Supporting Information

Synergism Between Few-Layer Black Phosphorus and Graphitic Carbon Nitride Enhances the Direct C–H Arylation under Visible Light Irradiation

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Contents

1. Materials

Red phosphorus (98.9%), tin (99.5%), tin(IV) iodide (95%), tert-butyl nitrite (t-BuONO), tetrafluoroboric acid (HBF_4, 50 wt% water), tetracycline hydrochloride (TC, 96%), acetonitrile (MeCN, 99.0%), and anilines were purchased from Alfa Aesar. Guanidine hydrochloride (GndCl, 98%,), LUDOX® HS-40 (colloidal silica 40 wt% suspension in H_2O), triethanolamine (TEOA, 99.0%), 2,2,6,6-tetramethylpiperidinoxyl (TEMPO, 98%), *N*-Boc pyrrole (98%), thiophene (99%), furan (99%) were purchased from Sigma Aldrich. Ammonium hydrogen difluoride (NH_4HF_2, >98%) was obtained from ROTH. Ethyl alcohol (EtOH, absolute, 99.9%), ethyl acetate (EtOAc, ≥ 99.5%), dimethyl sulfoxide (DMSO, 99.9%) dichloromethane (DCM, ≥ 99.0%), cyclohexane (99.8%), and *N*,*N*-dimethylformamide (DMF, 99.0%) were purchased from IsoLab chemicals. All chemicals and solvents were used as received without further purification unless it is noted.

1.1. Synthesis of bulk Black Phosphorus

The crystal BP was synthesized *via* low-pressure chemical vapor deposition method[1,2]. 10 mg of SnI_4, 20 mg of Sn, and 500 mg of red phosphorus were weighted and transported to specially designed quartz ampule. The vacuum sealed ampule was then placed in muffle to be thermally treated at set program given in the literature. Next, the ampoule was crushed under dry toluene and BP crystal was washed with ethanol in sonication bath. Finally, clean crystal was crushed under and stored under inert atmosphere.

1.2. Synthesis of graphitic carbon nitride (g-CN)

The g-CN was synthesized using hard template method utilizing Ludox® HS40 colloidal silica as template[3]. 4.0 g of guanidine hydrochloride, GndCl, dissolved in 4 mL distilled water was added to 10 g of Ludox® HS40 under vigorous stirring. Then, the solution was mixed and heated for 12 h at 50 °C. The obtained white solid was crushed and annealed in horizontal quartz-tube oven with reported heating program. To remove the silica template, the heat treated was reacted with hydrogen difluoride for 2 days. Finally, the resulting powder was washed with water/ethanol, dried, and stored for further use.

1.3. Charge migration study using photocatalytic TC degradation

The degradation of tetracycline hydrochloride (TC, 50 ppm) was performed in a double-walled cylindrical quartz reactor under a metal halogen lamp (white light, 150 W). The lamp was

placed 10 cm away from the quartz reactor system on the top of a magnetic stirrer. Next, 25 mg of photocatalyst was put into 100 mL of TC solution in DI water and the resulting mixture was let it stir under dark conditions for 0.5 h to reach adsorption-desorption equilibrium. After that, the visible light irradiation of photocatalytic degradation was started. Time-dependent measurements were taken by taking an equal amount of suspension from the solution at regular intervals. Followed by filtration (0.20 μm syringe filter), the absorbance of TC in the reaction mixture was determined by JASCO V730 spectrophotometer at a maximum wavelength of 357 nm (Figure S5). For the calculation of the degradation efficiency (%) of TC, the following equation was used.

$$Degradation\ Efficiency\ (\%) = \frac{A_0 - A_t}{A_0} \times 100$$

where A_0 is the initial concentration of TC, while A_t is the concentration after t period.

The scavenger experiment during the photodegradation process was examined by benzoquinone (BQ, 0.1 mmol/L) as electron scavenger under the same conditions mentioned above.

1.4. Materials Characterization

Transmission electron microscopy (TEM) images, high-angle annular dark field (HAADF) scanning transmission microscope (STEM) images and the corresponding EDS elemental mapping images were taken on Hitachi HT7700 with EXALENS (120 kV) working at high-resolution (HR) mode. The X-ray Diffraction (XRD) patterns were investigated with Bruker D8 Advance X-Ray diffractometer using Cu Kα radiation (1.54 A). Raman spectra data was obtained with Renishaw inVia Raman microscope (532 nm laser). Photoluminescence (PL) spectroscopy was measured by Agilent Cary Eclipse PL (320 nm). Time resolved photoluminescence (TRPL) spectroscopy of the semiconductors were done with an Edinburgh Instruments FLS1000 spectrometer (377 nm). The absorption properties were investigated using diffuse reflectance ultraviolet−visible−near-infrared (UV−Vis−NIR) spectroscopy via Shimadzu UV-3600 UV−Vis−NIR spectrophotometer. NMR spectra were obtained in CDCl3 using tetramethylsilane (TMS) as an internal standard on a Varian (running at 500 MHz for 1H NMR). Chemical shifts are provided in parts per million, while coupling constants (J values) are supplied in Hz (ppm). The letters s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and p (pentet) are used to represent different splitting patterns. The Bruker TopSpin

4.1.0 application was used to process NMR spectra. Silica Gel (Merck 60–200 mesh) and thick-walled glass columns were used for column chromatography. Using commercially manufactured 0.25 mm silica gel plates and a UV light for viewing, thin layer chromatography (TLC Merck Silica Gel 60 F254) was conducted (254 nm). The volume:volume ratio refers to the relative quantities of solvents in chromatography solvent mixtures.

1.5. Synthesis of aryl diazonium tetrafluoroborates[4]

To the 50 mL round-bottom flask with stirring bar, 5 mmol of corresponding aniline was placed in an ice bath. 3 mL of absolute ethanol and 1.25 mL of HBF_4 (50%, 10 mmol) were added. After the solution medium had cooled down, 1.40 mL of *tert*-butyl nitrite (10 mmol) was added dropwise. The reaction mixture was allowed to stir for 2 h at room temperature. Finally, resulting diazonium salt was washed several times with DCM using vacuum filtration, dried and stored at 4 °C for further use.

2. Catalyst characterization

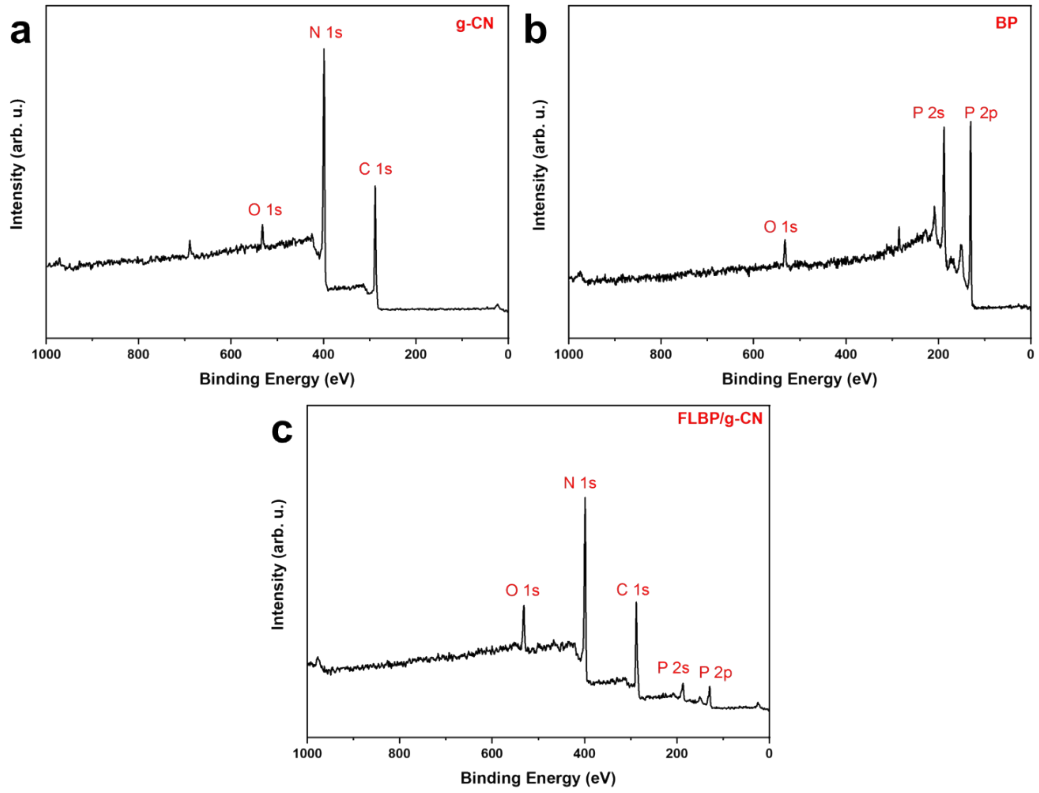


Figure S1. XPS survey spectra of **a.** BP, **b.** g-CN and **c.** FLBP/g-CN heterojunctions.

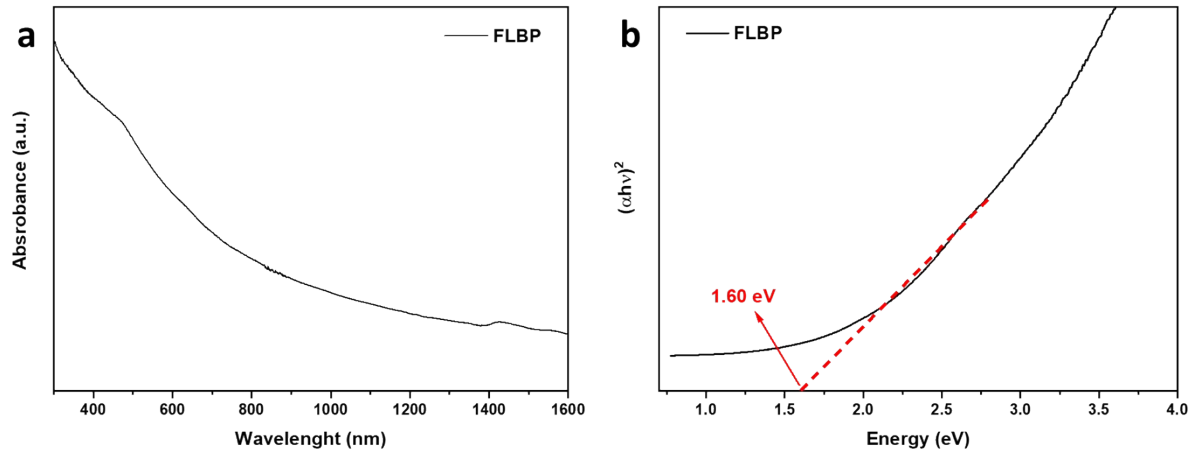


Figure S2. a. Absorbance spectra and **b.** Tauc plot of FLBP nanosheets.

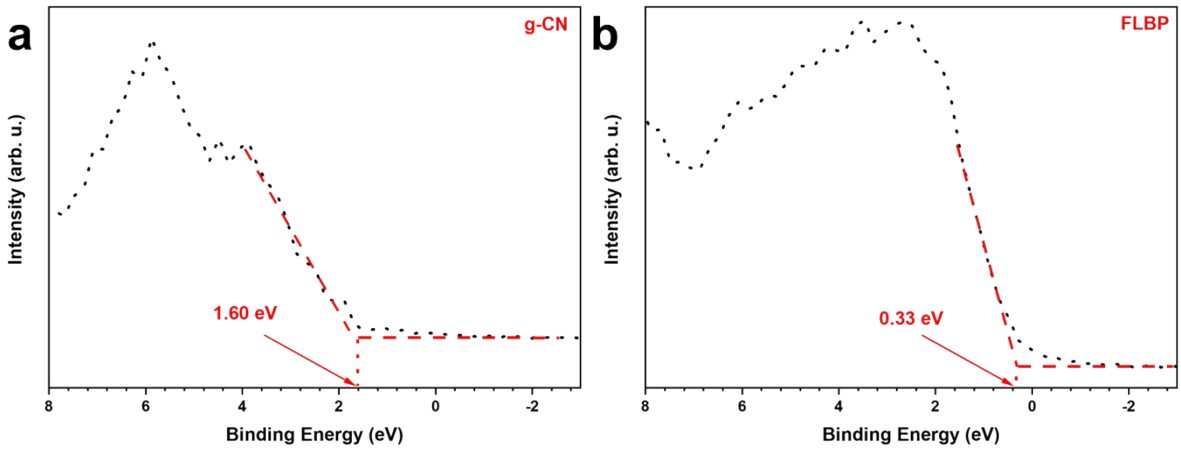


Figure S3. XPS valance band spectrum of **a.** pristine g-CN and **b.** FLBP nanosheets.

3. Reusability experiment and characterization

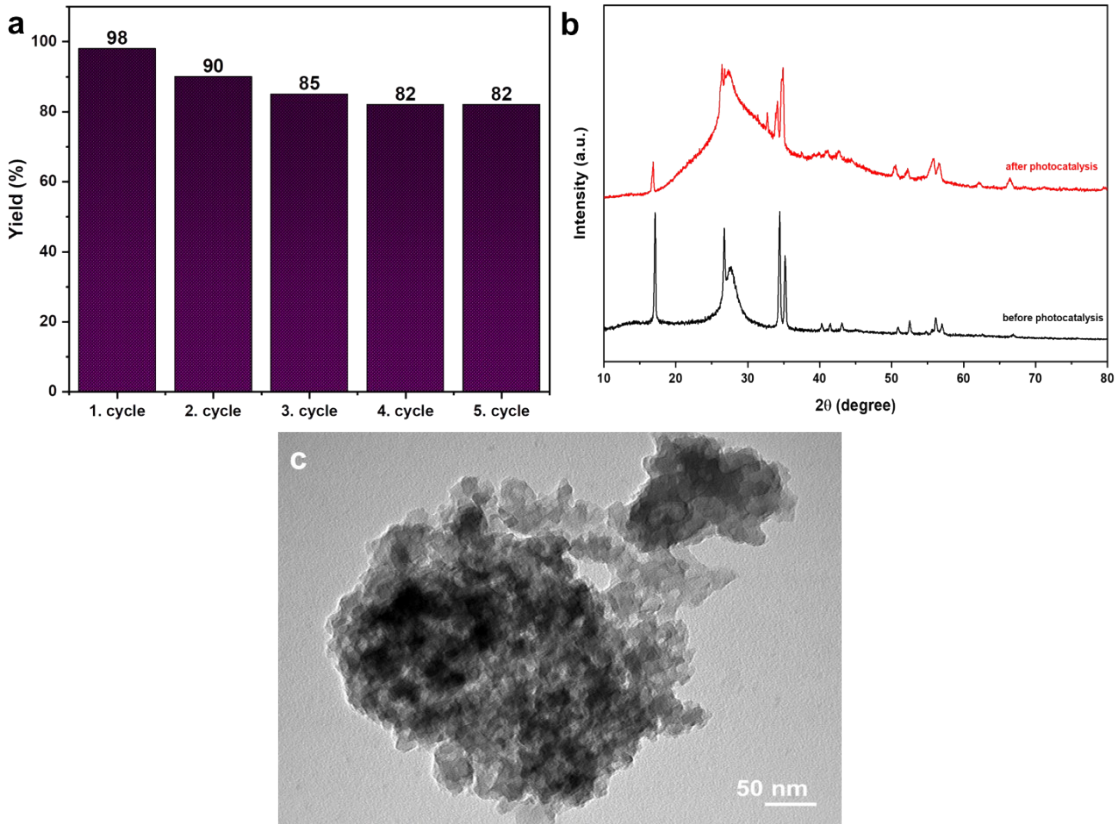


Figure S4. a. Five-run reusability test **b.** XRD pattern **c.** TEM image of FLBP/g-CN heterojunction.

It was observed that the XRD pattern (**Figure 7b**) after a five-run reusability test did not cause a change in the crystalline structure. In addition, it was determined from the TEM images in **Figure 7c** that it did not cause a change in the morphological structure. Positive reusability test results with XRD and TEM analyzes are strong evidence that a photocatalyst with high stability has been created.

4. Charge migration studies using degradation of TC

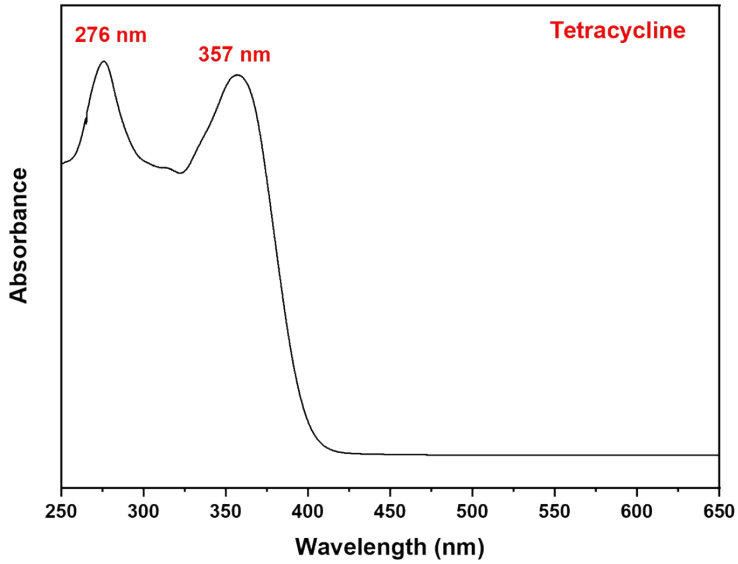


Figure S5. Absorbance spectrum of tetracycline (TC).

5. Comparison of C–H arylation performance with the literature

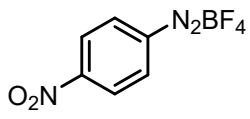
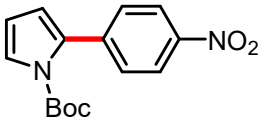
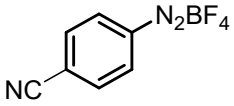
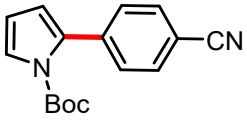
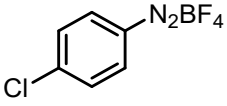
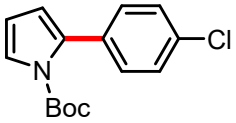
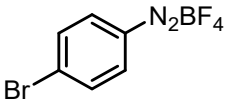
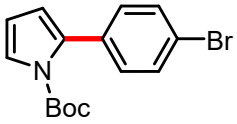
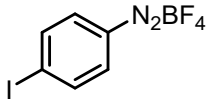
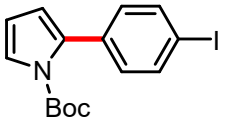
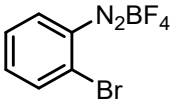
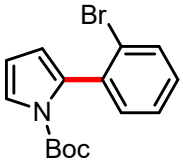
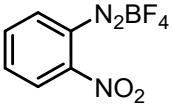
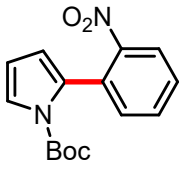
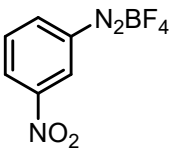
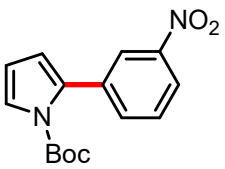
Table S1. Comparison of model reaction under different photocatalytic conditions in the literature.

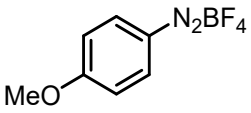
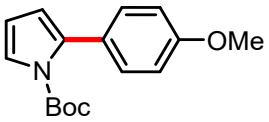
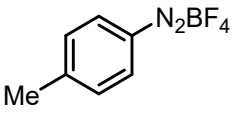
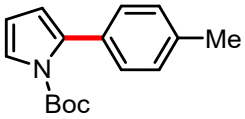
Entry	Photocatalyst	Catalyst mass (mg)	Time (h)	Light Source	Yield [%]	
1	Black Phosphorus[a]	5	2	White light (150 W metal halide lamp)	64	In this work
2	g-CN[a]	5	2	White light (150 W metal halide lamp)	56	In this work
3	$FLBP_{0.35}$/g-CN	5	2	White light (150 W metal halide lamp)	90	In this work
4	Bismuthene[a]	10	2	Versatile conditions	81	Ref[5]
5	Cercosporin	≥ 1	16	Sunlight	72	Ref[6]
6	$AcrH_2$	> 5	12	Blue LEDs (3 W)	34	Ref[7]
7	Porphyrin	< 1	3	Blue LED (λ = 455 nm)	78*	Ref[8]
8	$CpMn(CO)_3$	< 5	0.5	Blue LED (24 W, λ = 450 nm)	62*	Ref[9]
9	Eosin Y	< 1	2	530 nm LED (1 W)	61	Ref[10]
10	Immobilized BODIPY	5	2	Green LED (λ = 495–555 nm)	70*	Ref[11]
11	g-CN/rGO	4	1.5	Visible light (300 W Xenon lamp)	91*	Ref[12]
12	Fe_3O_4@$Cu_{2-x}S$–MoS_2F	2	1	Xenon lamp ((λ = 700 nm)	96*	Ref[13]
13	CNPVPy20	5	1	White LED (30 W)	95*	Ref[14]

[a]*The reaction was performed with* 1 *(20 equiv),* 2a *(0.25 mmol), and catalyst in 1.0 mL of DMSO * Furan was used as heteroarene.*

6. Substrate scope of the C–H bond formation

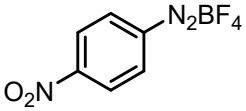
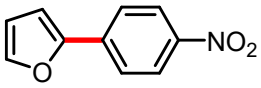
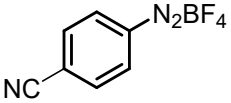
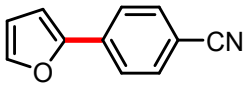
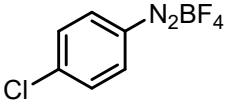
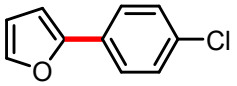
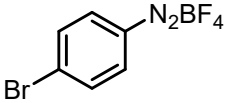
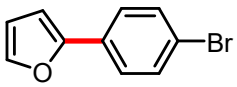
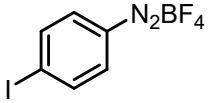
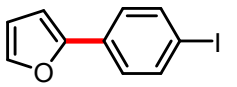
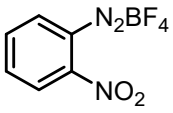
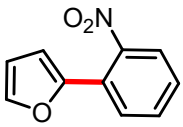
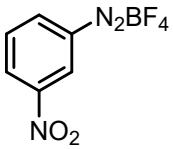
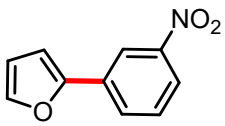
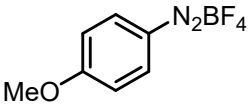
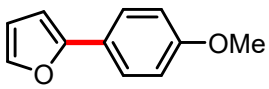
Table S2. Scope of aryl diazonium salts with *N*-Boc pyrrole.

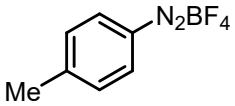
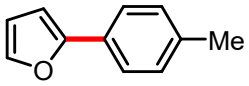
Entry	Substrate	Product	Yield(%)
1	 **2a**	 **3a**	90
2	 **2b**	 **3b**	77
3	 **2c**	 **3c**	68
4	 **2d**	 **3d**	70
5	 **2e**	 **3e**	66
6	 **2f**	 **3f**	63
7	 **2g**	 **3g**	66
8	 **2h**	 **3h**	60

9	 **2j**	 **3j**	**22**
10	 **2k**	 **3k**	**16**

*Conditions: 0,25 mmol of diazonium salt **2x**, 5 equiv. of N-Boc pyrrole (**1**), and 5 mg of catalyst in 1 mL of DMSO under irradiation of a white light (150 W) for 2 h at 25 °C. Isolated yield after purification with column chromatography on SiO_2 with cyclohexane/EtOAc as eluent.*

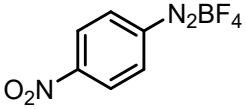
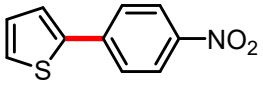
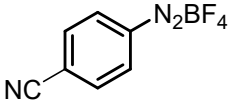
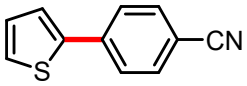
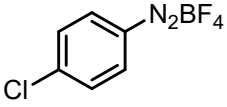
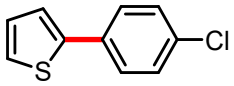
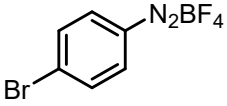
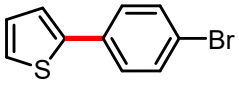
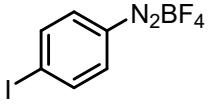
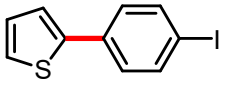
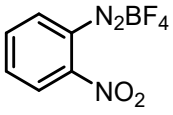
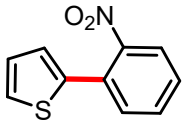
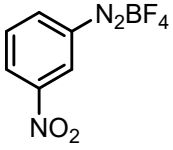
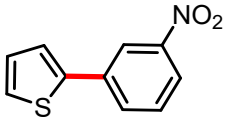
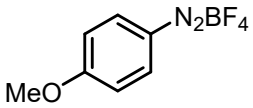
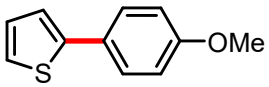
Table S3. Scope of aryl diazonium salts with furan.

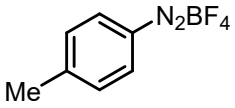
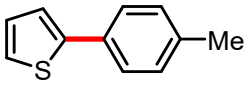
Entry	Substrate	Product	Yield(%)[a]
1	 **2a**	 **4a**	**82**
2	 **2b**	 **4b**	**94**
3	 **2c**	 **4c**	**75**
4	 **2d**	 **4d**	**76**
5	 **2e**	 **4e**	**82**
6	 **2g**	 **4g**	**95**
7	 **2h**	 **4h**	**74**
8	 **2j**	 **4j**	**65**

9	 **2k**	 **4k**	**20**

*Conditions: 0,25 mmol of diazonium salt **2x**, 1 mL of furan (**4**), and 5 mg of catalyst in 1 mL of DMSO under irradiation of a white light (150 W) for 2 h at 25 °C. Isolated yield after purification with column chromatography on SiO_2 with cyclohexane/EtOAc as eluent.*

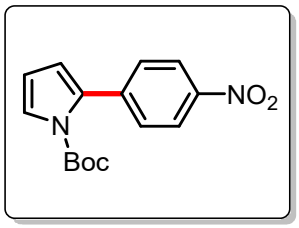
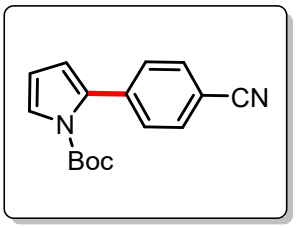
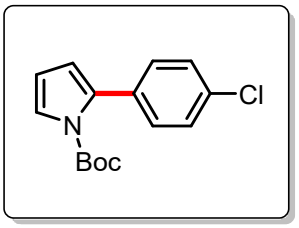
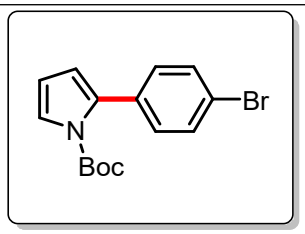
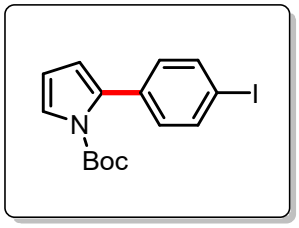
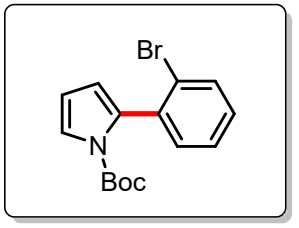
Table S4. Scope of aryl diazonium salts with thiophene.

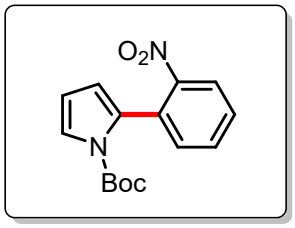
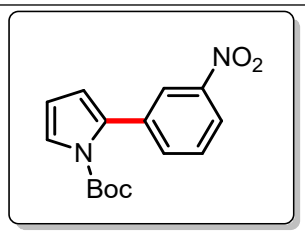
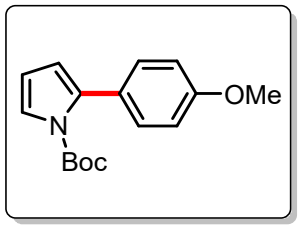
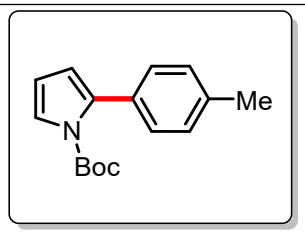
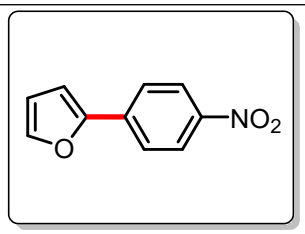
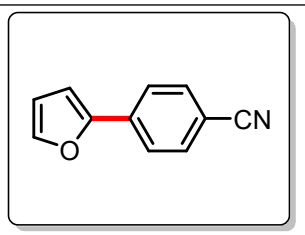
Entry	Substrate	Product	Yield(%)
1	 **2a**	 **5a**	**80**
2	 **2b**	 **5b**	**82**
3	 **2c**	 **5c**	**56**
4	 **2d**	 **5d**	**62**
5	 **2e**	 **5e**	**62**
6	 **2g**	 **5g**	**84**
7	 **2h**	 **5h**	**85**
8	 **2j**	 **5j**	**36**

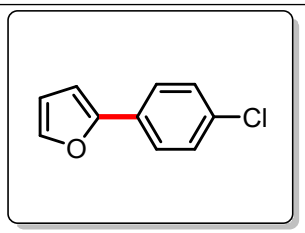
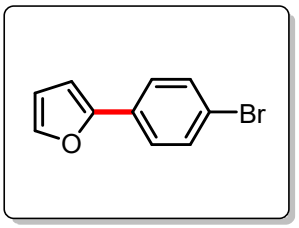
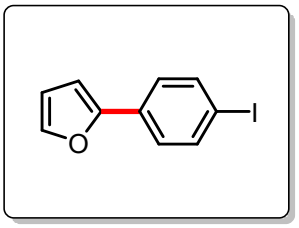
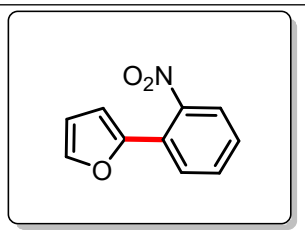
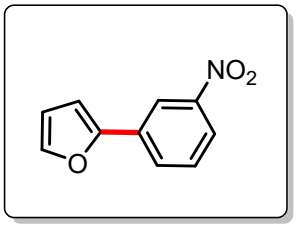
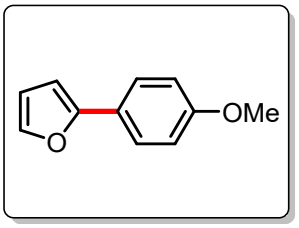
9		**2k**		**5k**	**54**

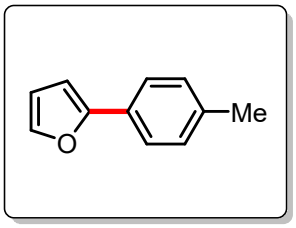
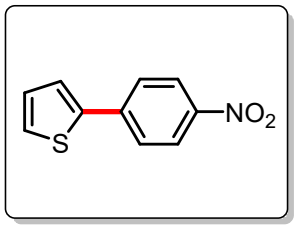
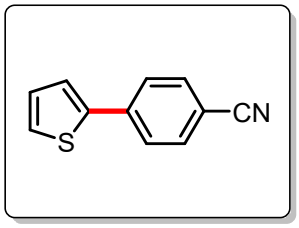
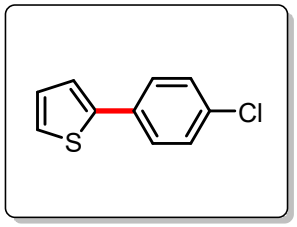
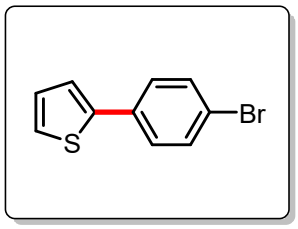
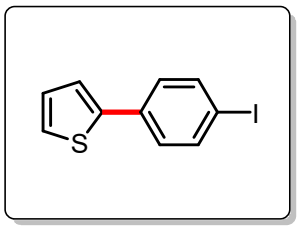
*Conditions: 0,25 mmol of diazonium salt **2x**, 1 mL of thiophene (**5**), and 5 mg of catalyst in 1 mL of DMSO under irradiation of a white light (150 W) for 4 h at 25 °C. Isolated yield after purification with column chromatography on SiO_2 with cyclohexane/EtOAc as eluent.*

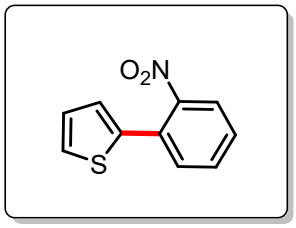
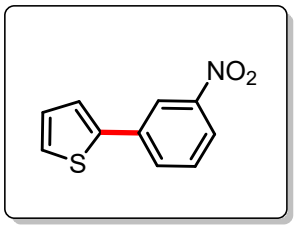
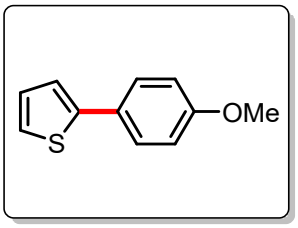
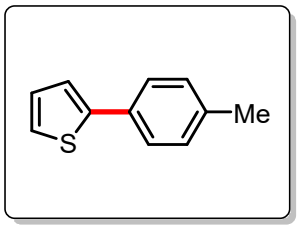
7. ^{1}H NMR characterization of C–H arylation products

	*N*-Boc-2-(4-nitrophenyl)pyrrole (**3a**)[15] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 – 8.20 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.50 (m, 2H), 7.41 – 7.40 (m, 1H), 6.33 – 6.31 (m, 1H), 6.28 – 6.26 (m, 1H), 1.43 (s, 9H).
	*N*-Boc-2-(4-cyanophenyl)pyrrole (**3b**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 77% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 – 7.62 (m, 2H), 7.46 – 7.44 (m, 2H), 7.39 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.28 – 6.24 (m, 2H), 1.41 (s, 9H).
	*N*-Boc-2-(4-chlorophenyl)pyrrole (**3c**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.27 (m, 5H), 6.24 – 6.22 (m, 1H), 6.19 (dd, *J* = 3.2, 1.8 Hz, 1H), 1.34 (s, 9H).
	*N*-Boc-2-(4-bromophenyl)pyrrole (**3d**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 – 7.47 (m, 2H), 7.37 – 7.35 (m, 1H), 7.24 – 7.22 (m, 2H), 6.24 – 6.22 (m, 1H), 6.20 – 6.18 (m, 1H), 1.41 (s, 9H).
	*N*-Boc-2-(4-iodophenyl)pyrrole (**3e**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 – 7.66 (m, 2H), 7.34 (br s, 1H), 7.09 – 7.08 (m, 2H), 6.22 (br s, 1H), 6.18 (br s, 1H), 1.40 (s, 9H).
	*N*-Boc-2-(2-bromophenyl)pyrrole (**3f**)[17] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.34 (m, 1H), 7.28 – 7.22 (m, 1H), 7.19 – 7.16 (m, 2H), 7.15 – 7.11 (m, 1H), 6.21 – 6.19 (m, 1H), 6.08 – 6.07 (m, 1H), 1.22 (s, 9H).

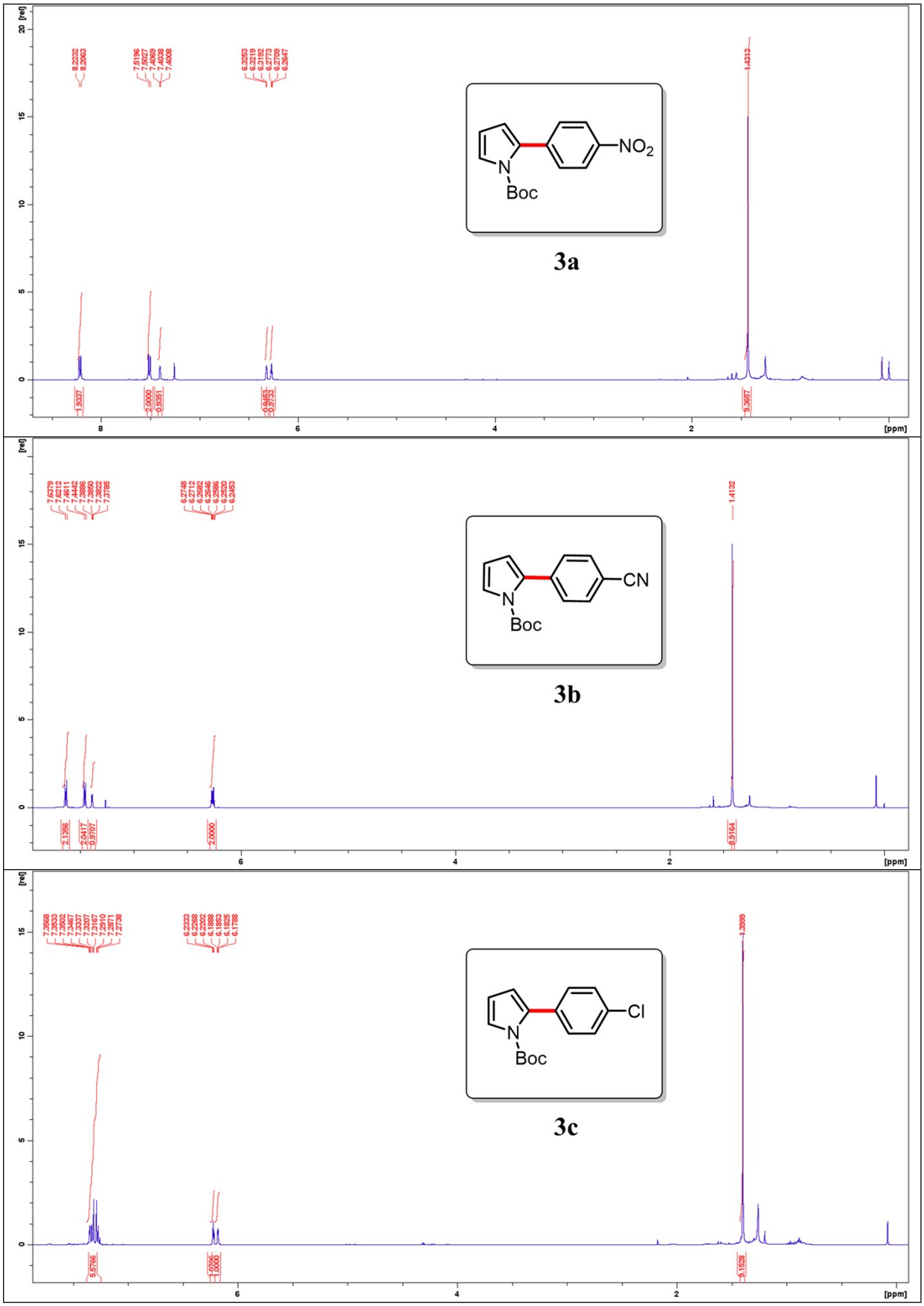
	*N*-Boc-2-(2-nitrophenyl)pyrrole (**3g**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 – 8.09 (m, 1H), 7.64 – 7.60 (m, 1H), 7.52 – 7.40 (m, 3H), 6.28 – 6.26 (m, 1H), 6.21 – 6.19 (m, 1H), 1.33 (s, 9H).
	*N*-Boc-2-(3-nitrophenyl)pyrrole (**3h**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 59% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (t, *J* = 1.95 1H), 8.17 – 8.14 (m, 1H), 7.70 – 7.67 (m, 1H), 7.53 (t, *J* = 8.0, 1H), 7.41 – 7.12 (m, 1H), 6.30 – 6.28 (m, 1H), 6.27 – 6.25 (m, 1H), 1.40 (s, 9H).
	*N*-Boc-2-(4-methoxyphenyl)pyrrole (**3j**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 22% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.24 (m, 1H), 7.20 – 7.18 (m, 2H), 6.82 – 6.80 (m, 2H), 6.14 – 6.12 (m, 1H), 6.07 – 6.05 (m, 1H), 3.76 (s, 3H), 1.31 (s, 9H).
	*N*-Boc-2-(4-methylphenyl)pyrrole (**3k**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 16% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.31 (m, 1H), 7.26 – 7.22 (m, 2H), 7.16 – 7.14 (m, 2H), 6.21 – 6.20 (m, 1H), 6.16 – 6.14 (m, 1H), 2.37 (s, 3H), 1.38 (s, 9H).
	2-(4-nitrophenyl)furan (**4a**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 – 8.22 (m, 2H), 7.79 – 7.77 (m, 2H), 7.57 – 7.56 (m, 1H), 6.88 – 6.86 (m, 1H), 6.55 (dd, *J* = 3.4, 1.8 Hz, 1H).
	2-(4-cyanophenyl)furan (**4b**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 94% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 – 7.31 (m, 2H), 7.64 – 7.62 (m, 2H), 7.53 – 7.52 (m, 1H), 6.81 (dd, *J* = 3.4, 0.5 Hz, 1H), 6.53 (dd, *J* = 3.4, 1.8 Hz, 1H).

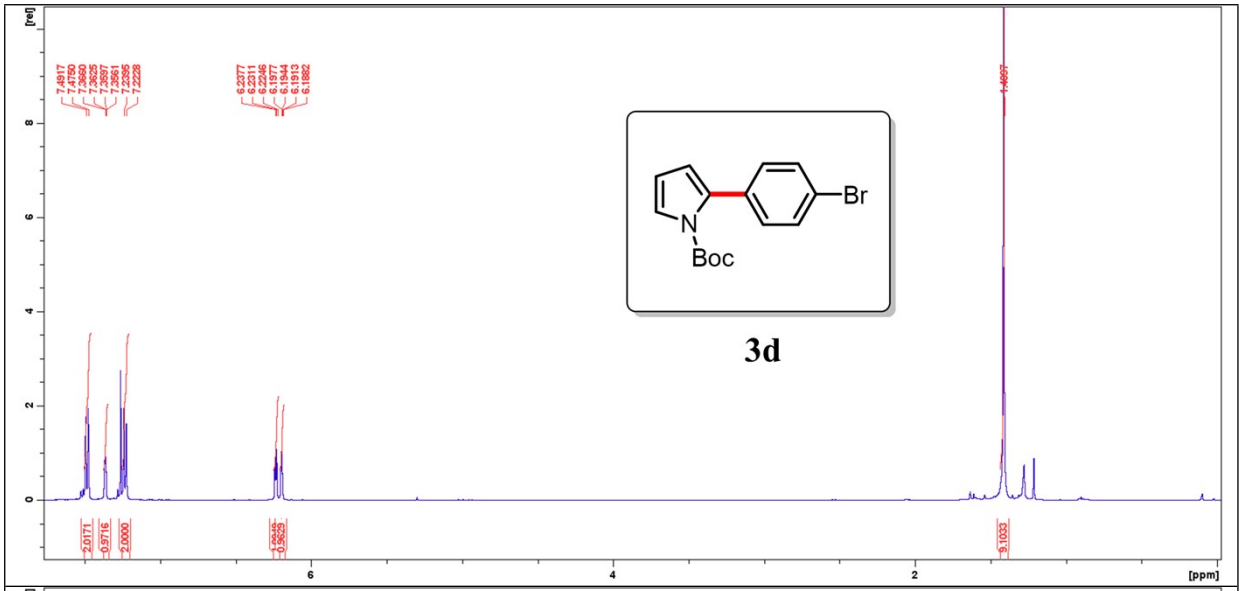
	2-(4-chlorophenyl)furan (**4c**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 – 7.31 (m, 2H), 7.47 – 7.46 (m, 1H), 7.36 – 7.34 (m, 2H), 6.64 – 6.63 (m, 1H), 6.48 – 6.46 (m, 1H).
	2-(4-bromophenyl)furan (**4d**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 – 7.47 (m, 5H), 6.66 (dd, *J* = 3.4, 0.4 Hz, 1H), 6.48 (dd, *J* = 3.4, 1.8 Hz, 1H).
	2-(4-iodophenyl)furan (**4e**)[18] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 – 7.70 (m, 2H), 7.48 – 7.47 (m, 1H), 7.42 – 7.39 (m, 2H), 6.67 (dd, *J* = 3.5, 0.4 Hz, 1H), 6.65 (dd, *J* = 3.4, 1.8 Hz, 1H).
	2-(2-nitrophenyl)furan (**4g**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 95% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 – 7.66 (m, 2H), 7.58 – 7.55 (m, 1H), 7.51 – 7.50 (m, 1H), 7.42 – 7.39 (m, 1H), 6.68 (dd, *J* = 3.6, 0.5 Hz, 1H), 6.50 (dd, *J* = 3.5, 1.8 Hz, 1H).
	2-(3-nitrophenyl)furan (**4h**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 – 8.48 (m, 1H), 8.10 – 8.08 (m, 1H), 7.97 – 7.95 (m, 1H), 7.56 – 7.53 (m, 2H), 6.82 (dd, *J* = 3.4, 0.4 Hz, 1H), 6.54 (dd, *J* = 3.4, 0.4 Hz, 1H).
	2-(4-methoxyphenyl)furan (**4j**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 – 7.60 (m, 2H), 7.43 (*br.* s, 1H), 6.94 – 6.92 (m, 2H), 6.52 – 6.51 (m, 1H), 6.46 (dd, *J* = 3.2, 1.6 Hz, 1H),

	3.84 (s, 3H).
	2-(4-methylphenyl)furan (**4k**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 20% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 – 7.55 (m, 2H), 7.45 – 7.44 (m, 1H), 7.20 – 7.18 (m, 2H), 6.60 (d, *J* = 3.4 Hz, 1H), 6.46 (dd, *J* = 3.3, 1.8 Hz, 1H), 2.36 (s, 3H).
	2-(4-nitrophenyl)thiophene (**5a**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 – 8.23 (m, 2H), 7.76 – 7.73 (m, 2H), 7.49 – 7.43 (m, 2H), 7.16 – 7.14 (m, 1H).
	2-(4-cyanophenyl)thiophene (**5b**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 – 7.62 (m, 4H), 7.42 – 7.38 (m, 2H), 7.14 – 7.11 (m, 1H).
	2-(4-chlorophenyl)thiophene (**5c**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 56% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.44 (m, 2H), 7.28 – 7.25 (m, 2H), 7.22 – 7.20 (m, 2H), 7.01 – 6.99 (m, 1H).
	2-(4-bromophenyl)thiophene (**5d**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.46 (m, 4H), 7.30 – 7.29 (m, 2H), 7.09 – 7.07 (m, 1H).
	2-(4-iodophenyl)thiophene (**5e**)[19] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 – 7.73 (m, 1H), 7.59 – 7.54 (m, 2H), 7.47 – 7.44 (m, 1H), 7.42 – 7.41 (m, 1H), 7.10 – 7.07 (m, 2H).

	2-(2-nitrophenyl)thiophene (**5g**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 – 7.53 (m, 2H), 7.21 – 7.19 (m, 2H), 7.16 – 7.14 (m, 2H), 6.94 – 6.92 (m, 1H).
	2–(3-nitrophenyl)thiophene (**5h**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 – 8.41 (m, 1H), 8.11 – 8.08 (m, 1H), 7.90 – 7.87 (m, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.43 – 7.41 (m, 1H), 7.38 – 7.36 (m, 1H), 7.14 – 7.11 (m, 1H).
	2-(4-methoxyphenyl)thiophene (5**j**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 36% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 – 7.53 (m, 2H), 7.22 – 7.20 (m, 2H), 7.07 – 7.04 (m, 1H), 6.93 – 6.91 (m, 2H), 3.84 (s, 3H).
	2-(4-methylphenyl)furan (5**k**)[16] isolation by column chromatography (cyclohexane/EtOAc: 90/10) in 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 – 7.42 (m, 2H), 7.20 – 7.16 (m, 2H), 7.12 – 7.10 (m, 2H), 7.00 – 6.97 (m, 1H), 2.29 (s, 3H).

8. ^{1}H NMR spectral data of the arylation products





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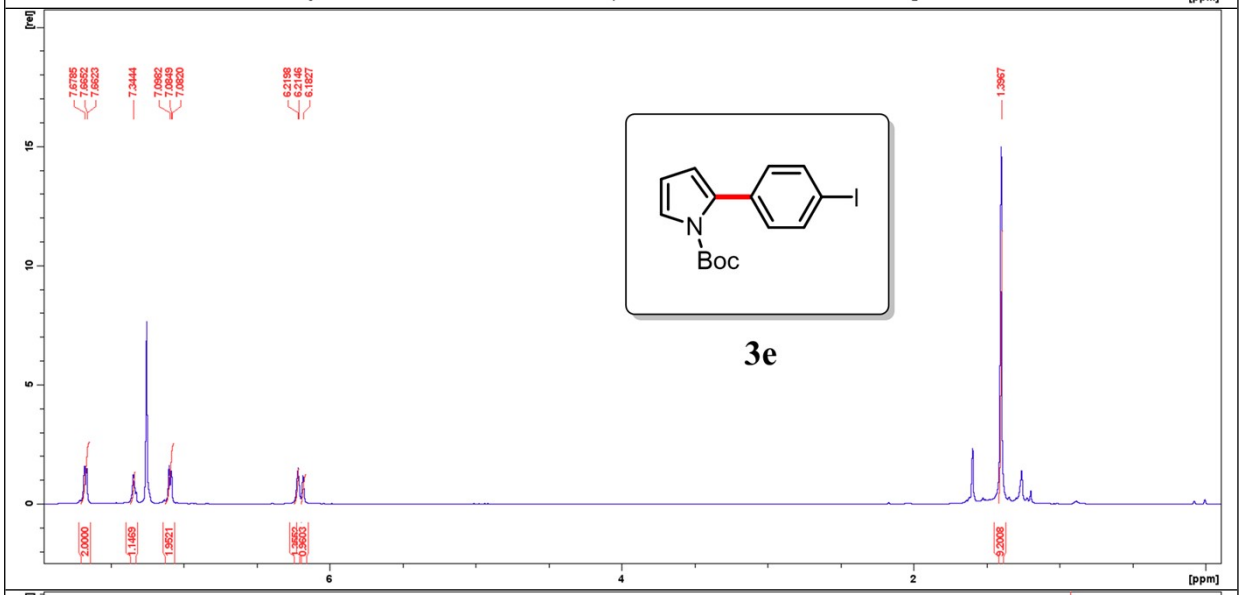

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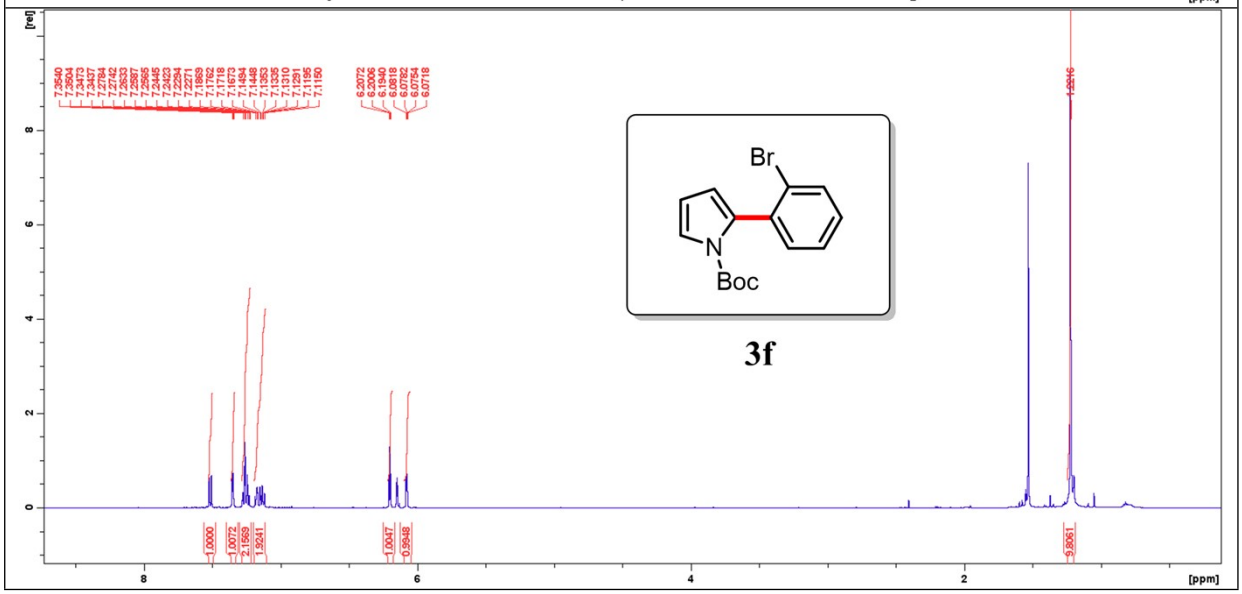

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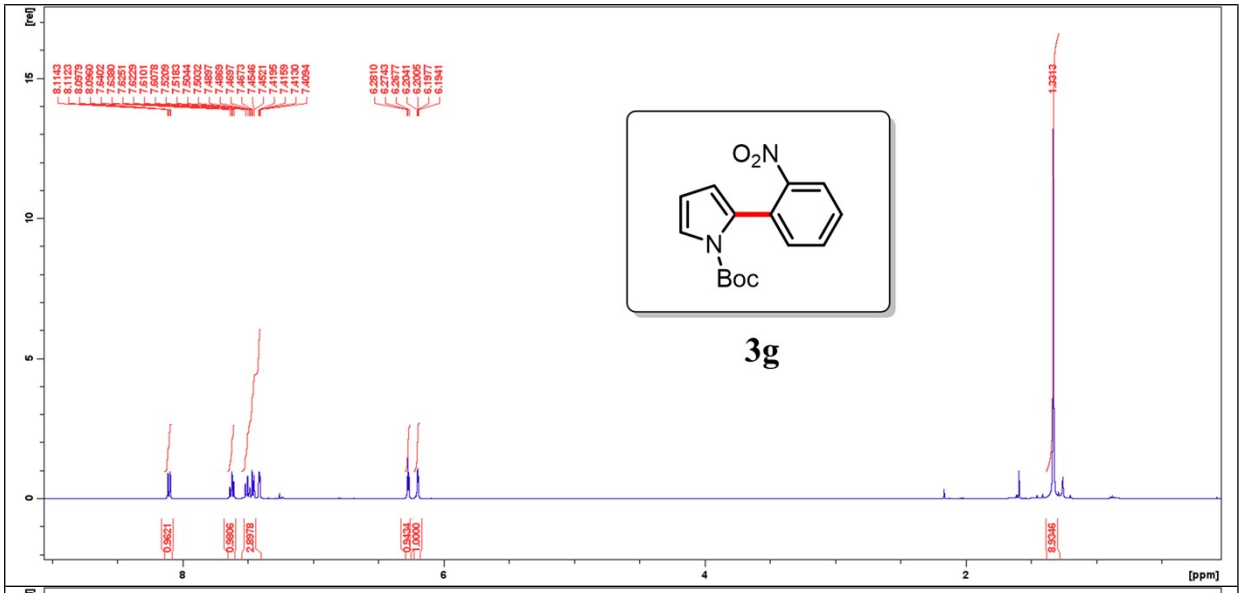

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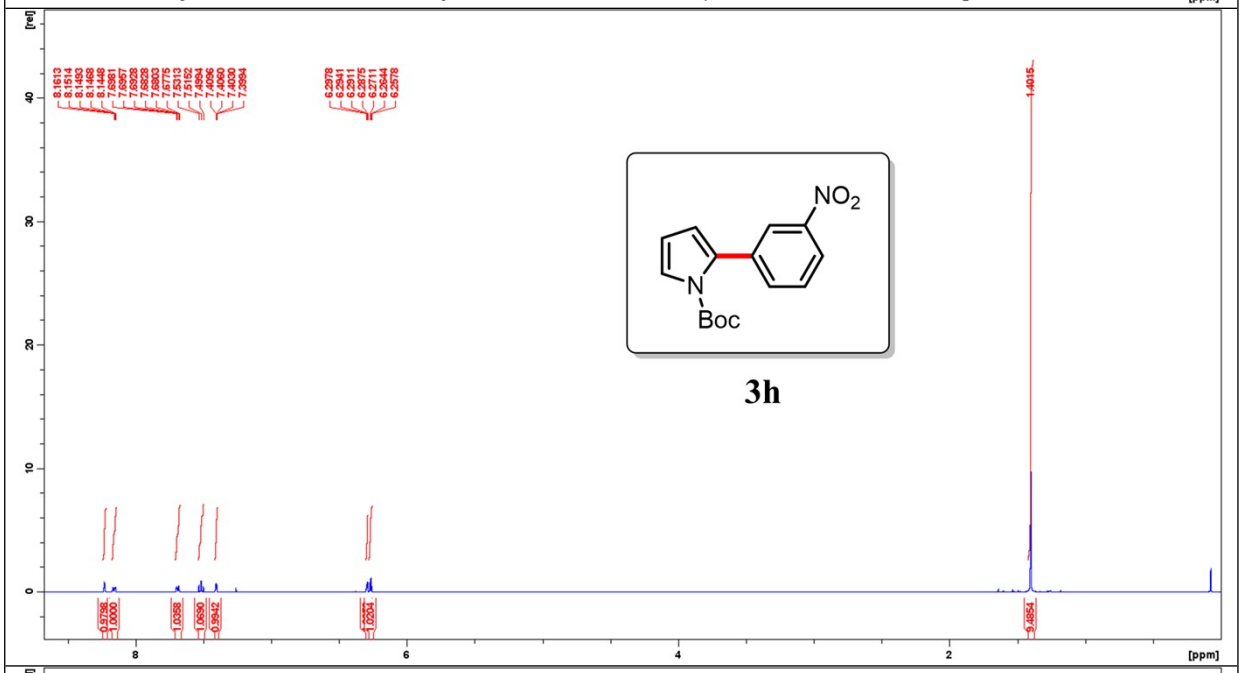

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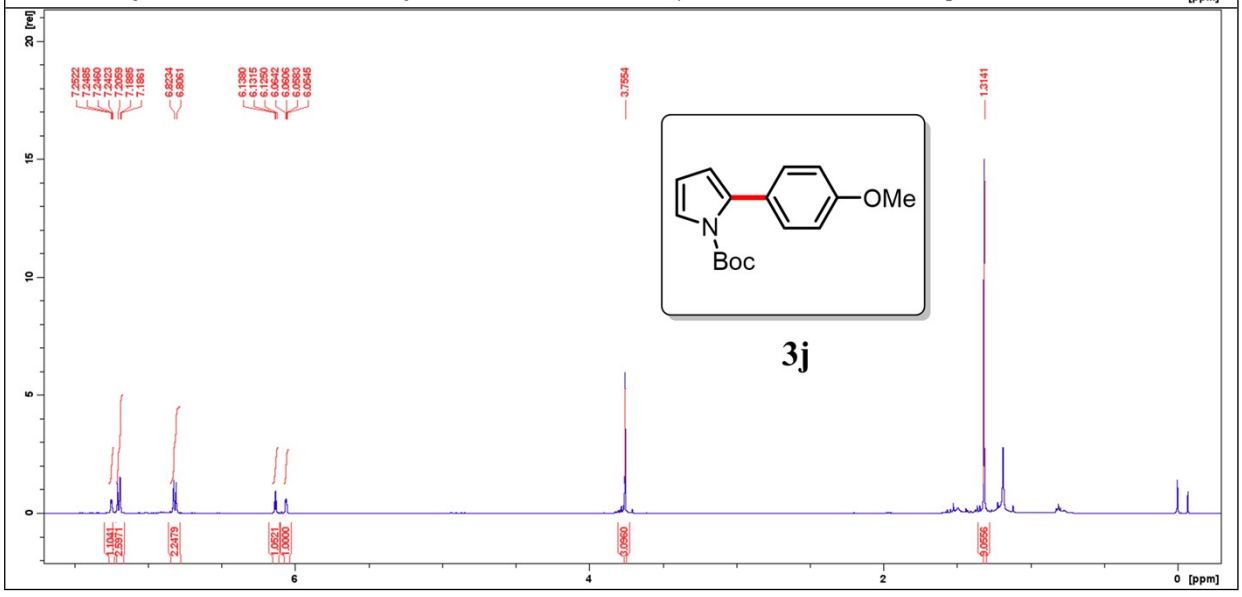

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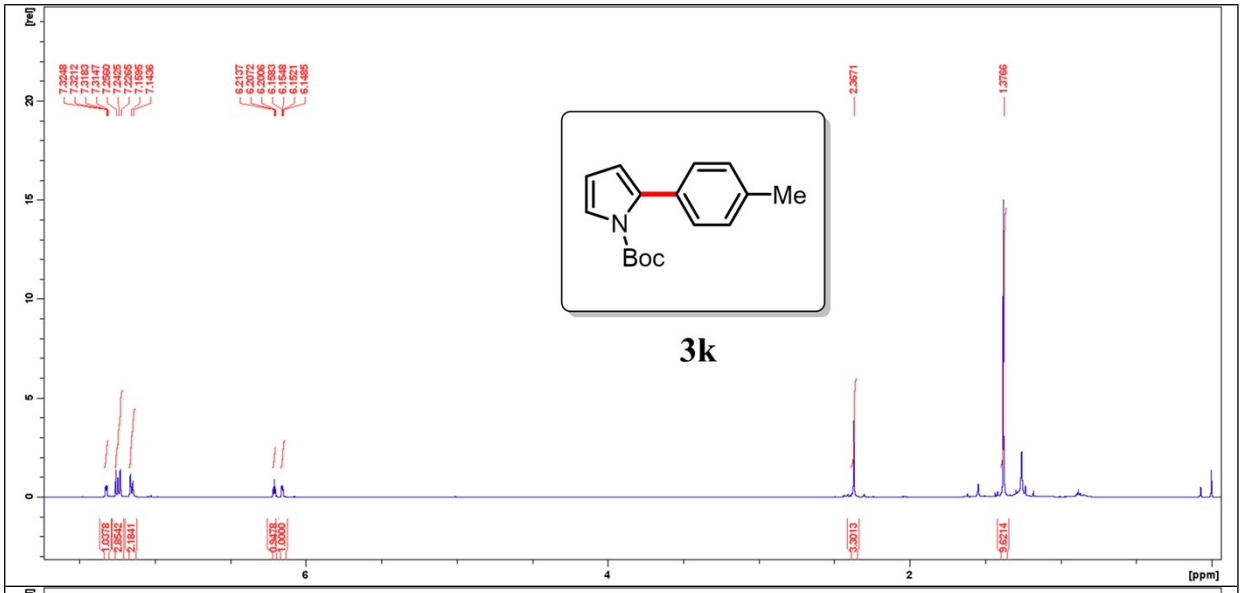

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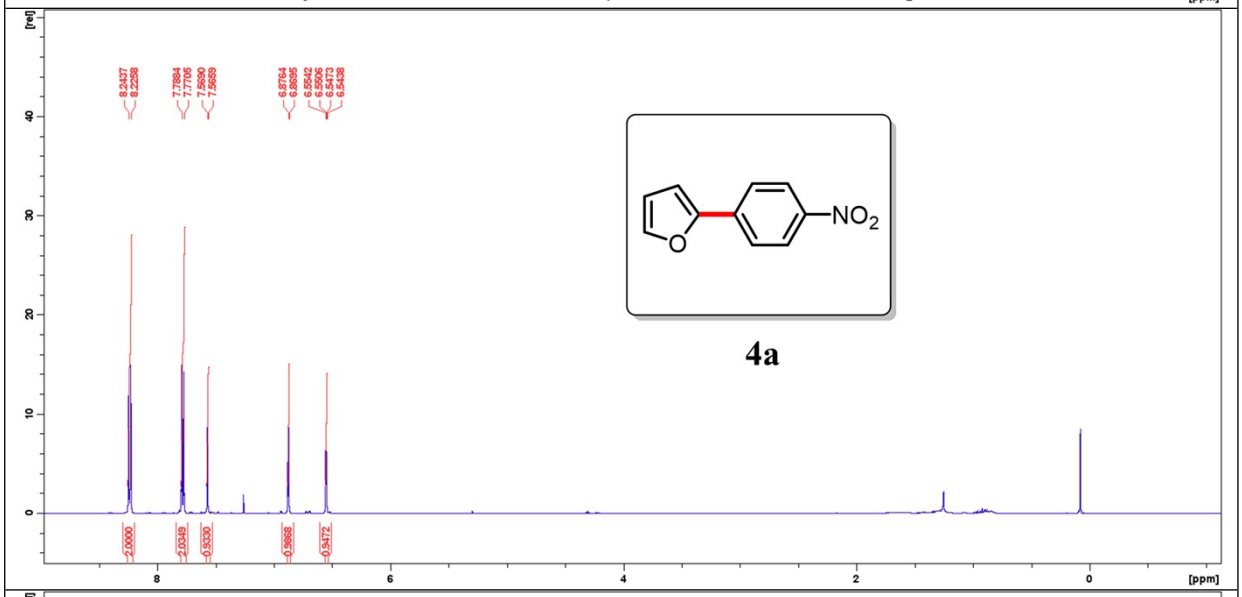

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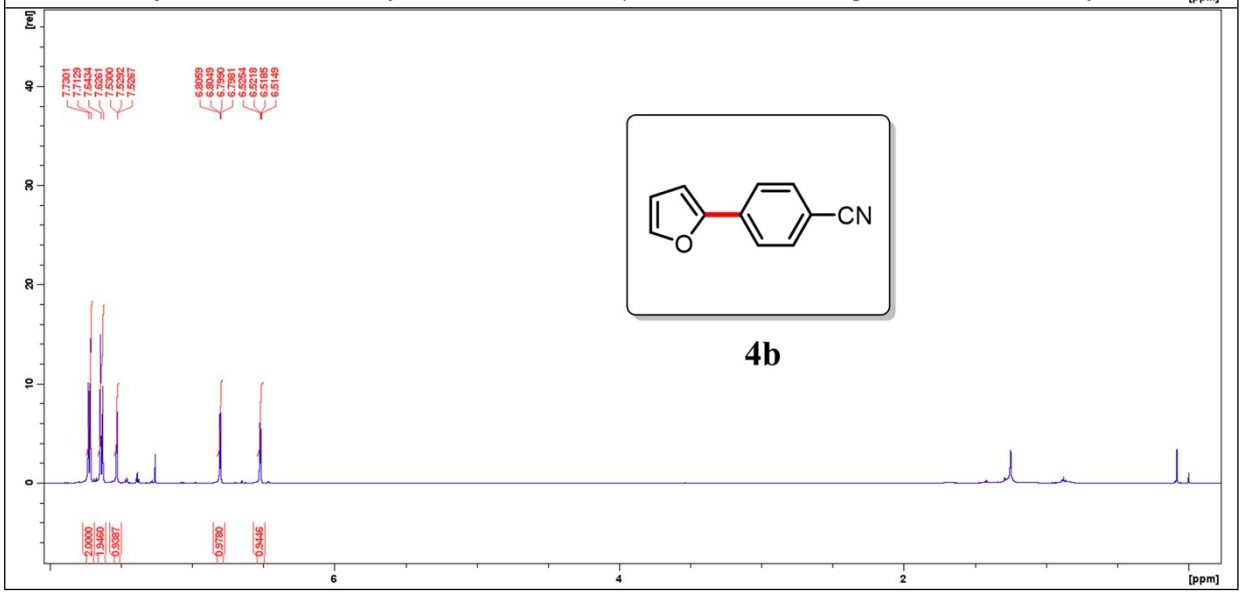

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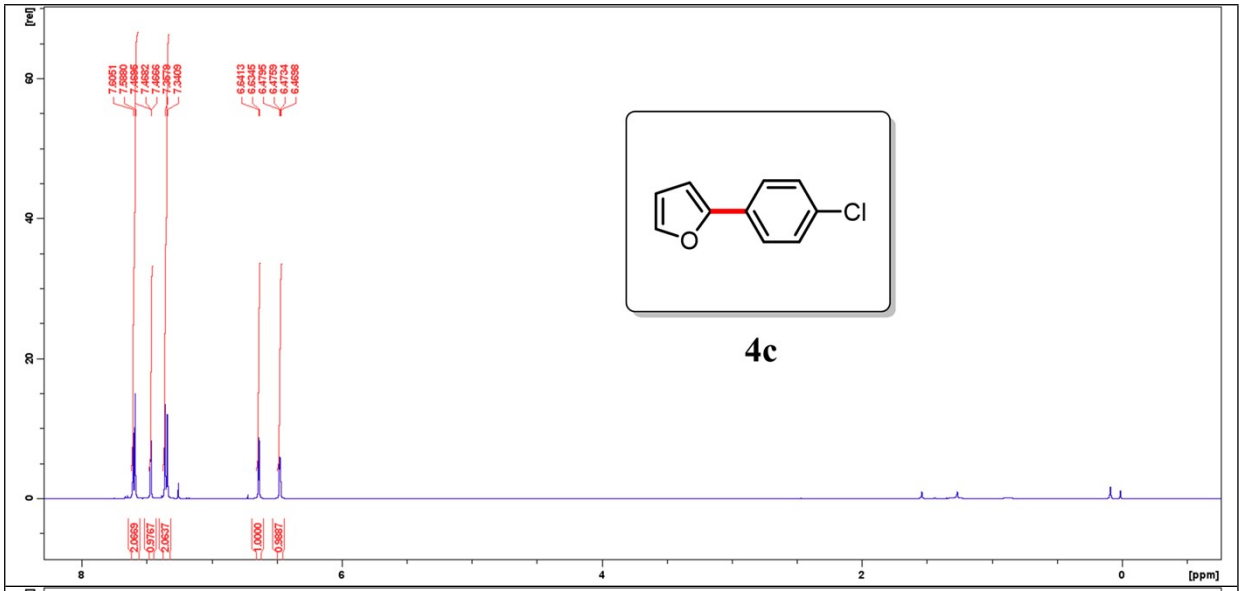
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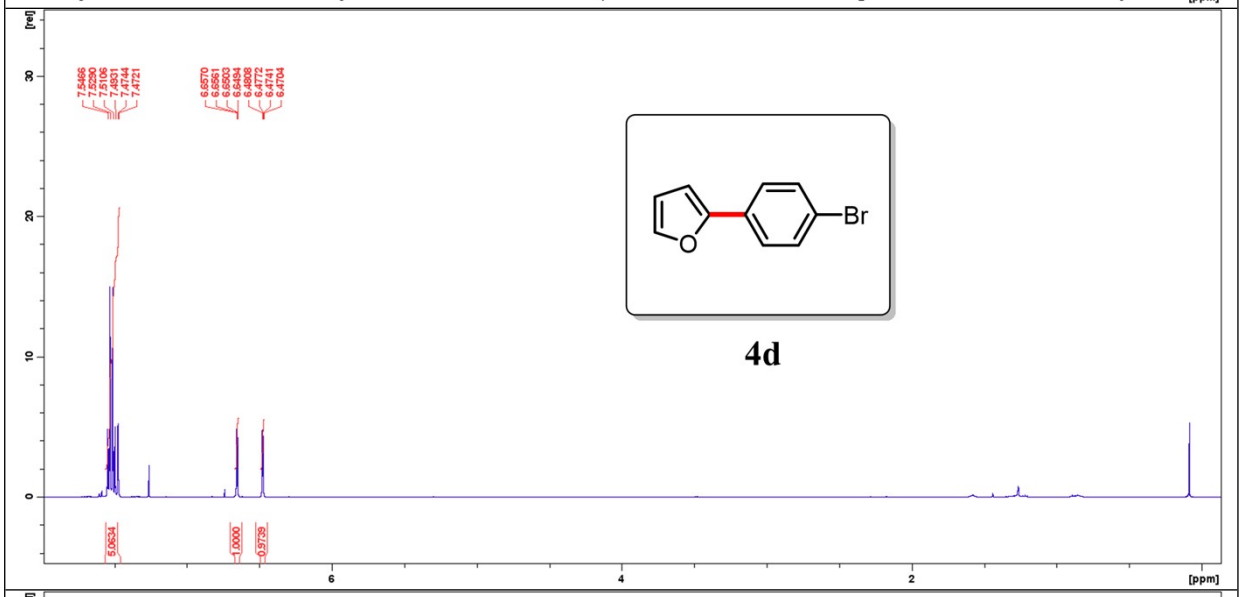
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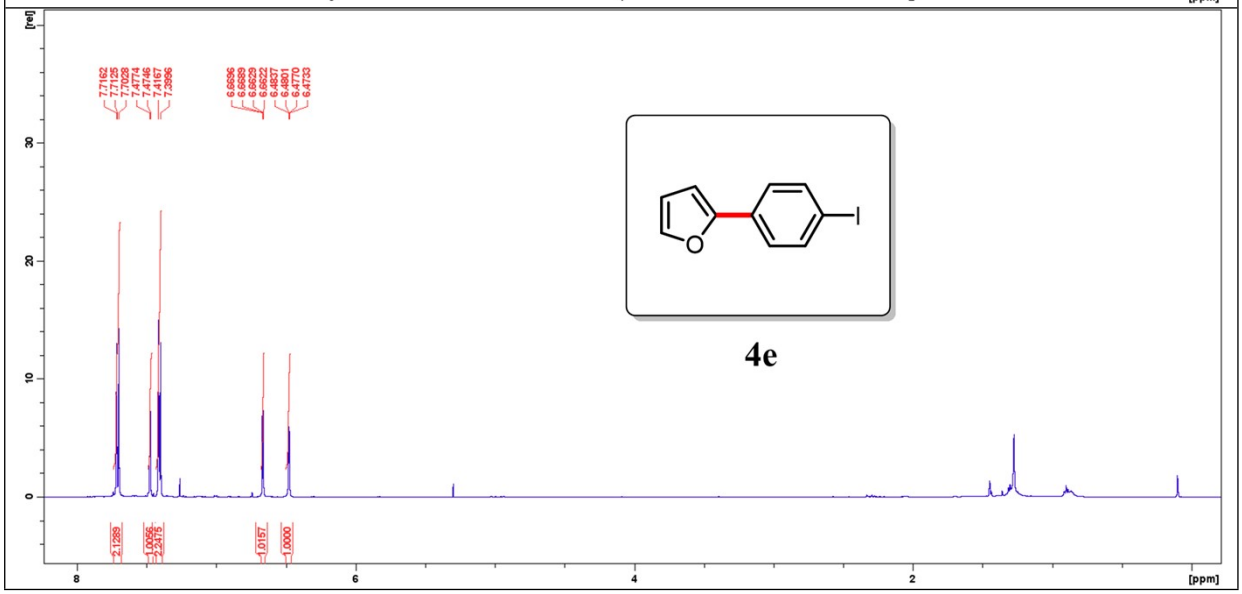
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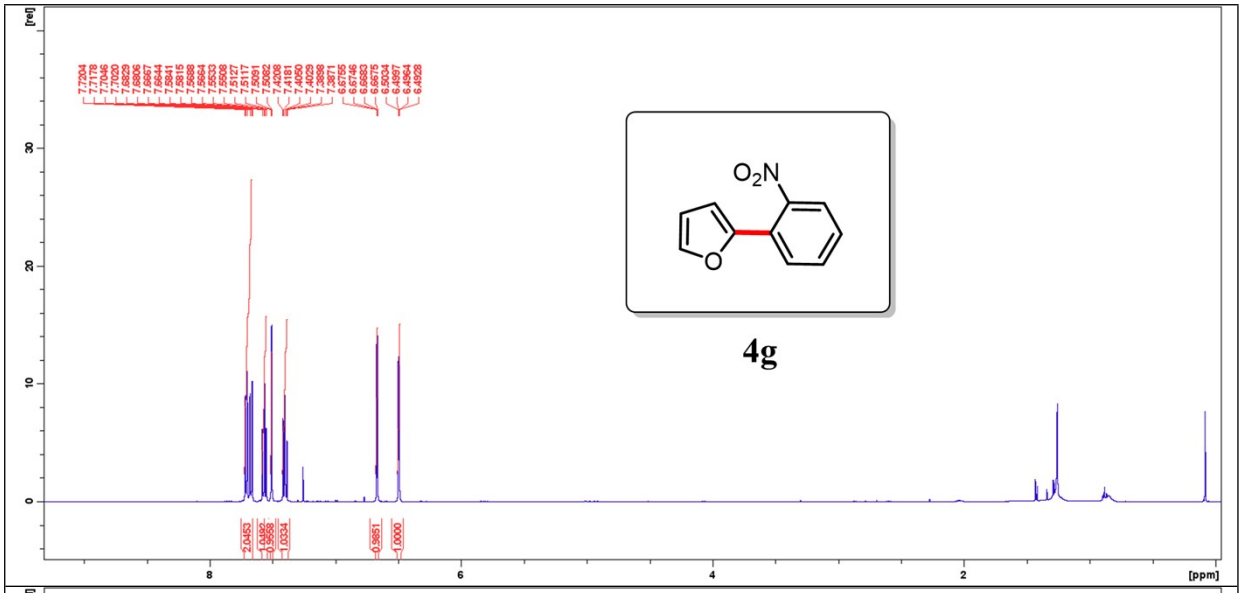
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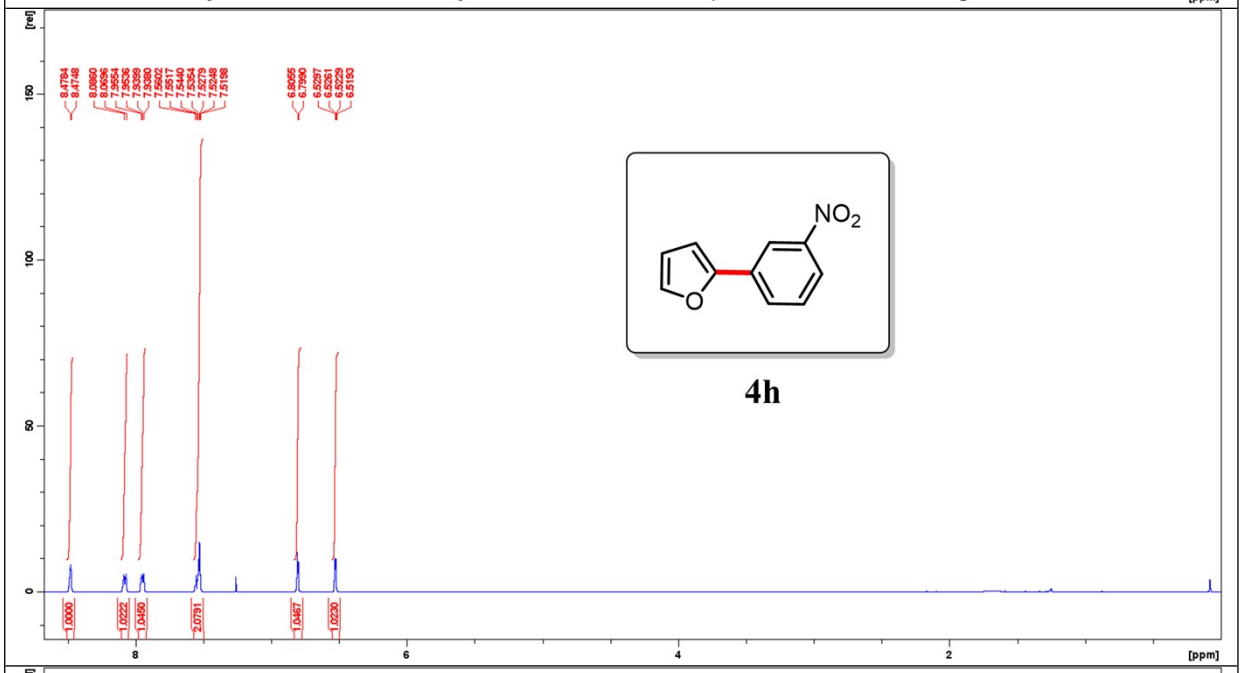
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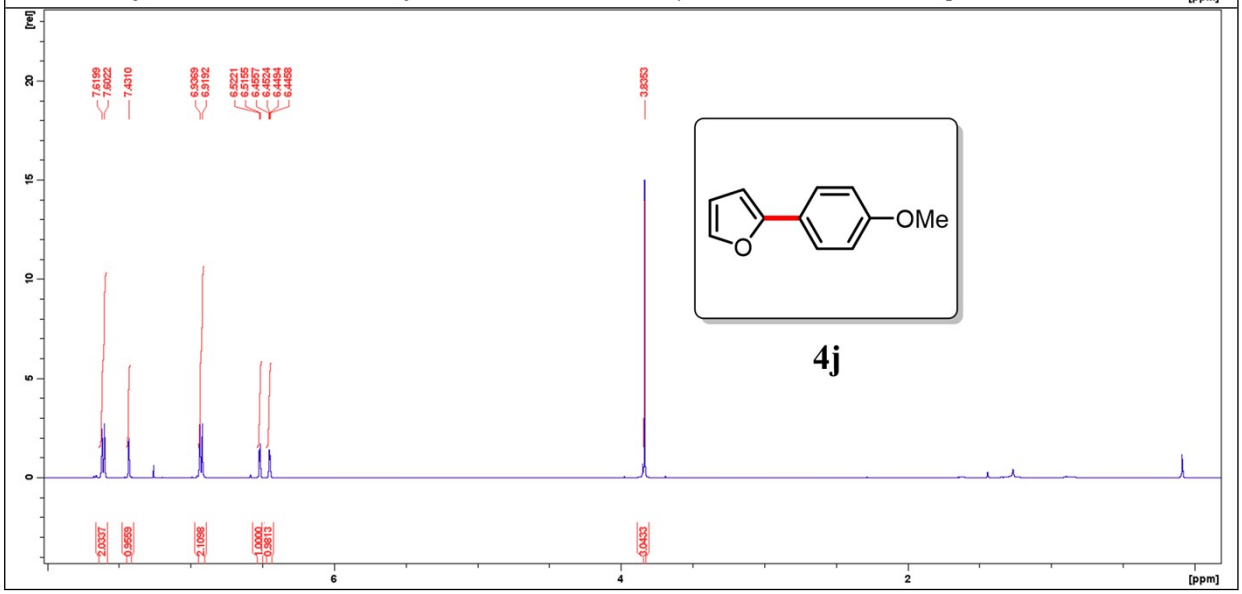
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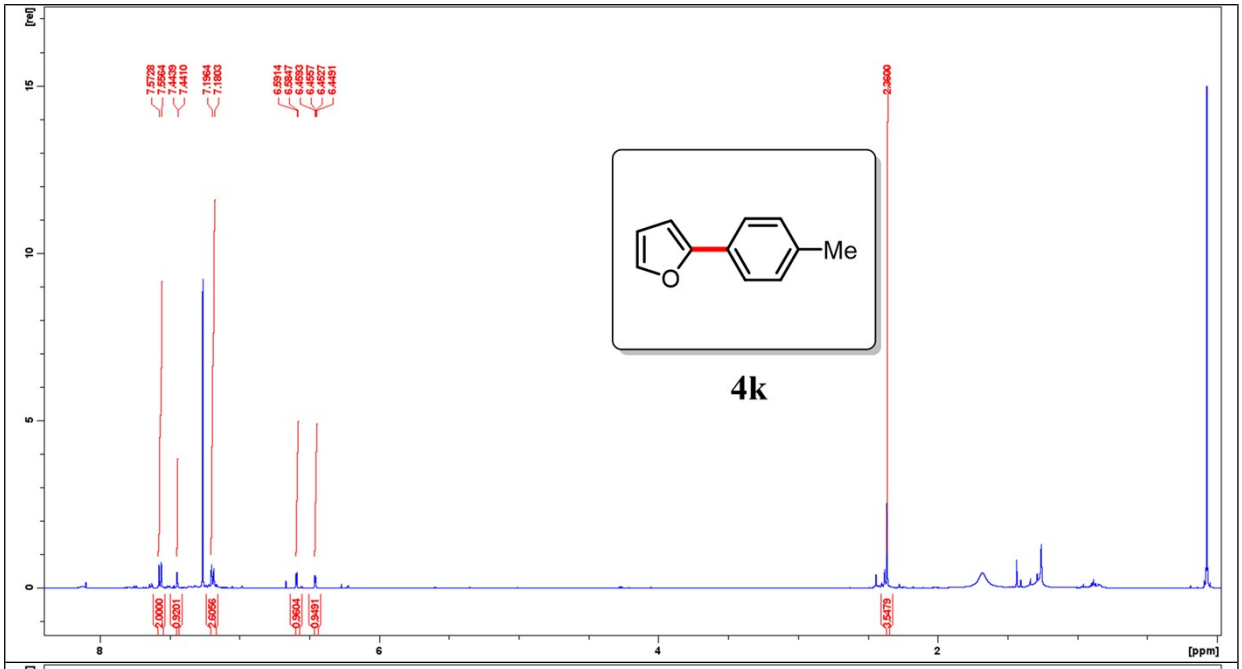

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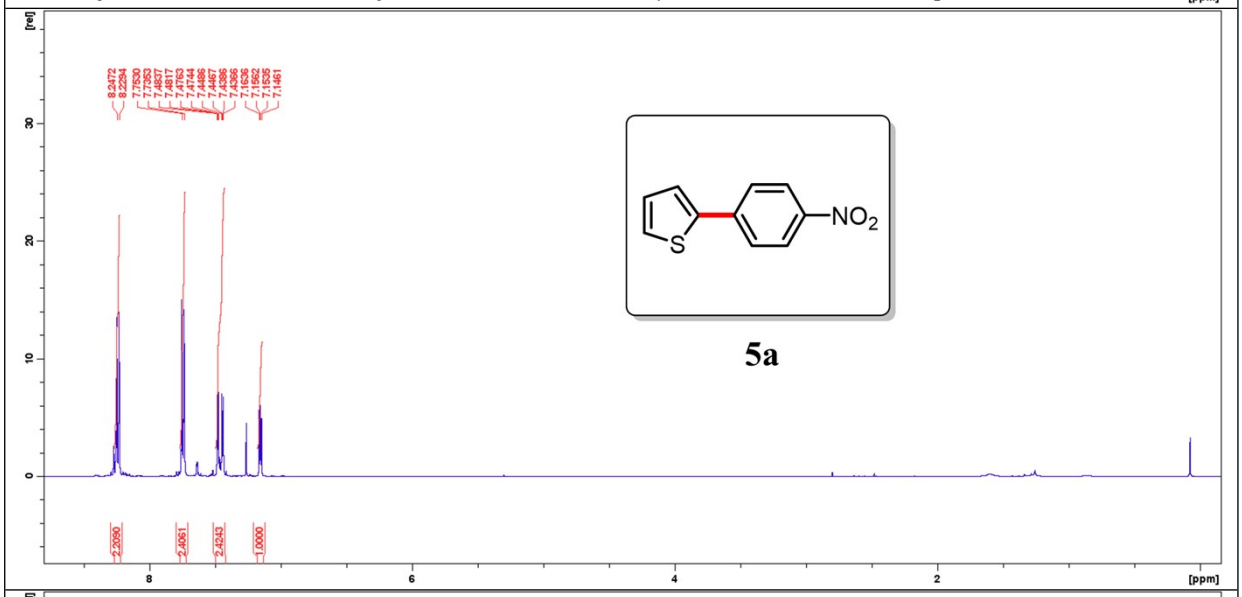

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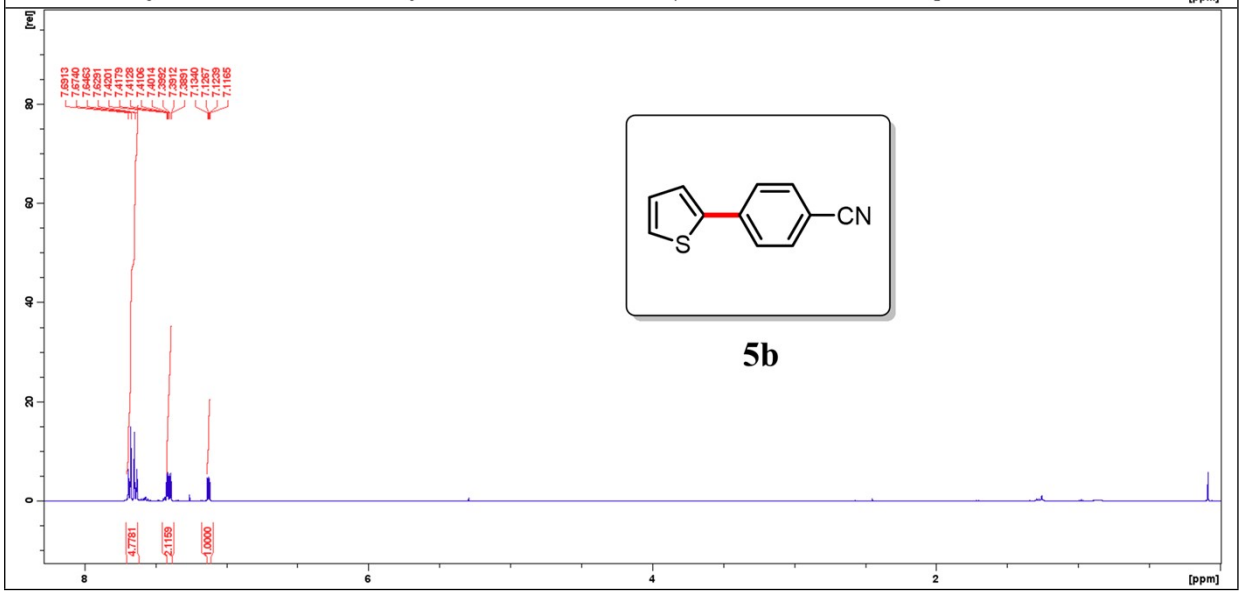

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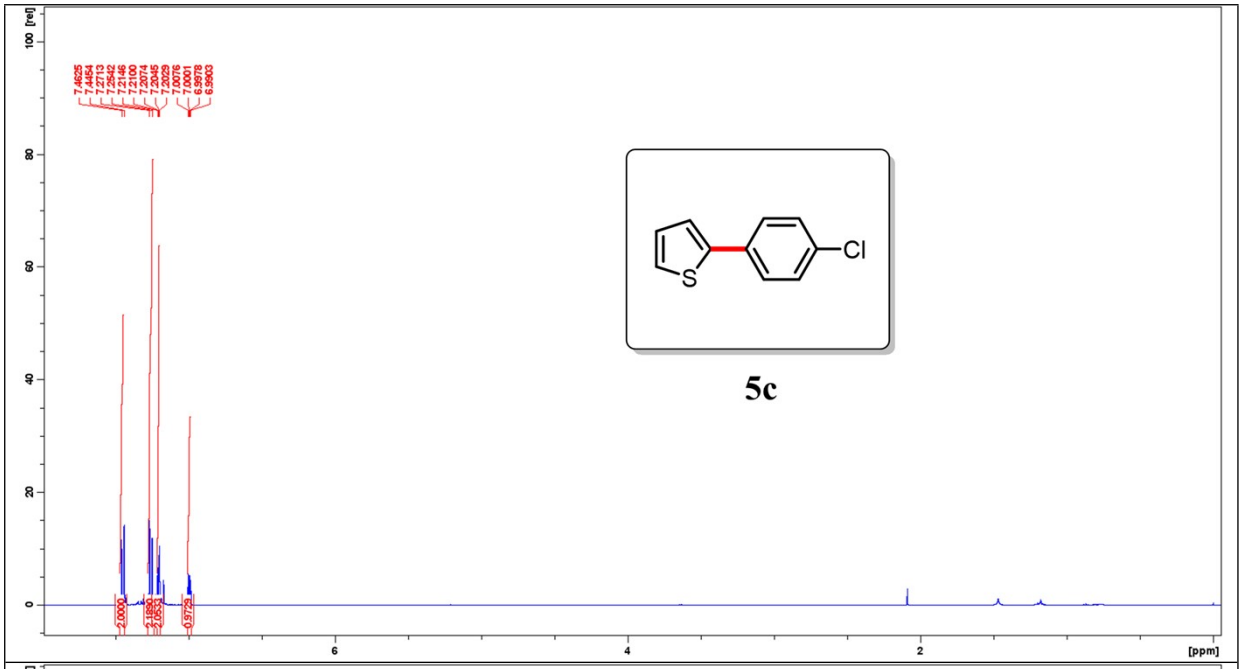

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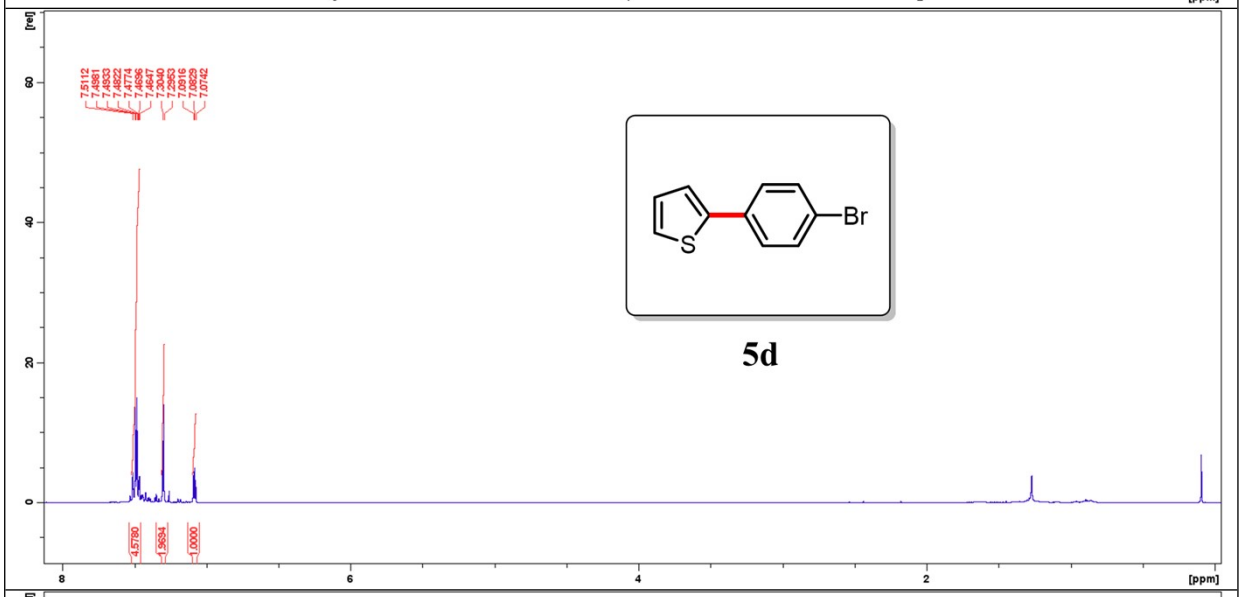

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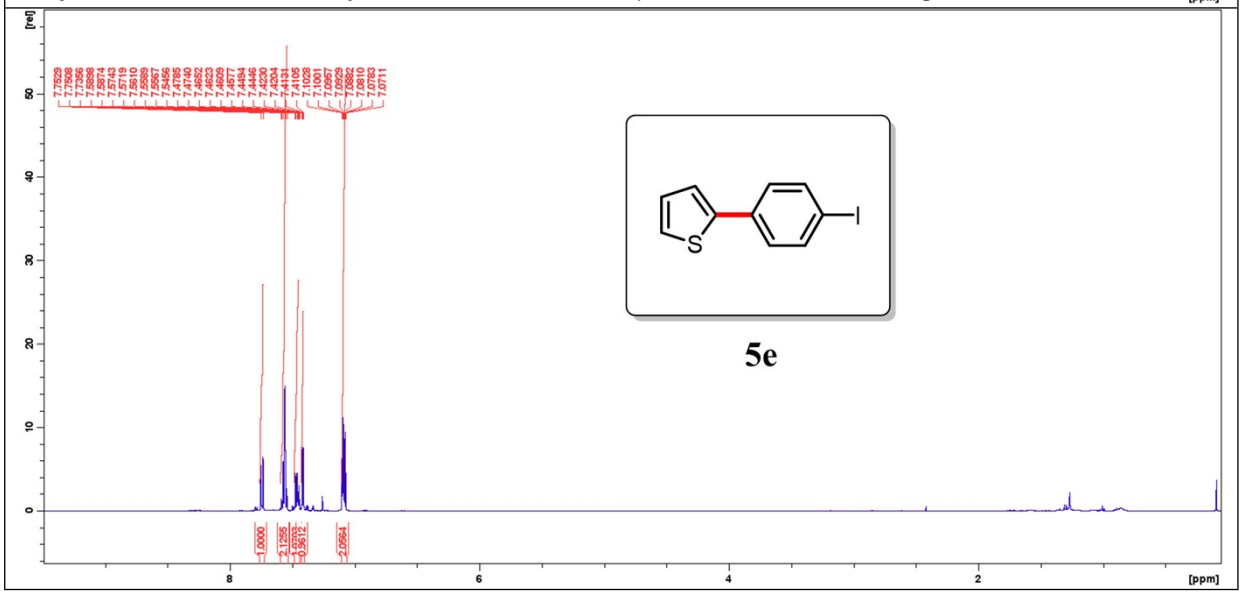

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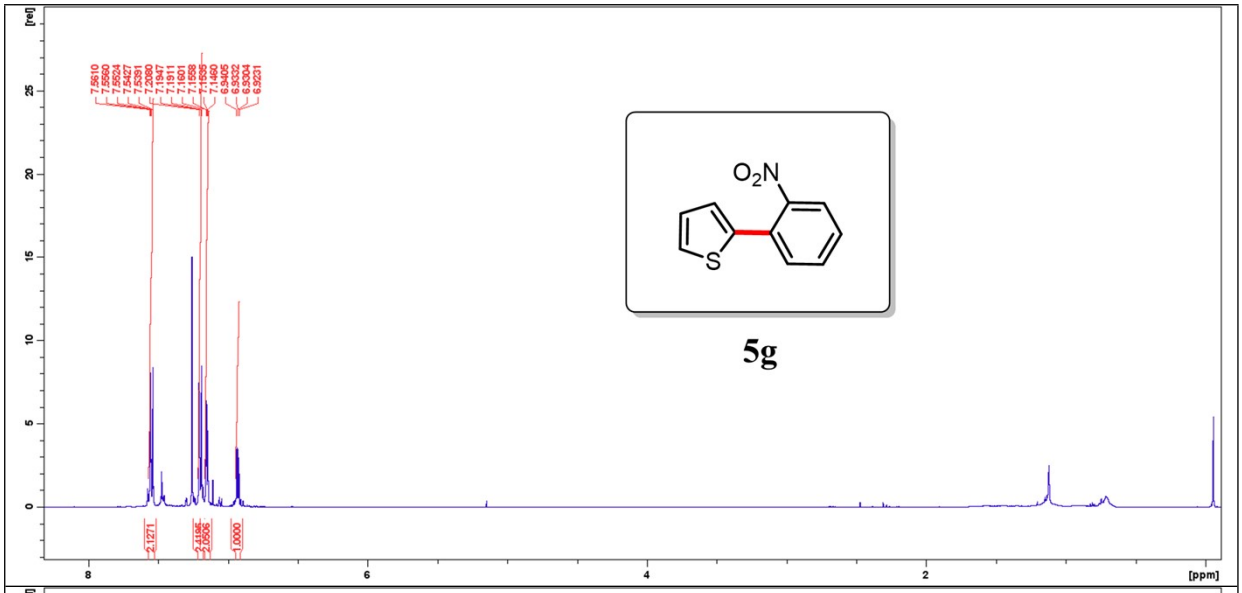

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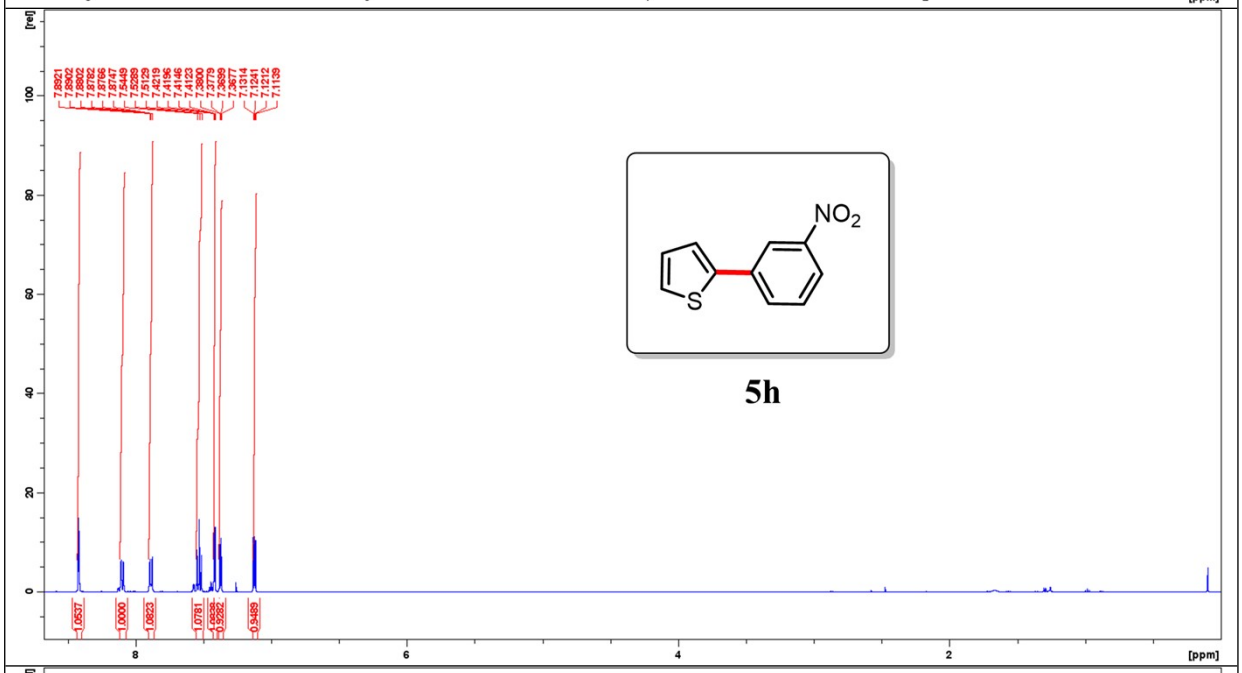

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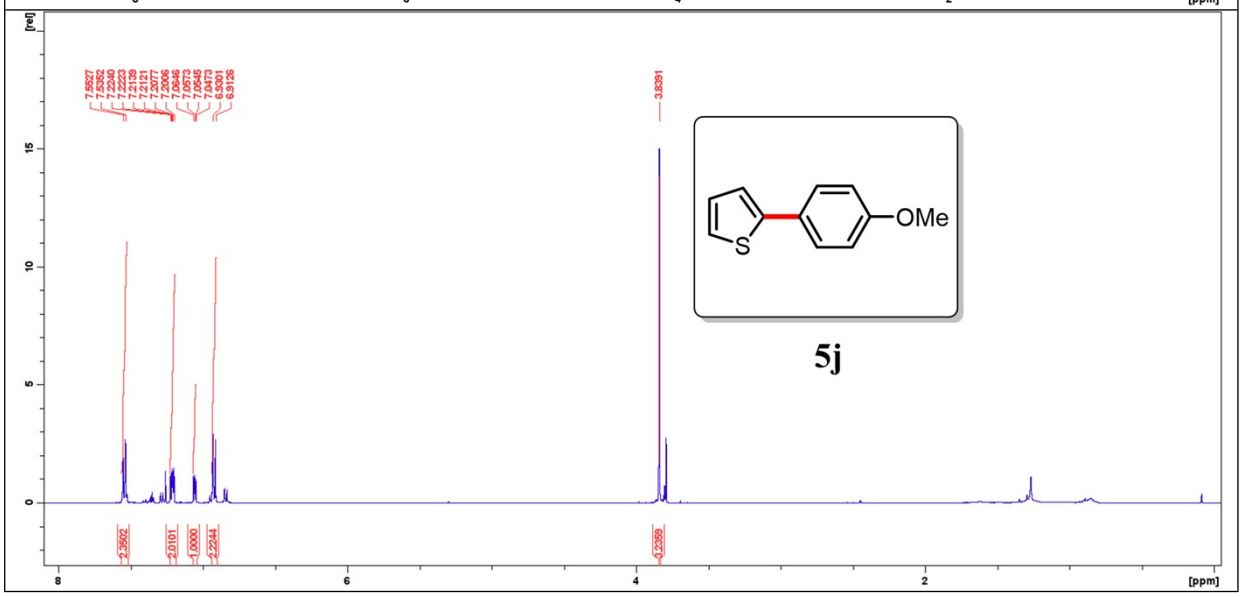

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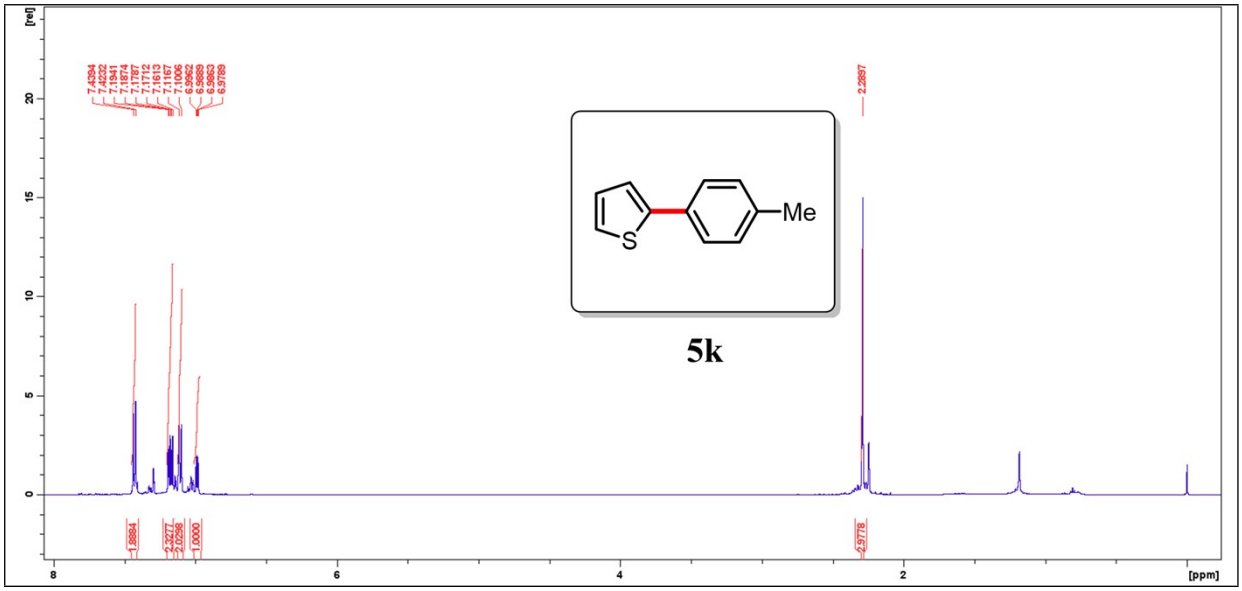
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5k

9. References

1 M. Zhao, H. Qian, X. Niu, W. Wang, L. Guan, J. Sha and Y. Wang, *Cryst. Growth Des.*, 2016, **16**, 1096–1103.

2 G. Tiouitchi, M. A. Ali, A. Benyoussef, M. Hamedoun, A. Lachgar, M. Benaissa, A. Kara, A. Ennaoui, A. Mahmoud, F. Boschini, H. Oughaddou, A. El Kenz and O. Mounkachi, *Mater. Lett.*, 2019, **236**, 56–59.

3 J. Xu, H.-T. Wu, X. Wang, B. Xue, Y.-X. Li and Y. Cao, *Phys. Chem. Chem. Phys.*, 2013, **15**, 4510.

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