# Supplementary Information

## Iron-Catalyzed Thioetherification of Thiols with Aryl Iodides

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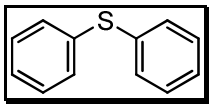
## 1. General information

All chemicals were purchased from Aldrich and Across chemicals and used without further purification. $FeCl_3$ (purity > 98 %) was purchased from Across chemicals and sublimated before being used. 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 sealable tube equipped with a magnetic stir bar was charged with $FeCl_3$ (8.0 mg, 0.05 mmol), ligand (0.05 mmol) and base (1.00 mmol) in a drybox under a nitrogen atmosphere. The aperture of the tube was then covered with a rubber septum and removed from the drybox. Under an argon atmosphere, thiophenol (0.050 mL, 0.50 mmol), iodobenzene (0.085 mL, 0.75 mmol) and solvent (0.5 mL) were added via syringe. The septum was then replaced by a teflon-coated screw cap and the reaction vessel was heated at 135 °C oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature and diluted with $CH_2Cl_2$ (20 mL). The resulting solution was filtered through a pad of celite then washed with $CH_2Cl_2$ (20 mL) and concentrated to give the crude material which was then purified by column chromatography ($SiO_2$, hexane or hexane/$CH_2Cl_2$) to yield **3**.

## 2.1 The representative example of Table 1 (Table 1, entry 2)



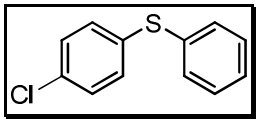

**Diphenyl sulfide 3a (Table 1, entry 2)[1].**

Following the general procedure for Table 1: $FeCl_3$ (8.0 mg, 0.05 mmol), **L2** (31.0 mg, 0.05 mmol) and NaO*t*Bu (96.0 mg, 1.00 mmol), then thiophenol (0.05 mL, 0.50 mmol), iodobenzene (0.085 mL, 0.75 mmol) and toluene (0.5 mL) to provide **3a** as a colorless oil (92 mg, 99% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.25-7.43 (m, 10 H); $^{13}$C

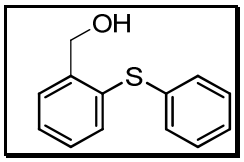
NMR (100 MHz, $CDCl_3$): δ = 127.0, 129.1, 131.0, 135.8.

## 3. General procedure for Table 2

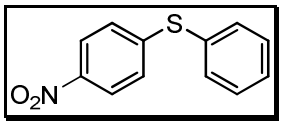
A sealable tube equipped with a magnetic stir bar was charged with $FeCl_3$ (16.0 mg, 0.10 mmol), **L2** (62.0 mg, 0.10 mmol) or **L4** (58.0 mg, 0.10 mmol), NaO*t*Bu (192.0 mg, 2.00 mmol) or KO*t*Bu (224 mg, 2 mmol) in a drybox under a nitrogen atmosphere. The aperture of the tube was then covered with a rubber septum and removed from the drybox. Under an argon atmosphere, aryl thiol (1.0 mmol), aryl iodide (1.5 mmol) and toluene (1.0 mL) were added via syringe. The septum was then replaced by a teflon-coated screw cap and the reaction vessel was heated at 135 °C oil bath. After stirring at this temperature for 24 h, the reaction mixture was cooled to room temperature and diluted with $CH_2Cl_2$ (20 mL). The resulting solution was directly filtered through a pad of celite then washed with $CH_2Cl_2$ (20 mL) and concentrated to give the crude material which was then purified by column chromatography ($SiO_2$, hexane or hexane/$CH_2Cl_2$) to give **3**.




**4-Chlorophenyl phenyl sulfide 3b (Table 2, entry 1)[2].** Following the general procedure for Table 2, using **L2** (62.0 mg, 0.10 mmol), NaO*t*Bu (192.0 mg, 2.00 mmol), thiophenol (0.10 mL, 1.00 mmol), 1-chloro-4-iodobenzene (358.0 mg, 1.5 mmol) to get **3b** as a colorless oil (201 mg, 91% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.35 (m, 9 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 127.4, 129.3, 131.2, 132.0, 133.0, 134.6, 135.0, 138.6.

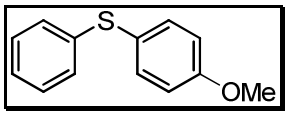



**(2-(Phenylthio)phenyl)methanol 3c (Table 2, entry 2)[3].** Following the general procedure for Table 2, using **L2** (62.0 mg, 0.10 mmol), NaO*t*Bu (192.0 mg, 2.00 mmol), thiophenol (0.10 mL, 1.00 mmol), 2-iodobenzyl alcohol (351.0 mg, 1.5 mmol), then purified by column chromatography ($SiO_2$, hexane:$CH_2Cl_2$ = 8:2) to provide **3c** as a colorless oil (183 mg, 85% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.18 (br s, 1 H), 4.76 (s, 2 H), 7.17-7.24 (m, 6 H), 7.25-7.38 (m, 2 H), 7.50 (d, *J* = 7.6 Hz, 1 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 63.1, 126.4, 128.1, 128.2, 128.3, 129.1, 129.3, 132.1, 133.7, 135.8, 142.2.



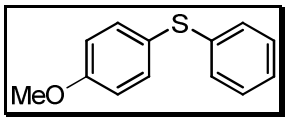

**4-Nitrophenyl phenyl sulfide 3d (Table 2, entry 3)[1].**

Following the general procedure for Table 2, using **L2** (62.0 mg, 0.10 mmol), NaO*t*Bu (192.0 mg, 2.00 mmol), thiophenol (0.10 mL, 1.00 mmol), 4-nitroiodobenzene (374.0 mg, 1.5 mmol), then purified by column chromatography ($SiO_2$, hexane:$CH_2Cl_2$ = 9:1) gave **3d** as a yellow oil (178 mg , 77% 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), 7.46-7.55 (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, 134.6, 145.1, 148.3.



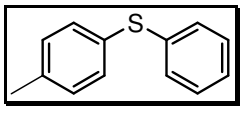

**4-Methoxyphenyl phenyl sulfide 3e (Table 2, entry 4)[4].**

Following the general procedure for Table 2, using **L2** (62.0 mg, 0.10 mmol), NaO*t*Bu (192.0 mg, 2.00 mmol), 4-methoxythiophenol (0.125 mL, 1.00 mmol), iodobenzene (0.17 mL, 1.50 mmol) to give **3e** as a colorless oil (180 mg, 83% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.68 (s, 3 H), 6.77 (d, *J* = 8.8 Hz, 2 H), 6.79-7.14 (m, 5 H), 7.30 (d, *J* = 8.8 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.2, 114.9, 124.3, 125.7, 128.2, 128.9, 135.3, 138.5, 159.8.



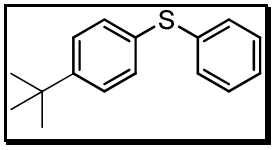

**4-Methoxyphenyl phenyl sulfide 3e (Table 2, entry 5)[4].**

Following the general procedure for Table 2, using **L4** (58.0 mg, 0.10 mmol), NaO*t*Bu (192.0 mg, 2.00 mmol), thiophenol (0.10 mL, 1.00 mmol), 4-iodoanisole (351.0 mg, 1.50 mmol) to give **3e** as a colorless oil (202 mg, 93% yield).

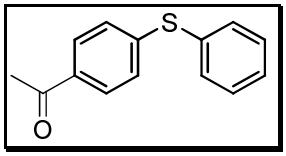



**4-Methylphenyl phenyl sulfide 3f (Table 2, entry 6)[1].**

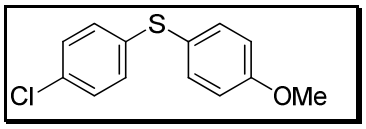
Following the general procedure for Table 2, using **L4** (58.0 mg, 0.10 mmol), NaO*t*Bu (192.0 mg, 2.00 mmol), thiophenol (0.10 mL, 1.00 mmol), 4-iodotoluene (327.0 mg, 1.50 mmol) to give **3f** as a colorless oil (189 mg, 94% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 7.21-7.44 (m, 9 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 21.0, 126.2, 128.9, 129.6, 130.0, 130.9, 132.2, 137.1, 137.4.



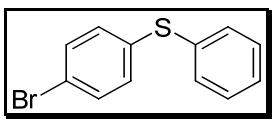

**4-*tert*-Butylphenyl phenyl sulfide 3g (Table 2, entry 7)[5].** Following the general procedure for Table 2, using **L4** (58.0 mg, 0.10 mmol), NaO*t*Bu (192.0 mg, 2.00 mmol), thiophenol (0.10 mL, 1.00 mmol), 4-*tert*-butyliodobenzene (0.27 mL, 1.50 mmol) to give **3g** as a colorless oil (220 mg, 91% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 9 H), 7.23-7.39 (m, 9 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 31.2, 34.5, 126.2, 126.5, 129.0, 130.2, 131.4, 136.6, 137.0, 150.5.




**4-Phenylsulfanylacetophenone 3h (Table 2, entry 7)[3].** Following the general procedure for Table 2, using **L4** (58.0 mg, 0.10 mmol), NaO*t*Bu (192.0 mg, 2.00 mmol), thiophenol (0.10 mL, 1.00 mmol), 4'-iodoacetophenone (369.0 mg, 1.5 mmol), then purified by column chromatography ($SiO_2$, hexane:$CH_2Cl_2$ = 9:1) to give **3h** as a yellow solid (218 mg , 95% yield). M.p.: 60-61 °C (lit.[3]: 63.0 °C); $^1$H NMR (600 MHz, $CDCl_3$): δ = 2.57 (s, 3 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 7.40-7.43 (m, 3 H), 7.41-7.42 (m, 2 H), 7.79 (d, *J* = 8.4 Hz, 2 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 26.4, 127.4, 128.7, 128.9, 129.6, 132.1, 133.9, 134.5, 144.9, 197.1.

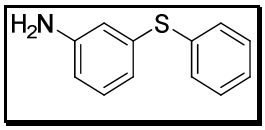



**4-Chlorophenyl 4-methoxyphenyl sulfide 3i (Table 2, entry 9)[6].** Following the general procedure for Table 2, using **L4** (58.0 mg, 0.10 mmol), NaO*t*Bu (192.0 mg, 2.00 mmol), 4-methoxythiophenol (0.125 mL, 1.00 mmol), 1-chloro-4-iodobenzene (358.0 mg, 1.5 mmol) to give **3i** as a colorless oil (192 mg, 77% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 7.07 (d, *J* = 8.4 Hz, 2 H), 7.18 (d, *J* = 8.8 Hz, 2 H), 7.40 (d, *J* = 8.8 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 55.3, 115.1, 123.7, 128.9, 129.2, 131.5, 135.4, 137.3, 160.0.

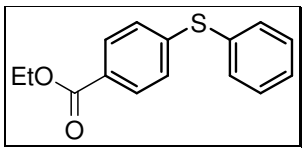



**4-Bromophenyl phenyl sulfide 3j (Table 2, entry 10)[5].** Following the general procedure for Table 2, using **L4** (58.0 mg, 0.10 mmol), NaO*t*Bu (192.0 mg, 2.00 mmol), thiophenol (0.10 mL, 1.0 mmol), 1-bromo-4-iodobenzene (424.0 mg, 1.5 mmol) to provide **3j** as a colorless oil (231 mg, 87% yield). $^1$H NMR

(400 MHz, $CDCl_3$): δ = 7.16 (d, *J* = 8.8 Hz, 2 H), 7.17-7.32 (m, 5 H), 7.40 (d, *J* = 8.8 Hz, 2 H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 120.9, 127.5, 129.3, 131.5, 132.1, 132.2, 134.9, 135.5.




**3-Phenylsulfanylaniline 3k (Table 2, entry 11)[4].**
Following the general procedure for Table 2, using **L4** (58.0 mg, 0.10 mmol), NaO*t*Bu (192.0 mg, 2.00 mmol), thiophenol (0.10 mL, 1.0 mmol), 3-iodoaniline (0.18 mL, 1.5 mmol) to provide **3k** as a yellow oil (186 mg, 92% yield). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 3.64 (br s, 2 H), 6.56-6.59 (m, 1 H), 6.56-6.67 (m, 1 H), 6.75-6.78 (m, 1 H), 7.01 (t, *J* = 8.0 Hz, 1 H), 7.25-7.41 (m, 5 H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 113.9, 117.1, 121.0, 126.9, 129.1, 129.9, 131.1, 135.8, 136.5, 147.1.

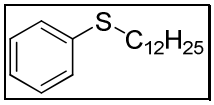



**4-Phenylsulfanyl-benzoic acid ethyl ester 3l (Table 2, entry 12)[3].** Following the general procedure for Table 2, using **L4** (58.0 mg, 0.10 mmol), thiophenol (0.10 mL, 1.00 mmol), ethyl-4-iodobenzoate (0.25 mL, 1.50 mmol), KO*t*Bu (224 mg, 2 mmol) to give **3l** as a colorless oil (187 mg, 72% yield). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.35 (t, *J* = 7.2 Hz, 3 H), 4.33 (q, *J* = 7.2 Hz, 2 H), 7.19 (d, *J* = 8.8 Hz, 2 H) , 7.34-7.39 (m, 3 H), 7.44-7.48 (m, 2 H), 7.88 (d, *J* = 8.8 Hz, 2 H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 14.2, 60.8, 127.6, 127.8, 128.4, 129.5, 130.0, 132.5, 133.5, 144.0, 166.1.

## 4. General procedure for Table 3

A sealable tube equipped with a magnetic stir bar was charged with $FeCl_3$ (8.0 mg, 0.05 mmol), ligand (0.05 mmol) and base (1.0 mmol) in a drybox under a nitrogen atmosphere. The aperture of the tube was then covered with a rubber septum and removed from the drybox. Under an argon atmosphere, 1-dodecanethiol (0.12 mL, 0.5 mmol), iodobenzene (0.085 mL, 0.75 mmol) and solvent (0.5 mL) were added via syringe. The septum was then replaced by a teflon-coated screw cap and the reaction vessel was heated at 135 °C oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature and diluted with $CH_2Cl_2$ (20 mL). The resulting solution was directly filtered through a pad of celite then washed with $CH_2Cl_2$ (20 mL) and concentrated to give the crude material which was then purified by column chromatography ($SiO_2$, hexane or hexane/$CH_2Cl_2$) to yield **5a**.

### 4.1 The representative example of Table 3 (Table 3, entry 11)

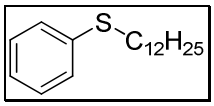


**Dodecyl phenyl sulfide 5a (Table 3, entry 11)**[7]

Following the general procedure for Table 3: using KO*t*Bu (112.0 mg, 1.0 mmol), 1-dodecanethiol (0.12 mL, 0.5 mmol), iodobenzene (0.085 mL, 0.75 mmol) in dioxane (0.5 mL) to provide **5a** as a colorless oil (136 mg, 98% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.86 (t, *J* = 6.8 Hz, 3 H), 1.24-1.66 (m, 20 H), 2.90 (t, *J* = 7.4 Hz, 2 H), 7.16-7.12 (m, 20 H), 7.31-7.23 (m, 5 H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.1, 22.7, 28.8, 29.1, 29.2, 29.3, 29.5, 29.6, 29.6, 31.9, 33.5 125.6, 128.8, 128.8, 137.0.

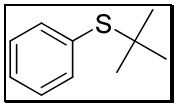
## 5. General procedure for Table 4

. A sealable tube equipped with a magnetic stir bar was charged with $FeCl_3$ (16.0 mg, 0.1 mmol), **L4** (58.0 mg, 0.10 mmol), KO*t*Bu (224.0 mg, 2.0 mmol) or $Cs_2CO_3$ (652.0 mg, 2.0 mmol) in a drybox under a nitrogen atmosphere. The aperture of the tube was then covered with a rubber septum and removed from the drybox. Under an argon atmosphere, alkyl thiol (1.0 mmol), aryl iodide (1.5 mmol) and dioxane (1.0 mL) were added via syringe. The septum was then replaced by a teflon-coated screw cap and the reaction vessel was heated at 135 °C oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature and diluted with $CH_2Cl_2$ (20 mL). The resulting solution was directly filtered through a pad of celite then washed with $CH_2Cl_2$ (20 mL) and concentrated to give the crude material which was then purified by column chromatography ($SiO_2$, hexane or hexane/$CH_2Cl_2$) to give **5**.



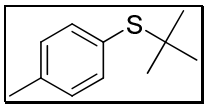
**Dodecyl phenyl sulfide 5a (Table 4, entry 1)**[7]**.**

Following the general procedure for Table 4, using KO*t*Bu (224.0 mg, 2.0 mmol), 1-dodecanethiol (0.24 mL, 1.0 mmol), iodobenzene (0.17 mL, 1.5 mmol) to provide **5a** as a colorless oil (270 mg, 97% yield).



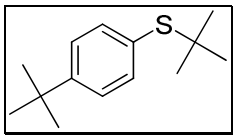
***tert*-Butyl phenyl sulfide 5b (Table 4, entry 2)**[8]**.**

Following the general procedure for Table 4, using KO*t*Bu (224.0 mg, 2.0 mmol), 2-methyl-2-propanethiol (0.113 mL, 1.0 mmol), iodobenzene (0.17 mL, 1.5 mmol) to give **5b** as a colorless oil (150 mg, 90% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.26 (s, 9 H), 7.31-7.33 (m, 3 H), 7.50-7.53 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 30.9, 45.8, 128.4, 128.6, 132.7, 137.4.



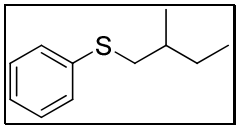
**1,1-Dimethylethyl 4-methylphenyl sulfide 5c (Table 4, entry 3)[9].**

Following the general procedure for Table 4, using KO*t*Bu (224.0 mg, 2.0 mmol), 2-methyl-2-propanethiol (0.113 mL, 1.0 mmol), 4-iodotoluene (327.0 mg, 1.5 mmol) to get **5c** as a colorless oil (158 mg, 88% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 9 H), 2.36 (s, 3 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.42 (d, *J* = 8.0 Hz, 2 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 21.2, 30.9, 45.5, 129.1, 129.2, 137.4, 138.7.



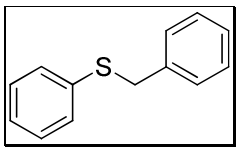
***tert*-Butyl(4-*tert*-butylphenyl)sulfane 5d (Table 4, entry 4)[10].**

Following the general procedure for Table 4, using KO*t*Bu (224.0 mg, 2.0 mmol), 2-methyl-2-propanethiol (0.113 mL, 1.0 mmol), 1-*tert*-butyl-4-iodobenzene (0.267 mL, 1.5 mmol) to get **5d** as a colorless oil (160 mg, 72% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 9 H), 1.30 (s, 9 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.43(d, *J* = 8.0 Hz, 2 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 31.0, 31.3, 34.6, 45.6, 125.5, 129.2, 137.1, 151.8; HREI-MS calcd. for $C_{14}H_{22}S$: 222.1442, Found: 222.1448.



**2-Methylbutyl phenyl sulfide 5e (Table 4, entry 5)[11].**

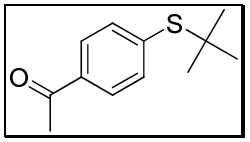
Following the general procedure for Table 4, using KO*t*Bu (224.0 mg, 2.0 mmol), 2-methyl-1-butanethiol (0.124 mL, 1.0 mmol), iodobenzene (0.351 mL, 1.5 mmol) to afford **5e** as a colorless oil (112 mg, 62% yield). $^1$H NMR (600 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7.5 Hz, 3 H), 0.98 (d, *J* = 7.2 Hz, 3 H), 1.24 (m, 1 H), 1.51 (m, 1 H), 1.62 (m, 1 H), 2.71 (dd, *J* = 7.2, 12.6 Hz, 1 H), 2.91 (dd,, *J* = 6.0, 12.6 Hz, 1 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 11.2, 18.8, 28.7, 34.4, 41.0, 125.7, 127.4,128.8, 137.0.



**Benzyl phenyl sulfide 5f (Table 4, entry 6)[12].**

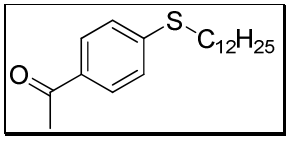
Following the general procedure for Table 4, using KO*t*Bu (224.0 mg, 2.0 mmol), α-toluenethiol (0.117 mL, 1.0 mmol), iodobenzene (0.351 mL, 1.5 mmol) to afford **5f** as a pink solid (150 mg, 75% yield). M.p.: 39.5-40.5 °C (lit.[12]: 40-41 °C);$^1$H NMR (400 MHz, $CDCl_3$): δ = 4.04 (s, 2 H), 7.09-7.23 (m, 10 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ

= 39.0, 126.3, 127.1, 128.5, 128.8, 128.8, 129.8, 136.3, 137.4.



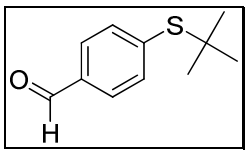

**1-(4-(*tert*-Butylthio)phenyl)ethanone 5g (Table 4, entry 7)[13].**

Following the general procedure for Table 4, using $Cs_2CO_3$ (652.0 mg, 2.0 mmol), 2-methyl-2-propanethiol (0.113 mL, 1.0 mmol), 4'-iodoacetopheonoe (369.0 mg, 1.5 mmol), then purified by column chromatography ($SiO_2$, hexane:$CH_2Cl_2$ = 9:1) to give **5g** as a colorless oil (133 mg, 64% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.3 (s, 9 H), 2.59 (s, 3 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 7.87 (d, *J* = 8.4 Hz, 2 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 26.7, 31.1, 46.9, 128.1, 136.8, 136.9, 139.4, 197.7; HREI-MS calcd. for $C_{12}H_{16}OS$: 208.0913, Found: 208.0922.



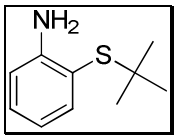

**4-Dodecylthioacetophenone 5h (Table 4, entry 8)[14].**

Following the general procedure for Table 4, using $Cs_2CO_3$ (652.0 mg, 2.0 mmol), 1-dodecanethiol (0.24 mL, 1.0 mmol), 4'-iodoacetopheonoe (369.0 mg, 1.5 mmol), then purified by column chromatography ($SiO_2$, hexane:$CH_2Cl_2$ = 9:1) to give **5h** as a white solid (369 mg, 99% yield). M.p.: 67-68 $^o$C (lit.[14]: 69.5-70.2 $^o$C); $^1$H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.6 Hz, 3 H), 1.24-1.69 (m, 20 H), 2.55 (s, 3 H), 2.96 (t, *J* = 7.4 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 7.83 (d, *J* = 8.4 Hz, 2 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.9, 28.9, 29.1, 29.3, 29.5, 29.5, 29.6, 29.6, 31.9, 32.0, 126.2, 128.7, 133.7, 145.0, 197.2.



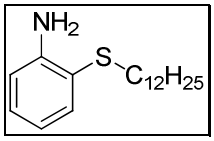

**4-(*tert*-Butylthio)benzaldehyde 5i (Table 4, entry 11)[15].**

Following the general procedure for Table 4, using $Cs_2CO_3$ (652.0 mg, 2.0 mmol), 2-methyl-2-propanethiol (0.113 mL, 1.0 mmol), 4-iodobenzaldehyde (348.0 mg, 1.5 mmol), then purified by column chromatography ($SiO_2$, hexane:$CH_2Cl_2$ = 10:1) to give **5i** as a colorless oil (150 mg, 77% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 9 H), 7.66 (d, *J* = 8.2 Hz, 2 H), 7.81 (d, *J* = 8.2 Hz, 2 H), 10.01 (s, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 31.2, 47.1, 129.3, 135.8, 136.9, 141.3, 191.5.



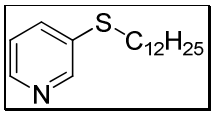

**2-(*tert*-Butylsulfanyl)aniline 5j (Table 4, entry 10)[16].**

Following the general procedure for Table 4, using KO*t*Bu (224.0 mg, 2.0 mmol), 2-methyl-2-propanethiol (0.113 mL, 1.0 mmol), 2-iodoaniline (329.0 mg, 1.5 mmol), then purified by column chromatography ($SiO_2$, hexane:$CH_2Cl_2$ = 9:1) to give **5j** as a deep blue oil (120 mg, 66% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.30 (s, 9 H), 4.69 (br s, 2 H), 6.76 (t, *J* = 7.4 Hz, 1 H), 6.9 (d, *J* = 8.0 Hz, 1 H), 7.16-7.24 (m, 1 H), 7.37-7.40 (m, 1 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 31.0, 48.0, 116.2, 117.4, 119.3, 130.6, 139.4, 148.1; HREI-MS calcd. for $C_{10}H_{15}NS$: 181.0921, Found: 181.0925.




**2-*n*-Dodecanesulfanylaniline 5k (Table 4, entry 11)[17].**

Following the general procedure for Table 4, using KO*t*Bu (224.0 mg, 2.0 mmol), 1-dodecanethiol (0.24 mL, 1.0 mmol), 2-iodoaniline (329.0 mg, 1.5 mmol), then purified by column chromatography ($SiO_2$, hexane:$CH_2Cl_2$ = 9:1) to give **5k** as a colorless oil (220 mg, 75% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.8 Hz, 3 H), 1.23-1.57 (m, 20 H), 2.71 (t, *J* = 7.2 Hz, 2 H), 4.31 (br s, 2 H), 6.60-6.80 (m, 2 H), 7.00-7.15 (m, 1 H), 7.30-7.40 (m, 1 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.7, 29.2, 29.3, 29.5, 29.57, 29.61, 29.62, 29.65, 31.9, 34.9, 114.8, 118.40, 118.43, 129.4, 135.6, 148.1.




**3-(Dodecylthio)pyridine 5l (Table 4, entry 12)[18].**

Following the general procedure for Table 4, using KO*t*Bu (224.0 mg, 2.0 mmol), 1-dodecanethiol (0.24 mL, 1.0 mmol), 3-iodopyridine (308.0 mg, 1.5 mmol), then purified by column chromatography ($SiO_2$, hexane:$CH_2Cl_2$ = 5:1) to give **5l** as a colorless oil (210 mg, 75% yield). $^1$H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 6.8 Hz, 3 H), 1.23-1.67 (m, 20 H), 2.93 (t, *J* = 7.2 Hz, 2 H), 7.71 (br s, 1 H), 7.73 (br s, 1 H), 8.41 (br s, 1 H), 8.53 (br s, 1 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 14.3, 22.9, 28.9, 29.3, 29.3, 29.5, 29.7, 29.7, 29.8, 32.1, 33.9, 123.9, 134.8, 137.1, 146.6, 149.7; HREI-MS calcd. for $C_{17}H_{29}NS$: 279.2014, Found: 279.2021.

## 6. References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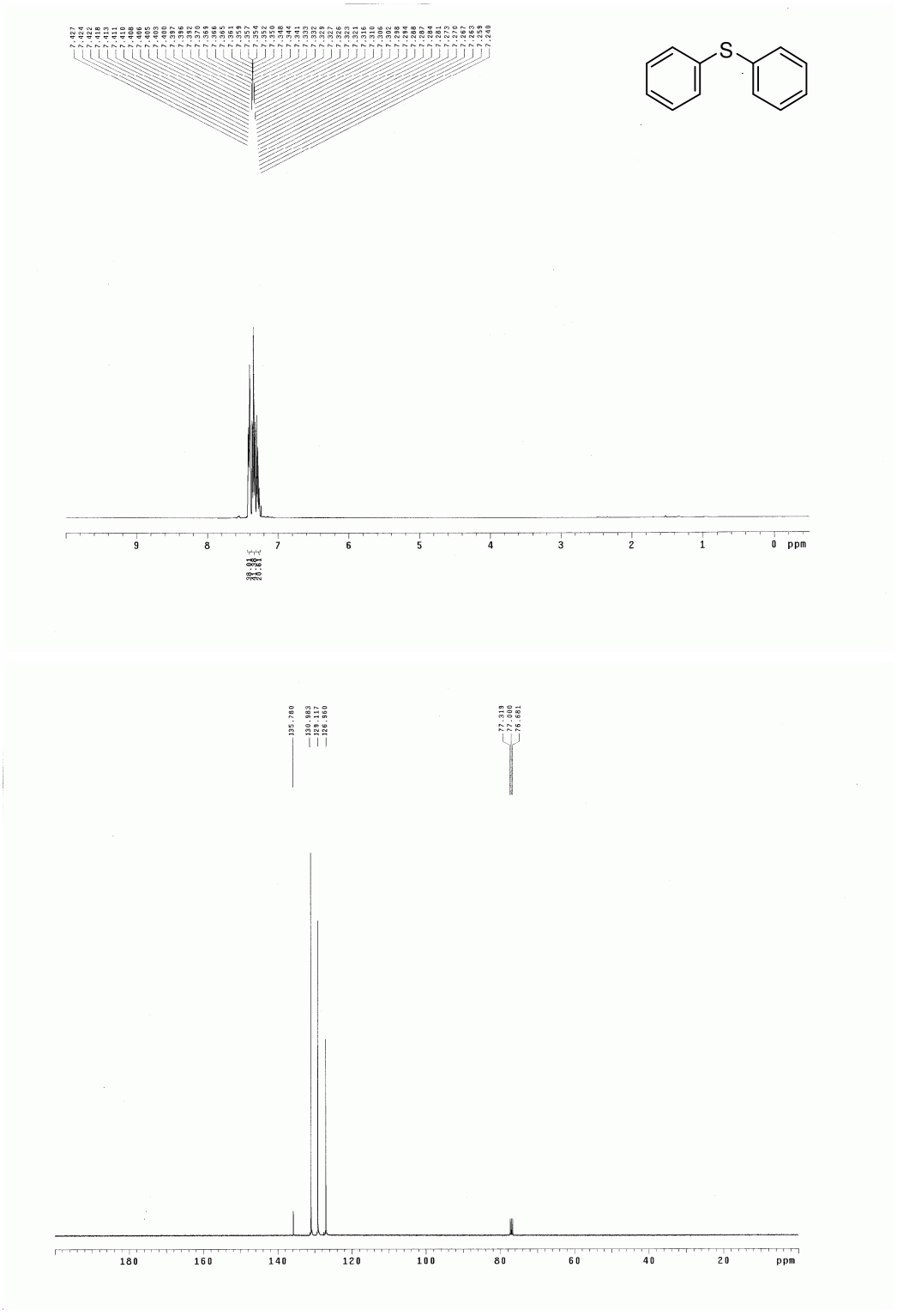
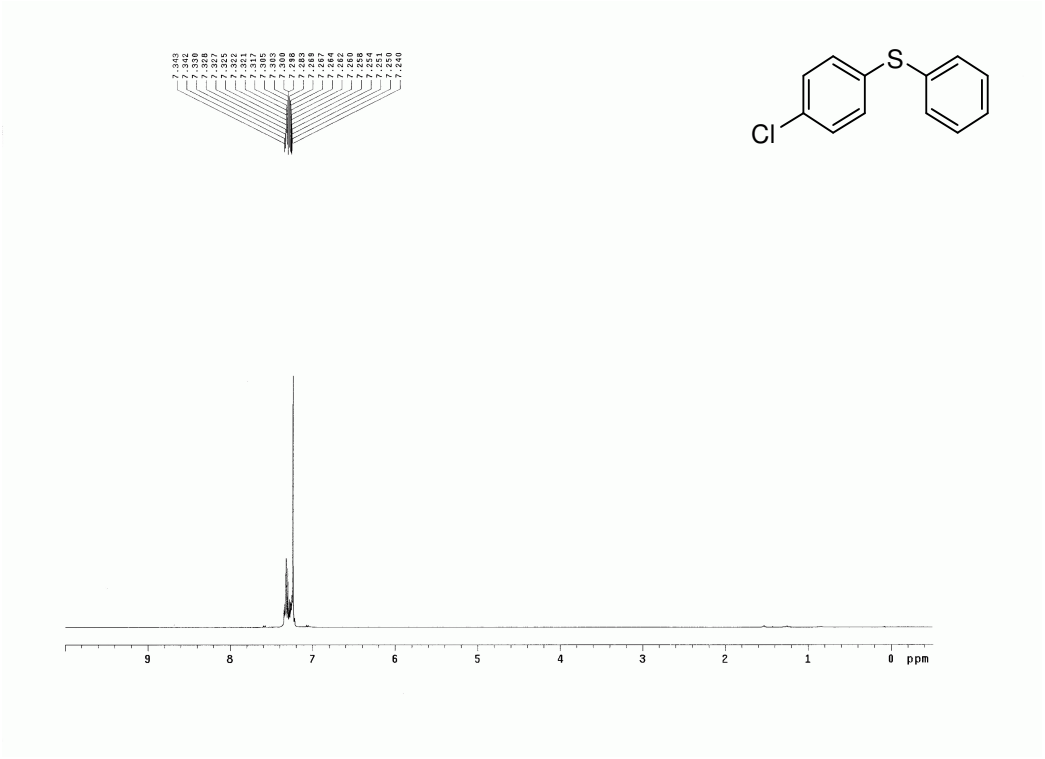
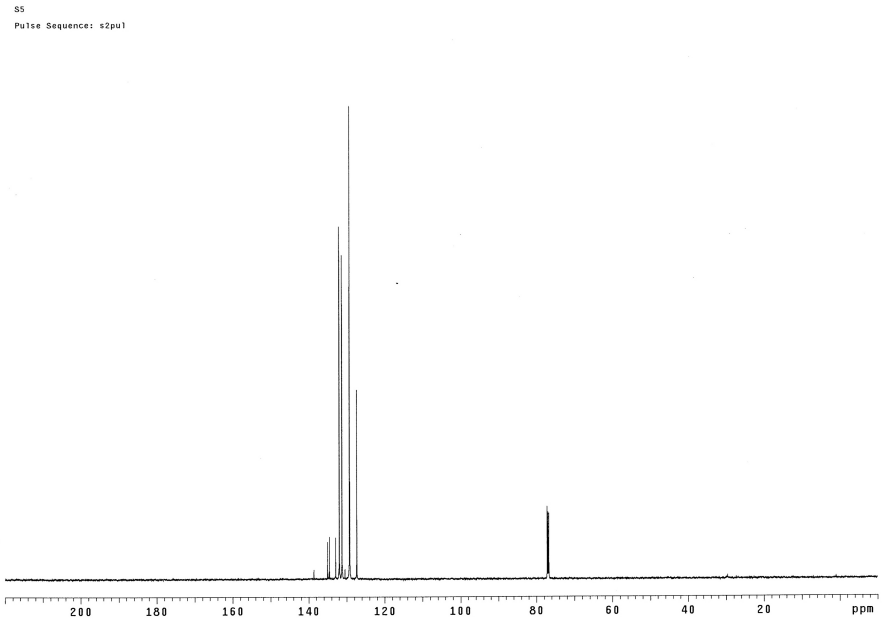
## 7. Spectra Data for Products:

## Diphenyl sulfide 3a

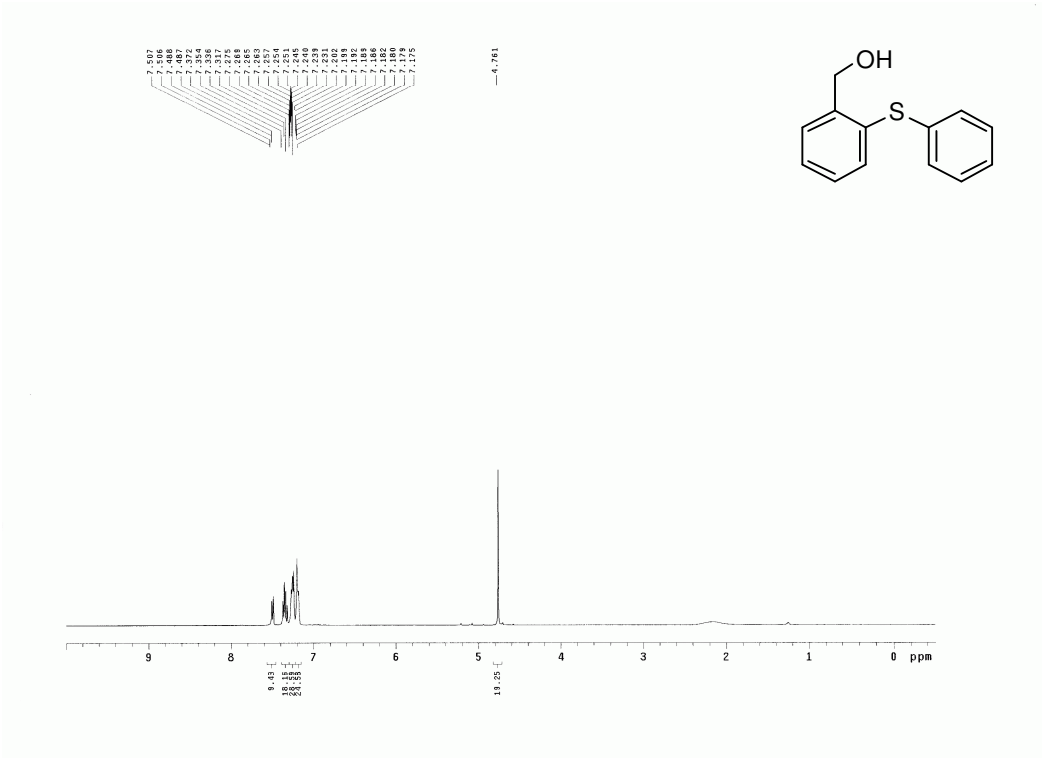


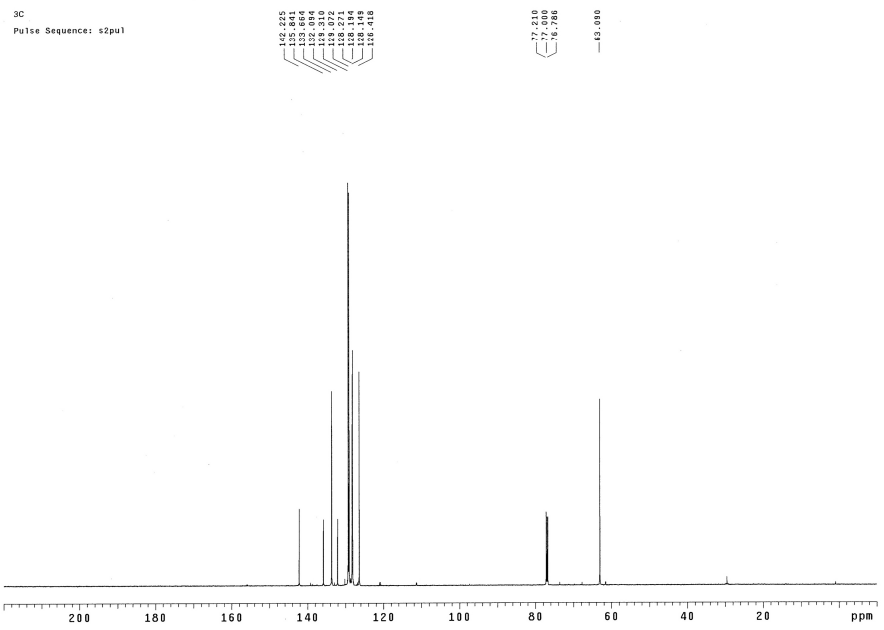

## 4-Chlorophenyl phenyl sulfide 3b



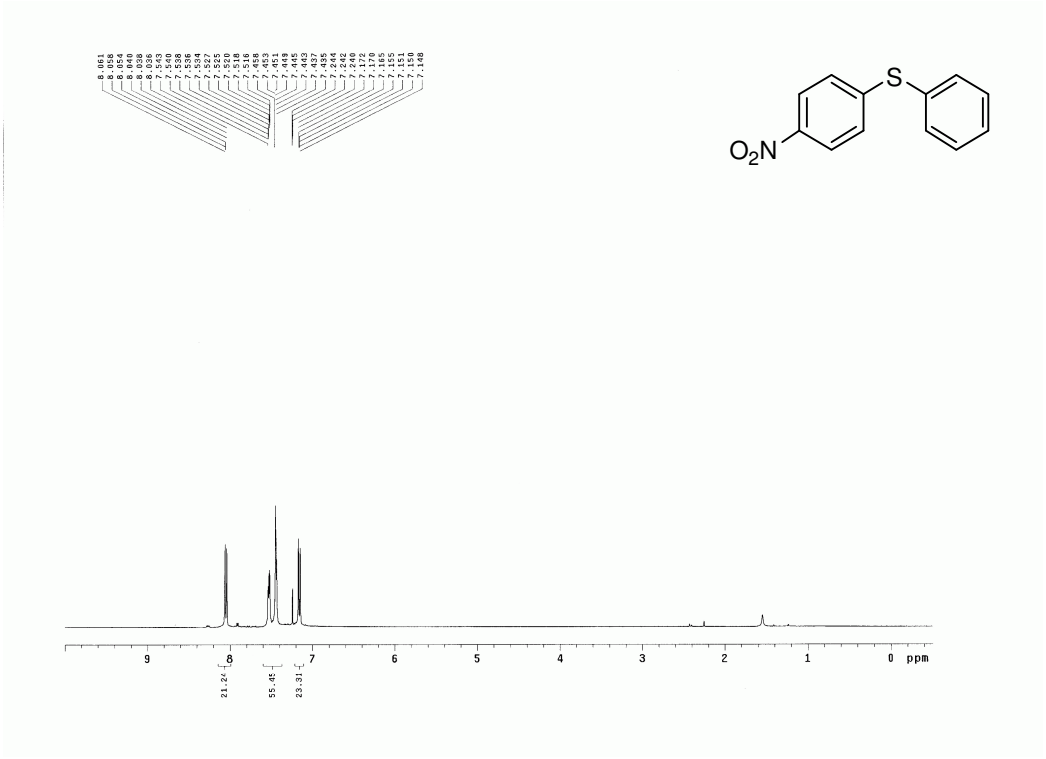



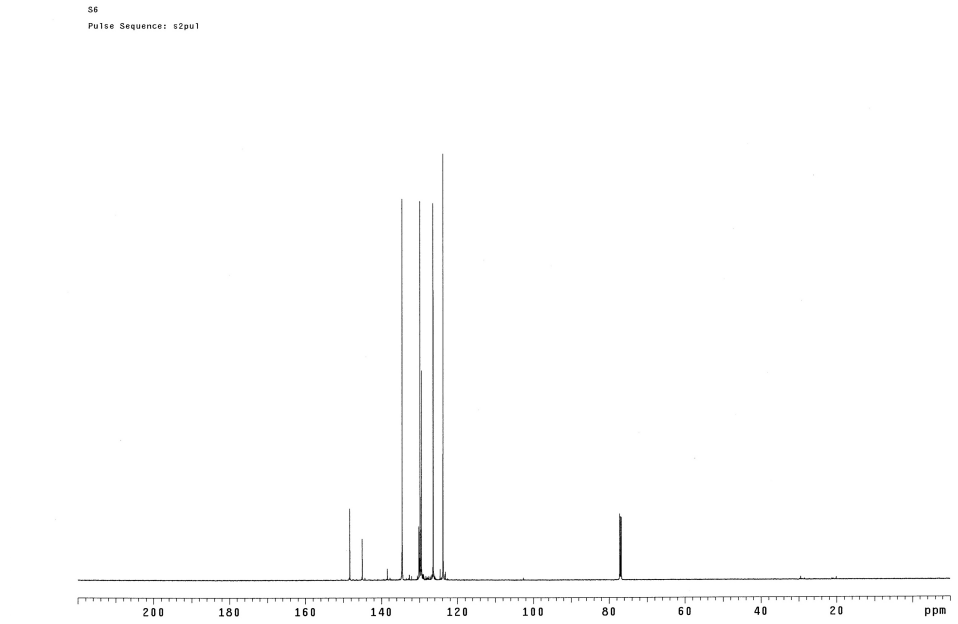

**(2-(Phenylthio)phenyl)methanol 3c**



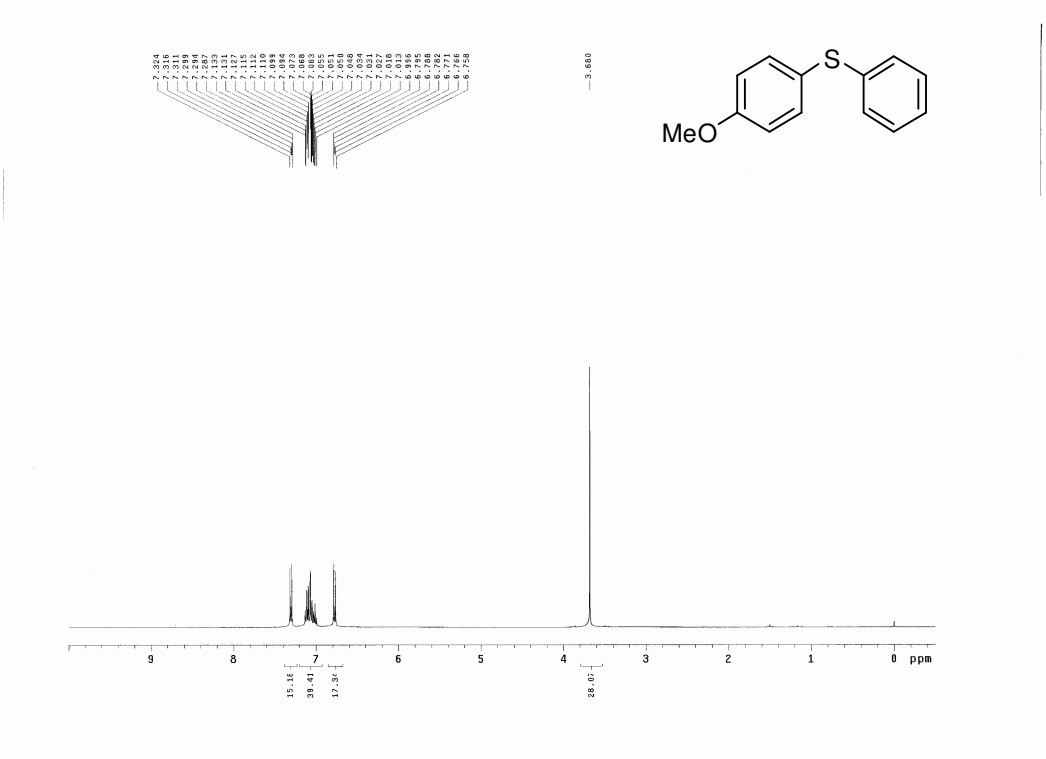



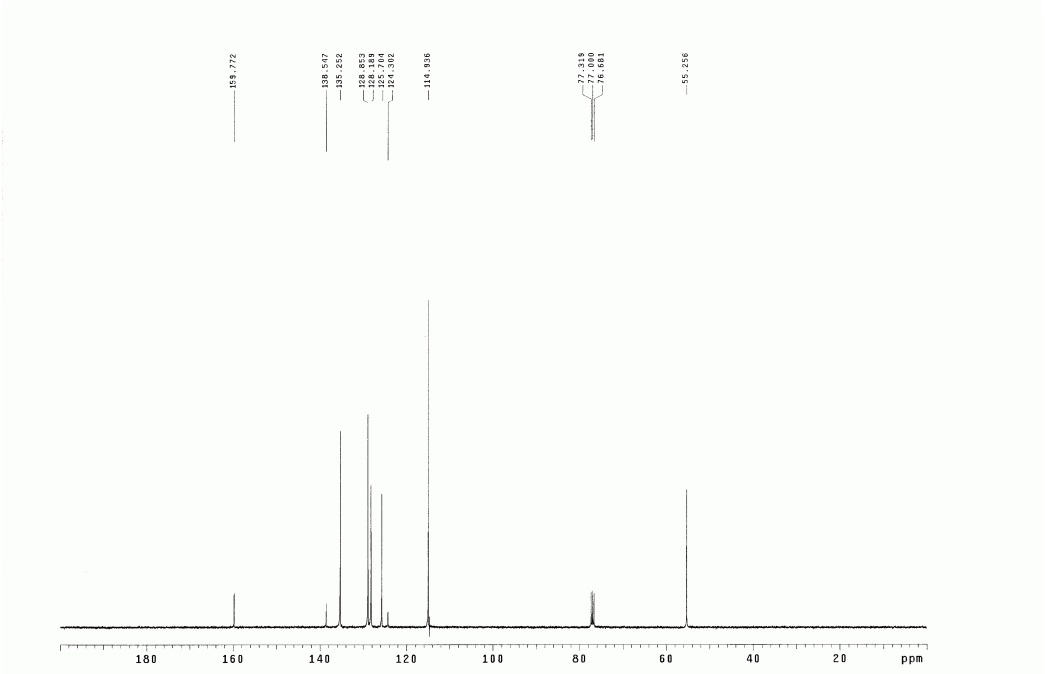

**4-Nitrophenyl phenyl sulfide 3d**



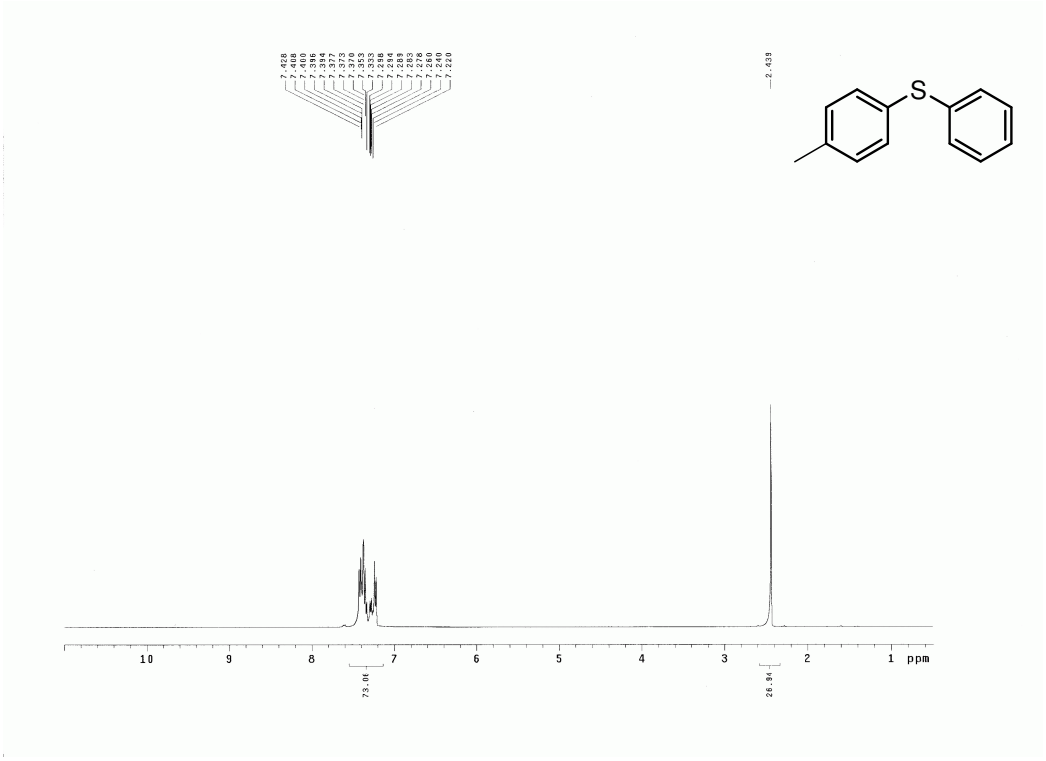



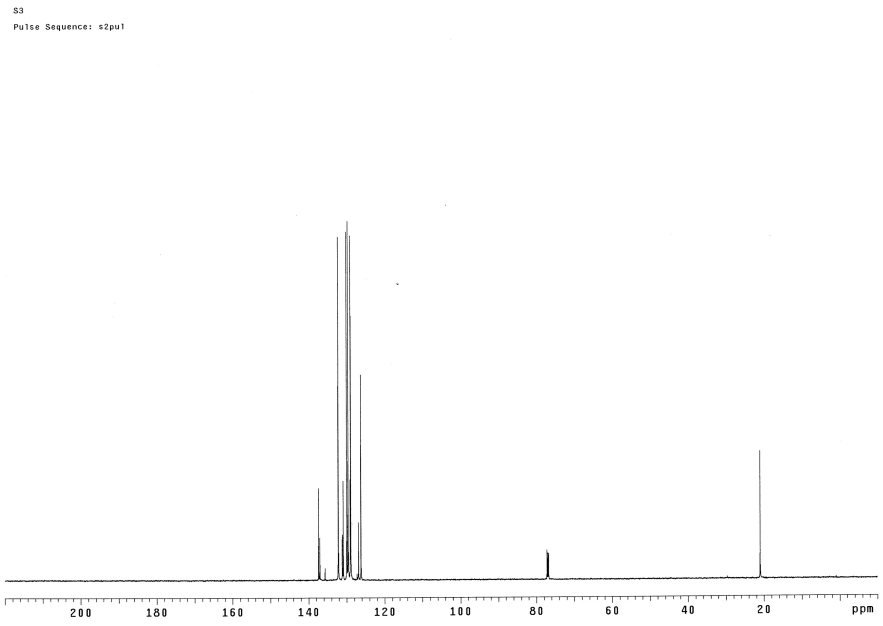

**4-Methoxyphenyl phenyl sulfide 3e**



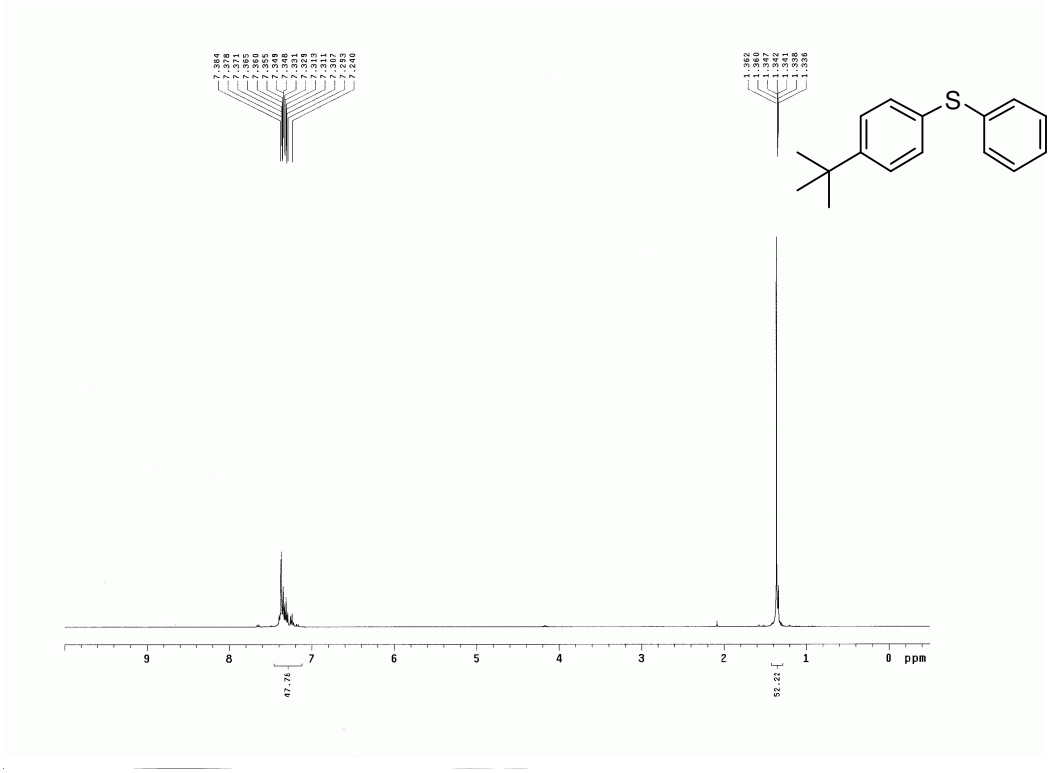



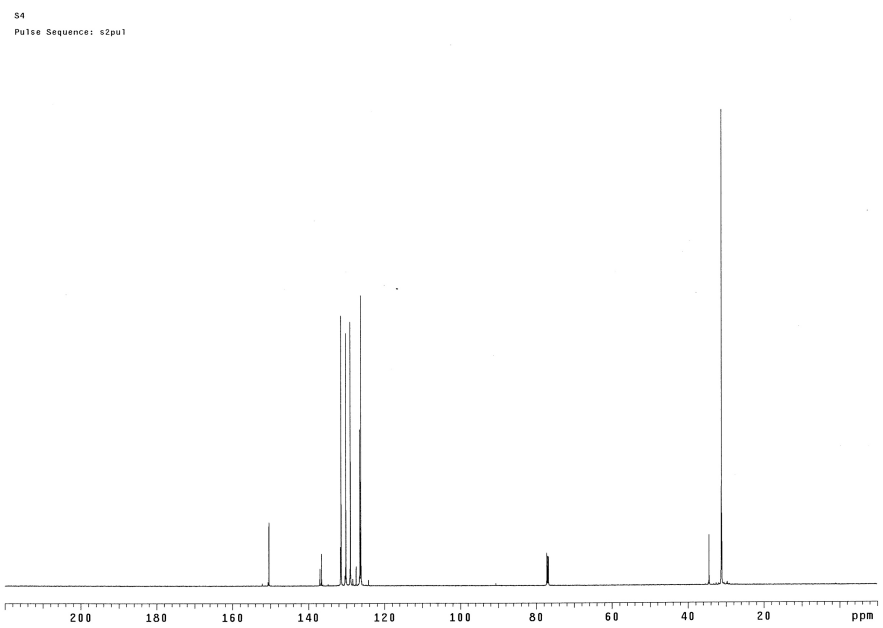

**4-Methylphenyl phenyl sulfide 3f**



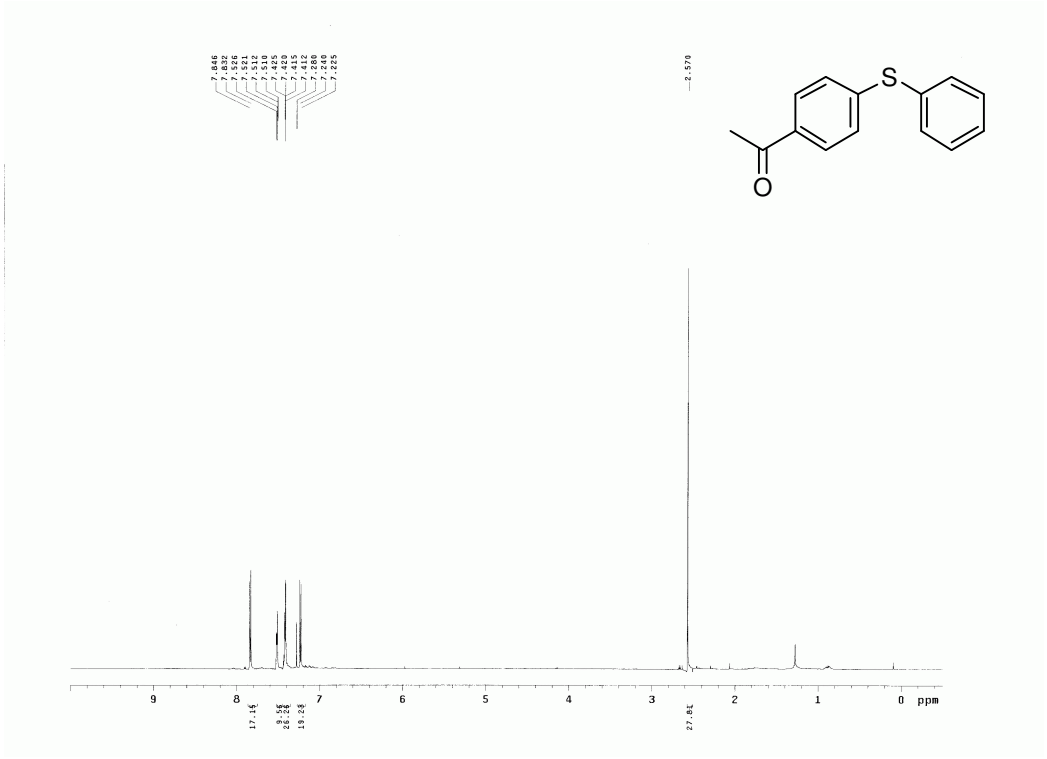



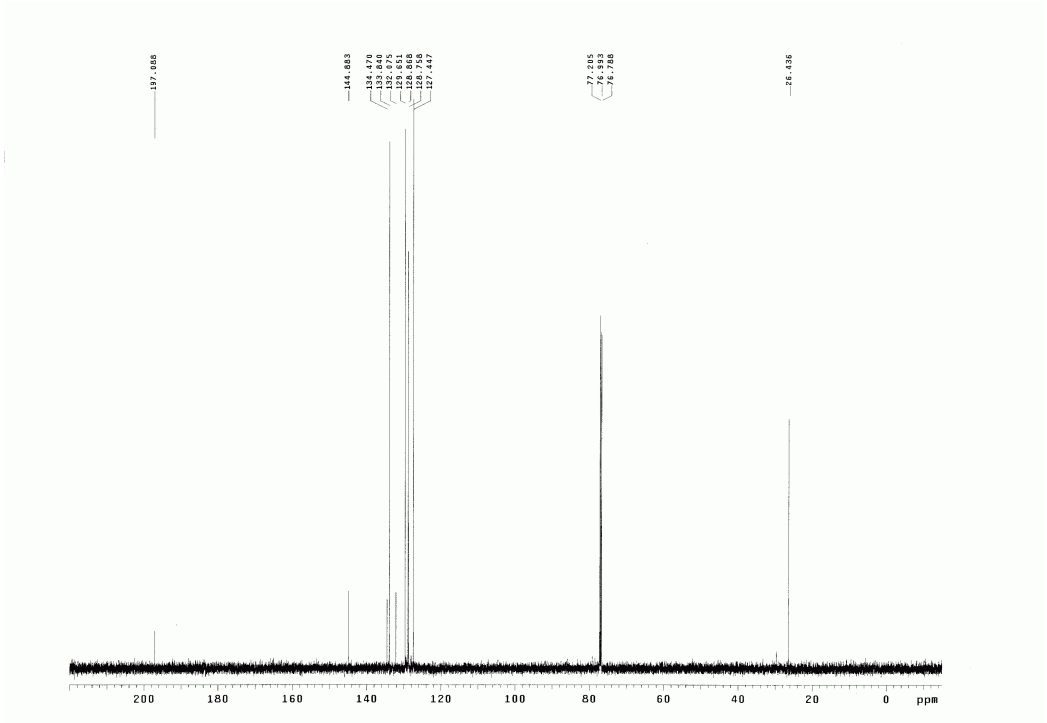

**4-*tert*-Butylphenyl phenyl sulfide 3g**



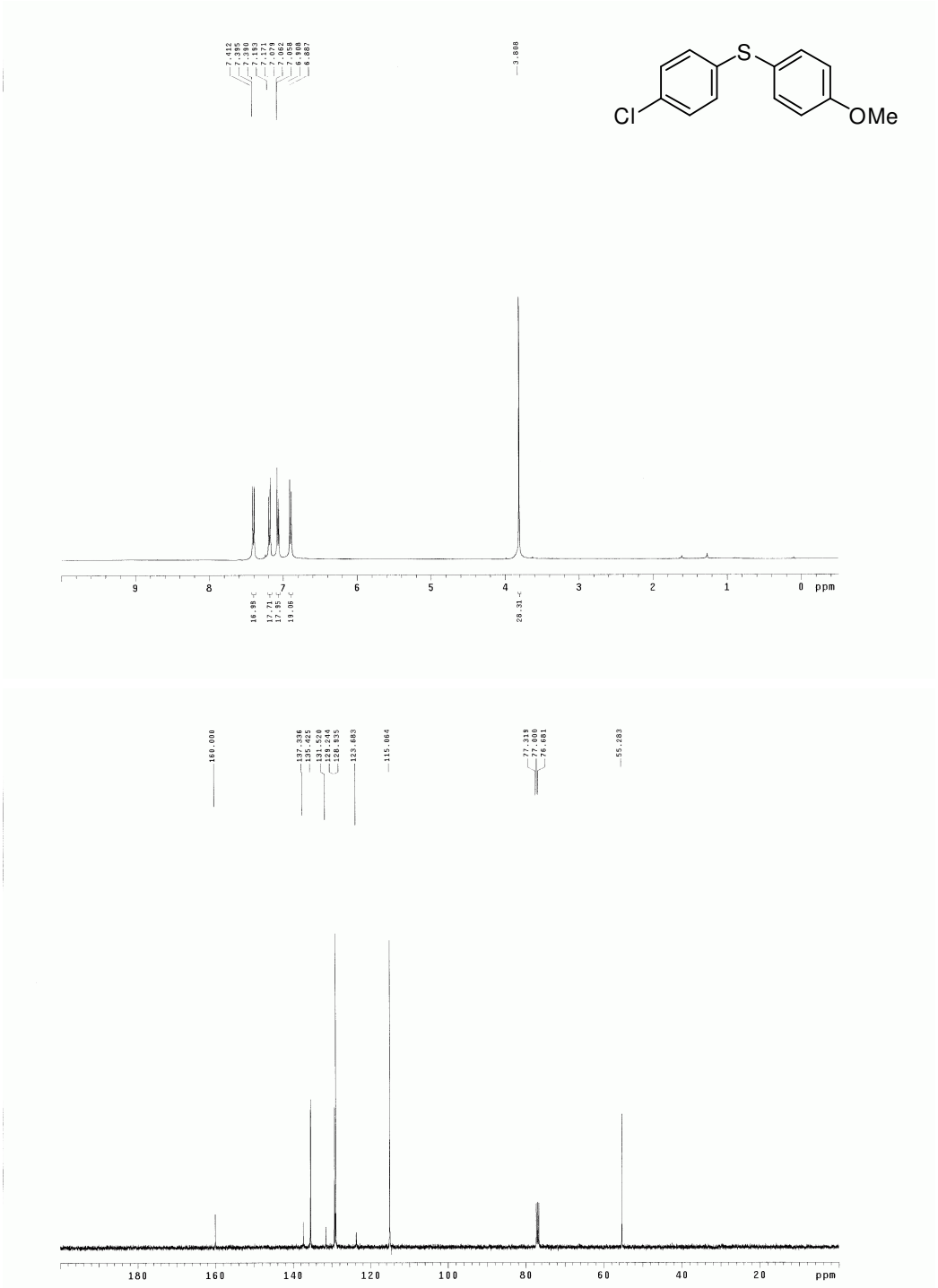




**4-Phenylsulfanylacetophenone 3h**

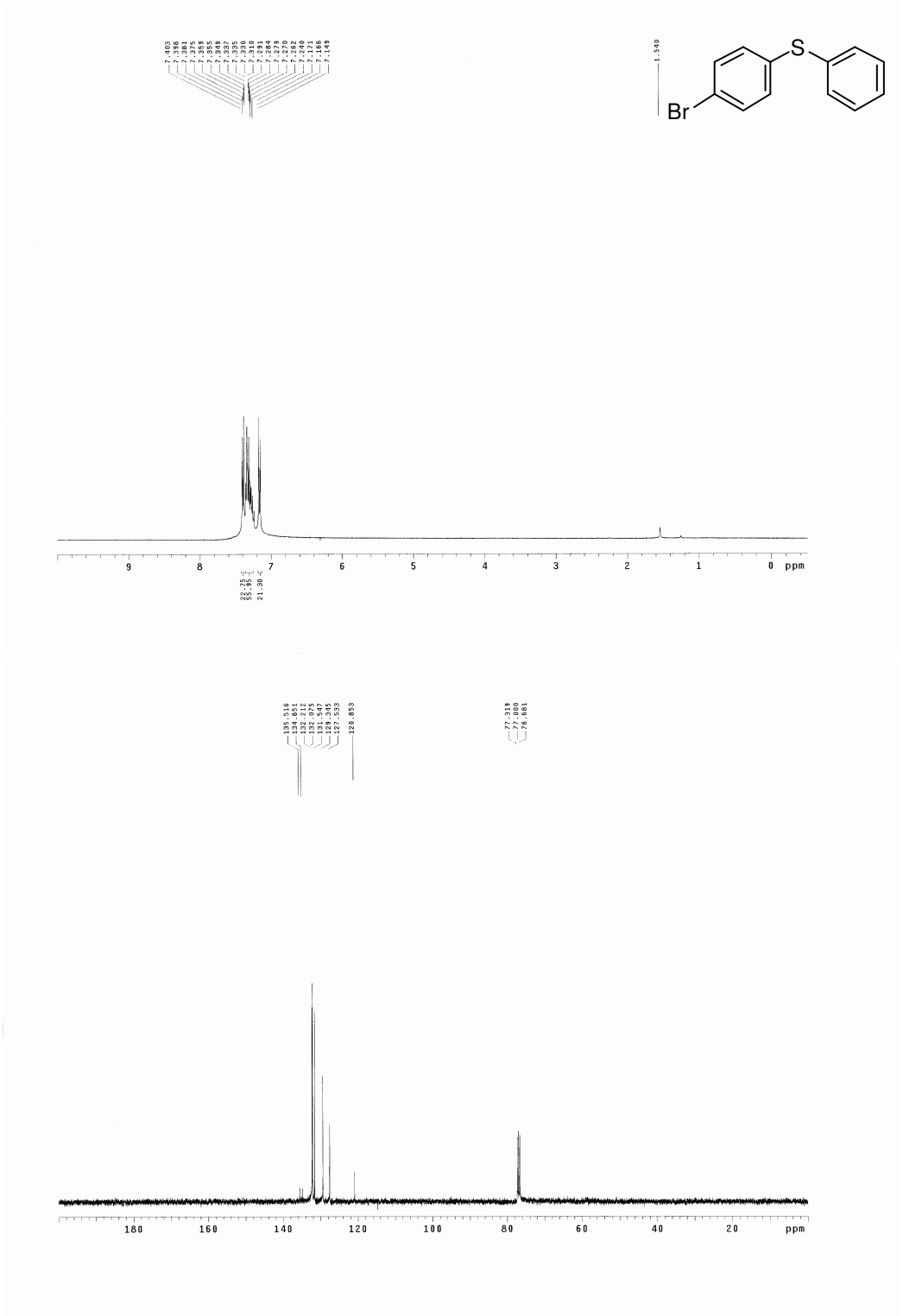


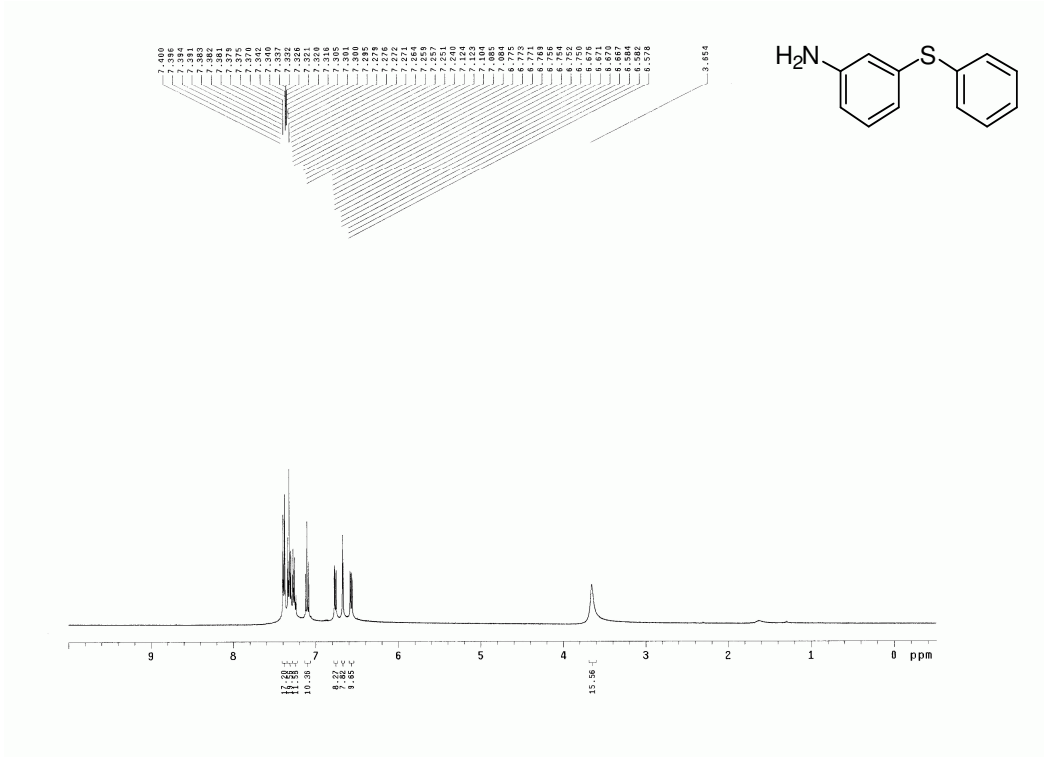

**4-Chlorophenyl 4-methoxyphenyl sulfide 3i**

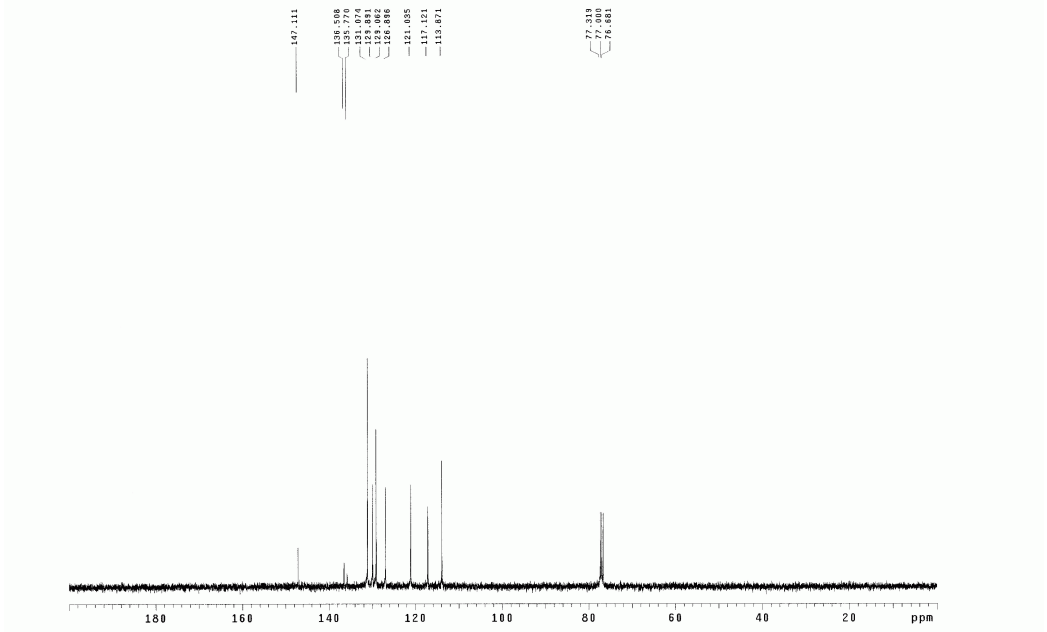



**4-Bromophenyl phenyl sulfide 3j**

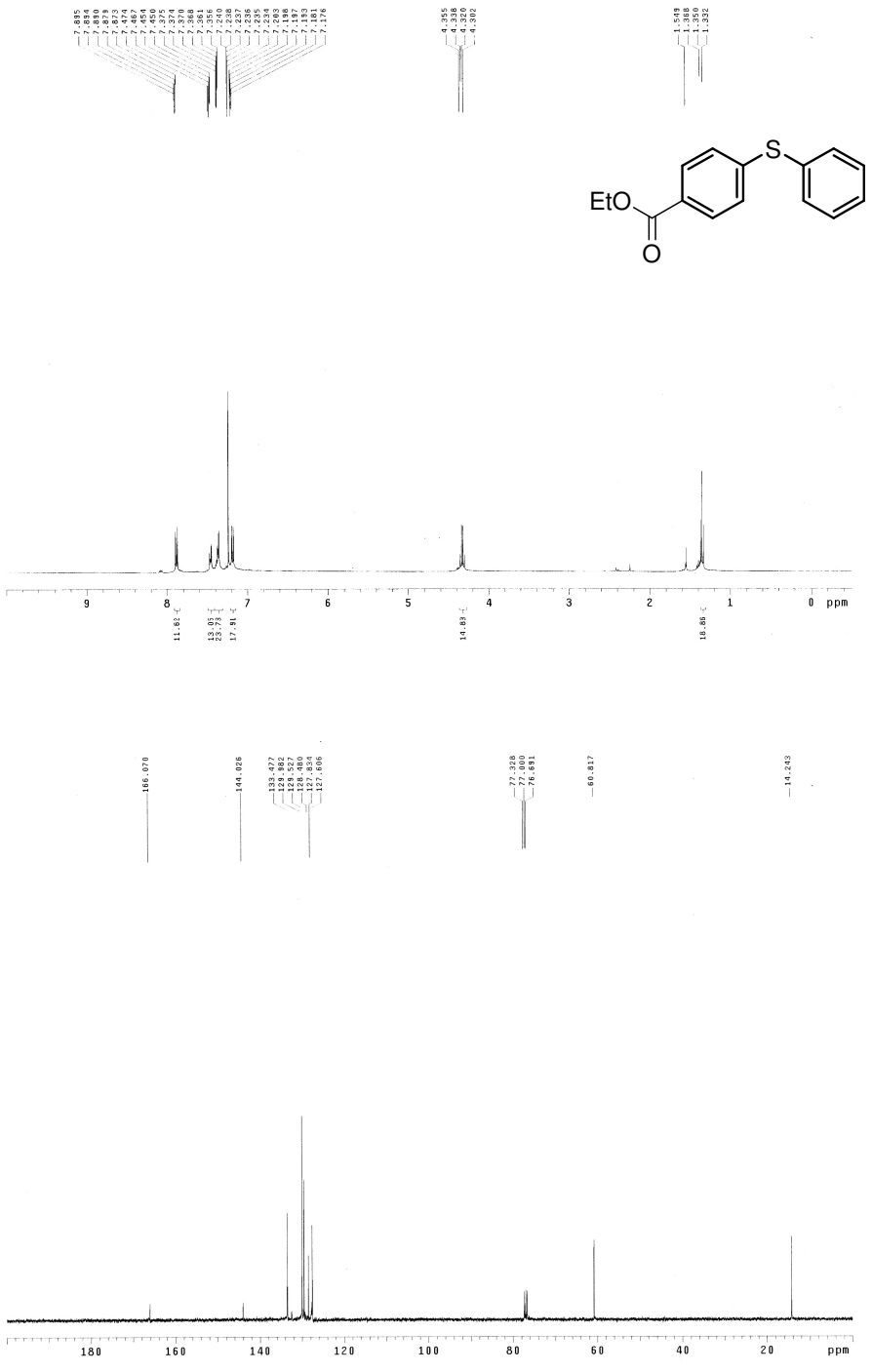



**3-Phenylsulfanylaniline 3k**

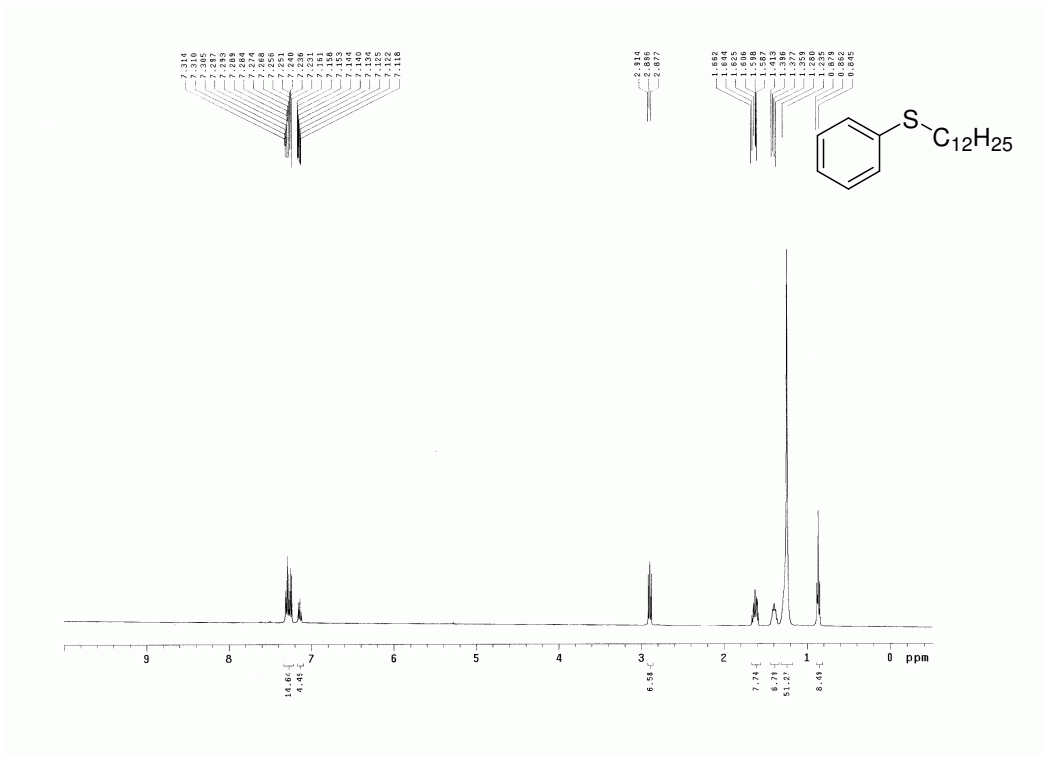


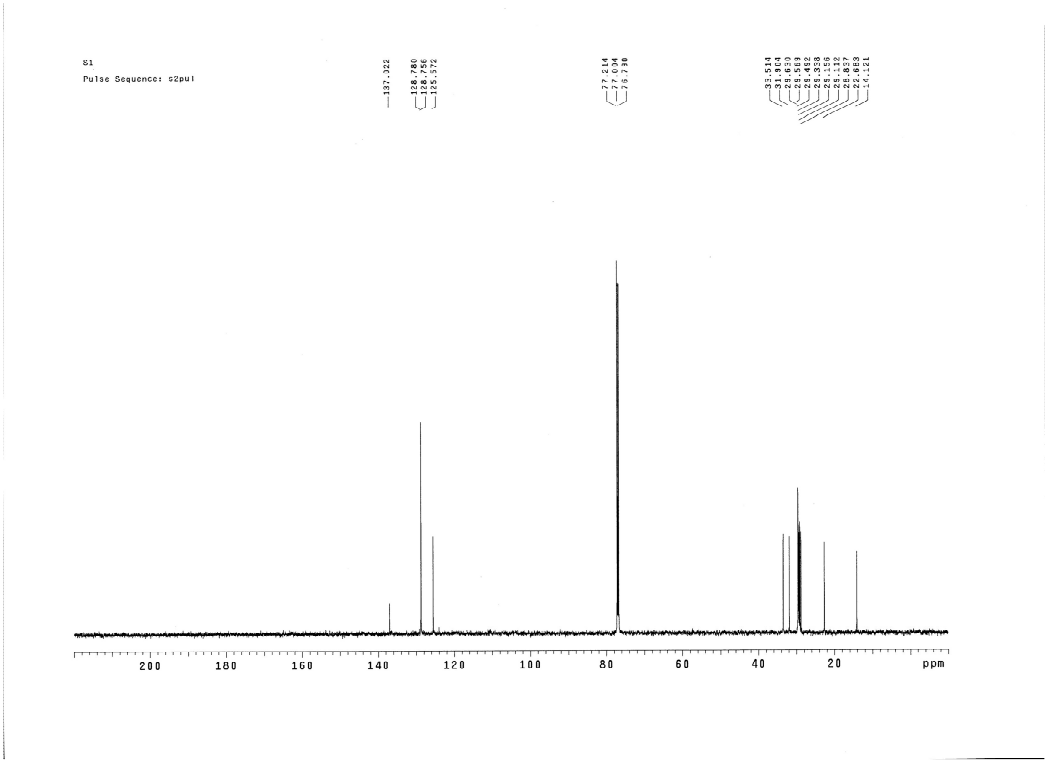




**4-Phenylsulfanyl-benzoic acid ethyl ester 3l**

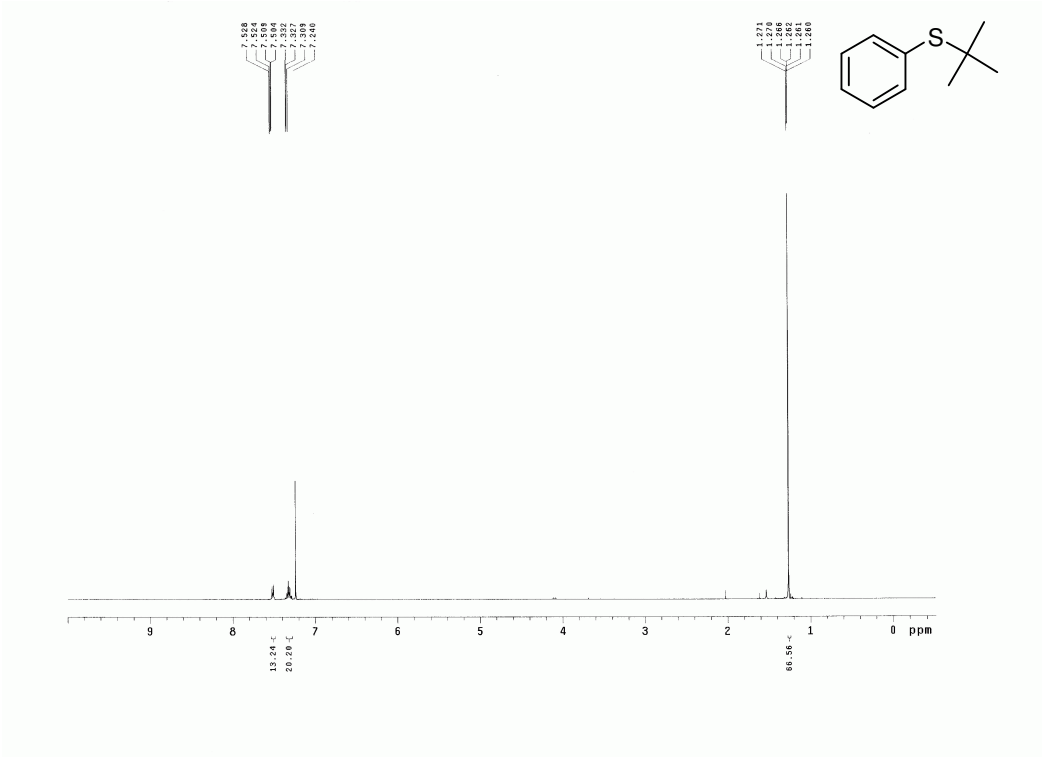


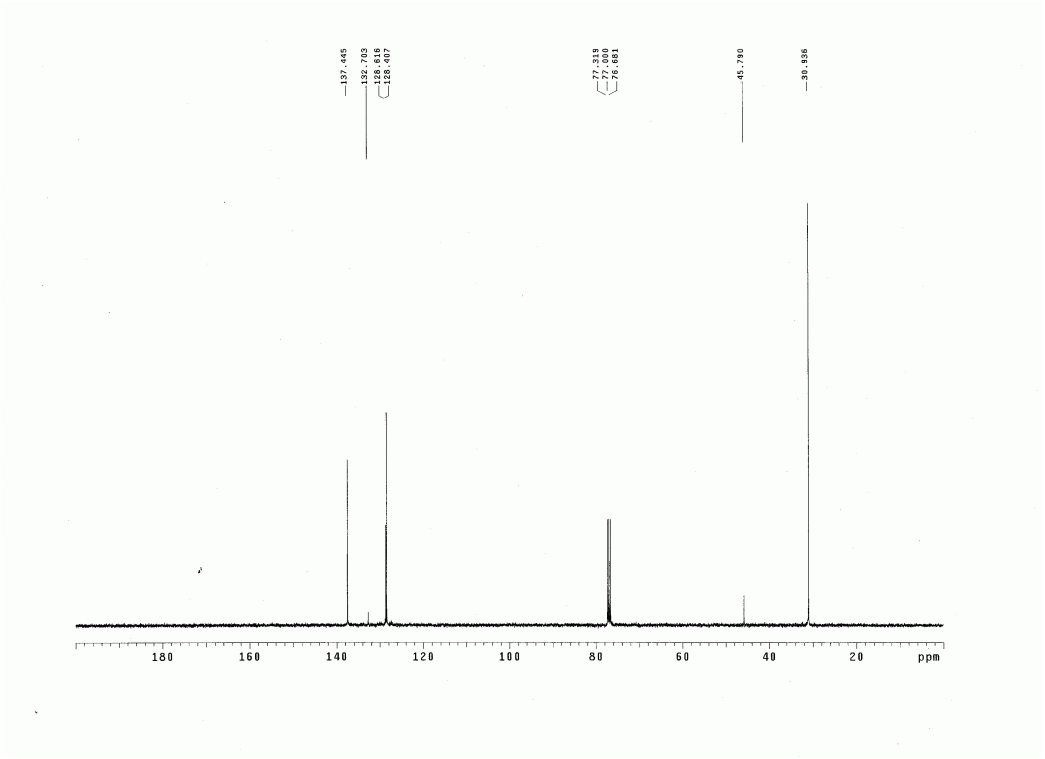

**Dodecyl phenyl sulfide 5a**



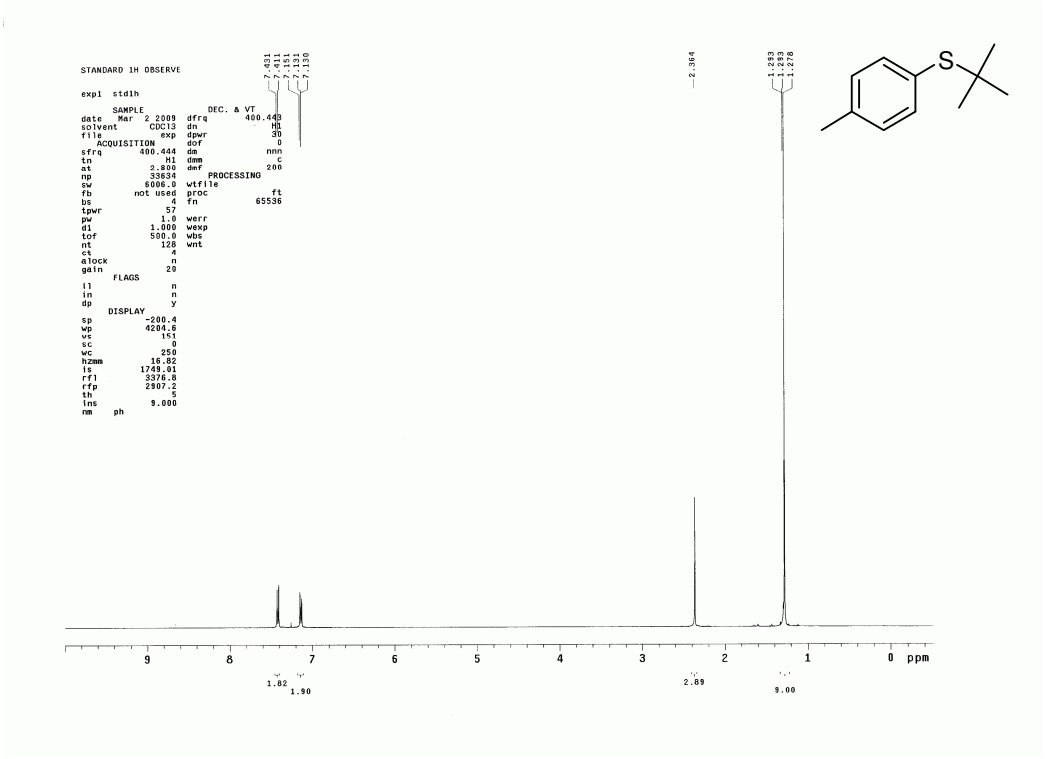



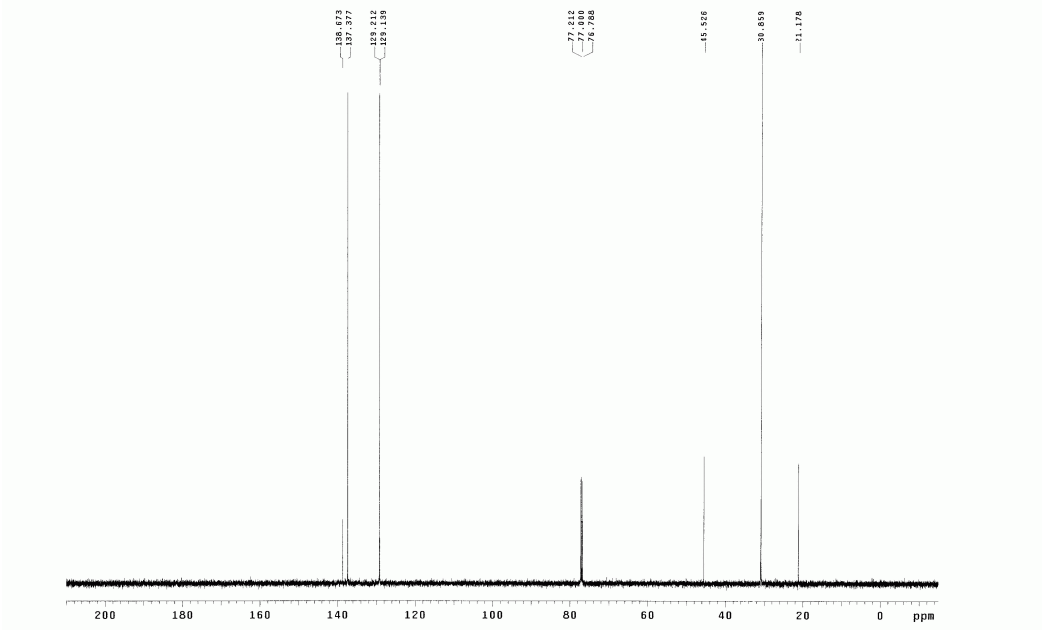

***tert*-Butyl phenyl sulfide 5b**



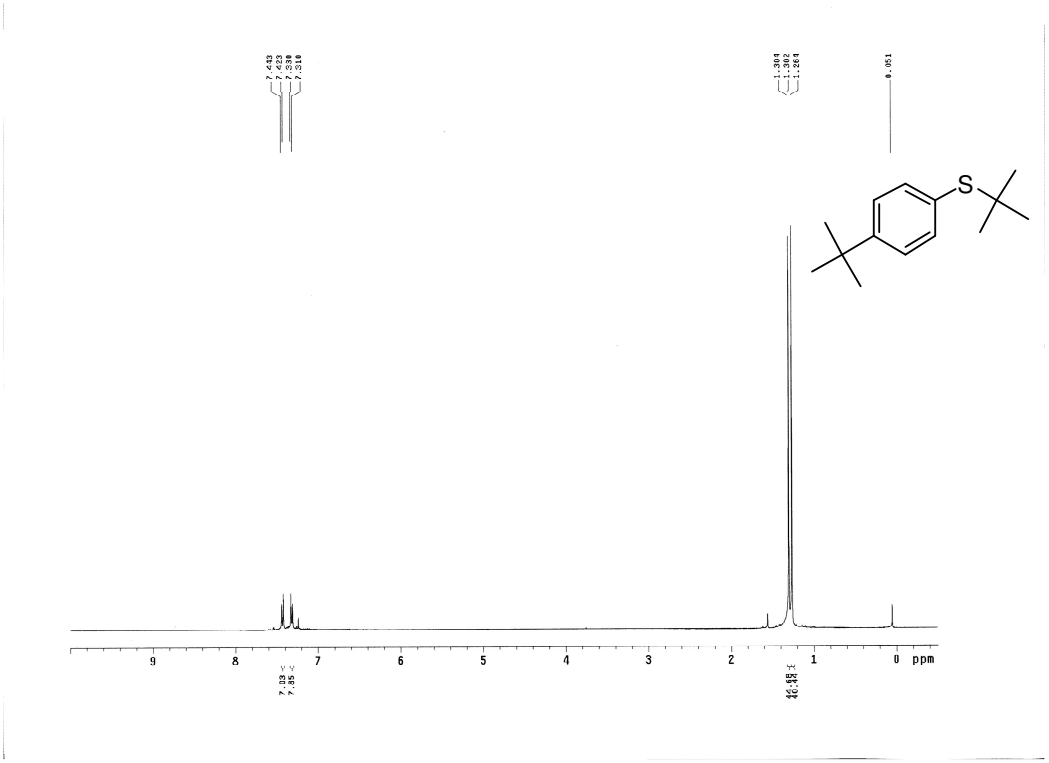



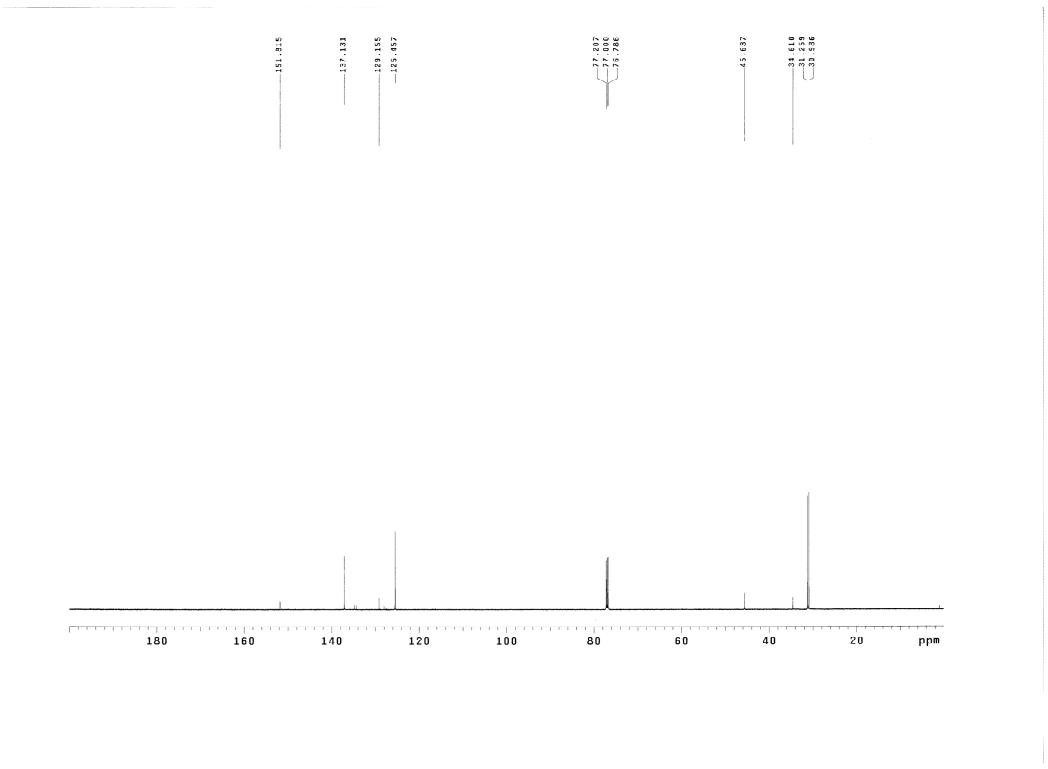

**1,1-Dimethylethyl 4-methylphenyl sulfide 5c**



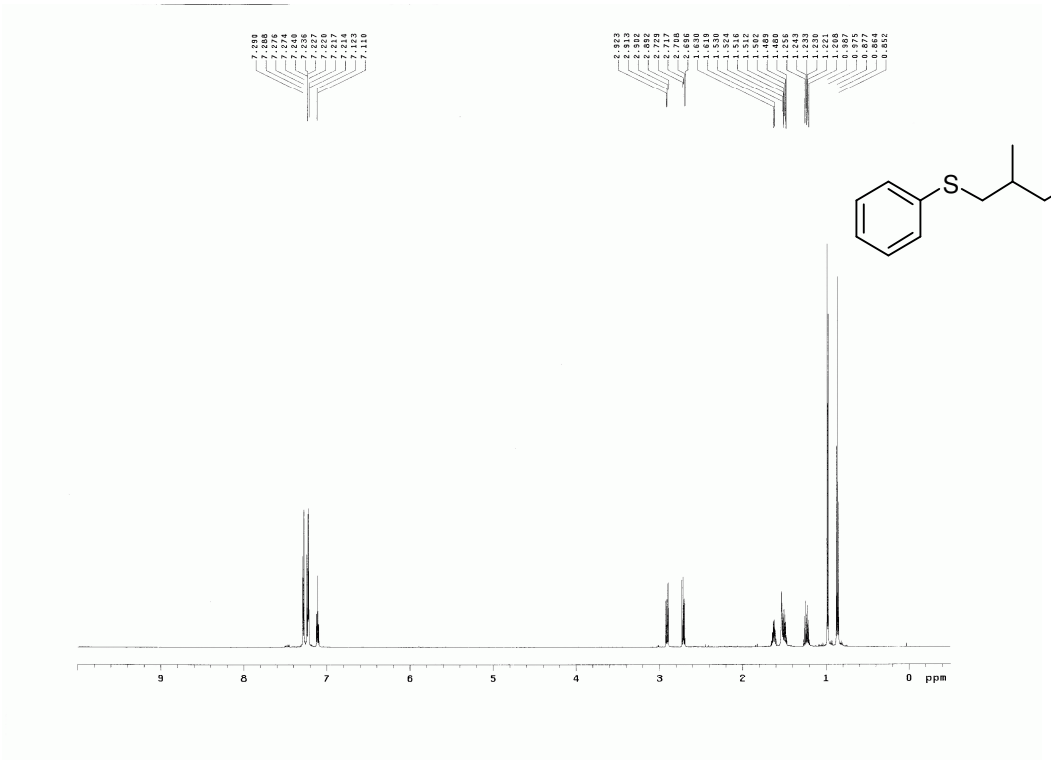



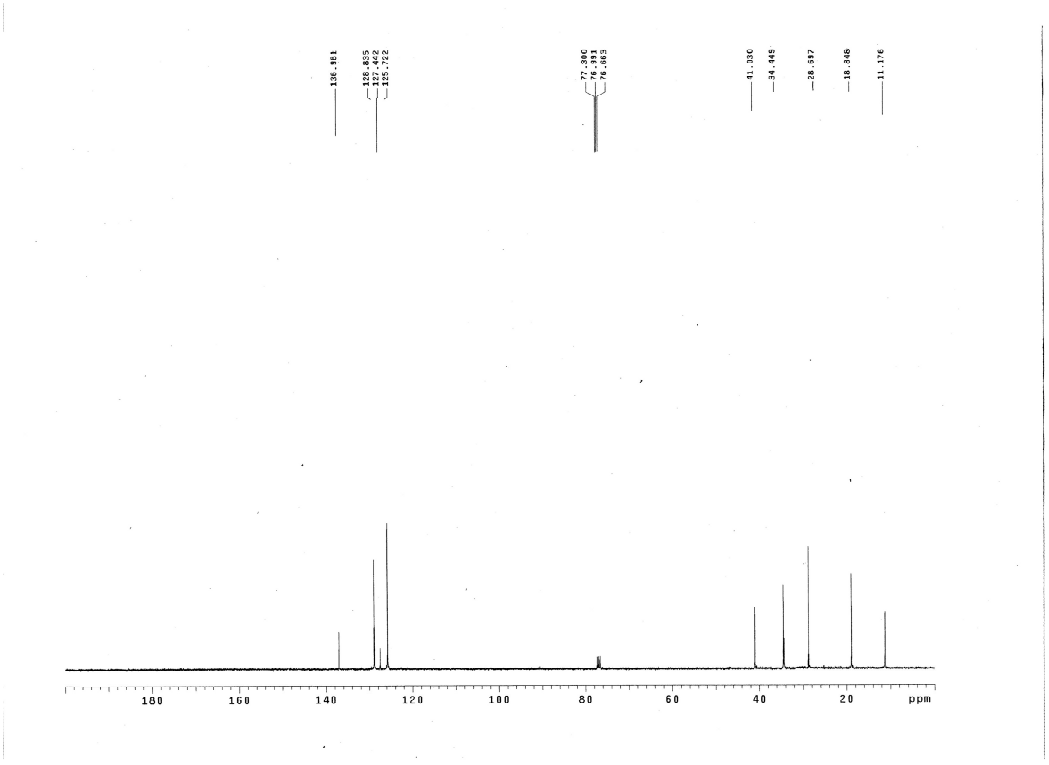

**_tert_-Butyl 4-_tert_-butylphenyl sulfide 5d**



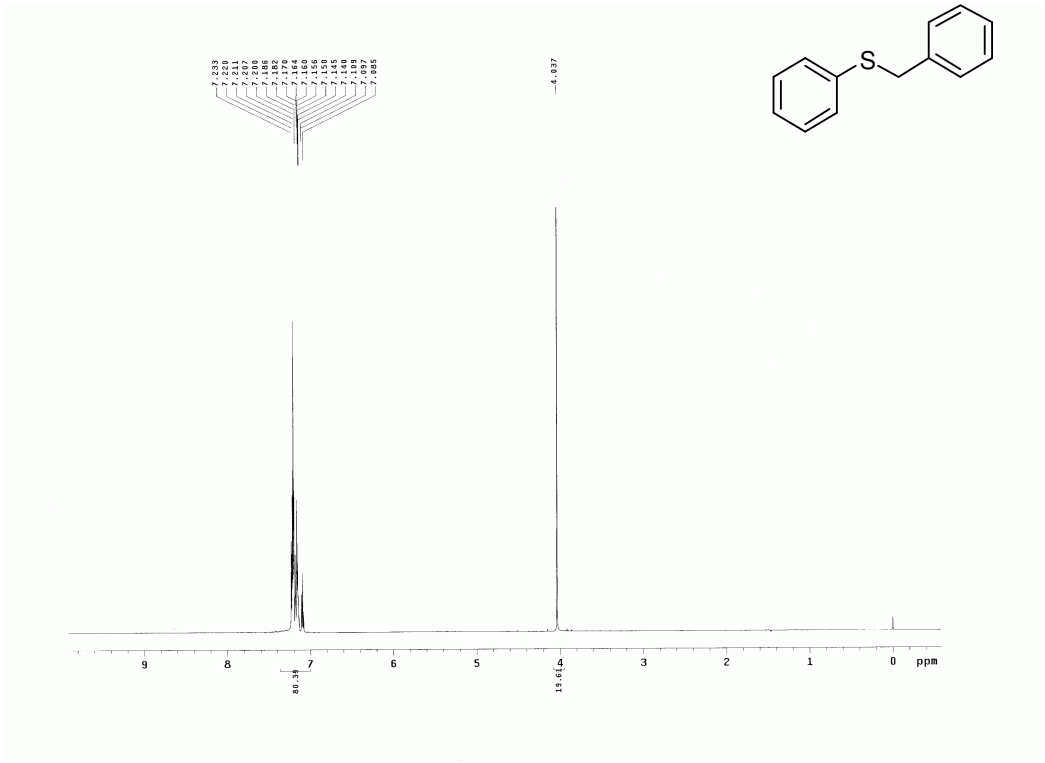



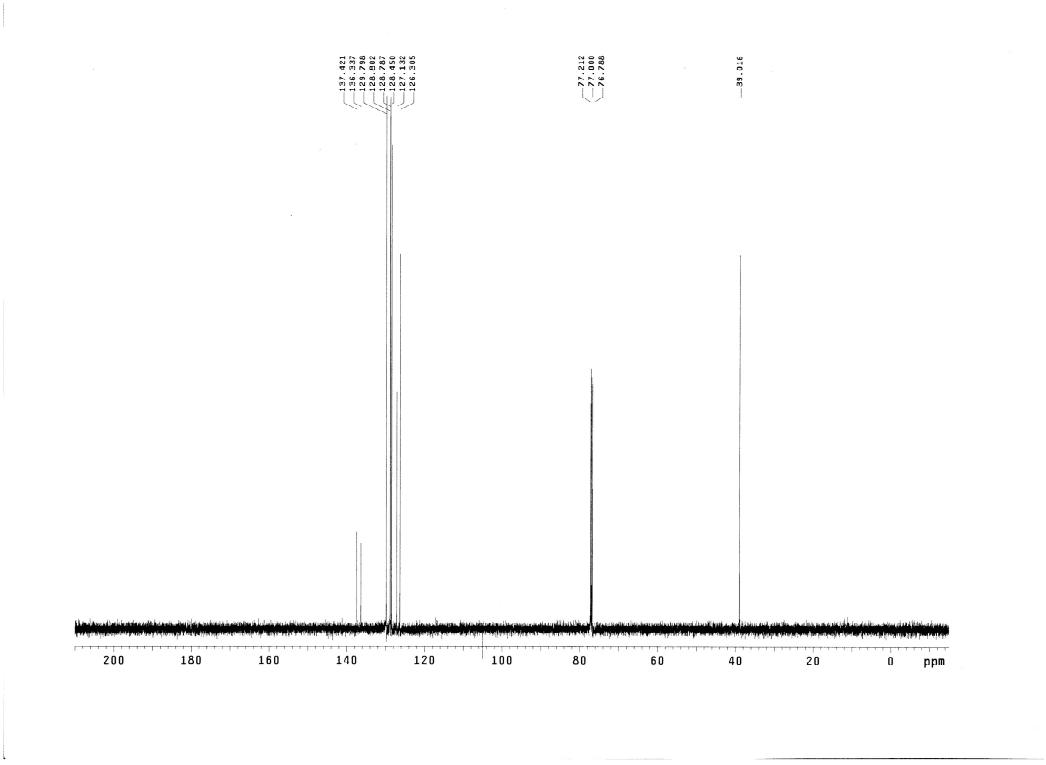

**2-Methylbutyl phenyl sulfide 5e**



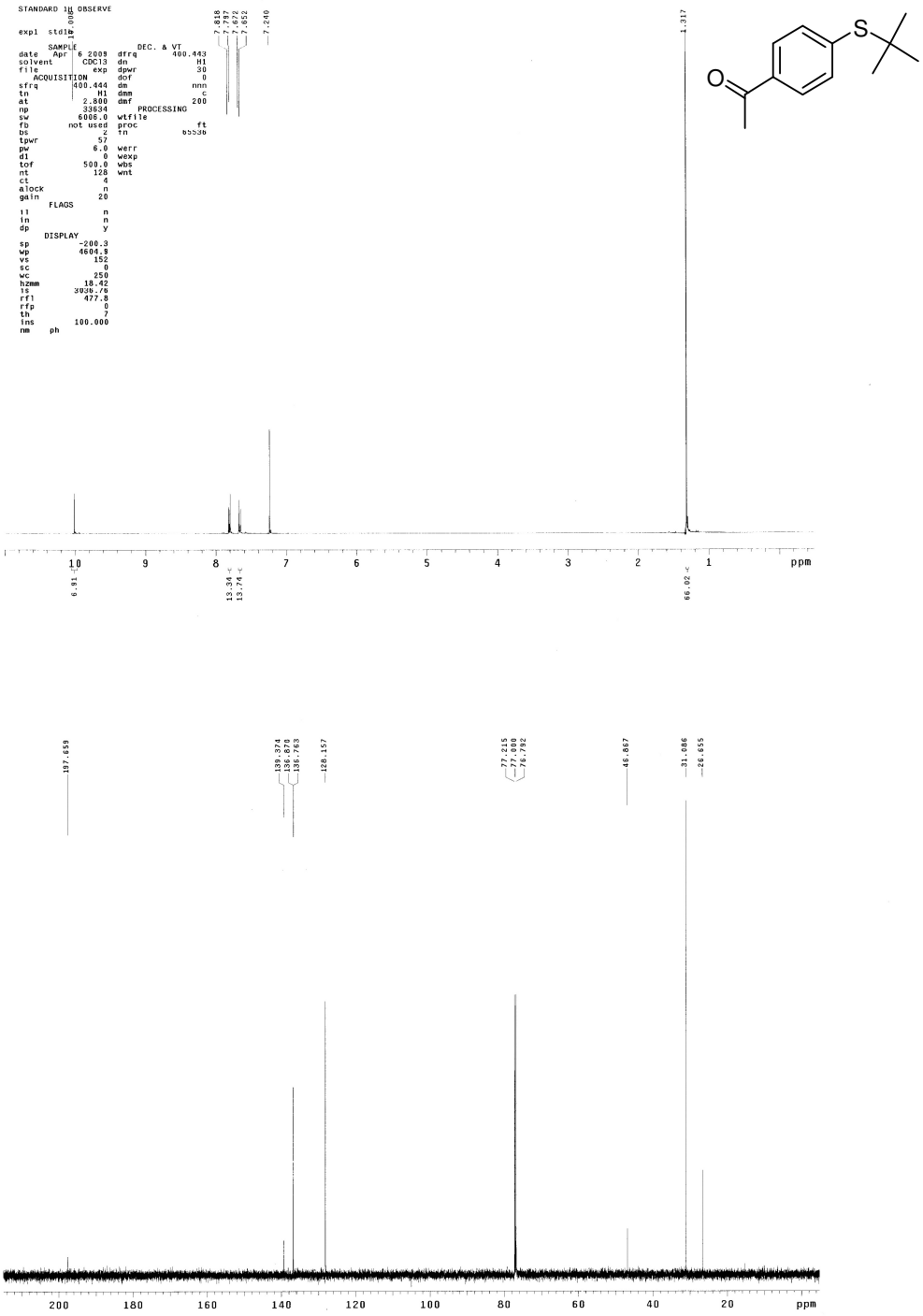




**Benzyl phenyl sulfide 5f**

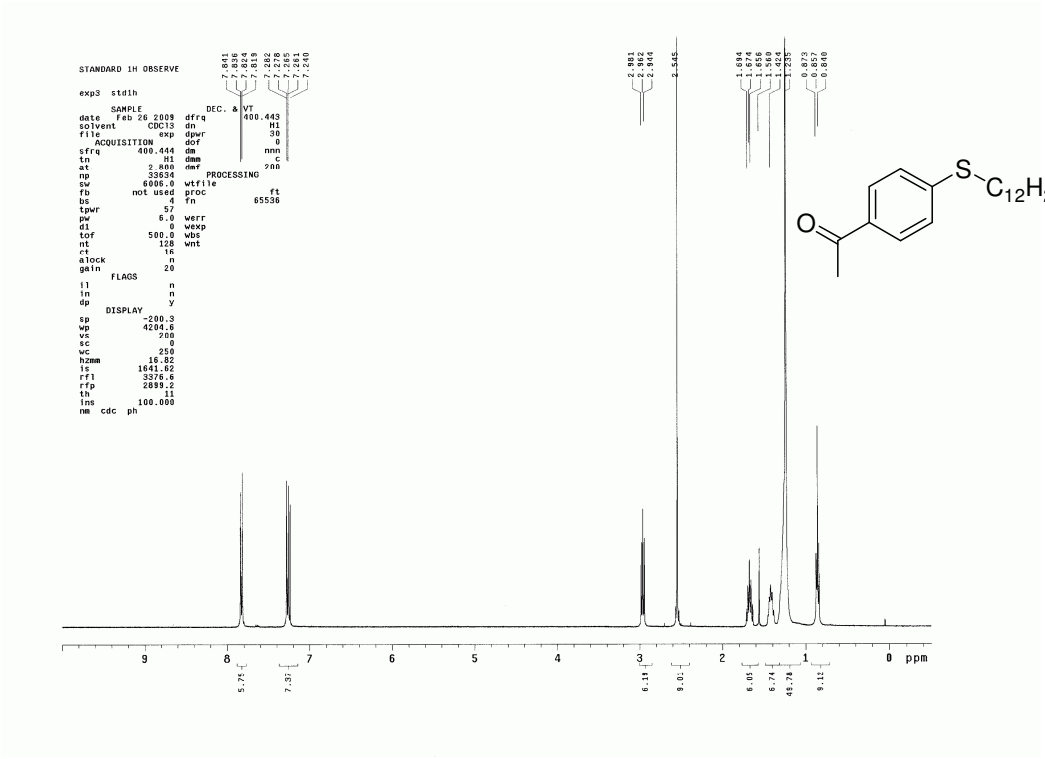


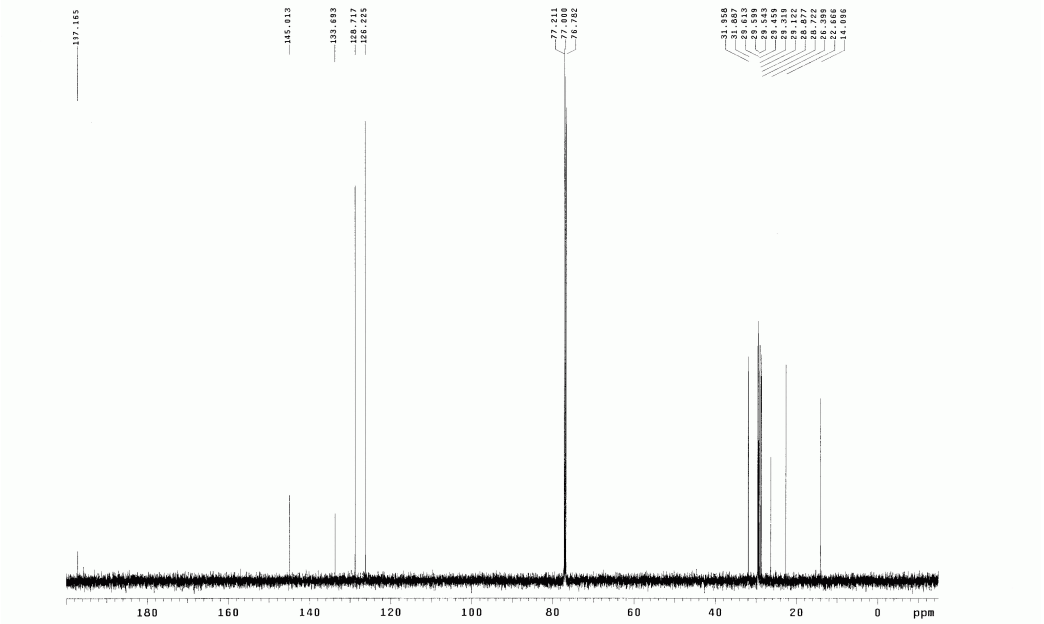




**1-(4-(*tert*-Butylthio)phenyl)ethanone 5g**

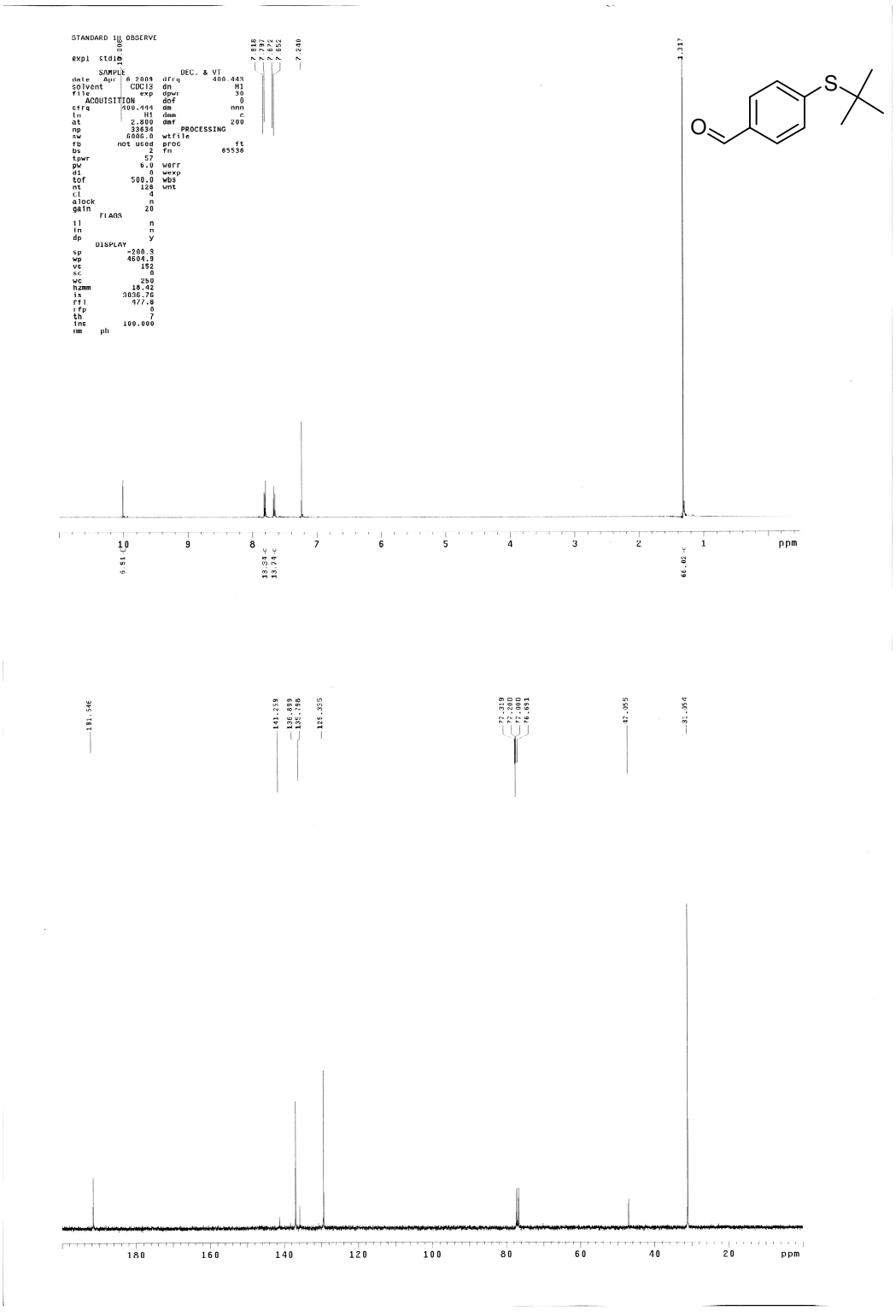



## 4-Dodecylthioacetophenone 5h

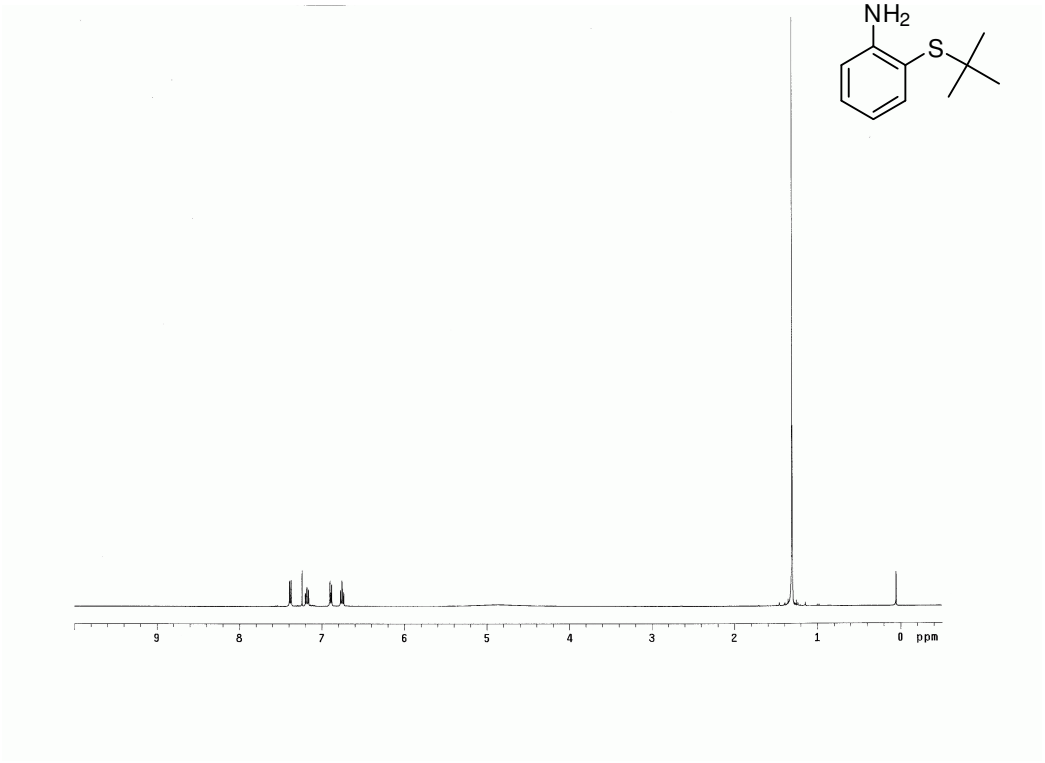


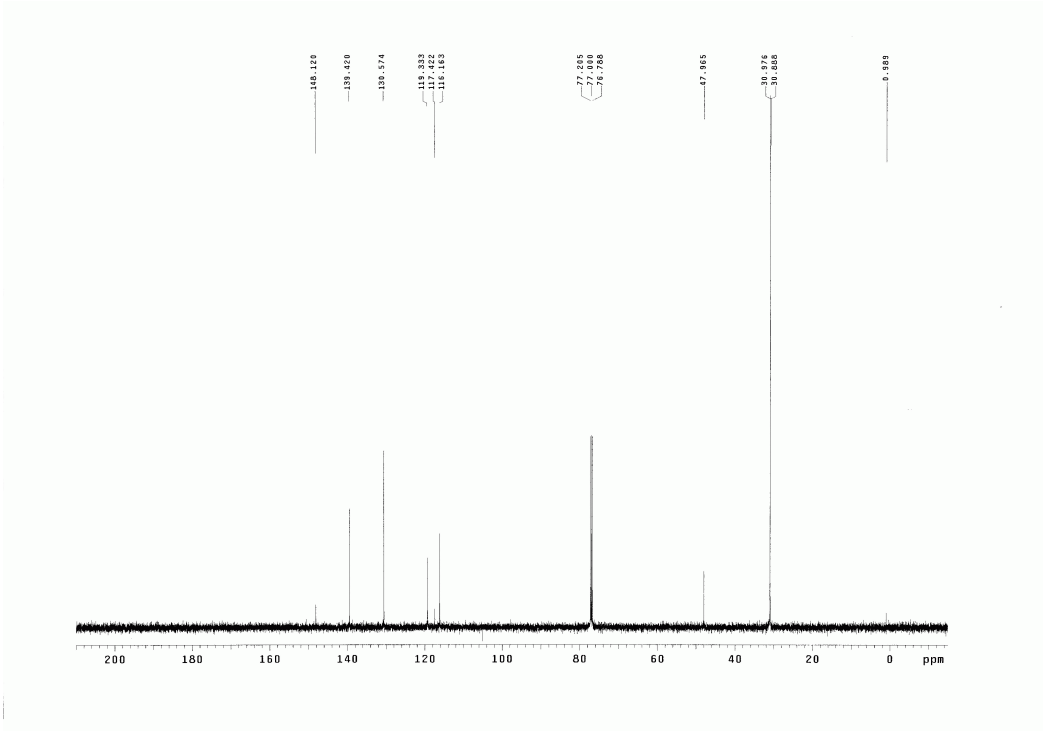




**4-(*tert*-Butylthio)benzaldehyde 5i**

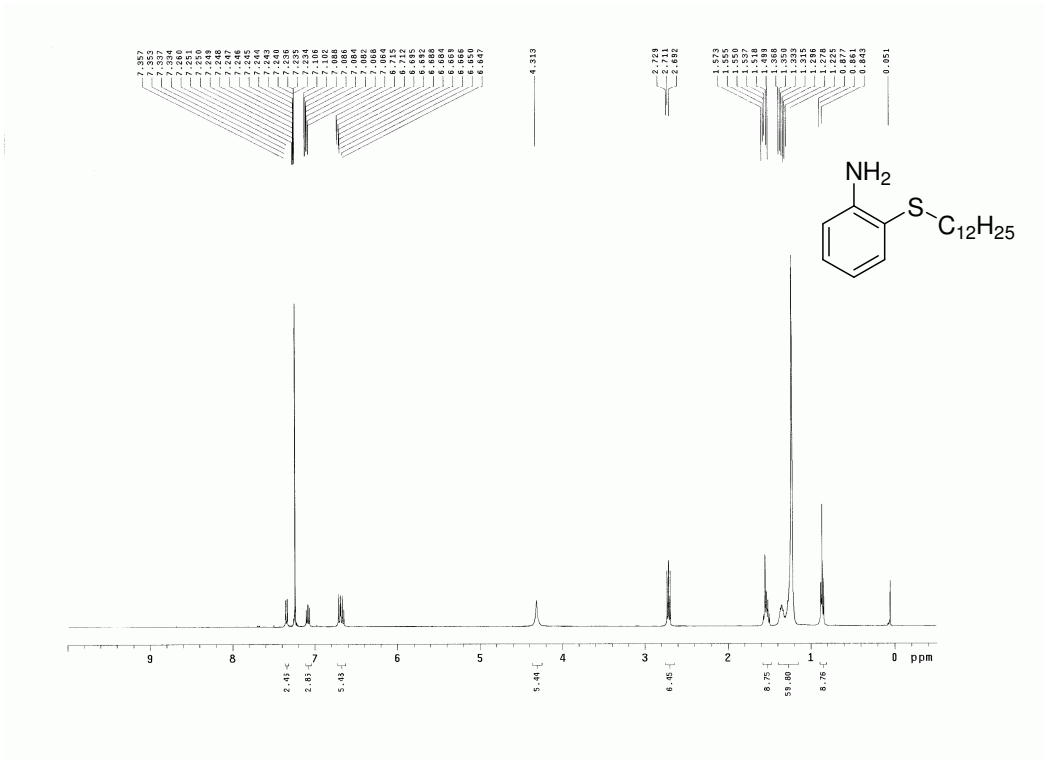


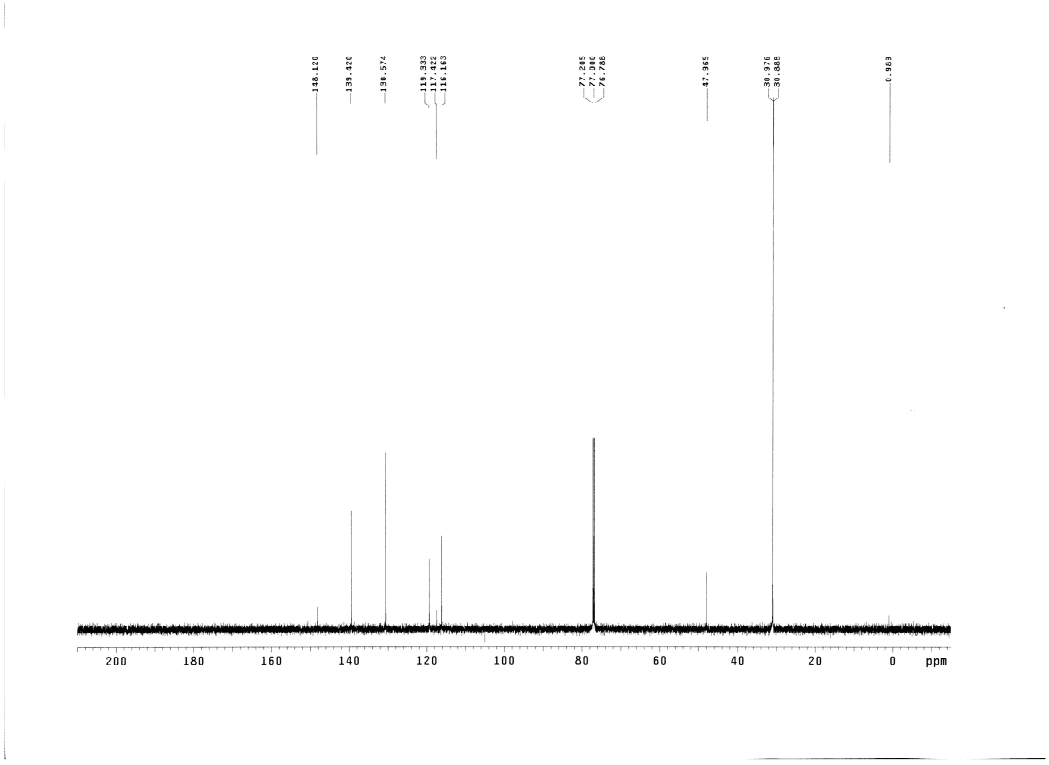

**2-(*tert*-Butylsulfanyl)aniline 5j**



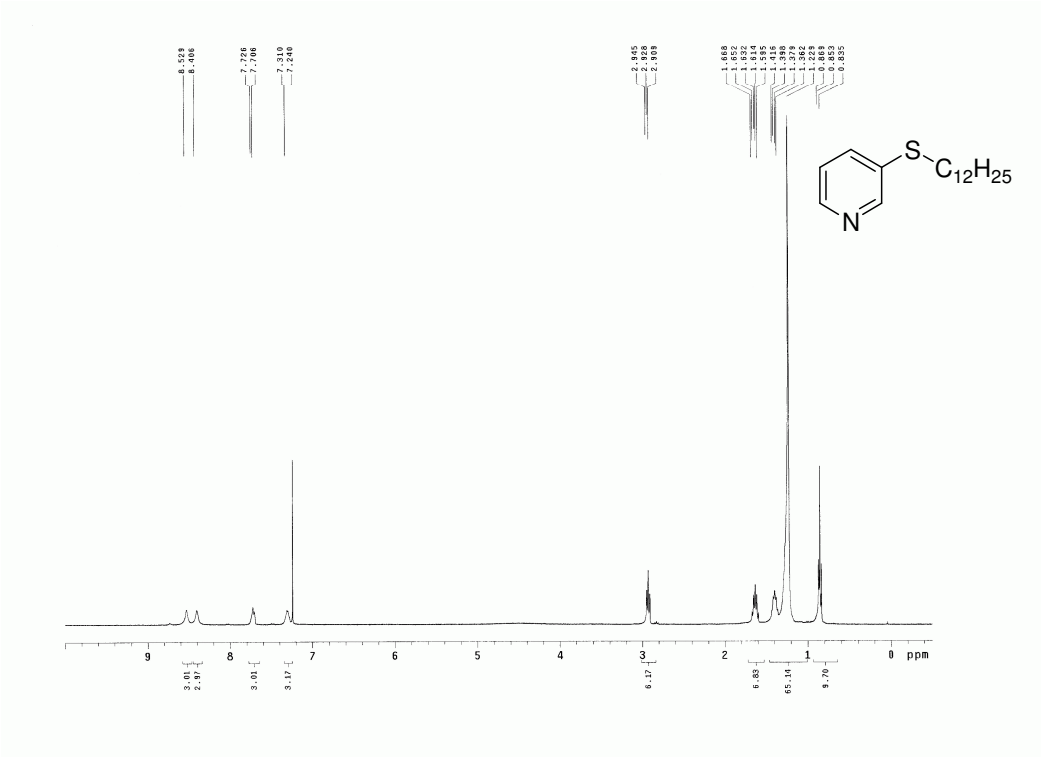



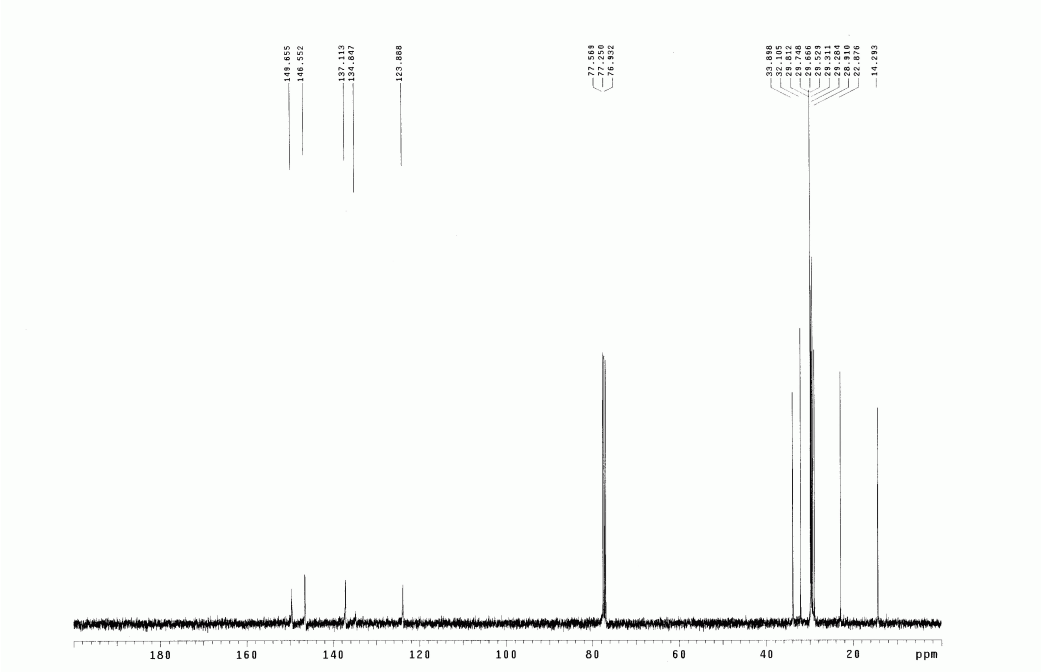

**2-*n*-Dodecanesulfanylaniline 5k**




**3-(Dodecylthio)pyridine 5l**


8.529
8.406
7.726
7.706
7.310
7.240
2.945
2.928
2.909
1.668
1.652
1.633
1.614
1.595
1.445
1.360
1.379
1.362
1.225
0.869
0.853
0.835
S
$C_{12}H_{25}$
N
9
8
7
6
5
4
3
2
1
0 ppm
3.01
2.91
3.01
3.17
6.17
6.83
65.14
9.70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146.552
137.113
134.647
123.888
77.568
77.250
76.932
33.898
32.105
29.812
29.738
29.666
29.523
29.331
29.284
28.910
22.876
14.293
180
160
140
120
100
80
60
40
20
ppm