Supporting Information

Copper-catalyzed Ring-opening C(sp^3)–N Coupling of Cycloketone Oxime Esters: Access to 1º, 2º and 3º Alkyl Amines

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Part 1. General Information

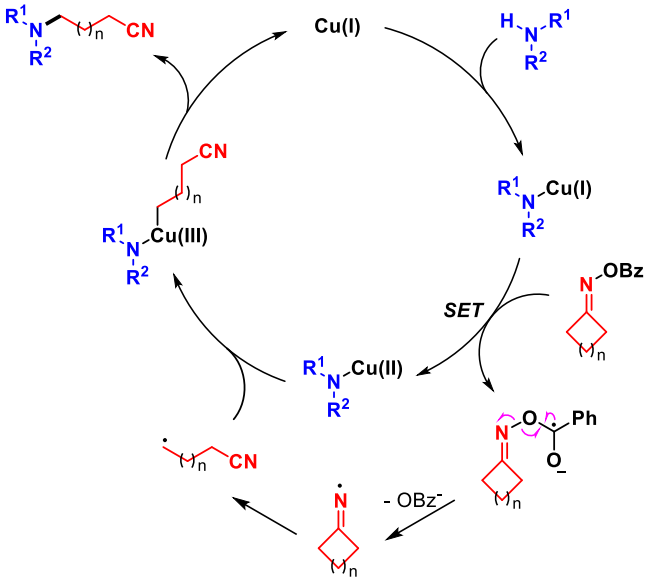
Material: Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere under anhydrous conditions and all reagents were purchased from commercial suppliers without further purification. Anhydrous tetrahydrofuran (THF) and ethanol (EtOH) were purchased from *Energy Chemical*. Anhydrous dimethylformamide (DMF), dichloromethane (DCM) were purchased from *J&K Scientific*. The diethyl ether (Et_2O) and toluene were distilled from sodium-benzophenone. Pyridine was distilled from calcium hydride. $Cu(OTf)_2$ (99.99%) was purchased from *Energy Chemical*.

Methods: Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (GF-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. Tsingdao silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography.

NMR spectra were recorded on a Brüker Advance 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz), Brüker Advance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) at ambient temperature. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^{1}H and $CDCl_3$ (77.2 ppm) for ^{13}C. The following abbreviations were used to explain the multiplicities. s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

IR spectra were recorded on an IRPrestige-21 FTIR spectrometer. High resolution mass spectrometric (HRMS) data were obtained using Brüker Apex IV RTMS

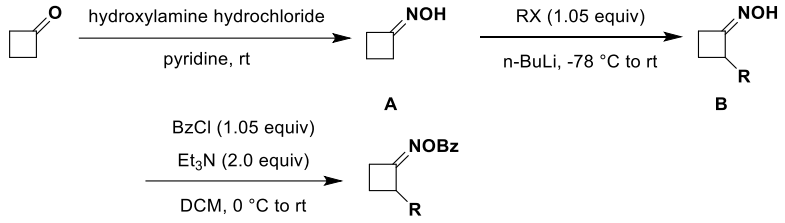
Part 2. Proposed catalytic cycle for the C(sp^3)–N coupling reaction



Part 3. Procedure and Characteristic Data for Substrates 1 and 2

Oxime esters **1b, 1e** are known compounds according to ref. 1; **1j** is known compound according to ref. 2; Phenylamine **2p** is known compound according to ref. 3; **2q** is known compound according to ref. 4. **2r** is known compound according to ref. 5. Other substrates are commercial available if not stated otherwise.

Procedure A



Synthesis of compound **A**

Cyclobutanone (1.50 mL, 20 mmol, 1.0 equiv) was added in a solution of the hydroxylamine hydrochloride (2.78 g, 40 mmol, 2.0 equiv) in dry pyridine (40 mL) at room temperature, and the mixture was stirred for 2 h at room temperature. Pyridine was removed under reduced pressure. The residue was diluted with water and extracted with EtOAc for three times. The combined organic layer was washed with brine and dried by anhydrous Na_2SO_4. The solution was concentrated and afforded the cyclobutanone oxime (~18 mmol, about 90% yield) as white solid, which carried forward to the next step without further purification.

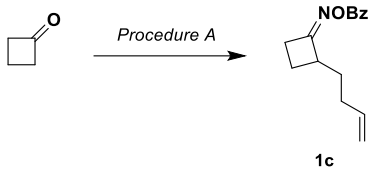
Synthesis of compound **B**

To a solution of cyclobutanone oxime (1.19 g, 14.0 mmol) in dry THF (28 mL) was added LDA (12.3 mL, 30.8 mmol, 2.5 M in THF, 2.2 equiv) dropwise at 0 °C, the mixture was stirred for 30 min at 0 °C. Then alkyl halide (14.7 mmol, 1.05 equiv) was added slowly at 0 °C, and the reaction was allowed to warm up to room temperature. After being stirred for 2 h, the reaction was quenched with cold water, and the yellow solution was extracted with EA. The combined organic layer was washed with water and dried over anhydrous Na_2SO_4. The solution was concentrated in *vacuo* and the residue was subjected to column chromatography to give a substituted cyclobutanone oxime (~11 mmol), which was used in the next step without further purification.

Synthesis of cyclobutanone oxime esters **1c-1d**

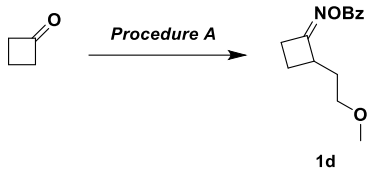
To a 50 mL dry Schlenk flask was added crude oxime (~11 mmol, 1.0 equiv) and 22 mL anhydrous DCM. Et_3N (3.10 mL, 22 mmol, 2.0 equiv) and BzCl (1.34 mL, 11.6 mmol, 1.05

equiv) were added dropwise sequentially at 0 °C. The mixture was stirred for 6 h at room temperature. The solution was diluted with water and extracted with ether for three times. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. The solution was concentrated in *vacuo* and the residue was purified by column chromatography to afford the desired product as yellow oil.



1c

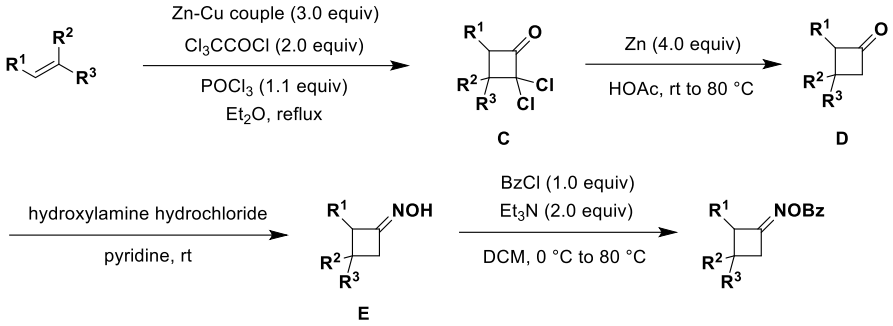
Substrate **1c** was obtained in 65% overall yield from cyclobutanone as yellow oil by column chromatography (PE/EA = 12/1) following the procedure A, by using 4-bromo-1-butene as the alkyl halide. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.4, 1.8 Hz, 2H), 7.58 (tt, J = 8.4, 1.2 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 5.85 – 5.78 (m, 1H), 5.06 (dd, J = 16.8, 1.8 Hz, 1H), 4.99 (dd, J = 16.8, 1.8 Hz, 1H), 3.46 – 3.40 (m, 1H), 3.14 – 3.08 (m, 1H), 3.03 – 2.97 (m, 1H), 2.27 – 2.21 (m, 1H), 2.21 – 2.16 (m, 2H), 2.01 – 1.96 (m, 1H), 1.80 – 1.74 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.7, 164.2, 137.8, 133.3, 129.7, 129.4, 128.6, 115.4, 45.3, 31.6, 31.1, 29.2, 21.1 ppm. **IR** νmax (film). 2923, 2850, 2245, 1738, 1514, 1606, 1459, 1264, 745, 711 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{15}H_{17}NNaO_2$ $[M+Na]^+$: 266.1151; found: 266.1150.



1d

Substrate **1d** was obtained in 60% overall yield from cyclobutanone as yellow oil by column chromatography (PE/EA = 12/1) following the procedure A, by using 1-bromo-2-methoxyethane as the alkyl halide. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.59 – 7.56 (m, 1H), 7.45 (dd, J = 15.0, 7.2 Hz, 2H), 3.56 – 3.41(m, 3H), 3.24 (s, 2H), 3.31 (s, 1H), 3.15 – 3.05 (m, 1H), 3.04 –2.98 (m, 1H), 2.33 – 2.21 (m, 2H), 2.17 – 2.11 (m, 1H), 1.94 – 1.88 (m, 1H), 1.85 – 1.79 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.4, 171.1, 164.1, 163.9, 133.2, 133.1, 129.52, 129.49, 129.1, 128.9, 128.5, 128.4, 70.1, 69.9, 58.6, 58.5, 43.5, 42.8, 32.1, 31.3, 29.2, 29.0, 21.0, 20.0 ppm. **IR** νmax (film). 2929, 1600, 1463, 1455, 1347, 1117, 746 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{14}H_{17}NNaO_3$ $[M+Na]^+$: 270.1101; found: 270.1105.

Procedure B



Synthesis of compound **C**

The alkene derivative (30 mmol, 1.0 equiv), Zn-Cu couple (11.6 g, 90 mmol, 3.0 equiv) were added in anhydrous ether (60 mL) under argon. To this mixture was added the solution of trichloroacetyl chloride (6.70 mL, 60 mmol, 2.0 equiv) and phosphorus oxychloride (3.08 mL, 33 mmol, 1.1 equiv) in ether (60 mL) dropwise at 0 °C under argon. The reaction was refluxed overnight. After the reaction was completed (as monitored by TLC) and cooled to room temperature, the mixture was filtered and the filtrate was washed with ether. The organic solution was washed with water, saturated $NaHCO_3$ (aq) and brine sequentially, then dried over anhydrous $MgSO_4$. The solution was concentrated at 15 °C, and the residue (~30 mmol) was used in the next step without further purification.

Synthesis of compound **D**

To the solution of 2,2-dichlorocyclobutanon (30 mmol, 1.0 equiv) in acetic acid (60 mL) was added zinc dust (7.85 g, 120 mmol, 4.0 equiv) under argon. The reaction was stirred at room temperature for 2 h and then heated at 80 °C for 5 h. The suspension was allowed to cool to room temperature and was diluted with water then extracted with ether for three times. The combined organic layer was neutralized with saturated $NaHCO_3$ (aq). The combined organic phase was washed with water and brine, dried over anhydrous $MgSO_4$. The solution was concentrated in *vacuo* at 15 °C and the desired ketone (~30 mmol) was used in the next step without further purification.

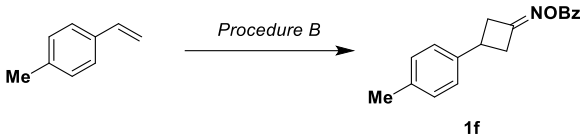
Synthesis of compound **E**

The ketone (20 mmol, 1.0 equiv) was added in a solution of the hydroxylamine hydrochloride (2.78 g, 40 mmol, 2.0 equiv) in dry pyridine (40 mL) at room temperature, and the solution was stirred for 2 h at room temperature. Pyridine was removed under reduced pressure. The residue was diluted with water and extracted with EA for three times. The combined organic layer was washed with brine and dried by anhydrous Na_2SO_4. The solution was concentrated and afforded

the cyclobutanone oxime (~18 mmol, about 90% yield) as white solid, which carried forward to the next step without further purification.

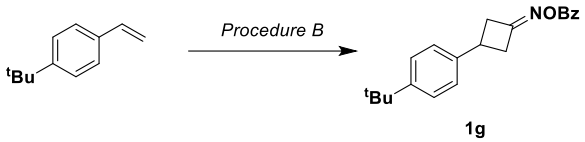
Synthesis of cyclobutanone oxime esters **1f-1i**

To a 50 mL dry Schlenk flask was added crude oxime (~11 mmol, 1.0 equiv) and 22 mL anhydrous DCM. Et_3N (3.10 mL, 22 mmol, 2.0 equiv) and BzCl (1.34 mL, 11.6 mmol, 1.05 equiv) were added dropwise sequentially at 0 °C. The mixture was stirred for 6 h at room temperature. The solution was diluted with water and extracted with ether for three times. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. The solution was concentrated in *vacuo* and the residue was purified by column chromatography to afford the desired product.



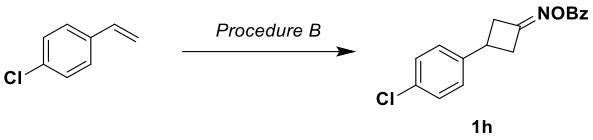
1f

Substrate **1f** was obtained in 68% overall yield as brown solid (m.p.61 °C) by column chromatography (PE/EA = 12/1) following the procedure B, by using 4-methylstyrene. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.4, 1.8 Hz, 2H), 7.55 (t, J = 7.8 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.15 (s, 4H), 3.63 (tt, J = 8.4, 8.4 Hz, 1H), 3.60 – 3.49 (m, 2H), 3.21 – 3.15 (m, 2H), 2.32 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.1, 163.8, 139.9, 136.3, 133.2, 129.5, 129.3, 128.8, 128.4, 126.1, 39.5, 39.4, 32.1, 20.9 ppm. **IR** νmax (film). 2966, 2253, 1497, 1481, 1408, 1377, 1036, 727 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{18}H_{17}NNaO_2$ $[M+Na]^+$: 302.1151; found: 302.1148.



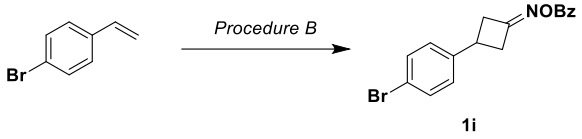
1g

Substrate **1g** was obtained in 60% overall yield as yellow solid (m.p.122 °C) by column chromatography (PE/EA = 14/1) following the procedure B, by using 4-tert-butylstyrene. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.4, 1.2 Hz, 2H), 7.59 (t, J = 7.8 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 3.69 (tt, J = 7.8, 7.8 Hz, 1H), 3.64 – 3.54 (m, 2H), 3.28 – 3.21 (m, 2H), 1.33 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.4, 164.1, 150.0, 140.1, 133.4, 129.8, 129.1, 128.6, 126.2, 125.8, 39.8, 39.6, 34.6, 32.3, 31.5 ppm; **IR** νmax (film). 2957, 2868, 1742, 1657, 1452, 1363, 1261, 1060, 1024, 880, 707 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{21}H_{23}NNaO_2$ $[M+Na]^+$: 344.1261; found: 344.1268.



1h

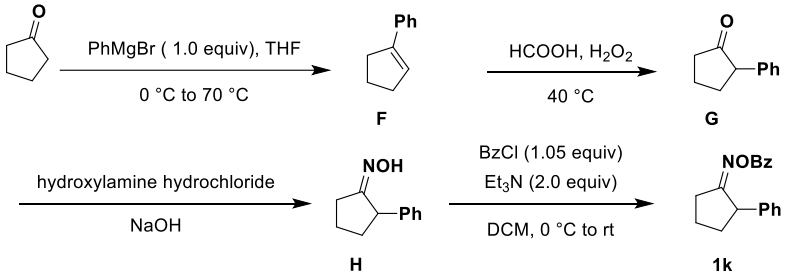
Substrate **1h** was obtained in 62% overall yield as yellow oil by column chromatography (PE/EA = 15/1) following the procedure B, by using 4-chlorostyrene. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 – 8.04 (m, 2H) , 7.58 (tt, J = 7.8, 1.2 Hz, 1H), 7.46 (tt, J = 7.8, 1.8 Hz, 2H), 7.32 (dd, J = 8.4, 1.8 Hz, 2H), 7.22 (dd, J = 8.4, 1.8Hz, 2H), 3.70 – 3.65 (m, 1H), 3.64 – 3.54 (m, 2H), 3.23 – 3.16 (m, 2H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.5, 163.9, 141.5, 133.4, 132.7, 129.6, 128.9, 128.6, 127.8, 39.6, 39.5, 32.0 ppm. **IR** νmax (film). 2924, 1713, 1591, 1494, 1363, 1261, 1165, 982, 828, 759 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{17}H_{14}ClNNaO_2$ $[M+Na]^+$: 322.0605; found: 322.0608.



1i

Substrate **1i** was obtained in 68% overall yield as yellow oil by column chromatography (PE/EA = 12/1) following the procedure B, by using 4-bromostyrene. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (dd, J = 7.8, 1.2 Hz, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.49 – 7.45 (m, 4H), 7.17 (d, J = 8.4 Hz, 2H), 3.69 – 3.65 (m, 1H), 3.64 – 3.56 (m, 2H), 3.25 – 3.17 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.5, 164.0, 142.1, 133.5, 132.0, 129.8, 129.0, 128.7, 128.2, 120.9, 39.7, 39.6, 32.2 ppm. **IR** νmax (film). 2918, 2850, 1826, 1737, 1391, 885, 851, 817, 708 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{17}H_{14}BrNNaO_2$ $[M+Na]^+$: 367.0100; found: 367.0111.

Synthesis of cyclopentanone oxime ester 1k



Synthesis of compound **F**

To the solution of phenylmagnesium bromide (10.0 mL, 30 mmol, 1.0 equiv, 3.0 M in Et_2O) in dry THF (60 mL) was added cyclopentone (2.65 mL, 30 mmol, 1.0 equiv) under argon at 0 °C and the mixture was allowed to warm to room temperature. Then the reaction was refluxed at 70 °C for 7 h. After the reaction was completed (as monitored by TLC), the solution was cooled to room

temperature and quenched with H_2O. The mixture was added the 6 M HCl (20 mL) and stirred for 30 min. The water layer was extracted with Et_2O for three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solution was concentrated in *vacuo* and the residue was purified by column chromatography (PE/EA = 15:1) to afford the alkene **F** in 55% yield (2.38 g, 16.5 mmol) as yellow oil.

Synthesis of compound **G**

Formic acid (0.69 mL, 18.2 mmol, 1.1 equiv) was mixed with H_2O_2 (1.82 mL, 16.5 mmol, 1.0 equiv, 30%) and the mixture was stirred for 15 min at 40 °C. Then this solution was added via syringe to **F** (2.38 g, 16.5 mmol, 1.0 equiv) and the mixture was stirred at room temperature overnight. After completed (as monitored by TLC), the reaction was quenched with sat. $NaHCO_3$ and extracted with Et_2O for three times then dried over anhydrous $MgSO_4$. The solution was concentrated in *vacuo* and the residue was purified by column chromatography (PE/EA = 15:1) to afford the ketone **G** in 50% yield (1.32 g, 8.3 mmol) as colorless oil.

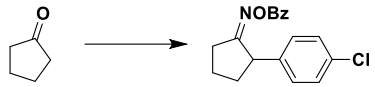
Synthesis of compound **H**

Phenylcyclopentanone **G** (1.32 g, 8.3 mmol, 1.0 equiv) was dissolved in EtOH (30 mL) and the solution of NaOH (33 mL, 16.6 mmol, 2.0 equiv, 0.5 M in H_2O) was added. Hydroxylamine hydrochloride (0.86 g, 12.4 mmol, 1.5 equiv) was added into the reaction and the reaction was allowed to warm to room temperature. After completed (as monitored by TLC), the reaction was diluted with water and extracted with EA for three times. The combined organic layer was washed with brine and dried over Na_2SO_4. The solution was concentrated in *vacuo* to afford the crude product **H** in 90% yield (1.29 g, 7.4 mmol), which was used in the next step without further purification.

Synthesis of cyclobutanone oxime ester **1k**

To a 50 mL dry Schlenk flask was added crude oxime (~11 mmol, 1.0 equiv) and 22 mL anhydrous DCM. Et_3N (3.10 mL, 22 mmol, 2.0 equiv) and BzCl (1.34 mL, 11.6 mmol, 1.05 equiv) were added dropwise sequentially at 0 °C. The mixture was stirred for 6 h at room temperature. The solution was diluted with water and extracted with ether for three times. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. The solution was concentrated in *vacuo* and the residue was purified by column chromatography (PE/EA = 15:1) to afford the oxime ester **1k** in 54% yield (1.66 g, 5.9 mmol) as yellow solid (m.p.75 °C). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (dd, J = 7.8, 1.8 Hz, 2H), 7.56 (t, J = 7.8 Hz, 1H), 7.44 (t, J = 7.2 Hz, 2H), 7.32 (d, J = 7.2 Hz, 2H), 7.31 (s, 2H), 7.24 – 7.20 (m, 1 H), 4.05 (td, J = 7.8, 1.8 Hz, 1H), 2.95 – 2.89 (m, 1H), 2.82 – 2.76 (m, 1H), 2.30 (dt, J = 19.2, 6.0 Hz, 1H), 2.06 – 1.95 (m, 2H), 1.87

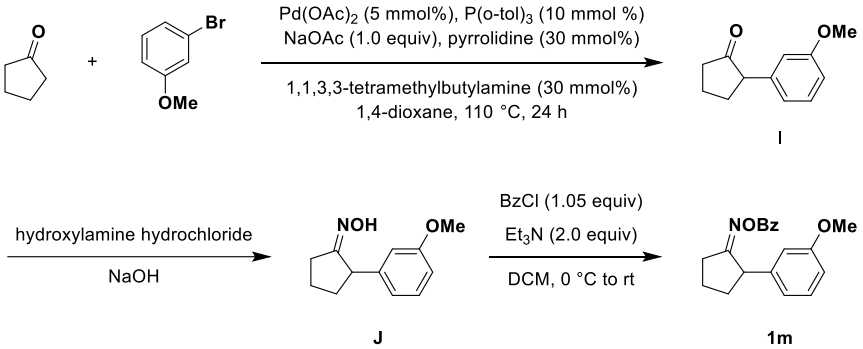
– 1.80 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 177.5, 163.8, 140.5, 133.2, 129.6, 129.3, 128.6, 128.5, 127.9, 126.8, 49.1, 34.8, 30.0, 22.5 ppm. **IR** νmax (film). 2972, 2900, 1451, 1406, 1394, 1250, 1230, 1055, 881 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{18}H_{17}NNaO_2$ $[M+Na]^+$: 302.1151; found: 302.1157.



1l

Substrate **1l** was obtained in 18% overall yield from cyclopentone as yellow solid (m.p.81 °C) by column chromatography (PE/EA = 16/1) following the method for the synthesis of cyclopentanone oxime ester **1k**, by using 4-chlorophenylmagnesium bromide. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (dd, J = 7.8, 1.2 Hz, 2H), 7.59 (tt, J = 7.2, 1.8 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.32 – 7.26 (m, 4H), 4.02 (t, J = 7.2 Hz, 1H), 2.98 – 2.92 (m, 1H), 2.83 – 2.76 (m, 1H), 2.35 – 2.30 (m, 1H), 2.05 – 1.96 (m, 2H), 1.89 – 1.82 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 177.2, 163.9, 138.9, 133.4, 132.8, 129.7, 129.4, 129.3, 128.9, 128.7, 48.7, 34.9, 30.0, 22.6 ppm. **IR** νmax (film). 2954, 2897, 1700, 1494, 1363, 1150, 986, 880, 750 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{18}H_{16}ClNNaO_2$ $[M+Na]^+$: 336.0762; found: 336.0754.

Synthesis of cyclopentanone oxime ester 1m



Synthesis of compound **I**

To a 500 mL dry Schlenk flask was added $Pd(OAc)_2$ (225 mg, 1.0 mmol, 0.05 equiv), $P(o\text{-}tol)_3$ (609 mg, 2.0 mmol, 0.1 equiv), NaOAc (1.64 g, 20.0 mmol, 1.0 equiv), pyrrolidine (0.49 mL, 6.0 mmol, 0.3 equiv), 1,1,3,3-tetramethylbutylamine (0.96 mL, 6.0 mmol, 0.3 equiv) and 1,4-dioxane (100 mL). Cyclopentanone (1.77 mL, 20.0 mmol, 1.0 equiv) and 3-bromoanisole (3.26 mL, 26.0 mmol, 1.3 equiv) were added into the mixture and the reaction was degassed for three times with argon. The mixture was sealed and allowed to stir at 110 °C for 24 h. After completed (as monitored by TLC), the reaction was cooled to room temperature. The mixture was filtered

through a small plug of silica gel and eluted with ethyl acetate. The filtrate was concentrated under *vacuo* and further purified by flash column chromatography (PE/EA= 12/1) to give the desired product **l** in 74 % yield (2.80 g, 14.8 mmol) as yellow oil.

Synthesis of compound **J**

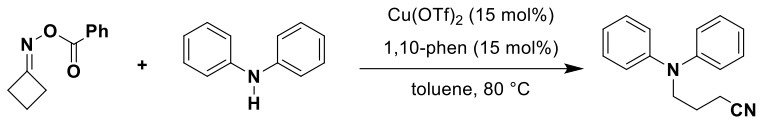
The ketone **l** (2.80 g, 14.7 mmol, 1.0 equiv) was dissolved in dry EtOH (0.25 M) and the solution of NaOH (59 mL, 29.4 mmol, 2.0 equiv, 0.5 M in H_2O) was added. Hydroxylamine hydrochloride (1.53 g, 22.1 mmol, 1.5 equiv) was added into the reaction and the mixture was allowed to react at room temperature. After completed (as monitored by TLC), the reaction was diluted with water and extracted with EA for three times. The combined organic layer was washed with brine and dried over Na_2SO_4. The solution was concentrated in *vacuo* to afford the crude product **J** in 92% yield (2.77 g, 13.5 mmol), which was used in the next step without further purification.

Synthesis of cyclobutanone oxime ester **1m**

To a 100 mL dry Schlenk flask was added crude oxime (13.5 mmol, 1.0 equiv) and anhydrous DCM (27.0 mL). Et_3N (3.75 mL, 27.0 mmol, 2.0 equiv) and BzCl (1.65 mL, 14.2 mmol, 1.05 equiv) were added dropwise sequentially at 0 °C. The mixture was stirred for 6 h at room temperature. The solution was diluted with water and extracted with ether for three times. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. The solution was concentrated in *vacuo* and the residue was purified by column chromatography (PE/EA = 15:1) to afford the oxime ester **1m** in 62% yield (2.59 g, 8.4 mmol) as yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, J = 7.2 Hz, 2H), 7.55 (tt, J = 7.2, 1.2 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.22 (t, J = 7.8 Hz, 1H), 6.90 – 6.89 (m, 2H), 6.76 (dd, J = 8.4, 2.4 Hz, 1H), 4.01 (t, J = 7.2 Hz, 1H), 3.78 (s, 3H), 2.92 – 2.87 (m, 1H), 2.80 – 2.74 (m, 1H), 2.30 – 2.25 (m, 1H), 2.04 – 1.92 (m, 2H), 1.87 – 1.77 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 177.3, 163.7, 159.6, 141.9, 133.1, 129.47, 129.45, 129.2, 128.4, 120.1, 113.9, 112.0, 55.1, 49.0, 34.6, 29.8, 22.4 ppm. **IR** νmax (film). 2932, 2850, 2784, 1820, 1700, 1420, 1250, 998, 793 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{19}H_{19}NNaO_3$ $[M+Na]^+$: 332.1257; found: 332.1247.

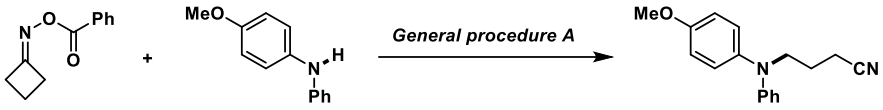
Part 4. General Procedure and Characteristic Data for Products 3 and 4

General procedure A



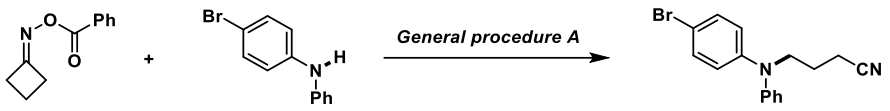
1a **2a** **3a**, 81%

To a 10 mL dry Schlenk flask was added **1a** (75.6 mg, 0.40 mmol, 2.0 equiv), $Cu(OTf)_2$ (10.8 mg, 0.03 mmol, 0.15 equiv), 1,10-phen (5.4 mg, 0.03 mmol, 0.15 equiv) and 2 mL dry toluene. Then **2a** (33.8 mg, 0.20 mmol, 1.0 equiv) was added at ambient temperature, and the reaction was degassed for three times with argon. The mixture was allowed to stir at 80 °C for 1.5 h. After completed (as monitored by TLC), the reaction was cooled to room temperature. The mixture was diluted with sat.$NaHCO_3$ and extracted with EA for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 10/1) afforded the desired product **3a** in 81% yield (38.3 mg, 0.16 mmol) as yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (t, J = 7.8 Hz, 4H), 6.99 – 6.97 (m, 6H), 3.85 (t, J = 7.2 Hz, 2H), 2.41 (t, J = 7.2 Hz, 2H), 2.01 (tt, J = 7.2, 7.2 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.8, 129.6, 122.1, 121.3, 119.4, 50.7, 23.7, 14.9 ppm; **IR** νmax (film).2923, 1770, 1493, 1374, 1245, 1059, 749, 694 cm^{-1}; **HRMS (ESI)** m/z calcd for $C_{16}H_{17}N_2$ $[M+H]^+$: 237.1386; found: 237.1389.



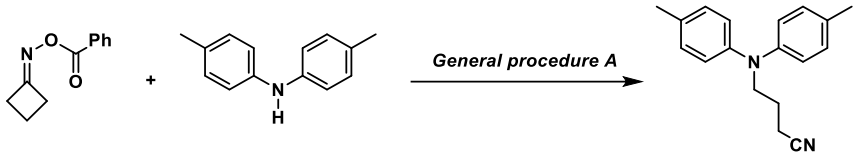
1a **2b** **3b**, 54%

Product **3b** was obtained in 54 % yield (28.7 mg, 0.11 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 5/1) following the general procedure A, except that **2b** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.19 (t, J = 7.8 Hz, 2H), 7.05 (d, J = 7.8 Hz, 2H), 6.90 (d, J = 7.8 Hz, 2H), 6.80 (t, J = 7.8 Hz, 1H), 6.74 (d, J = 7.8 Hz, 2H), 3.81 (s, 3H), 3.78 (t, J = 7.2 Hz, 2H), 2.41 (t, J = 7.2 Hz, 2H), 1.99 (tt, J = 7.2, 7.2 Hz, 2H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.9, 148.9, 140.3, 129.3, 127.4, 119.5, 119.1, 116.4, 115.2, 55.7, 50.9, 23.8, 14.9 ppm; **IR** νmax (film). 2924, 1770, 1595, 1808, 1498, 1243, 1033, 748 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{17}H_{18}N_2NaO$ $[M+Na]^+$: 289.1311; found: 289.1304.



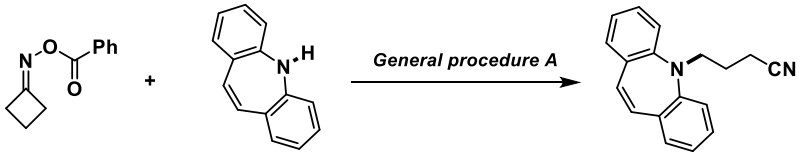
1a 2c **3c**, 60%

Product **3c** was obtained in 60% yield (37.7 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 7/1) following the general procedure A, except that **2c** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (d, J = 9.0 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.06 (t, J = 7.8 Hz, 1H), 7.02 (d, J = 7.8 Hz, 2H), 6.80 (d, J = 9.0 Hz, 2H), 3.82 (t, J = 7.2 Hz, 2H), 2.41 (t, J = 7.2 Hz, 2H), 1.99 (tt, J = 7.2, 7.2 Hz, 2H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.2, 147.1, 132.4, 129.9, 123.4, 122.9, 121.4, 119.2, 113.6, 50.7, 23.6, 14.9 ppm ; **IR** νmax (film). 2965, 1450, 1374, 1244, 1059, 913, 747 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{16}H_{15}BrN_2Na[M+Na]^+$: 337.0311; found: 337.0309.



1a 2d **3d**, 84%

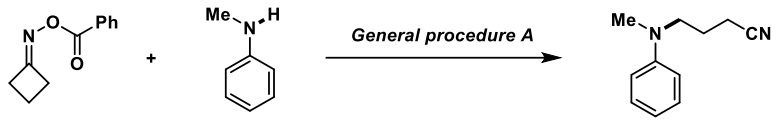
Product **3d** was obtained in 84% yield (44.4 mg, 0.17 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 8/1) following the general procedure A, except that **2d** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.07 (d, J = 8.4 Hz, 4H), 6.85 (d, J = 8.4 Hz, 4H), 3.78 (t, J = 7.2 Hz, 2H), 2.40 (t, J = 7.2 Hz, 2H), 2.29 (s, 6H), 1.97 (tt, J = 7.2, 7.2 Hz, 2H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.7, 131.4, 130.1, 121.3, 119.5, 50.8, 23.8, 20.7, 14.9 ppm; **IR** νmax (film). 2924, 2856, 1758, 1511, 1245. 1050, 810, 748 cm^{-1}; **IR** νmax (film). 2924, 2856, 1758, 1511, 1245. 1050, 810, 748 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{18}H_{20}N_2Na$ $[M+Na]^+$: 287.1519; found: 287.1514.



1a 2e **3e**, 78%

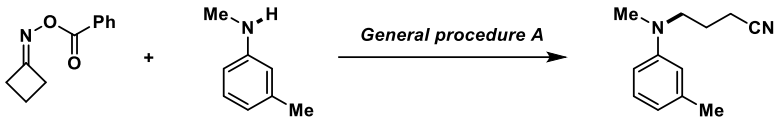
Product **3e** was obtained in 78% yield (40.6 mg, 0.16 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 8/1) following the general procedure A, except that **2e** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 (d, J = 7.8 Hz, 2H), 7.01 (t, J = 7.8 Hz, 4H), 6.75 (s, 2H), 3.85 (t, J = 6.6 Hz, 2H), 2.43 (t, J = 6.6 Hz, 2H), 1.90 (tt, J = 6.6, 6.6 Hz, 2H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.9, 134.2, 132.2, 129.5, 129.2, 124.0, 120.5, 48.8, 23.6,

14.5 ppm; **IR** νmax (film). 2923, 1770, 1758, 1697, 1557, 1275, 1246. 1056, 764, 749 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{18}H_{17}N_2$ $[M+H]^+$: 261.1386; found: 261.1382.



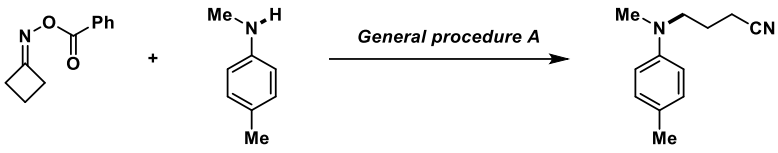
1a **2f** **3f**, 68%

Product **3f** was obtained in 68% yield (23.7 mg, 0.14 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 8/1) following the general procedure A, except that **2f** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 2H), 6.75 – 6.72 (m, 3H), 3.46 (t, J = 7.2 Hz, 2H), 2.95 (s, 3H), 2.38 (t, J = 7.2 Hz, 2H), 1.95 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.1, 129.5, 119.5, 117.2, 112.7, 51.4, 38.9, 23.3, 14.9 ppm; **IR** νmax (film). 2940, 1600, 1464, 1375, 1192, 1034, 752, 695 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{11}H_{14}N_2Na$ $[M+Na]^+$: 197.1049; found: 197.1054.



1a **2g** **3g**, 65%

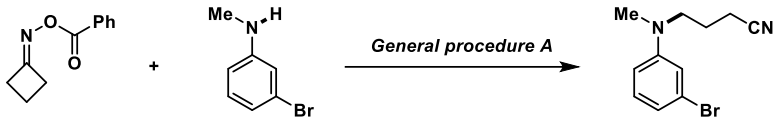
Product **3g** was obtained in 65% yield (24.5 mg, 0.13 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA =10/1) following the general procedure A, except that **2g** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.13 (t, J = 7.8 Hz, 1H), 6.57 (d, J = 7.8 Hz, 1H), 6.55 – 6.54 (m, 2H), 3.44 (t, J = 7.2 Hz, 2H), 2.94 (s, 3H), 2.38 (t, J = 7.2 Hz, 2H), 2.32 (s, 3H), 1.95 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.2, 139.2, 129.3, 119.6, 118.2, 113.6, 110.0, 51.4, 39.0, 23.4, 22.0, 14.9 ppm; **IR** νmax (film). 2922, 2851, 1764, 1602, 1498, 1377, 1176, 765, 692 cm^{-1}; **HRMS (ESI)** m/z calcd for $C_{12}H_{17}N_2$ $[M+H]^+$: 189.1386; found: 189.1386.



1a **2h** **3h**, 66%

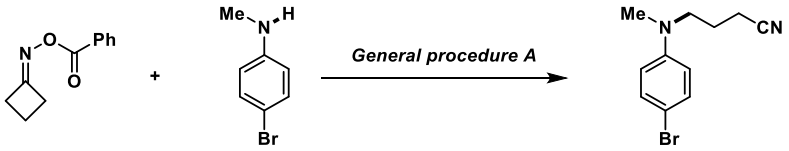
Product **3h** was obtained in 66% yield (24.8 mg, 0.13 mmol) as red oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 9/1) following the general procedure A, except that **2h** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.05 (d, J = 8.4 Hz, 2H), 6.66 (d, J

= 8.4 Hz, 2H), 3.40 (t, J = 7.2 Hz, 2H), 2.90 (s, 3H), 2.37 (t, J = 7.2 Hz, 2H), 2.25 (s, 3H), 1.92 (t, J = 6.6 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.2, 130.0, 126.7, 119.6, 113.4, 51.8, 39.1, 23.2, 20.3, 14.8 ppm; **IR** νmax (film). 2956, 2925, 2854, 1770, 1675, 1516, 1246, 1052, 816, 746 cm^{-1}; **HRMS (ESI)** m/z calcd for $C_{12}H_{17}N_2$ $[M+H]^+$: 189.1386; found: 189.1382.



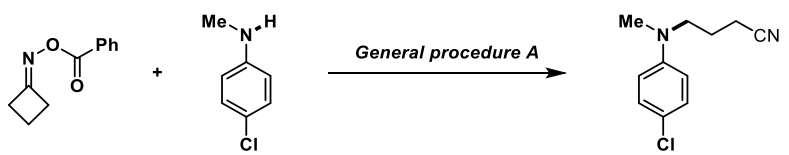
1a **2i** **3i**, 62%

Product **3i** was obtained in 62% yield (31.3 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 12/1) following the general procedure A, except that **2i** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.07 (t, J = 8.4 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.81 (s, 1H) 6.62 (dd, J = 8.4, 3.0 Hz, 1H), 3.44 (t, J = 7.2 Hz, 2H), 2.94 (s, 3H), 2.37 (t, J = 7.2 Hz, 2H), 1.93 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 150.2, 130.6, 123.7, 119.8, 119.3, 115.2, 111.1, 51.1, 38.9, 23.1, 14.8 ppm. **IR** νmax (film). 2925, 1592, 1555, 1493, 982, 753, 682 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{11}H_{13}BrN_2Na$ $[M+Na]^+$: 275.0154; found: 275.0156.



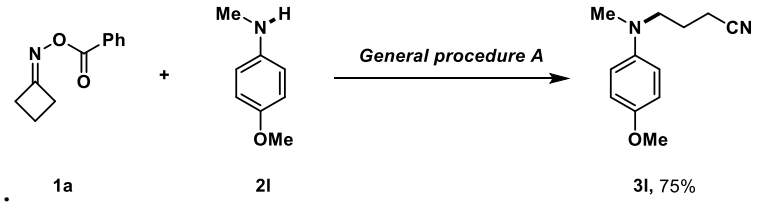
1a **2j** **3j**, 63%

Product **3j** was obtained in 63% yield (31.8 mg, 0.13 mmol) colorless oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 12/1) following the general procedure A, except that **2j** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.18 (d, J = 9.0 Hz, 2H), 6.63 (d, J = 9.0 Hz, 2H), 3.44 (t, J = 7.2 Hz, 2H), 2.93 (s, 3H), 2.38 (t, J = 7.2 Hz, 2H), 1.93 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.7, 129.2, 122.1, 119.4, 113.9, 51.5, 39.0, 23.1, 14.9 ppm; **IR** νmax (film). 2933, 1596, 1501, 1374, 1191, 1120, 811 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{11}H_{13}B_rN2Na$ $[M+Na]^+$: 275.0154; found: 275.0155.



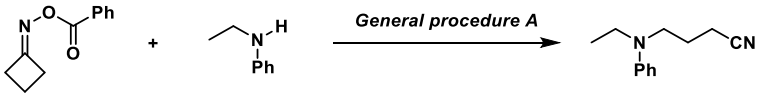
1a **2k** **3k**, 81%

Product **3k** was obtained in 81% yield (33.7 mg, 0.16 mmol) as colorless oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 12/1) following the general procedure A, except that **2k** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.31 (d, J = 9.0, 2H), 6.59 (d, J = 9.0, 2H), 3.44 (t, J = 7.2 Hz, 2H), 2.93 (s, 3H), 2.38 (t, J = 7.2 Hz, 2H), 1.93 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.0, 132.1, 119.3, 114.3, 109.2, 51.3, 39.0, 23.1, 14.9 ppm; **IR** νmax (film). 2920, 2850, 1650, 1472, 1339, 1277, 1012, 751 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{11}H_{13}ClN_2Na$ $[M+Na]^+$: 231.0659; found: 231.0664.



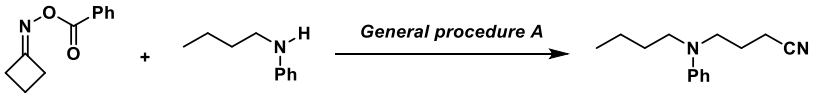
1a **2l** **3l**, 75%

Product **3l** was obtained in 75% yield (30.6 mg, 0.15 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 10/1) following the general procedure A, except that **2l** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.84 (d, J = 9.0 Hz, 2H), 6.75 (d, J = 9.0 Hz, 2H), 3.76 (s, 3H), 3.34 (t, J = 7.2 Hz, 2H), 2.86 (s, 3H), 2.40 (t, J = 7.2 Hz, 2H), 1.91 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.5, 144.3, 119.7, 115.6, 115.0, 55.9, 52.7, 39.8, 23.2, 14.9 ppm; **IR** νmax (film). 2921, 2850, 2367, 1512, 1245, 1083, 1035, 817 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{12}H_{16}N_2NaO$ $[M+Na]^+$: 227.1155; found: 227.1158.



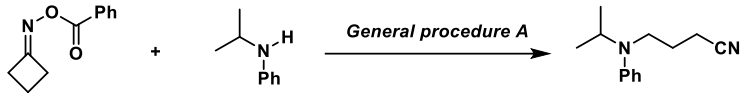
1a **2m** **3m**, 80%

Product **3m** was obtained in 80% yield (30.1 mg, 0.16 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 10/1) following the general procedure A, except that **2m** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$)δ 7.23 (t, J = 7.8 Hz, 2H), 6.70 (d, J = 7.8 Hz, 3H), 3.40 (t, J = 7.2 Hz, 2H), 3.37 (t, J = 7.2 Hz, 2H),2.39 (t, J = 7.2 Hz, 2H), 1.94 (tt, J = 7.2, 7.2 Hz, 2H), 1.15 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.6, 129.5, 119.6, 116.8, 112.9, 48.8, 45.9, 23.7, 14.8, 12.3 ppm; **IR** νmax (film). 2993, 1770, 1504, 1374, 1244, 1057, 913, 745 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{12}H_{17}N_2$ $[M+H]^+$: 189.1386; found: 189.1388.



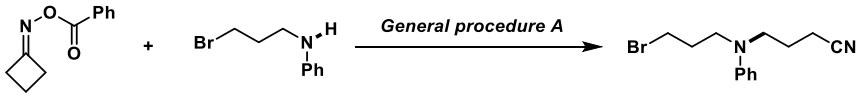
1a **2n** **3n**, 62%

Product **3n** was obtained in 62% yield (26.8 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 6/1) following the general procedure A, except that **2n** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 (t, J = 7.8 Hz, 2H), 6.71 – 6.68 (m, 3H), 3.42 (t, J = 7.2 Hz, 2H), 3.28 (t, J = 7.2 Hz, 2H), 2.38 (t, J = 7.2 Hz, 2H), 1.93 (tt, J = 7.2, 7.2 Hz, 2H), 1.56 (tt, J = 7.2, 7.2 Hz, 2H), 1.38 – 1.31 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.8, 129.5, 119.6, 116.7, 112.8, 51.8, 49.5, 29.4, 23.5, 20.4, 14.8, 14.1 ppm; **IR** νmax (film).2957, 2926, 2856, 1598, 1504, 1463, 1372, 1282, 747, 693 cm^{-1}; **HRMS (ESI) m/z** calcd for $C_{14}H_{21}N_2$ $[M+H]^+$: 217.1699; found: 217.1693.



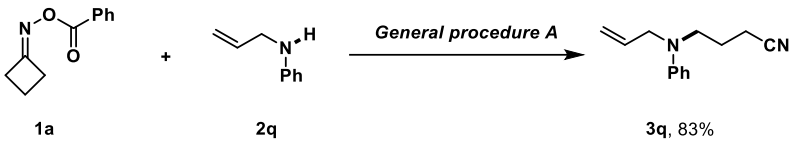
1a **2o** **3o**, 60%

Product **3o** was obtained in 60% yield (24.3 mg, 0.12 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 13/1) following the general procedure A, except that **2o** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 (t, J = 7.8 Hz, 2H), 6.82 (d, J = 7.8 Hz, 2H), 6.78 (t, J = 7.8 Hz, 1H), 3.98 – 3.93 (m, 1H), 3.24 (t, J = 7.2 Hz, 2H), 2.37 (t, J = 7.2 Hz, 2H), 1.87 (tt, J = 7.2, 7.2 Hz, 2H), 1.17 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.6, 129.3, 119.7, 118.4, 116.2, 51.3, 42.0, 24.3, 20.1, 14.8 ppm; **IR** νmax (film). 2956, 2920, 2850, 1770, 1459, 1376, 1244, 1098, 1059, 747 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{13}H_{19}N_2$ $[M+H]^+$: 203.1543; found: 203.1540.



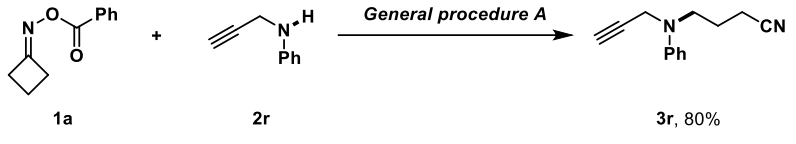
1a **2p** **3p**, 71%

Product **3p** was obtained in 71% yield (39.8 mg, 0.14 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 6/1) following the general procedure A, except that **2p** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 (t, J = 7.8 Hz, 2H), 6.76 – 6.73 (m, 3H), 3.47(tt, J = 7.2, 7.2 Hz, 4H), 3.44 (t, J = 3.0 Hz, 2H), 2.39 (t, J = 7.2 Hz, 2H), 2.13 (tt, J = 7.2, 7.2 Hz, 2H), 1.95 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.4, 129.6, 119.4, 117.7, 113.5, 50.1, 49.9, 31.3, 30.1, 23.4, 14.9 ppm. **IR** νmax (film). 2924, 1638, 1597, 1503, 1363, 1256, 749, 694 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{13}H_{17}BrN_2Na$ $[M+Na]^+$: 303.0467; found: 303.0465.



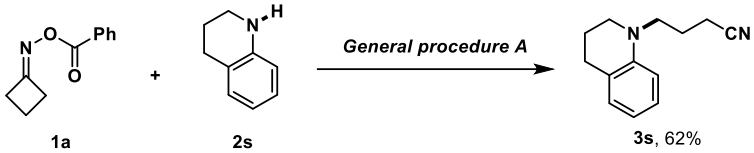
1a 2q **3q**, 83%

Product **3q** was obtained in 83% yield (33.2 mg, 0.17 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 8/1) following the general procedure A, except that **2q** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 2H), 6.74 – 6.71 (m, 3H), 5.87 – 5.81 (m, 1H), 5.18 (dd, J = 4.2, 1.8 Hz, 1H), 5.16 (dd, J = 4.2, 1.8 Hz, 1H), 3.93 (d, J = 4.8 Hz, 2H), 3.45 (t, J = 7.2 Hz, 2H), 2.40 (t, J = 7.2 Hz, 2H), 1.96 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.0, 133.9, 129.5, 119.5, 117.2, 116.8, 112.9, 54.1, 49.3, 23.6, 14.9 ppm; **IR** νmax (film). 2918, 2849, 1598, 1505, 1276, 926, 750, 693 cm^{-1}; **HRMS (ESI) m/z** calcd for $C_{13}H_{17}N_2$ $[M+H]^+$: 201.1386; found: 201.1390.



1a 2r **3r**, 80%

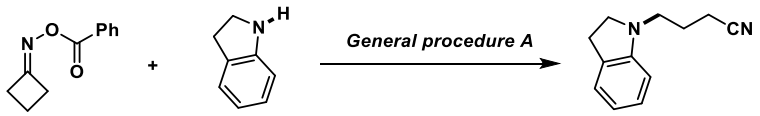
Product **3r** was obtained in 80% yield (31.7 mg, 0.16 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 12/1) following the general procedure A, except that **2r** was used to replace **2a**. **^{1}H NMR** (600 z, $CDCl_3$) δ 7.28 (t, J = 7.8 Hz, 2H), 6.87 (d, J = 7.2 Hz, 2H), 6.84 (t, J = 7.2 Hz, 1H), 4.02 (s, 2H), 3.50 (t, J = 7.2 Hz, 2H), 2.43 (t, J = 7.2 Hz, 2H), 2.23 (s, 1H), 2.00 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.8, 129.5, 119.5, 119.0, 114.8, 79.8, 72.7, 49.8, 41.3, 23.6, 14.9 ppm; **IR** νmax (film). 2995, 1770, 1759, 1374, 1245, 1057, 913, 747 cm^{-1}; **HRMS (ESI) m/z** calcd for $C_{13}H_{14}N_2Na[M+Na]^+$: 221.1049; found: 221.1055.



1a 2s **3s**, 62%

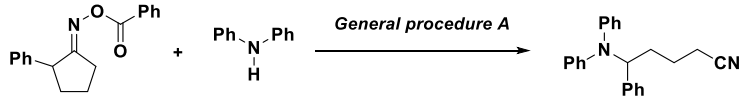
Product **3s** was obtained in 62% yield (24.8 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 8/1) following the general procedure A, except that **2s** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.05 (t, J = 7.8 Hz, 1H), 6.96 (d, J = 7.2 Hz, 1H), 6.60 (t, J = 7.2 Hz, 1H), 6.56 (d, J = 7.8 Hz, 1H), 3.40 (t, J = 7.2 Hz, 2H), 3.28 (t, J = 6.0 Hz, 2H), 2.76 (t, J = 6.0 Hz, 2H), 2.41 (t, J = 7.2 Hz, 2H), 1.99 – 1.94 (m, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.0, 129.5, 127.3, 122.9, 119.6, 116.4, 110.6, 50.2, 50.1, 28.1, 22.9, 22.3, 14.9

ppm; **IR** νmax (film). 2923, 1744, 1515, 1451, 1260, 1060, 1024, 880, 843, 812, 706 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{13}H_{16}N_2Na[M+Na]^+$: 223.1206; found: 223.1202.



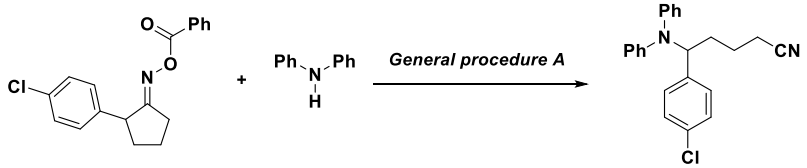
1a **2t** **3t**, 60%

Product **3t** was obtained in 60% yield (22.3 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 9/1) following the general procedure A, except that **2t** was used to replace **2a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.09 – 7.06 (m, 2H), 6.68 (t, J = 7.2 Hz, 1H), 6.50 (d, J = 7.8 Hz, 1H), 3.33 (t, J = 8.4 Hz, 2H), 3.19 (t, J = 7.2 Hz, 2H), 2.98 (t, J = 8.4 Hz, 2H), 2.48 (t, J = 7.2 Hz, 2H), 1.97 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.4, 130.0, 127.5, 124.7, 119.6, 118.3, 107.1, 53.7, 48.3, 28.7, 24.1, 14.8 ppm. **IR** νmax (film). 3063, 2927, 1742, 1689, 1492, 1451, 1399, 1260, 1059, 1024, 820, 705, 523 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{12}H_{14}N_2Na[M+Na]^+$: 209.1049; found: 209.1051.



1k **2a** **4j**, 51%

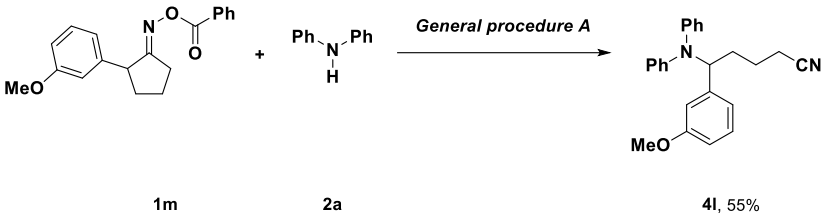
Product **4j** was obtained in 51% yield (33.3 mg, 0.10 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 6/1) following the general procedure A except that **1k** was used to replace **1a**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 (d, J = 6.0 Hz, 2H), 7.22 (d, J = 9.0 Hz, 4H), 7.20 (d, J = 9.0 Hz, 3H), 6.95 (t, J = 7.2 Hz, 2H), 6.83 (d, J = 9.0 Hz, 4H), 5.26 (t, J = 7.8 Hz, 1H), 2.35 – 2.26 (m, 2H), 2.23 – 2.16 (m, 1H), 2.15 – 2.09 (m, 1H), 1.83 – 1.73(m, 1H), 1.74 – 1.67 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.8, 141.1, 129.3, 128.5, 127.9, 127.5, 123.0, 122.1, 119.5, 61.6, 31.5, 23.2, 17.4 ppm. **IR** νmax (film). 2922, 2852, 1586, 1492, 1260, 800, 723, 698 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{23}H_{22}N_2Na$ $[M+Na]^+$: 349.1675; found: 349.1672.



1l **2a** **4k**, 53%

Product **4k** was obtained in 53% yield (38.2 mg, 0.11 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 7/1) following the general procedure A except

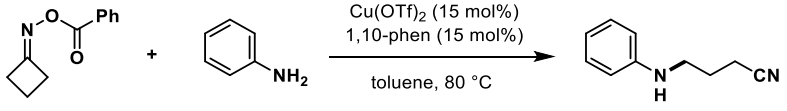
that **1l** was used to replace **1a.** **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 6H), 7.15 (d, J = 8.4 Hz, 2H), 6.97 (tt, J = 7.8, 1.2 Hz, 2H), 6.83 – 6.81 (m, 4H), 5.23 (t, J = 7.8 Hz, 1H), 2.35 – 2.27 (m, 2H), 2.20 – 2.15 (m, 1H), 2.11 – 2.05 (m, 1H), 1.83 – 1.76 (m, 1H), 1.71 – 1.64 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.5, 139.6, 133.3, 129.4, 129.3, 128.7, 123.0, 122.4, 119.4, 61.0, 31.5, 23.1, 17.4 ppm. **IR** νmax (film). 2950, 2908, 2843, 1786, 1504, 1248, 1059, 784 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{23}H_{21}ClN_2Na$ $[M+Na]^+$: 383.1285; found: 383.1283.



1m **2a** **4l**, 55%

Product **4l** was obtained in 55% yield (39.2 mg, 0.11 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 6/1) following the general procedure A except that **1m** was used to replace **1a.** **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 5H), 6.95 (tt, J = 7.2, 1.2 Hz, 2H), 6.87 – 6.83 (m, 5H), 6.77 – 6.76 (m, 2H), 5.21 (t, J = 7.8 Hz, 1H), 3.70 (s, 3H), 2.35 – 2.24 (m, 2H), 2.21 – 2.14 (m, 1H), 2.13 – 2.07 (m, 1H), 1.82 – 1.75 (m, 1H), 1.73 – 1.66 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.7, 146.8, 142.8, 129.5, 129.3, 123.1, 122.1, 120.3, 119.5, 113.7, 112.8, 61.7, 55.3, 31.6, 23.2, 17.4 ppm. **IR** νmax (film). 2934, 2878, 2732, 1790, 1424, 824, 778 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{24}H_{24}N_2NaO$ $[M+Na]^+$: 379.1781; found: 379.1779.

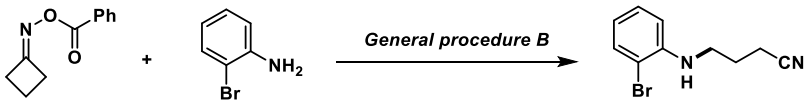
General procedure B



1a **2u** **3u**, 51%

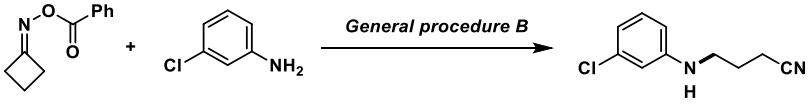
To a 10 mL dry Schlenk flask was added **1a** (37.8 mg, 0.20 mmol, 1.0 equiv), $Cu(OTf)_2$ (10.9 mg, 0.03 mmol, 0.15 equiv), 1,10-phen (5.4 mg, 0.03 mmol, 0.15 equiv) and 2 mL dry toluene. Then **2u** (36.5 μL, 0.40 mmol, 2.0 equiv) was added at ambient temperature, and the reaction was degassed for three times with argon. The mixture was allowed to stir at 80 °C for 1.5 h. After completed (as monitored by TLC), the reaction was cooled to room temperature. The mixture was diluted with sat.$NaHCO_3$ and extracted with EA for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 8/1) afforded the desired product **3u** in 51% yield (16.3 mg, 0.10 mmol) as yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.19 (t, J = 7.8 Hz, 2H), 6.74 (t, J = 7.8 Hz, 1H), 6.62

(d, J = 7.8 Hz, 2H), 3.71 (s, 1H), 3.31 (t, J = 7.2 Hz, 2H), 2.47 (t, J = 7.2 Hz, 2H), 1.96 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.6, 129.5, 119.5, 118.1, 113.0, 42.4, 25.4, 14.9 ppm; **IR** νmax (film). 2995, 1770, 1759, 1603, 1374, 1246, 1057, 913, 747 cm^{-1}; **HRMS (ESI) m/z** calcd for $C_{10}H_{13}N_2$ $[M+H]^+$: 161.1073; found: 161.1062.



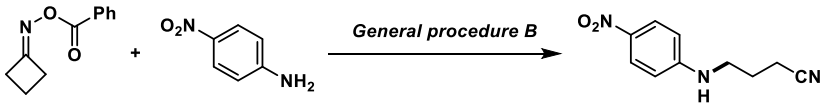
1a 2v 3v, 70%

Product **3v** was obtained in 70% yield (33.3 mg, 0.14 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 14/1) following the general procedure B, except that **2v** was used to replace **2u**. **^{1}H NMR** (600 MHz, $CDCl_3$)) δ 7.42 (dd, J = 7.8, 1.8 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 6.64 (d, J = 7.8 Hz, 1H), 6.60 (t, J = 7.8 Hz, 1H), 4.33 (s, 1H), 3.35 (dt, J = 6.0, 6.0 Hz, 2H), 2.47 (t, J = 7.2 Hz, 2H), 1.99 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.3, 132.7, 128.7, 119.3, 118.4, 111.3, 110.0, 42.2, 25.1, 14.9 ppm. **IR** νmax (film). 2993, 1770, 1595, 1507, 1374, 1244, 1054, 1018, 744 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{10}H_{11}BrN_2Na$ $[M+Na]^+$: 260.9998; found: 260.9999.



1a 2w 3w, 54%

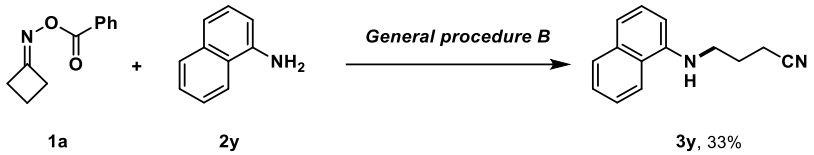
Product **3w** was obtained in 54% yield (21.0 mg, 0.11 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 10/1) following the general procedure B, except that **2w** was used to replace **2u**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.08 (t, J = 7.8 Hz, 1H), 6.69 (dd, J = 7.8, 1.8 Hz, 1H), 6.57 (t, J = 1.8 Hz, 1H), 6.48 (dd, J = 7.8, 1.8 Hz, 1H), 3.85 (s, 1H), 3.28 (t, J = 7.2 Hz, 2H), 2.46 (t, J = 7.2 Hz, 2H), 1.95 (tt, J =7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.8, 135.2, 130.5, 119.3, 117.8, 112.5, 111.3, 42.2, 25.1, 14.9 ppm; **IR** νmax (film). 2956, 2925, 2854, 1598, 1484, 1090, 987,36, 764, 682 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{10}H_{12}ClN_2$ $[M+H]^+$: 195.0684; found: 195.0681.



1a 2x 3x, 60%

Product **3x** was obtained in 60% yield (24.6 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 8/1) following the general procedure B, except that **2x** was used to replace **2u**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (d, J = 9.0 Hz, 2H), 6.57 (dd, J

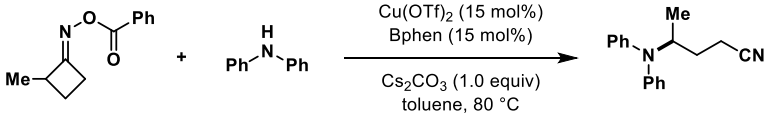
= 9.0 Hz, 2H), 4.76 (s, 1H), 3.44 (dt, J = 6.0, 6.0 Hz, 2H), 2.51 (t, J = 7.2 Hz, 2H), 2.03 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 152.9, 138.6, 126.6, 119.0, 111.4, 41.9, 24.9, 15.0 ppm. **IR** νmax (film). 3370, 2927, 1600, 1503, 1472, 1305, 1185, 1111, 833, 752, 694 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{10}H_{12}N_3O_2$ $[M+H]^+$: 206.0924; found: 206.0933.



1a **2y** **3y**, 33%

Product **3y** was obtained in 33% yield (13.9 mg, 0.07 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 6/1) following the general procedure B, except that **2y** was used to replace **2u**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 7.2 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 6.87 (dd, J = 9.0, 2.4 Hz, 1H), 6.82 (s, 1H), 3.89 (s, 1H), 3.42 (t, J = 7.2 Hz, 2H), 2.50 (t, J = 7.2 Hz, 2H), 2.04 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.2, 135.2, 129.3, 127.83, 127.78, 126.6, 126.1, 122.5, 119.5, 118.0, 104.7, 42.5, 25.2, 15.1 ppm. **IR** νmax (film). 2934, 2238, 1737, 1592, 1555, 1494, 1372, 1121, 982, 761, 683 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{14}H_{14}N_2Na$ $[M+Na]^+$: 233.1049; found: 233.1045.

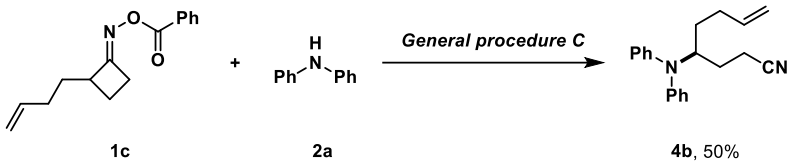
General procedure C



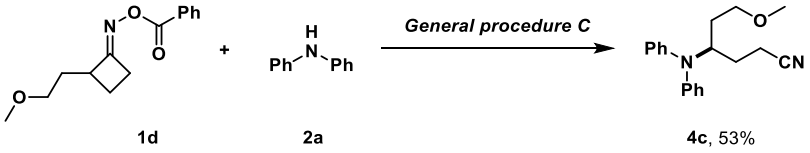
1b **2a** **4a**, 55%

To a 10 mL dry Schlenk flask was added **1b** (81.2 mg, 0.40 mmol, 2.0 equiv), $Cu(OTf)_2$ (10.8 mg, 0.03 mmol, 0.15 equiv), bathophenanthroline (10.0 mg, 0.03 mmol, 0.15 equiv), Cs_2CO_3 (65.2 mg, 0.20 mmol, 1.0 equiv) and 2mL dry toluene. Then **2a** (33.8 mg, 0.20 mmol, 1.0 equiv) was added at ambient temperature, and the reaction was degassed for three times with argon. The mixture was allowed to stir at 80 °C for 1.5 h. After completed (as monitored by TLC), the reaction was cooled to room temperature. The mixture was diluted with sat.$NaHCO_3$ and extracted with EA for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 8/1) afforded the desired product **4a** in 55% yield (27.5 mg, 0.11 mmol) as yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (t, J = 7.8 Hz, 4H), 7.02 (t, J = 7.8 Hz, 2H), 6.87 (d, J = 7.8 Hz, 4H), 4.30 (qt, J = 7.2, 7.2 Hz, 1H), 2.46 (t, J = 7.2 Hz, 2H), 2.01 (dt, J = 21.6, 7.2 Hz, 1H), 1.72 (dt, J = 21.6, 7.2 Hz, 1H), 1.24 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.3, 129.5, 123.1, 122.5,

119.6, 52.2, 30.9, 18.7, 15.0 ppm; **IR** νmax (film).2956, 2919, 2850, 1770, 1494, 1376, 1244, 1057, 747, 701 cm^{-1}; **HRMS (ESI) m/z** calcd for $C_{17}H_{19}N_2$ $[M+H]^+$: 251.1543; found: 251.1548.

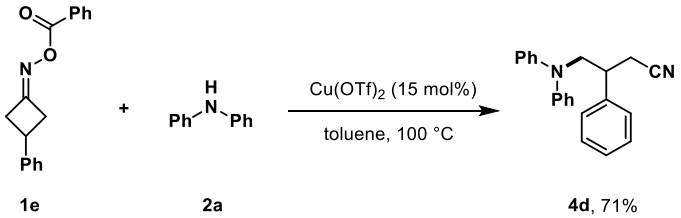


Product **4b** was obtained in 50% yield (29.0 mg, 0.10 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 12/1) following the general procedure C, except that **1c** was used to replace **1b**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 4H), 7.00 (t, J = 7.2 Hz, 2H), 6.90 (d, J = 7.8 Hz, 4H), 5.82 – 5.74 (m, 1H), 5.02 (dd, J = 9.6, 1.2 Hz, 1H), 5.00 (d, J = 1.2 Hz, 1H), 4.21 – 4.16 (m, 1H), 2.51 – 2.41 (m, 2H), 2.24 – 2.14 (m, 2H), 1.96 – 1.89 (m, 2H), 1.87 – 1.81 (m, 1H), 1.61 – 1.55 (m, 1H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 146.8, 137.6, 129.6, 123.1, 122.4, 119.8, 115.8, 57.1, 33.0, 31.2, 29.2, 15.0 ppm; **IR** νmax (film). 2994, 1770, 1493, 1383, 1244, 1057, 913, 746 cm^{-1}; **HRMS (ESI) m/z** calcd for $C_{20}H_{22}N_2Na$ $[M+Na]^+$: 313.1675; found: 313.1674.

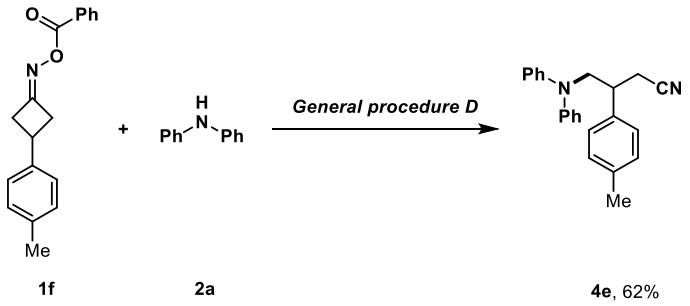


Product **4c** was obtained in 53% yield (31.2 mg, 0.11 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 10/1) following the general procedure C, except that **1d** was used to replace **1b**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 4H), 7.00 (t, J = 7.2Hz, 2H), 6.92 (dd, J = 8.4, 1.2 Hz, 4H), 4.42 – 4.37 (m, 1H), 3.45 – 3.43 (m, 2H), 3.29 (s, 3H), 2.54 – 2.48 (m, 1H), 2.44 – 2.39 (m, 1H), 2.02 – 1.90 (m, 3H), 1.73 (dt, J = 20.4, 6.0 Hz, 1H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 147.0, 129.6, 123.1, 122.4, 119.8, 69.7, 58.8, 55.0, 33.8, 30.0, 15.0 ppm. **IR** νmax (film) 2921, 2850, 1629, 1524, 830, 474 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{19}H_{22}N_2NaO[M+Na]^+$: 317.1624; found: 317.1625.

General procedure D

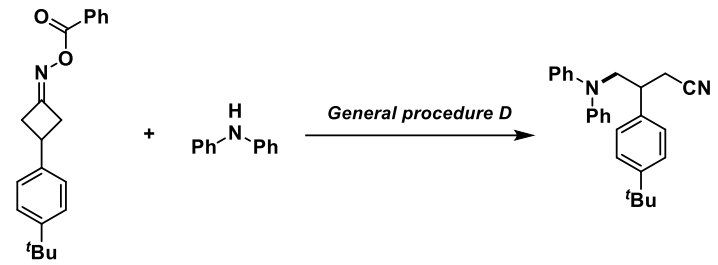


To a 10 mL dry Schlenk flask was added **1e** (106 mg, 0.40 mmol, 2.0 equiv), $Cu(OTf)_2$ (10.8 mg, 0.03 mmol, 0.15 equiv) and 2 mL dry toluene. Then **2a** (33.8 mg, 0.20 mmol, 1.0 equiv) was added at ambient temperature, and the reaction was degassed for three times with argon. The mixture was allowed to stir at 100 °C for 0.5 h. After completed (as monitored by TLC), the reaction was cooled to room temperature. The mixture was diluted with sat.$NaHCO_3$ and extracted with EA for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 8/1) afforded the desired product **4d** in 71% yield (44.3 mg, 0.14 mmol) as yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 3H), 7.28 – 7.22 (m, 6H), 6.99 (t, J = 7.5 Hz, 2H), 6.90 (d, J = 7.5 Hz, 4H), 4.09 (dd, J = 15.0, 8.5 Hz, 1H), 3.96 (dd, J = 15.0, 6.0 Hz, 1H), 3.45 – 3.39 (m, 1H), 2.82 (dd, J = 16.5, 6.0 Hz, 1H), 2.73 (dd, J = 16.5, 8.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.1, 139.6, 129.6, 129.2, 128.1, 127.6, 122.3, 121.6, 118.5, 57.2, 40.7, 22.2 ppm; **IR** νmax (film).2956, 2923, 2852, 1587, 1493, 1242, 750, 696 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{22}H_{20}N_2Na$ $[M+Na]^+$: 335.1519; found: 335.1515.



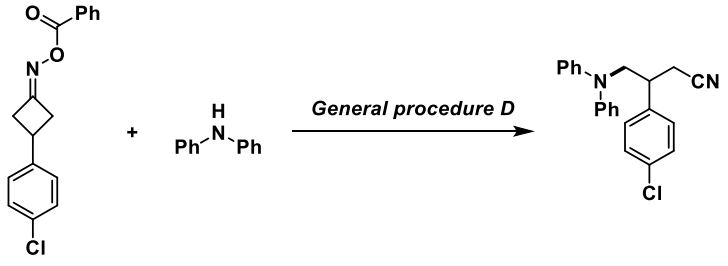
1f **2a** **4e**, 62%

Product **4e** was obtained in 62% yield (40.4 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 15/1) following the general procedure D, except that **1f** was used to replace **1e**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26 (t, J = 7.8 Hz, 4H), 7.16 (d, J = 7.8 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 6.98 (t, J = 7.8 Hz, 2H), 6.91 (d, J = 7.8 Hz, 4H), 4.05 (dd, J = 14.4, 8.4 Hz, 1H), 3.94 (dd, J = 14.4, 6.0 Hz, 1H), 3.40 – 3.35(m, 1H), 2.79 (dd, J = 16.8, 6.0 Hz, 1H), 2.70 (dd, J = 16.8, 8.4 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.2, 137.7, 136.5, 129.8, 129.6, 127.4, 122.3, 121.6, 118.6, 57.2, 40.3, 22.3, 21.2 ppm; **IR** νmax (film). 2994, 1770, 1588, 1493, 1374, 1244, 1057, 913, 747, 696 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{23}H_{22}N_2Na$ $[M+Na]^+$: 349.1675; found: 349.1684.



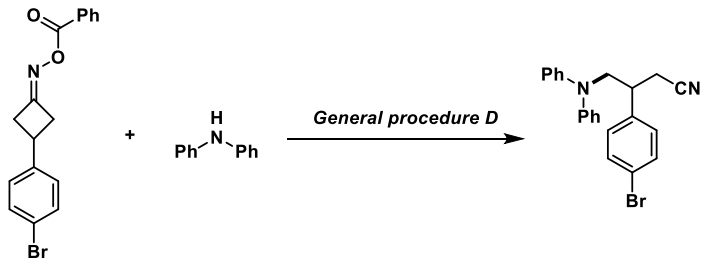
1g **2a** **4f**, 60%

Product **4f** was obtained in 60% yield (44.2 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 13/1) following the general procedure D, except that **1g** was used to replace **1e**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, J = 7.8 Hz, 2H), 7.25 (t, J = 7.8 Hz, 4H), 7.15 (d, J = 8.4 Hz, 2H), 6.98 (t, J = 7.8 Hz, 2H), 6.89 (d, J = 8.4 Hz, 4H), 4.08 (dd, J = 15.0, 8.4 Hz, 1H), 3.94 (dd, J = 15.0, 6.0 Hz, 1H), 3.42 – 3.38 (m, 1H), 2.80 (dd, J = 16.8, 6.0 Hz, 1H), 2.72 (dd, J = 16.8, 8.4 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 151.0, 148.2, 136.5, 129.6, 127.2, 126.0, 122.2, 121.6, 118.7, 57.2, 40.2, 34.7, 31.5, 22.2 ppm; **IR** νmax (film).2958, 2926, 1766, 1494, 1381, 1243, 1058, 747, 696 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{26}H_{28}N_2Na$ $[M+Na]^+$: 391.2145; found: 391.2147.



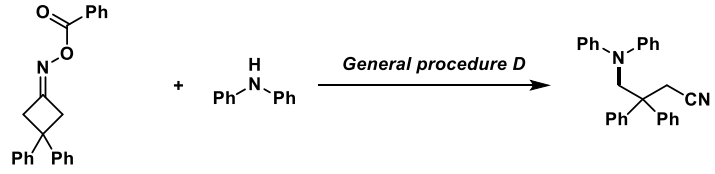
1h **2a** **4g**, 70%

Product **4g** was obtained in 70% yield (48.5 mg, 0.14 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 14/1) following the general procedure D, except that **1h** was used to replace **1e**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 (d, J = 7.8 Hz, 2H), 7.26 (t, J = 7.8 Hz, 4H), 7.16 (d, J = 7.8 Hz, 2H), 6.99 (t, J = 7.8 Hz, 2H), 6.89 (d, J = 7.8 Hz, 4H), 4.06 (dd, J = 15.0, 8.4 Hz, 1H), 3.94 (dd, J = 15.0, 6.0 Hz, 1H), 3.43 – 3.36 (m, 1H), 2.79 (dd, J = 16.8, 6.0 Hz, 1H), 2.70 (dd, J = 16.8, 8.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.0, 138.1, 133.9, 129.7, 129.3, 129.0, 122.5, 121.6, 118.2, 57.0, 40.2, 22.2 ppm; **IR** νmax (film). 2994, 1770, 1493, 1375, 1244, 1057, 913, 746 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{22}H_{19}ClN_2Na$ $[M+Na]^+$: 369.1129; found: 369.1124.



1i 2a **4h**, 52%

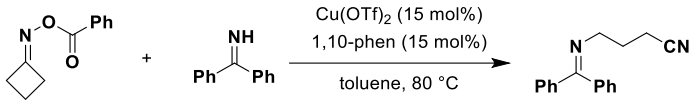
Product **4h** was obtained in 52% yield (40.6 mg, 0.10 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 18/1) following the general procedure D, except that **1i** was used to replace **1e**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.26 (t, J = 7.8 Hz, 4H), 7.10 (d, J = 8.4 Hz, 2H), 6.99 (t, J = 7.8 Hz, 2H), 6.88 (d, J = 7.8 Hz, 4H), 4.05 (dd, J = 15.0, 8.4 Hz, 1H), 3.94 (dd, J = 15.0, 6.0 Hz, 1H), 3.41 – 3.37 (m, 1H), 2.79 (dd, J = 16.8, 6.0 Hz, 1H), 2.70 (dd, J = 16.8, 8.4 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.0, 138.5, 132.3, 129.7, 129.3, 122.4, 122.0, 121.5, 118.2, 56.9, 40.2, 22.1 ppm. **IR** νmax (film).2994, 1770, 1491, 1374, 1244, 1057, 913, 746 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{22}H_{19}BrN_2Na$ $[M+Na]^+$: 413.0624; found: 413.0625.



1j 2a **4i**, 83%

Product **4i** was obtained in 83% yield (64.4 mg, 0.17 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 12/1) following the general procedure D, except that **1j** was used to replace **1e**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.34 (t, J = 7.8 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.16 (dt, J = 15.0, 7.8 Hz, 6H), 6.99 (t, J = 7.2 Hz, 2H), 6.74 (dd, J = 13.8, 7.8 Hz, 6H), 3.79 (d, J = 13.2 Hz, 1H), 3.33 (d, J = 16.2 Hz, 1H), 3.14 (d, J = 13.2 Hz, 1H), 2.76 (d, J = 16.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.7, 144.4, 135.8, 131.1, 129.2, 129.1, 128.3, 127.9, 127.3, 126.5, 125.9, 122.9, 118.6, 65.8, 44.4, 27.6 ppm. **IR** νmax (film).2923, 1770, 1759, 1491, 1445, 1246, 1060, 913, 745, 701 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{28}H_{25}N_2$ $[M+H]^+$: 389.2012; found: 389.2022.

Part 5. Procedure and Characteristic Data for Products 5-10



1a **5**, 62%

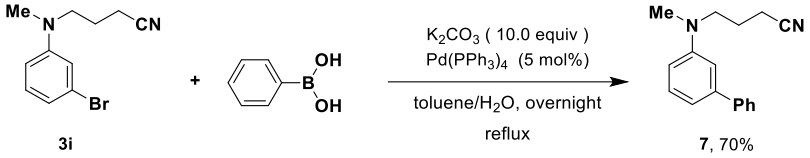
Product **5** was synthesized following the general procedure A: To a 10 mL dry Schlenk flask was added **1a** (75.6 mg, 0.40 mmol, 2.0 equiv), $Cu(OTf)_2$ (10.8 mg, 0.03 mmol, 0.15 equiv), 1,10-phen (5.4 mg, 0.03 mmol, 0.15 equiv) and 2 mL dry toluene. Then benzophenone imine (33.6 μL, 0.20 mmol, 1.0 equiv) was added at ambient temperature, and the reaction was degassed for three times with argon. The mixture was allowed to stir at 80 °C for 1.5 h. After completed (as monitored by TLC), the reaction was cooled to room temperature. The mixture was diluted with sat.$NaHCO_3$ and extracted with EA for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 14/1) afforded the desired product **5** in 62% yield (30.8 mg, 0.12 mmol) as yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61 (d, J = 7.2 Hz, 2H), 7.47 (t, J = 7.2 Hz, 2H), 7.44 (d, J = 7.2 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.2 Hz, 2H), 7.15 (d, J = 7.2 Hz, 2H), 3.43 (t, J = 6.6 Hz, 2H), 2.54 (t, J = 6.6 Hz, 2H), 2.02 (tt, J = 6.6, 6.6 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.6, 139.5, 136.7, 130.3, 128.8, 128.7, 128.4, 128.2, 127.7, 120.0, 51.6, 27.2, 15.2 ppm. **IR** νmax (film). 2921, 2851, 1624, 1446, 1275, 751, 642,428 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{17}H_{16}N_2Na$ $[M+Na]^+$: 271.1206; found: 271.1210.

The procedure for the synthesis of compound 6

5 **6**, 92%

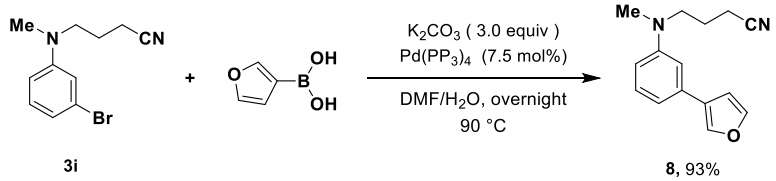
Substrate **5** (74.4 mg, 0.30 mmol, 1.0 equiv) was added to the solution of HCl (1.0 M)/CH_3OH (6 mL, v:v = 1:1). After being stirred at room temperature for 3 h, the mixture was concentrated in *vacuo* and the residue was diluted with water and extracted with EA for three times. The water layer was concentrated in *vacuo*. The product **6** was obtained in 92% yield (33.1 mg, 0.28 mmol) as white solid (m.p.127 °C). **^{1}H NMR** (600 MHz, D_2O) δ 3.12 (t, J = 7.2 Hz, 2H), 2.64 (t, J = 7.2 Hz, 2H), 2.05 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, D_2O) δ 120.5, 38.2, 22.7, 14.2 ppm. **IR** νmax (film). 2962, 1746, 1450, 1243, 1082, 1064, 1024, 749, 701 cm^{-1}.

The procedure for the synthesis of compound 7



To a solution of substrate **3i** (101 mg, 0.40 mmol, 1.0 equiv), phenylboronic acid (146 mg, 1.2 mmol, 3.0 equiv) and tetrakis(triphenylphosphine)palladium (23.1 mg, 0.02 mmol, 5.0 mol%) in 20 mL toluene was added the solution of K_2CO_3 (4.0 mL, 4.0 mmol, 10.0 equiv, 1.0 M in H_2O). The reaction was refluxed overnight under N_2. After completed (as monitored by TLC), the reaction was cooled to room temperature. The mixture was diluted with water, extracted with EA for three times and dried over anhydrous Na_2SO_4. The combined organic phase was concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 12/1) afforded the coupled product **7** in 70% yield (70.0 mg, 0.28 mmol) as yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.4, 1.8 Hz, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.34 (t, J = 7.8 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H) 6.96 (d, J = 7.8 Hz, 1H), 6.90 (t, J = 1.8 Hz, 1H), 6.73 (dd, J = 8.4, 2.4 Hz, 1H), 3.52 (t, J = 7.2 Hz, 2H), 3.01 (s, 3H), 2.40 (t, J = 7.2 Hz, 2H), 1.98 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.5, 142.7, 142.1, 129.8, 128.8, 127.42, 127.35, 119.5, 116.4, 111.73, 111.66, 51.4, 39.1, 23.4, 14.9 ppm. **IR** νmax (film).2924, 2854, 1770, 1759, 1596, 1460, 1376, 1246, 1056, 913, 748, 697 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{17}H_{18}N_2Na$ $[M+Na]^+$: 273.1362; found: 273.1364.

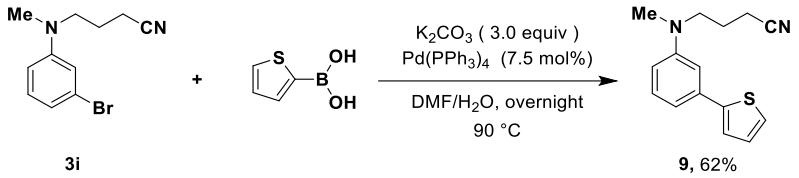
The procedure for the synthesis of compound 8



The substrate **3i** (101 mg, 0.40 mmol, 1.0 equiv), 3-furanboronic acid (67.1 mg, 0.60 mmol, 1.5 equiv) and tetrakis(triphenylphosphine)palladium (34.7 mg, 0.03 mmol, 7.5 mol%) was added into DMF (1.7 mL) and the solution of K_2CO_3 (1.2 mL, 1.2 mmol, 3.0 equiv, 1.0 M in H_2O) was added into the mixture under N_2. The reaction was allowed to stir for 12 h at 90 °C. After completed (as monitored by TLC), the reaction was cooled to room temperature, filtered and the filter residue was washed with EA. The combined organic phase was concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 12/1) afforded the coupled product **8** in 93% yield (89.3 mg, 0.37 mmol) as blown oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.46 (t,

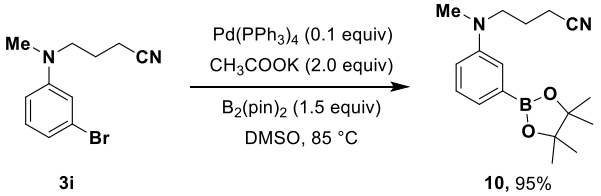
J = 1.8 Hz, 1H), 7.25 (t, J = 4.2 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 6.84 (s, 1H), 6.70 (s, 1H), 6.65 (dd, J = 7.8, 3.0 Hz, 1H), 3.50 (t, J = 7.2 Hz, 2H), 2.98 (s, 3H), 2.41 (t, J = 7.2 Hz, 2H), 1.97 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.6, 143.6, 138.7, 133.7, 129.9, 127.1, 119.6, 115.2, 111.6, 110.3, 109.2, 51.3, 38.9, 23.3, 14.9 ppm. **IR** νmax (film).2924, 1770, 1760, 1603, 1492, 1375, 1245, 1059, 913, 747 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{15}H_{16}N_2NaO$ $[M+Na]^+$: 263.1155; found: 263.1157.

The procedure for the synthesis of compound 9



The substrate **3i** (101 mg, 0.40 mmol, 1.0 equiv), 2-thiopheneboronic acid (76.8 mg, 0.60 mmol, 1.5 equiv) and tetrakis(triphenylphosphine)palladium (34.7 mg, 0.03 mmol, 7.5 mol%) was added into DMF (1.7 mL) and the solution of K_2CO_3 (1.2 mL, 1.2 mmol, 3.0 equiv, 1.0 M in H_2O) was added into the mixture under N_2. The reaction was allowed to stir for 12 h at 90 °C. After completed (as monitored by TLC), the reaction was cooled to room temperature, filtered and the filter residue was washed with EA. The combined organic phase was concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 12/1) afforded the coupled product **8** in 62% yield (63.5 mg, 0.25 mmol) as yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 (d, J = 3.6 Hz, 1H), 7.25 (t, J = 4.8 Hz, 2H), 7.07 (t, J = 4.8 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H), 6.94 (s, 1H), 6.67 (d, J = 7.8 Hz, 1H), 3.50 (t, J = 7.2 Hz, 2H), 3.00 (s, 3H), 2.40 (t, J = 7.2 Hz, 2H), 1.97 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.5, 145.2, 135.6, 130.0, 128.0, 124.7, 123.2, 119.5, 115.4, 112.0, 110.3, 51.4, 39.0, 23.3, 14.9 ppm. **IR** νmax (film). 2926, 1597, 1494, 1373, 1246, 1060, 913, 828, 747, 694 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{15}H_{16}N_2NaS$ $[M+Na]^+$: 279.0926; found: 279.0923.

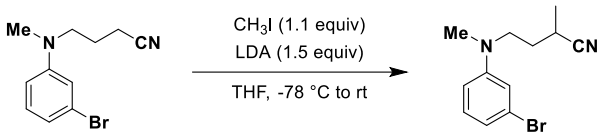
The procedure for the synthesis of compound 10



To a 10 mL dry Schlenk flask was added **3i** (127 mg, 0.50 mmol, 1.0 equiv), bis(pinacolato)diboron (191 mg, 0.75 mmol, 1.5 equiv), potassium acetate (98.1 mg, 1.0 mmol,

2.0 equiv), triphenylphosphine palladium (58.0 mg, 0.05 mmol, 0.1 equiv) and 2 mL anhydrous DMSO under N_2. The mixture was allowed to stir at 85 °C for 4 h. After completed (as monitored by TLC), the reaction was cooled to room temperature. The mixture was diluted with water and extracted with EA for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 6/1) afforded the desired product **10** in 95% yield (143 mg, 0.48 mmol) as yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (t, J =8.4 Hz, 1H), 7.20 (d, J = 7.2 Hz, 1H), 7.15 (d, J = 2.4 Hz, 1H), 6.85 (dd, J = 8.4, 2.4 Hz, 1H), 3.47 (t, J = 7.2 Hz, 2H), 2.98 (s, 3H), 2.38 (t, J = 7.2 Hz, 2H), 1.96 (tt, J = 7.2, 7.2 Hz, 2H), 1.34 (s, 12H).^{13}C NMR (150 MHz, $CDCl_3$) δ 148.7, 128.9, 123.9, 119.6, 118.9, 116.0, 83.8, 51.4, 39.1, 25.0, 23.4, 14.9 ppm. **IR** νmax (film). 2926, 1774, 1681, 1451, 1245, 1080, 1059, 1023, 913, 847, 744, 708 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{17}H_{25}BN_2NaO_2$ [M+Na]$^+$: 323.1901; found: 323.1907.

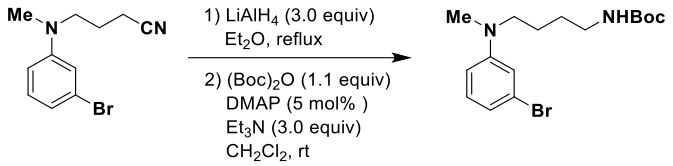
The procedure for the synthesis of compound 11



3i **11**, 65%

To a 10 mL dry Schlenk flask was added LDA (1.2 mL, 1.20 mmol, 1.5 equiv, 1.0 M in THF) at -78 °C under N_2. The **3i** (202 mg, 0.80 mmol, 1.0 equiv) in dry THF (0.5 mL) was added in Schlenk flask via syringe. The resulting solution was warmed to 0 °C for 30 minutes and cooled again to -78 °C. Methyl iodide (0.05 mL, 0.88 mmol, 1.1 equiv) was dissolved in dry THF (0.5 ml) at -78 °C. The lithiated species was transferred to the solution of CH_3I in THF dropwise at -78 °C. The reaction was stirred at -78 °C for 1 h. After completed (as monitored by TLC), the reaction was warmed to room temperature. The reaction was diluted with sat. NH_4Cl, and was extracted with Et_2O for three times. The combined organic phase was dried over anhydrous $MgSO_4$, and concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 8/1) afforded the desired product **11** in 65% yield (138 mg, 0.52 mmol) as yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (t, J = 8.4 Hz, 1H), 6.84 – 6.81 (m, 2H), 6.63 (dd, J = 8.4, 3.0 Hz, 1H), 3.57 – 3.51 (m, 1H), 3.45 (dt, J = 15.0, 7.8 Hz, 1H), 2.95 (s, 3H), 2.68 – 2.62 (m, 1H), 1.89 – 1.81 (m, 2H), 1.37 (d, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.1, 130.7, 123.8, 122.5, 119.7, 115.2, 111.0, 50.3, 38.9, 31.5, 23.4, 18.3 ppm. **IR** νmax (film). 2961, 1745, 1600, 1450, 1397, 1259, 1079, 1058, 1023, 879, 828, 705 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{12}H_{15}BrN_2Na$ [M+Na]$^+$: 289.0311; found: 289.0313.

The procedure for the synthesis of compound 12

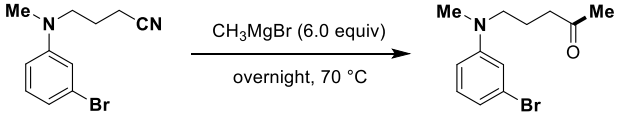


3i **12,** 45%

To a 10 mL dry Schlenk flask was added $LiAlH_4$ (45.5 mg, 1.2 mmol, 3.0 equiv) and dry Et_2O (5 mL) carefully at 0 °C. The **3i** (101 mg, 0.40 mmol, 1.0 equiv) was dissolved in Et_2O (2 mL) and added carefully to the solution of $LiAlH_4$. The mixture was refluxed for 2 h. After completed (as monitored by TLC), a solution of NaOH (10% in water) was added carefully. The mixture was extracted with Et_2O for three times. The combined organic phase was dried over anhydrous $MgSO_4$, and concentrated in *vacuo* to obtain the primary amine, which carried forward to the next step without further purification.

Di-tert-butyl dicarbonate (95.4 mg, 0.44 mmol, 1.1 equiv) and DMAP (2.4 mg, 0.02 mmol, 5 mol%) were added in DCM (2.6 mL) at room temperature and the mixture was stirred for 10 min. Et_3N (0.17 ml, 1.20 mmol, 3.0 equiv) and the above primary amine in DCM (2.4 mL) were added successively into the solution and the reaction was stirred overnight. After completed (as monitored by TLC), the reaction was diluted with water, extracted with DCM for three times and dried over $MgSO_4$. The solution was concentrated in *vacuo* and the residue was further purification by flash column chromatography (PE/EA = 6/1) to afford the desired product **12** in 45% overall yield (64.1 mg, 0.18 mmol) as yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.04 (t, J = 8.4 Hz, 1H), 6.77 (t, J = 2.4 Hz, 2H), 6.58 (dd, J = 8.4, 2.4 Hz, 1H), 4.53 (s, 1H), 3.31 (t, J = 7.2 Hz, 2H), 3.14 (dt, J = 7.2, 7.2 Hz, 2H), 2.90 (s, 3H), 1.60 - 1.56 (m, 2H), 1.52 - 1.48 (m, 2H), 1.44 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.1, 150.5, 130.5, 123.7, 118.8, 114.8, 110.7, 52.4, 40.5, 38.5, 29.9, 28.6, 27.9, 24.1 ppm. **IR** vmax (film). 2925, 1770, 1592, 1507, 1494, 1366, 1246, 1053, 913, 747 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{16}H_{25}BrN_2NaO_2$ $[M+Na]^+$: 379.0992; found: 379.0995.

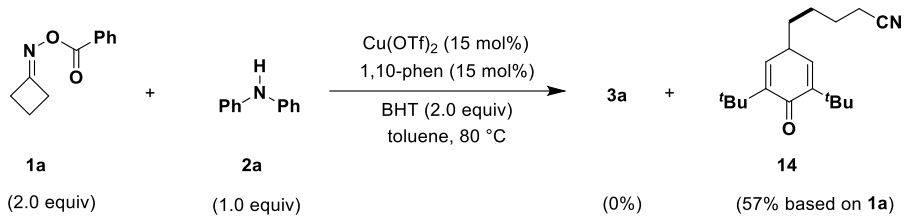
The procedure for the synthesis of compound 13



3i **13,** 72%

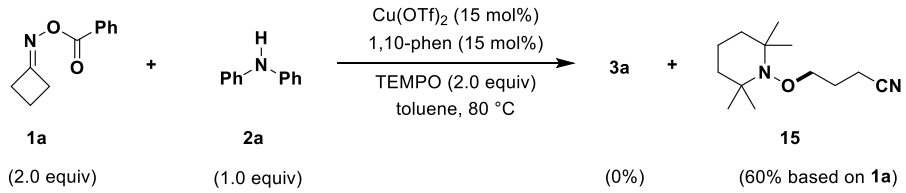
To a 10 mL dry Schlenk flask were added **3i** (152 mg, 0.60 mmol, 1.0 equiv) and 2 mL anhydrous Et_2O under N_2. Then the methylmagnesium bromide (1.2 mL, 3.60 mmol, 6.0 equiv, 3.0 M in ether) was added dropwise into this solution. The reaction was refluxed overnight. After completed (as monitored by TLC), the reaction was cooled to room temperature, and quenched with 1.0 M HCl. The mixture was allowed to stir for 3 h and extracted with Et_2O for five times. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 8/1) afforded the desired product **13** in 72% yield (116 mg, 0.43 mmol) as yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$ δ 7.05 (t, J = 8.4 Hz, 1H), 6.80 (s, 1H), 6.78 (d, J = 8.4 Hz, 1 H), 6.61 (dd, J = 8.4, 2.4 Hz, 1H), 3.29 (t, J = 7.2 Hz, 2H), 2.89 (s, 3H), 2.45 (t, J = 7.2 Hz, 2H), 2.12 (s, 3H), 1.83 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 208.2, 150.5, 130.5, 123.6, 118.9, 114.8, 110.7, 51.6, 40.5, 38.2, 30.1, 20.9 ppm; **IR** νmax (film). 2994, 1769, 1758, 1383, 1245, 1058, 913, 745, 707 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{12}H_{16}BrNNaO$ $[M+Na]^+$: 292.0307; found: 292.0308.

The procedure for the synthesis of compound 14



To a 10 mL dry Schlenk flask was added **1a** (75.6 mg, 0.40 mmol, 2.0 equiv), $Cu(OTf)_2$ (10.8 mg, 0.03 mmol, 0.15 equiv), 1,10-phen (5.4 mg, 0.03 mmol, 0.15 equiv), BHT (88.1 mg, 0.40 mmol, 2.0 equiv) and 2 mL dry toluene. Then **2a** (33.8 mg, 0.20 mmol, 1.0 equiv) was added at room temperature, and the reaction was degassed for three times with argon. The mixture was allowed to stir at 80 °C for 1.5 h. After completed (as monitored by TLC), the reaction was cooled to room temperature. The mixture was diluted with sat.$NaHCO_3$ and extracted with EA for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 10/1) afforded the desired product **14** in 57% yield based on **1a** (65.5 mg, 0.23 mmol) as yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.39 (s, 2H), 2.29 (t, J = 7.2 Hz, 2H), 1.75 (tt, J = 4.2, 4.2 Hz, 2H), 1.38 – 1.32 (m, 4H), 1.23 (s, 18H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 186.4, 147.5, 145.5, 119.4, 40.0, 39.8, 34.9, 29.7, 27.5, 21.1, 17.5 ppm. **IR** νmax (film). 2994, 1769, 1757, 1487, 1374, 1246, 1057, 913, 815, 744, 704 cm^{-1}; **HRMS** (ESI) m/z calcd for $C_{19}H_{29}NNaO$ $[M+Na]^+$: 310.2141; found: 310.2143.

The procedure for the synthesis of compound 15



To a 10 mL dry Schlenk flask was added **1a** (75.6 mg, 0.40 mmol, 2.0 equiv), $Cu(OTf)_2$ (10.8 mg, 0.03 mmol, 0.15 equiv), 1,10-phen (5.4 mg, 0.03 mmol, 0.15 equiv), TEMPO (2.5 mg, 0.40 mmol, 2.0 equiv) and 2 mL dry toluene. Then **2a** (33.8 mg, 0.20 mmol, 1.0 equiv) was added at room temperature, and the reaction was degassed for three times with argon. The mixture was allowed to stir at 80 °C for 1.5 h. After completed (as monitored by TLC), the reaction was cooled to room temperature. The mixture was diluted with sat. $NaHCO_3$ and extracted with EA for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. Further purification by flash column chromatography (PE/EA = 10/1) afforded the desired product **15** in 60% yield based on **1a** (53.8 mg, 0.24 mmol) as yellow oil. Compound **15** is a known compound according to ref.6.

Part 6. References

[1] Zhao, B.; Shi, Z. *Angew. Chem. Int. Ed.* **2017**, *56*, 12727.

[2] Nishimura, T.; Nishiguchi, Y.; Maeda, Y.; Uemura, S. *J. Org. Chem.* **2004**, *69*, 5342.

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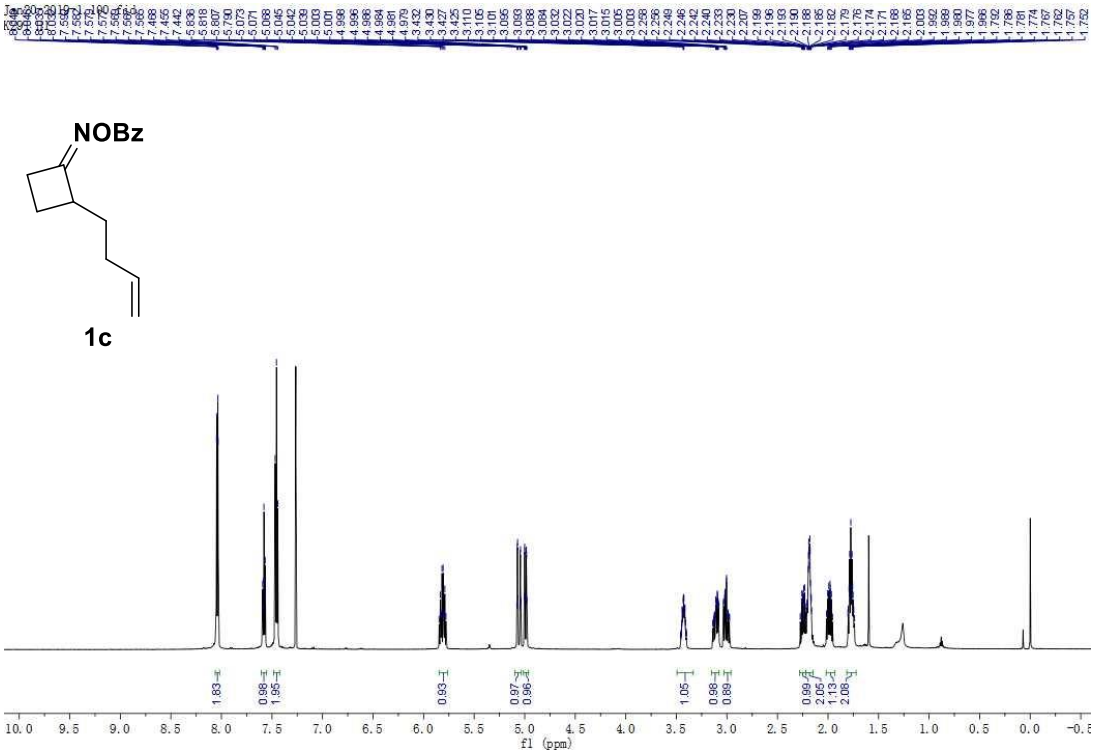
[4] Chanda, K.; Rej, S.; Liu, S.-Y.; Huang, M. H. *ChemCatChem* **2015**, *7*, 1813.

[5] Rajagopal, B.; Chou, C.-H.; Chung, C.-C.; Lin, P.-C. *Org. Lett.* **2014**, *16*, 3752.

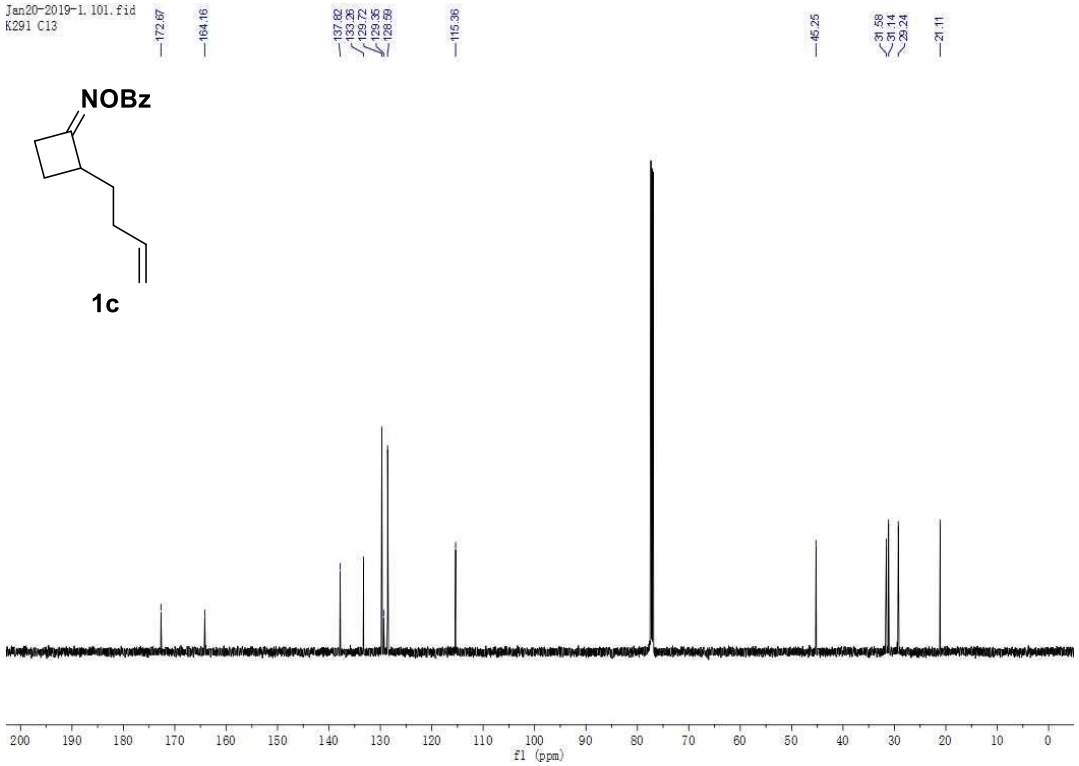
[6] Zhang, J.-Y.; Duan, X.-H.; Yang, J.-C.; Guo, L.-N. *J. Org. Chem.* **2018**, *83*, 4239.

Part 7: NMR spectra

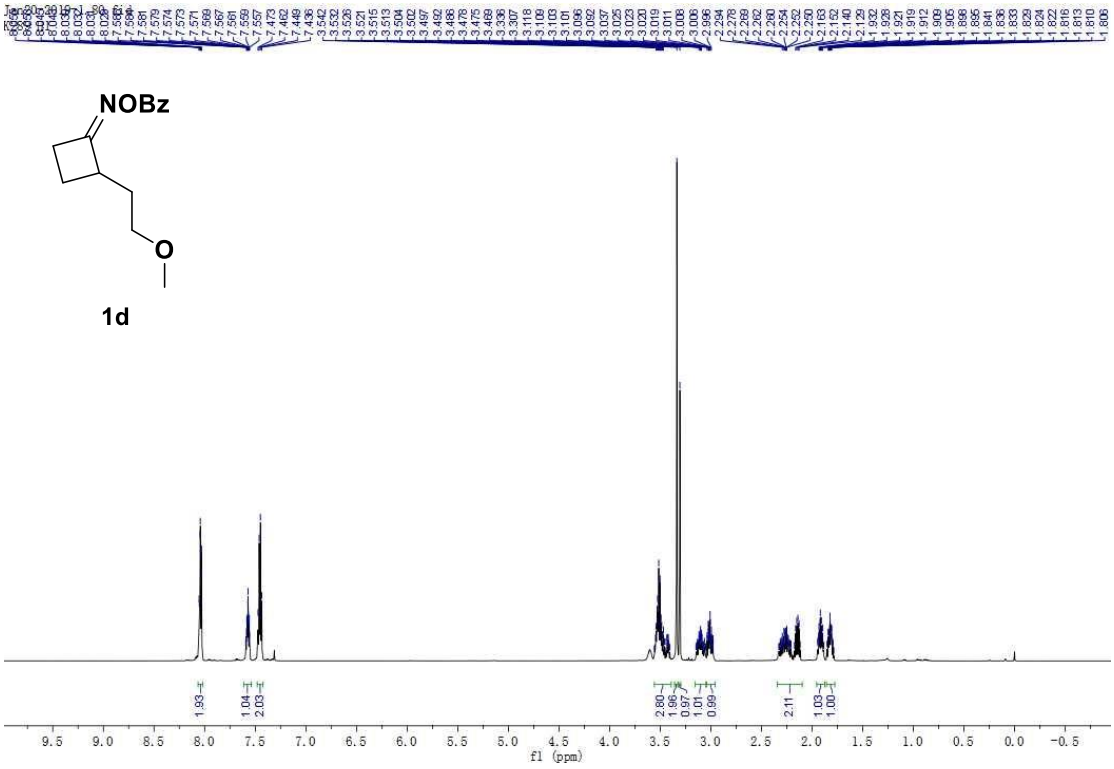
^{1}H NMR Spectra of **1c**



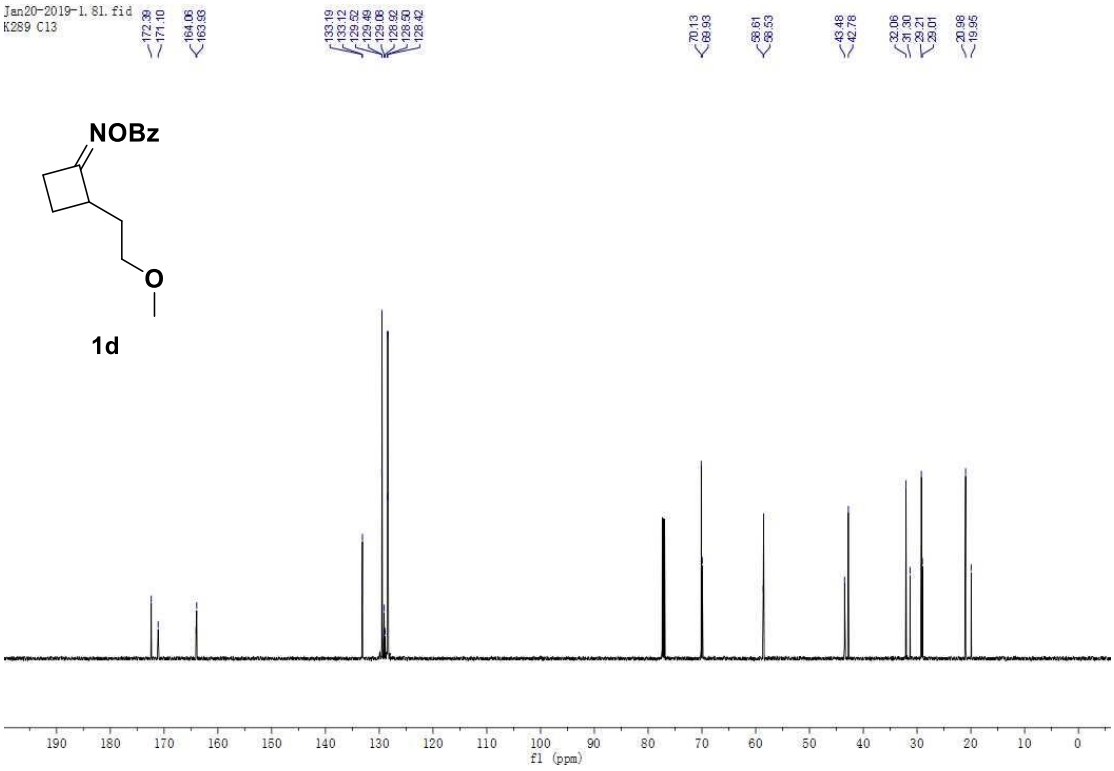
^{1}C NMR Spectra of **1c**



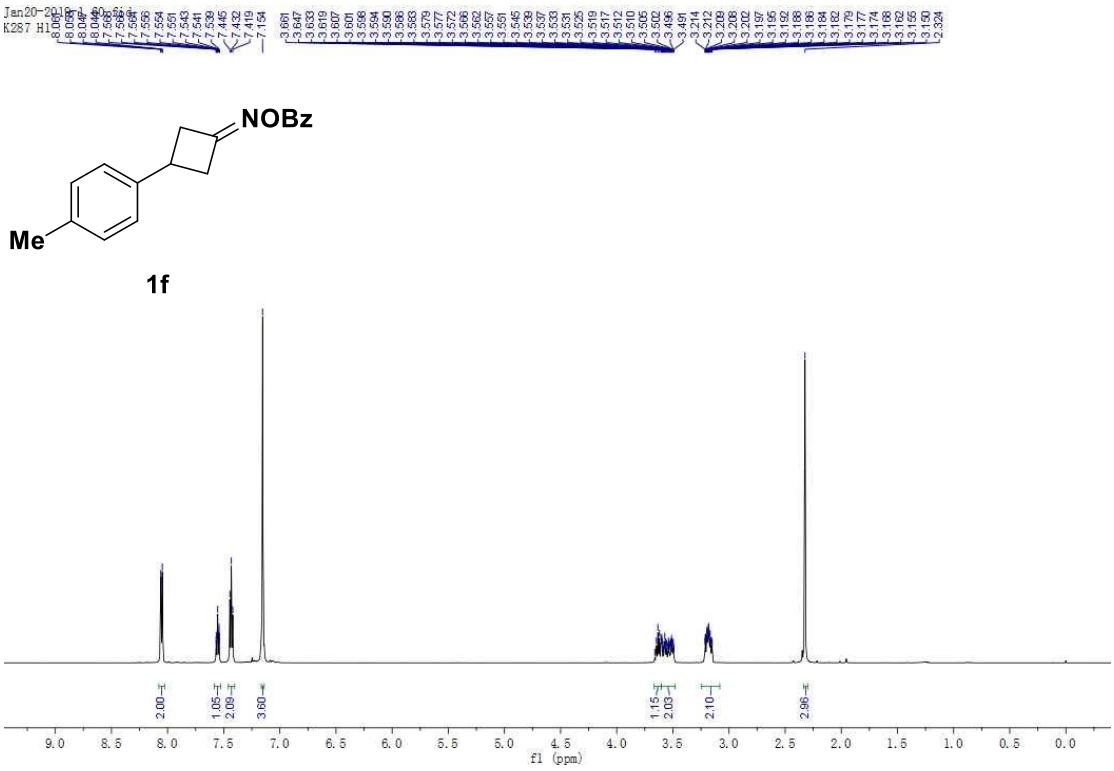
^{1}H NMR Spectra of **1d**



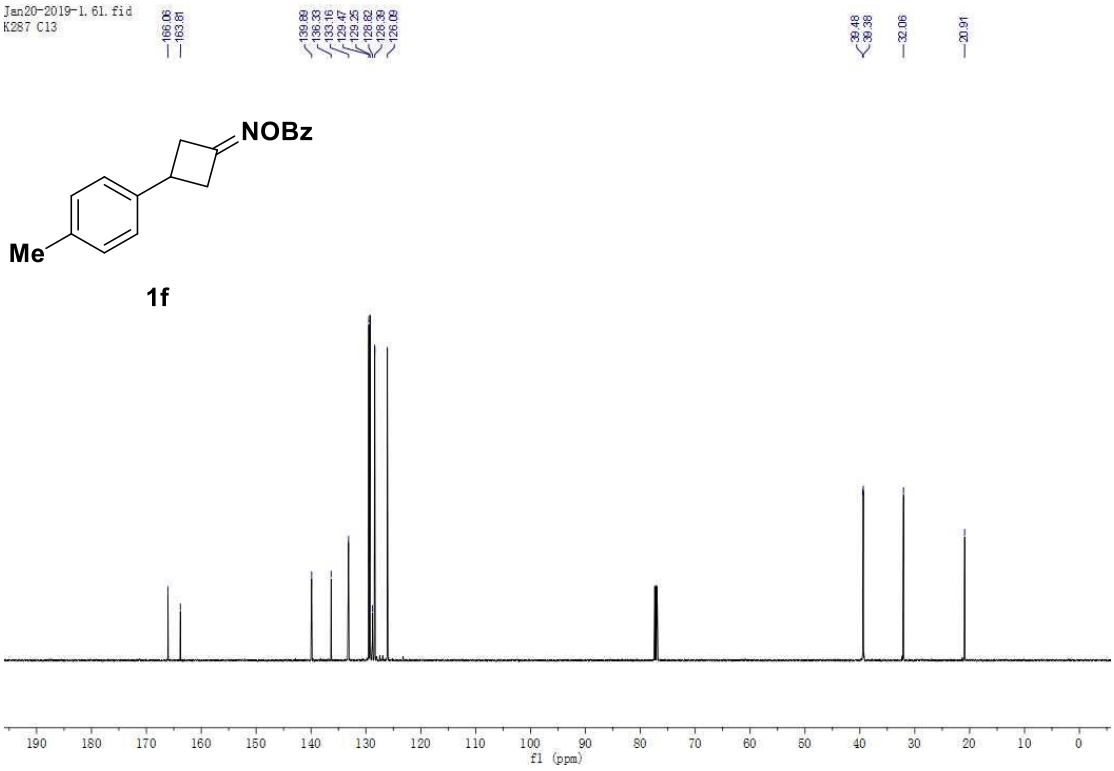
^{1}C NMR Spectra of **1d**



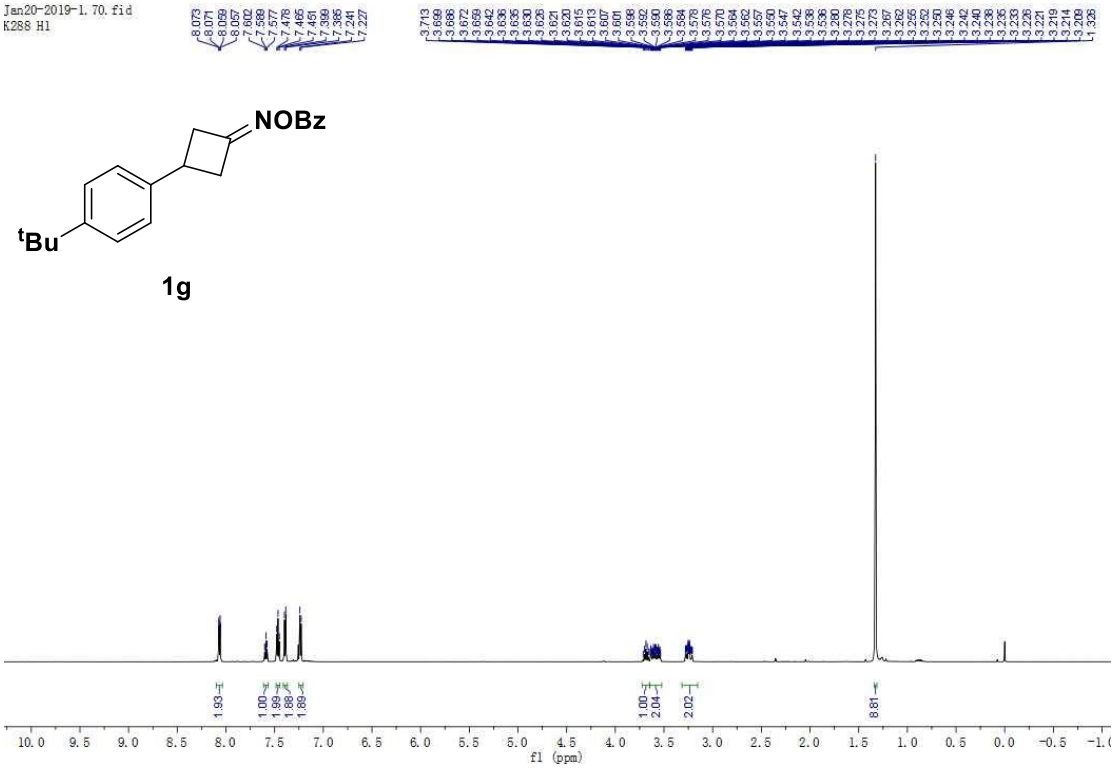
^{1}H NMR Spectra of **1f**



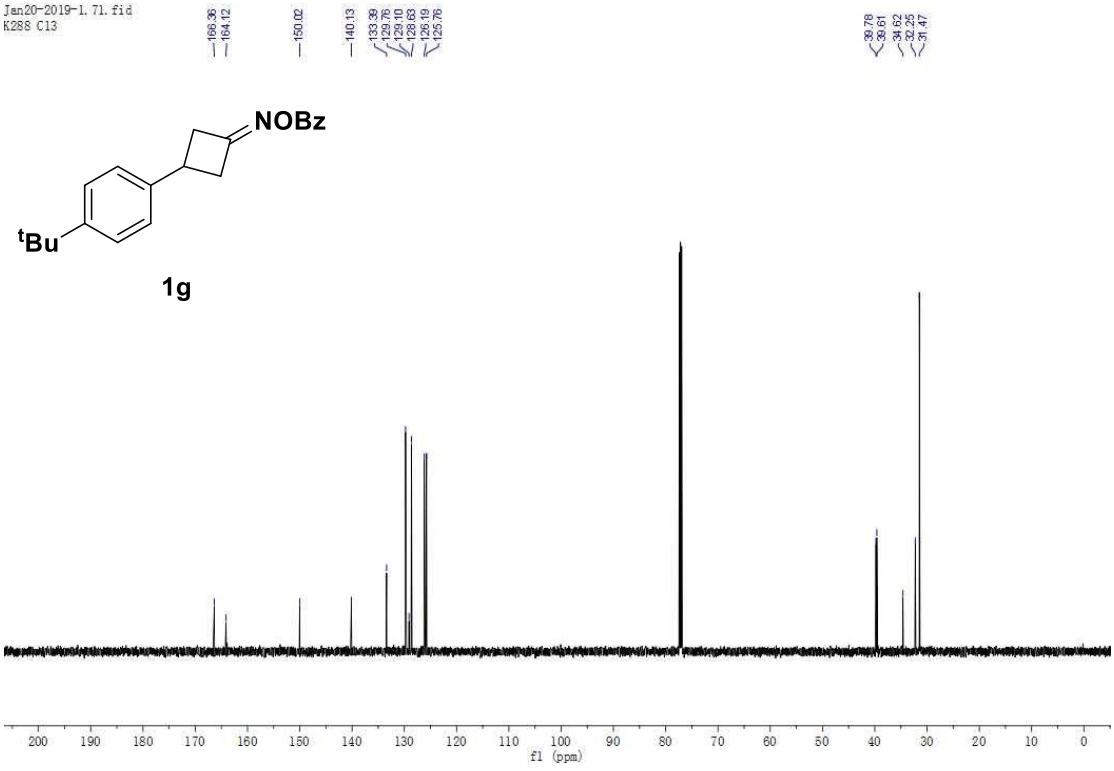
^{1}C NMR Spectra of **1f**



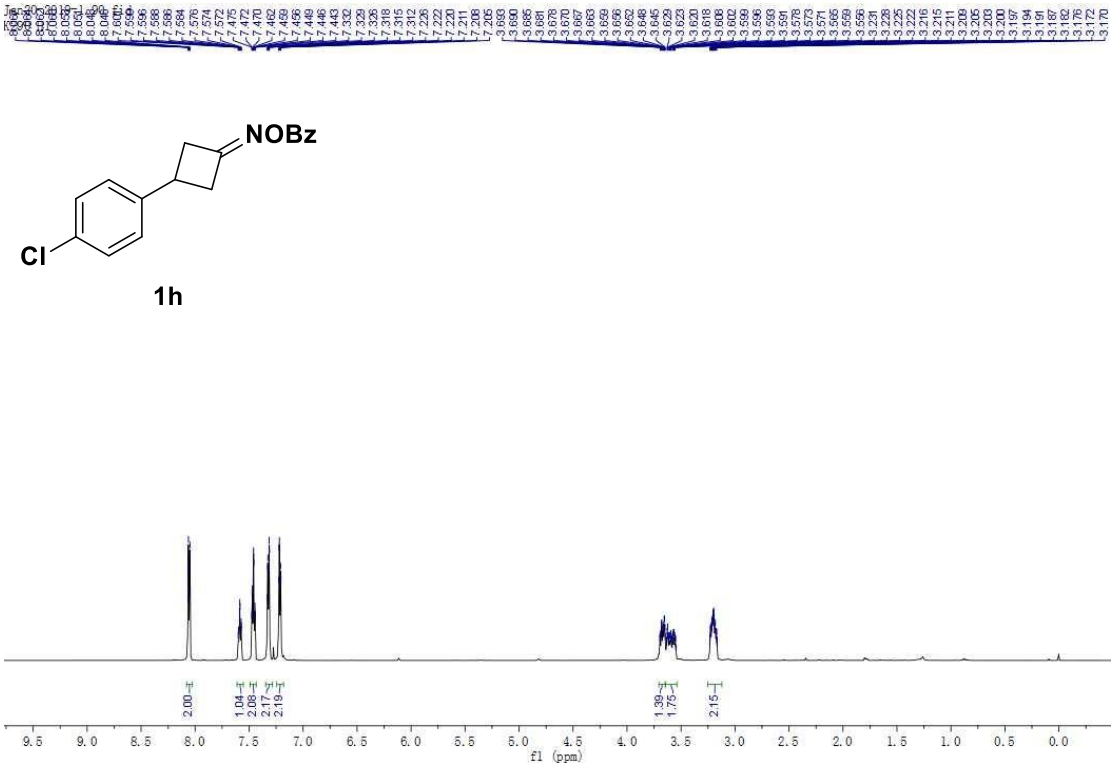
^{1}H NMR Spectra of **1g**



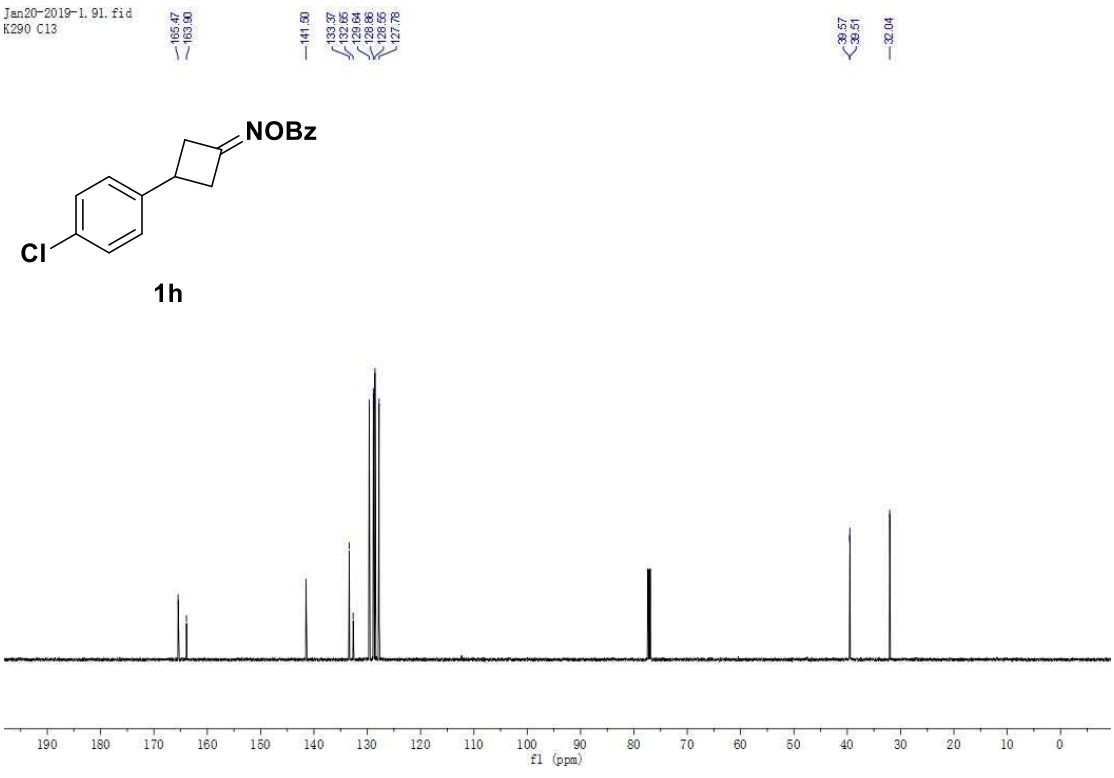
^{1}C NMR Spectra of **1g**



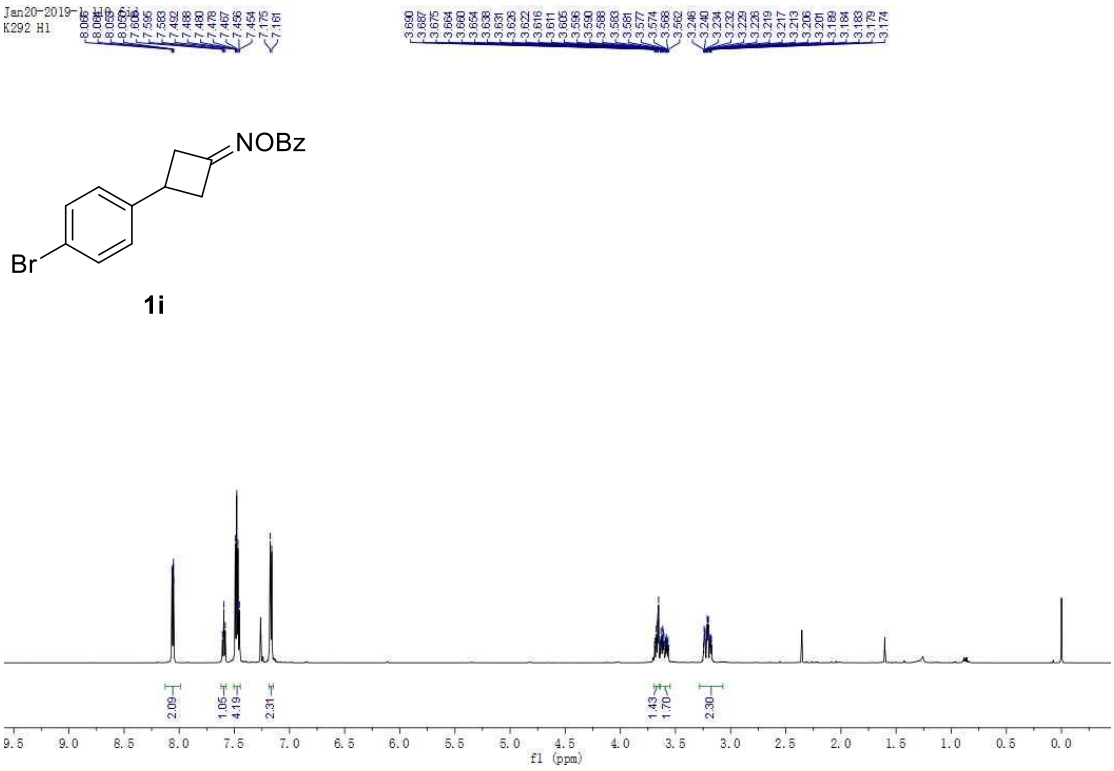
^{1}H NMR Spectra of **1h**



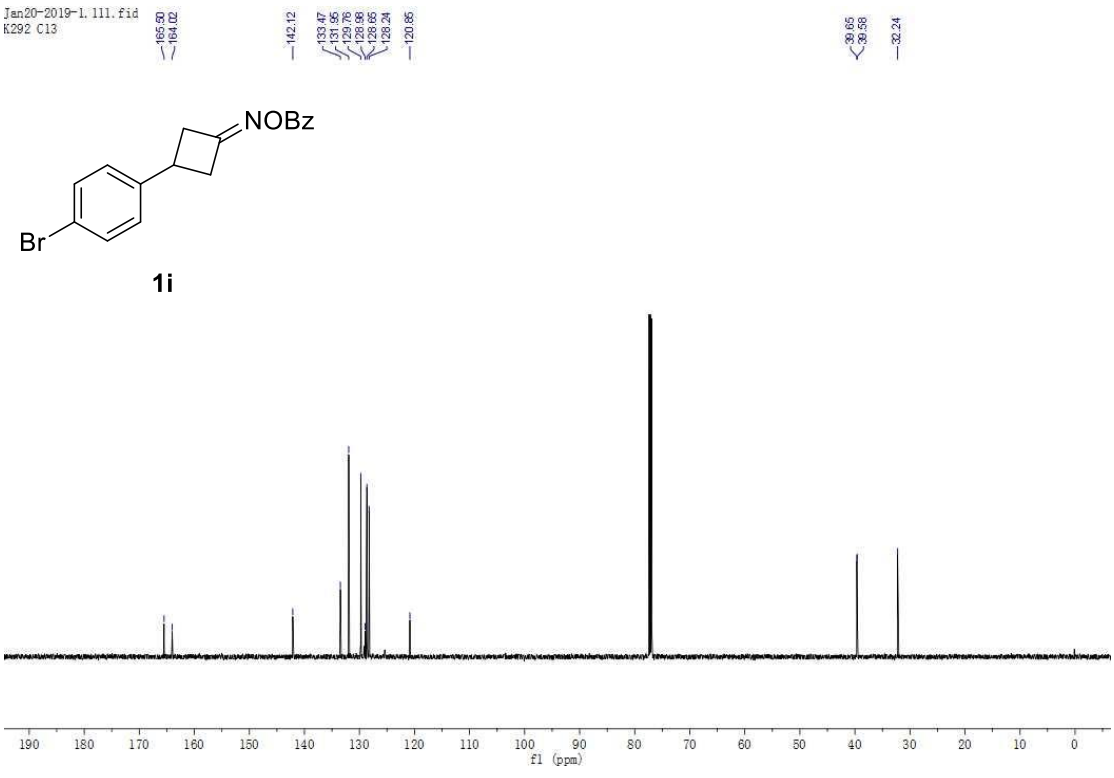
^{1}C NMR Spectra of **1h**



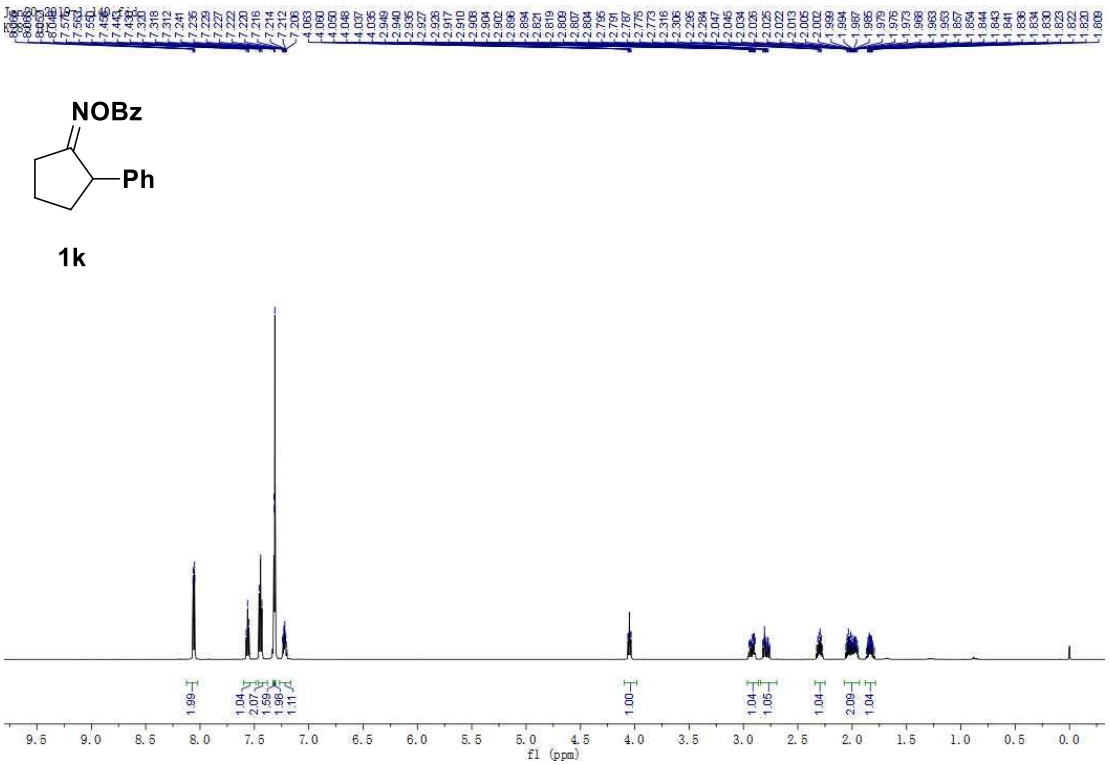
^{1}H NMR Spectra of **1i**



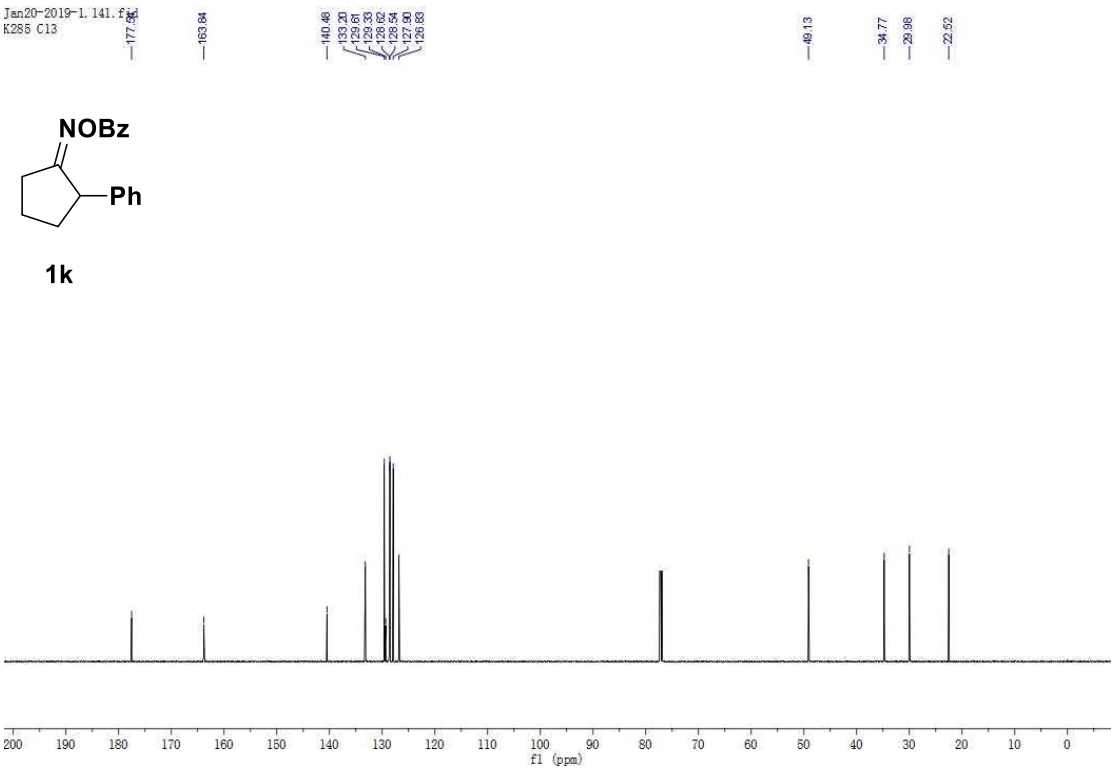
^{1}C NMR Spectra of **1i**



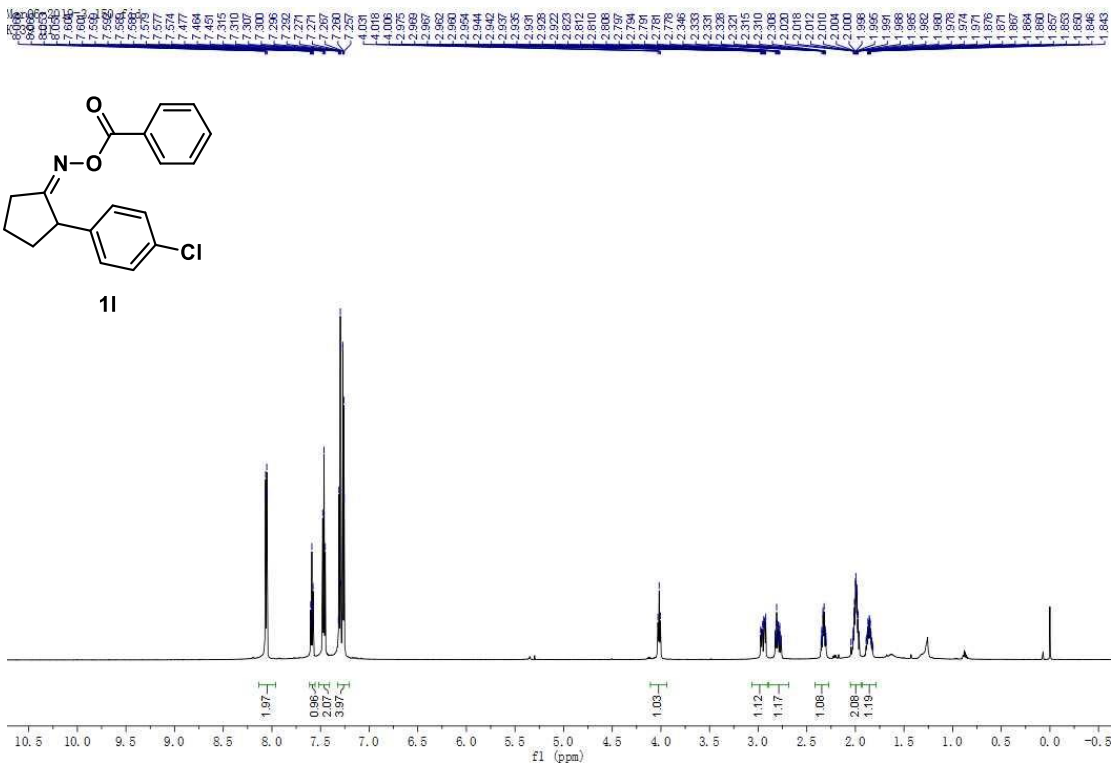
^{1}H NMR Spectra of **1k**



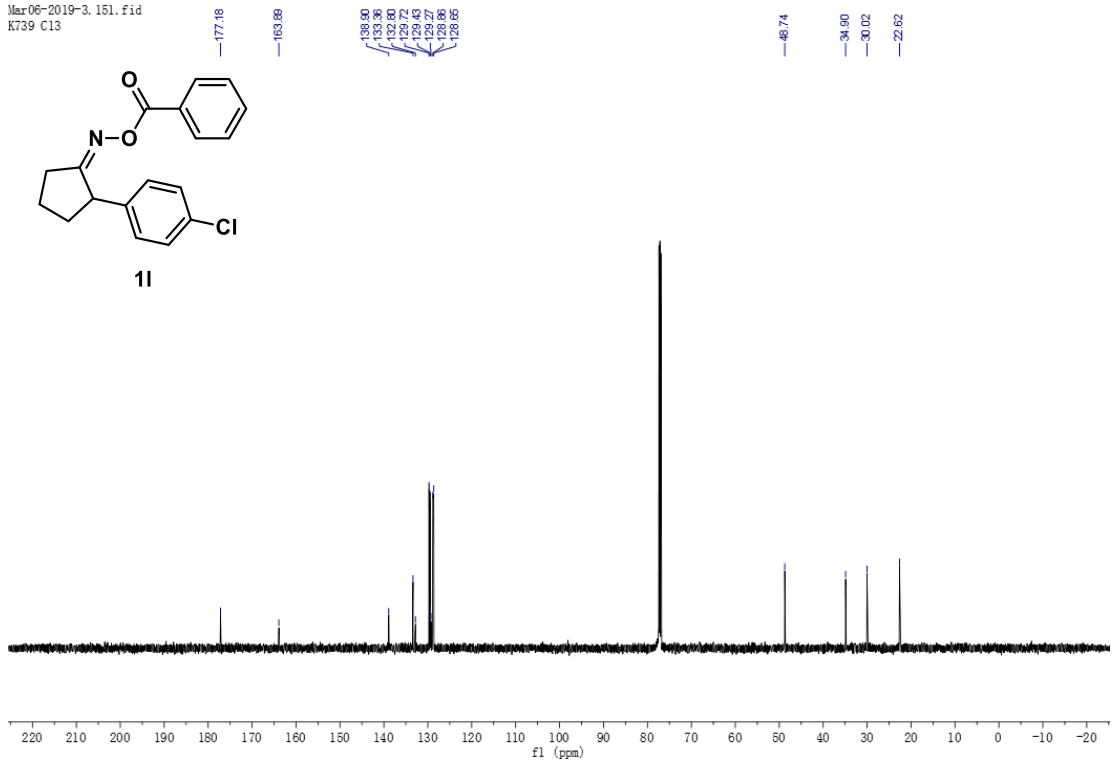
^{1}C NMR Spectra of **1k**



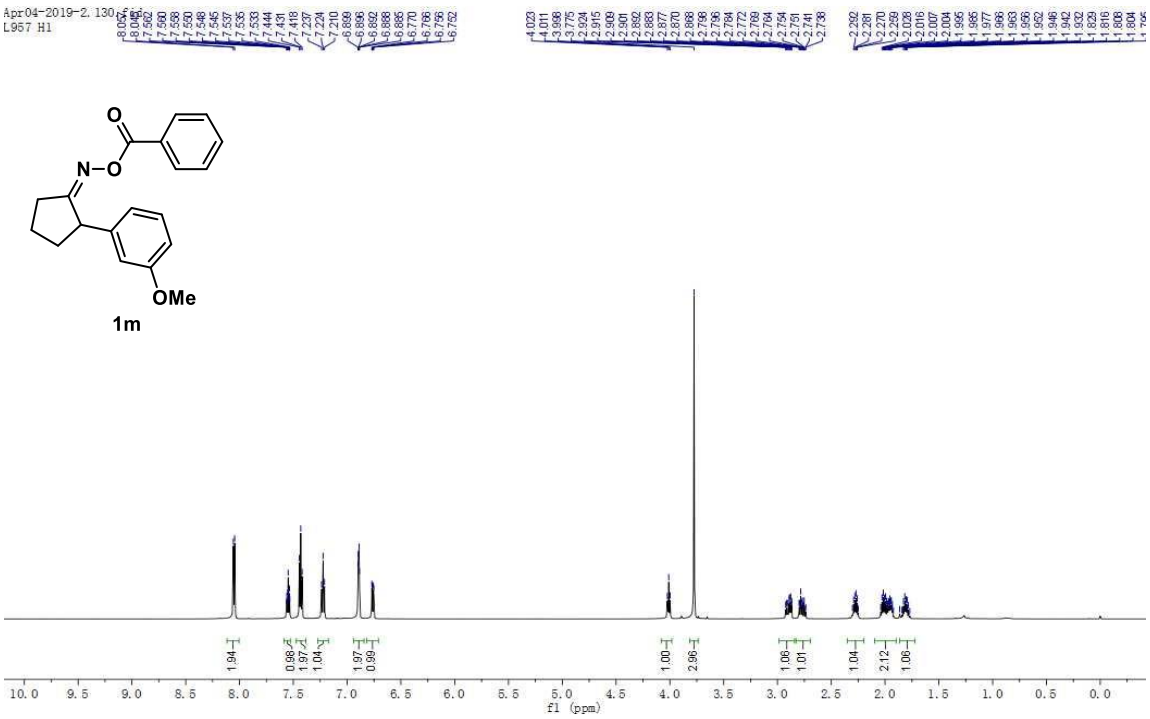
^{1}H NMR Spectra of **1l**



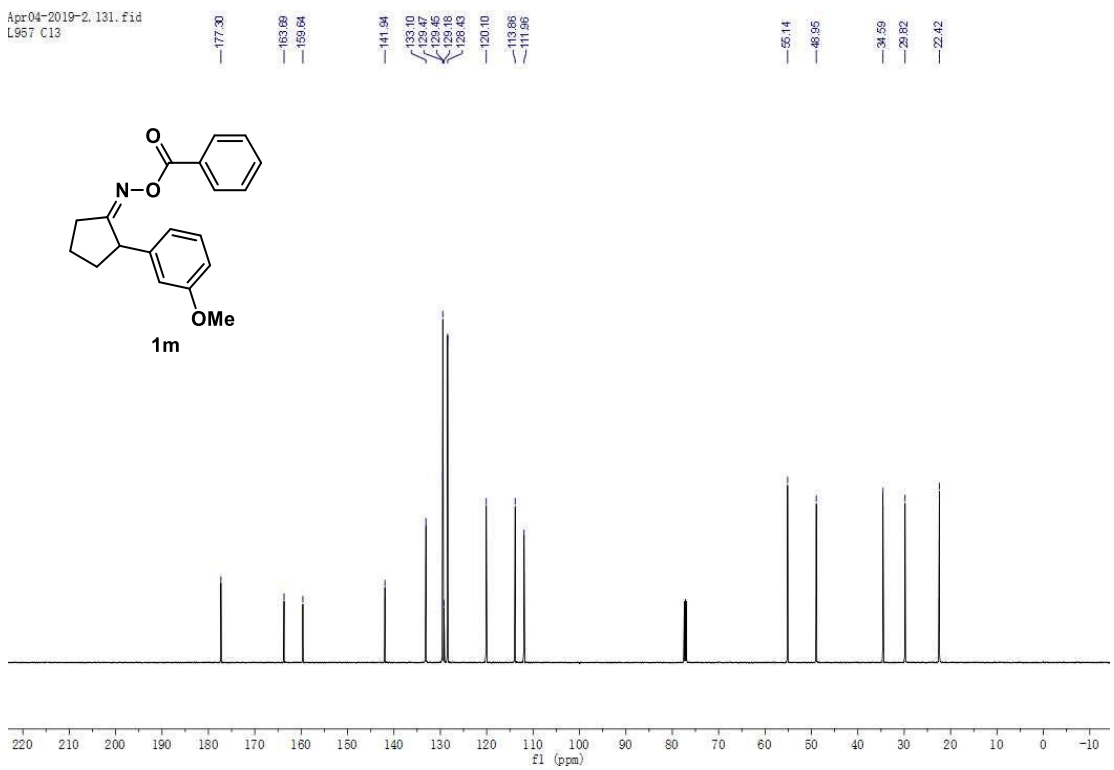
^{1}C NMR Spectra of **1l**



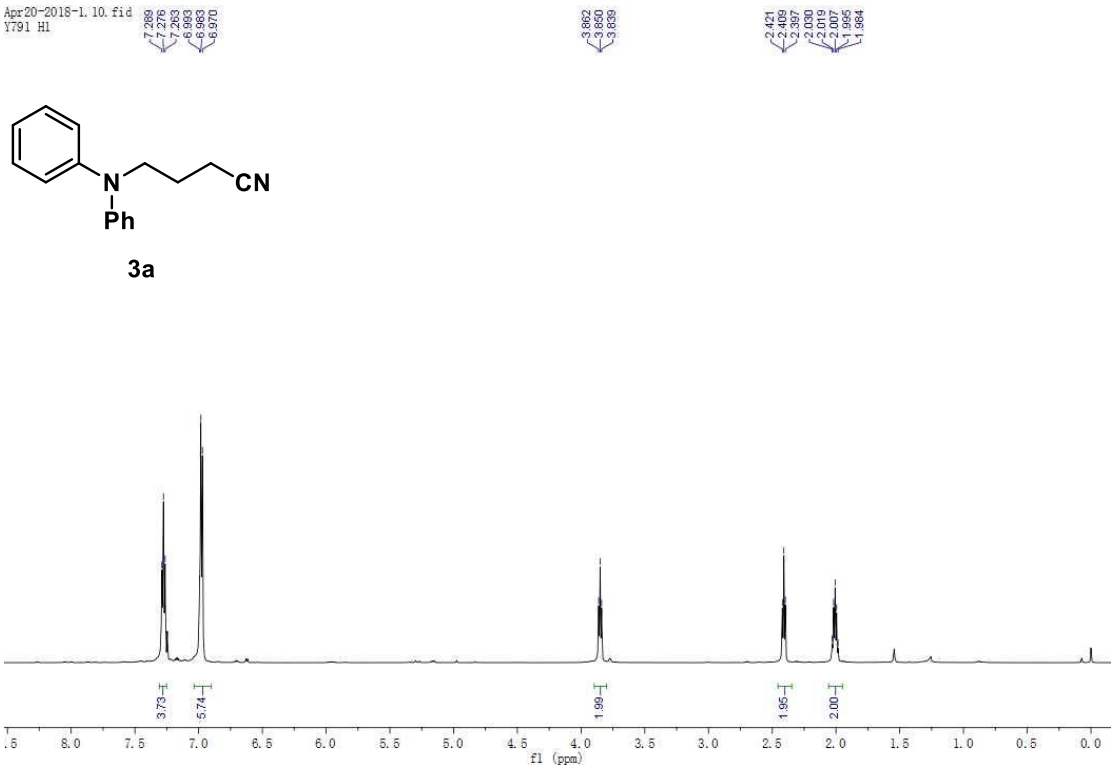
^{1}H NMR Spectra of **1m**



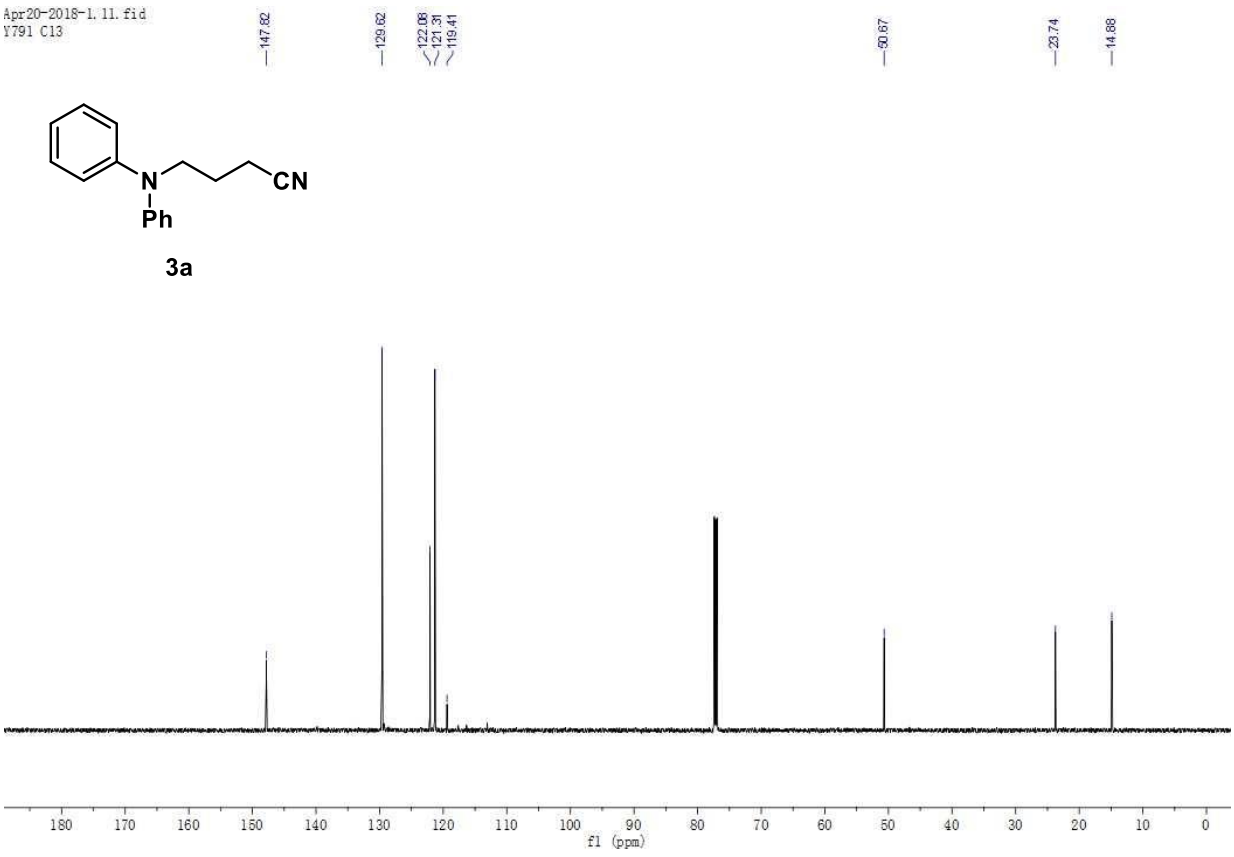
^{1}C NMR Spectra of **1m**



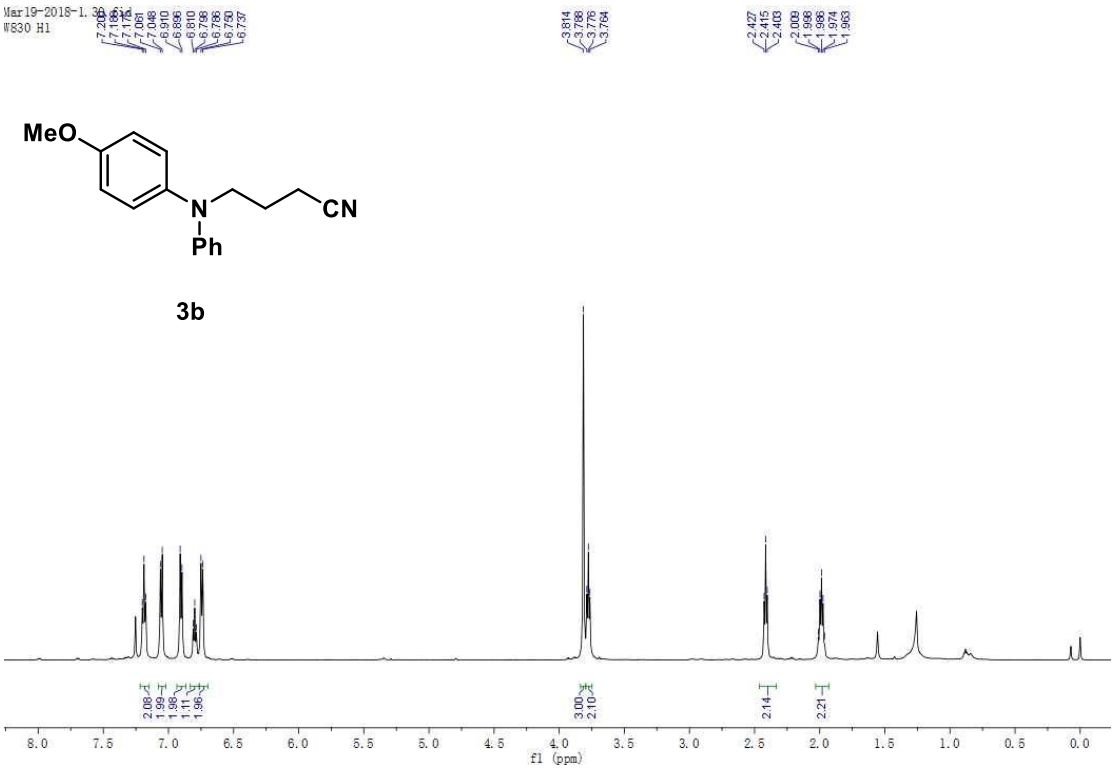
^{1}H NMR Spectra of **3a**



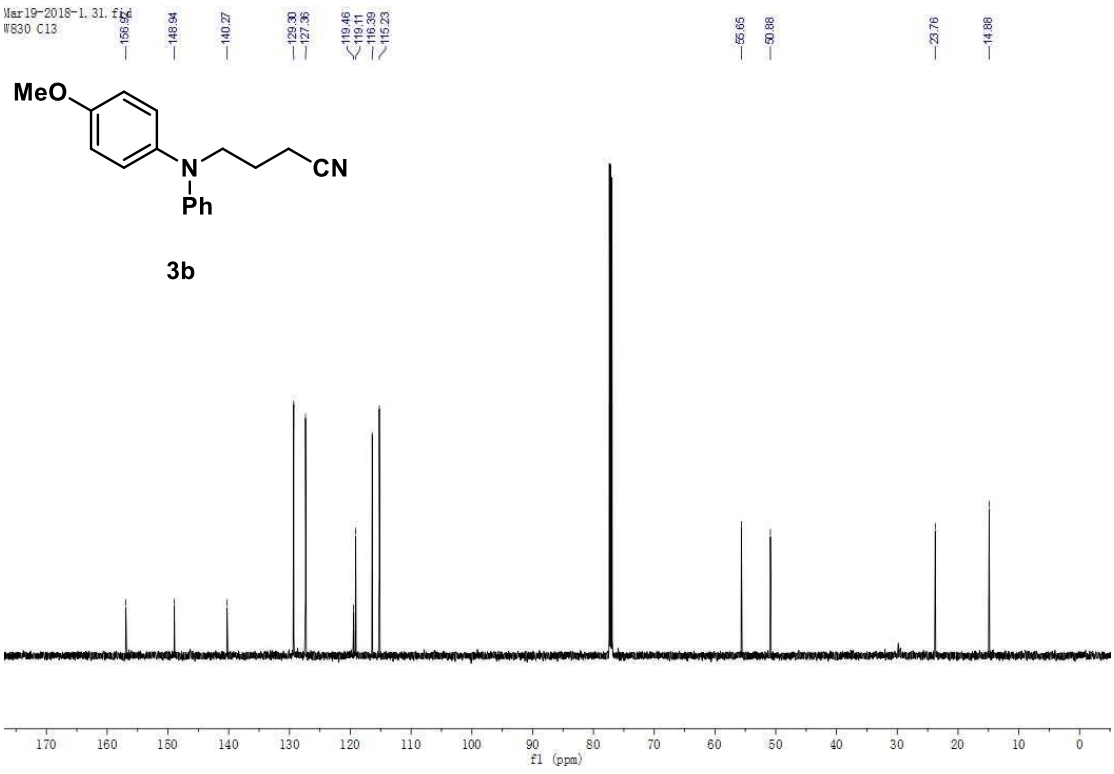
^{1}C NMR Spectra of **3a**



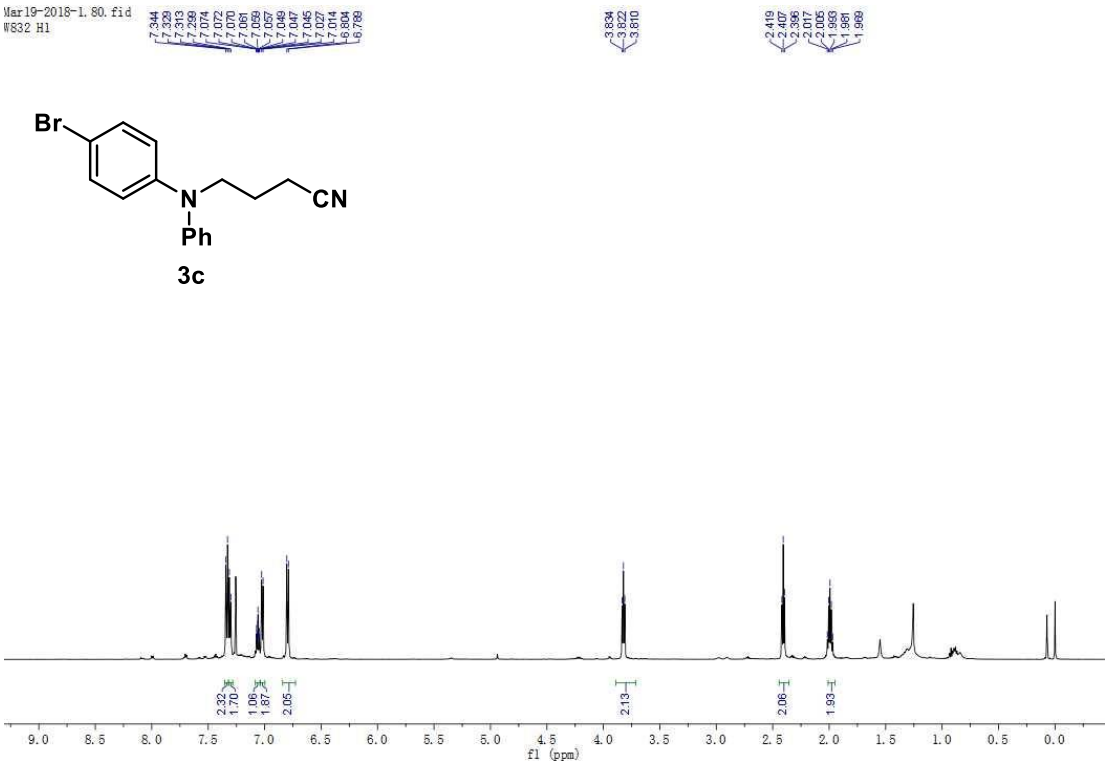
^{1}H NMR Spectra of **3b**



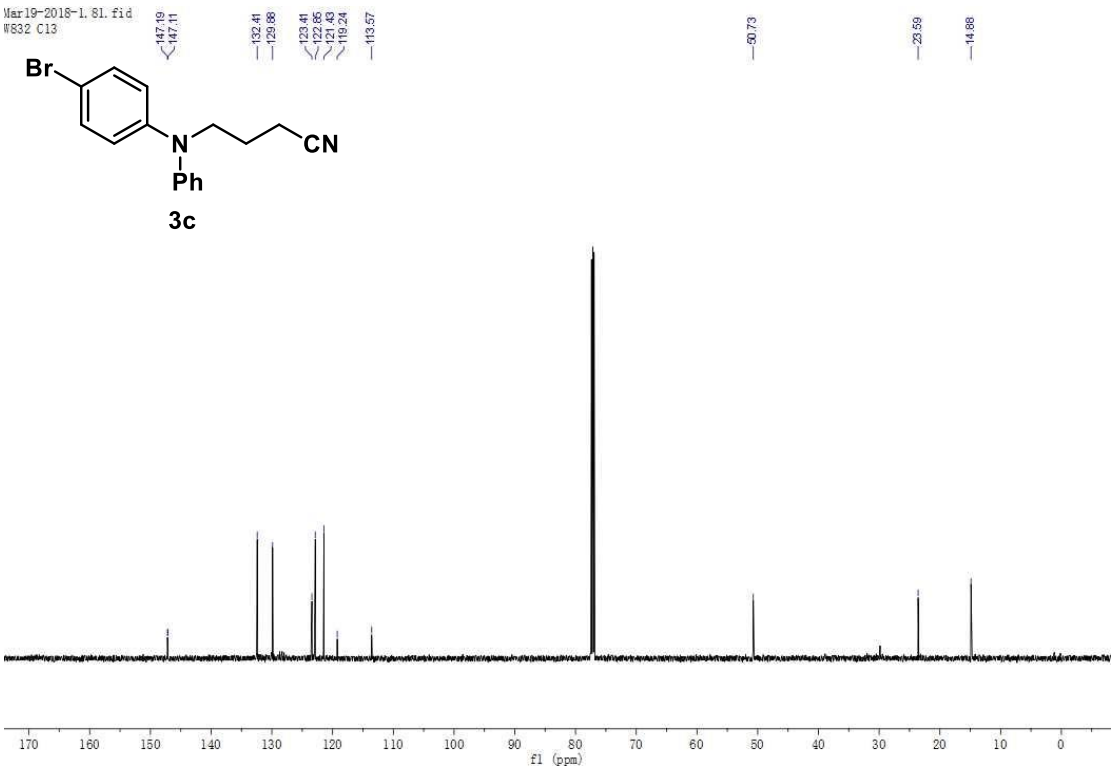
^{1}C NMR Spectra of **3b**



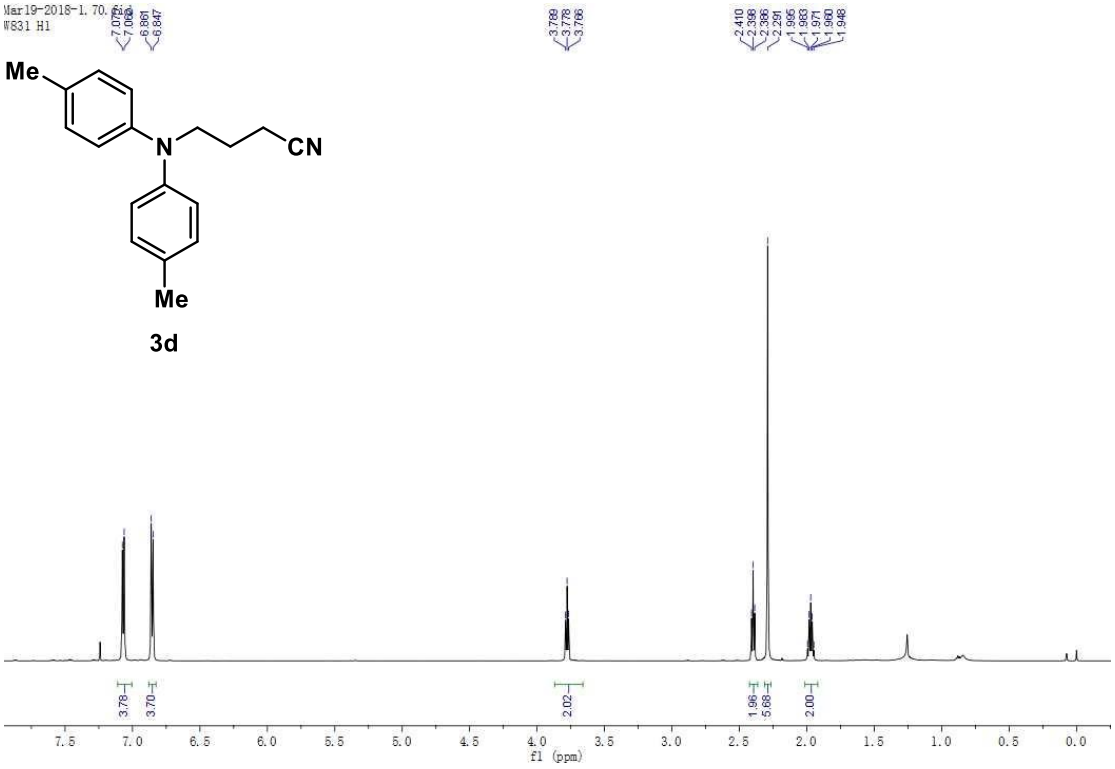
^{1}H NMR Spectra of **3c**



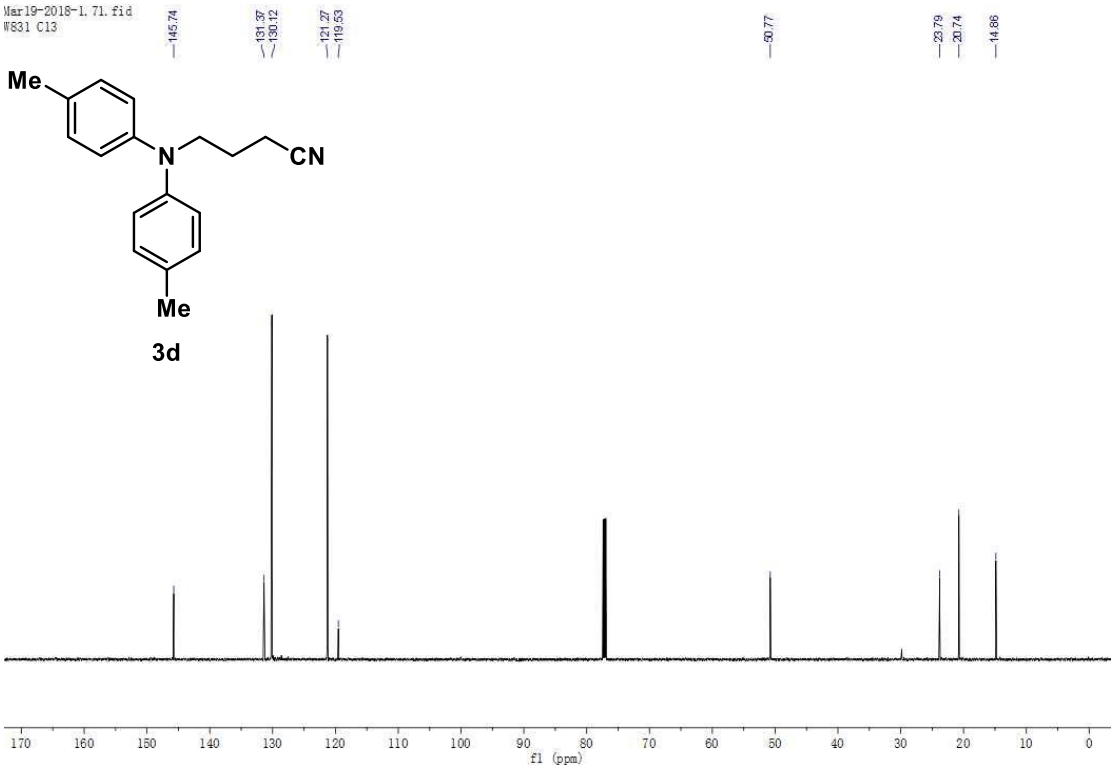
^{1}C NMR Spectra of **3c**



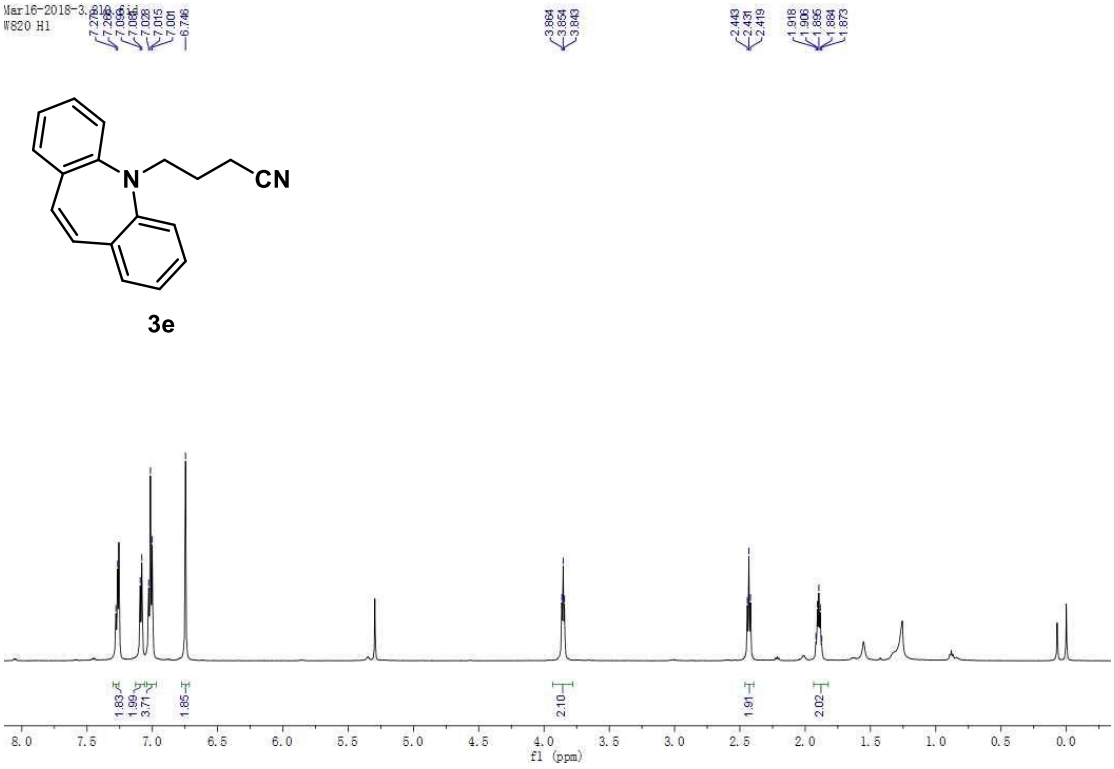
^{1}H NMR Spectra of **3d**



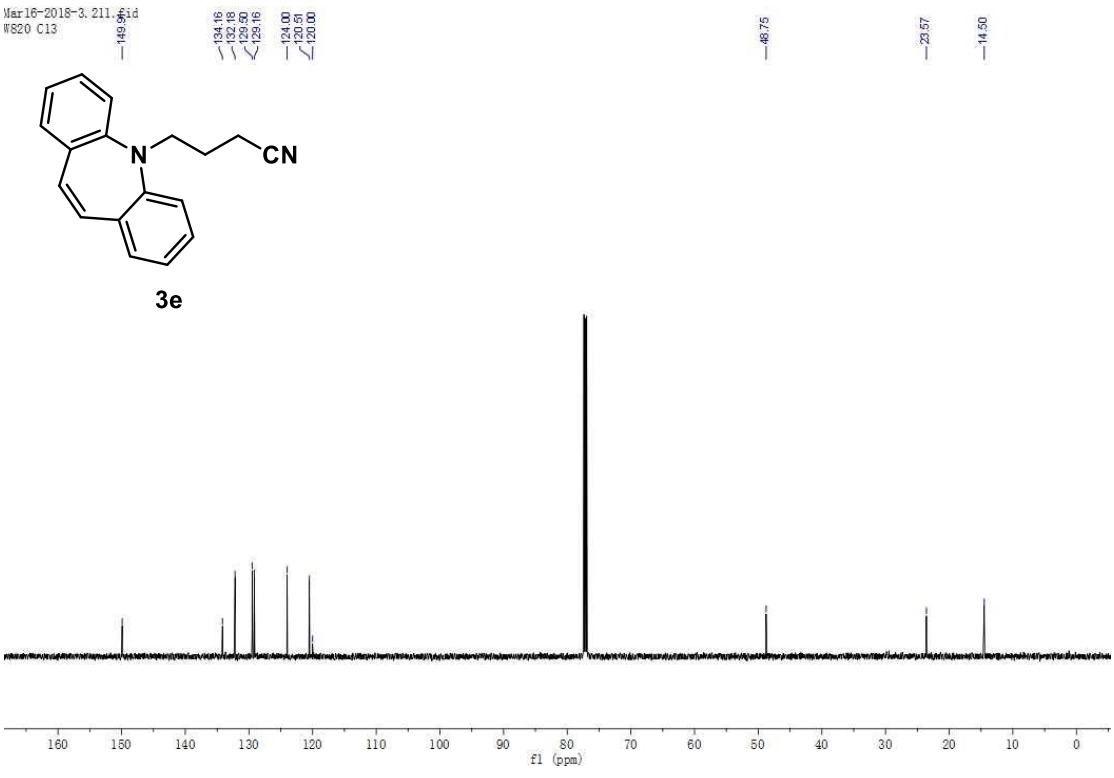
^{1}C NMR Spectra of **3d**



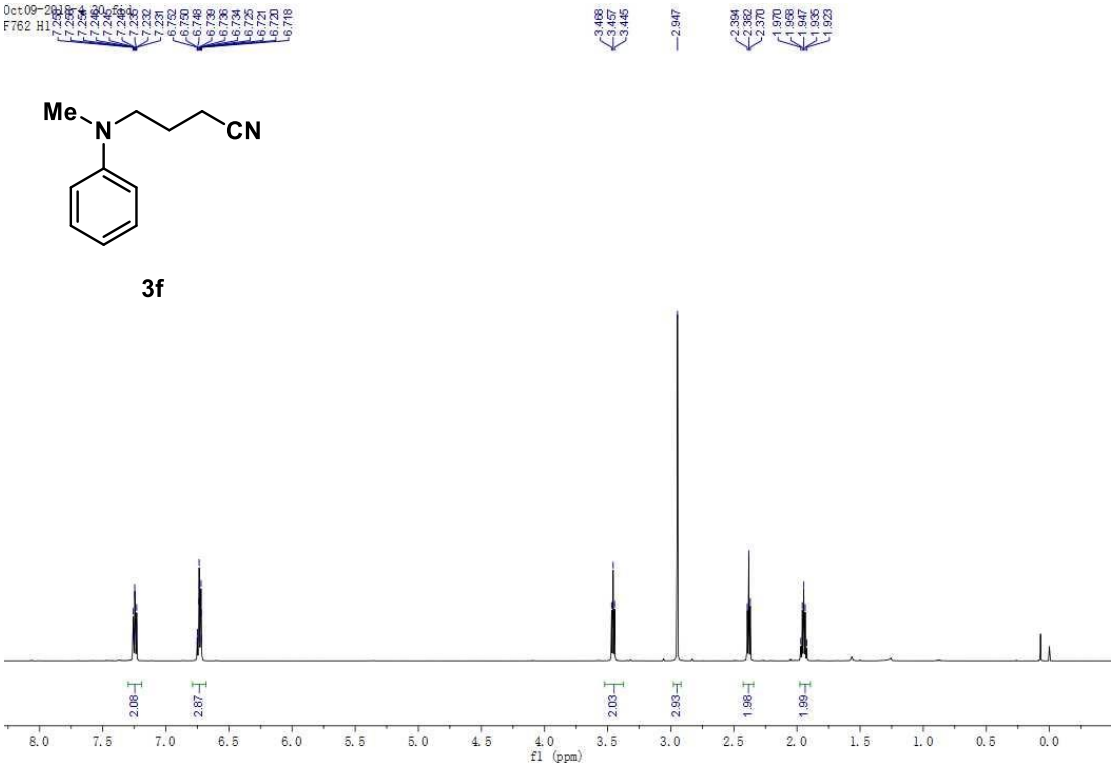
^{1}H NMR Spectra of **3e**



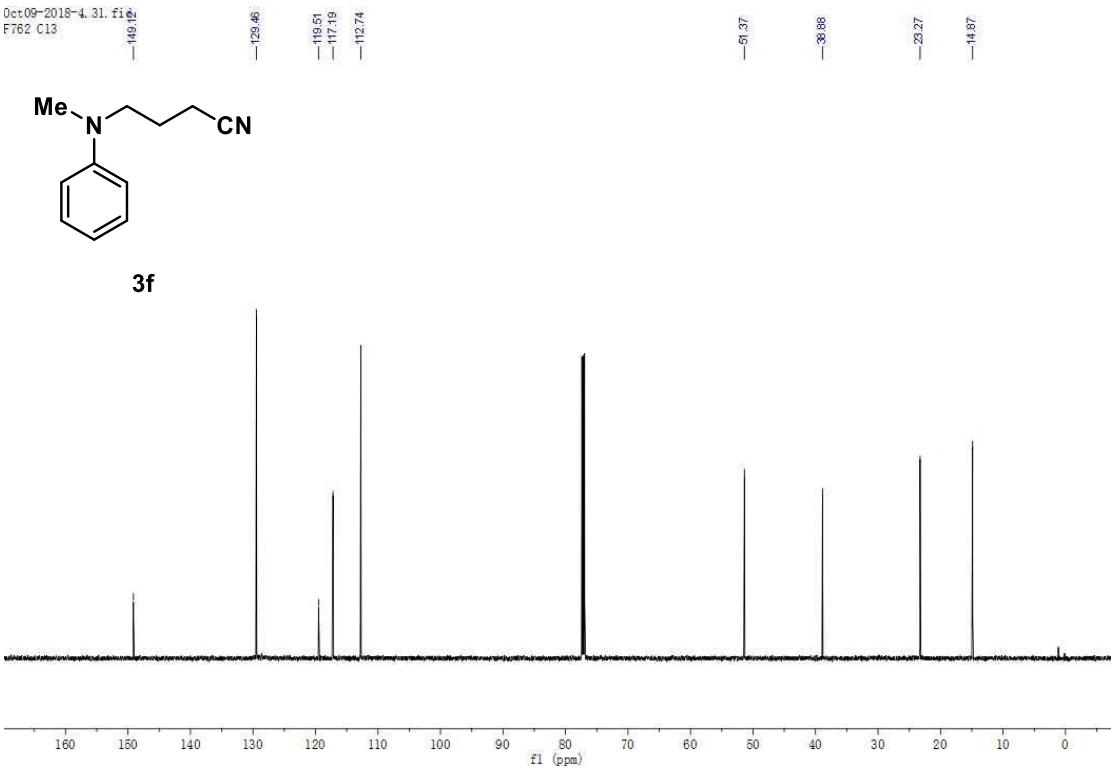
^{1}C NMR Spectra of **3e**



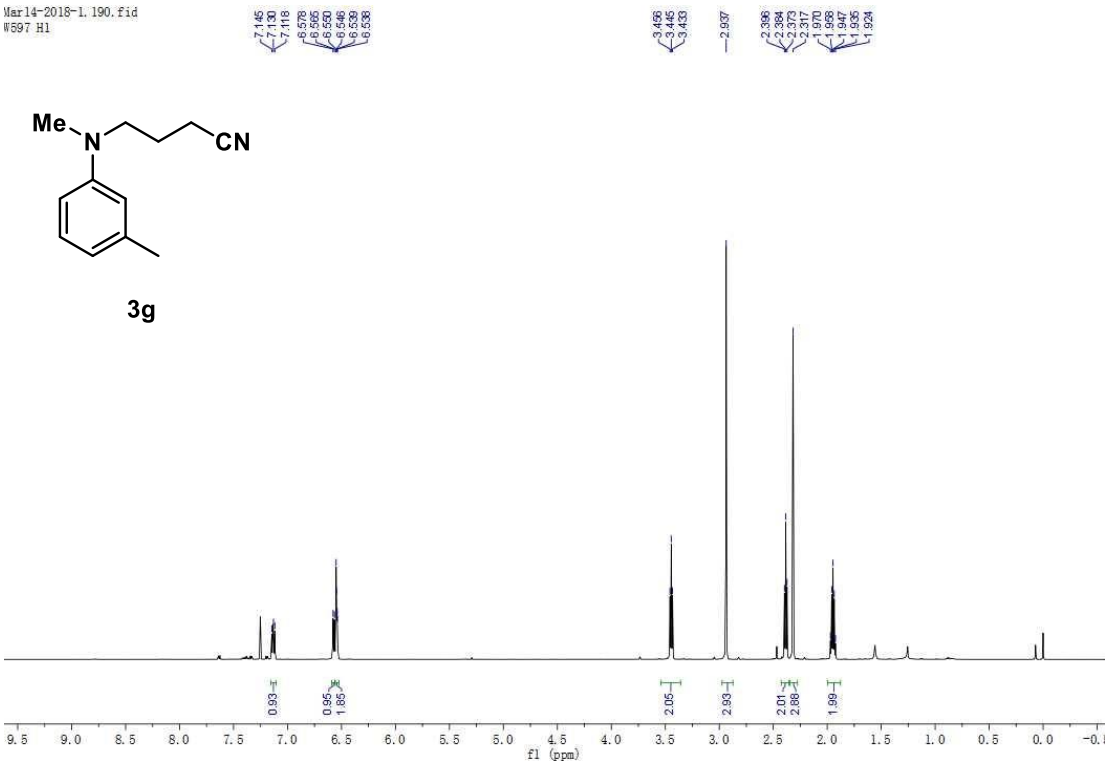
^{1}H NMR Spectra of **3f**



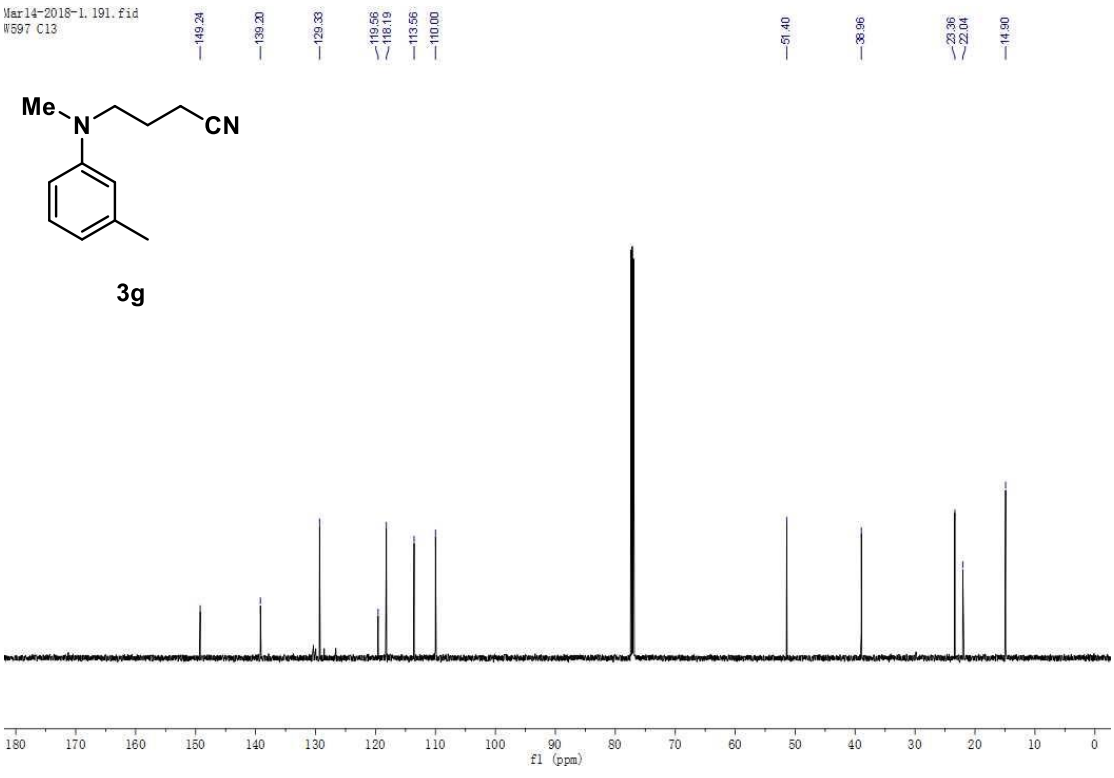
^{1}C NMR Spectra of **3f**



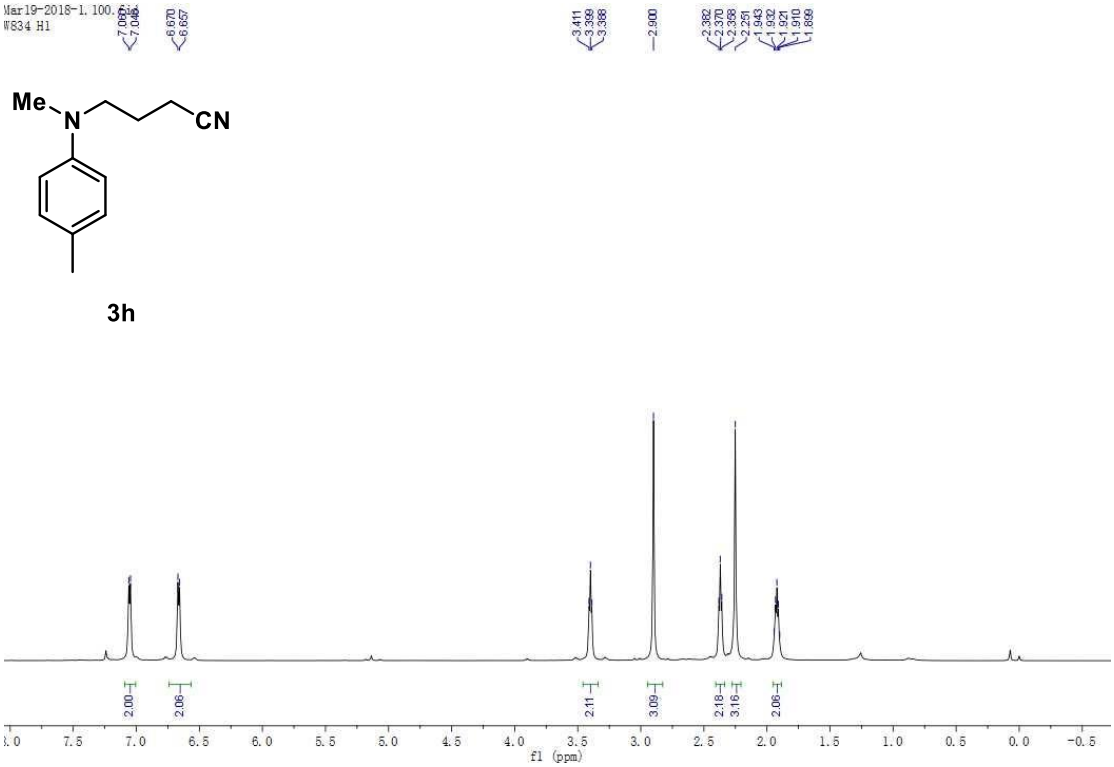
^{1}H NMR Spectra of **3g**



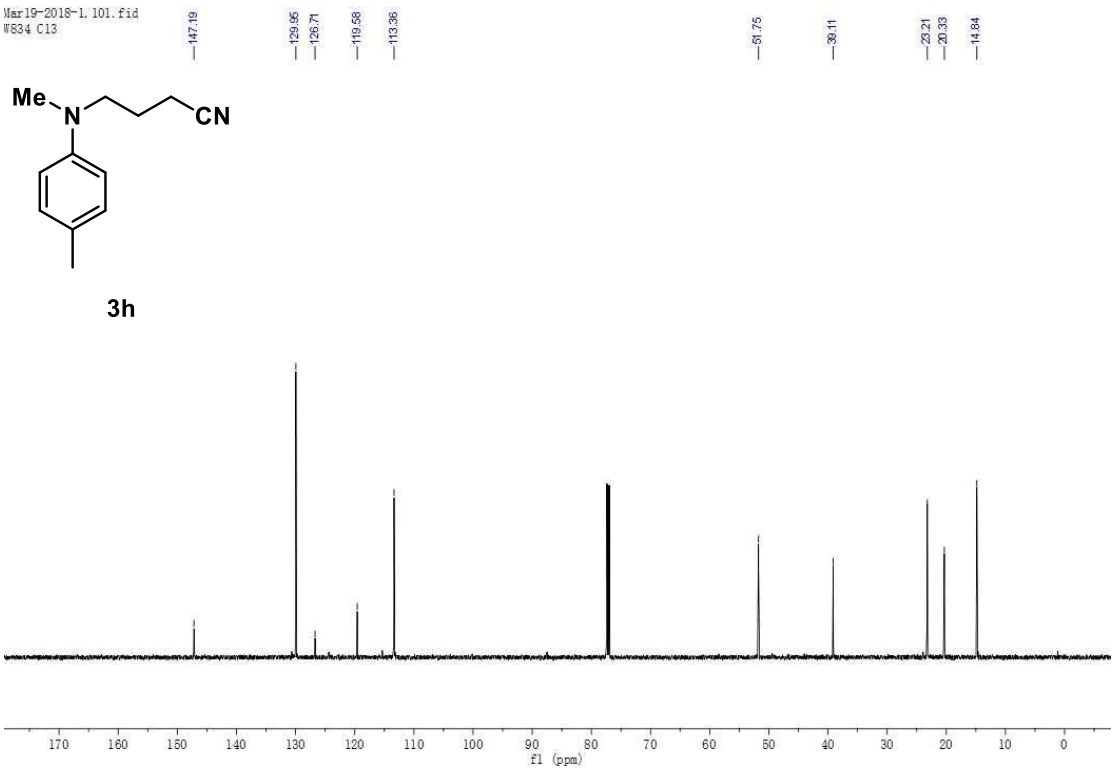
^{1}C NMR Spectra of **3g**



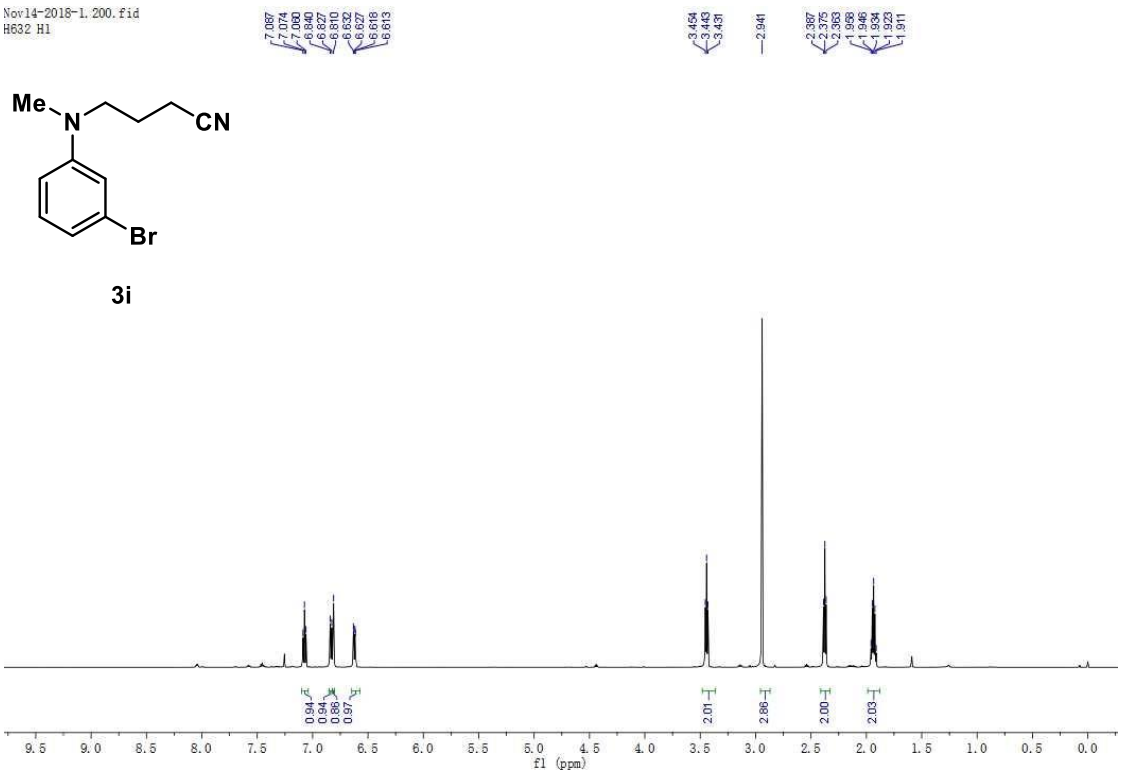
^{1}H NMR Spectra of **3h**



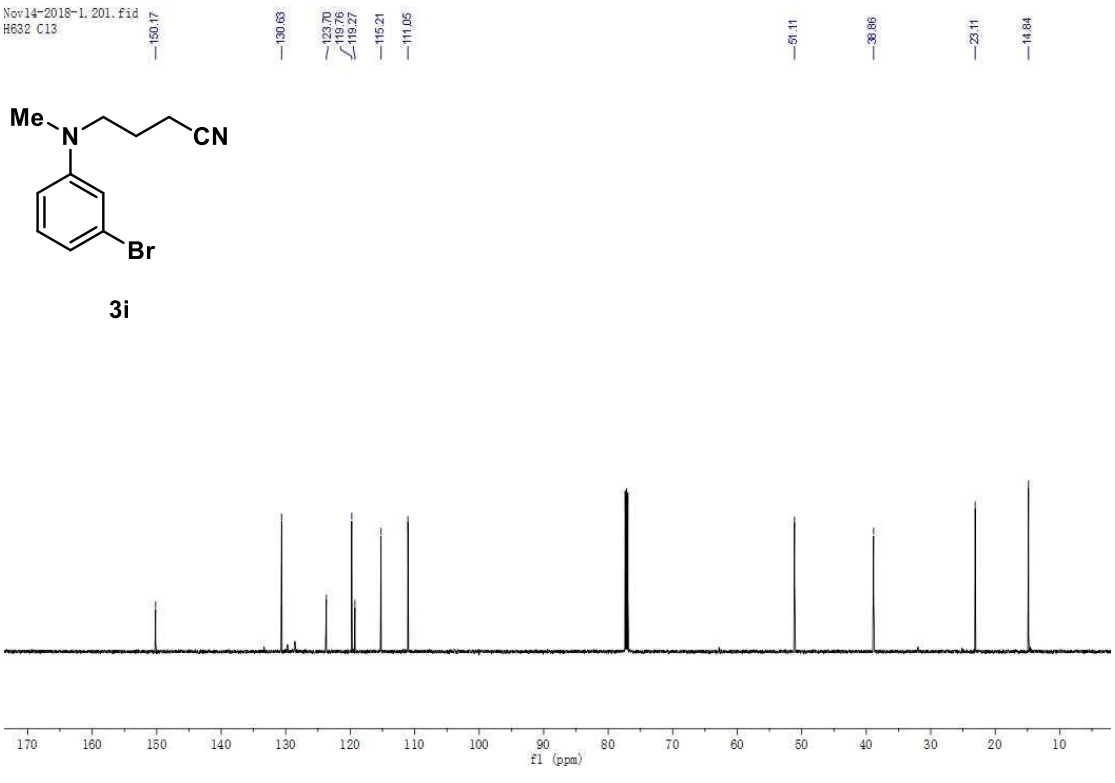
^{1}C NMR Spectra of **3h**



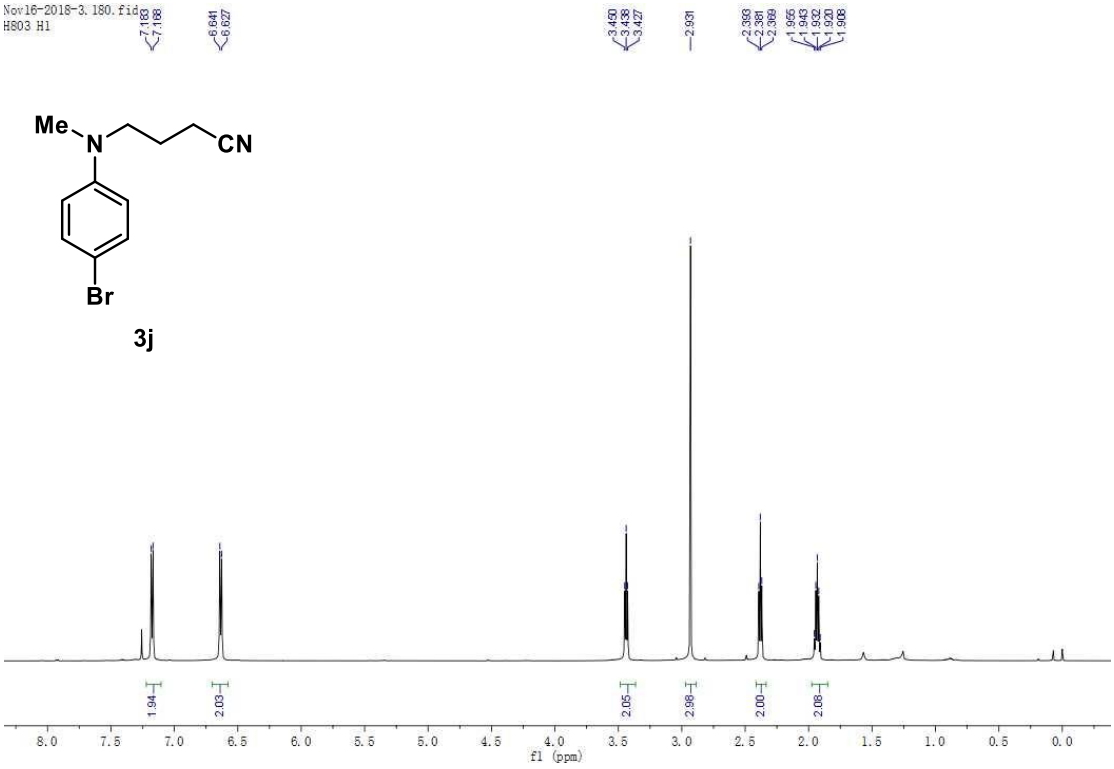
^{1}H NMR Spectra of **3i**



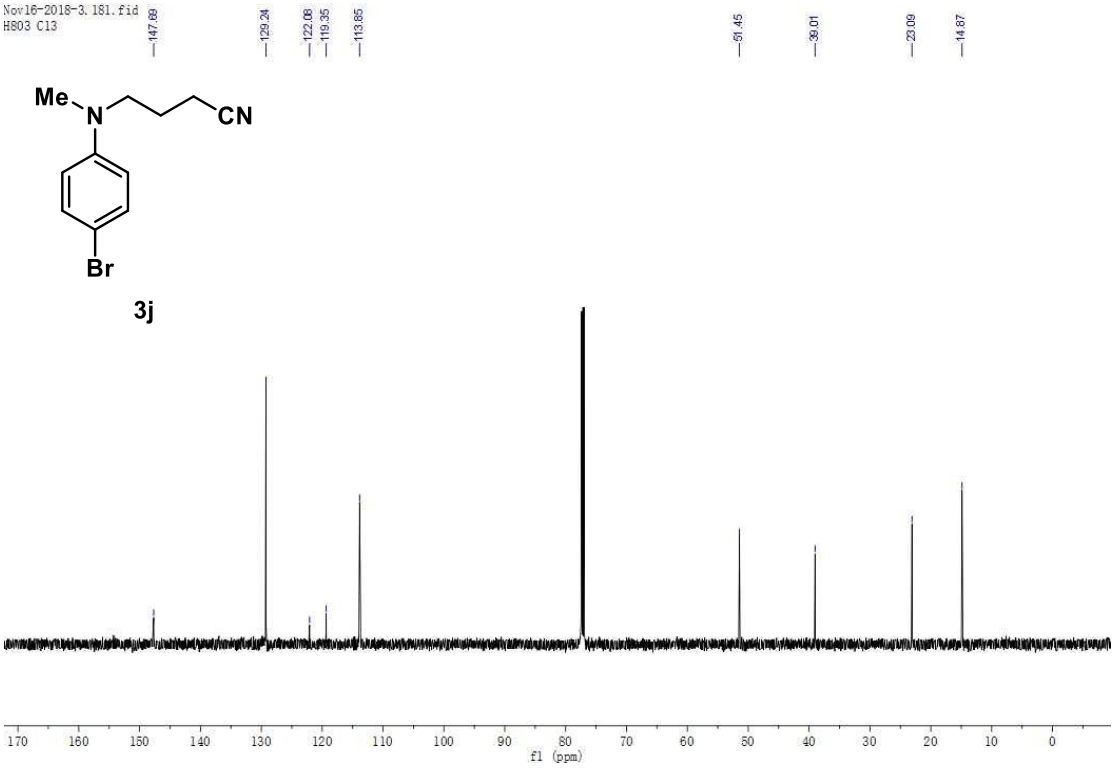
^{1}C NMR Spectra of **3i**



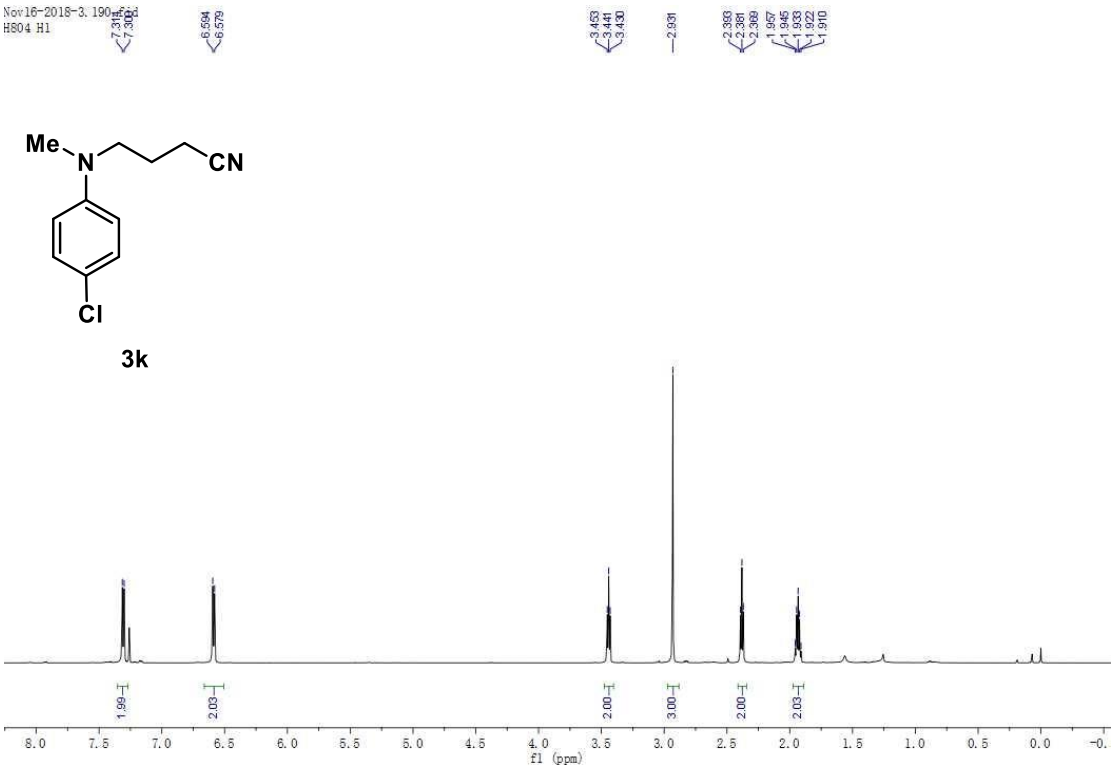
^{1}H NMR Spectra of **3j**



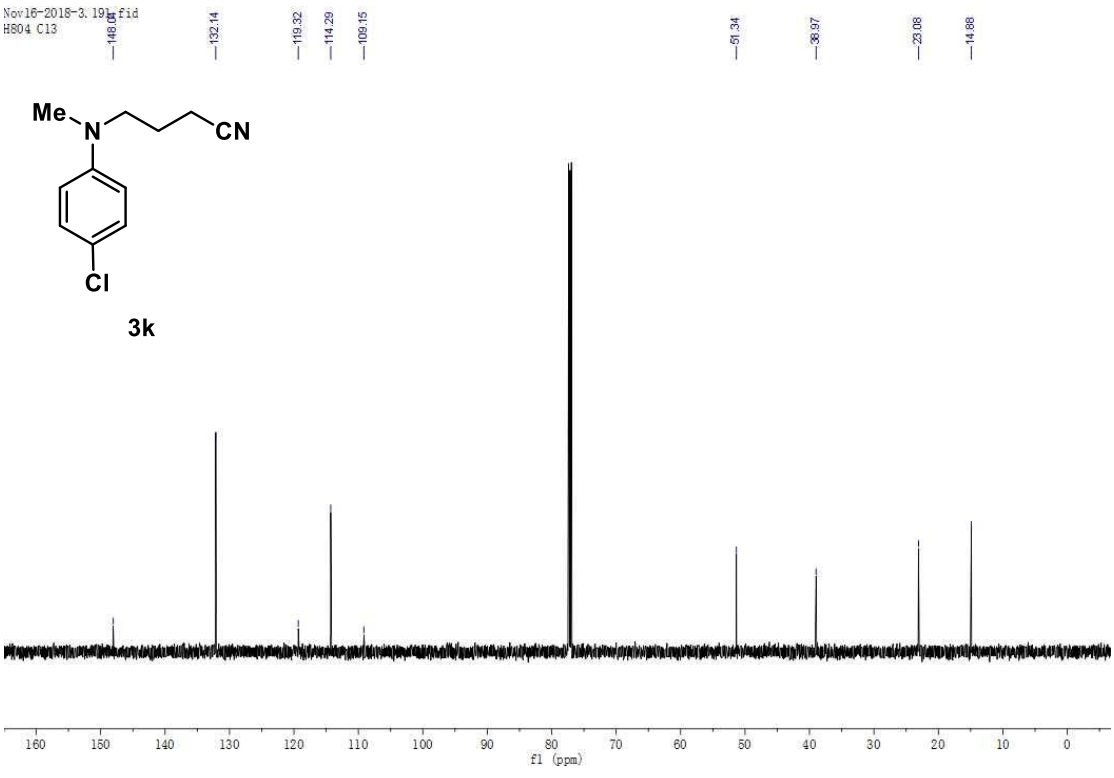
^{1}C NMR Spectra of **3j**



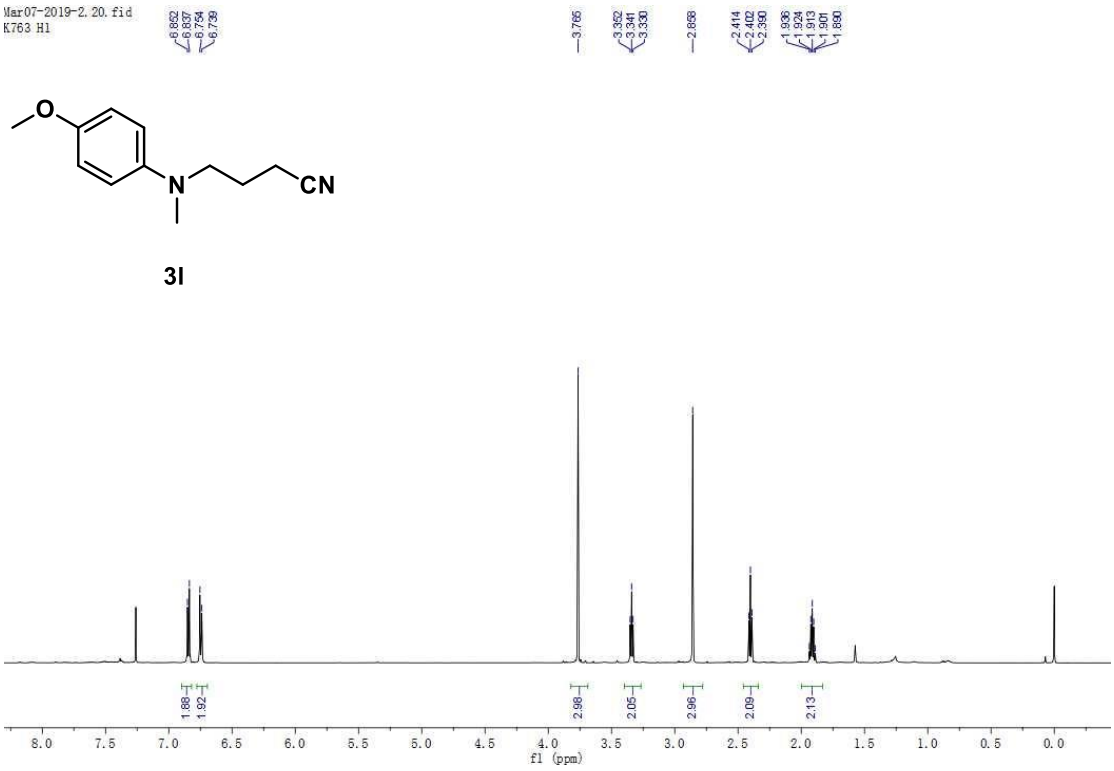
^{1}H NMR Spectra of **3k**



^{1}C NMR Spectra of **3k**

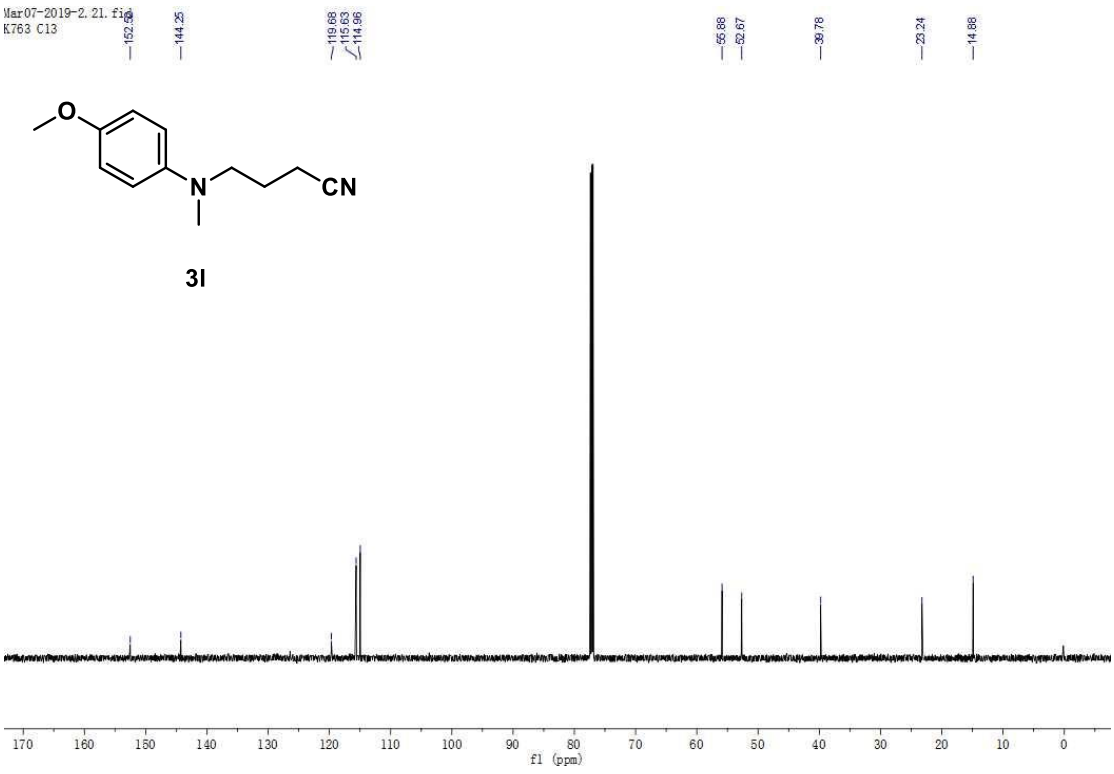


^{1}H NMR Spectra of **3l**



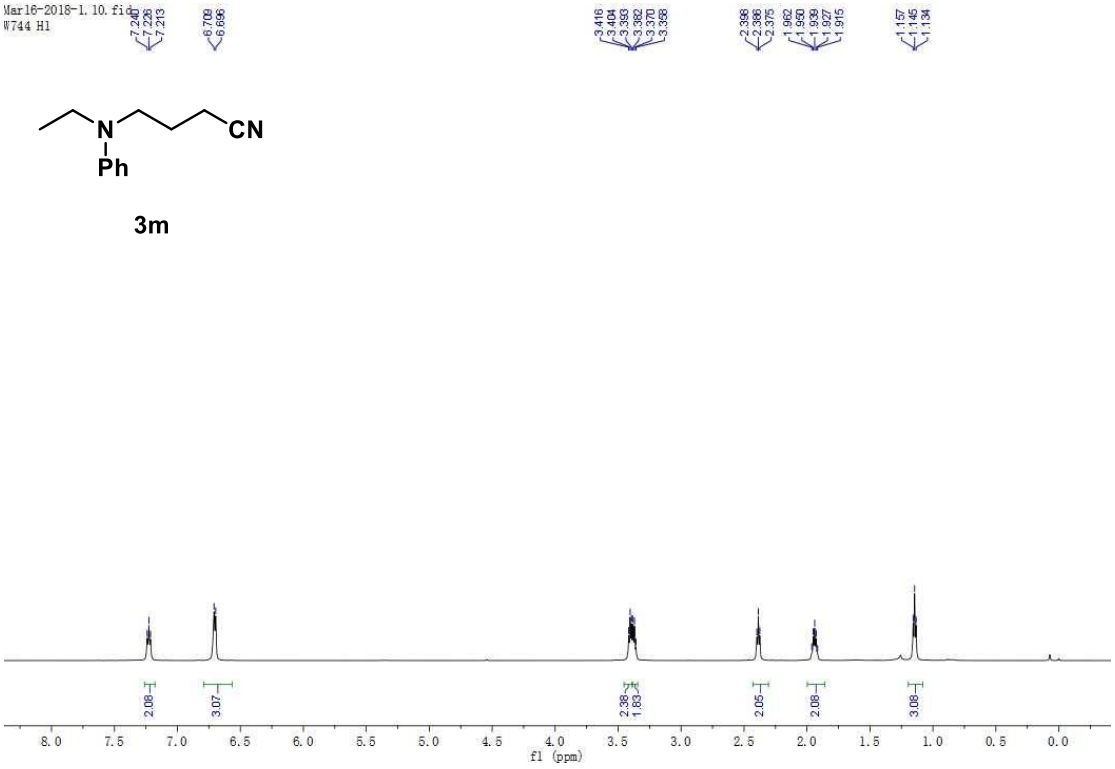
3l

^{1}C NMR Spectra of **3l**



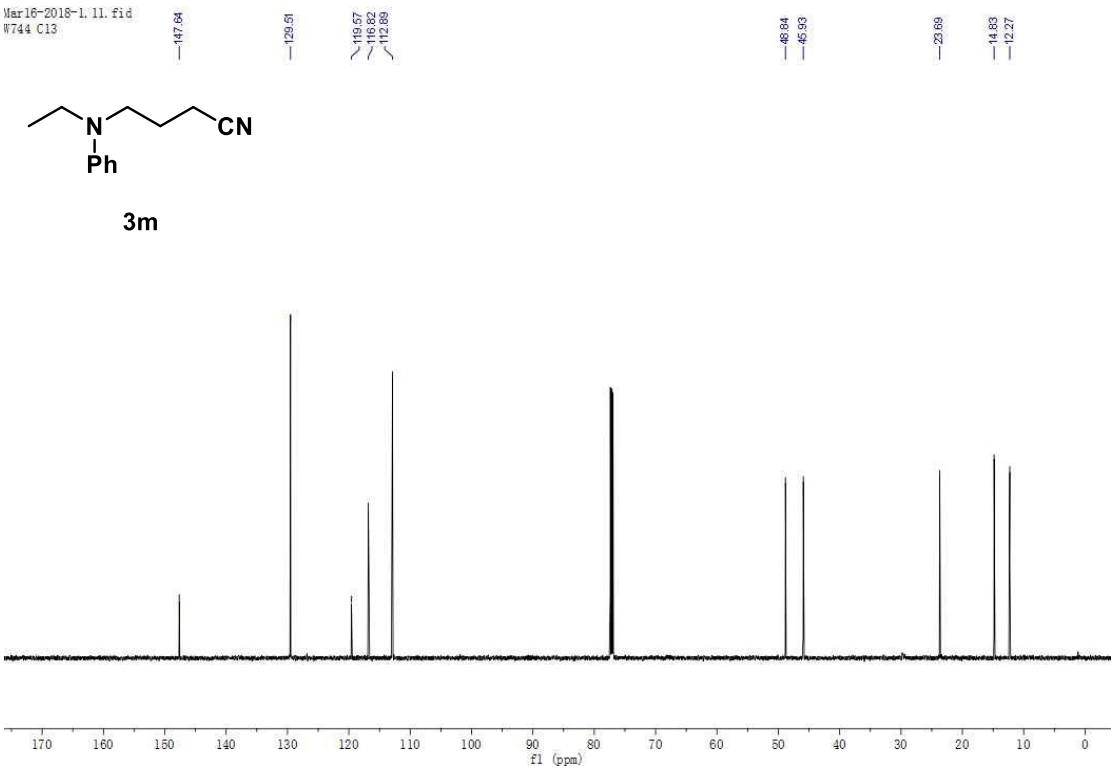
3l

^{1}H NMR Spectra of **3m**



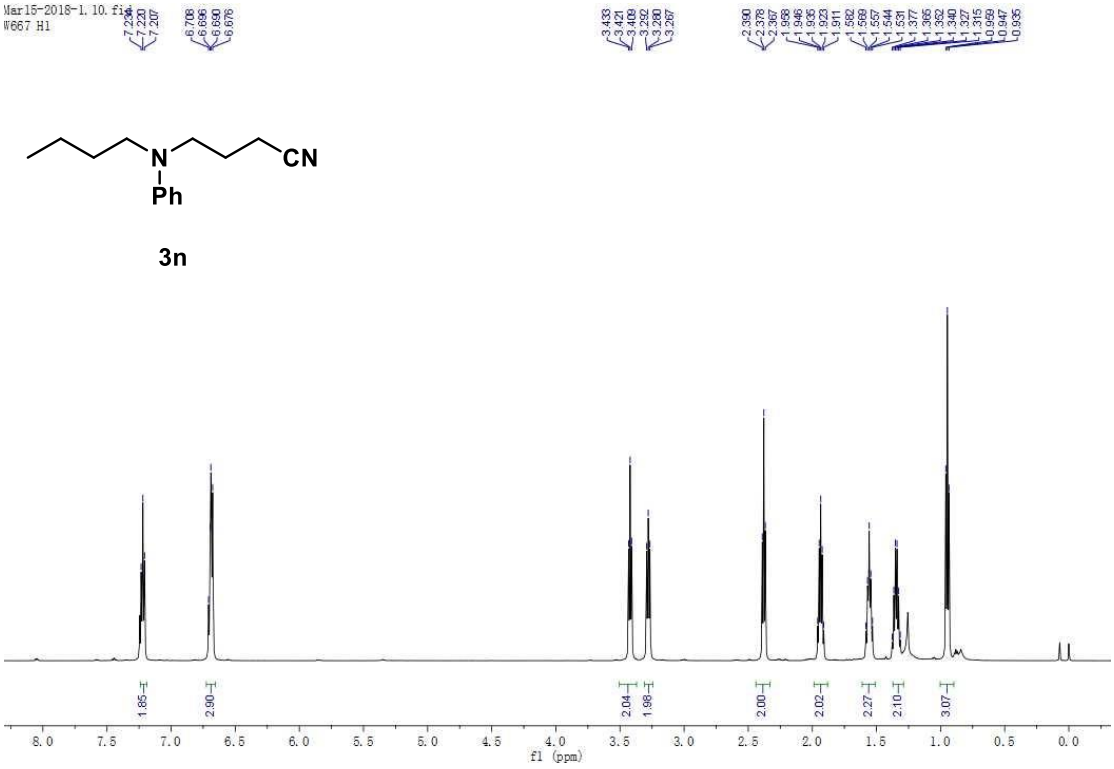
3m

^{1}C NMR Spectra of **3m**



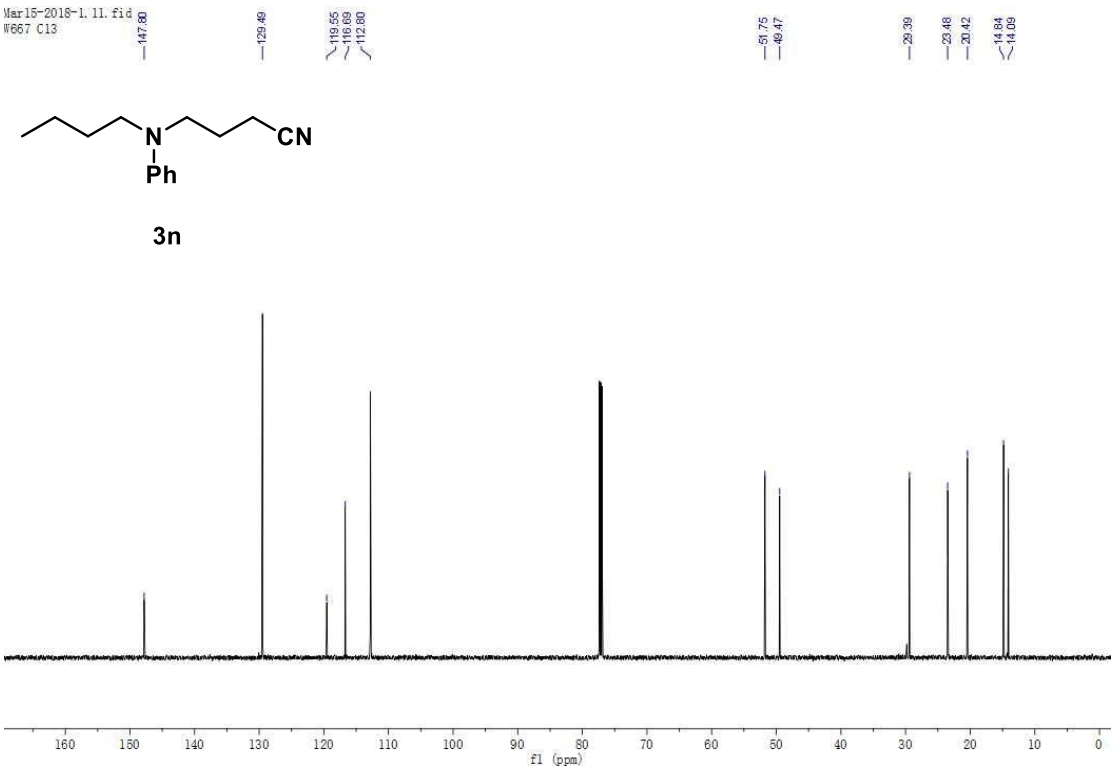
3m

^{1}H NMR Spectra of **3n**



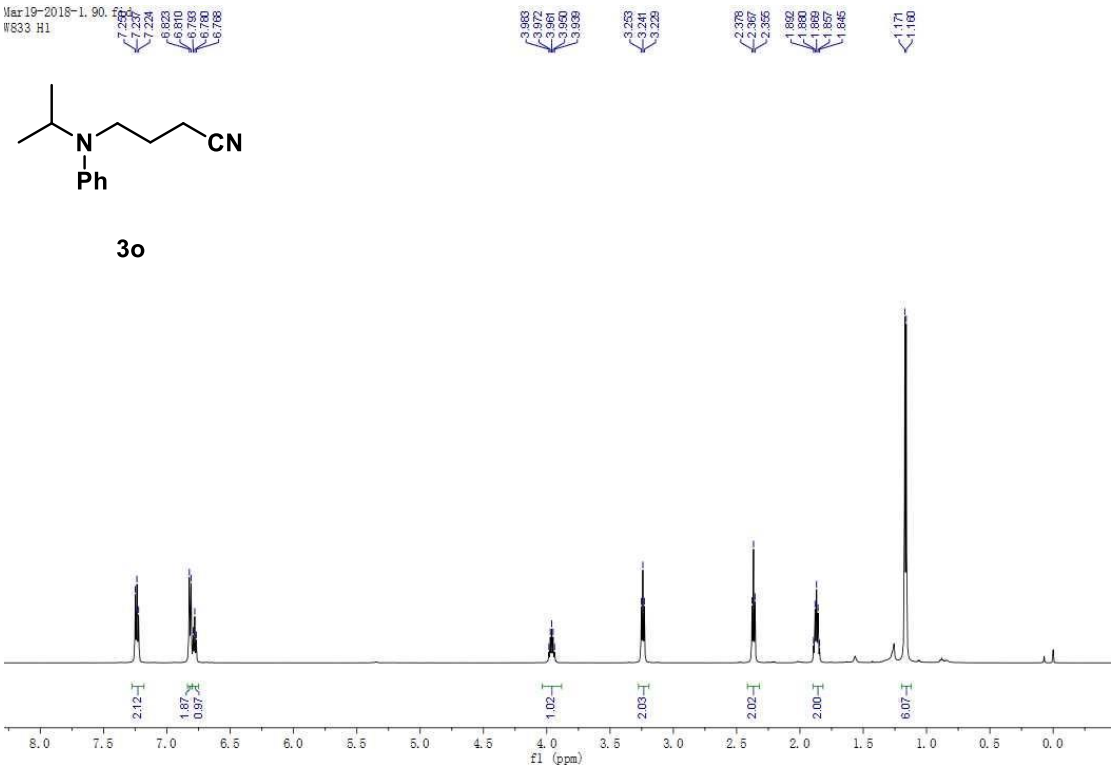
3n

^{1}C NMR Spectra of **3n**



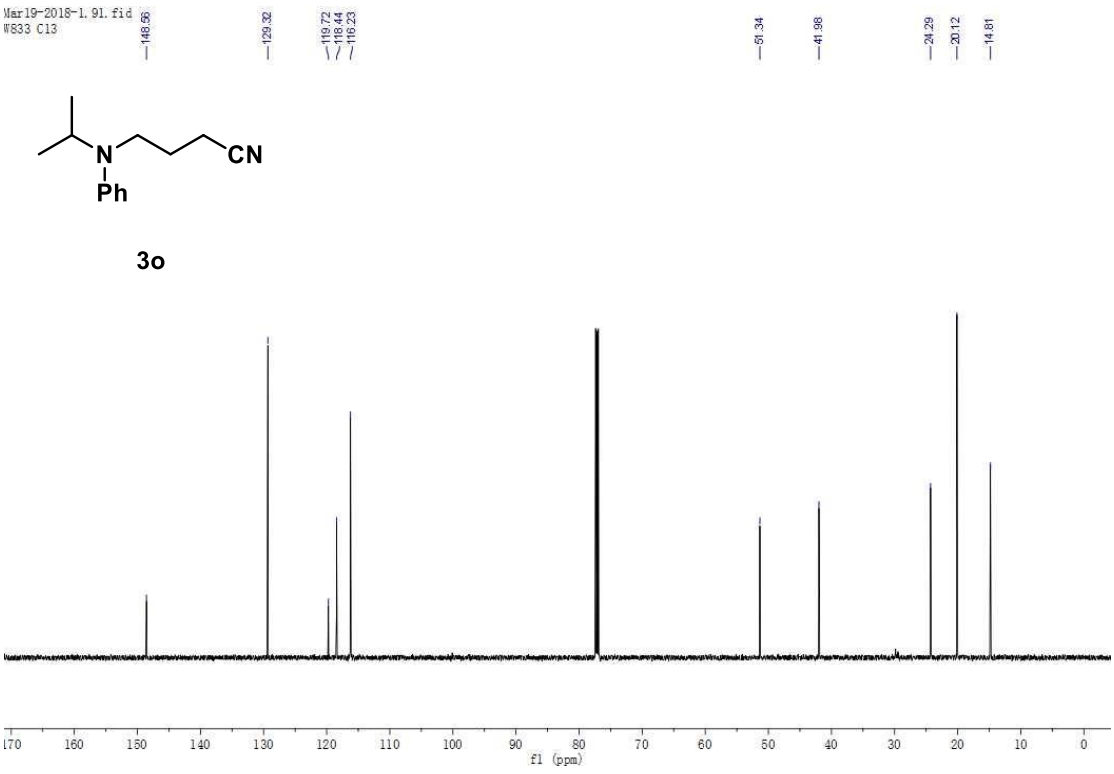
3n

^{1}H NMR Spectra of **3o**



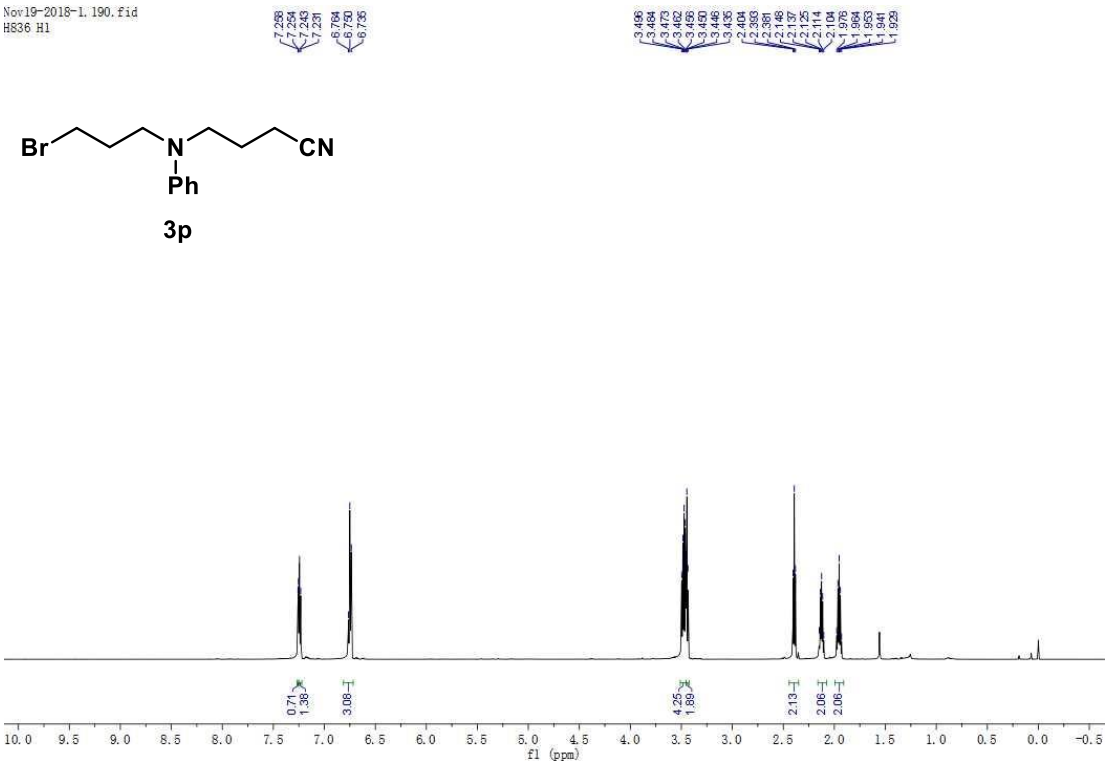
3o

^{1}C NMR Spectra of **3o**

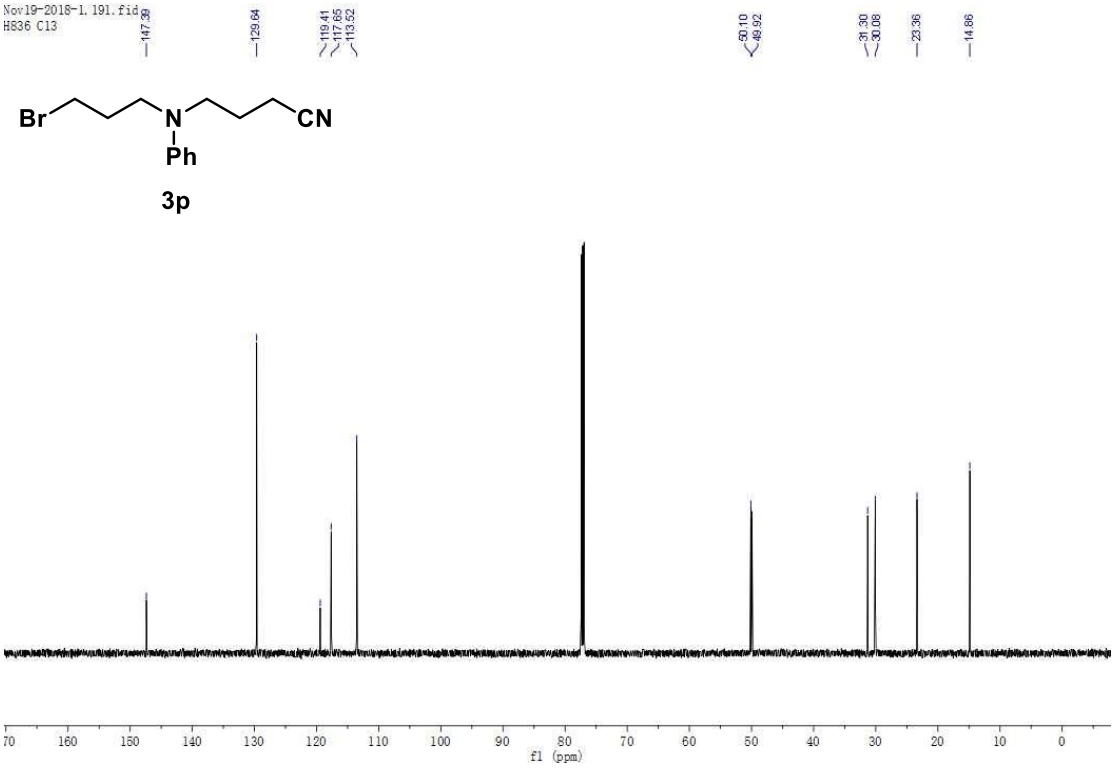


3o

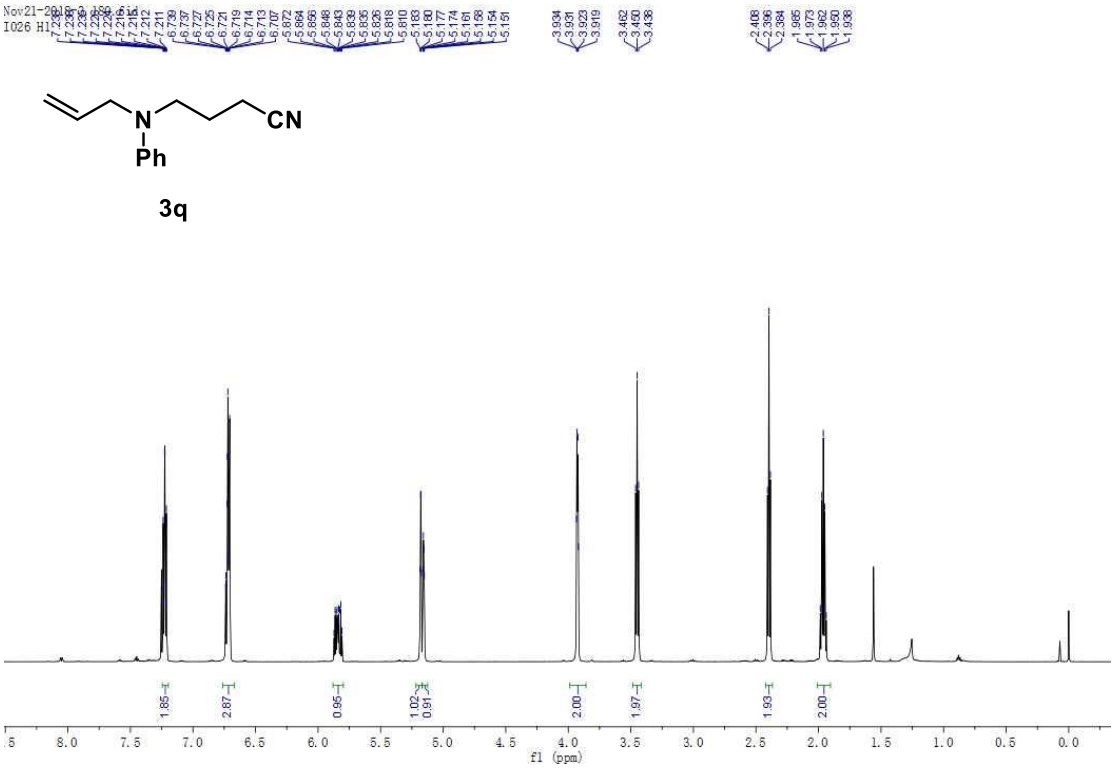
^{1}H NMR Spectra of **3p**



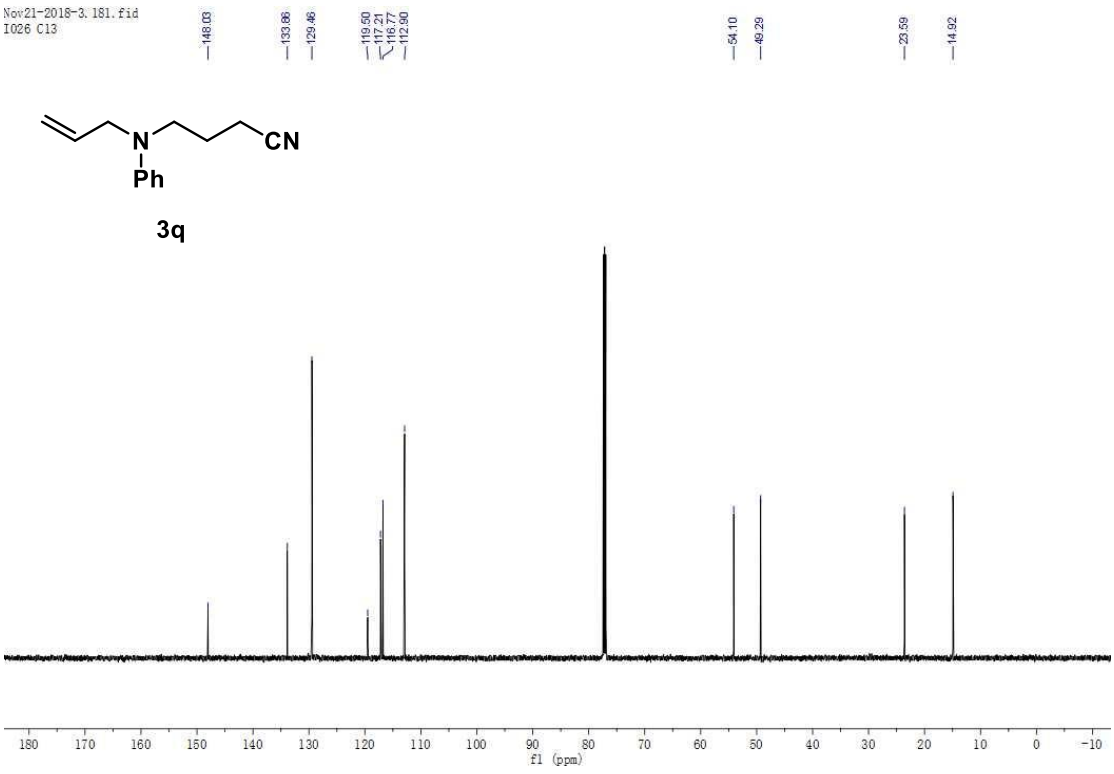
^{1}C NMR Spectra of **3p**



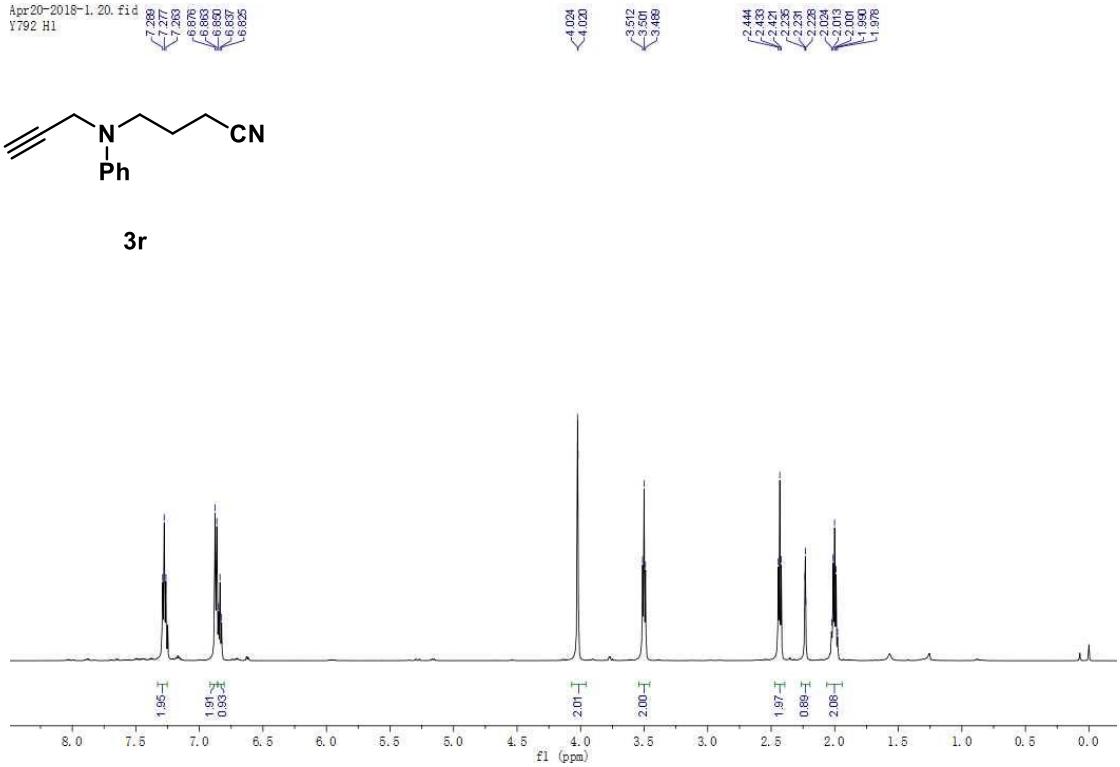
^{1}H NMR Spectra of **3q**



^{1}C NMR Spectra of **3q**

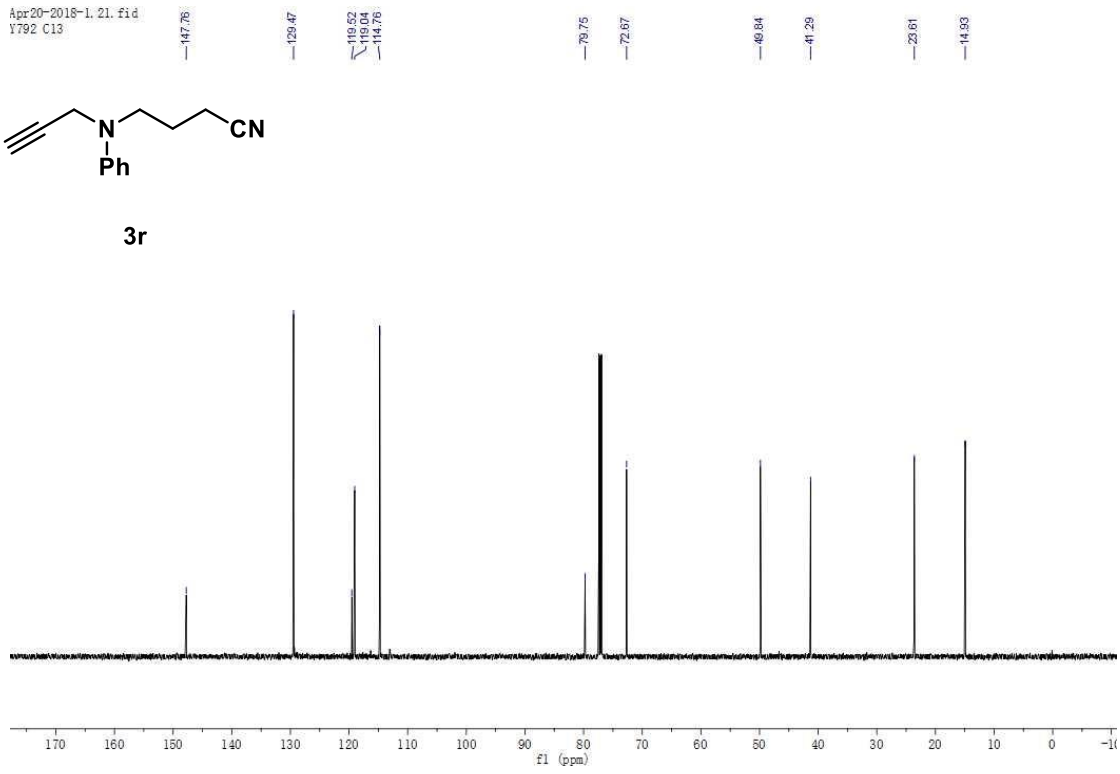


^{1}H NMR Spectra of **3r**



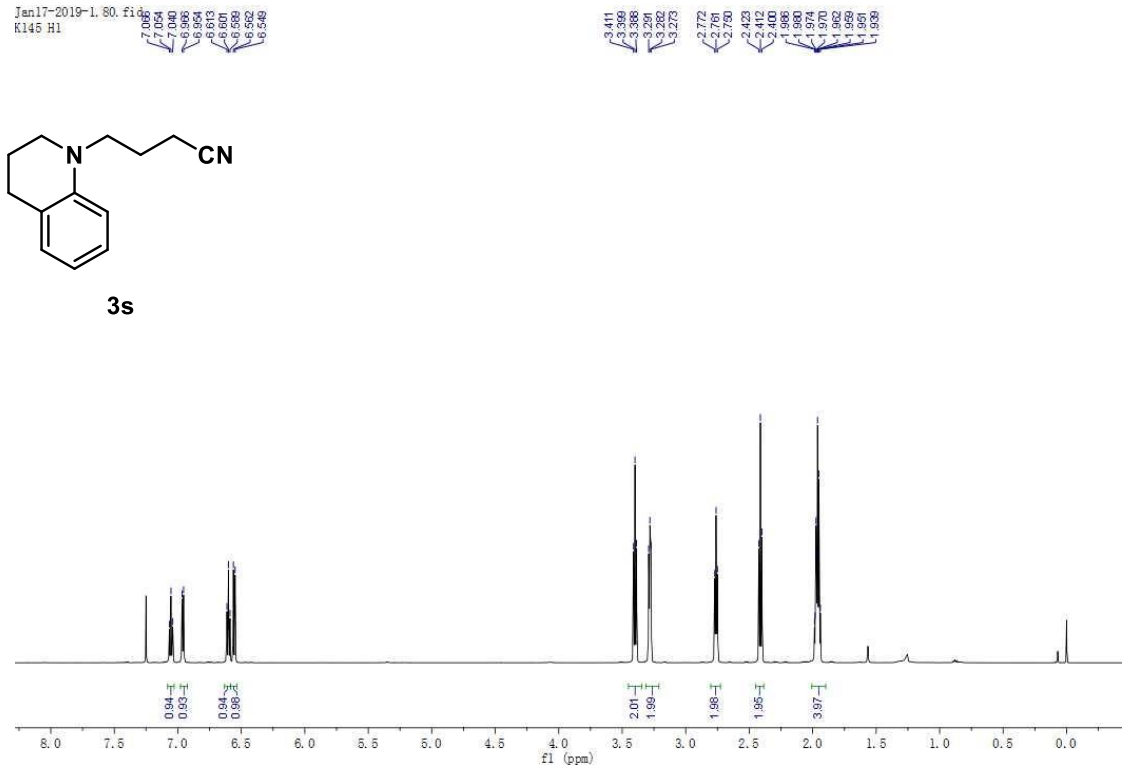
3r

^{1}C NMR Spectra of **3r**

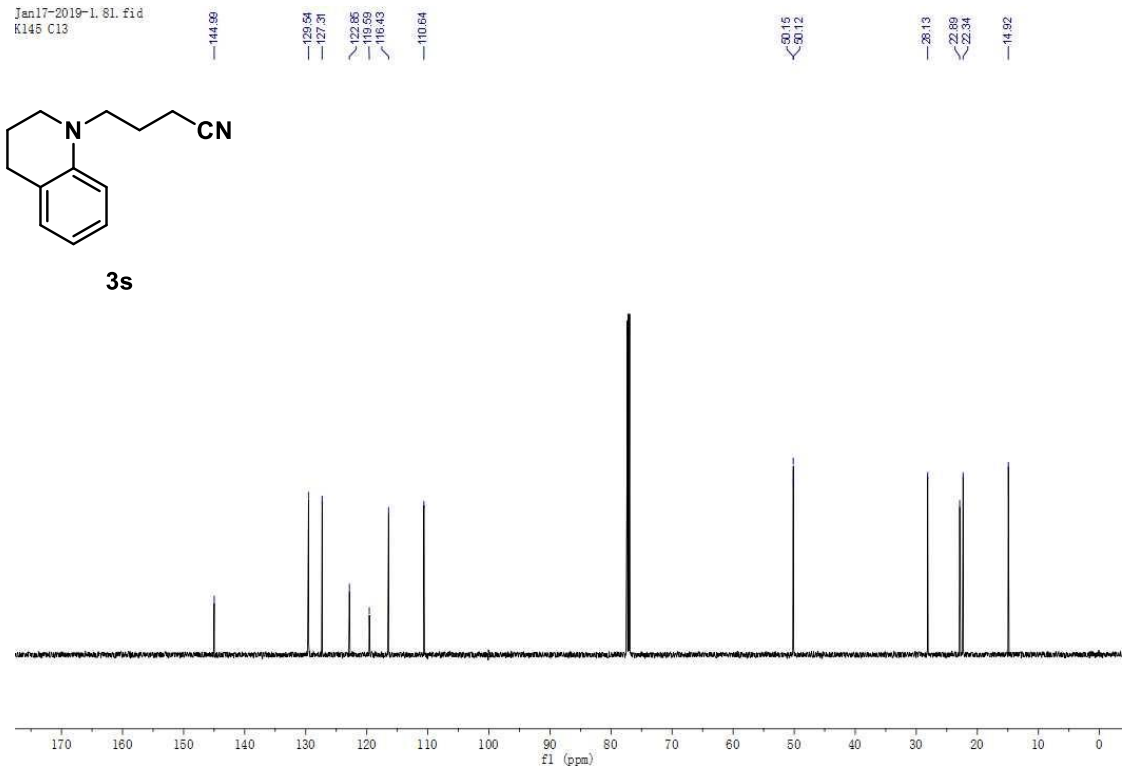


3r

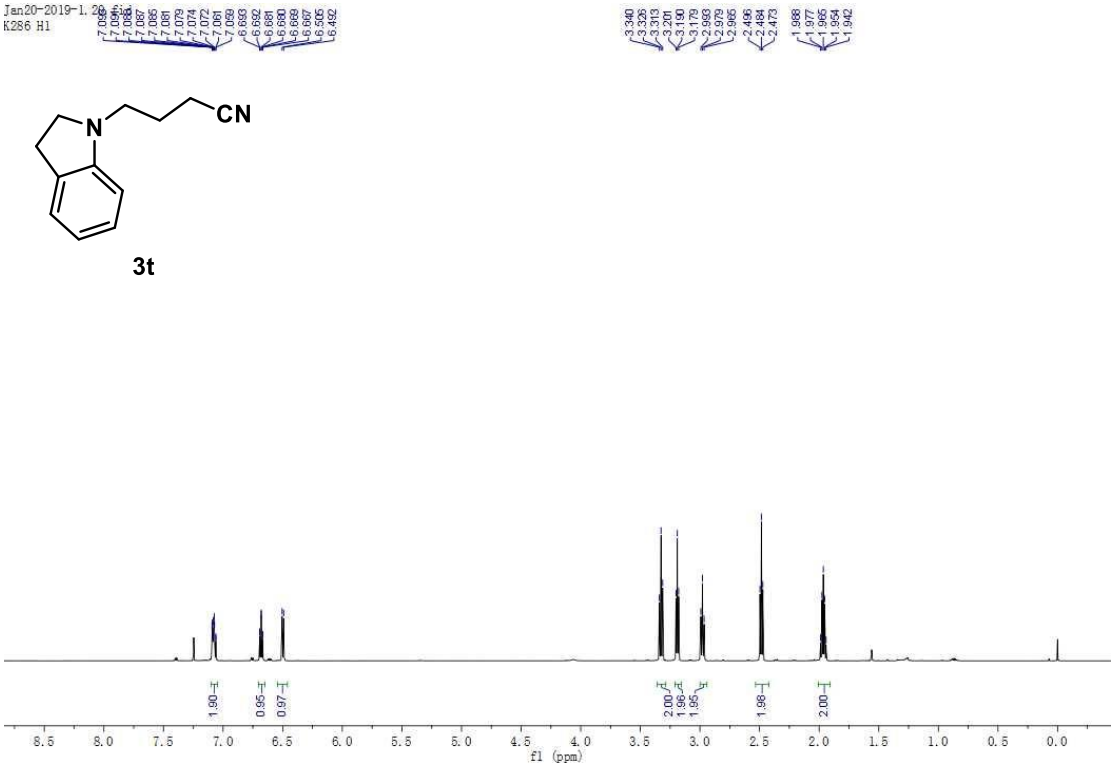
^{1}H NMR Spectra of **3s**



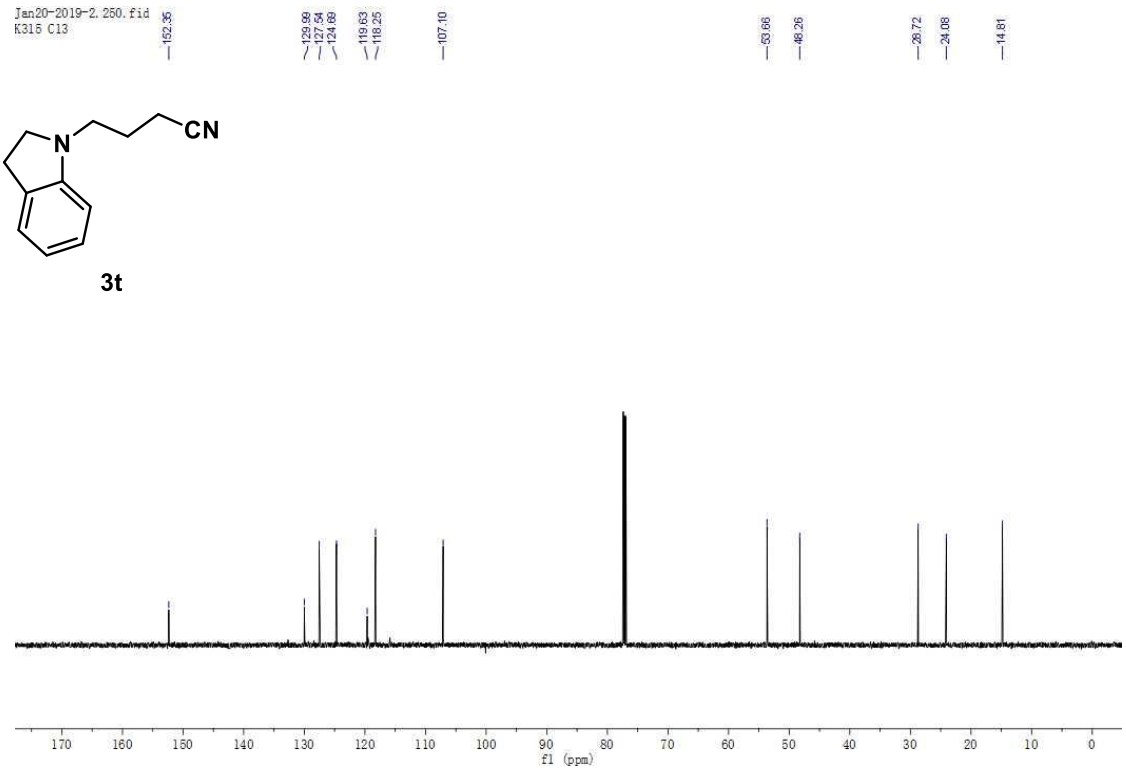
^{1}C NMR Spectra of **3s**



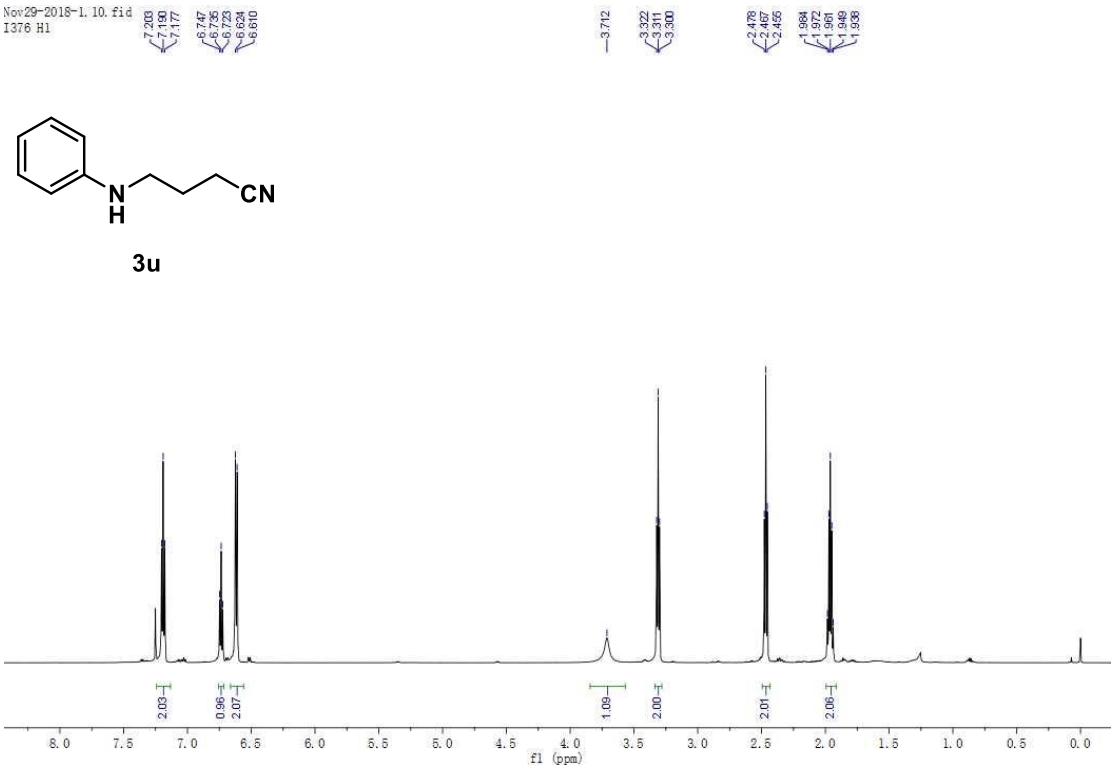
^{1}H NMR Spectra of **3t**



^{1}C NMR Spectra of **3t**

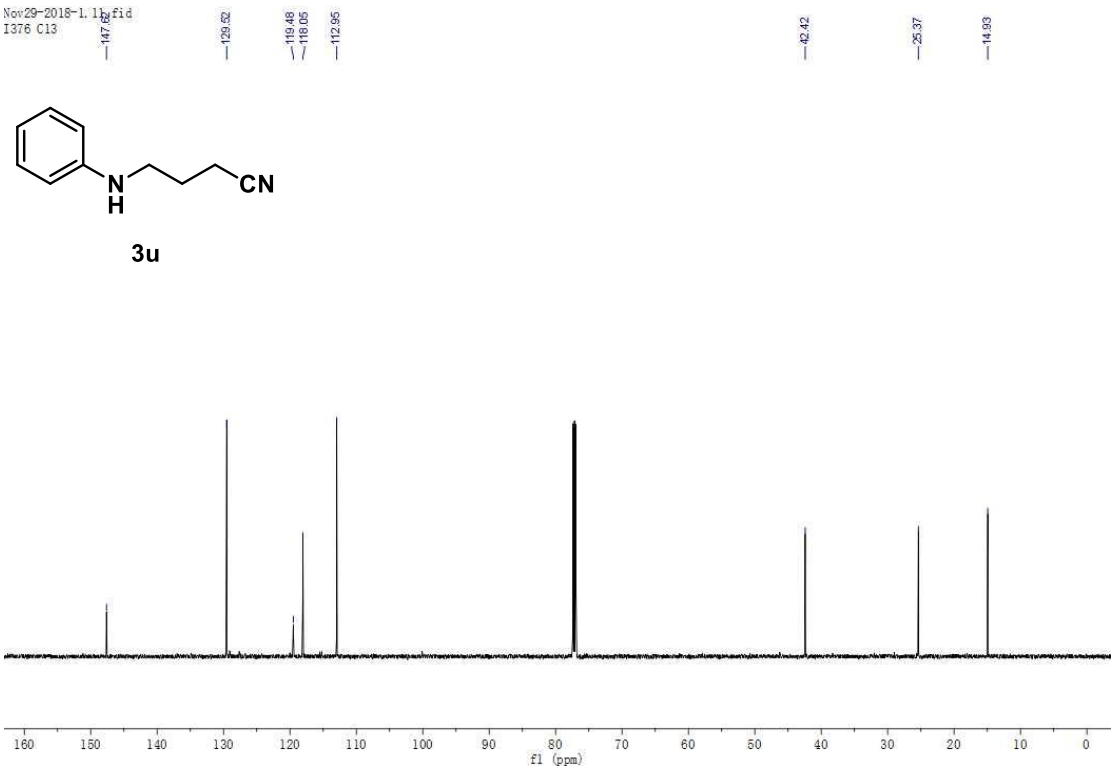


^{1}H NMR Spectra of **3u**



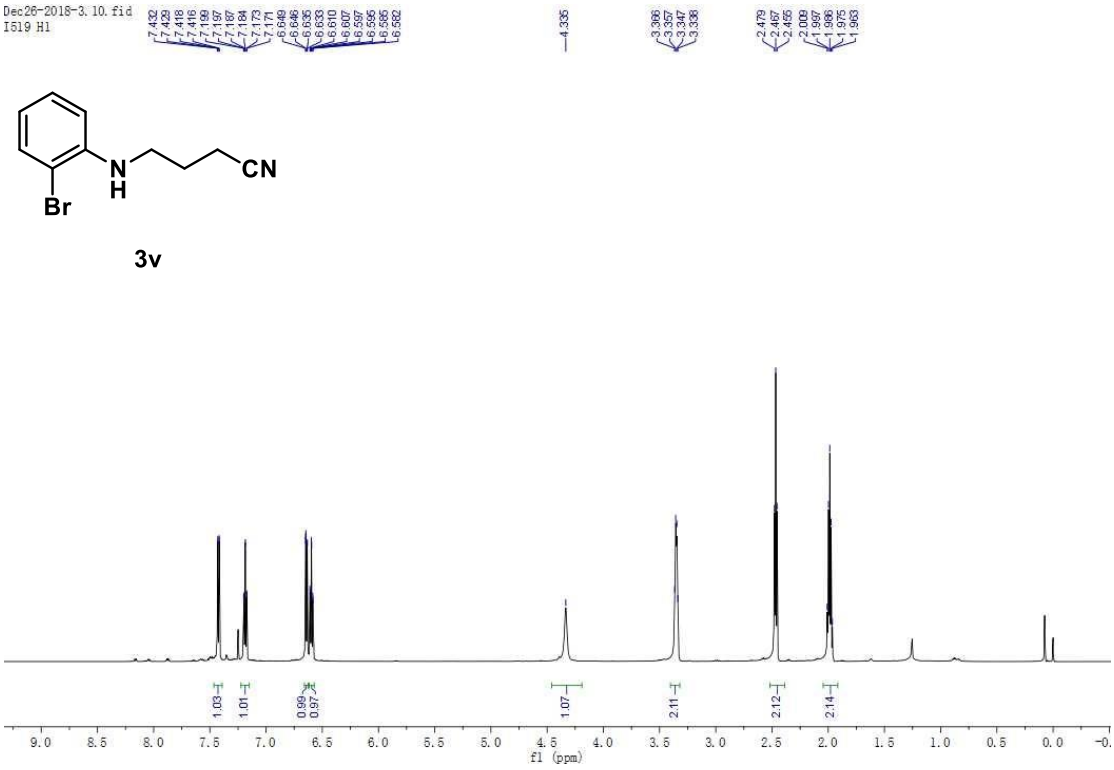
3u

^{1}C NMR Spectra of **3u**



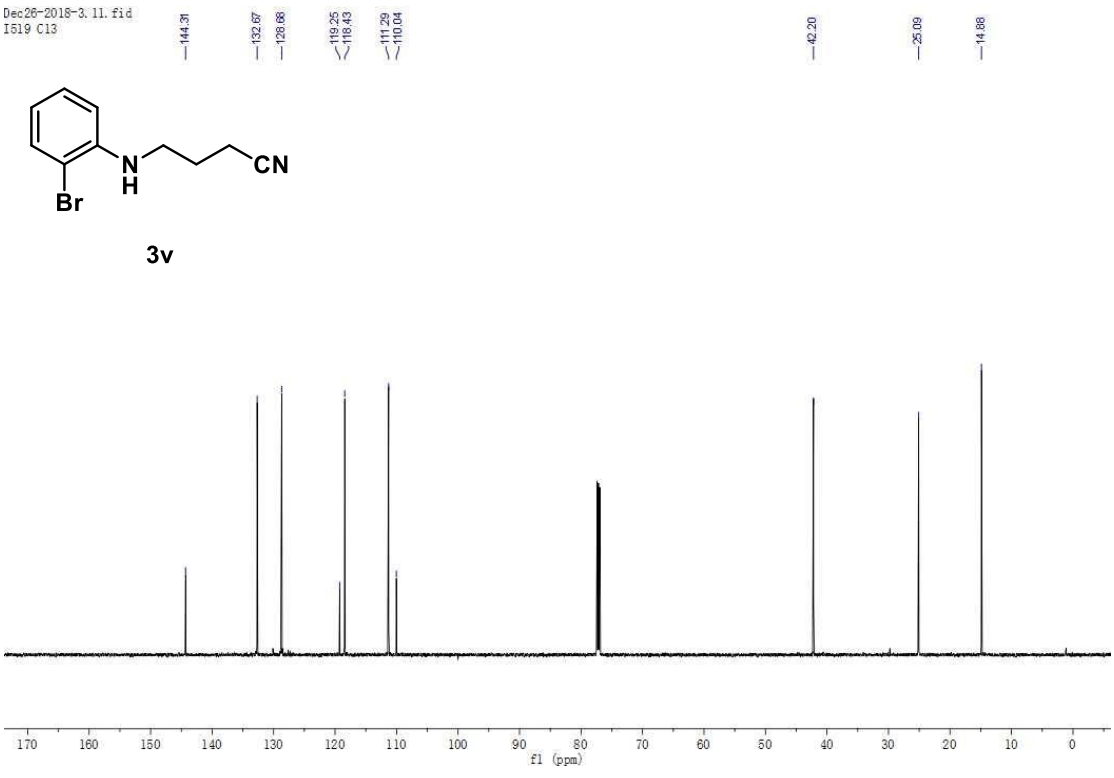
3u

^{1}H NMR Spectra of **3v**



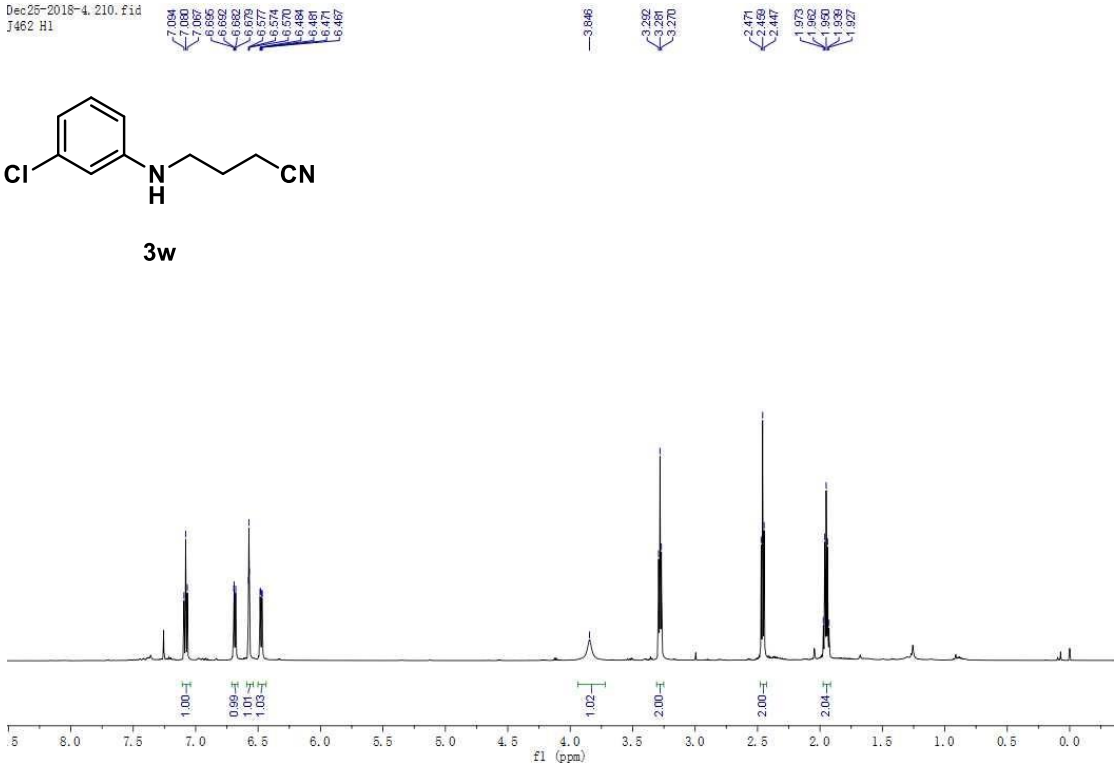
3v

^{1}C NMR Spectra of **3v**

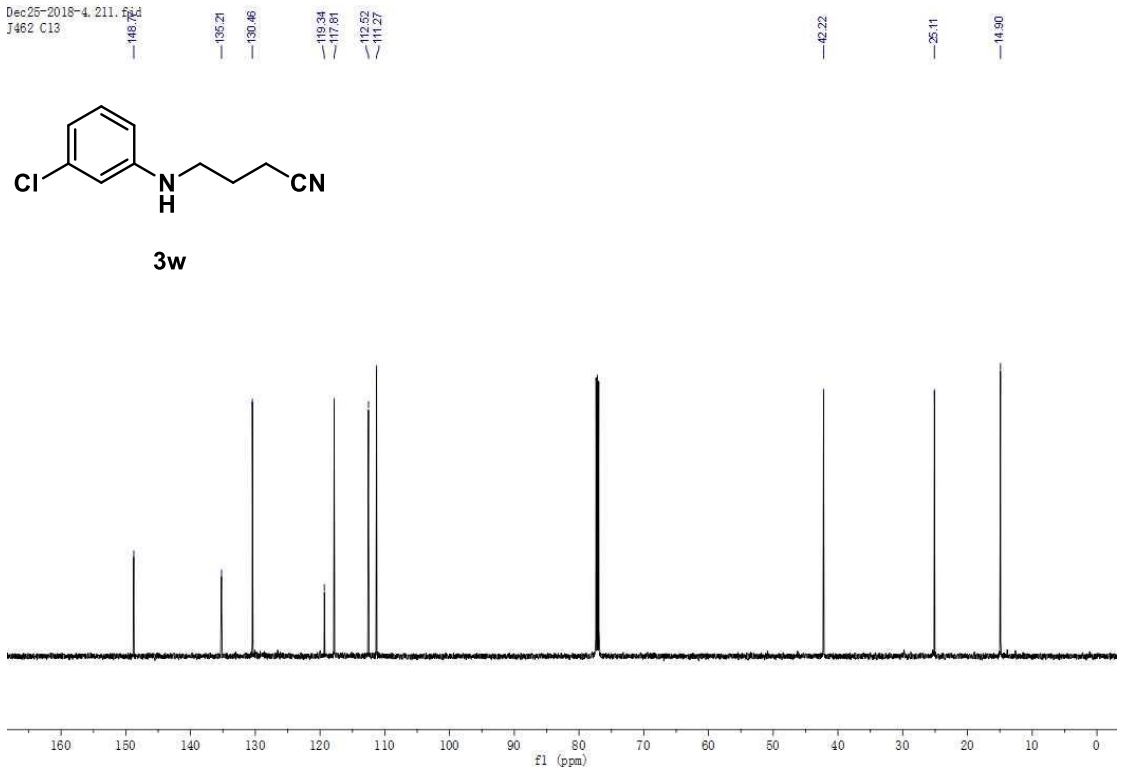


3v

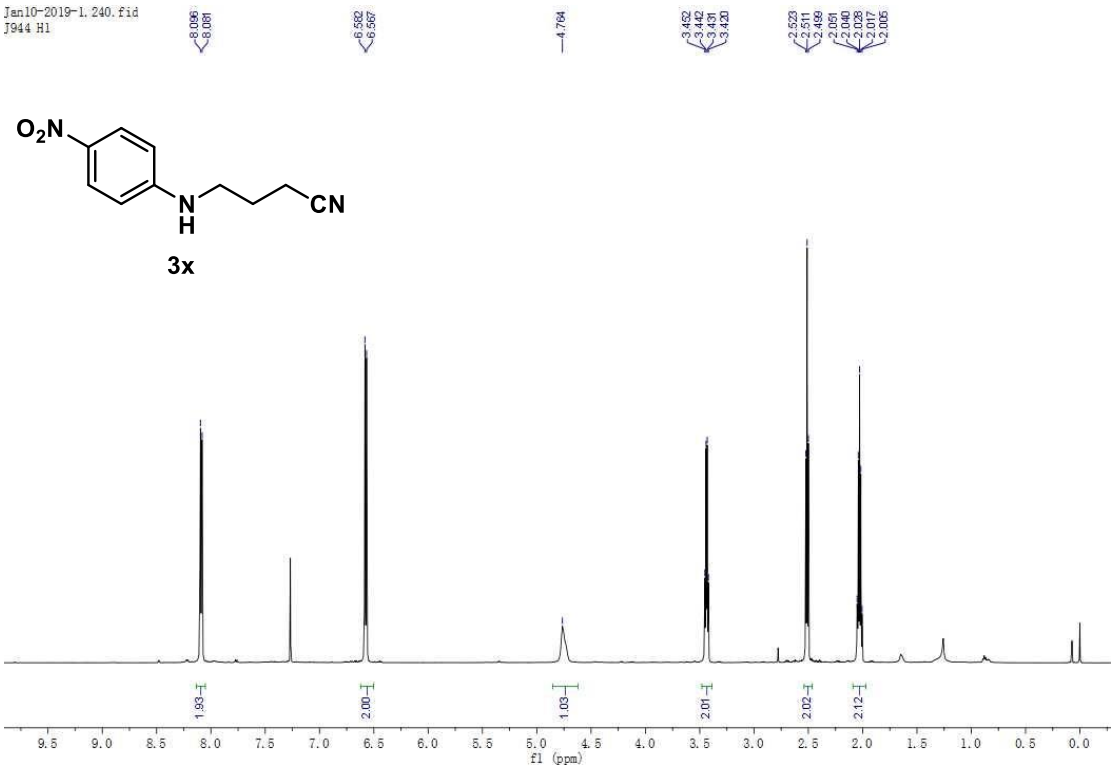
^{1}H NMR Spectra of **3w**



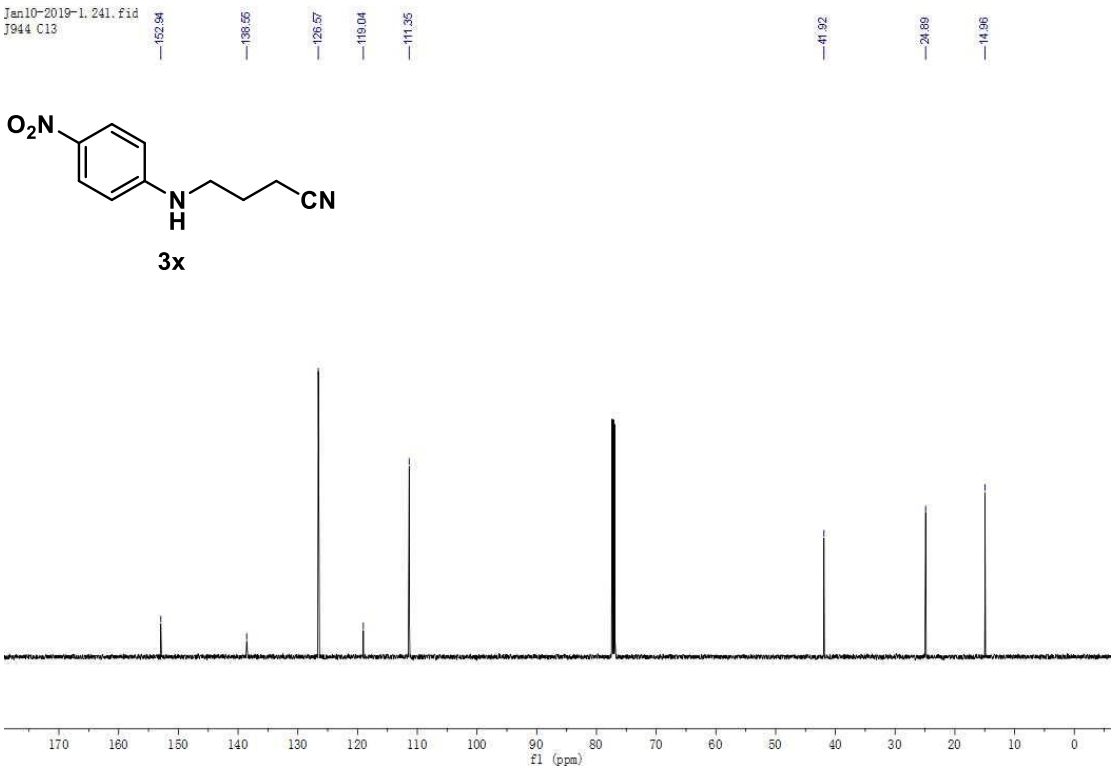
^{1}C NMR Spectra of **3w**



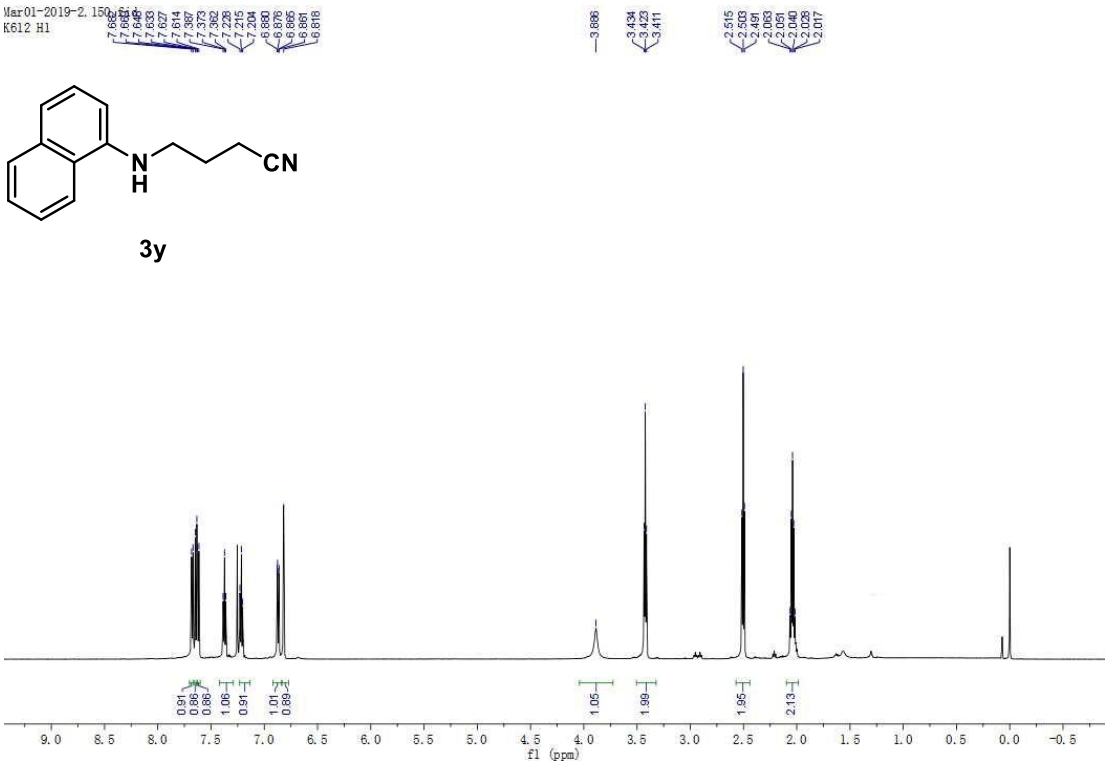
^{1}H NMR Spectra of **3x**



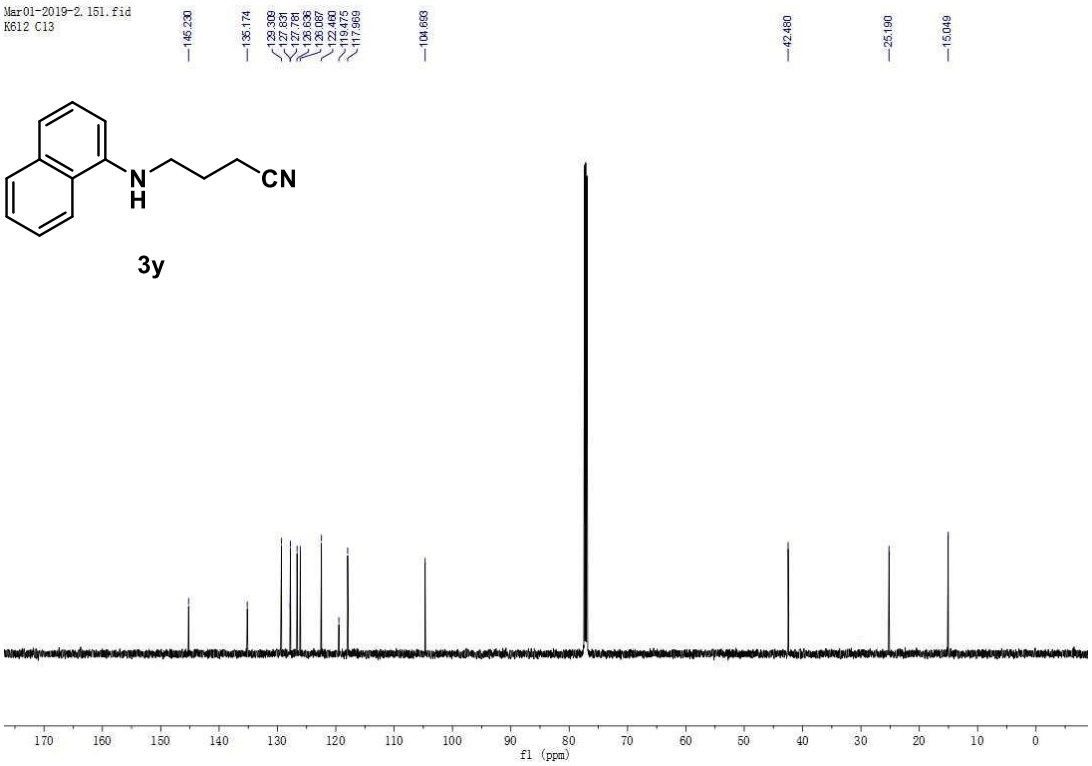
^{1}C NMR Spectra of **3x**



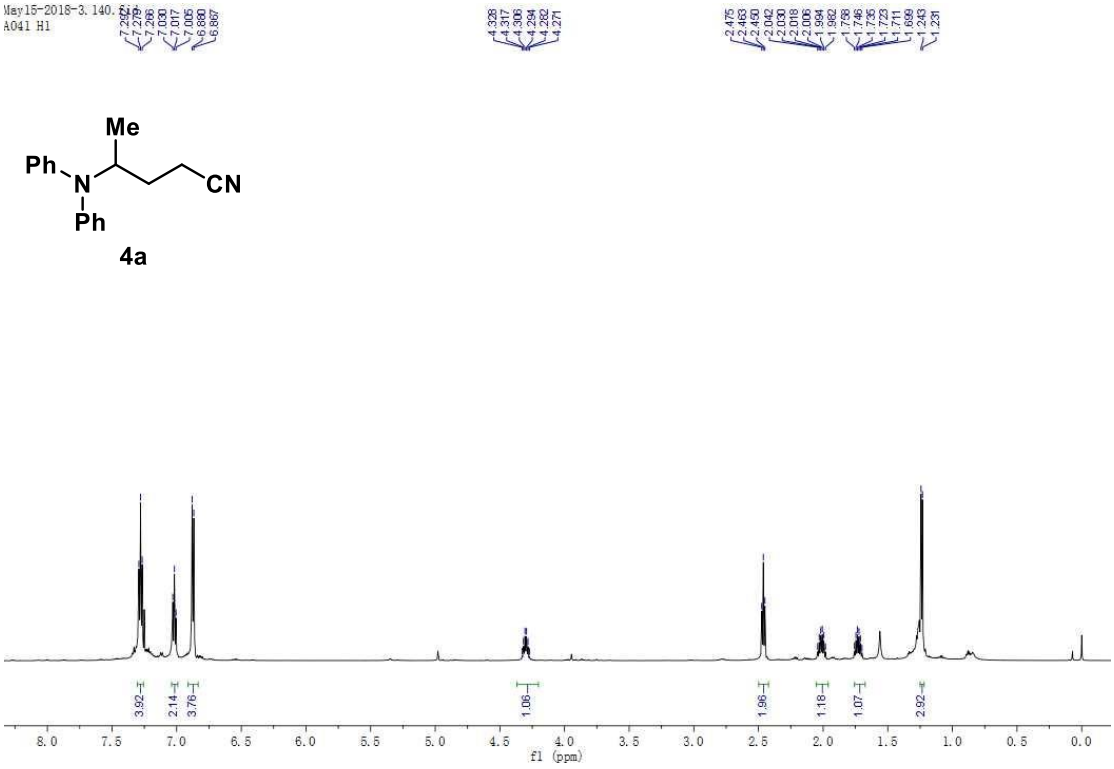
^{1}H NMR Spectra of **3y**



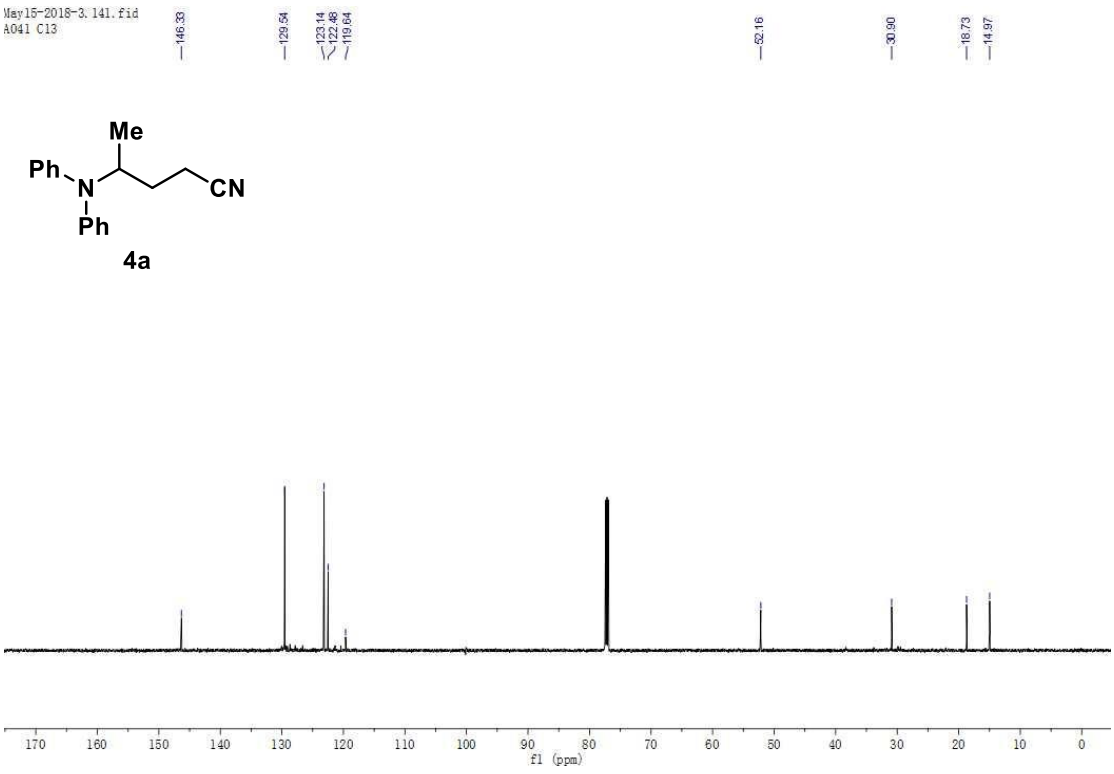
^{1}C NMR Spectra of **3y**



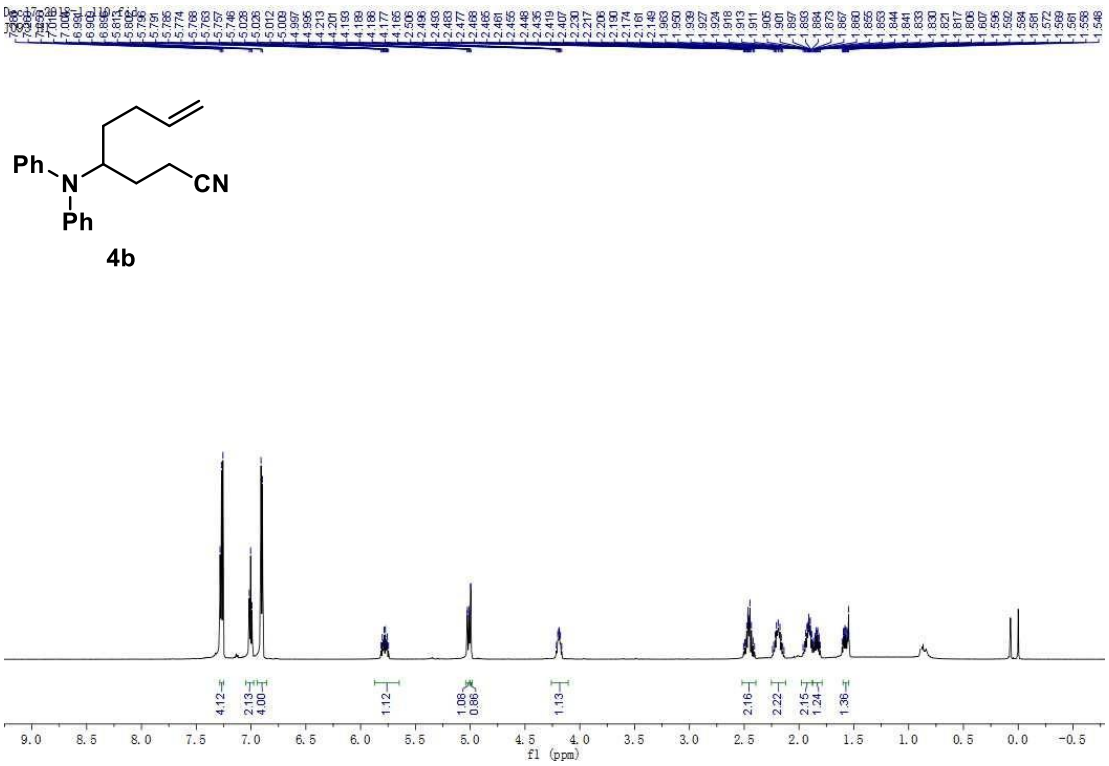
^{1}H NMR Spectra of **4a**



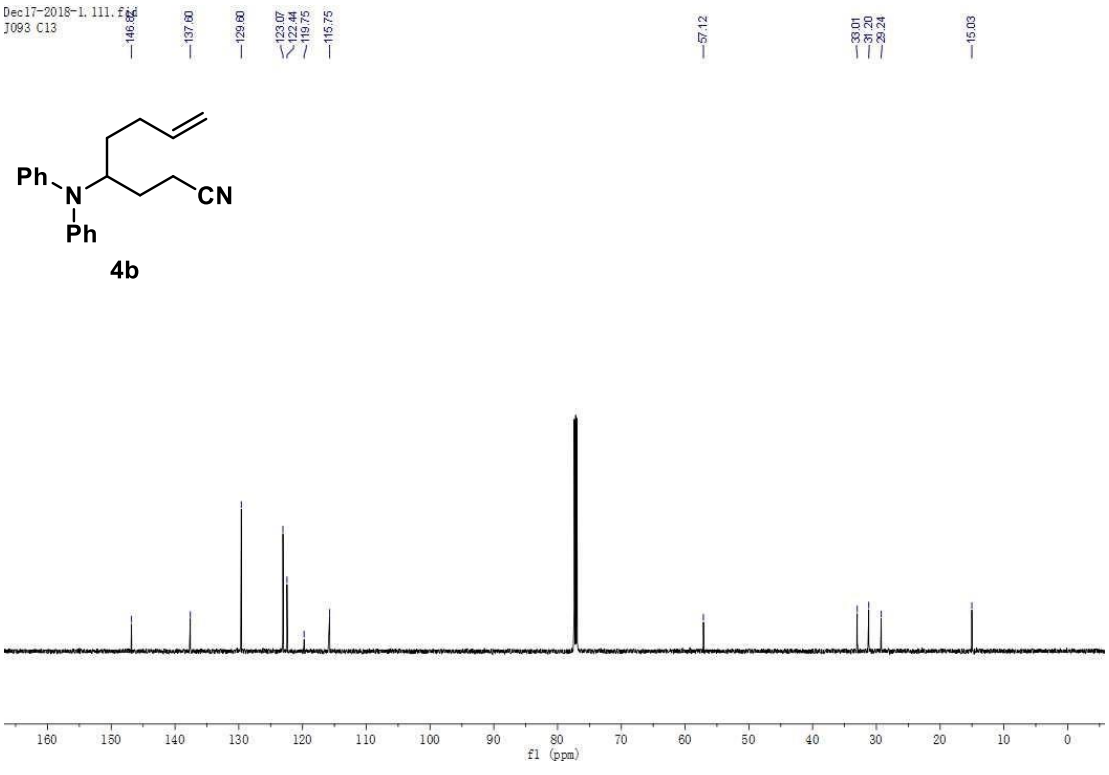
^{1}C NMR Spectra of **4a**



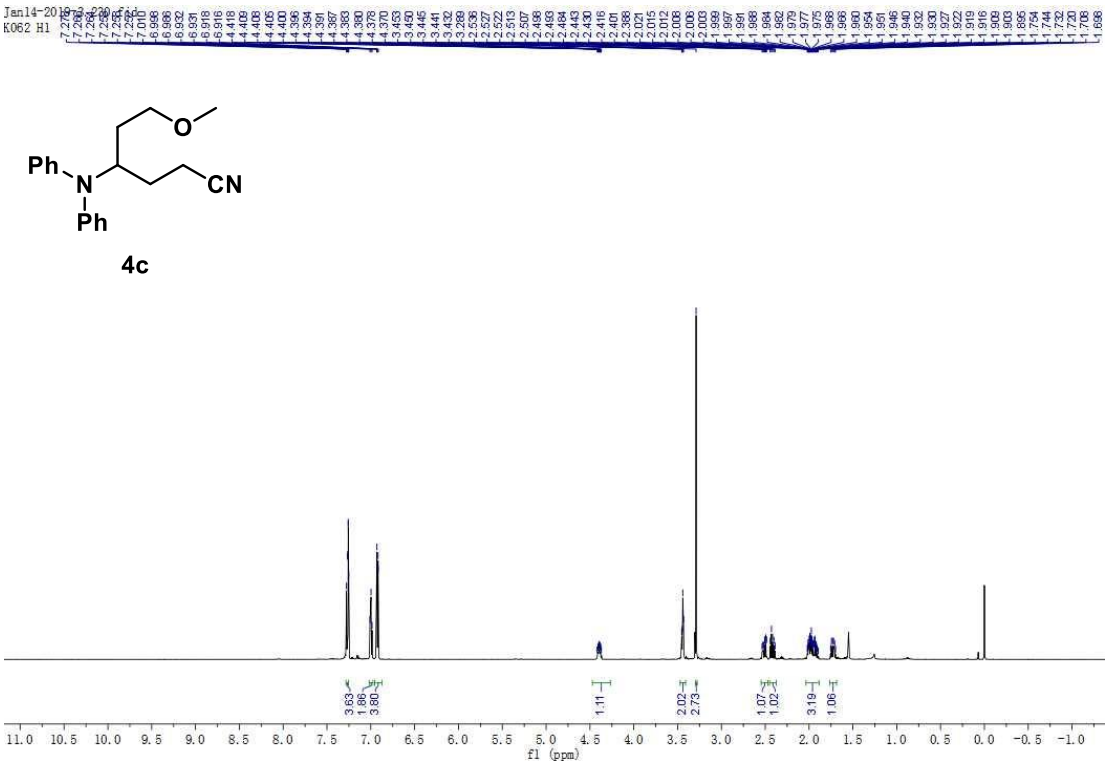
^{1}H NMR Spectra of **4b**



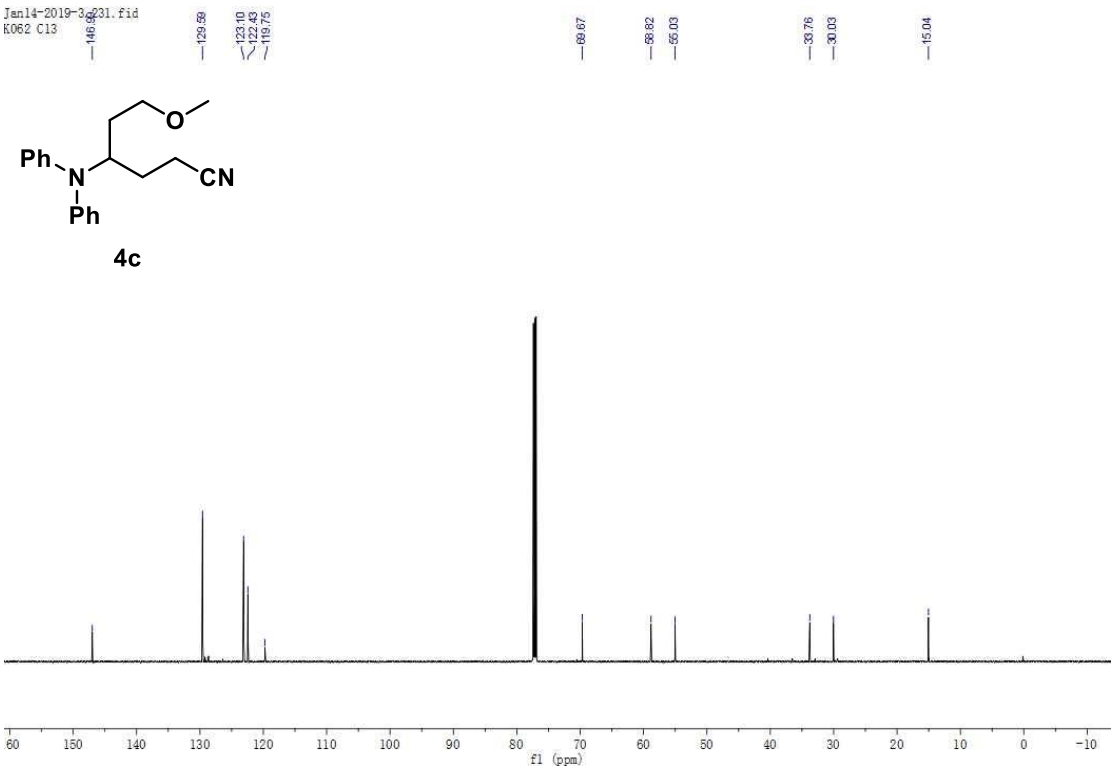
^{1}C NMR Spectra of **4b**



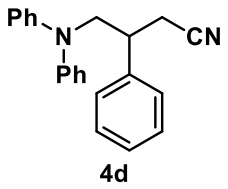
[1]H NMR Spectra of **4c**



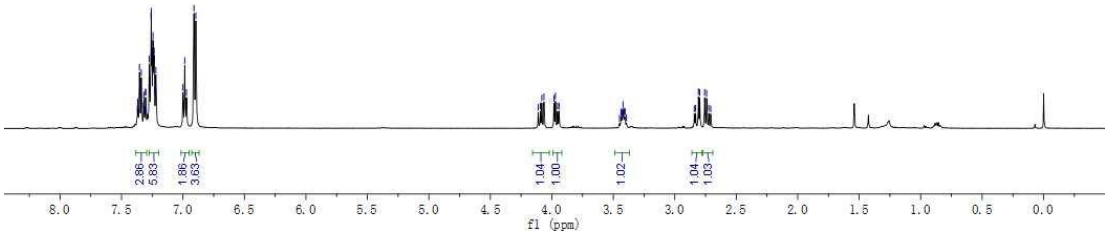
[1] C NMR Spectra of **4c**



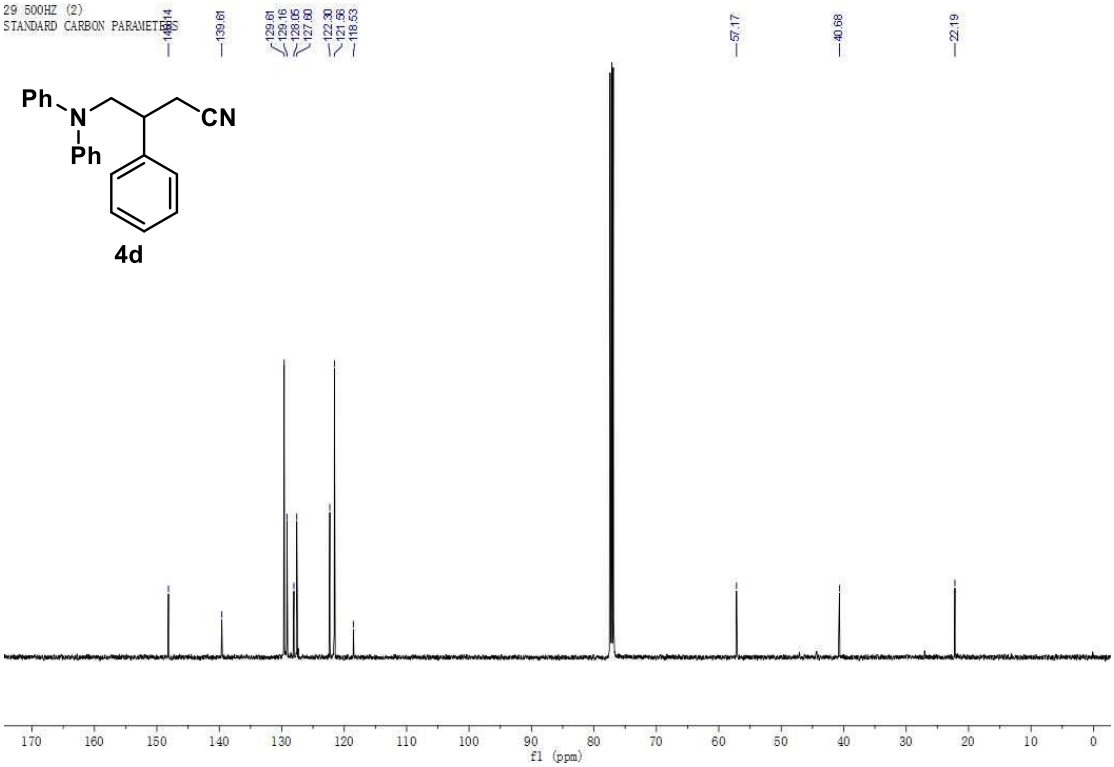
^{1}H NMR Spectra of **4d**



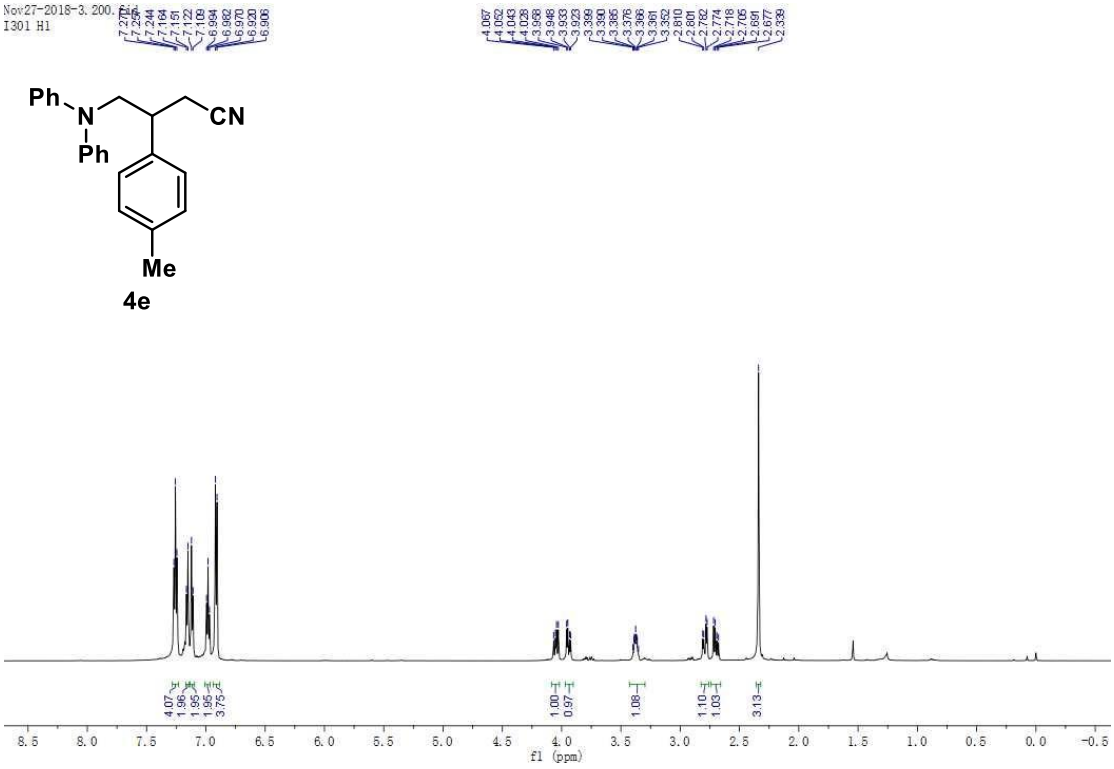
4d



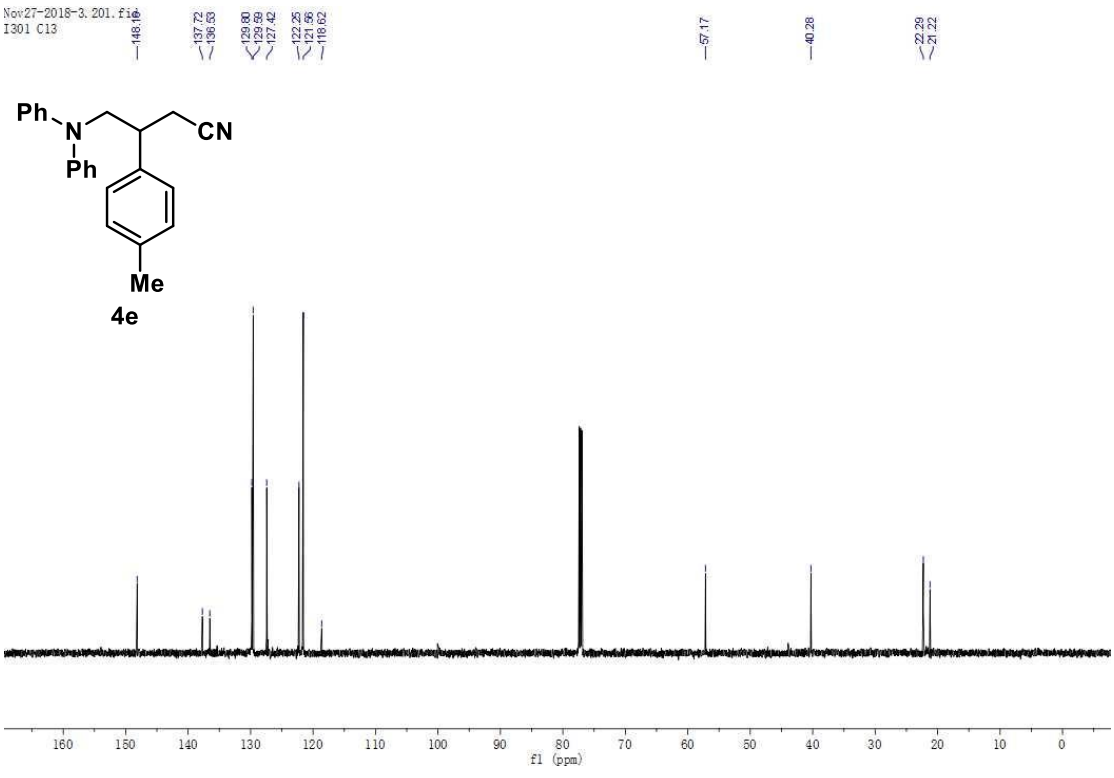
^{1}C NMR Spectra of **4d**



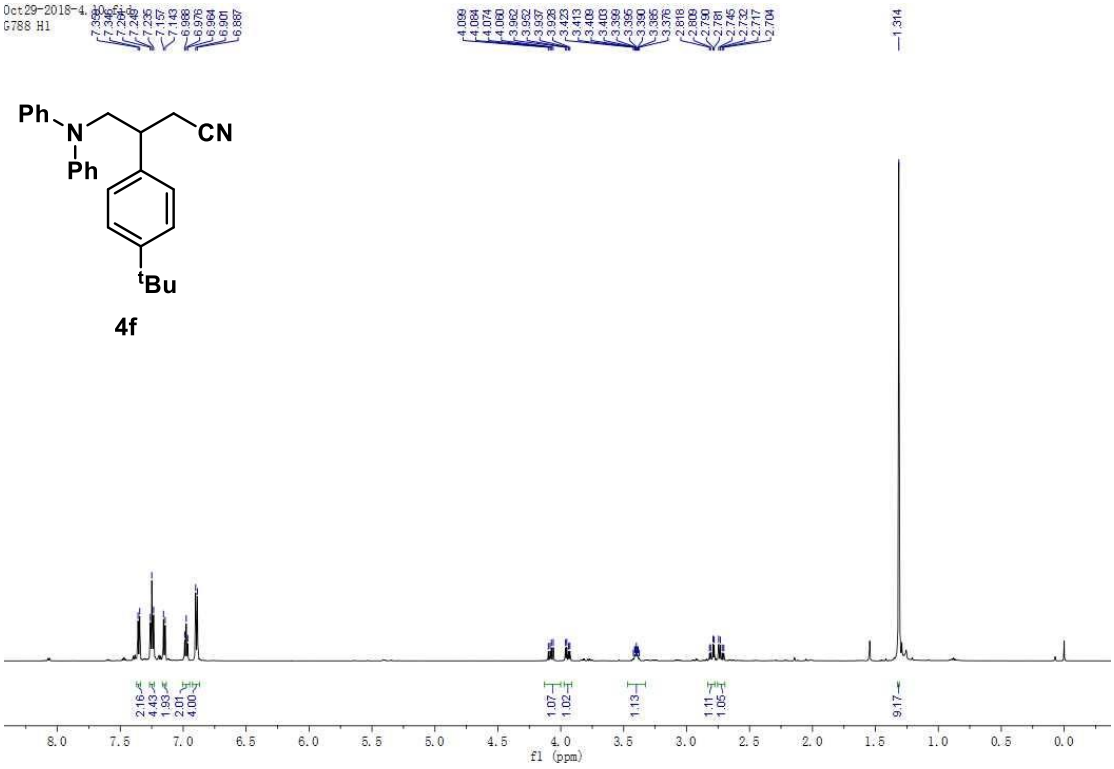
^{1}H NMR Spectra of **4e**



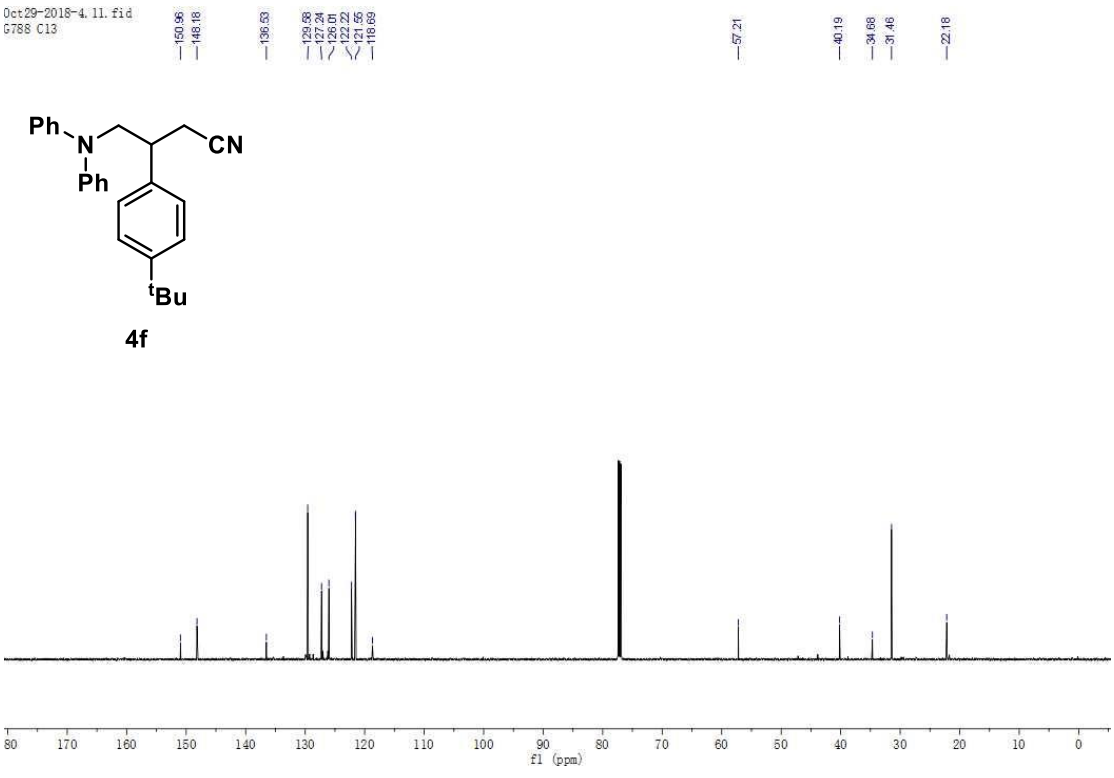
^{1}C NMR Spectra of **4e**



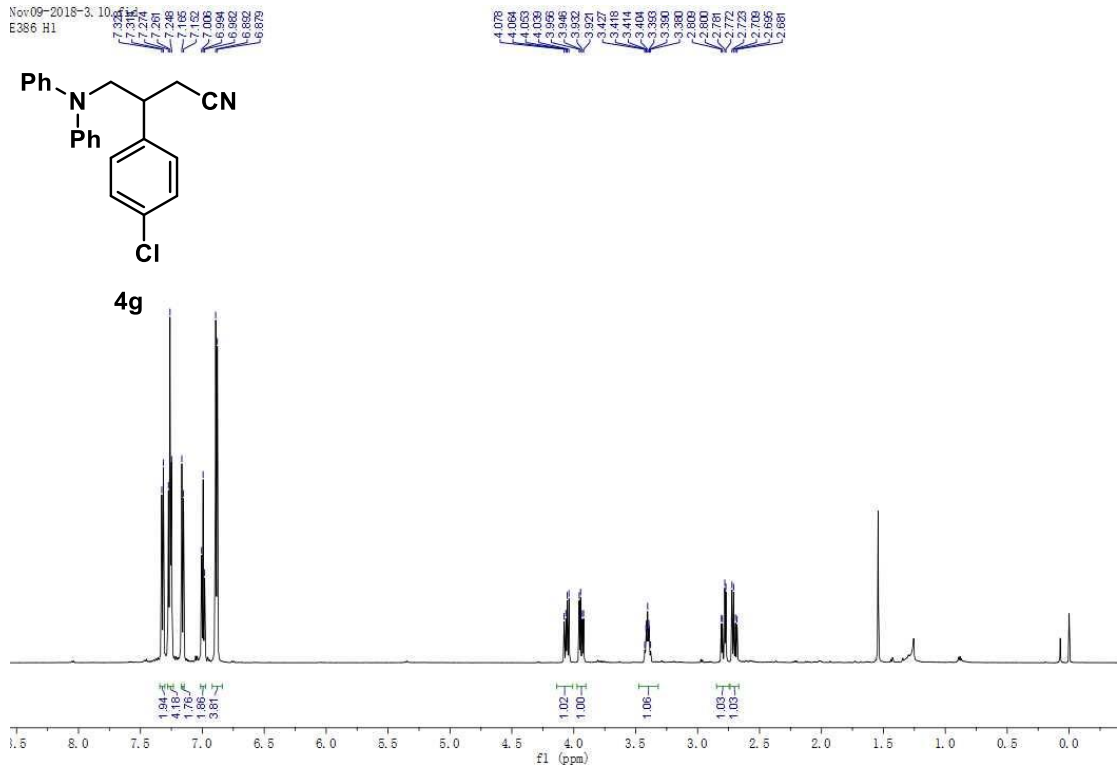
^{1}H NMR Spectra of **4f**



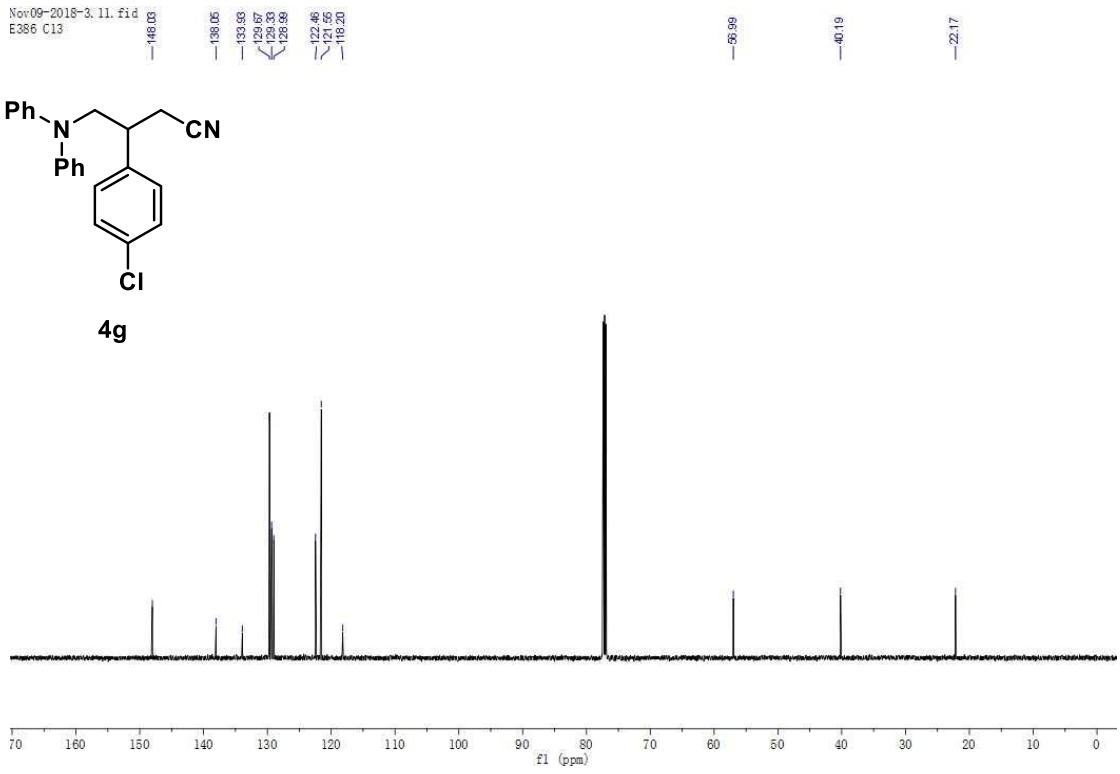
^{1}C NMR Spectra of **4f**



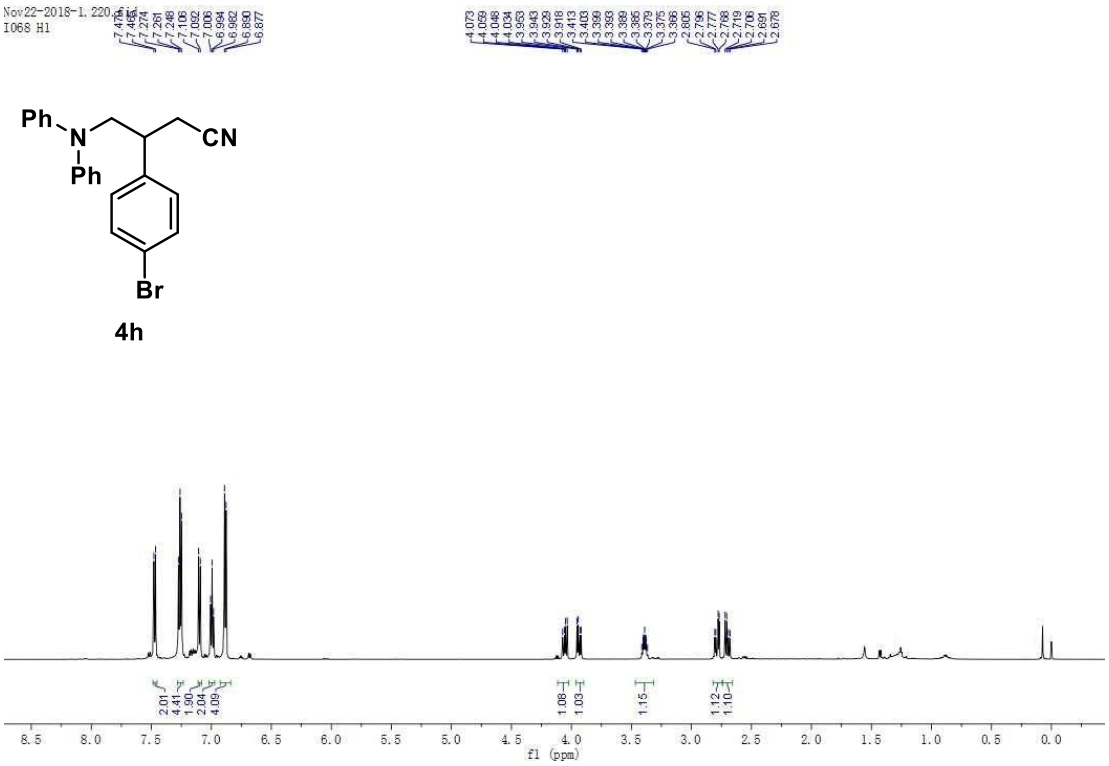
^{1}H NMR Spectra of **4g**



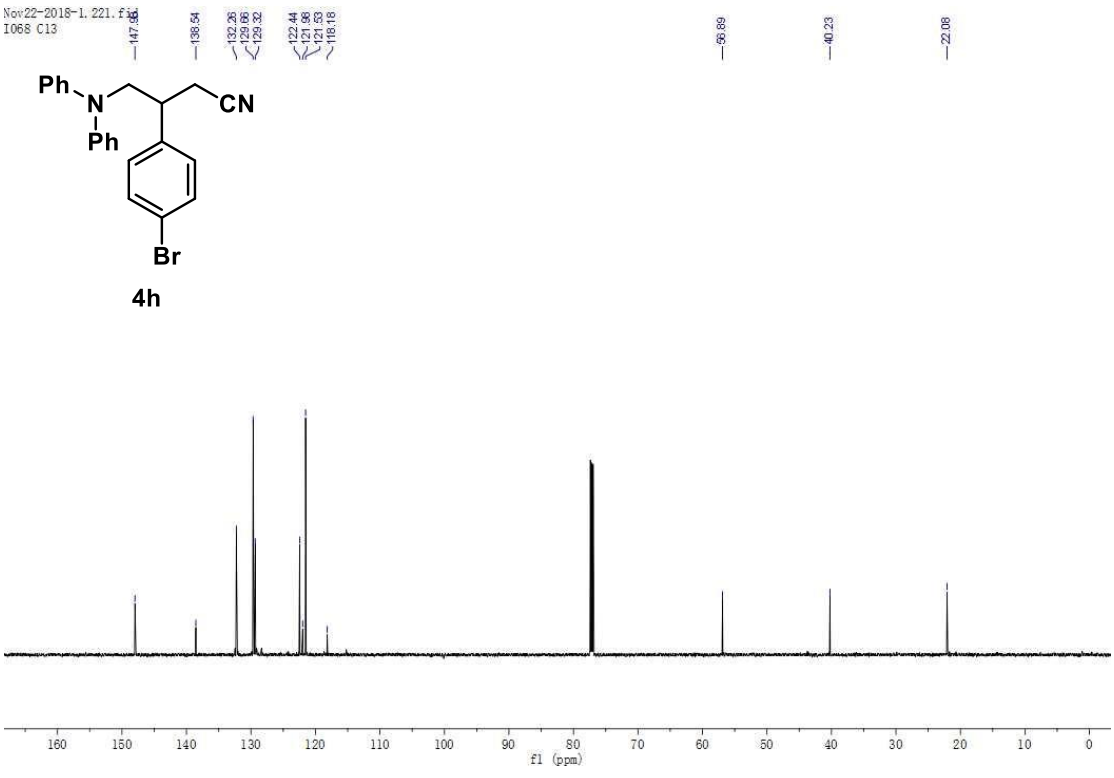
^{1}C NMR Spectra of **4g**



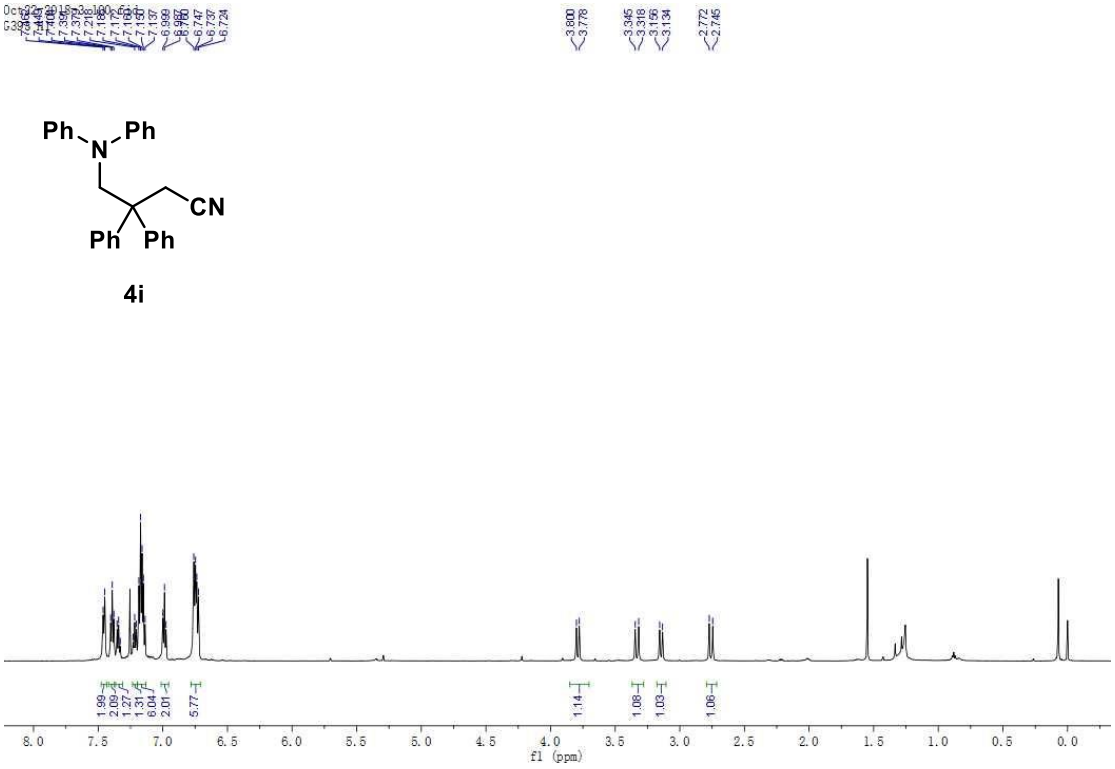
^{1}H NMR Spectra of **4h**



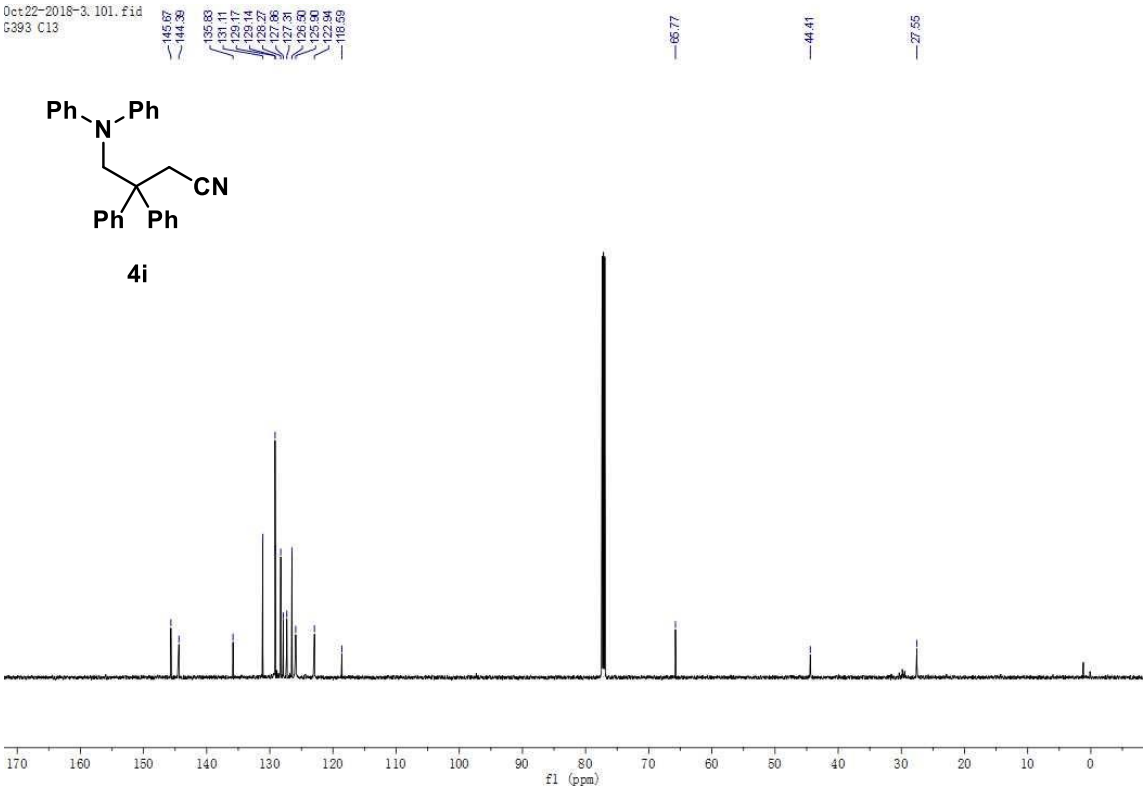
^{1}C NMR Spectra of **4h**



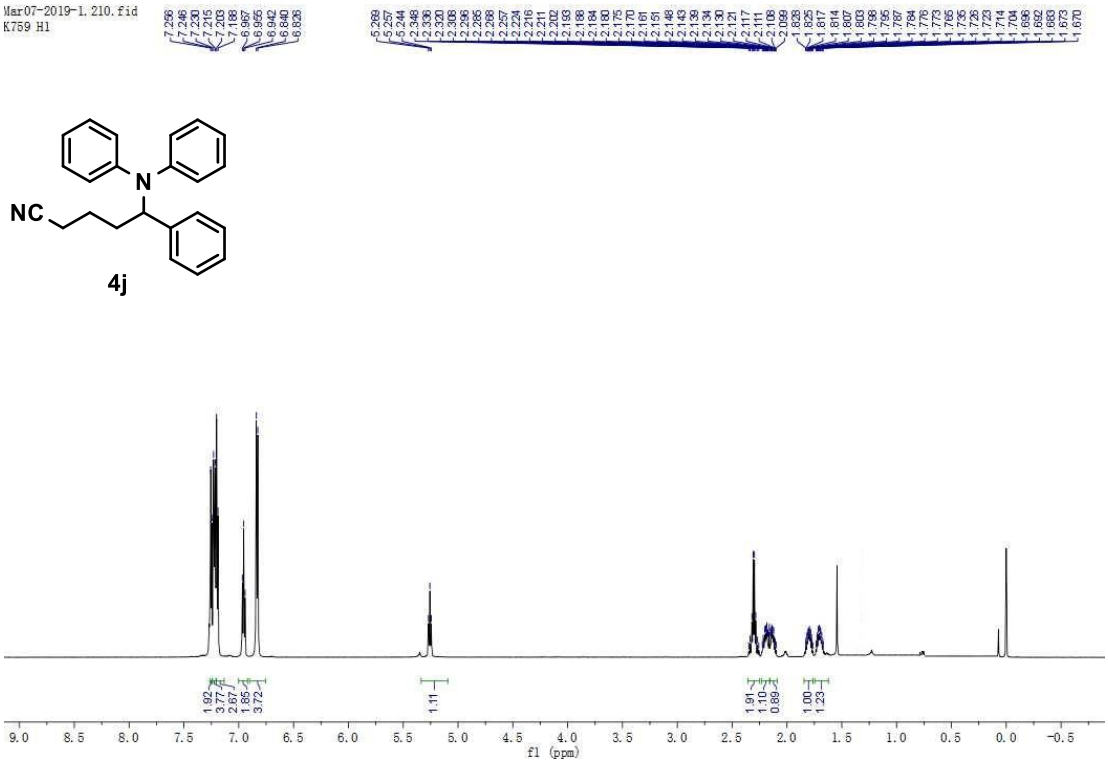
^{1}H NMR Spectra of **4i**



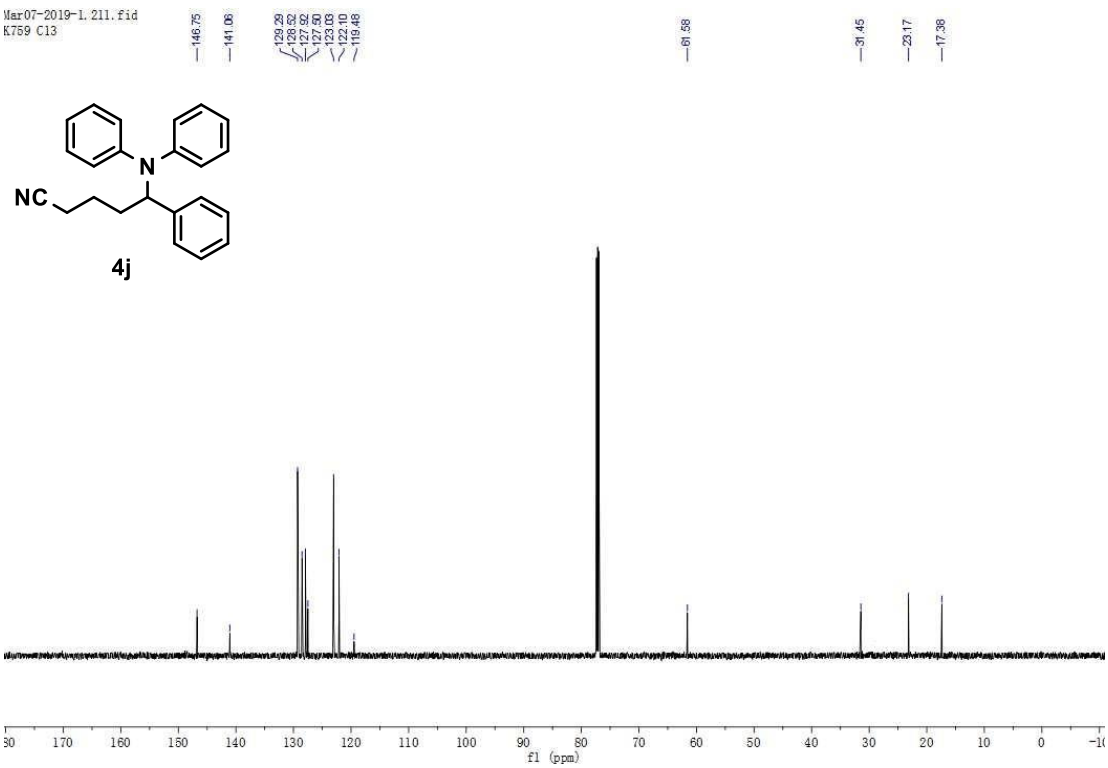
^{1}C NMR Spectra of **4i**



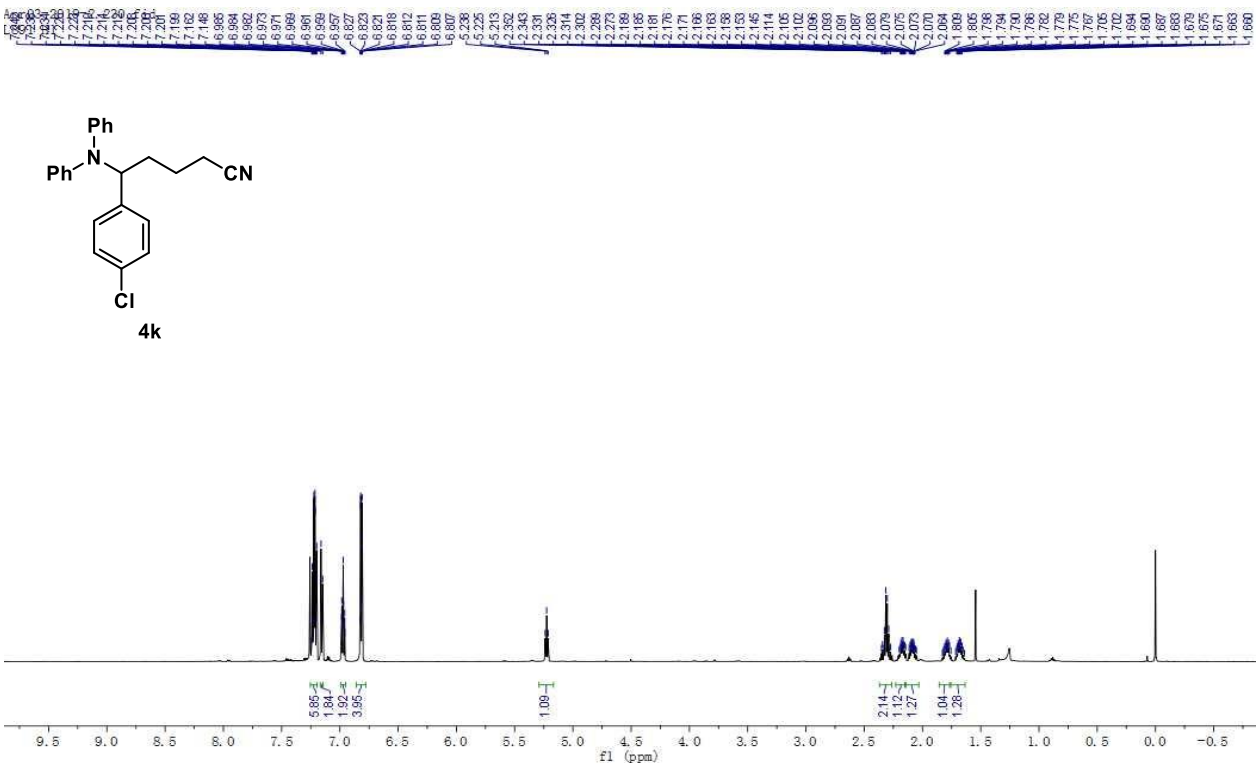
^{1}H NMR Spectra of **4j**



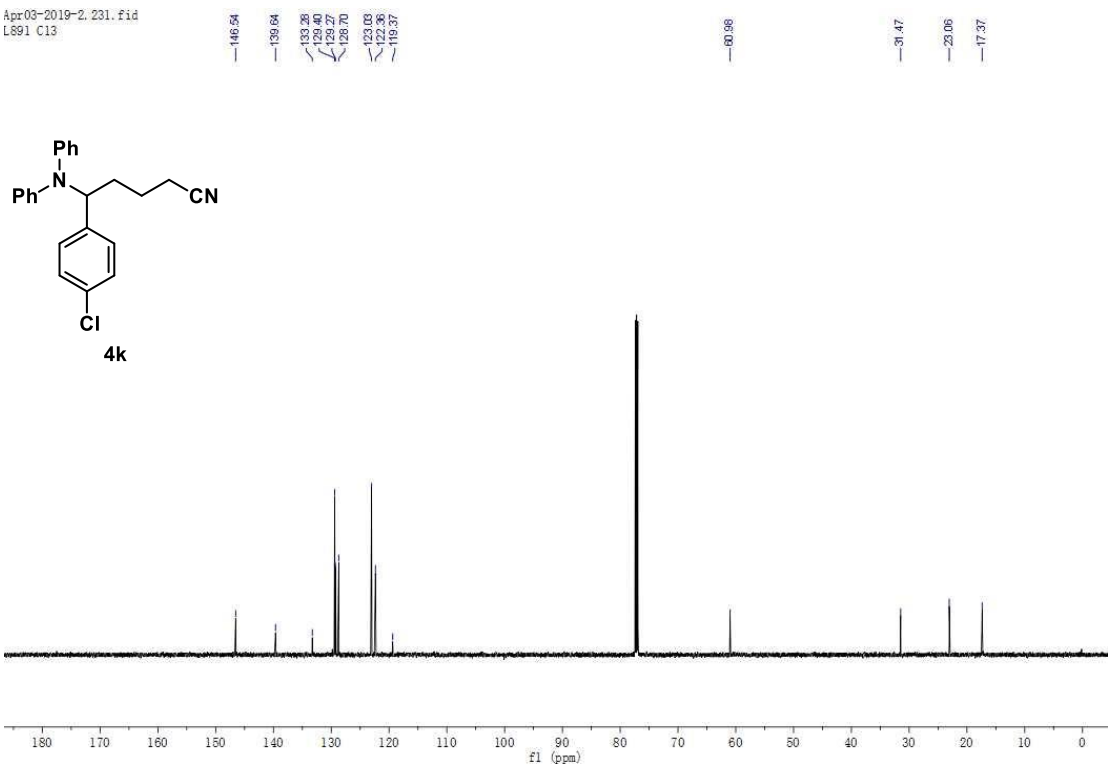
^{1}C NMR Spectra of **4j**



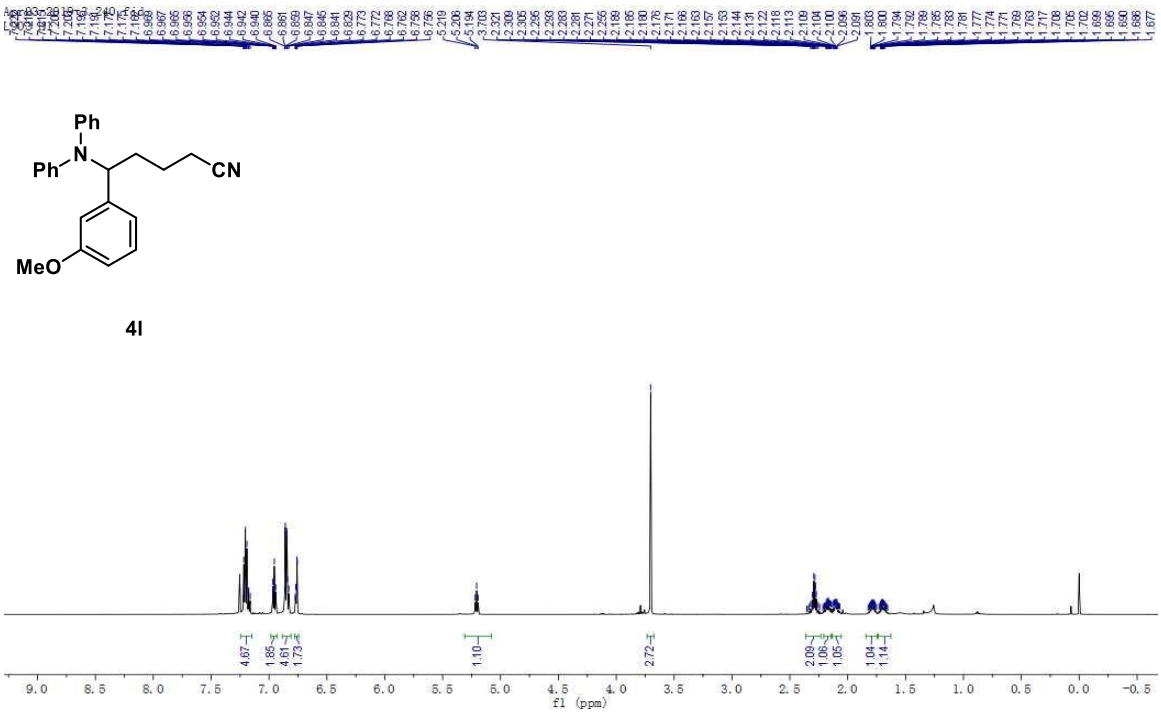
^{1}H NMR Spectra of **4k**



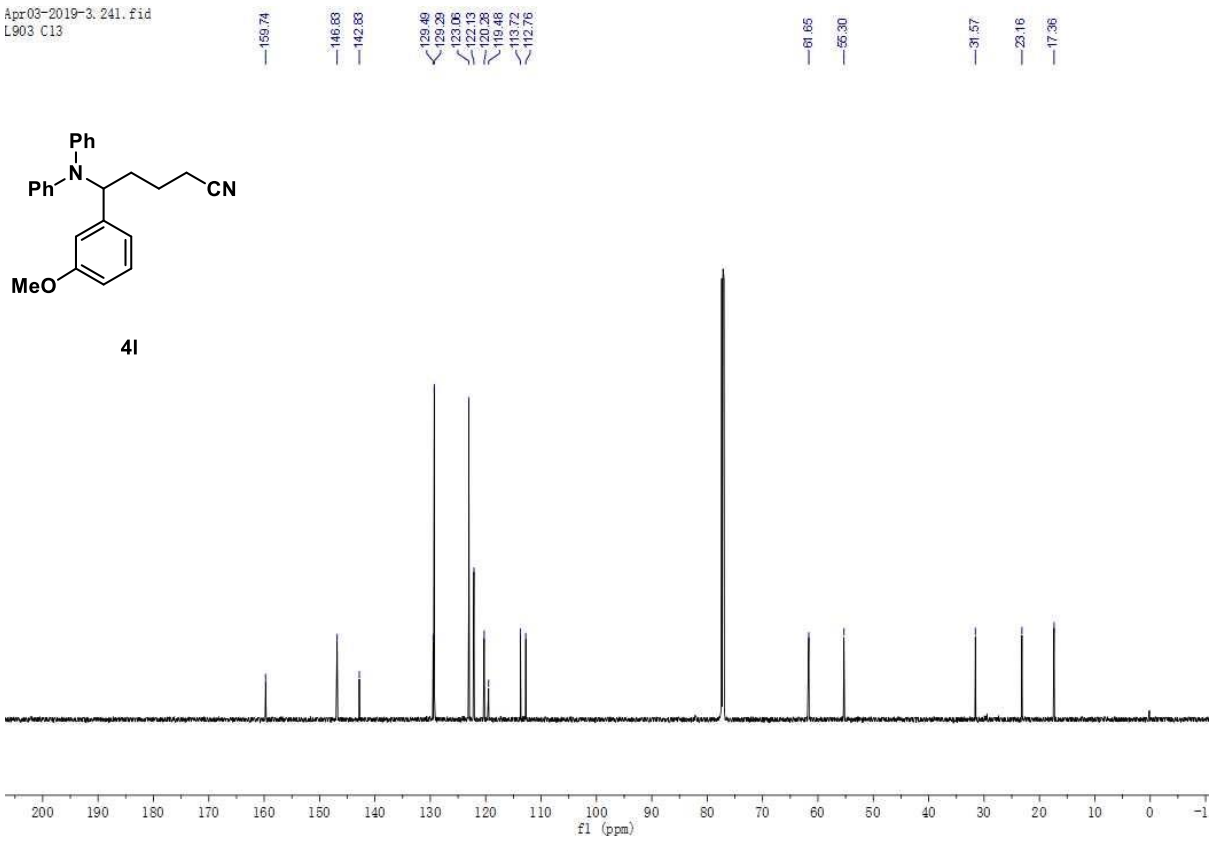
^{1}C NMR Spectra of **4k**



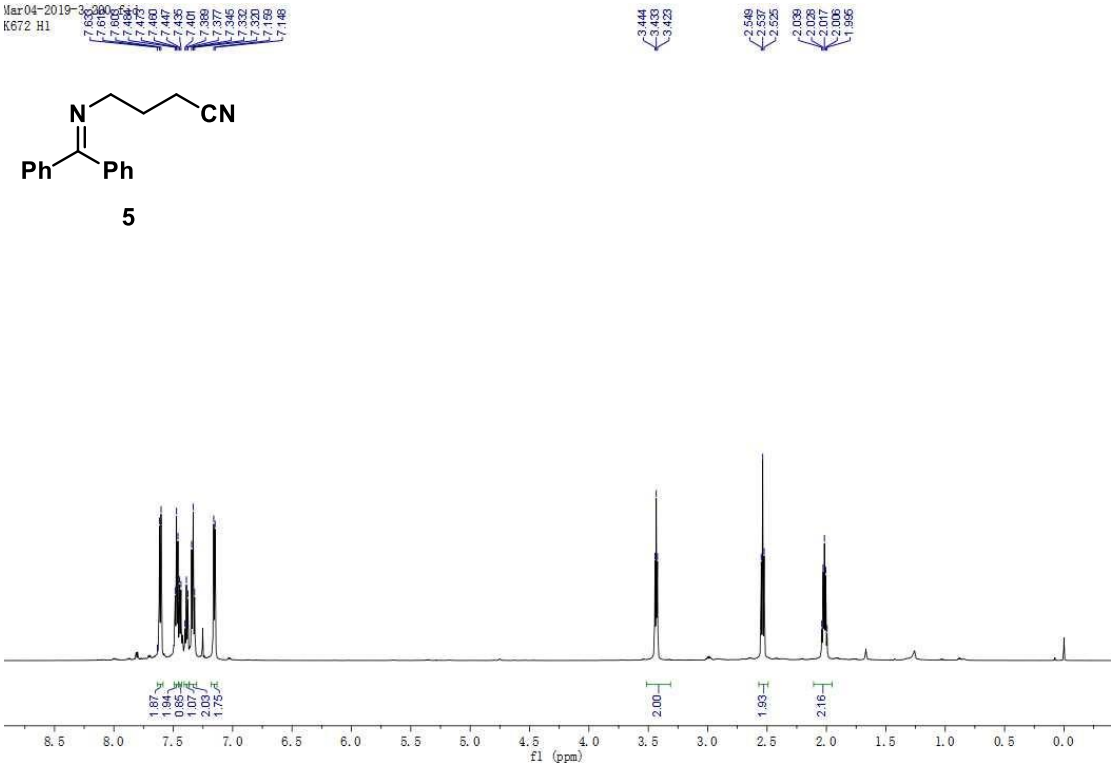
^{1}H NMR Spectra of **4l**



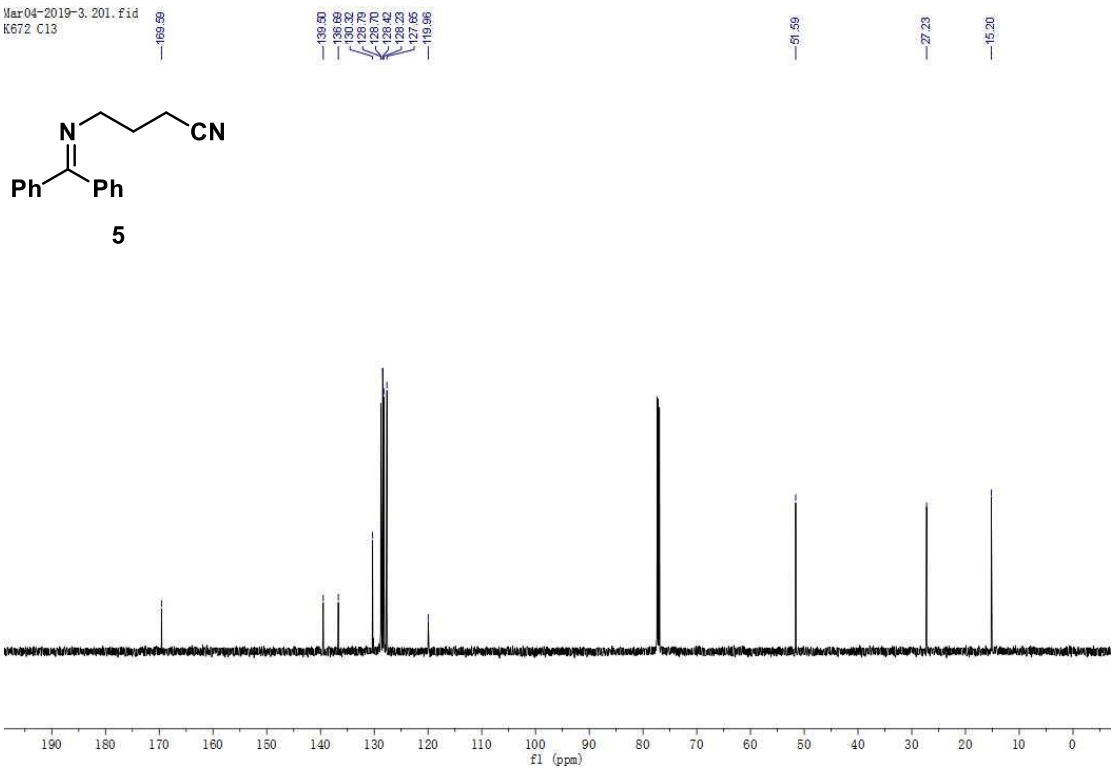
^{1}C NMR Spectra of **4l**



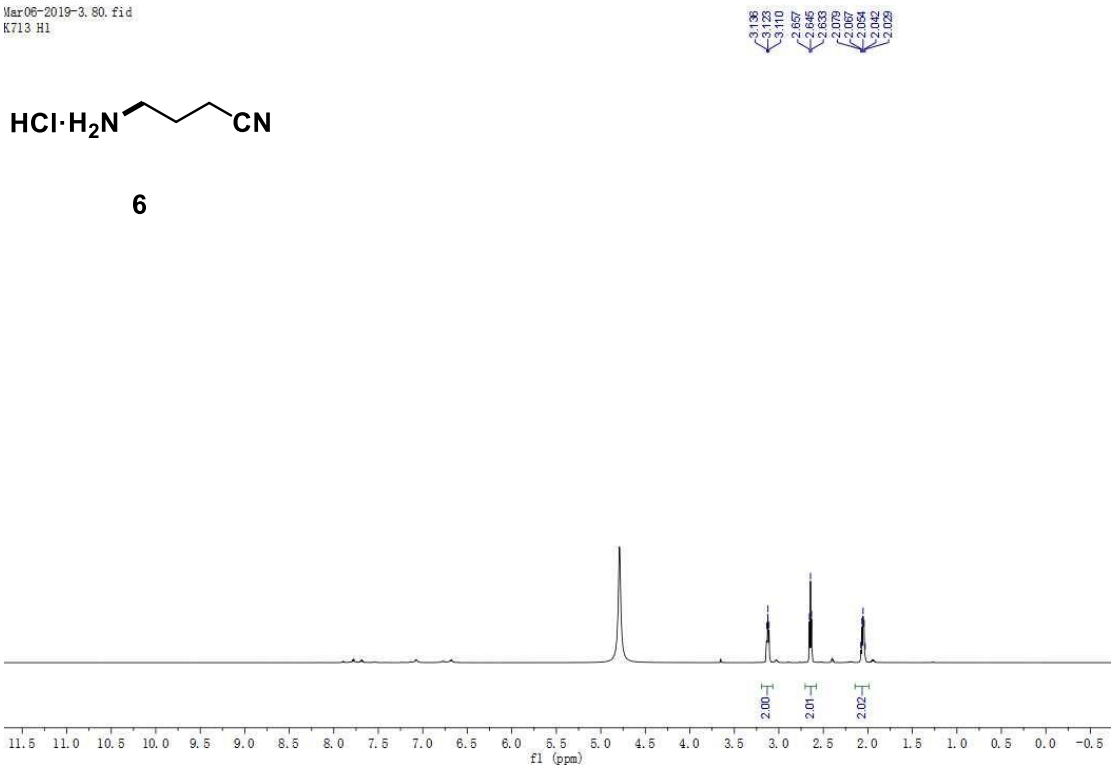
^{1}H NMR Spectra of **5**



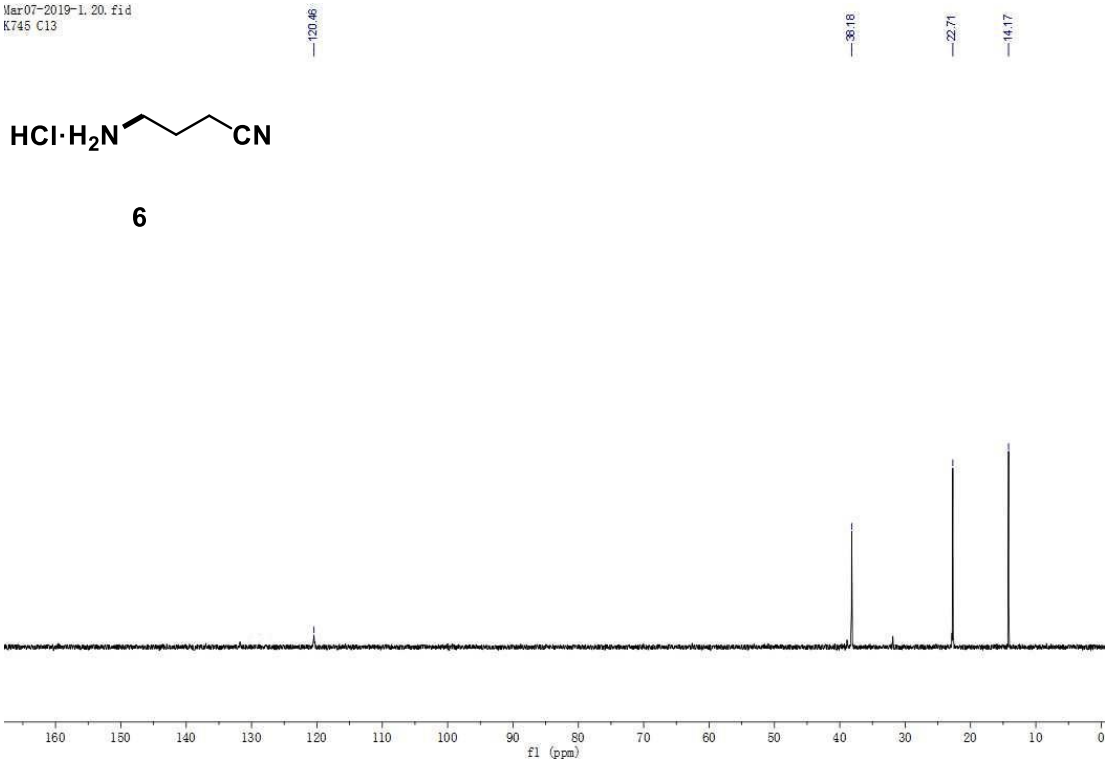
^{1}C NMR Spectra of **5**



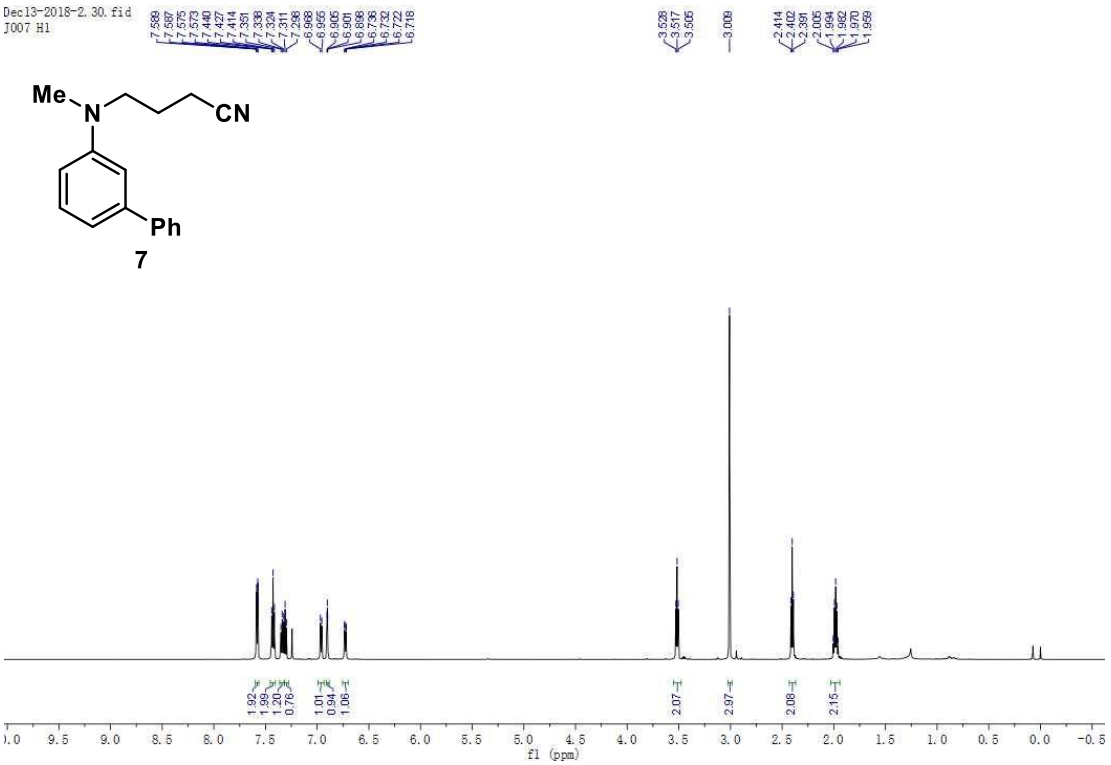
^{1}H NMR Spectra of **6**



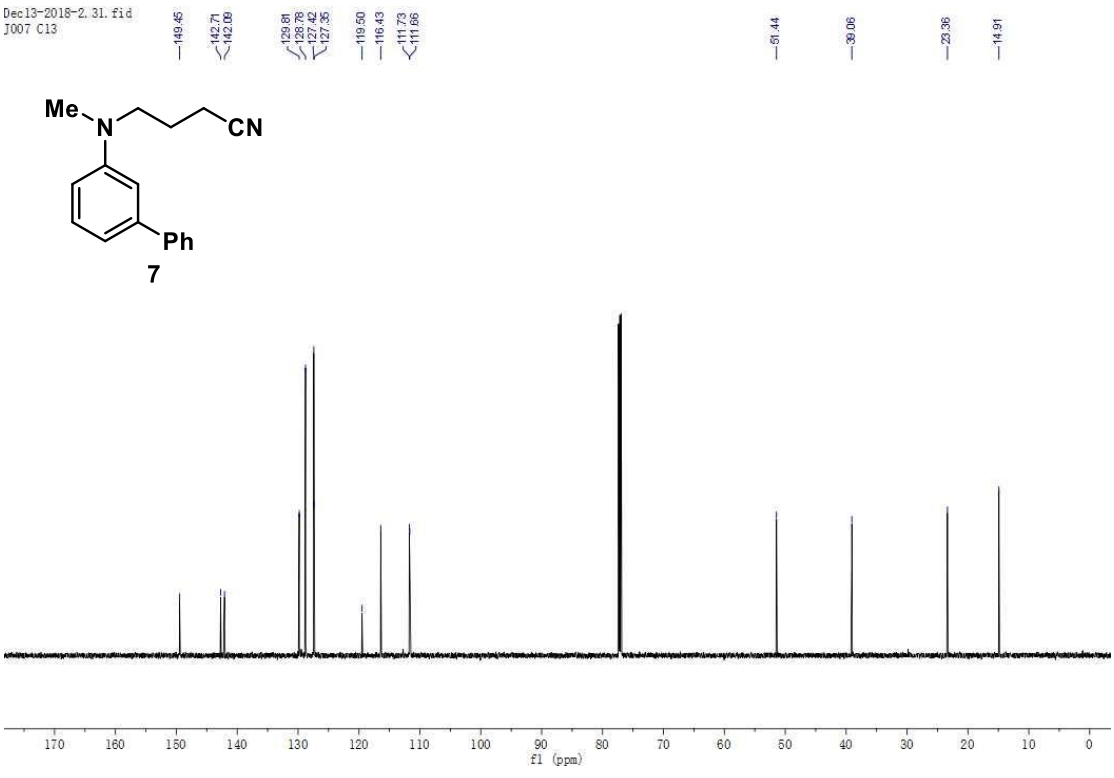
^{1}C NMR Spectra of **6**



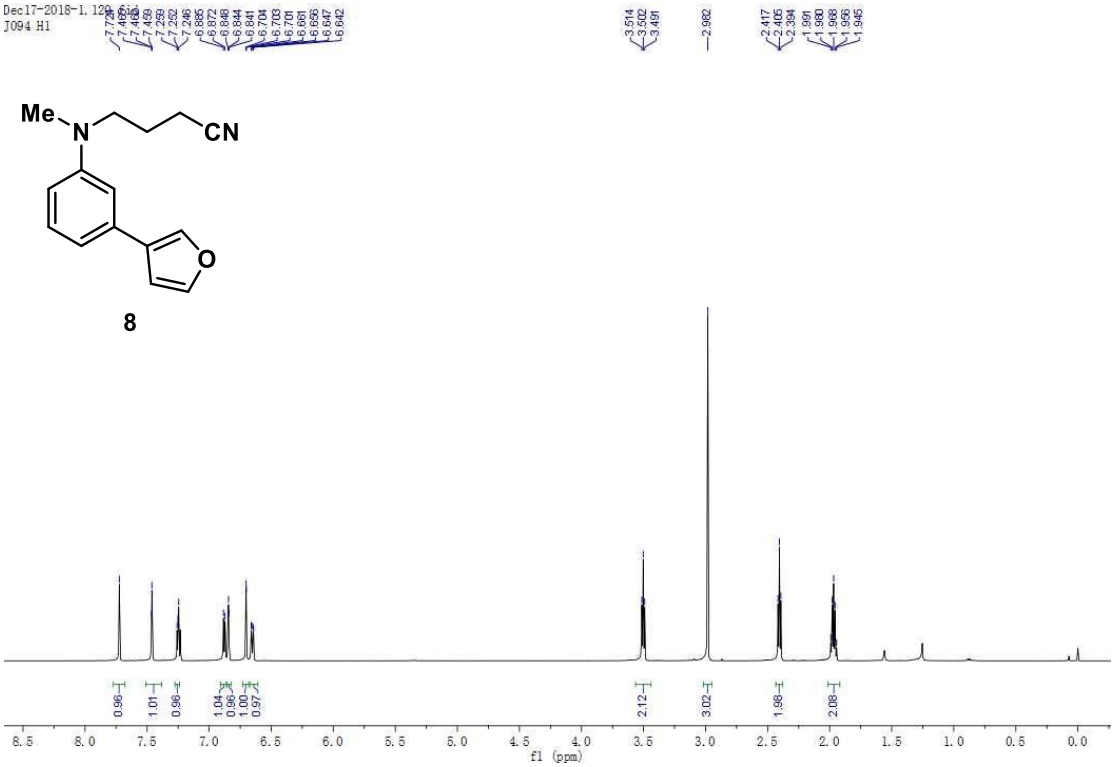
^{1}H NMR Spectra of **7**



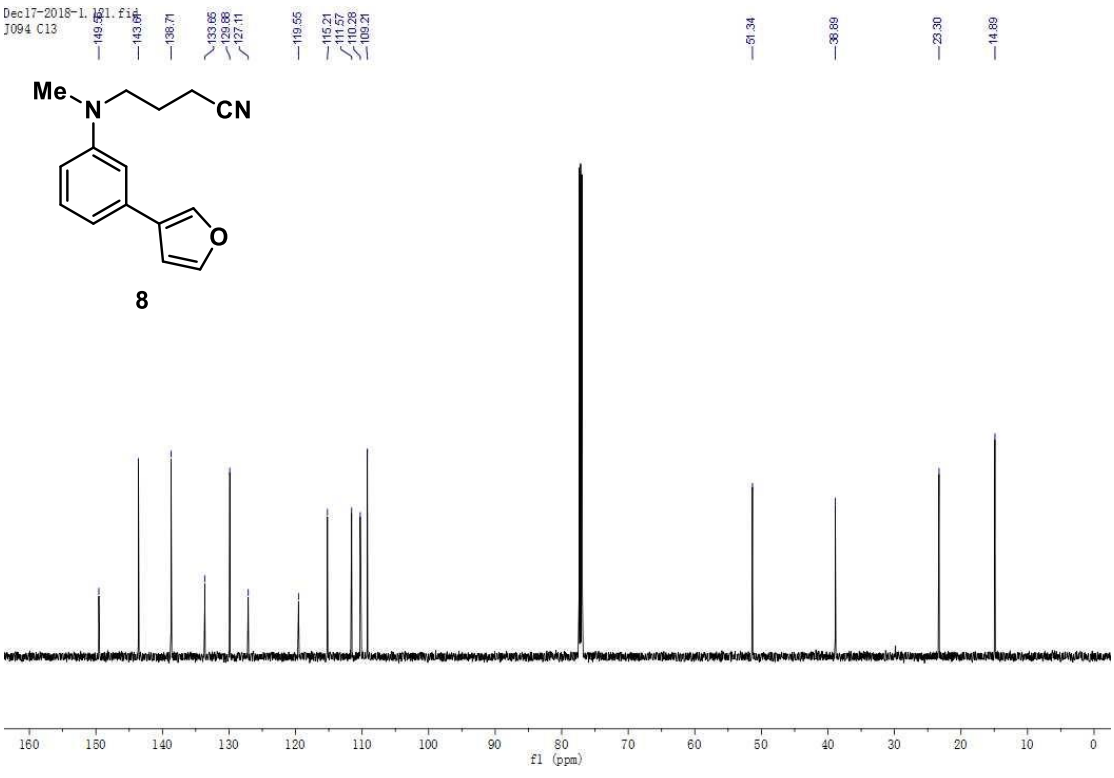
^{1}C NMR Spectra of **7**



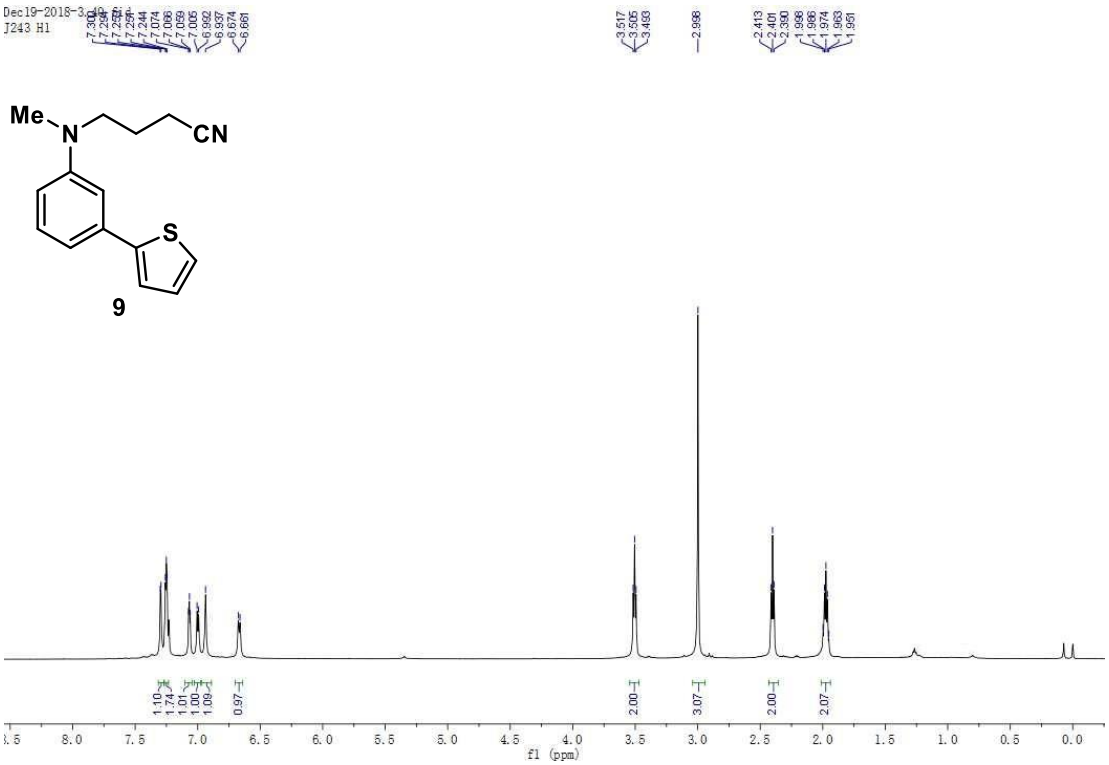
^{1}H NMR Spectra of **8**



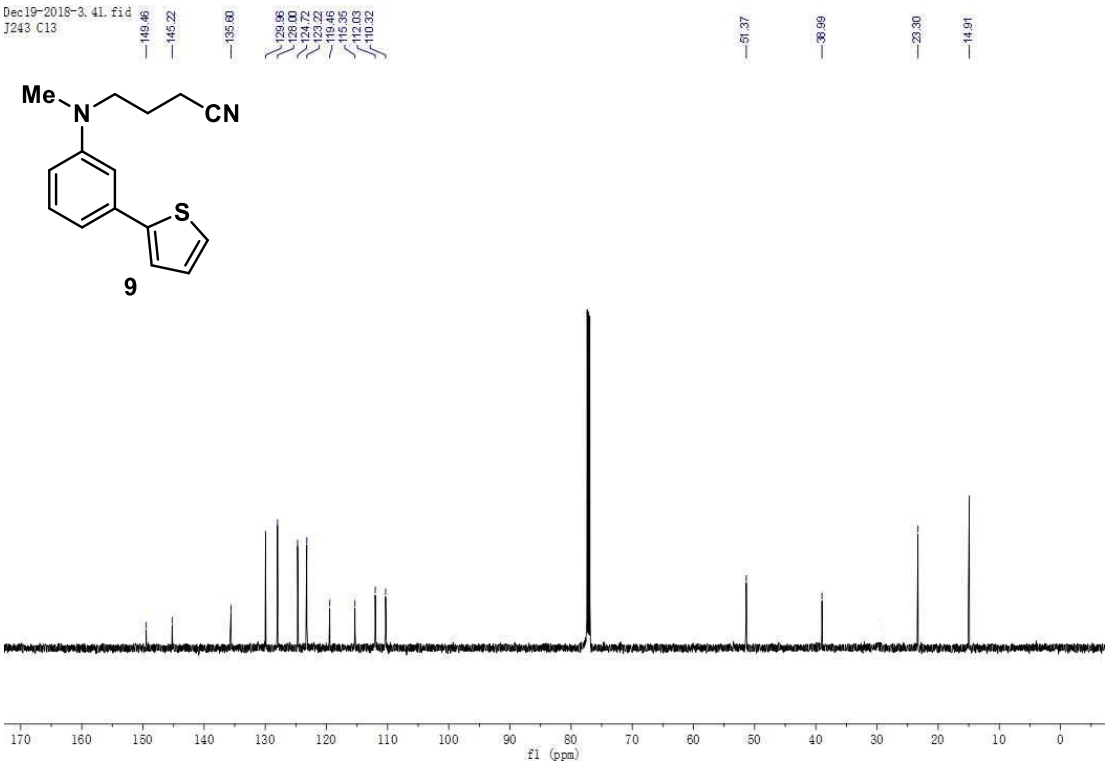
^{1}C NMR Spectra of **8**



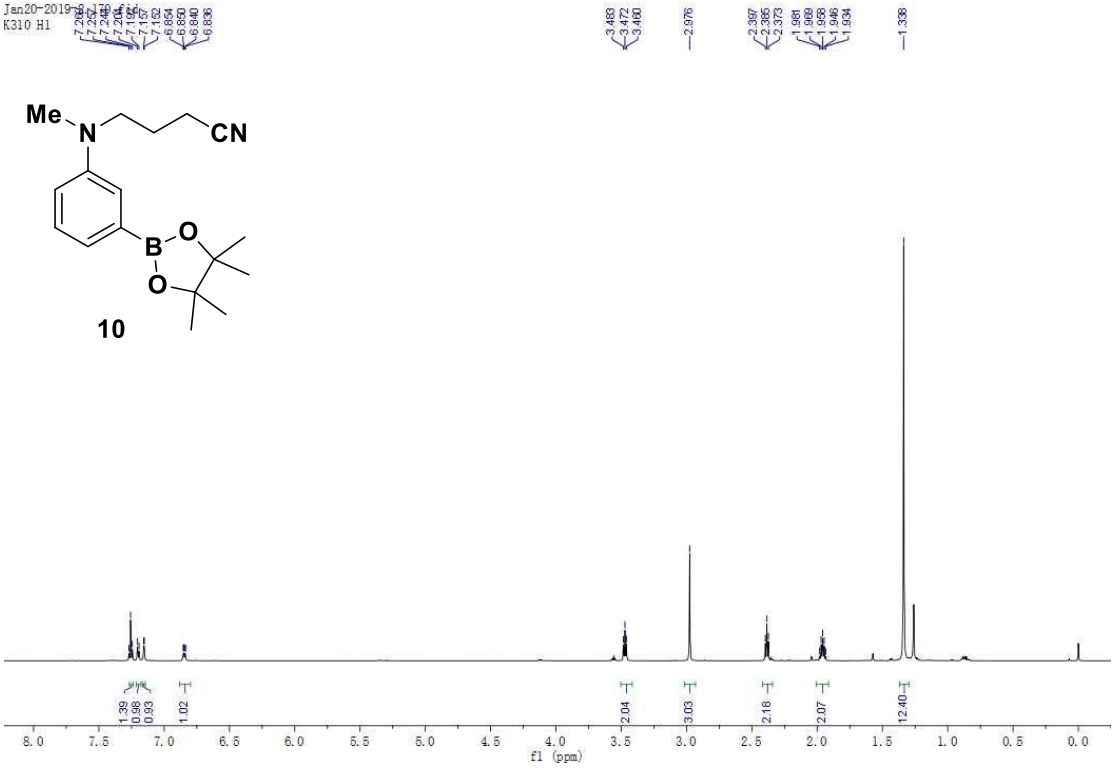
^{1}H NMR Spectra of **9**



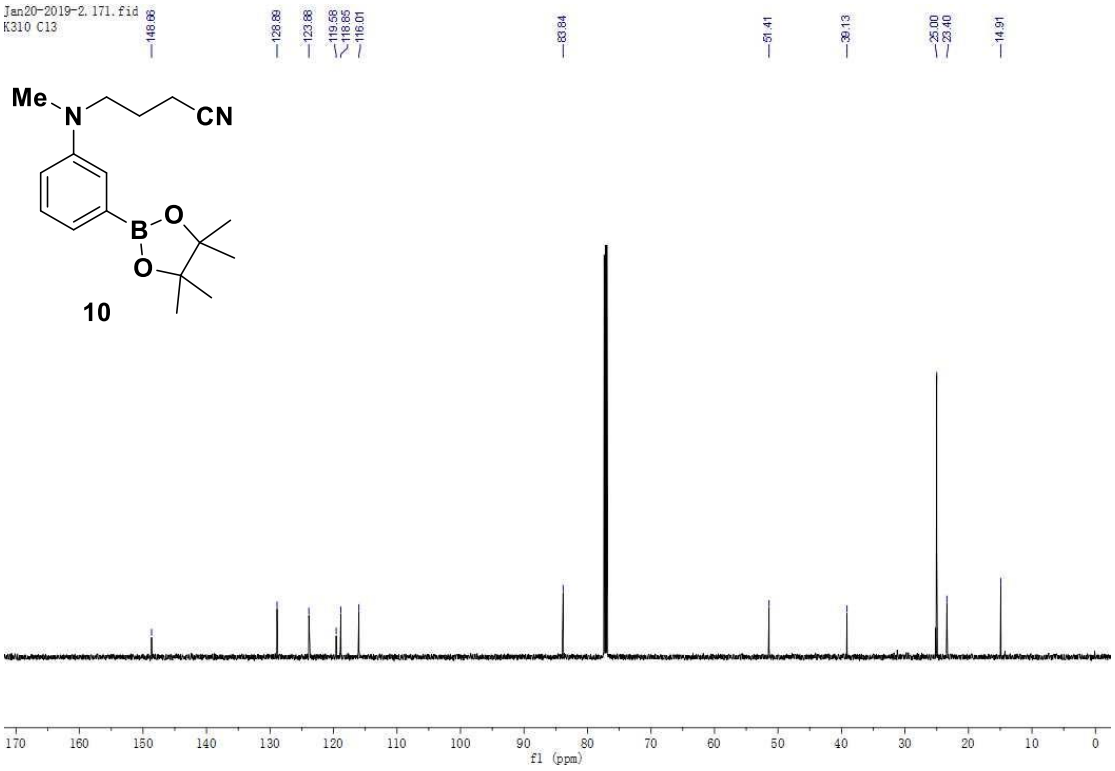
^{1}C NMR Spectra of **9**



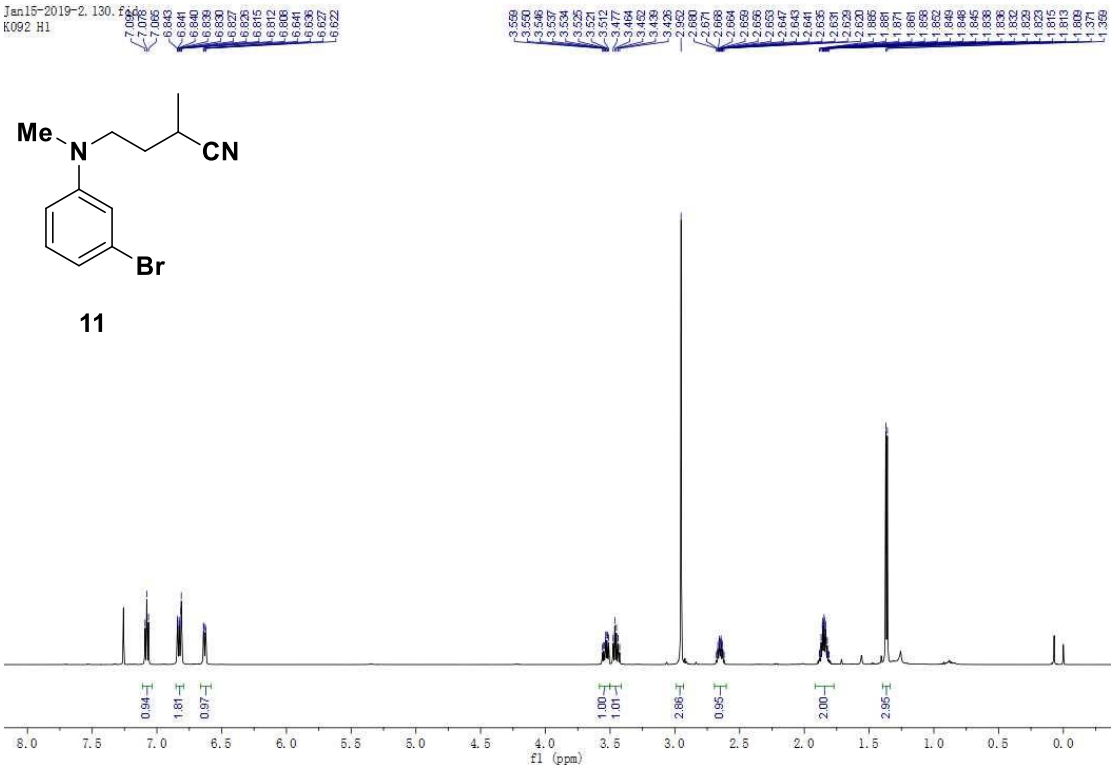
^{1}H NMR Spectra of **10**



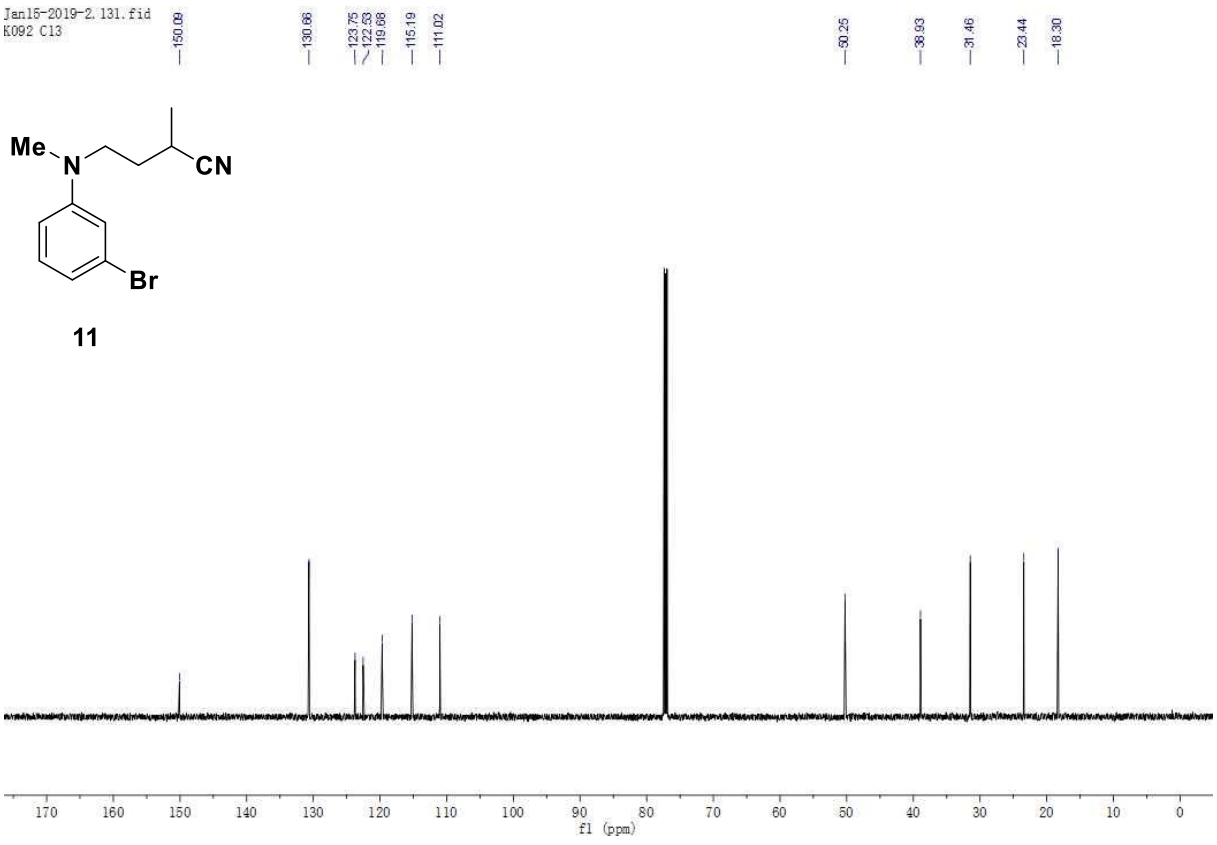
^{1}C NMR Spectra of **10**



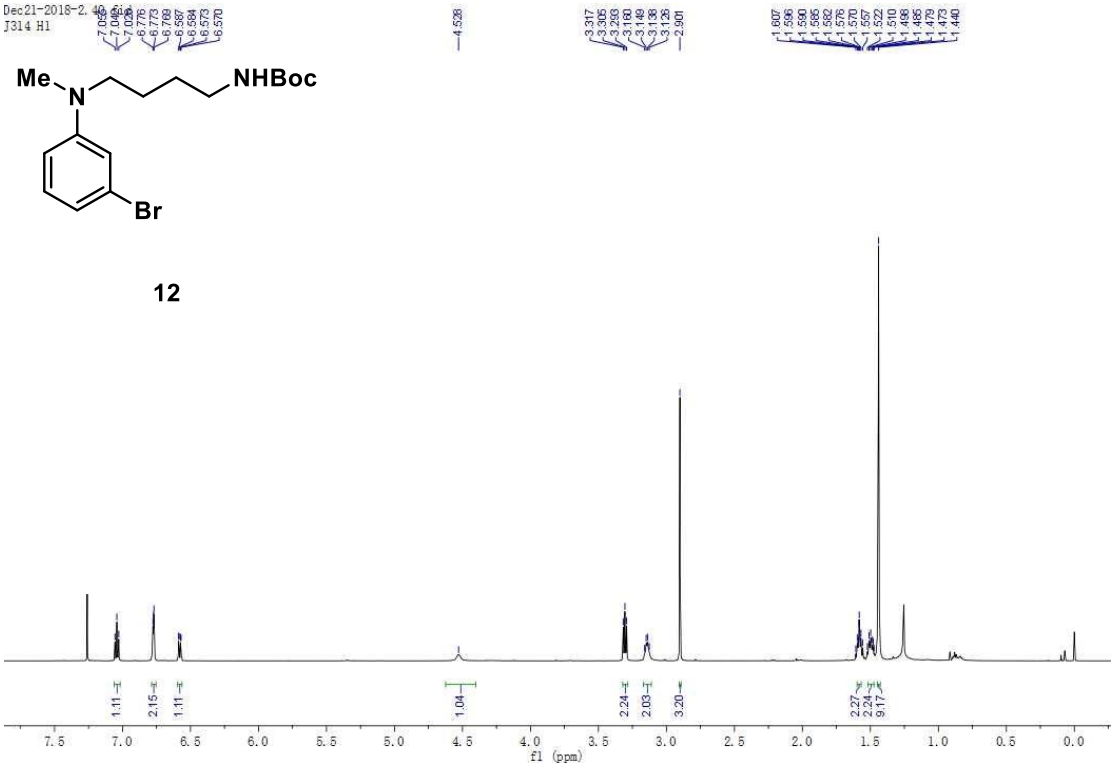
^{1}H NMR Spectra of **11**



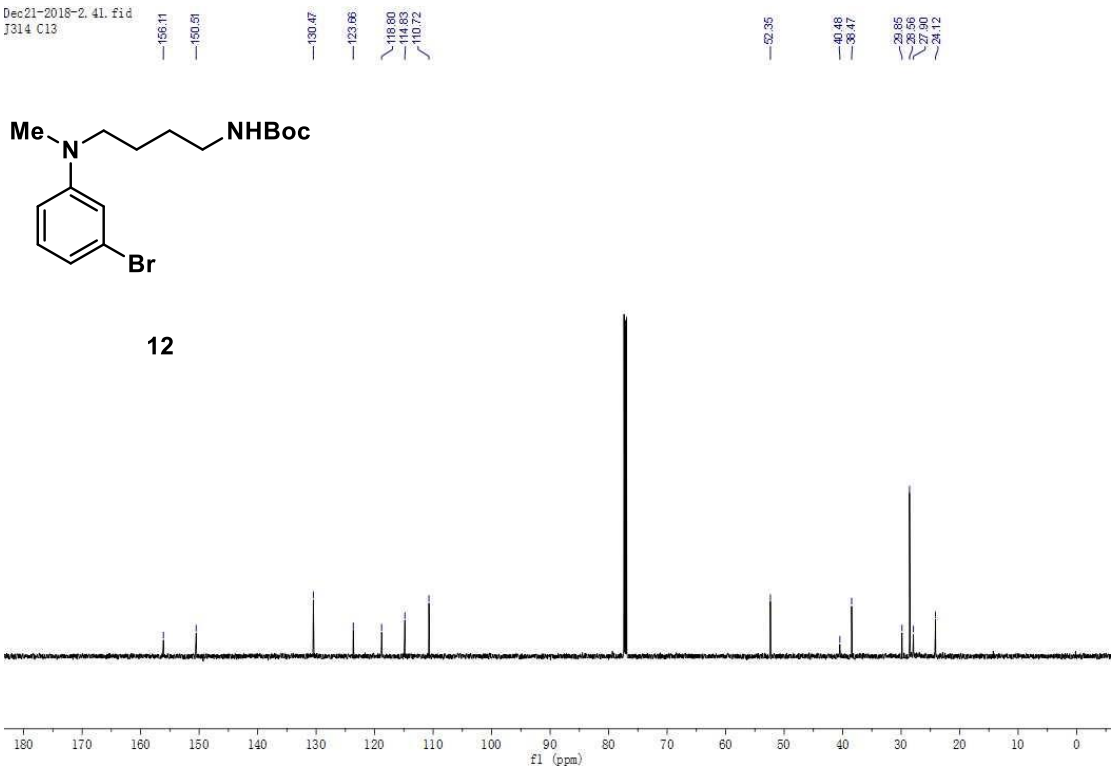
^{1}C NMR Spectra of **11**



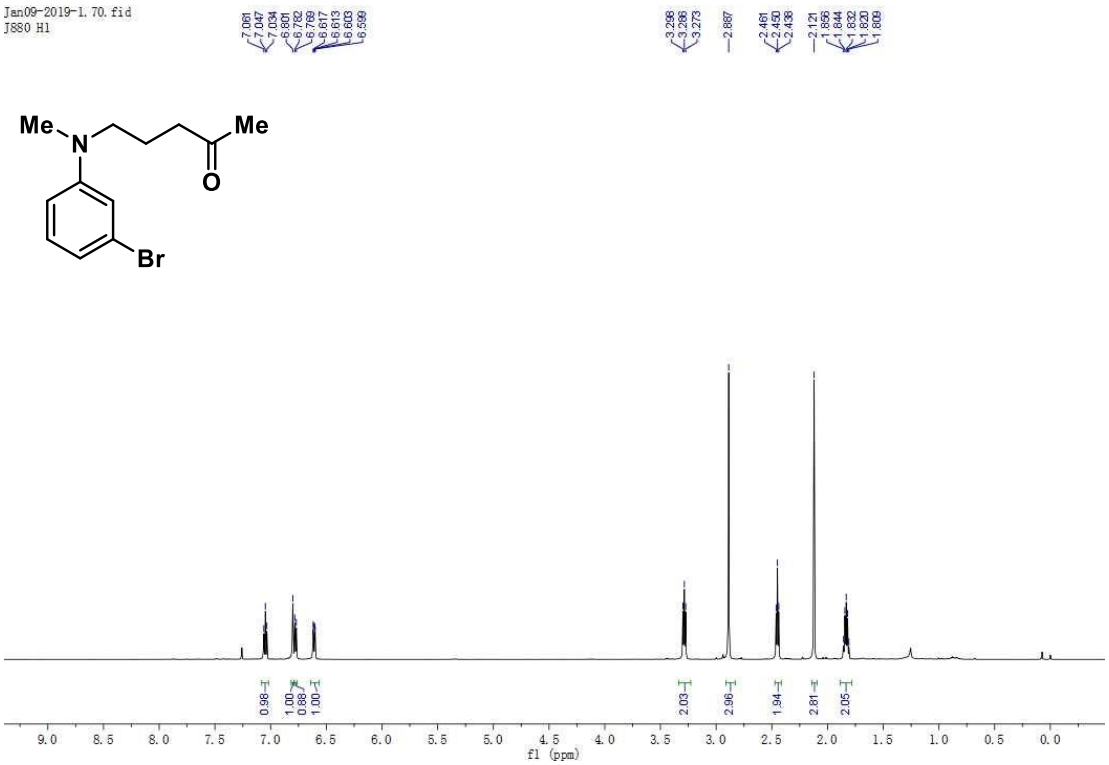
^{1}H NMR Spectra of **12**



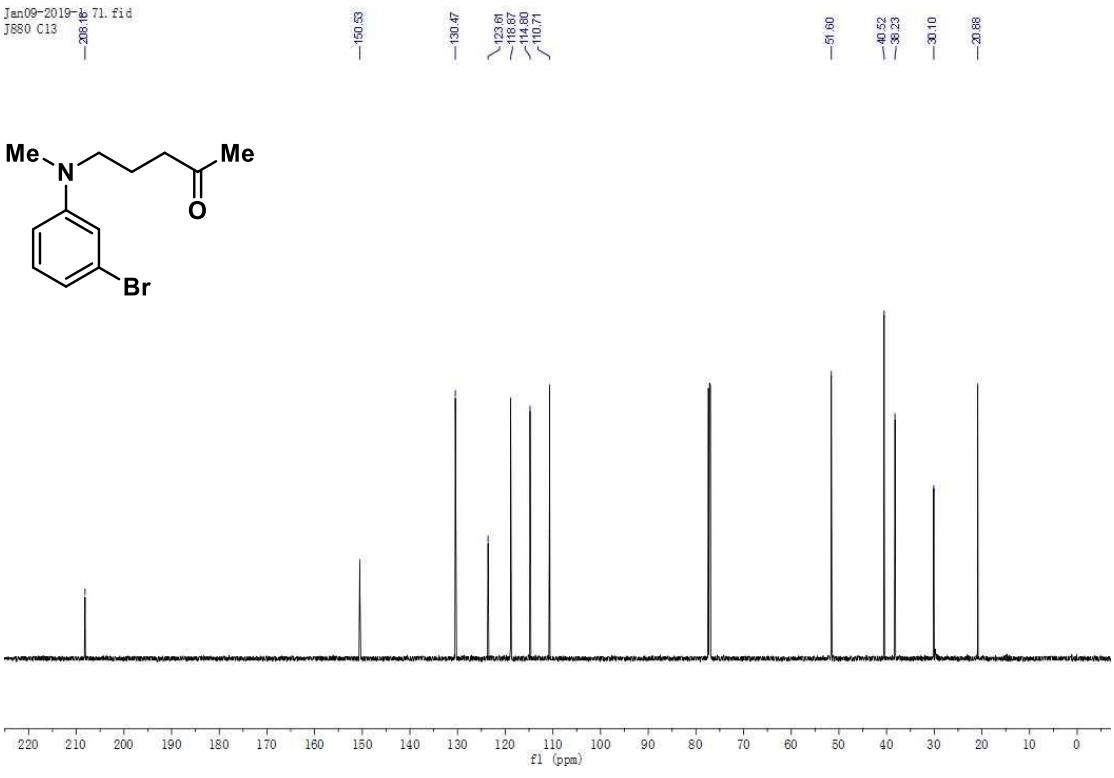
^{1}C NMR Spectra of **12**



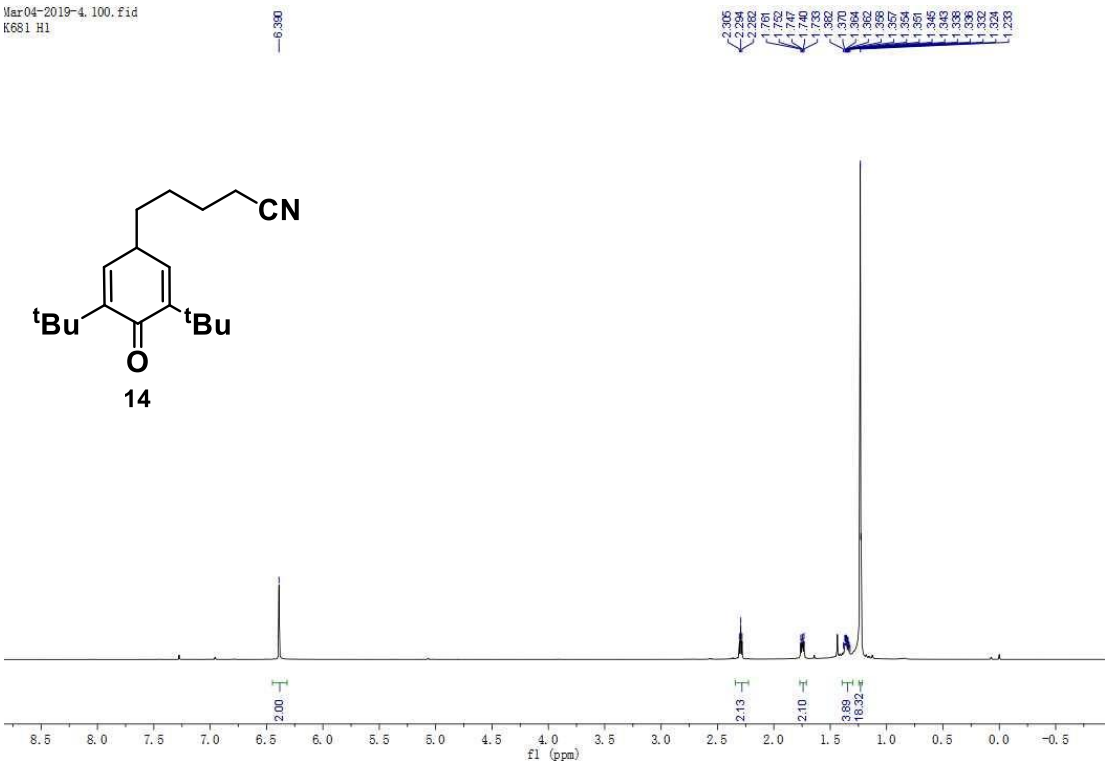
^{1}H NMR Spectra of **13**



^{1}C NMR Spectra of **13**



^{1}H NMR Spectra of **14**



^{1}C NMR Spectra of **14**