Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Intermolecular Alkene Arylcyanation Using BnSCN as Cyanide Source via Reductive Strategy: Access to 3,3-Disubstituted Oxindoles

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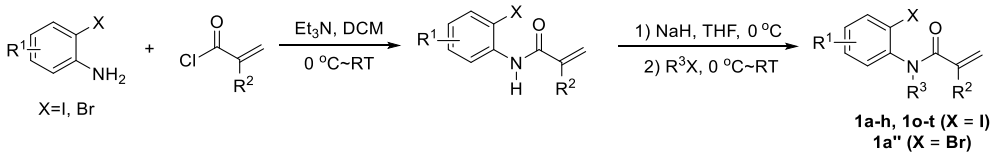
1. General Information

DMF solvent was dried from CaH_2 and purified by distillation before being used. Purifications of reactions products were carried out by column chromatography on silica gel (200-300 mesh) using a mixture of petroleum ether (60-90°C) and ethyl acetate as eluent. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) were measured on a Brucker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm, δ) downfield from residual solvents peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), … Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). GC-MS data were recorded on a GCMS-QP2010 instrument. Electrospray mass spectra were obtained using Bruker micrOTOF-Q II 10410 Mass Spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.

2. General Procedure

2.1 Synthesis of Aryl Halides (Procedure A) [1]

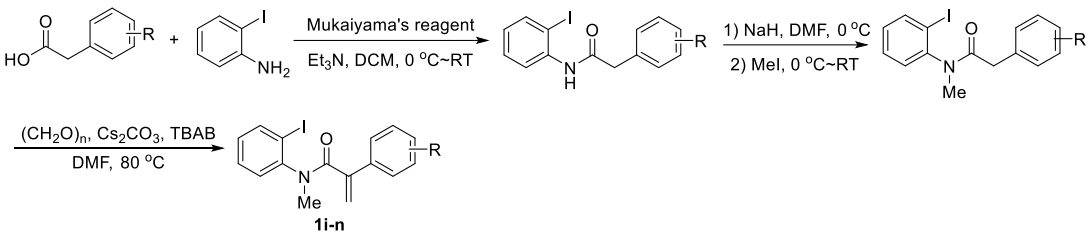


To a mixture of 2-haloaniline (1.0 mmol, 1.0 equiv), DMAP (6.0 mg, 0.05 mmol, 5 mol%), and Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv) in DCM (4.0 mL) was added acryloyl chloride (1.2 mmol, 1.2 equiv) at -20 °C dropwise. After stirring at -20 °C for 30 min and then room temperature overnight, the mixture was quenched with saturated $NaHCO_3$, extracted with DCM, washed with brine, and dried over anhydrous Na_2SO_4. After filtration and concentration, the obtained crude amide was used in next step without further purification.

NaH (80 mg, 60% in mineral oil, 2.0 mmol, 2.0 equiv) was added to a solution of

the above crude amide in THF (4.0 mL) at 0 °C in portions. After stirring for 20 min at 0 °C, RX (3.0 mmol, 3.0 equiv) was added dropwise and the reaction mixture was stirred at room temperature for another 2 h. The reaction was quenched with water and the resulting mixture was extracted with EtOAc twice. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, followed by filtration and concentration of organic phase. The residue was separated by column chromatography on silica gel with eluent (PE/EtOAc = 15 : 1 ~ 5 : 1) to afford the corresponding products **1a-h, 1o-t, 1a"**.

2.2 Synthesis of Aryl Halides (Procedure B) [2]



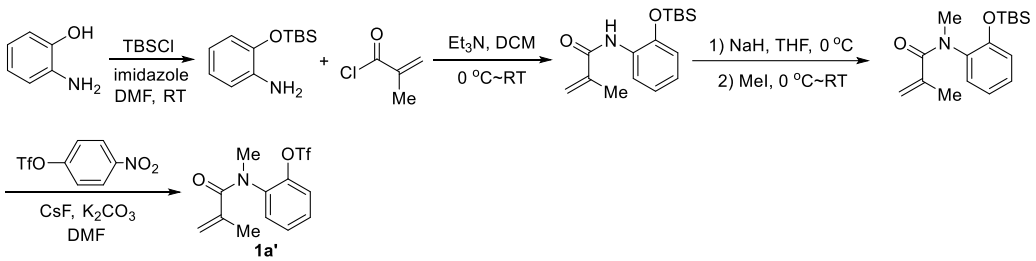
To a solution of the corresponding carboxylic acid (5.0 mmol, 1.0 equiv) dissolved in DCM (12.5 mL) cooled to 0 °C, Mukaiyama's reagent (6.0 mmol, 1.2 equiv), 2-iodoaniline (1.3141 g, 6.0 mmol, 1.2 equiv) and NEt_3 (1.5179 g, 15.0 mmol, 3.0 equiv) were added. The resulting solution is gradually warmed to room temperature and stirred until complete consumption of starting materials as indicated by TLC. The reaction mixture was diluted with DCM, and sequentially washed with 1 M HCl (2x) and brine (1x). The organic phase was dried over Na_2SO_4, filtered and concentrated in vacuo to afford a crude residue that was used without further purification.

The crude residue is re-dissolved in DMF (12.5 mL) and cooled to 0 °C. To this solution, NaH (300.0 mg, 60% in mineral oil, 7.5 mmol, 1.5 equiv) was added in one portion and the solution was stirred for 10 minutes. To this mixture, MeI (1.4194 g, 10.0 mmol, 2.0 equiv) was added dropwise. The reaction was gradually warmed to room temperature to stir until complete consumption of starting material as indicated

by TLC. The reaction mixture was quenched with aqueous saturated NH_4Cl and diluted with EtOAc. The reaction is extracted with EtOAc three times and washed with brine. The combined organic layers were sequentially dried over Na_2SO_4, filtered and concentrated in vacuo to afford a crude residue that was used without further purification.

The crude residue is re-dissolved in DMF (25 mL), and to this solution, paraformaldehyde (1.2020 g, 20.0 mmol, 4.0 equiv), Cs_2CO_3 (3.0 equiv), and tetrabutylammonium bromide (363.7 mg, 1.5 mmol, 0.3 equiv) were added. The resulting mixture was heated to 80 °C in a preheated oil bath and stirred until complete consumption of starting material as indicated by TLC. The reaction mixture was quenched with saturated NH_4Cl and diluted with EtOAc. The reaction is extracted with EtOAc three times and washed with brine. The combined organic layers were sequentially dried over Na_2SO_4, filtered and concentrated in vacuo to afford the crude product. The residue was separated by column chromatography on silica gel with eluent (PE/EtOAc = 10 : 1) to afford the corresponding products **1i-n**.

2.3 Synthesis of Aryl Triflates 1a' [3]



To a solution of 2-aminophenol (1.091g, 10 mmol, 1.0 equiv) and imidazole (1.02 g, 10 mmol, 1.0 equiv) in DMF (10 mL) was added a solution of TBSCl (1.65 g, 11 mmol, 1.1 equiv) in DMF (5 mL). The mixture was stirred at room temperature overnight. After the reaction was complete (monitored by TLC), the mixture was quenched with saturated NH_4Cl solution (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine (10 mL × 2), dried over anhydrous Na_2SO_4 and filtrated. Removal of the solvent under reduced pressure gave

a yellow oil residue which was used for the next step without further purification.

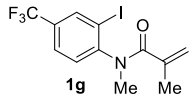
To a solution of TBS-protected aminophenol (669.3 mg, 3 mmol, 1.0 equiv) and triethylamine (0.87 mL, 6 mmol, 2.0 equiv) in DCM (4 mL) at 0 °C was added dropwise a solution of acryloyl chloride (376.2g, 3.6 mmol, 1.2 equiv) in DCM (1 mL) over 15 min. After stirring for another 30 min, the mixture was warmed to room temperature and stirred until the amine was consumed completely (monitored by TLC). The resulting solution was concentrated, and the residue was dissolved in EtOAc (5 mL) and filtered. The organic layer was washed with 5% HCl solution (3 × 5 mL), saturated $NaHCO_3$ solution (5 mL) and brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue (yellow oil) was used for the next step without further purification.

To a stirred mixture of NaH (60% dispersion in mineral oil) (0.24 g, 6 mmol, 2.0 equiv) in dry THF (5 mL) was added amide (657.6 mg, 3 mmol, 1.0 equiv) at 0 °C under N_2. After being stirred at rt for 30 min, the reaction was cooled to 0 °C and MeI (0.57 mL, 9 mmol, 3.0 equiv) was added dropwise. The mixture was then stirred at room temperature overnight. After the reaction was complete (monitored by TLC), the mixture was quenched with saturated aqueous NH_4Cl at 0 °C and extracted with EtOAc (4 mL × 3). The combined extracts were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/EtOAc = 10 : 1) to afford the N-protected amide.

To a solution of the N-protected amide (305.2 mg, 1 mmol, 1.0 equiv) in DMF (6 mL) was added CsF (759.6 mg, 5 mmol, 5.0 equiv). After stirring at 0 °C for 30 min, 4-nitrophenyltriflate (325.2 mg, 1.2 mmol, 1.2 equiv) and K_2CO_3 (276.4 mg, 2 mmol, 2.0 equiv) were introduced. The reaction mixture became yellow due to the generation of 4-nitrophenol. At the end of the reaction (followed by TLC), the yellow solution was diluted with H_2O (8 mL) and extracted with EtOAc. The combined organic phases were washed with 1 N NaOH solution and saturated brine, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel (PE/EtOAc = 10 : 1) to afford the aryl triflate **1a'** as white solid (581.9 mg, 60% yield

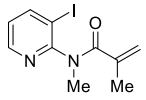
over four steps).

Substrates **1a-f, 1i-j, 1o, 1r, 1a'** and **1a''** were prepared according to the corresponding literature reports. Analytical data (^{1}H NMR, ^{13}C NMR) matches with the literature reports.[4]



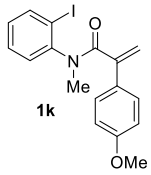
1g

N-(2-iodo-4-(trifluoromethyl)phenyl)-N-methylmethacrylamide (1g). 1g was prepared according to general procedure 2.1 and purified by column chromatography on silica gel (PE/EtOAc = 10 : 1) to obtain **1g** as white solid (232.5 mg, 63% yield). m.p. 94.3-96.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.63 (s, 1H), 7.30 (d, *J* = 4.8 Hz, 1H), 5.04 (s, 2H), 3.25 (s, 3H), 1.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.3, 150.3, 139.6, 137.1, 131.0 (q, *J* = 34.3 Hz), 129.3, 126.5, 122.4 (q, *J* = 271.2 Hz), 119.7, 98.9, 36.6, 20.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -62.6 (s, 3F); HRMS (ESI) calcd for $C_{12}H_{12}F_3INO$ $[M+H]^+$ 369.9910, found 369.9910.



1h

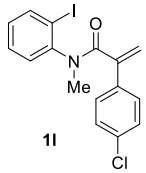
N-(3-iodopyridin-2-yl)-N-methylmethacrylamide (1h). 1h was prepared according to general procedure 2.1 and purified by column chromatography on silica gel (PE/EtOAc = 5 : 1) to obtain **1h** as white solid (151.0 mg, 50% yield). m.p. 54.0-55.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 6.93 (t, *J* = 6.0 Hz, 1H), 4.92 (s, 2H), 3.24 (s, 3H), 1.89 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.7, 158.1, 148.8, 148.7, 140.7, 123.9, 118.5, 94.0, 35.1, 20.1; HRMS (ESI) calcd for $C_{10}H_{12}IN_2O$ $[M+H]^+$ 302.9989, found 302.9990.



1k

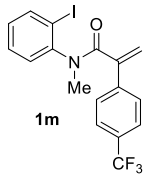
N-(2-iodophenyl)-2-(4-methoxyphenyl)-N-methylacrylamide (1k). 1k was prepared according to general procedure 2.2 and purified by column chromatography

on silica gel (PE/EtOAc = 10 : 1) to obtain **1k** as colorless oil (628.8 mg, 32% yield). Two rotamers were observed in 17:3 (0.85:0.15) ratio. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (t, *J* = 7.4 Hz, 0.15H), 7.75 (t, *J* = 8.4 Hz, 0.85H), 7.58-7.55 (m, 0.30H), 7.46-7.41 (m, 0.15H), 7.31-7.28 (m, 0.15H), 7.10-7.03 (m, 2.55H), 6.94-6.85 (m, 1.20H), 6.79-6.74 (m, 2.55H), 5.74 (d, *J* = 4.4 Hz, 0.15H), 5.53 (d, *J* = 4.8 Hz, 0.15H), 5.49 (d, *J* = 5.2 Hz, 0.85H), 5.25 (d, *J* = 5.6 Hz, 0.85H), 3.84-3.78 (m, 3.00H), 3.29 (d, *J* = 4.8 Hz, 2.55H), 3.17 (d, *J* = 5.2 Hz, 0.45H); **^{13}C NMR** (100 MHz, $CDCl_3$) of the major peaks: δ 170.6, 159.5, 145.5, 144.8, 139.8, 129.7, 129.5, 129.2, 128.8, 127.4, 115.3, 113.7, 99.2, 55.3, 36.3; HRMS (ESI) calcd for $C_{17}H_{17}INO_2$ $[M+H]^+$ 394.0298, found 394.0298.



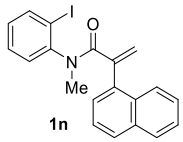
1l

2-(4-chlorophenyl)-N-(2-iodophenyl)-N-methylacrylamide (1l). 1l was prepared according to general procedure 2.2 and purified by column chromatography on silica gel (PE/EtOAc = 10 : 1) to obtain **1l** as white solid (794.0 mg, 40% yield). m.p. 110.7-111.3 °C; Two rotamers were observed in 17:3 (0.85:0.15) ratio. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11 (s, 0.15H), 7.94 (d, *J* = 8.0 Hz, 0.45H), 7.78-7.66 (m, 4.55H), 7.46-7.44 (m, 2.24H), 7.36 (d, *J* = 7.6 Hz, 0.15H), 7.21 (d, *J* = 8.4 Hz, 0.85H), 7.07 (t, *J* = 6.6 Hz, 0.15H), 6.91 (d, *J* = 7.2 Hz, 0.85H), 6.74 (t, *J* = 8.0 Hz, 0.85H), 6.00 (s, 0.15H), 5.74 (s, 0.15H), 5.70 (s, 0.85H), 5.47 (s, 0.85H), 3.34 (s, 2.55H), 3.18 (s, 0.45H); **^{13}C NMR** (100 MHz, $CDCl_3$) of the major peaks: δ 170.1, 145.3, 145.2, 139.7, 134.0, 132.9, 132.8, 129.6, 129.1, 128.7, 128.2, 128.0, 127.4, 126.1, 126.1, 125.3, 123.6, 117.2, 99.1, 36.2; HRMS (ESI) calcd for $C_{16}H_{14}ClINO$ $[M+H]^+$ 397.9803, found 397.9803.



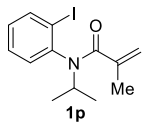
1m

N-(2-iodophenyl)-N-methyl-2-(4-(trifluoromethyl)phenyl)acrylamide (1m). **1m** was prepared according to general procedure 2.2 and purified by column chromatography on silica gel (PE/EtOAc = 10 : 1) to obtain **1m** as white solid (646.5 mg, 30% yield). m.p. 94.3-96.1 °C; Two rotamers were observed in 17:3 (0.85:0.15) ratio. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 0.15H), 7.75 (d, *J* = 8.0 Hz, 1.43H), 7.69 (d, *J* = 8.0 Hz, 0.30H), 7.47 (d, *J* = 7.6 Hz, 2.55H), 7.32-7.24 (m, 2.70H), 7.07 (t, *J* = 7.6 Hz, 1.30H), 6.90 (t, *J* = 7.6 Hz, 1.30H), 6.76 (d, *J* = 8.0 Hz, 1.20H), 5.97 (s, 0.15H), 5.79 (s, 0.15H), 5.75 (s, 0.85H), 5.43 (s, 0.85H), 3.30 (s, 2.55H), 3.19 (s, 0.45H); **^{13}C NMR** (100 MHz, $CDCl_3$) of the major peaks: δ 169.4, 145.1, 144.5, 140.4, 140.0, 129.7, 129.3, 128.9, 126.5, 125.3, 125.2, 125.2, 125.2, 119.8, 99.1, 36.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -162.6 (s, 3F); HRMS (ESI) calcd for $C_{17}H_{14}F_3INO$ $[M+H]^+$ 432.0067, found 432.0070.



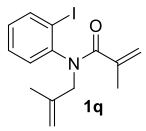
1n

N-(2-iodophenyl)-N-methyl-2-(naphthalen-1-yl)acrylamide (1n). **1n** was prepared according to general procedure 2.2 and purified by column chromatography on silica gel (PE/EtOAc = 10 : 1) to obtain **1n** as white solid (764.1 mg, 37% yield). m.p. 73.6-82.2 °C; Two rotamers were observed in 17:3 (0.85:0.15) ratio. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (d, J = 7.6 Hz, 0.15H), 7.75 (d, J = 8.0 Hz, 0.85H), 7.58 (d, J = 7.6 Hz, 0.30H), 7.44 (t, J = 7.4 Hz, 0.15H), 7.38 (d, J = 7.6 Hz, 0.3H), 7.30 (d, J = 6.4 Hz, 0.15H), 7.19 (d, J = 7.6 Hz, 1.90H), 7.08 (d, J = 6.0 Hz, 2.80H), 6.90 (t, J = 7.4 Hz, 0.85H), 6.78 (d, J = 7.6 Hz, 0.85H), 5.86 (s, 0.15H), 5.67 (s, 0.15H), 5.62 (s, 0.85H), 5.33 (s, 0.85H), 3.29 (s, 2.55H), 3.17 (s, 0.45H); **^{13}C NMR** (100 MHz, $CDCl_3$) of the major peaks: δ 169.6, 145.1, 144.2, 139.8, 135.2, 133.7, 129.5, 129.2, 128.7, 128.3, 127.3, 117.8, 99.0, 36.2; HRMS (ESI) calcd for $C_{20}H_{17}INO$ $[M+H]^+$ 414.0349, found 414.0350.



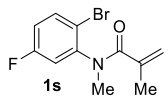
1p

N-(2-iodophenyl)-N-isopropylmethacrylamide (1p). 1p was prepared according to general procedure 2.1 and purified by column chromatography on silica gel (PE/EtOAc = 10 : 1) to obtain **1p** as white solid (131.7 mg, 40% yield). m.p. 62.9-69.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 4.97 (s, 2H), 4.60 (p, *J* = 6.6 Hz, 1H), 1.88 (s, 3H), 1.41 (d, *J* = 6.4 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.1, 141.1, 140.2, 130.7, 129.1, 128.5, 119.0, 102.9, 50.0, 22.3, 20.8, 19.3; HRMS (ESI) calcd for $C_{13}H_{17}INO$ $[M+H]^+$ 330.0349, found 330.0349.



1q

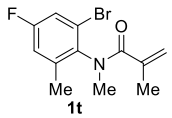
N-(2-iodophenyl)-N-(2-methylallyl)methacrylamide (1q). 1q was prepared according to general procedure 2.1 and purified by column chromatography on silica gel (PE/EtOAc = 10 : 1) to obtain **1q** as colorless oil (259.2 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 4.98-4.85 (m, 5H), 3.42 (d, *J* = 14.8 Hz, 1H), 1.79 (s, 3H), 1.73 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.1, 144.8, 140.2, 140.1, 140.1, 130.7, 129.2, 128.6, 118.6, 113.8, 99.8, 54.0, 20.7; HRMS (ESI) calcd for $C_{14}H_{17}INO$ $[M+H]^+$ 342.0349, found 342.0349.



1s

N-(2-bromo-5-fluorophenyl)-N-methylmethacrylamide (1s). 1s was prepared according to general procedure 2.1 and purified by column chromatography on silica gel (PE/EtOAc = 10 : 1) to obtain **1s** as yellow oil (184.3 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57-7.54 (m, 1H), 6.94-6.92 (m, 2H), 5.00 (s, 2H), 3.22 (s, 3H), 1.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.6, 161.8 (d, *J* = 248.4 Hz), 139.8, 134.5 (d, *J* = 8.7 Hz), 119.0, 117.3 (d, *J* = 3.0 Hz), 117.2 (d, *J* = 22.7 Hz), 116.5 (d, *J*

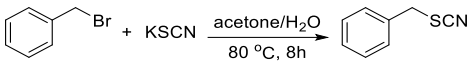
= 22.0 Hz), 36.3, 20.1; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -112.3 (s, 1F); HRMS (ESI) calcd for $C_{11}H_{12}BrFNO$ $[M+H]^+$ 272.0081, found 272.0085.



1t

N-(2-bromo-4-fluoro-6-methylphenyl)-N-methylmethacrylamide (1t). 1t was prepared according to general procedure 2.1 and purified by column chromatography on silica gel (PE/EtOAc = 10 : 1) to obtain **1t** as white solid; (199.5 mg, 70% yield). m.p. 56.7-59.5 °C; Two rotamers were observed in 9:1 (1.8:0.2) ratio. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22-7.18 (m, 1H), 6.95-6.91 (m, 1H), 5.32 (s, 0.10H), 5.28 (s, 0.10H), 5.00 (s, 0.90H), 4.96 (s, 0.90H), 3.23 (s, 0.30H), 3.16 (s, 2.70H), 2.28 (s, 2.70H), 2.25 (s, 0.30H), 2.06 (s, 0.30H), 1.84-1.79 (s, 2.70H); **^{13}C NMR** (100 MHz, $CDCl_3$) of the major peaks: δ 171.6, 171.5, 162.1, 159.6, 139.7, 139.6, 139.6, 124.5, 124.4, 118.5, 118.2, 117.1, 116.9, 35.4, 20.1, 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -112.0 (s, 1F); HRMS (ESI) calcd for $C_{12}H_{14}BrFNO$ $[M+H]^+$ 286.0237, found 286.0235.

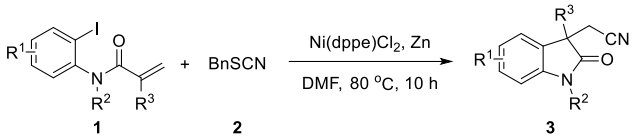
2.4 Synthesis of Benzyl Thiocyanate [5]



Benzyl bromide (1.710 g, 10.0 mmol, 1.0 equiv) and potassium thiocyanate (1.458 g, 15.0 mmol, 1.5 equiv) were added to 75 mL of water/acetone solution (4:1 vol %) in a Schlenk flask and heated at 80 °C for 8 h. After the completion, the layers were separated, and the aqueous layer was further extracted with diethylether (3 × 15 mL). The organic fractions were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc = 30 : 1) to afford the benzyl thiocyanate **2a** as white solid; m.p. 40.7-42.3 °C; (1.283 g, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40-7.34 (m, 5H), 4.14 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 134.3, 129.1, 128.9, 128.8, 112.0, 38.3; HRMS (ESI) calcd for C_8H_8NS $[M+H]^+$ 150.0372, found

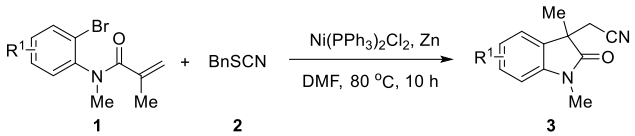
150.0376.

2.5 Typical Procedure for Isolated Products (Condition A)



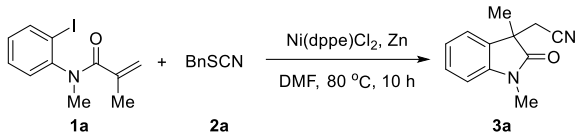
To a 25 mL of Schlenk tube were added N-arylacrylamide **1** (0.2 mmol, 1.0 equiv), benzylthiocyanate **2** (35.8 mg, 0.24 mmol, 1.2 equiv), $Ni(dppe)Cl_2$ (10.6 mg, 0.02 mmol, 10 mol%), zinc (39.6 mg, 0.6 mmol, 3.0 equiv). The mixture was evacuated and backfilled with N_2 for three times, DMF (1 mL) was then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 10 h, the reaction mixture was cooled to room temperature. The reaction was diluted with EtOAc (40 mL). After washed with water (2 × 15 mL) and brine (15 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure at 40 °C. The residue was purified with silica gel chromatography to give pure product **3**.

2.6 Typical Procedure for Isolated Products (Condition B)



To a 25 mL of Schlenk tube were added N-arylacrylamide **1** (0.2 mmol, 1.0 equiv), benzylthiocyanate **2** (35.8 mg, 0.24 mmol, 1.2 equiv), $Ni(PPh_3)_2Cl_2$ (14.0 mg, 0.02 mmol, 10 mol%), zinc (39.6 mg, 0.6 mmol, 3.0 equiv). The mixture was evacuated and backfilled with N_2 for three times, DMF (1 mL) was then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 10 h, the reaction mixture was cooled to room temperature. The reaction was diluted with EtOAc (40 mL). After washed with water (2 × 15 mL) and brine (15 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure at 40 °C. The residue was purified with silica gel chromatography to give pure product **3**.

2.7 Gram-scale Synthesis of Product 3a



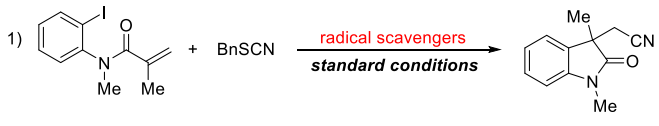
1a **2a** **3a**

A dry 100 mL Schlenk tube equipped with a stir bar was charged with N-arylacrylamide **1a** (1.2 g, 4.0 mmol, 1.0 equiv), benzylthiocyanate **2a** (715.3 mg, 4.8 mmol, 1.2 equiv), and then Ni(dppe)Cl_2 (211.2 mg, 0.4 mmol, 10 mol%), zinc (784.8 mg, 12 mmol, 3.0 equiv) were added in sequence. The mixture was evacuated and backfilled with N_2 for three times, DMF (20 mL) were then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 10 h, the reaction mixture was cooled to room temperature. The reaction was diluted with EtOAc (150 mL). After washed with water (2 × 50 mL) and brine (50 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure at 40 °C. The residue was purified with column chromatography on silica gel using PE/ EtOAc (6 : 1) as eluent to afford desired product **3a** as colorless oil (672.7 mg, 84% yield).

3. Mechanistic Investigations

3.1 Radical Trapping Experiments

1) Radical trapping experiments



1a **2a** **3a**

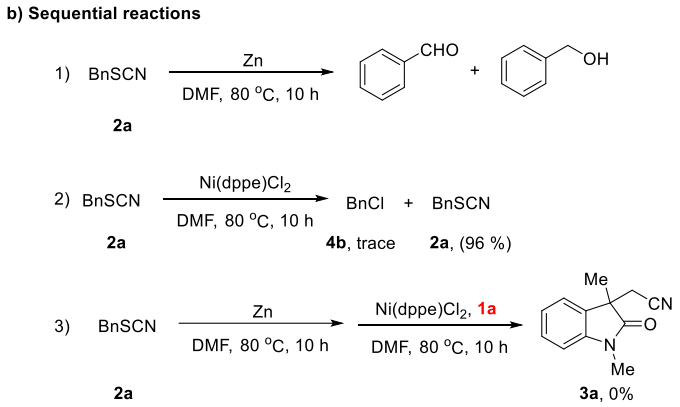
radical scavenger	yield of **3a**
TEMPO (2.0 equiv)	0%
BHT (2.0 equiv)	74%
1,1'-diphenylethylene (2.0 equiv)	49%

Experimental Procedure: To a 25 mL of Schlenk tube were added N-arylacrylamide **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), benzylthiocyanate **2a** (35.8 mg, 0.24 mmol, 1.2 equiv), Ni(dppe)Cl_2 (10.6 mg, 0.02 mmol, 10 mol%), zinc (39.6 mg, 0.6 mmol, 3.0

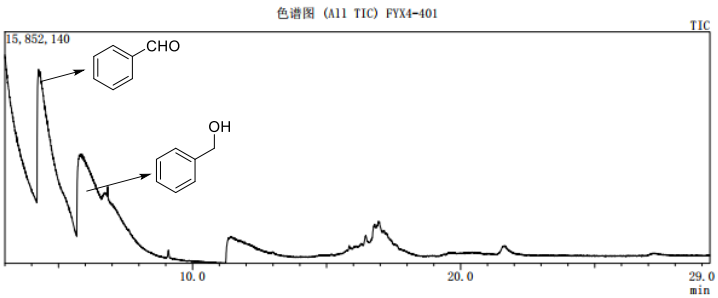
equiv). The mixture was evacuated and backfilled with N_2 for three times, radical scavenger (0.4 mmol, 2.0 equiv), DMF (1 mL) was then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 10 h, the reaction mixture was cooled to room temperature. The reaction was diluted with EtOAc (40 mL). After washed with water (2 × 15 mL) and brine (15 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure at 40 °C. The residue was purified with silica gel chromatography to give pure product **3a**.

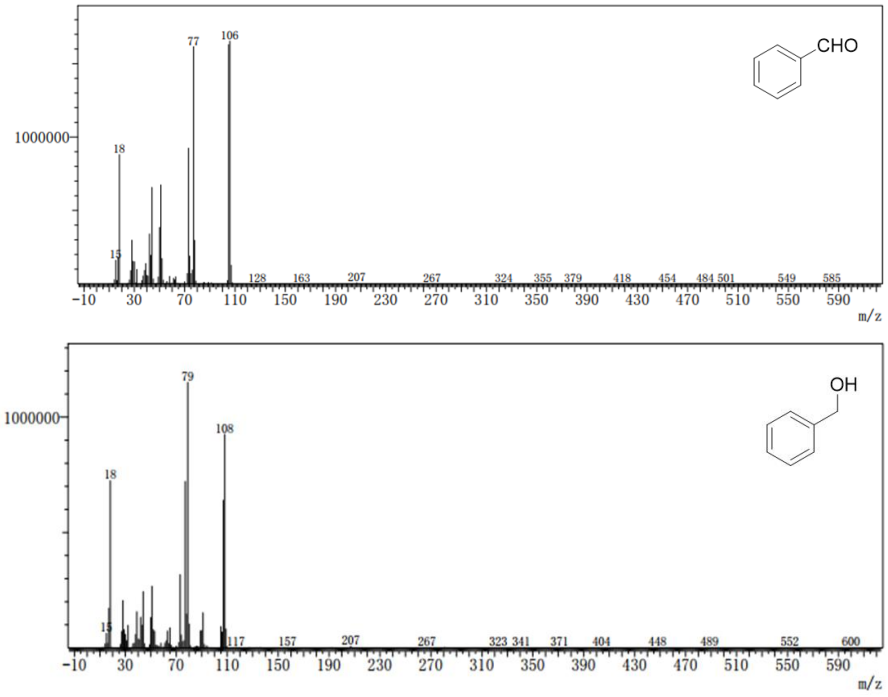
Conclusion: These results excluded the possibility of free radical intermediate involving in this reaction system.

3.2 Sequential Reactions

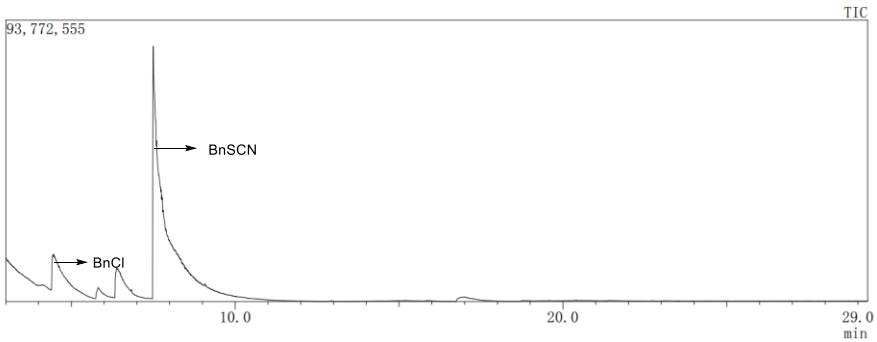


Experimental Procedure 1: To a 25 mL of Schlenk tube were added benzylthiocyanate **2a** (35.8 mg, 0.24 mmol), zinc (39.6 mg, 0.6 mmol). The mixture was evacuated and backfilled with N_2 for three times, DMF (1 mL) was then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 10 h, the reaction mixture was detected by TLC and GC-MS.





Experimental Procedure 2: To a 25 mL of Schlenk tube were added benzylthiocyanate **2a** (35.8 mg, 0.24 mmol), Ni(dppe)Cl_2 (10.6 mg, 0.02 mmol, 10 mol%). The mixture was evacuated and backfilled with N_2 for three times, DMF (1 mL) was then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 10 h, the reaction mixture was cooled to room temperature and detected by TLC and GC-MS. The reaction was then diluted with EtOAc (40 mL). After washed with water (2 × 15 mL) and brine (15 mL), the organic layer was dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure at 40 °C. The residue was purified with silica gel chromatography to recover **2a** (34.4 mg, 96%).

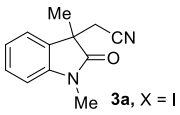


Experimental Procedure 3: To a 25 mL of Schlenk tube were added benzylthiocyanate **2a** (35.8 mg, 0.24 mmol), zinc (39.6 mg, 0.6 mmol). The mixture

was evacuated and backfilled with N_2 for three times, DMF (1 mL) was then added. The Schlenk tube was screw capped and put into a preheated oil bath (80 °C). After stirring for 10 h, N-arylacrylamide **1a** (60.2 mg, 0.2 mmol, 1.0 equiv), Ni(dppe)Cl_2 (10.6 mg, 0.02 mmol, 10 mol%) was added under N_2 atmosphere. After stirring for another 10 h, the reaction mixture was cooled to room temperature. Then the reaction was monitored by TLC.

Conclusion: These findings might rule out the formation of $Zn(CN)_2$ in situ.

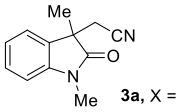
4. Characterization Data of Products



3a, X = I

2-(1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (3a)

3a was prepared according to general procedure 2.5 using **1a** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3a** as colorless oil (35.3 mg, 88% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.24 (s, 3H), 2.70 (dd, *J* = 114.8, 16.8 Hz, 2H), 1.52 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.4, 142.6, 130.9, 129.1, 123.2, 123.1, 116.6, 108.6, 44.8, 26.5, 26.3, 22.1; HRMS (ESI) calcd for $C_{12}H_{13}N_2O$ $[M+H]^+$ 201.1022, found 201.1022.

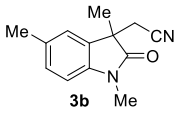


3a, X = OTf

2-(1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (3a, X = OTf)

3a was prepared according to general procedure 2.5 using **1a'** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3a** as colorless oil (34.1 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.23 (s, 3H), 2.70 (dd, *J* = 112.4, 16.8 Hz, 2H), 1.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.4, 142.6, 130.9, 129.1, 123.1, 123.0, 116.5, 108.6, 44.7, 26.4, 26.2, 22.1; HRMS

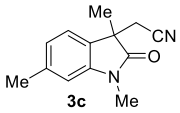
(ESI) calcd for $C_{12}H_{13}N_2O$ $[M+H]^+$ 201.1022, found 201.1022.



3b

2-(1,3,5-trimethyl-2-oxoindolin-3-yl)acetonitrile (3b)

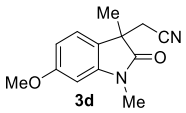
3b was prepared according to general procedure 2.5 using **1b** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3b** as colorless oil (32.2 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.22 (s, 3H), 2.70 (dd, *J* = 112.8, 16.4 Hz, 2H), 2.37 (s, 3H), 1.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.3, 140.1, 132.8, 130.9, 129.3, 123.8, 116.6, 108.3, 44.7, 26.4, 26.1, 22.1, 21.0; HRMS (ESI) calcd for $C_{13}H_{15}N_2O$ $[M+H]^+$ 215.1179, found 215.1179.



3c

2-(1,3,6-trimethyl-2-oxoindolin-3-yl)acetonitrile (3c)

3c was prepared according to general procedure 2.5 using **1c** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3c** as colorless oil (36.0 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.73 (s, 1H), 3.22 (s, 3H), 2.68 (dd, *J* = 112.8, 16.4 Hz, 2H), 2.40 (s, 3H), 1.50 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.7, 142.7, 139.4, 128.0, 123.6, 122.8, 116.7, 109.5, 44.6, 26.4, 26.3, 22.2, 21.8; HRMS (ESI) calcd for $C_{13}H_{15}N_2O$ $[M+H]^+$ 215.1179, found 215.1181.

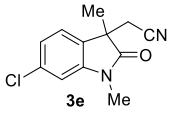


3d

2-(6-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (3d)

3d was prepared according to general procedure 2.5 using **1d** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 5 : 1) to obtain **3d** as white solid (33.6 mg, 73% yield). m.p. 70.5-72.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.49 (s, 1H), 3.84 (s, 3H), 3.22 (s, 3H), 2.68 (dd, *J* = 111.6, 16.4 Hz, 2H), 1.50 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ

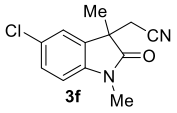
178.0, 160.8, 143.9, 123.7, 122.8, 116.7, 106.7, 96.7, 55.5, 44.4, 26.5, 26.4 22.2; HRMS (ESI) calcd for $C_{13}H_{15}N_2O_2$ $[M+H]^+$ 231.1128, found 231.1131.



3e

2-(6-chloro-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (3e)

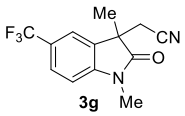
3e was prepared according to general procedure 2.5 using **1e** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3e** as white solid (38.0 mg, 81% yield). m.p. 65.6-65.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.90 (s, 1H), 3.22 (s, 3H), 2.69 (dd, *J* = 111.2, 16.4 Hz, 2H), 1.50 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.3, 143.9, 135.1, 129.2, 124.0, 123.0, 116.3, 109.4, 44.6, 26.6, 26.1, 22.1; HRMS (ESI) calcd for $C_{12}H_{12}ClN_2O$ $[M+H]^+$ 235.0633, found 235.0631.



3f

2-(5-chloro-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (3f)

3f was prepared according to general procedure 2.5 using **1f** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3f** as colorless oil (13.7 mg, 29% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 3.23 (s, 3H), 2.72 (dd, *J* = 97.6, 16.8 Hz, 2H), 1.52 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.0, 141.2, 132.5, 129.2, 128.7, 123.7, 116.2, 109.7, 45.1, 26.6, 26.1, 22.2; HRMS (ESI) calcd for $C_{12}H_{12}ClN_2O$ $[M+H]^+$ 235.0633, found 235.0635.

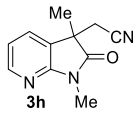


3g

2-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)acetonitrile (3g)

3g was prepared according to general procedure 2.5 using **1g** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3g** as colorless oil (17.7 mg, 33% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67-7.64 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 3.29 (s, 3H), 2.76 (dd, *J* = 104.8, 16.4 Hz, 2H), 1.55 (s, 3H);

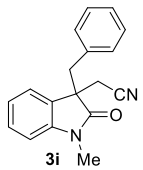
^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 145.7, 131.4, 127.1 (q, *J* = 3.9 Hz), 125.6 (q, *J* = 32.7 Hz), 122.7, 120.2 (q, *J* = 3.5 Hz), 116.0, 108.6, 45.0, 26.7, 26.1, 22.1; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -112.3 (s, 3F); HRMS (ESI) calcd for $C_{13}H_{12}F_3N_2O$ $[M+H]^+$ 269.0896, found 269.0896.



3h

2-(1,3-dimethyl-2-oxo-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetonitrile (3h)

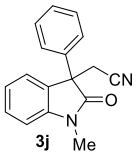
3h was prepared according to general procedure 2.5 using **1h** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 3 : 1) to obtain **3h** as colorless oil (23.0 mg, 57% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 5.2 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 6.2 Hz, 1H), 3.25 (s, 3H), 2.67 (dd, *J* = 135.2, 16.4 Hz, 2H), 1.49 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.0, 156.0, 148.0, 130.8, 125.3, 118.7, 116.3, 44.4, 25.7, 25.6, 21.6; HRMS (ESI) calcd for $C_{11}H_{12}N_3O$ $[M+H]^+$ 202.0975, found 202.0979.



3i

2-(3-benzyl-1-methyl-2-oxoindolin-3-yl)acetonitrile (3i)

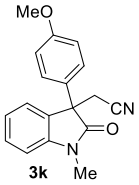
3i was prepared according to general procedure 2.5 using **1i** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3i** as colorless oil (44.2 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.14-7.03 (m, 4H), 6.83 (d, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 3.22 (q, *J* = 12.1 Hz, 2H), 2.99-2.82 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.1, 143.2, 134.1, 129.7, 129.18, 128.3, 127.7, 127.0, 123.8, 122.8, 116.5, 108.3, 50.4, 42.3, 26.1, 25.0; HRMS (ESI) calcd for $C_{18}H_{17}N_2O$ $[M+H]^+$ 263.1179, found 263.1179.



3j

2-(1-methyl-2-oxo-3-phenylindolin-3-yl)acetonitrile (3j)

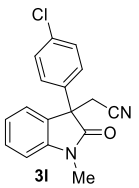
3j was prepared according to general procedure 2.5 using **1j** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3j** as colorless oil (38.9 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.34 (s, 5H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 3.41-3.03 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.7, 143.6, 136.4, 129.7, 129.4, 129.0, 128.4 126.7, 125.2, 123.4, 116.4, 109.0, 52.6, 26.8, 26.4; HRMS (ESI) calcd for $C_{17}H_{15}N_2O$ $[M+H]^+$ 263.1179, found 263.1182.



3k

2-(3-(4-methoxyphenyl)-1-methyl-2-oxoindolin-3-yl)acetonitrile (3k)

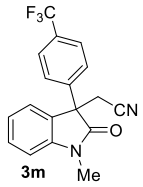
3k was prepared according to general procedure 2.5 using **1k** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 5 : 1) to obtain **3k** as colorless oil (36.3 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 3.38-2.93 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.9, 159.5, 143.5, 129.6, 129.5, 128.2, 128.0, 125.1, 123.3, 116.5, 114.2, 108.9, 55.2, 51.9, 26.7, 26.5; HRMS (ESI) calcd for $C_{18}H_{17}N_2O_2$ $[M+H]^+$ 293.1285, found 293.1285.



3l

2-(3-(4-chlorophenyl)-1-methyl-2-oxoindolin-3-yl)acetonitrile (3l)

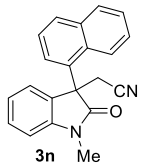
3l was prepared according to general procedure 2.5 using **1l** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3l** as colorless oil (36.7 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.31 (s, 4H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 3.38-2.96 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.2, 143.4, 134.8, 134.5, 129.9, 129.0, 128.8, 128.2, 125.1, 123.5, 116.2, 109.1, 52.0, 26.7, 26.4; HRMS (ESI) calcd for $C_{17}H_{14}ClN_2O$ $[M+H]^+$ 297.0789, found 297.0789.



3m

2-(1-methyl-2-oxo-3-(4-(trifluoromethyl)phenyl)indolin-3-yl)acetonitrile (3m)

3m was prepared according to general procedure 2.5 using **1m** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3m** as colorless oil (42.3 mg, 64% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62-7.46 (m, 6H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 3.44-3.00 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.8, 143.4, 140.3, 130.5 (q, *J* = 51.4 Hz), 130.1, 128.5, 127.3, 125.8 (q, *J* = 3.7 Hz), 125.1, 123.7 (q, *J* = 270.5 Hz), 123.6, 116.1, 109.3, 52.4, 26.8, 26.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -62.8 (s, 3F); HRMS (ESI) calcd for $C_{18}H_{14}F_3N_2O$ $[M+H]^+$ 331.1053, found 331.1052.

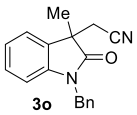


3n

2-(1-methyl-3-(naphthalen-1-yl)-2-oxoindolin-3-yl)acetonitrile (3n)

3n was prepared according to general procedure 2.5 using **1n** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3n** as colorless oil (40.6 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82-7.75 (m, 4H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.47-7.45 (m, 4H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 3.50-3.11 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.6, 143.5, 133.7,

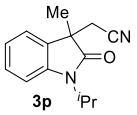
132.9, 132.8, 129.7, 129.4, 128.9, 128.2, 127.4, 126.6, 126.4, 126.0, 125.2, 124.0, 123.4, 116.4, 109.0, 52.8, 26.7, 26.2; HRMS (ESI) calcd for $C_{21}H_{17}N_2O$ $[M+H]^+$ 313.1335, found 313.1333.



3o

2-(1-benzyl-3-methyl-2-oxoindolin-3-yl)acetonitrile (3o)

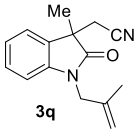
3o was prepared according to general procedure 2.5 using **1o** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3o** as colorless oil (44.2 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.6 Hz, 1H), 7.34-7.21 (m, 6H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 4.93 (s, 2H), 2.78 (dd, *J* = 104.4, 16.4 Hz, 2H), 1.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.6, 141.7, 135.2, 130.9, 129.0, 128.8, 127.8, 127.1, 123.2, 123.1, 116.5, 109.7, 44.9, 43.9, 26.2, 22.5; HRMS (ESI) calcd for $C_{18}H_{17}N_2O$ $[M+H]^+$ 277.1335, found 277.1335.



3p

2-(1-isopropyl-3-methyl-2-oxoindolin-3-yl)acetonitrile (3p)

3p was prepared according to general procedure 2.5 using **1p** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3p** as colorless oil (38.8 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 6.0 Hz, 1H), 7.32 (t, *J* = 6.8 Hz, 1H), 7.15-7.03 (m, 2H), 4.62 (s, 1H), 2.70 (dd, *J* = 89.6, 16.8 Hz, 2H), 1.49 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.1, 141.1, 140.2, 130.7, 129.1, 128.5, 119.0, 102.9, 50.0, 22.3, 20.8, 19.28, 19.26; HRMS (ESI) calcd for $C_{14}H_{17}N_2O$ $[M+H]^+$ 229.1335, found 229.1335.

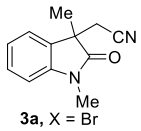


3q

2-(3-methyl-1-(2-methylallyl)-2-oxoindolin-3-yl)acetonitrile (3q)

3q was prepared according to general procedure 2.5 using **1q** and **2a** and was

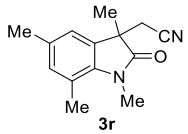
purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3q** as colorless oil (36.6 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 4.91 (d, *J* = 34.0 Hz, 2H), 4.29 (dd, *J* = 20.0 Hz, 16.8 Hz, 2H), 2.75 (dd, *J* = 103.2, 16.8 Hz, 2H), 1.73 (s, 3H), 1.54 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.4, 142.0, 138.5, 130.8, 129.1, 123.2, 123.0, 116.6, 112.8, 109.7, 45.9, 44.9, 26.2, 22.6, 19.8; HRMS (ESI) calcd for $C_{15}H_{17}N_2O$ $[M+H]^+$ 241.3355, found 241.3355.



3a, X = Br

2-(1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (3a, X = Br)

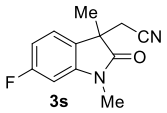
3a was prepared according to general procedure 2.6 using **1a**" and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3a** as colorless oil (24.5 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.25 (s, 3H), 2.71 (dd, *J* = 116.8, 16.8 Hz, 2H), 1.53 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.5, 142.6, 131.0, 129.2, 123.2, 123.1, 116.6, 108.7, 44.8, 26.5, 26.3, 22.1; HRMS (ESI) calcd for $C_{12}H_{13}N_2O$ $[M+H]^+$ 201.1022, found 201.1022.



3r

2-(1,3,5,7-tetramethyl-2-oxoindolin-3-yl)acetonitrile (3r)

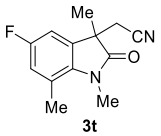
3r was prepared according to general procedure 2.6 using **1r** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3r** as colorless oil (16.9 mg, 37% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.10 (s, 1H), 6.88 (s, 1H), 3.49 (s, 3H), 2.83-2.53 (m, 5H), 2.31 (s, 3H), 1.48 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 178.2, 137.9, 133.3, 132.7, 131.7, 121.6, 120.0, 116.7, 44.2, 29.8, 26.5, 22.6, 20.8, 18.8; HRMS (ESI) calcd for $C_{14}H_{17}N_2O$ $[M+H]^+$ 229.1135, found 229.1135.



3s

2-(6-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)acetonitrile (3s)

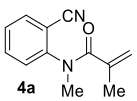
3s was prepared according to general procedure 2.6 using **1s** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3s** as colorless oil (13.6 mg, 31% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45-7.38 (m, 1H), 6.81 (t, *J* = 8.8 Hz, 1H), 6.65 (d, *J* = 8.8 Hz, 1H), 3.23 (s, 3H), 2.69 (dd, *J* = 112.0, 16.8 Hz, 2H), 1.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.7, 163.5 (d, *J* = 245.2 Hz), 144.2 (d, *J* = 11.5 Hz), 126.2 (d, *J* = 2.7 Hz), 124.3 (d, *J* = 9.8 Hz), 116.4, 109.3 (d, *J* = 22.4 Hz), 97.6 (d, *J* = 27.5 Hz), 44.5, 26.6, 26.3, 22.2; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -110.4 (s, 1F); HRMS (ESI) calcd for $C_{12}H_{12}FN_2O$ $[M+H]^+$ 219.0928, found 219.0928.



3t

2-(5-fluoro-1,3,7-trimethyl-2-oxoindolin-3-yl)acetonitrile (3t)

3t was prepared according to general procedure 2.6 using **1t** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **3t** as colorless oil (21.4 mg, 31% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.03 (d, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 9.6 Hz, 1H), 3.50 (s, 3H), 2.84-2.54 (m, 5H), 1.48 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 178.0, 158.9 (d, *J* = 241.3 Hz), 136.3 (d, *J* = 2.3 Hz), 133.1 (d, *J* = 8.3 Hz), 122.0 (d, *J* = 7.4 Hz), 118.9 (d, *J* = 22.6 Hz), 116.3, 108.8 (d, *J* = 24.2 Hz), 44.7, 29.9, 26.4, 22.5, 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -119.9 (s, 1F); HRMS (ESI) calcd for $C_{13}H_{14}FN_2O$ $[M+H]^+$ 233.1085, found 233.1085.



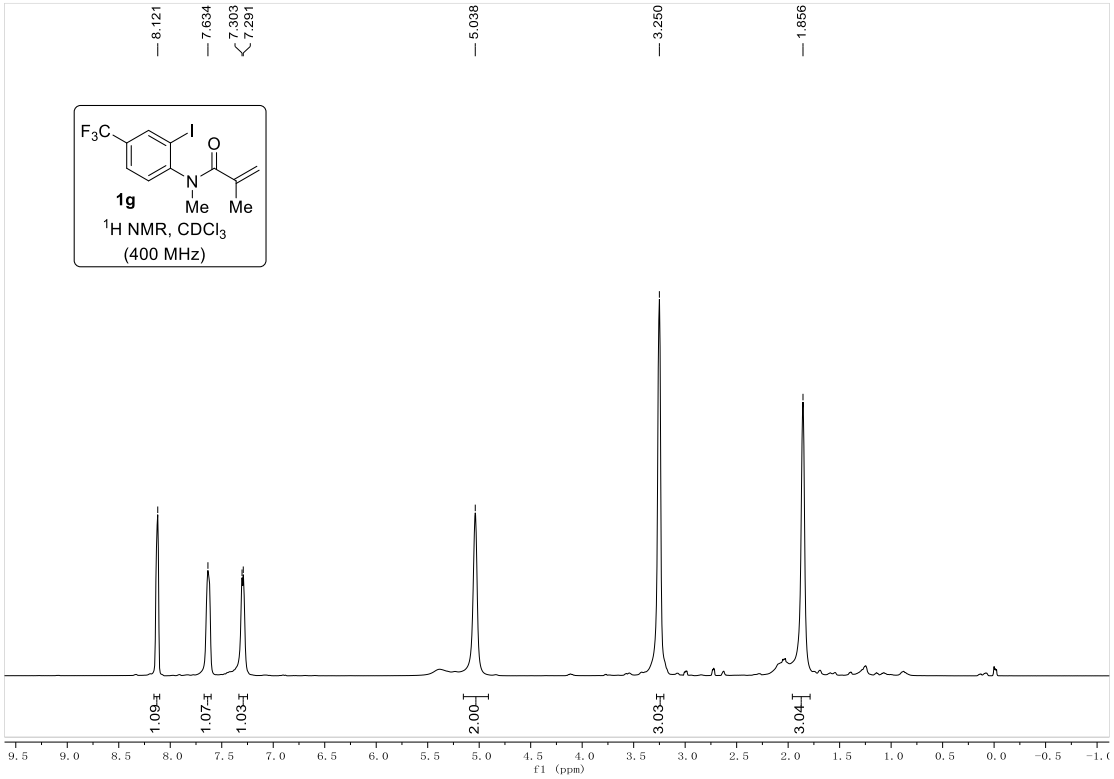
4a

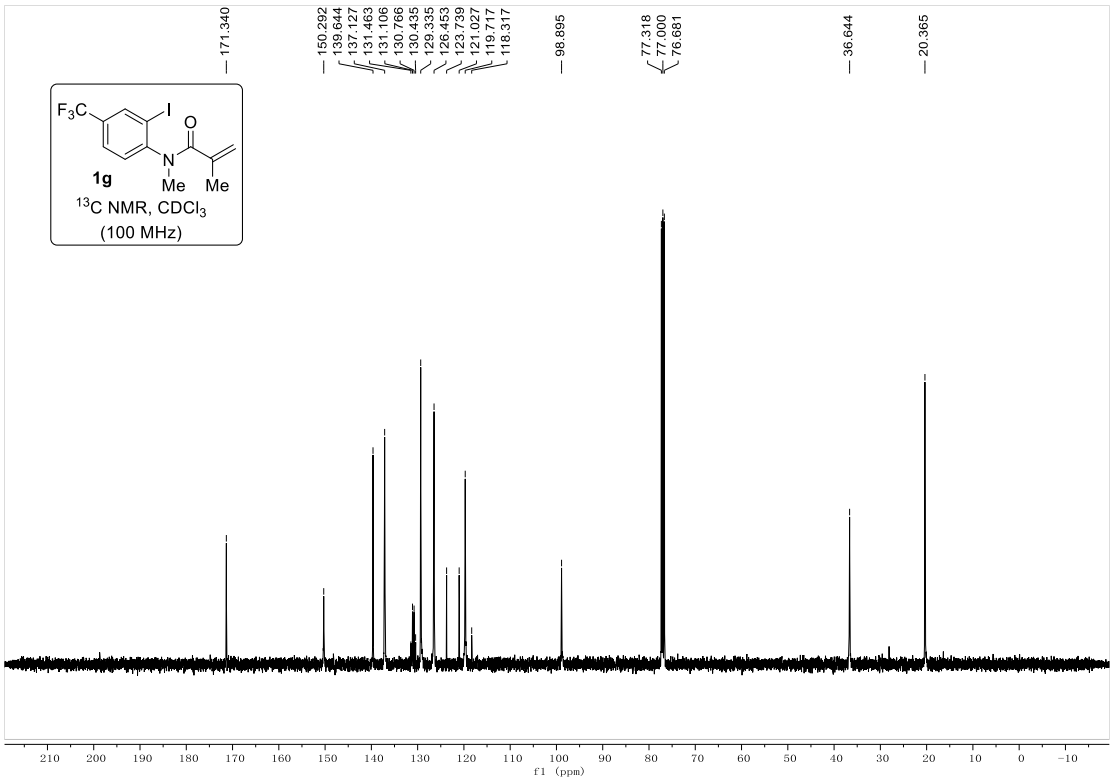
2-(5-fluoro-1,3,7-trimethyl-2-oxoindolin-3-yl)acetonitrile (4a)

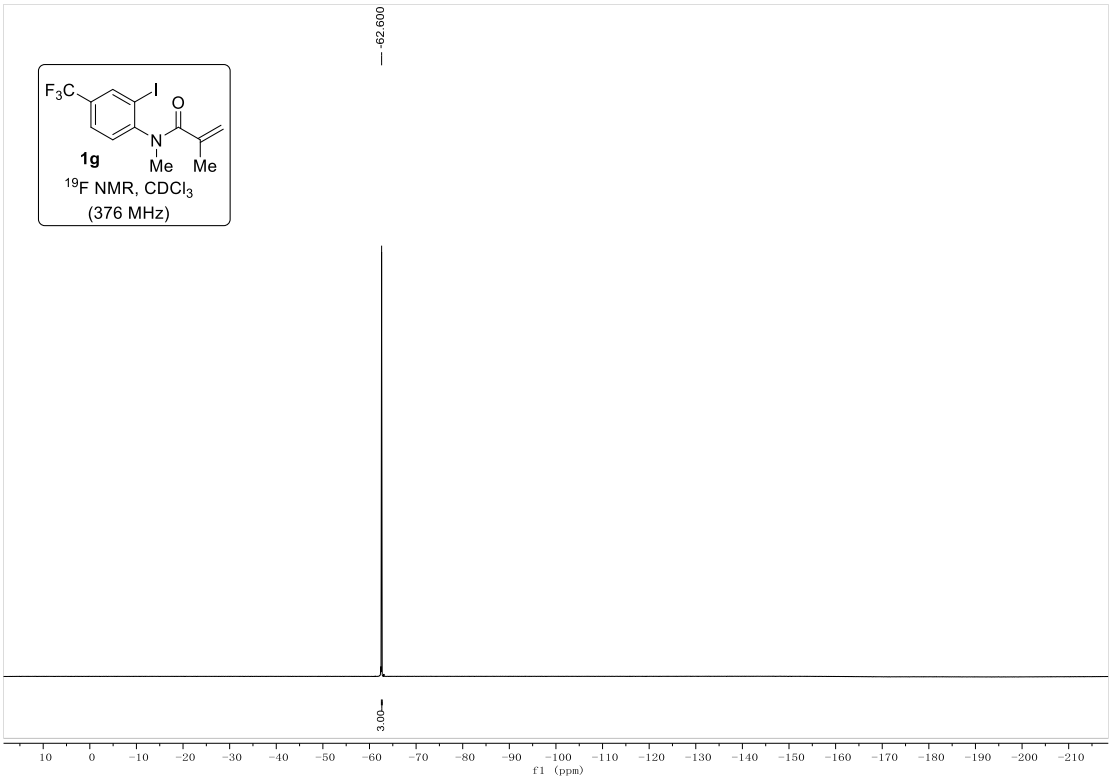
4a was obtained using **1a** and **2a** and was purified by silica gel column chromatography (PE/EtOAc = 6 : 1) to obtain **4a** as colorless oil (12.0 mg, 30% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 6.0 Hz, 1H), 5.07 (d, *J* = 41.6 Hz, 2H), 3.40 (s, 3H), 1.89 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.7, 147.5, 139.9, 133.9, 133.8, 128.7, 127.85, 120.0, 116.2, 111.9, 37.7, 20.1; HRMS (ESI) calcd for $C_{12}H_{13}N_2O$ $[M+H]^+$ 201.1022, found 201.1022.

5. Data of the ^{1}H、^{13}C and ^{19}F NMR Spectra



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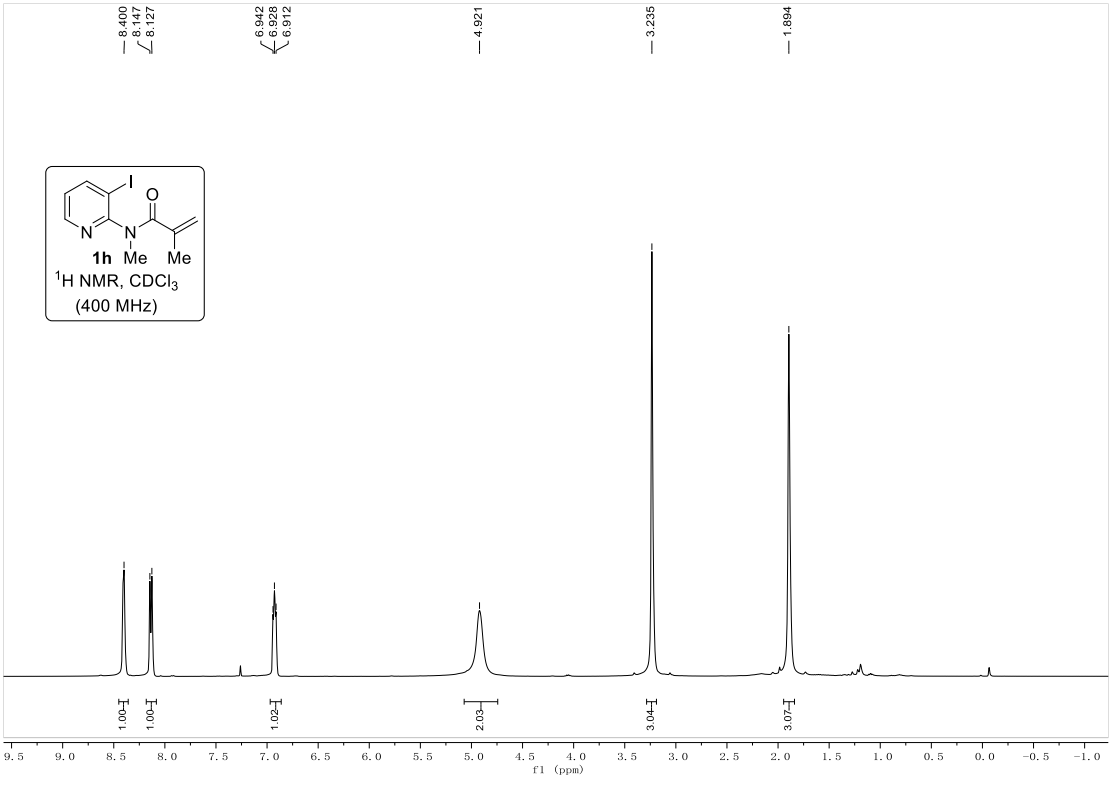
F3C
I
O
N
Me
Me
1g
19F NMR, CDCl3
(376 MHz)
3.00
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)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8.147
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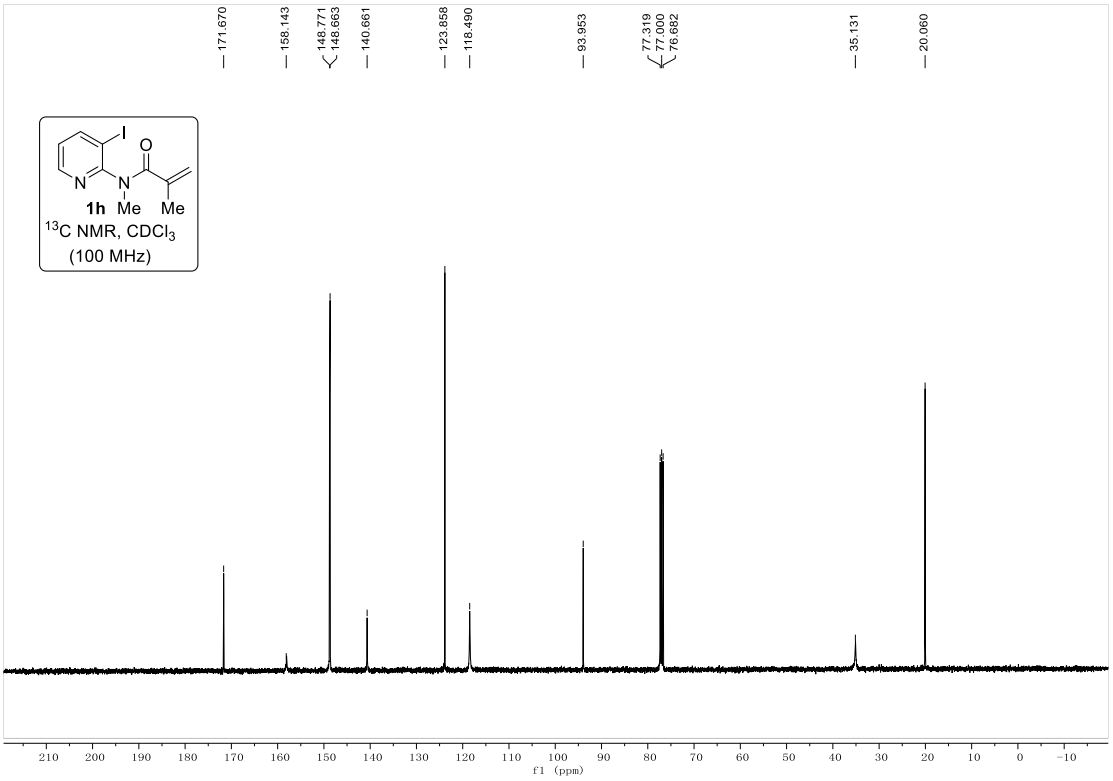
6.942
6.928
6.912
4.921
3.235
1.894
I
O
N
N
Me
Me
1h
1H NMR, CDCl3
(400 MHz)
1.00
1.00
1.02
2.03
3.04
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)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148.663
140.661
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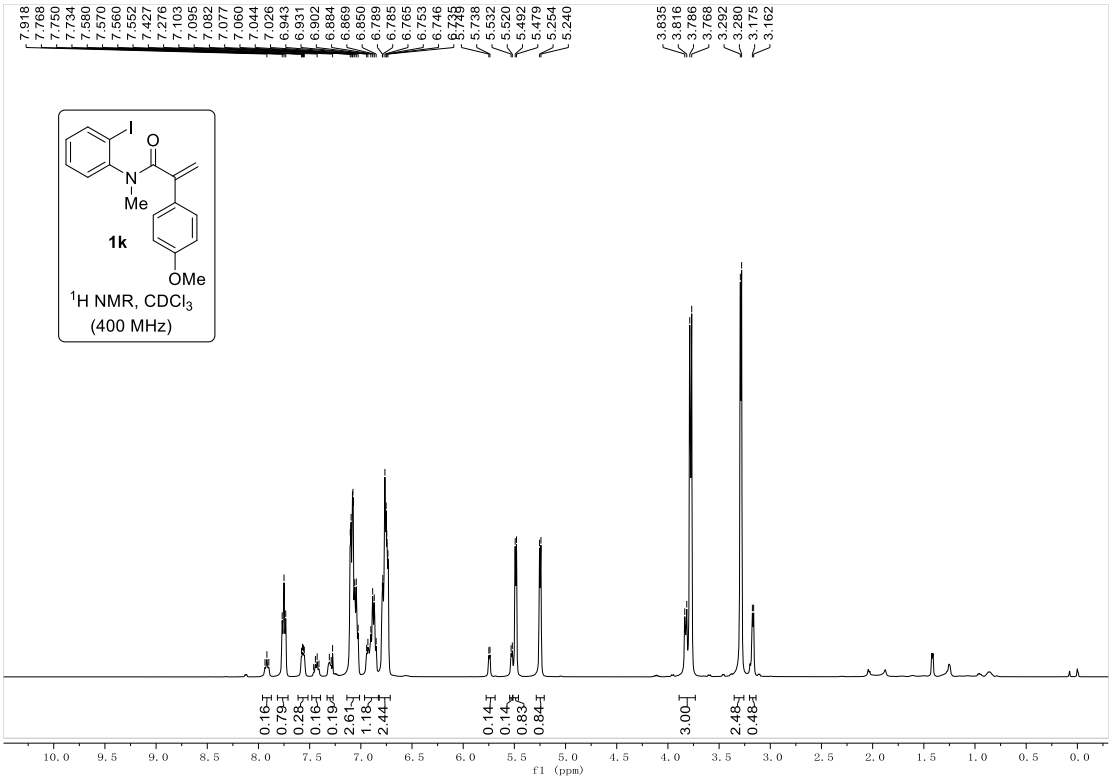
93.953
77.319
77.000
76.682
35.131
20.060
1h Me Me
13C NMR, CDCl3
(100 MHz)
f1 (ppm)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7.570
7.560
7.552
7.427
7.276
7.103
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7.077
7.060
7.044
7.026
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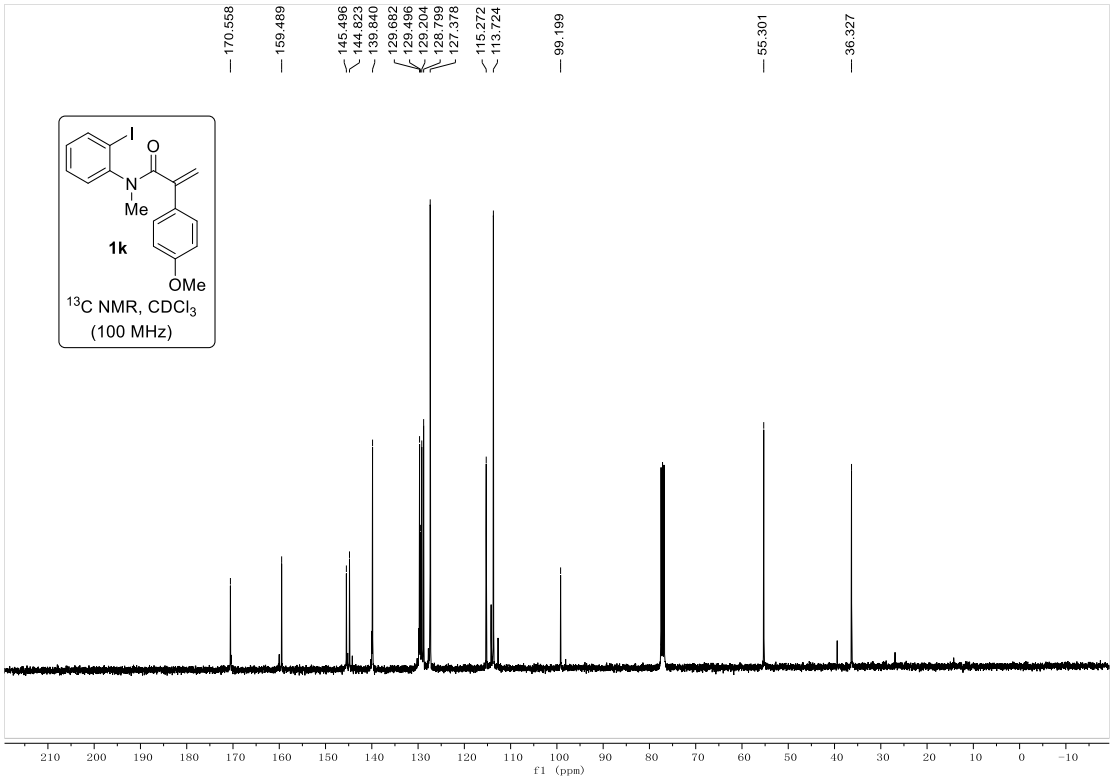
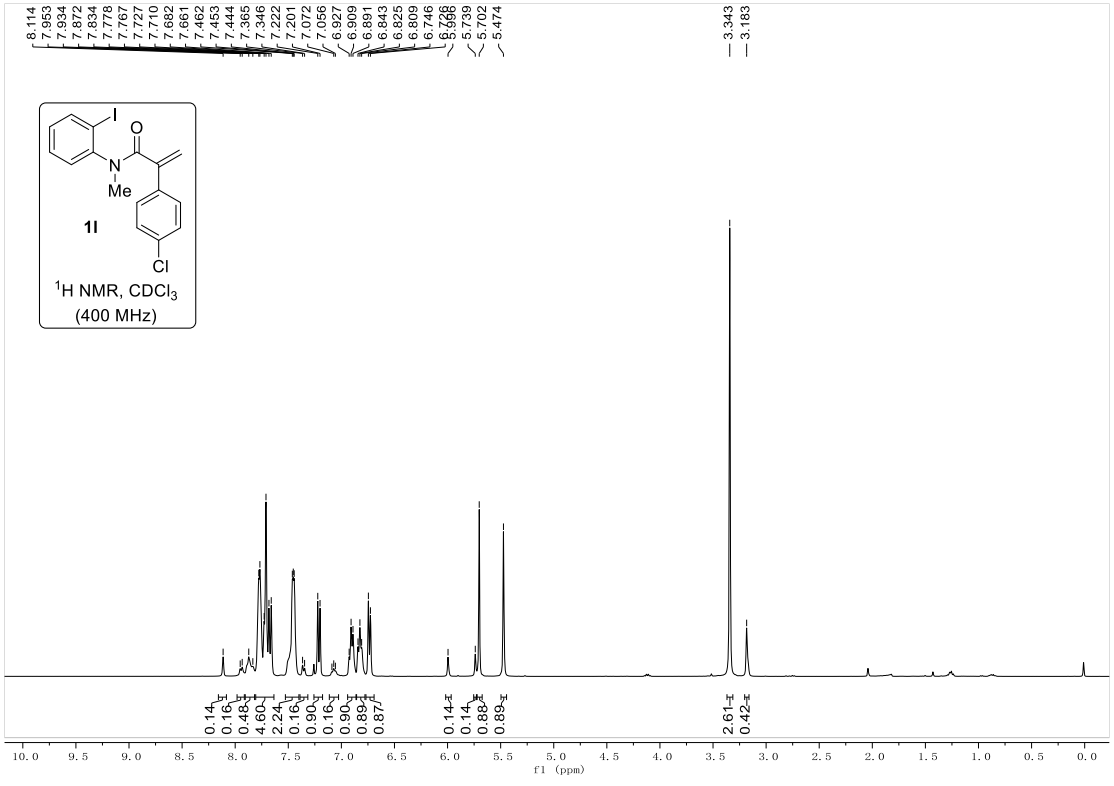
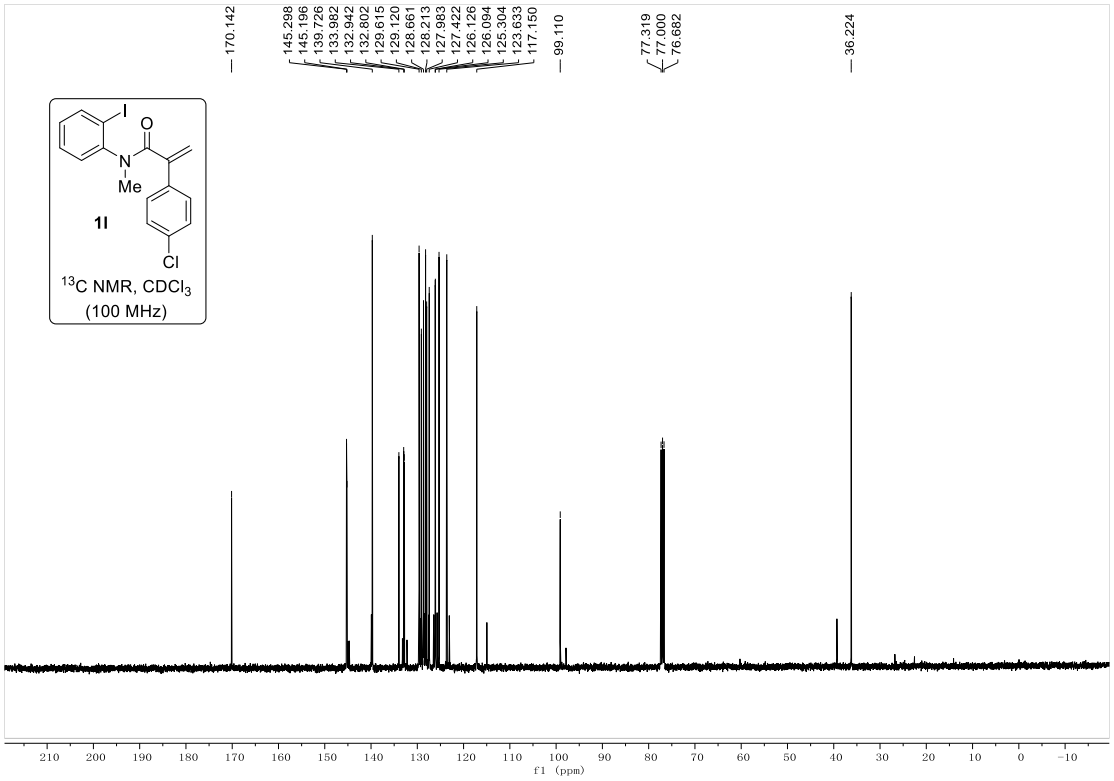
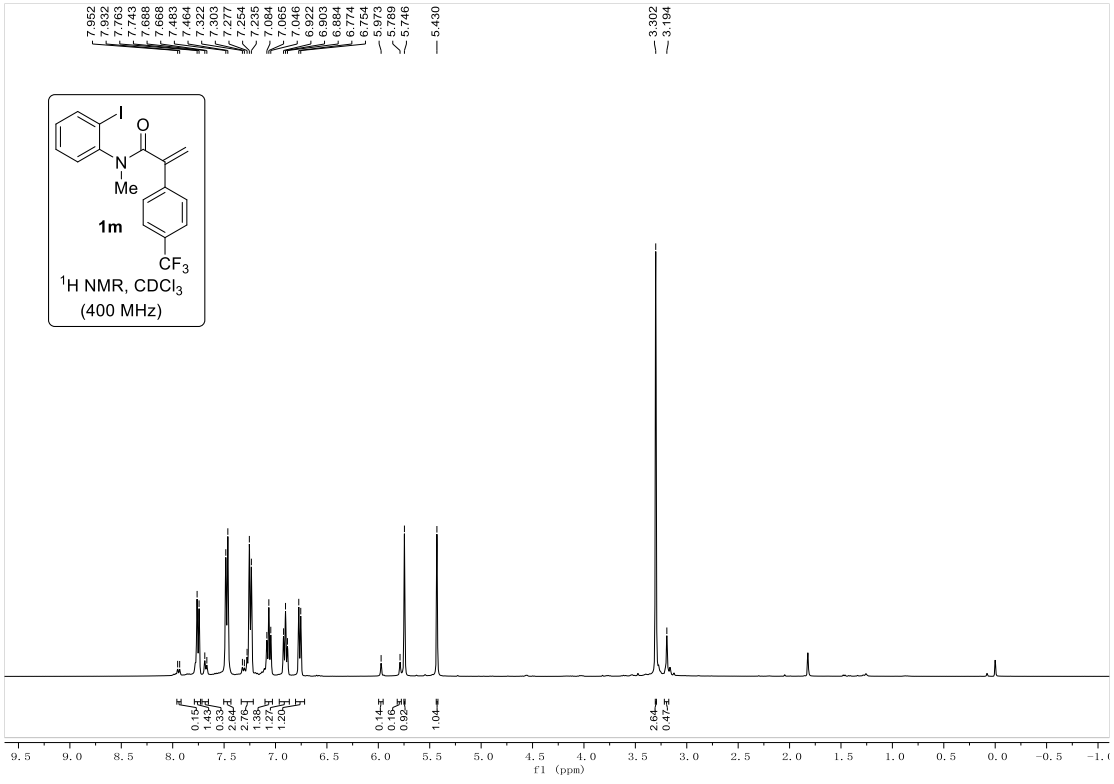
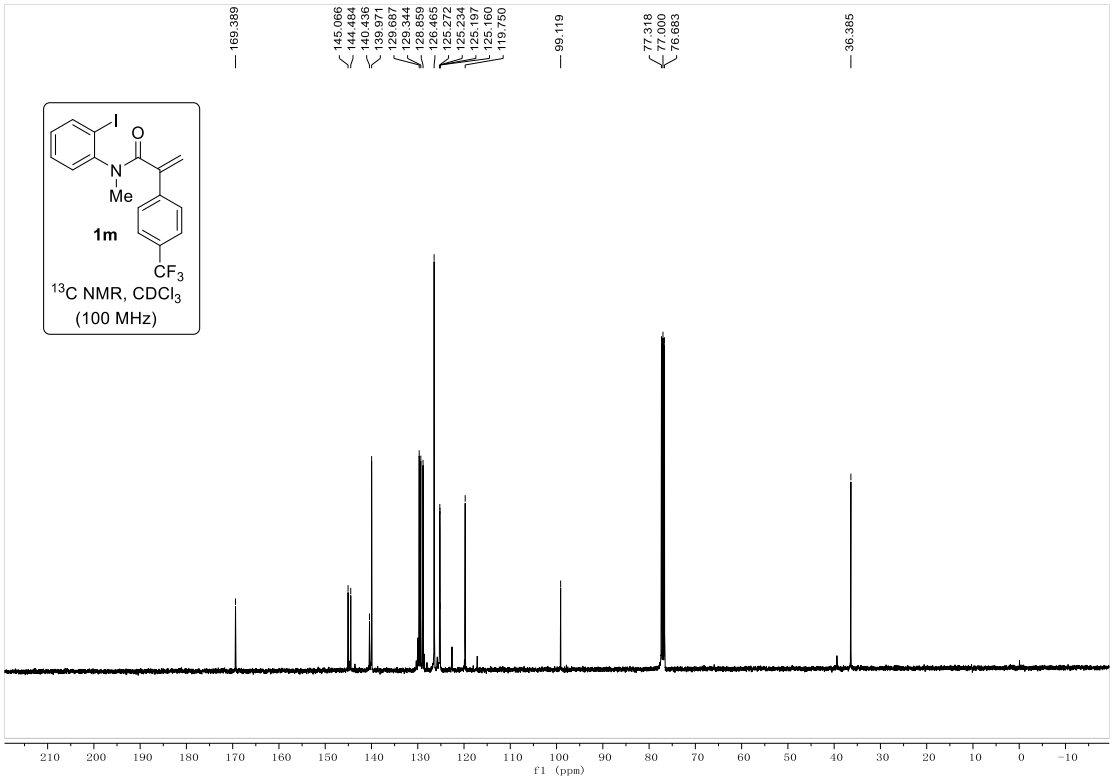
6.931
6.902
6.884
6.869
6.850
6.789
6.785
6.765
6.753
6.746
5.738
5.532
5.520
5.492
5.479
5.254
5.240
3.835
3.816
3.786
3.768
3.292
3.280
3.175
3.162
Me
1k
OMe
1H NMR, CDCl3
(400 MHz)
0.16
0.79
0.28
0.16
0.19
2.61
1.18
2.44
0.14
0.14
0.83
0.84
3.00
2.48
0.48
f1 (ppm)

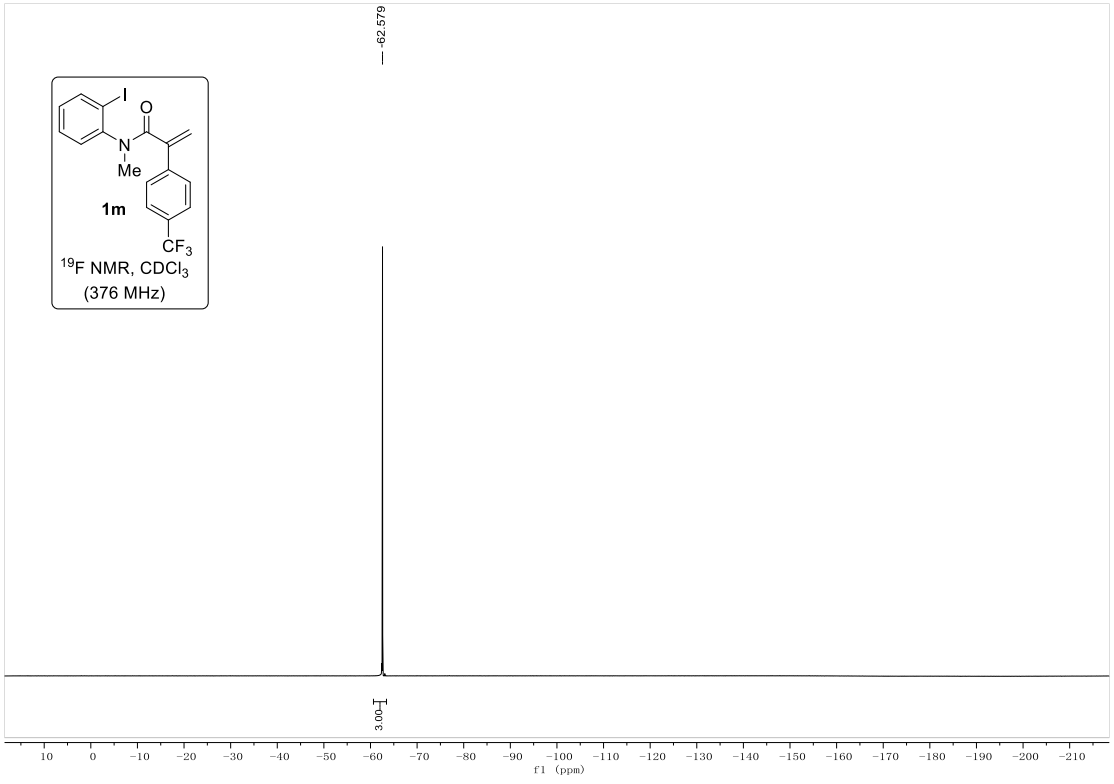

170.558
159.489
145.496
144.823
139.840
129.682
129.496
129.204
128.799
127.378
115.272
113.724
99.199
55.301
36.327
1k
OMe
13C NMR, CDCl3
(100 MHz)
f1 (ppm)

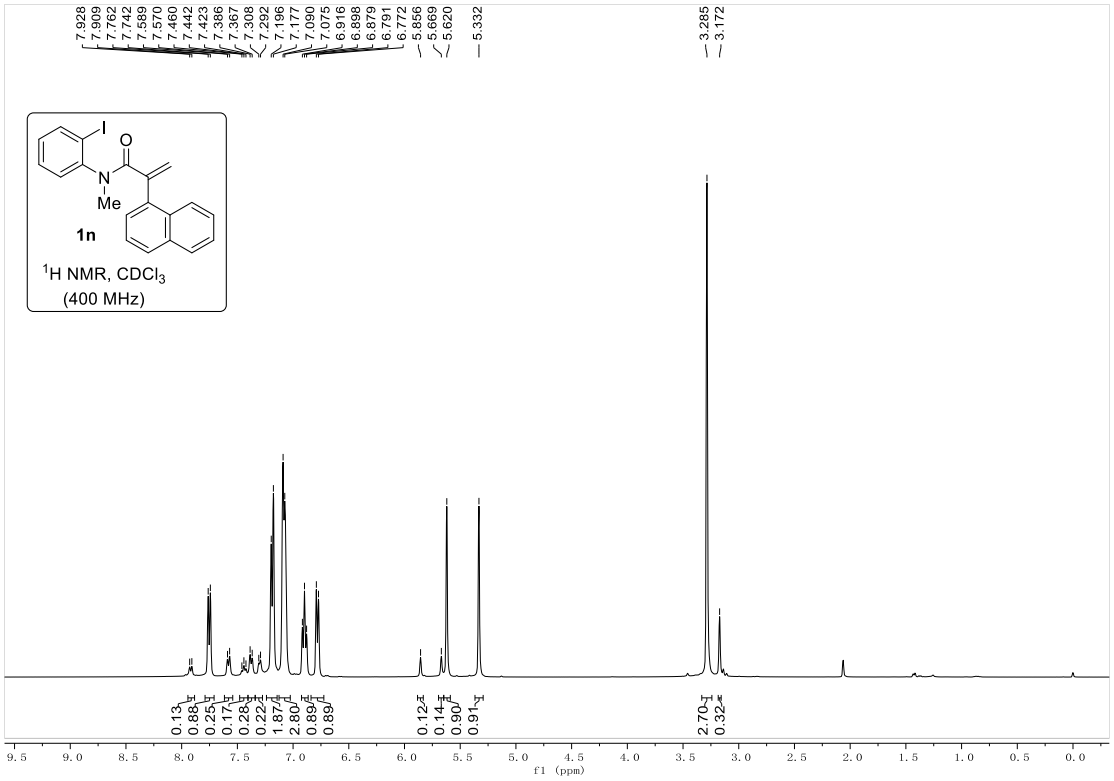

8.114
7.953
7.934
7.872
7.834
7.778
7.767
7.727
7.710
7.682
7.661
7.462
7.453
7.444
7.365
7.346
7.222
7.201
7.072
7.056
6.927
6.909
6.891
6.843
6.825
6.809
6.746
6.726
5.998
5.739
5.702
5.474
3.343
3.183
1l
Cl
1H NMR, CDCl3
(400 MHz)
0.14
0.16
0.48
4.60
2.24
0.16
0.90
0.16
0.90
0.89
0.87
0.14
0.14
0.88
0.89
2.61
0.42
f1 (ppm)

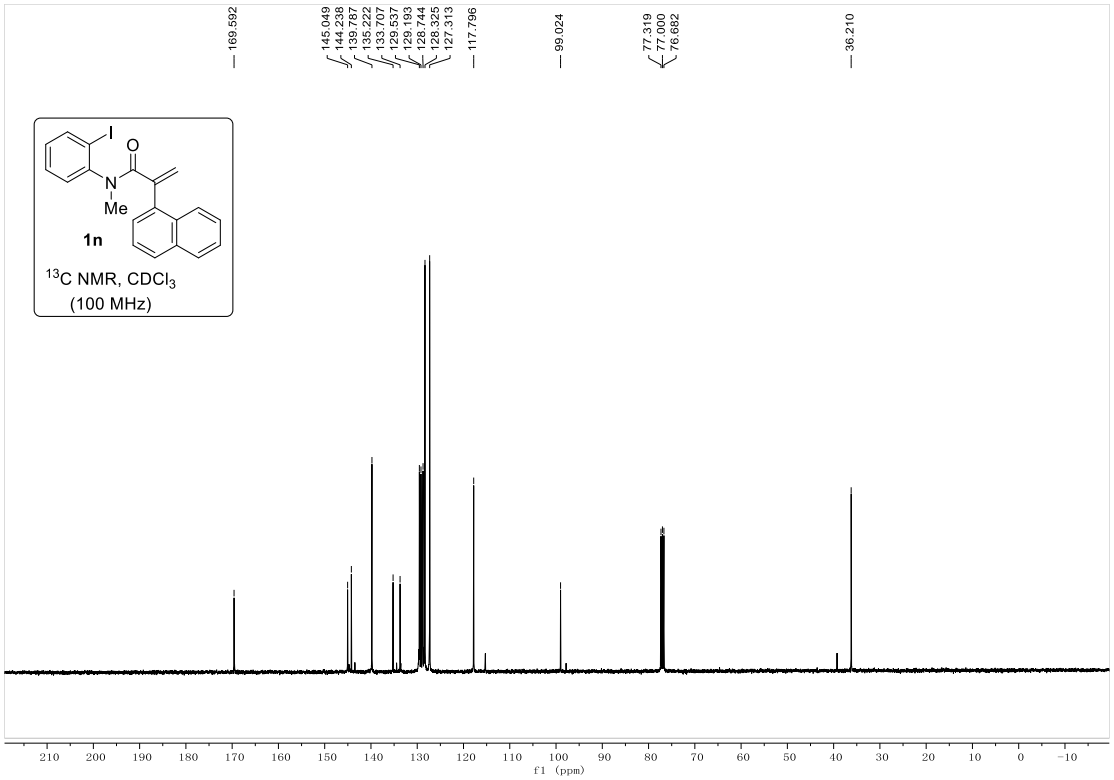

170.142
145.298
145.196
139.726
133.982
132.942
132.802
129.615
129.120
128.661
128.213
127.983
127.422
126.126
126.094
125.304
123.633
117.150
99.110
77.319
77.000
76.682
36.224
1l
^{13}C NMR, CDCl$_3$
(100 MHz)
f1 (ppm)

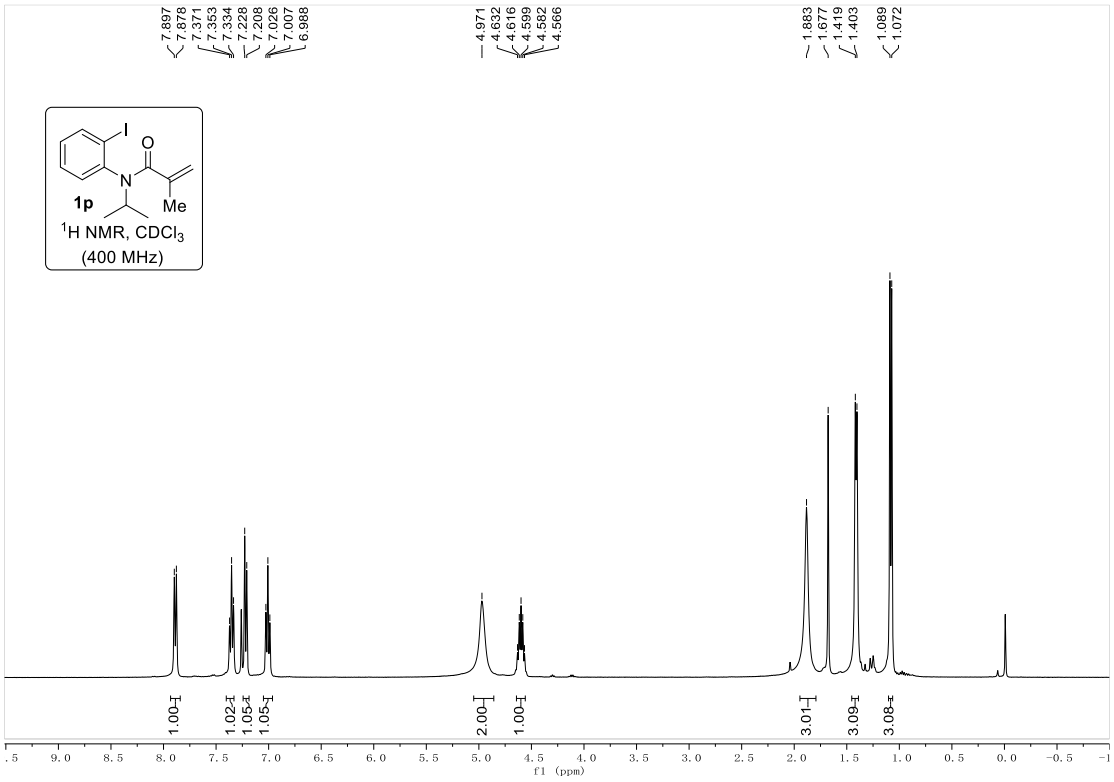

7.952
7.932
7.763
7.743
7.688
7.668
7.483
7.464
7.322
7.303
7.277
7.254
7.235
7.084
7.065
7.046
6.922
6.903
6.884
6.774
6.754
5.973
5.789
5.746
5.430
3.302
3.194
1m
^{1}H NMR, CDCl$_3$
(400 MHz)
f1 (ppm)

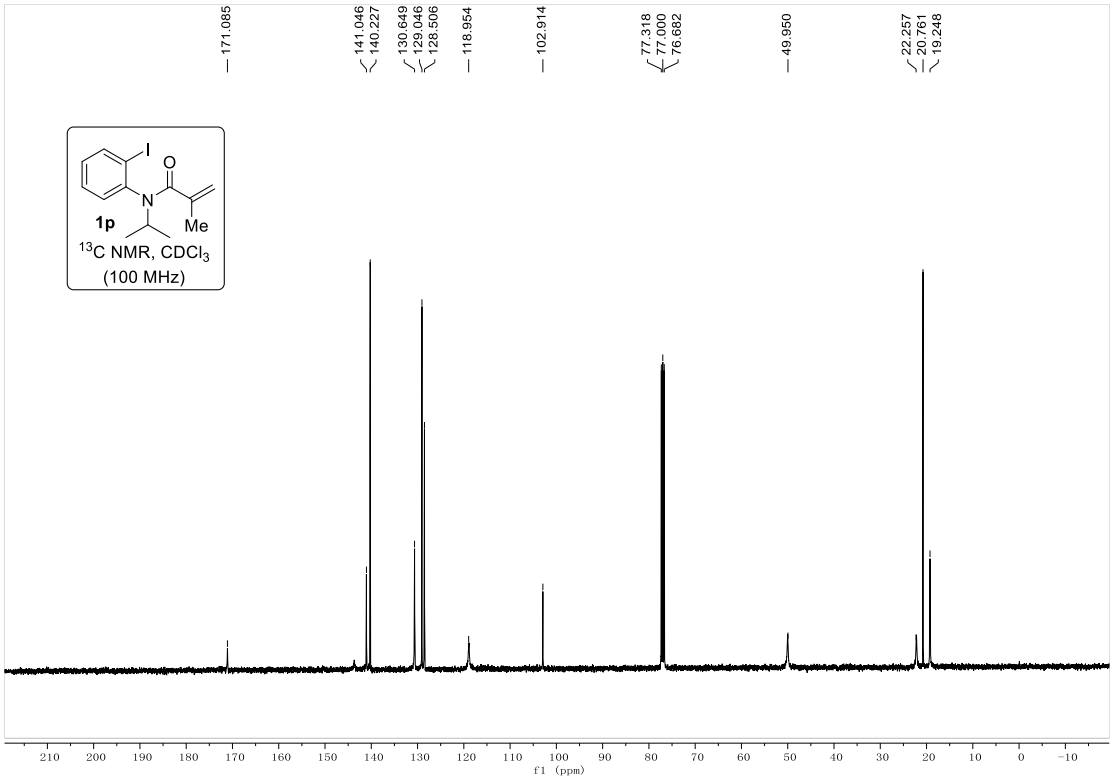

169.389
145.066
144.484
140.436
139.971
129.687
129.344
128.859
126.465
125.272
125.234
125.197
125.160
119.750
99.119
77.318
77.000
76.683
36.385
1m
^{13}C NMR, CDCl$_3$
(100 MHz)
f1 (ppm)

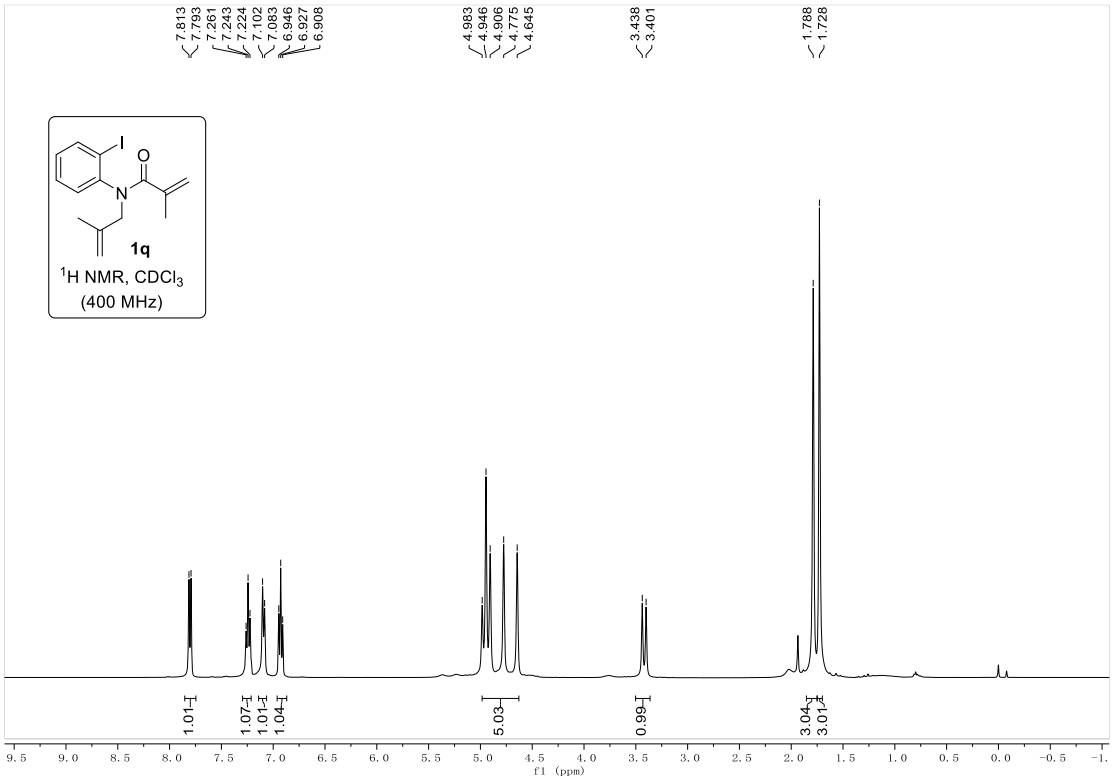

-62.579
3.00
1m
^{19}F NMR, CDCl$_3$
(376 MHz)
f1 (ppm)

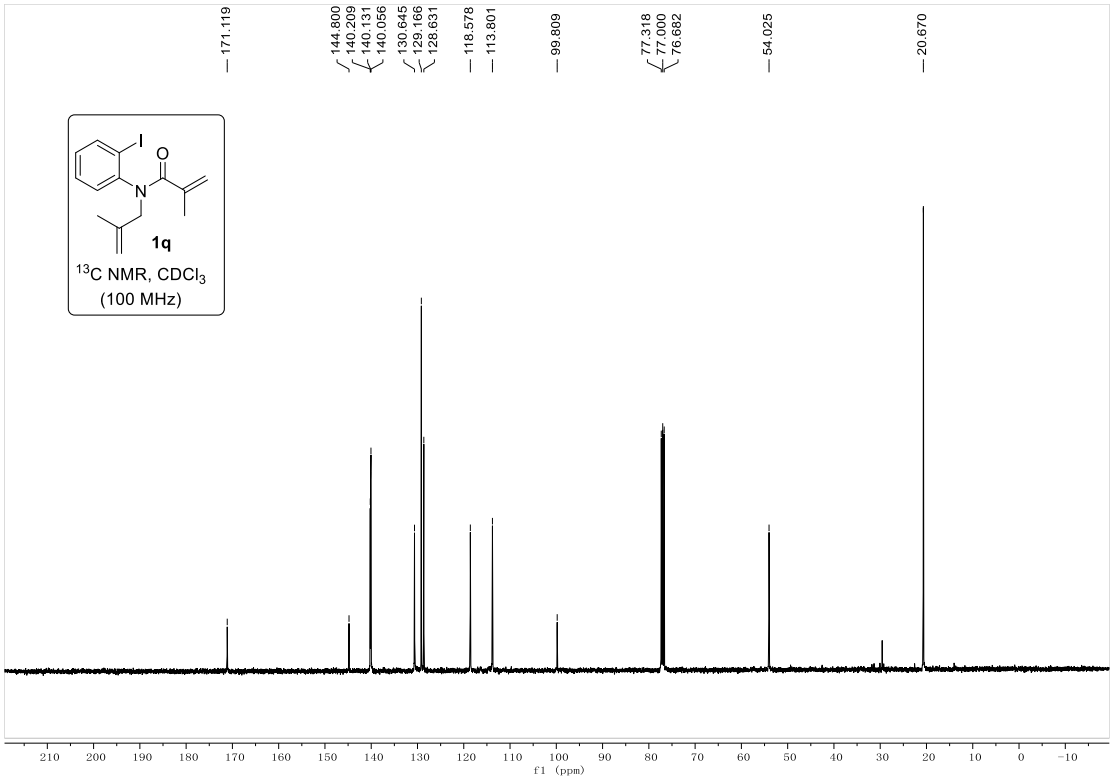

7.928
7.909
7.762
7.742
7.589
7.570
7.460
7.442
7.423
7.386
7.367
7.308
7.292
7.196
7.177
7.090
7.075
6.916
6.898
6.879
6.791
6.772
5.856
5.669
5.620
5.332
3.285
3.172
I
O
N
Me
1n
1H NMR, CDCl3
(400 MHz)
0.13
0.88
0.25
0.17
0.28
0.22
1.87
2.80
0.89
0.89
0.12
0.14
0.90
0.91
2.70
0.32
f1 (ppm)

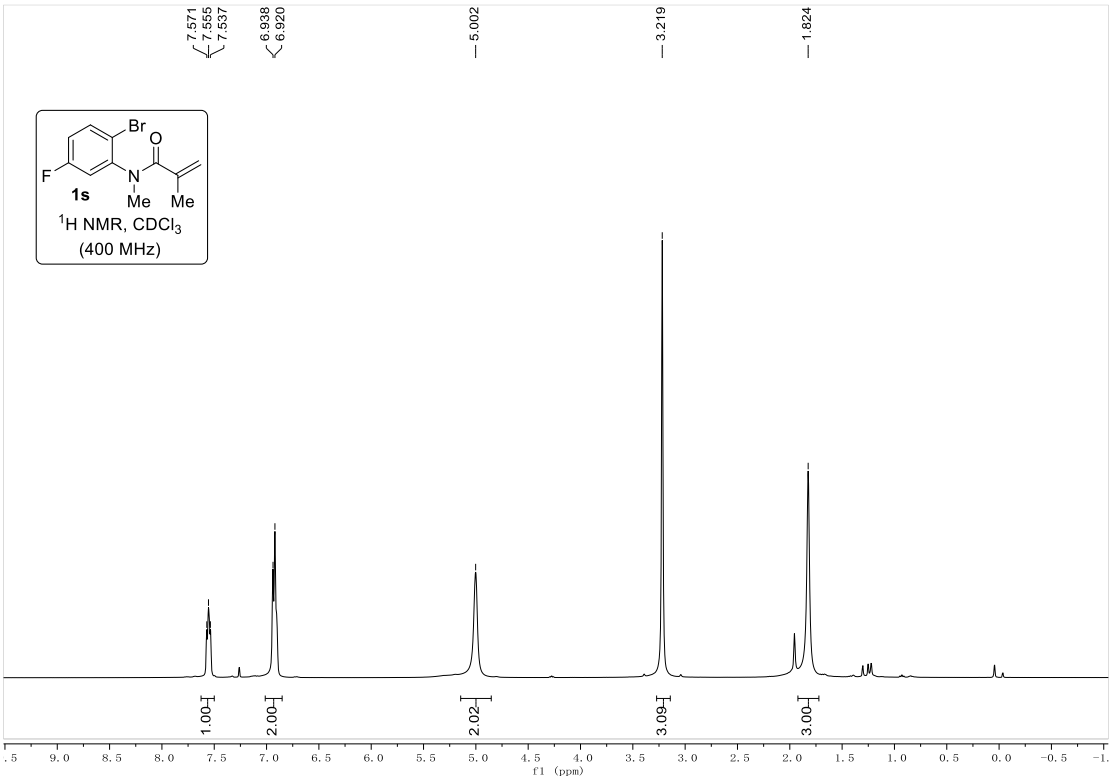

169.592
145.049
144.238
139.787
135.222
133.707
133.537
129.193
128.744
128.325
127.313
117.796
99.024
77.319
77.000
76.682
36.210
I
O
N
Me
1n
13C NMR, CDCl3
(100 MHz)
f1 (ppm)

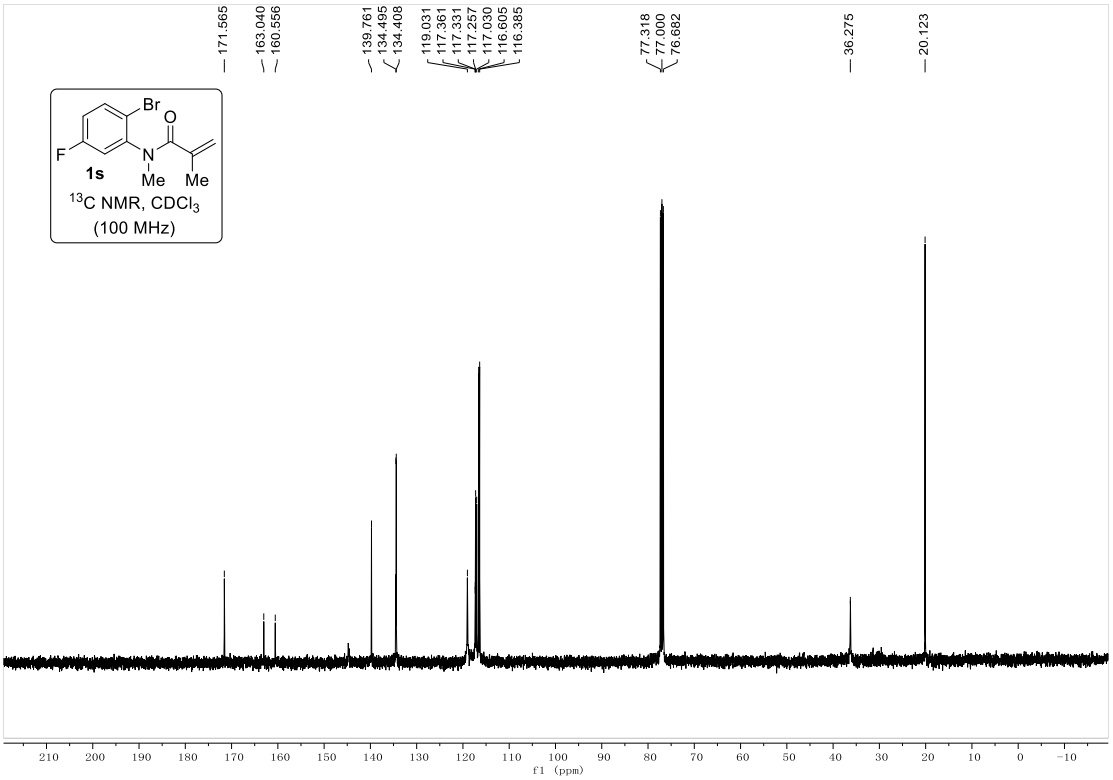

7.897
7.878
7.371
7.353
7.334
7.228
7.208
7.026
7.007
6.988
4.971
4.632
4.616
4.599
4.582
4.566
1.883
1.677
1.419
1.403
1.089
1.072
1p
1H NMR, CDCl3
(400 MHz)
1.00
1.02
1.05
1.05
2.00
1.00
3.01
3.09
3.08
f1 (ppm)

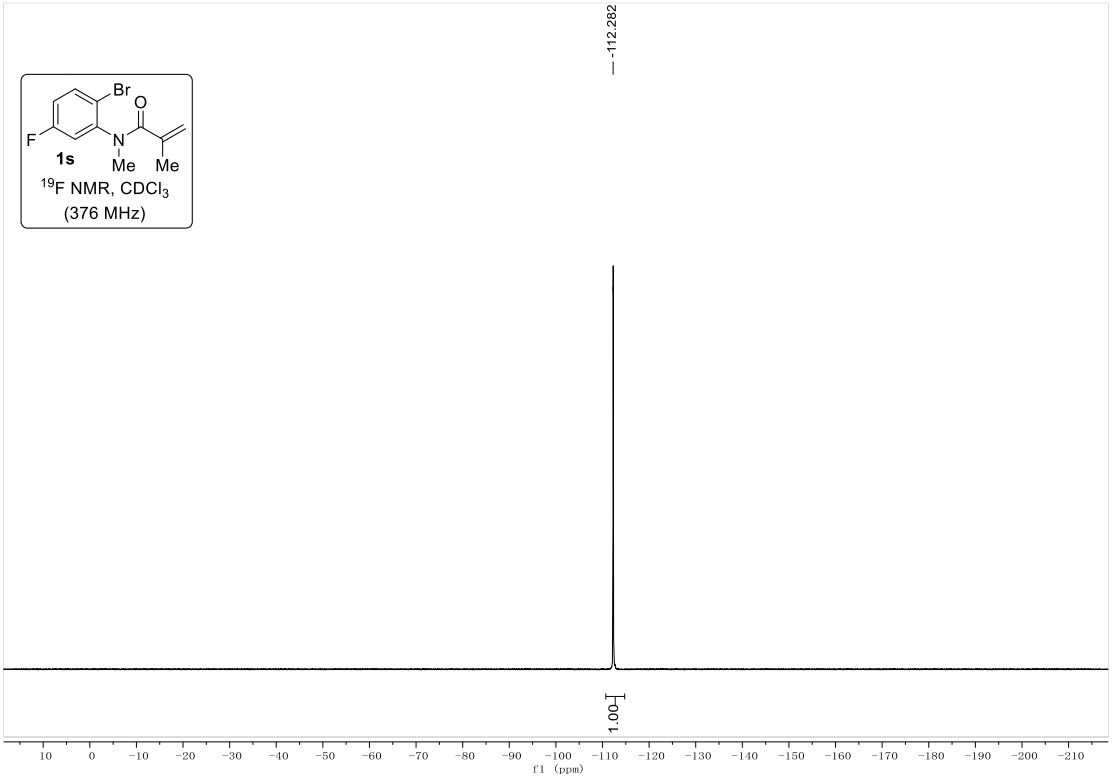

171.085
141.046
140.227
130.649
129.046
128.506
118.954
102.914
77.318
77.000
76.682
49.950
22.257
20.761
19.248
1p
13C NMR, CDCl3
(100 MHz)
f1 (ppm)

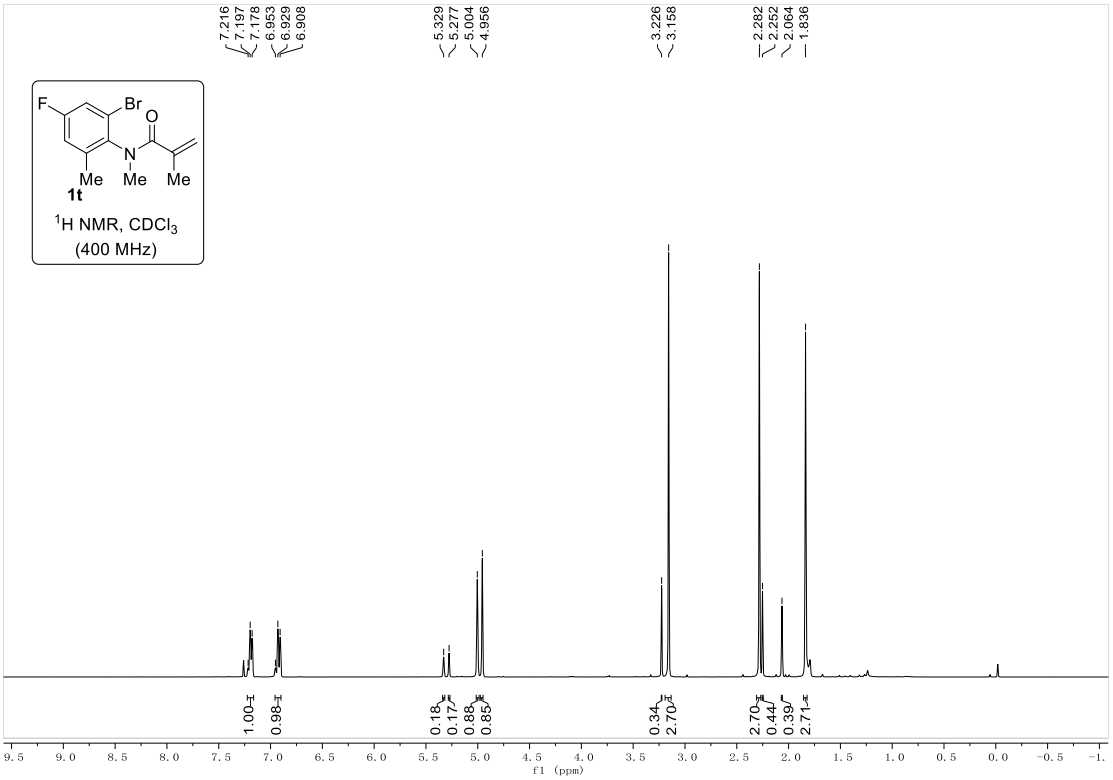

7.813
7.793
7.261
7.243
7.224
7.102
7.083
6.946
6.927
6.908
4.983
4.946
4.906
4.775
4.645
3.438
3.401
1.788
1.728
1q
1H NMR, CDCl3
(400 MHz)
1.01
1.07
1.01
1.04
5.03
0.99
3.04
3.01
f1 (ppm)

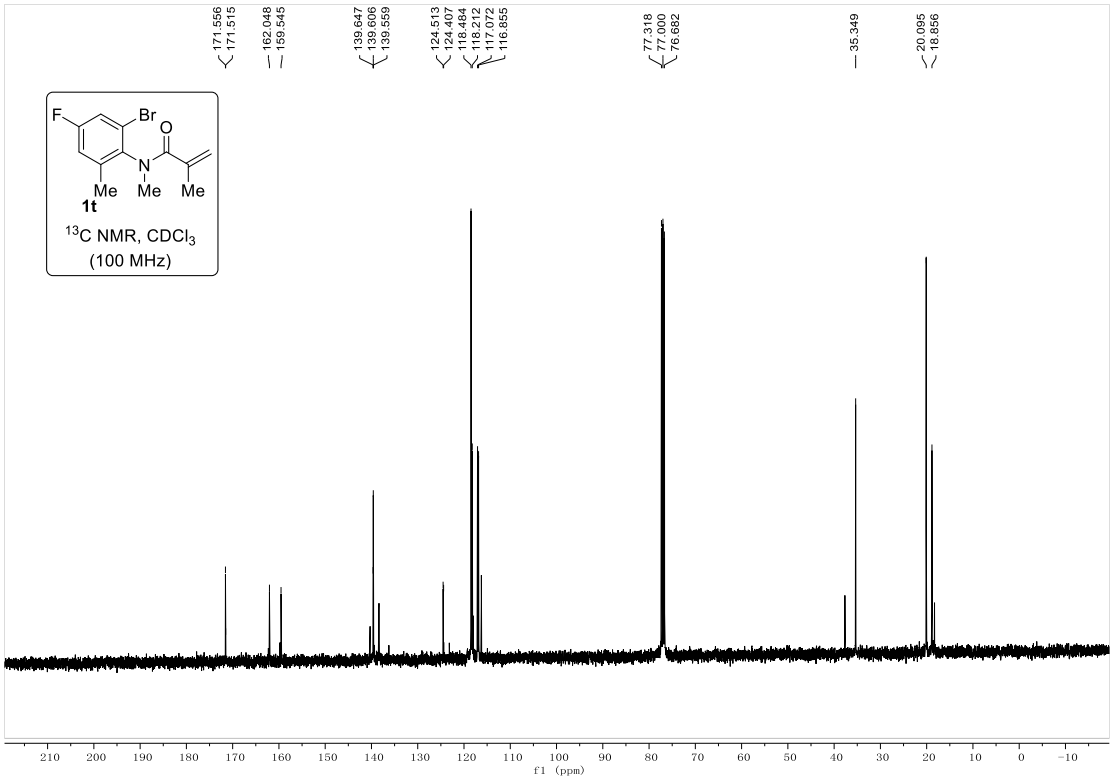

171.119
144.800
140.209
140.131
140.056
130.645
129.166
128.631
118.578
113.801
99.809
77.318
77.000
76.682
54.025
20.670
1q
13C NMR, CDCl3
(100 MHz)
f1 (ppm)

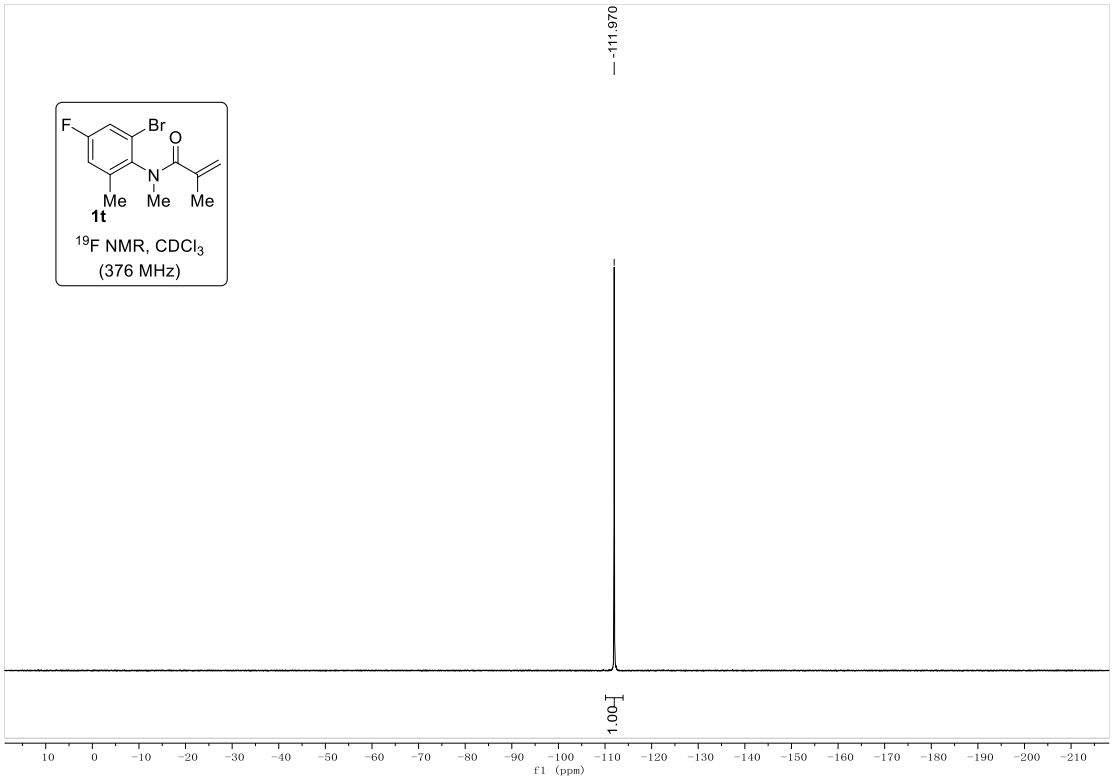

7.571
7.555
7.537
6.938
6.920
5.002
3.219
1.824
Br
O
F
N
1s
Me
Me
^{1}H NMR, $CDCl_3$
(400 MHz)
1.00
2.00
2.02
3.09
3.00
f1 (ppm)

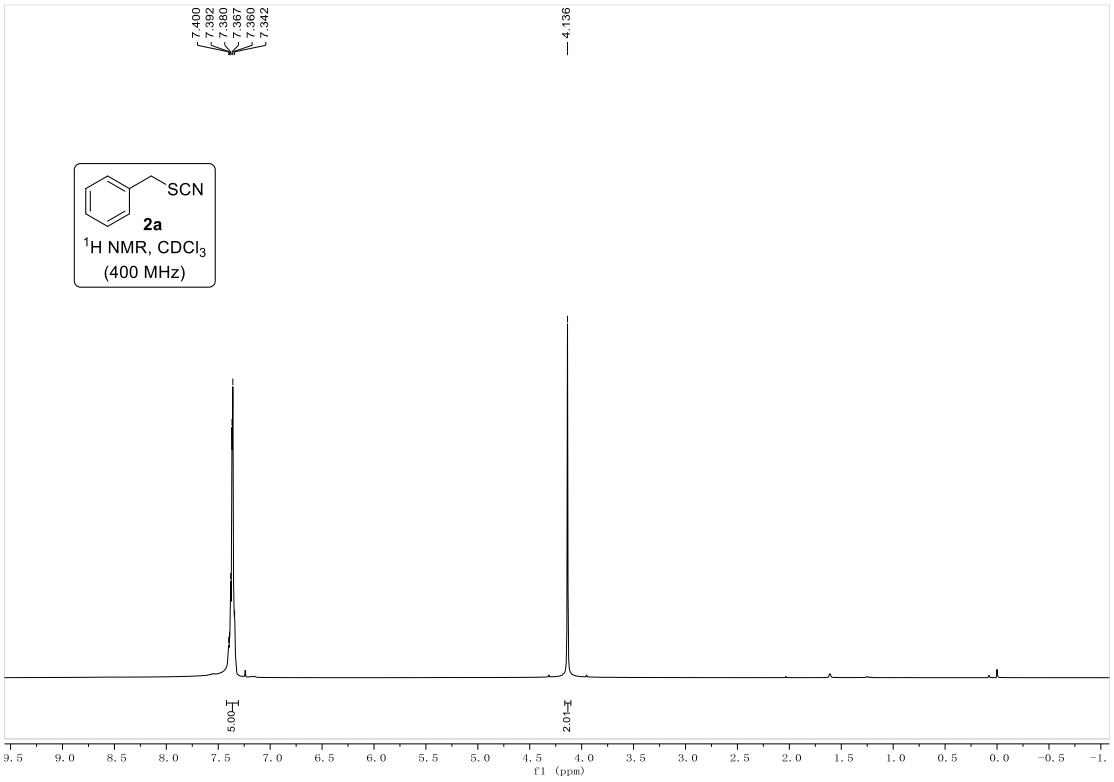

171.565
163.040
160.556
139.761
134.495
134.408
119.031
117.361
117.331
117.257
117.030
116.605
116.385
77.318
77.000
76.682
36.275
20.123
Br
O
F
N
1s
Me
Me
^{13}C NMR, $CDCl_3$
(100 MHz)
f1 (ppm)

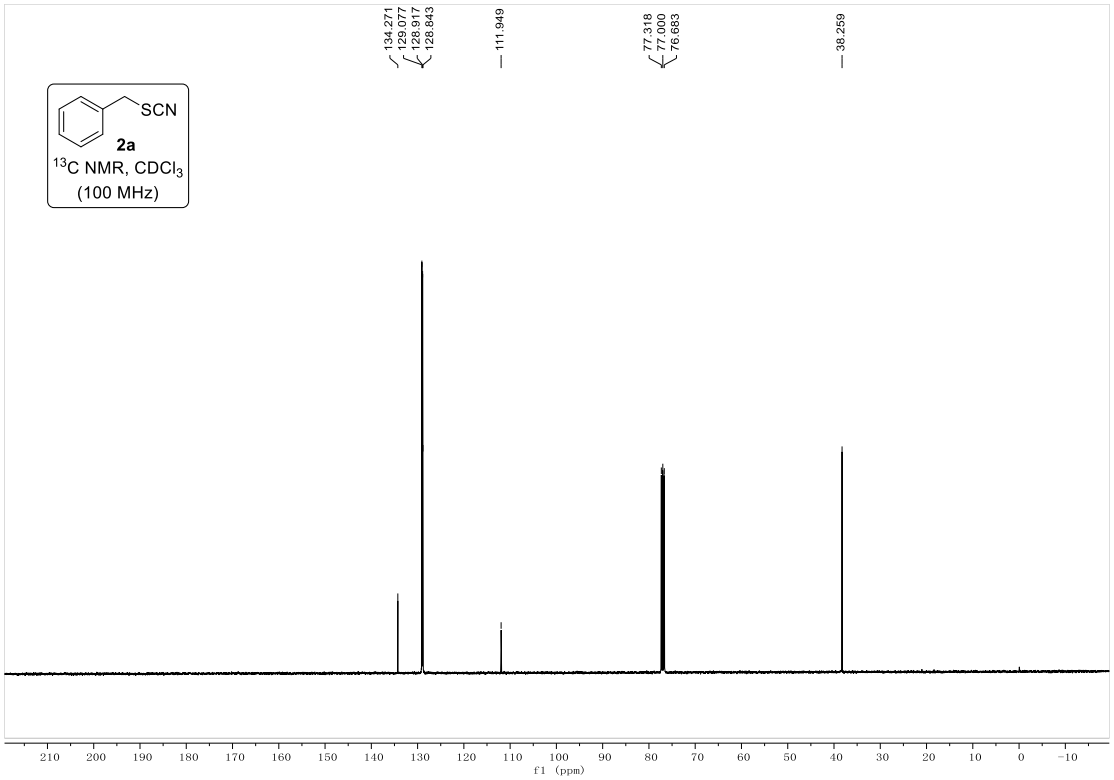

-112.282
Br
O
F
N
Me
Me
1s
^{19}F NMR, CDCl$_3$
(376 MHz)
1.00
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

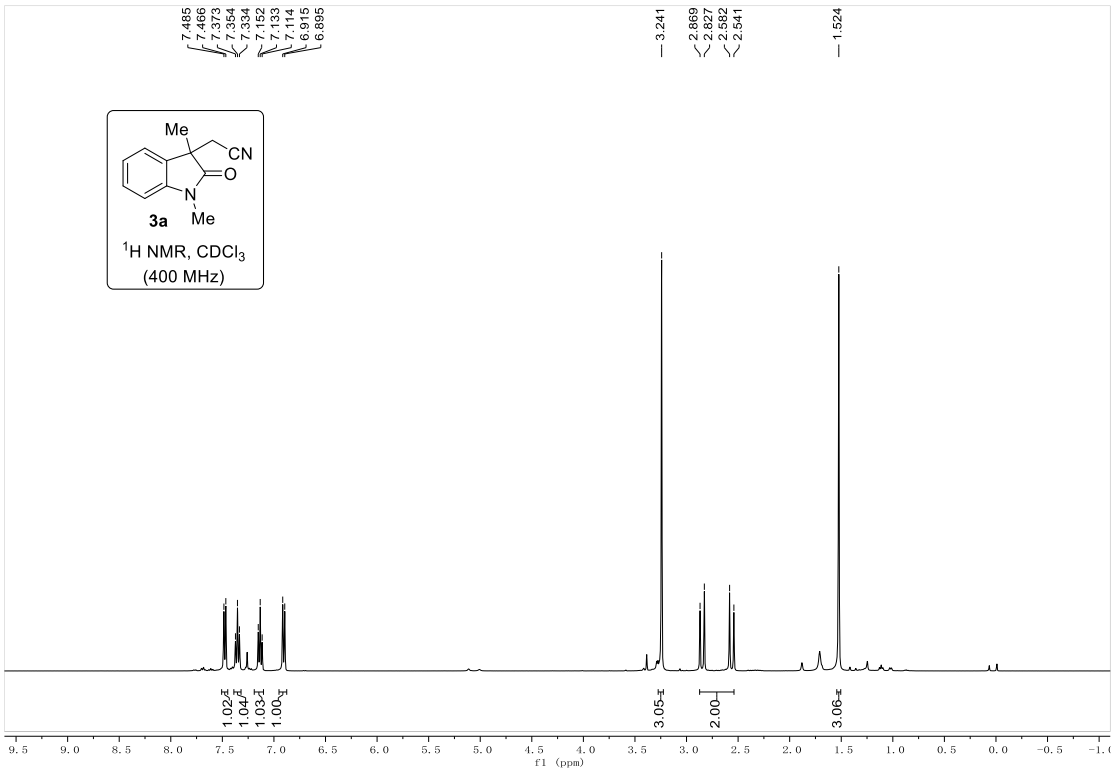

7.216
7.197
7.178
6.953
6.929
6.908
5.329
5.277
5.004
4.956
3.226
3.158
2.282
2.252
2.064
1.836
F
Br
O
N
Me
Me
Me
1t
^{1}H NMR, CDCl$_3$
(400 MHz)
1.00
0.98
0.18
0.17
0.88
0.85
0.34
2.70
2.70
0.44
0.39
2.71
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.
f1 (ppm)

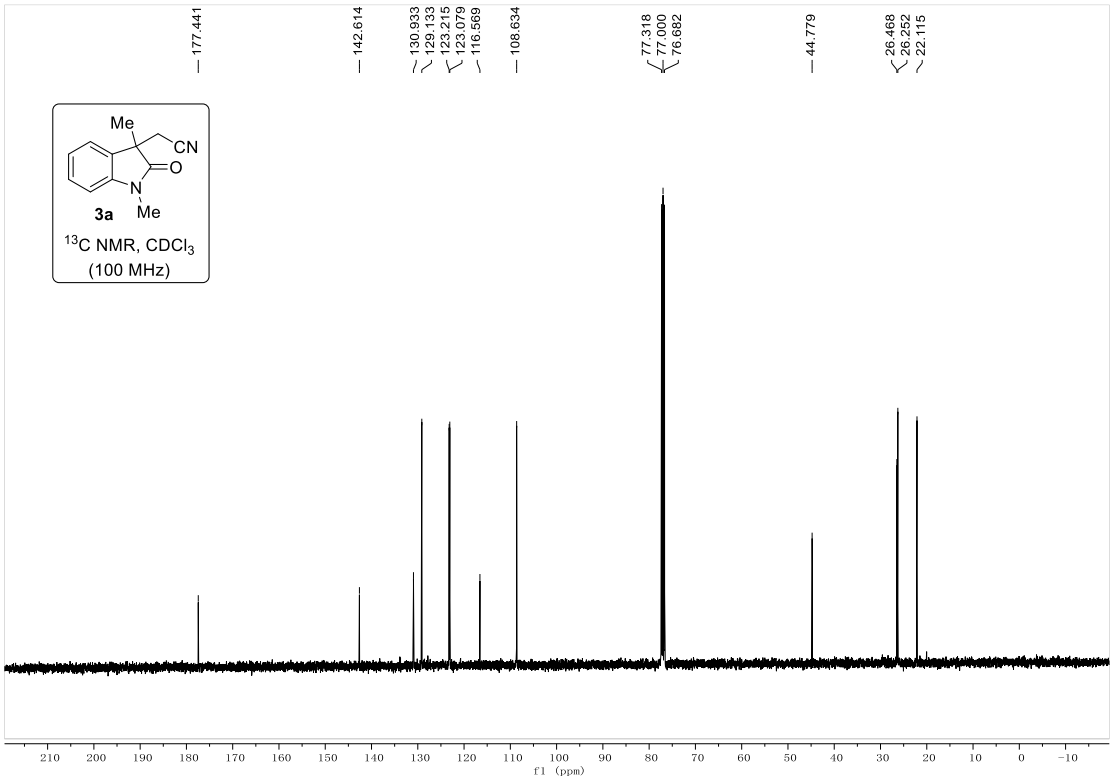

171.556
171.515
162.048
159.545
139.647
139.606
139.559
124.513
124.407
118.484
118.212
117.072
116.855
77.318
77.000
76.682
35.349
20.095
18.856
F
Br
O
N
Me
Me
Me
1t
^{13}C NMR, CDCl$_3$
(100 MHz)
f1 (ppm)

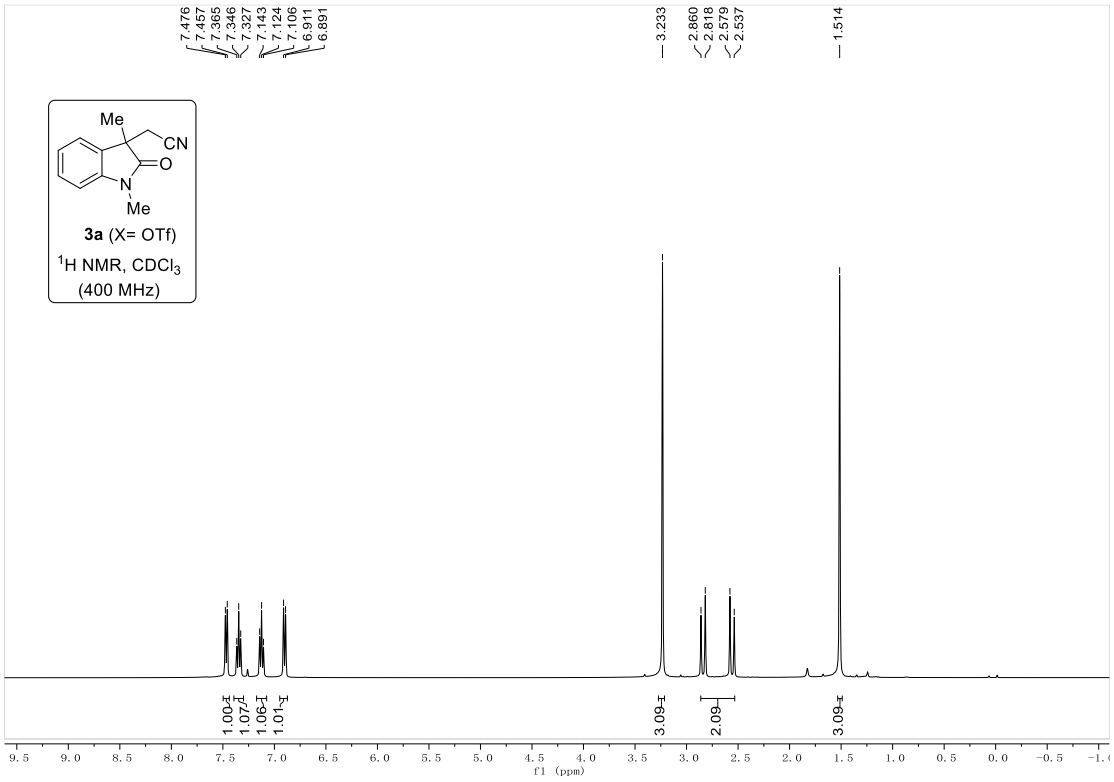

-111.970
F
Br
O
N
Me
Me
Me
1t
^{19}F NMR, CDCl$_3$
(376 MHz)
1.00
f1 (ppm)

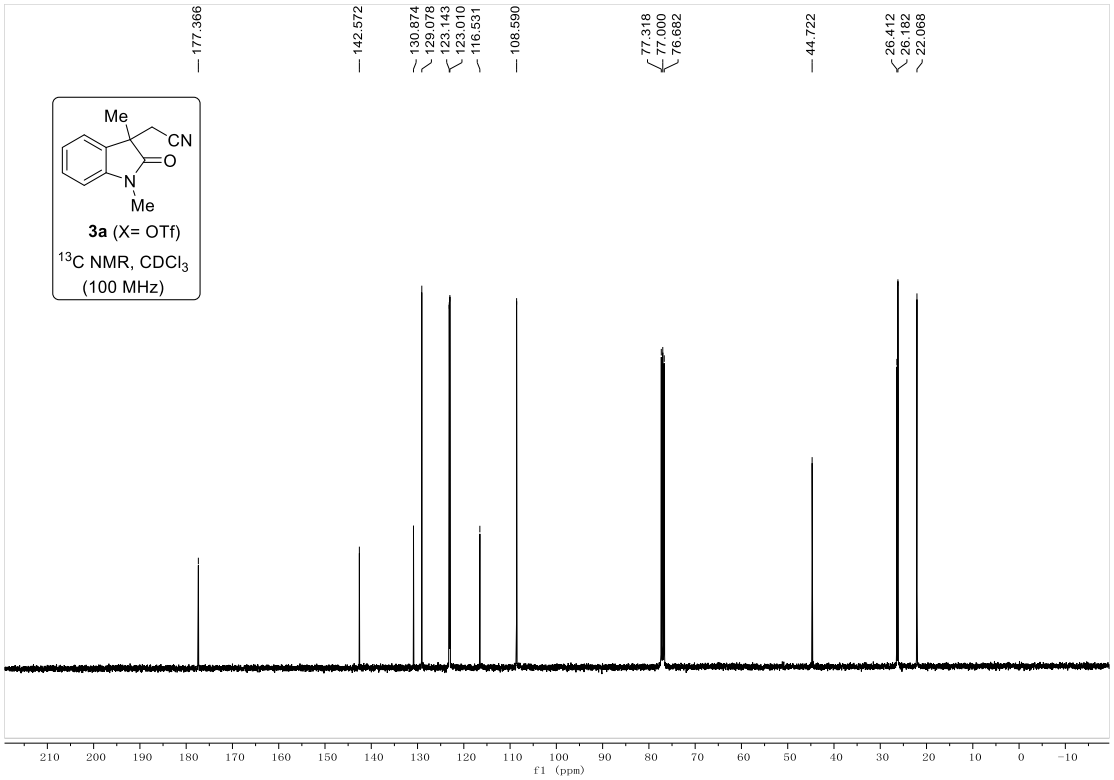

7.400
7.392
7.380
7.367
7.360
7.342
4.136
SCN
2a
^{1}H NMR, CDCl$_3$
(400 MHz)
5.00
2.01
f1 (ppm)

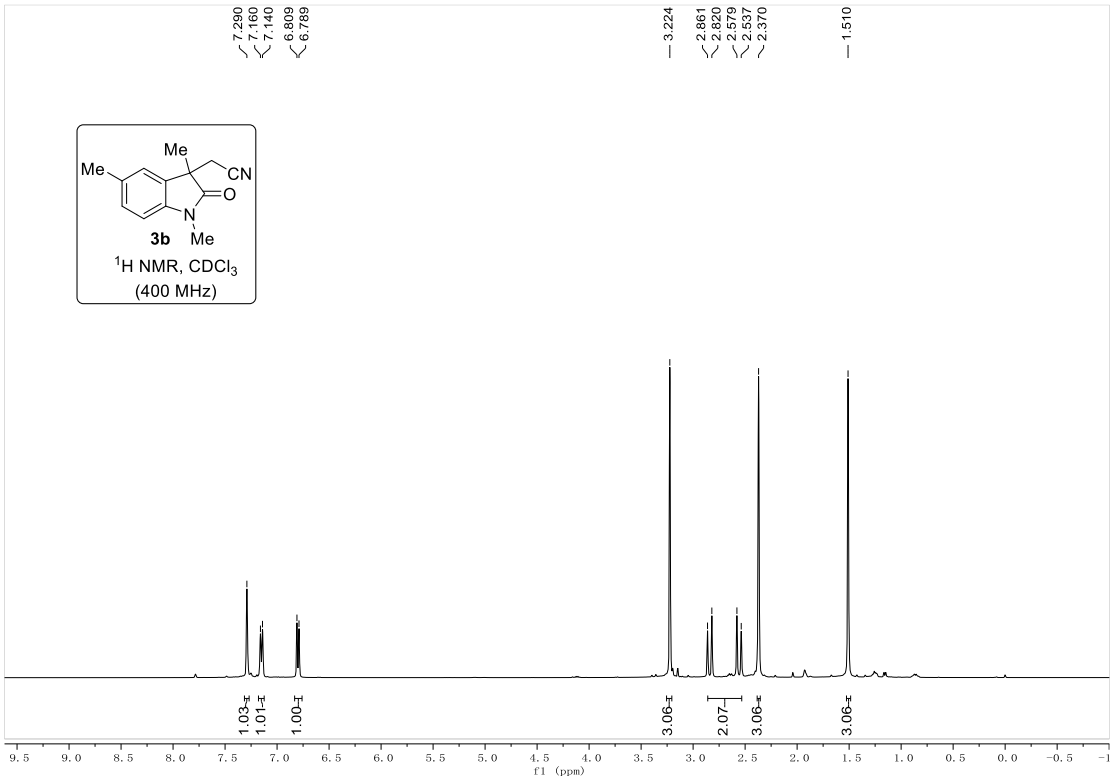

134.271
129.077
128.917
128.843
111.949
77.318
77.000
76.683
38.259
SCN
2a
^{13}C NMR, CDCl$_3$
(100 MHz)
f1 (ppm)

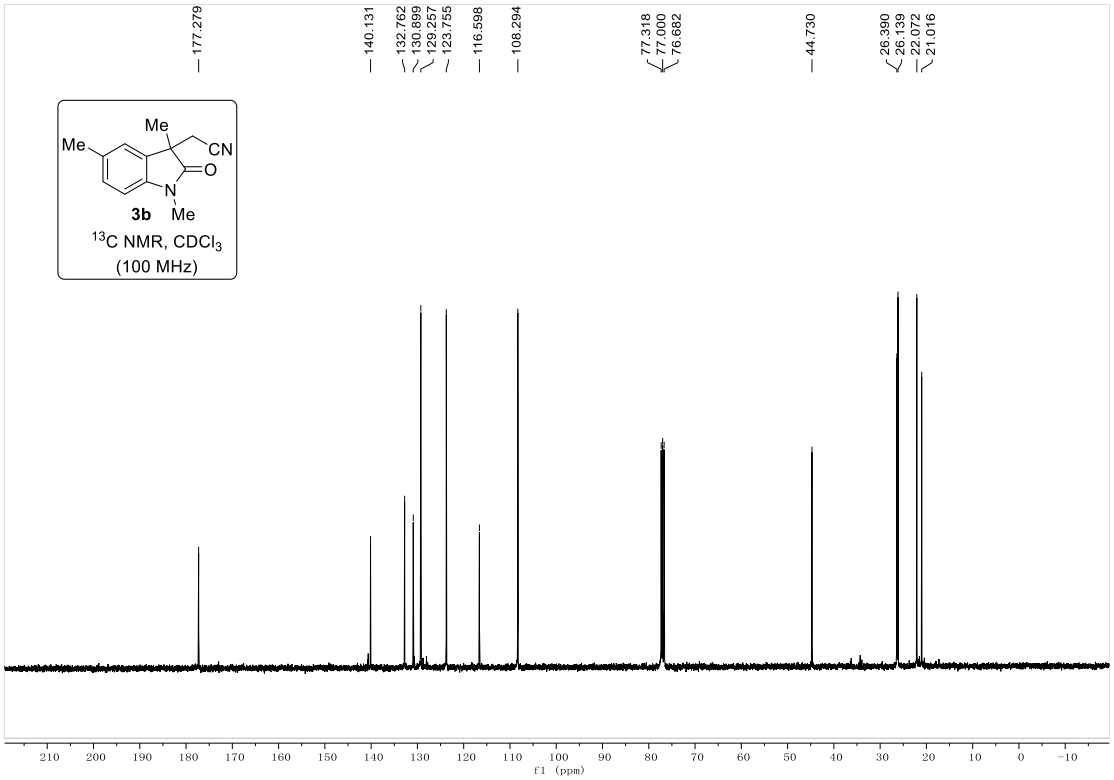

7.485
7.466
7.373
7.354
7.334
7.152
7.133
7.114
6.915
6.895
3.241
2.869
2.827
2.582
2.541
1.524
Me
CN
O
N
Me
3a
1H NMR, CDCl3
(400 MHz)
1.02
1.04
1.03
1.00
3.05
2.00
3.06
f1 (ppm)

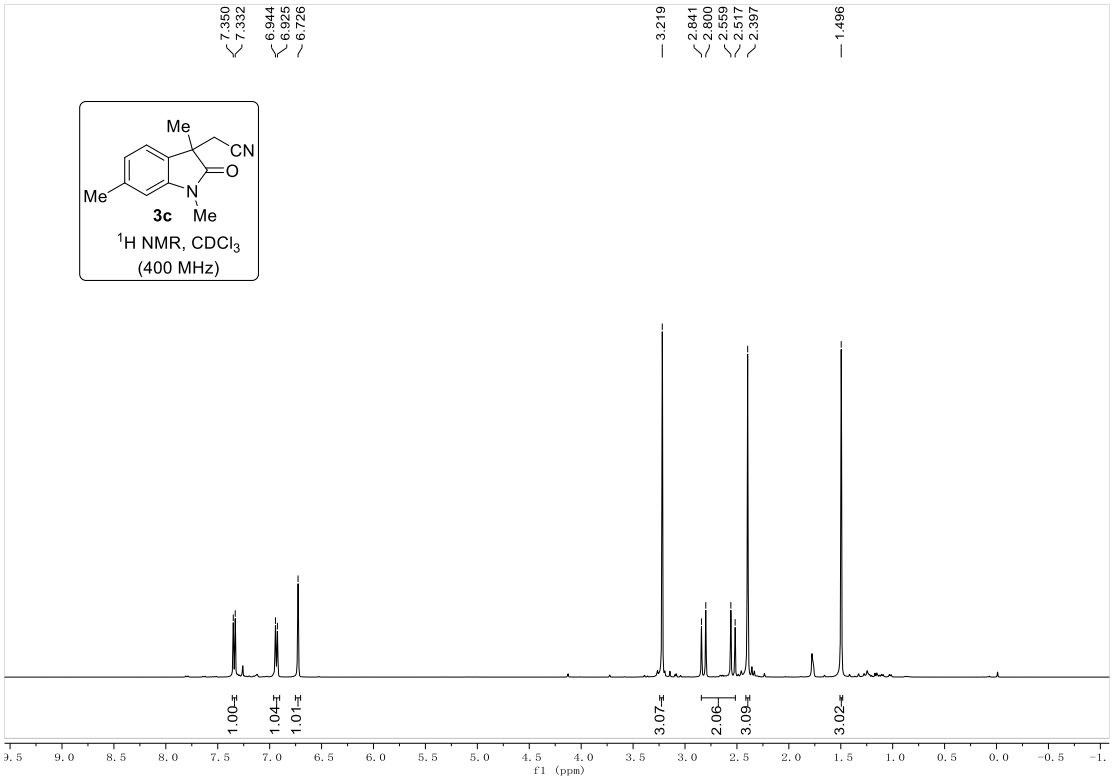

177.441
142.614
130.933
129.133
123.215
123.079
116.569
108.634
77.318
77.000
76.682
44.779
26.468
26.252
22.115
Me
CN
O
N
Me
3a
13C NMR, CDCl3
(100 MHz)
f1 (ppm)

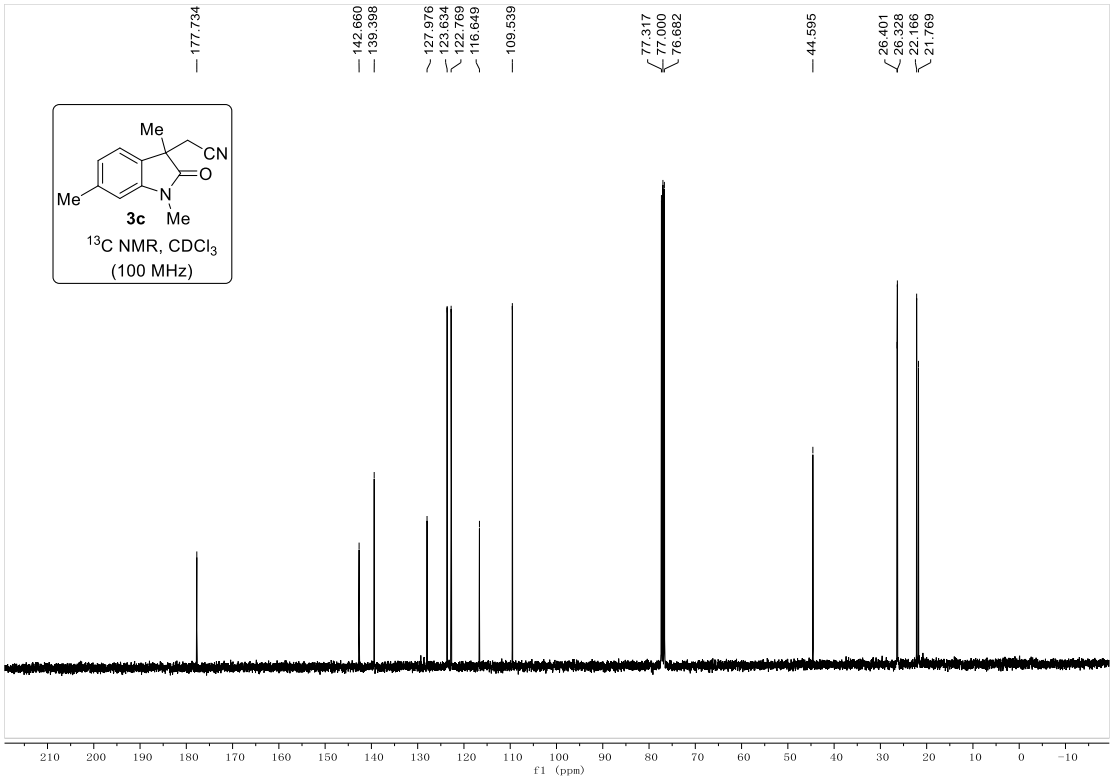

7.476
7.457
7.365
7.346
7.327
7.143
7.124
7.106
6.911
6.891
3.233
2.860
2.818
2.579
2.537
1.514
Me
CN
O
N
Me
3a (X= OTf)
1H NMR, CDCl3
(400 MHz)
1.00
1.07
1.06
1.01
3.09
2.09
3.09
f1 (ppm)

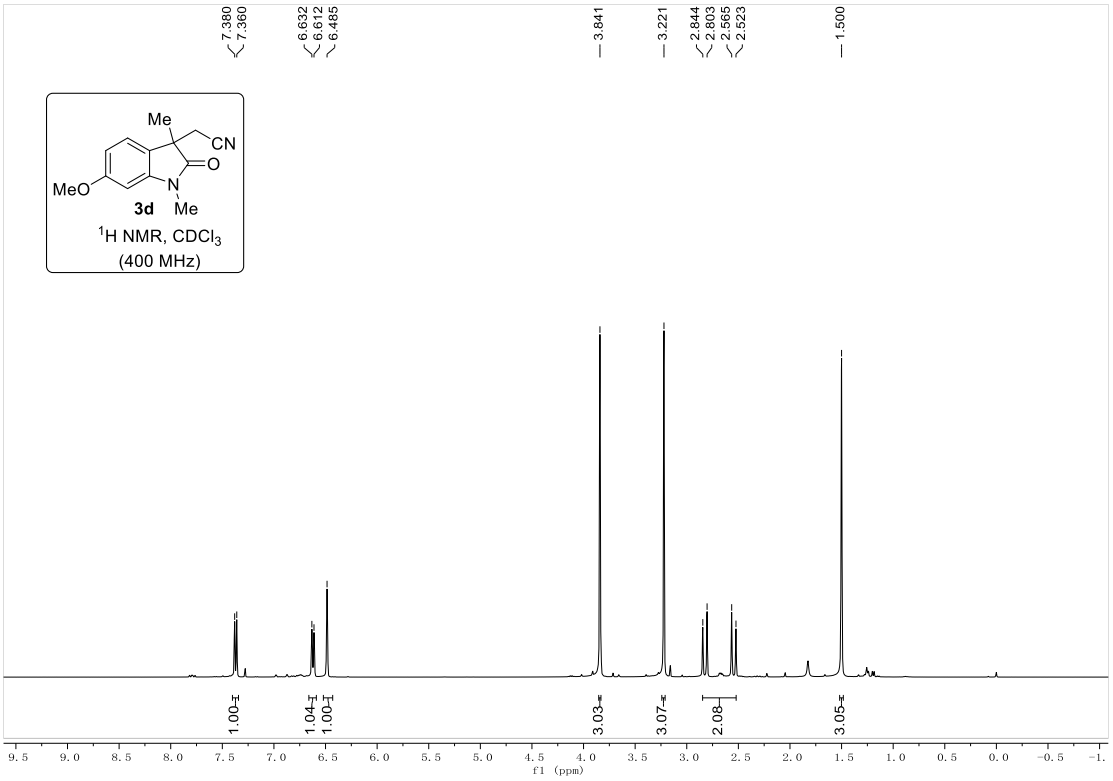

177.366
142.572
130.874
129.078
123.143
123.010
116.531
108.590
77.318
77.000
76.682
44.722
26.412
26.182
22.068
Me
CN
O
N
Me
3a (X= OTf)
13C NMR, CDCl3
(100 MHz)
f1 (ppm)

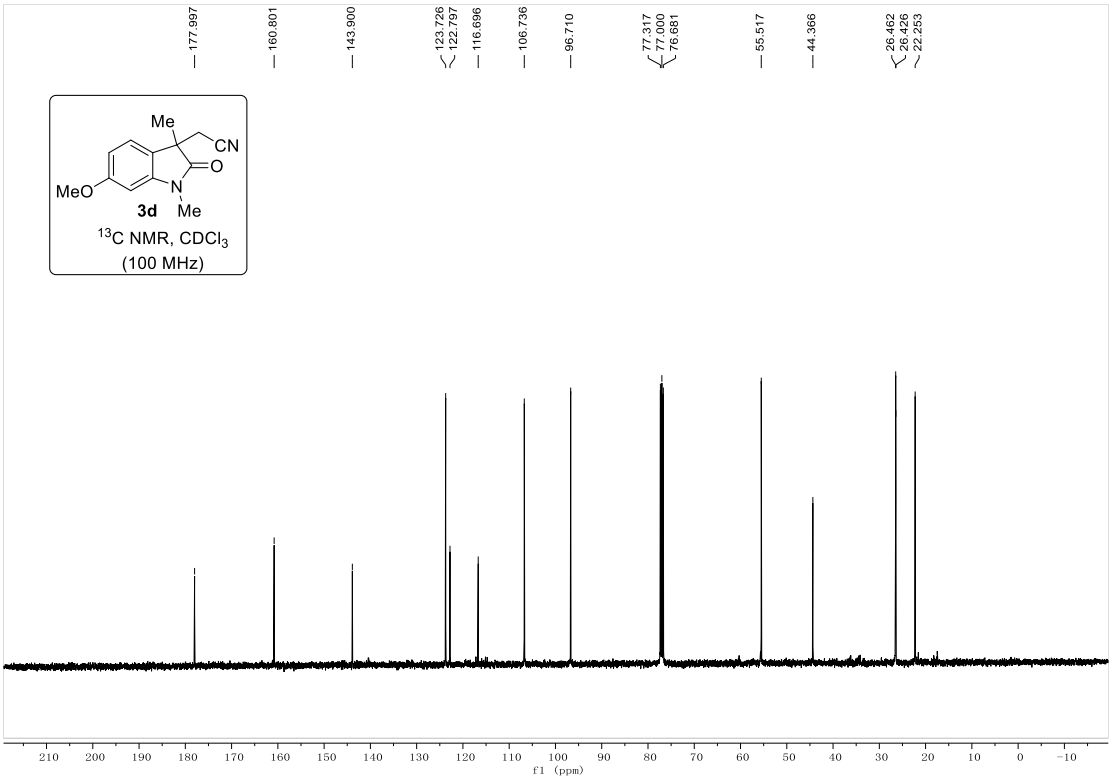

7.290
7.160
7.140
6.809
6.789
3.224
2.861
2.820
2.579
2.537
2.370
1.510
Me
Me
CN
O
N
Me
3b
^{1}H NMR, CDCl$_3$
(400 MHz)
1.03
1.01
1.00
3.06
2.07
3.06
3.06
f1 (ppm)

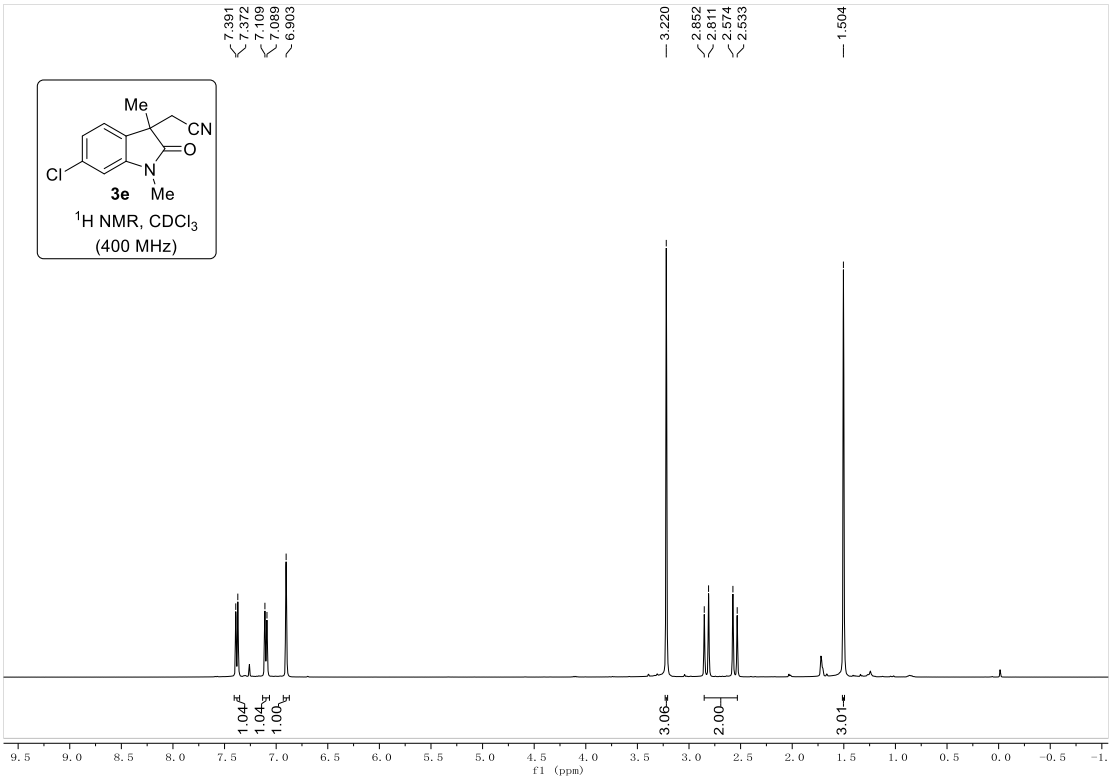

177.279
140.131
132.762
130.899
129.257
123.755
116.598
108.294
77.318
77.000
76.682
44.730
26.390
26.139
22.072
21.016
Me
Me
CN
O
N
Me
3b
^{13}C NMR, CDCl$_3$
(100 MHz)
f1 (ppm)


7.350
7.332
6.944
6.925
6.726
3.219
2.841
2.800
2.559
2.517
2.397
1.496
Me
CN
O
Me
N
3c Me
1H NMR, CDCl3
(400 MHz)
1.00
1.04
1.01
3.07
2.06
3.09
3.02
f1 (ppm)


177.734
142.660
139.398
127.976
123.634
122.769
116.649
109.539
77.317
77.000
76.682
44.595
26.401
26.328
22.166
21.769
Me
CN
O
Me
N
3c Me
13C NMR, CDCl3
(100 MHz)
f1 (ppm)


7.380
7.360
6.632
6.612
6.485
3.841
3.221
2.844
2.803
2.565
2.523
1.500
Me
CN
O
MeO
N
Me
3d
^{1}H NMR, CDCl$_3$
(400 MHz)
1.00
1.04
1.00
3.03
3.07
2.08
3.05
f1 (ppm)


177.997
160.801
143.900
123.726
122.797
116.696
106.736
96.710
77.317
77.000
76.681
55.517
44.366
26.462
26.426
22.253
Me
CN
O
MeO
N
Me
3d
^{13}C NMR, CDCl$_3$
(100 MHz)
f1 (ppm)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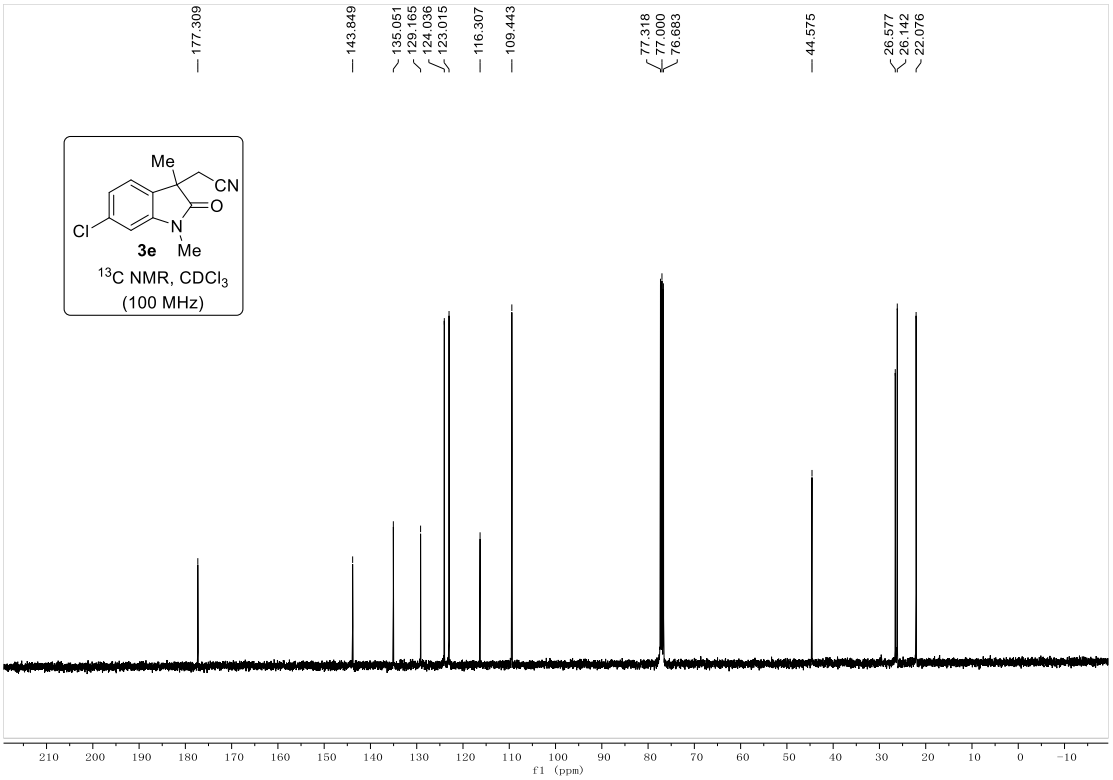
7.372
7.109
7.089
6.903
3.220
2.852
2.811
2.574
2.533
1.504
Me
CN
O
Cl
N
Me
3e
1H NMR, CDCl3
(400 MHz)
1.04
1.04
1.00
3.06
2.00
3.01
f1 (ppm)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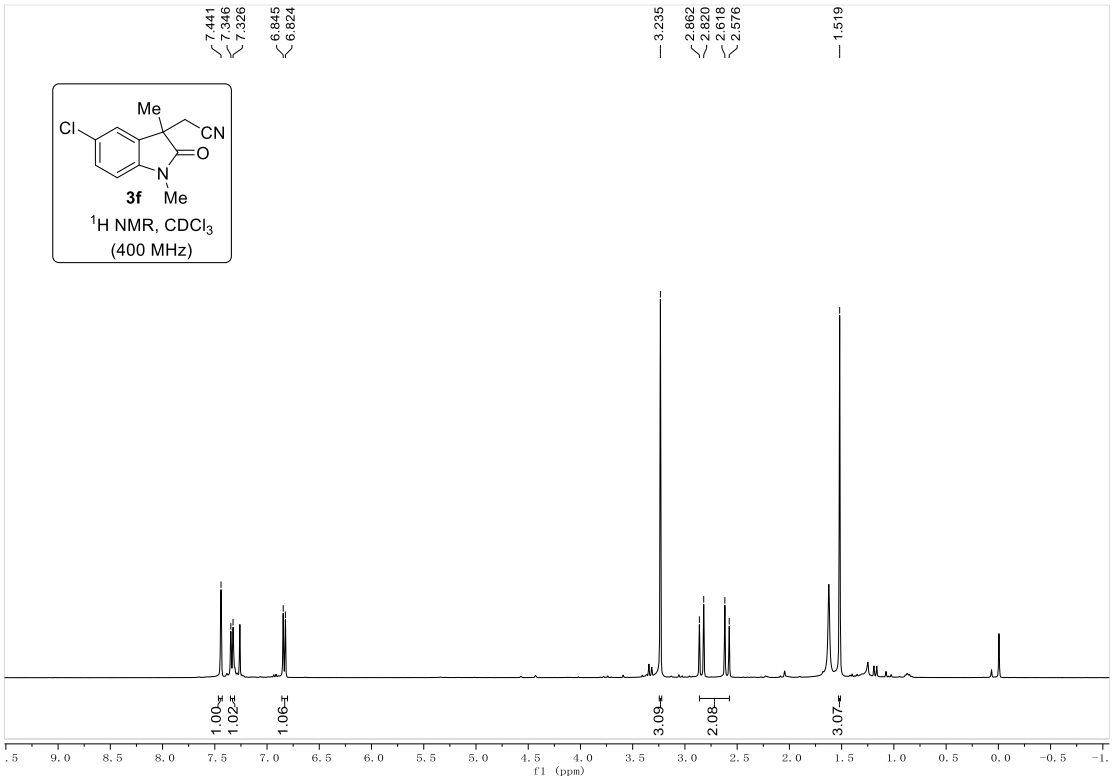
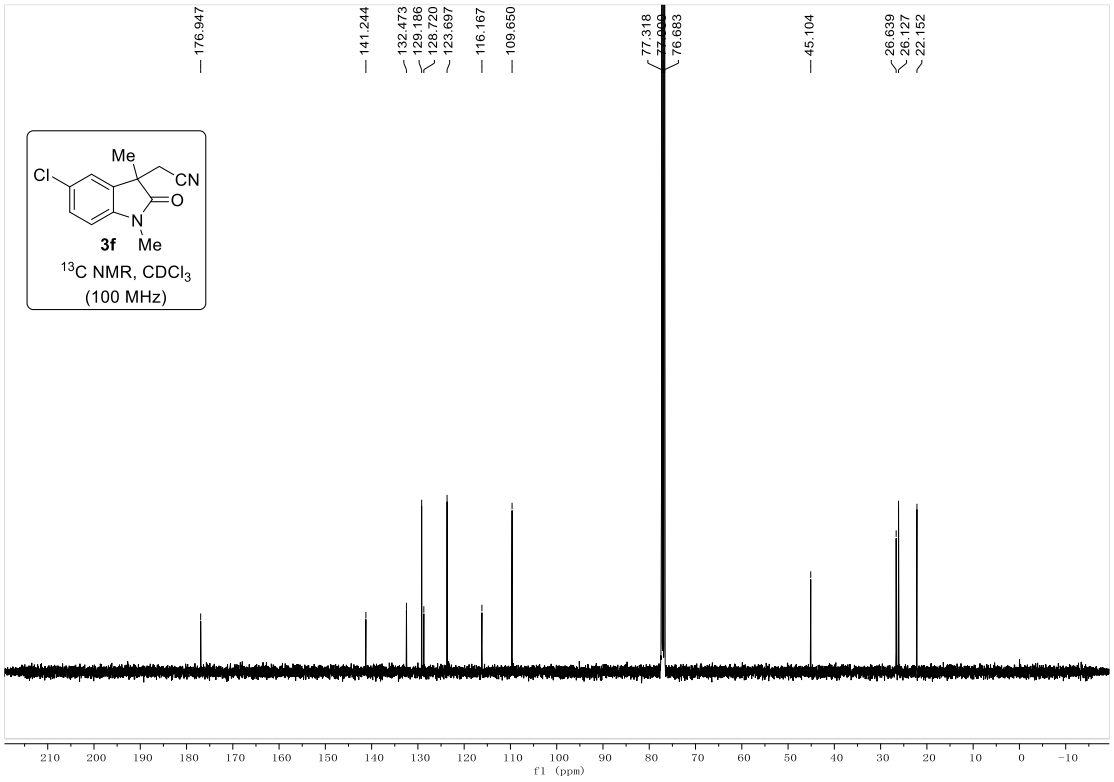
143.849
135.051
129.165
124.036
123.015
116.307
109.443
77.318
77.000
76.683
44.575
26.577
26.142
22.076
Me
CN
O
Cl
N
Me
3e
13C NMR, CDCl3
(100 MHz)
f1 (ppm)


7.441
7.346
7.326
6.845
6.824
3.235
2.862
2.820
2.618
2.576
1.519
Me
Cl
CN
O
N
Me
3f
^{1}H NMR, CDCl$_3$
(400 MHz)
1.00
1.02
1.06
3.09
2.08
3.07
f1 (ppm)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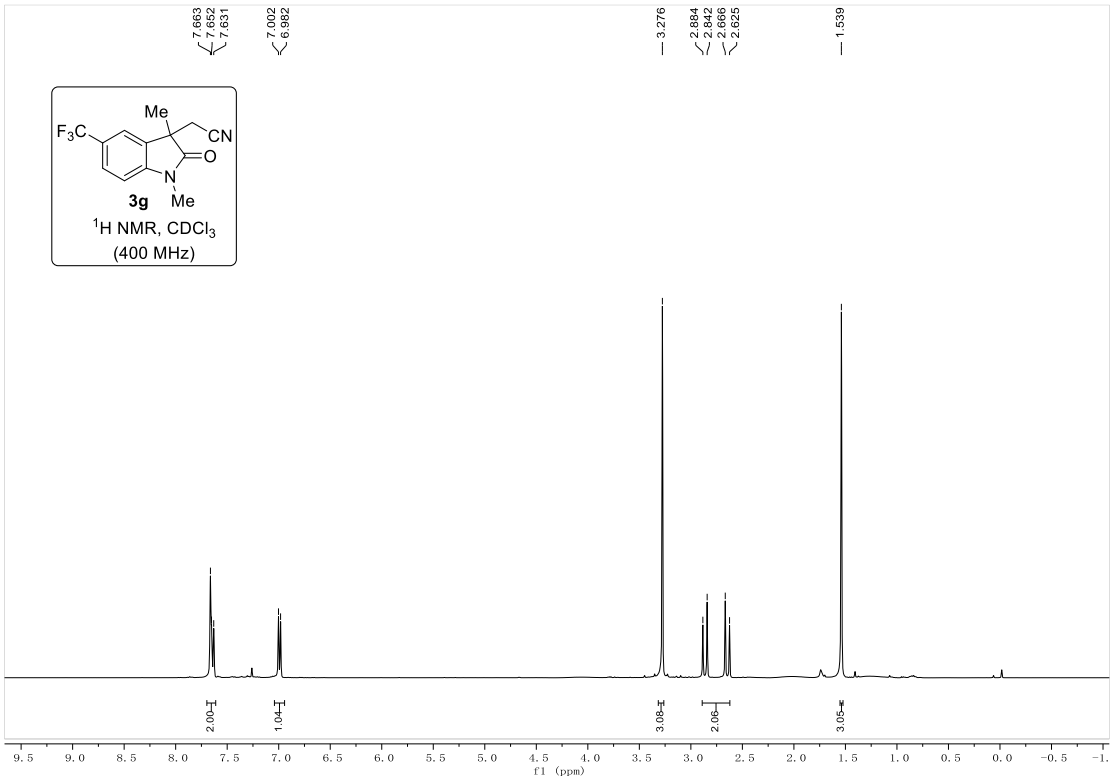
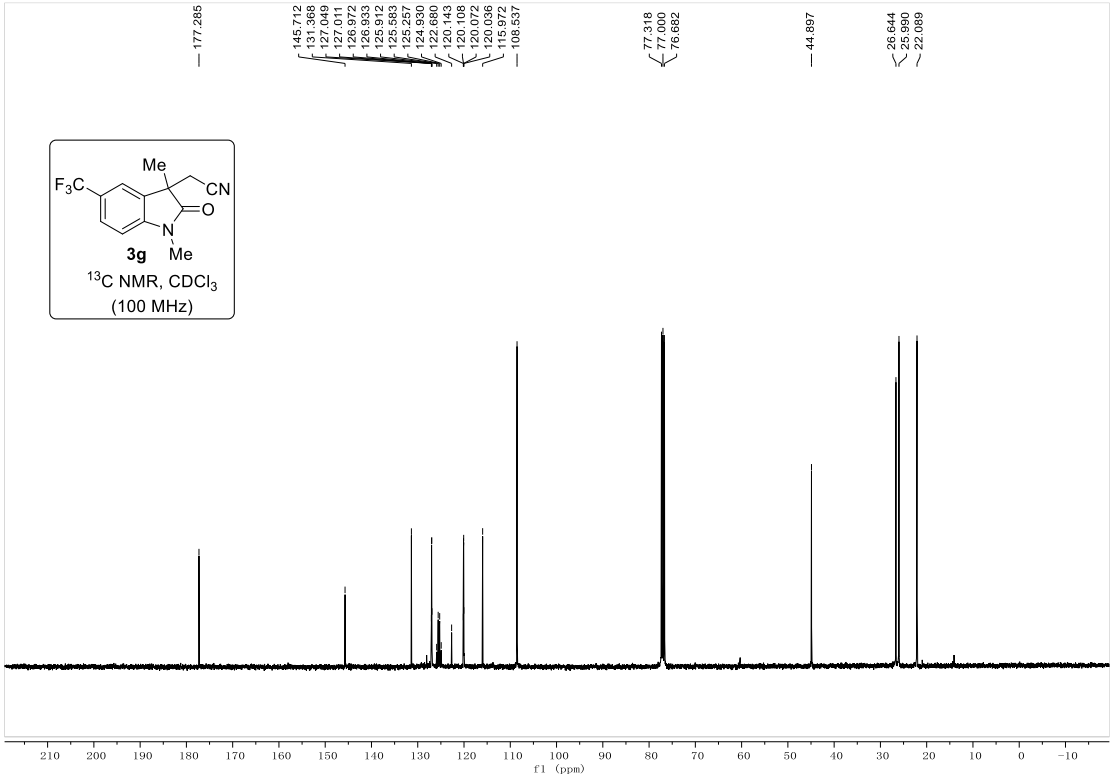
141.244
132.473
129.186
128.720
123.697
116.167
109.650
77.318
77.000
76.683
45.104
26.639
26.127
22.152
Me
Cl
CN
O
N
Me
3f
^{13}C NMR, CDCl$_3$
(100 MHz)
f1 (ppm)


7.663
7.652
7.631
7.002
6.982
3.276
2.884
2.842
2.666
2.625
1.539
Me
F3C
CN
O
N
Me
3g
1H NMR, CDCl3
(400 MHz)
2.00
1.04
3.08
2.06
3.05
f1 (ppm)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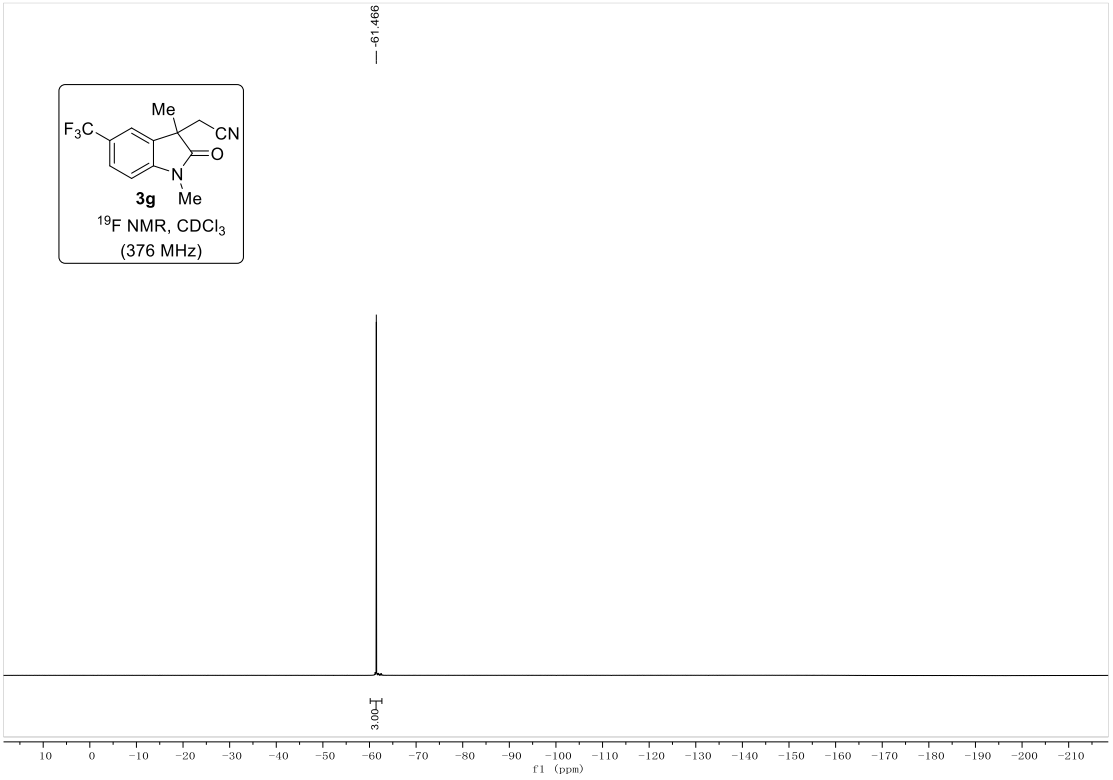
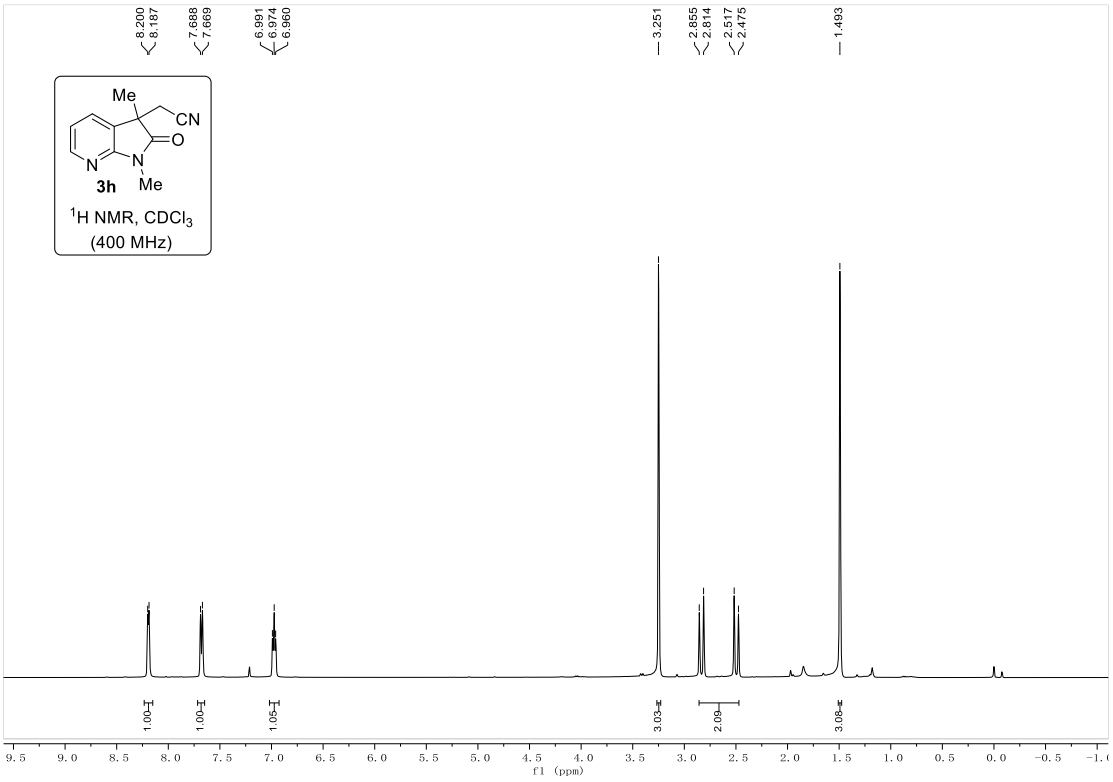
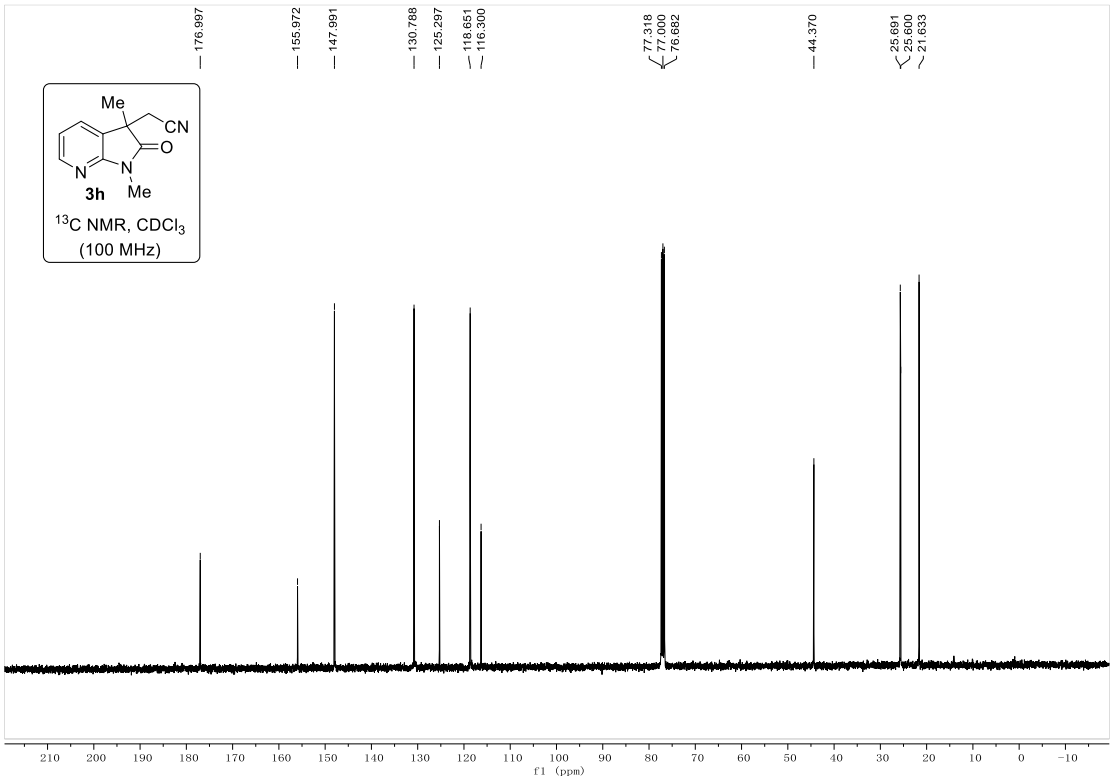
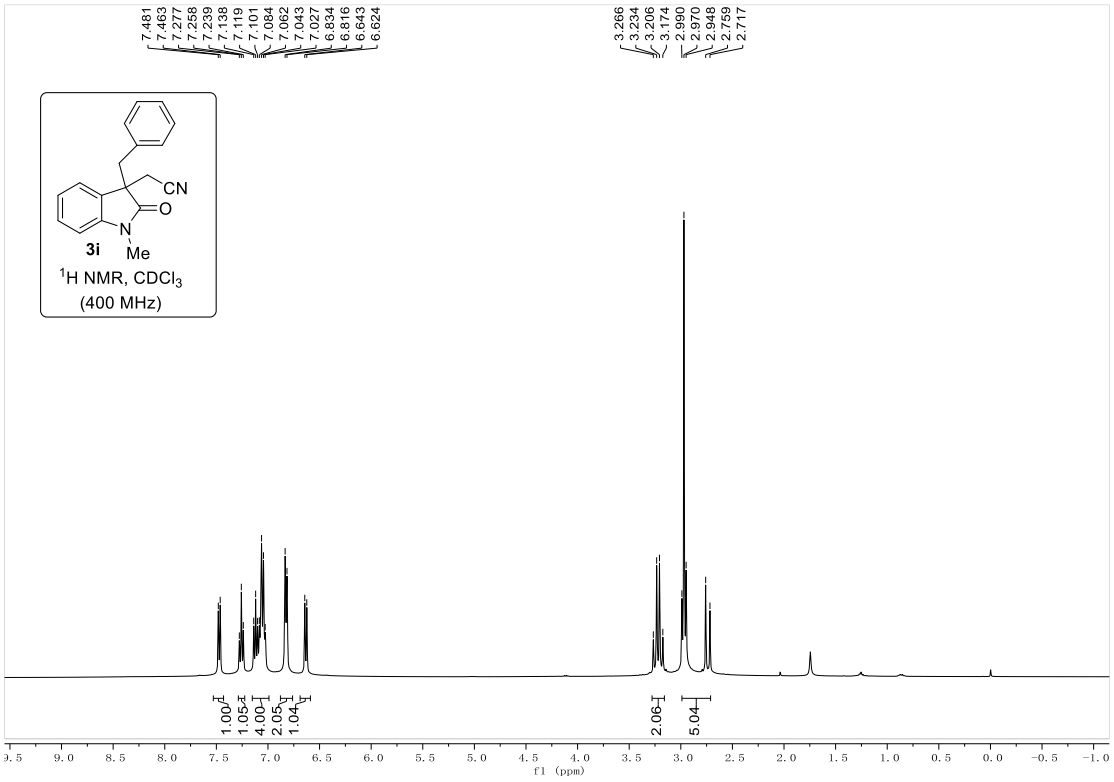
145.712
131.388
127.049
127.011
126.972
126.933
125.912
125.583
125.257
124.930
122.680
120.143
120.108
120.072
120.036
115.972
108.537
77.318
77.000
76.682
44.897
26.644
25.990
22.089
Me
F3C
CN
O
N
Me
3g
13C NMR, CDCl3
(100 MHz)
f1 (ppm)


-61.466
Me
F3C
CN
O
N
Me
3g
19F NMR, CDCl3
(376 MHz)
3.00
f1 (ppm)


8.200
8.187
7.688
7.669
6.991
6.974
6.960
3.251
2.855
2.814
2.517
2.475
1.493
Me
CN
O
N
N
Me
3h
1H NMR, CDCl3
(400 MHz)
1.00
1.00
1.05
3.03
2.09
3.08
f1 (ppm)


176.997
155.972
147.991
130.788
125.297
118.651
116.300
77.318
77.000
76.682
44.370
25.691
25.600
21.633
Me
CN
O
N
N
Me
3h
13C NMR, CDCl3
(100 MHz)
f1 (ppm)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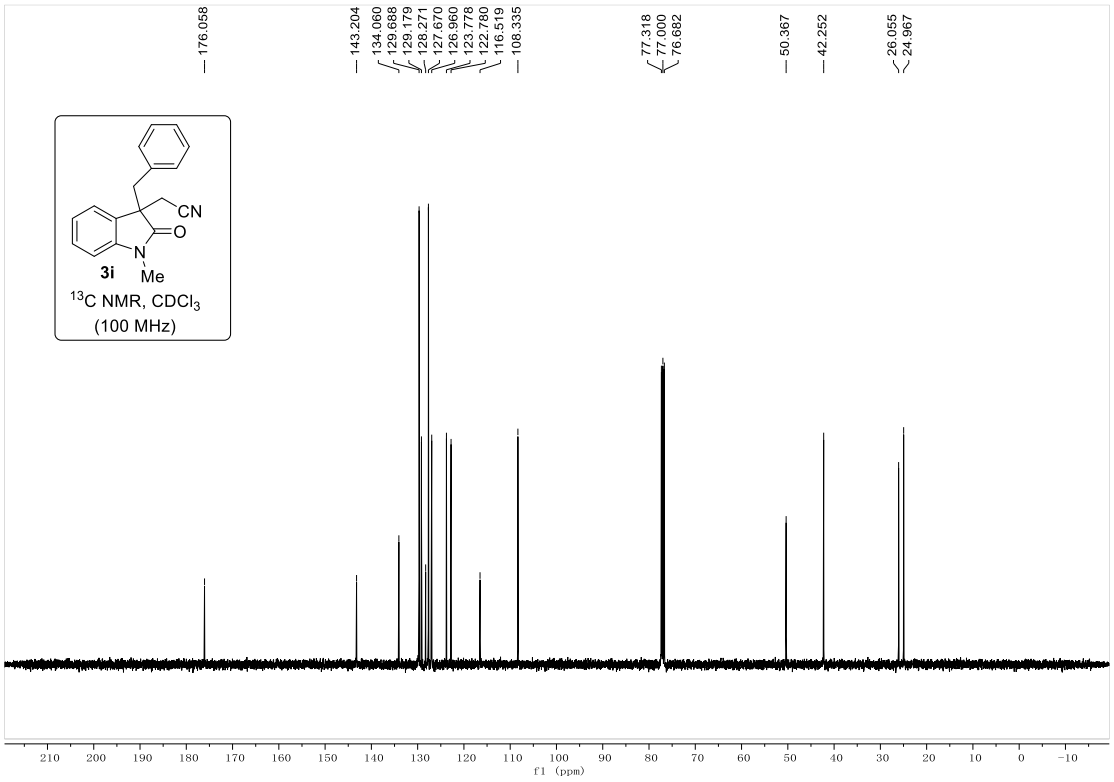
7.463
7.277
7.258
7.239
7.138
7.119
7.101
7.084
7.062
7.043
7.027
6.834
6.816
6.643
6.624
3.266
3.234
3.206
3.174
2.990
2.970
2.948
2.759
2.717
CN
O
N
Me
3i
1H NMR, CDCl3
(400 MHz)
1.00
1.05
4.00
2.05
1.04
2.06
5.04
f1 (ppm)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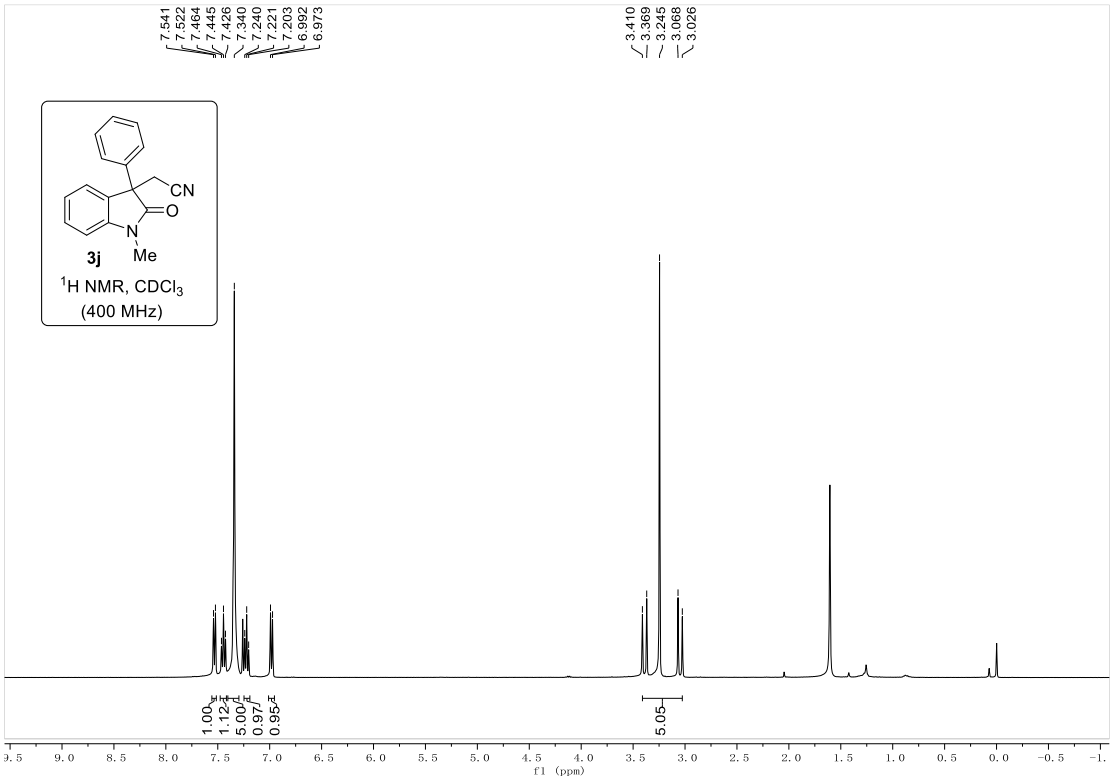
143.204
134.060
129.688
129.179
128.271
127.670
126.960
123.778
122.780
116.519
108.335
77.318
77.000
76.682
50.367
42.252
26.055
24.967
CN
O
N
Me
3i
13C NMR, CDCl3
(100 MHz)
f1 (ppm)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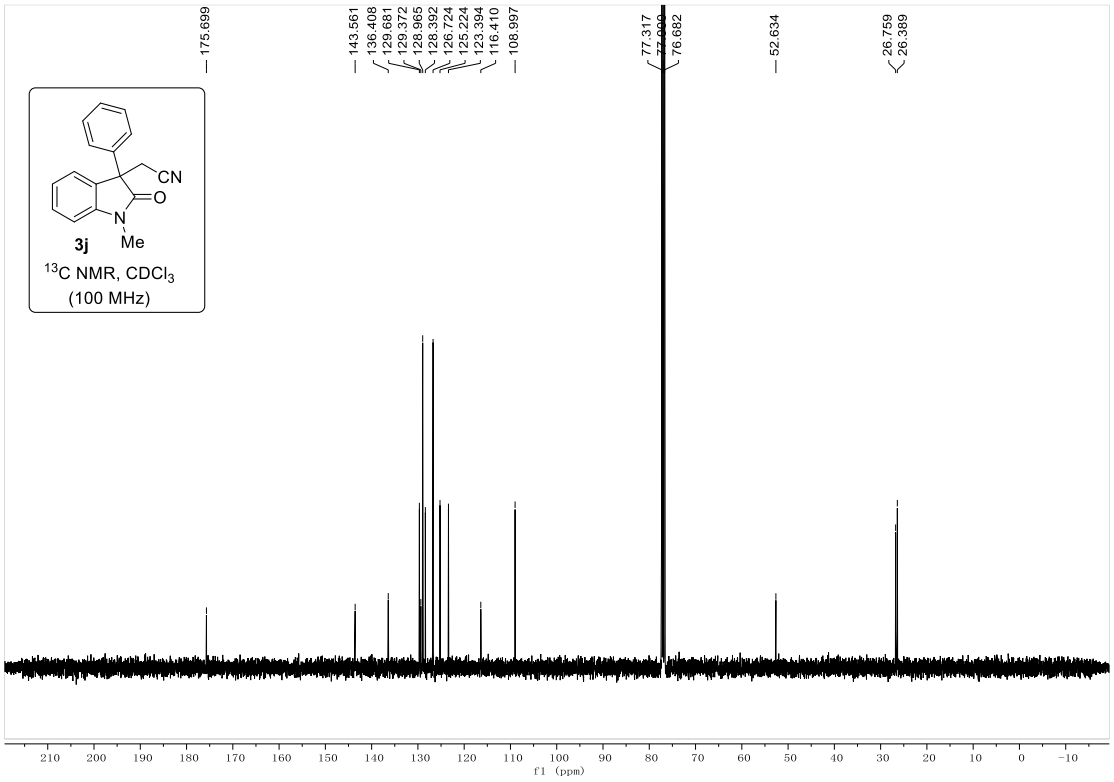
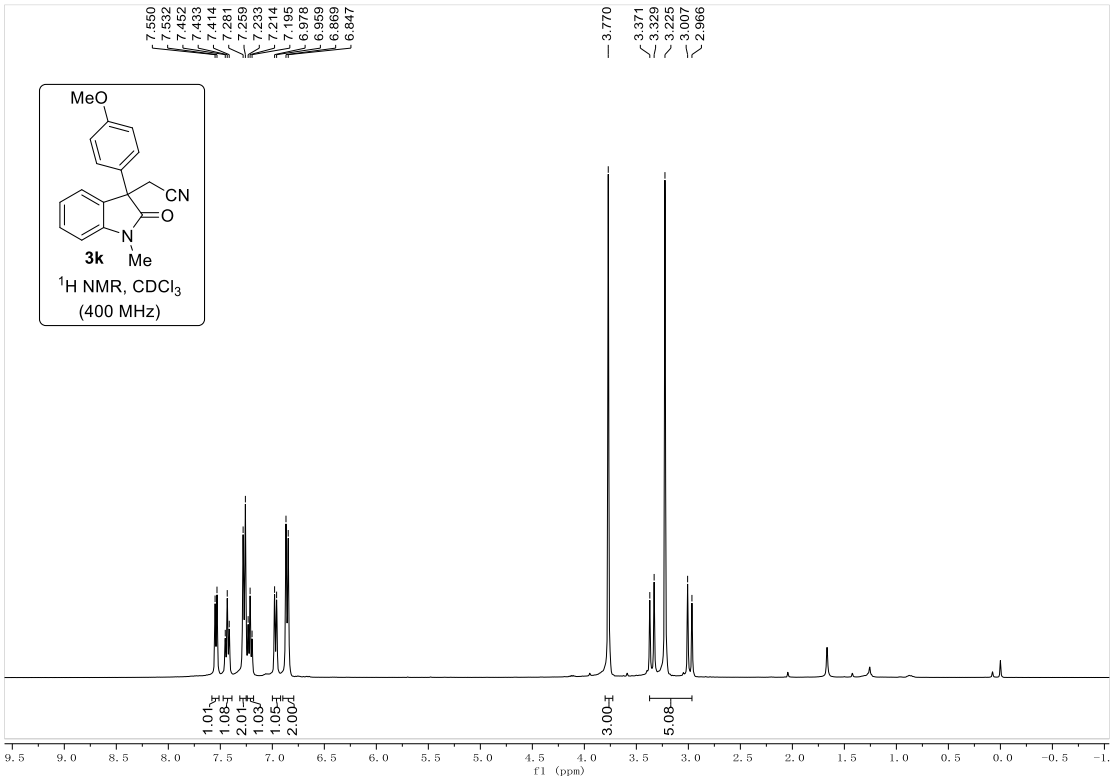
7.522
7.464
7.445
7.426
7.340
7.240
7.221
7.203
6.992
6.973
3.410
3.369
3.245
3.068
3.026
CN
O
N
Me
3j
1H NMR, CDCl3
(400 MHz)
1.00
1.12
5.00
0.97
0.95
5.05
f1 (ppm)


175.699
143.561
136.408
129.681
129.372
128.965
128.392
126.724
125.224
123.394
116.410
108.997
77.317
77.000
76.682
52.634
26.759
26.389
CN
O
N
Me
3j
13C NMR, CDCl3
(100 MHz)
f1 (ppm)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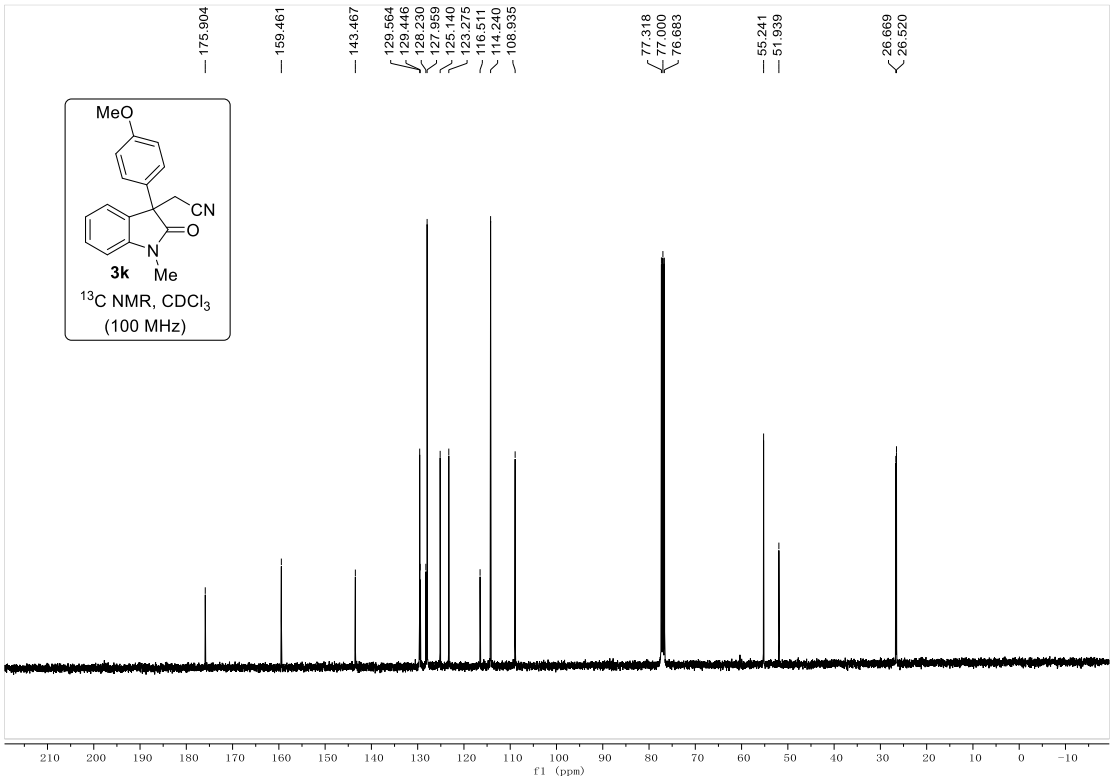
7.532
7.452
7.433
7.414
7.281
7.259
7.233
7.214
7.195
6.978
6.959
6.869
6.847
3.770
3.371
3.329
3.225
3.007
2.966
MeO
CN
O
N
Me
3k
1H NMR, CDCl3
(400 MHz)
1.01
1.08
2.01
1.03
1.05
2.00
3.00
5.08
f1 (ppm)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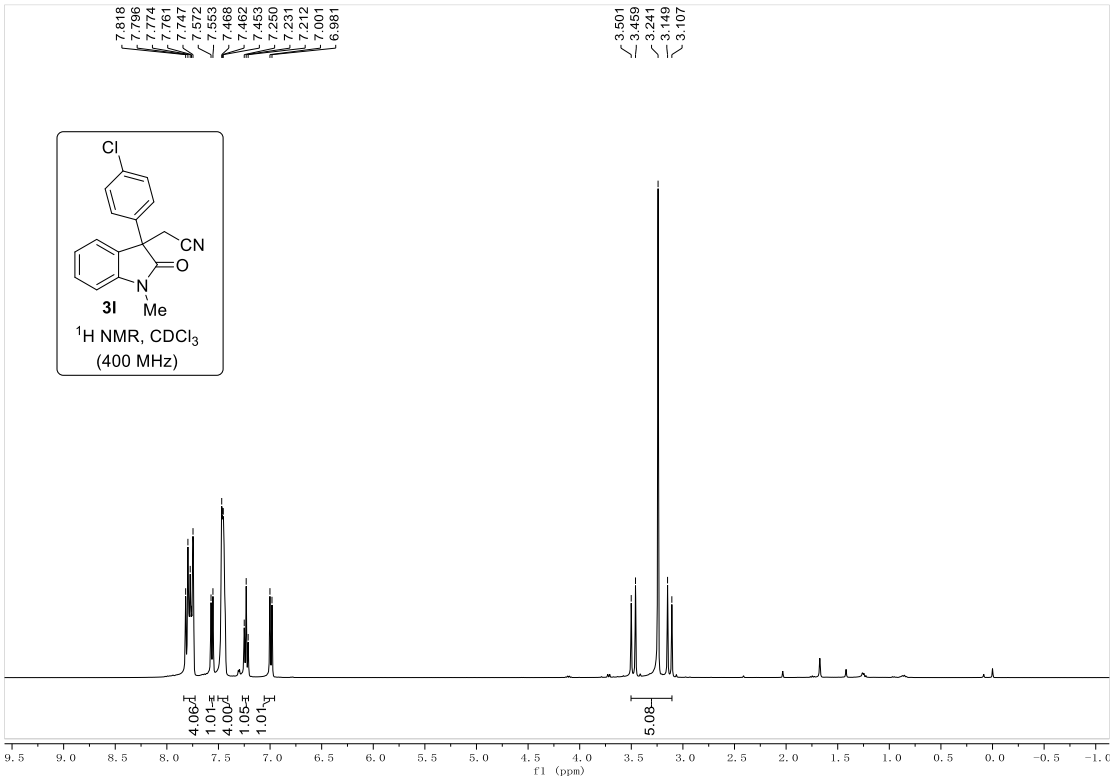
143.467
129.564
129.446
128.230
127.959
125.140
123.275
116.511
114.240
108.935
77.318
77.000
76.683
55.241
51.939
26.669
26.520
MeO
CN
O
N
Me
3k
13C NMR, CDCl3
(100 MHz)
f1 (ppm)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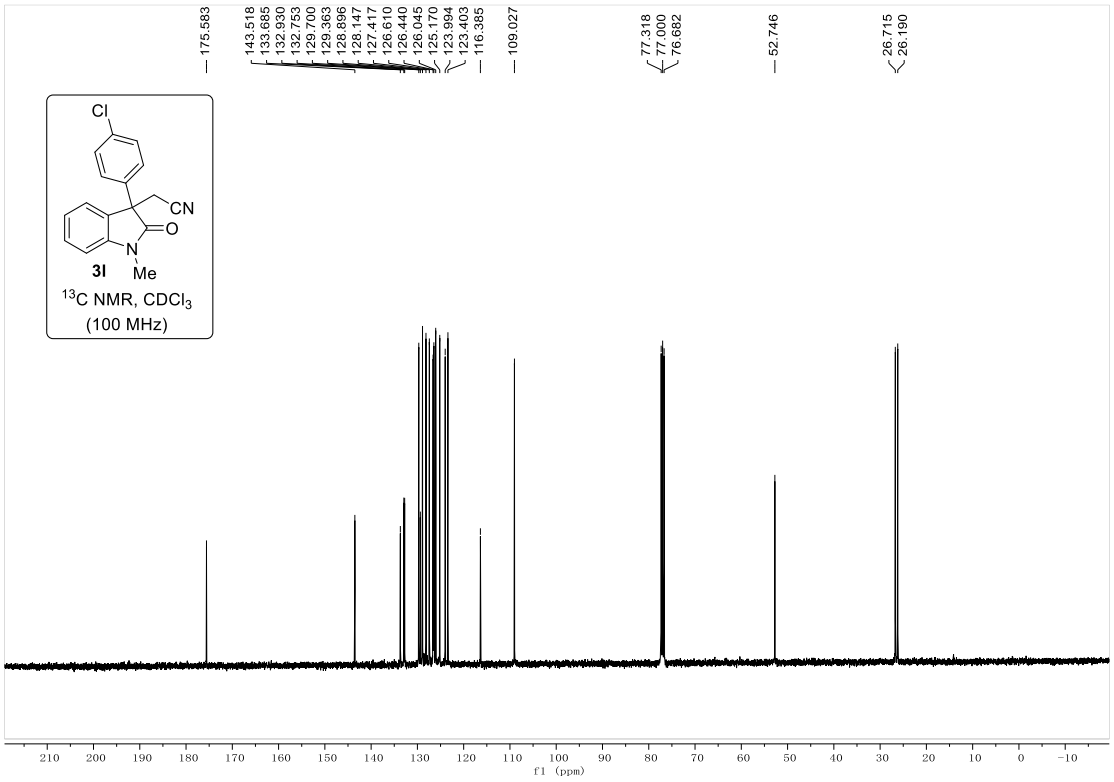
7.796
7.774
7.761
7.747
7.572
7.553
7.468
7.462
7.453
7.250
7.231
7.212
7.001
6.981
3.501
3.459
3.241
3.149
3.107
Cl
CN
O
N
Me
3l
1H NMR, CDCl3
(400 MHz)
4.06
1.01
4.00
1.05
1.01
5.08
f1 (ppm)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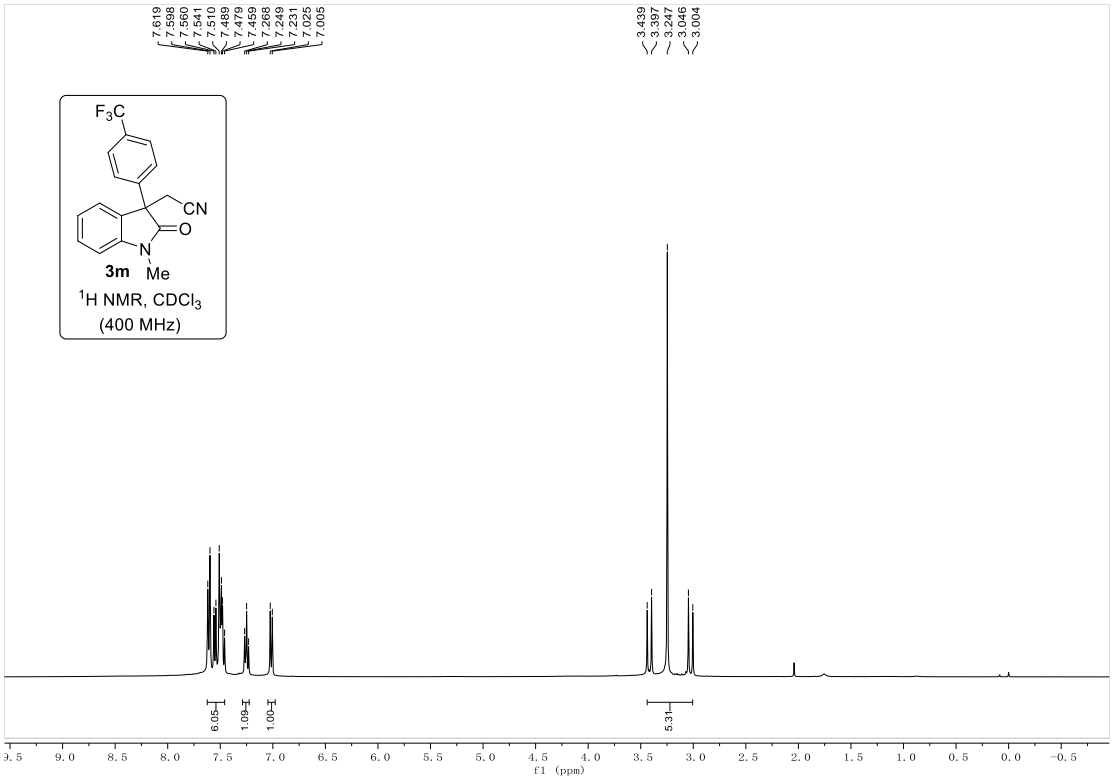
143.518
133.685
132.930
132.753
129.700
129.363
128.896
128.147
127.417
126.610
126.440
126.045
125.170
123.994
123.403
116.385
109.027
77.318
77.000
76.682
52.746
26.715
26.190
Cl
CN
O
N
Me
3l
13C NMR, CDCl3
(100 MHz)
f1 (ppm)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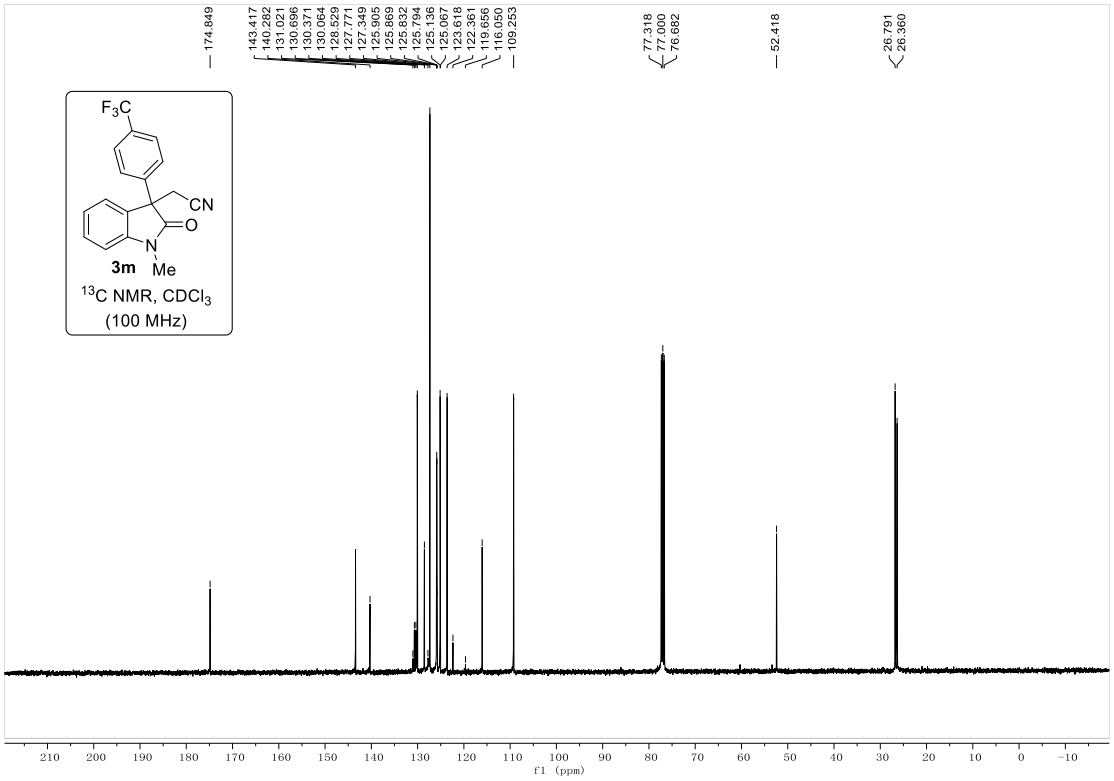
7.560
7.541
7.510
7.488
7.479
7.459
7.268
7.249
7.231
7.025
7.005
3.439
3.397
3.247
3.046
3.004
F3C
CN
O
N
Me
3m
1H NMR, CDCl3
(400 MHz)
6.05
1.09
1.00
5.31
f1 (ppm)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130.064
128.529
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127.349
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125.832
125.794
125.136
125.067
123.618
122.361
119.656
116.050
109.253
77.318
77.000
76.682
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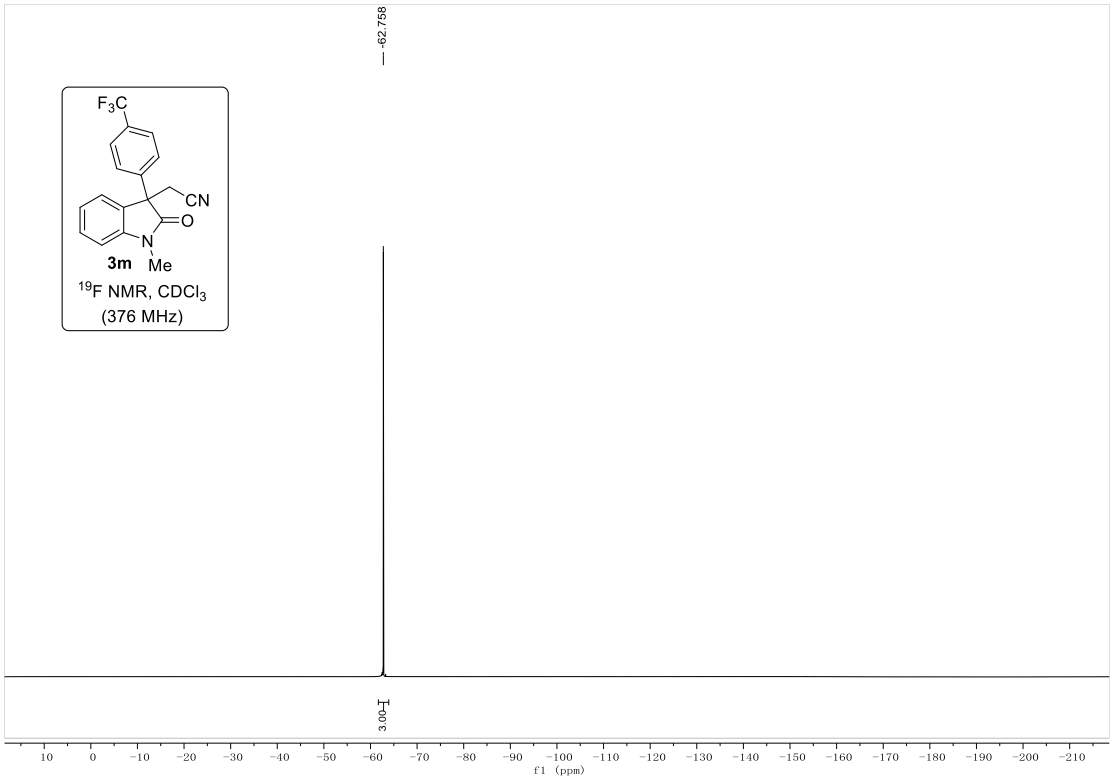
26.360
F3C
CN
O
N
Me
3m
13C NMR, CDCl3
(100 MHz)
f1 (ppm)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19F NMR, CDCl3
(376 MHz)
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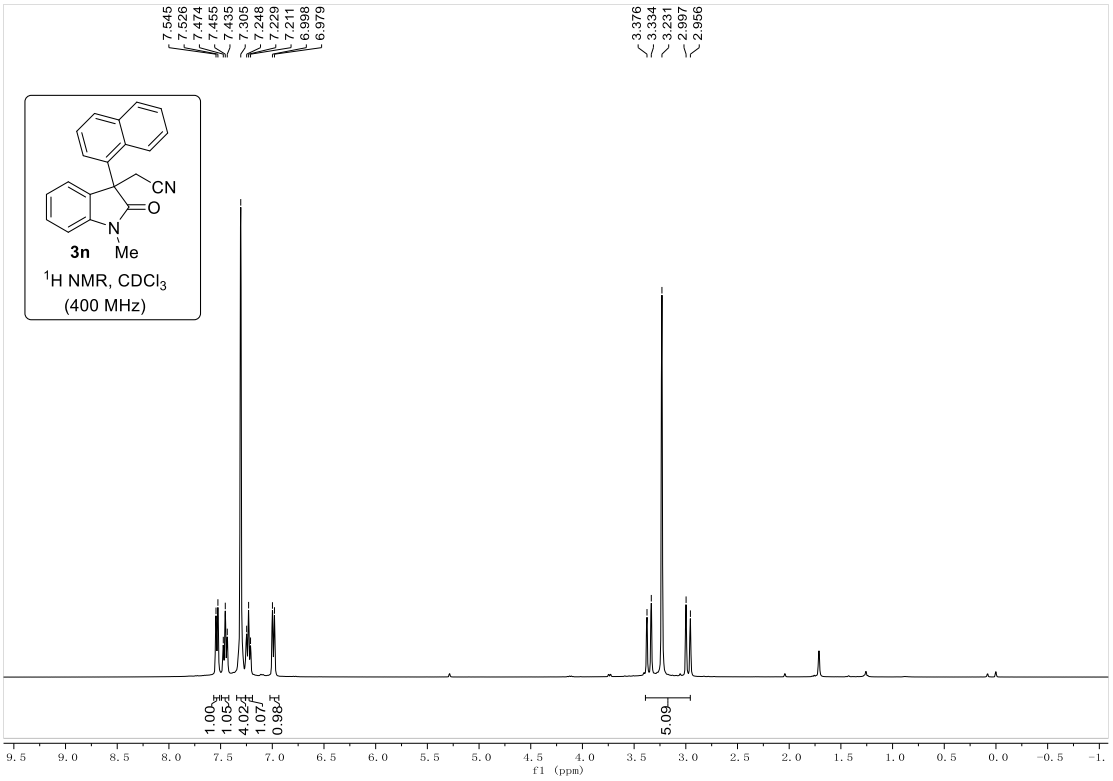
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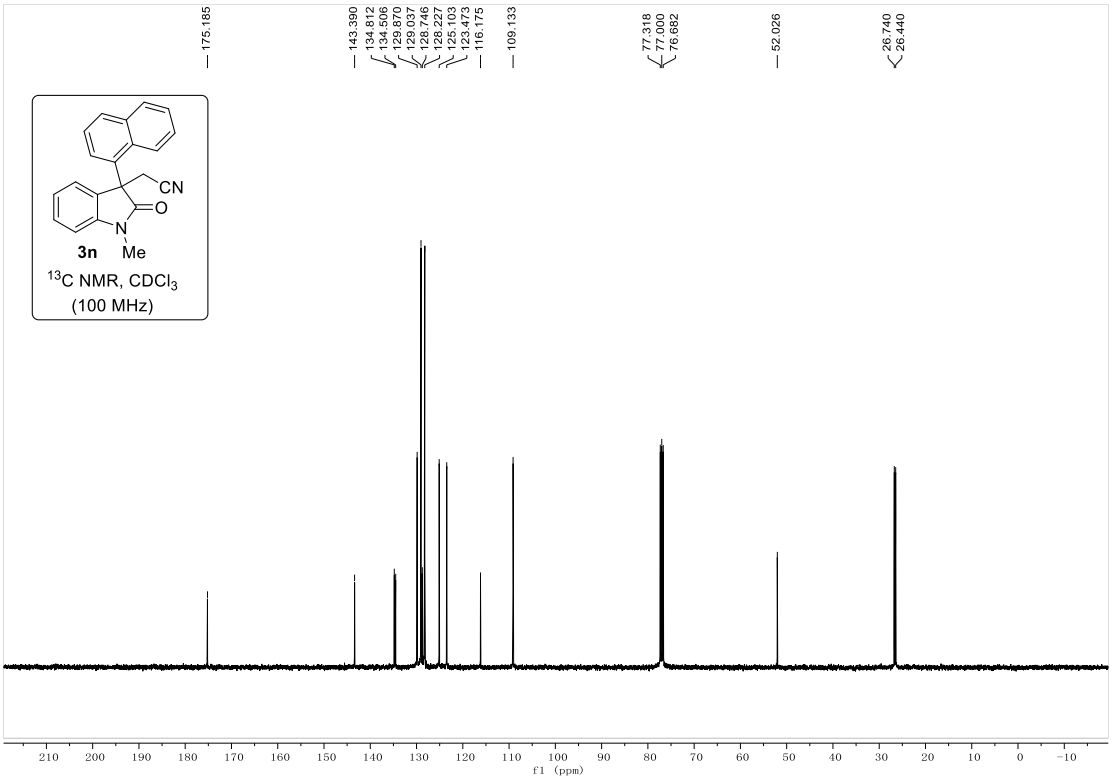
7.455
7.435
7.305
7.248
7.229
7.211
6.998
6.979
3.376
3.334
3.231
2.997
2.956
CN
O
N
Me
3n
1H NMR, CDCl3
(400 MHz)
1.00
1.05
4.02
1.07
0.98
5.09
f1 (ppm)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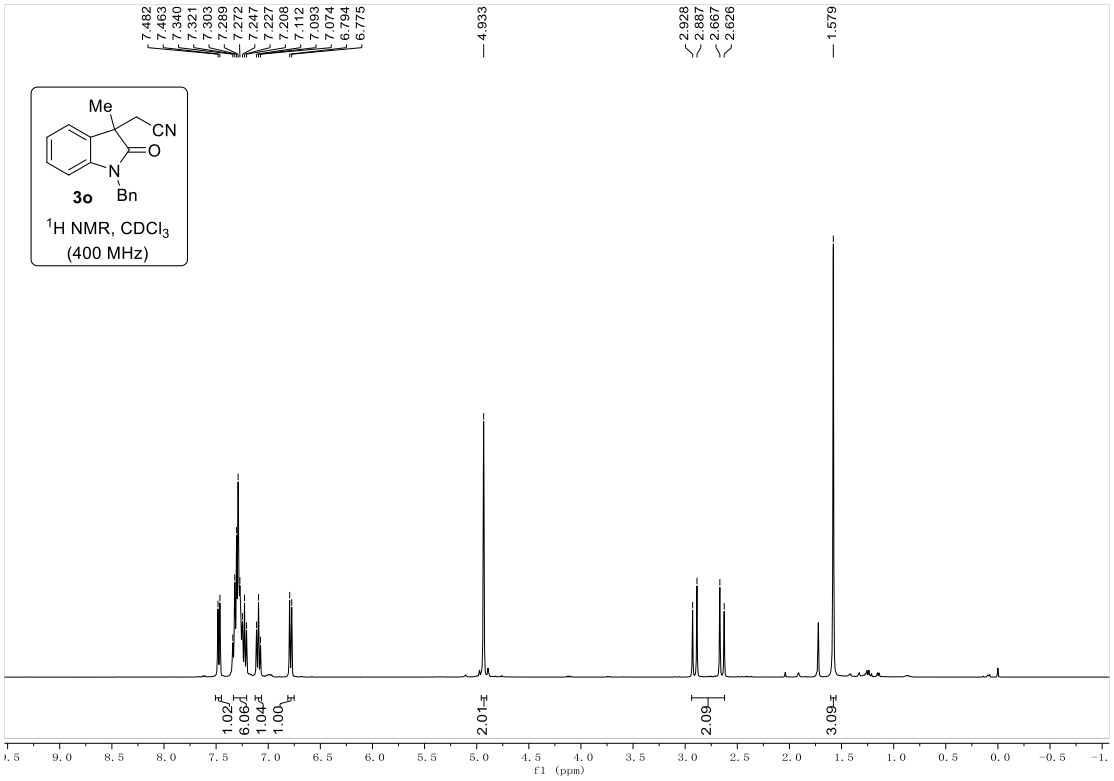
134.506
129.870
129.037
128.746
128.227
125.103
123.473
116.175
109.133
77.318
77.000
76.682
52.026
26.740
26.440
CN
O
N
Me
3n
13C NMR, CDCl3
(100 MHz)
f1 (ppm)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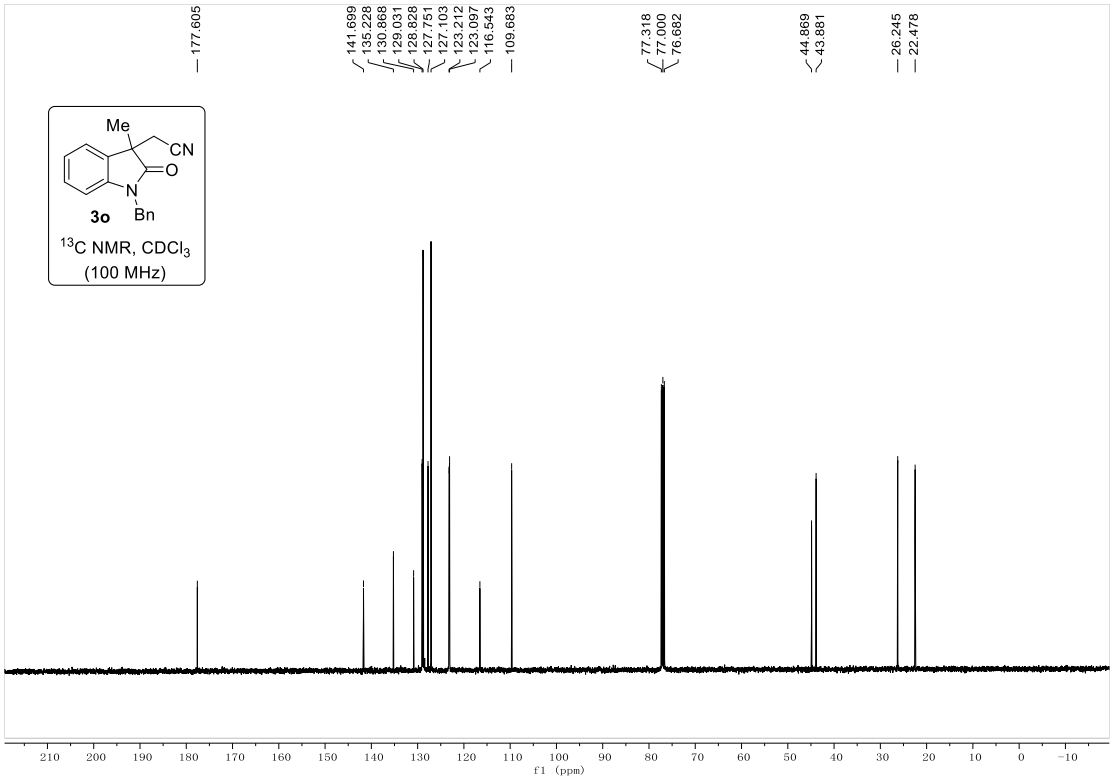
7.289
7.272
7.247
7.227
7.208
7.112
7.093
7.074
6.794
6.775
4.933
2.928
2.887
2.667
2.626
1.579
Me
CN
O
N
Bn
3o
1H NMR, CDCl3
(400 MHz)
1.02
6.06
1.04
1.00
2.01
2.09
3.09
f1 (ppm)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130.868
129.031
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127.751
127.103
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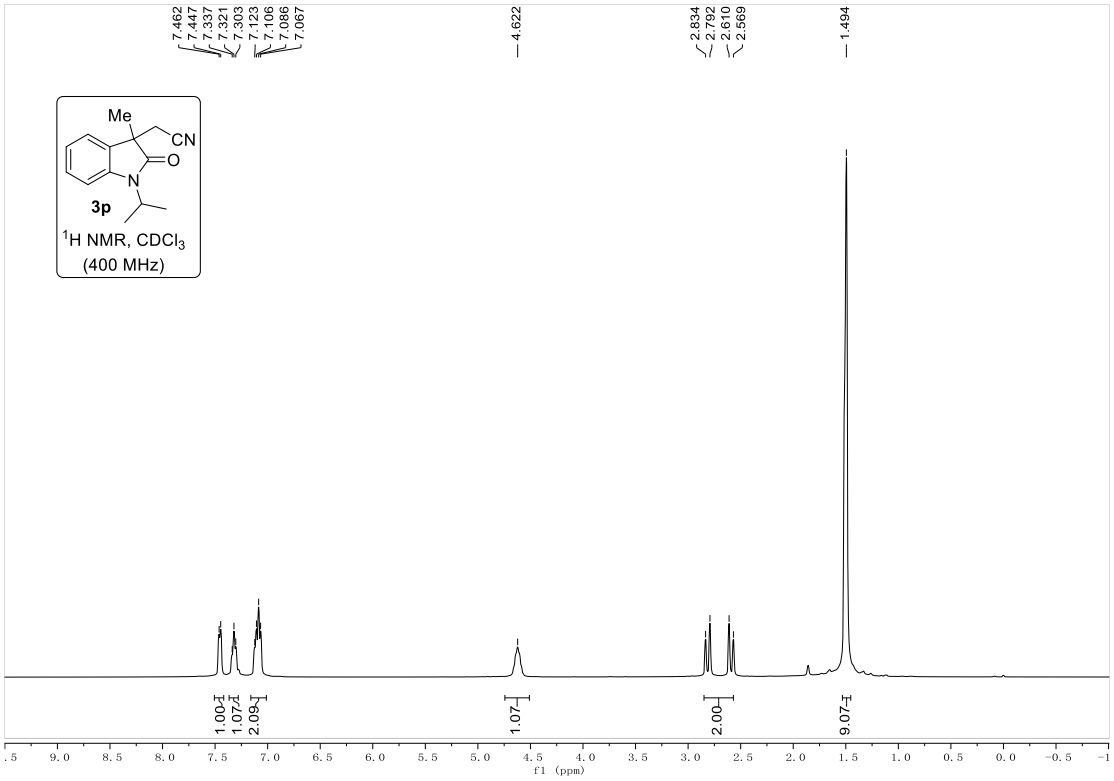
123.097
116.543
109.683
77.318
77.000
76.682
44.869
43.881
26.245
22.478
Me
CN
O
N
Bn
3o
13C NMR, CDCl3
(100 MHz)
f1 (ppm)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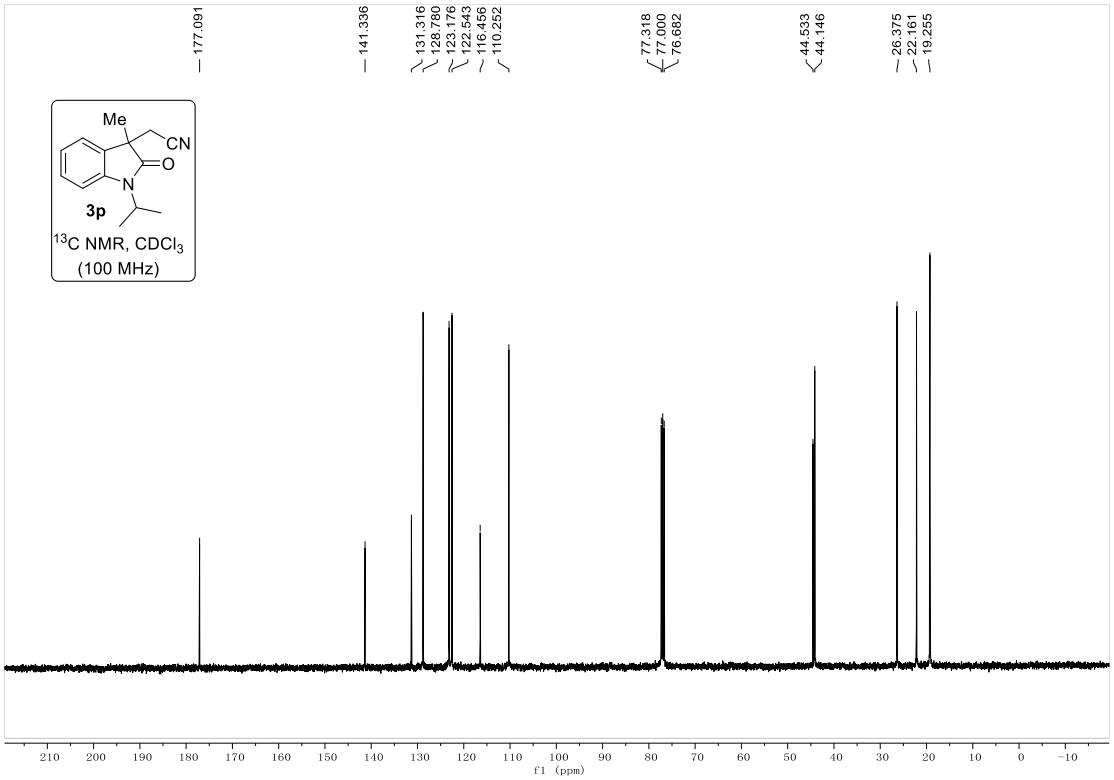
7.337
7.321
7.303
7.123
7.106
7.086
7.067
4.622
2.834
2.792
2.610
2.569
1.494
Me
CN
O
N
3p
1H NMR, CDCl3
(400 MHz)
1.00
1.07
2.09
1.07
2.00
9.07
f1 (ppm)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128.780
123.176
122.543
116.456
110.252
77.318
77.000
76.682
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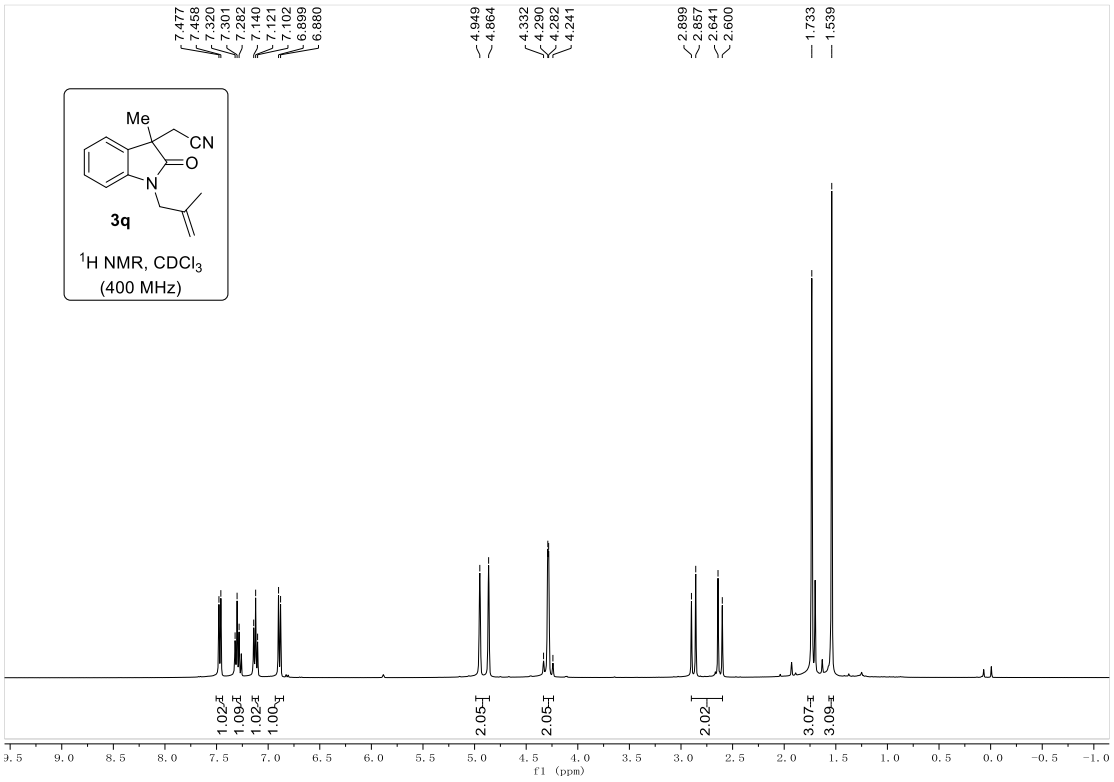
44.146
26.375
22.161
19.255
Me
CN
O
N
3p
13C NMR, CDCl3
(100 MHz)
f1 (ppm)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7.140
7.121
7.102
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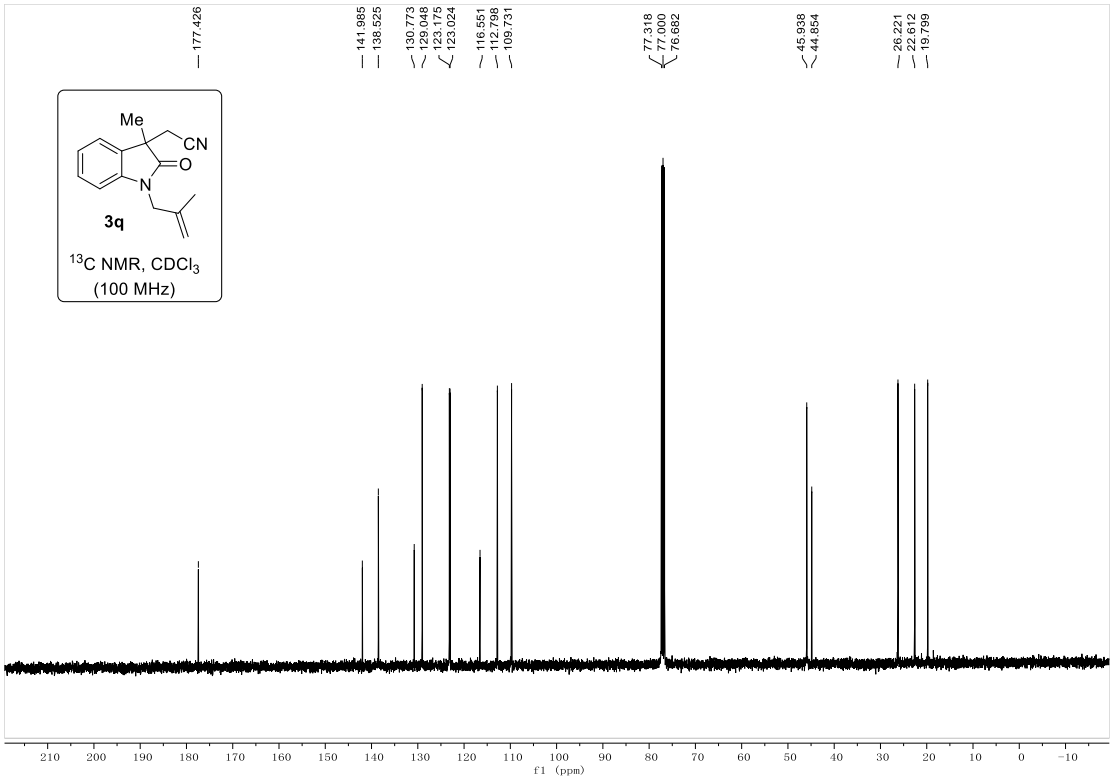
6.880
4.949
4.864
4.332
4.290
4.282
4.241
2.899
2.857
2.641
2.600
1.733
1.539
Me
CN
O
N
3q
1H NMR, CDCl3
(400 MHz)
1.02
1.09
1.02
1.00
2.05
2.05
2.02
3.07
3.09
f1 (ppm)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116.551
112.798
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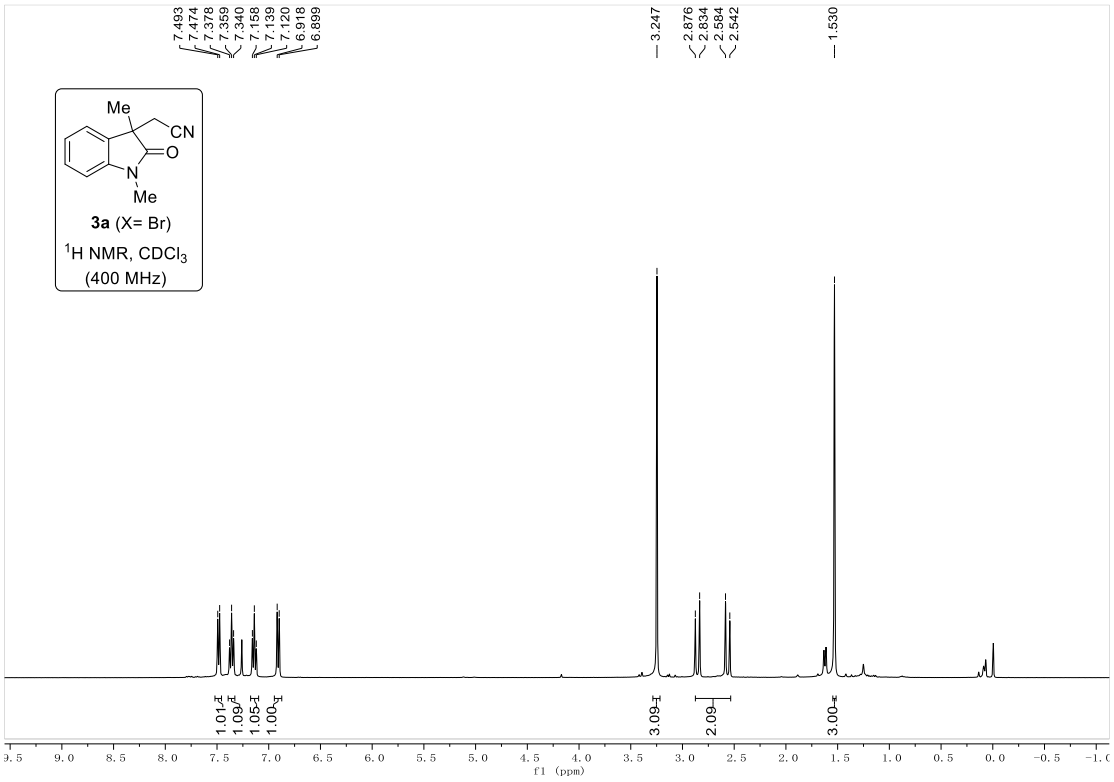
77.318
77.000
76.682
45.938
44.854
26.221
22.612
19.799
Me
CN
O
N
3q
13C NMR, CDCl3
(100 MHz)
f1 (ppm)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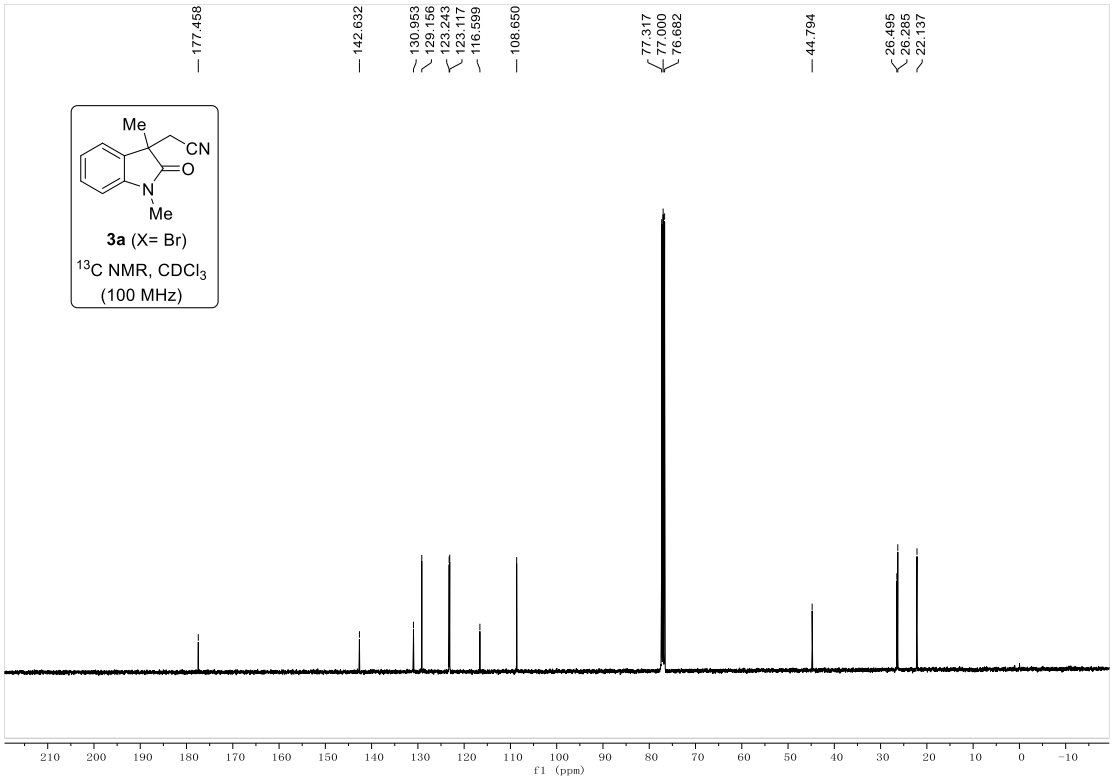
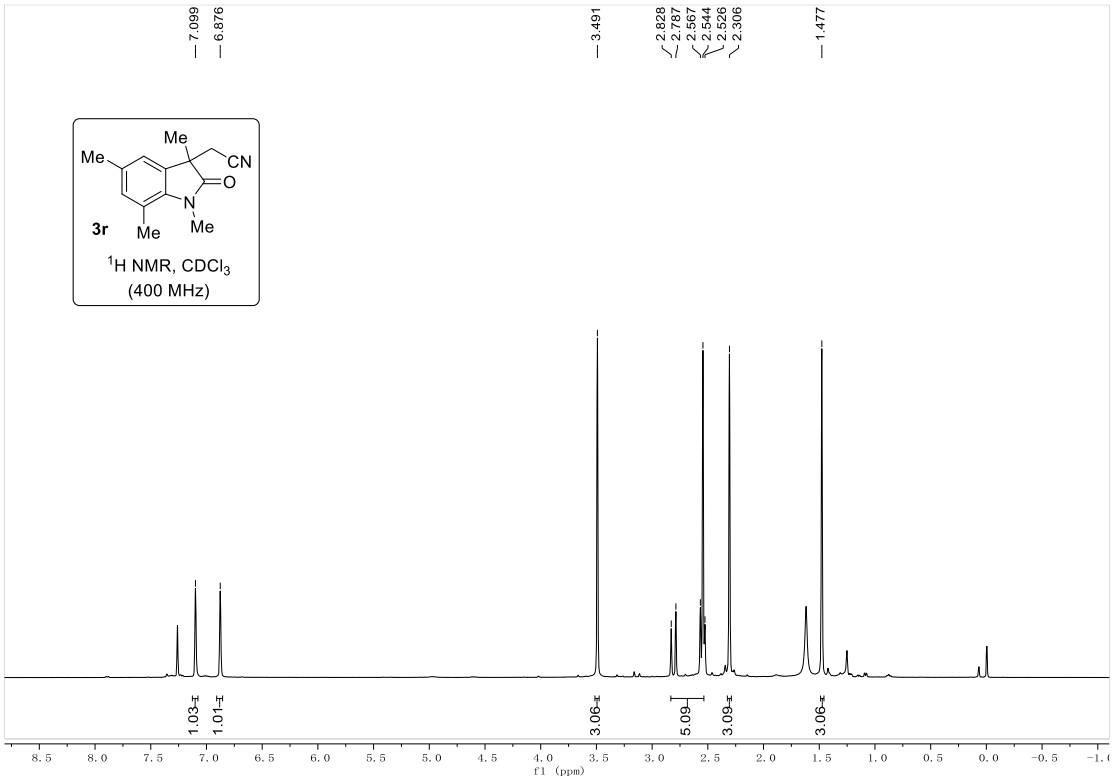
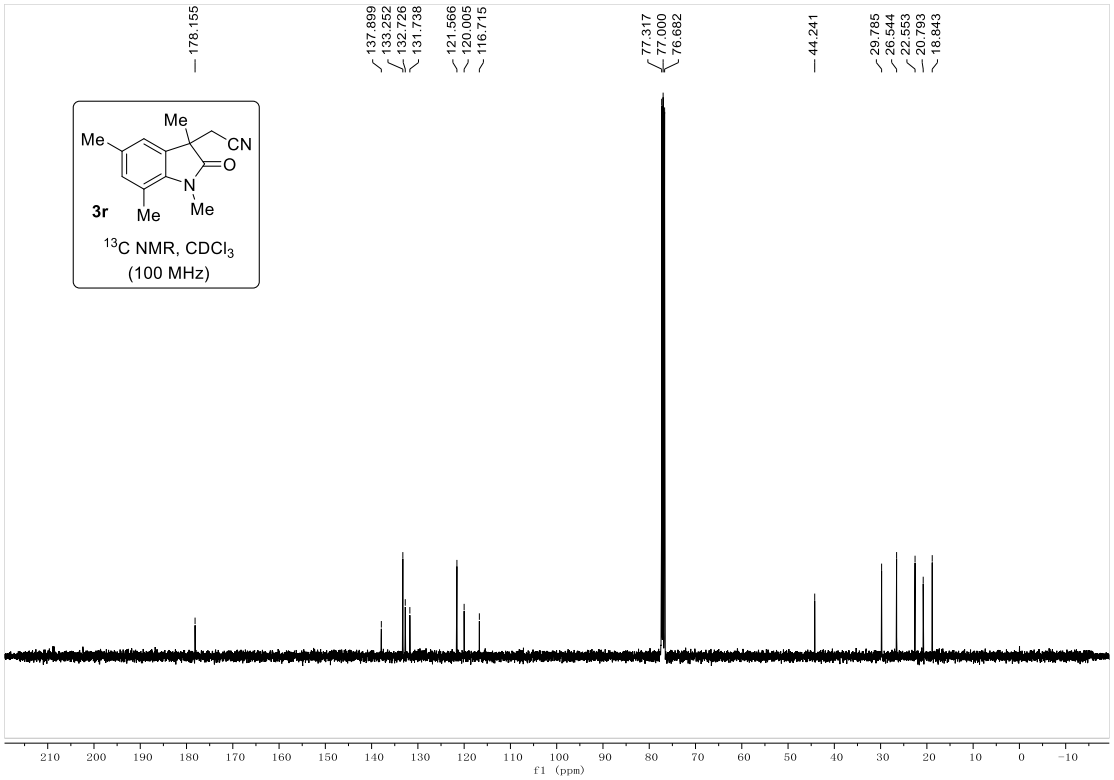
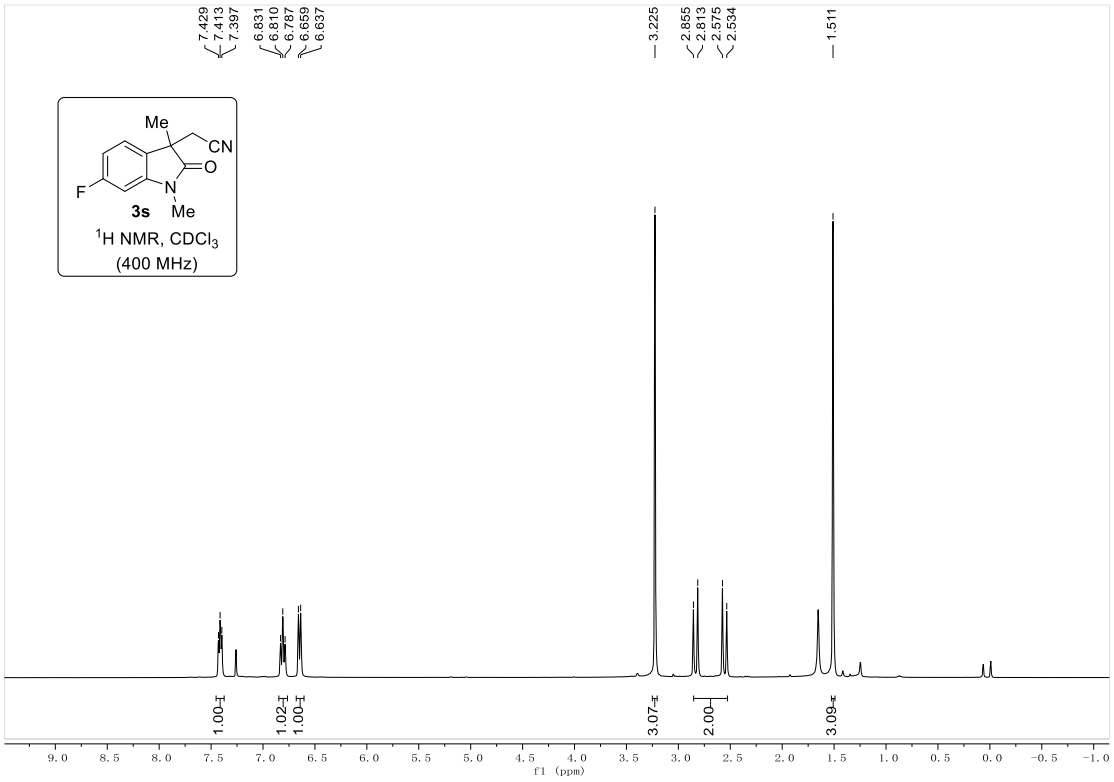
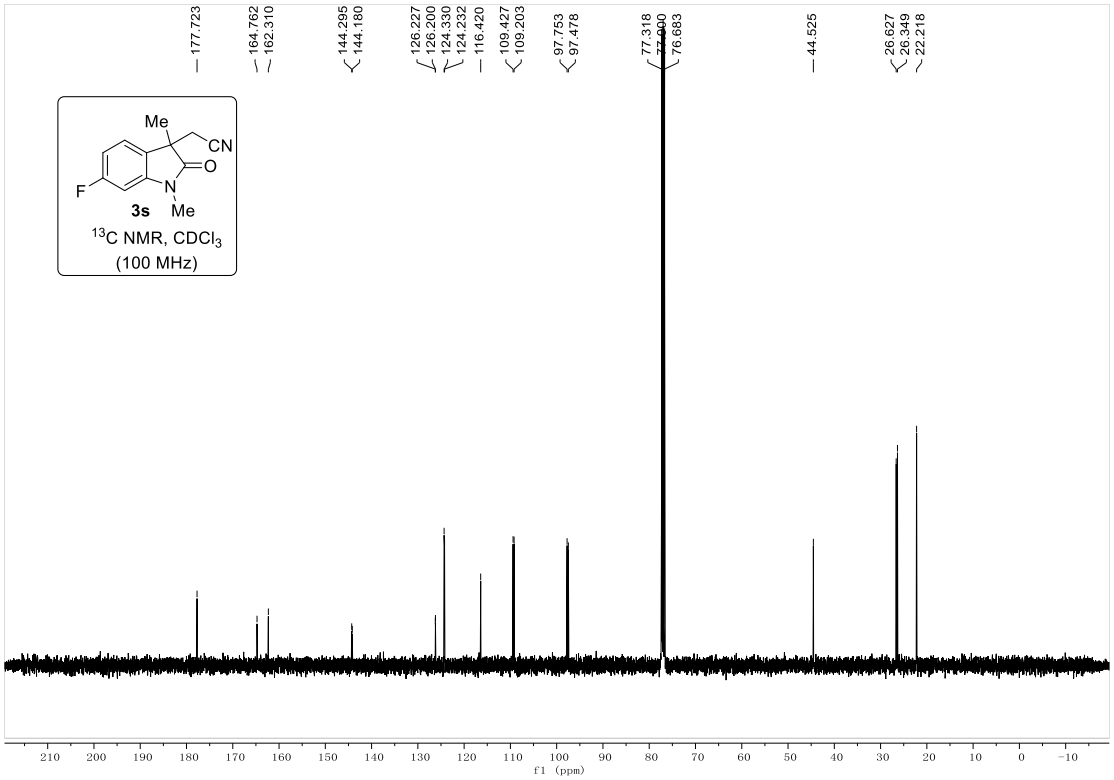
7.359
7.340
7.158
7.139
7.120
6.918
6.899
3.247
2.876
2.834
2.584
2.542
1.530
Me
CN
O
N
Me
3a (X= Br)
1H NMR, CDCl3
(400 MHz)
1.01
1.09
1.05
1.00
3.09
2.09
3.00
f1 (ppm)

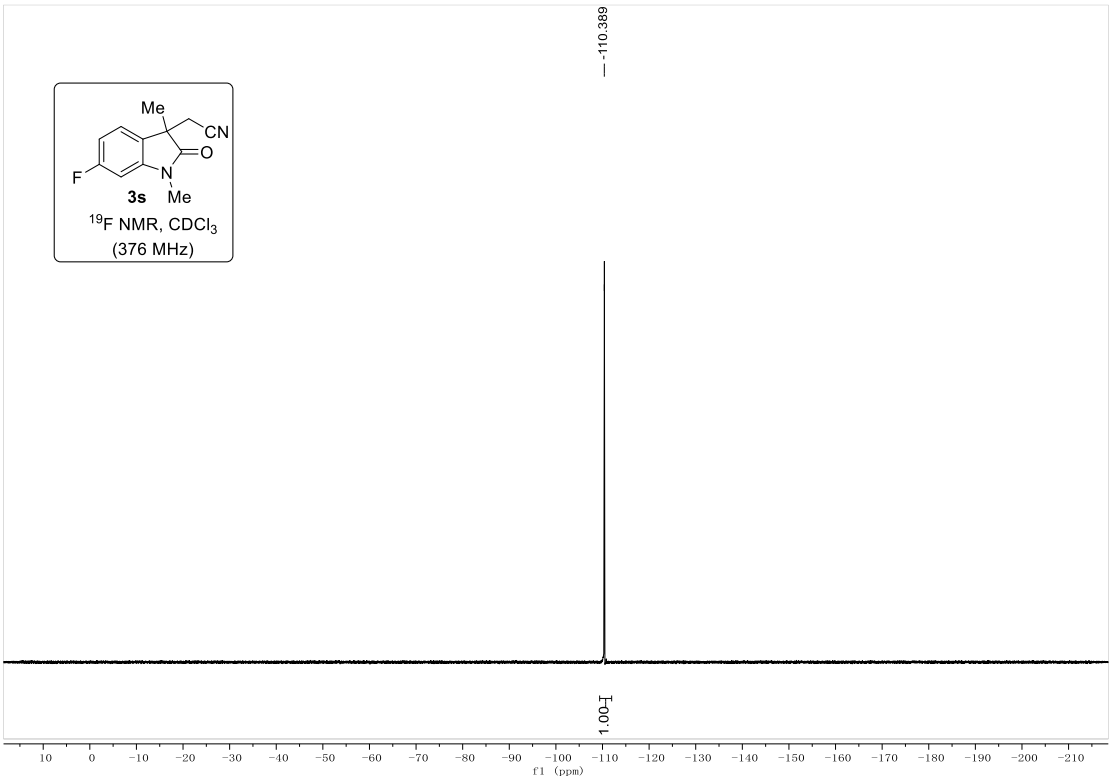

177.458
142.632
130.953
129.156
123.243
123.117
116.599
108.650
77.317
77.000
76.682
44.794
26.495
26.285
22.137
Me
CN
O
N
Me
3a (X= Br)
13C NMR, CDCl3
(100 MHz)
f1 (ppm)

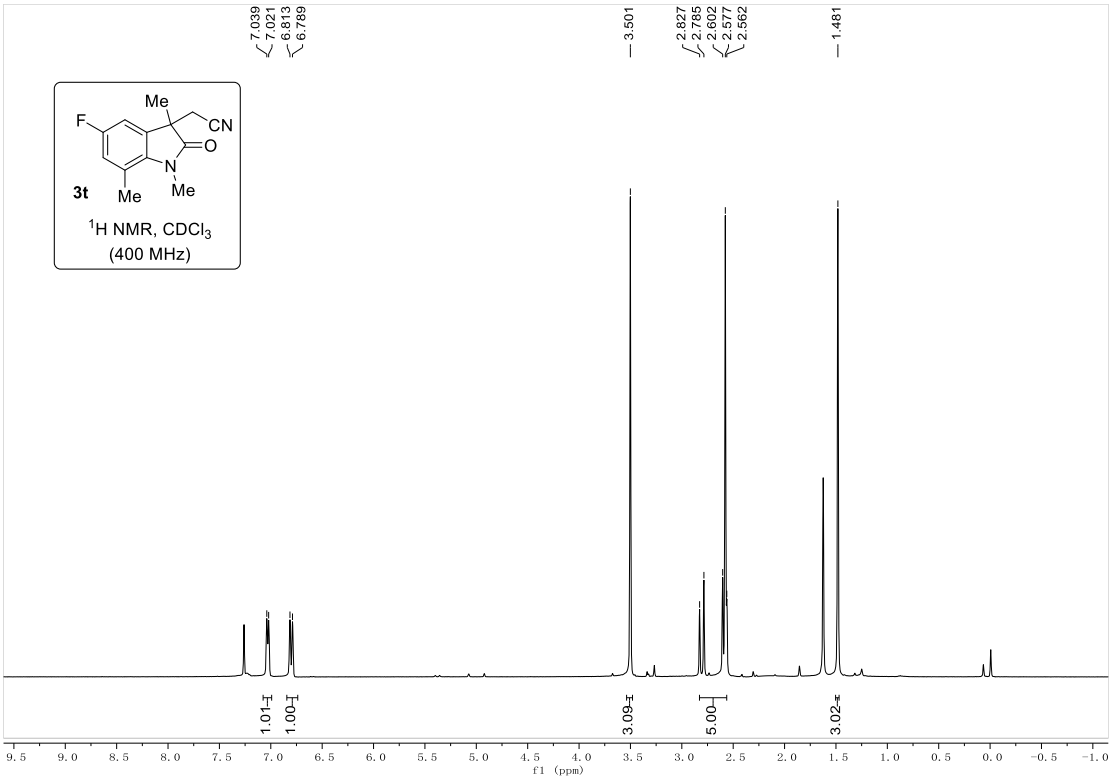

7.099
6.876
3.491
2.828
2.787
2.567
2.544
2.526
2.306
1.477
Me
Me
CN
O
N
Me
3r
Me
Me
1H NMR, CDCl3
(400 MHz)
1.03
1.01
3.06
5.09
3.09
3.06
f1 (ppm)

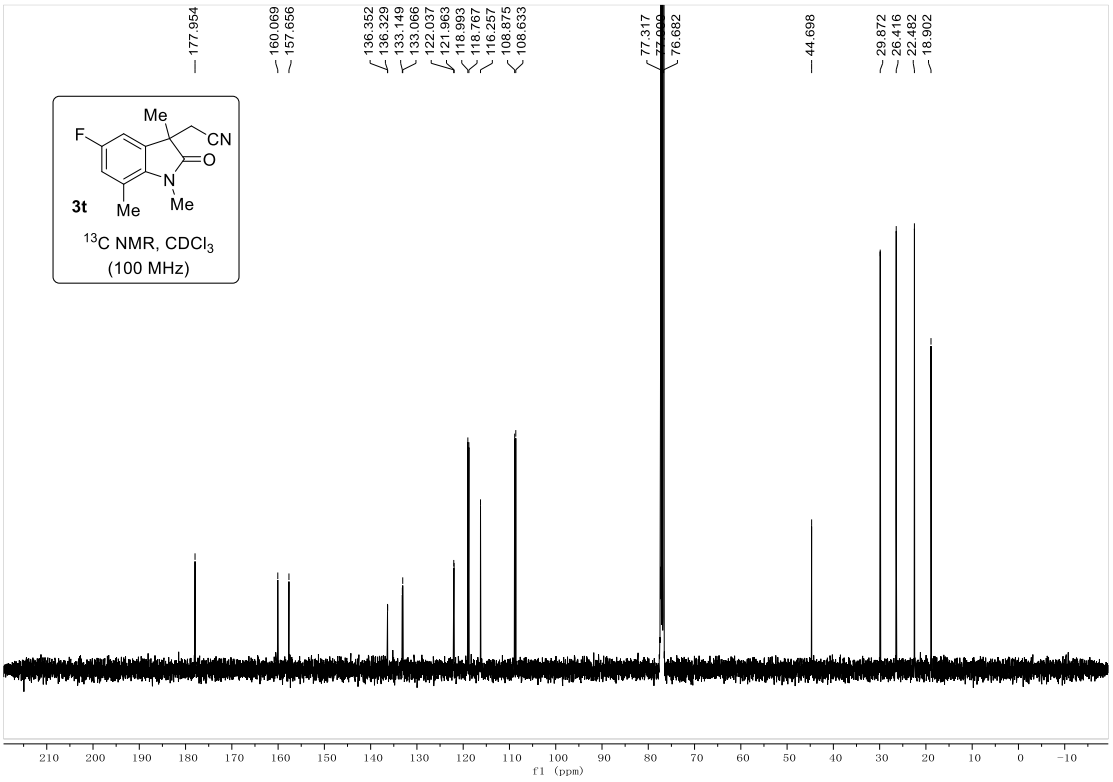

178.155
137.899
133.252
132.726
131.738
121.566
120.005
116.715
77.317
77.000
76.682
44.241
29.785
26.544
22.553
20.793
18.843
Me
Me
CN
O
N
Me
3r
Me
Me
13C NMR, CDCl3
(100 MHz)
f1 (ppm)

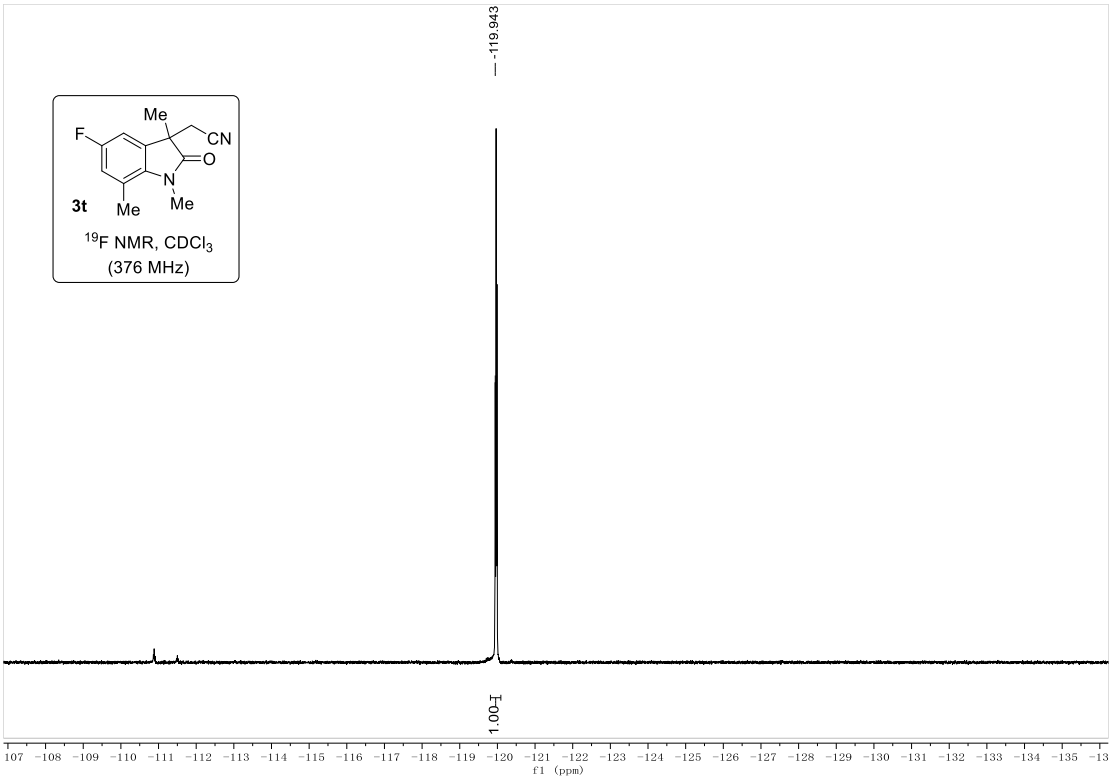

7.429
7.413
7.397
6.831
6.810
6.787
6.659
6.637
3.225
2.855
2.813
2.575
2.534
1.511
Me
CN
O
F
N
Me
3s
^{1}H NMR, CDCl$_3$
(400 MHz)
1.00
1.02
1.00
3.07
2.00
3.09
f1 (ppm)

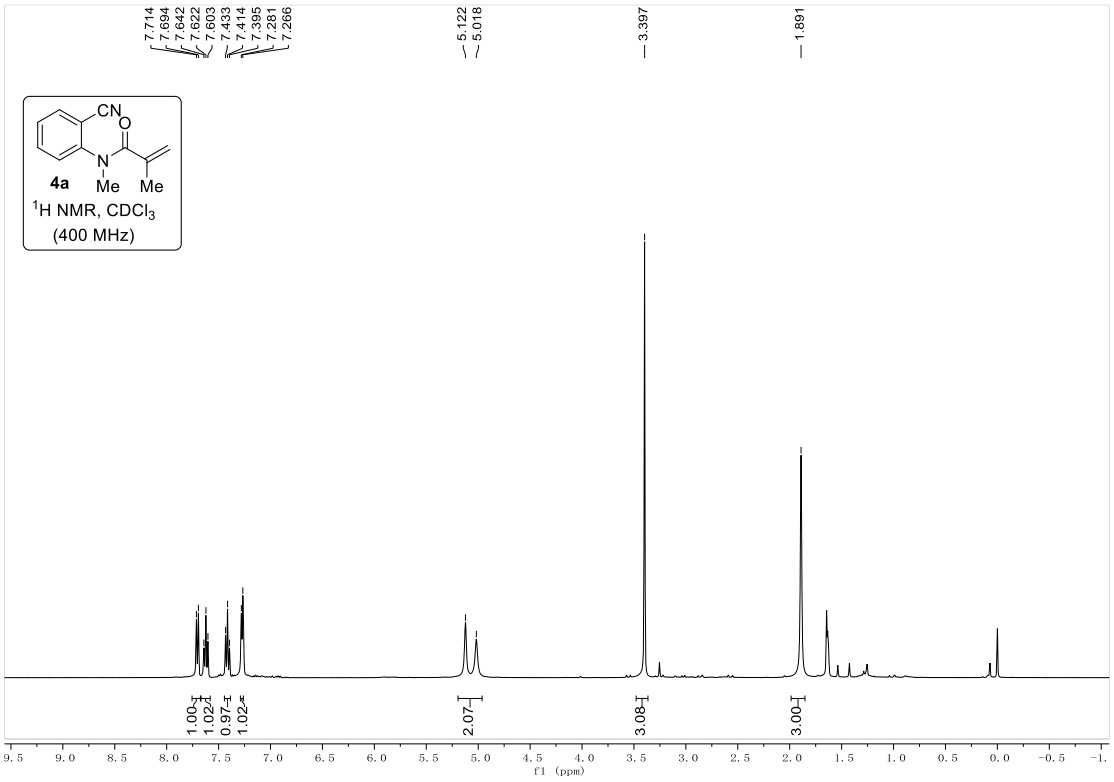

177.723
164.762
162.310
144.295
144.180
126.227
126.200
124.330
124.232
116.420
109.427
109.203
97.753
97.478
77.318
77.000
76.683
44.525
26.627
26.349
22.218
Me
CN
O
F
N
Me
3s
^{13}C NMR, CDCl$_3$
(100 MHz)
f1 (ppm)

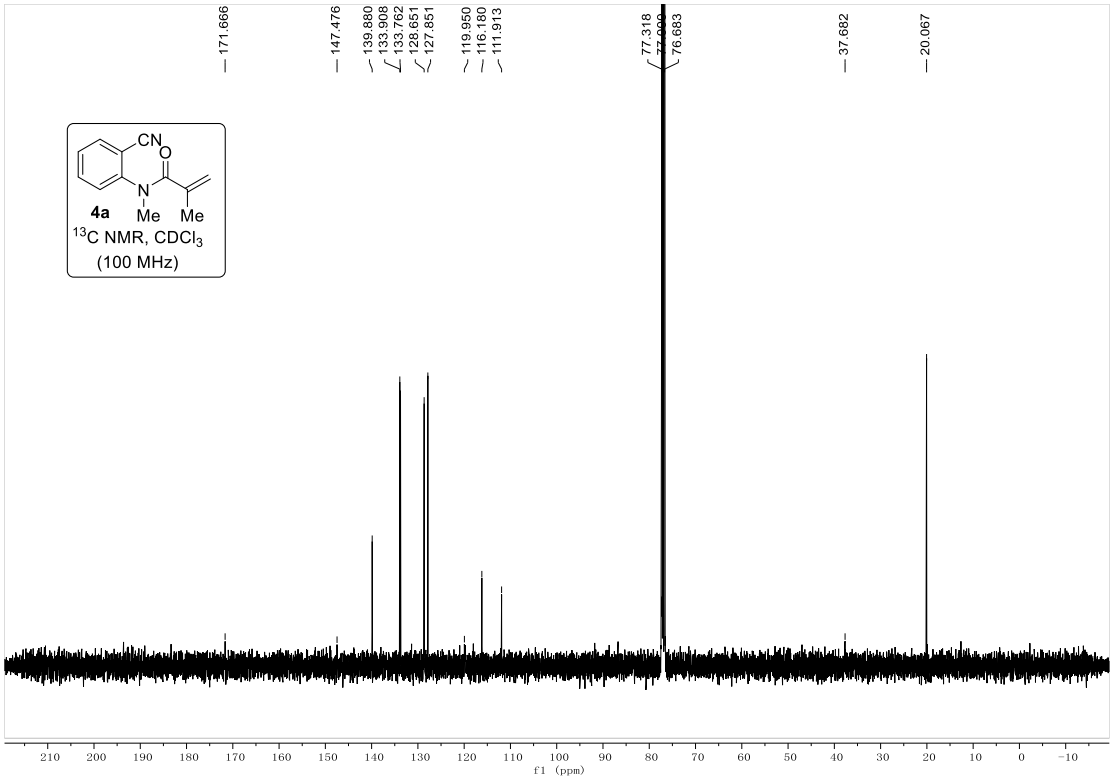

-110.389
Me
CN
O
F
N
Me
3s
^{19}F NMR, CDCl$_3$
(376 MHz)
1.00
f1 (ppm)


7.039
7.021
6.813
6.789
3.501
2.827
2.785
2.602
2.577
2.562
1.481
Me
F
CN
O
N
Me
3t
Me
Me
^{1}H NMR, CDCl$_3$
(400 MHz)
1.01
1.00
3.09
5.00
3.02
f1 (ppm)


177.954
160.069
157.656
136.352
136.329
133.149
133.066
122.037
121.963
118.993
118.767
116.257
108.875
108.633
77.317
77.000
76.682
44.698
29.872
26.416
22.482
18.902
Me
F
CN
O
N
Me
3t
Me
^{13}C NMR, CDCl$_3$
(100 MHz)
f1 (ppm)


-119.943
Me
F
CN
O
N
Me
3t
Me
^{19}F NMR, CDCl$_3$
(376 MHz)
1.00
f1 (ppm)


7.714
7.694
7.642
7.622
7.603
7.433
7.414
7.395
7.281
7.266
5.122
5.018
3.397
1.891
CN
O
N
Me
Me
4a
1H NMR, CDCl3
(400 MHz)
1.00
1.02
0.97
1.02
2.07
3.08
3.00
f1 (ppm)


171.666
147.476
139.880
133.908
133.762
128.651
127.851
119.950
116.180
111.913
77.318
76.683
37.682
20.067
CN
O
N
Me
Me
4a
13C NMR, CDCl3
(100 MHz)
f1 (ppm)

6. References:

[1] (a) W. Dong, Y. Liu, B. Hu, K. Ren, Y. Li, X. Xie, Y. Jiang and Z. Zhang, *Chem. Commun.* 2015, **51**, 4587−4590. (b) W. Kong, Q. Wang and J. Zhu, *J. Am. Chem. Soc.* 2015, **137**, 16028−16031.

[2] A. Yen and M. Lautens, *Org. Lett.* 2018, **20**, 4323–4327.

[3] Y. Li, K. Wang, Y. Ping, Y. Wang and W. Kong, *Org. Lett.* 2018, **20**, 921–924.

[4] Y. Feng, S. Yang, S. Zhao, D.-P. Zhang, X. Li, H. Liu, Y. Dong and F.-G. Sun, *Org. Lett.* 2020, **22**, 6734-6738.

[5] W. T. Eckenhoff, A. B. Biernesser and T. Pintauer, *Inorg. Chem.* 2012, **51**, 11917–11929.