

Supplementary information

Aerobic Oxidative Synthesis of Quinazolinones and Benzothiazoles in the Presence of Laccase/DDQ as a Bioinspired Cooperative Catalytic System under Mild Conditions

Nadia Ghorishi, Zahra Shokri, Reza Moradi, Amira Abdelrasoul, Amin Rostami*

1. General Information

All chemicals and solvents were bought from the Merck and Aldrich Chemical Companies and used without further purification. Laccase from *Trametes versicolor* (CAS Number: 0080498153, Product Number: 38429-10G) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Melting points were obtained on an Electrothermal 9100 apparatus and are uncorrected. ¹H NMR spectra were recorded on BrukerAvance spectrometer (250 and 400 MHz).

2. Analytical data of the products

2-Phenylquinazolin-4(3*H*)-one (Table 2, entry 1):¹ $R_f = 0.50$ (*n*-hexane/ethyl acetate: 3:1), ¹H NMR (DMSO-*d*₆, 250 MHz): δ (ppm)= 12.49 (s, 1H), 8.16-8.14 (m, 3H), 7.80-7.69 (m, 2H), 7.54-7.49 (m, 4H).

2-(4-Methylphenyl)quinazolin-4(3*H*)-one (Table 2, entry 2):¹ $R_f = 0.53$ (*n*-hexane/ethyl acetate: 3:1), ¹H NMR (DMSO-*d*₆, 250 MHz): δ (ppm)= 12.38 (s, 1H), 8.18-8.09 (m, 3H), 7.79 (t, $J = 7.2$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.06 (d, $J = 8.5$ Hz, 2H), 3.82 (s, 3H).

2-(3-Methoxyphenyl)quinazolin-4(3*H*)-one (Table 2, entry 4):¹ $R_f = 0.55$ (*n*-hexane/ethyl acetate: 3:1), ¹H NMR (250 MHz, DMSO-*d*₆): δ (ppm)= 12.53 (s, 1H), 8.14 (d, $J = 7.7$ Hz, 1H), 7.83-7.74 (m, 4H), 7.54-7.42 (m, 2H), 7.14 (d, $J = 8.0$ Hz, 1H), 3.85 (s, 3H).

2-(2-Methoxyphenyl)quinazolin-4(3*H*)-one (Table 2, entry 5):¹ $R_f = 0.55$ (*n*-hexane/ethyl acetate: 3:1), ¹H NMR (250 MHz, DMSO-*d*₆): δ (ppm)= 12.10 (s, 1H), 8.13 (d, $J = 7.5$ Hz, 1H), 7.81-7.52 (m, 5H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.10-7.07 (m, 1H), 3.84 (s, 3H).

2-(3-Bromophenyl)quinazolin-4(3*H*)-one (Table 2, entry 8):² $R_f = 0.60$ (*n*-hexane/ethyl acetate: 3:1), ¹H NMR (DMSO-*d*₆, 400 MHz): δ (ppm)= 12.62 (br s, 1H), 8.37(s, 1H), 8.20 (d, $J = 7.5$ Hz, 1H), 8.17 (d, $J = 7.5$ Hz, 1H), 7.88-7.76 (m, 3H), 7.57-7.50 (m, 2H).

2-(3-Fluorophenyl)quinazolin-4(3*H*)-one (Table 2, entry 9): $R_f = 0.6$ (*n*-hexane/ethyl acetate: 3:1), ¹H NMR (DMSO-*d*₆, 400 MHz): δ (ppm)= 12.60 (s, 1H), 8.15 (d, $J = 7.7$ Hz, 1H), 8.06-7.97 (m, 2H), 7.86-7.72 (m, 2H), 7.63-7.40 (m, 3H).

2-phenylbenzothiazole (Table 5, entry 1):³ $R_f = 0.60$ (*n*-hexane/ethyl acetate: 2:1), ¹H NMR (CDCl₃, 250 MHz): δ (ppm) = 8.10-8.08 (m, 3H), 7.91 (d, 1H, $J = 7.5$ Hz), 7.50-7.49 (m, 4H), 7.42-7.36 (m, 1H).

2-(4-fluorophenyl)benzothiazole (Table 5, entry 6):³ $R_f = 0.65$ (*n*-hexane/ethyl acetate: 2:1), ¹H NMR (CDCl₃, 250 MHz): δ (ppm)= 8.12-8.05 (m, 3H), 7.90 (d, 1H, $J = 7.5$ Hz), 7.50 (t, 1H, $J = 7.2$ Hz), 7.39 (t, 1H, $J = 7.2$ Hz), 7.26-7.15 (m, 2H).

2-(benzothiazol-2-yl)-4-bromophenol (Table 5, entry 13): $R_f = 0.55$ (*n*-hexane/ethyl acetate: 2:1), ¹H NMR (CDCl₃, 250 MHz): δ (ppm)= 12-13 (s, 1H), 7.94 (dd, 2H, $J = 19.5, 8.0$ Hz), 7.56 (d, 1H, $J = 2.0$ Hz), 7.54-7.41 (m, 3H), 6.98 (d, 1H, $J = 8.8$ Hz).

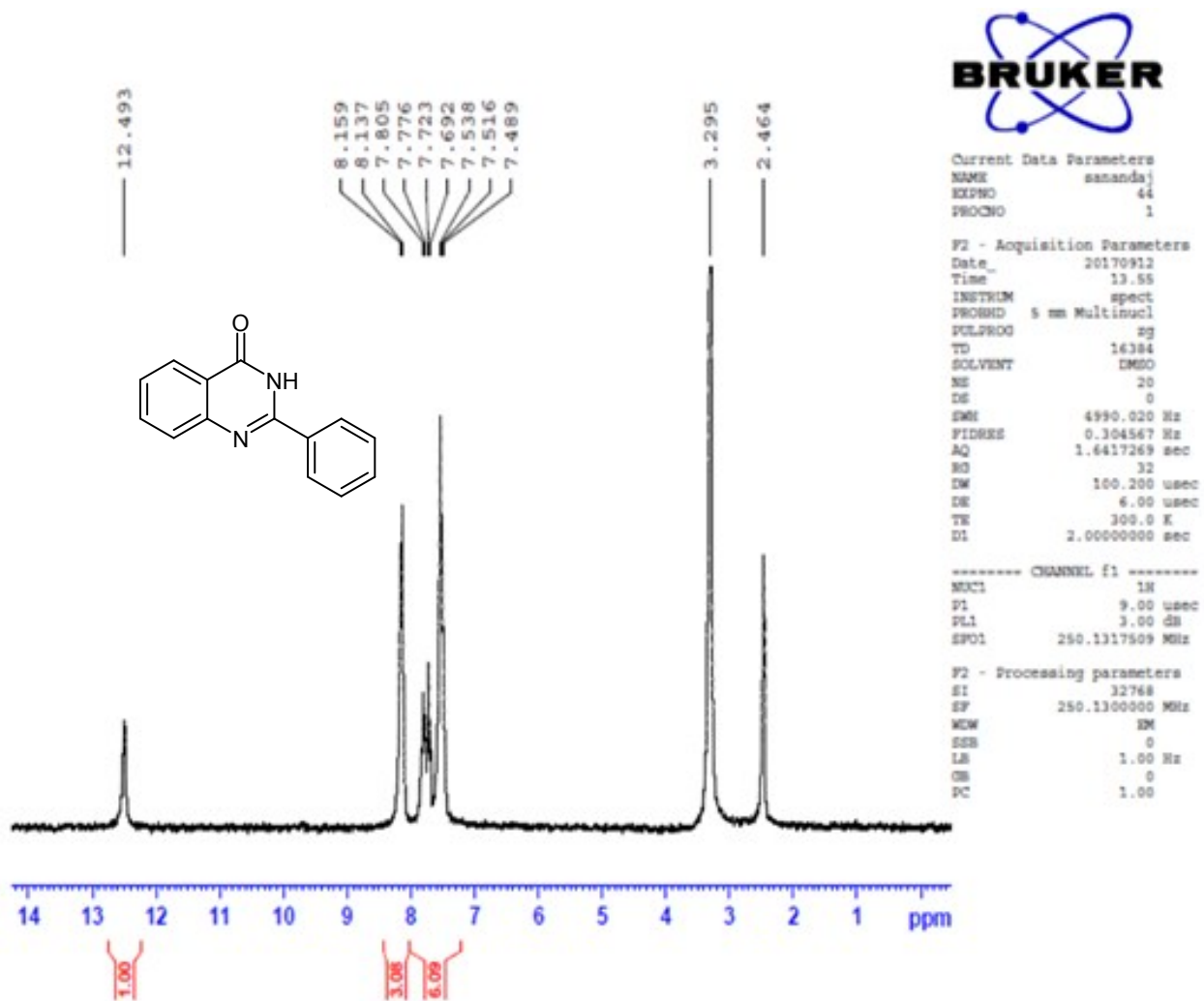
2-(3-nitrophenyl)benzothiazole (Table 5, entry 18):³ $R_f = 0.7$ (*n*-hexane/ethyl acetate: 2:1), ¹H NMR (CDCl₃, 250 MHz): δ (ppm)= 8.93 (s, 1H), 8.43 (d, 1H, $J = 7.7$ Hz), 8.34 (d, 1H, $J = 8.0$ Hz), 8.12 (d, 1H, $J = 7.7$ Hz), 7.96 (d, 1H, $J = 7.7$ Hz), 7.70 (t, 1H, $J = 8.0$ Hz), 7.55-7.42 (m, 2H).

2-(5-methylfuran-2-yl)benzothiazole (Table 5, entry 19): $R_f = 0.6$ (*n*-hexane/ethyl acetate: 2:1), ¹H NMR (CDCl₃, 250 MHz): δ (ppm)= 8.03 (d, 1H, $J = 8.2$ Hz), 7.86 (d, 1H, $J = 8.0$ Hz), 7.46 (m, 1H), 7.34 (m, 1H), 7.07 (d, 1H, $J = 3.0$ Hz), 6.18 (d, 1H, $J = 3.0$ Hz), 2.43 (s, 3H).

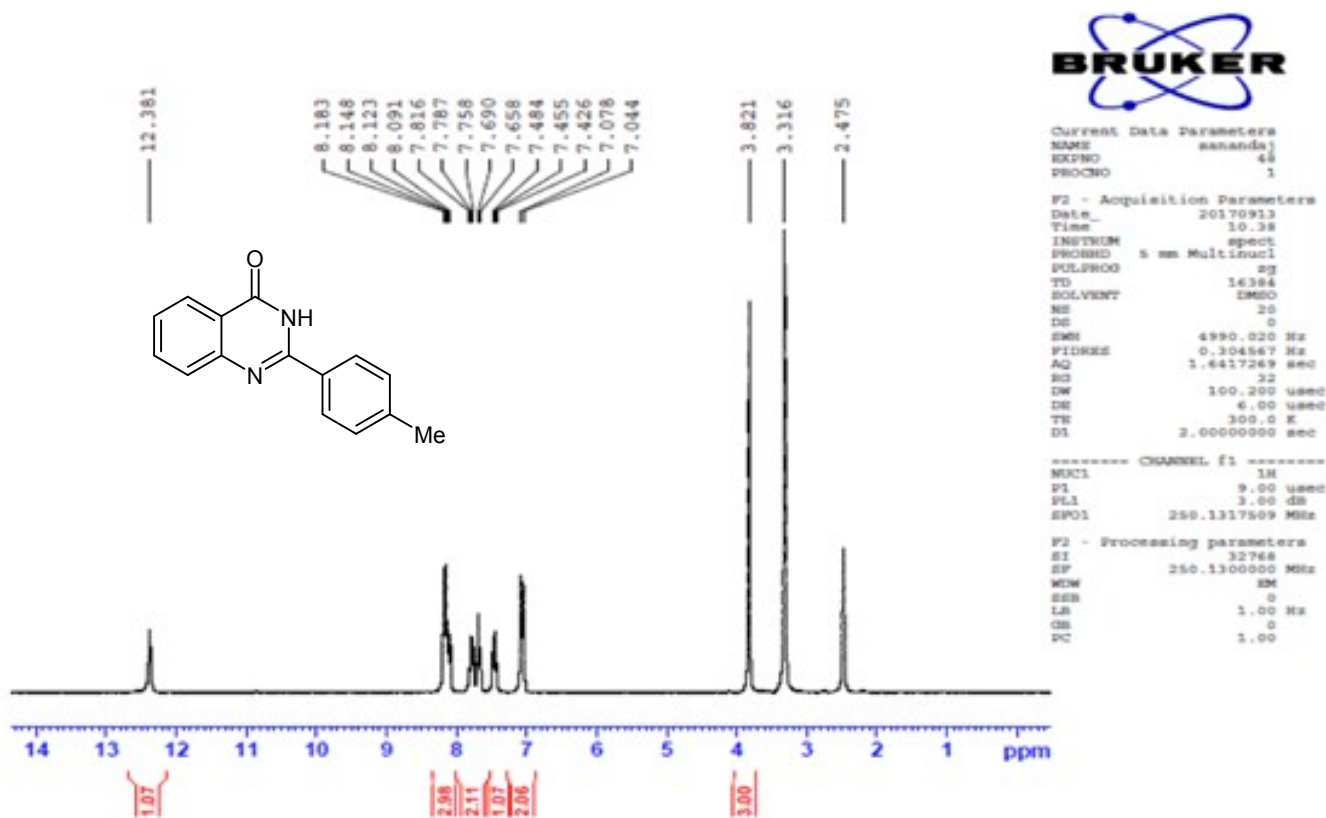
2-(naphthalen-1-yl)benzothiazole (Table 5, entry 20):³ $R_f = 0.6$ (*n*-hexane/ethyl acetate: 2:1), ¹H NMR (CDCl₃, 250 MHz): δ (ppm)= 8.57 (br s, 1H), 8.21 (d, 1H, $J = 7.2$ Hz), 8.12 (d, 1H, $J = 8$ Hz), 7.97-7.92 (m, 4H), 7.57-7.49 (m, 4H), 7.43-7.37 (m, 1H).

3. ¹H NMR of the products

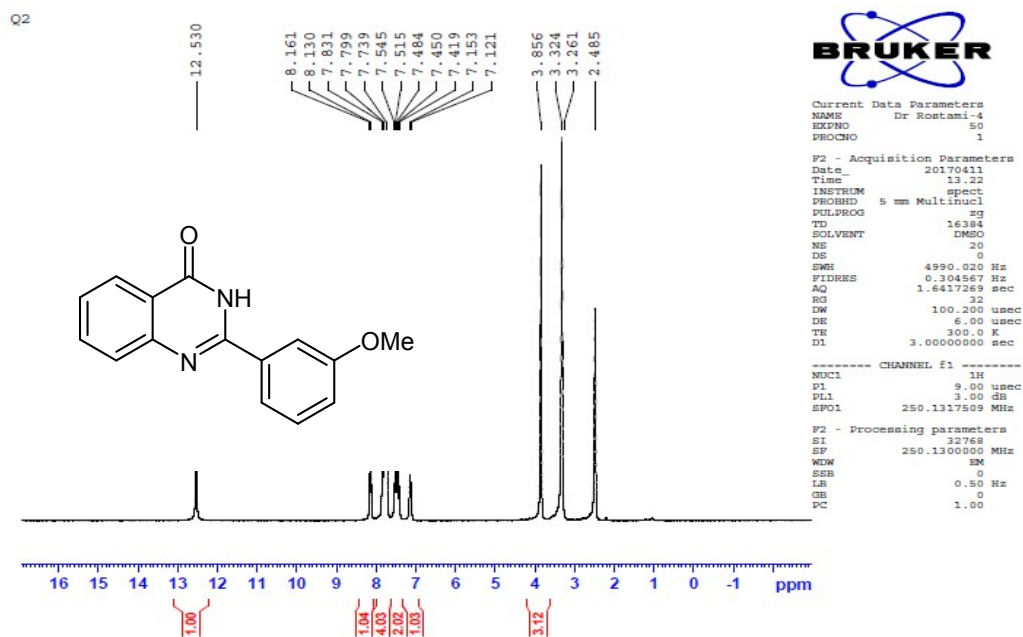
¹HNMR (Table 2, entry 1)



¹HNMR (Table 2, entry 2)

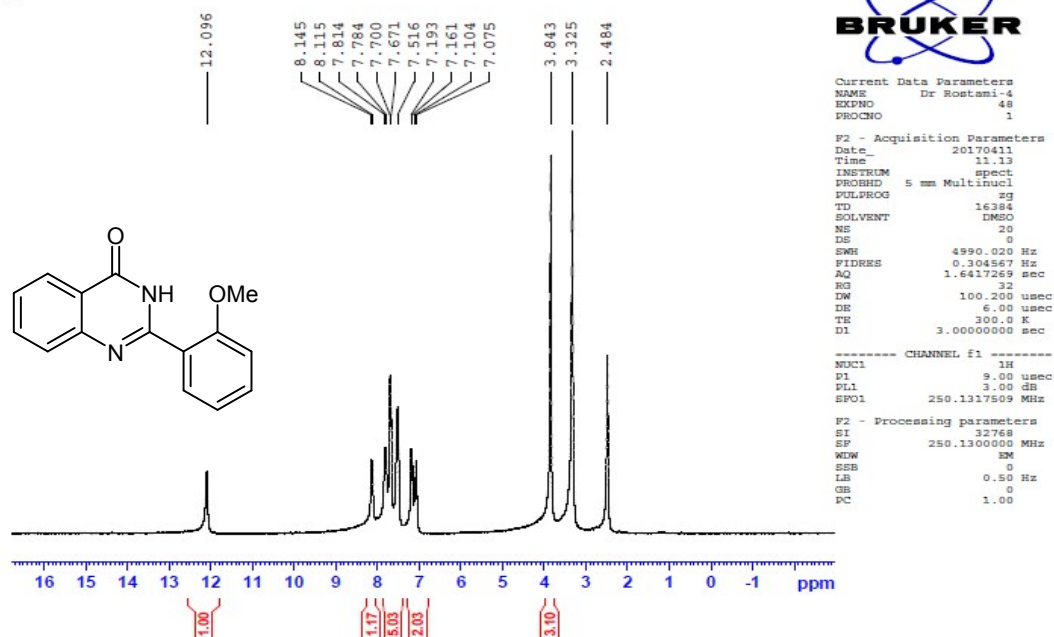


¹HNMR (Table 2, entry 4)

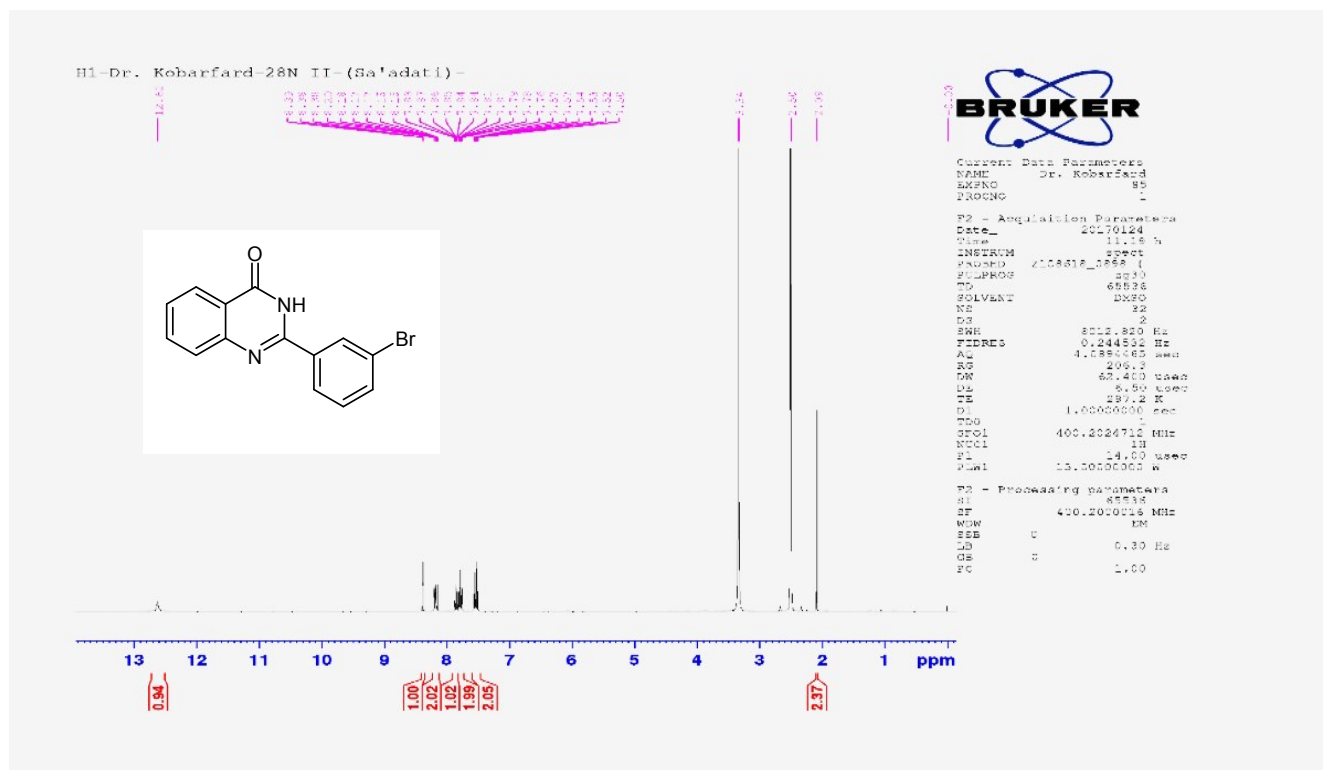


¹H NMR (Table 2, entry 5)

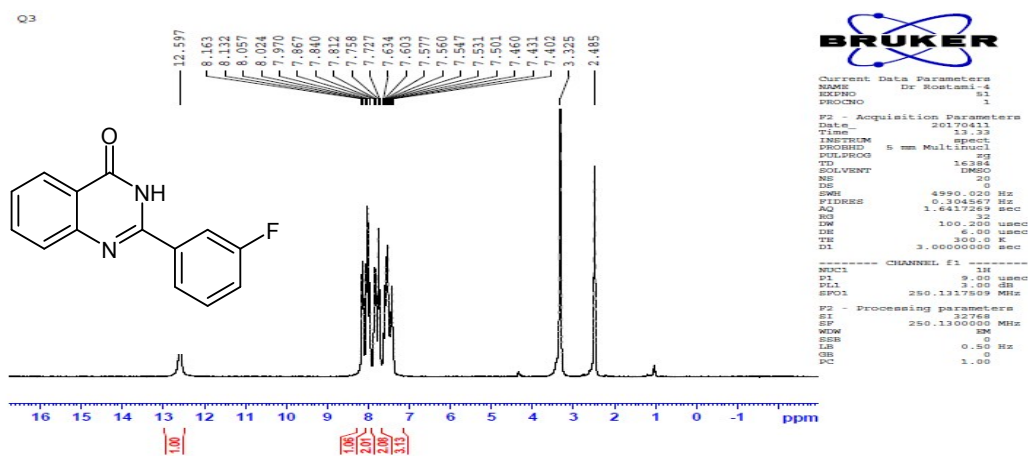
Q1



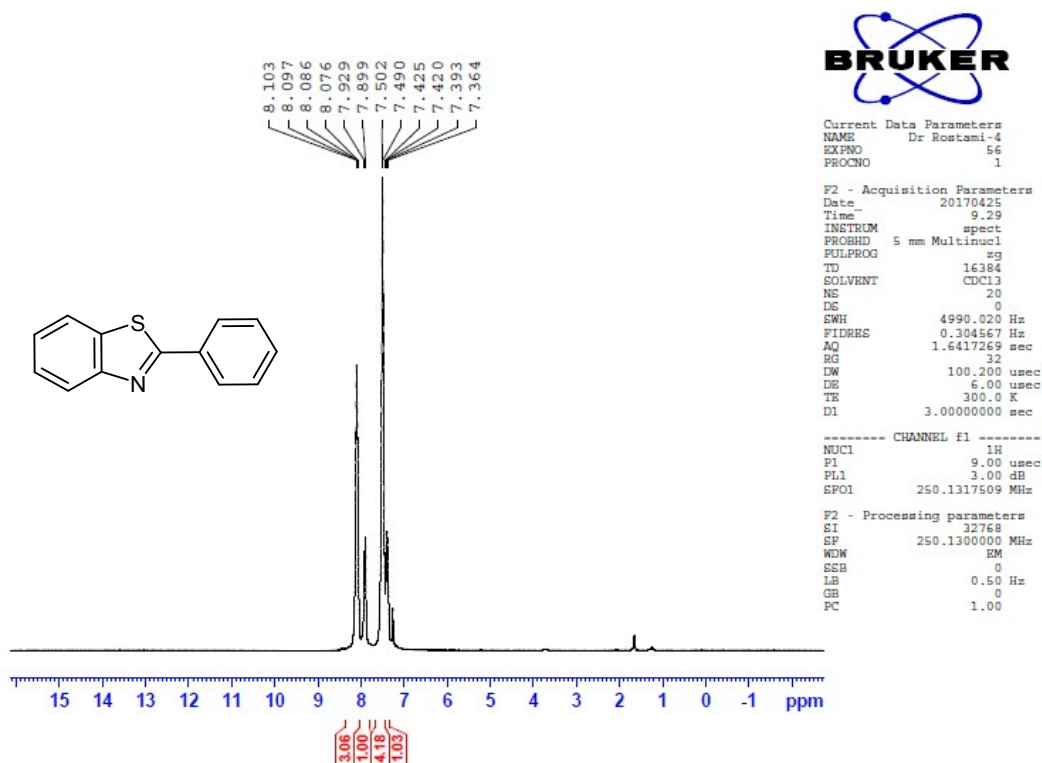
¹HNMR (Table 2, entry 8)



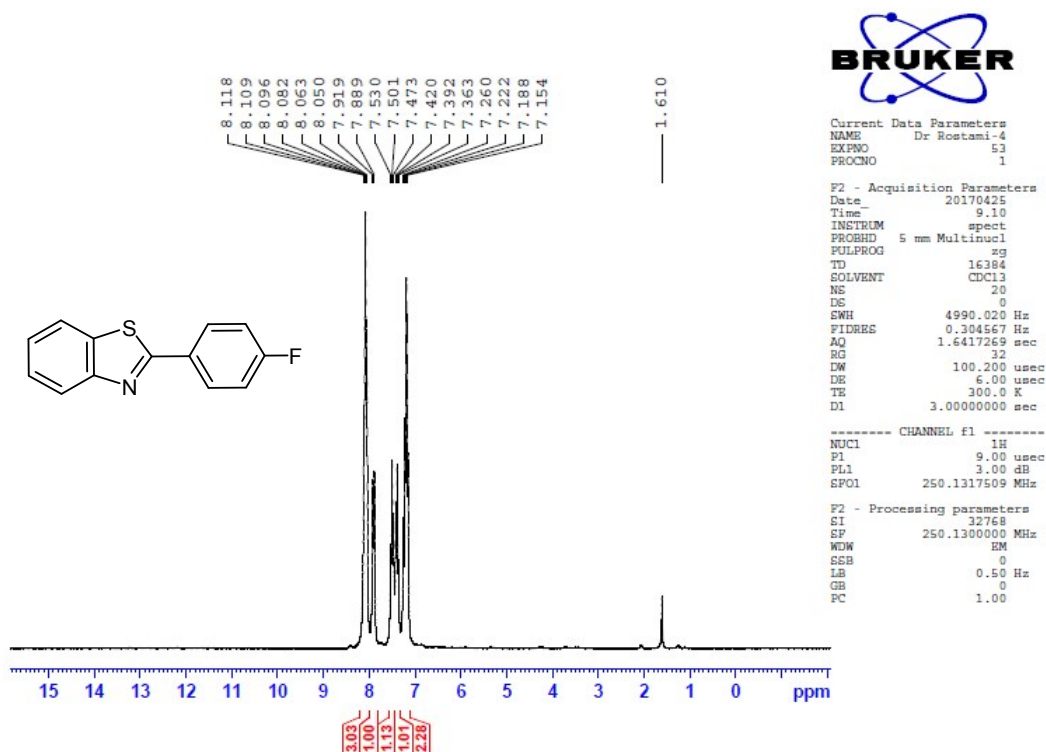
¹HNMR (Table 2, entry 9)



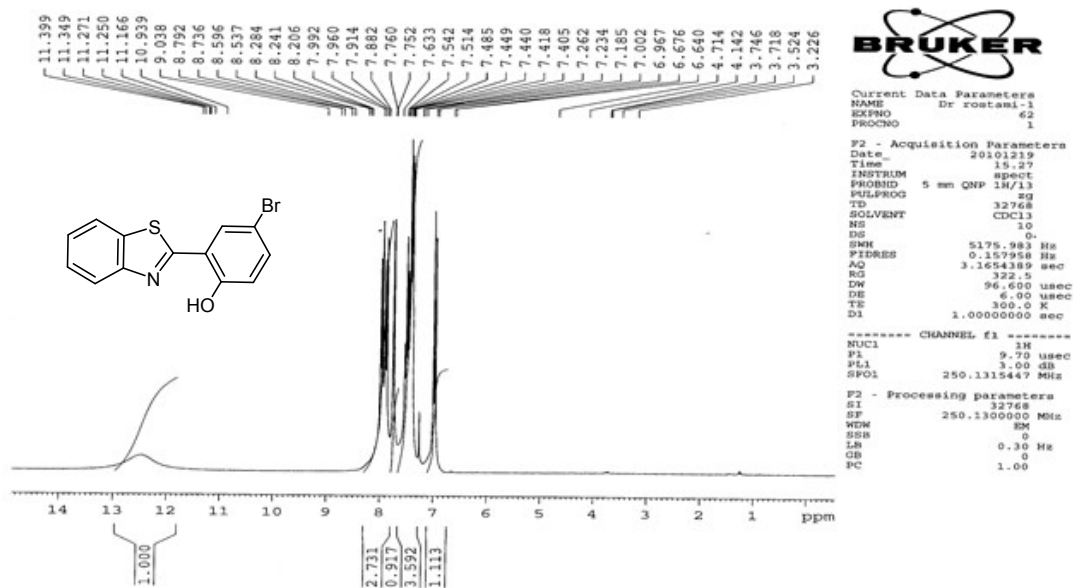
¹HNMR (Table 5, entry 1)



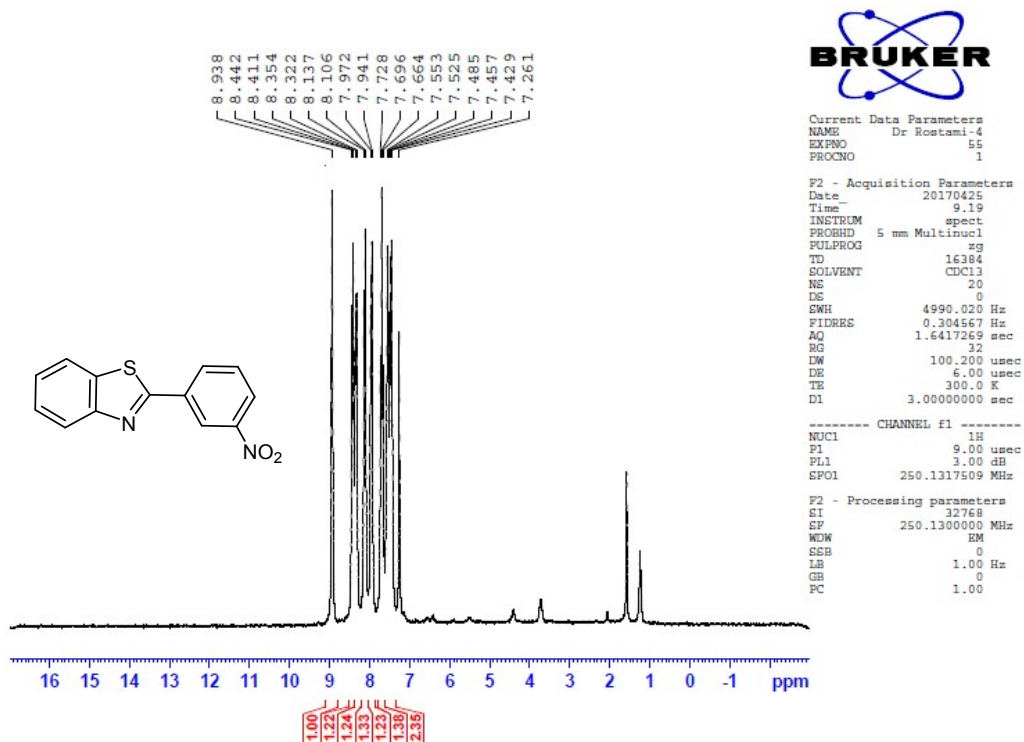
¹HNMR (Table 5, entry 6)



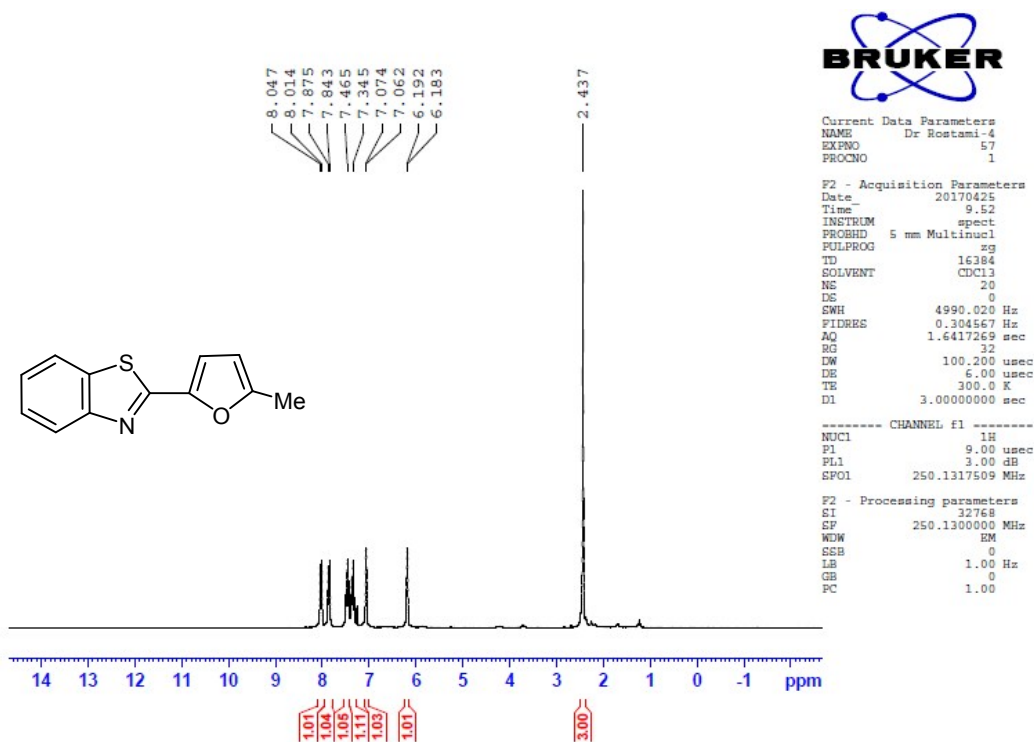
¹HNMR (Table 5, entry 13)



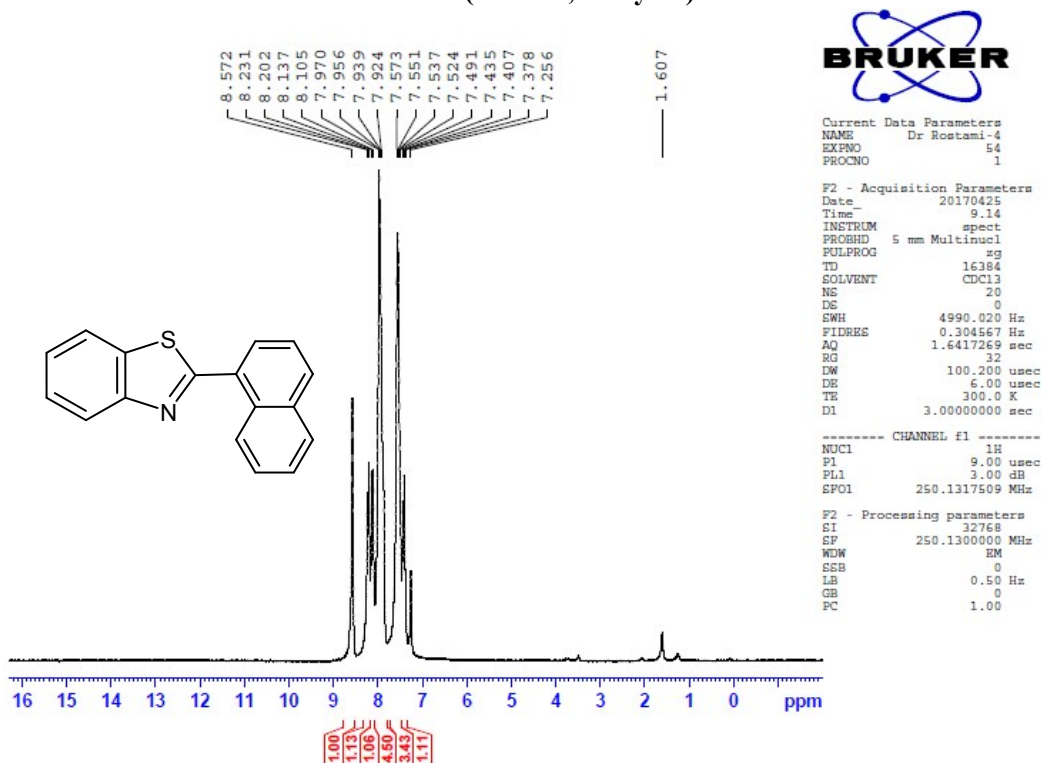
¹HNMR (Table 5, entry 18)



¹HNMR (Table 5, entry 19)



¹HNMR (Table 5, entry 20)



References

1. K. Upadhyaya, R. Kumar, T. Sanjeev, K. Shukla, R. Pati Tripathi, *J. Org. Chem.*, 2016, **81**, 5046.
2. J. Fang, J. Zhou, *J. Org. Chem.*, 2011, **76**, 7730.
3. X. L. Yang, C. M. Xu, S. M. Lin, J. X. Chen, J. C. Ding, H. Y. Wu, W. K. Sua, *J. Braz. Chem. Soc.*, 2010, **21**, 37.