Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Black Phosphorous as a Metal-Free, Visible-Light-Active Heterogeneous Photoredox Catalyst for the Direct C-H Arylation of Heteroarenes

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1. General Information

Chemicals: Red Phosphorus (98.9%), Sn (99.5%), tetrafluoroboric acid and tin(IV) iodide (SnI_4, 95%) were purchased from Alfa Aesar. Ethyl alcohol (absolute) and aniline derivatives were purchased from Sigma-Aldrich. Dimethylsulfoxide (DMSO) was purchased from Merck. *tert*-Butyl nitrite(*t*BuONO) was purchased from J&K scientific. All materials were purchased from commercial suppliers and used without further purification.

Instrumentation: X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Thermo Scientific X-ray photoelectron spectrometer with an aluminum anode (Al Kα, 1468.3 eV). Sample's crystal structure was investigated by a Bruker D8 Advance X-ray Diffractometer (Cu Kα, 1.5406 Å). Transmission electron microscopy (TEM) was performed on a Hitachi HT7800 TEM instrument (120 kV) working at a high-resolution (HR) mode. Raman spectra were recorded using a Renishaw inVia Raman microscope (excitation source 532 nm). Absorption spectra were recorded on a Shimadzu UV-3600 UV−vis−NIR spectrophotometer. Atomic force microscopy (AFM) measurements were done by using Bruker Dimension Icon AFM. Scanning electron microscopy (SEM) images were recorded with Zeiss Ultra Plus Field Emission Scanning Electron Microscope. ^{1}H-NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ solution with internal solvent signal peak at 7.26 ppm. Proton NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t =triplet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet), and coupling constants (Hz). All C-H arylation products are known in the literature and were identified by comparison with the previously reported NMR data. All reactions were monitored by column chromatography using Merck silica gel 60 (230-400 mesh ASTM) as the stationary phase and ethyl acetate/n-hexane were used as eluents; visualization was accomplished with short wave UV light (254 nm).

Homemade photocatalytic reaction setup: A homemade system was used for all photocatalytic reactions (**Figure S1**). The homemade system is formed by a jacketed reaction flask (25 mL) with a teflon stopcock, , a magnetic stirrer, a teflon-coated stir bar, a Philips CDM-SA/T 150W/942 1CT/12 metal halide lamp with appropriate power supply (150 Watt, 13330 Lumen) and mirrors that are placed at all the walls of the setup in order to gain maximum light efficiency. The reaction temperature was kept constant at 25 °C by using a water-circulator bath.

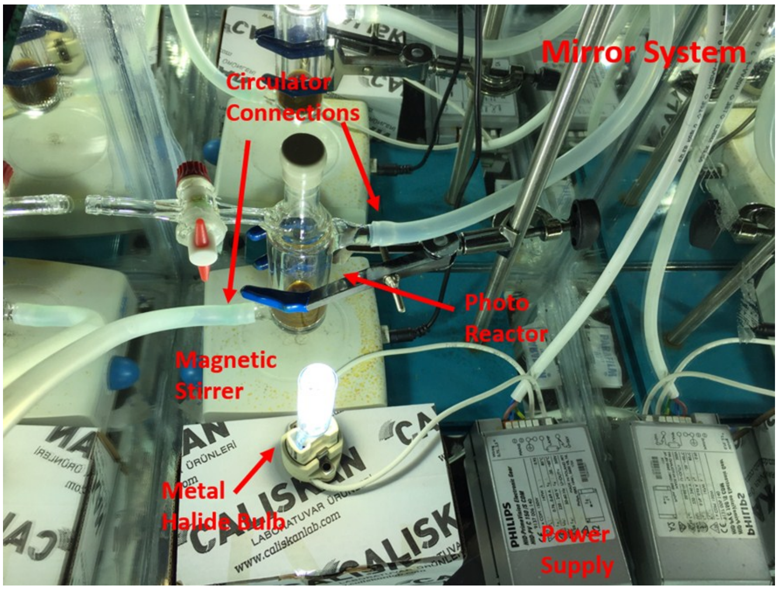


Figure S1. The homemade photocatalytic reaction setup used in the photocatalysis experiments.

2. General Procedures

2.1. Synthesis of BP crystals and their exfoliation into BP nanosheets

Black phosphorus was synthesized by using chemical vapor transport method.[1] Mineralizers (Sn, I) that are being added to ampoule with phosphorus source (Red Phosphorus) are crucial in the synthesis of BP. In a typical synthesis, Red Phosphorus (500 mg), Sn powder (20 mg) and SnI_4 (10 mg) were transferred into a quartz ampoule with 10 cm length and 1.5 cm diameter. The ampoule was sealed under vacuum (0.06 mbar) and it was placed horizontally into a muffle furnace. Firstly, the temperature was raised to 620 °C within 5 hours and kept at this temperature for 5h. Next, it was slowly cooled down to 485 °C and maintained there for 2h followed by natural cooling to room temperature. Ampoule was cracked in dry toluene at room temperature and single crystal BP was obtained (Figure S2). The yielded BP crystals were sonicated in absolute ethanol to remove the impurities (Sn and SnI_4). Purified BP crystals were transferred into a Schlenk flask and vacuum sealed for the further use.

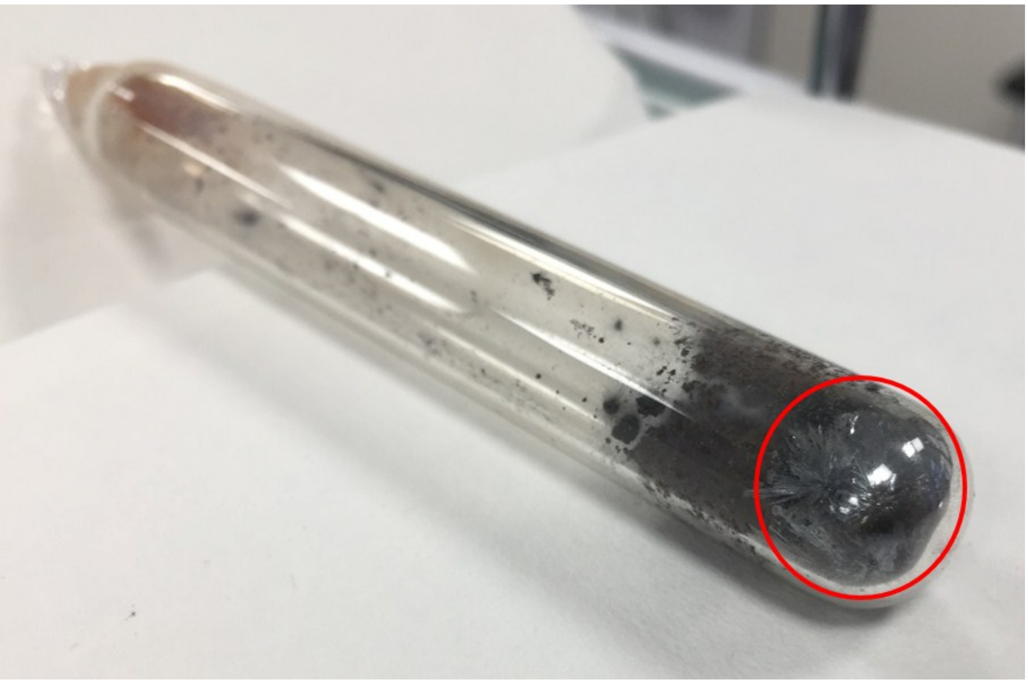


Figure S2. A photography of as-prepared BP crystal in the quartz ampoule

In order to obtain BP nanosheets dispersed in a solvent, 10 mg BP crystals were added into the desired solvent (5 mL) under inert conditions and the resulting mixture was sonicated for 8 hours in a sonicator bath (200W) at 6-7 °C in dark (**Figure S3**). The resultant BP dispersion in DMSO is directly employed as a photoredox catalyst in the C-H arylation reactions.

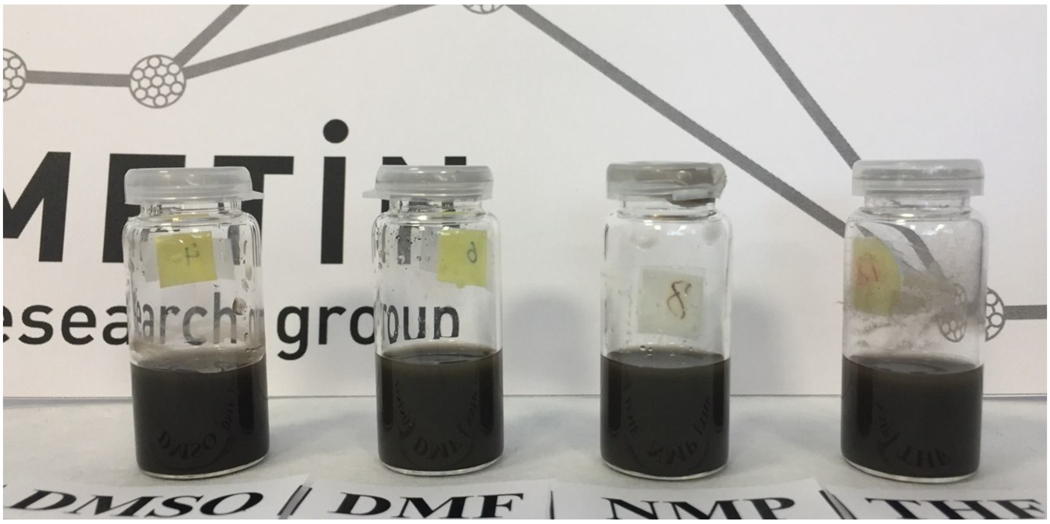


Figure S3. Exfoliated BP nanosheets in various solvents (as prepared), from left to right: DMSO, DMF, NMP and THF.

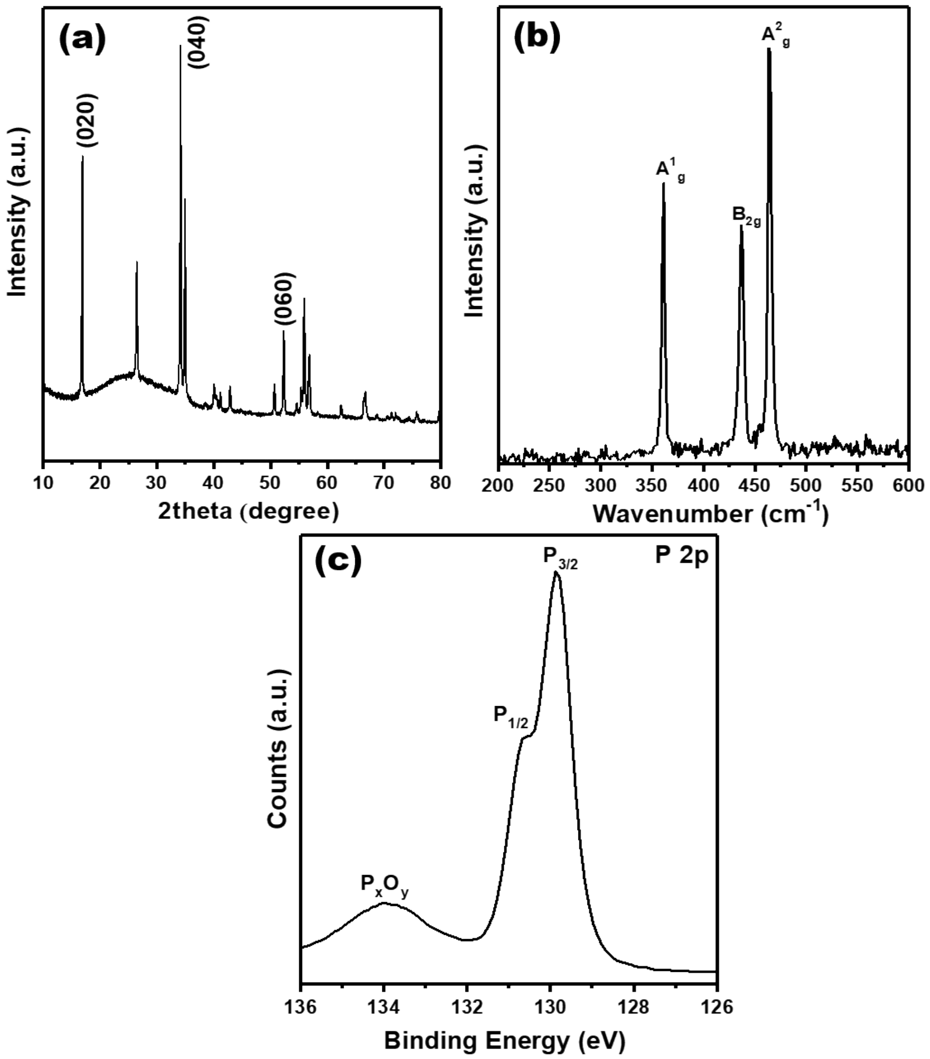


Figure S4. (a) XRD pattern and (b) Raman spectrum and (c) high-resolution XPS spectrum for P 2p core-level of BP after the fifth run of the reusability test.

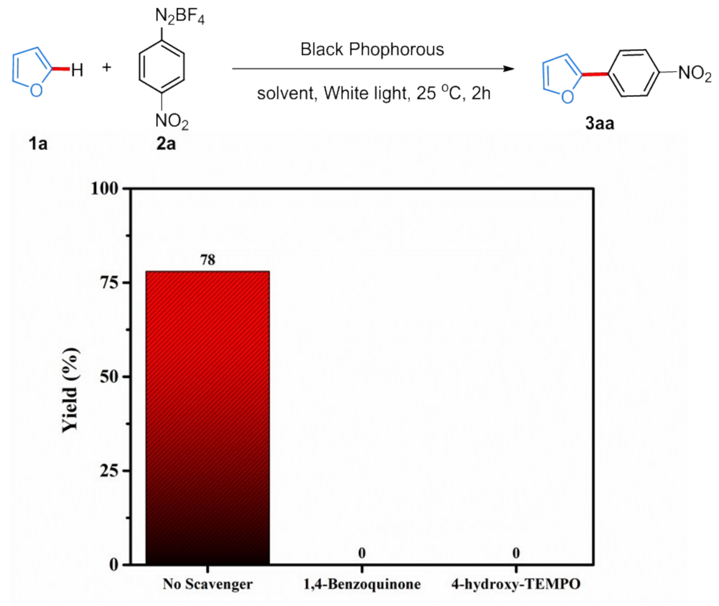


Figure S5. The control experiment with radical scavenger (1,4-benzoquinone and 4-hydroxy-TEMPO) for the photocatalytic C-H arylation of 4-nitrodiazonium tetrafloroborate with furan. Reaction conditions: (1) 0.25 mmol **1a**, 10 mg BP, 5 mL DMSO and furan (2.5 mmol), irradiation with white light for 2 h; (2) the reaction in the presence of 1,4-Benzoquinone (1.25 mmol) as a scavenger. (3) the reaction in the presence of 4-hydroxy-TEMPO (0.5 mmol) as a scavenger. All the yields are determined by column chromatography.

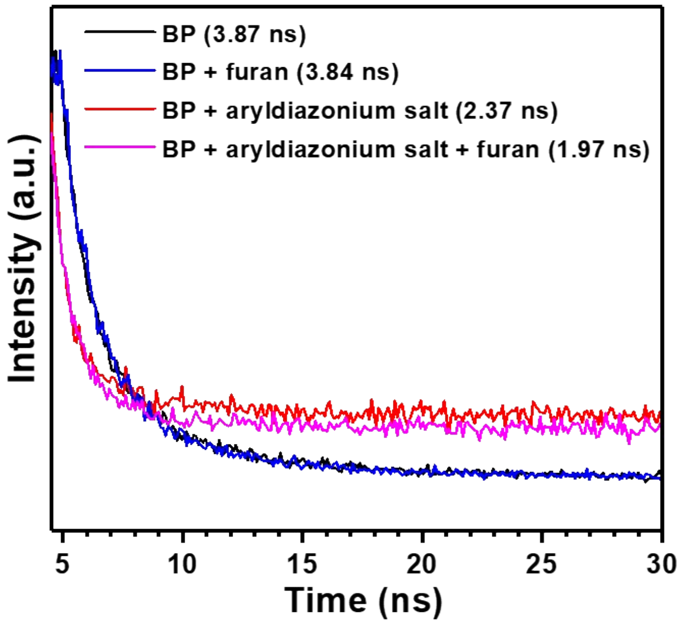


Figure S6. Time-resolved photoluminescence spectroscopy analysis of pristine BP, BP + furan, BP + aryldiazonium salt, BP + aryldiazonium salt + furan. The numerical values given in the parenthesis are the calculated lifetimes for each sample.

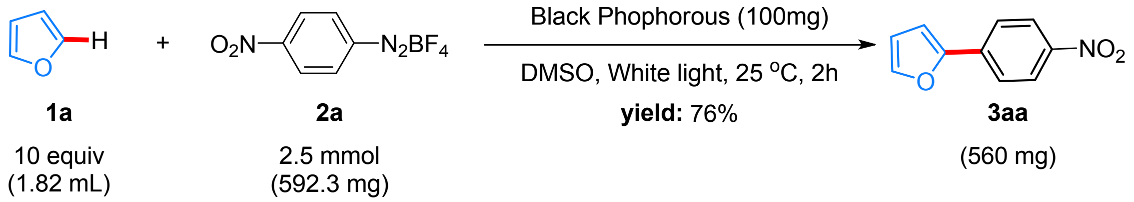
2.2. General procedure for the synthesis of aryl diazonium tetrafluoroborates[1]

The appropriate aniline (5 mmol) was dissolved in a mixture of 3 mL of absolute ethanol and HBF_4 (50%, 1.25 mL, 10 mmol). After cooling the reaction mixture to 4 °C using ice bath and the *tert*-butyl nitrile (1.40 mL, 10 mmol) was added dropwise. The resulting mixture was stirred for 2h at room temperature. Diethyl ether was added until precipitation of diazonium tetrafluoroborate, which is filtered, washed several times with diethyl ether (3x 10mL) and dried under vacuum.

2.3. General procedure for the BP-catalyzed photocatalytic reaction of aryl diazonium tetrafluoroborates with furan

DMSO was dried over 4Å molecular sieves overnight and degassed with Argon for 10 minutes to get rid of dissolved oxygen before the sonication procedure. Then, BP (10 mg) which was being held under an argon atmosphere, was transferred into 5 mL of DMSO. Sonication was conducted under dark conditions for 8h at 6 ^{o}C to ensure the stability of BP. Subsequently, this exfoliated black phosphorus and aryl diazonium tetrafluoroborate (1 equiv, 0.25 mmol) were added to a 25 mL photoreactor equipped with a magnetic stirring bar. Then, furan (10 equiv, 2.5 mmol) was added via micropipette to the reaction mixture. The photoreactor was irradiated through the reactor's plane bottom side using white light. After 2 h of irradiation the reaction mixture was transferred to separating funnel, diluted with EtOAc (10 mL) and washed with brine (3x10mL). The combined organic layers were separated, dried over Na_2SO_4, filtered and concentrated in evaporator. The residue was purified by column chromatography on SiO_2 using EtOAc/Hexanes as eluent.

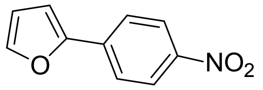
2.4. Scale-up synthesis



100 mg black phosphorus added into the degassed and dried 50 mL of DMSO was sonicated at 6 ^{o}C for 8 hours under dark conditions. Subsequently, this exfoliated black phosphorus and 4-nitrobenzenediazonium tetrafluoroborate (1 equiv, 2.5 mmol, 592 mg) were added to a 25

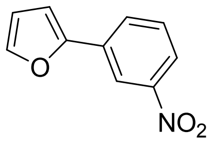
mL photoreactor equipped with a magnetic stirring bar. Then, furan (10 equiv, 25 mmol, 1.82 mL) was added via micropipette to the reaction mixture. The photo reactor was irradiated through the reactor's plane bottom side using white light. After 2 h of irradiation the reaction mixture was transferred to separating funnel, diluted with EtOAc (100 mL) and washed with brine (3x100 mL). The combined organic layers were separated, dried over Na_2SO_4, filtered and concentrated in evaporator. The residue was purified by column chromatography on silica gel eluted with EtOAc/hexane (1:9) to give the product (**3aa**) as a yellow solid (360 mg, 76% yield).

2-(4-nitrophenyl)furan[2]



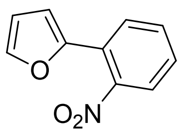
3aa was obtained as yellow solid (36.8mg, 78% yield); **R_f** (hexane): 0.28; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26-8.24 (m, 2H), 7.80-7.78 (m, 2H), 7.57 (d, *J* =1.6 Hz, 1H), 6.88 (d, *J* = 3.5 Hz, 1H), 6.55 (dd, *J* = 3.5, 1.8 Hz, 1H).

2-(3-nitrophenyl)furan[4]



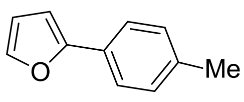
3ab was obtained as colorless solid (35.9mg, 76% yield); **R_f**(hexane): 0.27; ^1H NMR (400 MHz, $CDCl_3$) δ 8.49 (m, 1H), 8.06-8.04 (m, 1H), 7.93-7.91 (m, 1H), 7.53-7.49 (m, 2H), 6.78 (d, 1H, *J* = 3.4 Hz), 6.51 (dd, *J* = 3.4, 1.8 Hz,1H).

2-(2-nitrophenyl)furan[4]



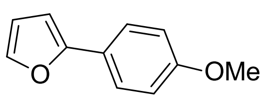
3ac was obtained as colorless solid (39.7mg, 84% yield); **R_f**(hexane): 0.26; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73-7.67 (m, 2H), 7.59-7.56 (m, 1H), 7.51-7.50 (m, 1H), 7.43-7.39 (m, 1H), 6.67 (dd, *J* = 3.4, 0.6 Hz, 1H), 6.50 (dd, *J* = 3.4, 1.8 Hz, 1H).

2-(*p*-tolyl)furan[3]



3ad was obtained as colorless oil (16.5 mg, 42% yield); **R_f** (hexane): 0.77; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.46 (m, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.62-6.60 (m, 1H), 6.48-6.47 (m, 1H), 2.38 (s, 3H).

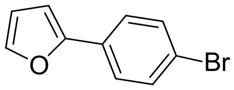
2-(4-methoxyphenyl)furan[3]



3ae was obtained as colorless solid (17.4mg, 40% yield); **R_f**(hexane): 0.54; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.9 Hz, 2H), 7.43 (dd, *J* =

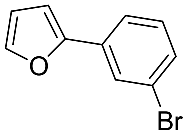
1.8, 0.7 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.52 (dd, *J* = 3.3, 0.7 Hz, 1H), 6.45 (dd, *J* = 3.3, 1.8 Hz, 1H), 3.84 (s, 3H).

2-(4-bromophenyl)furan[2]



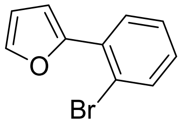
3af was obtained as white solid (42.4mg, 76% yield); **R_f** (hexane): 0.84; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 4H), 7.48 (d, *J* = 1.5 Hz, 1H), 6.66 (d, *J* = 3.4 Hz, 1H), 6.48 (dd, *J* = 3.4, 1.9 Hz, 1H).

2-(3-bromophenyl)furan[2]



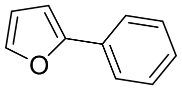
3ag was obtained as colorless oil (41.2mg, 74% yield); **R_f** (hexane): 0.85; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (t, *J* = 1.7 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.51 (d, *J* = 1.5 Hz, 1H), 7.42-7.40 (m, 1H), 7.30 – 7.28 (m, 1H), 6.71 (d, *J* = 3.4 Hz, 1H), 6.52 (dd, *J* = 3.4, 1.8 Hz, 1H).

2-(2-bromophenyl)furan[2]



3ah was obtained as colorless oil (44mg, 79% yield); **R_f** (hexane): 0.79; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.65 (dd, *J* = 8.0,1.1 Hz, 1H), 7.52 (d, *J* = 1.7 Hz, 1H), 7.36 (ddd, *J* = 7.8, 7.3, 1.2 Hz,1H), 7.17 (d, *J* = 3.4 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.3, 1.6 Hz, 1H), 6.53 (dd, *J* = 3.4, 1.8 Hz, 1H).

2-phenylfuran[2]



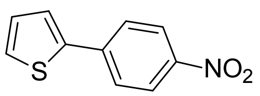
3ai was obtained as yellow oil (20mg, 55% yield); **R_f** (hexane): 0.65; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2H), 7.39 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.18 – 7.16 (m, 1H), 6.57 (dd, *J* = 3.3, 0.8 Hz, 1H), 6.39 (dd, *J* = 3.4, 1.8 Hz, 1H).

2.5. General procedure for the reaction of aryl diazonium tetrafluoroborates with thiophene

10 mg black phosphorus added into the degassed and dried 5 mL of DMSO was sonicated at 6 ^oC for 8 hours under dark conditions. Subsequently, this exfoliated black phosphorus and aryl diazonium tetrafluoroborate (1 equiv, 0.25 mmol) were added to a 25 mL photoreactor equipped with a magnetic stirring bar. Then, thiophene (10 equiv, 2.5 mmol) was added via micropipette to the reaction mixture. The photo reactor was irradiated through the reactor's plane bottom side using white light. After 2 h, of irradiation the reaction mixture was transferred to separating funnel, diluted with ethyl acetate and washed with water (3x10 mL).

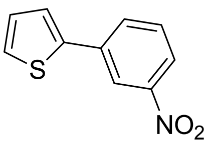
Then the organic layer was separated, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on SiO_2 using EtOAc/Hexane as eluent.

2-(4-nitrophenyl)thiophene[5]



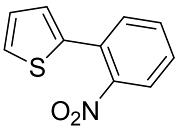
3ba was obtained as yellow solid (38.5mg, 75% yield); **R_f** (hexane): 0.27; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.9 Hz, 2H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.48 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.44 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.15 (dd, *J* = 5.1, 3.7 Hz, 1H).

2-(3-nitrophenyl)thiophene[4]



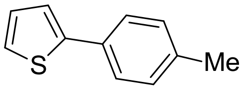
3bb was obtained as colorless oil (38mg, 74% yield); **R_f** (hexane): 0.30; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40-8.39 (m, 1H), 8.10-8.07 (m, 1H), 7.87 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.53-7.49 (m, 1H), 7.40 (dd, *J* = 3.7, 1.1 Hz, 1H) , 7.36 (dd, *J* = 5.1, 1.1 Hz, 1H) , 7.11 (dd, *J* = 5.1, 3.7 Hz, 1H).

2-(2-nitrophenyl)thiophene[4]



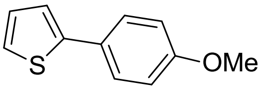
3bc was obtained as colorless oil (41mg, 80% yield); **R_f** (hexane): 0.31; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.60-7.54 (m, 2H), 7.48-7.44 (m, 1H), 7.42 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.10-7.07 (m, 2H).

2-(*p*-tolyl)thiophene[3]



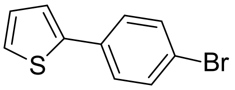
3bd was obtained as yellow oil (19.6mg, 45% yield); **R_f** (hexane): 078; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.29-7.28 (m, 1H), 7.27-7.26 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.08 (dd, *J* = 5.1, 3.6 Hz, 1H), 2.39 (s, 3H).

2-(4-methoxyphenyl)thiophene[3]



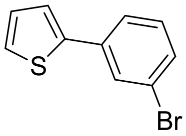
3be was obtained as colorless solid (19mg, 40% yield); **R_f** (hexane): 0.55; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.9 Hz, 2H), 7.23-7.21 (m, 2H), 7.06 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.94-6.92 (m, 2H), 3.85 (s, 3H).

2-(4-bromophenyl)thiophene[2]



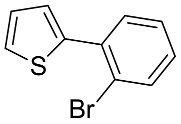
3bf was obtained as white solid (44.8mg, 75% yield); **R_f** (hexane): 085; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.47 (m, 4H), 7.31-7.30 (m, 2H), 7.10-7.08 (m, 1H).

2-(3-bromophenyl)thiophene[2]



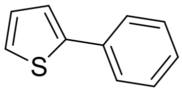
3bg was obtained as colorless oil (42.4mg, 71% yield); **R$_f$** (hexane): 084; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80 (t, *J* = 1.8 Hz, 1H), 7.58 – 7.56 (m, 1H), 7.45 – 7.43 (m, 1H), 7.36 – 7.35 (m, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.14 – 7.12 (m, 1H).

2-(2-bromophenyl)thiophene[2]



3bh was obtained as colorless oil (46.6mg, 78% yield); **R$_f$** (hexane): 084; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.40 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.33 (td, *J* = 7.7, 1.2 Hz, 1H), 7.30 (dd, *J* = 3.5, 1.2 Hz, 1H), 7.18 (ddd, *J* = 8.0, 7.7, 1.7 Hz, 1H), 7.11 (dd, *J* = 5.1, 3.6 Hz, 1H).

2-phenylthiophene[3]



3bi was obtained as colorless oil (20.8mg, 52% yield); **R$_f$** (hexane): 075; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.62-7.60 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.39-7.35 (t, *J* = 7.6 Hz, 2H), 7.32-7.30 (dd, *J* = 3.5, 1.1 Hz, 1H), 7.29-7.26 (m, 2H), 7.06-7.09 (dd, *J* = 5.1, 3.6 Hz, 1H).

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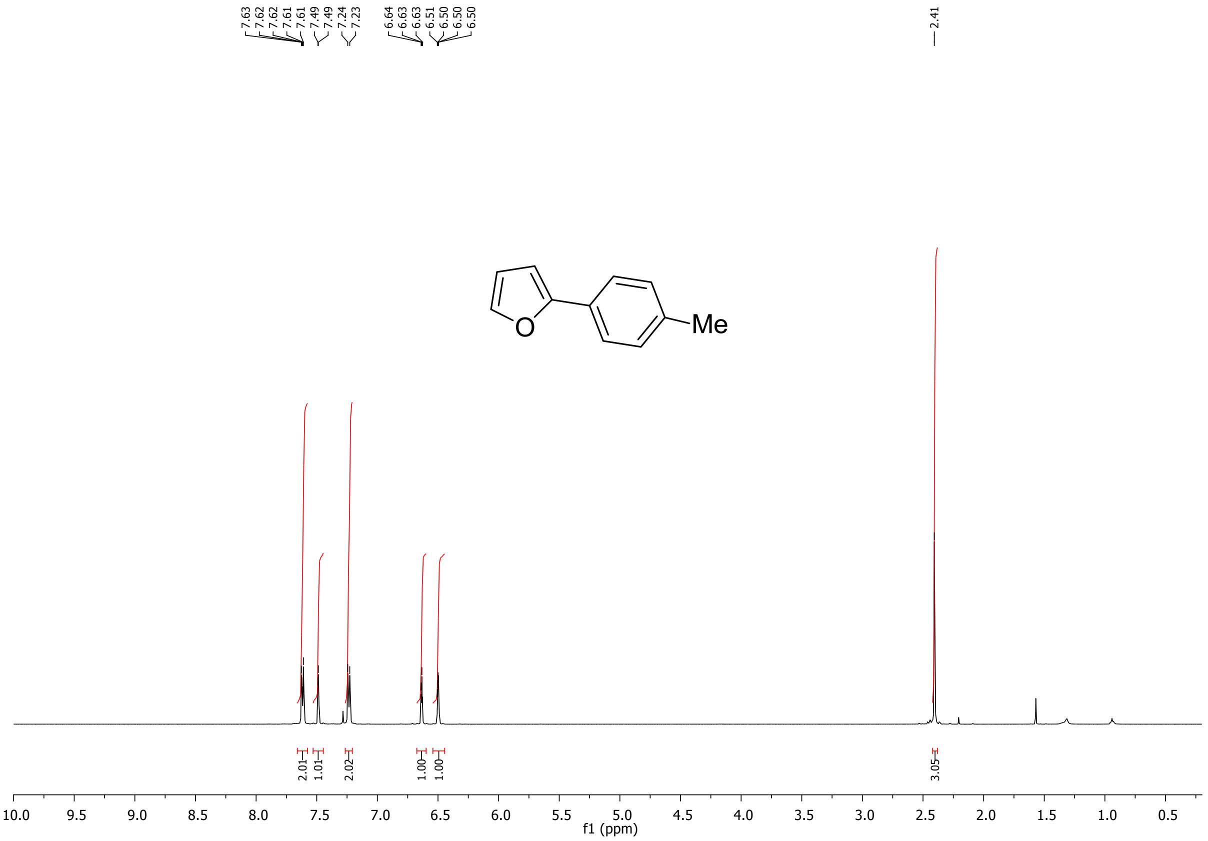
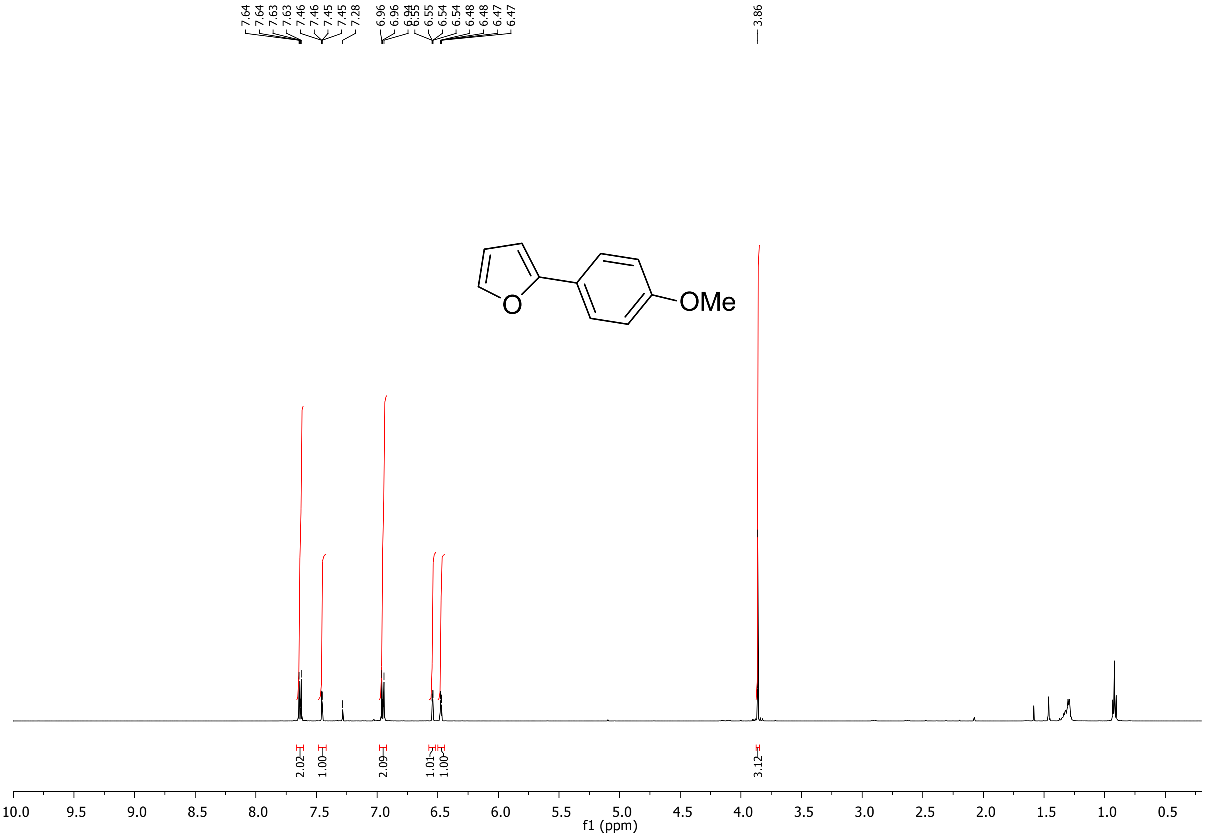
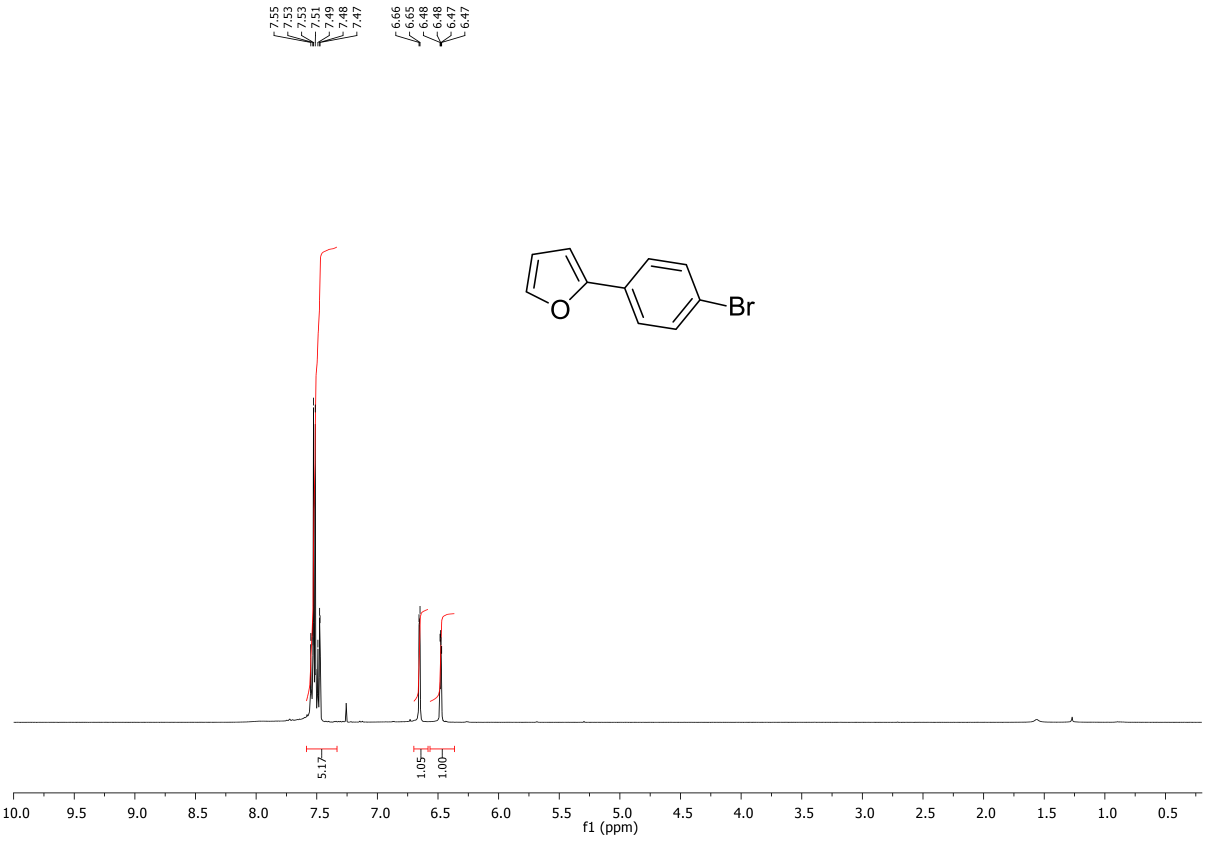
^{1}H-NMR spectra of the products



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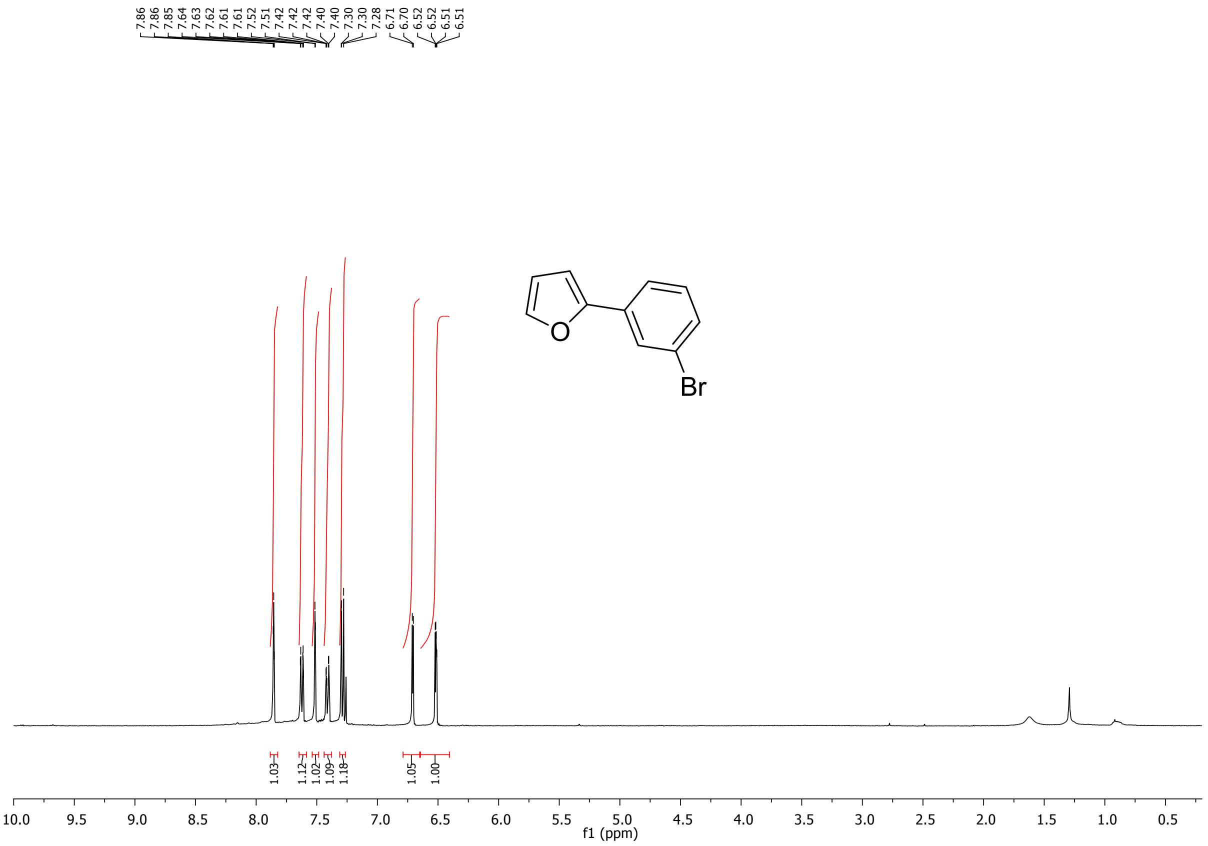
O
Br
5.17
1.05
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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7.30
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6.51
O
Br
1.03
1.12
1.02
1.09
1.18
1.05
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
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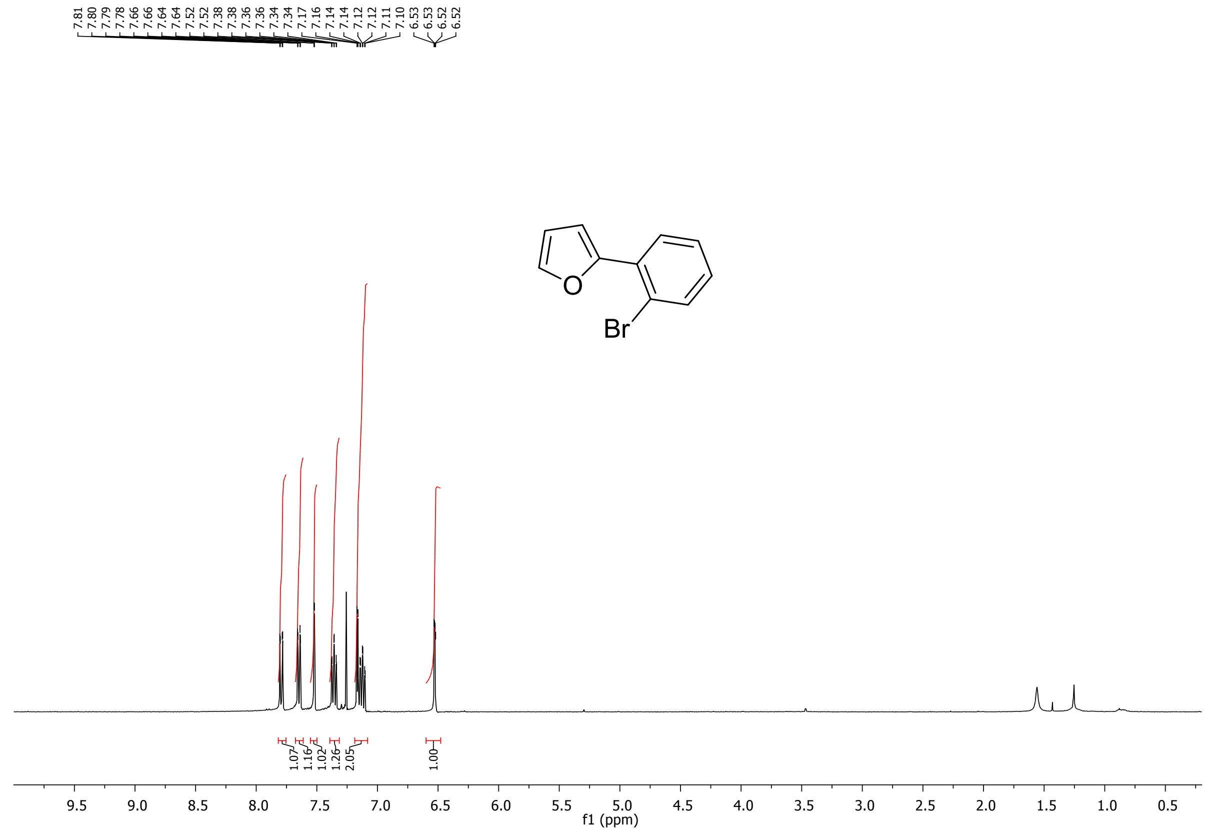
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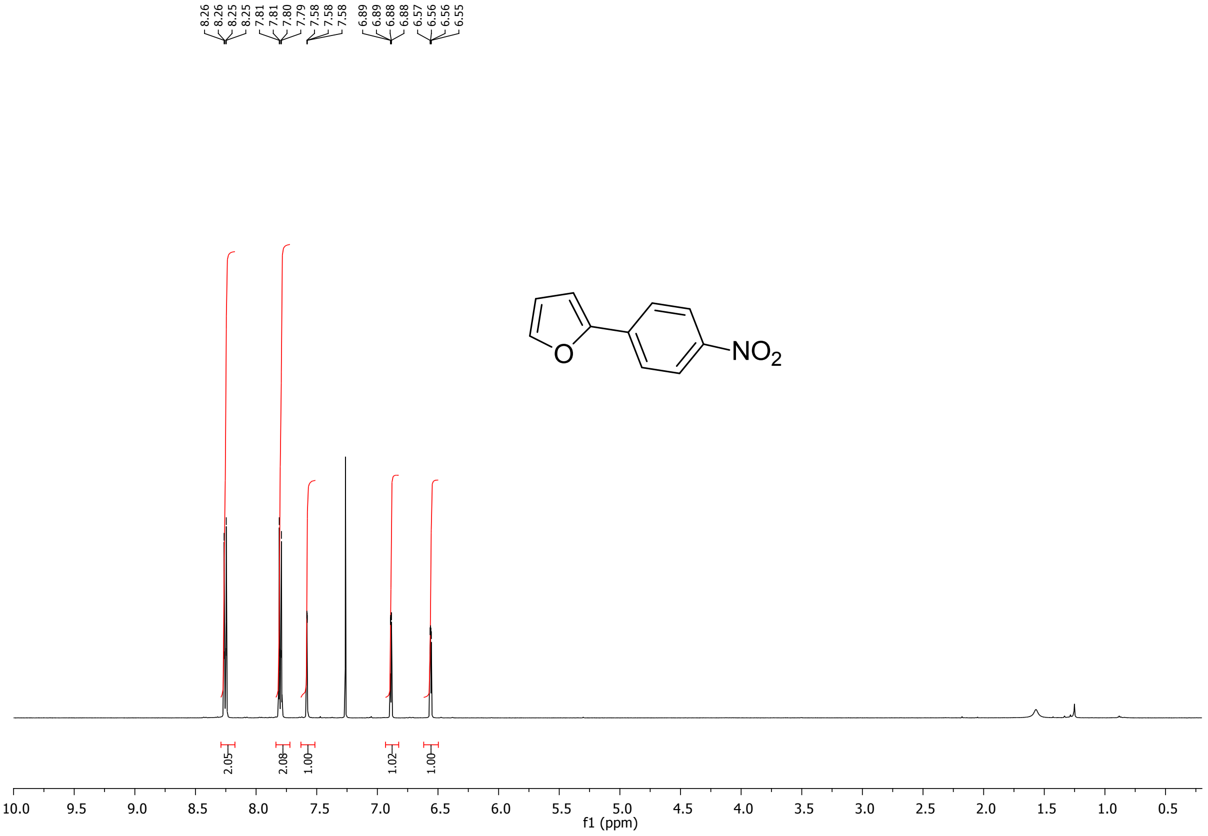
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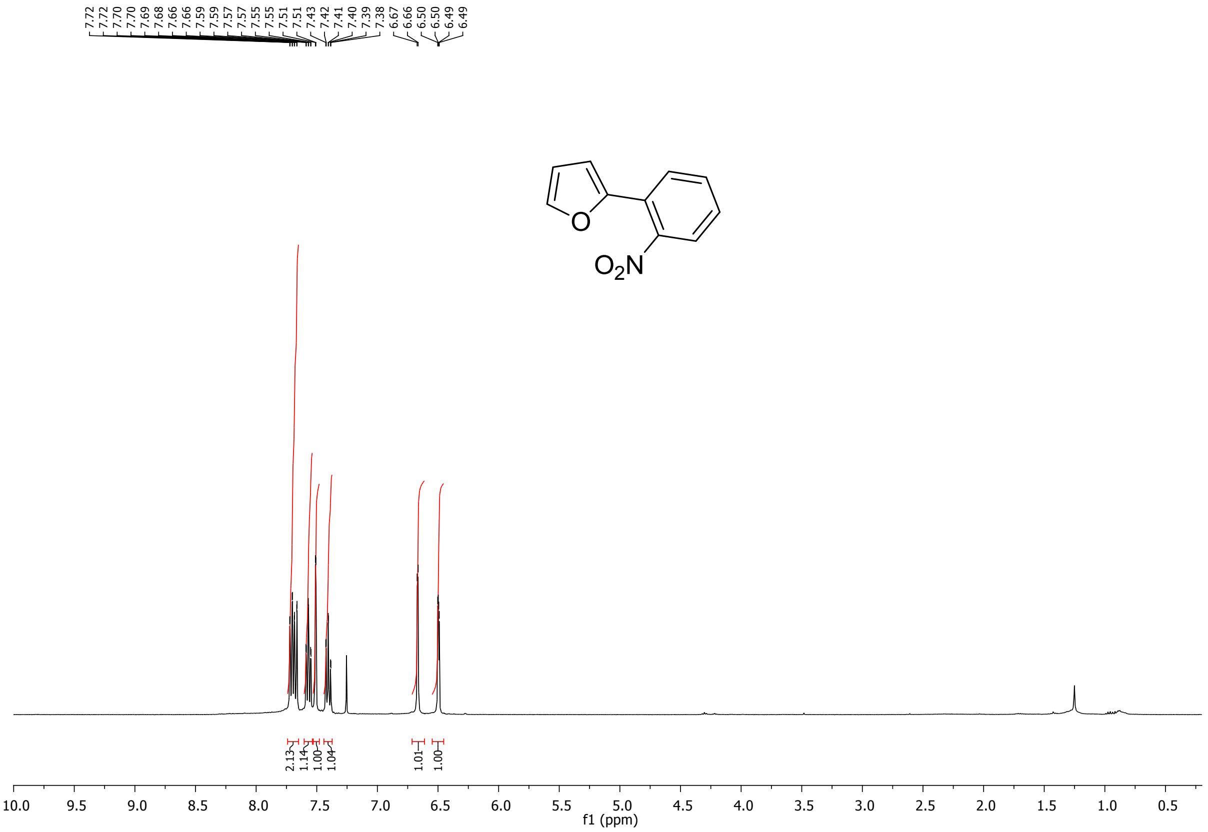
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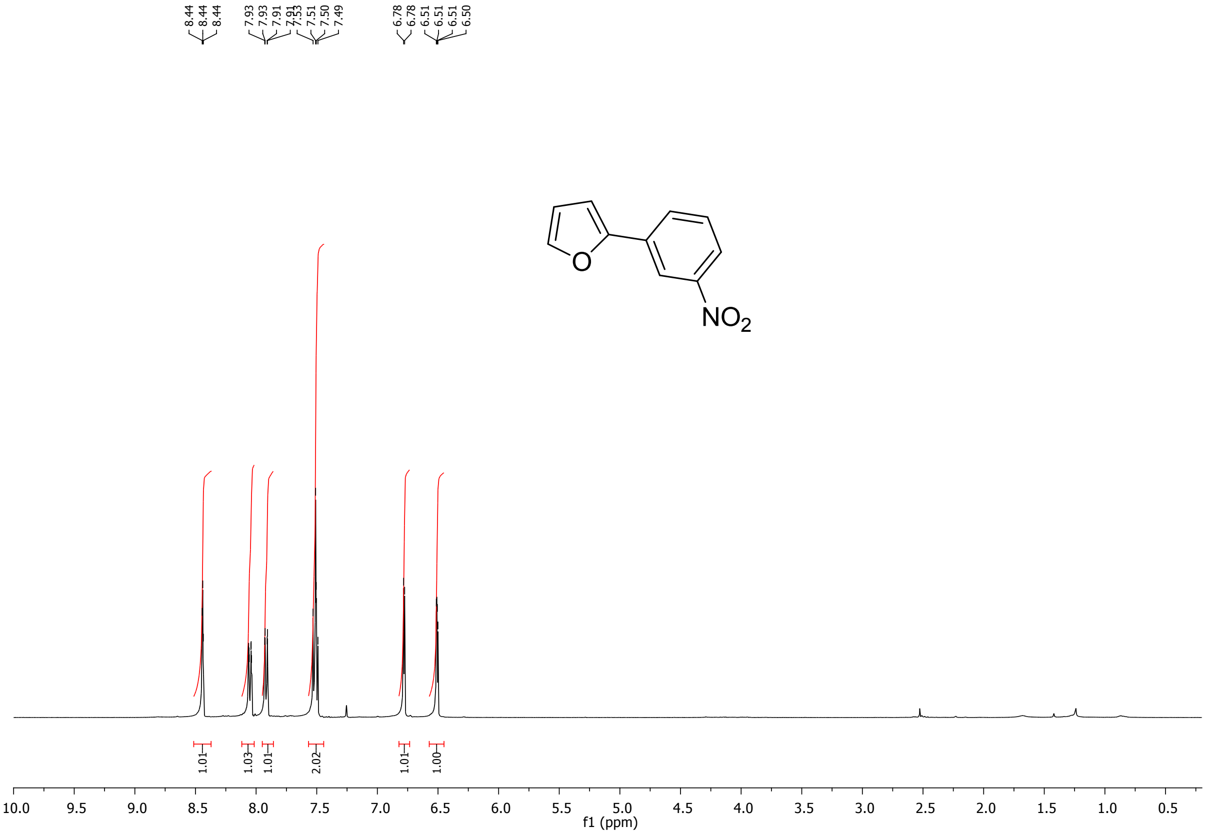
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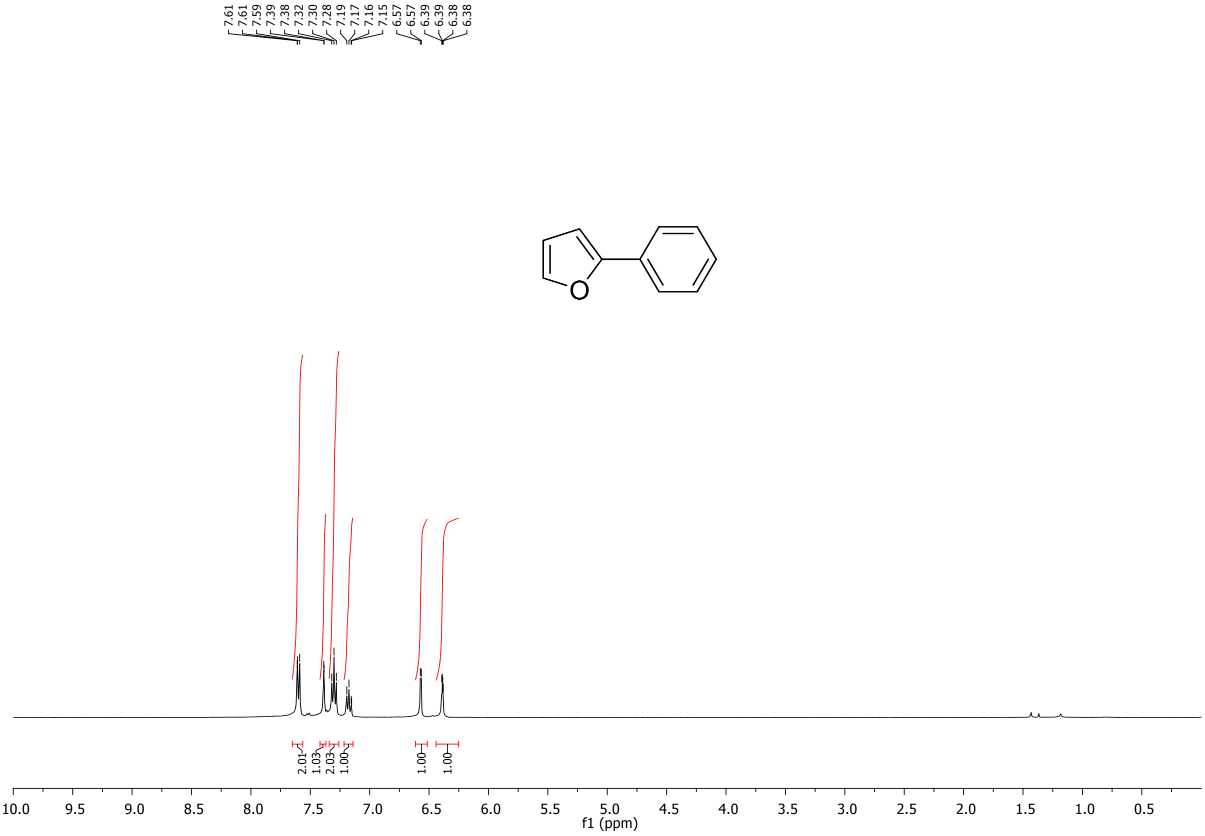
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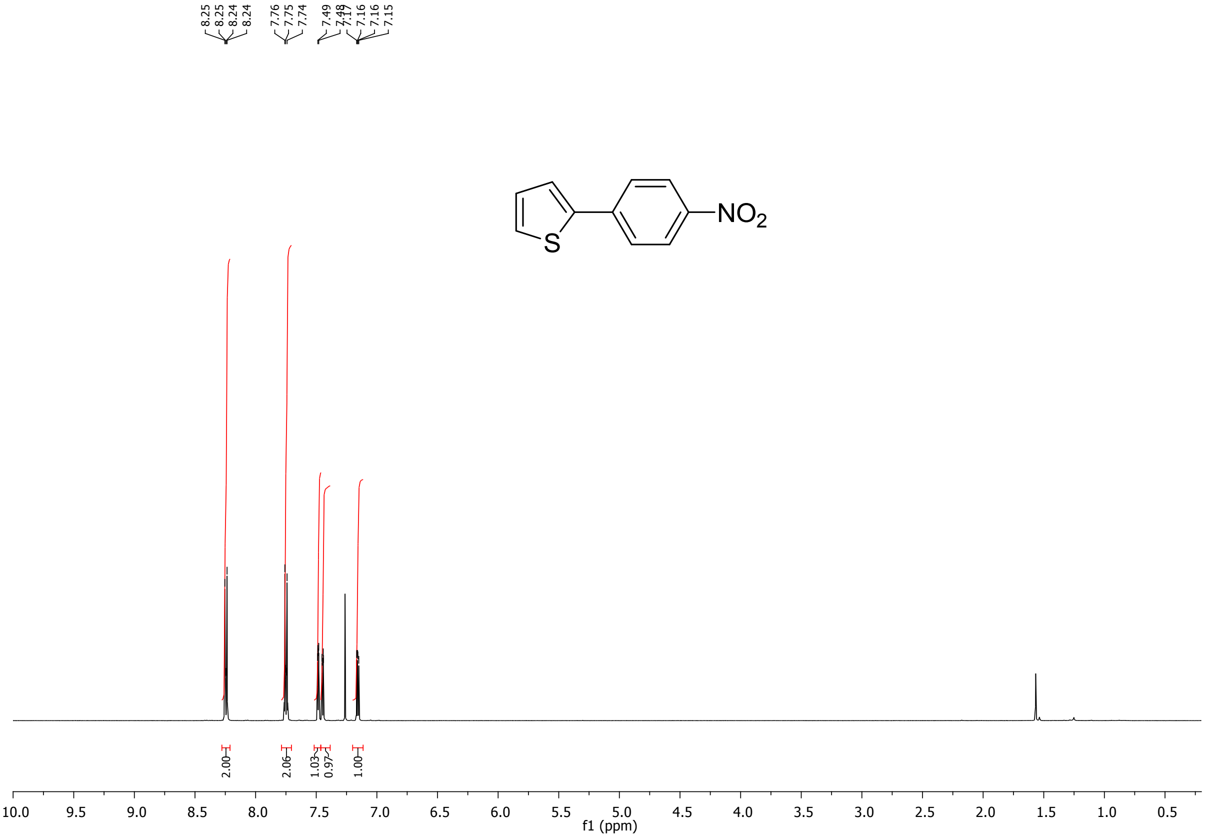
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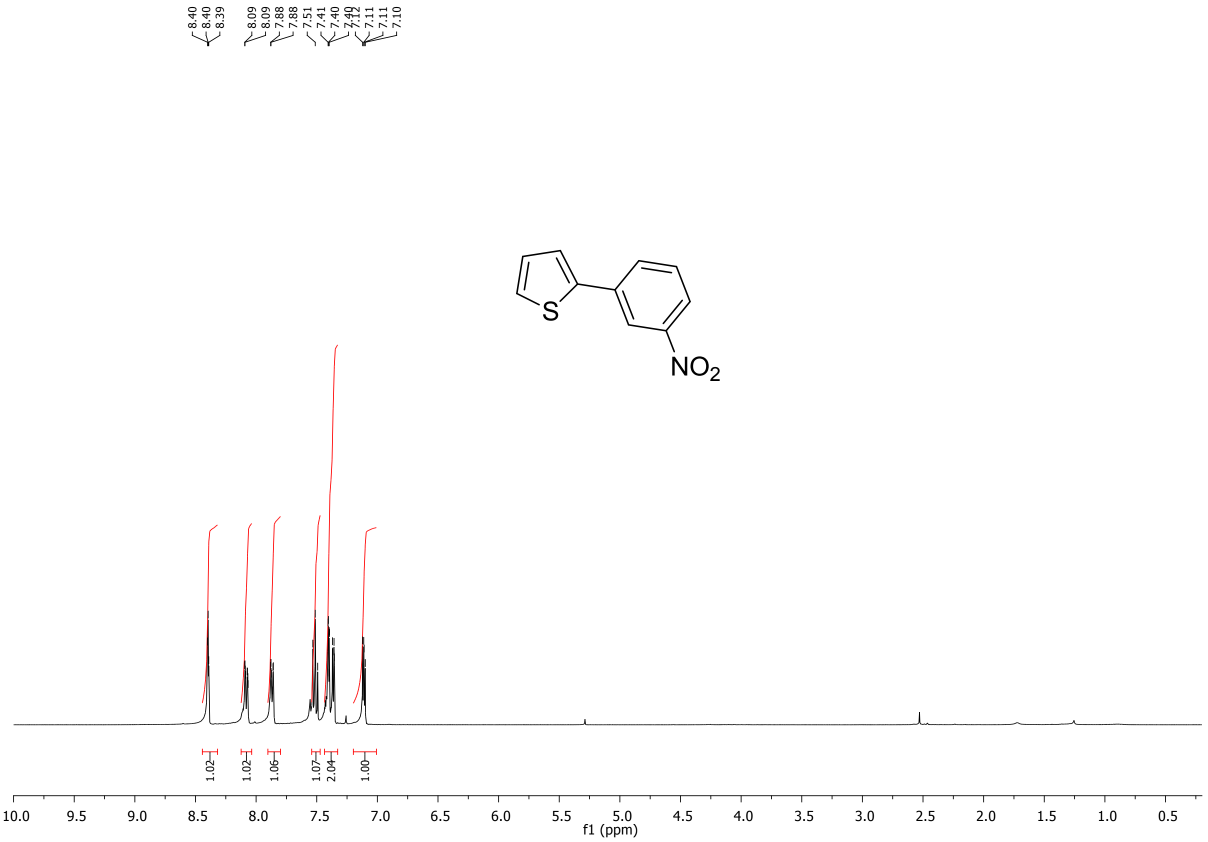
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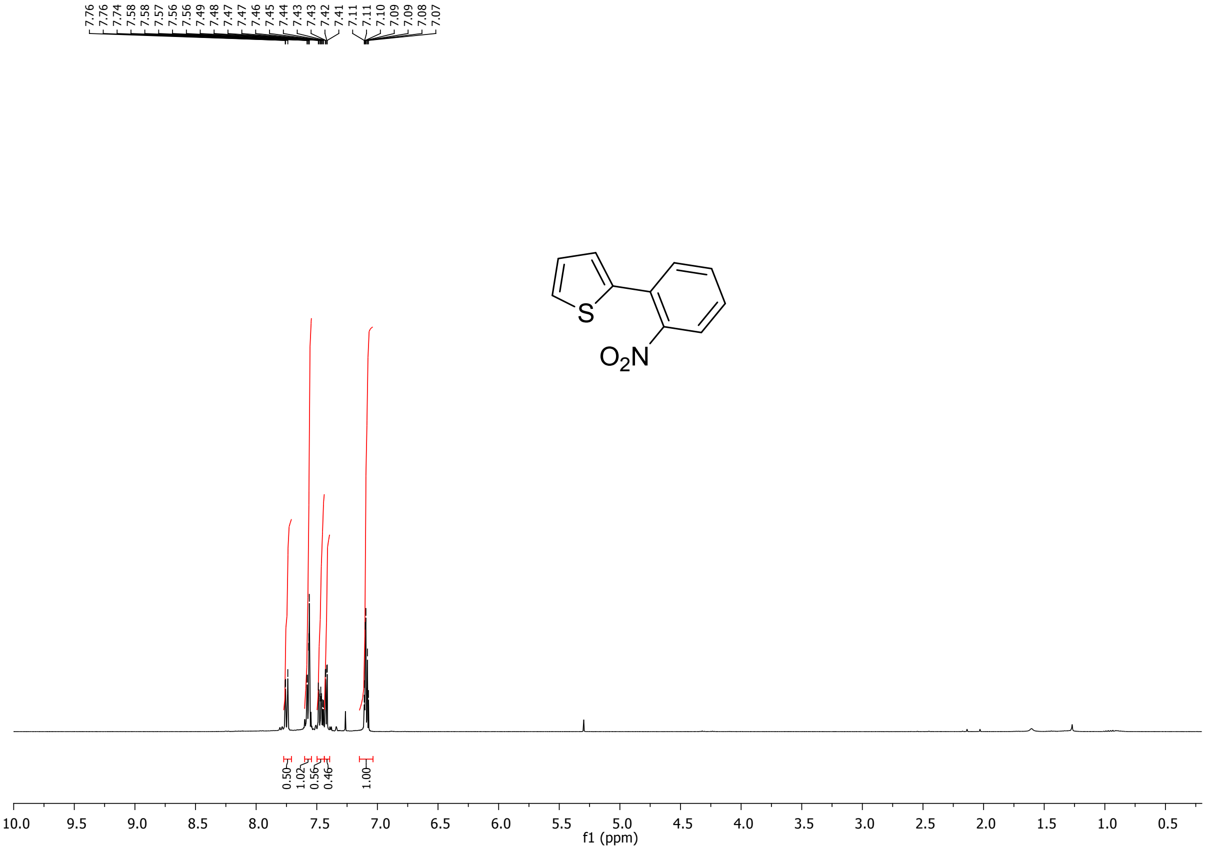
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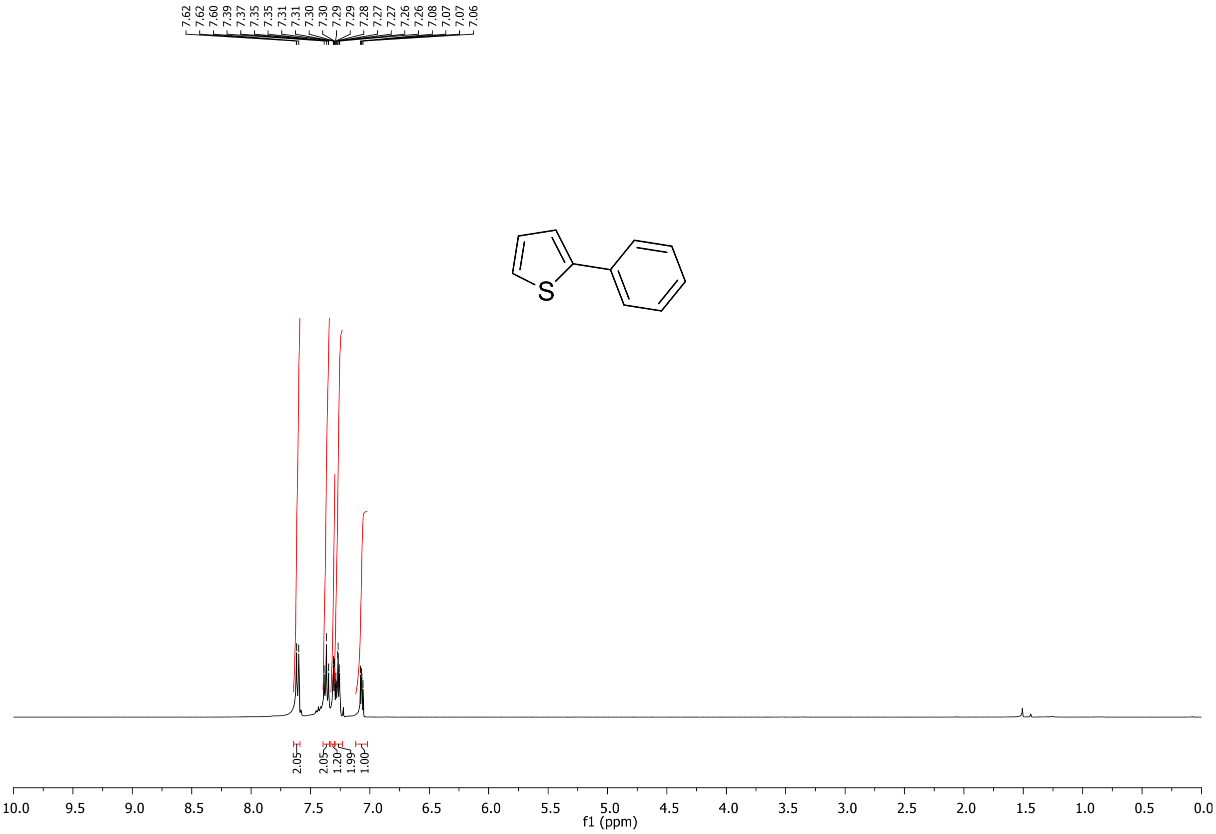
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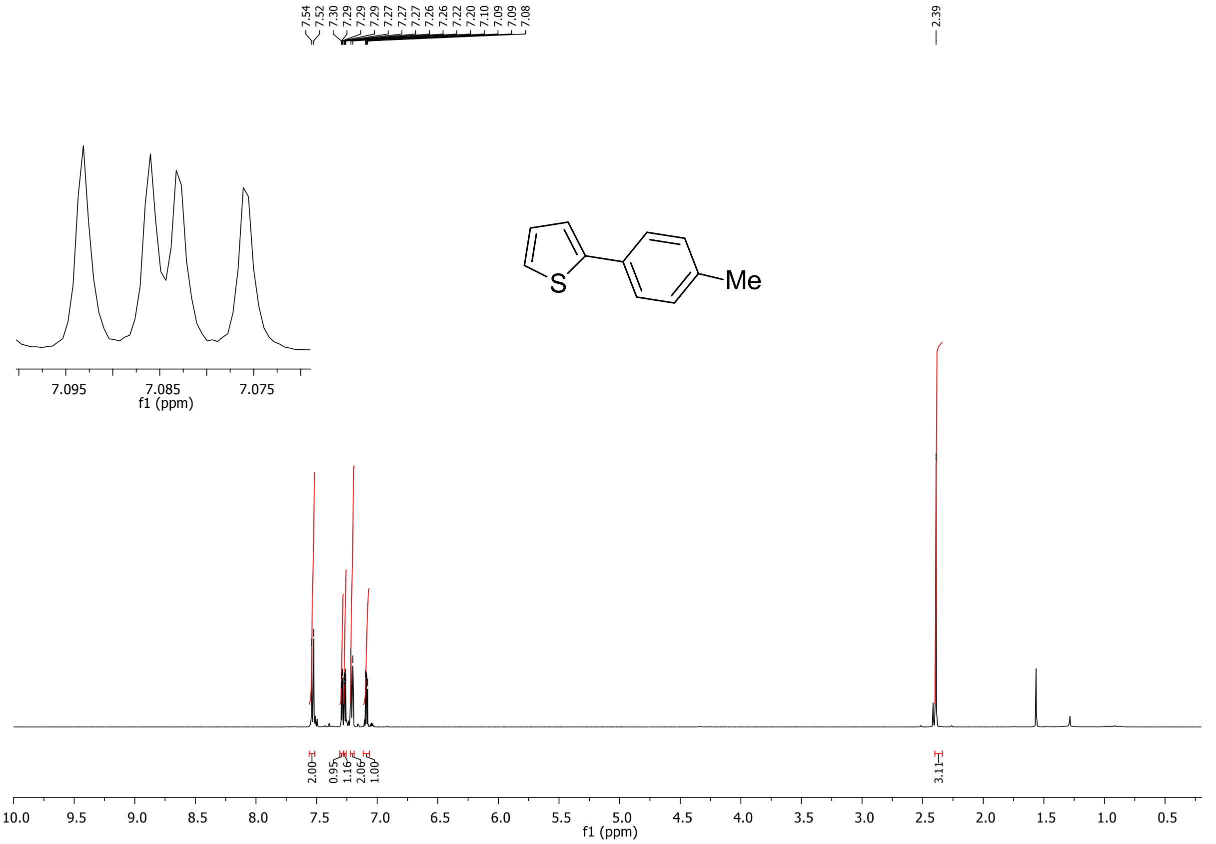
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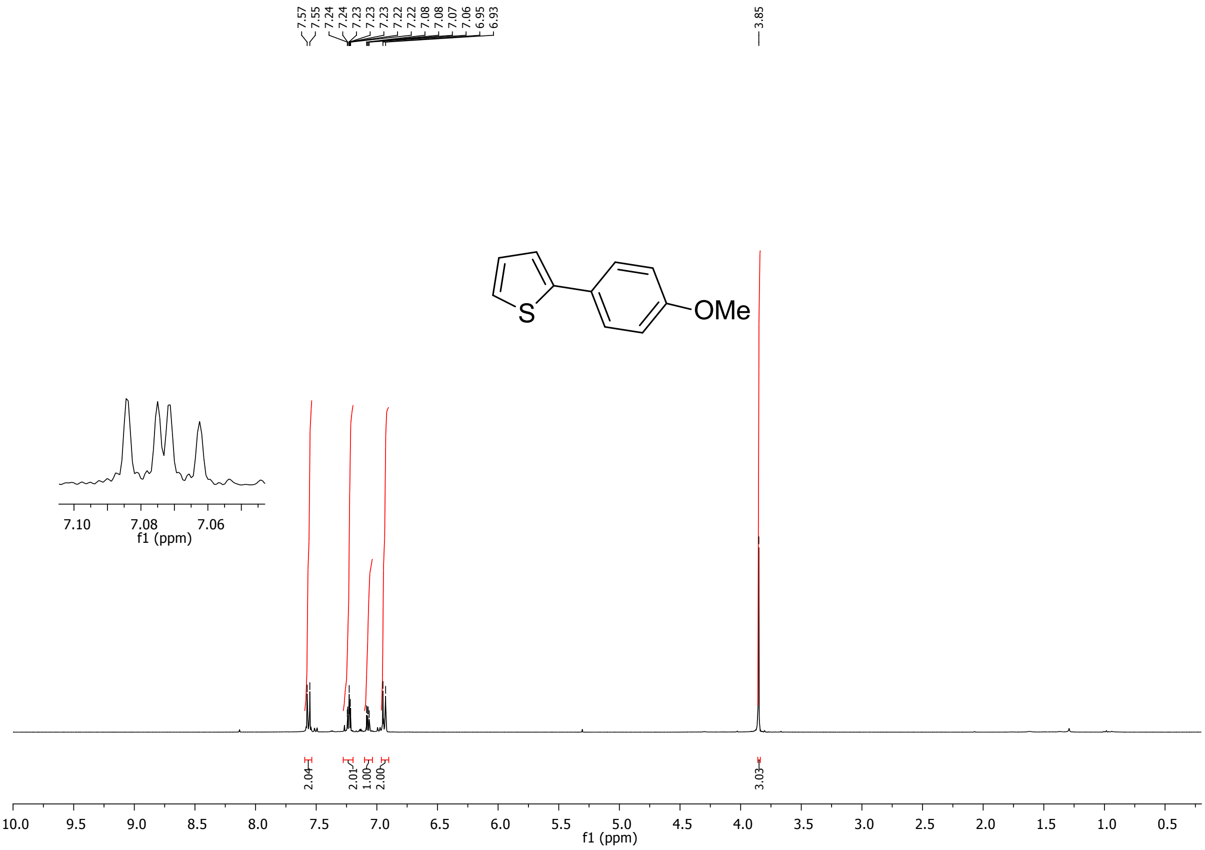
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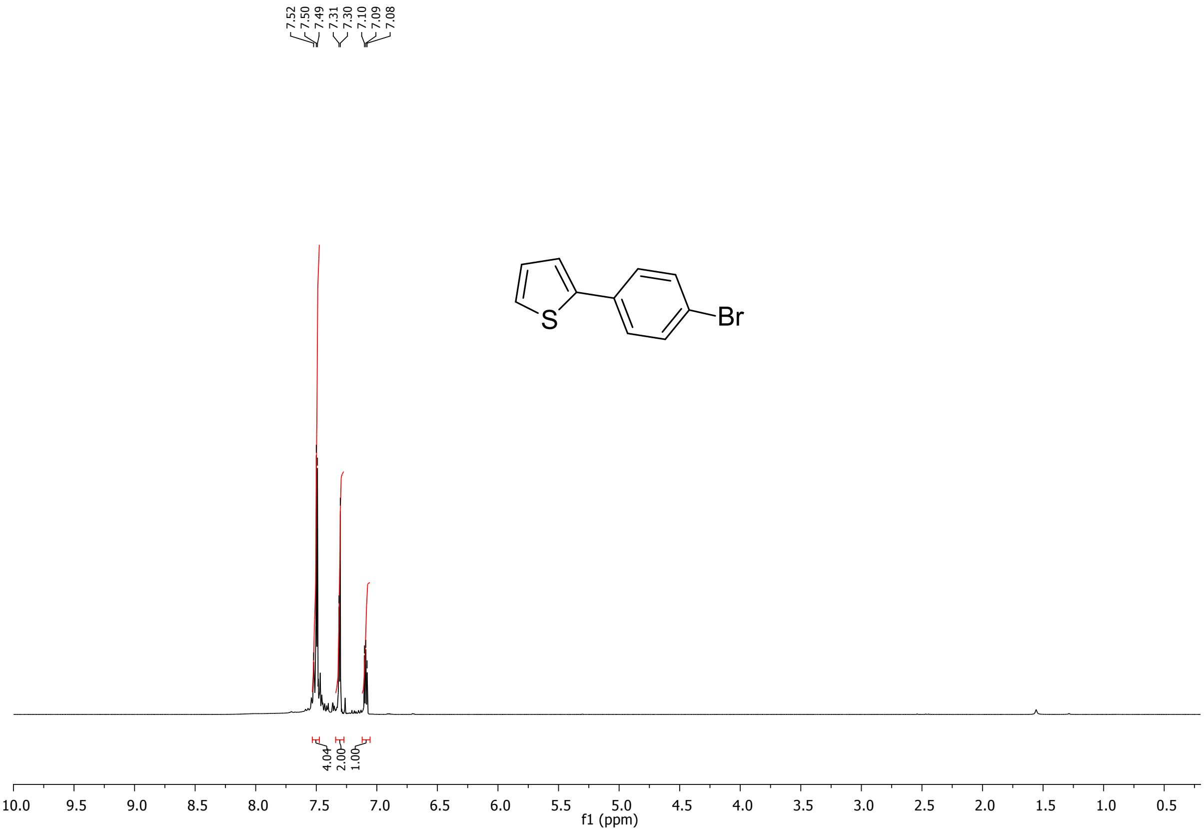
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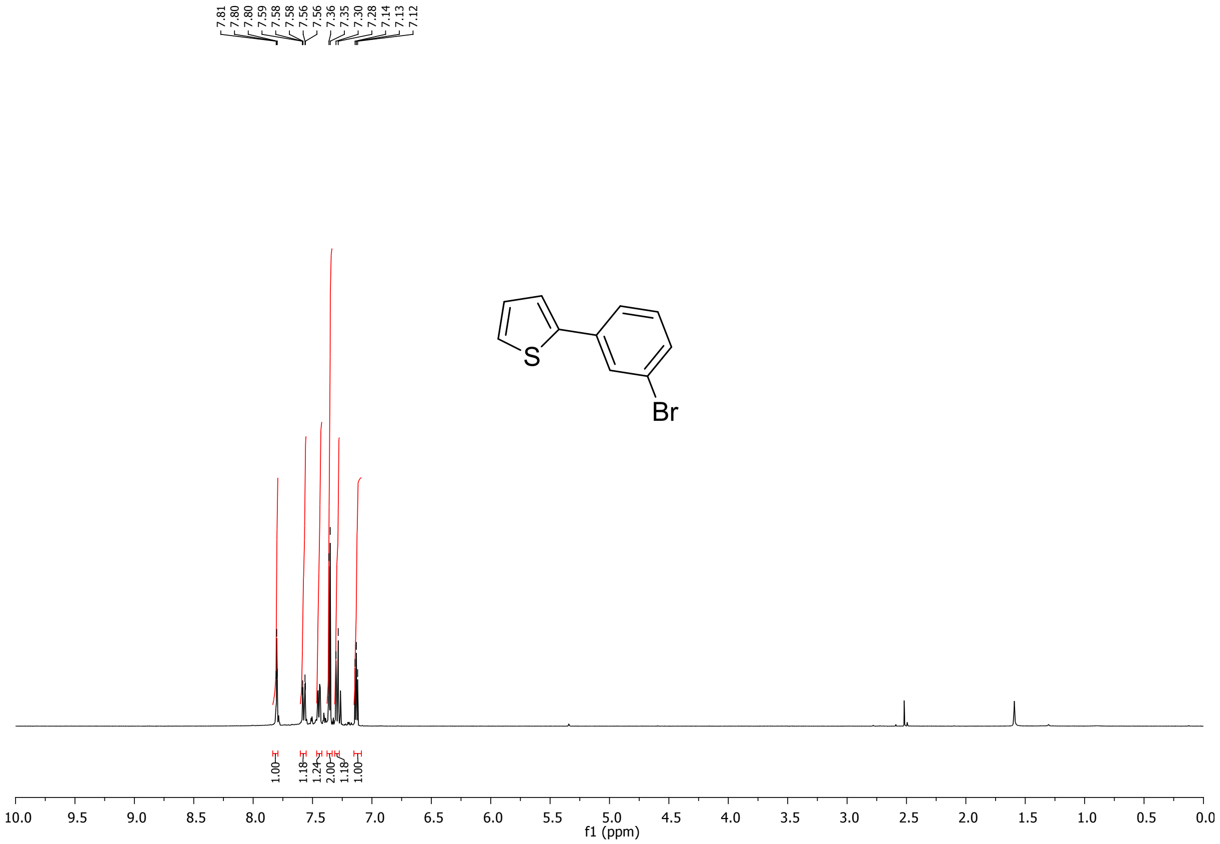
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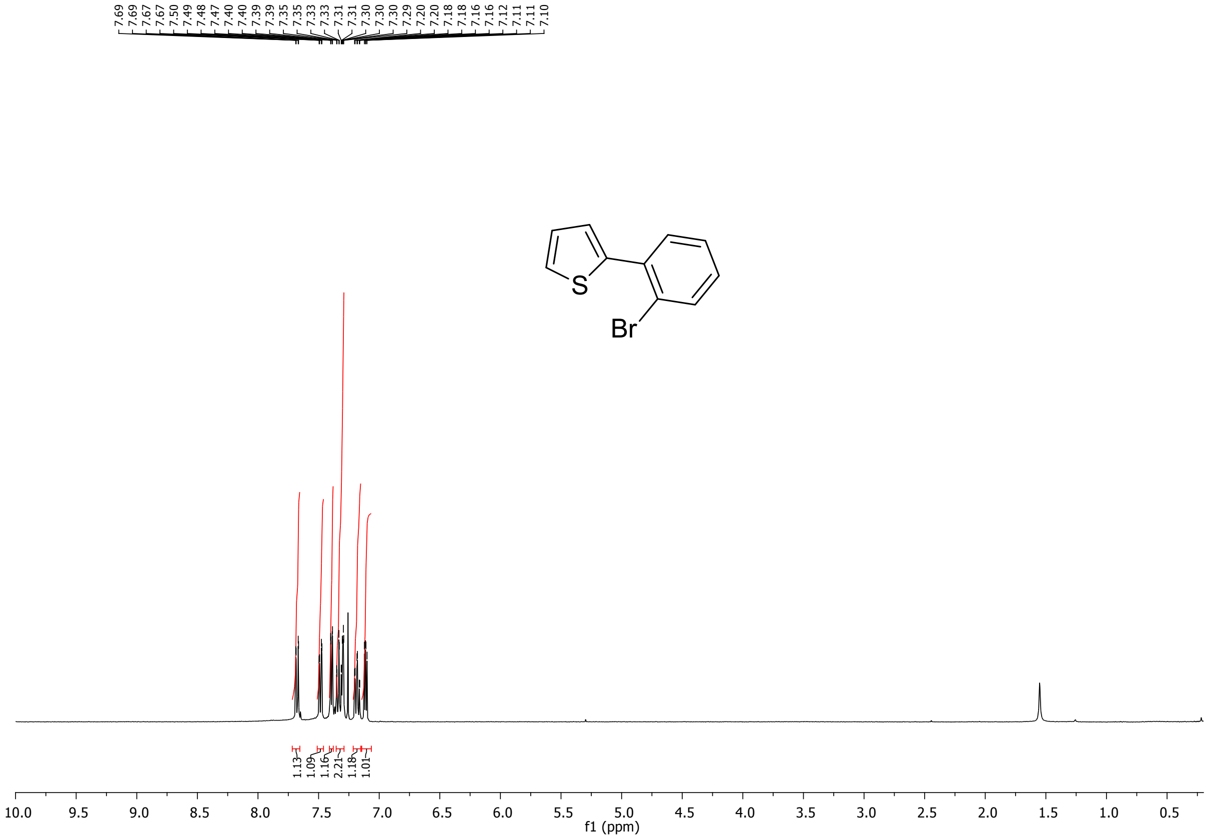
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