

Supporting Information

for

**KOH-Mediated Synthesis of Amides from Azides and
1,3-Dicarbonyl Compounds**

Zhuoran Yang, Yao Xu, Xiaoming Liao, Wenjun Wang, Chang Lyu * and Xiaoxiang
Zhang *

College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037,
People's Republic of China.

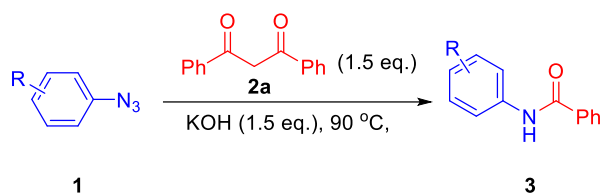
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General Considerations

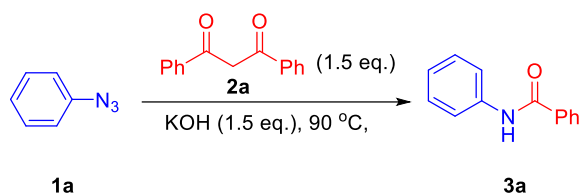
Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. Analytical thin layer chromatography (TLC) was performed using precoated silica gel plates. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and a gradient solvent system (petroleum ether/ethyl acetate as the eluant). ¹H NMR spectra were recorded on 400/600 MHz spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s (singlet), bs (broad singlet), d (doublet), t (triplet), dd(doublet of doublets), or m (multiplet). The number of protons (n) for a given resonance is indicated by nH, and coupling constants are reported as *J* values in Hz. All the starting materials **1** were prepared by the reported methods. ¹

General procedure for the synthesis of *N*-phenylbenzamides



To a 5 mL test tube were added phenyl azide **1** (0.1 mmol, 1 equiv), dibenzoylmethane **2a** (0.15 mmol, 1.5 equiv), KOH (0.15 mmol, 1.5 equiv), and 1,4-dioxane (1 mL). The reaction solution was then put into an aluminum heating block and stirred at 90 °C and reacted for two hours under air, which was monitored by TLC analysis. Upon completion, the reaction mixture was directly subjected to purification by flash column chromatography on silica gel to give the desired *N*-phenylbenzamides **3** (eluent: petrol ether/ethyl acetate = 10:1).

General procedure for the mechanism research



To a 5 mL test tube were added azidobenzene **1a** (0.1 mmol, 1 equiv), dibenzoylmethane **2a** (0.15 mmol, 1.5 equiv), KOH (0.15 mmol, 1.5 equiv), and 1,4-dioxane (1 mL). The reaction solution was then put into an aluminum heating block and stirred at 90 °C and reacted for two hours under air, which was monitored by TLC analysis. Upon completion, the reaction mixture was directly sent to check the crude NMR. After careful checking the crude NMR, we found the methyl peak of toluene, which confirmed our mechanism hypothesis.

Figure S1. ^1H NMR Spectra of Crude products (600 MHz, CDCl_3).

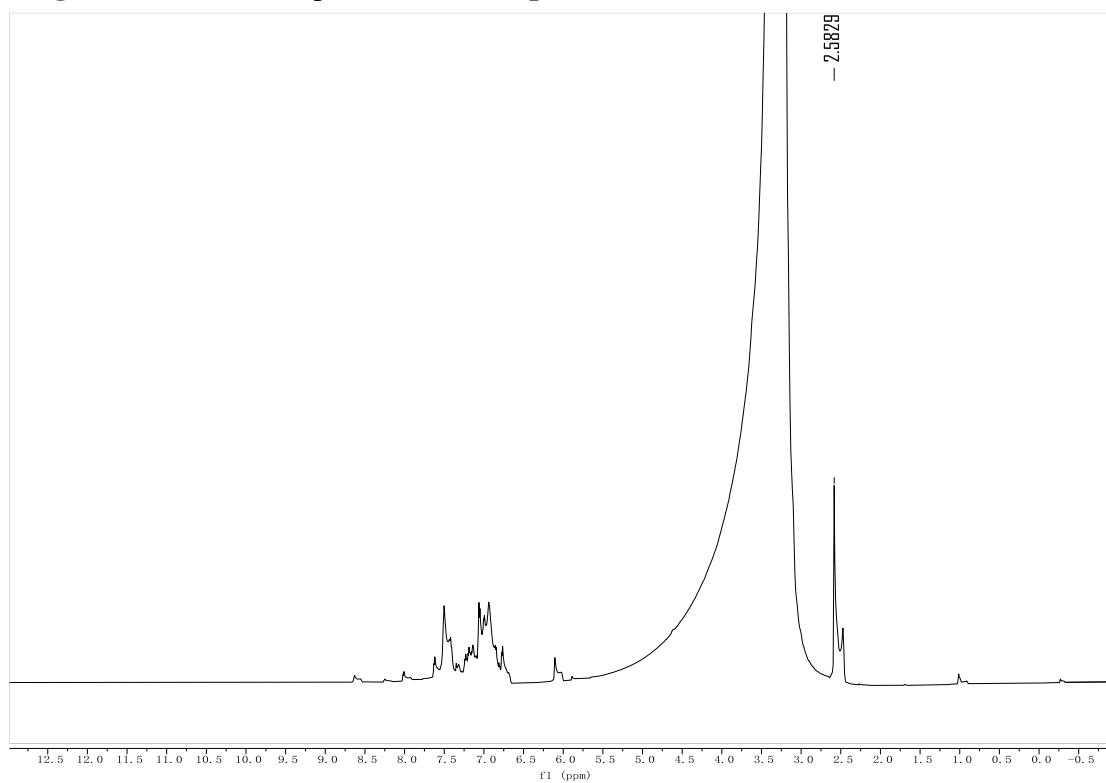
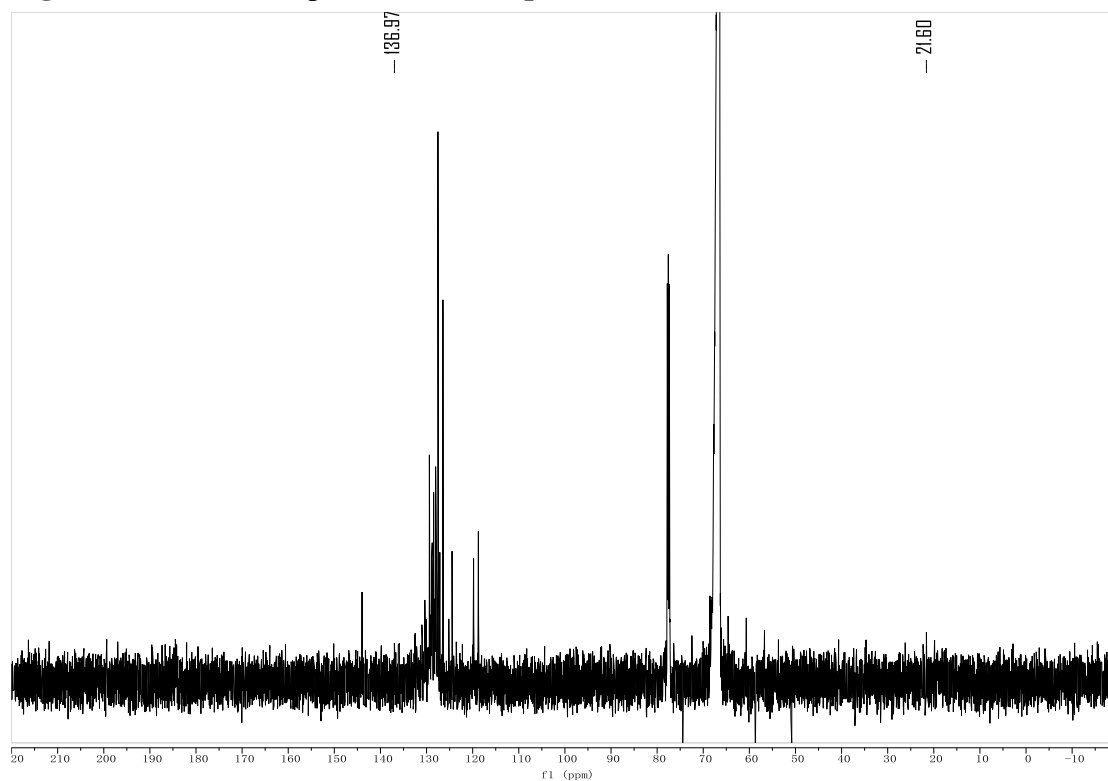
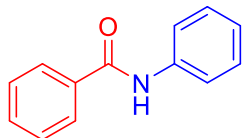


Figure S2. ^{13}C NMR Spectra of Crude products (151 MHz, CDCl_3).



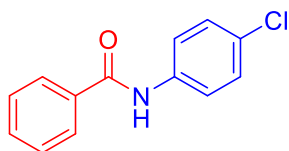
Characterization data of compounds 3

N-phenyl benzamide (3a)



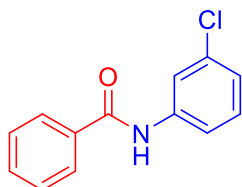
Known compound ²: 83% yield; ¹H NMR (CDCl₃, 600 MHz) δ: 7.15-7.17 (m, 1H), 7.37-7.40 (m, 2H), 7.49-7.51 (m, 2H), 7.55-7.57 (m, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.80 (br, 1H), 7.88 (d, *J* = 7.2 Hz, 2H). ¹³C NMR (CDCl₃, 151 MHz) δ 165.8, 137.9, 135.0, 131.8, 129.1, 128.8, 127.0, 124.6, 120.2.

N-(4-chlorophenyl) benzamide (3b)



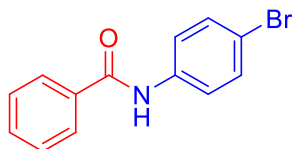
Known compound ²: 65% yield; ¹H NMR (CDCl₃, 600 MHz) δ: 7.34 (d, *J* = 8.4 Hz, 2H), 7.49-7.51 (m, 2H), 7.56-7.58 (m, 1H), 7.60-7.61 (m, 2H), 7.81 (br, 1H), 7.86 (d, *J* = 7.8 Hz, 2H).

N-(3-chlorophenyl) benzamide (3c)



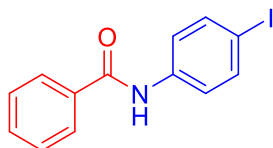
Known compound ³: 50% yield; ¹H NMR (CDCl₃, 600 MHz) δ: 7.12-7.14 (m, 1H), 7.26-7.30 (m, 1H), 7.48-7.50 (m, 3H), 7.55-7.58 (m, 1H), 7.77-7.78 (m, 1H), 7.85-7.87 (m, 2H).

N-(4-bromophenyl) benzamide (3d)



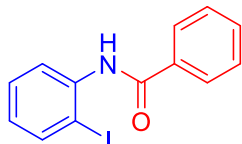
Known compound ²: 77% yield; ¹H NMR (CDCl₃, 600 MHz) δ: 7.48-7.51 (m, 4H), 7.55-7.58 (m, 3H), 7.80 (br, 1H), 7.86 (d, *J* = 7.2 Hz, 2H).

N-(4-iodophenyl) benzamide (3e)



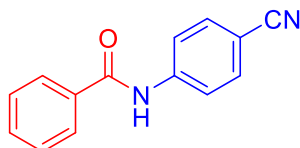
Known compound ²: 62% yield; ¹H NMR (CDCl₃, 600 MHz) δ : 7.44 (d, J = 9 Hz, 2H), 7.50 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 7.2 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.75 (br, 1H), 7.86 (d, J = 7.2 Hz, 2H).

***N*-(2-iodophenyl) benzamide (3f)**



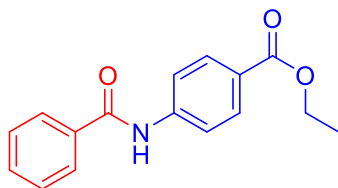
Known compound ²: 76% yield; ¹H NMR (CDCl₃, 400 MHz) δ : 6.89 (m, 1H), 7.41 (m, 1H), 7.51-7.55 (m, 2H), 7.57-7.61 (m, 1H), 7.81-7.84 (m, 2H), 7.97-7.99 (m, 2H), 8.30 (br, 1H), 8.46-8.48 (m, 1H).

***N*-(4-cyanophenyl) benzamide (3g)**



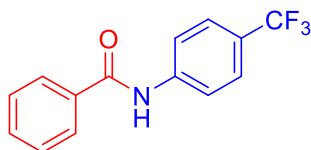
Known compound ²: 35% yield; ¹H NMR (CDCl₃, 600 MHz) δ : 7.51-7.54 (m, 2H), 7.59-7.62 (m, 1H), 7.67 (d, J = 7.8 Hz, 2H), 7.80 (d, J = 7.8 Hz, 2H), 7.88 (d, J = 7.8 Hz, 2H), 7.96 (br, 1H).

Ethyl 4-benzamido benzoate (3h)



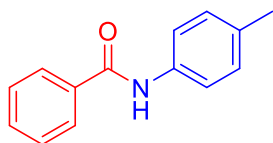
Known compound ⁴: 48% yield; ¹H NMR (CDCl₃, 600 MHz) δ : 7.44 (d, J = 9 Hz, 2H), 7.50 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 7.2 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.75 (br, 1H), 7.86 (d, J = 7.2 Hz, 2H).

***N*-(4-(trifluoromethyl) phenyl) benzamide (3i)**



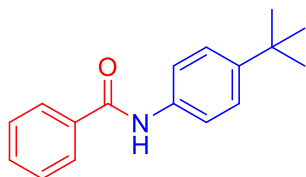
Known compound ⁵: 40% yield; ¹H NMR (CDCl₃, 400 MHz) δ : 7.50-7.54 (m, 2H), 7.57-7.62 (m, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.87-7.89 (m, 2H), 7.92 (br, 1H).

***N*-(*p*-tolyl) benzamide (3k)**



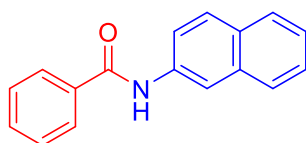
Known compound ²: 84 % yield; ¹H NMR (CDCl₃, 600 MHz) δ : 2.34 (s, 3H), 7.17 (d, J = 8.4 Hz, 2H), 7.47-7.56 (m, 5H), 7.81 (br, 1H), 7.86 (d, J = 7.2 Hz, 2H).

***N*-(4-(*tert*-butyl) phenyl) benzamide (3m)**



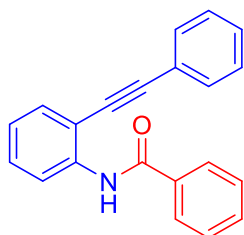
Known compound ⁶: 69% yield; ¹H NMR (CDCl₃, 600 MHz) δ : 1.33 (s, 9H), 7.39-7.40 (m, 2H), 7.48-7.50 (m, 2H), 7.54-7.57 (m, 3H), 7.79 (br, 1H), 7.86-7.88 (m, 2H).

***N*-(naphthalen-1-yl) benzamide (3n)**



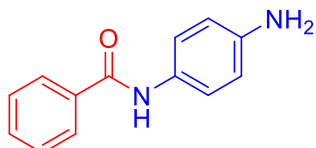
Known compound ⁷: 51% yield; ¹H NMR (CDCl₃, 400 MHz) δ : 7.51-7.60 (m, 6H), 7.76 (d, J = 8.4 Hz, 1H), 7.90-7.93 (m, 2H), 8.00 (d, J = 7.2 Hz, 2H), 8.05 (d, J = 7.2 Hz, 1H), 8.22 (br, 1H).

***N*-phenylbenzamide (3o)**



Known compound ⁸: 56% yield; ¹H NMR (CDCl₃, 400 MHz) δ : 5.39-5.42 (m, 2H), 6.16-6.24 (m, 2H), 6.74-6.75 (m, 1H), 6.83-6.91 (m, 2H), 7.21-7.28 (m, 2H), 7.46-7.50 (m, 2H), 7.61 (d, J = 7.6 Hz, 2H), 8.84 (br, 1H)

***N*-(4-aminophenyl) benzamide (3p)**



Known compound ⁹: 63% yield; ¹H NMR (CDCl₃, 400 MHz) δ : 3.69 (br, 2H), 6.70 (d,

$J = 8.4$ Hz, 2H), 7.39-7.41 (m, 2H), 7.45-7.49 (m, 2H), 7.51-7.55 (m, 1H), 7.67 (br, 1H), 7.84-7.86 (m, 2H).

Figure S5. ^1H NMR Spectra of compound **3b** (600 MHz, CDCl_3).

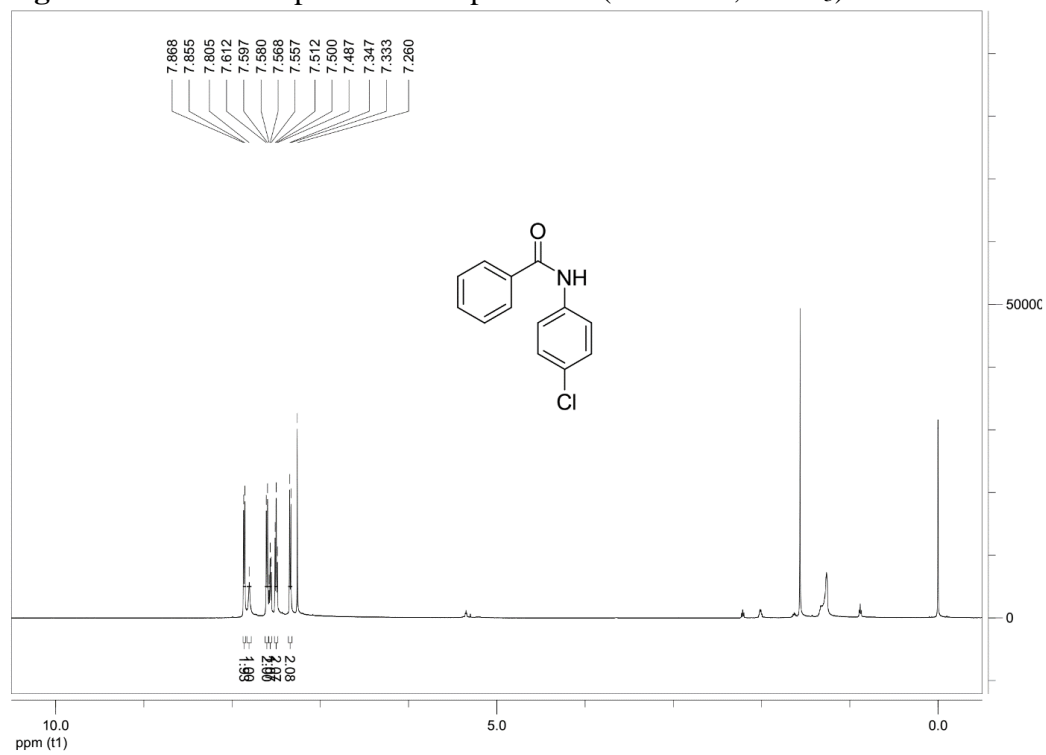


Figure S6. ^1H NMR Spectra of compound **3c** (600 MHz, CDCl_3).

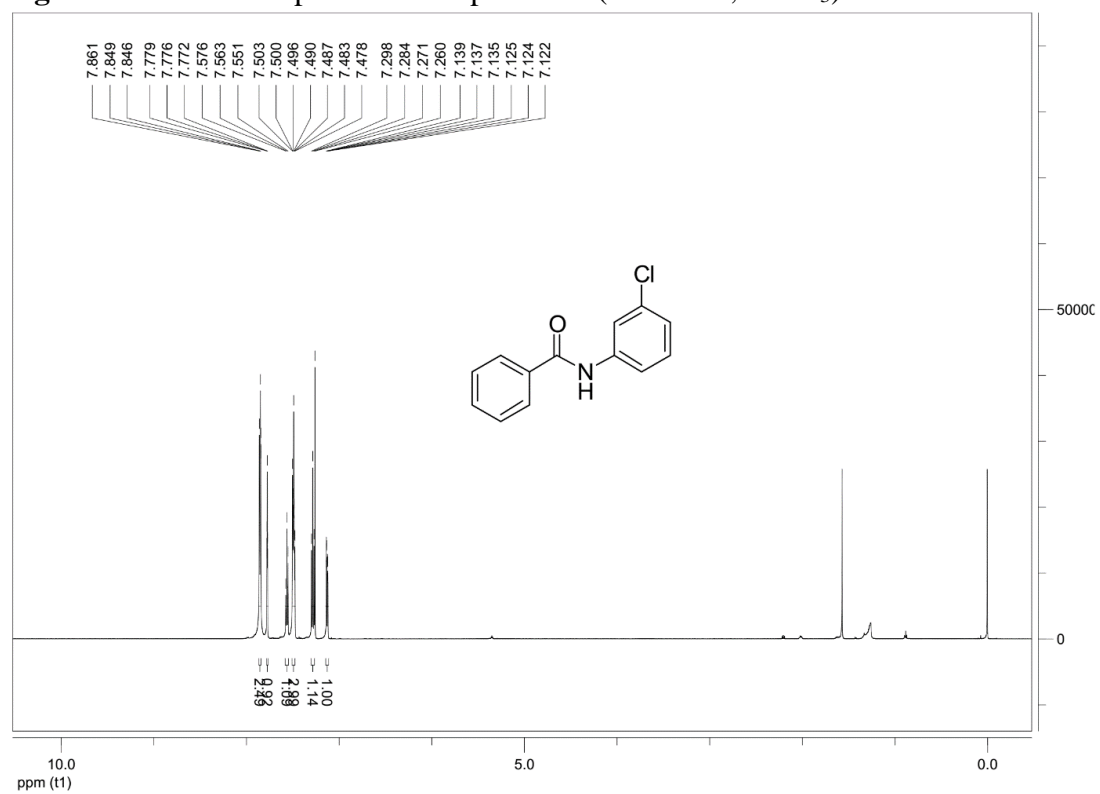


Figure S9. ^1H NMR Spectra of compound **3f** (400 MHz, CDCl_3).

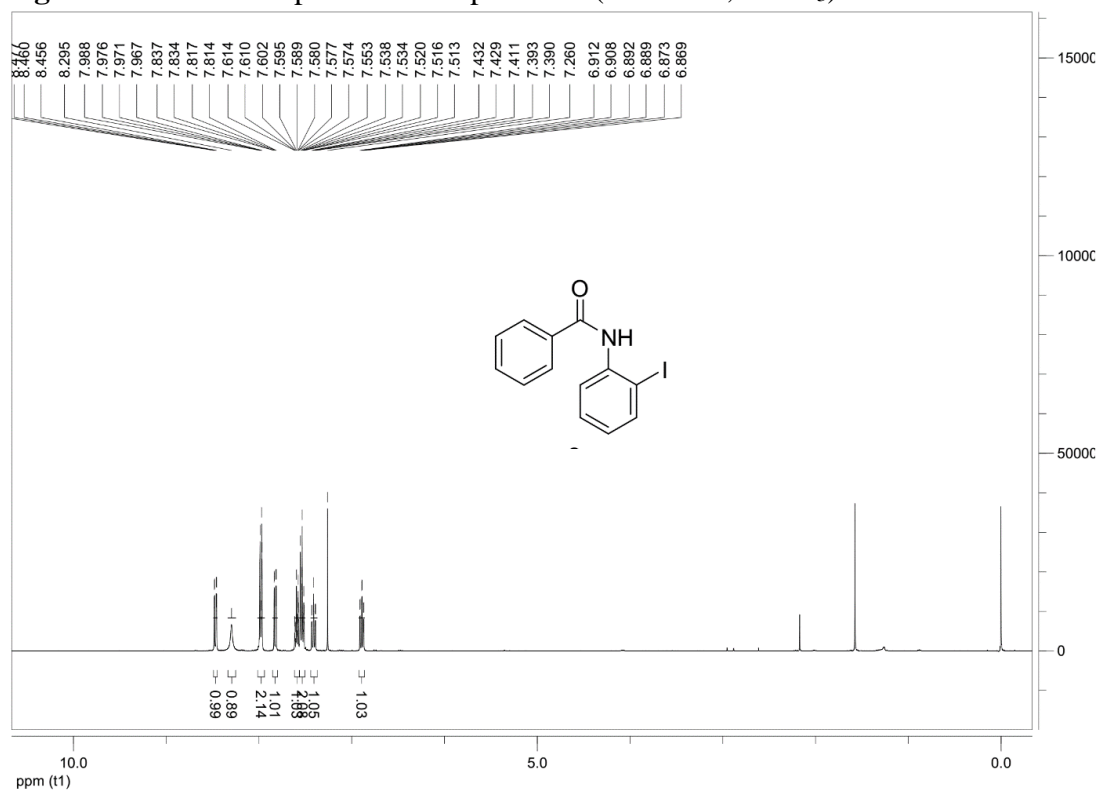


Figure S10. ^1H NMR Spectra of compound **3g** (600 MHz, CDCl_3).

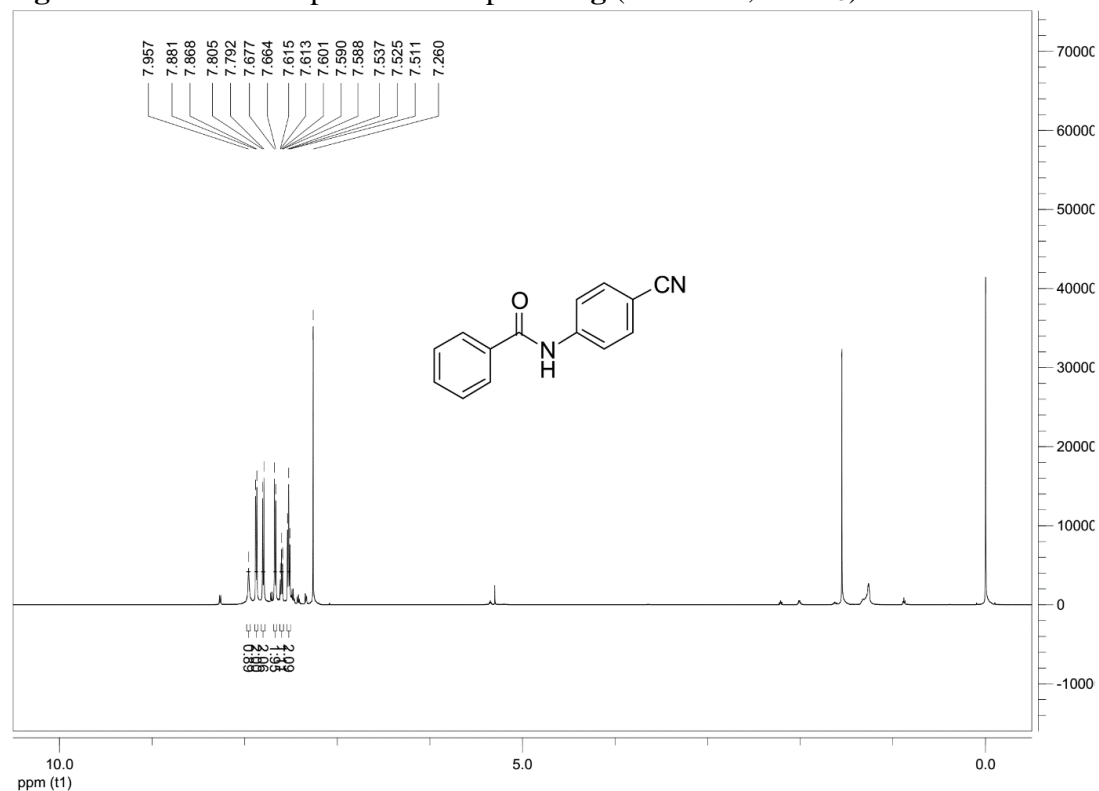


Figure S11. ^1H NMR Spectra of compound **3h** (600 MHz, CDCl_3).

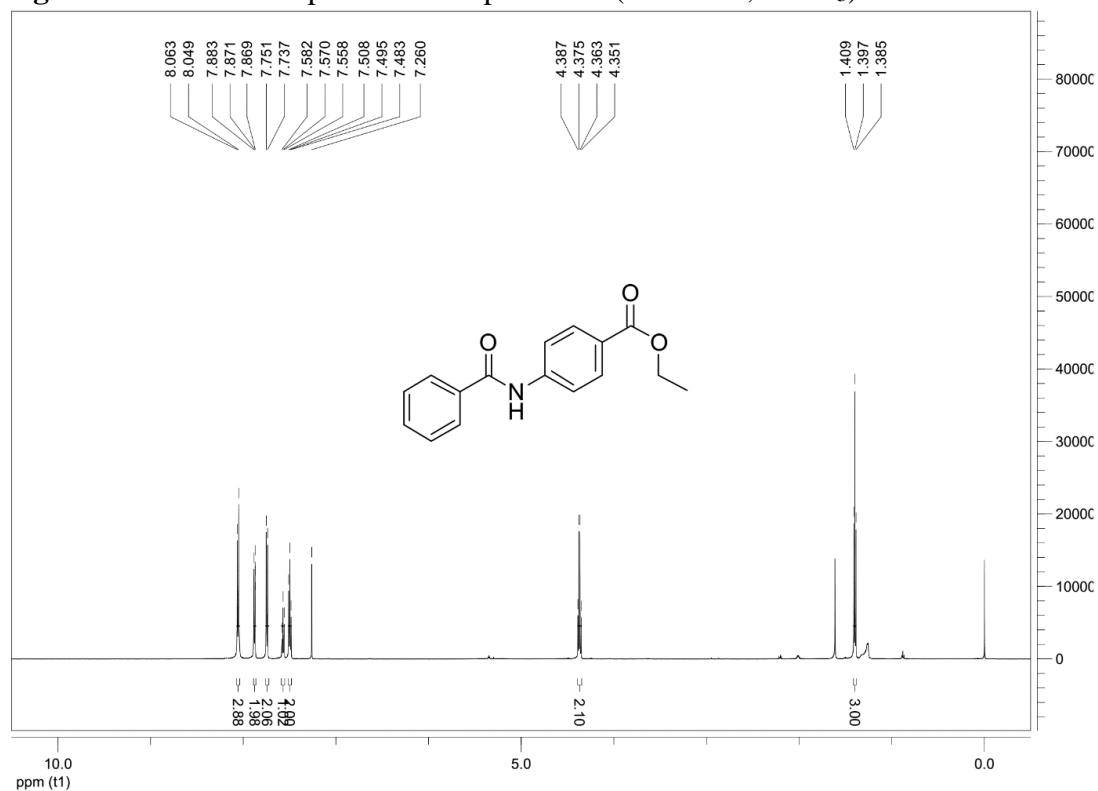


Figure S12. ^1H NMR Spectra of compound **3i** (400 MHz, CDCl_3).

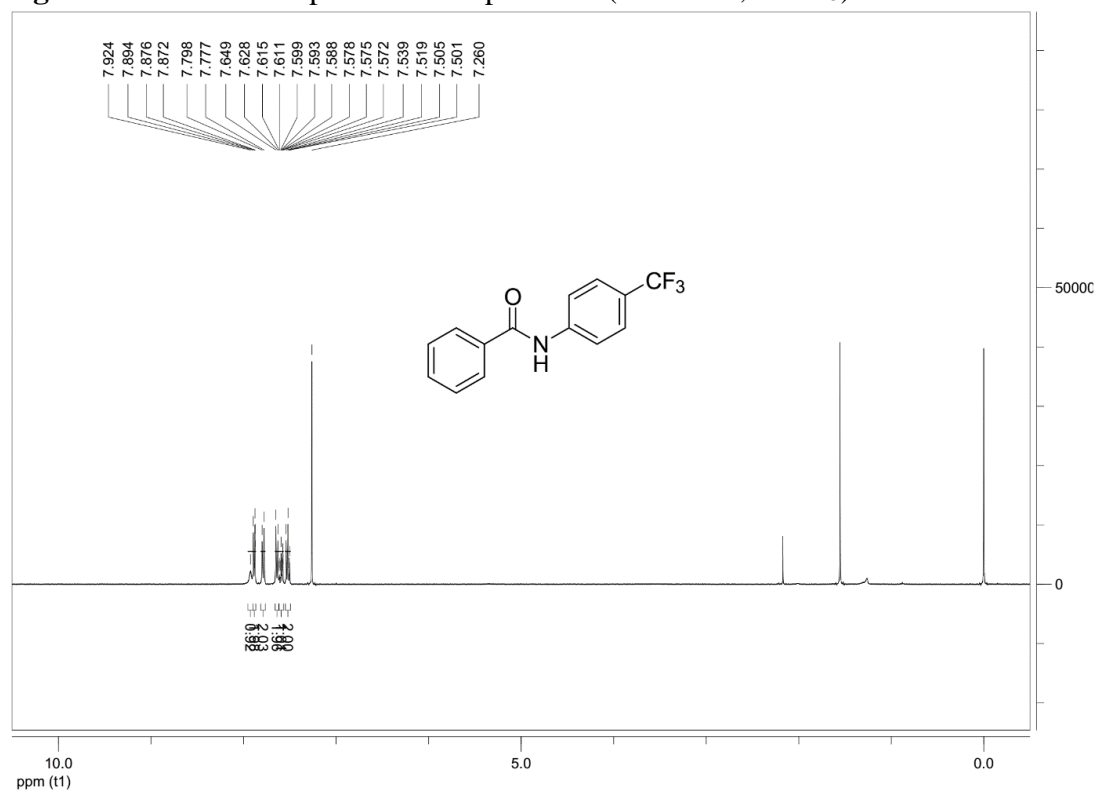


Figure S13. ^1H NMR Spectra of compound **3k** (600 MHz, CDCl_3).

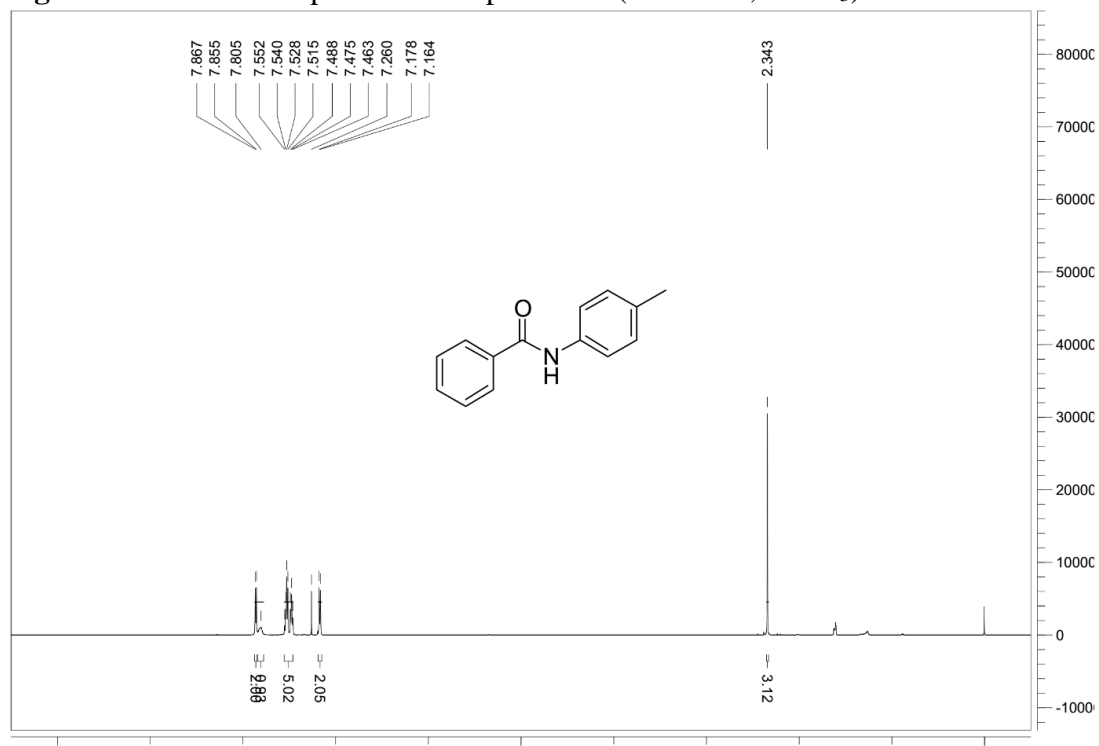


Figure S14. ^1H NMR Spectra of compound **3m** (600 MHz, CDCl_3).

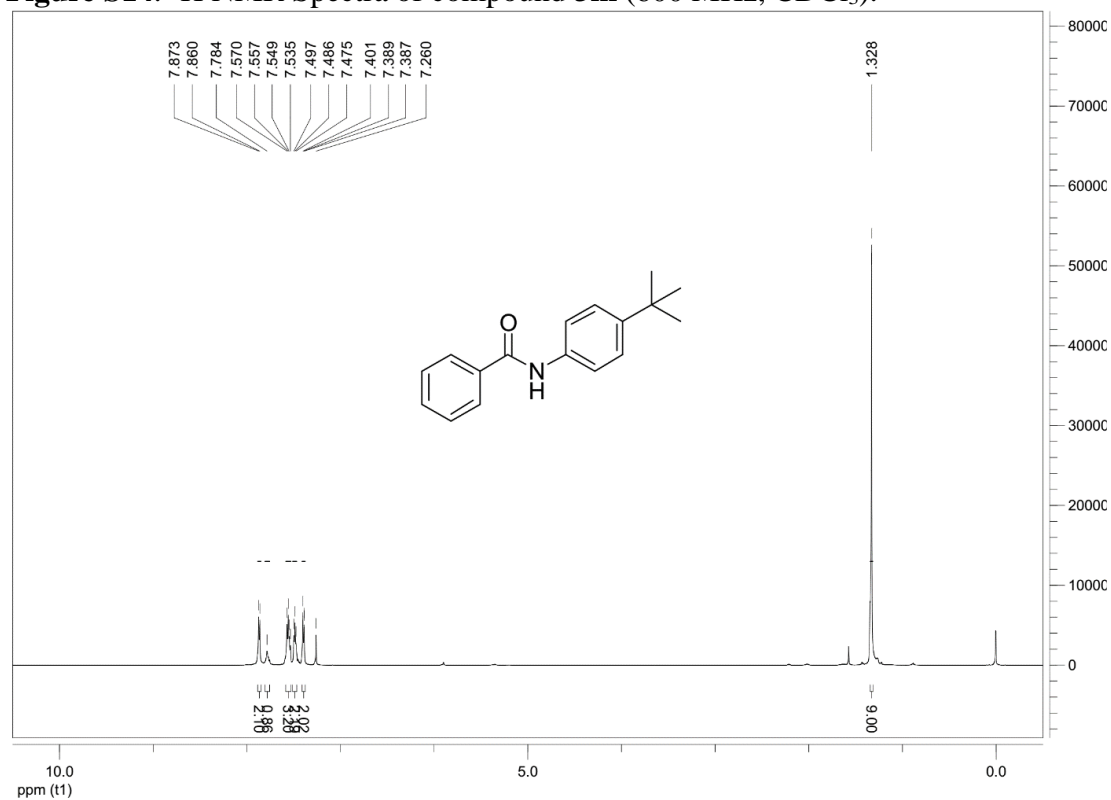


Figure S15. ^1H NMR Spectra of compound **3n** (400 MHz, CDCl_3).

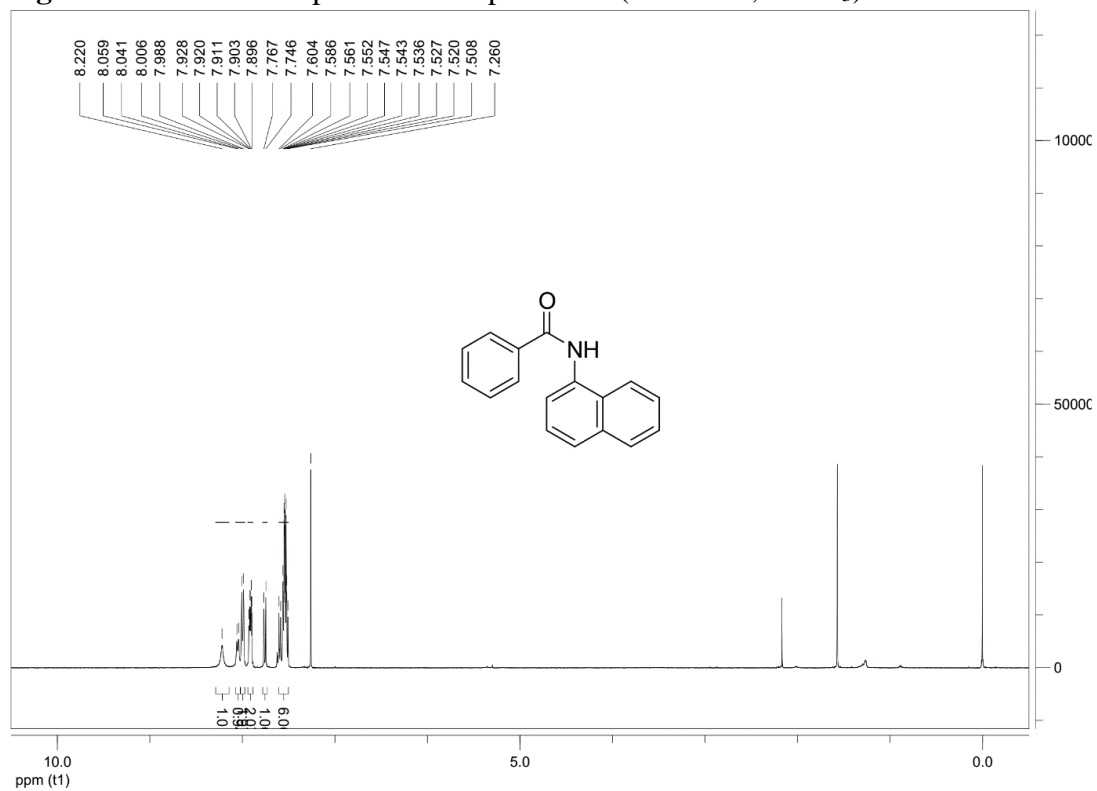


Figure S16. ^1H NMR Spectra of compound **3o** (400 MHz, CDCl_3).

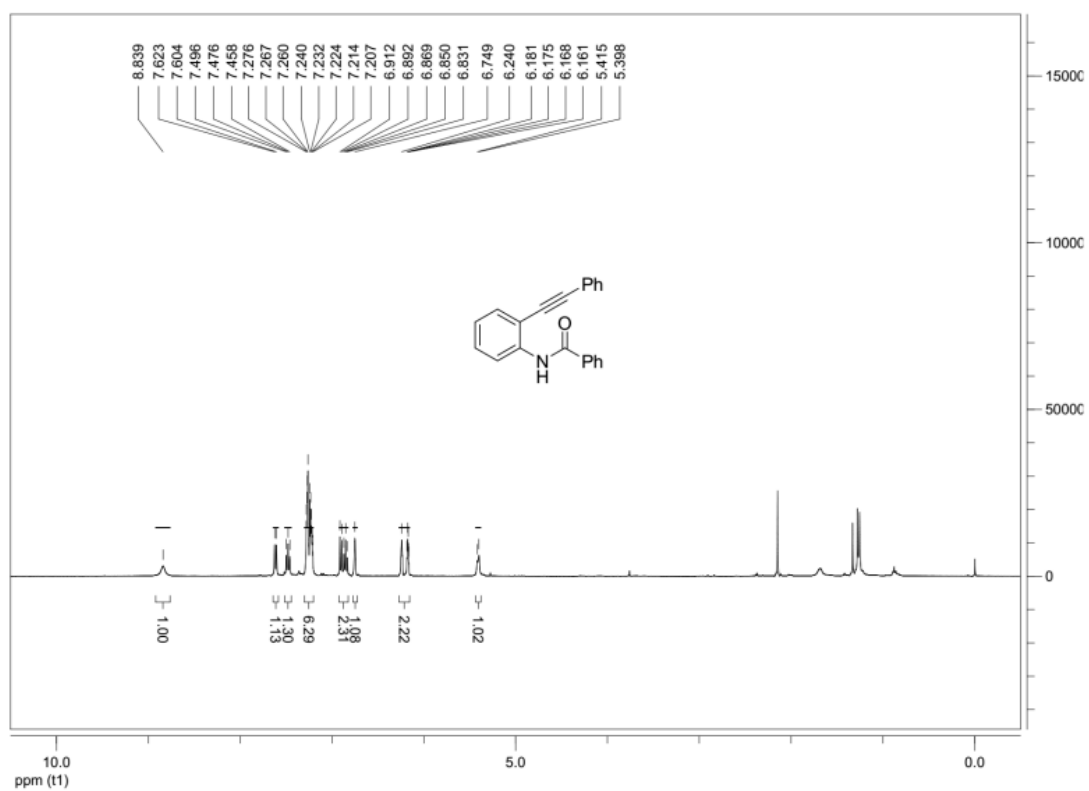


Figure S17. ^1H NMR Spectra of compound **3p** (400 MHz, CDCl_3).

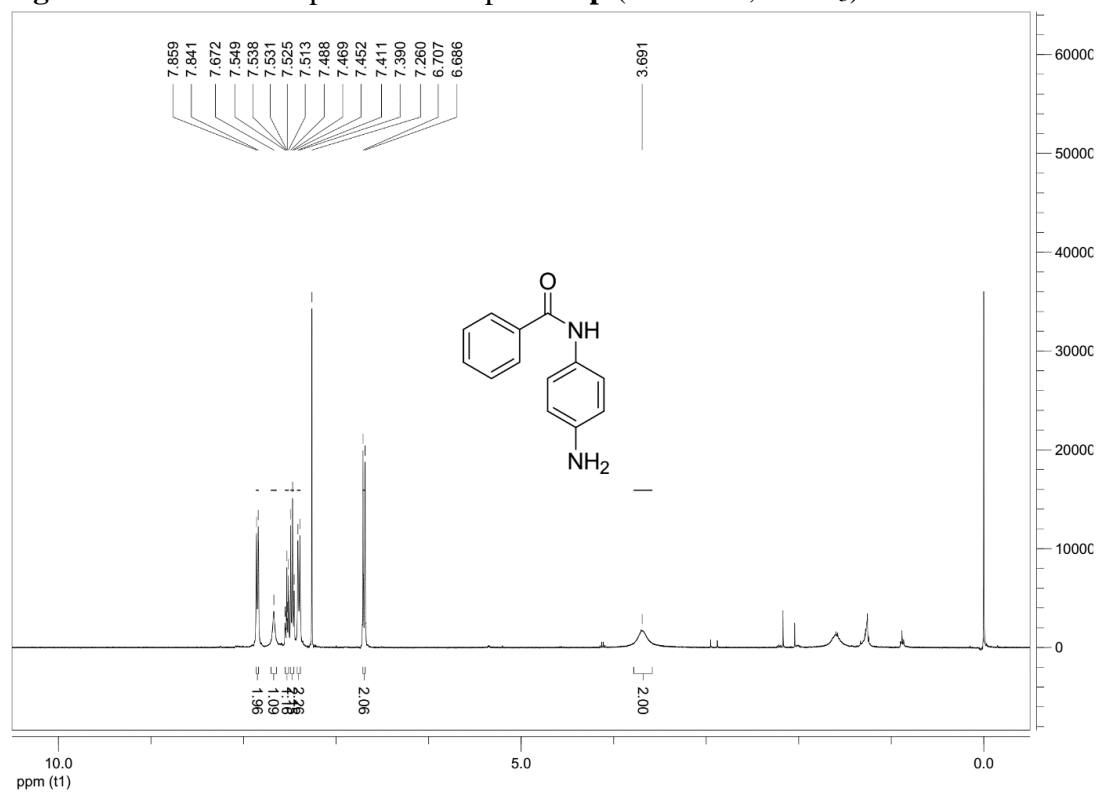
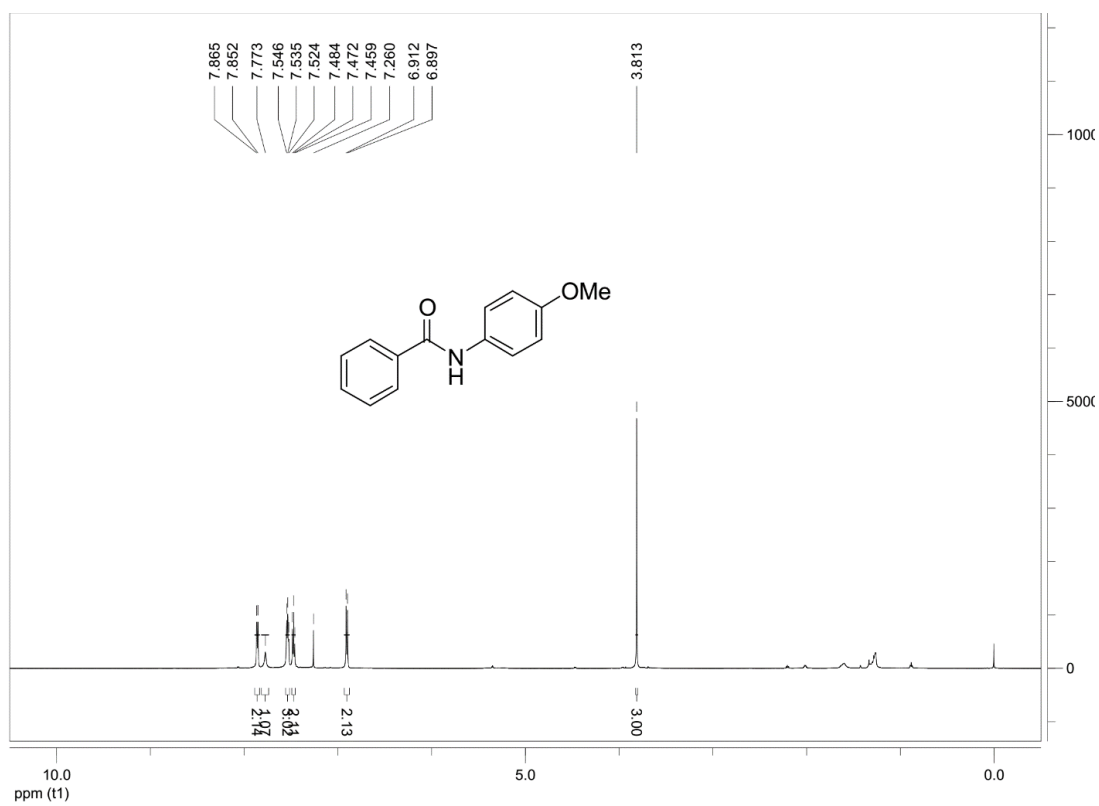


Figure S18. ^1H NMR Spectra of compound **3q** (600 MHz, CDCl_3).



References

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