

Supporting Information

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

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Table of Contents

Part 1. General Information-----	S2
Part 2. Proposed catalytic cycle for the C(<i>sp</i> ³)-N coupling reaction-----	S2
Part 3. Procedure and Characteristic Data for Substrates 1 and 2 -----	S3
Part 4. General Procedure and Characteristic Data for Products 3 and 4 -----	S11
Part 5. Procedure and Characteristic Data for Products 5-10 -----	S26
Part 6. References-----	S32
Part 7. NMR Spectra-----	S33

Part 1. General Information

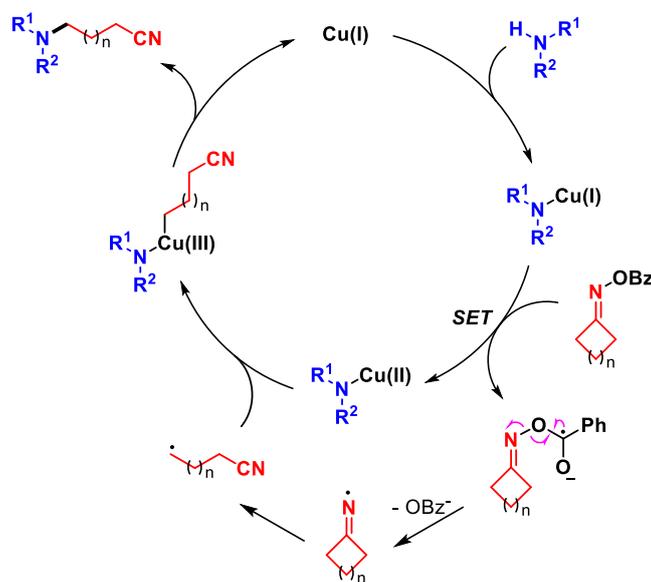
Material: Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere under anhydrous conditions and all reagents were purchased from commercial suppliers without further purification. Anhydrous tetrahydrofuran (THF) and ethanol (EtOH) were purchased from *Energy Chemical*. Anhydrous dimethylformamide (DMF), dichloromethane (DCM) were purchased from *J&K Scientific*. The diethyl ether (Et₂O) 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 Bruker Advance 600 (¹H: 600 MHz, ¹³C: 150 MHz), Bruker Advance 500 (¹H: 500 MHz, ¹³C: 125 MHz) at ambient temperature. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ¹H and CDCl₃ (77.2 ppm) for ¹³C. 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 Bruker Apex IV RTMS

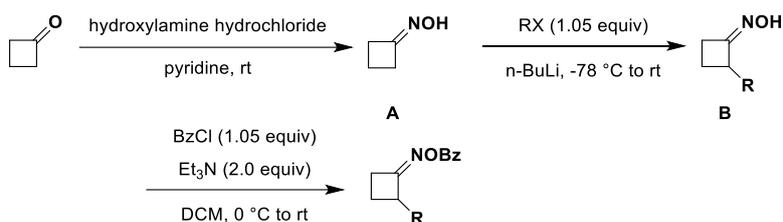
Part 2. Proposed catalytic cycle for the C(sp³)-N coupling reaction



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 Na₂SO₄. 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.

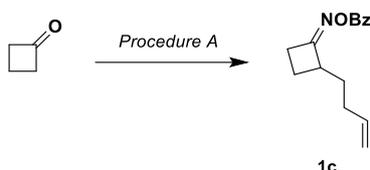
Synthesis of compound B

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 Na₂SO₄. 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.

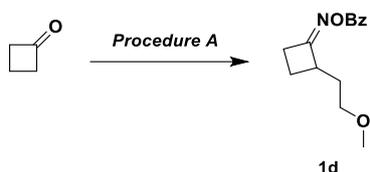
Synthesis of cyclobutanone oxime esters **1c-1d**

To a 50 mL dry Schlenk flask was added crude oxime (~11 mmol, 1.0 equiv) and 22 mL anhydrous DCM. Et₃N (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 MgSO₄. The solution was concentrated in *vacuo* and the residue was purified by column chromatography to afford the desired product as yellow oil.

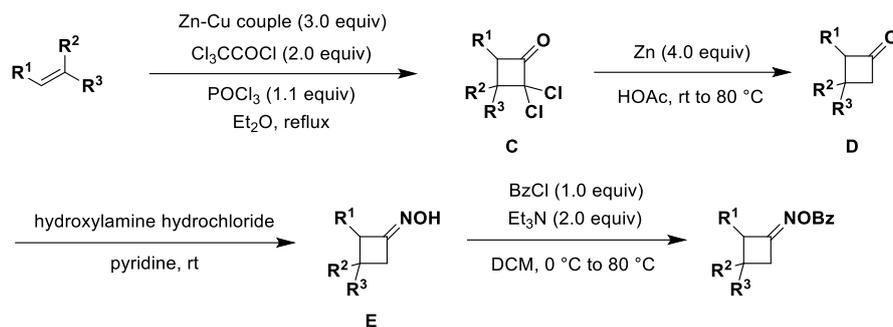


Substrate **1c** was obtained in 65% overall yield from cyclobutanone as yellow oil by column chromatography (PE/EA = 12/1) following the procedure A, by using 4-bromo-1-butene as the alkyl halide. **¹H NMR** (600 MHz, CDCl₃) δ 8.04 (dd, J = 8.4, 1.8 Hz, 2H), 7.58 (tt, J = 8.4, 1.2 Hz, 1H), 7.46 (t, 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). **¹³C NMR** (150 MHz, CDCl₃) 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** v_{max} (film). 2923, 2850, 2245, 1738, 1514, 1606, 1459, 1264, 745, 711 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₅H₁₇NNaO₂ [M+Na]⁺: 266.1151; found: 266.1150.



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. **¹H NMR** (600 MHz, CDCl₃) 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). **¹³C NMR** (150 MHz, CDCl₃) 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** v_{max} (film). 2929, 1600, 1463, 1455, 1347, 1117, 746 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₄H₁₇NNaO₃ [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 NaHCO₃ (aq) and brine sequentially, then dried over anhydrous MgSO₄. 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-dichlorocyclobutanone (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 NaHCO₃ (aq). The combined organic phase was washed with water and brine, dried over anhydrous MgSO₄. The solution was concentrated *in vacuo* at 15 °C and the desired ketone (~30 mmol) was used in the next step without further purification.

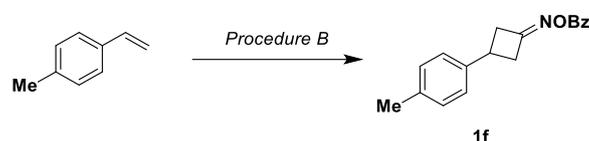
Synthesis of compound E

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 Na₂SO₄. The solution was concentrated and afforded

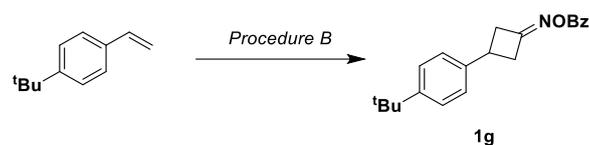
the cyclobutanone oxime (~18 mmol, about 90% yield) as white solid, which carried forward to the next step without further purification.

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

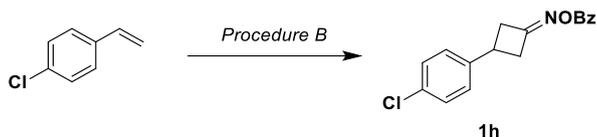
To a 50 mL dry Schlenk flask was added crude oxime (~11 mmol, 1.0 equiv) and 22 mL anhydrous DCM. Et₃N (3.10 mL, 22 mmol, 2.0 equiv) and BzCl (1.34 mL, 11.6 mmol, 1.05 equiv) were added dropwise sequentially at 0 °C. The mixture was stirred for 6 h at room temperature. The solution was diluted with water and extracted with ether for three times. The combined organic layer was washed with water and dried over anhydrous MgSO₄. The solution was concentrated in *vacuo* and the residue was purified by column chromatography to afford the desired product.



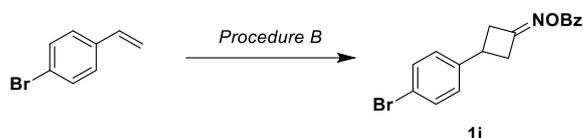
Substrate **1f** was obtained in 68% overall yield as brown solid (m.p.61 °C) by column chromatography (PE/EA = 12/1) following the procedure B, by using 4-methylstyrene. **¹H NMR** (600 MHz, CDCl₃) δ 8.05 (dd, J = 8.4, 1.8 Hz, 2H), 7.55 (t, J = 7.8 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.15 (s, 4H), 3.63 (tt, J = 8.4, 8.4 Hz, 1H), 3.60 – 3.49 (m, 2H), 3.21 – 3.15 (m, 2H), 2.32 (s, 3H). **¹³C NMR** (150 MHz, CDCl₃) 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** v_{max} (film). 2966, 2253, 1497, 1481, 1408, 1377, 1036, 727 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₈H₁₇NNaO₂ [M+Na]⁺: 302.1151; found: 302.1148.



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. **¹H NMR** (600 MHz, CDCl₃) 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). **¹³C NMR** (150 MHz, CDCl₃) 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** v_{max} (film). 2957, 2868, 1742, 1657, 1452, 1363, 1261, 1060, 1024, 880, 707 cm⁻¹; **HRMS** (ESI) m/z calcd for C₂₁H₂₃NNaO₂ [M+Na]⁺: 344.1261; found: 344.1268.

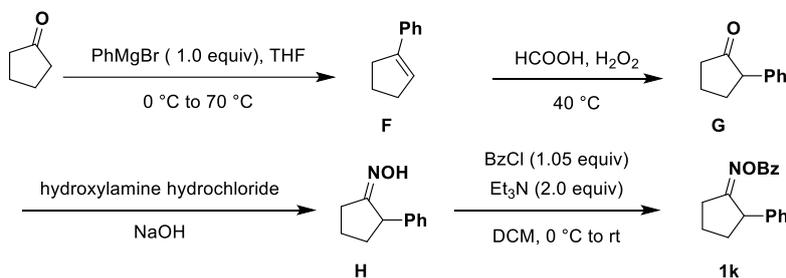


Substrate **1h** was obtained in 62% overall yield as yellow oil by column chromatography (PE/EA = 15/1) following the procedure B, by using 4-chlorostyrene. **¹H NMR** (600 MHz, CDCl₃) δ 8.07 – 8.04 (m, 2H), 7.58 (tt, J = 7.8, 1.2 Hz, 1H), 7.46 (tt, J = 7.8, 1.8 Hz, 2H), 7.32 (dd, J = 8.4, 1.8 Hz, 2H), 7.22 (dd, J = 8.4, 1.8 Hz, 2H), 3.70 – 3.65 (m, 1H), 3.64 – 3.54 (m, 2H), 3.23 – 3.16 (m, 2H). **¹³C NMR** (150 MHz, CDCl₃) 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** v_{max} (film). 2924, 1713, 1591, 1494, 1363, 1261, 1165, 982, 828, 759 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₇H₁₄ClNNaO₂ [M+Na]⁺: 322.0605; found: 322.0608.



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. **¹H NMR** (600 MHz, CDCl₃) 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). **¹³C NMR** (150 MHz, CDCl₃) 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** v_{max} (film). 2918, 2850, 1826, 1737, 1391, 885, 851, 817, 708 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₇H₁₄BrNNaO₂ [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 Et₂O) in dry THF (60 mL) was added cyclopentanone (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 H₂O. The mixture was added the 6 M HCl (20 mL) and stirred for 30 min. The water layer was extracted with Et₂O for three times. The combined organic layer was washed with brine and dried over MgSO₄. 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 H₂O₂ (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. NaHCO₃ and extracted with Et₂O for three times then dried over anhydrous MgSO₄. 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.

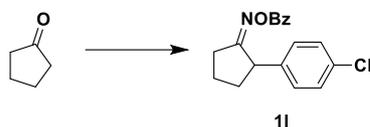
Synthesis of compound **H**

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 H₂O) 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 Na₂SO₄. 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**

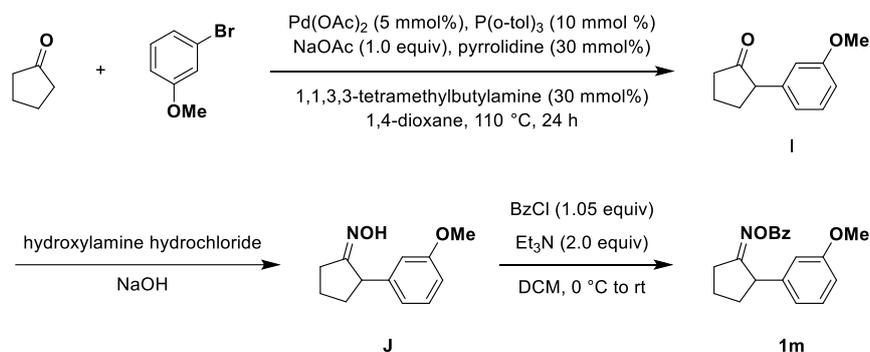
To a 50 mL dry Schlenk flask was added crude oxime (~11 mmol, 1.0 equiv) and 22 mL anhydrous DCM. Et₃N (3.10 mL, 22 mmol, 2.0 equiv) and BzCl (1.34 mL, 11.6 mmol, 1.05 equiv) were added dropwise sequentially at 0 °C. The mixture was stirred for 6 h at room temperature. The solution was diluted with water and extracted with ether for three times. The combined organic layer was washed with water and dried over anhydrous MgSO₄. 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). ¹H NMR (600 MHz, CDCl₃) 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 ν_{max} (film). 2972, 2900, 1451, 1406, 1394, 1250, 1230, 1055, 881 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$: 302.1151; found: 302.1157.



Substrate **11** was obtained in 18% overall yield from cyclopentanone 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. ^1H 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 ν_{max} (film). 2954, 2897, 1700, 1494, 1363, 1150, 986, 880, 750 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{16}\text{ClNNaO}_2$ $[\text{M}+\text{Na}]^+$: 336.0762; found: 336.0754.

Synthesis of cyclopentanone oxime ester **1m**



Synthesis of compound **I**

To a 500 mL dry Schlenk flask was added $\text{Pd}(\text{OAc})_2$ (225 mg, 1.0 mmol, 0.05 equiv), $\text{P}(\text{o-tol})_3$ (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 **I** in 74 % yield (2.80 g, 14.8 mmol) as yellow oil.

Synthesis of compound **J**

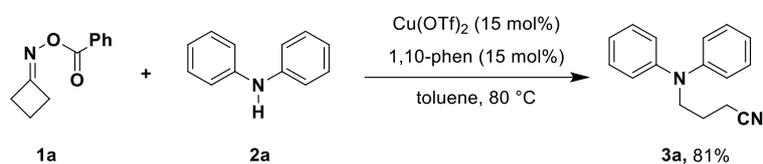
The ketone **I** (2.80 g, 14.7 mmol, 1.0 equiv) was dissolved in dry EtOH (0.25 M) and the solution of NaOH (59 mL, 29.4 mmol, 2.0 equiv, 0.5 M in H₂O) was added. Hydroxylamine hydrochloride (1.53 g, 22.1 mmol, 1.5 equiv) was added into the reaction and the mixture was allowed to react at room temperature. 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 Na₂SO₄. 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**

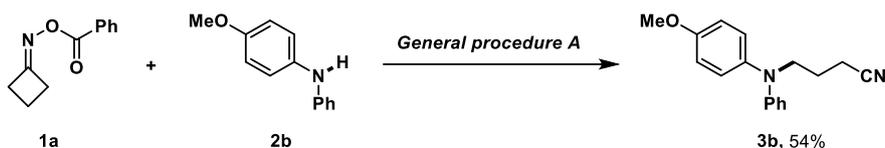
To a 100 mL dry Schlenk flask was added crude oxime (13.5 mmol, 1.0 equiv) and anhydrous DCM (27.0 mL). Et₃N (3.75 mL, 27.0 mmol, 2.0 equiv) and BzCl (1.65 mL, 14.2 mmol, 1.05 equiv) were added dropwise sequentially at 0 °C. The mixture was stirred for 6 h at room temperature. The solution was diluted with water and extracted with ether for three times. The combined organic layer was washed with water and dried over anhydrous MgSO₄. 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. ¹H NMR (600 MHz, CDCl₃) 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). ¹³C NMR (150 MHz, CDCl₃) 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 v_{max} (film). 2932, 2850, 2784, 1820, 1700, 1420, 1250, 998, 793 cm⁻¹; HRMS (ESI) m/z calcd for C₁₉H₁₉NNaO₃ [M+Na]⁺: 332.1257; found: 332.1247.

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

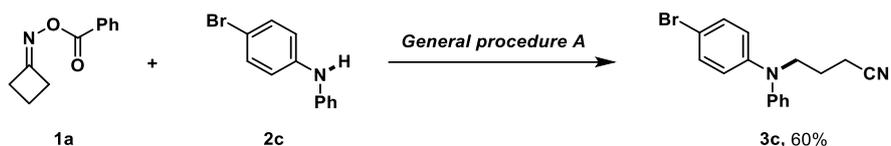
General procedure A



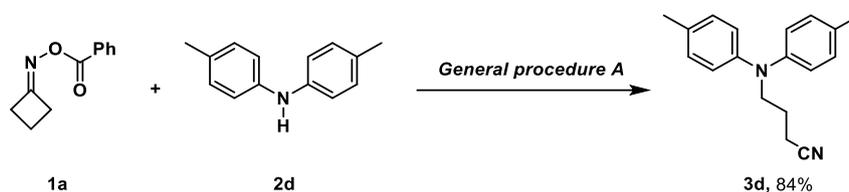
To a 10 mL dry Schlenk flask was added **1a** (75.6 mg, 0.40 mmol, 2.0 equiv), $\text{Cu}(\text{OTf})_2$ (10.8 mg, 0.03 mmol, 0.15 equiv), 1,10-phen (5.4 mg, 0.03 mmol, 0.15 equiv) and 2 mL dry toluene. Then **2a** (33.8 mg, 0.20 mmol, 1.0 equiv) was added at ambient temperature, and the reaction was 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. $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 147.8, 129.6, 122.1, 121.3, 119.4, 50.7, 23.7, 14.9 ppm; **IR** ν_{max} (film). 2923, 1770, 1493, 1374, 1245, 1059, 749, 694 cm^{-1} ; **HRMS (ESI)** m/z calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2$ $[\text{M}+\text{H}]^+$: 237.1386; found: 237.1389.



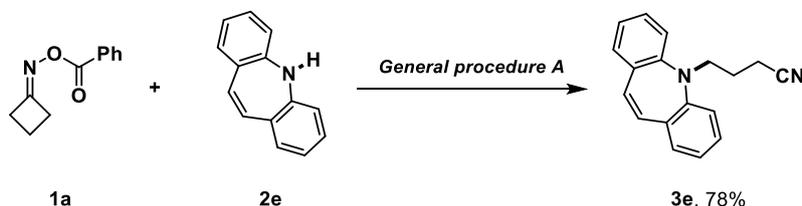
Product **3b** was obtained in 54 % yield (28.7 mg, 0.11 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 5/1) following the general procedure A, except that **2b** was used to replace **2a**. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.19 (t, $J = 7.8$ Hz, 2H), 7.05 (d, $J = 7.8$ 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). $^{13}\text{C NMR}$ (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** ν_{max} (film). 2924, 1770, 1595, 1808, 1498, 1243, 1033, 748 cm^{-1} ; **HRMS (ESI)** m/z calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{NaO}$ $[\text{M}+\text{Na}]^+$: 289.1311; found: 289.1304.



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**. **¹H NMR** (600 MHz, CDCl₃) 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). **¹³C NMR** (150 MHz, CDCl₃) 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** v_{max} (film). 2965, 1450, 1374, 1244, 1059, 913, 747 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₆H₁₅BrN₂Na[M+Na]⁺: 337.0311; found: 337.0309.

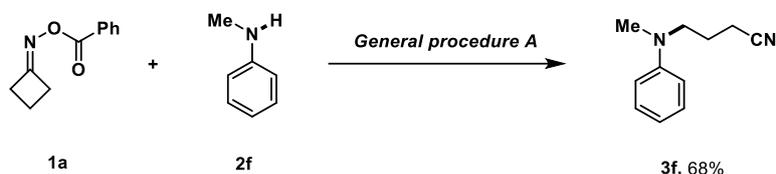


Product **3d** was obtained in 84% yield (44.4 mg, 0.17 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 8/1) following the general procedure A, except that **2d** was used to replace **2a**. **¹H NMR** (600 MHz, CDCl₃) δ 7.07 (d, J = 8.4 Hz, 4H), 6.85 (d, J = 8.4 Hz, 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). **¹³C NMR** (150 MHz, CDCl₃) δ 145.7, 131.4, 130.1, 121.3, 119.5, 50.8, 23.8, 20.7, 14.9 ppm; **IR** v_{max} (film). 2924, 2856, 1758, 1511, 1245. 1050, 810, 748 cm⁻¹; **IR** v_{max} (film). 2924, 2856, 1758, 1511, 1245. 1050, 810, 748 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₈H₂₀N₂Na [M+Na]⁺: 287.1519; found: 287.1514.

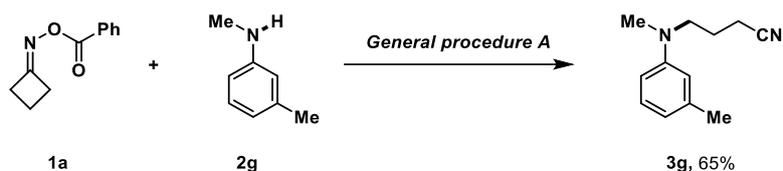


Product **3e** was obtained in 78% yield (40.6 mg, 0.16 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 8/1) following the general procedure A, except that **2e** was used to replace **2a**. **¹H NMR** (600 MHz, CDCl₃) δ 7.27 (d, J = 7.8 Hz, 2H), 7.01 (t, J = 7.8 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). **¹³C NMR** (150 MHz, CDCl₃) δ 149.9, 134.2, 132.2, 129.5, 129.2, 124.0, 120.5, 48.8, 23.6,

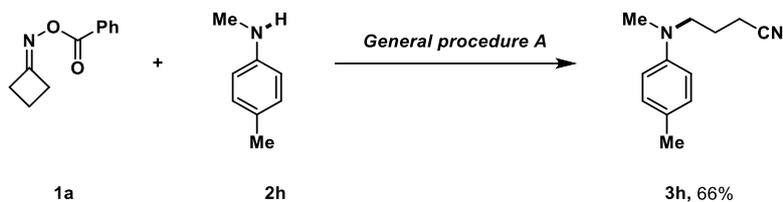
14.5 ppm; **IR** ν_{max} (film). 2923, 1770, 1758, 1697, 1557, 1275, 1246. 1056, 764, 749 cm^{-1} ;
HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2$ $[\text{M}+\text{H}]^+$: 261.1386; found: 261.1382.



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**. **^1H 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** ν_{max} (film). 2940, 1600, 1464, 1375, 1192, 1034, 752, 695 cm^{-1} ; **HRMS** (ESI) m/z calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 197.1049; found: 197.1054.

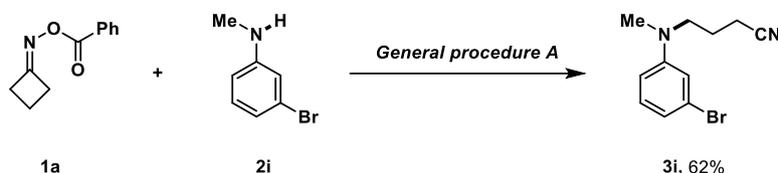


Product **3g** was obtained in 65% yield (24.5 mg, 0.13 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 10/1) following the general procedure A, except that **2g** was used to replace **2a**. **^1H NMR** (600 MHz, CDCl_3) δ 7.13 (t, $J = 7.8$ Hz, 1H), 6.57 (d, $J = 7.8$ 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** ν_{max} (film). 2922, 2851, 1764, 1602, 1498, 1377, 1176, 765, 692 cm^{-1} ; **HRMS** (ESI) m/z calcd for $\text{C}_{12}\text{H}_{17}\text{N}_2$ $[\text{M}+\text{H}]^+$: 189.1386; found: 189.1386.

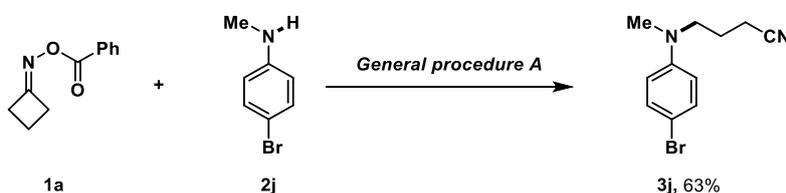


Product **3h** was obtained in 66% yield (24.8 mg, 0.13 mmol) as red oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 9/1) following the general procedure A, except that **2h** was used to replace **2a**. **^1H NMR** (600 MHz, CDCl_3) δ 7.05 (d, $J = 8.4$ Hz, 2H), 6.66 (d, J

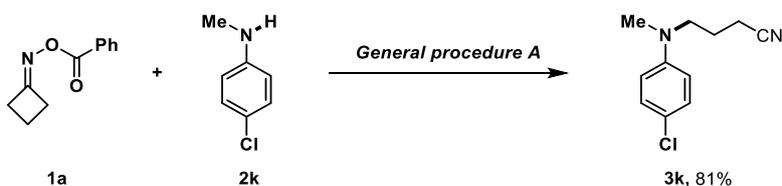
= 8.4 Hz, 2H), 3.40 (t, J = 7.2 Hz, 2H), 2.90 (s, 3H), 2.37 (t, J = 7.2 Hz, 2H), 2.25 (s, 3H), 1.92 (t, J = 6.6 Hz, 2H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 147.2, 130.0, 126.7, 119.6, 113.4, 51.8, 39.1, 23.2, 20.3, 14.8 ppm; **IR** ν_{max} (film). 2956, 2925, 2854, 1770, 1675, 1516, 1246, 1052, 816, 746 cm^{-1} ; **HRMS (ESI)** m/z calcd for $\text{C}_{12}\text{H}_{17}\text{N}_2$ $[\text{M}+\text{H}]^+$: 189.1386; found: 189.1382.



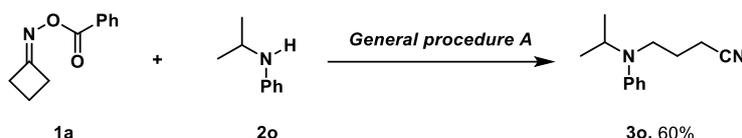
Product **3i** was obtained in 62% yield (31.3 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 12/1) following the general procedure A, except that **2i** was used to replace **2a**. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.07 (t, J = 8.4 Hz, 1H), 6.83 (d, 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). $^{13}\text{C NMR}$ (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** ν_{max} (film). 2925, 1592, 1555, 1493, 982, 753, 682 cm^{-1} ; **HRMS (ESI)** m/z calcd for $\text{C}_{11}\text{H}_{13}\text{BrN}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 275.0154; found: 275.0156.



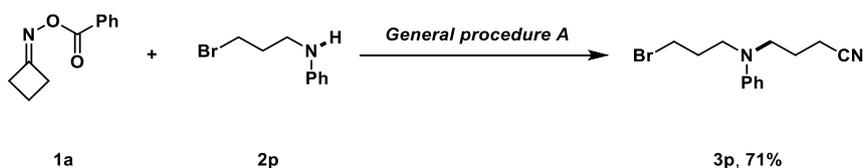
Product **3j** was obtained in 63% yield (31.8 mg, 0.13 mmol) colorless oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 12/1) following the general procedure A, except that **2j** was used to replace **2a**. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.18 (d, J = 9.0 Hz, 2H), 6.63 (d, 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). $^{13}\text{C NMR}$ (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** ν_{max} (film). 2933, 1596, 1501, 1374, 1191, 1120, 811 cm^{-1} ; **HRMS (ESI)** m/z calcd for $\text{C}_{11}\text{H}_{13}\text{BrN}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 275.0154; found: 275.0155.



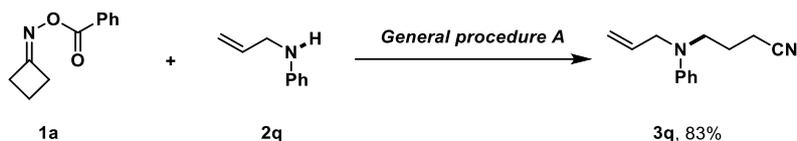
Product **3n** was obtained in 62% yield (26.8 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 6/1) following the general procedure A, except that **2n** was used to replace **2a**. **¹H NMR** (600 MHz, CDCl₃) δ 7.22 (t, J = 7.8 Hz, 2H), 6.71 – 6.68 (m, 3H), 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). **¹³C NMR** (150 MHz, CDCl₃) 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** ν_{max} (film). 2957, 2926, 2856, 1598, 1504, 1463, 1372, 1282, 747, 693 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₄H₂₁N₂ [M+H]⁺: 217.1699; found: 217.1693.



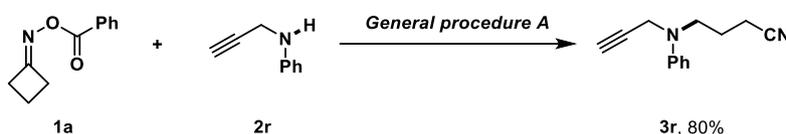
Product **3o** was obtained in 60% yield (24.3 mg, 0.12 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 13/1) following the general procedure A, except that **2o** was used to replace **2a**. **¹H NMR** (600 MHz, CDCl₃) δ 7.24 (t, J = 7.8 Hz, 2H), 6.82 (d, J = 7.8 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). **¹³C NMR** (150 MHz, CDCl₃) δ 148.6, 129.3, 119.7, 118.4, 116.2, 51.3, 42.0, 24.3, 20.1, 14.8 ppm; **IR** ν_{max} (film). 2956, 2920, 2850, 1770, 1459, 1376, 1244, 1098, 1059, 747 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₃H₁₉N₂ [M+H]⁺: 203.1543; found: 203.1540.



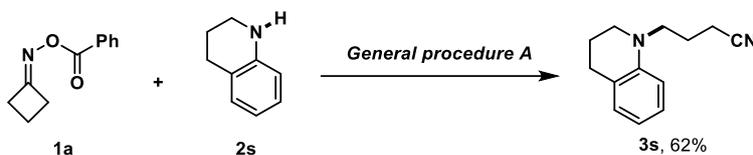
Product **3p** was obtained in 71% yield (39.8 mg, 0.14 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 6/1) following the general procedure A, except that **2p** was used to replace **2a**. **¹H NMR** (600 MHz, CDCl₃) δ 7.24 (t, J = 7.8 Hz, 2H), 6.76 – 6.73 (m, 3H), 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). **¹³C NMR** (150 MHz, CDCl₃) 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** ν_{max} (film). 2924, 1638, 1597, 1503, 1363, 1256, 749, 694 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₃H₁₇BrN₂Na [M+Na]⁺: 303.0467; found: 303.0465.



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**. **¹H NMR** (600 MHz, CDCl₃) 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). **¹³C NMR** (150 MHz, CDCl₃) 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** ν_{max} (film). 2918, 2849, 1598, 1505, 1276, 926, 750, 693 cm⁻¹; **HRMS (ESI) m/z** calcd for C₁₃H₁₇N₂ [M+H]⁺: 201.1386; found: 201.1390.

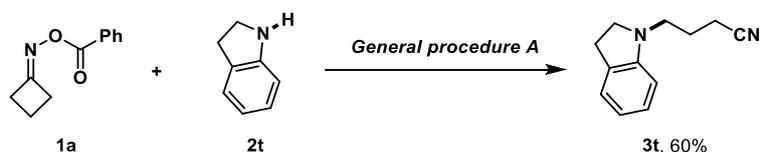


Product **3r** was obtained in 80% yield (31.7 mg, 0.16 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 12/1) following the general procedure A, except that **2r** was used to replace **2a**. **¹H NMR** (600 MHz, CDCl₃) δ 7.28 (t, J = 7.8 Hz, 2H), 6.87 (d, J = 7.2 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). **¹³C NMR** (150 MHz, CDCl₃) 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** ν_{max} (film). 2995, 1770, 1759, 1374, 1245, 1057, 913, 747 cm⁻¹; **HRMS (ESI) m/z** calcd for C₁₃H₁₄N₂Na[M+Na]⁺: 221.1049; found: 221.1055.

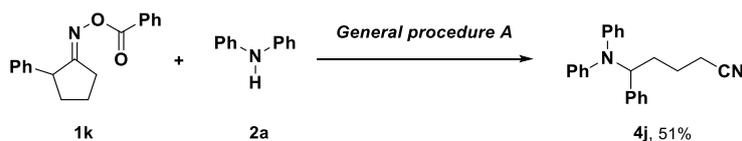


Product **3s** was obtained in 62% yield (24.8 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 8/1) following the general procedure A, except that **2s** was used to replace **2a**. **¹H NMR** (600 MHz, CDCl₃) δ 7.05 (t, J = 7.8 Hz, 1H), 6.96 (d, J = 7.2 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). **¹³C NMR** (150 MHz, CDCl₃) 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

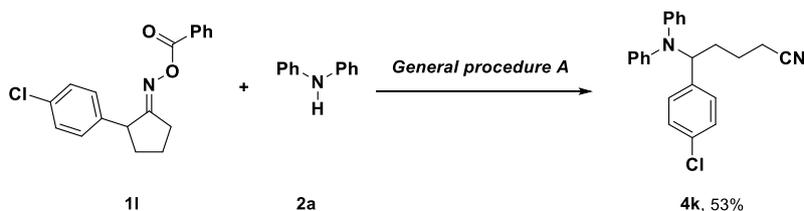
ppm; **IR** ν_{max} (film). 2923, 1744, 1515, 1451, 1260, 1060, 1024, 880, 843, 812, 706 cm^{-1} ; **HRMS** (ESI) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{Na}[\text{M}+\text{Na}]^+$: 223.1206; found: 223.1202.



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**. **^1H 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** ν_{max} (film). 3063, 2927, 1742, 1689, 1492, 1451, 1399, 1260, 1059, 1024, 820, 705, 523 cm^{-1} ; **HRMS** (ESI) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Na}[\text{M}+\text{Na}]^+$: 209.1049; found: 209.1051.

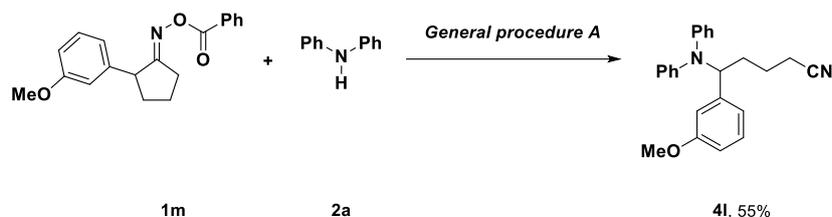


Product **4j** was obtained in 51% yield (33.3 mg, 0.10 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 6/1) following the general procedure A except that **1k** was used to replace **1a**. **^1H NMR** (600 MHz, CDCl_3) δ 7.25 (d, $J = 6.0$ Hz, 2H), 7.22 (d, $J = 9.0$ 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** ν_{max} (film). 2922, 2852, 1586, 1492, 1260, 800, 723, 698 cm^{-1} ; **HRMS** (ESI) m/z calcd for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{Na} [\text{M}+\text{Na}]^+$: 349.1675; found: 349.1672.



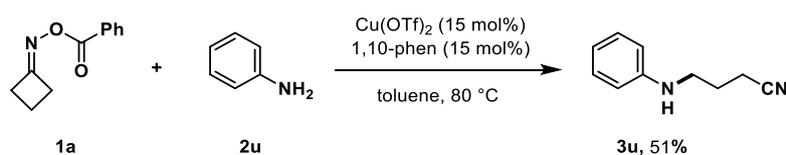
Product **4k** was obtained in 53% yield (38.2 mg, 0.11 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 7/1) following the general procedure A except

that **1l** was used to replace **1a**. **¹H NMR** (600 MHz, CDCl₃) 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). **¹³C NMR** (150 MHz, CDCl₃) 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** v_{max} (film). 2950, 2908, 2843, 1786, 1504, 1248, 1059, 784 cm⁻¹; **HRMS** (ESI) m/z calcd for C₂₃H₂₁ClN₂Na [M+Na]⁺: 383.1285; found: 383.1283.



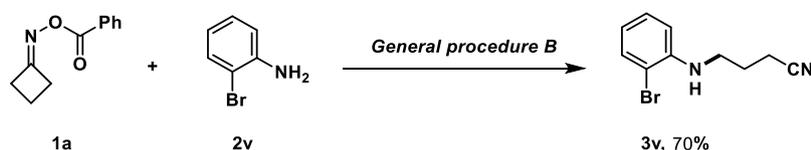
Product **4l** was obtained in 55% yield (39.2 mg, 0.11 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 6/1) following the general procedure A except that **1m** was used to replace **1a**. **¹H NMR** (600 MHz, CDCl₃) δ 7.22 – 7.16 (m, 5H), 6.95 (tt, J = 7.2, 1.2 Hz, 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). **¹³C NMR** (150 MHz, CDCl₃) 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** v_{max} (film). 2934, 2878, 2732, 1790, 1424, 824, 778 cm⁻¹; **HRMS** (ESI) m/z calcd for C₂₄H₂₄N₂NaO [M+Na]⁺: 379.1781; found: 379.1779.

General procedure B

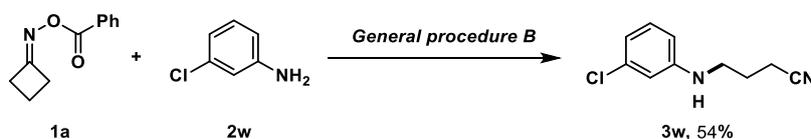


To a 10 mL dry Schlenk flask was added **1a** (37.8 mg, 0.20 mmol, 1.0 equiv), Cu(OTf)₂ (10.9 mg, 0.03 mmol, 0.15 equiv), 1,10-phen (5.4 mg, 0.03 mmol, 0.15 equiv) and 2 mL dry toluene. Then **2u** (36.5 μL, 0.40 mmol, 2.0 equiv) was added at ambient temperature, and the reaction was degassed for three 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.NaHCO₃ and extracted with EA for three times. The combined organic layer was dried over anhydrous Na₂SO₄ 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. **¹H NMR** (600 MHz, CDCl₃) δ 7.19 (t, J = 7.8 Hz, 2H), 6.74 (t, J = 7.8 Hz, 1H), 6.62

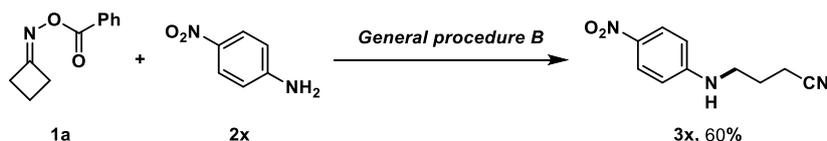
(d, $J = 7.8$ Hz, 2H), 3.71 (s, 1H), 3.31 (t, $J = 7.2$ Hz, 2H), 2.47 (t, $J = 7.2$ Hz, 2H), 1.96 (tt, $J = 7.2, 7.2$ Hz, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 147.6, 129.5, 119.5, 118.1, 113.0, 42.4, 25.4, 14.9 ppm; IR ν_{max} (film). 2995, 1770, 1759, 1603, 1374, 1246, 1057, 913, 747 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{13}\text{N}_2$ $[\text{M}+\text{H}]^+$: 161.1073; found: 161.1062.



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**. ^1H 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 ν_{max} (film). 2993, 1770, 1595, 1507, 1374, 1244, 1054, 1018, 744 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{11}\text{BrN}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 260.9998; found: 260.9999.

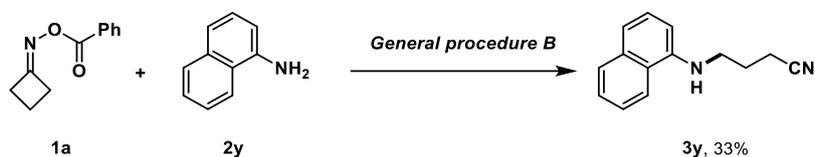


Product **3w** was obtained in 54% yield (21.0 mg, 0.11 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 10/1) following the general procedure B, except that **2w** was used to replace **2u**. ^1H NMR (600 MHz, CDCl_3) δ 7.08 (t, $J = 7.8$ Hz, 1H), 6.69 (dd, $J = 7.8, 1.8$ 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 ν_{max} (film). 2956, 2925, 2854, 1598, 1484, 1090, 987, 36, 764, 682 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{12}\text{ClN}_2$ $[\text{M}+\text{H}]^+$: 195.0684; found: 195.0681.



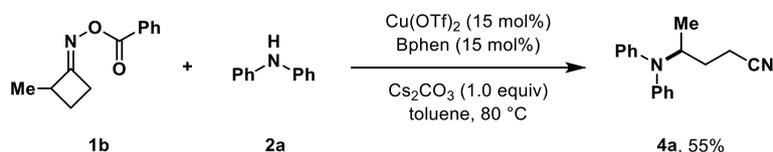
Product **3x** was obtained in 60% yield (24.6 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 8/1) following the general procedure B, except that **2x** was used to replace **2u**. ^1H NMR (600 MHz, CDCl_3) δ 8.09 (d, $J = 9.0$ Hz, 2H), 6.57 (dd, $J = 7.8, 1.8$ Hz, 1H), 6.48 (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 ν_{max} (film). 2956, 2925, 2854, 1598, 1484, 1090, 987, 36, 764, 682 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{12}\text{N}_3$ $[\text{M}+\text{H}]^+$: 194.0899; found: 194.0899.

= 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 ν_{max} (film). 3370, 2927, 1600, 1503, 1472, 1305, 1185, 1111, 833, 752, 694 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{12}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 206.0924; found: 206.0933.



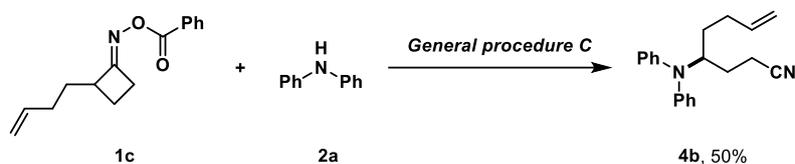
Product **3y** was obtained in 33% yield (13.9 mg, 0.07 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 6/1) following the general procedure B, except that **2y** was used to replace **2u**. ^1H NMR (600 MHz, CDCl_3) δ 7.68 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 9.0 Hz, 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 ν_{max} (film). 2934, 2238, 1737, 1592, 1555, 1494, 1372, 1121, 982, 761, 683 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 233.1049; found: 233.1045.

General procedure C

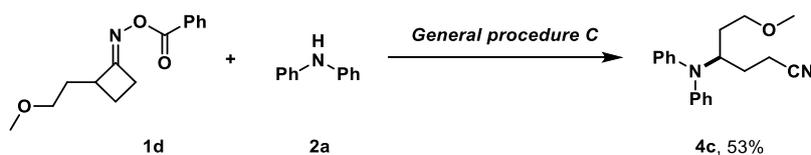


To a 10 mL dry Schlenk flask was added **1b** (81.2 mg, 0.40 mmol, 2.0 equiv), $\text{Cu}(\text{OTf})_2$ (10.8 mg, 0.03 mmol, 0.15 equiv), bathophenanthroline (10.0 mg, 0.03 mmol, 0.15 equiv), Cs_2CO_3 (65.2 mg, 0.20 mmol, 1.0 equiv) and 2 mL dry toluene. Then **2a** (33.8 mg, 0.20 mmol, 1.0 equiv) was 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 = 8/1) afforded the desired product **4a** in 55% yield (27.5 mg, 0.11 mmol) as yellow oil. ^1H 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** ν_{max} (film). 2956, 2919, 2850, 1770, 1494, 1376, 1244, 1057, 747, 701 cm^{-1} ; **HRMS (ESI)** m/z calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2$ $[\text{M}+\text{H}]^+$: 251.1543; found: 251.1548.

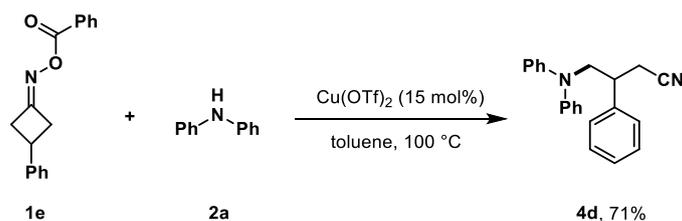


Product **4b** was obtained in 50% yield (29.0 mg, 0.10 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 12/1) following the general procedure C, except that **1c** was used to replace **1b**. **^1H NMR** (600 MHz, CDCl_3) δ 7.28 – 7.26 (m, 4H), 7.00 (t, J = 7.2 Hz, 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** ν_{max} (film). 2994, 1770, 1493, 1383, 1244, 1057, 913, 746 cm^{-1} ; **HRMS (ESI)** m/z calcd for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 313.1675; found: 313.1674.

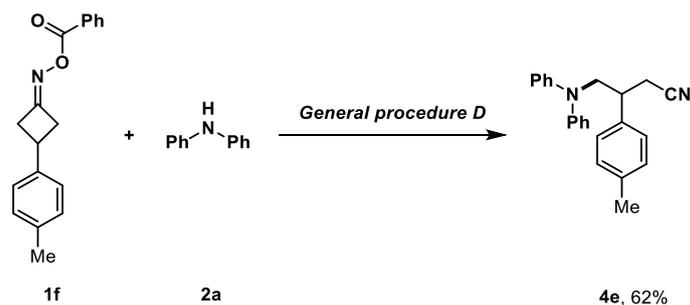


Product **4c** was obtained in 53% yield (31.2 mg, 0.11 mmol) as brown oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 10/1) following the general procedure C, except that **1d** was used to replace **1b**. **^1H NMR** (600 MHz, CDCl_3) δ 7.28 – 7.25 (m, 4H), 7.00 (t, J = 7.2 Hz, 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** ν_{max} (film) 2921, 2850, 1629, 1524, 830, 474 cm^{-1} ; **HRMS (ESI)** m/z calcd for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{NaO}$ $[\text{M}+\text{Na}]^+$: 317.1624; found: 317.1625.

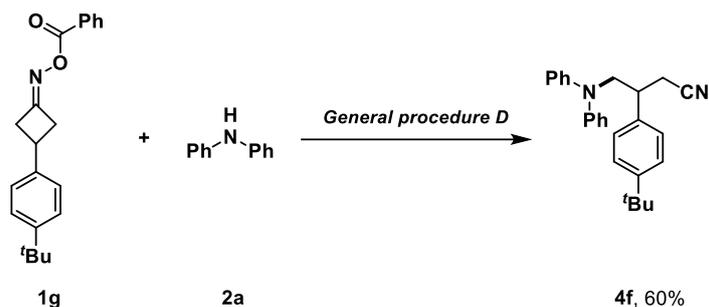
General procedure D



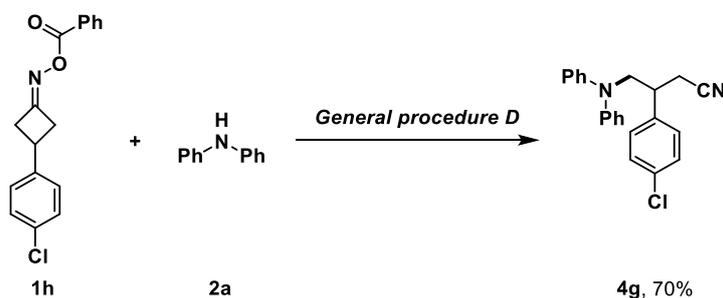
To a 10 mL dry Schlenk flask was added **1e** (106 mg, 0.40 mmol, 2.0 equiv), Cu(OTf)₂ (10.8 mg, 0.03 mmol, 0.15 equiv) and 2 mL dry toluene. Then **2a** (33.8 mg, 0.20 mmol, 1.0 equiv) was added at ambient temperature, and the reaction was degassed for three times with argon. The mixture was allowed 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.NaHCO₃ and extracted with EA for three times. The combined organic layer was dried over anhydrous Na₂SO₄ 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. **¹H NMR** (500 MHz, CDCl₃) 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). **¹³C NMR** (125 MHz, CDCl₃) 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** v_{max} (film).2956, 2923, 2852, 1587, 1493, 1242, 750, 696 cm⁻¹; **HRMS** (ESI) m/z calcd for C₂₂H₂₀N₂Na [M+Na]⁺: 335.1519; found: 335.1515.



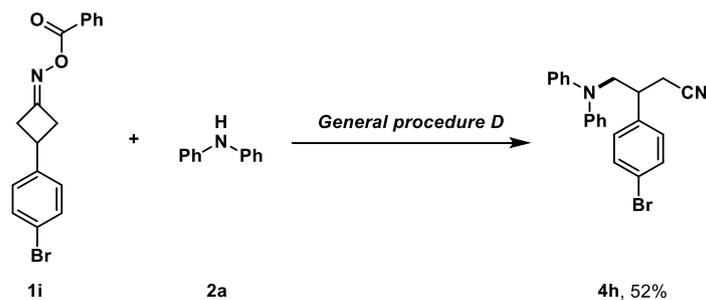
Product **4e** was obtained in 62% yield (40.4 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 15/1) following the general procedure D, except that **1f** was used to replace **1e**. **¹H NMR** (600 MHz, CDCl₃) δ 7.26 (t, J = 7.8 Hz, 4H), 7.16 (d, J = 7.8 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). **¹³C NMR** (150 MHz, CDCl₃) 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** v_{max} (film). 2994, 1770, 1588, 1493, 1374, 1244, 1057, 913, 747, 696 cm⁻¹; **HRMS** (ESI) m/z calcd for C₂₃H₂₂N₂Na [M+Na]⁺: 349.1675; found: 349.1684.



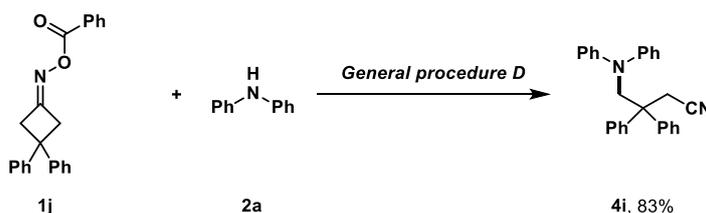
Product **4f** was obtained in 60% yield (44.2 mg, 0.12 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 13/1) following the general procedure D, except that **1g** was used to replace **1e**. **¹H NMR** (600 MHz, CDCl₃) δ 7.35 (d, J = 7.8 Hz, 2H), 7.25 (t, J = 7.8 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). **¹³C NMR** (150 MHz, CDCl₃) 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** v_{max} (film). 2958, 2926, 1766, 1494, 1381, 1243, 1058, 747, 696 cm⁻¹; **HRMS** (ESI) m/z calcd for C₂₆H₂₈N₂Na [M+Na]⁺: 391.2145; found: 391.2147.



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**. **¹H NMR** (600 MHz, CDCl₃) 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). **¹³C NMR** (150 MHz, CDCl₃) 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** v_{max} (film). 2994, 1770, 1493, 1375, 1244, 1057, 913, 746 cm⁻¹; **HRMS** (ESI) m/z calcd for C₂₂H₁₉ClN₂Na [M+Na]⁺: 369.1129; found: 369.1124.

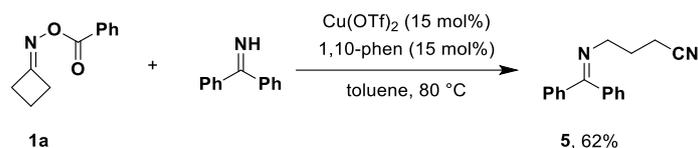


Product **4h** was obtained in 52% yield (40.6 mg, 0.10 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 18/1) following the general procedure D, except that **1i** was used to replace **1e**. **¹H NMR** (600 MHz, CDCl₃) δ 7.47 (d, J = 8.4 Hz, 2H), 7.26 (t, J = 7.8 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). **¹³C NMR** (150 MHz, CDCl₃) 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** ν_{max} (film).2994, 1770, 1491, 1374, 1244, 1057, 913, 746 cm⁻¹; **HRMS** (ESI) m/z calcd for C₂₂H₁₉BrN₂Na [M+Na]⁺: 413.0624; found: 413.0625.



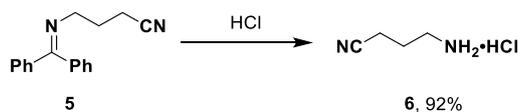
Product **4i** was obtained in 83% yield (64.4 mg, 0.17 mmol) as yellow oil in a 0.20 mmol scale synthesis by column chromatography (PE/EA = 12/1) following the general procedure D, except that **1j** was used to replace **1e**. **¹H NMR** (600 MHz, CDCl₃) δ 7.46 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.8 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). **¹³C NMR** (150 MHz, CDCl₃) 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** ν_{max} (film).2923, 1770, 1759, 1491, 1445, 1246, 1060, 913, 745, 701 cm⁻¹; **HRMS** (ESI) m/z calcd for C₂₈H₂₅N₂ [M+H]⁺: 389.2012; found: 389.2022.

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



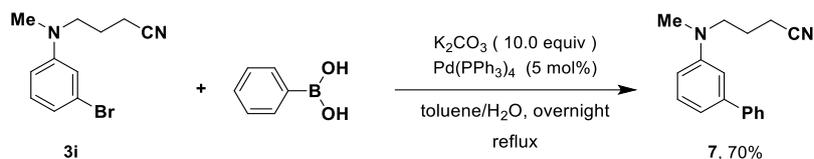
Product **5** was synthesized following the general procedure A: To a 10 mL dry Schlenk flask was added **1a** (75.6 mg, 0.40 mmol, 2.0 equiv), Cu(OTf)₂ (10.8 mg, 0.03 mmol, 0.15 equiv), 1,10-phen (5.4 mg, 0.03 mmol, 0.15 equiv) and 2 mL dry toluene. Then benzophenone imine (33.6 μL , 0.20 mmol, 1.0 equiv) was added at ambient temperature, and the reaction was degassed for three times with argon. The mixture was allowed to stir at 80 $^\circ\text{C}$ for 1.5 h. After completed (as monitored by TLC), the reaction was cooled to room temperature. The mixture was diluted with sat. NaHCO₃ and extracted with EA for three times. The combined organic layer was dried over anhydrous Na₂SO₄ 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. ¹H NMR (600 MHz, CDCl₃) 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). ¹³C NMR (150 MHz, CDCl₃) 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 ν_{max} (film). 2921, 2851, 1624, 1446, 1275, 751, 642, 428 cm⁻¹; HRMS (ESI) m/z calcd for C₁₇H₁₆N₂Na [M+Na]⁺: 271.1206; found: 271.1210.

The procedure for the synthesis of compound 6



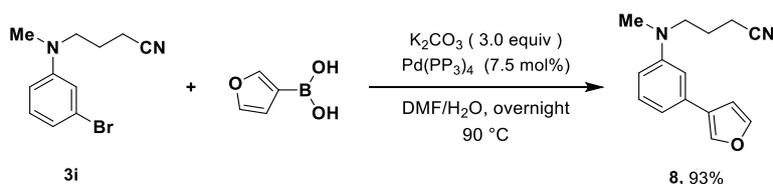
Substrate **5** (74.4 mg, 0.30 mmol, 1.0 equiv) was added to the solution of HCl (1.0 M)/CH₃OH (6 mL, v:v = 1:1). After being stirred at room temperature for 3 h, the mixture was concentrated in *vacuo* and the residue was diluted with water and extracted with EA for three times. The water layer was concentrated in *vacuo*. The product **6** was obtained in 92% yield (33.1 mg, 0.28 mmol) as white solid (m.p. 127 $^\circ\text{C}$). ¹H NMR (600 MHz, D₂O) 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). ¹³C NMR (150 MHz, D₂O) δ 120.5, 38.2, 22.7, 14.2 ppm. IR ν_{max} (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. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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** ν_{max} (film).2924, 2854, 1770, 1759, 1596, 1460, 1376, 1246, 1056, 913, 748, 697 cm^{-1} ; **HRMS** (ESI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 273.1362; found: 273.1364.

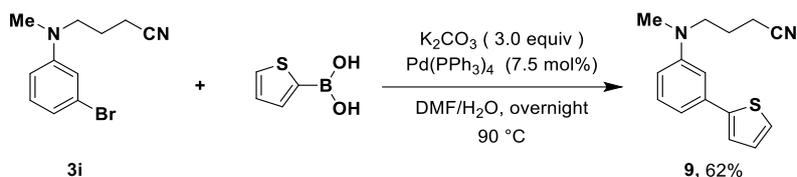
The procedure for the synthesis of compound 8



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. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.72 (s, 1H), 7.46 (t,

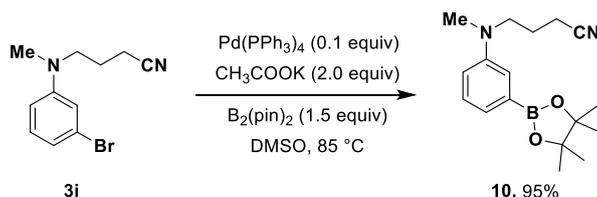
$J = 1.8$ Hz, 1H), 7.25 (t, $J = 4.2$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 6.84 (s, 1H), 6.70 (s, 1H), 6.65 (dd, $J = 7.8, 3.0$ Hz, 1H), 3.50 (t, $J = 7.2$ Hz, 2H), 2.98 (s, 3H), 2.41 (t, $J = 7.2$ Hz, 2H), 1.97 (tt, $J = 7.2, 7.2$ Hz, 2H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 149.6, 143.6, 138.7, 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** ν_{max} (film). 2924, 1770, 1760, 1603, 1492, 1375, 1245, 1059, 913, 747 cm^{-1} ; **HRMS** (ESI) m/z calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{NaO}$ $[\text{M}+\text{Na}]^+$: 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. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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** ν_{max} (film). 2926, 1597, 1494, 1373, 1246, 1060, 913, 828, 747, 694 cm^{-1} ; **HRMS** (ESI) m/z calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{NaS}$ $[\text{M}+\text{Na}]^+$: 279.0926; found: 279.0923.

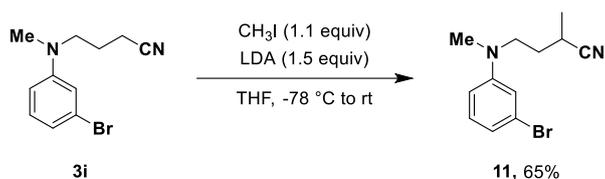
The procedure for the synthesis of compound 10



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,

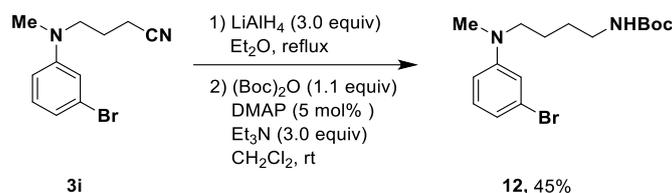
2.0 equiv), triphenylphosphine palladium (58.0 mg, 0.05 mmol, 0.1 equiv) and 2 mL anhydrous DMSO under N₂. The mixture was allowed to stir at 85 °C for 4 h. After completed (as monitored by TLC), the reaction was cooled to room temperature. The mixture was diluted with water and extracted with EA for three times. The combined organic layer was dried over anhydrous Na₂SO₄ 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. ¹H NMR (600 MHz, CDCl₃) 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). ¹³C NMR (150 MHz, CDCl₃) 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** ν_{max} (film). 2926, 1774, 1681, 1451, 1245, 1080, 1059, 1023, 913, 847, 744, 708 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₇H₂₅BN₂NaO₂ [M+Na]⁺: 323.1901; found: 323.1907.

The procedure for the synthesis of compound **11**



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 N₂. 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 CH₃I 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. NH₄Cl, and was extracted with Et₂O for three times. The combined organic phase was dried over anhydrous MgSO₄, 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. ¹H NMR (600 MHz, CDCl₃) 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). ¹³C NMR (150 MHz, CDCl₃) 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** ν_{max} (film). 2961, 1745, 1600, 1450, 1397, 1259, 1079, 1058, 1023, 879, 828, 705 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₂H₁₅BrN₂Na [M+Na]⁺: 289.0311; found: 289.0313.

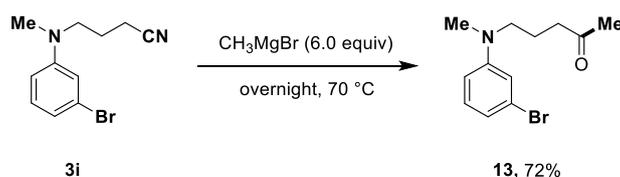
The procedure for the synthesis of compound 12



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.

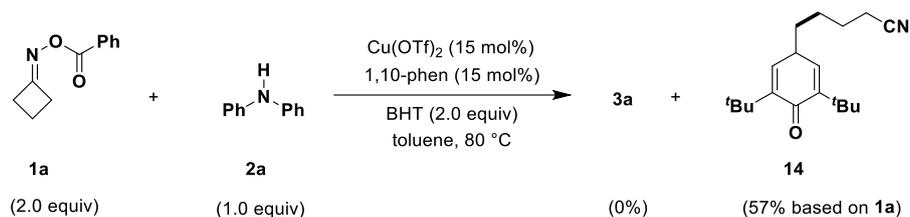
Di-tert-butyl dicarbonate (95.4 mg, 0.44 mmol, 1.1 equiv) and DMAP (2.4 mg, 0.02 mmol, 5 mol%) were added in DCM (2.6 mL) at room temperature and the mixture was stirred for 10 min. Et_3N (0.17 mL, 1.20 mmol, 3.0 equiv) and the above primary amine in DCM (2.4 mL) were added successively into the solution 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. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 ν_{max} (film). 2925, 1770, 1592, 1507, 1494, 1366, 1246, 1053, 913, 747 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{25}\text{BrN}_2\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 379.0992; found: 379.0995.

The procedure for the synthesis of compound 13



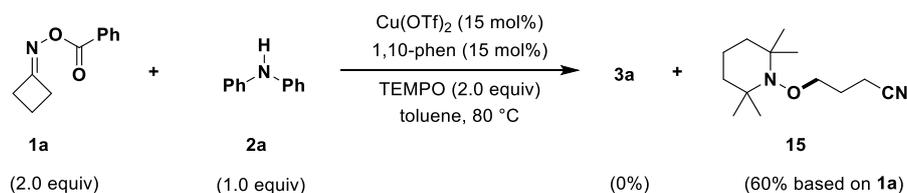
To a 10 mL dry Schlenk flask were added **3i** (152 mg, 0.60 mmol, 1.0 equiv) and 2 mL anhydrous Et₂O under N₂. Then the methylmagnesium bromide (1.2 mL, 3.60 mmol, 6.0 equiv, 3.0 M in ether) was added dropwise into this solution. The reaction was refluxed overnight. After completed (as monitored by 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 Et₂O for five times. The combined organic layer was dried over anhydrous MgSO₄ 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. **¹H NMR** (600 MHz, CDCl₃) δ 7.05 (t, J = 8.4 Hz, 1H), 6.80 (s, 1H), 6.78 (d, J = 8.4 Hz, 1H), 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). **¹³C NMR** (150 MHz, CDCl₃) 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** ν_{max} (film). 2994, 1769, 1758, 1383, 1245, 1058, 913, 745, 707 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₂H₁₆BrNNaO [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.NaHCO₃ and extracted with EA for three times. The combined organic layer was dried over anhydrous Na₂SO₄ 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. **¹H NMR** (600 MHz, CDCl₃) 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). **¹³C NMR** (150 MHz, CDCl₃) 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** ν_{max} (film). 2994, 1769, 1757, 1487, 1374, 1246, 1057, 913, 815, 744, 704 cm⁻¹; **HRMS** (ESI) m/z calcd for C₁₉H₂₉NNaO [M+Na]⁺: 310.2141; found: 310.2143.

The procedure for the synthesis of compound 15



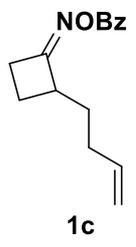
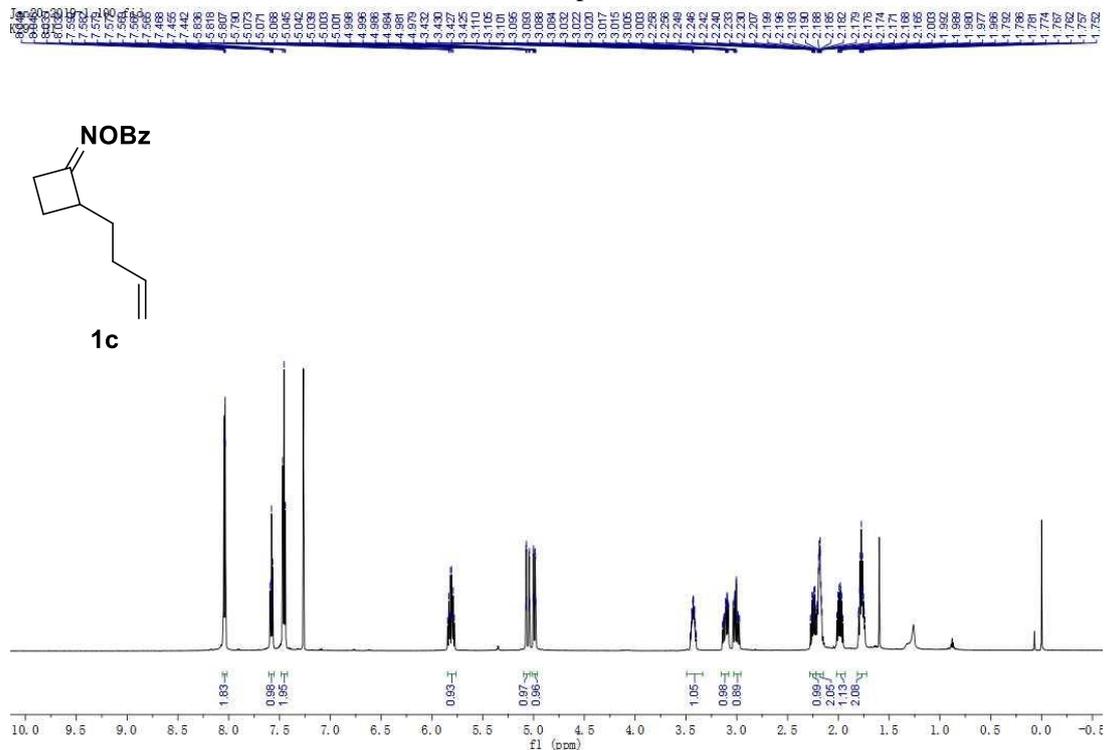
To a 10 mL dry Schlenk flask was added **1a** (75.6 mg, 0.40 mmol, 2.0 equiv), $\text{Cu}(\text{OTf})_2$ (10.8 mg, 0.03 mmol, 0.15 equiv), 1,10-phen (5.4 mg, 0.03 mmol, 0.15 equiv), TEMPO (2.5 mg, 0.40 mmol, 2.0 equiv) and 2 mL dry toluene. Then **2a** (33.8 mg, 0.20 mmol, 1.0 equiv) was added at room 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

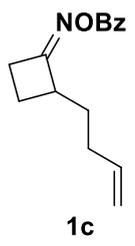
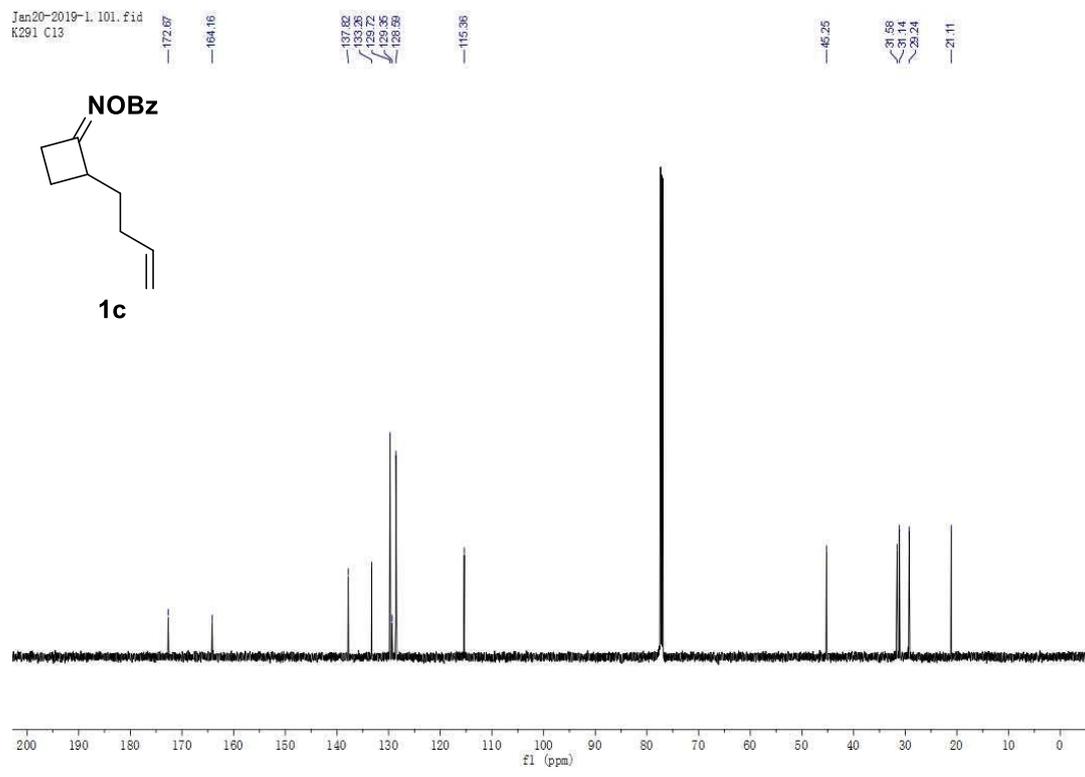
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- [2] Nishimura, T.; Nishiguchi, Y.; Maeda, Y.; Uemura, S. *J. Org. Chem.* **2004**, *69*, 5342.
- [3] Quach, T. D.; Batey, R. A. *Org. Lett.* **2003**, *5*, 4397.
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- [5] Rajagopal, B.; Chou, C.-H.; Chung, C.-C.; Lin, P.-C. *Org. Lett.* **2014**, *16*, 3752.
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Part 7: NMR spectra

¹H NMR Spectra of **1c**

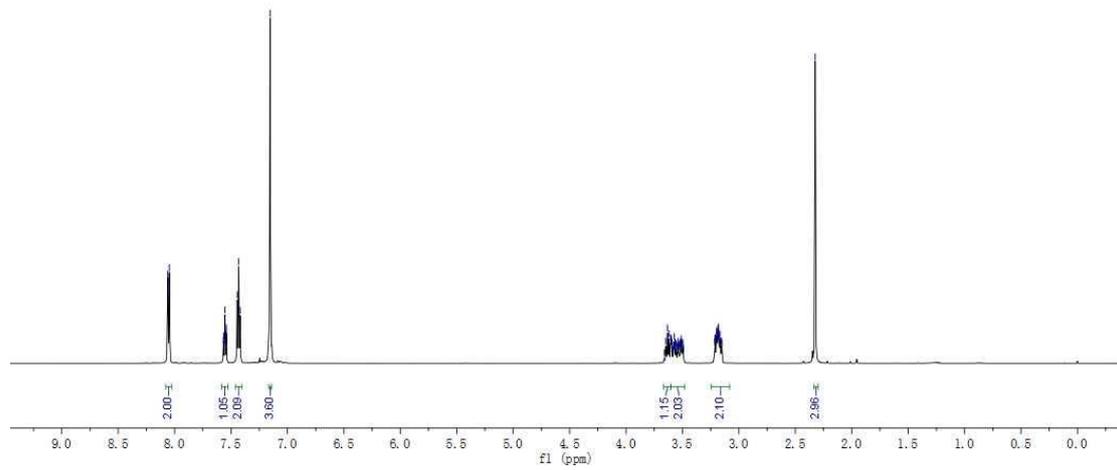
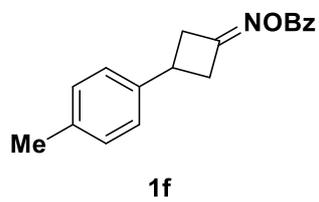


¹³C NMR Spectra of **1c**



¹H NMR Spectra of 1f

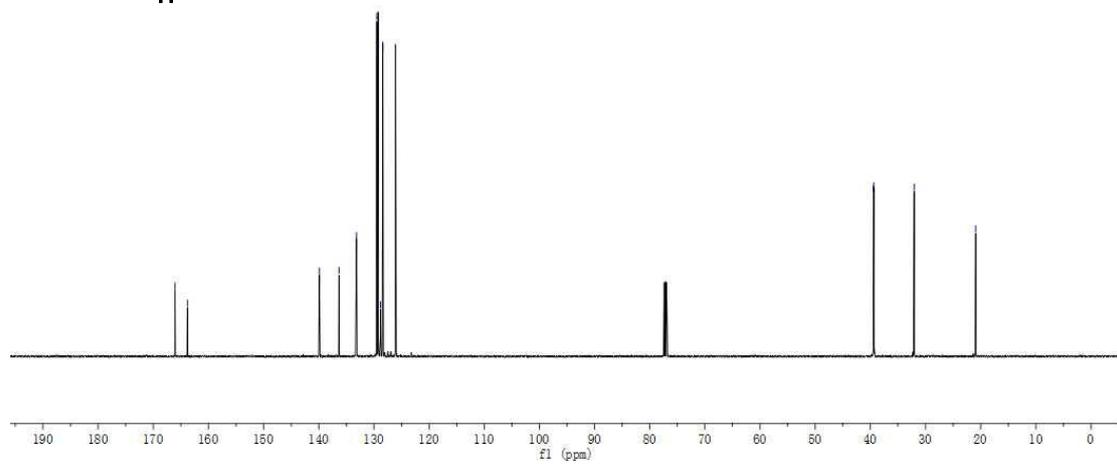
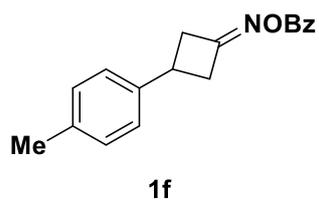
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1.6765
1.6701
1.6637
1.6573
1.6509
1.6445
1.6381
1.6317
1.6253
1.6189
1.6125
1.6061
1.5997
1.5933
1.5869
1.5805
1.5741
1.5677
1.5613
1.5549
1.5485
1.5421
1.5357
1.5293
1.5229
1.5165
1.5101
1.5037
1.4973
1.4909
1.4845
1.4781
1.4717
1.4653
1.4589
1.4525
1.4461
1.4397
1.4333
1.4269
1.4205
1.4141
1.4077
1.4013
1.3949
1.3885
1.3821
1.3757
1.3693
1.3629
1.3565
1.3501
1.3437
1.3373
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1.3245
1.3181
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1.3053
1.2989
1.2925
1.2861
1.2797
1.2733
1.2669
1.2605
1.2541
1.2477
1.2413
1.2349
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1.2221
1.2157
1.2093
1.2029
1.1965
1.1901
1.1837
1.1773
1.1709
1.1645
1.1581
1.1517
1.1453
1.1389
1.1325
1.1261
1.1197
1.1133
1.1069
1.1005
1.0941
1.0877
1.0813
1.0749
1.0685
1.0621
1.0557
1.0493
1.0429
1.0365
1.0301
1.0237
1.0173
1.0109
1.0045
0.9981
0.9917
0.9853
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0.9533
0.9469
0.9405
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0.9213
0.9149
0.9085
0.9021
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0.8701
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0.5501
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0.5373
0.5309
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0.4989
0.4925
0.4861
0.4797
0.4733
0.4669
0.4605
0.4541
0.4477
0.4413
0.4349
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0.4221
0.4157
0.4093
0.4029
0.3965
0.3901
0.3837
0.3773
0.3709
0.3645
0.3581
0.3517
0.3453
0.3389
0.3325
0.3261
0.3197
0.3133
0.3069
0.3005
0.2941
0.2877
0.2813
0.2749
0.2685
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0.2429
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0.2109
0.2045
0.1981
0.1917
0.1853
0.1789
0.1725
0.1661
0.1597
0.1533
0.1469
0.1405
0.1341
0.1277
0.1213
0.1149
0.1085
0.1021
0.0957
0.0893
0.0829
0.0765
0.0701
0.0637
0.0573
0.0509
0.0445
0.0381
0.0317
0.0253
0.0189
0.0125
0.0061
0.0000



¹³C NMR Spectra of 1f

Jan20-2019-1.61.fid
F287 C13

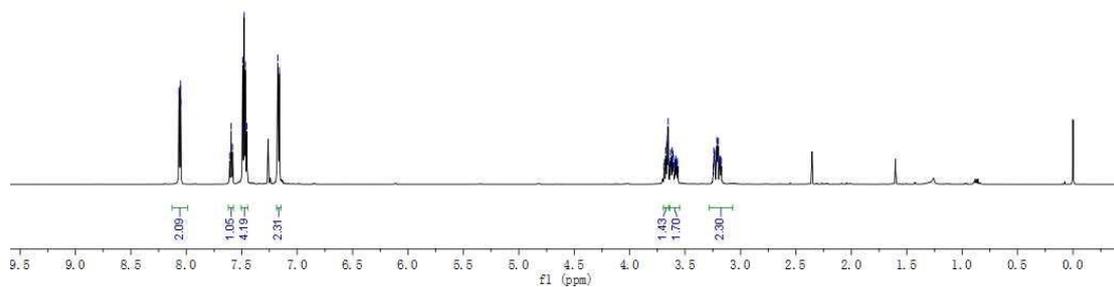
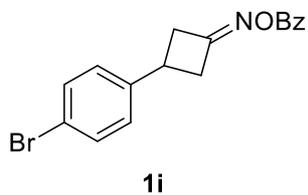
166.06
163.81
139.80
136.33
133.16
129.47
129.25
128.90
126.09
39.48
38.38
32.06
20.91



¹H NMR Spectra of **1i**

Jan20-2019-
K292 H1

8.089
8.087
8.085
8.083
7.856
7.854
7.482
7.480
7.478
7.476
7.454
7.175
7.161
3.690
3.687
3.675
3.664
3.660
3.654
3.638
3.631
3.622
3.616
3.611
3.605
3.590
3.588
3.583
3.581
3.577
3.574
3.568
3.246
3.240
3.232
3.226
3.226
3.219
3.217
3.213
3.205
3.201
3.189
3.184
3.183
3.179
3.174

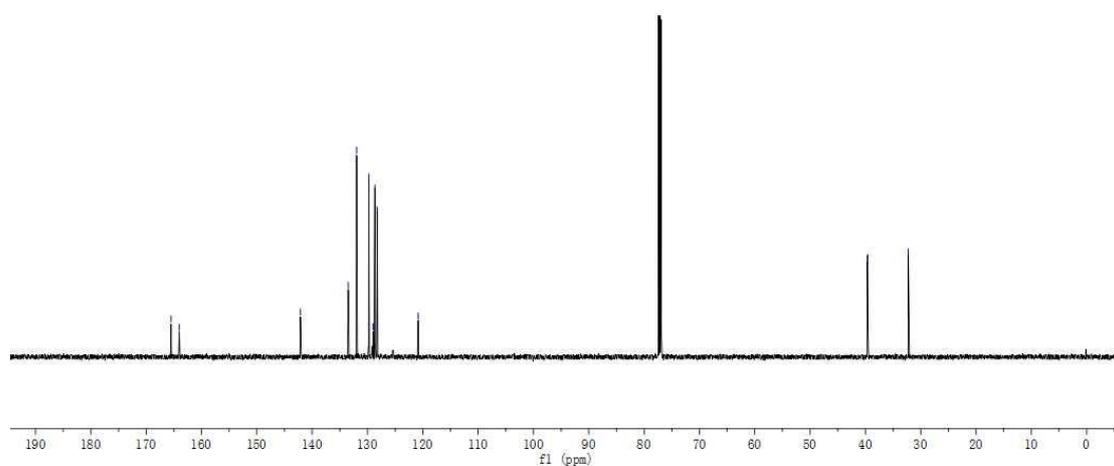
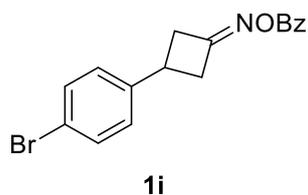


¹³C NMR Spectra of **1i**

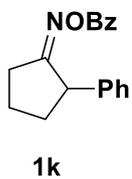
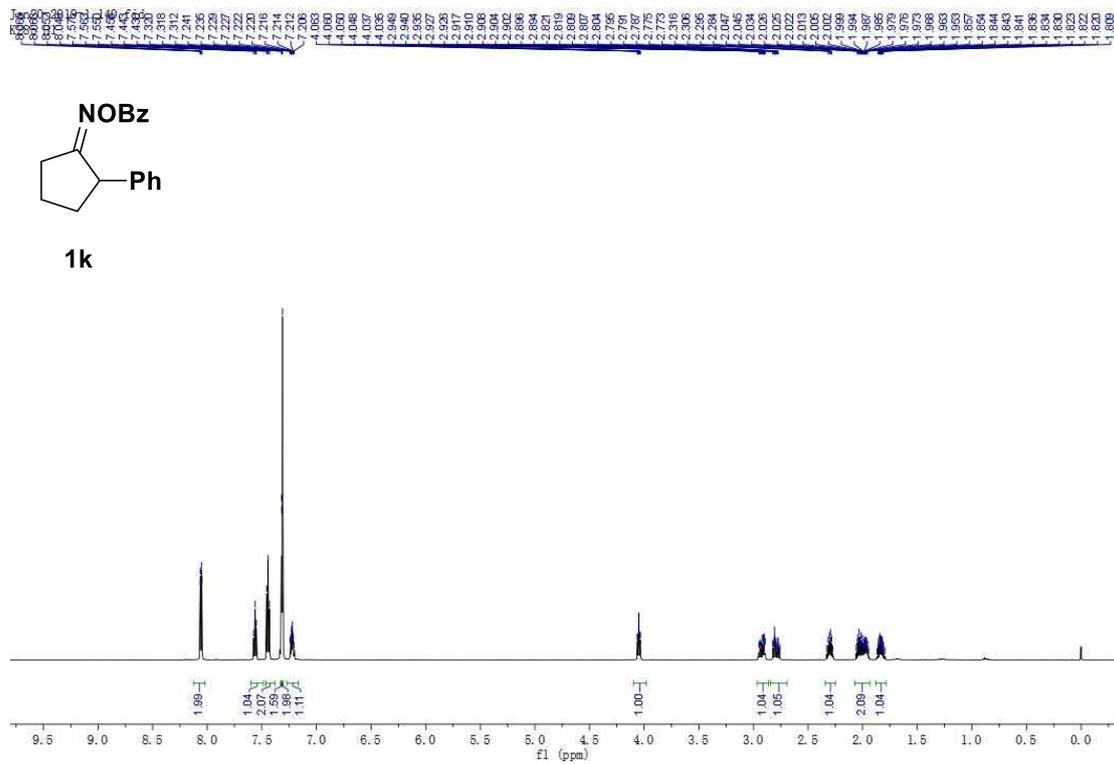
Jan20-2019-1.111.fid
K292 C13

165.67
164.02
142.12
133.47
131.65
129.76
128.98
128.65
128.24
120.85

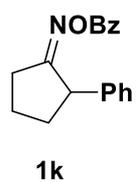
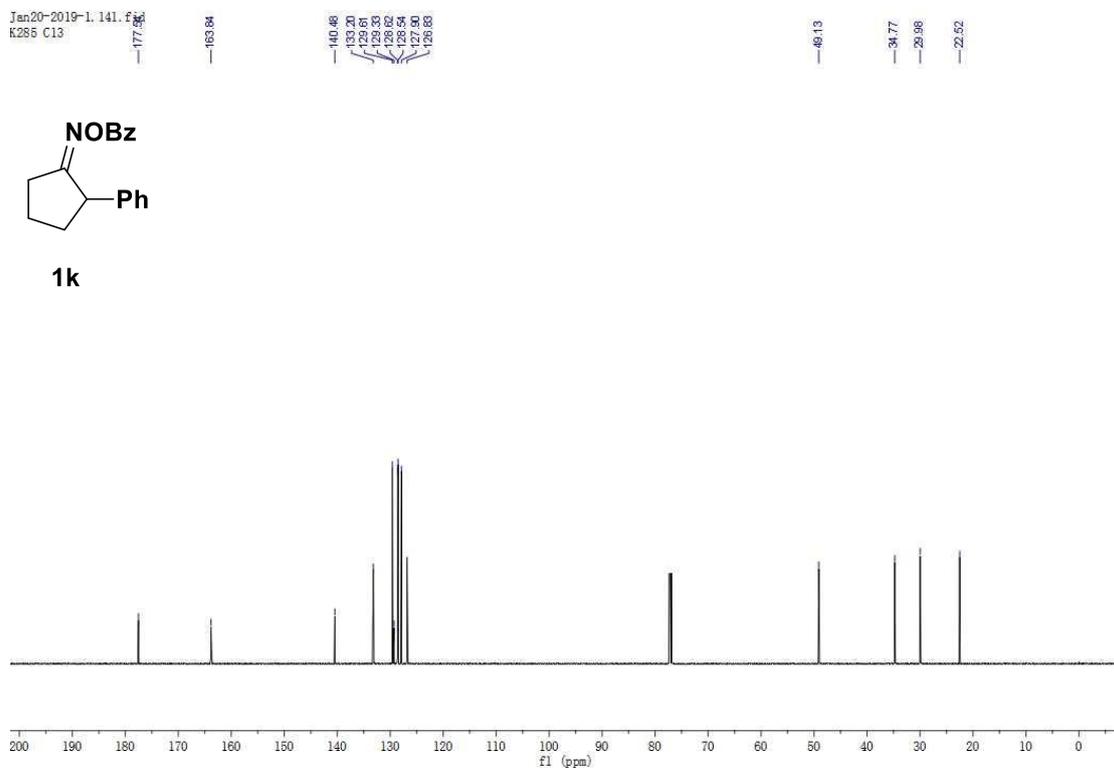
38.65
38.65
32.24



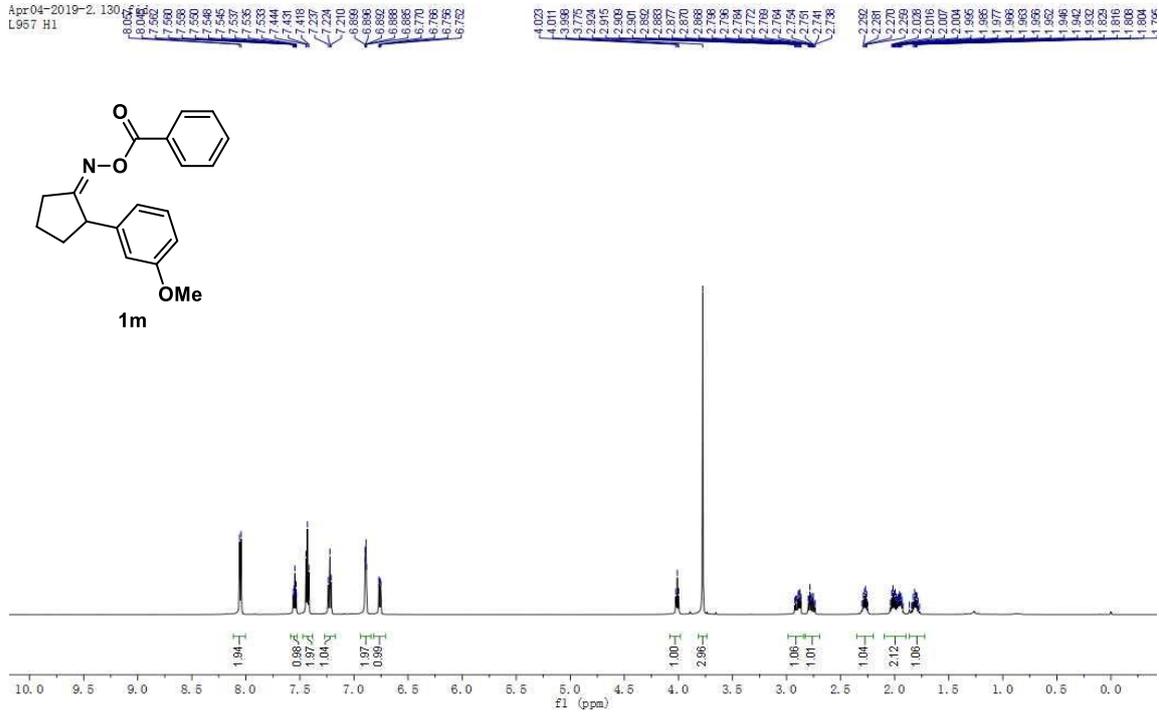
¹H NMR Spectra of 1k



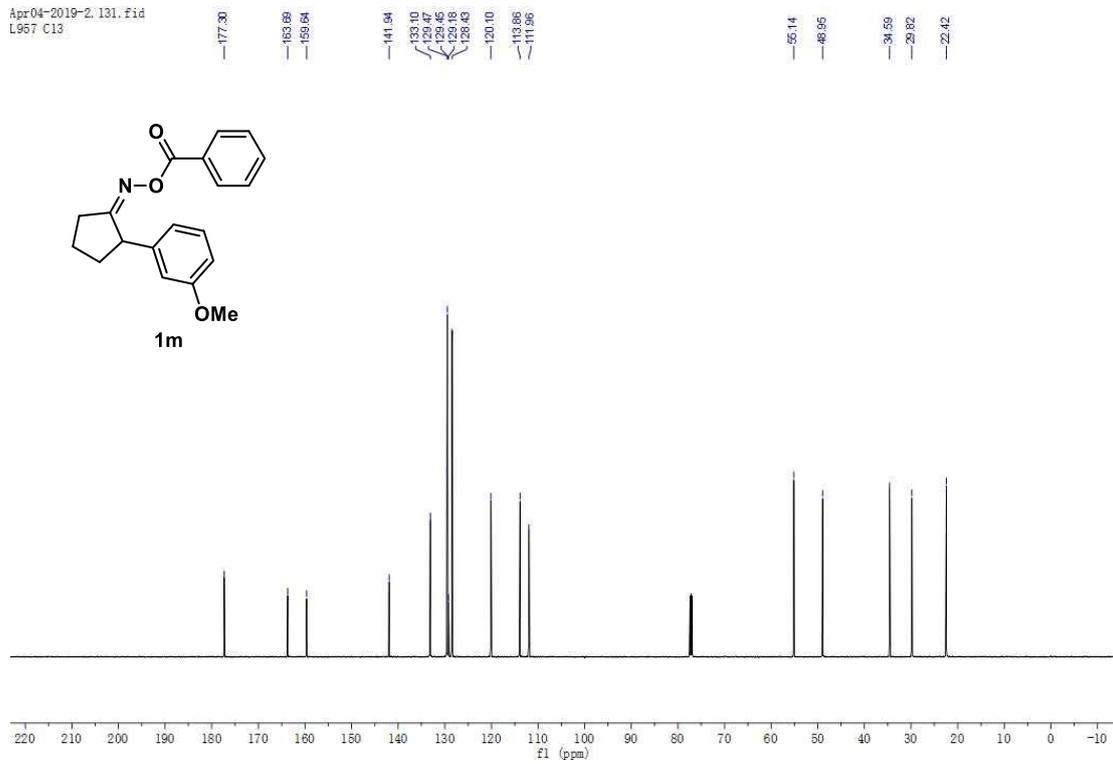
¹³C NMR Spectra of 1k



¹H NMR Spectra of **1m**



¹³C NMR Spectra of **1m**



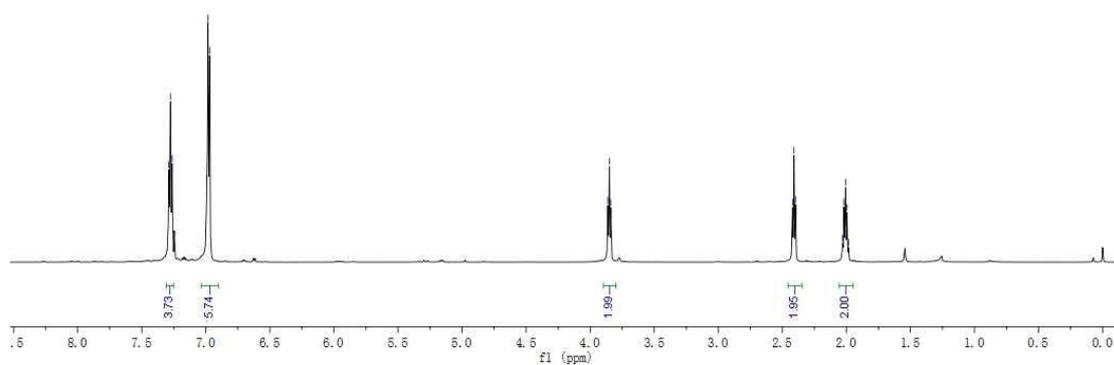
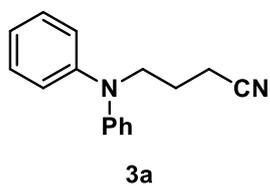
¹H NMR Spectra of **3a**

Apr20-2018-1.10.fid
Y791 H1

7.289
7.263
6.993
6.970

3.862
3.850
3.839

2.421
2.397
2.030
2.019
2.007
1.995
1.984



¹³C NMR Spectra of **3a**

Apr20-2018-1.11.fid
Y791 C13

147.62

129.62

122.08

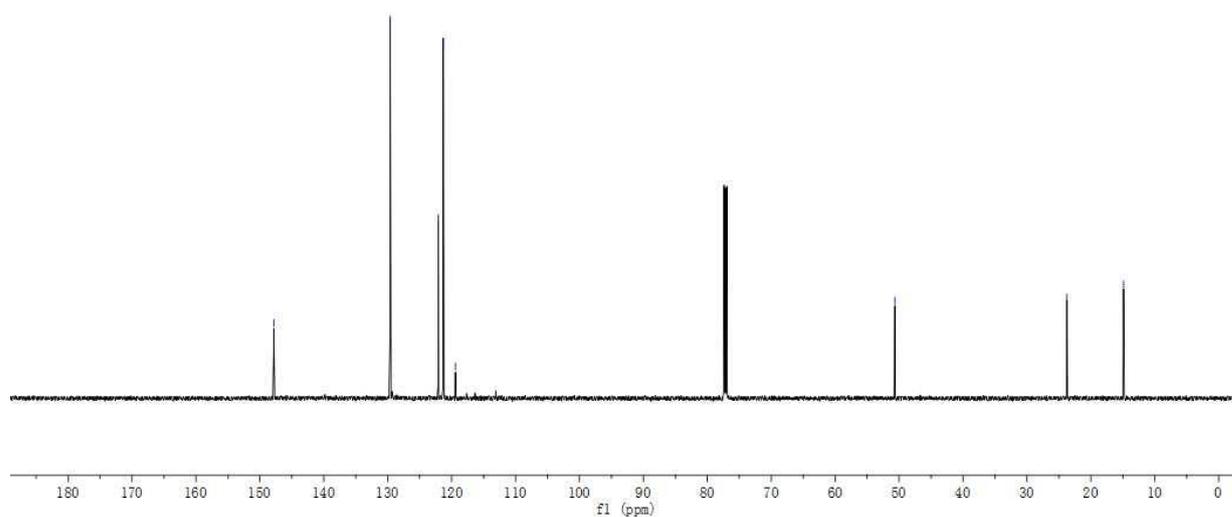
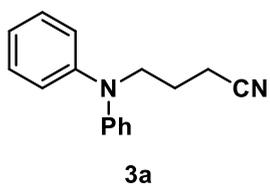
121.31

119.41

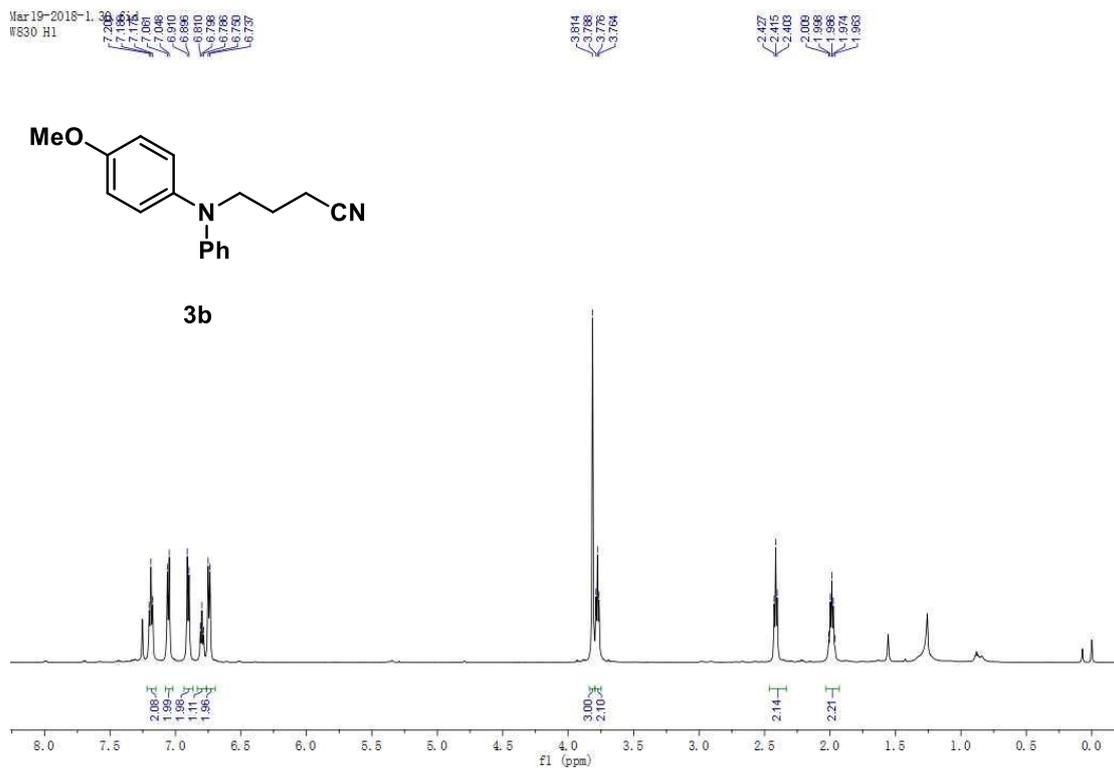
60.67

23.74

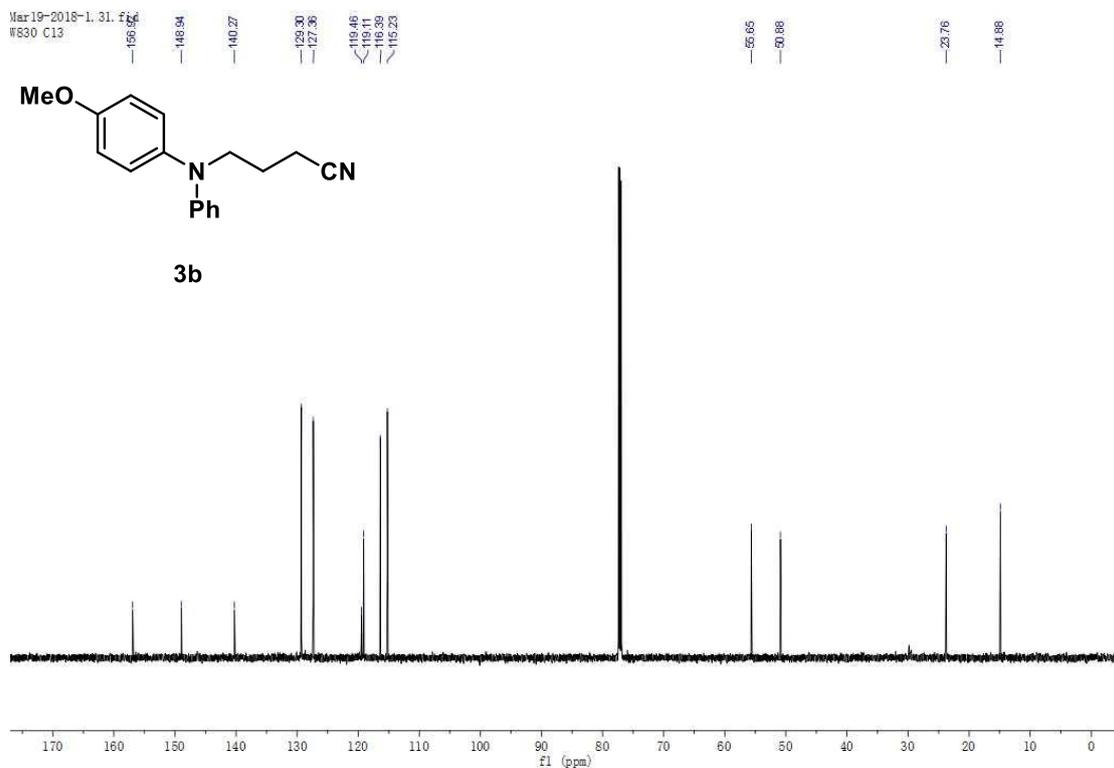
14.88



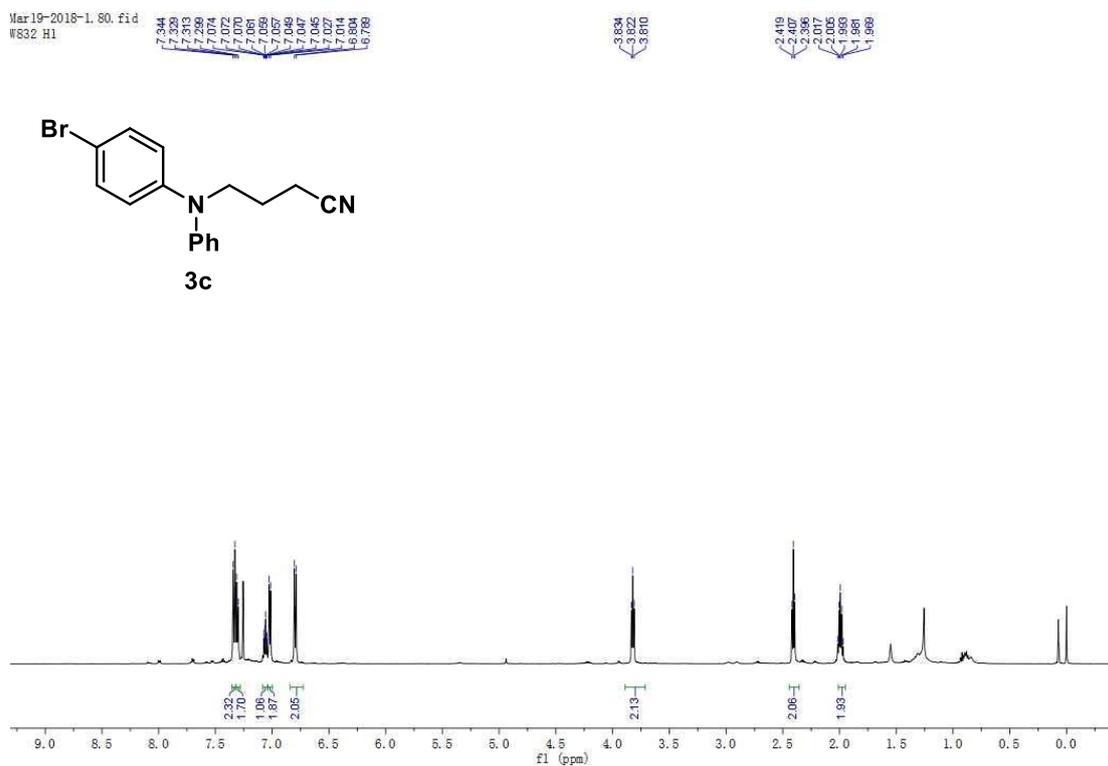
¹H NMR Spectra of **3b**



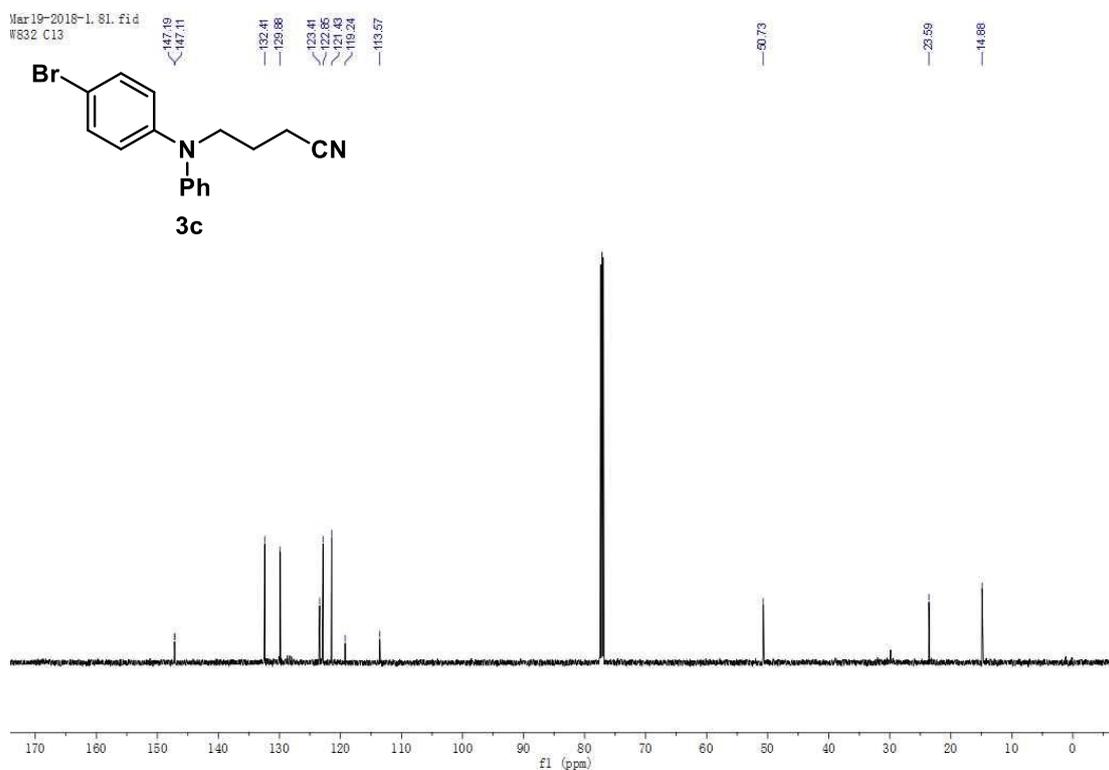
¹³C NMR Spectra of **3b**



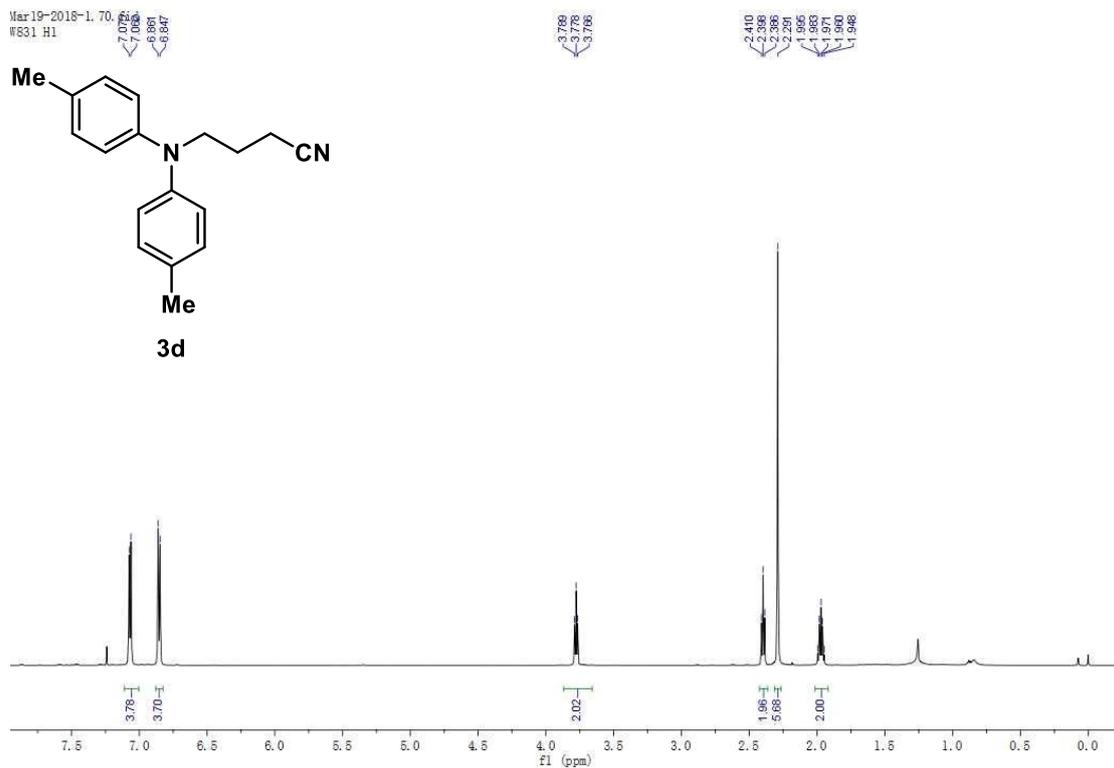
¹H NMR Spectra of 3c



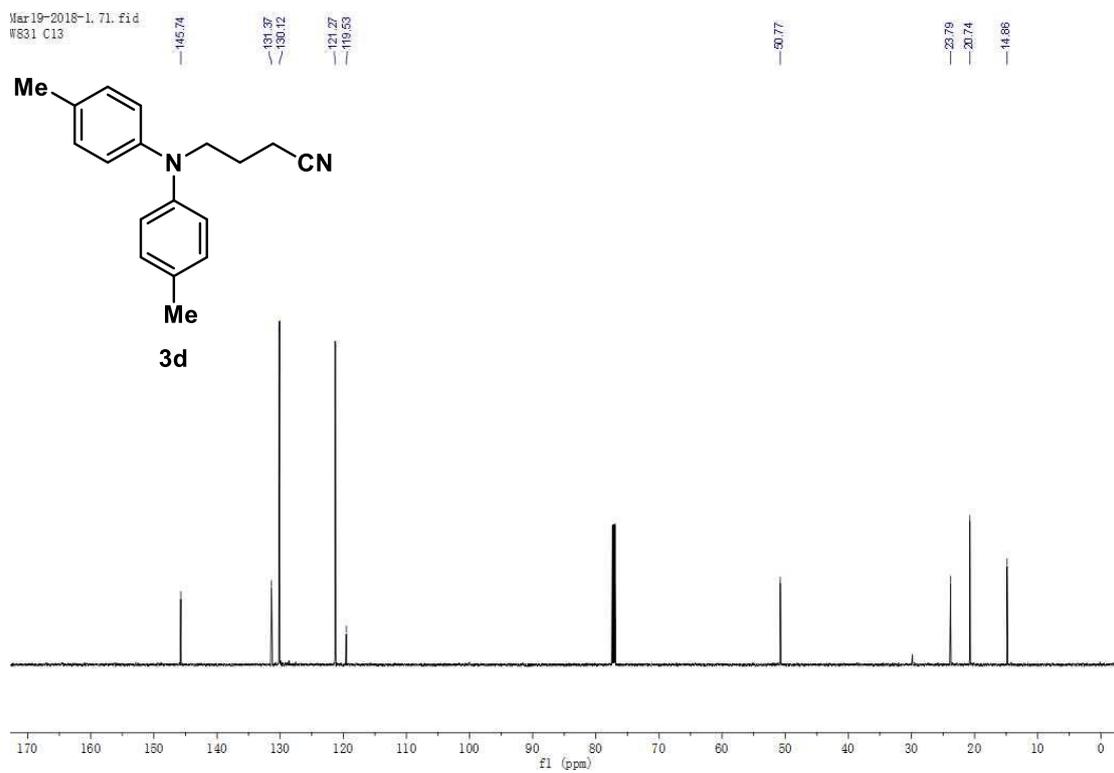
¹³C NMR Spectra of 3c



¹H NMR Spectra of 3d

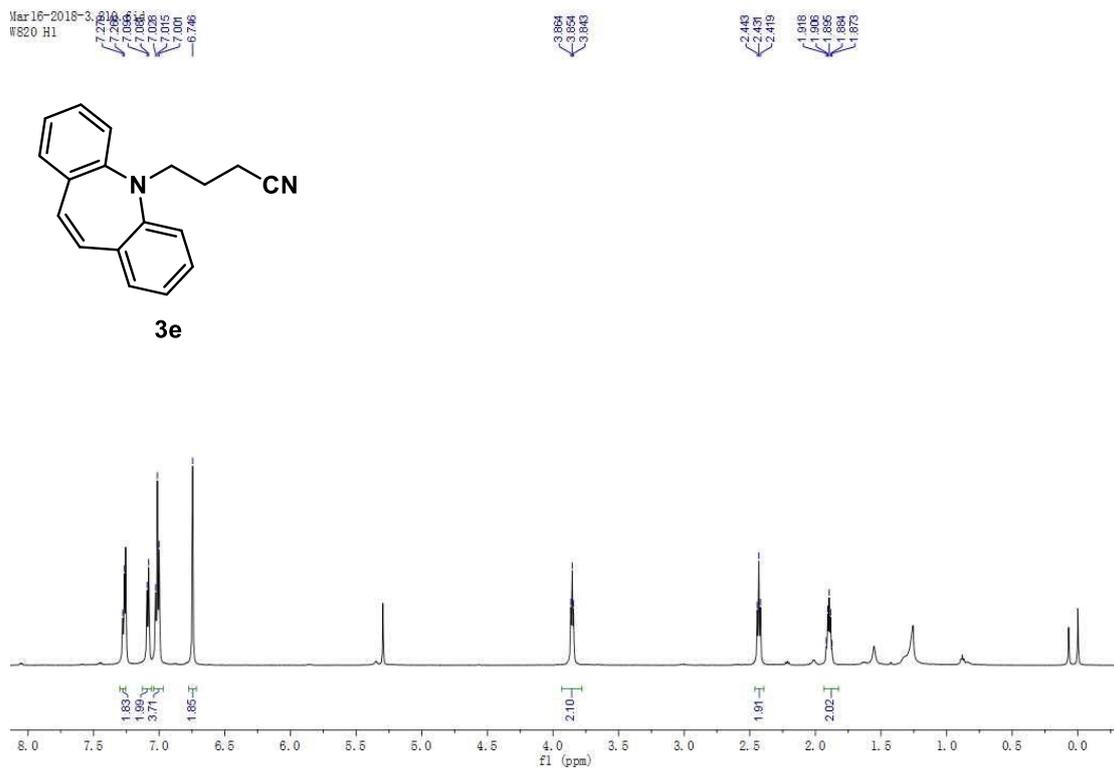
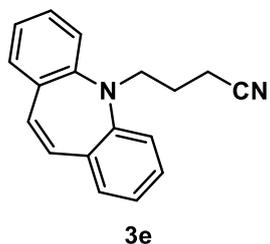


¹³C NMR Spectra of 3d



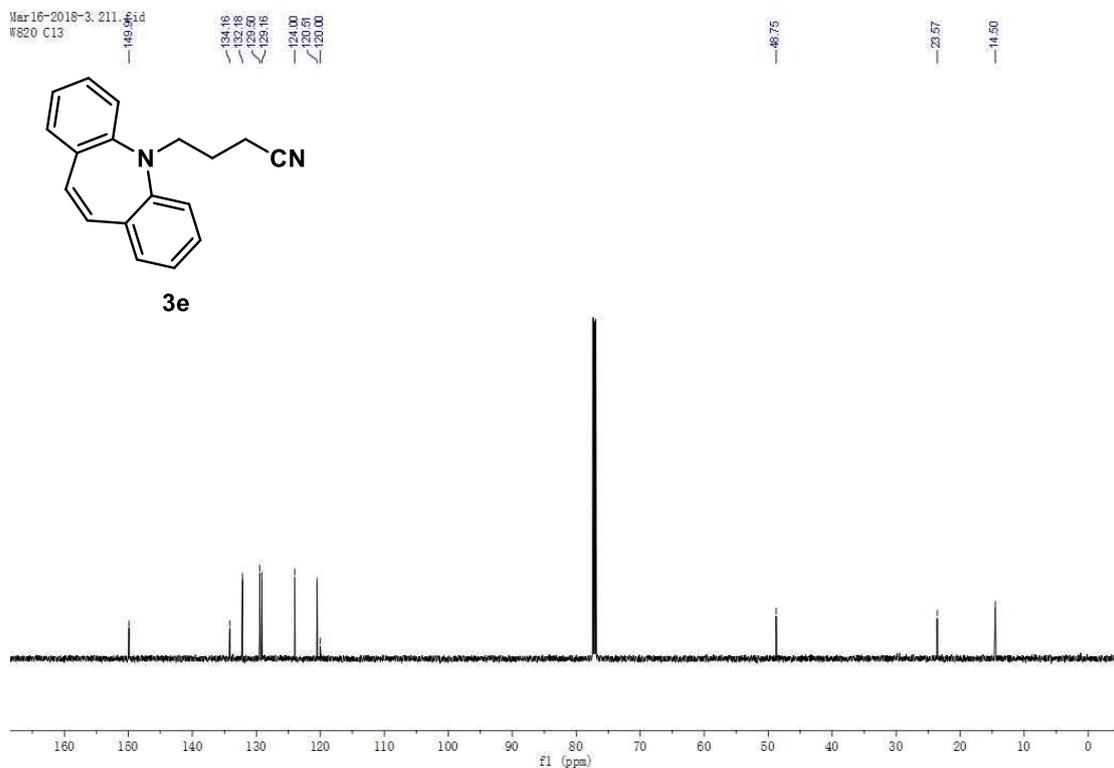
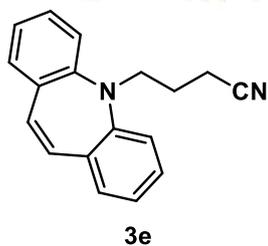
¹H NMR Spectra of 3e

Mar 16-2018-3
#820 H1



¹³C NMR Spectra of 3e

Mar 16-2018-3.211
#820 C13

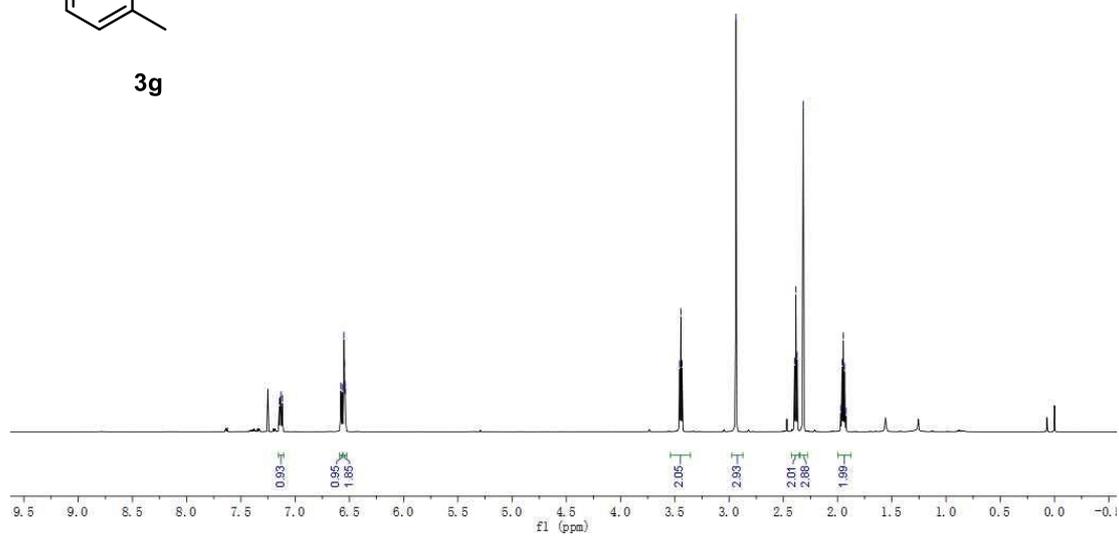
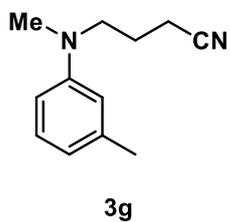


¹H NMR Spectra of 3g

Mar14-2018-1.190.fid
#697 H1

7.145
7.136
7.118
6.578
6.565
6.550
6.546
6.538

2.456
2.433
2.957
2.305
2.384
2.373
2.317
1.970
1.947
1.935
1.924

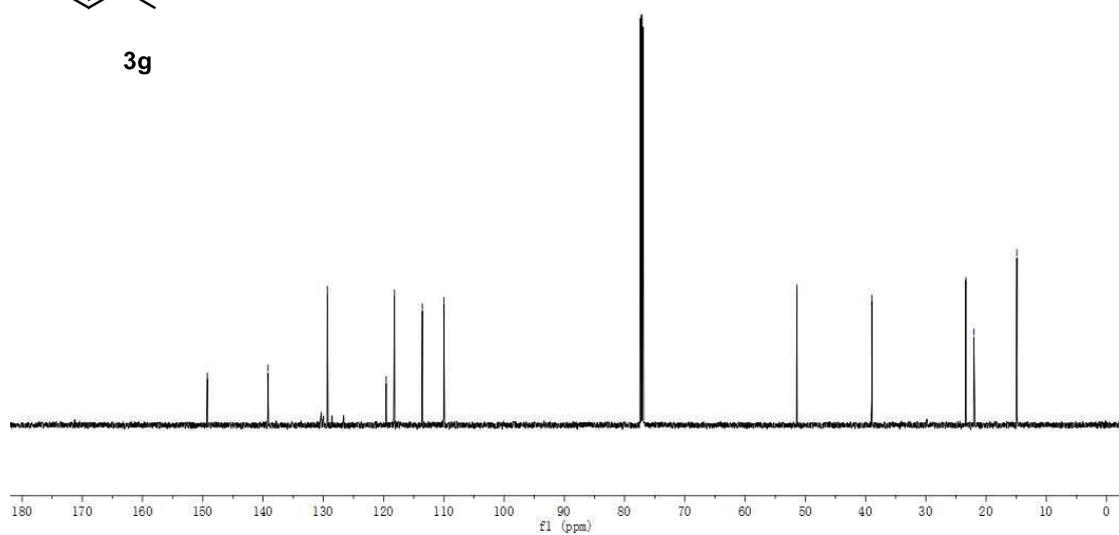
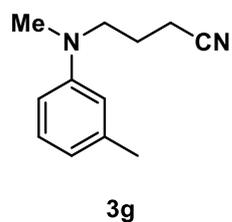


¹³C NMR Spectra of 3g

Mar14-2018-1.191.fid
#597 C13

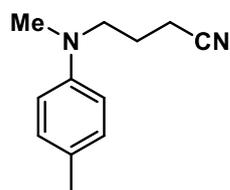
149.24
138.20
120.33
119.56
116.19
113.56
110.00

51.40
38.96
23.96
22.04
14.90

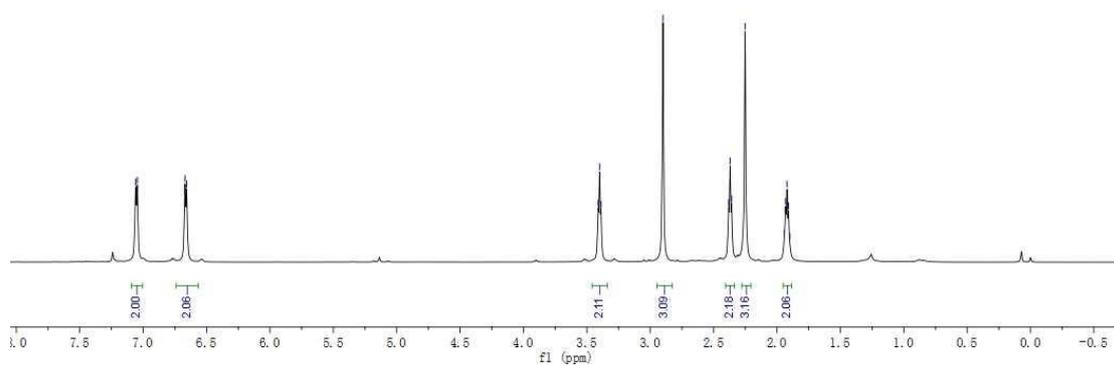


¹H NMR Spectra of 3h

Mar19-2018-1.100.
#834 H1

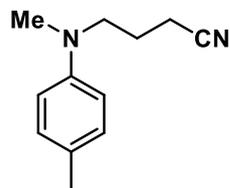


3h

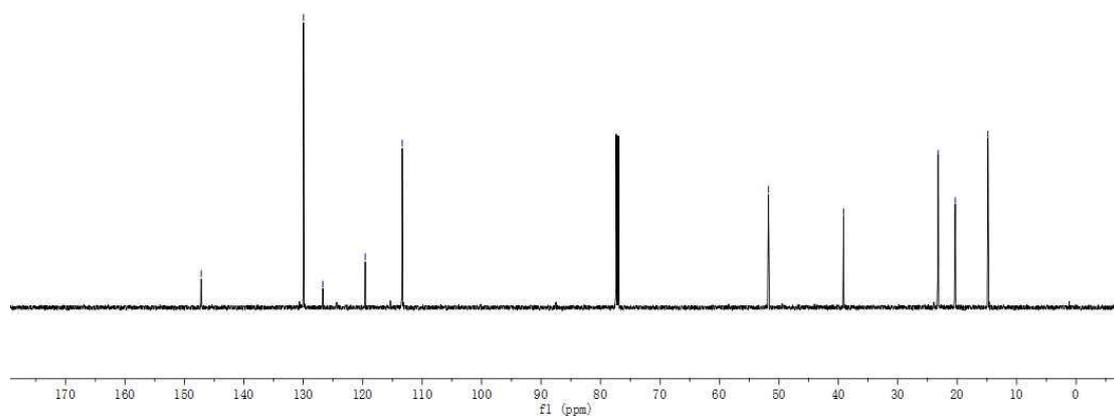


¹³C NMR Spectra of 3h

Mar19-2018-1.101.fid
#834 C13



3h



¹H NMR Spectra of **3i**

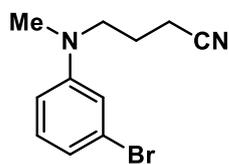
Nov14-2018-1. 200. fid
H632 H1

7.087
7.074
7.060
6.840
6.827
6.810
6.632
6.627
6.618
6.603

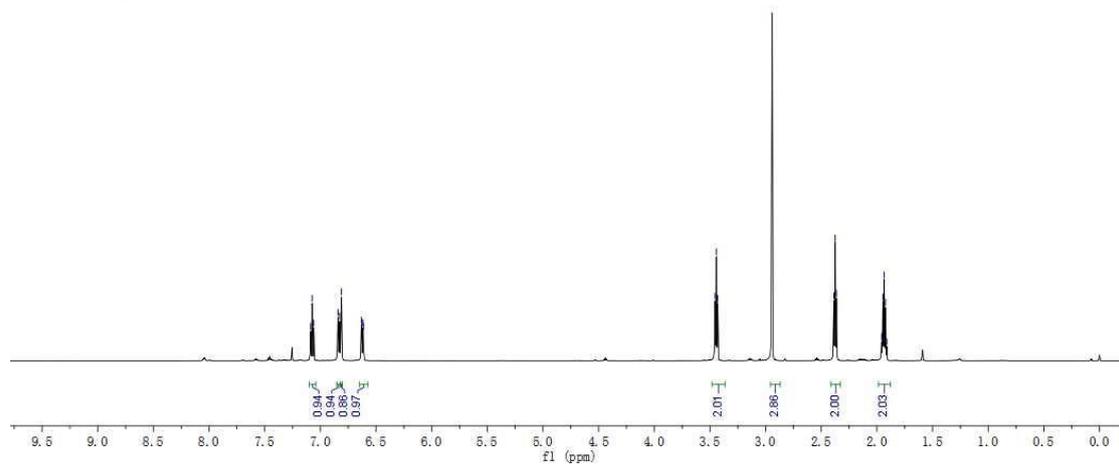
3.454
3.443
3.431

2.941

2.387
2.375
2.363
1.968
1.946
1.923
1.911



3i



¹³C NMR Spectra of **3i**

Nov14-2018-1. 201. fid
H632 C13

150.17

130.03

123.70

119.76

115.21

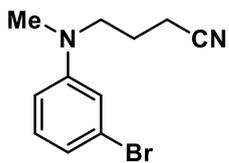
111.05

51.11

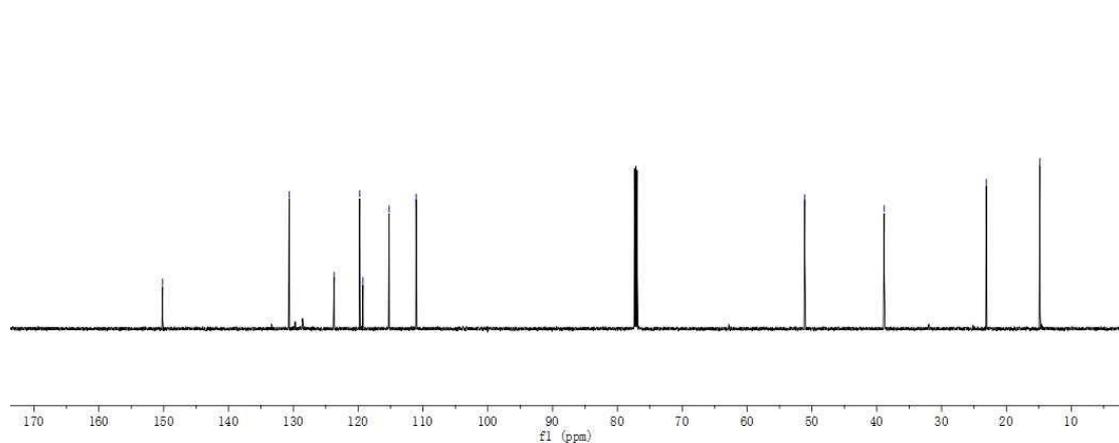
38.86

22.11

14.84



3i



¹H NMR Spectra of 3j

Nov16-2018-3.180.fid
H803 H1

7.188
7.188

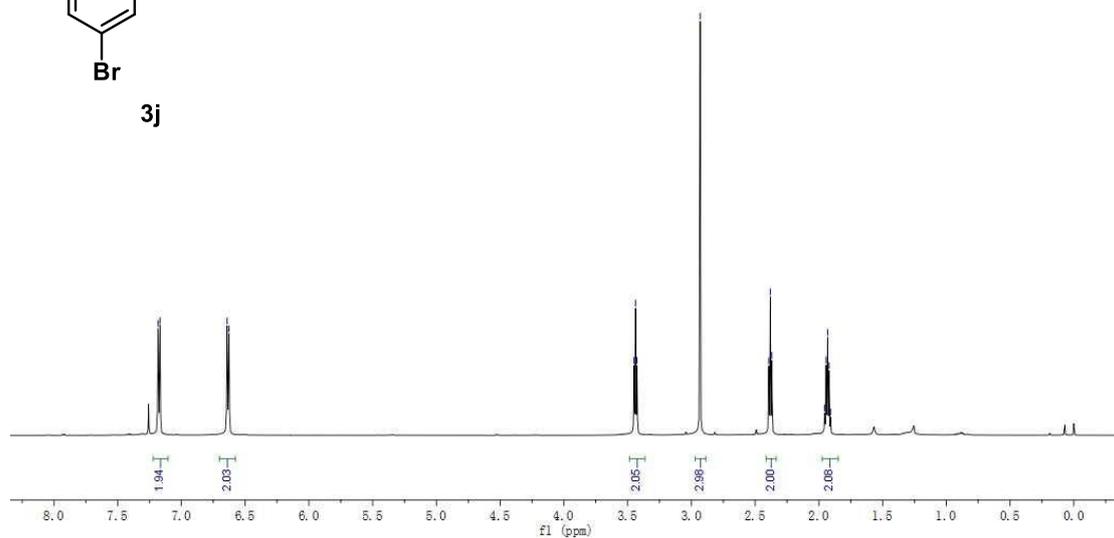
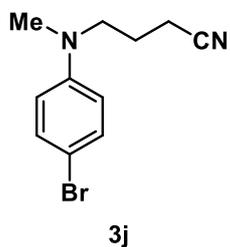
6.641
6.627

3.430
3.438
3.427

2.991

2.363
2.381
2.369

1.955
1.943
1.932
1.921
1.908



¹³C NMR Spectra of 3j

Nov16-2018-3.181.fid
H803 C13

147.68

128.24

122.06

119.35

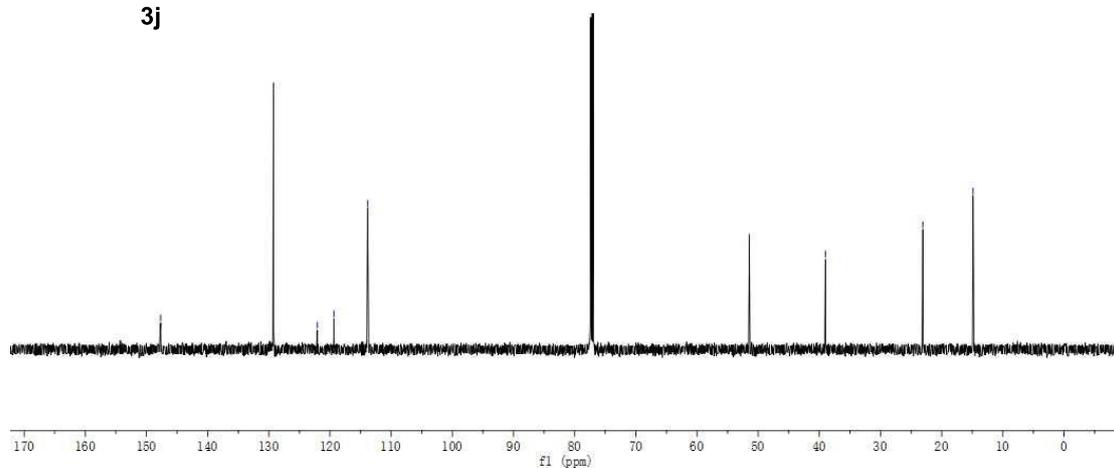
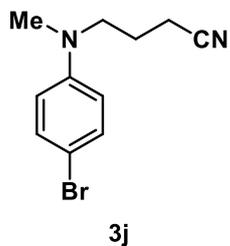
113.85

51.45

39.01

22.09

14.87



¹H NMR Spectra of 3k

Nov16-2018-3.190.fid
H804 H1

7.348
7.308

6.564
6.579

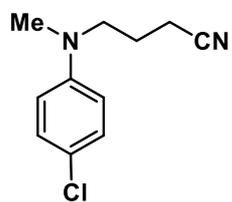
3.423
3.411
3.410

2.931

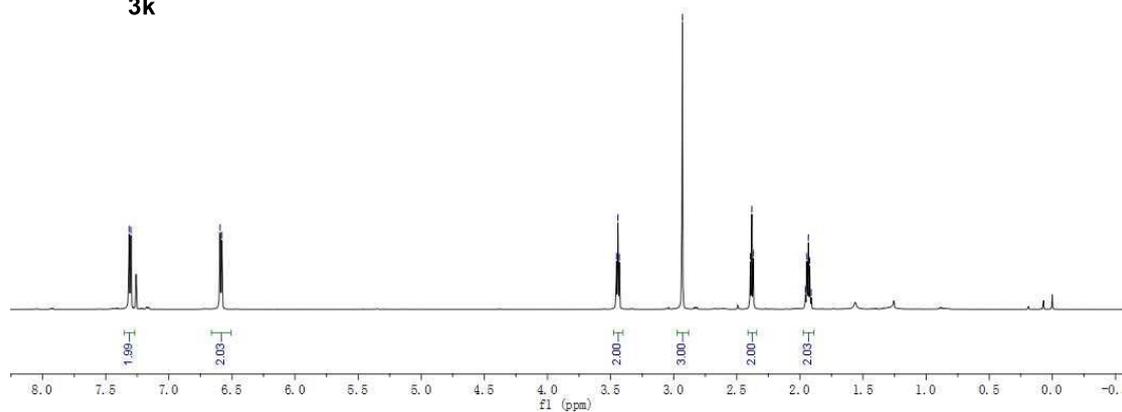
2.383
2.381

2.369

1.945
1.922
1.910



3k



¹³C NMR Spectra of 3k

Nov16-2018-3.191.fid
H804 C13

148.05

132.14

119.32

114.29

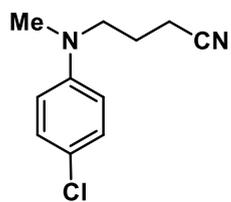
109.15

51.54

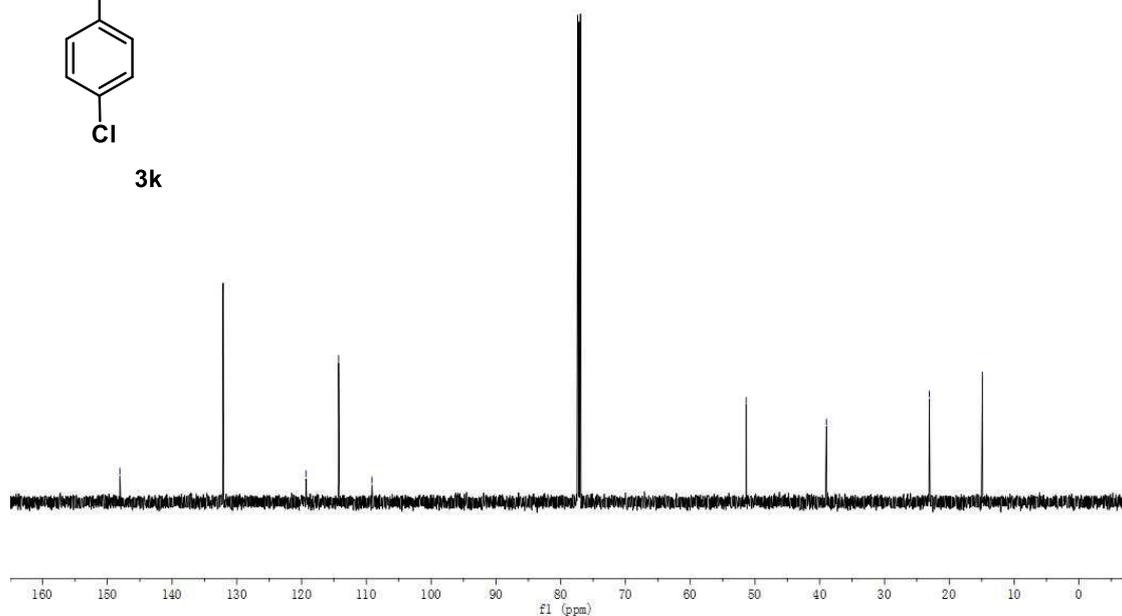
38.97

23.08

14.88



3k



¹H NMR Spectra of **3I**

Mar07-2019-2.20.fid
K763 H1

6.8632
6.8637
6.754
6.739

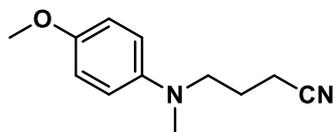
3.765

3.352
3.341
3.330

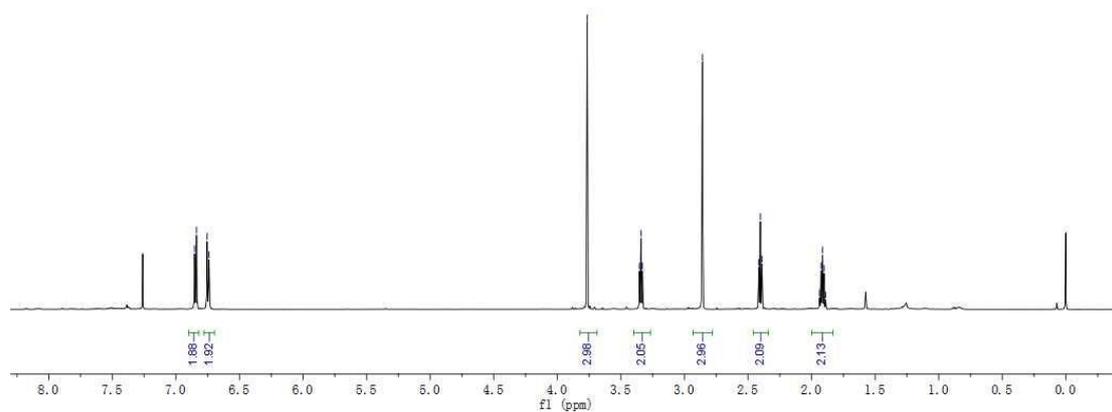
2.898

2.414
2.403
2.390

1.936
1.925
1.913
1.901
1.890



3I



¹³C NMR Spectra of **3I**

Mar07-2019-2.21.fid
K763 C13

162.86
144.25

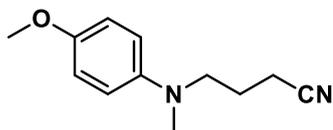
119.68
115.63
114.96

55.88
52.87

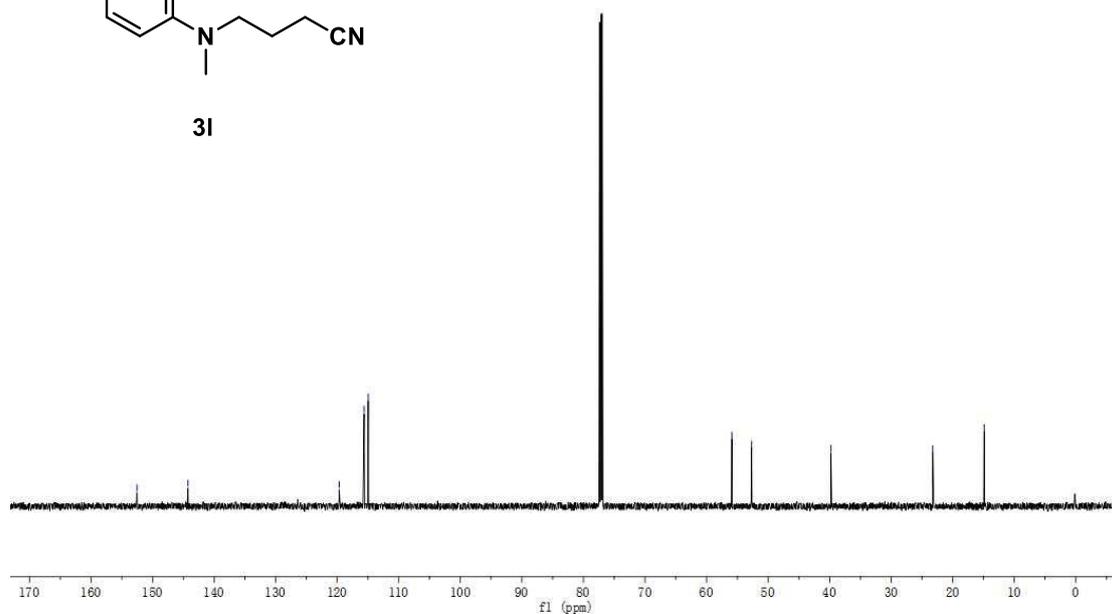
38.78

23.24

14.86



3I



¹H NMR Spectra of **3m**

Mar16-2018-1.10.fid
#744 H1

7.240
7.228
7.218

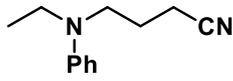
6.709
6.696

3.416
3.404
3.393
3.382
3.370
3.358

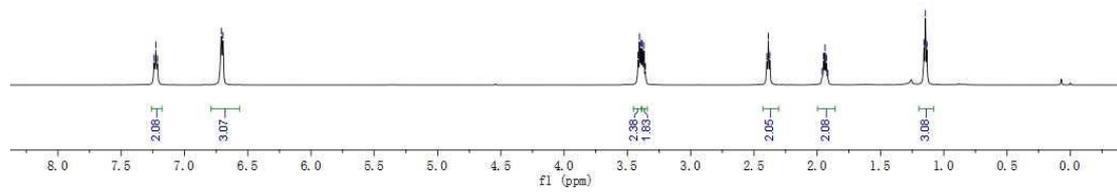
2.388
2.386
2.375

1.962
1.950
1.937
1.915

1.157
1.145
1.134



3m



¹³C NMR Spectra of **3m**

Mar16-2018-1.11.fid
#744 C13

147.64

129.51

119.57
116.82
112.88

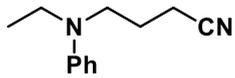
48.84

46.93

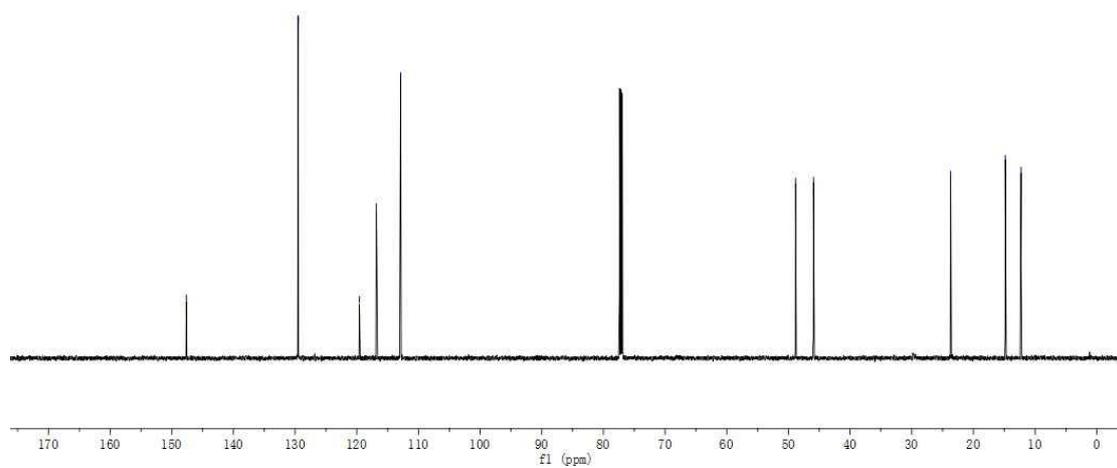
23.89

14.83

12.27



3m

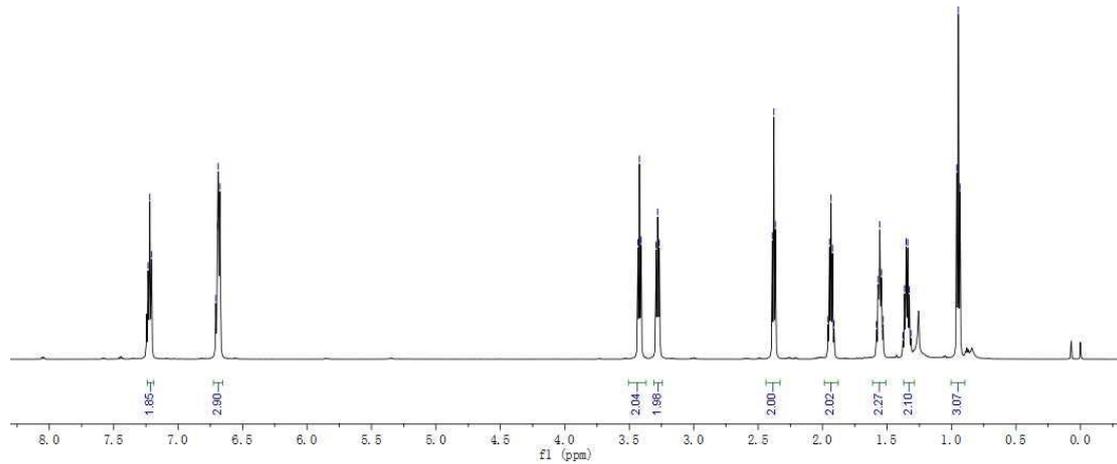
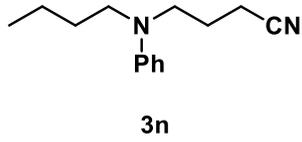


¹H NMR Spectra of **3n**

Mar15-2018-1.10.f1d
#667 H1

3.433
3.421
3.252
3.200
3.207

2.900
2.378
2.367
1.968
1.956
1.945
1.923
1.911
1.562
1.550
1.539
1.544
1.531
1.377
1.365
1.353
1.340
1.327
1.315
0.969
0.957
0.945



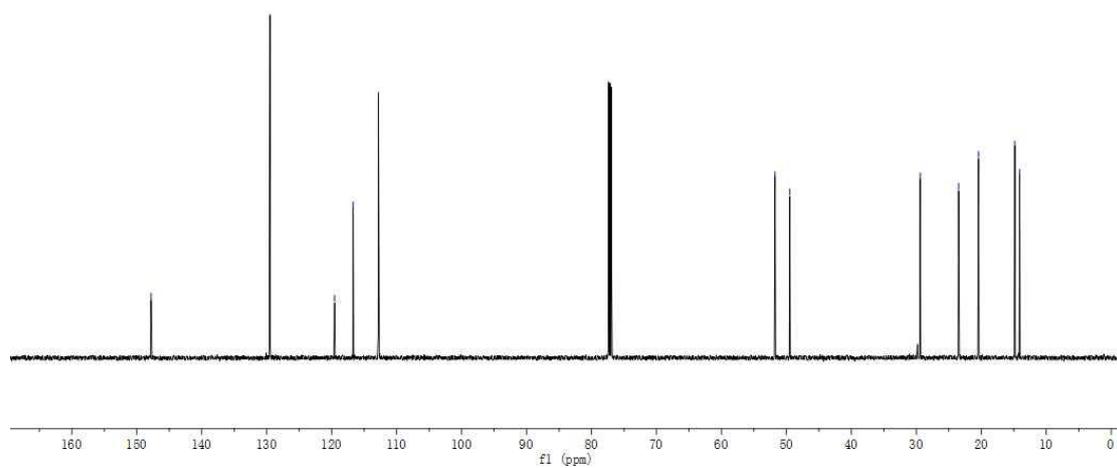
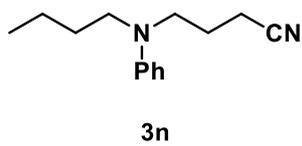
¹³C NMR Spectra of **3n**

Mar15-2018-1.11.f1d
#667 C13

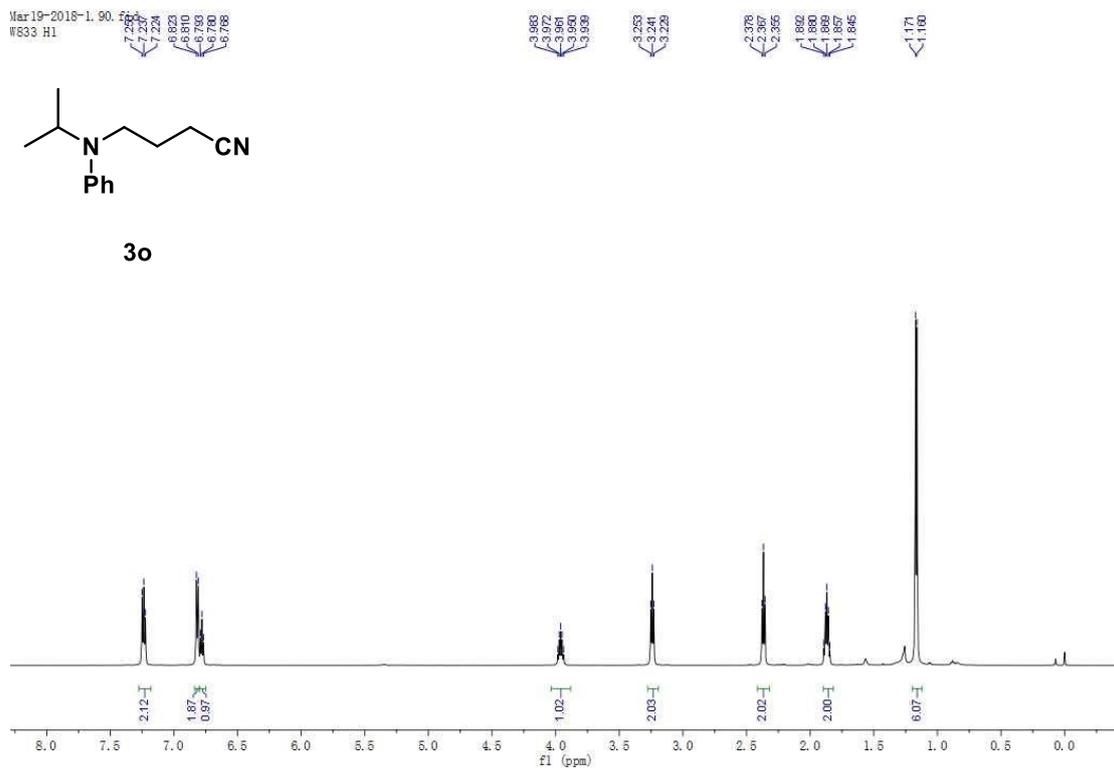
147.80
129.49
119.55
116.69
112.80

51.75
48.17

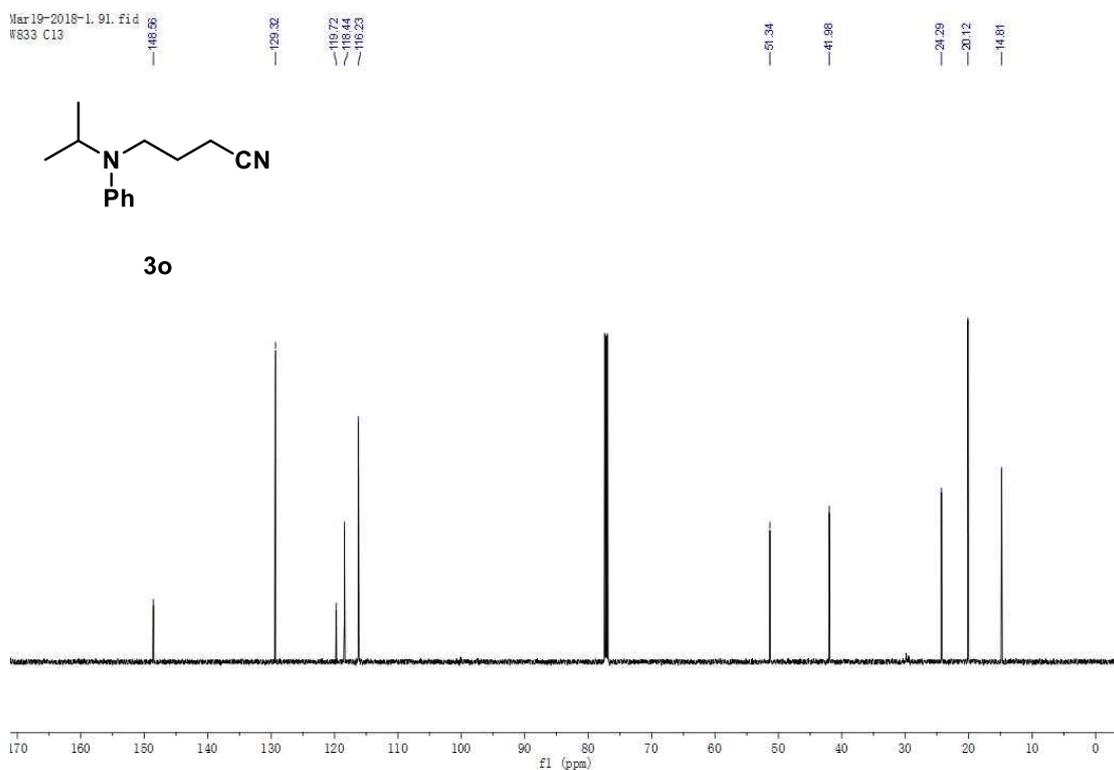
29.39
23.48
20.42
14.84
14.09



¹H NMR Spectra of **3o**



¹³C NMR Spectra of **3o**

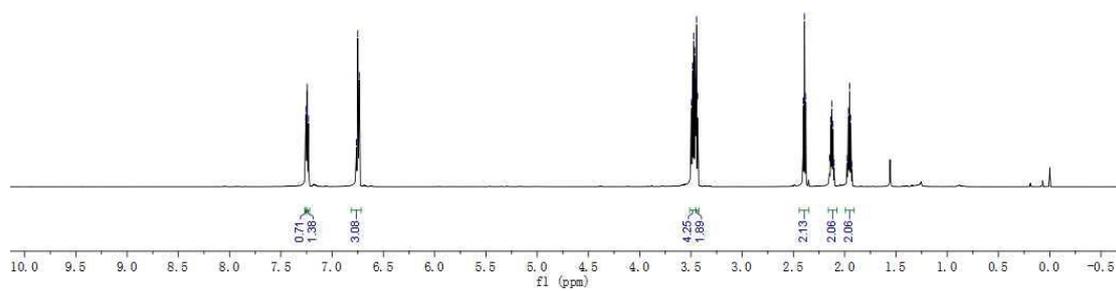
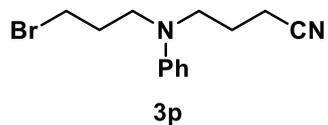


¹H NMR Spectra of 3p

Nov19-2018-1.190.fid
HS36 H1

7.288
7.264
7.231
7.201
6.784
6.750
6.735

3.493
3.484
3.473
3.452
3.450
3.446
3.435
2.404
2.383
2.368
2.356
2.137
2.125
2.114
2.104
1.994
1.953
1.941
1.929

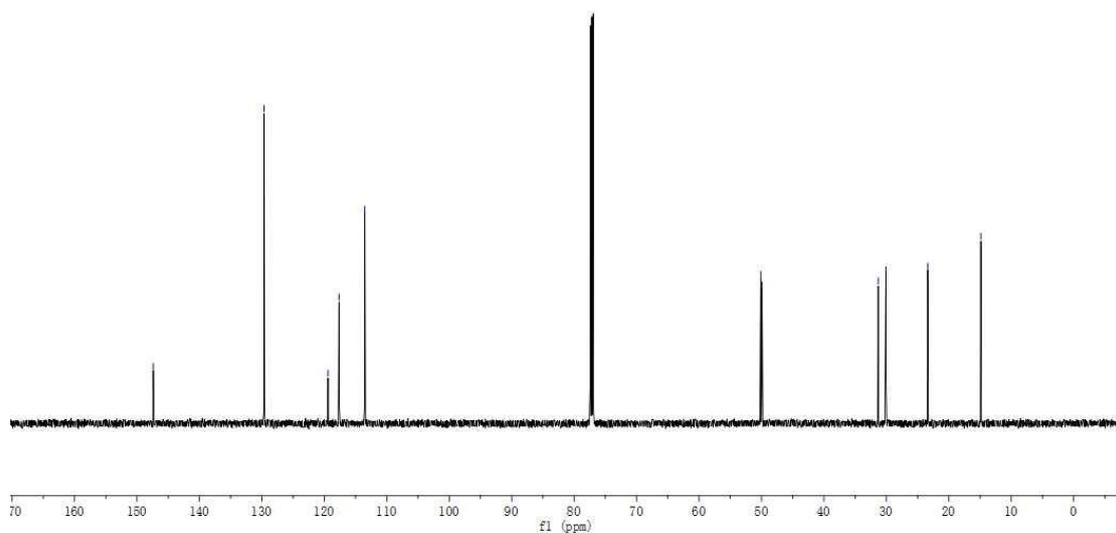
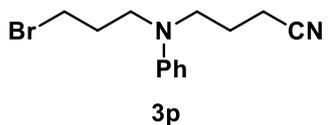


¹³C NMR Spectra of 3p

Nov19-2018-1.191.fid
HS36 C13

147.36
120.64
119.41
115.52
113.52

50.10
49.82
31.30
30.08
23.36
14.88



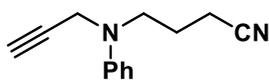
¹H NMR Spectra of 3r

Apr20-2018-1. 20. fid
Y792 H1

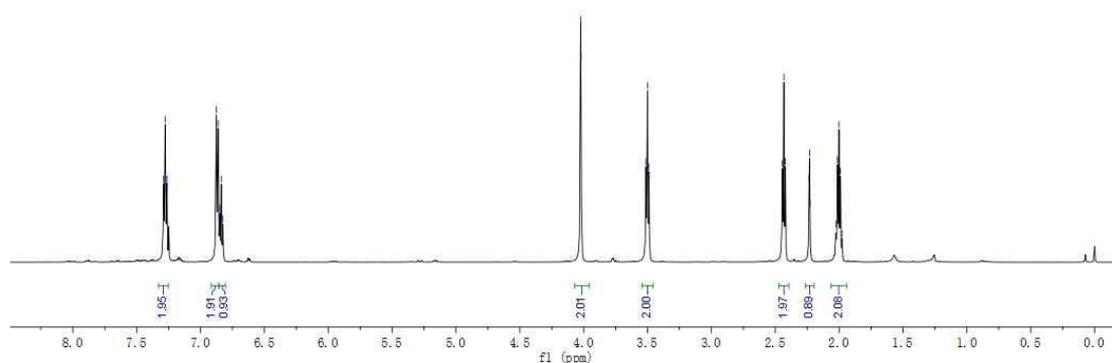
7.289
7.277
6.876
6.863
6.852
6.825

4.024
4.020
3.512
3.502
3.489

2.444
2.433
2.422
2.256
2.231
2.228
2.024
2.013
1.990
1.978



3r



¹³C NMR Spectra of 3r

Apr20-2018-1. 21. fid
Y792 C13

147.76

129.47

119.52
119.04
114.76

79.75

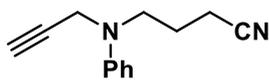
72.67

46.84

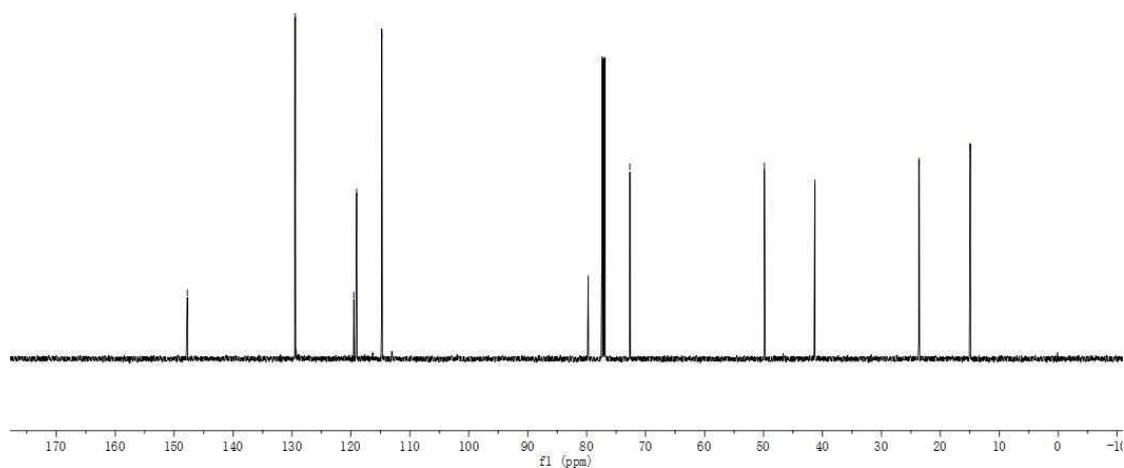
41.29

23.81

14.93



3r

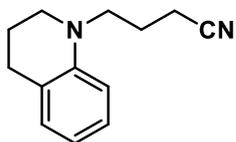


¹H NMR Spectra of 3s

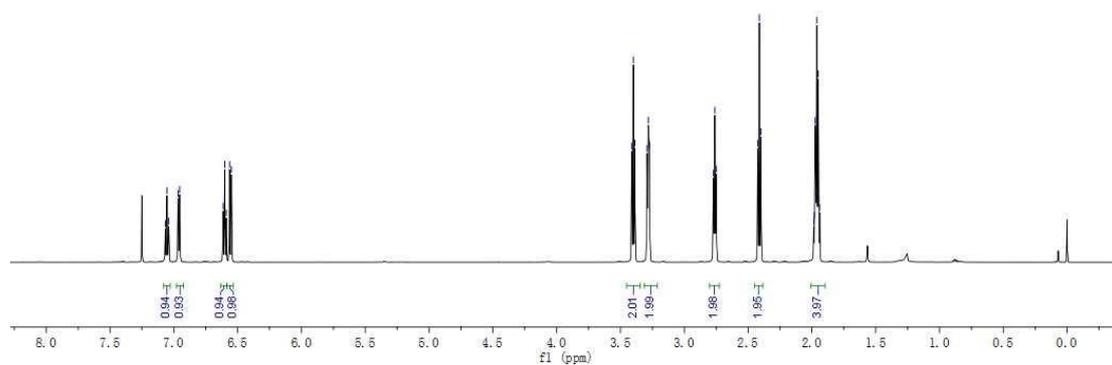
Jan17-2019-1.80.fid
K145 H1

7.086
7.054
6.996
6.964
6.813
6.801
6.582
6.549

3.411
3.389
3.366
3.292
3.262
3.273
2.772
2.761
2.750
2.423
2.400
1.988
1.980
1.974
1.962
1.959
1.951



3s



¹³C NMR Spectra of 3s

Jan17-2019-1.81.fid
K145 C13

144.99

128.54

127.31

122.85

119.59

116.43

110.64

50.15

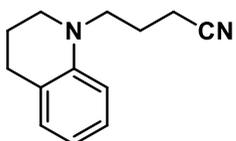
50.12

28.13

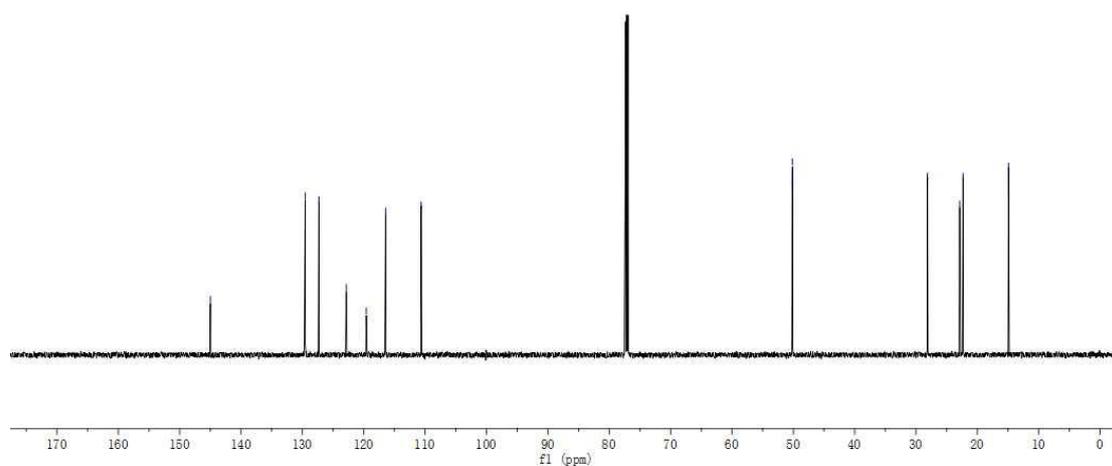
22.89

22.54

14.92



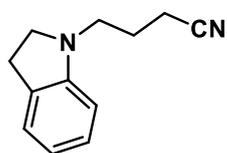
3s



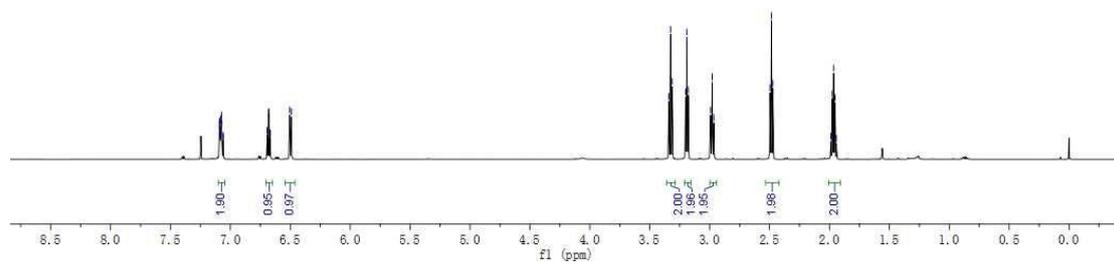
¹H NMR Spectra of 3t

Jan20-2019-1.250
K286 H1

3.340
3.326
3.201
3.190
3.179
2.963
2.965
2.486
2.473
1.988
1.977
1.965
1.954
1.942



3t



¹³C NMR Spectra of 3t

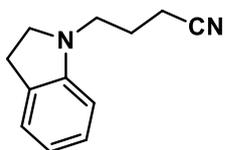
Jan20-2019-2.250.fid
K316 C13

152.36
129.99
127.54
124.88
118.63
118.25
107.10

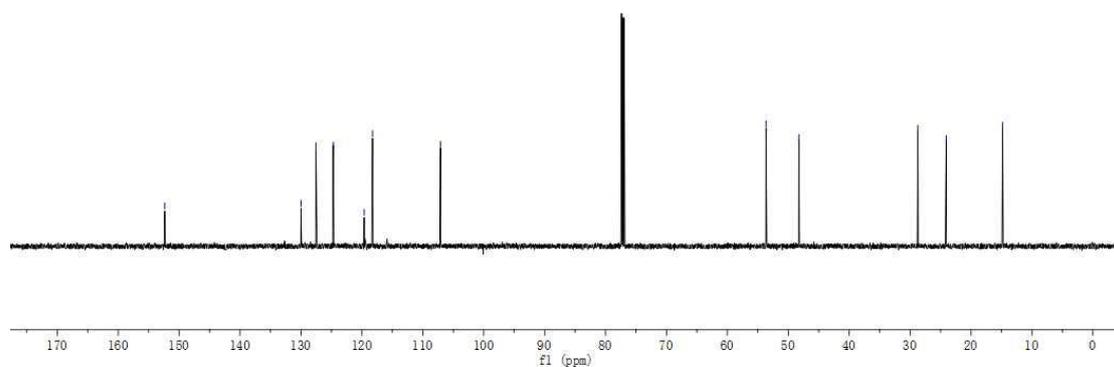
53.86
48.26

28.72
24.03

14.81



3t



¹H NMR Spectra of **3u**

Nov29-2018-1.10.fid
1376 H1

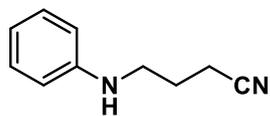
7.203
7.177
6.747
6.735
6.723
6.610

3.712

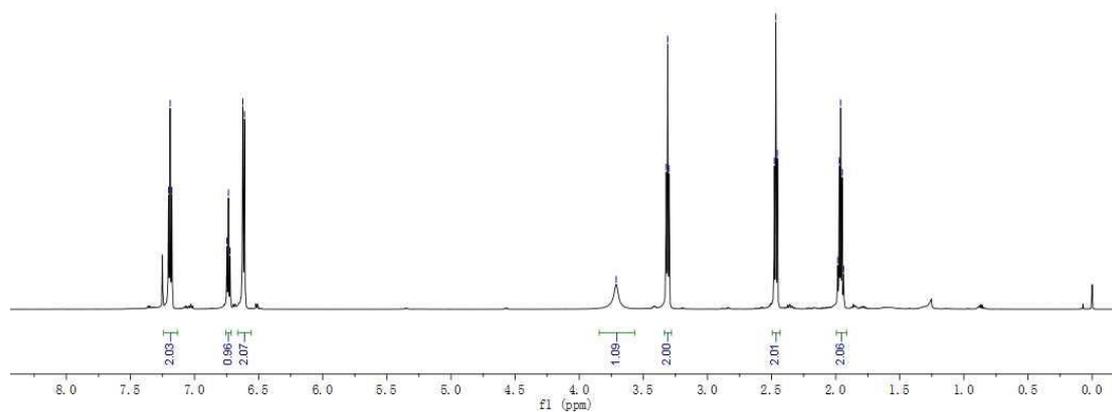
3.322
3.311
3.300

2.429
2.455

1.984
1.972
1.960
1.948
1.938



3u



¹³C NMR Spectra of **3u**

Nov29-2018-1.11.fid
1376 C13

147.62

129.52

116.48

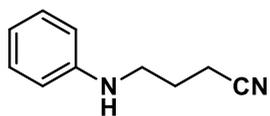
116.03

112.95

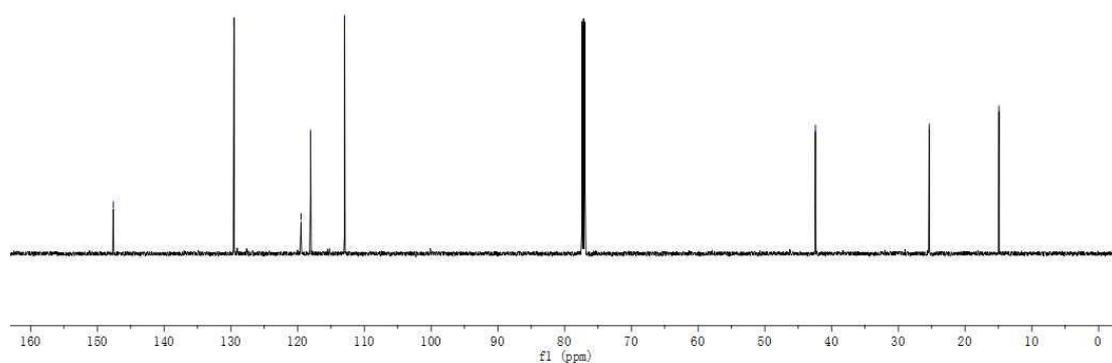
42.42

25.37

14.93

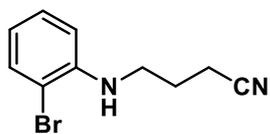


3u

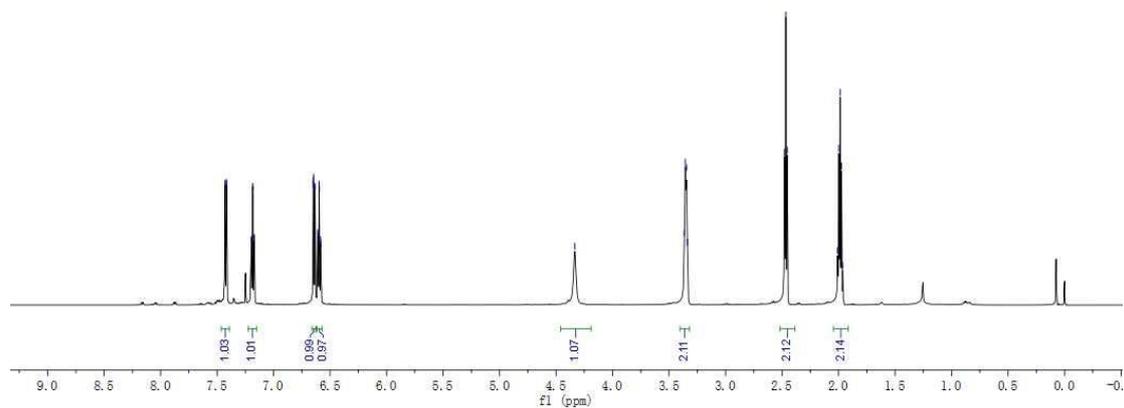


¹H NMR Spectra of 3v

Dec26-2018-3.10.fid
1619 H1

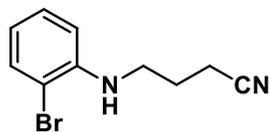


3v

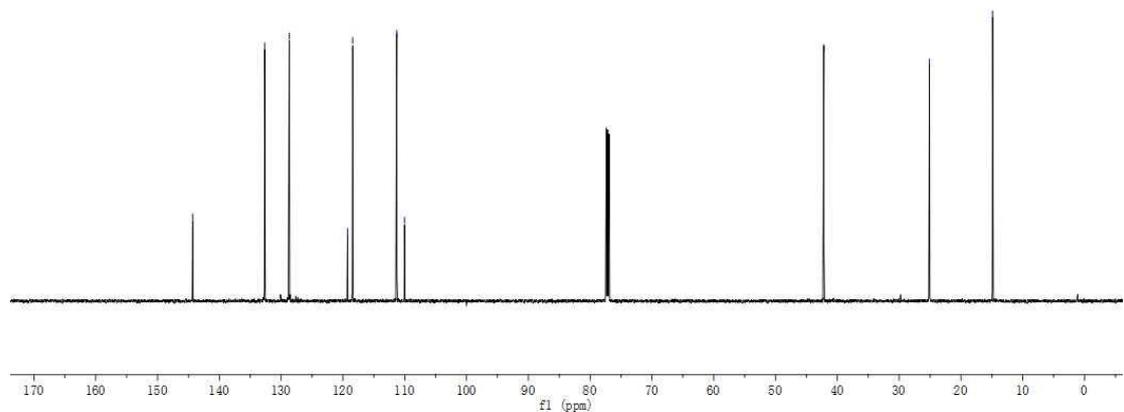


¹³C NMR Spectra of 3v

Dec26-2018-3.11.fid
1619 C13



3v



¹H NMR Spectra of 3w

Dec25-2018-4.210.fid
J462 H1

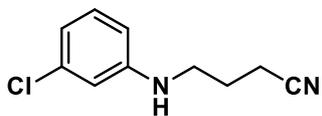
7.084
7.080
6.895
6.662
6.679
6.574
6.570
6.484
6.481
6.471
6.467

3.846

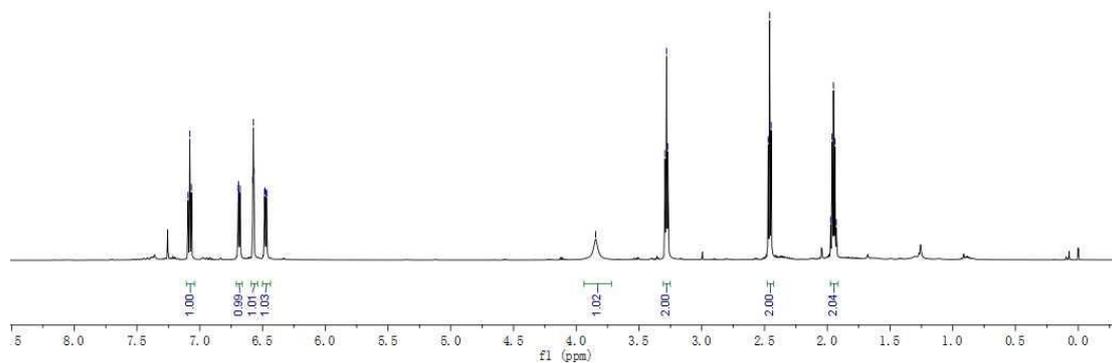
2.262
2.261
2.270

2.471
2.459
2.447

1.973
1.962
1.950
1.938
1.927



3w



¹³C NMR Spectra of 3w

Dec25-2018-4.211.fid
J462 C13

148.764

136.21

130.46

119.34

117.81

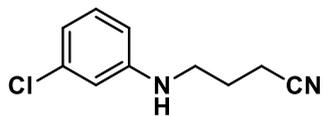
112.52

111.27

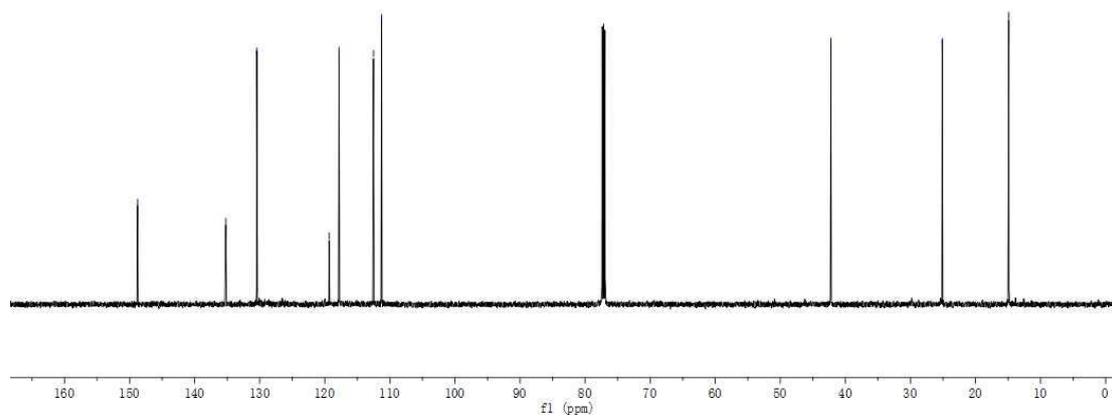
42.22

25.11

14.90



3w



¹H NMR Spectra of 3x

Jan10-2019-1. 240. fid
J944 H1

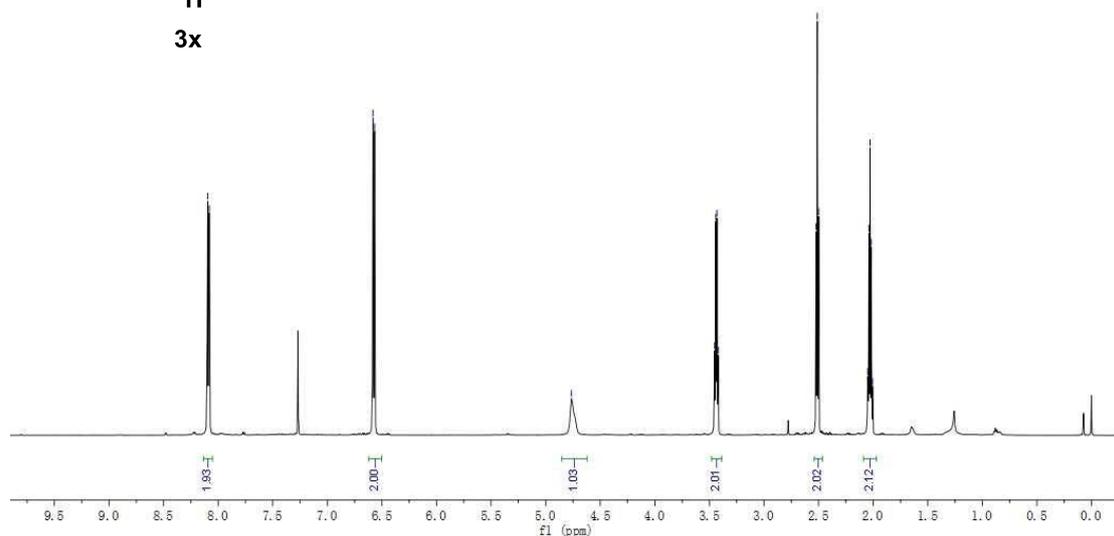
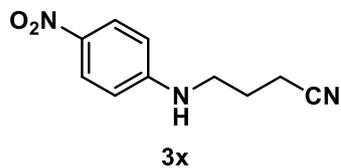
8.086
8.081

6.562
6.567

4.764

3.463
3.442
3.431
3.420

2.523
2.511
2.489
2.061
2.038
2.017
2.005



¹³C NMR Spectra of 3x

Jan10-2019-1. 241. fid
J944 C13

152.94

138.55

126.57

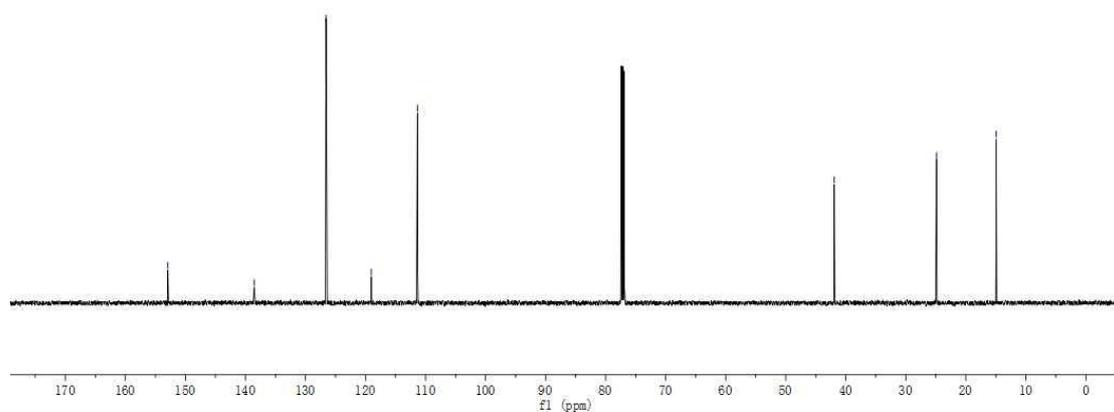
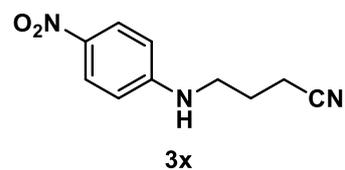
119.04

111.35

41.92

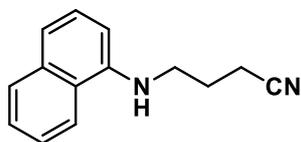
24.89

14.96

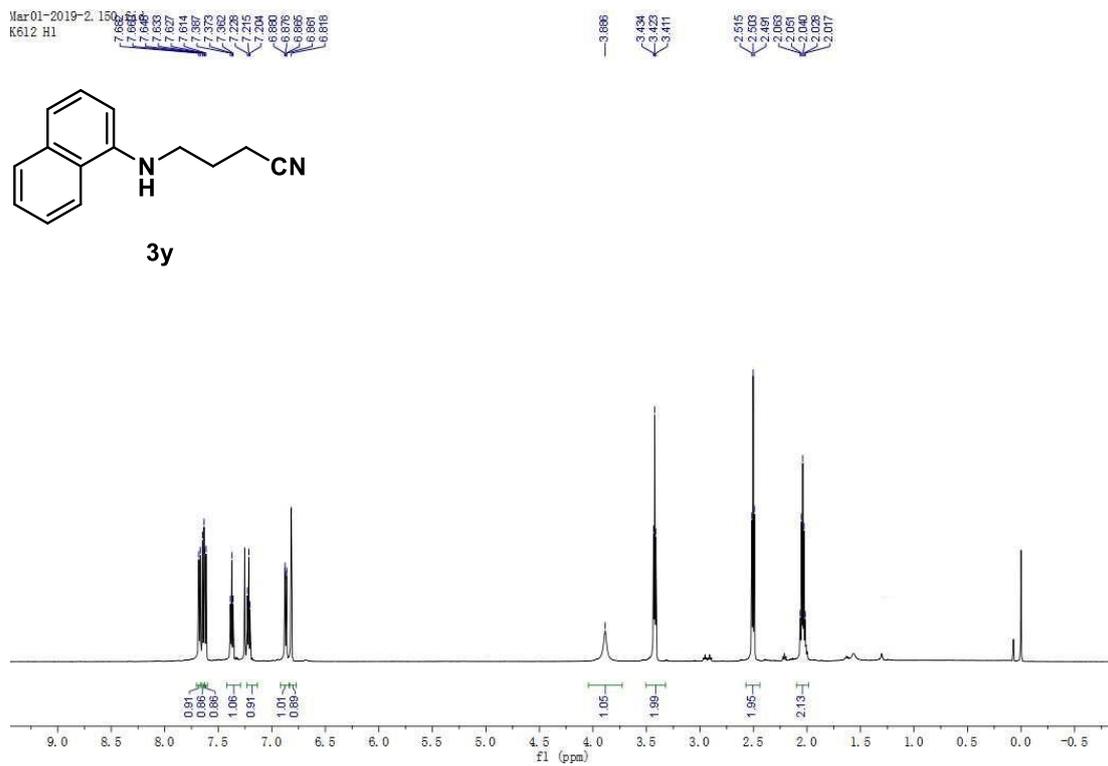


¹H NMR Spectra of 3y

Mar01-2019-2.150
K612 H1

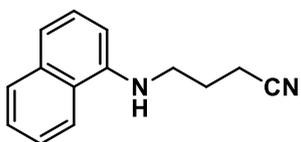


3y

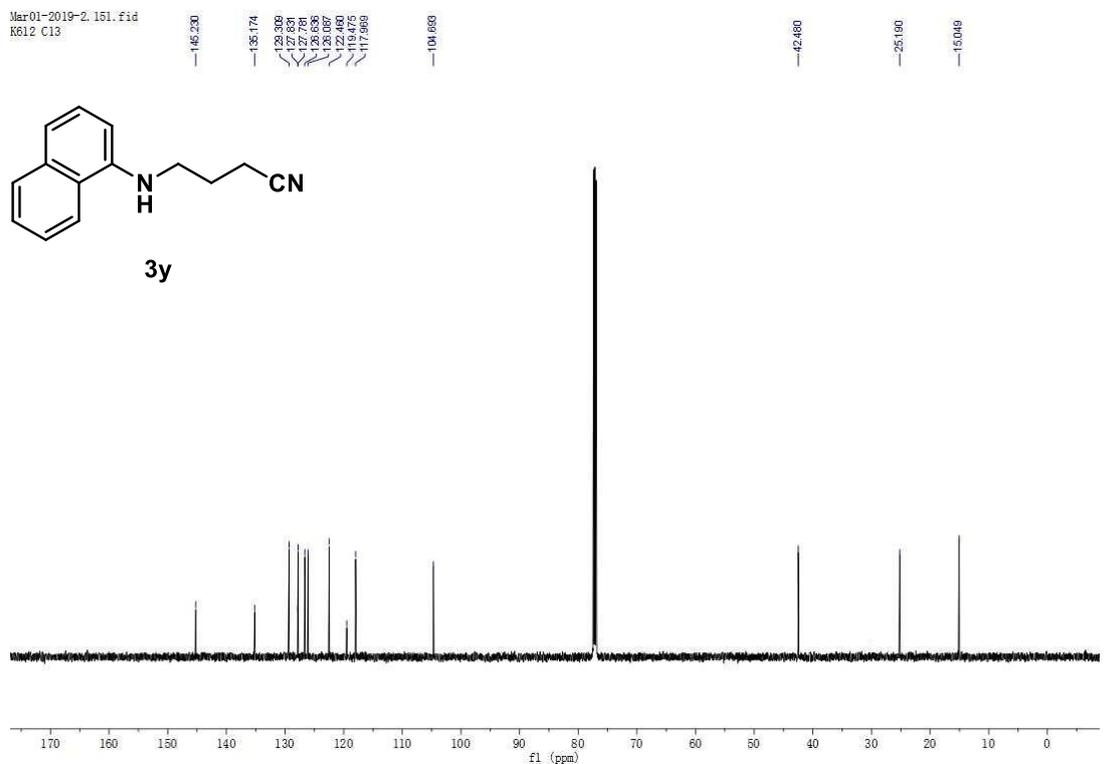


¹³C NMR Spectra of 3y

Mar01-2019-2.151.Fid
K612 C13



3y



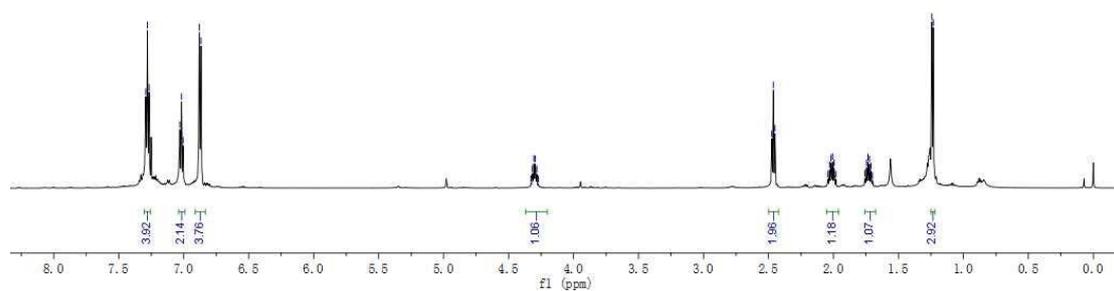
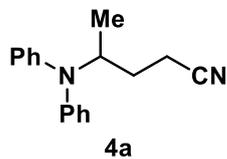
¹H NMR Spectra of 4a

May15-2018-3.140.
A041 H1

7.262
7.276
7.286
7.017
7.005
6.880
6.867

4.328
4.317
4.306
4.284
4.262
4.271

2.475
2.463
2.450
2.042
2.030
2.018
2.006
1.994
1.982
1.796
1.735
1.723
1.711
1.698
1.281

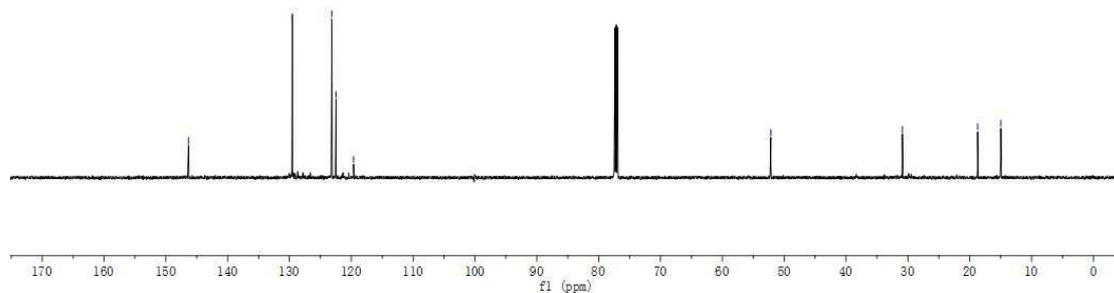
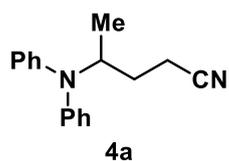


¹³C NMR Spectra of 4a

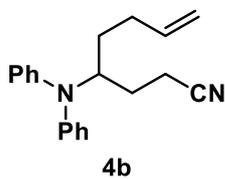
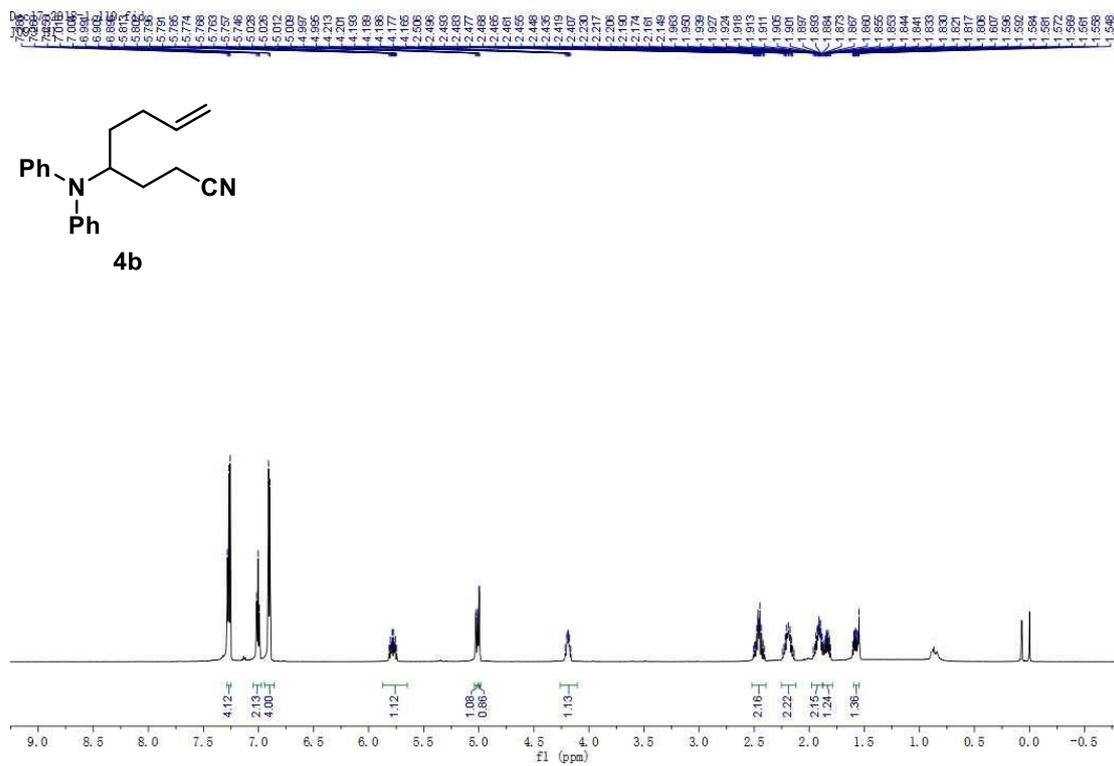
May15-2018-3.141.fid
A041 C13

146.35
128.54
123.14
122.46
119.64

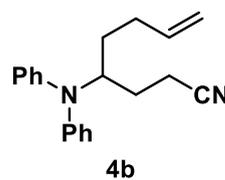
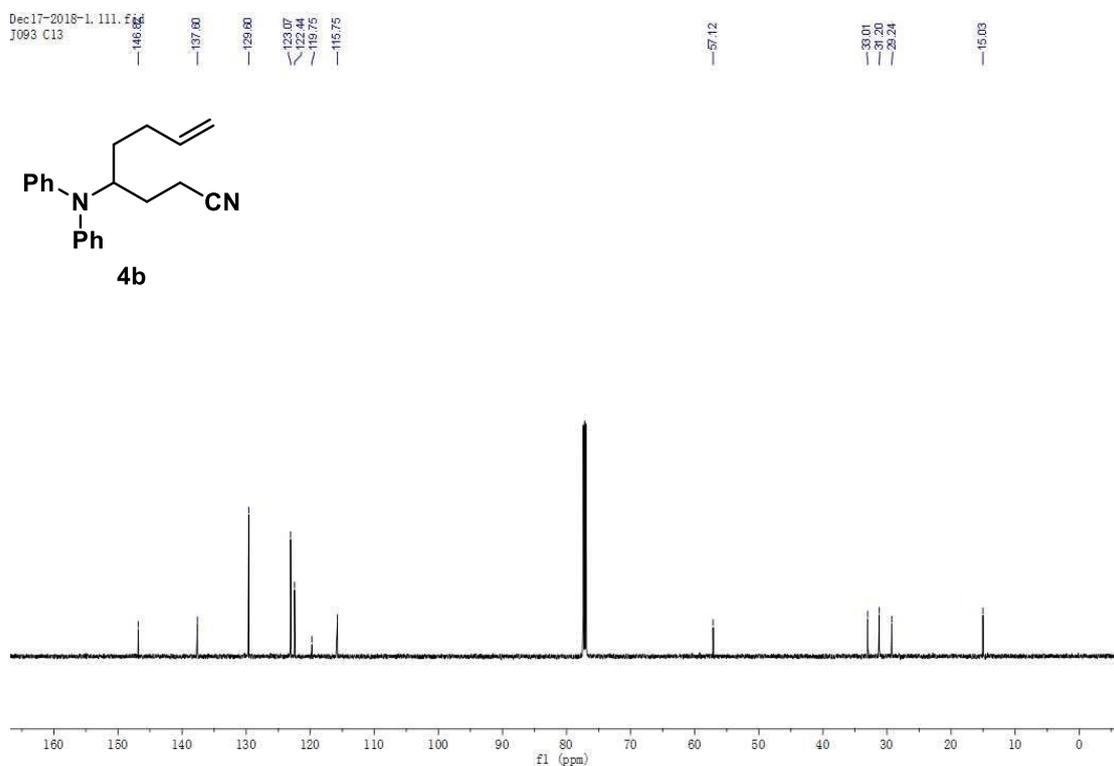
62.16
30.90
18.73
14.97



¹H NMR Spectra of 4b

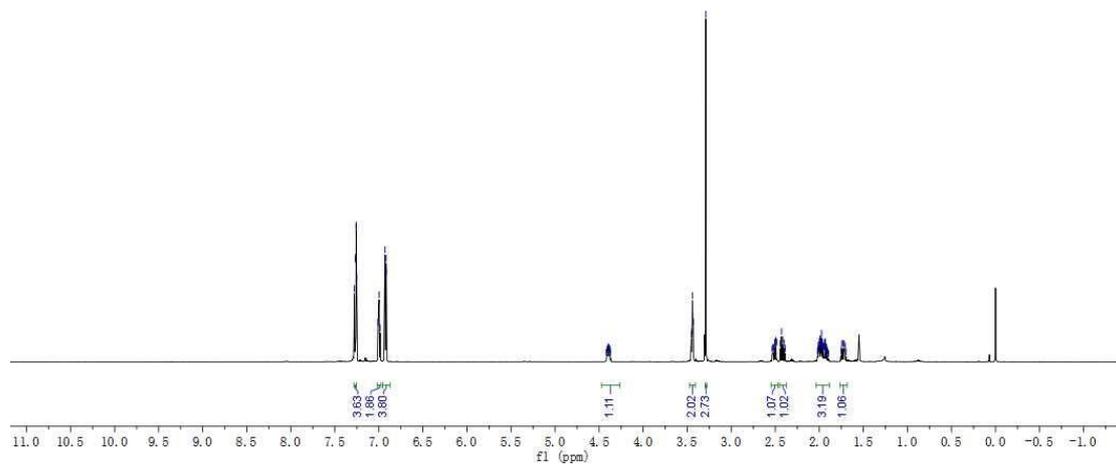
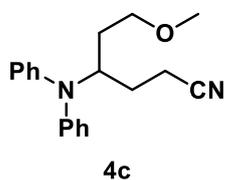


¹³C NMR Spectra of 4b



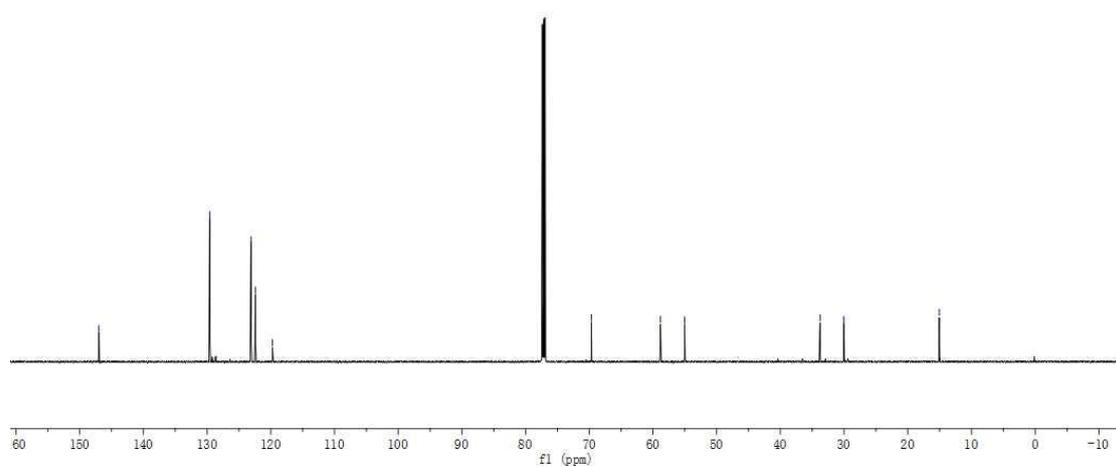
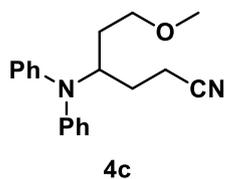
¹H NMR Spectra of 4c

Jan14-2019
K062 H1
7.278
7.258
7.256
7.254
7.252
7.010
6.998
6.986
6.952
6.918
6.916
4.418
4.408
4.406
4.405
4.400
4.396
4.384
4.382
4.367
4.363
4.360
4.378
4.376
3.453
3.450
3.445
3.441
3.429
3.298
2.536
2.527
2.522
2.520
2.507
2.498
2.483
2.484
2.478
2.430
2.416
2.401
2.388
2.377
2.015
2.012
2.008
2.006
2.000
1.999
1.997
1.991
1.988
1.984
1.981
1.979
1.977
1.975
1.965
1.962
1.958
1.954
1.951
1.951
1.949
1.946
1.932
1.930
1.927
1.922
1.916
1.916
1.909
1.903
1.895
1.895
1.744
1.732
1.720
1.708
1.688



¹³C NMR Spectra of 4c

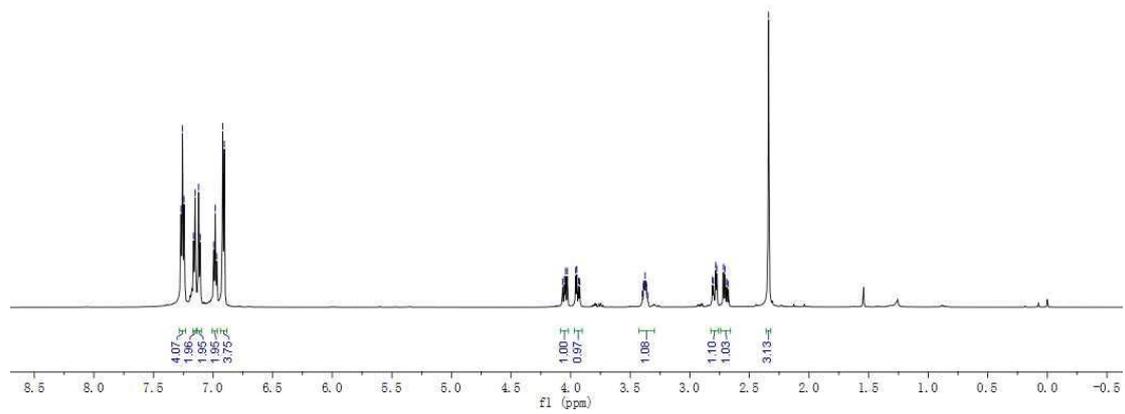
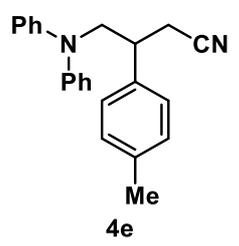
Jan14-2019-3031.fid
K062 C13
146.86
129.59
123.10
122.43
119.75
69.87
58.82
55.03
33.76
30.03
15.04



¹H NMR Spectra of 4e

Nov27-2018-3. 200.
I301 H1

4.067
4.062
4.056
4.028
3.968
3.948
3.933
3.929
3.904
3.885
3.876
3.866
3.852
2.810
2.801
2.792
2.718
2.705
2.691
2.677
2.326

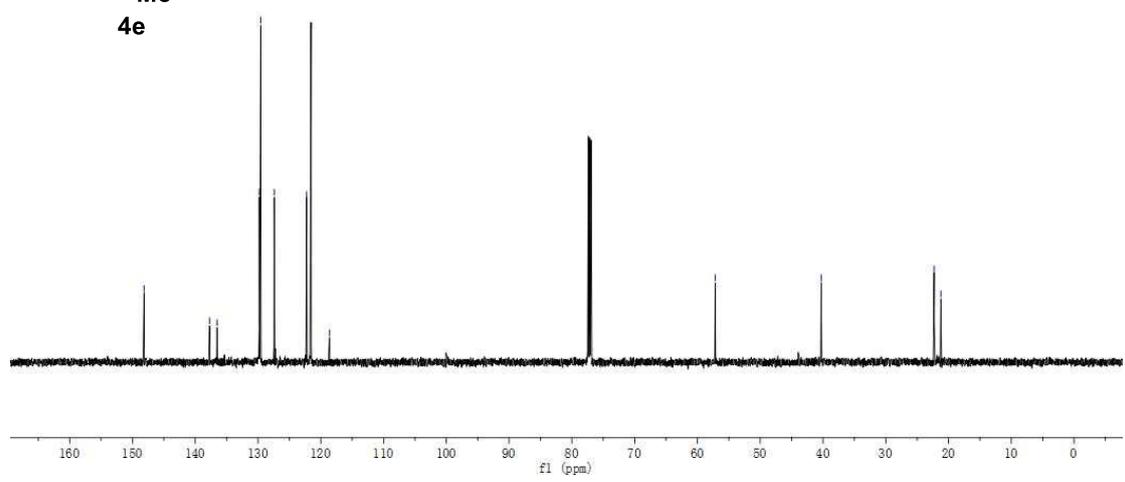
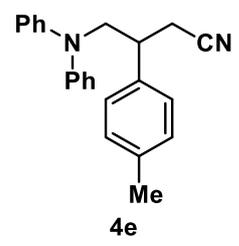


¹³C NMR Spectra of 4e

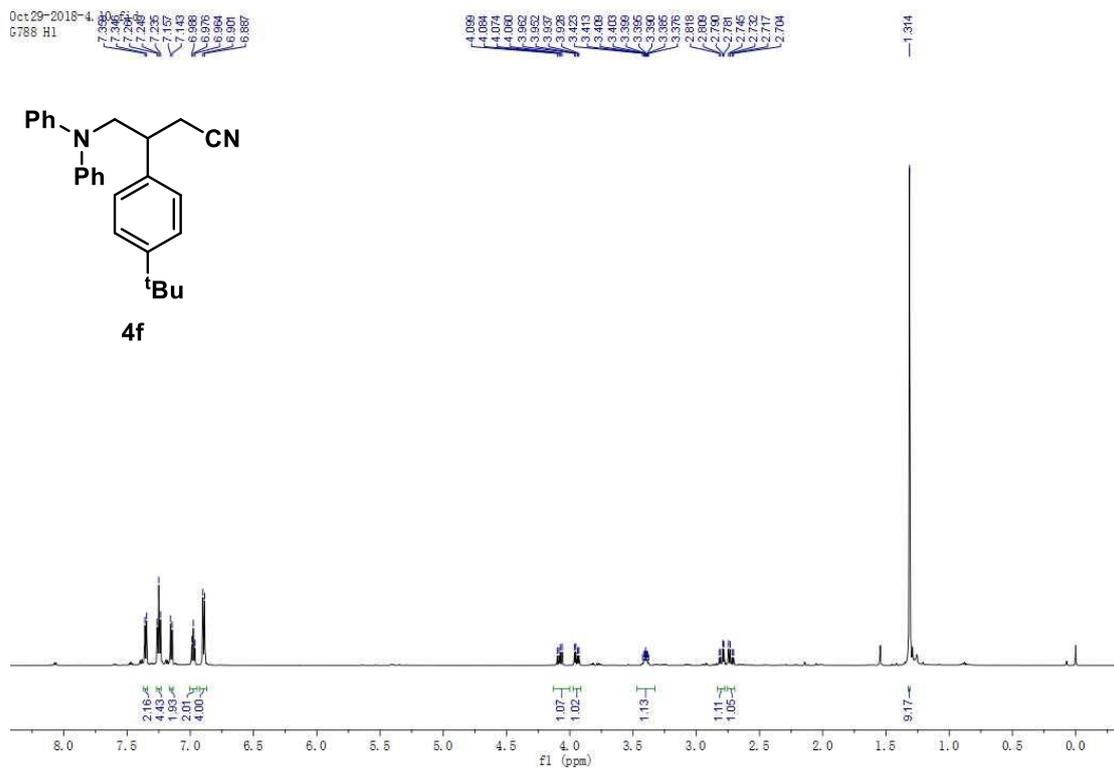
Nov27-2018-3. 201. f1a
I301 C13

148.16
137.72
136.53
128.00
127.39
127.42
122.29
121.66
116.62

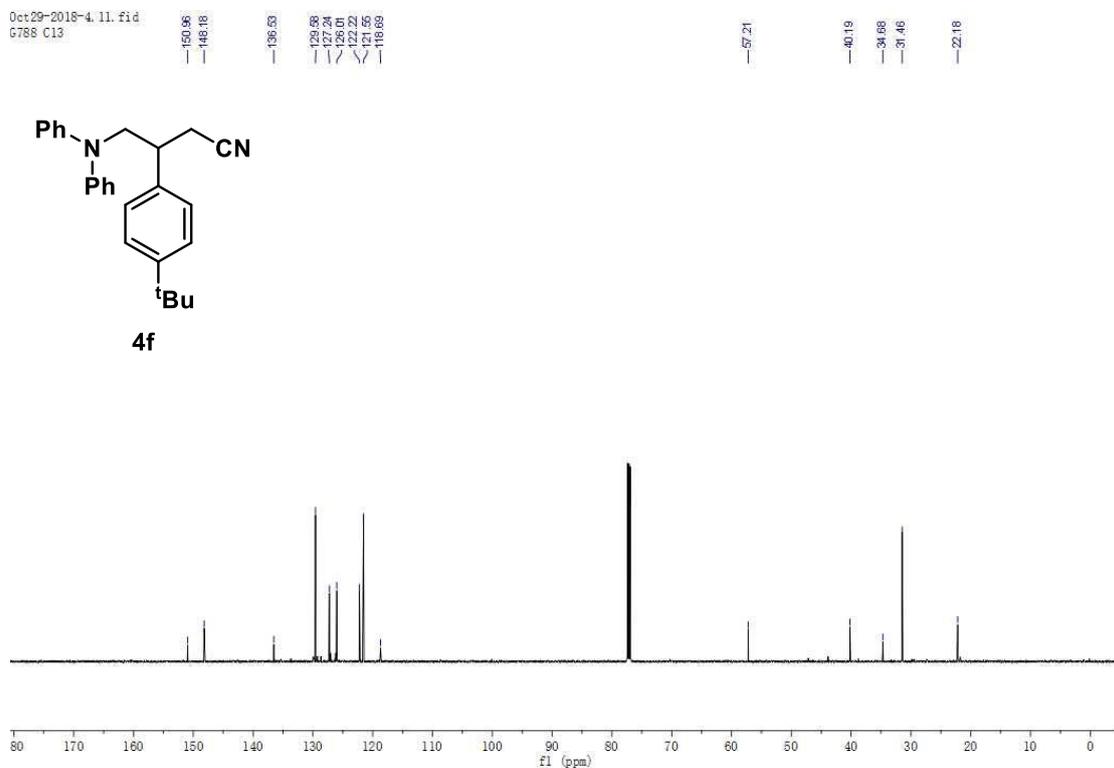
57.17
40.28
22.29
21.22



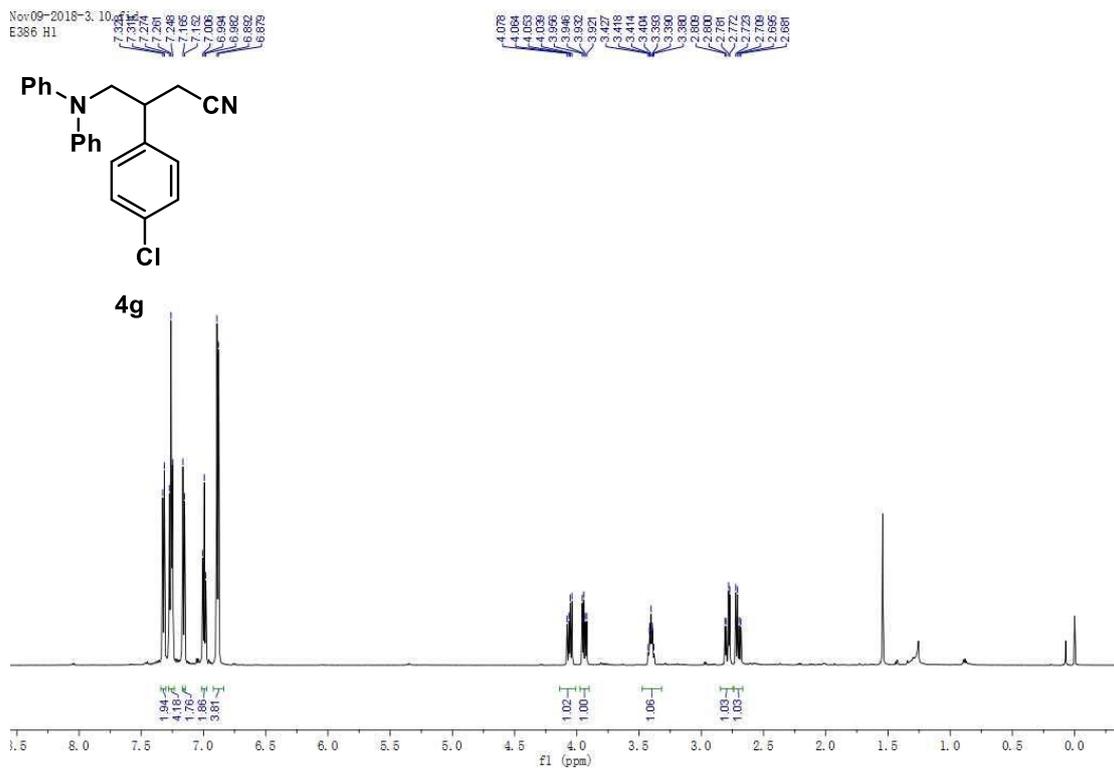
¹H NMR Spectra of 4f



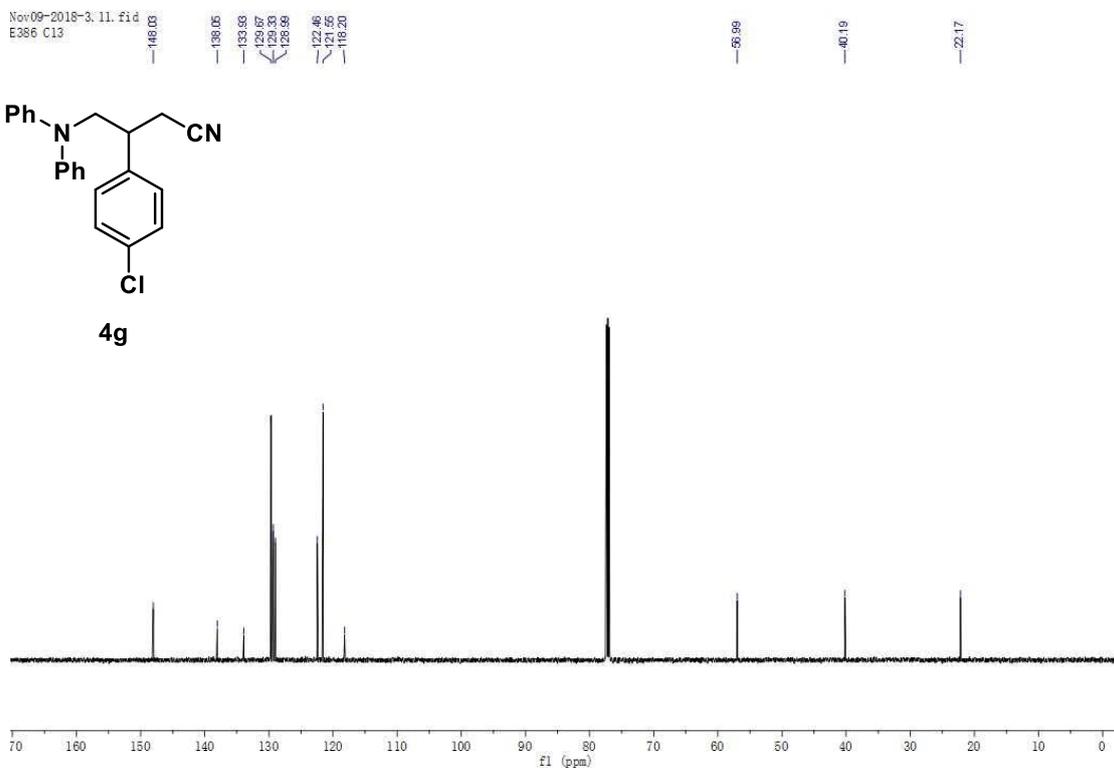
¹³C NMR Spectra of 4f



¹H NMR Spectra of 4g



¹³C NMR Spectra of 4g

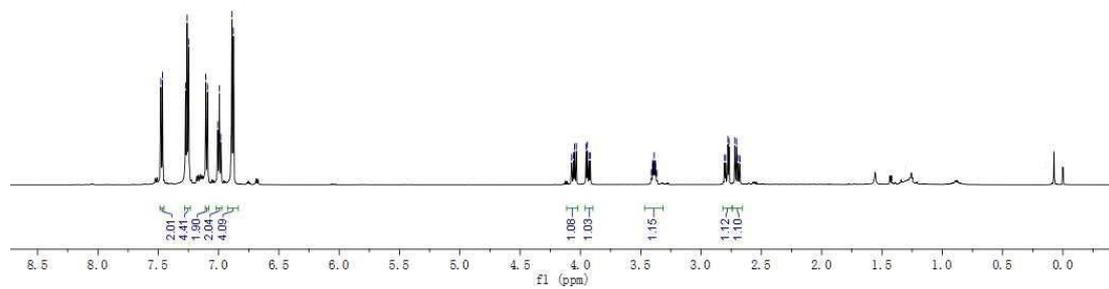
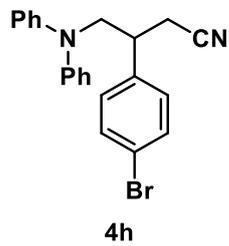


¹H NMR Spectra of 4h

Nov22-2018-1. 220.
1068 H1

7.476
7.473
7.271
7.248
7.106
7.002
6.994
6.962
6.890
6.877

4.073
4.069
4.065
4.034
3.953
3.943
3.926
3.922
3.913
3.433
3.399
3.389
3.385
3.385
3.379
3.375
3.366
3.366
2.777
2.777
2.768
2.719
2.681
2.678



¹³C NMR Spectra of 4h

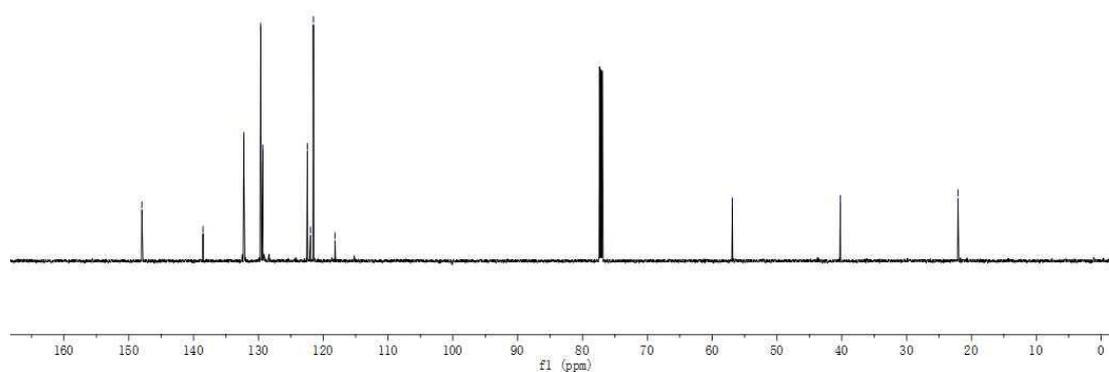
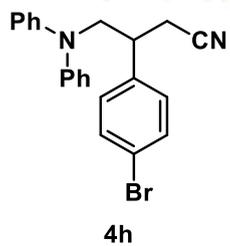
Nov22-2018-1. 221. f34
1068 C13

147.84
138.54
132.28
128.06
128.32
122.44
121.83
118.18

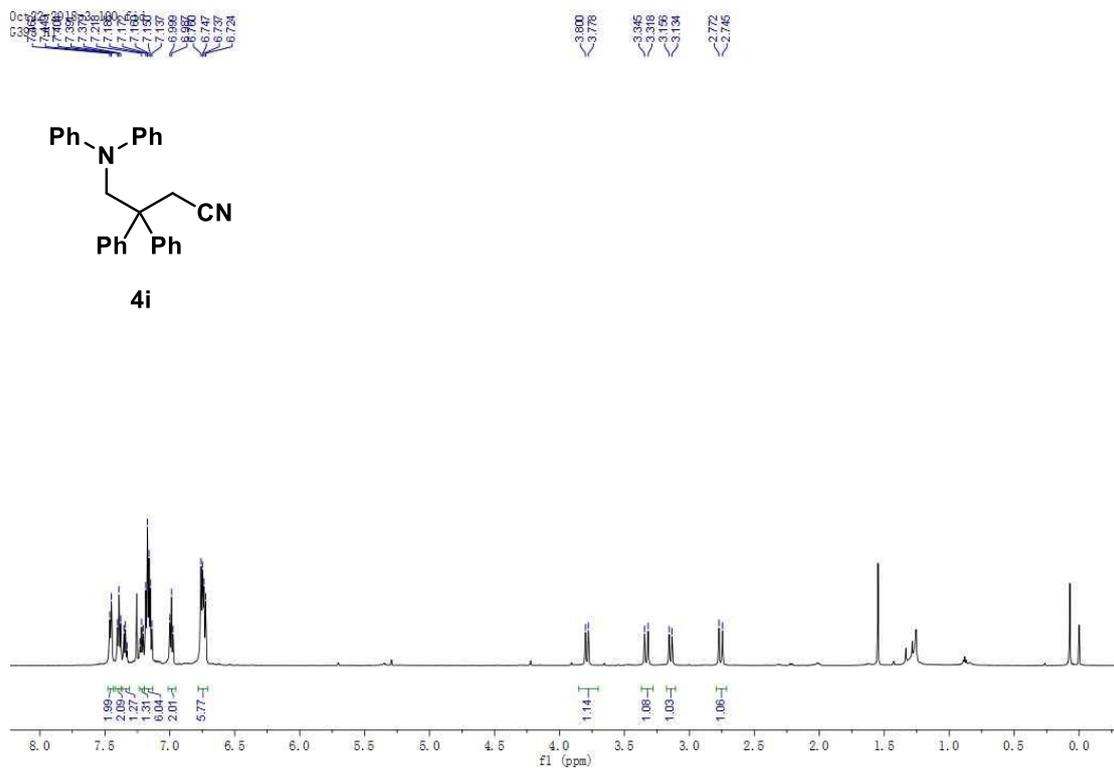
56.89

40.23

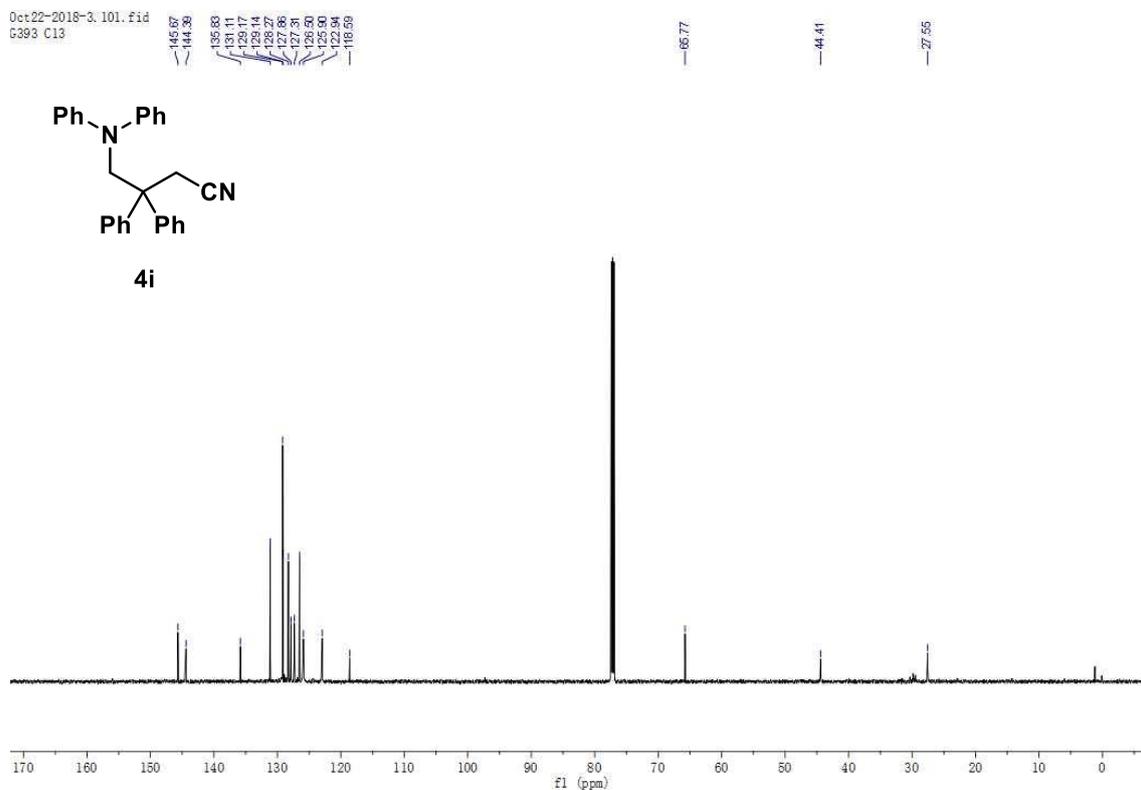
22.09



¹H NMR Spectra of **4i**



¹³C NMR Spectra of **4i**

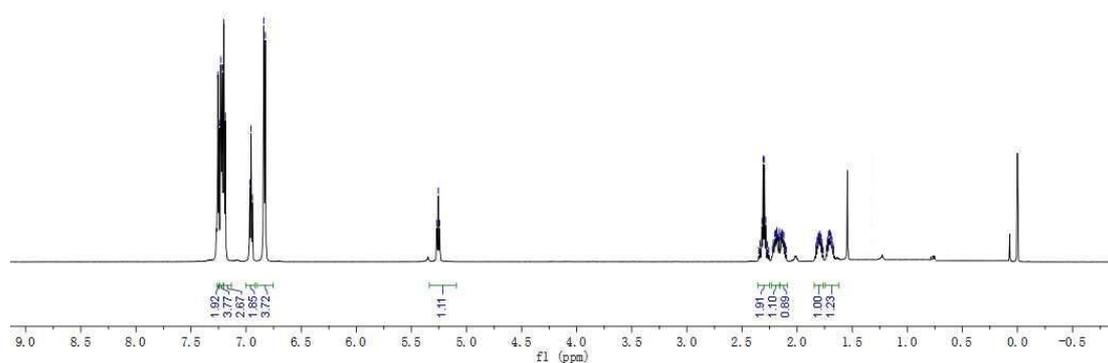
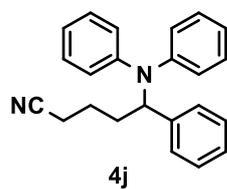


¹H NMR Spectra of 4j

Mar07-2019-1. 210. fid
K759 H1

7.293
7.246
7.243
7.240
7.203
7.188
6.897
6.890
6.840
6.833

5.289
5.257
4.141
2.948
2.938
2.930
2.908
2.895
2.885
2.857
2.224
2.216
2.202
2.193
2.188
2.184
2.175
2.170
2.161
2.148
2.143
2.136
2.134
2.130
2.117
2.111
2.109
2.099
1.925
1.817
1.814
1.807
1.798
1.788
1.765
1.757
1.754
1.735
1.725
1.714
1.704
1.695
1.682
1.673
1.670



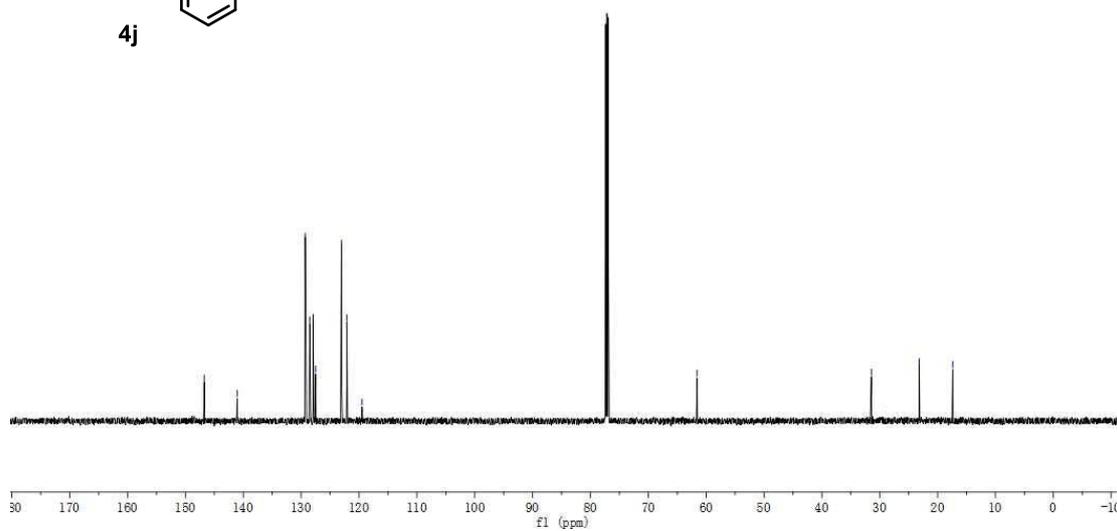
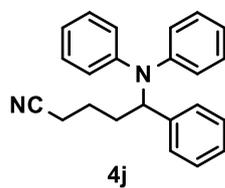
¹³C NMR Spectra of 4j

Mar07-2019-1. 211. fid
K759 C13

146.75
141.06
129.29
128.92
128.82
127.80
123.03
122.10
119.48

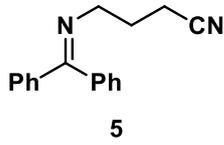
61.56

31.45
23.17
17.36

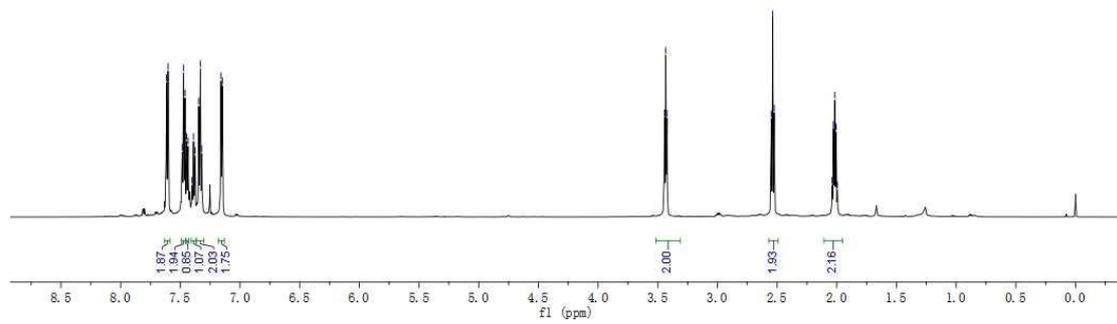


¹H NMR Spectra of 5

Mar04-2019-3.201.fid
K672 H1

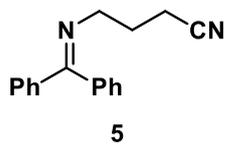


3.444
3.423
2.549
2.537
2.525
2.038
2.017
2.006
1.985



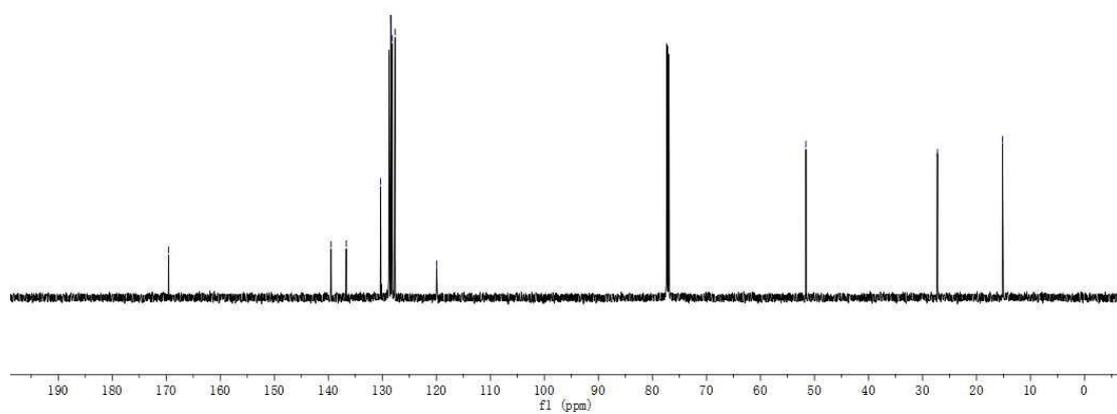
¹³C NMR Spectra of 5

Mar04-2019-3.201.fid
K672 C13



138.30
137.32
130.32
128.70
128.42
127.62
119.95

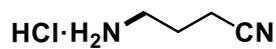
51.59
27.23
15.20



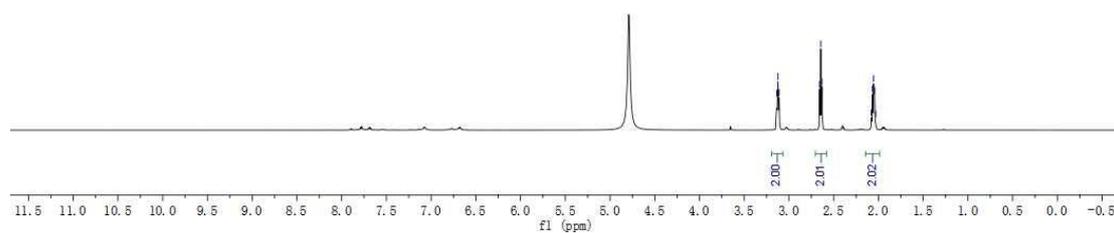
¹H NMR Spectra of 6

Mar06-2019-3_80.fid
K713 H1

3.136
3.170
3.170
2.657
2.657
2.653
2.079
2.067
2.064
2.029



6



¹³C NMR Spectra of 6

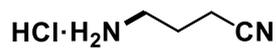
Mar07-2019-1_20.fid
K745 C13

120.46

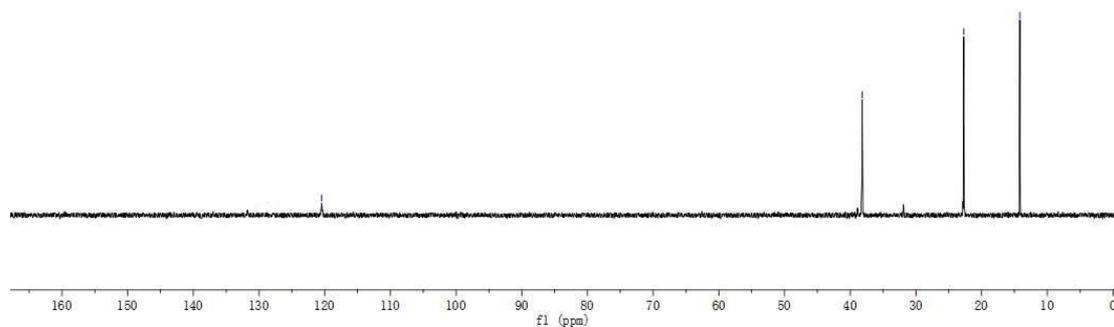
38.18

22.71

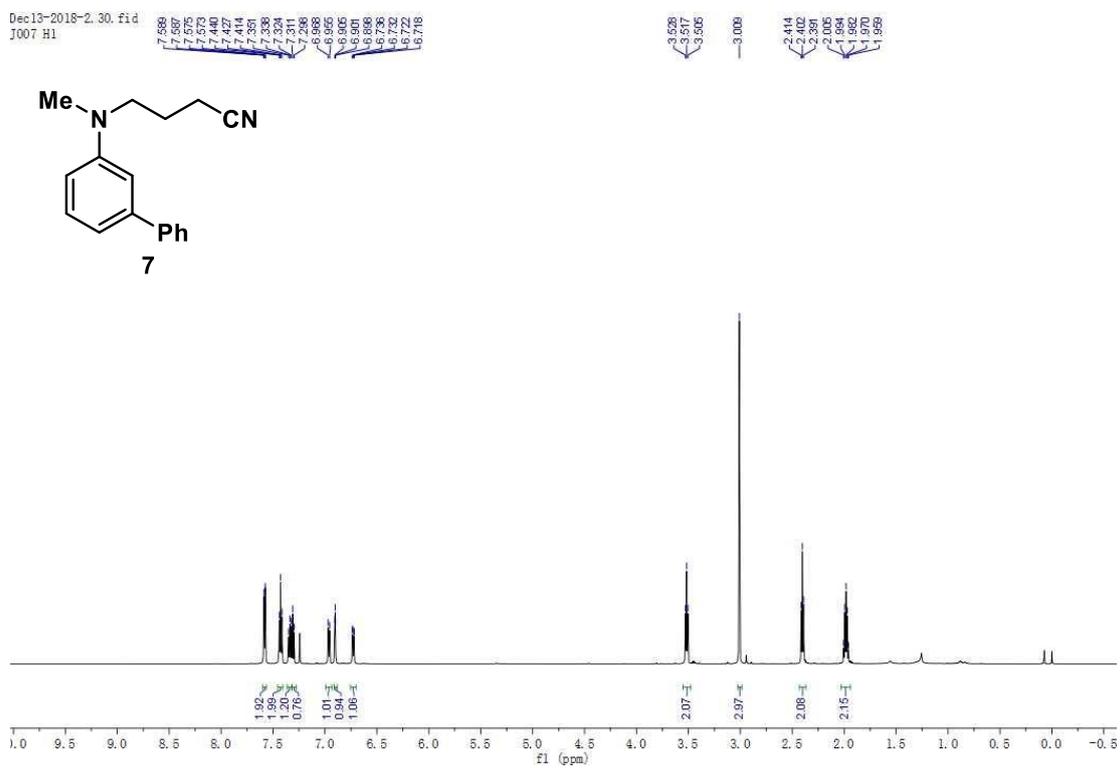
14.17



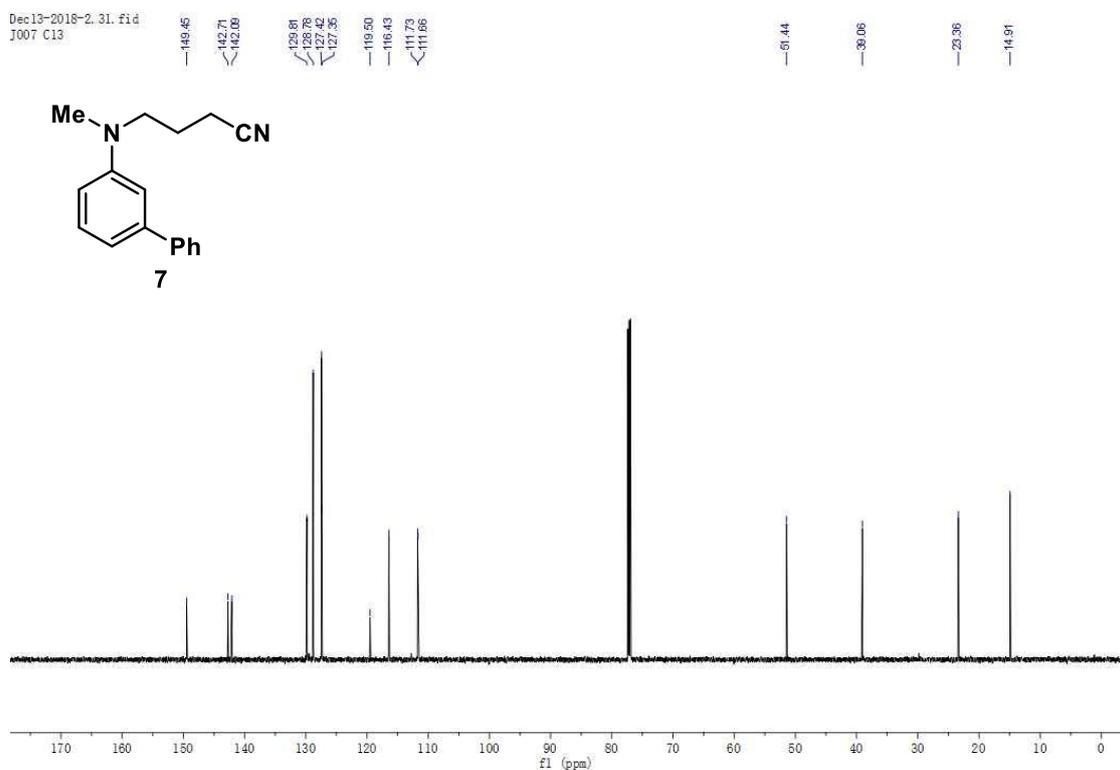
6



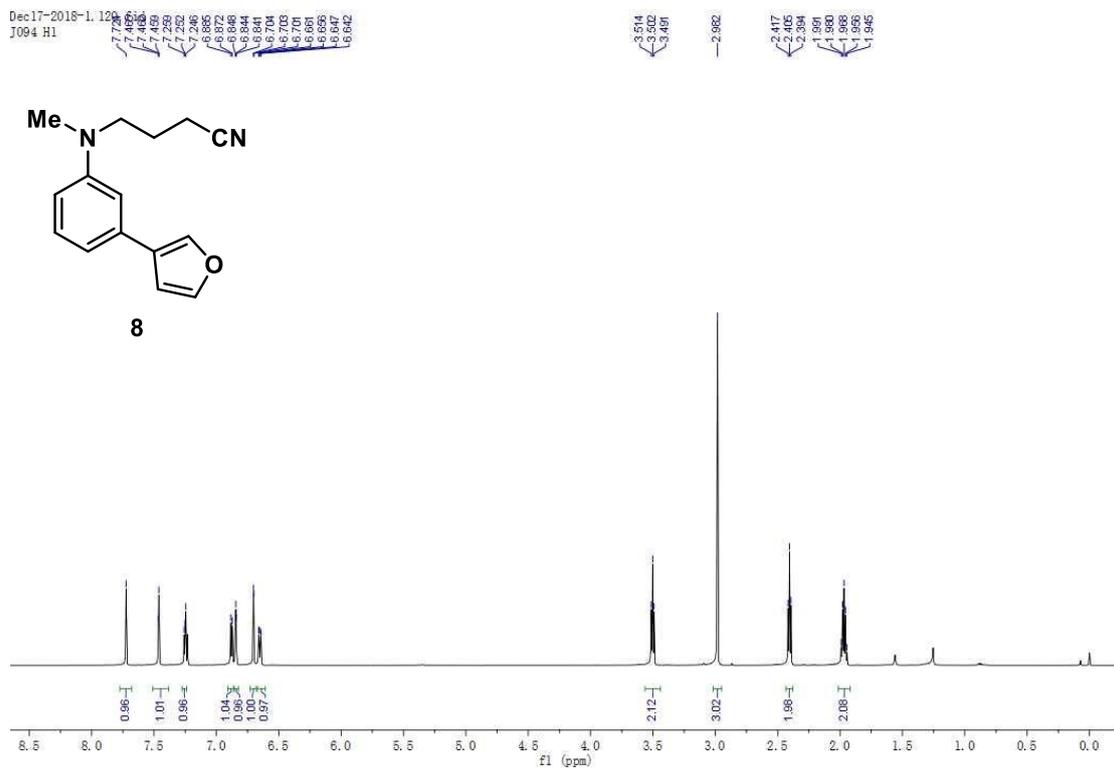
¹H NMR Spectra of 7



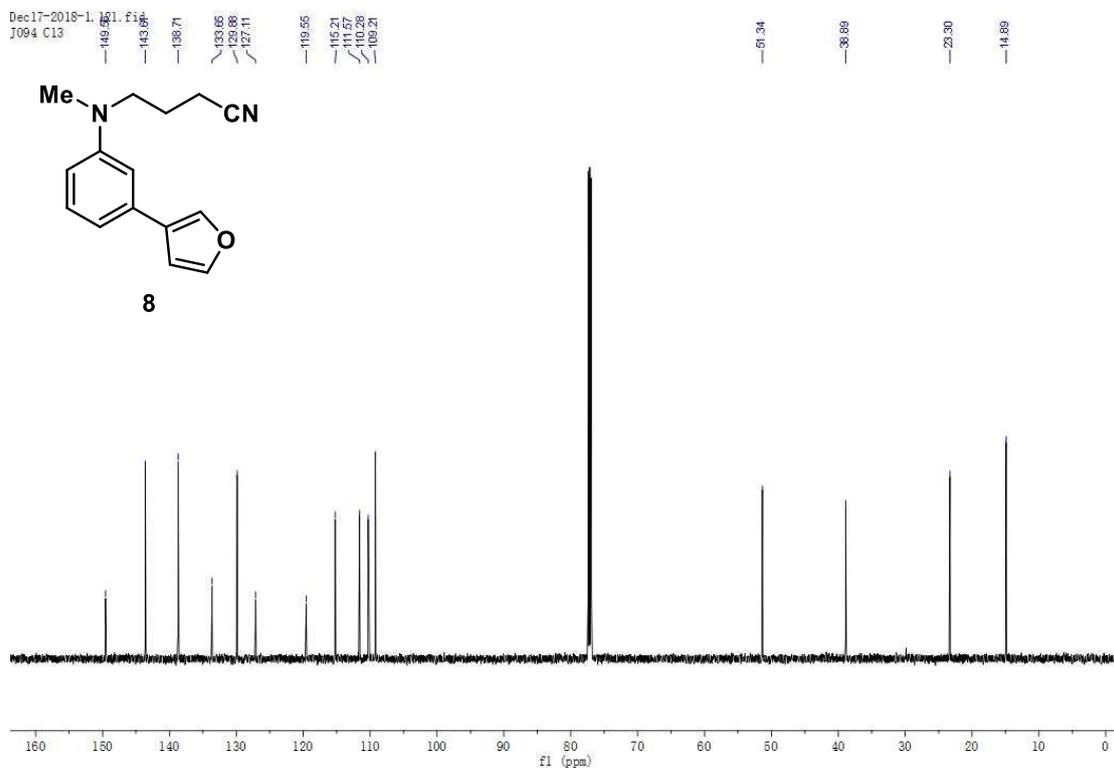
¹³C NMR Spectra of 7



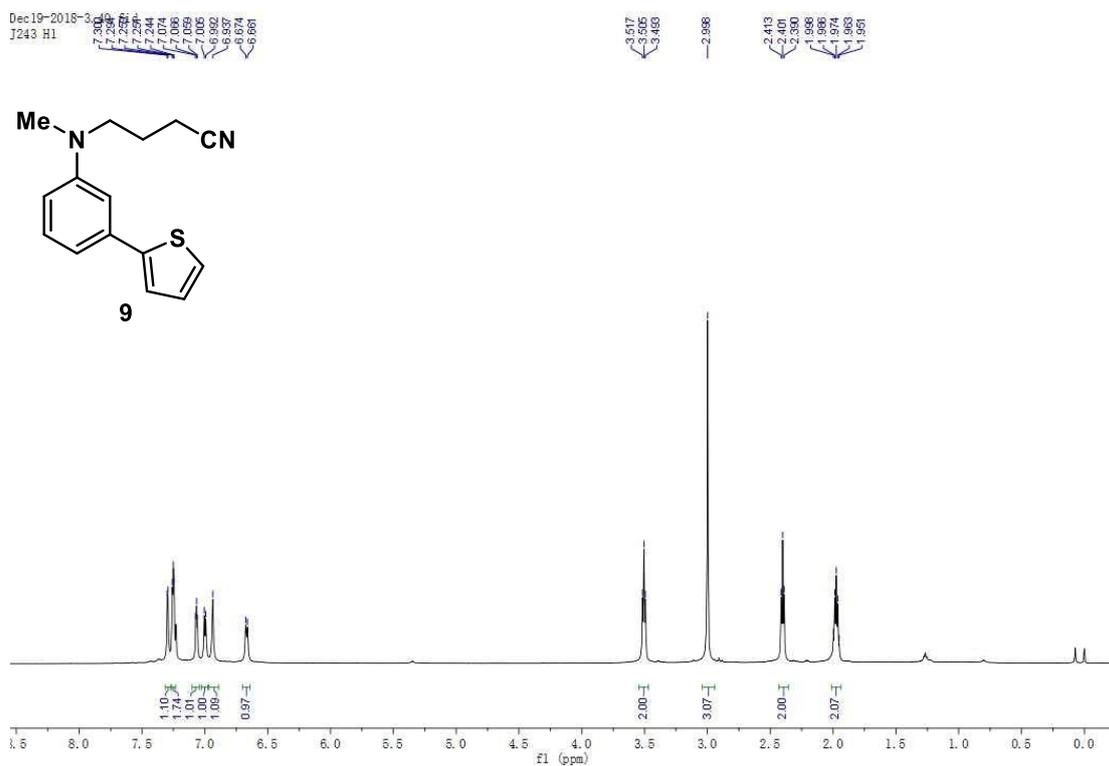
¹H NMR Spectra of 8



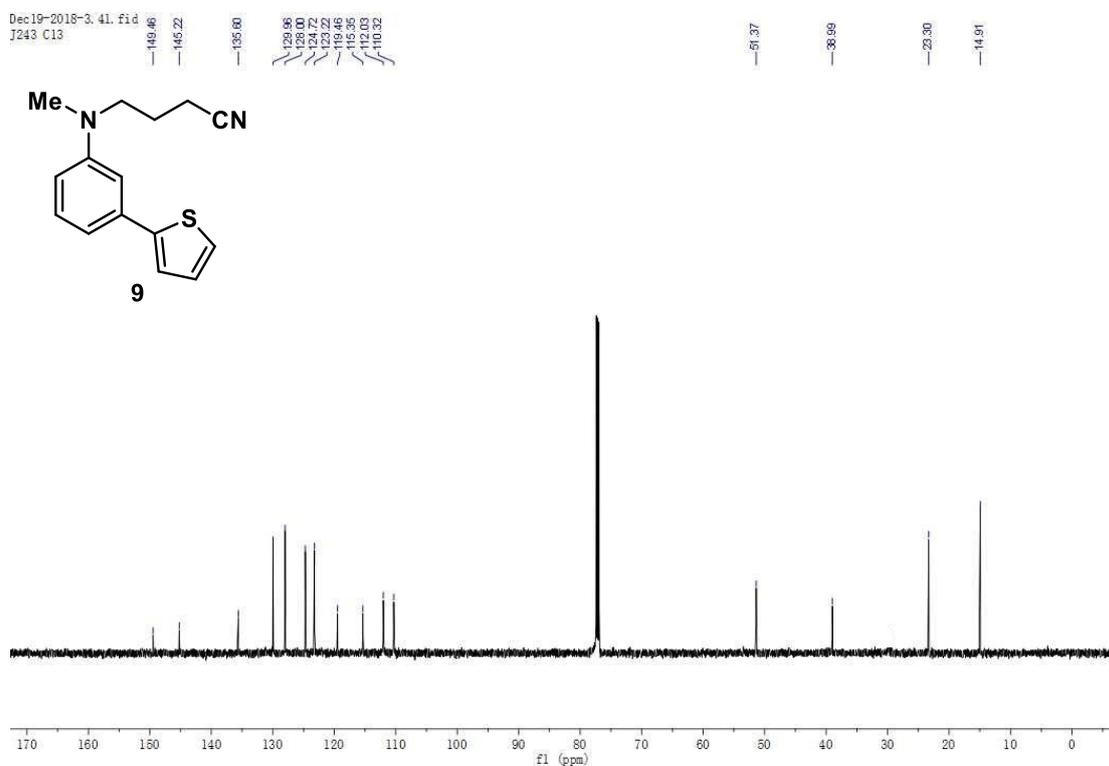
¹³C NMR Spectra of 8



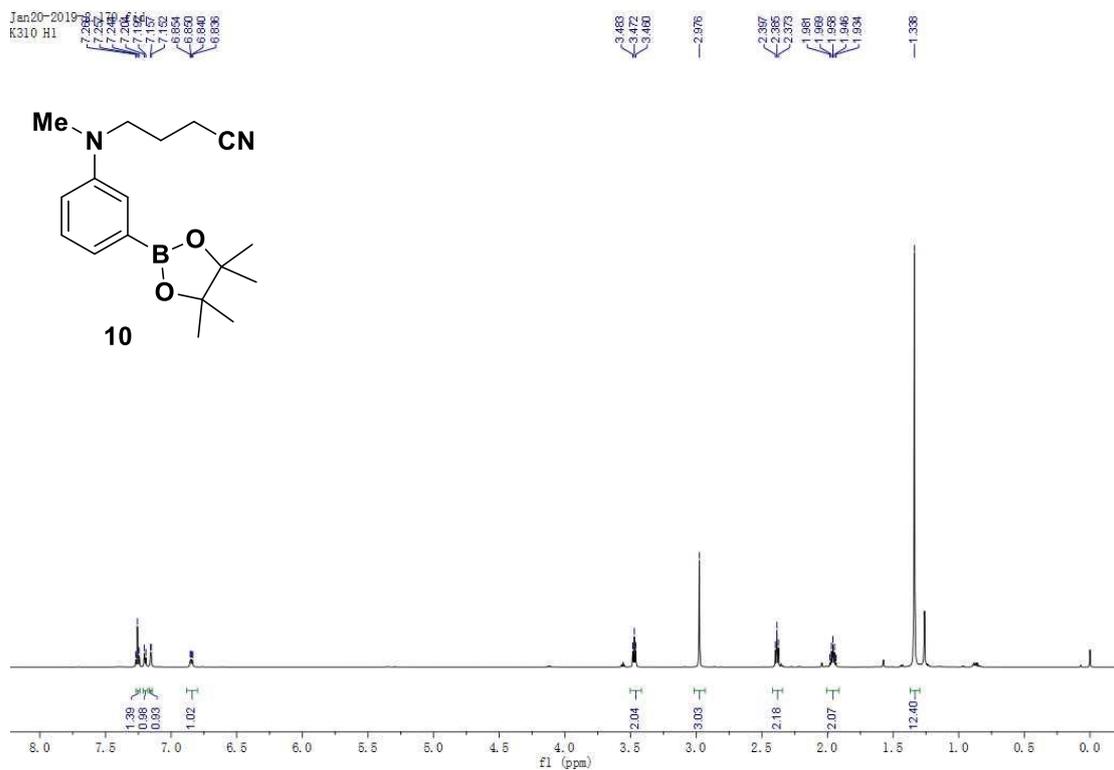
¹H NMR Spectra of 9



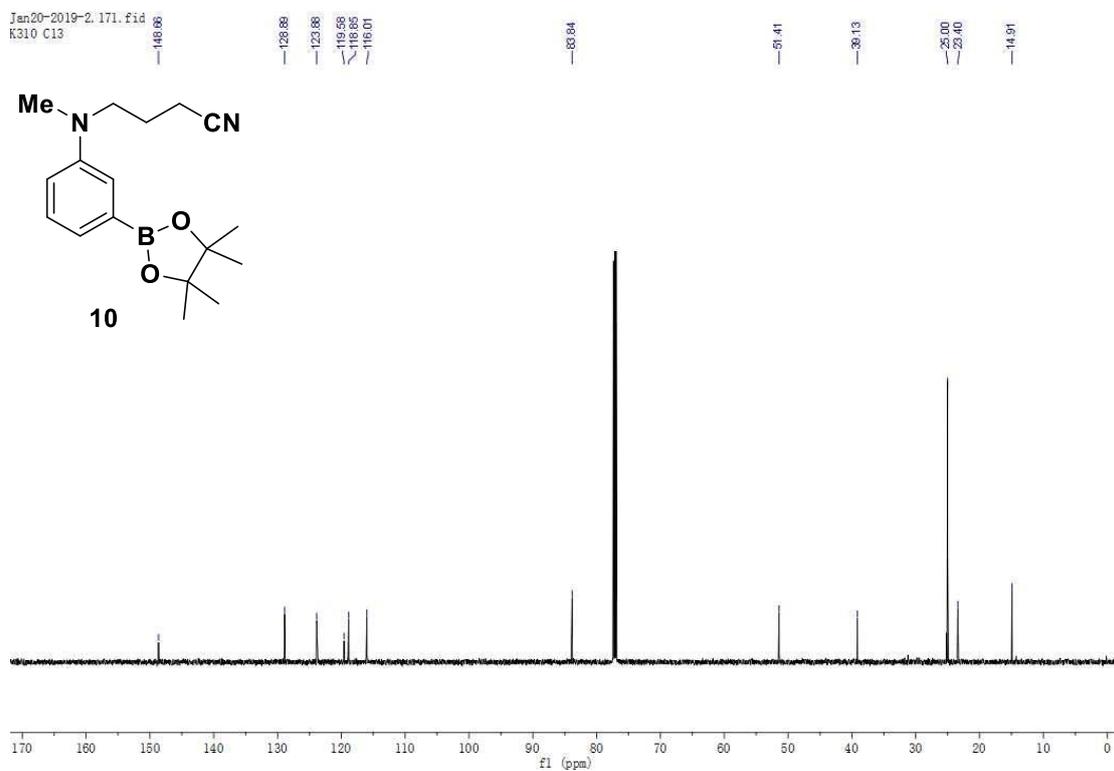
¹³C NMR Spectra of 9



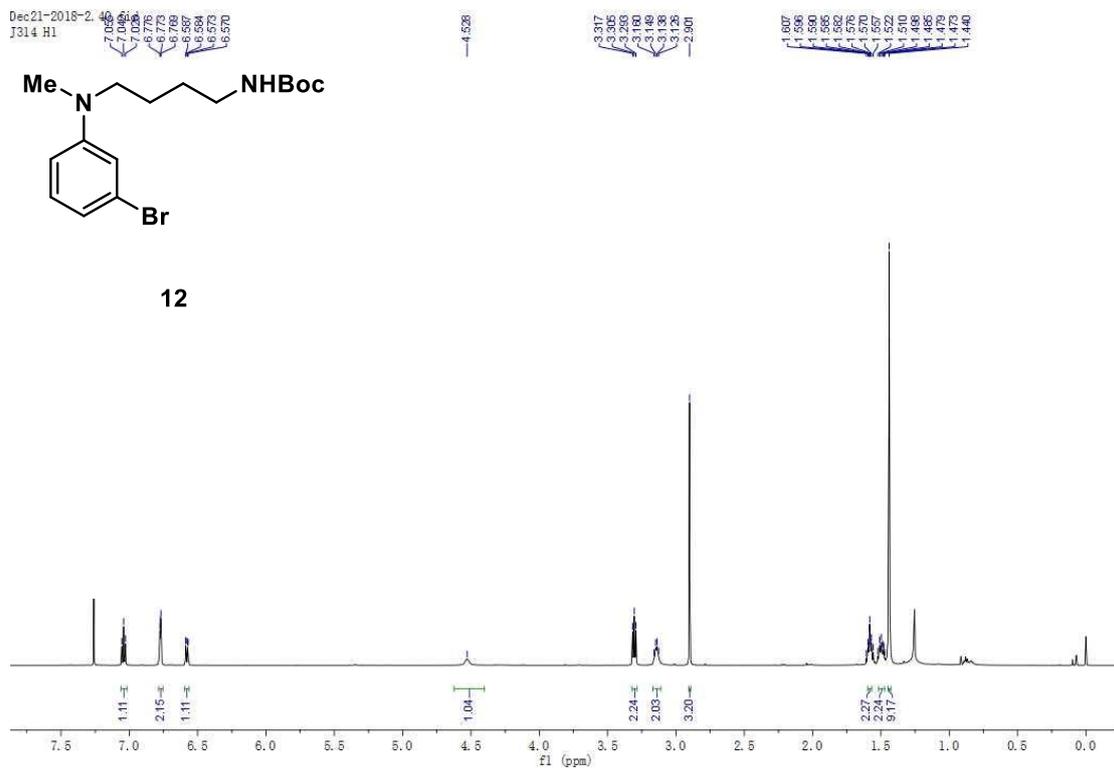
¹H NMR Spectra of 10



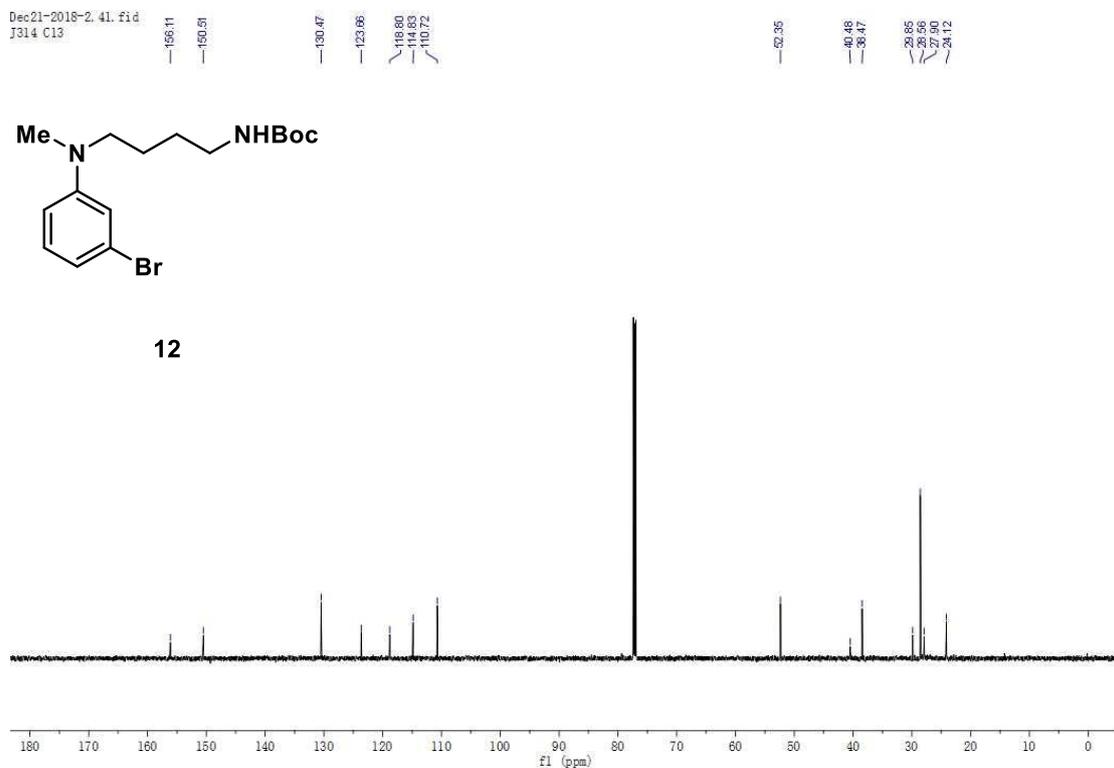
¹³C NMR Spectra of 10



¹H NMR Spectra of 12



¹³C NMR Spectra of 12

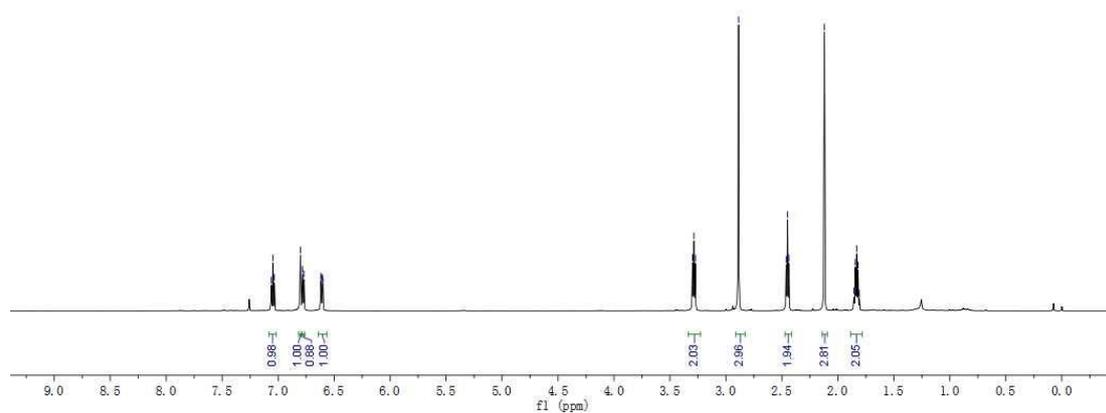
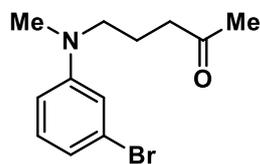


¹H NMR Spectra of 13

Jan09-2019-1. 70. fid
J880 H1

7.081
7.047
6.801
6.782
6.769
6.617
6.603
6.599

3.298
3.286
3.273
2.867
2.481
2.450
2.438
2.121
1.856
1.844
1.832
1.820
1.809



¹³C NMR Spectra of 13

Jan09-2019-1. 71. fid
J880 C13

206.16

150.53

130.47

123.61

116.80

110.71

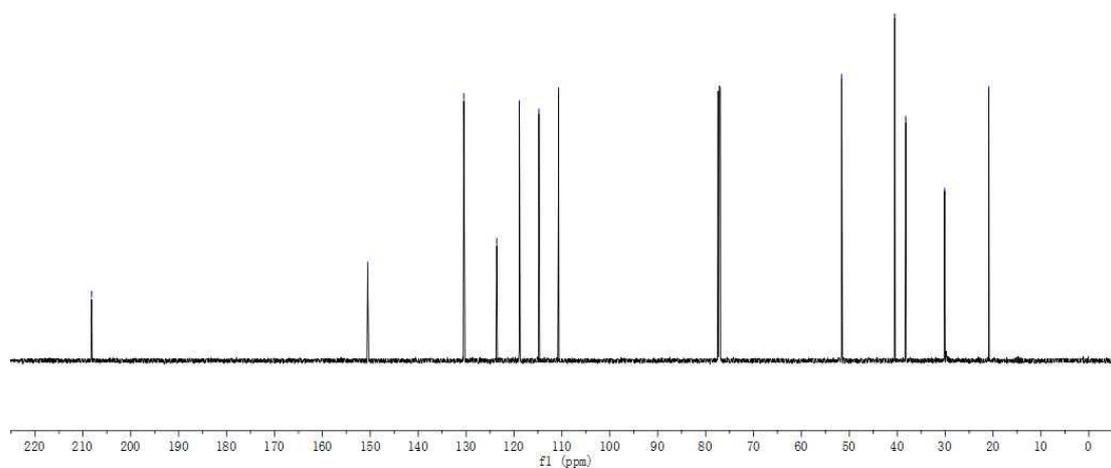
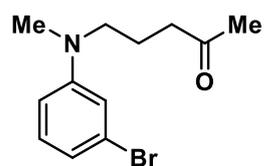
51.80

40.52

38.23

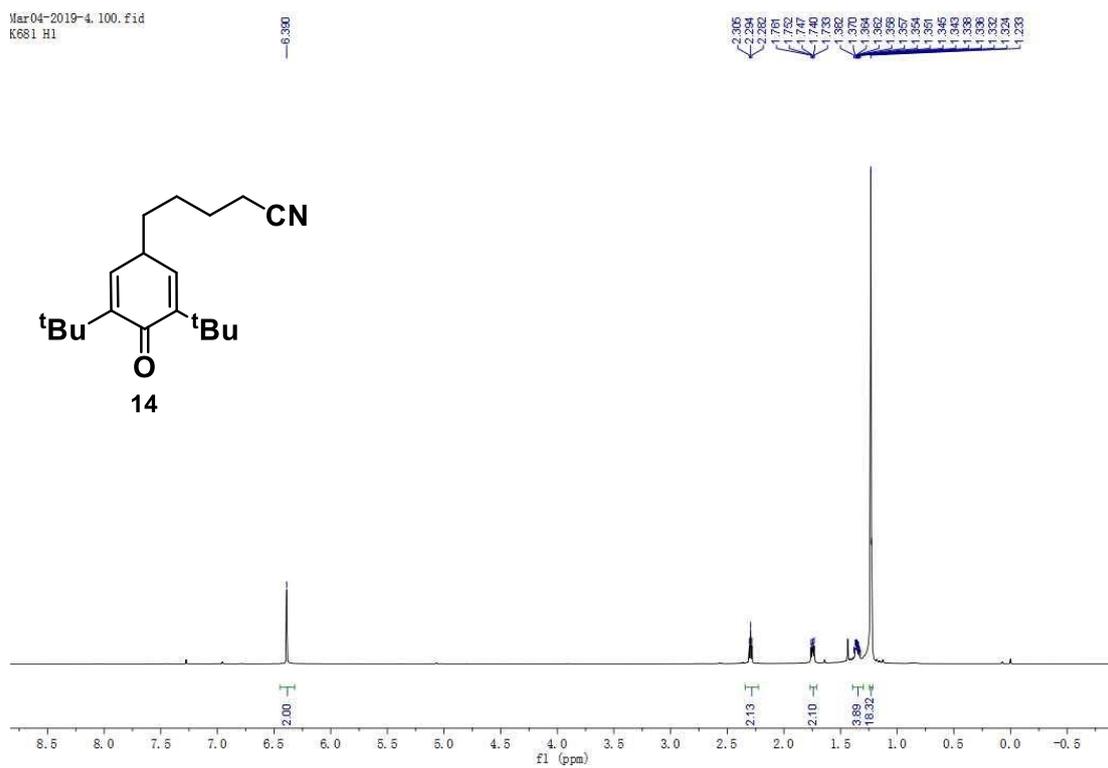
30.10

20.88



¹H NMR Spectra of 14

Mar04-2019-4.100.fid
E681 H1



¹³C NMR Spectra of 14

Mar04-2019-4.101.fid
E681 C13

