Supplementary Information

Formic acid-promoted hydrodeoxygenation reactions over by carbon encapsulated Co nanoparticles

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Experimental

Materials

$Co(NO_3)_2·6H_2O$, 1,4-benzenedicarboxylic acid (H_2BDC), dicyandiamide and all substrates were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). All of the solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Vulcan XC-72 carbon black was purchased from Cabot Corp. (USA). All of the chemicals were directly used as received.

Catalyst preparation

Firstly, 223.1 mg of $Co(NO_3)_2·6H_2O$ was dissolved in 7.5 mL of *N,N*-dimethyl formamide (DMF) to form a transparent solution, followed by the addition of 7.5 mL of DMF containing 382 mg of H_2BDC. The mixture was refluxed at 120 °C for 30 min, and then 0.6 g of Vulcan XC-72 carbon black and 7.5 mL of DMF were added. The mixture was further refluxed for 4-5 h at 120 °C, and then the solvent was evaporated off. The as-obtained black powder was grinded with 4 g of dicyandiamide, and then the composite was subjected to be pyrolyzed at 800 °C under N_2 for 2 h. The as-prepared black powder was treated by H_2SO_4 (1 M) at 80 °C overnight to remove the loosely bonded Co nanoparticles. Then, the obtained catalyst was collected by centrifugation, washed with deionized water, and dried under vacuum. The as-prepared catalyst was abbreviated as Co@NC-800.The NC-800 catalyst was prepared following the same procedure of Co@NC-800 catalyst without the addition of $Co(NO_3)_2·6H_2O$. The Co@C-800 catalyst was prepared following the same procedure of Co@NC-800 catalyst without the addition of dicyandiamide. The Co-MOF catalyst was prepared following the same procedure of Co@NC-800 catalyst without the addition of Vulcan XC-72 carbon black.

Catalyst characterization

TEM images of the samples were performed on an FEI Talos F200X instrument. The sample was firstly dispersed in ethanol and dropped onto copper grids for observation. XRD patterns of the catalysts were collected on a Bruker D8 Advance powder diffractometer (Cu K_α). All XRD patterns were collected in the 2θ range of 10–80° with a scanning rate of 0.016 °/s. XPS was conducted on a Thermo Scientific ESCALAB Xi+ spectrometer with a monochromatized Al K_α source (1486.6 eV).

General procedure of the hydrodeoxygenation of sulfoxides

0.25 mmol of the sulfoxide, 1 mmol of formic acid and 30 mg of Co@NC-800 were charged into a 50 mL stainless steel autoclave and then 10 mL of solvent was added. The autoclave was sealed, flushed with nitrogen for 30 min and then pressurized with 10 bar nitrogen. The autoclave was heated from room temperature to 100 °C within a few minutes, and then the reaction was performed for a certain time under the stirring speed of 1000 RPM. After reaction, the autoclave was cooled down to room temperature. The catalyst was filtered and washed thoroughly with ethanol. The clear liquid reaction solution was analyzed by gas chromatography (GC). The products were confirmed by nuclear magnetic resonance (NMR) technologies. To isolate these products, the reaction mixture was first concentrated under reduced pressure and then purified by silica gel chromatography eluting using hexane and dichloromethane (hexane/ethyl acetate = 4/1) as the eluent. The structures of the purified products were characterized by ^{1}H NMR.

Analytic methods

Products was analyzed on an Agilent 7890A GC instrument with a cross-linked capillary DB-5 column (30 m × 250 μm × 0.25 μm) equipped with a flame ionization detector (FID). N_2 was used as the carrier gas with a flow rate of 2 mL·min^{-1}. Standard analysis conditions were described as follows: injector temperature 280 °C, detector

temperature 300 °C, column temperature program: from 50 °C (hold for 1.5 min) to 250 °C (hold for 3 min) at a heating rate of 10 °C·min^{-1}. The content of each compound was determined based on the internal standard method.

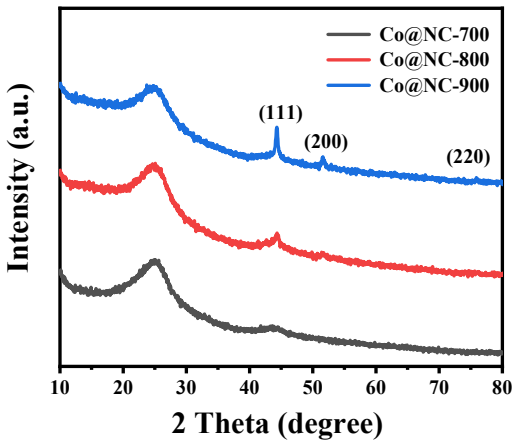


Fig. S1 XRD patterns of the Co@NC-T catalysts.

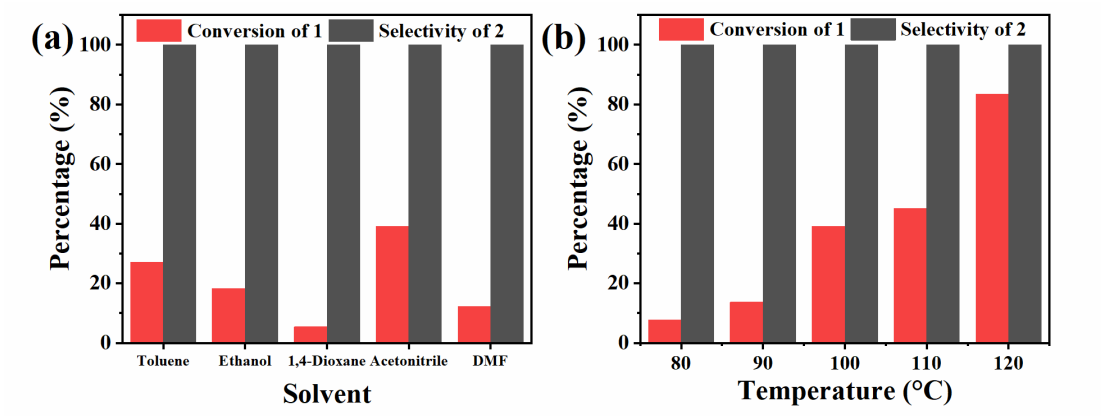


Fig. S2 Optimization of reaction conditions by using different (a) solvents and (b) temperatures. Reaction conditions: diphenyl sulfoxide (0.25 mmol), formic acid (1 mmol), Co@NC-800 catalyst (30 mg), solvent (10 mL), N_2 (10 bar), and 4 h..

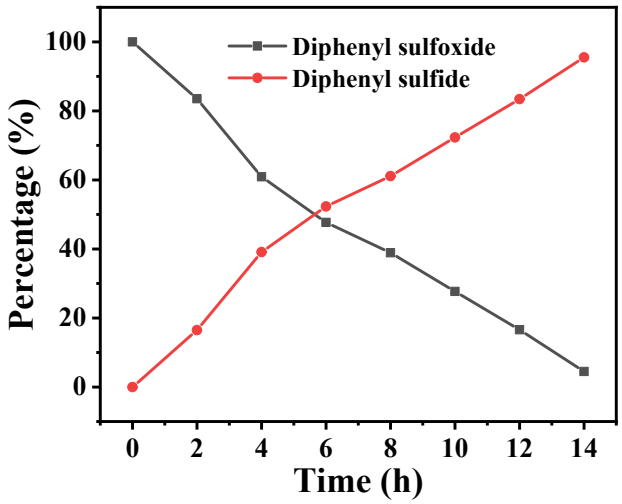


Fig. S3 Time dependent course for the catalytic transfer hydrodeoxygenation of diphenyl sulfoxide. Reaction conditions: diphenyl sulfoxide (0.25 mmol), formic acid (1 mmol), Co@NC-800 (30 mg), solvent (10 mL), N_2 (10 bar), 100 °C and 0-14 h.

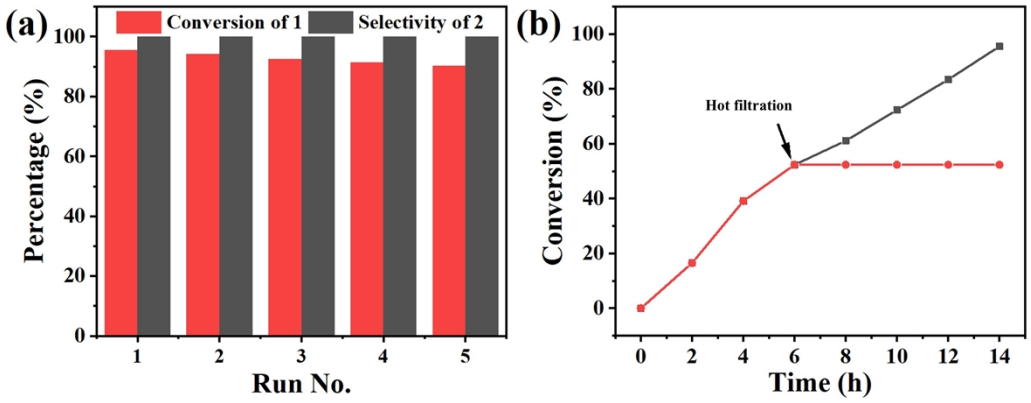
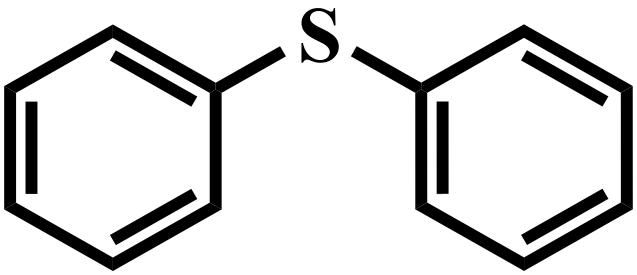


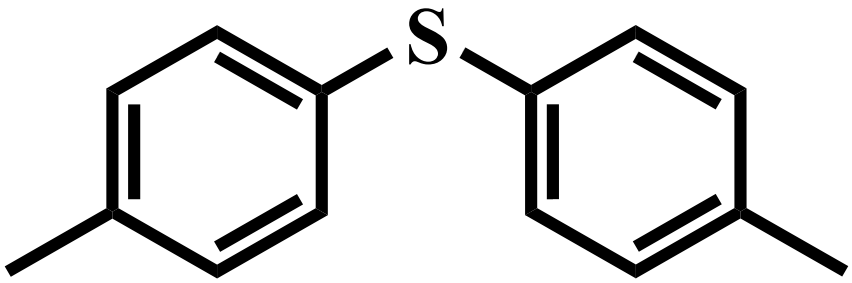
Fig. S4 (a) Catalyst recycling and (b) hot filtration test for the catalyst Co@NC-800 catalyst for the catalytic transfer hydrodeoxygenation of sulfoxide to sulfide. Reaction conditions: diphenyl sulfoxide (0.25 mmol), formic acid (1 mmol), Co@NC-800 (30 mg), acetonitrile (10 mL), N_2 (10 bar), 100 °C and 14 h.

Diphenyl sulfide



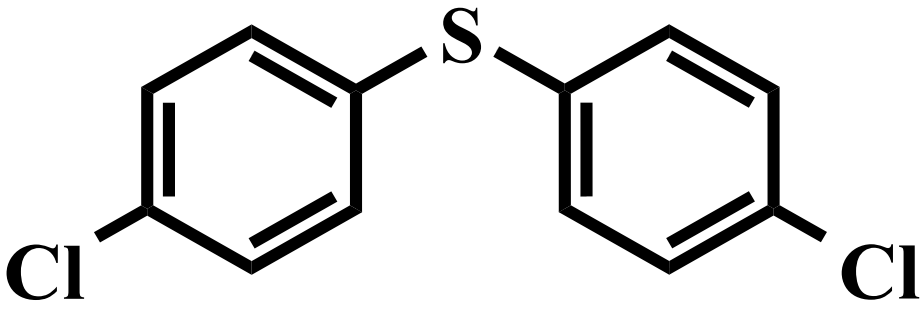
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 4H), 7.34 (ddd, *J* = 7.7, 6.8, 1.2 Hz, 4H), 7.30 – 7.26 (m, 2H).

Di-p-tolyl sulphide



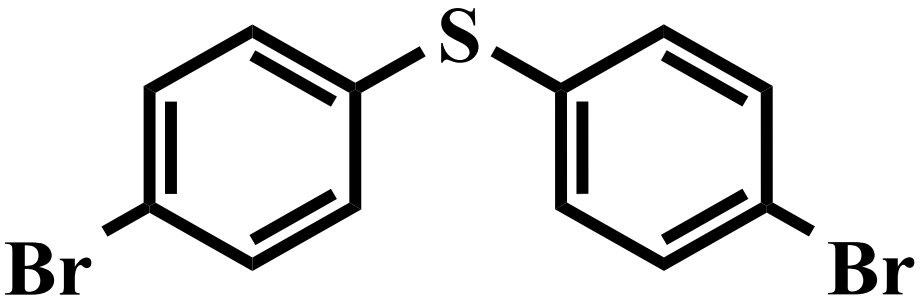
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.2 Hz, 4H), 7.11 (d, *J* = 7.9 Hz, 4H), 2.33 (s, 6H).

4,4'-Dichloro diphenyl sulfide



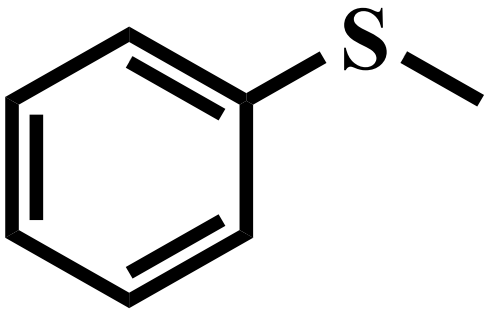
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 – 7.23 (m, 4H), 7.23 – 7.21 (m, 4H).

Bis(4-bromophenyl) sulphide



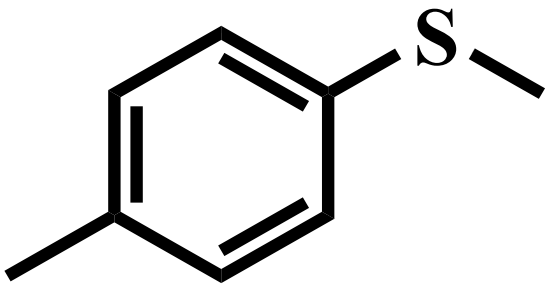
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 – 7.40 (m, 4H), 7.22 – 7.16 (m, 4H).

Thioanisole



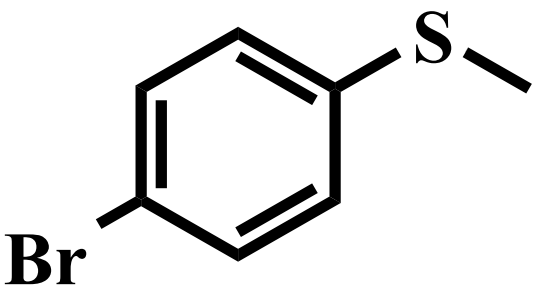
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 4H), 7.15 (tt, *J* = 7.2, 1.7 Hz, 1H), 2.50 (s, 3H).

(4-Methylthio)toluene



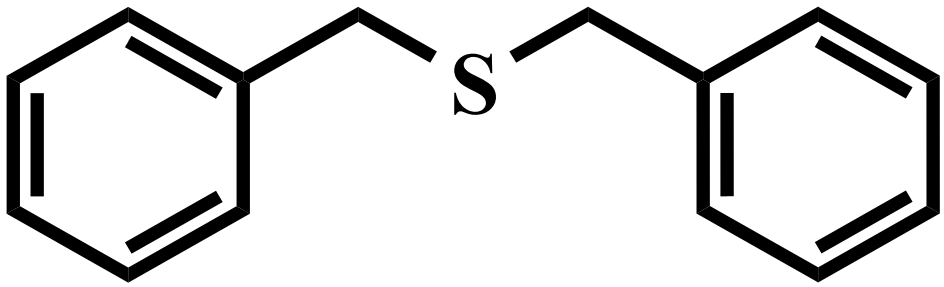
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.48 (s, 3H), 2.34 (s, 3H).

4-Bromothioanisole



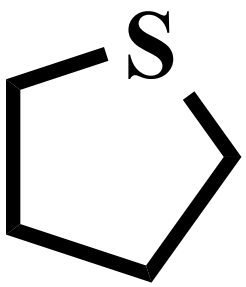
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.13 – 7.09 (m, 2H), 2.46 (s, 3H).

Dibenzyl sulphide



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 – 7.20 (m, 8H), 7.18 (tt, *J* = 6.3, 1.7 Hz, 2H), 3.53 (s, 4H).

Tetrahydrothiophene



^{1}H NMR (600 MHz, Chloroform-*d*) δ 2.85 – 2.78 (m, 4H), 1.95 – 1.88 (m, 4H).

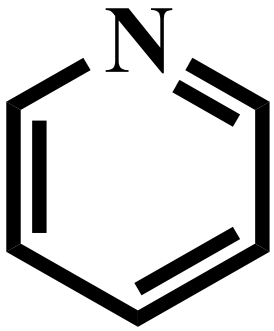
Dibutyl sulfide

^{1}H NMR (600 MHz, Chloroform-*d*) δ 2.53 – 2.47 (m, 4H), 1.55 (p, *J* = 7.4 Hz, 4H), 1.39 (h, *J* = 7.4 Hz, 4H), 0.90 (t, *J* = 7.4 Hz, 6H).

Dodecyl methyl sulfide

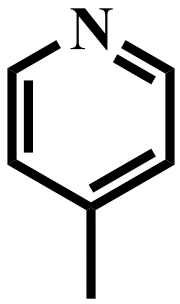
^{1}H NMR (600 MHz, Chloroform-*d*) δ 2.50 – 2.45 (m, 2H), 2.08 (s, 3H), 1.58 (tt, *J* = 8.9, 6.5 Hz, 2H), 1.39 – 1.32 (m, 2H), 1.26 (d, *J* = 9.1 Hz, 16H), 0.87 (t, *J* = 7.0 Hz, 3H).

Pyridine



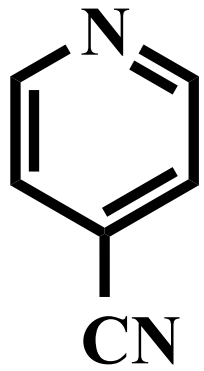
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 – 8.55 (m, 2H), 7.63 (tt, *J* = 7.6, 1.8 Hz, 1H), 7.24 (ddd, *J* = 7.6, 4.3, 1.5 Hz, 2H).

4-Methylpyridine



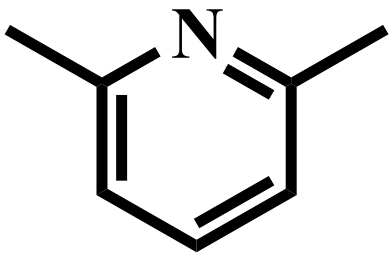
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 – 8.37 (m, 2H), 7.11 – 7.02 (m, 2H), 2.31 (s, 3H).

4-Cyanopyridine



^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 – 8.77 (m, 2H), 7.52 (dt, *J* = 4.3, 1.1 Hz, 2H).

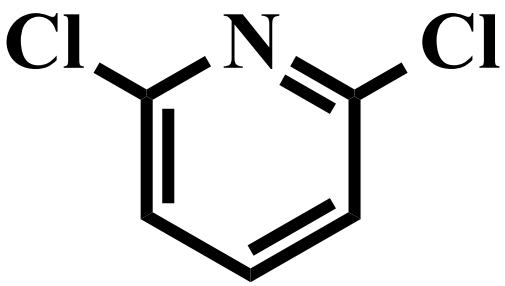
2,6-Lutidine



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 2H), 2.50

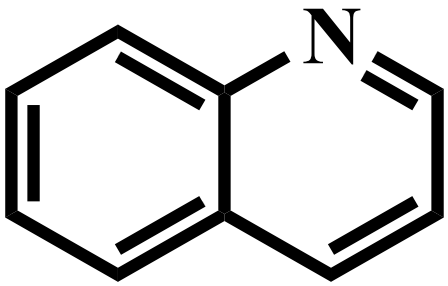
(s, 6H).

2,6-Dichloropyridine

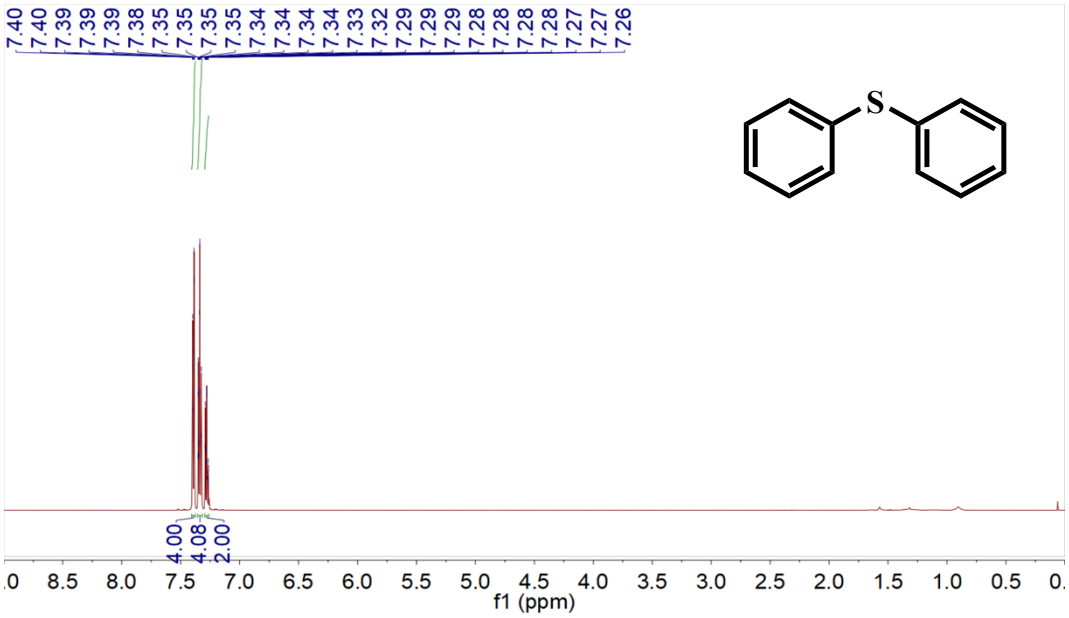


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (t, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 2H).

Quinoline



^{1}H NMR (600 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.16 – 8.06 (m, 2H), 7.79 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.8, 1.1 Hz, 1H), 7.36 (dd, *J* = 8.2, 4.2 Hz, 1H).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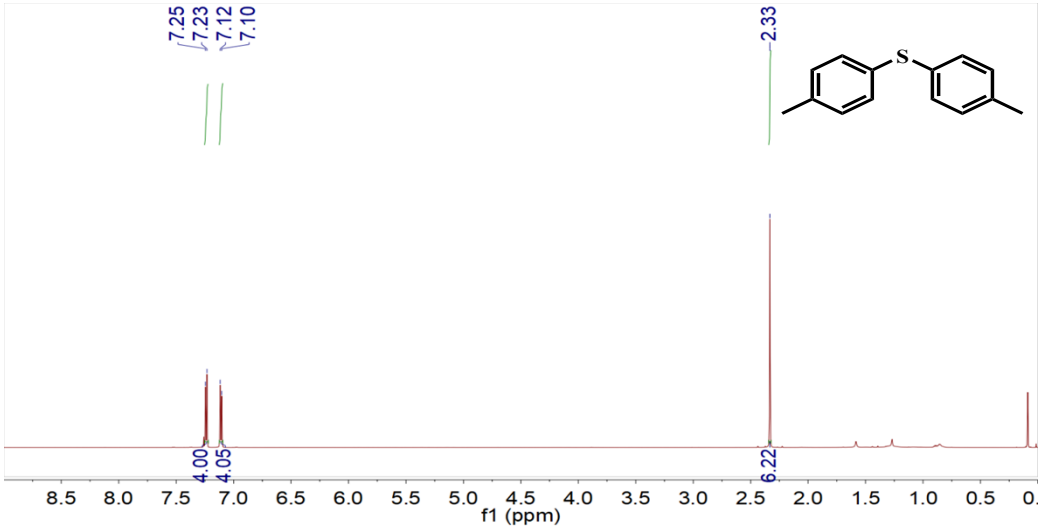
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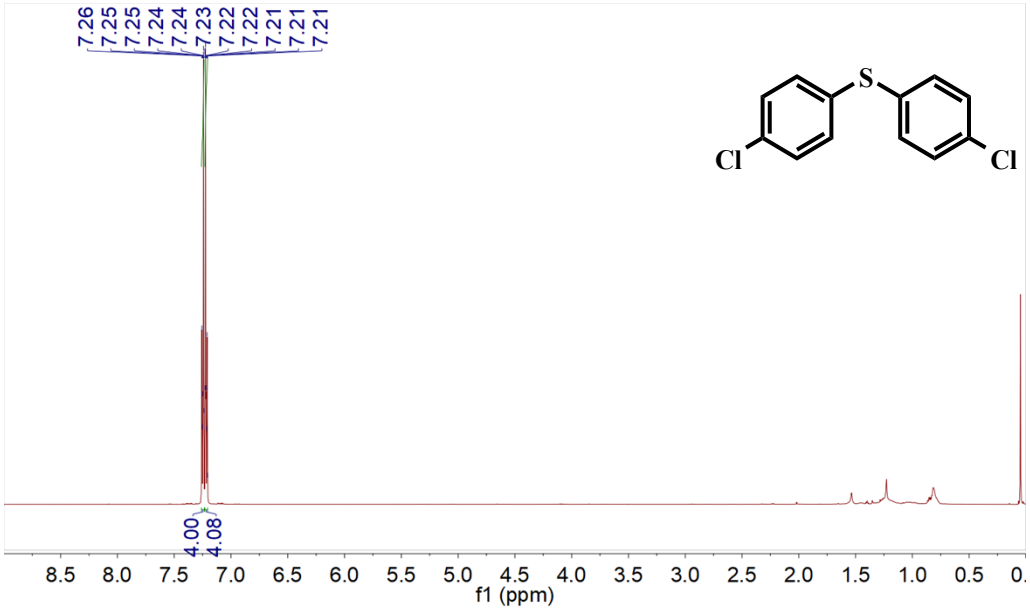
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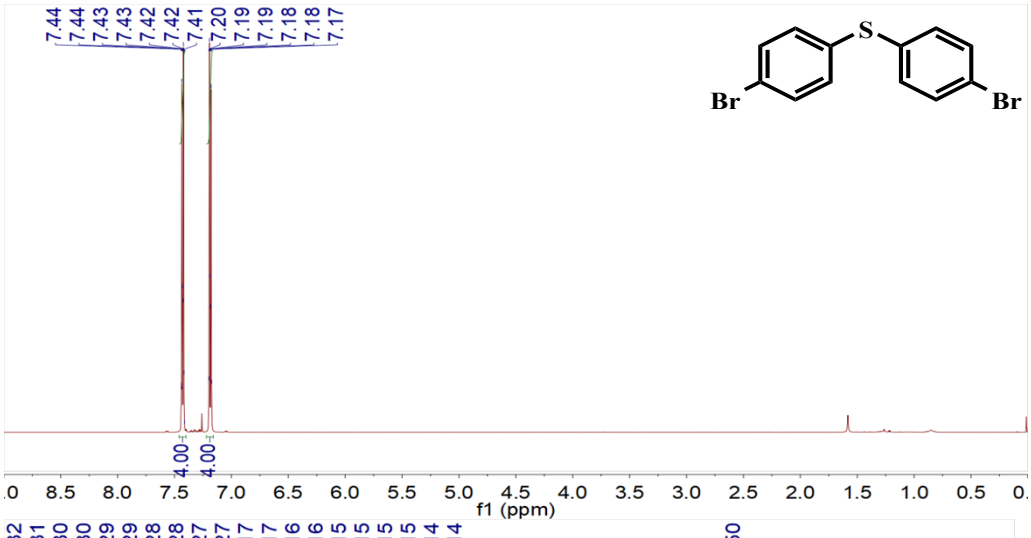
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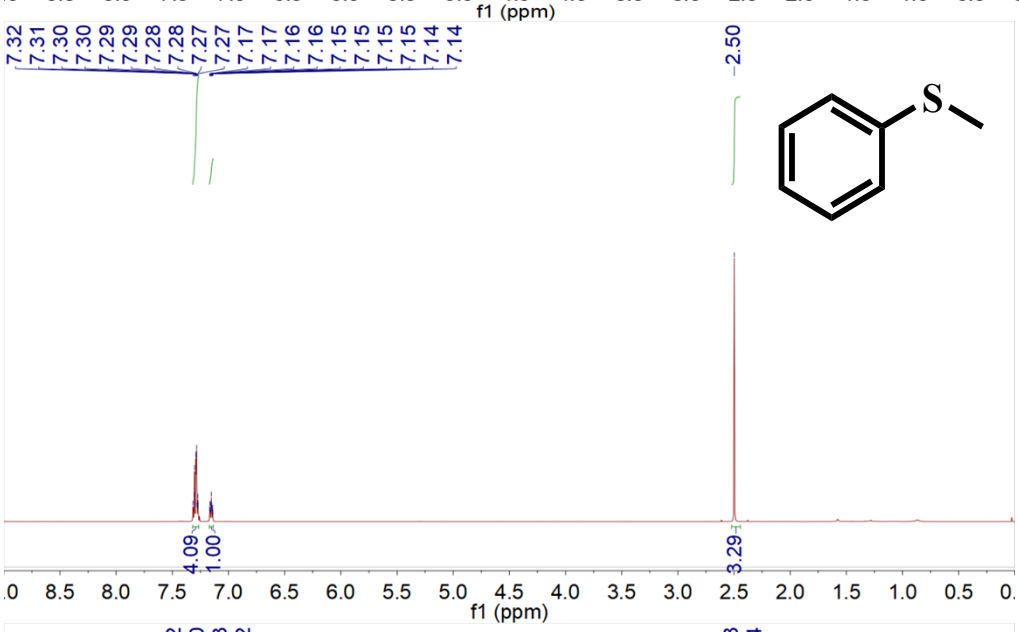
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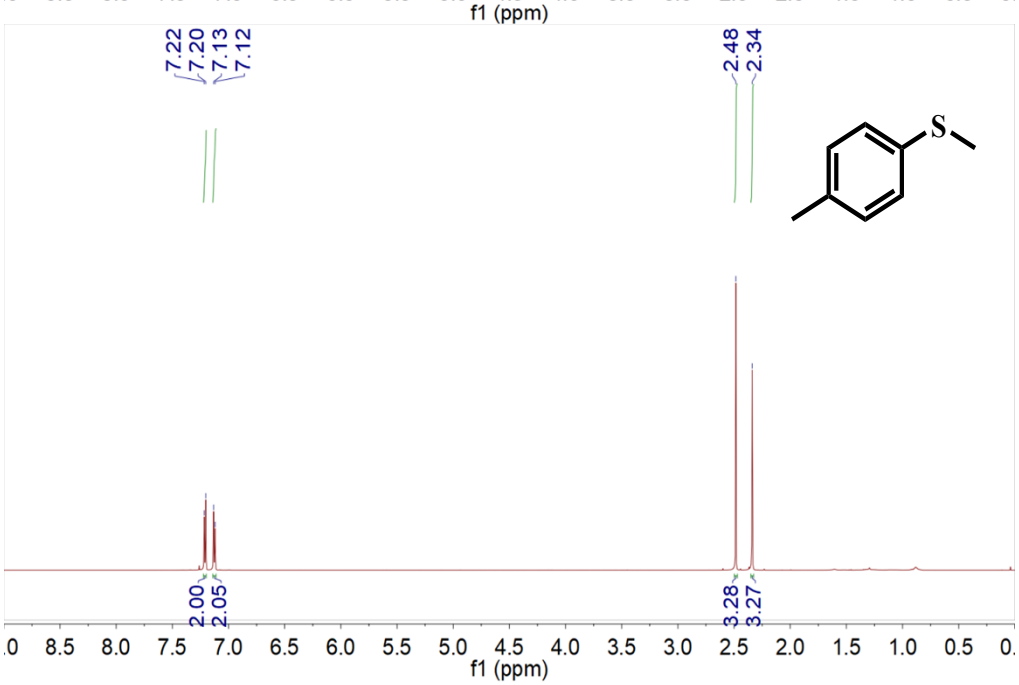
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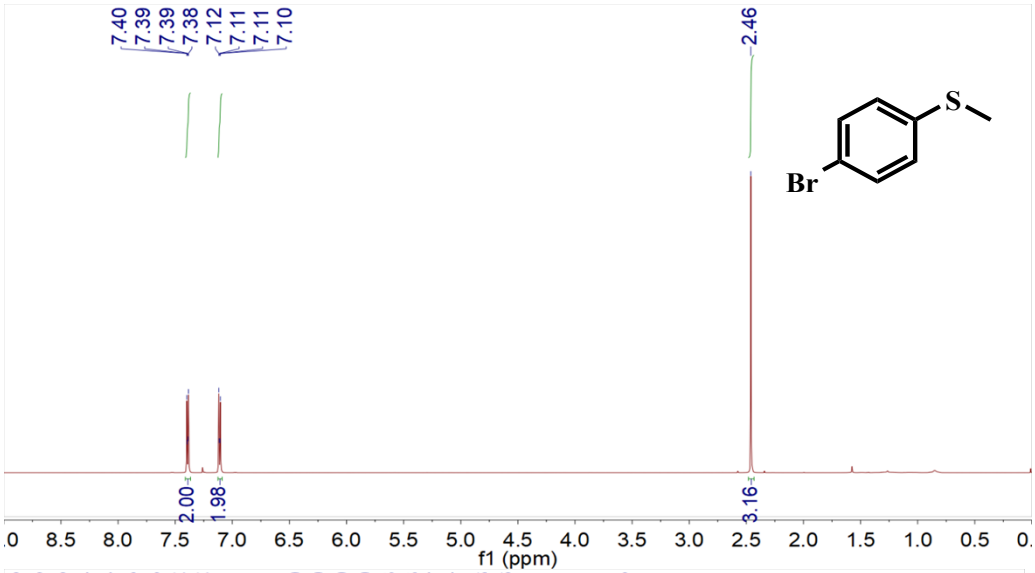
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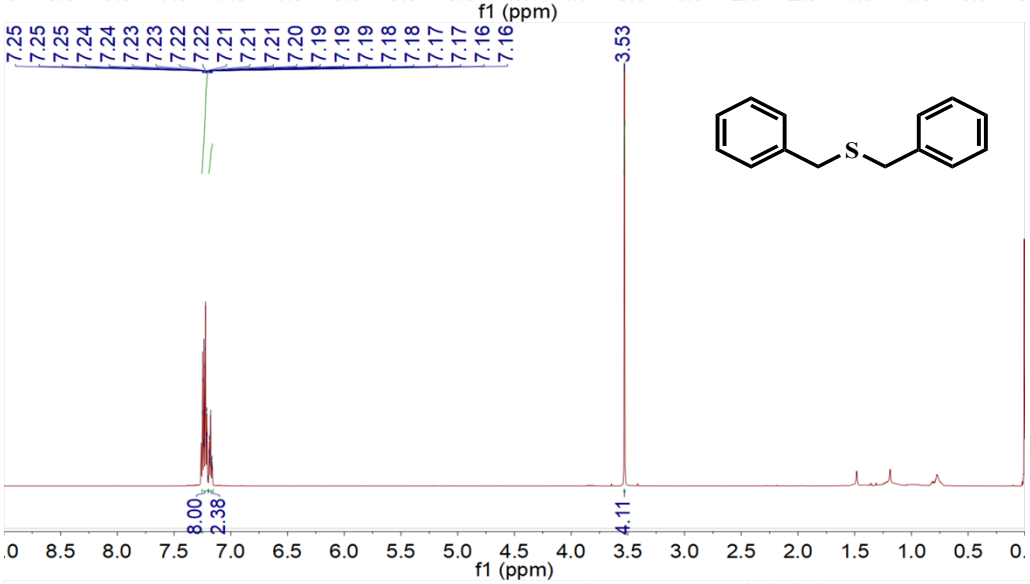
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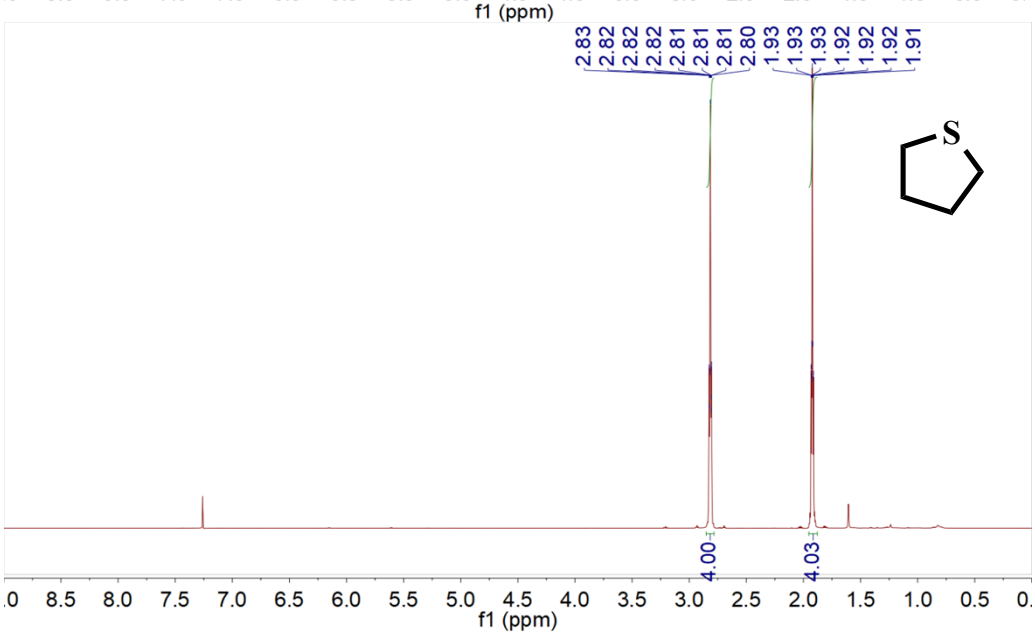
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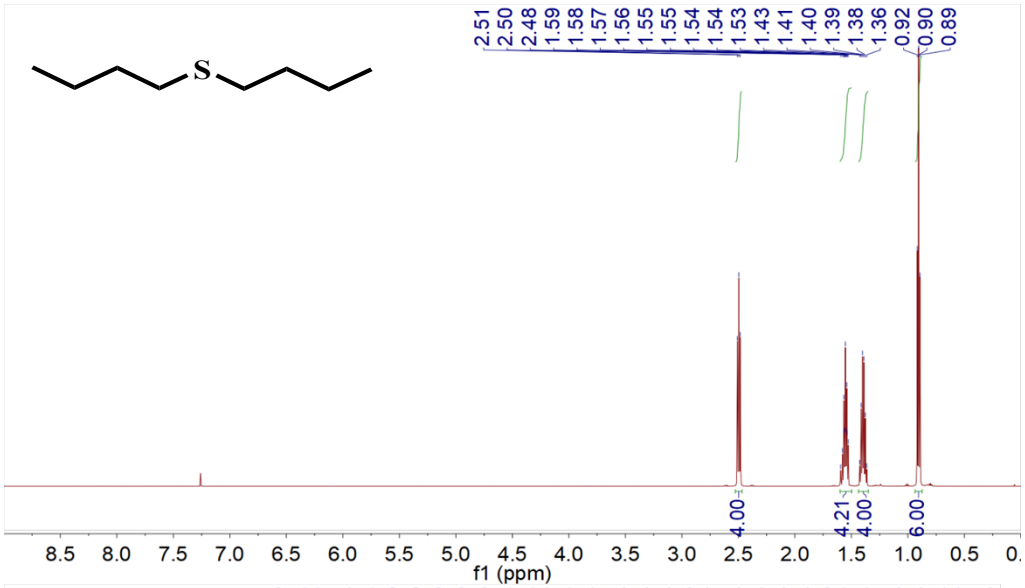
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4.00 4.21 4.00 6.00
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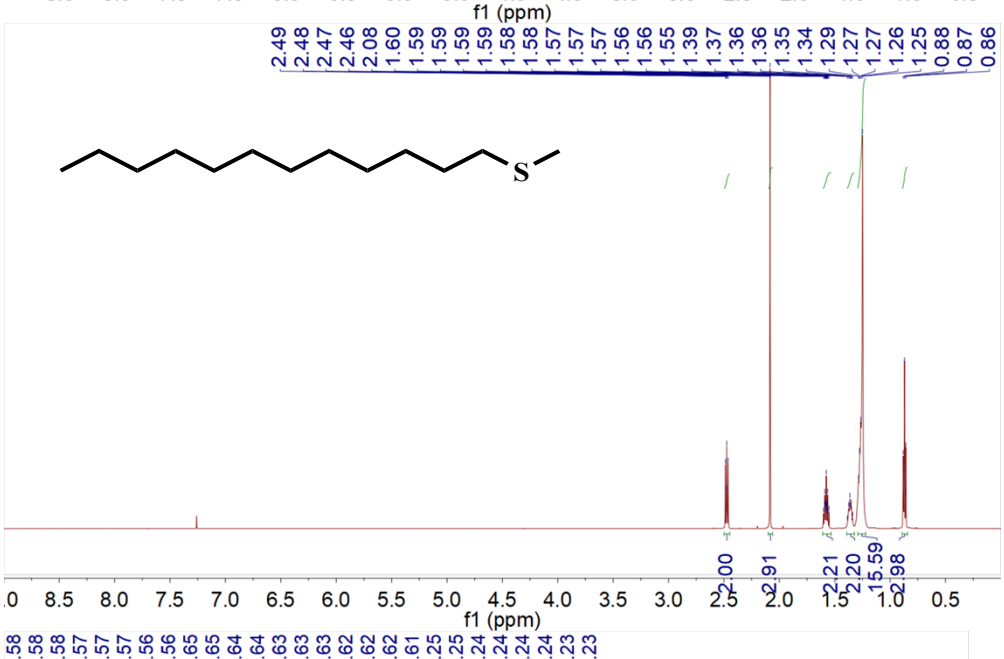
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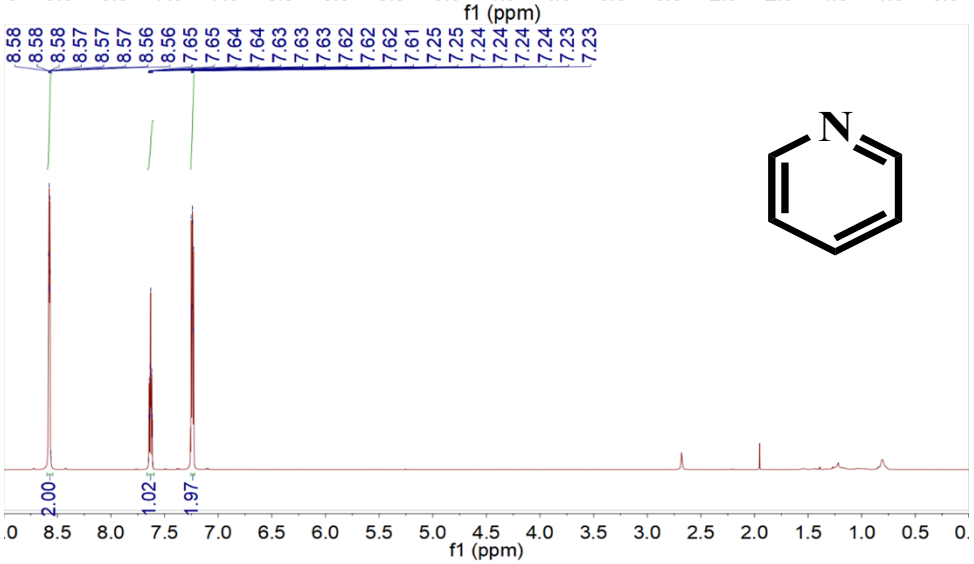
f1 (ppm)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2.00 1.02 1.97
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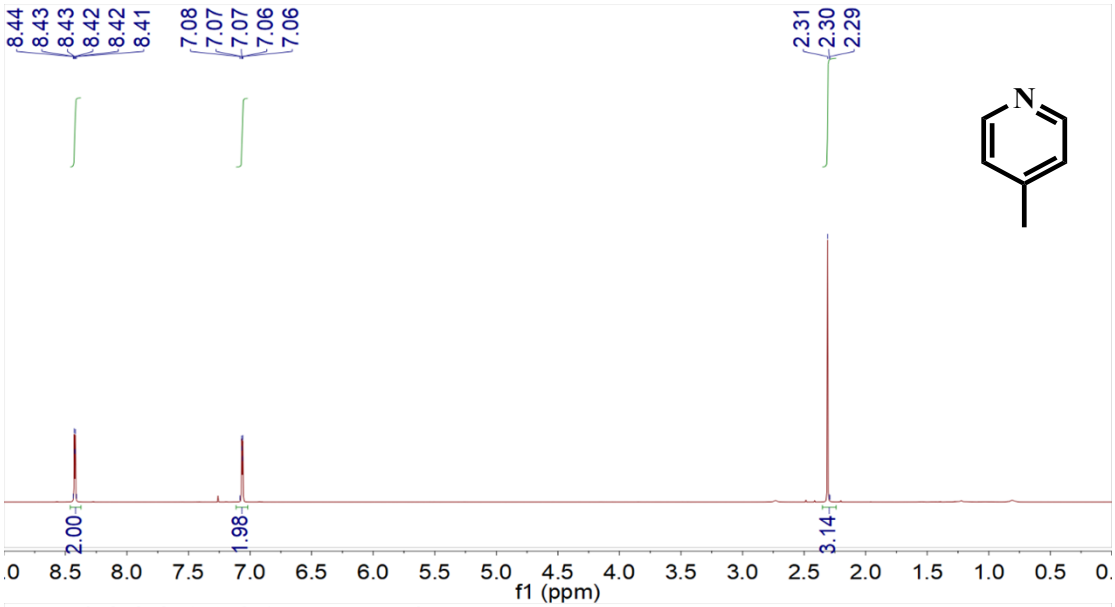
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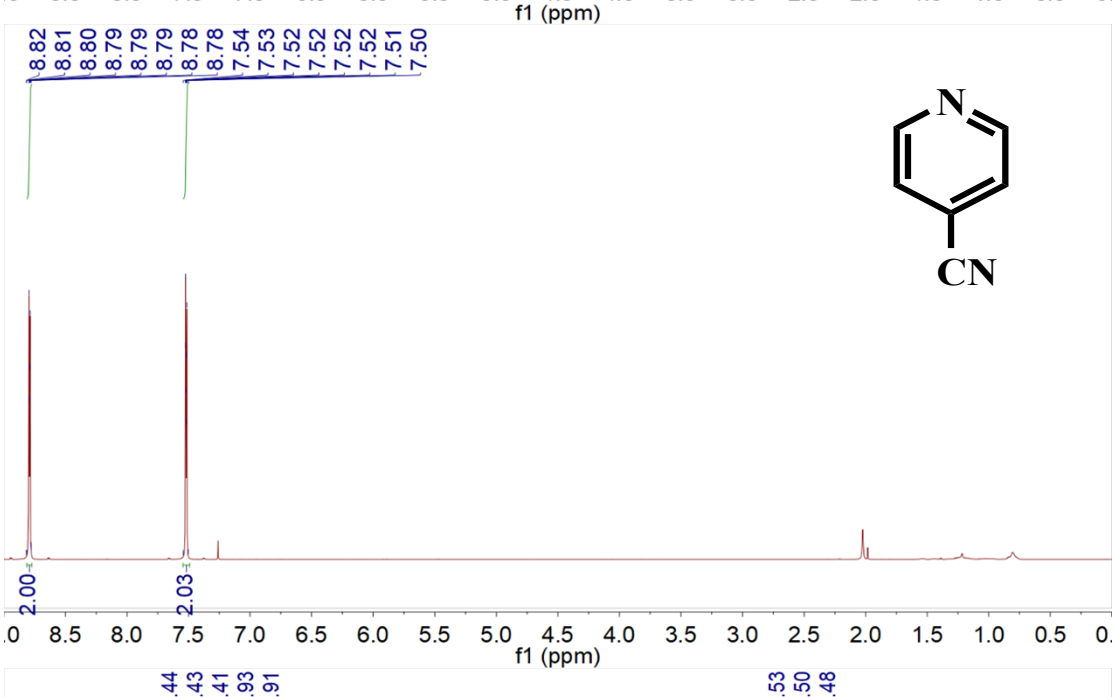
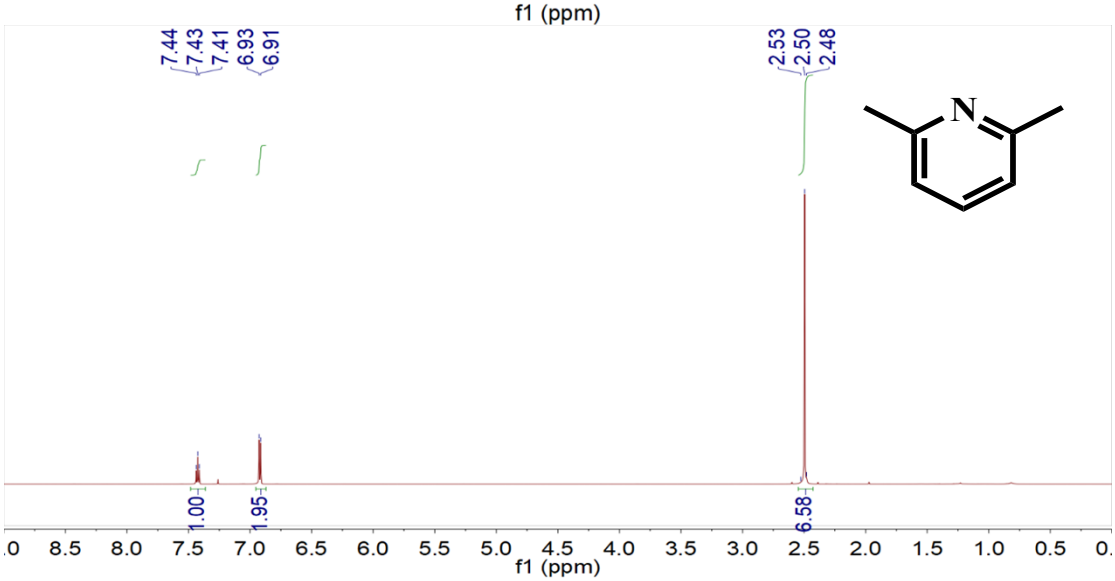
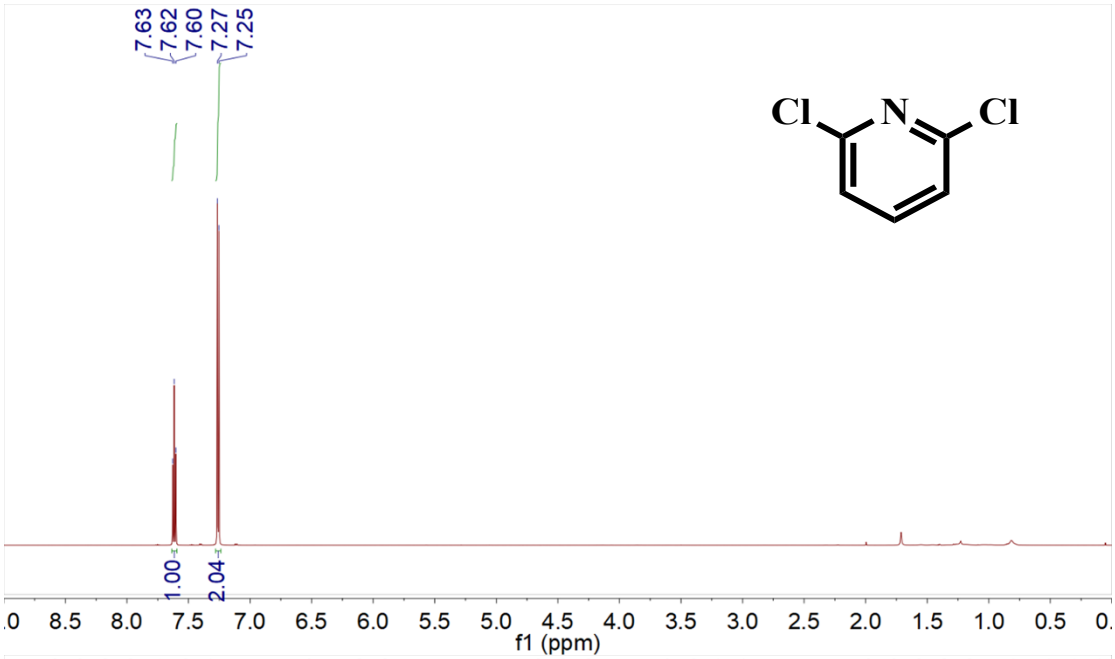
7.06
2.31
2.30
2.29
N
2.00
1.98
3.14
f1 (ppm)


8.82
8.81
8.80
8.79
8.79
8.79
8.78
8.78
7.54
7.53
7.52
7.52
7.52
7.52
7.51
7.50
N
CN
2.00
2.03
f1 (ppm)


7.44
7.43
7.41
6.93
6.91
2.53
2.50
2.48
N
1.00
1.95
6.58
f1 (ppm)


7.63
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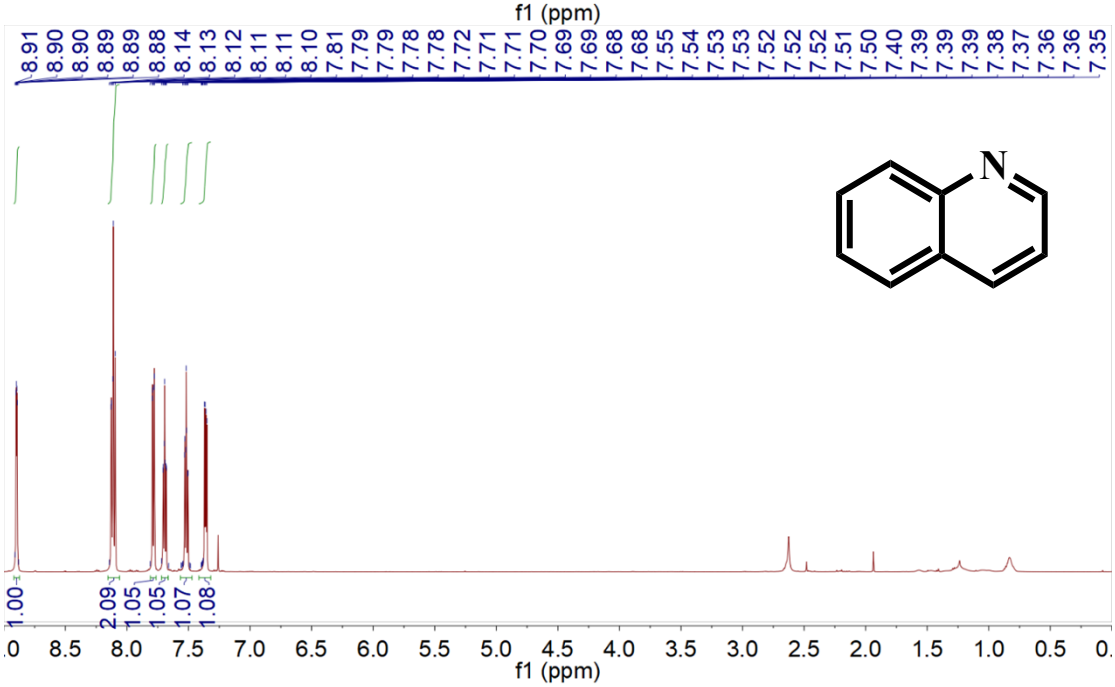
7.60
7.27
7.25
Cl
N
Cl
1.00
2.04
f1 (ppm)


8.91
8.90
8.90
8.89
8.89
8.88
8.14
8.13
8.12
8.11
8.11
8.10
7.81
7.79
7.79
7.78
7.78
7.72
7.71
7.71
7.70
7.69
7.69
7.68
7.68
7.55
7.54
7.53
7.53
7.52
7.52
7.52
7.51
7.50
7.40
7.39
7.39
7.39
7.38
7.37
7.36
7.36
7.35
N
1.00
2.09
1.05
1.05
1.07
1.08
f1 (ppm)