SUPPORTING INFORMATION

A General Method for Copper-Catalyzed Arylation of Arene C-H Bonds

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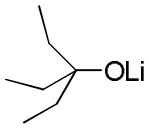
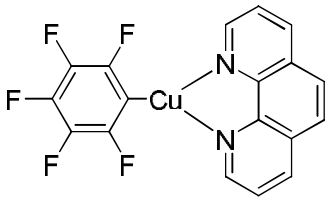
Experimental Section

General considerations. Reactions were performed in 1-dram vials with PTFE/Liner caps. Flash chromatography was performed on 60Å silica gel (Sorbent Technologies). Purification by preparative HPLC was performed on a Shimadzu Prominence LC (LC-20AB) equipped with a SPD-20A UV-Vis detector and a Varian Dynamax (250 mm x 21.4 mm) column. GC-MS analyses were performed on a Shimadzu GCMS-QP5000 chromatograph equipped with a Restek column (Rtx-XLB, 30 m x 0.25 mm I.D.). The ^{1}H, ^{19}F and ^{13}C NMR were recorded on a GE QE-300 spectrometer using residual solvent peak as a reference. Hexafluorobenzene (1% in C_6D_6, δ = -164.9) was employed as an external standard in ^{19}F NMR spectra. Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA. IR spectra were obtained using ThermoNicolet Avatar 370 FT-IR instrument. Analytical thin layer chromatography was performed on silica gel IB-F (Baker-flex) by J. T. Baker.

Materials. The following starting materials were obtained from commercial sources and were used without further purification: 4-iodotoluene, 4-iodobenzotrifluoride, 4-bromotoluene, 4-bromobenzotrifluoride, 1,4-difluorobenzene, 1,2,4,5-tetrafluorobenzene, pentafluorobenzene, 4-bromobiphenyl, and 1,3-dibromobenzene were bought from Oakwood. 1,10-Phenanthroline, copper(I) iodide, DMF, 2,3-benzofuran, 1-iodonapthalene, 4,5-dimethylthiazole, 1-phenylpyrazole, benzothiophene, 2,3,5,6-tetrafluorotoluene, pyrimidine, 2-chloropyridine, 4-bromobenzophenone, 1,4-diiodobenzene, 2,4-difluorobenzophenone, and alpha-bromostyrene were obtained from Acros. Potassium phosphate, *m*-xylene, 2-bromopyridine, 1,3-dinitrobenzene, bromomethylenecyclohexane, 2-iodotoluene, 3-iodotoluene, pentachlorobenzene, 1,3-dichlorobenzene, 3-nitrobenzonitrile, pyridazine, pyridine N-oxide, 2-picoline N-oxide, anhydrous DMPU, n-butyllithium (2.0 M solution in cyclohexane), and 2-iodophenol were purchased from Aldrich. Iodobenzene, 1-methyl-1,2,4-triazole, 3-chlorothiophene, benzothiazole, caffeine, 2-chlorothiophene, thiophene, 2-chloroquinoline, 2,3,5,6-tetrafluoroanisole, and 3-ethyl-3-pentanol were from Alfa Aesar. Lithium *t*-butoxide was bought from Strem. 2-Iodopyridine and 4-bromo-1-butene were purchased from TCI. *t*-Butanol (OD) was from Cambridge Isotope Laboratories, Inc. 1,2,4,5-Tetrachlorobenzene was purchased from Eastman Organic Chemicals. 1-(But-3-enyloxy)-2-iodobenzene was prepared from *o*-iodophenol.[1] 2-Phenylpyridine oxide was synthesized from 2-phenylpyridine.[2]

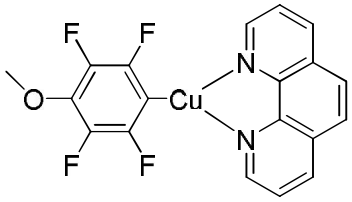


Lithium 3-ethyl-3-pentoxide. A flamed-dried 200 mL Schlenk flask was charged with a magnetic stirrer and phenanthroline indicator (5 mg). The flask was evacuated and backfilled three times by argon. Anhydrous pentane (20 mL) and a 2M solution of n-BuLi in cyclohexane (50 mL) were added at 0 ^{o}C to form a reddish-brown solution. 3-Ethyl-3-pentanol (predried by distillation from Mg turnings) was added dropwise with stirring until the solution became colorless. The reaction mixture was warmed up to room temperature following by solvent removal under vacuum affording a yellow solid. The crude product was dissolved in pentane (10 mL), filtered through Celite® under argon atmosphere. Celite® was washed by additional pentane (10 mL). The filtrate was kept at – 20 ^{o}C for a week affording 9.5 g (78%) of a colorless crystalline product. This compound is known.[3]



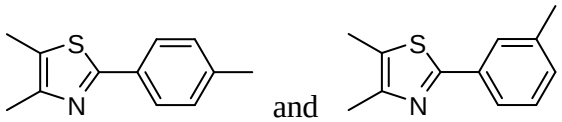
Pentafluorophenylcopper-phenanthroline complex 1. To a mixture of copper (I) chloride (1.99 g, 20 mmol) and *t*-BuOLi (1.50 g, 18.8 mmol) in a 50 mL Schlenk flask under Ar atmosphere was added dry THF (25 mL). The pale yellow reaction mixture was vigorously stirred at 40 ^{o}C for 4 hours followed by addition of pentafluorobenzene (5.04 g, 30 mmol) in one portion and stirring for an additional hour. The pale yellow solution was evaporated to dryness under reduced pressure and the residue was dissolved in dry toluene (30 mL) followed by filtration through a pad of Celite® under argon atmosphere. The filtrate was evaporated to dryness under reduced pressure at 45 ^{o}C and the residue was dissolved in dry CH_2Cl_2 (50 mL). To this mixture was added a solution of phenanthroline (3.60 g, 20 mmol) in CH_2Cl_2 (20 mL). An immediate precipitate of an orange solid was observed. The mixture was stirred for 5 minutes followed by filtration under argon atmosphere. An orange solid (4.0 g, 52% yield) was obtained. It can be recrystallized from a mixture (1/2) of DCM and DMPU at – 30 ^{o}C affording dark orange needles. The connectivity was verified by X-ray crystallography; however, it was not possible to fully refine the structure due to twinning of

the crystals. ^{1}H NMR (300 MHz, DMF-d_7) δ 7.87-7.97 (m, 2H), 8.14 (s, 2H), 8.70 (d, J = 8.5 Hz, 2H), 9.13 (d, J = 2.5 Hz, 2H). ^{19}F NMR (282 MHz, DMF-d_7) δ -166.2- -165.9 (m, 2F), -165.2 (t, J_F = 20 Hz, 1F), -112.9- -112.4 (m, 2F). ^{13}C NMR (75 MHz, DMF-d_7) δ 125.0, 127.5, 129.6, 134.2-138.3 (m), 137.7, 136.0-139.8 (m), 145.5, 148.0-151.6 (m), 150.5. FT-IR (neat, cm^{-1}) υ 1511, 1486, 1432, 1423, 1416, 1035, 934, 839, 770, 725. The complex is sensitive to temperature and atmospheric moisture and satisfactory elemental analyses could not be obtained.



4-Methoxytetrafluorophenylcopper-phenanthroline complex 2. To a mixture of copper (I) chloride (1.0 g, 10 mmol) and *t*-BuOLi (0.76 g, 9.5 mmol) in a 50 mL Schlenk flask under Ar atmosphere was added dry THF (12 mL). The pale yellow reaction mixture was vigorously stirred at 40 ^{o}C for 4 hours followed by addition of 2,3,5,6-tetrafluoroanisole (2.0 g, 11.1 mmol) in one portion and stirring overnight at 40 ^{o}C. The pale yellow suspension was evaporated to dryness under reduced pressure and the residue was dissolved in dry toluene (20 mL) followed by filtration through a pad of Celite® under argon atmosphere. The filtrate was evaporated to dryness under reduced pressure at 45 ^{o}C and the residue was dissolved in dry CH_2Cl_2 (5 mL). To this mixture was added a solution of phenanthroline (0.58 g, 3.2 mmol) in CH_2Cl_2 (5 mL). The rust-colored solution was stirred for 5 minutes at room temperature and then kept at -30 ^{o}C for 2 days. Rust-colored crystals were collected and washed by a small amount of CH_2Cl_2 affording 0.52 g (38%) of the product. The structure was verified by X-ray crystallography. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.93 (s, 3H), 7.83-7.90 (m, 2H), 7.96 (s, 2H), 8.45-8.52 (m, 2H), 9.17 (s, 2H). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -161.0- -160.4 (m, 2F), -113.8- -113.0 (m, 2F). FT-IR (neat, cm^{-1}) υ 1476, 1423, 1075, 949, 929, 841, 757, 727. It was impossible to obtain a good quality ^{13}C spectrum of **2** due to low solubility in common NMR solvents coupled with instability in solution. The complex is sensitive to temperature and atmospheric moisture and satisfactory elemental analyses could not be obtained.

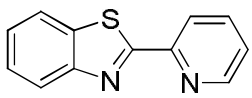
General procedure for coupling reactions. Outside the glovebox a 1-dram vial equipped with a magnetic stir bar was charged with haloarene, phenanthroline (10 mol%), substrate, and solvent (DMF or a 1/1 mixture of DMF and xylenes). If anhydrous DMPU was used, the reaction was set up inside the glovebox. The vial was flushed with argon, capped and placed inside a glovebox. To this mixture was added CuI (10 mol %) and base (1.7-4.0 equiv). The sealed vial was then taken out of the glovebox, stirred at room temperature for 5 min and placed in a preheated oil bath. After the completion of the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (50 mL). The resulting solution was washed with brine (15 mL), dried over anhydrous $MgSO_4$, and concentrated under vacuum to a volume of about 1 mL. The mixture containing the product was subjected to column chromatography on silica gel (hexanes followed by appropriate solvent to elute the products). After concentrating the fractions containing the product, the residue was dried under reduced pressure to yield pure product.



4,5-Dimethyl-2-*p*-tolylthiazole and 4,5-dimethyl-2-*m*-tolylthiazole (Scheme 3): Copper(I) iodide (19 mg, 0.1 mmol), 4,5-dimethylthiazole (113 mg, 1.0 mmol), p-bromotoluene (513 mg, 3.0 mmol), *t*-BuOK (224 mg, 2.0 mmol), and DMF (1.0 mL) at 140 ^oC for 10 minutes. After column chromatography (hexanes, then 10% ethyl acetate in hexanes) and preparative HPLC (5% ethyl acetate in hexanes) 17 mg (8.4%) of a yellow solid (4,5-dimethyl-2-*p*-tolylthiazole) and 15 mg (7.4%) of a colorless oil (4,5-dimethyl-2-*m*-tolylthiazole) were obtained. These compounds are known.[4]

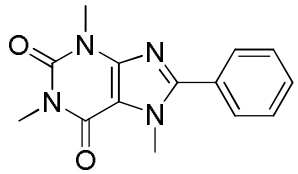
- 4,5-Dimethyl-2-*p*-tolylthiazole: ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 9H), 7.20 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H).

- 4,5-Dimethyl-2-*m*-tolylthiazole: ^1H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 9H), 7.18 (d, J = 7.5 Hz, 1H), 7.25-7.32 (m, 1H), 7.63 (d, J = 7.5 Hz, 1H), 7.71 (s, 1H).

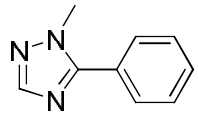


2-(Pyridin-2-yl)benzo[d]thiazole (Entry 1, Table 1): Copper(I) iodide (19 mg, 0.1 mmol), 2-bromopyridine (316 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), benzothiazole (135 mg, 1.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and DMF (0.6 mL), 120 ^oC, 5 hours. After

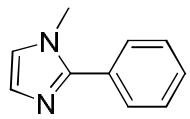
column chromatography (hexanes, then 20% ethyl acetate in hexanes) 190 mg (89%) of a colorless solid was obtained. R_f = 0.36 (1/4 ethyl acetate/hexanes). This compound is known.[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.45 (m, 2H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.84 (dt, *J* = 7.7 Hz, 1.6 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 8.36 (d, *J* = 7.7 Hz, 1H), 8.68 (d, *J* = 4.4 Hz, 1H).



1,3,7-Trimethyl-8-phenyl-1H-purine-2,6(3H,7H)-dione (Entry 2, Table 1): Copper(I) iodide (19 mg, 0.1 mmol), caffeine (194 mg, 1.0 mmol), iodobenzene (408 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), *t*-BuOLi (160 mg, 2.0 mmol), and DMF (0.5 mL), 110 ^{o}C, 5 hours. After column chromatography (hexanes, then 20% hexanes in ethyl acetate) 230 mg (85%) of a colorless solid was obtained. R_f = 0.25 (1/1 ethyl acetate/hexanes). This compound is known.[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.43 (s, 3H), 3.62 (s, 3H), 4.05 (s, 3H), 7.50-7.60 (m, 3H), 7.65-7.72 (m, 2H).

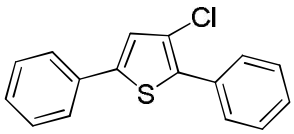


1-Methyl-5-phenyl-1H-1,2,4-triazole (Entry 3, Table 1): Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (408 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 1-methyl-1,2,4-triazole (83 mg, 1.0 mmol), *t*-BuOLi (160 mg, 1.7 mmol), and DMF (0.6 mL), 100 ^{o}C, 5 hours. After column chromatography (hexanes, then 20% hexanes in ethyl acetate) 140 mg (88%) of a light tan oil was obtained. R_f = 0.23 (1/1 ethyl acetate/hexanes). This compound is known.[7] ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00 (s, 3H), 7.48-7.54 (m, 3H), 7.64-7.70 (m, 2H), 7.94 (s, 1H).

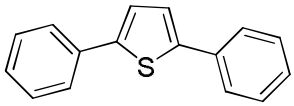


1-Methyl-2-phenylimidazole (Entry 4, Table 1): Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (408 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 1-methylimidazole (82 mg, 1.0 mmol), Et_3COLi (207 mg, 1.7 mmol), and anhydrous DMPU (0.5 mL), 125 ^{o}C, 12 hours. After column chromatography (hexanes, then 1/1 ethyl

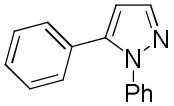
acetate/hexanes) 130 mg (82%) of a colorless solid was obtained. R_f = 0.56 (ethyl acetate). This compound is known.[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.73 (s, 3H), 6.96 (d, *J* = 1.0 Hz, 1H), 7.11 (d, *J* = 1.0 Hz, 1H), 7.38-7.48 (m, 3H), 7.59-7.64 (m, 2H).



3-Chloro-2,5-diphenylthiophene (Entry 5, Table 1): Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (612 mg, 3.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 3-chlorothiophene (118.5 mg, 1.0 mmol), Et_3COLi (305 mg, 2.5 mmol), and anhydrous DMPU (0.6 mL), 125 ^{o}C, 15 hours. After column chromatography (hexanes) 235 mg (87%) of a colorless solid was obtained. R_f = 0.36 (hexanes), mp 63.5-64.5 ^{o}C (from pentane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (s, 1H), 7.29-7.49 (m, 6H), 7.55-7.62 (m, 2H), 7.69-7.76 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.2, 125.6, 126.0, 128.6, 128.7, 129.0, 129.1, 129.5, 132.8, 133.8, 135.9, 142.6. FT-IR (neat, cm^{-1}) υ 1483, 863, 828, 756, 718, 694. Anal calcd for $C_{16}H_{11}SCl$ (270.78 g/mol): C, 70.97; H, 4.09; Found. C, 70.85; H, 4.04.

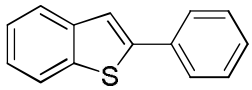


2,5-Diphenylthiophene (Entry 6, Table 1): Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (612 mg, 3.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), thiophene (84 mg, 1.0 mmol), Et_3COLi (366 mg, 3.0 mmol), and anhydrous DMPU (0.6 mL), 125 ^{o}C, 15 hours. After column chromatography (hexanes) 200 mg (85%) of a colorless solid was obtained. R_f = 0.24 (SiO_2, hexanes). This compound is known.[9] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.32 (m, 4H), 7.39 (t, *J* = 7.7 Hz, 4H), 7.63 (d, *J* = 7.7 Hz, 4H).

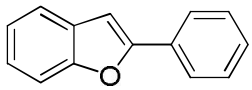


1,5-Diphenyl-1H-pyrazole (Entry 7, Table 1): Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (408 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 1-phenylpyrazole (144 mg, 1.0 mmol), Et_3COLi (207 mg, 1.7 mmol), and anhydrous DMPU (0.5 mL), 125 ^{o}C, 12 hours. After column chromatography (hexanes, then 10% ethyl acetate in hexanes) 115 mg (52%) of a colorless solid was obtained. R_f = 0.41 (1/4 ethyl acetate/hexanes). This

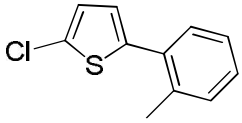
compound is known.[10] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.51 (d, *J* = 1.7 Hz, 1H), 7.20-7.26 (m, 2H), 7.26-7.35 (m, 8H), 7.72 (d, *J* = 1.7 Hz, 1H).



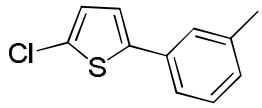
2-Phenylbenzo[b]thiophene (Entry 8, Table 1) : Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (408 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), benzo[b]thiophene (134 mg, 1.0 mmol), Et_3COLi (207 mg, 1.7 mmol), and anhydrous DMPU (0.5 mL), 125 ^oC, 12 hours. After column chromatography (hexanes) 180 mg (86%) of a colorless solid was obtained. R_f = 0.33 (hexanes). This compound is known.[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.47 (m, 5H), 7.55 (s, 1H), 7.67-7.86 (m, 4H).



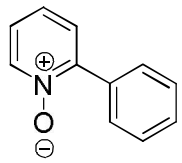
2-Phenylbenzofuran (Entry 9, Table 1): Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (408 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), benzofuran (118 mg, 1.0 mmol), Et_3COLi (207 mg, 1.7 mmol), and anhydrous DMPU (0.5 mL), 125 ^oC, 12 hours. After column chromatography (hexanes) 117 mg (60%) of a colorless solid was obtained. R_f = 0.27 (hexanes). This compound is known.[11] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (s, 1H), 7.20-7.40 (m, 3H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 2H).



2-Chloro-5-*o*-tolylthiophene (Entry 10, Table 1): Copper(I) iodide (19 mg, 0.1 mmol), 2-iodotoluene (218 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 2-chlorothiophene (237 mg, 2.0 mmol), *t*-BuOLi (160 mg, 2.0 mmol), and anhydrous DMPU (0.6 mL), 125 ^oC, 12 hours. After column chromatography (hexanes) 185 mg of a colorless oil (89%) was obtained. R_f = 0.54 (hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 3H), 6.73 (d, *J* = 3.9 Hz, 1H), 6.82 (d, *J* = 3.9 Hz, 1H), 7.10-7.20 (m, 3H), 7.24-7.29 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 126.1, 126.5, 126.6, 128.7, 129.8, 130.8, 131.3, 133.8, 136.6, 142.3. FT-IR (neat, cm^{-1}) υ 1487, 1455, 1003, 799, 756, 721. Anal calcd for $C_{11}H_9ClS$ (208.71 g/mol): C, 63.30; H, 4.35; Found. C, 62.83; H, 4.32.



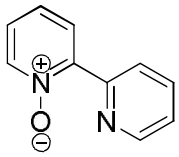
2-Chloro-5-*m*-tolylthiophene (Entry 11, Table 1): Copper(I) iodide (19 mg, 0.1 mmol), 3-iodotoluene (218 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 2-chlorothiophene (237 mg, 2.0 mmol), *t*-BuOLi (160 mg, 2.0 mmol), and anhydrous DMPU (0.6 mL), 125 ^{o}C, 12 hours. After column chromatography (hexanes) 190 mg of a colorless solid (91%) was obtained. R_f = 0.55 (hexanes), mp 37-38.5 ^{o}C (from hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H), 6.89 (d, *J* = 3.9 Hz, 1H), 7.06 (d, *J* = 3.9 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.24-7.35 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.0, 122.7, 123.3, 126.8, 127.6, 129.2, 129.4, 129.5, 134.2, 139.2, 143.7. FT-IR (neat, cm^{-1}) υ 1603, 1488, 1446, 1211, 796, 782, 688. Anal calcd for $C_{11}H_9ClS$ (208.71 g/mol): C, 63.30; H, 4.35; Found. C, 63.28; H, 4.30.



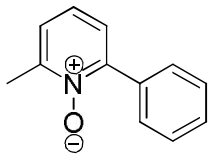
2-Phenylpyridine 1-oxide and 2,6-diphenylpyridine 1-oxide (Entry 1, Table 2): Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (408 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), pyridine *N*-oxide (95 mg, 1.0 mmol), *t*-BuOLi (145 mg, 1.8 mmol), and anhydrous DMPU (0.5 mL), 125 ^{o}C, 1 hour. After column chromatography (ethyl acetate, then 15% MeOH in ethyl acetate) 50 mg of 2,6-diphenylpyridine 1-oxide (20%) was obtained as an off-white solid. Additionally, 2-phenylpyridine 1-oxide (100 mg, 58%) was obtained as a colorless solid. These compounds are known.[7,12]

2-Phenylpyridine 1-oxide: R_f = 0.46 (3/7 methanol/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17-7.34 (m, 2H), 7.38-7.53 (m, 4H), 7.80 (dd, *J* = 7.7 Hz, 1.7 Hz, 2H), 8.33 (d, *J* = 6.0 Hz, 1H).

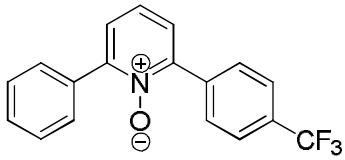
2,6-Diphenylpyridine 1-oxide: R_f = 0.30 (1/1 ethyl acetate/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.52 (m, 9H), 7.80-7.87 (m, 4H).



2,2'-Bipyridine 1-oxide (Entry 2, Table 2): Copper(I) iodide (19 mg, 0.1 mmol), 2-iodopyridine (410 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), pyridine *N*-oxide (95 mg, 1.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and DMF (0.6 mL), 120 ^oC, 5 hours. After column chromatography (hexanes, then 7/3 ethyl acetate/hexanes) 70 mg (41%) of a light tan solid was obtained. R_f = 0.34 (ethyl acetate). This compound is known.[13] ^1H NMR (300 MHz, $CDCl_3$) δ 6.29 (t, *J* = 6.7 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 7.27-7.44 (m, 2H), 7.77-7.98 (m, 3H), 8.56 (dd, *J* = 5.0 Hz, 1.0 Hz, 1H).

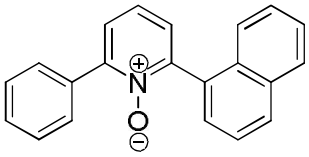


2-Methyl-6-phenylpyridine 1-oxide (Entry 3, Table 2): Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (408 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 2-picoline *N*-oxide (109 mg, 1.0 mmol), *t*-BuOLi (145 mg, 1.8 mmol), and anhydrous DMPU (0.5 mL), 125 ^oC, 1 hour. After column chromatography (ethyl acetate, then 5% MeOH in ethyl acetate) and preparative HPLC (5% MeOH in ethyl acetate) 80 mg (43%) of a light tan solid was obtained. R_f = 0.24 (ethyl acetate). This compound is known.[14] ^1H NMR (300 MHz, $CDCl_3$) δ 2.56 (s, 3H), 7.13-7.34 (m, 3H), 7.37-7.51 (m, 3H), 7.77 (dd, *J* = 7.8 Hz, 1.7 Hz, 2H).

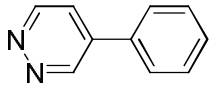


2-Phenyl-6-(4-(trifluoromethyl)phenyl)pyridine 1-oxide (Entry 4, Table 2): Copper(I) iodide (19 mg, 0.1 mmol), 4-iodobenzotrifluoride (544 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 2-phenylpyridine *N*-oxide (171 mg, 1.0 mmol), *t*-BuOLi (160 mg, 2.0 mmol), and anhydrous DMPU (0.6 mL), 125 ^oC, 1 hour. After column chromatography (hexanes, then 1/1 ethyl acetate/hexanes) 252 mg (80%) of a light tan solid was obtained. R_f = 0.44 (1/1 ethyl acetate/hexanes), mp 150-151 ^oC (from ether). ^1H NMR (300 MHz, $CDCl_3$) δ 7.33-7.42 (m, 2H), 7.43-7.51 (m, 4H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.79-7.84 (m, 2H), 7.96 (d,

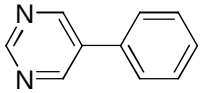
J = 8.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 124.4 (q, $J_{C\text{-}F}$ = 273 Hz), 125.4, 125.5, 125.6, 126.6, 127.4, 128.7, 130.0, 130.6, 131.6 (q, $J_{C\text{-}F}$ = 33.5 Hz), 133.5, 137.4, 149.0, 150.7. FT-IR (neat, cm^{-1}) υ 1372, 1327, 1281, 1165, 1121, 1071, 854, 844, 800, 768 Anal calcd for $C_{18}H_{12}F_3NO$ (315.29 g/mol): C, 68.57; H, 3.84; N, 4.44; Found. C, 68.71; H, 3.91; N, 4.41.



2-(Naphthalen-1-yl)-6-phenylpyridine 1-oxide (Entry 5, Table 2): Copper(I) iodide (19 mg, 0.1 mmol), 1-iodonapthalene (508 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 2-phenylpyridine *N*-oxide (171 mg, 1.0 mmol), *t*-BuOLi (160 mg, 2.0 mmol), and anhydrous DMPU (0.6 mL), 125 °C, 1 hour. After column chromatography (hexanes, then 1/1 ethyl acetate/hexanes) 270 mg (91%) of a light tan solid was obtained. R_f = 0.31 (1/1 ethyl acetate/hexanes), mp 167-168 °C (from ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.50 (m, 7H), 7.52-7.60 (m, 4H), 7.86-7.98 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.5, 124.9, 125.8, 125.9, 126.6, 127.1, 127.3, 127.8, 128.2, 128.6, 129.0, 129.9, 130.1, 130.3, 131.7, 133.6, 134.0, 150.4, 151.0. FT-IR (neat, cm^{-1}) υ 1372, 1245, 843, 782, 764. Anal calcd for $C_{21}H_{15}NO$ (297.35 g/mol): C, 84.82; H, 5.08; N, 4.71; Found. C, 84.56; H, 5.05; N, 4.64.

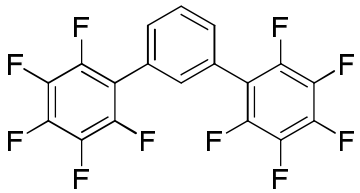


4-Phenylpyridazine (Entry 6, Table 2): Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (204 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), pyridazine (160 mg, 2.0 mmol), Et_3COLi (207 mg, 1.7 mmol), and anhydrous DMPU (0.5 mL), 125 °C, 12 hours. After column chromatography (hexanes, then 1/1 ethyl acetate/hexanes) 94 mg (60%) of a light tan solid was obtained. R_f = 0.40 (ethyl acetate). This compound is known.[15] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.59 (m, 3H), 7.60-7.70 (m, 3H), 9.21 (dd, J = 5.5 Hz, 1.0 Hz, 1H), 9.45 (dd, J = 2.2 Hz, 1.0 Hz, 1H).

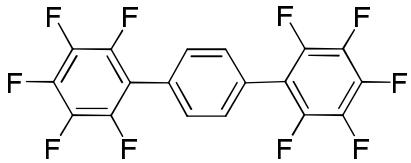


5-Phenylpyrimidine (Entry 7, Table 2): Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (204 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), pyrimidine (160 mg, 2.0

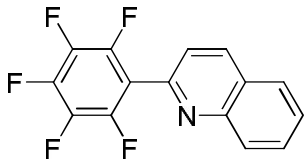
mmol), Et_3COLi (207 mg, 1.7 mmol), and anhydrous DMPU (0.5 mL), 125 ^oC, 12 hours. After column chromatography (hexanes, then 1/1 ethyl acetate/hexanes) 48 mg (31%) of a light tan solid was obtained. R_f = 0.55 (ethyl acetate). This compound is known.[16] ^1H NMR (300 MHz, $CDCl_3$) δ 7.42-7.61 (m, 5H), 8.95 (s, 2H), 9.20 (s, 1H).



1,3-Dipentafluorophenylbenzene (Entry 1, Table 3): Copper(I) iodide (29 mg, 0.15 mmol), pentafluorobenzene (504 mg, 3.0 mmol), 1,10-phenanthroline (27 mg, 0.15 mmol), 1,3-dibromobenzene (236 mg, 1.0 mmol), K_3PO_4 (848 mg, 4.0 mmol), and DMF/xylenes (1/1, 0.8 mL), 125 ^oC, 24 hours. After column chromatography (hexanes) 210 mg (51%) of a colorless solid was obtained. R_f = 0.38 (hexanes). This compound is known.[17] ^1H NMR (300 MHz, $CDCl_3$) δ 7.47-7.58 (m, 3H), 7.60-7.67 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -163.8- -163.5 (m, 4F), -156.4 (t, J_F = 21.0 Hz, 2F), -145.0 (dd, J_F = 23.0 Hz, 7.6 Hz, 4F).

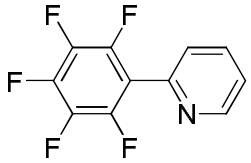


1,4-Dipentafluorophenylbenzene (Entry 2, Table 3): Copper(I) iodide (29 mg, 0.15 mmol), pentafluorobenzene (504 mg, 3.0 mmol), 1,10-phenanthroline (27 mg, 0.15 mmol), 1,4-diiodobenzene (330 mg, 1.0 mmol), K_3PO_4 (848 mg, 4.0 mmol), and DMF (0.8 mL), 125 ^oC, 12 hours. After column chromatography (hexanes) 300 mg (73%) of a colorless solid was obtained. R_f = 0.30 (hexanes). This compound is known.[18] ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (s, 4H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -163.4- -163.0 (m, 4F), -156.2- -155.8 (m, 2F), -144.6 (dd, J_F = J_F = 23.0 Hz, 7.6 Hz, 4F).

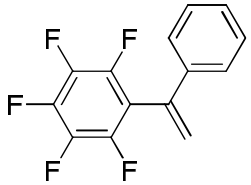


2-(Pentafluorophenyl)quinoline (Entry 3, Table 3): Copper(I) iodide (19 mg, 0.1 mmol), pentafluorobenzene (252 mg, 1.5 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 2-chloroquinoline (163.5 mg, 1.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and DMF/xylenes (1/1,

0.5 mL), 125 °C, 24 hours. After column chromatography (hexanes) 250 mg (85%) of a colorless solid was obtained. R_f = 0.42 (1/9 ethyl acetate/hexanes), mp 168-169.5 °C (from pentane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 1H), 7.63 (dt, *J* = 7.8 Hz, 0.5 Hz, 1H), 7.79 (dt, *J* = 7.8 Hz, 0.5 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.29 (d, *J* = 8.5 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -163.5- -162.9 (m, 2F), -155.3- -154.9 (m, 1F), -144.4 (d, J_F = 21.0 Hz, 2F). FT-IR (neat, cm^{-1}) υ 1493, 1077, 986, 906, 836, 789 Anal calcd for $C_{15}H_6NF_5$ (295.21 g/mol): C, 61.03; H, 2.05; N, 4.74; Found. C, 61.03; H, 1.97; N, 4.61.

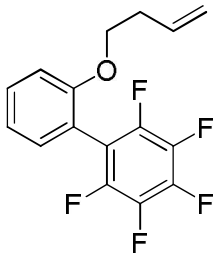


2-(Pentafluorophenyl)pyridine (Entry 4, Table 3): Copper(I) iodide (19 mg, 0.1 mmol), 2-chloropyridine (113.5 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), pentafluorobenzene (252 mg, 1.5 mmol), K_3PO_4 (424 mg, 2.0 mmol), and DMF/xylenes (0.6 mL), 150 °C, 24 hours. After column chromatography (hexanes, then 10% ethyl acetate in hexanes) 100 mg (41%) of a colorless solid was obtained. R_f = 0.41 (1/4 AcOEt/hexanes). This compound is known.[17] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (ddd, *J* = 8.0 Hz, 5.0 Hz, 1.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.80-7.88 (m, 1H), 8.74-8.80 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -163.6- -163.3 (m, 2F), -155.5- -155.1 (m, 1F), -144.9 (dd, J_F = 23.0 Hz, 7.6 Hz, 2F).

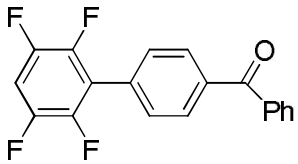


1,2,3,4,5-Pentafluoro-6-(1-phenylvinyl)benzene (Entry 5, Table 3): Copper(I) iodide (19 mg, 0.1 mmol), α-bromostyrene (183 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), pentafluorobenzene (252 mg, 1.5 mmol), K_3PO_4 (424 mg, 2.0 mmol), and DMF/xylenes (1/1, 0.6 mL), 125 °C, 24 hours. After column chromatography (hexanes) 220 mg (81%) of a colorless oil was obtained. R_f = 0.42 (hexanes). This compound is known.[19] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.44 (s, 1H), 6.06 (s, 1H), 7.22-7.39 (m, 5H). ^{19}F NMR (282

MHz, $CDCl_3$) δ -163.9- -163.4 (m, 2F), -156.9- -156.5 (m, 1F), -141.9 (dd, J_F = 23.0 Hz, 7.6 Hz, 2F).

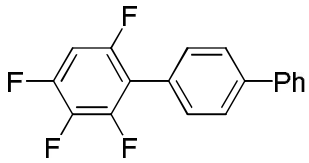


2'-(But-3-enyloxy)-2,3,4,5,6-pentafluorobiphenyl (Entry 6, Table 3): Copper(I) iodide (19 mg, 0.1 mmol), 1-(but-3-enyloxy)-2-iodobenzene (274 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), pentafluorobenzene (252 mg, 1.5 mmol), K_3PO_4 (424 mg, 2.0 mmol), and DMF (0.6 mL), 125 ^oC, 12 hours. After column chromatography (hexanes, then 10% ethyl acetate in hexanes) 280 mg (89%) of a colorless oil was obtained. R_f = 0.33 (hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 2.43 (q, J = 6.6 Hz, 2H), 4.04 (t, J = 6.6 Hz, 2H), 5.01 (s, 1H), 5.06 (d, J = 5.5 Hz, 1H), 5.68-5.85 (m, 1H), 7.02 (d, J = 7.8 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 6.6 Hz, 1H), 7.43 (dt, J = 7.8 Hz, 1.5 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -165.3- -164.9 (m, 2F), -158.2- -157.8 (m, 1F), -141.8- -141.4 (m, 2F). ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.1, 68.1, 112.8, 113.4 (t, J_{C-F} = 15.7 Hz), 116.2, 117.4, 121.2, 131.5, 132.2, 136.4, 136.1-139.5 (m), 139.5-142.9 (m), 143.1-146.9 (m), 157.0. FT-IR (neat, cm^{-1}) υ 1493, 1250, 1063, 987, 752 Anal calcd for $C_{16}H_{11}OF_5$ (314.25 g/mol): C, 61.15; H, 3.53; Found. C, 61.58; H, 3.50.

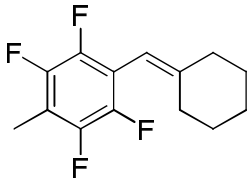


Phenyl(2',3',5',6'-tetrafluorobiphenyl-4-yl)methanone (Entry 7, Table 3): Copper(I) iodide (19 mg, 0.1 mmol), 1,2,4,5-tetrafluorobenzene (300 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 4-bromobenzophenone (261 mg, 1.0 mmol), K_3PO_4 (500 mg, 2.4 mmol), and anhydrous DMPU (0.5 mL), 120 ^oC, 12 hours. After column chromatography (hexanes, then 5% ethyl acetate in hexanes) 170 mg (52%) of a colorless solid was obtained. R_f = 0.42 (1/9 ethyl acetate/hexanes), mp 108-111 ^oC (from pentane). ^1H NMR (300 MHz, $CDCl_3$) δ 7.05-7.18 (m, 1H), 7.45-7.65 (m, 5H), 7.80-7.88 (m, 2H), 7.92 (d, J = 7.5 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -145.5- -145.3 (m, 2F), -140.5- -140.2 (m,

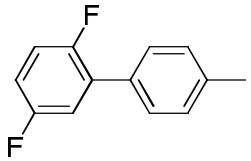
2F). ^{13}C NMR (75 MHz, $CDCl_3$) δ 106.0 (t, J_{C-F} = 21.5 Hz), 121.1 (t, J_{C-F} = 16.8 Hz), 128.7, 128.9, 130.5, 130.6, 131.9, 133.0, 137.9, 138.8, 142.4-146.2 (m), 145.0-148.8 (m), 196.2. FT-IR (neat, cm^{-1}) υ 1645, 1492, 1283, 936, 852, 701 Anal calcd for $C_{19}H_{10}OF_4$ (330.28 g/mol): C, 69.09; H, 3.05; Found. C, 68.99; H, 3.02.



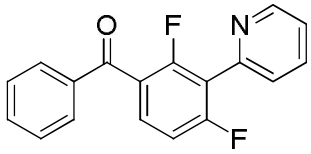
2,3,4,6-Tetrafluoro-4'-phenylbiphenyl (Entry 8, Table 3): Copper(I) iodide (19 mg, 0.1 mmol), 1,2,3,5-tetrafluorobenzene (300 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 4-bromobiphenyl (231 mg, 1.0 mmol), K_3PO_4 (500 mg, 2.4 mmol), and anhydrous DMPU (0.5 mL), 125 ^oC, 24 hours. After column chromatography (hexanes) 210 mg (70%) of a colorless solid was obtained. R_f = 0.23 (hexanes). This compound is known.[20] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.83-6.95 (m, 1H), 7.34-7.55 (m, 5H), 7.60-7.74 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -166.8- -166.3 (m, 1F), -137.3 (d, J_F = 21.0 Hz, 1F), -135.3- -135.0 (m, 1F), -120.0 (t, J_F = 10.0 Hz, 1F).



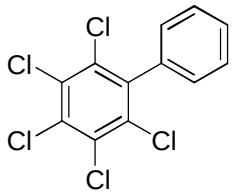
1-(Cyclohexylidenemethyl)-2,3,5,6-tetrafluoro-4-methylbenzene (Entry 9, Table 3): Copper(I) iodide (19 mg, 0.1 mmol), 2,3,5,6-tetrafluorotoluene (245 mg, 1.5 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), bromomethylenecyclohexane (175 mg, 1.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and anhydrous DMPU (0.6 mL), 125 ^oC, 12 hours. After column chromatography (hexanes) 245 mg (95%) of a colorless oil was obtained. R_f = 0.60 (hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50-1.70 (m, 6H), 2.05 (s, 2H), 2.24 (t, J = 2.2 Hz, 3H), 2.31 (t, J = 6.0 Hz, 2H), 5.79 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -147.3 (dd, J_F = 21.0 Hz, 13.3 Hz, 2F), -147.3 (dd, J_F = 21.0 Hz, 13.3 Hz, 2F). ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.9, 26.8, 27.9, 28.9, 31.6, 37.5, 106.6, 114.2 (t, J = 19.5 Hz), 115.3 (t, J = 19.5 Hz), 142.3-146.0 (m), 143.6-147.4 (m), 151.0. FT-IR (neat, cm^{-1}) υ 2934, 2857, 1475, 1287, 1064, 951, 922 Anal calcd for $C_{14}H_{14}F_4$ (258.25 g/mol): C, 65.11; H, 5.46; Found. C, 64.74; H, 5.33.



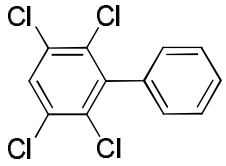
2,5-Difluoro-4'-methylbiphenyl (Entry 10, Table 3): Copper(I) iodide (19 mg, 0.1 mmol), 4-iodotoluene (218 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 1,4-difluorobenzene (228 mg, 2.0 mmol), Et_3COLi (207 mg, 1.7 mmol), and anhydrous DMPU (0.5 mL), 125 ^oC, 12 hours. After column chromatography (hexanes) 110 mg (54%) of a colorless oil was obtained. R_f = 0.42 (hexanes). This compound is known.[17] ^1H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 6.91-7.02 (m, 1H), 7.03-7.18 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.43 (dd, *J* = 7.8 Hz, 1.2 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -125.9 (br s, 1F), -120.9 (br s, 1F).



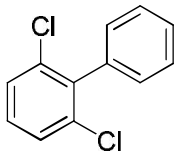
2,4-Difluoro-3-(pyridin-2-yl)benzophenone (Entry 11, Table 3): Copper(I) iodide (19 mg, 0.1 mmol), 2-iodopyridine (205 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 2,4-difluorobenzophenone (436 mg, 2.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and anhydrous DMPU (0.6 mL), 125 ^oC, 24 hours. After column chromatography (hexanes, then 1/1 ethyl acetate/hexanes) 200 mg (68%) of a light tan oil was obtained. R_f = 0.45 (1/1 ethyl acetate/hexanes). ^1H NMR (300 MHz, $CDCl_3$) δ 7.11 (dt, *J* = 8.8 Hz, 1.2 Hz, 1H), 7.26-7.33 (m, 1H), 7.39-7.50 (m, 3H), 7.51-7.64 (m, 2H), 7.75 (dt, *J* = 7.8 Hz, 2.0 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 2H), 8.72 (d, *J* = 4.4 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.3- -113.2 (m, 1F), -110.2- -110.0 (m, 1F). ^{13}C NMR (75 MHz, $CDCl_3$) δ 112.8 (dd, *J* = 24.0 Hz, 4.5 Hz), 119.2 (t, *J* = 18.5, Hz), 121.9, 123.8, 124.3 (dd, *J* = 15.5 Hz, 3.5 Hz), 126.5, 129.1, 130.2, 132.1 (dd, *J* = 10.8 Hz, 6.8 Hz), 134.0, 137.0, 137.9, 149.1, 150.4, 158.7 (dd, *J* = 257.3 Hz, 7.0 Hz), 162.7 (dd, *J* = 257.3 Hz, 7.0 Hz), 192.8. FT-IR (neat, cm^{-1}) υ 1667, 1618, 1592, 1448, 1420, 1321, 1269, 1013, 832, 797, 789, 748, 719 Anal calcd for $C_{18}H_{11}F_2NO$ (295.28 g/mol): C, 73.22; H, 3.75; N, 4.74; Found. C, 72.55; H, 3.88; N, 4.74.



2,3,4,5,6-Pentachlorobiphenyl (Entry 12, Table 3): Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (408 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 1,2,3,4,5-pentachlorobenzene (250 mg, 1.0 mmol), *t*-BuOLi (160 mg, 2 mmol), and DMF (0.5 mL), 120 ^{o}C, 12 hours. After column chromatography (hexanes) 297 mg (91%) of a colorless solid was obtained. R_f = 0.54 (hexanes). This compound is known.[21] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.21 (m, 2H), 7.44-7.52 (m, 3H).



2,3,5,6-Tetrachlorobiphenyl (Entry 13, Table 3): Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (204 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 1,2,4,5-tetrachlorobenzene (432 mg, 2.0 mmol), *t*-BuOLi (160 mg, 2 mmol), and DMPU (0.6 mL), 125 ^{o}C, 12 hours. After column chromatography (hexanes) 217 mg (74 %) of a colorless solid was obtained. R_f = 0.51 (hexanes). This compound is known.[22] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17-7.22 (m, 2H), 7.44-7.52 (m, 3H), 7.64 (s, 1H).

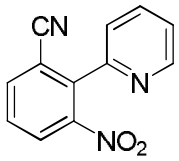


2,6-Dichlorobiphenyl (Entry 14, Table 3):

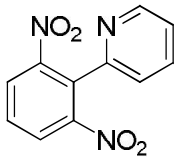
- Using Et_3COLi base: Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (204 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 1,3-dichlorobenzene (220 mg, 1.5 mmol), Et_3COLi (207 mg, 1.7 mmol), and anhydrous DMPU (0.5 mL), 125 ^{o}C, 12 hours. After column chromatography (hexanes) 96 mg (43 %) of a colorless oil was obtained. R_f = 0.49 (hexanes). This compound is known.[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18-7.30 (m, 3H), 7.38-7.50 (m, 5H).

- Using *t*-BuOLi base: Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (204 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 1,3-dichlorobenzene (220 mg, 1.5 mmol), *t*-

BuOLi (160 mg, 2.0 mmol), and DMPU (0.5 mL), 125 ^{o}C, 12 hours. After column chromatography (hexanes) 40 mg (18 %) of a colorless oil was obtained.



3-Nitro-2-(pyridin-2-yl)benzonitrile (Entry 15, Table 3): Copper(I) iodide (19 mg, 0.1 mmol), 2-iodopyridine (410 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 3-nitrobenzonitrile (148 mg, 1.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and anhydrous DMPU (0.6 mL), 125 ^{o}C, 24 hours. After column chromatography (hexanes, then 1/1 ethyl acetate/hexanes) 115 mg (51%) of a light tan solid was obtained. R_f = 0.45 (1/1 ethyl acetate/hexanes), mp 107-109 ^{o}C (from ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (ddd, *J* = 8.0 Hz, 4.5 Hz, 1.0 Hz, 1H), 7.60 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.89 (dt, *J* = 8.0 Hz, 1.7 Hz, 1H), 7.99 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 8.16 (dd, *J* = 8.0 Hz, 1 Hz, 1H), 8.69 (dt, *J* = 4.5 Hz, 1.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 115.8, 116.4, 124.4, 124.7, 128.8, 130.3, 132.8, 137.3, 137.5, 139.4, 150.7, 152.4. FT-IR (neat, cm^{-1}) υ 2230, 1589, 1548, 1528, 1372, 815, 799, 783, 754, 733 Anal calcd for $C_{12}H_7N_3O_2$ (225.20 g/mol): C, 64.00; H, 3.13; N, 18.66; Found. C, 64.27; H, 3.13; N, 18.40.



2-(2,6-Dinitrophenyl)pyridine (Entry 16, Table 3) : Copper(I) iodide (19 mg, 0.1 mmol), 2-iodopyridine (205 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), 1,3-dinitrobenzene (336 mg, 2.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and anhydrous DMPU (0.6 mL), 125 ^{o}C, 22 hours. After column chromatography (hexanes, then 35 % ethyl acetate in hexanes) 176 mg (72%) of a colorless solid was obtained. R_f = 0.47 (1/1 ethyl acetate/hexanes), mp 160-162 ^{o}C (from hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.41 (m, 2H), 7.71-7.83 (m, 2H), 8.15 (d, *J* = 7.8 Hz, 2H), 8.63-8.67 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 124.0, 124.2, 128.2, 130.4, 130.6, 137.2, 150.6, 150.8, 151.2. FT-IR (neat, cm^{-1}) υ 1524, 1362, 821, 793, 752, 721, 706 Anal calcd for $C_{12}H_7N_3O_2$ (245.19 g/mol): C, 53.88; H, 2.88; N, 17.14; Found. C, 53.86; H, 2.71; N, 16.87.

Control arylation reaction (CuI omitted):

- Using 4-iodotoluene as the coupling partner: 1,10-phenanthroline (18 mg, 0.1 mmol), pentafluorobenzene (252 mg, 1.5 mmol), 4-iodotoluene (218 mg, 1.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and DMF (0.6 mL) at 125 °C, 12 h. No product was detected.

- Using 2-iodopyridine as the coupling partner: 1,10-phenanthroline (18 mg, 0.1 mmol), pentafluorobenzene (252 mg, 1.5 mmol), 2-iodopyridine (205 mg, 1.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and DMF (0.6 mL) at 125 °C, 12 h. A trace of arylated product was detected.

Reaction of benzothiophene and iodoarenes in the presence of *t*-BuOD:

- Using iodobenzene: Copper(I) iodide (19 mg, 0.1 mmol), iodobenzene (408 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), benzothiophene (134 mg, 1.0 mmol), *t*-BuOLi (160 mg, 2.0 mmol), *t*-BuOD (150 mg, 2.0 mmol), and anhydrous DMPU (0.5 mL), 125 ^{o}C. The reaction was stopped after 1 hour (15% conversion by GC). The unreacted starting material was recovered by column chromatography (hexanes). NMR integration showed 20% D incorporation in starting material at 2-position (δ 7.45 ppm).

- Using 4-iodotoluene: Copper(I) iodide (19 mg, 0.1 mmol), 4-iodotoluene (436 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), benzothiophene (134 mg, 1.0 mmol), *t*-BuOLi (160 mg, 2.0 mmol), *t*-BuOD (150 mg, 2.0 mmol), and anhydrous DMPU (0.5 mL), 125 ^{o}C. The reaction was stopped after 1 hour (13% conversion by GC). The unreacted starting material was recovered by column chromatography (hexanes). NMR integration showed 25% D incorporation in starting material at 2-position (δ 7.45 ppm).

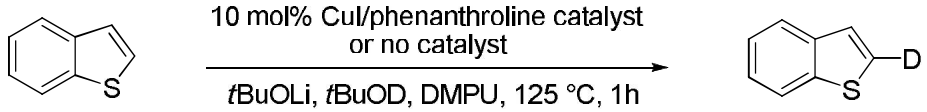
- Using 4-iodobenzotrifluoride: Copper(I) iodide (19 mg, 0.1 mmol), 4-iodobenzotrifluoride (544 mg, 2.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), benzothiophene (134 mg, 1.0 mmol), *t*-BuOLi (160 mg, 2.0 mmol), *t*-BuOD (150 mg, 2.0 mmol), and DMPU (0.5 mL), 125 ^{o}C. The reaction was stopped after 1 hour (34% conversion by GC). The unreacted starting material was recovered by column chromatography (hexanes). NMR integration showed 26% of D incorporation in starting material at 2-position (δ 7.45 ppm).

^{19}F NMR study of the reaction intermediate: Copper(I) iodide (190 mg, 1.0 mmol), 1,10-phenanthroline (180 mg, 1.0 mmol), pentafluorobenzene (252 mg, 1.5 mmol), K_3PO_4 (424 mg, 2.0 mmol), and DMF (3.0 mL) at 125 °C. The reaction mixture was analyzed by ^{19}F NMR at different reaction times. At t = 0, only C_6F_5H was observed by ^{19}F NMR. At t = 1h, only pentafluorophenylcopper phenanthroline complex was present in the reaction mixture.

Table S1. ^{19}F NMR spectrum of the reaction mixture and $C_6F_5Cu(Phen)$ complex

	Reaction mixture at t = 0	Reaction mixture at t = 1 h	$C_6F_5Cu(Phen)$
o-F	-142.2 (d, $J_{F\text{-}F}$ = 10 Hz, 2F)	-113.5- -113.0 (m, 2F)	-112.9- -112.4 (m, 2F)
m-F	-166.3- -166.0 (m, 2F)	-166.4- -166.0 (m, 2F)	-166.2- -165.9 (m, 2F)
p-F	-158.5 (t, J_F = 20 Hz, 1F)	-165.2 (t, J_F = 20 Hz, 1F)	-165.2 (t, J_F = 20 Hz, 1F)

H/D exchange reactions:



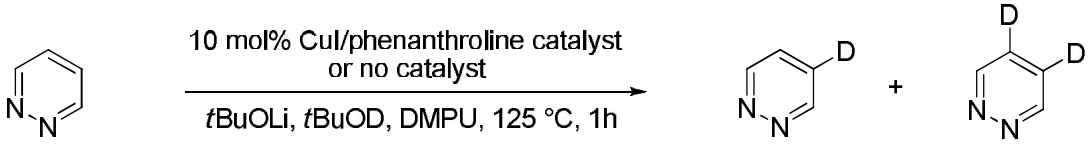
25-30% D incorporation

With copper(I) catalyst: Copper(I) iodide (19 mg, 0.1 mmol), benzothiophene (134 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), *t*-BuOD (375 mg, 5 mmol), *t*-BuOLi (160 mg, 2.0 mmol), and DMPU (0.7 mL) at 125 °C for 1 h. Benzothiophene was recovered by column chromatography (hexanes). NMR integration of the C-2 proton (δ 7.45 ppm) showed 30% D incorporation.

Without copper(I) catalyst: Benzothiophene (134 mg, 1.0 mmol), *t*-BuOD (375 mg, 5 mmol), *t*-BuOLi (160 mg, 2.0 mmol), and DMPU (0.7 mL) at 125 °C for 1 h. Benzothiophene was recovered by column chromatography (hexanes). NMR integration of the C-2 proton (δ 7.45 ppm) showed 30% D incorporation.

Using *t*-BuOCu: *t*-BuOCu (68.5 mg, 0.5 mmol), benzothiophene (67 mg, 0.5 mmol), 1,10-phenanthroline (90 mg, 0.5 mmol), *t*-BuOD (187.5 mg, 2.5 mmol), and anhydrous DMPU (0.4 mL) at 125 °C for 1 h. Benzothiophene was recovered by column chromatography (hexanes). NMR integration of the C-2 proton (δ 7.45 ppm) showed 60% D incorporation.

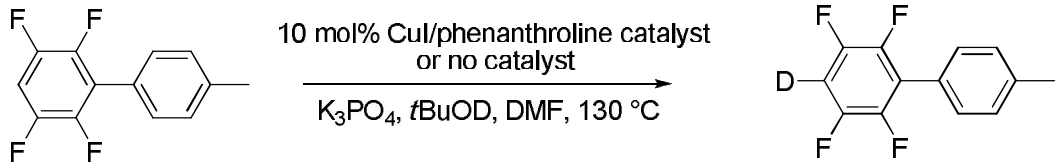
Using LiI: LiI (134 mg, 1.0 mmol), benzothiophene (134 mg, 1.0 mmol), *t*-BuOD (375 mg, 5 mmol), and anhydrous DMPU (0.7 mL) at 125 °C for 1 h. Benzothiophene was recovered by column chromatography (hexanes). Deuterium incorporation in starting material was not detected.



30-35% D incorporation

With copper(I) catalyst: Copper(I) iodide (19 mg, 0.1 mmol), pyridazine (80 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), *t*-BuOD (375 mg, 5 mmol), *t*-BuOLi (160 mg, 2.0 mmol), and anhydrous DMPU (0.7 mL) at 125 °C for 1 h. After column chromatography (5% MeOH in ethyl acetate) a mixture of pyridazine and DMPU was recovered. NMR integration (δ 7.29-7.35 ppm, m) showed 30% D incorporation in starting material.

Without copper(I) catalyst: Pyridazine (80 mg, 1.0 mmol), *t*-BuOD (375 mg, 5 mmol), *t*-BuOLi (160 mg, 2.0 mmol), and anhydrous DMPU (0.7 mL) at 125 °C for 1 h. After column chromatography (5% MeOH in ethyl acetate) a mixture of pyridazine and DMPU was recovered. NMR integration (δ 7.29-7.35 ppm, m) showed 30% D incorporation in starting material.



62-65% D incorporation

With copper(I) catalyst: Copper(I) iodide (9.6 mg, 0.05 mmol), 1,10-phenanthroline (9 mg, 0.05 mmol), 2,3,5,6-tetrafluoro-4'-methylbiphenyl (120 mg, 0.5 mmol), *t*-BuOD (375 mg, 5 mmol), K_3PO_4 (212 mg, 1.0 mmol), and DMF (0.4 mL) at 130° C for 24 h. The unreacted starting material was recovered by column chromatography (hexanes). NMR integration (δ 6.97-7.12 ppm, m) showed 65% of D incorporation in starting material.

Without copper(I) catalyst: 2,3,5,6-Tetrafluoro-4'-methylbiphenyl (120 mg, 0.5 mmol), *t*-BuOD (375 mg, 5 mmol), K_3PO_4 (212 mg, 1.0 mmol), and DMF (0.4 mL) at 130° C for 24 h. The unreacted starting material was recovered by column chromatography (hexanes). NMR integration (δ 6.97-7.12 ppm, m) showed 62% of D incorporation in starting material.

Competition reaction of pentafluorobenzene and 1,2,4,5-tetrafluorobenzene: Copper(I) iodide (19 mg, 0.1 mmol), 4-iodotoluene (218 mg, 1.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), pentafluorobenzene (1176 mg, 7.0 mmol), 1,2,4,5-tetrafluorobenzene (1050 mg, 7.0 mmol), K_3PO_4 (488 mg, 2.3 mmol), and DMF (0.8 mL) at 125 °C, 15 h. The molar ratio of arylation products 2,3,4,5,6-pentafluoro-4'-methylbiphenyl/2,3,5,6-tetrafluoro-4'-methyl-biphenyl was determined to be 3.0 by GC analysis of crude reaction mixture.

Competition reaction of 4-iodotoluene and 4-iodobenzotrifluoride: Copper(I) iodide (19 mg, 0.1 mmol), 4-iodotoluene (1526 mg, 7.0 mmol), 4-iodobenzotrifluoride (1904 mg, 7.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), pentafluorobenzene (168 mg, 1.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and DMF (1.0 mL) at 125 °C, 1 h. The molar ratio of arylation products 2,3,4,5,6-pentafluoro-4'-(trifluoromethyl)-biphenyl/2,3,4,5,6-pentafluoro-4'-methylbiphenyl was determined to be 4.0 by GC analysis of crude reaction mixture.

Competition reaction of 4-bromotoluene and 4-bromobenzotrifluoride: Copper(I) iodide (19 mg, 0.1 mmol), 4-iodotoluene (1526 mg, 7.0 mmol), 4-iodobenzotrifluoride (1904 mg, 7.0 mmol), 1,10-phenanthroline (18 mg, 0.1 mmol), pentafluorobenzene (168 mg, 1.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and DMF (1.0 mL) at 125 °C, 1 h. The molar ratio of arylation products 2,3,4,5,6-pentafluoro-4'-(trifluoromethyl)-biphenyl/2,3,4,5,6-pentafluoro-4'-methylbiphenyl was determined to be 4.0 by GC analysis of crude reaction mixture.

X-Ray Data for 4-Methoxy-2,3,5,6-tetrafluorophenylcopper-phenanthroline Complex 2

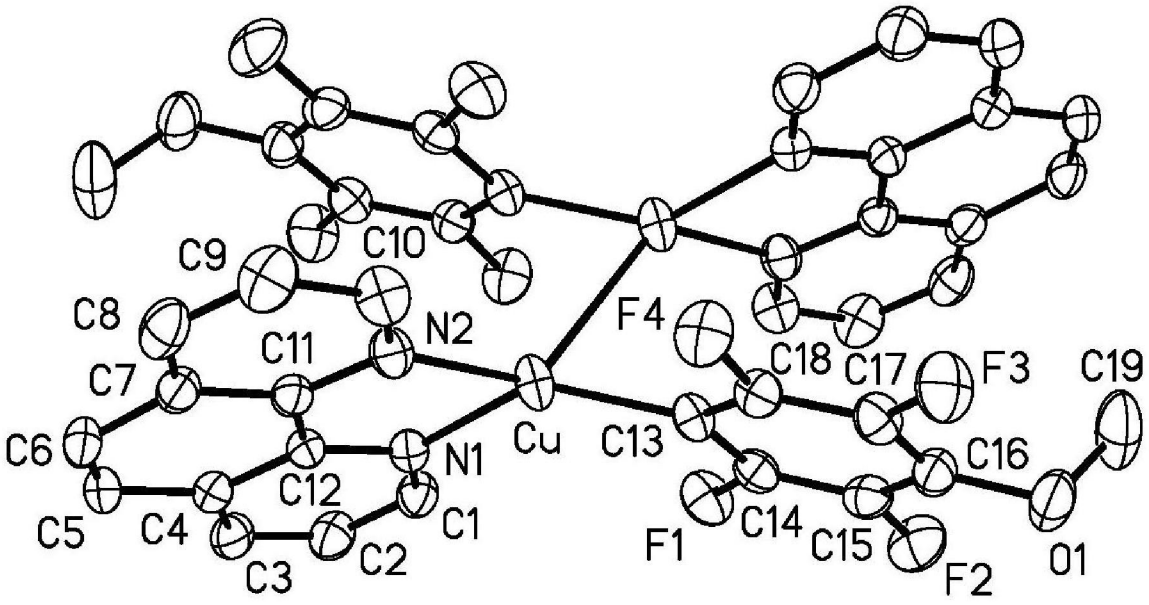
All measurements were made with a Siemens SMART platform diffractometer equipped with a 4K CCD APEX II detector. A hemisphere of data (1271 frames at 6 cm detector distance) was collected using a narrow-frame algorithm with scan widths of 0.30\% in omega and an exposure time of 30 s/frame. The data were integrated using the Bruker-Nonius SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A psi scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 3841 reflections having I>10\s(I), and these, along with other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be 2/m, and from the systematic absences noted the space group was shown unambiguously to be P2(1)/n. The asymmetric unit consists of one-half dimer situated about an inversion center.

Acknowledgment for use of MRSEC/TCSUH Facilities: This work made use of MRSEC/TCSUH Shared Experimental Facilities supported by the National Science Foundation under Award Number DMR-9632667 and the Texas Center for Superconductivity at the University of Houston.

Table S2. Crystal Data and Structure Refinement for 4-Methoxy-2,3,5,6-tetrafluorophenylcopper-phenanthroline Complex 2.

Empirical formula	$C_{38}H_{22}Cu_2F_8N_4O_2$
Formula weight	845.68
Temperature	223(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 9.3839(6) A alpha = 90 deg.
	b = 17.3423(11) A beta = 93.516(1) deg.
	c = 10.0786(6) A gamma = 90 deg.
Volume	1637.09(18) A^3
Z, Calculated density	2, 1.716 Mg/m^3
Absorption coefficient	1.389 mm^-1
F(000)	848
Crystal color and shape	Bright red column
Crystal size	0.45 x 0.15 x 0.15 mm
Theta range for data collection	2.34 to 25.09 deg.
Limiting indices	-11<=h<=11, 0<=k<=20, 0<=l<=11
Reflections collected/unique	8401/3001 [R(int) = 0.0434]
Completeness to theta = 25.09	99.5 %
Absorption correction	Empirical
Max. and min. transmission	0.9856 and 0.6505
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2082 / 0 / 245
Goodness-of-fit on F^2	0.996
Final R indices [I>4sigma(I)]	R1 = 0.0282, wR2 = 0.0760
R indices (all data)	R1 = 0.0400, wR2 = 0.0834
Largest diff. peak and hole	0.513 and -0.207 e.A^-3

Figure S1. Structural View (40% Ellipsoids) of 4-Methoxy-2,3,5,6-tetrafluorophenyl-copper-phenanthroline Complex 2 Showing Partial Atom Numbering Scheme.



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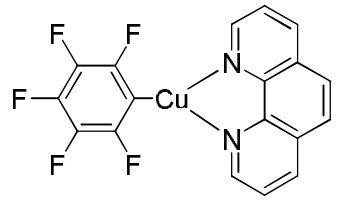
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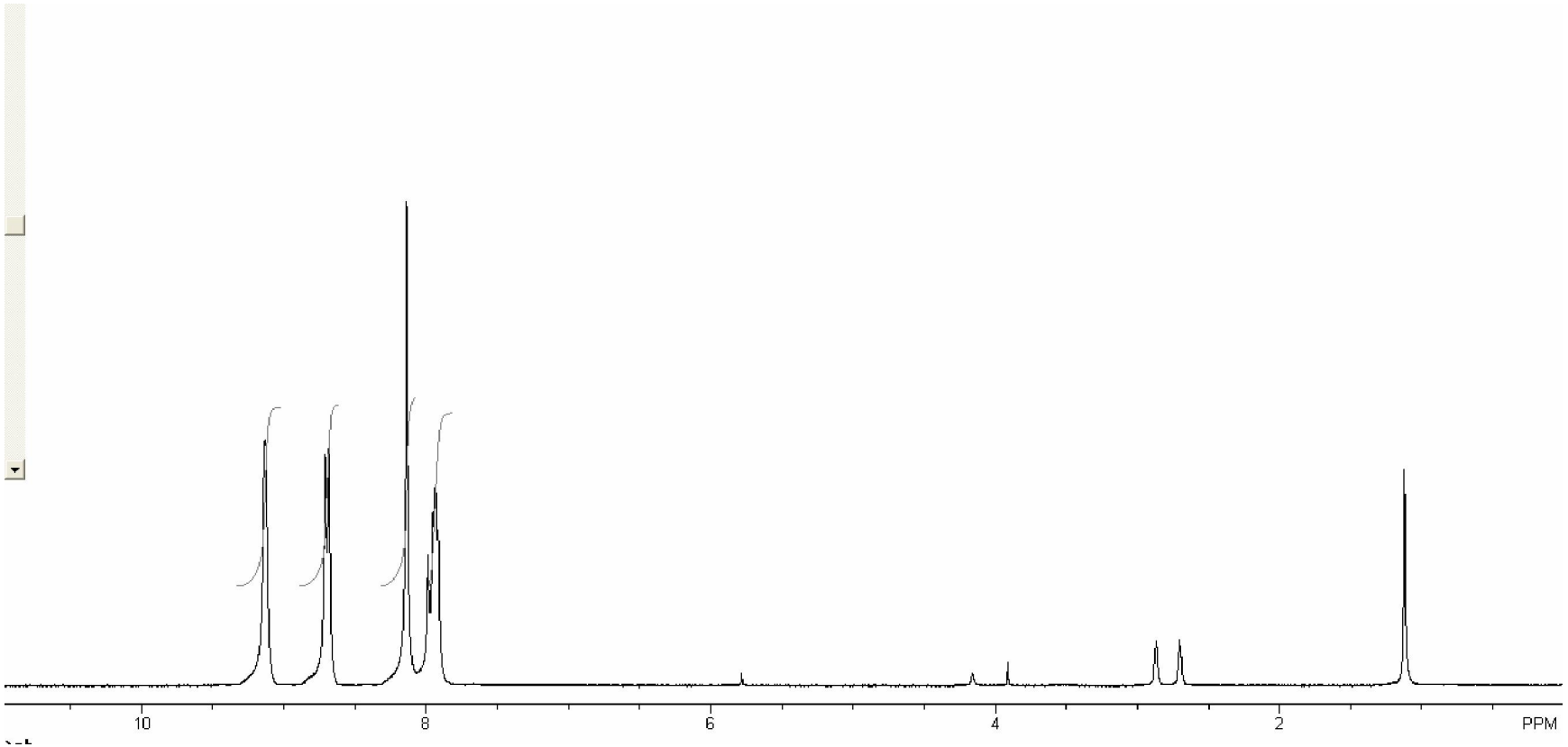
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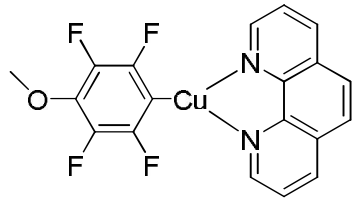
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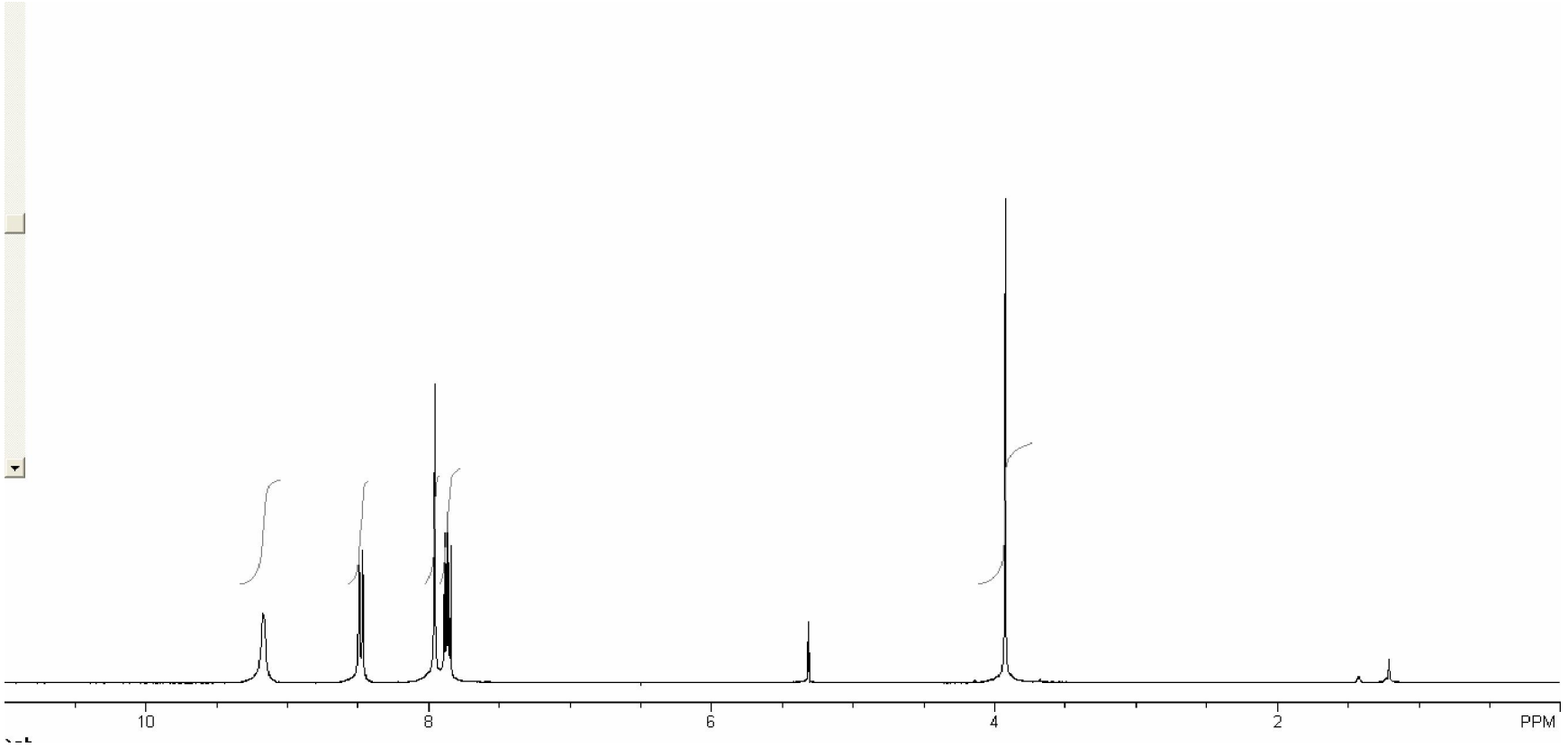
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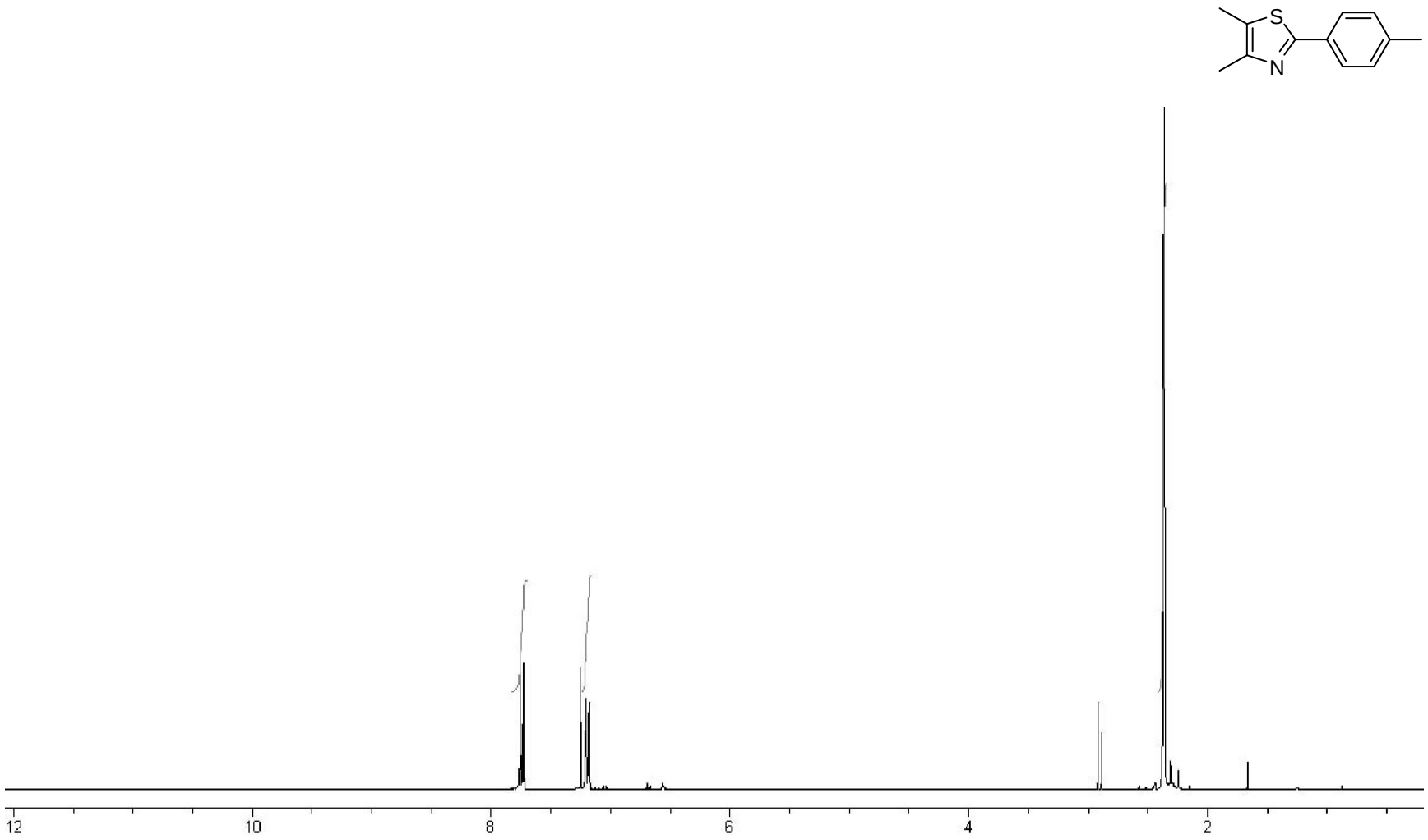
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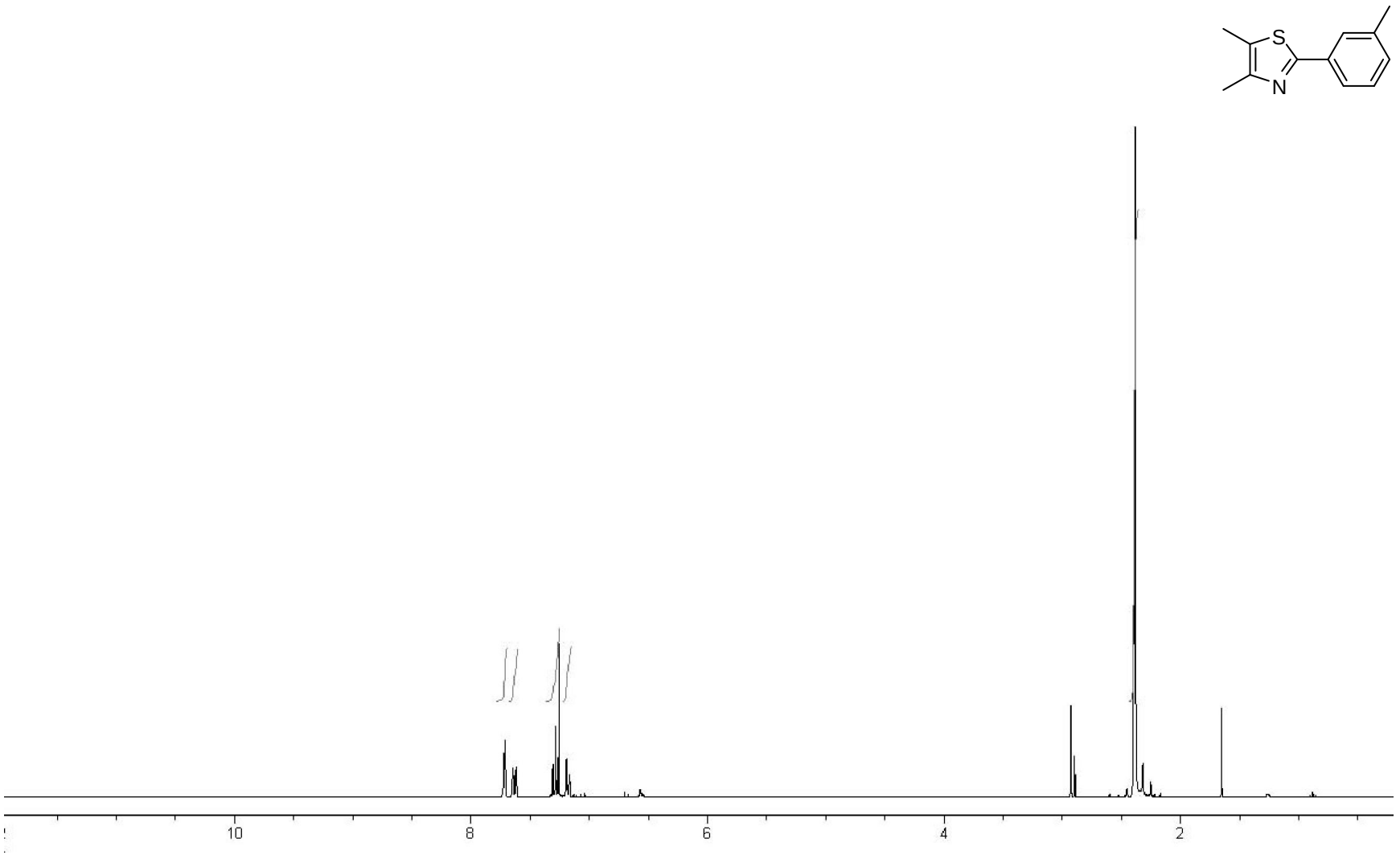
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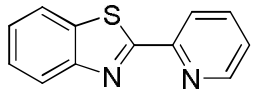
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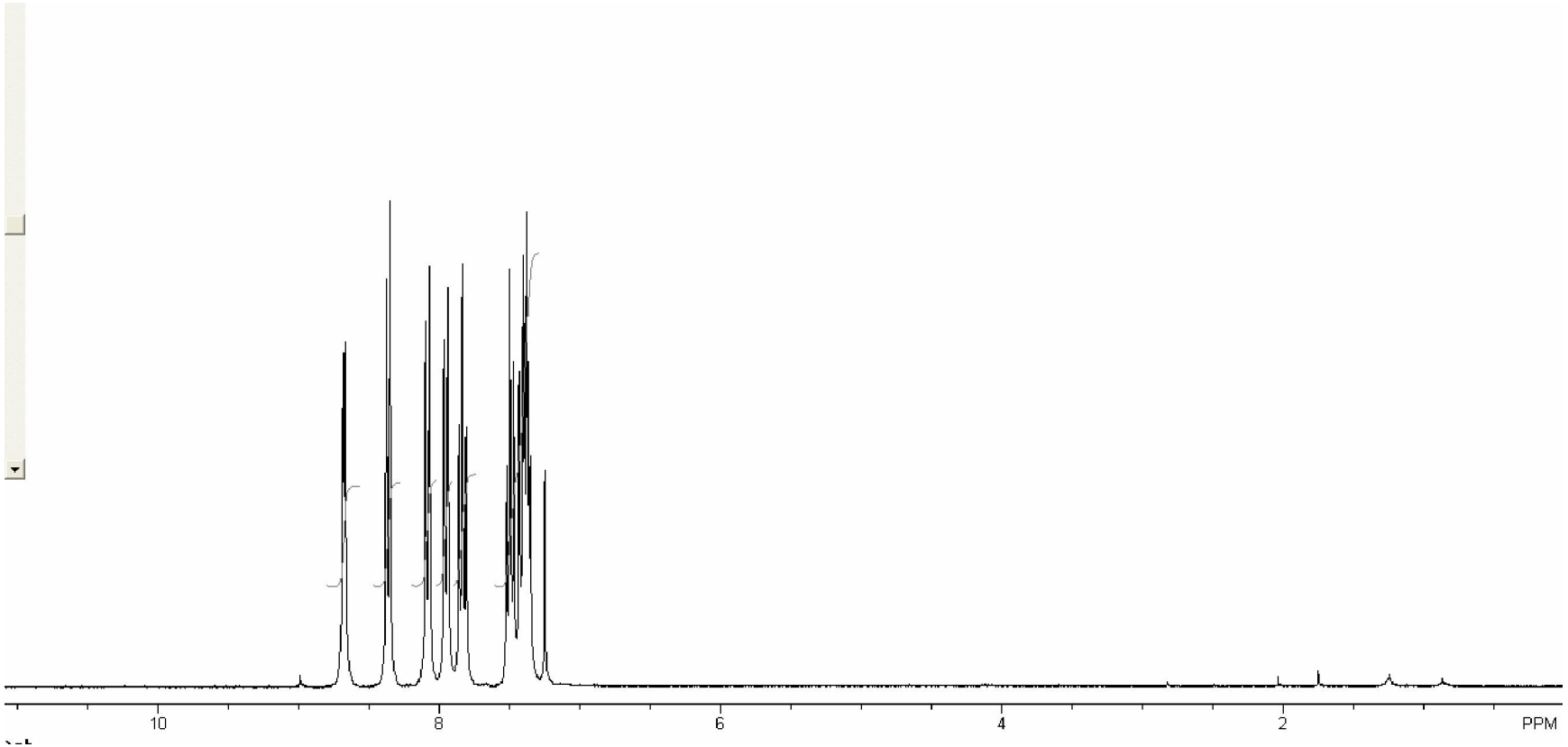
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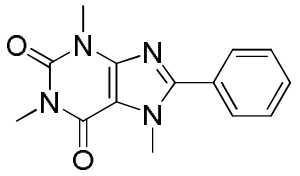
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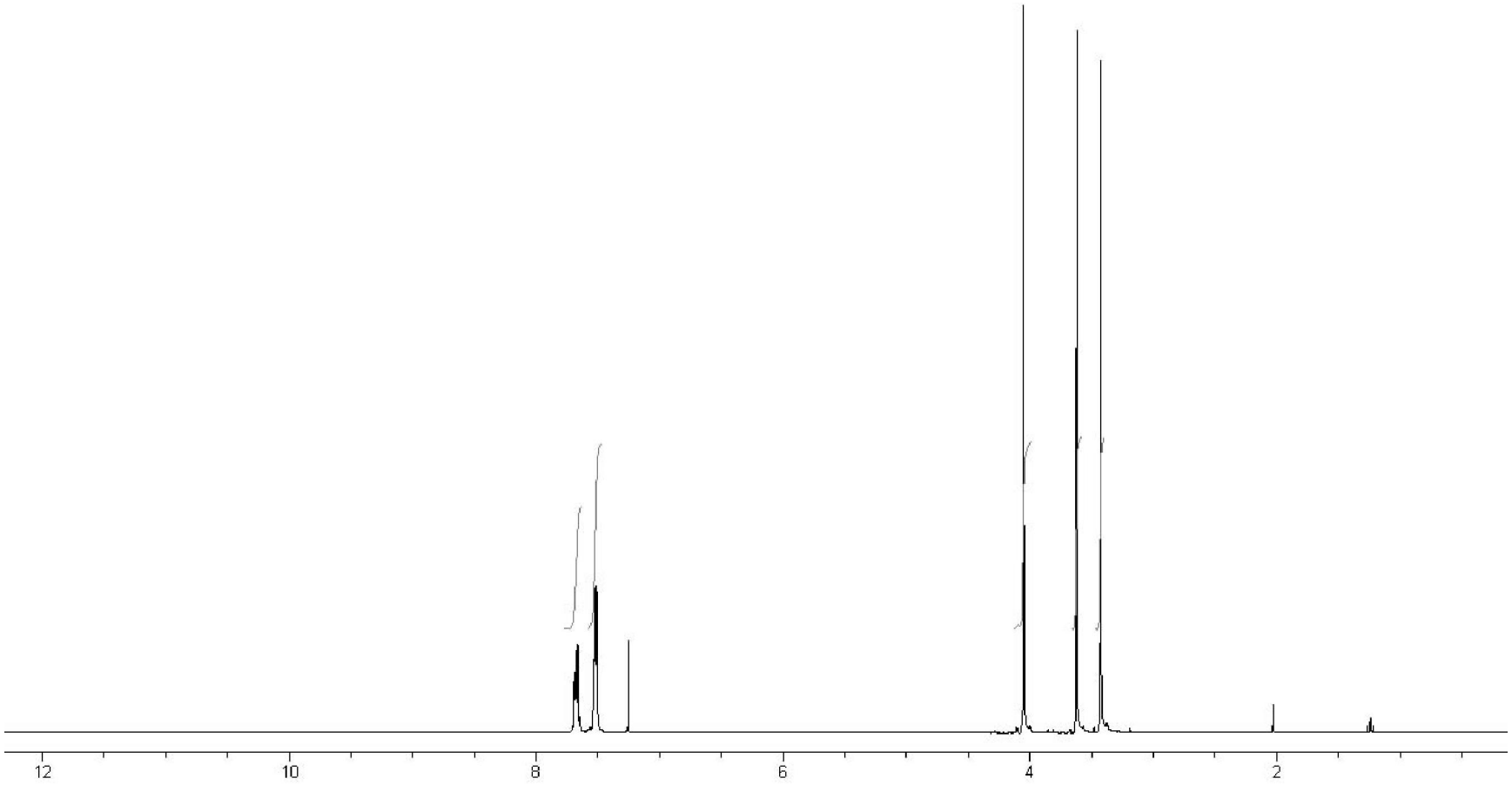
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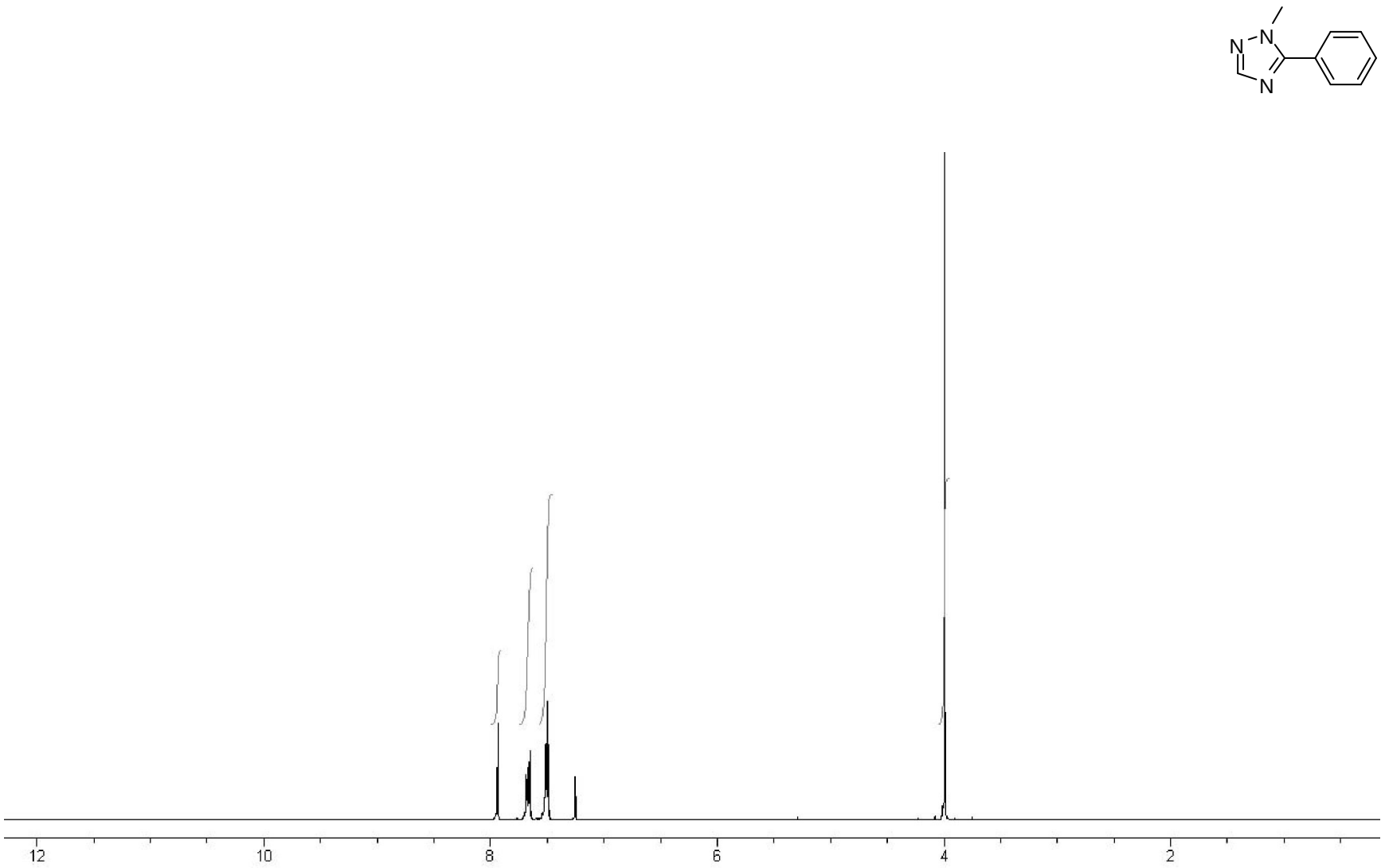
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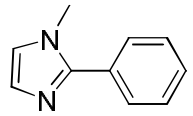
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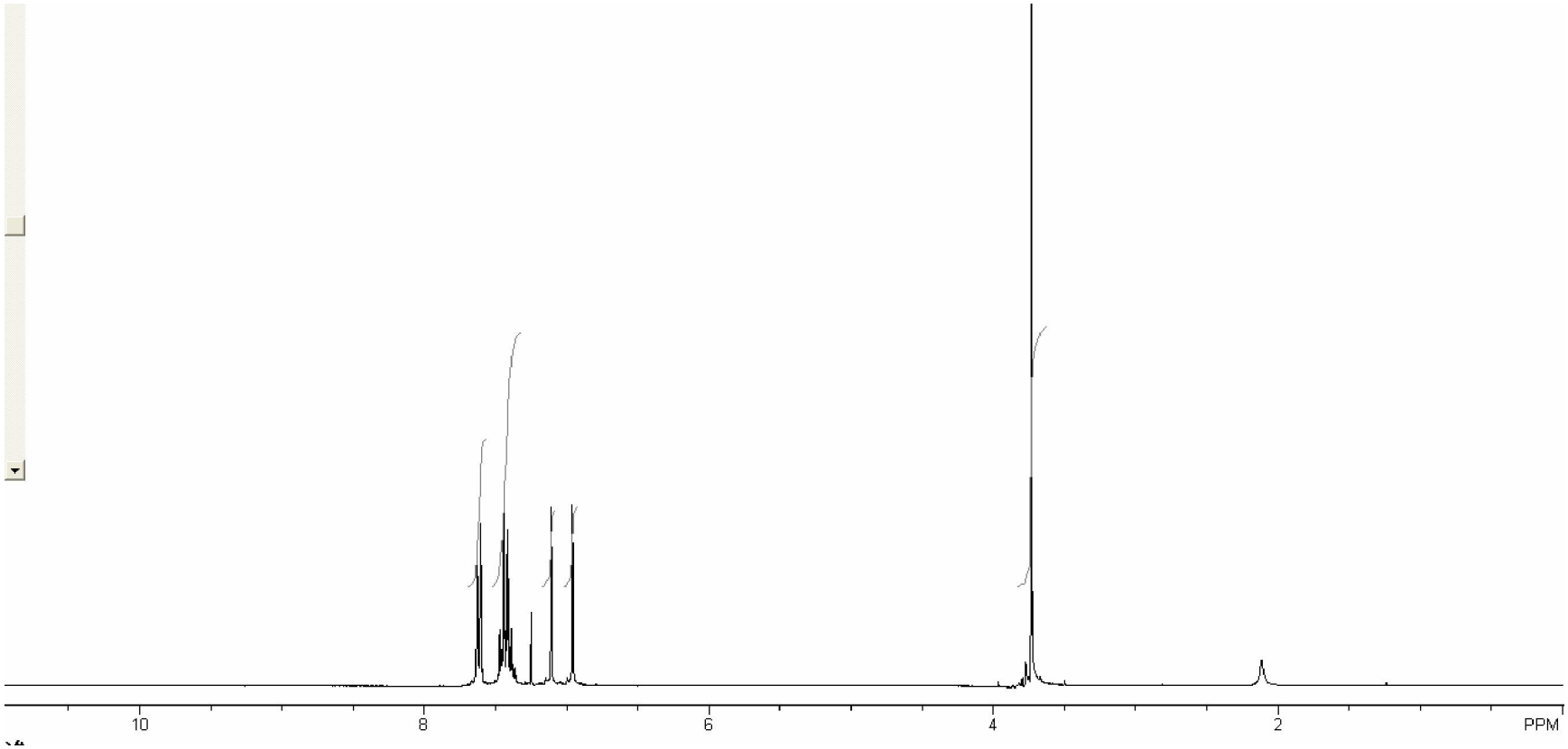
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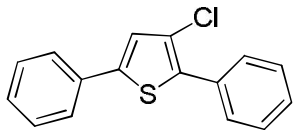
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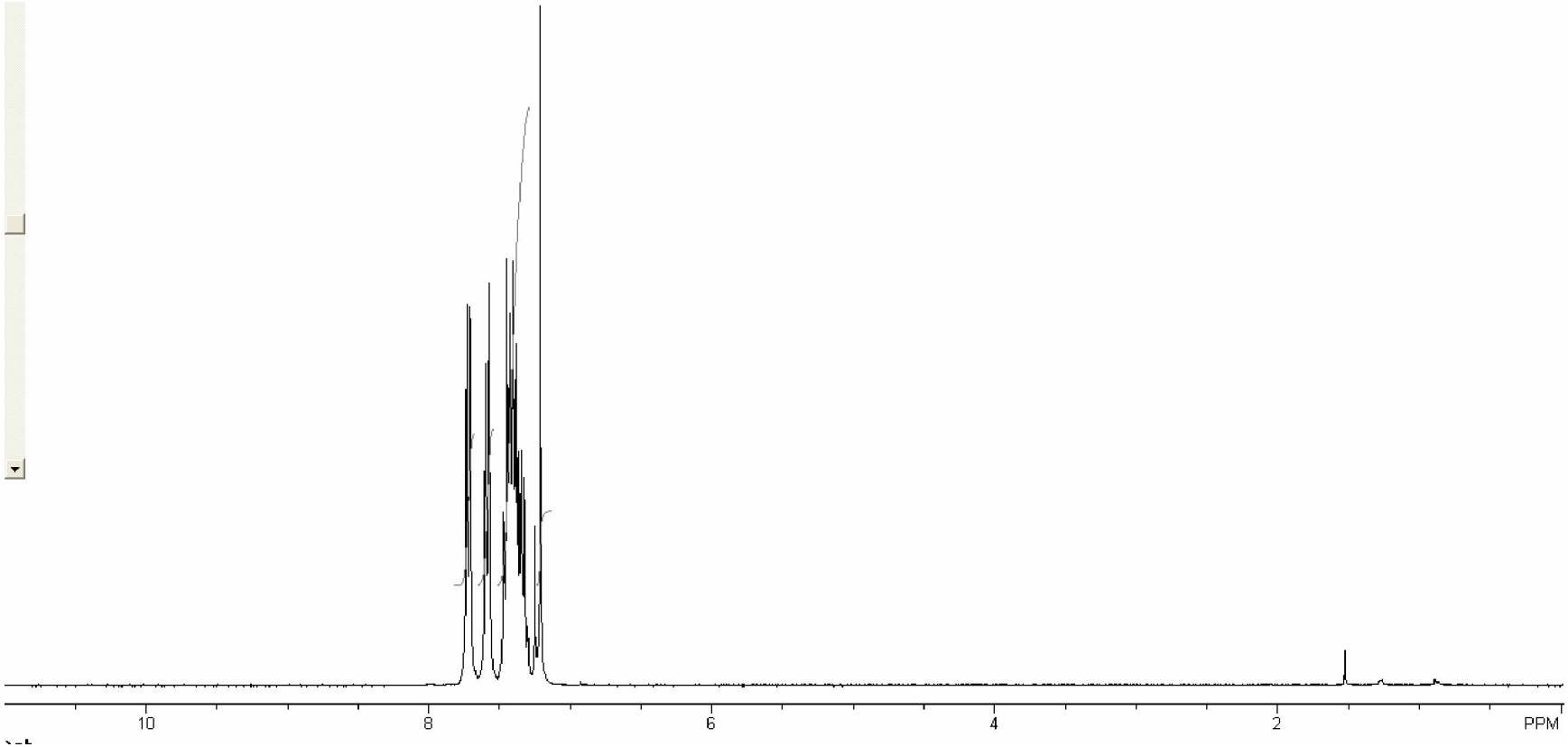
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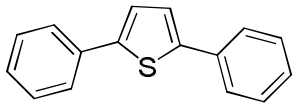
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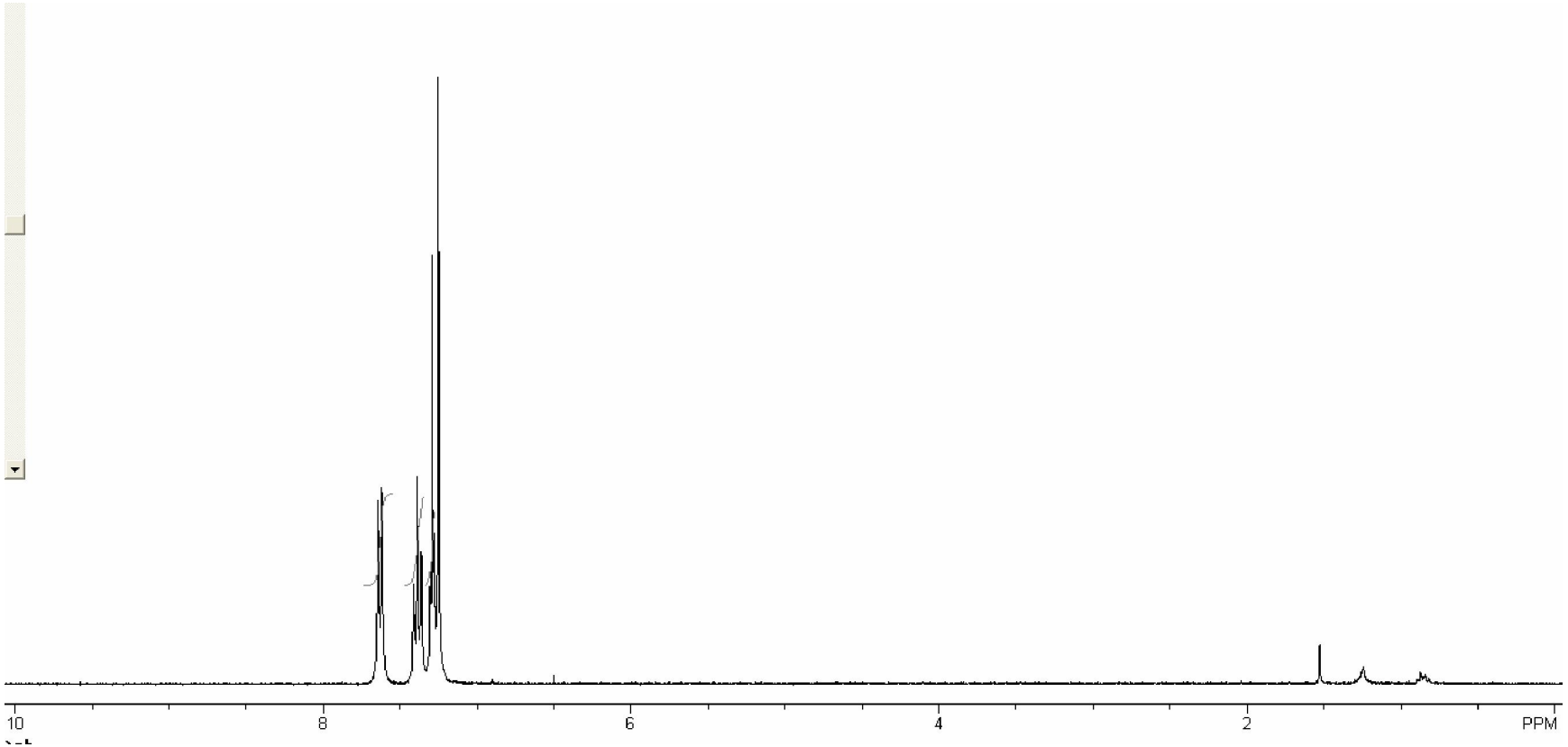
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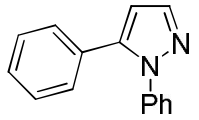
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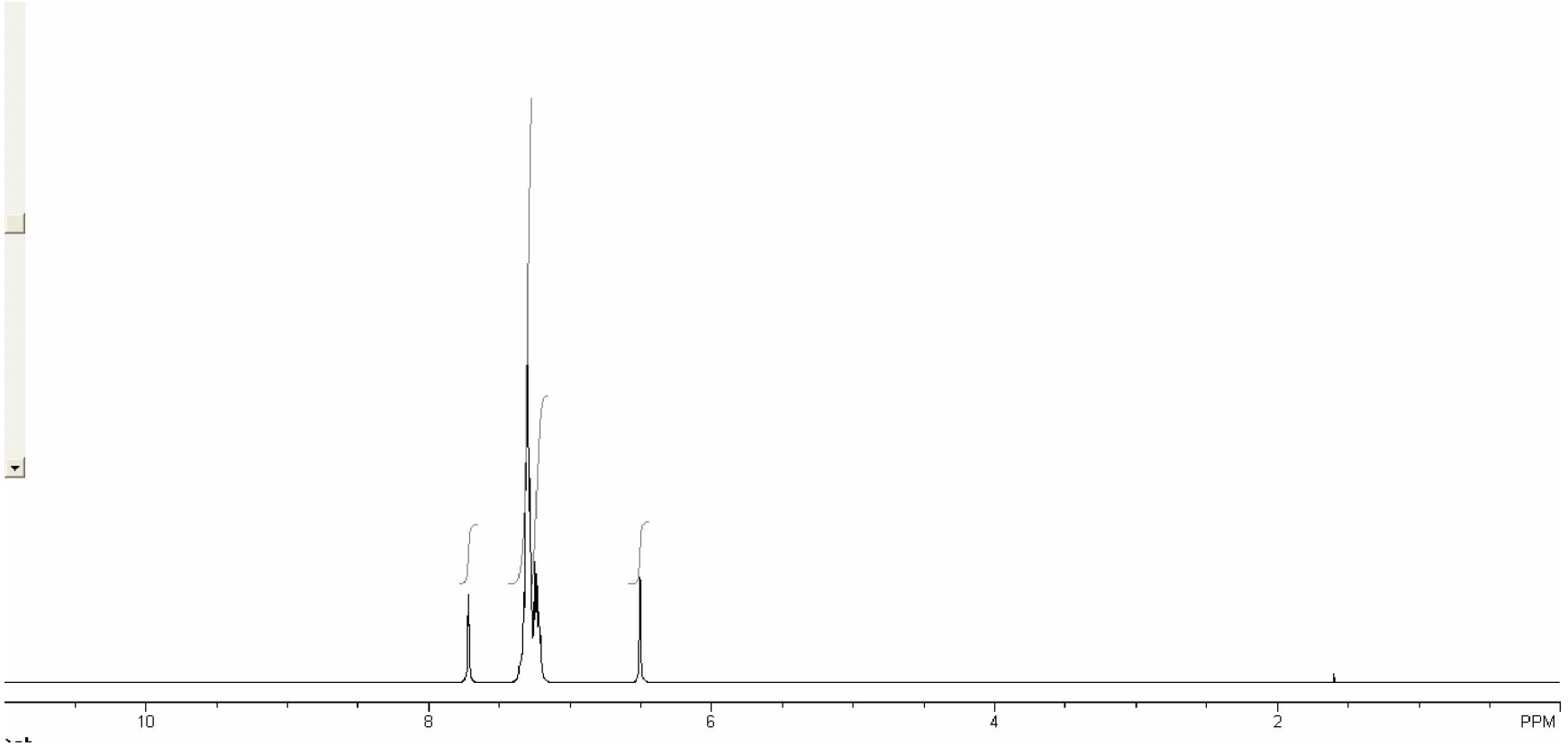
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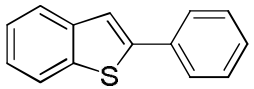
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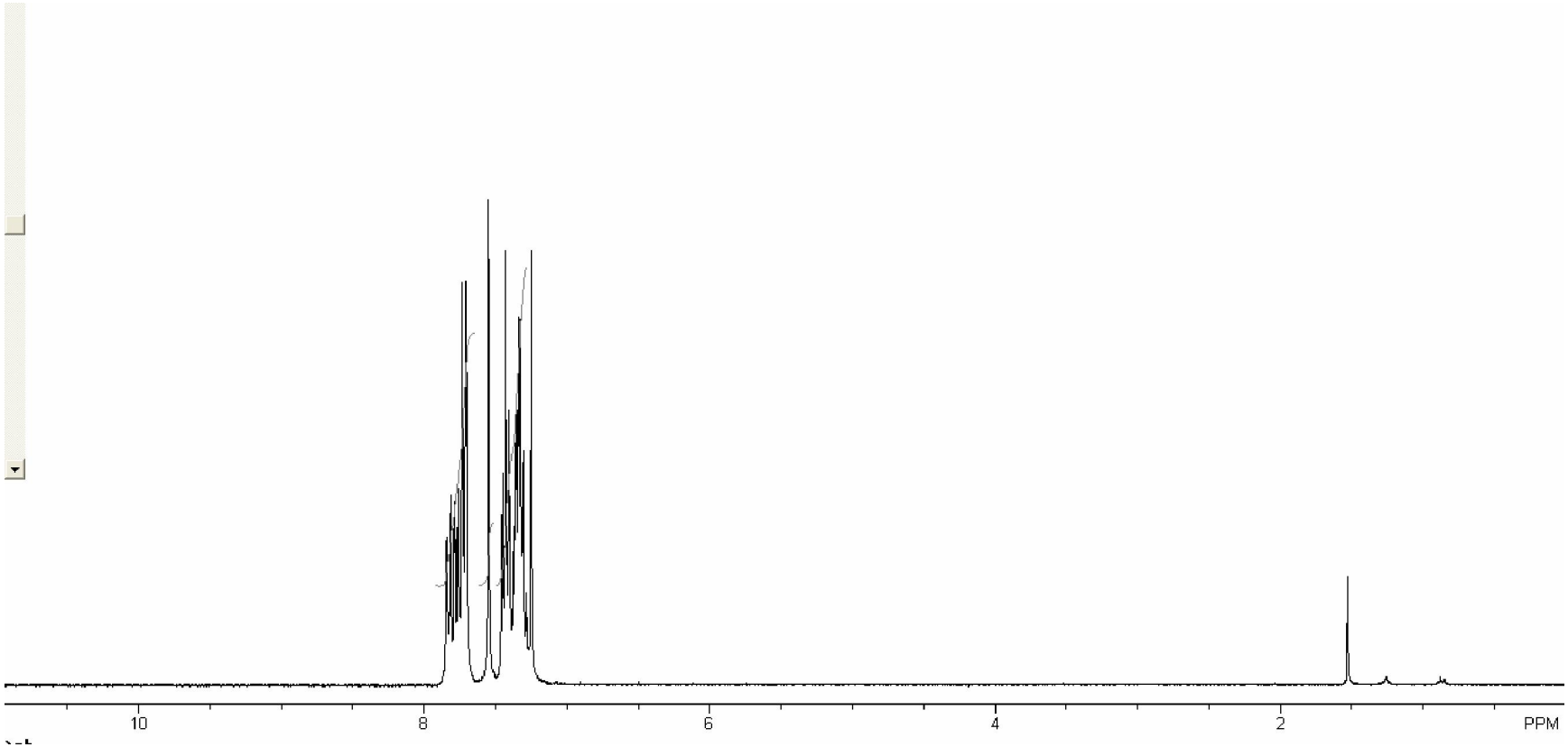
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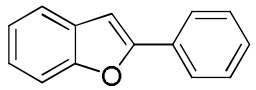
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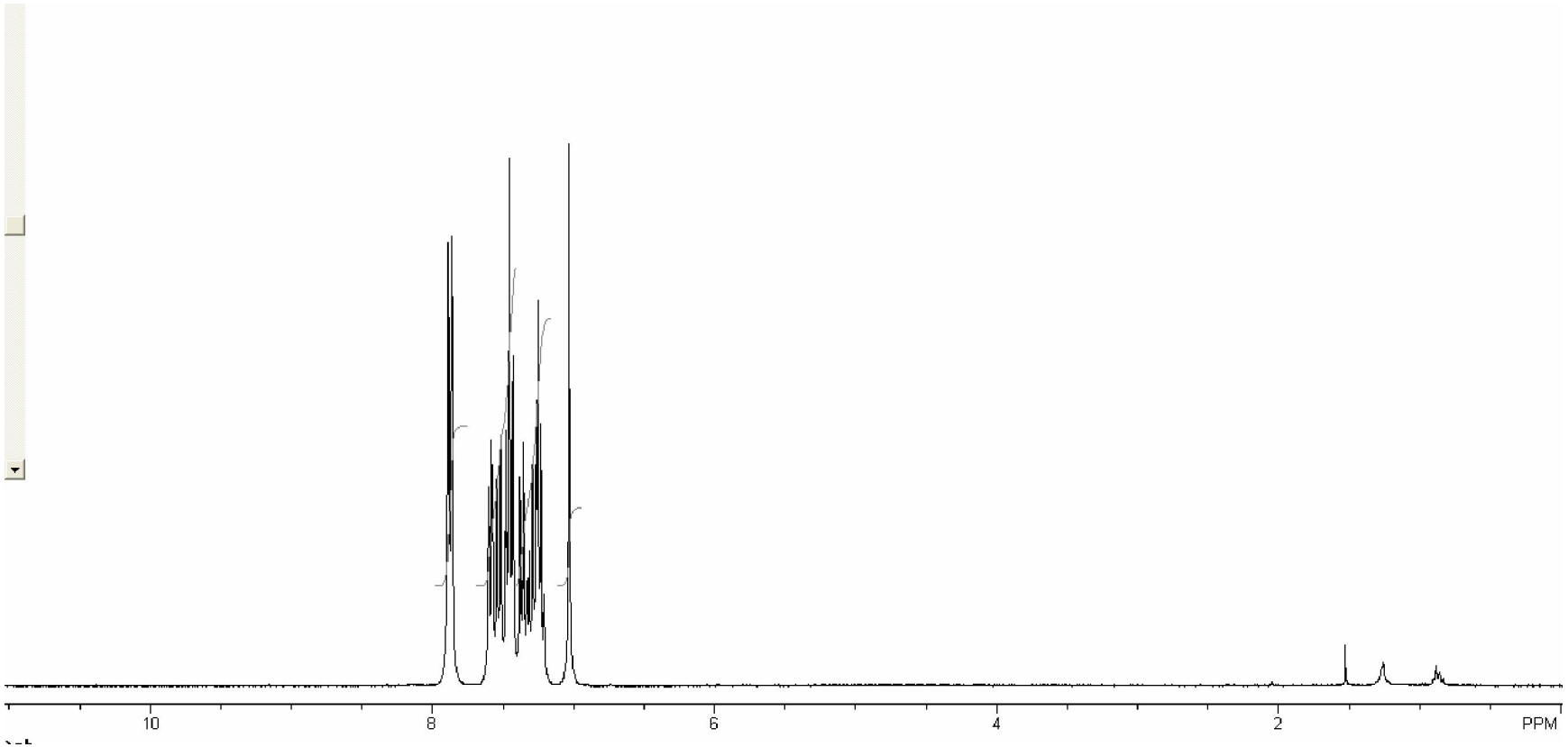
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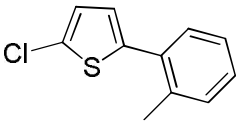
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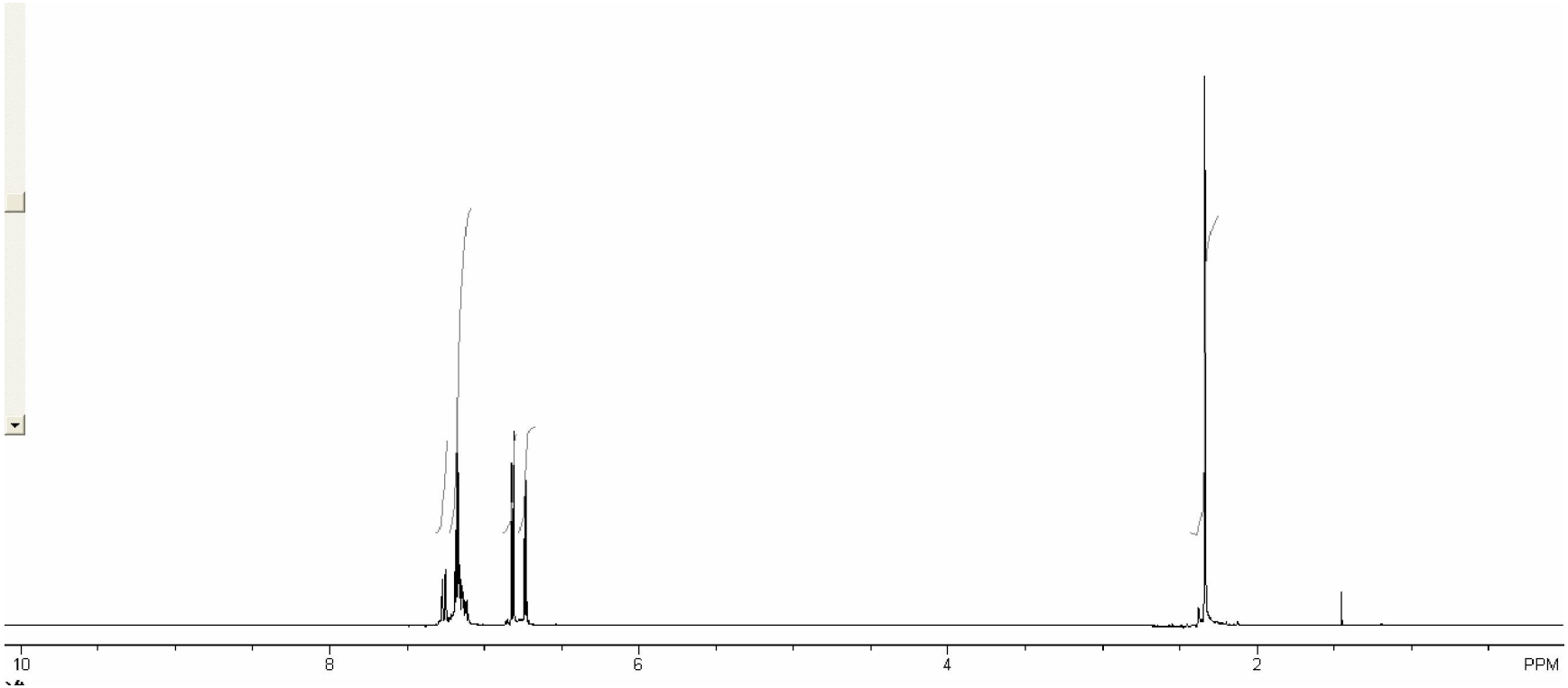
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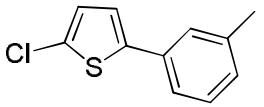
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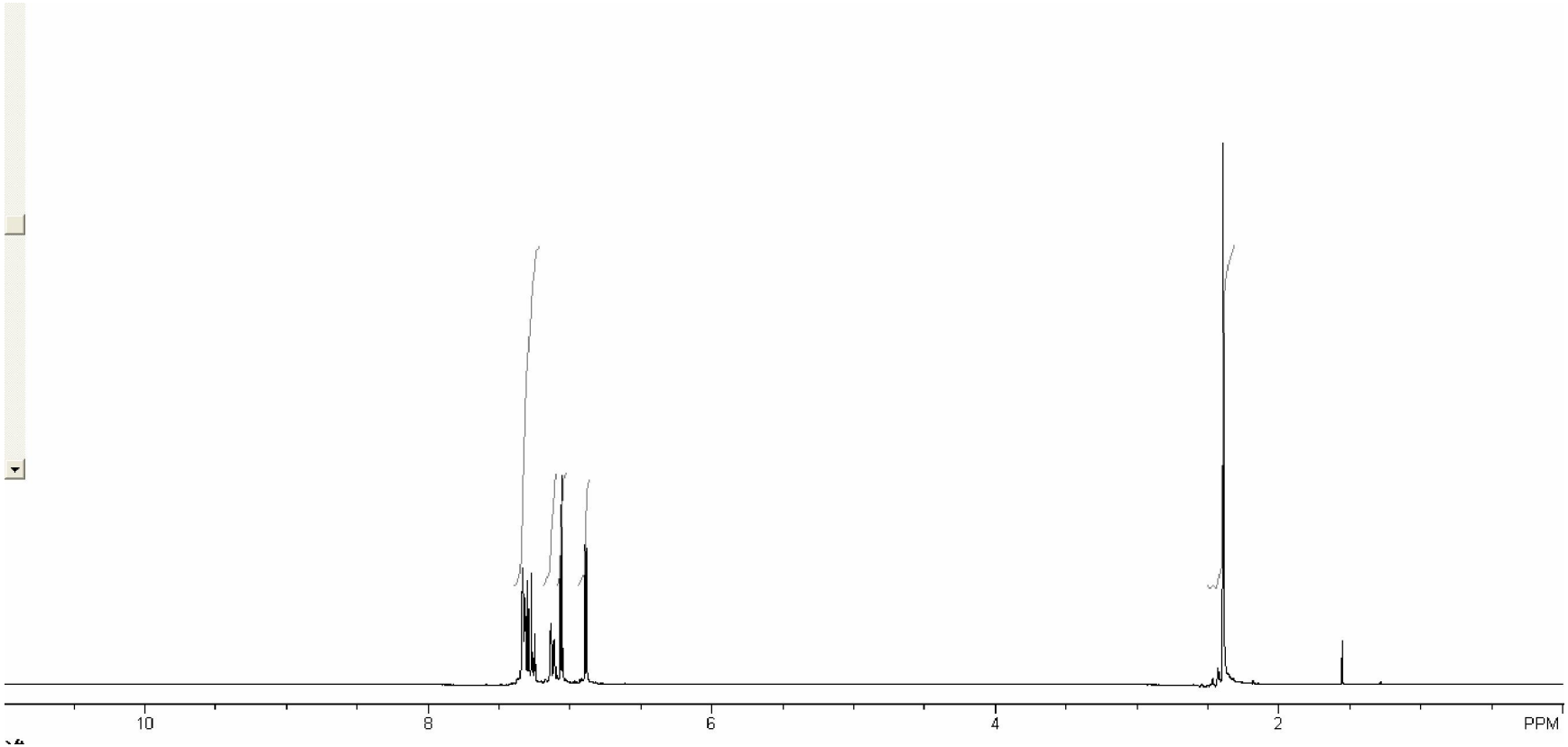
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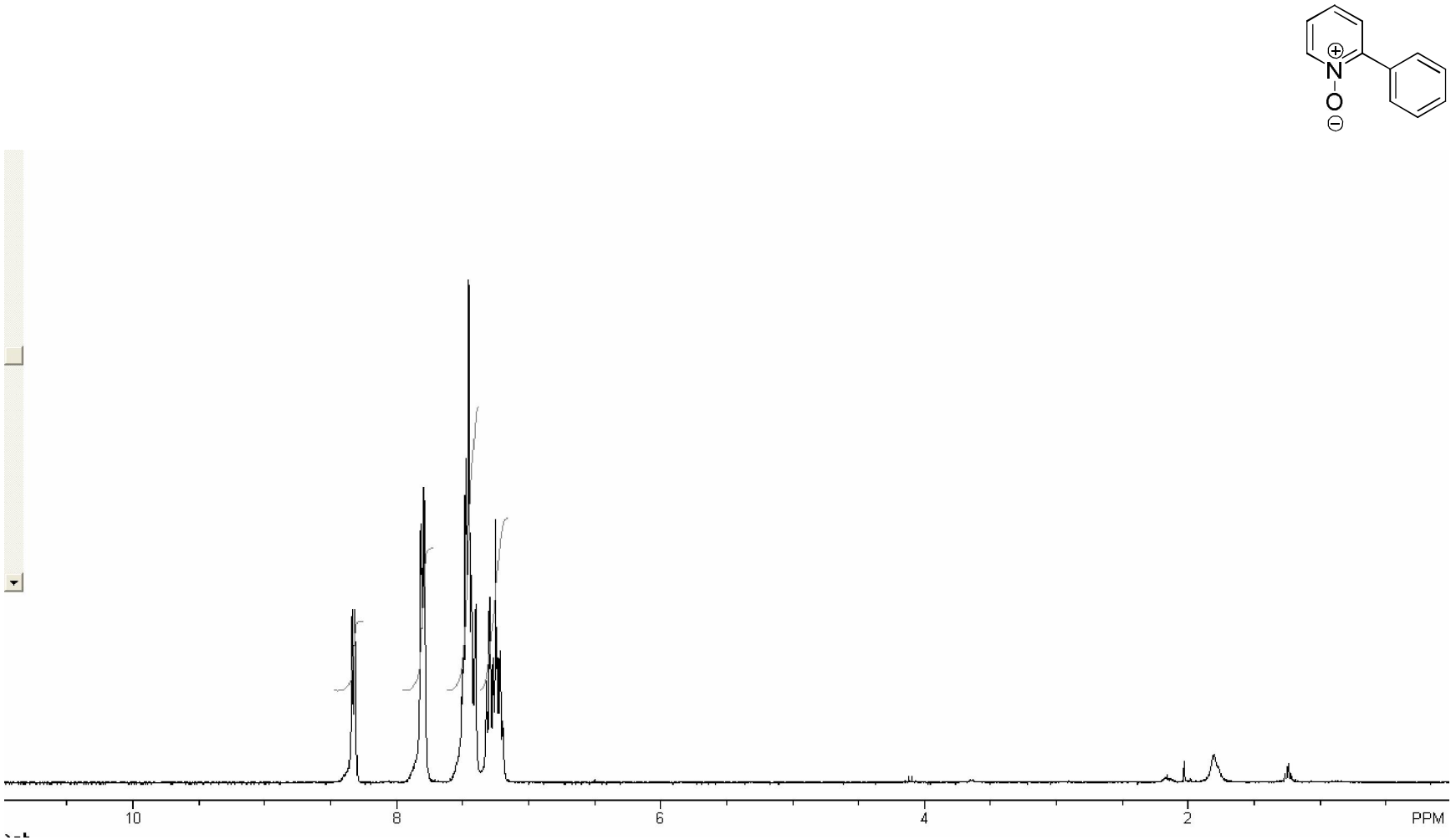
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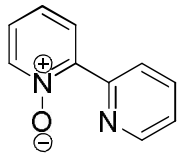
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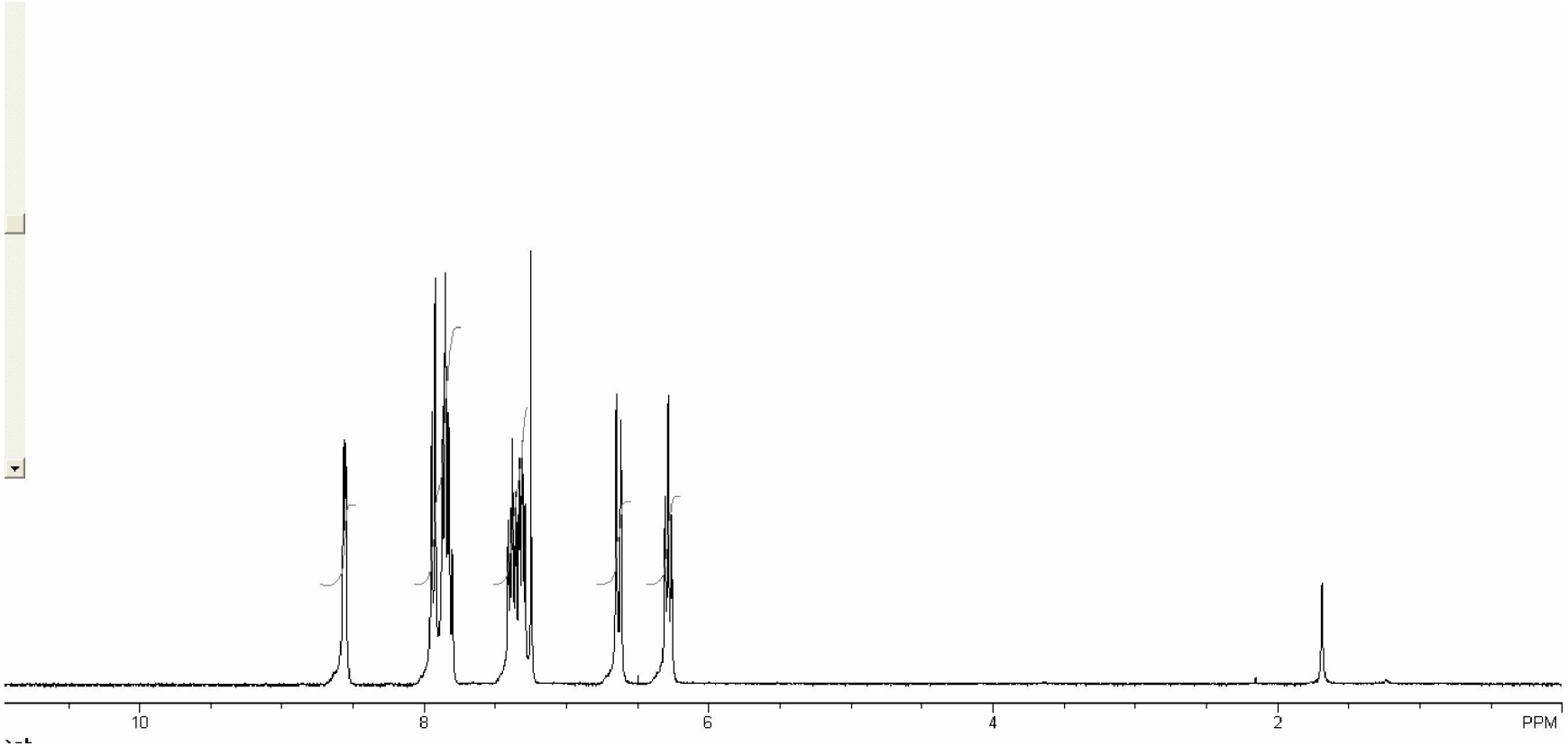
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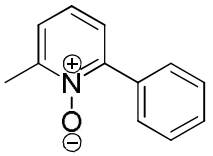

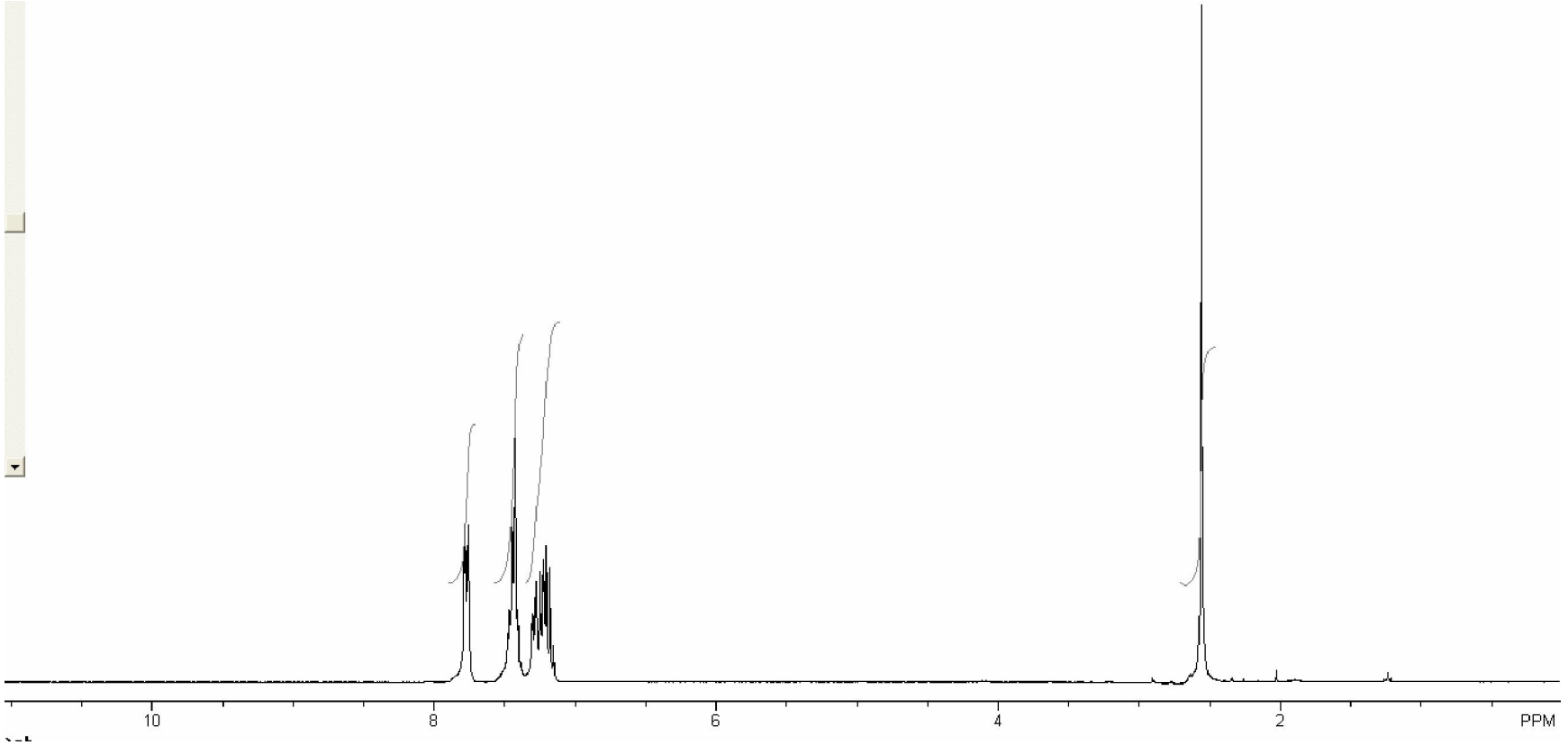
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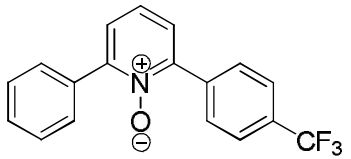
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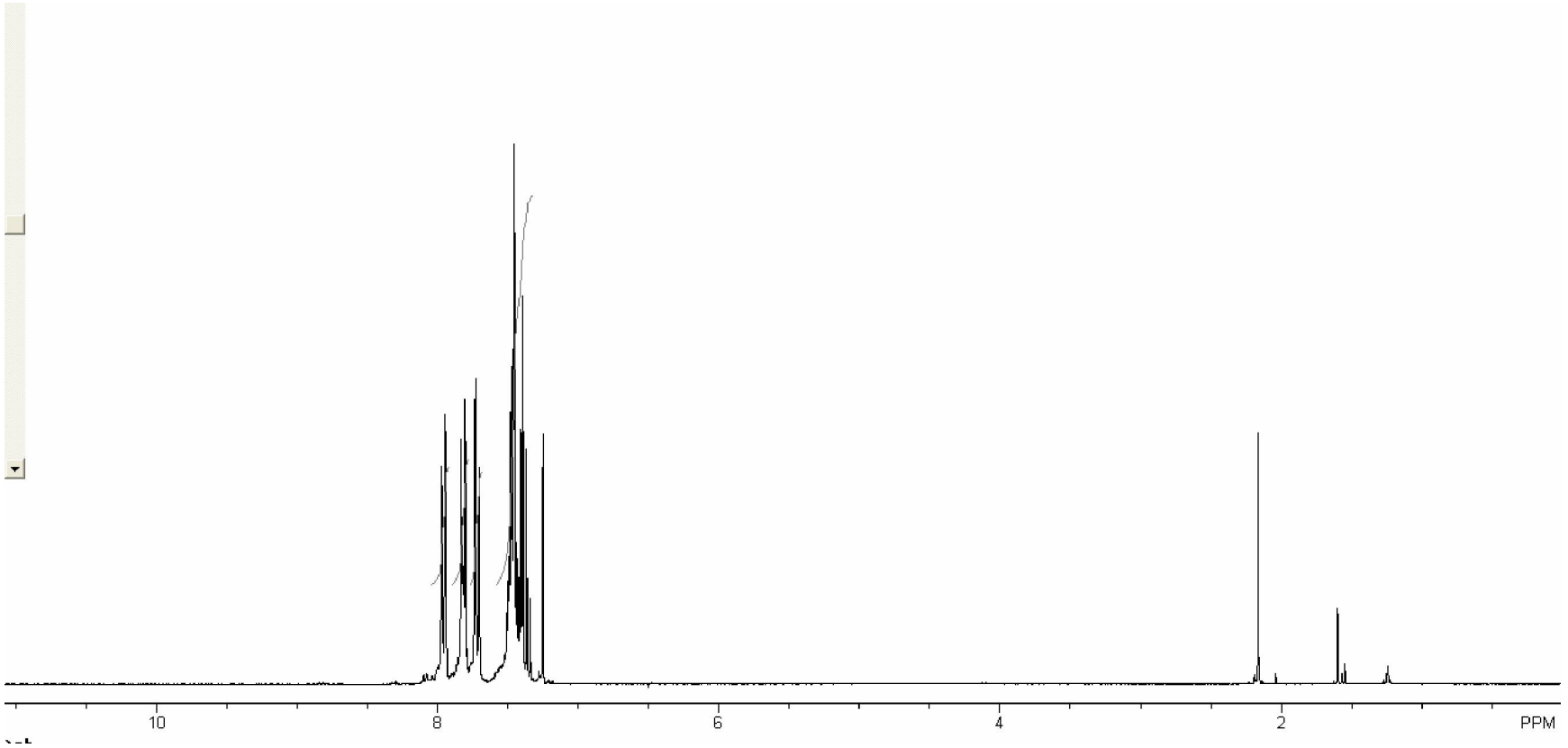
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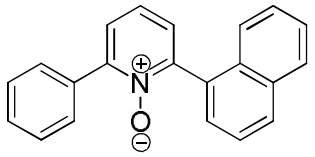

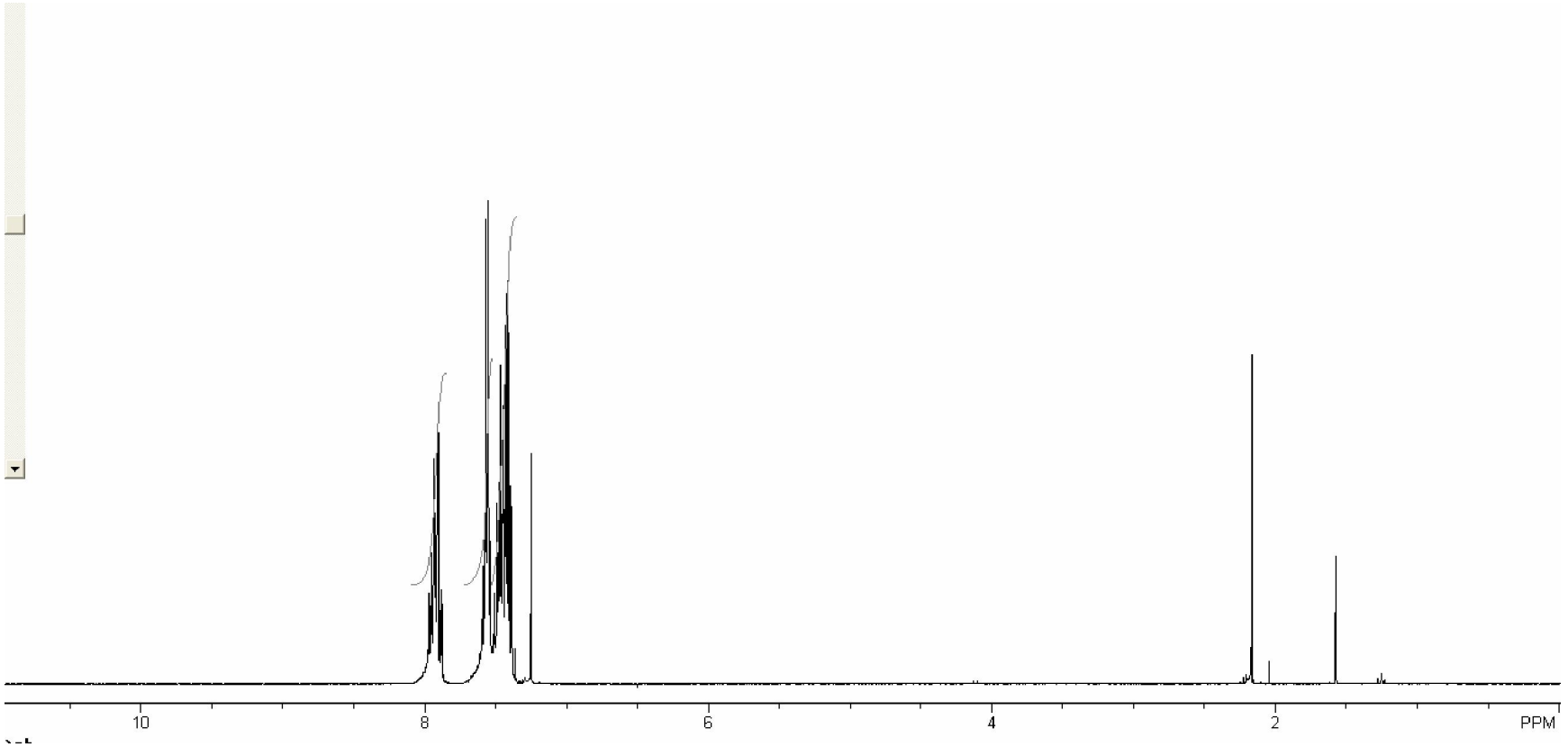
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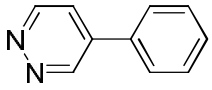
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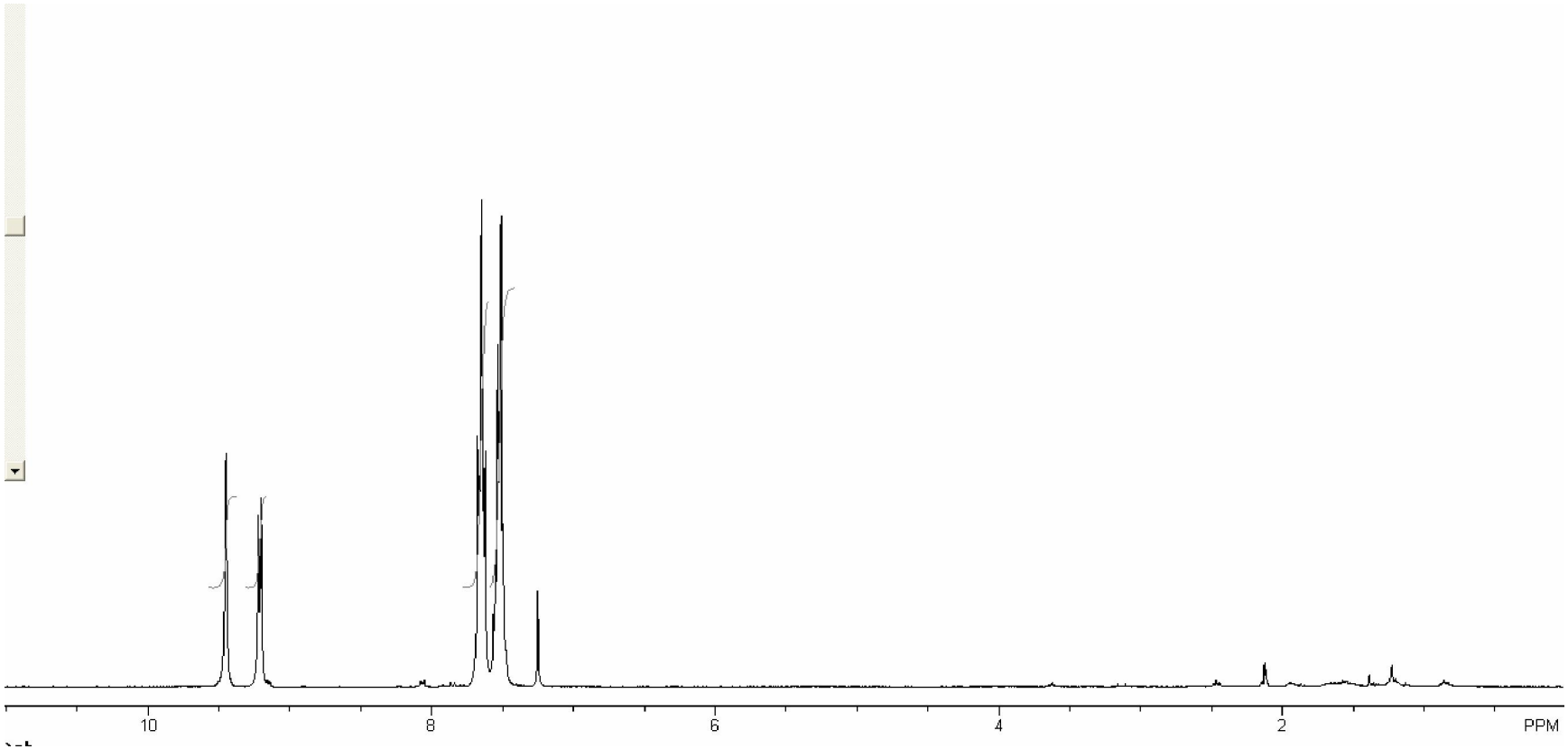
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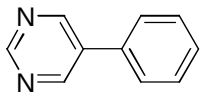
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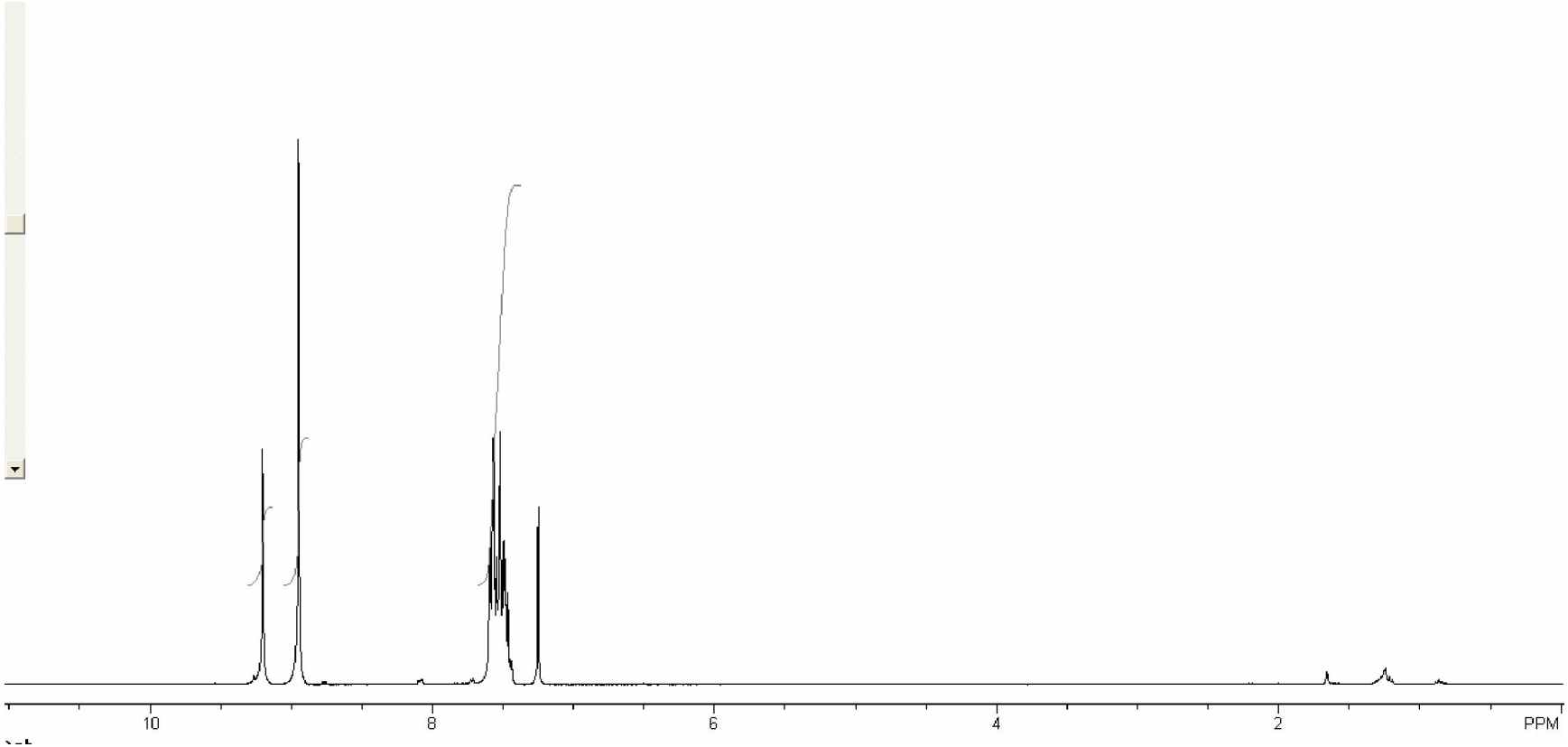
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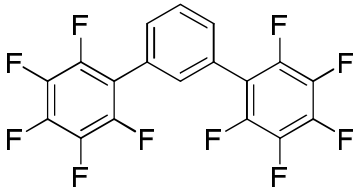
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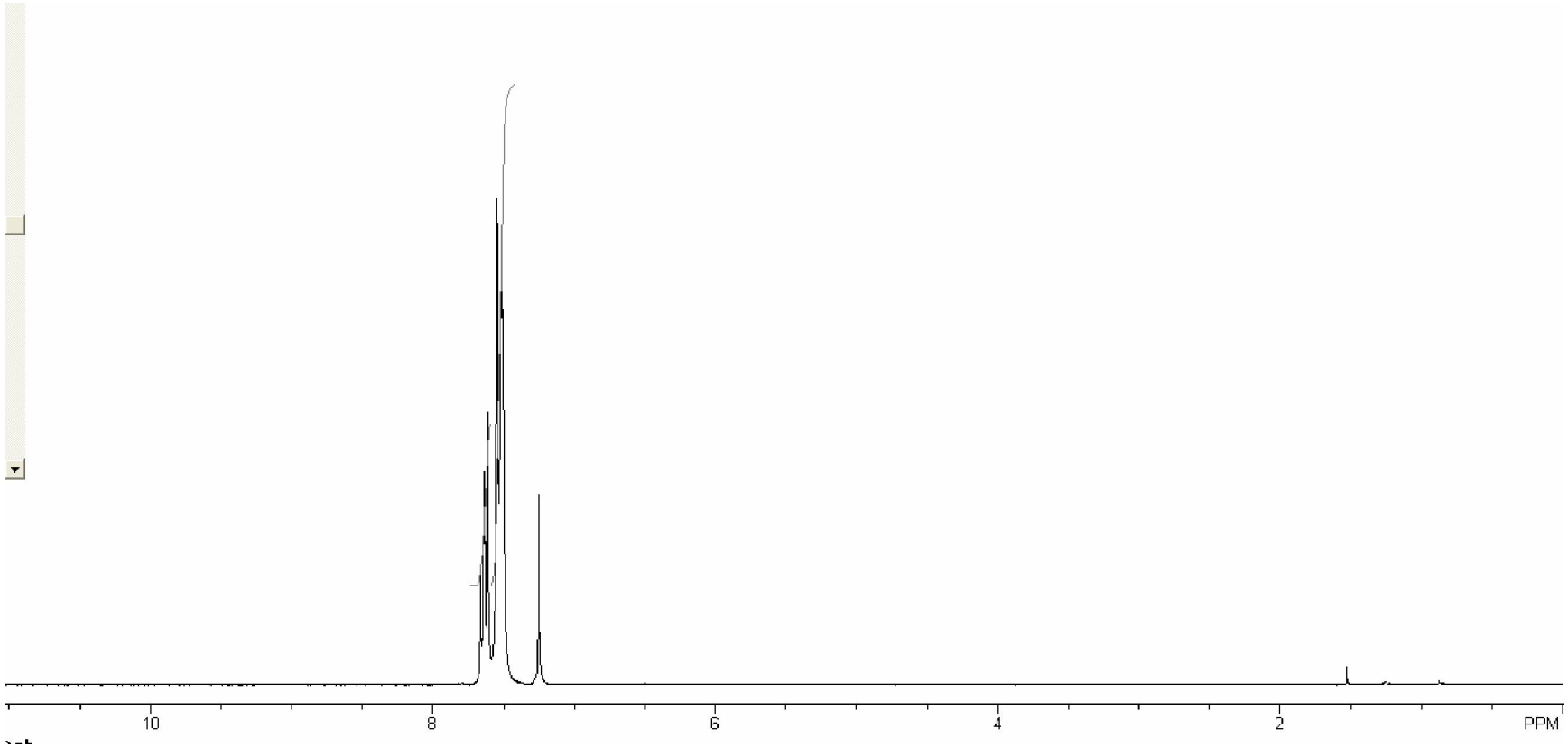
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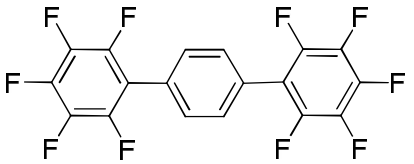
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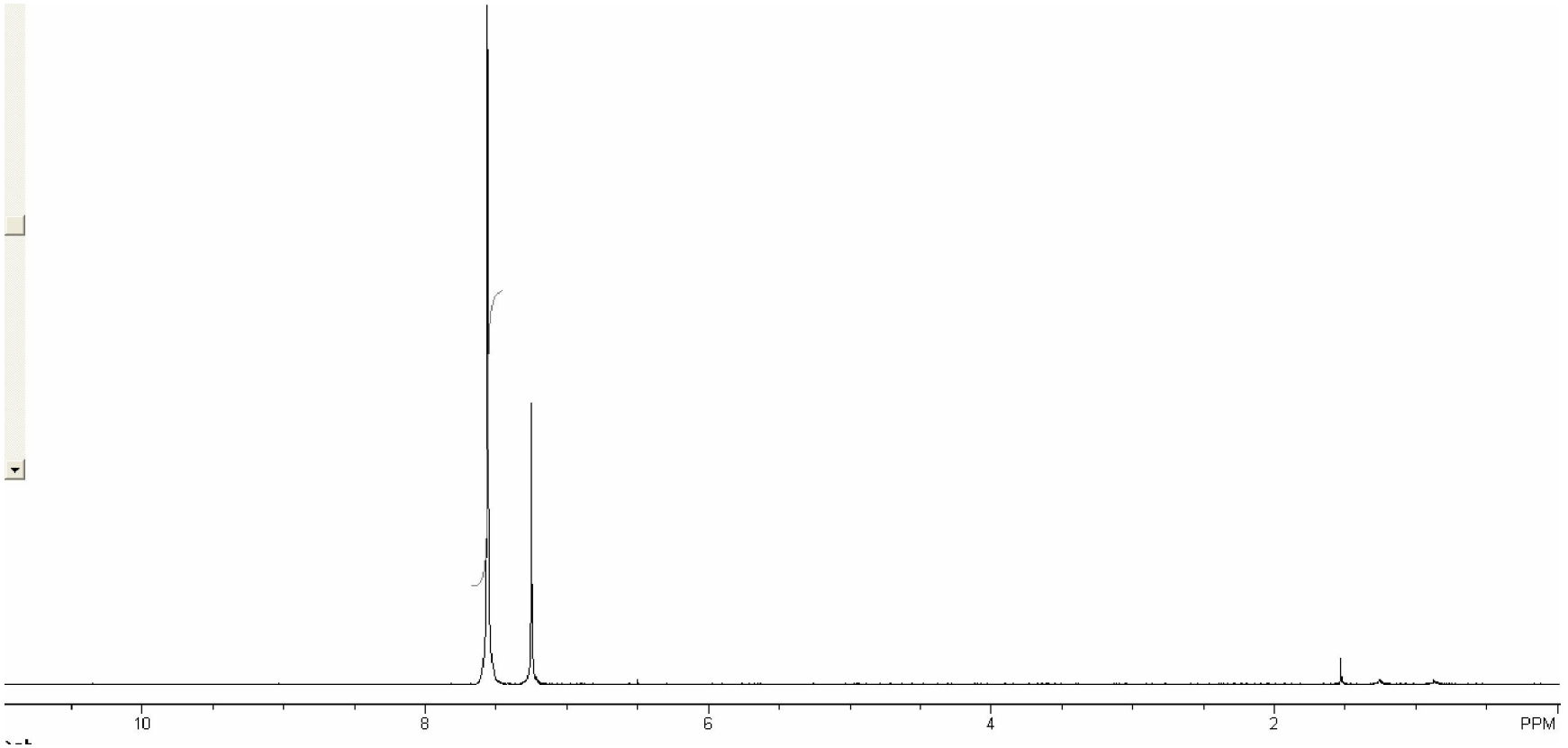
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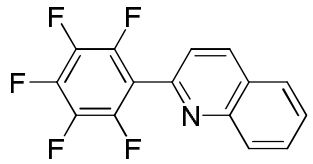
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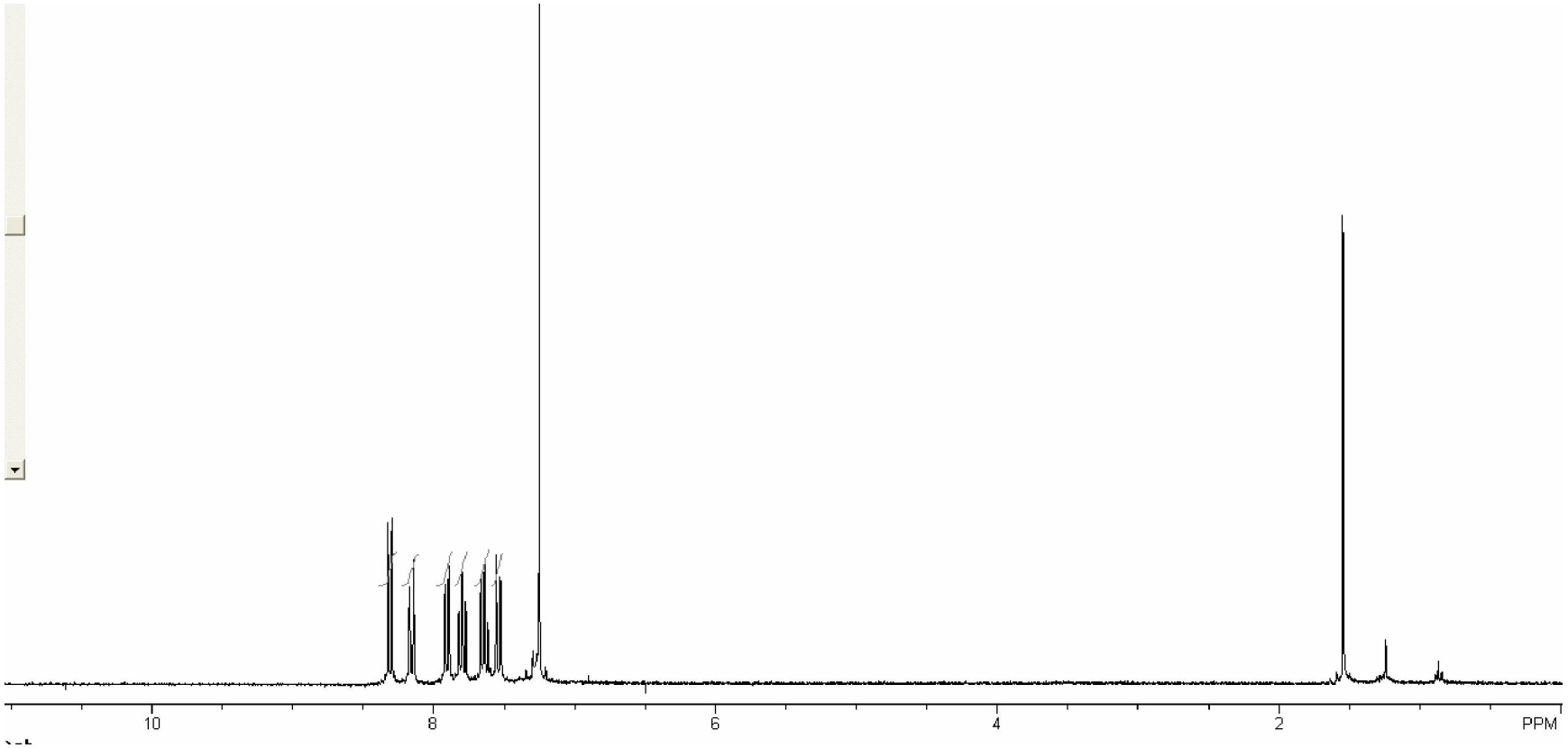
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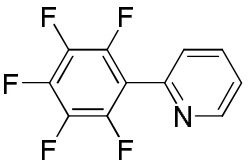
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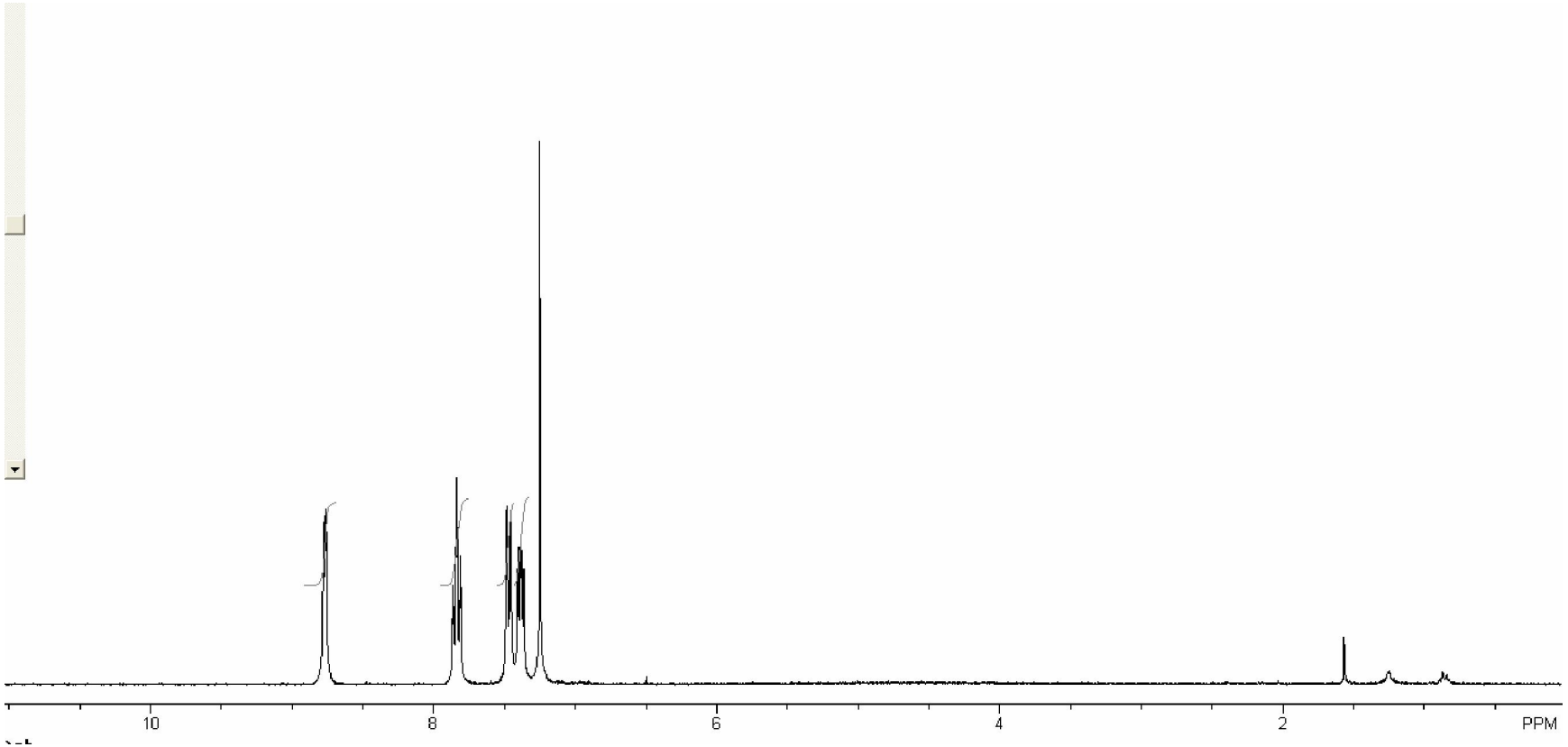
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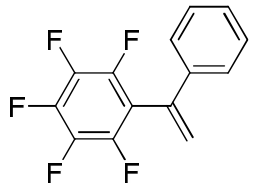
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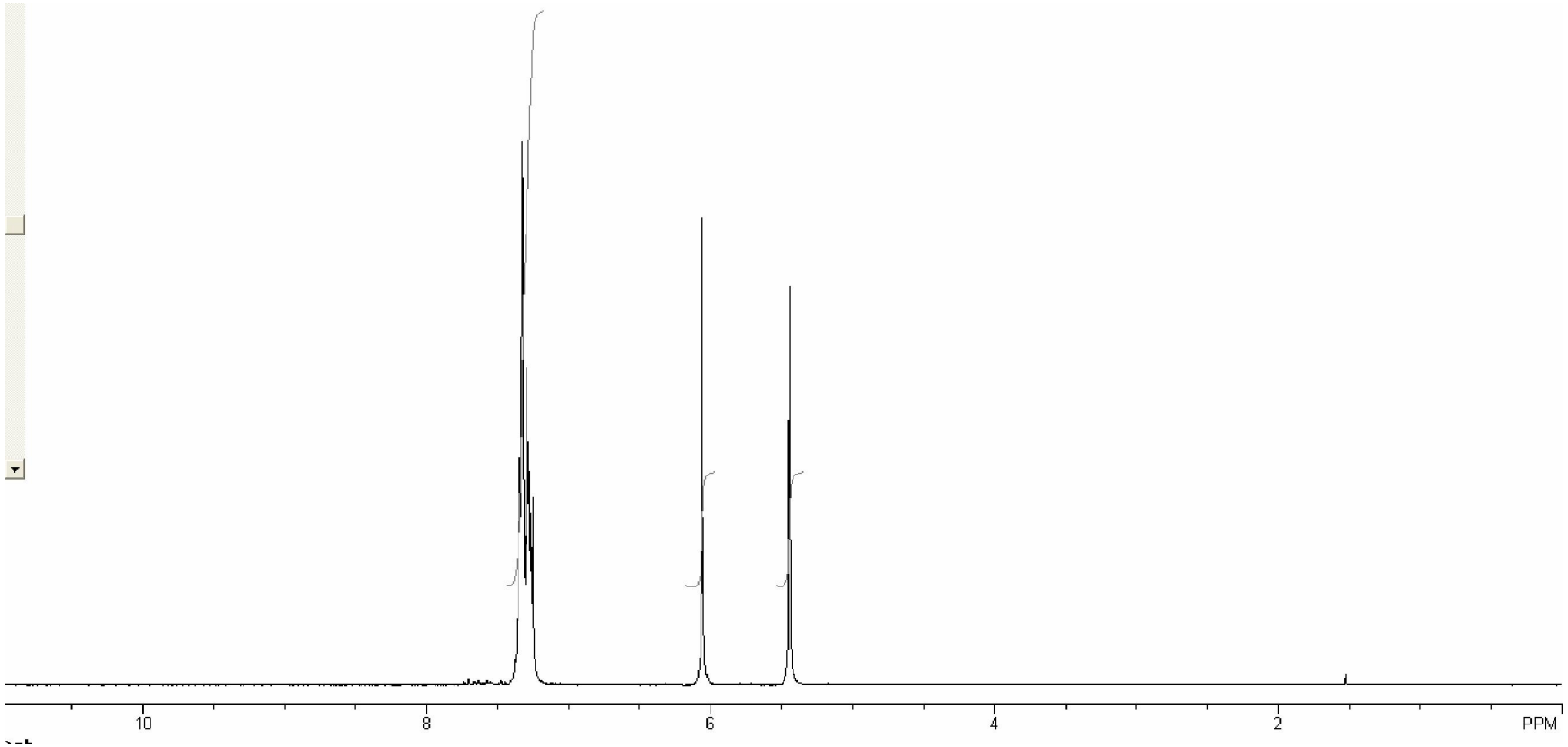
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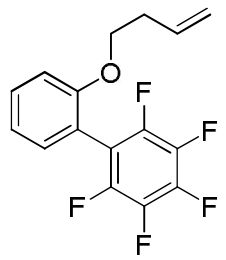
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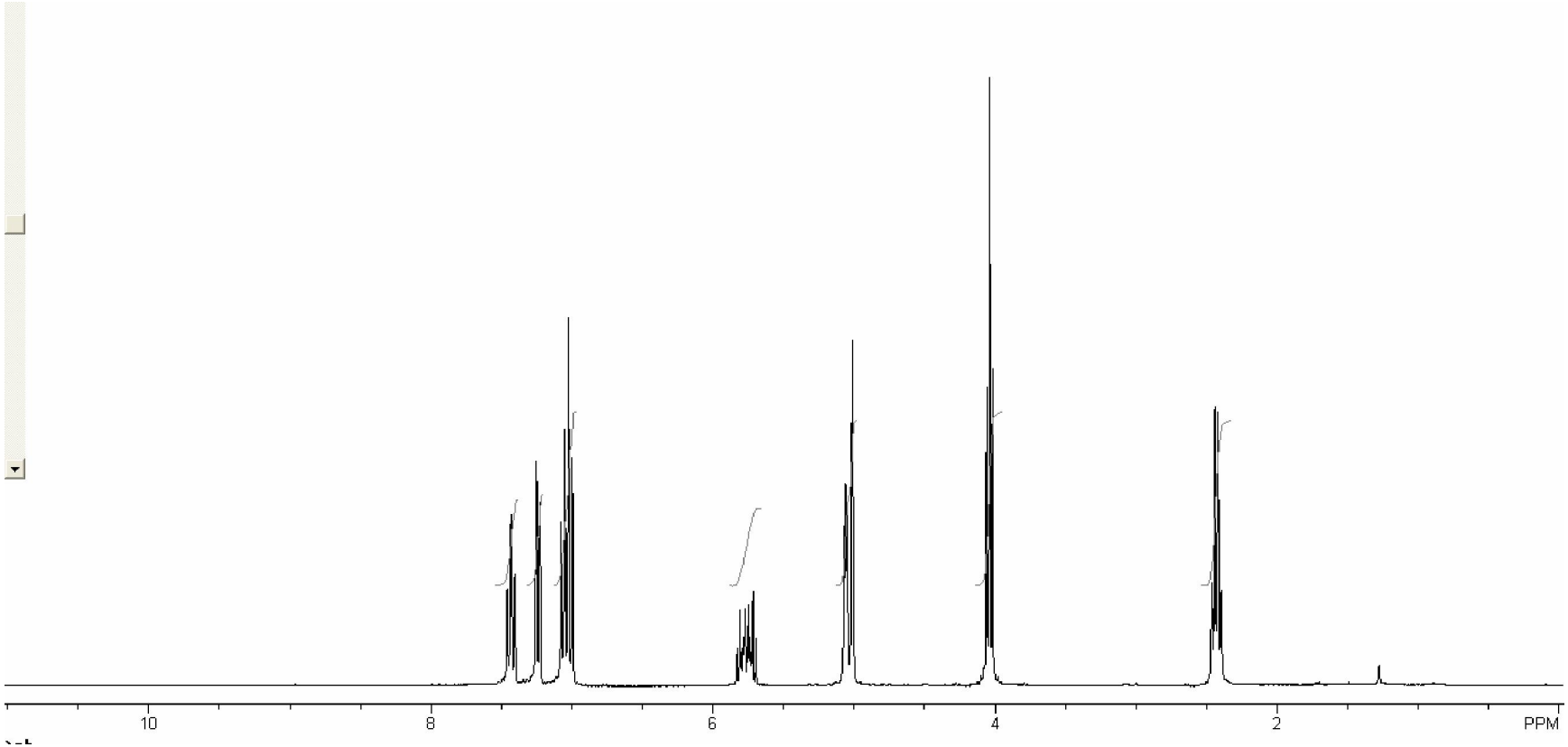
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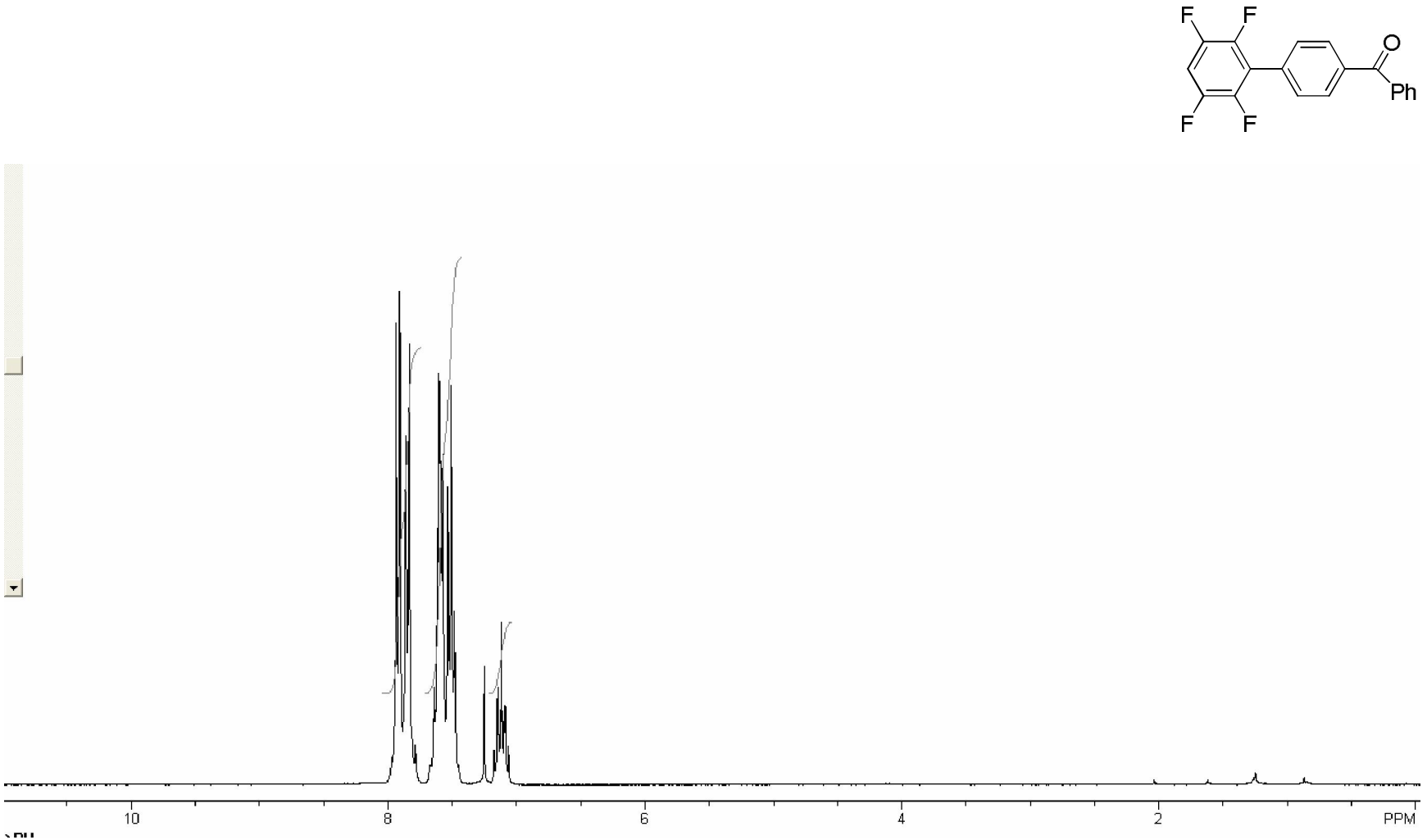
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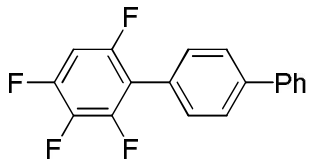
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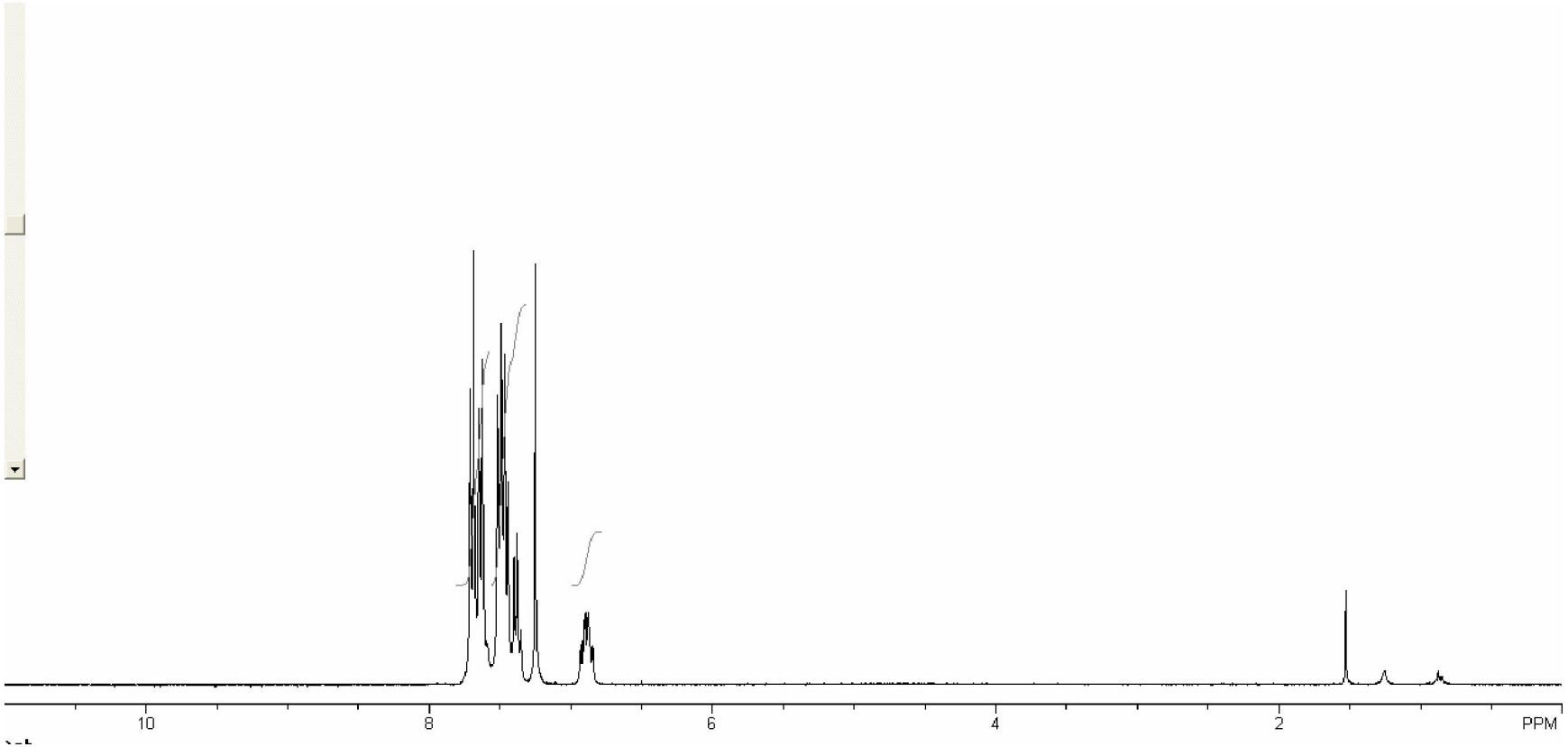
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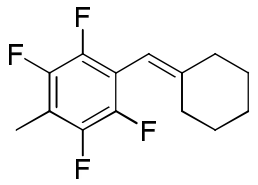
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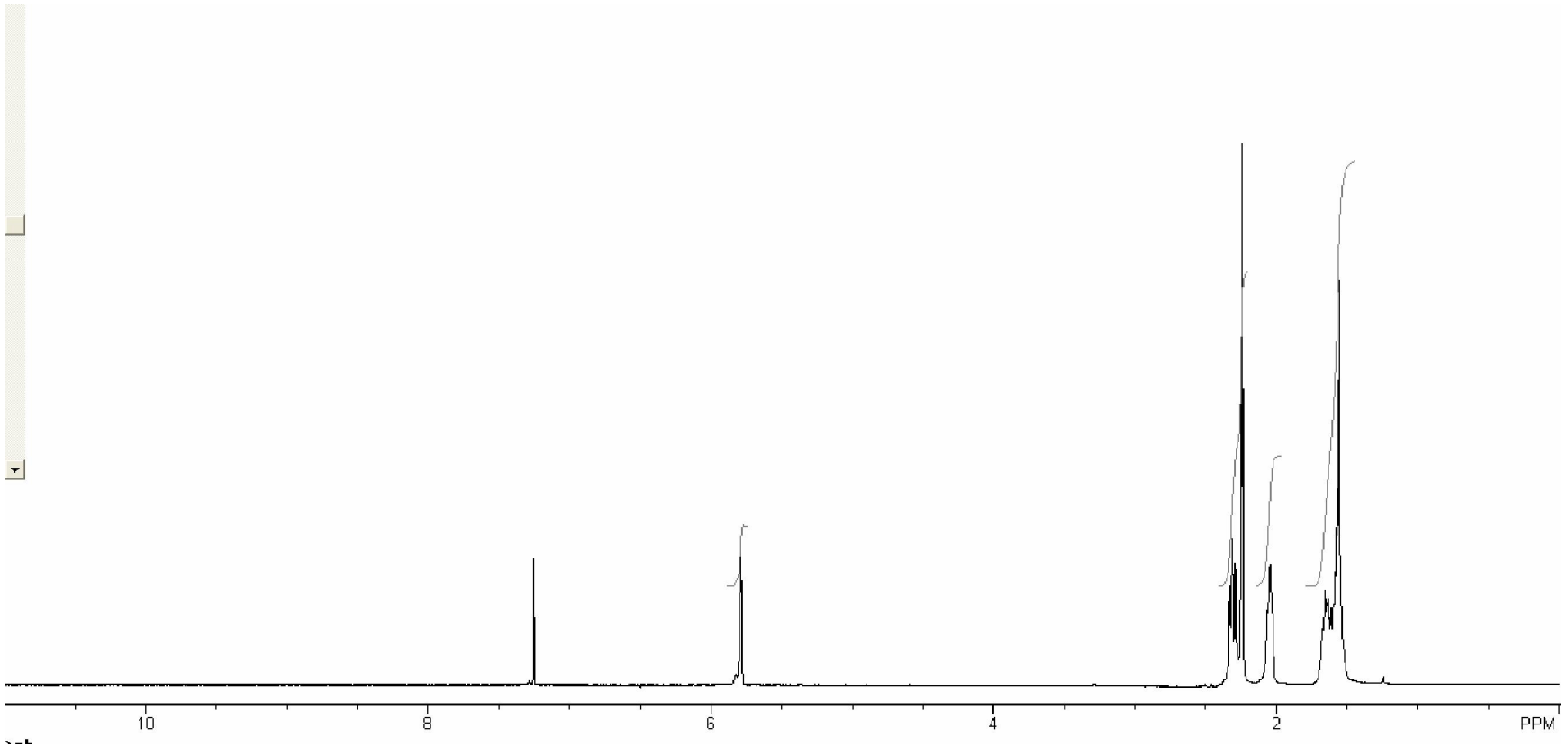
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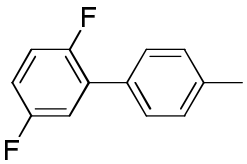
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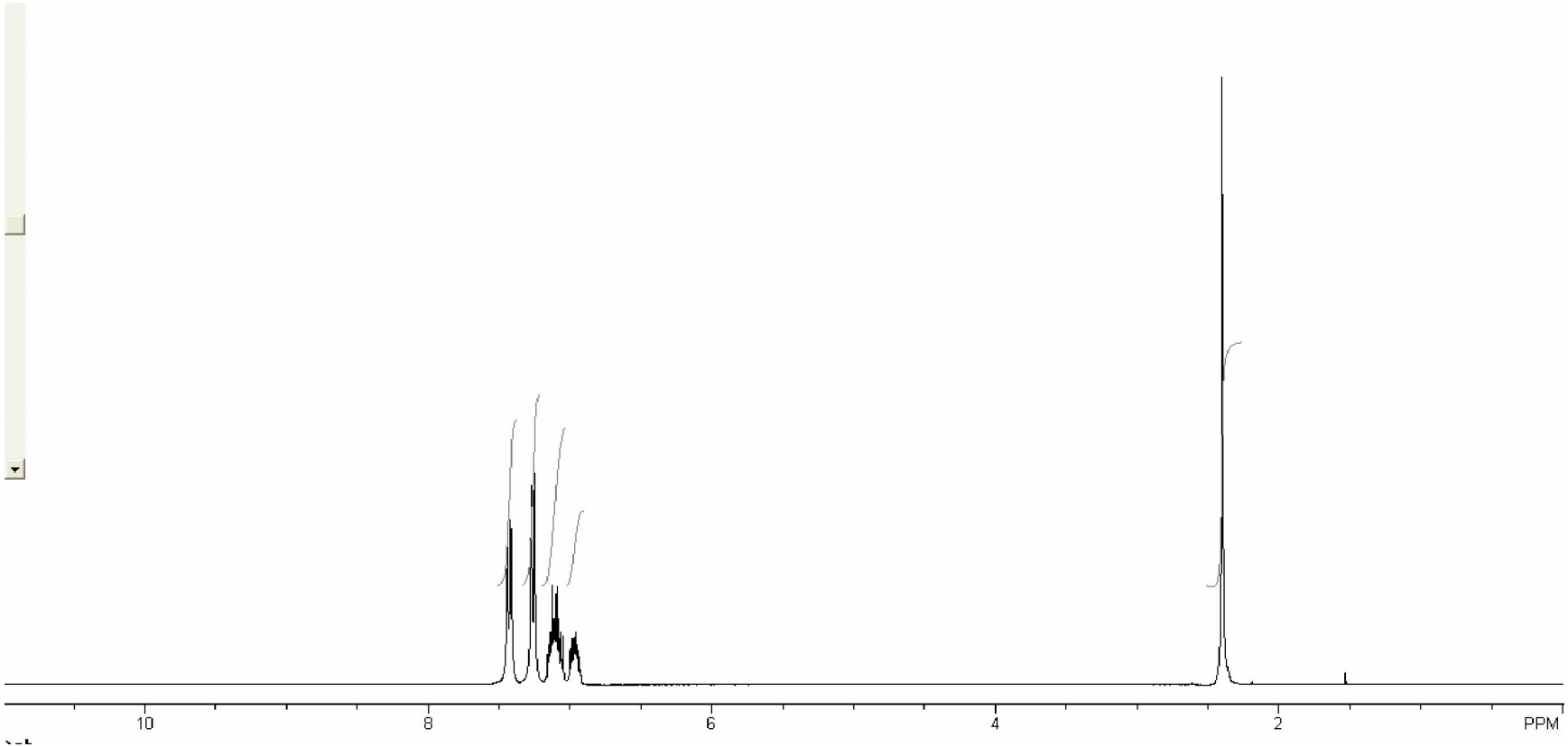
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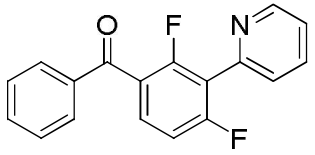
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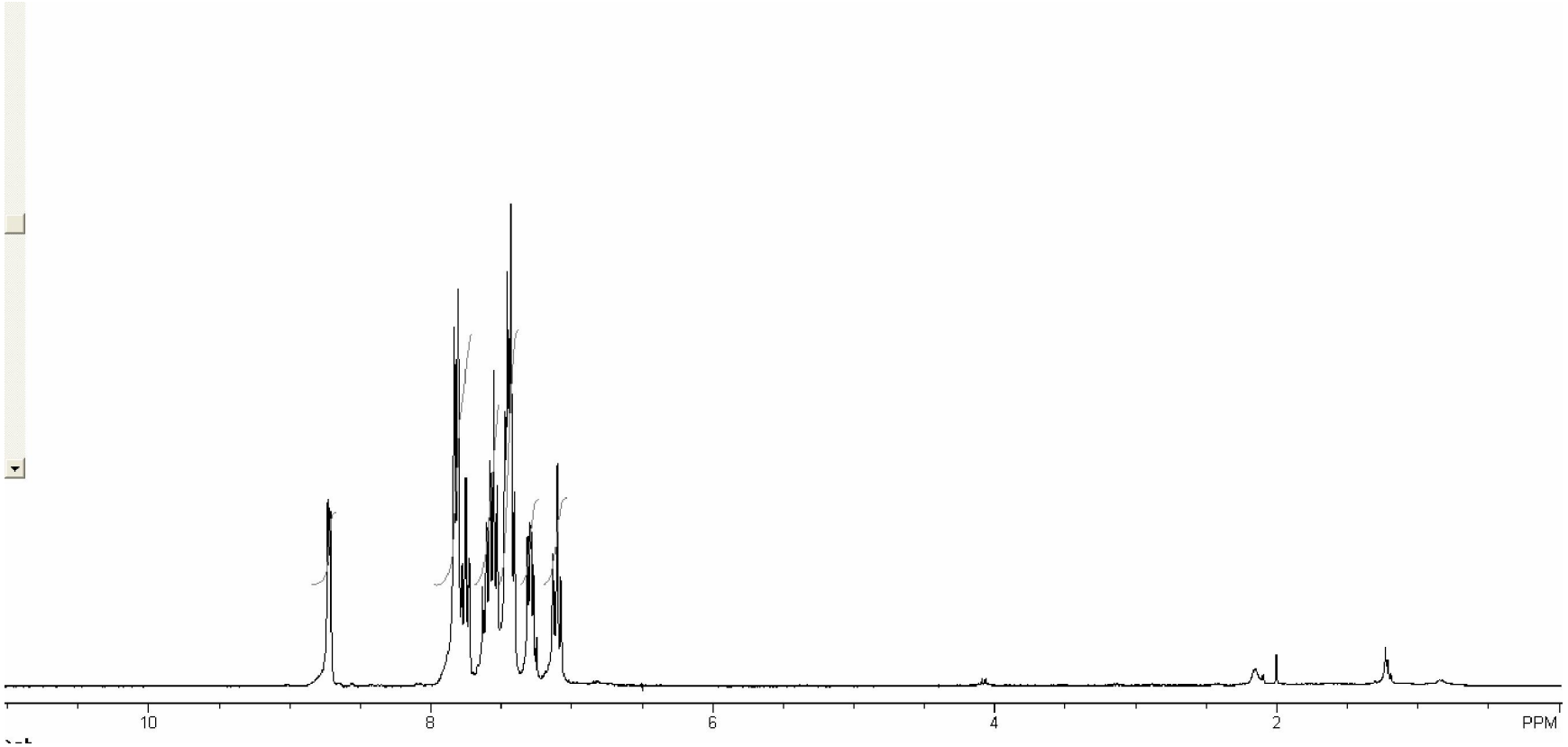
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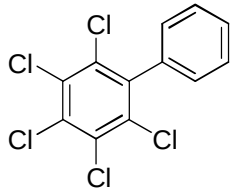
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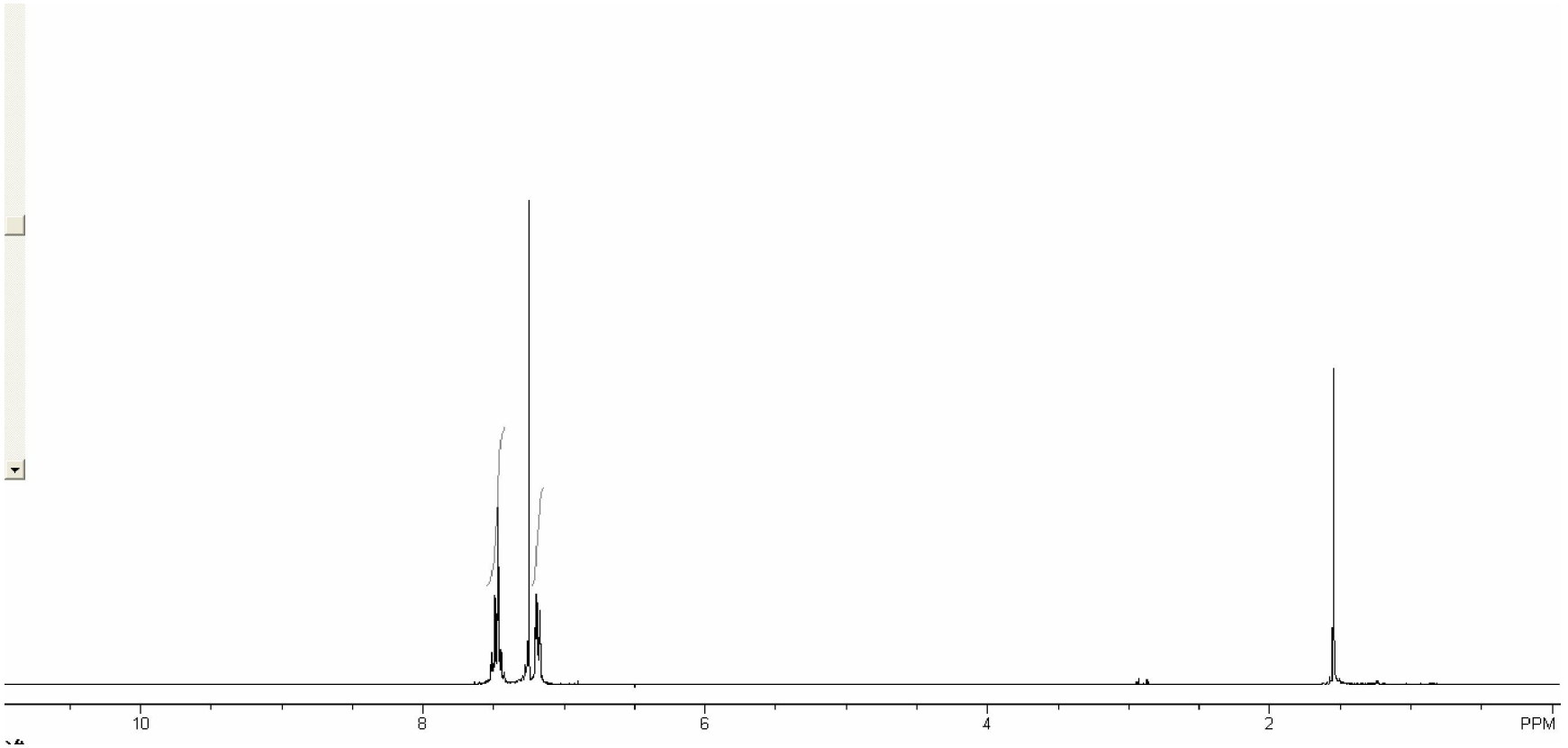
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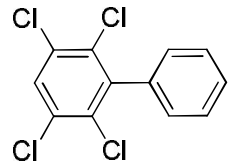
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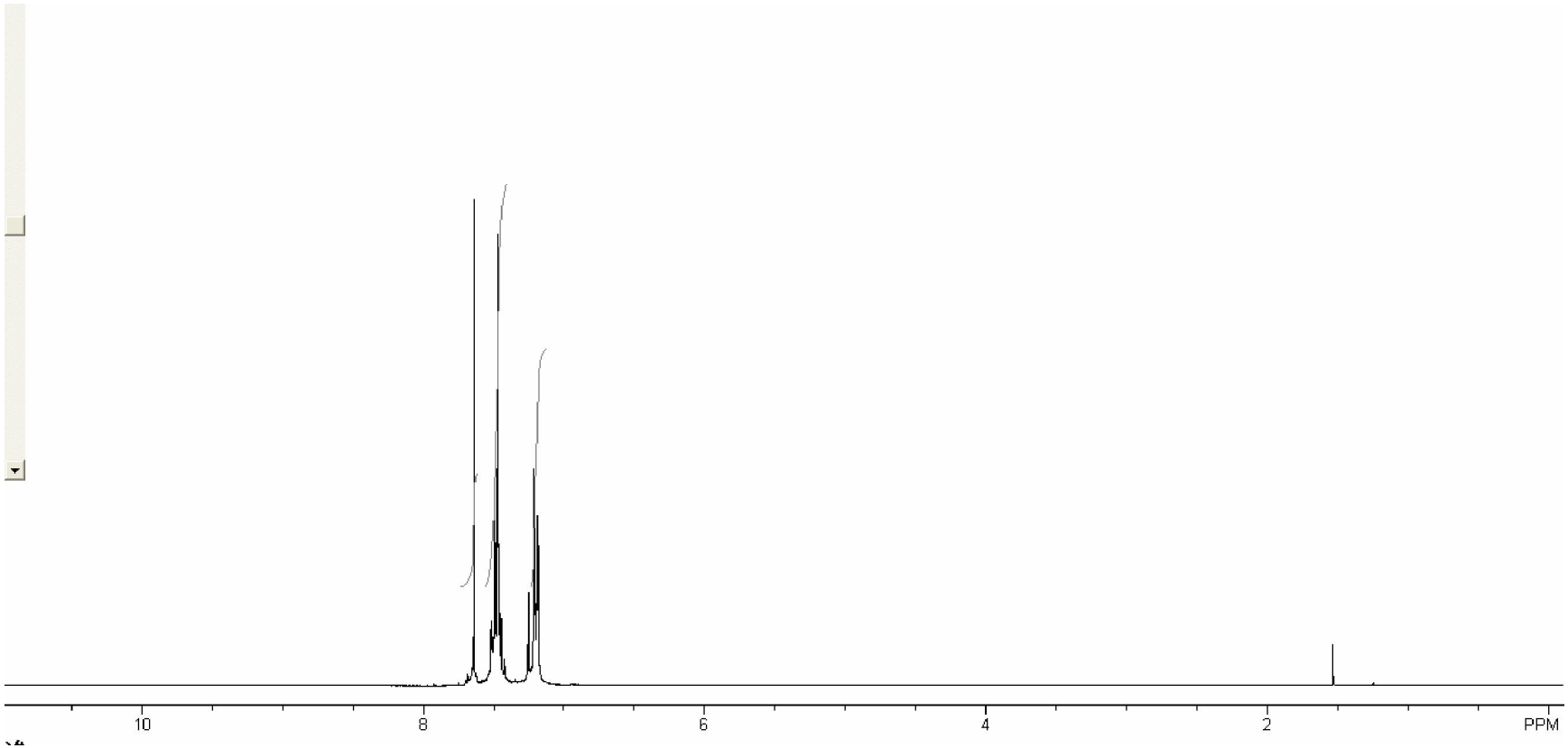
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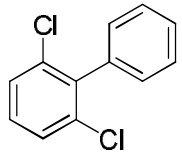
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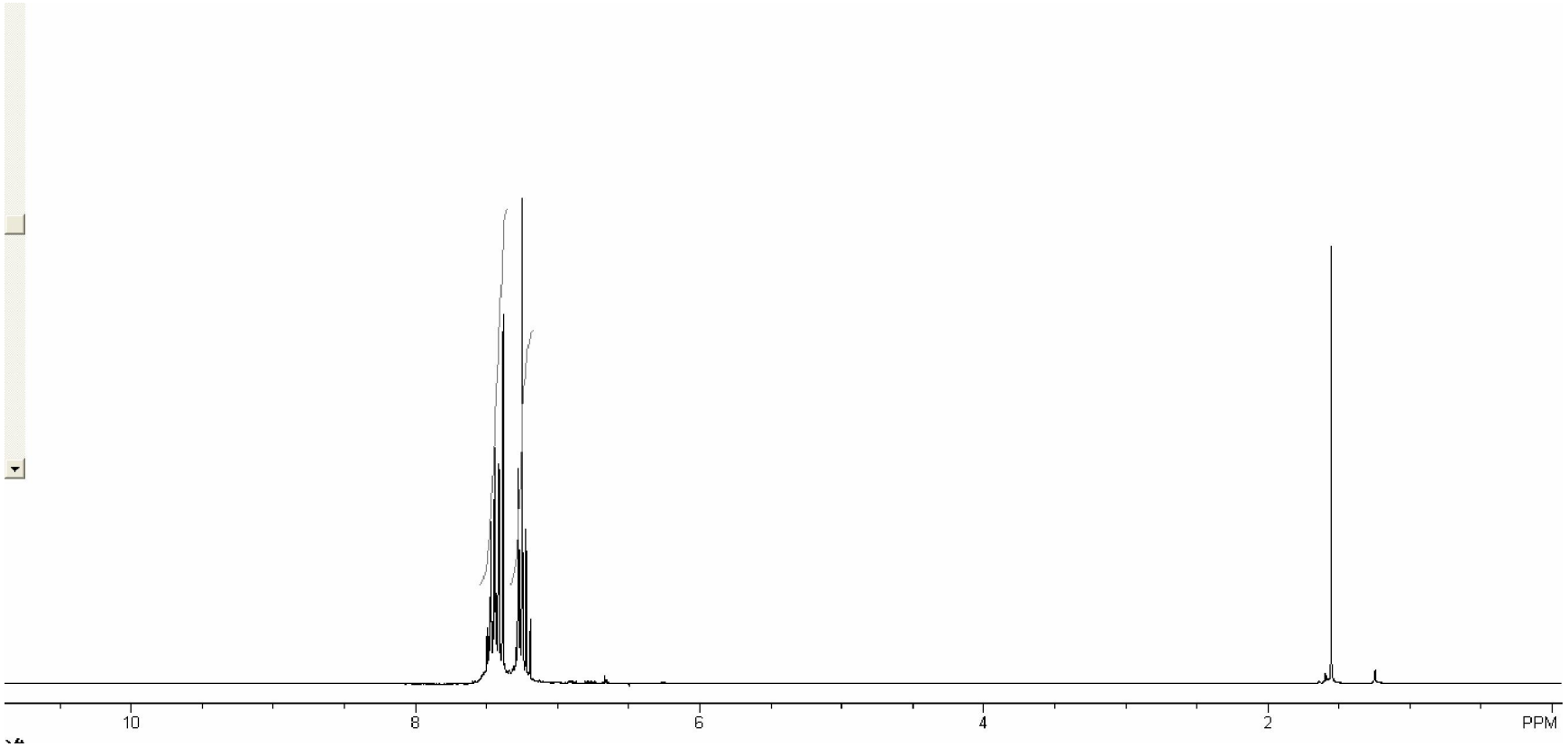
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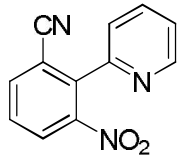
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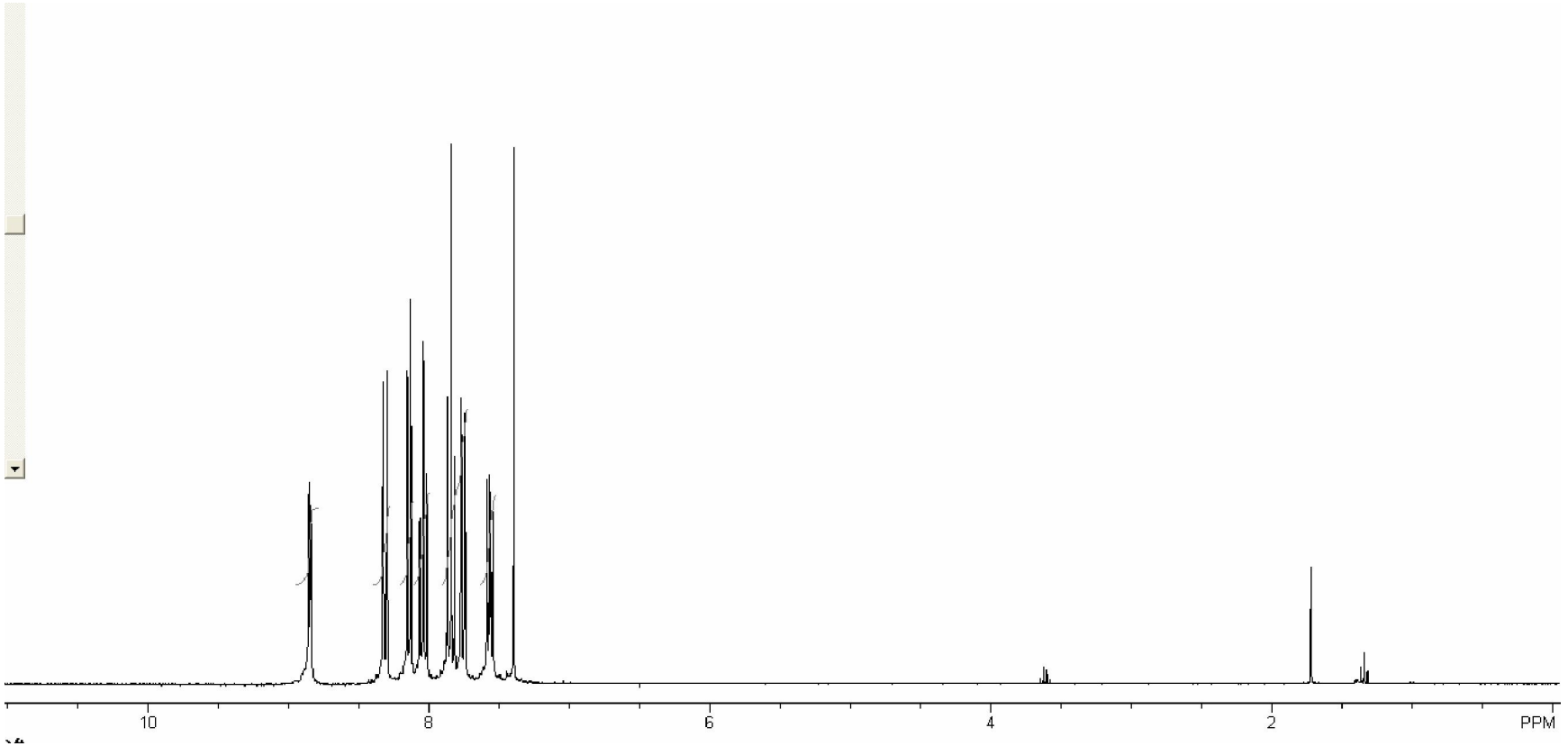
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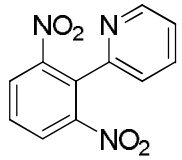
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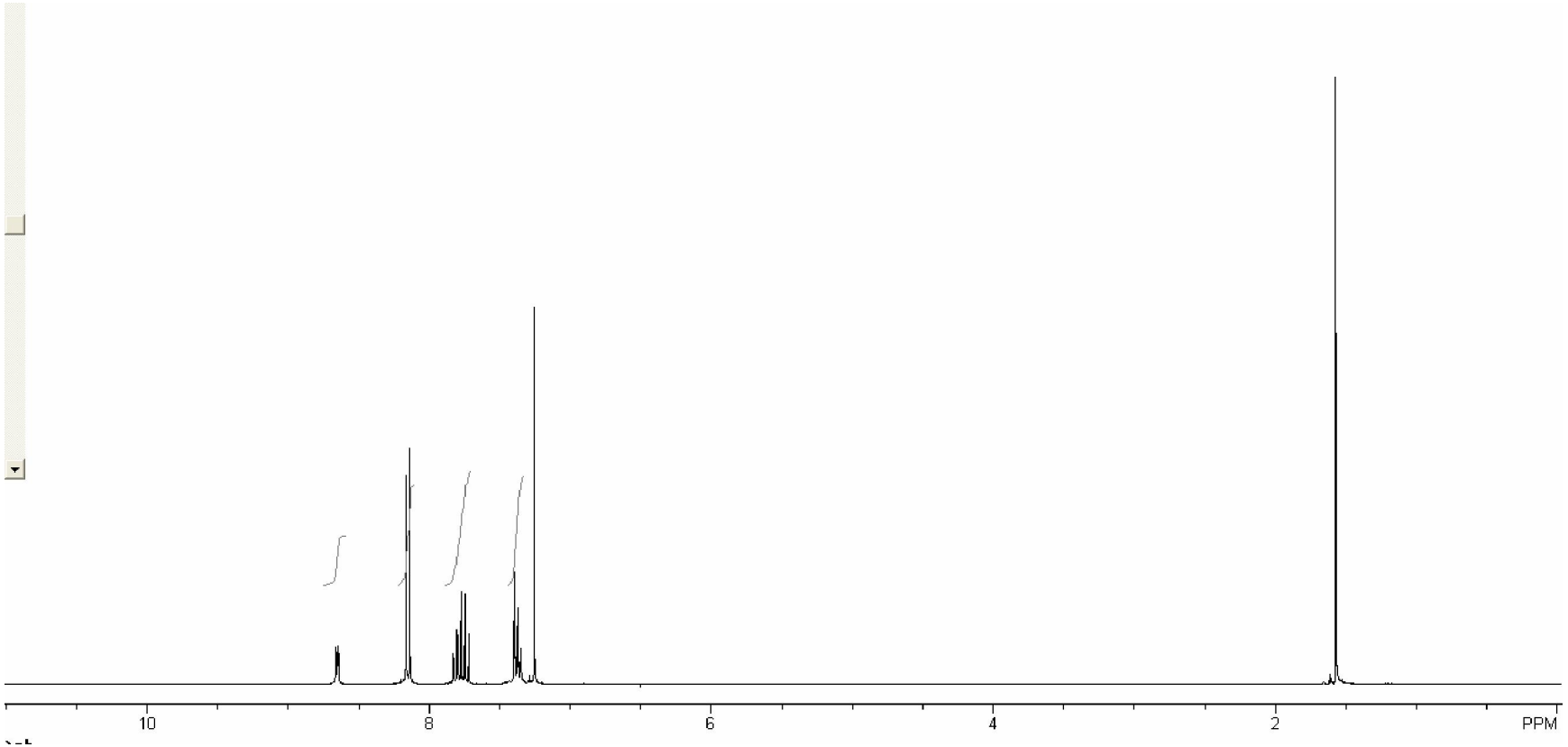
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