

Supporting Information

Iron catalyzed efficient synthesis of 2-arylbenzothiazoles from benzothiazole and olefins using environmentally benign molecular oxygen as oxidant

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1. General information:

Materials and Method:

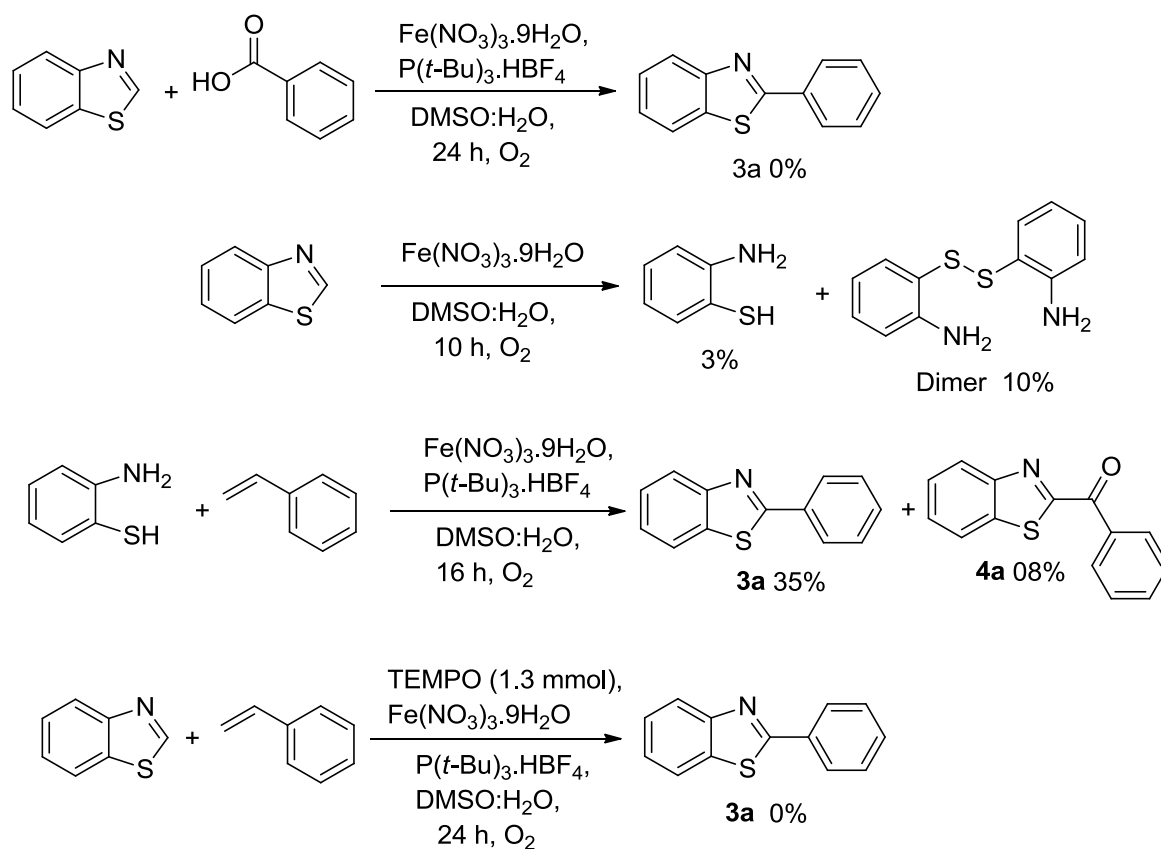
All chemicals and reagents were purchased from Sigma Aldrich, S. D. fine chemical and commercial suppliers. Solvents were purchased from commercial suppliers and used without purification. Reaction monitor by using TLC and Perkin Elmer Clarus 400 gas chromatography equipped with flame ionization detector with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm). GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness 0.25 μm df) (column flow 2 mLmin⁻¹, 80 °C to 240 °C at 10 °C/min rise.). GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness (df) = 0.25 μm) (column flow 2 mLmin⁻¹, 80 °C to 240 °C at 10 °C/min rise) was used for the mass analysis of the products. Products were purified by column chromatography on 100–200 mesh silica gels. The ¹H NMR spectra was recorded on Bruker-400 MHz spectrometer in CDCl₃ using tetramethylsilane (TMS) as internal standard. The ¹³C NMR spectra were recorded on Bruker-100 MHz spectrometer in CDCl₃. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as internal standard. *J* (coupling constant) values were reported in Hz. Splitting patterns of proton are described as s (singlet), d (doublet), dd (doublet of doublets), t (triplet) and m (multiplet). The products were confirmed by the comparison of their GC-MS spectra, and/or ¹H and ¹³C NMR spectra with those of authentic data.

2. General experimental procedure for arylation of benzothiazole with styrene:

To an oven dried 15 ml glass vial with a magnetic bar was charged with benzothiazole (1a, 1 mmol), styrene (2a, 2.5 mmol), ferric nitrate (5 mol %), P(*t*-Bu)₃.HBF₄ (25 mol%), and solvent (DMSO:H₂O, 3:1). The vial was then flush with oxygen and sealed with a cap. The reaction mixture was stirred at 120 °C for 24 h monitored by TLC and GC. After completion, cool the reaction mixture to room temperature. Extract the product with ethyl acetate (3×15

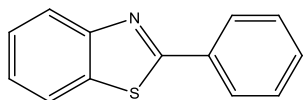
ml), dried the organic layer over Na_2SO_4 and evaporated to afford the crude product. The product was purified by column chromatography (silica gel, 100-200 mesh; petroleum ether/ethyl acetate) to afford the pure product. The product was confirmed by GC-MS, ^1H and ^{13}C NMR spectroscopic analysis.

Scheme S1. Control experiments.



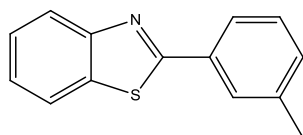
3. Spectral data of compounds:

2-Phenylbenzothiazole (3a)



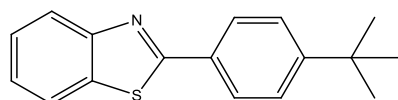
^1H NMR (CDCl_3 , 400 MHz) δ 8.10-8.07 (m, 3H), 7.89 (d, $J = 8$ Hz, 1H), 7.57-7.46 (m, 4H), 7.37 (t, $J = 8$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 168.05, 154.14, 135.05, 133.61, 130.95, 129.00, 127.60, 126.30, 125.17, 123.23, 121.60. GC-MS (EI): m/z $[\text{M}]^+$, 211 (100), 208 (26.6), 69 (16.1).

2-(3-Methylphenyl)benzothiazole (3b)



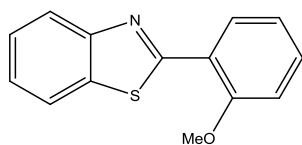
^1H NMR (CDCl_3 , 400 MHz) δ 8.07 (d, $J = 8$ Hz, 1H), 7.93 (s, 1H), 7.89-7.85 (m, 2H), 7.48 (t, $J = 8$ Hz, 1H), 7.37 (t, $J = 7.6$ Hz, 2H), 7.29 (d, $J = 7.6$ Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 168.32, 154.11, 138.85, 135.02, 133.50, 131.80, 128.91, 127.97, 126.27, 125.11, 124.85, 123.15, 121.59, 21.34. GC-MS (EI): m/z $[\text{M}]^+$, 225 (100), 108 (13), 69 (17.5).

2-(4-tert-Butylphenyl)benzothiazole (3c)



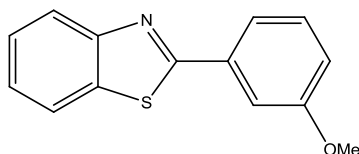
^1H NMR (CDCl_3 , 400 MHz) δ 8.07-8.01 (m, 3H), 7.87 (d, $J = 7.6$ Hz, 1H), 7.54-7.45 (m, 3H), 7.38-7.34 (m, 1H), 1.37 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 168.11, 154.50, 154.20, 134.97, 130.89, 127.48, 126.20, 125.95, 124.97, 123.07, 121.55, 34.96, 31.17. GC-MS (EI): m/z 267 (41.2) $[\text{M}]^+$, 252 (100), 224 (14.5), 73 (10.2), 45 (12.4).

2-(2-Methoxyphenyl)benzothiazole (3d)



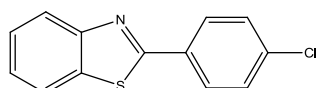
^1H NMR (MeOD, 400 MHz) δ 8.53 (dd, $J = 7.6, 1.6$ Hz, 1H), 8.09 (d, $J = 8$ Hz, 1H), 7.92 (d, $J = 7.6$ Hz, 1H), 7.50-7.43 (m, 2H), 7.37 (t, $J = 8$ Hz, 1H), 7.13 (t, $J = 8$ Hz, 1H), 7.06 (d, $J = 8.4$ Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 163.12, 157.23, 152.17, 136.12, 131.75, 129.55, 125.88, 124.57, 122.79, 122.30, 121.19, 121.16, 111.67, 55.70. GC-MS (EI): m/z 241 (100) $[\text{M}]^+$, 241(100), 240 (37.1), 212 (50), 211 (39.3), 210 (26.3), 209 (10.8), 208 (41), 136 (92.1), 109 (21), 108 (43.4), 92 (11.7), 82 (17.4), 77 (11.7), 69 (32.5), 63 (21.1), 45 (12.8).

2-(3-Methoxyphenyl)benzothiazole (3f)



^1H NMR (CDCl_3 , 400 MHz) δ 8.08 (d, $J = 8$ Hz, 1H), 7.90 (d, $J = 8$ Hz, 1H), 7.68-7.61 (m, 2H), 7.47 (t, $J = 8$ Hz, 1H), 7.42-7.37 (m, 2H), 7.04 (dd, $J = 8.4, 2$ Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.95, 160.06, 154.07, 135.06, 134.91, 130.02, 126.32, 125.23, 123.26, 121.61, 120.24, 117.36, 112.03, 55.51. GC-MS (EI): m/z 241 (100) $[\text{M}]^+$, 240 (71.7), 212 (23.8), 211 (38.3), 210 (27.8), 109 (12), 108 (17.8), 82 (11.2), 69 (20.6), 63 (14.4).

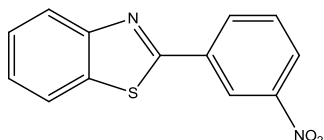
2-(4-Chlorophenyl)benzothiazole(3i)



^1H NMR (CDCl_3 , 400 MHz) δ 8.08-8.02 (m, 3H), 7.90 (d, $J = 8$ Hz, 1H), 7.55-7.46 (m, 3H), 7.42 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.64, 154.05, 137.04, 135.05,

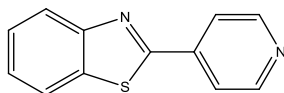
132.11, 129.28, 128.72, 126.49, 125.43, 123.29, 121.66. GC-MS (EI): m/z 245 (100) $[M]^+$, 210 (11.4), 108 (30.9), 82 (10.9), 69 (20.5).

2-(3-Nitrophenyl)benzothiazole(3m)



^1H NMR (CDCl_3 , 400 MHz) δ 8.93 (s, 1H), 8.41 (d, $J = 7.6$ Hz, 1H), 8.33 (dd, $J = 8, 1.2$ Hz, 1H), 8.11 (d, $J = 8$ Hz, 1H), 7.95 (d, $J = 8$ Hz, 1H), 7.69 (t, $J = 8$ Hz, 1H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.45 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 164.87, 153.94, 148.75, 135.28, 135.17, 132.99, 130.09, 126.83, 126.03, 125.17, 123.75, 122.32, 121.83. GC-MS (EI): m/z 256 (100) $[M]^+$, 211 (14.4), 210 (82.8), 209 (34.7), 183 (12), 139 (21.1), 69 (18.8), 63 (11.5).

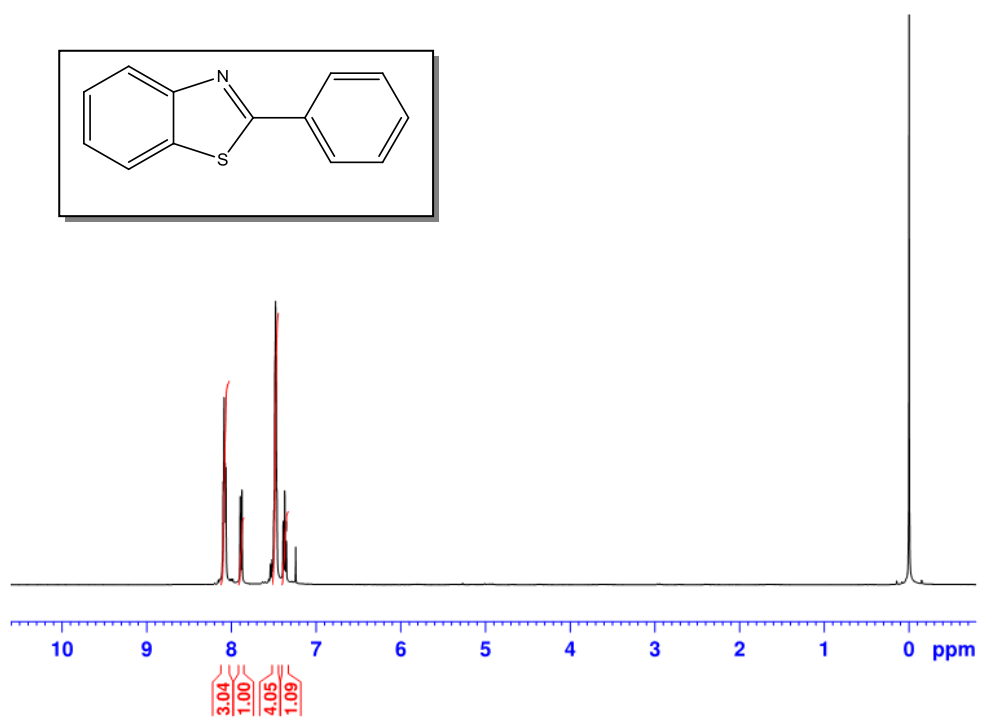
2-(Pyridin-4-yl)benzothiazole (3n)



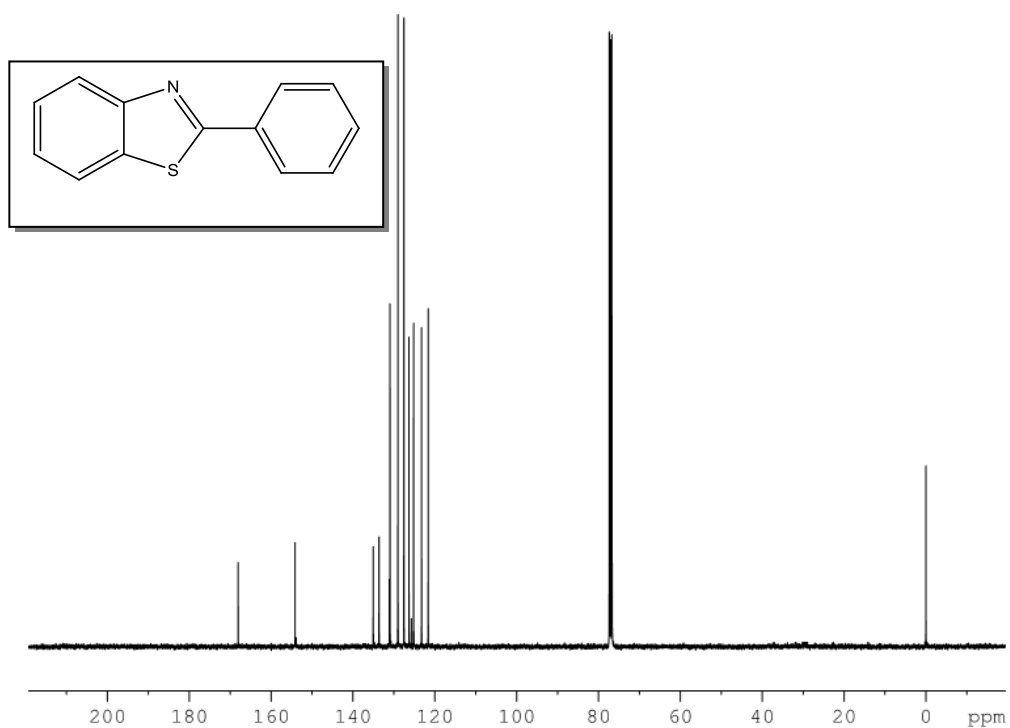
^1H NMR (CDCl_3 , 400 MHz) δ 8.78 (d, $J = 4.8$ Hz, 2H), 8.13 (d, $J = 8$ Hz, 1H), 7.96-7.94 (m, 3H), 7.55 (t, $J = 8$ Hz, 1H), 7.46 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 165.07, 153.97, 150.71, 140.52, 135.21, 126.83, 126.21, 123.93, 121.87, 121.22. GC-MS (EI): m/z 212 (100) $[M]^+$, 211(28.6), 186 (18.9), 185 (13.6), 108 (17.8), 82 (14.8), 69 (26.1), 63 (11), 51 (10).

4. Copies of ^1H NMR and ^{13}C NMR Spectra:

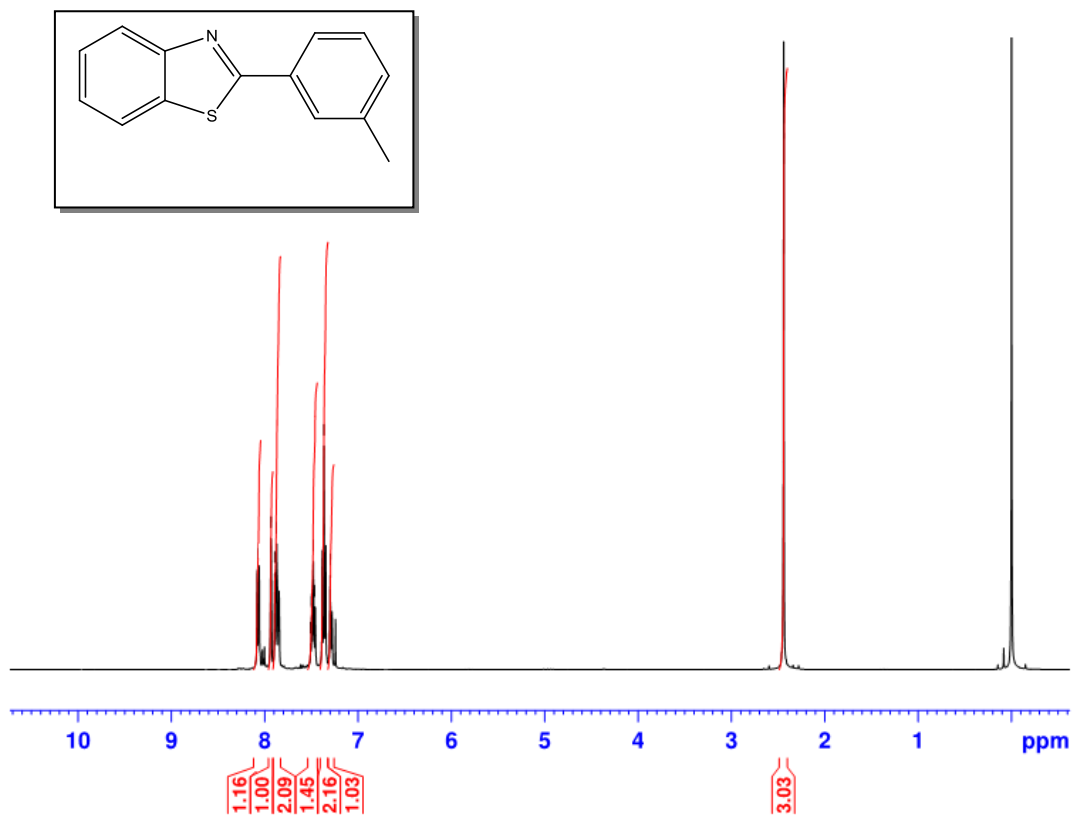
2-Phenylbenzothiazole ^1H NMR (*3a*)



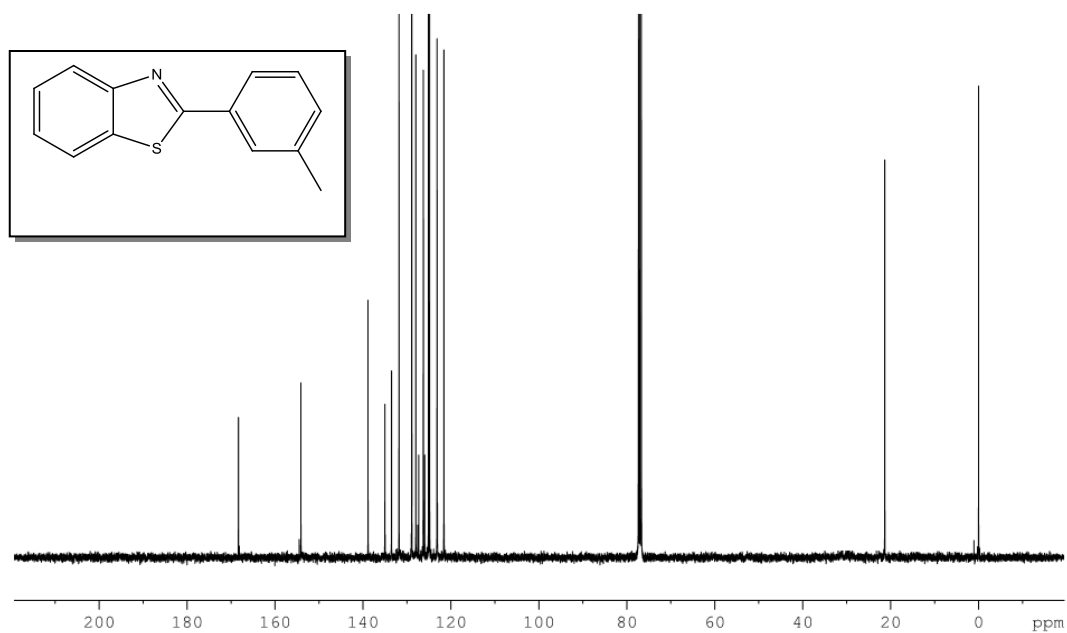
2-Phenylbenzothiazole ^{13}C NMR (*3a*)



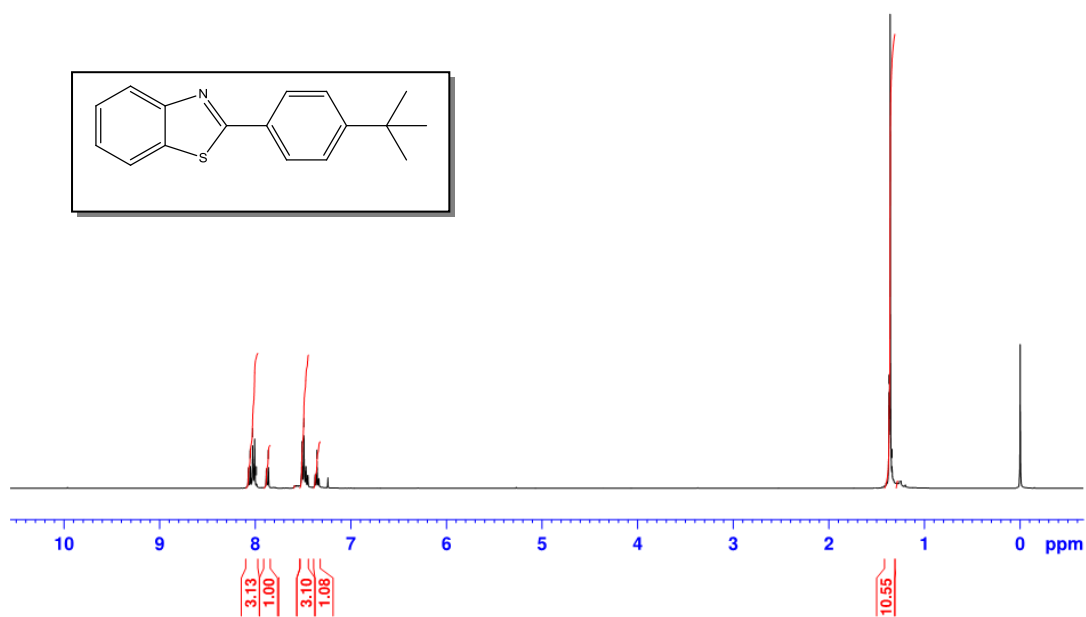
2-(3-Methylphenyl)benzothiazole ^1H NMR (3b)



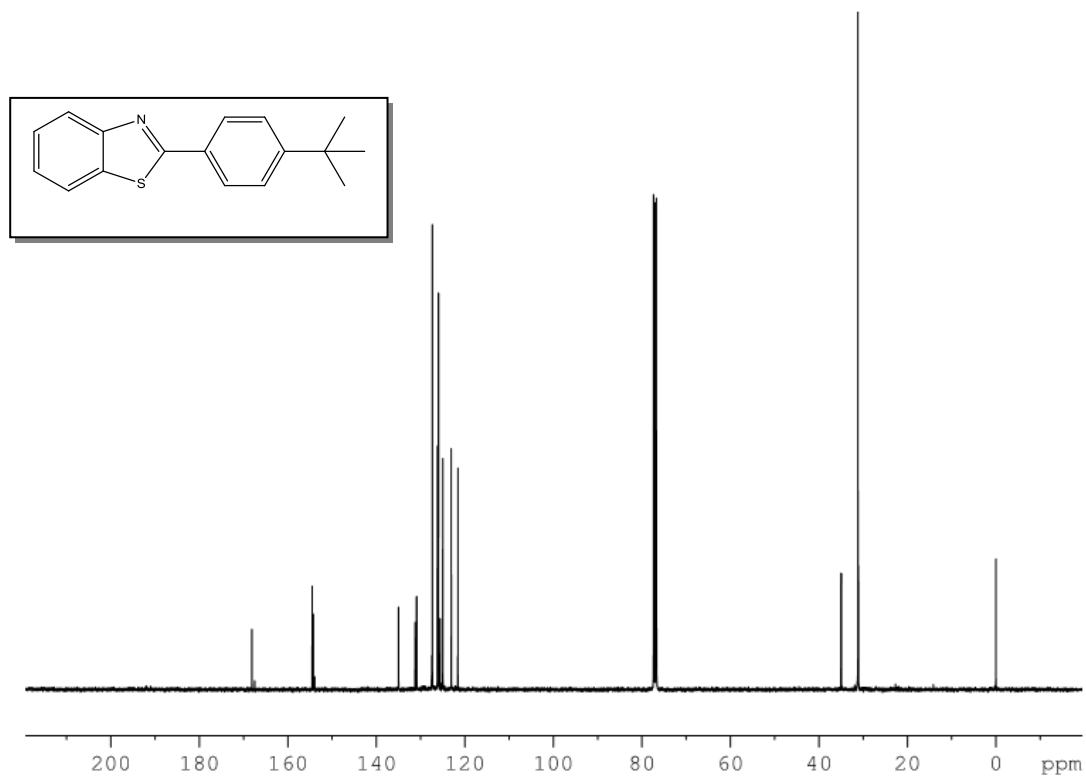
2-(3-Methylphenyl)benzothiazole ^{13}C NMR (3b)



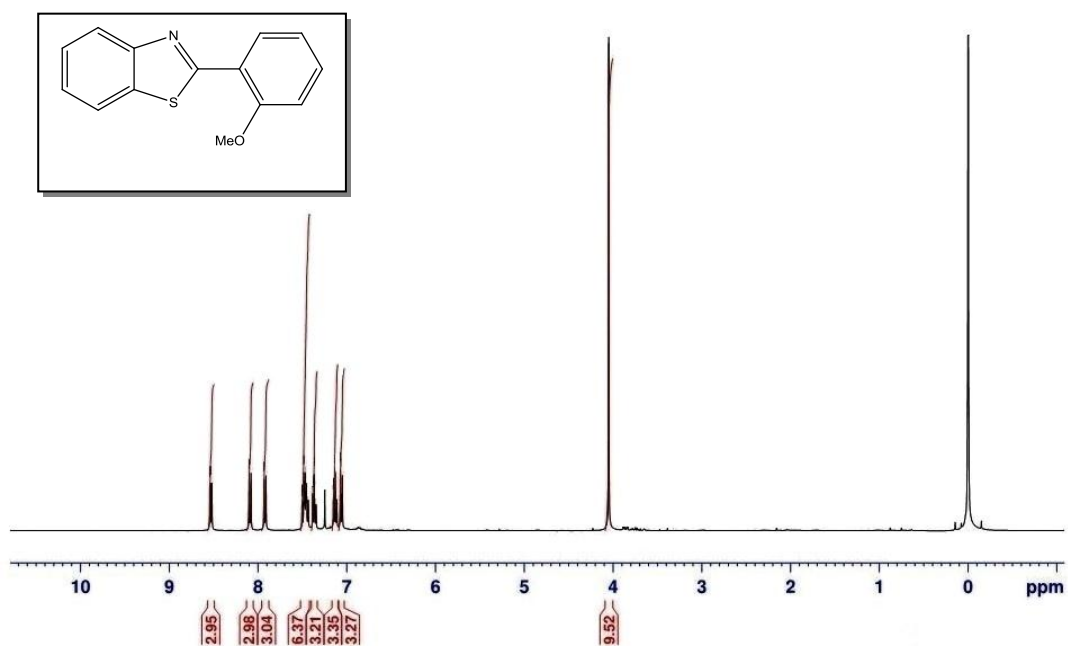
2-(4-tert-Butylphenyl)benzothiazole ^1H NMR (3c)



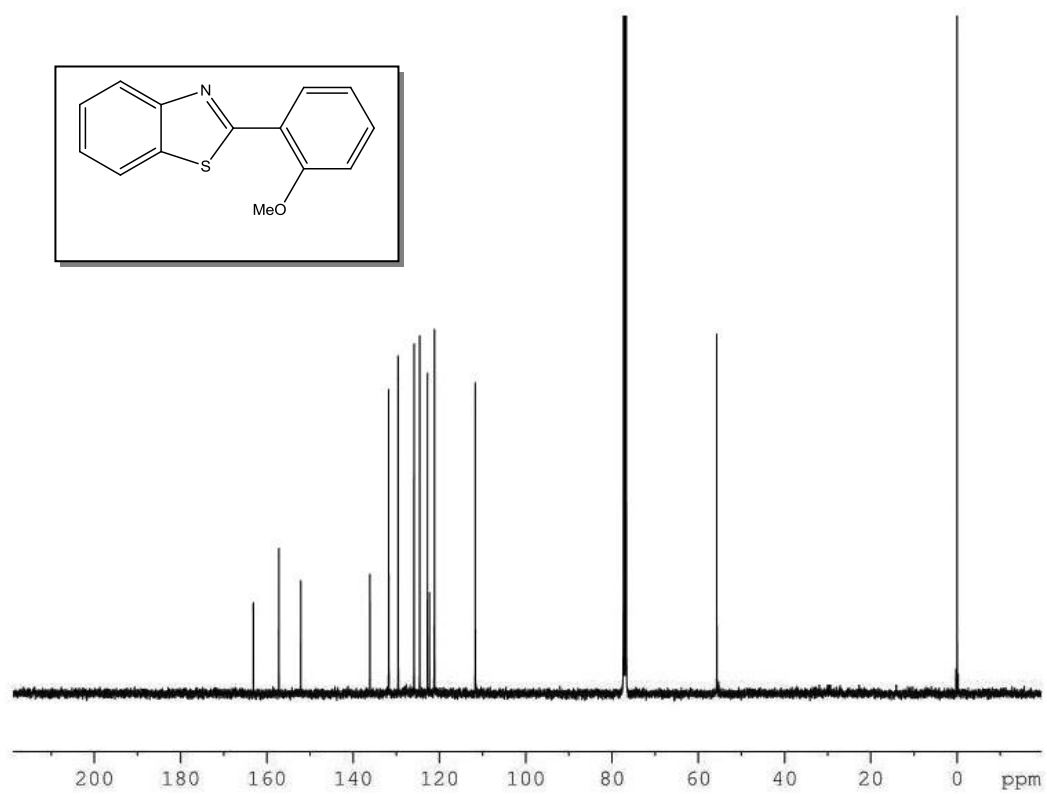
2-(4-tert-Butylphenyl)benzothiazole ^{13}C NMR (3c)



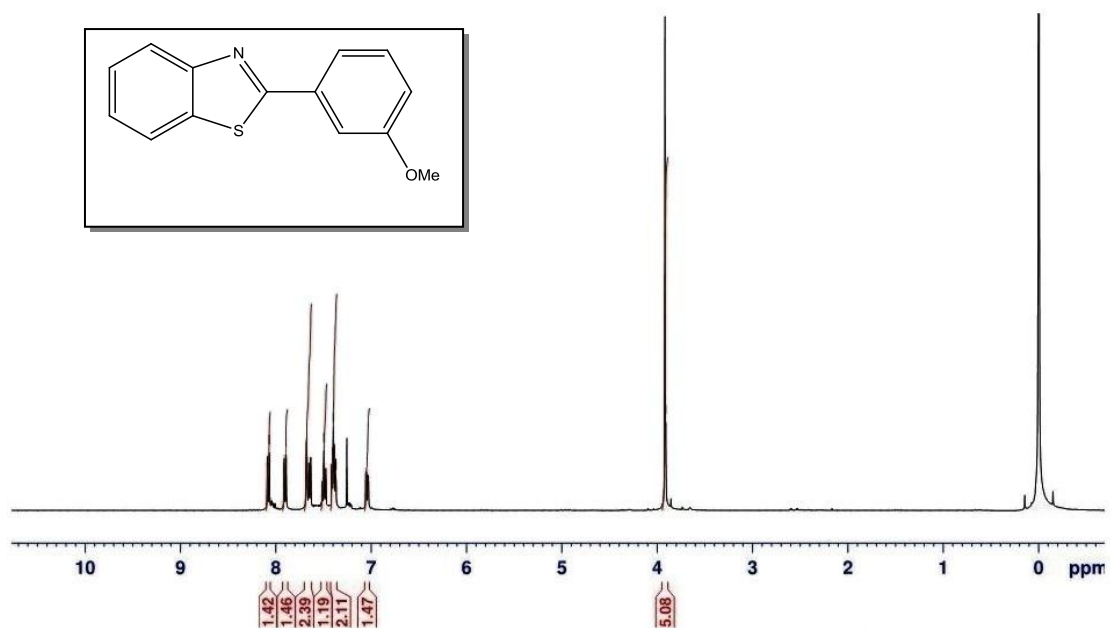
2-(2-Methoxyphenyl)benzothiazole ^1H NMR (3d)



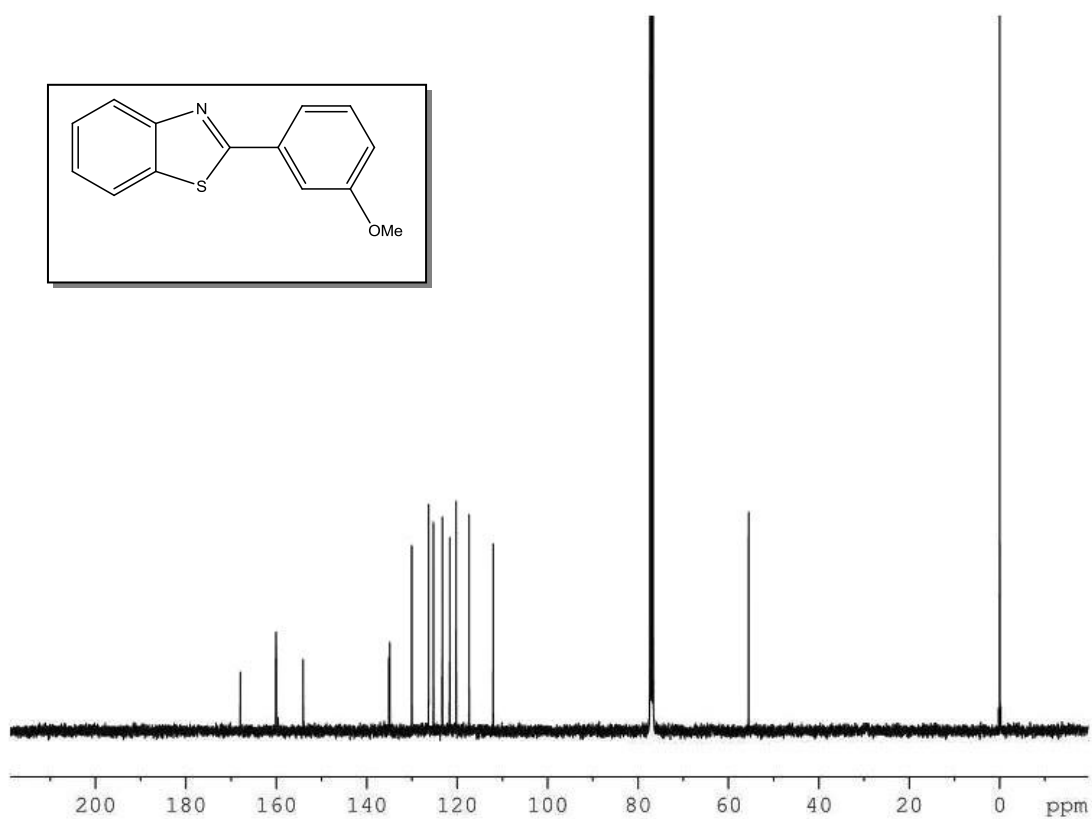
2-(2-Methoxyphenyl)benzothiazole ^{13}C NMR (3d)



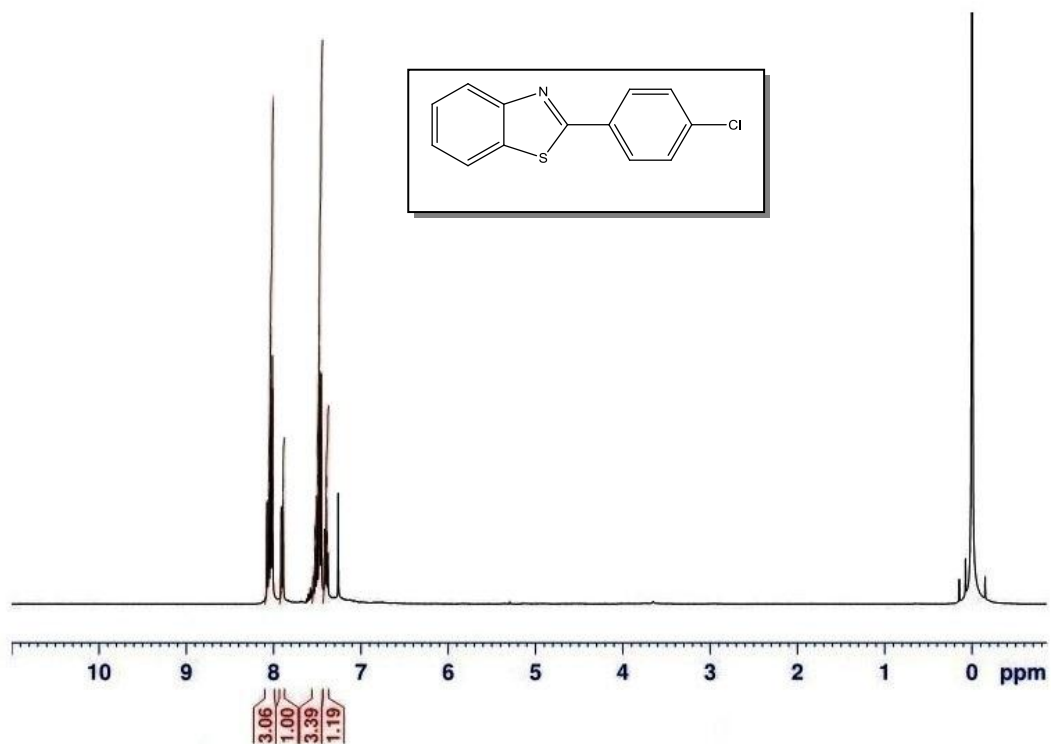
2-(3-Methoxyphenyl)benzothiazole ^1H NMR (3f)



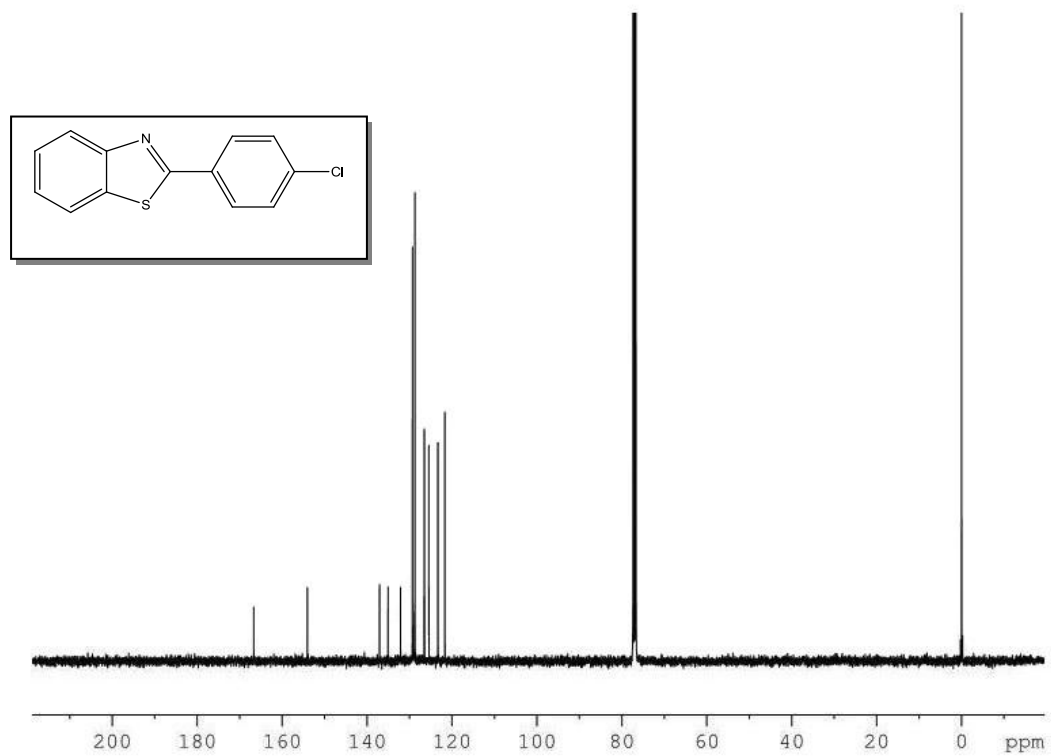
2-(3-Methoxyphenyl)benzothiazole ^{13}C NMR (3f)



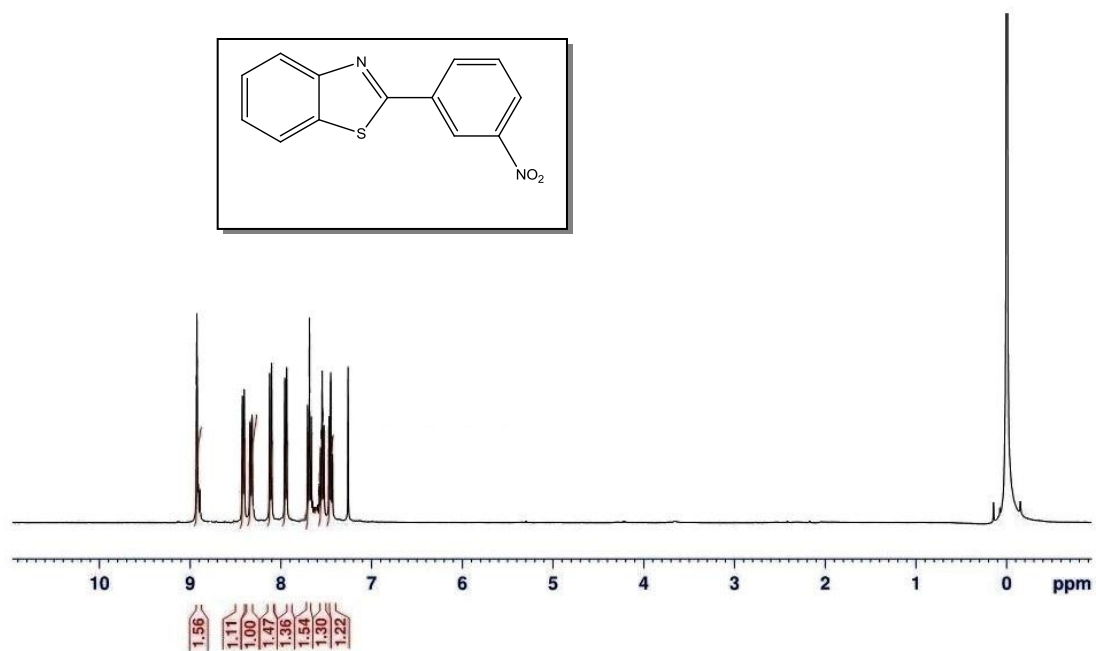
2-(4-Chlorophenyl)benzothiazole ^1H NMR (3i)



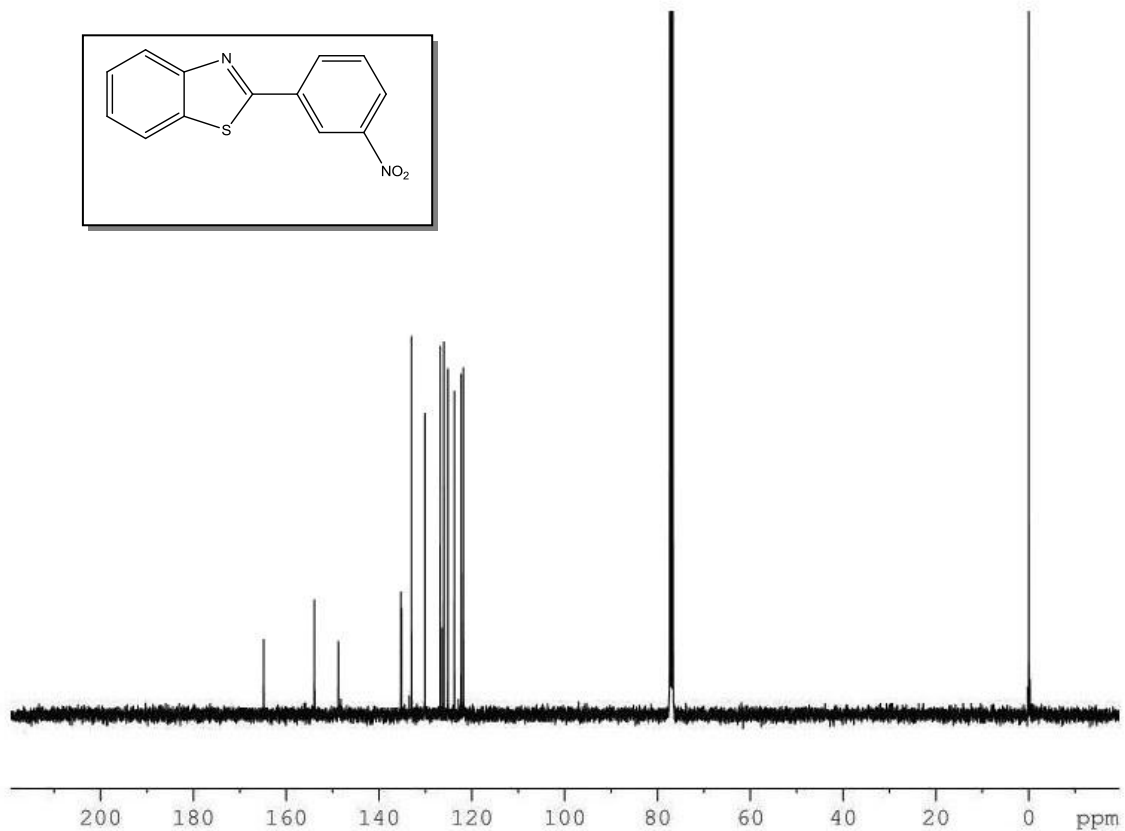
2-(4-Chlorophenyl)benzothiazole ^{13}C NMR (3i)



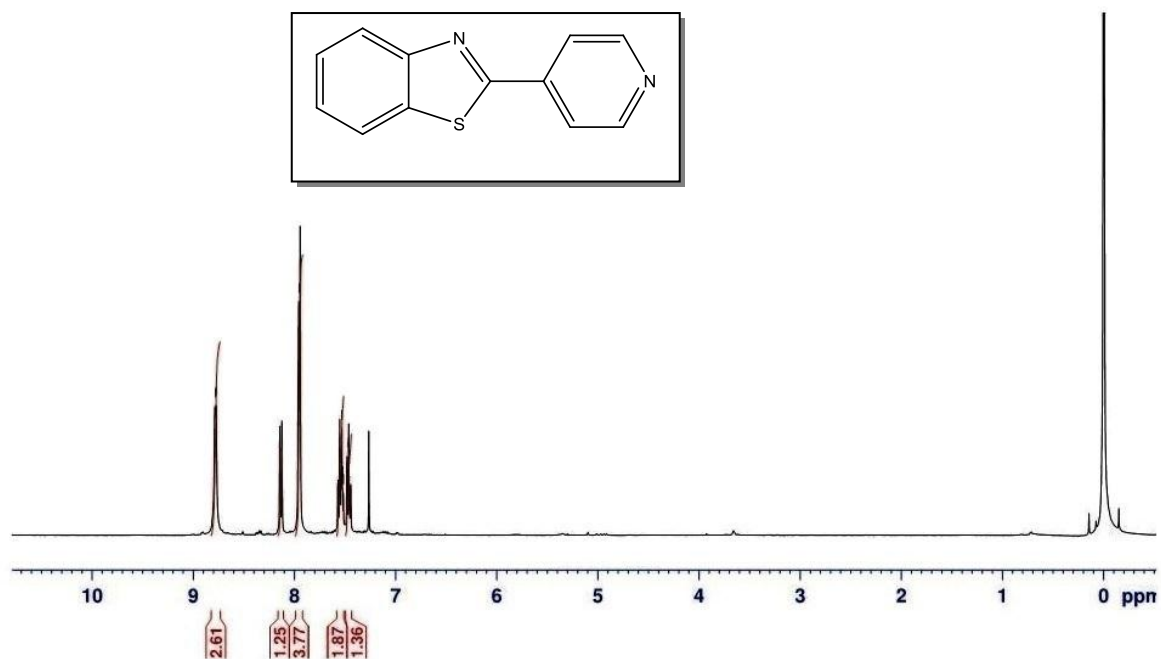
2-(3-Nitrophenyl)benzothiazole ^1H NMR (3m)



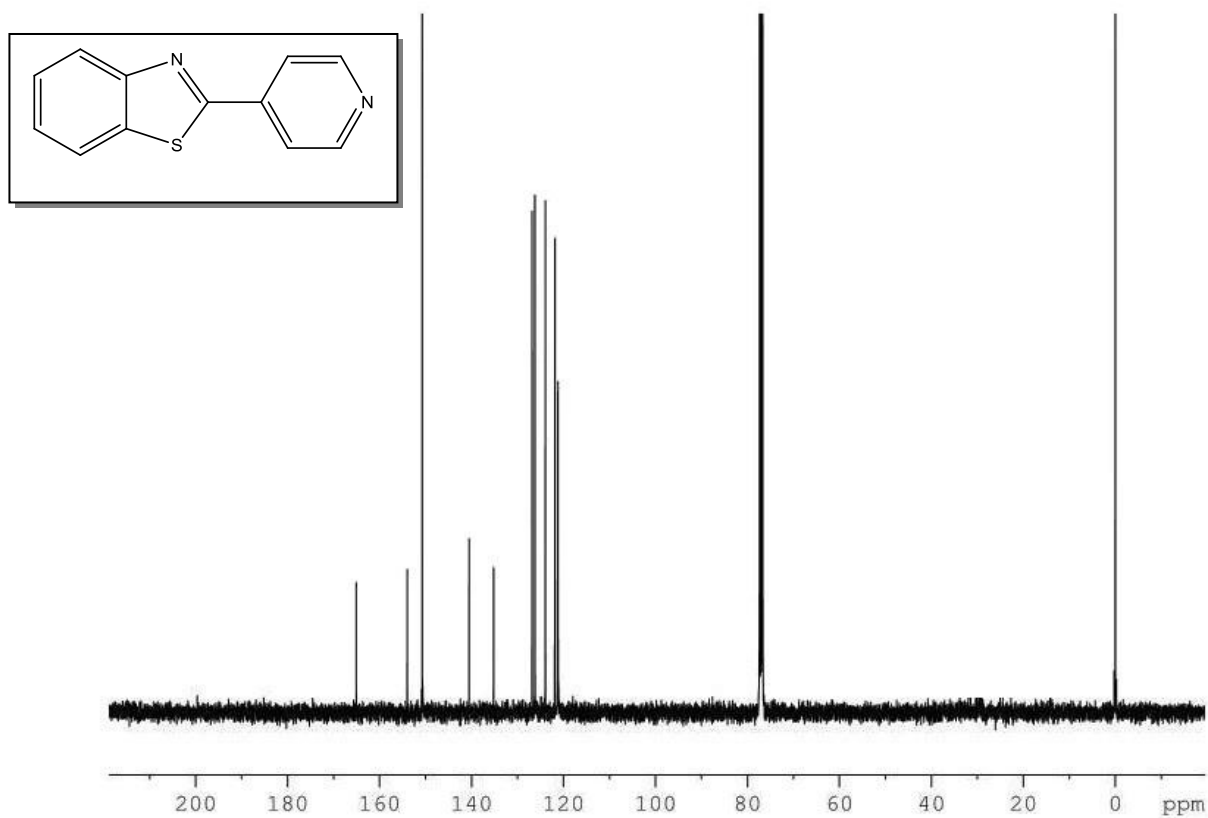
2-(3-Nitrophenyl)benzothiazole ^{13}C NMR (3m)



2-(Pyridin-4-yl)benzothiazole ^1H NMR (3n)



2-(Pyridin-4-yl)benzothiazole ^{13}C NMR (3n)



5. Reference:

1. S. Liu, R. Chen, X. Guo, H. Yang, G. Deng and C.-J. Li, *Green Chem.*, 2012, **14**, 1577–1580.
2. Y. Liao, H. Qi, S. Chen, P. Jiang, W. Zhou and G.-J. Deng, *Org. Lett.*, 2012, **14**, 6004–6007.
3. H. Deng, Z. Li, F. Ke, X. Zhou, *Chem. Eur. J.*, 2012, **18**, 4840–4843.
4. Y. Cheng, J. Yang, Y. Qu and P. Li, *Org. Lett.*, 2012, **14**, 98–101.
5. Y. Sun, W. Wu, W. Zeng, X. Wu and H. Jiang, *Org. Lett.*, 2013, **15**, 1598–1601.