



Supporting Information

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## Supporting Information

### Iron-Catalyzed *S*-Arylation of Thiols with Aryl Iodides

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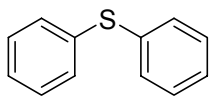
**Supporting Information Available.** Experimental details for compounds **3a-r** and <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of all compounds are included.

<b>General information</b>	<b>S2</b>
<b>General procedure for the <i>S</i>-arylation of thiols</b>	<b>S2</b>
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**General information:** All reagents were purchased from commercial suppliers and used without further purification. All experiments were carried out under argon. Flash chromatography was carried out with Merck silica gel 60 (63-200 mesh). Analytical TLC was performed with Merck silica gel 60 F<sub>254</sub> plates, and the products were visualized by UV detection. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR (300 or 400 MHz and 75 or 100 MHz, respectively) spectra were recorded in CDCl<sub>3</sub>. Chemical shifts ( $\delta$ ) are reported in ppm using TMS as internal standard, and spin-spin coupling constants ( $J$ ) are given in Hz. IR spectra were recorded on a Perkin-Elmer FT/IR 1760 as KBr pellets. Melting points were determined in open-end capillary tubes on a Büchi B-540 melting point apparatus and are uncorrected. Mass spectra were acquired on a Varian MAT 212 spectrometer (CI, 100 eV and EI, 70 eV). Microanalyses were obtained with a Vario EL element analyzer.

**General procedure for *S*-arylation of thiols:** A sealable tube equipped with a magnetic stir bar was charged with thiophenol (**1**, 1.0 equiv), NaOtBu (2.0 equiv) and FeCl<sub>3</sub> (0.10 equiv). The aperture of the tube was then covered with a rubber septum, and an argon atmosphere was established. Phenyl iodide (**2**, 1.5 equiv), *N,N'*-dimethylethylenediamine (0.20 equiv) and toluene (1 mL/mmol of **1**) were added via syringe. The septum was then replaced by a teflon-coated screw cap, and the reaction vessel was placed in a 135 °C oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature and diluted with dichloromethane. The resulting solution was directly filtered through a pad of silica and concentrated to afford the product, which was purified by silica gel chromatography to yield thioether **3**. The identity and purity of the known products was confirmed by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopic analysis, and the new products were fully characterized.

**Diphenyl sulfide<sup>1</sup> (3a).** Following the general procedure using thiophenol (0.05 mL, 0.48 mmol) and iodobenzene (80 mL, 0.72 mmol) provided 82.4 mg (91% yield) of the coupling product as a colorless liquid after purification by flash chromatography (pentane) of the crude oil.

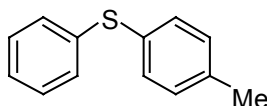


<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.22 (m, 10H)

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  135.7 (C), 131.0 (CH), 129.1 (CH), 127.0 (CH).

All spectral data correspond to those given in the literature.

**Phenyl tolyl sulfide<sup>1</sup> (3b).** Following the general procedure using thiophenol (0.05 mL, 0.48 mmol) and 4-iodotoluene (162.2 mg, 0.72 mmol) provided 95.5 mg (98% yield) of the coupling product as a pale yellow liquid after purification by flash chromatography (pentane) of the crude oil.



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41-7.16 (m, 9H), 2.42 (s, 3H).

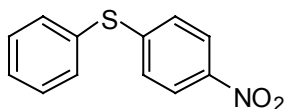
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.5 (C), 132.2 (C), 131.2 (CH), 129.9 (CH), 129.7 (CH), 128.9 (CH), 128.5 (C), 126.3 (CH), 20.9 (CH<sub>3</sub>).

All spectral data correspond to those given in the literature.

**4-Nitrophenyl phenyl sulfide<sup>1</sup> (3c).** Following the general procedure using thiophenol (0.08 mL, 0.77 mmol) and 4-iodonitrobenzene (119.6 mg, 0.47 mmol) provided 95.6 mg (88% yield) of the coupling product as a yellow solid after purification by flash chromatography (dichloromethane/pentane 3/7) of the crude oil.

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<sup>1</sup> T. Itoh, T. Mase, *Org. Lett.* **2004**, 6, 4587.



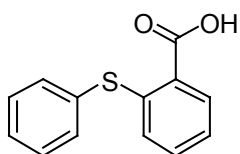
M.p. : 55-56 °C (lit.<sup>1</sup> 54-55 °C).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (d,  $J$  = 8.8 Hz, 2H), 7.55-7.52 (m, 2H), 7.46-7.44 (m, 3H), 7.17 (d,  $J$  = 8.8 Hz, 2H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.3 (C), 145.1 (C), 134.5 (CH), 130.2 (C), 129.9 (CH), 129.5 (CH), 126.5 (CH), 123.8 (CH).

All spectral data correspond to those given in the literature.

**2-Phenylthiobenzoic acid<sup>2</sup> (3d).** Following the general procedure using thiophenol (0.08 mL, 0.77 mmol) and 2-iodobenzoic acid (123 mg, 0.48 mmol) provided 101.1 mg (90% yield) of the coupling product as a white solid after washing the crude mixture with water and dichloromethane, further acidification with 1M HCl and extraction of the aqueous layer with dichloromethane.



M.p. : 166-168 °C (lit.<sup>2</sup> 166.5-167 °C).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.5 (bs, 1H) 8.14 (dd,  $J$  = 7.8, 1.6 Hz, 1H), 7.63-7.55 (m, 2H), 7.49-7.41 (m, 3H), 7.32-7.23 (m, 1H), 7.15 (dt,  $J$  = 7.6, 1.2 Hz, 1H), 6.82 (dd,  $J$  = 8.2, 0.9 Hz, 1H)

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  171.9 (C), 144.7 (C), 135.9 (CH), 133.2 (CH), 132.2 (CH), 132.1 (CH), 129.9 (CH), 129.3 (CH), 127.2 (CH), 125.3 (C), 124.3 (CH).

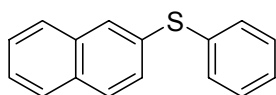
MS (EI)  $m/z$  (%) 230 ( $M^+$ , 100), 184 (36), 137 (66).

Calcd. for C<sub>13</sub>H<sub>10</sub>O<sub>2</sub>S: C, 67.80; H, 4.38; found C, 67.83; H, 4.20.

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<sup>2</sup> J. Nakayama, T. Fujita, M. Hoshino, *Chem. Lett.* **1982**, 1777.

**2-Naphthyl phenyl sulfide<sup>3</sup> (3e).** Following the general procedure using 2-naphthalenthioi (100 mg, 0.61 mmol) and iodobenzene (0.093 mL, 0.92 mmol) provided 122 mg (85% yield) of the coupling product as a white solid after purification by flash chromatography (pentane) of the crude oil.



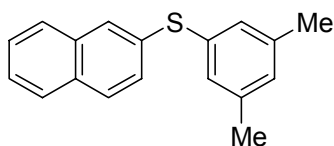
M.p. : 51-52 °C (lit.<sup>3</sup> 50 °C).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.73-7.58 (m, 4H), 7.36-7.13 (m, 8H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  135.9 (C), 133.8 (C), 133.0 (C), 132.3 (C), 130.9 (CH), 129.9 (CH), 129.3 (CH), 128.9 (CH), 128.8 (CH), 127.8 (CH), 127.4 (CH), 127.1 (CH), 126.6 (CH), 126.2 (CH).

All spectral data correspond to those given in the literature.

**3,5-Dimethylphenyl 2-naphthyl sulfide (3f).** Following the general procedure using 2-naphthalenthioi (100 mg, 0.61 mmol) and 5-iodo-*m*-xylene (0.13 mL, 0.92 mmol) provided 135 mg (84% yield) of the coupling product as a white solid after purification by flash chromatography (pentane) of the crude oil.



M.p. : 99-100 °C.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70-7.58 (m, 4H), 7.35-7.27 (m, 3H), 6.92 (s, 2H), 6.77 (s, 1H), 2.14 (s, 6H).

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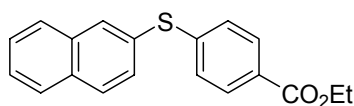
<sup>3</sup> C. Mispelaere-Canivet, J.-F. Spindler, S. Perrio, P. Beslin, *Tetrahedron* **2005**, *61*, 5253.

$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.9 (C), 134.9 (C), 133.8 (C), 133.6 (C), 132.2 (C), 129.3 (CH), 129.2 (CH), 129.0 (CH), 128.8 (CH), 128.6 (CH), 127.8 (CH), 127.4 (CH), 126.6 (CH), 126.1 (CH), 21.4 ( $\text{CH}_3$ ).

MS (EI)  $m/z$  (%) 264 ( $\text{M}^+$ , 100), 249 (18), 234 (19).

Calcd. for  $\text{C}_{18}\text{H}_{16}\text{S}$ : C, 81.77; H, 6.10; found C, 81.49; H, 5.98.

**4-(Thio-2-naphthyl)benzoic acid ethylester (3g).** Following the general procedure using 2-naphthalenthioi (100 mg, 0.61 mmol) and 4-iodobenzoic acid ethylester (0.16 mL, 0.92 mmol) provided 152 mg (81% yield) of the coupling product as a white solid after purification by flash chromatography (dichloromethane/pentane 2/8) of the crude oil.



M.p. : 55-56 °C.

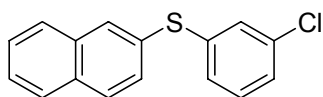
$^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91-7.90 (m, 1H), 7.83-7.79 (m, 2H), 7.75-7.65 (m, 3H), 7.44-7.39 (m, 2H), 7.37 (dd,  $J$  = 8.5, 1.9 Hz, 1H), 7.17-7.13 (m, 2H), 4.25 (q,  $J$  = 7.1 Hz, 2H), 1.27 (t,  $J$  = 7.1 Hz, 3H).

$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1 (C), 143.9 (C), 133.8 (C), 132.9 (C), 132.8 (CH), 130.9 (CH), 130.2 (CH), 130.1 (CH), 129.8 (C), 129.3 (CH), 127.9 (C), 128.8 (CH), 127.7 (CH), 126.9 (CH), 126.8 (CH), 61.0 ( $\text{CH}_2$ ), 14.5 ( $\text{CH}_3$ ).

MS (EI)  $m/z$  (%) 308 ( $\text{M}^+$ , 100), 280 (15), 263 (22), 234 (36), 115 (20).

Calcd. for  $\text{C}_{19}\text{H}_{16}\text{O}_2\text{S}$ : C, 74.00; H, 5.23; found C, 73.66; H, 5.23.

**3-Chlorophenyl 2-naphthyl sulfide (3h).** Following the general procedure using 2-naphthalenthioi (100 mg, 0.61 mmol) and 1-iodo-3-chlorobenzene (0.14 mL, 0.92 mmol) provided 140 mg (85% yield) of the coupling product as a white solid after purification by flash chromatography (pentane) of the crude oil.



M.p. : 64-65 °C.

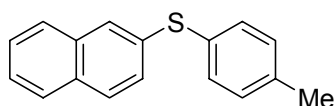
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 1.6$  Hz, 1H), 7.72-7.62 (m, 3H), 7.39-7.35 (m, 2H), 7.31 (dd,  $J = 8.5, 1.9$  Hz, 1H), 7.18-7.17 (m, 1H), 7.05 (s, 3H).

$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.9 (C), 134.9 (C), 133.8 (C), 132.7 (C), 131.6 (CH), 131.1 (C), 130.1 (CH), 129.4 (CH), 129.3 (CH), 129.2 (CH), 127.9 (CH), 127.8 (CH), 127.6 (CH), 126.8 (CH), 126.7 (CH).

MS (EI)  $m/z$  (%) 272 ( $\text{M}^+ + 2$ , 33), 270 ( $\text{M}^+$ , 100), 234 (50), 115 (19).

Calcd. for  $\text{C}_{16}\text{H}_{11}\text{ClS}$ : C, 70.97; H, 4.09; found C, 70.68; H, 4.23.

**4-Methylphenyl 2-naphthyl sulfide<sup>4</sup> (3i).** Following the general procedure using 2-naphthalenthioi (100 mg, 0.61 mmol) and 4-iodotoluene (205 mg, 0.92 mmol) provided 145 mg (96% yield) of the coupling product as a white solid after purification by flash chromatography (pentane) of the crude oil.



M.p. : 67-68 °C (lit.<sup>4</sup> 66-67 °C)

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67-7.57 (m, 4H), 7.36-7.29 (m, 2H), 7.26-7.22 (m, 3H), 7.03 (d,  $J = 7.7$  Hz, 2H), 2.24 (s, 3H).

$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.6 (C), 134.4 (C), 133.8 (C), 132.1 (CH), 132.0 (C), 131.4 (C), 130.1 (CH), 128.7 (CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 127.3 (CH), 126.5 (CH), 125.9 (CH), 21.3 ( $\text{CH}_3$ ).

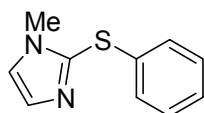
All spectral data correspond to those given in the literature.

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<sup>4</sup> T. Nakazawa, N. Hirose, K. Itabashi, *Synthesis* **1989**, 955.



**2-(Phenylsulfanyl)-*N*-methylimidazole (3j).** Following the general procedure using 2-mercapto-*N*-methylimidazole (100 mg, 0.86 mmol) and iodobenzene (0.14 mL, 1.29 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (560.4 mg, 1.72 mmol) as base provided 86 mg (52% yield) of the coupling product as a yellow oil after purification by flash chromatography (ethyl acetate) of the crude oil.



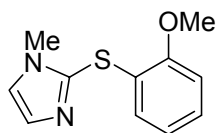
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.20-7.14 (m, 2H), 7.10-7.04 (m, 4H), 6.98 (d,  $J$  = 1.4 Hz, 1H), 3.54 (s, 3H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.9 (C), 134.9 (C), 130.1 (CH), 129.2 (CH), 127.9 (CH), 126.5 (CH), 123.8 (CH), 33.9 (CH<sub>3</sub>).

MS (EI)  $m/z$  (%) 190 (M<sup>+</sup>, 75), 189 (100), 91 (16), 51 (18).

Calcd. for C<sub>10</sub>H<sub>10</sub>NS: C, 63.13; H, 5.30; N, 14.72; found C, 62.83; H, 5.28; N, 14.81.

**2-(2-Methoxyphenylsulfanyl)-*N*-methylimidazole (3k).** Following the general procedure using 2-mercapto-*N*-methylimidazole (100 mg, 0.86 mmol) and 2-iodoanisole (0.18 mL, 1.29 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (560.4 mg, 1.72 mmol) as base provided 134 mg (71% yield) of the coupling product as a yellow oil after purification by flash chromatography (ethyl acetate) of the crude oil.



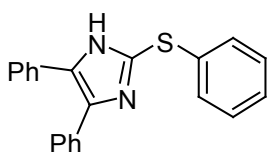
<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.10-7.03 (m, 2H), 7.02-7.00 (m, 1H), 6.77-6.68 (m, 2H), 6.52-6.49 (m, 1H), 3.78 (s, 3H), 3.54 (s, 3H).

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  155.6 (C), 137.2 (C), 130.3 (CH), 127.6 (CH), 127.3 (CH), 124.0 (CH), 123.9 (CH), 121.5 (CH), 110.8 (CH), 55.9 (CH<sub>3</sub>), 33.8 (CH<sub>3</sub>).

MS (EI)  $m/z$  (%) 220 ( $M^+$ , 9), 189 (100).

Calcd. for  $C_{11}H_{12}N_2OS$ : C, 59.97; H, 5.49; N, 12.72; found C, 60.01; H, 5.43; N, 12.84.

**4,5-Diphenyl-2-(phenylsulfanyl)imidazole (3l).** Following the general procedure using 4,5-diphenyl-2-imidazolethiol (126.4 mg, 0.48 mmol) and iodobenzene (0.08 mL, 0.72 mmol) provided 96.8 mg (61% yield) of the coupling product as a white solid after purification by flash chromatography (ethyl acetate) of the crude oil.



M.p. : 207-209 °C

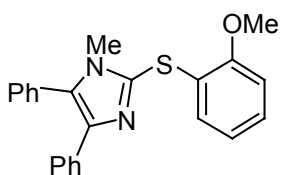
$^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.62 (dd,  $J$  = 8.3, 1.1 Hz, 4H), 7.39 (d,  $J$  = 6.0 Hz, 1H), 7.21 (m, 6H), 7.02 (t,  $J$  = 7.8 Hz, 4H).

$^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  137.4 (CH), 134.0 (C), 130.2 (CH), 129.5 (CH), 129.4 (CH), 128.6 (CH), 127.7 (CH), 127.7 (CH), 127.4 (CH), 127.3 (CH), 94.4 (C).

MS (EI)  $m/z$  (%) 328 ( $M^+$ , 100), 165 (12).

Calcd. for  $C_{21}H_{16}N_2S$ : C, 76.80; H, 4.91; N, 8.53; found C, 76.65; H, 5.22; N, 8.45.

**4,5-Diphenyl-2-(2-methoxyphenylsulfanyl)imidazole (3m).** Following the general procedure using 4,5-diphenyl-2-imidazolethiol (126.4 mg, 0.48 mmol) and 2-iodoanisole (0.10 mL, 0.72 mmol) and  $K_3PO_4$  (204.4 mg, 0.96 mmol) as base provided 56.4 mg (33% yield) of the coupling product as a white solid after purification by flash chromatography (ethyl acetate) of the crude oil.



M.p. : 170-172 °C

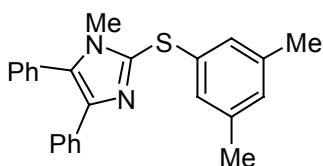
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (dd,  $J = 7.7, 1.7$  Hz, 4H), 7.27-7.12 (m, 8H), 6.88-6.75 (m, 2H), 3.83 (s, 3H).

$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.0 (C), 137.4 (C), 131.6 (CH), 129.1 (CH), 128.6 (CH), 127.7 (CH), 127.6 (CH), 127.3 (C), 122.3 (C), 121.8 (CH), 111.4 (CH), 56.2 ( $\text{CH}_3$ ).

MS (EI)  $m/z$  (%) 358 ( $\text{M}^+$ , 65), 327 (100).

Calcd. for  $\text{C}_{23}\text{H}_{20}\text{N}_2\text{OS}$ : C, 73.71; H, 5.06; N, 7.82; found C, 73.69; H, 5.34; N, 7.65.

**2-(3,5-Dimethylphenylsulfanyl)-4,5-diphenylimidazole (3n).** Following the general procedure using 4,5-diphenyl-2-imidazolethiol (126.4 mg, 0.48 mmol) and 5-iodo-*m*-xylene (0.11 mL, 0.72 mmol) provided 54.7 mg (32% yield) of the coupling product as a pale yellow solid after purification by flash chromatography (ethyl acetate) of the crude oil.



M.p. : 143-145 °C

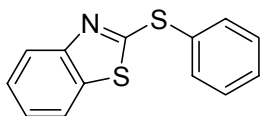
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44-7.40 (m, 4H), 7.26-7.21 (m, 6H), 6.99 (s, 2H), 6.83 (s, 1H), 2.22 (s, 6H).

$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ . 139.1 (C), 138.3 (C), 133.0 (C), 132.3 (C), 129.4 (CH), 128.5 (CH), 127.9 (CH), 127.8 (CH), 127.5 (CH), 104.7 (C), 21.2 ( $\text{CH}_3$ ).

MS (EI)  $m/z$  (%) 356 ( $\text{M}^+$ , 100).

Calcd. for  $\text{C}_{24}\text{H}_{22}\text{N}_2\text{S}$ : C, 77.49; H, 5.65; N, 7.86; found C, 77.10; H, 5.91; N, 7.66.

**2-Phenylsulfanyl-benzothiazole<sup>5</sup> (3o).** Following the general procedure using 2-mercaptobenzothiazole (100 mg, 0.58 mmol) and iodobenzene (0.09 mL, 0.87 mmol) provided 128 mg (91% yield) of the coupling product as a yellow oil after purification by flash chromatography (pentane/dichloromethane 9/1) of the crude oil.

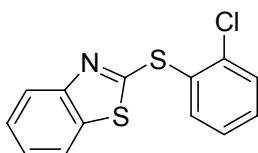


<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78-7.76 (m, 1H), 7.63-7.61 (m, 2H), 7.54-7.51 (m, 1H), 7.42-7.33 (m, 3H), 7.28 (dt,  $J$  = 7.8, 1.4 Hz, 1H), 7.14 (dt,  $J$  = 7.4, 1.1 Hz, 1H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.6 (C), 153.9 (C), 135.2 (C), 135.3 (CH), 130.5 (CH), 129.9 (CH), 126.2 (CH), 124.3 (CH), 121.9 (CH), 120.8 (CH).

All spectral data correspond to those given in the literature.

**2-(2-Chlorophenylsulfanyl)benzothiazole (3p).** Following the general procedure using 2-mercaptobenzothiazole (100 mg, 0.58 mmol) and 1-iodo-2-chlorobenzene (0.10 mL, 0.87 mmol) provided 128 mg (80% yield) of the coupling product as a white solid after purification by flash chromatography (dichloromethane/pentane 1/1) of the crude oil.



M.p. : 55-56 °C.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.79-7.83 (m, 1H), 7.68 (dd,  $J$  = 7.7, 1.7 Hz, 1H), 7.59-7.56 (m, 1H), 7.47 (dd,  $J$  = 7.9, 1.5 Hz, 1H), 7.36-7.16 (m, 4H).

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  166.9 (C), 153.8 (C), 138.9 (C), 137.0 (CH), 135.8 (C), 131.8 (CH), 130.8 (CH), 129.5 (C), 127.9 (CH), 126.3 (CH), 124.6 (CH), 122.2 (CH), 120.9 (CH).

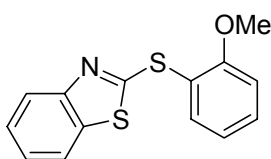
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<sup>5</sup> C. Savarin, J. Srogl, L. S. Liebeskind, *Org. Lett.* **2002**, 4, 4309.

MS (EI)  $m/z$  (%) 277 ( $M^+$ , 13), 242 (100), 108 (21).

Calcd. for  $C_{13}H_8ClNS_2$ : C, 56.21; H, 2.90; N, 5.04; found C, 56.45; H, 3.15; N, 5.05.

**2-(2-Methoxyphenylsulfanyl)benzothiazole (3q).** Following the general procedure using 2-mercaptobenzothiazole (100 mg, 0.58 mmol) and 2-iodoanisole (0.12 mL, 0.87 mmol) provided 145 mg (91% yield) of the coupling product as a white solid after purification by flash chromatography (dichloromethane) of the crude oil.



M.p. : 71-72 °C.

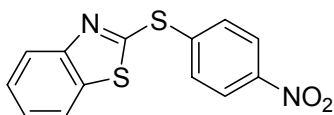
$^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.79-7.77 (m, 1H), 7.60 (dd,  $J$  = 7.7, 1.6 Hz, 1H), 7.55-7.52 (m, 1H), 6.97-6.92 (m, 1H); 6.74-6.66 (m, 1H), 6.61 (dt,  $J$  = 7.5, 1.4 Hz, 1H), 7.44-7.39 (m, 1H), 7.31-7.27 (m, 1H), 7.17-7.13 (m, 1H), 3.75 (s, 3H).

$^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  169.8 (C), 159.9 (C), 154.0 (C), 137.4 (CH), 135.6 (C), 132.8 (CH), 125.9 (CH), 124.0 (CH), 121.8 (CH), 121.5 (CH), 120.7 (CH), 117.7 (C), 111.9 (CH), 56.1 ( $CH_3$ ).

MS (EI)  $m/z$  (%) 273 ( $M^+$ , 15), 242 (100).

Calcd. for  $C_{14}H_{11}NOS_2$ : C, 61.51; H, 4.06; N, 5.12; found C, 61.64; H, 4.29; N, 5.03.

**2-(4-Nitrophenylsulfanyl)benzothiazole (3r).** Following the general procedure using 2-mercaptobenzothiazole (100 mg, 0.58 mmol) and 4-iodonitrobenzene (220 mg, 0.87 mmol) provided 134 mg (80% yield) of the coupling product as an orange solid after purification by flash chromatography (dichloromethane) of the crude oil.



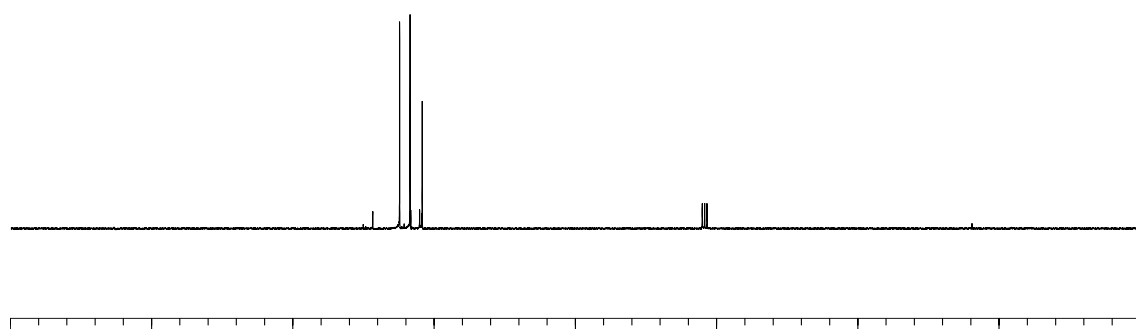
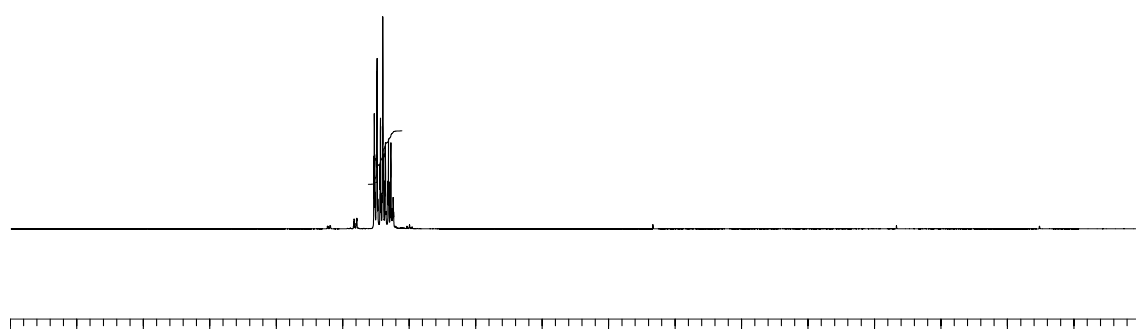
M.p. : 95-96 °C.

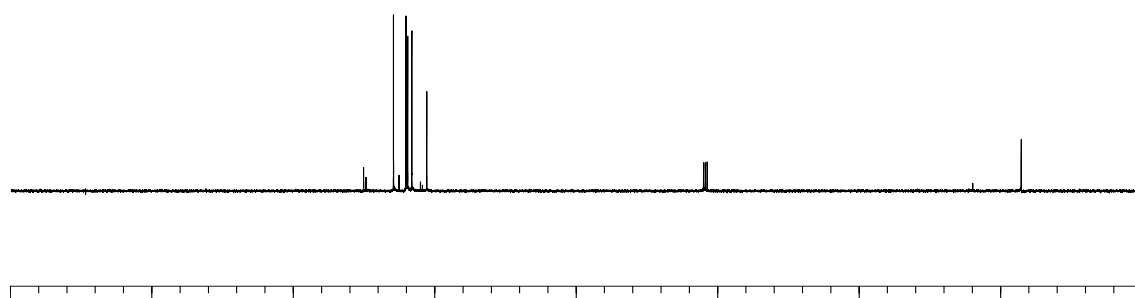
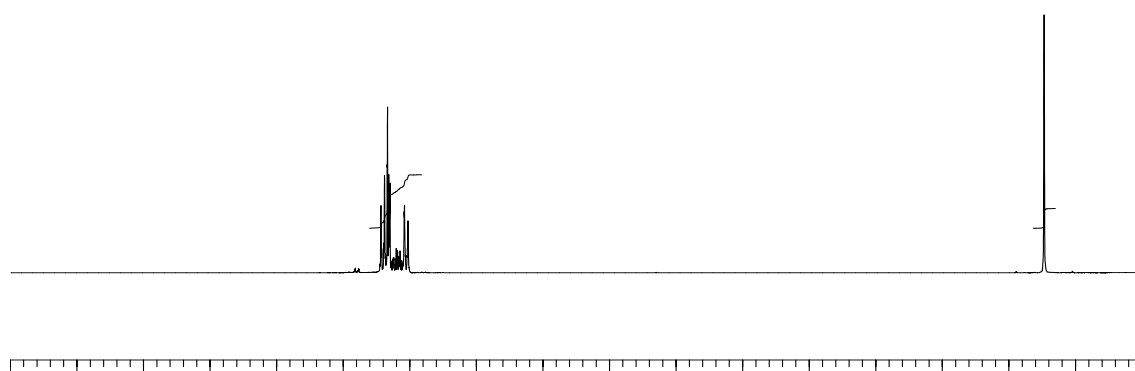
$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15-8.11 (m, 2H), 7.88-7.85 (m, 1H), 7.69-7.65 (m, 3H), 7.41-7.25 (m, 2H).

$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8 (C), 153.4 (C), 147.9 (C), 140.0 (C), 136.2 (C), 132.7 (CH), 126.7 (CH), 125.5 (CH), 124.5 (CH), 122.8 (CH), 121.2 (CH).

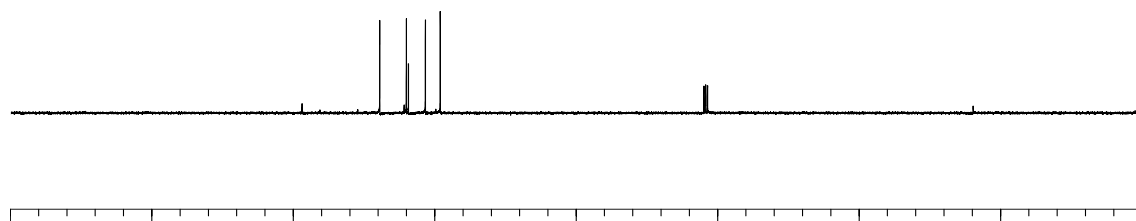
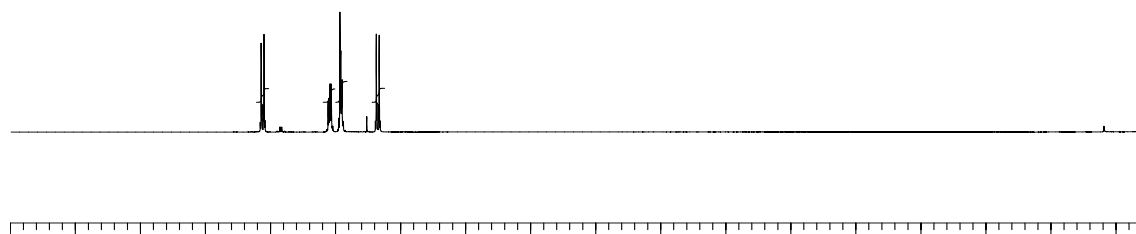
MS (EI)  $m/z$  (%) 290 ( $\text{M}^+$ , 10), 288 (100), 241 (39).

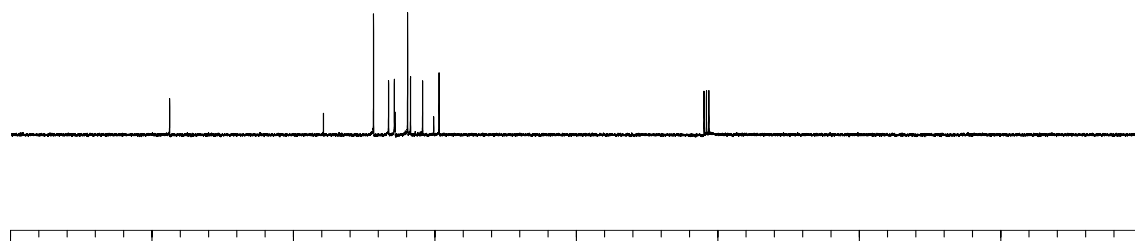
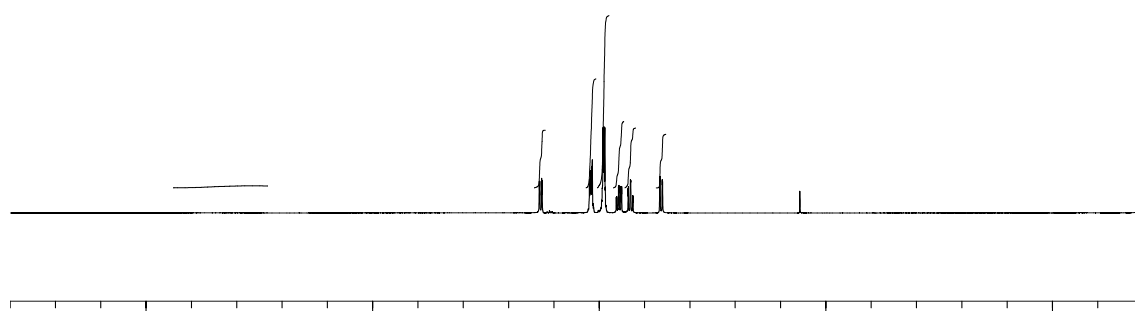
All spectral data correspond to those given in the literature.

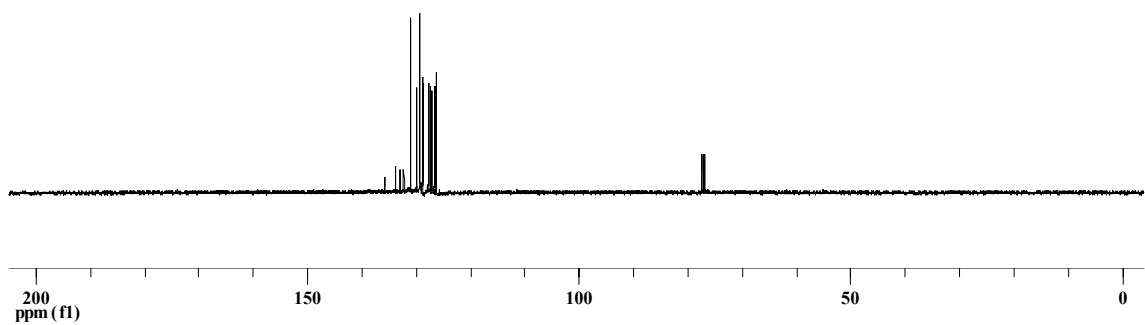
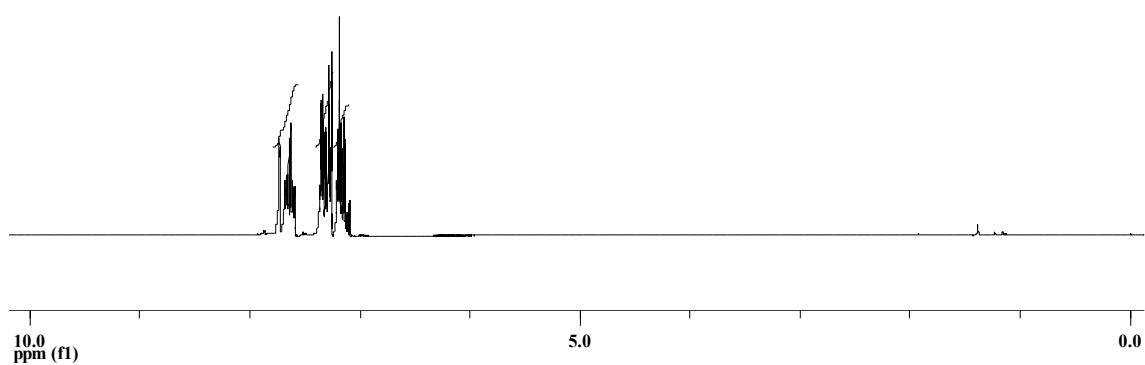
**Diphenyl sulfide (3a)**

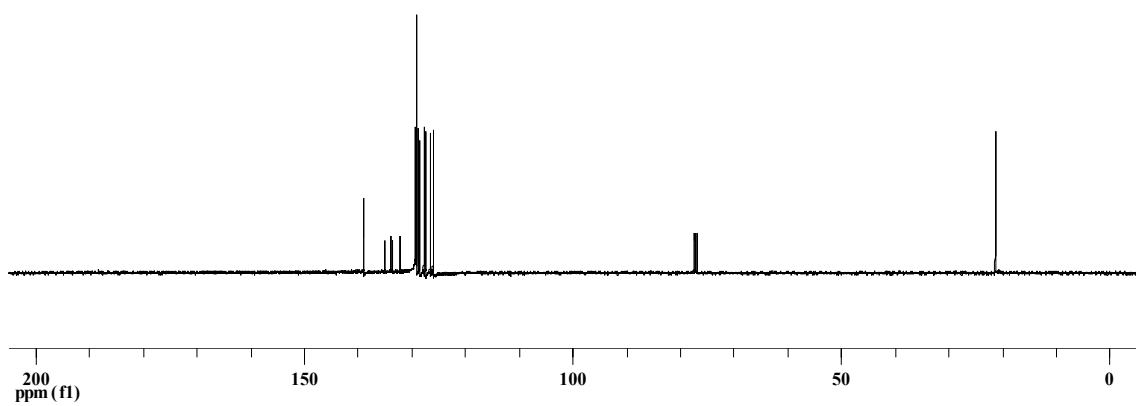
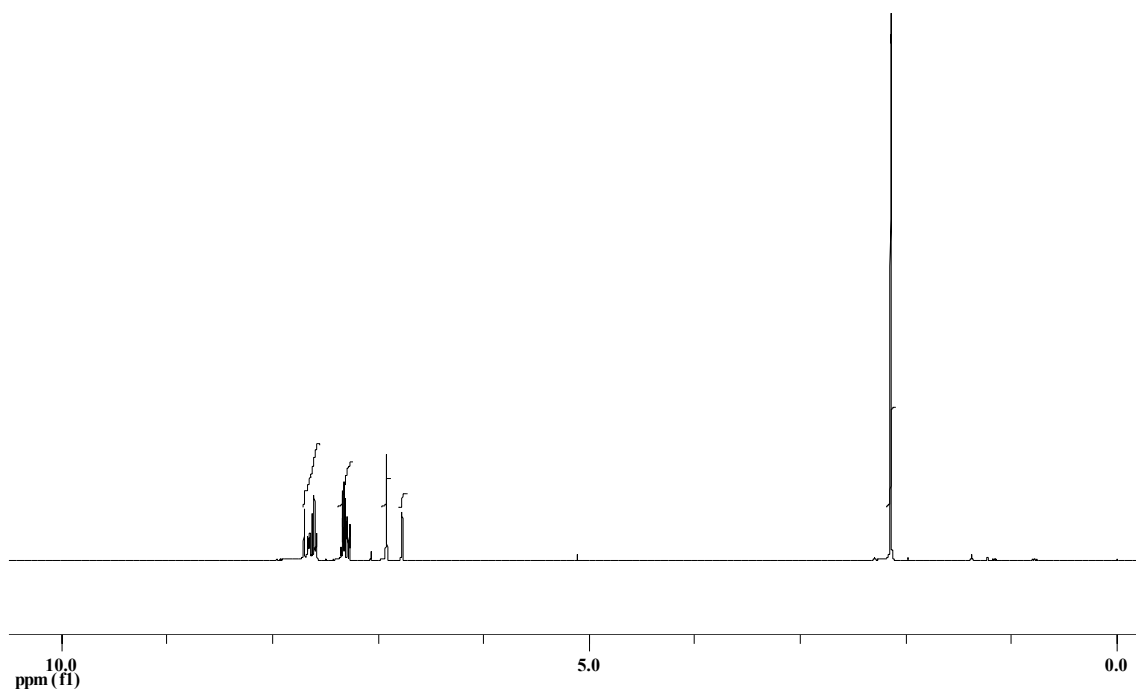
**Phenyl tolyl sulfide (3b)**

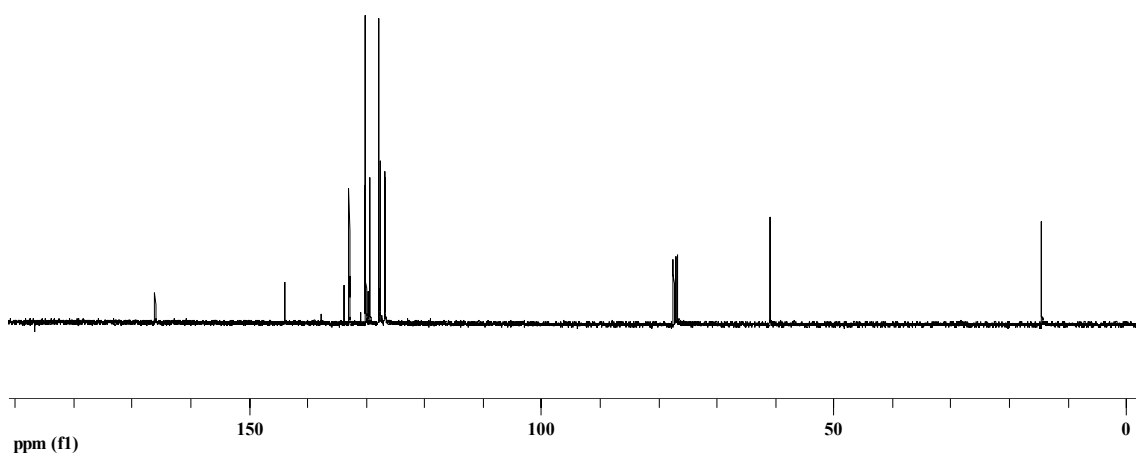
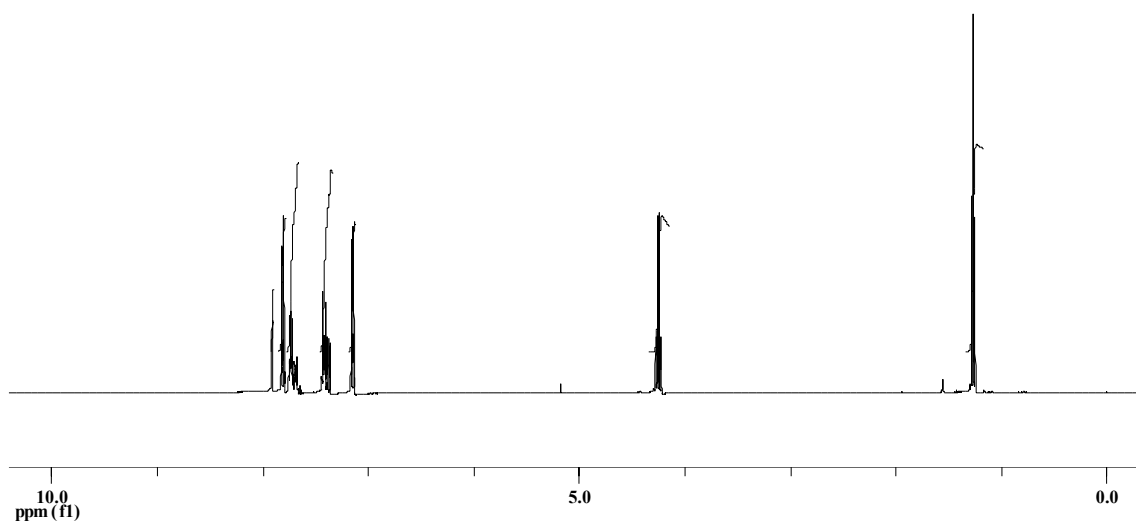


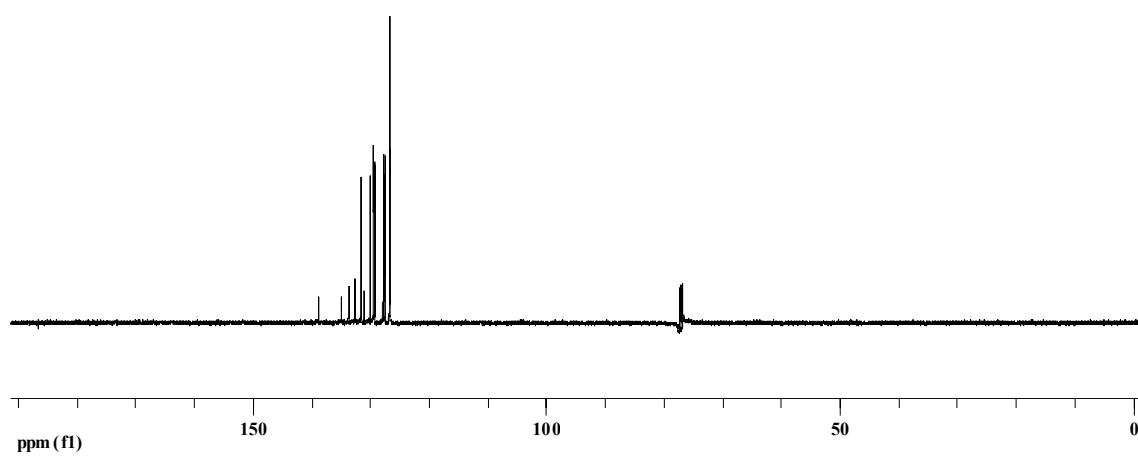
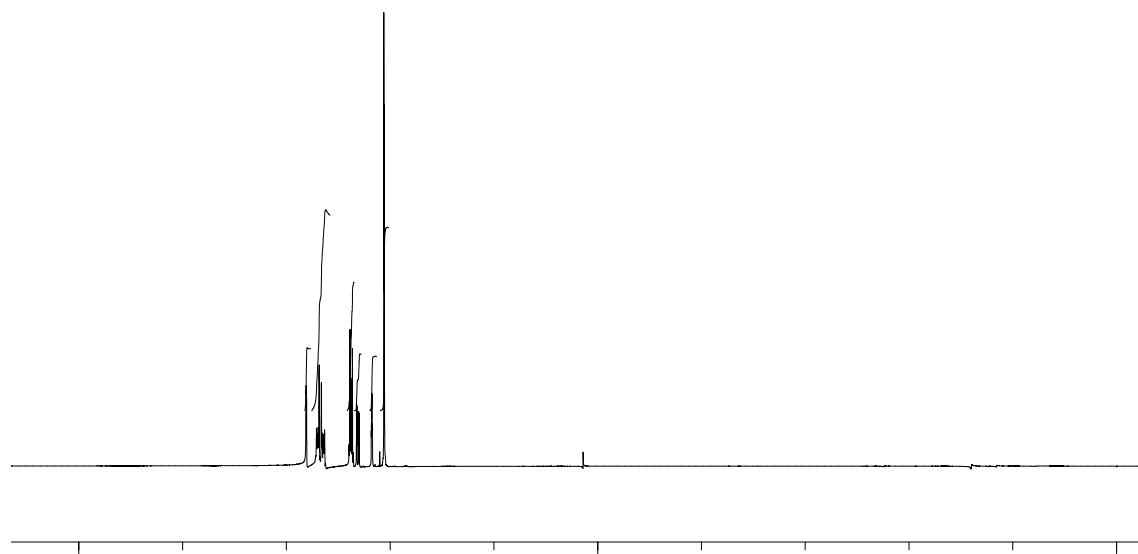
**4-Nitrophenyl phenyl sulfide (3c)**

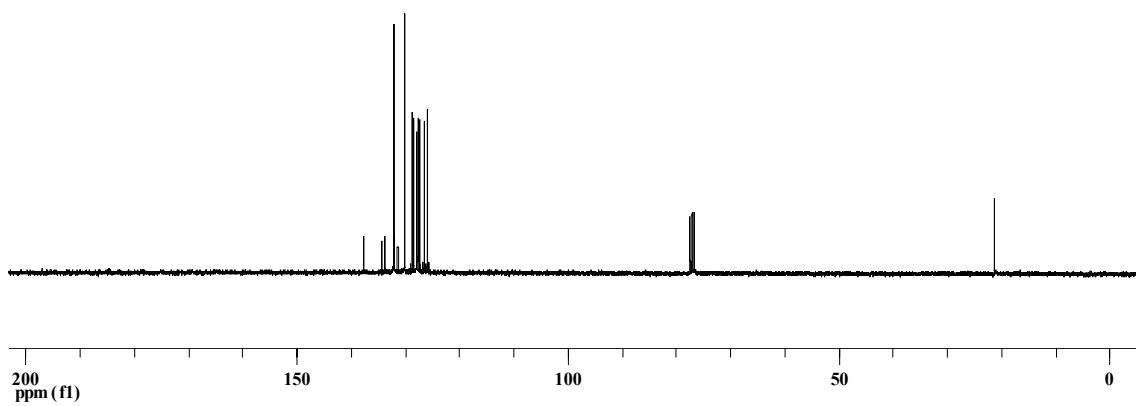
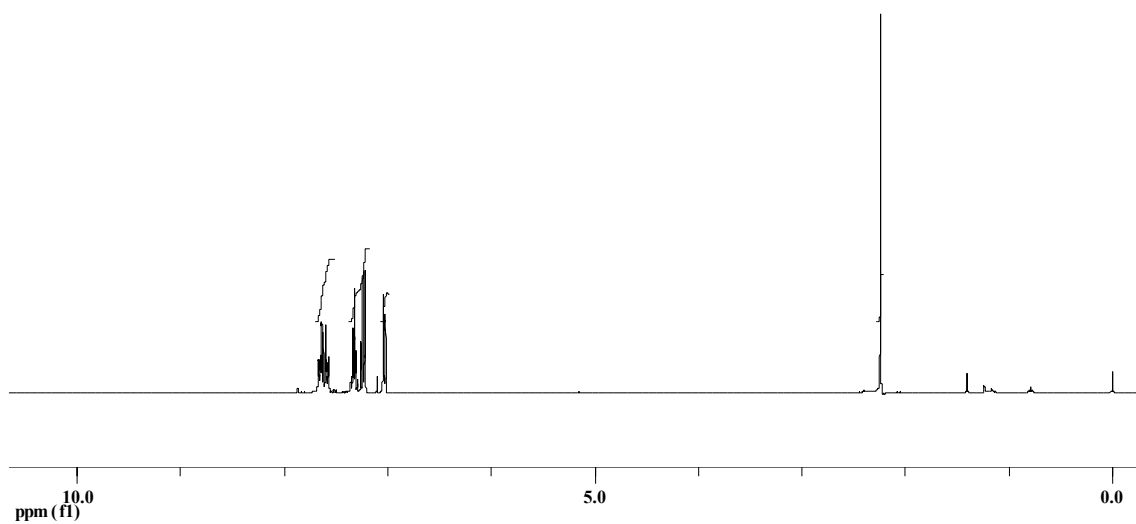
**2-Phenylthiobenzoic acid (3d)**

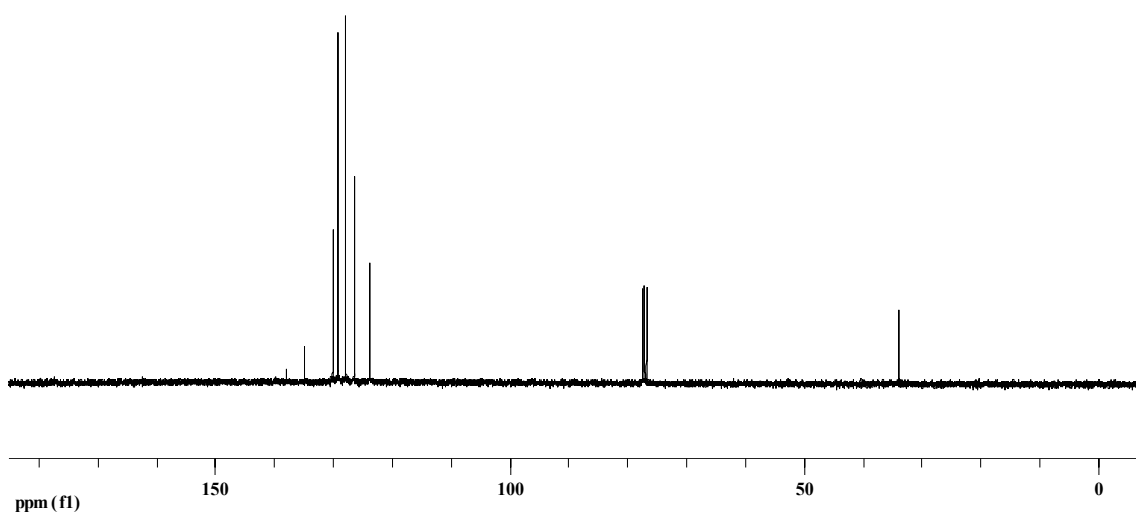
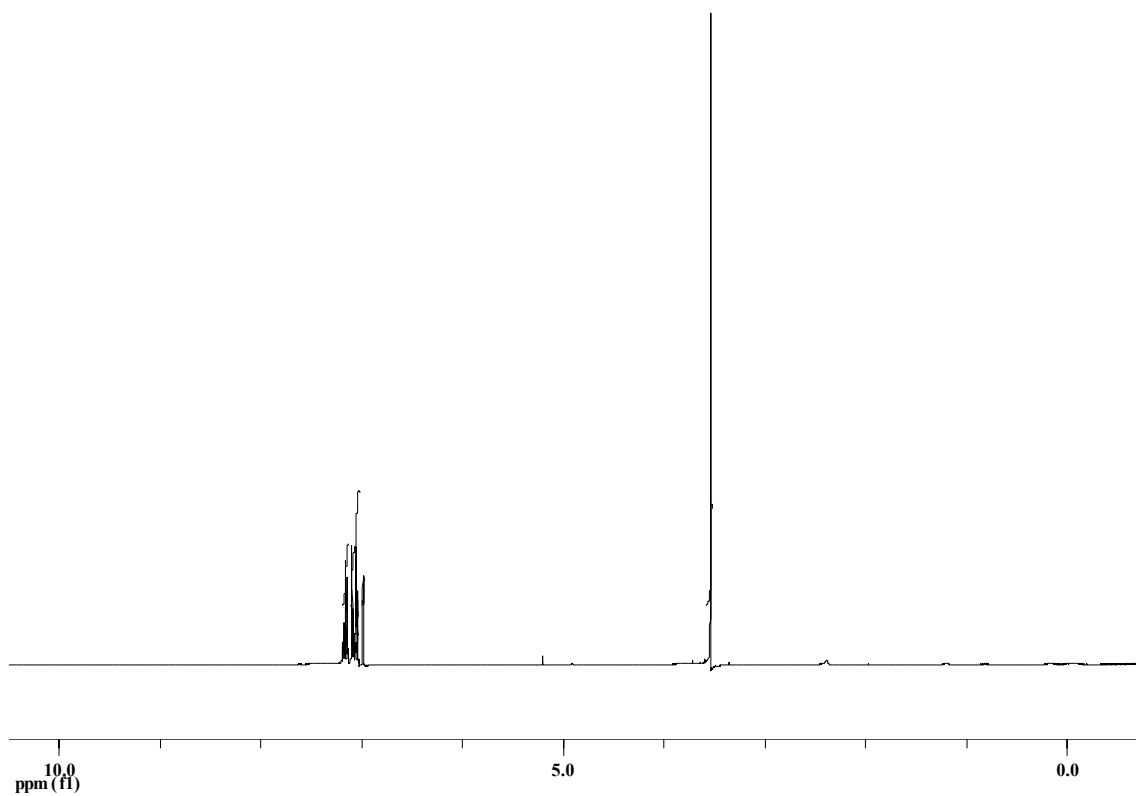
**2-Naphthyl phenyl sulfide (3e)**

**3,5-Dimethylphenyl 2-naphthyl sulfide (3f)**

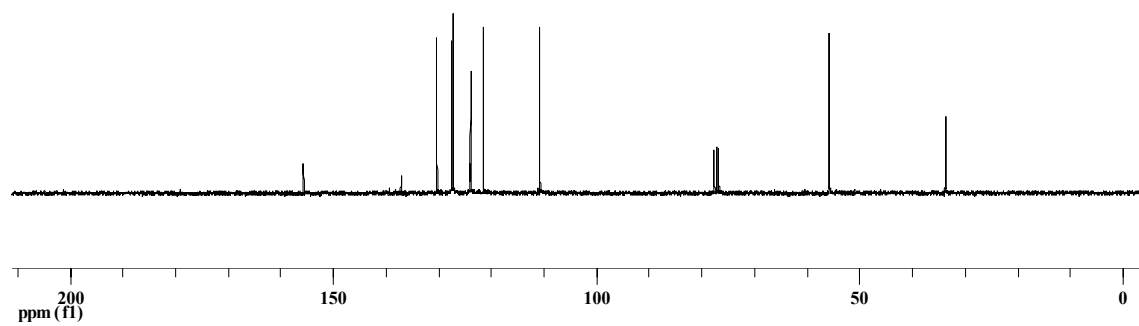
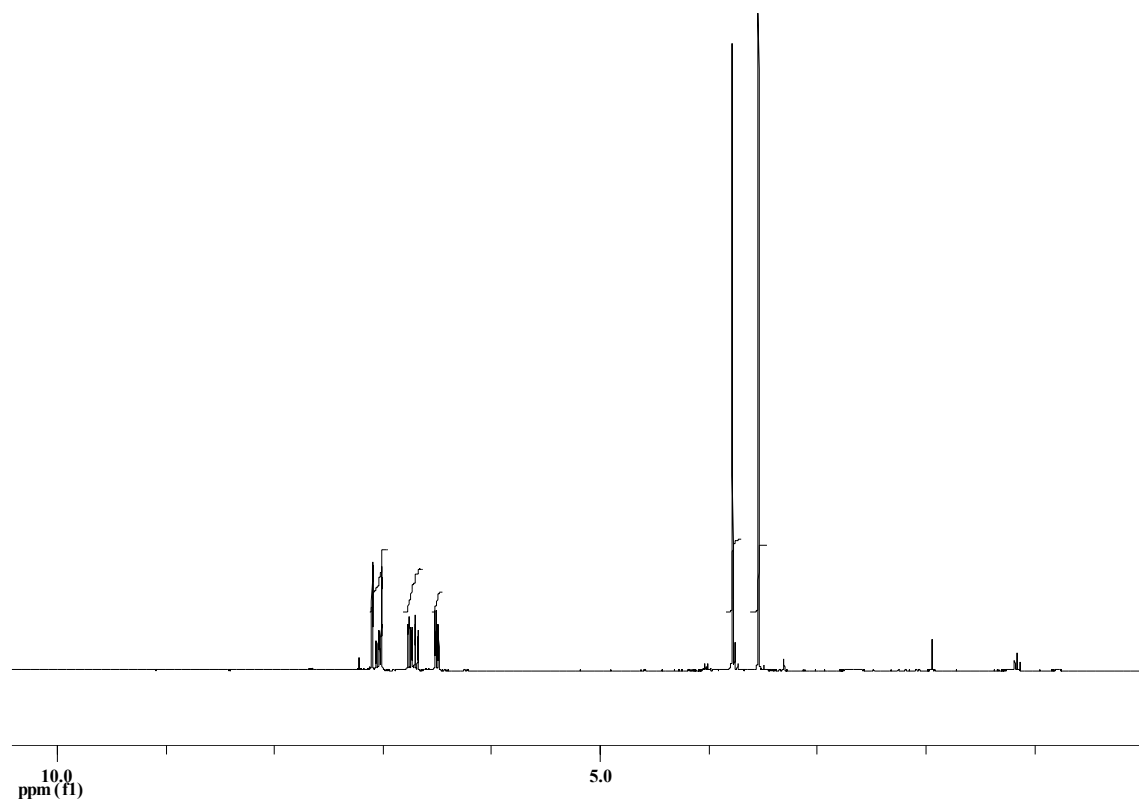
**4-(Thio-2-naphthyl)benzoic acid ethylester (3g)**

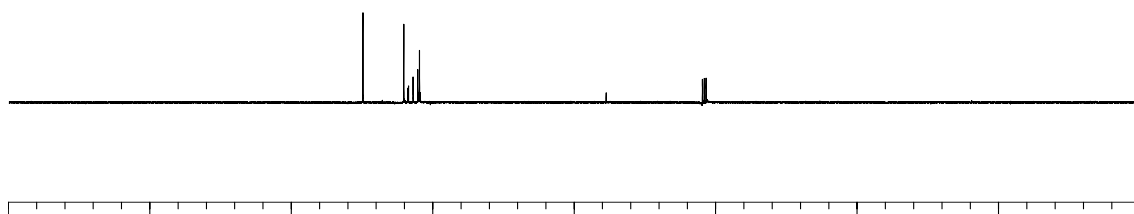
**3-Chlorophenyl 2-naphthyl sulfide (3h)**

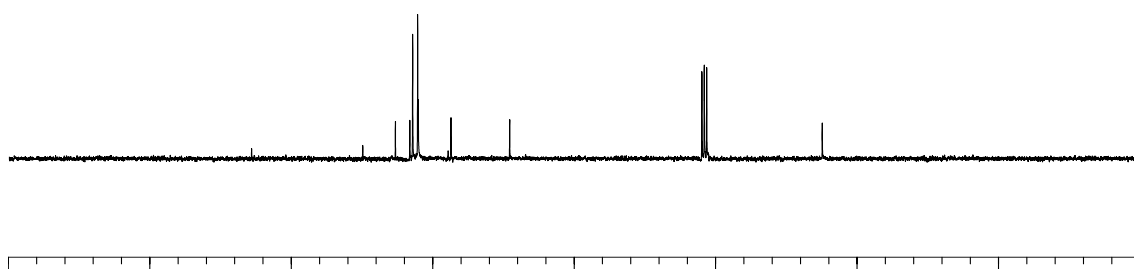
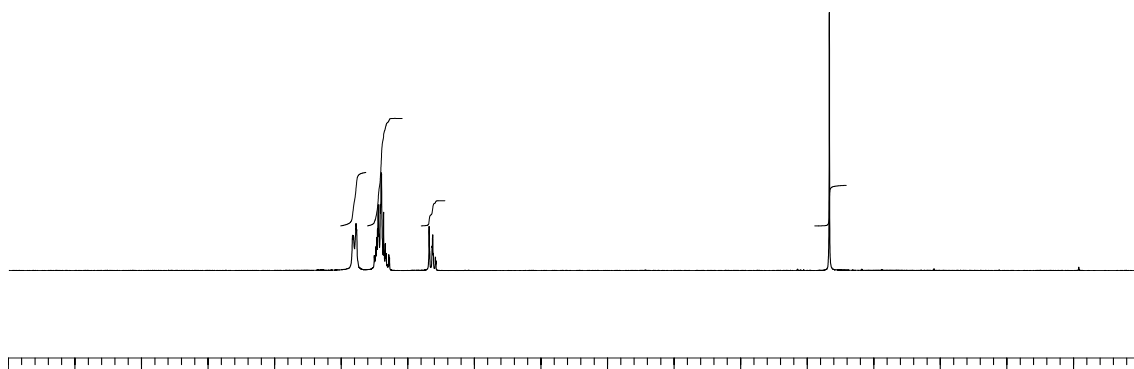
**4-Methylphenyl 2-naphthyl sulfide (3i)**

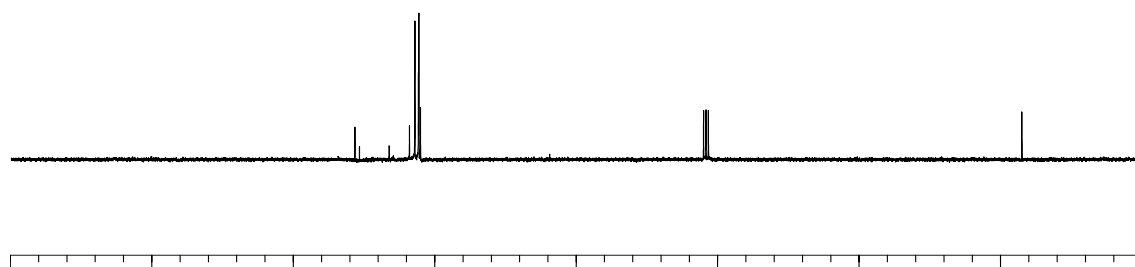
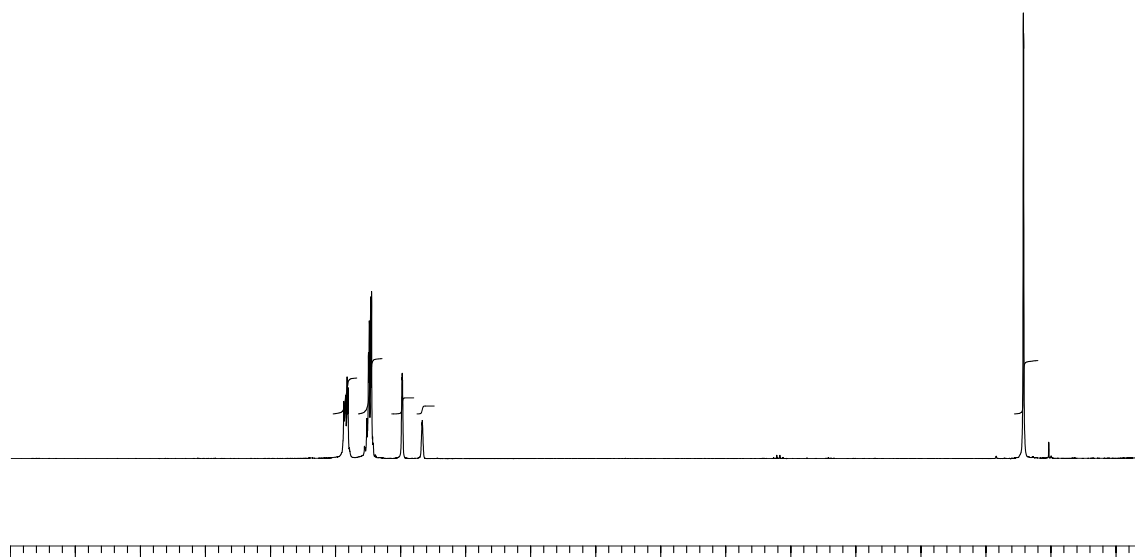
**2-(Phenylsulfanyl)-*N*-methylimidazole (3j)**

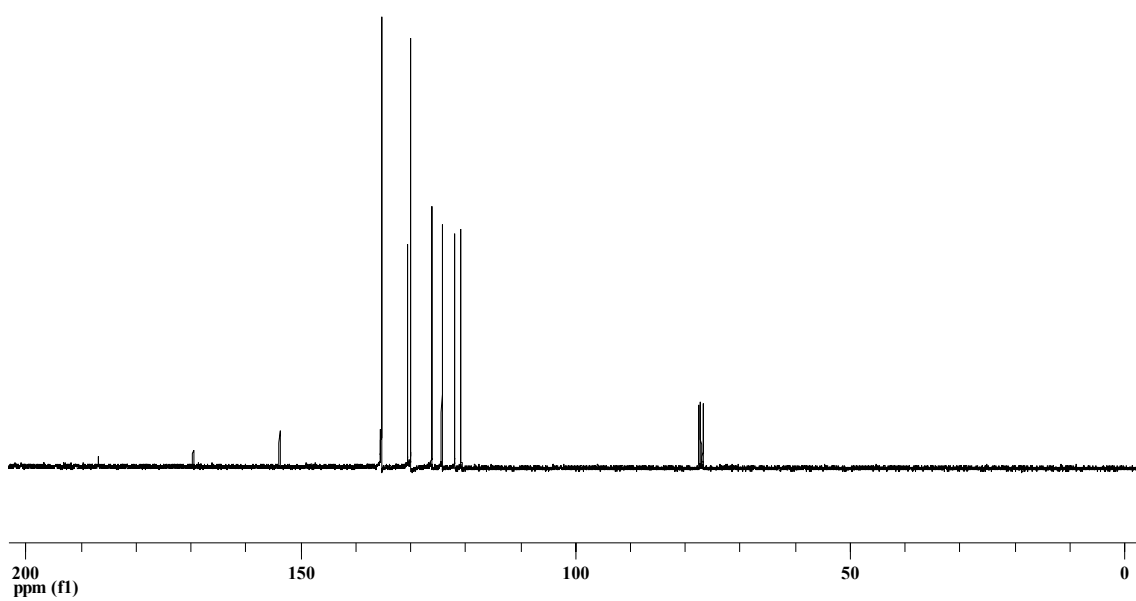
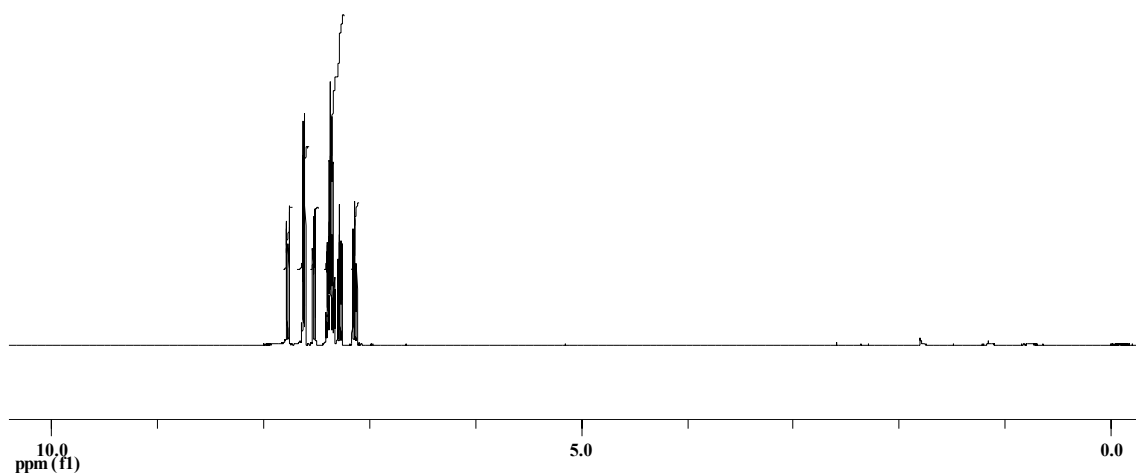


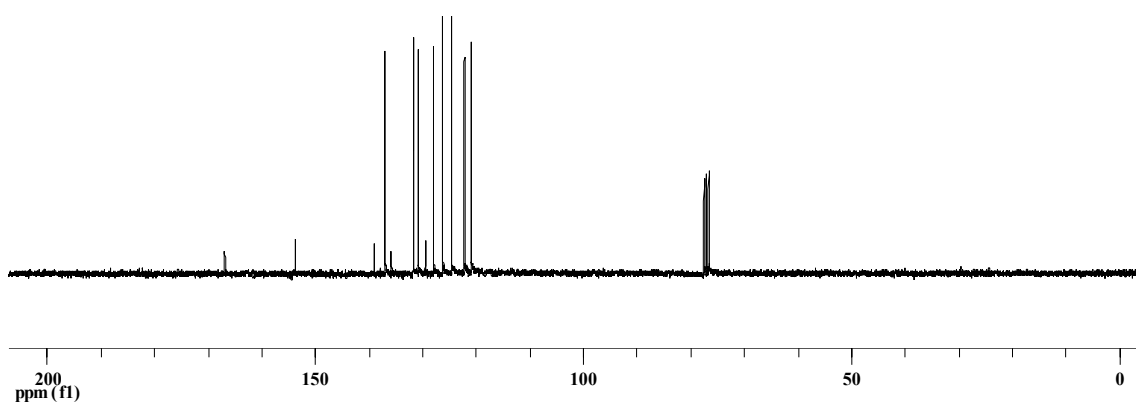
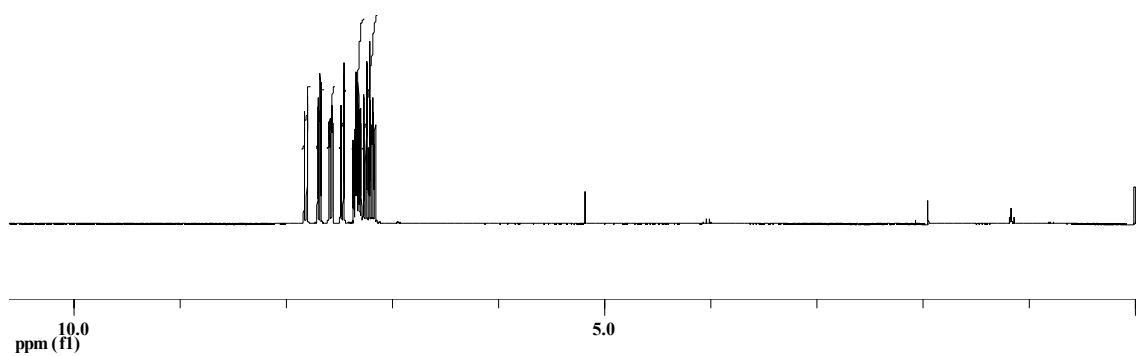
**2-(2-Methoxyphenylsulfanyl)-*N*-methylimidazole (3k)**

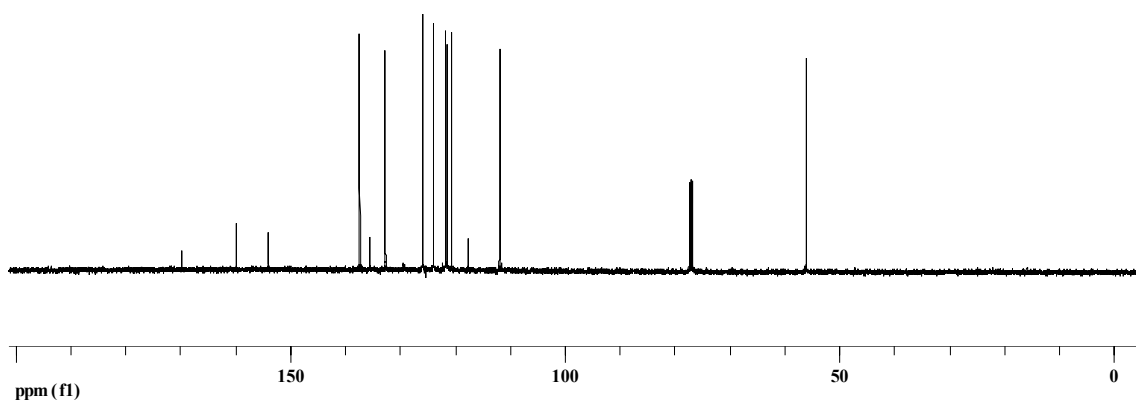
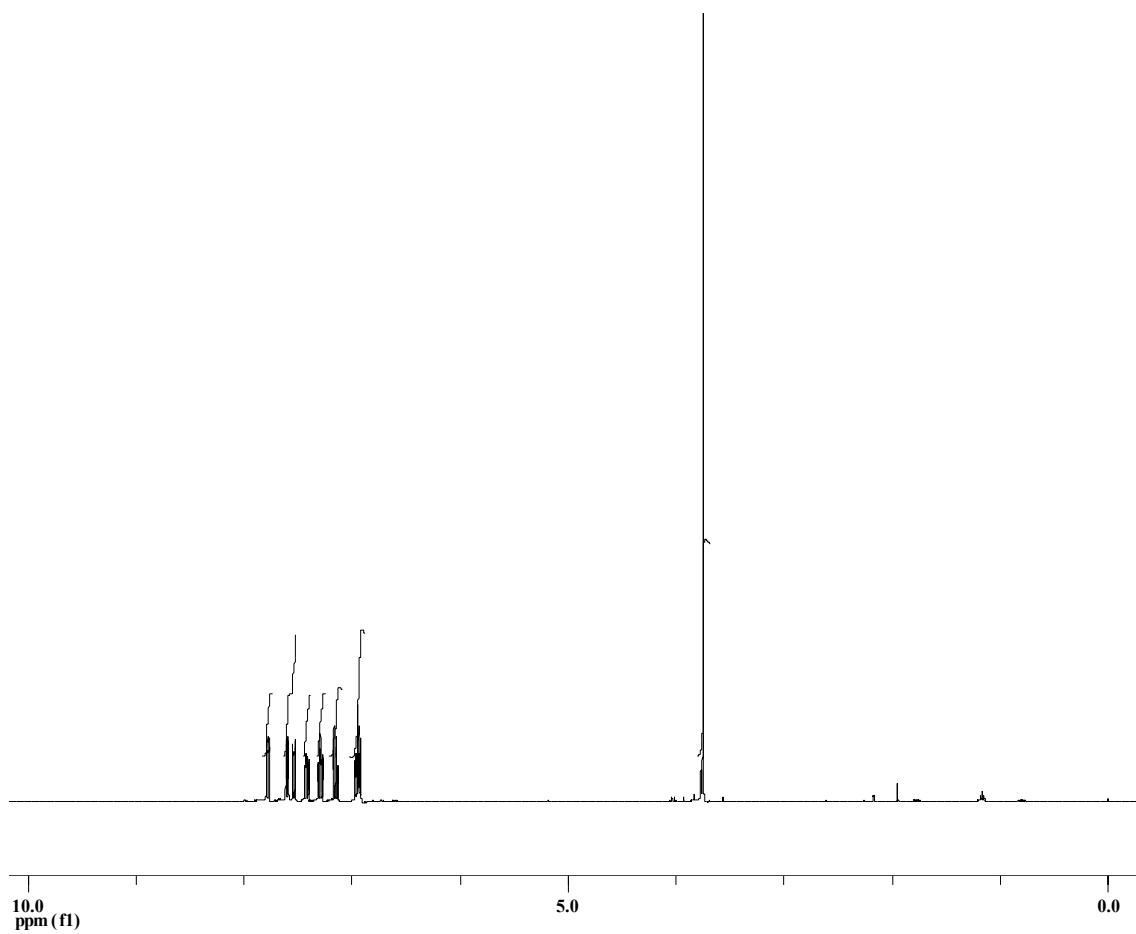
**4,5-Diphenyl-2-(phenylsulfanyl)imidazole (3l)**

**4,5-Diphenyl-2-(2-methoxyphenylsulfanyl)imidazole (3m)**

**2-(3,5-Dimethylphenylsulfanyl)-4,5-diphenylimidazole (3n)**

**2-Phenylsulfanyl-benzothiazole (3o)**

**2-(2-Chlorophenylsulfanyl)benzothiazole (3p)**

**2-(2-Methoxyphenylsulfanyl)benzothiazole (3q)**

**2-(4-Nitrophenylsulfanyl)benzothiazole (3r)**