

Supplementary information

Reusable and efficient $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ /cationic 2,2'-bipyridyl system catalyzed S-arylation of aryl halides with thiols in water under air

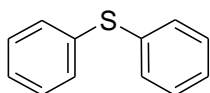
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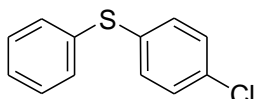
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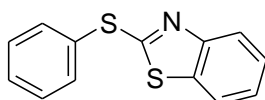
Diphenyl sulfide (4a)

Colorless oil. ^1H NMR (CDCl_3 , 200 MHz) $\delta = 7.22\text{--}7.36$ (m, 10H); ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 135.8$ (2C), 131.0 (4C), 129.1 (4C), 126.9 (2C).



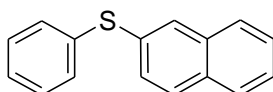
4-Chlorophenylphenyl sulfide (4b)

Colorless oil. ^1H NMR (CDCl_3 , 200 MHz) $\delta = 7.25\text{--}7.34$ (m, 9H); ^{13}C NMR (CDCl_3 , 50 MHz) $\delta = 127.4$, 129.2 (2C), 129.3 (2C), 131.3 (2C), 132.0, 132.9 (2C), 134.7, 135.1.



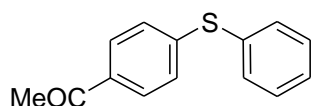
2-Phenylsulfanylbenzothiazole (4c)

Colorless oil. ^1H NMR (CDCl_3 , 200 MHz) $\delta = 7.25$ (d, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.46–7.52 (m, 3H), 7.64 (d, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 7.0$ Hz, 2H), 7.88 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR (CDCl_3 , 50 MHz) $\delta = 120.7$, 121.8, 124.2, 124.4, 126.0, 129.9 (2C), 130.3, 132.6, 135.2 (2C), 135.4, 153.8.



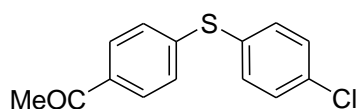
2'-Naphthalylphenyl sulfide (4d)

Pale yellow solid. Mp 50–51 °C (lit.² 51–52 °C). ^1H NMR (CDCl_3 , 200 MHz) $\delta = 7.25\text{--}7.49$ (m, 8H), 7.71–7.84 (m, 4H); ^{13}C NMR (CDCl_3 , 50 MHz) $\delta = 126.1$, 126.5, 127.0, 127.4, 127.7, 128.7, 128.8, 129.2 (2C), 129.8, 130.9 (2C), 132.2, 133.0, 133.8, 135.8.



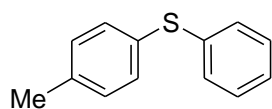
4-Phenylsulfanylacetophenone (4e)

Pale yellow solid. Mp 62–64 °C (lit.³ 62.6–63.6 °C). ¹H NMR (CDCl₃, 200 MHz) δ = 2.54 (s, 3H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.37–7.42 (m, 3H), 7.45–7.52 (m, 2H), 7.81 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ = 26.4, 127.5 (2C), 128.7 (2C), 128.8 (2C), 129.6, 132.1, 133.8 (2C), 134.5, 144.8, 197.0.



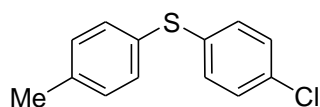
1-(4-(4-Chlorophenylthio)phenyl)ethanone (4f)

Pale orange solid. Mp 40–42 °C (lit.⁴ 40–42 °C). ¹H NMR (CDCl₃, 200 MHz) δ = 2.56 (s, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 4H), 7.83 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ = 26.3, 127.7 (2C), 128.8 (2C), 129.5 (2C), 130.4, 134.8 (2C), 143.7, 144.6, 147.8, 196.7.



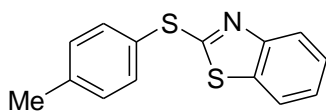
4-Tolylphenylsulfide (4g)

Pale yellow oil. ¹H NMR (CDCl₃, 200 MHz) δ = 2.33 (s, 3H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.16–7.24 (m, 5H), 7.27 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ = 21.1, 126.4, 129.0 (2C), 129.8 (2C), 130.0 (2C), 131.4, 132.2 (2C), 137.0, 137.5.



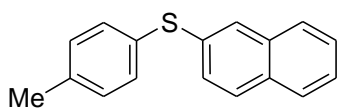
4'-Chlorophenyl-4-tolylsulfide (4h)

White solid. Mp 70–72 °C (lit.¹ 71.0–71 °C). ¹H NMR (CDCl₃, 200 MHz) δ = 2.33 (s, 3H), 7.11–7.17 (m, 4H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ = 21.1, 129.0 (2C), 130.1 (2C), 130.7, 130.9 (2C), 132.3, 132.7 (2C), 135.9, 138.0.



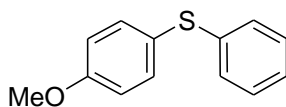
2-(*p*-Tolylthio)benzo[*d*]thiazole (4i)

White solid. Mp 70–72 °C (lit.⁵ 70–72 °C). ¹H NMR (CDCl₃, 200 MHz) δ = 2.38 (s, 3H), 7.15–7.24 (m, 3H), 7.33–7.36 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 3H), 7.83 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (CDCl₃, 50 MHz) δ = 21.5, 120.8, 121.8, 124.2, 126.1, 126.2, 130.8 (2C), 135.4, 135.6 (2C), 141.1, 154.0, 170.8.



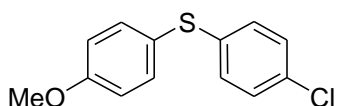
2'-Naphthalyl-4-tolylsulfide (4j)

White solid. Mp 66–67 °C (lit.¹ 66–67 °C). ¹H NMR (CDCl₃, 200 MHz) δ = 2.28 (s, 3H), 7.05–7.73 (m, 11H); ¹³C NMR (CDCl₃, 50 MHz) δ = 21.1, 125.7, 126.2, 126.6, 126.7, 127.4, 127.7, 127.9, 128.4, 128.9 (2C), 130.0 (2C), 132.1, 132.5, 133.5, 134.3.



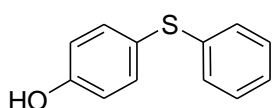
1-Methoxy-4-phenylthiobenzene (4k)

Colorless oil.⁶ ¹H NMR (CDCl₃, 200 MHz) δ = 3.81 (s, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.10–7.16 (m, 3H), 7.20–7.22 (m, 2H), 7.40 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ = 55.3, 114.9 (2C), 124.2, 125.7, 128.2 (2C), 128.8 (2C), 135.3 (2C), 138.6, 159.7.



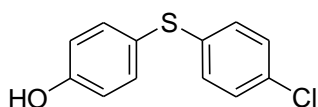
4'-Chlorophenyl-4-methoxyphenylsulfide (4l)

White solid. Mp 60–62 °C (lit.⁷ 60.5–61.5 °C). ¹H NMR (CDCl₃, 200 MHz) δ = 3.83 (s, 3), 6.90 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ = 55.4, 115.1 (2C), 128.9, 129.4 (2C), 132.1 (2C), 132.5 (2C), 132.8, 133.4, 159.2.



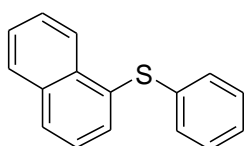
4-Phenylsulfanylphenol (4m)

Colorless oil.⁸ ¹H NMR (CDCl₃, 200 MHz) δ = 4.81 (s, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 7.14–7.18 (m, 3H), 7.21–7.26 (m, 2H), 7.36 (d, *J* = 8.6 Hz, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ = 116.5 (2C), 124.6, 125.9, 128.3 (2C), 128.9 (2C), 135.3 (2C), 138.4, 155.7.



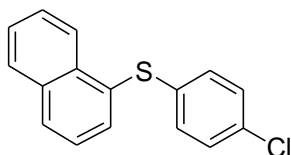
4-(4-Chlorophenylthio)phenol (4n)

Pale yellow solid. Mp 54–55 °C (lit.⁹ 54–55 °C). ¹H NMR (CDCl₃, 200 MHz) δ = 5.11 (s, 1H), 6.61 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 9.0 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ = 116.6 (2C), 129.0, 129.5 (2C), 132.6, 133.3 (2C), 135.5 (2C), 138.4, 156.0.



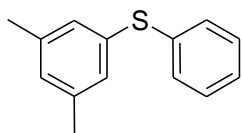
1-Naphthylphenylsulfide (4o)

Colorless oil.¹⁰ ¹H NMR (CDCl₃, 200 MHz) δ = 7.12–7.23 (m, 5H), 7.42 (d, J = 8.4 Hz, 1H), 7.49–7.53 (m, 2H), 7.66 (d, J = 8.4 Hz, 1H), 7.83–7.87 (m, 2H), 8.35–8.37 (m, 1H); ¹³C NMR (CDCl₃, 50 MHz) δ = 125.5, 125.8, 126.1, 126.4, 126.9, 128.5, 129.0 (2C), 129.1 (2C), 129.2, 131.2, 132.5, 133.6, 134.3, 136.7.



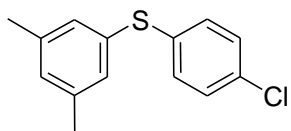
4-Chlorophenyl-1-naphthylsulfide (4p)

Colorless oil.⁹ ¹H NMR (CDCl₃, 200 MHz) δ = 7.04 (d, J = 8.8 Hz, 2H), 7.14 (d, J = 8.8 Hz, 2H), 7.37–7.75 (m, 3H), 7.66 (d, J = 7.0 Hz, 1H), 7.83–7.88 (m, 2H), 8.29–8.34 (m, 1H); ¹³C NMR (CDCl₃, 50 MHz) δ = 125.8 (2C), 126.5, 127.1, 129.1 (2C), 129.6, 129.9 (2C), 130.5, 131.9, 132.9 (2C), 133.6, 134.8, 135.7.



3,5-Dimethylphenylphenylsulfide (4q)

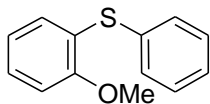
Colorless oil.¹¹ ¹H NMR (CDCl₃, 200 MHz) δ = 2.26 (s, 6H), 6.88 (s, 1H), 6.99 (s, 2H), 7.24–7.34 (m, 5H); ¹³C NMR (CDCl₃, 50 MHz) δ = 21.2 (2C), 126.7, 129.1 (2C), 129.2 (2C), 129.3, 130.6 (2C), 134.9 (2C), 136.5, 138.9 (2C).



1-[(4-Chlorophenyl)thio]-3,5-dimethylbenzene (4r)

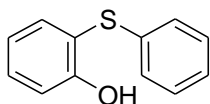
Colorless oil.¹² ¹H NMR (CDCl₃, 200 MHz) δ = 2.27 (s, 6H), 6.90 (s, 1H), 6.98 (s, 2H), 7.24 (d, J =

1.8 Hz, 4H); ^{13}C NMR (CDCl_3 , 50 MHz) δ = 21.2 (2C), 129.2, 129.4 (2C), 129.5 (2C), 131.6 (2C), 132.6, 134.2, 135.3, 139.1 (2C).



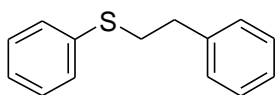
1-Methoxy-2-(phenylthio)benzene (4s)

Colorless oil. ^1H NMR (CDCl_3 , 200 MHz) δ = 3.82 (s, 3H), 6.85–6.91 (m, 2H), 7.07 (d, J = 7.6 Hz, 1H), 7.20–7.26 (m, 2H), 7.27–7.32 (m, 4H); ^{13}C NMR (CDCl_3 , 50 MHz) δ = 55.9, 110.8, 121.2, 124.0, 127.1, 128.1, 129.3 (2C), 131.4 (2C), 131.8, 134.5, 157.0.



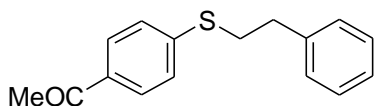
2-Phenylsulfanyphenol (4t)

Colorless oil. ^1H NMR (CDCl_3 , 200 MHz) δ = 6.44 (s, 1H), 6.83 (t, J = 6.2 Hz, 1H), 6.95–7.07 (m, 4H), 7.12 (m, 2H), 7.28 (m, 1H), 7.40 (d, J = 5.6 Hz, 1H); ^{13}C NMR (CDCl_3 , 50 MHz) δ = 115.5, 116.0, 121.3, 126.1, 126.9, 129.1 (2C), 132.3 (2C), 135.8, 136.9, 157.0.



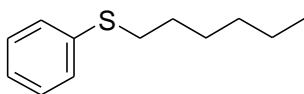
Phenethylphenylsulfide (4u)

Pale yellow oil. ^1H NMR (CDCl_3 , 200 MHz) δ = 2.98 (t, J = 7.7 Hz, 2H), 3.25 (t, J = 7.8 Hz, 2H), 7.13–7.38 (m, 10H); ^{13}C NMR (CDCl_3 , 50 MHz) δ = 35.4, 37.0, 125.8, 126.6, 127.1 (2C), 128.5 (2C), 128.9 (2C), 129.0 (2C), 136.4, 139.5.



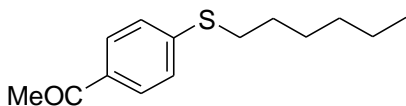
1-(4-(Phenethylthio)phenyl)ethanone (4v)

Pale yellow solid. Mp 48–50 °C. ^1H NMR (CDCl_3 , 400 MHz) δ = 2.55 (s, 3H), 2.97 (t, J = 8.0 Hz, 2H), 3.23 (t, J = 8.0 Hz, 2H), 7.20–7.25 (m, 3H), 7.29–7.33 (m, 4H), 7.85 (d, J = 8.8 Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ = 26.3, 33.4, 35.1, 126.5 (2C), 126.6, 128.4 (2C), 128.5 (2C), 128.7 (2C), 133.9, 139.6, 144.1, 197.0. Found: C, 74.86; H, 6.49.; S, 12.19. Calcd. for $\text{C}_{16}\text{H}_{16}\text{OS}$: C, 74.96; H, 6.29. S, 12.51.



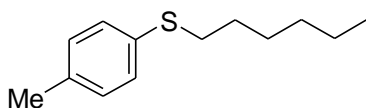
Hexylphenylsulfide (4w)

Pale yellow oil. ^1H NMR (CDCl_3 , 400 MHz) δ = 0.88 (t, J = 6.6 Hz, 3H), 1.23–1.33 (m, 4H), 1.38–1.46 (m, 2H), 1.60–1.68 (m, 2H), 2.91 (t, J = 7.2 Hz, 2H), 7.13–7.17 (m, 1H), 7.24–7.33 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz) δ = 14.0, 22.5, 28.5, 29.2, 31.4, 33.7, 125.6, 128.8 (2C), 128.9 (2C), 137.1. Found: C, 74.61; H, 9.48.; S, 16.39. Calcd. for $\text{C}_{12}\text{H}_{18}\text{S}$: C, 74.16; H, 9.34.; S, 16.50.



1-(4-(Hexylthio)phenyl)ethanone (4x)

Pale yellow solid. Mp 69–71 °C. ^1H NMR (CDCl_3 , 400 MHz) δ = 0.91 (t, J = 6.8 Hz, 3H), 1.29–1.36 (m, 4H), 1.43–1.50 (m, 2H), 1.67–1.74 (m, 2H), 2.56 (s, 3H), 2.99 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ = 13.7, 22.3, 26.1, 28.3, 28.5, 31.1, 31.7, 126.0 (2C), 128.4 (2C), 133.5, 137.6, 196.6. HRMS calcd for $\text{C}_{14}\text{H}_{20}\text{OS}$, 236.1236; found, 236.1235.



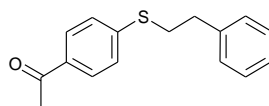
Hexyl(*p*-tolyl)sulfane (4y)

Colorless oil.¹⁵ ¹H NMR (CDCl₃, 200 MHz) δ = 0.86 (t, *J* = 6.5 Hz, 3H), 1.16–1.49 (m, 6H), 1.52–1.69 (m, 2H), 2.35 (s, 3H), 2.81 (t, *J* = 7.3 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H); ¹³C NMR (CDCl₃, 50 MHz): δ 13.9, 21.4, 22.6, 28.4, 29.0, 31.2, 34.3, 128.1 (2C), 129.5 (2C), 131.7, 136.0.

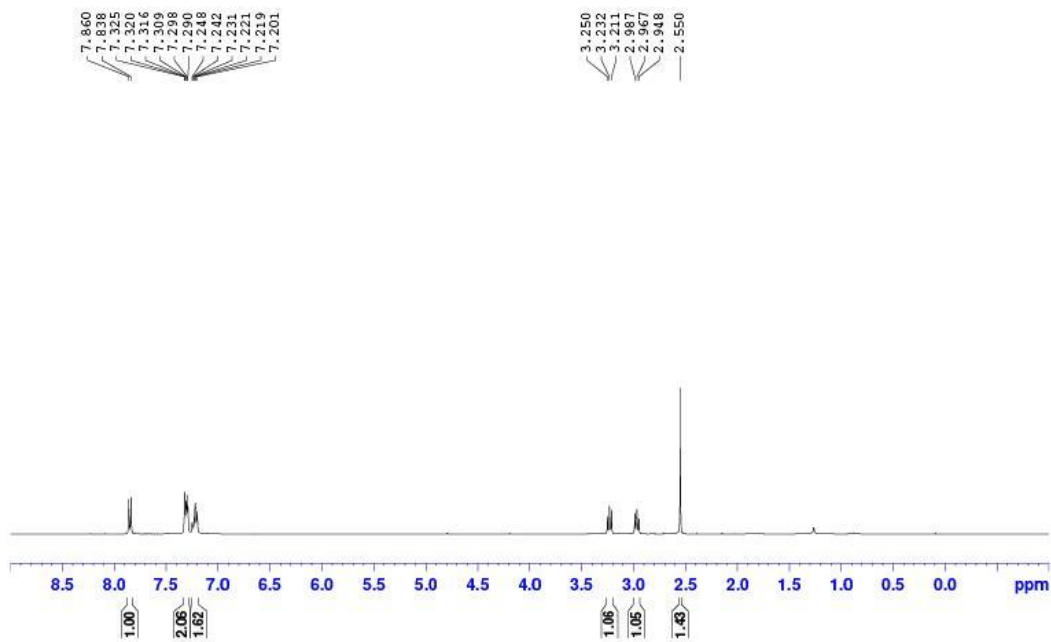
References

- [1] W.-Y. Wu, J.-C. Wang, F.-Y. Tsai, *Green Chem.* **2009**, *11*, 326–329.
- [2] C.-F. Fu, Y.-H. Liu, S.-M. Peng, S.-T. Liu, *Tetrahedron*, **2010**, *66*, 2119-2122..
- [3] Y. Feng, H. Wang, F. Sun, Y. Li, X. Fu, K. Jin, *Tetrahedron*, **2009**, *65*, 9737-9741.
- [4] M. J. Gorczynski, R. M. Leal, S. L. Mooberry, J. H. Bushwillwe, M. L. Brown, *Bioorg. Med. Chem.* **2004**, *12*, 1029–1036.
- [5] S. Murru, H. Ghosh, S. K. Sahoo and B.K. Patel, *Org. Lett.*, **2009**, *11*, 4254–4257.
- [6] C. G. Bates, R. K. Gujadhur, D. Venkataraman, *Org. Lett.* **2002**, *4*, 2803–2806.
- [7] D. Q. Qian, B. Lin, H. J. Shine, I. Y. Guzman-Jimenez and K. H. Whitmire, *J. Phys. Org. Chem.*, **2002**, *15*, 139–147.
- [8] M. J. Dickens, J. P. Gilday, T. J. Mowlem, D. A. Widdowson, *Tetrahedron*, **1991**, *47*, 8621–8634.
- [9] B. C. Ranu, A. Saba, R. Jana, *Adv. Synth. Catal.* **2007**, *349*, 2690–2696.
- [10] Y.-C. Wong, T. T. Jayanth, C.-H. Cheng, *Org. Lett.* **2006**, *8*, 5613–5616.
- [11] D. J. C. Prasad, A. B. Naidu, G. Sekar, *Tetrahedron Lett.* **2009**, *50*, 1411–1415.
- [12] M. S. Kabir, M. Lorenz, M. L. Van Linn, O. A. Namjoshi, S. Ara, J. M. Cook, *J. Org. Chem.* **2010**, *75*, 3626–3643.
- [13] Y.-J. Chen, H.-H. Chen, *Org. Lett.* **2006**, *8*, 5609–5612.
- [14] N. Taniguchi, *J. Org. Chem.*, **2007**, *72*, 1241–1245.
- [15] V. P. Reddy, A. V. Kumar, K. Swapna, K. R. Rao, *Org. Lett.*, **2009**, *11*, 1697–1700.

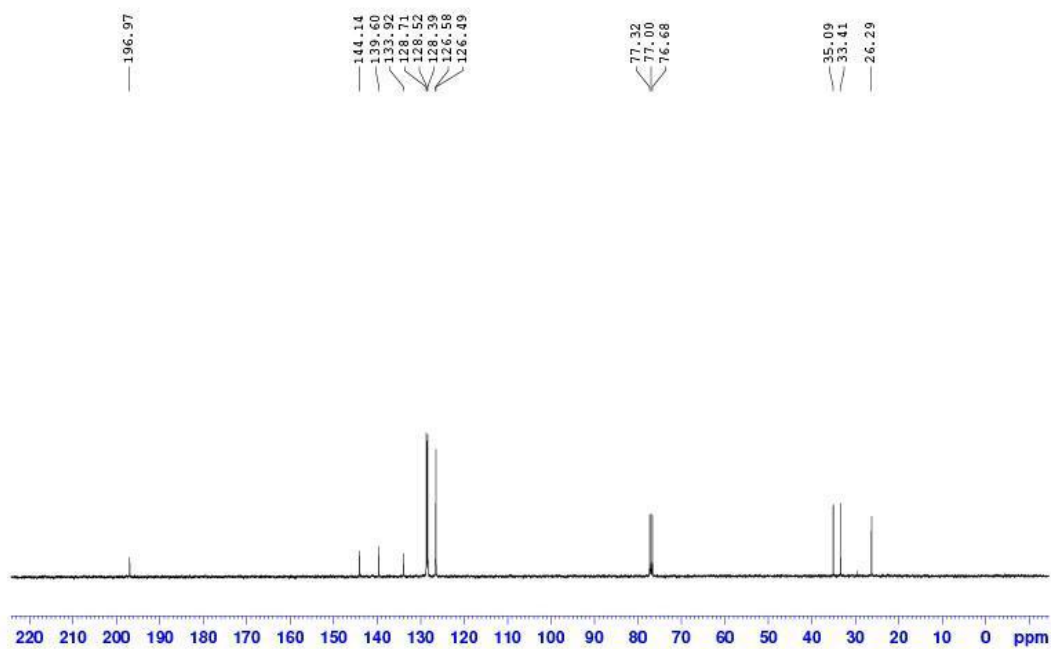
1-(4-(Phenethylthio)phenyl)ethanone (4v)

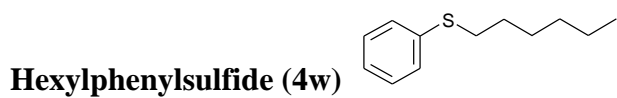


1-(4-(Phenethylthio)phenyl)ethanone

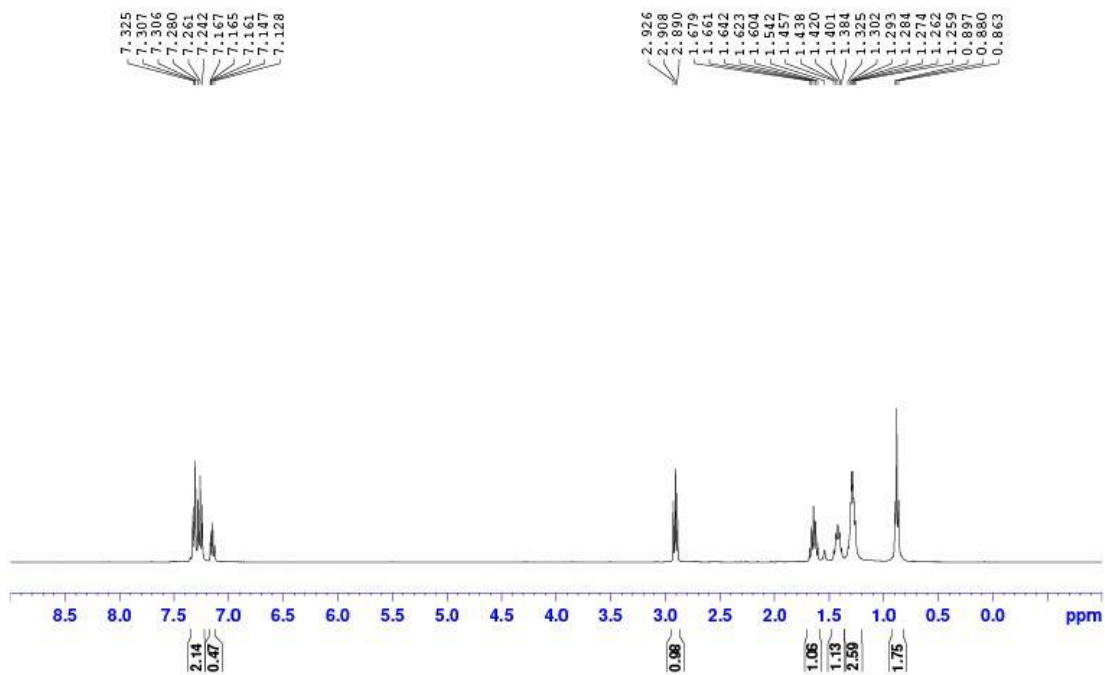


1-(4-(Phenethylthio)phenyl)ethanone

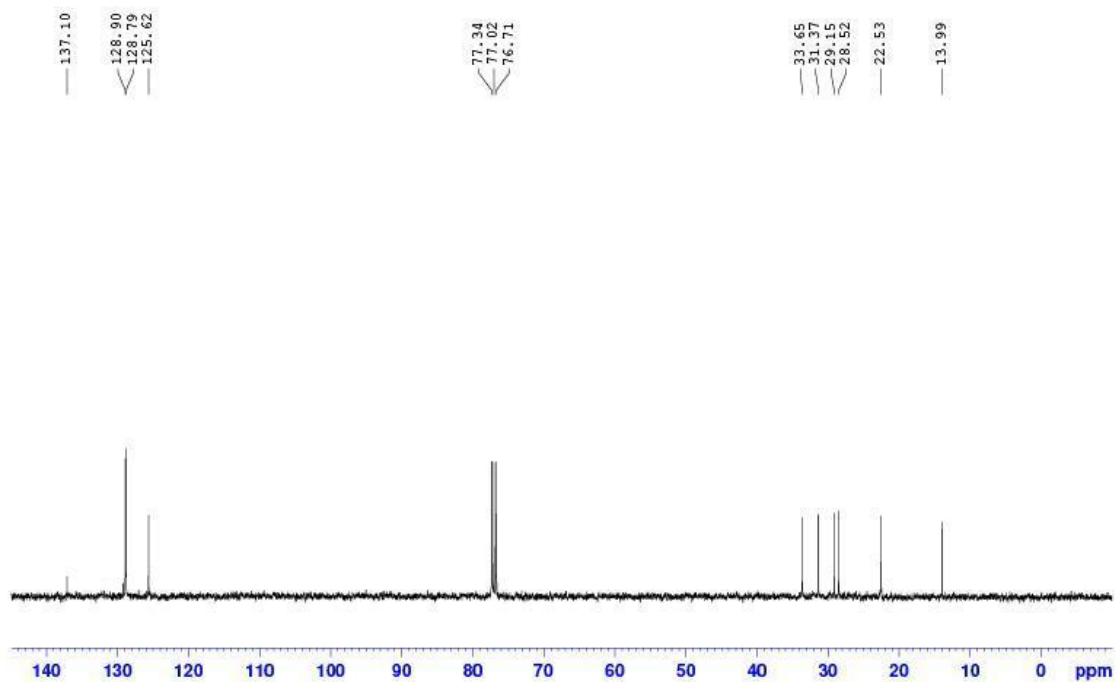




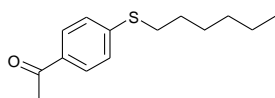
Hexylphenylsulfide



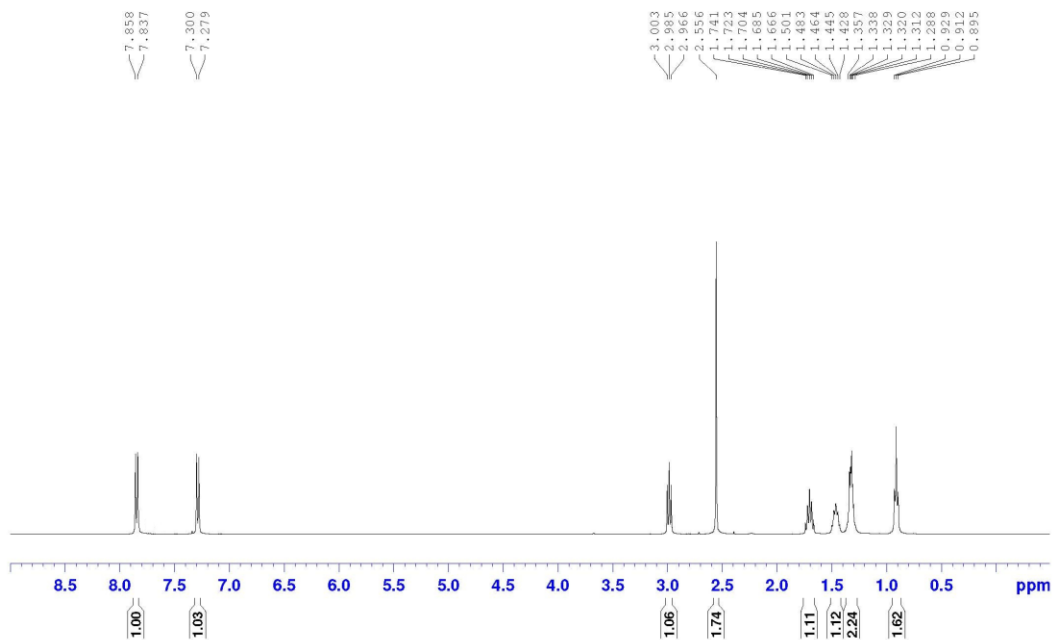
Hexylphenylsulfide



1-(4-(Hexylthio)phenyl)ethanone (4x)



1-(4-(Hexylthio)phenyl)ethanone



1-(4-(Hexylthio)phenyl)ethanone

