Electronic Supplementary Information

Direct *N*-acylation of azoles via metal-free catalyzed oxidative cross-coupling strategy

Jingjing Zhao,[ab] Pan Li,[a] Chungu Xia[a] and Fuwei Li*[a]

† State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China

‡ Graduate University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

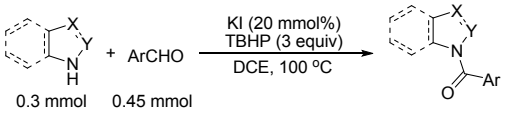
Email: fuweili@licp.cas.cn

Electronic Supplementary Information Contents:

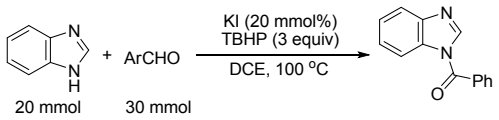
General Information:

All reagents purchased from commercial sources were used as received. The silica gel for column chromatography was supplied as 300–400 meshes. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE Ⅲ spectrometer and are referenced to the residual solvent signals (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C in $CDCl_3$). The HRMS spectra were recorded on a Bruker micrOTOF Q Ⅱ spectrometer.

General Procedure for *N*-Acylation of Azoles (3, 5):

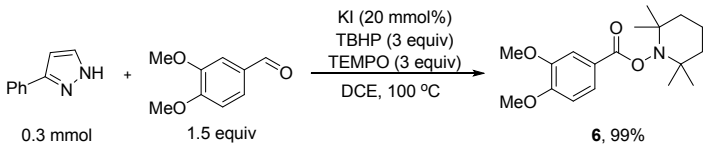


To a 15 mL pressure tube with a stir bar was added 0.3 mmol of azole **1**, **4**, 0.45 mmol of aldehyde **2** or benzil (1.5 equiv), followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired product **3**, **5**.

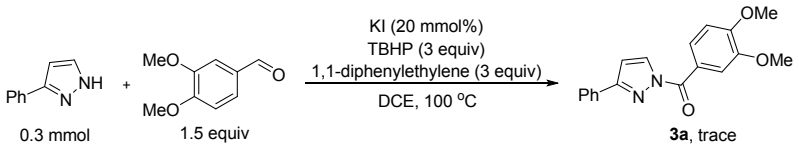


To a 100 mL round-bottom flask with a stir bar was added 20 mmol of benzoimidazole, 30 mmol of benzaldehyde (1.5 equiv), followed by 4 mmol of KI (0.2 equiv). Then 25 mL of DCE was added, followed by 60 mmol of TBHP (70% aqueous). The flask with a condenser was open in air. The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired product **5a** (3.78 g, 85% yield).

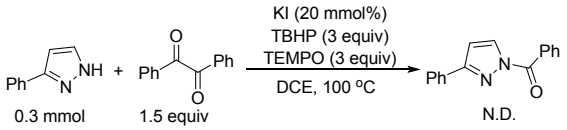
General Procedure for Radical Trapping Experiments:



To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 5-phenyl-1*H*-pyrazole **1a**, 0.45 mmol of 3,4-dimethoxybenzaldehyde **2a** (1.5 equiv), followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous) and 0.9 mmol of TEMPO (2,2,6,6-Tetramethylpiperidinooxy). The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford **6** in 99% yield.

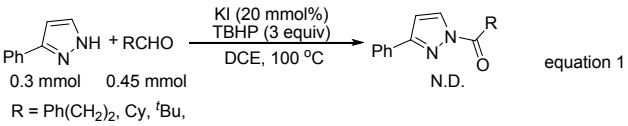


To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 5-phenyl-1*H*-pyrazole **1a**, 0.45 mmol of 3,4-dimethoxybenzaldehyde **2a** (1.5 equiv), followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous) and 0.9 mmol of 1,1-Diphenylethylene. The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature. Only trace **3a** was detected by GC-MS.

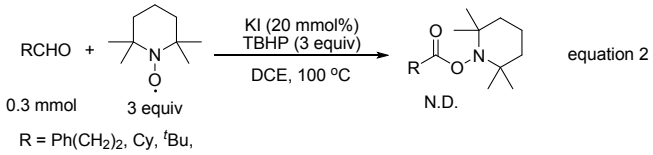


To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 5-phenyl-1*H*-pyrazole **1a**, 0.45 mmol of benzil (1.5 equiv), followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous) and 0.9 mmol of TEMPO. The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature. The desired product was not detected by GC-MS.

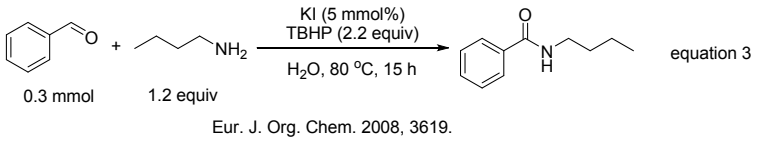
General Procedure for Control Experiments:



To a 15 mL pressure tube with a stir bar was added 0.3 mmol of pyrazole **1a**, 0.45 mmol of aliphatic aldehyde (1.5 equiv), followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature. The desired product was not detected by GC-MS. The pyrazole **1a** and corresponding aliphatic aldehyde were recovered, unusual product was not detected by GC-MS.

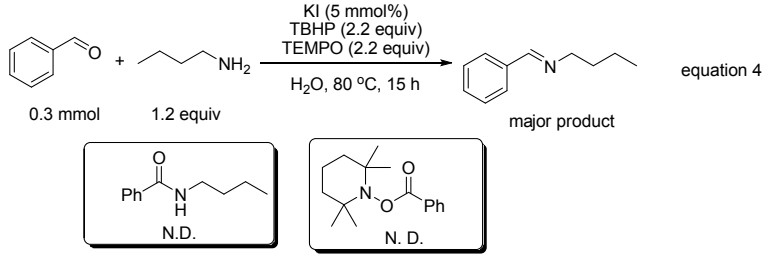


To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 3-phenylpropanal, 0.9 mmol of TEMPO, followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature. The corresponding aliphatic aldehyde was recovered, and the coupling product of 3-phenylpropanal and TEMPO was not detected by GC-MS.

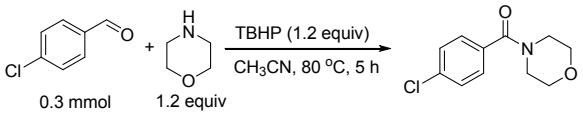


Eur. J. Org. Chem. 2008, 3619.

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of benzaldehyde, 0.36 mmol of butan-1-amine (1.2 equiv), followed by 0.015 mmol of KI (0.05 equiv). Then 3 mL of H_2O was added, followed by 0.66 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 80 ºC for 15 h, cooled to room temperature. The amide was detected as the major product by GC-MS.



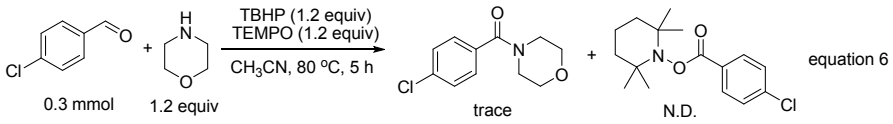
To a 15 mL pressure tube with a stir bar was added 0.3 mmol of benzaldehyde, 0.36 mmol of butan-1-amine (1.2 equiv), followed by 0.015 mmol of KI (0.05 equiv) and 0.66 mmol of TEMPO (2.2 equiv). Then 3 mL of H_2O was added, followed by 0.66 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 80 ºC for 15 h, cooled to room temperature. The amide and the coupling product of acyl radical and TEMPO were not detected by GC-MS. Instead, the imine product was observed as the major product by GC-MS.



Org. Lett. 2007, 9, 3429.

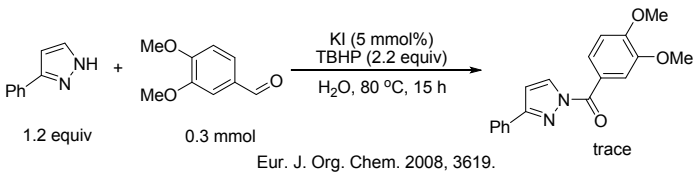
equation 5

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 4-chlorobenzaldehyde, 0.36 mmol of morpholine (1.2 equiv). Then 3 mL of CH_3CN was added, followed by 0.36 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 80 ºC for 5 h, cooled to room temperature. The amide was detected as the major product by GC-MS.



equation 6

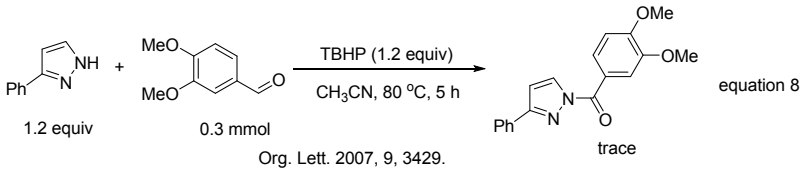
To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 4-chlorobenzaldehyde, 0.36 mmol of morpholine (1.2 equiv), followed by 0.66 mmol of TEMPO (2.2 equiv). Then 3 mL of CH_3CN was added, followed by 0.36 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 80 ºC for 5 h, cooled to room temperature. Only trace amide was detected by GC-MS. And the coupling product of acyl radical and TEMPO were not detected by GC-MS.



Eur. J. Org. Chem. 2008, 3619.

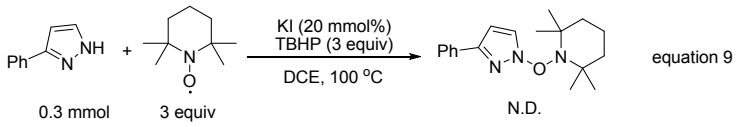
equation 7

To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 3,4-dimethoxybenzaldehyde **2a**, 0.36 mmol of 3-phenyl-1H-pyrazole **1a** (1.2 equiv), followed by 0.015 mmol of KI (0.05 equiv). Then 3 mL of H_2O was added, followed by 0.66 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 80 ºC for 15 h, cooled to room temperature. Only trace **3a** was detected by GC-MS.

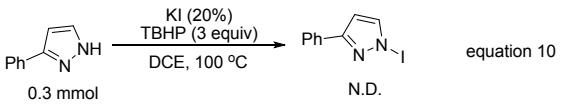


Org. Lett. 2007, 9, 3429.

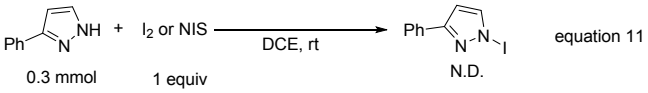
To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 3,4-dimethoxybenzaldehyde **2a**, 0.36 mmol of 3-phenyl-1H-pyrazole **1a** (1.2 equiv). Then 3 mL of CH_3CN was added, followed by 0.36 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 80 ºC for 5 h, cooled to room temperature. Only trace **3a** was detected by GC-MS.



To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 5-phenyl-1*H*-pyrazole **1a**, 0.9 mmol of TEMPO, followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature. The coupling product of **1a** and TEMPO was not detected by GC-MS.

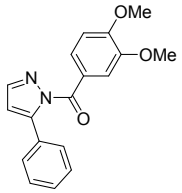


To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 5-phenyl-1*H*-pyrazole **1a**, followed by 0.06 mmol of KI (0.2 equiv). Then 3 mL of DCE was added, followed by 0.9 mmol of TBHP (70% aqueous). The reaction mixture was stirred at 100 ºC for 12 h, cooled to room temperature. The 1-iodo-3-phenyl-1*H*-pyrazole was not detected by GC-MS.



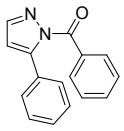
To a 15 mL pressure tube with a stir bar was added 0.3 mmol of 5-phenyl-1*H*-pyrazole **1a**, followed by 0.3 mmol of I_2 or NIS (1 equiv). Then 3 mL of DCE was added. The reaction mixture was stirred at room temperature for 12 h. The 1-iodo-3-phenyl-1*H*-pyrazole was not detected by GC-MS.

Characterization Data of Compounds 3a-3p:



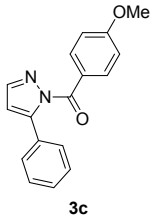
3a

(3,4-dimethoxyphenyl)(5-phenyl-1*H*-pyrazol-1-yl)methanone (3a) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.9 Hz, 1 H), 8.14 (dd, *J* = 8.5, 2.1 Hz, 1 H), 7.96 (d, *J* = 2.0 Hz, 1 H), 7.93–7.87 (m, 2 H), 7.50-7.36 (m, 3 H), 6.99 (t, *J* = 8.2 Hz, 1 H), 6.85 (d, *J* = 2.9 Hz, 1 H), 4.00 (s, 3 H), 3.98 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 155.6, 153.4, 148.3, 132.0, 132.0, 129.1, 128.8, 127.2, 126.3, 123.5, 114.7, 110.1, 106.7, 56.1, 56.0; HRMS (ESI) Calcd for $C_{18}H_{16}N_2NaO_3$ [M+Na] 331.1066, Found 331.1053.



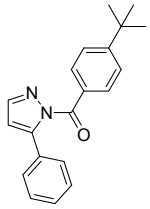
3b

phenyl(5-phenyl-1*H*-pyrazol-1-yl)methanone (3b) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.9 Hz, 1 H), 8.31–8.25 (m, 2 H), 7.93–7.87 (m, 2 H), 7.68–7.62 (m, 1 H), 7.58–7.51 (m, 2 H), 7.47–7.37 (m, 3 H), 6.87 (d, *J* = 2.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 155.9, 133.0, 131.9, 131.8, 131.7, 131.5, 129.2, 128.7, 128.0, 126.4, 107.2; HRMS (ESI) Calcd for $C_{16}H_{12}N_2NaO$ [M+Na] 271.0844, Found 271.0842.



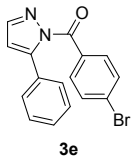
3c

(4-methoxyphenyl)(5-phenyl-1*H*-pyrazol-1-yl)methanone (3c) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (t, *J* = 3.6 Hz, 1 H), 8.42–8.35 (m, 2 H), 7.92–7.89 (m, 2 H), 7.50–7.37 (m, 3 H), 7.05–6.99 (m, 2 H), 6.84 (d, *J* = 2.9 Hz, 1 H), 3.91 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 163.6, 155.5, 134.5, 132.0, 131.8, 129.0, 128.7, 126.3, 123.5, 113.4, 106.7, 55.5; HRMS (ESI) Calcd for $C_{17}H_{14}N_2NaO_2$ [M+Na] 301.0962, Found 301.0947.



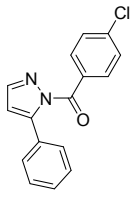
3d

(4-(*tert*-butyl)phenyl)(5-phenyl-1*H*-pyrazol-1-yl)methanone (3d) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.9 Hz, 1 H), 8.31 – 8.22 (m, 2 H), 7.96 – 7.88 (m, 2 H), 7.61 – 7.54 (m, 2 H), 7.50 – 7.37 (m, 3 H), 6.86 (d, *J* = 2.9 Hz, 1 H), 1.40 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 156.8, 155.7, 132.0, 131.9, 131.7, 129.1, 128.7, 128.5, 126.4, 125.1, 106.9, 35.1, 31.1; HRMS (ESI) Calcd for $C_{20}H_{20}N_2NaO$ [M+Na] 327.1460, Found 327.1468.



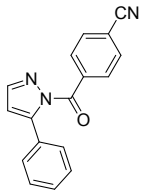
3e

(4-bromophenyl)(5-phenyl-1*H*-pyrazol-1-yl)methanone (3e) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1 H), 8.18–8.13 (m, 1 H), 7.85–7.83 (m, 1 H), 7.78–7.72 (m, 2 H), 7.68 (dd, *J* = 8.6, 1.9 Hz, 2 H), 7.51–7.39 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 144.1, 142.6, 132.4, 132.0, 131.6, 131.0, 128.4, 125.9, 125.4, 120.7, 115.4; HRMS (ESI) Calcd for $C_{14}H_9BrN_2NaO$ [M+Na] 322.9782, Found 322.9790.



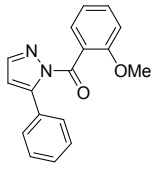
3f

(4-chlorophenyl)(5-phenyl-1*H*-pyrazol-1-yl)methanone (3f) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.9 Hz, 1 H), 8.31–8.23 (m, 2 H), 7.93–7.84 (m, 2 H), 7.54–7.50 (m, 2 H), 7.48–7.38 (m, 3 H), 6.88 (d, *J* = 2.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 156.1, 139.6, 133.4, 131.7, 131.6, 129.8, 129.3, 128.8, 128.4, 126.4, 107.4; HRMS (ESI) Calcd for $C_{16}H_{11}ClN_2NaO$ [M+Na] 305.0448, Found 305.0452.



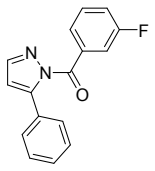
3g

4-(5-phenyl-1*H*-pyrazole-1-carbonyl)benzonitrile (3g) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.9 Hz, 1 H), 8.34 (d, *J* = 8.2 Hz, 2 H), 7.90–7.79 (m, 4 H), 7.48–7.40 (m, 3 H), 6.91 (d, *J* = 2.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 156.6, 135.4, 132.1, 131.7, 131.6, 131.2, 129.5, 128.8, 126.4, 117.9, 116.1, 108.0; HRMS (ESI) Calcd for $C_{17}H_{11}N_3NaO$ [M+Na] 296.0794, Found 296.0794.



3h

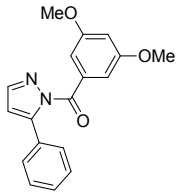
(2-methoxyphenyl)(5-phenyl-1*H*-pyrazol-1-yl)methanone (3h) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 2.9 Hz, 1 H), 7.86–7.78 (m, 2 H), 7.59–7.50 (m, 2 H), 7.42–7.35 (m, 3 H), 7.09–7.03 (m, 2 H), 6.81 (d, *J* = 2.9 Hz, 1 H), 3.82 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 157.9, 155.7, 132.7, 131.9, 131.1, 130.5, 129.1, 128.6, 126.4, 122.7, 120.2, 111.6, 107.3, 55.9; HRMS (ESI) Calcd for $C_{17}H_{14}N_2NaO_2$ [M+Na] 301.0954, Found 301.0947.



3i

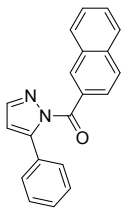
(3-fluorophenyl)(5-phenyl-1*H*-pyrazol-1-yl)methanone (3i) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.9 Hz, 1 H), 8.11–8.07 (m, 1 H), 8.07–8.02 (m, 1 H), 7.92–7.86 (m, 2 H), 7.51 (td, *J* = 8.0, 5.6 Hz, 1 H), 7.48–7.38 (m, 3 H), 7.35 (tdd, *J* = 8.3, 2.6, 0.9 Hz, 1 H), 6.89 (d, *J* = 2.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.1 ($^{1}J_{CF}$ = 246.8 Hz), 156.3, 133.4 ($^{3}J_{CF}$ = 7.8 Hz), 131.8, 131.6, 129.7 ($^{3}J_{CF}$ = 7.8 Hz), 129.4, 128.8, 127.7 ($^{4}J_{CF}$ = 3.2 Hz), 126.4, 120.1

($^2J_{CF}$ = 21.3 Hz), 119.0 ($^1J_{CF}$ = 24.1 Hz), 107.6; HRMS (ESI) Calcd for $C_{16}H_{11}FN_2NaO$ [M+Na] 289.0740, Found 289.0748.



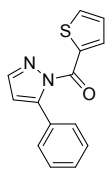
3j

(3,5-dimethoxyphenyl)(5-phenyl-1*H*-pyrazol-1-yl)methanone (3j) [Newcompound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 2.9 Hz, 1 H), 7.93–7.85 (m, 2 H), 7.46–7.39 (m, 5 H), 6.87 (d, *J* = 2.9 Hz, 1 H), 6.73 (t, *J* = 2.3 Hz, 1 H), 3.87 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 160.2, 155.9, 133.0, 132.0, 131.8, 129.2, 128.8, 126.3, 109.6, 107.2, 105.9, 55.6; HRMS (ESI) Calcd for $C_{18}H_{16}N_2NaO_3$ [M+Na] 331.1054, Found 331.1053.



3k

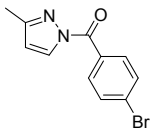
naphthalen-2-yl(5-phenyl-1*H*-pyrazol-1-yl)methanone (3k) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1 H), 8.54 (d, *J* = 2.9 Hz, 1 H), 8.31–8.24 (m, 1 H), 8.03 (d, *J* = 8.1 Hz, 1 H), 7.97 (d, *J* = 8.7 Hz, 1 H), 7.94–7.91 (m, 3 H), 7.67–7.63 (m, 1 H), 7.61–7.57 (m, 1 H), 7.50–7.37 (m, 3 H), 6.90 (d, *J* = 2.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 155.9, 135.4, 134.1, 132.2, 131.8, 129.7, 129.2, 128.8, 128.6, 127.7, 127.6, 127.1, 126.7, 126.4, 107.1; HRMS (ESI) Calcd for $C_{20}H_{14}N_2NaO$ [M+Na] 321.1000, Found 321.0998.



3l

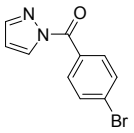
(5-phenyl-1*H*-pyrazol-1-yl)(thiophen-2-yl)methanone (3l) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 3.9, 1.3 Hz, 1 H), 8.46 (d, *J* = 2.9 Hz, 1 H), 7.98 (dd, *J* = 5.3,

3.3 Hz, 2 H), 7.84 (dd, *J* = 5.0, 1.3 Hz, 1 H), 7.53–7.46 (m, 2 H), 7.43 (ddd, *J* = 7.4, 3.7, 1.3 Hz, 1 H), 7.22 (dd, *J* = 4.9, 4.0 Hz, 1 H), 6.86 (d, *J* = 2.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 155.5, 138.5, 137.7, 132.2, 131.7, 130.8, 129.2, 128.8, 127.2, 126.4, 107.3; HRMS (ESI) Calcd for $C_{14}H_{10}N_2NaOS$ [M+Na] 277.0398, Found 277.0406.



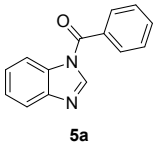
3m

(4-bromophenyl)(3-methyl-1*H*-pyrazol-1-yl)methanone (3m) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 2.7 Hz, 1 H), 8.08–7.99 (m, 2 H), 7.67–7.61 (m, 2 H), 6.34 (d, *J* = 2.8 Hz, 1 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 154.7, 133.1, 131.4, 131.1, 130.5, 128.1, 110.5, 14.0; HRMS (ESI) Calcd for $C_{11}H_9BrN_2NaO$ [M+Na] 286.9786, Found 286.9790.



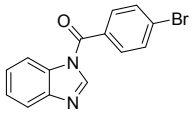
3n

(4-bromophenyl)(1*H*-pyrazol-1-yl)methanone (3n) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 2.9, 0.5 Hz, 1 H), 8.08–7.99 (m, 2 H), 7.80 (d, *J* = 0.7 Hz, 1 H), 7.71–7.62 (m, 2 H), 6.53 (dd, *J* = 2.8, 1.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 144.7, 133.1, 131.4, 130.4, 130.2, 128.3, 109.7; HRMS (ESI) Calcd for $C_{10}H_7BrN_2NaO$ [M+Na] 272.9639, Found 272.9634.



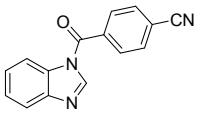
5a

(1*H*-benzo[*d*]imidazol-1-yl)(phenyl)methanone (5a)[1]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1 H), 8.22–8.19 (m, 1 H), 7.87–7.83 (m, 1 H), 7.81 (dd, *J* = 5.2, 3.3 Hz, 2 H), 7.74–7.67 (m, 1 H), 7.62–7.58 (m, 2 H), 7.49–7.41 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.1, 143.1, 133.2, 132.9, 132.1, 129.5, 129.1, 125.8, 125.3, 120.6, 115.5; HRMS (ESI) Calcd for $C_{14}H_{11}N_2O$ [M+H] 223.0866, Found 223.0866.



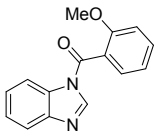
5b

(1*H*-benzo[*d*]imidazol-1-yl)(4-bromophenyl)methanone (5b) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1 H), 8.18–8.13 (m, 1 H), 7.85–7.83 (m, 1 H), 7.78–7.72 (m, 2 H), 7.68 (dd, *J* = 8.6, 1.9 Hz, 2 H), 7.51–7.39 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 144.1, 142.6, 132.4, 132.0, 131.6, 131.0, 128.4, 125.9, 125.4, 120.7, 115.4; HRMS (ESI) Calcd for $C_{14}H_9BrN_2NaO$ [M+Na] 322.9782, Found 322.9790.



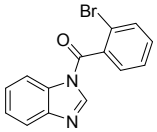
5c

4-(1*H*-benzo[*d*]imidazole-1-carbonyl)benzonitrile (5c) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.14 (m, 1 H), 8.12 (s, 1 H), 7.97–7.88 (m, 4 H), 7.87–7.82 (m, 1 H), 7.51–7.43 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 144.1, 142.3, 136.7, 132.9, 131.8, 129.9, 126.3, 125.9, 120.9, 117.4, 116.8, 115.5; HRMS (ESI) Calcd for $C_{15}H_9N_3NaO$ [M+Na] 270.0630, Found 270.0638.



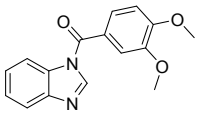
5d

(1*H*-benzo[*d*]imidazol-1-yl)(2-methoxyphenyl)methanone (5d) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30–8.21 (m, 1 H), 7.97 (s, 1 H), 7.86–7.73 (m, 1 H), 7.59 (m, 1 H), 7.54 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.48–7.37 (m, 2 H), 7.14 (td, *J* = 7.5, 0.8 Hz, 1 H), 7.06 (d, *J* = 8.4 Hz, 1 H), 3.78 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 156.5, 144.1, 143.6, 133.5, 131.6, 129.9, 125.7, 125.1, 122.9, 121.2, 120.3, 115.5, 111.6, 55.7; HRMS (ESI) Calcd for $C_{15}H_{12}N_2NaO_2$ [M+Na] 275.0794, Found 275.0791.



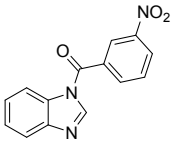
5e

(1*H*-benzo[*d*]imidazol-1-yl)(2-bromophenyl)methanone (5e) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 5.4 Hz, 1 H), 7.90 (s, 1 H), 7.87–7.81 (m, 1 H), 7.76–7.74 (m, 1 H), 7.60–7.39 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 144.2, 142.7, 135.3, 133.5, 132.6, 131.3, 129.2, 127.9, 126.029, 125.5, 120.6, 119.7, 115.4; HRMS (ESI) Calcd for $C_{14}H_9BrN_2NaO$ [M+Na] 322.9793, Found 322.9790.



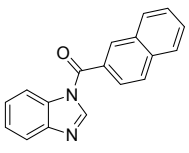
5f

(1*H*-benzo[*d*]imidazol-1-yl)(3,4-dimethoxyphenyl)methanone (5f) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1 H), 8.17–8.09 (m, 1 H), 7.89–7.80 (m, 1 H), 7.48–7.38 (m, 4 H), 7.06–6.95 (m, 1 H), 4.00 (s, 3 H), 3.96 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 153.5, 149.4, 144.0, 143.1, 132.3, 125.5, 125.0, 124.8, 124.1, 120.4, 115.2, 112.3, 110.4, 56.2, 56.1; HRMS (ESI) Calcd for $C_{16}H_{14}N_2NaO_3$ [M+Na] 305.0902, Found 305.0897.



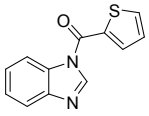
5g

(1*H*-benzo[*d*]imidazol-1-yl)(3-nitrophenyl)methanone (5g) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (t, *J* = 1.9 Hz, 1 H), 8.56 (ddd, *J* = 8.3, 2.2, 1.0 Hz, 1 H), 8.23–8.17 (m, 1 H), 8.16 (s, 1 H), 8.16–8.12 (m, 1 H), 7.91–7.81 (m, 2 H), 7.54–7.44 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 148.4, 144.1, 142.1, 134.8, 134.5, 131.8, 130.5, 127.6, 126.3, 125.9, 124.5, 120.9, 115.5; HRMS (ESI) Calcd for $C_{14}H_{10}N_3O_3$ [M+H] 268.0712, Found 268.0717.



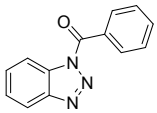
5h

(1*H*-benzo[*d*]imidazol-1-yl)(naphthalen-2-yl)methanone (5h) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 2 H), 8.26–8.19 (m, 1 H), 8.04 (d, *J* = 8.5 Hz, 1 H), 7.96 (d, *J* = 8.7 Hz, 2 H), 7.90–7.83 (m, 2 H), 7.72–7.66 (m, 1 H), 7.65–7.60 (m, 1 H), 7.50–7.42 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.1, 143.2, 135.3, 132.2, 131.1, 129.9, 129.2, 129.0, 128.0, 127.5, 125.7, 125.2, 125.0, 120.6, 115.4; HRMS (ESI) Calcd for $C_{18}H_{12}N_2NaO$ [M+Na] 295.0849, Found 295.0842.



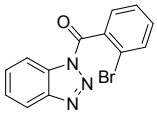
5i

(1*H*-benzo[*d*]imidazol-1-yl)(thiophen-2-yl)methanone (5i) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1 H), 8.23–8.14 (m, 1 H), 7.88–7.80 (m, 2 H), 7.81–7.76 (m, 1 H), 7.50–7.39 (m, 2 H), 7.28–7.26 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 143.9, 142.2, 135.7, 134.5, 134.3, 132.2, 128.2, 125.7, 125.2, 120.5, 115.3; HRMS (ESI) Calcd for $C_{12}H_9N_2OS$ [M+H] 229.0431, Found 229.0430.



5j

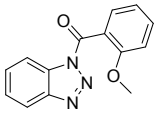
(1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenyl)methanone (5j)[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.3 Hz, 1 H), 8.25–8.19 (m, 2 H), 8.17 (d, *J* = 8.3 Hz, 1 H), 7.74–7.67 (m, 2 H), 7.62–7.52 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 145.7, 133.7, 132.3, 131.7, 131.5, 130.4, 128.4, 126.3, 120.2, 114.8; HRMS (ESI) Calcd for $C_{13}H_9N_3NaO$ [M+Na] 246.0630, Found 246.0638.



5m

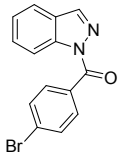
1*H*-benzo[*d*][1,2,3]triazol-1-yl)(2-bromophenyl)methanone (5m) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 8.3, 0.7 Hz, 1 H), 8.16 (dd, *J* = 8.3, 0.7 Hz, 1 H), 7.77–7.70 (m, 2 H), 7.64–7.60 (m, 1 H), 7.60–7.54 (m, 1 H), 7.53–7.44 (m, 2 H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 166.4, 146.2, 135.0, 133.2, 132.5, 131.3, 130.7, 130.1, 127.2, 126.7, 120.6, 120.4, 114.4; HRMS (ESI) Calcd for $C_{13}H_8BrN_3NaO$ [M+Na] 323.9736, Found 323.9743.



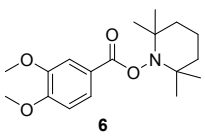
5n

(1*H*-benzo[*d*][1,2,3]triazol-1-yl)(2-methoxyphenyl)methanone (5n) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.3 Hz, 1 H), 8.13 (d, *J* = 8.3 Hz, 1 H), 7.69 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 1 H), 7.63–7.50 (m, 3 H), 7.12 (td, *J* = 7.5, 0.8 Hz, 1 H), 7.06 (d, *J* = 8.4 Hz, 1 H), 3.77 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 157.8, 146.0, 133.5, 131.4, 130.3, 130.2, 126.1, 122.7, 120.5, 120.1, 114.4, 111.7, 55.8; HRMS (ESI) Calcd for $C_{14}H_{11}N_3NaO_2$ [M+Na] 276.0738, Found 276.0743.



5o

(4-bromophenyl)(1*H*-indazol-1-yl)methanone (5o) [New compound]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 8.4, 0.7 Hz, 1 H), 8.21 (d, *J* = 0.6 Hz, 1 H), 8.01-7.93 (m, 2 H), 7.83-7.76 (m, 1 H), 7.68-7.65 (m, 2 H), 7.64-7.61 (m, 1 H), 7.48-7.39 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 140.6, 140.1, 132.6, 132.1, 131.3, 129.7, 127.3, 126.1, 125.0, 121.0, 115.9; HRMS (ESI) Calcd for $C_{14}H_9BrN_2NaO$ [M+Na] 322.9789, Found 322.9790.



6

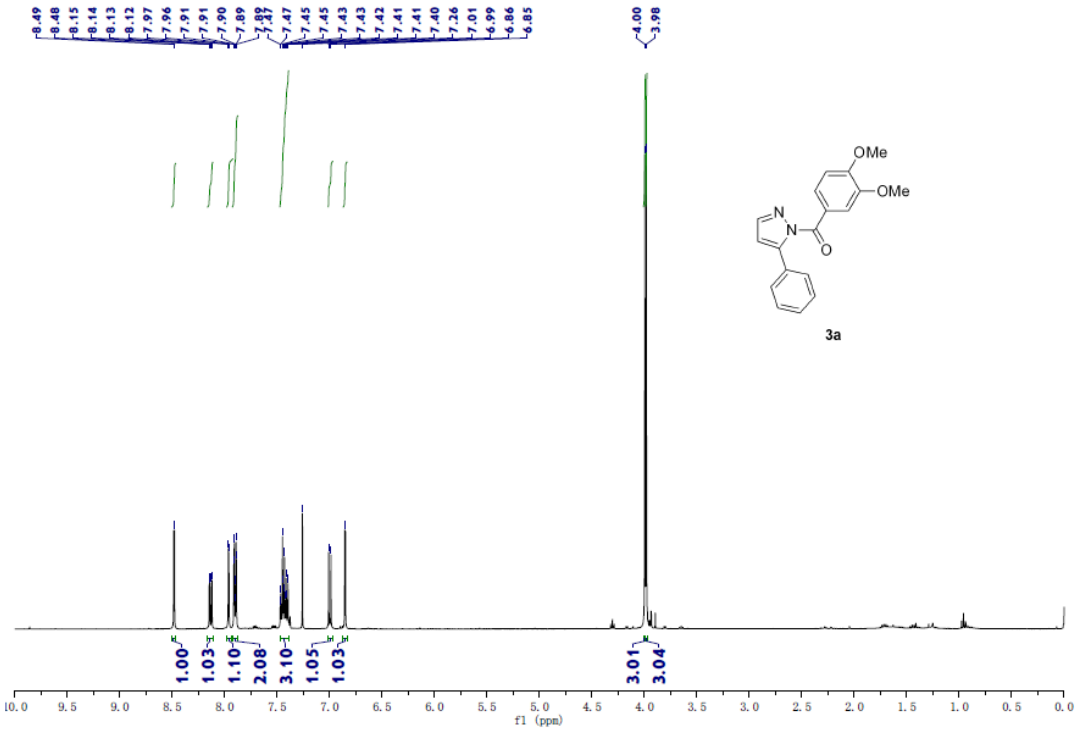
2,2,6,6-tetramethylpiperidin-1-yl 3,4-dimethoxybenzoate (6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.4, 1.5 Hz, 1 H), 7.54 (d, *J* = 1.5 Hz, 1 H), 6.86 (d, *J* = 8.4 Hz, 1 H), 3.89 (s, 6 H), 1.76-1.39 (m, 6 H), 1.22 (s, 6 H), 1.07 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 152.7, 148.6, 123.0, 121.9, 112.1, 110.1, 60.1, 55.8, 55.77, 38.8, 31.8, 20.6, 16.8; HRMS (ESI) Calcd for $C_{18}H_{27}NNaO_4$ [M+Na] 344.1825, Found 344.1832.

References:

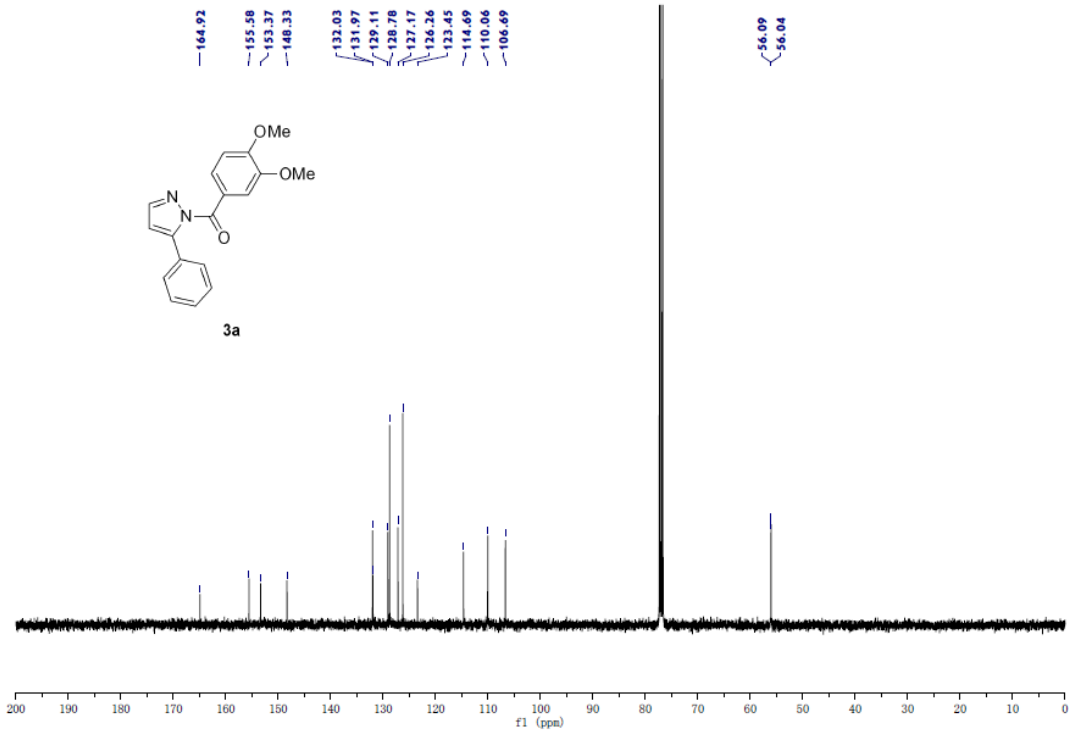
(1) H. R. J. Yajnanarayana and W. G. Harry, *J. Org. Chem.* 1991, **56**, 865.

(2) (a) R. K. Alam and P. Alfredo, *J. Org. Chem.* 1990, **65**, 3679; (b) N. G. Gaylord and J. M. Naughton, *J. Org. Chem.* 1957, **22**, 1022.

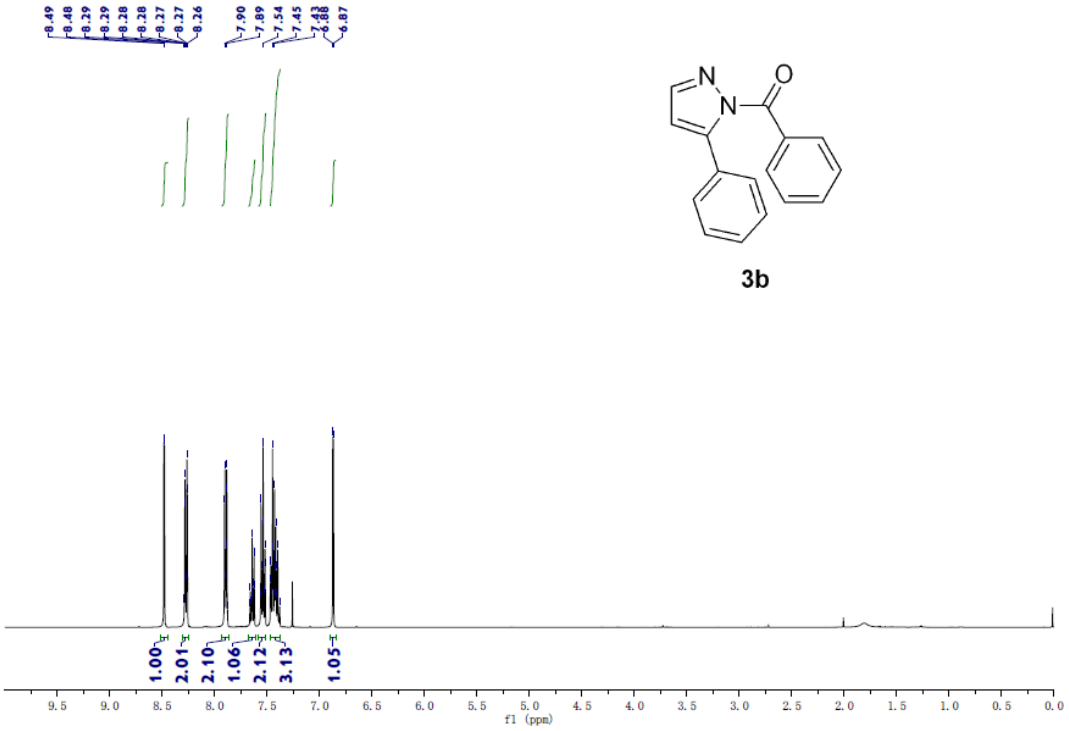
Copies of ^{1}H and ^{13}C NMR Spectra



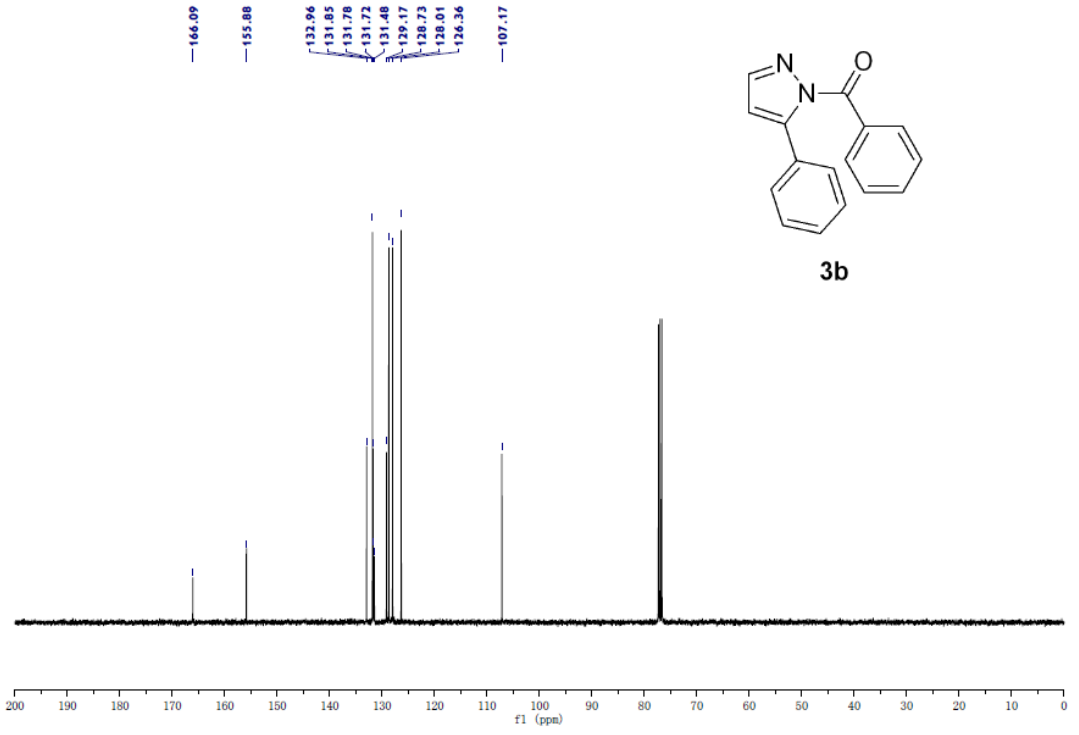
^{1}H NMR of product **3a**



^{13}C NMR of product **3a**



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



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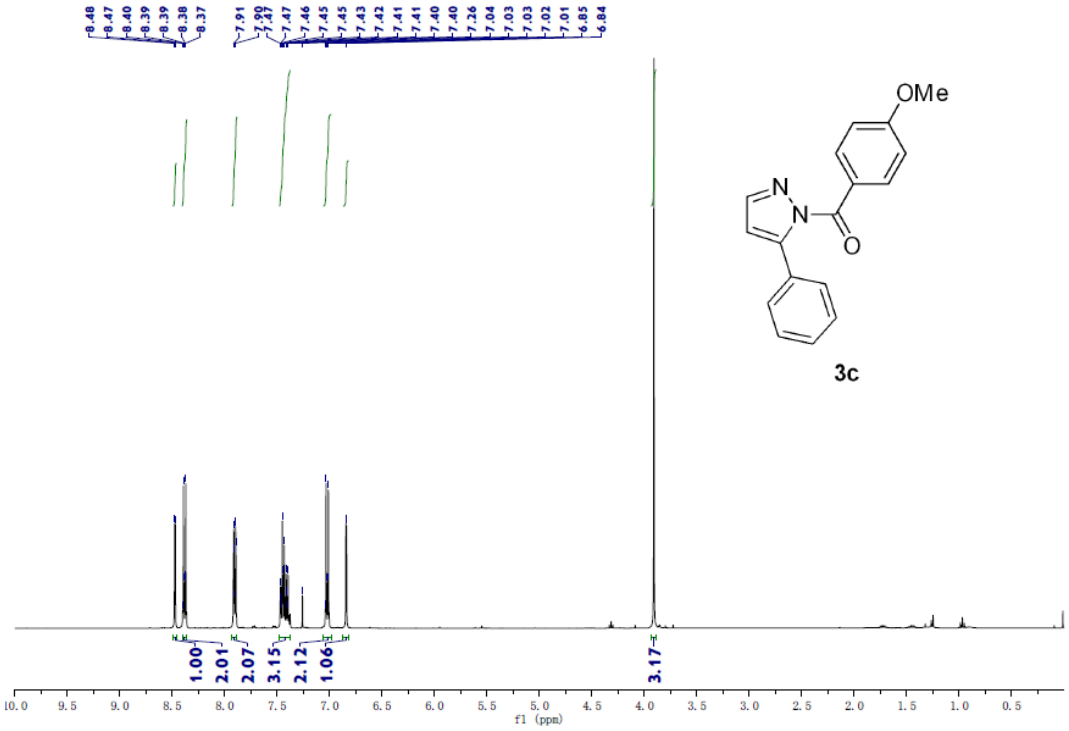
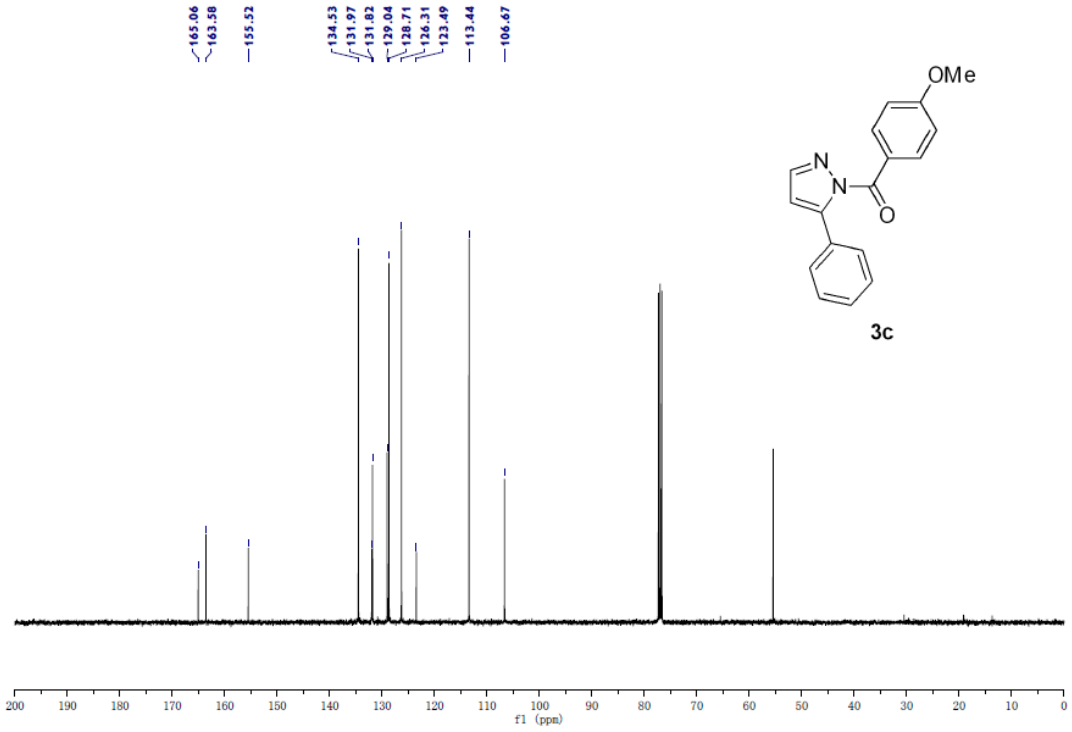
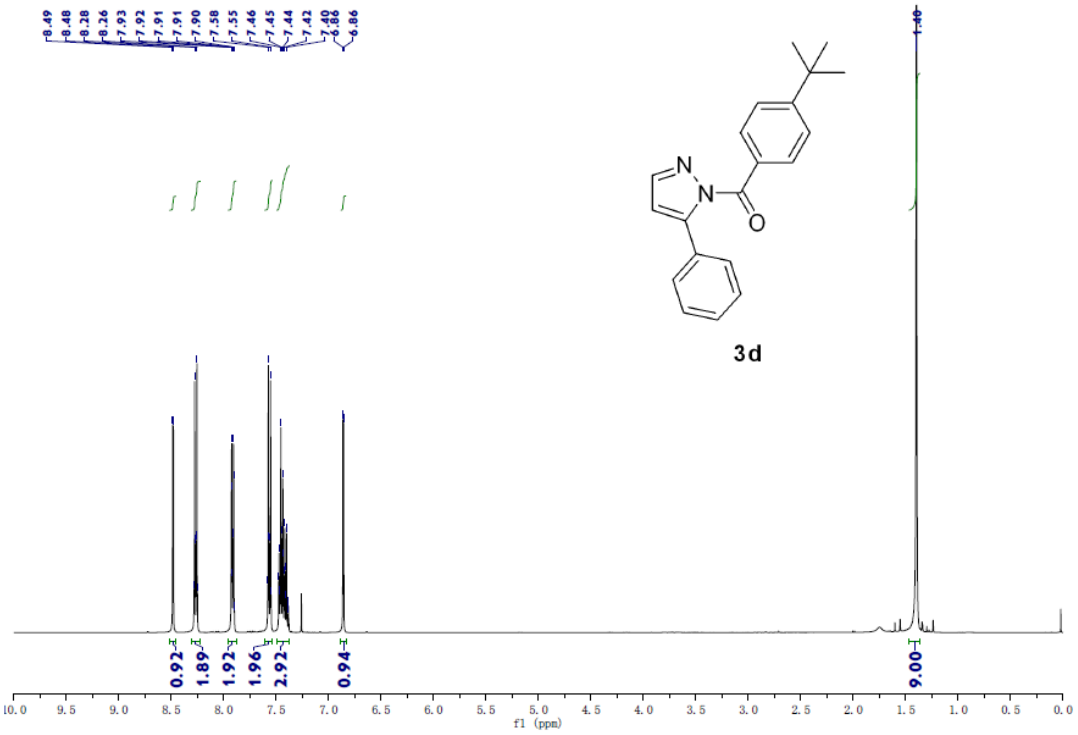


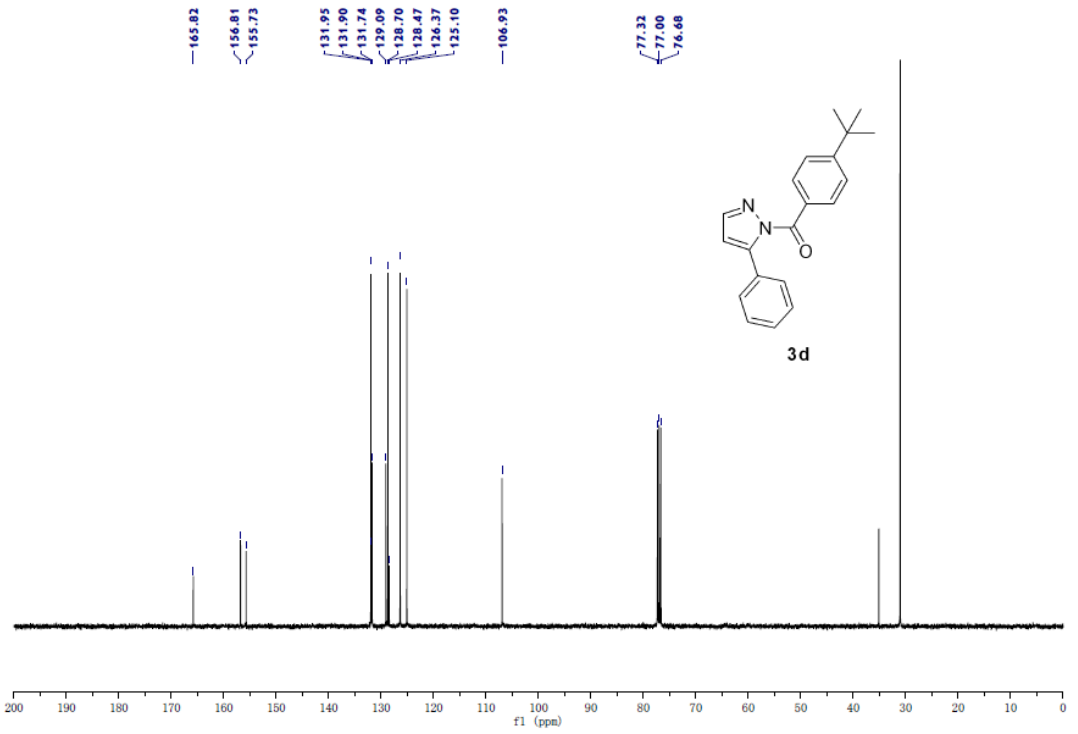
^{1}H NMR of product **3c**



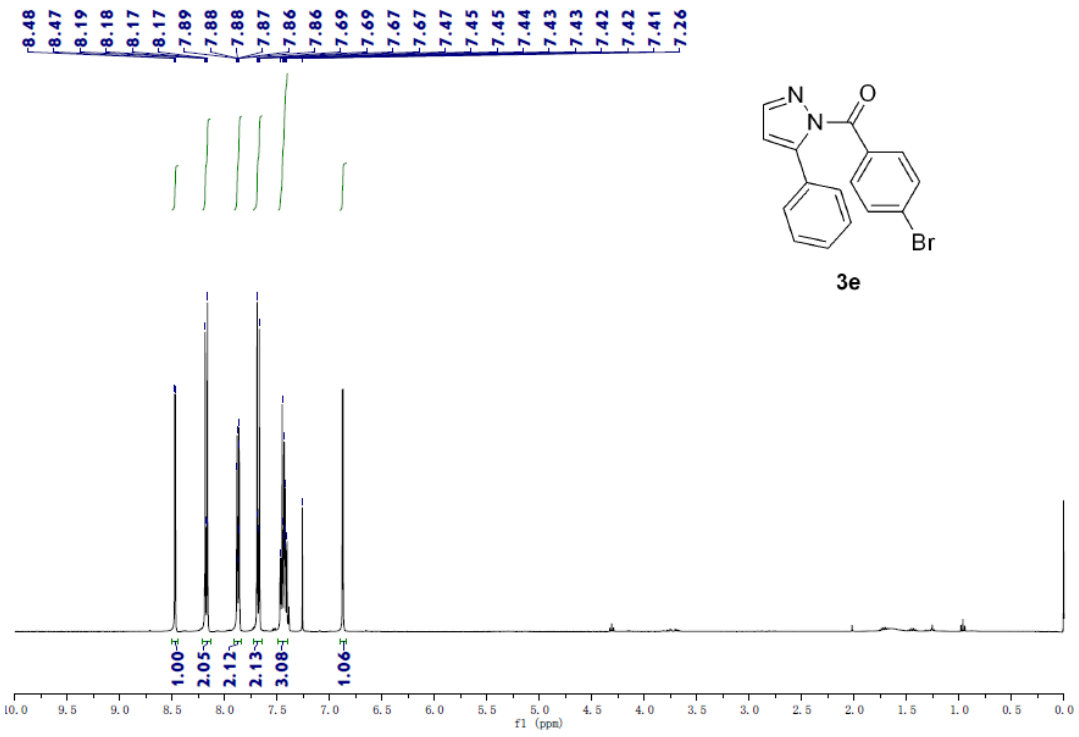
^{13}C NMR of product **3c**



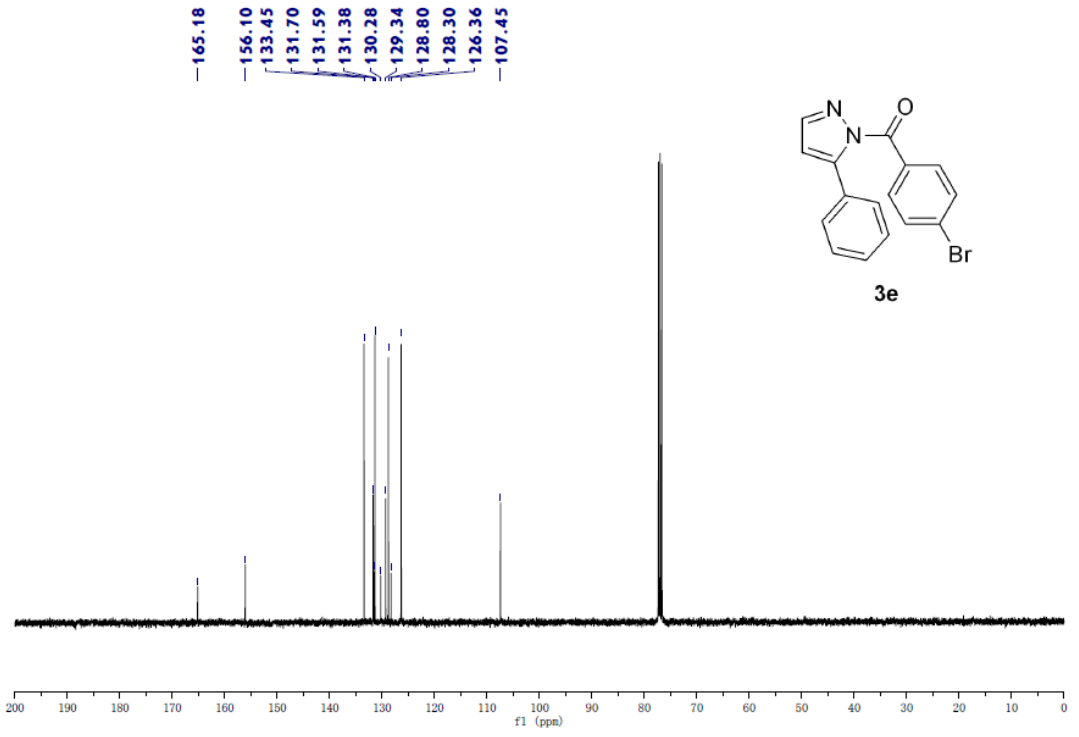
^{1}H NMR of product **3d**



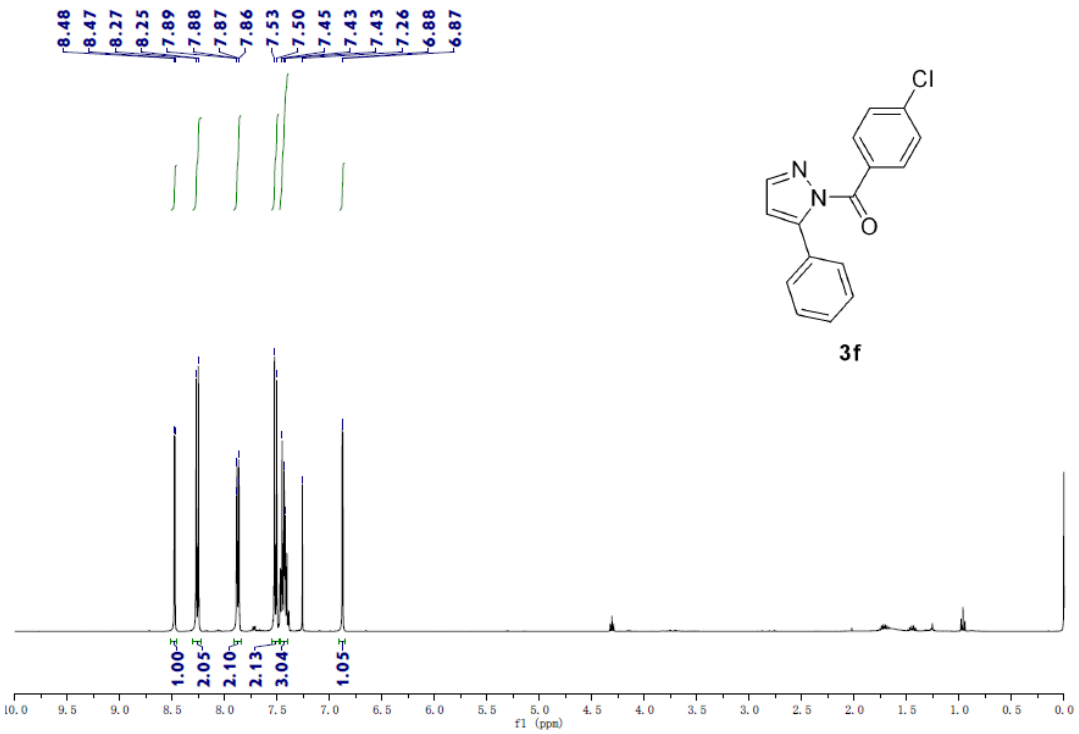
^{13}C NMR of product **3d**



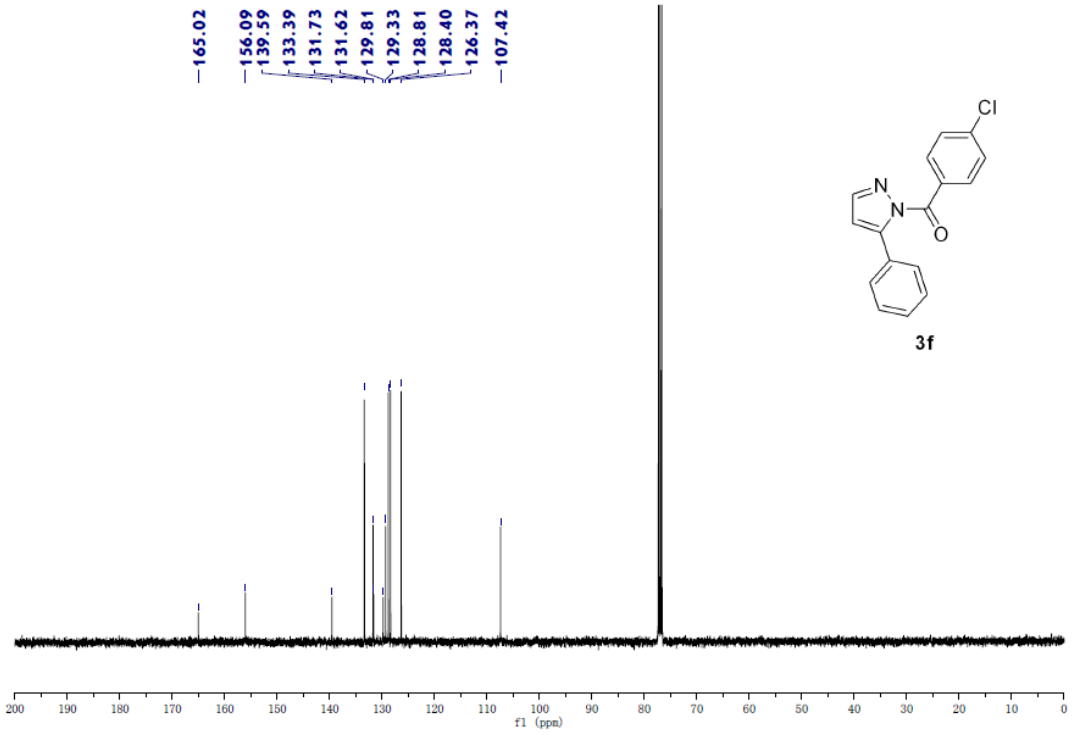
^{1}H NMR of product **3e**



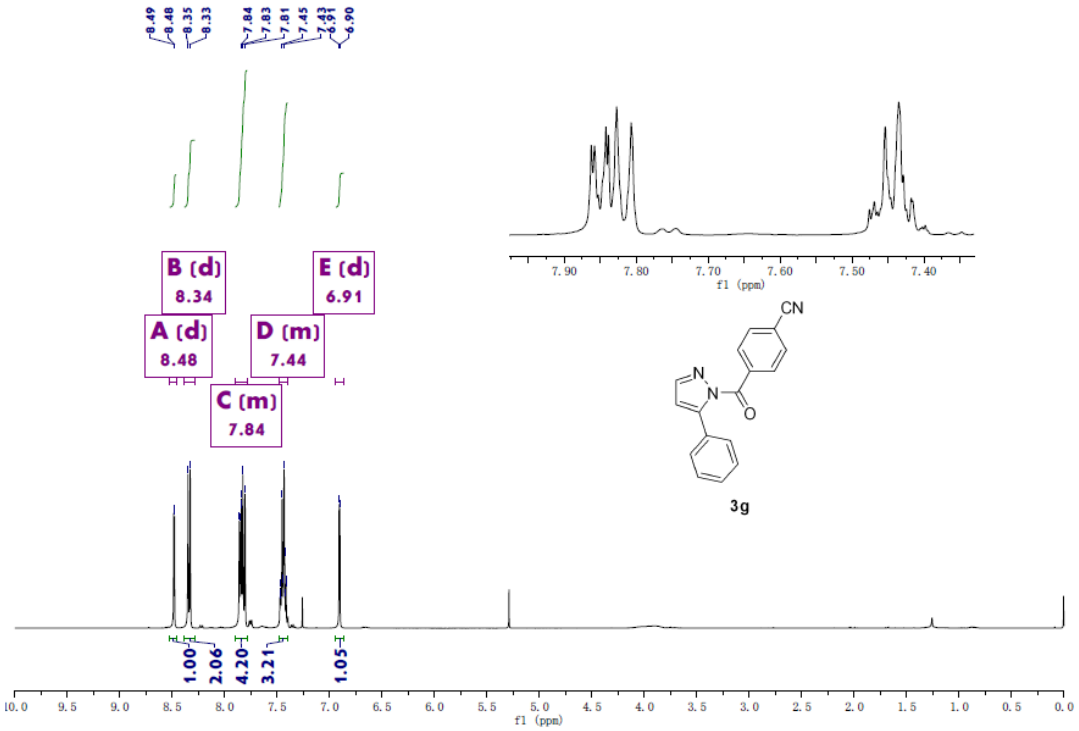
^{13}C NMR of product **3e**



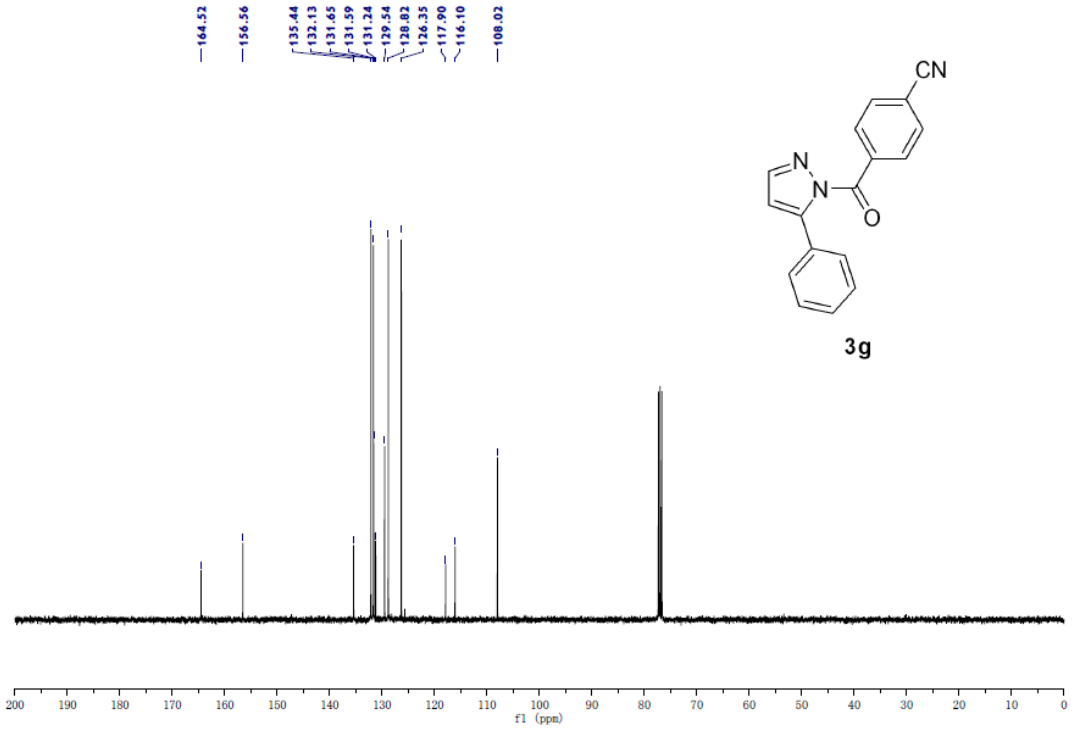
^{1}H NMR of product **3f**



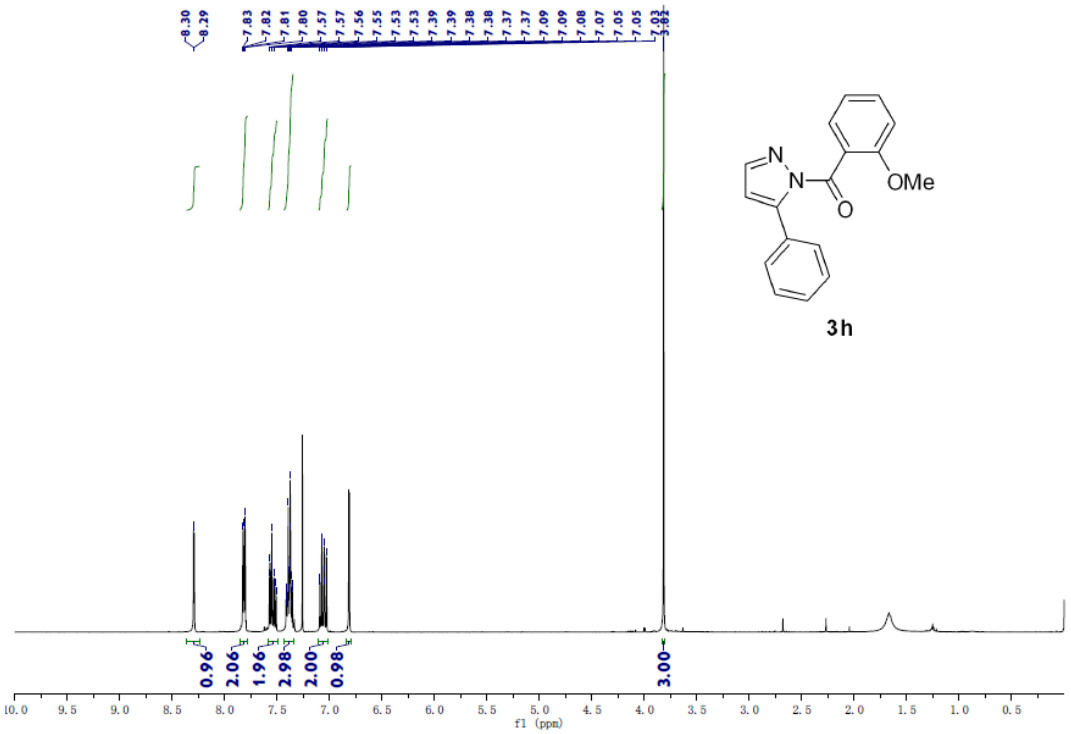
^{13}C NMR of product **3f**



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



^{13}C NMR of product **3g**



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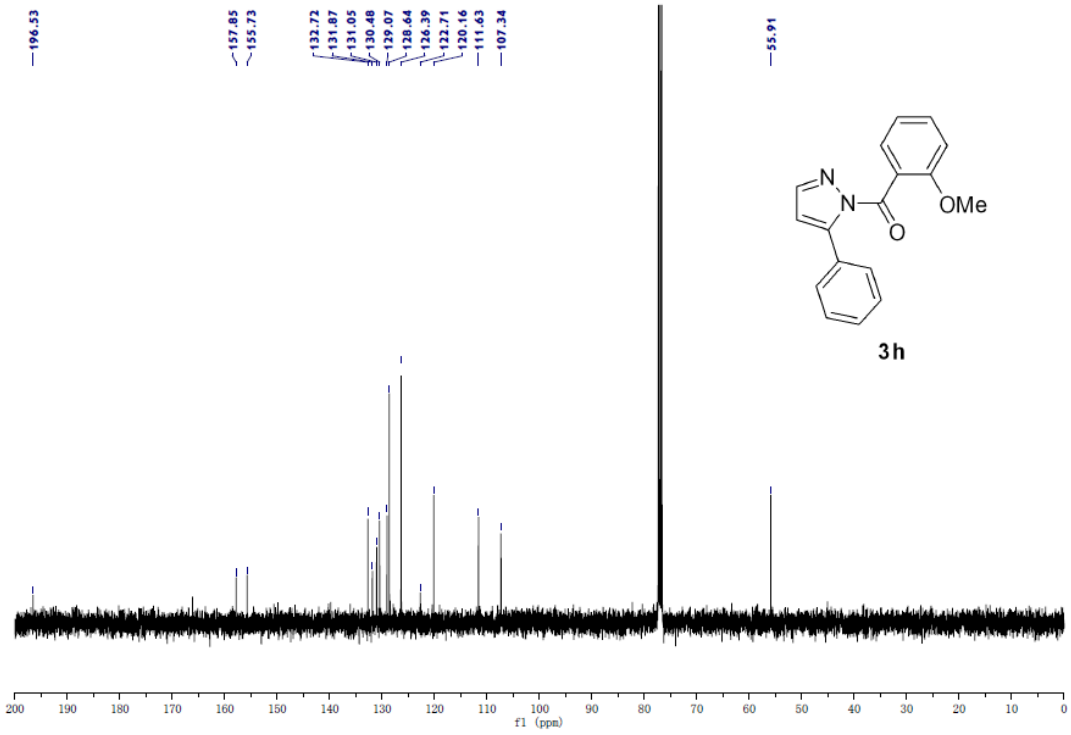
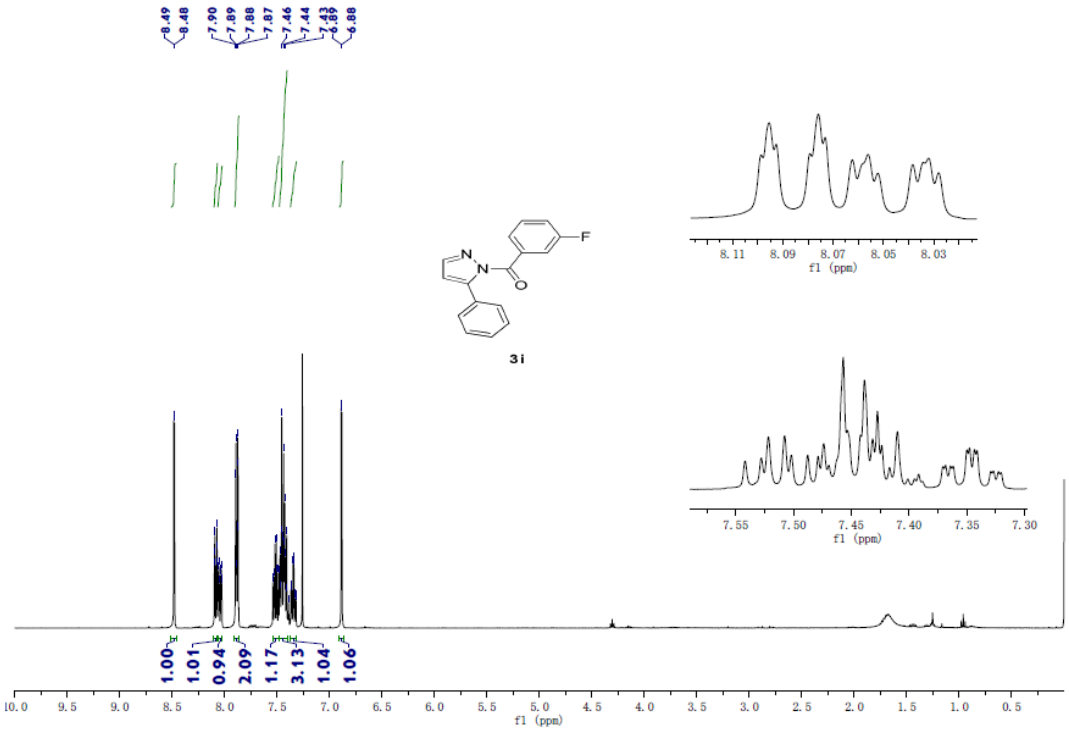
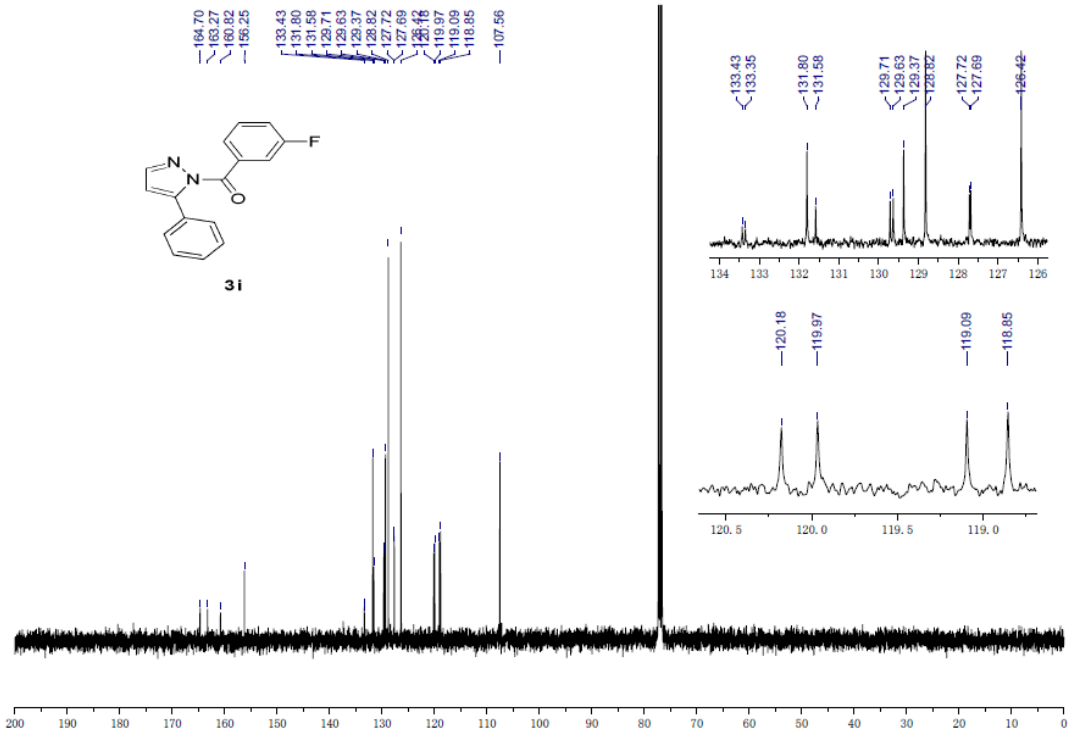


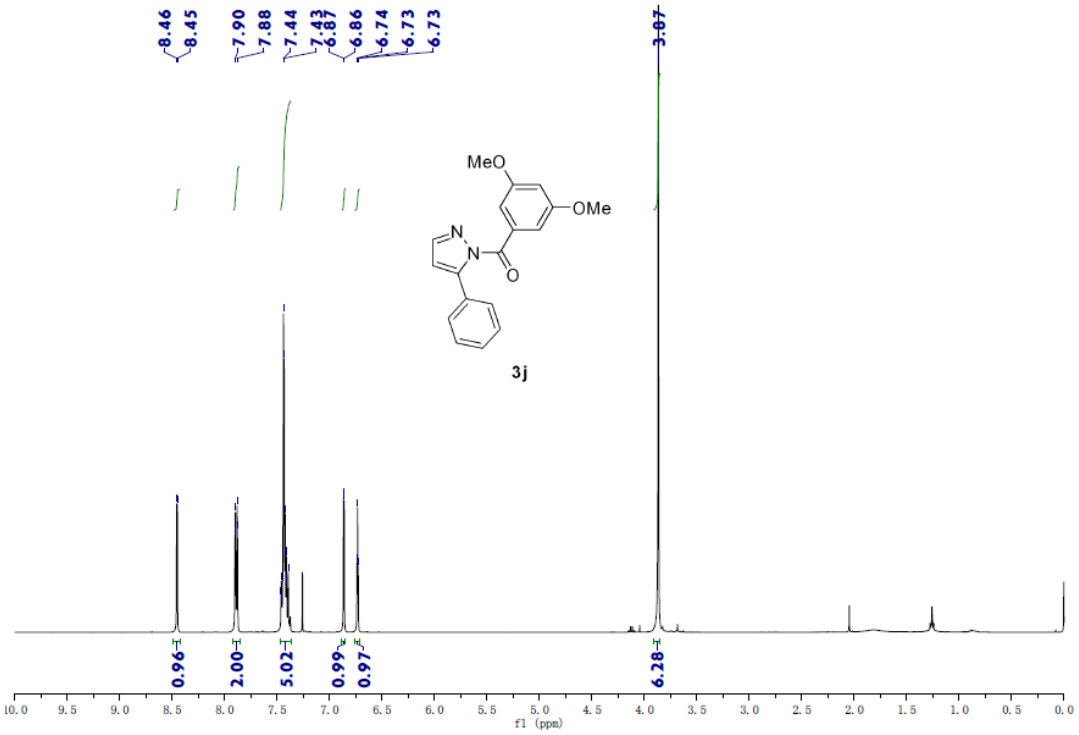
^{13}C NMR of product **3h**



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



^{13}C NMR of product **3i**



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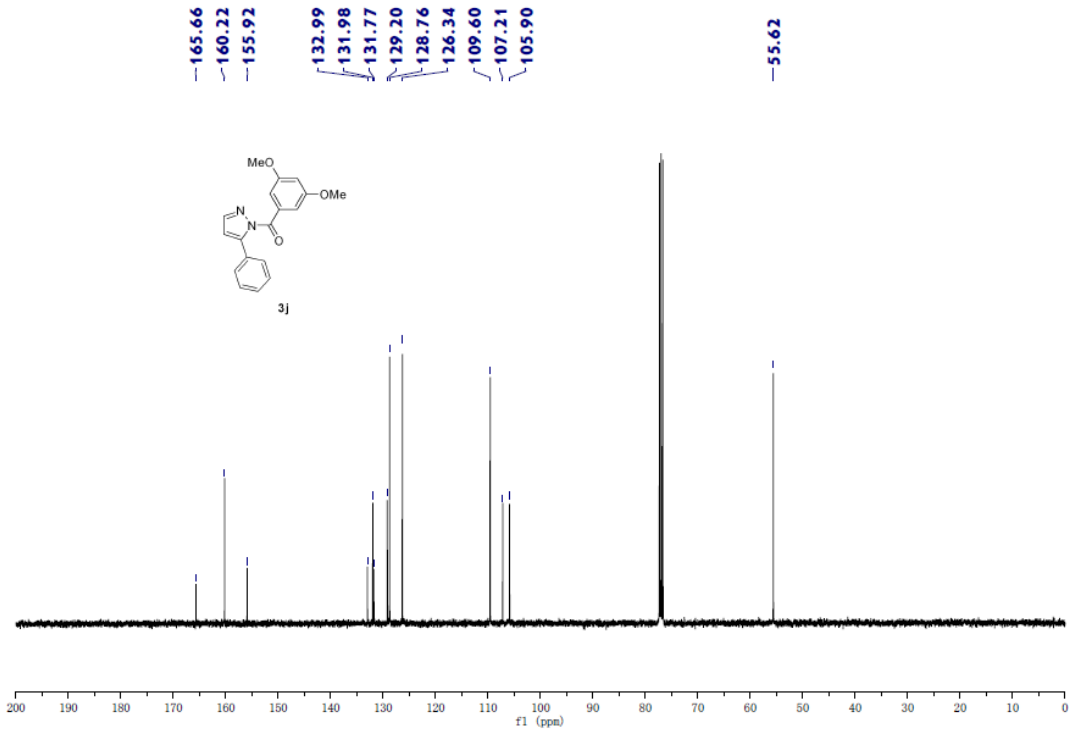

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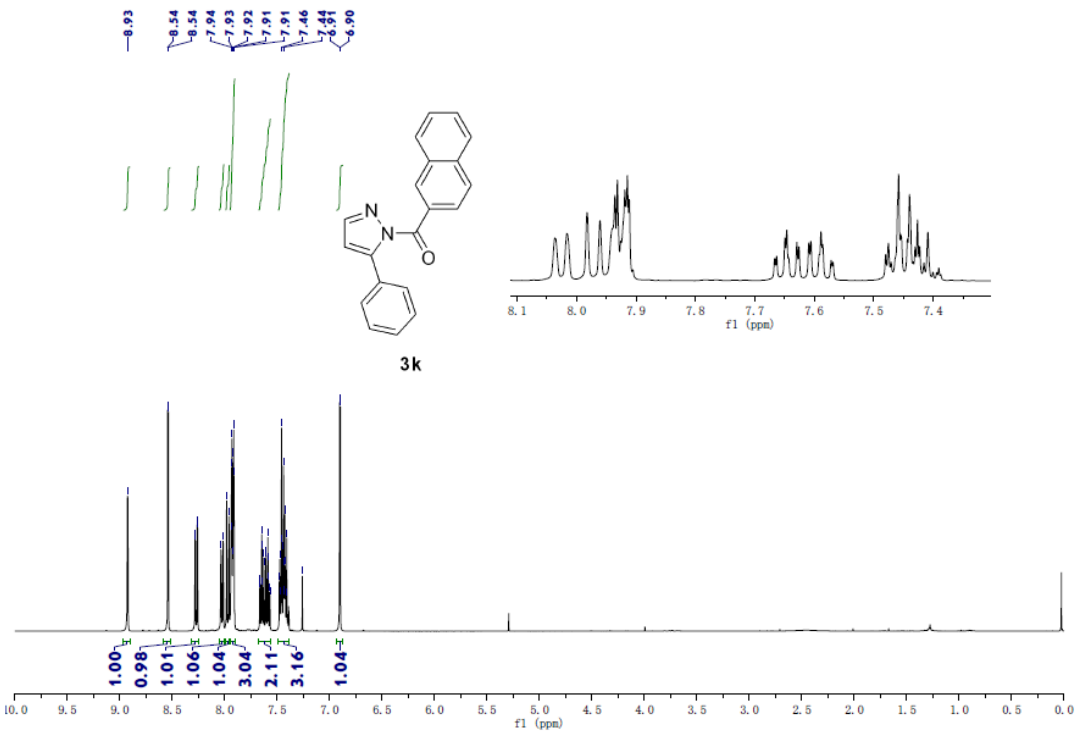

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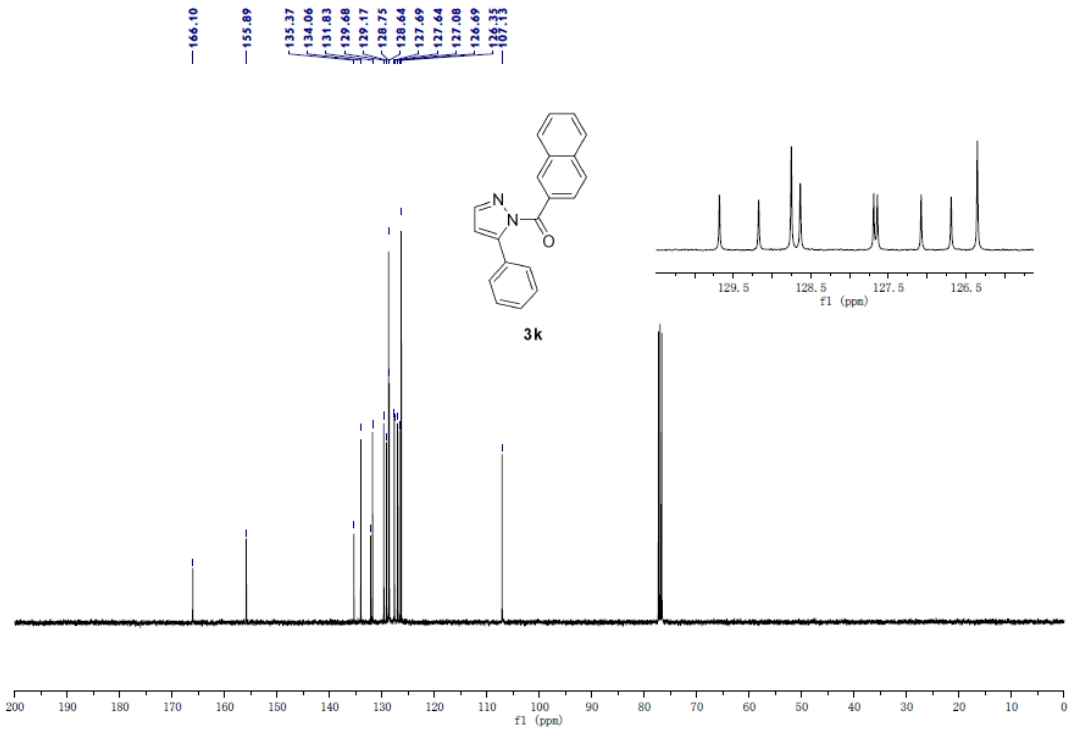

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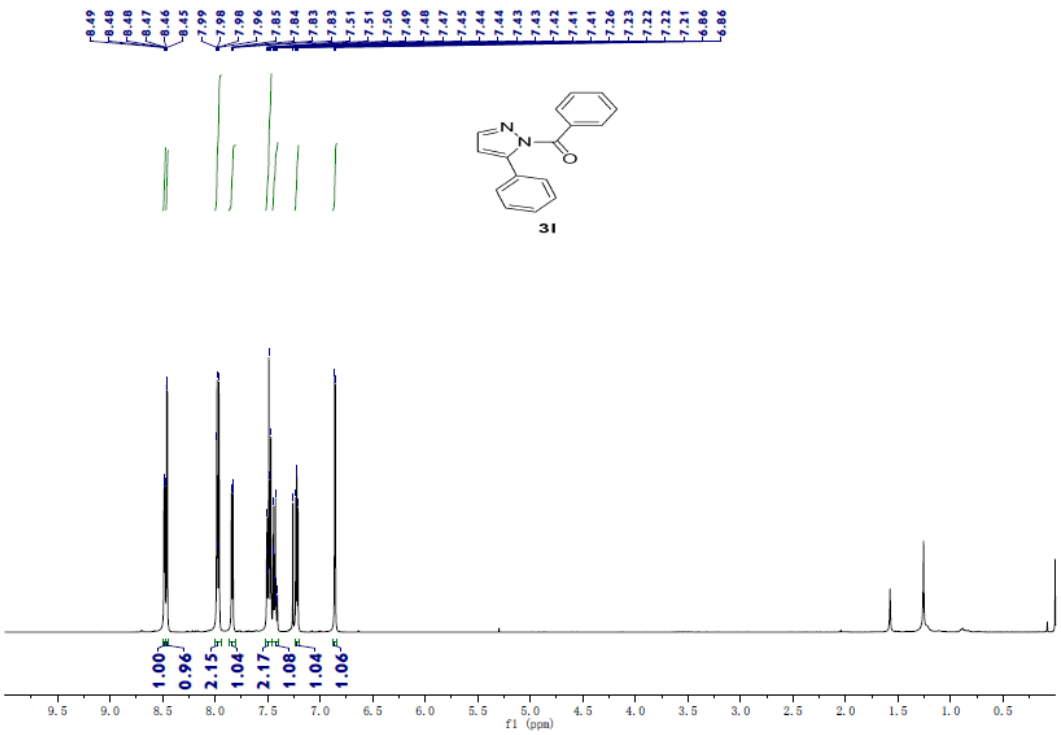
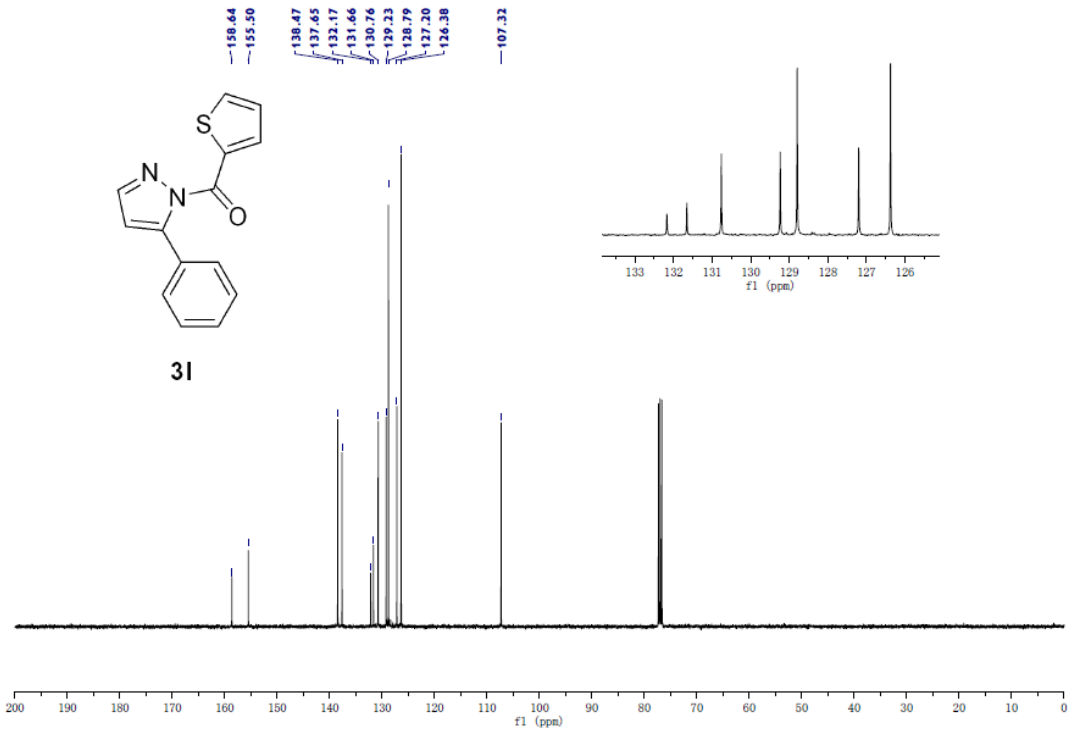
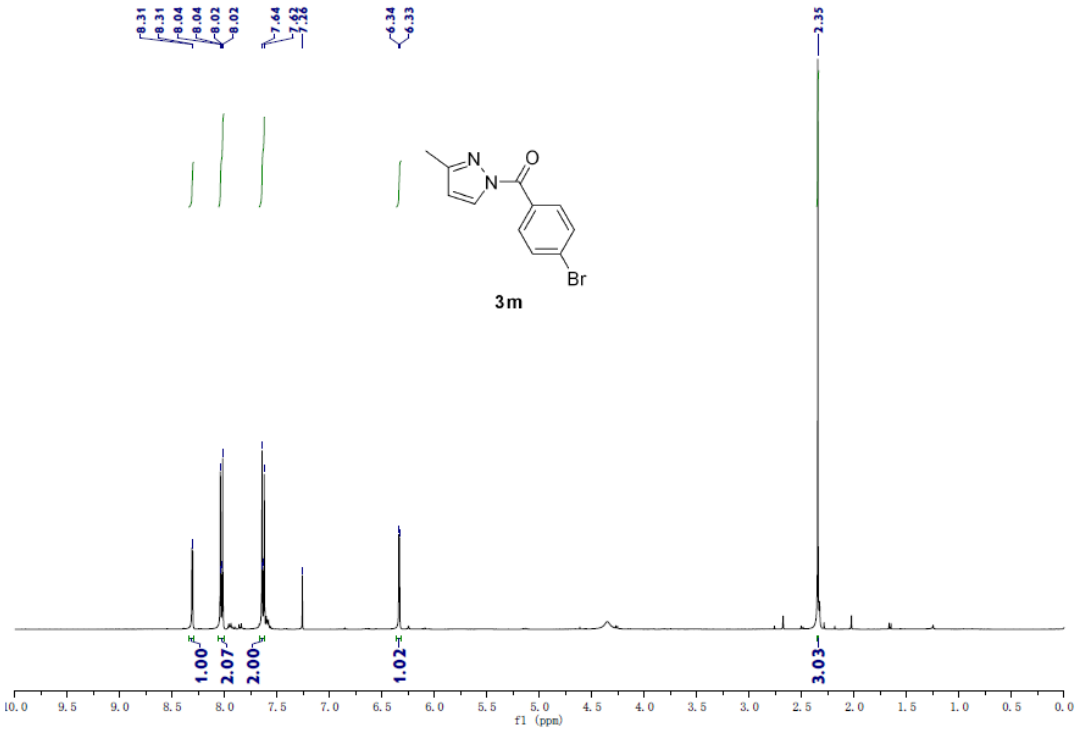


^{1}H NMR of product **3l**



^{13}C NMR of product **3l**



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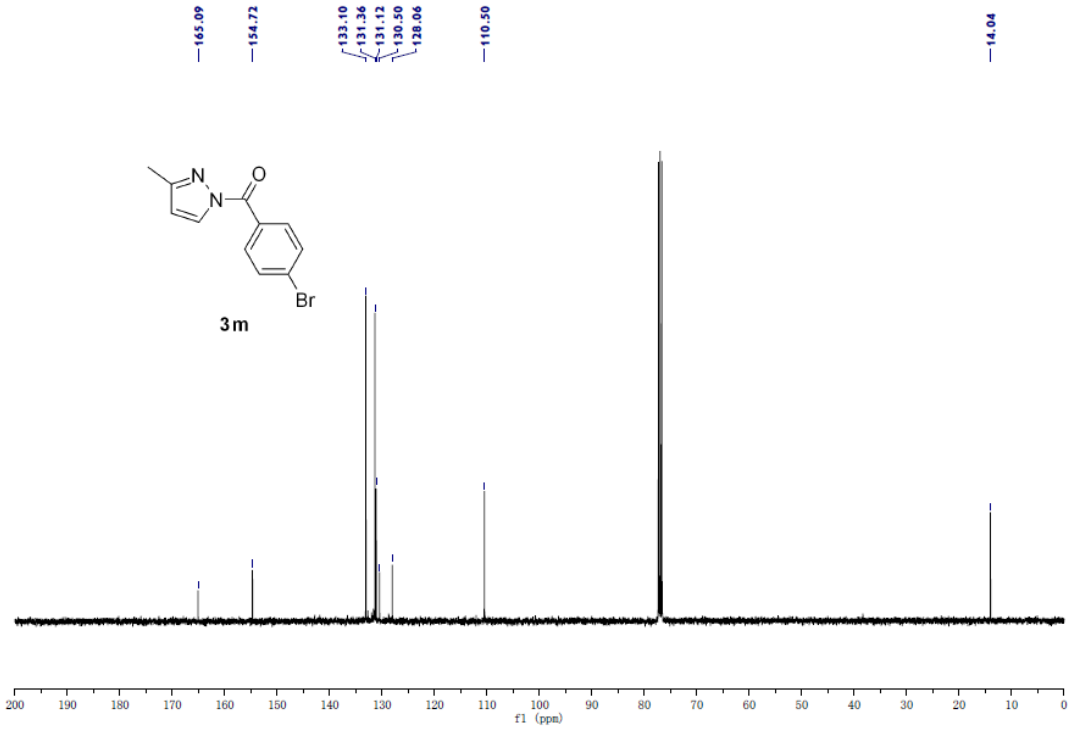

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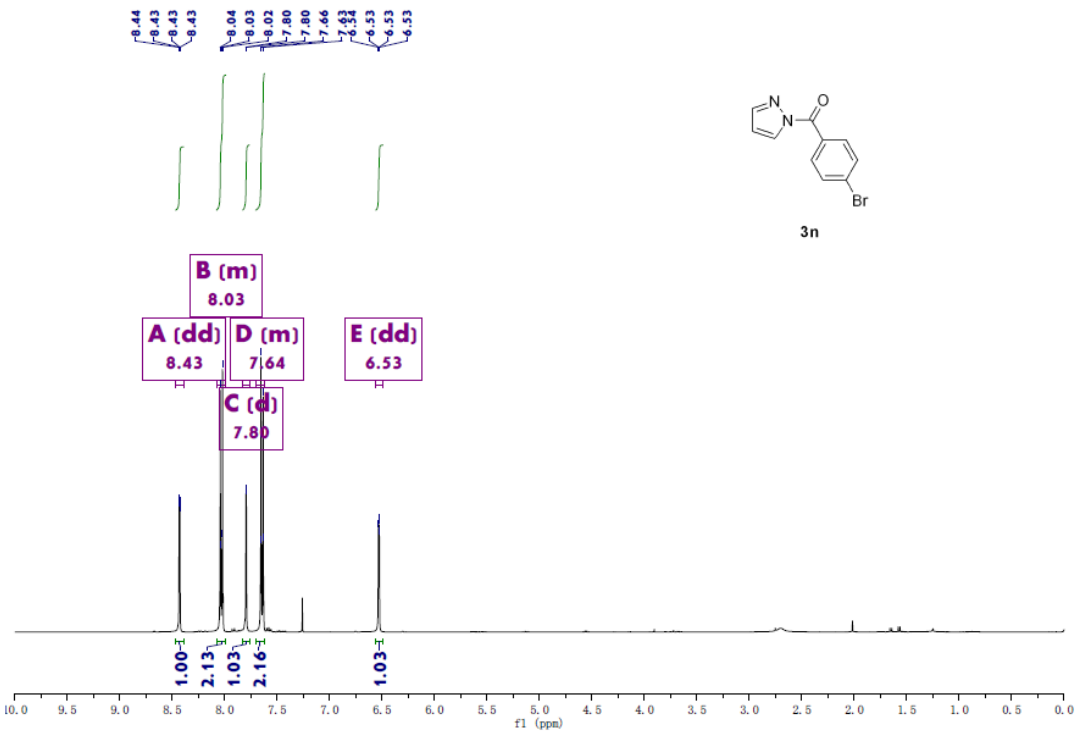

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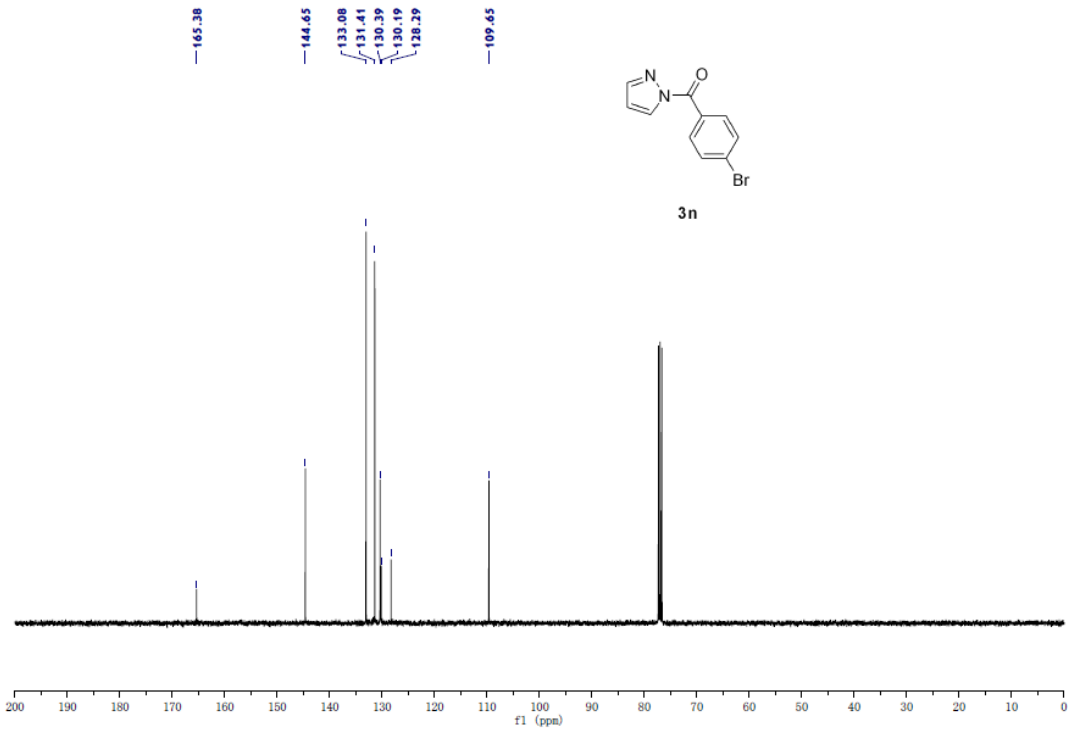

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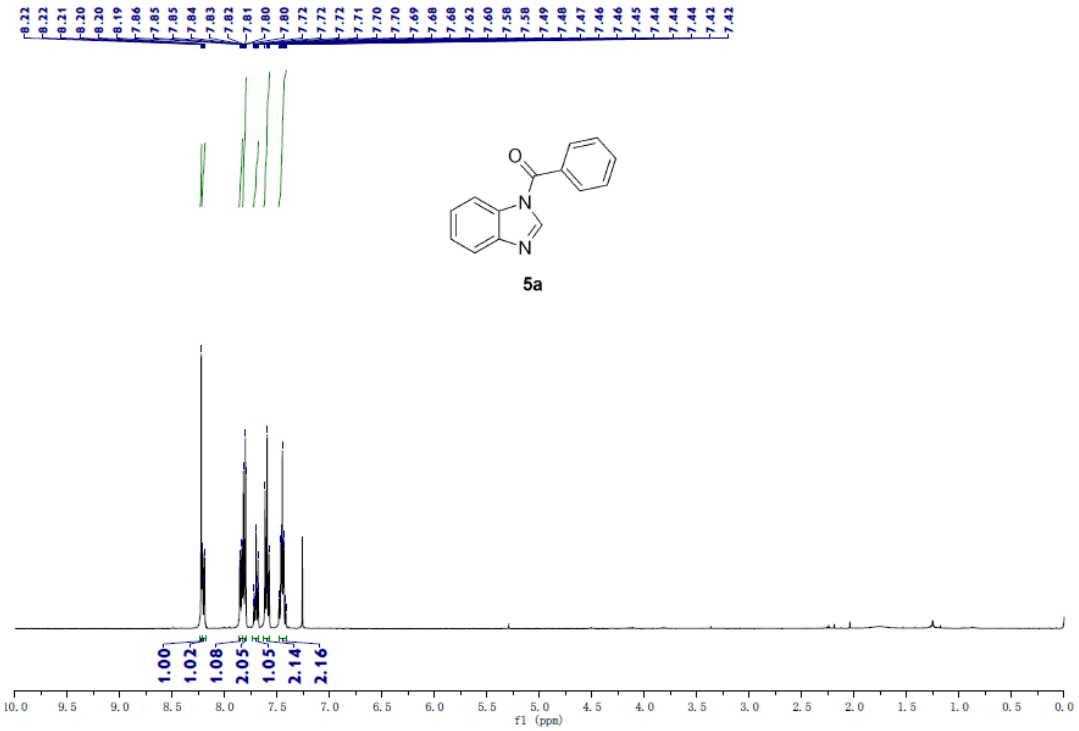
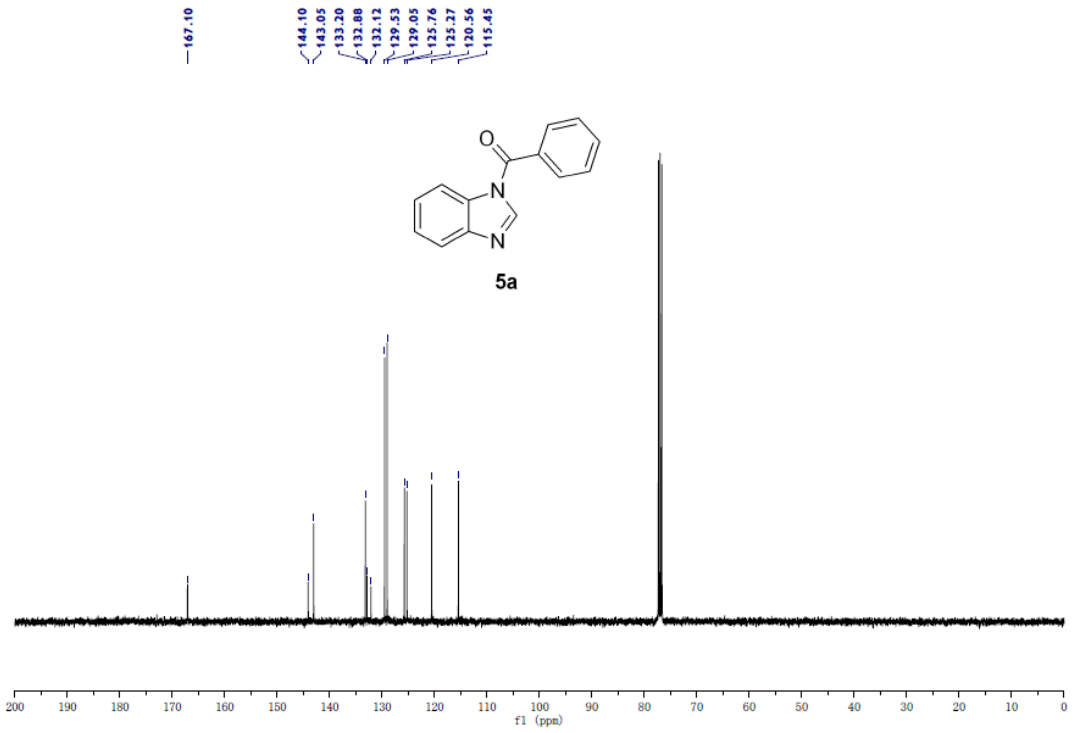
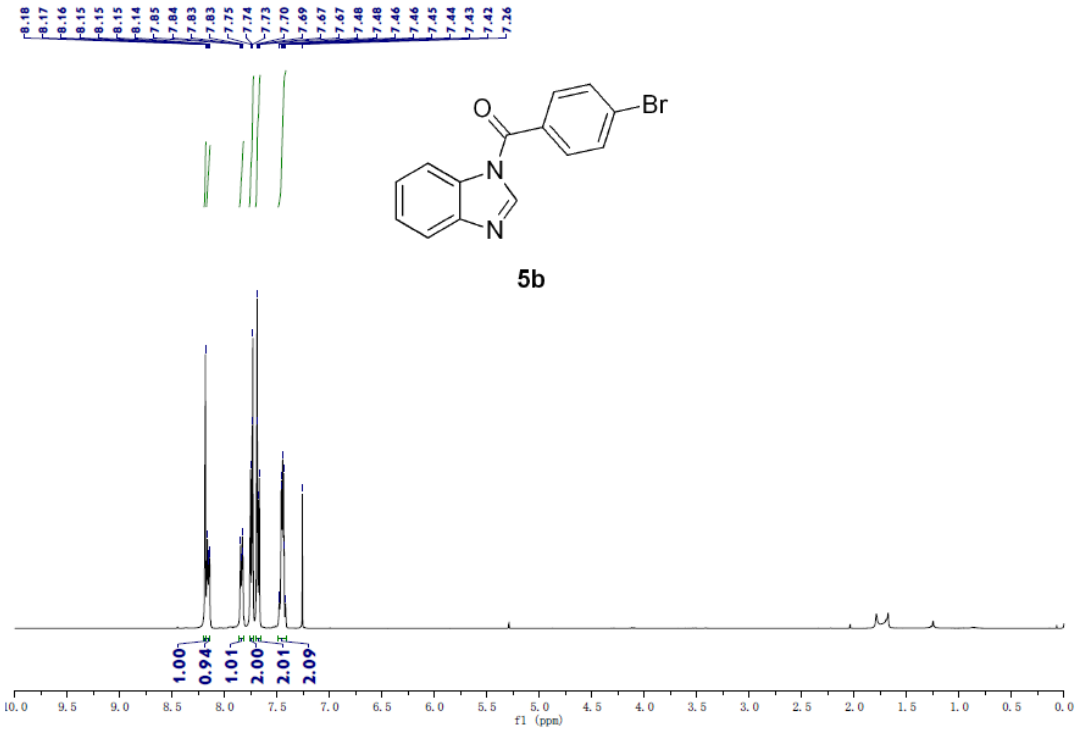


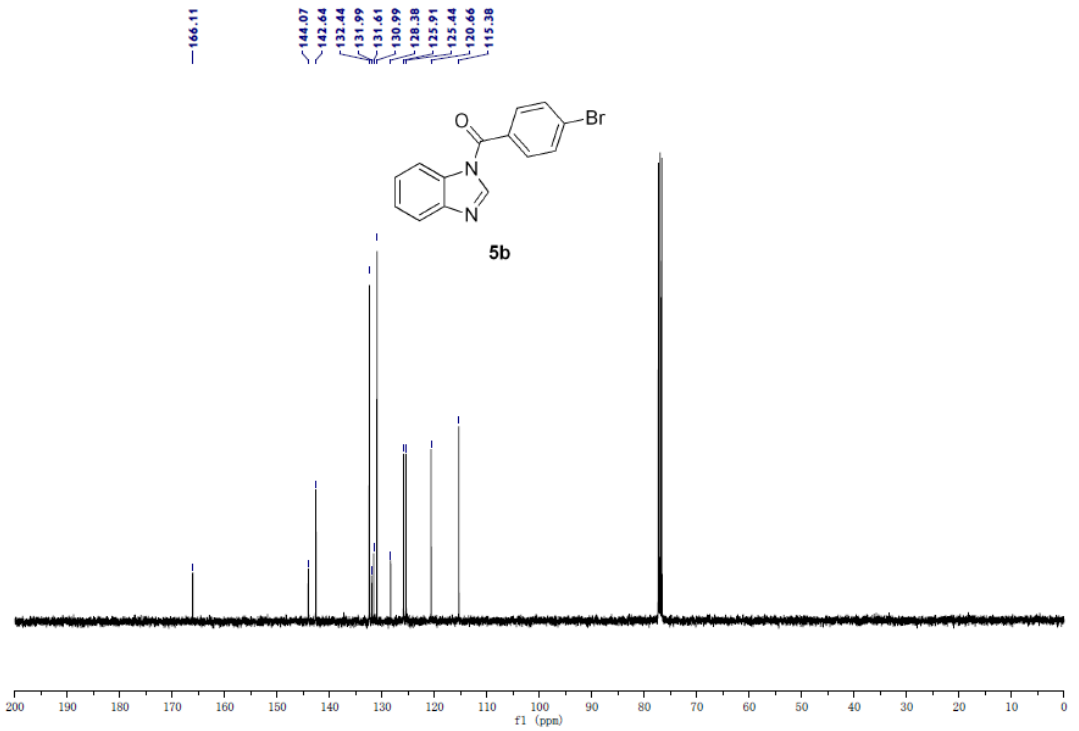
^{1}H NMR of product **5a**



^{13}C NMR of product **5a**



^{1}H NMR of product **5b**



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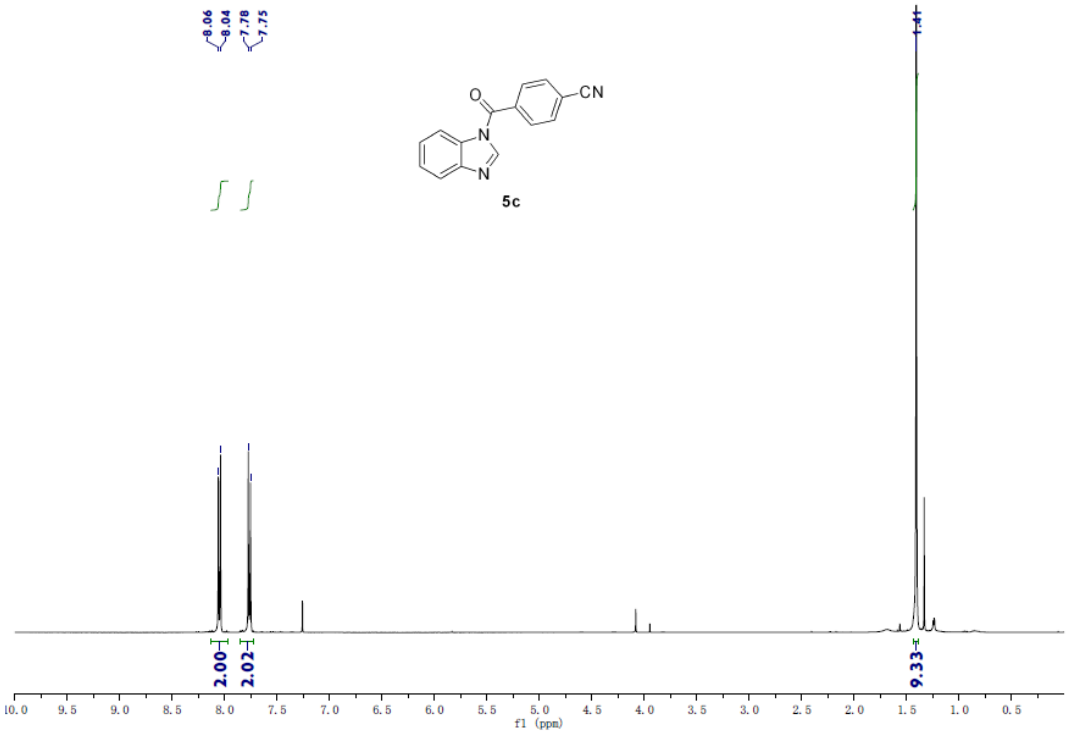

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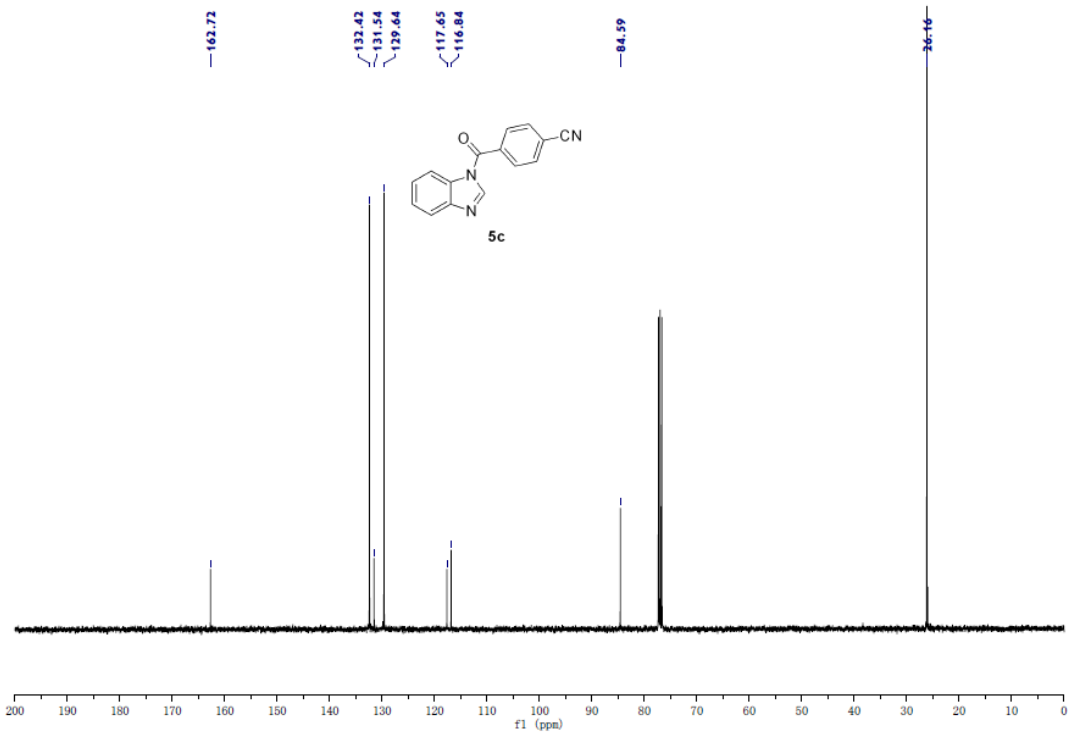

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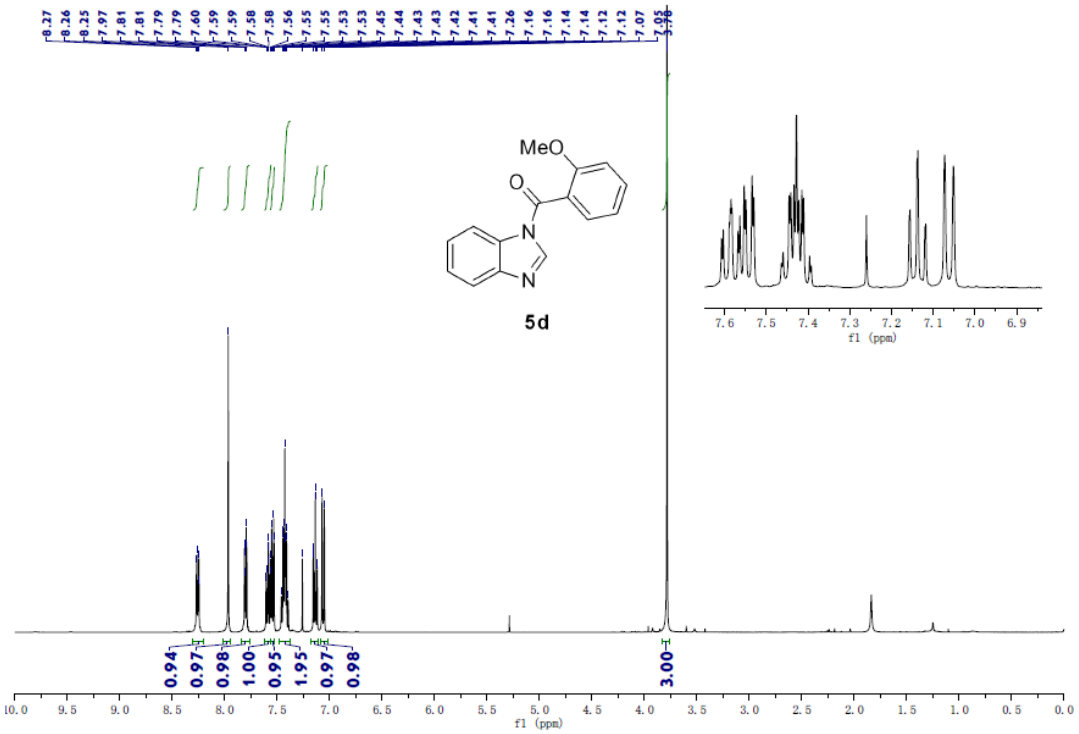
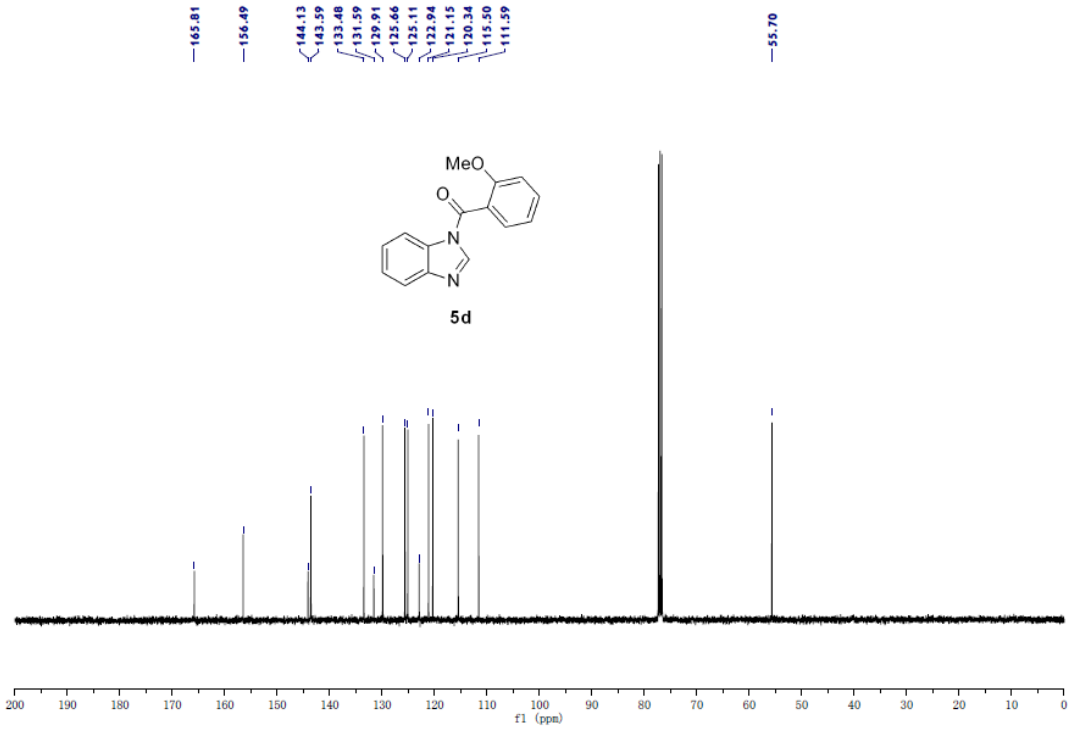
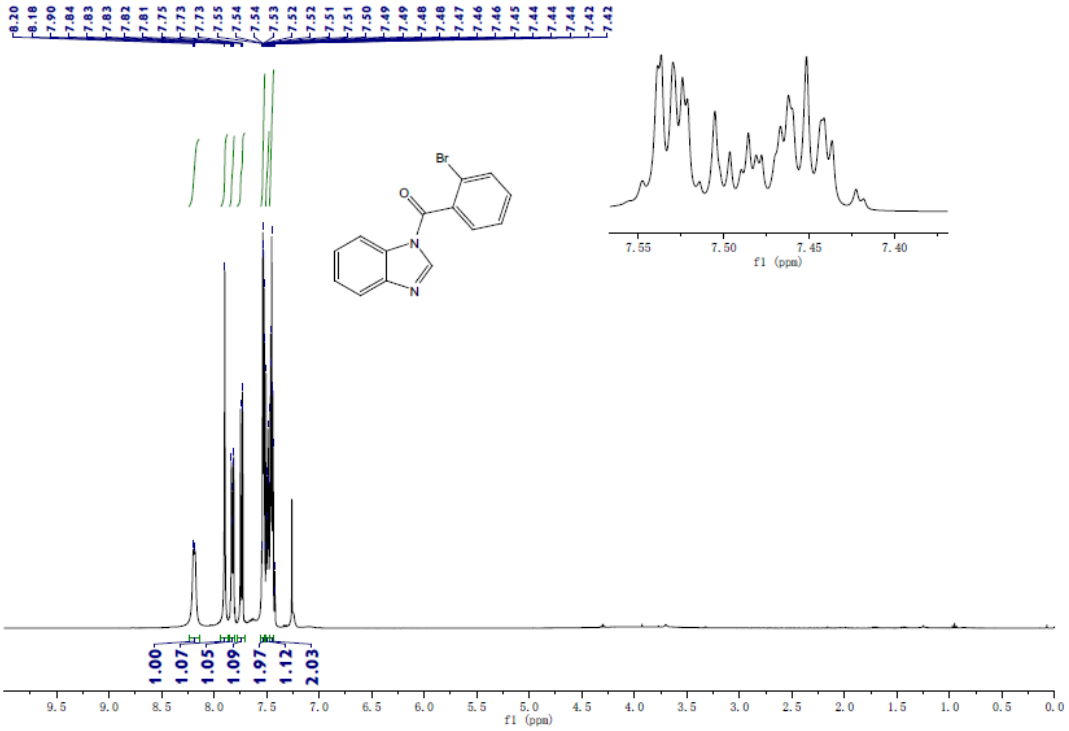


^{1}H NMR of product **5d**



^{13}C NMR of product **5d**



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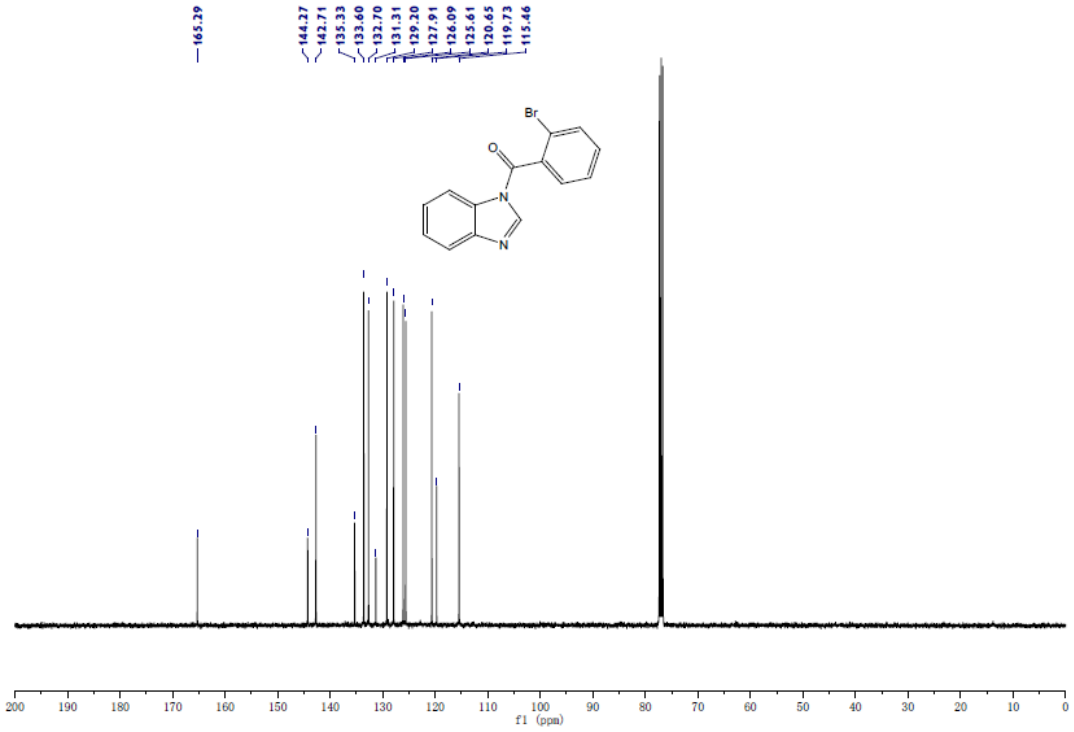

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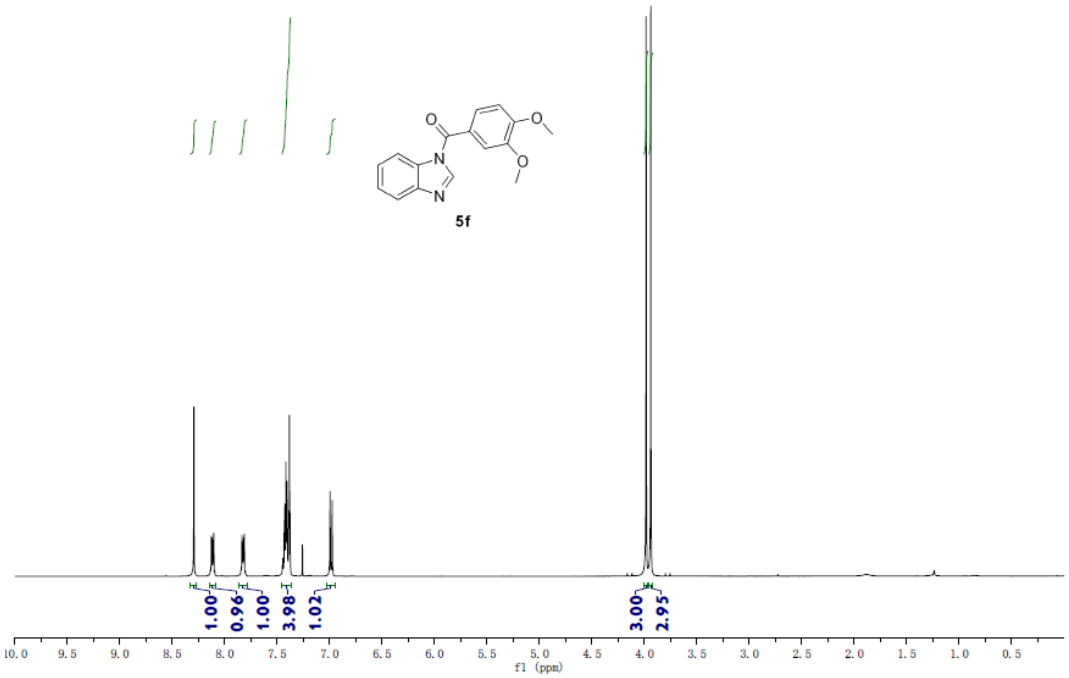
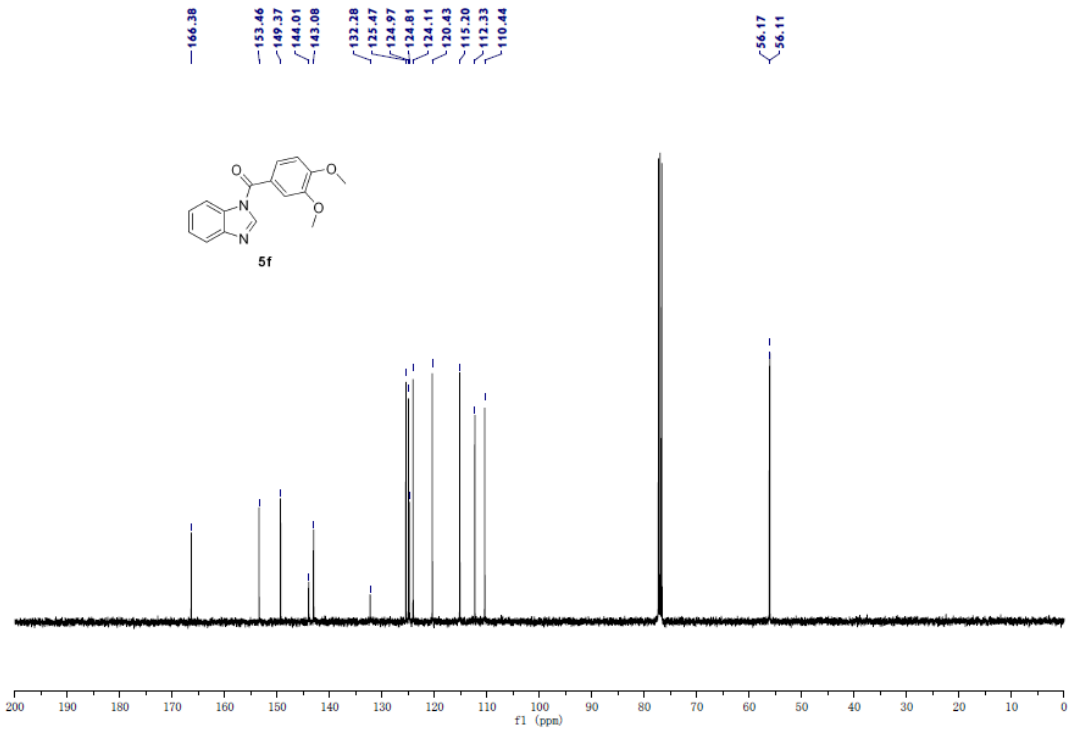
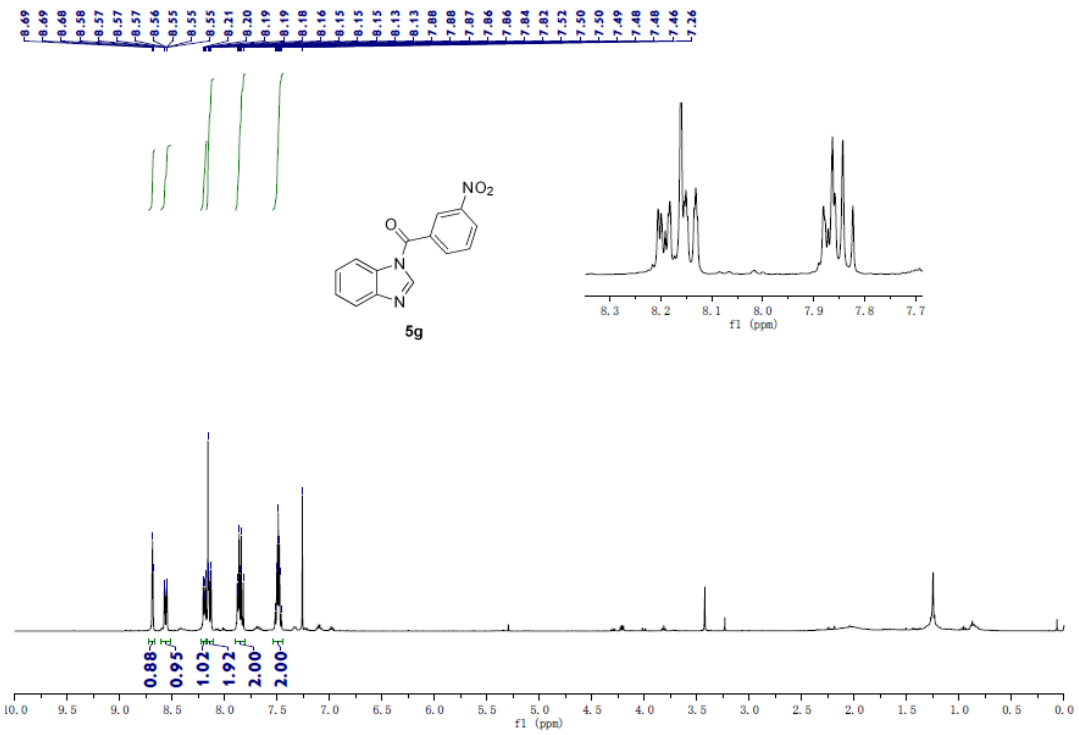


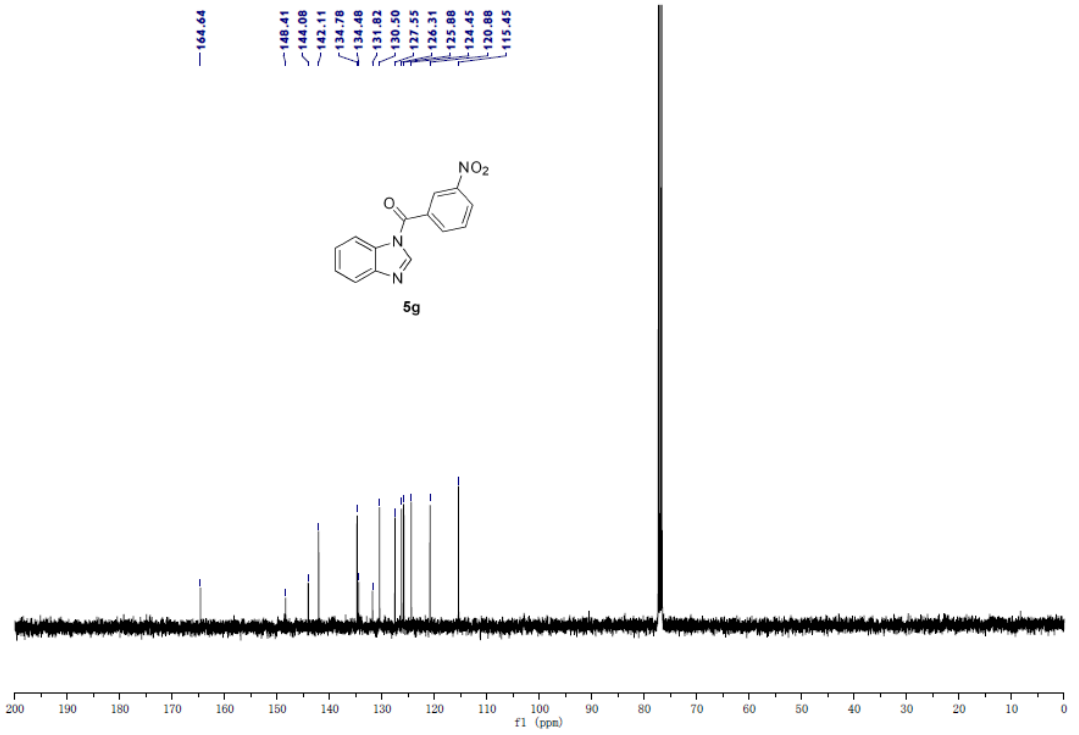
^{1}H NMR of product **5f**



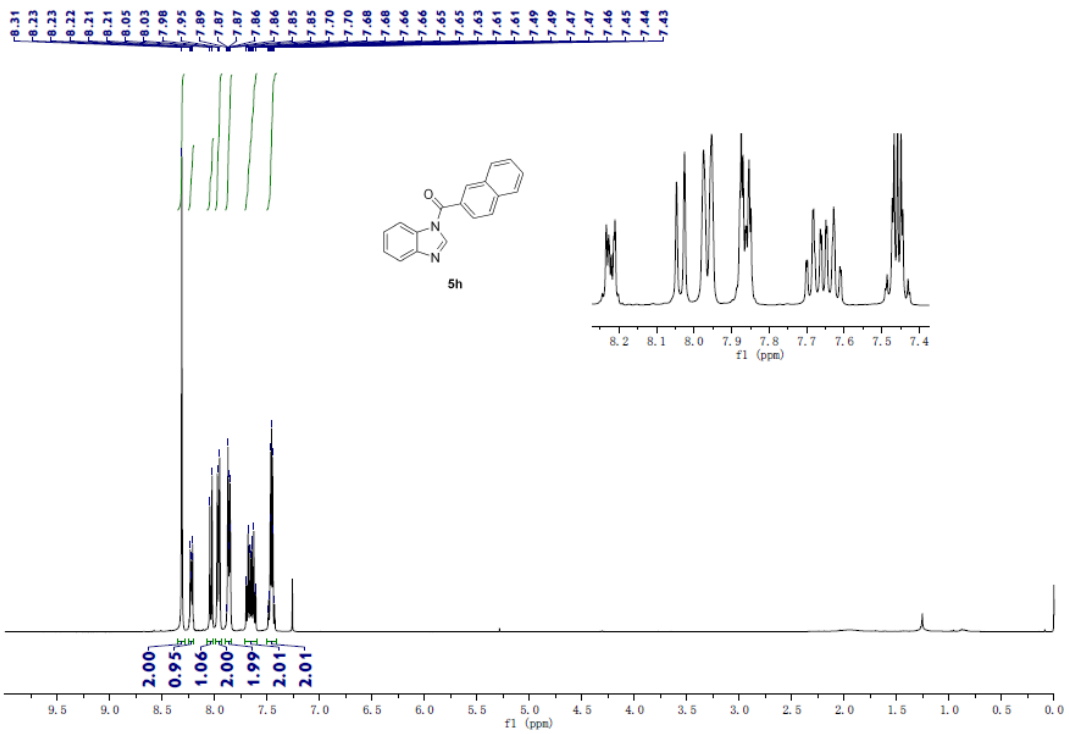
^{13}C NMR of product **5f**



^{1}H NMR of product **5g**



^{13}C NMR of product **5g**



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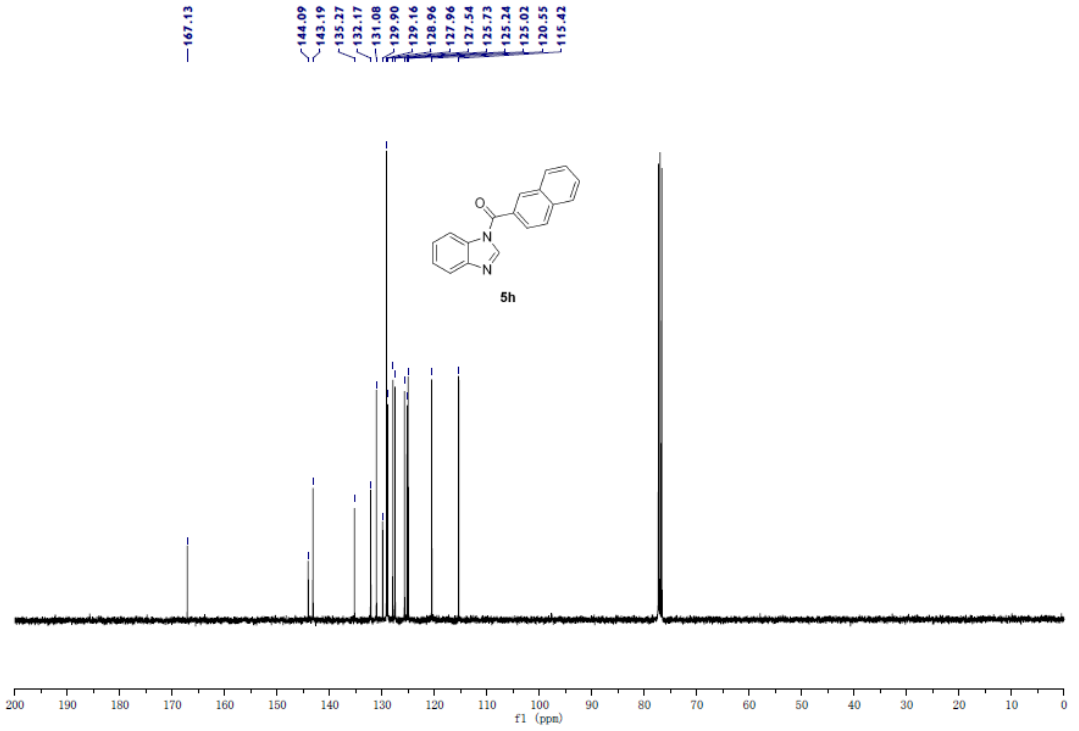

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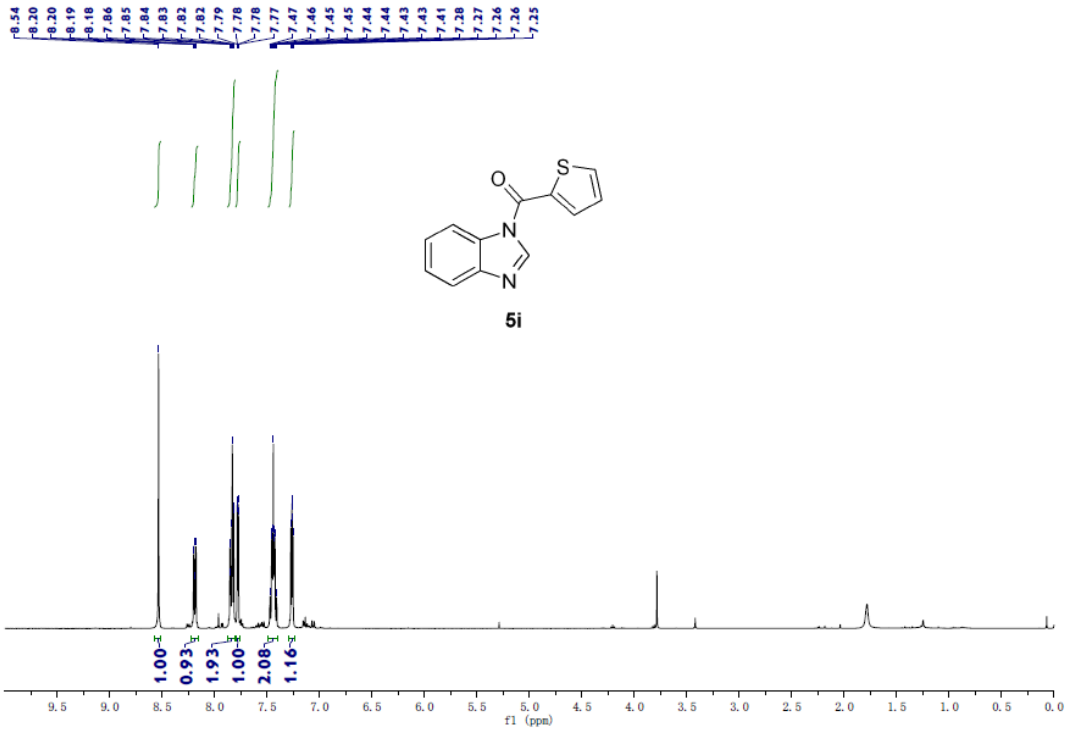
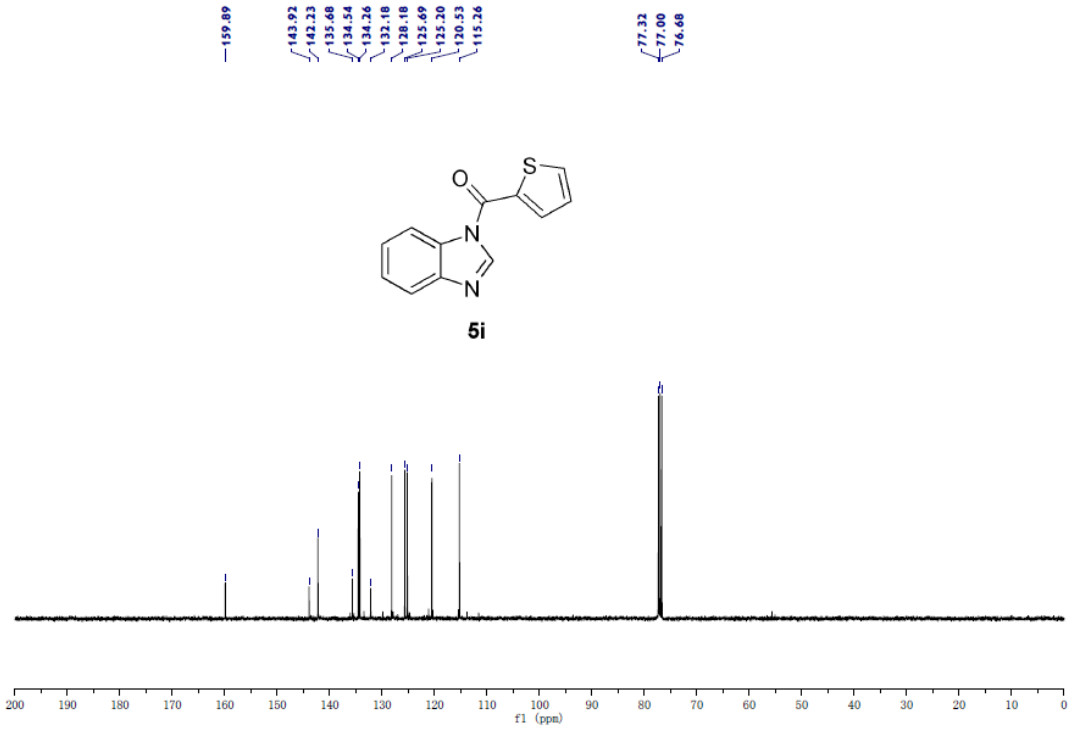


^{1}H NMR of product **5i**



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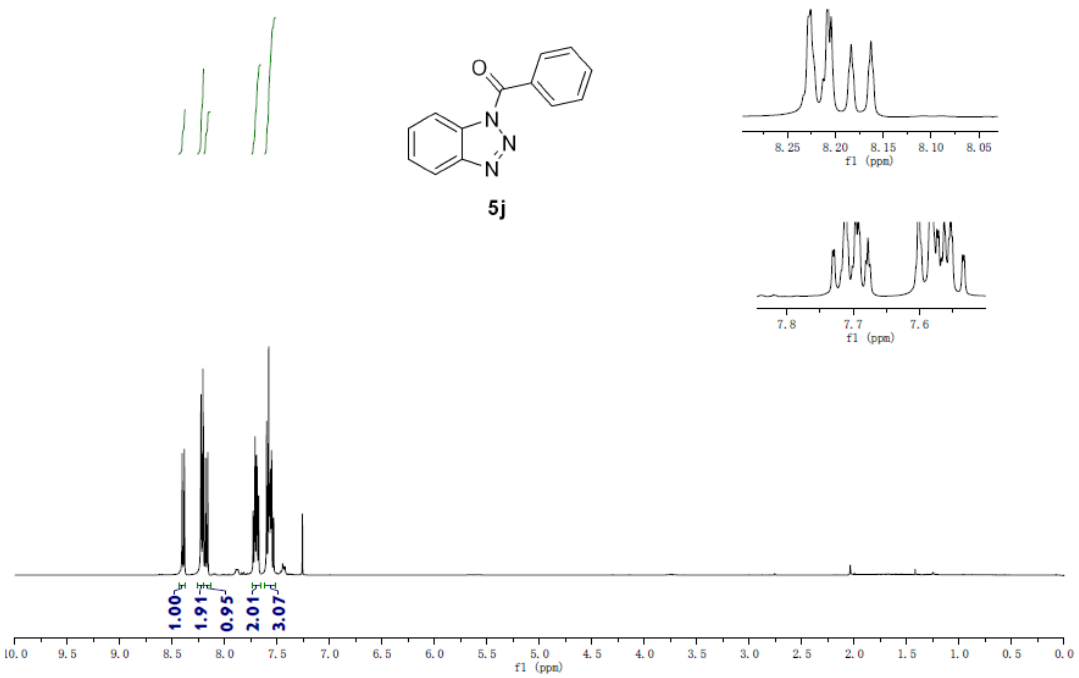

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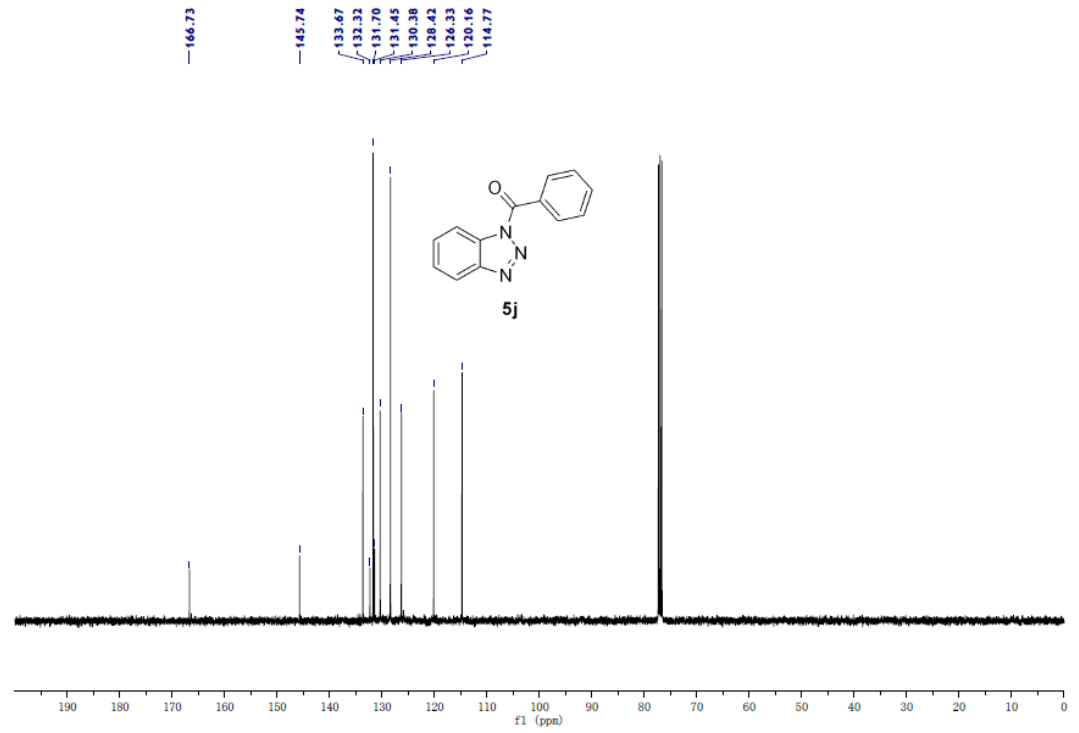

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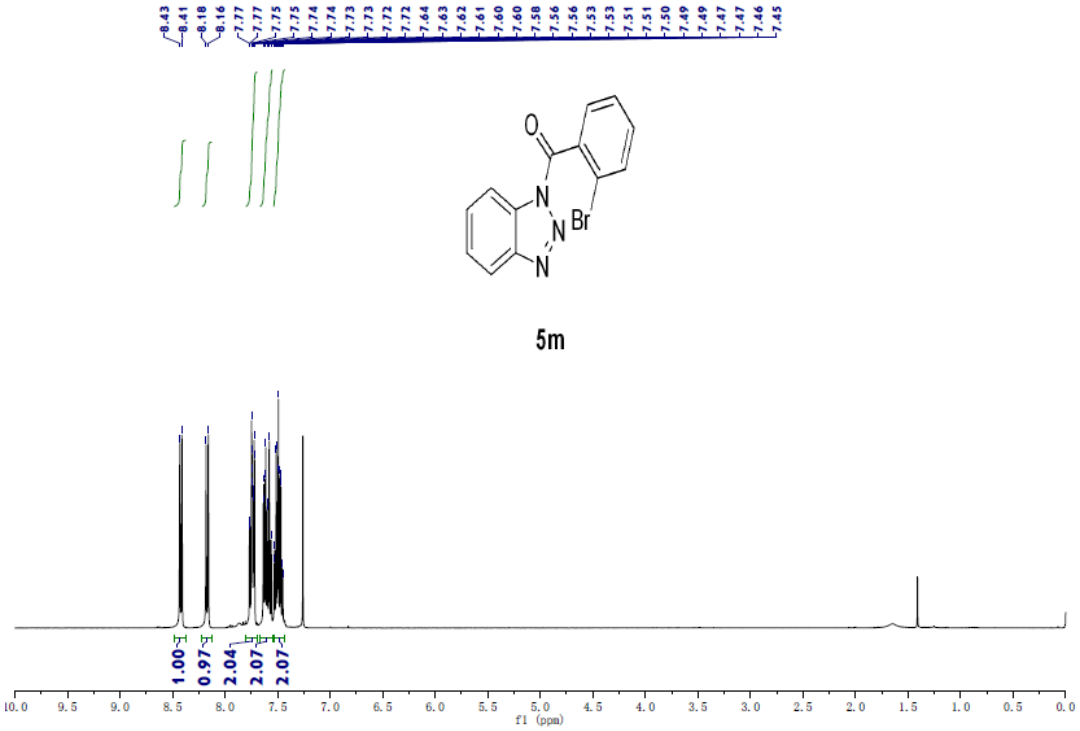
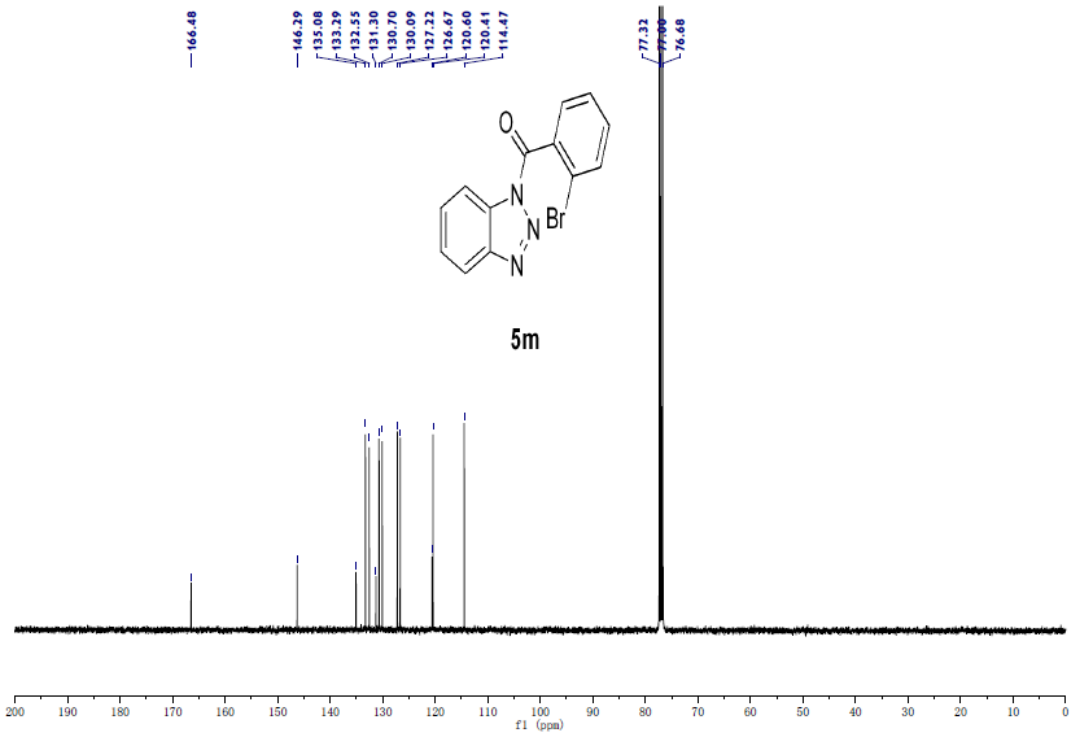


^{1}H NMR of product **5m**



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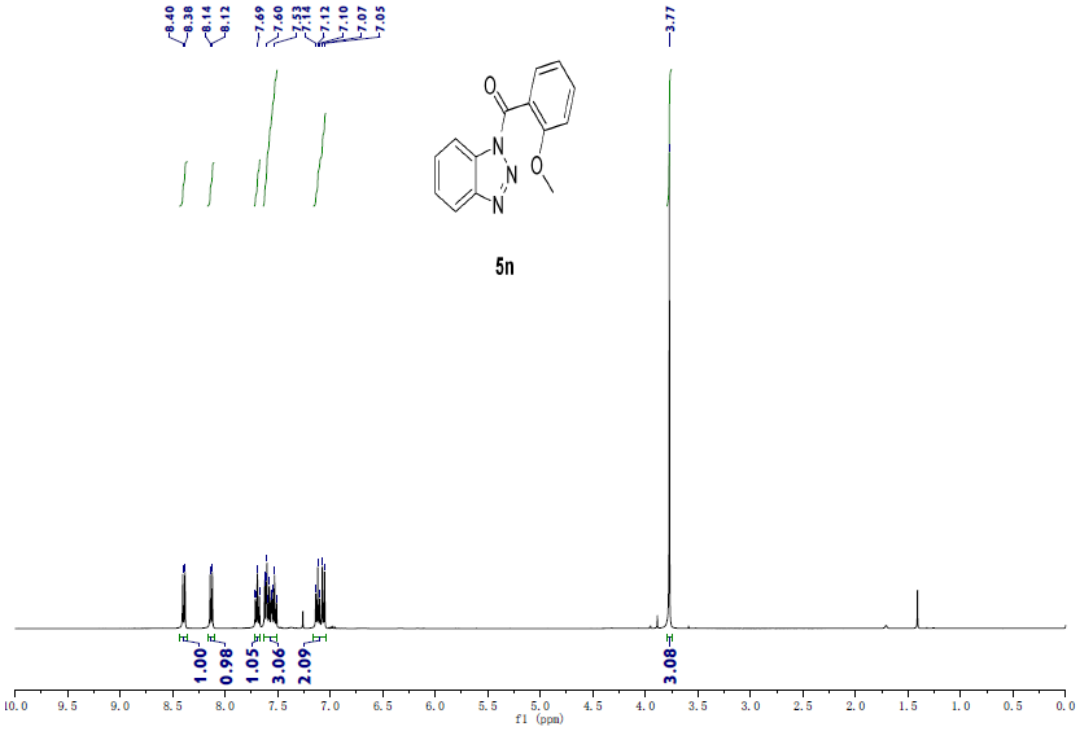

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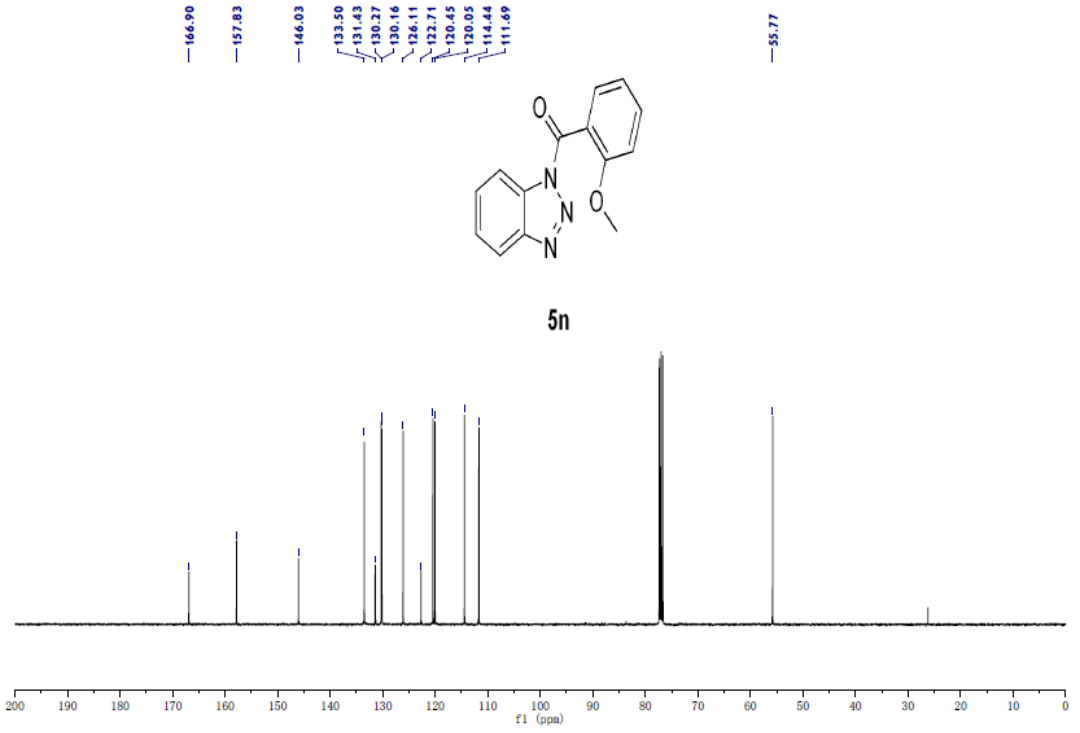

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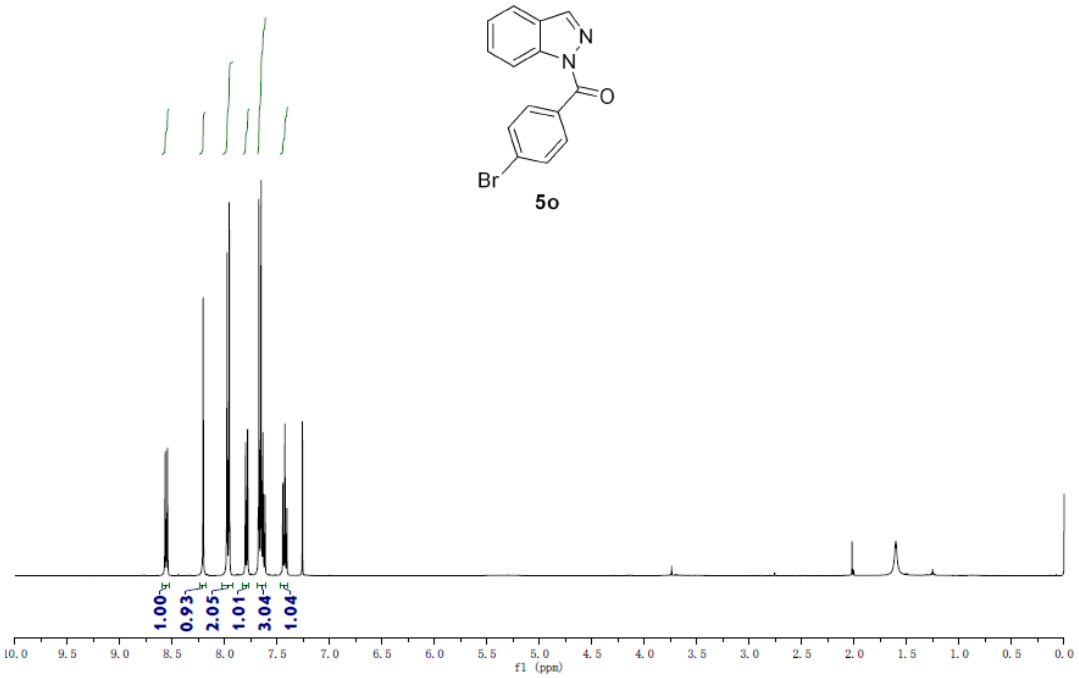
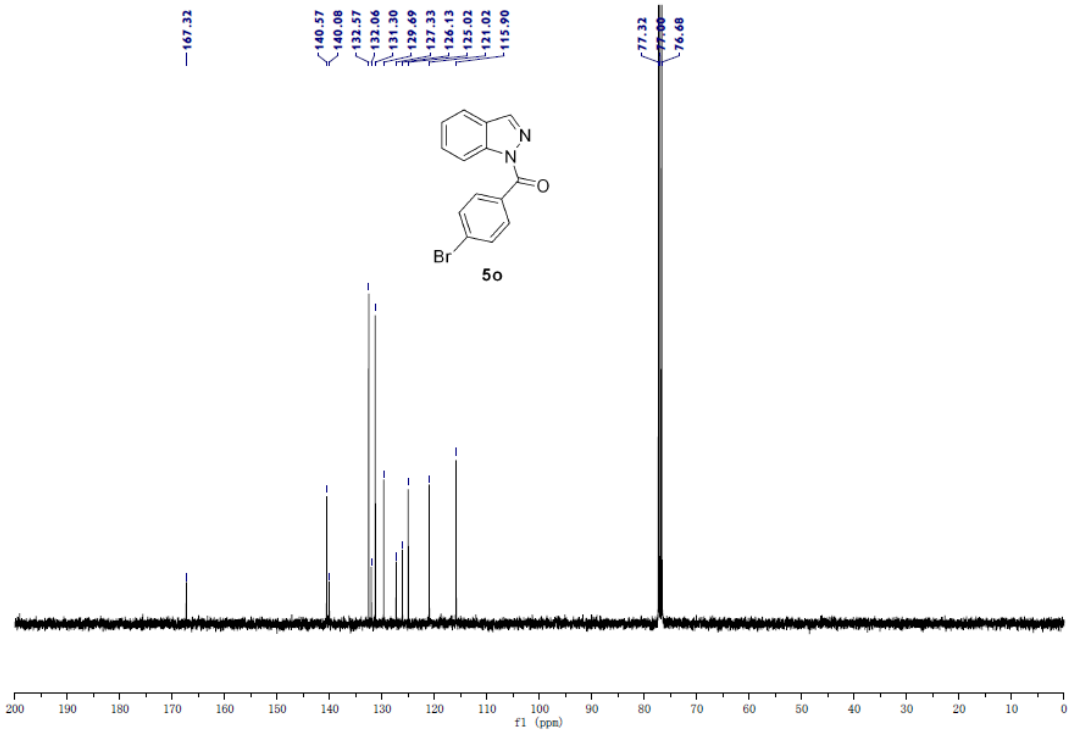


^{1}H NMR of product **5o**



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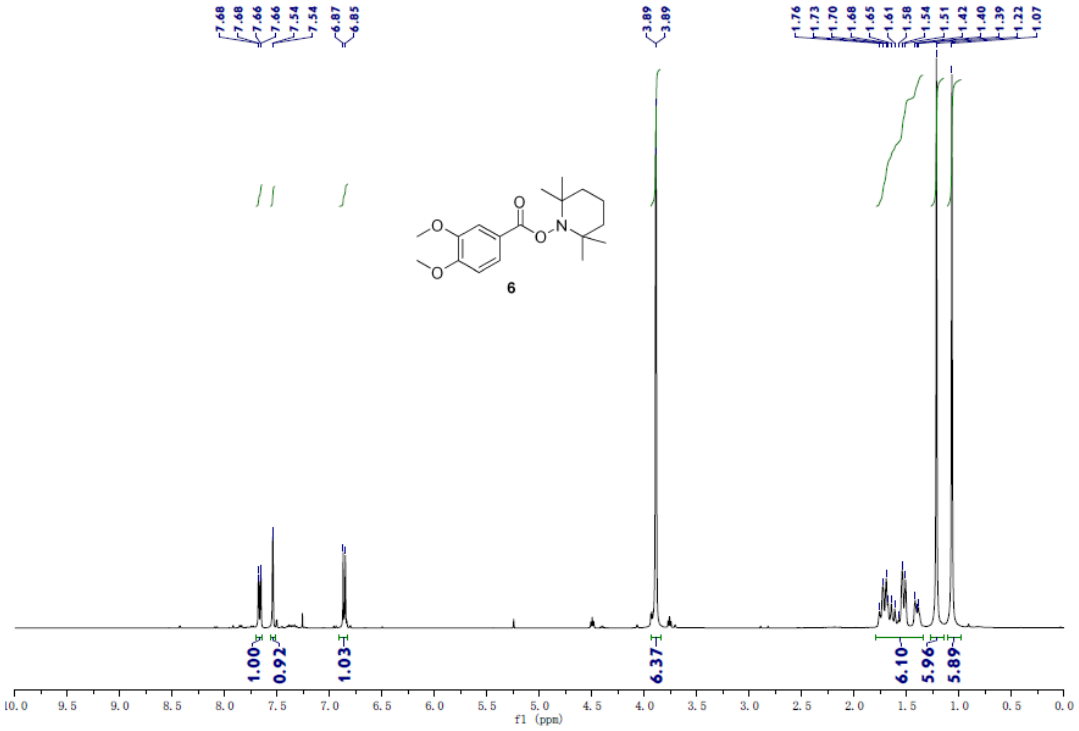
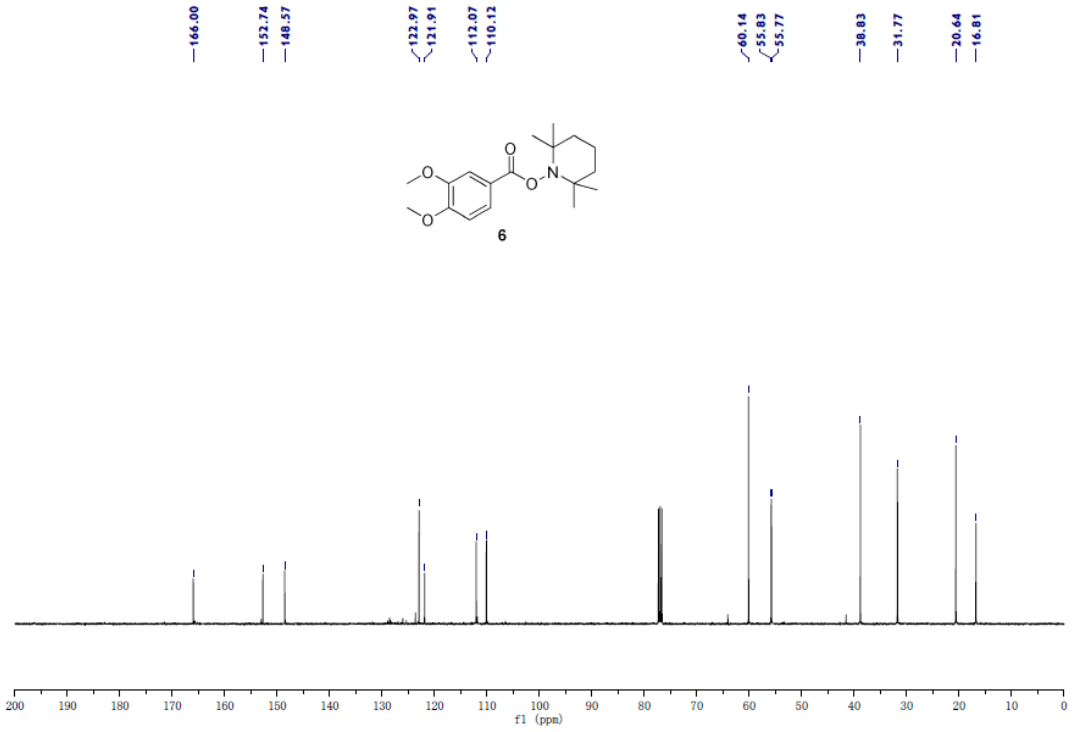


^{1}H NMR of product **6**



^{13}C NMR of product **6**