

Supporting information

Palladium Nanoparticles Immobilized on Nano-Silica Triazine Dendritic Polymer: A Recyclable and Sustainable Nanoreactor for C-S Cross- Coupling Reaction

Amir Landarani-Isfahani, Iraj Mohammadpoor-Baltork,* Valiollah Mirkhani,* Majid
Moghadam, Shahram Tangestaninejad and Hadi Amiri Rudbari

Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran

Tel: +98-313-7934927; Fax: +98-313-6689732; E-mail: imbaltork@sci.ui.ac.ir;
mirkhani@sci.ui.ac.ir

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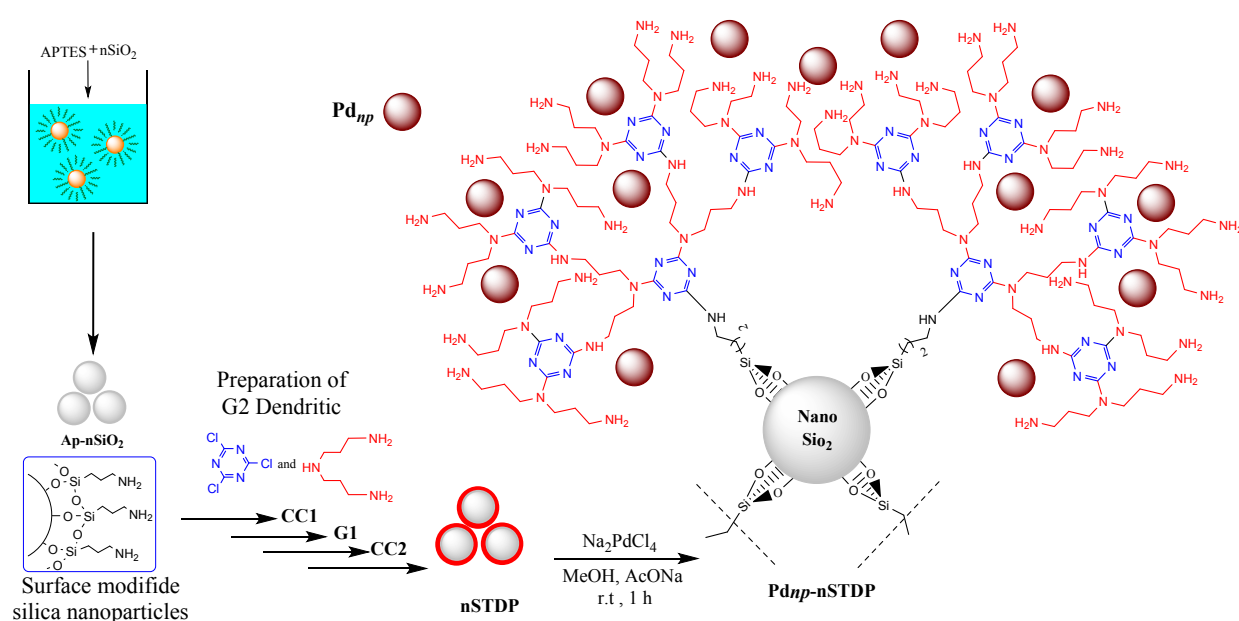


Figure S1. Schematic illustration of preparation of palladium nanoparticles immobilized on nano silica triazine dendritic polymer (Pd_{np}-nSTDP) catalyst.

1. Preparation of Pd_{np}-nSTDP¹

Activation of Nano-Silica:

In a round-bottomed flask equipped with a condenser and a magnetic stirrer, a mixture of nano-silica (10 g, 40–100 nm) and concentrated HCl (80 mL, 6M) was heated in an oil-bath at 120 °C for 24 h. The mixture was filtered and the white powder was washed with distilled water until neutral pH. The solid was dried under vacuum at 120 °C.

Preparation of Propylamine-Functionalized Nano-Silica (AP-nSiO₂)

(AP-nSiO₂): In a round-bottomed flask equipped with a condenser and a magnetic stirrer, a mixture of activated nanosilica (3 g) and 3-aminopropyltrimethoxysilane (APTS) (8 mL) in 50 mL of anhydrous toluene was stirred under reflux conditions for 8 h. The reaction mixture was filtered and the solid material was washed with toluene in a continuous extraction apparatus (Soxhlet) to remove the unreacted starting material, and dried in a vacuum oven at 110 °C.

Preparation of CC1-nSiO₂

The AP-nSiO₂ (2 g, 0.99 mmol g) 1 was added to a solution of cyanuric chloride (1.85 g, 10 mmol) and diisopropylethylamine (DIPEA) (10 mmol, 1.7 mL) in THF (10 mL). The reaction mixture was shaken overnight at room temperature. The solid material

was separated by filtration, washed with hot THF for 12 h in a Soxhlet apparatus to remove the unreacted starting materials and then dried in a vacuum oven at 50 °C.

Preparation of nano-silica-supported triazine dendritic polymer (G1)

To a slurry of CC1-nSiO₂ (1 g) in DMF (12 mL) was added bis(3-aminopropyl)amine (8.11 mmol, 1 mL) and DIPEA (8.11 mmol, 1.4 mL). The reaction mixture was stirred at 80 °C for 16 h. The solid material was filtered, washed with hot ethanol for 12 h in a Soxhlet apparatus to remove the unreacted starting materials and then dried in a vacuum oven at 50 °C.

Preparation of CC2-nSiO₂

Nano-silica-supported triazine dendritic polymer, G1 (1 g, 0.45 mmol) was added to a solution of cyanuric chloride (1.66 g, 9 mmol) and DIPEA (9 mmol, 1.56 mL) in THF (20 mL). The reaction mixture was agitated at room temperature for 16 h. The reaction mixture was filtered and the solid was washed with hot THF for 16 h in a Soxhlet apparatus to remove the unreacted starting materials. Finally, the CC2-nSiO₂ was dried in a vacuum oven at 50 °C.

Preparation of nano-silica supported triazine dendritic polymer (G2 or nSTDP)

To a slurry of CC2-nSiO₂ (1 g, 0.36 mmol) in DMF (20 mL) was added bis(3-aminopropyl)amine (9.36 mmol, 1.14 mL) and DIPEA (9.36 mmol, 1.61 mL). The reaction mixture was agitated at 80 °C for 16 h and then filtered. The resulting nano-silica-supported dendritic polymer (G2 or nSTDP) was washed with hot ethanol for 24 h in a Soxhlet apparatus to remove unreacted starting materials and dried in a vacuum oven at 50 °C.

Preparation of nano-Silica triazine dendritic polymer supported palladium nanoparticles (Pd_{np}-nSTDP)

A mixture of PdCl₂ (240 mg, 1.36 mmol) and NaCl (88 mg, 1.52 mmol) in methanol (8 mL) was stirred at room temperature for 24 h and then filtered. The filtrates were diluted with methanol (40 mL) and nSTDP (1 g, 0.21 mmol) was added to this solution. The resulting mixture was stirred at 60 °C for 24 h. At the end of the reaction, the mixture was cooled to room temperature, sodium acetate (0.76 g, 9.28 mmol) was added and stirred at room temperature for 1 h. The solid was filtered, washed with methanol, water and acetone, to remove the unreacted starting materials

and then dried in vacuum to afford Pd_{np}-nSTDP catalyst (1.07 g) as a light gray solid. Palladium analysis (ICP): 1.27%. Average particle diameter: 3.1±0.5 nm (based on TEM and particle size analyses).

The Pd_{np}-nSTDP catalyst was characterized by FT-IR spectroscopy, thermogravimetric analysis (TGA), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray (EDX), transmission electron microscopy (TEM) and elemental analysis.¹

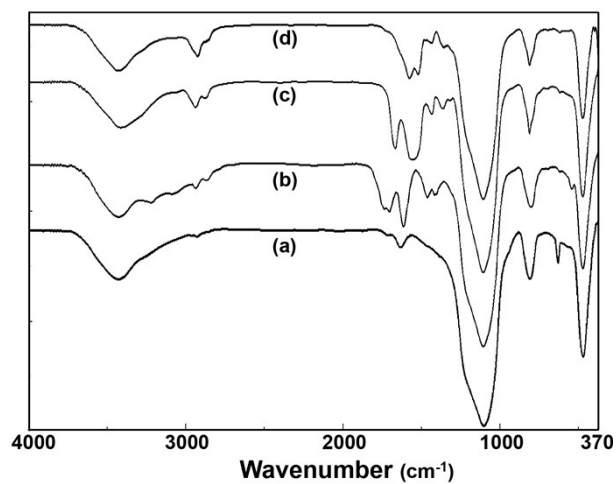


Figure S2. The FT-IR spectra of: a) AP-nSiO₂; b) CC1-nSiO₂; c) G1 and d) G2 (nSTDP).

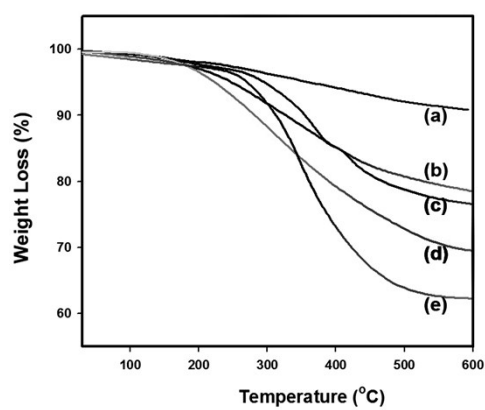


Figure S3. TGA spectra of: a) AP-nSiO₂; b) CC1-nSiO₂; c) G1; d) CC2-nSiO₂ and e) G2.

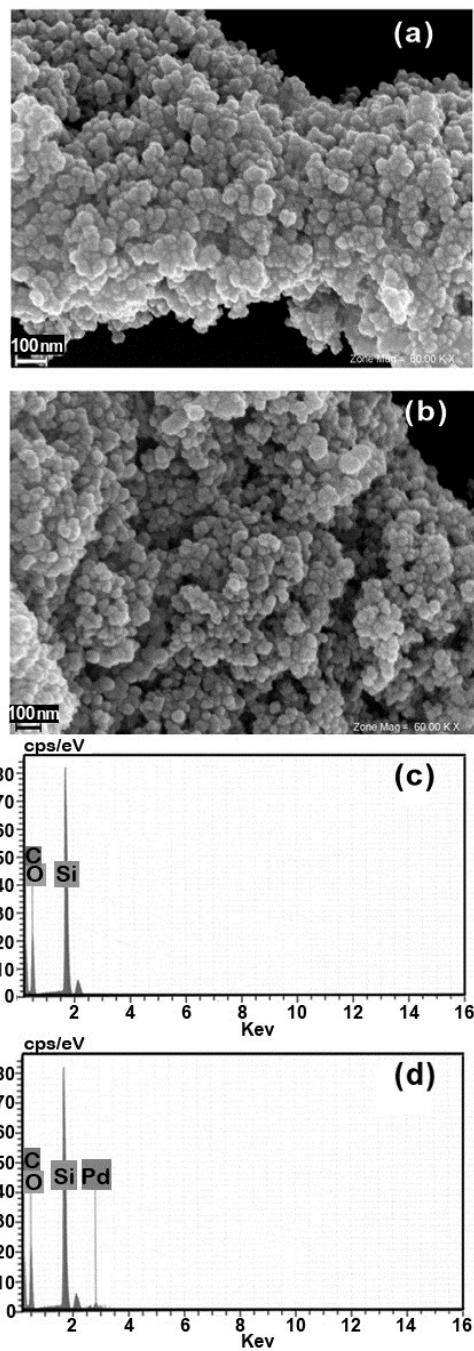


Figure S4. FE-SEM images of: a) nSTDP and b) Pd_{np}-nSTDP. SEM-EDX spectra of: c) nSTDP and d) Pd_{np}-nSTDP.

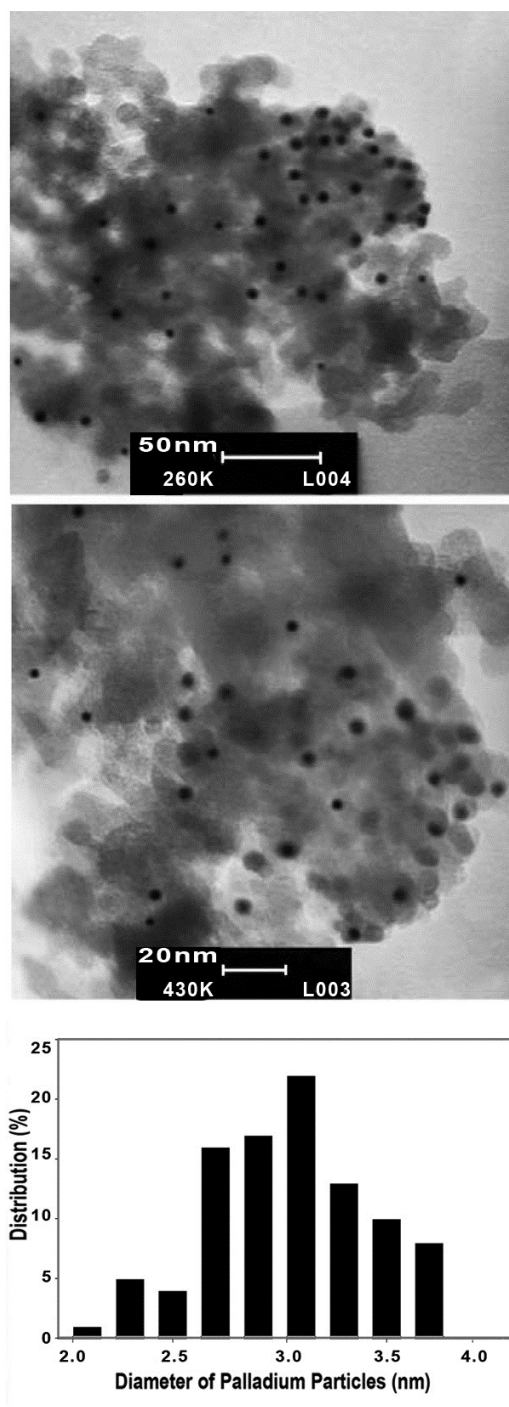
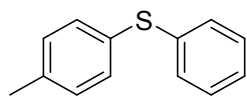


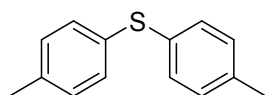
Figure S5. TEM image and particle size distribution results for Pd_{np}-nSTDP catalyst.

2. Spectroscopic Data of The Products:



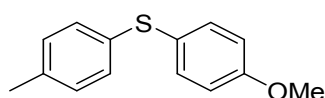
phenyl(*p*-tolyl)sulfide (Table 2, entry 1)

Colourless oil (Lit.² oil). IR (KBr) $\nu = 2923, 2860, 1598, 1445, 1325, 1107, 1036, 873, 807, 688 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.29$ (d, $J = 8.0 \text{ Hz}$, 2H), 7.10 (d, $J = 7.6 \text{ Hz}$, 2H), 7.14 (t, $J = 8.0 \text{ Hz}$, 2H), 7.05 (t, $J = 8 \text{ Hz}$, 1H), 6.82 (d, $J = 7.6 \text{ Hz}$, 2H), 2.30 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 137.22, 137.11, 134.34, 129.80, 129.43, 128.31, 125.61, 124.57, 20.98$.



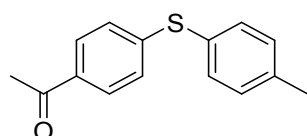
di-*p*-tolylsulfide (Table 2, entry 2)

Mp: 57-58 °C (Lit.³ 56.1 °C). IR (KBr) $\nu = 2920, 2855, 1592, 1486, 1397, 801 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.37$ (d, $J = 8.0 \text{ Hz}$, 4H), 7.09 (d, $J = 8.0 \text{ Hz}$, 4H), 2.31 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 136.25, 133.00, 129.60, 129.14, 20.98$.



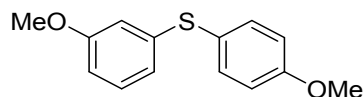
(4-methoxyphenyl)(*p*-tolyl)sulfide (Table 2, entry 3)

Mp: 44-45 °C (Lit.⁴ 44 °C) IR (KBr) $\nu = 2917, 2835, 1590, 1491, 1400, 1245, 1102, 835, 805 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.35$ (d, $J = 6.8 \text{ Hz}$, 2H), 7.12 (d, $J = 7.2 \text{ Hz}$, 2H), 7.05 (d, $J = 7.2 \text{ Hz}$, 2H), 6.86 (d, $J = 6.8 \text{ Hz}$, 2H), 3.79 (s, 3H), 2.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 159.42, 136.09, 134.35, 129.75, 129.32, 128.49, 125.56, 114.83, 55.33, 20.98$.



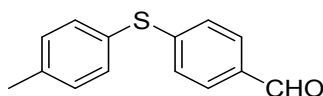
1-(4-(*p*-tolylthio)phenyl)ethanone (Table 2, entry 4)

Mp: 90-92 °C (Lit.⁴ 90-91 °C). IR (KBr) ν = 2922, 2867, 1675, 1587, 1490, 1399, 1150, 960, 817 cm^{-1} . ¹H NMR (400 MHz, CDCl₃): δ = 7.81 (d, J = 6.8 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.25 (d, 8.0 Hz, 2H), 7.18 (d, J = 6.8 Hz, 2H), 2.56 (s, 3H), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 195.21, 139.39, 135.65, 134.54, 133.08, 130.56, 130.38, 128.84, 126.62, 26.49, 21.31.



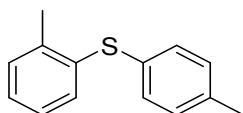
(3-methoxyphenyl)(4-methoxyphenyl)sulfide (Table 2, entry 9)

Colourless oil (Lit.⁵ Oil). IR (KBr) ν = 2955, 2835, 1590, 1477, 1283, 1246, 1162, 1039, 862, 772, 606 cm^{-1} . ¹H NMR (400 MHz, CDCl₃): δ = 7.34 (d, J = 8.4 Hz, 2H), 7.05 (t, J = 8.0 Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 6.66 (dt, J = 6.8, 2.0 Hz, 2H), 6.61-6.60 (m, 1H), 3.73 (s, 3H), 3.64 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 160.07, 159.97, 135.69, 129.92, 129.72, 120.24, 119.58, 113.13, 112.56, 111.32, 55.37, 55.30.



4-(*p*-tolylthio)benzaldehyde (Table 2, entry 11)

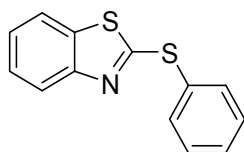
Mp: 70-72 °C (Lit.⁶ 69-70 °C). IR (KBr) ν = 2938, 2922, 2810, 1720, 1590, 1455, 1032, 850 cm^{-1} . ¹H NMR (400 MHz, CDCl₃): δ = 9.96 (s, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 7.6 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 2.30 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 198.10, 144.91, 135.70, 133.20, 131.18, 130.01, 128.96, 128.38, 126.63, 30.94.



***o*-tolyl(*p*-tolyl)sulfide (Table 2, entry 12)**

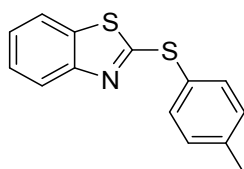
Colourless oil (Lit.⁷ Oil). IR (KBr) ν = 2921, 2860, 1590, 1490, 1466, 1180, 804, 748 cm^{-1} . ¹H NMR (400 MHz, CDCl₃): δ = 7.36 (d, J = 8.0 Hz, 2H), 7.15-7.14 (m, 3H), 7.12-7.05 (m,

3H), 2.30 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 137.15, 135.71, 130.12, 130.01, 129.96, 126.89, 126.35, 125.10, 120.26, 119.55, 21.05, 20.96.



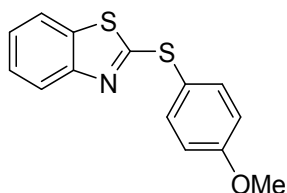
2-(phenylthio)benzo[d]thiazole (Table 3, 3a)

Yellow oil (Lit.⁸ Oil). IR (KBr) ν = 2922, 1626, 1580, 1452, 1403, 1135, 1107, 873, 751 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 7.86 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.55 (d, 8.0 Hz, 1H), 7.45-7.39 (m, 3H), 7.35 (t, J = 8.4 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 170.23, 154.16, 135.61, 135.40, 130.25, 129.83, 129.71, 125.95, 124.20, 121.85, 120.69.



2-(p-tolylthio)benzo[d]thiazole (Table 3, 3b)

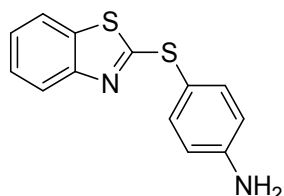
Mp: 69-70 °C (Lit.⁹ 72-73 °C) IR (KBr) ν = 2931, 2857, 1590, 1493, 1454, 1421, 1081, 1003, 814, 725, 755 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 7.86 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 8.4 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.26 (t, J = 8.4 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 172.03, 154.18, 141.73, 136.18, 133.50, 131.61, 126.17, 124.11, 121.74, 120.77, 120.14, 20.96.



2-(4-methoxyphenylthio)benzo[d]thiazole (Table 3, 3c)

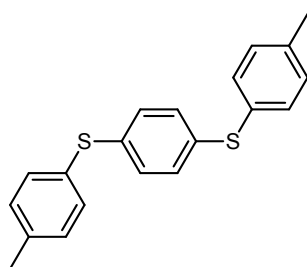
Mp: 60-62 °C (Lit.¹⁰ 61-63 °C). IR (KBr) ν = 2966, 2837, 1588, 1492, 1455, 1291, 1033, 1024, 830, 758 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 7.85 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.8 Hz, 2H), 7.61 (d, 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H), 6.99 (d, J

= 8.8 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 172.06, 161.73, 154.19, 136.11, 137.64, 126.13, 124.09, 121.76, 120.77, 120.16, 115.54, 55.50.



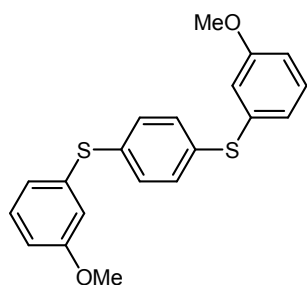
4-(benzo[d]thiazol-2-ylthio)aniline (Table 3, 3d)

Mp: 124-125 °C (Lit.¹¹ 122-123 °C). IR (KBr) ν = 3360, 3015, 2922, 1607, 1476, 1445, 1251, 1157, 807, 749 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 7.62 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 6.74 (d, J = 8.4 Hz, 2H), 3.99 (brs, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 159.41, 146.15, 136.11, 134.38, 129.75, 129.30, 128.51, 125.50, 116.21, 114.65.



1,4-Bis(*p*-tolylthio)benzene (Table 4, 1D)

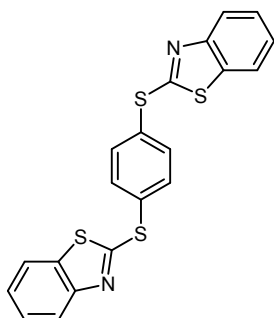
Mp 141-142 °C. IR (KBr) ν = 3023, 1608, 1448, 1391, 1139, 884, 720 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 7.45 (s, 4H), 7.40 (d, J = 7.6 Hz, 4H), 7.13 (d, J = 7.6 Hz, 4H), 2.34 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ = 130.62, 129.32, 128.01, 126.34, 124.64, 120.91, 20.78. Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{S}_2$: C, 74.49; H, 5.63; S, 19.89. Found: C, 74.25; H, 5.60; S, 20.01.



1,4-Bis((3-methoxyphenyl)thio)benzene (Table 4, 2D)

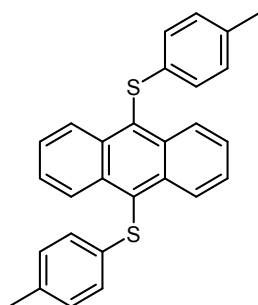
Mp 139-141 °C. IR (KBr) ν = 3038, 1621, 1457, 1401, 1132, 920, 750 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 7.37 (s, 4H), 7.23 (t, J = 8.0, 2H), 7.15-7.12 (m, 4H), 6.80 (ddt, J = 7.6,

2.0, 1.2 Hz, 2H), 3.75 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 160.17, 138.72, 138.31, 129.95, 119.62, 113.08, 112.47, 55.33$. Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{S}_2$: C, 67.76; H, 5.12; S, 18.09. Found: C, 67.43; H, 5.15; S, 18.20



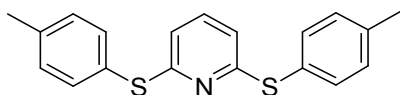
1,4-Bis(benzo[d]thiazol-2-ylthio)benzene (Table 4, 3D)

Mp 231-233 °C. IR (KBr) $\nu = 3010, 1654, 1563, 1459, 1380, 1240, 790, 724 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.81$ (d, $J = 8.0$, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.53 (s, 4H), 7.35 (td, $J = 8.4, 1.2$ Hz, 2H), 7.22 (td, $J = 8.4, 1.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.83, 136.53, 133.24, 131.90, 129.03, 126.35, 125.20, 124.65, 122.15$. Anal. Calcd. for $\text{C}_{20}\text{H}_{12}\text{N}_2\text{S}_4$: C, 58.79; H, 2.96; N, 6.86; S, 31.39. Found: C, 58.50; H, 3.0; N, 6.79; S, 31.52.



9,10-Bis(p-tolylthio)anthracene (Table 4, 4D)

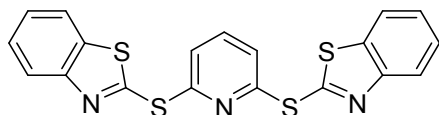
Mp 188-190 °C. IR (KBr) $\nu = 3013, 1611, 1448, 1390, 1121, 884, 720 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.99$ (dd, $J = 7.2, 3.6$ Hz, 4H), 7.58 (dd, $J = 7.2, 3.6$ Hz, 4H), 6.96 (d, $J = 8.4$ Hz, 4H), 6.92 (d, $J = 7.6$ Hz, 4H), 2.24 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 132.32, 129.17, 129.07, 126.35, 125.19, 124.60, 122.14, 120.91, 20.79$. Anal. Calcd. for $\text{C}_{28}\text{H}_{22}\text{S}_2$: C, 79.58; H, 5.25; S, 15.17. Found: C, 79.29; H, 5.28; S, 15.26.



2,6-bis(p-tolylthio)pyridine (Table 4, 5D)

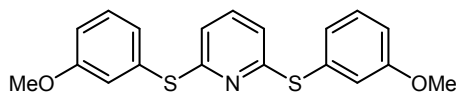
Mp: 194-195 °C (Lit.¹² 194-195 °C). IR (KBr) $\nu = 2982, 1632, 1595, 1410, 1387, 1170, 1056, 830, 732 \text{ cm}^{-1}$. ^1H NMR (400 MHz, DMSO-d_6): $\delta = 7.22$ - 7.19 (m, 4H), 7.18 (t, $J = 8.0$ Hz, 1H), 7.05 (d, $J = 8.0$ Hz, 4H), 6.29 (d, $J = 8.0$ Hz, 2H), 2.26 (s, 6H). ^{13}C NMR (100 MHz,

DMSO- d_6): δ = 164.12, 140.11, 138.52, 135.52, 130.70, 126.24, 119.02, 21.36. Anal. Cald. For $C_{19}H_{17}NS_2$: C, 70.55; H, 5.30; N, 4.33; S, 19.83, Found: C, 70.50; H, 5.24; N, 4.30; S, 19.96.



2,6-bis(benzo[d]thiazol-2-ylthio)pyridine (Table 4, 6D)

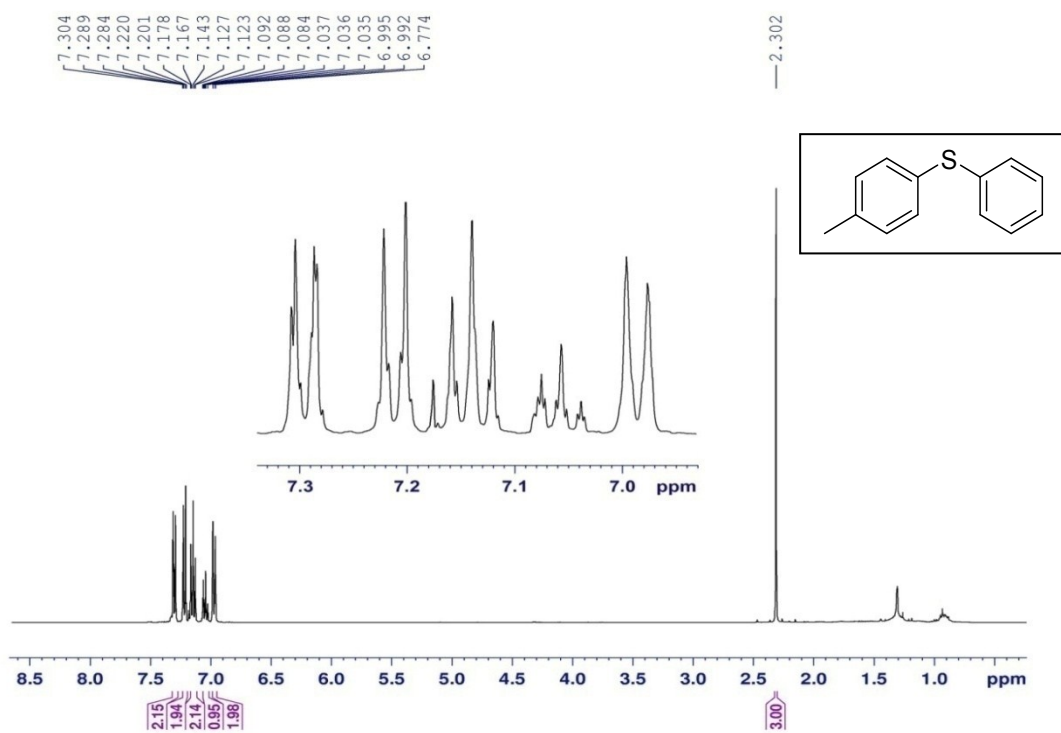
Mp: 188-189 °C (Lit.¹² 185-186 °C). IR (KBr) ν = 3056, 1640, 1544, 1404, 1132, 785, 757 cm^{-1} . 1H NMR (400 MHz, DMSO- d_6): δ = 7.99-7.94 (m, 3H), 7.84 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.6 Hz, 2H), 7.54-7.50 (m, 2H), 7.44-7.40 (m, 2H). ^{13}C NMR (100 MHz, DMSO- d_6): δ = 162.55, 154.67, 152.66, 149.90, 137.30, 136.08, 126.40, 125.10, 122.49, 120.95. Anal. Cald. For $C_{19}H_{11}N_3S_4$: C, 55.72; H, 2.71; N, 10.26; S, 31.32, Found: C, 55.46; H, 2.74; N, 10.21; S, 31.46.



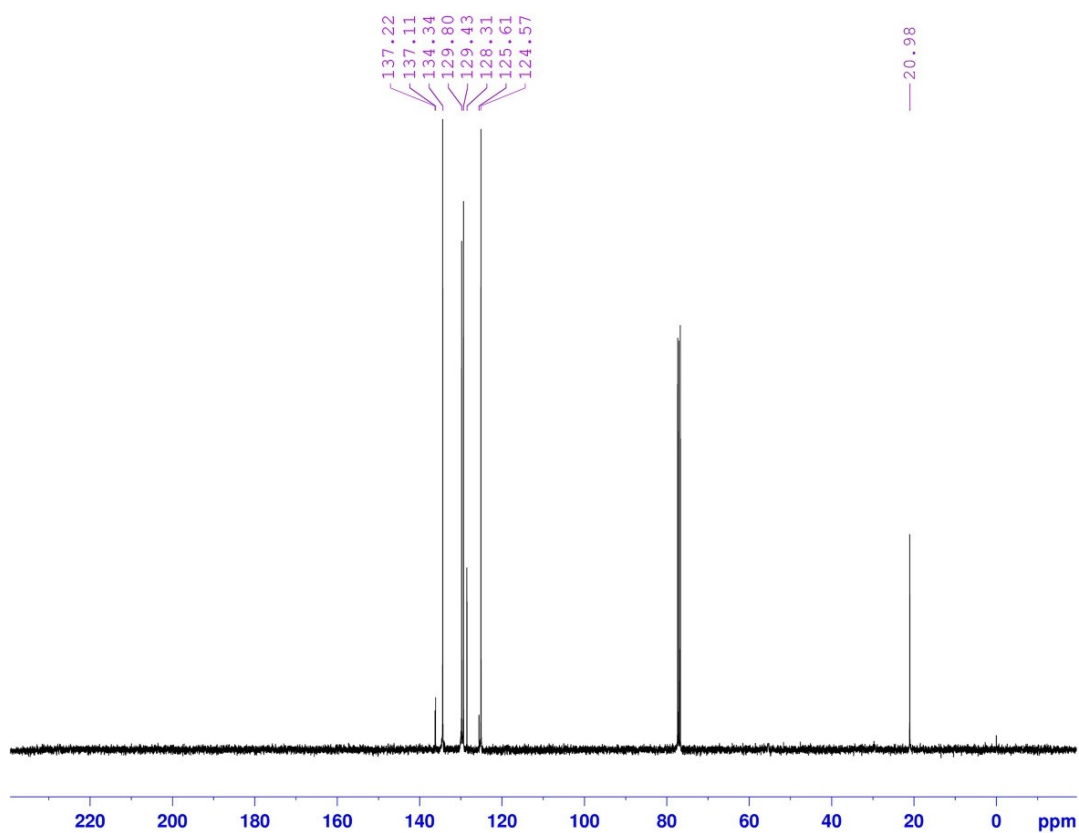
2,6-Bis((3-methoxyphenyl)thio)pyridine (Table 4, 7D)

Mp 142-144 °C. IR (KBr) ν = 3066, 1643, 1538, 1395, 1122, 772, 750 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ = 7.24- (t, J = 8.0 Hz, 2H), 7.15-7.06 (m, 5H), 6.88 (ddt, J = 7.6, 2.0, 1.2 Hz, 2H), 6.48 (d, J = 7.6 Hz, 2H), 3.74 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.24, 137.23, 131.84, 130.49, 127.25, 123.20, 119.96, 117.19, 115.44, 55.33. Anal. Cald. for $C_{19}H_{17}NO_2S_2$: C, 64.20; H, 4.20; N, 3.94; S, 18.04. Found: C, 64.33; H, 4.18; N, 3.88; S, 17.94.

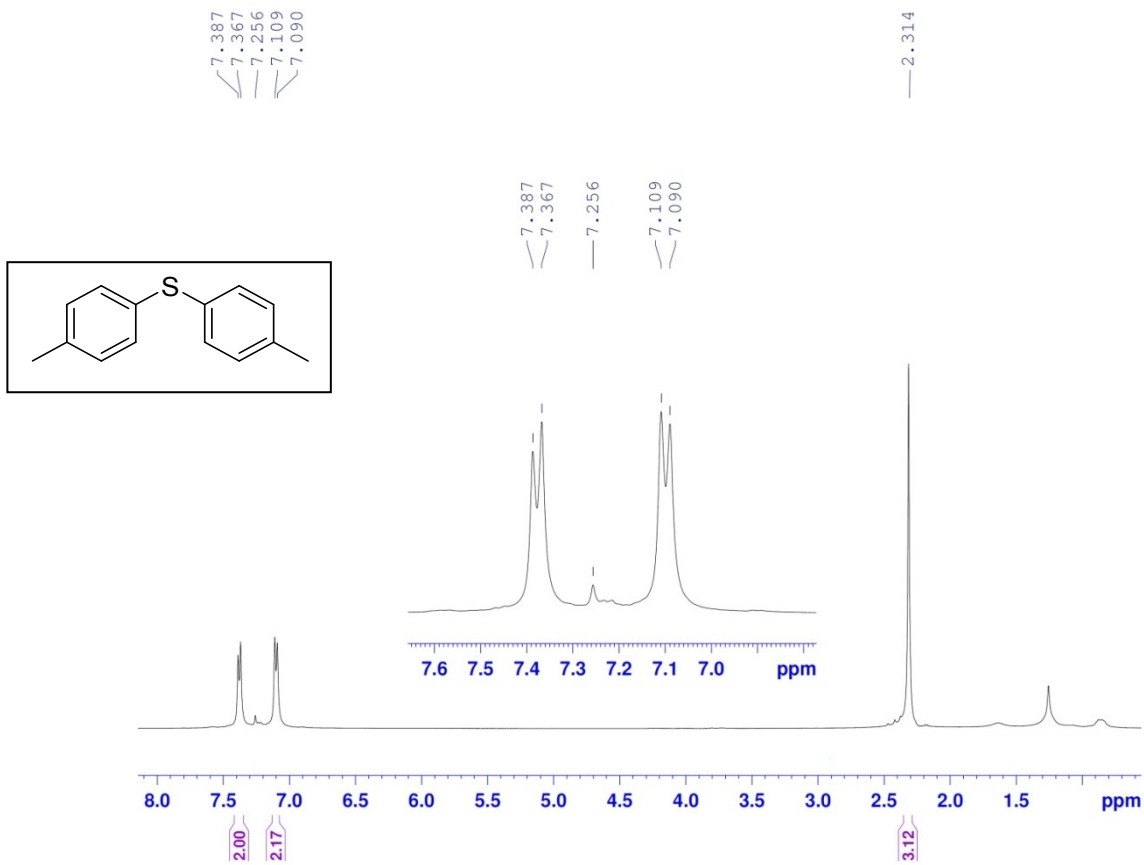
3. ^1H and ^{13}C NMR Spectra of the Products:



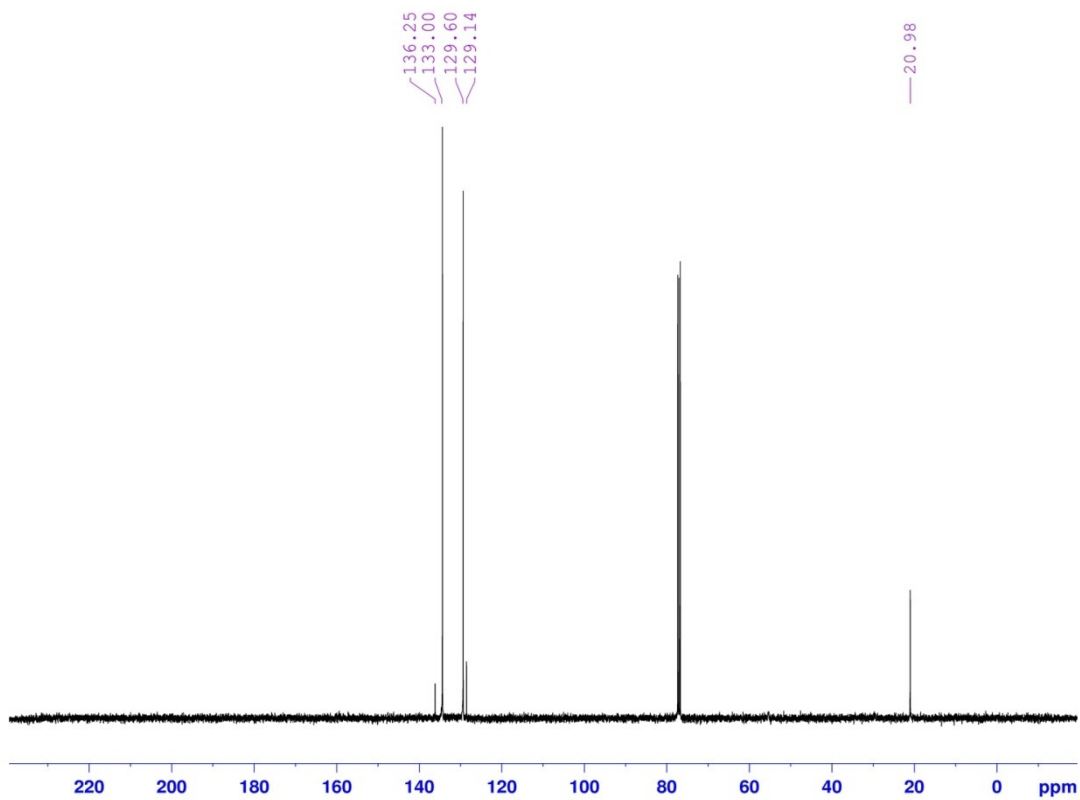
^1H NMR of phenyl(*p*-tolyl)sulfide



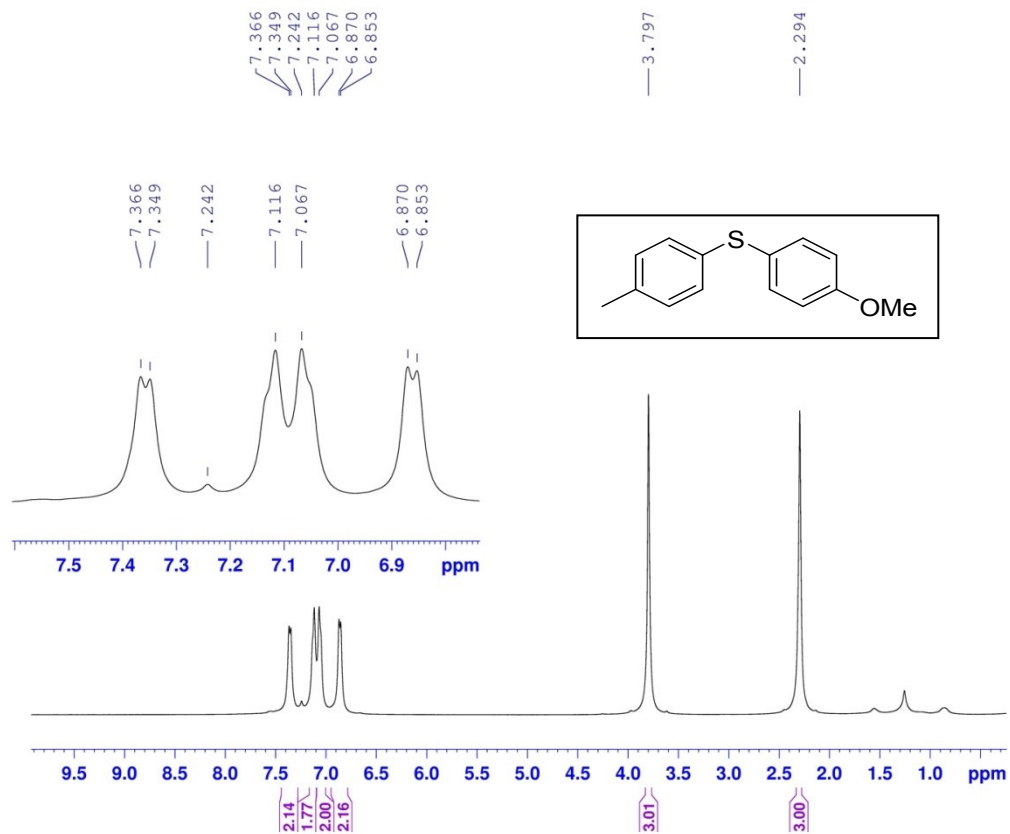
^{13}C NMR of phenyl(*p*-tolyl)sulfide



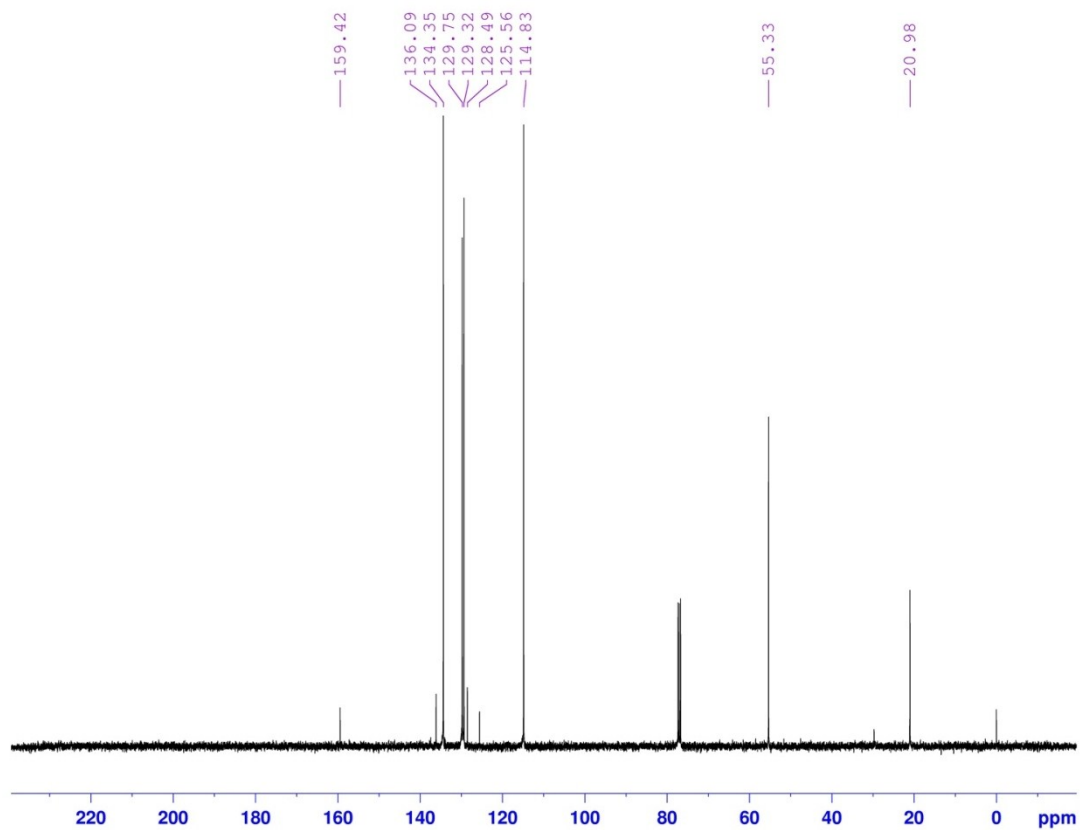
¹H NMR of di-*p*-tolylsulfide



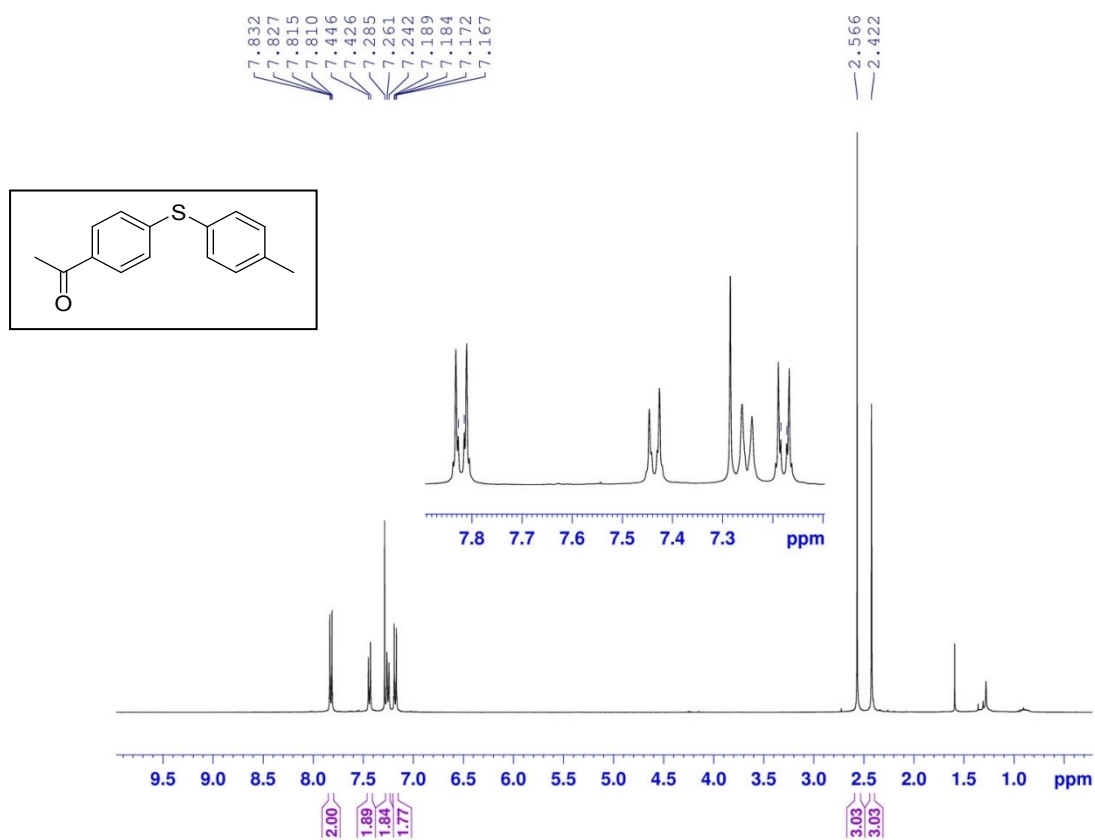
¹³C NMR of di-*p*-tolylsulfide



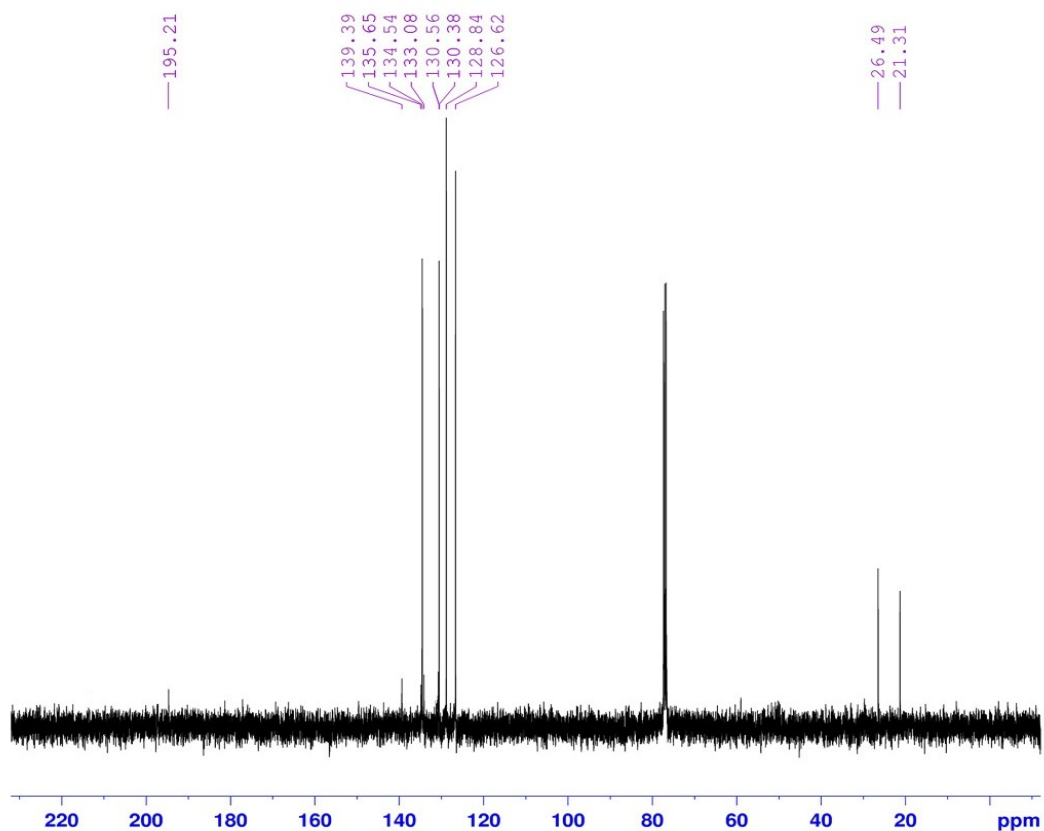
¹H NMR of (4-methoxyphenyl)(*p*-tolyl)sulfide



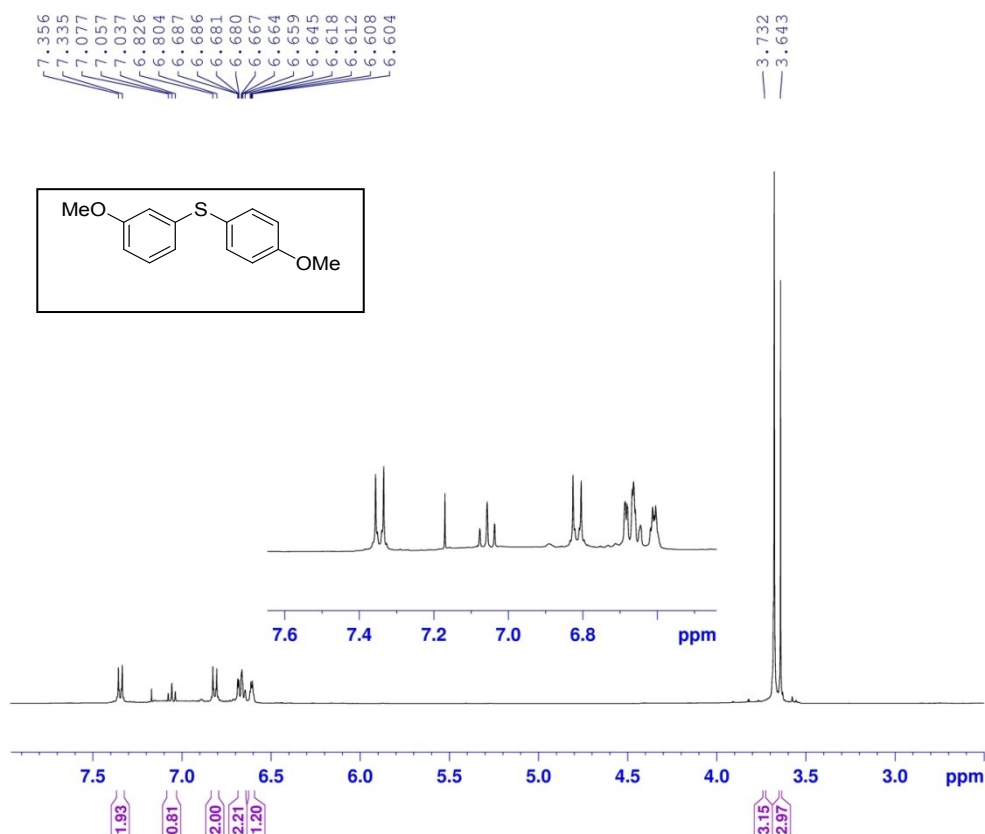
¹³C NMR of (4-methoxyphenyl)(*p*-tolyl)sulfide



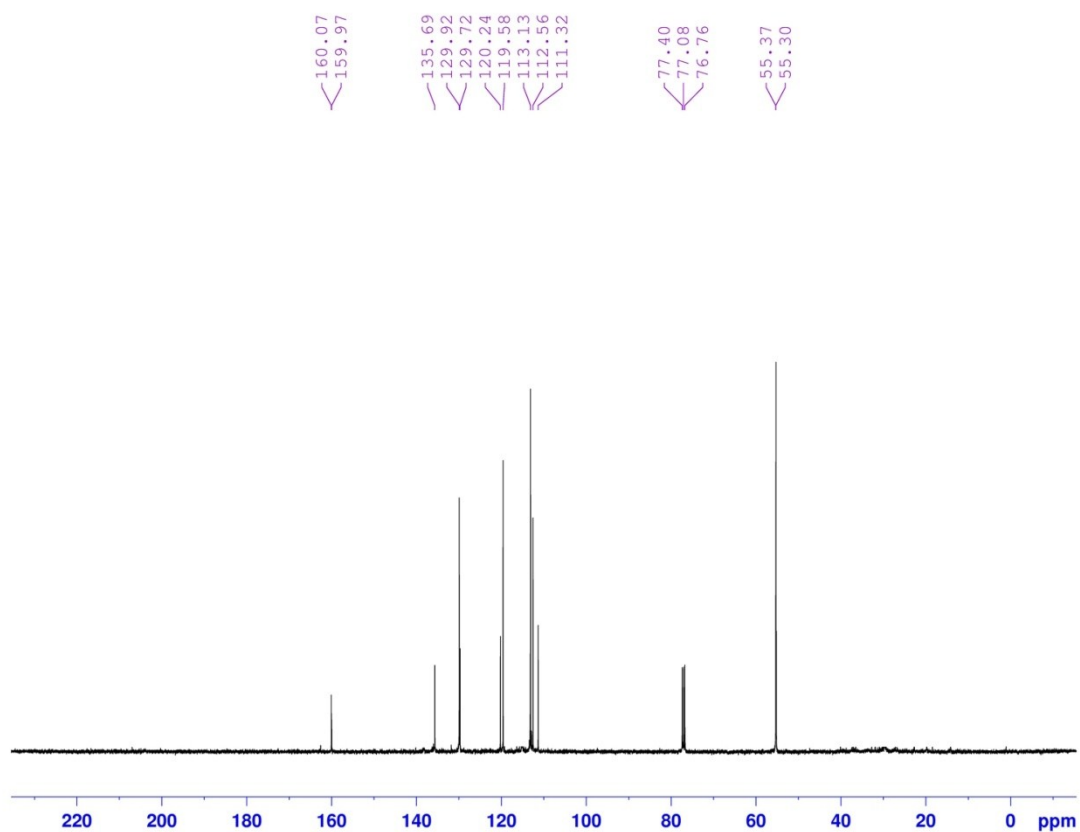
¹H NMR of 1-(4-(*p*-tolylthio)phenyl)ethanone



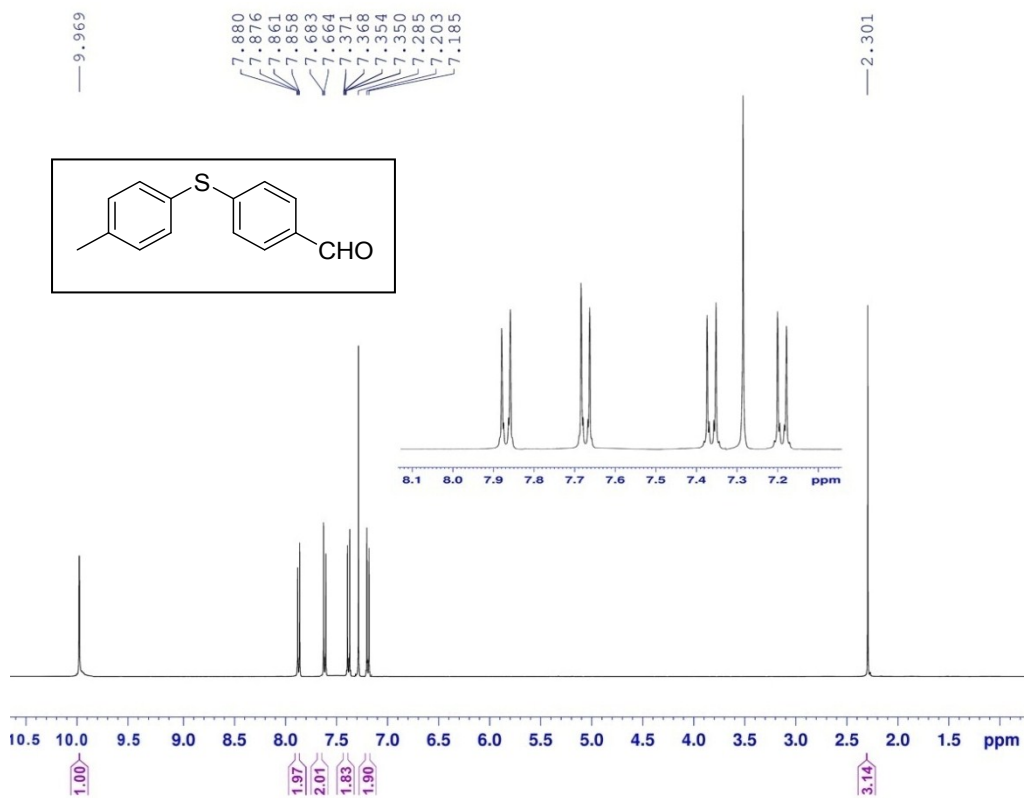
¹³C NMR of 1-(4-(*p*-tolylthio)phenyl)ethanone



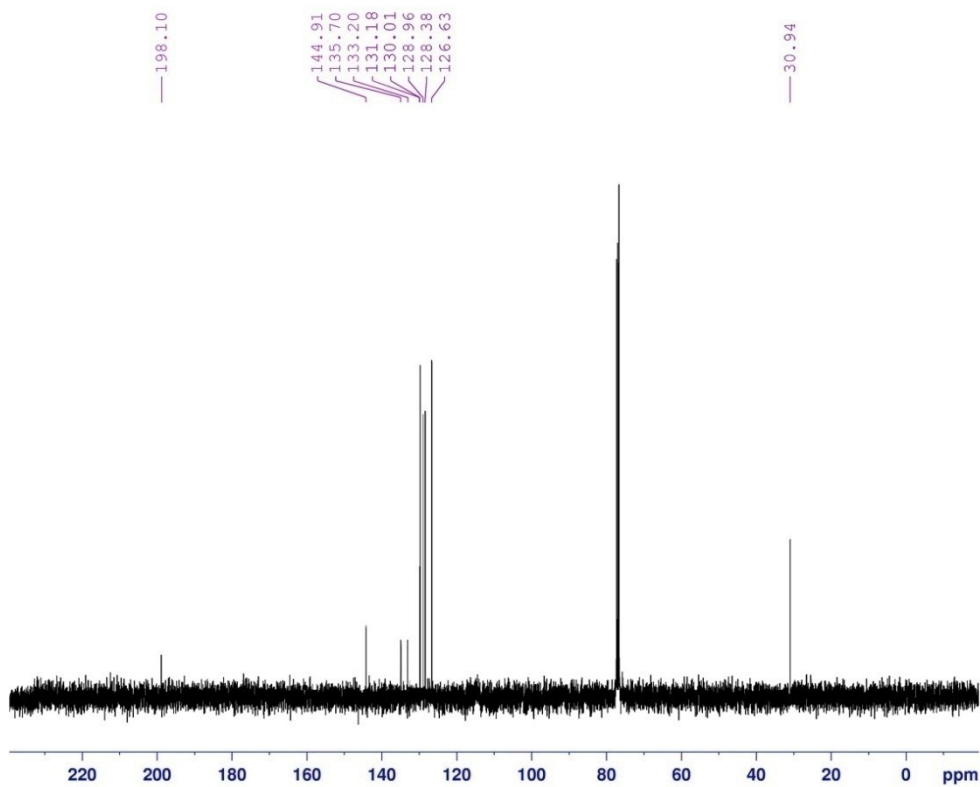
¹H NMR of (3-methoxyphenyl)(4-methoxyphenyl)sulfide



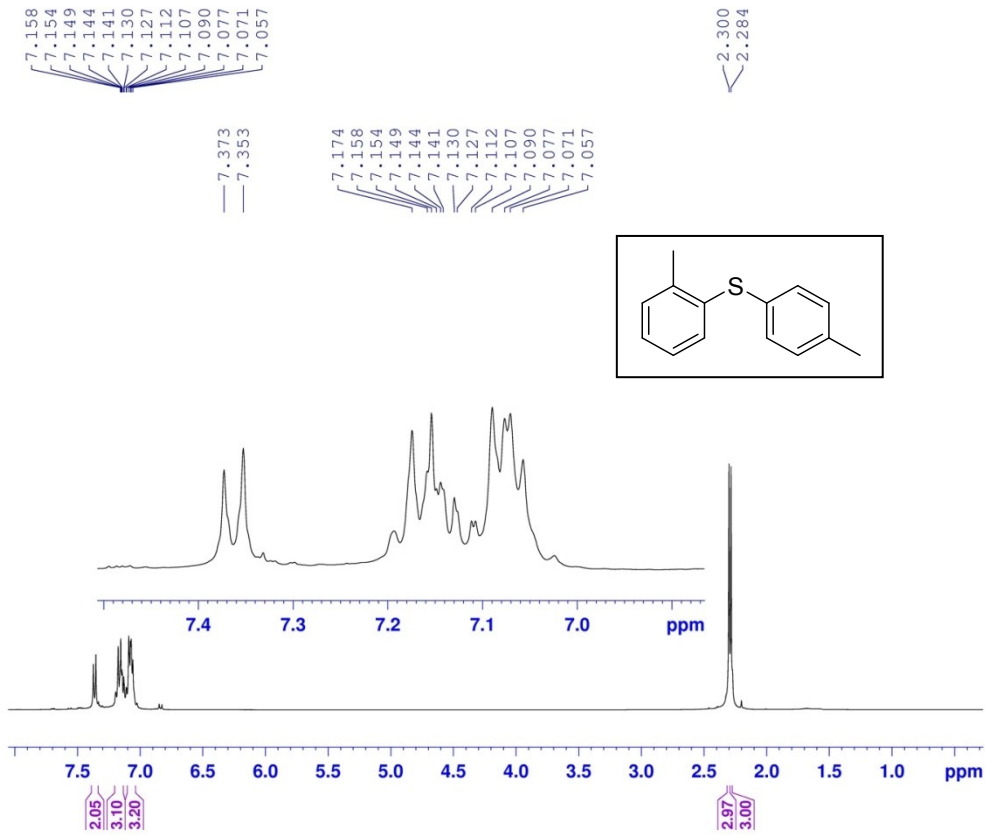
¹³C NMR of (3-methoxyphenyl)(4-methoxyphenyl)sulfide



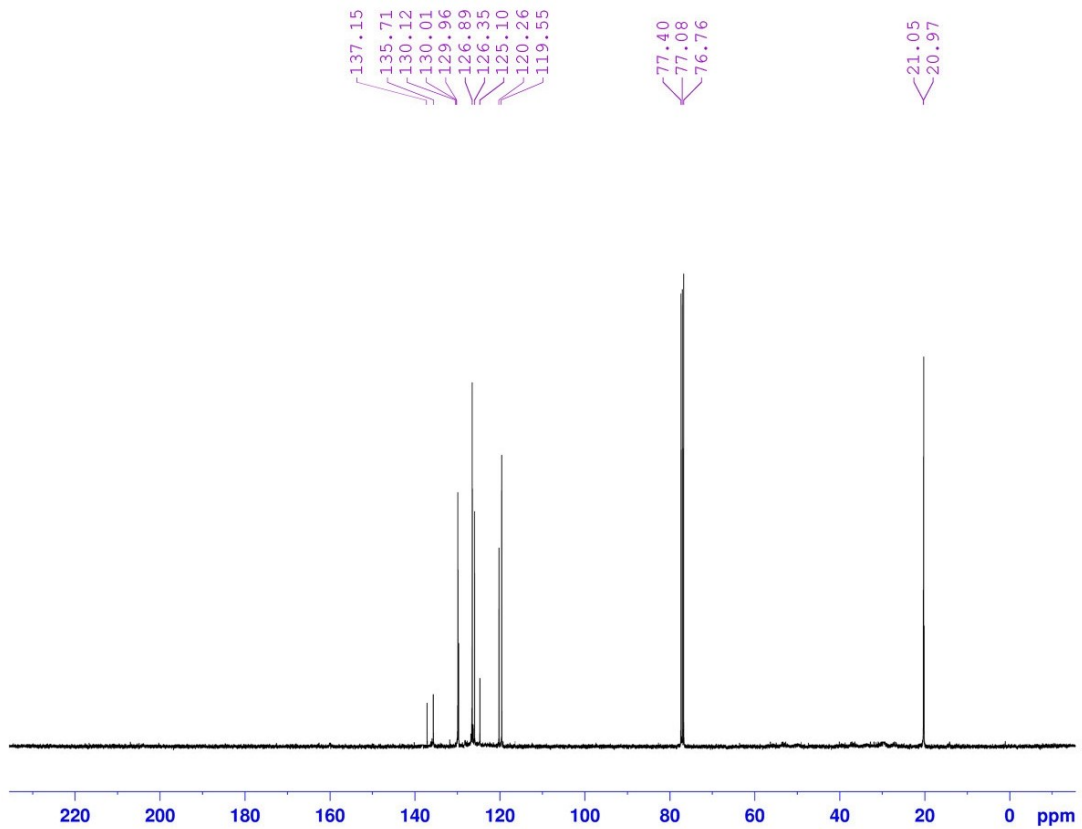
¹H NMR of 4-(*p*-tolylthio)benzaldehyde



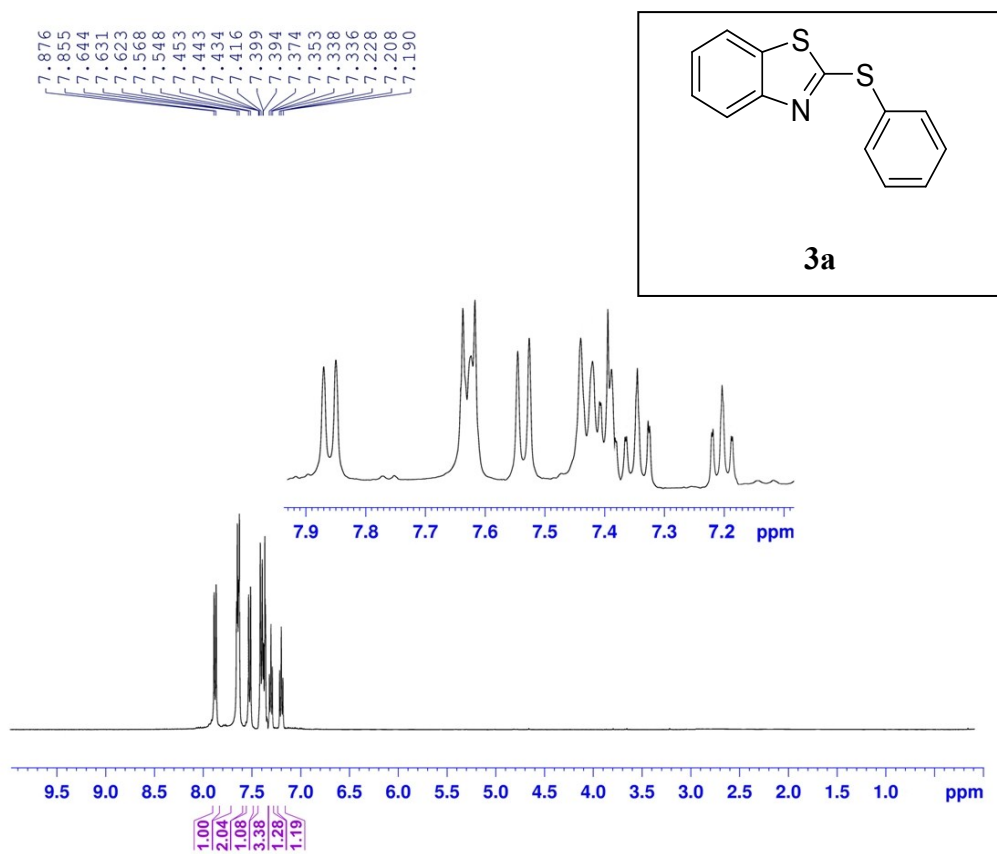
¹³C NMR of 4-(*p*-tolylthio)benzaldehyde



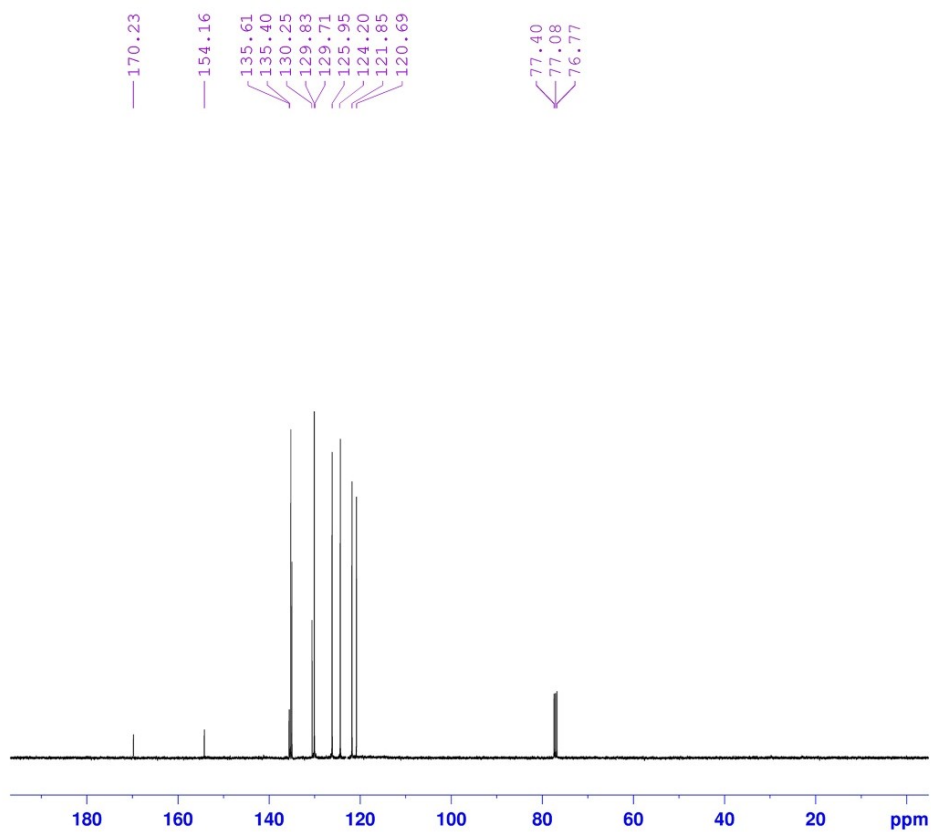
¹H NMR of *o*-tolyl(*p*-tolyl)sulfide



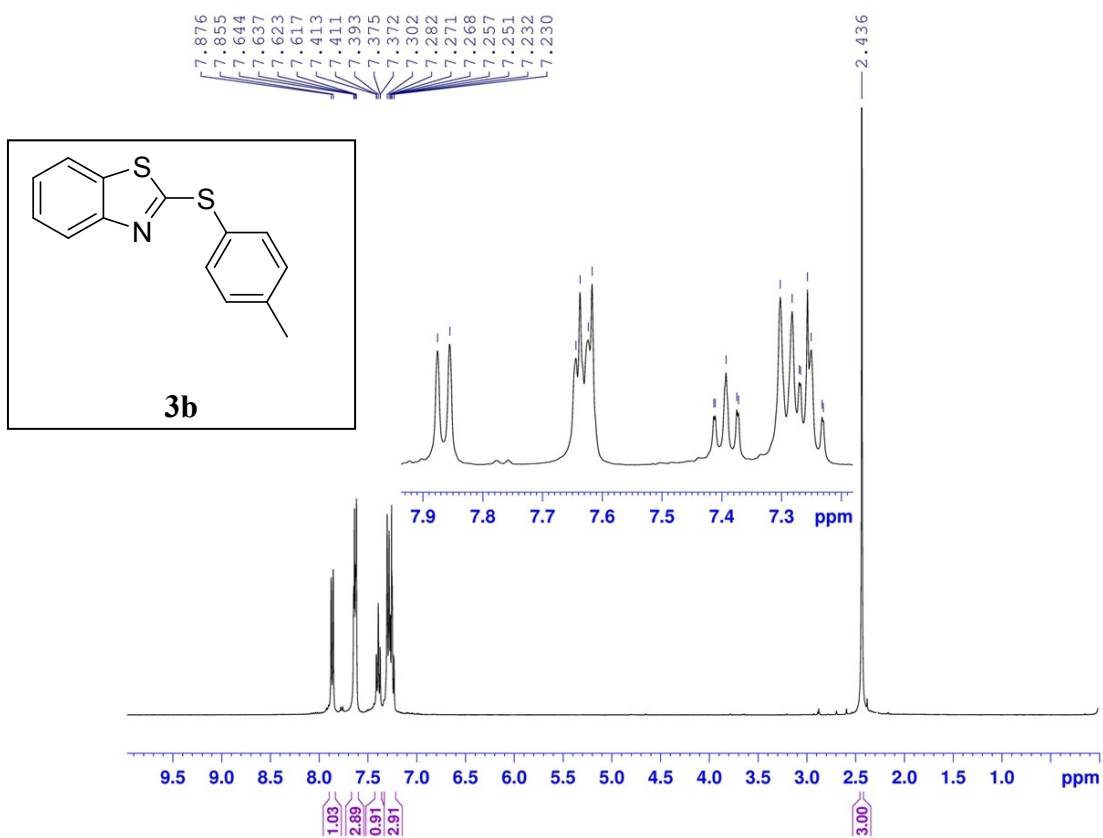
¹³C NMR of *o*-tolyl(*p*-tolyl)sulfide



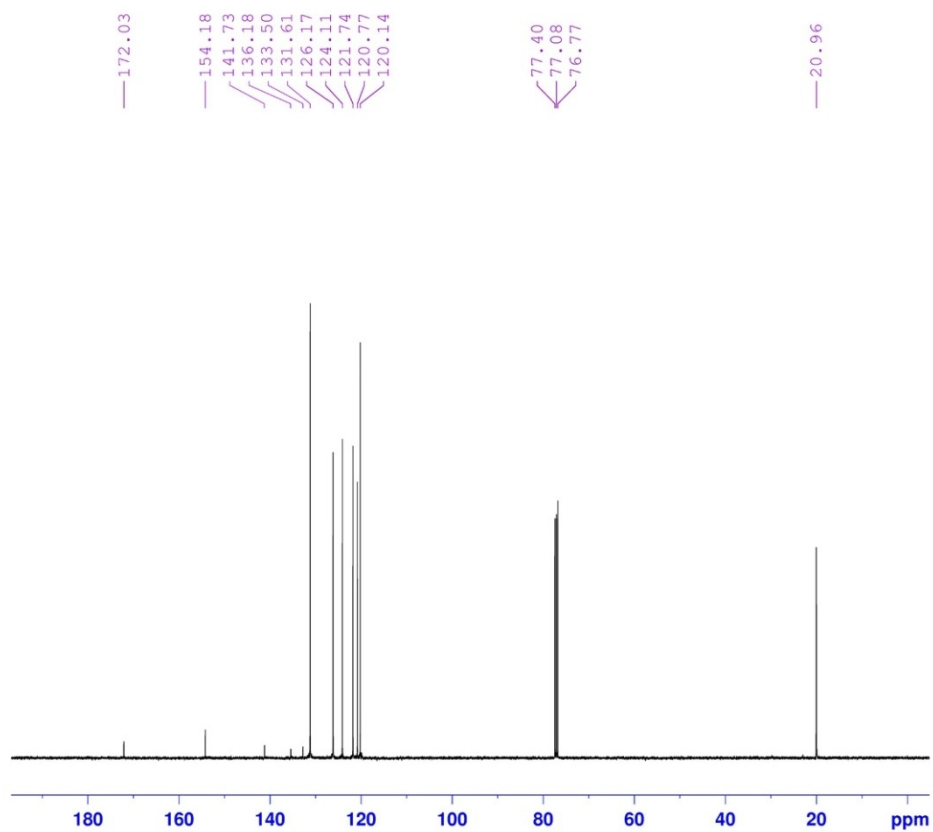
¹H NMR of 2-(phenylthio)benzo[*d*]thiazole



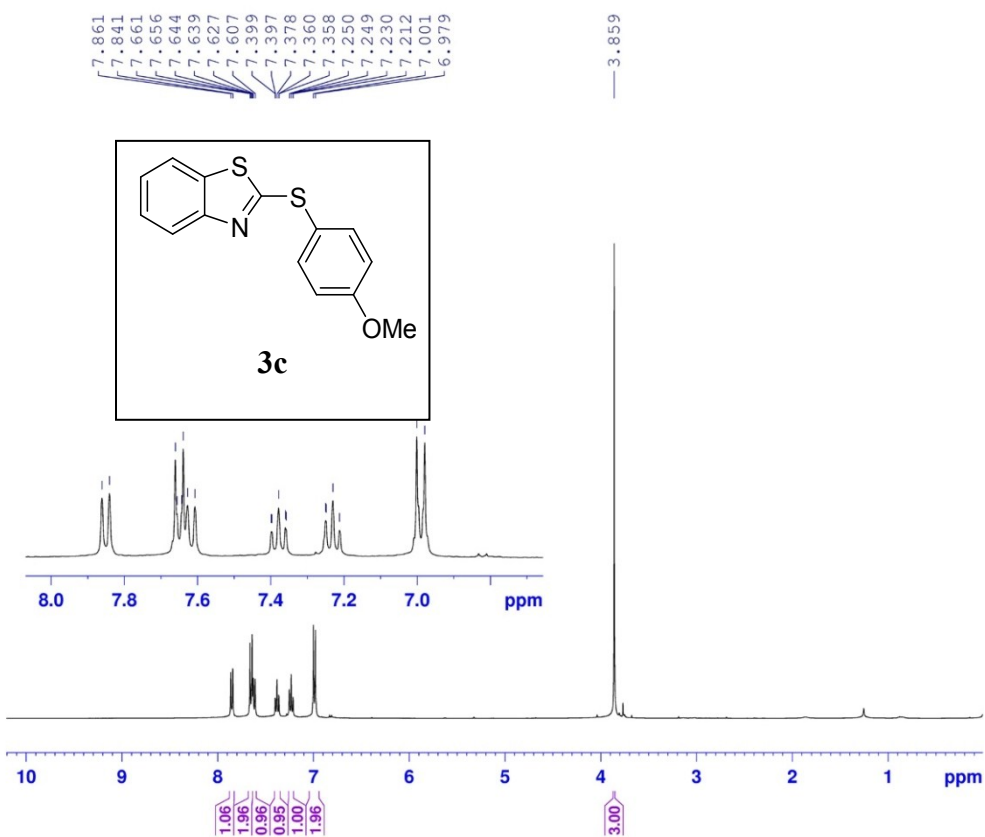
¹³C NMR of 2-(phenylthio)benzo[*d*]thiazole



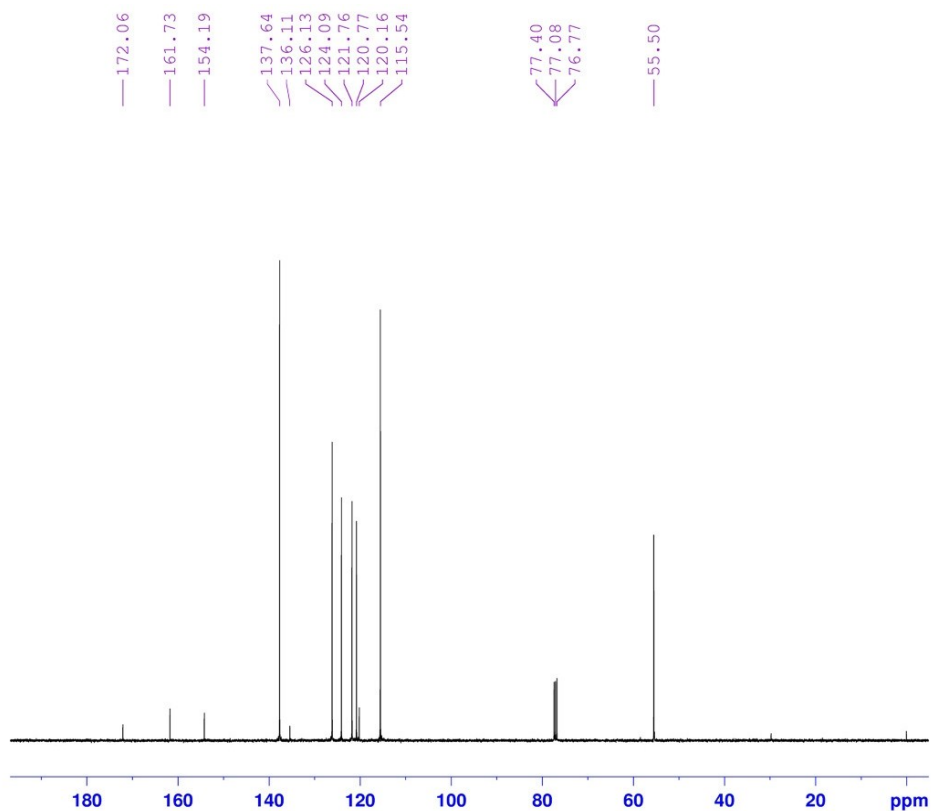
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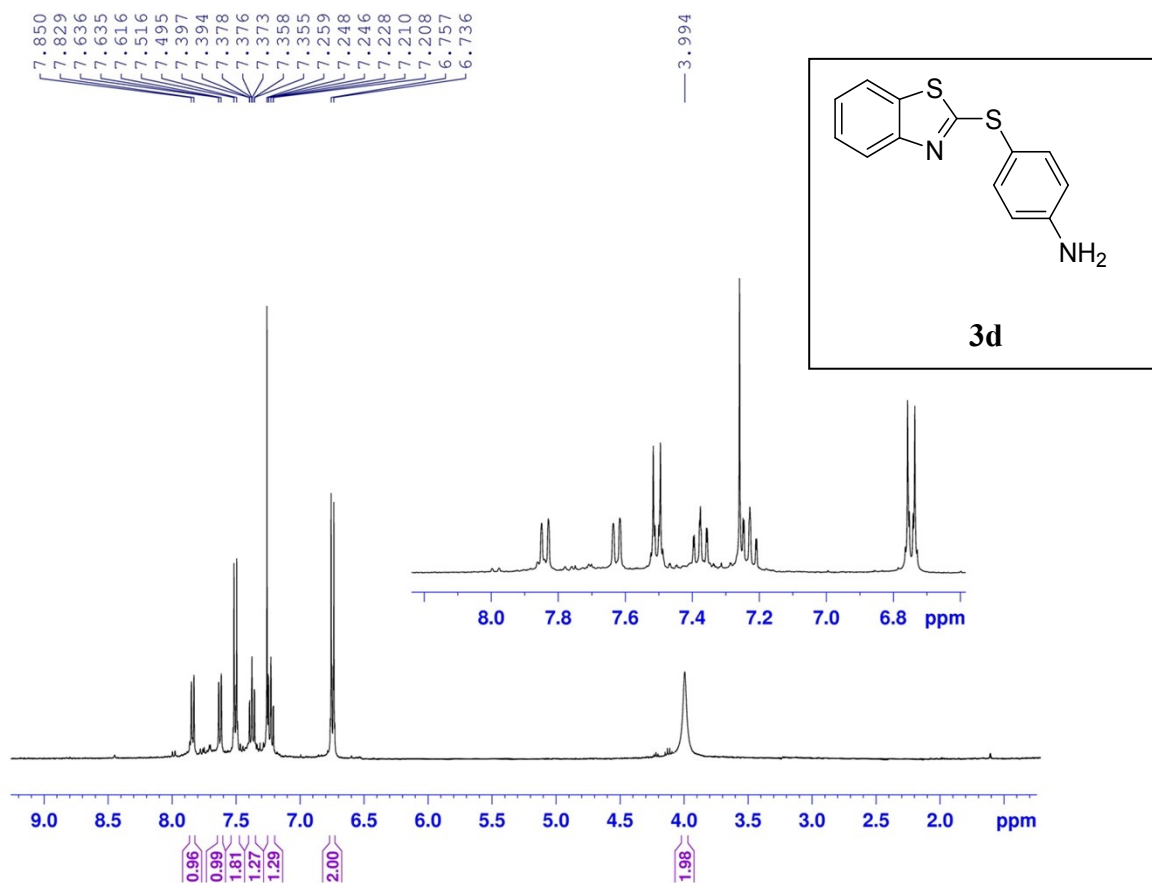
^{13}C NMR of 2-(*p*-tolylthio)benzo[*d*]thiazole



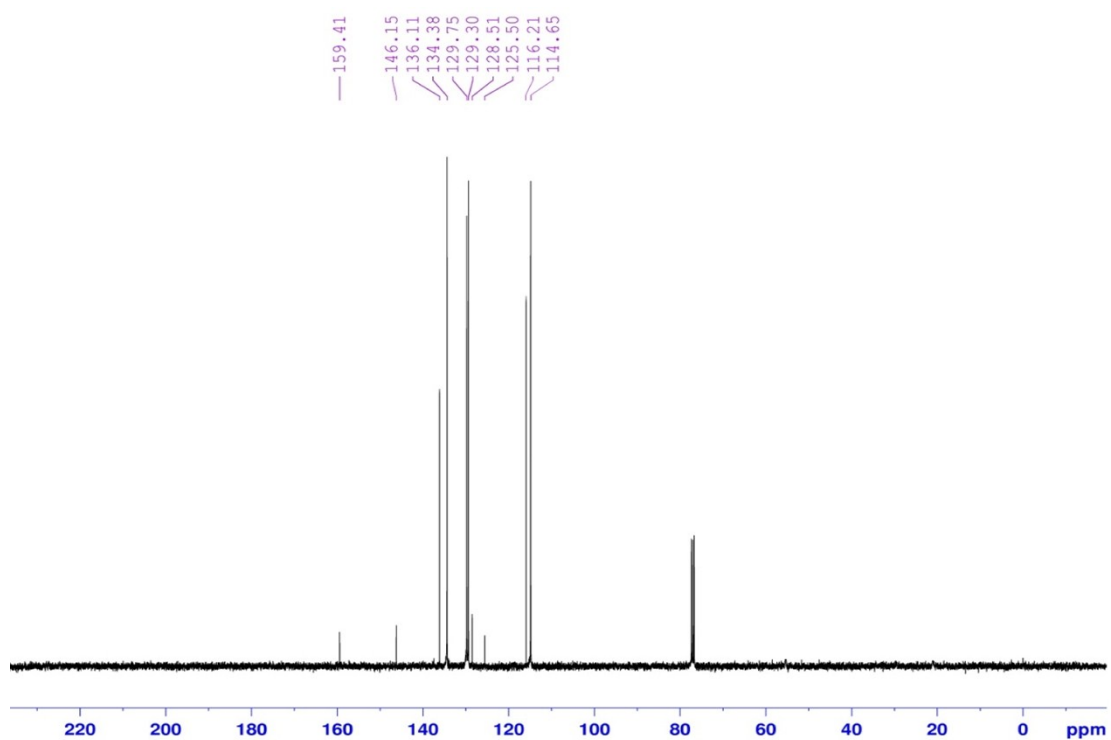
^1H NMR of 2-(4-methoxyphenylthio)benzo[*d*]thiazole



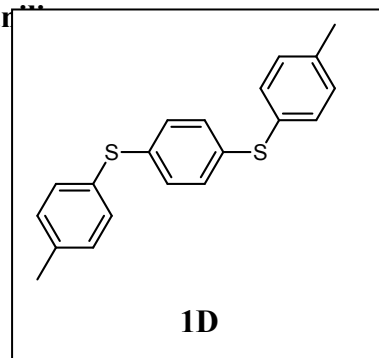
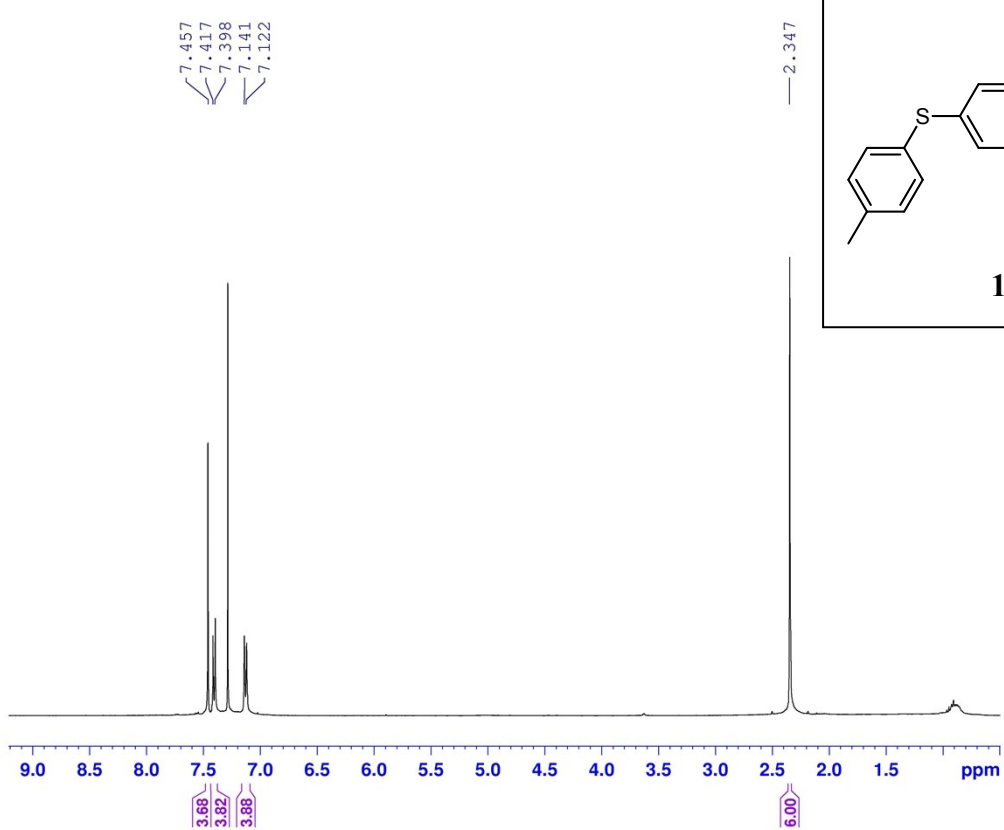
¹³C NMR of 2-(4-methoxyphenylthio)benzo[d]thiazole



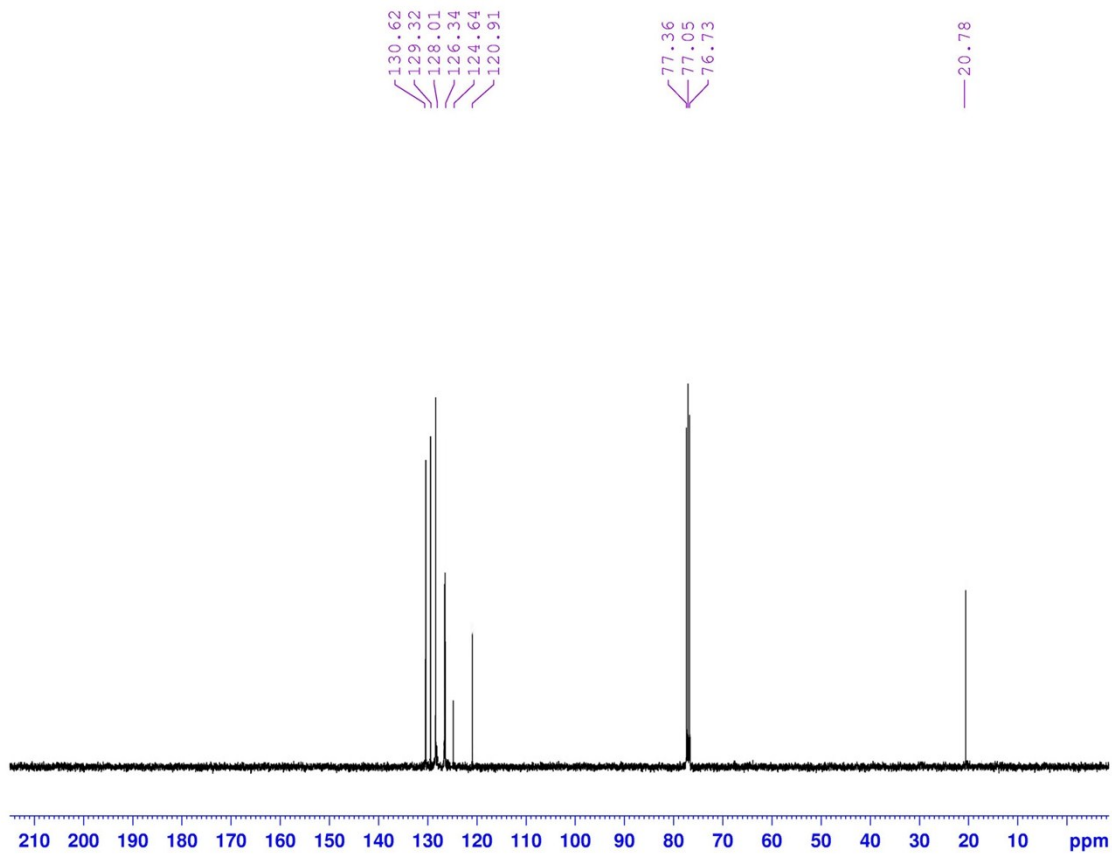
¹H NMR of 4-(benzo[d]thiazol-2-ylthio)aniline



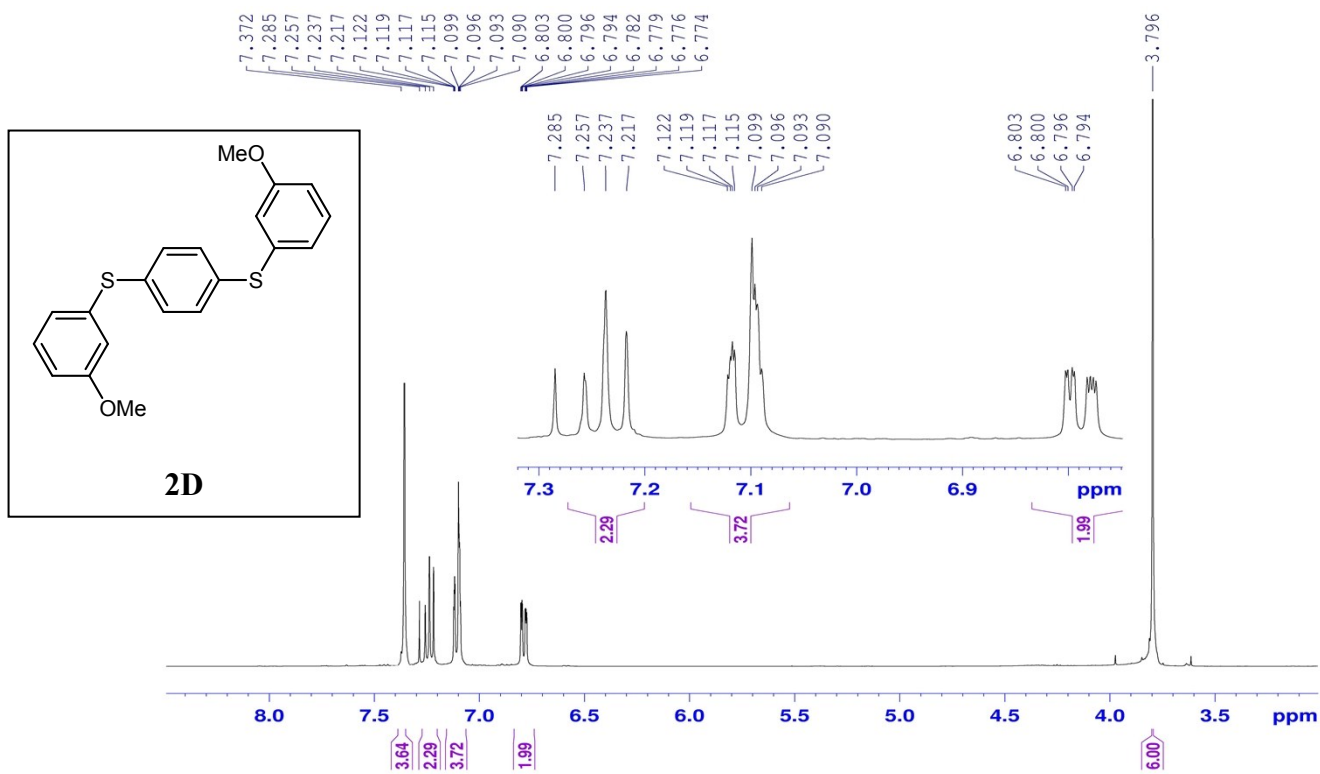
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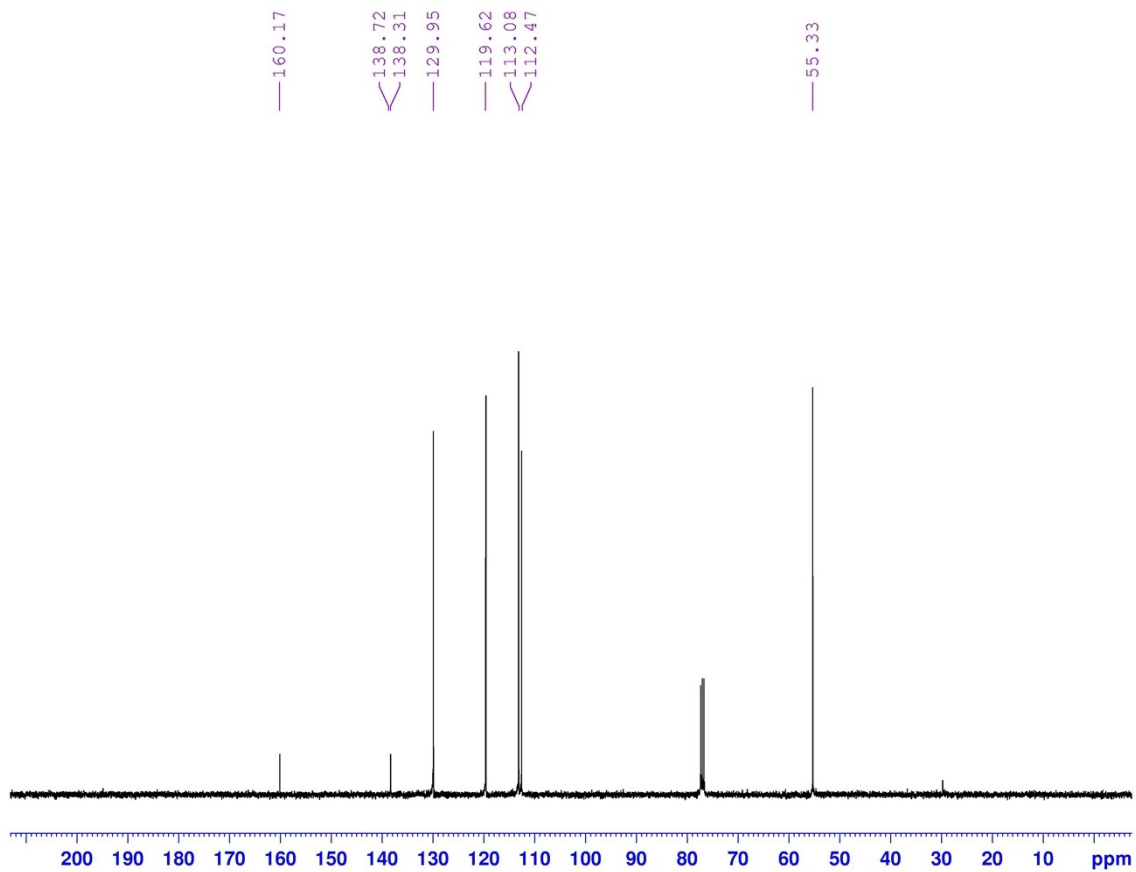
¹H NMR of 1,4-Bis(*p*-tolylthio)benzene



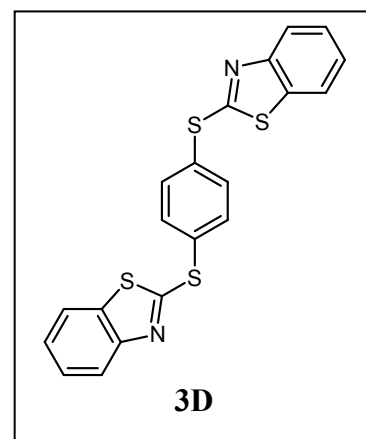
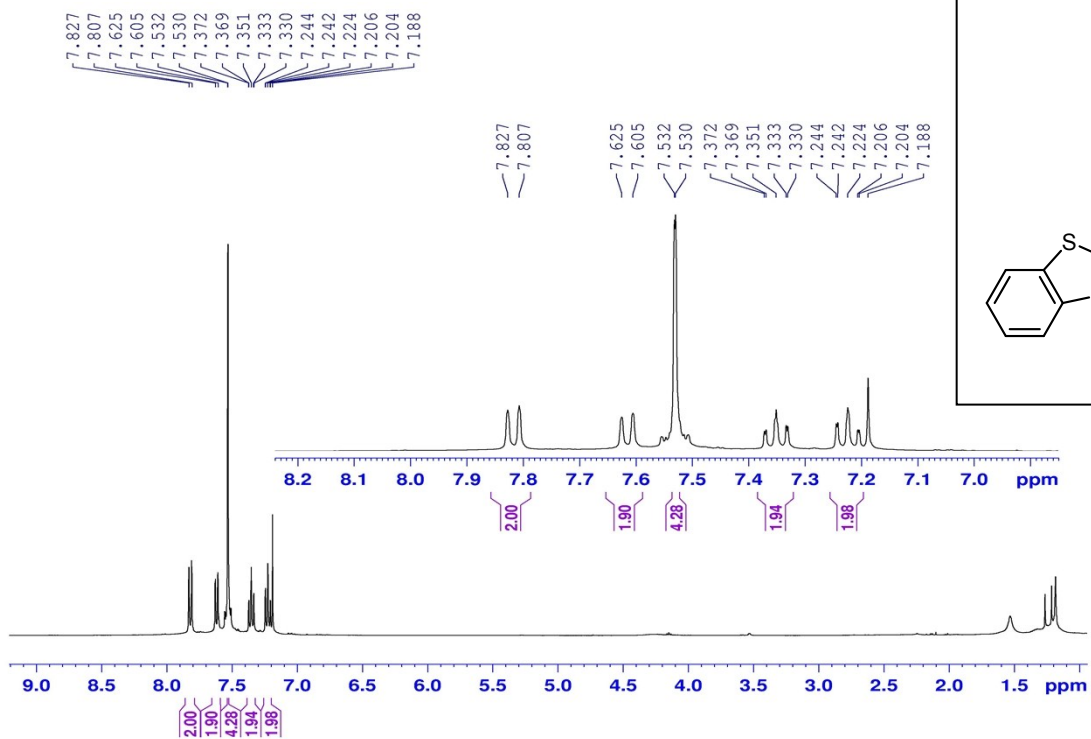
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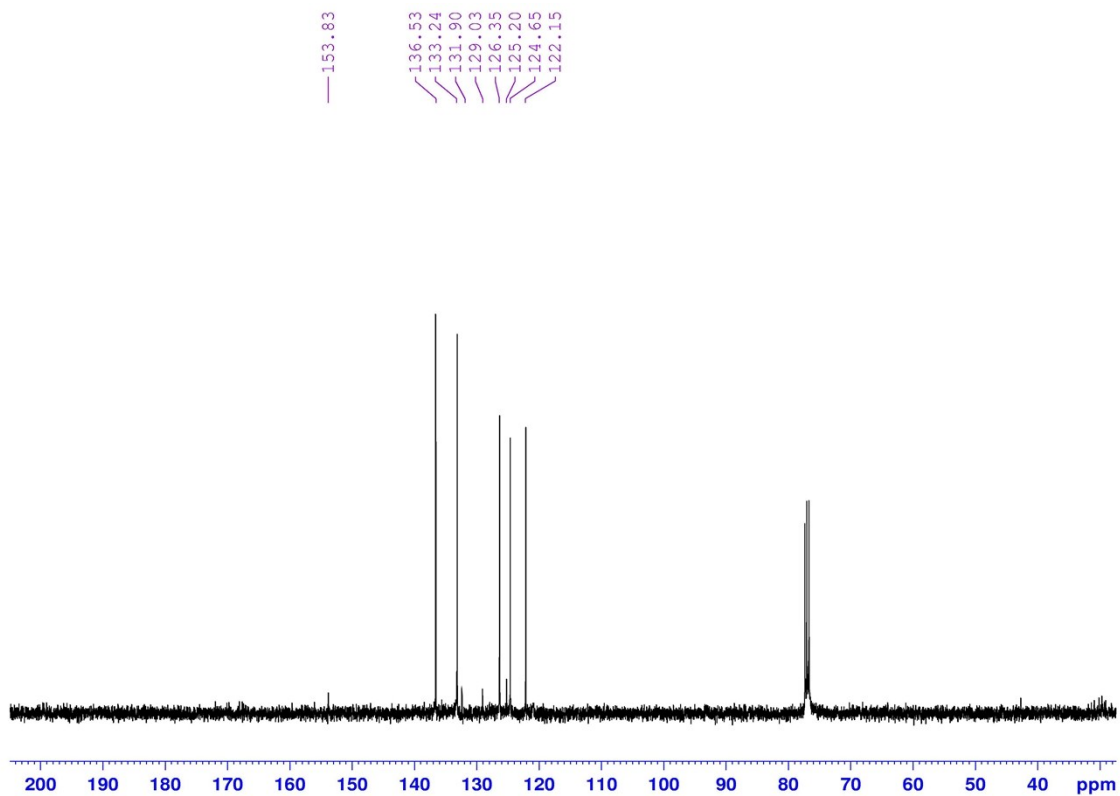
¹H NMR of 1,4-Bis((3-methoxyphenyl)thio)benzene



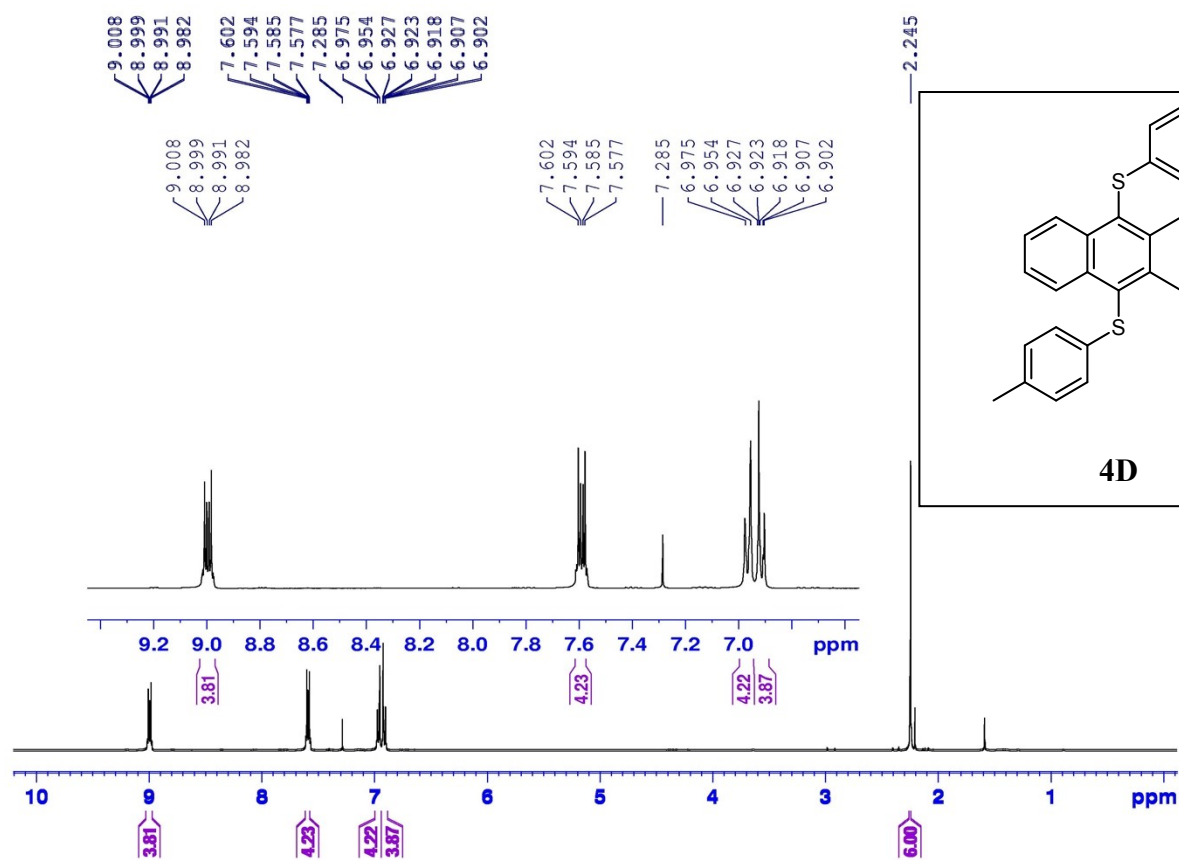
^{13}C NMR of 1,4-Bis((3-methoxyphenyl)thio)benzene



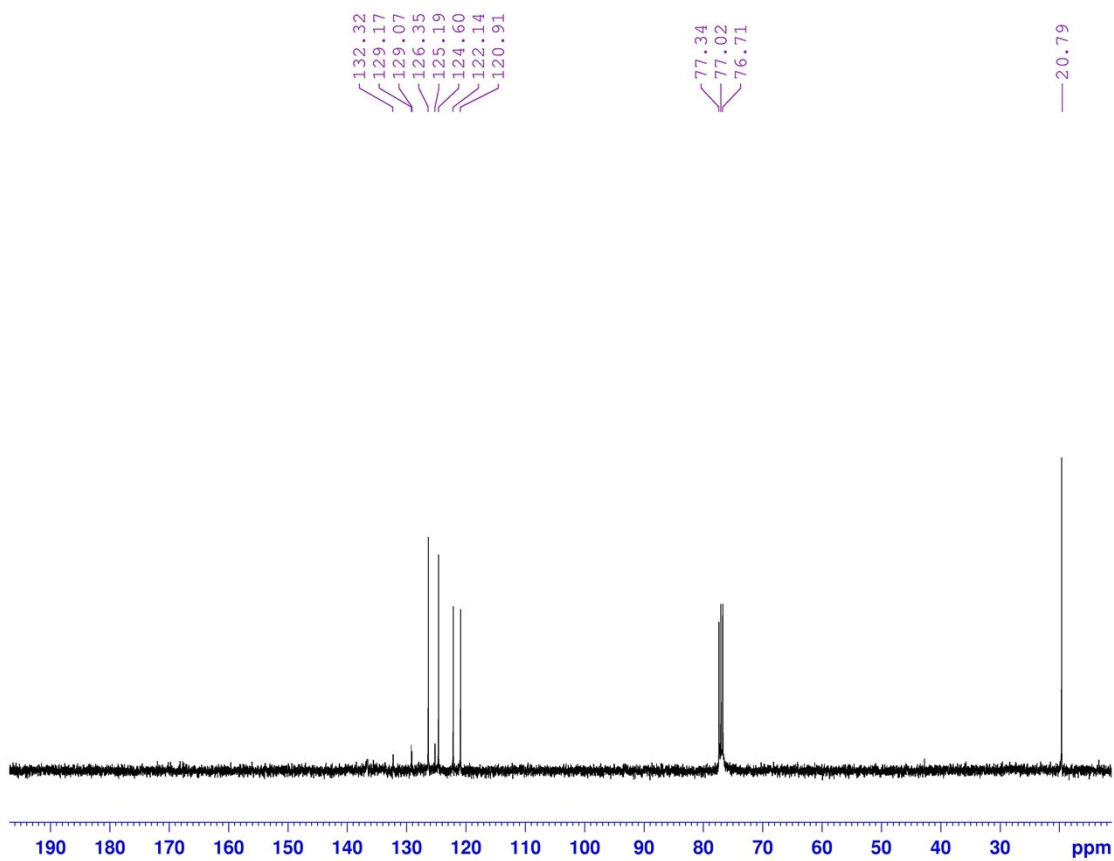
^1H NMR of 1,4-Bis(benzo[d]thiazol-2-ylthio)benzene



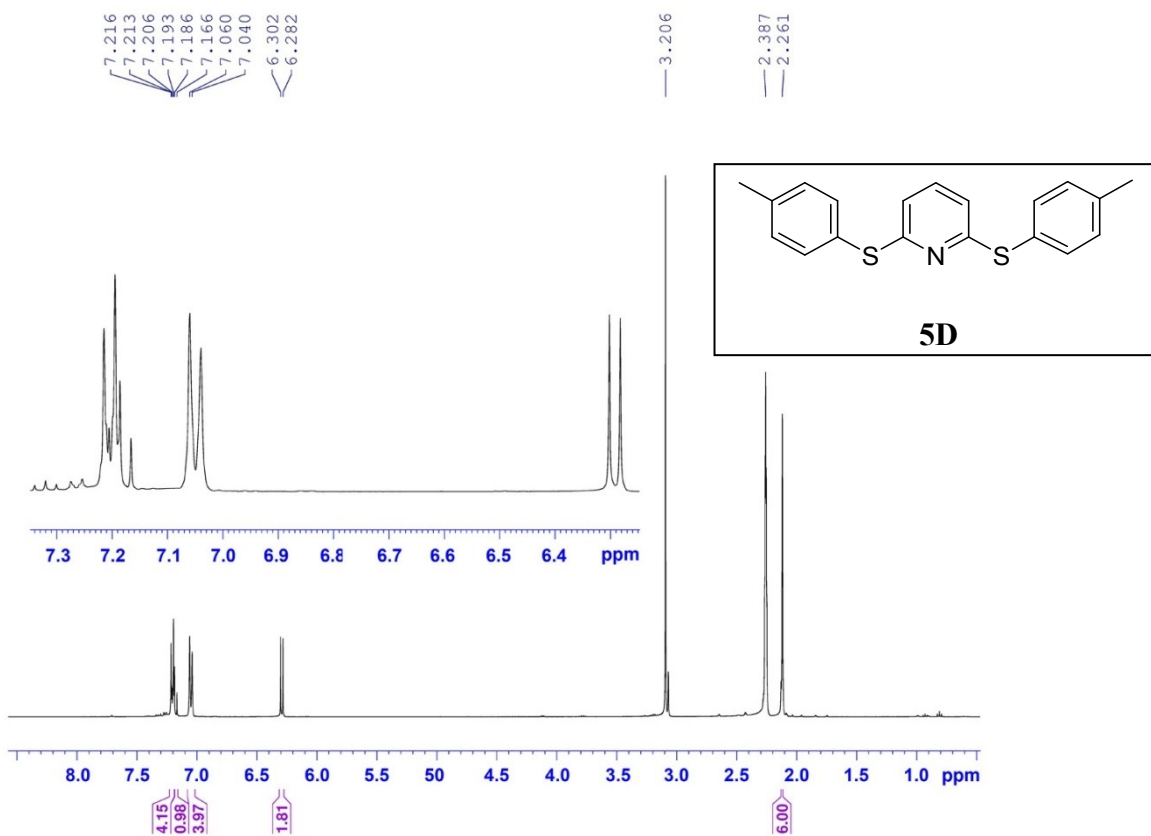
¹³C NMR of 1,4-Bis(benzo[d]thiazol-2-ylthio)benzene



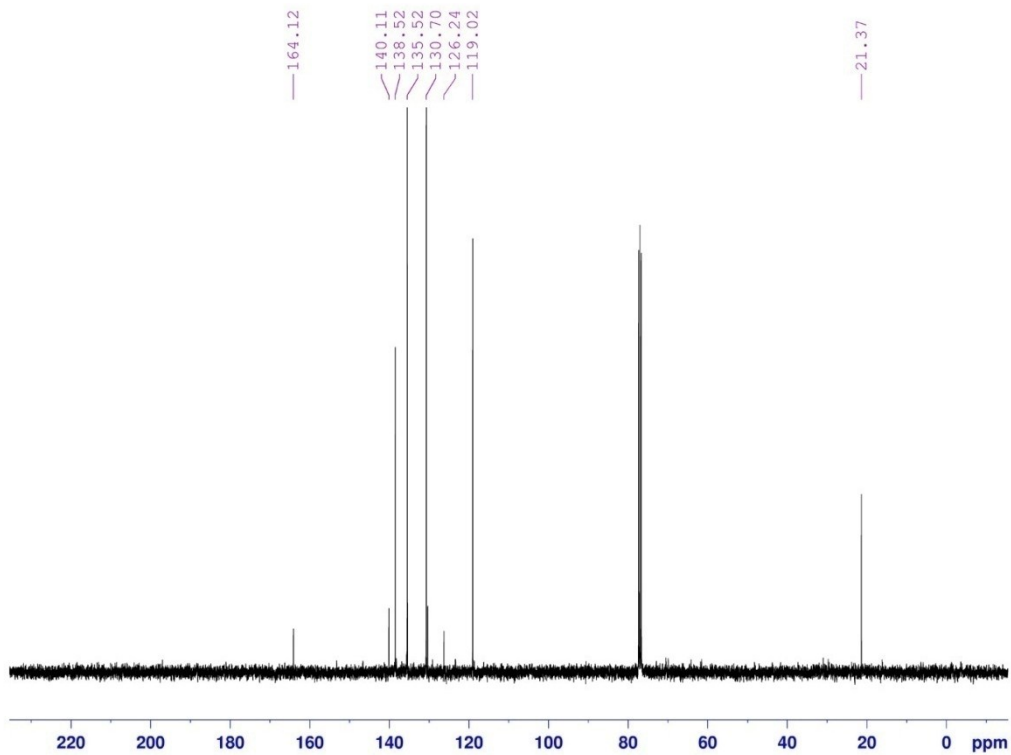
¹H NMR of 9,10-Bis(*p*-tolylthio)anthracene



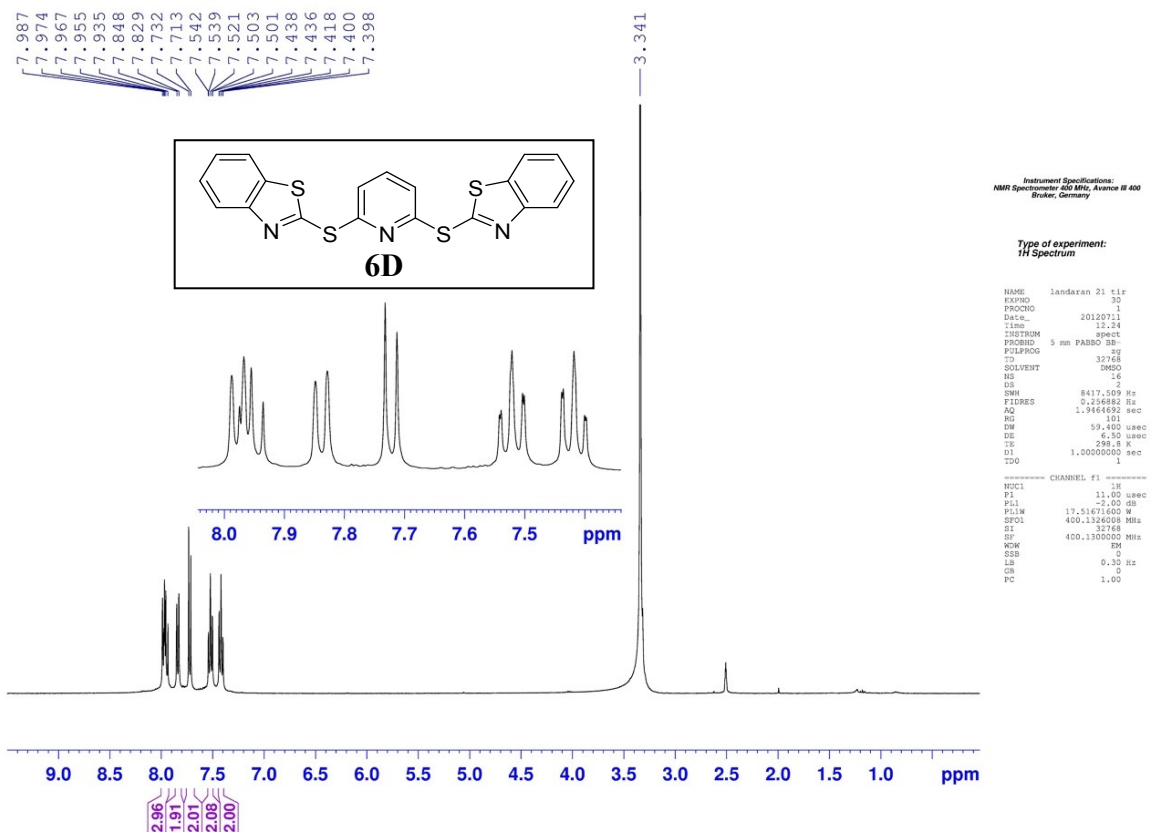
¹³C NMR of 9,10-Bis(*p*-tolylthio)anthracene



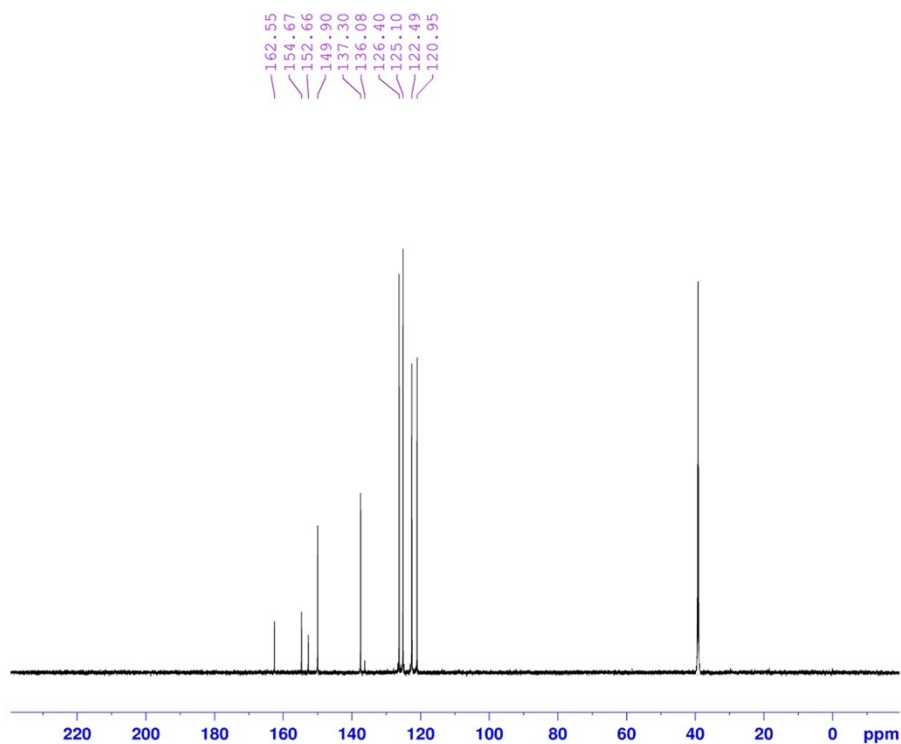
¹H NMR of 2,6-bis(benzo[*d*]thiazol-2-ylthio)pyridine



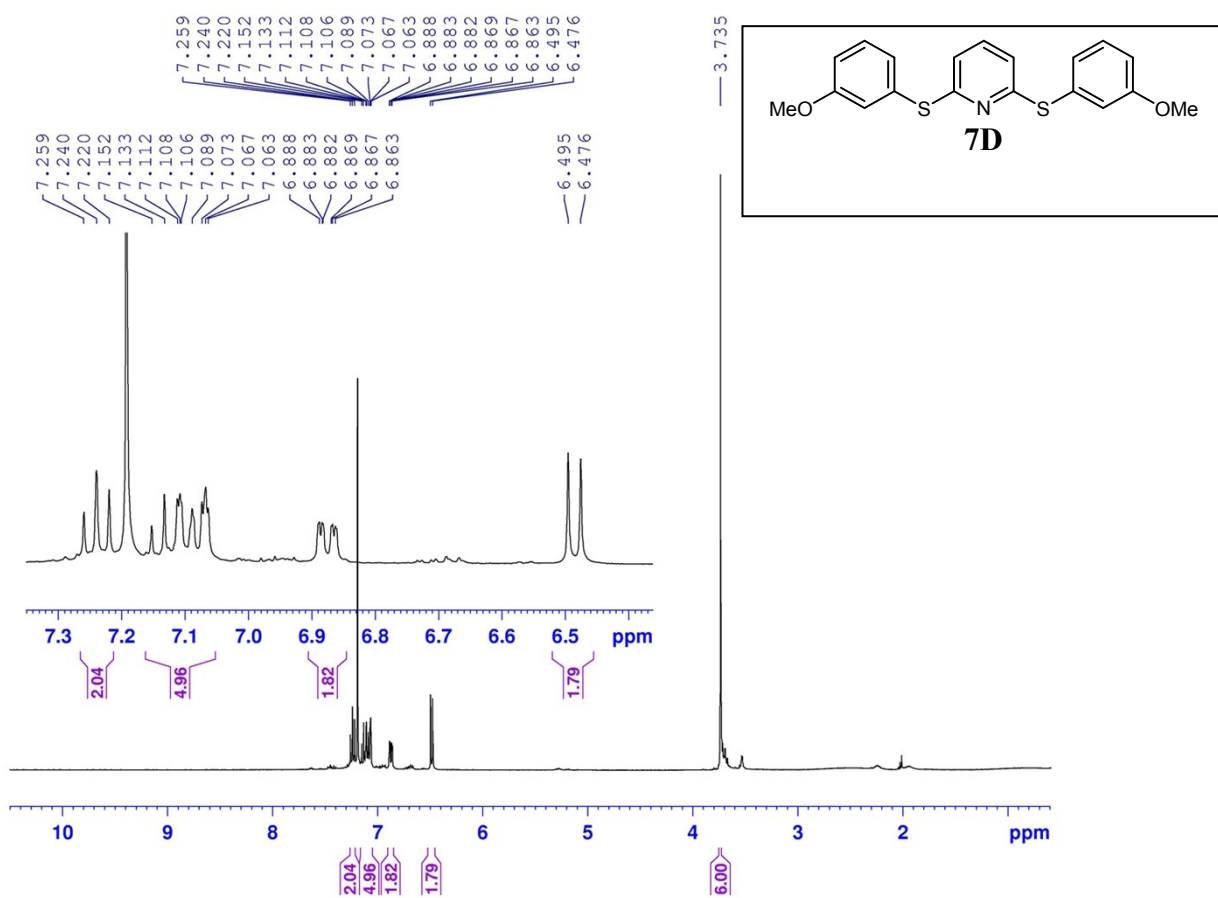
^{13}C NMR of 2,6-bis(*p*-tolylthio)pyridine



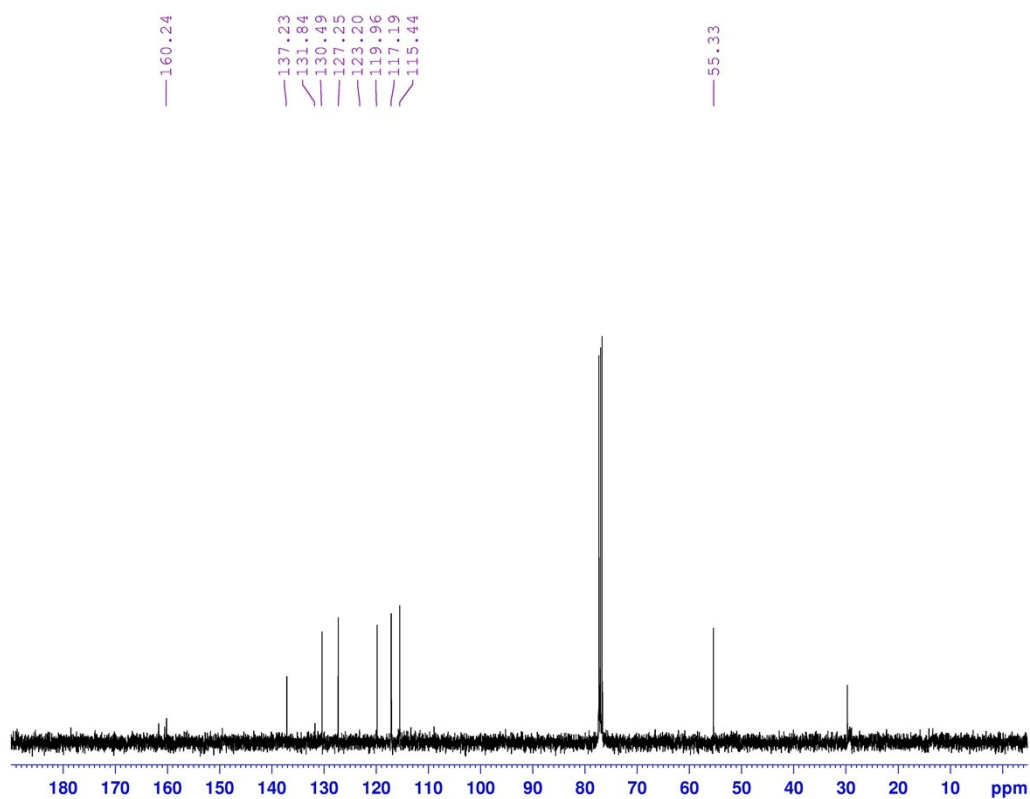
¹H NMR of 2,6-bis(benzo[*d*]thiazol-2-ylthio)pyridine



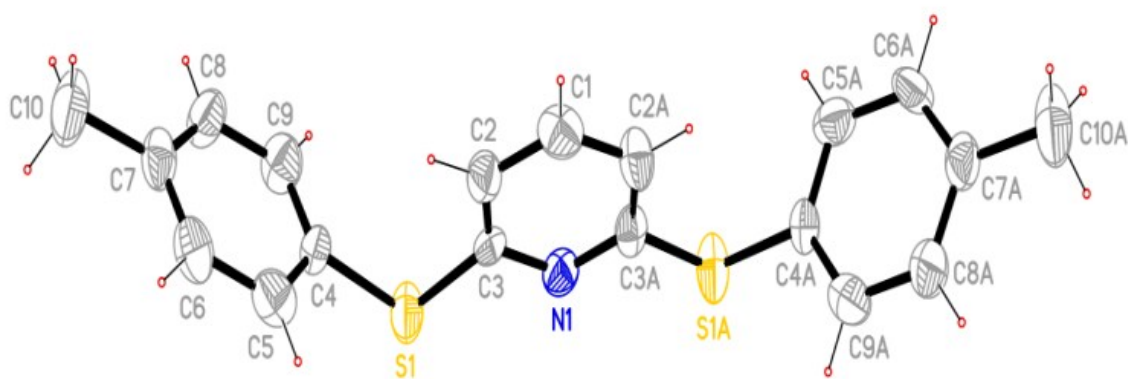
¹³C NMR of 2,6-bis(benzo[*d*]thiazol-2-ylthio)pyridine



^1H NMR of 2,6-Bis((3-methoxyphenyl)thio)pyridine



^{13}C NMR of 2,6-Bis((3-methoxyphenyl)thio)pyridine



4. Figure 1. X-ray crystal structure of 5D

5.**Table 1 Crystal Data and Structure Refinement for Compound 5D.**

| | |
|-----------------------------|--|
| Empirical formula | $C_{19}H_{17}NS_2$ |
| Formula weight | 323.45 |
| Temperature | 298(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, C2/c |
| Unit cell dimensions | $a = 12.837(3)$ Å $\alpha = 90^\circ$ $b = 8.8654(18)$ Å $\beta = 105.87(3)^\circ$ $c = 15.322(3)$ Å $\gamma = 90^\circ$ |
| Volume | 1677.2(6) Å ³ |
| Z, Calculated density | 4, 1.281 Mg/m ³ |
| Absorption coefficient | 0.313 mm ⁻¹ |
| F(000) | 680 |

| | |
|-----------------------------------|---|
| Crystal size | 0.21 x 0.11 x 0.09 mm |
| Theta range for data collection | 2.764 to 24.999° |
| Limiting indices | -15<=h<=15, -10<=k<=10, -18<=l<=18 |
| Reflections collected / unique | 3709 / 1435 [R(int) = 0.1340] |
| Completeness to theta = 24.999 | 96.5% |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 1435 / 0 / 102 |
| Goodness-of-fit on F ² | 1.215 |
| Final R indices [I>2sigma(I)] | R1 = 0.1168, wR2 = 0.1411 |
| R indices (all data) | R1 = 0.1915, wR2 = 0.1602 |
| Largest diff. peak and hole | 0.235 and -0.271 e.A ⁻³ |

6. REFERENCES

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