SUPPORTING INFORMATION

In Situ Generation and Trapping of Aryllithium and Arylpotassium Species by Halogen, Sulfur, and Carbon Electrophiles

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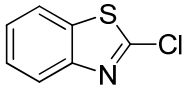
Experimental Section

General considerations. Reactions were performed in 1-dram or 2-dram vials with PTFE/Liner caps. Flash chromatography was performed on 60Å silica gel (Sorbent Technologies). Purification by preparative TLC was performed on Analtech silica gel plates 2000 microns with UV-254 indicator. Purification by HPLC was performed on 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 spectra were recorded on GE QE-300 or ECA 500 spectrometer using TMS or residual solvent peak as a standard. Melting points are uncorrected. 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 Fluka silica gel/TLC-cards with fluorescent indicator 254 nm.

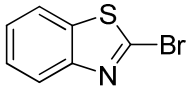
Materials. The following starting materials were obtained from commercial sources and were used without further purification: pentafluorobenzene, 1,3,5-trifluorobenzene, diphenyl disulfide, 1,2,4,5-tetrafluorobenzene, carbon tetrabromide, iodine monochloride, caffeine, 4-chlorobenzaldehyde, benzophenone, potassium phosphate, *m*-xylene, pyridine-*N*-oxide, 1-butylimidazole, cyclohexanecarboxaldehyde, 1-phenylpyrazole, pentachlorobenzene, benzothiazole, benzoxazole, 2-chlorothiophene, carbon tetrachloride, 1,2-diiodotetrafluoroethane, 2,3,5,6-tetrafluoroanisole, 2-phenylpyridine, 3,5-difluorobenzonitrile, 3-fluoronitrobenzene, potassium *t*-butoxide, lithium *t*-butoxide, and sulfur. 2-Phenylpyridine oxide was prepared from 2-phenylpyridine.[1] 1-Phenyl-1H-1,2,4-triazole and 1-phenylbenzimidazole are known.[2] 2,3,5,6-Tetrafluorobiphenyl is known[3] and was prepared according to previously described method. [4]

General procedure for halogenation. Outside the glovebox a 1-dram or 2-dram vial equipped with a magnetic stir bar was charged with substrate (1.0-2.0 mmol) and halogenating reagent (1.0-3.0 equiv). The vial was flushed with argon, capped and placed inside a glovebox. To this mixture anhydrous DMF or a mixture (1/1) of DMF and xylenes

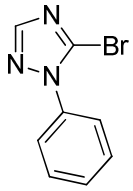
(1.0 mL) was added, followed by base (K_3PO_4 or t-BuOLi, 2.0-4.0 equiv). The sealed vial was taken out of the glovebox and placed in a preheated oil bath (50-130 ^oC) for the indicated time. The reaction mixture was allowed to cool to room temperature and subjected to flash chromatography on silica gel. After concentrating the fractions containing the product, the residue was dried under reduced pressure to yield pure halogenation product.



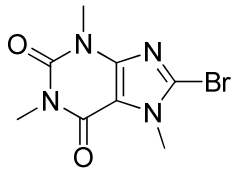
2-Chlorobenzo[d]thiazole (Entry 1, Table 1): Benzothiazole (135 mg, 1.0 mmol), carbon tetrachloride (308 mg, 2.0 mmol), t-BuOLi (200 mg, 2.5 mmol), and DMF/*m*-xylene (1.0 mL), 100 ^oC, 1 hour. After column chromatography (10% AcOEt in hexanes) 135 mg (80%) of a light tan oil was obtained. R_f = 0.53 (SiO_2, AcOEt/hexanes 1/4). This compound is known.[5] ^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.52 (m, 2H), 7.74-7.81 (m, 1H), 7.91-7.98 (m, 1H).



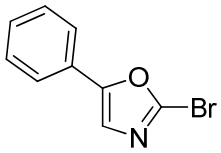
2-Bromobenzo[d]thiazole (Entry 2, Table 1): Benzothiazole (135 mg, 1.0 mmol), carbon tetrabromide (498 mg, 1.5 mmol), K_3PO_4 (636 mg, 3.0 mmol), and DMF (1.0 mL), 120 ^oC, 5 hours. After column chromatography (10% AcOEt in hexanes) 175 mg (82%) of a light tan oil was obtained. R_f = 0.53 (SiO_2, AcOEt/hexanes 1/4). This compound is known.[6] ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.50 (m, 2H), 7.78-7.82 (m, 1H), 7.96-8.01 (m, 1H).



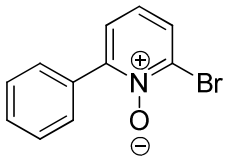
5-Bromo-1-phenyl-1H-1,2,4-triazole (Entry 3, Table 1): 1-Phenyl-1H-1,2,4-triazole (145 mg, 1.0 mmol), dibromotetrafluoroethane (520 mg, 2.0 mmol), t-BuOLi (240 mg, 3.0 mmol), and DMF (2.0 mL), 100 ^oC, 3 hours. After preparative TLC (30% AcOEt in hexanes), 173 mg (77%) of a white solid was obtained. R_f=0.21 (SiO_2, hexanes/AcOEt 9/1). This compound is known.[7] ^1H NMR (300 MHz, $CDCl_3$) δ 7.48-7.61 (m, 5H), 8.05 (s, 1H).



8-Bromo-3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione (Entry 4, Table 1): Caffeine (194 mg, 1.0 mmol), dibromotetrafluoroethane (780 mg, 3.0 mmol), t-BuOLi (320 mg, 4.0 mmol), and DMF (2.0 mL), 100 ^{o}C, 13 hours. After column chromatography (gradient 10%-15% AcOEt in CH_2Cl_2) 176 mg (65%) of a white solid was obtained. R_f=0.25 (SiO_2, hexanes/AcOEt 1/1). This compound is known.[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.40 (s, 3H), 3.56 (s, 3H), 3.97 (s, 3H).

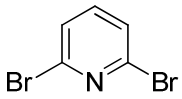


2-Bromo-5-phenyloxazole (Entry 5, Table 1): 5-Phenyloxazole (145 mg, 1.0 mmol), 1,2-dibromotetrafluoroethane (520 mg, 2.0 mmol), t-BuOLi (160 mg, 2.0 mmol), and DMF/*m*-xylenes (1.0 mL), 60 ^{o}C, 1 hour. After column chromatography (20% AcOEt in hexanes) 180 mg (80%) of a light tan oil was obtained. R_f = 0.51 (SiO_2, AcOEt/hexanes 1/4). This compound is known.[9] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.31-7.46 (m, 3H), 7.56-7.62 (m, 2H).

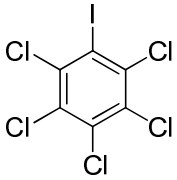


2-Bromo-6-phenylpyridine 1-oxide (Entry 6, Table 1): 2-Phenylpyridine oxide (171 mg, 1.0 mmol), carbon tetrabromide (830 mg, 2.5 mmol), t-BuOLi (320 mg, 4.0 mmol), and DMF/*m*-xylenes (1.0 mL), 60 ^{o}C, 1 hour. After column chromatography (3/2 AcOEt/hexanes) 140 mg (56%) of a light tan solid was obtained. R_f = 0.22 (SiO_2, AcOEt/hexanes 1/1), mp 117-119 ^{o}C (from AcOEt/hexanes 1/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (t, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.43-7.49 (m, 3H), 7.65 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.76-7.81 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.4, 126.5, 128.7, 129.9, 130.0, 130.4, 133.2, 135.1, 151.5. FT-IR (neat, cm^{-1}) υ 2929, 1534, 1458, 1367,

1247, 1052, 842, 792, 784, 768, 702. Anal calcd for $C_{11}H_8BrNO$ (250.09 g/mol): C, 52.83; H, 3.22; N, 5.60; Found. C, 52.94; H, 3.32; N, 5.43.

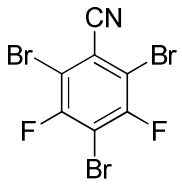


2,6-Dibromopyridine (Entry 7, Table 1): Pyridine oxide (95 mg, 1.0 mmol), carbon tetrabromide (830 mg, 2.5 mmol), t-BuOLi (240 mg, 3.0 mmol), and *m*-xylene (1.5 mL), 100 ^{o}C, 1 hour. After column chromatography (20% AcOEt in hexanes) 70 mg (30%) of a light tan solid was obtained. R_f = 0.49 (SiO_2, AcOEt/hexanes 1/4). This compound is known.[10] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.48 (m, 3H).

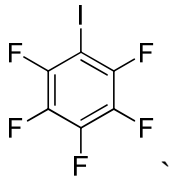


Pentachloroiodobenzene (Entry 8, Table 1): Pentachlorobenzene (250.5 mg, 1.0 mmol), ICl (243.8 mg, 1.5 mmol), t-BuOLi (240 mg, 3.0 mmol), and DMF (1.5 mL), 120 ^{o}C, 3 hours. After column chromatography (hexanes) 340 mg (90%) of a colorless solid was obtained. R_f = 0.57 (SiO_2, hexanes). This compound is known.[11] ^{13}C NMR (75 MHz, $CDCl_3$) δ 103.6, 131.1, 134.6, 138.6.

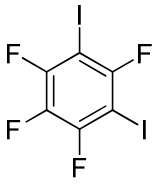
2-Bromo-1-fluoro-3-nitrobenzene (Entry 9, Table 1): 3-Fluoronitrobenzene (141 mg, 1.0 mmol), carbon tetrabromide (498 mg, 1.5 mmol), t-BuOLi (200 mg, 2.5 mmol), and DMF (1.0 mL), 60 ^{o}C, 2 hours. After column chromatography (10% AcOEt in hexanes) 120 mg (55%) of a yellow solid was obtained. R_f = 0.19 (SiO_2, hexanes), mp 42-44 ^{o}C (from AcOEt/hexanes 1/9). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (dt, J = 8.3 Hz, 1.0 Hz, 1H), 7.41-7.51 (m, 1H), 7.60-7.68 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 104.2 (d, J_{C-F} = 24.0 Hz), 120.5 (d, J_{C-F} = 22.8 Hz), 121.4 (d, J_{C-F} = 3.6 Hz), 129.6 (d, J_{C-F} = 8.4 Hz), 151.6 (br s), 160.3 (d, J_{C-F} = 251.3 Hz). FT-IR (neat, cm^{-1}) υ 1533, 1456, 1356, 1292, 1264, 944, 814, 799, 736, 704. Anal calcd for $C_6H_3BrFNO_2$ (220.00 g/mol): C, 32.76; H, 1.37; N, 6.37; Found. C, 32.86; H, 1.26; N, 6.28.



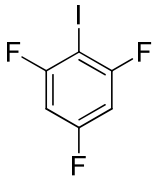
2,4,6-Tribromo-3,5-difluorobenzonitrile (Entry 10, Table 1): 3,5-Difluorobenzonitrile (139 mg, 1.0 mmol), carbon tetrabromide (1160 mg, 3.5 mmol), t-BuOLi (320 mg, 4.0 mmol), and DMF/*m*-xylene (1.5 mL), 60 ^{o}C, 2 hours. After column chromatography (15% AcOEt in hexanes) and preparative HPLC (5% AcOEt in hexanes) 150 mg (40%) of a colorless solid was obtained. R_f = 0.58 (SiO_2, AcOEt/hexanes 1/4). This compound is known.[12] ^{19}F NMR (282 MHz, $CDCl_3$) δ -169.0 (s, 2F).



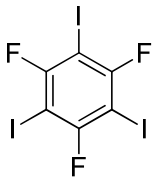
Pentafluoroiodobenzene (Entry 11, Table 1): Pentafluorobenzene (252 mg, 1.5 mmol), iodine (254 mg, 1.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and DMF (1.0 mL), 130 ^{o}C, 2 hours. After column chromatography (pentane) 250 mg (85%) of a colorless oil was obtained. R_f = 0.51 (SiO_2, hexanes). This compound is known.[13] ^{19}F NMR (282 MHz, $CDCl_3$) δ -157.6- -157.4 (m, 2F), -150.3 (t, J_F = 21.0 Hz, 1F), -117.4- -117.2 (m, 2F).



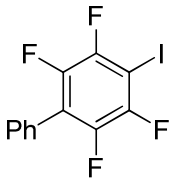
1,2,3,5-Tetrafluoro-4,6-diiodobenzene (Entry 12, Table 1): 1,2,3,5-Tetrafluorobenzene (300 mg, 2.0 mmol), iodine (1524 mg, 6.0 mmol), t-BuOLi (640 mg, 8.0 mmol), and DMF (1.5 mL), 60 ^{o}C, 3 hours. After column chromatography (pentane) 523 mg (95%) of a colorless oil was obtained. R_f = 0.68 (SiO_2, hexanes). This compound is known.[14] ^{13}C NMR (125 MHz, $CDCl_3$) δ 64.8-65.6 (m), 134.7.0-137.3 (m), 150.6-152.9 (m), 154.0-157.8 (m).



1,3,5-Trifluoro-2-iodobenzene (Entry 13, Table 1): 1,3,5-Trifluorobenzene (396 mg, 3.0 mmol), ICl (162.5 mg, 1.0 mmol), t-BuOLi (160 mg, 2.0 mmol), and DMF (1.0 mL), 60 ^{o}C, 1 hour. After column chromatography (pentane) 150 mg (58%) of a colorless oil was obtained. R_f = 0.57 (SiO_2, hexanes). This compound is known.[15] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.66-6.77 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -168.1- -168.0 (m, 2F), -106.1- -105.9 (m, 1F).



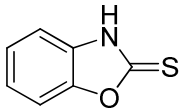
1,3,5-Trifluoro-2,4,6-triiodobenzene (Entry 14, Table 1): A 1 dram vial was charged with DMF (2.0 mL), 1,3,5-trifluorobenzene (132 mg, 1.0 mmol), ICl (492 mg, 3.0 mmol), and t-BuOLi (320 mg, 4.0 mmol) in the order listed. The reaction mixture was heated at 60 ^{o}C for 4 hours. After column chromatography (10% AcOEt in hexanes) 165 mg (32%) of a colorless solid was obtained. R_f = 0.36 (SiO_2, hexanes). This compound is known.[13] ^{19}F NMR (282 MHz, $CDCl_3$) δ -147.6 (s, 3F).



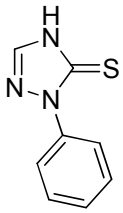
2,3,5,6-tetrafluoro-4-iodobiphenyl (Entry 15, Table 1): A 2 dram vial was charged with DMF (1.0 mL), 2,3,5,6-tetrafluorobiphenyl (226 mg, 1.0 mmol), I_2 (508 mg, 2.0 mmol), and t-BuOLi (240 mg, 3.0 mmol), 50 ^{o}C, 3 hours. After column chromatography (10% CH_2Cl_2 in hexanes) 342 mg (97%) of a colorless solid was obtained. R_f = 0.49 (SiO_2, hexanes). This compound is known.[15] ^{1}H NMR (500 MHz, $CDCl_3$) δ7.40-7.55 (m, 5H).

General procedure for reaction with sulfur electrophiles.

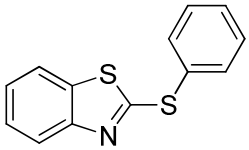
Outside the glovebox a 1-dram or 2-dram vial equipped with a magnetic stir bar was charged with substrate (1.0-2.0 mmol) and sulfur electrophile (2.0-8.0 equiv). The vial was flushed with argon, capped and placed inside a glovebox. To this mixture anhydrous DMF or DMPU (1.0-2.0 mL) was added, followed by base (K_3PO_4, t-BuOK, or t-BuOLi, 1.5-3.0 equiv). The sealed vial was taken out of the glovebox and placed in a preheated oil bath (80-130 ^oC) for the indicated time. The reaction mixture was allowed to cool to room temperature, quenched with 15% aqueous citric acid, extracted with AcOEt, washed with brine, dried over anhydrous $MgSO_4$, filtered, and subjected to flash chromatography on silica gel or preparative TLC. After concentrating the fractions containing the product, the residue was dried under reduced pressure to yield pure product.



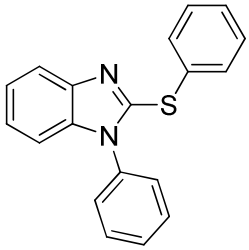
2(3H)-Benzoxazolethione (Entry 1, Table 2): Benzoxazole (119 mg, 1.0 mmol), sulfur (256 mg, 8.0 mmol), t-BuOLi (240 mg, 3.0 mmol), and DMF (1.0 mL), 80 ^oC, 12 hours. After column chromatography (gradient 10 % to 20% AcOEt in hexanes) 136 mg (90%) of a yellow solid was obtained. R_f=0.57 (SiO_2, AcOEt/hexanes 1/1). This compound is known.[16] ^1H NMR (300 MHz, $CDCl_3$) δ 7.20-7.40 (m, 4H), 10.9 (br s, 1H).



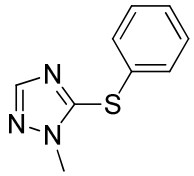
1,2-Dihydro-2-phenyl-3H-1,2,4-triazole-3-thione (Entry 2, Table 2): 1-Phenyl-1H-1,2,4-triazole (290 mg, 2.0 mmol), sulfur (512 mg, 16.0 mmol), t-BuOLi (320 mg, 4.0 mmol), and DMF (2.0 mL), 80 ^oC, 12 hours. After column chromatography (40% AcOEt in hexanes) 264 mg (74%) of a white crystalline solid was obtained. R_f=0.38 (SiO_2, AcOEt/hexanes 1/1). This compound is known.[17] ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.47 (m, 1H), 7.48-7.56 (m, 2H), 7.92-7.98 (m, 3H), 13.1 (br s, 1H).



2-Phenylsulfanyl-benzothiazole (Entry 3, Table 2): Benzothiazole (135 mg, 1.0 mmol), diphenyl disulfide (328 mg, 1.5 mmol), K_3PO_4 (636 mg, 3.0 mmol), and DMF (1.0 mL), 100 ^oC, 13 hours. After column chromatography (gradient 10%-20% CH_2Cl_2 in hexanes) 209 mg (85%) of a yellow oil was obtained. R_f=0.39 (SiO_2, CH_2Cl_2/hexanes 1/1). This compound is known.[18] ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (dt, *J*=7.5 Hz, 1.1 Hz, 1H), 7.41 (dt, *J*=7.8 Hz, 1.6 Hz, 1H), 7.44-7.56 (m, 3H), 7.63-7.68 (m, 1H), 7.72-7.77 (m, 2H), 7.86-7.91 (m, 1H).

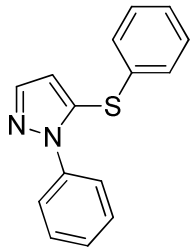


1-Phenyl-2-(phenylthio)-1H-benzimidazole (Entry 4, Table 2): 1-Phenylbenzimidazole (388 mg, 2.0 mmol), diphenyl disulfide (873 mg, 4.0 mmol), t-BuOLi (320 mg, 4.0 mmol), and DMF (2.0 mL), 130 ^oC, 12 hours. After column chromatography (30% CH_2Cl_2 in hexanes, CH_2Cl_2, then 30% AcOEt in CH_2Cl_2) 512 mg (84%) of a light tan solid was obtained. R_f=0.52 (SiO_2, hexane/AcOEt 3/1). Analytical sample was recrystallized from hexanes/AcOEt, mp 92-94 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.09-7.15 (m, 1H), 7.17-7.54 (m, 12H), 7.56-7.80 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.2, 119.7, 122.9, 123.5, 127.6, 128.4, 129.1, 129.4, 129.7, 131.1, 132.4, 135.7, 137.5, 143.4, 149.5. FT-IR (neat, cm^{-1}) υ 1497, 1424, 1343, 1260, 1220. Anal calcd for $C_{19}H_{14}N_2S$ (302.39 g/mol): C, 75.47; H, 4.67; N, 9.26; Found. C, 75.41; H, 4.60; N, 9.21.

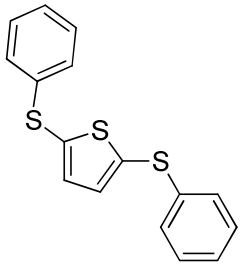


1-Methyl-5-(phenylthio)-1H-1,2,4-triazole (Entry 5, Table 2): 1-Methyl-1H-1,2,4-triazole (166 mg, 2.0 mmol), diphenyl disulfide (655 mg, 3.0 mmol), t-BuOLi (240 mg, 3.0 mmol), and DMF (2.0 mL), 80 ^oC, 12 hours. After column chromatography (1:1 hexanes/CH_2Cl_2, then 1:1 AcOEt/hexanes) 212 mg (55%) of a light yellow oil was obtained. R_f=0.53 (SiO_2,

AcOEt/hexanes 1/1). This compound is known.[19] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3H), 7.30-7.42 (m, 5H), 7.92 (s, 1H).



1-Phenyl-5-(phenylthio)-1H-pyrazole (Entry 6, Table 2): 1-Phenyl-1H-pyrazole (144 mg, 1.0 mmol), diphenyl disulfide (437 mg, 2.0 mmol), t-BuOK (224 mg, 2.0 mmol), and DMF (1.0 mL), 130 ^{o}C, 36 hours. After column chromatography (gradient 10%-20% AcOEt in hexanes) 204 mg (81%) of a yellow oil was obtained. R_f=0.59 (SiO_2, hexanes/AcOEt 3/1).^{1}H NMR (300 MHz, $CDCl_3$) δ 6.61 (d, *J*=1.7 Hz, 1H), 7.06-7.26 (m, 5H), 7.31-7.50 (m, 5H), 7.74 (d, *J*=1.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 114.9, 125.5, 127.0, 128.2, 128.6, 128.9, 129.3, 132.4, 135.4, 139.4, 140.7. FT-IR (neat, cm^{-1}) υ 3066, 1598, 1583, 1500, 1478, 1440, 1380, 1100, 1072. Anal calcd for $C_{15}H_{12}N_2S$ (252.33 g/mol): C, 71.40; H, 4.79; N, 11.10; Found. C, 71.28; H, 4.74; N, 10.88.

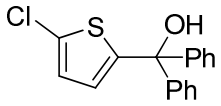


2,5-bis(Phenylthio)thiophene (Entry 7, Table 2): 2-Chlorothiophene (118 mg, 1.0 mmol), diphenyl disulfide (437 mg, 2.0 mmol), t-BuOLi (160 mg, 2.0 mmol), and DMPU (1.0 mL), 130 ^{o}C, 12 hours. After column chromatography (gradient 1%-10% CH_2Cl_2 in hexanes) and subsequent preparative TLC (5% CH_2Cl_2 in hexanes) 248 mg (82%) of a yellow oil was obtained. R_f=0.47 (SiO_2, hexanes/CH_2Cl_2 9/1). This compound is known.[20] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12-7.22 (m, 12H).

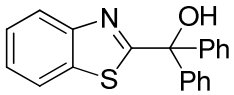
General procedure for reaction with carbon electrophiles.

Outside the glovebox a 1-dram or 2-dram vial equipped with a magnetic stir bar was charged with substrate (1.0-2.0 mmol) and aldehyde or ketone (3.0 equiv). The vial was flushed with

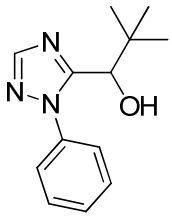
argon, capped and placed inside a glovebox. To this mixture anhydrous DMF (1.0-2.0 mL) was added, followed by base (K_3PO_4 or t-BuOLi, 1.5-3.0 equiv). The sealed vial was taken out of the glovebox and was placed in a preheated oil bath (60-105 ^oC) or stirred at RT for the indicated time. The reaction mixture was allowed to cool to room temperature, quenched with 15% citric acid, extracted with AcOEt, washed with brine, dried over anhydrous $MgSO_4$, filtered and subjected to flash chromatography on silica gel or preparative TLC. After concentrating the fractions containing the product, the residue was dried under reduced pressure to yield pure product.



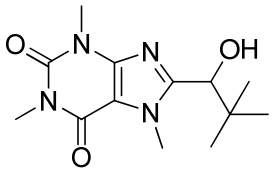
(5-Chlorothiophen-2-yl)diphenylmethanol (Entry 1, Table 3): 2-Chlorothiophene (118 mg, 1.0 mmol), benzophenone (474 mg, 3.0 mmol), t-BuOLi (120 mg, 1.5 mmol), and DMF (1.0 mL), 105 ^oC, 20 hours. After preparative TLC (10% CH_2Cl_2 in hexanes) 123 mg (41%) of a light pink solid was obtained. R_f=0.32 (SiO_2, CH_2Cl_2/hexanes 1/1). Analytical sample was recrystallized from hexanes, mp 112-114 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 2.92 (s, 1H), 6.48 (d, *J*=3.9 Hz, 1H), 6.75 (d, *J*=3.9 Hz, 1H), 7.25-7.45 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 80.4, 125.8, 126.2, 127.4, 128.1, 128.3, 130.5, 146.0, 150.8. FT-IR (neat, cm^{-1}) υ 3445, 1489, 1446, 1334, 1215, 1165, 1123. Anal calcd for $C_{17}H_{13}ClOS$ (300.80 g/mol): C, 67.88; H, 4.36; Found. C, 67.86; H, 4.26.



α,α-Diphenyl-2-benzothiazolemethanol (Entry 2, Table 3): Benzothiazole (135 mg, 1.0 mmol), benzophenone (546 mg, 3.0 mmol), t-BuOLi (160 mg, 2.0 mmol), and DMF (1.0 mL), 80 ^oC, 13 hours. After column chromatography (gradient 10%-20% CH_2Cl_2 in hexanes) 247 mg (77%) of a white solid was obtained. R_f=0.23 (SiO_2, CH_2Cl_2/hexanes 1/1). This compound is known.[21] ^1H NMR (300 MHz, $CDCl_3$) δ 4.43 (s, 1H), 7.30-7.41 (m, 7H), 7.43-7.52 (m, 5H), 7.80-7.85 (m, 1H), 7.99-8.04 (m, 1H).

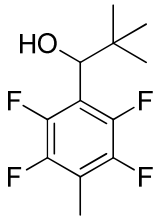


2,2-dimethyl-1-(1-phenyl-1H-1,2,4-triazol-5-yl)propan-1-ol (Entry 3, Table 3): 1-Phenyl-1H-1,2,4-triazole (145 mg, 1.0 mmol), pivaldehyde (258 mg, 3.0 mmol), t-BuOLi (120 mg, 1.5 mmol), and DMF (1.0 mL), 100 ^{o}C, 12 hours. After preparative TLC (10% AcOEt in CH_2Cl_2) 153 mg (66%) of white solid was obtained. R_f=0.38 (SiO_2, hexane/AcOEt 1/1). Analytical sample was recrystallized from hexanes/AcOEt, mp 108-110 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (s, 9H), 2.95 (d, *J*=9.7 Hz, 1H), 4.55 (d, *J*=9.7 Hz, 1H), 7.24-7.58 (m, 5H), 8.03 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 37.1, 73.2, 126.2, 129.7, 129.8, 137.6, 151.0, 156.5. FT-IR (neat, cm^{-1}) υ 3294, 2955, 2901, 1597, 1504, 1473, 1386, 1297, 1273, 1185, 1104, 1063, 1037. Anal calcd for $C_{13}H_{17}N_3O$ (231.29 g/mol): C, 67.51; H, 7.41; N, 18.17; Found. C, 67.64; H, 7.50; N, 18.19.

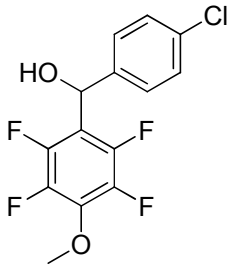


8-(1-Hydroxy-2,2-dimethylpropyl)-1,3,7-trimethyl-1H-purine-2,6(3H,7H)-dione (Entry 4, Table 3): Caffeine (194 mg, 1.0 mmol), pivaldehyde (258 mg, 3.0 mmol), t-BuOLi (120 mg, 1.5 mmol), and DMF (1.0 mL), 105 ^{o}C, 12 hours. After column chromatography (gradient 50%-60% AcOEt in CH_2Cl_2) 255 mg (91%) of a white solid was obtained. R_f=0.26 (SiO_2, AcOEt/CH_2Cl_2 1/1). Analytical sample was recrystallized from hexanes/AcOEt, mp 169-171 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (s, 9H), 3.04 (d, *J*=8.5 Hz, 1H), 3.39 (s, 3H), 3.55 (s, 3H), 3.99 (s, 3H), 4.47 (d, *J*=8.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.8, 28.1, 29.9, 33.0, 37.5, 73.7, 107.7, 147.6, 151.8, 154.0, 155.6. FT-IR (neat, cm^{-1}) υ 3446, 2952, 1694, 1641, 1541, 1435, 1366, 1220, 1080. Anal calcd for $C_{13}H_{20}N_4O_3$ (280.32 g/mol): C, 55.70; H, 7.19; N, 19.99; Found. C, 55.80; H, 7.33; N, 19.97.

Control experiment: If the reaction was performed under the conditions described above, but without added base, product formation was not observed.

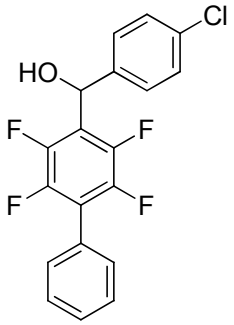


(2,2-Dimethyl-1-(2,3,5,6-tetrafluoro-4-methylphenyl)propan-1-ol (Entry 5, Table 3): 2,3,5,6-Tetrafluorotoluene (164 mg, 1.0 mmol), pivaldehyde (258 mg, 3.0 mmol), t-BuOLi (120 mg, 1.5 mmol), and DMF (1.0 mL), RT, 12 hours. After preparative TLC (50% CH_2Cl_2 in hexanes) 171 mg (68%) of a white solid was obtained. Analytical sample was recrystallized from hexanes, mp 59-61 °C. R_f=0.53 (SiO_2, CH_2Cl_2/hexanes 1/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, *J*=1.4 Hz, 9H), 2.27 (t, *J*=2.1 Hz, 3H), 2.47 (dt, *J*=10.0 Hz, 3.0 Hz, 1H), 4.78 (d, *J*=10.0 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -147.5- -146.9 (m, 2F), -145.2-144.7 (m, 2F). ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.5-8.0 (m), 25.8, 37.4, 76.0-76.2 (m), 115.0-115.6 (m), 117.3-117.8 (m), 142.0-144.3 (m), 145.6-147.4 (m). FT-IR (neat, cm^{-1}) υ 3474, 2964, 1479, 1393, 1369, 1279, 1259, 1095, 1050. Anal calcd for $C_{12}H_{14}F_4O$ (250.23 g/mol): C, 57.60; H, 5.64; Found. C, 57.65; H, 5.67.

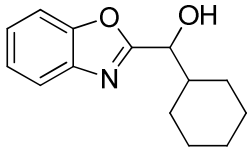


(4-Chlorophenyl)(2,3,5,6-tetrafluoro-4-methoxyphenyl)methanol (Entry 6, Table 3): 2,3,5,6-Tetrafluoroanisole (180 mg, 1.0 mmol), 4-chlorobenzaldehyde (422 mg, 3.0 mmol), t-BuOLi (120 mg, 1.5 mmol), and DMF (1.0 mL), RT, 2 hours. After column chromatography (gradient 30%-60% CH_2Cl_2 in hexanes) 300 mg (93%) of a colorless oil was obtained. R_f=0.45 (SiO_2, hexanes/CH_2Cl_2 1/4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.64 (dt, *J*=7.5 Hz, 1.1 Hz, 1H), 4.08 (t, *J*=1.4 Hz, 3H), 6.18 (d, *J*=7.5 Hz, 1H), 7.33 (s, 4H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -160.6- -160.4 (m, 2F), -148.2- -148.0 (m, 2F). ^{13}C NMR (75 MHz, $CDCl_3$) δ 62.6 (t, $J_{C\text{-}F}$=3.6 Hz), 67.4 (quintet, $J_{C\text{-}F}$=2.4 Hz), 114.5-115.4 (m), 127.4, 129.3, 134.4, 138.3-140.0 (m), 140.1, 142.8-143.9 (m), 146.6-147.3 (m). FT-IR (neat, cm^{-1}) υ 3387, 1651, 1491, 1438, 1416, 1196, 1132, 1092. Anal calcd for $C_{14}H_9ClF_4O_2$ (320.67 g/mol): C, 52.44;

H, 2.83; Found. C, 52.40; H, 2.88. At elevated temperatures, base-catalyzed formation of p-chlorobenzyl p-chlorobenzoate is observed.



(4-Chlorophenyl)(2,3,5,6-tetrafluorobiphenyl-4-yl)methanol (Entry 7, Table 3): 2,3,5,6-Tetrafluorobiphenyl (226 mg, 1.0 mmol), 4-chlorobenzaldehyde (422 mg, 3.0 mmol), t-BuOLi (120 mg, 1.5 mmol), and DMF (1.0 mL), 60 ^{o}C, 6 hours. After column chromatography (gradient 30%-60% CH_2Cl_2 in hexanes) 311 mg (85%) of a white solid was obtained. R_f=0.33 (SiO_2, hexanes/CH_2Cl_2 1/1). Analytical sample was recrystallized from hexanes/AcOEt, mp 142-144 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.69 (d, *J*=6.0 Hz, 1H), 6.30 (d, *J*=6.0 Hz, 1H), 7.34-7.56 (m, 9H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -147.3- -147.0 (m, 2F), -146.6- -146.4 (m, 2F). ^{13}C NMR (75 MHz, $CDCl_3$) δ 67.5 (quintet, J_{C-F}=2.4 Hz), 120.3-121.1 (m, 2C), 127.2, 127.2-127.4 (m), 128.9, 129.1, 129.5, 130.2-130.4 (m), 134.2, 139.6, 142.2-143.4 (m), 145.4-146.7 (m). FT-IR (neat, cm^{-1}) υ 3309, 1479, 1438, 1304, 1179, 1096, 1053. Anal calcd for $C_{19}H_{11}ClF_4O$ (366.84 g/mol): C, 62.23; H, 3.02; Found. C, 62.38; H, 2.94. At elevated temperatures, base-catalyzed formation of p-chlorobenzyl p-chlorobenzoate is observed.



Benzo[d]oxazol-2-yl(cyclohexyl)methanol (Entry 8, Table 3): Benzoxazole (119 mg, 1.0 mmol), cyclohexanecarboxaldehyde (337 mg, 3.0 mmol), K_3PO_4 (636 mg, 3.0 mmol), and DMF (1.0 mL), 80 ^{o}C, 11 hours. After column chromatography (gradient 5%-15% AcOEt in CH_2Cl_2) 232 mg (50%) of yellow solid was obtained. R_f=0.53 (SiO_2, AcOEt/CH_2Cl_2 1/9). Analytical sample was recrystallized from hexanes/AcOEt, mp 121-123 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05-1.40 (m, 5H), 1.53-1.87 (m, 5H), 1.91-2.06 (m, 1H), 3.70 (br s, 1H), 4.74 (d, *J*=5.9 Hz, 1H), 7.29-7.37 (m, 2H), 7.48-7.55 (m, 1H), 7.66-7.74 (m, 1H). ^{13}C NMR

(75 MHz, $CDCl_3$) δ 26.0, 26.2, 26.4, 27.8, 29.1, 43.3, 72.8, 111.0, 120.1, 124.7, 125.2, 140.6, 150.9, 167.7. FT-IR (neat, cm^{-1}) υ 3280, 2920, 2853, 1615, 1570, 1456, 1242, 1232, 1117. Anal calcd for $C_{14}H_{17}NO_2$ (231.29 g/mol): C, 72.70; H, 7.41; N, 6.06; Found. C, 72.85; H, 7.42; N, 6.03.

Control experiment: If the reaction was performed under the conditions described above, but without added base, product formation was not observed.

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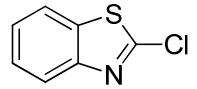

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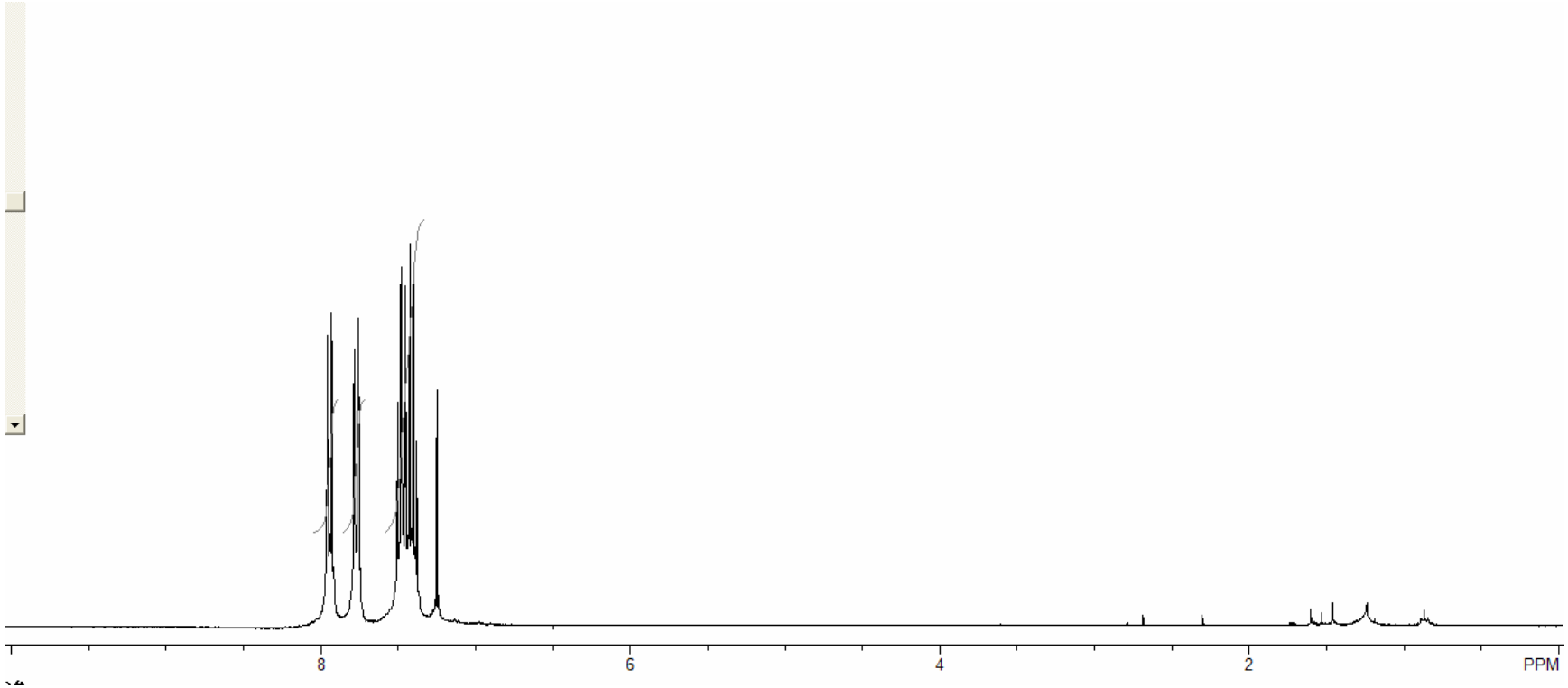

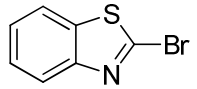

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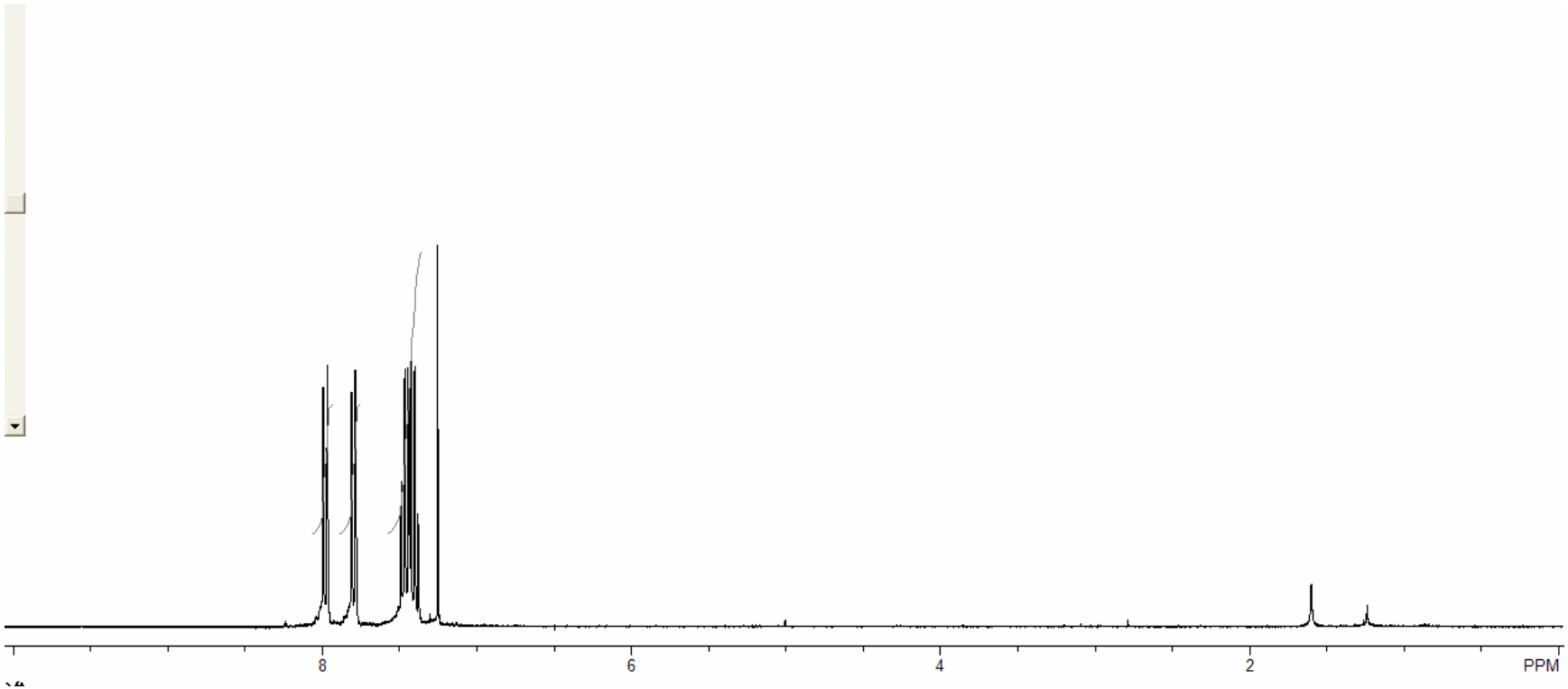

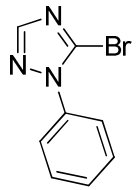

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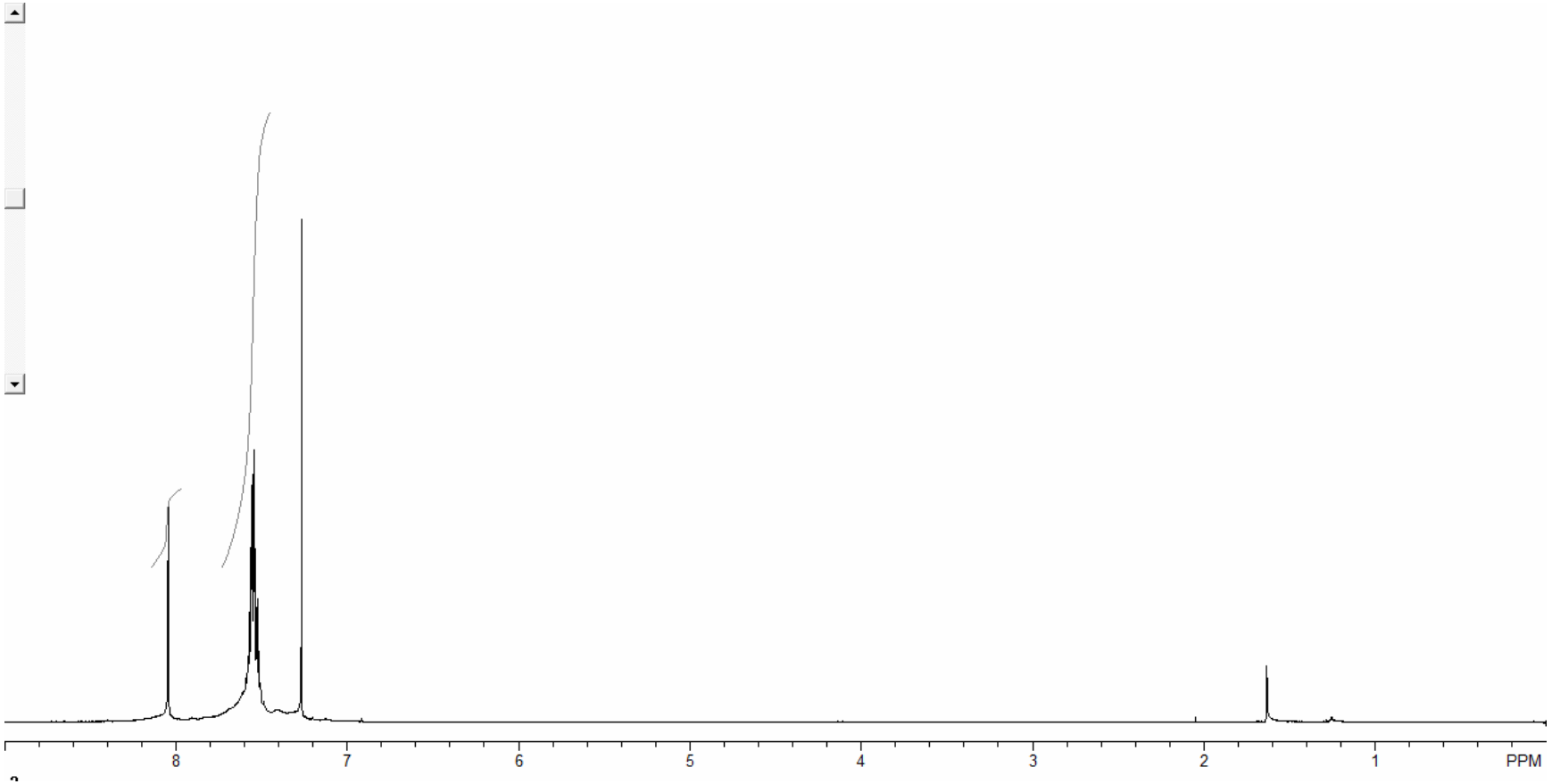

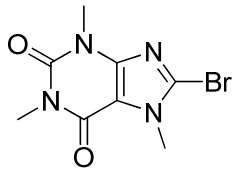

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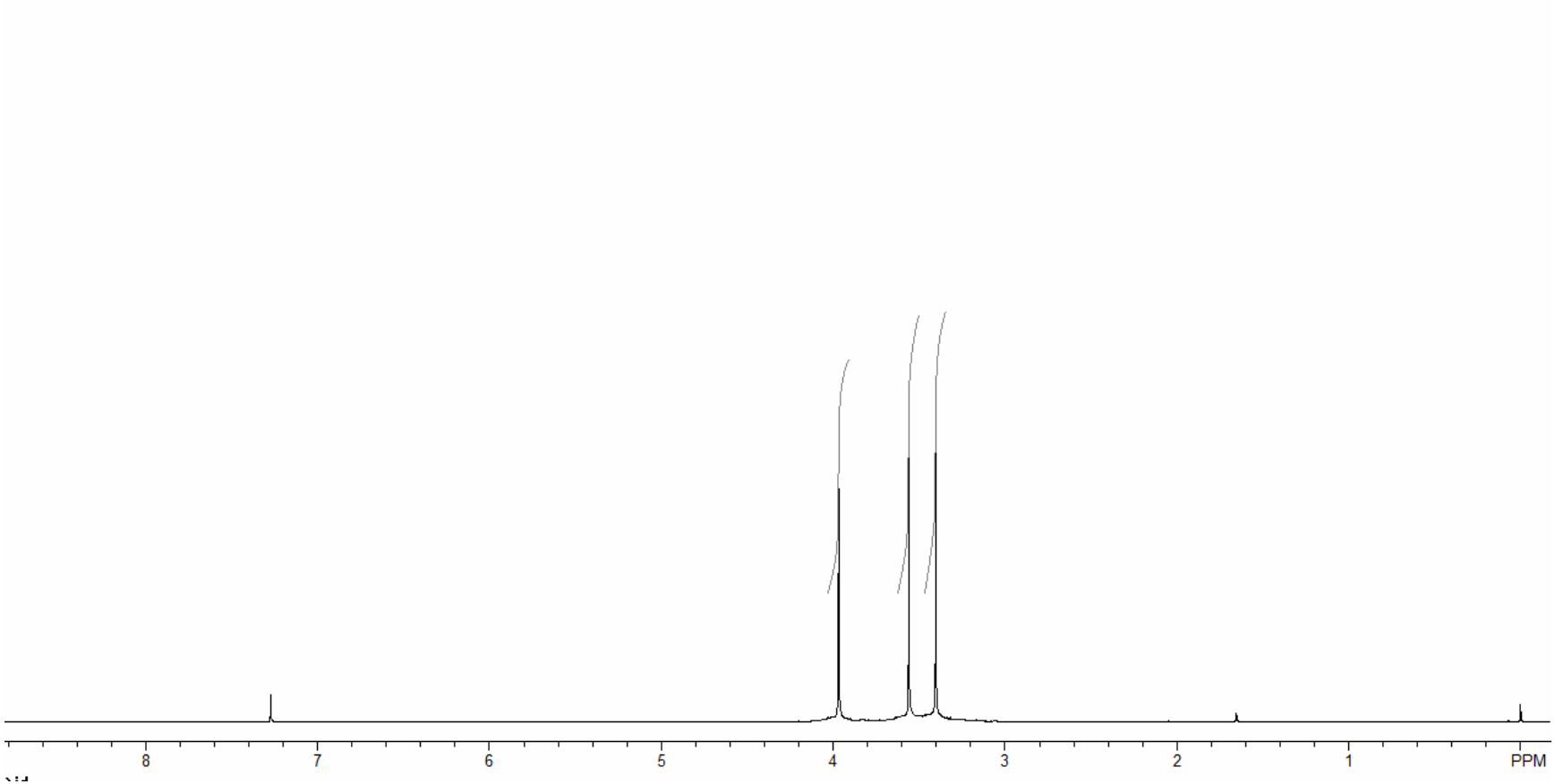
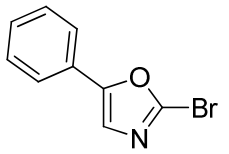
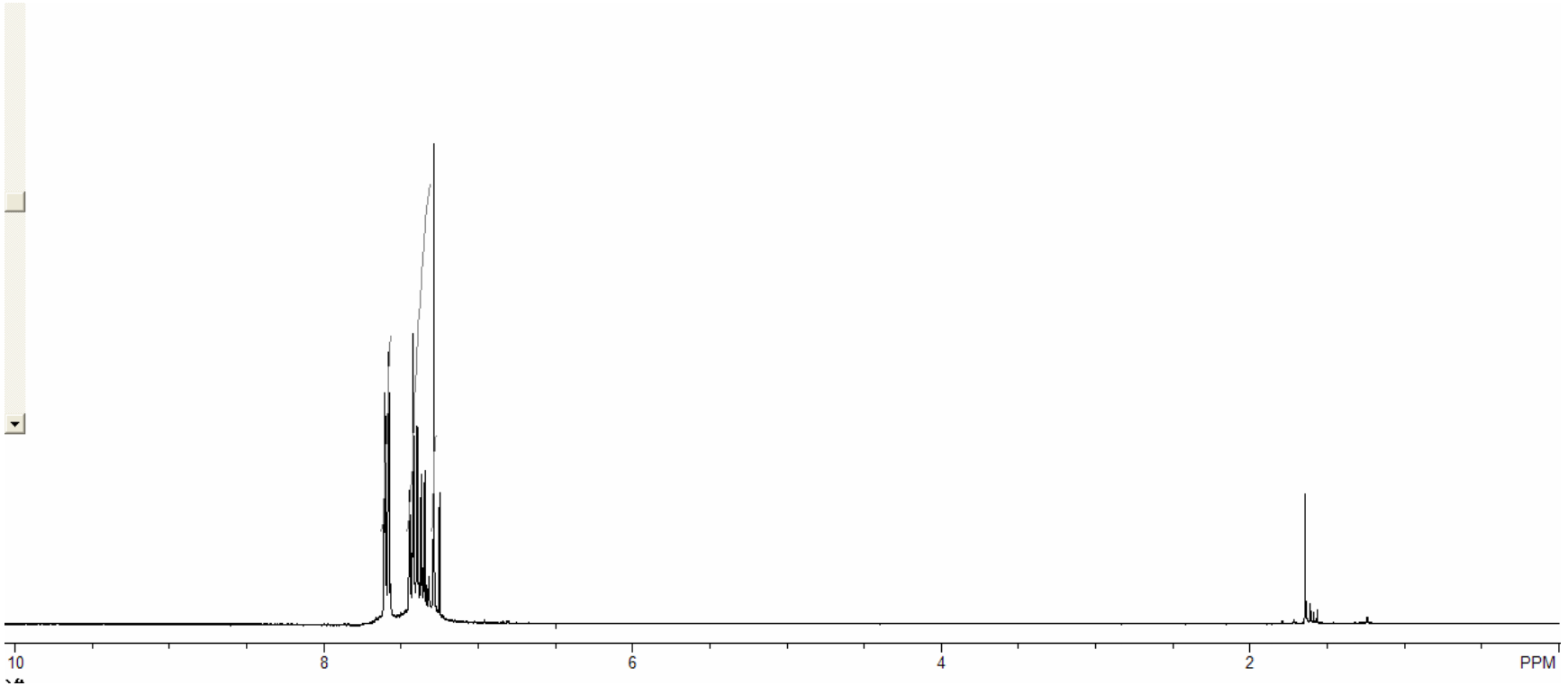
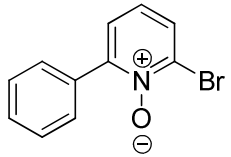




(Entry 5, Table 1)





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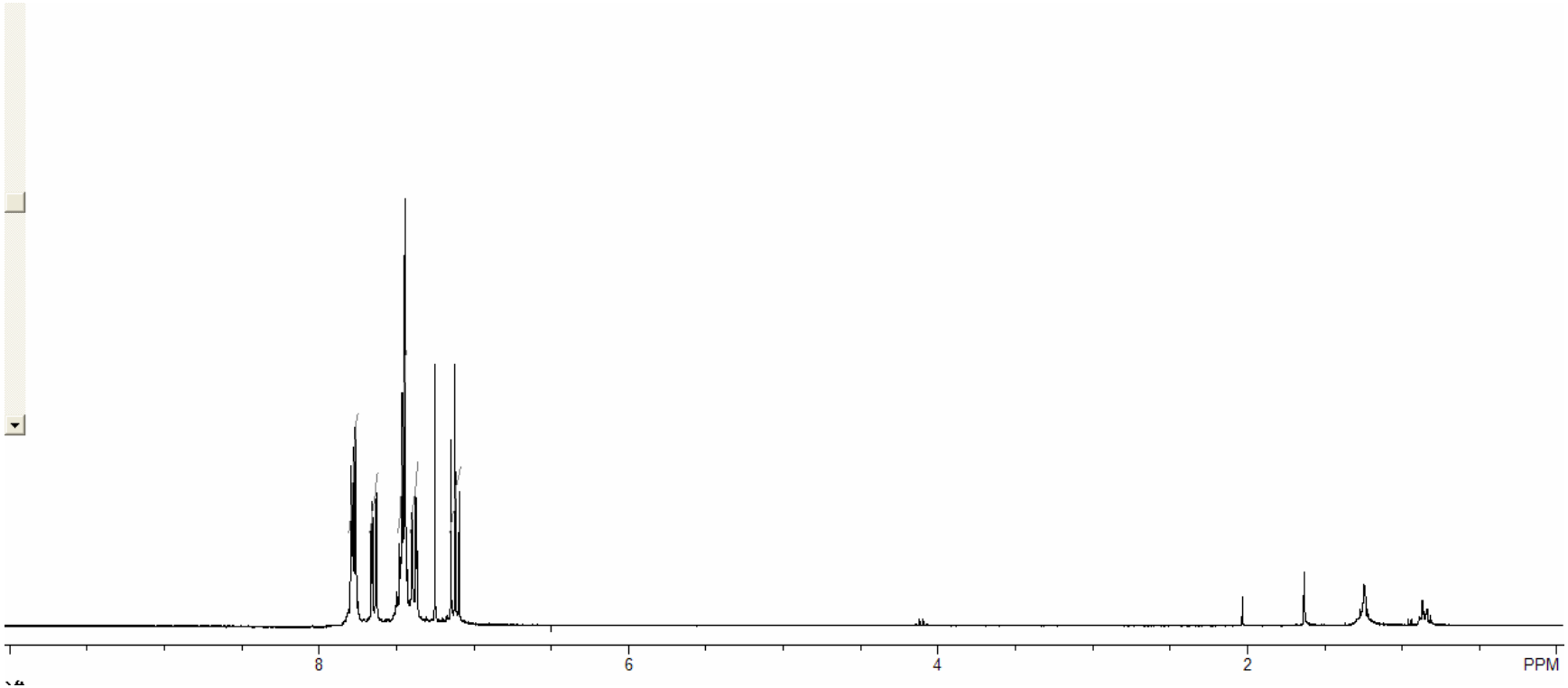

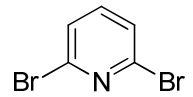

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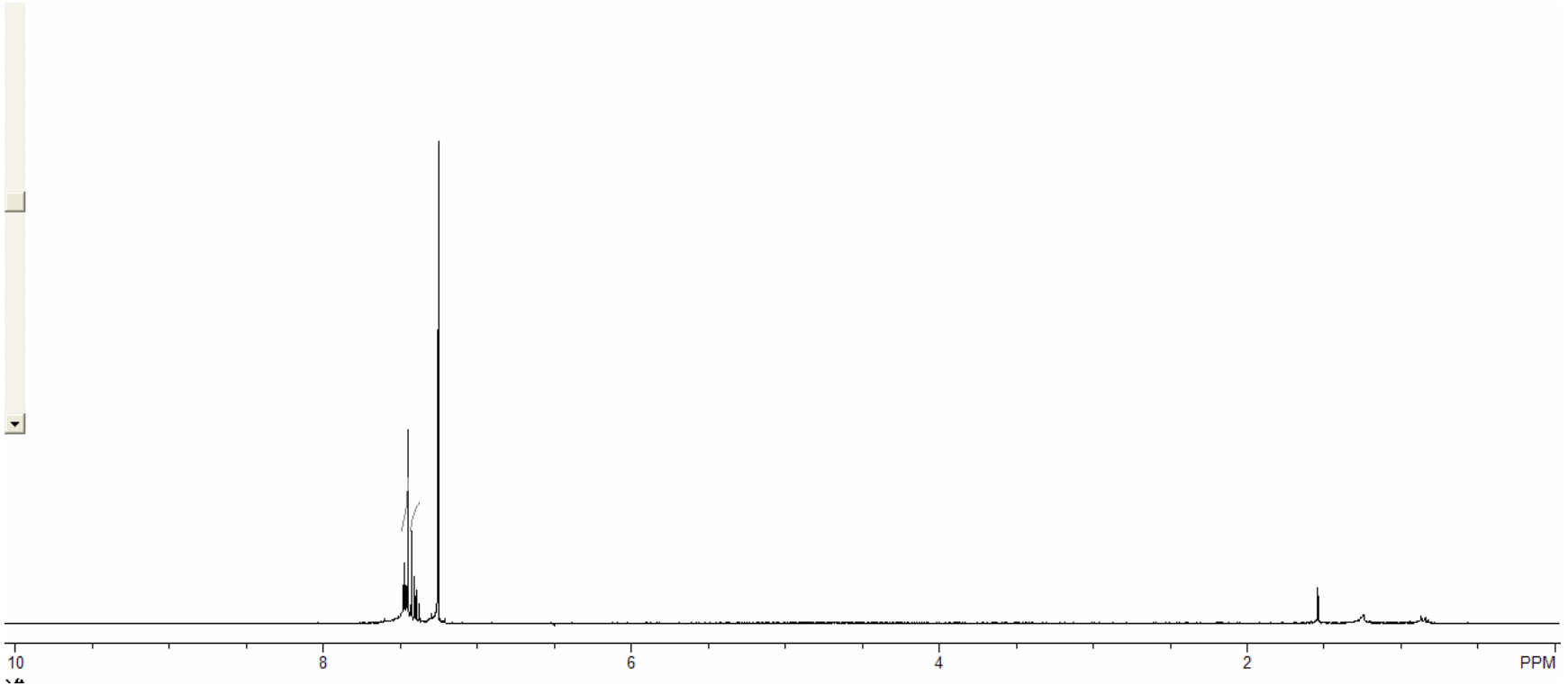

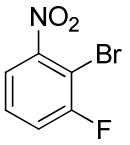

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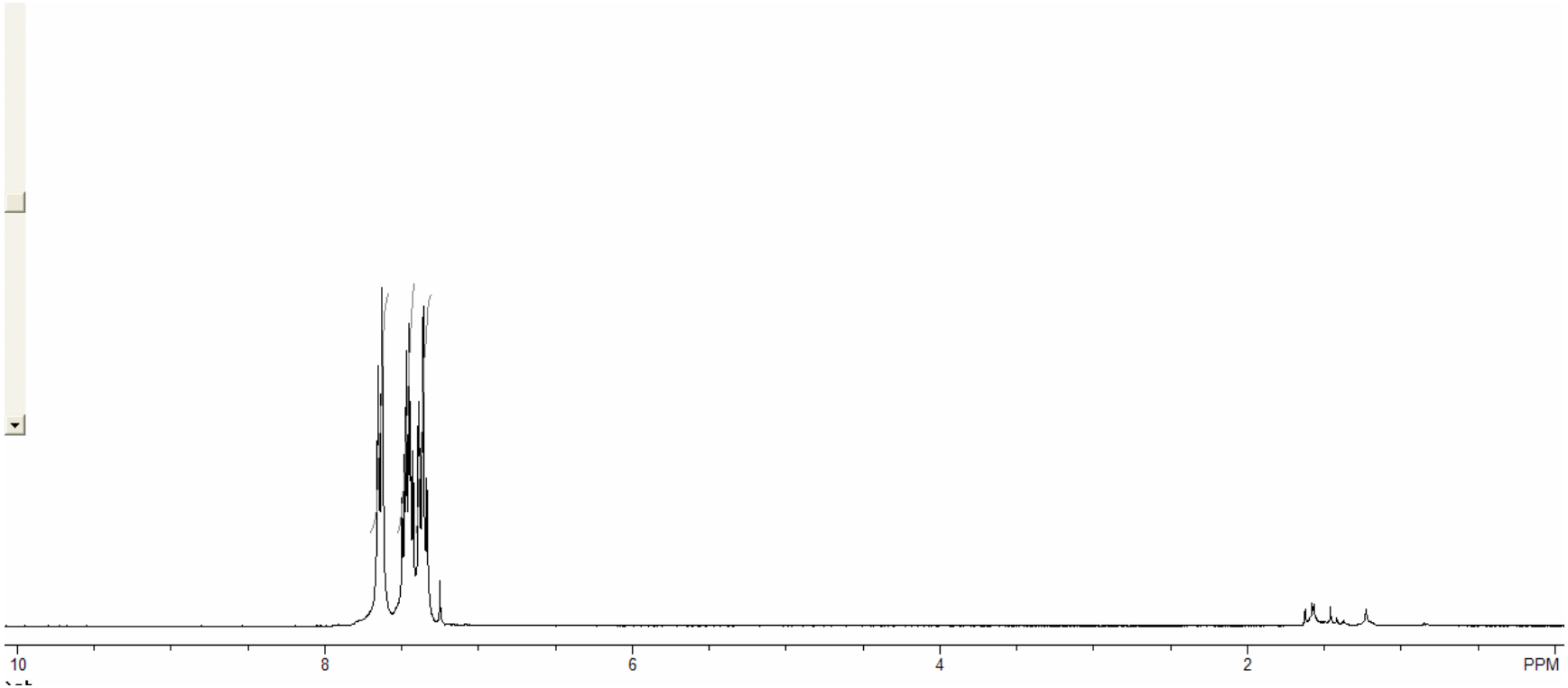

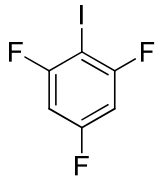

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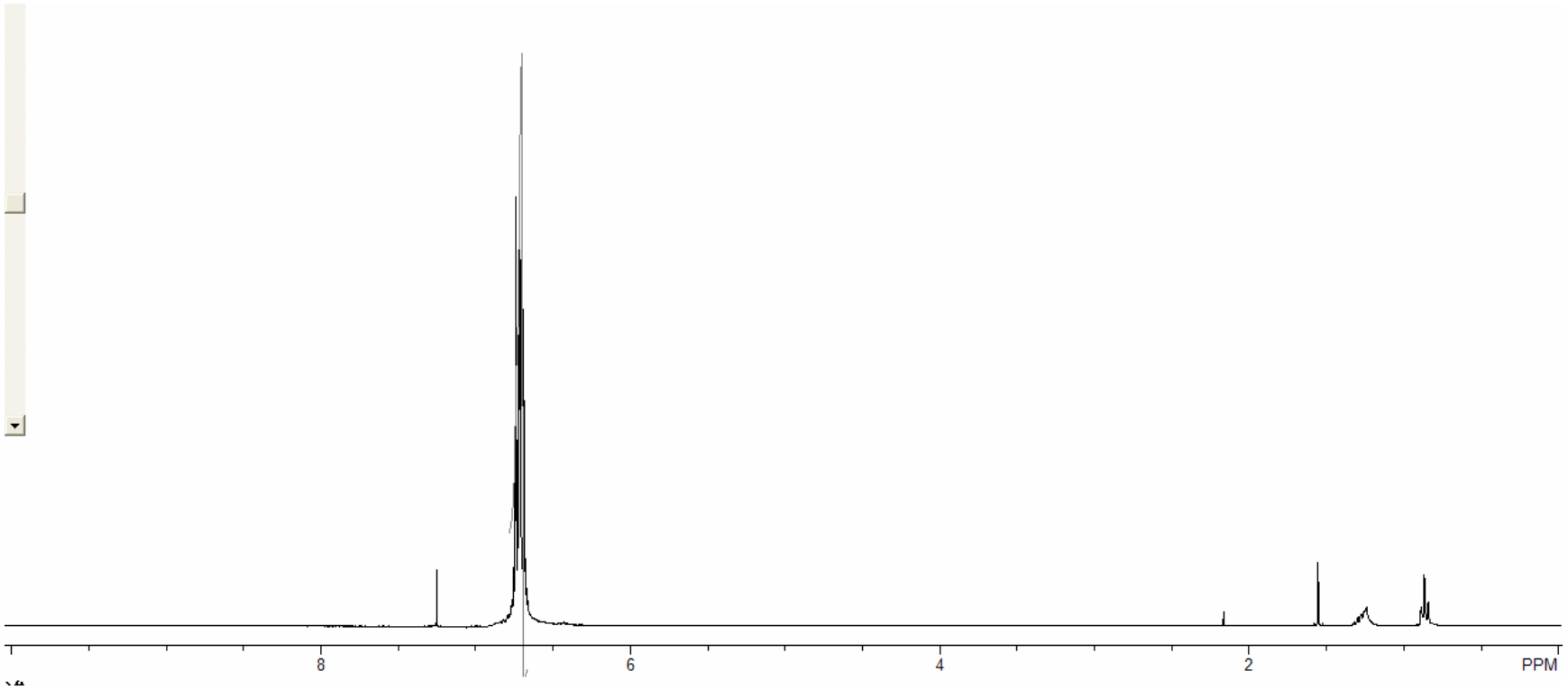

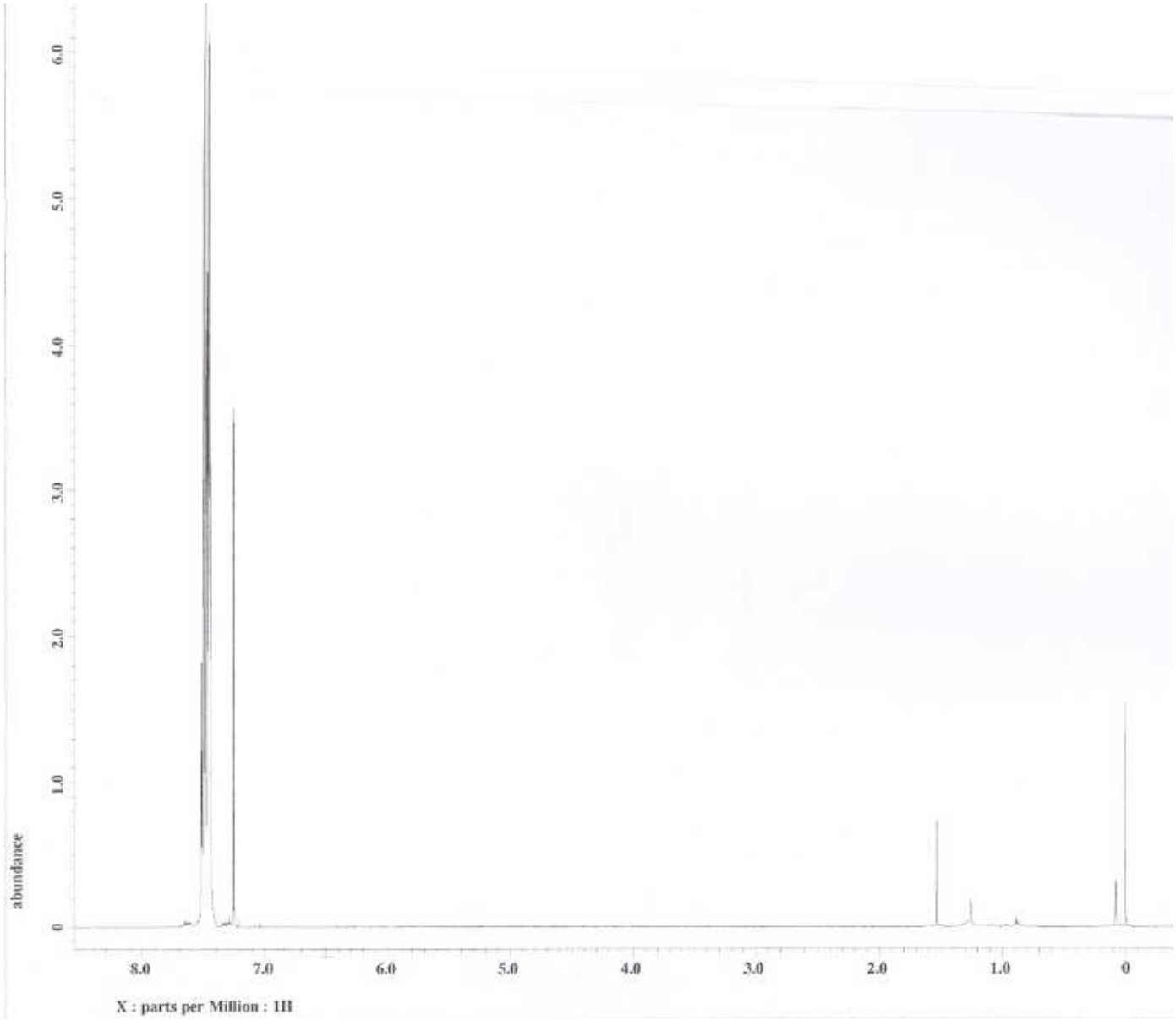

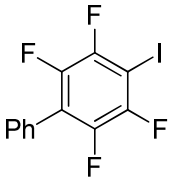

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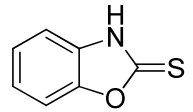

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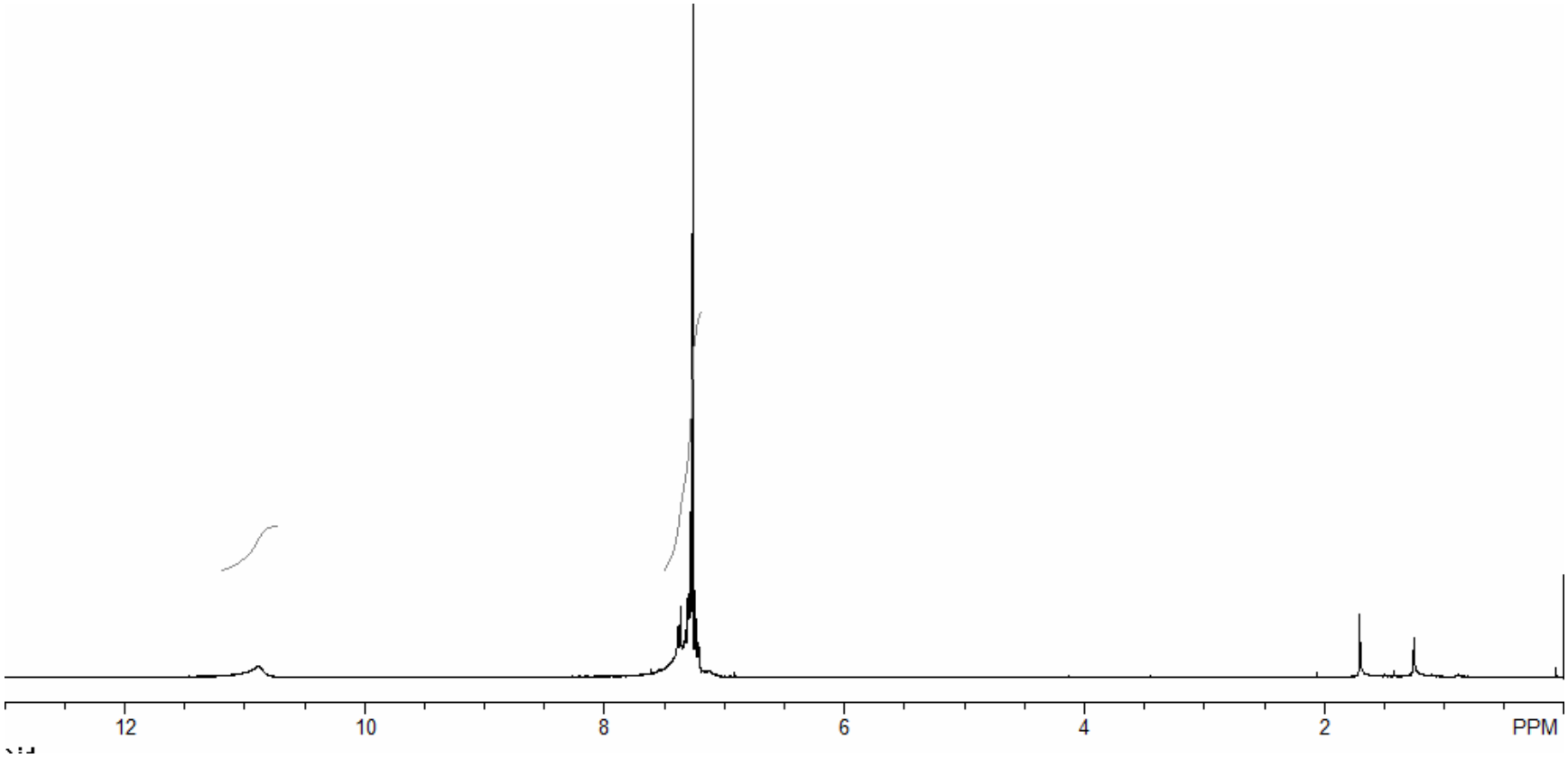

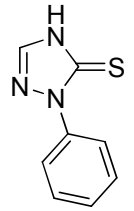

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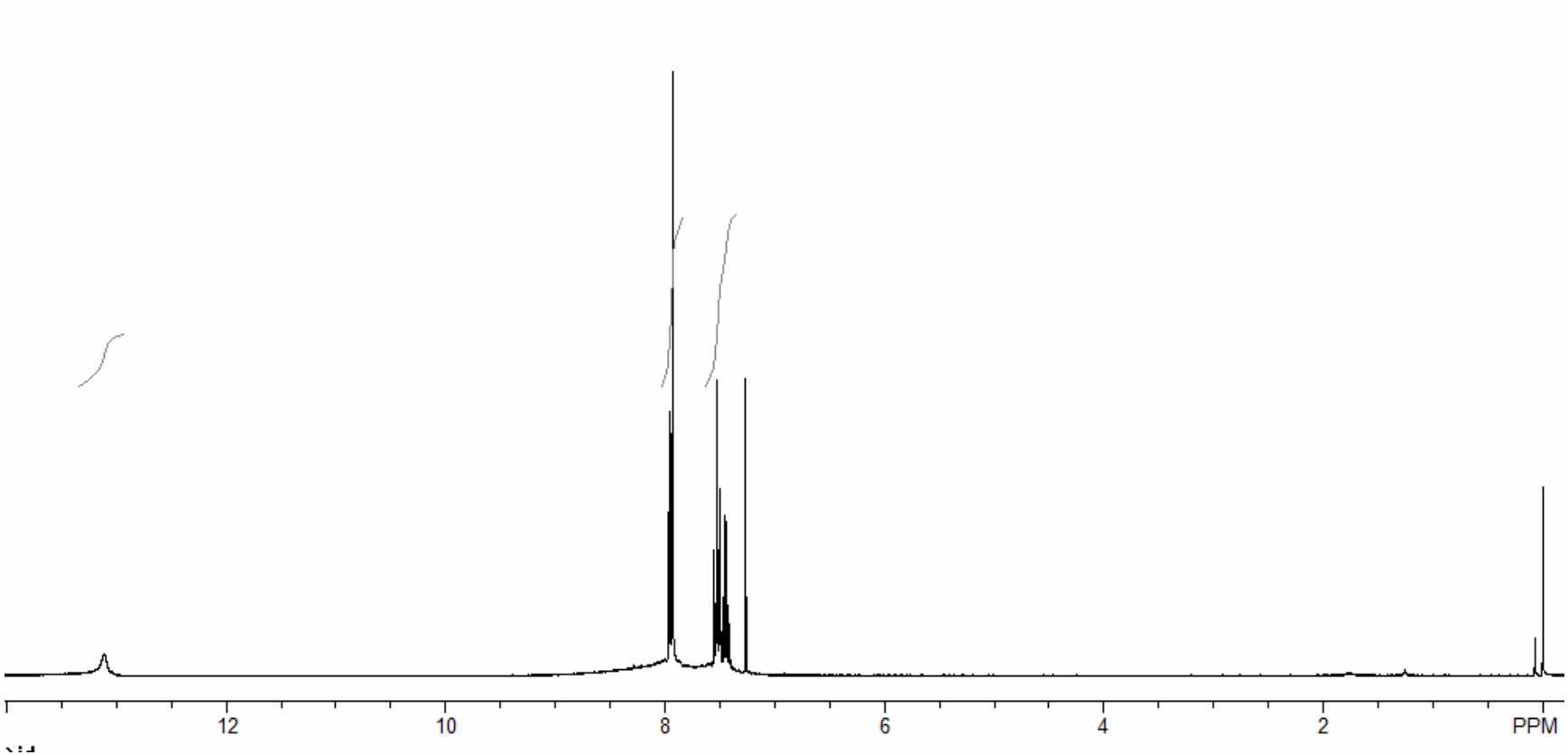

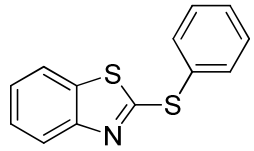

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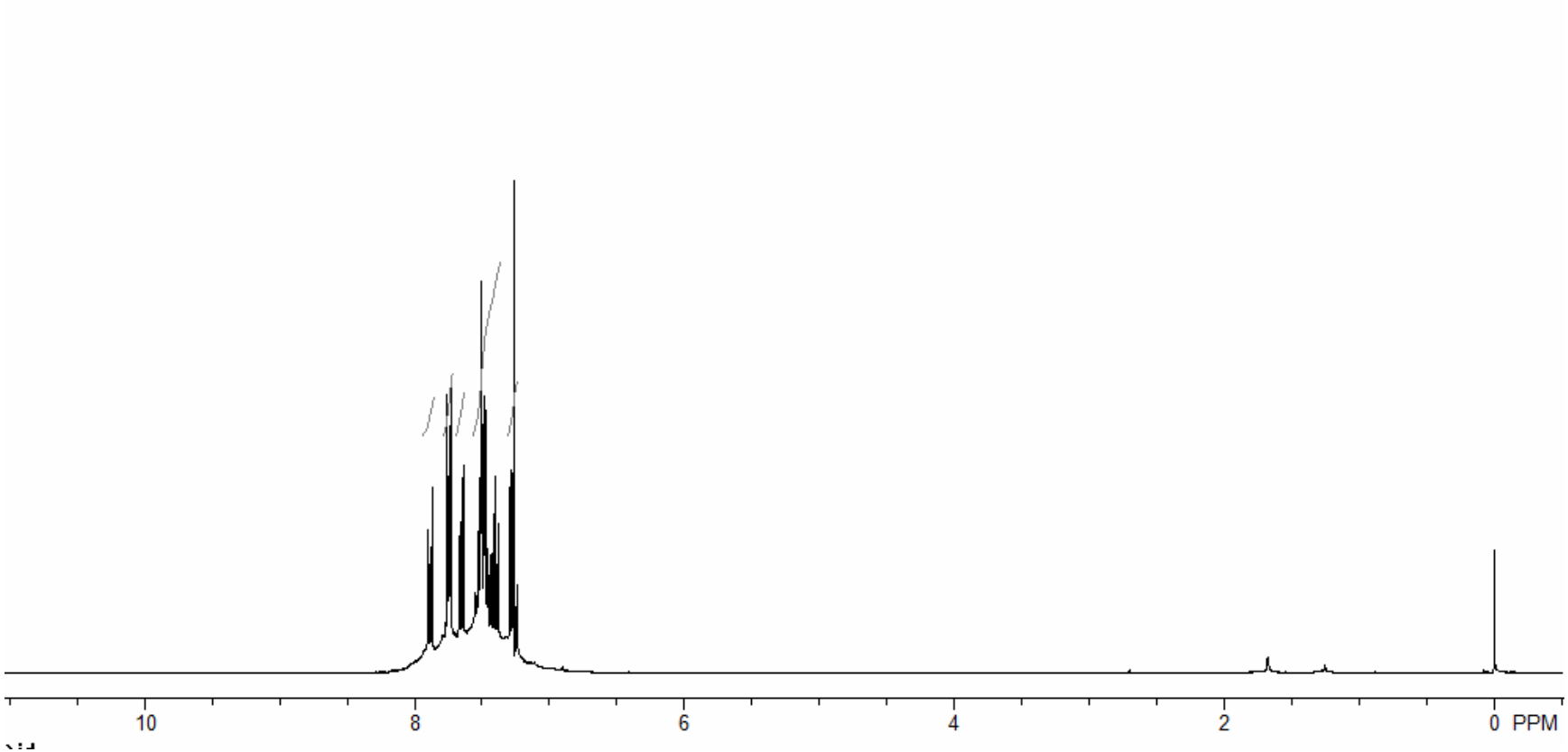

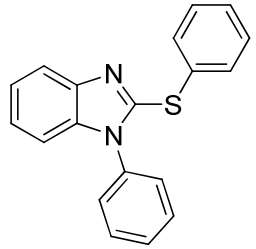

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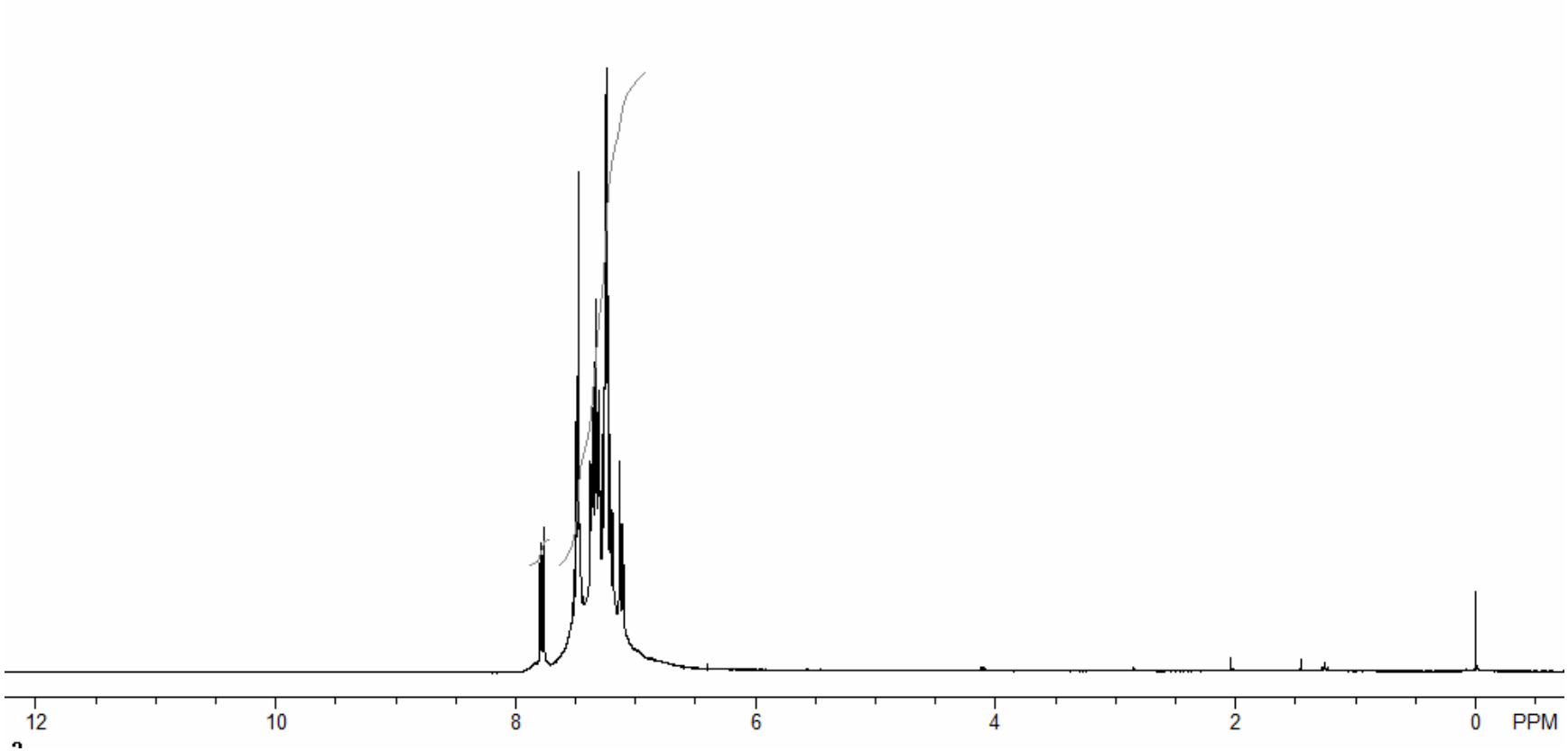

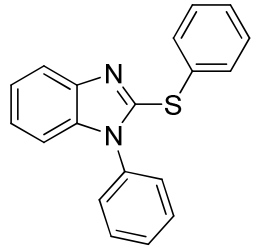

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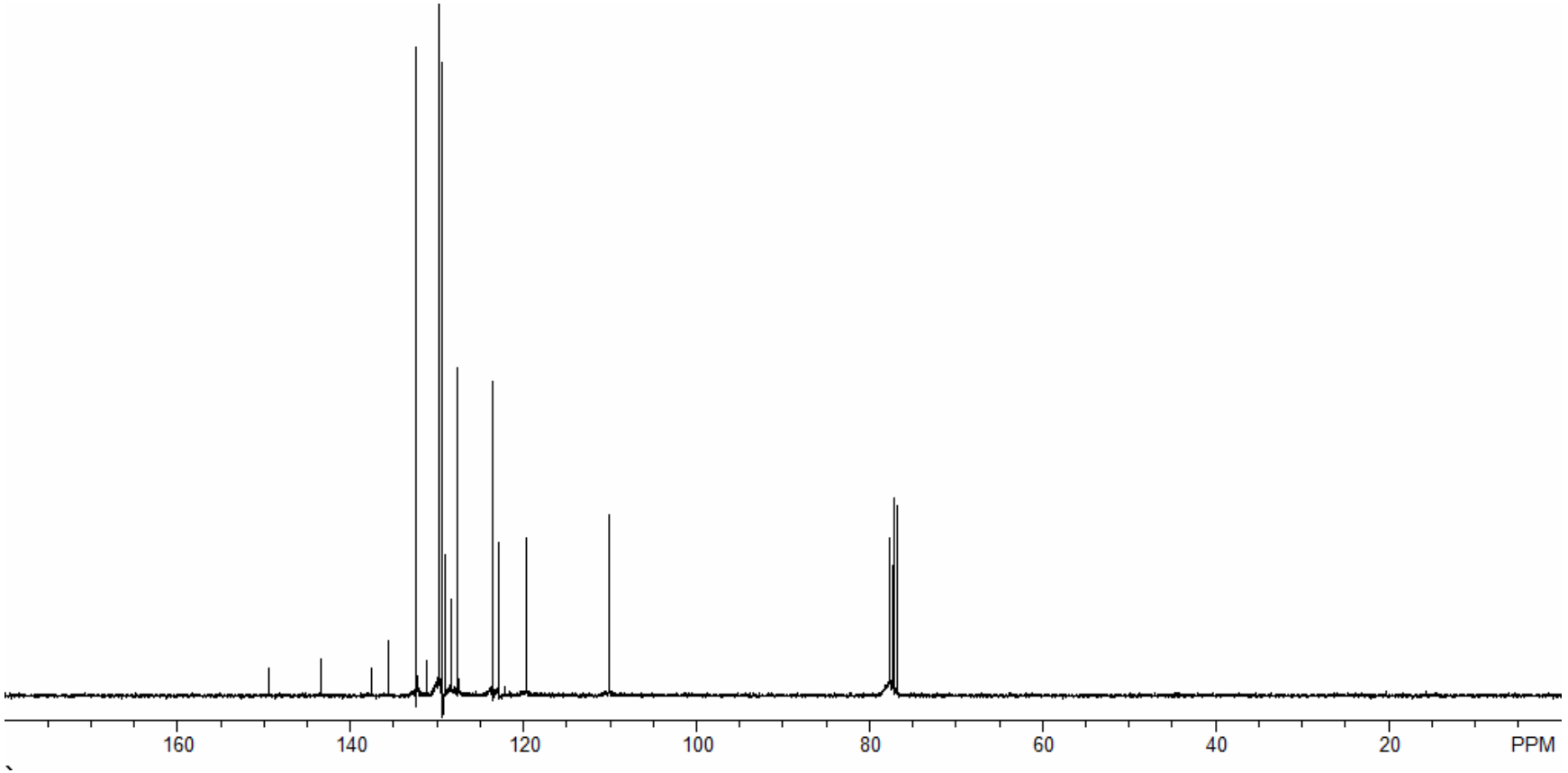

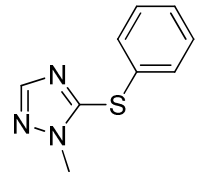

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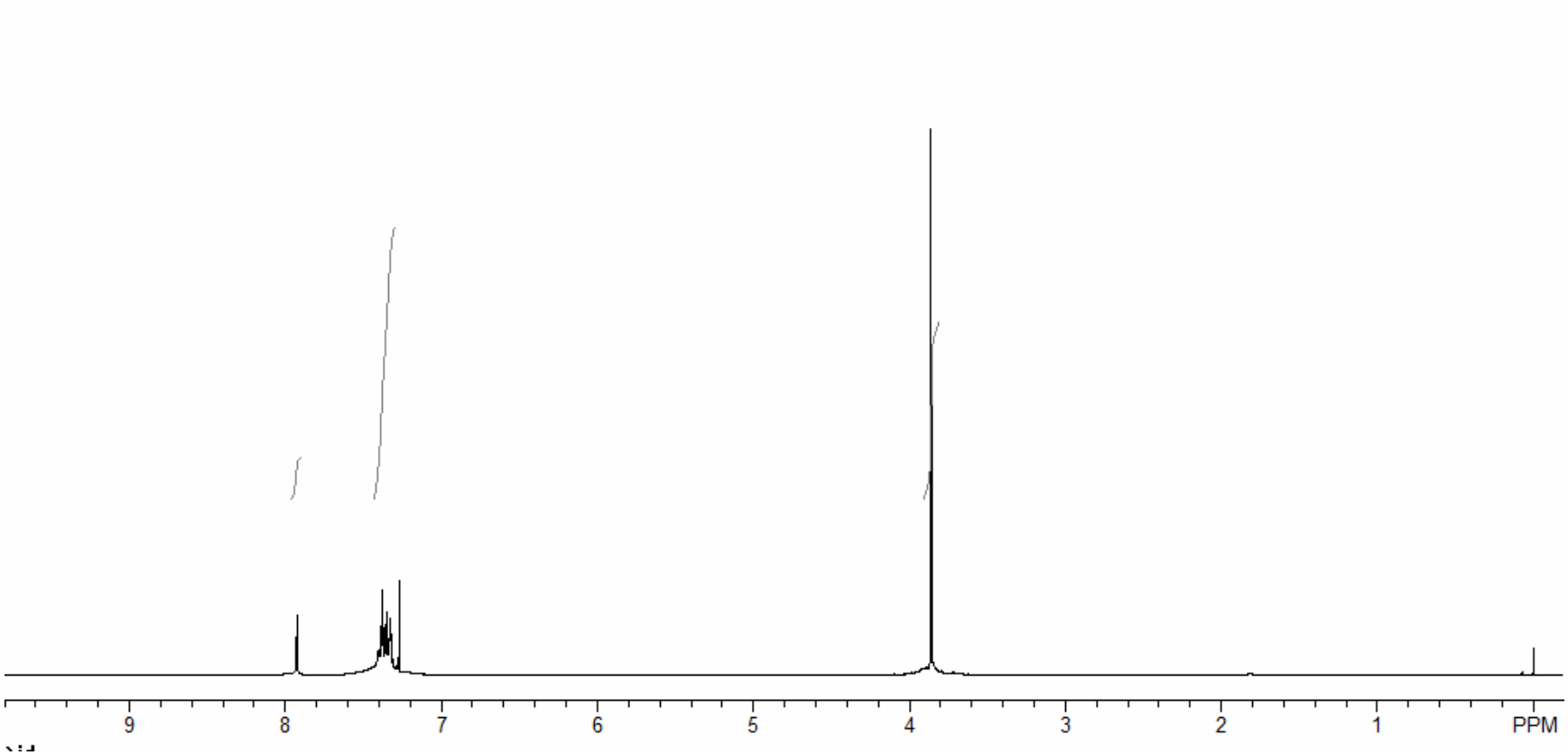

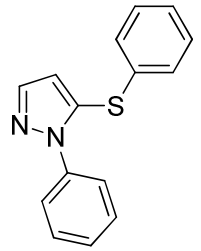

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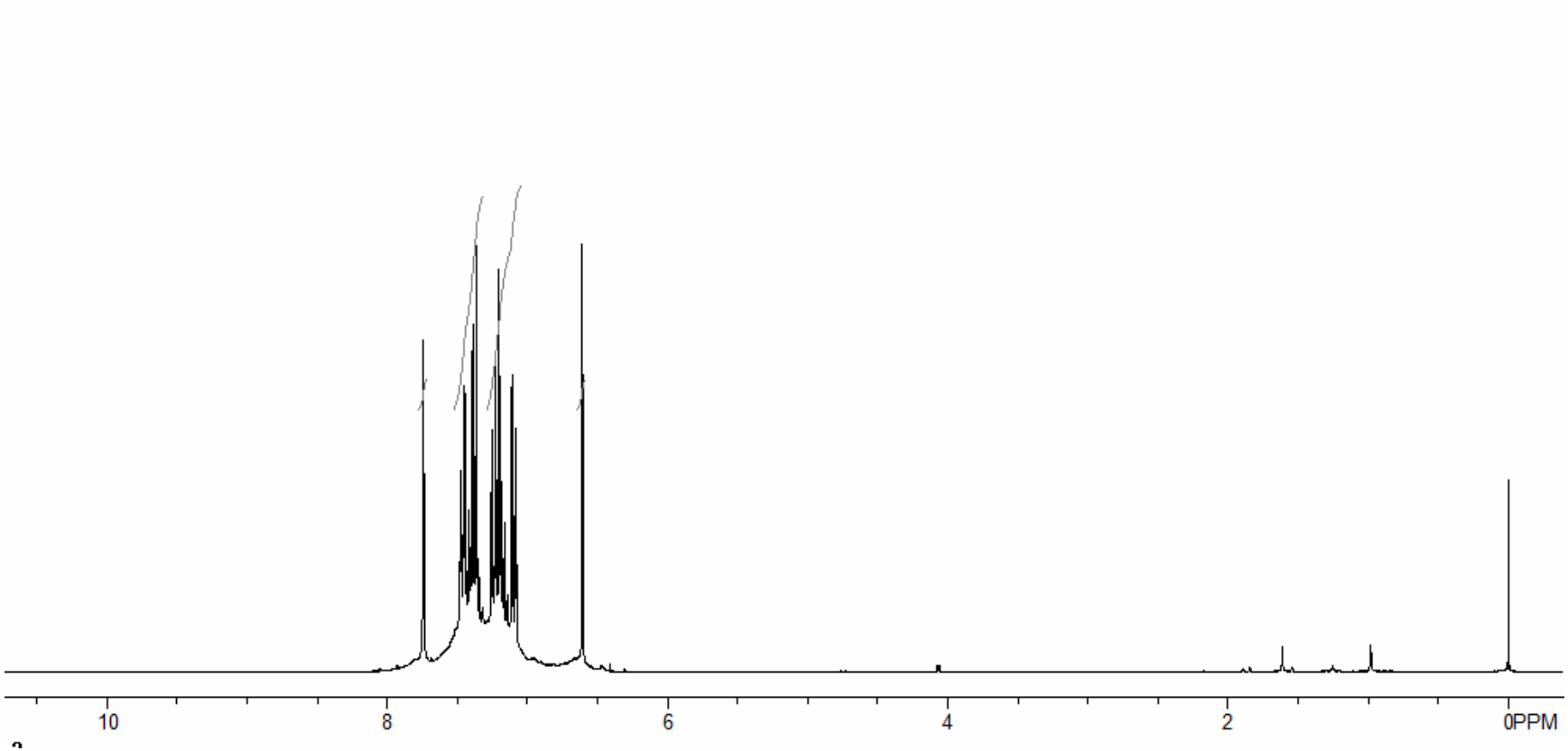

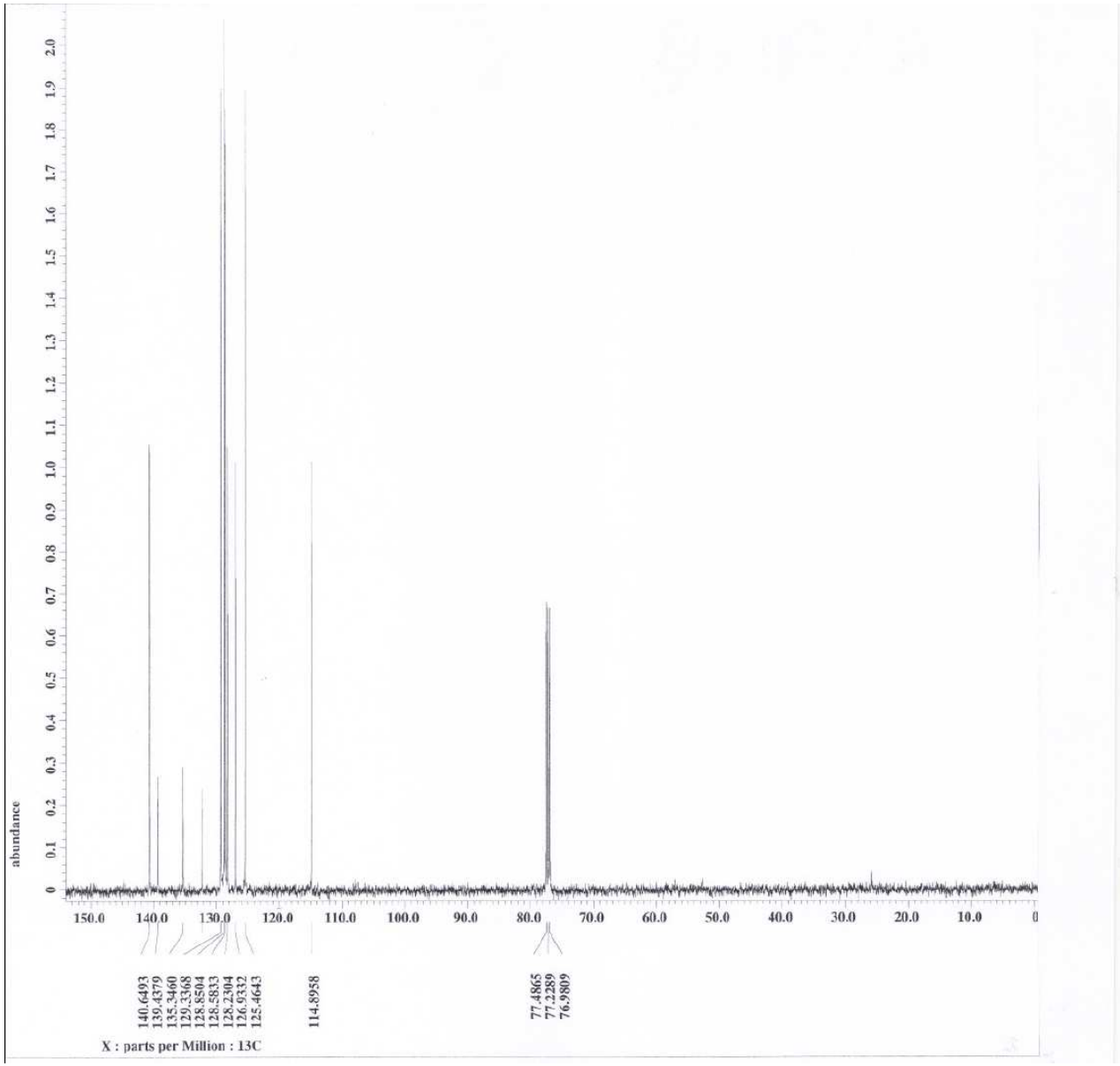

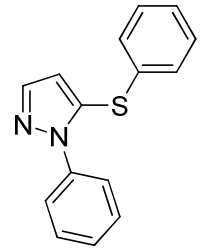

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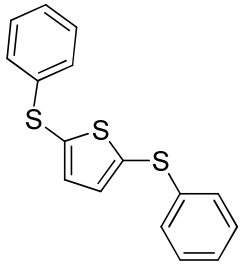

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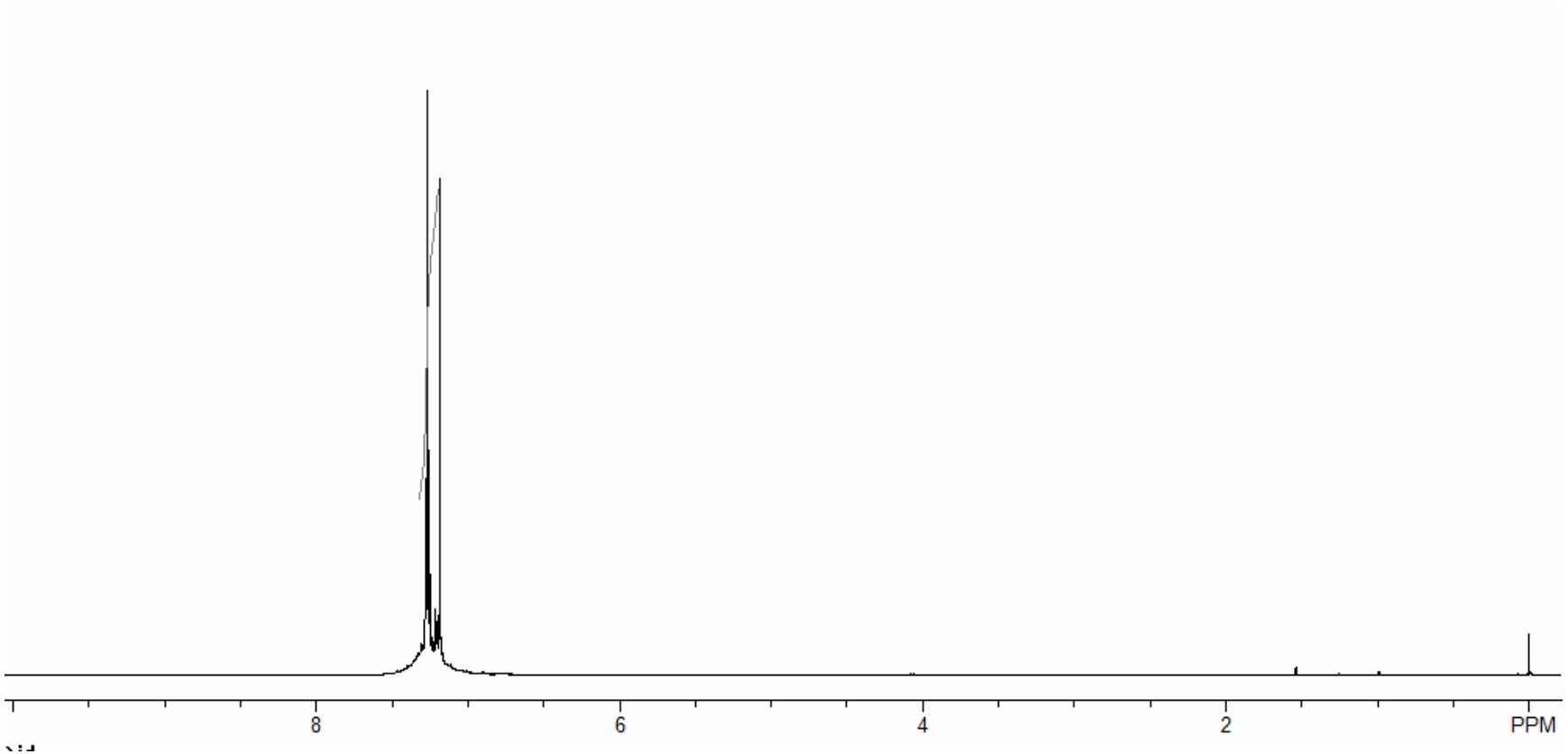

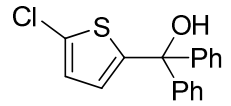

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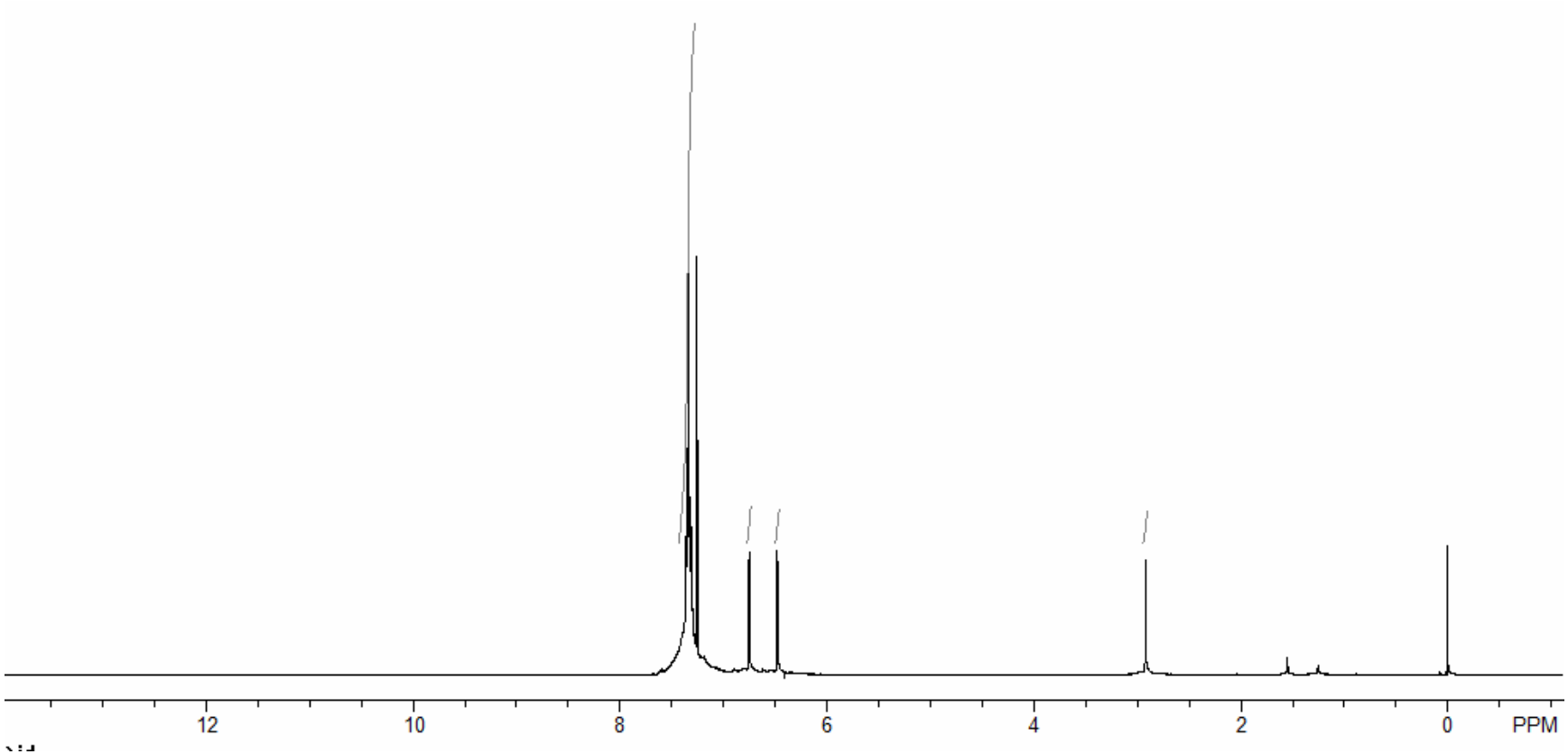

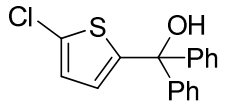

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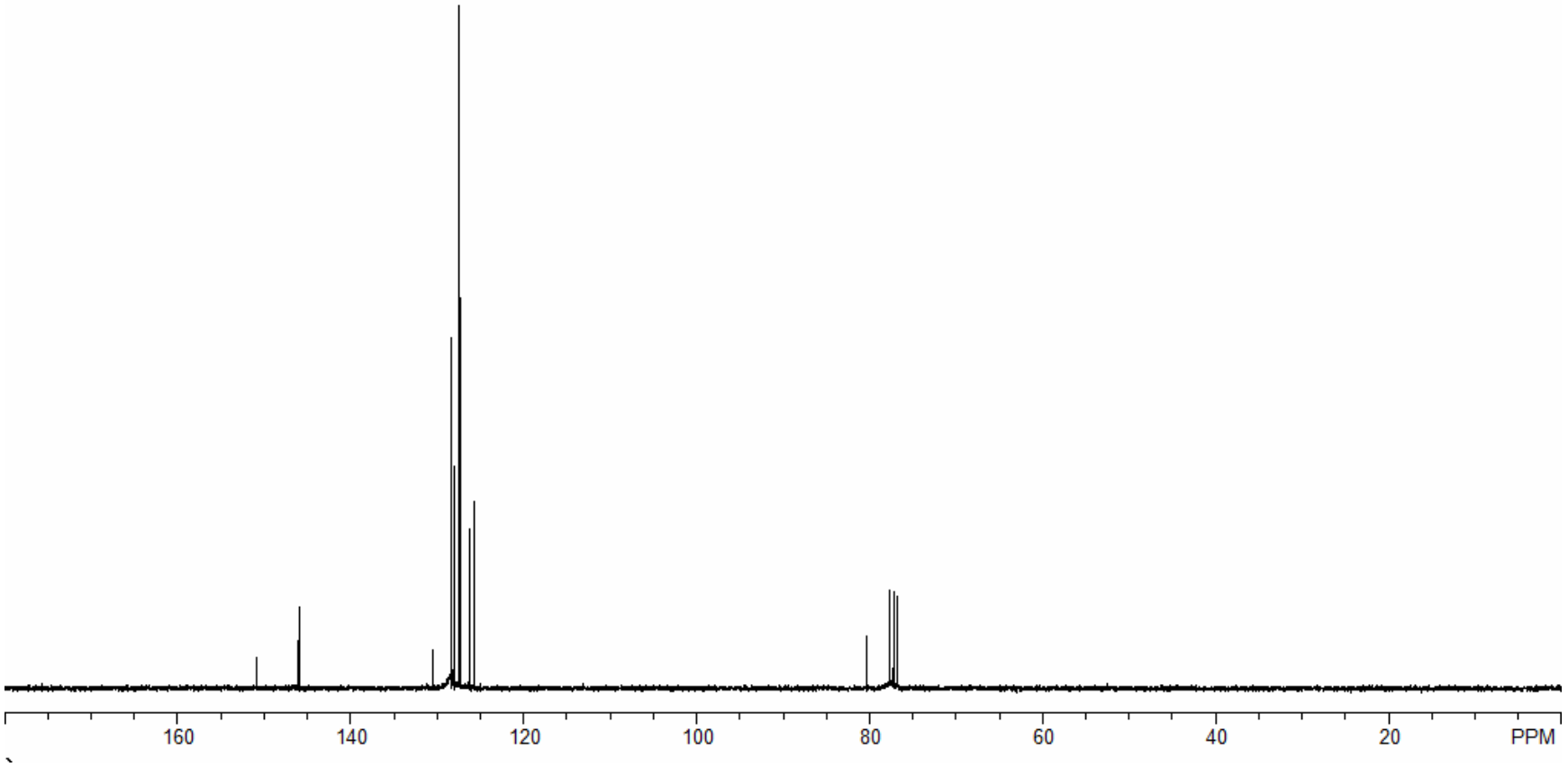

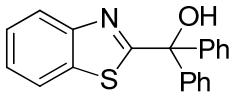

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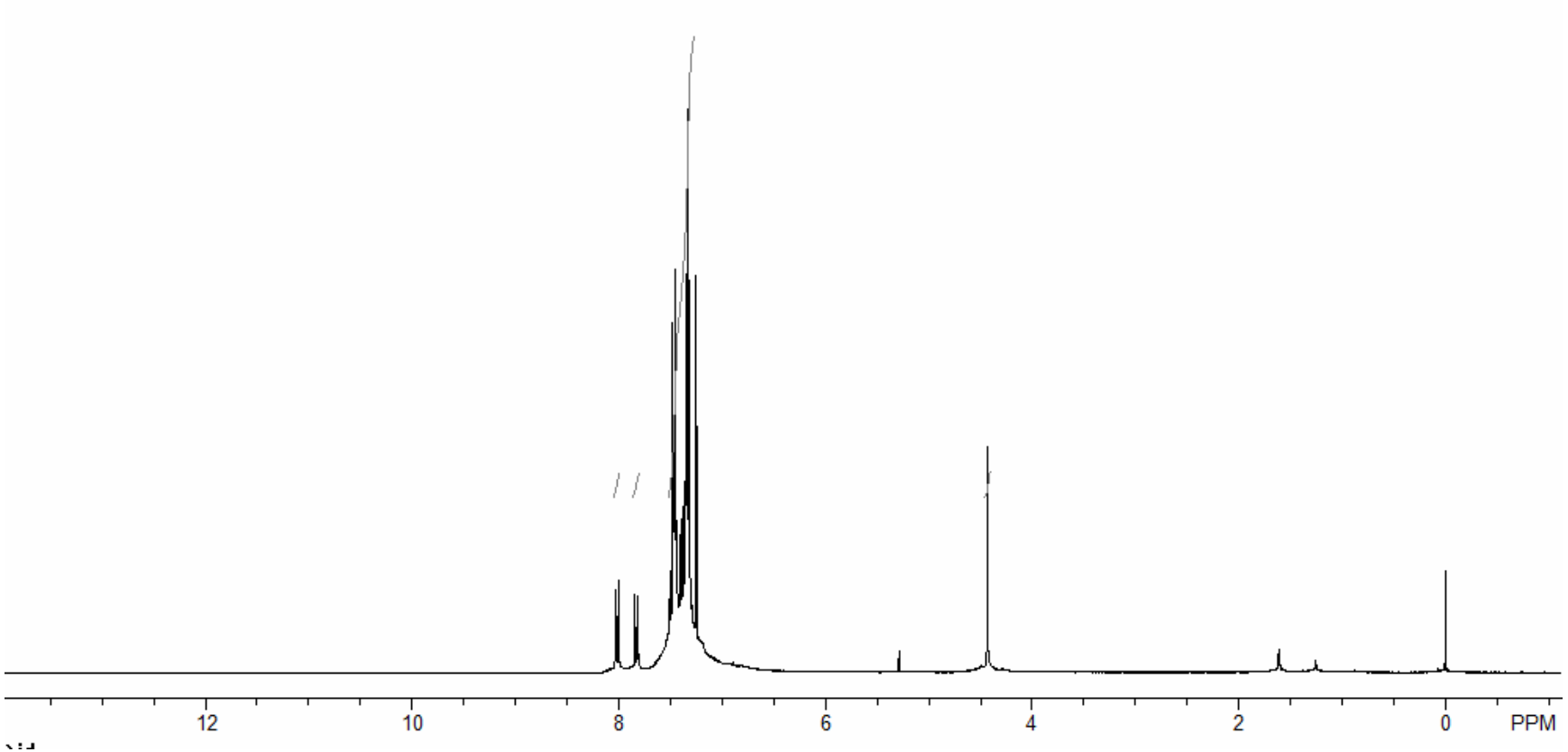

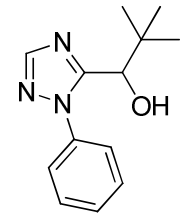

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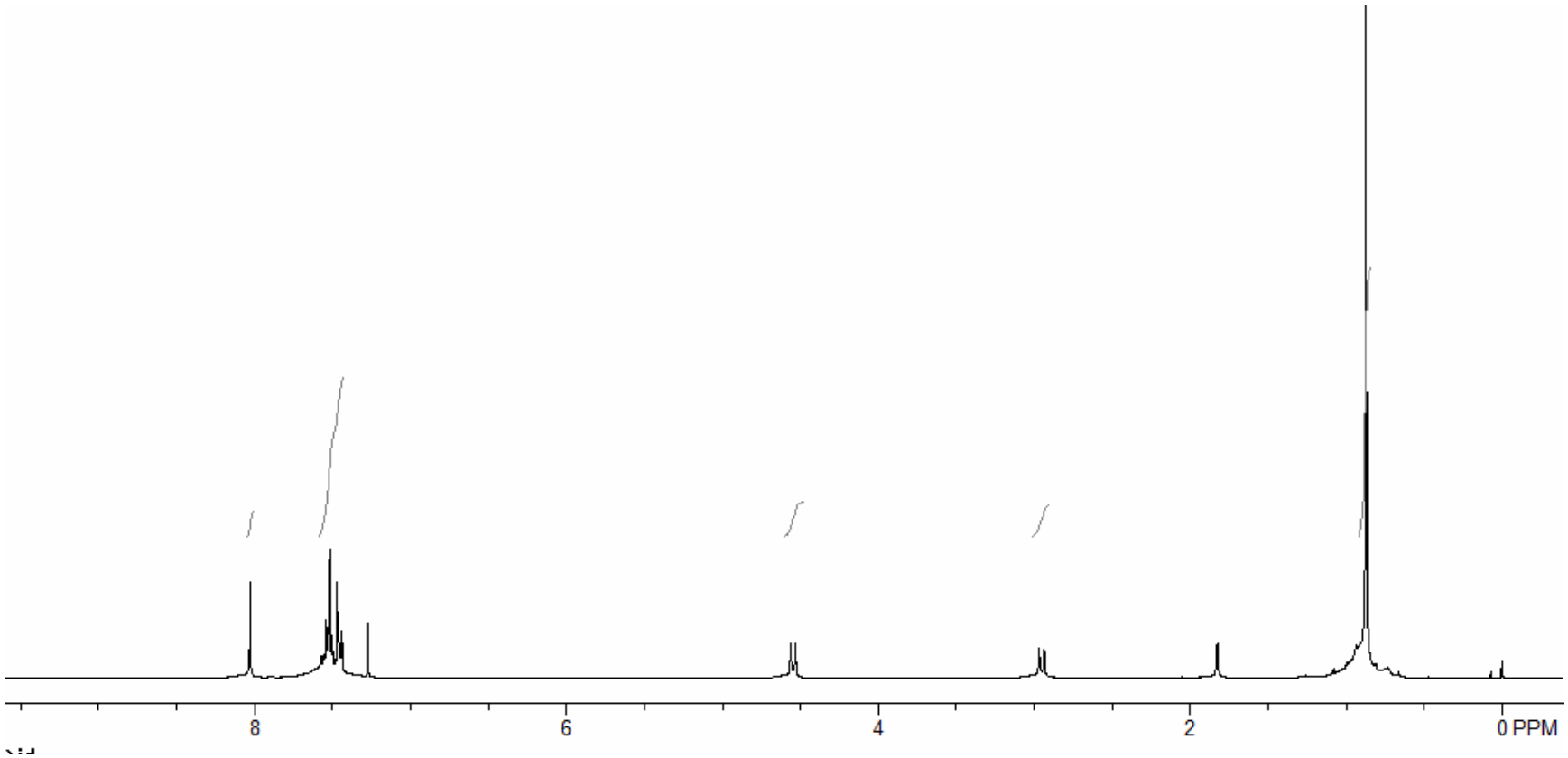

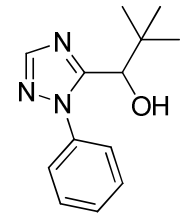

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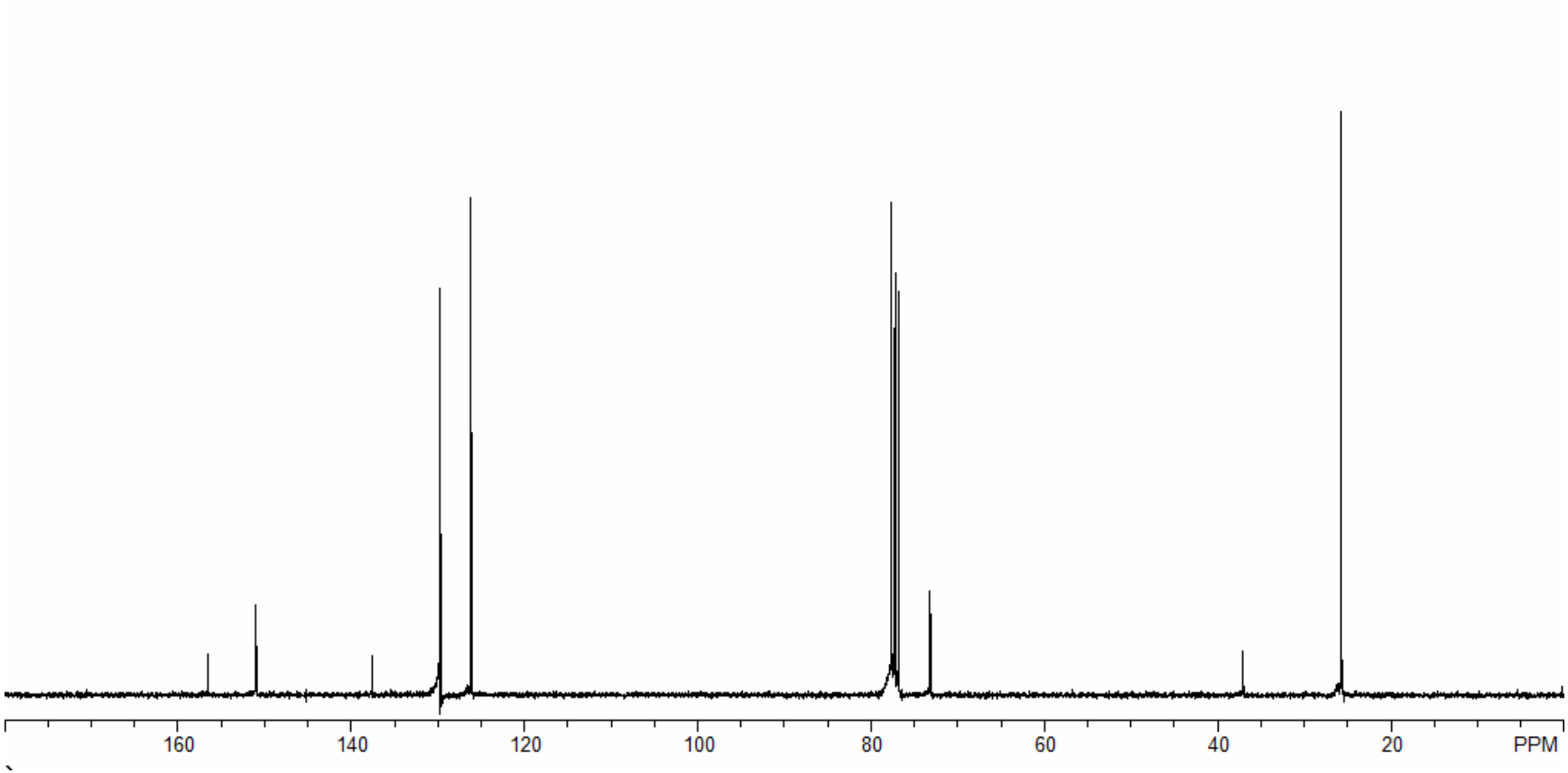

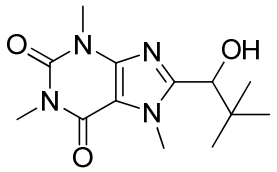

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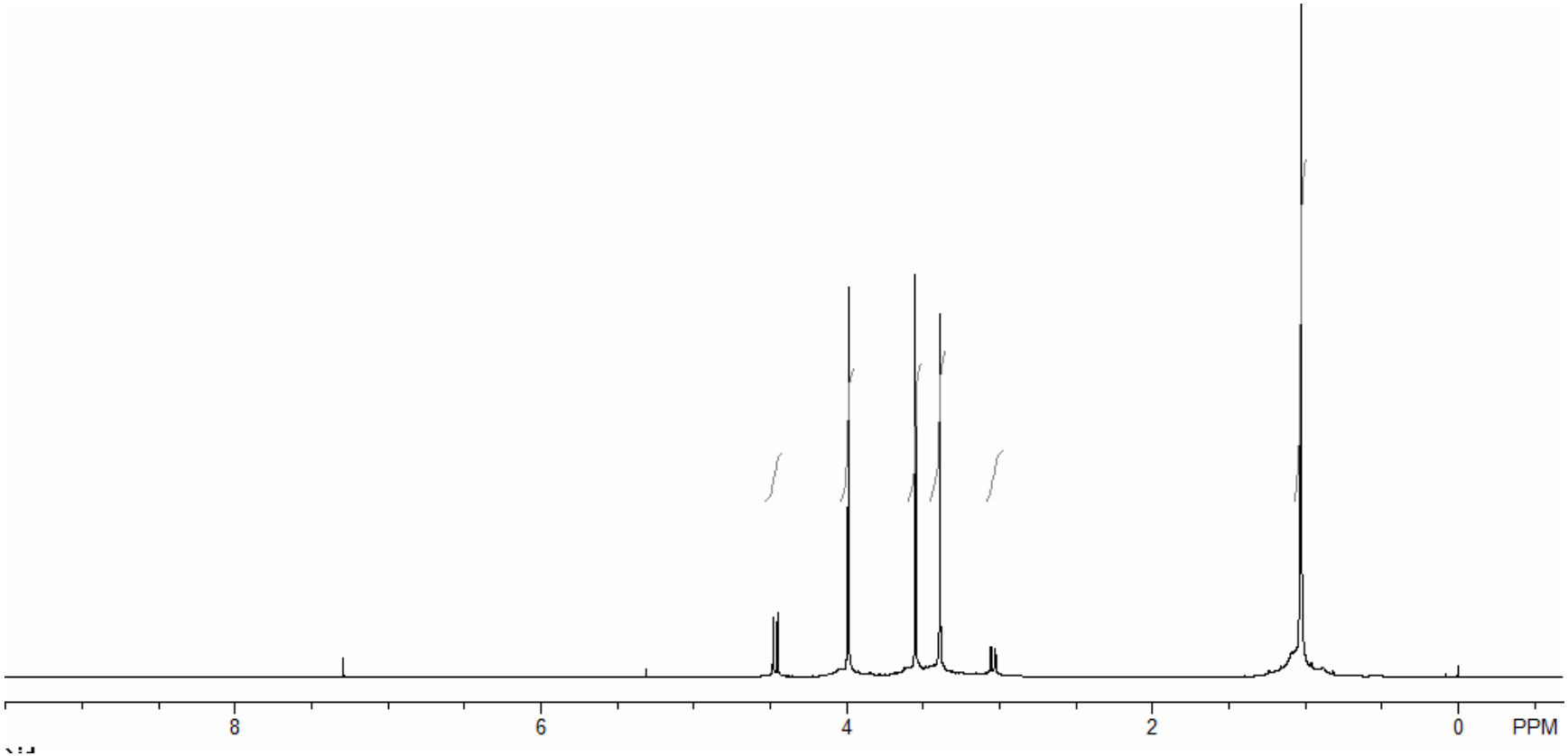

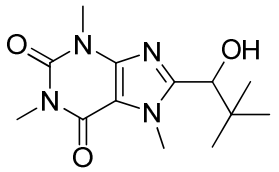

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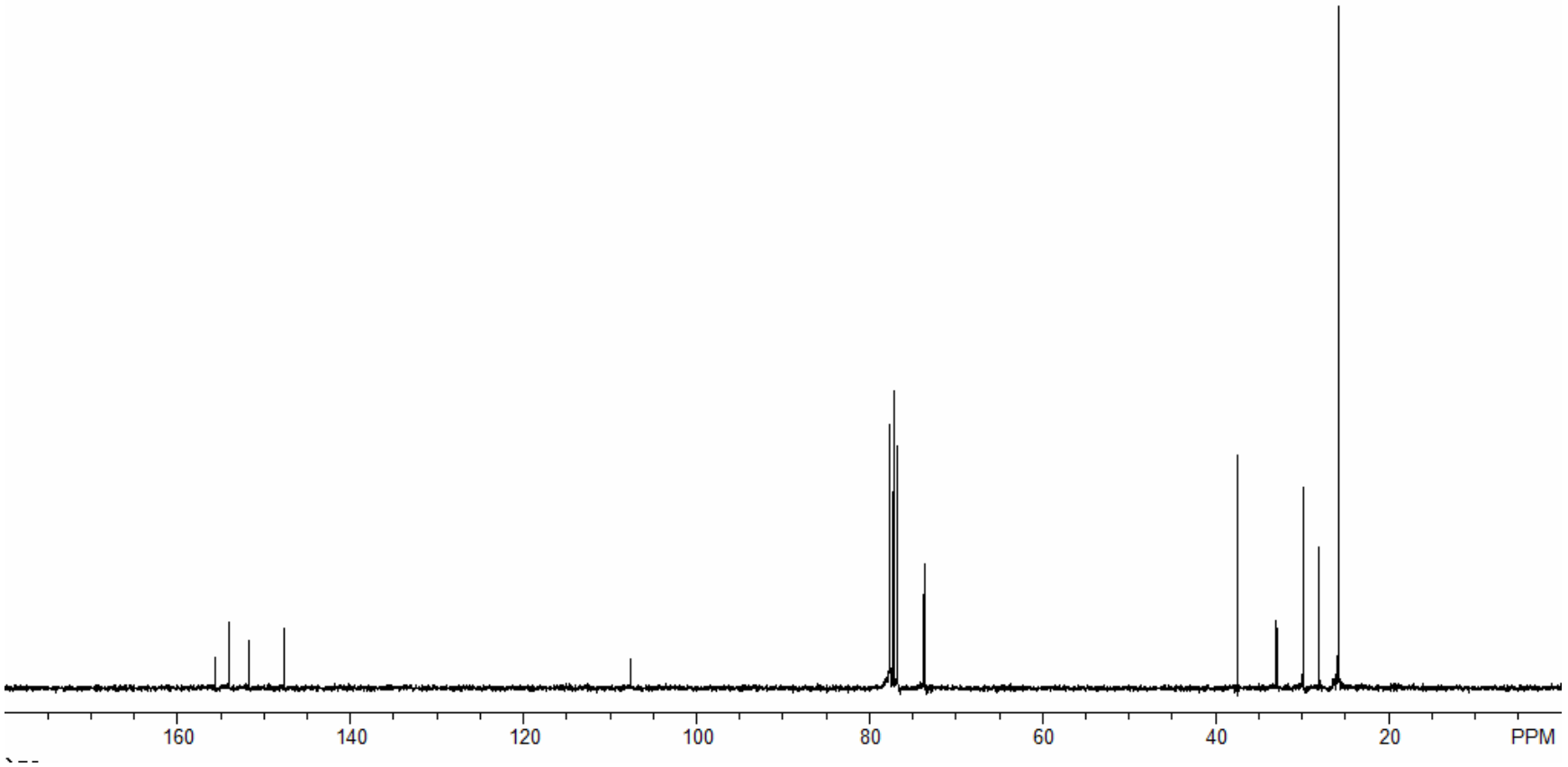

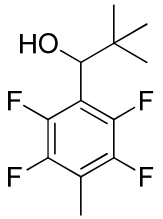

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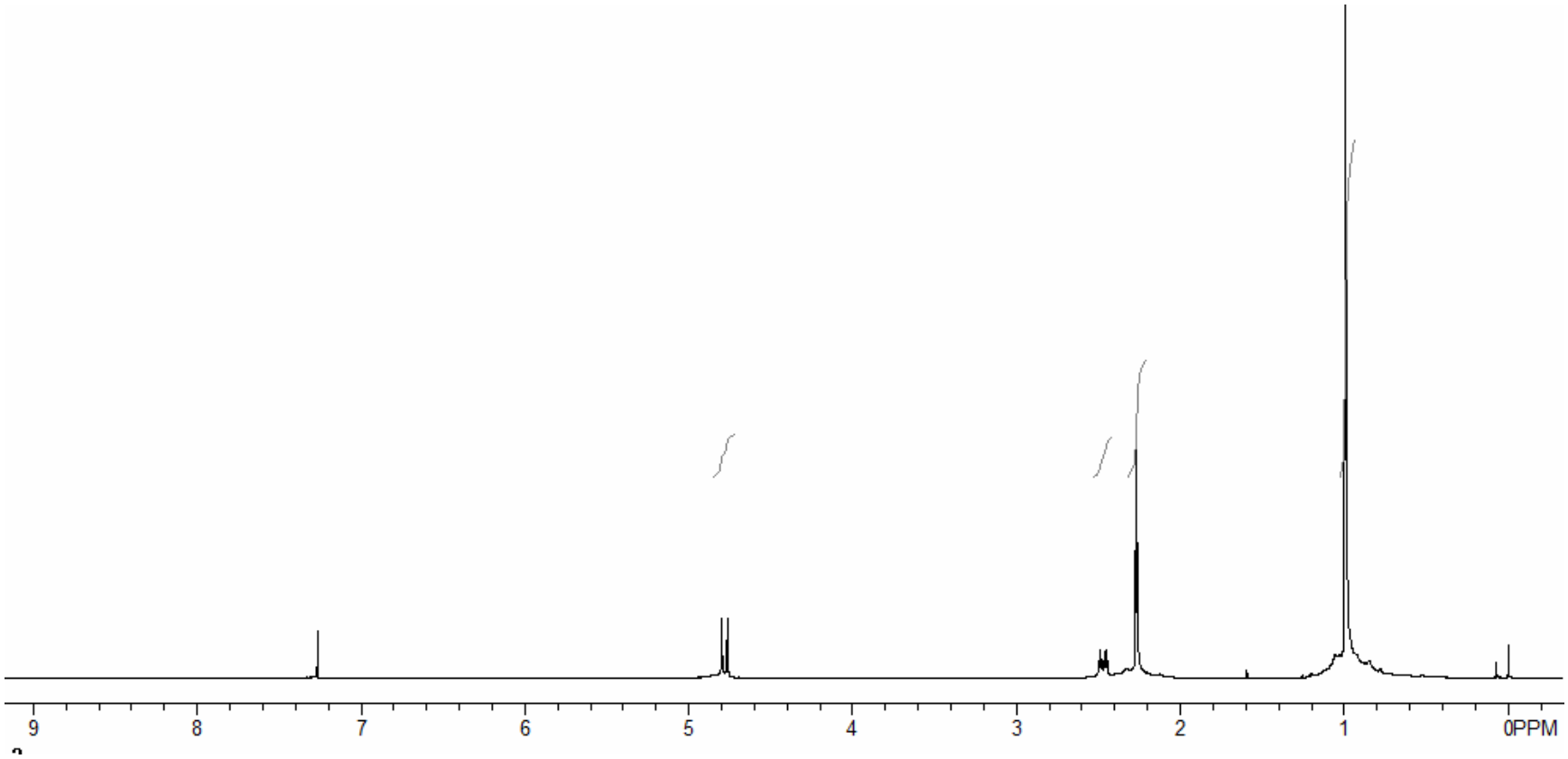

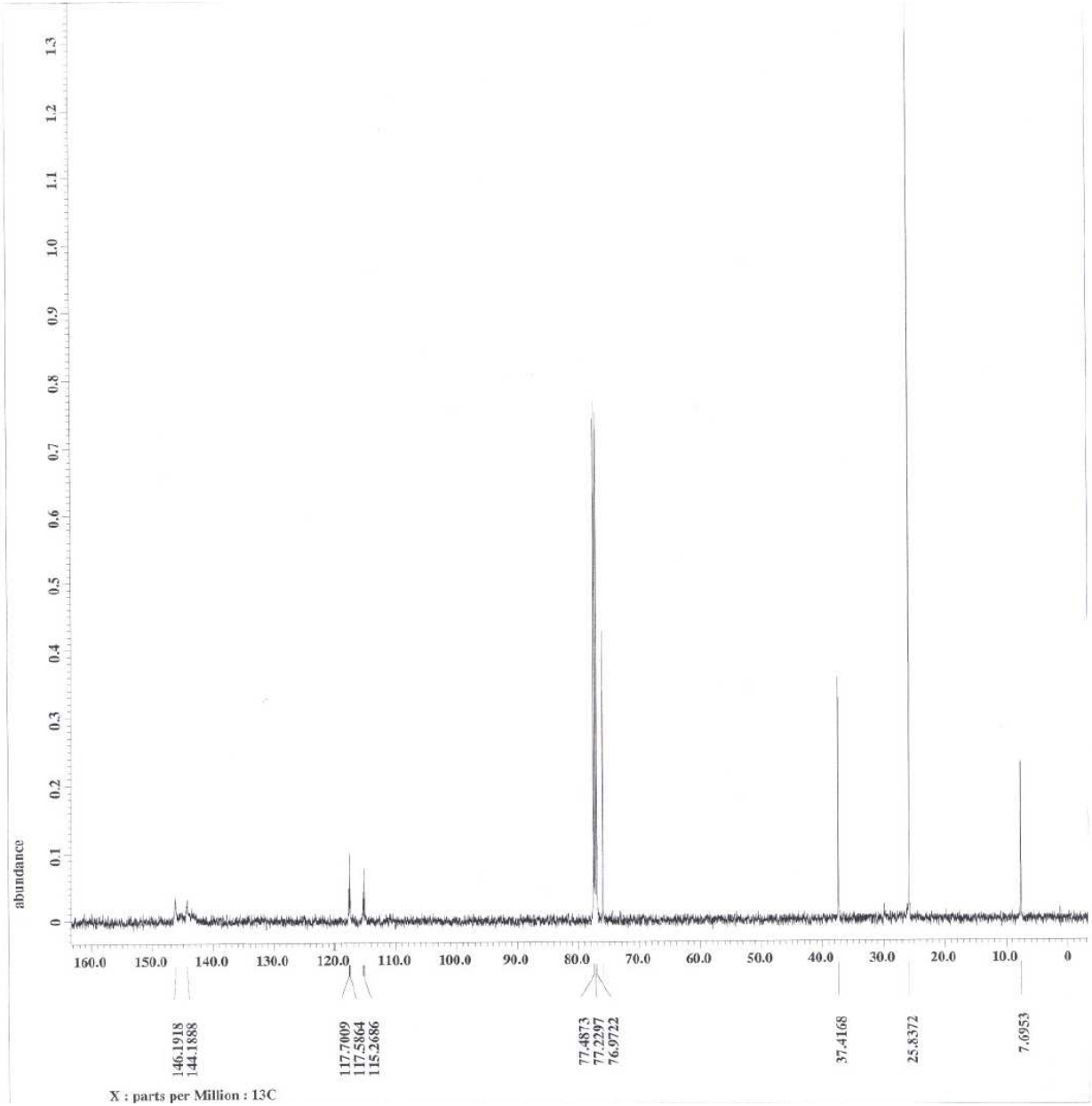

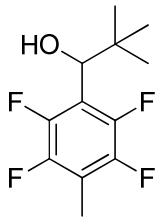

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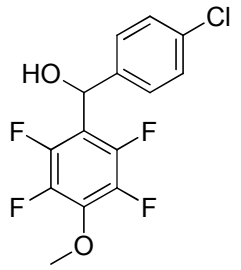

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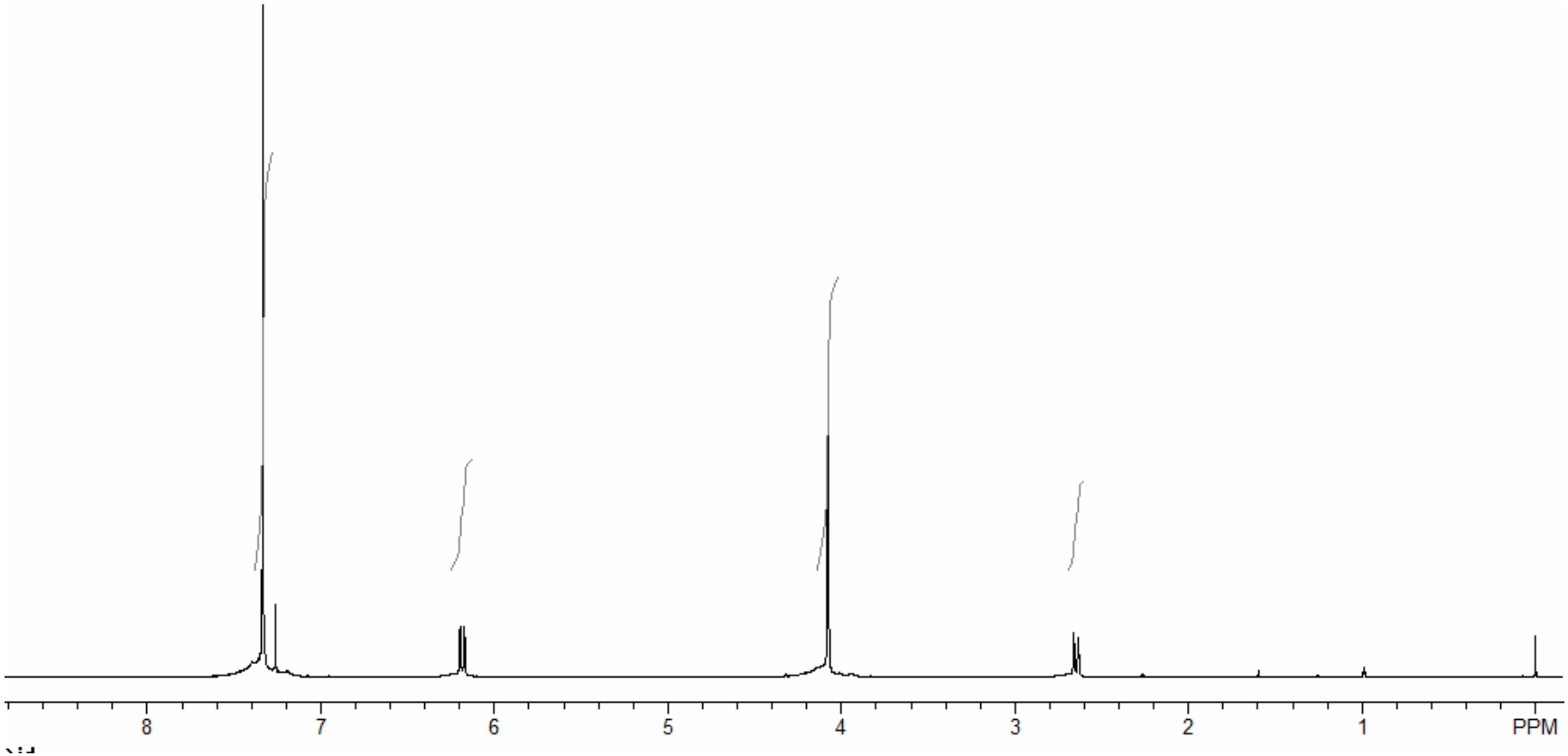

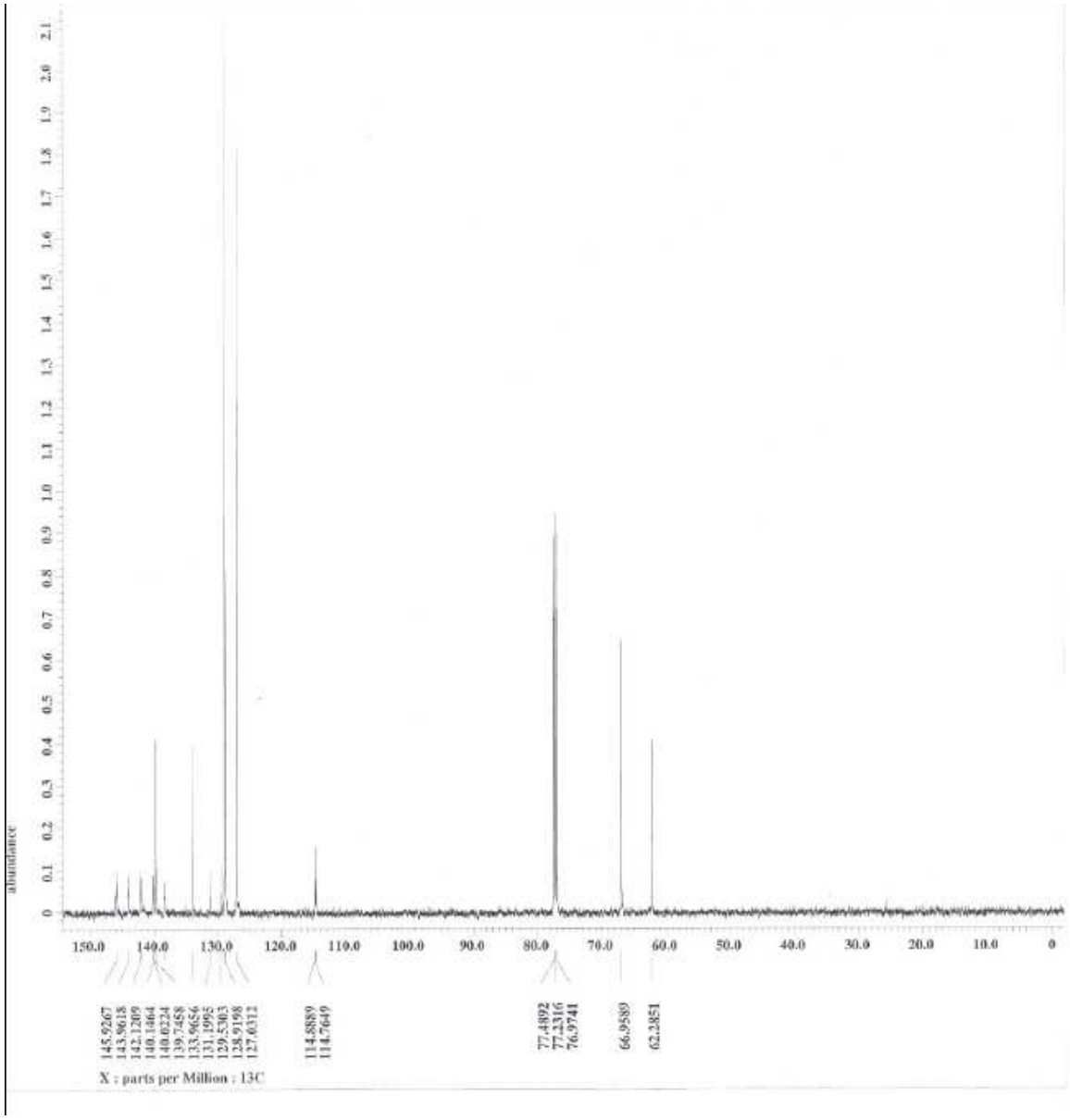

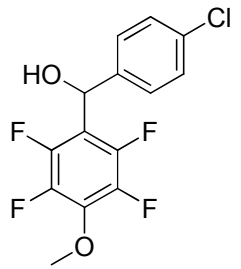

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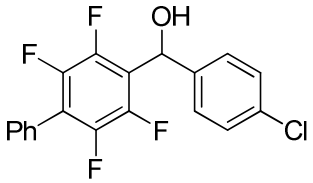

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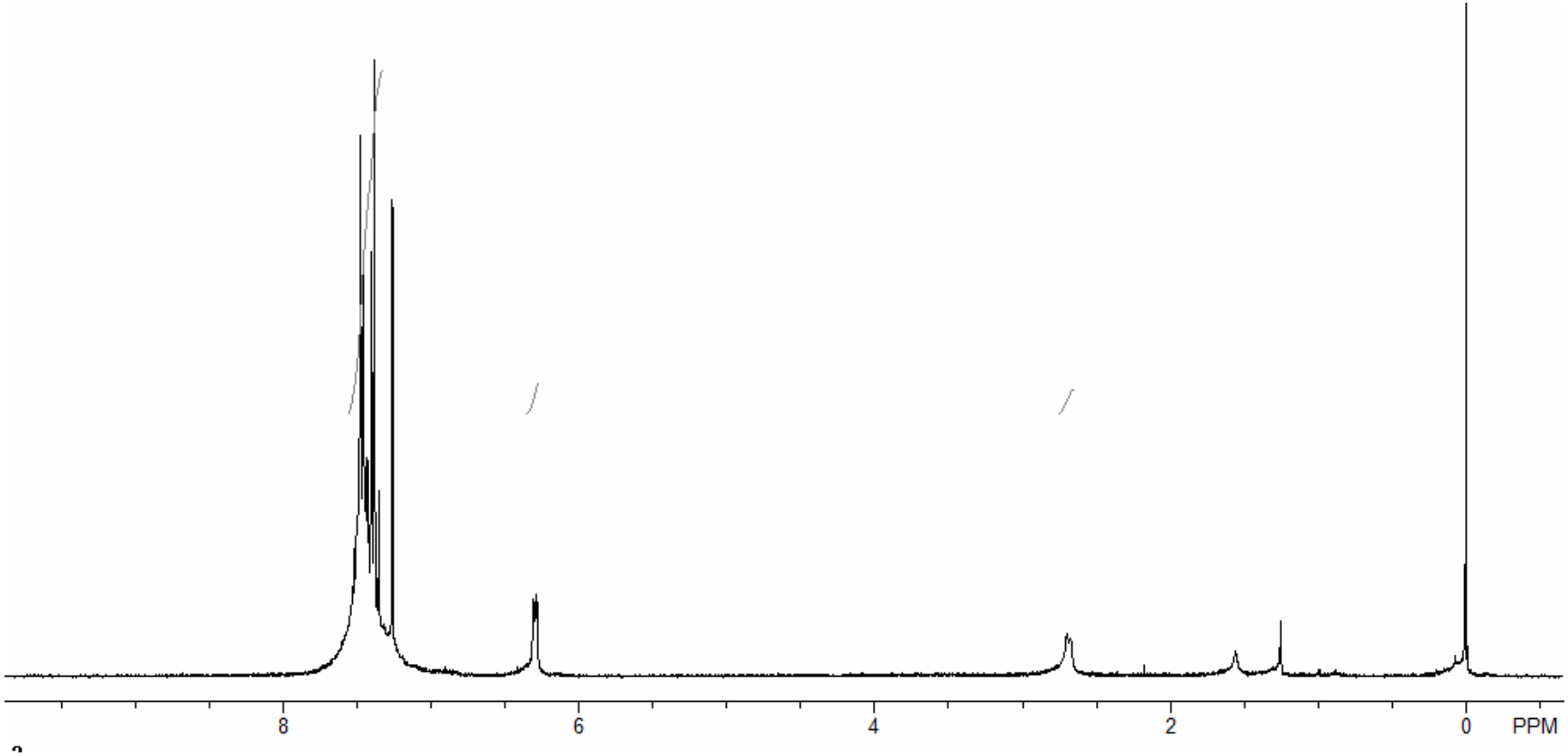

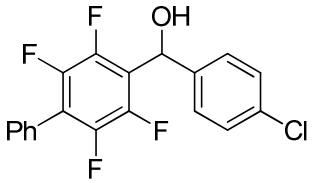

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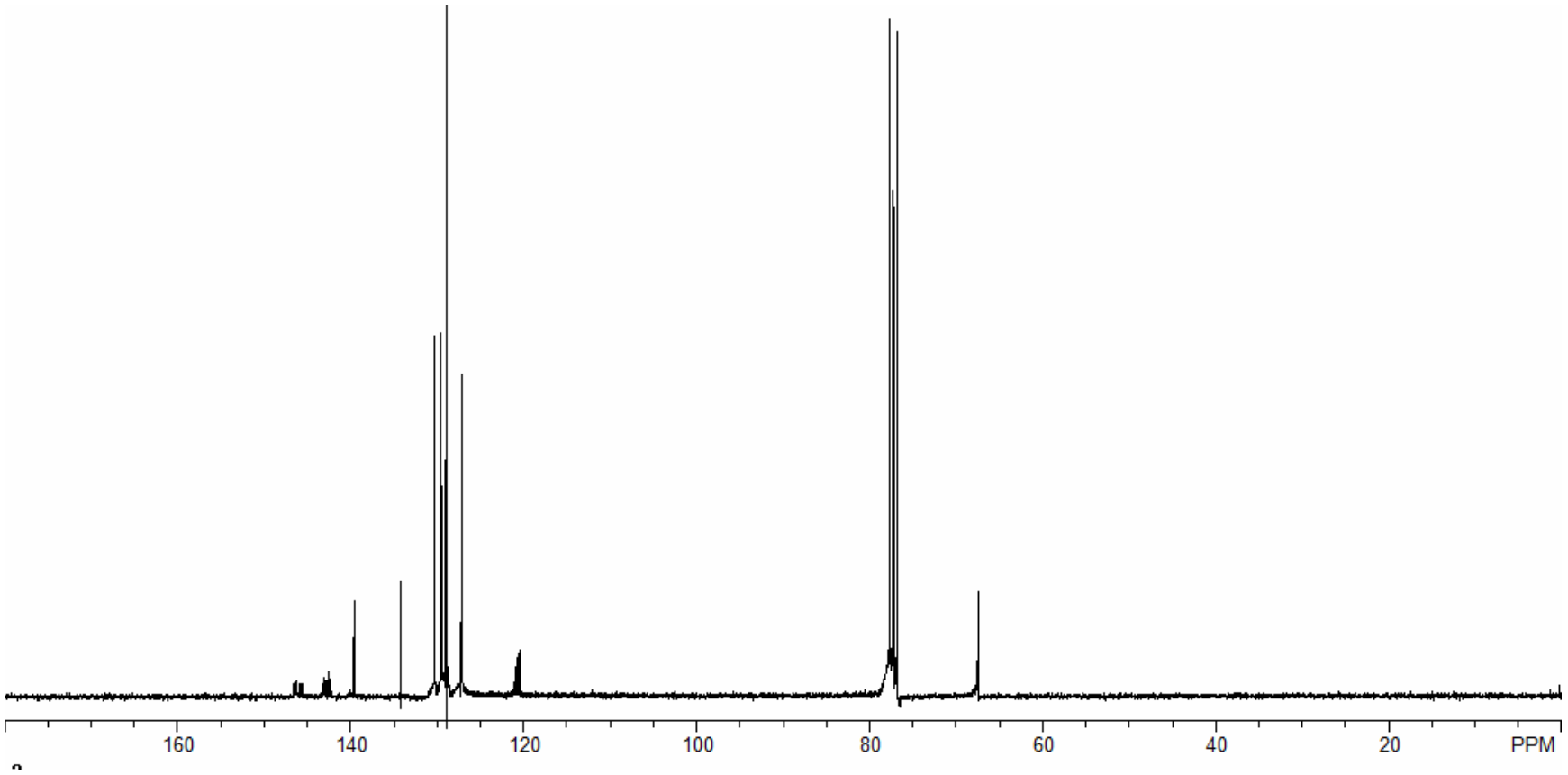

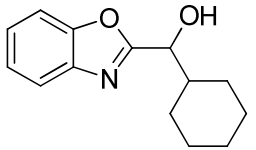

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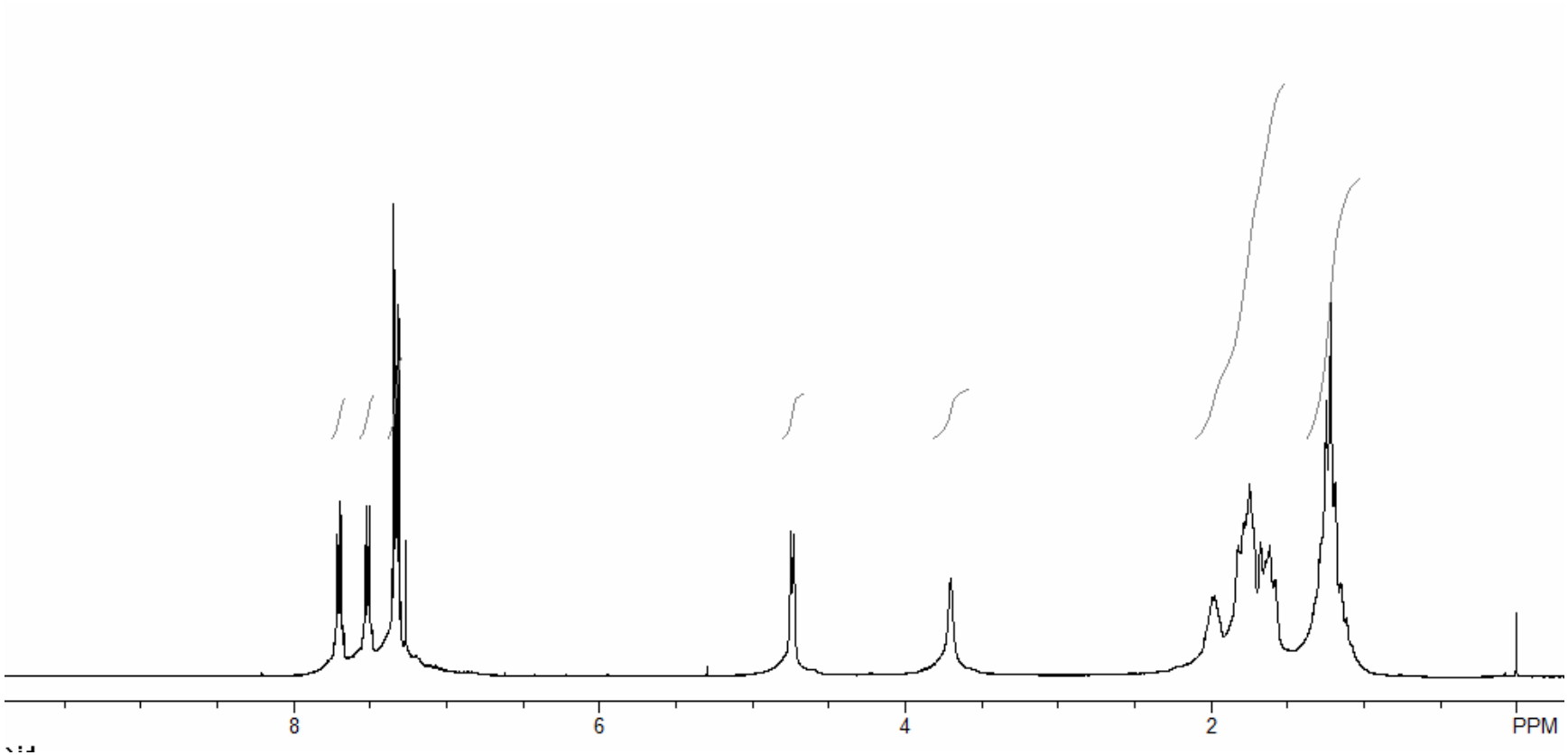

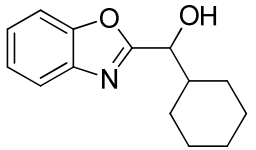

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