Supplementary Information

Synthesis of CuO on mesoporous silica and its applications for coupling reactions of thiols with aryl iodides

Chin-Keng Chen,[a] Yan-Wun Chen,[b] Che-Hung Lin,[a] Hong-Ping Lin*[b] and Chin-Fa Lee*[a]

[a]Department of Chemistry, National Chung Hsing University, Taichung, Taiwan 402, ROC. E-mail: cfalee@dragon.nchu.edu.tw

[b]Department of Chemistry, National Cheng Kung University, Tainan, Taiwan 701, ROC. E-mail: hplin@mail.ncku.edu.tw

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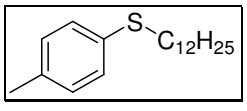
1. General information

All chemicals were purchased from commercial suppliers and used without further purification. Toluene was dried over sodium; dioxane, DME and DMF were dried over CaH_2 and stored in the presence of activated molecular sieve. All reactions were carried out under an inert atmosphere. Flash chromatography was performed on Merck silica gel 60 (230-400 mesh). NMR spectra were recorded on a Varian Unity Inova-600 or a Varian Mercury-400 instrument using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constant (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, b = broad. Melting points (m.p.) were determined using a Büchi 535 apparatus and are reported uncorrected. GC-MS analyses were performed on a GC-MS analysis on HP 5890 GC equipped with HP 5972 MS. High-resolution mass spectra were carried out on a Jeol JMS-HX 110 spectrometer by the services at the National Chung Hsing University.

2. General procedure for Table 1

A 4-mL sealable vial equipped with a magnetic stir bar was charged with base (1.5 mmol) under a nitrogen atmosphere. The aperture of the vial was then covered with a rubber septum. Under a nitrogen atmosphere, CuO on mesoporous silica (12.8 mg, 0.01 mmol), 1-dodecanethiol (0.29 mL, 1.2 mmol), 4-iodotoluene (218.0 mg, 1.00 mmol) and solvent (1.0 mL) were added via syringe. The septum was then replaced by a screw cap containing a PTFE septum, and the reaction vessel was heated at 110 °C oil bath. After stirring at this temperature for 21 h, the heterogeneous mixture was cooled to room temperature and diluted with EtOAc (20 mL). The resulting solution was filtered through a pad of celite then washed with EtOAc (20 mL) and concentrated to give the crude material which was then purified by column chromatography (SiO_2, hexane) to yield **3a**.

2.1 The representative example of Table 1



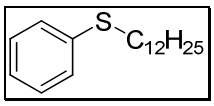
Dodecyl-*p*-tolyl sulfide (Table 1, entry 4)[1]

Following the general procedure for Table 1, using Cs_2CO_3 (488.0 mg, 1.5 mmol) and DMSO (1.0 mL) to give **3a** as a colorless oil (254 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 3 H), 1.23-1.63 (m, 20 H), 2.30 (s, 3 H), 2.85 (t, *J* = 7.2 Hz, 2 H), 7.07 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.0, 22.7, 28.8, 29.2, 29.2, 29.3, 29.5, 29.6, 29.6, 31.9, 34.4,

129.6, 129.8, 133.2, 135.8.

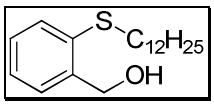
3. General procedure for Table 2, entries 1-12 (method A)

A 4-mL sealable vial equipped with a magnetic stir bar was charged with Cs_2CO_3 (488.0, 1.5 mmol) and CuO on mesoporous silica (12.8 mg, 0.01 mmol) under a nitrogen atmosphere. The aperture of the vial was then covered with a rubber septum, aryl iodide (1.00 mmol), DMSO or dioxane (1.0 mL) were added via syringe. The aliphatic thiol (1.2 mmol) was added via syringe, and the vial sealed with a cap containing a PTFE septum and the reaction vessel was heated at 110 °C oil bath. After stirring at this temperature for 21 h, the heterogeneous mixture was cooled to room temperature and diluted with EtOAc (20 mL). The resulting solution was directly filtered through a pad of celite then washed with EtOAc (20 mL) and concentrated to give the crude material which was then purified by column chromatography (SiO_2, hexane and CH_2Cl_2 or Ethyl acetate) to yield **3**.



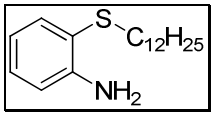
Dodecyl phenyl sulfide 3b (Table 2, entry 1)[2].

Following the method A, using 1-dodecanethiol (0.29 mL, 1.2 mmol), iodobenzene (0.115 mL, 1.00 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane) to provide **3b** as a colorless oil (257 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.4 Hz, 3 H), 1.23-1.66 (m, 20 H), 2.90 (t, *J* = 7.6 Hz, 2 H), 7.11-7.31 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.8, 29.1, 29.3, 29.5, 29.6, 29.6, 29.7, 31.9, 33.6, 125.6, 128.8, 128.8, 137.1.



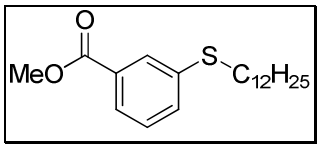
(2-(Dodecylthio)phenyl)methanol 3c (Table 2, entry 2).

Following the method A, using 1-dodecanethiol (0.29 mL, 1.2 mmol), 2-iodobenzyl alcohol (234.0 mg, 1.00 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3c** as a white solid (220 mg, 72% yield). M.p.: 38-39 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.76 (t, *J* = 6.4 Hz, 3 H), 1.13-1.54 (m, 20 H), 1.96 (br s, 1 H), 2.80 (t, *J* = 7.6 Hz, 2 H), 4.65 (s, 2 H), 7.01-7.26 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 28.8, 29.1, 29.2, 29.4, 29.5, 29.5, 29.5, 31.8, 33.9, 63.4, 126.1, 127.9, 128.0, 129.2, 135.0, 140.4; HREI-MS calcd. for $C_{19}H_{32}SO$: 308.2174, Found: 308.2166.



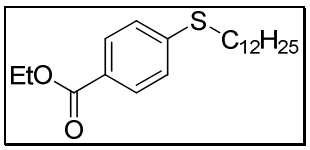
2-*n*-Dodecanesulfanylaniline 3d (Table 2, entry 3)[3].

Following the method A, using 1-dodecanethiol (0.29 mL, 1.2 mmol), 2-iodoaniline (219 mg, 1.00 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3d** as a colorless oil (201 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.4 Hz, 3 H), 1.23-1.58 (m, 20 H), 2.71 (t, *J* = 7.2 Hz, 2 H), 4.31 (br s, 2 H), 6.65-6.72 (m, 2 H), 7.06-7.11 (m, 1 H), 7.33-7.36 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 28.7, 29.1, 29.3, 29.5, 29.5, 29.6, 29.6, 31.9, 34.8, 114.7, 114.7, 118.3, 129.3, 135.5, 148.0.



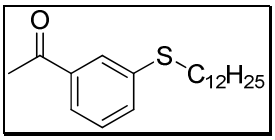
Methyl 3-(dodecylthio)benzoate 3e (Table 2, entry 4).

Following the method A, using CuO on mesoporous silica (64.0 mg, 0.05 mmol), 1-dodecanethiol (0.29 mL, 1.2 mmol), methyl-3-iodobenzoate (262 mg, 1.00 mmol) in dioxane, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3e** as a colorless oil (0.291 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 3 H), 1.23-1.69 (m, 20 H), 2.94 (t, *J* = 7.2 Hz, 2 H), 3.90 (s, 3 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.45-7.47 (m, 1H), 7.78-7.81 (m, 1H), 7.94-7.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.5, 28.6, 28.8, 29.0, 29.2, 29.3, 29.4, 29.5, 29.5, 31.7, 33.1, 51.9, 126.4, 128.5, 129.0, 130.6, 132.5, 138.0, 166.3; HREI-MS calcd. for $C_{20}H_{32}SO_2$: 336.2123, Found: 2119.



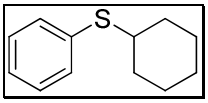
Ethyl 4-(dodecylthio)benzoate 3f (Table 2, entry 5).

Following the method A, using 1-dodecanethiol (0.29 mL, 1.2 mmol), ethyl-4-iodobenzoate (0.17 mL, 1.00 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3f** as a yellow oil (275 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 3 H), 1.24-1.69 (m, 23 H), 2.96 (t, *J* = 7.2 Hz, 2 H), 4.34 (q, *J* = 7.2 Hz, 2 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.90 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 14.1, 22.5, 28.5, 28.7, 29.0, 29.2, 29.3, 29.4, 29.4, 31.7, 31.8, 60.4, 125.9, 126.6, 129.6, 144.2, 165.8; HREI-MS calcd. for $C_{21}H_{34}SO_2$: 350.2280, Found: 350.2271.



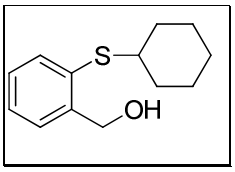
1-(3-(Dodecylthio)phenyl)ethanone 3g (Table 2, entry 6).

Following the method A, using CuO on mesoporous silica (64.0 mg, 0.05 mmol), 1-dodecanethiol (0.29 mL, 1.2 mmol), 3'-iodoacetophenone (0.14 mL, 1.00 mmol) in dioxane, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3g** as a yellow solid (310 mg, 97% yield). M.p.: 44-45 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.2 Hz, 3 H), 1.25-1.70 (m, 20 H), 2.59 (s, 3 H), 2.96 (t, J = 7.2 Hz, 2 H), 7.37 (t, J = 7.6 Hz, 1 H), 7.48-7.50 (m, 1H), 7.71-7.73 (m, 1H), 7.88-7.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.5, 26.2, 28.6, 28.7, 28.9, 29.1, 29.3, 29.4, 29.4, 31.7, 33.0, 125.1, 127.5, 128.6, 132.5, 137.4, 138.3, 196.9; HREI-MS calcd. for $C_{20}H_{32}SO$: 320.2174, Found: 320.2184.



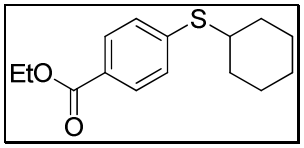
Cyclohexyl phenyl sulfide 3h (Table 2, entry 7)[4].

Following the method A, using cyclohexyl mercaptan (0.15 mL, 1.2 mmol), iodobenzene (0.115 mL, 1.00 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane) to provide **3h** as a yellow oil (130 mg, 68% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.20-1.39 (m, 5 H), 1.58-1.61 (m, 1 H), 1.74-1.77 (m, 2 H), 1.95-2.01 (m, 2 H), 3.06-3.11 (m, 1 H), 7.19-7.30 (m, 3 H), 7.37-7.40 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.7, 25.9, 33.2, 46.4, 126.5, 128.6, 131.7, 135.1.



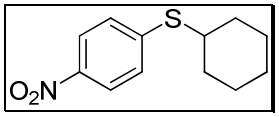
(2-(Cyclohexylthio)phenyl)methanol 3i (Table 2, entry 8).

Following the method A, using cyclohexyl mercaptan (0.15 mL, 1.2 mmol), 2-iodobenzyl alcohol (234.0 mg, 1.00 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3i** as a yellow oil (211 mg, 95% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21-1.42 (m, 5 H), 1.58-1.62 (m, 1 H), 1.73-1.78 (m, 2 H), 1.94-1.97 (m, 2 H), 2.37 (br s, 1 H), 3.06-3.13 (m, 1 H), 4.78 (s, 2 H), 7.22-7.25 (m, 2 H), 7.34-7.38 (m, 1 H), 7.42-7.44 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6, 25.9, 33.3, 47.1, 63.7, 127.1, 127.8, 128.2, 132.8, 133.1, 142.3; HREI-MS calcd. for $C_{13}H_{18}SO$: 222.1078, Found: 222.1074.



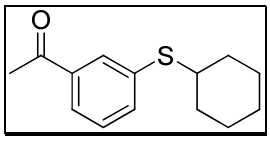
Ethyl 4-(cyclohexylthio)benzoate 3j (Table 2, entry 9).

Following the method A, using cyclohexyl mercaptan (0.15 mL, 1.2 mmol), ethyl-4-iodobenzoate (0.17 mL, 1.00 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3j** as a colorless oil (192 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23-1.45 (m, 8 H), 1.61-1.64 (m, 1 H), 1.76-1.79 (m, 2 H), 2.00-2.02 (m, 2 H), 3.24-3.29 (m, 1 H), 4.34 (q, *J* = 7.6 Hz, 2 H) 7.32 (d, *J* = 8.4 Hz, 2 H), 7.91 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 25.6, 25.8, 33.0, 45.0, 60.7, 127.4, 128.5, 129.7, 142.7, 166.2; HREI-MS calcd. for $C_{15}H_{20}SO_2$: 264.1184, Found: 264.1181.



Cyclohexyl(4-nitrophenyl)sulfane 3k (Table 2, entry 10).

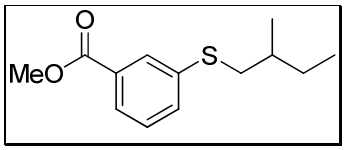
Following the method A, using cyclohexyl mercaptan (0.15 mL, 1.2 mmol), 1-iodo-4-nitrobenzene (249.0 mg, 1.00 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3k** as a yellow oil (226 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24-1.46 (m, 5 H), 1.64-1.67 (m, 1 H), 1.78-1.81 (m, 2 H), 2.02-2.05 (m, 2 H), 3.30-3.36 (m, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 8.09 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.7, 26.0, 32.8, 44.7, 123.8, 127.6, 145.0, 146.9; HREI-MS calcd. for $C_{12}H_{15}NSO_2$: 237.0823, Found: 237.0820.



1-(3-(Cyclohexylthio)phenyl)ethanone 3l (Table 2, entry 11).

Following the method A, using CuO on mesoporous silica (64.0 mg, 0.05 mmol), cyclohexyl mercaptan (0.15 mL, 1.2 mmol), 3'-iodoacetophenone (0.14 mL, 1.00 mmol) in dioxane, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3l** as a yellow oil (191 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27-1.44 (m, 5 H), 1.62-1.65 (m, 1 H), 1.78-1.80 (m, 2 H), 1.98-2.00 (m, 2 H), 2.60 (s, 3 H), 3.15-3.20 (m, 1 H), 7.38 (t, *J* = 7.6 Hz, 1 H), 7.56-7.58 (m, 1H), 7.77-7.80 (m, 1H), 7.96-7.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.6, 25.8, 26.5, 33.1, 46.4, 126.3, 128.8, 130.9, 135.8, 136.3, 137.5, 197.4; HREI-MS calcd. for $C_{14}H_{18}$ SO:

234.1078, Found: 234.1069.

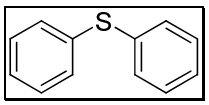


Methyl 3-(2-methylbutylthio)benzoate 3m (Table 2, entry 12).

Following the method A, using CuO on mesoporous silica (64.0 mg, 0.05 mmol), 2-methyl-1-butanethiol (0.155 mL, 1.2 mmol), methyl-3-iodobenzoate (262 mg, 1.00 mmol) in dioxane, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3m** as a colorless oil (217 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.2 Hz, 3 H), 1.01 (d, *J* = 6.4 Hz, 3 H), 1.21-1.32 (m, 1 H), 1.45-1.57 (m, 1 H), 1.61-1.69 (m, 1 H), 2.77 (dd, *J* = 7.6, 12.8 Hz, 1 H), 2.97 (dd, *J* = 6.0, 12.8 Hz, 1 H), 3.89 (s, 3 H), 7.31 (t, *J* = 7.6 Hz, 1 H), 7.45-7.48 (m, 1H), 7.77-7.80 (m, 1H), 7.94-7.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1, 18.8, 28.7, 34.4, 40.3, 52.1, 126.4, 128.6, 129.0, 130.7, 132.6, 138.4, 166.6; HREI-MS calcd. for $C_{13}H_{18}SO_2$: 238.1028, Found: 238.1033.

General procedure for Table 2, entries 13-24 (method B)

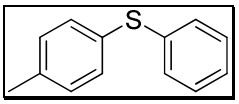
A 4-mL sealable vial equipped with a magnetic stir bar was charged with Cs_2CO_3 (488.0, 1.5 mmol) and CuO on mesoporous (12.8 mg, 0.01 mmol) in DMSO or dioxane (1.0 mL) under a nitrogen atmosphere. The aperture of the vial was then covered with a rubber septum, aryl iodide (1.10 mmol) and aliphatic thiol (1.0 mmol) were added via syringe, and the vial sealed with a cap containing a PTFE septum and the reaction vessel was heated at 110 °C oil bath. After stirring at this temperature for 21 h, the heterogeneous mixture was cooled to room temperature and diluted with EtOAc (20 mL). The resulting solution was directly filtered through a pad of celite then washed with EtOAc (20 mL) and concentrated to give the crude material which was then purified by column chromatography (SiO_2, hexane/CH_2Cl_2 or hexane/EtOAc) to yield **3.**



Diphenyl sulfide 3n (Table 2, entry 13)[5].

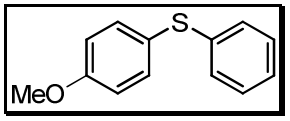
Following the method B, using Cs_2CO_3 (489.0 mg, 1.5 mmol), thiophenol (0.10 mL, 1.0 mmol), iodobenzene (0.12 mL, 1.1 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane) to provide **3n** as a colorless oil (178 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18-7.32 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$):

δ = 127.0, 129.2, 131.0, 135.8.



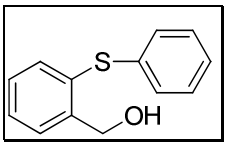
4-Methylphenyl phenyl sulfide 3o (Table 2, entry 14)[5].

Following the method B, using Cs_2CO_3 (489.0 mg, 1.5 mmol), thiophenol (0.10 mL, 1.0 mmol), 4-iodotoluene (240 mg, 1.1 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane) to provide **3o** as a colorless oil (190 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 7.10-7.30 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 126.3, 129.0, 129.7, 130.0, 131.2, 132.2, 137.1, 137.5.



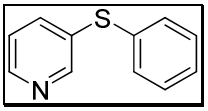
4-Methoxyphenyl phenyl sulfide 3p (Table 2 entry 15)[6].

Following the method B, using Cs_2CO_3 (489.0 mg, 1.5 mmol), thiophenol (0.10 mL, 1.0 mmol), 4-iodoanisole (257 mg, 1.1 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:CH_2Cl_2 = 10:1) to provide **3p** as a colorless oil (143 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 3 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 7.08-7.25 (m, 5 H), 7.40 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 114.9, 124.3, 125.7, 128.2, 128.9, 135.3, 138.6, 159.8.



(2-(Phenylthio)phenyl)methanol 3q (Table 2, entry 16)[7].

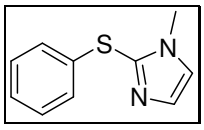
Following the method B, using Cs_2CO_3 (489.0 mg, 1.5 mmol), thiophenol (0.10 mL, 1.0 mmol), 2-iodobenzyl alcohol (257 mg, 1.1 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:CH_2Cl_2 = 8:2) to provide **3q** as a colorless oil (173 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02 (t, *J* = 6.4 Hz, 1 H), 4.76 (d, *J* = 6.4 Hz, 2 H), 7.15-7.21 (m, 6 H), 7.23-7.28 (m, 2 H), 7.50 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.3, 126.5, 128.3, 128.4, 129.1, 129.4, 132.3, 133.8, 135.9, 142.3.



3-Pyridyl phenyl sulfide 3r (Table 2, entry 17)[8].

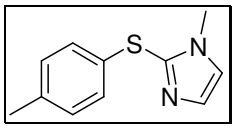
Following the method B, using Cs_2CO_3 (489.0 mg, 1.5 mmol), thiophenol (0.10 mL, 1.0 mmol), 3-iodopyridine (225 mg, 1.1 mmol) in DMSO, then purified by column

chromatography (SiO_2, hexane:CH_2Cl_2 = 8:2) to provide **3r** as a yellow oil (163 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12-7.15 (m, 1 H), 7.15-7.34 (m, 5 H), 7.51-7.55 (m, 1 H), 8.39-8.41 (m, 1 H), 8.52 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.6, 127.6, 129.2, 131.5, 133.3, 133.7, 137.6, 147.6, 150.8.



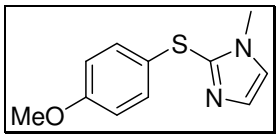
2-(Phenylsulfanyl)-*N*-methylimidazole 3s (Table 2, entry 18)[5].

Following the method B, using Cs_2CO_3 (489.0 mg, 1.5 mmol), 2-mercapto-1-methylimidazole (114 mg, 1.0 mmol), iodobenzene (0.12 mL, 1.1 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:EA = 3:1) to provide **3r** as a yellow oil (141 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (s, 3 H), 7.06 (d, *J* = 0.8 Hz, 1 H), 7.10-7.20 (m, 4 H), 7.20-7.28 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.6, 123.7, 126.3, 127.7, 129.0, 129.8, 134.6, 137.6.



1-Methyl-2-(*p*-toylsulfanyl)-1*H*-imidazole 3t (Table 2, entry 19)[9].

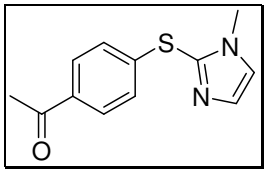
Following the method B, using Cs_2CO_3 (489.0 mg, 1.5 mmol), 2-mercapto-1-methylimidazole (114 mg, 1.0 mmol), 4-iodotoluene (240 mg, 1.1 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:EA = 3:1) to provide **3s** as a yellow oil (178 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H), 3.62 (s, 3 H), 7.00-7.08 (m, 3 H), 7.08-7.18 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.5, 33.4, 123.4, 128.2, 129.4,129.6, 130.4, 136.3, 138.1.



2-(4-Methoxyphenylthio)-1-methyl-1*H*-imidazole 3u (Table 2, entry 20)

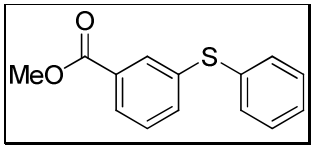
Following the method B, using 2-mercapto-1-methylimidazole (114 mg, 1.0 mmol), 4-iodoanisole (257 mg, 1.1 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:EA = 3:1) to provide **3u** as a yellow oil (158 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.37 (s, 3 H), 3.51 (s, 3 H), 6.53-6.60 (m, 2 H), 6.74 (d, *J* = 1.2 Hz, 1 H), 6.85 (d, *J* = 1.2 Hz, 1 H), 6.87-7.05 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.4, 54.9, 114.5, 123.2, 123.9, 129.2, 131.2, 139.1, 158.8;

HREI-MS calcd. for:220.0670, Found: 220.0671.



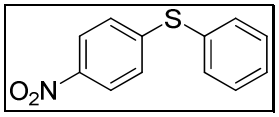
1-(4-(1-Methyl-1*H*-imidazol-2-ylthio)phenyl)ethanone 3v (Table 3, entry 21).

Following the method B, using Cs_2CO_3 (489.0 mg, 1.5 mmol), 2-mercapto-1-methylimidazole (114 mg, 1.0 mmol), 4'-iodoacetophenone (271 mg 1.1 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:EA = 2:1) to provide **3v** as a yellow oil (179 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.52 (s, 3 H), 3.63 (s, 3 H), 7.00-7.09 (m, 2 H), 7.10-7.14 (m, 1 H), 7.20-7.25 (m, 1 H), 7.78-7.82 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.1, 33.5, 124.2, 125.9, 128.7, 130.2, 134.4, 135.6, 142.0, 196.6; HREI-MS calcd. for $C_{12}H_{12}SON_2$: 232.0670, Found: 232.0660.



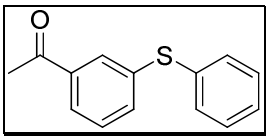
Methyl 3-phenylsulfanylbenzoate 3w (Table 2, entry 22)[6]

Following the method B, using CuO on mesoporous silica (64.0 mg, 0.05 mmol), thiophenol (0.10 mL, 1.0 mmol), methyl-3-iodobenzoate (288 mg, 1.1 mmol) in dioxane, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3w** as a colorless oil (184 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 7.21-7.32 (m, 6 H), 7.38-7.41 (m, 1 H), 7.80-7.83 (m, 1 H), 7.93-7.94 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.1, 127.6, 127.9, 129.1, 129.3, 131.1, 131.3, 131.6, 134.5, 134.6, 137.0, 166.3.



4-Nitrophenyl phenyl sulfide 3x (Table 2, entry 23)[5]**.**

Following the method B, using thiophenol (0.10 mL, 1.0 mmol), 4-nitroiodobenzene (274 mg, 1.1 mmol) in DMSO, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3x** as a yellow oil (215 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (d, *J* = 8.8 Hz, 2 H), 7.43-7.45 (m, 3 H), 7.46-7.54 (m, 2 H), 8.05 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 123.8, 126.4, 129.5, 130.0, 130.2, 134.5, 145.1, 148.3.



1-(3-(Phenylthio)phenyl)ethanone 3y (Table 2, entry 24)

Following the method B, using thiophenol (0.10 mL, 1.0 mmol), 3'-iodoacetophenone (0.155 mL, 1.1 mmol) in dioxane, then purified by column chromatography (SiO_2, hexane:EA = 9:1) to provide **3y** as a yellow oil (163 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 3 H), 7.28-7.38 (m, 6 H), 7.43-7.46 (m, 1 H), 7.77-7.79 (m, 1 H), 7.77-7.78 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.4, 126.4, 127.6, 129.2, 129.2, 129.7, 131.6, 134.2, 134.4, 137.3, 137.7, 197.1; HREI-MS calcd. for $C_{14}H_{12}SO$: 228.0609, Found: 228.0601.

4. Fig. S1

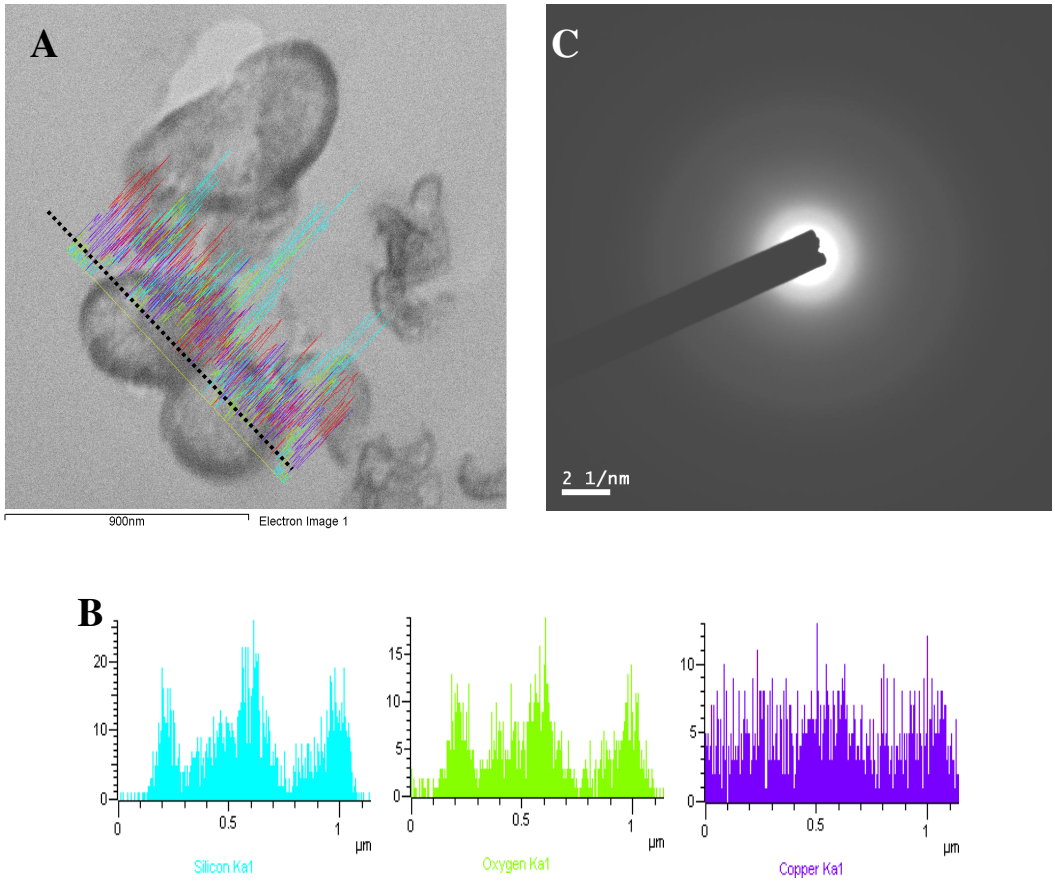


Fig. S1 Scanning transmission-electronmicroscopy image (STEM), in conjunction with EDX elemental mapping and line profiles revealed that the shell of the mesoporous silica composed of Si, O and Cu. The similar element distribution profiles indicate that the CuO is well dispersed within the mesoporous silica. (A) HAADF-STEM image. (B) Line profiles of Si, O, and Cu recorded along the dashed line shown in **Figure S1(A).** (C) The selected area electron diffraction pattern of the shell of the CuO on mesoporous silica sample.

5. Fig. S2

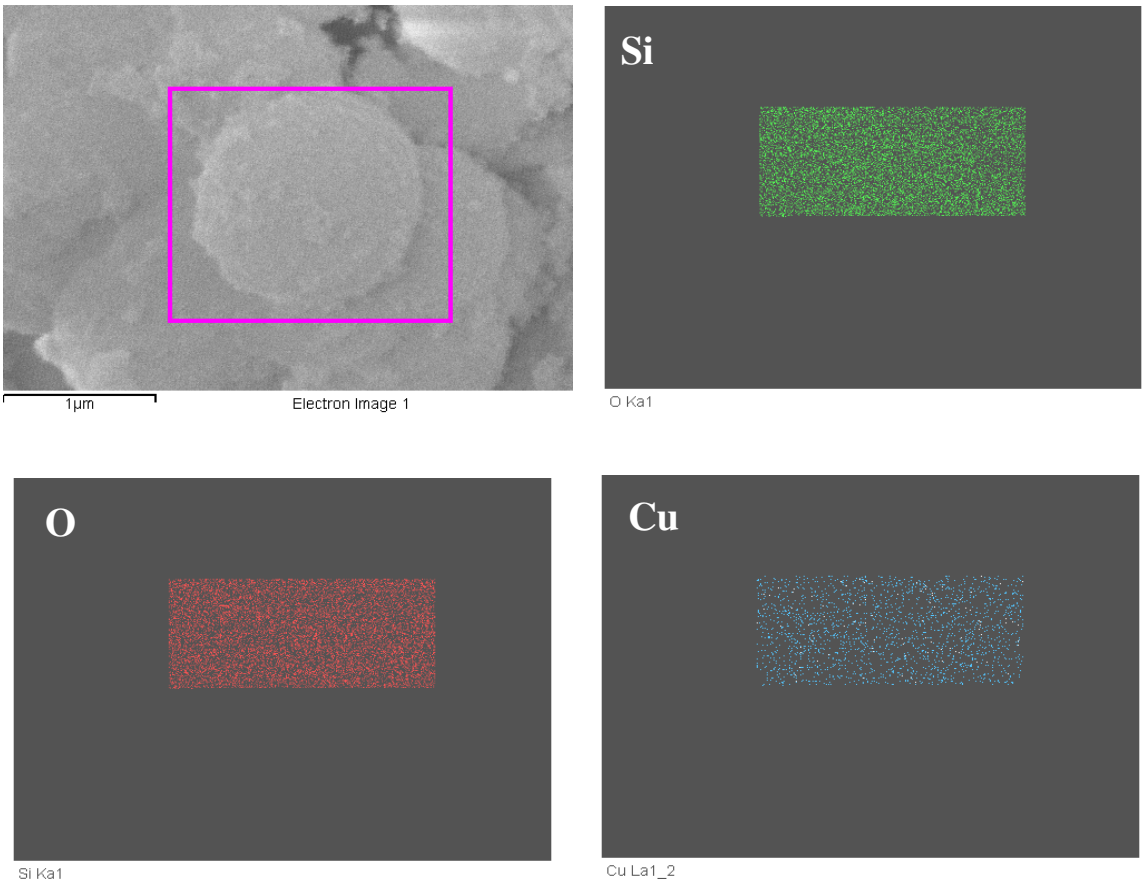


Fig. S2 The SEM image and the corresponding energy dispersive X-ray (EDX) spectroscopic mapping images of the Si, O and Cu elements in the CuO on mesoporous silica sample. The element distribution images indicate that the CuO is well dispersed within the mesoporous silica. In order to save the experimental time, only half area of the bracket in the SEM image was scanned.

6. Fig. S3

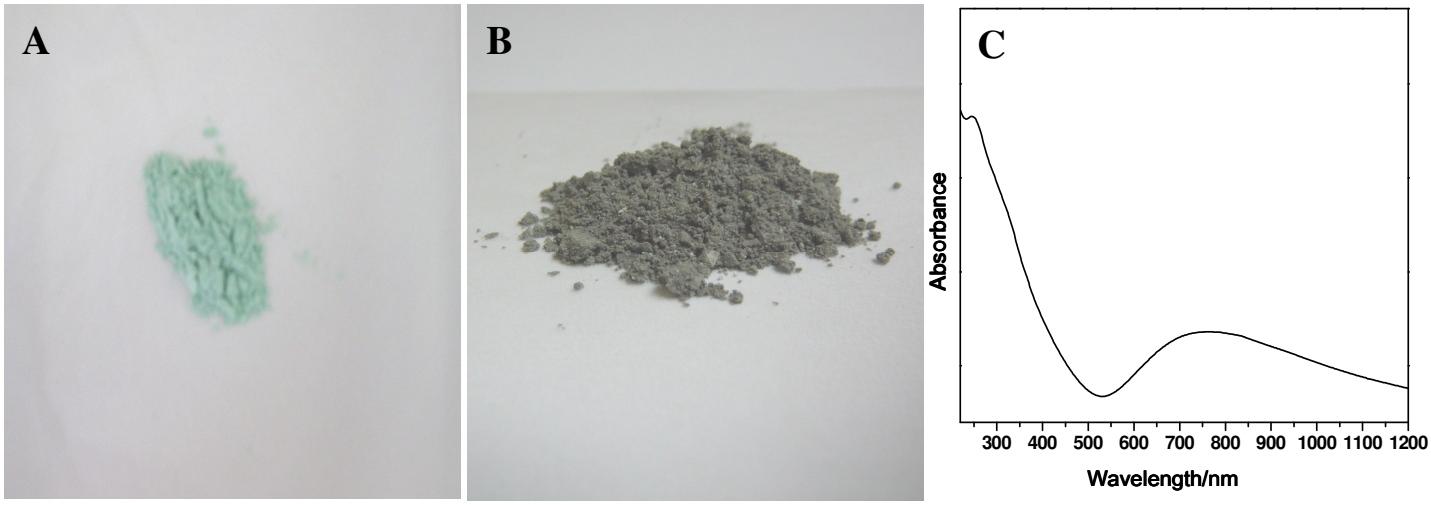


Fig. S3 Optical micrographs of the CuO-containing mesoporous silica samples at same chemical composition (Cu/Si molar ratio ≈ 10) synthesized by using different synthetic method. (A) CuO on mesoporous silica prepared by using the method we proposed. (B) CuO/mesoporous silica obtained from the typical impregnation method. (C) UV-vis DR spectroscopy of the CuO on mesoporous silica sample in Figure S3 A.

7. TEM images of the catalyst after catalysis

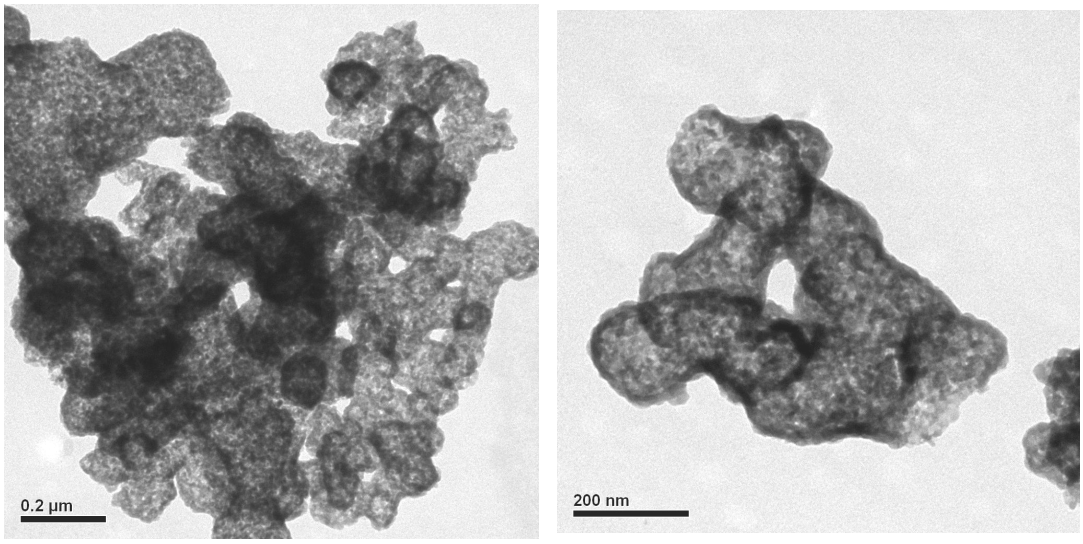


Fig. S4 TEM images of the CuO on mesoporous silica after fourth run reaction

8. References

1. K. Ajiki, M. Hirano and K. Tanaka, *Org. Lett.*, 2005, **7**, 4193.
2. S. D. Pastor and E. T. Hessell, *J. Org. Chem.*, 1985, **50**, 4812.
3. Z. Duan, S. Ranjit, P. Zhang and X. Liu, *Chem. Eur. J.*, 2009, **15**, 3666.
4. C. G. Bates, R. K. Gujadhur, D. Venkataraman, *Org. Lett.*, 2002, **4**, 2803.
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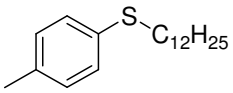
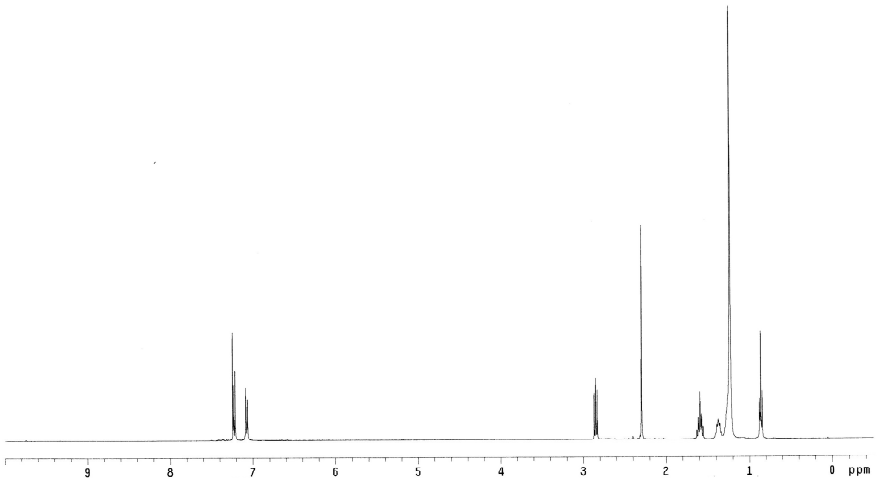
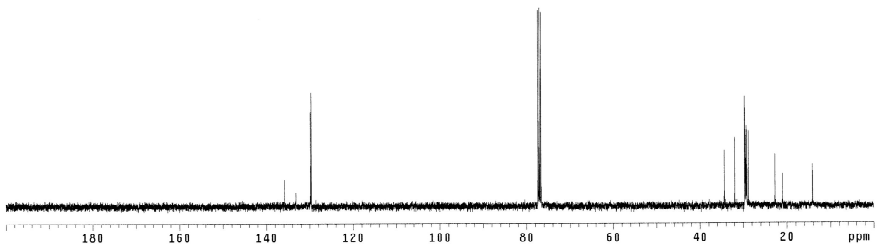
8. N. Taniguch, and T. Onami, *J. Org. Chem.,* 2004, **69**, 915.
9. U. Schopfer and A. Schlapbach, *Tetrahedron*, 2001, **57**, 3069.

9. Spectra Data for Products

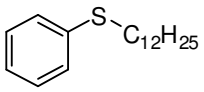
Dodecyl-*p*-tolyl sulfide 3a

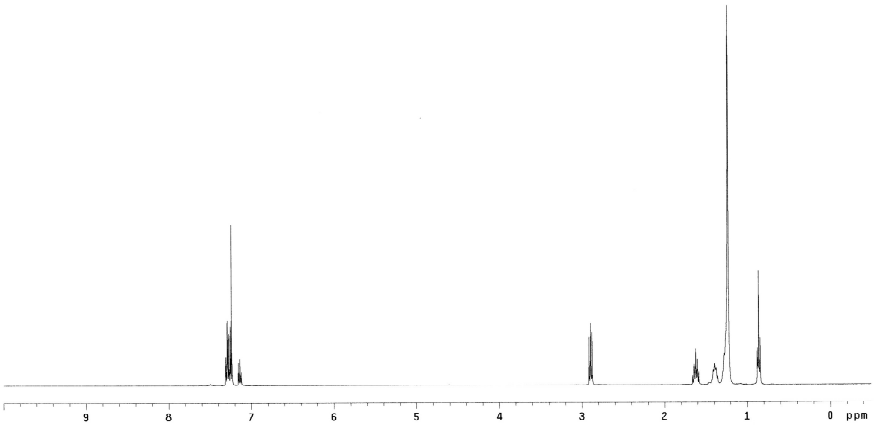


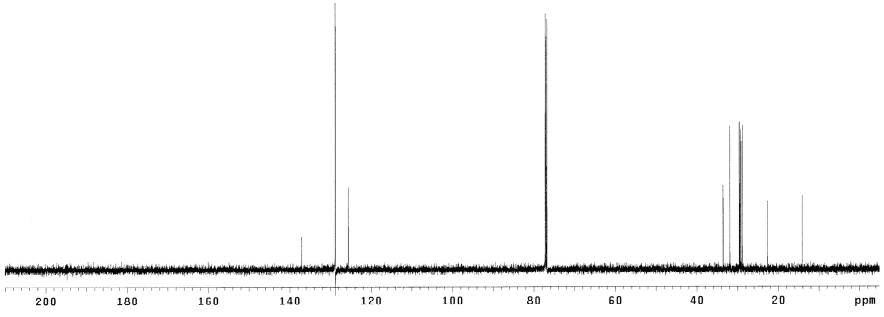




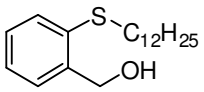
Dodecyl phenyl sulfide 3b

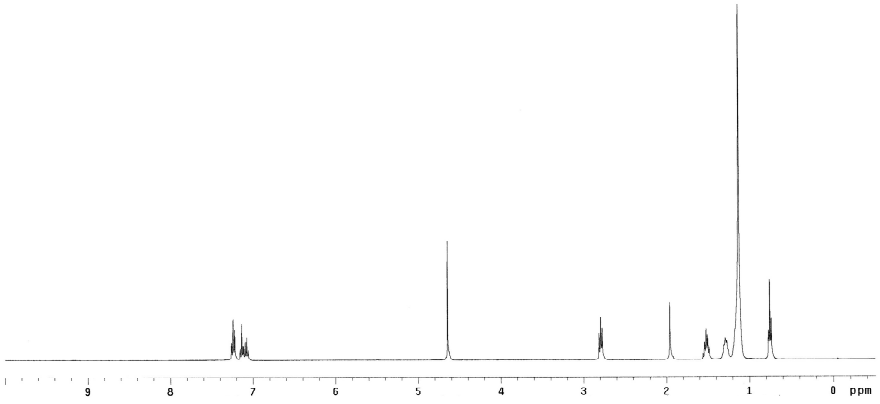


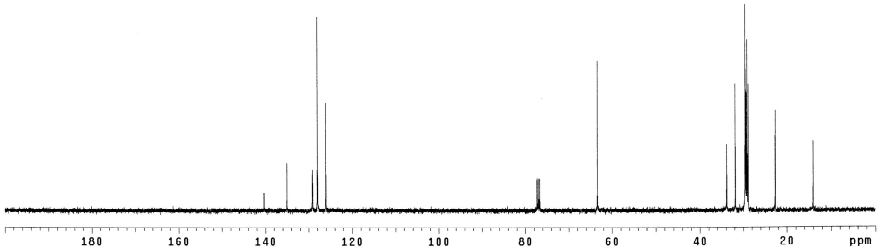




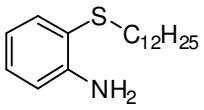
(2-(Dodecylthio)phenyl)methanol 3c

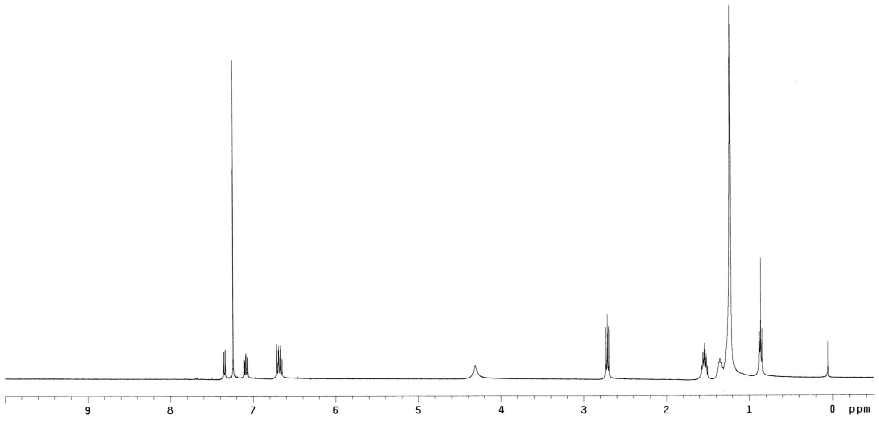


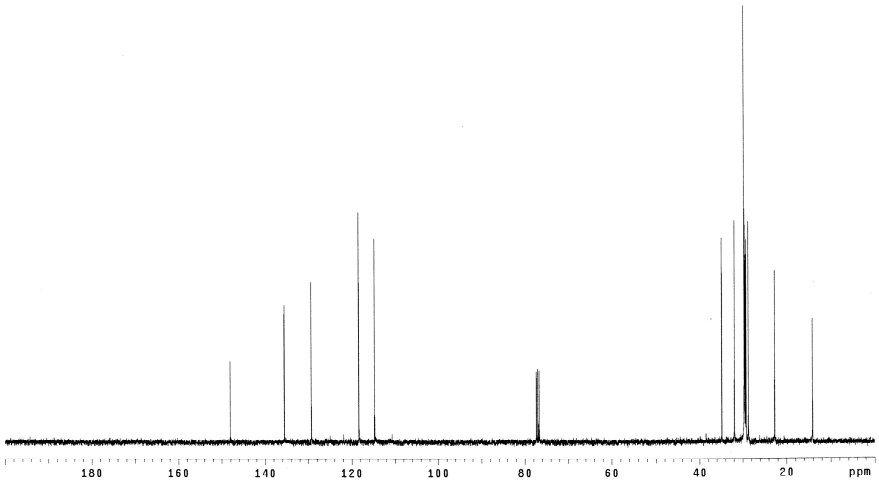




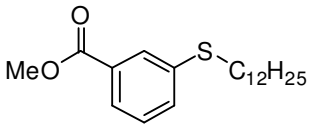
2-*n*-Dodecanesulfanylaniline 3d

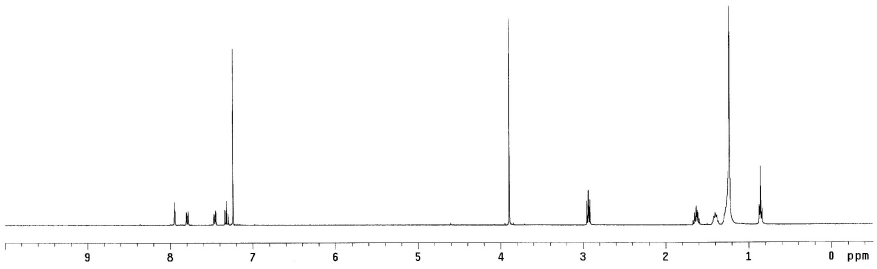


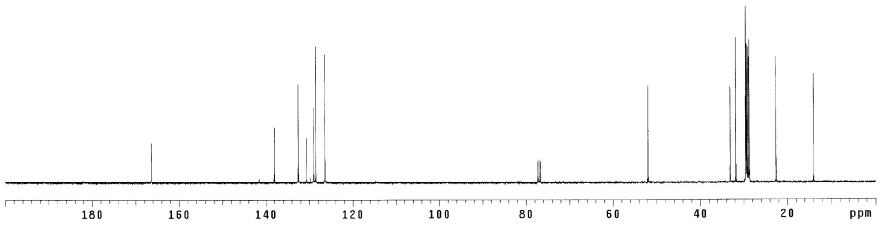




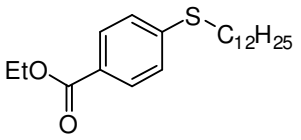
Methyl 3-(dodecylthio)benzoate 3e

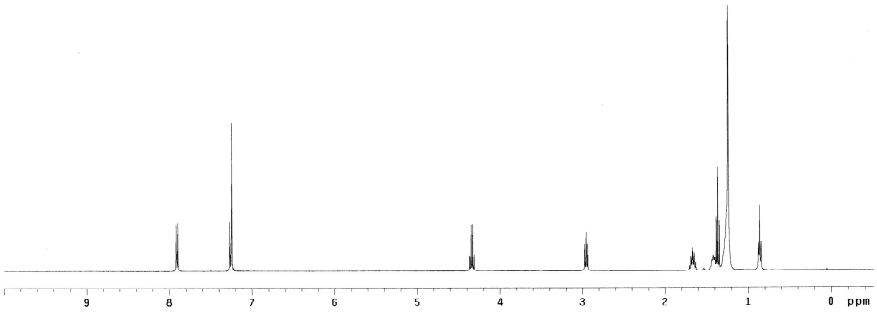


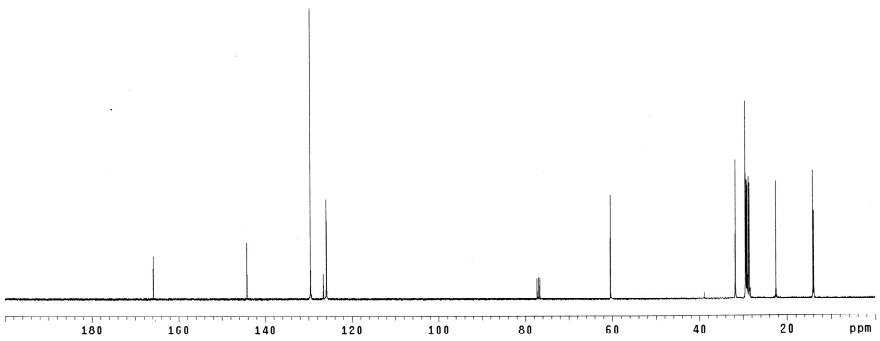




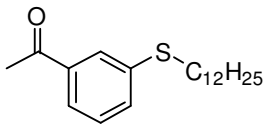
Ethyl 4-(dodecylthio)benzoate 3f

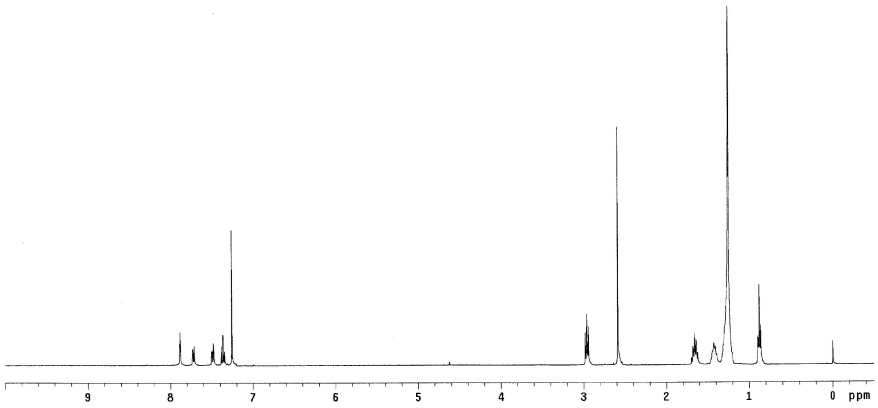


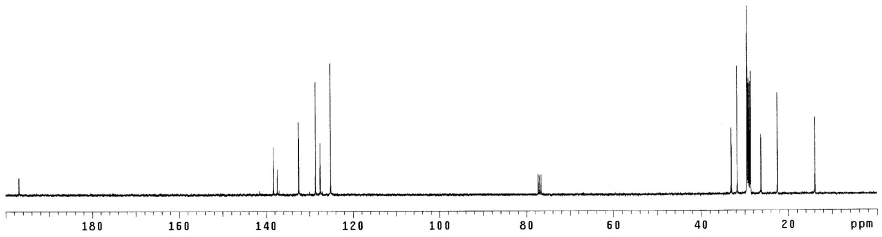




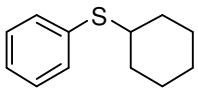
1-(3-(Dodecylthio)phenyl)ethanone 3g

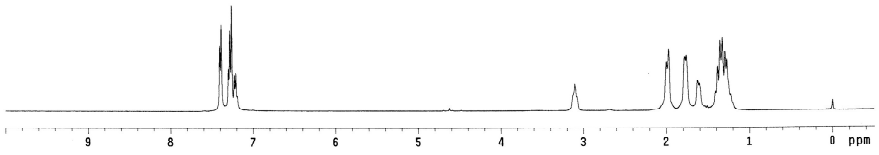


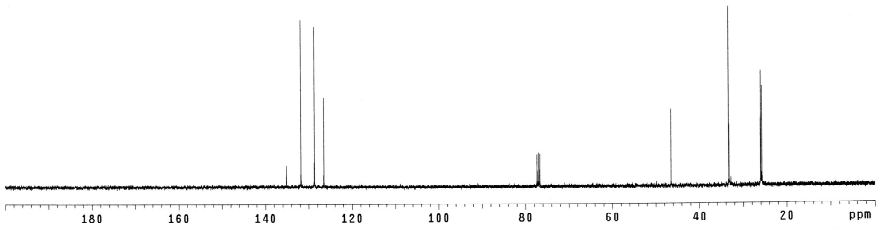




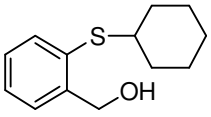
Cyclohexyl phenyl sulfide 3h

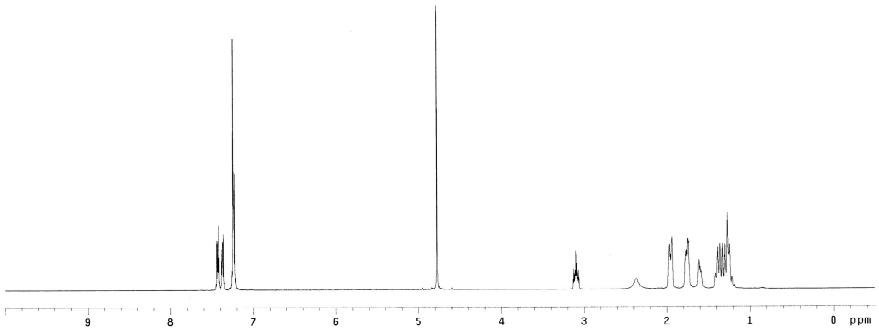


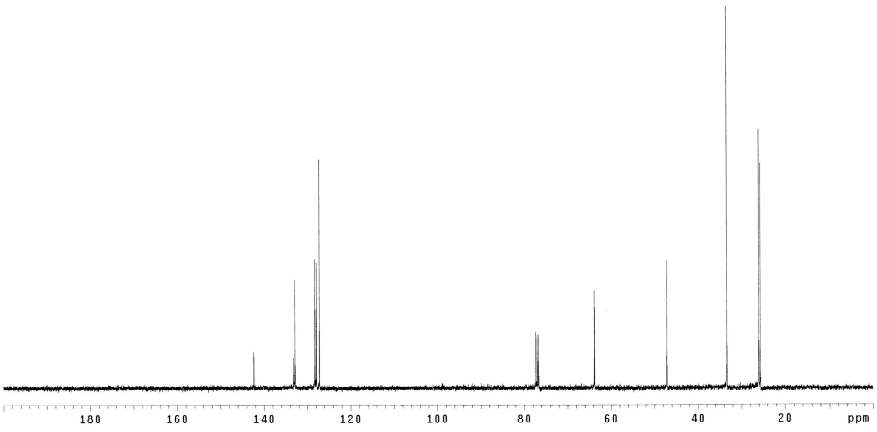




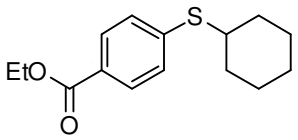
(2-(Cyclohexylthio)phenyl)methanol 3i

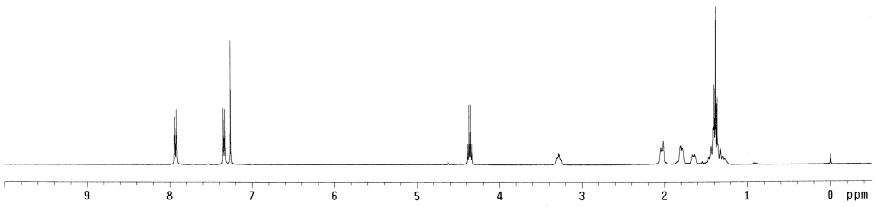


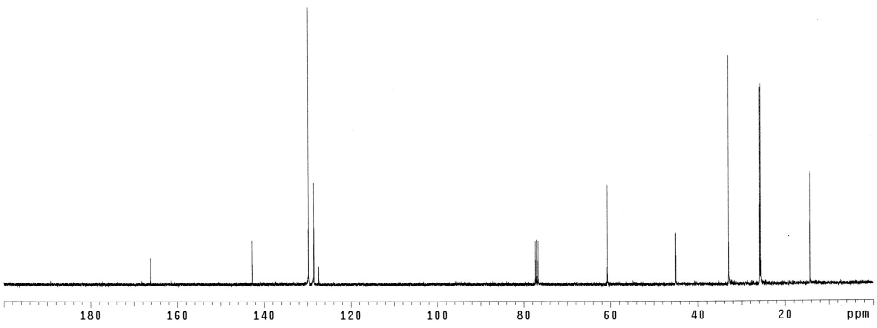




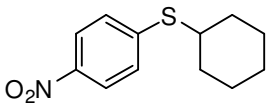
Ethyl 4-(cyclohexylthio)benzoate 3j

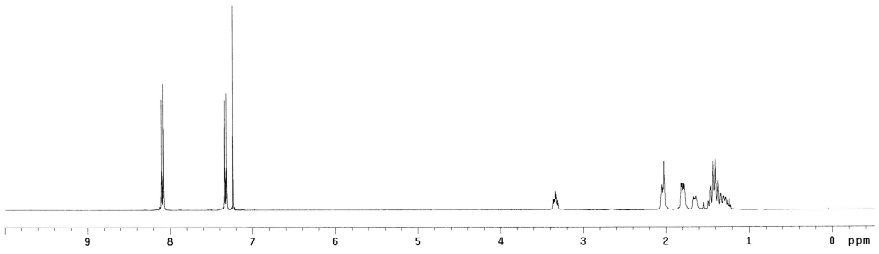


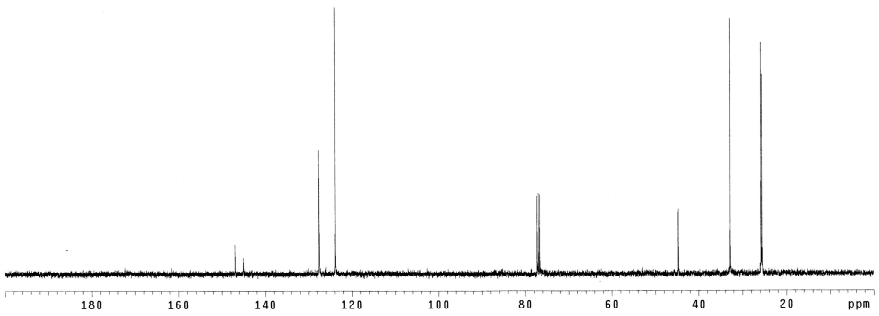




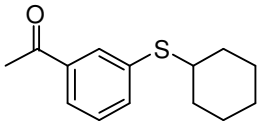
Cyclohexyl-(4-nitrophenyl)-sulfide 3k

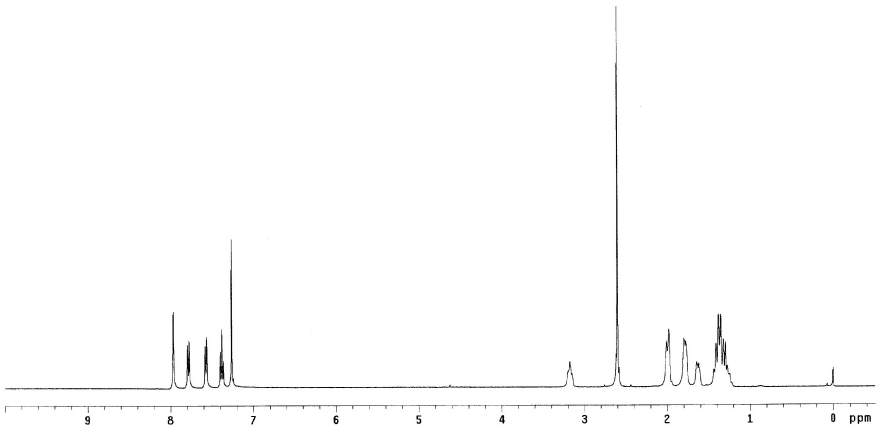


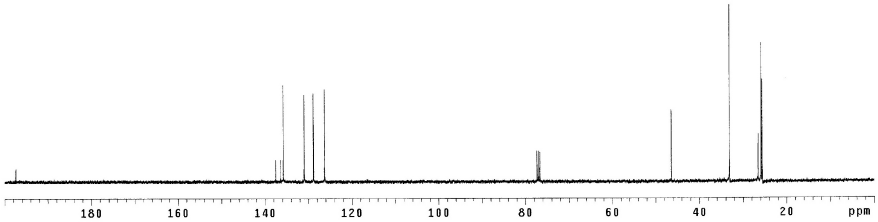




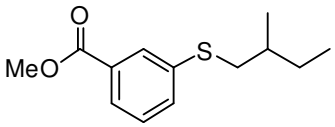
1-(3-(Cyclohexylthio)phenyl)ethanone 3l

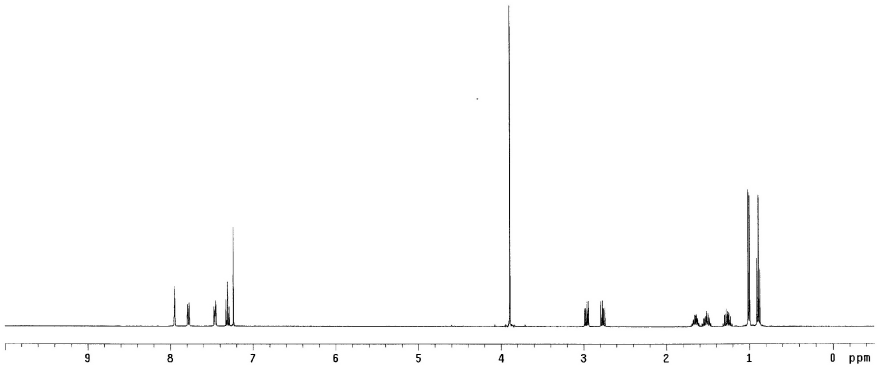


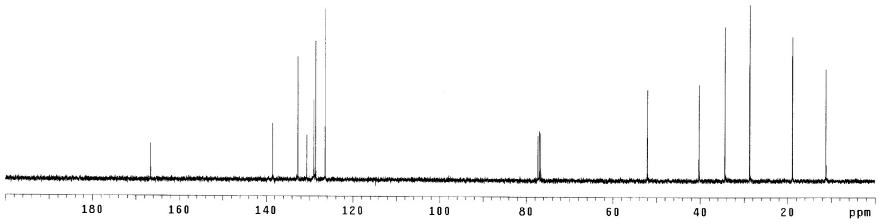




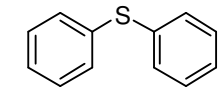
Methyl 3-(2-methylbutylthio)benzoate 3m

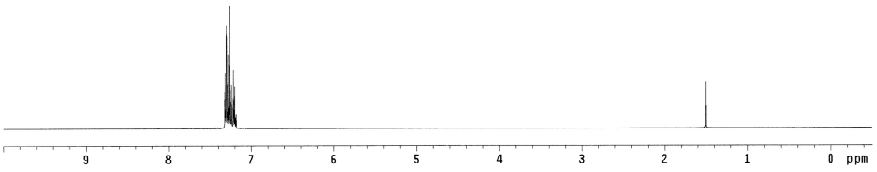


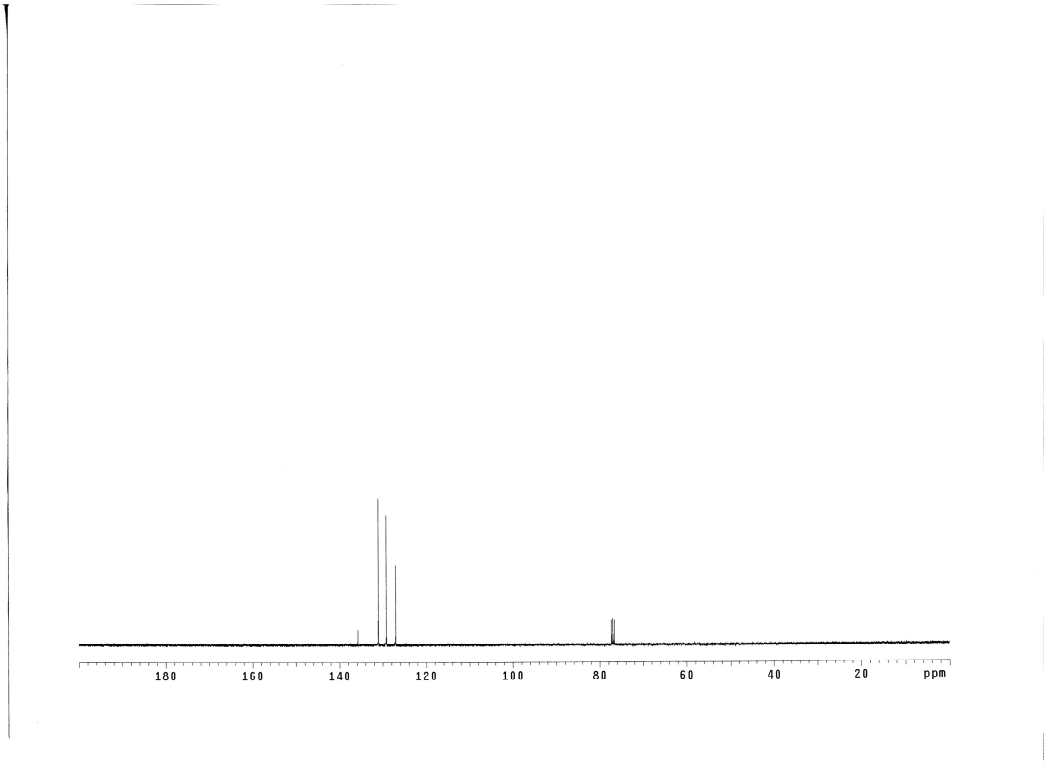




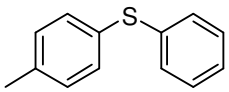
Diphenyl sulfide 3n

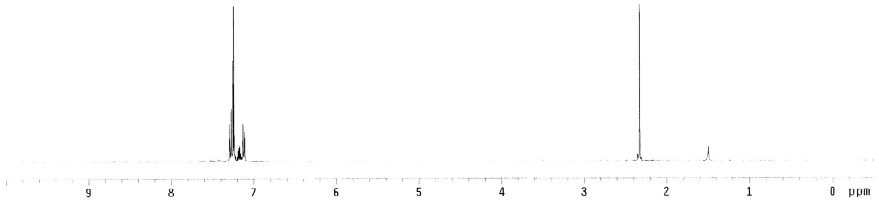


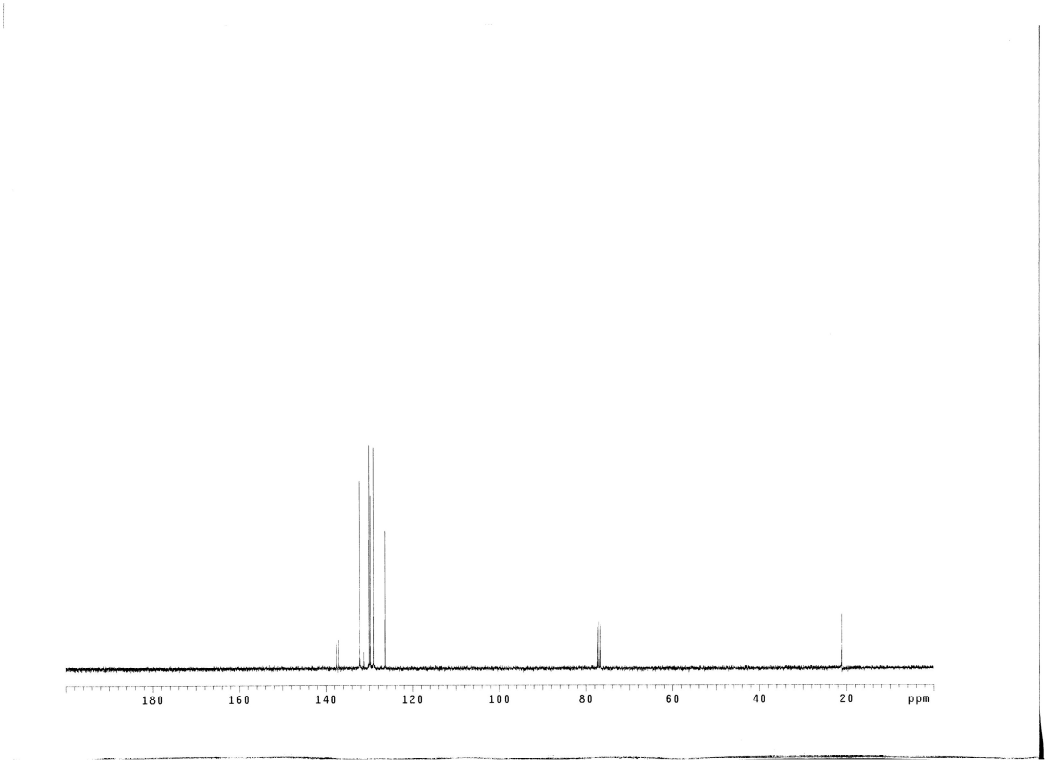




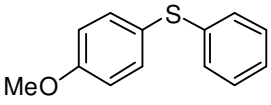
4-Methylphenyl phenyl sulfide 3o

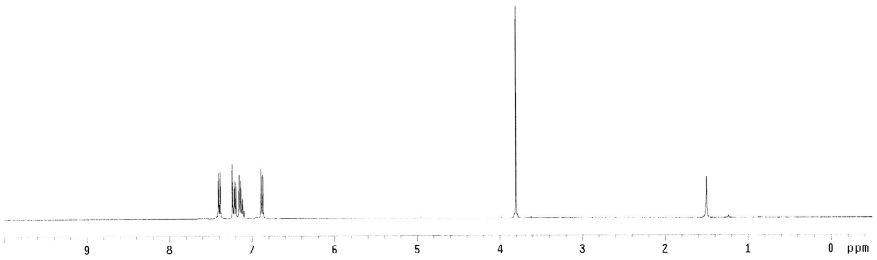


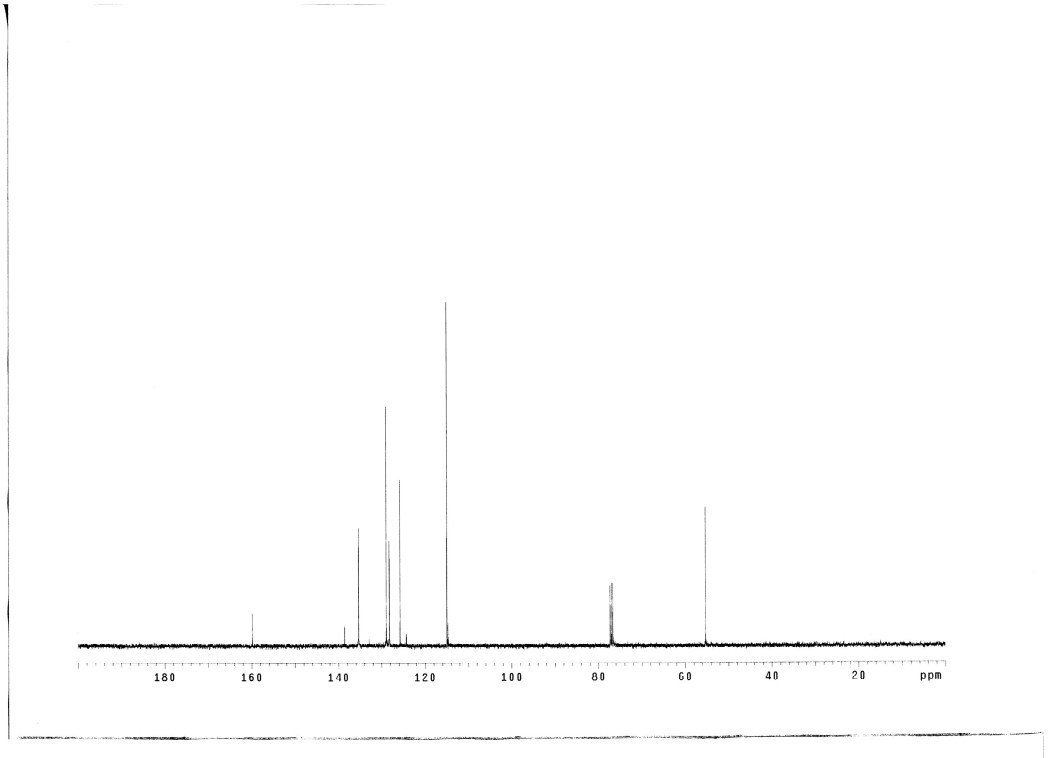




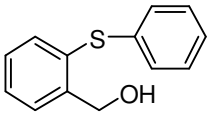
4-Methoxyphenyl phenyl sulfide 3p

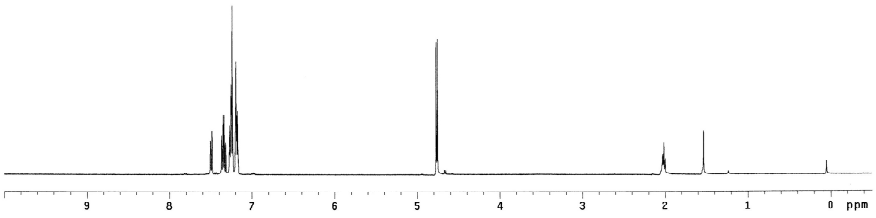


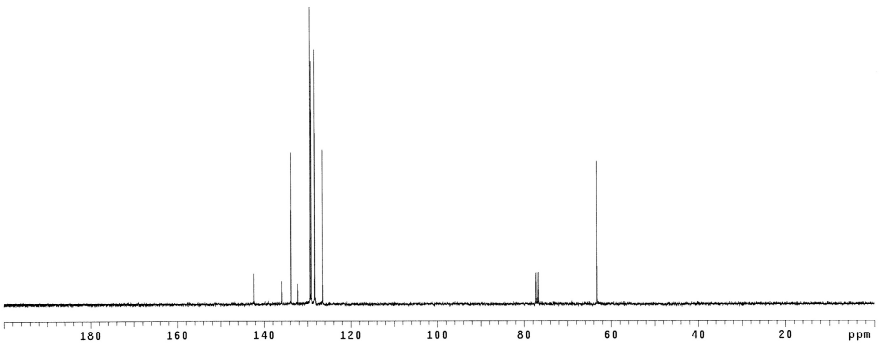




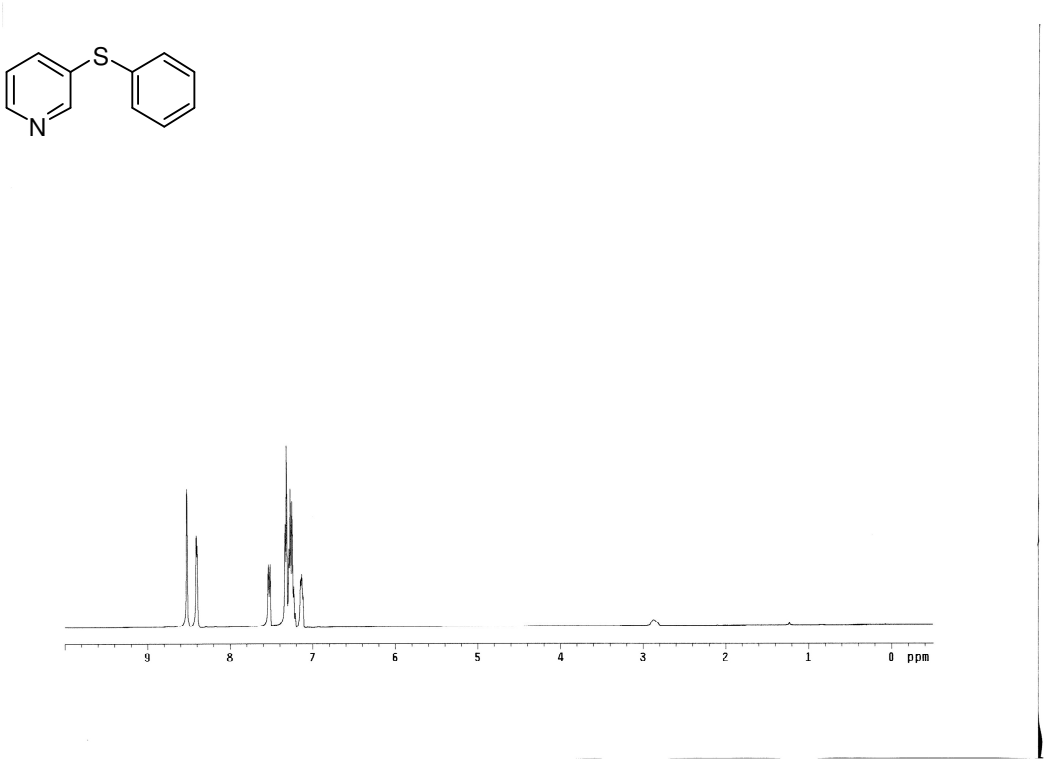
(2-(Phenylthio)phenyl)methanol 3q

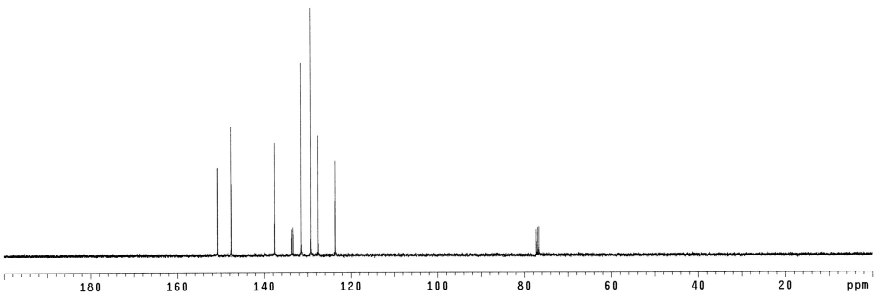




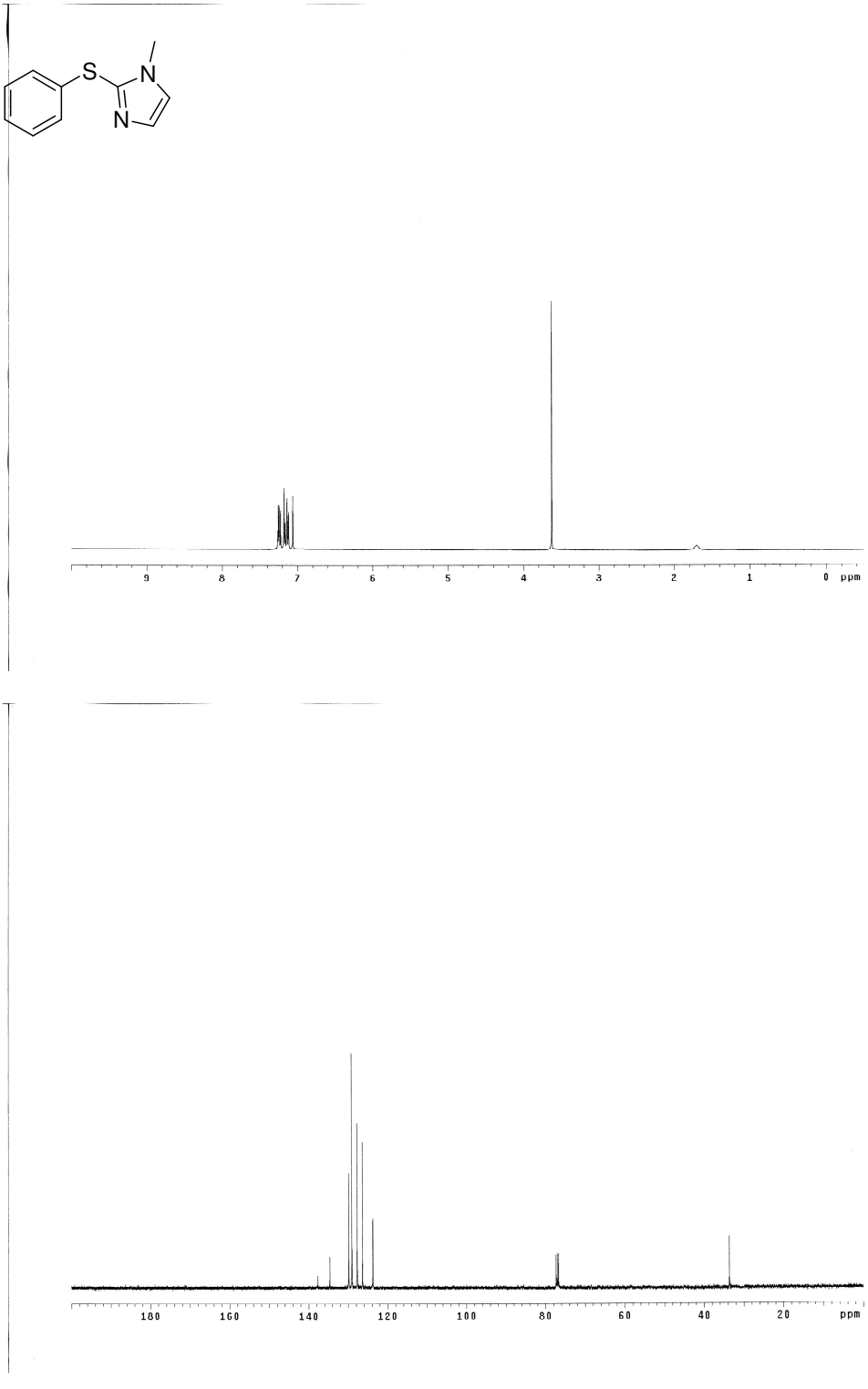


3-Pyridyl phenyl sulfide 3r

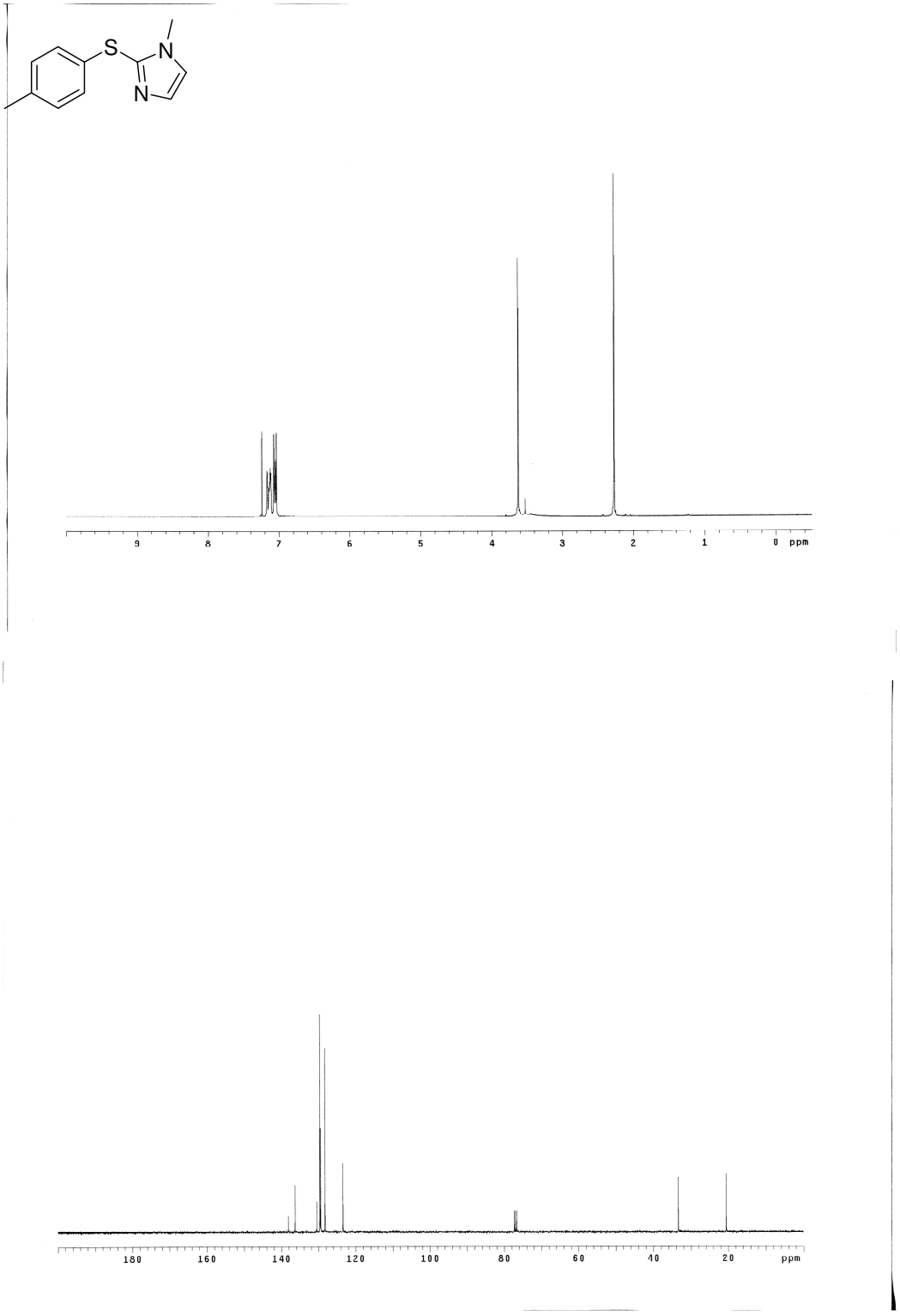




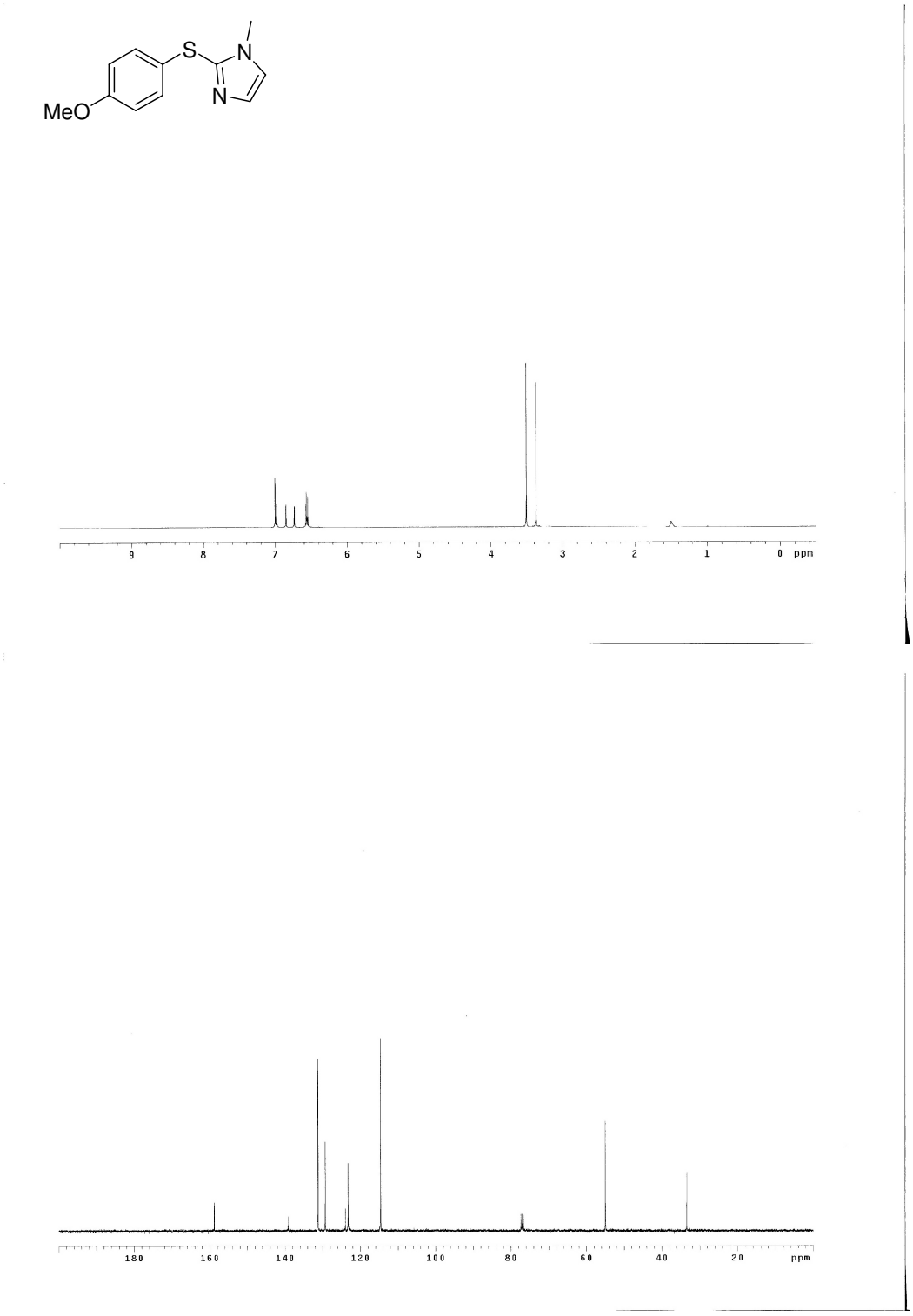
2-(Phenylsulfanyl)-*N*-methylimidazole 3s



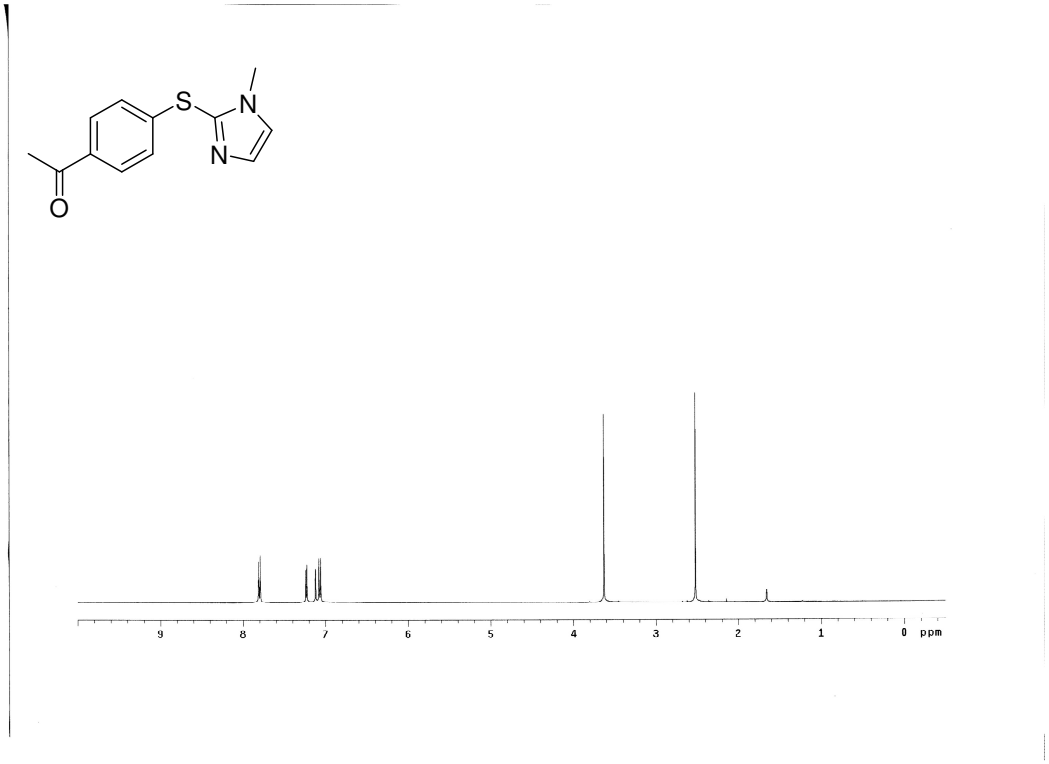
1-Methyl-2-(*p*-toylsulfanyl)-1*H*-imidazole 3t

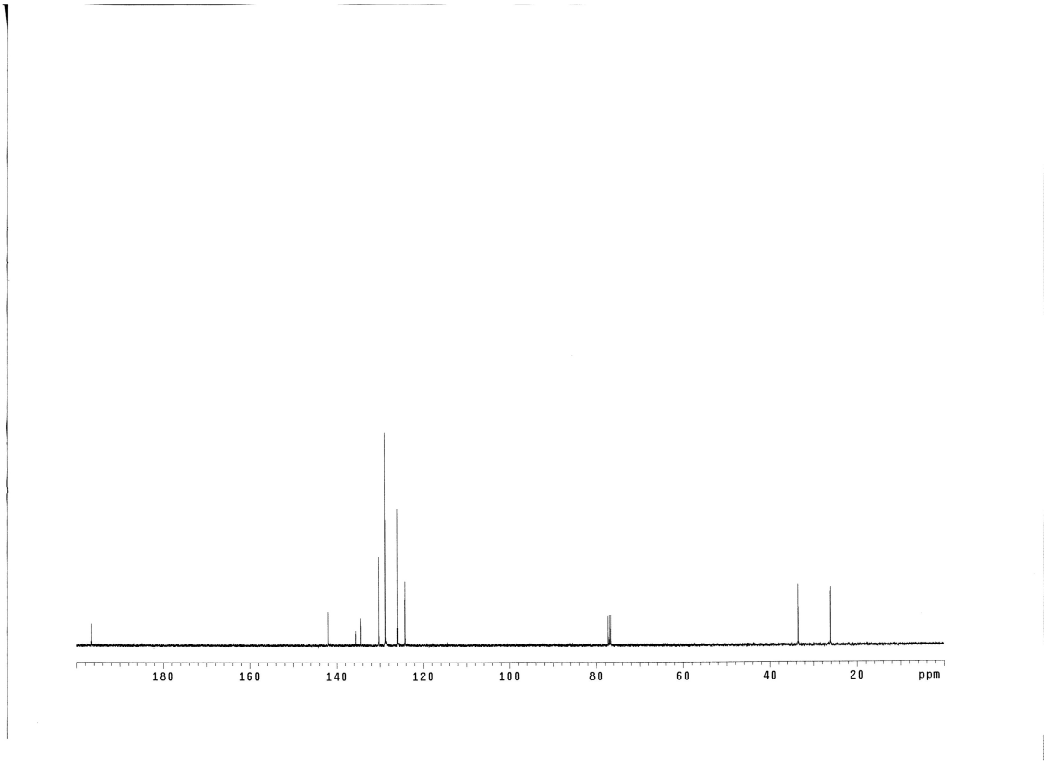


2-(4-Methoxyphenylthio)-1-methyl-1H-imidazole 3u

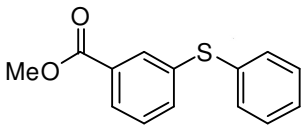


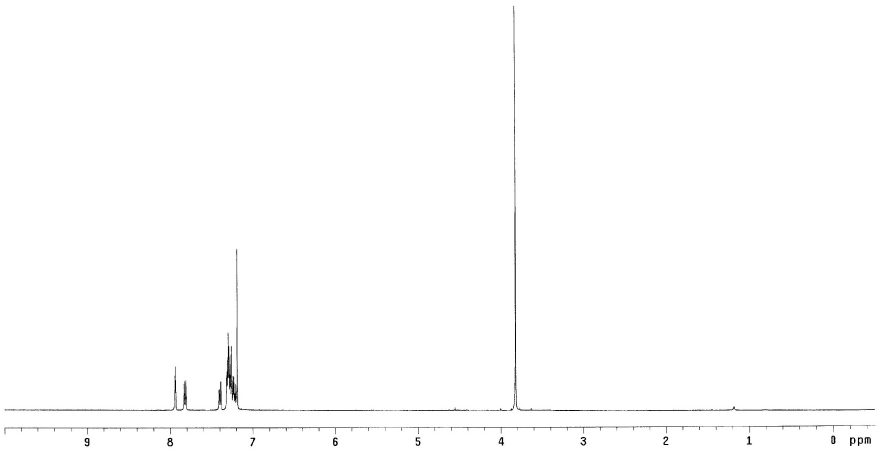
1-(4-(1-Methyl-1*H*-imidazol-2-ylthio)phenyl)ethanone 3v

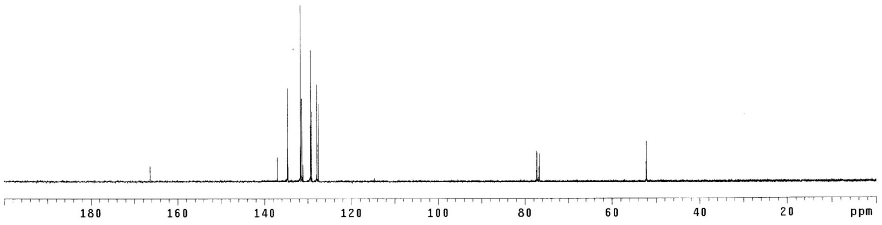




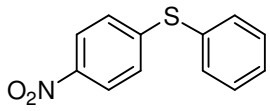
Methyl 3-phenylsulfanylbenzoate 3w

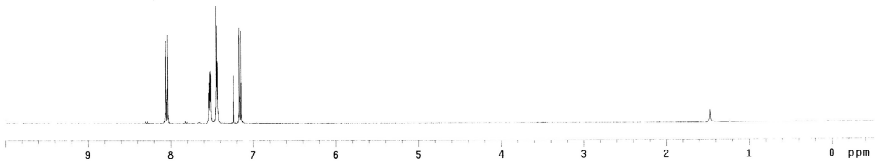


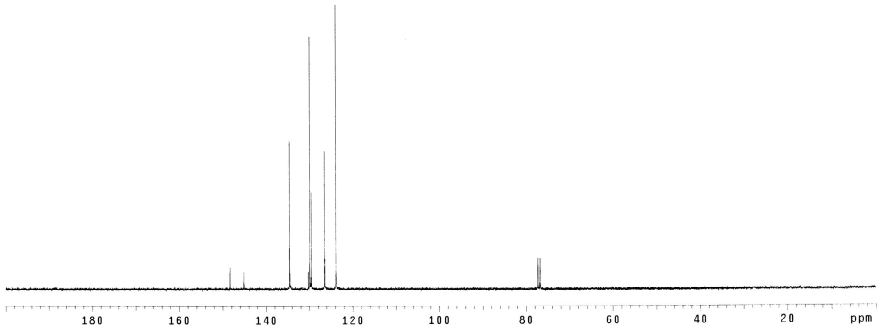




4-Nitrophenyl phenyl sulfide 3x







1-(3-(Phenylthio)phenyl)ethanone 3y