Supporting Information

Desulfonylcyanamidation of *α,β*-Unsaturated Sulfones with *N*-tosyl *N*-Aryl Cyanamides (NCTS): Access to *N*-Cyanoenaminones

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1. General information

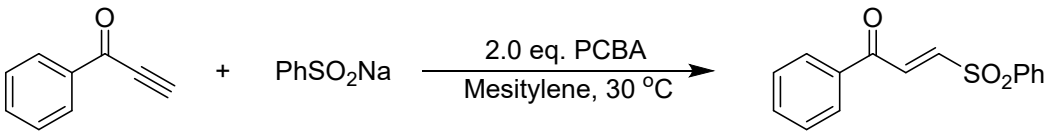
All experiments were carried out under an atmosphere of air. Flash column chromatography was performed over silica gel 48-75 μm. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded on Bruker-AV (500 MHz, 471 MHZ and 126 MHz, respectively) instrument internally referenced to $SiMe_4$ or chloroform signals. HRMS was recorded using waters G2-Xs qtof mass spectrometer. The new compounds were characterized by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, MS and HRMS. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{19}F NMR, ^{13}C NMR data and MS data with those of literature. The Substrates **1**[1] and **2**[2,3] was synthesized according to the reported methods.

Trichloromethane ($CHCl_3$), dichloromethane, dichloroethane and ethyl acetate were freshly distilled from CaH_2; tetrahydrofuran (THF), toluene and ether were dried with sodium benzophenone and distilled before use.

Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. All reagents and solvents were used as received from commercial sources (*Energy Chemical, J&K®, Adamas-beta®, Bidepharm*) without further purification.

2. Experimental procedure

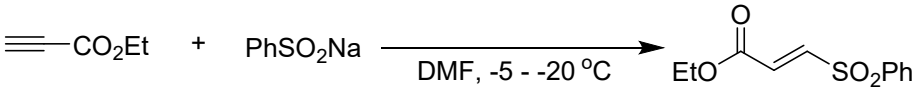
2.1 General Procedure for the synthesis of *α,β*-unsaturated *γ*-keto sulfones[1]



To a dried round bottle flask with a magnetic stirring bar were added the 1-phenylprop-2-yn-1-one (10 mmol), sodium benzosulfinate (20 mmol), and 4-chlorobenzoic acid (20 mmol), followed by the addition of mesitylene (50 mL). The reaction mixture was stirred at room temperature for 50 h. The solvent was removed under reduced pressure, and theresidue was purified by column chromatography on

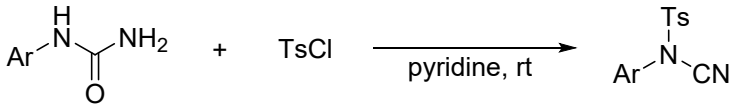
silica gel to afford *α,β*-unsaturated *γ*-keto sulfone.

2.2 General Procedure for the synthesis of (*E*)-3-(phenylsulfonyl)acrylates[3]



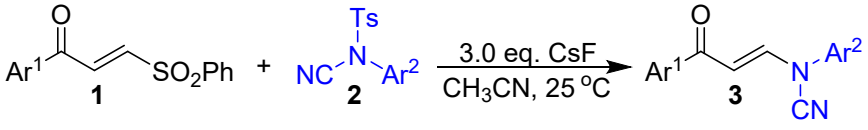
A solution of sodium arylsulfinate (1 mmol) in DMF (3 mL) was cooled to -5 °C. Then, dialkylacetylenedicarboxylate (1 mmol) inDMF(2 mL)was added dropwise, and the mixturewas stirredfor 24 h at room temperature. The mixture was poured onto H_2O (15 mL), extracted with AcOEt(30 mL), dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue waspurified by a silica gel column chromatography using hexane/AcOEt (7:1) as an eluent to give (*E*)-3-(phenylsulfonyl)acrylate.

2.3 General Procedure for the synthesis of NCTS[2]



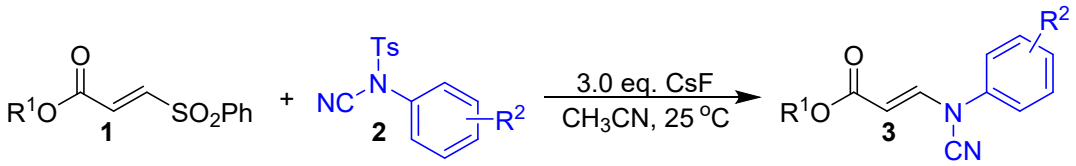
To a mixture of arylurea (1 equiv) and pyridine (150 mL) was added ptoluenesulfonyl chloride (2.5 equiv, 105.8 g) over 3 minutes at room temperature. The reaction mixture was stirred at the same temperature for 20 minutes, and then poured into ice-cooled water (1 L) with vigorous stirring. The formed precipitate was filtered, washed with water and purified by chromatography on silica gel, yielding N-cyano-N-(2-cyanophenyl)-4-methylbenzenesulfonamide.

2.4 CsF-promoted desulycyanamidation of *α,β*-unsaturated sulfones with NCTS



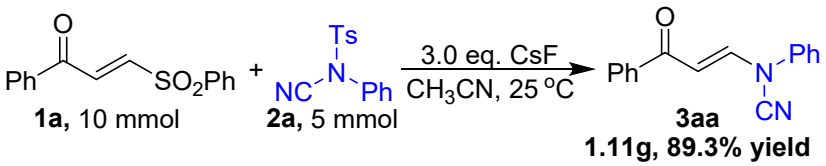
In a 10 mL of sealed tube, a mixture of *α,β*-unsaturated *γ*-keto sulfones **1** (0.4 mmol), NCTS **2** (0.2 mmol), CsF (0.6 mmol) and CH_3CN (2.0 mL) was stirred at room temperature. After completion of the reaction (detected by TLC), the reaction mixture was concentrated under reduced pressure. The residue was separated by column

chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to afford *N*-cyanoenaminones.



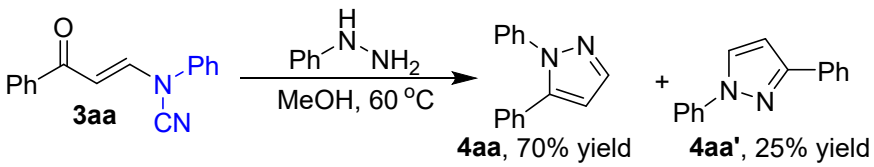
In a 10 mL of sealed tube, a mixture of (*E*)-3-(phenylsulfonyl)acrylates **1** (0.4 mmol), NCTS **2** (0.2 mmol), CsF (0.6 mmol) and CH_3CN (2.0 mL) was stirred at room temperature. After completion of the reaction (detected by TLC), the reaction mixture was concentrated under reduced pressure. The residue was separated by column chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to afford *N*-cyanoenaminesters.

2.5 Gram-scale of **1a**.



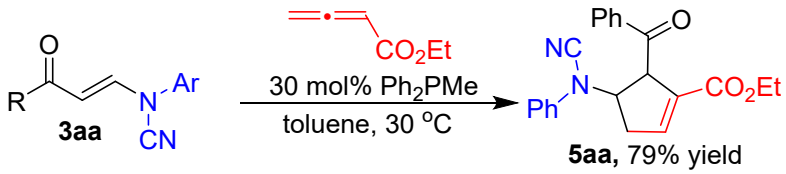
In a 10 mL of sealed tube, a mixture of *α,β*-unsaturated *γ*-keto sulfones **1a** (10 mmol, 2.7g), NCTS **2a** (5 mmol, 1.36g), CsF (15 mmol, 2.28g) and CH_3CN (30.0 mL) was stirred at room temperature. After completion of the reaction (detected by TLC), the reaction mixture was concentrated under reduced pressure. The residue was separated by column chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to afford *N*-cyanoenaminone **3aa** with 89.3% yield (1.11 g).

2.6 The transformation of the product **3aa.**



The **3aa** (0.2 mmol, 49.6 mg) in methanol (1.5 mL) were added to a10 mL flask fitted

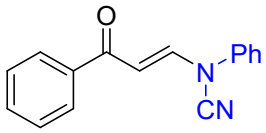
with a reflux condenser and magnetic stirring. Phenyl hydrazine (0.2 mmol; 2.16 g) was then added, and the reactions were heated to 60 °C and remained under magneic stirringfor an additional 4 to 6 h with monitoring via TLC. After completingthe reaction times, the mixtures were allowed to reach room temperature. The residue was separated by column chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to afford **4aa** in 70% yield and **4aa'** in 25% yield.



In a 10 mL of sealed tube, a mixture of **3aa** (0.2 mmol; 42.2 mg), allenoates **2** (0.24 mmol; 26.9 mg), PhPME (0.06 mmol; 12 mg) and toluene (2 mL) was stirred at 30 °C for 1.0 h. After completion of the reaction (detected by TLC), the reaction mixture was concentrated under reduced pressure. The residue was separated by column chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to afford **5aa**, 56.9 mg, 79% yield.

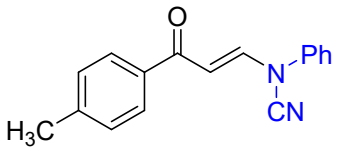
3. Characterization data of the products

(*E*)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)-*N*-phenylcyanamide (3aa)



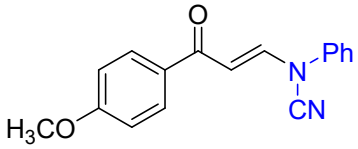
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3aa** as a white solid (47.13 mg, 95% yield); m.p.: 87 – 89 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.77 (d, *J* = 13.2 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.49 (dd, *J* = 13.7, 7.2 Hz, 4H), 7.35 (dd, *J* = 16.0, 7.9 Hz, 3H), 7.06 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.31, 141.17, 137.93, 137.57, 133.22, 130.27, 128.75, 128.30, 127.47, 119.69, 108.54, 108.46; HRMS (ESI) m/z calcd. for $C_{16}H_{13}N_2O$ $[M+H]^+$ = 249.1022, found 249.1026.

(*E*)-*N*-(3-oxo-3-(p-tolyl)prop-1-en-1-yl)-*N*-phenylcyanamide (3ba)



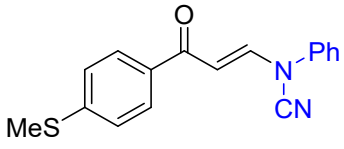
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ba** as a yellow solid (50.84 mg, 97% yield); m.p.: 83 – 85 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 13.1 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.37 – 7.32 (m, 1H), 7.05 (d, *J* = 13.1 Hz, 1H), 6.98 – 6.96 (m, 1H), 3.88 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.71, 163.75, 140.43, 138.03, 130.67, 130.47, 130.25, 127.34, 119.60, 113.97, 108.71, 108.48, 55.55; for $C_{17}H_{14}N_2O$ $[M+H]^+$ = 263.1179, found 263.1177.

(*E*)-*N*-(3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)-*N*-phenylcyanamide (3ca)



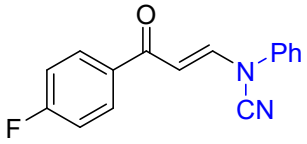
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ca** as a yellow solid (51.17 mg, 92% yield); m.p.: 81 – 83 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.97 (m, 2H), 7.73 (dd, *J* = 13.1, 2.5 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.38 – 7.30 (m, 3H), 7.04 (dd, *J* = 13.1, 2.7 Hz, 1H), 6.97 – 6.95 (m, 2H), 3.86 (d, *J* = 3.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.61, 163.70, 140.36, 137.99, 130.63, 130.44, 130.21, 127.28, 119.53, 113.94, 108.66, 108.43, 55.53; HRMS (ESI) m/z calcd. for $C_{17}H_{15}N_2O_2$ $[M+H]^+$ = 279.1128, found 279.1125.

(*E*)-*N*-(3-(4-(methylthio)phenyl)-3-oxoprop-1-en-1-yl)-*N*-phenylcyanamide (3da)



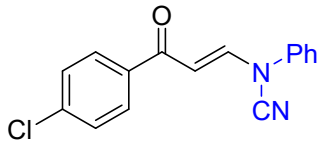
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3da** as a yellow solid (42.34 mg, 72% yield); m.p.: 146 – 148 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.76 (d, *J* = 13.1 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.39 – 7.34 (m, 3H), 7.32 – 7.29 (m, 2H), 7.04 (d, *J* = 13.1 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.15, 146.32, 140.91, 137.98, 133.77, 130.27, 128.73, 127.44, 125.09, 119.68, 108.61, 108.31, 14.78; HRMS (ESI) m/z calcd. $C_{17}H_{15}N_2OS$ $[M+H]^+$ = 295.0900, found 295.0902.

(*E*)-*N*-(3-(4-fluorophenyl)-3-oxoprop-1-en-1-yl)-*N*-phenylcyanamide (3ea)



The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ea** as a white solid (47.89 mg, 90% yield); m.p.: 127 – 130 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.77 (d, *J* = 13.1 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.35 (dd, *J* = 13.1, 7.8 Hz, 3H), 7.16 (t, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 13.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.69, 165.81 (d, *J* = 255.2 Hz), 141.40, 133.91 (d, *J* = 2.9 Hz), 130.92 (d, *J* = 9.4 Hz), 137.90, 130.30, 127.53, 119.69, 115.87 (d, *J* = 21.9 Hz), 108.47, 108.00; ^{19}F NMR (471 MHz, $CDCl_3$) δ -104.78; HRMS (ESI) m/z calcd. for $C_{16}H_{12}FN_2O$ $[M+H]^+$ = 267.0928, found 267.0928.

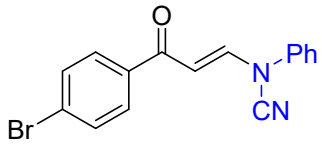
(*E*)-*N*-(3-(4-chlorophenyl)-3-oxoprop-1-en-1-yl)-*N*-phenylcyanamide (3fa)



The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:20) to afford **3fa** as a yellow solid (53.02 mg, 94% yield); m.p.: 117 – 119 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J*

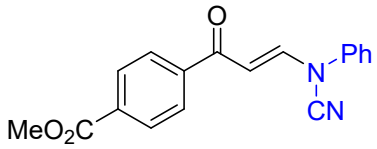
= 8.6 Hz, 1H), 7.78 (d, *J* = 13.1 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.38 – 7.35 (m, 1H), 7.00 (d, *J* = 13.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.02, 141.65, 139.68, 137.88, 135.89, 130.32, 129.70, 129.07, 127.61, 119.75, 108.43, 107.93; HRMS (ESI) m/z calcd. for $C_{16}H_{12}ClN_2O$ $[M+H]^+$ = 283.0633, found 283.0631.

(*E*)-*N*-(3-(4-bromophenyl)-3-oxoprop-1-en-1-yl)-*N*-phenylcyanamide(3ga)



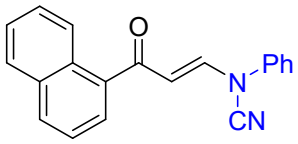
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ga** as a yellow solid (59.98 mg, 92% yield); m.p.: 112 – 113 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.84 (m, 2H), 7.78 (d, *J* = 13.1 Hz, 1H), 7.65 – 7.63 (m, 2H), 7.51 – 7.48 (m, 2H), 7.36 (t, *J* = 8.5 Hz, 3H), 6.99 (d, *J* = 13.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.21, 141.69, 137.85, 136.29, 132.05, 130.32, 129.79, 128.40, 127.61, 119.74, 108.42, 107.86; HRMS (ESI) m/z calcd. for $C_{16}H_{12}BrN_2O$ $[M+H]^+$ = 327.0128, found 327.0131.

Methyl (*E*)-4-(3-(*N*-phenylcyanamido)acryloyl)benzoate (3ha)



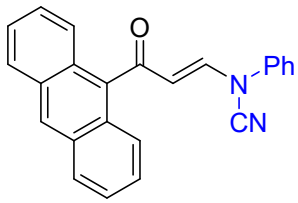
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ha** as a white solid (58.15 mg, 95% yield); m.p.: 150 – 151 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.1 Hz, 1H), 7.79 (d, *J* = 8.9 Hz, 2H), 7.49 – 7.35 (m, 5H), 7.30 – 7.26 (m, 2H), 7.24 – 7.22 (m, 2H), 6.64 (d, *J* = 13.6 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.85, 154.47, 141.37, 137.78, 132.04, 131.20, 130.25, 128.89, 128.28, 127.82, 127.54, 124.28, 123.91, 123.18, 120.00, 115.87, 113.00, 108.61, 56.63; HRMS (ESI) m/z calcd. for $C_{18}H_{15}N_2O_3$ $[M+H]^+$ = 307.1077, found 307.1081.

(*E*)-*N*-(3-(naphthalen-1-yl)-3-oxoprop-1-en-1-yl)-*N*-phenylcyanamide (3ia)



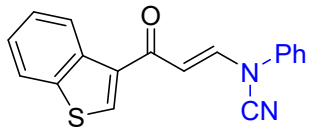
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ia** as a yellow solid (48.29 mg, 81% yield); m.p.: 124 – 126 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 9.4 Hz, 1H), 7.67 (d, *J* = 13.4 Hz, 1H), 7.58 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.47 – 7.41 (m, 2H), 7.34 – 7.29 (m, 3H), 6.86 (d, *J* = 13.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.44, 141.63, 137.85, 136.54, 133.92, 132.44, 130.31, 128.57, 127.78, 127.60, 127.49, 126.63, 125.62, 124.56, 119.90, 113.16, 108.54; HRMS (ESI) m/z calcd. for $C_{17}H_{14}F_3N_2O$ $[M+H]^+$ = 319.1053, found 319.1050.

(*E*)-*N*-(3-(anthracen-9-yl)-3-oxoprop-1-en-1-yl)-*N*-phenylcyanamide (3ja)



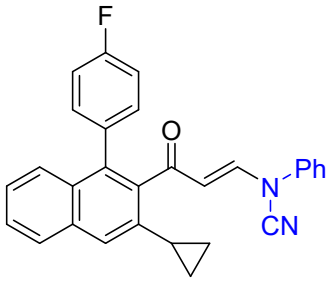
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ja** as a yellow solid (57.78 mg, 83% yield); m.p.: 129 – 131 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.04 – 8.02 (m, 2H), 7.95 – 7.93 (m, 2H), 7.54 – 7.48 (m, 4H), 7.39 – 7.32 (m, 2H), 7.30 – 7.22 (m, 2H), 7.14 – 7.07 (m, 2H), 6.73 (d, *J* = 13.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.90, 143.72, 137.50, 134.03, 131.11, 130.27, 128.93, 128.82, 128.07, 127.81, 126.99, 125.64, 124.92, 120.20, 116.15, 108.27; HRMS (ESI) m/z calcd. for $C_{24}H_{17}N_2O$ $[M+H]^+$ = 349.1335, found 349.1335.

(*E*)-*N*-(3-(benzo[b]thiophen-3-yl)-3-oxoprop-1-en-1-yl)-*N*-phenylcyanamide (3ka)



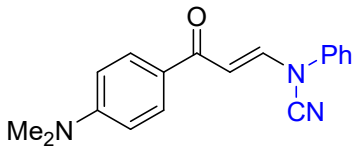
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ka** as a yellow solid (58.98 mg, 97% yield); m.p.: 132 – 134 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.2 Hz, 1H), 8.18 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 13.1 Hz, 1H), 7.43 – 7.28 (m, 4H), 7.27 – 7.17 (m, 3H), 6.85 (d, *J* = 13.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.92, 140.03, 137.97, 136.84, 136.79, 135.77, 130.26, 127.35, 125.89, 125.73, 125.68, 122.39, 119.54, 110.10, 108.65; HRMS (ESI) m/z calcd. for $C_{18}H_{13}N_2OS$ $[M+H]^+$ = 305.0743, found 305.0742.

(*E*)-*N*-(3-(3-cyclopropyl-1-(4-fluorophenyl)naphthalen-2-yl)-3-oxoprop-1-en-1-yl)-*N*-phenylcyanamide (3la)



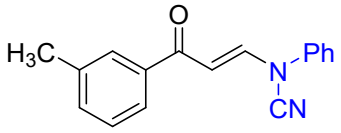
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3la** as a white solid (79.51 mg, 92% yield); m.p.: 142 – 145 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.67z (m, 1H), 7.52 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.34 – 7.31 (m, 3H), 7.26 – 7.16 (m, 5H), 6.14 (d, *J* = 13.6 Hz, 1H), 2.18 – 2.13 (m, 1H), 1.40 – 1.38 (m, 2H), 1.07 – 1.05 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.68, 162.91 (d, *J* = 249.0 Hz), 158.43, 148.10, 143.57, 141.87, 137.39, 133.12, 130.32, 131.93 (d, *J* = 8.2 Hz), 131.23 (d, *J* = 3.5 Hz), 130.15, 129.18, 127.91, 126.17, 125.96, 124.92, 120.26, 115.72 (d, *J* = 21.6 Hz), 114.78, 108.08, 15.68, 11.04; ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.26; HRMS (ESI) m/z calcd. for $C_{29}H_{22}FN_2O$ $[M+H]^+$ = 433.1711, found 433.1711.

(*E*)-*N*-(3-(4-(dimethylamino)phenyl)-3-oxoprop-1-en-1-yl)-*N*-phenylcyanamide (3ma)



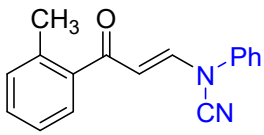
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ma** as a white solid (55.89 mg, 96% yield); m.p.: 144 – 146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 2H), 7.60 (d, *J* = 13.1 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.27 – 7.20 (m, 3H), 6.98 (d, *J* = 13.1 Hz, 1H), 6.60 – 6.56 (m, 2H), 2.97 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.75, 152.56, 137.98, 137.12, 129.62, 129.10, 125.98, 124.17, 118.35, 109.79, 107.95, 107.92, 38.98; HRMS (ESI) m/z calcd. for $C_{18}H_{17}N_3O$ $[M+H]^+$ = 292.1444, found 292.1446.

(*E*)-*N*-(3-oxo-3-(*m*-tolyl)prop-1-en-1-yl)-*N*-phenylcyanamide (3na)



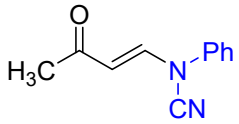
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3na** as a white solid (48.75 mg, 93% yield); m.p.: 40 – 42 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.54 (dd, *J* = 10.4, 6.7 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 8.1 Hz, 1H), 6.71 (d, *J* = 13.4 Hz, 1H), 2.49 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.93, 141.37, 138.54, 137.82, 137.50, 131.68, 131.15, 130.29, 128.20, 127.55, 125.75, 119.87, 112.68, 108.52, 20.57; HRMS (ESI) m/z calcd. for $C_{17}H_{15}N_2O$ $[M+H]^+$ = 263.1179, found 263.1177.

(*E*)-*N*-(3-oxo-3-(*o*-tolyl)prop-1-en-1-yl)-*N*-phenylcyanamide (3oa)



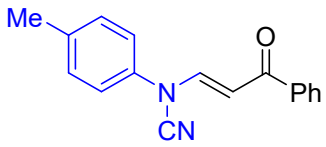
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3oa** as a white solid (47.70 mg, 91% yield); m.p.: 41 – 43 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.46 (t, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 6.9 Hz, 3H), 7.27 (t, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 13.4 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.94, 141.38, 138.56, 137.84, 137.52, 131.70, 131.17, 130.30, 128.22, 127.56, 125.77, 119.87, 112.68, 108.53, 20.58; HRMS (ESI) m/z calcd. for $C_{17}H_{15}N_2O$ $[M+H]^+$ = 263.1179, found 263.1179.

(*E*)-*N*-(3-oxobut-1-en-1-yl)-*N*-phenylcyanamide (3pa)



The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:20) to afford **3pa** as a colorless liquid (34.61 mg, 93% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 3H), 7.36 – 7.31 (m, 3H), 6.27 (d, *J* = 13.5 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.72, 139.77, 137.75, 130.28, 127.56, 119.91, 112.68, 108.46, 29.67; HRMS (ESI) m/z calcd. for $C_{11}H_{11}N_2O$ $[M+H]^+$ = 217.0972, found 217.0976.

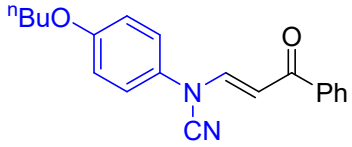
(*E*)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)-*N*-(*p*-tolyl)cyanamide (3ab)



The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3ab** as a orange solid (42.98 mg, 82% yield); m.p.: 58 – 60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.97 (m, 2H), 7.72 (d, *J* = 13.2 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.26 (q, *J* = 8.7 Hz, 4H), 7.01 (d, *J* = 13.2 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.38, 141.77, 137.75, 137.66, 135.52, 133.15, 130.77, 128.73, 128.28,

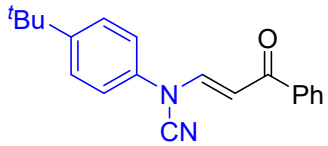
120.00, 108.83, 108.06, 20.92; HRMS (ESI) m/z calcd. for $C_{17}H_{15}N_2O$ $[M+H]^+$ = 263.1179, found 263.1182.

(*E*)-*N*-(4-butoxyphenyl)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)cyanamide (3ac)



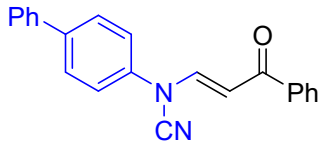
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ac** as a yellow solid (59.54 mg, 93% yield); m.p.: 80 – 82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 7.64 (d, *J* = 13.2 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.26 (m, 2H), 6.98 – 6.92 (m, 3H), 3.97 (t, *J* = 6.5 Hz, 2H), 1.81 – 1.75 (m, 2H), 1.50 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.40, 158.77, 142.85, 137.69, 133.10, 130.59, 128.71, 128.25, 122.62, 115.86, 109.30, 107.56, 68.21, 31.17, 19.21, 13.85; HRMS (ESI) m/z calcd. for $C_{20}H_{21}N_2O$ $[M+H]^+$ = 321.1598, found 321.1601.

(*E*)-*N*-(4-(*tert*-butyl)phenyl)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)cyanamide (3ad)



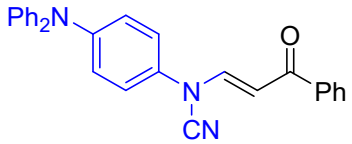
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ad** as a white solid (58.39 mg, 96% yield); m.p.: 95 – 97 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.97 (m, 2H), 7.75 (d, *J* = 13.2 Hz, 1H), 7.58 (dd, *J* = 10.5, 4.2 Hz, 1H), 7.50 – 7.47 (m, 4H), 7.31 – 7.26 (m, 2H), 7.03 (d, *J* = 13.2 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.36, 150.96, 141.65, 137.71, 135.41, 133.10, 128.71, 128.28, 127.16, 119.65, 108.74, 108.15, 34.68, 31.25; HRMS (ESI) m/z calcd. for $C_{20}H_{21}N_2O$ $[M+H]^+$ = 305.1648, found 305.1648.

(*E*)-*N*-([1,1'-biphenyl]-4-yl)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)cyanamide (3ae)



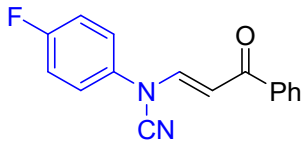
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ae** as a white solid (37.59 mg, 58% yield); m.p.: 128 – 130 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.81 (d, *J* = 13.2 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.59 (dd, *J* = 12.6, 7.3 Hz, 3H), 7.52 – 7.38 (m, 7H), 7.09 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.33, 141.05, 140.58, 139.30, 137.58, 136.99, 133.25, 129.04, 128.82, 128.77, 128.32, 128.01, 127.05, 120.00, 108.58, 108.52; HRMS (ESI) m/z calcd. for $C_{22}H_{17}N_2O$ $[M+H]^+$ = 325.1335, found 325.1337.

(*E*)-*N*-(4-(diphenylamino)phenyl)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)cyanamide (3af)



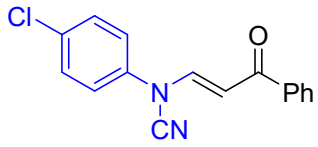
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3af** as a yellow solid (71.40 mg, 86% yield); m.p.: 129 – 131 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.4 Hz, 2H), 7.58 (d, *J* = 13.2 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 4H), 7.10 (d, *J* = 9.0 Hz, 2H), 7.03 – 6.97 m, 8H), 6.90 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.36, 146.66, 145.98, 141.25, 136.63, 132.07, 130.35, 128.53, 127.68, 127.23, 123.83, 122.82, 122.63, 120.68, 107.96, 106.77; HRMS (ESI) m/z calcd. for $C_{28}H_{22}N_3O$ $[M+H]^+$ = 416.1757, found 416.1761.

(*E*)-*N*-(4-fluorophenyl)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)cyanamide (3ag)



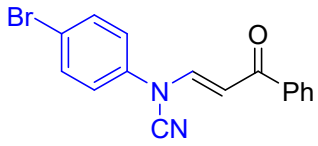
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ag** as a white solid (50.55 mg, 95% yield); m.p.: 101 – 103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 13.2 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.35 (m, 2H), 7.21 – 7.18 (m, 2H), 7.02 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.27, 161.52 (d, *J* = 249.1 Hz), 141.59, 137.51, 134.09, 133.31, 128.80, 128.31, 122.39 (d, *J* = 8.5 Hz), 117.31 (d, *J* = 23.6 Hz), 108.66, 108.47; ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.95; $C_{16}H_{12}FN_2O$ $[M+H]^+$ = 371.0569, found 371.0568.

(*E*)-*N*-(4-chlorophenyl)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)cyanamide (3ah)



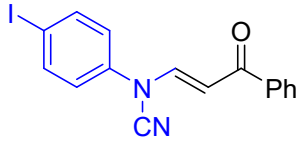
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ah** as a orange solid (45.69 mg, 81% yield); m.p.: 123 – 125 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.97 (m, 2H), 7.70 (d, *J* = 13.1 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.47 – 7.44 (m, 2H), 7.33 – 7.30 (m, 2H), 7.06 (d, *J* = 13.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.17, 140.63, 137.44, 136.51, 133.37, 133.22, 130.41, 128.81, 128.33, 121.00, 108.89, 108.21; HRMS (ESI) m/z calcd. for $C_{16}H_{12}ClN_2O$ $[M+H]^+$ = 283.0633, found 283.0637.

(*E*)-*N*-(4-bromophenyl)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)cyanamide (3ai)



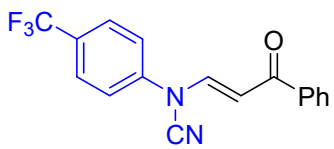
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ai** as a orange solid (50.16 mg, 80% yield); m.p.: 156 – 158 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 13.1 Hz, 1H), 7.51 (t, *J* = 7.1 Hz, 3H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 13.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.10, 139.40, 136.38, 135.99, 132.32, 127.76, 127.28, 120.12, 119.79, 107.92, 107.07; HRMS (ESI) m/z calcd. for $C_{16}H_{12}BrN_2O$ $[M+H]^+$ = 327.0128, found 327.0128.

(*E*)-*N*-(4-iodophenyl)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)cyanamide (3aj)



The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3aj** as a yellow solid (48.61 mg, 65% yield); m.p.: 102 – 103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.98 (m, 2H), 7.83 – 7.80z (m, 2H), 7.71 (d, *J* = 13.1 Hz, 1H), 7.61 (dd, *J* = 10.5, 4.2 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.15 – 7.13 (m, 2H), 7.08 (d, *J* = 13.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.19, 140.24, 139.28, 137.77, 137.41, 133.37, 128.80, 128.31, 121.24, 109.07, 108.03, 91.63; HRMS (ESI) m/z calcd. for $C_{16}H_{12}IN_2O$ $[M+H]^+$ = 374.9989, found 374.9987.

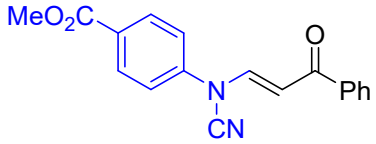
(*E*)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)-*N*-(4-(trifluoromethyl)phenyl)cyanamide (3ak)



The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ak** as a yellow solid (38.56 mg, 61% yield); m.p.: 152 – 153 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J*

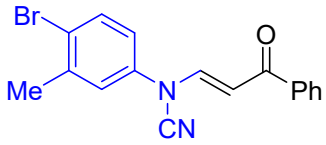
= 7.9 Hz, 1H), 7.82 (d, *J* = 13.1 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.62 (t, *J* = 7.1 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.16 (d, *J* = 13.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.08, 140.70, 139.35, 137.31, 133.52, 129.30 (q, *J* = 33.8 Hz), 128.85, 128.37, 127.61 (q, *J* = 3.6 Hz), 123.43 (q, *J* = 272.2 Hz), 119.02, 109.78, 107.65; HRMS (ESI) m/z calcd. for $C_{17}H_{11}F_3N_2O$ $[M+H]^+$ = 317.0896, found 317.0897.

Methyl (*E*)-4-(*N*-(3-oxo-3-phenylprop-1-en-1-yl)cyanamido)benzoate (3al)



The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3al** as a white solid (45.91 mg, 75% yield); m.p.: 126 – 127 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.14 (m, 1H), 8.02 – 7.97 (m, 1H), 7.85 (d, *J* = 13.1 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.16 (d, *J* = 13.1 Hz, 1H), 3.95 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.10, 165.65, 141.34, 139.39, 137.34, 133.45, 131.81, 128.83, 128.76, 128.36, 118.31, 109.63, 107.66, 52.47; HRMS (ESI) m/z calcd. for $C_{18}H_{15}N_2O_3$ $[M+H]^+$ = 307.1077, found 307.1079.

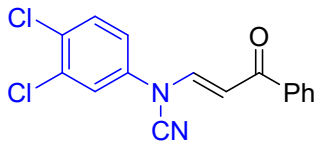
(*E*)-*N*-(4-bromo-3-methylphenyl)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)cyanamide (3am)



The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3am** as a white solid (49.64 mg, 73% yield); m.p.: 147 – 149 °C; ^{1}H NMR (500 MHz, CDCl3) δ 7.98 – 7.96 (m, 2H), 7.71 (d, J = 13.1 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.49 (dd, J = 10.6, 4.7 Hz, 2H), 7.24 (d, J = 2.8 Hz, 1H), 7.07 – 7.04 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.17, 140.63, 140.52, 137.44, 137.00, 133.90, 133.31, 128.77, 128.30, 123.27,

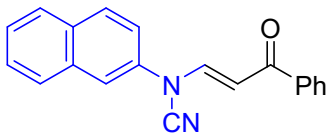
121.64, 118.33, 108.71, 108.21, 23.20; HRMS (ESI) m/z calcd. for $C_{17}H_{14}BrN_2O$ $[M+H]^+$ = 341.0284, found 341.0281.

(*E*)-*N*-(3,4-dichlorophenyl)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)cyanamide (3an)



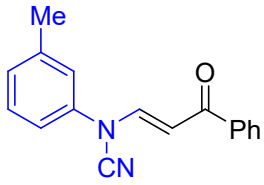
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3an** as a yellow solid (41.71 mg, 66% yield); m.p.: 133 – 135 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.98 (m, 2H), 7.69 (d, *J* = 13.1 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.52 (dd, *J* = 9.3, 5.4 Hz, 3H), 7.25 (dd, *J* = 9.5, 3.5 Hz, 1H), 7.10 (d, *J* = 13.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.04, 139.73, 137.29, 137.13, 134.58, 133.51, 131.85, 131.62, 128.85, 128.36, 121.41, 118.61, 109.53, 107.70; HRMS (ESI) m/z calcd. for $C_{16}H_{10}Cl_2N_2O$ $[M+H]^+$ = 317.0243, found 317.0244.

(*E*)-*N*-(naphthalen-2-yl)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)cyanamide (3ao)



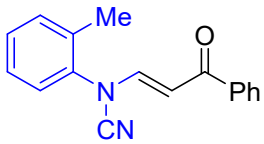
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ao** as a yellow solid (56.04 mg, 94% yield); m.p.: 137 – 139 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 2H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.78 – 7.70 (m, 3H), 7.62 (d, *J* = 1.7 Hz, 1H), 7.47 (dd, *J* = 13.4, 6.6 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.38 – 7.34 (m, 2H), 6.99 (d, *J* = 13.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.22, 140.15, 136.51, 134.13, 132.31, 132.18, 130.79, 129.57, 127.70, 127.26, 126.85, 126.72, 126.70, 125.80, 116.89, 116.34, 107.59, 107.51; HRMS (ESI) m/z calcd. for for $C_{20}H_{15}N_2O$ $[M+H]^+$ = 299.1179, found 299.1182.

(*E*)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)-*N*-(*m*-tolyl)cyanamide (3ap)



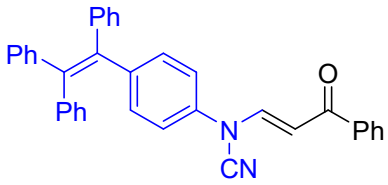
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ap** as a white solid (46.13 mg, 88% yield); m.p.: 125 – 127 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.98 (m, 2H), 7.77 (d, *J* = 13.2 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.16 (d, *J* = 11.9 Hz, 2H), 7.05 (d, *J* = 13.2 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.39, 141.33, 140.69, 137.88, 137.62, 133.20, 130.03, 128.75, 128.30, 128.26, 120.25, 119.98, 116.72, 108.28, 21.44; HRMS (ESI) m/z calcd. for $C_{17}H_{15}N_2O$ $[M+H]^+$ = 263.1179, found 263.1183.

(*E*)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)-*N*-(o-tolyl)cyanamide (3aq)



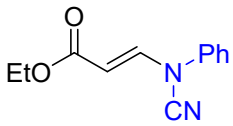
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3aq** as a yellow solid (46.13 mg, 88% yield); m.p.: 119 – 121 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.39 – 7.32 (m, 4H), 6.70 (d, *J* = 13.2 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.45, 144.72, 137.69, 136.07, 134.60, 133.07, 132.20, 130.16, 128.70, 128.23, 128.04, 126.30, 109.72, 106.76, 17.47; HRMS (ESI) m/z calcd. for $C_{17}H_{15}N_2O$ $[M+H]^+$ = 263.1179, found 263.1184.

(*E*)-*N*-(3-oxo-3-phenylprop-1-en-1-yl)-*N*-(4-(1,2,2-triphenylvinyl)phenyl)cyanamide (3ar)



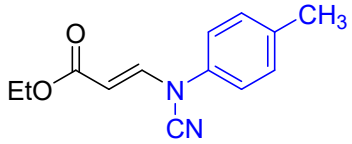
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:15) to afford **3ar** as a white solid (68.29 mg, 68% yield); m.p.: 185 – 187 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 13.1 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.05 – 6.98 (m, 13H), 6.94 – 6.91 (m, 7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.22, 142.21, 142.08, 142.07, 141.92, 141.26, 140.03, 137.98, 136.51, 134.73, 132.14, 132.02, 130.20, 130.18, 130.13, 127.67, 127.21, 126.94, 126.86, 126.68, 125.92, 125.78, 125.70, 117.76, 107.36, 107.24; HRMS (ESI) m/z calcd. for $C_{36}H_{27}N_3O$ $[M+H]^+$ = 503.2118, found 503.2115.

Ethyl (*E*)-3-(*N*-phenylcyanamido)acrylate (3qa)[4]



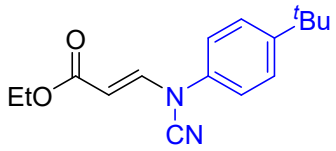
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3qa** as a yellow liquid (40.19 mg, 93% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 13.6 Hz, 1H), 7.47 (dd, *J* = 8.2, 7.7 Hz, 2H), 7.35 – 7.31 (dd, *J* = 13.0, 7.6 Hz, 3H), 5.90 (d, *J* = 13.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.01, 140.73, 137.77, 130.22, 127.40, 119.84, 108.59, 105.04, 60.70, 14.29; HRMS (ESI) m/z calcd. for $C_{12}H_{13}N_2O_2$ $[M+H]^+$ = 217.0977, found 217.0972.

Ethyl (*E*)-3-(*N*-(*p*-tolyl)cyanamido)acrylate (3qb)[4]



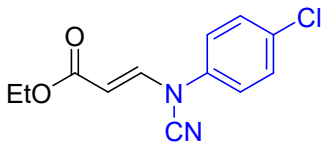
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3ab** as a yellow liquid (34.97 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 13.6 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.84 (d, *J* = 13.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.12, 141.35, 137.73, 135.33, 130.73, 120.27, 108.96, 104.54, 60.64, 20.89, 14.29; HRMS (ESI) m/z calcd. for $C_{13}H_{15}N_2O_2$ $[M+H]^+$ = 231.1134, found 231.1130.

Ethyl (*E*)-3-(*N*-(4-(tert-butyl)phenyl)cyanamido)acrylate (3qd)[4]



The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3qd** as a colorless liquid (48.98 mg, 90% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 13.6 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 5.85 (d, *J* = 13.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.33 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.12, 150.95, 141.28, 135.17, 127.14, 119.95, 108.92, 104.56, 60.64, 34.68, 31.24, 14.30; HRMS (ESI) m/z calcd. for $C_{17}H_{20}N_2O_2$ $[M+H]^+$ = 273.1598, found 273.1602.

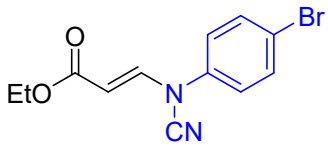
Ethyl (E)-3-(N-(4-chlorophenyl)cyanamido)acrylate (3qh)[4]



The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3qh** as a yellow solid (43.50 mg, 87% yield); m.p.: 65 – 66 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 21.9, 11.2 Hz, 3H), 7.26 (d, *J* = 8.7 Hz, 2H), 5.91 (d, *J* = 13.6 Hz, 1H), 4.24 (q, *J* =

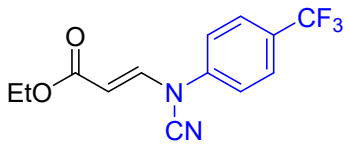
7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.83, 140.21, 136.33, 133.18, 130.38, 121.18, 108.26, 105.65, 60.84, 14.28; HRMS (ESI) m/z calcd. for $C_{12}H_{12}ClN_2O_2$ $[M+H]^+$ = 251.0587, found 251.0587.

Ethyl (*E*)-3-(*N*-(4-bromophenyl)cyanamido)acrylate (3qi)[4]



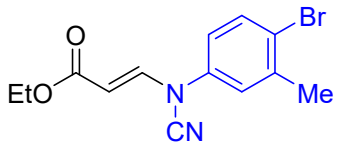
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3qi** as a white solid (46.45 mg, 79% yield); m.p.: 86 – 88 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.49 (d, J = 13.6 Hz, 1H), 7.22 – 7.19 (m, 2H), 5.92 (d, J = 13.6 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.81, 140.04, 136.88, 133.33, 121.34, 120.79, 108.15, 105.75, 60.85, 14.28; HRMS (ESI) m/z calcd. for $C_{12}H_{12}BrN_2O_2$ $[M+H]^+$ = 295.0082, found 295.0081.

Ethyl (*E*)-3-(*N*-(4-(trifluoromethyl)phenyl)cyanamido)acrylate (3qk)[4]



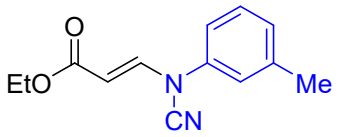
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3qk** as a white solid (40.90 mg, 72% yield); m.p.: 98 – 100 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 13.5 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 6.02 (d, J = 13.5 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.65, 140.59, 138.91, 129.23 (q, J = 33.3 Hz), 127.57 (q, J = 3.6 Hz), 123.42 (q, J = 272.1 Hz), 119.03, 107.59, 106.79, 60.98, 14.26; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.52; HRMS (ESI) m/z calcd. for $C_{13}H_{12}F_3N_2O_2$ $[M+H]^+$ = 285.0851, found 285.0849.

Ethyl (*E*)-3-(*N*-(4-bromo-3-methylphenyl)cyanamido)acrylate (3qm)[4]



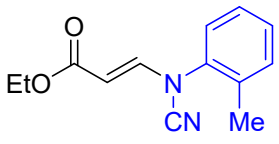
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3qm** as a white solid (51.74 mg, 84% yield); m.p.: 67 – 69 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.6 Hz, 1H), 7.50 (d, *J* = 13.6 Hz, 1H), 7.19 (d, *J* = 2.7 Hz, 1H), 7.01 (dd, *J* = 8.6, 2.8 Hz, 1H), 5.90 (d, *J* = 13.6 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.92, 140.51, 140.27, 136.86, 133.89, 123.24, 121.88, 118.54, 108.29, 105.46, 60.81, 23.17, 14.29; HRMS (ESI) m/z calcd. for $C_{13}H_{14}BrN_2O_2$ $[M+H]^+$ = 309.0233, found 309.0229.

Ethyl (*E*)-3-(*N*-(*m*-tolyl)cyanamido)acrylate (3qp)[4]



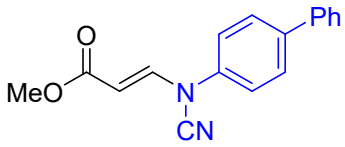
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3qp** as a yellow liquid (34.97 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 13.6 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.12 (dd, *J* = 13.8, 8.5 Hz, 3H), 5.89 (d, *J* = 13.6 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.13, 140.91, 140.65, 137.74, 129.98, 128.20, 120.48, 116.92, 108.73, 104.86, 60.69, 21.40, 14.29; HRMS (ESI) m/z calcd. for $C_{13}H_{15}N_2O_2$ $[M+H]^+$ = 231,1134, found 231,1130.

Ethyl (*E*)-3-(*N*-(*o*-tolyl)cyanamido)acrylate (3qq)[4]



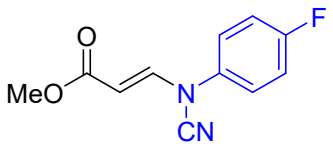
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3qq** as a yellow liquid (28.99 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 (d, *J* = 5.9 Hz, 1H), 5.42 (d, *J* = 13.6 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.01, 143.94, 135.46, 134.89, 132.14, 130.17, 128.00, 126.54, 110.10, 102.92, 60.58, 17.34, 14.27; HRMS (ESI) m/z calcd. for $C_{13}H_{15}N_2O_2$ $[M+H]^+$ = 231,1134, found 231,1134.

Methyl (*E*)-3-(*N*-([1,1'-biphenyl]-4-yl)cyanamido)acrylate (3re)[4]



The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3re** as a white solid (47.83 mg, 86% yield); m.p.: 101 – 103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.61 – 7.56 (m, 3H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 9.2 Hz, 3H), 5.94 (d, *J* = 13.6 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.46, 140.85, 140.57, 139.32, 136.82, 129.04, 128.81, 128.00, 127.04, 120.14, 108.51, 104.73, 51.87; HRMS (ESI) m/z calcd. for $C_{17}H_{14}F_3N_2O$ $[M+H]^+$ = 279.1128, found 279.1133.

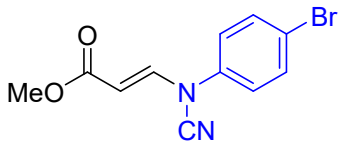
Methyl (*E*)-3-(*N*-(4-fluorophenyl)cyanamido)acrylate (3rg)



The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3aa** as a white solid (39.61 mg, 90% yield); m.p.: 59 – 61 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 13.6 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.13 – 7.08 (m, 2H), 5.77 (d, *J* = 13.6 Hz, 1H),

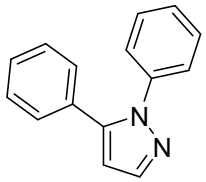
3.70 (s, 3H); ^{3}C NMR (126 MHz, $CDCl_3$) δ 165.29, 160.49 (d, *J* = 249.0 Hz), 140.36, 132.79 (d, *J* = 2.8 Hz), 121.62 (d, *J* = 8.9 Hz), 116.25 (d, *J* = 23.2 Hz), 107.66, 103.56, 50.83; ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.93; HRMS (ESI) m/z calcd. for $C_{11}H_{10}FN_2O_2$ $[M+H]^+$ = 221,0721, found 221,0721.

Methyl (*E*)-3-(N-(4-bromophenyl)cyanamido)acrylate (3ri)



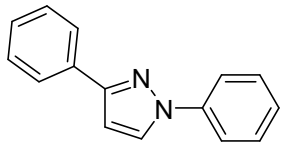
The general procedure was followed and then purified by silica column chromatography (ethyl acetate/petroleum ether = 1:10) to afford **3ri** as a white solid (46.47 mg, 83% yield); m.p.: 75 – 77 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 13.6 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 5.92 (d, *J* = 13.6 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.25, 140.24, 136.85, 133.35, 121.30, 120.82, 108.07, 105.28, 51.95; HRMS (ESI) m/z calcd. for $C_{11}H_{10}BrN_2O$ $[M+H]^+$ = 280.9920, found 280.9925.

1,5-diphenyl-1H-pyrazole (4aa)[5]



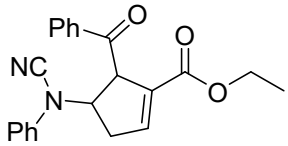
A white solid (30.81 mg, 70% yield); m.p.: 47 – 49 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 1.6 Hz, 1H), 7.36 – 7.25 (m, 8H), 7.25 – 7.20 (m, 2H), 6.50 (d, *J* = 1.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.01, 140.34, 140.16, 130.63, 128.91, 128.79, 128.48, 128.22, 127.43, 125.23, 107.88; HRMS (ESI) m/z calcd. for $C_{15}H_{13}N_2$ $[M+H]^+$ = 221.1073, found 221.1073.

1,3-diphenyl-1H-pyrazole (4aa′)



A white solid (11.00 mg, 25% yield); m.p.: 73 – 75 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 15.2, 4.8 Hz, 3H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.50 – 7.41 (m, 4H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.95, 140.25, 133.14, 129.44, 128.68, 128.05, 128.01, 126.36, 125.86, 119.08, 105.05; HRMS (ESI) m/z calcd. for $C_{11}H_{10}BrN_2O$ $[M+H]^+$ = 221.1073, found 221.1073.

Ethyl 5-benzoyl-4-(N-phenylcyanamido)cyclopent-1-ene-1-carboxylate (5aa)



A colorless liquid (56.90 mg, 79% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 3H), 5.22 – 5.21 (m, 1H), 4.73 – 4.69 (m, 1H), 4.12 – 4.01 (m, 2H), 3.32 – 3.26 m, 1H), 3.03 – 2.98 (m, 1H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.96, 162.96, 142.70, 139.36, 136.45, 135.51, 133.80, 129.86, 128.80, 128.75, 124.76, 117.46, 111.73, 63.18, 60.92, 55.97, 38.45, 13.86; HRMS (ESI) m/z calcd. for $C_{22}H_{21}N_2O_3$ $[M+H]^+$ = 361.1547, found 361.1552.

4. X-ray Crystal Structure for 3aa

Suitable crystals of compound **3aa** was obtained by slowly evaporating a mixture of dichloromethane and hexane solution at ambient temperature. A colorless crystal of **3aa** was mounted on a glass fiber at a random orientation.

A Single colourless needle-shaped crystals of **3aa** was used as supplied. A suitable crystal with dimensions 0.40 × 0.15 × 0.05 mm3 was selected and mounted on a Bruker D8 Venture diffractometer. The crystal was kept at a steady T = 170.00 K during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using dual methods and by using Olex2 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2019/2 (Sheldrick, 2015) using full matrix least squares minimisation on F2. The ellipsoids are shown at 30% probability levels. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2504276 for compound **3aa**.

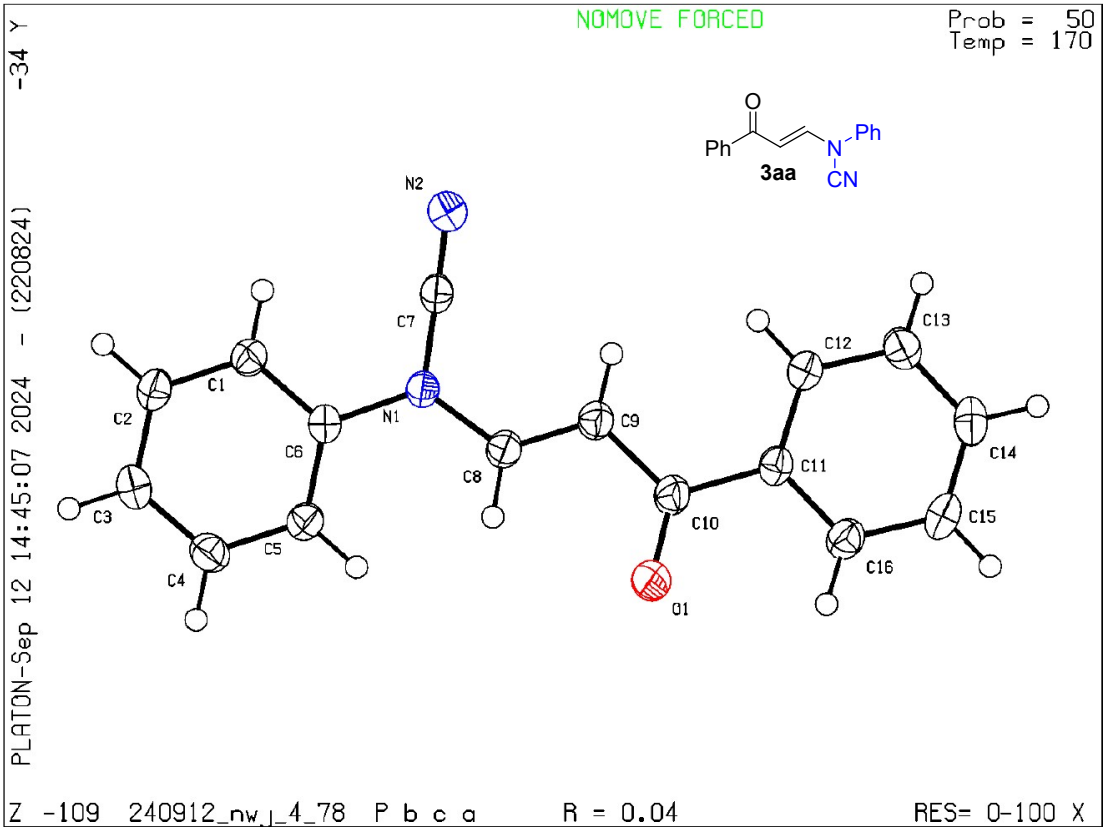


Table 1 Crystal data and structure refinement for 240912_NWJ_4_78.

Identification code	240912_NWJ_4_78
Empirical formula	$C_{16}H_{12}N_2O$
Formula weight	248.28
Temperature/K	170.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	10.9912(4)
b/Å	7.7964(3)
c/Å	29.0779(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2491.74(16)
Z	8
ρ_{calc}g/cm^3	1.324
μ/mm^{-1}	0.428
F(000)	1040.0
Crystal size/mm^3	0.18 × 0.09 × 0.07
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.774 to 121.308
Index ranges	-14 ≤ h ≤ 14, -10 ≤ k ≤ 10, -37 ≤ l ≤ 37
Reflections collected	38346
Independent reflections	2864 [R_{int} = 0.0557, R_{sigma} = 0.0381]
Data/restraints/parameters	2864/0/172
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0413, wR_2 = 0.1107
Final R indexes [all data]	R_1 = 0.0507, wR_2 = 0.1142
Largest diff. peak/hole / e Å^{-3}	0.49/-0.60

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 240912_NWJ_4_78. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	3154.1(9)	1958.6(18)	6498.1(3)	64.7(4)
N1	5885.5(8)	3860.5(11)	5670.9(3)	24.8(2)
N2	7542.5(10)	5701.0(15)	5980.0(3)	42.6(3)

C1	6827.6(9)	4175.0(13)	4916.3(3)	27.6(2)	
C2	6889.2(10)	3765.9(14)	4452.5(4)	30.1(2)	
C3	6075.4(10)	2616.3(14)	4258.8(4)	30.7(2)	
C4	5185.5(11)	1890.3(15)	4533.5(4)	32.3(2)	
C5	5115.1(10)	2280.2(14)	4999.8(4)	29.8(2)	
C6	5940.1(9)	3417.7(12)	5191.4(3)	23.2(2)	
C7	6775.2(10)	4851.1(14)	5841.2(3)	28.7(2)	
C8	5003.5(9)	3250.4(14)	5975.6(3)	28.2(2)	
C9	4951.1(10)	3556.1(14)	6424.0(4)	28.5(2)	
C10	3947.5(10)	2785.5(16)	6690.2(4)	32.1(3)	
C11	3928.6(9)	2953.2(13)	7201.9(3)	26.5(2)	
C12	4861.4(10)	3726.3(14)	7449.6(4)	31.3(2)	
C13	4830.4(12)	3745.9(16)	7927.7(4)	36.6(3)	
C14	3858.3(11)	3017.4(15)	8158.6(4)	35.6(3)	
C15	2917.9(11)	2256.7(15)	7915.6(4)	34.8(3)	
C16	2952.2(10)	2216.1(15)	7438.9(4)	31.7(2)	

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 240912_NWJ_4_78. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	47.9(6)	119.0(10)	27.3(4)	-0.4(5)	-3.2(4)	-41.1(6)
N1	25.6(4)	26.9(4)	21.9(4)	0.4(3)	1.9(3)	0.1(3)
N2	45.4(6)	51.6(6)	30.7(5)	-5.7(4)	3.5(4)	-16.0(5)
C1	25.1(5)	30.7(5)	26.9(5)	-0.4(4)	1.7(4)	-0.1(4)
C2	28.6(5)	35.3(5)	26.4(5)	2.4(4)	5.1(4)	2.0(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 240912_NWJ_4_78. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	35.0(6)	33.8(5)	23.4(5)	-1.3(4)	0.2(4)	6.3(4)
C4	35.7(6)	31.2(5)	29.9(5)	-3.5(4)	-2.5(4)	-2.2(4)
C5	31.6(5)	29.3(5)	28.4(5)	0.5(4)	3.3(4)	-3.9(4)
C6	25.1(5)	22.5(4)	22.0(5)	1.3(3)	1.0(4)	5.3(3)
C7	32.0(5)	31.6(5)	22.4(5)	-0.5(4)	4.3(4)	-1.5(4)
C8	25.4(5)	33.7(5)	25.4(5)	3.0(4)	0.7(4)	-0.5(4)
C9	29.1(5)	31.2(5)	25.1(5)	2.3(4)	0.8(4)	-0.6(4)
C10	26.9(5)	44.5(6)	24.9(5)	4.2(4)	-0.6(4)	-1.9(4)
C11	26.2(5)	29.3(5)	24.0(5)	3.6(4)	1.9(4)	2.8(4)
C12	33.5(6)	34.3(5)	26.1(5)	2.4(4)	2.7(4)	-5.4(4)
C13	45.3(7)	37.7(6)	26.7(5)	-1.5(4)	-1.0(5)	-6.3(5)
C14	48.1(7)	34.8(6)	23.8(5)	1.7(4)	6.4(5)	4.3(5)
C15	34.4(6)	38.0(6)	31.9(5)	6.3(5)	10.9(4)	2.3(5)
C16	26.3(5)	38.0(6)	30.8(5)	3.9(4)	2.2(4)	0.0(4)

Table 4 Bond Lengths for 240912_NWJ_4_78.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C10	1.2198(14)	C5	C6	1.3853(15)
N1	C6	1.4378(12)	C8	C9	1.3267(14)
N1	C7	1.3407(13)	C9	C10	1.4754(14)
N1	C8	1.3968(13)	C10	C11	1.4938(14)
N2	C7	1.1460(15)	C11	C12	1.3903(15)
C1	C2	1.3876(14)	C11	C16	1.3989(14)
C1	C6	1.3927(14)	C12	C13	1.3908(15)
C2	C3	1.3859(16)	C13	C14	1.3839(17)
C3	C4	1.3839(16)	C14	C15	1.3855(17)
C4	C5	1.3917(15)	C15	C16	1.3870(16)

Table 5 Bond Angles for 240912_NWJ_4_78.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N1	C6	117.77(8)	C8	C9	C10	118.35(10)
C7	N1	C8	117.91(8)	O1	C10	C9	120.62(10)
C8	N1	C6	124.22(9)	O1	C10	C11	119.50(10)
C2	C1	C6	119.66(10)	C9	C10	C11	119.82(9)
C3	C2	C1	120.81(10)	C12	C11	C10	122.93(9)
C4	C3	C2	119.08(10)	C12	C11	C16	119.25(10)

Table 5 Bond Angles for 240912_NWJ_4_78.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	C4	C5	120.82(10)	C16	C11	C10	117.73(9)
C6	C5	C4	119.68(10)	C11	C12	C13	120.30(10)
C1	C6	N1	118.97(9)	C14	C13	C12	119.96(11)
C5	C6	N1	121.09(9)	C13	C14	C15	120.28(10)
C5	C6	C1	119.93(9)	C14	C15	C16	119.95(10)
N2	C7	N1	178.94(11)	C15	C16	C11	120.25(10)
C9	C8	N1	126.32(10)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 240912_NWJ_4_78.

Atom	*x*	*y*	*z*	U(eq)
H1	7387.88	4967.61	5045.63	33
H2	7496.66	4280.23	4265.41	36
H3	6127.69	2330.65	3941.8	37
H4	4615.62	1116.2	4402.13	39
H5	4504.15	1768.7	5185.83	36
H8	4380.77	2548.37	5849.54	34
H9	5545.01	4253.89	6570.06	34
H12	5522.86	4243.44	7291.48	38
H13	5476.25	4259.12	8095.66	44
H14	3835.65	3038.99	8485.17	43
H15	2250.03	1763.23	8075.3	42
H16	2310.14	1685.65	7272.69	38

5. Reference

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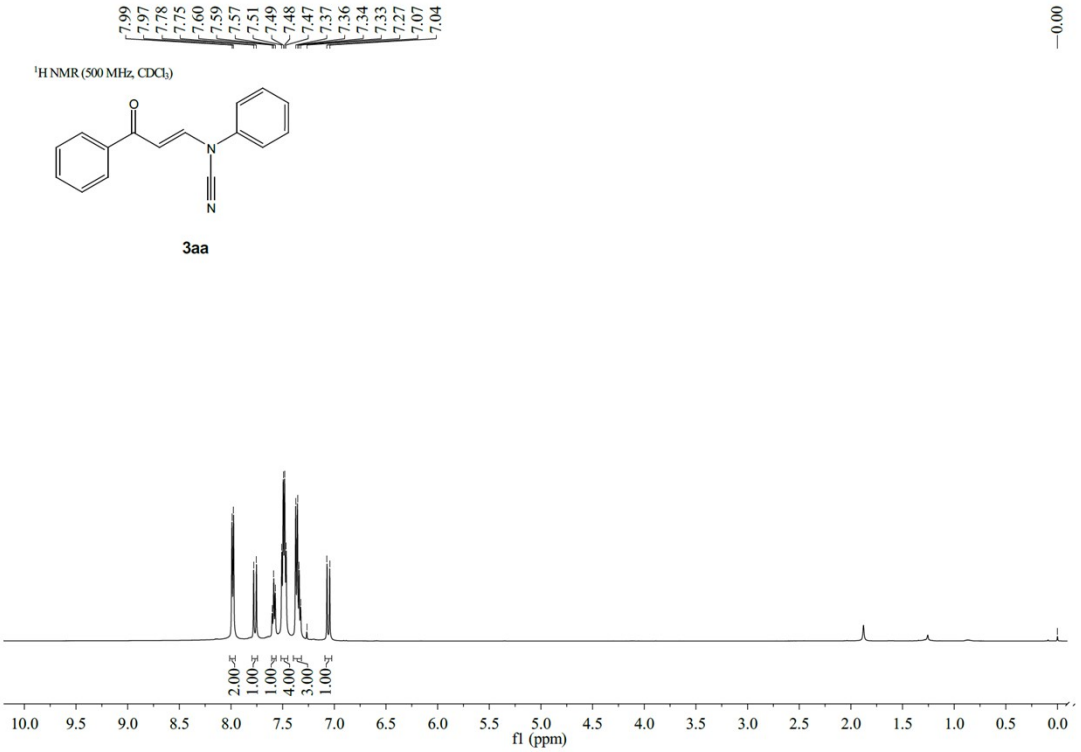
6. ^{1}H, ^{13}C, ^{19}F NMR spectra of compounds.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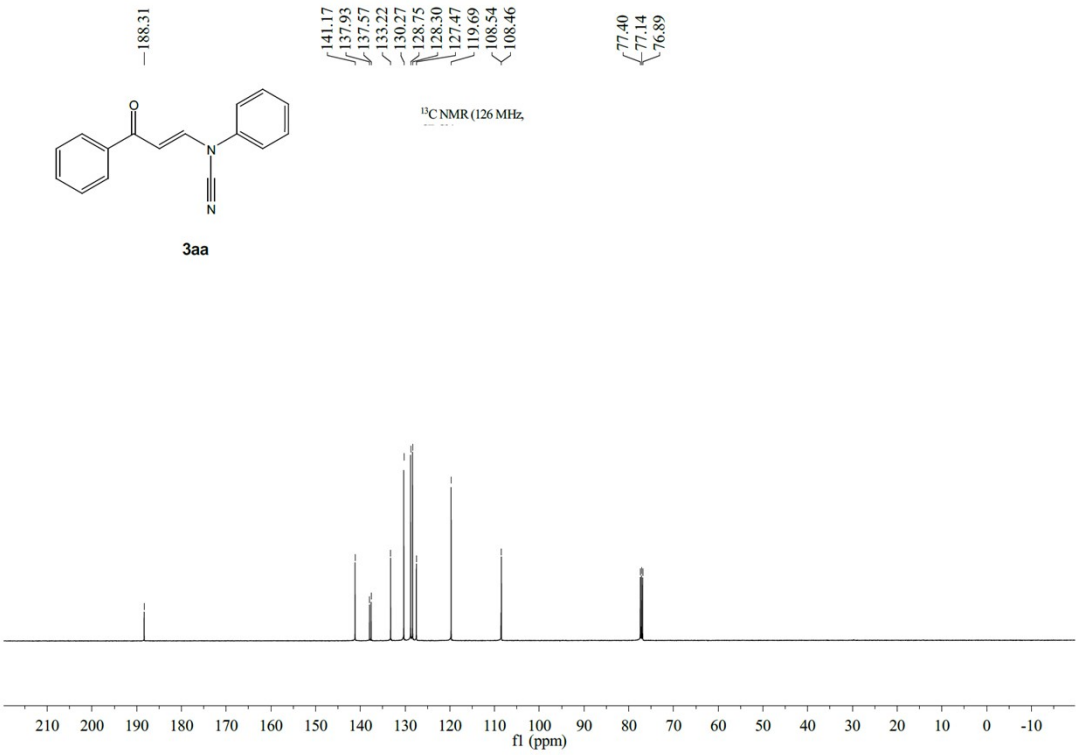
7.97
7.78
7.75
7.60
7.59
7.57
7.51
7.49
7.48
7.47
7.37
7.36
7.34
7.33
7.27
7.07
7.04
0.00
^{1}H NMR (500 MHz, CDCl$_3$)
O
N
N
3aa
2.00
1.00
1.00
4.00
3.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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137.93
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133.22
130.27
128.75
128.30
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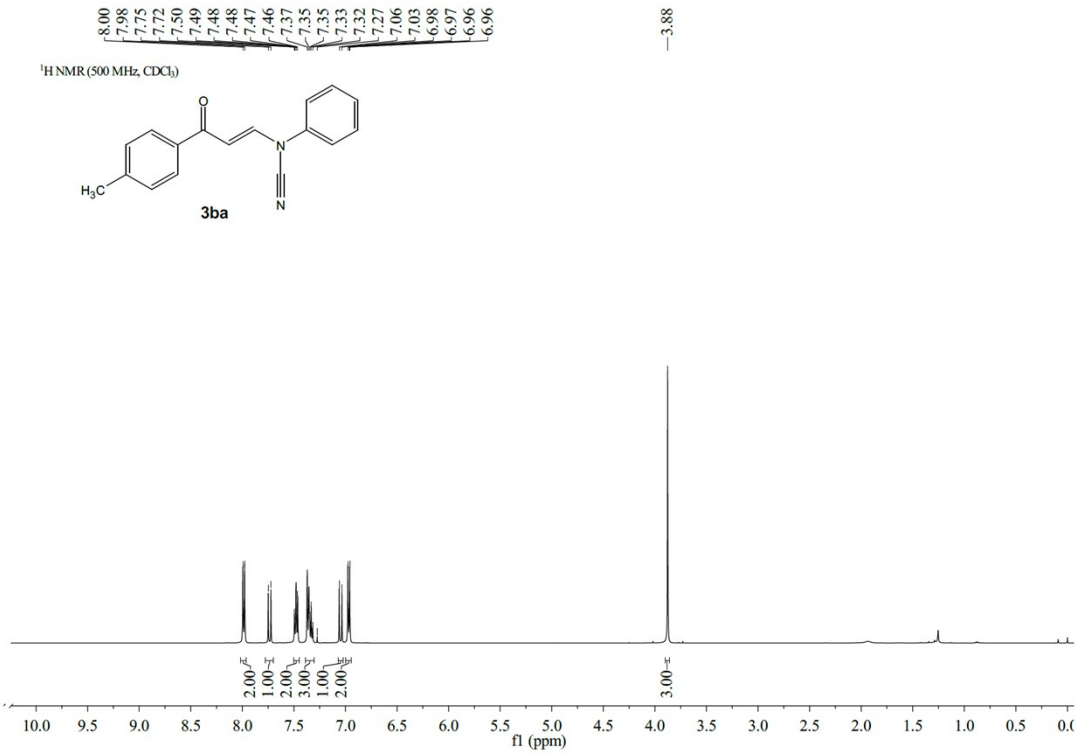
108.54
108.46
77.40
77.14
76.89
^{13}C NMR (126 MHz,
O
N
N
3aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.33
7.32
7.27
7.06
7.03
6.98
6.97
6.96
6.96
3.88
1H NMR (500 MHz, CDCl3)
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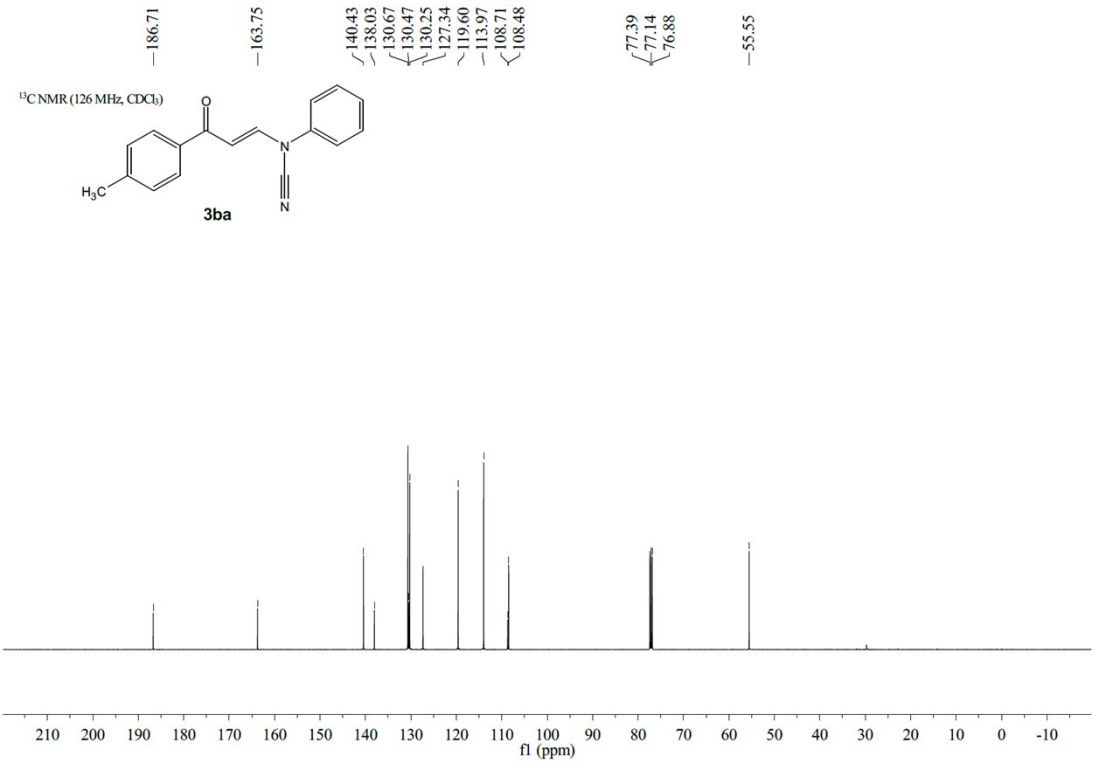
N
H3C
N
3ba
2.00
1.00
2.00
3.00
1.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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130.47
130.25
127.34
119.60
113.97
108.71
108.48
77.39
77.14
76.88
55.55
13C NMR (126 MHz, CDCl3)
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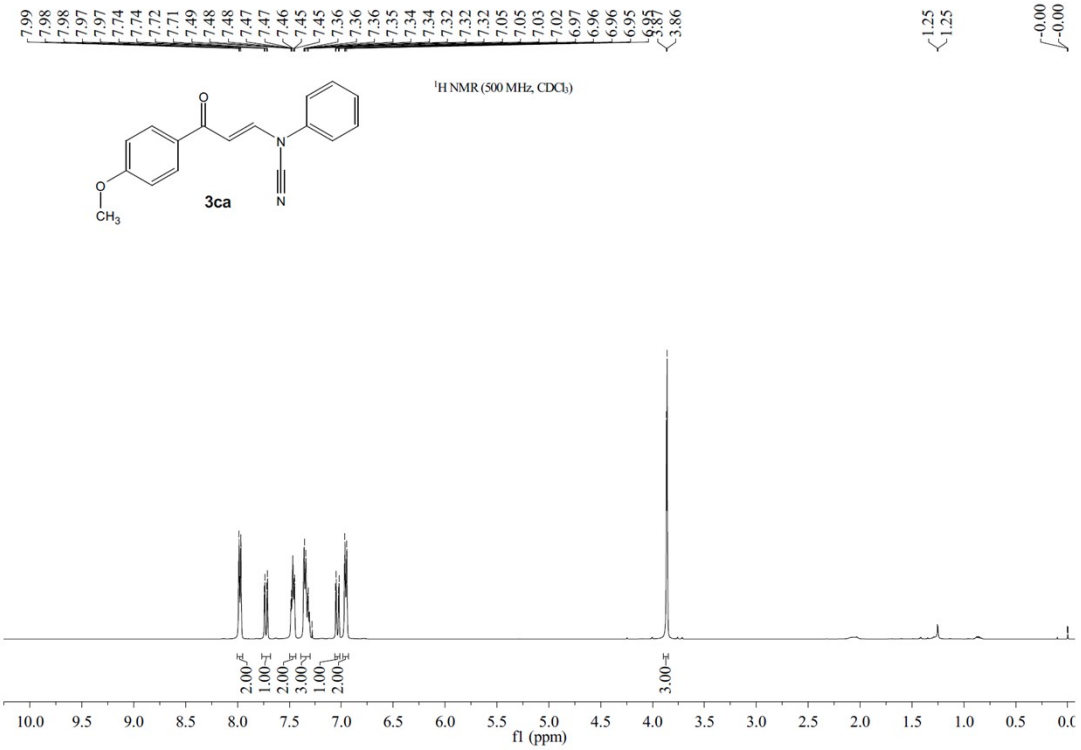
N
H3C
N
3ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.03
7.02
6.97
6.96
6.96
6.95
6.95
3.87
3.86
1.25
1.25
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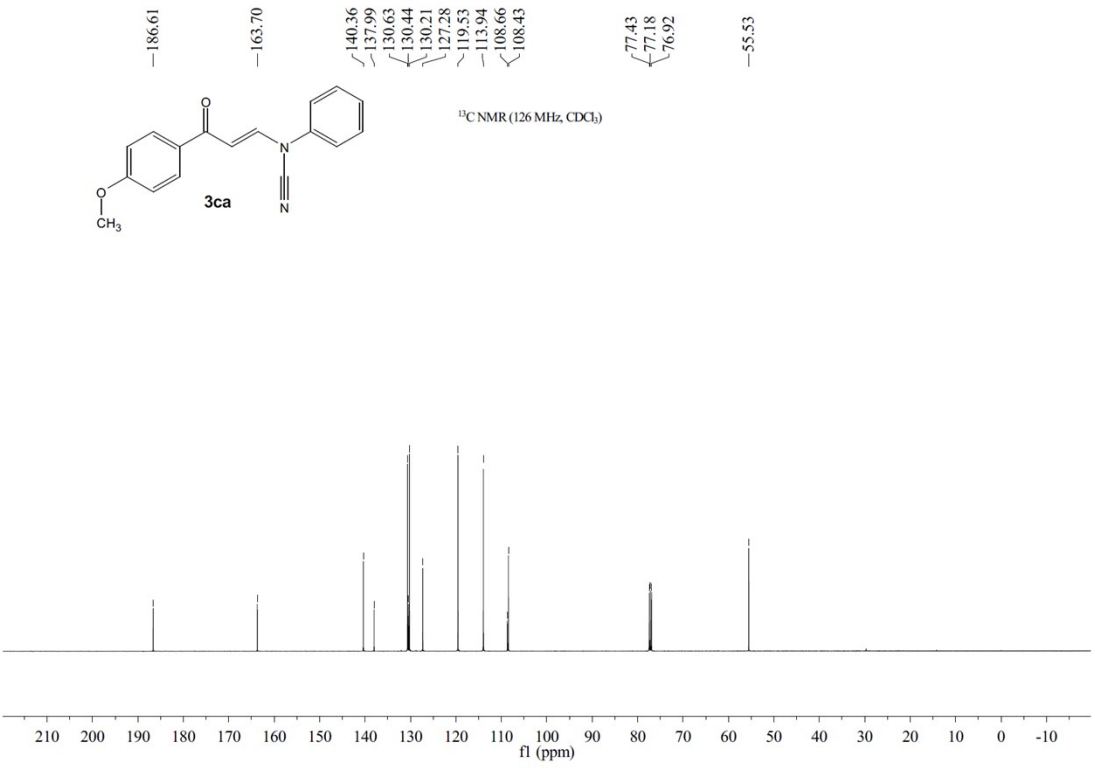
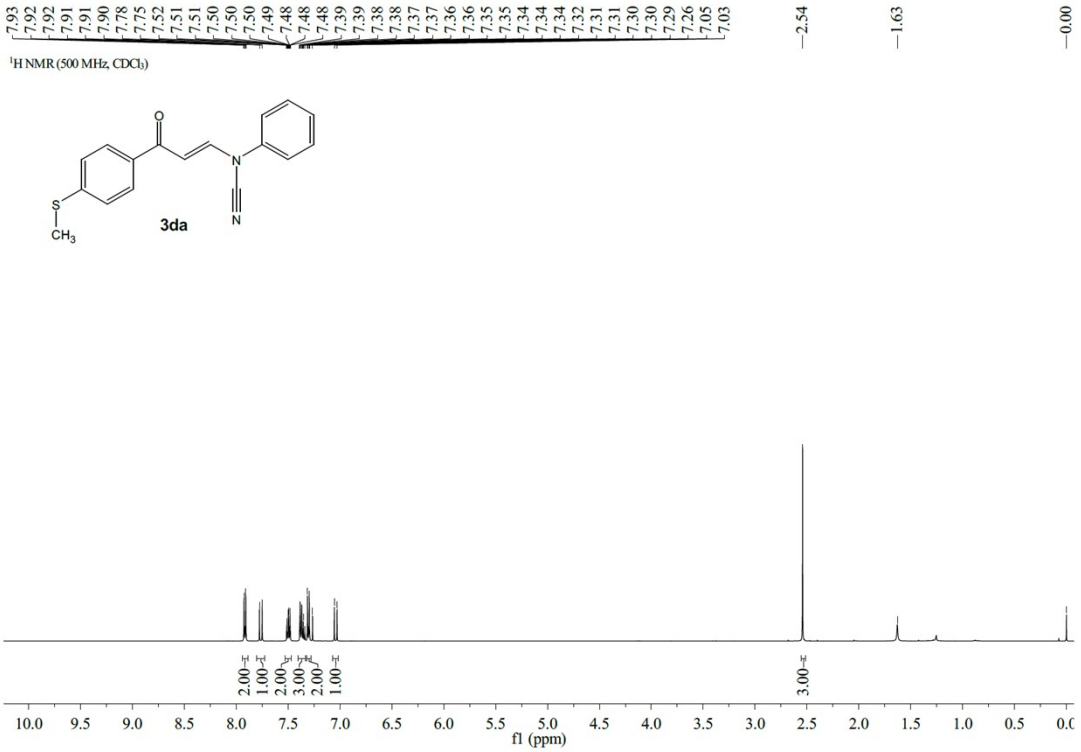
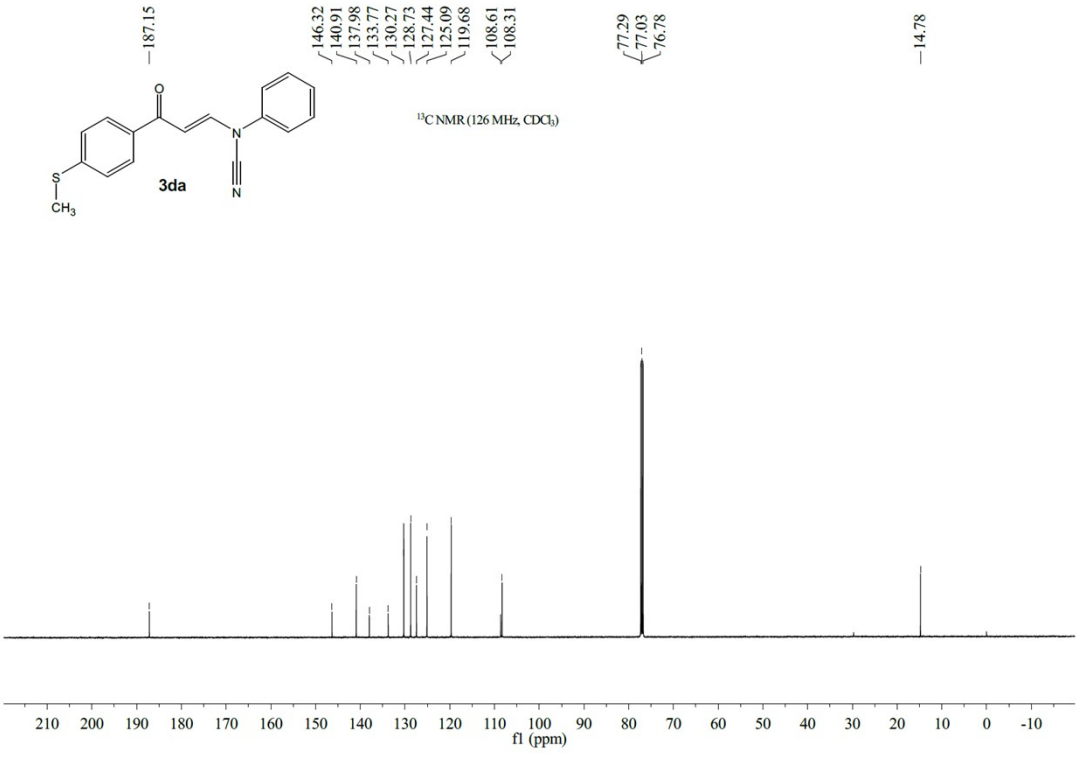
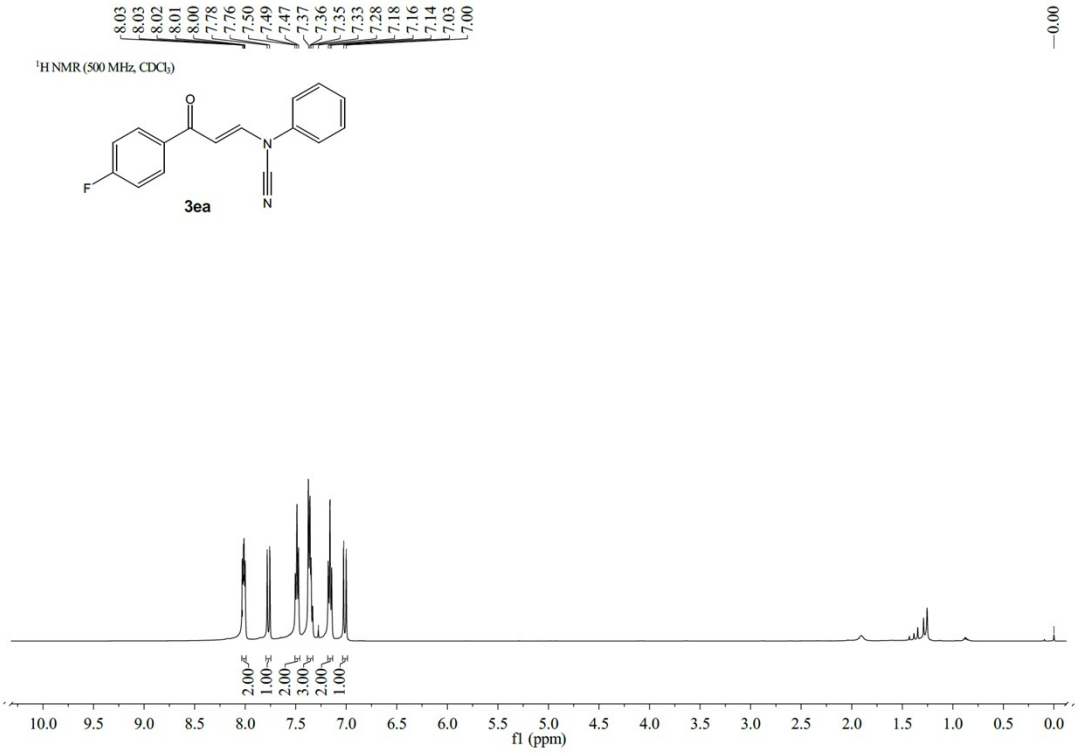
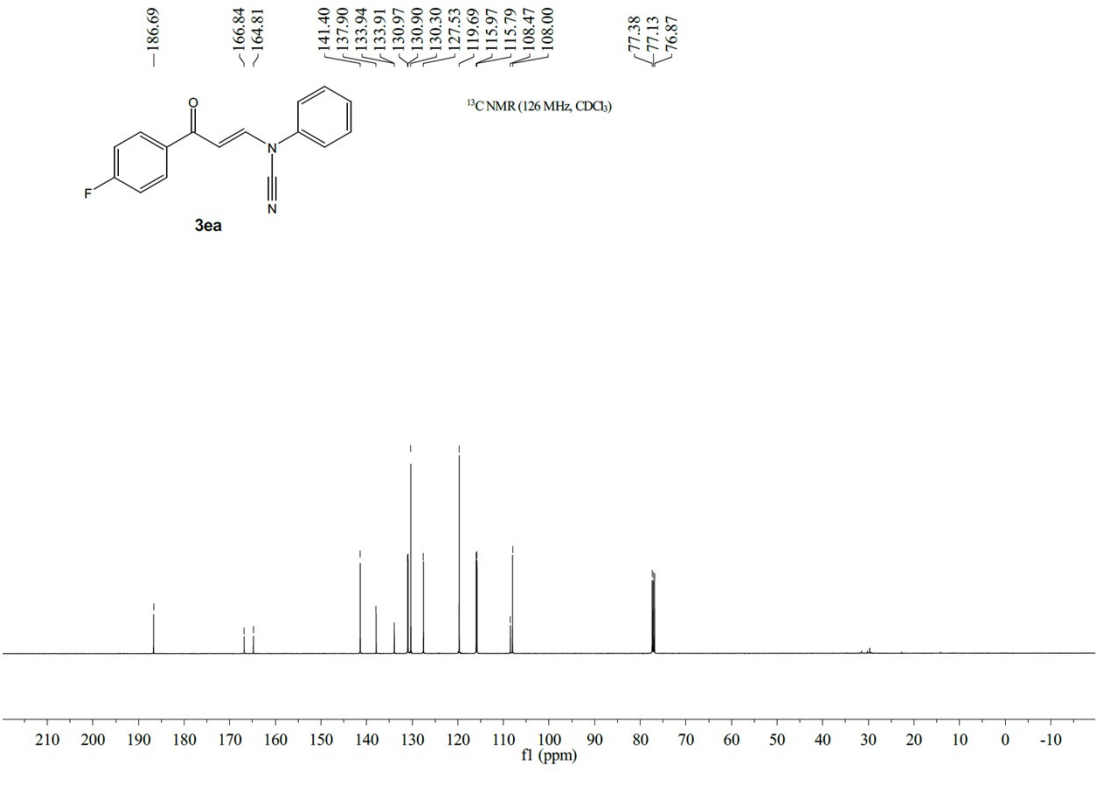
N
O
CH3
N
3ca
2.00
1.00
2.00
3.00
1.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


186.61
163.70
140.36
137.99
130.63
130.44
130.21
127.28
119.53
113.94
108.66
108.43
77.43
77.18
76.92
55.53
13C NMR (126 MHz, CDCl3)
O
N
O
CH3
N
3ca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

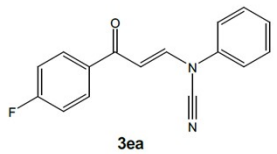

7.93
7.92
7.92
7.91
7.91
7.90
7.78
7.75
7.52
7.51
7.51
7.50
7.50
7.50
7.49
7.48
7.48
7.48
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.32
7.31
7.31
7.30
7.30
7.29
7.26
7.05
7.03
2.54
1.63
0.00
1H NMR (500 MHz, CDCl3)
O
N
S
CH3
N
3da
2.00
1.00
2.00
3.00
2.00
1.00
3.00
10.0
9.5
9.0
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
f1 (ppm)


187.15
146.32
140.91
137.98
133.77
130.27
128.73
127.44
125.09
119.68
108.61
108.31
77.29
77.03
76.78
14.78
13C NMR (126 MHz, CDCl3)
O
N
S
CH3
N
3da
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.03
8.03
8.02
8.01
8.00
7.78
7.76
7.50
7.49
7.47
7.37
7.36
7.35
7.33
7.28
7.18
7.16
7.14
7.03
7.00
0.00
1H NMR (500 MHz, CDCl3)
O
N
F
N
3ea
2.00
1.00
2.00
3.00
2.00
1.00
10.0 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
f1 (ppm)

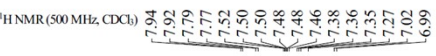

186.69
166.84
164.81
141.40
137.90
133.94
133.91
130.97
130.90
130.30
127.53
119.69
115.97
115.79
108.47
108.00
77.38
77.13
76.87
13C NMR (126 MHz, CDCl3)
O
N
F
N
3ea
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

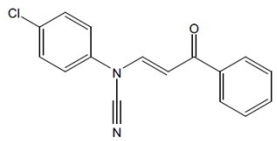
^{19}F NMR (471 MHz, $CDCl_3$)



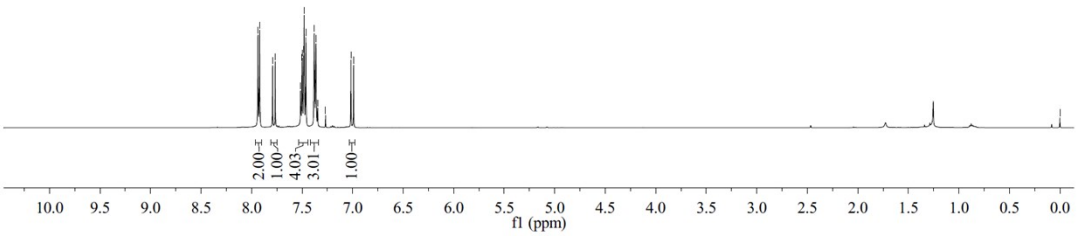
3ea

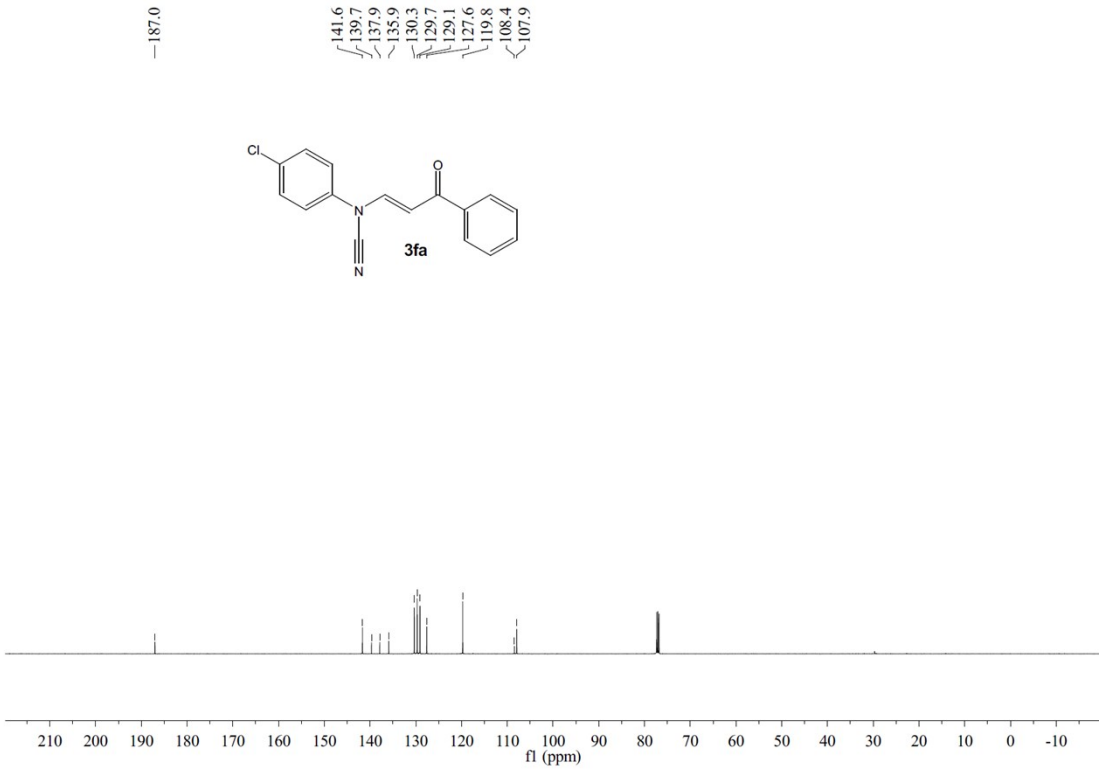
^{1}H NMR (500 MHz, $CDCl_3$)

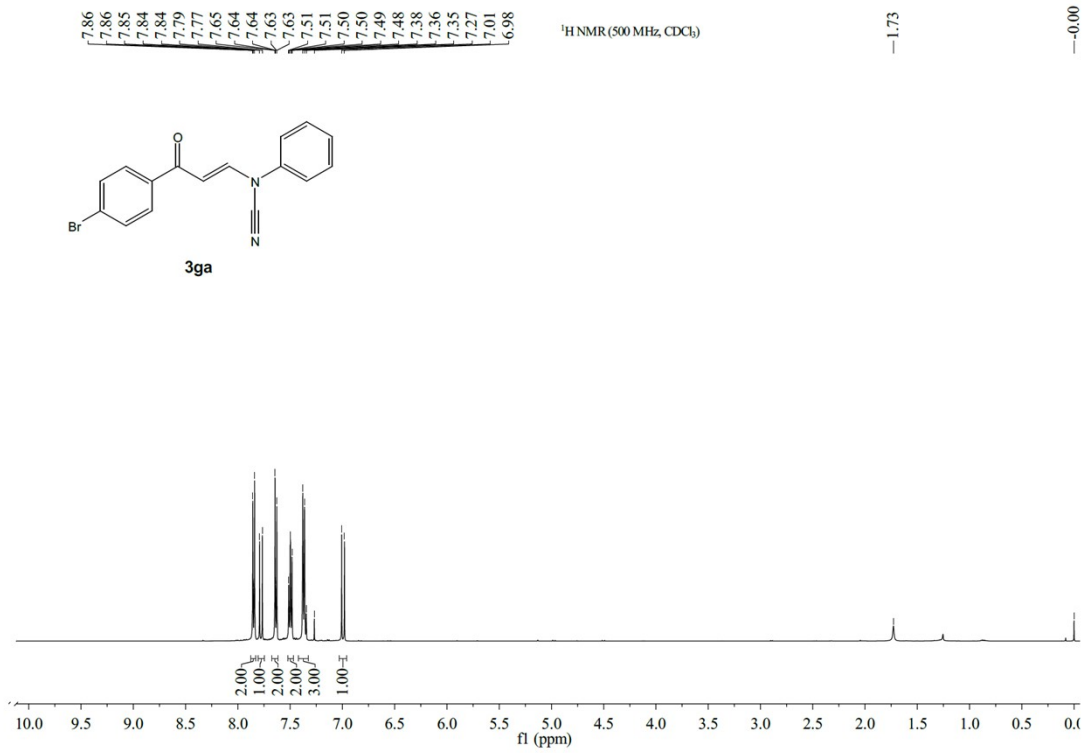


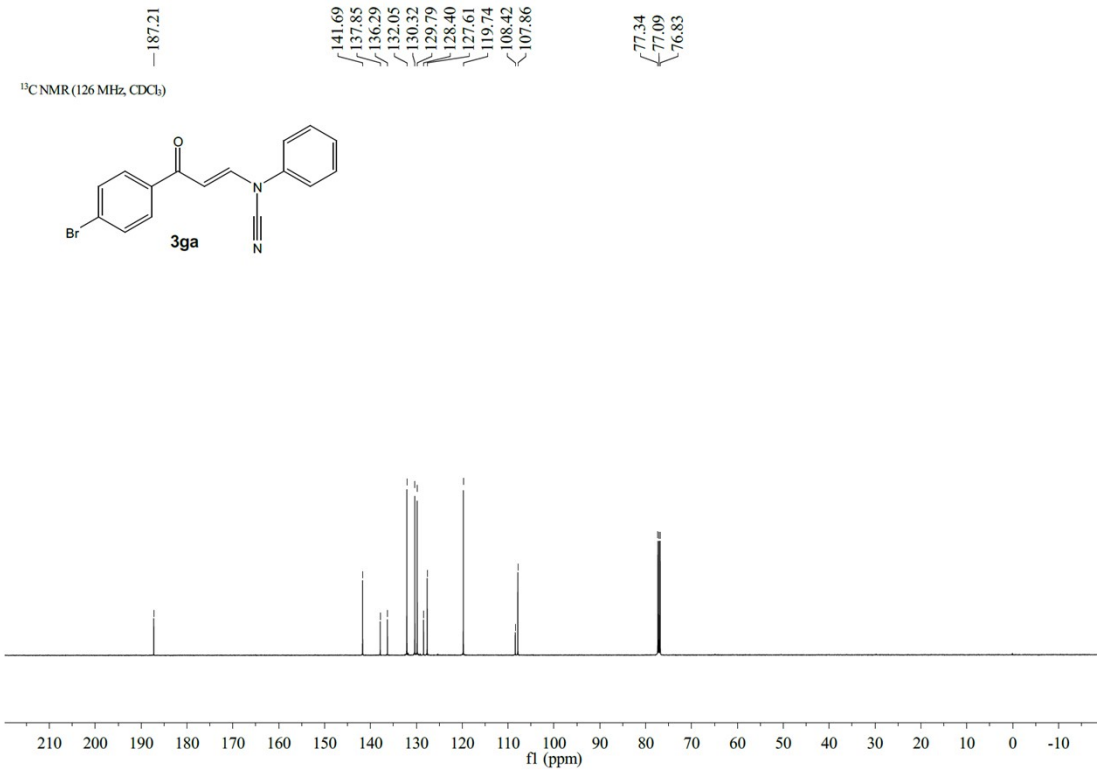


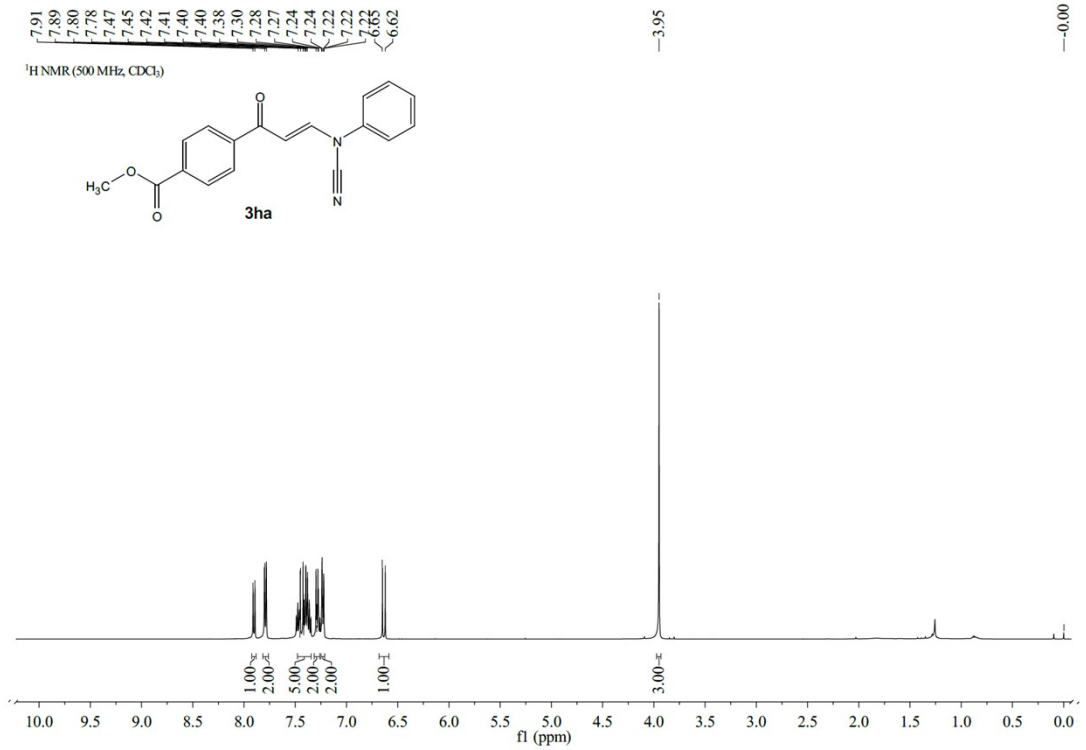
3fa

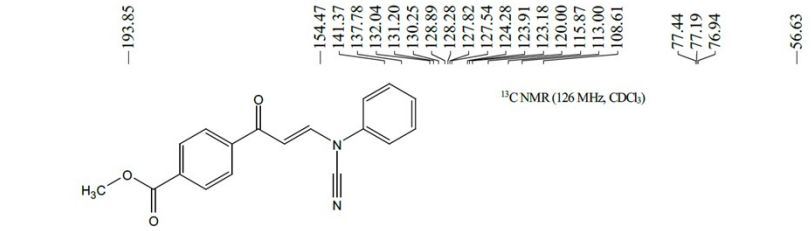



187.0
141.6
139.7
137.9
135.9
130.3
129.7
129.1
127.6
119.8
108.4
107.9
Cl
O
N
N
3fa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

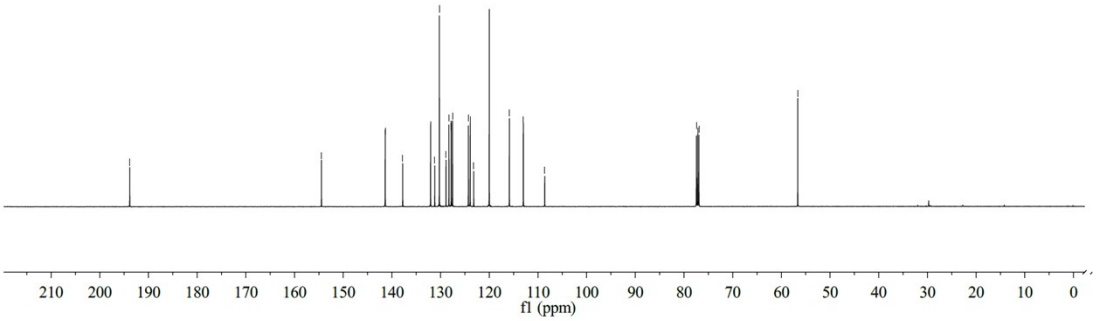

7.86
7.86
7.85
7.84
7.84
7.79
7.77
7.65
7.64
7.64
7.63
7.63
7.51
7.51
7.50
7.50
7.49
7.48
7.38
7.36
7.35
7.27
7.01
6.98
^{1}H NMR (500 MHz, CDCl$_3$)
1.73
0.00
O
N
Br
N
3ga
2.00
1.00
2.00
2.00
3.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


187.21
141.69
137.85
136.29
132.05
130.32
129.79
128.40
127.61
119.74
108.42
107.86
77.34
77.09
76.83
13C NMR (126 MHz, CDCl3)
O
N
Br
N
3ga
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.91
7.89
7.80
7.78
7.47
7.45
7.42
7.41
7.40
7.40
7.38
7.30
7.28
7.27
7.24
7.24
7.22
7.22
7.22
6.65
6.62
3.95
0.00
1H NMR (500 MHz, CDCl3)
O
N
H3C
O
O
N
3ha
1.00
2.00
5.00
2.00
2.00
1.00
3.00
10.0 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
f1 (ppm)

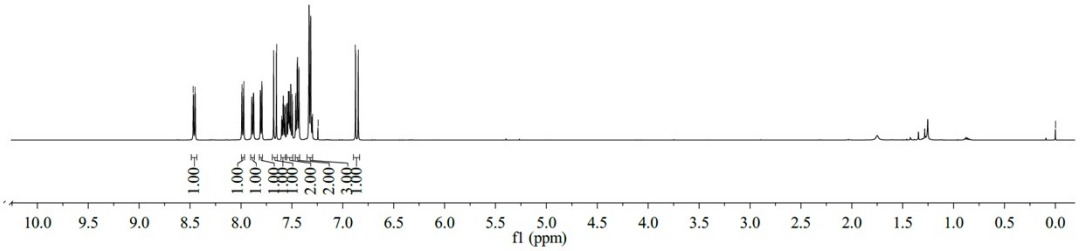

193.85
154.47
141.37
137.78
132.04
131.20
130.25
128.89
128.28
127.82
127.54
124.28
123.91
123.18
120.00
115.87
113.00
108.61
77.44
77.19
76.94
56.63
13C NMR (126 MHz, CDCl3)
O
N
CN
H3C
O
O

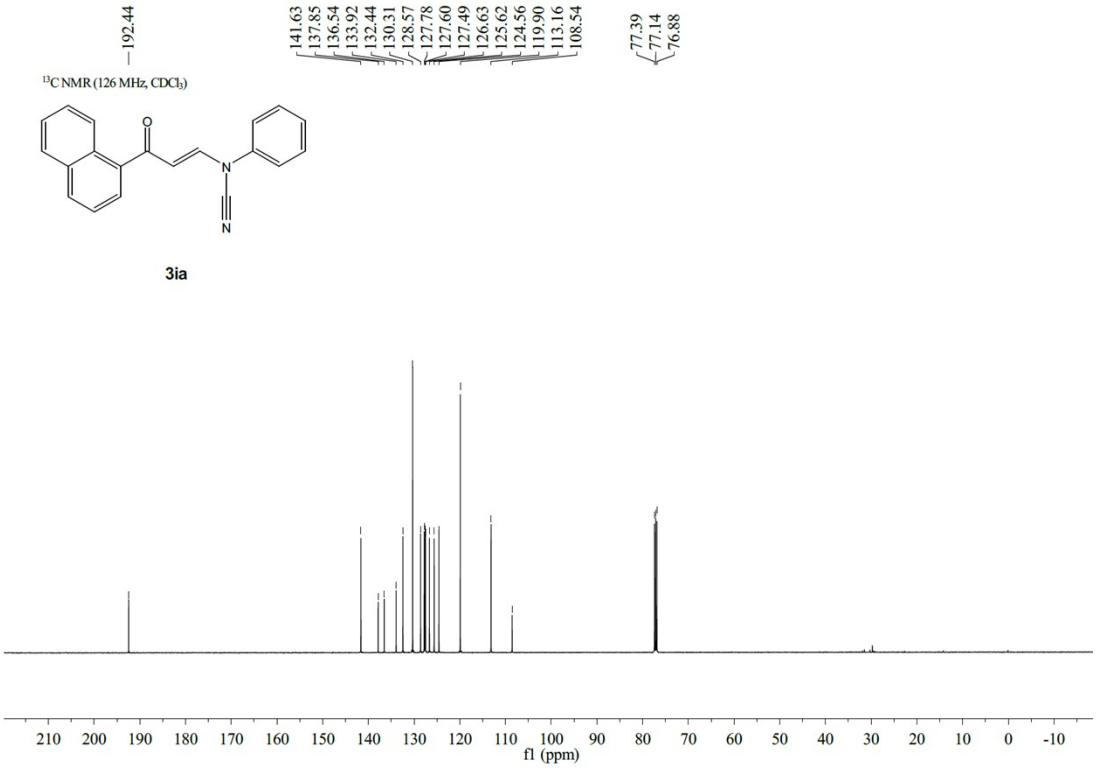
3ha

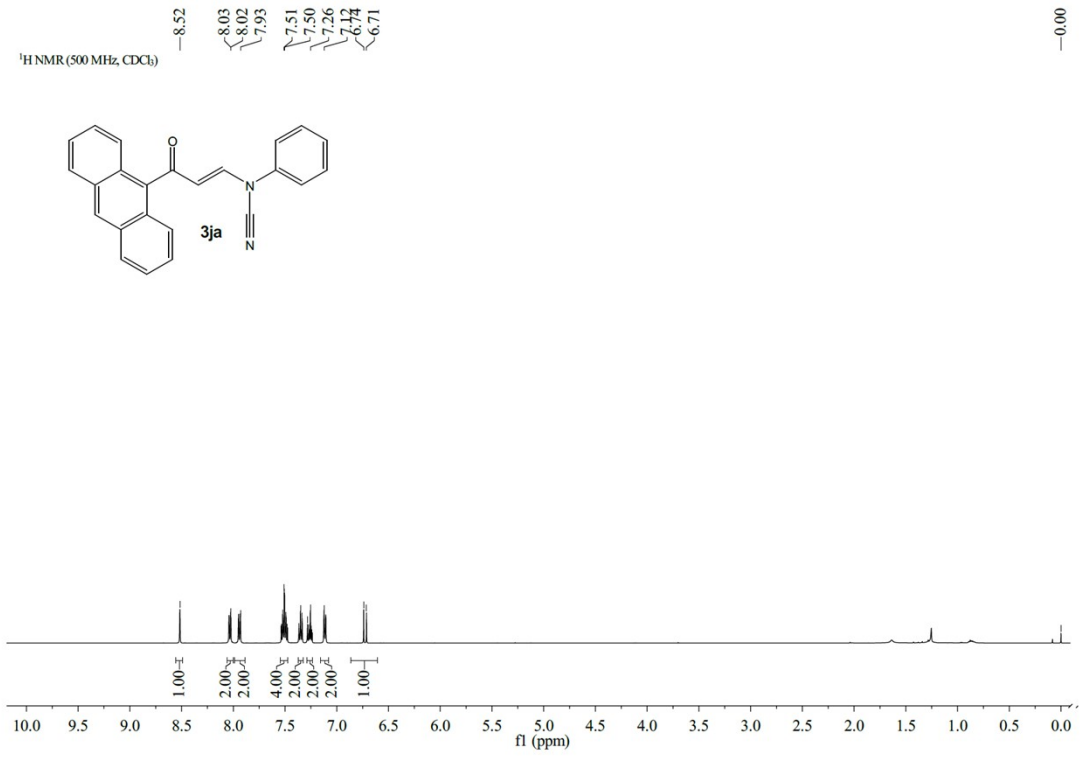

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

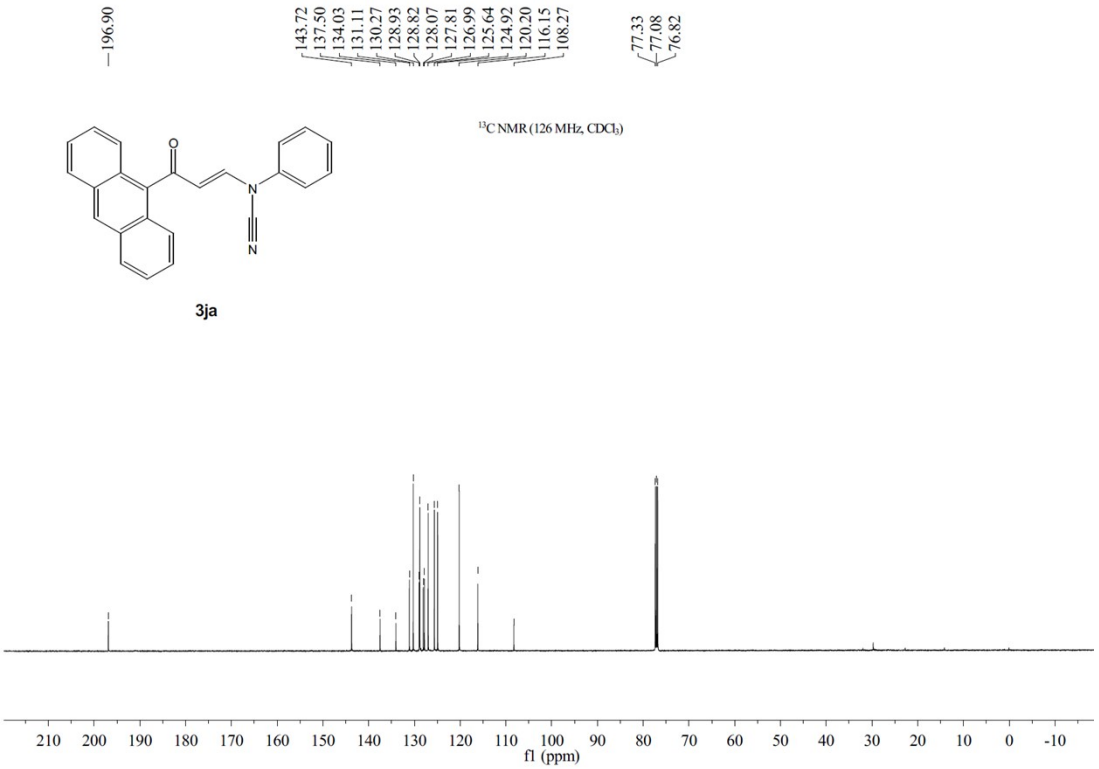

8.47
8.45
7.68
7.65
7.44
7.43
7.33
7.31
6.87
6.85
0.00
1H NMR (500 MHz, CDCl3)
O
N
CN

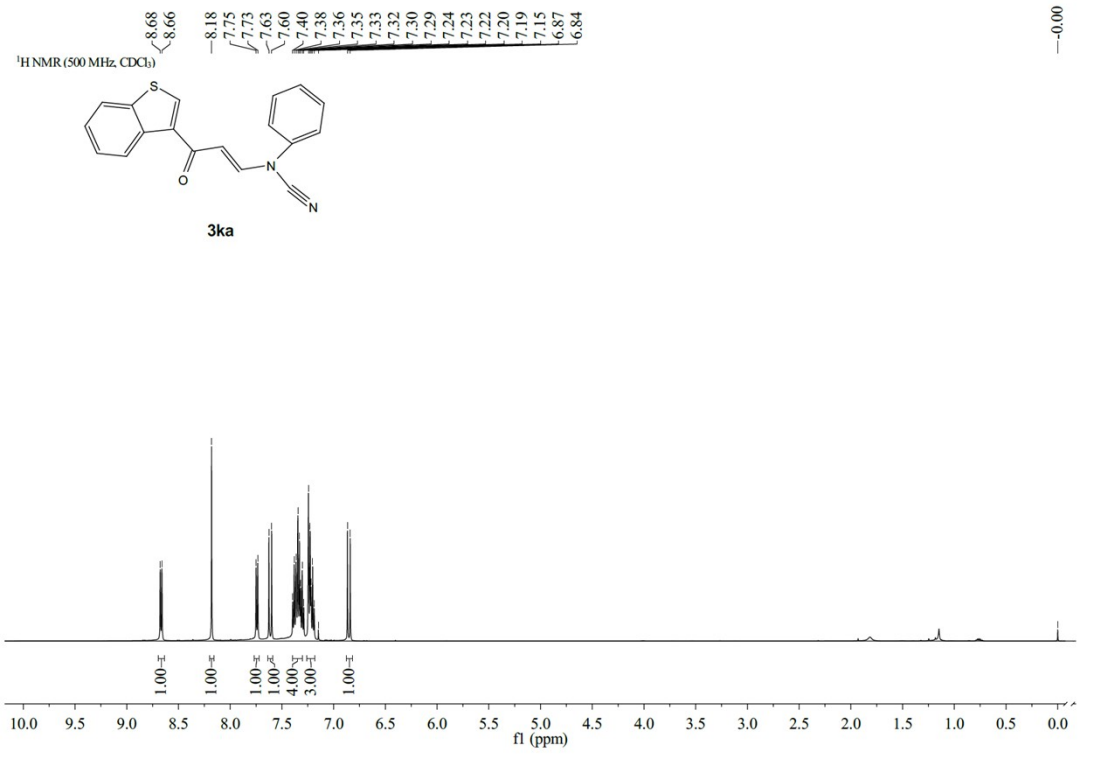
3ia

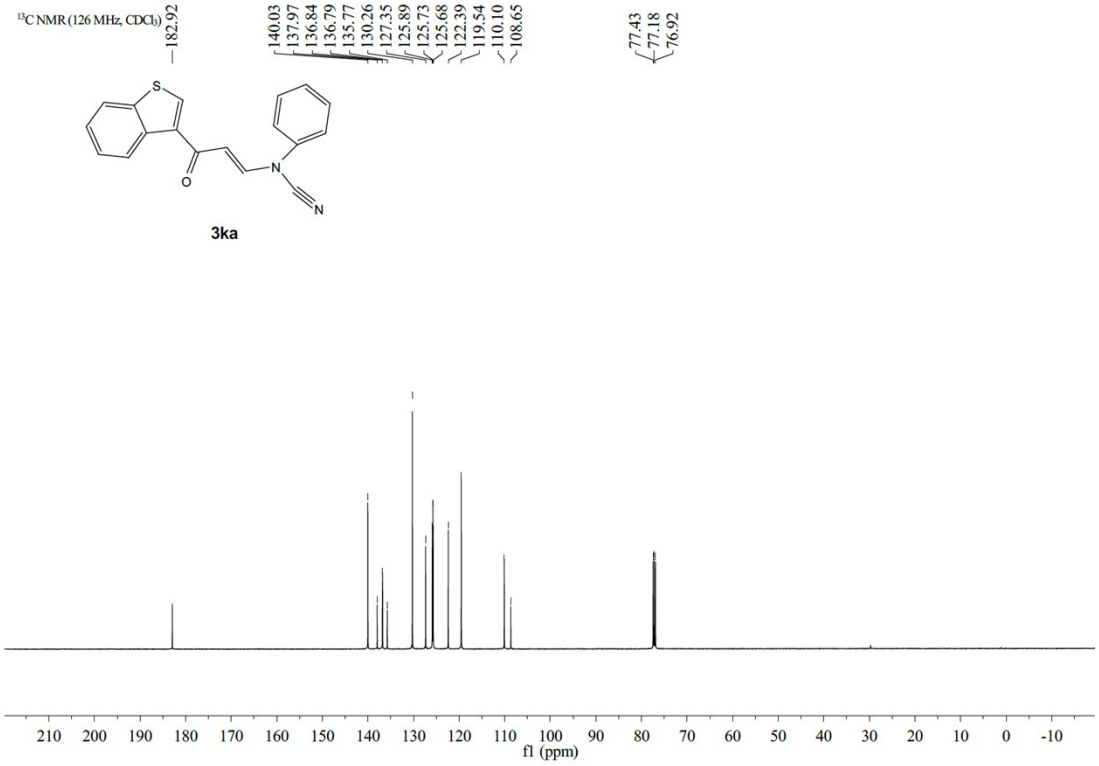

1.00
1.00
1.00
1.00
1.00
2.00
2.00
3.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

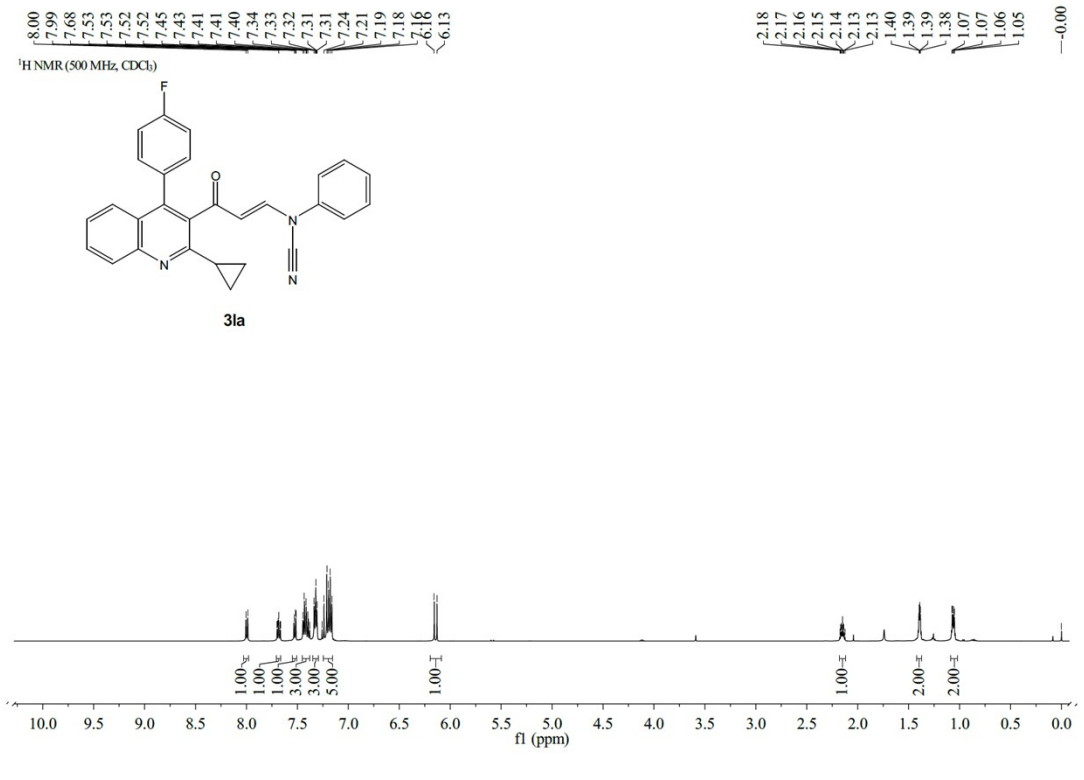

192.44
141.63
137.85
136.54
133.92
132.44
130.31
128.57
127.78
127.60
127.49
126.63
125.62
124.56
119.90
113.16
108.54
77.39
77.14
76.88
13C NMR (126 MHz, CDCl3)
O
N
N
3ia
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.52
8.03
8.02
7.93
7.51
7.50
7.26
7.12
6.74
6.71
0.00
1H NMR (500 MHz, CDCl3)
O
N
N
3ja
1.00
2.00
2.00
4.00
2.00
2.00
2.00
1.00
10.0 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
f1 (ppm)

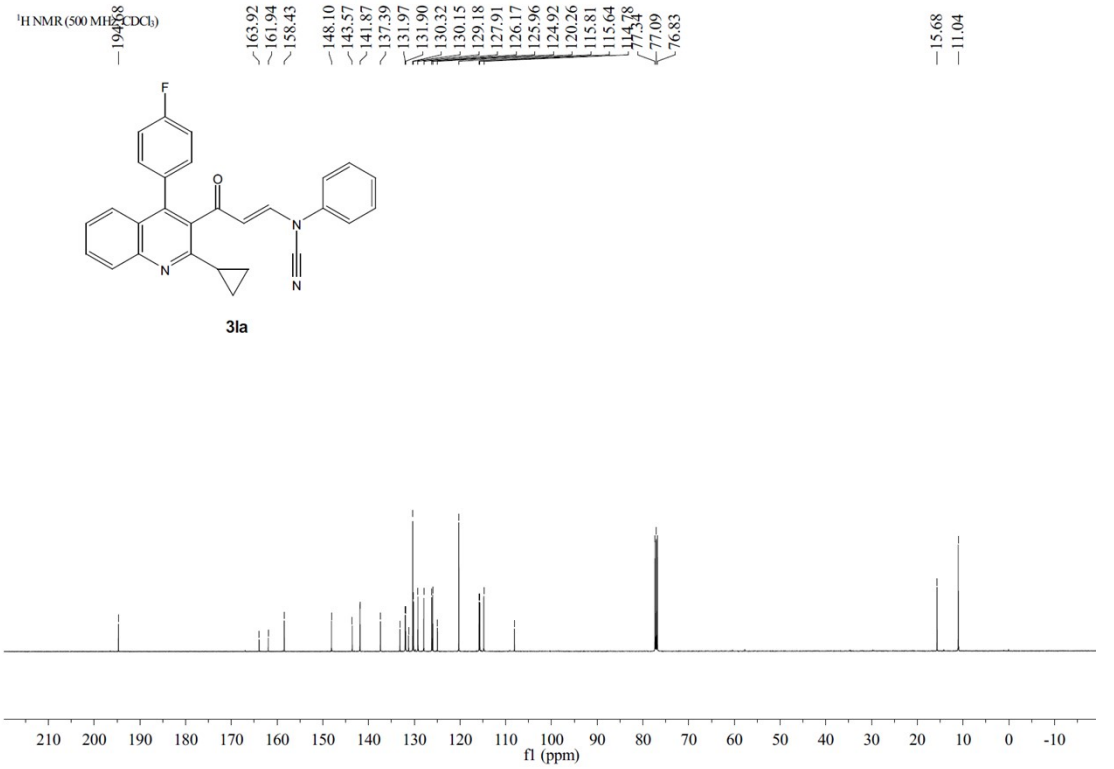

196.90
143.72
137.50
134.03
131.11
130.27
128.93
128.82
128.07
127.81
126.99
125.64
124.92
120.20
116.15
108.27
77.33
77.08
76.82
13C NMR (126 MHz, CDCl3)
O
N
N
3ja
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.68
8.66
8.18
7.75
7.73
7.63
7.60
7.40
7.38
7.36
7.35
7.33
7.32
7.30
7.29
7.24
7.23
7.22
7.20
7.19
7.15
6.87
6.84
0.00
1H NMR (500 MHz, CDCl3)
S
O
N
N
3ka
1.00
1.00
1.00
1.00
4.00
3.00
1.00
10.0 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
f1 (ppm)

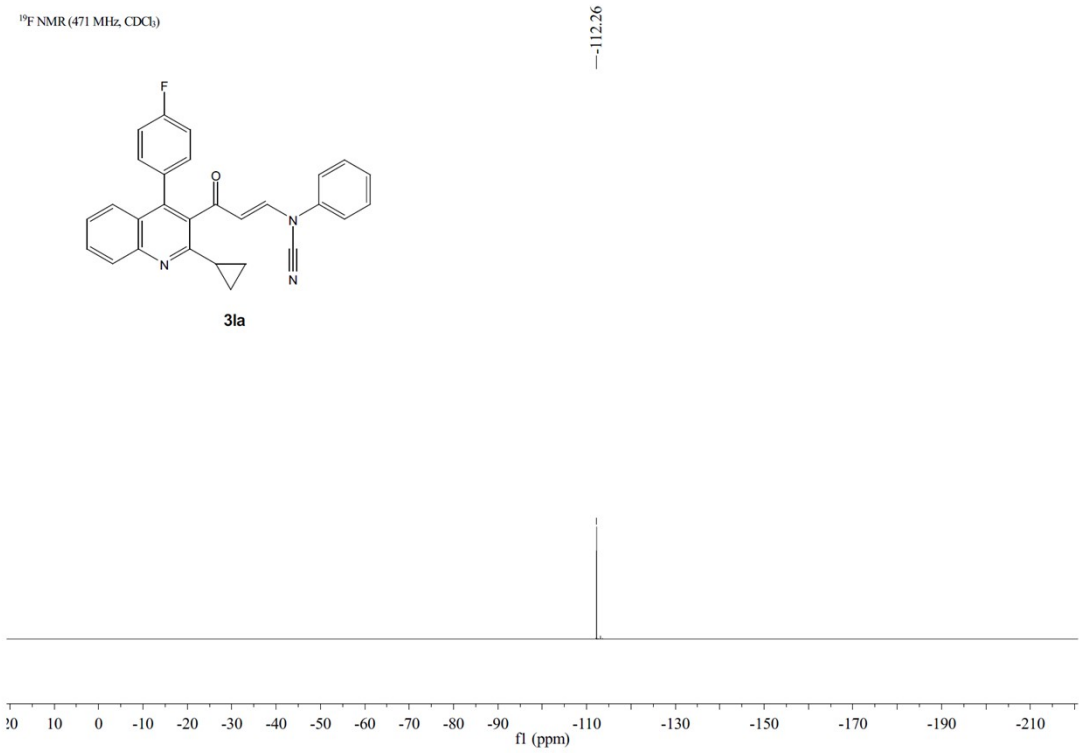

13C NMR (126 MHz, CDCl3)
182.92
140.03
137.97
136.84
136.79
135.77
130.26
127.35
125.89
125.73
125.68
122.39
119.54
110.10
108.65
77.43
77.18
76.92
S
O
N
N
3ka
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

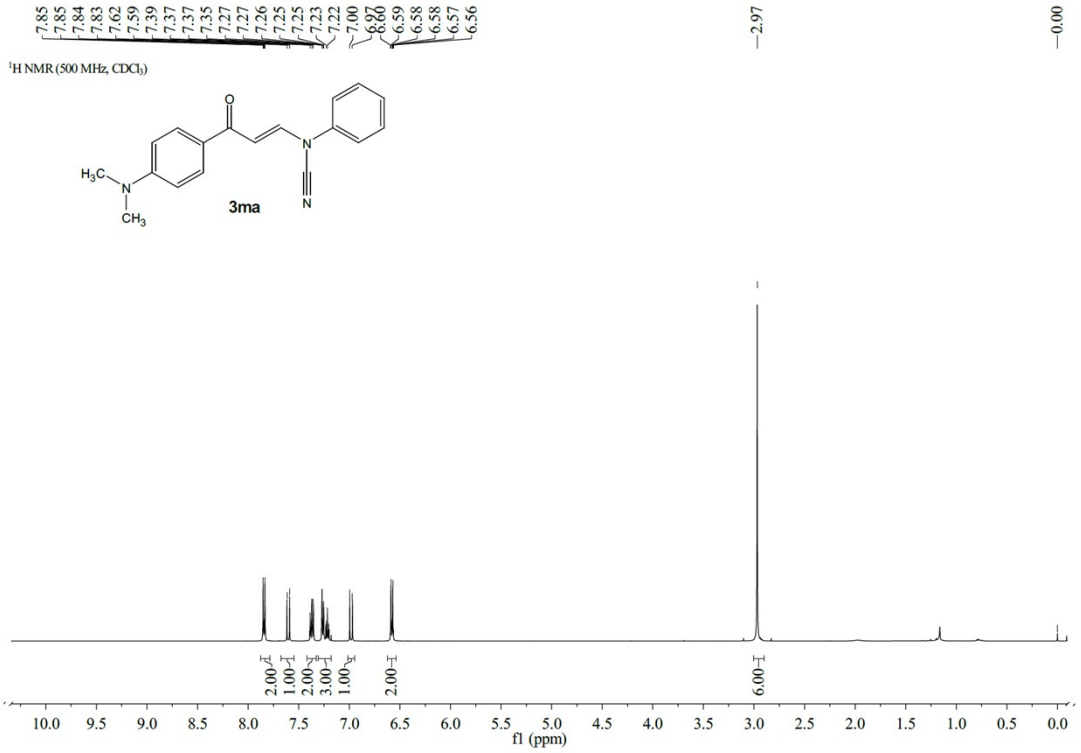

8.00
7.99
7.68
7.53
7.53
7.52
7.52
7.45
7.43
7.41
7.41
7.40
7.34
7.33
7.32
7.31
7.31
7.24
7.21
7.19
7.18
7.16
6.18
6.13
2.18
2.17
2.16
2.15
2.14
2.13
2.13
1.40
1.39
1.39
1.38
1.07
1.07
1.06
1.05
-0.00
1H NMR (500 MHz, CDCl3)
F
O
N
N
N
3la
1.00
1.00
1.00
3.00
5.00
1.00
1.00
2.00
2.00
10.0 9.5 9.0 8.5 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
f1 (ppm)

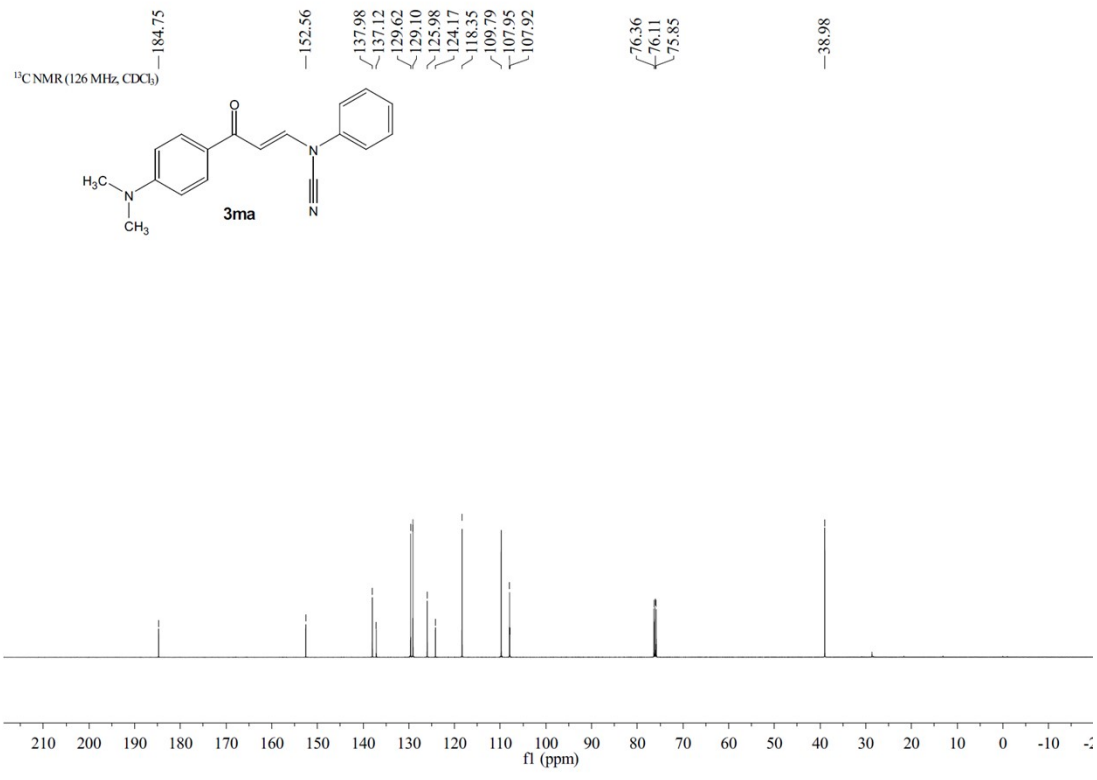
^{1}H NMR (500 MHz, $CDCl_3$)

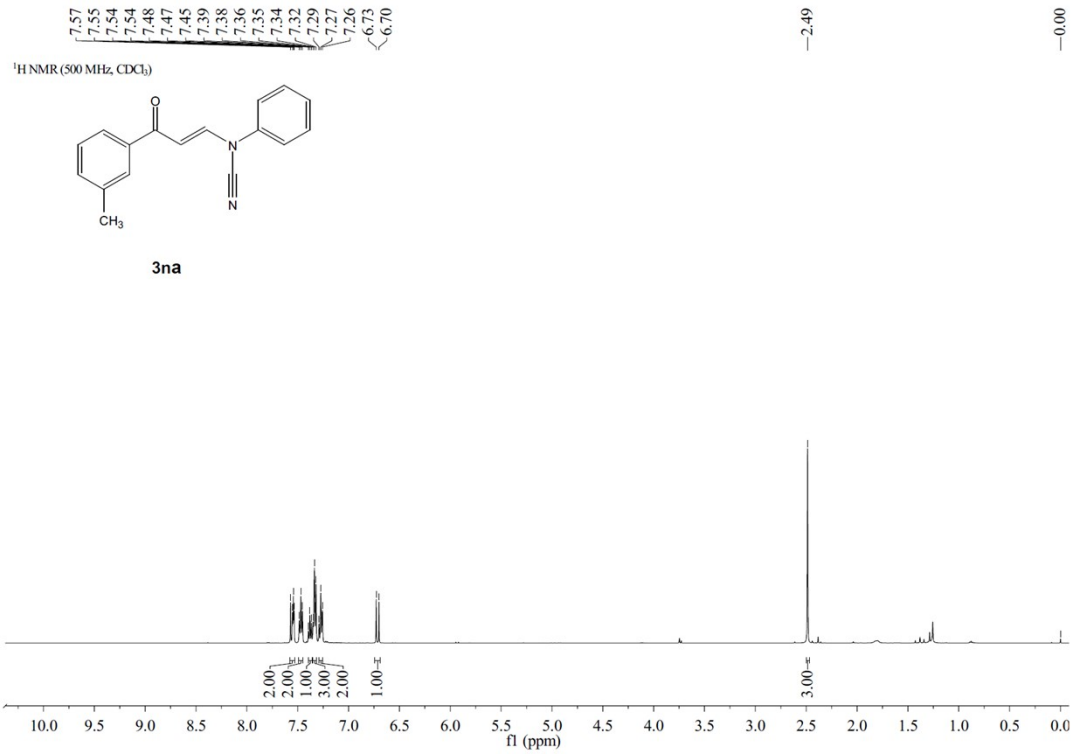


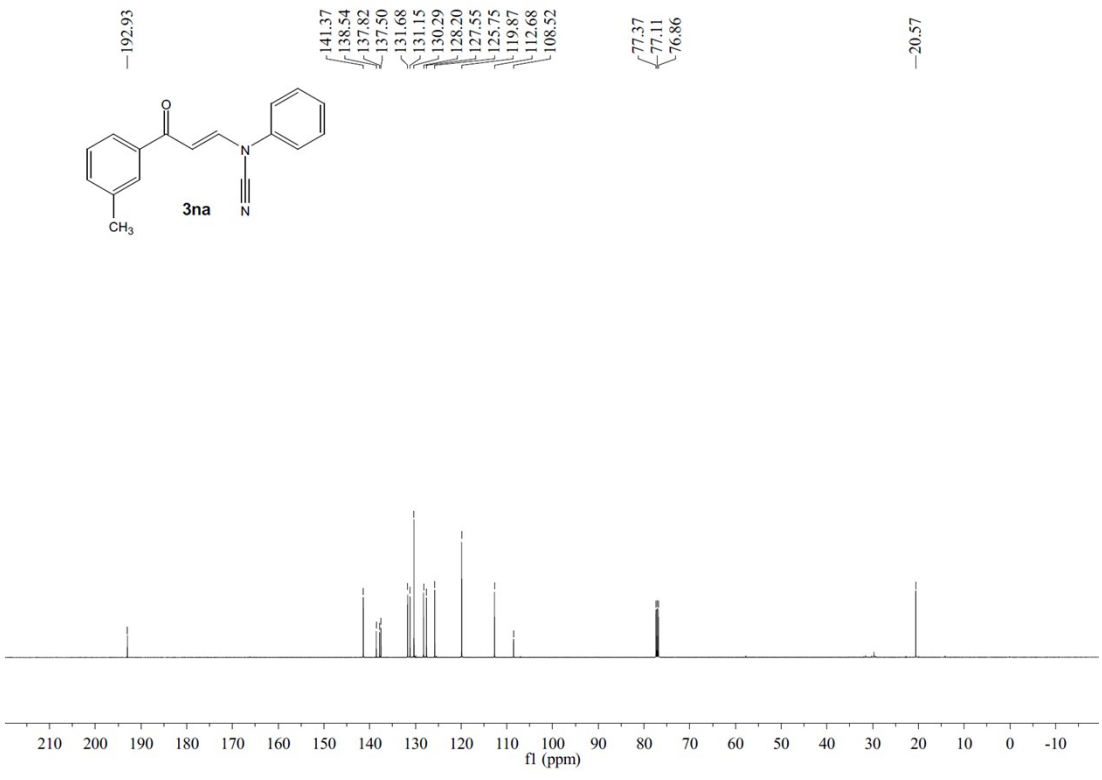
^{19}F NMR (471 MHz, $CDCl_3$)

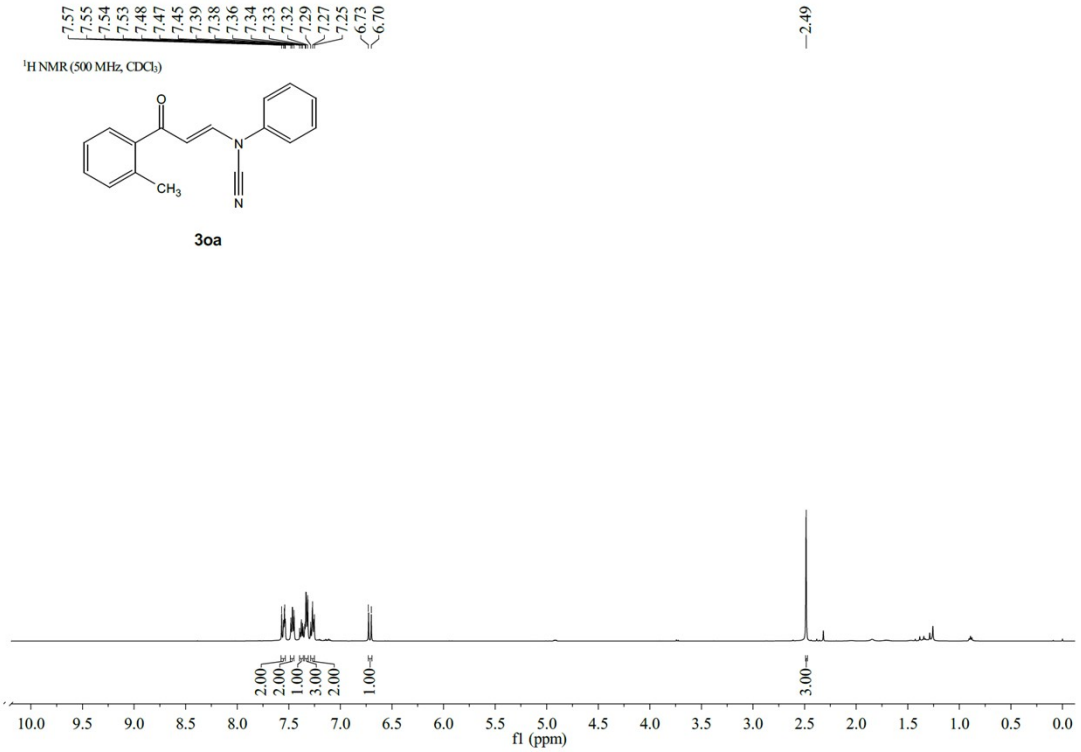


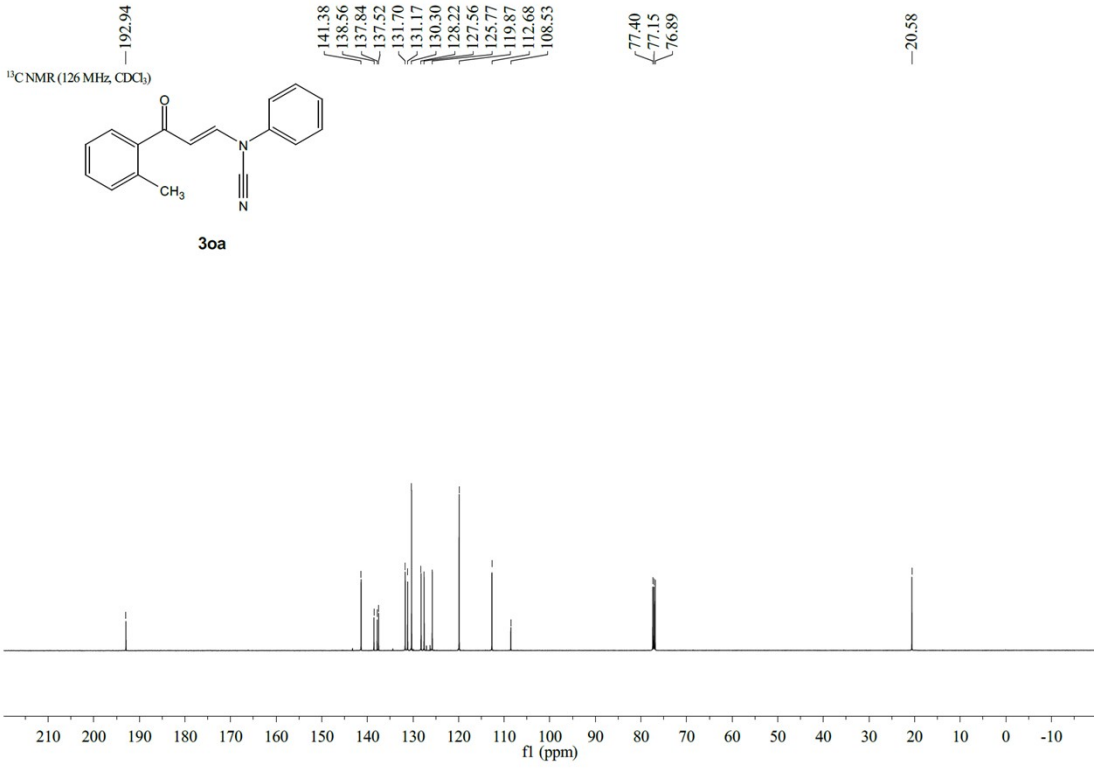

7.85
7.85
7.84
7.83
7.62
7.59
7.39
7.37
7.37
7.35
7.27
7.27
7.26
7.25
7.25
7.23
7.22
7.00
6.97
6.60
6.59
6.58
6.58
6.57
6.56
2.97
0.00
1H NMR (500 MHz, CDCl3)
3ma
2.00
1.00
2.00
3.00
1.00
2.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

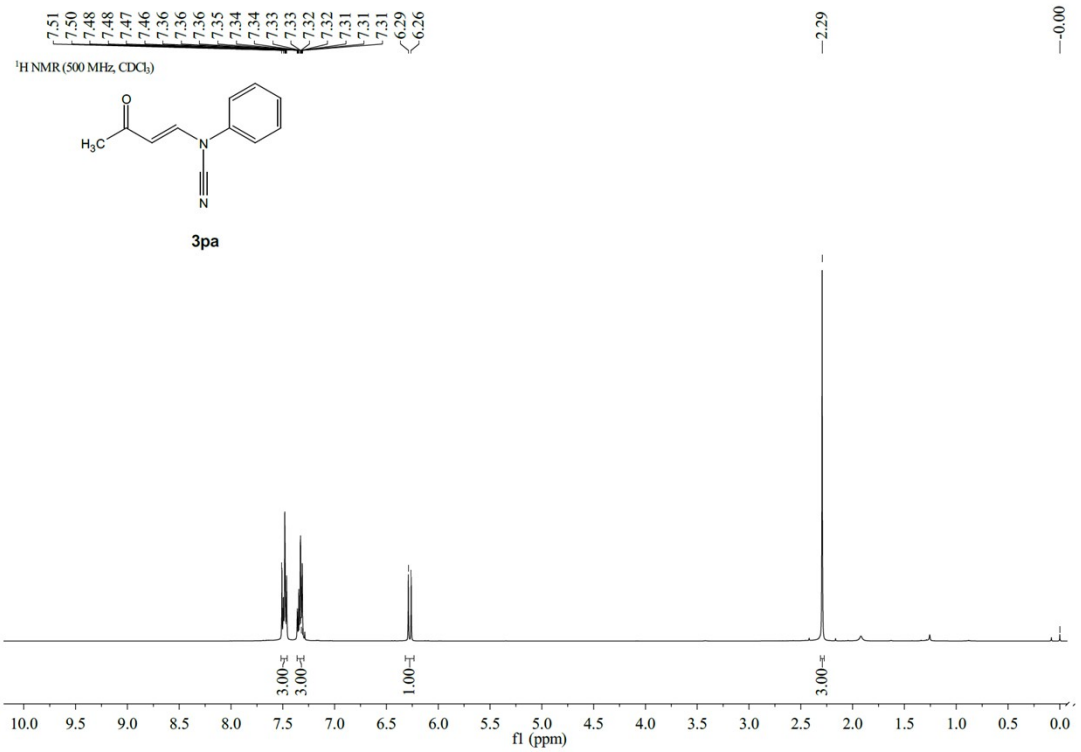

184.75
152.56
137.98
137.12
129.62
129.10
125.98
124.17
118.35
109.79
107.95
107.92
76.36
76.11
75.85
38.98
13C NMR (126 MHz, CDCl3)
3ma
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

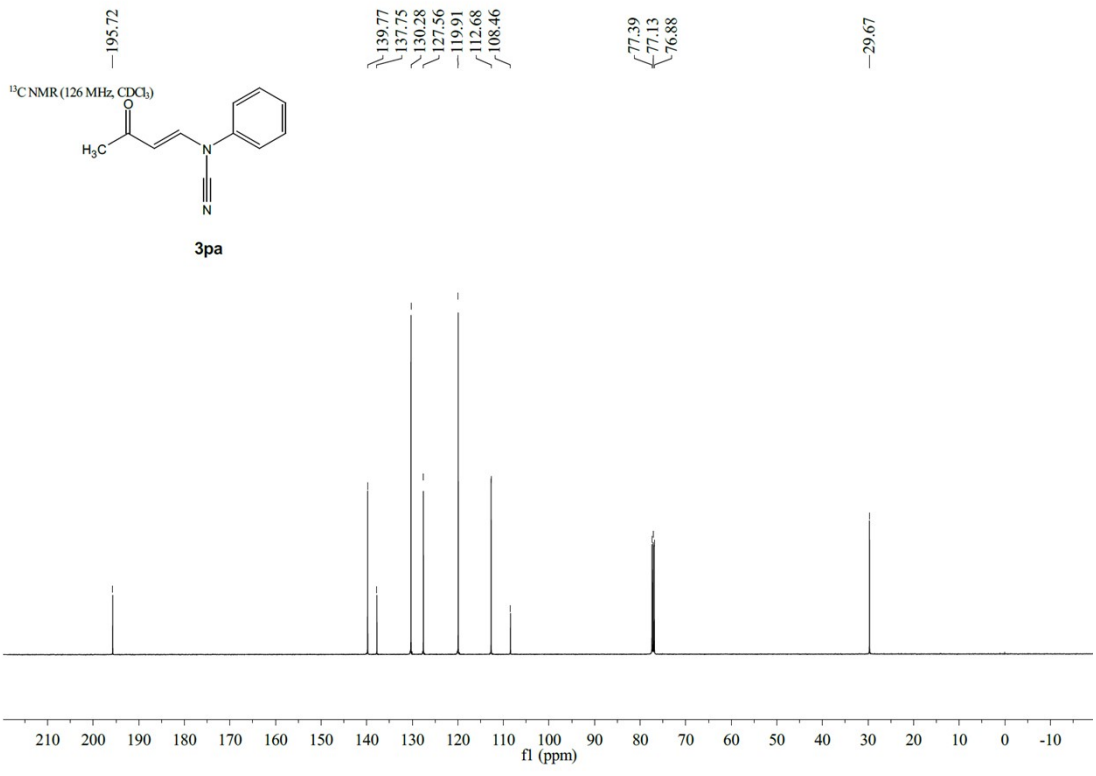

7.57
7.55
7.54
7.54
7.48
7.47
7.45
7.39
7.38
7.36
7.35
7.34
7.32
7.29
7.27
7.26
6.73
6.70
2.49
0.00
1H NMR (500 MHz, CDCl3)
O
N
N
CH3
3na
2.00
2.00
1.00
3.00
2.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

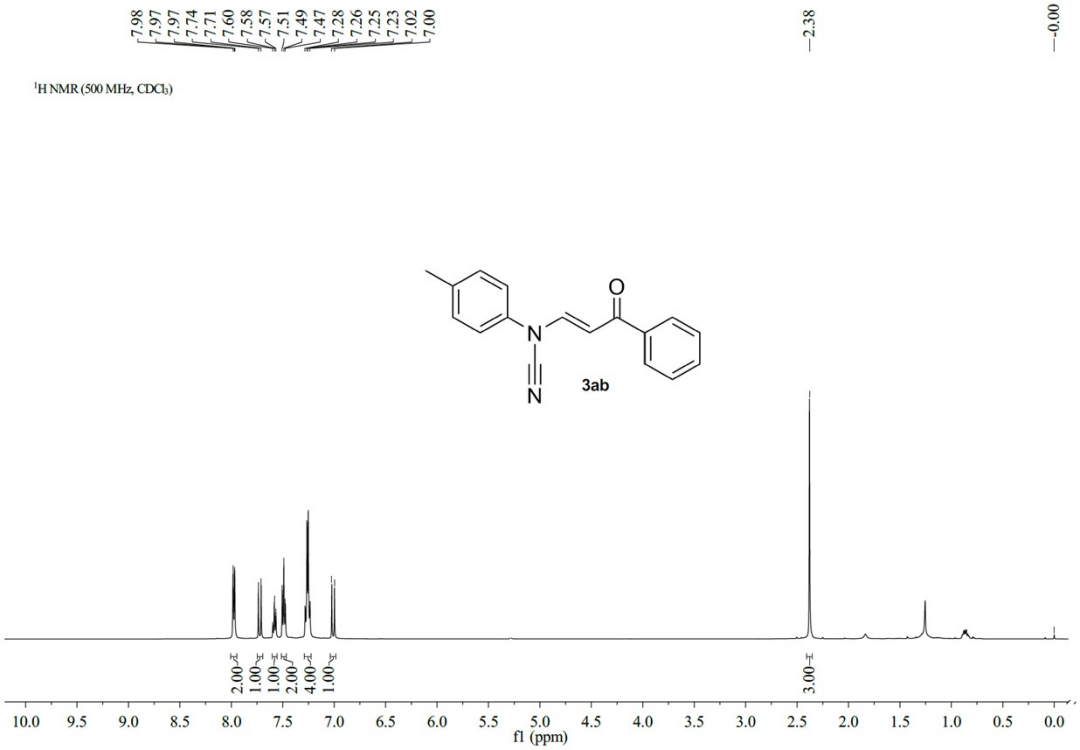

192.93
141.37
138.54
137.82
137.50
131.68
131.15
130.29
128.20
127.55
125.75
119.87
112.68
108.52
77.37
77.11
76.86
20.57
O
N
N
CH3
3na
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

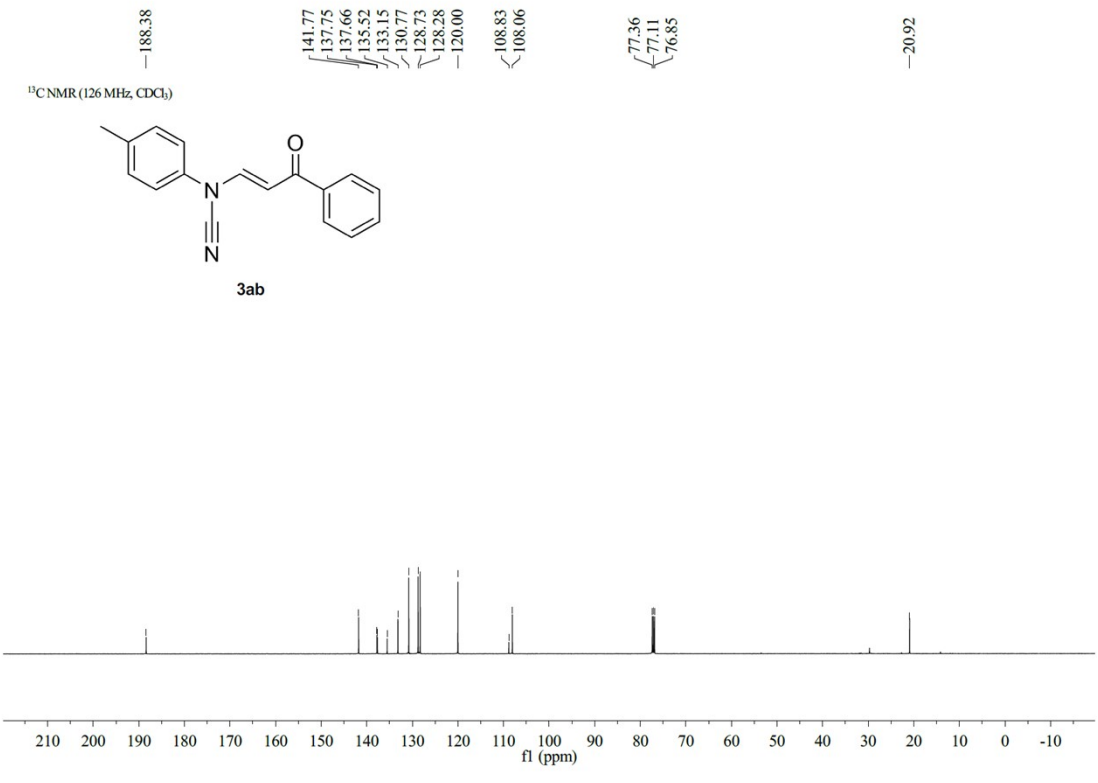

7.57
7.55
7.54
7.53
7.48
7.47
7.45
7.39
7.38
7.36
7.34
7.33
7.32
7.29
7.27
7.25
6.73
6.70
2.49
^{1}H NMR (500 MHz, CDCl$_3$)
O
N
CH$_3$
N
3oa
2.00
2.00
1.00
3.00
2.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

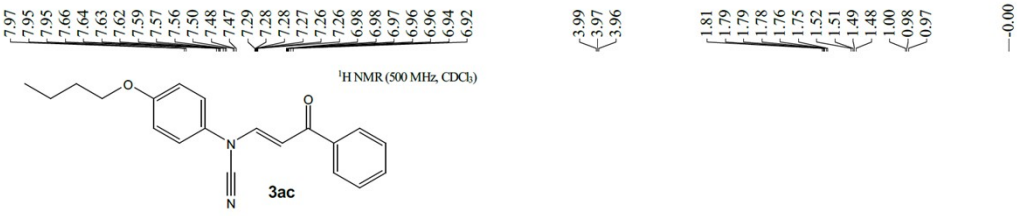

192.94
141.38
138.56
137.84
137.52
131.70
131.17
130.30
128.22
127.56
125.77
119.87
112.68
108.53
77.40
77.15
76.89
20.58
^{13}C NMR (126 MHz, CDCl$_3$)
O
N
CH$_3$
N
3oa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

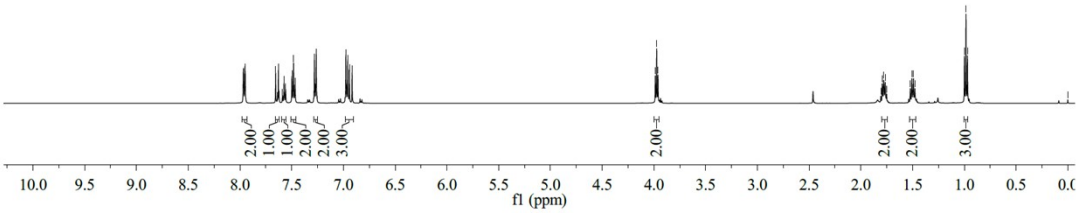

7.51
7.50
7.48
7.48
7.47
7.46
7.36
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.31
6.29
6.26
2.29
0.00
1H NMR (500 MHz, CDCl3)
3pa
3.00
3.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

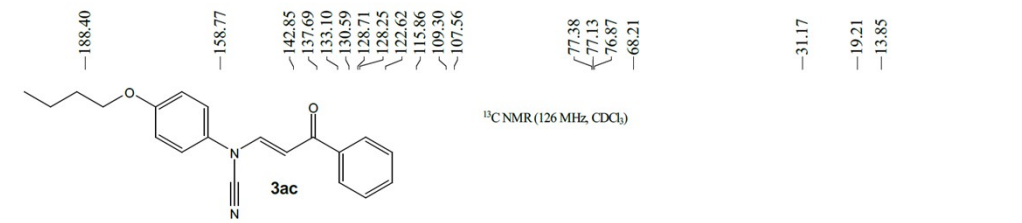

195.72
139.77
137.75
130.28
127.56
119.91
112.68
108.46
77.39
77.13
76.88
29.67
13C NMR (126 MHz, CDCl3)
3pa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

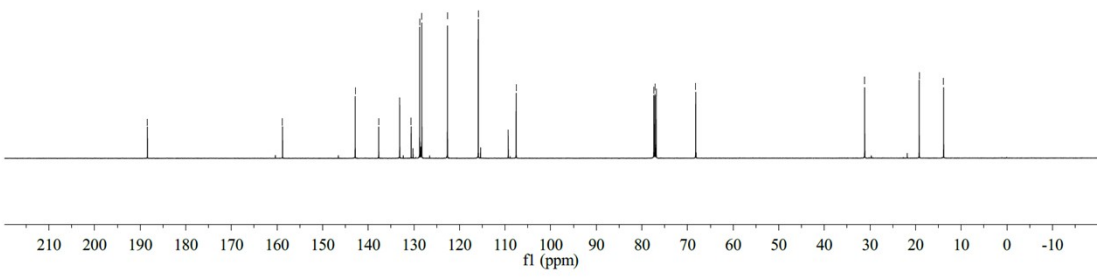

7.98
7.97
7.97
7.74
7.71
7.60
7.58
7.57
7.51
7.49
7.47
7.28
7.26
7.25
7.23
7.02
7.00
2.38
-0.00
1H NMR (500 MHz, CDCl3)
O
N
N
3ab
2.00
1.00
1.00
2.00
4.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

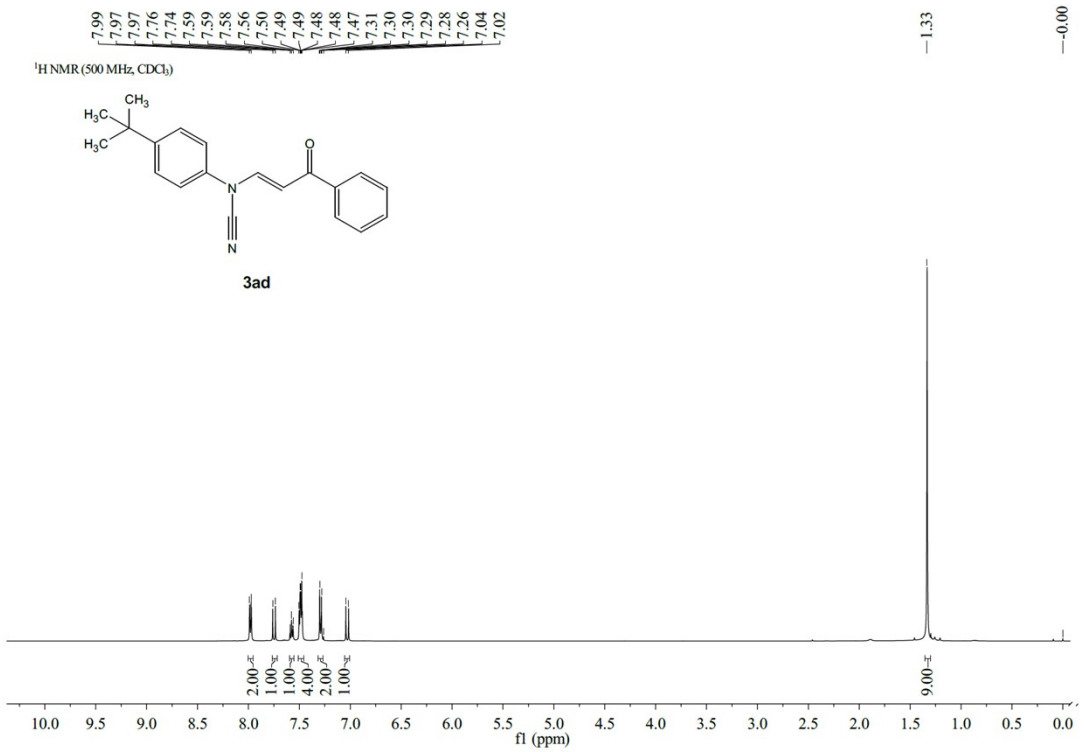

188.38
141.77
137.75
137.66
135.52
133.15
130.77
128.73
128.28
120.00
108.83
108.06
77.36
77.11
76.85
20.92
13C NMR (126 MHz, CDCl3)
O
N
N
3ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

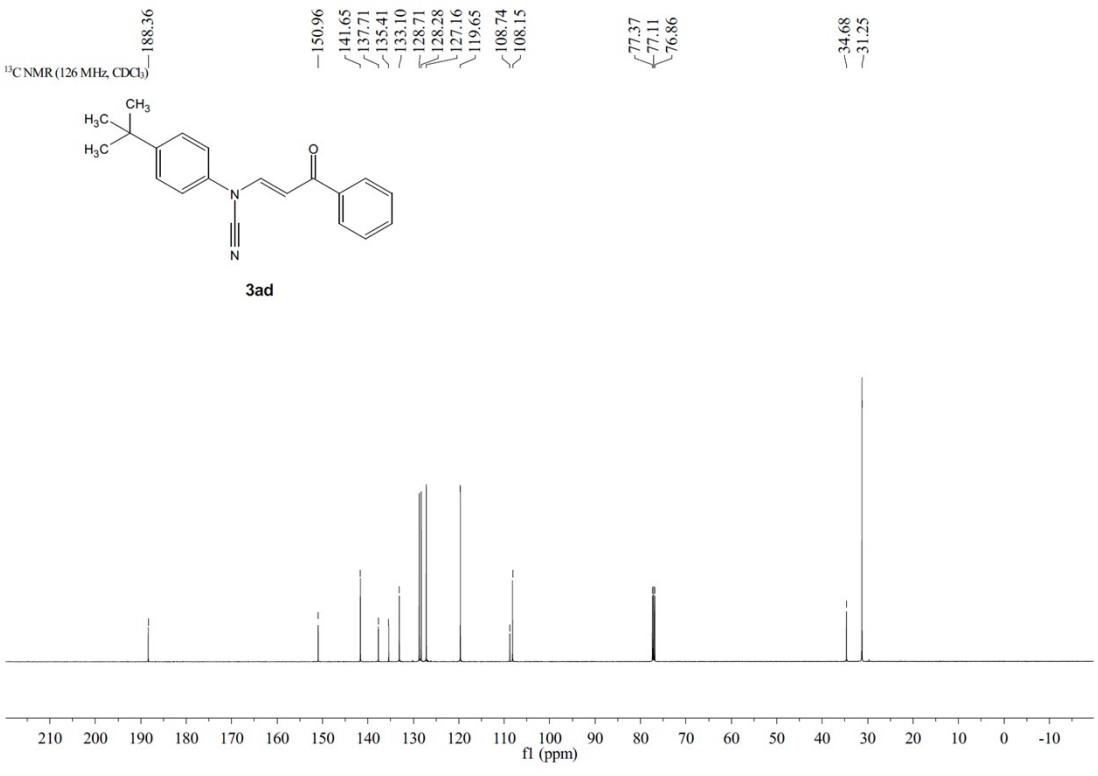

7.97
7.95
7.95
7.66
7.64
7.63
7.62
7.59
7.57
7.56
7.50
7.48
7.47
7.29
7.28
7.28
7.27
7.26
7.26
6.98
6.98
6.97
6.96
6.96
6.94
6.92
3.99
3.97
3.96
1.81
1.79
1.79
1.78
1.76
1.75
1.52
1.51
1.49
1.48
1.00
0.98
0.97
-0.00
1H NMR (500 MHz, CDCl3)
O
N
N
3ac

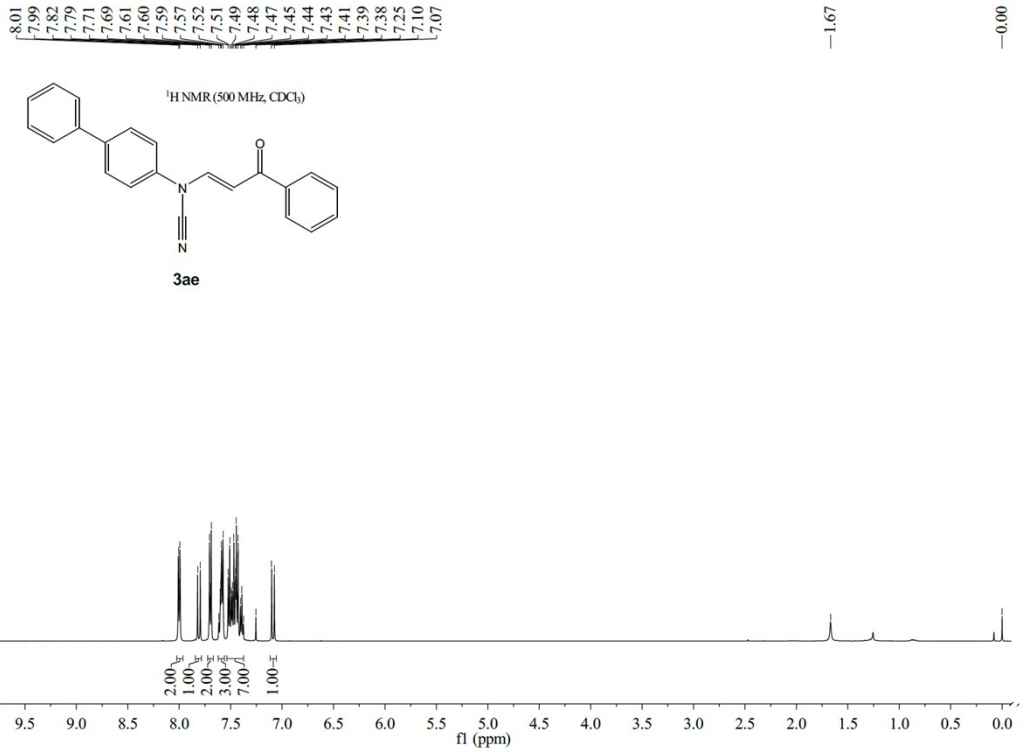

2.00
1.00
1.00
2.00
2.00
3.00
2.00
2.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

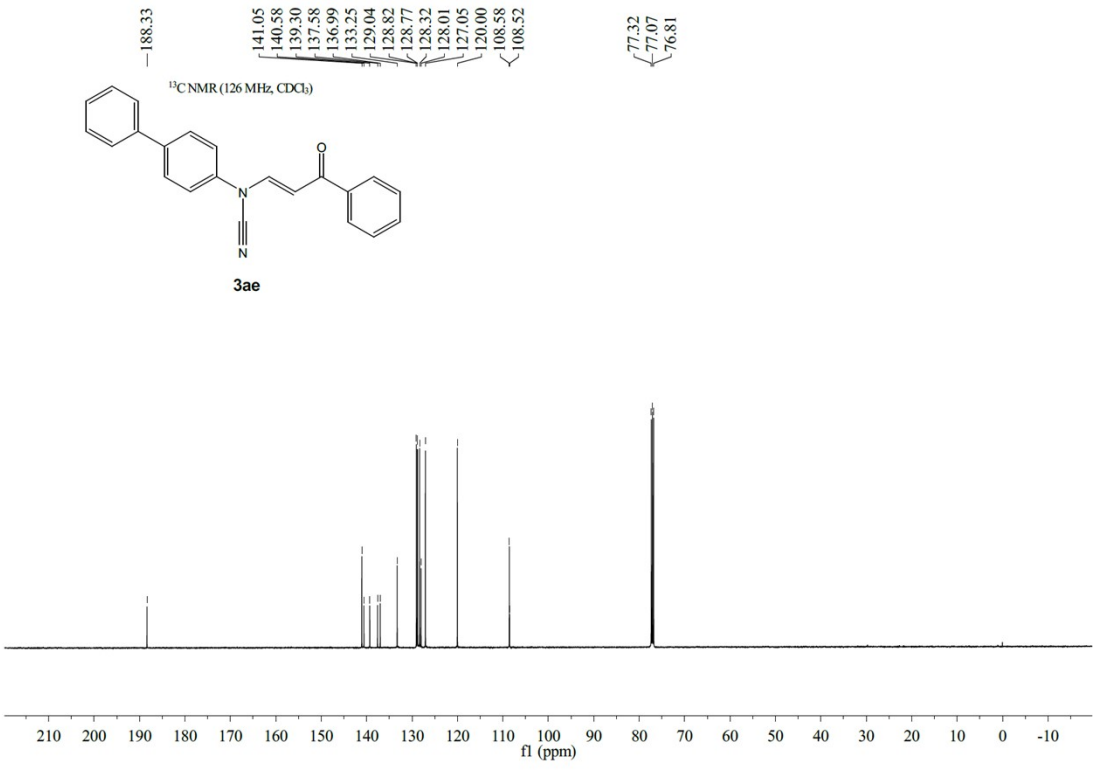

188.40
158.77
142.85
137.69
133.10
130.59
128.71
128.25
122.62
115.86
109.30
107.56
77.38
77.13
76.87
68.21
31.17
19.21
13.85
13C NMR (126 MHz, CDCl3)
O
N
N
3ac

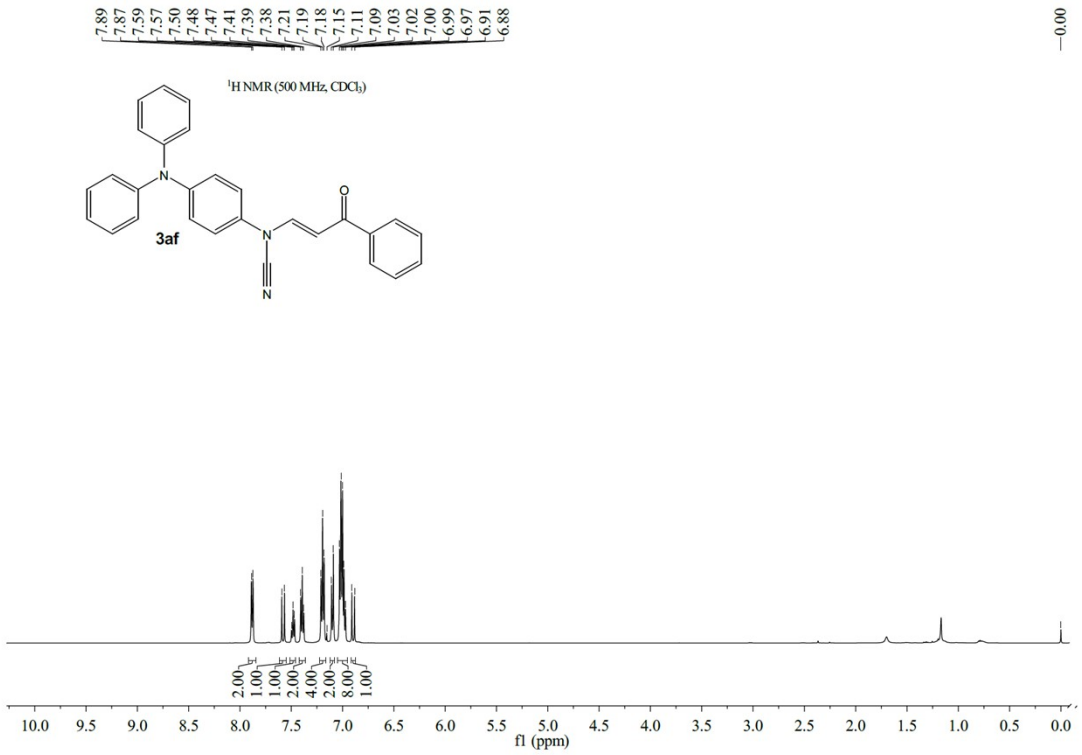

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

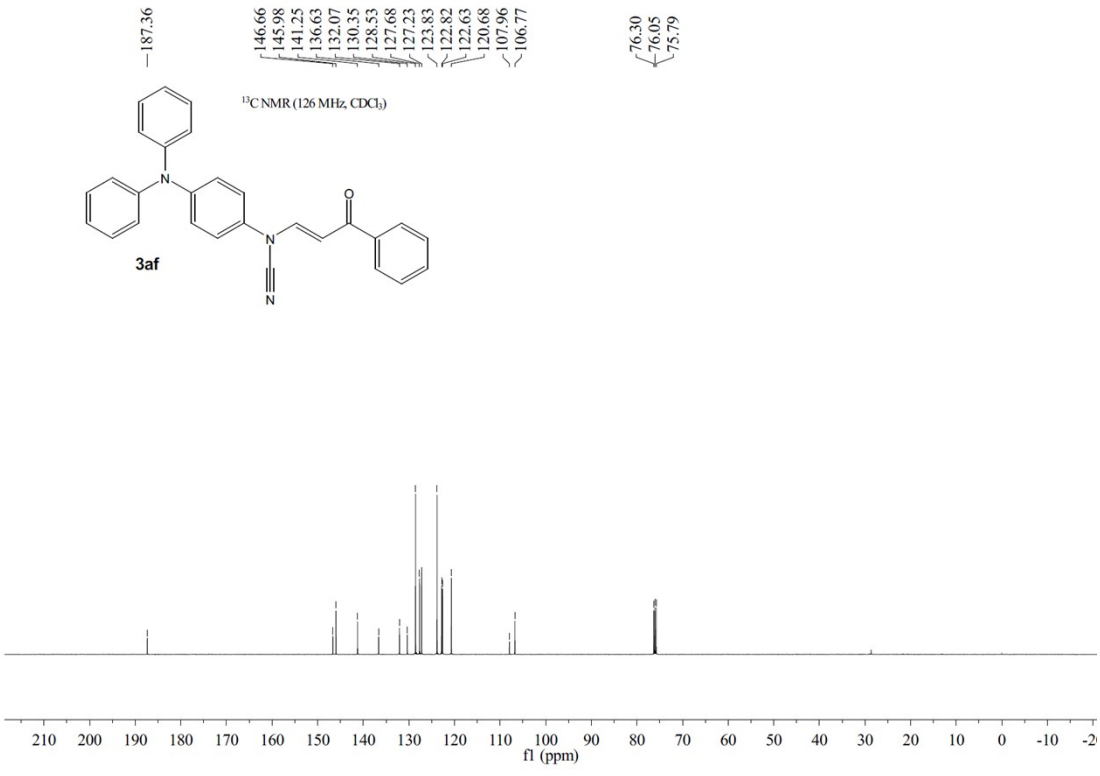

7.99
7.97
7.97
7.76
7.74
7.59
7.59
7.58
7.56
7.50
7.49
7.49
7.48
7.48
7.47
7.31
7.30
7.30
7.29
7.28
7.26
7.04
7.02
1.33
0.00
1H NMR (500 MHz, CDCl3)
CH3
H3C
H3C
O
N
N
3ad
2.00
1.00
1.00
4.00
2.00
1.00
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

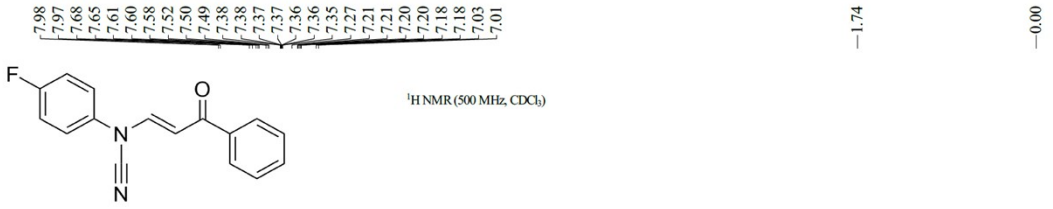

188.36
150.96
141.65
137.71
135.41
133.10
128.71
128.28
127.16
119.65
108.74
108.15
77.37
77.11
76.86
34.68
31.25
13C NMR (126 MHz, CDCl3)
CH3
H3C
H3C
O
N
N
3ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.01
7.99
7.82
7.79
7.71
7.69
7.61
7.60
7.59
7.57
7.52
7.51
7.49
7.48
7.47
7.45
7.44
7.43
7.41
7.39
7.38
7.25
7.10
7.07
1.67
0.00
1H NMR (500 MHz, CDCl3)
O
N
N
3ae
2.00
1.00
2.00
3.00
7.00
1.00
10.0 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
f1 (ppm)

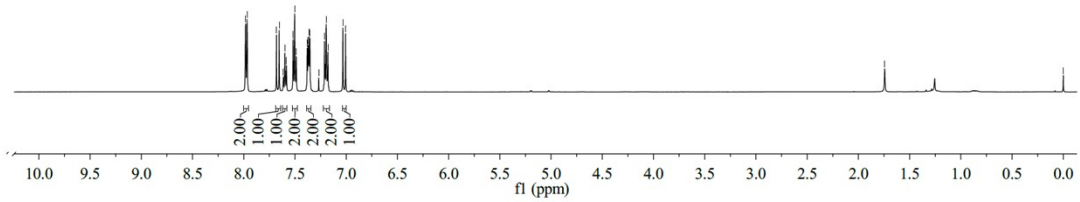

188.33
141.05
140.58
139.30
137.58
136.99
133.25
129.04
128.82
128.77
128.32
128.01
127.05
120.00
108.58
108.52
77.32
77.07
76.81
13C NMR (126 MHz, CDCl3)
O
N
N
3ae
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.89
7.87
7.59
7.57
7.50
7.48
7.47
7.41
7.39
7.38
7.21
7.19
7.18
7.15
7.11
7.09
7.03
7.02
7.00
6.99
6.97
6.91
6.88
0.00
^{1}H NMR (500 MHz, CDCl$_3$)
3af
2.00
1.00
1.00
2.00
4.00
2.00
8.00
1.00
f1 (ppm)


187.36
146.66
145.98
141.25
136.63
132.07
130.35
128.53
127.68
127.23
123.83
122.82
122.63
120.68
107.96
106.77
76.30
76.05
75.79
^{13}C NMR (126 MHz, CDCl$_3$)
3af
f1 (ppm)

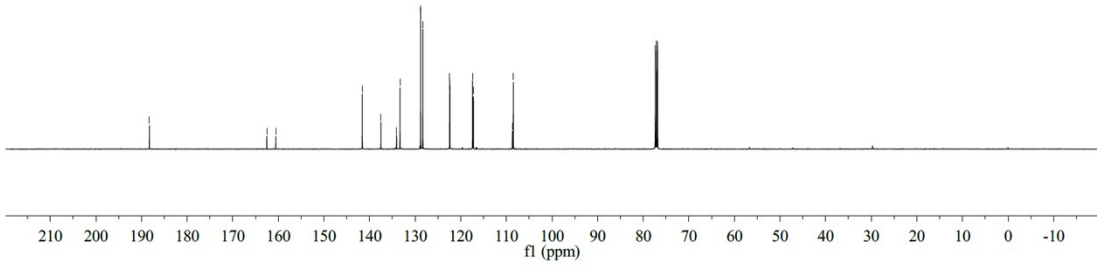

7.98
7.97
7.68
7.65
7.61
7.60
7.58
7.52
7.50
7.49
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.27
7.21
7.21
7.20
7.20
7.18
7.18
7.03
7.01
1.74
0.00
F
O
N
N
1H NMR (500 MHz, CDCl3)

3ag

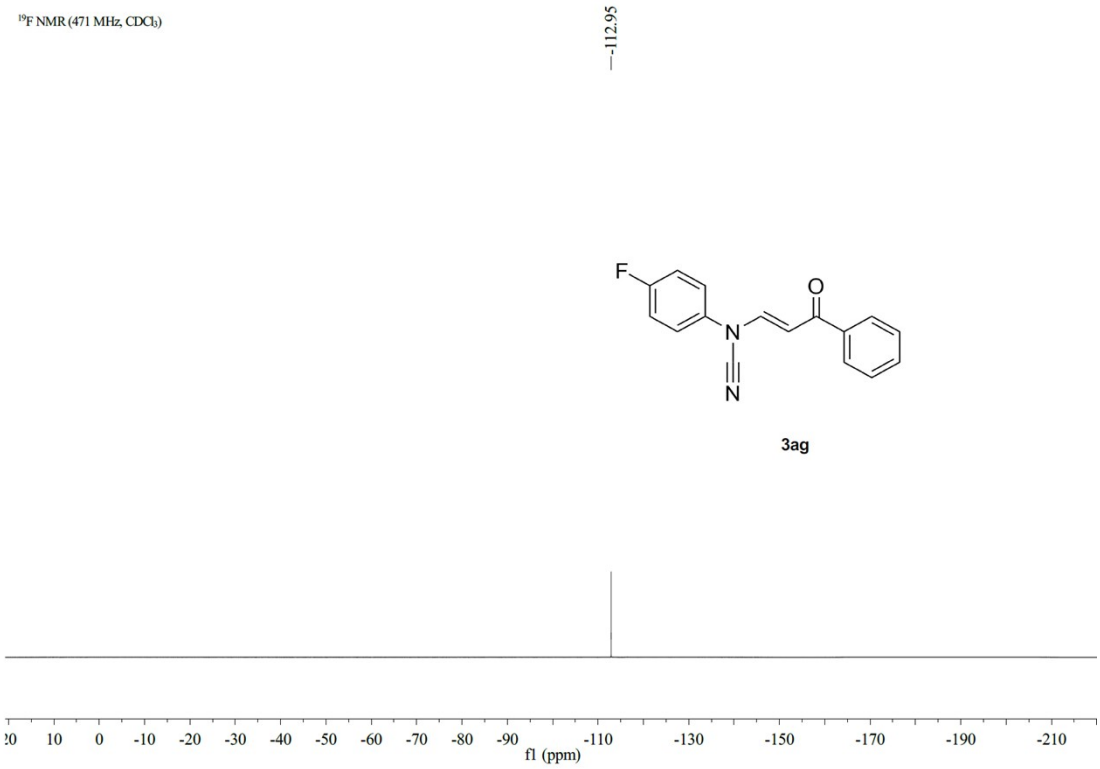

2.00
1.00
1.00
2.00
2.00
2.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

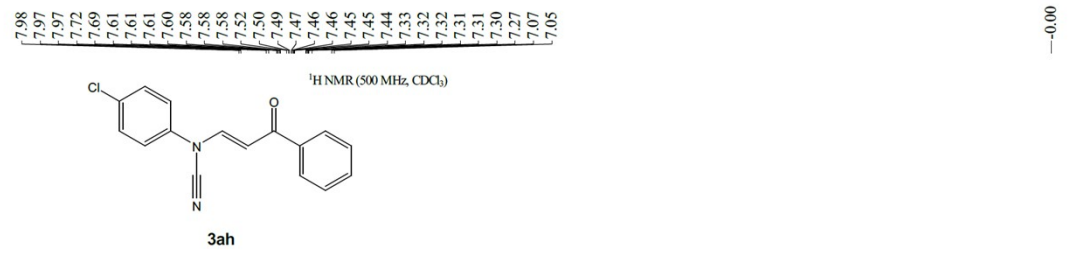

188.27
162.51
160.53
141.59
137.51
134.09
133.31
128.80
128.31
122.44
122.37
117.41
117.23
108.66
108.47
77.34
77.09
76.83
F
O
N
N
13C NMR (126 MHz, CDCl3)

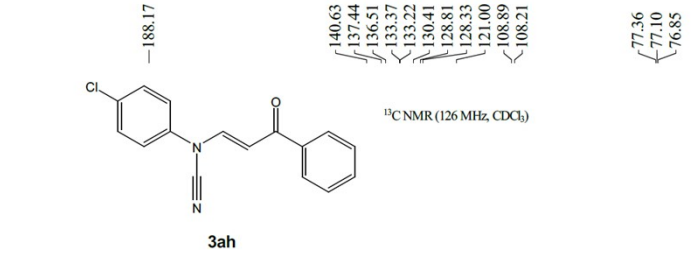
3ag


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

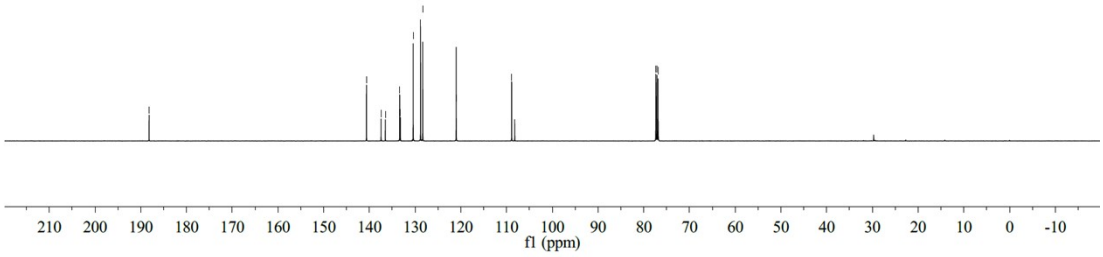
^{19}F NMR (471 MHz, $CDCl_3$)

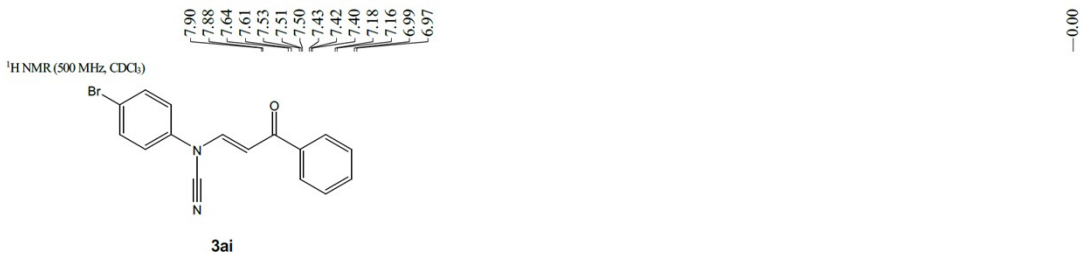




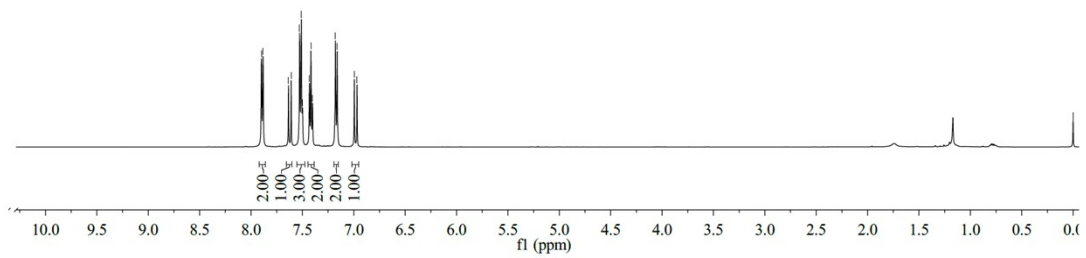

188.17
140.63
137.44
136.51
133.37
133.22
130.41
128.81
128.33
121.00
108.89
108.21
77.36
77.10
76.85
Cl
O
N
N
^{13}C NMR (126 MHz, CDCl$_3$)

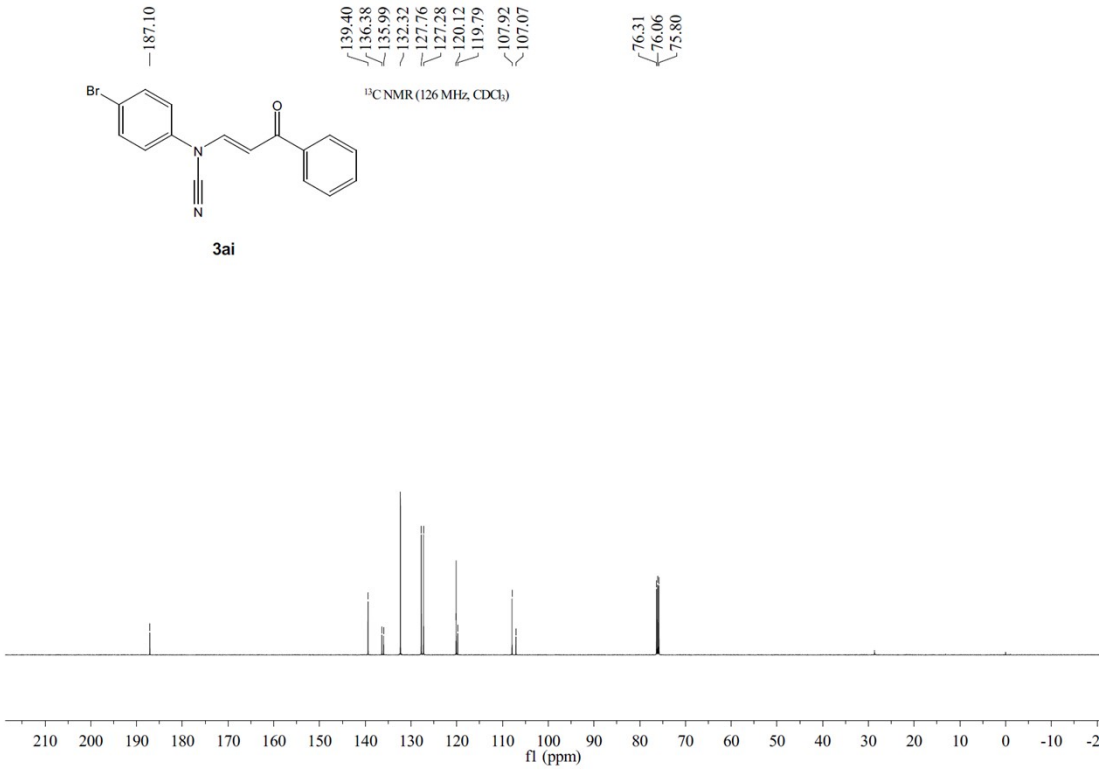
3ah

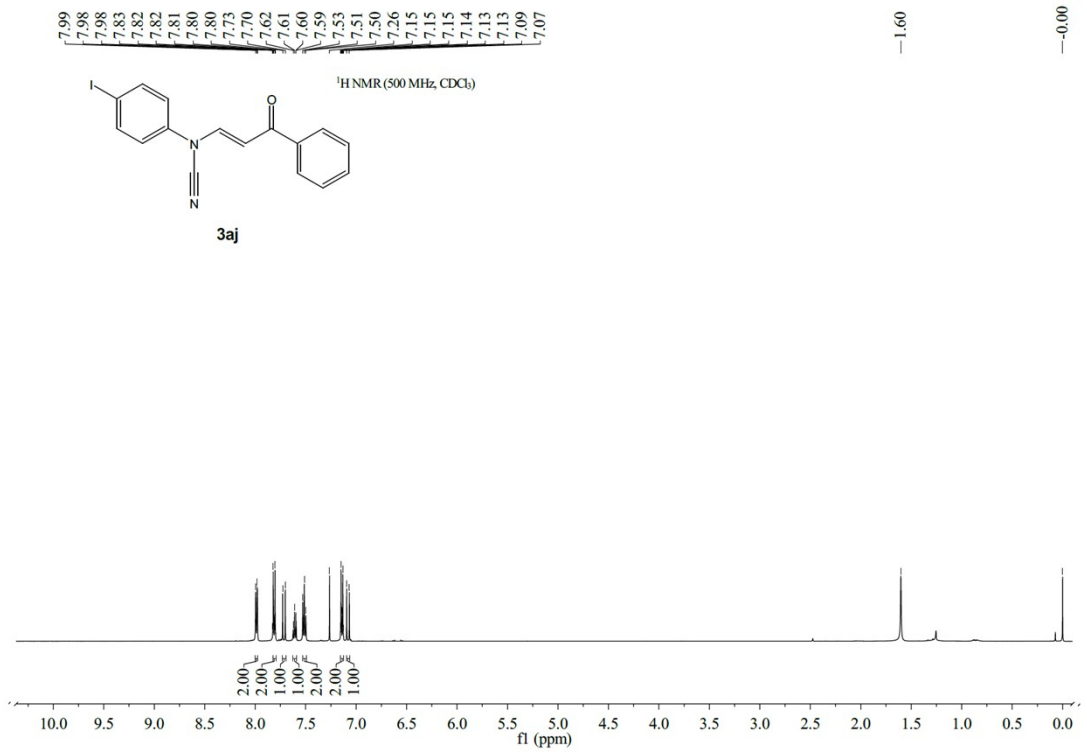

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

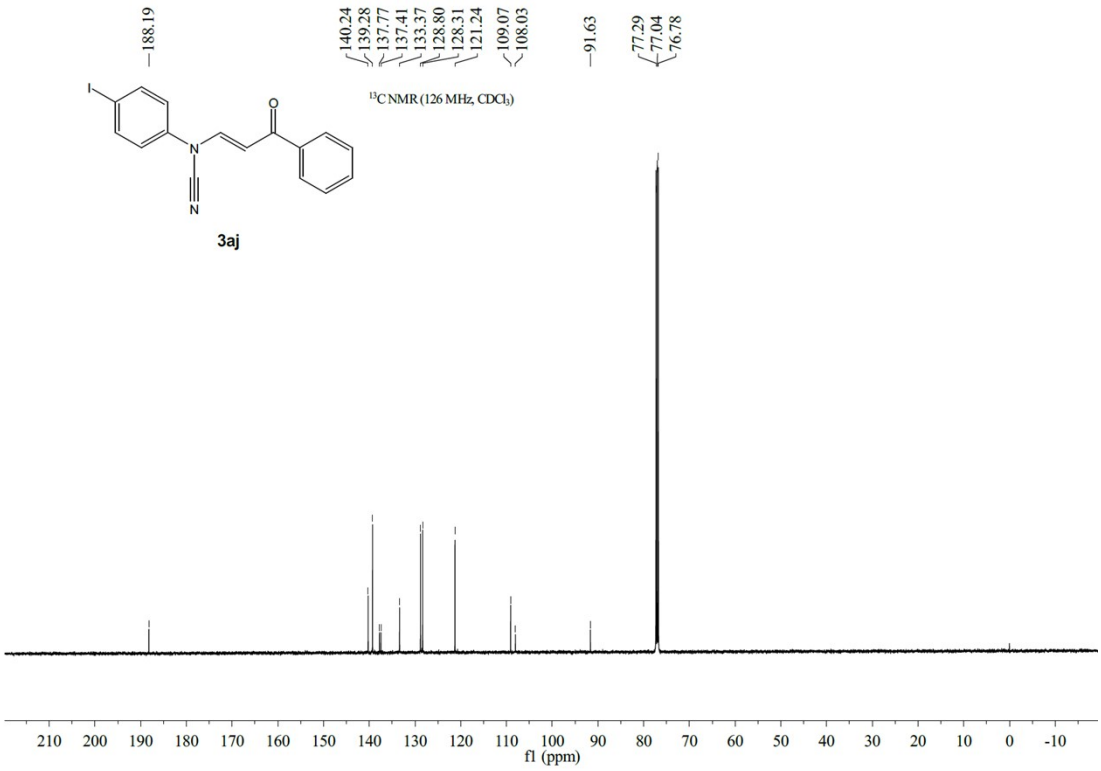

7.90
7.88
7.64
7.61
7.53
7.51
7.50
7.43
7.42
7.40
7.18
7.16
6.99
6.97
0.00
^{1}H NMR (500 MHz, CDCl$_3$)
Br
O
N
N

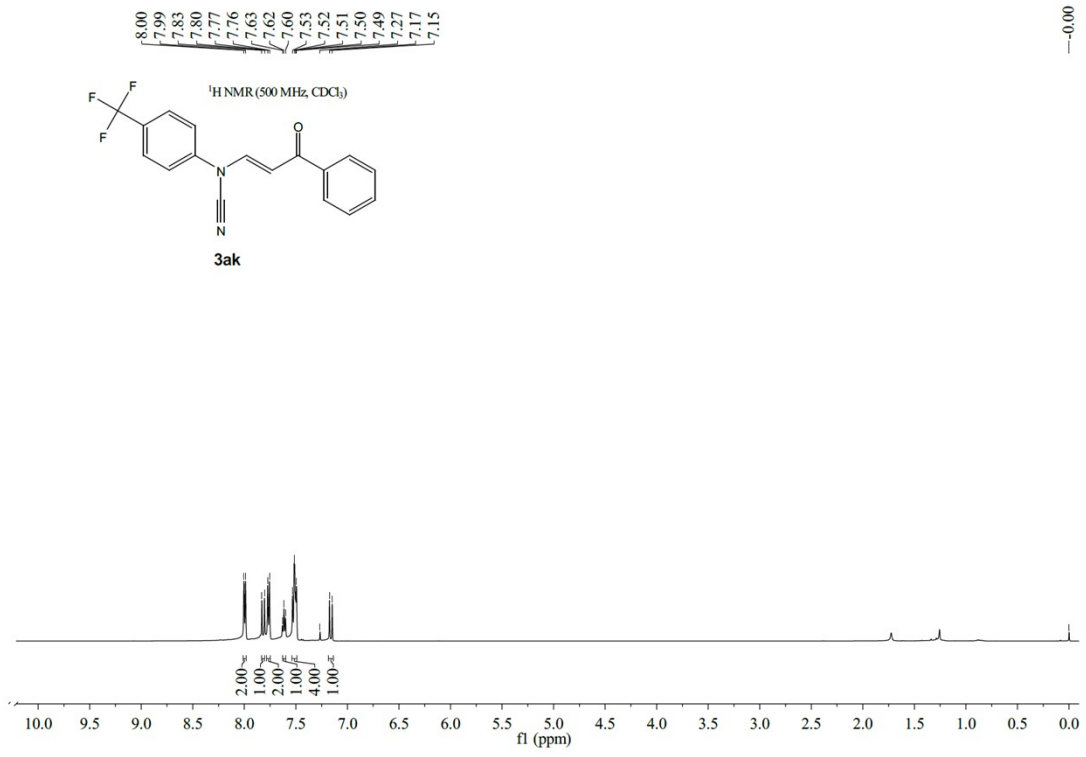
3ai

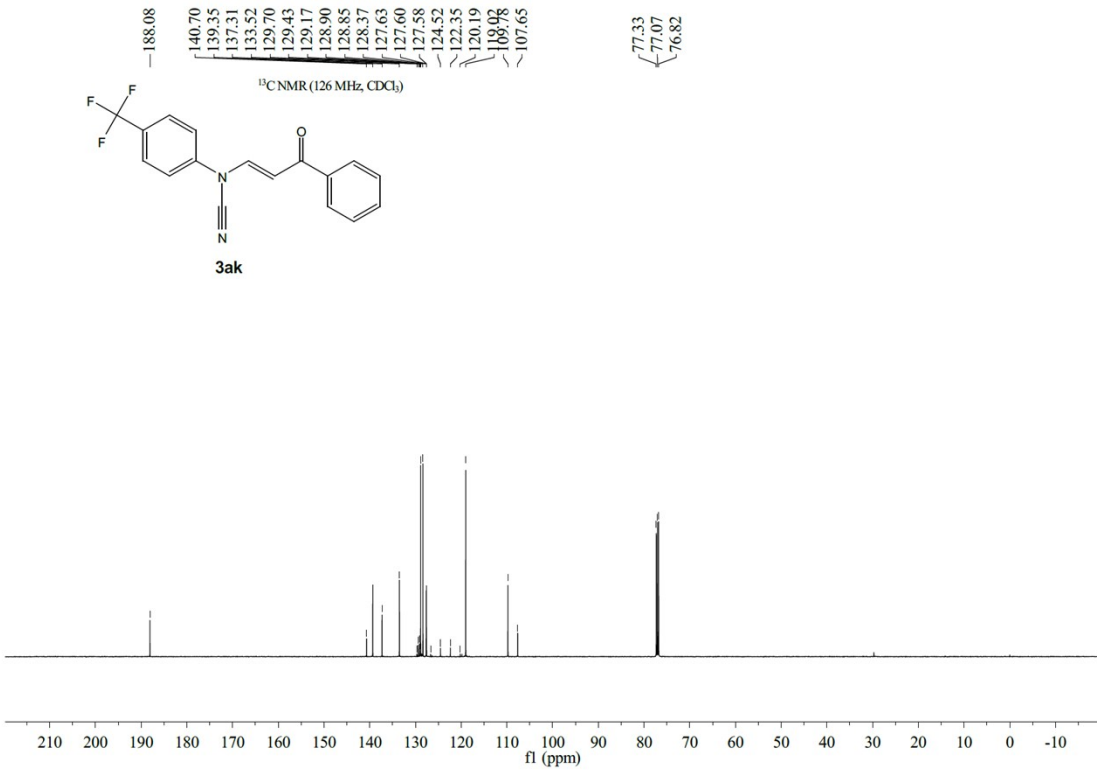

2.00
1.00
3.00
2.00
2.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

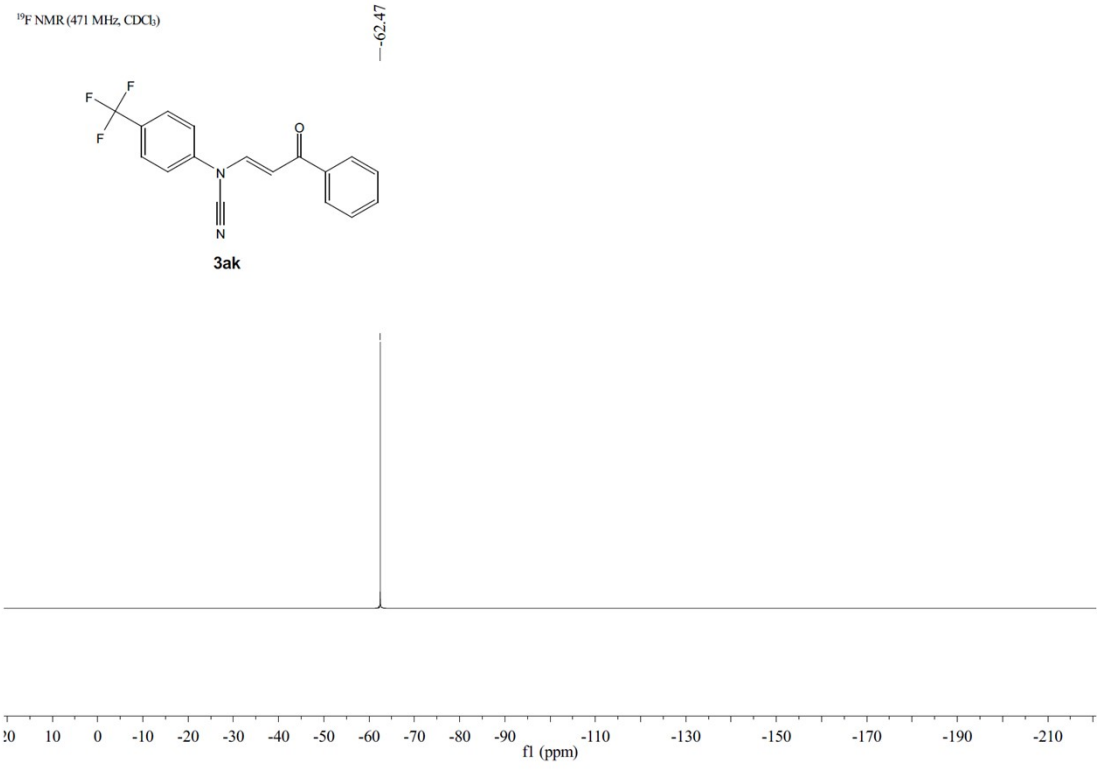

187.10
139.40
136.38
135.99
132.32
127.76
127.28
120.12
119.79
107.92
107.07
76.31
76.06
75.80
Br
O
N
N
13C NMR (126 MHz, CDCl3)
3ai
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

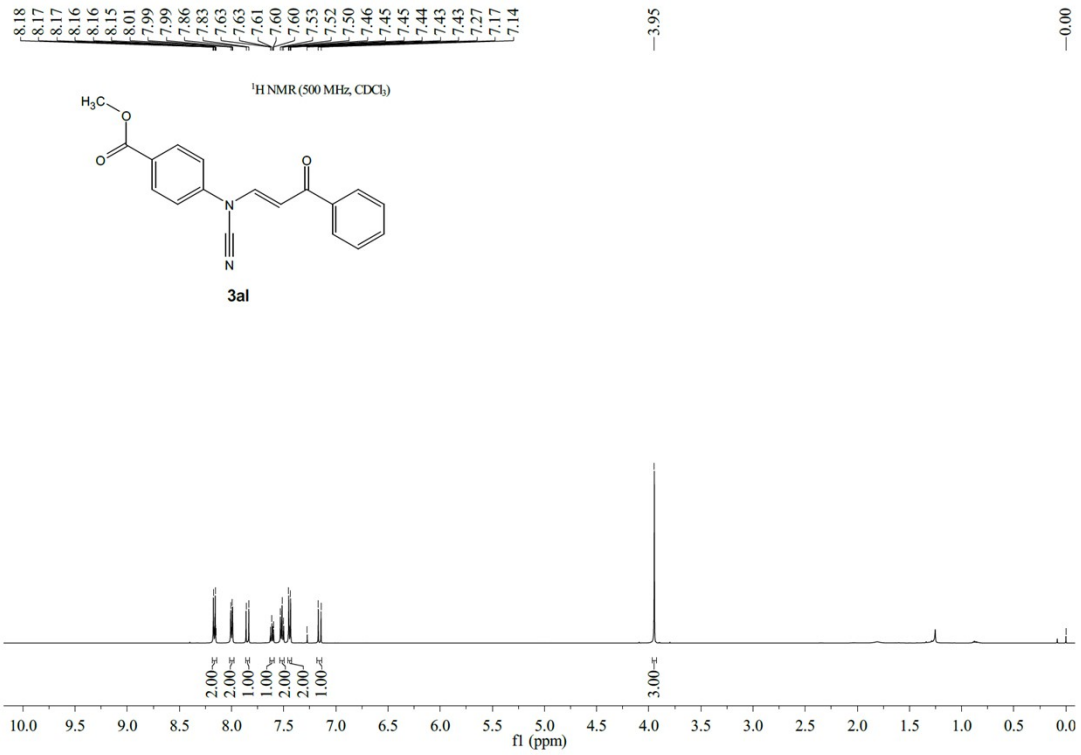

7.99
7.98
7.98
7.83
7.82
7.82
7.81
7.80
7.80
7.73
7.70
7.62
7.61
7.60
7.59
7.53
7.51
7.50
7.26
7.15
7.15
7.15
7.14
7.13
7.13
7.09
7.07
1.60
0.00
I
O
N
N
1H NMR (500 MHz, CDCl3)
3aj
2.00
2.00
1.00
1.00
2.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

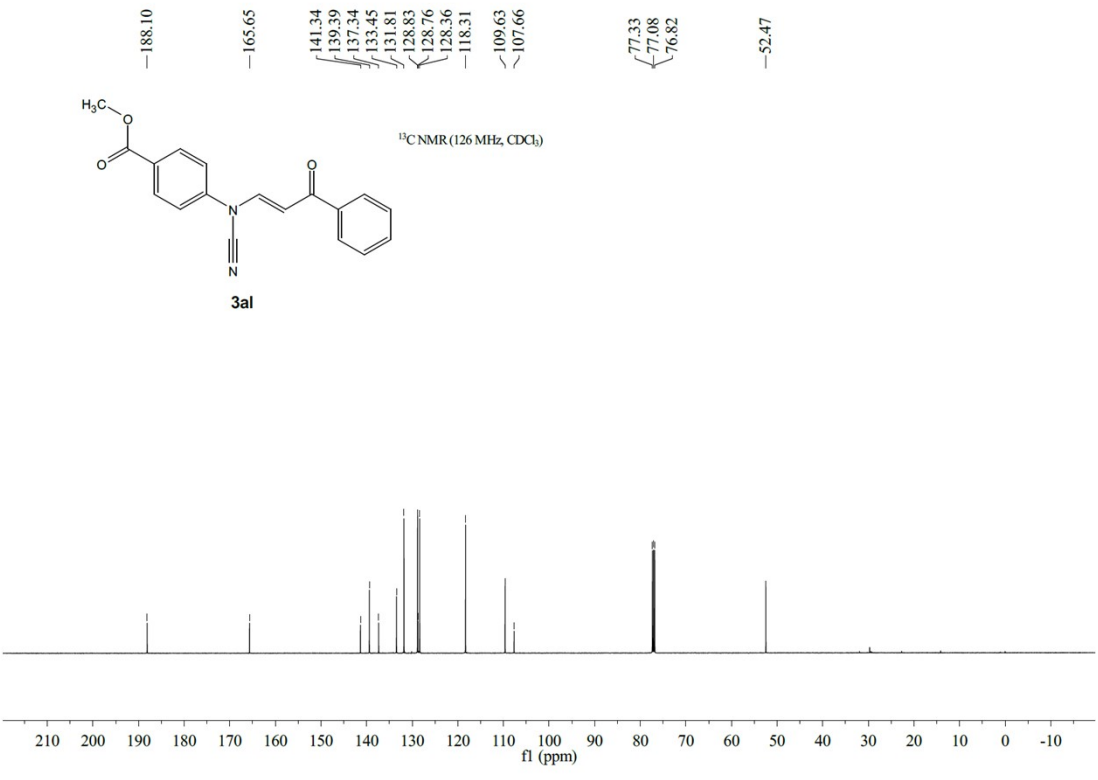

188.19
140.24
139.28
137.77
137.41
133.37
128.80
128.31
121.24
109.07
108.03
91.63
77.29
77.04
76.78
13C NMR (126 MHz, CDCl3)
I
O
N
N
3aj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

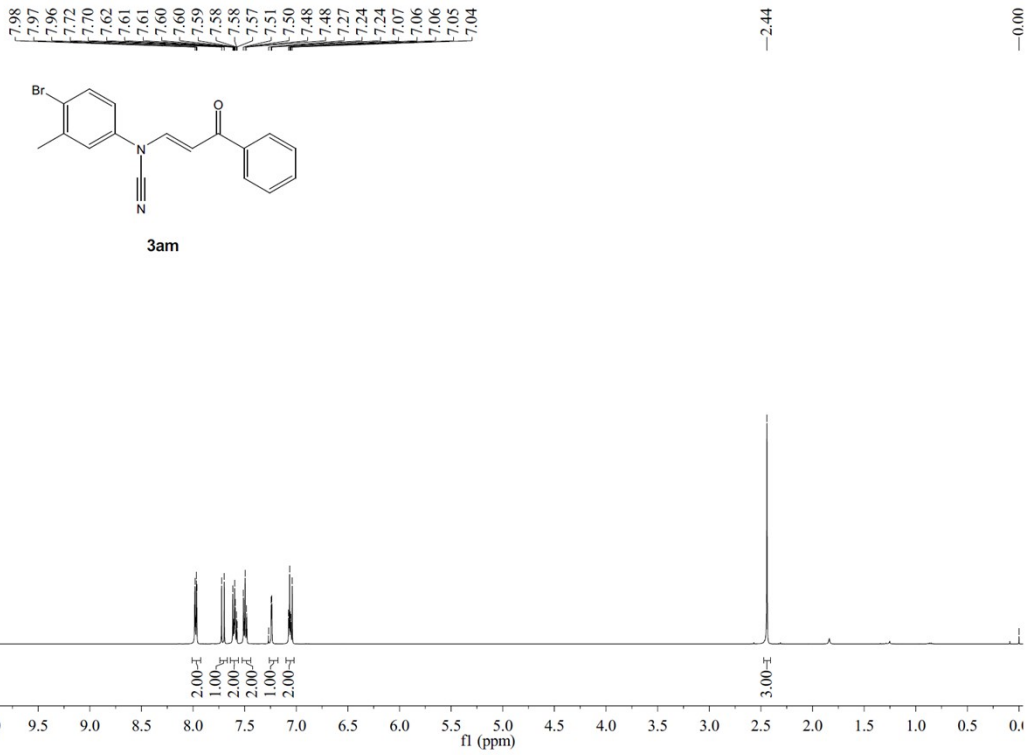

8.00
7.99
7.83
7.80
7.77
7.76
7.63
7.62
7.60
7.53
7.52
7.51
7.50
7.49
7.27
7.17
7.15
0.00
1H NMR (500 MHz, CDCl3)
F
F
F
O
N
N
3ak
2.00
1.00
2.00
1.00
4.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


188.08
140.70
139.35
137.31
133.52
129.70
129.43
129.17
128.90
128.85
128.37
127.63
127.60
127.58
124.52
122.35
120.19
109.98
109.78
107.65
77.33
77.07
76.82
13C NMR (126 MHz, CDCl3)
F
F
F
O
N
N
3ak
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

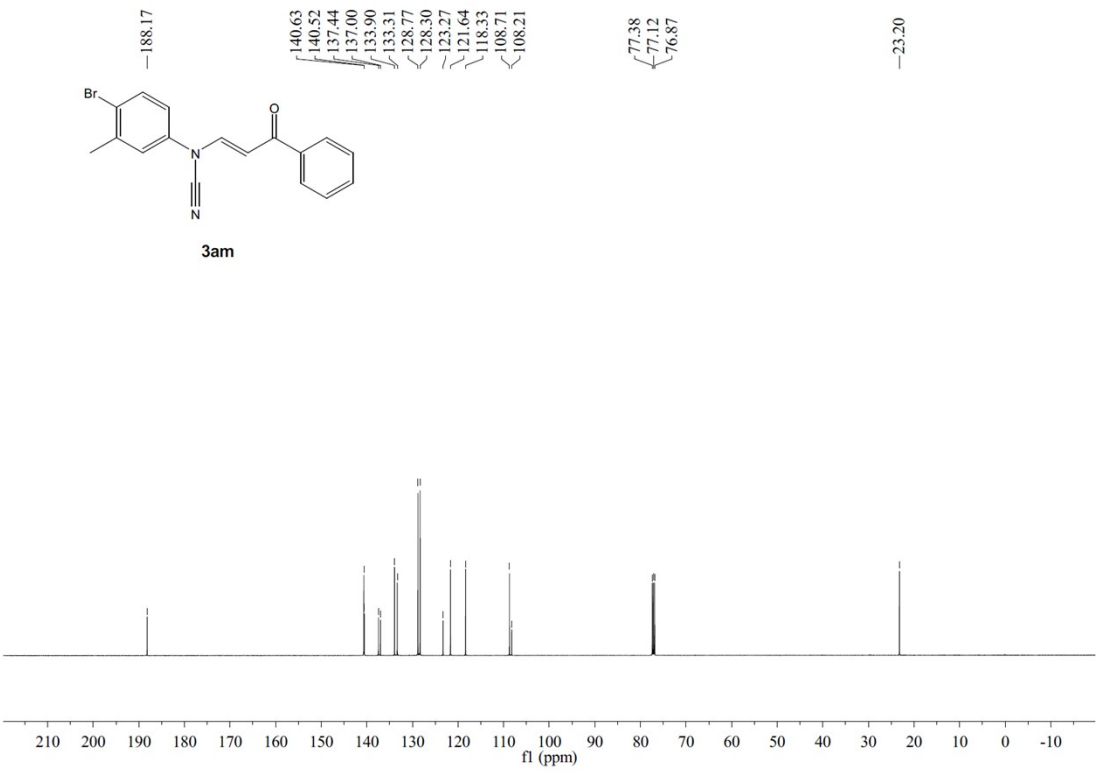

19F NMR (471 MHz, CDCl3)
-62.47
F
F
F
O
N
N
3ak
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)


8.18
8.17
8.17
8.16
8.16
8.15
8.01
7.99
7.99
7.86
7.83
7.63
7.63
7.61
7.60
7.60
7.53
7.52
7.50
7.46
7.45
7.45
7.44
7.43
7.43
7.27
7.17
7.14
3.95
0.00
1H NMR (500 MHz, CDCl3)
3al
2.00
2.00
1.00
1.00
2.00
2.00
1.00
3.00
10.0 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
f1 (ppm)


188.10
165.65
141.34
139.39
137.34
133.45
131.81
128.83
128.76
128.36
118.31
109.63
107.66
77.33
77.08
76.82
52.47
13C NMR (126 MHz, CDCl3)
3al
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

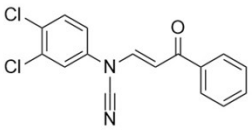

7.98
7.97
7.96
7.72
7.70
7.62
7.61
7.61
7.60
7.60
7.59
7.58
7.58
7.57
7.51
7.50
7.48
7.48
7.27
7.24
7.24
7.07
7.06
7.06
7.05
7.04
2.44
0.00
Br
O
N
N
2.00
1.00
2.00
2.00
1.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

3am

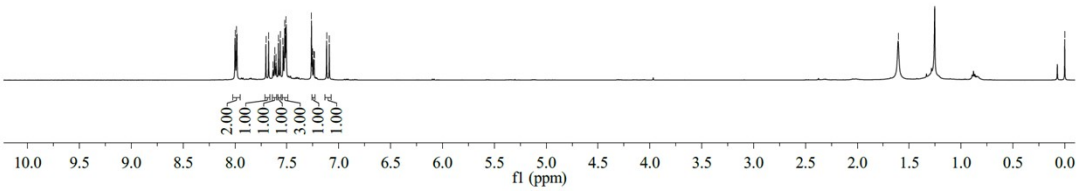

188.17
140.63
140.52
137.44
137.00
133.90
133.31
128.77
128.30
123.27
121.64
118.33
108.71
108.21
77.38
77.12
76.87
23.20
Br
O
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

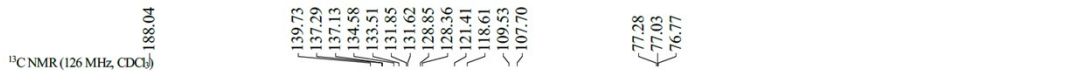
3am

^{1}H NMR (500 MHz, $CDCl_3$)

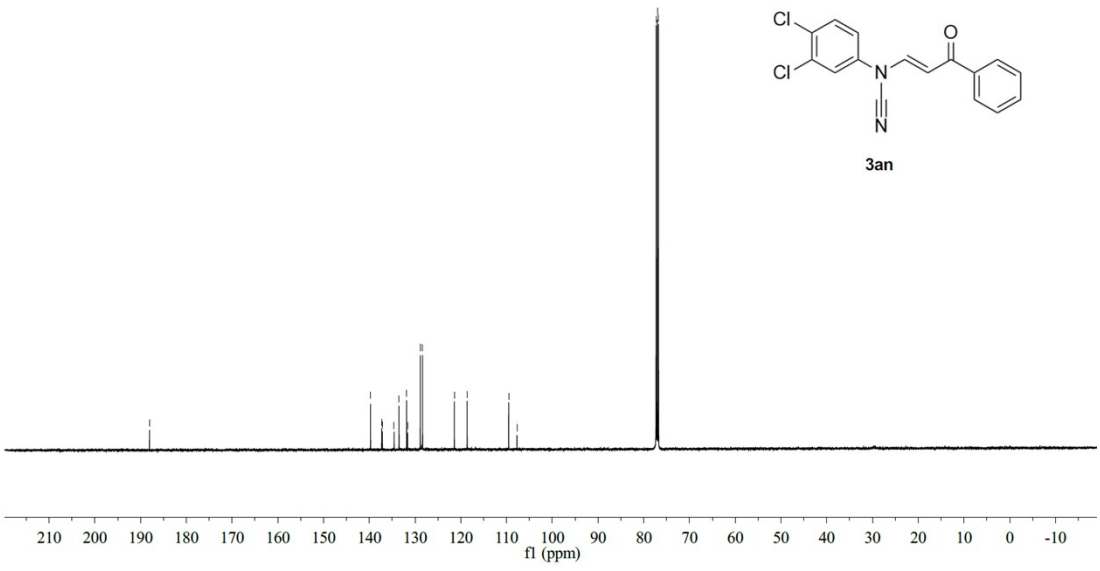


3an

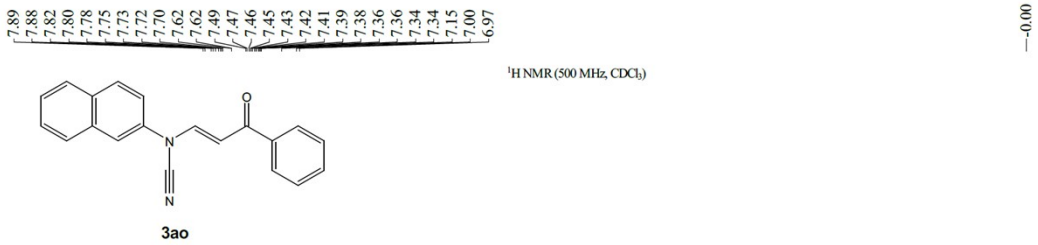


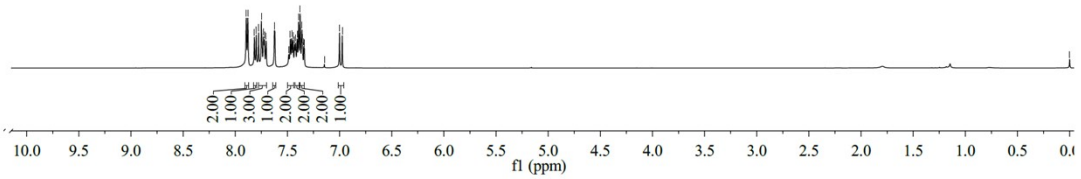


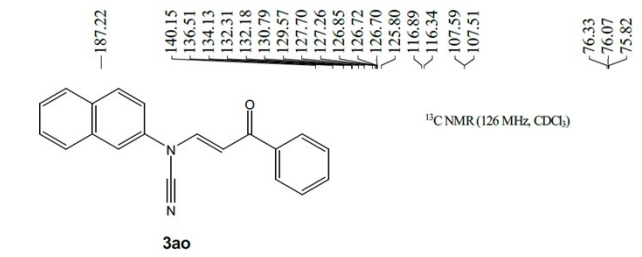
^{13}C NMR (126 MHz, $CDCl_3$)

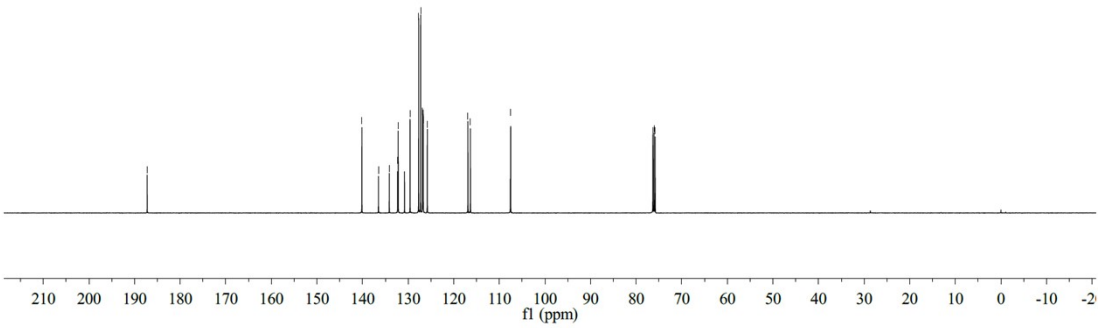


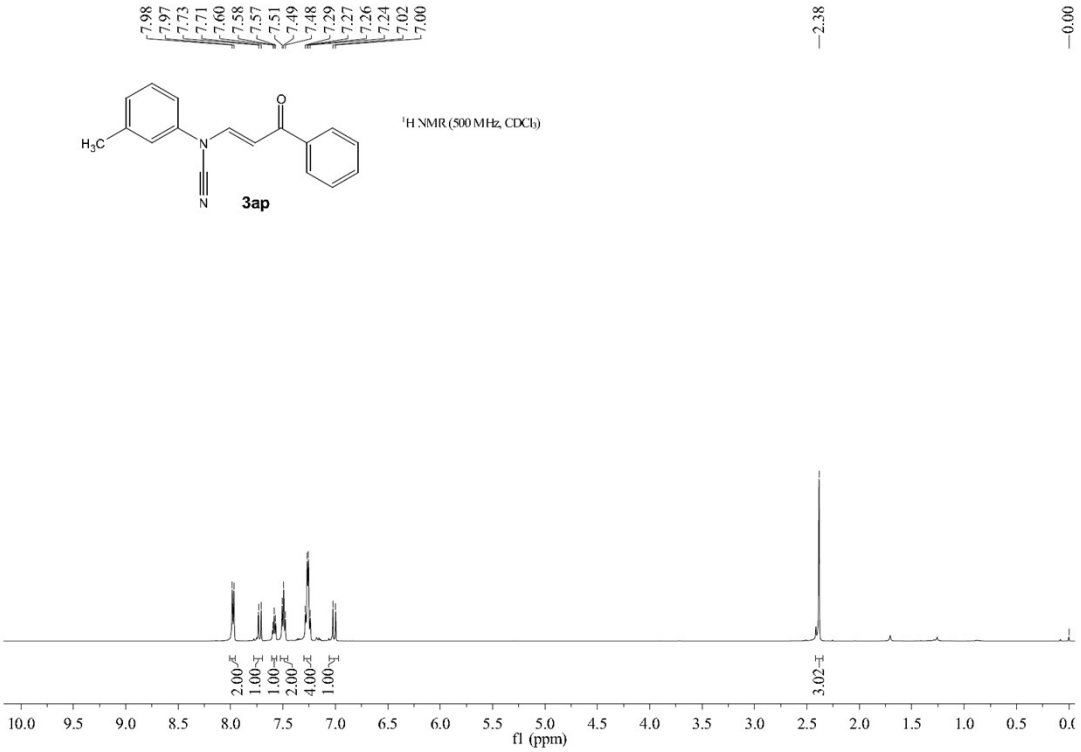
3an

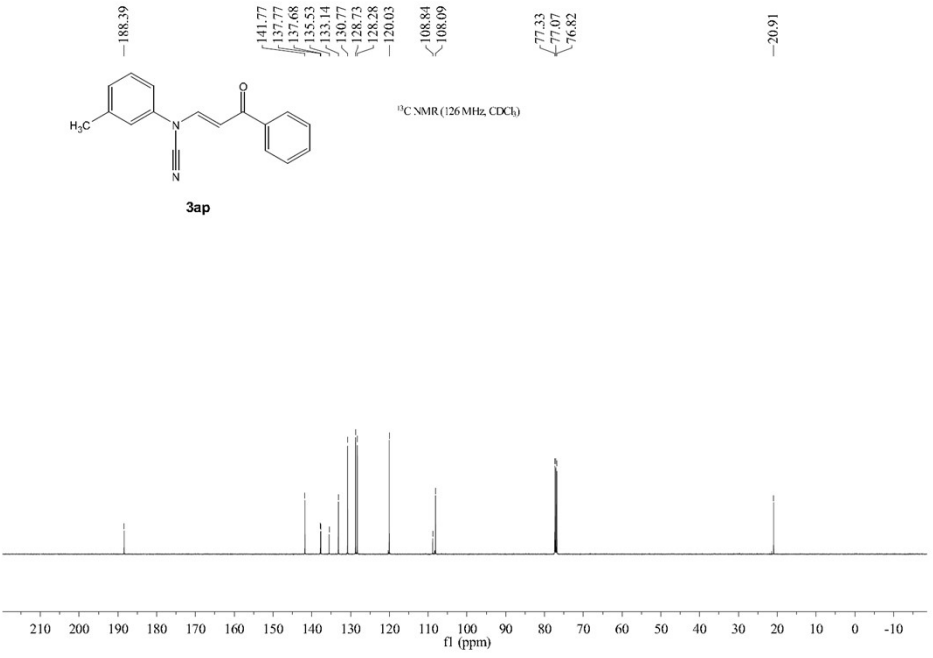

7.89
7.88
7.82
7.80
7.78
7.75
7.73
7.72
7.70
7.62
7.62
7.49
7.47
7.46
7.45
7.43
7.42
7.41
7.39
7.38
7.36
7.36
7.34
7.34
7.15
7.00
6.97
-0.00
^{1}H NMR (500 MHz, CDCl$_3$)
O
N
N
3ao

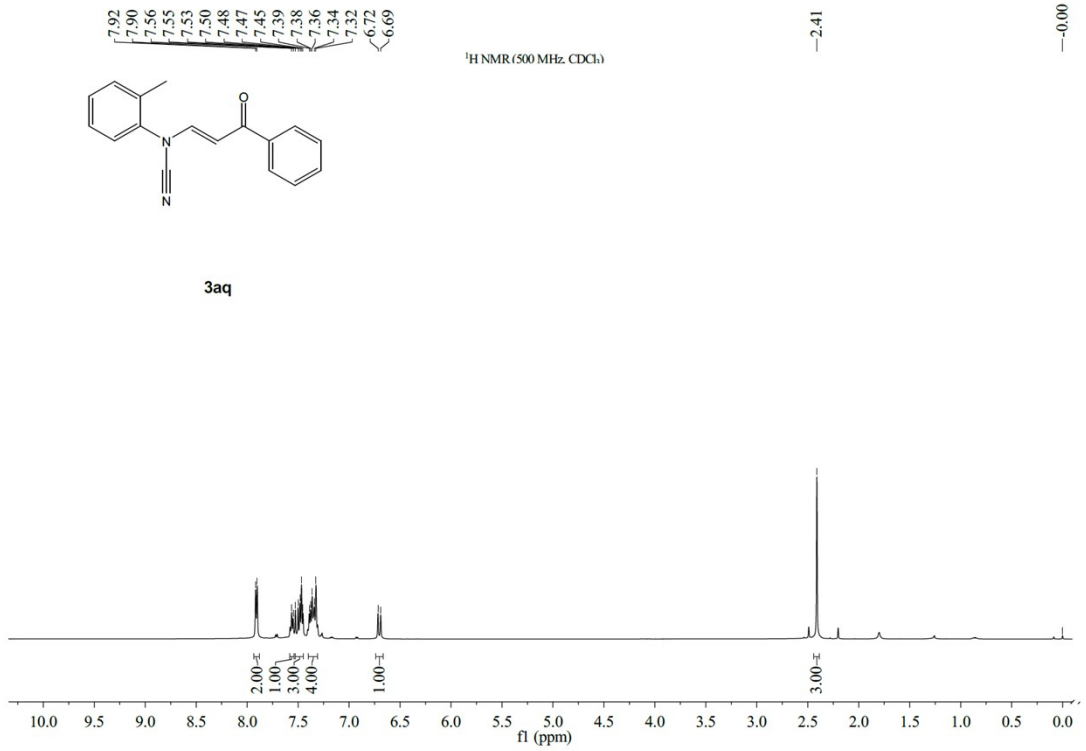

2.00
1.00
3.00
1.00
2.00
2.00
2.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

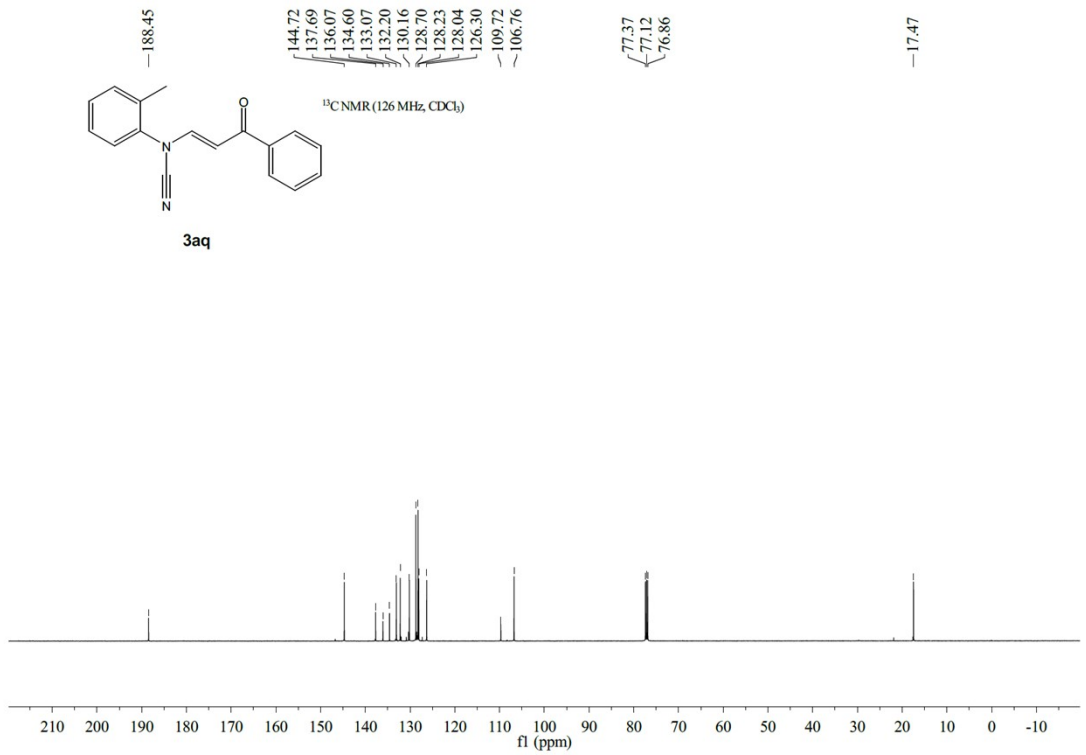

187.22
140.15
136.51
134.13
132.31
132.18
130.79
129.57
127.70
127.26
126.85
126.72
126.70
125.80
116.89
116.34
107.59
107.51
76.33
76.07
75.82
^{13}C NMR (126 MHz, CDCl$_3$)
O
N
N
3ao

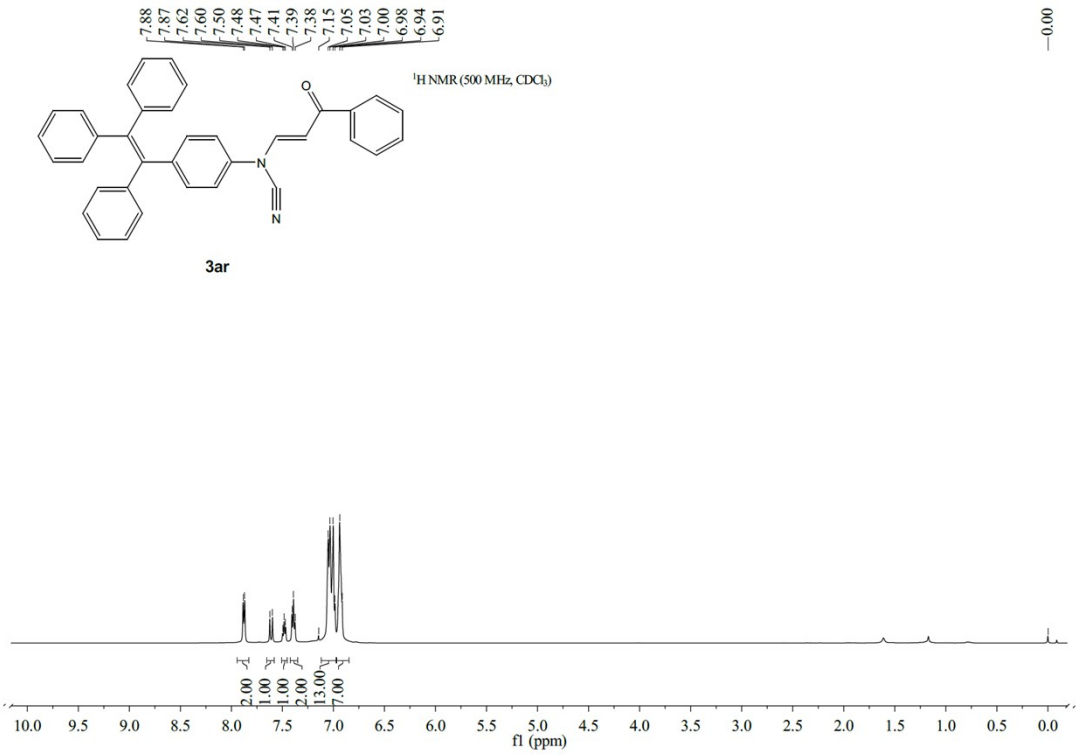

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

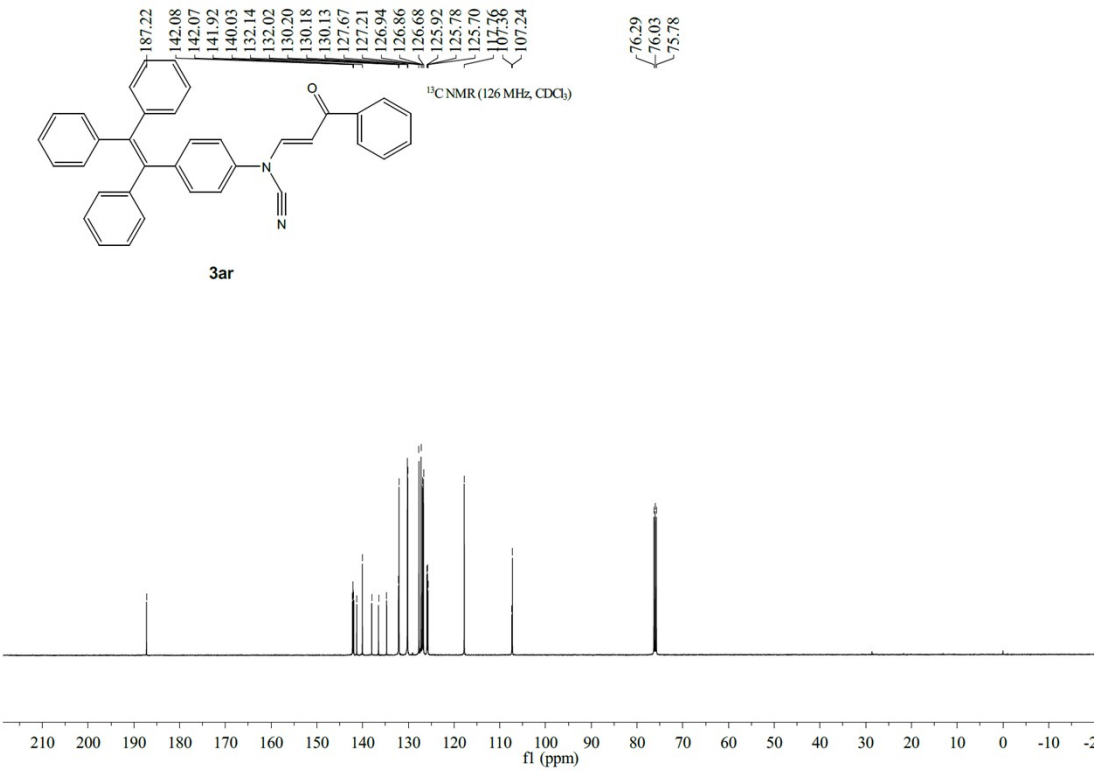

7.98
7.97
7.73
7.71
7.60
7.58
7.57
7.51
7.49
7.48
7.29
7.27
7.26
7.24
7.02
7.00
2.38
0.00
O
H3C
N
N
3ap
1H NMR (500 MHz, CDCl3)
2.00
1.00
1.00
2.00
4.00
1.00
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

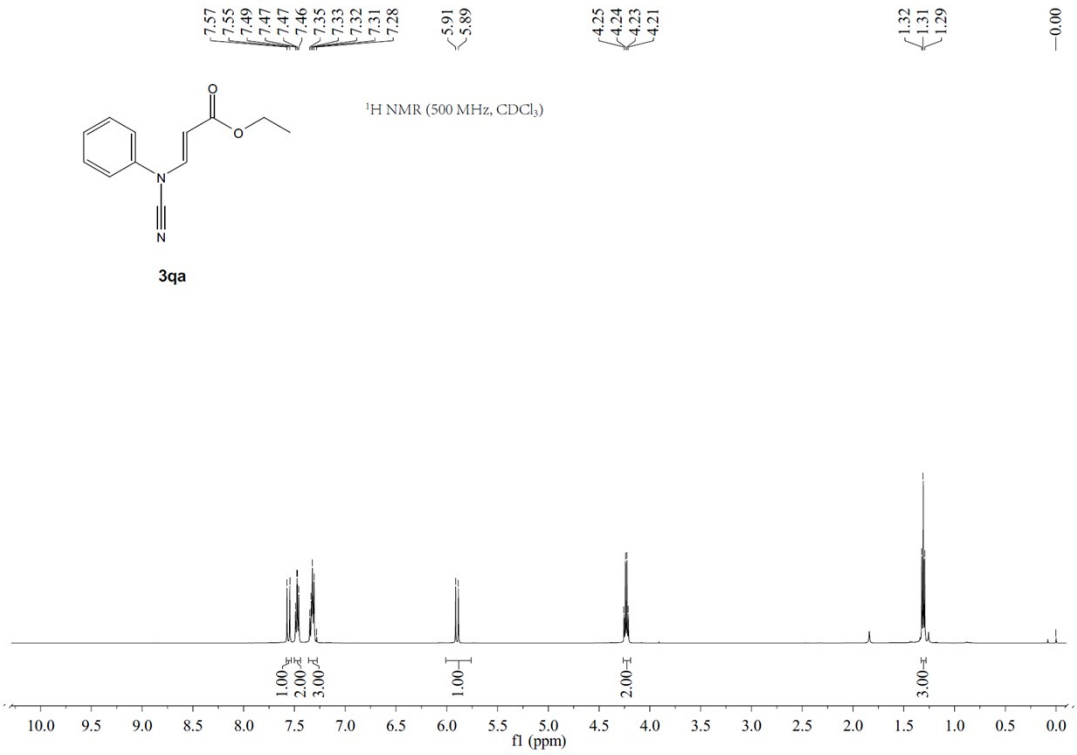

188.39
141.77
137.77
137.68
135.53
133.14
130.77
128.73
128.28
120.03
108.84
108.09
77.33
77.07
76.82
20.91
O
H3C
N
N
3ap
13C NMR (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

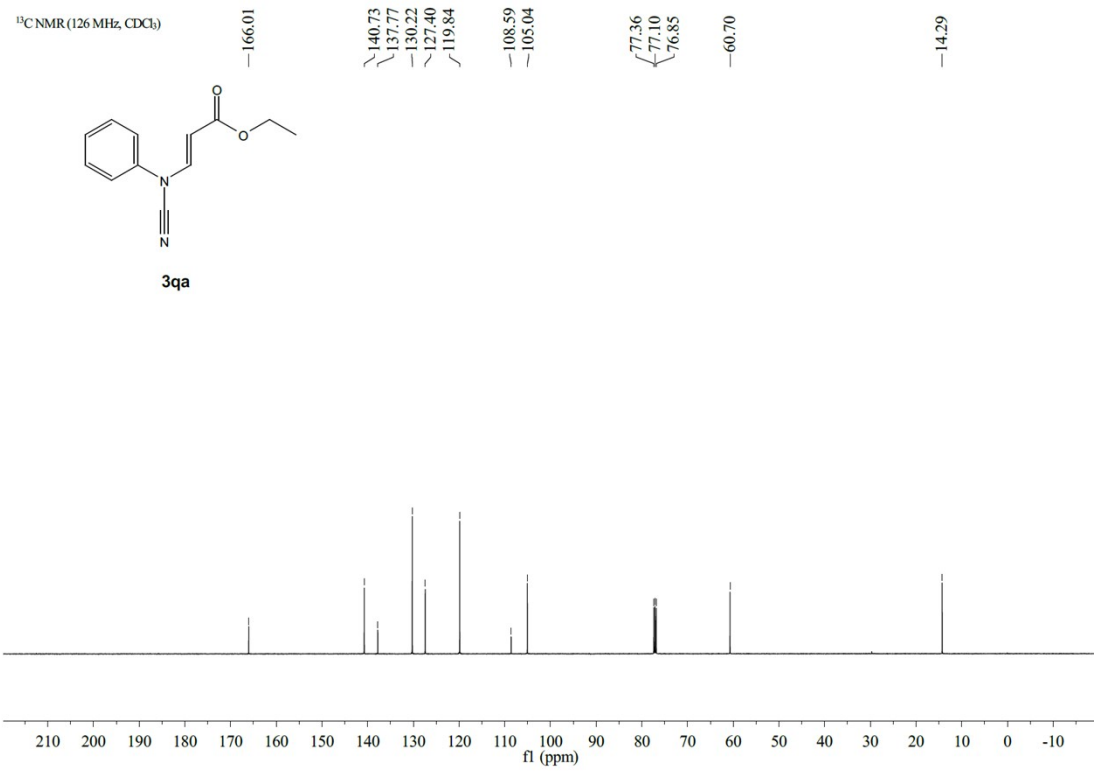

7.92
7.90
7.56
7.55
7.53
7.50
7.48
7.47
7.45
7.39
7.38
7.36
7.34
7.32
6.72
6.69
2.41
0.00
^{1}H NMR (500 MHz, CDCl$_3$)
O
N
N
3aq
2.00
1.00
3.00
4.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


188.45
144.72
137.69
136.07
134.60
133.07
132.20
130.16
128.70
128.23
128.04
126.30
109.72
106.76
77.37
77.12
76.86
17.47
^{13}C NMR (126 MHz, CDCl$_3$)
O
N
N
3aq
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

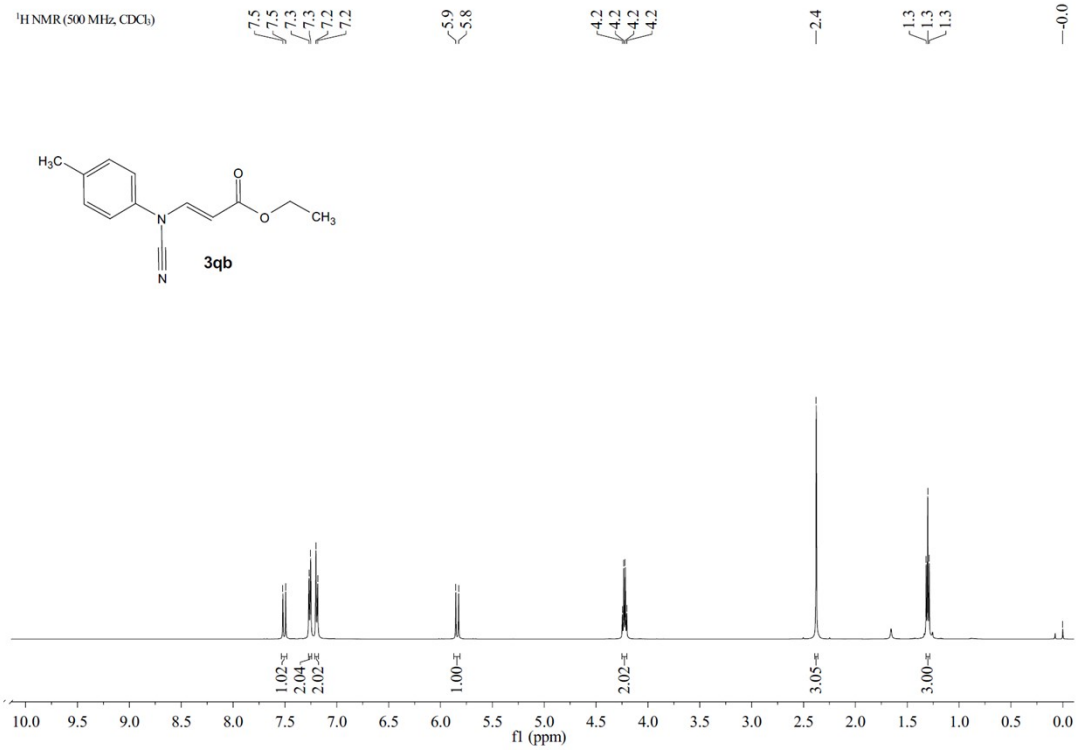

7.88
7.87
7.62
7.60
7.50
7.48
7.47
7.41
7.39
7.38
7.15
7.05
7.03
7.00
6.98
6.94
6.91
0.00
^{1}H NMR (500 MHz, CDCl$_3$)
O
N
N
3ar
2.00
1.00
1.00
2.00
13.00
7.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


187.22
142.08
142.07
141.92
140.03
132.14
132.02
130.20
130.18
130.13
127.67
127.21
126.94
126.86
126.68
125.92
125.78
125.70
107.36
107.24
76.29
76.03
75.78
^{13}C NMR (126 MHz, CDCl$_3$)
O
N
N
3ar
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

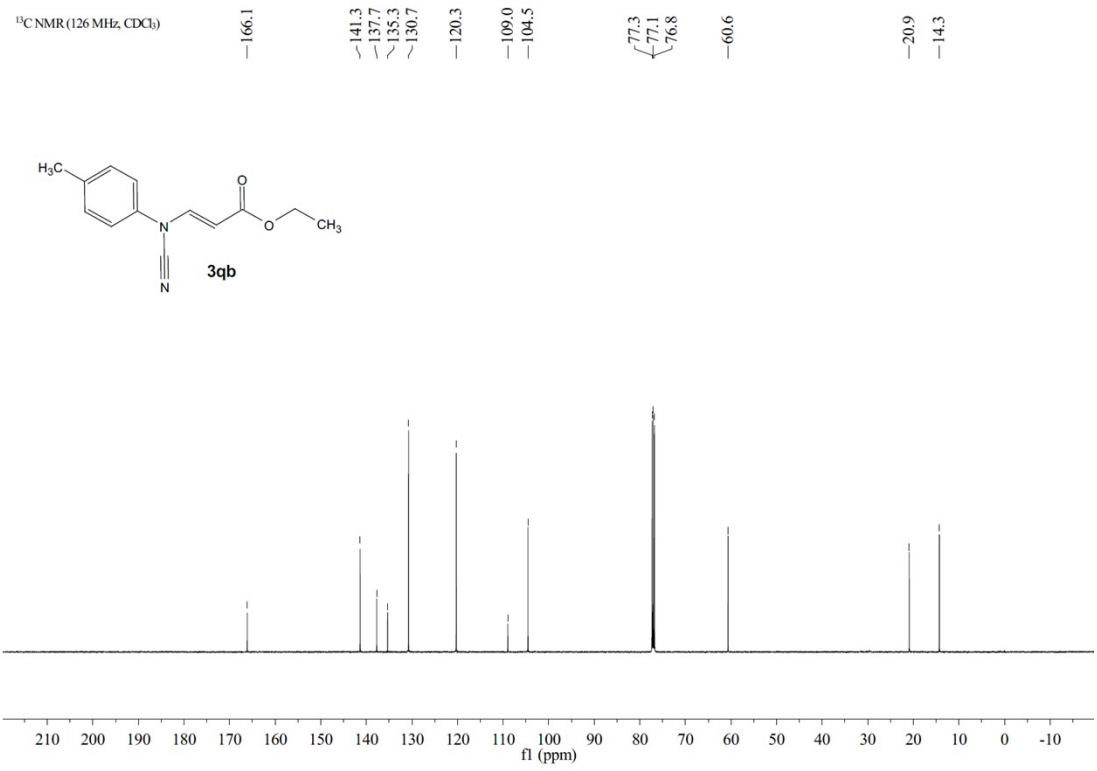

7.57
7.55
7.49
7.47
7.47
7.46
7.35
7.33
7.32
7.31
7.28
5.91
5.89
4.25
4.24
4.23
4.21
1.32
1.31
1.29
0.00
1H NMR (500 MHz, CDCl3)
O
O
N
N
3qa
1.00
2.00
3.00
1.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

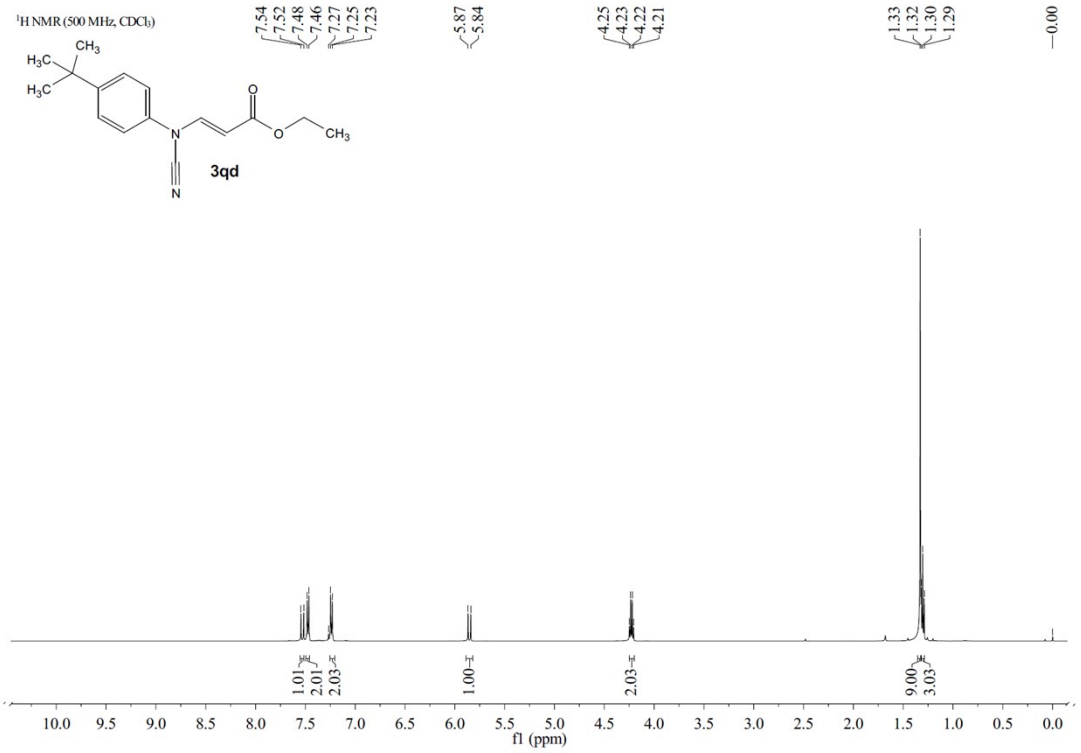

13C NMR (126 MHz, CDCl3)
166.01
140.73
137.77
130.22
127.40
119.84
108.59
105.04
77.36
77.10
76.85
60.70
14.29
O
O
N
N
3qa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

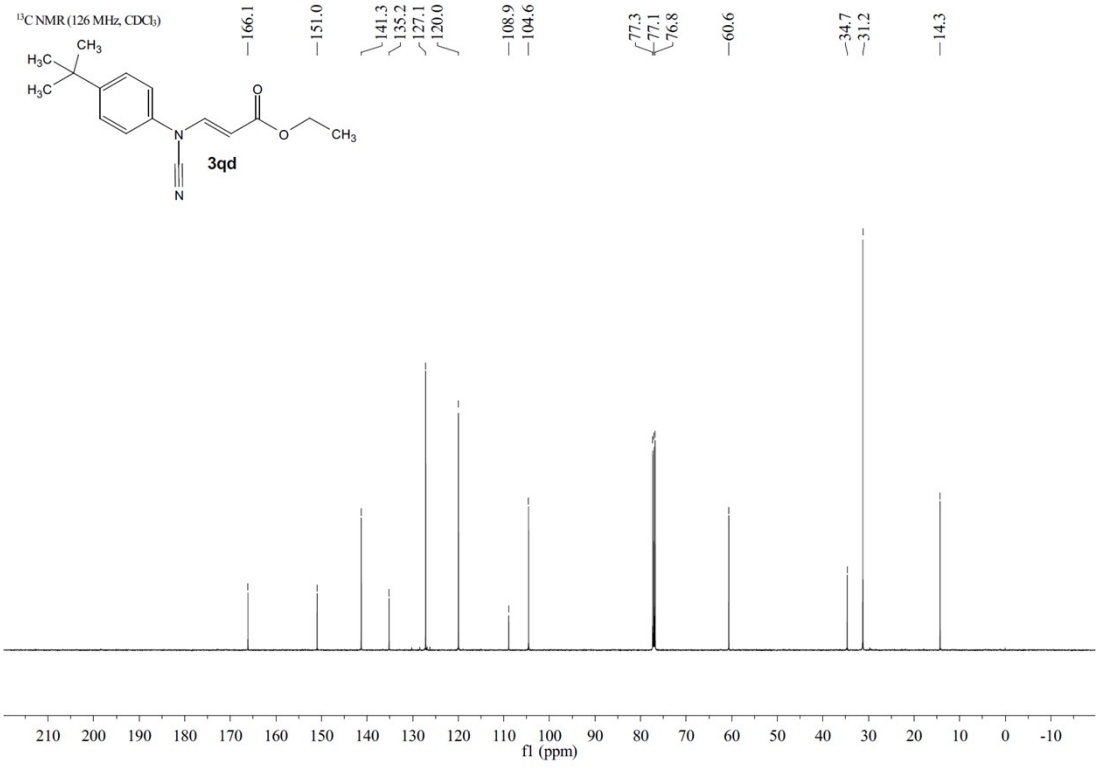
^{1}H NMR (500 MHz, CDCl$_3$)



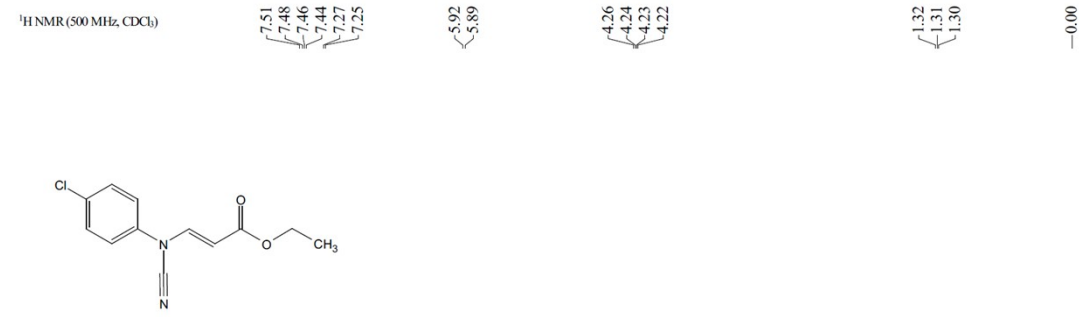
^{13}C NMR (126 MHz, CDCl$_3$)



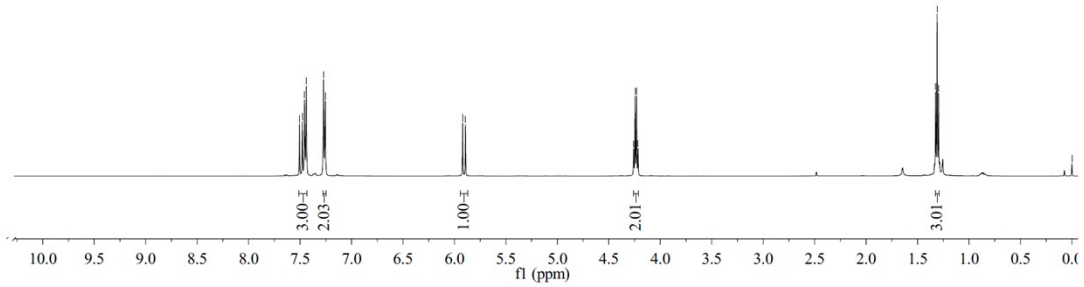

^{1}H NMR (500 MHz, CDCl$_3$)
7.54
7.52
7.48
7.46
7.27
7.25
7.23
5.87
5.84
4.25
4.23
4.22
4.21
1.33
1.32
1.30
1.29
0.00
3qd
1.01
2.01
2.03
1.00
2.03
9.00
3.03
f1 (ppm)


^{13}C NMR (126 MHz, CDCl$_3$)
166.1
151.0
141.3
135.2
127.1
120.0
108.9
104.6
77.3
77.1
76.8
60.6
34.7
31.2
14.3
3qd
f1 (ppm)

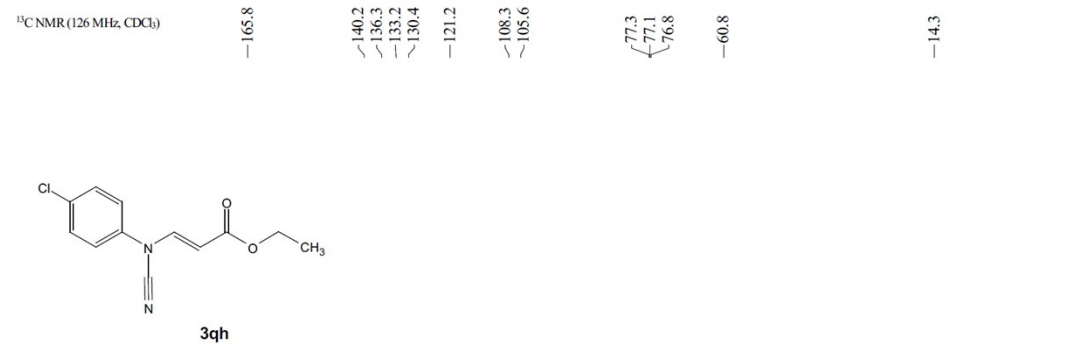
^{1}H NMR (500 MHz, $CDCl_3$)



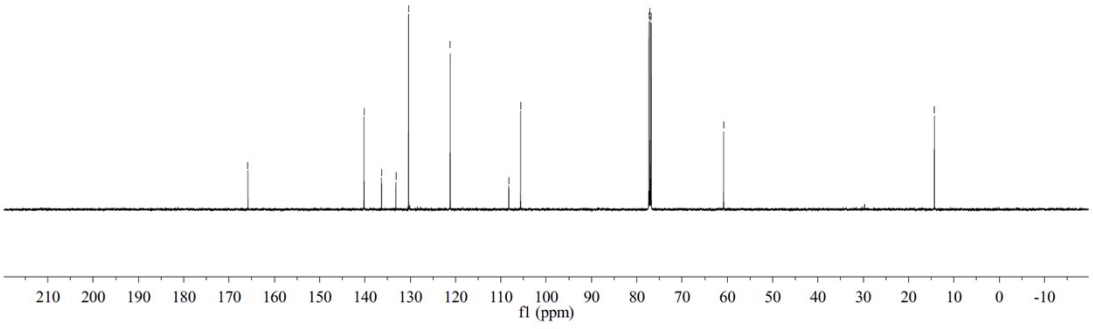
3qh

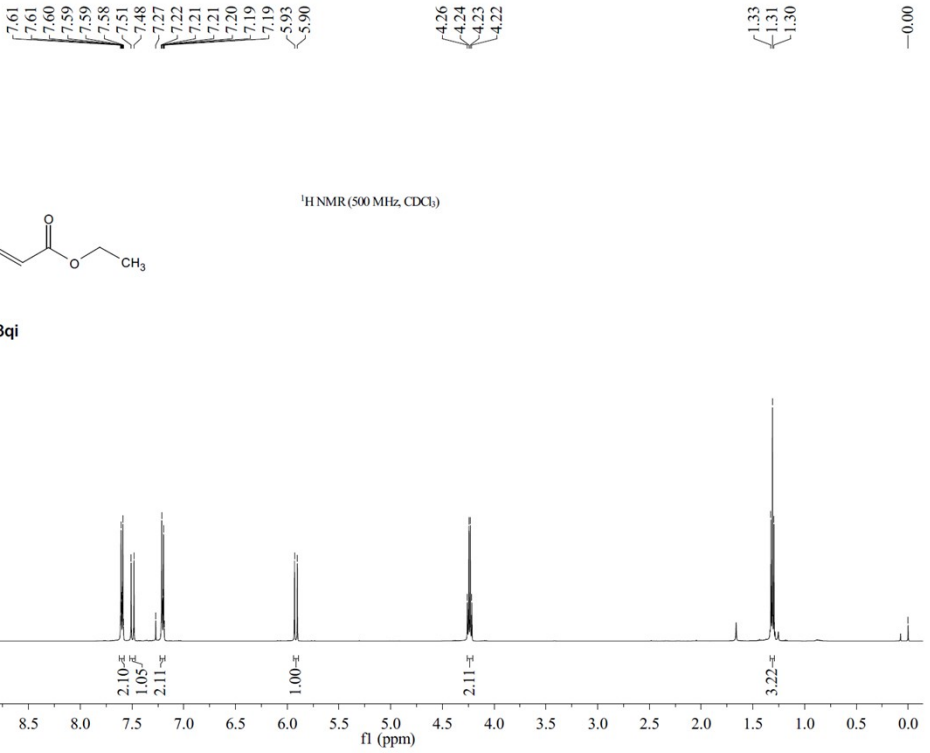


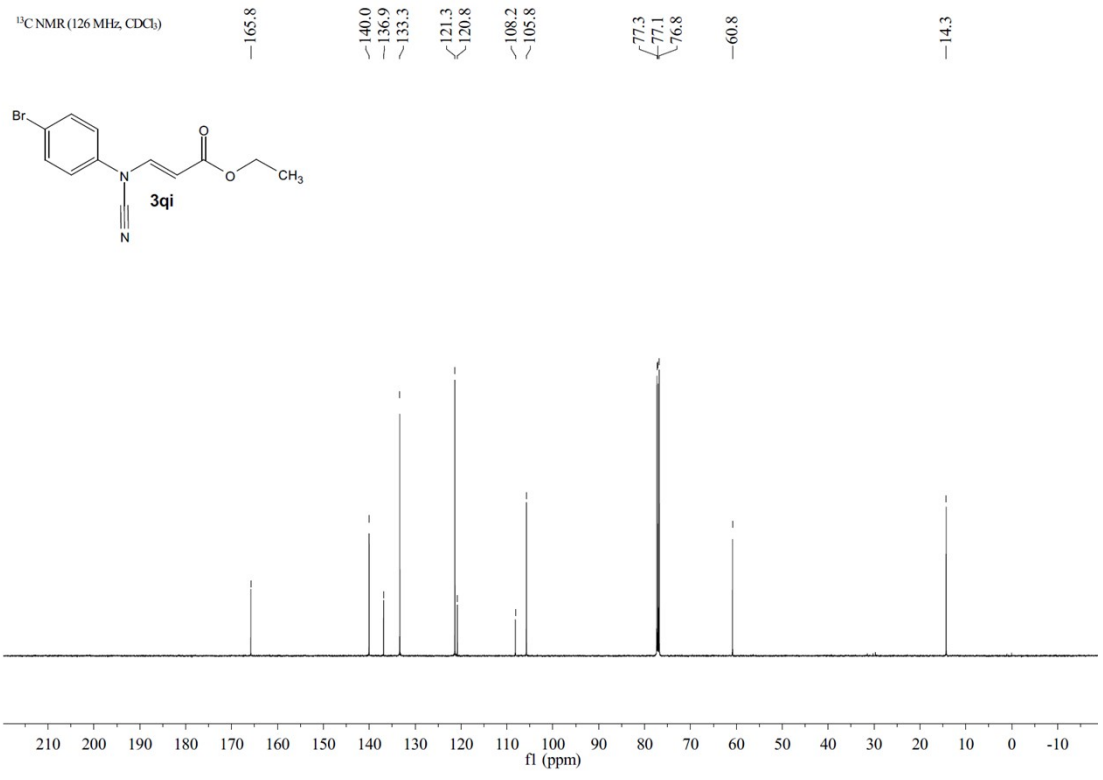
^{13}C NMR (126 MHz, $CDCl_3$)



3qh

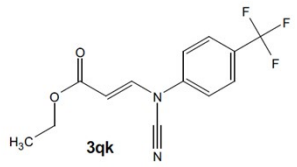



7.61
7.61
7.60
7.59
7.59
7.58
7.51
7.48
7.27
7.22
7.21
7.21
7.20
7.19
7.19
5.93
5.90
4.26
4.24
4.23
4.22
1.33
1.31
1.30
0.00
Br
O
N
O
CH3
N
3qi
1H NMR (500 MHz, CDCl3)
2.10
1.05
2.11
1.00
2.11
3.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

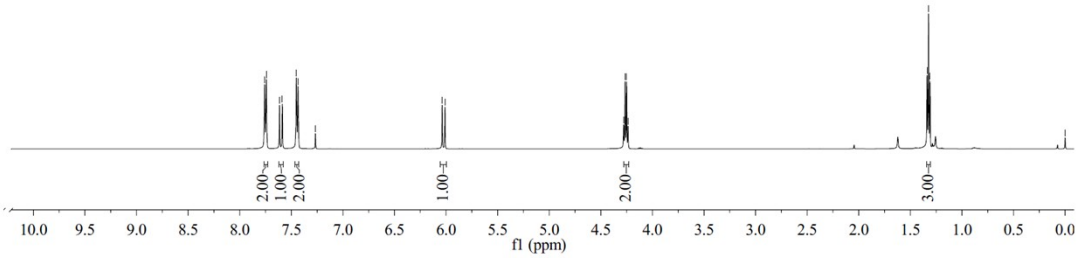

13C NMR (126 MHz, CDCl3)
165.8
140.0
136.9
133.3
121.3
120.8
108.2
105.8
77.3
77.1
76.8
60.8
14.3
Br
O
N
O
CH3
N
3qi
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR (500 MHz, $CDCl_3$)

7.76, 7.74, 7.61, 7.59, 7.45, 7.43, 7.27, 6.04, 6.01, 4.28, 4.26, 4.25, 4.24, 1.34, 1.32, 1.31, 0.00

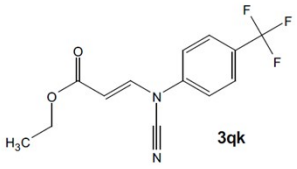


3qk

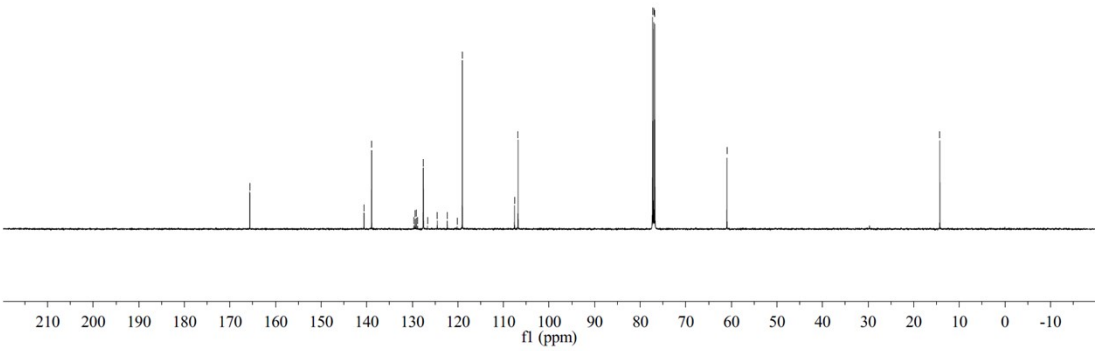


^{13}C NMR (126 MHz, $CDCl_3$)

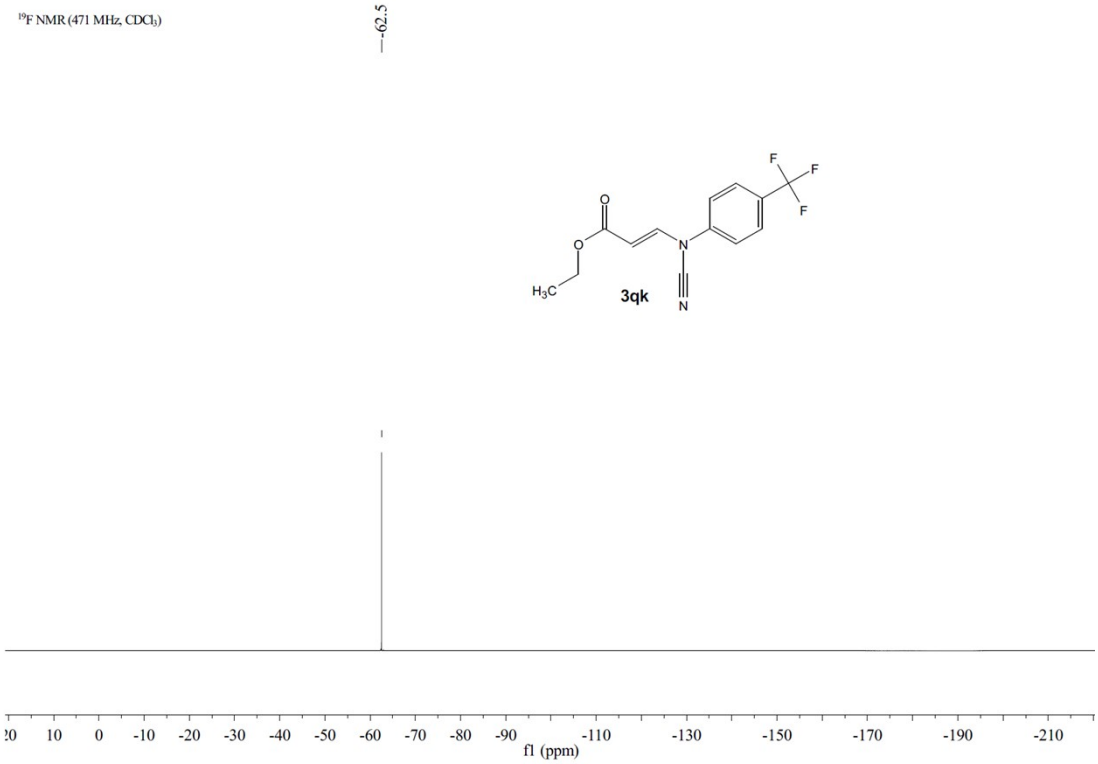
165.65, 140.59, 138.91, 127.61, 127.58, 127.56, 127.53, 109.03, 107.39, 106.79, 77.29, 77.04, 76.78, 60.98, 14.26

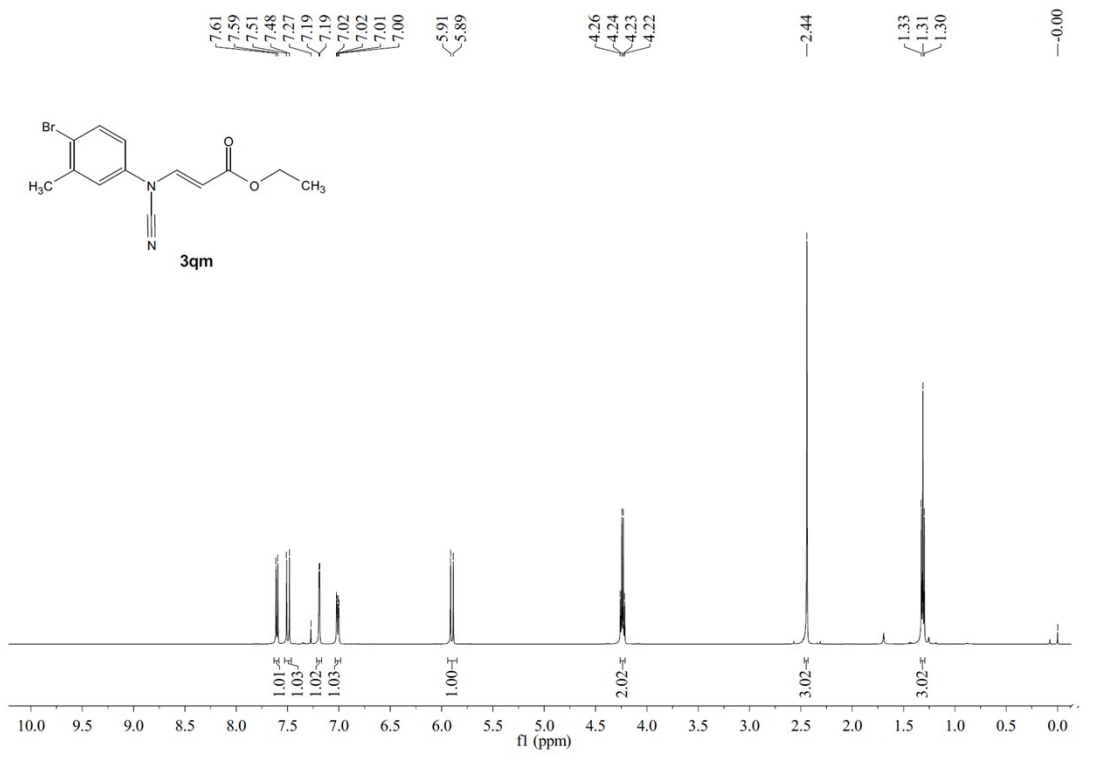


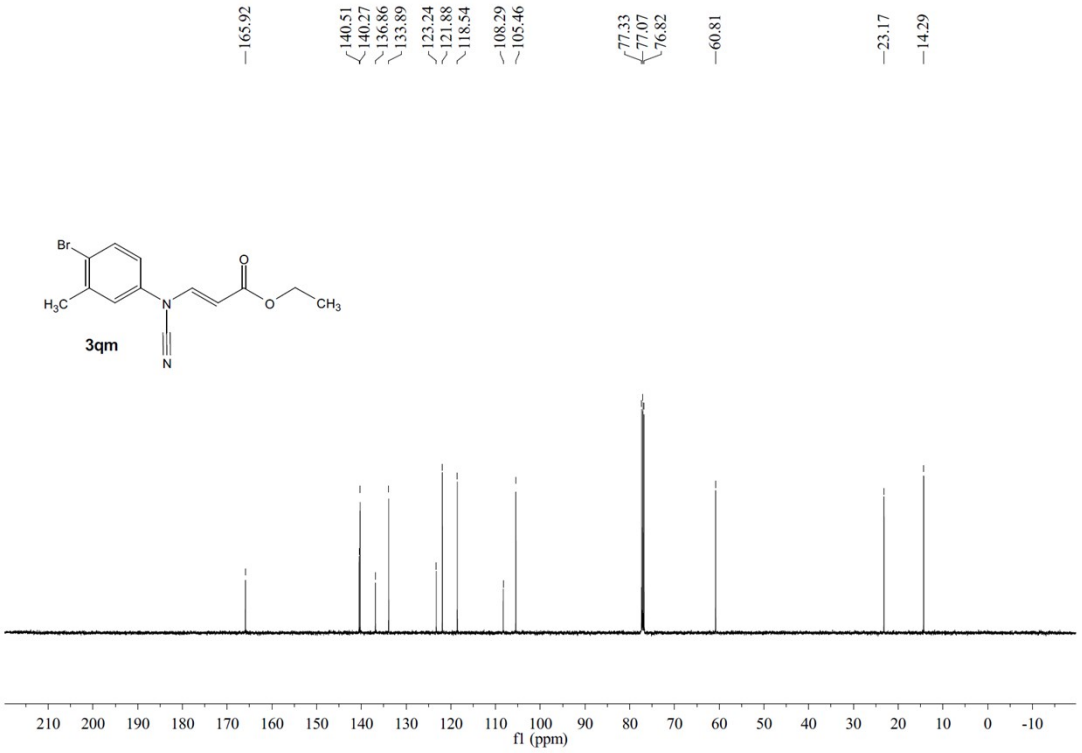
3qk

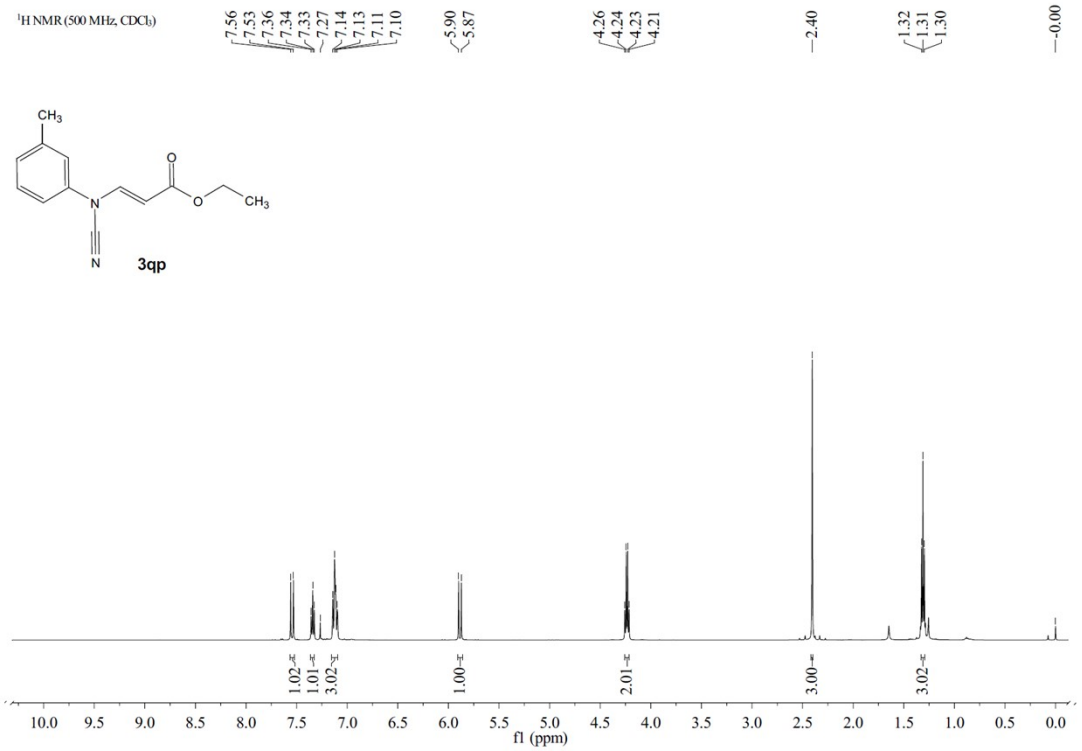


^{19}F NMR (471 MHz, $CDCl_3$)



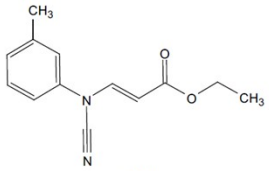



165.92
140.51
140.27
136.86
133.89
123.24
121.88
118.54
108.29
105.46
77.33
77.07
76.82
60.81
23.17
14.29
Br
H3C
N
O
O
CH3
N
3qm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

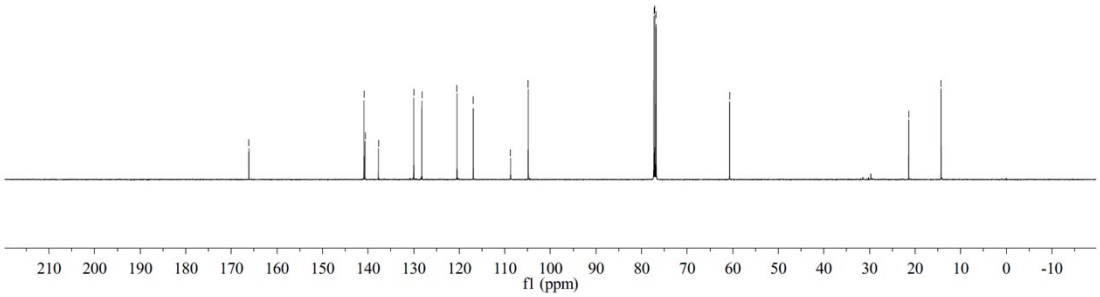

1H NMR (500 MHz, CDCl3)
7.56
7.53
7.36
7.34
7.33
7.27
7.14
7.13
7.11
7.10
5.90
5.87
4.26
4.24
4.23
4.21
2.40
1.32
1.31
1.30
0.00
CH3
N
O
O
CH3
N
3qp
1.02
1.01
3.02
1.00
2.01
3.00
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

^{13}C NMR (126 MHz, $CDCl_3$)

166.13
140.91
140.65
137.74
129.98
128.20
120.48
116.92
108.73
104.86
77.31
77.05
76.80
60.69
21.40
14.29

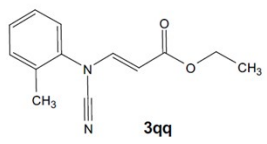


3qp

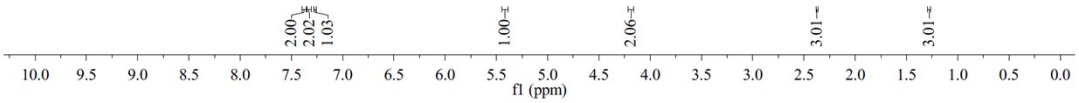


^{1}H NMR (500 MHz, $CDCl_3$)

7.39
7.37
7.36
7.34
7.33
7.32
7.30
7.27
7.26
5.43
5.40
4.21
4.20
4.18
4.17
2.37
1.59
1.29
1.28
1.26
0.00

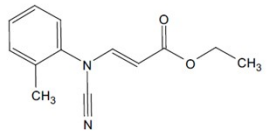


3qq

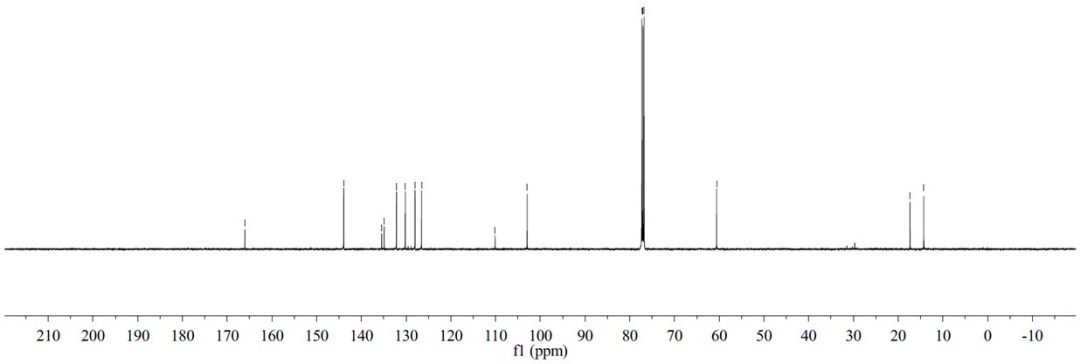


^{13}C NMR (126 MHz, $CDCl_3$)

166.01
143.94
135.46
134.89
132.14
130.17
128.00
126.54
110.10
102.92
77.29
77.04
76.79
60.58
17.34
14.27

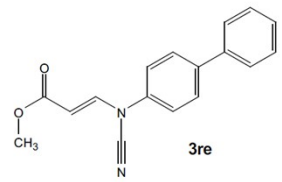


3qq

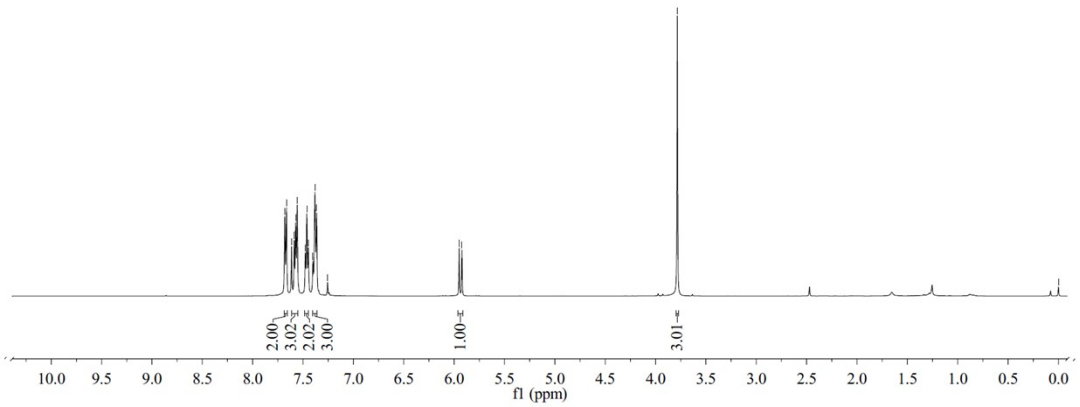


^{1}H NMR (500 MHz, $CDCl_3$)

7.68
7.66
7.61
7.59
7.57
7.56
7.48
7.46
7.45
7.40
7.38
7.36
7.26
5.95
5.92
3.78
0.00

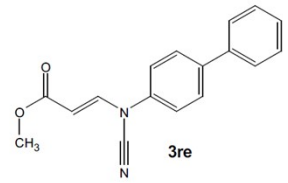


3re

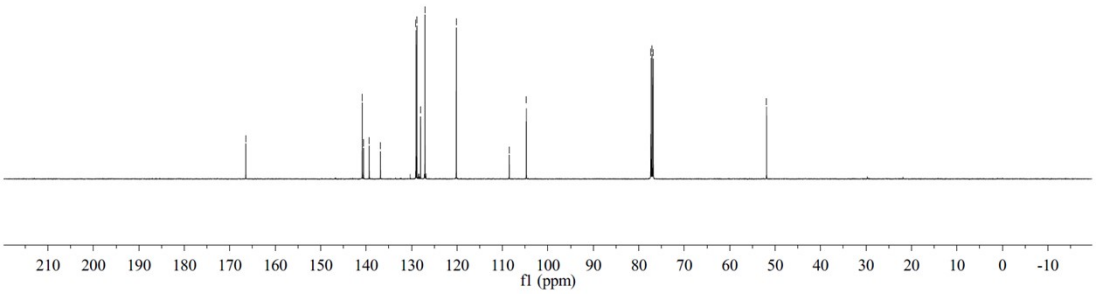


^{13}C NMR (126 MHz, $CDCl_3$)

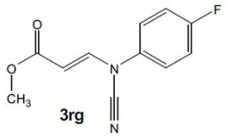
166.46
140.85
140.57
139.32
136.82
129.04
128.81
128.00
127.04
120.14
108.51
104.73
77.33
77.08
76.82
51.87



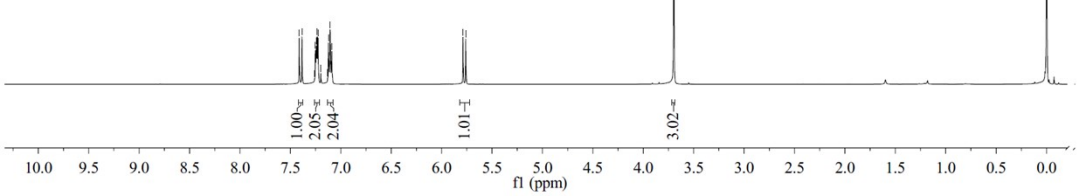
3re

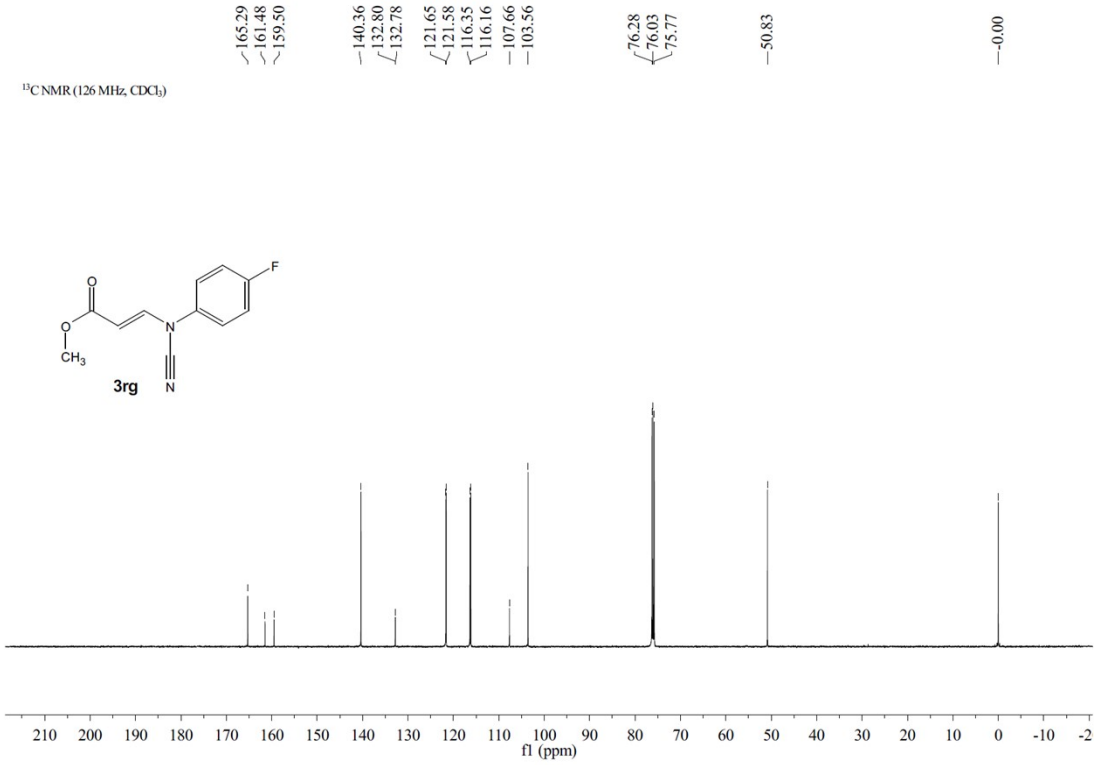


^{1}H NMR (500 MHz, $CDCl_3$)



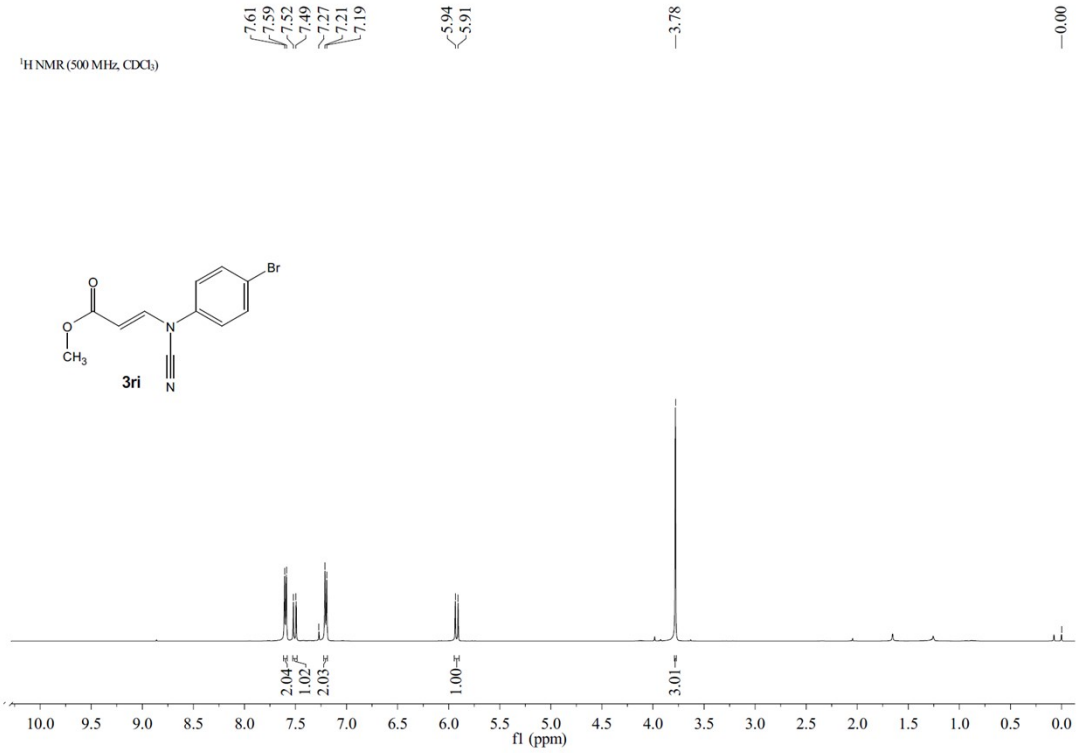
3rg



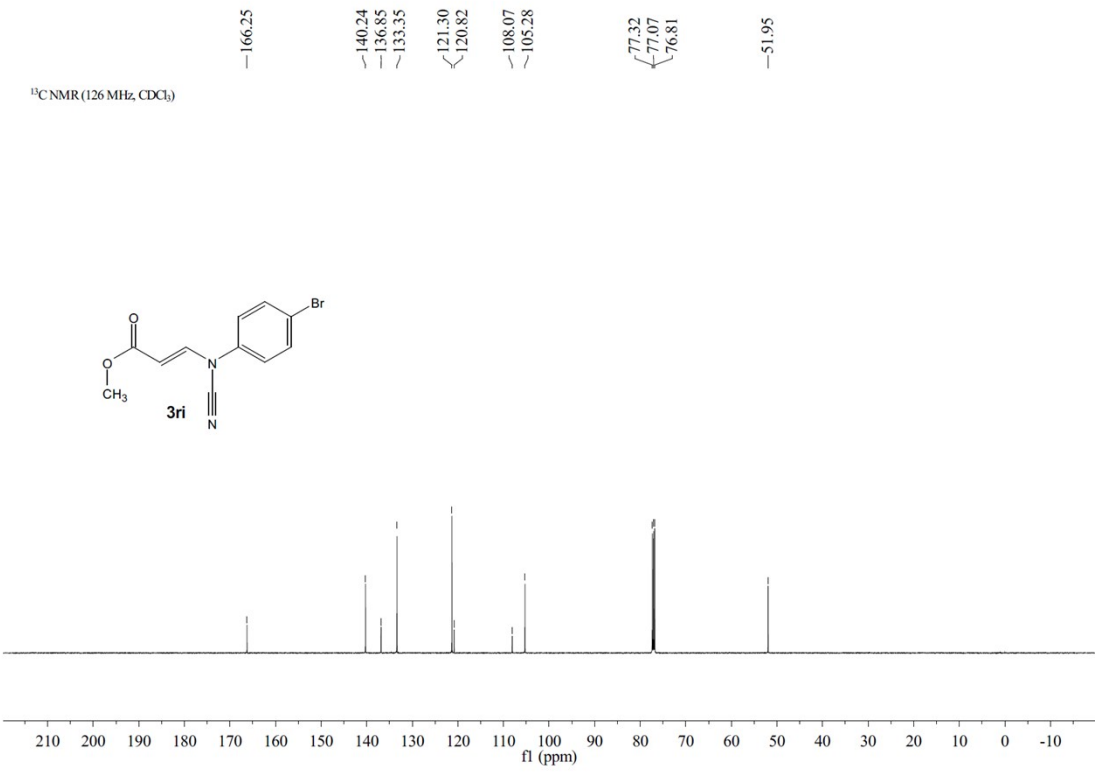

165.29
161.48
159.50
140.36
132.80
132.78
121.65
121.58
116.35
116.16
107.66
103.56
76.28
76.03
75.77
50.83
0.00
13C NMR (126 MHz, CDCl3)
O
O
CH3
N
F
3rg
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)


-112.93
19F NMR (471 MHz, CDCl3)
O
O
CH3
N
F
3rg
N
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

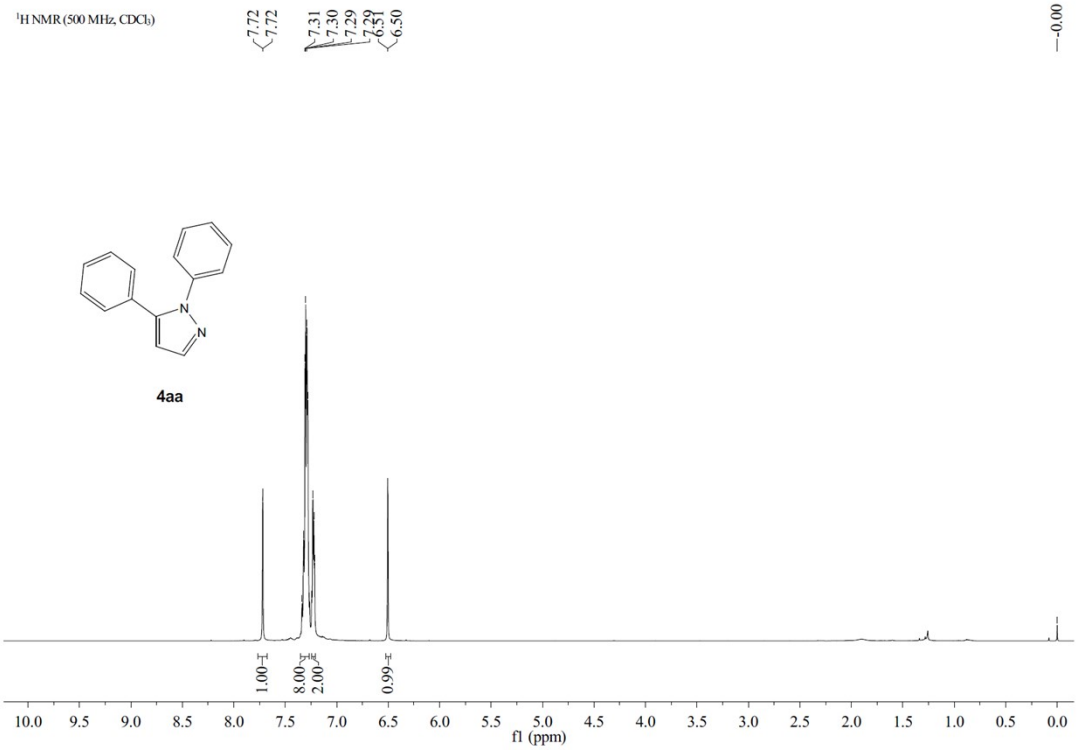
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

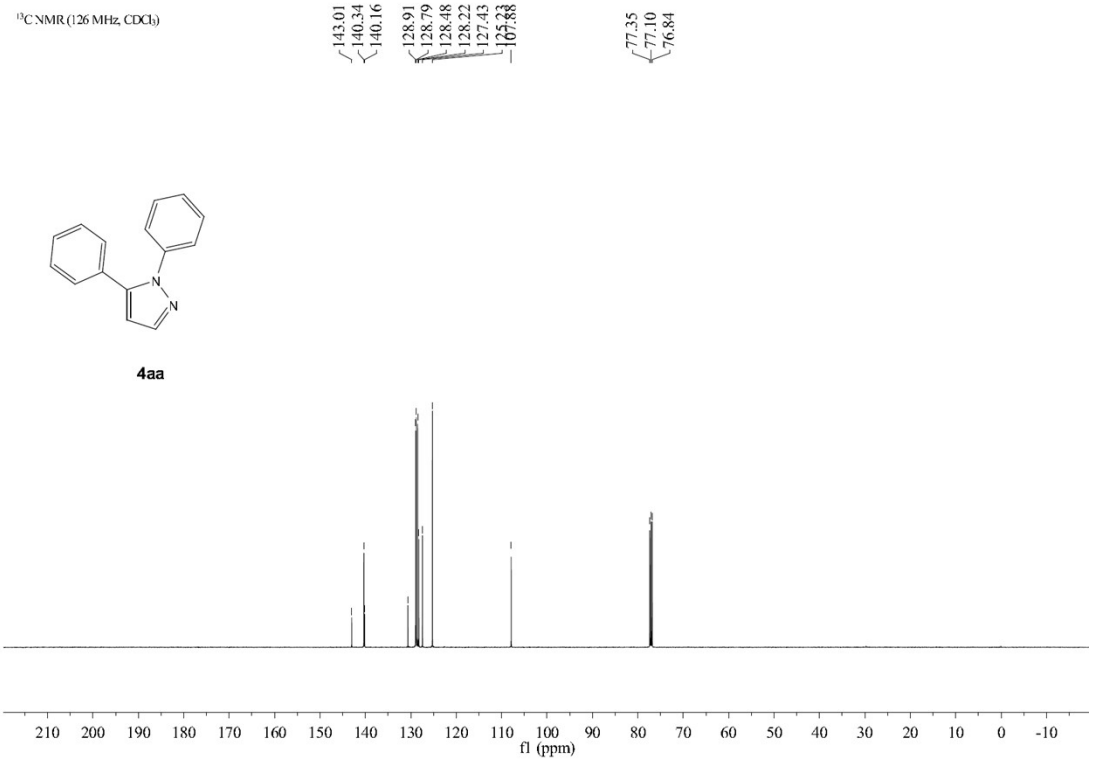


^{1}H NMR (500 MHz, $CDCl_3$)

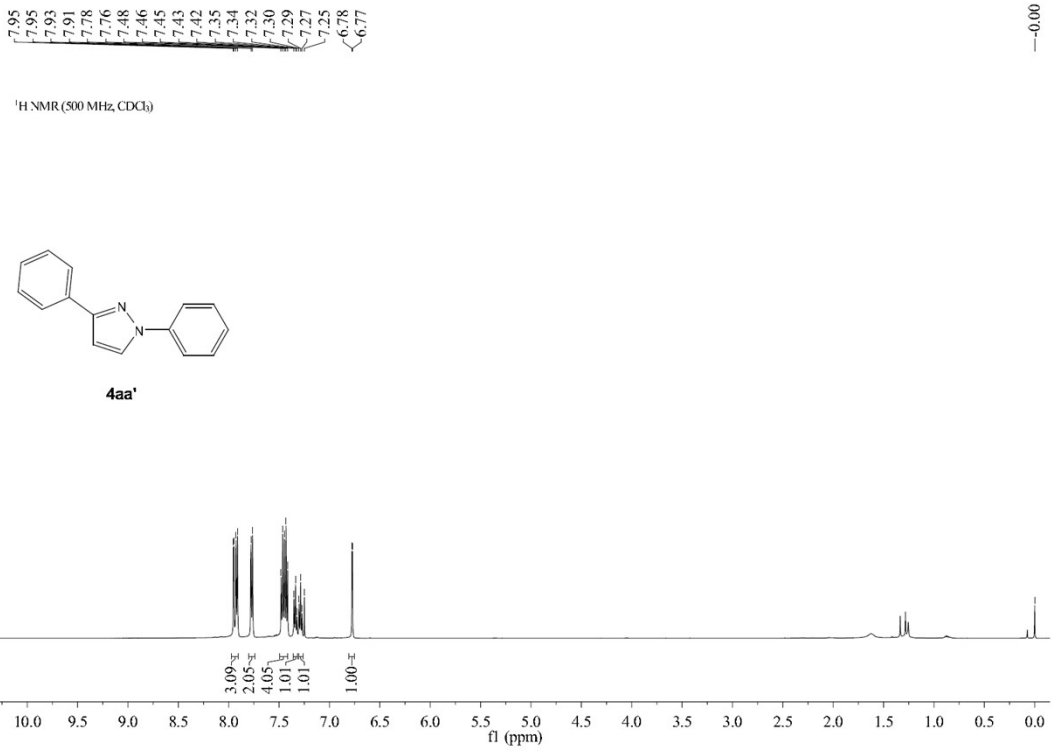


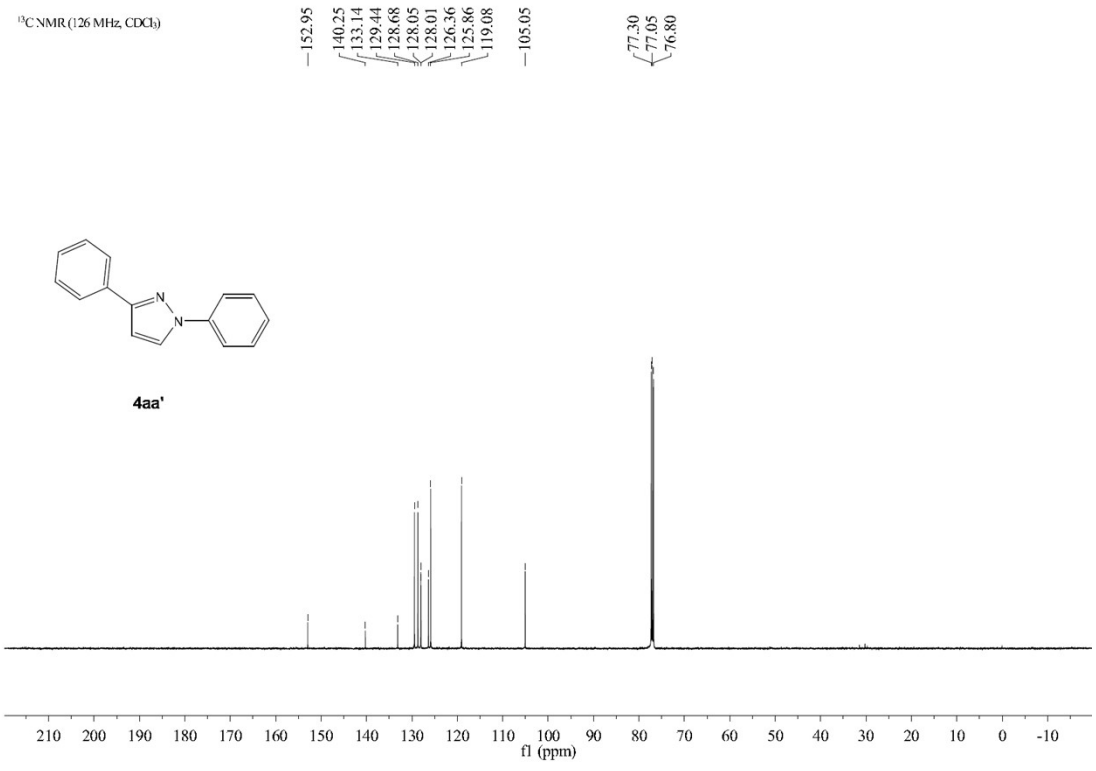
4aa

^{13}C NMR (126 MHz, $CDCl_3$)

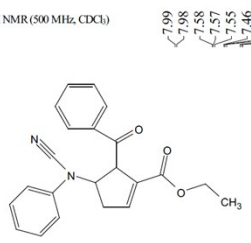


4aa

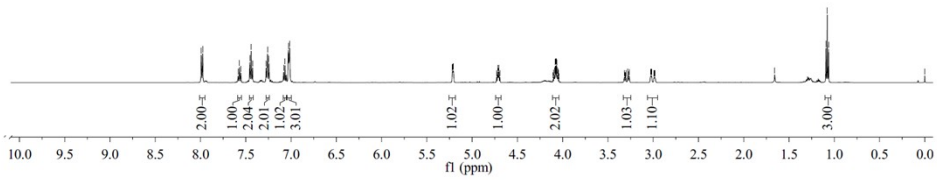

7.95
7.95
7.93
7.91
7.78
7.76
7.48
7.46
7.45
7.43
7.42
7.35
7.34
7.32
7.30
7.29
7.27
7.25
6.78
6.77
0.00
1H NMR (500 MHz, CDCl3)
4aa'
3.09
2.05
4.05
1.01
1.01
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


13C NMR (126 MHz, CDCl3)
152.95
140.25
133.14
129.44
128.68
128.05
128.01
126.36
125.86
119.08
105.05
77.30
77.05
76.80
4aa'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

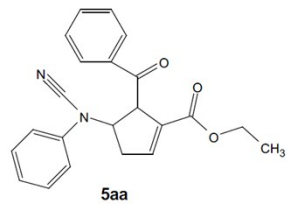
^{1}H NMR (500 MHz, $CDCl_3$)



5aa



^{13}C NMR (126 MHz, $CDCl_3$)



5aa