SUPPORTING INFORMATION

Deoxygenative Arylation of Secondary Amides by Merging Iridium Catalysis with Electrochemical Radical Cross-coupling

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1. General Information

All the electrochemical reactions were carried out in an undivided cell equipped with two graphite rods (φ = 6mm) unless otherwise stated. Concentration under reduced pressure was performed by rotary evaporation at 35 – 40 °C at an appropriate pressure. Purified compounds were further dried under vacuum (10^{-6}-10^{-3} bar). The analytical thin layer chromatography (TLC) was performed on HSGF/UV254 plates. The flash chromatography was performed on Huanghai silica gel (200-300 mesh) by standard techniques eluting with solvents as indicated. Yields refer to purified and spectroscopically pure compounds or mixture of constitutional isomers. All air- and moisture-sensitive manipulations were performed using standard Schlenk and glove-box techniques under an atmosphere of argon or nitrogen.

Anhydrous DCM, anhydrous DCE, anhydrous 1,4-dioxane, anhydrous DMSO, anhydrous DMF, and anhydrous CH_3CN were purchased from J&K Scientific Ltd. All deuterated solvents were purchased from J&K Scientific Ltd. All other commercial reagents were used as supplied unless otherwise stated.

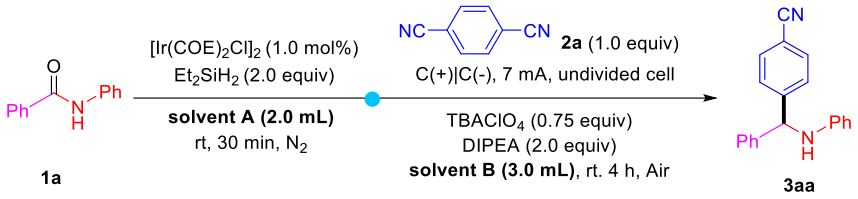
Electrolyzation of the reaction mixture was achieved using adjustable DC regulated power supply HSPY-60-002 (MS-60 V 200 mA) (Beijing Hanchengpuyuan Technology Co., Ltd.).

Nuclear magnetic resonance (NMR) spectra were recorded on Varian 400 MHz, Varian 500 MHz, Agilent 400 MHz or Bruker AM 400 (400 MHz) spectrometers. Chemical shifts (δ values) were reported in ppm relative to internal TMS (^{1}H NMR) or $CDCl_3$ (^{1}H NMR) or $CDCl_3$ (^{13}C NMR), respectively. The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broadened.

HRMS (ESI) were determined on Agilent 6224 TOF LC/MS. IR spectra were obtained on Bruker Tensor 27 instruments with Bruker Platinum ATR accessory. Melting points (m.p.) were measured on a RY-I apparatus and uncorrected.

2. Optimization of reaction conditions

Table S1. Solvent screening[a]

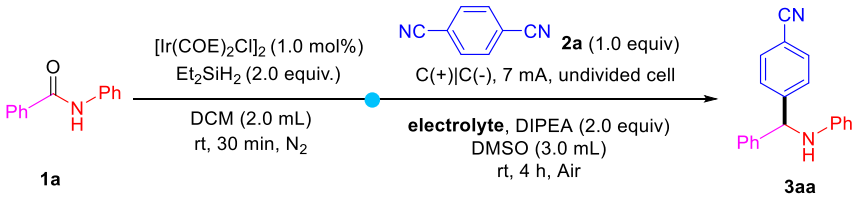


Entry	Solvent A	Solvent B	Yield (%)[b]
1	DCM	DCM	27
2	DCM	DMSO	48
3	DCM	DMF	46
4	DCM	MeCN	32
5	DCM	1,4-dioxane	trace
6	DCE	DMF	30
7	MeCN	DMSO	trace
8	THF	DMSO	16

[a]Reaction conditions: A mixture of **1a** (0.20 mmol), Et_2SiH_2 (0.40 mmol) and $[Ir(COE)_2Cl]_2$ (1.0 mol%) was stirred in solvent A (2.0 mL) for 30 min at room temperature. The resulting solution was added to a mixture of **2a** (0.20 mmol), $TBAClO_4$ (0.15 mmol), DIPEA (0.40 mmol) and solvent B (3.0 mL) in an undivided cell, a pair of graphite rod electrodes (φ = 6.0 mm) was placed and the mixture was electrolyzed at a current of 7.0 mA for 4 h with stirring.

[b]Determined by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as internal standard.

Table S2. Electrolyte screening[a]



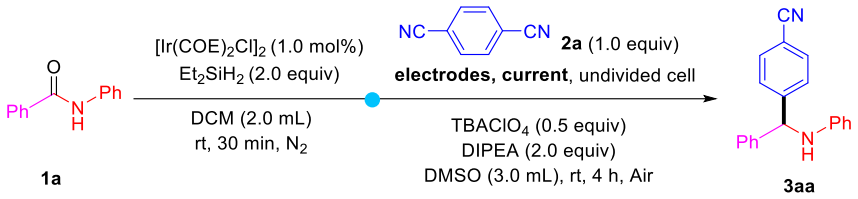
Entry	electrolyte	yield (%)[b]
1	^{n}Bu$_4$NClO$_4$ (0.75 equiv)	48
2	^{n}Bu$_4$NClO$_4$ (0.25 equiv)	30
3	^{n}Bu$_4$NClO$_4$ (0.5 equiv)	51

4	$^{n}Bu_4NClO_4$ (1.0 equiv)	41
5	$^{n}Bu_4NBF_4$ (0.5 equiv)	43
6	$^{n}Bu_4NPF_6$ (0.5 equiv)	40
7	$^{n}Bu_4NBr$ (0.5 equiv)	29
8	$^{n}Bu_4NF$ (0.5 equiv)	11
9	$^{n}Bu_4NOAc$ (0.5 equiv)	34

[a]Reaction conditions: A mixture of **1a** (0.20 mmol), Et_2SiH_2 (0.40 mmol) and $[Ir(COE)_2Cl]_2$ (1.0 mol%) was stirred in CH_2Cl_2 (2.0 mL) for 30 min at room temperature. The resulting solution was added to a mixture of **2a** (0.20 mmol), electrolyte, DIPEA (0.40 mmol) and DMSO (3.0 mL) in an undivided cell, a pair of graphite rod electrodes (φ = 6.0 mm) was placed and the mixture was electrolyzed at a current of 7.0 mA for 4 h with stirring.

[b]Determined by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as internal standard.

Table S3. Current and electrode screening[a]



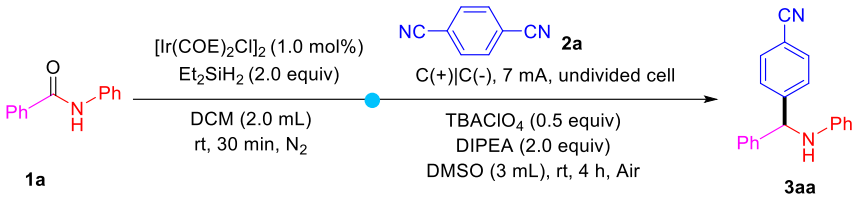
Entry	electrodes	current (mA)	yield (%)[b]
1	C(+)|C(-)	5	11
2	C(+)|C(-)	7	48
3	C(+)|C(-)	9	61
4	C(+)|C(-)	11	44
5[c]	C(+)|Ni(-)	9	20
6	Pt(+)|Pt(-)	9	32

[a]Reaction conditions: A mixture of **1a** (0.20 mmol), Et_2SiH_2 (0.40 mmol) and $[Ir(COE)_2Cl]_2$ (1.0 mol%) was stirred in CH_2Cl_2 (2.0 mL) for 30 min at room temperature. The resulting solution was added to a mixture of **2a** (0.20 mmol), $TBAClO_4$ (0.10 mmol), DIPEA (0.40 mmol) and DMSO (3.0 mL) in an undivided cell, both electrodes were placed and the mixture was electrolyzed at a constant current for 4 h with stirring.

[b]Determined by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as internal standard.

[c]Without addition of DIPEA.

Table S4. Substrate ratio screening[a]

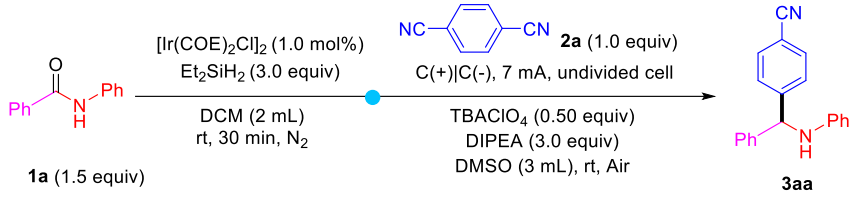


Entry	amount of 1a (mmol)	amount of 2a (mmol)	yield (%)[b]
1	0.4	0.2	63
2	0.3	0.2	67
3	0.2	0.2	61
4	0.2	0.3	56
5	0.2	0.4	59

[a]Reaction conditions: A mixture of **1a** (x mmol), Et_2SiH_2 (2 mmol) and $[Ir(COE)_2Cl]_2$ (1.0 mol%) was stirred in solvent A (2.0 mL) for 30 min at room temperature. The resulting solution was added to a mixture of **2a** (y mmol), $TBAClO_4$ (0.10 mmol), DIPEA (0.40 mmol) and solvent B (3.0 mL) in an undivided cell, a pair of graphite rod electrodes (φ = 6.0 mm) were placed and the mixture was electrolyzed at a current of 9.0 mA for 4 h with stirring.

[b]Determined by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as internal standard.

Table S5. Reaction time screening[a]



Entry	reaction time	yield (%)[b]
1	2h	70
2	2.5h	81 (74)[c]
3	3h	73
5	4h	67

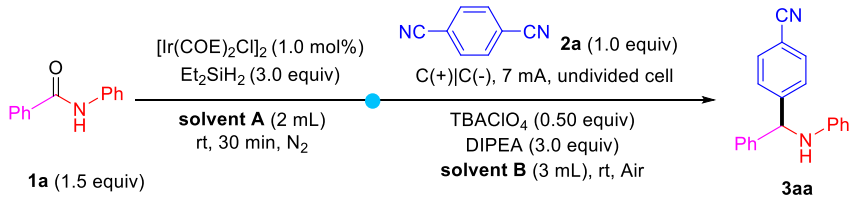
[a]Reaction conditions: A mixture of **1a** (0.30 mmol), Et_2SiH_2 (0.60 mmol) and $[Ir(COE)_2Cl]_2$ (1.0 mol%) was stirred in solvent A (2.0 mL) for 30 min at room temperature. The resulting solution was added to a mixture of **2a** (0.20 mmol), $TBAClO_4$ (0.10 mmol), DIPEA (0.60 mmol) and solvent B (3.0 mL) in an

undivided cell, a pair of graphite rod electrodes (φ = 6.0 mm) was placed and the mixture was electrolyzed at a current of 9.0 mA for a certain time with stirring.

[b]Determined by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as internal standard.

[c]Isolated yield.

Table S6. Alternative solvent screening[a]



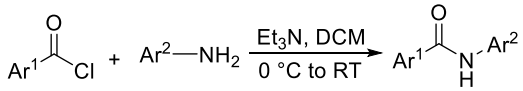
Entry	Solvent A	Solvent B	Yield (%)[b]
1	THF	DMSO	72
2	EtOH	DMSO	n.d.
3	DMF	DMSO	n.d.
4	DMAc	DMSO	n.d.
5	toluene	DMSO	59
6	diglyme	DMSO	trace
7	PhCF3	DMSO	70
8	DMSO	DMSO	12
9	benzene	DMSO	42
10	EtOAc	DMSO	trace
11	DCM	DMF	77
12	DCM	DMAc	35

[a]Reaction conditions: A mixture of **1a** (0.30 mmol), Et_2SiH_2 (0.60 mmol) and $[Ir(COE)_2Cl]_2$ (1.0 mol%) was stirred in solvent A (2.0 mL) for 30 min at room temperature. The resulting solution was added to a mixture of **2a** (0.20 mmol), $TBAClO_4$ (0.10 mmol), DIPEA (0.60 mmol) and solvent B (3.0 mL) in an undivided cell, a pair of graphite rod electrodes (φ = 6.0 mm) was placed and the mixture was electrolyzed at a current of 9.0 mA for 2.5 h with stirring.

[b]Determined by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as internal standard.

3. Experimental Procedures

General Procedure for the Synthesis of Amides



The amides were synthesized according to the reported literature.[1] To a round bottom flask equipped with a magnetic stir bar was added amine (10.0 mmol, 1.0 equiv), triethylamine (1.4 mL, 10.5 mmol, 1.05 equiv), and DCM (20 mL). After the solution was cooled to 0 °C, acyl chloride (10.5 mmol, 1.05 equiv) was added dropwise into the solution. The mixture was warmed gradually to room temperature and stirred for 16 hours. Then the reaction was quenched by water and extracted by ethyl acetate (3 × 20 mL). Subsequently, the combined organic phase was washed by HCl (aq., 1.0 M), saturated aqueous sodium bicarbonate, and brine in sequence. The organic phase was dried by magnesium sulfate, and the solvent was removed under reduced pressure. The residue was recrystallized from petroleum ether-ethyl acetate to afford the corresponding amide.

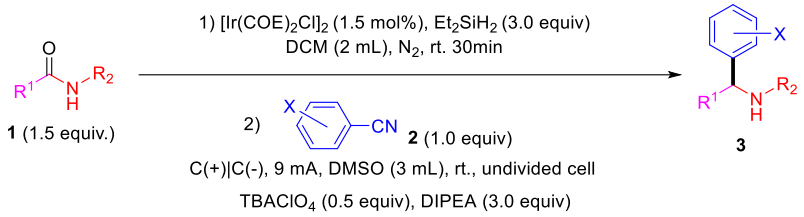
Reaction Apparatus used in electrolyze process

All materials used to make the tube-type electrolytic cell were purchased from domestic corporation, both anode and cathode used in the reaction were graphite rod (Φ = 6mm). Electrolyzation of the reaction mixture was achieved using adjustable DC regulated power supply HSPY-60-002 (MS-60 V 200 mA) (Beijing Hanchengpuyuan Technology Co., Ltd.).

Figure S1. Materials used to make the tube-type electrolytic cell

Figure S2. Power supply used in the electrolyze process

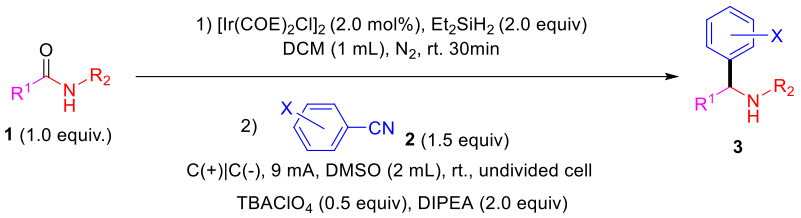
General Procedure for the Synthesis of α-diarylamines



To an oven-dried Schlenk tube equipped with a magnetic stir bar was added amide **1** (0.30 mmol, 1.5 equiv) and $[Ir(COE)_2Cl]_2$ (0.0030 mmol, 1.5 mol%, 2.9 mg) in a nitrogen filled glovebox. Then the tube was removed from the glovebox. To this mixture, anhydrous dichloromethane (DCM, 2.0 mL) and diethylsilane (0.60 mmol, 3.0 equiv, 81.0 μL) were added via a gastight syringe under an argon atmosphere. The mixture was allowed to stir for 30 min in an air-conditioned room of 25 ºC. Subsequently, the resulting mixture was dropped to a solution of aromatic nitrile **2** (0.2 mmol, 1.0 equiv), tetrabutylammonium perchlorate ($TBAClO_4$, 0.10 mmol, 0.50 equiv.), and N,N-Diisopropylethylamine (DIPEA, 0.60 mmol, 3.0 equiv.) in anhydrous dimethyl sulfoxide (DMSO, 3 mL) in an undivided electrolysis cell (10 mL). Then, both graphite rod electrodes (φ = 6.0 mm) were placed and the mixture

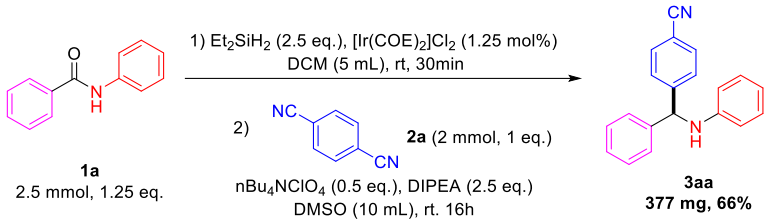
was electrolyzed at a constant current of 9.0 mA at room temperature. After a certain reaction time, the electrodes were removed and washed with EtOAc (20 mL), and the combined organic mixture was washed with water (20 mL) and then extracted with DCM (3×10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using petroleum ether/EtOAc as eluent on silica gel to obtain the desired α-diarylamines.

General Procedure for the Late-stage functionalization



To an oven-dried Schlenk tube equipped with a magnetic stir bar was added amide **1** (0.10 mmol, 1.0 equiv) and $[Ir(COE)_2Cl]_2$ (0.0020 mmol, 2 mol%, 1.9 mg) in a nitrogen filled glovebox. Then the tube was removed from the glovebox. To this mixture, anhydrous dichloromethane (DCM, 1.0 mL) and diethylsilane (0.20 mmol, 2.0 equiv, 27.0 μL) were added via a gastight syringe under an argon atmosphere. The mixture was allowed to stir for 30 min in an air-conditioned room of 25 ºC. Subsequently, the resulting mixture was dropped to a solution of aromatic nitrile **2** (0.15 mmol, 1.5 equiv), tetrabutylammonium perchlorate ($TBAClO_4$, 0.05 mmol, 0.25 equiv.), and N,N-Diisopropylethylamine (DIPEA, 0.20 mmol, 2.0 equiv.) in anhydrous dimethyl sulfoxide (DMSO, 2 mL) in an undivided electrolysis cell (10 mL). Then, both graphite rod electrodes (φ = 6.0 mm) were placed and the mixture was electrolyzed at a constant current of 9.0 mA at room temperature. After a certain reaction time, the electrodes were removed and washed with EtOAc (20 mL), and the combined organic mixture was washed with water (20 mL) and then extracted with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using petroleum ether/EtOAc as eluent on silica gel to obtain the desired α-diarylamines.

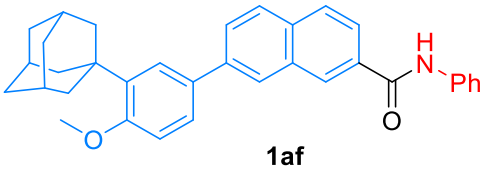
Scale-up Experiment for the Synthesis of α-diarylamine 3aa



To an oven-dried Schlenk tube equipped with a magnetic stir bar was added amide **1a** (2.50 mmol, 1.25 equiv) and $[Ir(COE)_2Cl]_2$ (0.025 mmol, 1.25 mol%, 24.0 mg) in a nitrogen filled glovebox. Then the tube was removed from the glovebox. To this mixture, anhydrous dichloromethane (DCM, 5.0 mL) and diethylsilane (5.0 mmol, 2.5 equiv, 0.67 mL) were added via a gastight syringe under an argon atmosphere. The mixture was allowed to stir for 30 min in an air-conditioned room of 25 °C. Subsequently, the resulting mixture was dropped to a solution of aromatic nitrile **2a** (2.0 mmol, 1.0 equiv), tetrabutylammonium perchlorate ($TBAClO_4$, 0.50 mmol, 0.25 equiv.), and N,N-Diisopropylethylamine (DIPEA, 5.0 mmol, 2.0 equiv.) in anhydrous dimethyl sulfoxide (DMSO, 10 mL) in an undivided electrolysis cell (20 mL). Then, both graphite rod electrodes (φ = 6.0 mm) were placed and the mixture was electrolyzed at a constant current of 9.0 mA at room temperature for 16 hours. The electrodes were removed and washed with EtOAc (20 mL), and the combined organic mixture was washed with water (20 mL) and then extracted with EtOAc (3×20 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using petroleum ether/EtOAc = 20:1 as eluent on silica gel to obtain the desired α-diarylamine **3aa** in 66% yield.

4. New Substrate Characterization

6-(3-(adamantan-1-yl)-4-methoxyphenyl)-N-phenyl-2-naphthamide (1af)



1af

The title compound **1af** was prepared according to the general procedure as described above. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 5/1) to afford a white solid, 44% yield.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.38 (m, 1H), 8.05 – 7.90 (m, 5H), 7.85 – 7.79 (m, 1H), 7.75 – 7.67 (m, 2H), 7.63 – 7.59 (m, 1H), 7.58 – 7.52 (m, 1H), 7.45 – 7.35 (m, 2H), 7.22 – 7.14 (m, 1H), 7.04 – 6.98 (m, 1H), 3.91 (s, 3H), 2.23 – 2.16 (m, 6H), 2.15 – 2.08 (m, 3H), 1.87 – 1.75 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 165.75, 158.92, 141.08, 139.03, 138.06, 135.30, 132.50, 131.67, 131.36, 129.30, 129.12, 128.81, 127.30, 126.77, 125.94, 125.69, 124.74, 124.54, 123.83, 120.22, 112.14, 55.16, 40.63, 37.22, 37.13, 29.12.

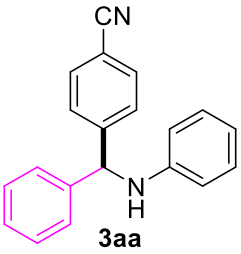
HRMS ESI^{+} (m/z) calc'd for $C_{34}H_{34}NO_2$ $[M+H]^{+}$, 488.2584; found, 488.2587.

IR (neat) ν (cm^{-1}) = 3054, 2930, 2226, 1541, 1430, 1247, 1047, 940, 755, 694

Melting point: 225.2 – 226.8 °C

5. Product Characterization

4-(phenyl(phenylamino)methyl)benzonitrile (3aa)[2]



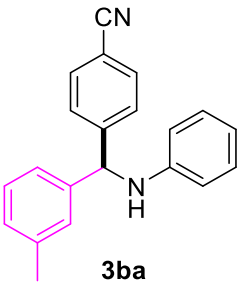
3aa

The title compound **3aa** was prepared according to the general procedure as described above in 74% yield, 42.0 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a pale-yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, 2H, *J* = 8.2 Hz), 7.52 (d, 2H, *J* = 8.2 Hz), 7.38 – 7.26 (m, 5H), 7.08 – 7.17 (m, 2H), 6.76 – 6.70 (m, 1H), 6.55 – 6.46 (m, 2H), 5.52 (s, 1H), 4.21 (br, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.20, 146.73, 141.84, 132.64, 129.28, 129.14, 128.12, 127.99, 127.64, 118.80, 118.36, 113.55, 111.20, 62.97 ppm.

4-((phenylamino)(m-tolyl)methyl)benzonitrile (3ba)[2]



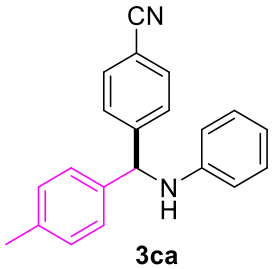
3ba

The title compound **3ba** was prepared according to the general procedure as described above in 87% yield, 52.1 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, 2H, *J* = 8.2 Hz), 7.51 (d, 2H, *J* = 8.2 Hz), 7.24 – 7.19 (m, 1H), 7.16 – 7.03 (m, 5H), 6.74 – 6.68 (m, 1H), 6.46 – 6.52 (m, 2H), 5.46 (s, 1H), 4.22 (br, 1H), 2.31 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.40, 146.87, 141.91, 138.96, 132.65, 129.31, 129.06, 128.92, 128.34, 127.98, 124.71, 118.91, 118.31, 113.58, 111.10, 63.02, 21.52 ppm.

4-((phenylamino)(p-tolyl)methyl)benzonitrile (3ca)[2]



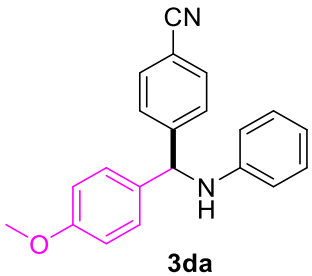
3ca

The title compound **3ca** was prepared according to the general procedure as described above in 92% yield, 54.9 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, 2H, *J* = 8.2 Hz), 7.52 (d, 2H, *J* = 8.2 Hz), 7.28 – 7.22 (m, 1H), 7.18 – 7.04 (m, 5H), 6.78 – 6.70 (m, 1H), 6.57 – 6.46 (m, 2H), 5.47 (s, 1H), 4.27 (br, 1H), 2.33 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.87, 144.21, 136.39, 135.33, 130.00, 127.19, 126.67, 125.31, 124.94, 116.26, 115.65, 110.93, 108.43, 60.06, 18.51 ppm.

4-((4-methoxyphenyl)(phenylamino)methyl)benzonitrile (3da)[2]



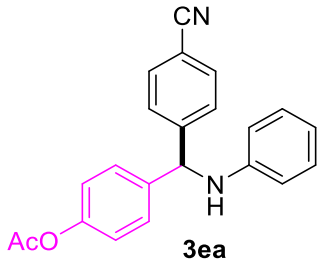
3da

The title compound **3da** was prepared according to the general procedure as described above in 61% yield, 38.3 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, 2H, *J* = 7.2 Hz), 7.52 (d, 2H, *J* = 7.3 Hz), 7.21 – 7.17 (m, 2H), 7.16 – 7.10 (m, 2H), 6.90 – 6.85 (m, 2H), 6.77 – 6.70 (m, 1H), 6.54 – 6.46 (m, 2H), 5.48 (s, 1H), 4.19 (br, 1H), 3.80 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.34, 148.54, 146.78, 134.07, 132.61, 129.27, 128.85, 127.91, 118.87, 118.26, 114.44, 113.53, 111.05, 62.31, 55.34 ppm.

4-((4-cyanophenyl)(phenylamino)methyl)phenyl acetate (3ea)



3ea

The title compound **3ea** was prepared according to the general procedure as described above in 51% yield, 34.7 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 10/1) to afford a yellow oil.

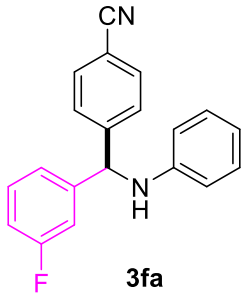
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, 2H, *J* = 8.4 Hz), 7.52 (d, 2H, *J* = 8.1 Hz), 7.31 – 7.28 (m, 2H), 7.17 – 7.12 (m, 2H), 7.10 – 7.05 (m, 2H), 6.78 – 6.72 (m, 1H), 6.53 – 6.48 (m, 2H), 5.53 (s, 1H), 4.23 (br, 1H), 2.30 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.46, 150.33, 147.87, 146.61, 139.30, 132.71, 129.31, 128.81, 128.03, 122.26, 118.75, 118.47, 113.58, 111.34, 62.36, 21.14 ppm.

HRMS ESI$^+$ (m/z) calc'd for $C_{22}H_{18}N_2O_2Na$ $[M+Na]^+$, 365.1256; found, 365.1261.

IR (neat) ν (cm^{-1}) = 3387, 3051, 2927, 2852, 2227, 1923, 1754, 1600, 1500, 1429, 1369, 1312, 1194, 1165, 1045, 910, 750, 729, 692.

4-((3-fluorophenyl)(phenylamino)methyl)benzonitrile (3fa)[3]



3fa

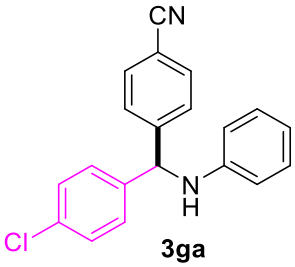
The title compound **3fa** was prepared according to the general procedure as described above in 61% yield, 37.0 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, 2H, *J* = 8.3 Hz), 7.50 (d, 2H, *J* = 8.0 Hz), 7.36 – 7.29 (m, 1H), 7.18 – 7.08 (m, 3H), 7.05 – 6.96 (m, 2H), 6.81 – 6.73 (m, 1H), 6.56 – 6.43 (m, 2H), 5.52 (s, 1H), 4.23 (br, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.17 (d, *J* = 247.6 Hz), 147.53, 146.47, 144.22 (d, *J* = 6.5 Hz), 132.78, 130.72 (d, *J* = 8.3 Hz), 129.33, 128.06, 123.17 (d, *J* = 3.1 Hz), 118.66, 118.64, 115.08 (d, *J* = 21.2 Hz), 114.52 (d, *J* = 22.2 Hz), 113.64, 111.59, 62.48 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -111.37 – -111.88 (m, 1F) ppm.

4-((4-chlorophenyl)(phenylamino)methyl)benzonitrile (3ga)[3]



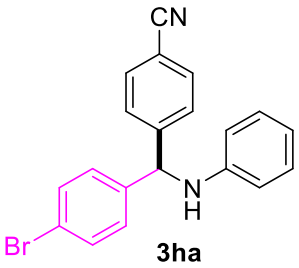
3ga

The title compound **3ga** was prepared according to the general procedure as described above in 54% yield, 34.2 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 40/1) to afford a brown oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, 2H, *J* = 8.3 Hz), 7.48 (d, 2H, *J* = 7.7 Hz), 7.34 (d, 2H, *J* = 8.4 Hz), 7.26 – 7.21 (m, 2H), 7.16 – 7.10 (m, 2H), 6.78 – 6.71 (m, 1H), 6.54 – 6.47 (m, 2H), 5.50 (s, 1H), 4.17 (br, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.69, 146.49, 140.20, 133.96, 132.76, 129.34, 129.31, 128.95, 128.94, 128.06, 118.63, 113.65, 111.53, 62.28 ppm.

4-((4-bromophenyl)(phenylamino)methyl)benzonitrile (3ha)



3ha

The title compound **3ha** was prepared according to the general procedure as described above in 60% yield, 43.5 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, 2H, *J* = 8.2 Hz), 7.52 – 7.43 (m, 4H), 7.22 – 7.10 (m, 4H), 6.79 – 6.71 (m, 1H), 6.54 – 6.48 (m, 2H), 5.49 (s, 1H), 4.16 (br, 1H) ppm.

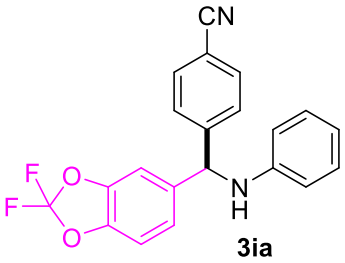
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.55, 146.42, 140.67, 132.71, 132.23, 129.29, 129.21, 128.01, 122.03, 118.63, 118.55, 113.62, 111.55, 62.32 ppm.

HRMS ESI+ (m/z) calc'd for $C_{20}H_{15}BrN_2$ $[M+Na]^+$, 385.0311; found, 385.0317.

IR (neat) ν (cm-1) = 3361, 2919, 2580, 2226, 1599, 1502, 1315, 1263, 1069, 1008, 861, 810, 751, 693.

Melting point: 82.0 – 83.8 °C.

4-((2,2-difluorobenzo[d][1,3]dioxol-5-yl)(phenylamino)methyl)benzonitrile (3ia)



3ia

The title compound **3ia** was prepared according to the general procedure as described above in 42% yield, 30.9 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, 2H, *J* = 8.0 Hz), 7.47 (d, 2H, *J* = 8.1 Hz), 7.19 – 7.10 (m, 2H), 7.08 – 6.98 (m, 3H), 6.82 – 6.72 (m, 1H), 6.57 – 6.44 (m, 2H), 5.50 (s, 1H), 4.14 (br, 1H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.44, 146.29, 144.31, 143.36, 137.93, 132.86, 131.65 (t, *J* = 256.7 Hz) 129.36, 128.03, 122.82, 118.82, 118.56, 113.67, 111.73, 109.83, 108.78, 62.52 ppm.

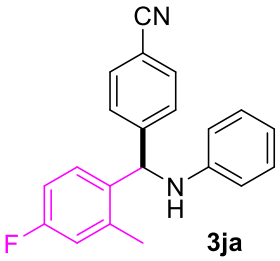
^{9}F NMR (376 MHz, Chloroform-*d*) δ -49.87 – -49.99 (m, 2F) ppm.

HRMS ESI$^+$ (m/z) calc'd for $C_{21}H_{15}F_2N_2O_2$ $[M+H]^+$, 365.1096; found, 365.1099.

IR (neat) ν (cm^{-1}) 3334, 2961, 2228, 1733, 1614, 1493, 1306, 1283, 1196, 1030, 907, 794, 693, 647.

Melting point: 66.5 – 68.0 °C.

4-((4-fluoro-2-methylphenyl)(phenylamino)methyl)benzonitrile (3ja)



3ja

The title compound **3ja** was prepared according to the general procedure as described above in 43% yield, 27.2 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, 2H, *J* = 8.0 Hz), 7.46 (d, 2H, *J* = 8.0 Hz), 7.18 – 7.10 (m, 2H), 7.07 – 6.99 (m, 1H), 6.98 – 6.91 (m, 1H), 6.87 – 6.79 (m, 1H), 6.78 – 6.70 (m, 1H), 6.53 – 6.43 (m, 2H), 5.68 (s, 1H), 4.07 (s, 1H), 2.35 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.50 (d, *J* = 246.8 Hz), 144.88, 144.07, 136.05 (d, *J* = 8.0 Hz), 132.84 (d, *J* = 3.0 Hz), 130.02, 126.77, 126.71, 125.90, 116.12, 115.76, 115.13 (d, *J* = 21.4 Hz), 110.57, 110.54 (d, *J* = 20.7 Hz), 108.79, 56.01, 16.88 ppm.

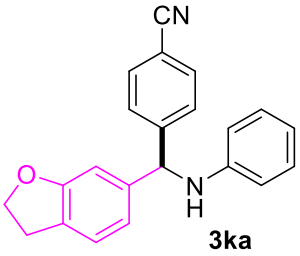
^{19}F NMR (128 MHz, Chloroform-*d*) δ -114.81 – -114.98 (m, 1F) ppm.

HRMS ESI$^+$ (m/z) calc'd for $C_{21}H_{17}FN_2Na$ $[M+Na]^+$, 339.1268; found, 339.1267.

IR (neat) ν (cm^{-1}) 3387, 2920, 2228, 1724, 1599, 1496, 1428, 1310, 1268, 1237, 1175, 953, 908, 862, 817, 729, 691.

Melting point: 135.2 – 137.2 °C.

4-((2,3-dihydrobenzofuran-6-yl)(phenylamino)methyl)benzonitrile (3ka)



3ka

The title compound **3ka** was prepared according to the general procedure as described above in 81% yield, 52.8 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 10/1) to afford a yellow oil.

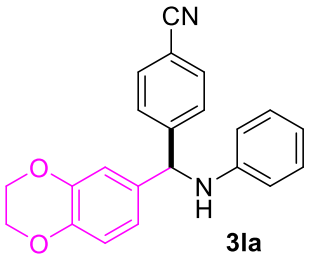
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, 2H, *J* = 8.1 Hz), 7.52 (d, 2H, *J* = 8.3 Hz), 7.16 – 7.10 (m, 2H), 7.09 – 7.05 (m, 1H), 7.03 – 6.99 (m, 1H), 6.76 – 6.70 (m, 2H), 6.53 – 6.45 (m, 2H), 5.44 (s, 1H), 4.56 (t, 2H, *J* = 8.7 Hz), 4.18 (br, 1H), 3.17 (t, 2H, *J* = 8.7 Hz) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.96, 148.70, 146.82, 134.14, 132.61, 129.26, 128.03, 127.85, 127.70, 124.24, 118.88, 118.23, 113.52, 110.99, 109.60, 71.48, 62.62, 29.66 ppm.

HRMS ESI$^+$ (m/z) calc'd for $C_{22}H_{18}N_2ONa$ $[M+Na]^+$, 349.1311; found, 349.1312.

IR (neat) ν (cm^{-1}) = 3381, 3053, 2961, 2894, 2225, 2078, 1600, 1488, 1427, 1313, 1242, 1100, 981, 816, 749, 691.

4-((2,3-dihydrobenzo[b][1,4]dioxin-6-yl)(phenylamino)methyl)benzonitrile (3la)



3la

The title compound **3la** was prepared according to the general procedure as described above in 59% yield, 40.2 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 50/1) to afford a pale-yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, 2H, *J* = 8.3 Hz), 7.51 (d, 2H, *J* = 8.4 Hz), 7.17 – 7.09 (m, 2H), 6.86 – 6.80 (m, 1H), 6.79 – 6.69 (m, 3H), 6.52 – 6.45 (m, 2H), 5.40 (s, 1H), 4.23 (s, 4H) 4.18 (br, 1H) ppm.

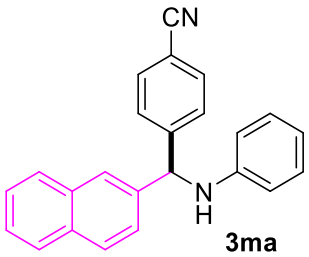
^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.35, 146.72, 143.82, 143.33, 135.20, 132.57, 129.20, 127.82, 120.50, 118.77, 118.24, 117.76, 116.38, 113.51, 111.07, 64.33, 64.29, 62.33 ppm.

HRMS ESI$^+$ (m/z) calc'd for $C_{22}H_{19}N_2O_2$ $[M+H]^+$, 343.1441; found, 343.1448.

IR (neat) ν (cm^{-1}) = 3386, 2927, 2874, 2226, 1598, 1499, 1428, 1283, 1253, 1201, 1064, 915, 886, 813, 747, 730, 691.

Melting point: 73.0 – 74.8 °C.

4-(naphthalen-2-yl(phenylamino)methyl)benzonitrile (3ma)[3]



3ma

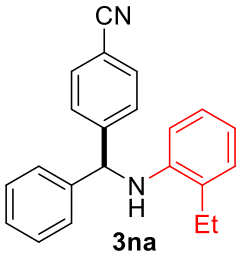
The title compound **3ma** was prepared according to the general procedure as described above in 80% yield, 53.8 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.76 (m, 4H), 7.64 (d, 2H, *J* = 8.3 Hz), 7.58 (d, 2H, *J* = 8.1 Hz), 7.55 – 7.49 (m, 2H), 7.45 – 7.40 (m, 1H), 7.22 – 7.14 (m, 2H), 6.82 – 6.75 (m, 1H), 6.63 – 6.54 (m, 2H), 5.72 (s, 1H), 4.35 (br, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.10, 146.84, 139.12, 133.44, 133.02, 132.70, 129.36, 129.17,

128.22, 128.07, 127.80, 126.65, 126.57, 126.50, 125.39, 118.84, 118.47, 113.70, 111.31, 63.10 ppm.

4-(((2-ethylphenyl)amino)(phenyl)methyl)benzonitrile (3na)



3na

The title compound **3na** was prepared according to the general procedure as described above in 59% yield, 37.1 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a brown oil.

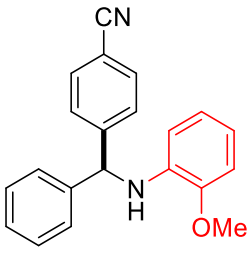
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, 2H, *J* = 8.1 Hz), 7.52 (d, 2H, *J* = 8.2 Hz), 7.41 – 7.25 (m, 5H), 7.17 – 7.09 (m, 1H), 7.05 – 6.94 (m, 1H), 6.79 – 6.70 (m, 1H), 6.38 – 6.28 (m, 1H), 5.58 (s, 1H), 4.14 (br, 1H), 2.54 (q, 2H, *J* = 7.8 Hz), 1.29 (t, 3H, *J* = 7.5 Hz) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.38, 144.06, 142.09, 132.71, 129.23, 128.16, 128.00, 127.62, 126.94, 118.88, 118.23, 111.51, 111.19, 62.82, 24.04, 12.87 ppm.

HRMS ESI$^+$ (m/z) calc'd for $C_{22}H_{21}N_2$ $[M+H]^+$, 313.1699; found, 313.1701.

IR (neat) ν (cm-1) = 3429, 2964, 2872, 1601, 1502, 1452, 1304, 1261, 1130, 1057, 1023, 909, 851, 812, 744, 698, 636.

4-(((2-methoxyphenyl)amino)(phenyl)methyl)benzonitrile (3oa)



3oa

The title compound **3oa** was prepared according to the general procedure as described above in 91% yield, 57.1 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, 2H, *J* = 8.4 Hz), 7.50 (d, 2H, *J* = 8.2 Hz), 7.31 – 7.27 (m, 1H), 7.25 – 7.21 (m, 1H), 7.15 – 7.10 (m, 2H), 6.96 – 6.90 (m, 2H), 6.74 – 6.69 (m, 1H), 6.56 – 6.51 (m,

2H), 5.91 (s, 1H), 3.79 (s, 3H) ppm.

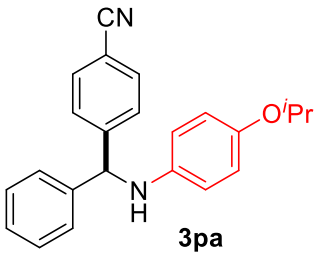
^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.52, 148.66, 147.11, 132.33, 129.81, 129.21, 129.10, 128.24, 127.99, 121.07, 118.04, 113.50, 118.98, 111.08, 110.75, 56.57, 55.50 ppm.

HRMS ESI$^+$ (m/z) calc'd for $C_{21}H_{18}N_2ONa$ $[M+Na]^+$, 337.1311; found, 337.1316.

IR (neat) ν (cm^{-1}) = 3428, 2964, 2227, 1601, 1501, 1457, 1304, 1261, 1130, 1057, 1023, 908, 851, 811, 744, 698.

Melting point: 137.0 – 138.8 °C.

(1,3-dimethyl-1H-imidazol-3-ium-2-yl)(phenyl((2-(trifluoromethoxy)phenyl)amino)methyl) dihydroborate (3pa)



3pa

The title compound **3pa** was prepared according to the general procedure as described above in 50% yield, 34.2 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a dark semi-solid.

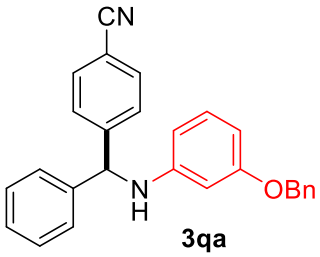
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, 2H, *J* = 8.1 Hz), 7.53 (d, 2H, *J* = 8.2 Hz), 7.38 – 7.27 (m, 5H), 6.71 (d, 2H, *J* = 8.6 Hz), 6.44 (d, 2H, *J* = 8.6 Hz), 5.43 (s, 1H), 4.44 – 4.29 (m, 1H), 3.98 (br, 1H), 1.27 (d, *J* = 6.1 Hz, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.67, 148.59, 142.13, 141.10, 132.61, 129.09, 128.03, 127.99, 127.58, 118.85, 117.67, 114.71, 111.09, 70.98, 63.75, 22.19 ppm.

HRMS ESI$^+$ (m/z) calc'd for $C_{23}H_{22}N_2ONa$ $[M+Na]^+$, 365.1624; found, 365.1630.

IR (neat) ν (cm^{-1}) = 3375, 3030, 2973, 2227, 1661, 1603, 1505, 1406, 1376, 1228, 1112, 951, 820, 731, 697.

4-(((3-(benzyloxy)phenyl)amino)(phenyl)methyl)benzonitrile (3qa)



3qa

The title compound **3qa** was prepared according to the general procedure as described above in 77% yield, 60.4 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 50/1) to afford a brown semi-solid.

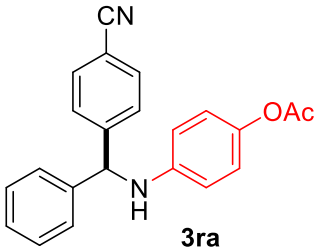
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, 2H, *J* = 8.3 Hz), 7.50 (d, 2H, *J* = 8.2 Hz), 7.37 – 7.29 (m, 8H), 7.28 – 7.26 (m, 1H), 7.26 – 7.22 (m, 1H), 7.06 – 7.00 (m, 1H), 6.39 – 6.34 (m, 1H), 6.16 – 6.12 (m, 1H), 6.13 – 6.11 (m, 1H), 5.48 (s, 1H), 4.93 (s, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.99, 148.14, 148.08, 141.77, 137.07, 132.63, 130.05, 129.14, 128.57, 128.14, 127.96, 127.92, 127.65, 127.43, 118.82, 111.19, 106.91, 104.39, 100.53, 69.86, 62.89 ppm.

HRMS ESI$^+$ (m/z) calc'd for $C_{27}H_{22}N_2ONa$ $[M+Na]^+$, 413.1624; found, 413.1626.

IR (neat) ν (cm^{-1}) = 3387, 3030, 2924, 2227, 1597, 1493, 1452, 1301, 1187, 1158, 1023, 907, 816, 728, 693.

4-(((4-cyanophenyl)(phenyl)methyl)amino)phenyl acetate (3ra)



3ra

The title compound **3ra** was prepared according to the general procedure as described above in 66% yield, 45.5 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 10/1) to afford a colorless oil.

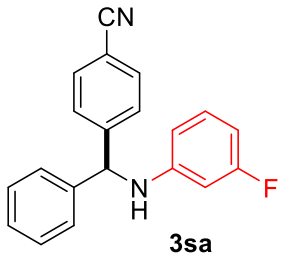
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, 2H, *J* = 8.4 Hz), 7.51 (d, 2H, *J* = 8.1 Hz), 7.38 – 7.25 (m, 5H), 6.87 – 6.80 (m, 2H), 6.52 – 6.42 (m, 2H), 5.46 (s, 1H), 4.22 (br, 1H), 2.24 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.16, 147.99, 144.67, 142.65, 141.67, 132.68, 129.18, 128.19, 127.99, 127.60, 122.19, 118.76, 113.96, 111.28, 63.28, 21.08 ppm.

HRMS ESI^{+} (m/z) calc'd for $C_{22}H_{18}N_2O_2Na$ $[M+Na]^+$, 365.1260; found, 365.1264.

IR (neat) ν (cm^{-1}) = 3380, 2226, 1742, 1606, 1505, 1367, 1190, 1011, 903, 825, 728, 697, 617.

4-(((3-fluorophenyl)amino)(phenyl)methyl)benzonitrile (3sa)[3]



3sa

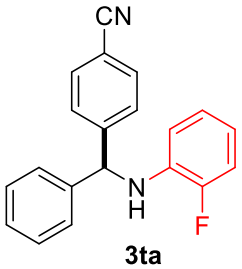
The title compound **3sa** was prepared according to the general procedure as described above in 57% yield, 34.4 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a pale-yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, 2H, *J* = 8.3 Hz), 7.50 (d, 2H, *J* = 8.2 Hz), 7.40 – 7.28 (m, 3H), 7.28 – 7.23 (m, 2H), 7.10 – 7.01 (m, 1H), 6.47 – 6.38 (m, 1H), 6.34 – 6.26 (m, 1H), 6.21 – 6.14 (m, 1H), 5.50 (s, 1H), 4.34 (br, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.88 (d, *J* = 243.5 Hz), 148.43 (d, *J* = 10.6 Hz), 147.60, 141.30, 132.72, 130.39 (d, *J* = 10.2 Hz), 129.23, 128.30, 127.95, 127.59, 118.70, 111.42, 109.39 (d, *J* = 2.5 Hz), 104.88 (d, *J* = 21.6 Hz), 100.48 (d, *J* = 25.6 Hz), 62.83 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.38 – -112.47 (m, 1F) ppm.

4-(((2-fluorophenyl)amino)(phenyl)methyl)benzonitrile (3ta)[3]



3ta

The title compound **3ta** was prepared according to the general procedure as described above in 46% yield, 27.8 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a brown oil.

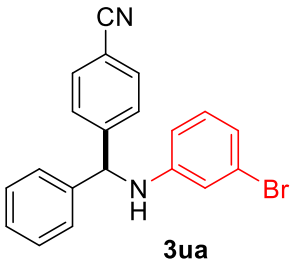
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, 2H, *J* = 8.4 Hz), 7.53 (d, 2H, *J* = 8.2 Hz), 7.40 – 7.28 (m, 5H), 7.04 – 6.98 (m, 1H), 6.90 – 6.83 (m, 1H), 6.71 – 6.60 (m, 1H), 6.43 – 6.37 (m, 1H,), 5.54 (s, 1H),

4.49 (br, 1H). ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.57 (d, *J* = 239.1 Hz), 147.74, 141.31, 135.21 (d, *J* = 11.6 Hz), 132.72, 129.21, 128.27, 127.95, 127.55, 124.54 (d, *J* = 3.7 Hz), 118.72, 117.82 (d, *J* = 6.9 Hz), 114.57 (d, *J* = 18.5 Hz), 113.25 (d, *J* = 2.9 Hz), 111.42, 62.58 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -135.56 – -135.85 (m, 1F) ppm.

4-(((3-bromophenyl)amino)(phenyl)methyl)benzonitrile (3ua)



3ua

The title compound **3ua** was prepared according to the general procedure as described above in 55% yield, 39.6 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a yellow oil.

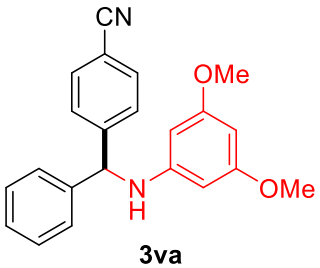
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, 2H, *J* = 8.4 Hz), 7.49 (d, 2H, *J* = 8.2 Hz), 7.39 – 7.28 (m, 3H), 7.28 – 7.22 (m, 2H), 7.00 – 6.92 (m, 1H), 6.87 – 6.81 (m, 1H), 6.69 – 6.63 (m, 1H), 6.44 – 6.36 (m, 1H), 5.50 (d, 1H, *J* = 3.8 Hz), 4.27 (br, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.92, 147.47, 141.25, 132.73, 130.57, 129.24, 128.32, 127.93, 127.58, 123.21, 121.24, 118.69, 116.36, 112.05, 111.46, 62.66 ppm.

HRMS ESI^{+} (m/z) calc'd for $C_{20}H_{16}BrN_2$ $[M+H]^{+}$, 363.0491; found, 363.0494.

IR (neat) ν (cm^{-1}) = 3382, 3062, 2920, 2227, 1592, 1478, 1410, 1318, 1083, 986, 906, 768, 723, 698.

4-(((3,5-dimethoxyphenyl)amino)(phenyl)methyl)benzonitrile (3va)



3va

The title compound **3va** was prepared according to the general procedure as described above in 49% yield, 33.6 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1)

to afford a dark oil.

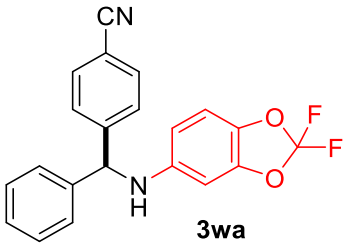
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.24 (m, 5H), 5.91 (s, 1H), 5.71 (s, 2H), 5.51 (s, 1H), 4.26 (br, 1H), 3.68 (s, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.65, 148.67, 148.11, 141.72, 132.64, 129.15, 128.15, 127.95, 127.64, 118.82, 111.18, 92.63, 90.40, 62.91, 55.14 ppm.

HRMS ESI$^+$ calc'd for $C_{22}H_{20}N_2O_2Na$ $[M+Na]^+$, 367.1417; found, 367.1413.

IR (neat) ν (cm^{-1}) = 2974, 2923, 2227, 1732, 1506, 1371, 1228, 1180, 1112, 1045, 952, 821, 730, 699.

4-(((2,2-difluorobenzo[d][1,3]dioxol-5-yl)amino)(phenyl)methyl)benzonitrile (3wa)



3wa

The title compound **3wa** was prepared according to the general procedure as described above in 67% yield, 48.6 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, 2H, *J* = 8.4 Hz), 7.51 (d, 2H, *J* = 8.1 Hz), 7.40 – 7.27 (m, 5H), 6.83 – 6.76 (m, 1H), 6.30 – 6.26 (m, 1H), 6.19 – 6.14 (m, 1H), 5.46 (s, 1H), 4.28 (br, 1H).

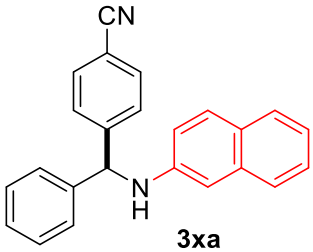
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.53, 144.52, 143.70, 141.18, 136.37, 132.71, 131.66 (t, *J* = 252.5 Hz), 129.22, 128.29, 127.91, 127.46, 118.62, 111.44, 109.73, 107.41, 96.15, 63.40 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -50.43 (s, 2F) ppm.

HRMS ESI$^+$ calc'd for $C_{21}H_{15}F_2N_2O_2$ $[M+H]^+$, 365.1096; found, 365.1100.

IR (neat) ν (cm^{-1}) = 3377, 3064, 2962, 2228, 1727, 1498, 1451, 1410, 1308, 1228, 1196, 1177, 1140, 1066, 906, 820, 730, 699, 648.

4-((naphthalen-2-ylamino)(phenyl)methyl)benzonitrile (3xa)



3xa

The title compound **3xa** was prepared according to the general procedure as described above in 47% yield, 31.5 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.58 (m, 4H), 7.58 – 7.53 (m, 2H), 7.49 – 7.44 (m, 1H), 7.40 – 7.29 (m, 6H), 7.23 – 7.17 (m, 1H), 6.93 – 6.87 (m, 1H), 6.61 – 6.54 (m, 1H), 5.65 (s, 1H), 4.38 (br, 1H).

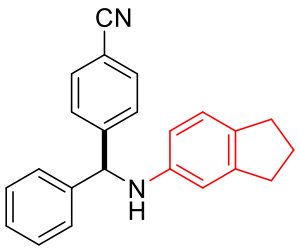
^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.31, 141.65, 139.10, 132.16, 130.07, 126.59, 126.53, 125.67, 125.60, 125.43, 125.21, 125.09, 125.02, 123.88, 123.52, 120.00, 115.27, 108.68, 103.54, 60.36 ppm.

HRMS ESI$^+$ calc'd for $C_{24}H_{19}N_2$ $[M+H]^+$, 335.1543; found, 335.1541.

IR (neat) ν (cm^{-1}) 3354, 2918, 2849, 2229, 1767, 1600, 1489, 1322, 1230, 1144, 1034, 868, 821, 794, 753, 692.

Melting point: 167.0 – 169.0 °C.

4-(((2,3-dihydro-1H-inden-5-yl)amino)(phenyl)methyl)benzonitrile (3ya)



3ya

The title compound **3ya** was prepared according to the general procedure as described above in 60% yield, 39.0 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a dark solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, 2H, *J* = 8.2 Hz), 7.52 (d, 2H, *J* = 8.2 Hz), 7.36 – 7.23 (m, 5H), 7.00 – 6.93 (d, 1H, *J* = 8.0 Hz), 6.43 – 6.39 (m, 1H), 6.34 – 6.26 (m, 1H), 5.47 (s, 1H), 4.09 (br, 1H), 2.81 – 2.73 (m, 4H), 2.04– 1.97 (m, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.58, 145.61, 145.55, 142.18, 134.14, 132.62, 129.11, 128.03,

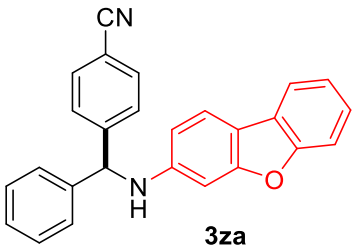
128.01, 127.66, 124.81, 118.89, 111.79, 111.07, 109.74, 63.39, 33.15, 31.94, 25.68 ppm.

HRMS ESI^{+} (m/z) calc'd for $C_{23}H_{20}N_2Na$ $[M+Na]^+$, 347.4162; found, 347.4163.

IR (neat) ν (cm^{-1}) = 3385, 3027, 2841, 2227, 1609, 1493, 1329, 1283, 908, 808, 728, 697, 631.

Melting point: 66.2 – 67.8 °C.

4-((dibenzo[b,d]furan-3-ylamino)(phenyl)methyl)benzonitrile (3za)



3za

The title compound **3za** was prepared according to the general procedure as described above in 53% yield, 39.6 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 50/1) to afford a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.75 (m, 1H), 7.73 – 7.71 (m, 1H), 7.70 – 7.65 (m, 1H), 7.64 – 7.59 (m, 2H), 7.56 – 7.51 (m, 2H), 7.45 – 7.41 (m, 1H), 7.39 – 7.35 (m, 2H), 7.34 – 7.28 (m, 4H), 6.66 – 6.56 (m, 2H), 5.60 (s, 1H), 4.55 (br, 1H). ppm.

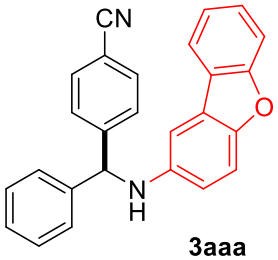
^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.17, 147.48, 145.74, 140.47, 139.36, 130.09, 126.61, 125.58, 125.46, 125.06, 124.47, 122.24, 121.73, 119.72, 118.00, 116.30, 112.12, 109.52, 109.09, 108.60, 101.35, 61.16 ppm.

HRMS ESI^{+}(m/z) calc'd for $C_{26}H_{19}N_2O$ $[M+H]^+$, 375.1492; found, 375.1494.

IR (neat) ν (cm^{-1}) = 3387, 3055, 2228, 1634, 1603, 1489, 1455, 1278, 1188, 1159, 1127, 1016, 908, 846, 812, 724, 698, 633.

Melting point: 65.0 – 66.1 °C.

4-((dibenzo[b,d]furan-2-ylamino)(phenyl)methyl)benzonitrile (3aaa)



3aaa

The title compound **3aaa** was prepared according to the general procedure as described above in 48% yield, 35.9 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.71 (m, 2H), 7.64 (d, 2H, *J* = 8.2 Hz), 7.58 (d, 2H, *J* = 8.2 Hz), 7.52 – 7.46 (m, 1H), 7.42 – 7.38 (m, 1H), 7.37 – 7.31 (m, 5H), 7.27 – 7.22 (m, 1H), 7.01 – 6.95 (m, 1H), 6.73 – 6.66 (m, 1H), 5.60 (s, 1H), 4.27 (br, 1H) ppm.

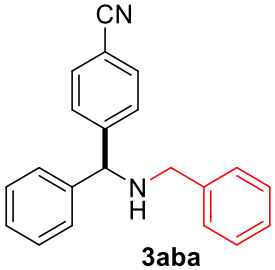
^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.31, 153.27, 145.15, 144.48, 138.82, 130.11, 126.63, 125.67, 125.42, 125.06, 122.60, 122.16, 120.12, 118.64, 116.77, 116.20, 112.64, 108.73, 108.55, 108.03, 93.08, 60.52 ppm.

HRMS ESI$^+$ (m/z) calc'd for $C_{26}H_{18}N_2ONa$ $[M+Na]^+$, 397.1311; found, 397.1319.

IR (neat) ν (cm^{-1}) = 3387, 3055, 2227, 1633, 1602, 1481, 1448, 1185, 1104, 1019, 907, 837, 803, 727, 697, 606.

Melting point: 58.3 – 60.2 °C.

4-((benzylamino)(phenyl)methyl)benzonitrile (3aba)[3]



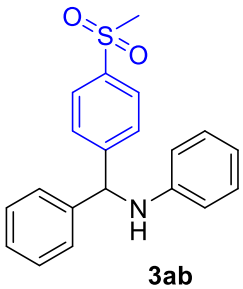
3aba

The title compound **3aba** was prepared according to the general procedure as described above in 66% yield, 39.1 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1) to afford a pale-yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (s, 4H), 7.41 – 7.15 (m, 10H), 4.87 (s, 1H), 3.71 (s, 2H), 1.85 (s, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.43, 142.74, 139.90, 132.41, 128.87, 128.53, 128.15, 128.11, 127.70, 127.31, 127.21, 118.96, 110.84, 66.20, 51.85 ppm.

N-((4-(methylsulfonyl)phenyl)(phenyl)methyl)aniline (3ab)[3]



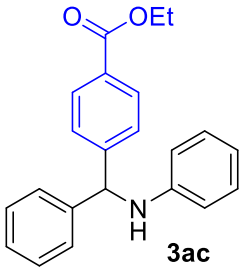
3ab

The title compound **3ab** was prepared according to the general procedure as described above in 54% yield, 36.2 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 5/1) to afford a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, 2H, *J* = 8.2 Hz), 7.61 (d, 2H, *J* = 8.3 Hz), 7.38 – 7.27 (m, 5H), 7.17 – 7.08 (m, 2H), 6.78 – 6.69 (m, 1H), 6.55 – 6.44 (m, 2H), 5.55 (s, 1H), 4.24 (br, 1H), 3.04 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.22, 146.73, 141.88, 139.42, 129.28, 129.14, 128.17, 128.12, 127.94, 127.64, 118.36, 113.57, 62.91, 44.51 ppm.

ethyl 4-(phenyl(phenylamino)methyl)benzoate (3ac)



3ac

The title compound **3ac** was prepared according to the general procedure as described above in 57% yield, 37.8 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 5/1) to afford a yellow semi-solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, 2H, *J* = 8.4 Hz), 7.46 (d, 2H, *J* = 8.2 Hz), 7.35 – 7.29 (m, 4H) 7.29 – 7.25 (m, 1H), 7.14 – 7.08 (m, 2H), 6.73 – 6.68 (m, 1H), 6.55 – 6.49 (m, 2H), 5.53 (s, 1H), 4.35 (q, 2H, *J* = 7.1 Hz), 4.23 (br, 1H), 1.37 (t, 3H, *J* = 7.1 Hz) ppm.

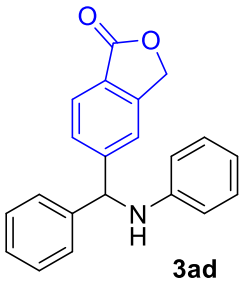
^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.41, 147.85, 147.07, 142.39, 130.09, 129.63, 129.20, 128.95, 127.77, 127.61, 127.28, 118.02, 113.56, 62.98, 60.94, 14.36 ppm.

HRMS ESI$^+$ (m/z) calc'd for $C_{22}H_{21}NO_2Na$ $[M+Na]^+$, 354.1465; found, 354.1462.

IR (neat) ν (cm^{-1}) = 3386, 2980, 2851, 1709, 1661, 1600, 1500, 1269, 1174, 1102, 894, 852, 747, 693,

619.

5-(phenyl(phenylamino)methyl)isobenzofuran-1(3H)-one (3ad)



3ad

The title compound **3ad** was prepared according to the general procedure as described above in 66% yield, 41.6 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 5/1) to afford a yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 1H), 7.60 – 7.53 (m, 2H), 7.38 – 7.27 (m, 5H), 7.17 – 7.10 (m, 2H), 6.76 – 6.71 (m, 1H), 6.57 – 6.49 (m, 2H), 5.59 (s, 1H), 5.25 (d, 2H, J = 3.6 Hz), 4.31 (br, 1H) ppm.

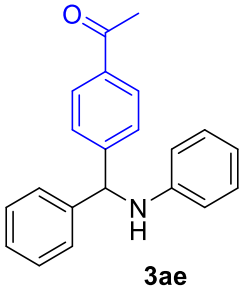
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.85, 150.00, 147.45, 146.81, 142.04, 129.31, 129.18, 128.54, 128.14, 127.66, 126.15, 124.99, 120.59, 118.37, 113.59, 69.67, 63.26 ppm.

HRMS ESI^{+} (m/z) calc'd for $C_{21}H_{18}NO_2$ $[M+H]^{+}$, 316.1332; found, 316.1337.

IR (neat) ν (cm^{-1}) = 3381, 3053, 1749, 1599, 1500, 1451, 1432, 1361, 1316, 1264, 1045, 1003, 873, 847, 733, 692.

Melting point: 108.0 – 109.5 °C.

1-(4-(phenyl(phenylamino)methyl)phenyl)ethan-1-one (3ae)



3ae

The title compound **3ae** was prepared according to the general procedure as described above in 44% yield, 26.3 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 20/1)

to afford a yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, 2H, *J* = 8.2 Hz), 7.49 (d, 2H, *J* = 8.1 Hz), 7.37 – 7.26 (m, 5H), 7.12 – 7.07 (m, 2H), 6.78 – 6.65 (m, 1H), 6.58 – 6.45 (m, 2H), 5.53 (s, 1H), 4.25 (br, 1H), 2.57 (s, 3H) ppm.

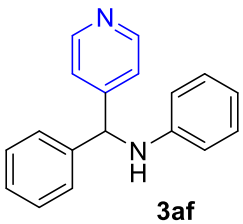
^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.12, 145.59, 144.41, 139.69, 133.70, 126.60, 126.38, 126.32, 125.23, 124.99, 124.87, 115.48, 110.95, 60.38, 24.02 ppm.

HRMS ESI$^+$ (m/z) calc'd for $C_{21}H_{19}NONa$ $[M+Na]^+$, 324.1359; found, 324.1360.

IR (neat) ν (cm^{-1}) = 3387, 3061, 2228, 1728, 1593, 1496, 1310, 1201, 1120, 1091, 1023, 905, 848, 728, 697.

Melting point: 94.0 – 95.8 °C.

N-(phenyl(pyridin-4-yl)methyl)aniline (3af)[4]



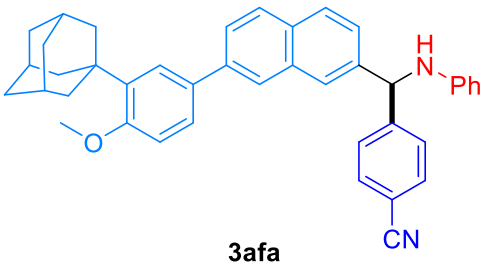
3af

The title compound **3af** was prepared according to the general procedure as described above in 39% yield, 20.4 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 3/1) to afford a pale-yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 – 8.51 (m, 2H), 7.38 – 7.28 (m, 7H), 7.16 – 7.11 (m, 2H), 6.76 – 6.71 (m, 1H), 6.55 – 6.49 (m, 2H), 5.46 (d, 1H, *J* = 2.7 Hz), 4.21 (br, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.73, 150.21, 146.77, 141.56, 129.27, 129.11, 128.14, 127.69, 122.34, 118.32, 113.54, 62.39 ppm.

4-((6-(3-(adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)(phenylamino)methyl)benzonitrile (3afa)



3afa

The title compound **3afa** was prepared according to the general procedure as described above in 56% yield, 31.9 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 10/1) to afford a white solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.97 – 7.95 (m, 1H), 7.89 – 7.85 (m, 1H), 7.84 – 7.79 (m, 1H), 7.76 – 7.72 (m, 2H), 7.67 – 7.63 (m, 3H), 7.61 – 7.55 (m, 2H), 7.54 – 7.49 (m, 1H), 7.42 – 7.37 (m, 1H), 7.19 – 7.13 (m, 2H), 7.01 – 6.96 (m, 1H), 6.78 – 6.72 (m, 1H), 6.59 – 6.54 (m, 2H), 5.69 (s, 1H), 4.31 (br, 1H), 3.90 (s, 3H), 2.21 – 2.16 (m, 6H), 2.12 – 2.07 (m, 3H), 1.83 – 1.77 (m, 6H).

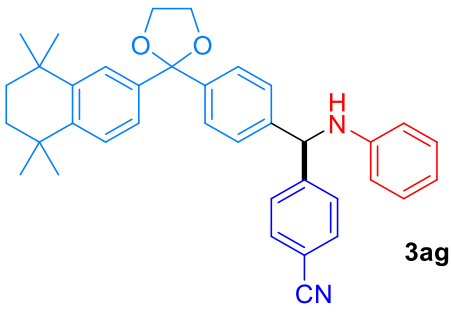
^{13}C NMR (101 MHz, Chloroform-d) δ 158.73, 148.12, 146.81, 139.63, 138.97, 138.68, 133.35, 132.83, 132.68, 132.15, 129.32, 129.25, 128.35, 128.19, 126.45, 126.28, 125.87, 125.64, 125.61, 124.77, 118.80, 118.42, 113.64, 112.12, 111.30, 63.11, 55.20, 40.62, 37.15, 29.72, 29.13.

HRMS ESI$^+$ (m/z) calc'd for $C_{41}H_{39}N_2O$ $[M+H]^+$, 575.3057; found, 575.3059.

IR (neat) ν (cm^{-1}) = 2935, 2227, 1560, 1519, 1247, 1039, 941, 755, 692.

Melting point: 79.0 – 80.5 °C.

4-((phenylamino)(4-(2-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-1,3-dioxolan-2-yl)phenyl)methyl)benzonitrile (3aga)



3aga

The title compound **3aga** was prepared according to the general procedure as described above in 61% yield, 33.0 mg. It was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 10/1) to afford a colorless solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.67 – 7.57 (m, 2H), 7.54 – 7.47 (m, 4H), 7.45 – 7.41 (m, 1H), 7.29

– 7.19 (m, 3H), 7.18 – 7.07 (m, 3H), 6.82 – 6.66 (m, 1H), 6.61 – 6.41 (m, 2H), 5.49 (s, 1H), 4.18 (br, 1H), 4.03 (s, 4H), 1.66 (s, 4H), 1.24 (s, 12H).

^{13}C NMR (101 MHz, Chloroform-d) δ 148.09, 146.70, 144.72, 144.60, 142.48, 141.41, 138.45, 132.60, 129.26, 127.98, 127.40, 126.97, 126.40, 123.84, 123.43, 118.80, 118.33, 113.52, 111.18, 109.30, 64.87, 62.71, 35.08, 35.03, 34.33, 34.12, 31.87, 31.82.

HRMS ESI$^+$ (m/z) calc'd for $C_{37}H_{39}N_2O_2$ $[M+H]^+$, 543.3006; found, 543.3010.

IR (neat) ν (cm^{-1}) = 2954, 2891, 2228, 1598, 1523, 1279, 1080, 790, 654.

Melting point: 65.0 – 66.7 °C.

6. Preliminary Mechanistic Studies

^{1}H NMR experiments

To explore the reaction mechanism of this deoxygenative cross coupling reaction, ^{1}H NMR experiments were performed to probe the intermediates generated by the iridium-catalyzed reduction of amide **1a** as shown in Figure S3.

Pure starting material **1a** is shown in spectrum (i), and starting material **1a** with Et_2SiH_2 is shown in the spectrum (ii). After treating the above solution with the iridium catalyst for a few minutes, amide **1a** was fully converted, and a newly generated intermediate, imine, was witnessed as the major species in the ^{1}H NMR spectrum (iii), which is likely to be produced via the intermediary of silylhemiaminal.[5,6]

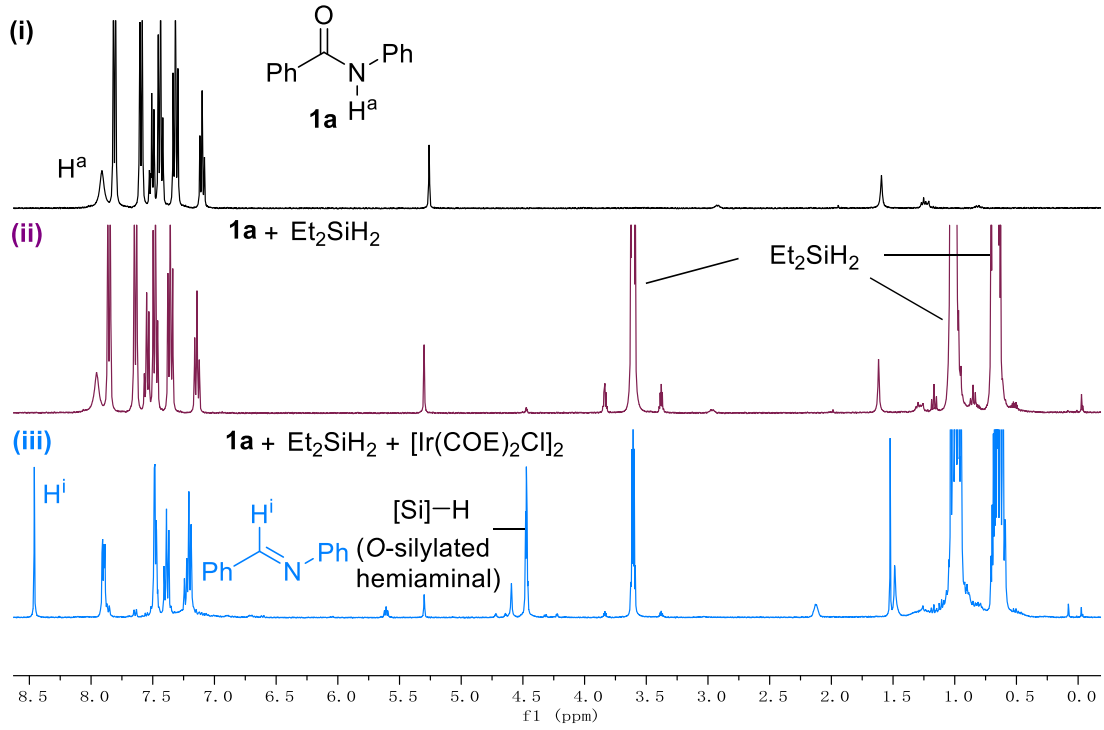


Figure S3. ^{1}H NMR spectra (400 MHz) in the iridium-catalyzed reduction of amide 1a.

i) Amide **1a** (0.10 mmol) in CD_2Cl_2 (1.0 mL). ii) Amide **1a** (0.10 mmol) and Et_2SiH_2 (0.20 mmol, 2.0 equiv.) in CD_2Cl_2 (1.0 mL). iii) Amide **1a** (0.10 mmol), Et_2SiH_2 (0.20 mmol, 2.0 equiv.), and $[Ir(COE)_2Cl]_2$ (1.0 mol %) in CD_2Cl_2 (1.0 mL), 5 min.

Control experiments

Some control experiments were conducted on the cross-coupling reaction as shown in Figure S4.

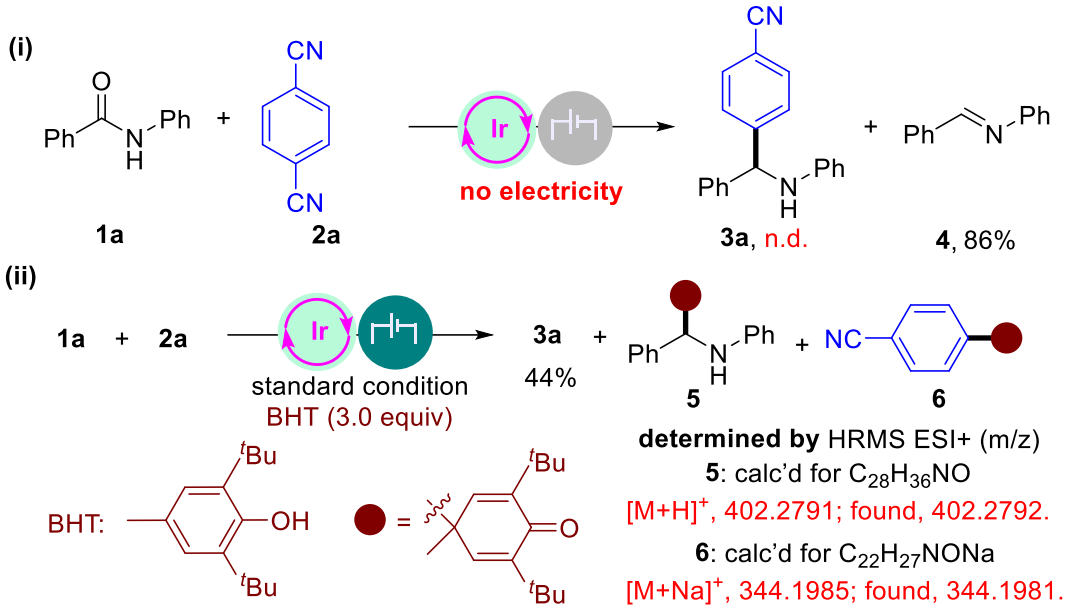


Figure S4. Control experiments

(i) A mixture of **1a** (0.30 mmol), Et_2SiH_2 (0.60 mmol), $[Ir(COE)_2Cl]_2$ (1.0 mol%), and DCM (2.0 mL) was pre-mixed for 30 min. Subsequently, the mixture was added to a tube-type undivided cell with another solution of **2a** (0.2 mmol) and $TBAClO_4$ (0.10 mmol) in DMSO (3.0 mL) while both graphite rod electrodes were placed. Then the reaction mixture was stirred without electricity for 2.5 hours. No desired product **3aa** was detected, and imine **4** was detected in 86% yield.

(ii) A mixture of **1a** (0.30 mmol), Et_2SiH_2 (0.60 mmol), $[Ir(COE)_2Cl]_2$ (1.0 mol%), and DCM (2.0 mL) was pre-mixed for 30 min. Subsequently, the mixture was added to a tube-type undivided cell with another solution of **2a** (0.20 mmol), $TBAClO_4$ (0.10 mmol), and butylated hydroxytoluene (BHT, 0.60 mmol) in DMSO (3.0 mL) while both graphite rod electrodes were placed, then the reaction mixture was electrolyzed in a current of 9.0 mA for 2.5 hours. Product **3aa** was obtained in a low yield of 47%, and the corresponding radical-BHT adducts **5** and **6** were detected by HRMS. **HRMS ESI**$^+$ (m/z) **5**: calc'd for $C_{28}H_{36}NO$ $[M+H]^+$, 402.2791; found, 402.2792. **6**: (m/z) calc'd for $C_{22}H_{27}NONa$ $[M+H]^+$, 344.1985; found, 344.1981.

7. References

[1] F. Buckingham, S. Calderwood, B. Checa, T. Keller, M. Tredwell, T. L. Collier, I. M. Newington, R. Bhalla, M. Glaser, V. Gouverneur, *J. Fluorine Chem.* **2015**, *180*, 33-39.

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8. NMR Spectra

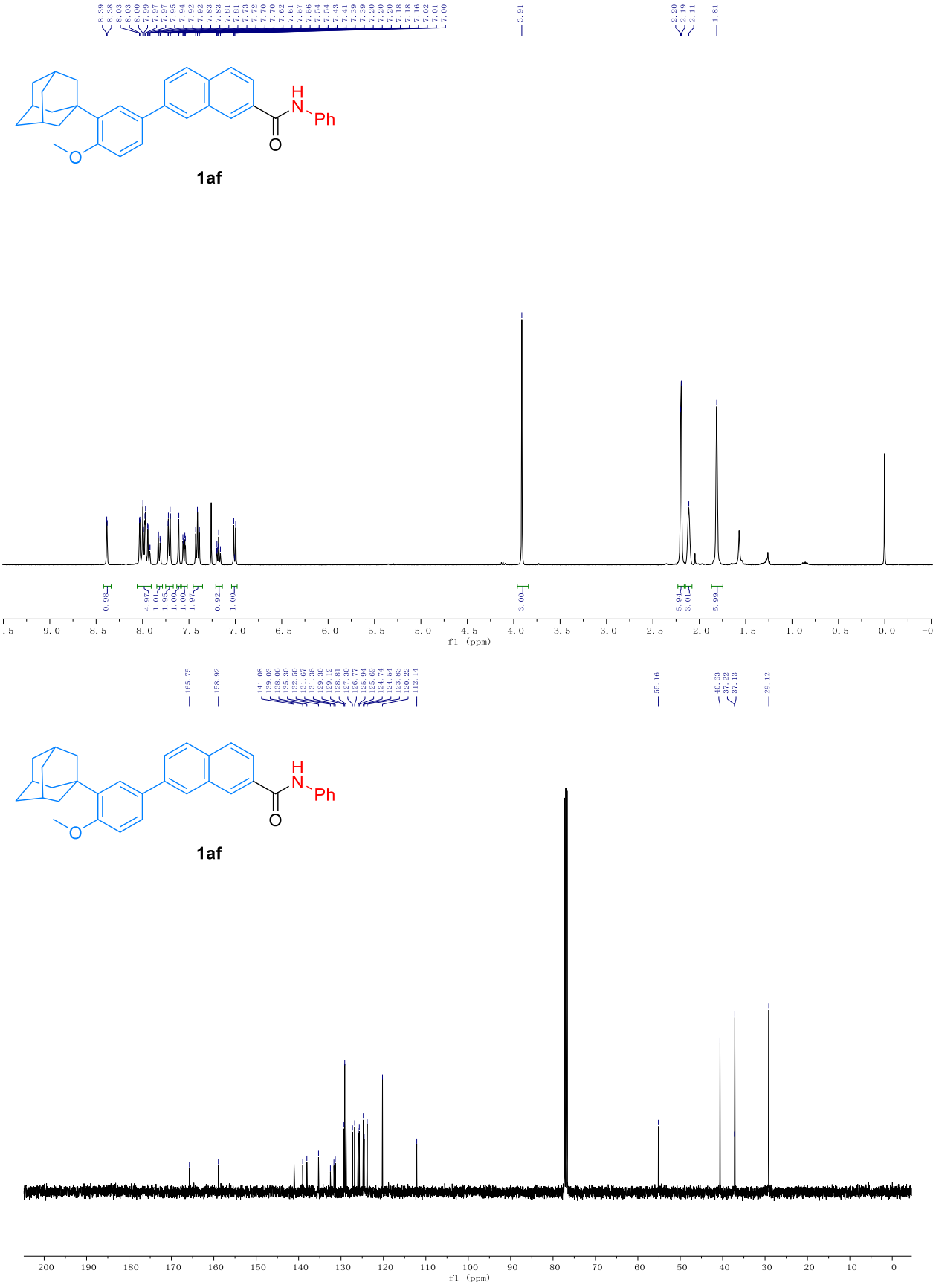


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **1af**

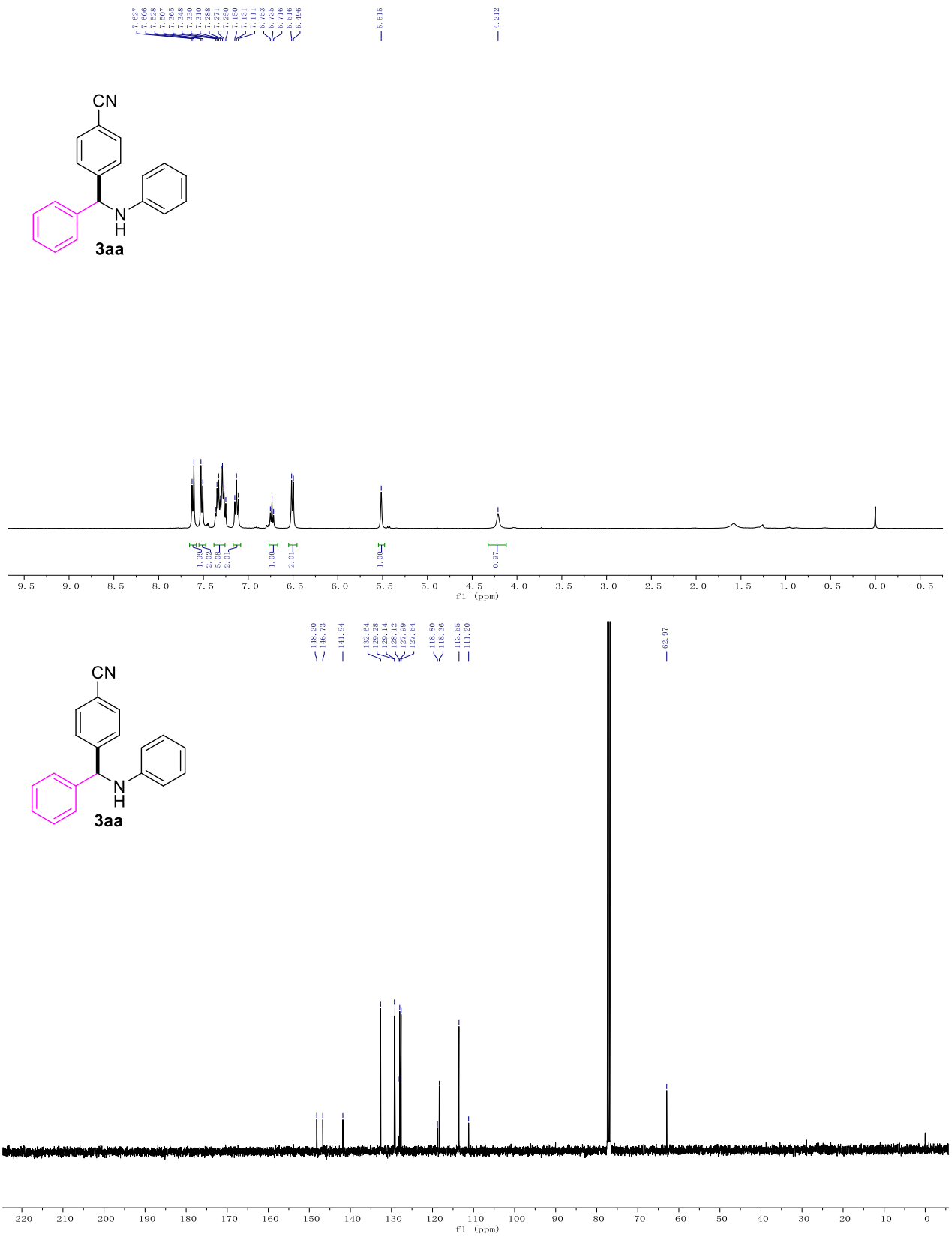


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3aa**

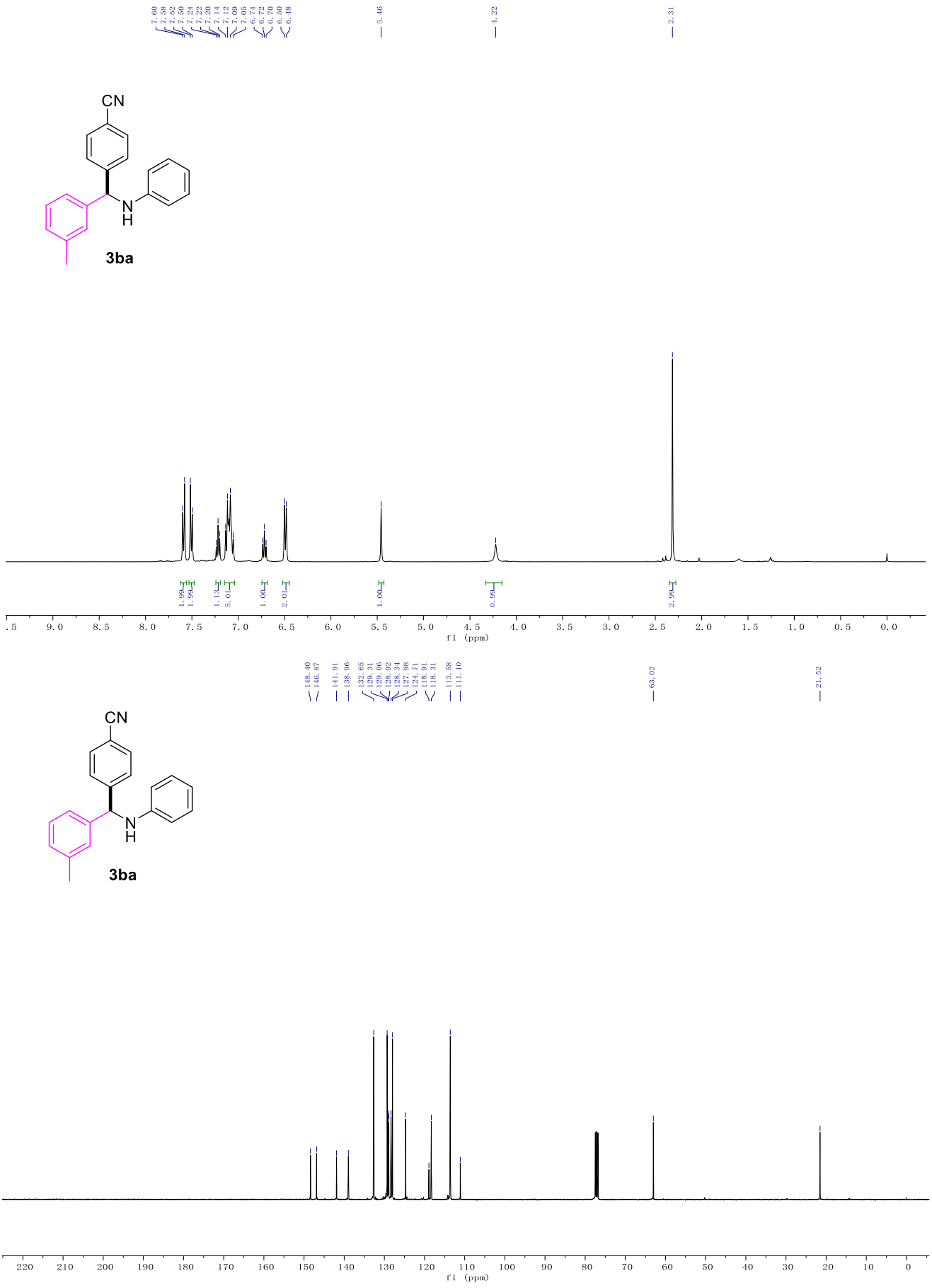
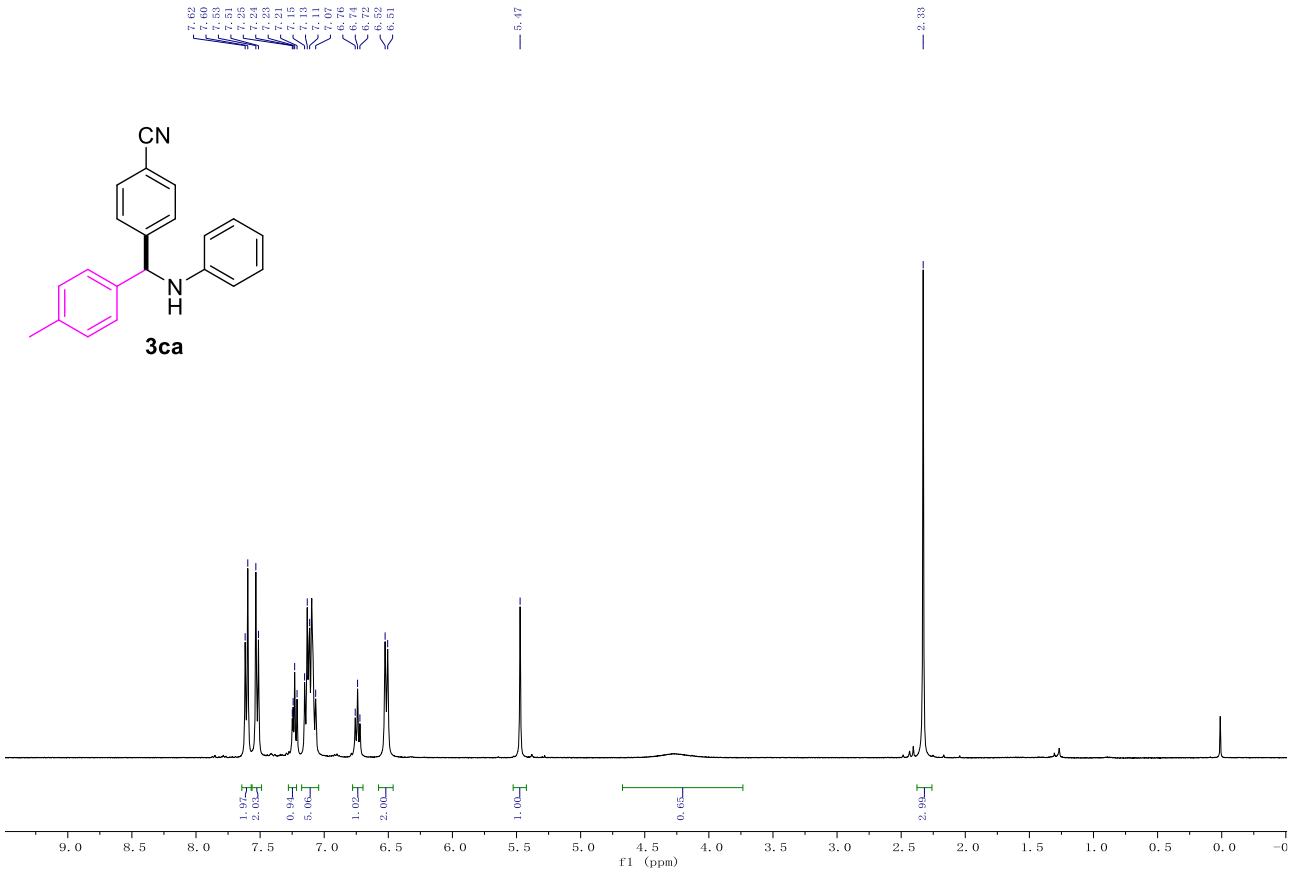


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3ba**



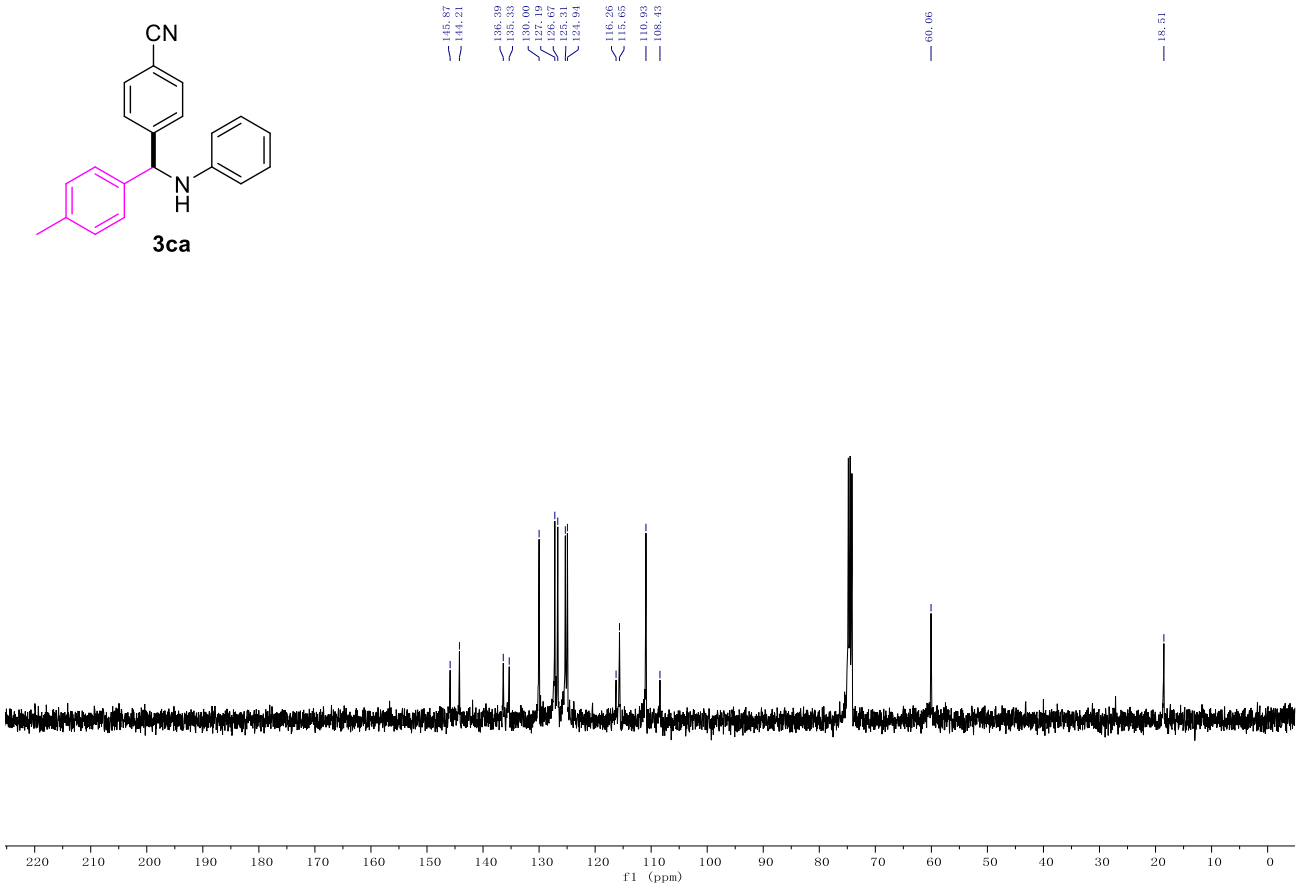


Figure S8. **^{1}H NMR** (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3ca**

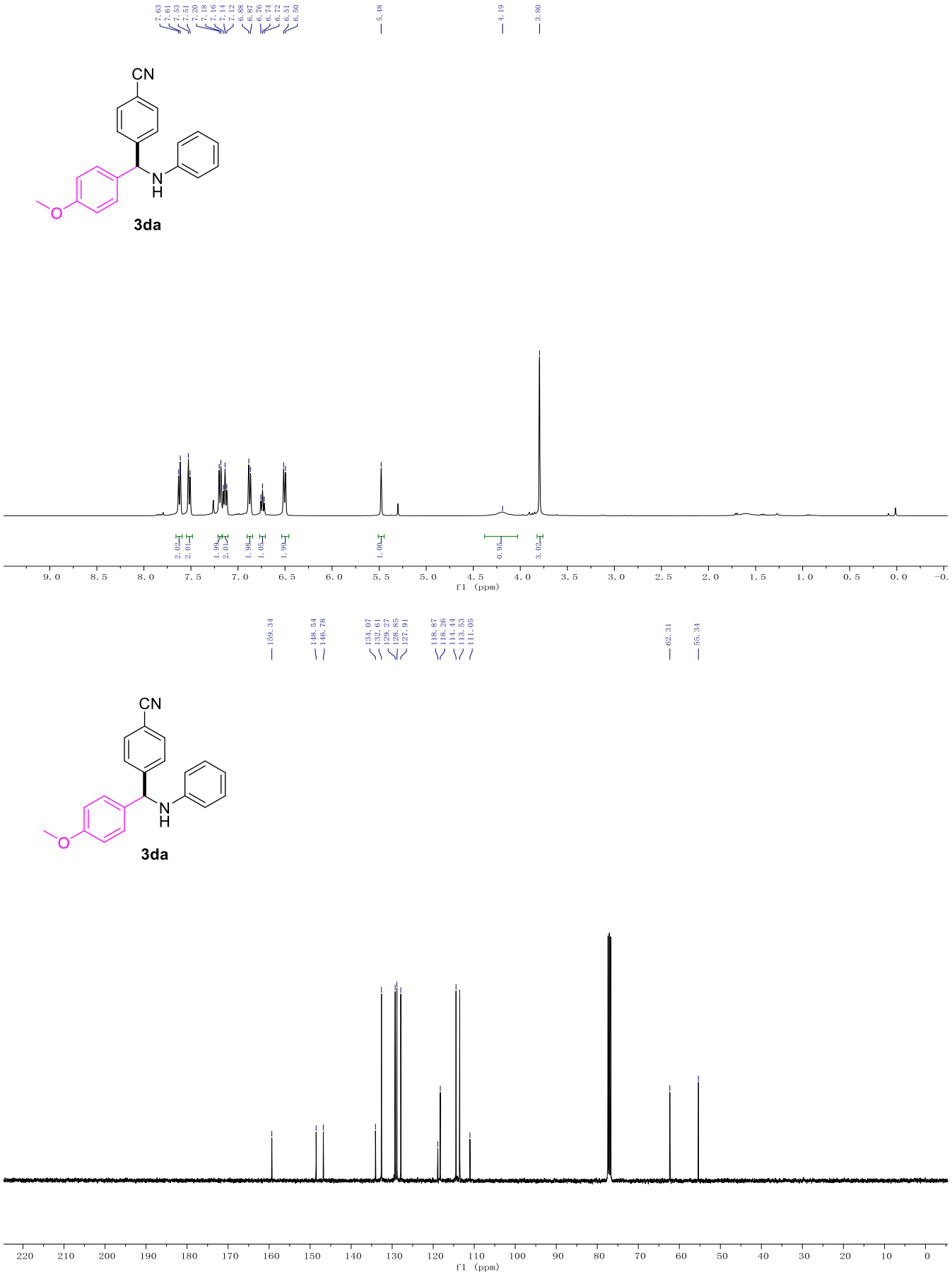


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3da**

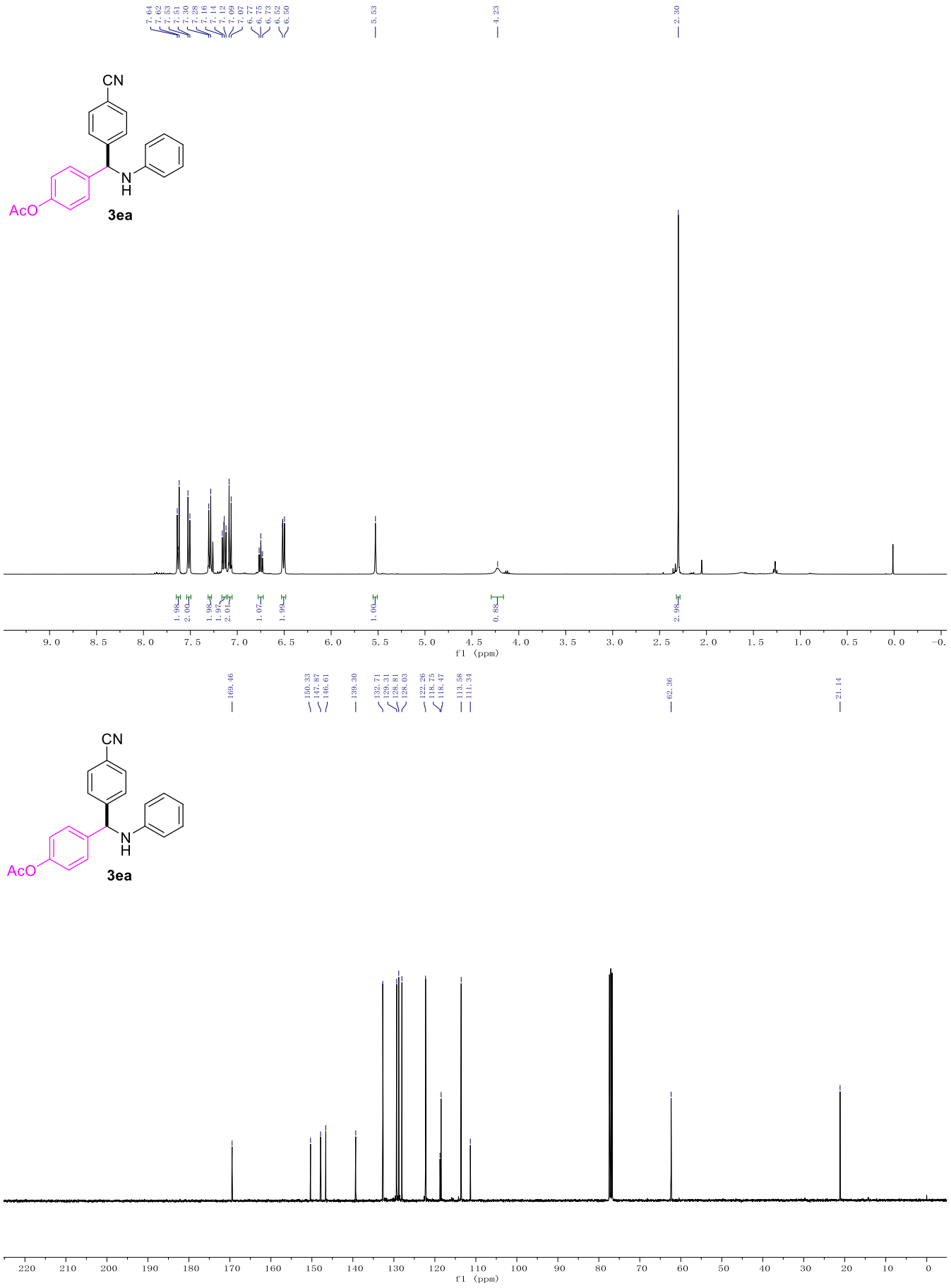
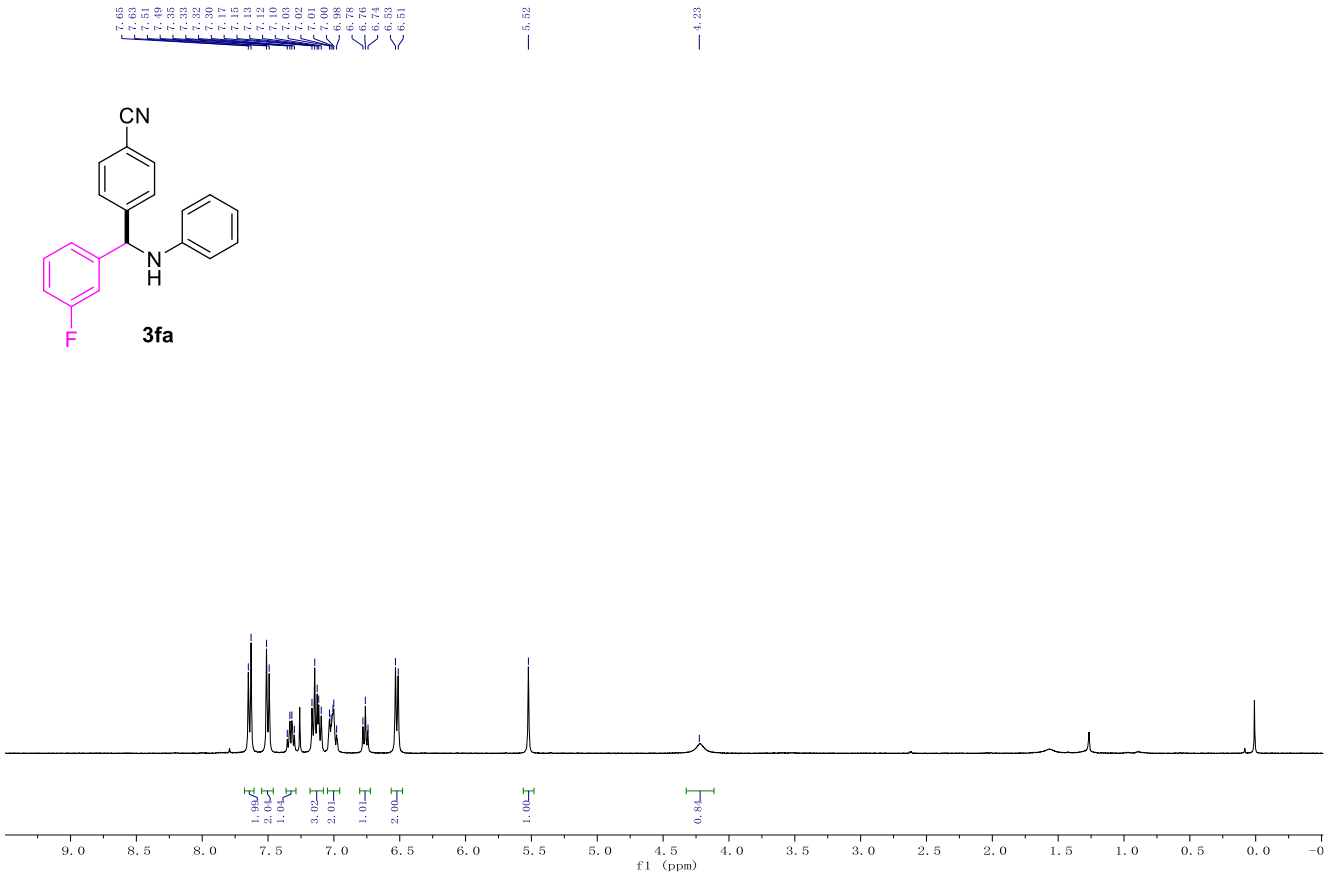
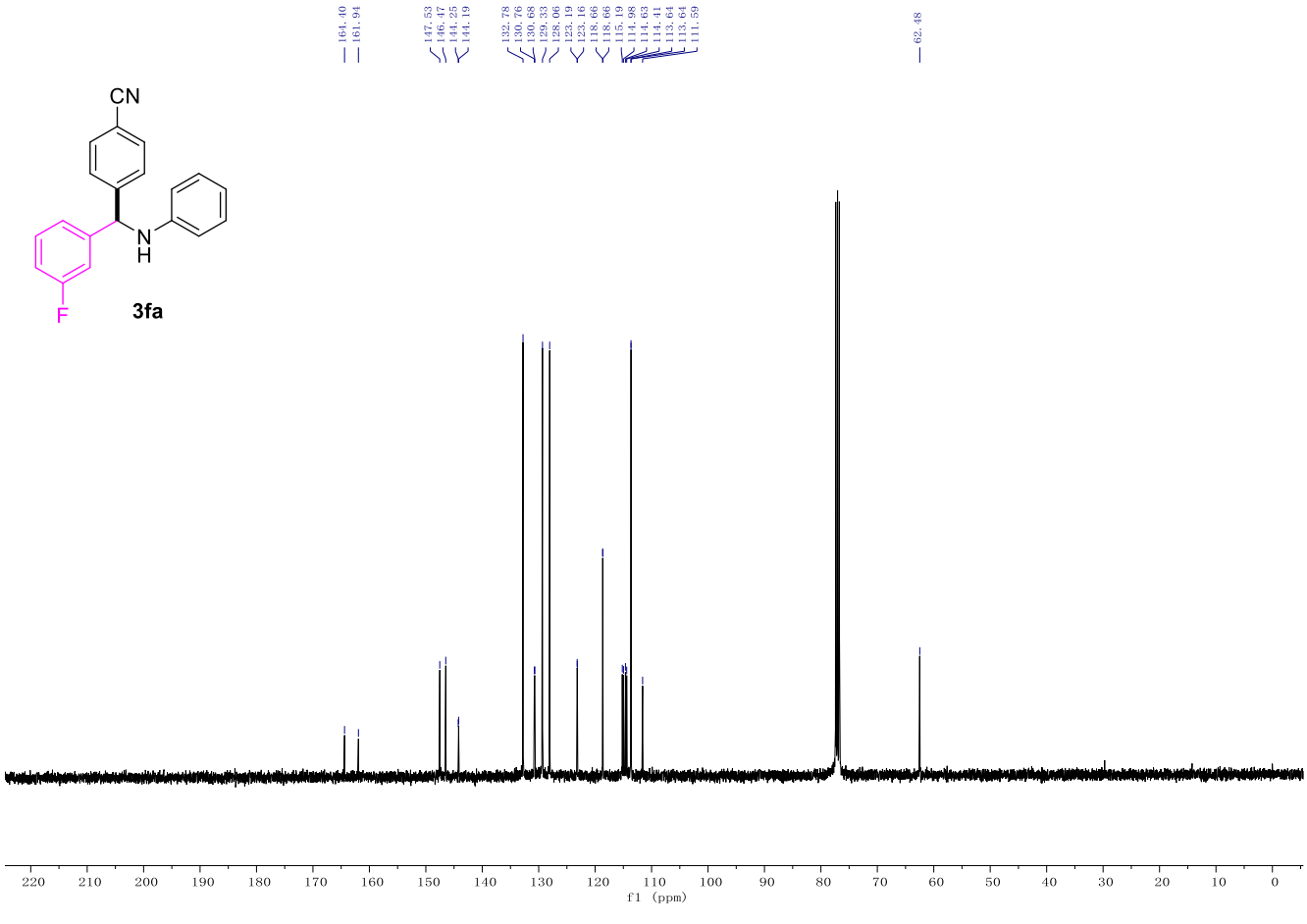


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3ea**


7.65
7.63
7.51
7.49
7.35
7.33
7.32
7.30
7.17
7.15
7.13
7.12
7.10
7.08
7.02
7.01
7.00
6.98
6.78
6.76
6.74
6.53
6.51
5.52
4.23
CN
N
H
F
3fa
1.99
2.04
1.04
3.02
2.01
1.01
2.00
1.00
0.84
f1 (ppm)


164.40
161.94
147.53
146.47
144.25
144.19
132.78
130.76
130.68
129.33
128.06
123.19
123.16
118.66
118.66
115.19
114.98
114.63
114.41
113.64
113.64
111.59
62.48
CN
N
H
F
3fa
f1 (ppm)

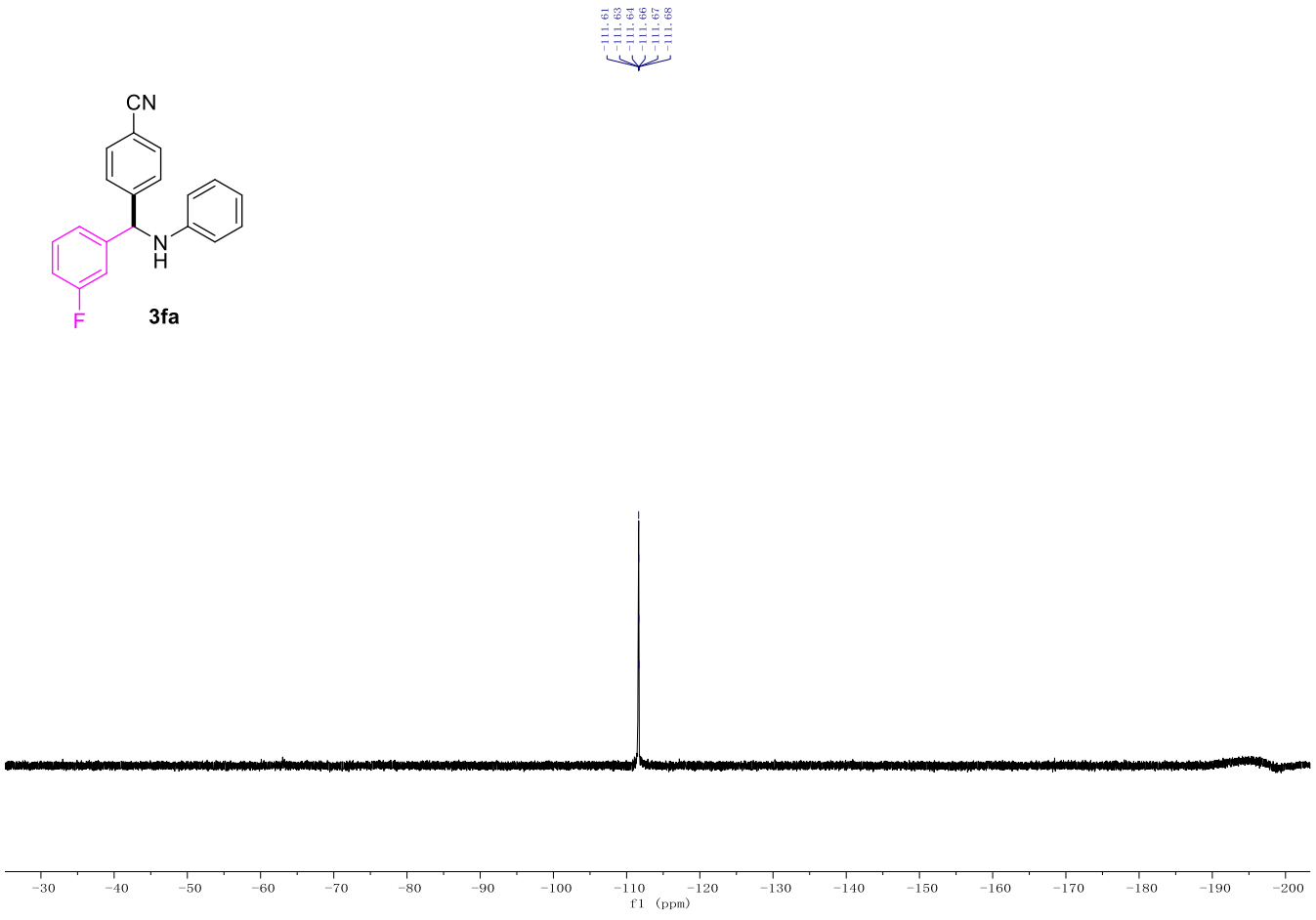


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) and **^{19}F NMR** (376 MHz, $CDCl_3$) of **3fa**

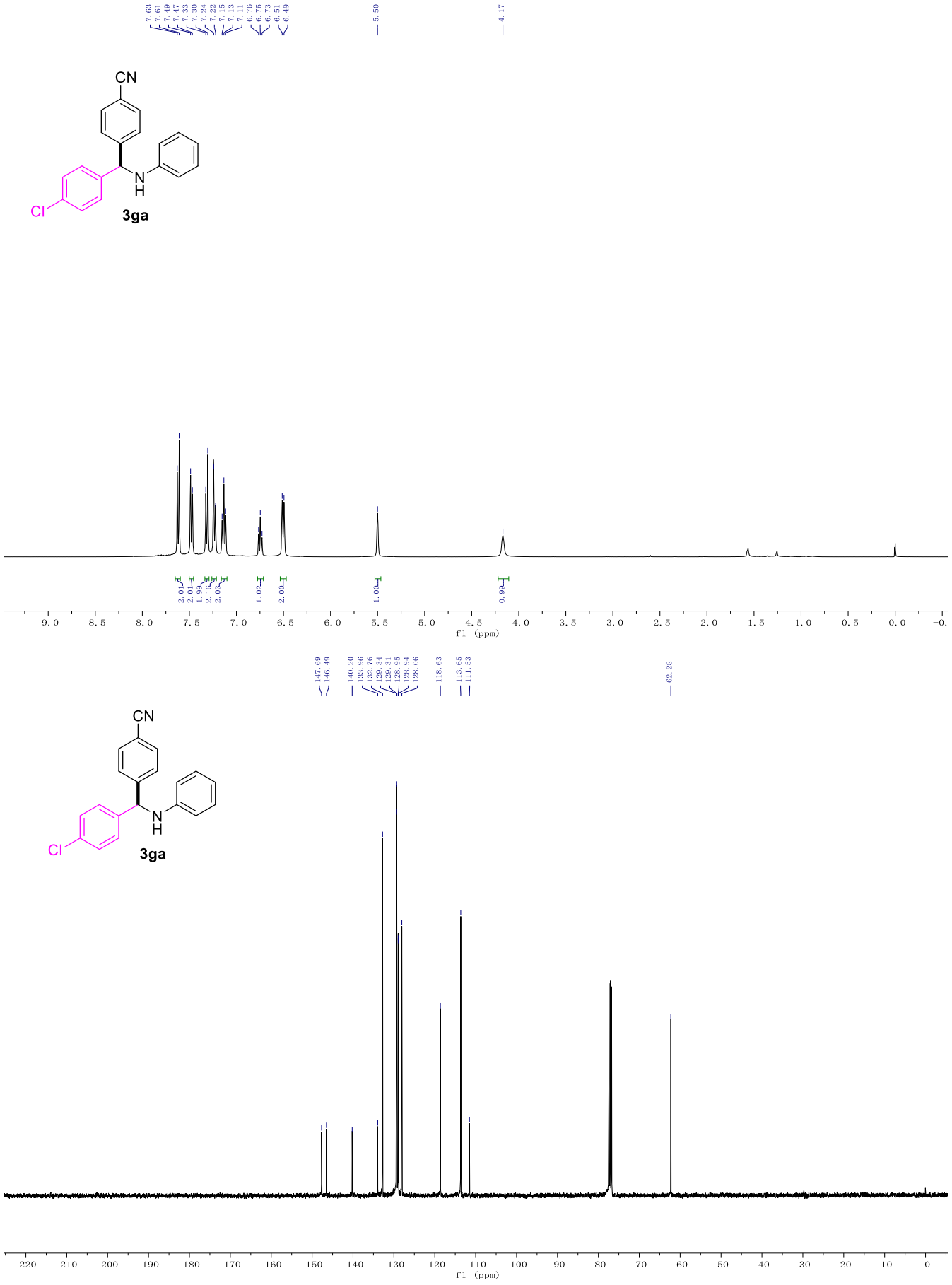


Figure S12. ^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C NMR** (101 MHz, $CDCl_3$) of **3ga**

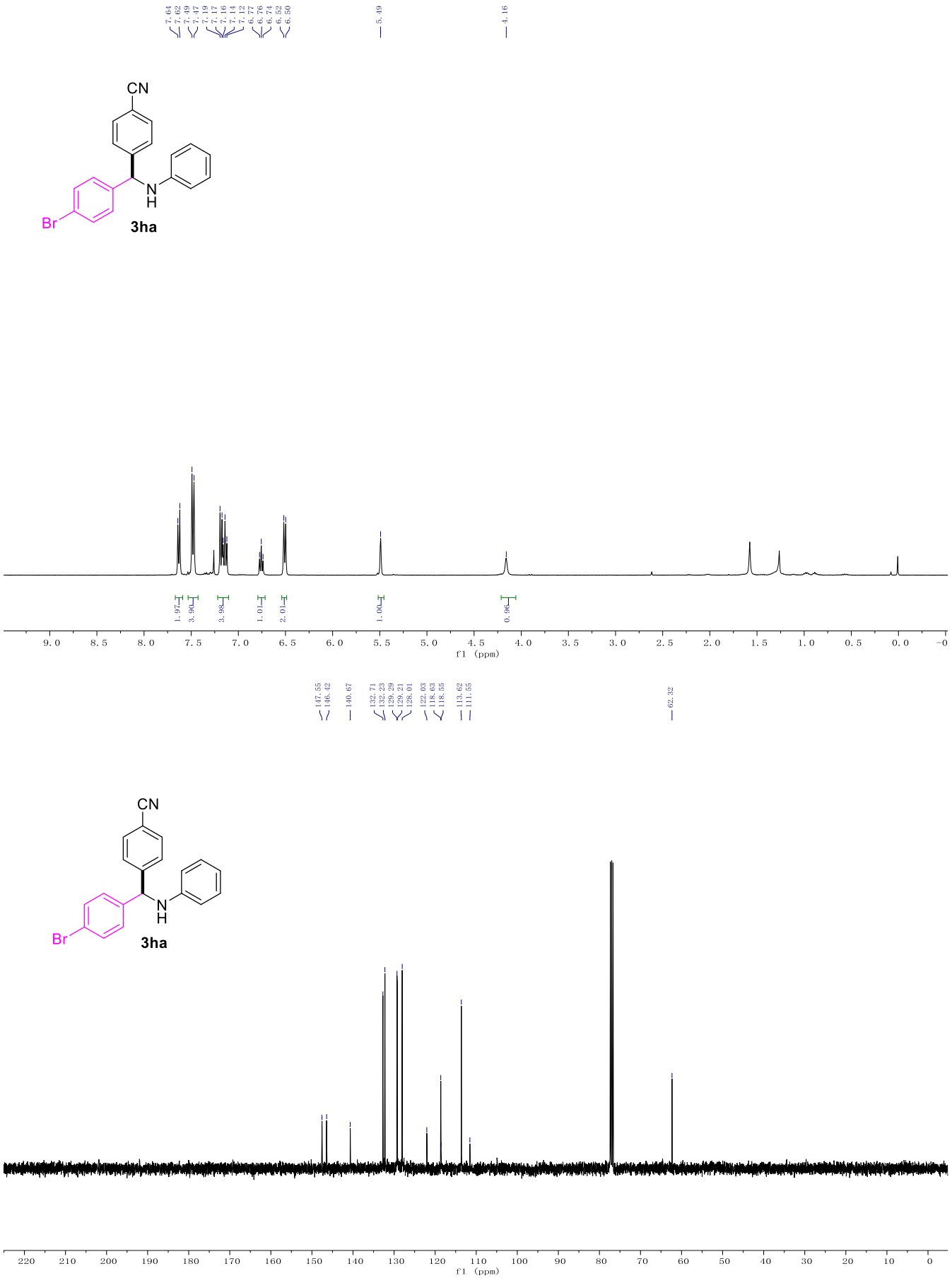
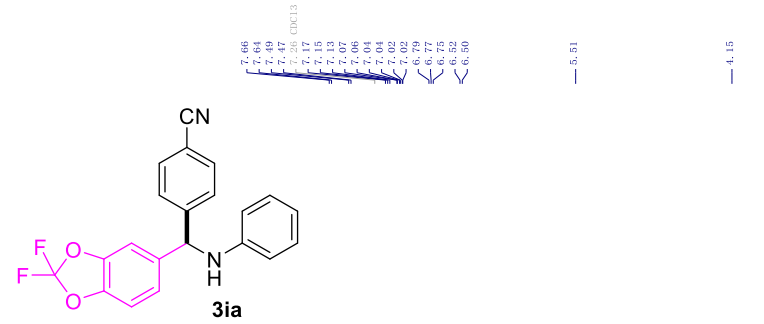
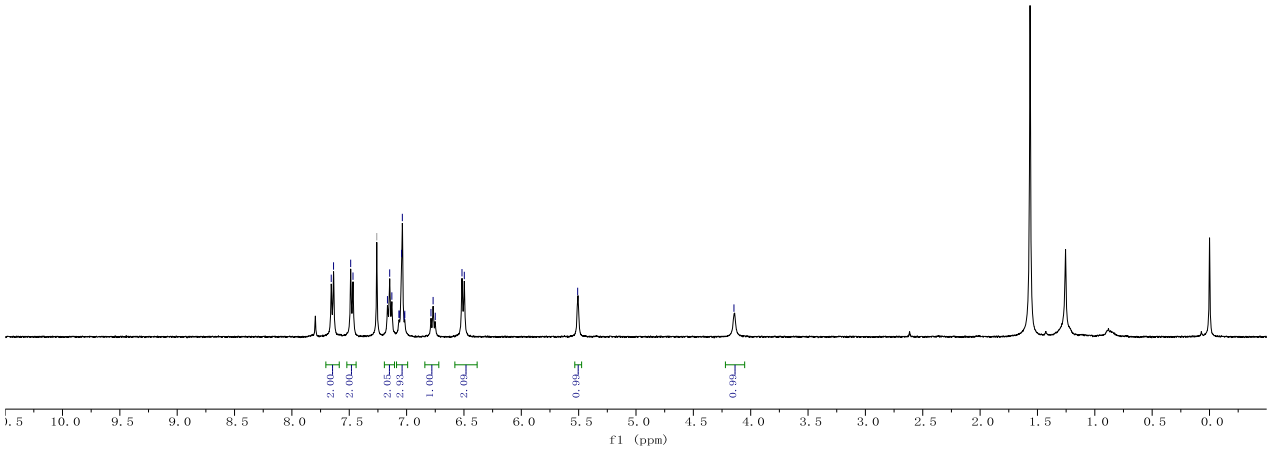


Figure S13. ^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C NMR** (101 MHz, $CDCl_3$) of **3ha**

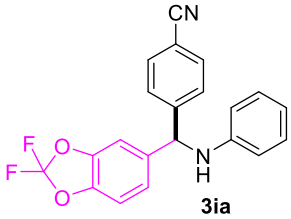

7.66
7.64
7.49
7.47
7.26 CDCl3
7.17
7.15
7.13
7.07
7.06
7.04
7.04
7.02
7.02
6.79
6.77
6.75
6.52
6.50
5.51
4.15

CN
F
O
F
O
N
H

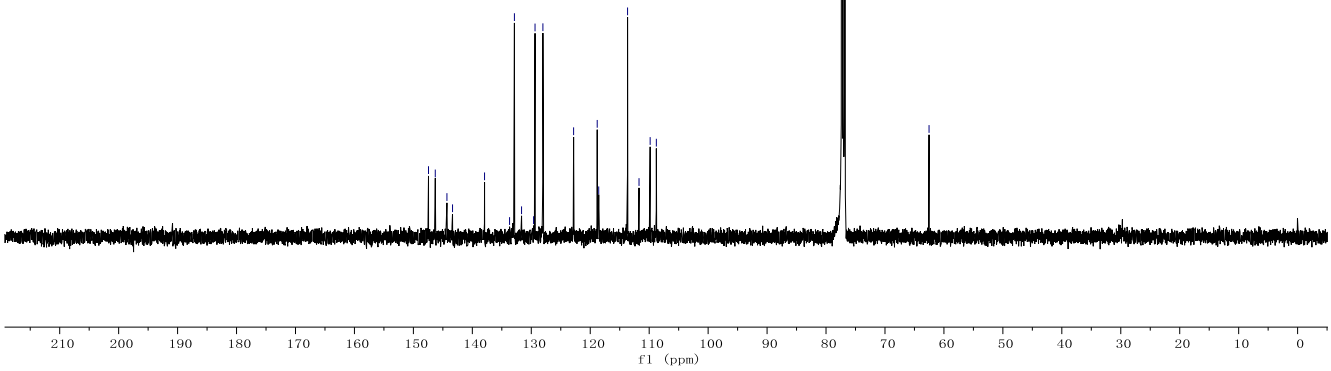
3ia


2.00
2.00
2.05
2.93
1.00
2.09
0.99
0.99
f1 (ppm)


147.44
146.29
144.31
143.36
137.93
133.69
132.86
131.65
129.61
129.36
128.03
122.82
118.82
118.56
113.67
111.73
109.83
108.78
62.52


CN
F
O
F
O
N
H

3ia


f1 (ppm)

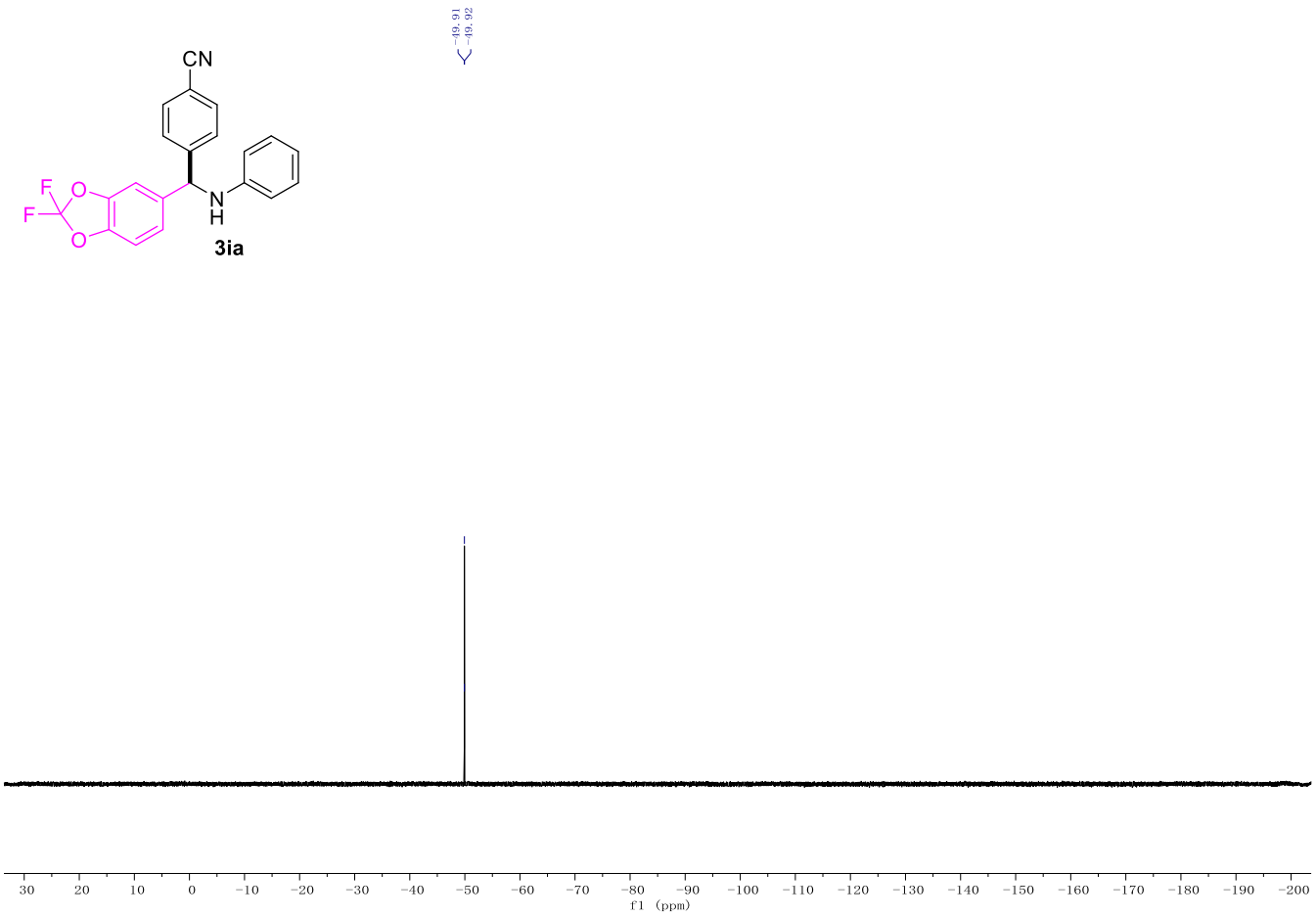
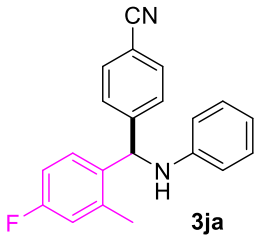
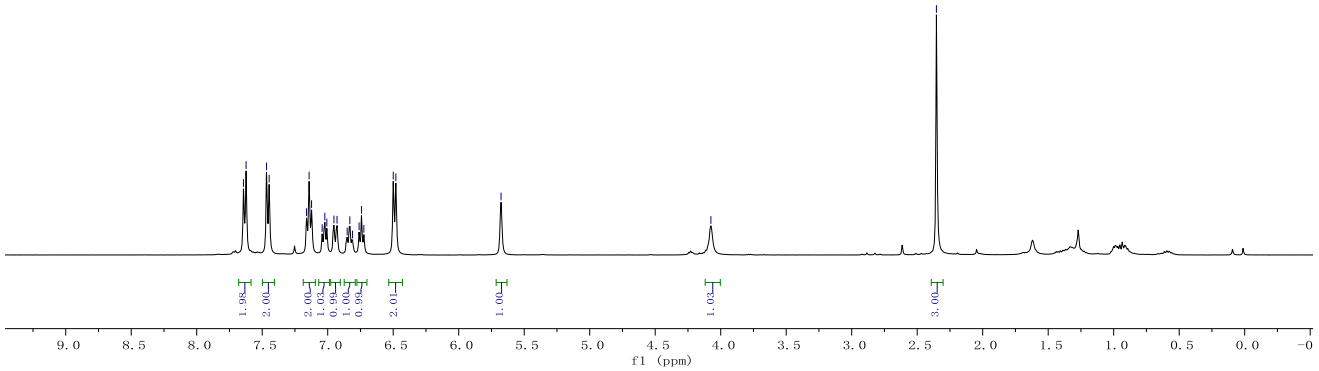


Figure S14. **^{1}H NMR** (400 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) and **^{19}F NMR** (376 MHz, $CDCl_3$) of **3ia**

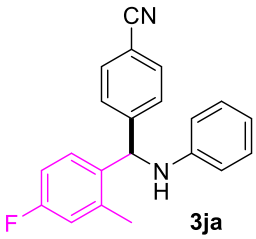

7.64
7.62
7.47
7.45
7.16
7.14
7.12
7.04
7.02
7.01
6.95
6.93
6.85
6.83
6.81
6.76
6.74
6.72
6.50
6.48
5.68
4.07
2.35


CN
N
H
F

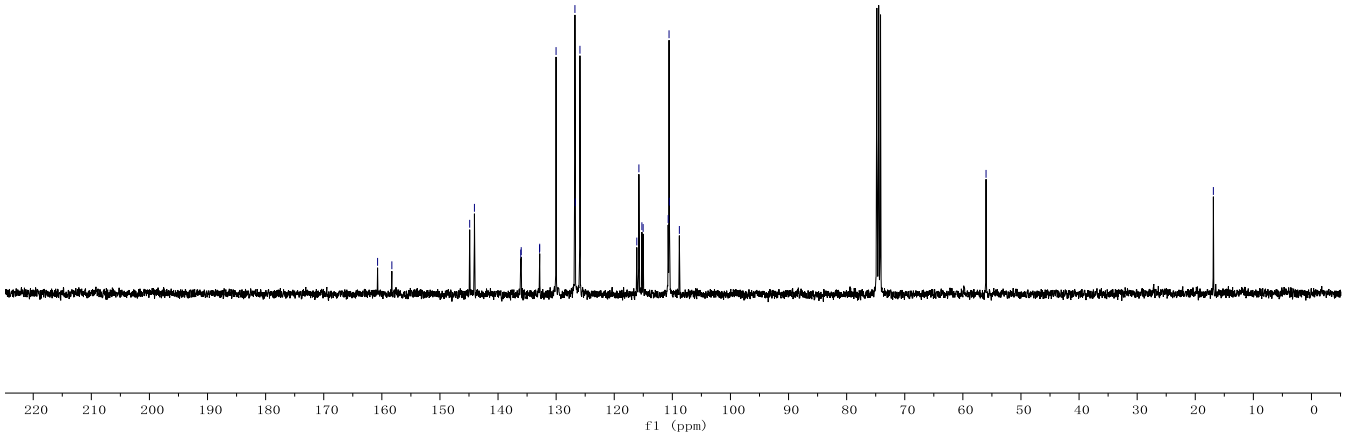
3ja


1.98
2.00
2.00
1.03
0.99
1.00
0.99
2.01
1.00
1.03
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.73
158.28
144.88
144.07
136.09
136.01
132.86
132.83
130.02
126.77
126.71
125.90
116.12
115.76
115.24
115.09
110.72
110.57
110.51
108.79
56.01
16.88


CN
N
H
F

3ja


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

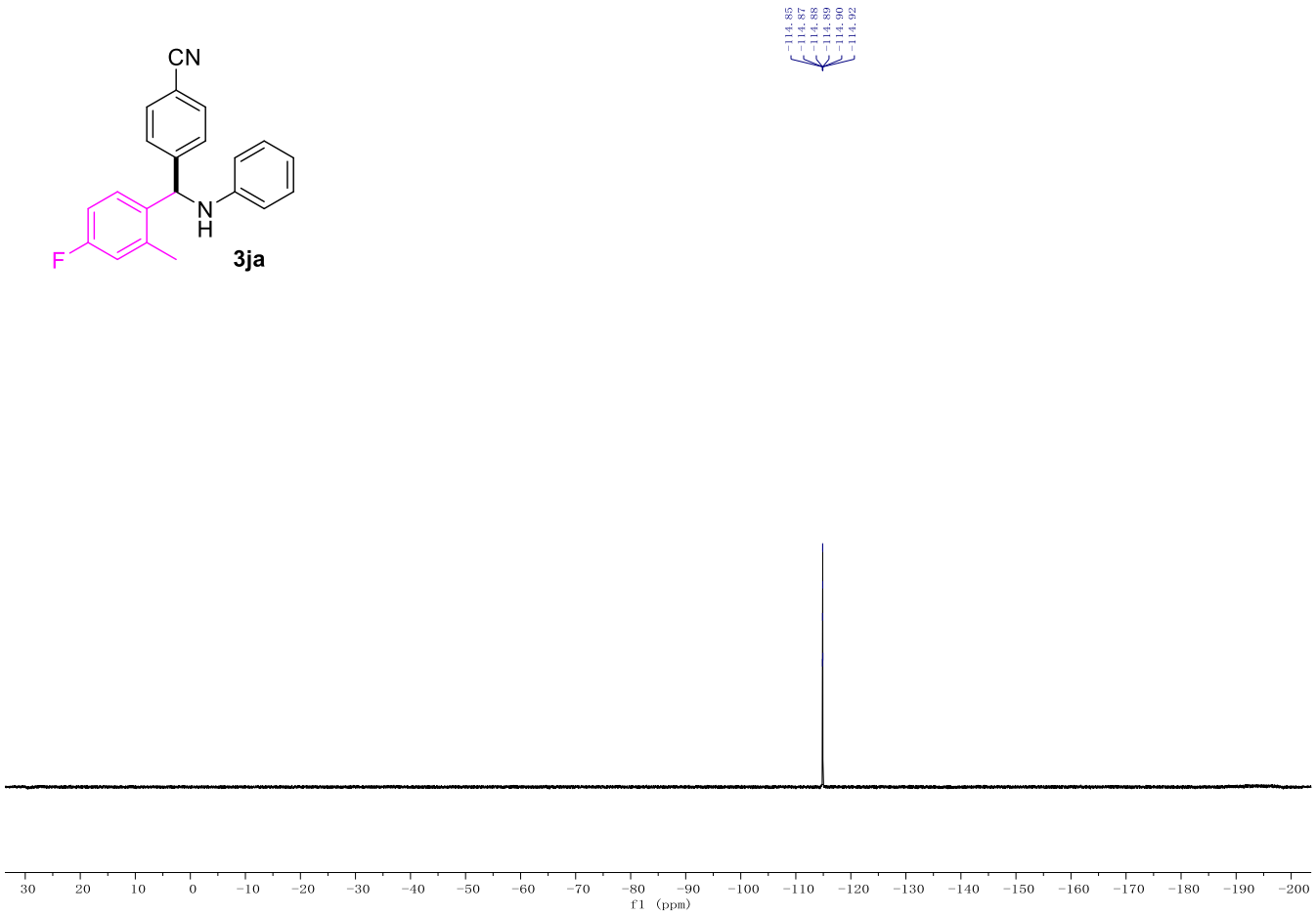


Figure S15. **^{1}H NMR** (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) and **^{19}F NMR** (376 MHz, $CDCl_3$) of **3ja**

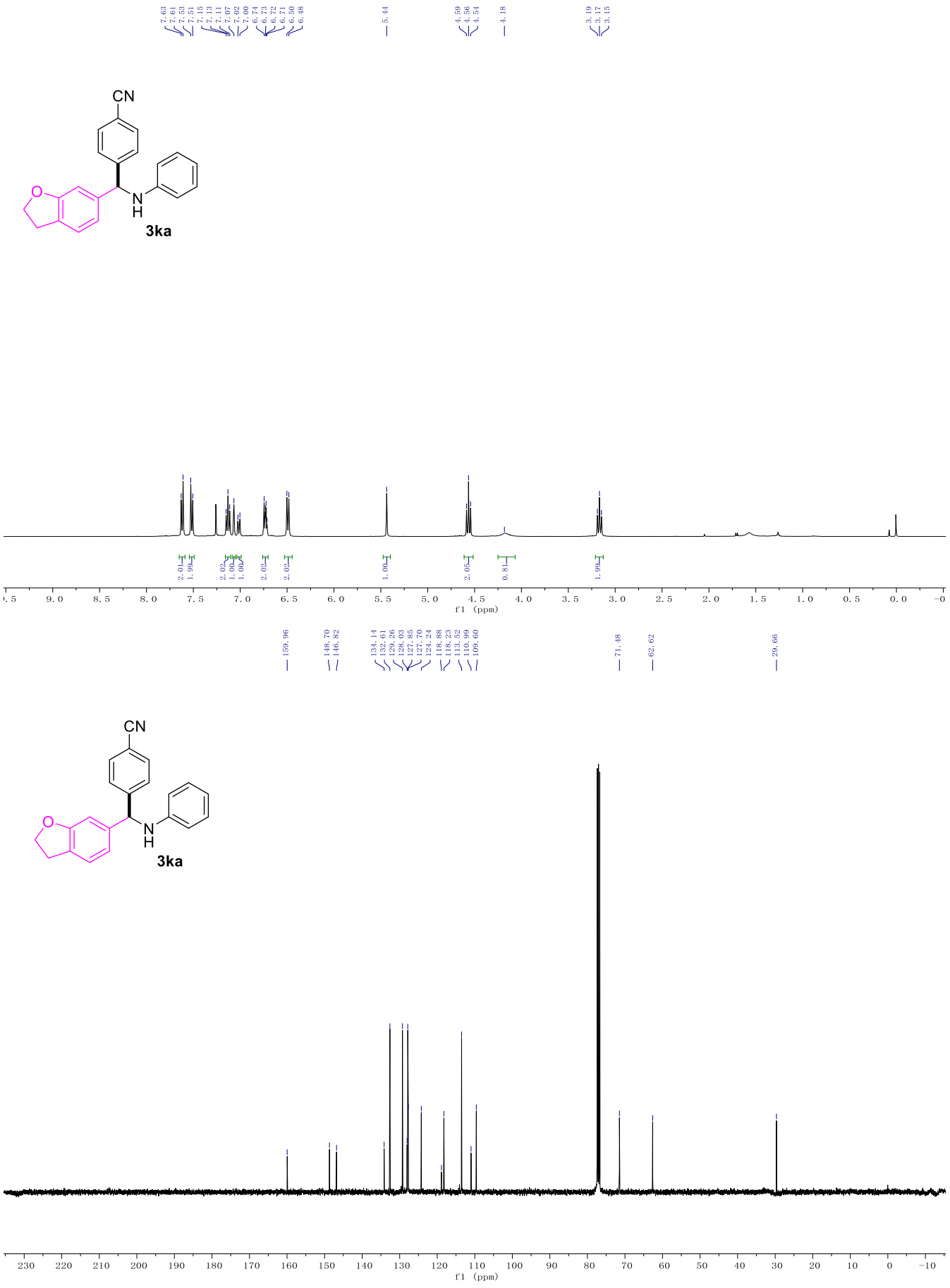


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3ka**

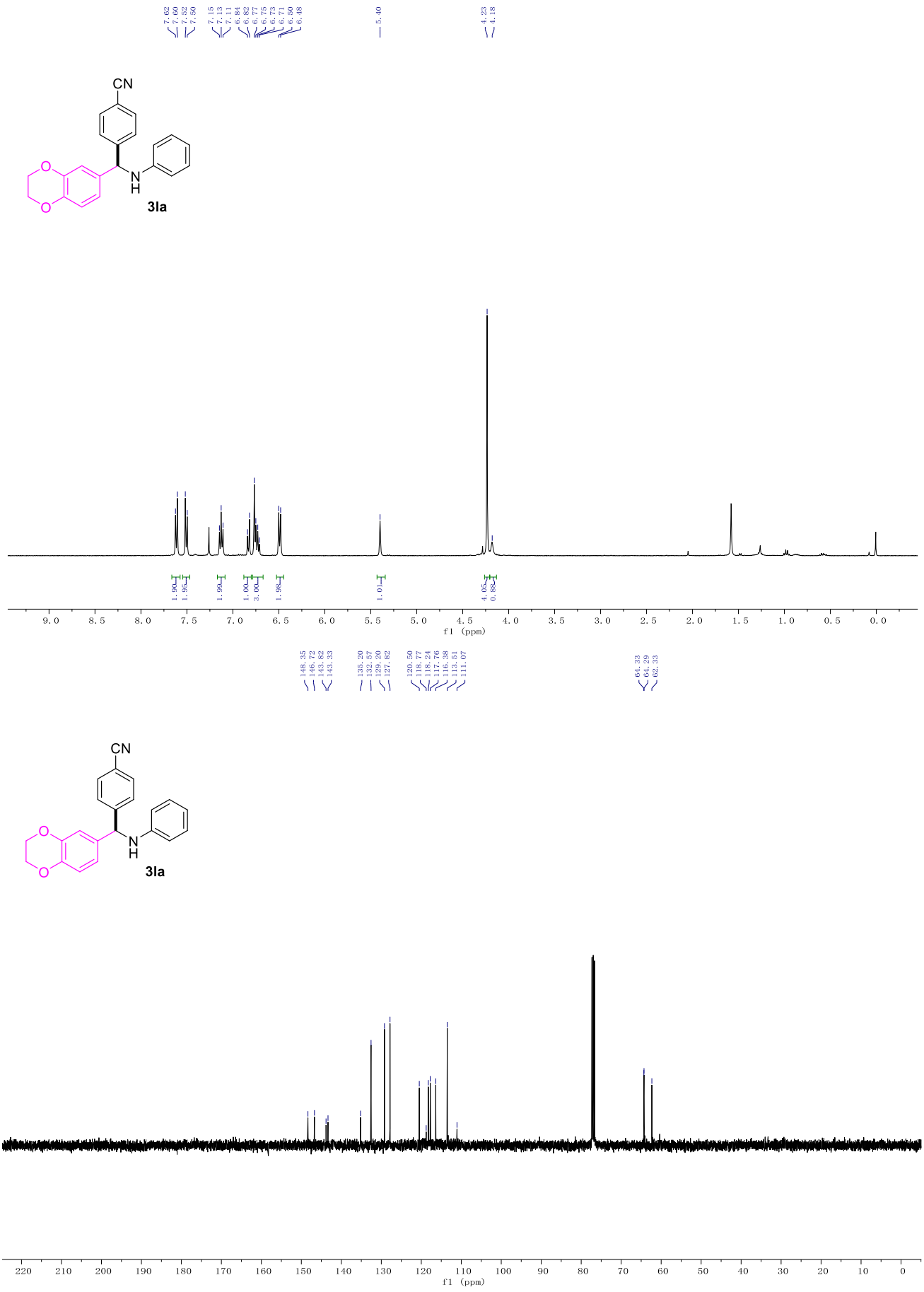


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$)of **3la**

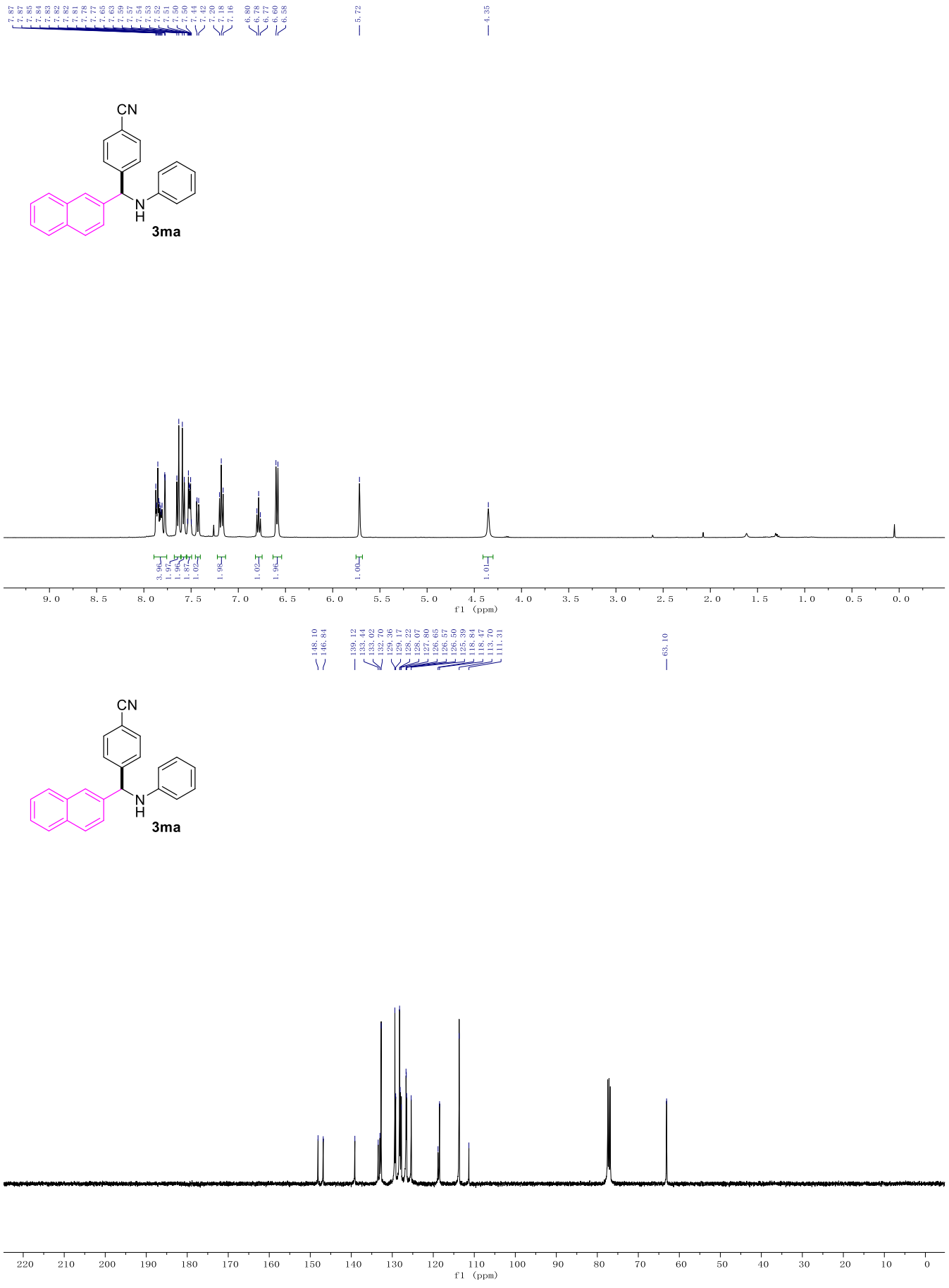


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3ma**

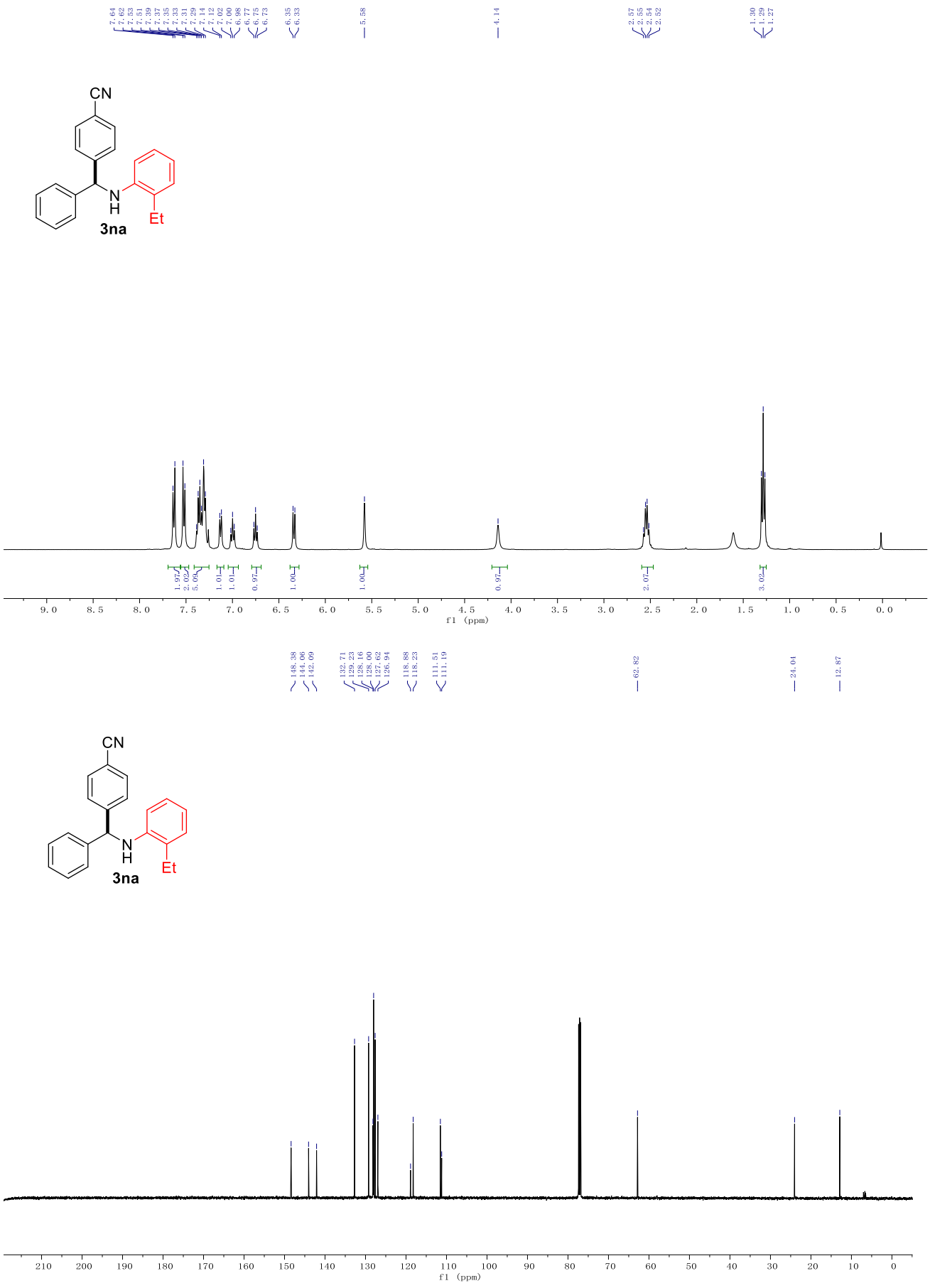


Figure S19. ^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C NMR** (101 MHz, $CDCl_3$) of **3na**

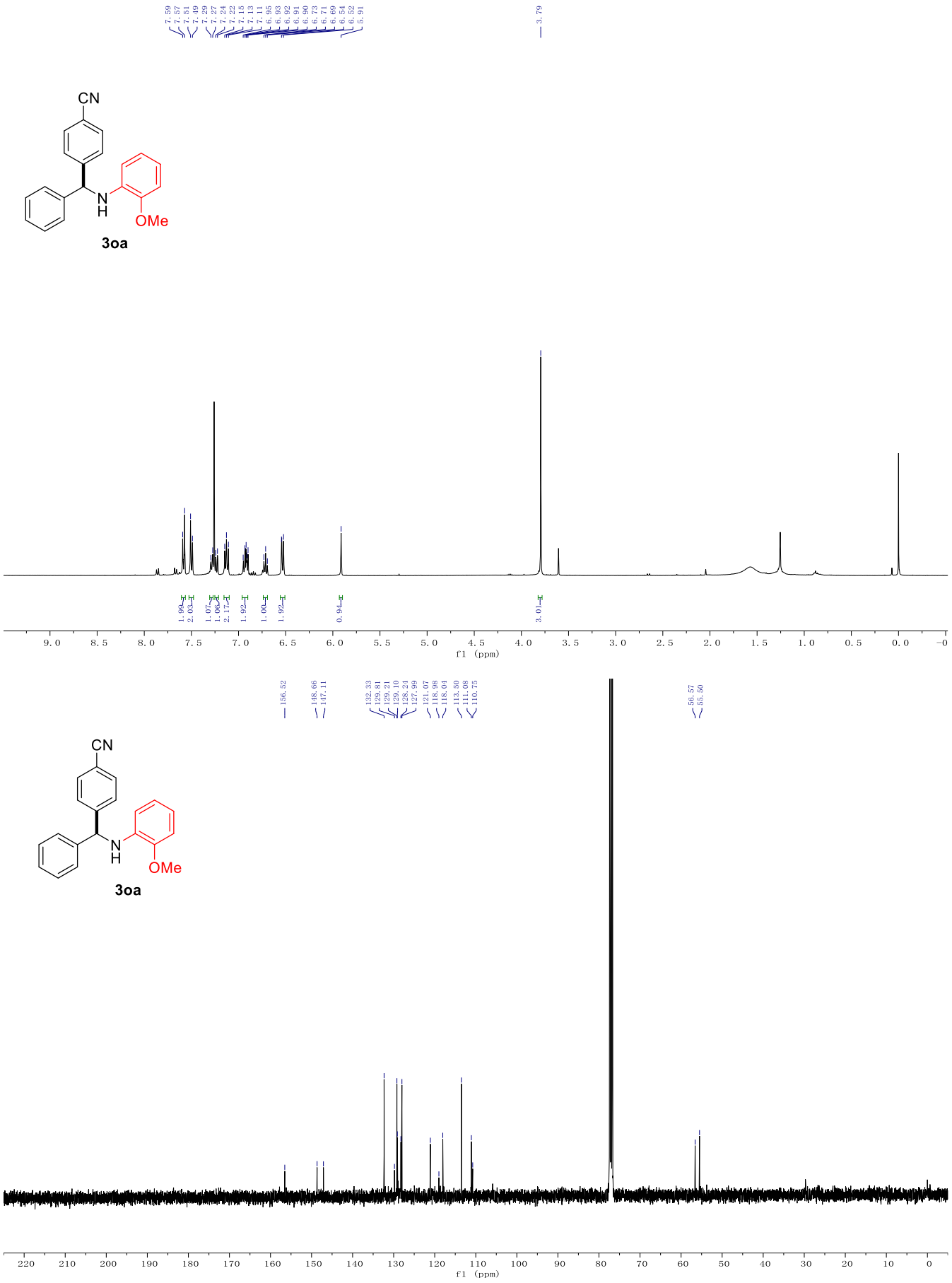


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3oa**

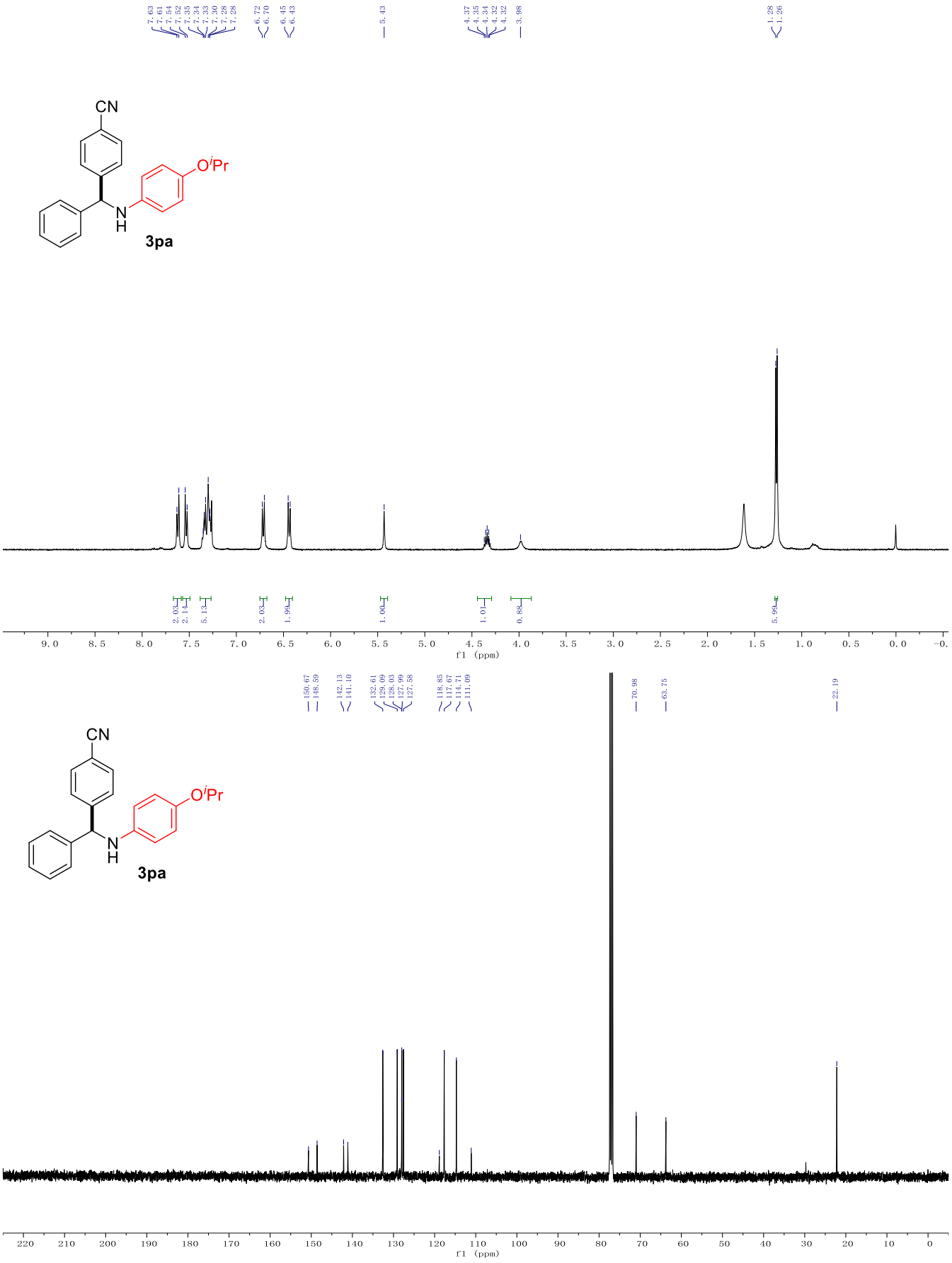


Figure S21. ^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C NMR** (101 MHz, $CDCl_3$) of **3pa**

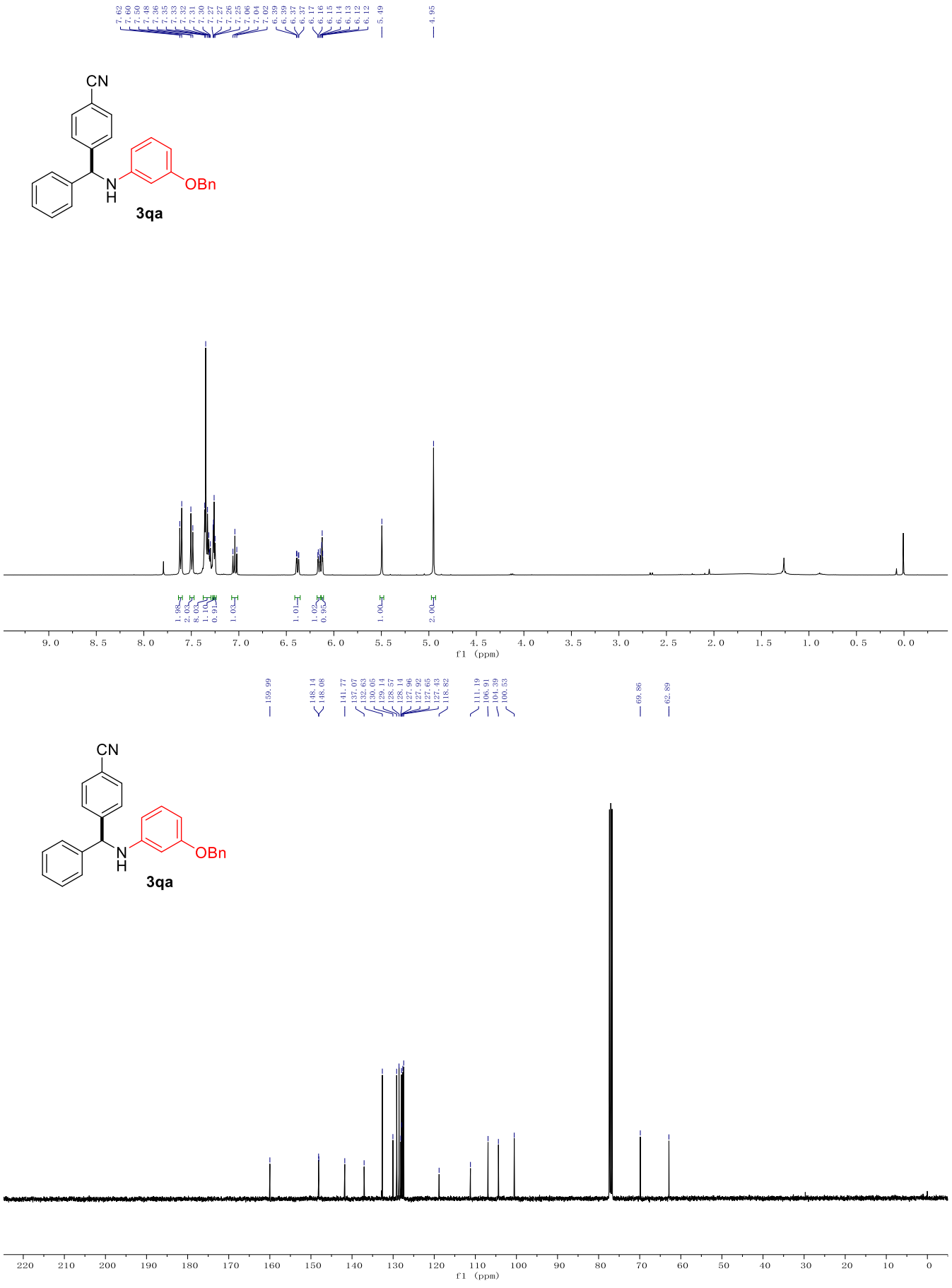


Figure S22. ^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C NMR** (101 MHz, $CDCl_3$) of **3qa**

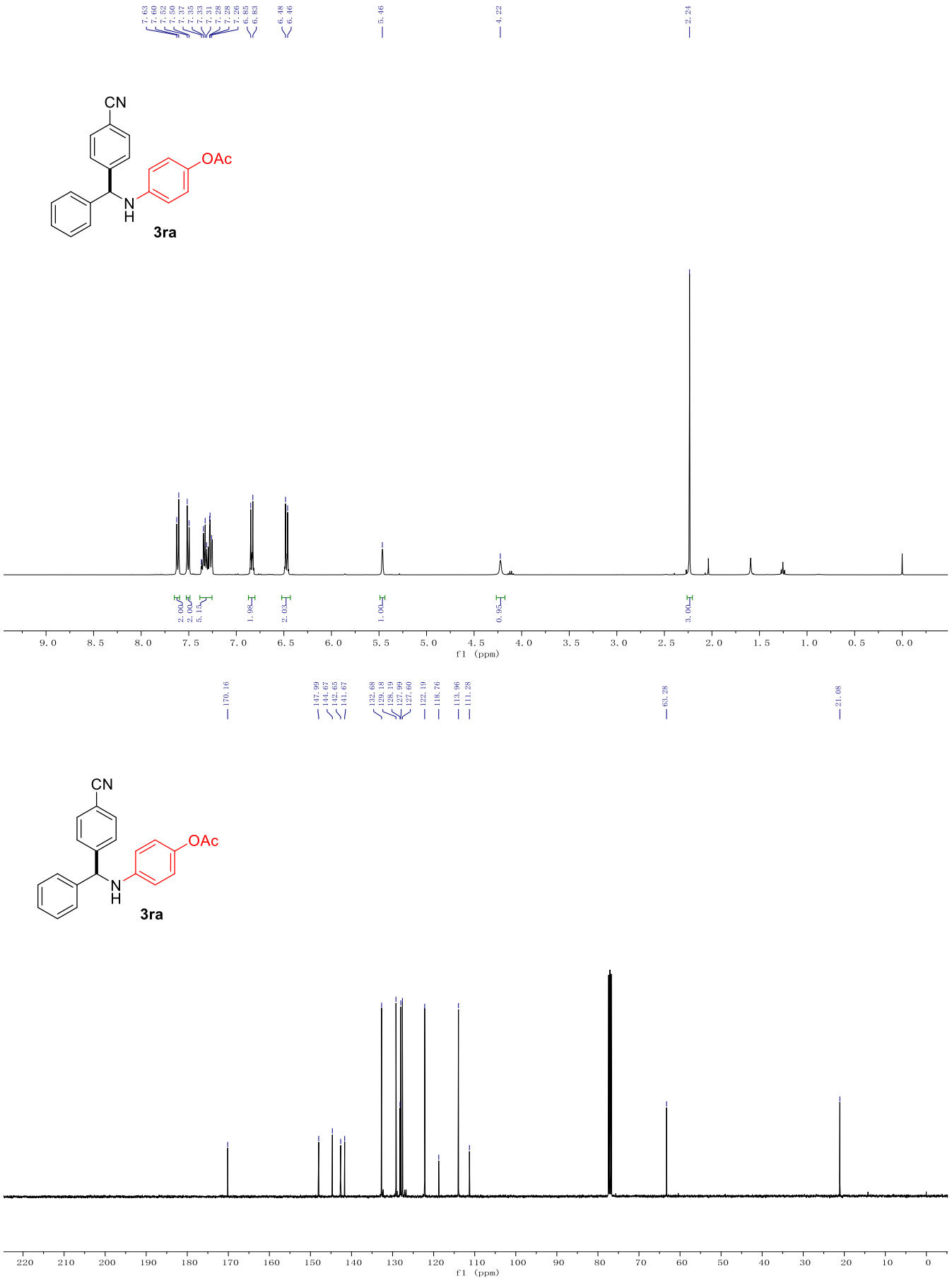
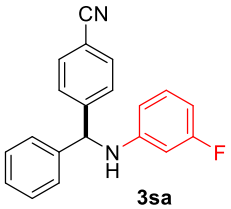
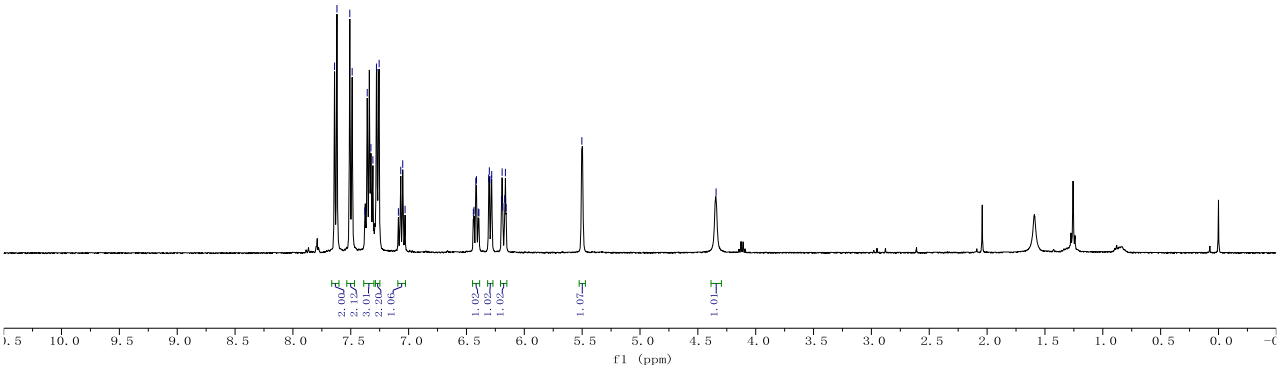


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3ra**

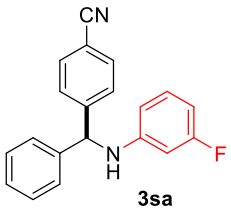

7.64
7.62
7.51
7.49
7.38
7.36
7.33
7.31
7.28
7.25
7.09
7.07
7.05
7.03
6.44
6.43
6.42
6.41
6.40
6.39
6.31
6.30
6.29
6.28
6.20
6.19
6.18
6.17
6.16
6.16
5.50
4.34


CN
N
H
F

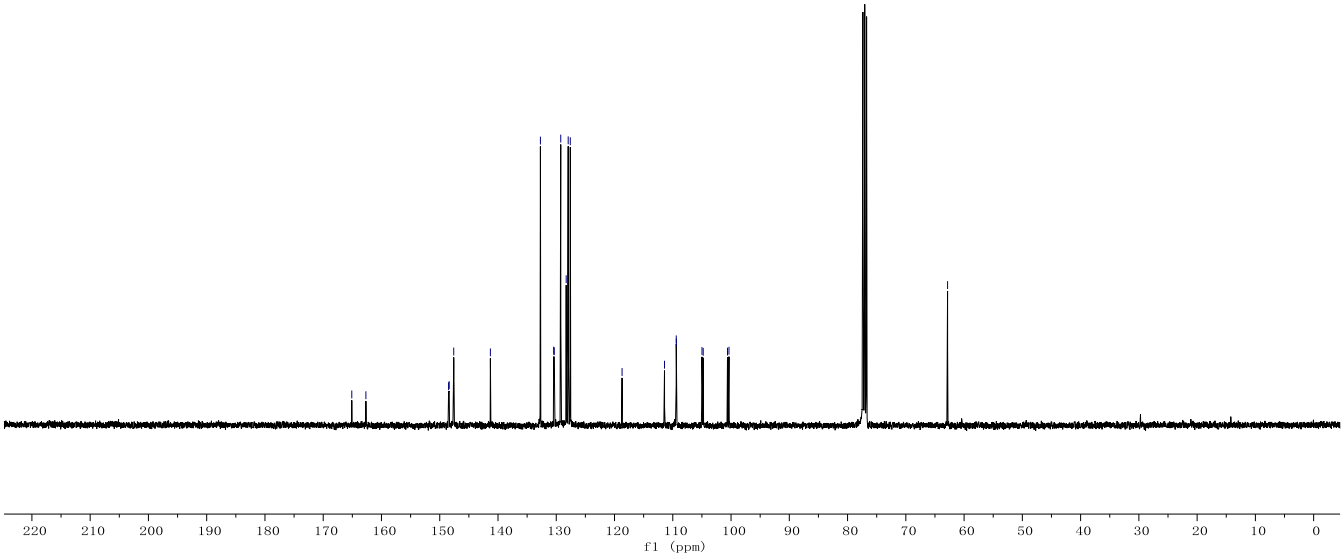
3sa


2.00
2.12
3.01
2.20
1.06
1.02
1.02
1.02
1.07
1.01
f1 (ppm)


165.10
162.67
148.48
148.38
147.60
141.30
132.72
130.44
130.34
129.23
128.30
127.95
127.59
118.70
111.42
109.41
109.38
104.99
104.78
100.61
100.35
62.83


CN
N
H
F

3sa


f1 (ppm)

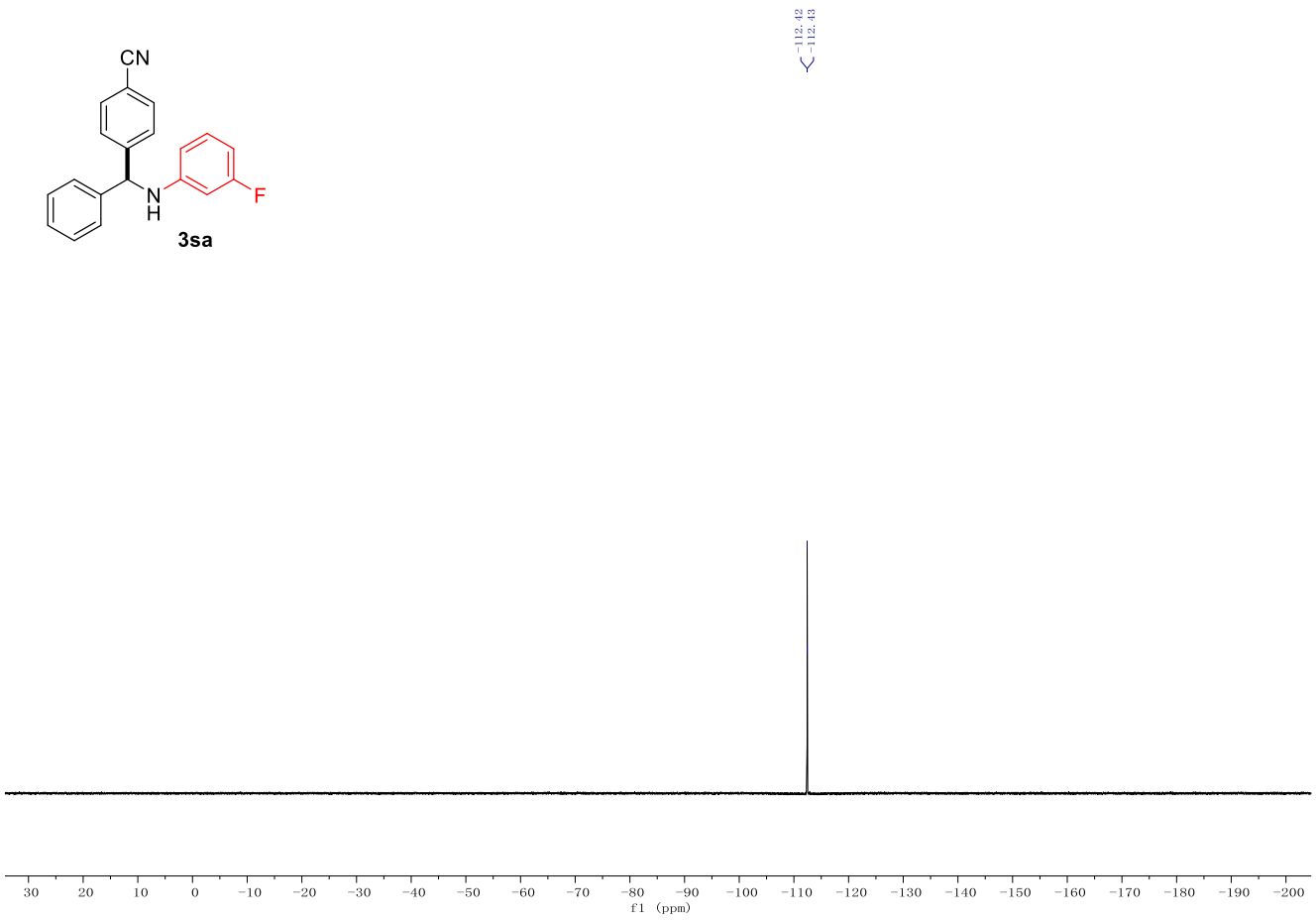
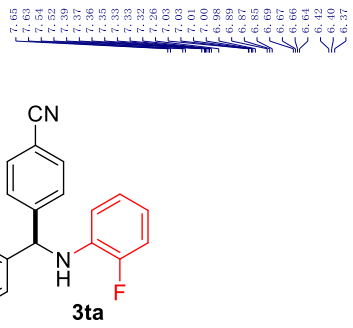
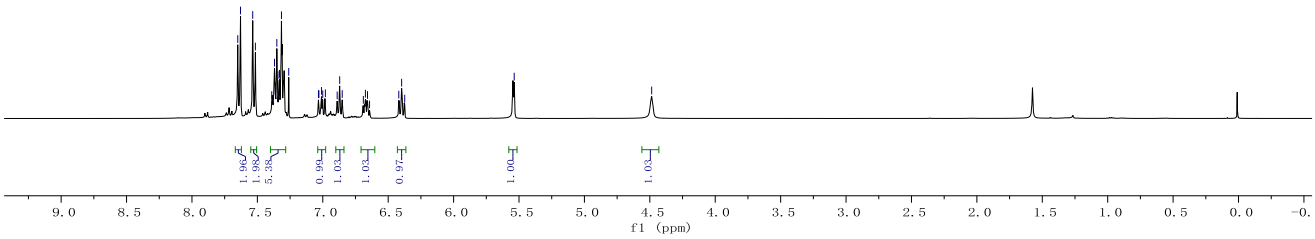
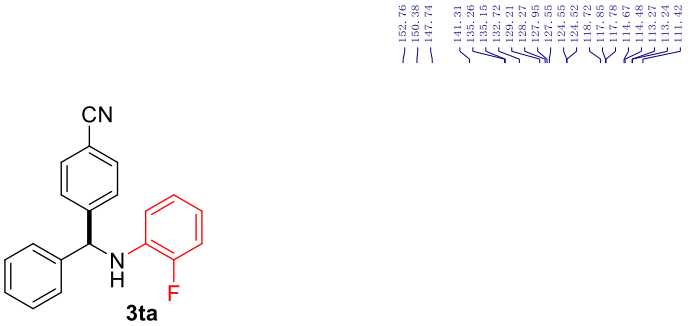
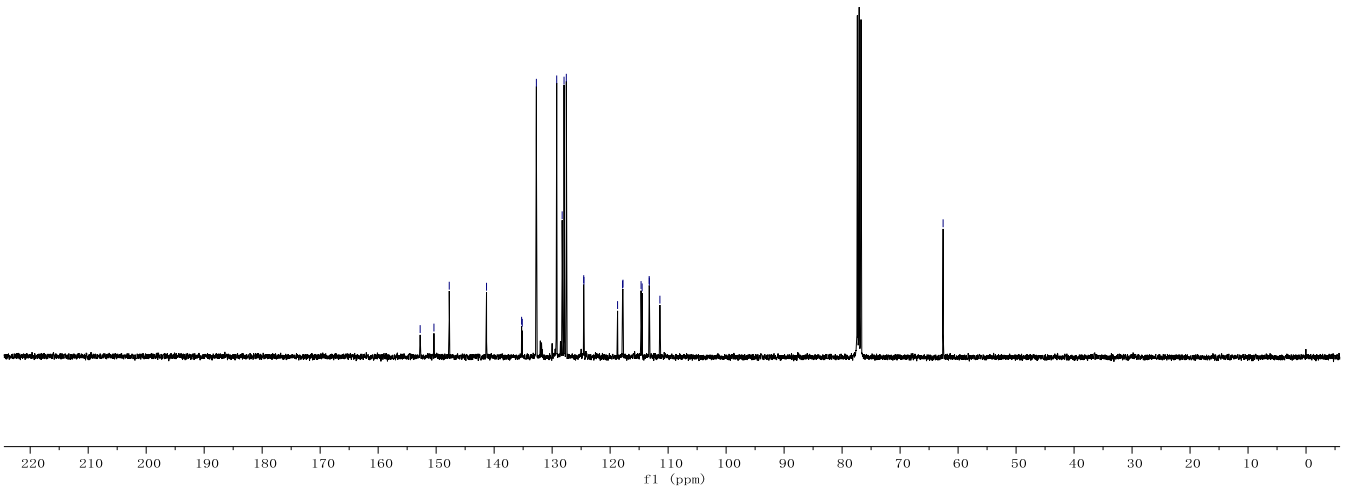


Figure S24. **^{1}H NMR** (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) and **^{19}F NMR** (376 MHz, $CDCl_3$) of **3sa**


7.65
7.63
7.54
7.52
7.39
7.37
7.36
7.35
7.33
7.32
7.26
7.03
7.01
7.00
6.98
6.89
6.87
6.85
6.69
6.67
6.66
6.64
6.42
6.40
6.37
5.54
4.49
CN
N
H
F
3ta


1.96
1.98
5.38
0.99
1.03
1.03
0.97
1.00
1.03
f1 (ppm)


152.76
150.38
147.74
141.31
135.26
135.15
132.72
129.21
128.27
127.95
127.55
124.55
124.52
118.72
117.85
117.78
114.67
114.48
113.27
113.24
111.42
62.58
CN
N
H
F
3ta


f1 (ppm)

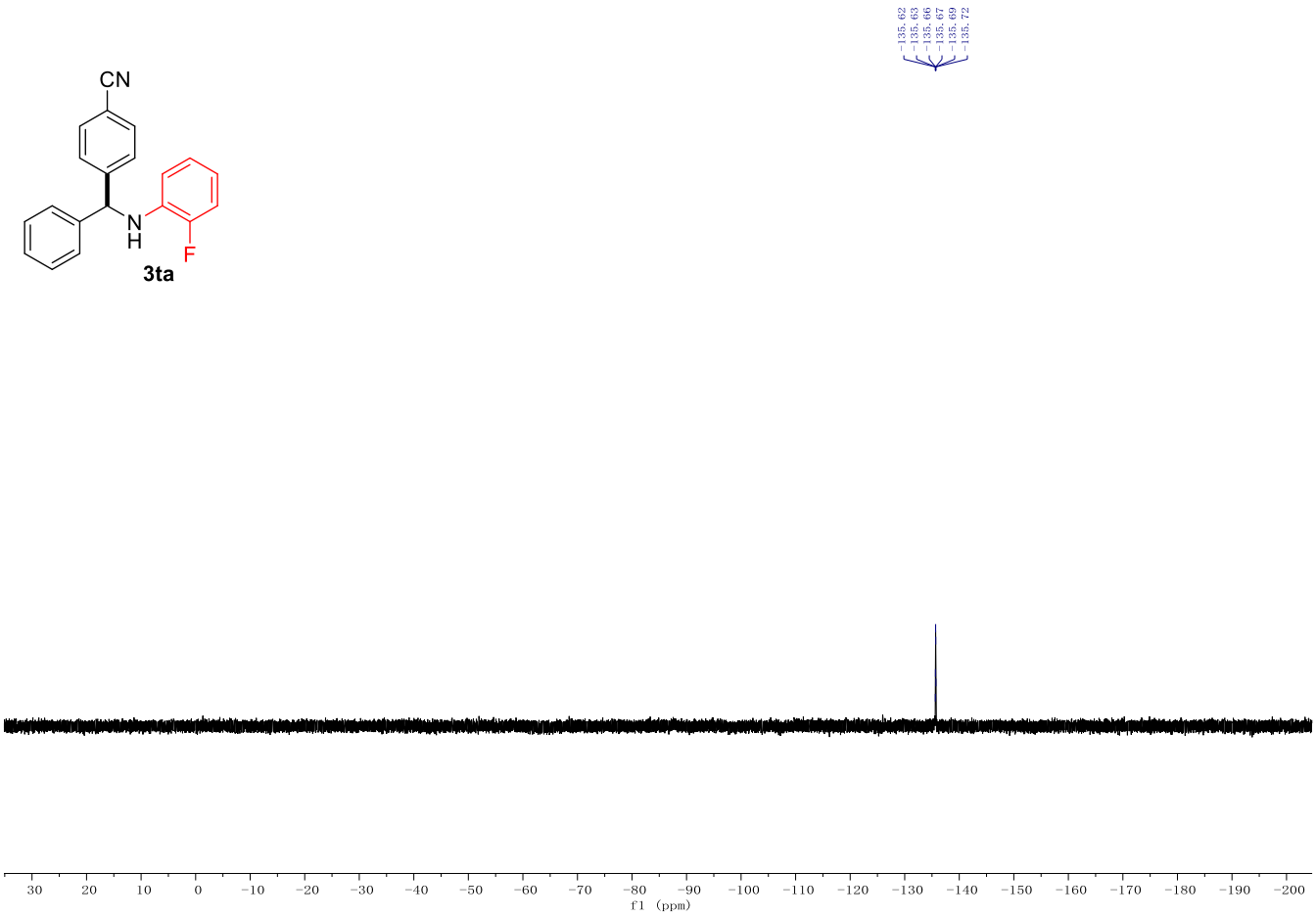


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) and **^{19}F NMR** (376 MHz, $CDCl_3$) of **3ta**

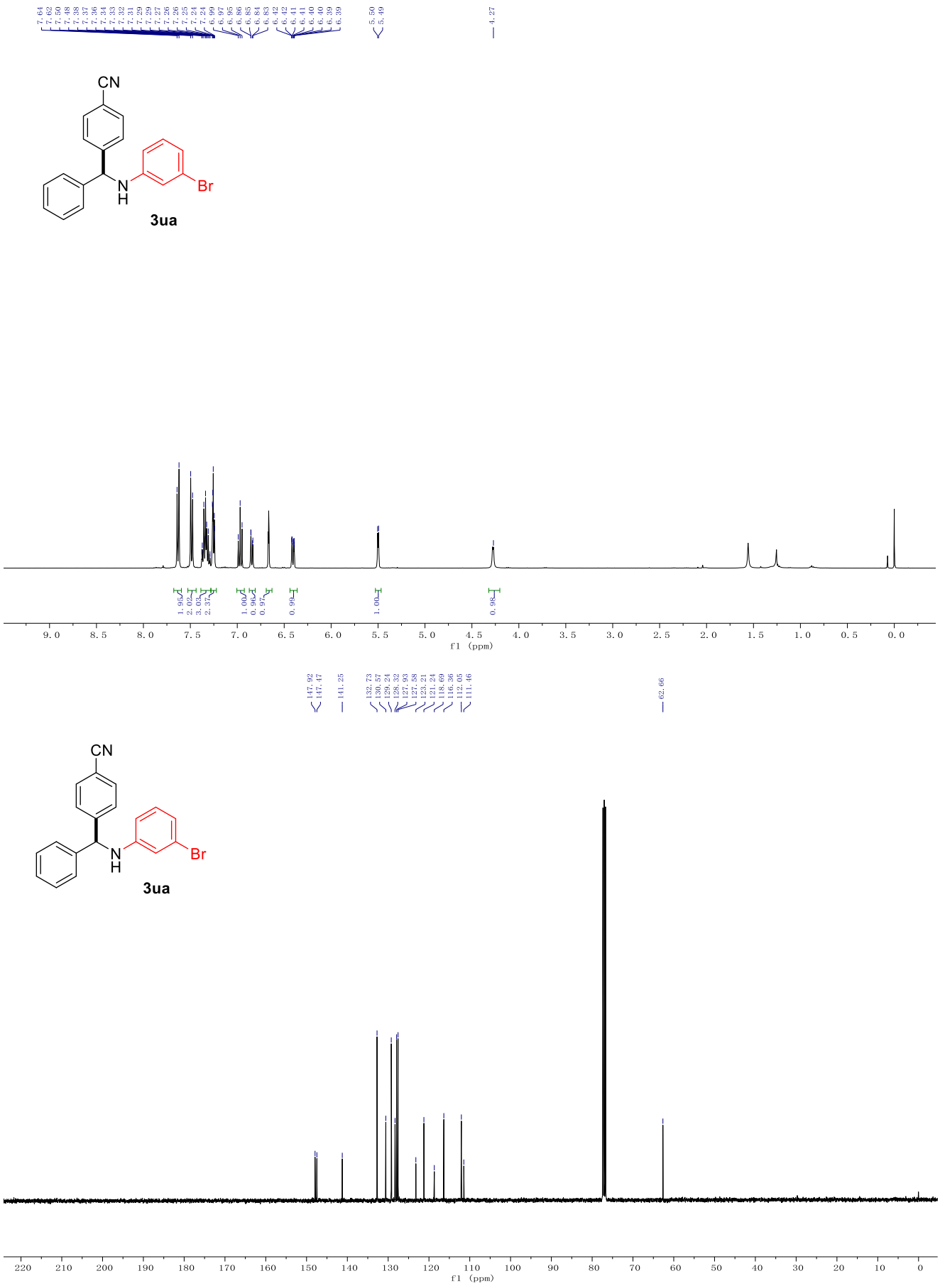


Figure S26. ^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C NMR** (101 MHz, $CDCl_3$) of **3ua**

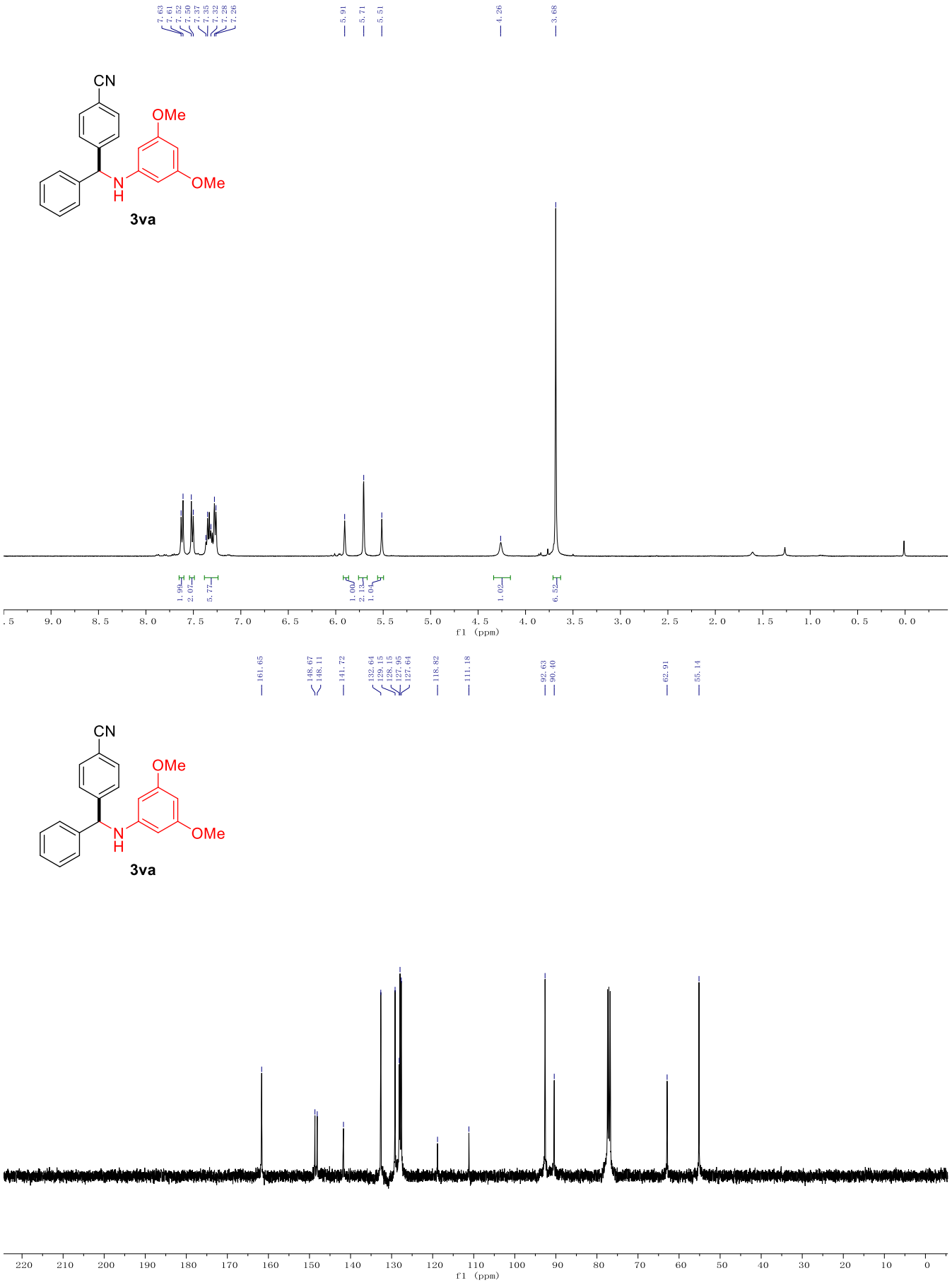
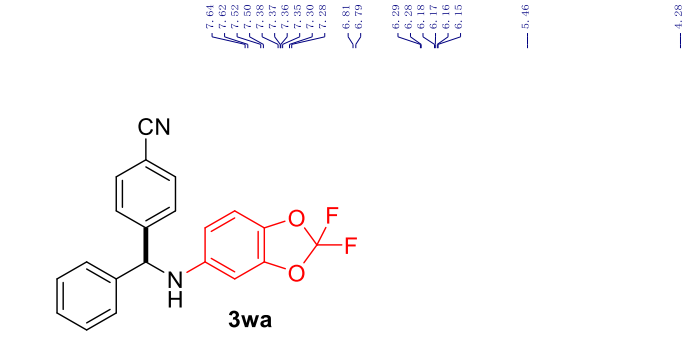
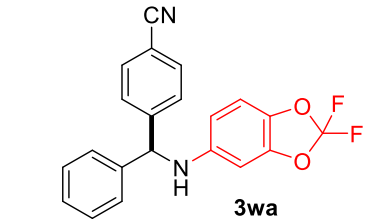


Figure S27. ^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C NMR** (101 MHz, $CDCl_3$) of **3va**


CN
O
F
F
O
N
H
3wa

7.64
7.62
7.52
7.50
7.38
7.37
7.36
7.35
7.30
7.28
6.81
6.79
6.29
6.28
6.18
6.17
6.16
6.15
5.46
4.28
2.04
2.09
5.41
1.02
0.98
1.00
1.00
0.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


CN
O
F
F
O
N
H
3wa

147.53
144.52
143.70
141.18
136.37
134.19
132.71
131.66
129.22
129.14
128.29
127.91
127.46
118.62
111.44
109.73
107.42
96.15
63.41
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

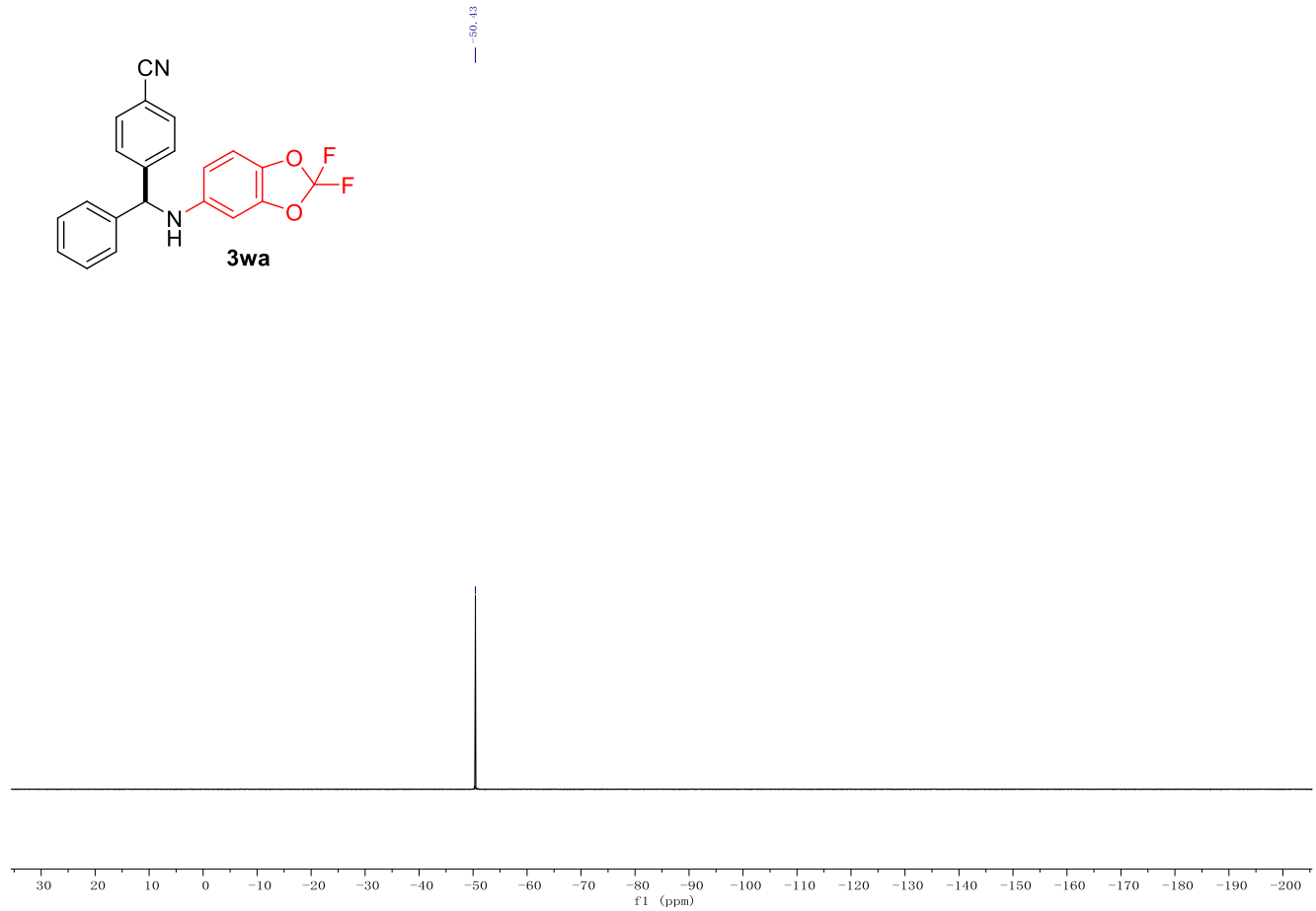


Figure S28. ^{1}**H NMR** (400 MHz, $CDCl_3$), ^{13}**C NMR** (101 MHz, $CDCl_3$) and ^{19}**F NMR** (376 MHz, $CDCl_3$) of **3wa**

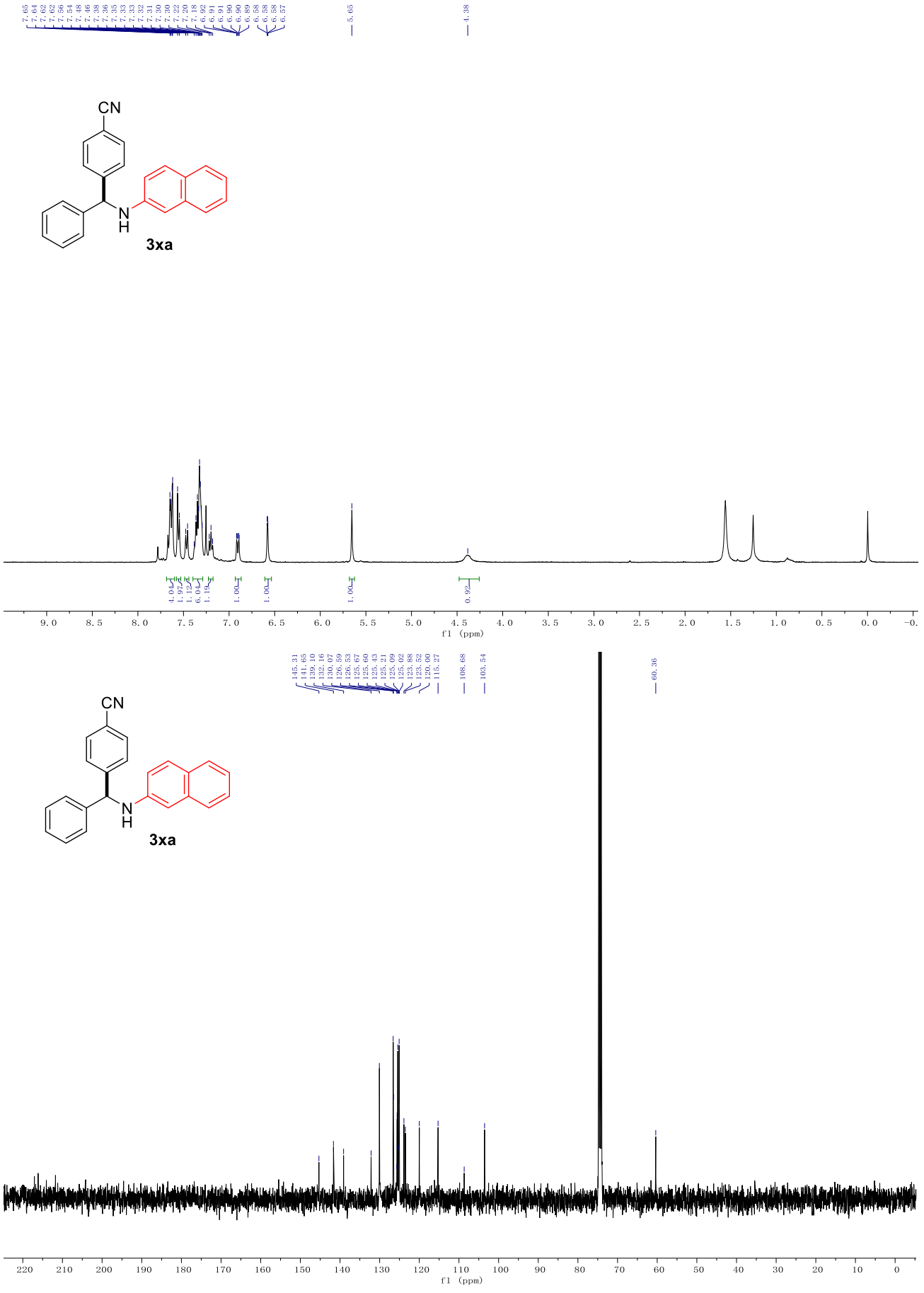


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3xa**

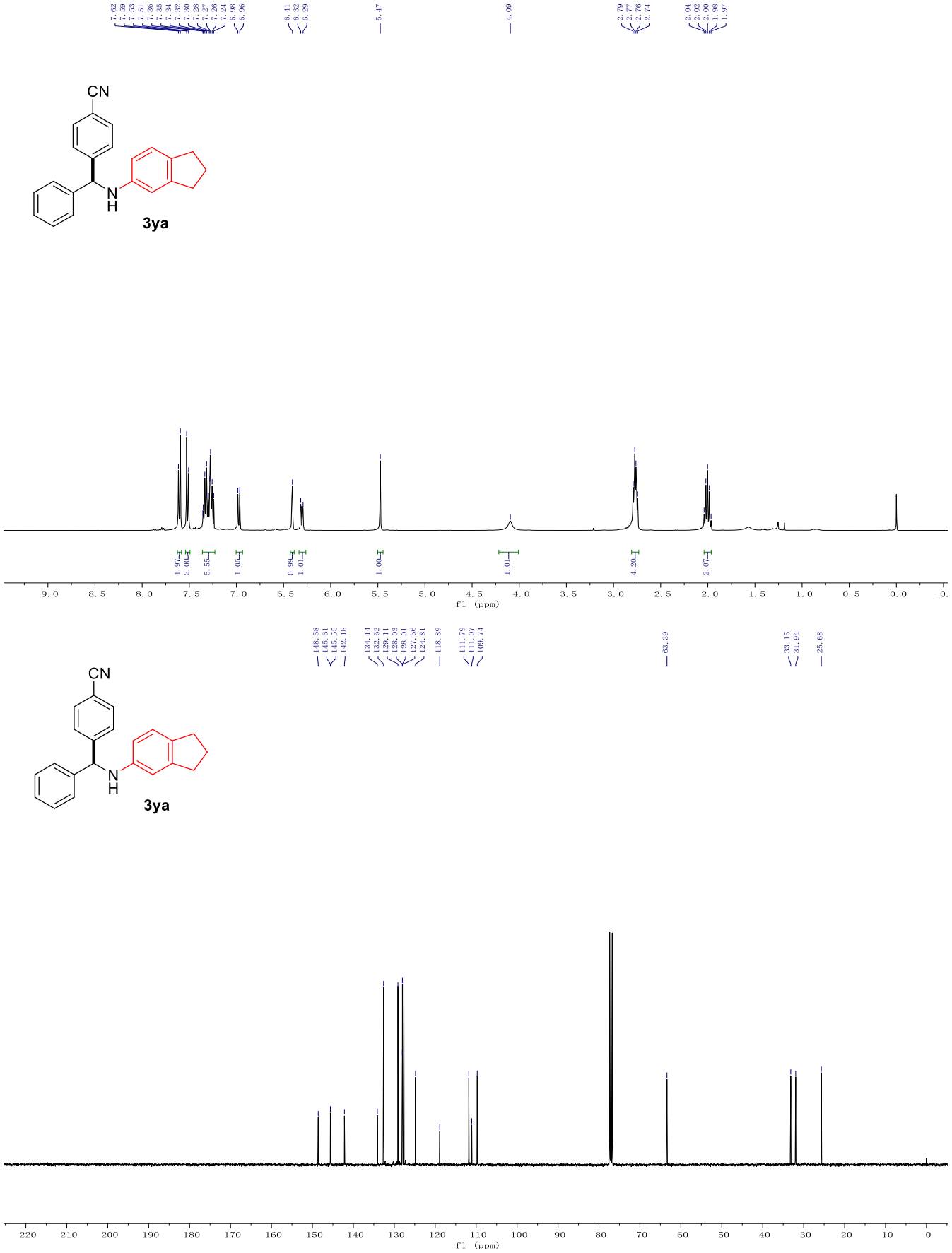


Figure S30. ^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C NMR** (101 MHz, $CDCl_3$) of **3ya**

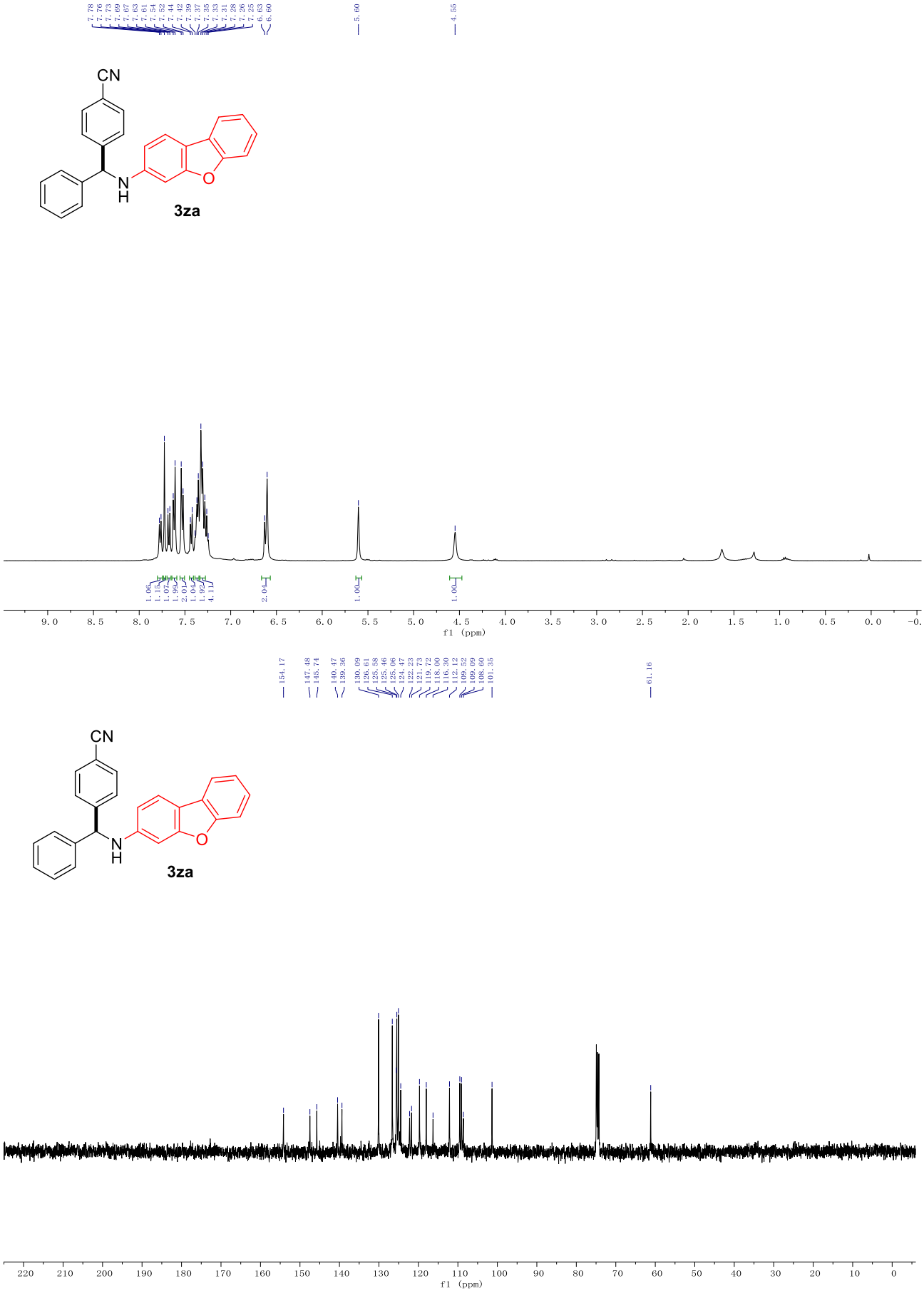


Figure S31. ^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C NMR** (101 MHz, $CDCl_3$) of **3za**

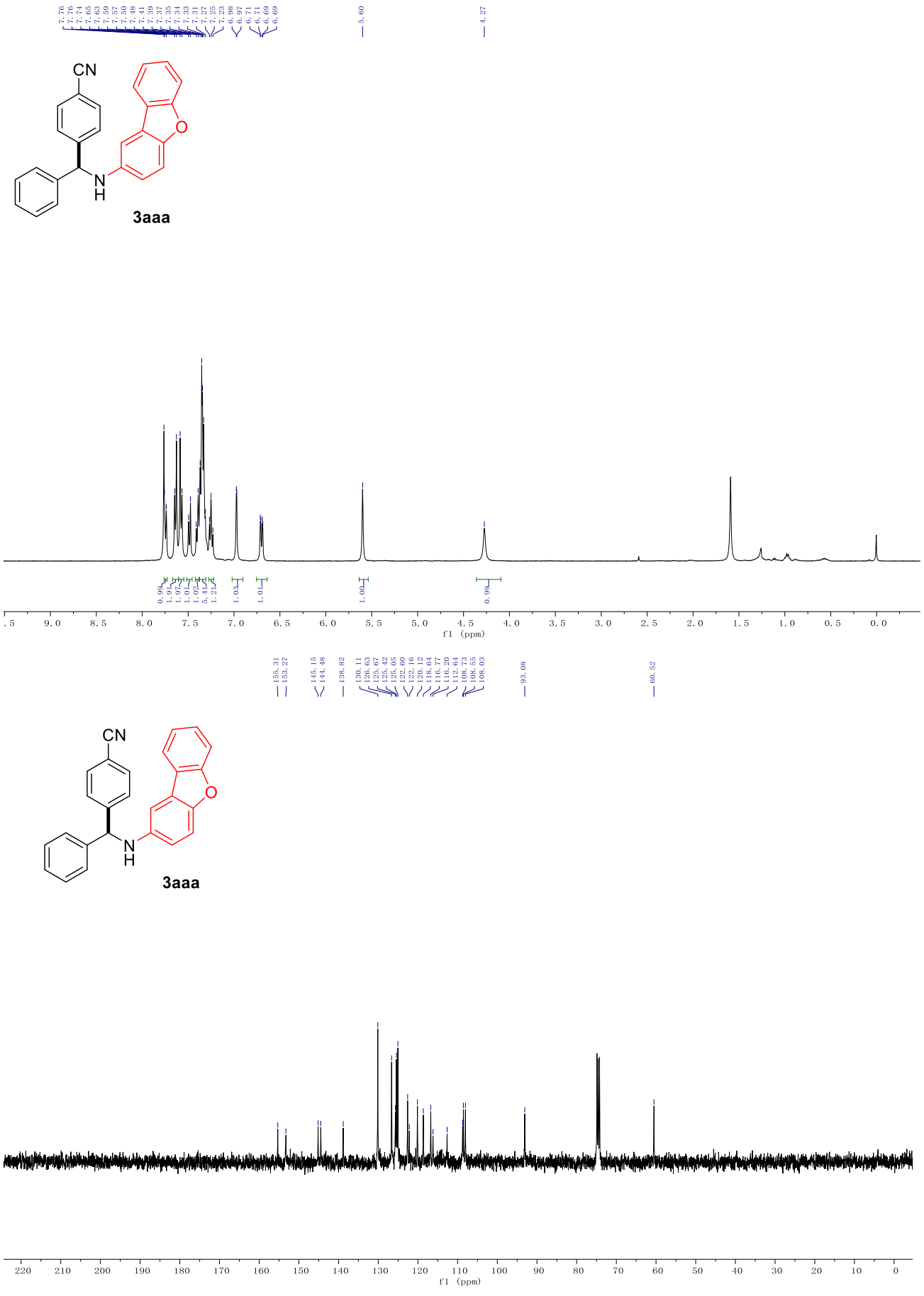


Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3aaa**

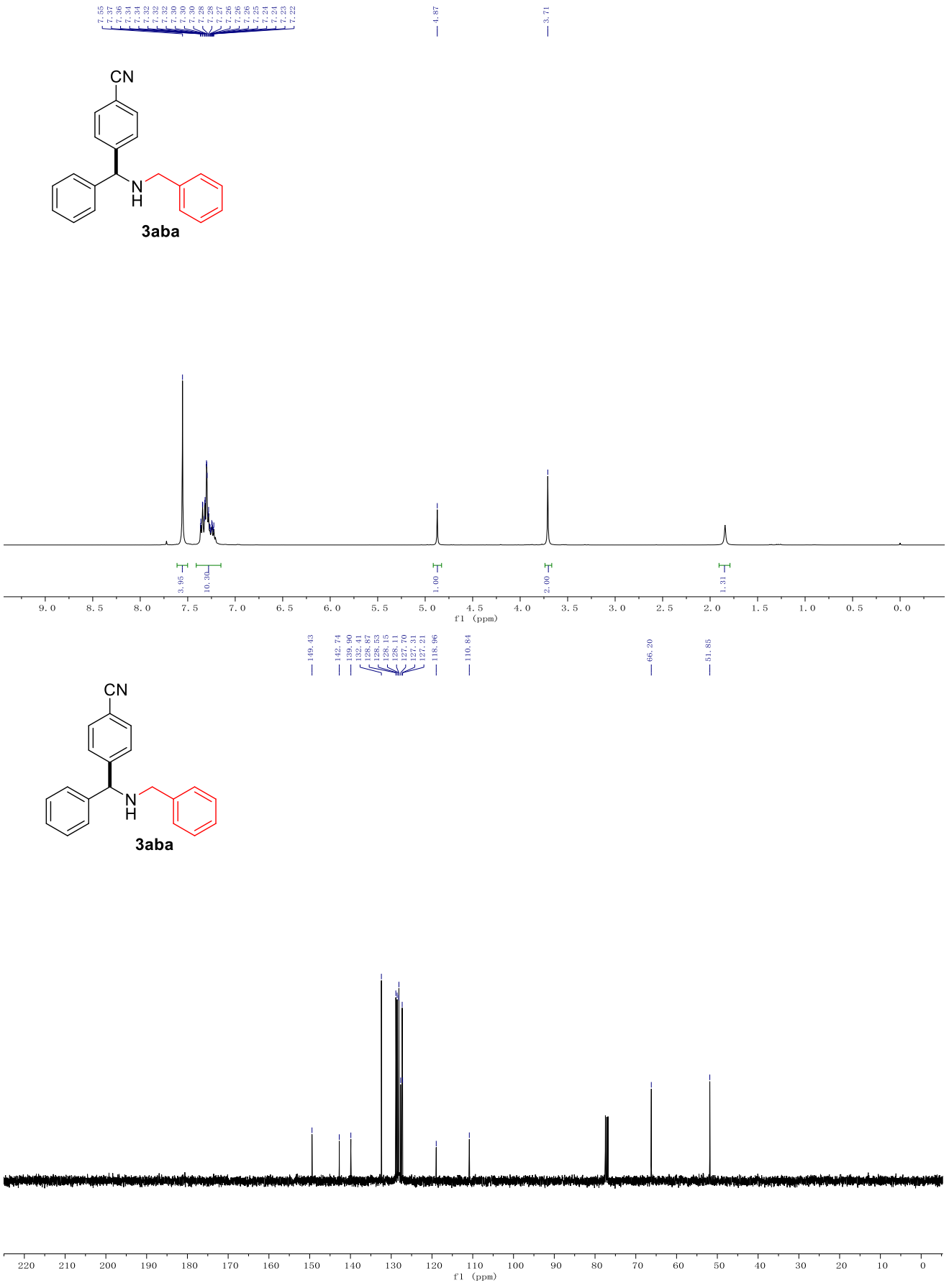


Figure S33. **^{1}H NMR** (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3aba**

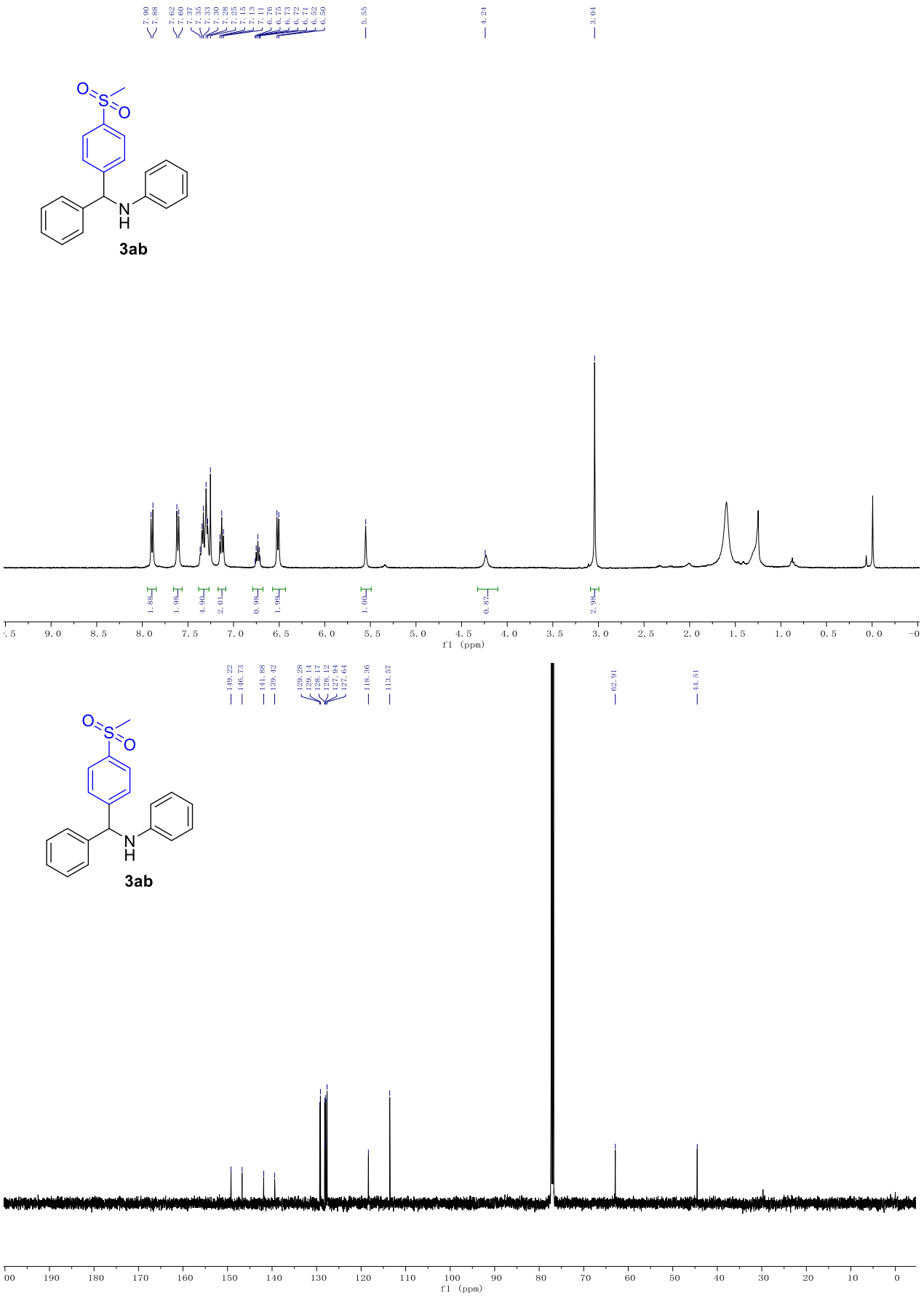


Figure S34. **^{1}H NMR** (400 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) of **3ab**

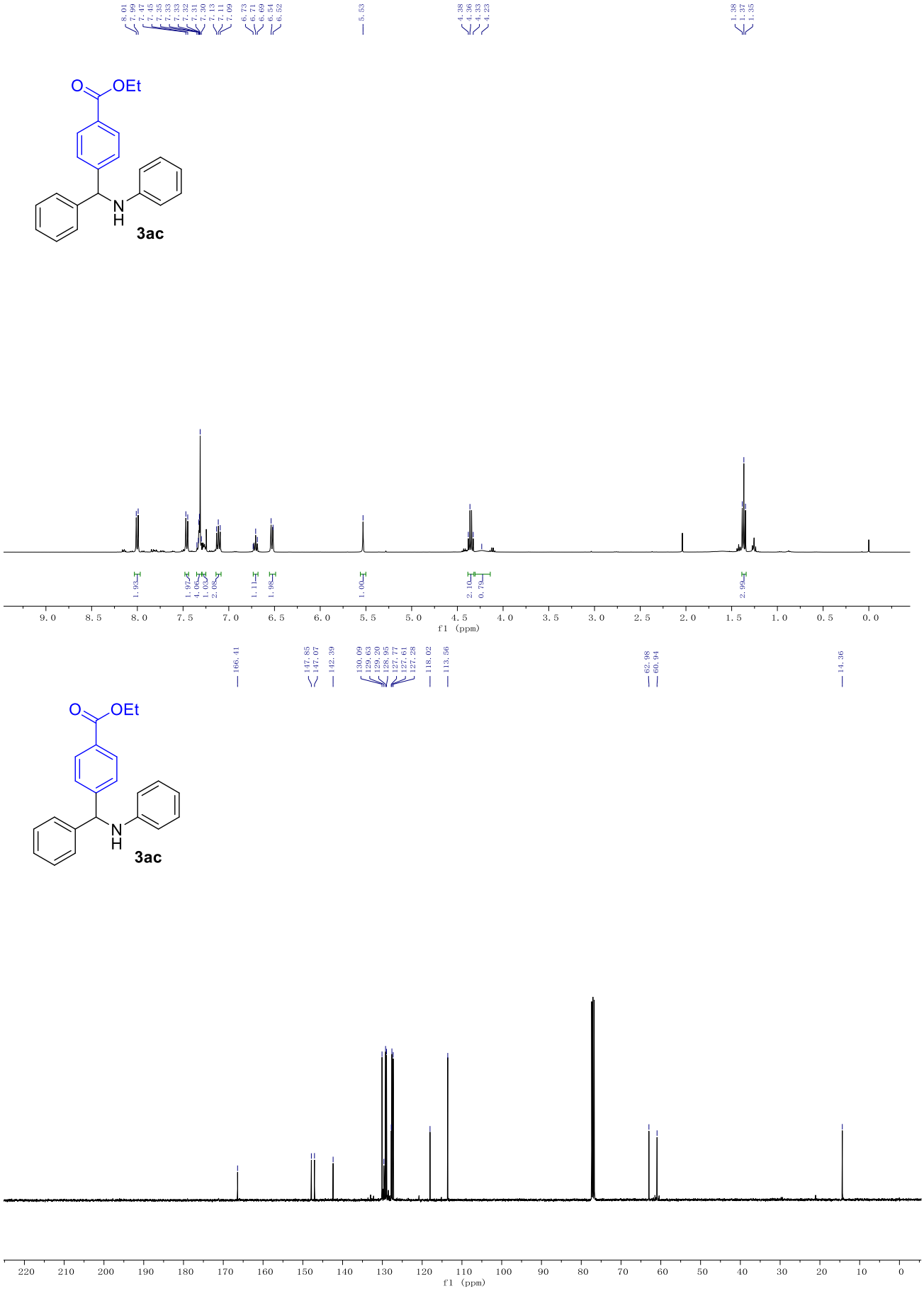


Figure S35. ^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C NMR** (126 MHz, $CDCl_3$) of **3ac**

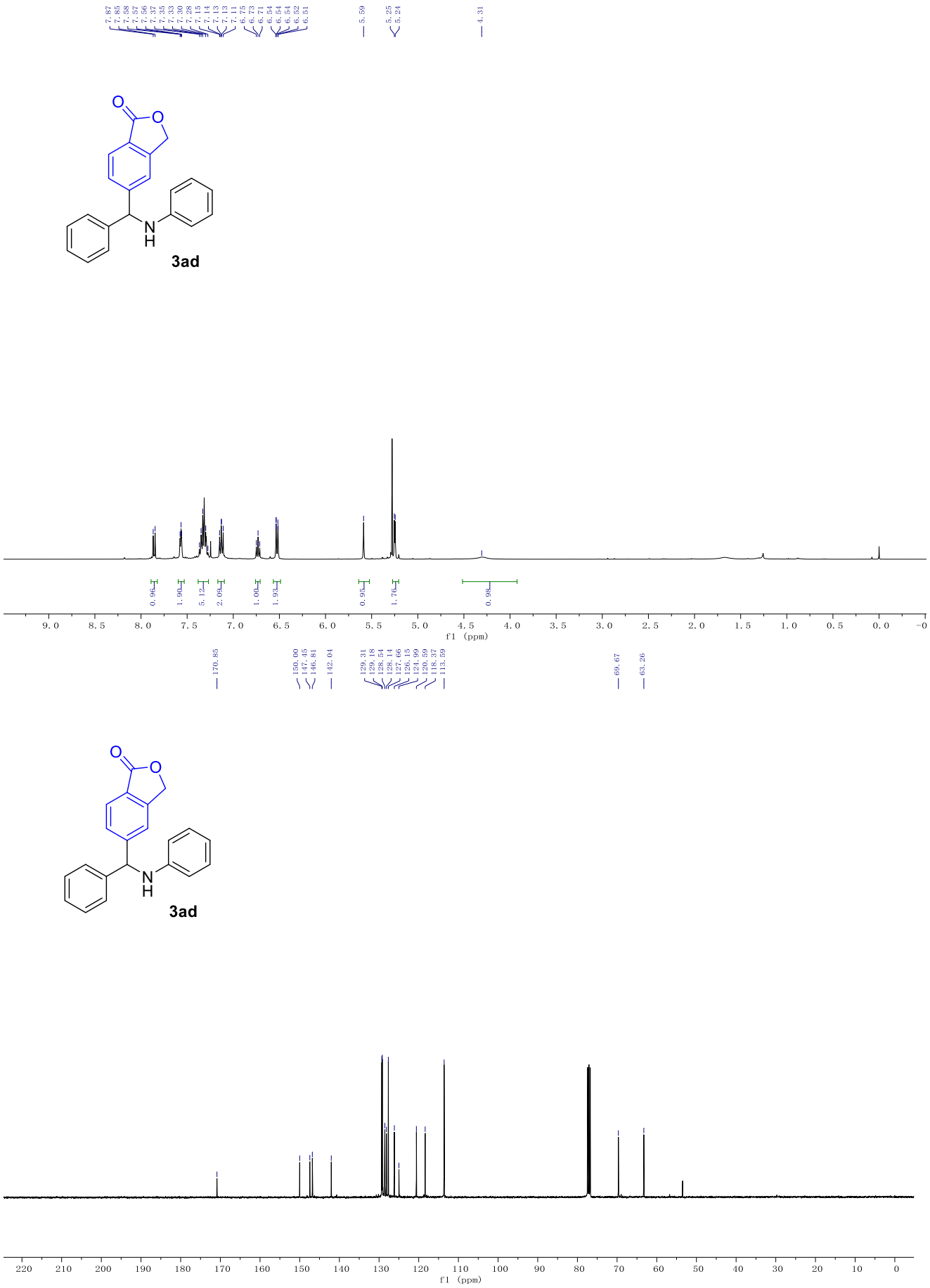


Figure S36. ^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C NMR** (101 MHz, $CDCl_3$) of **3ad**

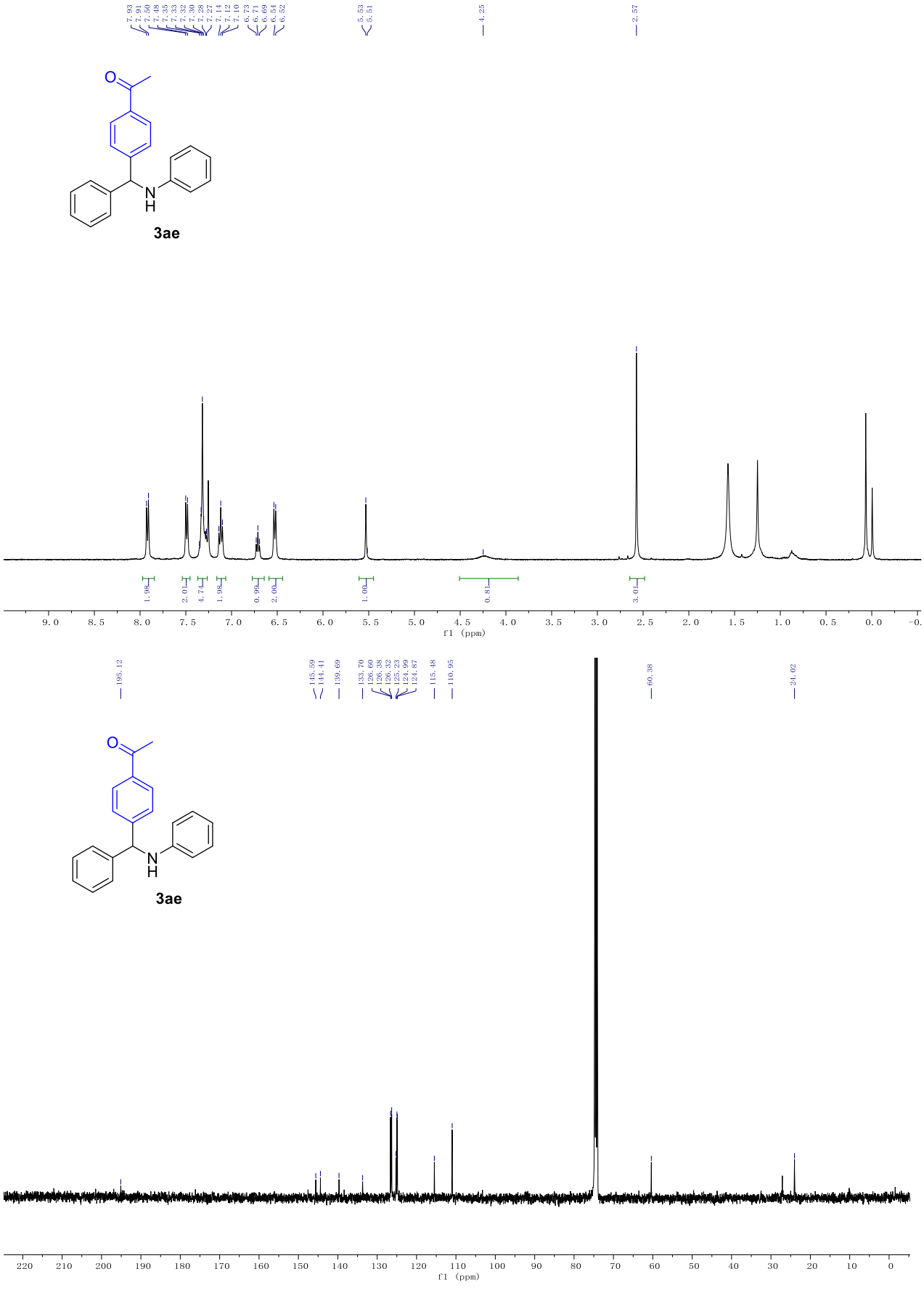


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) of **3ae**

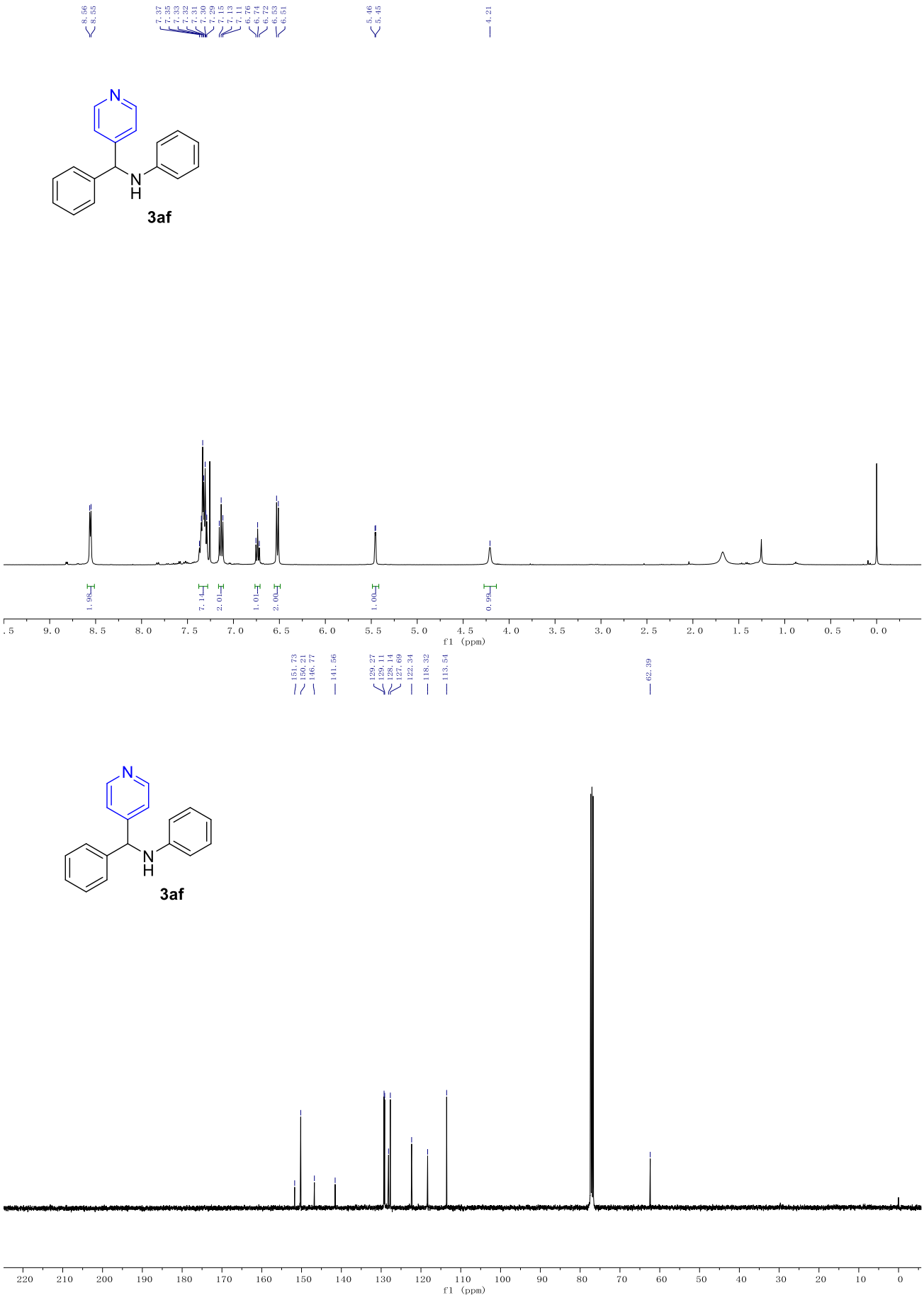


Figure S38. ^{1}**H NMR** (400 MHz, $CDCl_3$) and ^{13}**C NMR** (101 MHz, $CDCl_3$) of **3af**

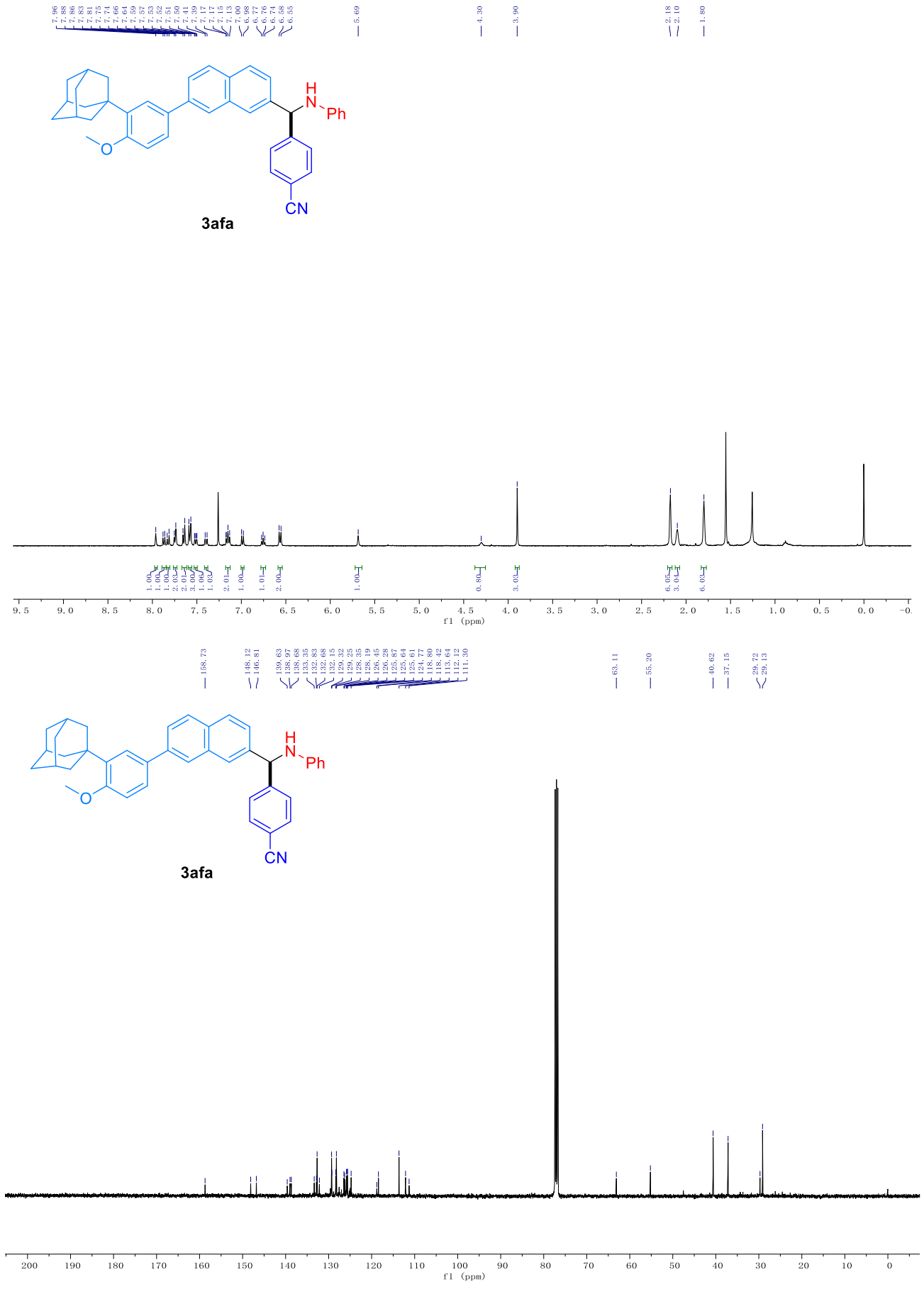


Figure S39. **^{1}H NMR** (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3afa**

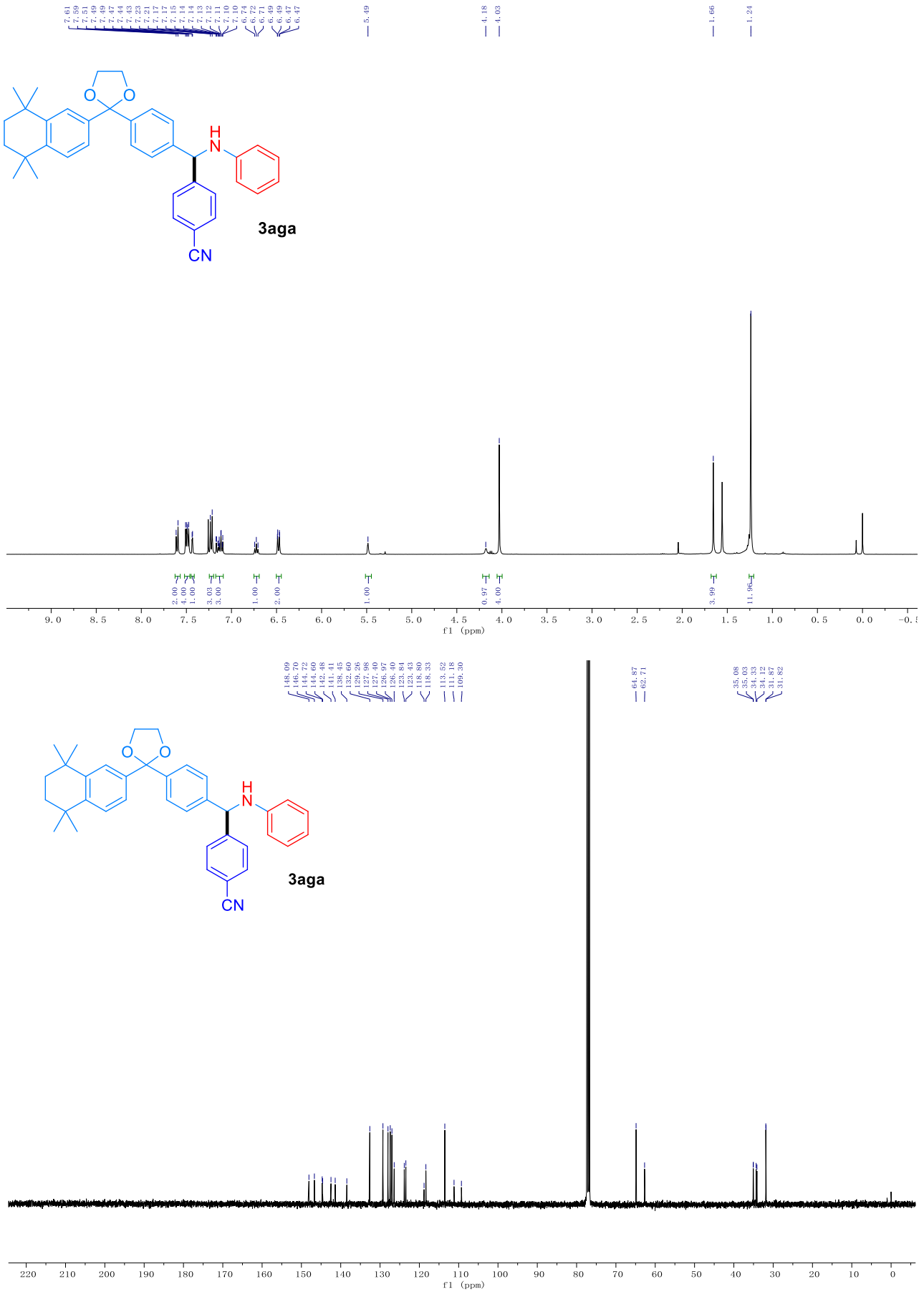


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) of **3aga**