Electronic Supplementary Information

Pd-Catalyzed *ortho*-C–H Arylation of Free Anilines with Arylboric Acids Forming *o*-Amino Biaryls

Ying Lin,[a,#] Changxu Ye,[a,#] Meng Zhou,[a] Zhi Tang,[a,*] Long Liu,[a,*] Yuansheng Wang,[a]

Lingling Wang,[a] and Tieqiao Chen[a,*]

[a]Key Laboratory of Ministry of Education for Advanced Materials in Tropical Island Resources, Hainan Provincial Key Laboratory of Fine Chemical, Hainan Provincial Fine Chemical Engineering Research Center, Hainan University, Haikou, 570228, China.

[*]E-mail: tangzhijoe@hnu.edu.cn; hainanliulong@hainanu.edu.cn.; chentieqiao@hnu.edu.cn

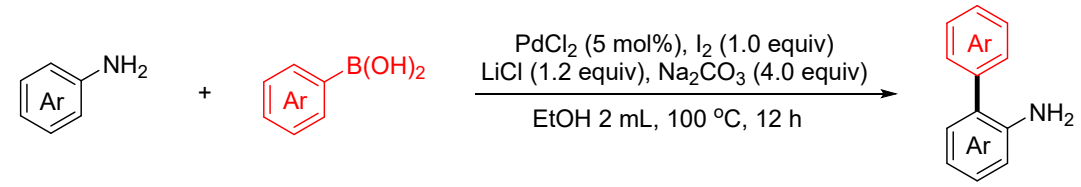
Table of contents

1. General Information

All experiments were carried out under air atmosphere using standard Schlenk techniques or in a dry glovebox. All heating (heating module) and stirring were conducted on the IKA (Model: RCT B S025). Solvents were dried over Na metal or CaH_2, and were distilled under nitrogen prior to use. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. Column chromatography was performed using Silica Gel 60 (200–300 mesh). The reactions were monitored by GC and GC-MS, GC-MS data were recorded on GC-MS QP 2010 plus, and GC analysis was performed on GC 2014. The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker ADVANCE III spectrometer at 400 MHz, 100 MHz, and 376 MHz respectively, and chemical shifts were reported in parts per million (ppm). The following abbreviations were used to explain the multiplicities: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (multiple), td (triplet of doublets). Melting points were measured using a melting point instrument and are uncorrected. HRMS were recorded on a LCMS-IT-TOF instrument by the ESI. All solvents, reagents and acid were purchased from Energy Chemical, Alfa Aesar and Aladdin.

2. Experimental Section

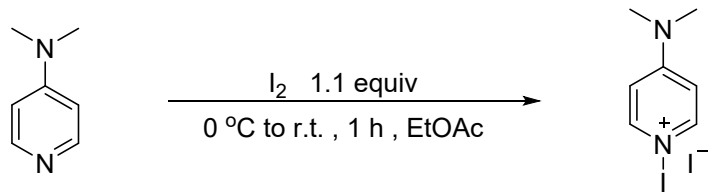
(a) General Experimental Procedure



1, 0.2 mmol **2**, 1.5 equiv **3**

To a 25 mL Schlenk tube, aniline **1** (0.20 mmol) and phenylboronic acid **2** (0.30 mmol, 1.5 equiv), $PdCl_2$ (0.01 mmol, 5 mol%), I_2 (0.20 mmol, 1.0 equiv), LiCl (0.24 mmol, 1.2 equiv) and Na_2CO_3 (0.8 mmol, 4.0 equiv) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Then the mixture was cooled to room temperature. The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether and ethyl acetate (PE/EA) as eluent.

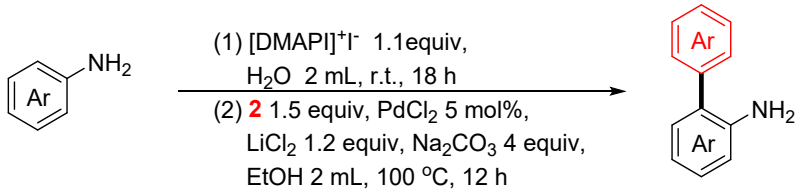
(b) Procedure for the synthesis of [DMAPI$^+$]I$^-$.[1]



8, DMAP, 16 mmol **9**, [DMAPI$^+$]I$^-$, 66 %

DMAP (2.0 g, 16 mmol, 1.0 equiv) and ethyl acetate (20 mL) were added to a flask of 100 mL, stirred at 0 °C, and then a solution of ethyl acetate (10 mL) of I_2 (4.5 g, 17.6 mmol, 1.1 equiv) was slowly dripped into the flask. After addition, the reaction temperature was heated to room temperature and stirred for 1 hour. The resulting solids are filtered through a Buchner funnel and washed with ethyl acetate. The obtained solid was thoroughly dried under vacuum to obtain compound **9**, with a yield of 66% (3.95 g).

(c) One-pot two-step synthesis of *o*-Amino Biaryls.

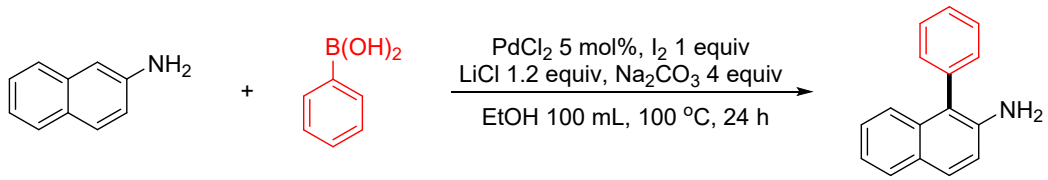


1, 0.2 mmol **3**

To a 25-mL Schlenk tube, aniline **1** (0.20 mmol), [DMAPI$^+$]I$^-$ (82.7 mg, 0.22 mmol) and H_2O (2 mL), were stirred at room temperature for 18 hours. In the appeal Schlenk tube, phenylboronic acid **2** (36.6 mg, 0.30 mmol), $PdCl_2$ (1.8 mg, 0.01 mmol), LiCl (10.2 mg, 0.24 mmol) , Na_2CO_3 (84.8 mg, 0.80 mmol) and EtOH (2 mL) are added and stirred at 100 °C for 12 hours. The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether and ethyl acetate (PE/EA) as eluent.

3. Application Experiments

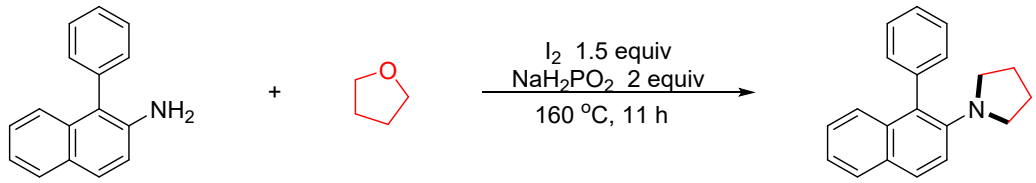
(a) Gram scale reaction.



1a 10 mmol | **2a** 1.5 equiv | **3a** 70% yield, 1.53 g

To a 250 mL three necked flask, **1a** (1.43 g, 10 mmol), **2a** (1.83 g, 15 mmol), $PdCl_2$ (0.09 g, 0.5 mmol), I_2 (2.54 mg, 10 mmol), LiCl (0.51 g, 12 mmol), Na_2CO_3 (4.24 g, 40 mmol) and EtOH (100 mL), were stirred under reflux at 100 °C for 24 h. **3a** was purified by column chromatography in 70% yield (1.53 g).

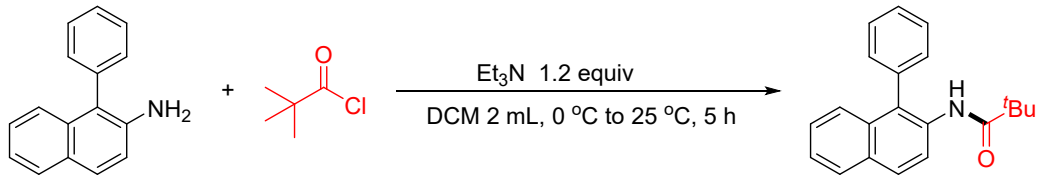
(b) Deoxyamination reaction.[2]



3a, 0.2 mmol | 2 mL | **4**, 92% isolated yield

To a 25 mL Schlenk tube, **1a** (28.6 mg, 0.20 mmol), **THF** (2 mL), I_2 (76.2 mg, 0.30 mmol), and NaH_2PO_2 (35.2 mg, 0.40 mmol), were stirred at 160 °C for 11 hours. Product **4** was purified by column chromatography in 92% yield (50.8 mg).

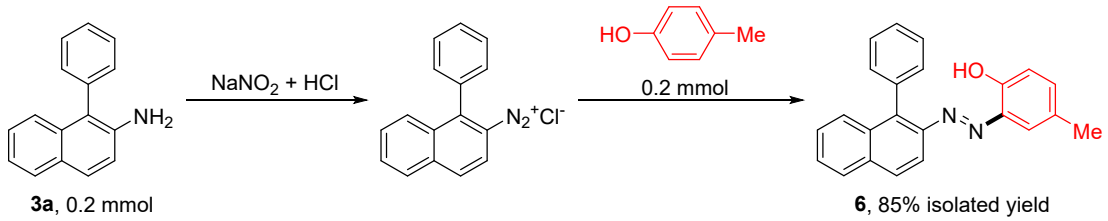
(c) Amidation reaction.[3]



3a, 0.2 mmol | 1.1 equiv | **5**, 97% isolated yield

To a 25 mL Schlenk tube, **1a** (28.6 mg, 0.20 mmol), **pivaloyl chloride** (26.4 mg, 0.22 mmol), Et_3N (24.2 mg, 0.24 mmol), and DCM (2 mL), were stirred at 0 °C to 5 °C for 5 hours. Product **5** was purified by column chromatography in 97% yield (58.5 mg).

(d) Diazotization reaction[4]

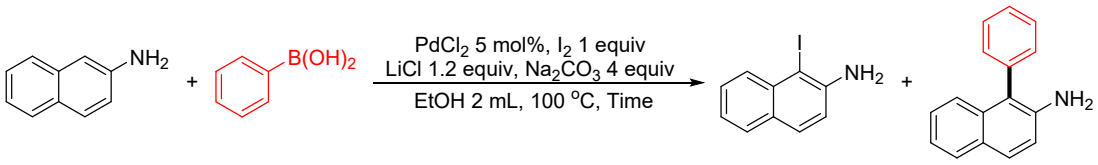


3a, 0.2 mmol

6, 85% isolated yield

To a 100 mL three necked flask, **3a** (1.43 g, 0.2 mmol), $NaNO_2$ (1.83 g, 0.28 mmol), and 5% NaOH solution (12 mL), were stirred at 5 °C. Then add 20% HCl solution to the flask slowly and stir for 30 min. In the flask of appeal, the solution of 15% Na_2CO_3 (8 mL) containing ***p*-cresol** (23.8 mg, 0.22 mmol) was slowly added, continued to stir for 15min, and then heated to room temperature for 15 min. The resulting solids are filtered through a Buchner funnel and washed with water. The obtained solid was thoroughly dried under vacuum to obtain compound **6**, with a yield of 85% (57.4 mg).

4. Experiment of Reaction Monitoring.[a]

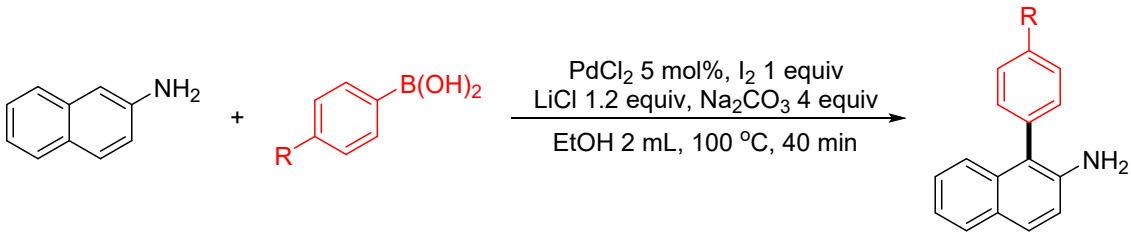


1a, 0.2 mmol **2a**, 1.5 equiv **7** **3a**

Entry	Time (min)	**7** Yield%[b]	**3a** Yield%[b]
1	30	36	22
2	35	37	30
3	40	22	39
4	60	trace	64
5	90	trace	71
6	120	trace	74
7	240	trace	81

[a]Reaction conditions: To a 25 mL Schlenk tube, 2-Naphthylamine **1a** (28.6 mg, 0.20 mmol), phenylboronic acid **2a** (36.6 mg, 0.3 mmol), $PdCl_2$ (1.8 mg, 0.01 mmol), I_2 (50.8 mg, 0.20 mmol), LiCl (10.2 mg, 0.24 mmol) and Na_2CO_3 (84.8 mg, 0.80 mmol), were stirred at 100 °C. [b]GC yield dodecane as an internal standard.

5. Experiment of Hammett Analysis.[a]

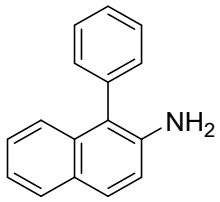


1a, 0.2 mmol **2**, 1.5 equiv **3**

Entry	-R	Yield%[b]
1	-OMe	31
2	-Me	30
3	-^{t}Bu	30
4	-H	39
5	-CF_3	45
6	-CN	55

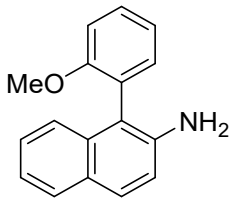
[a]Reaction conditions: To a 25 mL Schlenk tube, 2-Naphthylamine **1a** (28.6 mg, 0.20 mmol), **2** (0.3 mmol, 1.5 equiv), $PdCl_2$ (1.8 mg, 0.01 mmol), I_2 (50.8 mg, 0.20 mmol), LiCl (10.2 mg, 0.24 mmol) and Na_2CO_3 (84.8 mg, 0.80 mmol), were stirred at 100 °C for 40 min. [b]GC yield dodecane as an internal standard.

6. Characterization Data for the Products



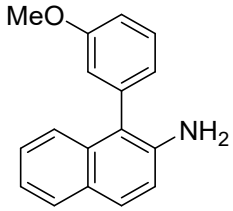
1-phenylnaphthalen-2-amine (3a).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and phenylboronic acid **2a** (0.30 mmol, 36.6 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 20/1) yielded the title compound **3a** in 81% (35.5 mg) as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.80 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.46–7.40 (m, 2H), 7.39–7.25 (m, 3H), 7.09 (d, *J* = 8.7 Hz, 1H), 3.75 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.1, 137.2, 133.8, 131.0, 129.3, 128.8, 128.0, 127.9, 127.6, 126.3, 124.3, 122.2, 119.9, 118.2. This compound is known.[5]



1-(2-methoxyphenyl)naphthalen-2-amine (3b).

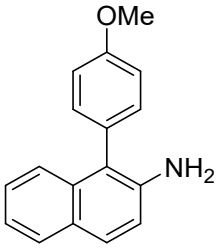
The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (2-methoxyphenyl)boronic acid **2b** (0.30 mmol, 45.6 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3b** in 49% (24.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.66 (m, 2H), 7.46–7.42 (m, 1H), 7.28–7.17 (m, 4H), 7.13–7.08 (m, 2H), 7.04 (d, *J* = 8.7 Hz, 1H), 3.69 (s, 3H), 3.17 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.9, 141.4, 133.9, 132.8, 129.4, 128.8, 128.1, 128.0, 126.2, 125.4, 124.3, 122.1, 121.4, 118.2, 116.7, 111.8, 55.8. This compound is known.[6]



1-(3-methoxyphenyl)naphthalen-2-amines (3c).

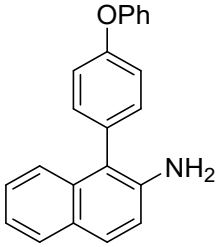
The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (3-methoxyphenyl)boronic acid **2c** (0.30 mmol, 45.6 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title

compound **3c** in 74% (36.9 mg) as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.67 (m, 2H), 7.49–7.42 (m, 1H), 7.35–7.19 (m, 3H), 7.04 (d, *J* = 8.7 Hz, 1H), 7.01–6.89 (m, 3H), 3.83 (s, 3H), 3.73 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.3, 141.0, 138.6, 133.7, 130.4, 128.8, 127.9, 127.9, 126.4, 124.3, 123.1, 122.2, 119.8, 118.1, 115.9, 113.5, 55.3. This compound is known.[5]



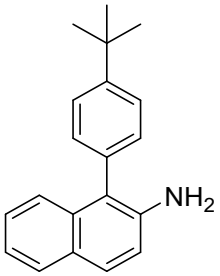
1-(4-methoxyphenyl)naphthalen-2-amine (3d).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (4-methoxyphenyl)boronic acid **2d** (0.30 mmol, 45.6 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 ^{o}C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3d** in 67% (33.4 mg) as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.59 (m, 2H), 7.25–7.11 (m, 5H), 7.02–6.94 (m, 3H), 3.81 (s, 3H), 3.63 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.0, 141.4, 134.2, 132.0, 129.1, 128.6, 128.1, 127.9, 126.3, 124.3, 122.1, 119.6, 118.1, 114.8, 55.4. This compound is known.[7]



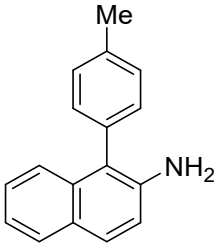
1-(4-phenoxyphenyl)naphthalen-2-amine (3e).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (4-phenoxyphenyl)boronic acid **2e** (0.30 mmol, 64.2 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 ^{o}C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3e** in 65% (40.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.60 (m, 2H), 7.34–7.30 (m, 2H), 7.27–7.21 (m, 4H), 7.17–7.15 (m, 1H), 7.11–7.05 (m, 5H), 6.96 (d, *J* = 2.2 Hz, 1H), 3.67 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.0, 156.9, 141.3, 134.0, 132.3, 131.6, 129.9, 128.8, 128.0, 128.0, 126.4, 124.2, 123.7, 122.2, 119.3, 119.3, 119.2, 118.1. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{22}H_{17}NO$: 312.1383; found: 312.1381.



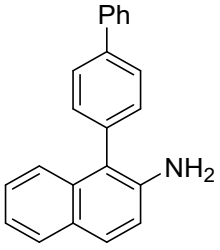
1-(4-(tert-butyl)phenyl)naphthalen-2-amine (3f).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (4-(tert-butyl)phenyl)boronic acid **2f** (0.30 mmol, 53.4 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3f** in 71% (39.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.66 (m, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.37–7.16 (m, 5H), 7.02 (d, *J* = 8.7 Hz, 1H), 3.67 (s, 2H), 1.40 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.3, 141.2, 134.0, 130.5, 128.6, 128.0, 127.9, 126.2, 126.2, 124.5, 122.1, 120.0, 118.1, 34.7, 31.5. This compound is known.[7]



1-(p-tolyl)naphthalen-2-amine (3g).

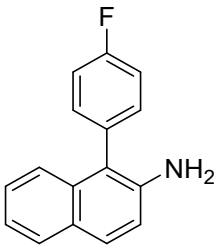
The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and *p*-tolylboronic acid **2g** (0.30 mmol, 40.8 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3g** in 67% (29.9 mg) as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.66 (m, 2H), 7.38–7.29 (m, 3H), 7.28–7.18 (m, 4H), 7.03 (d, *J* = 8.7 Hz, 1H), 3.71 (s, 2H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.2, 137.2, 134.0, 133.9, 130.8, 130.0, 128.6, 128.0, 127.9, 126.2, 124.3, 122.1, 120.0, 118.1, 21.4. This compound is known.[5]



1-([1,1'-biphenyl]-4-yl)naphthalen-2-amine (3h).

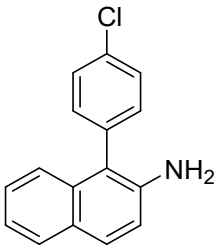
The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and [1,1'-biphenyl]-4-ylboronic acid **2h** (0.30 mmol,

59.4 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3h** in 68% (40.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.72 (m, 6H), 7.56–7.50 (m, 4H), 7.46–7.43 (m, 2H), 7.39–7.26 (m, 2H), 7.12 (d, *J* = 8.7 Hz, 1H), 3.43 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.0, 140.8, 140.4, 136.1, 133.8, 131.4, 128.9, 128.9, 128.1, 128.0, 127.5, 127.2, 126.4, 124.3, 122.3, 119.7, 118.2. This compound is known.[8]



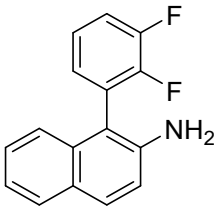
1-(4-fluorophenyl)naphthalen-2-amine (3i).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (4-fluorophenyl)boronic acid **2i** (0.30 mmol, 42.0 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3i** in 64% (30.3 mg) as a yellow solid; mp: 130–131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.73 (m, 2H), 7.41–7.37 (m, 2H), 7.35–7.25 (m, 5H), 7.08 (d, *J* = 8.7 Hz, 1H), 3.29 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.3 (d, *J* = 244.9 Hz), 141.2, 133.9, 132.9 (d, *J* = 3.4 Hz), 132.7 (d, *J* = 7.9 Hz), 129.0, 128.0, 128.0, 126.5, 124.0, 122.3, 118.8, 118.1, 116.3 (d, *J* = 21.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.62. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{16}H_{12}FN$: 238.1027; found: 238.1028.



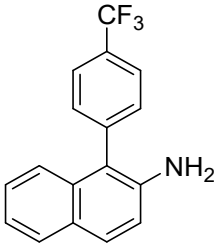
1-(4-chlorophenyl)naphthalen-2-amine (3j).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (4-fluorophenyl)boronic acid **2j** (0.30 mmol, 46.8 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3j** in 66% (33.4 mg) as a white solid; mp: 153–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.66 (m, 2H), 7.59–7.48 (m, 2H), 7.34–7.30 (m, 2H), 7.29–7.20 (m, 3H), 7.03 (d, *J* = 8.8 Hz, 1H), 3.69 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, CDCl3) δ 141.1, 135.6, 133.6, 133.6, 132.5, 129.6, 129.1, 128.0, 128.0, 126.5, 123.9, 122.3, 118.4, 118.1. This compound is known.[9]



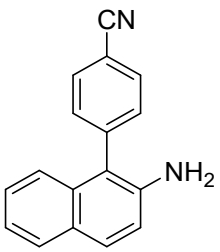
1-(2,3-difluorophenyl)naphthalen-2-amine (3k).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (2,3-difluorophenyl)boronic acid **2k** (0.30 mmol, 47.4 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3k** in 48% (24.5 mg) as a yellow solid; mp: 125–126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.71 (m, 2H), 7.34–7.18 (m, 5H), 7.15–7.09 (m, 1H), 7.05 (d, J = 8.8 Hz, 1H), 3.73 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.5 (dd, J_1 = 248.3 Hz, J_2 = 13.0 Hz), 148.8 (dd, J_1 = 247.1 Hz, J_2 = 11.9 Hz), 141.8 133.4, 129.9, 128.1, 127.9, 126.9, 126.6(d, J = 14.0 Hz), 125.0 (d, J = 5.0 Hz), 124.9 (d, J = 2.1 Hz), 123.5, 122.5, 118.1, 117.0 (d, J = 17.0 Hz), 111.6 (d, J = 2.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.54 (d, J = 21.2 Hz), -137.75 (d, J = 22.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{16}H_{11}F_2N$: 256.0932; found: 256.0905.



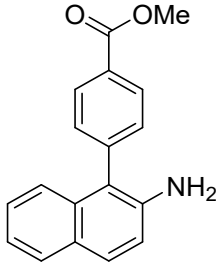
1-(4-(trifluoromethyl)phenyl)naphthalen-2-amine (3l).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (4-(trifluoromethyl)phenyl)boronic acid **2l** (0.30 mmol, 57.0 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3l** in 70% (40.2 mg) as a white solid; mp: 105–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.74 (t, J = 8.2 Hz, 2H), 7.53 (d, J = 7.9 Hz, 2H), 7.32–7.17 (m, 3H), 7.05 (d, J = 8.8 Hz, 1H), 3.69 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.3, 141.0, 133.4, 131.5, 129.8 (d, J = 32.3 Hz), 129.4, 128.1, 127.9, 126.7, 126.3 (q, J = 3.7 Hz), 125.6, 123.7, 122.4, 121.7 (q, J = 270.6 Hz), 118.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.50. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{17}H_{12}F_3N$: 288.0995; found: 288.0993.



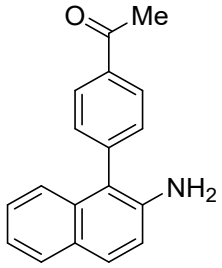
4-(2-aminonaphthalen-1-yl)benzonitrile (3m).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (4-cyanophenyl)boronic acid **2m** (0.30 mmol, 44.1 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3m** in 52% (25.4 mg) as a white solid; mp: 212–213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.81 (m, 2H), 7.74 (t, *J* = 7.9 Hz, 2H), 7.54–7.49 (m, 2H), 7.33–7.22 (m, 2H), 7.17–7.14 (m, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 3.68 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.7, 140.9, 133.1, 133.1, 132.1, 129.7, 128.2, 127.9, 126.9, 123.4, 122.6, 118.9, 118.2, 117.5, 111.5. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{17}H_{12}N_2$: 245.1073; found: 245.1073.



methyl 4-(2-aminonaphthalen-1-yl)benzoate (3n).

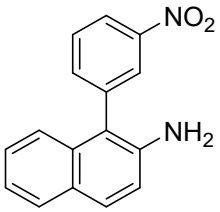
The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (4-(methoxycarbonyl)phenyl)boronic acid **2n** (0.30 mmol, 54.0 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3n** in 35% (19.4 mg) as a yellow solid; mp: 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27–8.17 (m, 2H), 7.75–7.70 (m, 2H), 7.51–7.44 (m, 2H), 7.30–7.20 (m, 3H), 7.03 (d, *J* = 8.7 Hz, 1H), 3.97 (s, 3H), 3.70 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.1, 142.5, 140.9, 133.3, 131.2, 130.6, 129.4, 129.3, 128.1, 127.9, 126.6, 123.8, 122.4, 118.6, 118.2, 52.3. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{18}H_{15}NO_2$: 278.1176; found: 278.1176.



1-(4-(2-aminonaphthalen-1-yl)phenyl)ethan-1-one (3o).

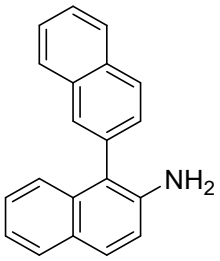
The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (4-acetylphenyl)boronic acid **2o** (0.30 mmol, 49.2 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3o** in 42% (21.9 mg) as a yellow solid; mp: 215–216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18–8.12 (m, 2H), 7.73 (t, *J* = 8.5 Hz, 2H), 7.55–7.48 (m, 2H), 7.32–7.20 (m, 3H), 7.05 (d, *J* =

8.7 Hz, 1H), 3.71 (s, 2H), 2.69 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.0, 142.7, 140.9, 136.3, 133.3, 131.4, 129.3, 128.1, 127.9, 126.6, 123.8, 122.4, 118.5, 118.2, 26.8. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{18}H_{15}NO$: 262.1226; found: 262.1228.



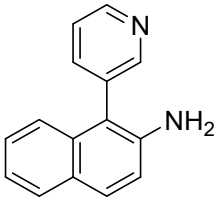
1-(3-nitrophenyl)naphthalen-2-amine (3p).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and (3-nitrophenyl)boronic acid **2p** (0.30 mmol, 50.1 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3p** in 63% (33.3 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36–8.23 (m, 2H), 7.78–7.70 (m, 4H), 7.34–7.22 (m, 2H), 7.16–7.13 (m, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 3.69 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.1, 141.2, 139.2, 137.7, 133.3, 130.4, 129.8, 128.2, 128.0, 127.0, 126.2, 123.3, 122.7, 122.6, 118.2, 116.8. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{16}H_{12}N_2O_2$: 265.0972; found: 265.0972.



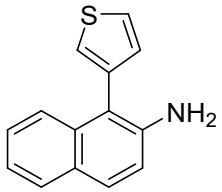
[1,2'-binaphthalen]-2-amine (3q).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and naphthalen-1-ylboronic acid **2q** (0.30 mmol, 51.6 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3q** in 74% (39.8 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.95–7.93 (m, 1H), 7.91–7.84 (m, 2H), 7.78–7.70 (m, 2H), 7.58–7.50 (m, 2H), 7.49–7.47 (m, 1H), 7.35–7.28 (m, 1H), 7.28–7.20 (m, 2H), 7.07 (d, *J* = 8.7 Hz, 1H), 3.74 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.3, 134.7, 134.0, 133.9, 132.8, 129.9, 129.1, 129.0, 128.9, 128.0, 128.0, 128.0, 127.9, 126.4, 126.3, 126.2, 124.3, 122.3, 119.7, 118.2. This compound is known.[5]



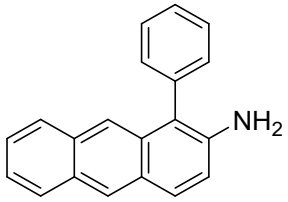
1-(pyridin-3-yl)naphthalen-2-amine (3r).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg) and pyridin-3-ylboronic acid **2r** (0.30 mmol, 36.9 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in EtOH (2 mL) was vigorously stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 1/1) yielded the title compound **3r** in 46% (20.3 mg) as a black oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.2 Hz, 1H), 8.70 (s, 1H), 7.83–7.77 (m, 3H), 7.58–7.55 (m, 1H), 7.36–7.27 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 3.49 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.6, 148.6, 141.7, 139.4, 133.7, 133.3, 129.7, 128.2, 128.0, 126.9, 124.3, 123.5, 122.5, 118.1, 115.3. This compound is known.[10]



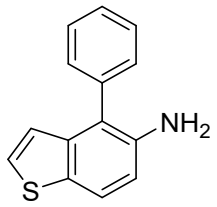
1-(thiophen-3-yl)naphthalen-2-amine (3s).

Follow the procedure for the one-pot two-step. To a 25 mL Schlenk tube, naphthalen-2-amine **1a** (0.20 mmol, 28.6 mg), [DMAPI$^+$]I$^-$ (82.7 mg, 0.22 mmol) and H_2O (2 mL), were stirred at room temperature for 18 h. In the appeal Schlenk tube, thiophen-3-ylboronic acid **2s** (0.30 mmol, 38.4 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), LiCl (0.24 mmol, 10.2 mg) , Na_2CO_3 (0.80 mmol, 84.8 mg) and EtOH (2 mL) are added and stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 20/1) yielded the title compound **3s** in 44% (19.9 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.61 (dd, J_1 = 3.0 Hz, 1H, J_2 = 2.9 Hz), 7.46 (d, *J* = 8.4 Hz, 1H), 7.40 (dd, J_1 = 1.2 Hz, J_2 = 1.2 Hz, 1H), 7.38–7.34 (m, 1H), 7.31–7.27 (m, 1H), 7.20 (dd, J_1 = 1.2 Hz, J_2 = 1.2 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 3.66 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.0, 136.9, 134.2, 129.9, 129.0, 128.0, 126.5, 126.5, 124.7, 124.2, 122.3, 118.0, 114.5. HRMS (ESI) m/z: [M+H]$^+$ calcd. for $C_{14}H_{11}NS$: 226.0685; found: 226.0686.



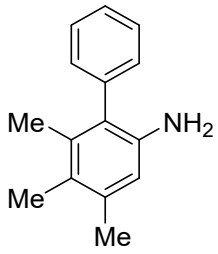
1-phenylanthracen-2-amine (3t).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, anthracen-2-amine **1t** (0.20 mmol, 38.6 mg) and phenylboronic acid **2a** (0.30 mmol, 36.6 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and $NaHCO_3$ (0.80 mmol, 67.2 mg) in DMSO (2 mL) was vigorously stirred at 140 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3t** in 53% (28.5 mg) as a yellow solid; mp: 129–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.94–7.86 (m, 2H), 7.79–7.68 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 2H), 7.51 (m, 1H), 7.47–7.42 (m, 2H), 7.32 (s, 2H), 7.09 (d, *J* = 9.0 Hz, 1H), 3.54 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.0, 137.3, 132.6, 132.3, 131.2, 129.5, 129.4, 129.3, 128.0, 127.8, 127.6, 126.4, 125.3, 124.0, 121.7, 119.9, 117.5. This compound is known.[11]



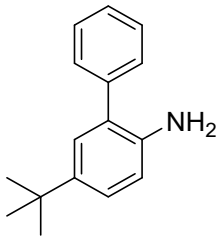
4-phenylbenzo[b]thiophen-5-amine (3u).

The representative general procedure mentioned above was followed. To a 25 mL Schlenk tube, benzo[b]thiophen-5-amine **1u** (0.20 mmol, 29.8 mg) and phenylboronic acid **2a** (0.30 mmol, 36.6 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), I_2 (0.20 mmol, 50.8 mg), LiCl (0.24 mmol, 10.2 mg) and Na_2CO_3 (0.80 mmol, 84.8 mg) in DMSO (2 mL) was vigorously stirred at 140 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3u** in 50% (22.5 mg) as a yellow solid; mp: 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.66 (m, 1H), 7.55–7.48 (m, 2H), 7.47–7.38 (m, 3H), 7.30 (d, *J* = 5.5 Hz, 1H), 6.93–6.86 (m, 2H), 3.66 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.3, 140.2, 137.4, 130.4, 130.1, 129.1, 127.6, 126.6, 123.0, 122.2, 121.3, 115.1. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{14}H_{11}NS$: 226.0685; found: 226.0686.



4,5,6-trimethyl-[1,1'-biphenyl]-2-aminev (3v).

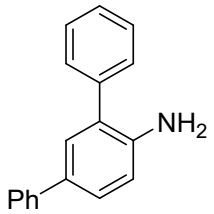
Follow the procedure for the one-pot two-step. To a 25 mL Schlenk tube, 3,4,5-trimethylaniline **1v** (0.20 mmol, 27.0 mg), $[DMAPI^+]I^-$ (82.7 mg, 0.22 mmol) and H_2O (2 mL), were stirred at room temperature for 18 h. In the appeal Schlenk tube, phenylboronic acid **2a** (0.30 mmol, 36.6 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), LiCl (0.24 mmol, 10.2 mg) , Na_2CO_3 (0.80 mmol, 84.8 mg) and EtOH (2 mL) are added and stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3v** in 40% (16.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.47 (m, 2H), 7.38–7.32 (m, 1H), 7.26–7.20 (m, 2H), 6.53 (s, 1H), 3.27 (s, 2H), 2.27 (s, 3H), 2.14 (s, 3H), 1.93 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.4, 139.2, 136.3, 135.2, 130.3, 129.0, 127.1, 126.3, 125.1, 114.5, 20.9, 17.8, 15.2. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{15}H_{17}N$: 212.1434; found: 212.1434.



1-(6-bromonaphthalen-2-yl)pyrrolidine (3w).

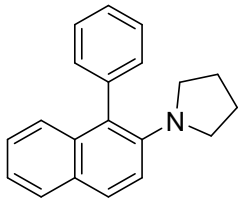
Follow the procedure for the one-pot two-step. To a 25 mL Schlenk tube, 4-(tert-butyl)aniline **1v** (0.20 mmol, 29.8 mg), $[DMAPI^+]I^-$ (82.7 mg, 0.22 mmol) and H_2O (2 mL), were stirred at room temperature for 18 h. In the appeal Schlenk tube, phenylboronic acid **2a** (0.30 mmol, 36.6 mg),

$PdCl_2$ (0.01 mmol, 1.8 mg), LiCl (0.24 mmol, 10.2 mg) , Na_2CO_3 (0.80 mmol, 84.8 mg) and EtOH (2 mL) are added and stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3w** in 51% (22.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.42 (m, 4H), 7.33–7,38 (m, 1H), 7.23–7.15 (m, 2H), 6.74 (d, *J* = 8.3 Hz, 1H), 3.68 (s, 2H), 1.31 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.6, 141.0, 140.1, 129.2, 128.8, 127.4, 127.3, 127.1, 125.4, 115.5, 34.0, 31.6. .This compound is known.[5]



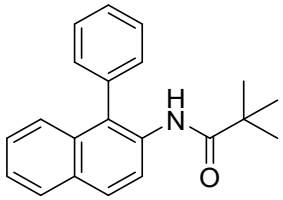
[1,1':3',1''-terphenyl]-4'-amine (3x).

Follow the procedure for the one-pot two-step. To a 25 mL Schlenk tube, [1,1'-biphenyl]-4-amine **1x** (0.20 mmol, 33.8 mg), [DMAPI$^+$]I$^-$ (82.7 mg, 0.22 mmol) and H_2O (2 mL), were stirred at room temperature for 18 h. In the appeal Schlenk tube, phenylboronic acid **2a** (0.30 mmol, 36.6 mg), $PdCl_2$ (0.01 mmol, 1.8 mg), LiCl (0.24 mmol, 10.2 mg) , Na_2CO_3 (0.80 mmol, 84.8 mg) and EtOH (2 mL) are added and stirred at 100 °C for 12 h. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **3x** in 49% (23.9 mg) as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.55 (m, 2H), 7.47–7.52 (m, 4H), 7.44–7.45 (m, 1H), 7.43–7.37 (m, 4H), 7.30–7.25 (m, 2H), 6.85 (d, *J* = 8.1 Hz, 1H), 3.86 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.0, 141.0, 139.4, 131.7, 129.2, 129.2, 128.9, 128.7, 127.9, 127.4, 127.1, 126.4, 126.3, 116.0. This compound is known.[5]



1-(1-phenylnaphthalen-2-yl)pyrrolidine (4).

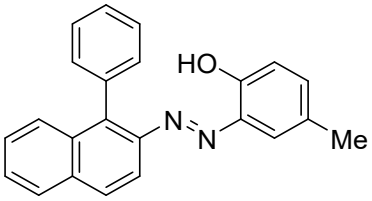
Follow the procedure for the deoxyamination reaction above. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 40/1) yielded the title compound **4** in 92% (50.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.75 (m, 2H), 7.49–7.38 (m, 6H), 7.31–7.21 (m, 4H). 3.03–3.00 (m, 4H), 1.78 (t, *J* = 3.4 Hz, 1H), 1.77 (t, *J* = 3.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.1, 140.5, 134.5, 132.1, 128.1, 127.9, 127.6, 127.2, 126.5, 125.9, 124.3, 121.8, 117.1, 51.0, 25.6. This compound is known.[12]



***N*-(1-phenylnaphthalen-2-yl)pivalamide (5).**

Follow the procedure for the amidation reaction above. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 20/1) yielded the title compound **5** in 97% (58.5 mg) as a white solid; mp: 166-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 9.0 Hz, 1H), 7.93 (d, *J* = 9.0 Hz,

1H), 7.89 (d, J = 8.0 Hz, 1H), 7.64–7.61 (m, 2H), 7.58–7.54 (m, 1H), 7.45–7.35 (m, 6H), 1.08 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 176.4, 135.8, 133.4, 132.5, 130.5, 130.5, 129.4, 128.4, 127.9, 127.2, 126.2, 125.6, 124.6, 120.3, 39.7, 27.2. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{21}H_{21}NO$: 304.1696; found: 304.1698.



4-methyl-2-((1-phenylnaphthalen-2-yl)diazenyl)phenol (6).

Follow the procedure for the deoxyamination reaction above. Purification by filtering and washing with water yielded the title compound **6** in 85% (50.8 mg) as a orange solid; mp: 146-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 (s, 1H), 8.19 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 7.4 Hz, 1H), 7.75 (d, J = 1.5 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.60–7.56 (m, 4H), 7.48–7.42 (m, 3H), 7.07 (dd, J_1 = 8.4 Hz, J_2 = 1.9 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 2.36 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 149.8, 145.5, 140.3, 137.5, 136.5, 134.7, 133.9, 133.1, 130.4, 129.1, 128.9, 128.5, 128.2, 128.0, 127.6, 126.8, 117.9, 113.9, 20.3. HRMS (ESI) m/z: $[M+H]^+$ caled. for $C_{15}H_{17}N$: 212.1434; found: 212.1434. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{23}H_{18}N_2O$: 339.1492; found: 339.1484.

7. References

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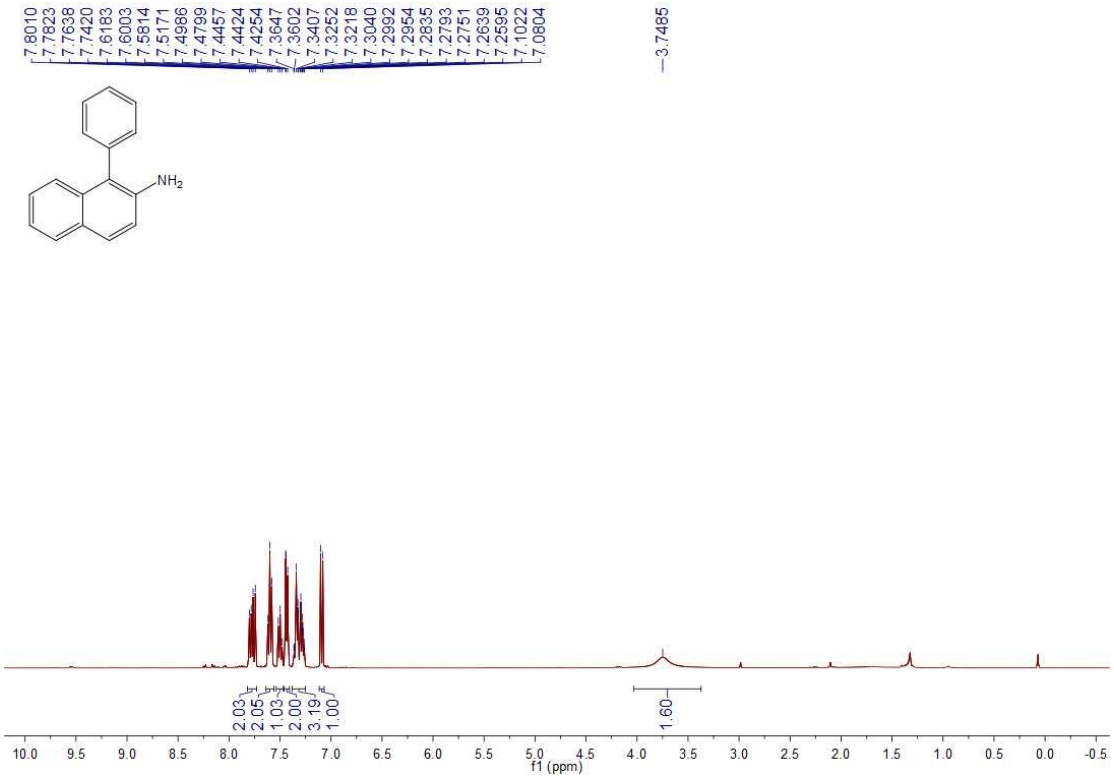
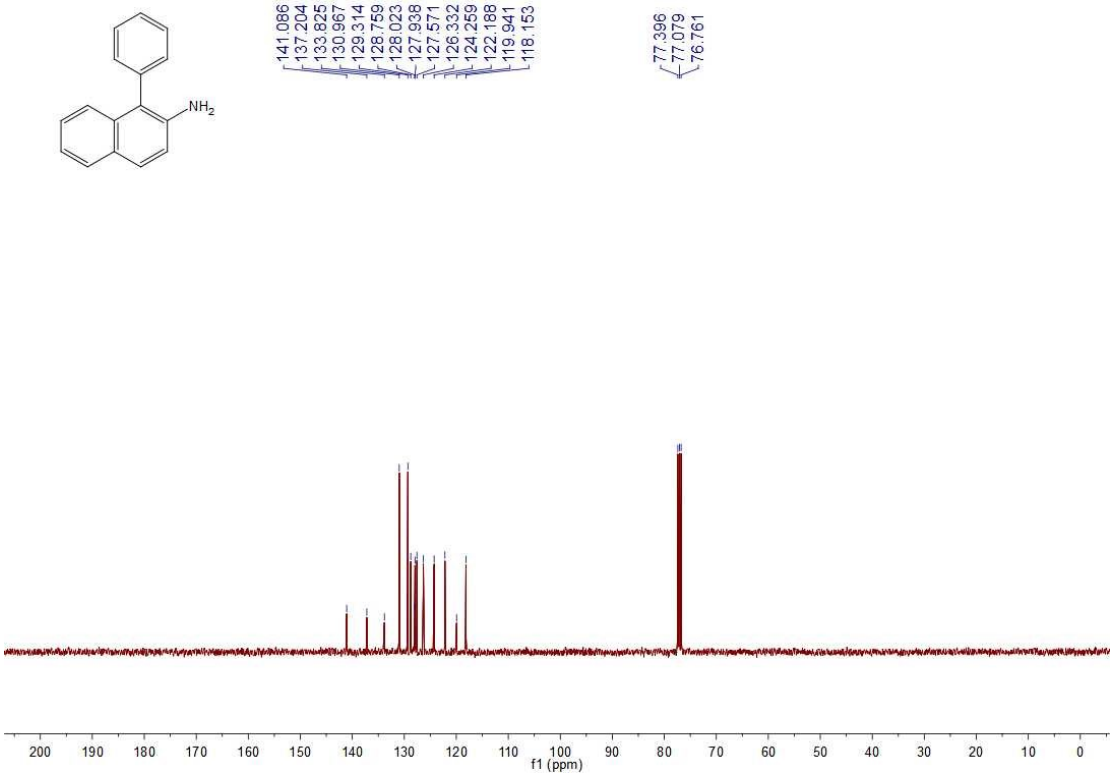
8. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra of the Products.

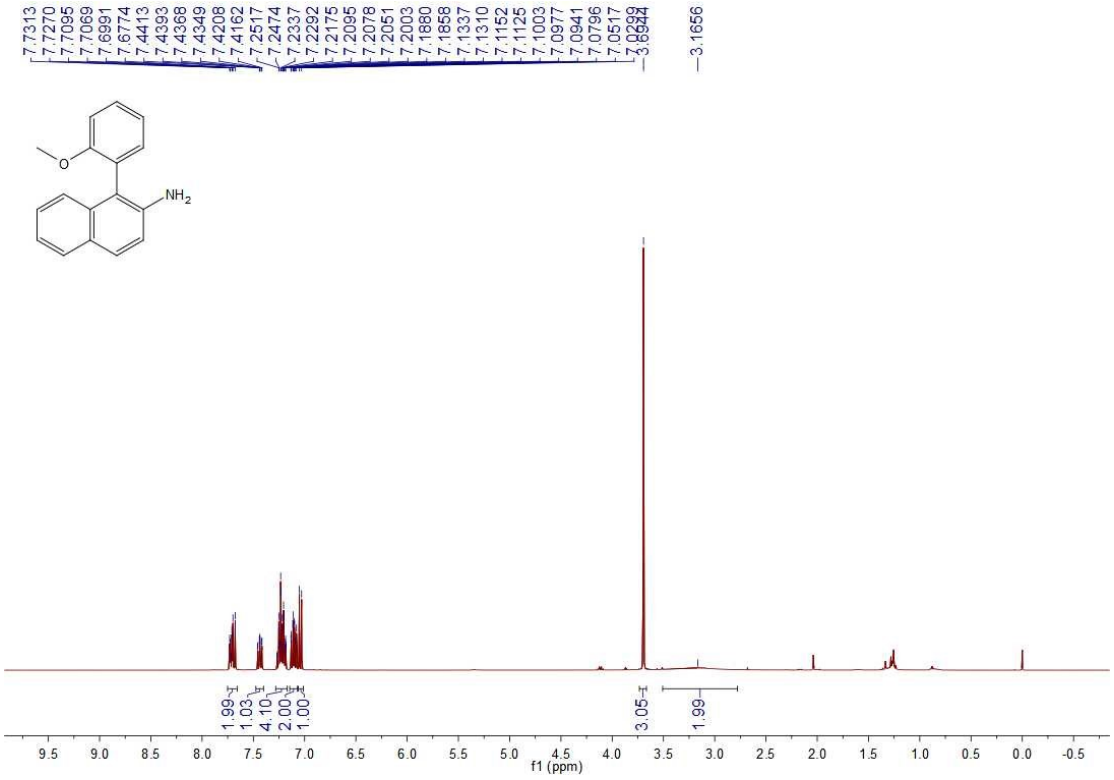
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-phenylnaphthalen-2-amine (**3a**).



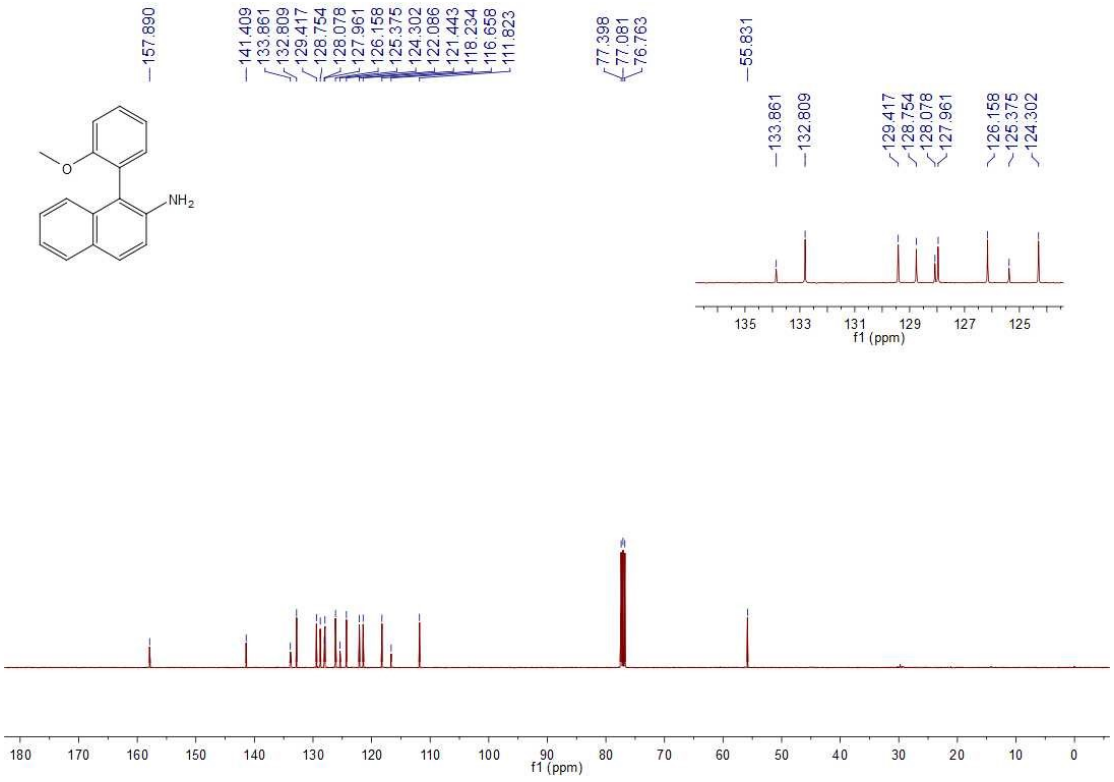
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-phenylnaphthalen-2-amine (**3a**).



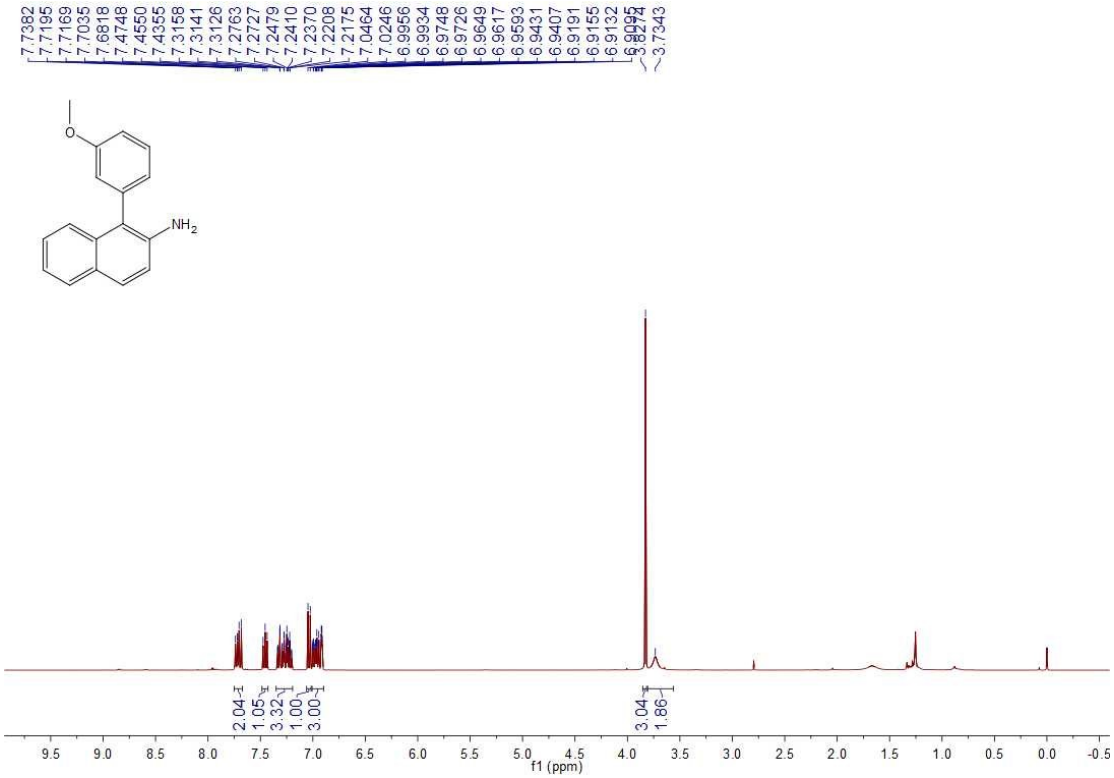
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(2-methoxyphenyl)naphthalen-2-amine (**3b**).



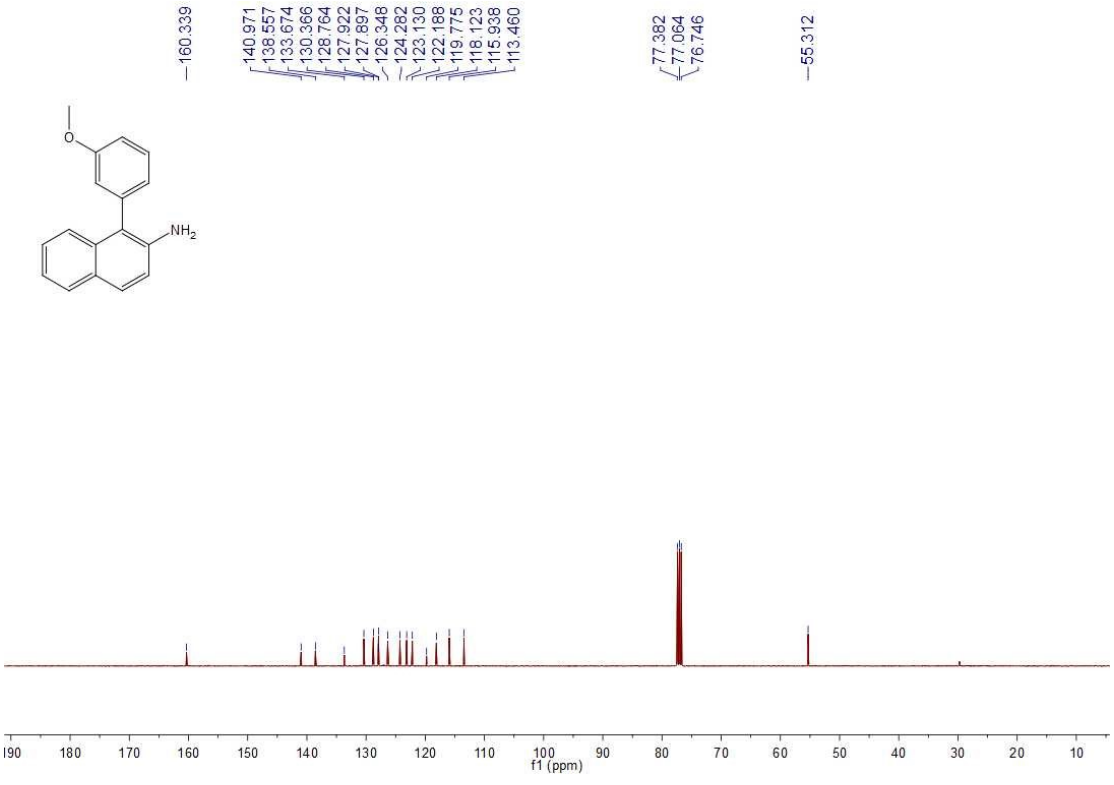
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 1-(2-methoxyphenyl)naphthalen-2-amine (**3b**).



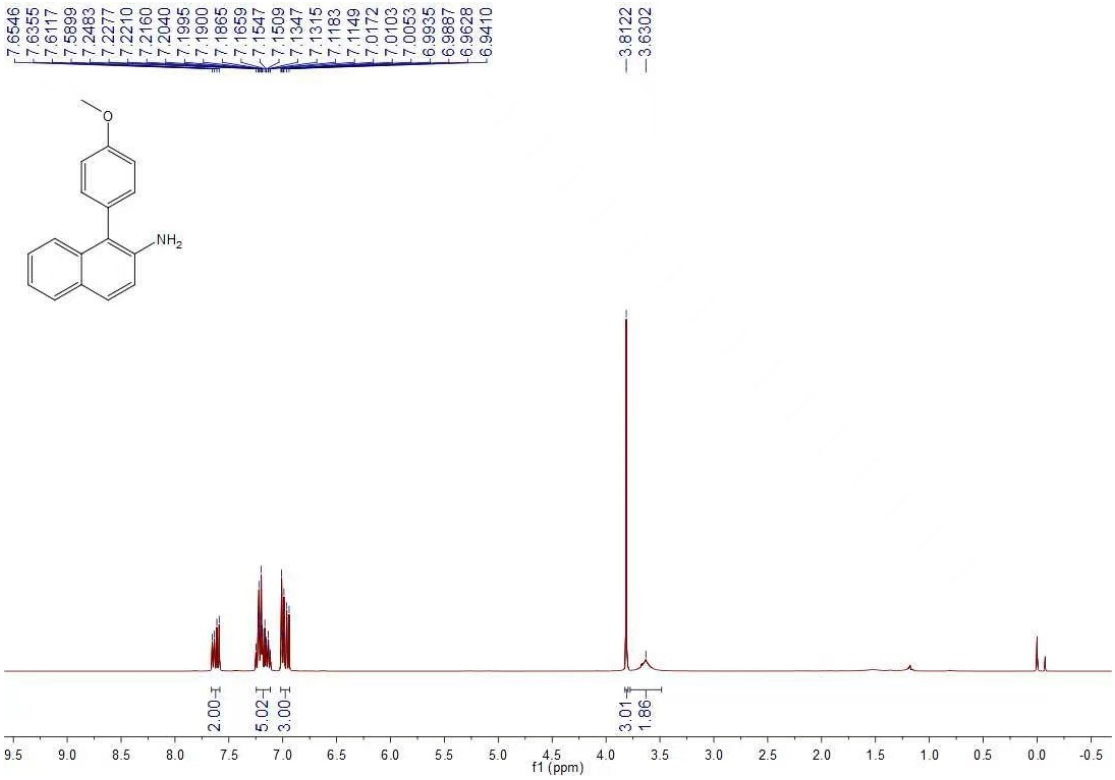
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(3-methoxyphenyl)naphthalen-2-amines (**3c**).



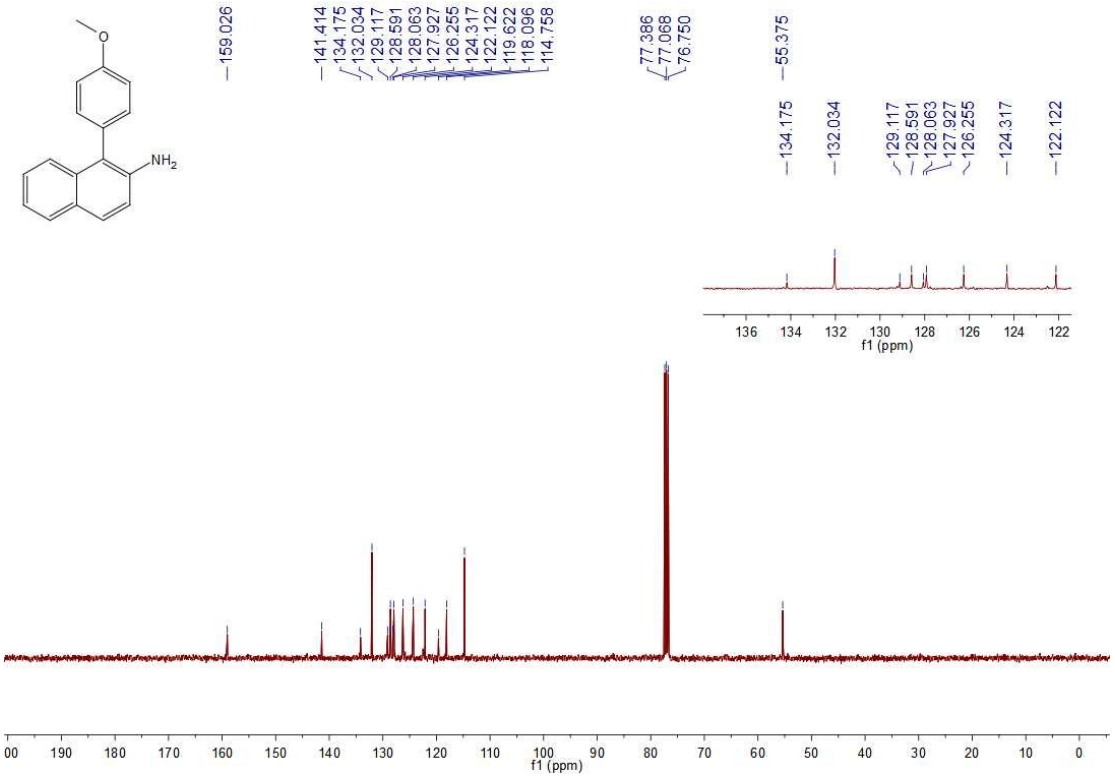
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 1-(3-methoxyphenyl)naphthalen-2-amines (**3c**).



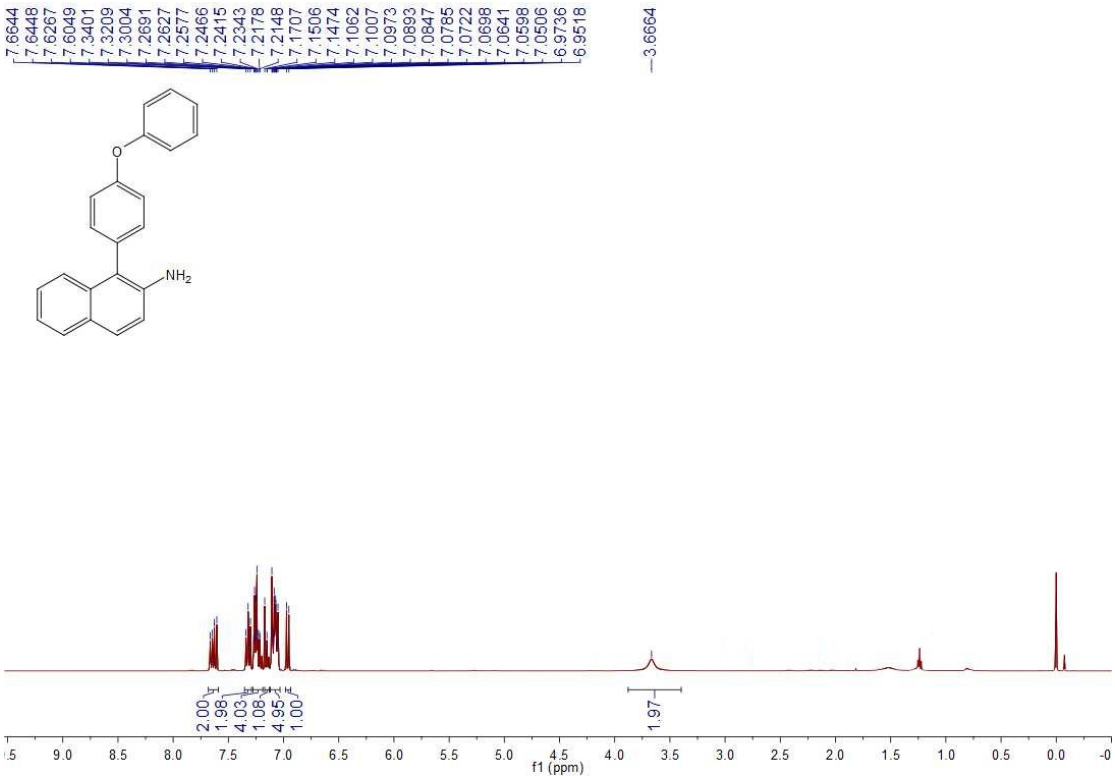
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(4-methoxyphenyl)naphthalen-2-amine (**3d**).



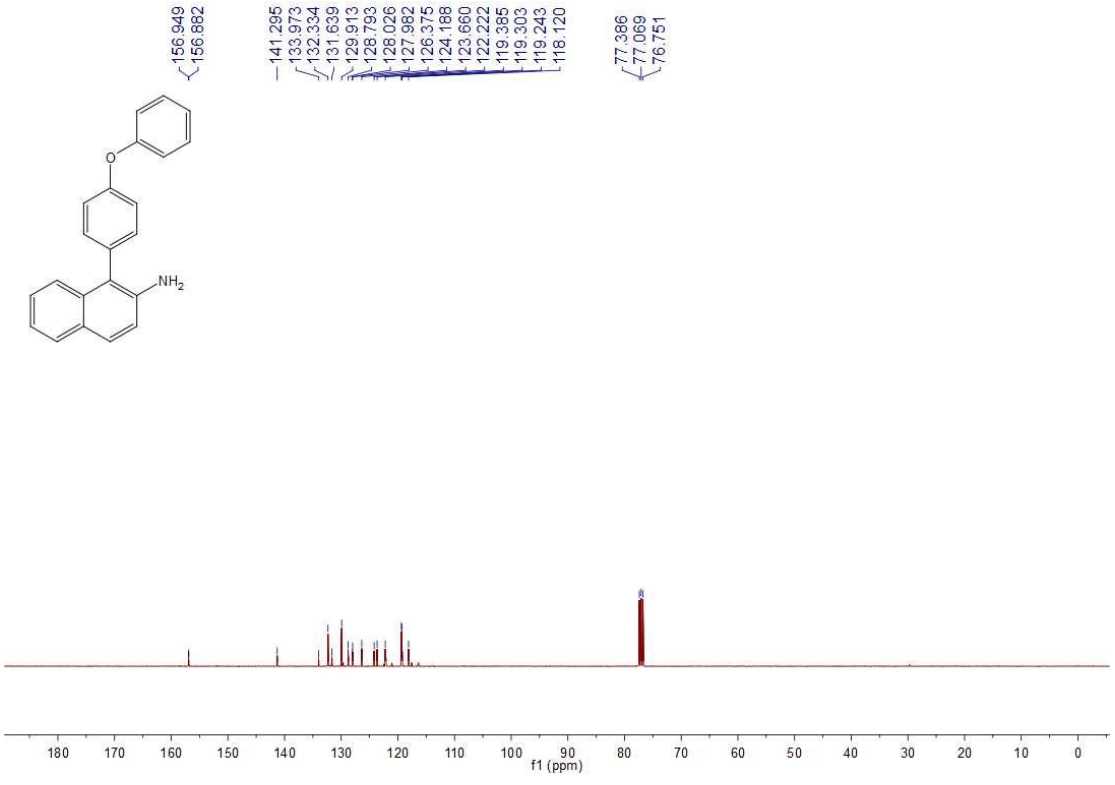
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-(4-methoxyphenyl)naphthalen-2-amine (**3d**).



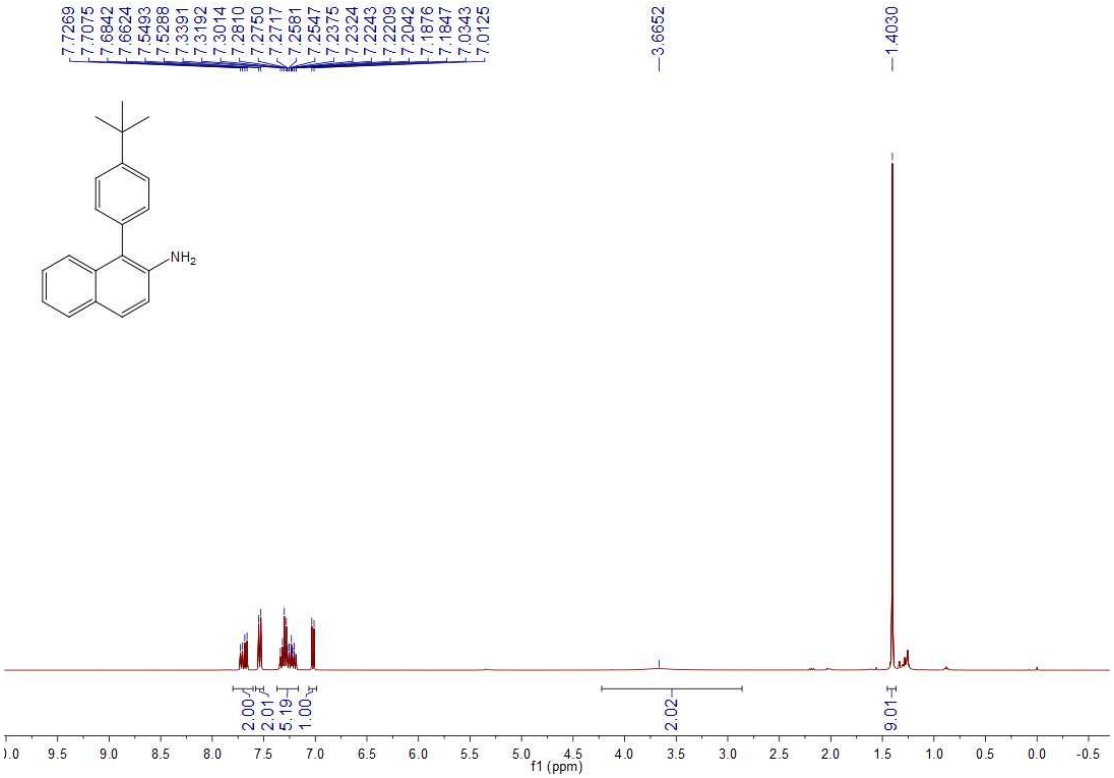
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(4-phenoxyphenyl)naphthalen-2-amine (**3e**).



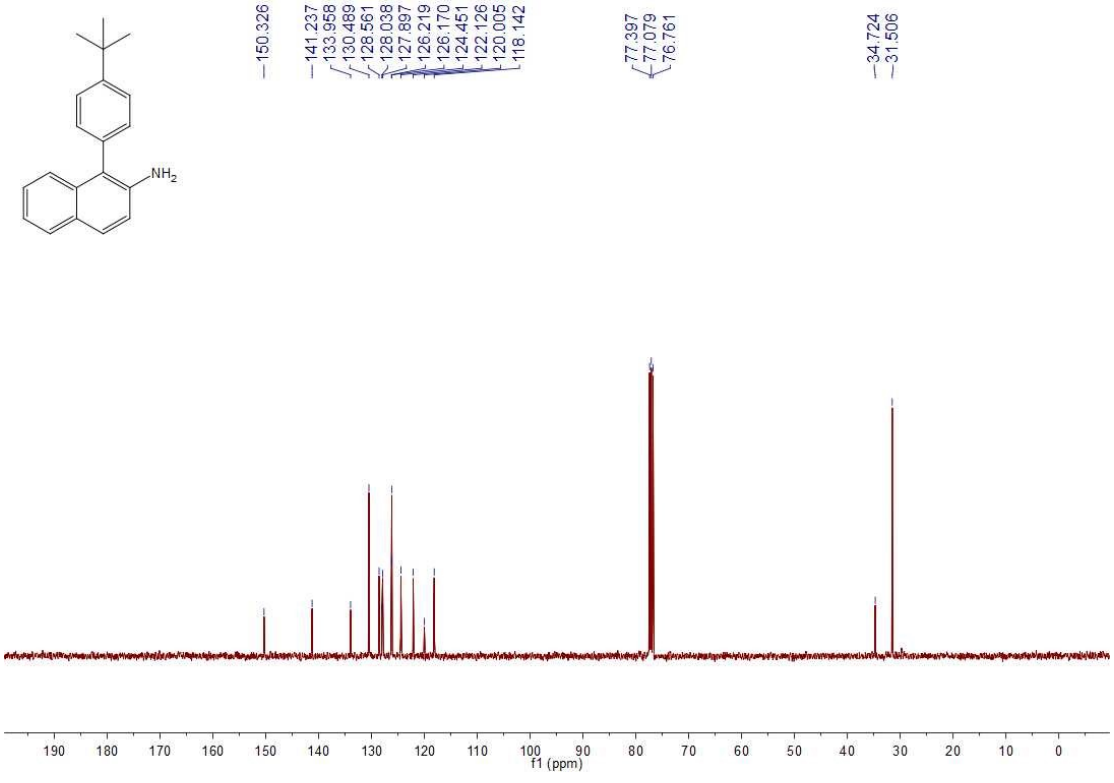
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-(4-phenoxyphenyl)naphthalen-2-amine (**3e**).



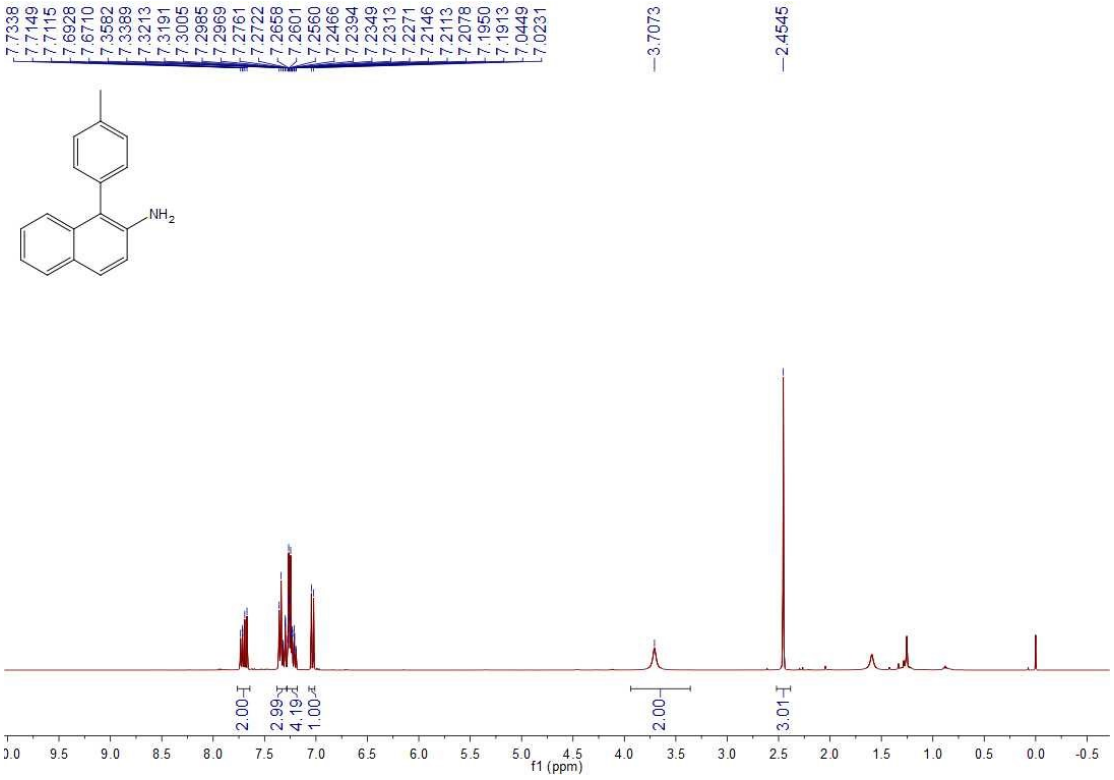
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(4-(tert-butyl)phenyl)naphthalen-2-amine (**3f**).



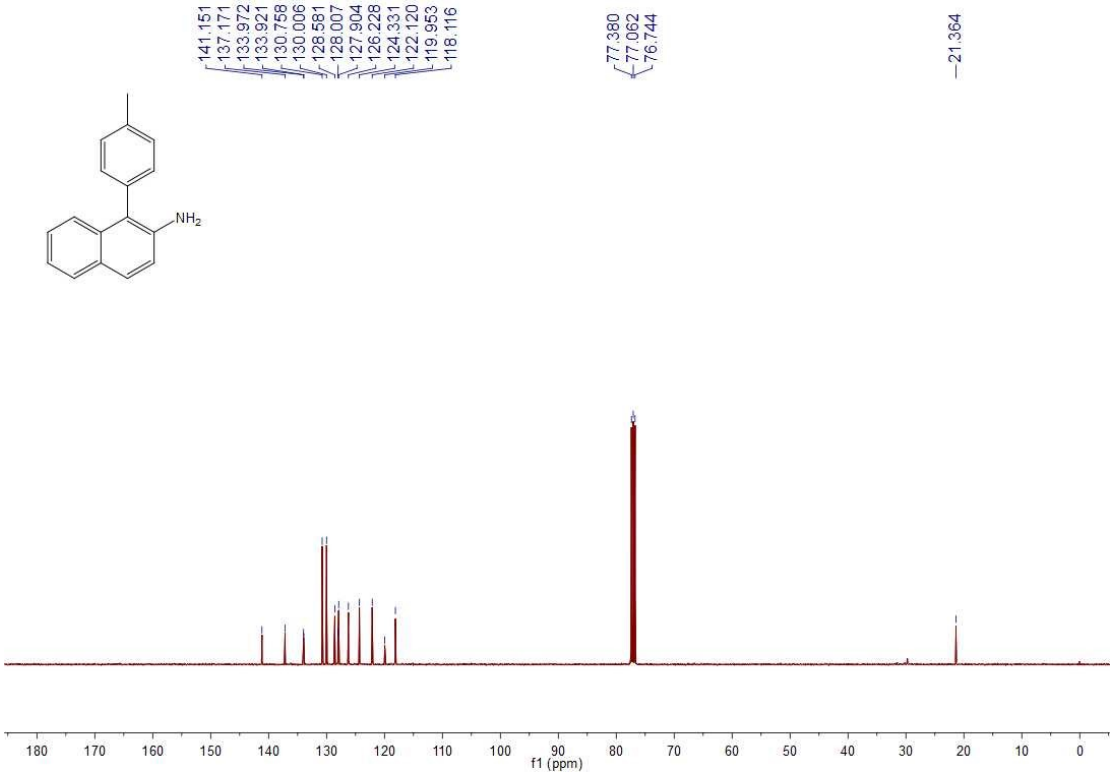
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 1-(4-(tert-butyl)phenyl)naphthalen-2-amine (**3f**).



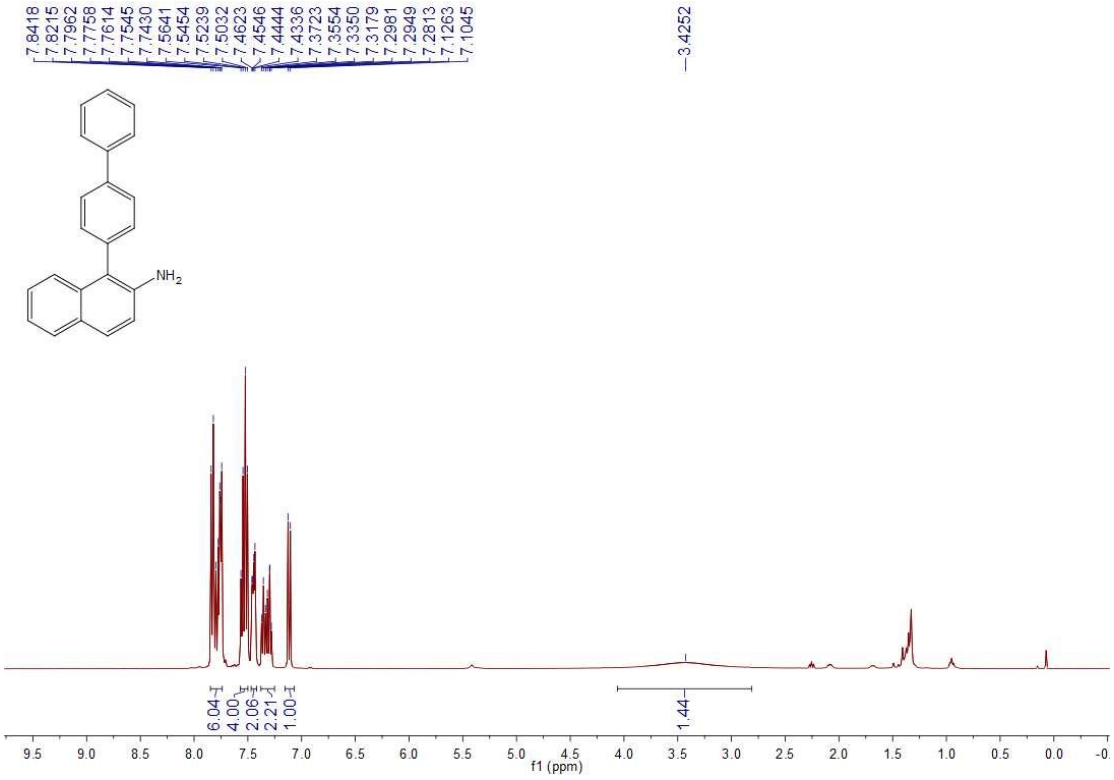
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(p-tolyl)naphthalen-2-amine (**3g**).



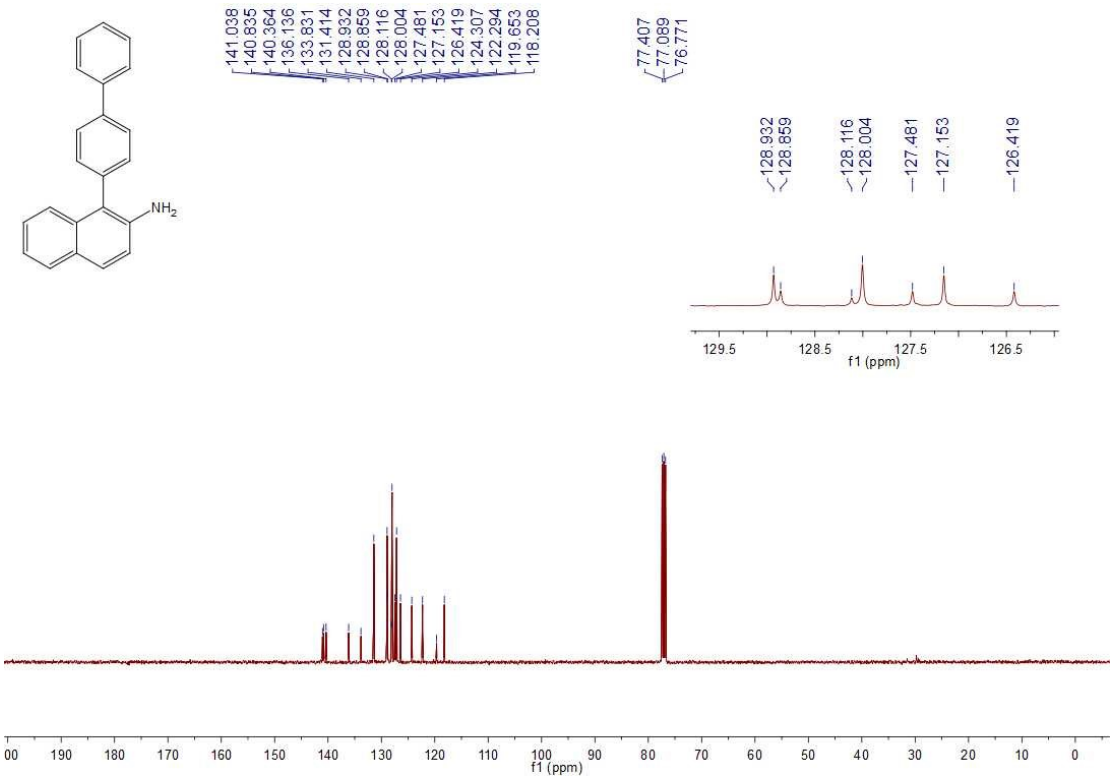
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-(p-tolyl)naphthalen-2-amine (**3g**).



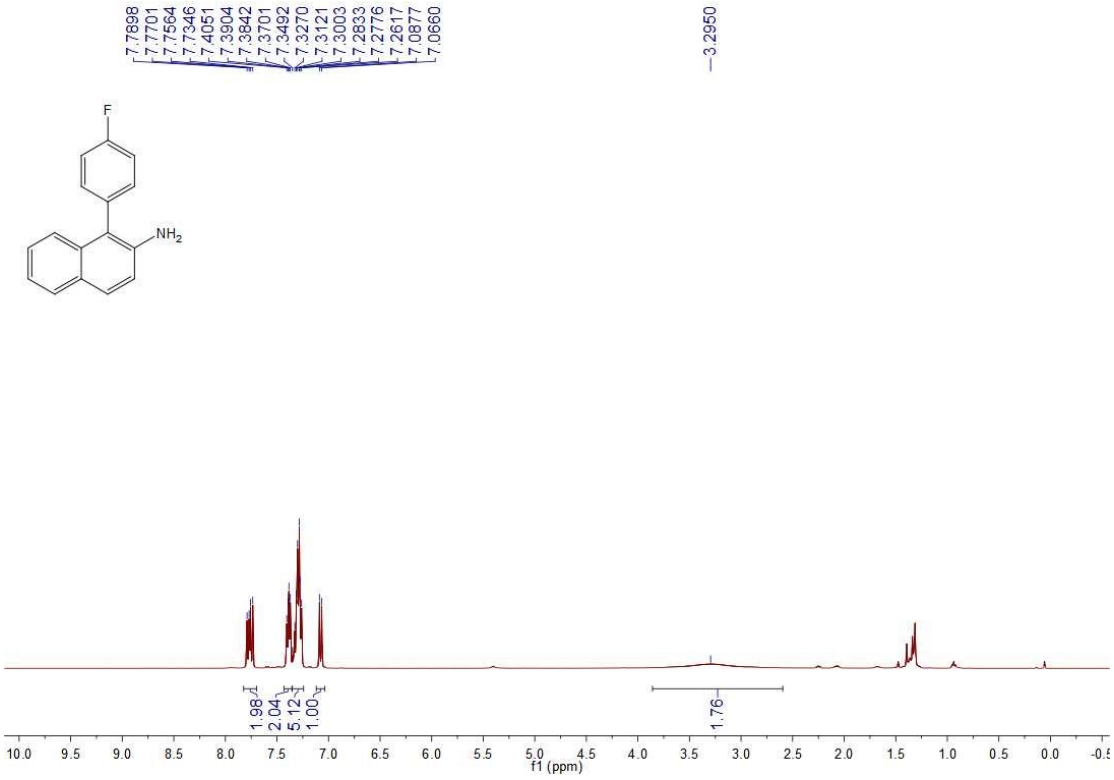
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-([1,1'-biphenyl]-4-yl)naphthalen-2-amine (**3h**).



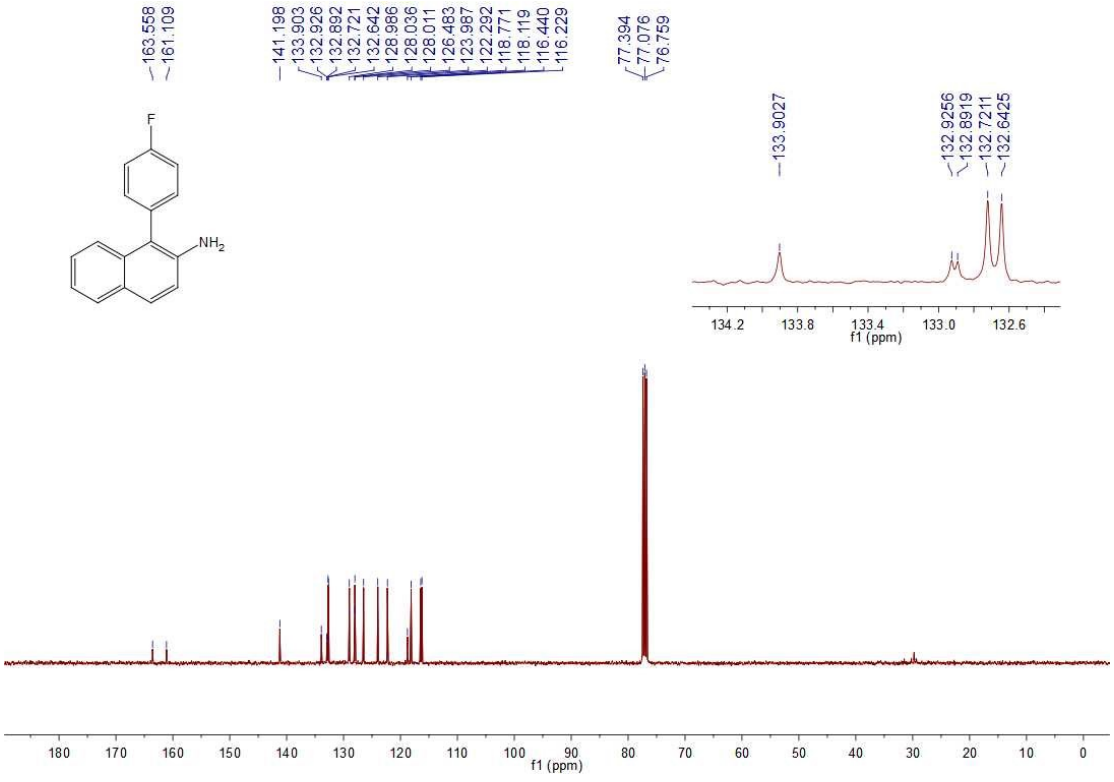
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 1-([1,1'-biphenyl]-4-yl)naphthalen-2-amine (**3h**).



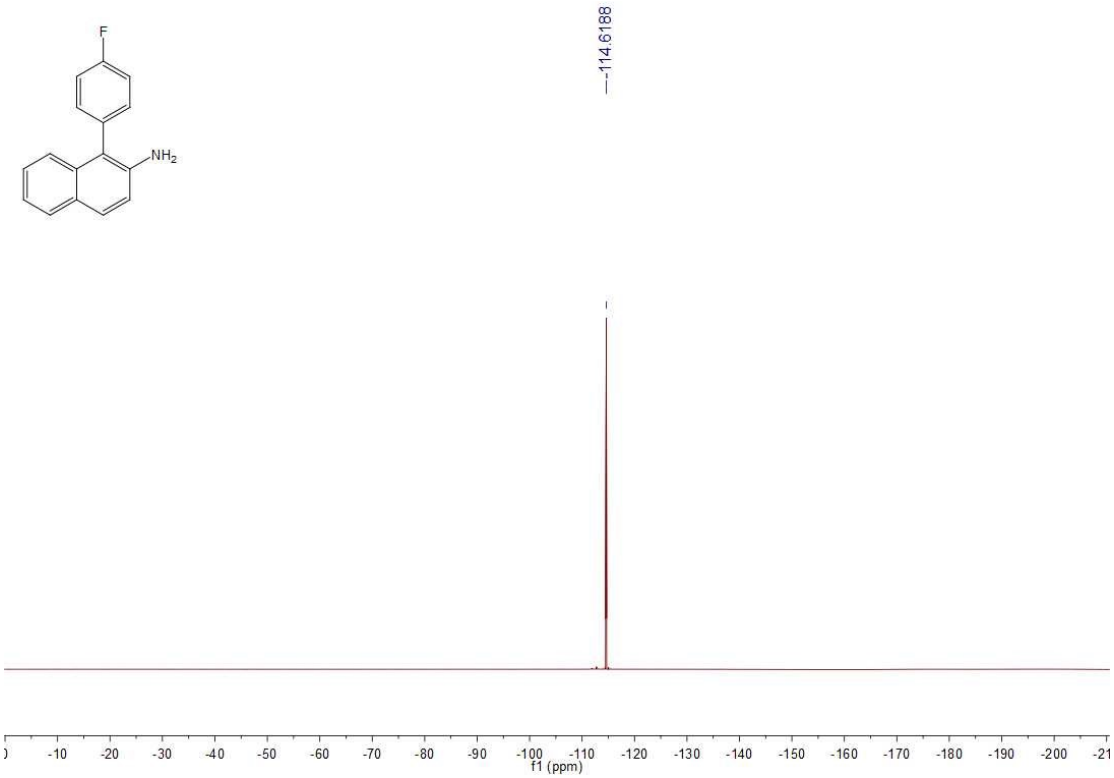
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(4-fluorophenyl)naphthalen-2-amine (**3i**).



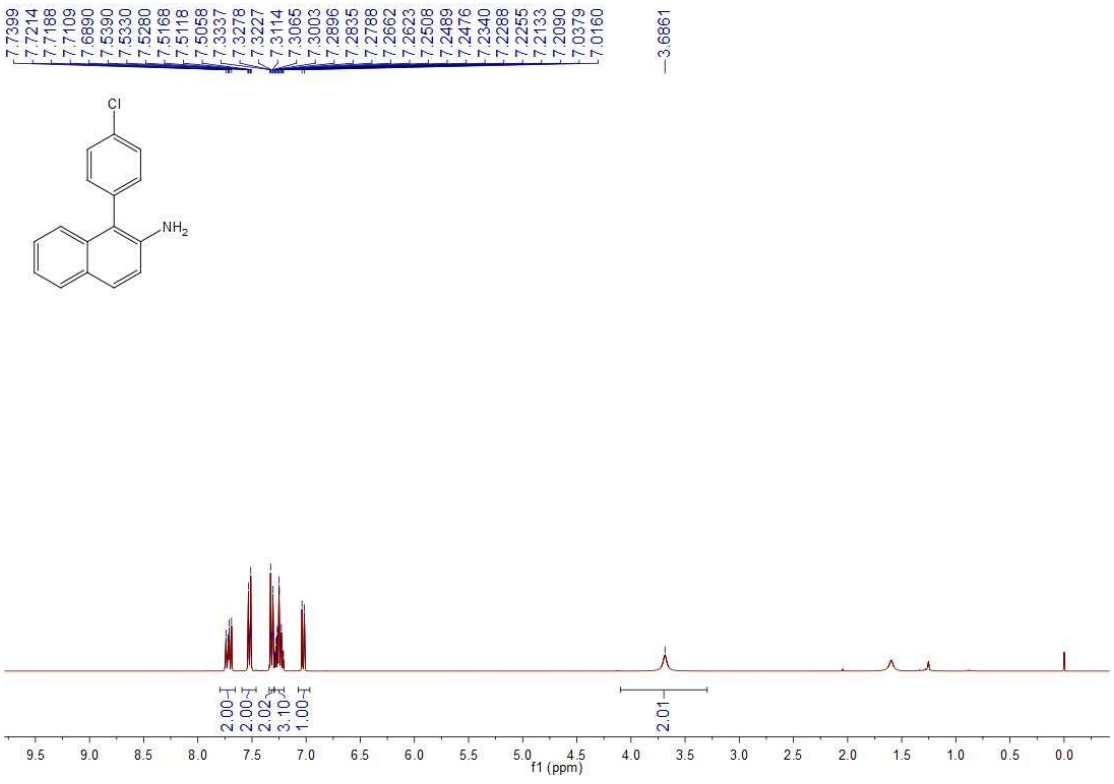
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum for 1-(4-fluorophenyl)naphthalen-2-amine (**3i**).



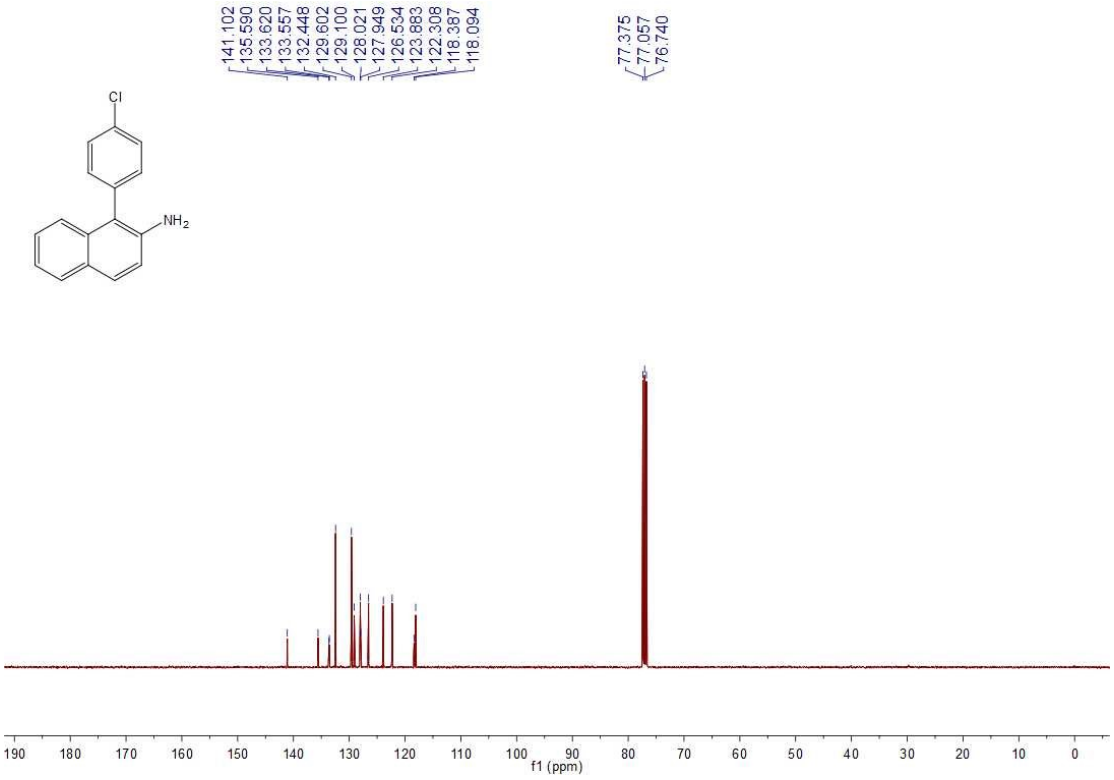
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 1-(4-fluorophenyl)naphthalen-2-amine (**3i**).



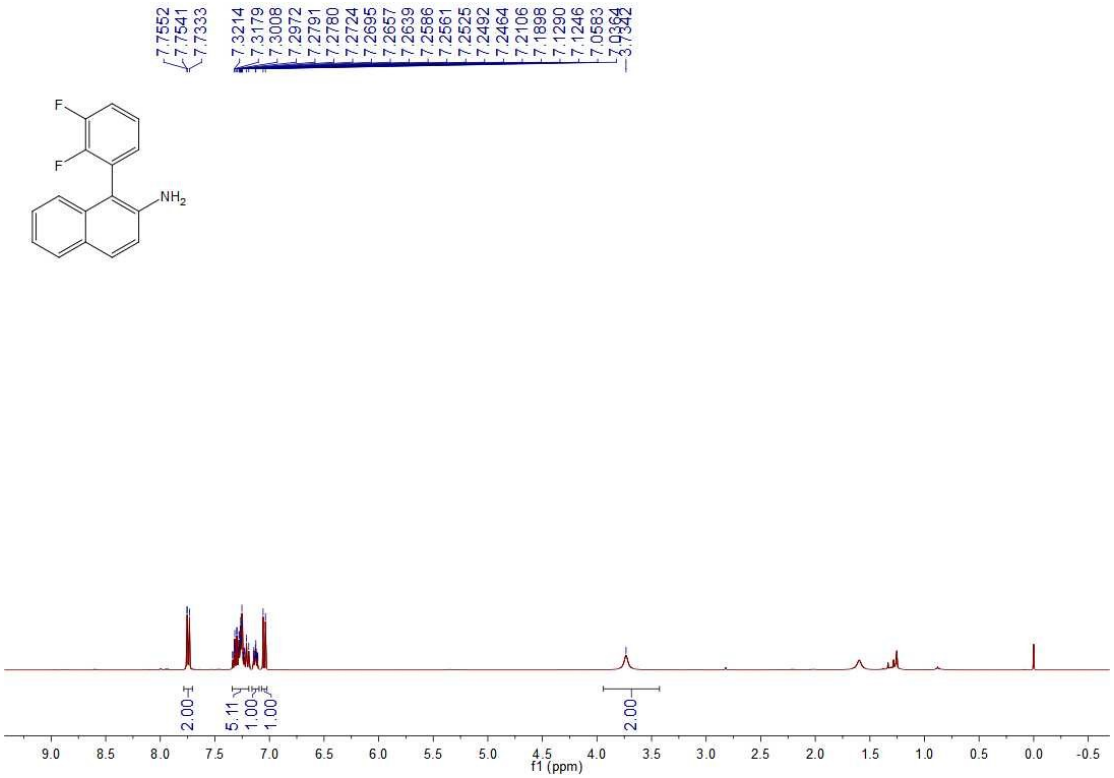
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(4-chlorophenyl)naphthalen-2-amine (**3j**).



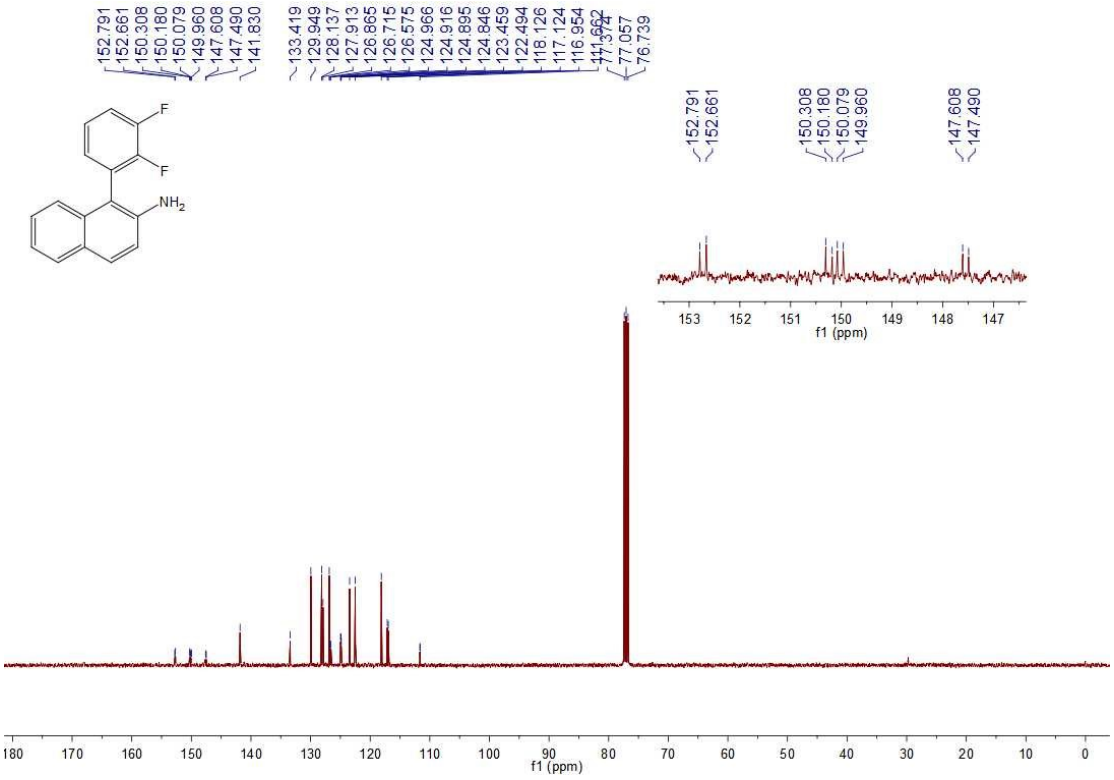
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-(4-chlorophenyl)naphthalen-2-amine (**3j**).



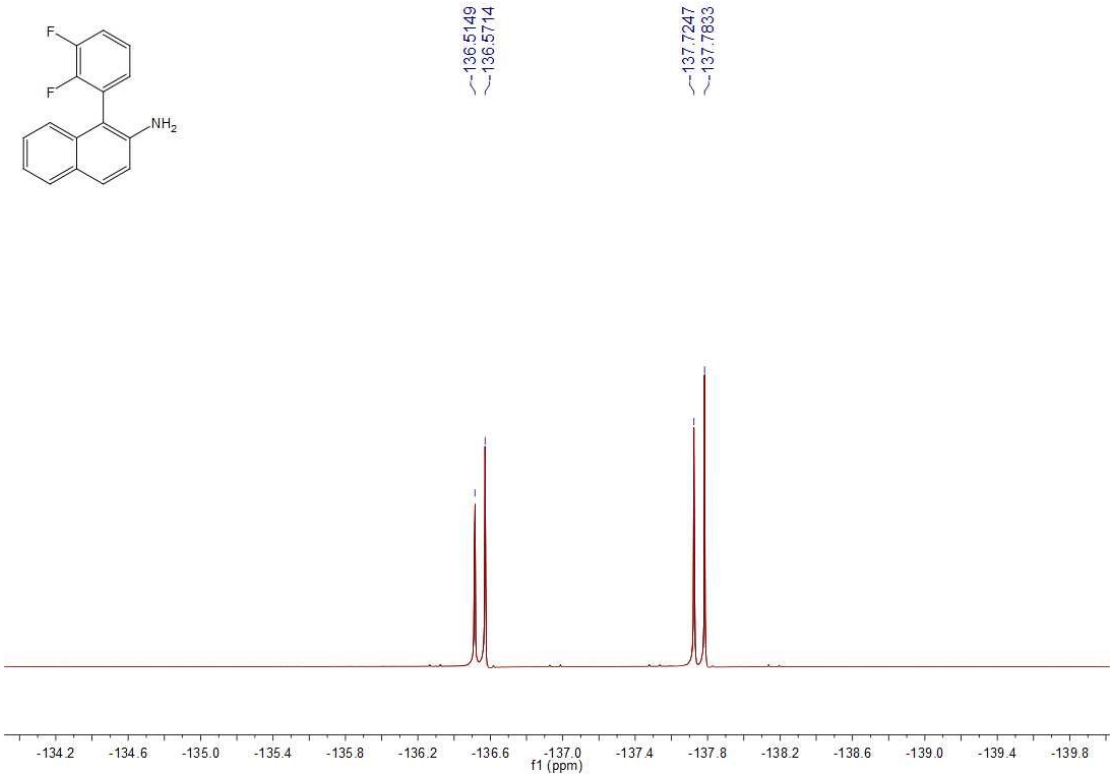
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(2,3-difluorophenyl)naphthalen-2-amine (**3k**).



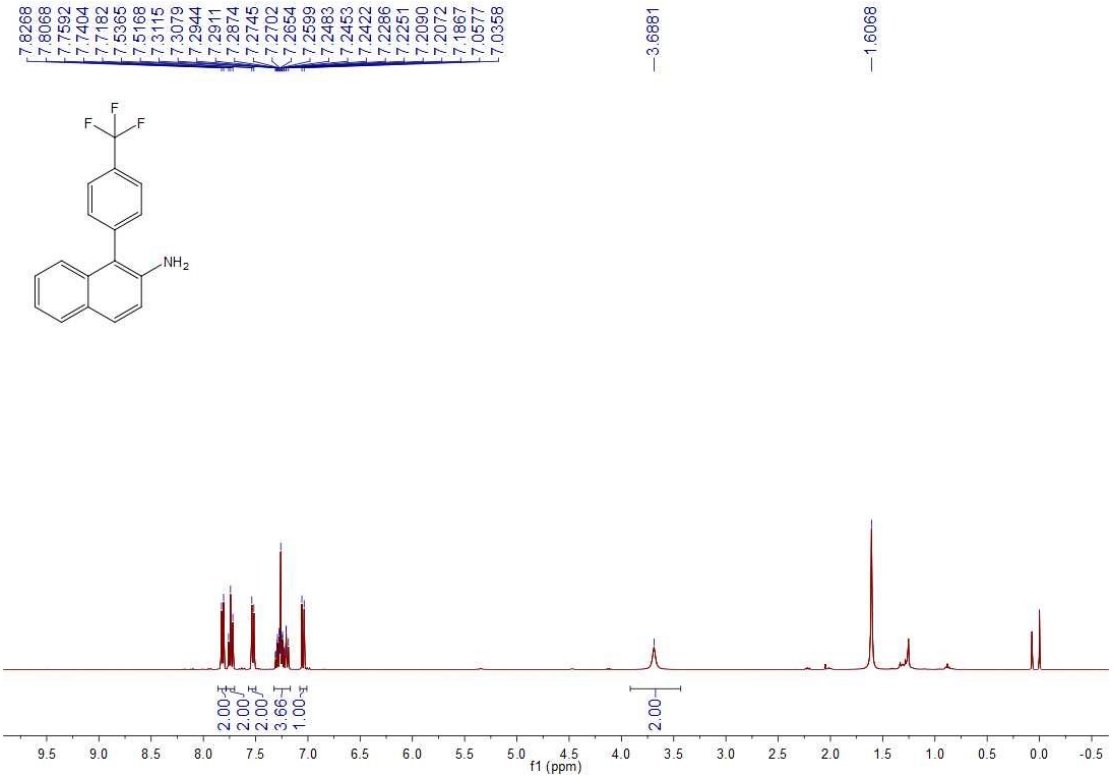
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-(2,3-difluorophenyl)naphthalen-2-amine (**3k**).



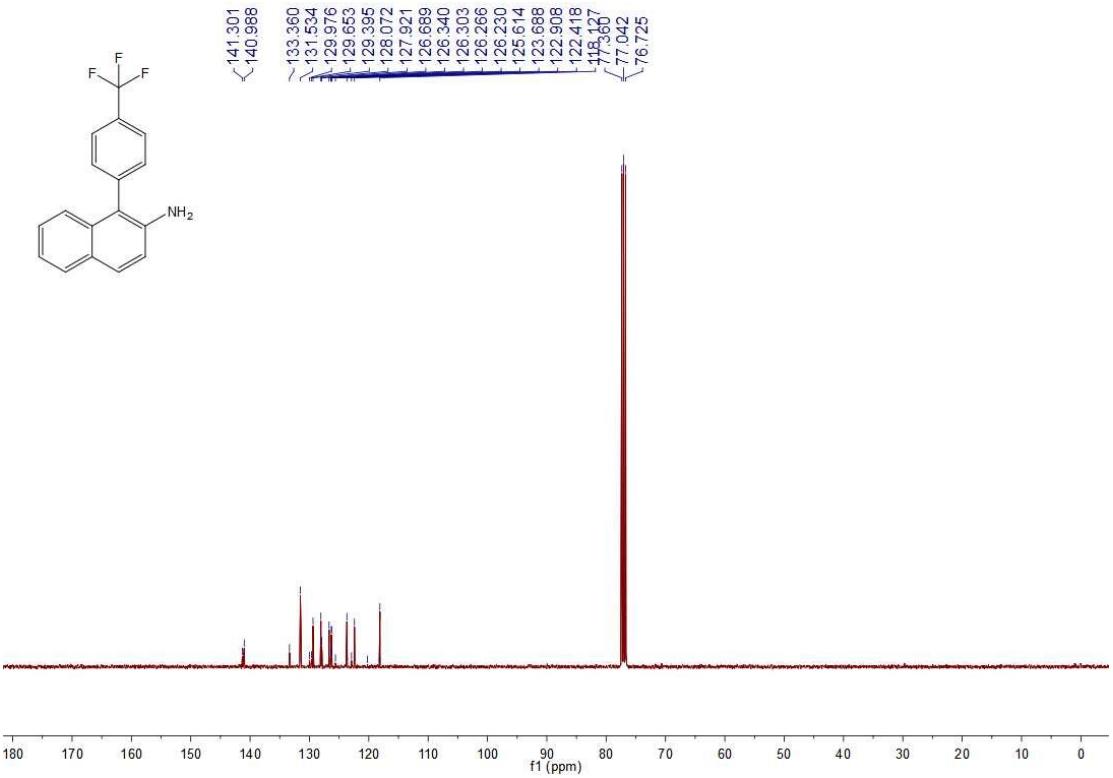
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 1-(2,3-difluorophenyl)naphthalen-2-amine (**3k**).



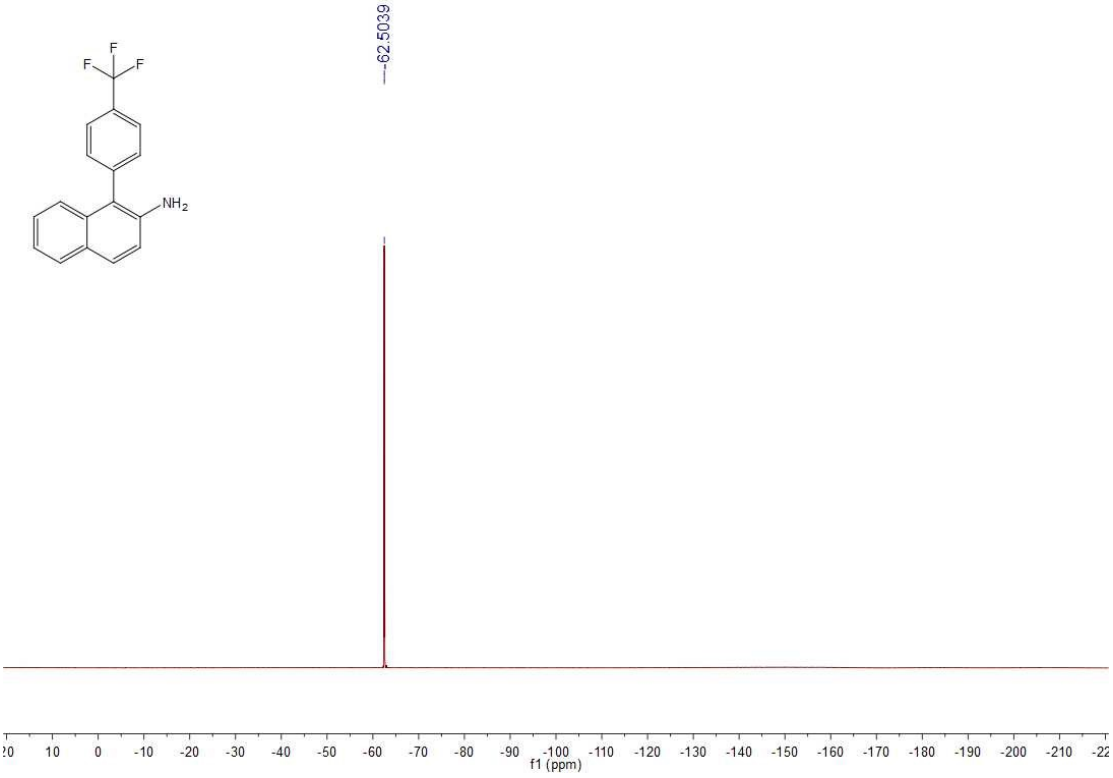
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(4-(trifluoromethyl)phenyl)naphthalen-2-amine (**3l**).



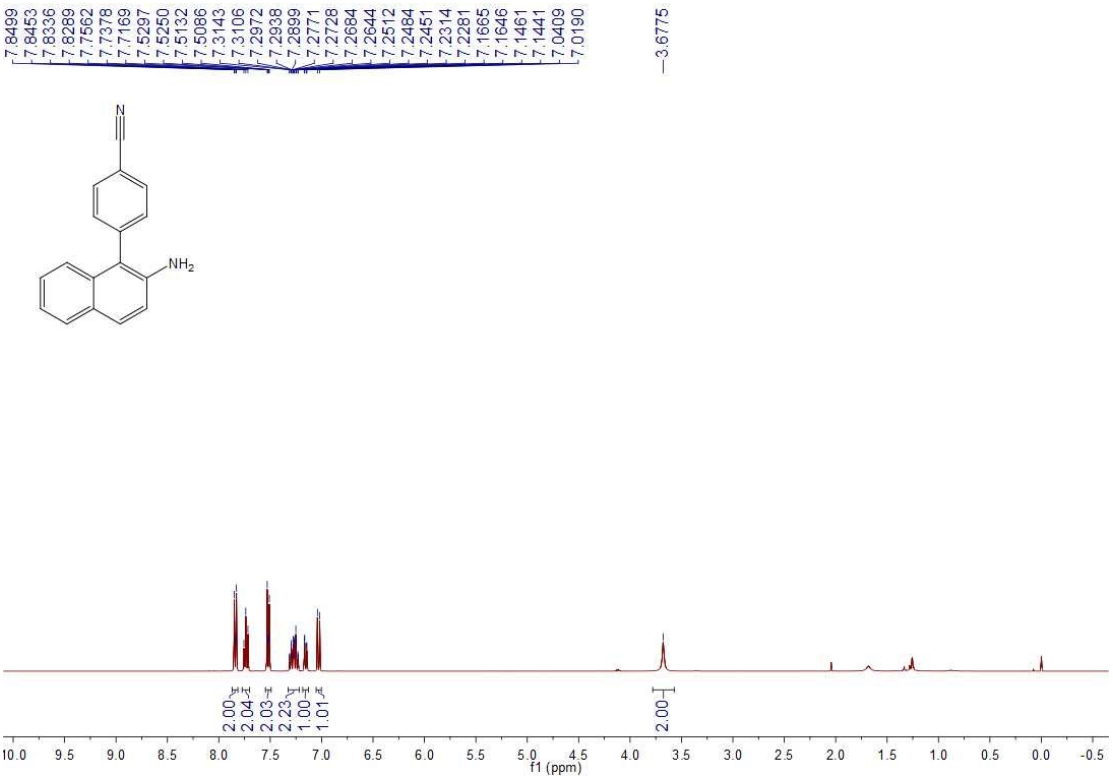
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-(4-(trifluoromethyl)phenyl)naphthalen-2-amine (**3l**).



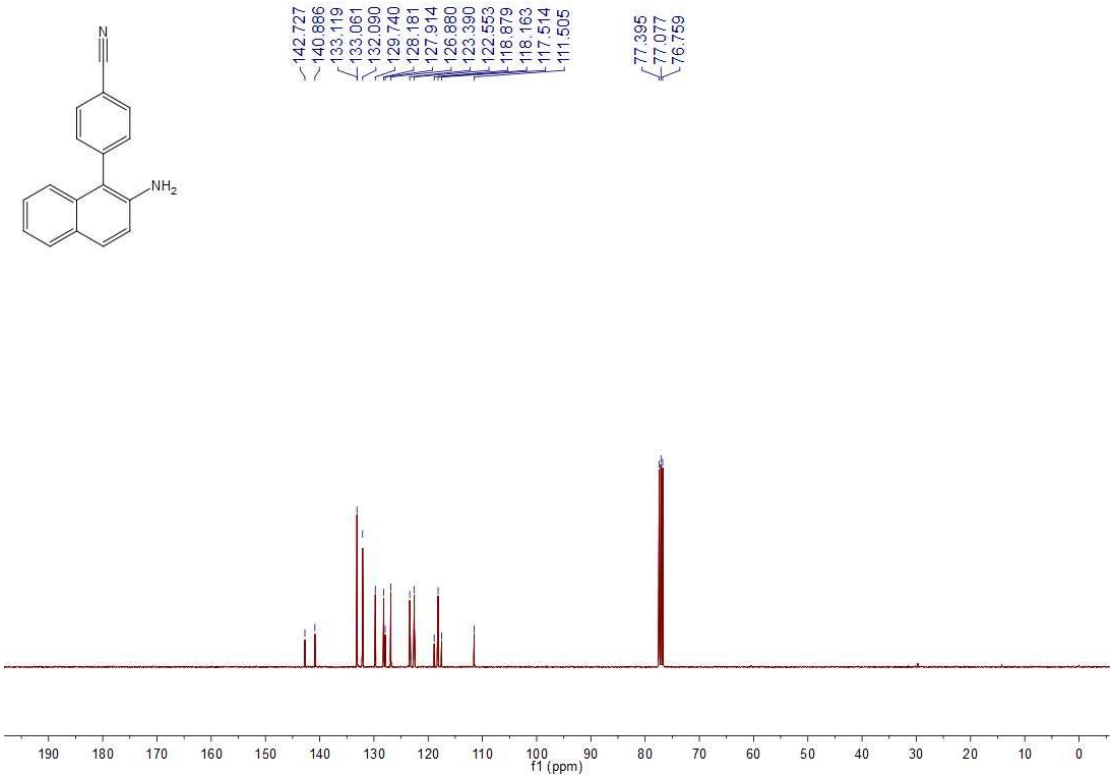
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 1-(4-(trifluoromethyl)phenyl)naphthalen-2-amine (**3l**).



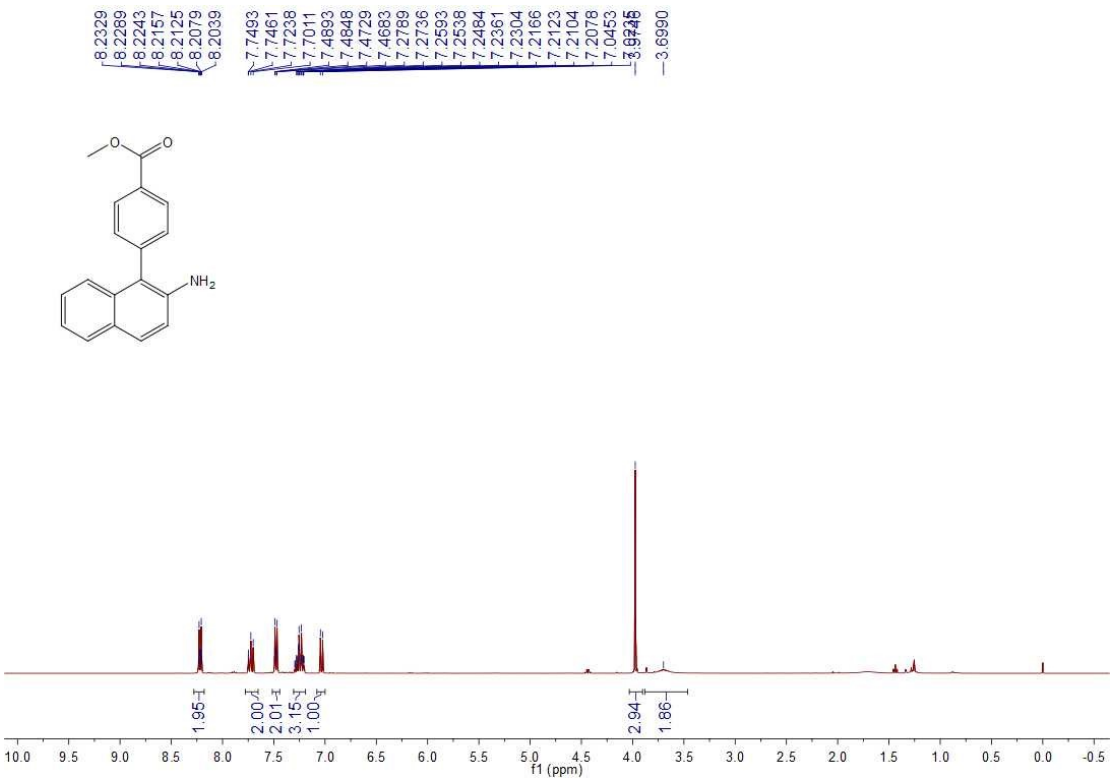
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4-(2-aminonaphthalen-1-yl)benzonitrile (**3m**).



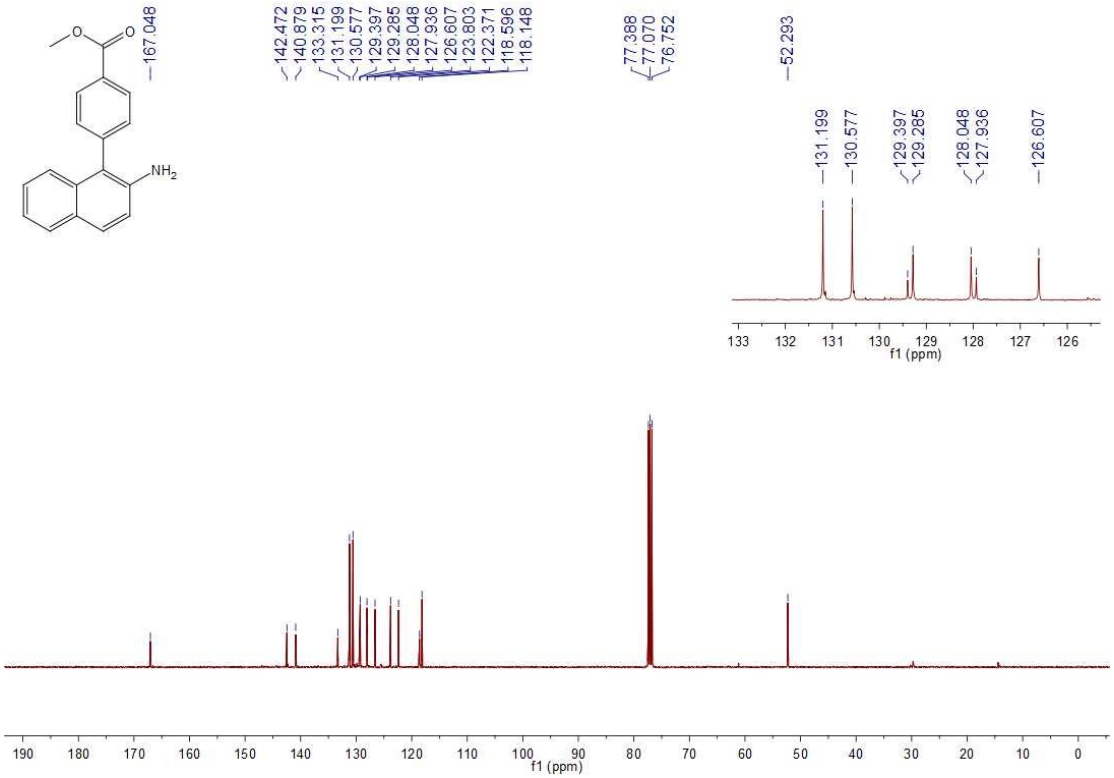
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 4-(2-aminonaphthalen-1-yl)benzonitrile (**3m**).



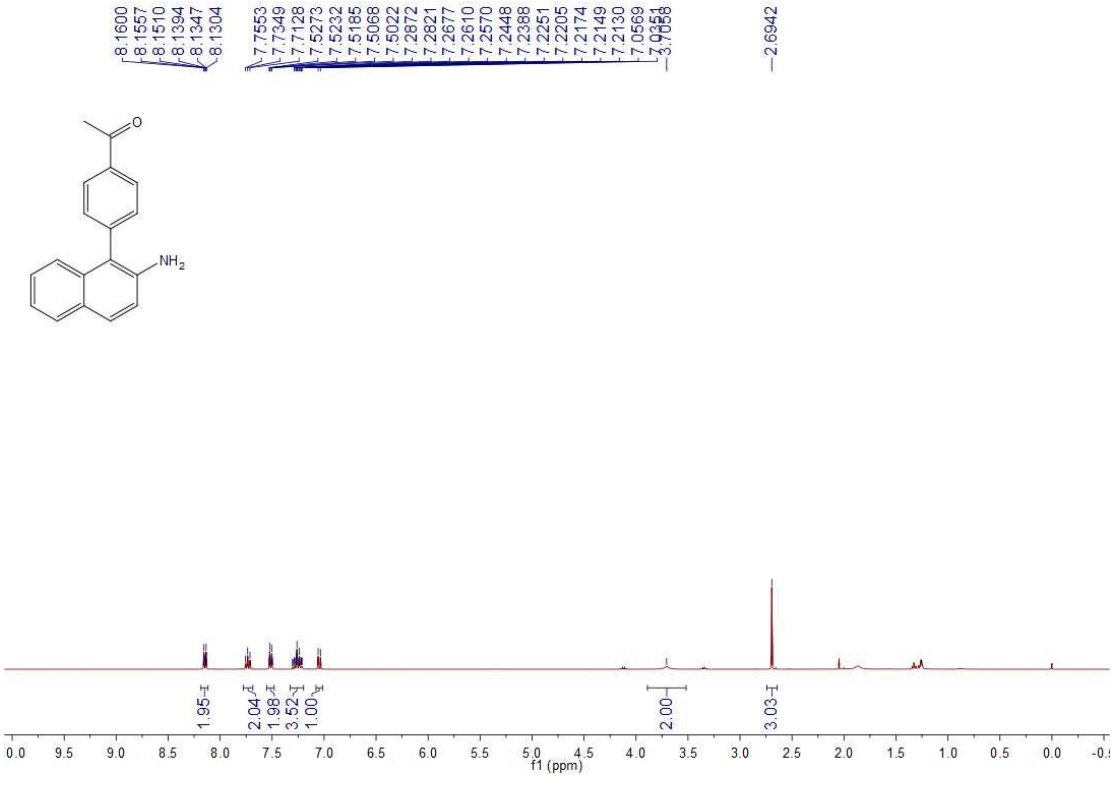
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for methyl 4-(2-aminonaphthalen-1-yl)benzoate (**3n**).



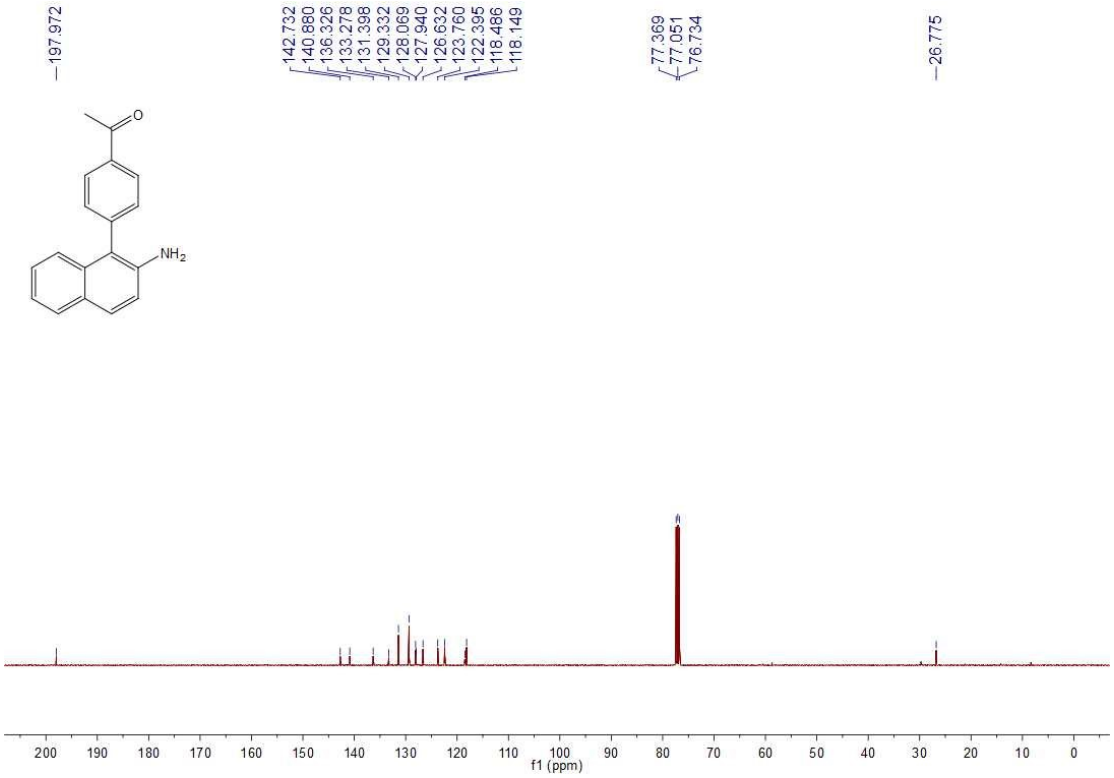
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for methyl 4-(2-aminonaphthalen-1-yl)benzoate (**3n**).



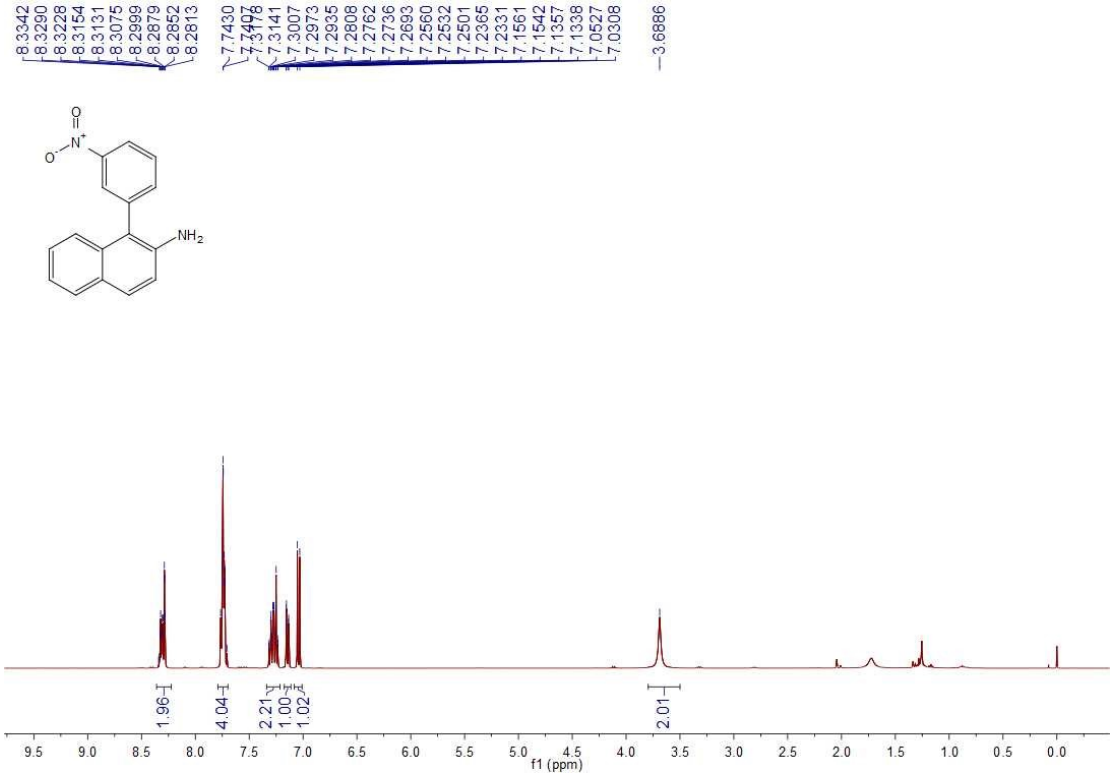
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(4-(2-aminonaphthalen-1-yl)phenyl)ethan-1-one (**3o**).



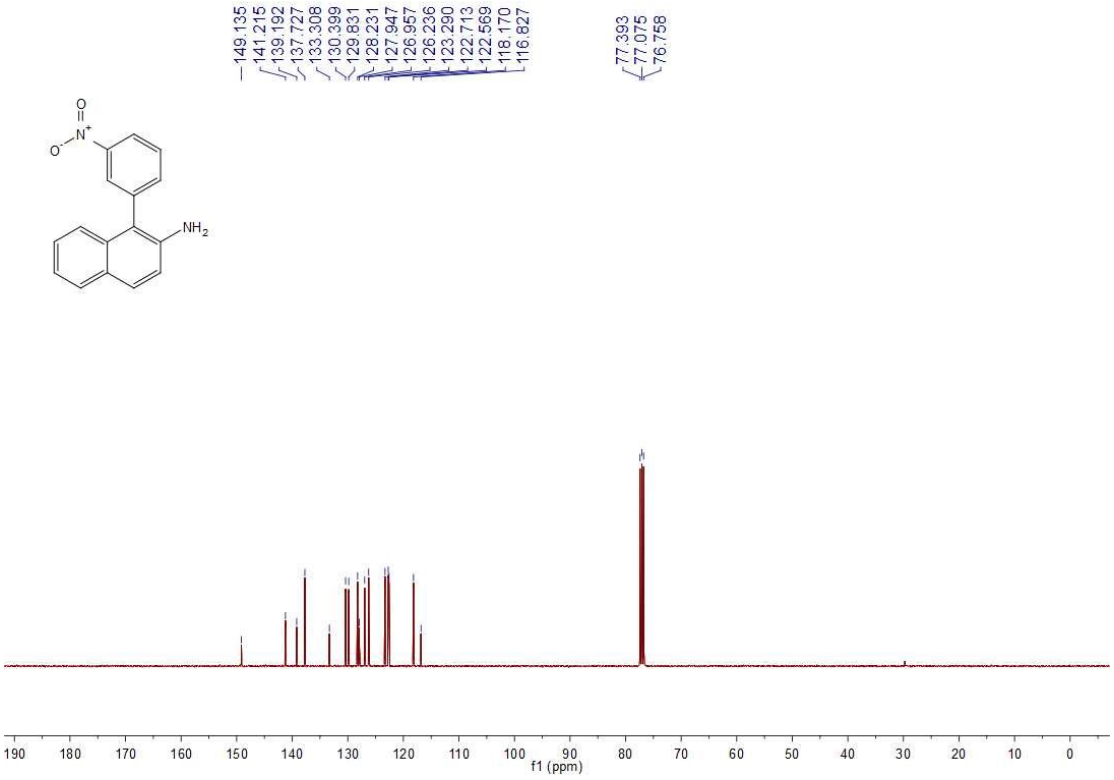
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-(4-(2-aminonaphthalen-1-yl)phenyl)ethan-1-one (**3o**).



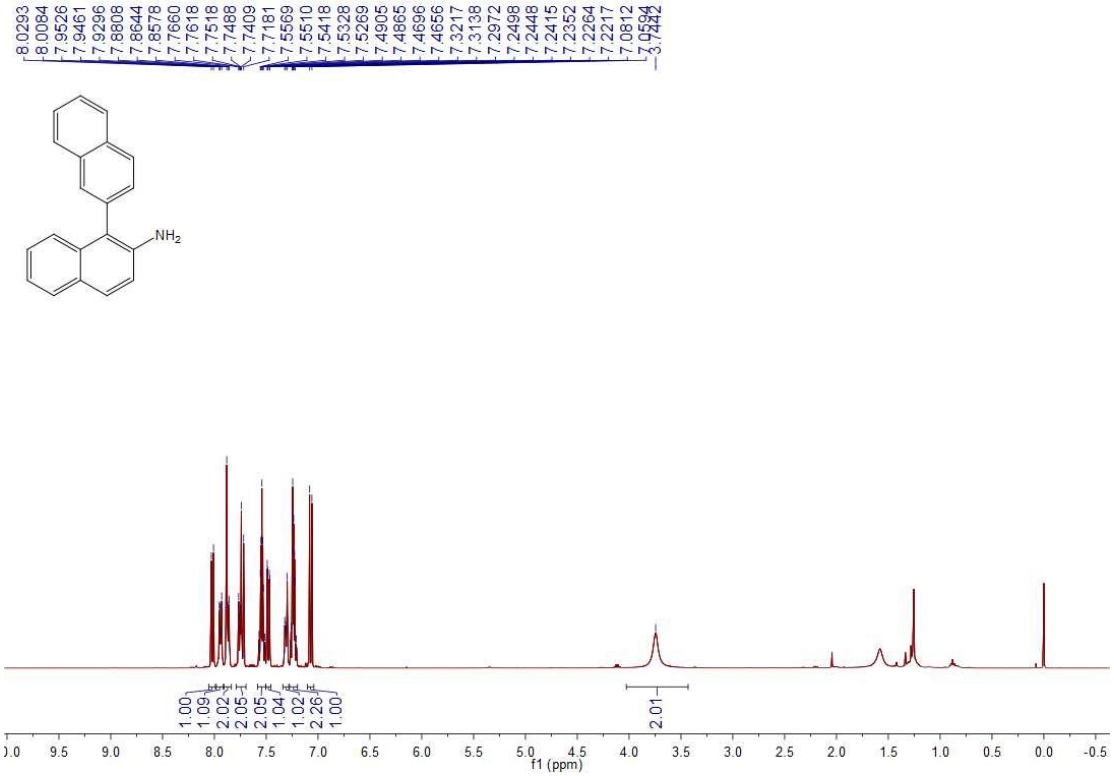
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(3-nitrophenyl)naphthalen-2-amine (**3p**).



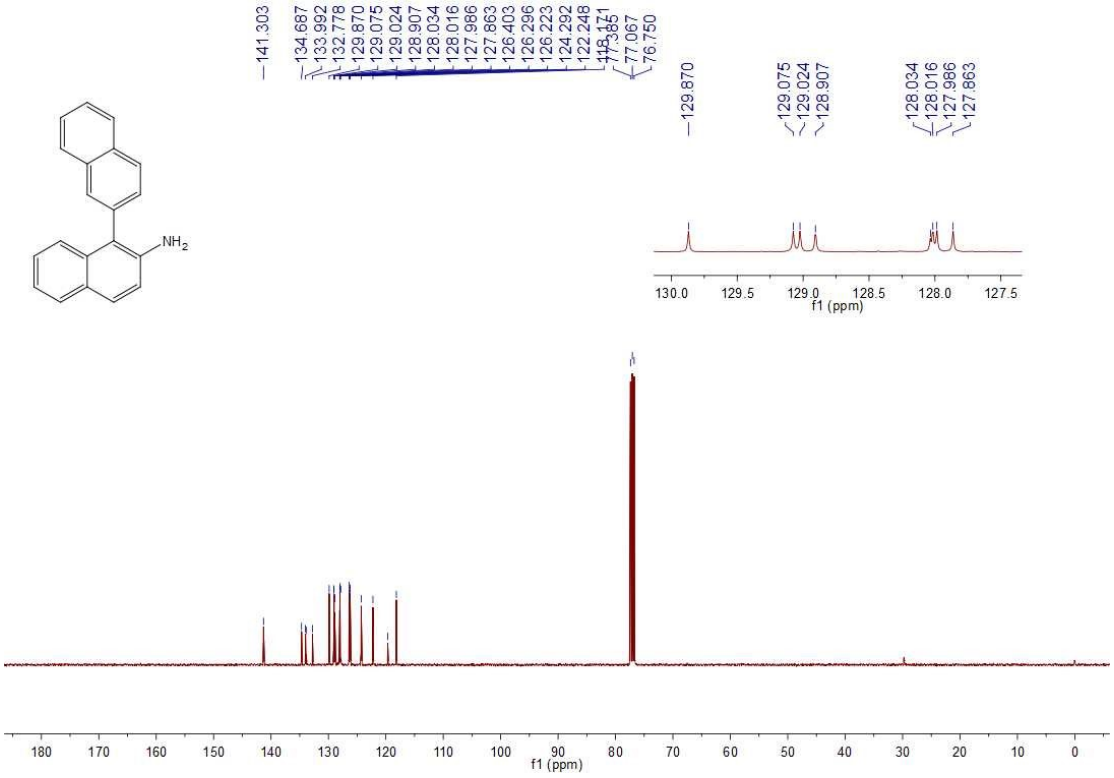
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-(3-nitrophenyl)naphthalen-2-amine (**3p**).



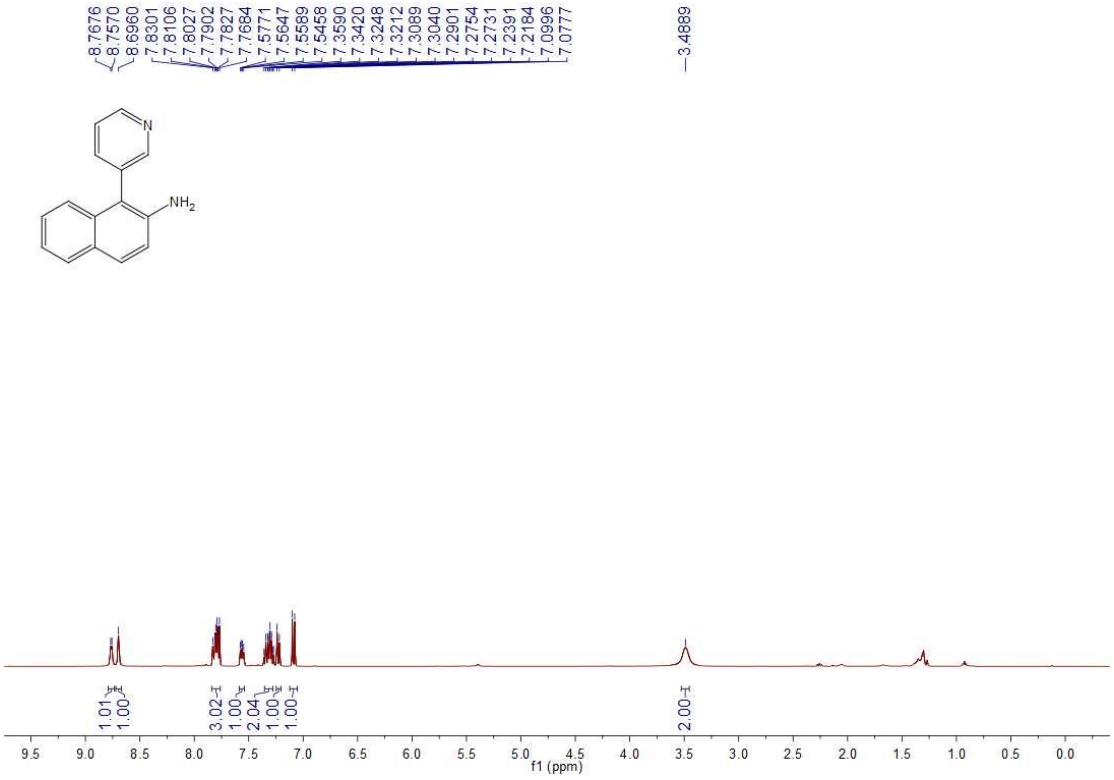
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for [1,2'-binaphthalen]-2-amine (**3q**).



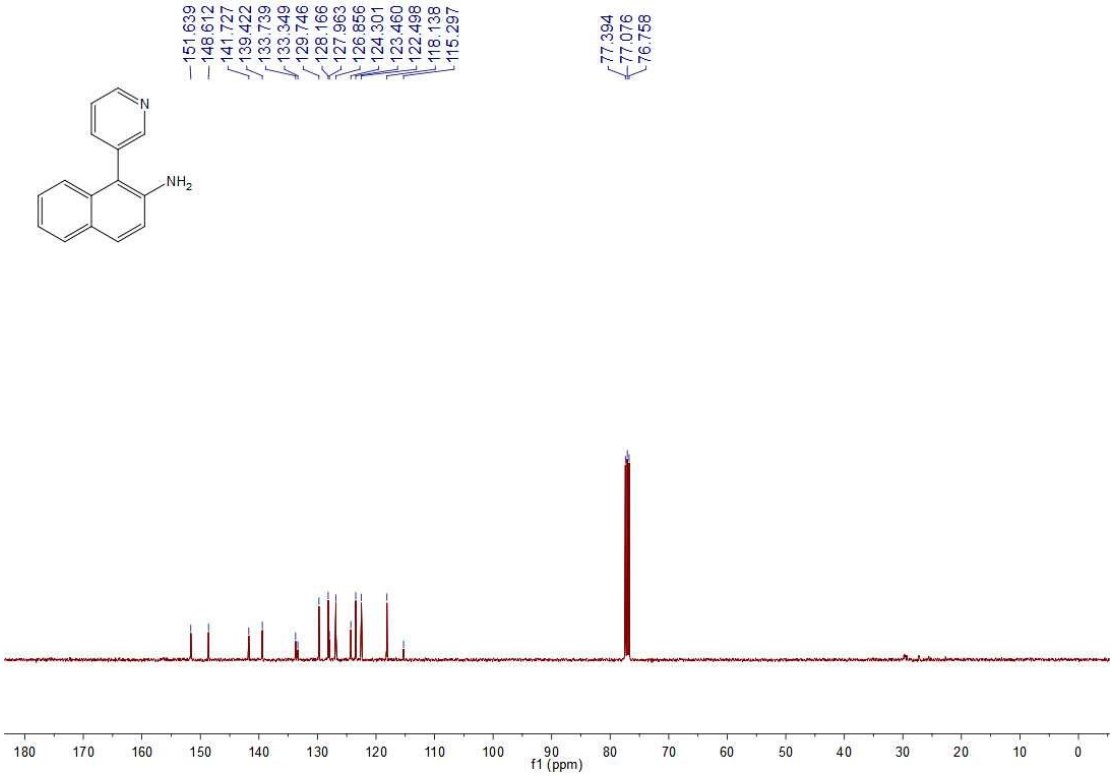
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for [1,2'-binaphthalen]-2-amine (**3q**).



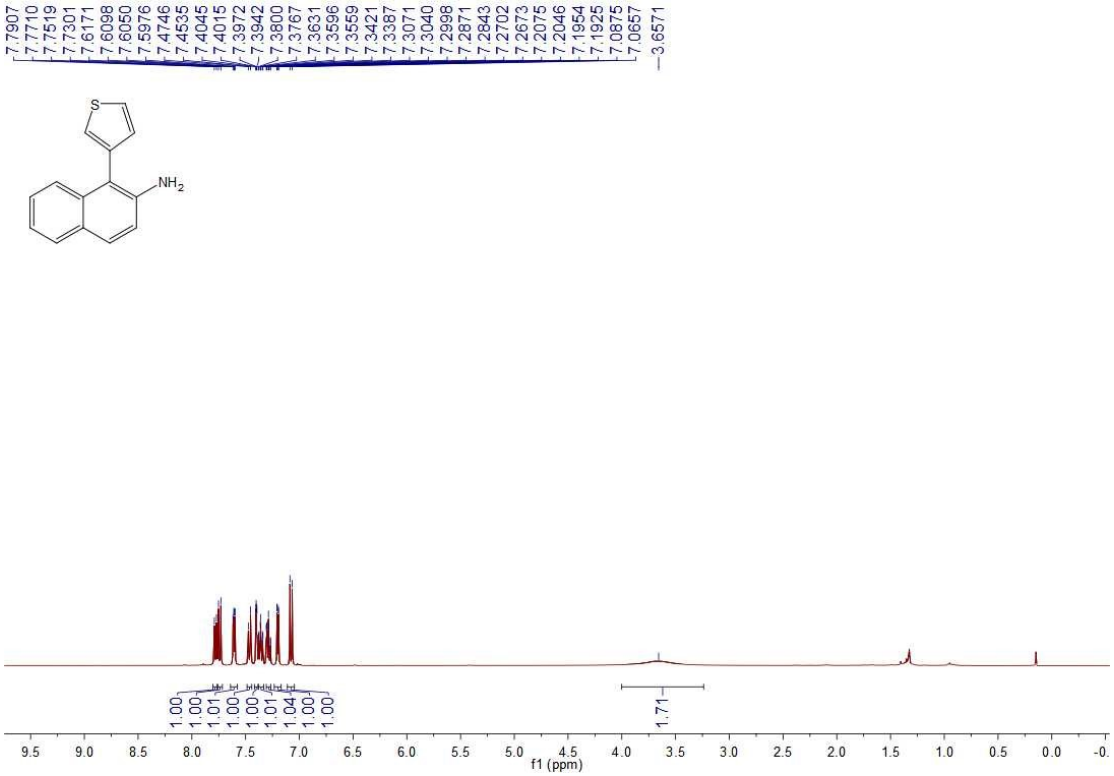
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(pyridin-3-yl)naphthalen-2-amine (**3r**).



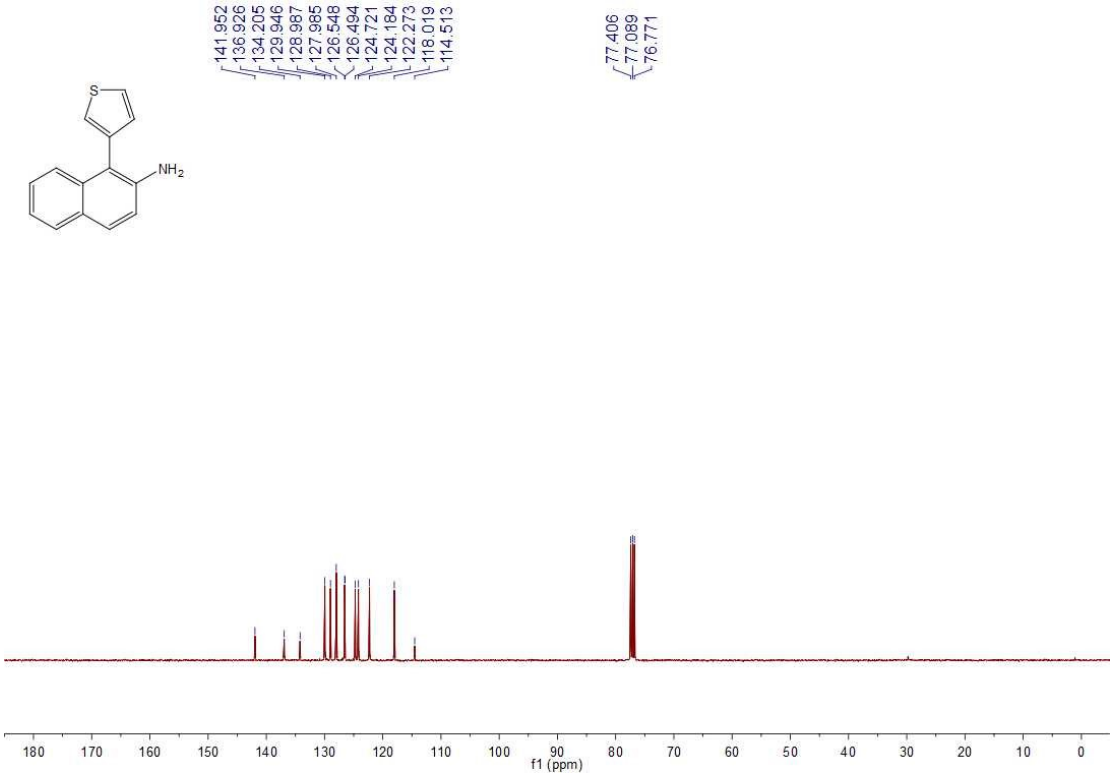
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-(pyridin-3-yl)naphthalen-2-amine (**3r**).



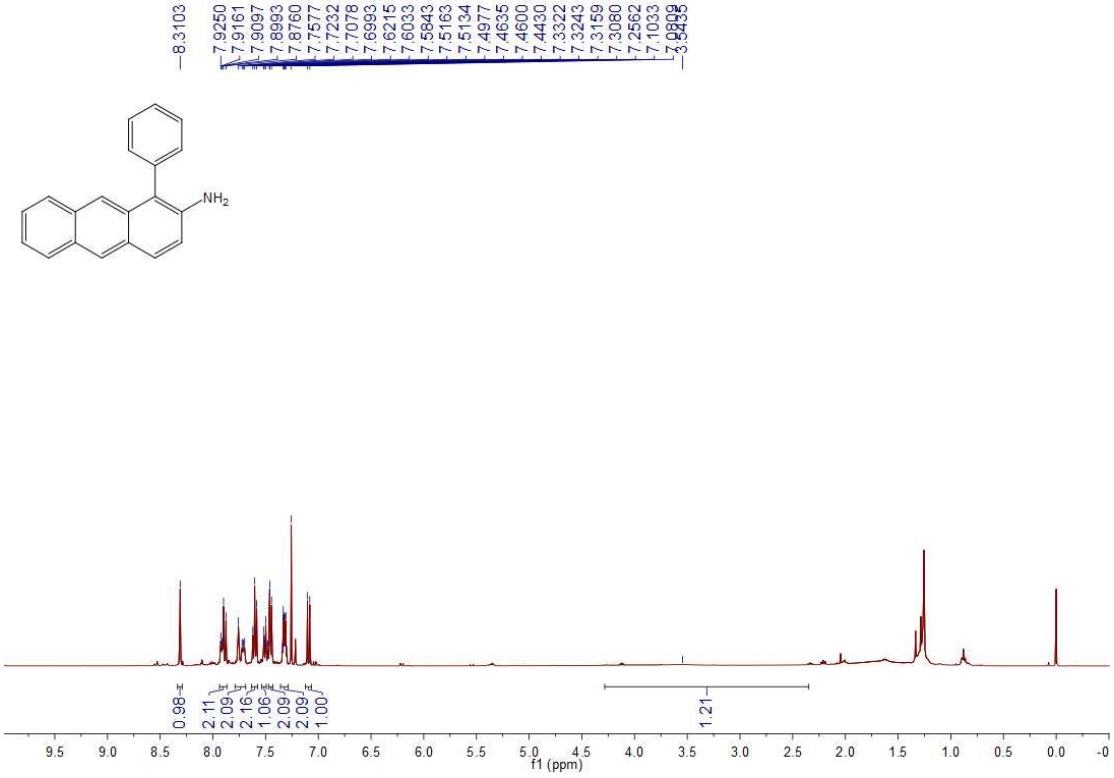
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(thiophen-3-yl)naphthalen-2-amine (**3s**).



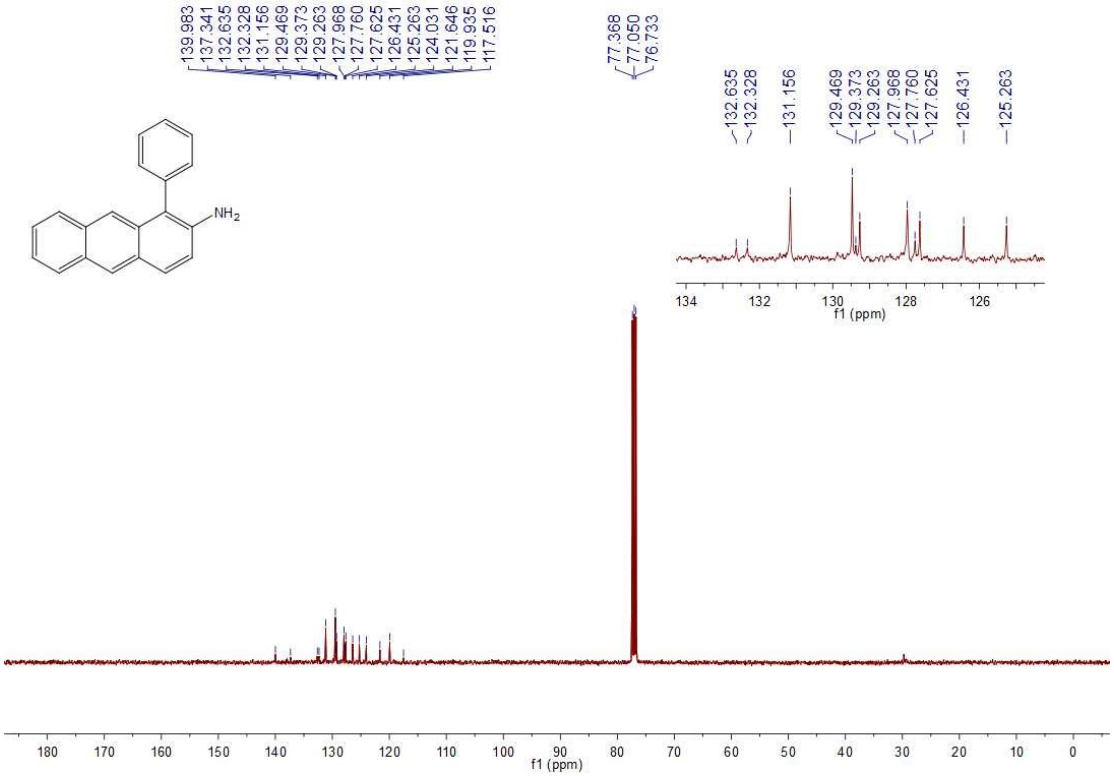
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-(thiophen-3-yl)naphthalen-2-amine (**3s**).



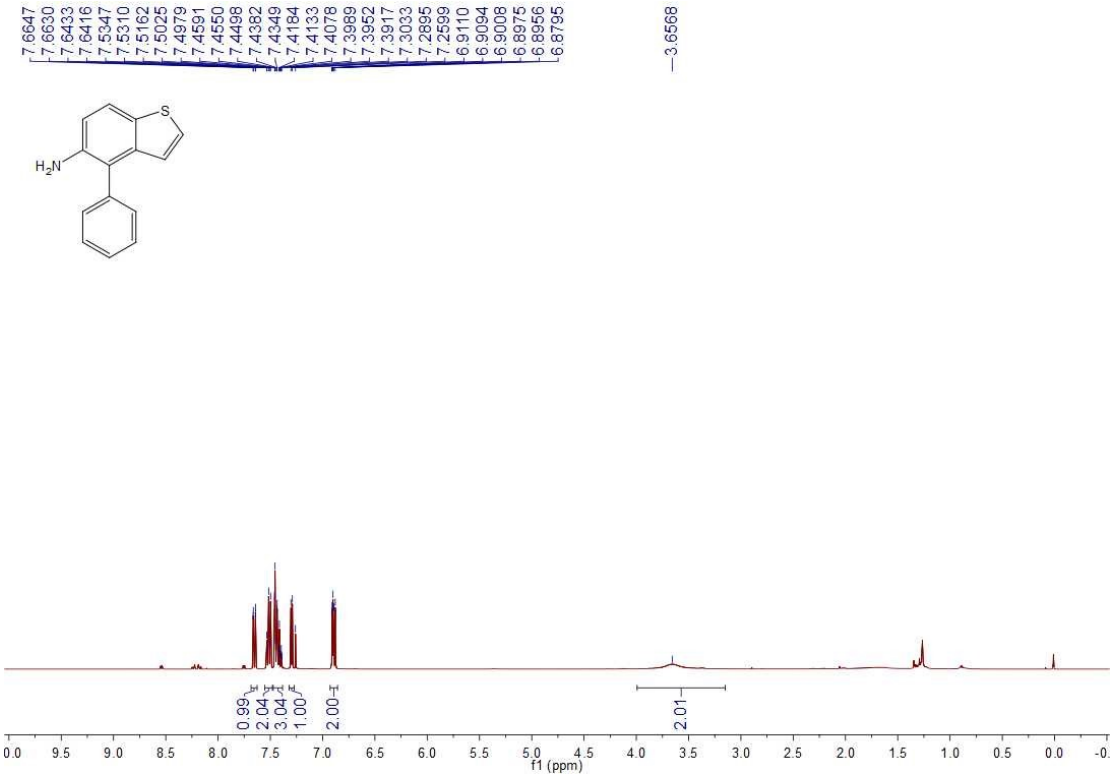
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-phenylanthracen-2-amine (**3t**).



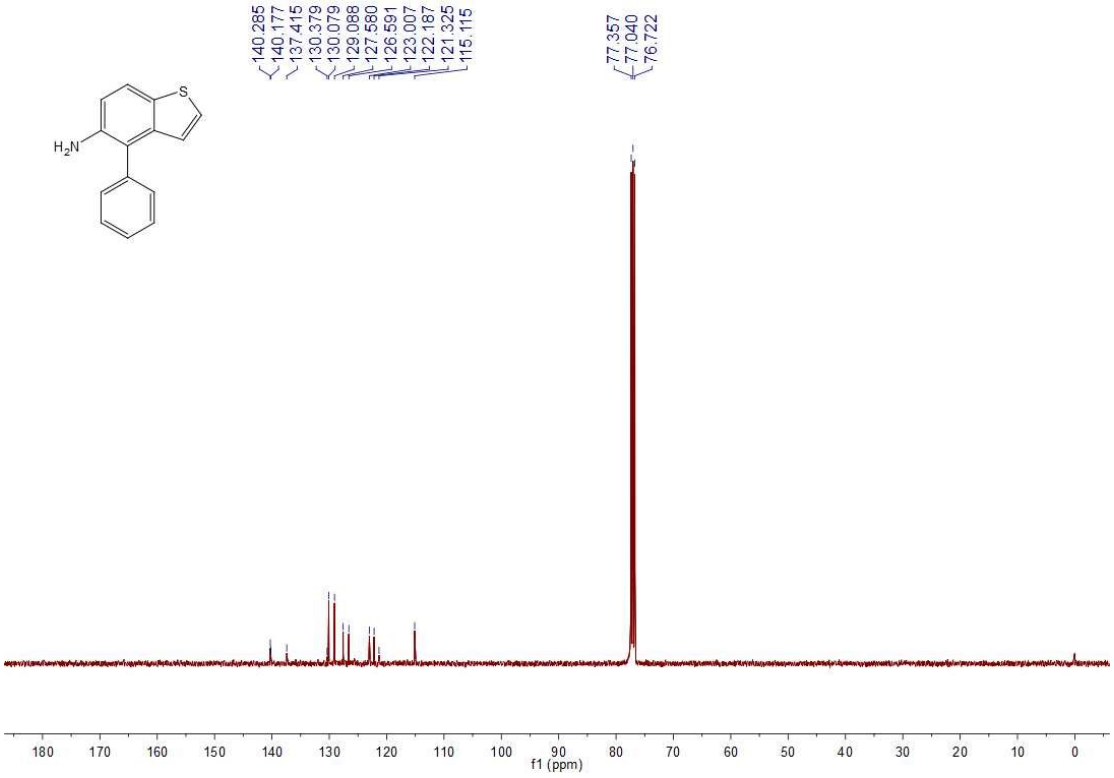
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-phenylanthracen-2-amine (**3t**).



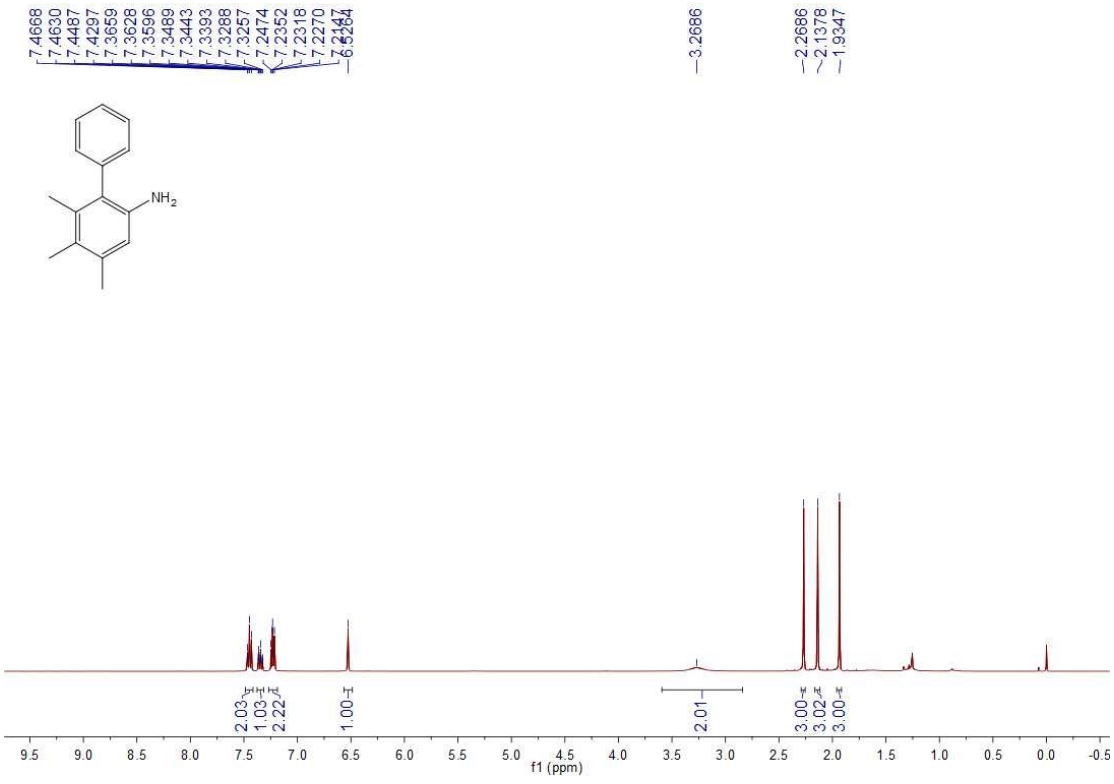
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4-phenylbenzo[b]thiophen-5-amine (**3u**).



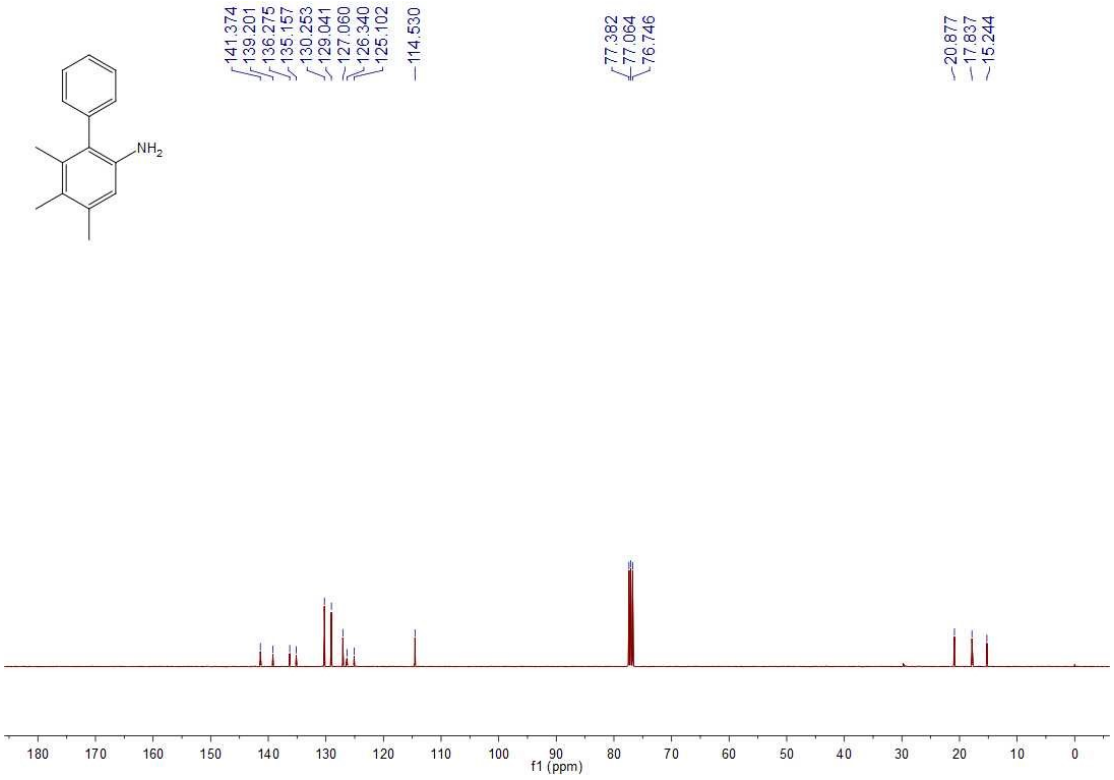
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 4-phenylbenzo[b]thiophen-5-amine (**3u**).



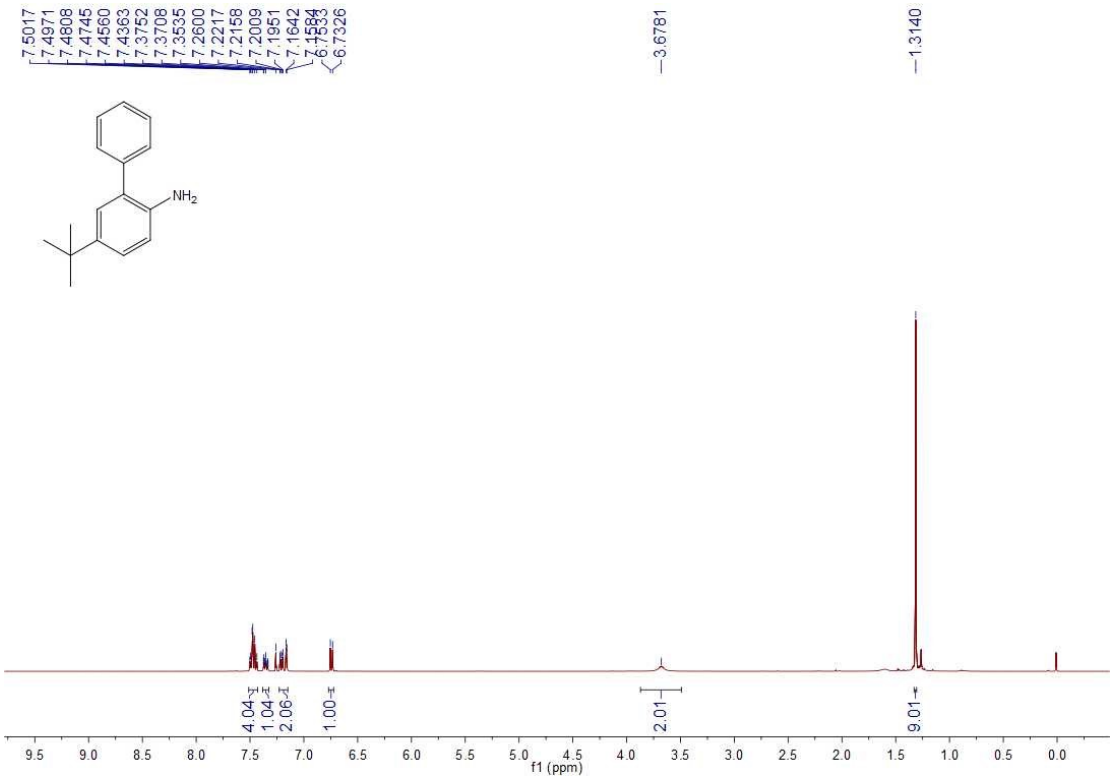
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4,5,6-trimethyl-[1,1'-biphenyl]-2-aminev (**3v**).



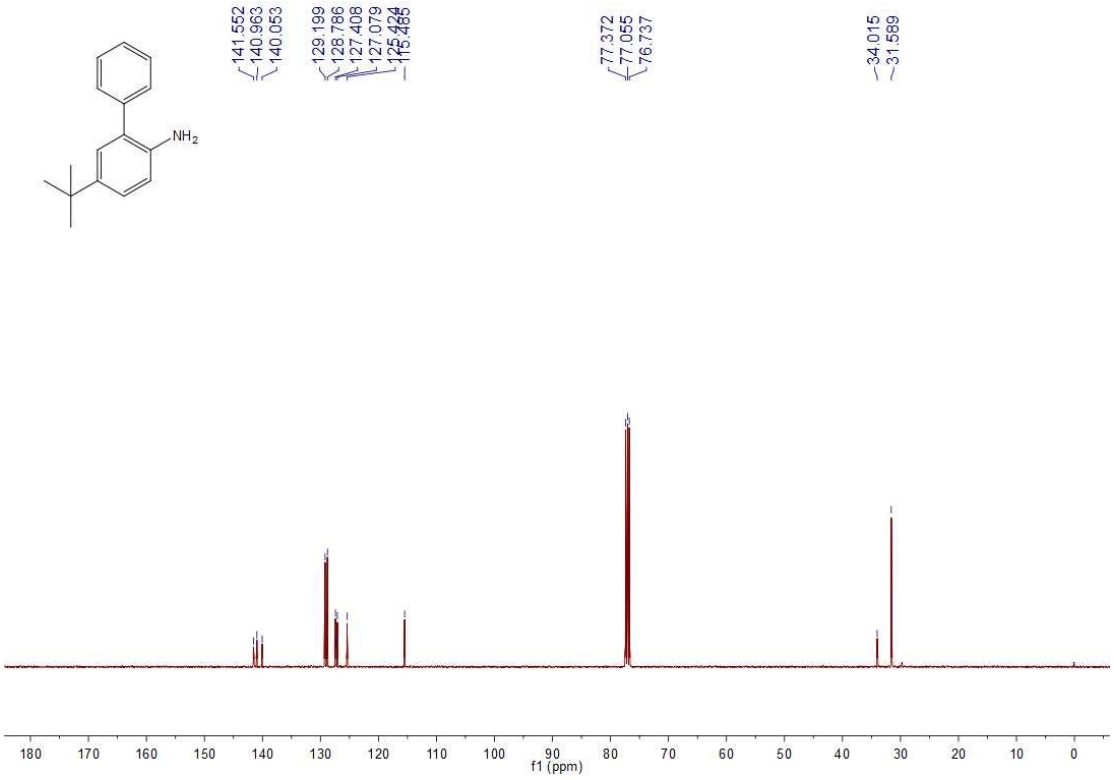
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 4,5,6-trimethyl-[1,1'-biphenyl]-2-aminev (**3v**).



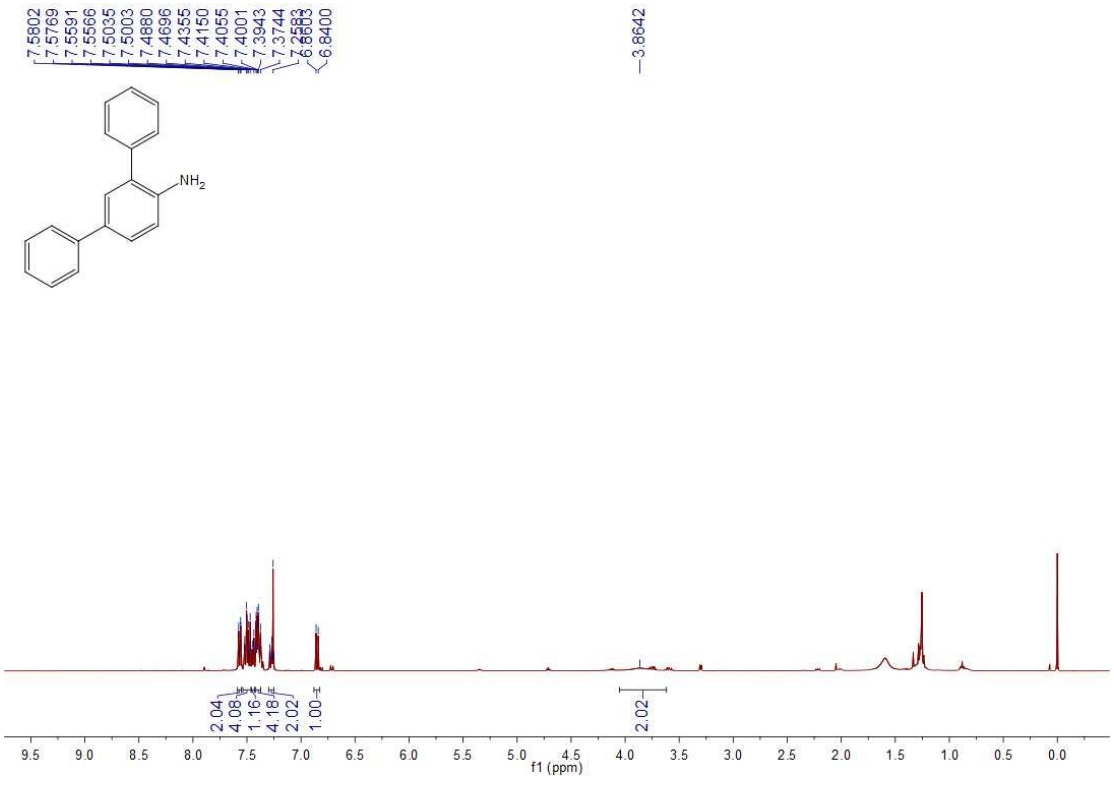
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(6-bromonaphthalen-2-yl)pyrrolidine (**3w**).



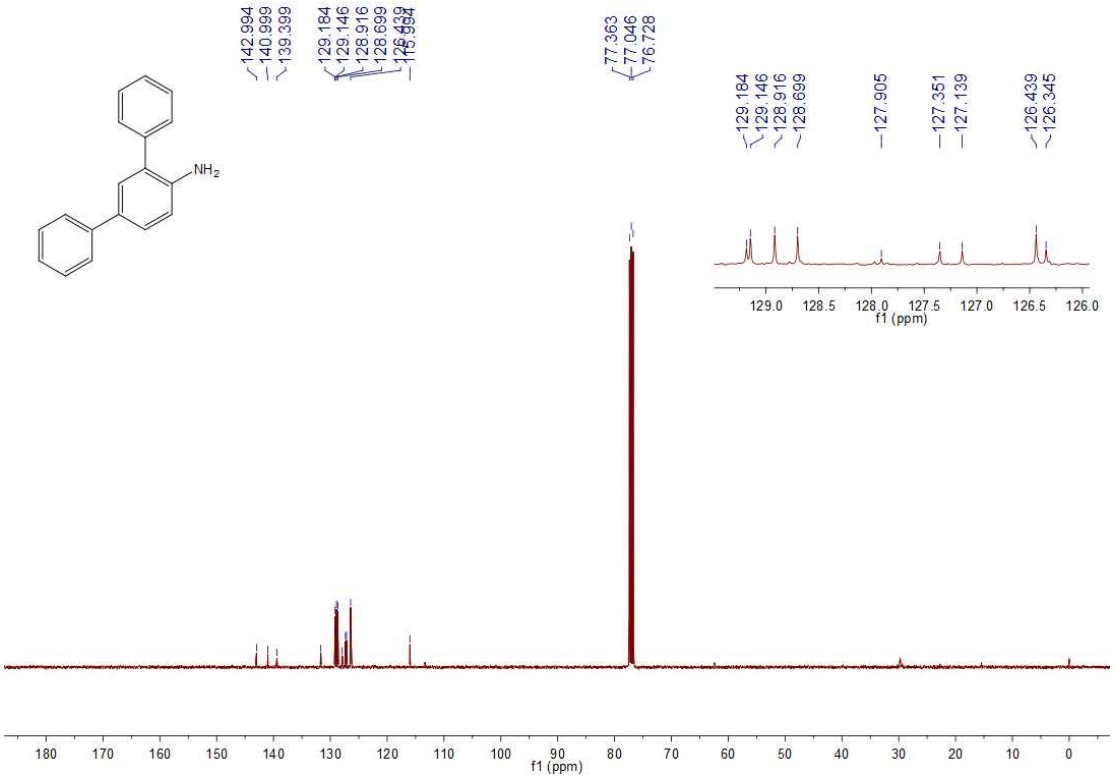
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-(6-bromonaphthalen-2-yl)pyrrolidine (**3w**).



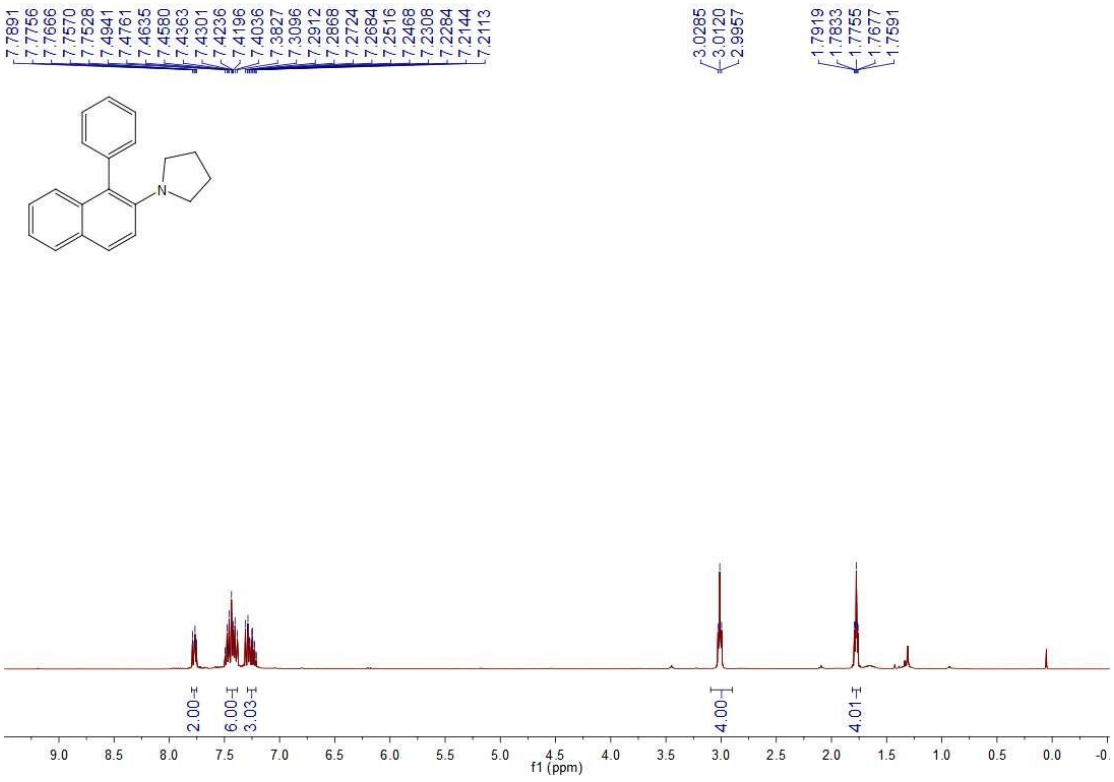
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for [1,1':3',1"-terphenyl]-4'-amine (**3x**).



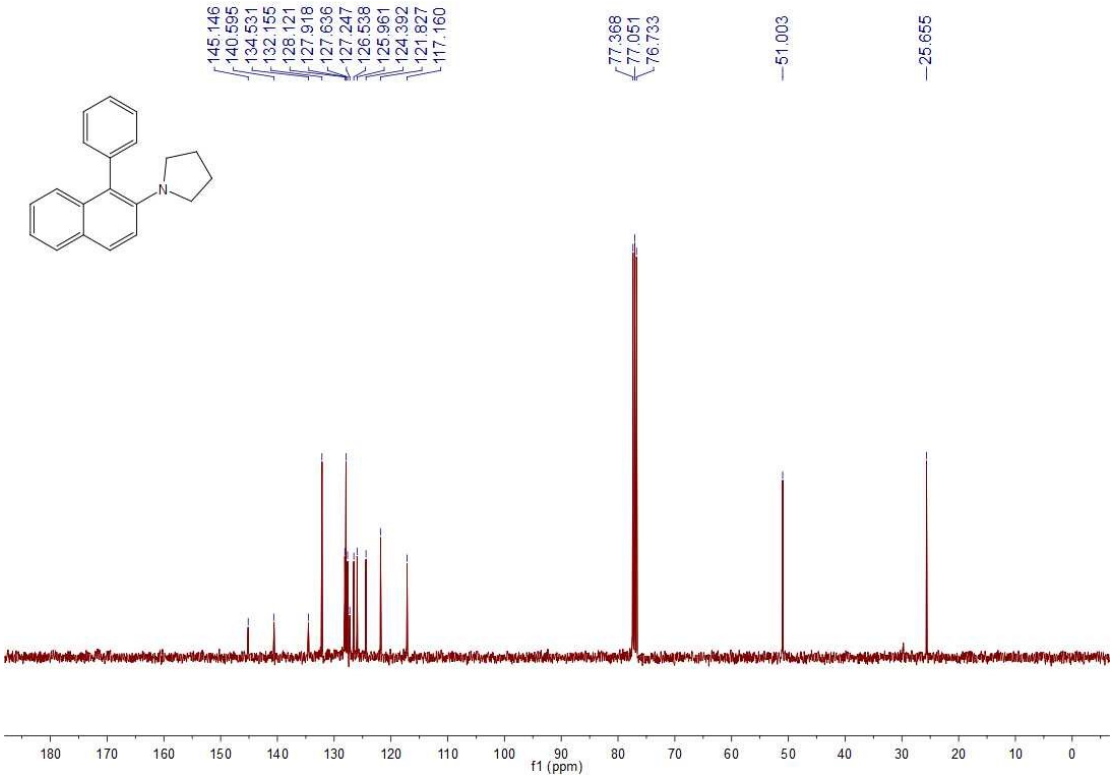
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for [1,1':3',1"-terphenyl]-4'-amine (**3x**).



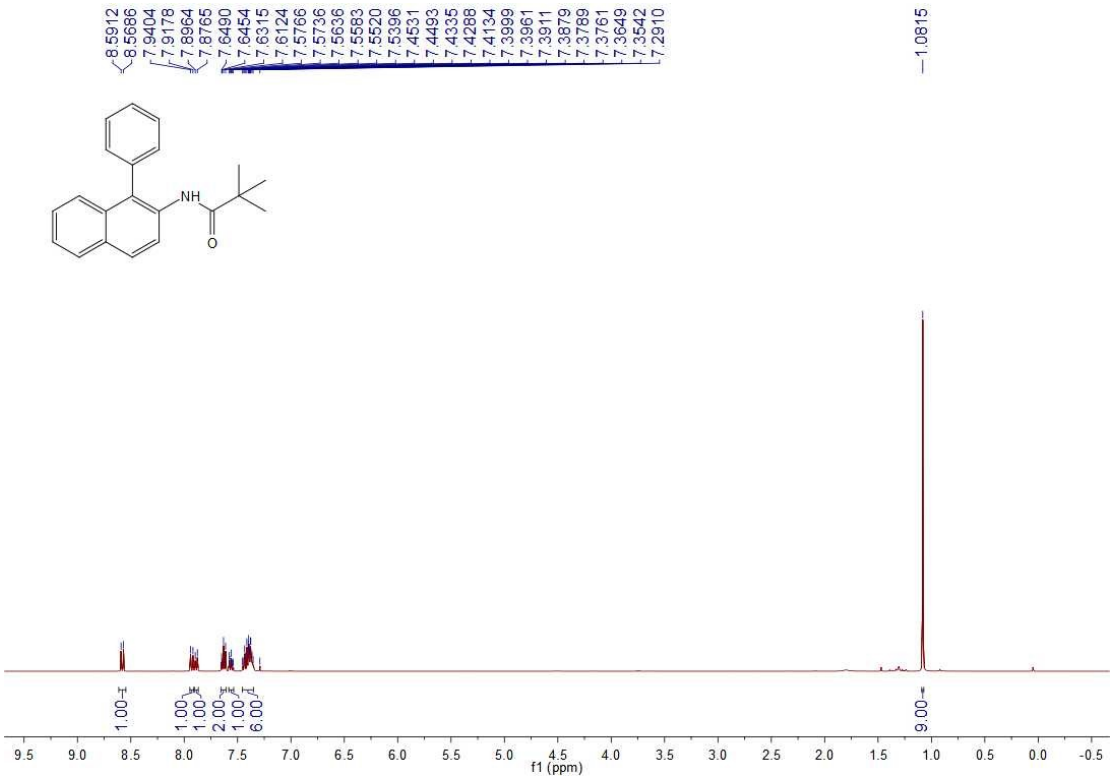
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 1-(1-phenylnaphthalen-2-yl)pyrrolidine (**4**).



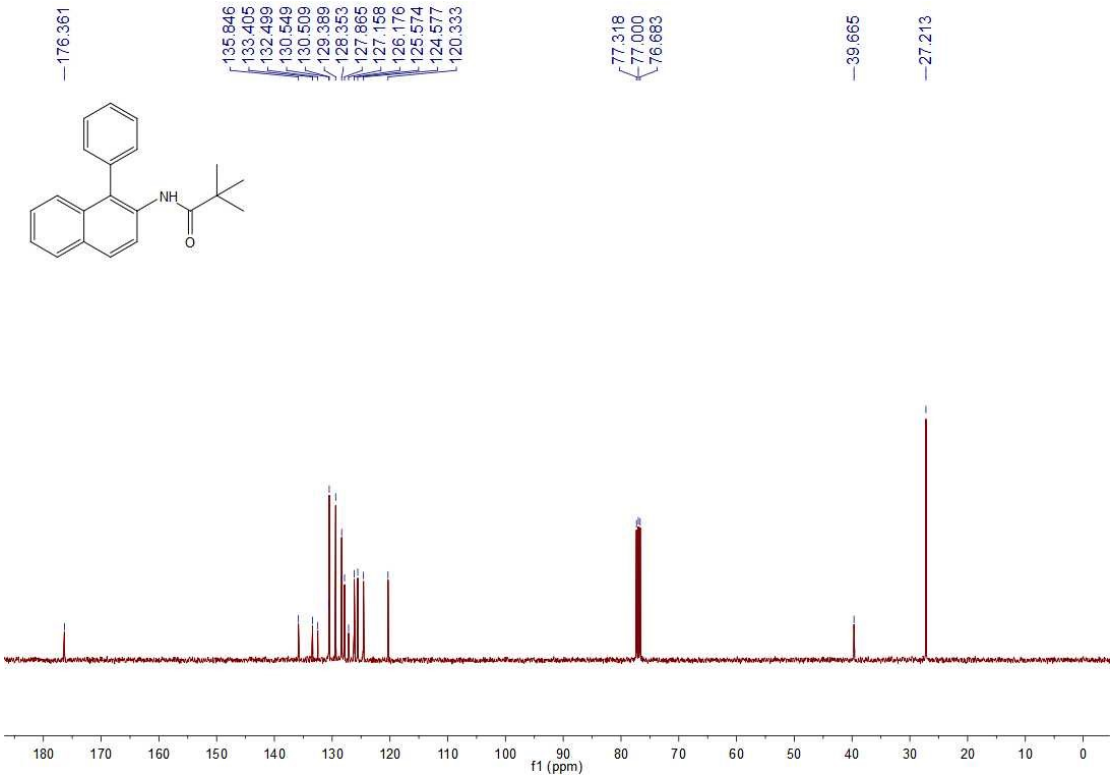
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 1-(1-phenylnaphthalen-2-yl)pyrrolidine (**4**).



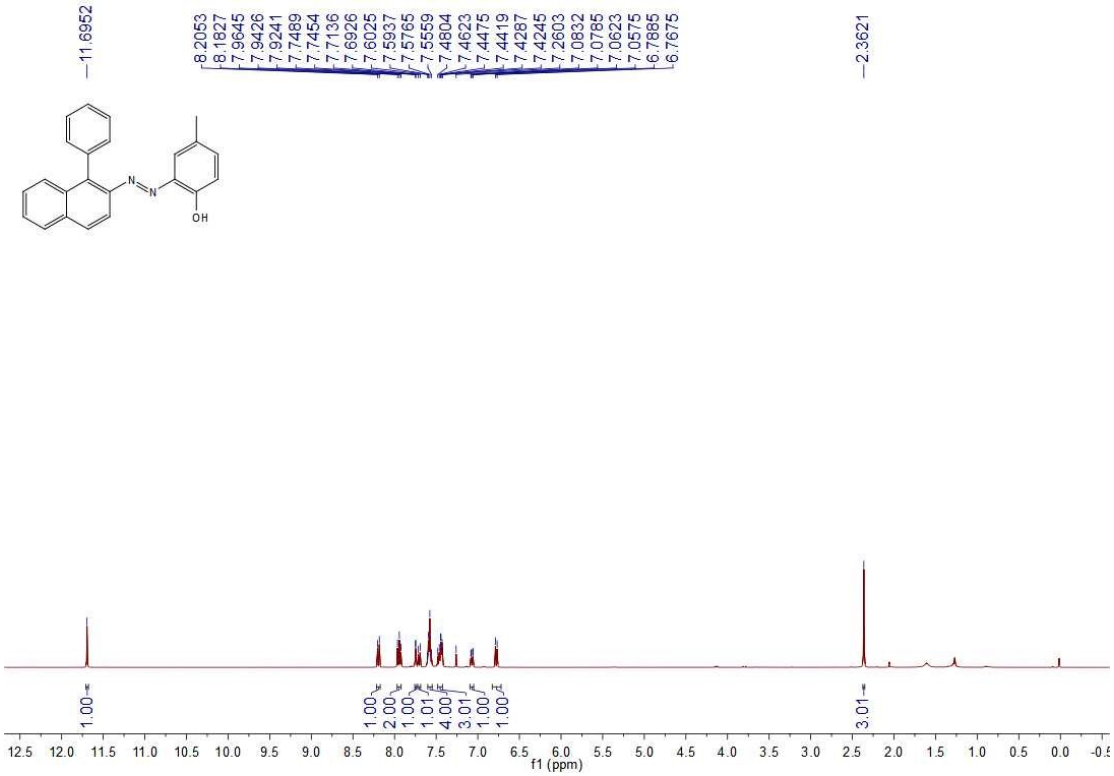
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for N-(1-phenylnaphthalen-2-yl)pivalamide (**5**).



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for N-(1-phenylnaphthalen-2-yl)pivalamide (**5**).



^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4-methyl-2-((1-phenylnaphthalen-2-yl)diazenyl)phenol (**6**).



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum for 4-methyl-2-((1-phenylnaphthalen-2-yl) diazenyl)phenol (**6**).