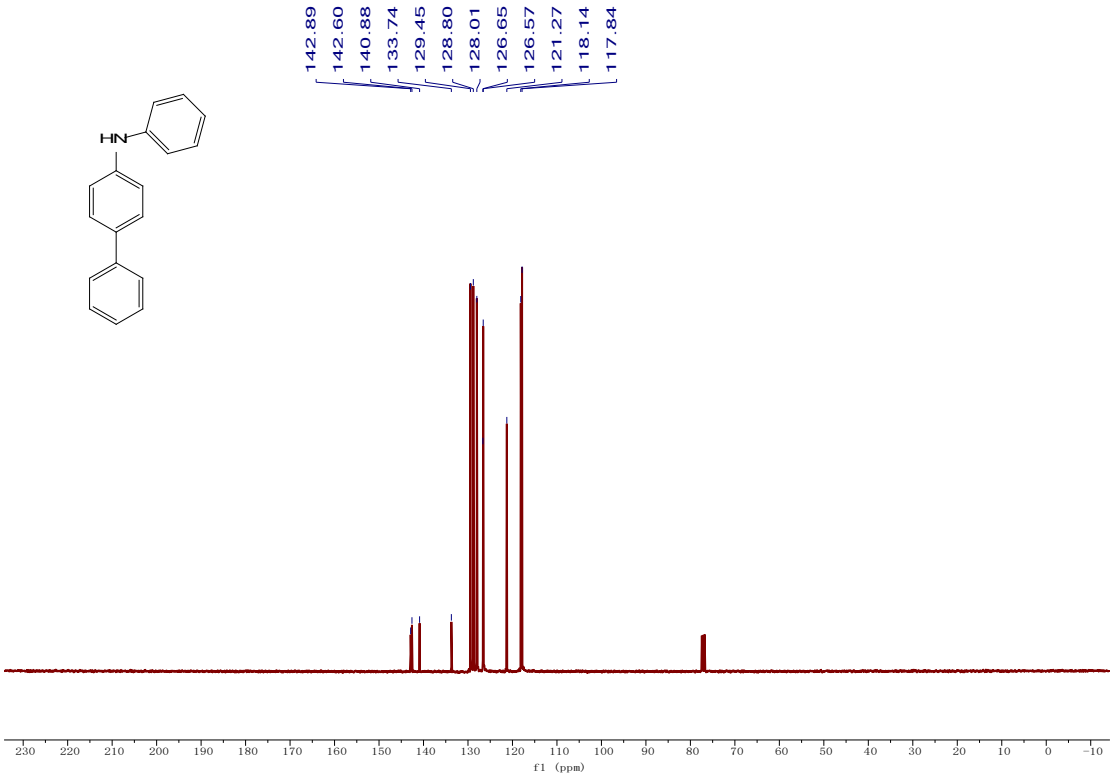




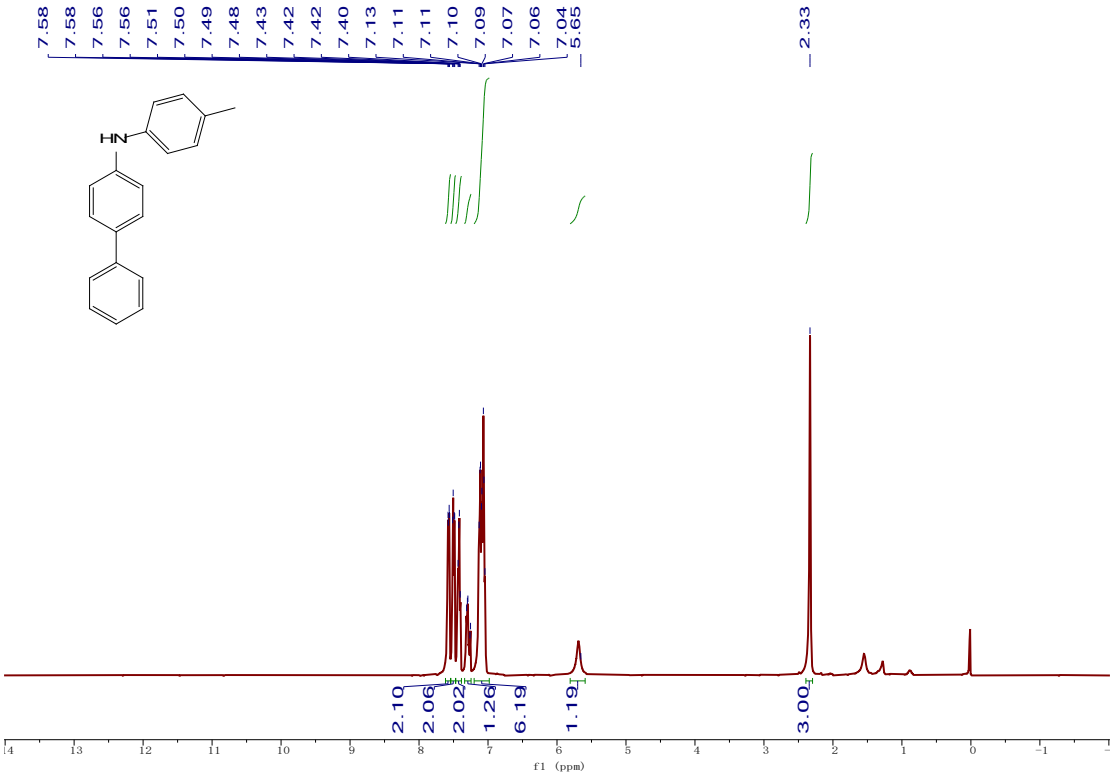
3.3 ^{1}H NMR and ^{13}C NMR spectra of products 3a~3r.

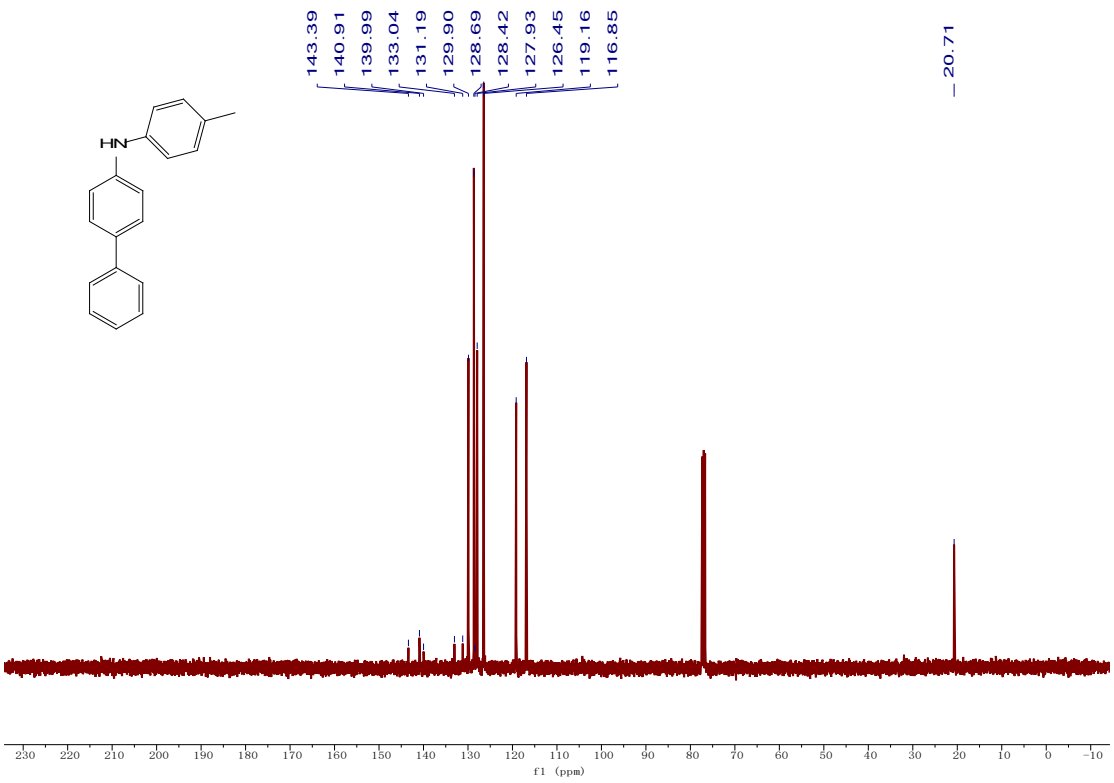
N-phenyl-[1,1'-biphenyl]-4-amine (3a)



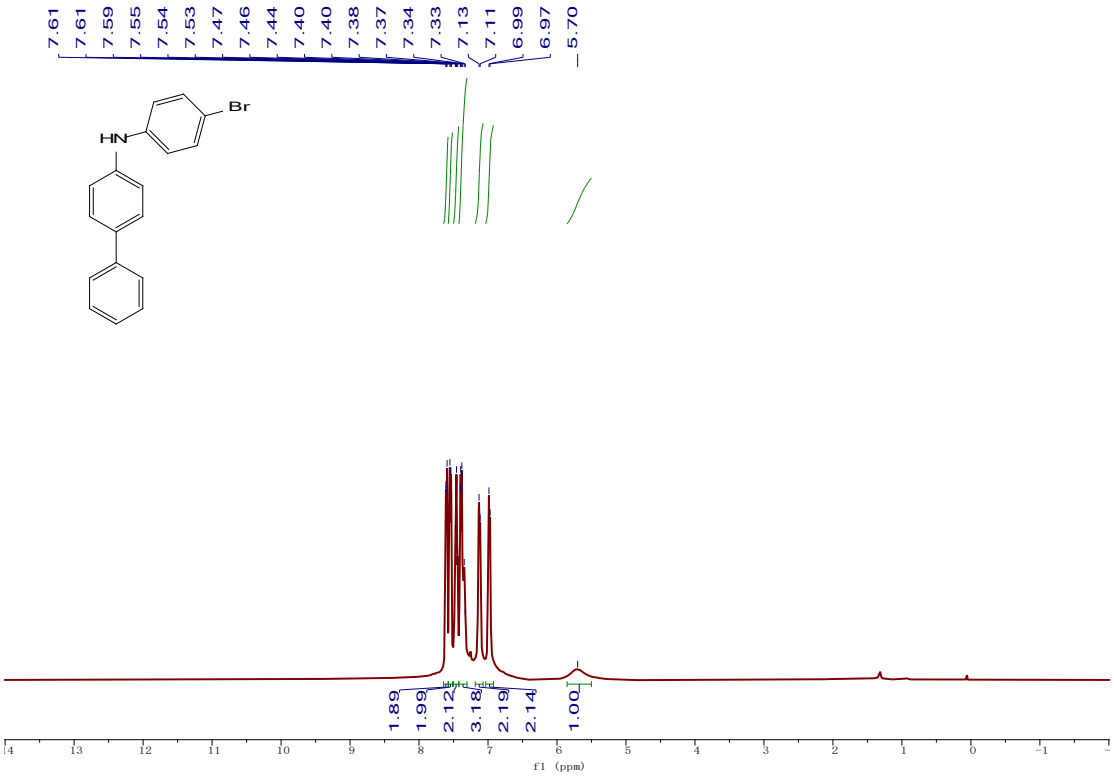


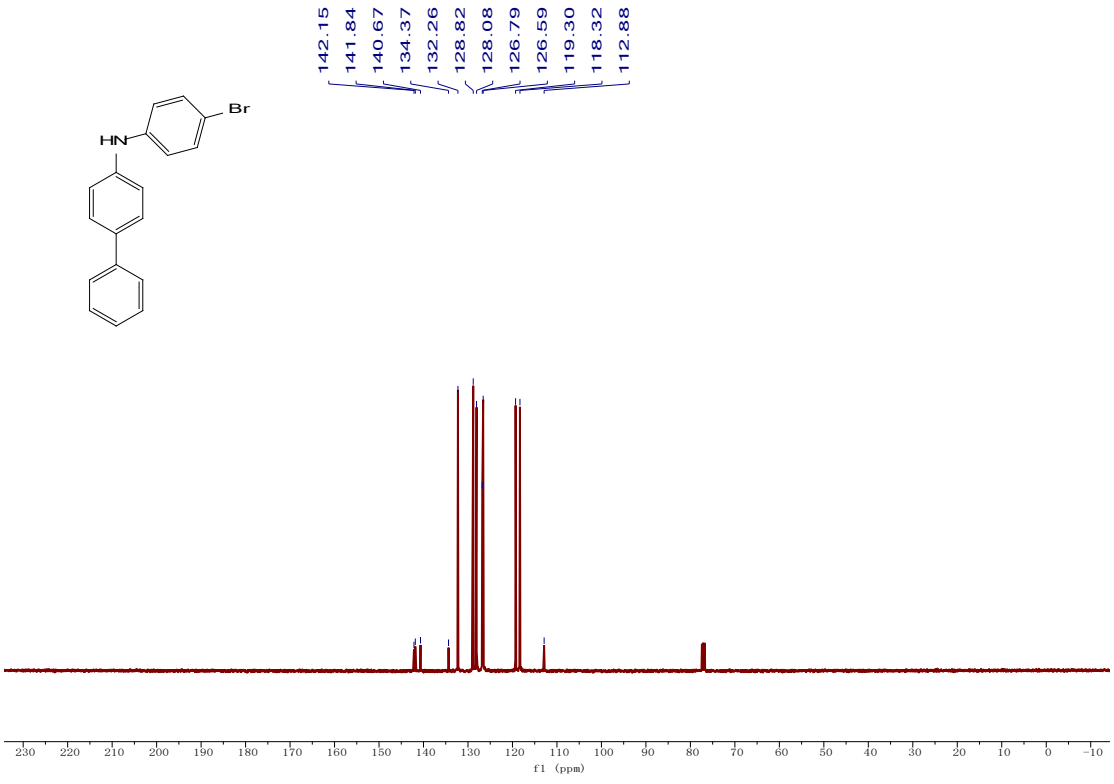
N-(p-tolyl)-[1,1'-biphenyl]-4-amine (3b)



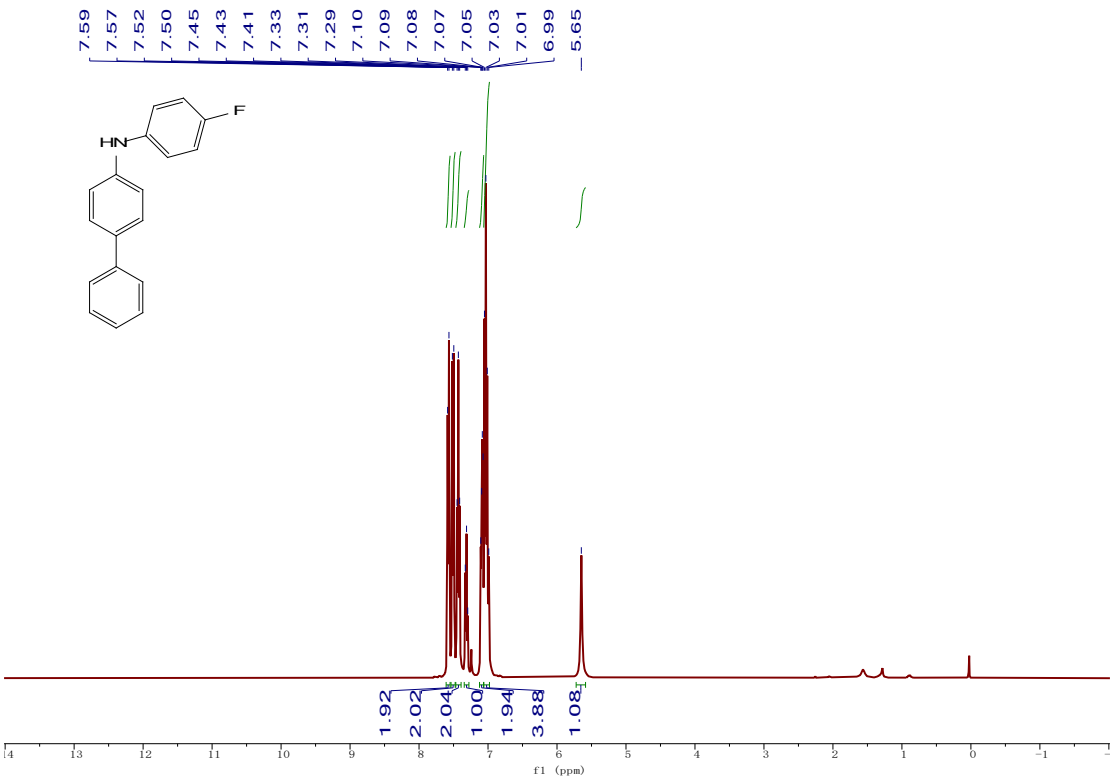


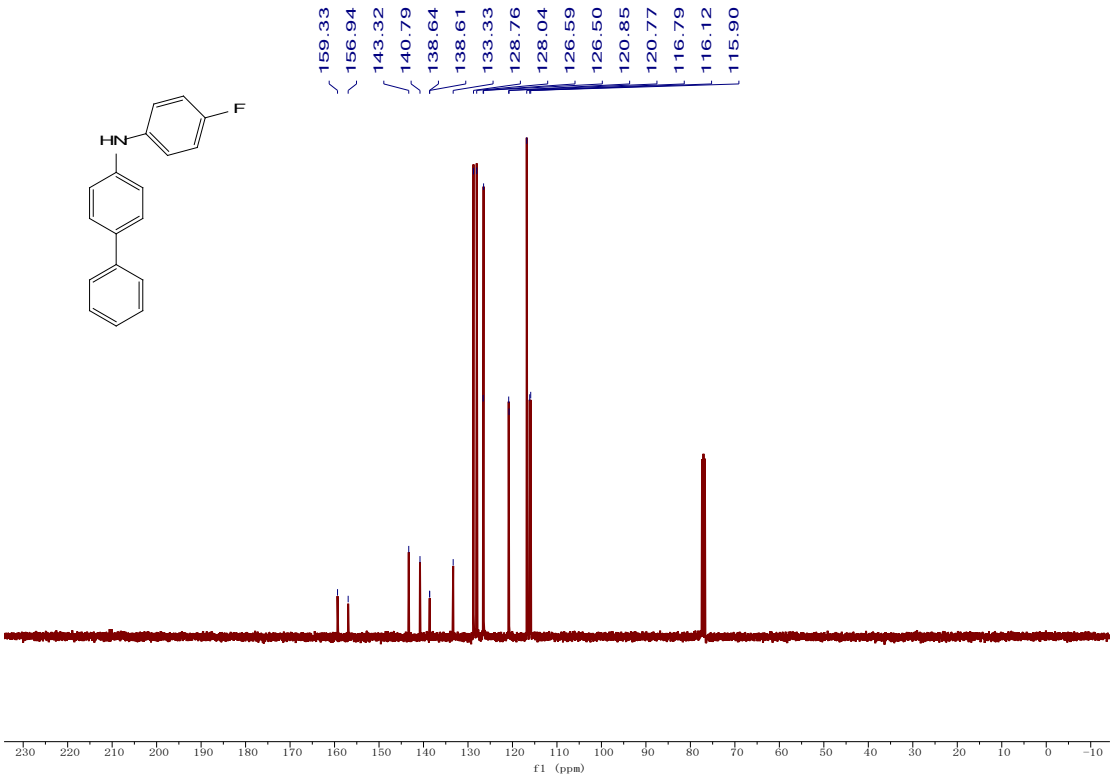
N-(4-bromophenyl)-[1,1'-biphenyl]-4-amine (3c)



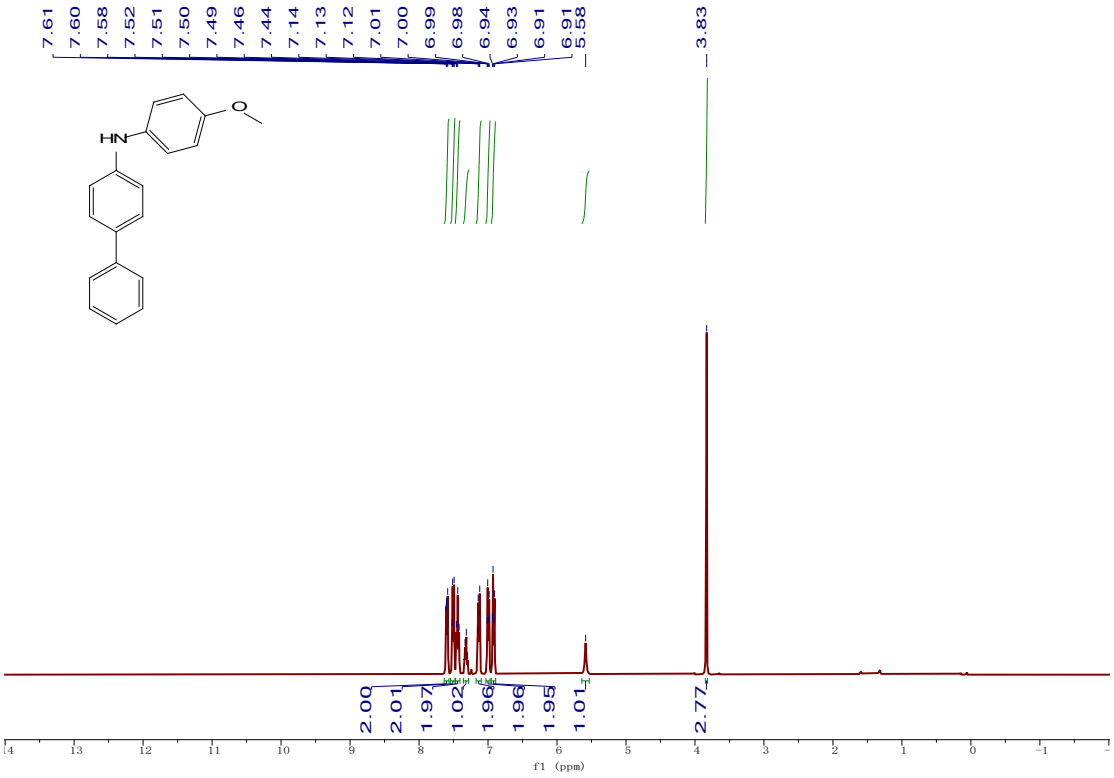


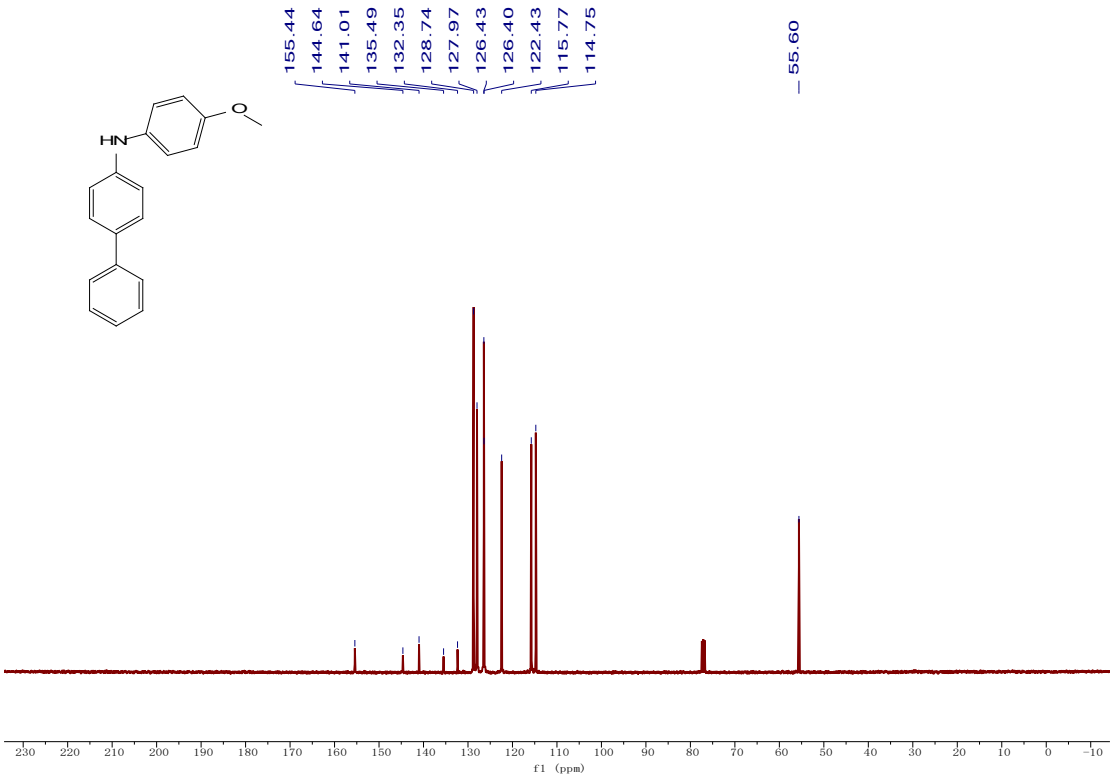
N-(4-fluorophenyl)-[1,1'-biphenyl]-4-amine (3d)



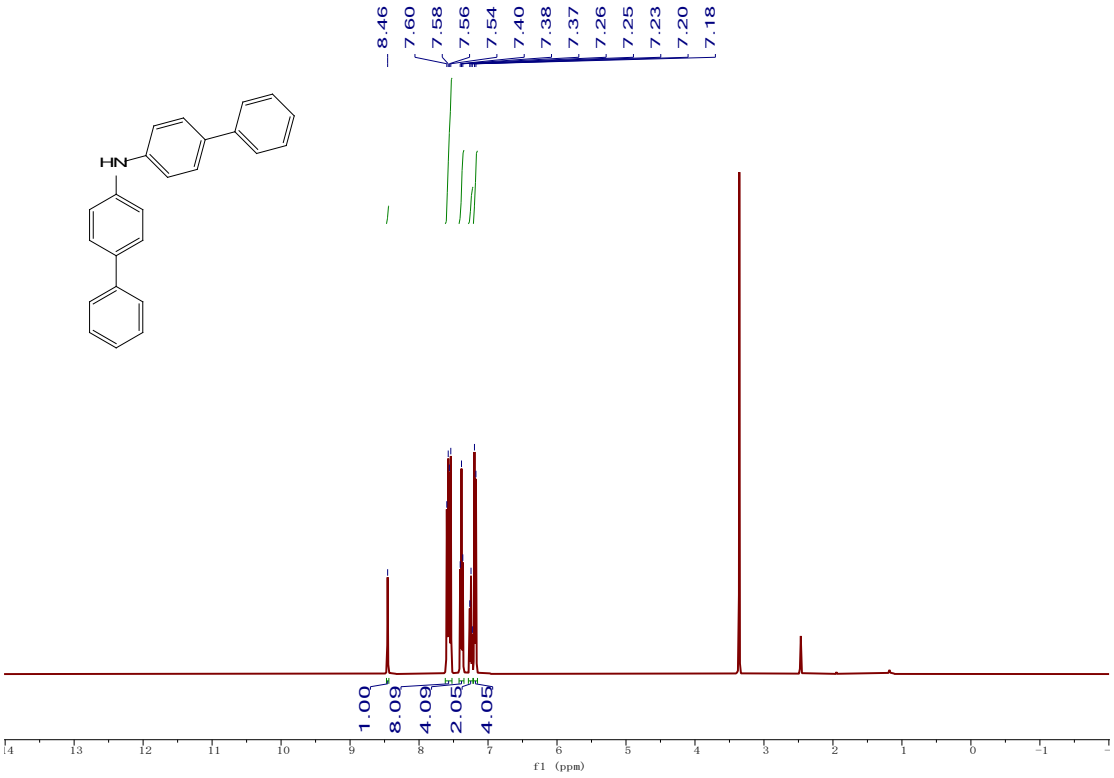


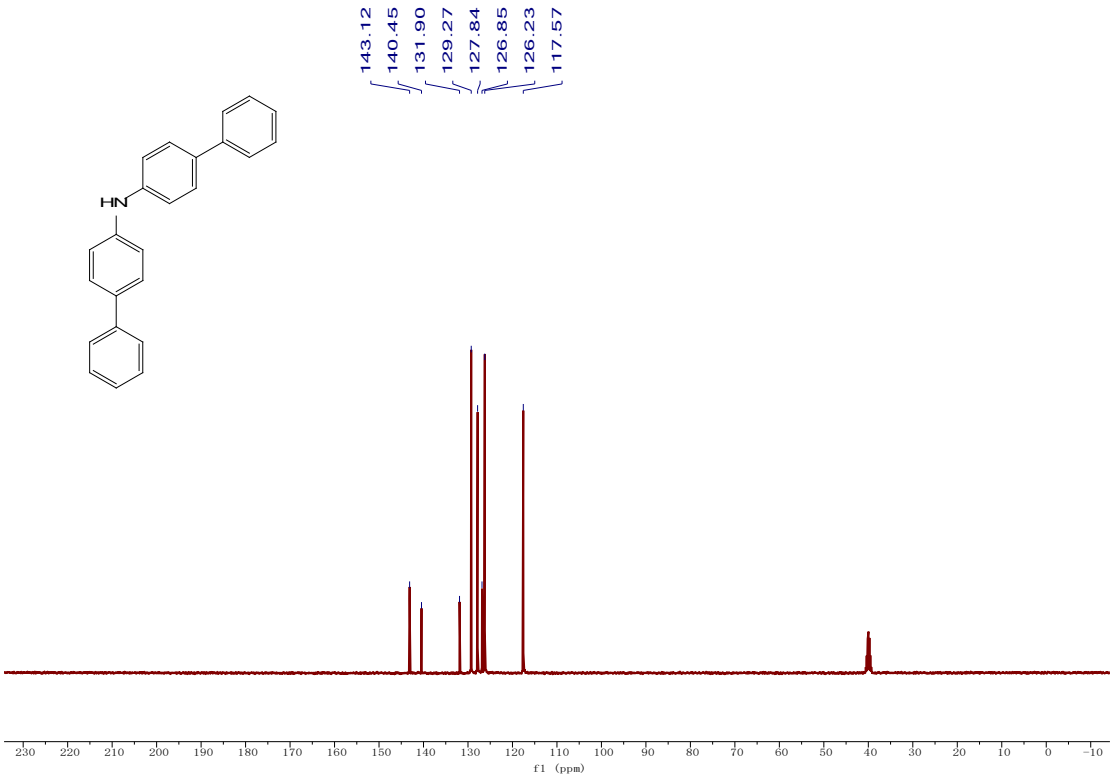
N-(4-methoxyphenyl)-[1,1'-biphenyl]-4-amine (3e)



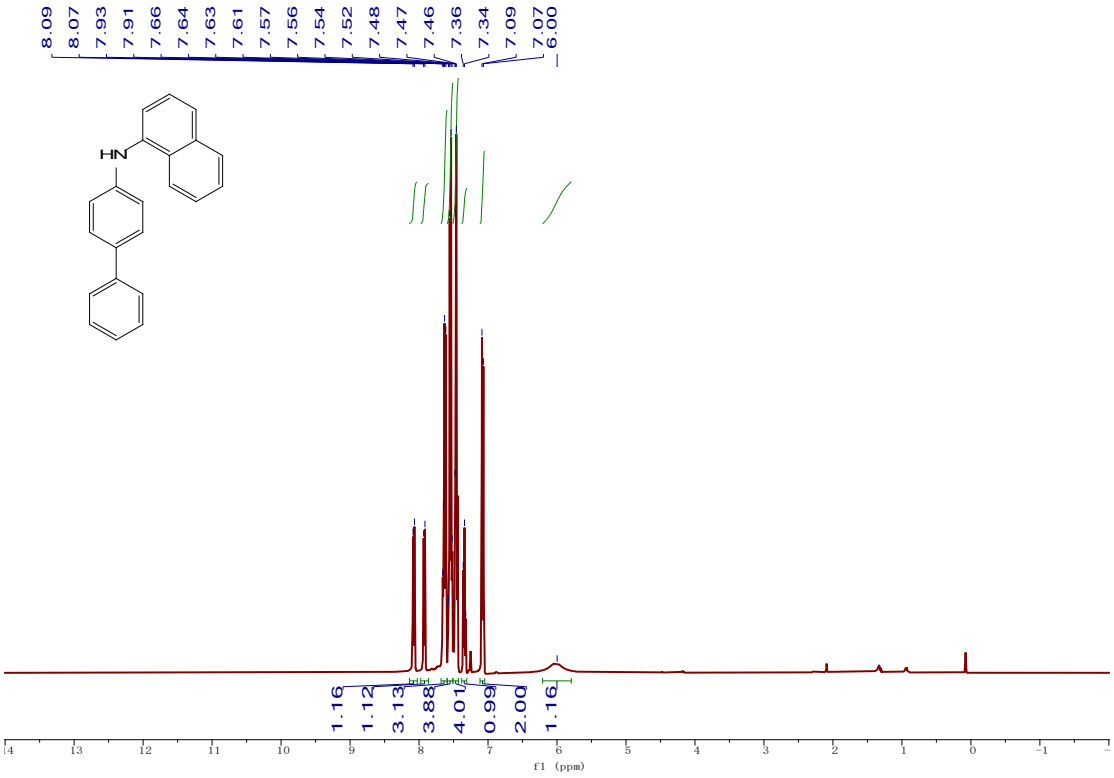


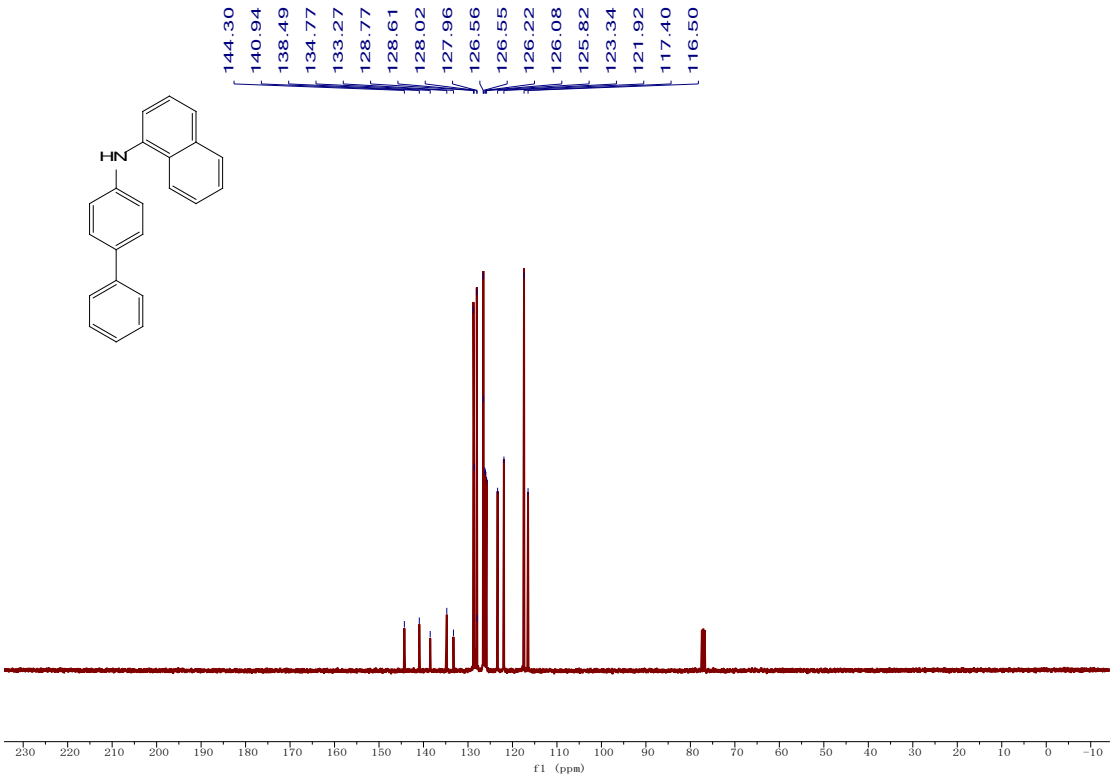
di([1,1'-biphenyl]-4-yl)amine (3f)



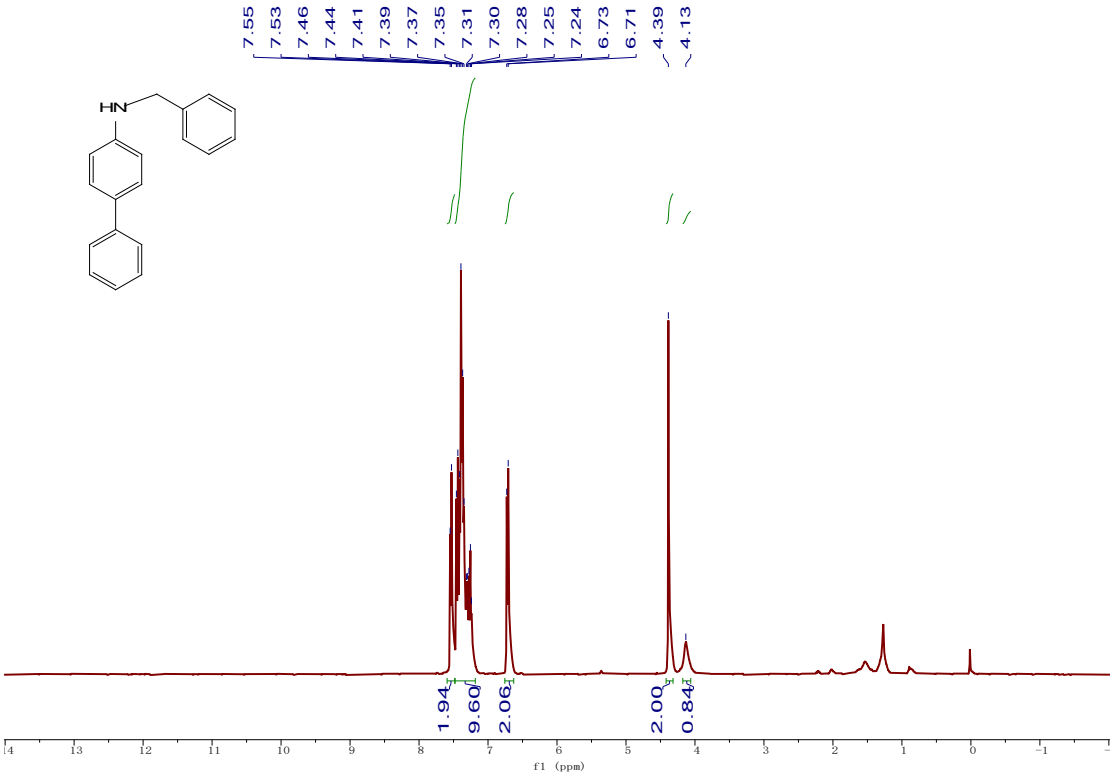


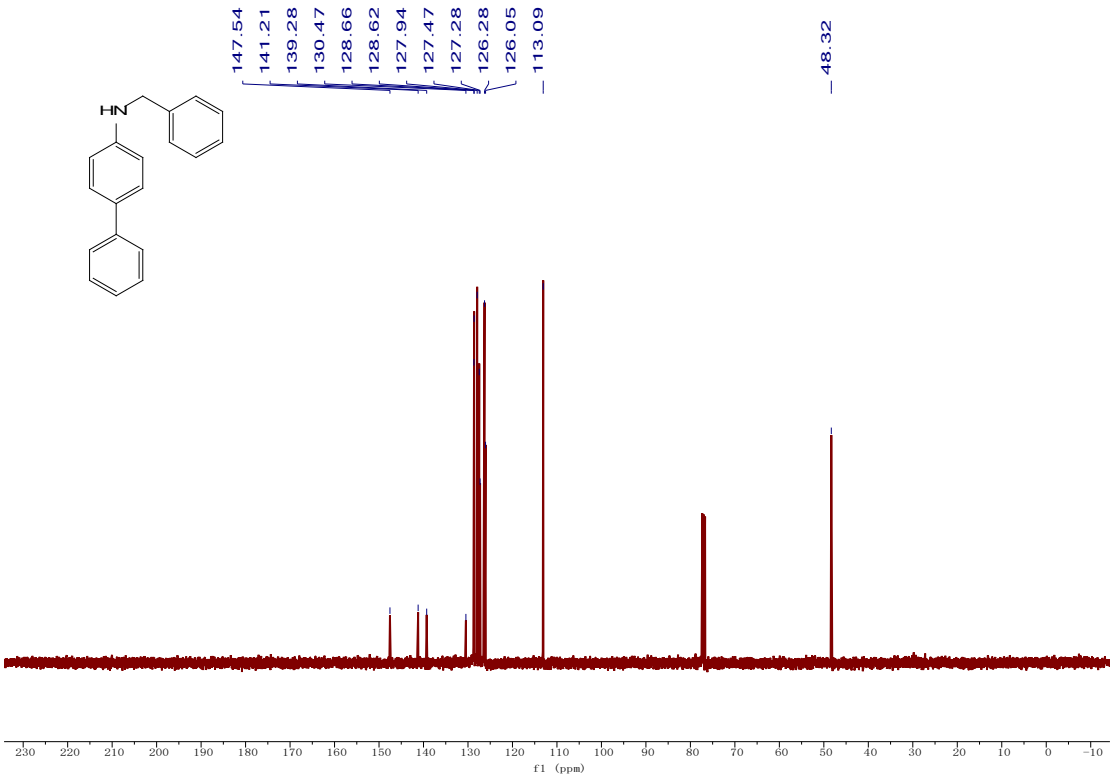
N-([1,1'-biphenyl]-4-yl)naphthalen-1-amine (3g)



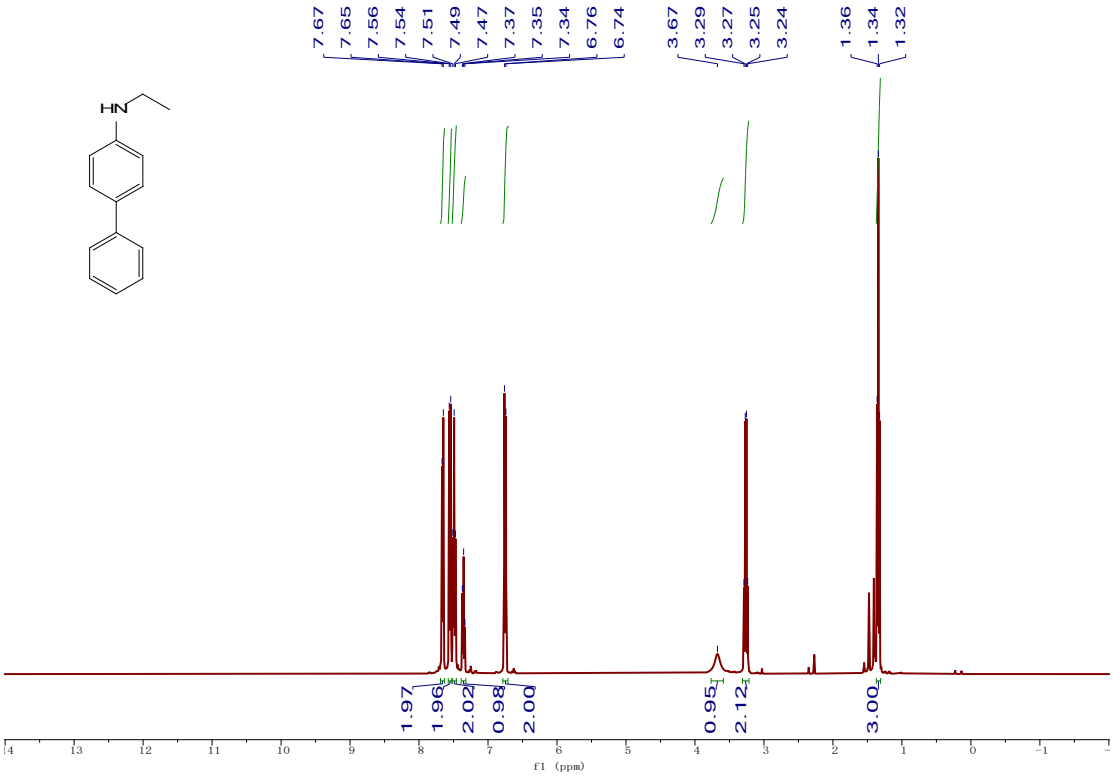


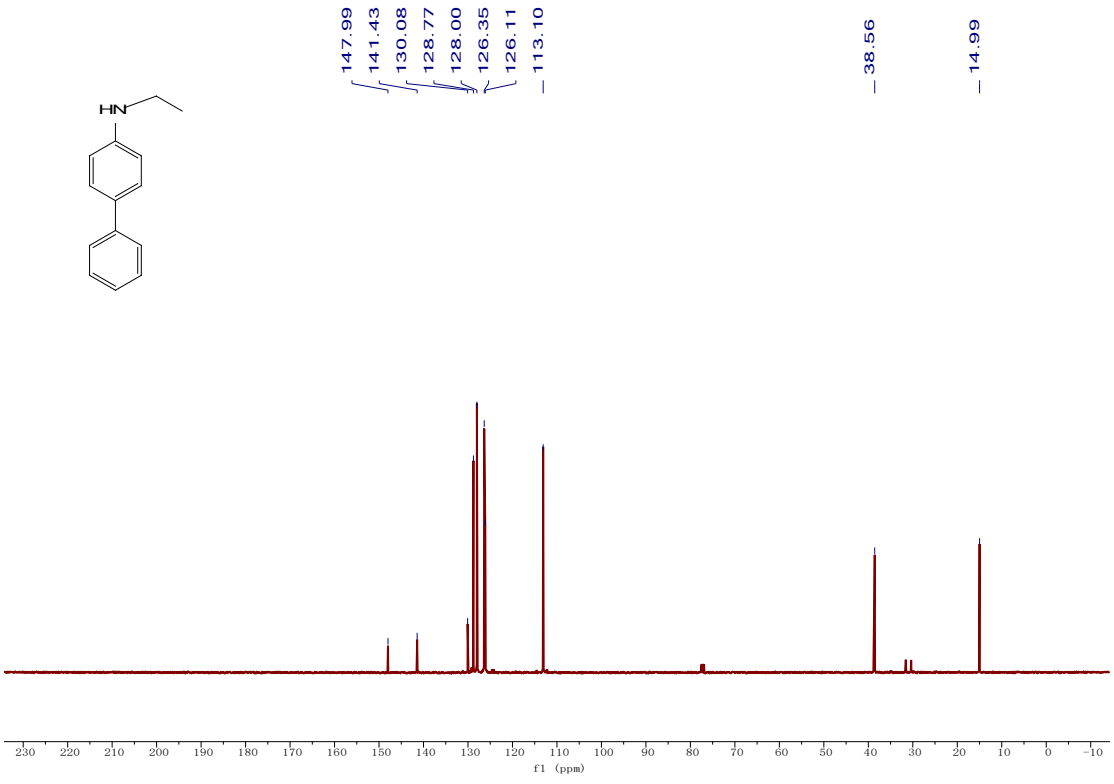
N-benzyl-[1,1'-biphenyl]-4-amine (3h)



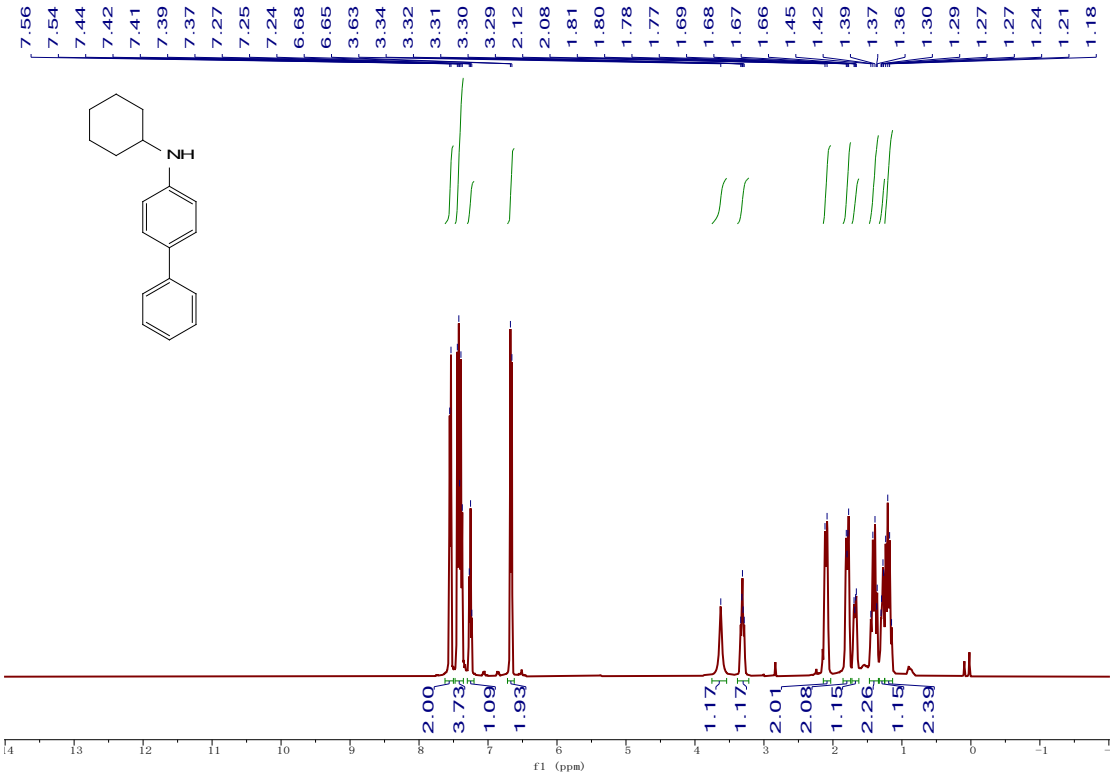


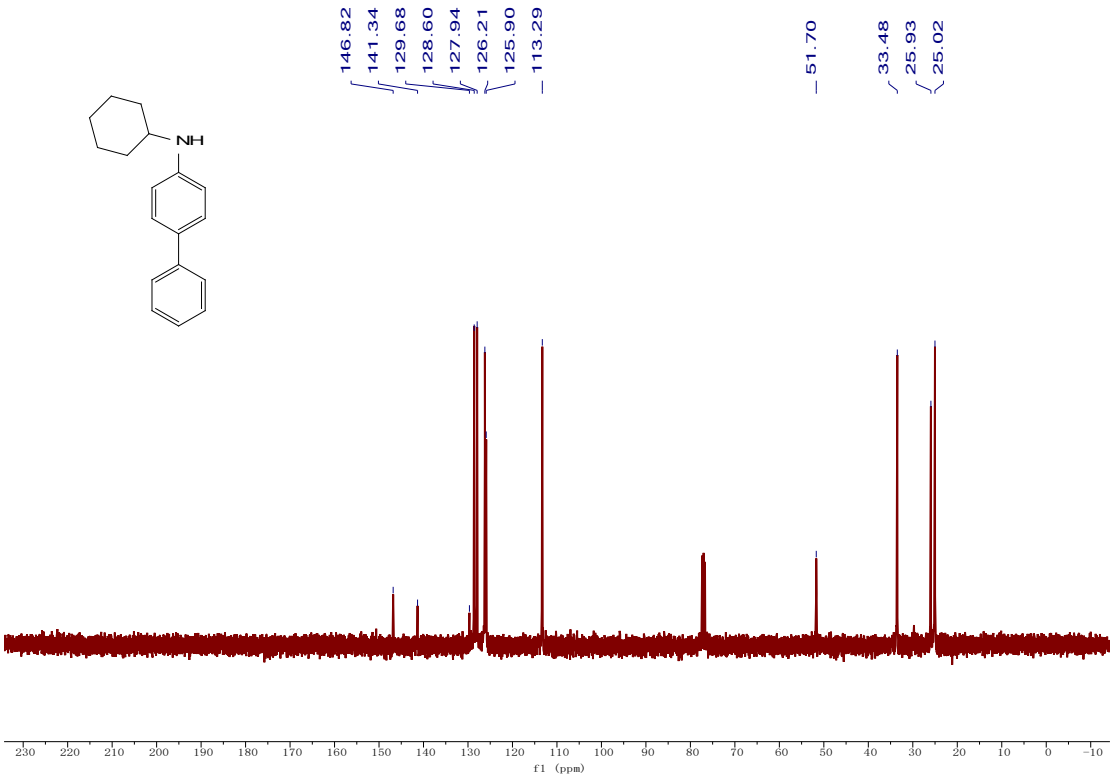
N-ethyl-[1,1'-biphenyl]-4-amine (3i)



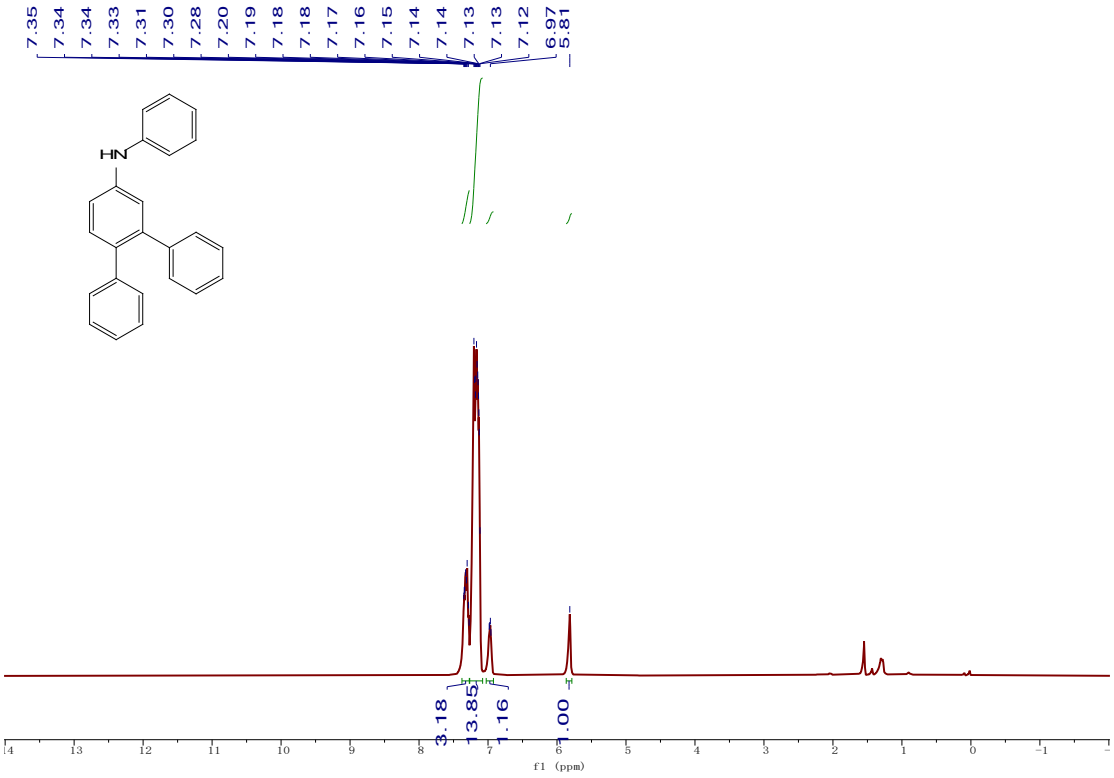


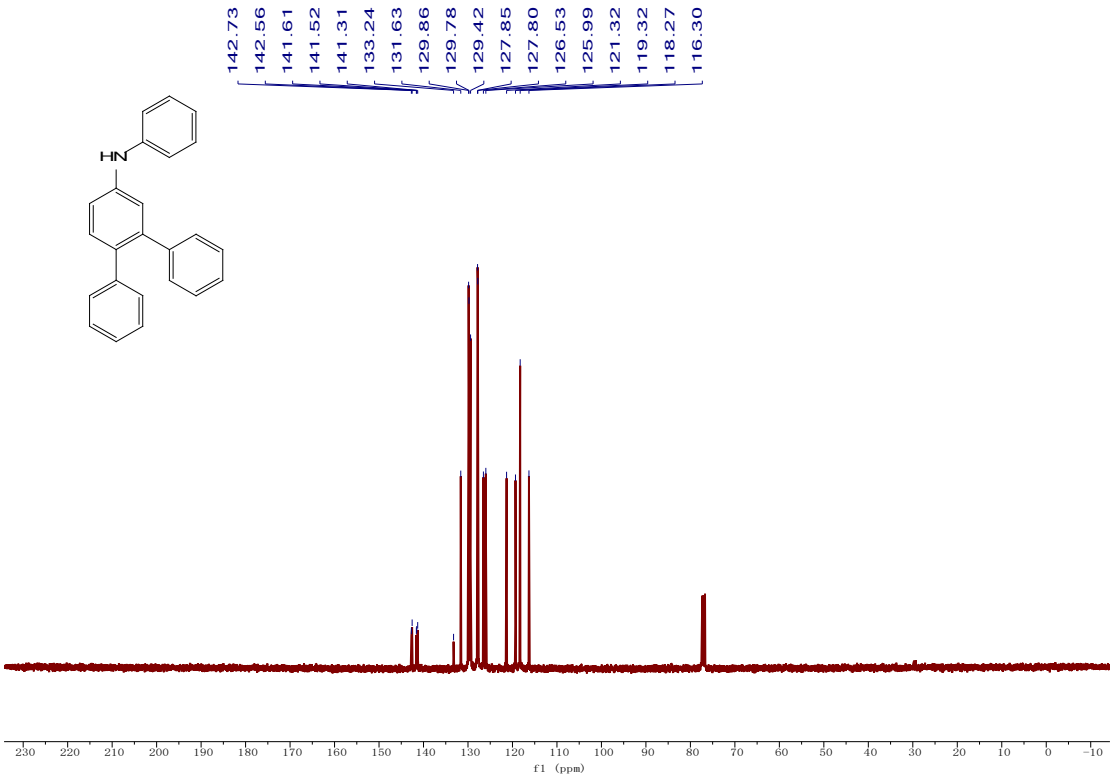
N-(cyclohexylmethyl)-[1,1'-biphenyl]-4-amine (3j)



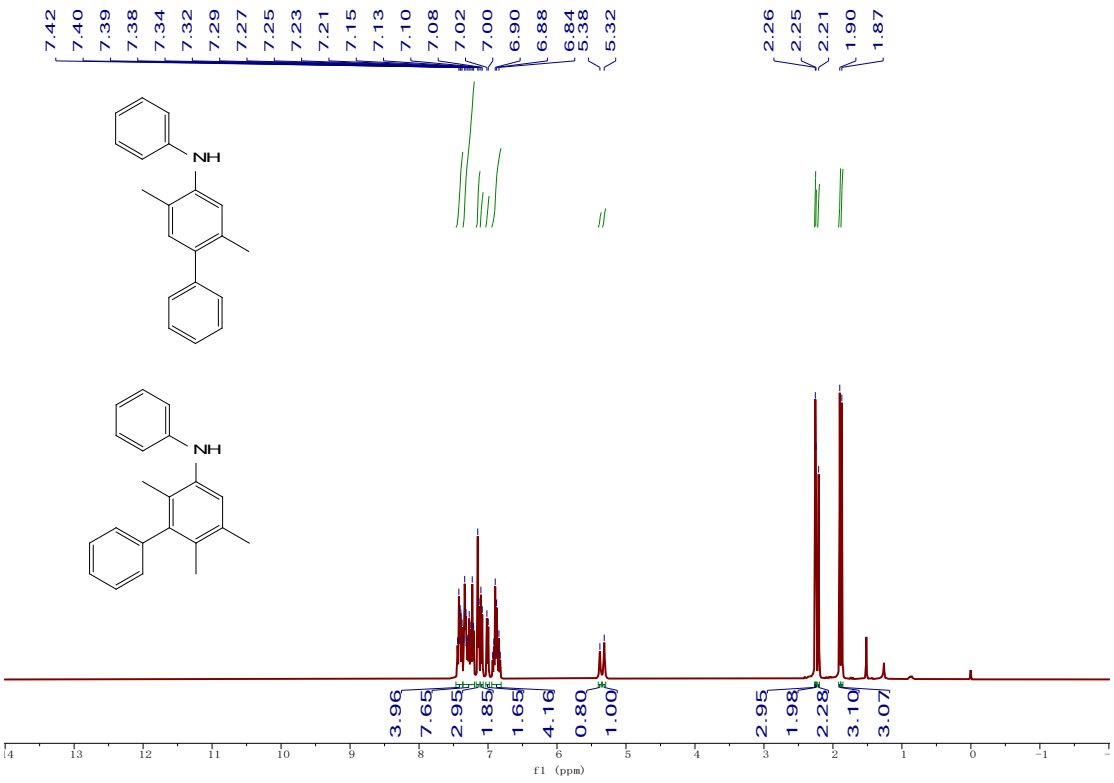


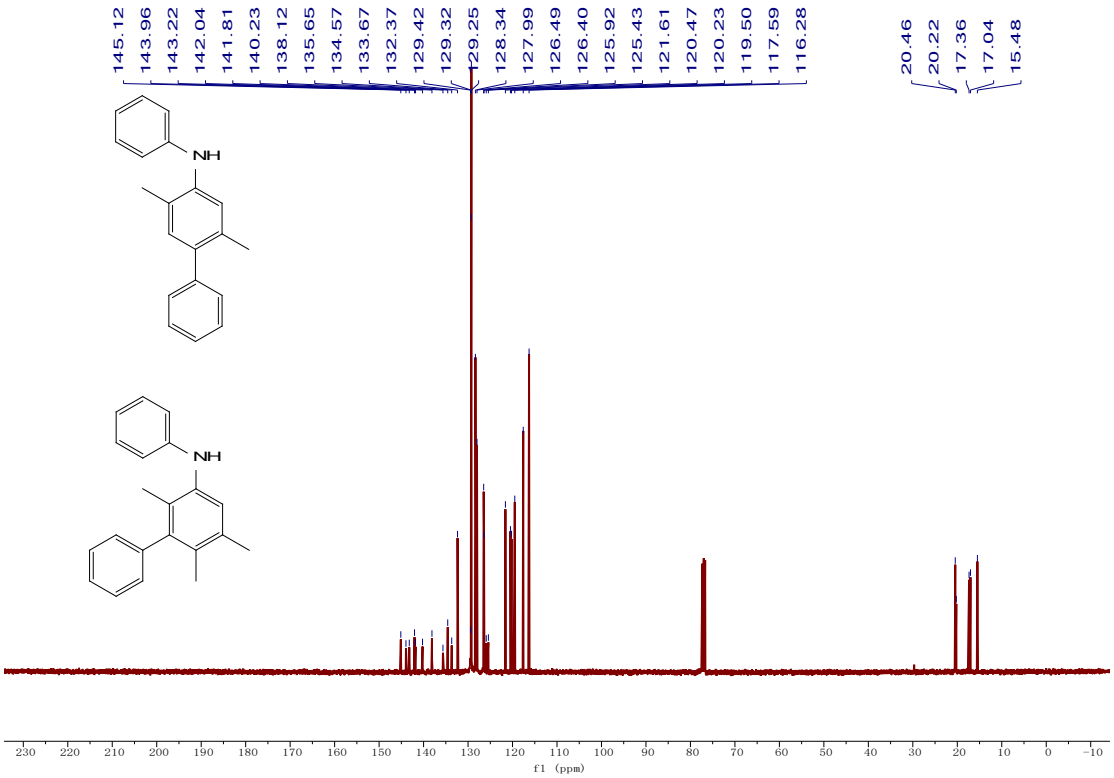
N-phenyl-[1,1':2',1''-terphenyl]-4'-amine (3k)



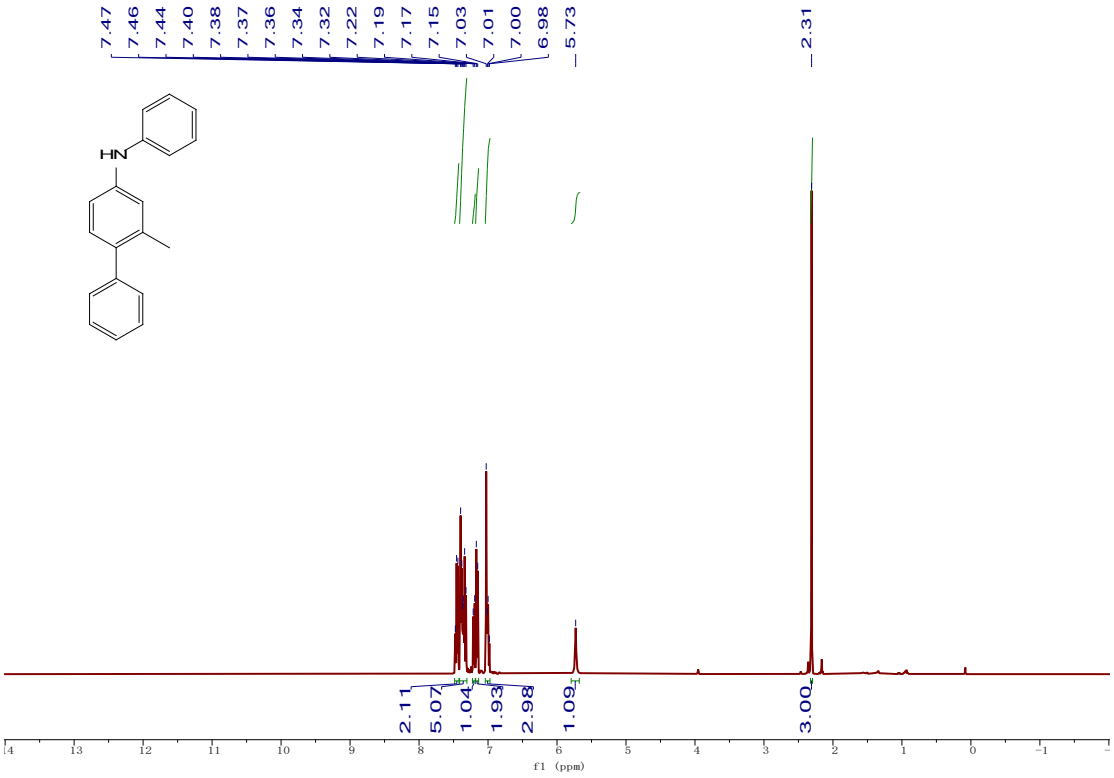


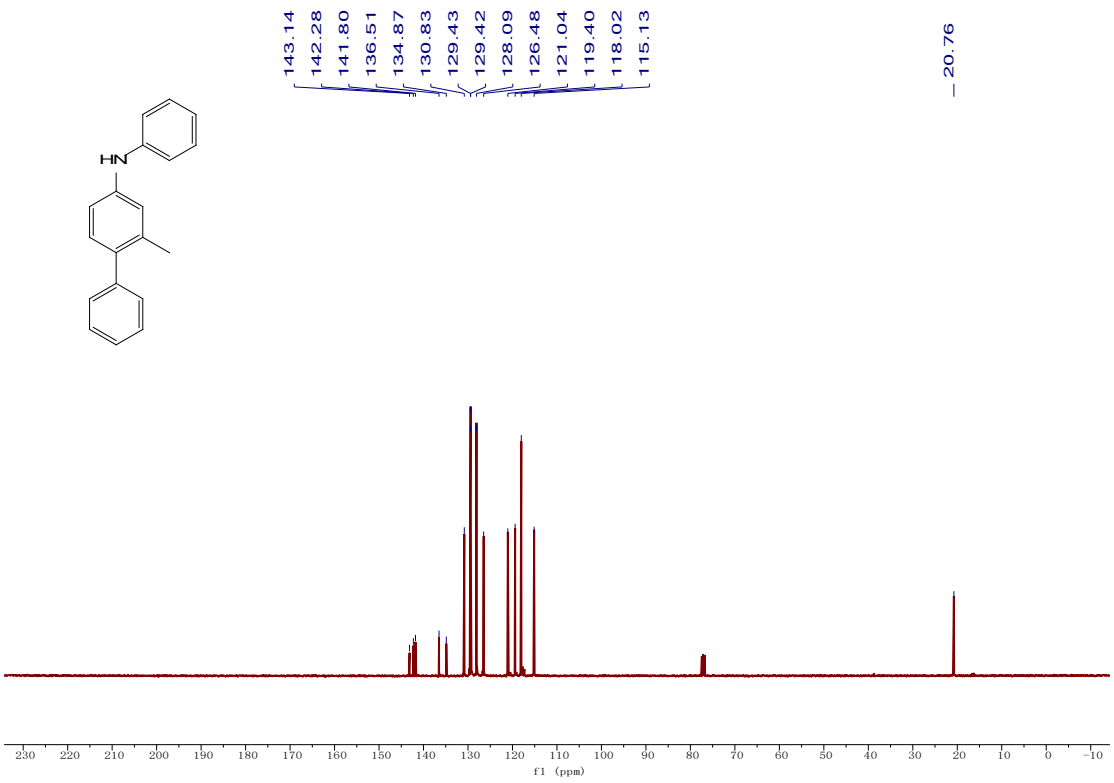
2,5-dimethyl-N-phenyl-[1,1'-biphenyl]-4-amine (3l) and 2,5,6-trimethyl-N-phenyl-[1,1'-biphenyl]-3-amine (3l')



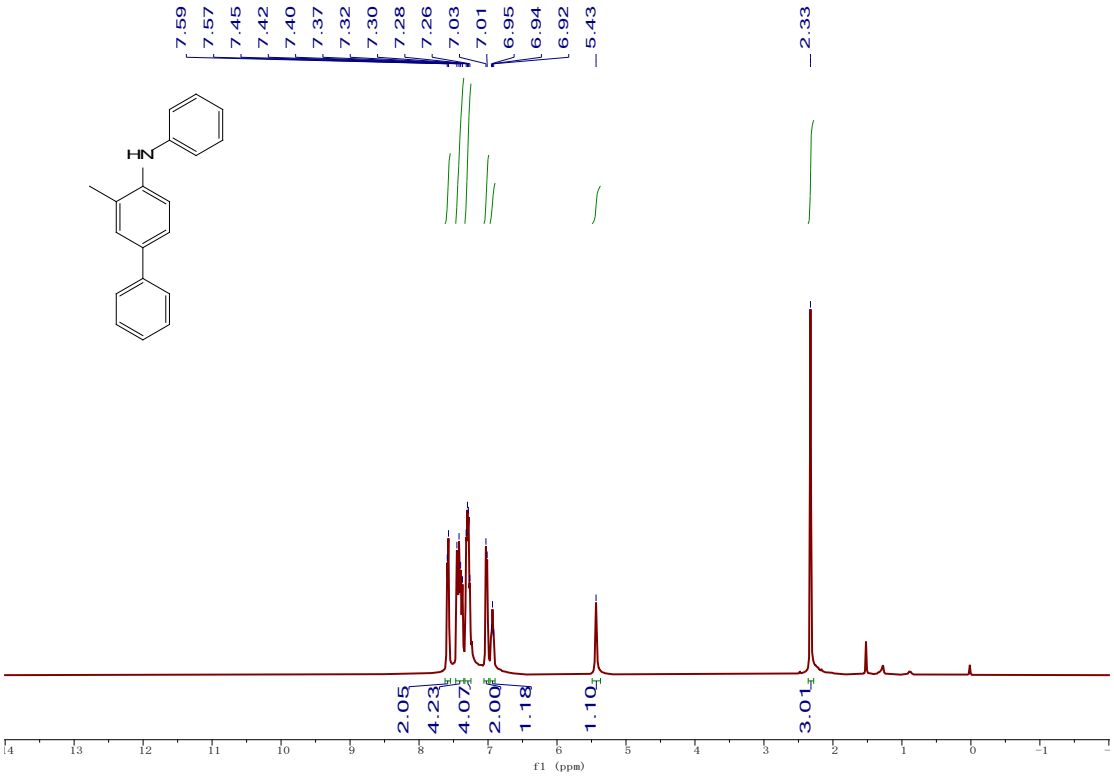


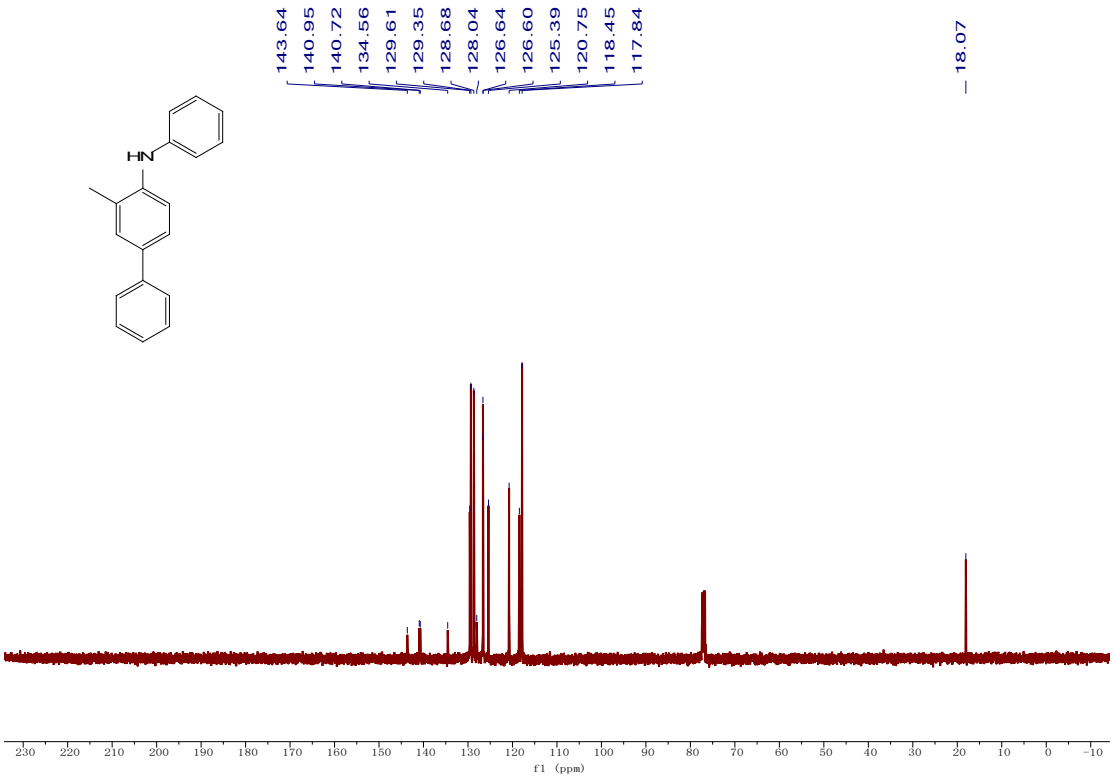
2-methyl-N-phenyl-[1,1'-biphenyl]-4-amine (3m)



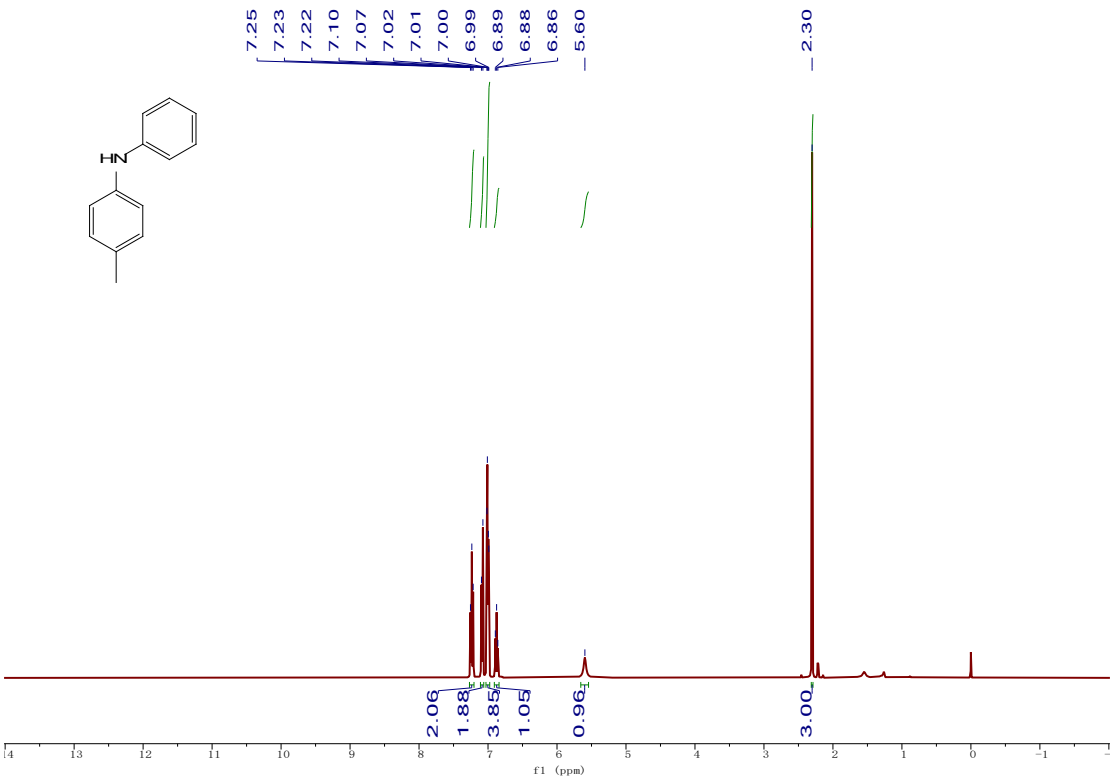


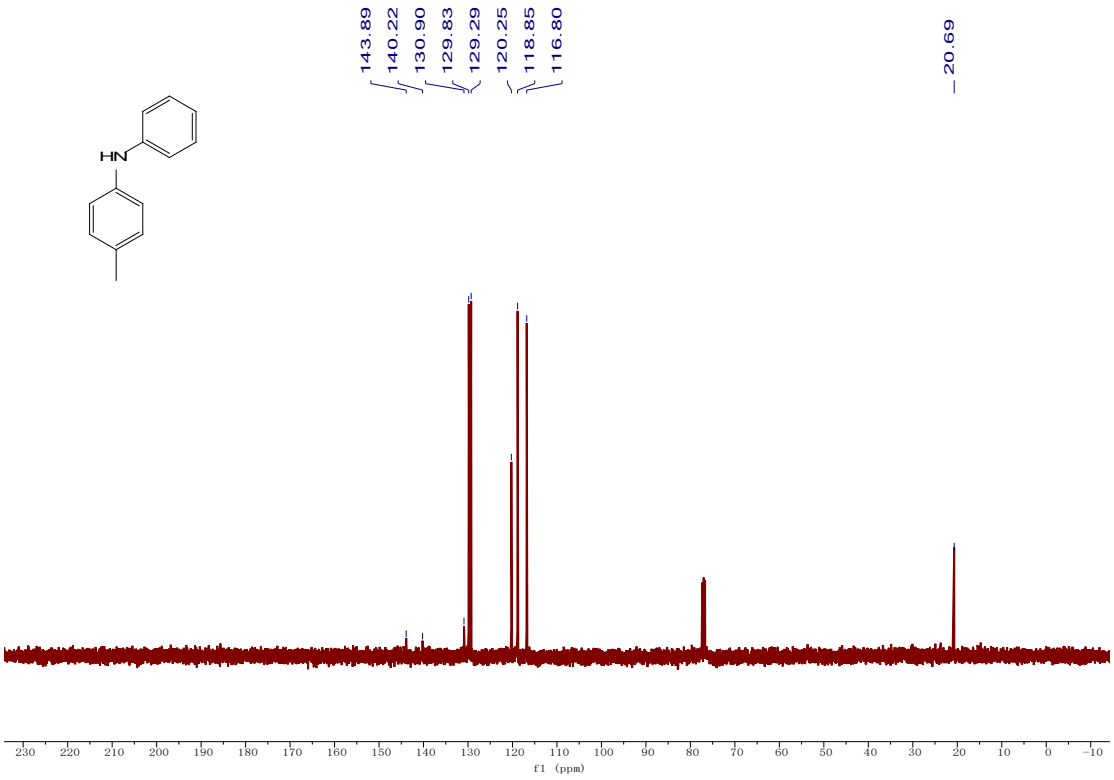
3-methyl-N-phenyl-[1,1'-biphenyl]-4-amine (3n)





4-methyl-N-phenylaniline (3p)





4-(5-iodopentyl)-N-phenylaniline (3q)