

**Highly active and magnetically retrievable nanoferrite-DOPA-copper catalyst for the
coupling of thiophenols with aryl halides**

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Supporting Information

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Experimental section

Synthesis of magnetic nano-ferrites

FeSO₄·7H₂O (13.9 g) and Fe₂(SO₄)₃ (20 g) were dissolved in 500 mL water in a 1000 mL beaker. Ammonium hydroxide (25%) was added slowly to adjust the pH of the solution to 10. The reaction mixture was then continually stirred for 1 h at 60 °C. The precipitated nanoparticles were separated magnetically, washed with water until the pH reached 7, and then dried under vacuum at 60 °C for 2 h. Ferrite was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). This magnetic nano-ferrite (Fe₃O₄) was then used for further chemical modification.

Surface modification of nano-ferrites (nano-FeDOPA)

Nano-Fe₃O₄ (2 gm) was dispersed in 25 mL water by sonication for 30 min. Dopamine hydrochloride (1 gm) dissolved in 5 mL of water was added to this solution and again sonicated for 2 h. The amine-functionalized nanomaterial was then precipitated using acetone, isolated by centrifugation, and dried under vacuum at 60 °C for 2 h.

Synthesis of nano-FeDOPACu, catalyst

Amine-functionalized nano-Fe₃O₄ (1 gm) was dispersed in water-methanol mixture (1:1). CuCl₂·2H₂O (100 mg) solution in water was added to the reaction mixture. Hydrazine monohydrate solution in water was added drop wise to bring the pH of this mixture to 9, followed by the addition of 0.1 gm of NaBH₄. The reaction mixture was then stirred for 24 h at room temperature. The product was allowed to settle, washed several times with water and acetone, and dried under vacuum at 60 °C for 2 h. Catalyst characterization by X-ray diffraction (XRD) (Fig. 1d) and transmission electron microscopy (TEM) (Fig. 1c) confirm the anchoring of Cu nanoparticles on ferrite surfaces. The weight percentage of Cu in the catalyst was found to be 0.82% by ICP-AES analysis.

Synthesis of diary sulfide

Aryl halide (1.0 mmol), thiophenol (1.2 mmol) and nano-FeDOPACu catalyst (100 mg) were placed in a crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. Isopropanol (5 mL) was added to the reaction mixture. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system, operated at 120 °C (temperature monitored by a built-in infrared sensor), 100 Watts and 10–60 psi for 25-45 min (Table 3). After completion of the reaction, the catalyst was easily removed from reaction

mixture using an external magnet. After separation of catalyst, the solid product was filtered off or extracted with ethyl acetate and purified by column chromatography.

All products listed in Table 3 are known in the literature and were identified by comparison of their FT-IR, ^1H , and ^{13}C NMR with literature data.¹⁻⁶ The ^1H and ^{13}C NMR spectra for all the compound (Table 3) is given below.

References:

1. S. M. Agawane and J. M. Nagarkar, *Tetrahedron Lett.*, 2011, **52**, 5220.
2. K. Swapna, S. N. Murthy, M. T. Jyothi and Y. V. D. Nageswar, *Org. Biomol. Chem.*, 2011, **9**, 5989.
3. V. K. Akkilagunta and R. R. Kakulapati, *J. Org. Chem.*, 2011, **76**, 6819.
4. X. Y. Zhang, X. Y. Zhang, and S. R. Guo., *Journal of Sulfur Chemistry*, 2011, **32**, 23.
5. H. J. Yoon, J. W. Choi, H. Kang, T. Kang, S. M. Lee, B. H. Jun, Y. S. Lee, *Synlett*, 2010, 2518.
6. (a) Y. Zhang, K. N. Ngeow and J. Y. Ying, *Org. Lett.*, 2007, **9**, 3495; (b) A. Saxena, A. Kumar and S. Mozumdar, *Appl. Catal., A*, 2007, **317**, 210; (c) S. Jammi, P. Barua, L. Rout, P. Saha and T. Punniyamurthy, *Tetrahedron Lett.*, 2008, **49**, 1484; (d) H. J. Cristau, B. Chabaud, A. Chene and H. Christol, *Synthesis*, 1981, 892; (e) C. Millois and P. Diaz, *Org. Lett.*, 2000, **2**, 1705; (f) V. Percec, J.-Y. Bae and D. H. Hill, *J. Org. Chem.*, 1995, **60**, 6895; (g) K. Takagi, *Chem. Lett.*, 1987, 2221.

Table 1 Optimization of reaction condition

Entry	Solvent	Base	Temp	Times	Yield ^a
1	H ₂ O	NaOH	100 °C	24 h	-
2	H ₂ O	K ₂ CO ₃	100 °C	24 h	-
3	H ₂ O	Cs ₂ CO ₃	100 °C	24 h	-
4	DMF	K ₂ CO ₃	153 °C	24 h	70%
5	DMF	Cs ₂ CO ₃	153 °C	24 h	70%
6	THF	K ₂ CO ₃	65 °C	24 h	65%
7	THF	Cs ₂ CO ₃	65 °C	24 h	66%
8	CH ₃ CN	K ₂ CO ₃	82 °C	24 h	63%
9	CH ₃ CN	Cs ₂ CO ₃	82 °C	24 h	65%
10	THF:iPrOH	K ₂ CO ₃	reflux	24 h	77%
11	THF:iPrOH	Cs ₂ CO ₃	reflux	24 h	76%
12	iPrOH	Cs ₂ CO ₃	82 °C	24 h	79%
13	iPrOH	K ₂ CO ₃	82 °C	24 h	81%
14	iPrOH	K ₂ CO ₃	120 °C	25 min	98% ^b

a) Reaction condition: 1.2 mmol of thiophenol, 1.0 mmol of aryl halide, 100 mg of nano-FeDOPACu catalyst.
 b) Reaction condition: 1.2 mmol of thiophenol, 1.0 mmol of aryl halide, 100 mg of nano-FeDOPACu catalyst.
 MW, 120 °C, Power 100 Watt.

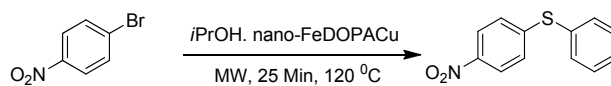
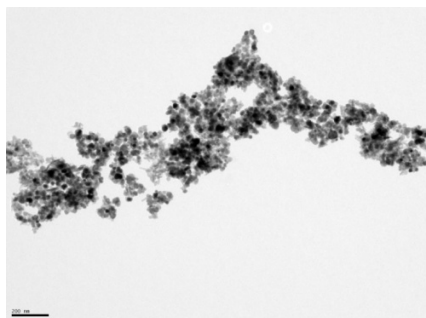
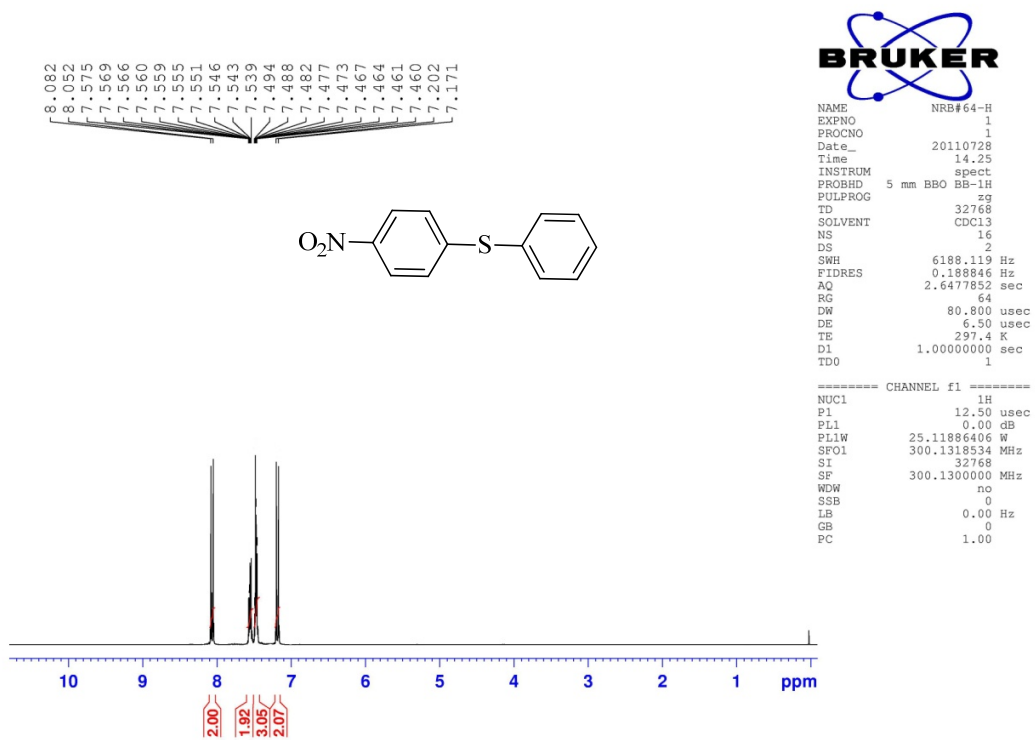


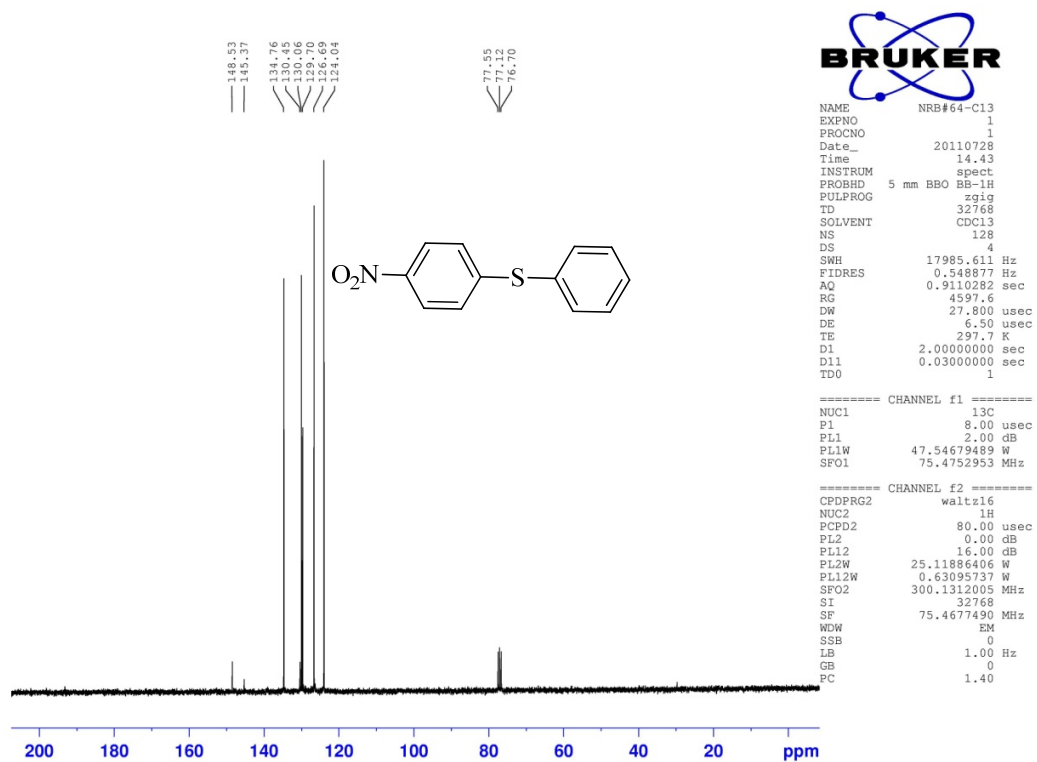
Table 4 Recycling of catalyst

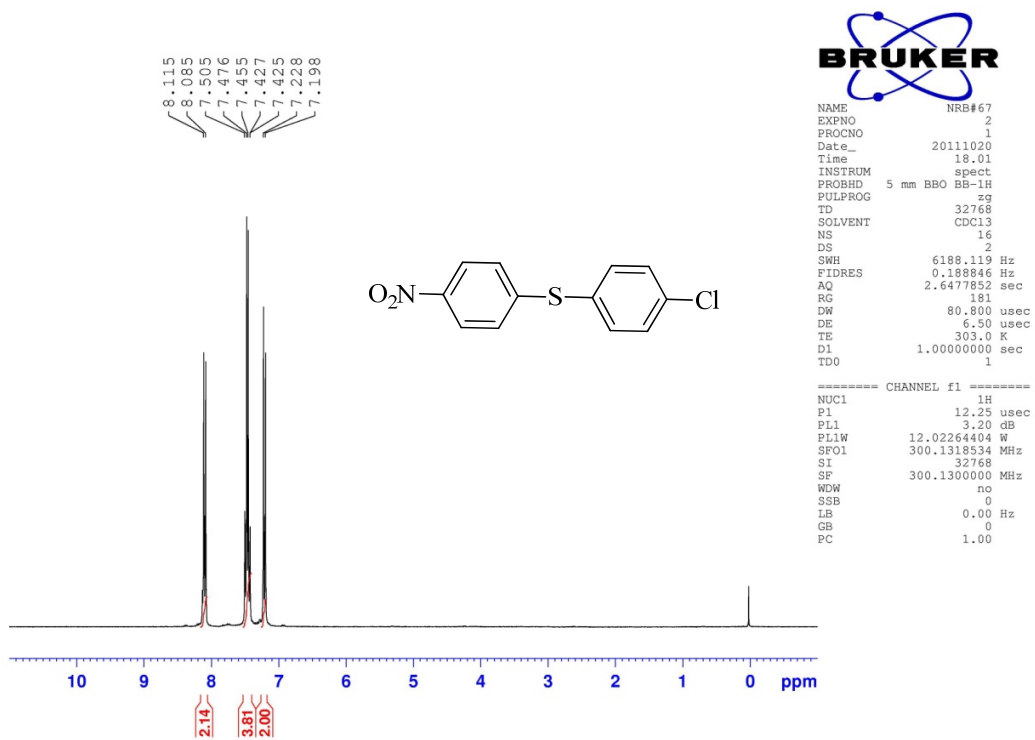
No of cycles	Yield
1	98%
2	97%
3	97%

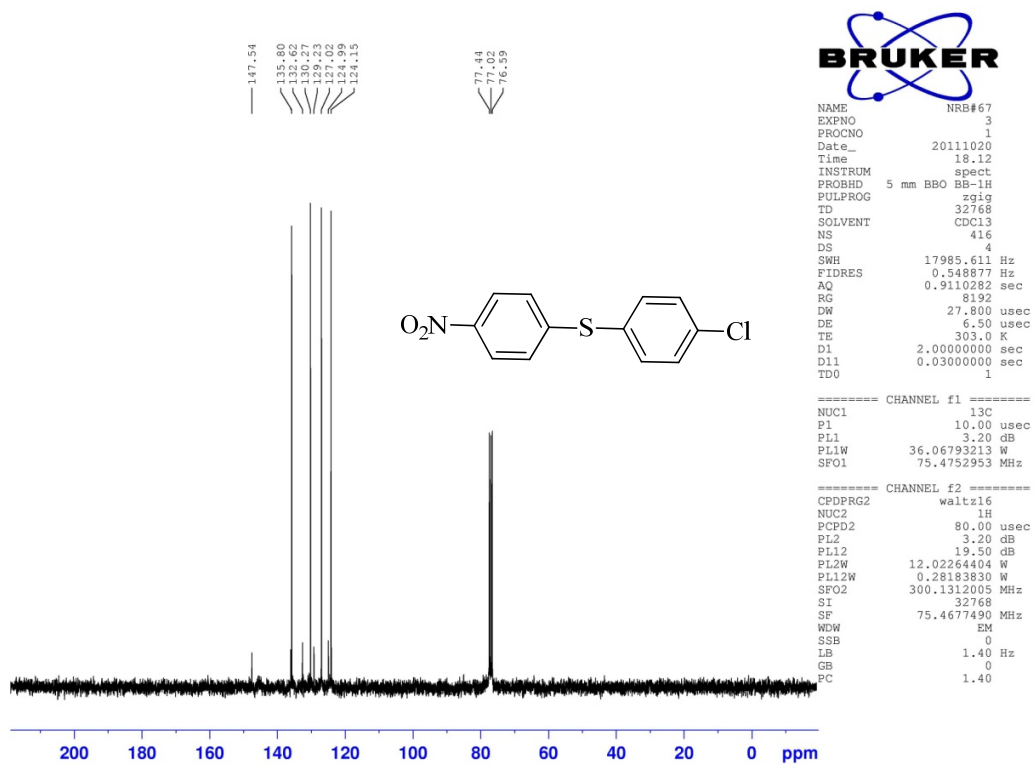
Figure 1 TEM image of catalyst after three cycles

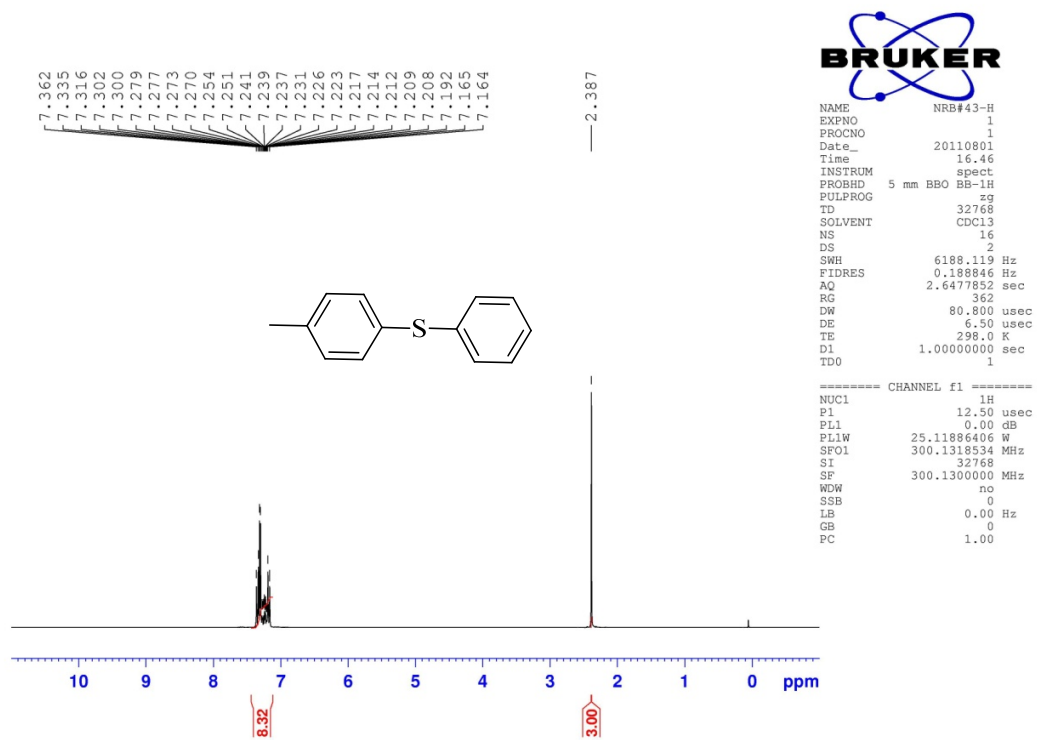


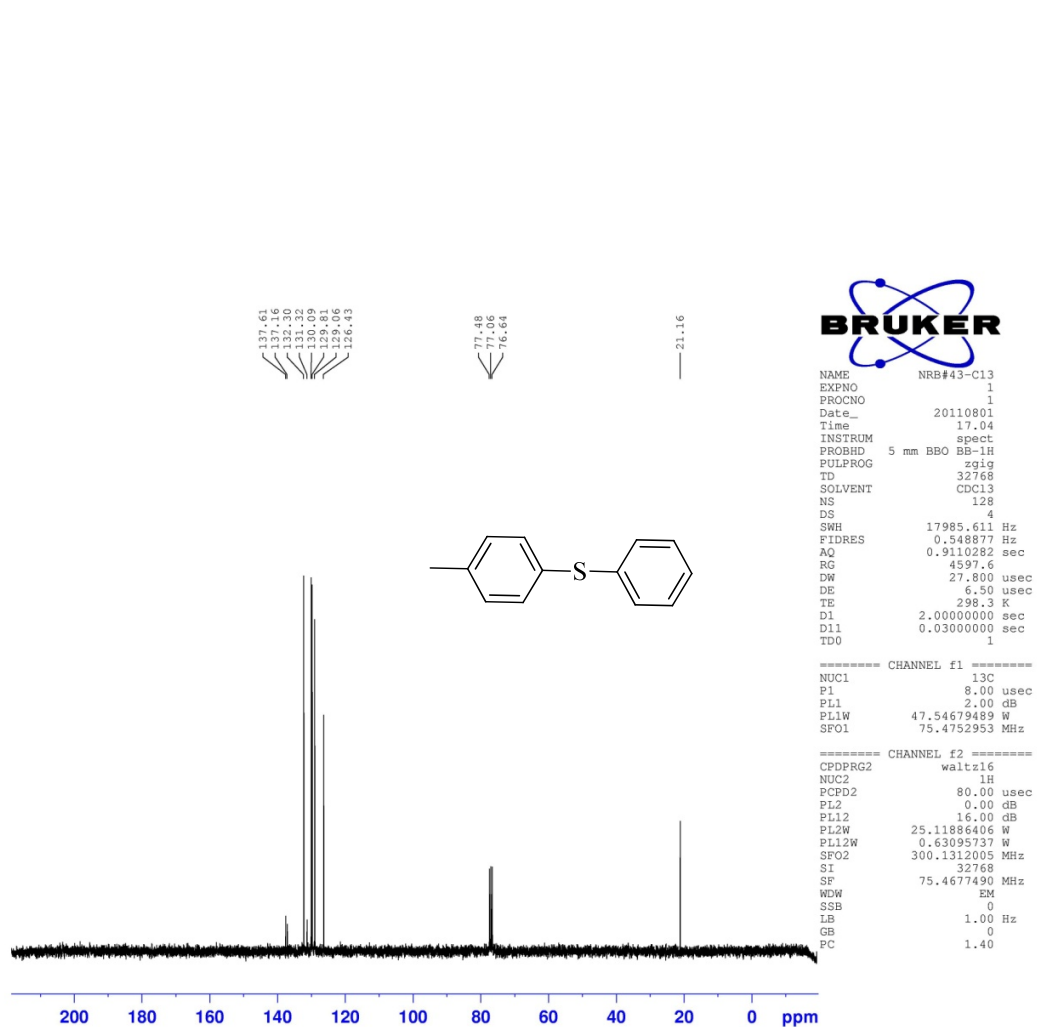


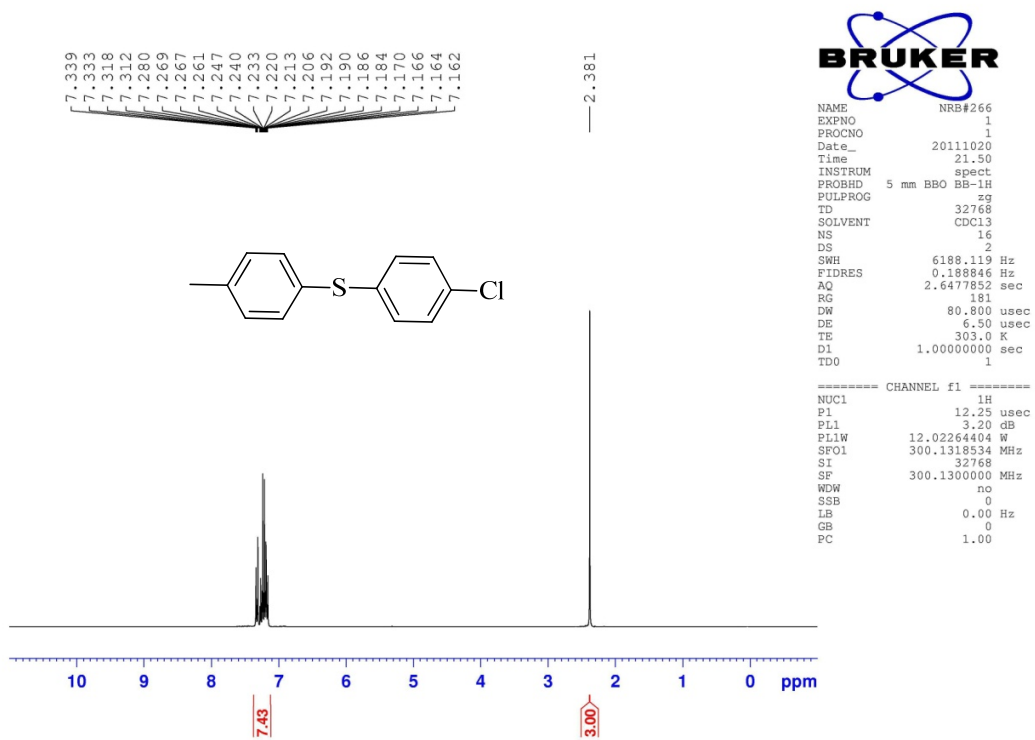


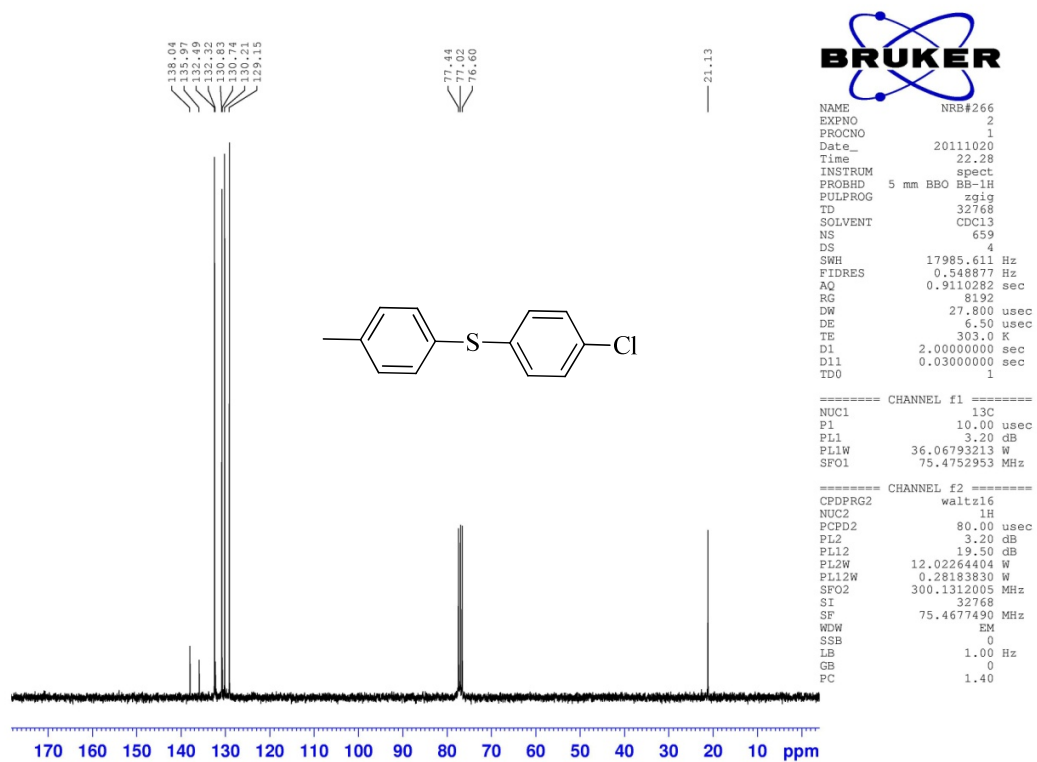


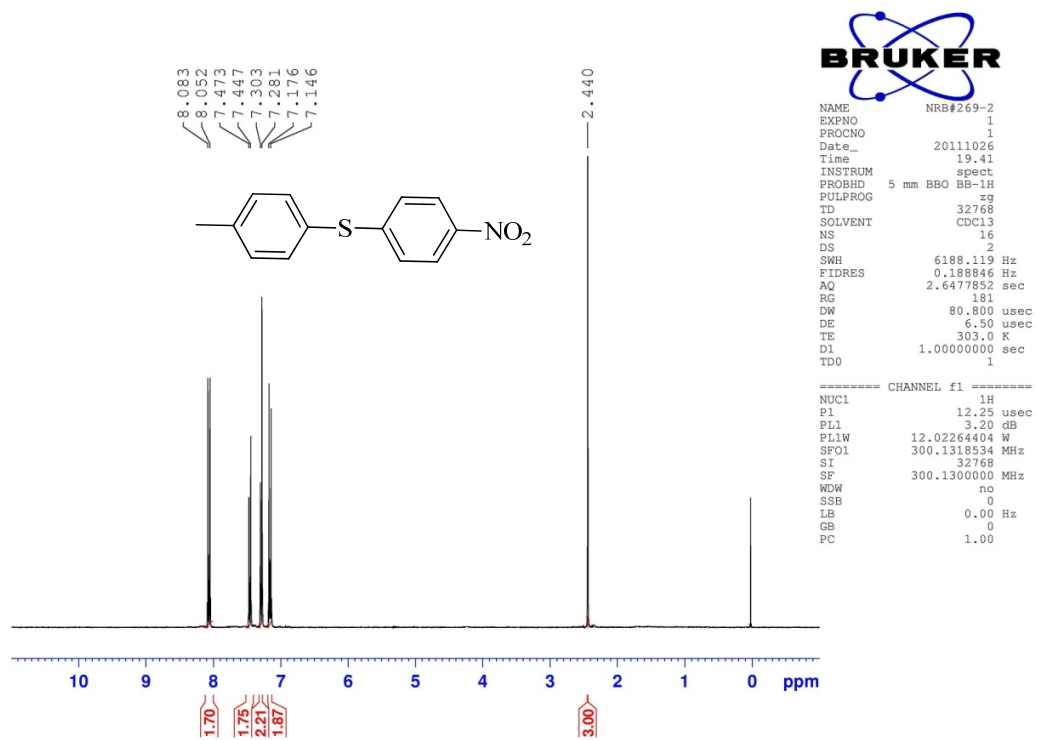


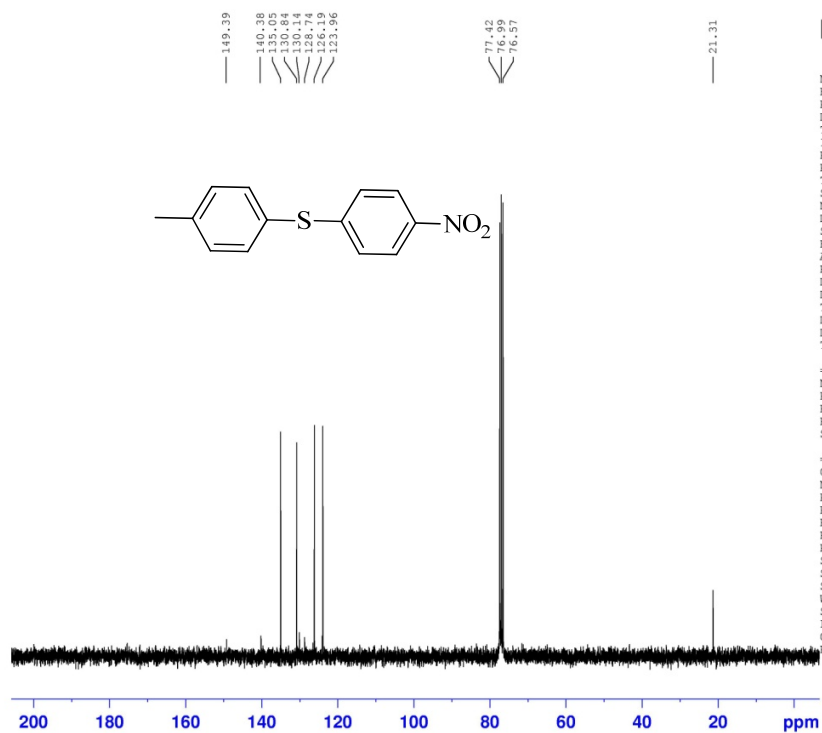








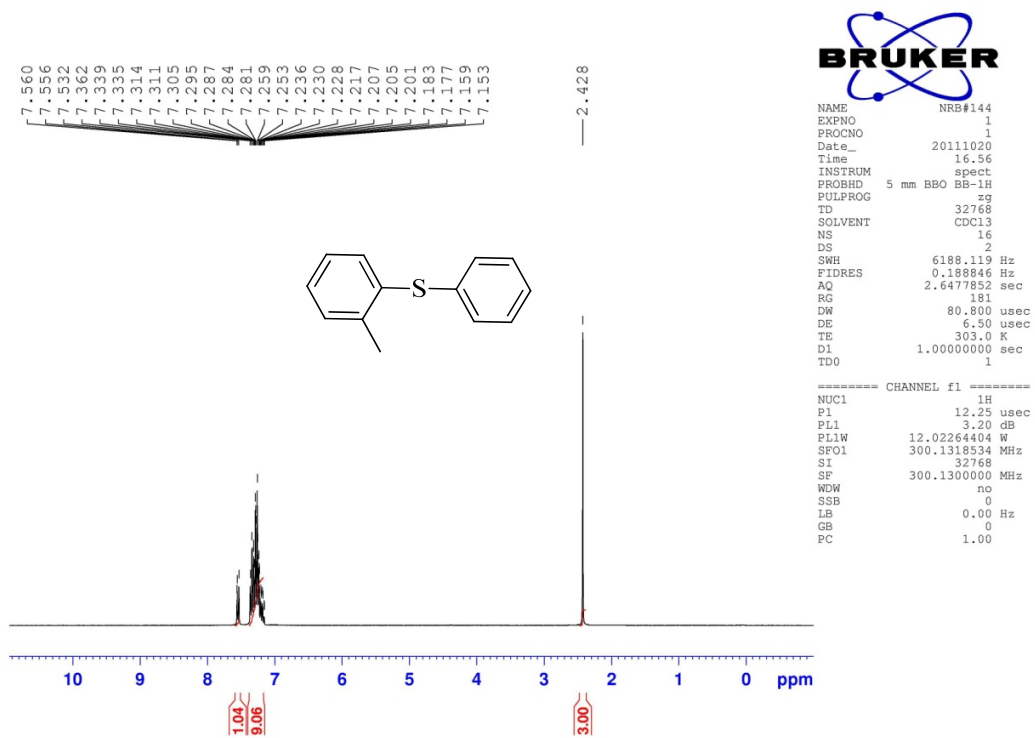


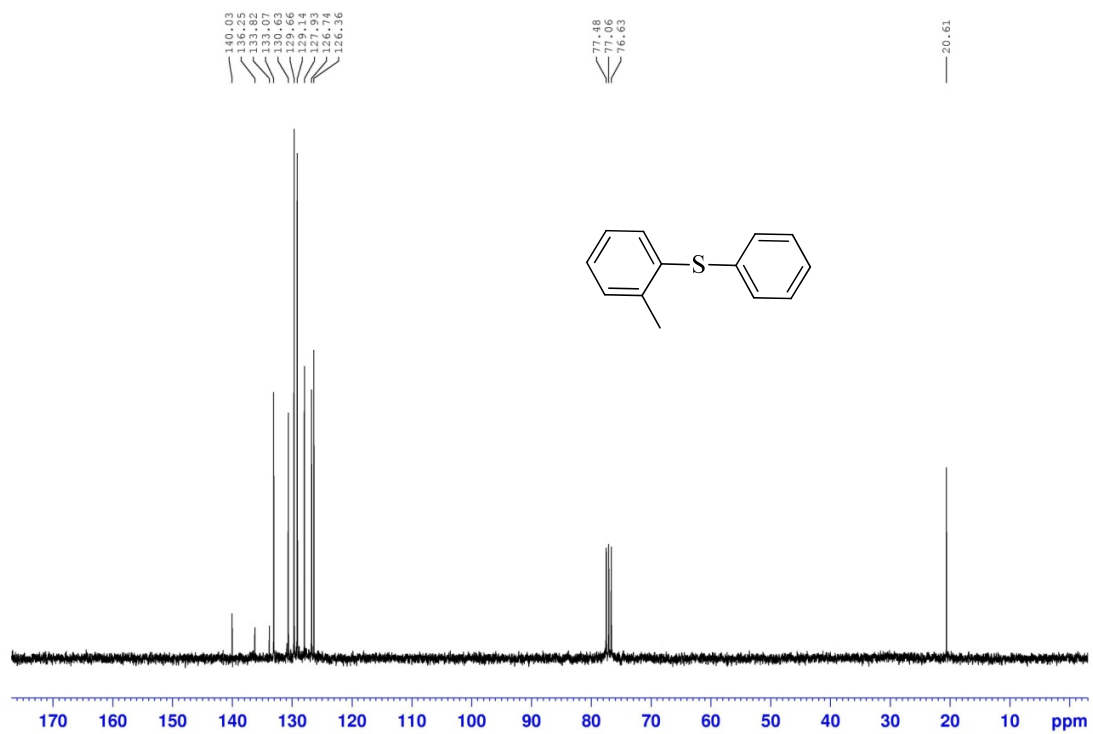


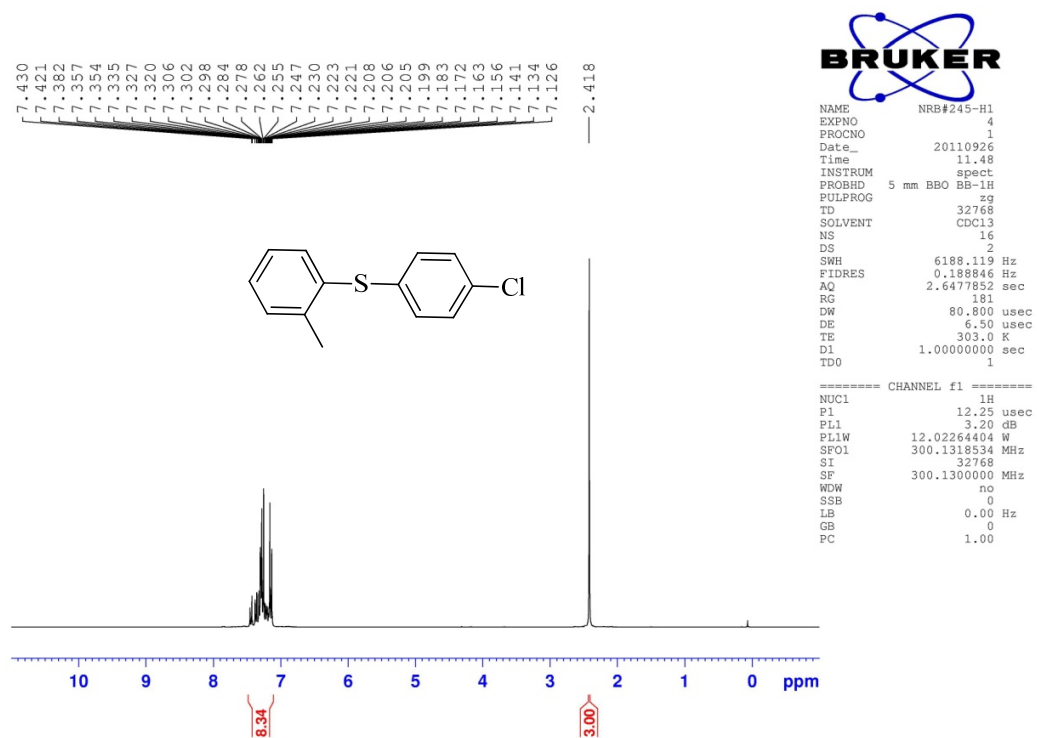
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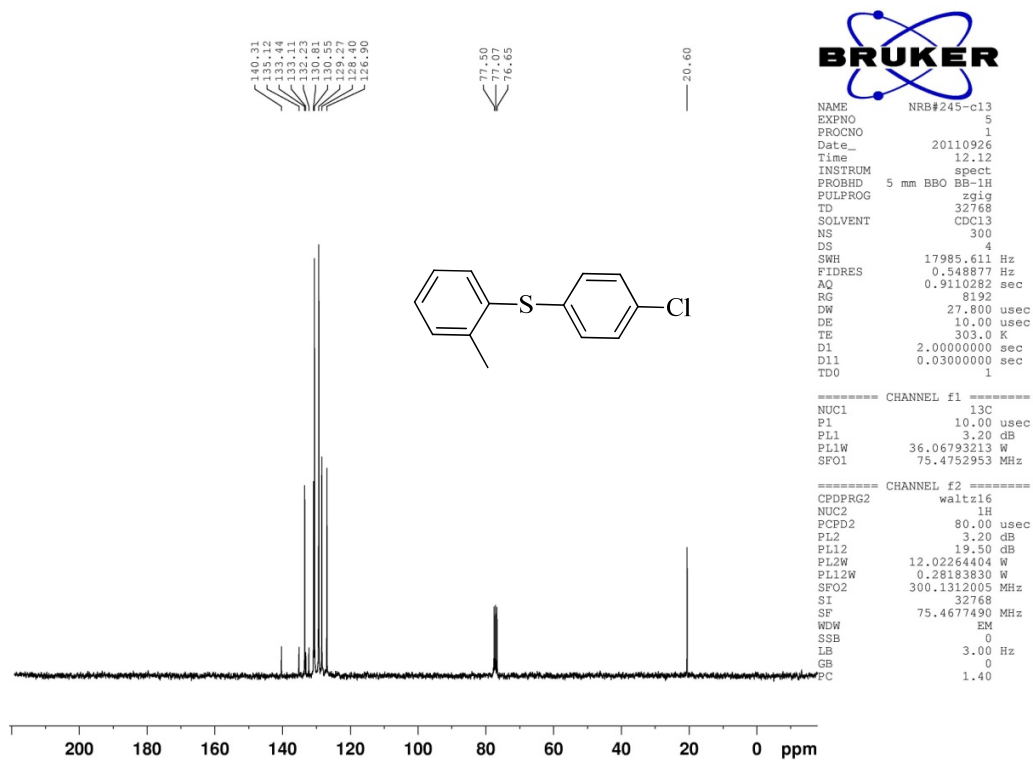
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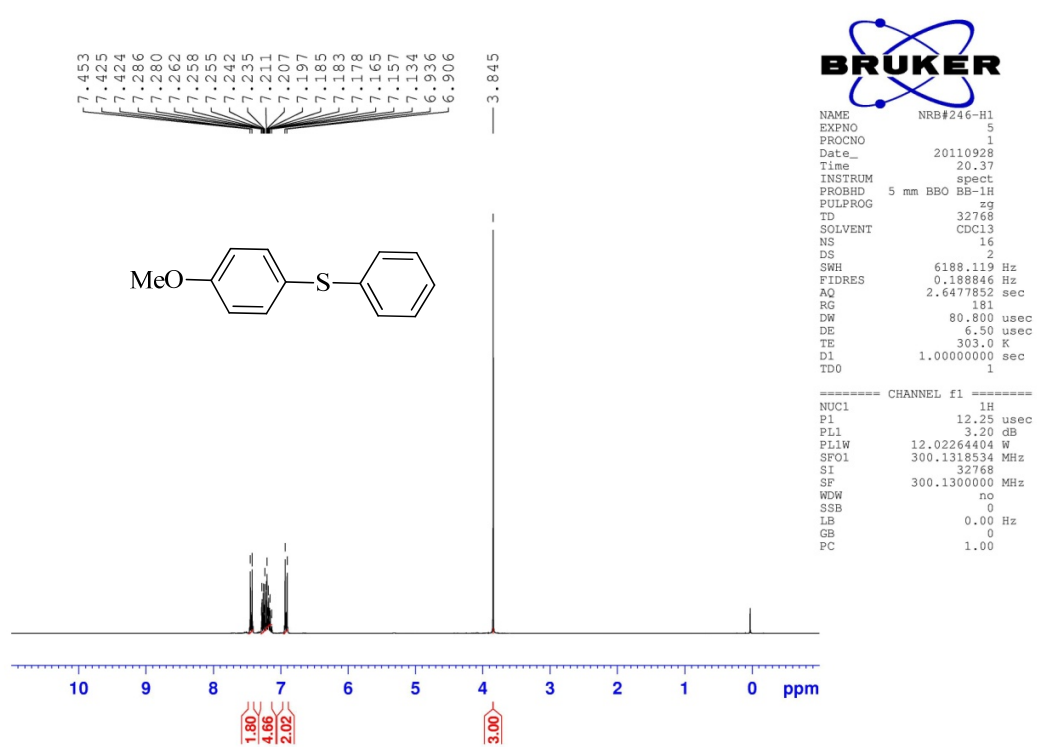
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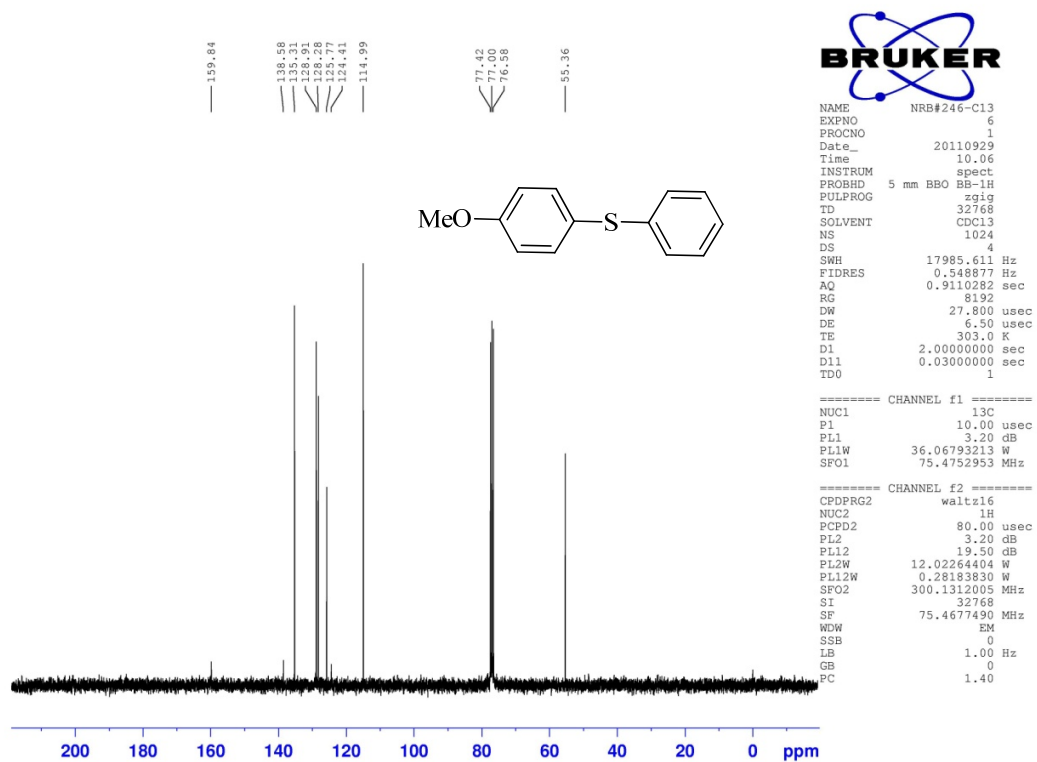


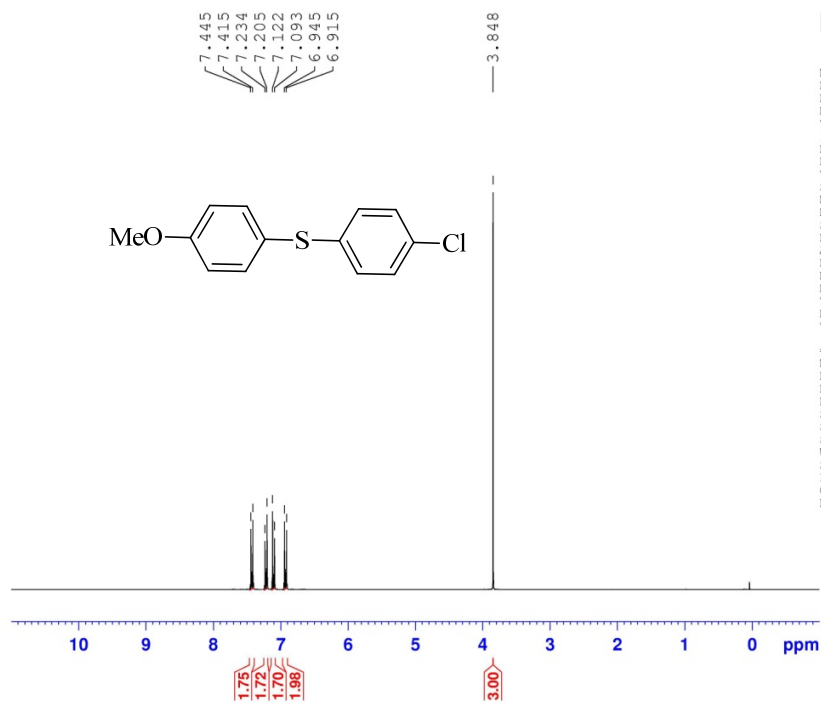












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