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Electronic Supplementary Information

Oxidoreductive Coupling of Thiols with Aryl Halides Catalyzed by Copper on Iron

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General

Unless otherwise indicated, all starting materials were obtained from commercial suppliers, and were used without further purification. Analytical thin-layer chromatography (TLC) was performed on Merck DC pre coated TLC plates with 0.25 mm Kieselgel 60 F_{254}. Visualization was performed with a 254 nm UV lamp. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-250 spectrometer in $CDCl_3$. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards (δ 7.26 for ^1H, δ 77.0 for ^{13}C). Coupling constants (*J*) are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), m (multiplet). Combination gas chromatography and low resolution mass spectrometry was obtained on an Agilent 6890N Gas Chromatograph (30 m x 0.25 mm column with 0.25 µm HP-5MS coating, He carrier gas) and Agilent 5973 Mass Spectrometer (Ion source: EI+, 70eV, 230°C; interface: 300°C). IR spectra were obtained on a Bruker IFS55 spectrometer on a single-reflection diamond ATR unit. All melting points were measured on Büchi 501 apparatus and are uncorrected. High-resolution mass spectra were recorded on an Agilent Technologies 6210 Time of Flight mass spectrometer.

The Preparation of Copper on Iron Catalyst

To a round-bottom flask was charged with Iron powder (5 g, 89.5 mmol) and water (deoxygenated with argon) (50 mL). The aqueous solution of $CuSO_4$ (125.6 mg, 0.79 mmol) (50ml) was dropped in the mixture under argon atmosphere over 1h and strirred with KPG-stirrer vigorously for 3 h. The catalyst was separated with magnet and washed with deoxygenated water (5×20 mL) than acetone (3×20 mL) and dried under reduced pressure.

General Procedure for the Catalyst screening

A mixture of iodobenzene (56 µL, 0.5 mmol), thiophenol (51 µL, 0.5 mmol), 5 mol% Cu/Fe (5 wt%) (32 mg, 0.025 mmol Cu), K_2CO_3 (76 mg, 0.55 mmol, 1.1 eq.), and 1-butanol (100 µL) were heated for 5h at 100 ºC. After allowing the mixture to cool to room temperature, the mixture was diluted with ethyl acetate (0.5 mL) than sample was taken and the conversion was determined by GC analysis

Solvent screening

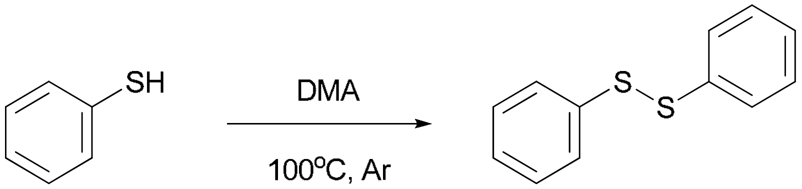
A mixture of iodobenzene (56 µL, 0.5 mmol), thiophenol (51 µL, 0.5 mmol), 5 mol% Cu/Fe (1 wt%) (156 mg, 0.025 mmol Cu), base (1.1 eq.), and the solvent (500 µL) were heated at 100 ºC. After 0.5; 1; 2; 3; 4; 6; 8 and 12 hour samples were taken and the conversions were determined by GC analysis

Cu on Fe catalyst recycling

A mixture of iodobenzene (56 µL, 0.5 mmol), thiophenol (51 µL, 0.5 mmol), 5 mol% Cu/Fe (1 wt%) (156 mg, 0.025 mmol Cu), base (1.1 eq.), and DMA (100 µL) were heated at 100 ºC. After 8 h reaction mixture was cooled, the catalyst was separated with magnet and washed with ethyl acetate (2×5 mL) water (2×5 mL) and acetone (3×5 mL), dried under vacuum and was reused.

Entry	Cu/Fe	conversion[%]
1	1st run	100
2	2nd run	100
3	3rd run	100
4	4th run	98
5	5th run	80

Study of disulfide formation[a]



Entry	K_2CO_3 (eq.)	(mol%) Cu/Fe (5wt%)	Time (min)	Conversion[b] (%)
1	-	-	1	55
2	-	-	30	55
3	1.1	-	1	63
4	1.1	-	30	61
5	-	5	1	65
6	-	5	30	69
7	1.1	5	1	70
8	1.1	5	30	65

[a] Reaction conditions: 0.5 mmol thiophenol, 500µl DMA

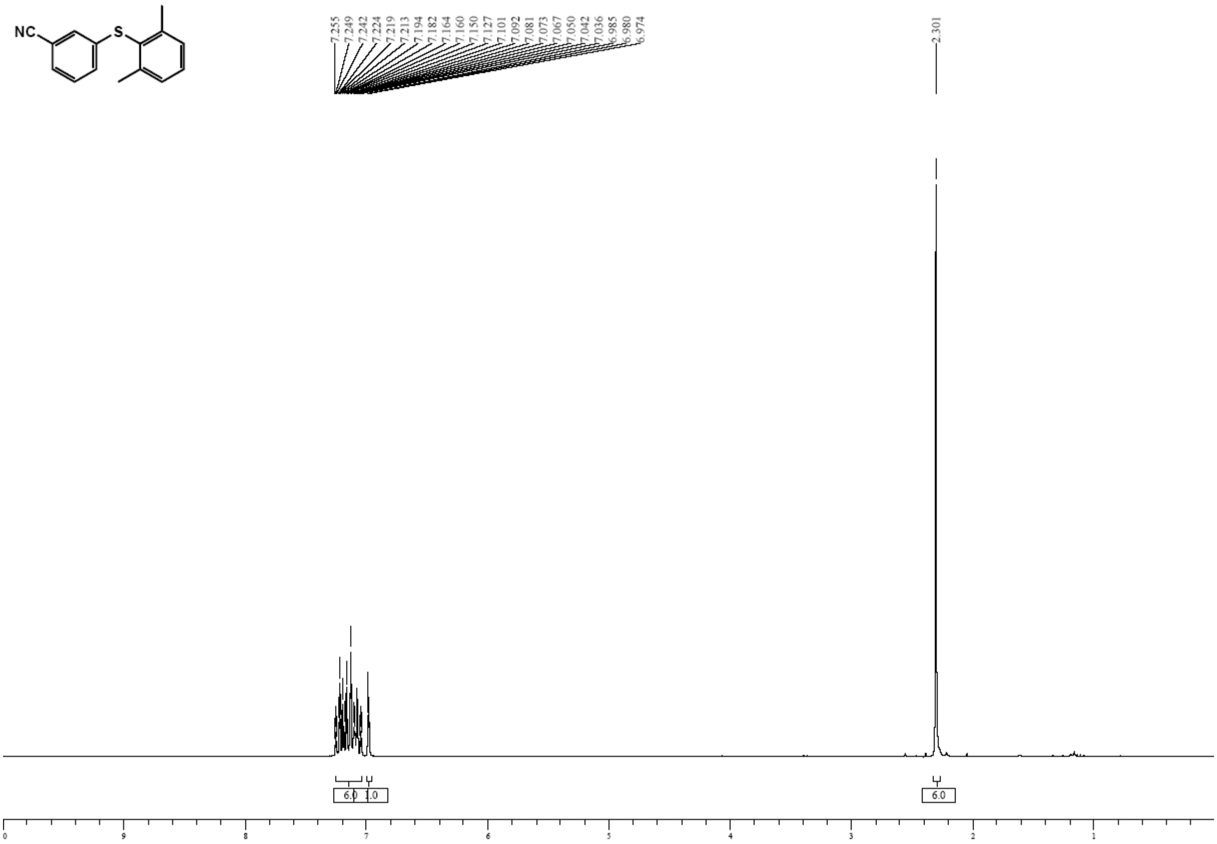
[b] 2*disulfide/(2*disulfide+thiophenol) ratio, determined by GC.

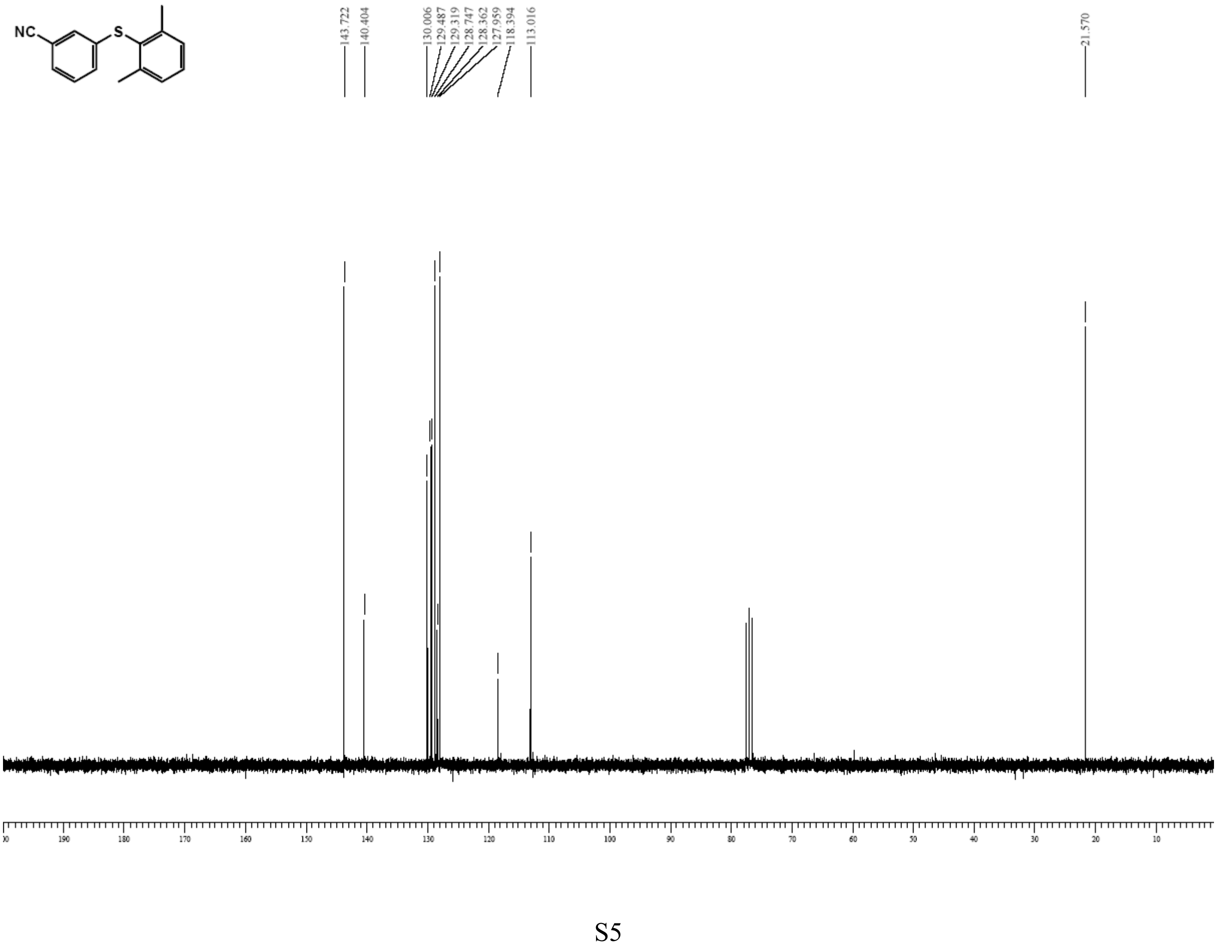
General Procedure for the Synthesis of Sulfides

A mixture of aryl halide (0.5 mmol, 1 eq.), thiol (0.5 mmol, 1 eq.), 5 mol% Cu/Fe (5 wt%) (32 mg, 0.025 mmol Cu), K_2CO_3 (76 mg, 0.55 mmol, 1.1 eq), and DMA (100 μL) were heated for 8-48h at 100ºC. After allowing the mixture to cool to room temperature, the mixture was diluted with ethyl acetate (5 mL). The catalyst was separated with magnet and washed with ethyl acetate (2×5 mL) and with water (2×5 mL). The organic phase was separated and dried with Na_2SO_4, filtered, and the solvent was removed under vacuum, and the residue was purified by chromatography on silica gel to give desired aryl sulfide.

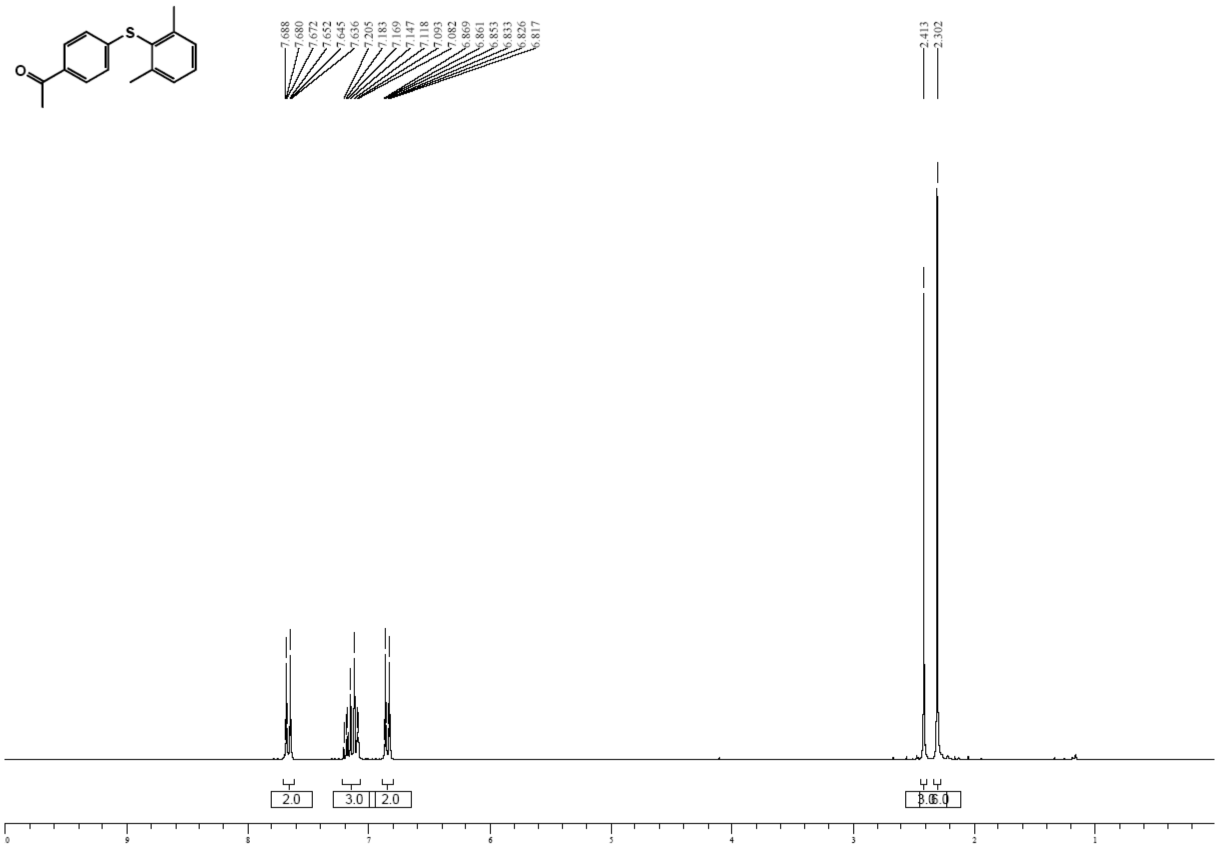
NMR spectra of the new compounds

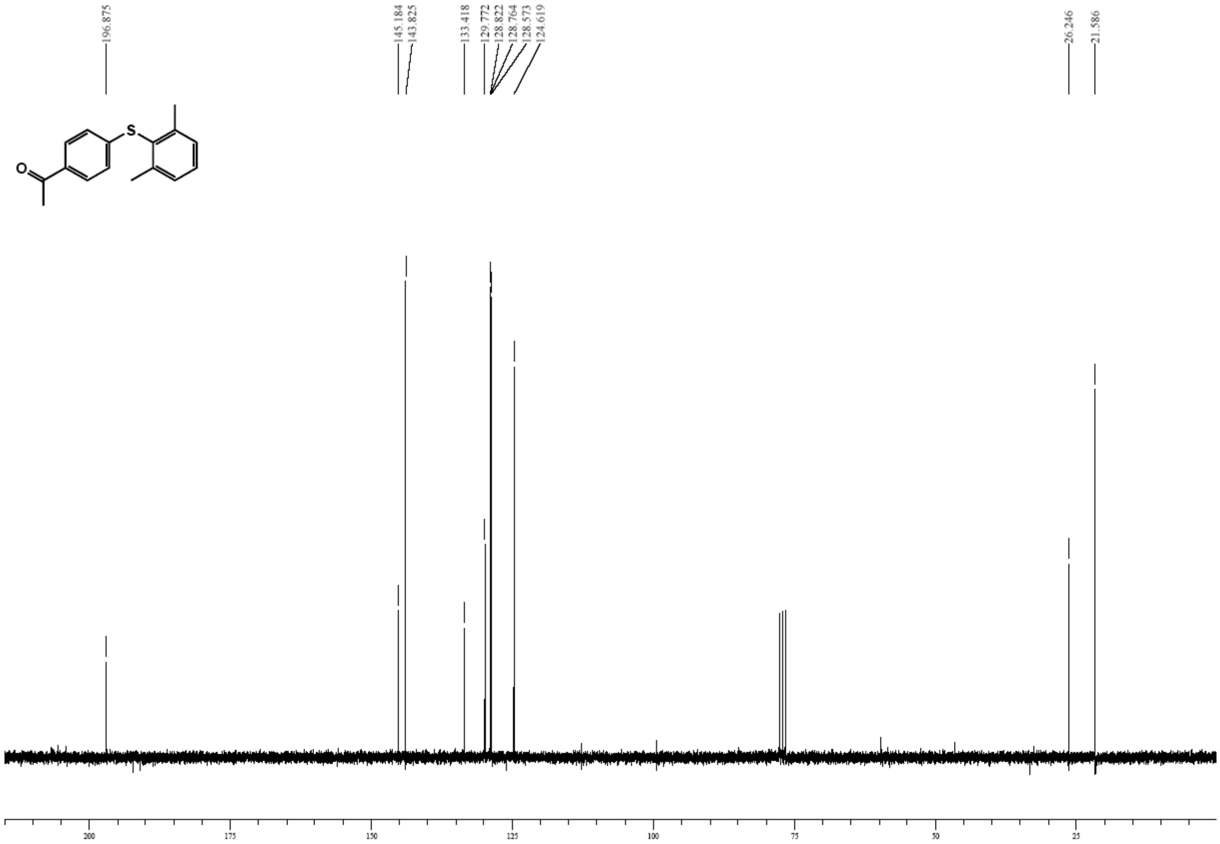
3-(2,6-diMethylphenylthio)benzonitrile (3k)



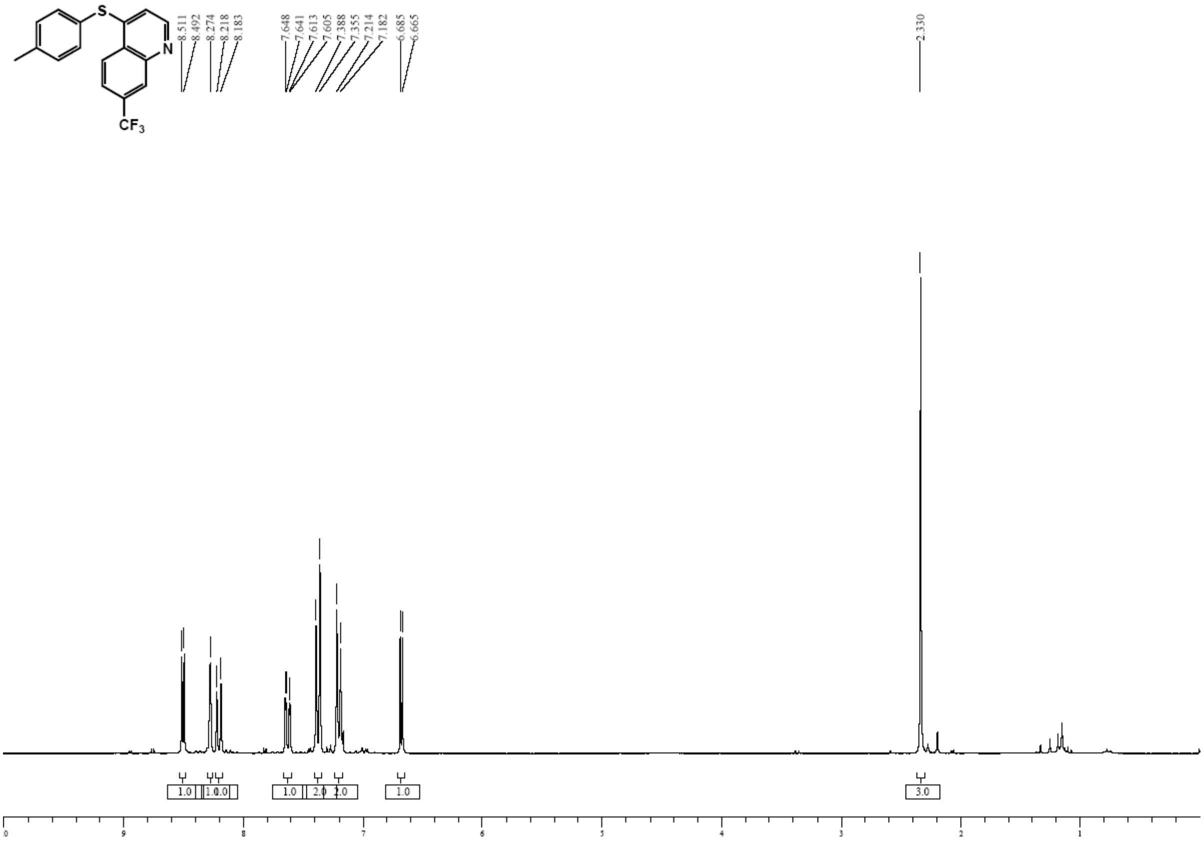


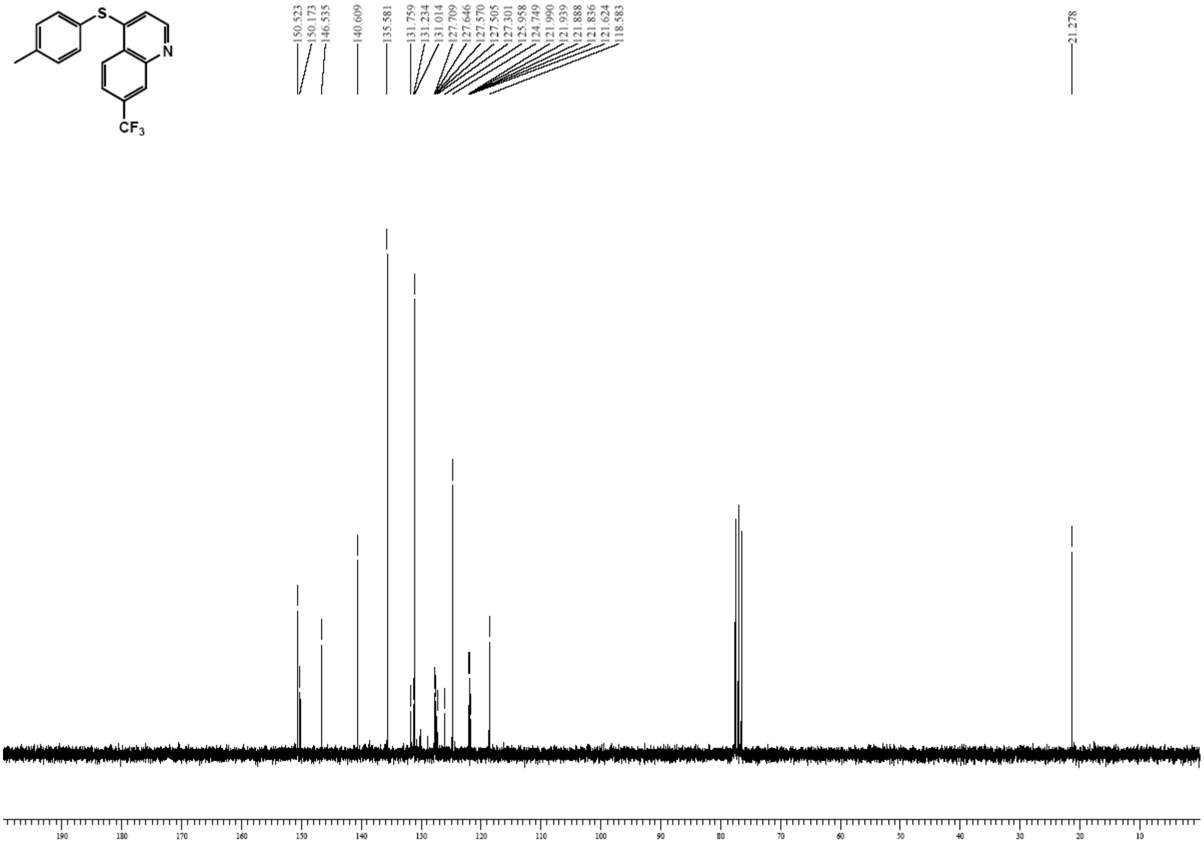
4-(2,6-diMethylphenylthio)benzophenone (3l)



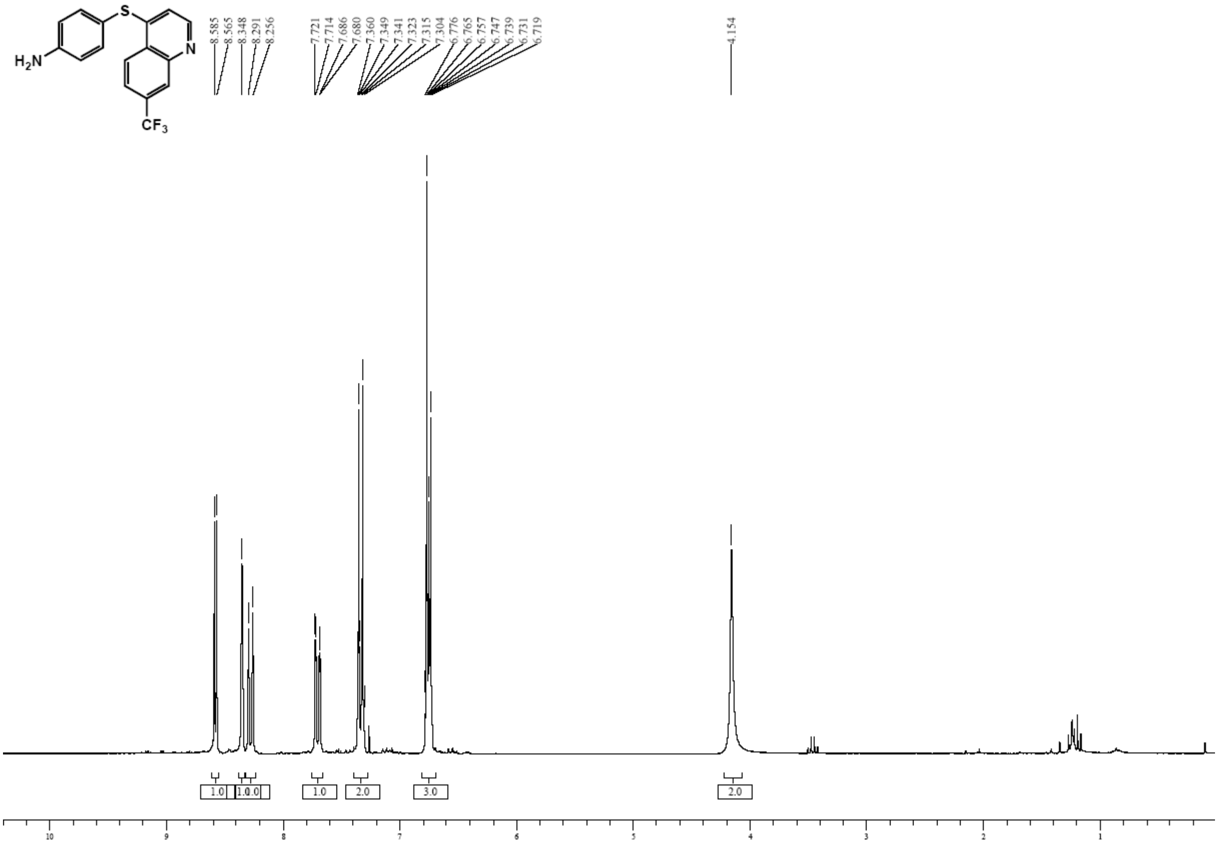


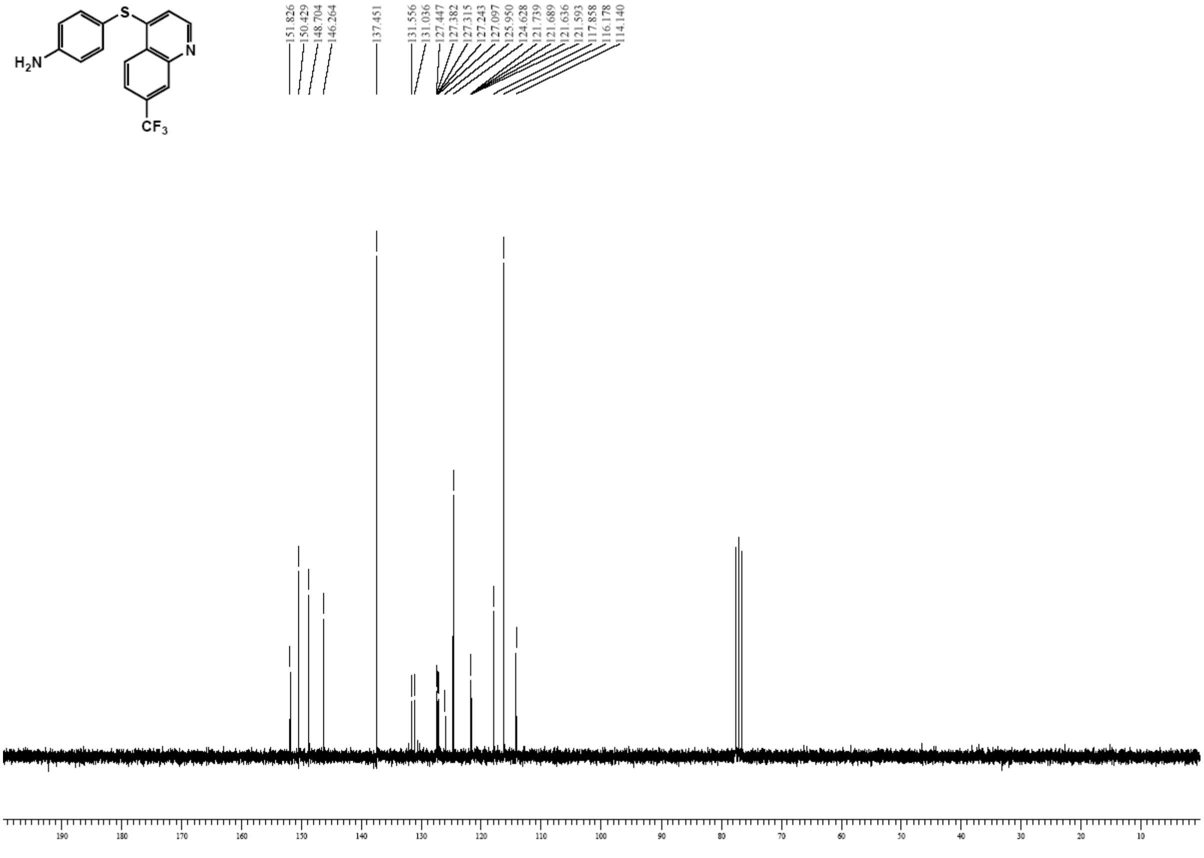
4-(4-Methylphenylthio)-7-(trifluoromethyl)quinoline (3p)



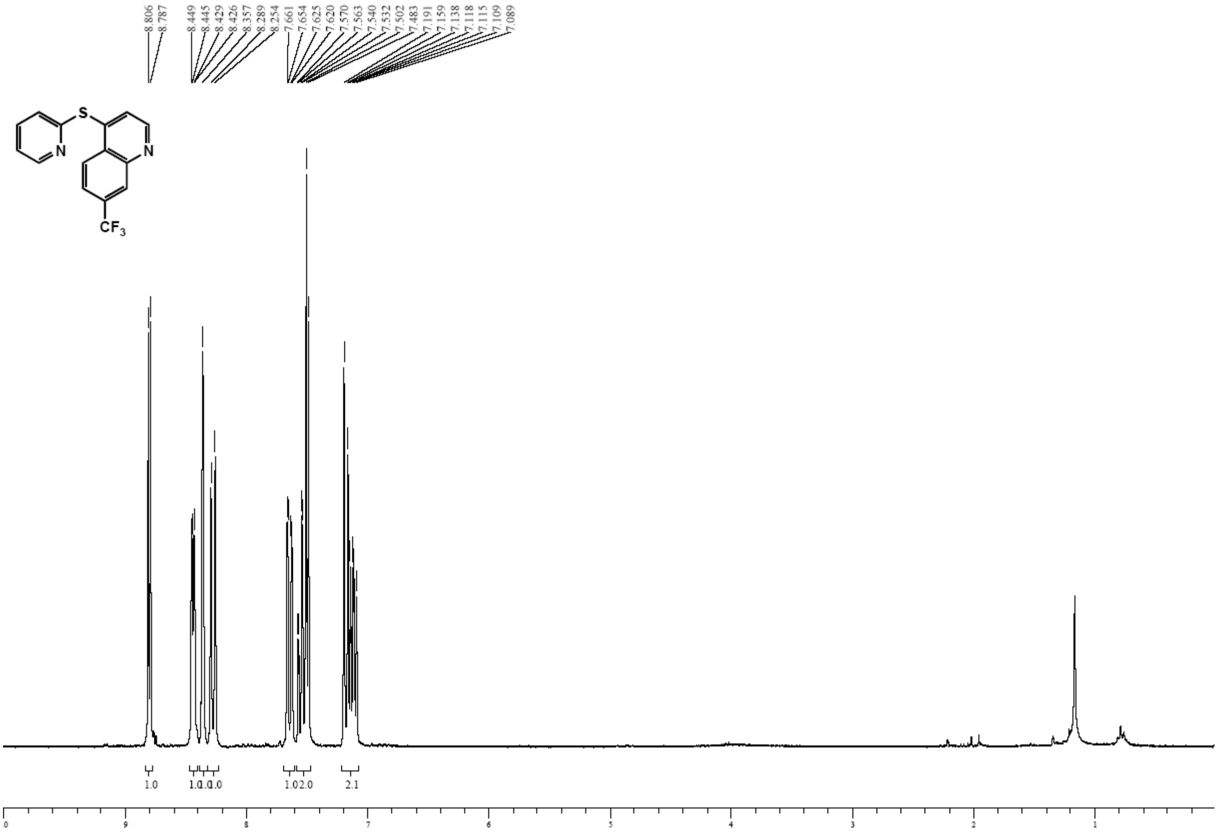


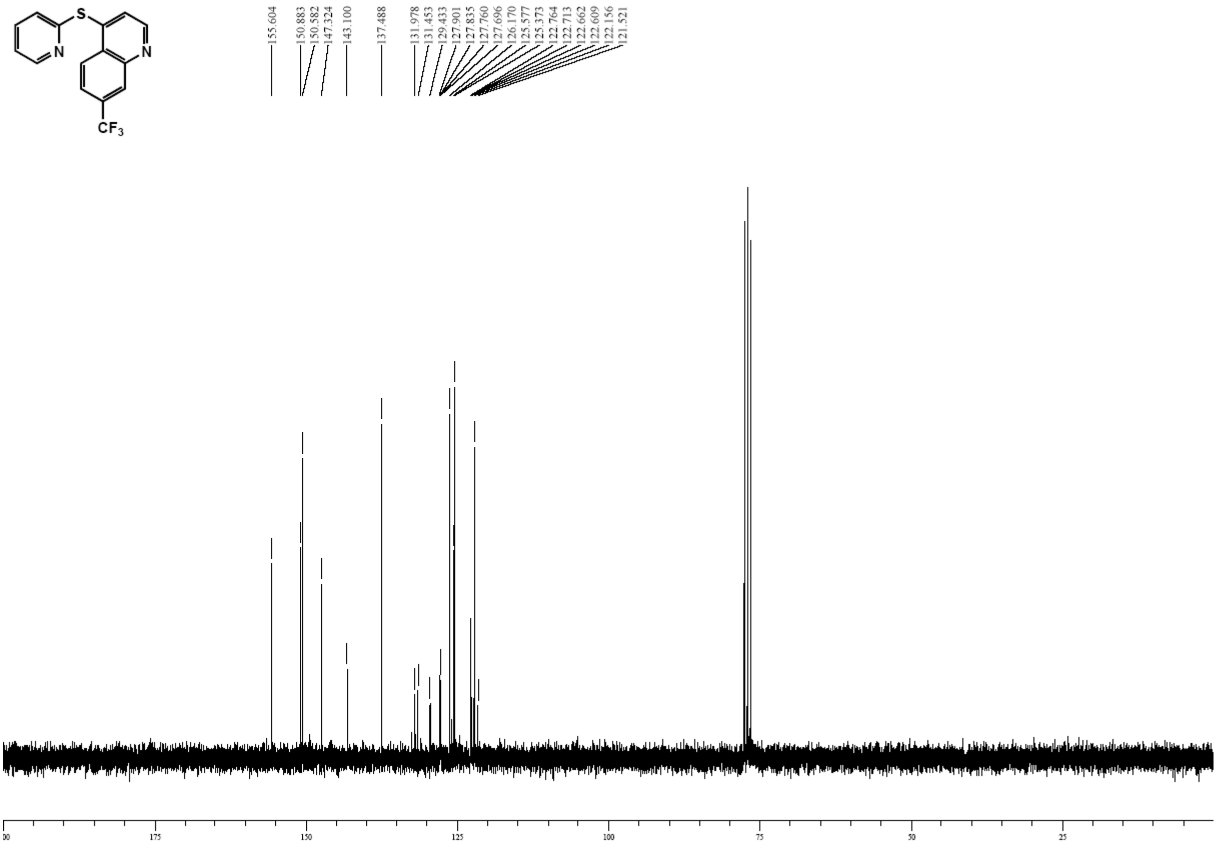
4-(4-Aminolphenylthio)-7-(trifluoromethyl)quinoline (3q)



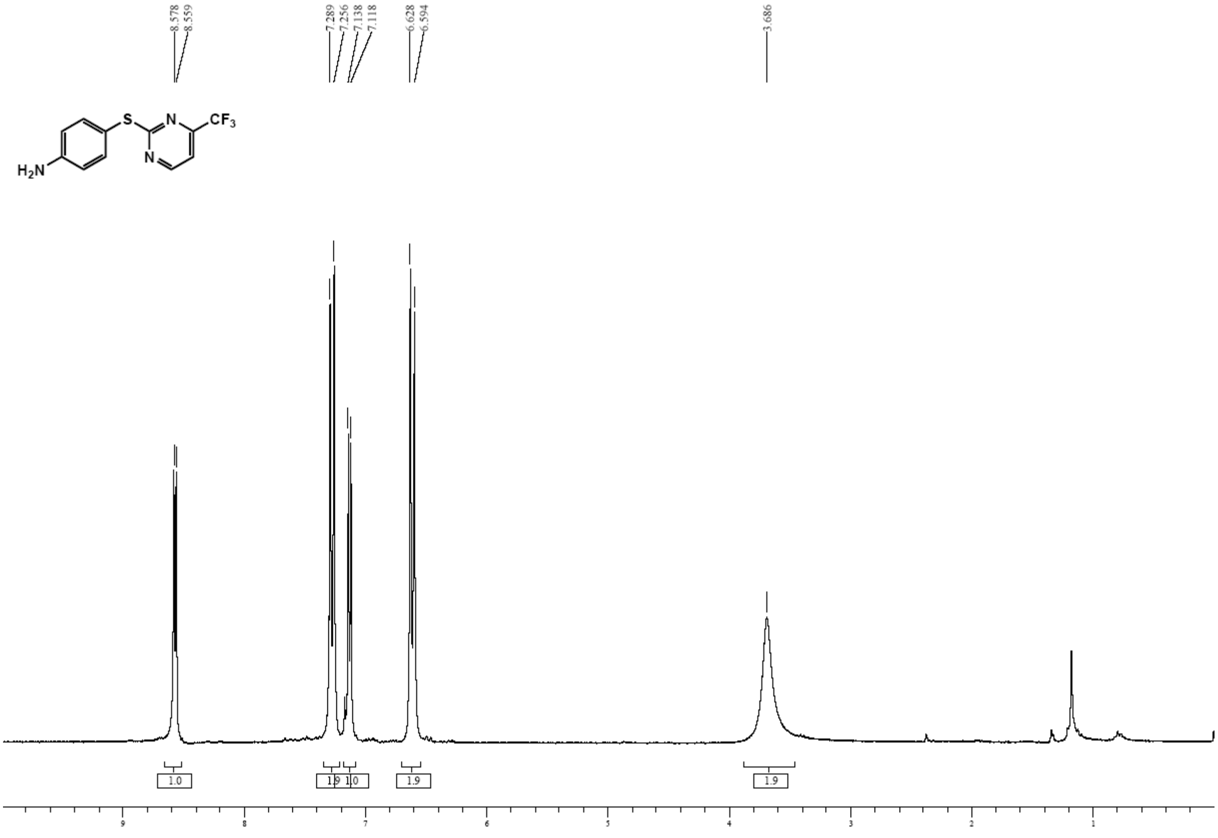


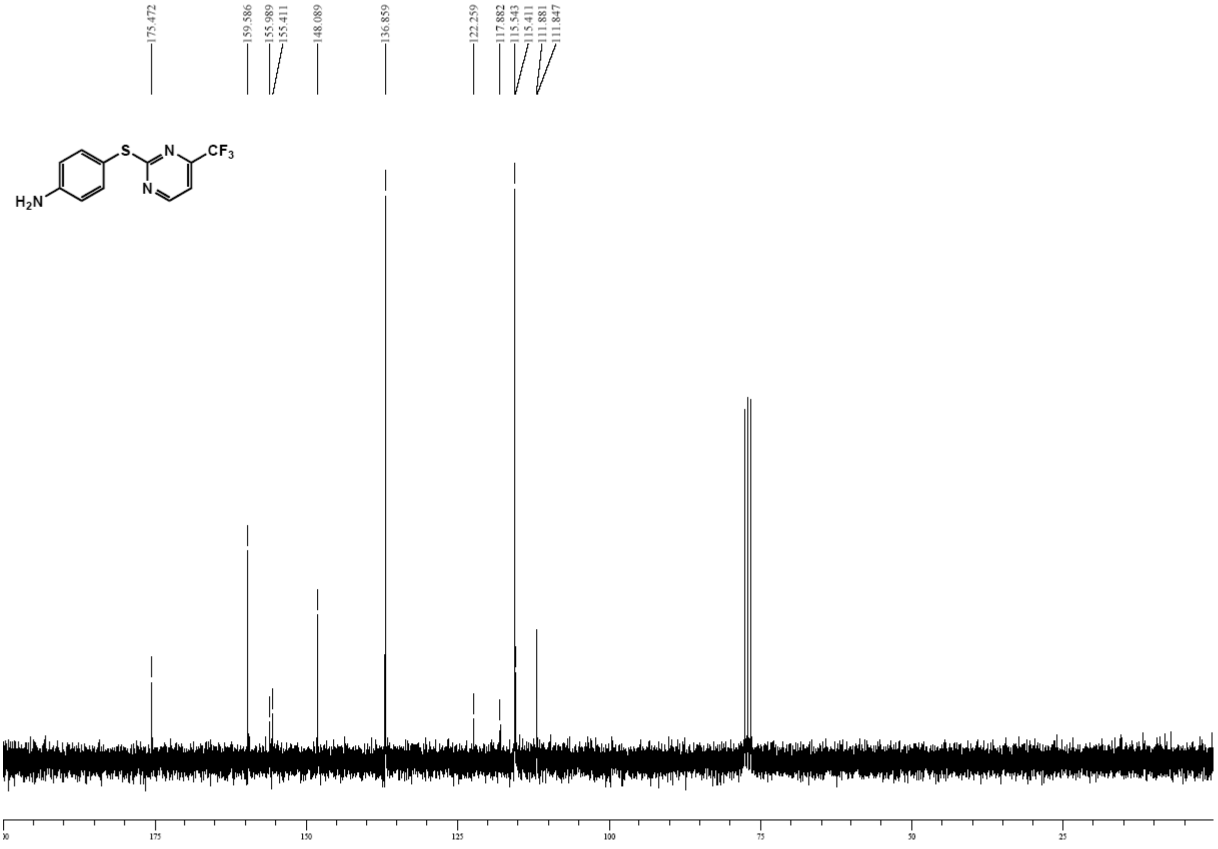
4-(2-pyridylthio)-7-(trifluoromethyl)quinoline (3r)





2-(4-Aminolphenylthio)-4-(trifluoromethyl)pyrimidine (3s)





2-(2-pyridylthio)-4-(trifluoromethyl)pyrimidine (3t)