SUPPORTING INFORMATION

Mechanochemical Solid-State Synthesis of 2-Aminothiazoles, Quinoxalines and Bezoylbenzofurans from Ketones by One-Pot Sequential Acid- and Base-Mediated Reactions

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Contents

Spectral Data of Products

*2-Amino-4-(p-bromophenyl)thiazole (**2a**).*[1] Pale yellow solid; R_f 0.40 (25 % EtOAc/petroleum ether); mp 170–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 (brs, 2H), 6.73 (s, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H).

*2-Phenylamino-4-(p-bromophenyl)thiazole (**2b**).*[2] Pale yellow solid; R_f 0.50 (5% EtOAc/petroleum ether); mp 132–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 7.07–7.11 (m, 1H), 7.35–7.40 (m, 4H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H).

*2-(p-Bromophenyl)amino-4-(p-bromophenyl)thiazole (**2c**).*[3] Pale yellow solid; R_f 0.65 (5% EtOAc/petroleum ether); mp 158–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.39 (brs, 1H), 7.46 (d, 8.9 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.71(d, *J* = 8.7 Hz, 2H).

*2-(p-Chlorophenyl)amino-4-(p-bromophenyl)thiazole (**2d**).*[2] White solid; R_f 0.65 (5% EtOAc/petroleum ether); mp 160–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.37 (d, 8.9 Hz, 2H), 7.41 (brs, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.71(d, *J* = 8.7 Hz, 2H).

*2-(p-Tolyl)amino-4-(p-bromophenyl)thiazole (**2e**).*[2] Colorless solid; R_f 0.68 (5% EtOAc/petroleum ether); mp 160–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 6.78 (s, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.39 (brs, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H).

*2-(2-Benzylidenehydrazinyl)-4-(p-bromophenyl)thiazole (**2g**).*[4] Pale brown solid; R_f 0.40 (10% EtOAc/petroleum ether); mp 216–218 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 1H), 7.34–7.38 (m, 3H), 7.40–7.42 (m, 3H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H).

2-(2-(*p*-Bromobenzylidene)hydrazinyl)-4-(*p*-bromophenyl)thiazole *(**2h**)*.[5] Pale brown solid; R_f 0.30 (10% EtOAc/petroleum ether); mp 200–202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.36 (s, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H).

*4-(p-Bromophenyl)-2-(2-(p-methoxybenzylidene)hydrazinyl)thiazole (**2i**).*[5] Pale brown solid; R_f 0.50 (10% EtOAc/petroleum ether); mp 198–200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.84 (s, 3H), 6.86 (s, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.45 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H).

*2-Amino-4,5-diphenylthiazole (**2j**).*[6] Colorless crystalline; R_f 0.50 (25% EtOAc/petroleum ether); mp 176–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.10 (s, 2H), 7.21–7.29 (m, 8H), 7.44–7.47 (m, 2H).

*2-Amino-8H-indeno[1,2-d]thiazole (**4a**).*[7] Pale brown solid; R_f 0.20 (10% EtOAc/petroleum ether); mp 192–194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 2H), 5.06 (brs, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H).

*2-Phenylamino-8H-indeno[1,2-d]thiazole (**4b**)*.[8] Off-white solid; R_f 0.42 (5% EtOAc/petroleum ether); mp 172–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 2H), 7.13–7.16 (m, 1H), 7.22–7.26 (m, 1H), 7.34–7.43 (m, 5H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.66 (d, *J* = 7.3 Hz, 1H).

*2-(p-Bromophenyl)quinoxaline (**5a**)*.[9] Pale orange yellow solid; R_f 0.50 (10% EtOAc/petroleum ether); mp 122–124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.74–7.83 (m, 2H), 8.09 (d, *J* = 8.2 Hz, 2H), 8.11–8.16 (m, 2H), 9.30 (s, 1H).

*2-(p-Bromophenyl)-6/7-methylquinoxaline (**5b+5b'**)*.[10] Pale yellow solid; R_f 0.50 (10% EtOAc/petroleum ether); isomers ratio (ca. 1:1); mp 136–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (s, 3H), 7.58–7.64 (m, 1H), 7.68–7.70 (m, 2H), 7.89 (s, 1H), 7.92 (s, 1H), 7.99–8.08 (m, 3H), 9.23 (s, 0.5H), 9.25 (s, 0.5H). (It should be noted that the spectral data are for an inseparable mixture with only the signal at δ ca. 9.2 split up as two signals. For each of these signals, the integration is accounted for 0.5 proton.)

*11H-indeno[2,1-b]quinoxaline (**6a**)*.[11] Pale yellow solid; R_f 0.35 (10% EtOAc/petroleum ether); mp 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (s, 2H), 7.52–7.57 (m, 2H), 7.65–7.67 (m, 1H), 7.70–7.77 (m, 2H), 8.10 (d, *J* = 9.6 Hz, 1H), 8.17 (d, *J* = 7.2 Hz, 1H), 8.26 (d, *J* = 7.2 Hz, 1H).

*2-Benzofuranyl-(p-bromophenyl)methanone (**7a**)*.[12] White solid; R_f 0.75 (5% EtOAc/petroleum ether); mp 170–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.55 (s, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 2H).

*(p-Bromophenyl)(5,7-dibromo-2-benzofuranyl)methanone (**7b**)*.[13] White solid; R_f 0.80 (5% EtOAc/petroleum ether); mp 198–200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 1.7 Hz, 1H), 8.03 (d, *J* = 8.6 Hz, 2H).

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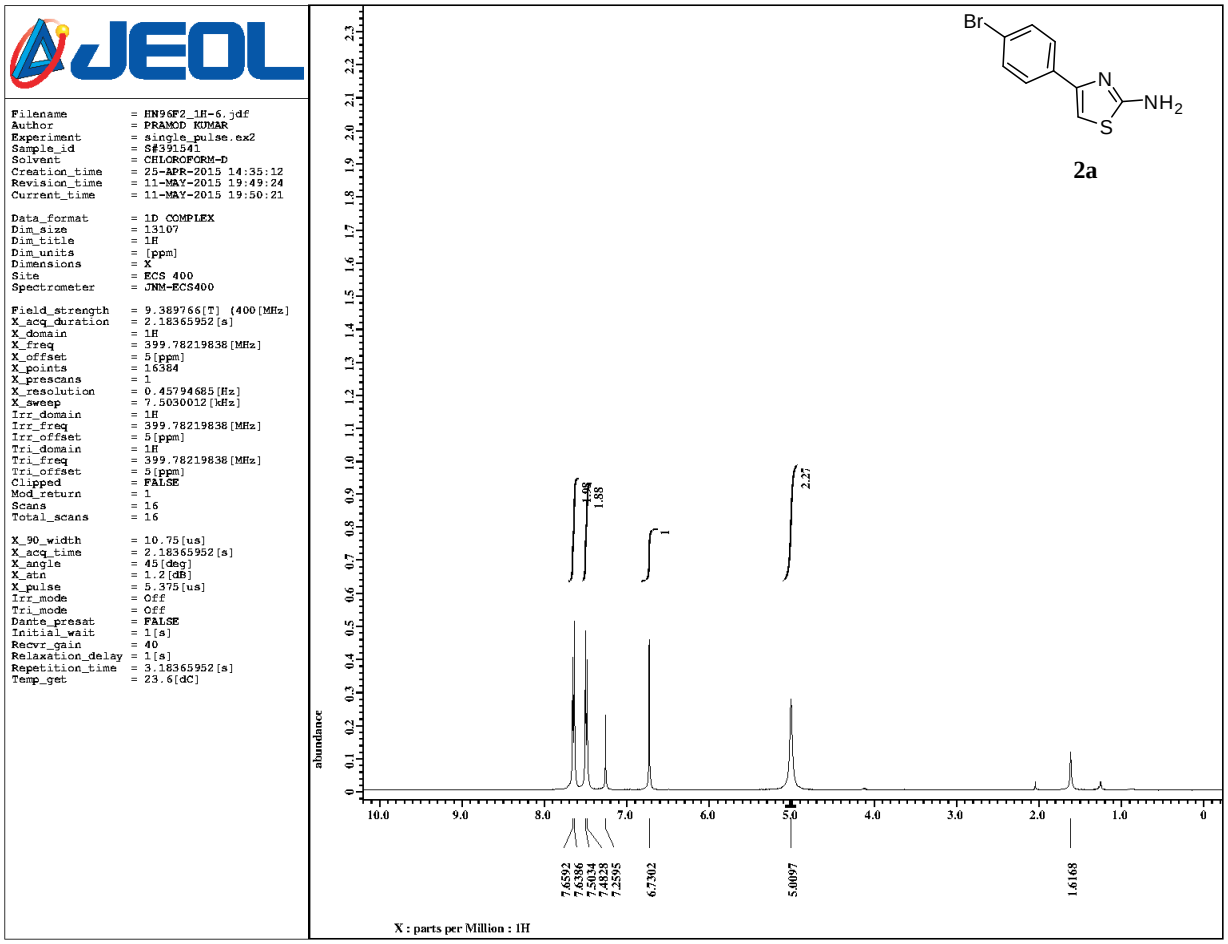

Figure S1. ^{1}H NMR spectrum of 2-amino-4-(*p*-bromophenyl)thiazole in $CDCl_3$.

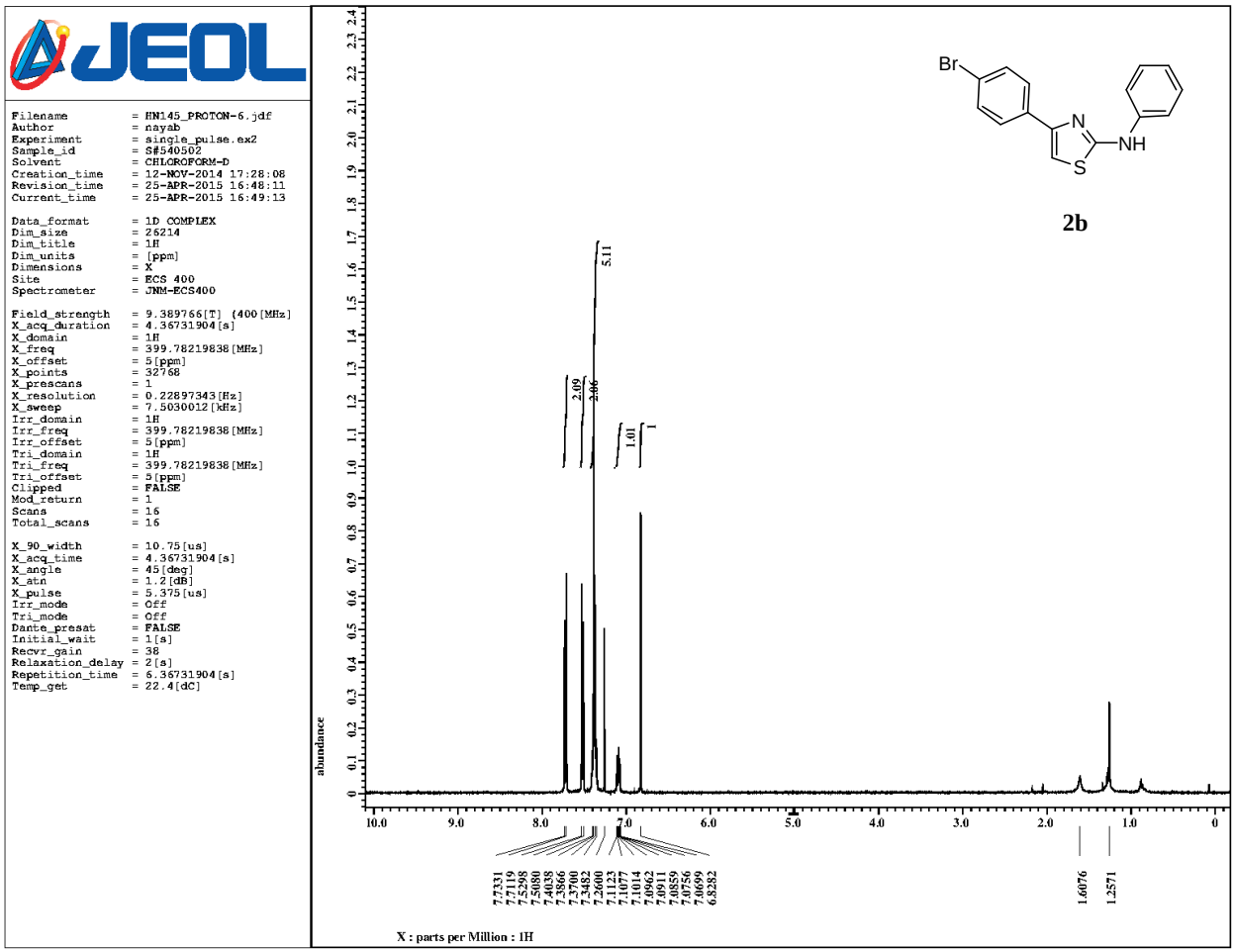

Figure S2. ^{1}H NMR spectrum of 2-phenylamino-4-(*p*-bromophenyl)thiazole in $CDCl_3$.

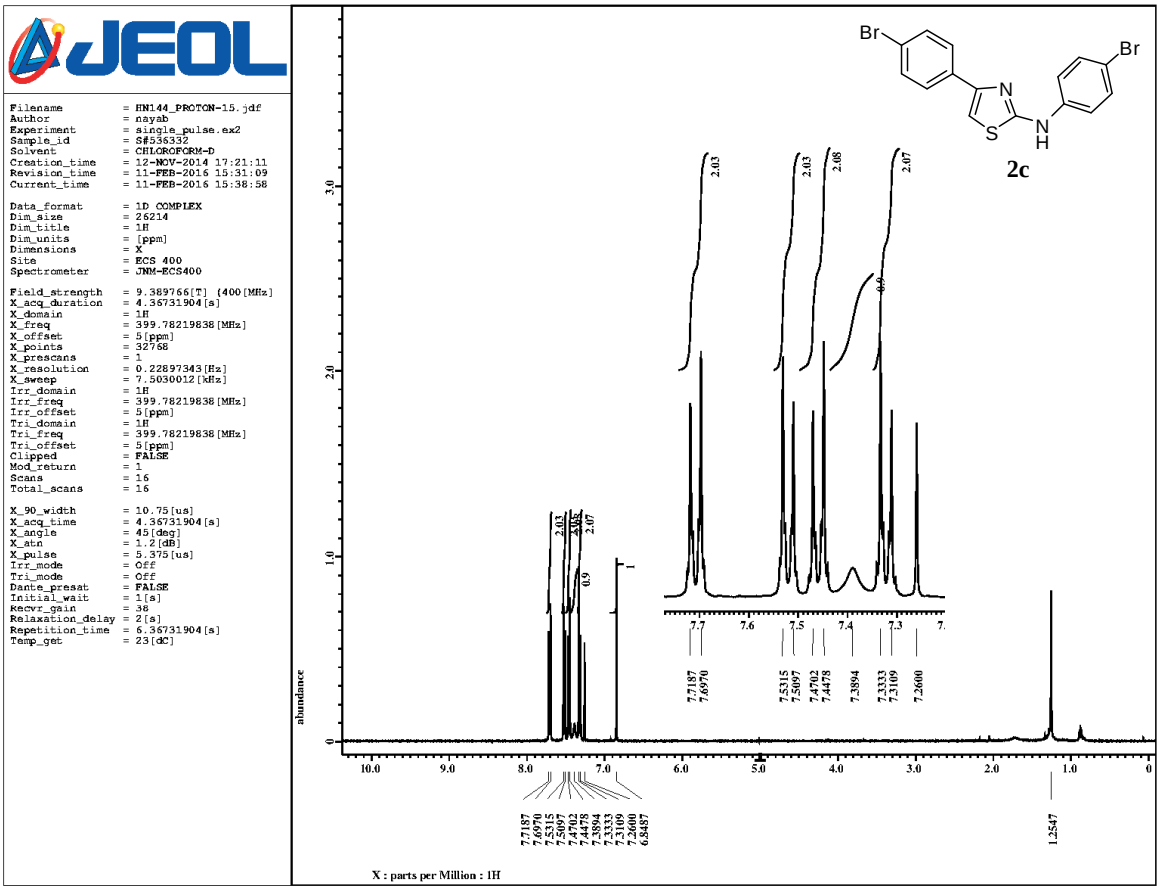

Figure S3. ^{1}H NMR spectrum of 2-(*p*-bromophenyl)amino-4-(*p*-bromophenyl)thiazole in $CDCl_3$.

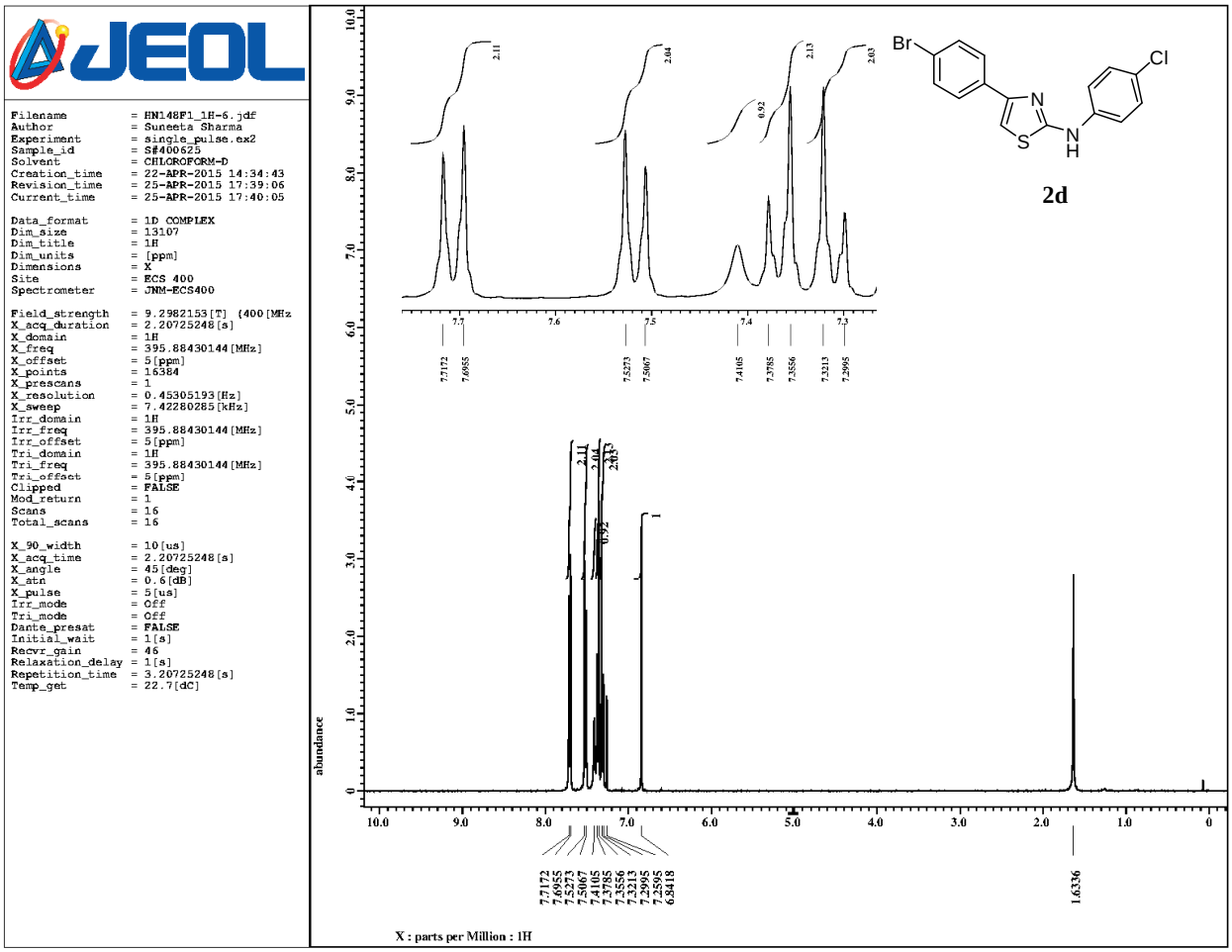

Figure S4. ^{1}H NMR spectrum of 2-(*p*-chlorophenyl)amino-4-(*p*-bromophenyl)thiazole in $CDCl_3$.

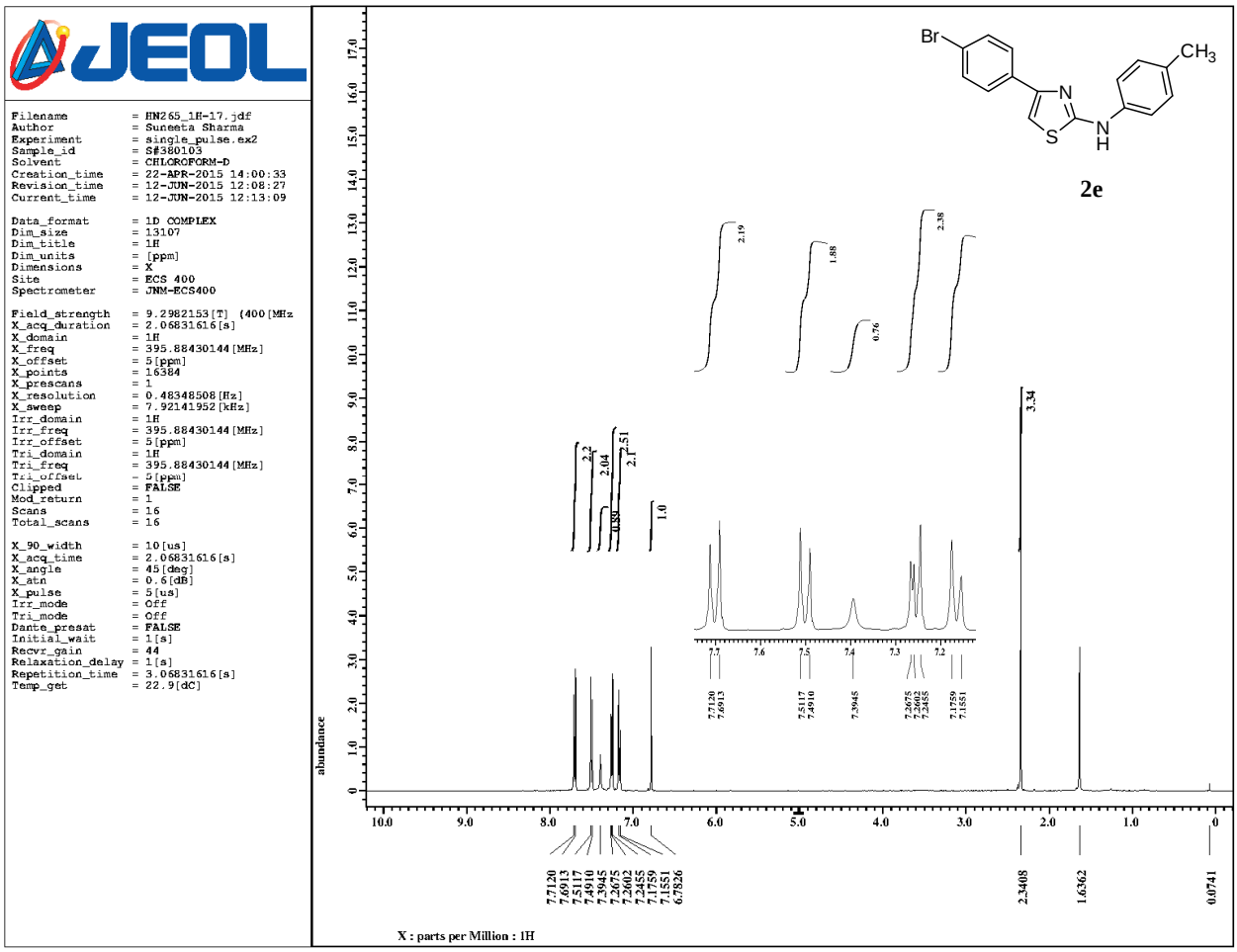

Figure S5. ^{1}H NMR spectrum of 2-(*p*-tolyl)amino-4-(*p*-bromophenyl)thiazole in $CDCl_3$.

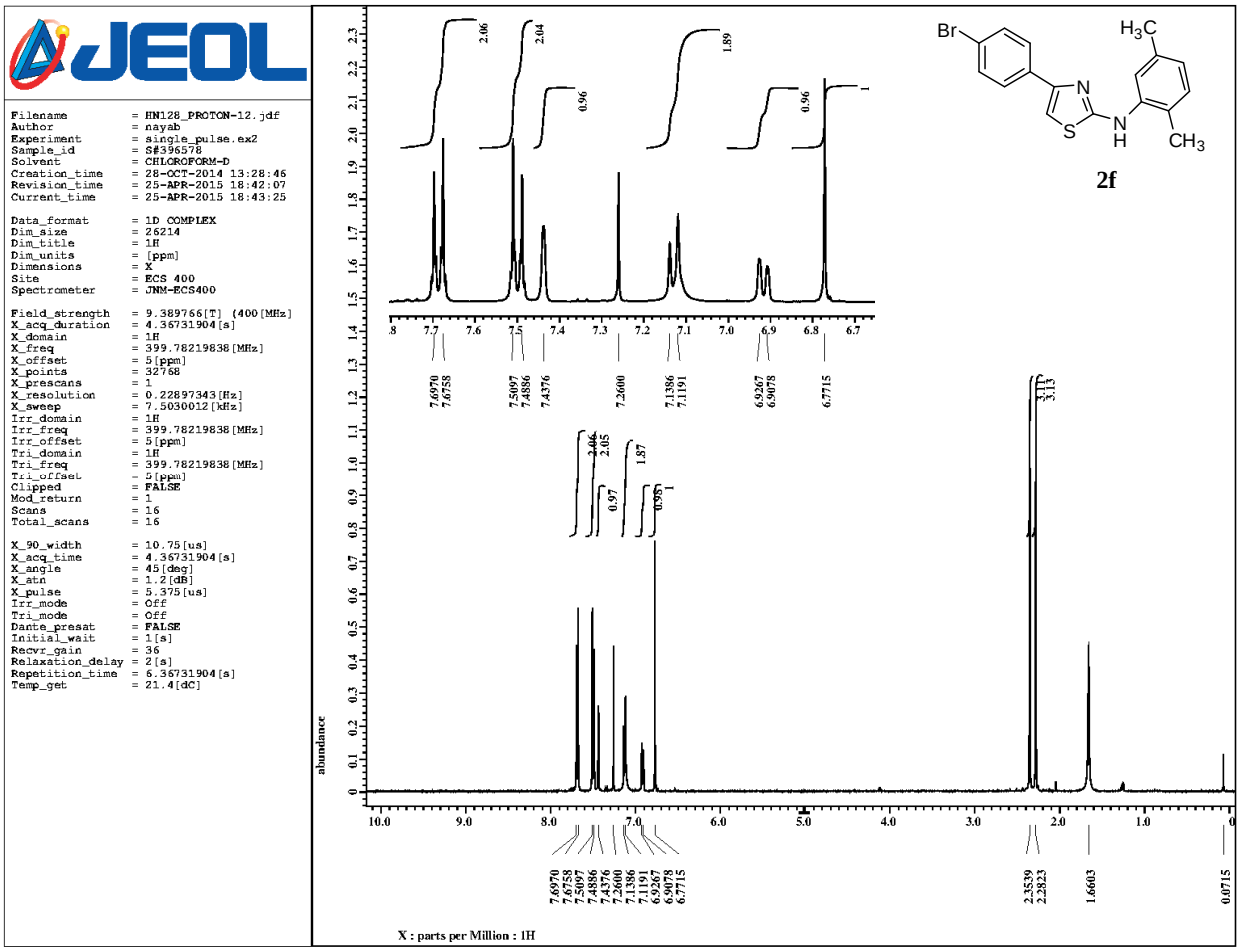

Figure S6. ^{1}H NMR spectrum of 2-(2,5-dimethylphenyl)amino-4-(*p*-bromophenyl)thiazole in $CDCl_3$.

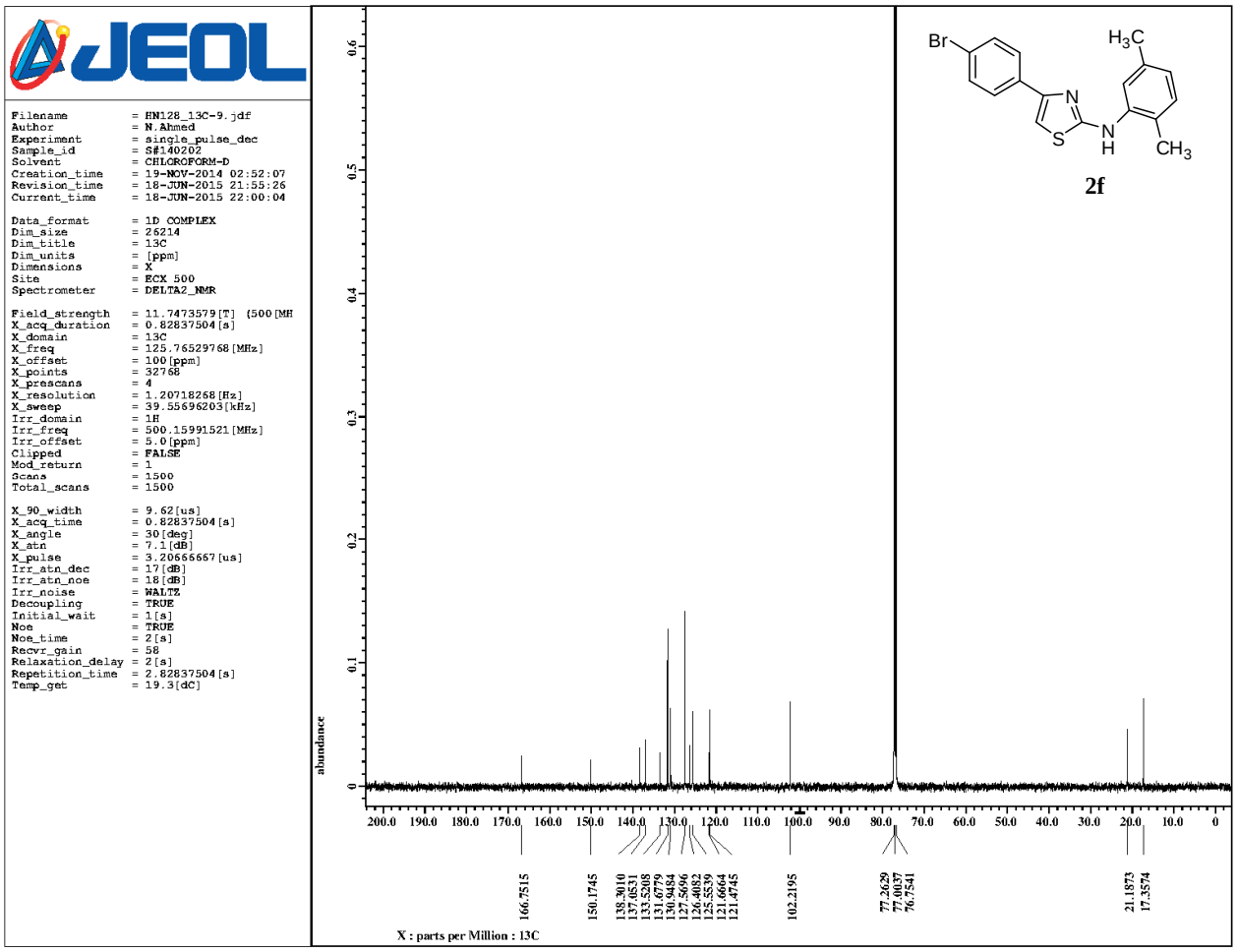

Figure S7. ^{13}C NMR spectrum of 2-(2,5-dimethylphenyl)amino-4-(*p*-bromophenyl)thiazole in $CDCl_3$.

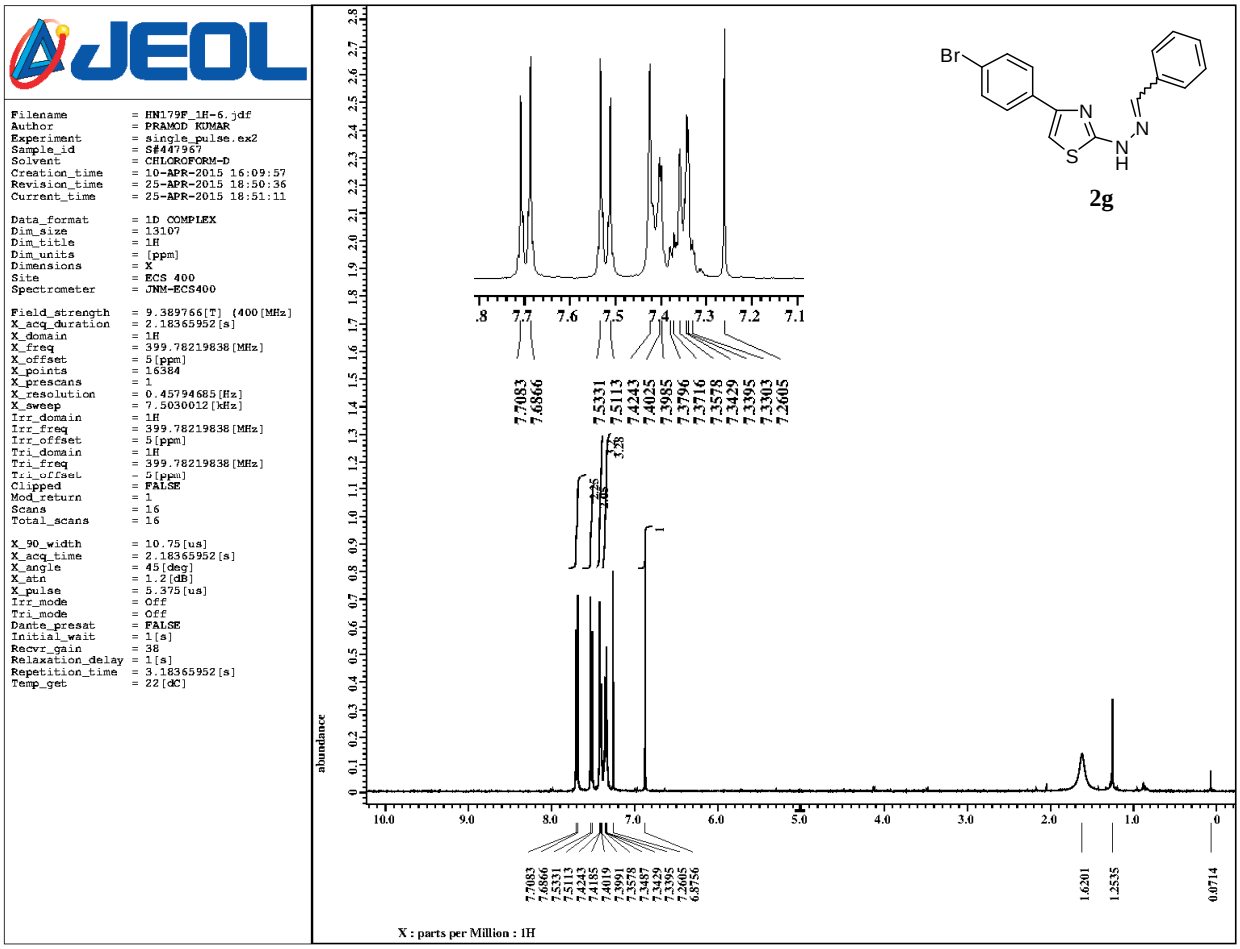

Figure S8. ^{1}H NMR spectrum of 2-(2-benzylidenehydrazinyl)-4-(*p*-bromophenyl)thiazole in $CDCl_3$.

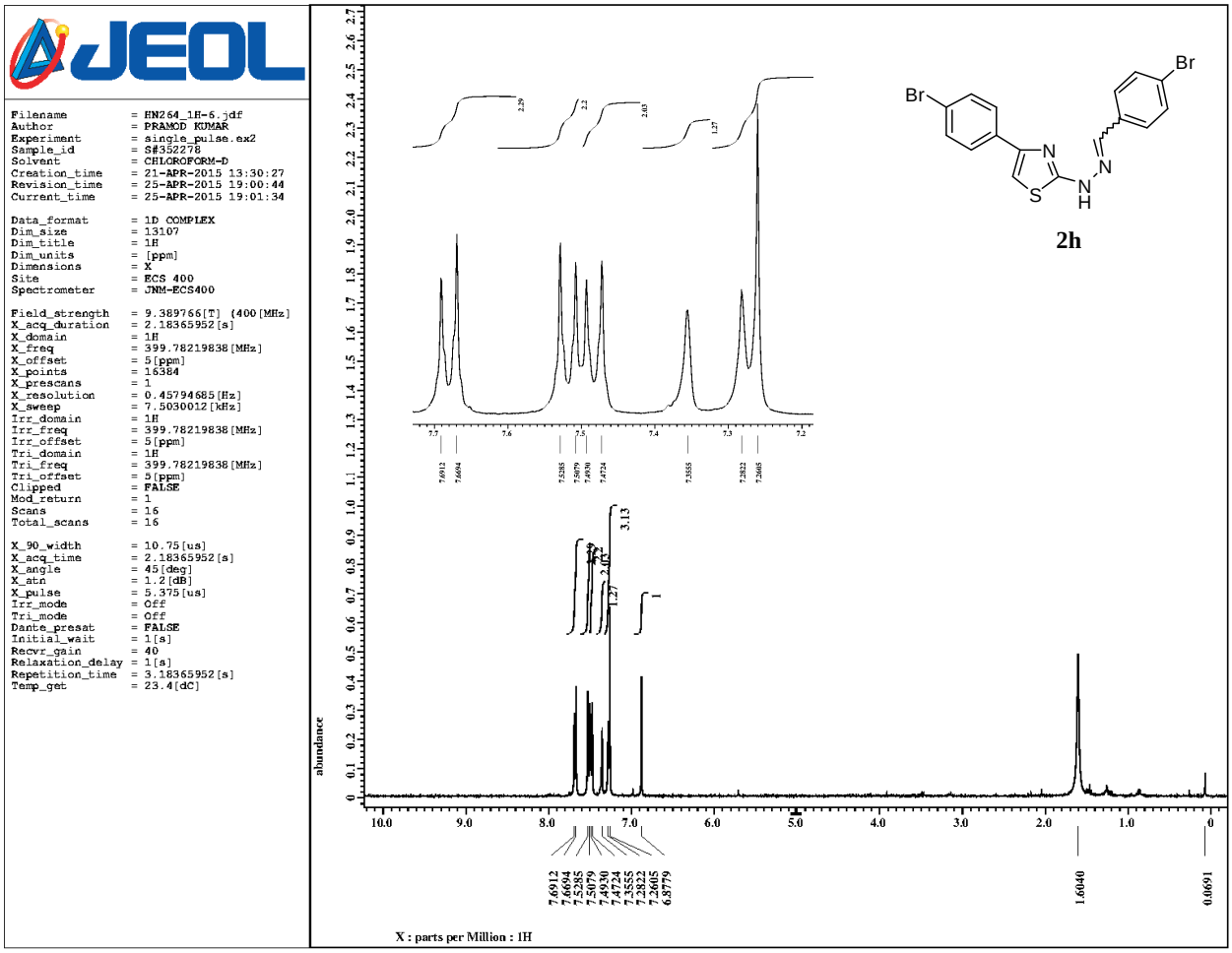

Figure S9. ^{1}H NMR spectrum of 2-(2-(*p*-bromobenzylidene)hydrazinyl)-4-(*p*-bromophenyl)thiazole in $CDCl_3$.

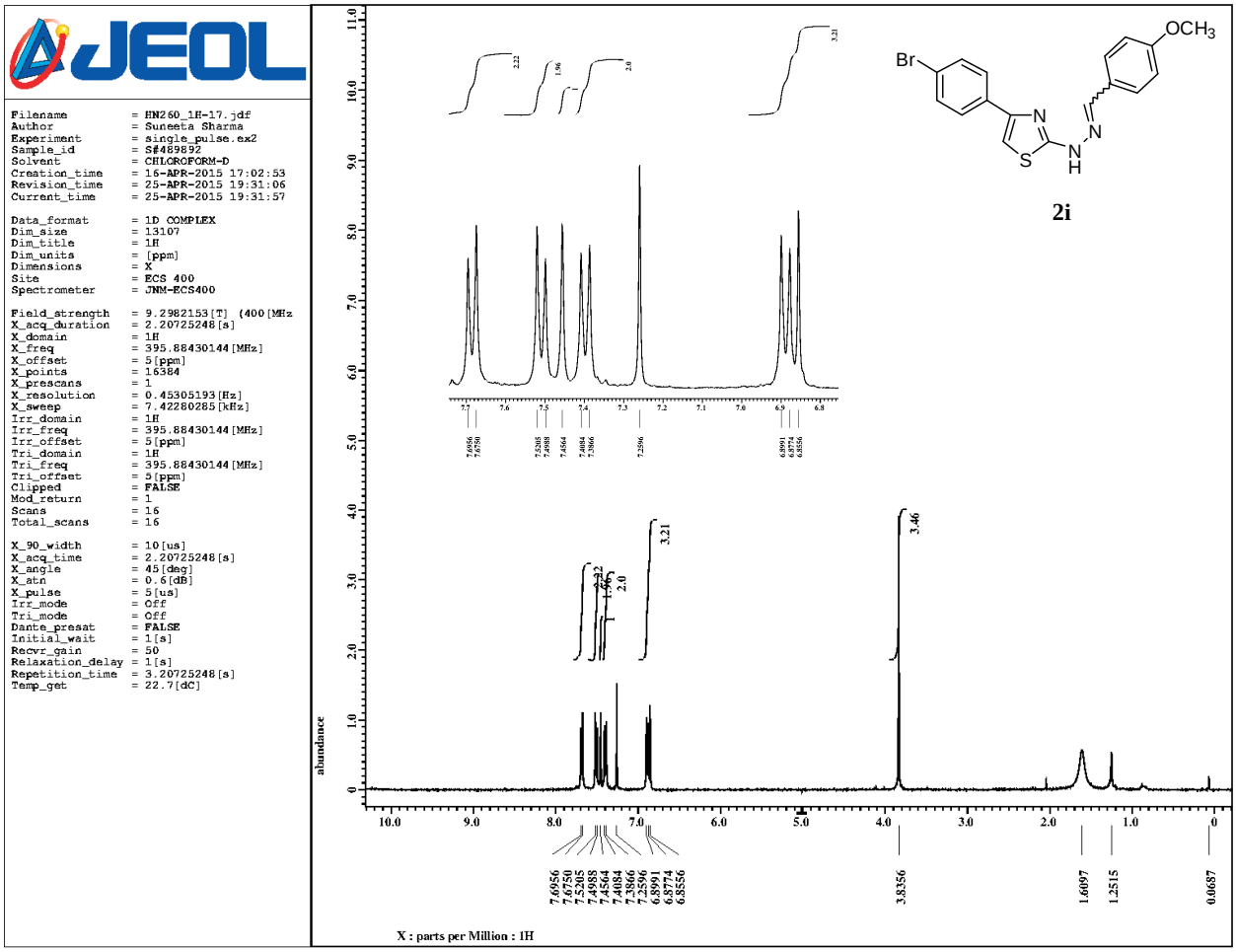

Figure S10. ^{1}H NMR spectrum of 4-(*p*-bromophenyl)-2-(2-(*p*-methoxybenzylidene)hydrazinyl) thiazole in $CDCl_3$.

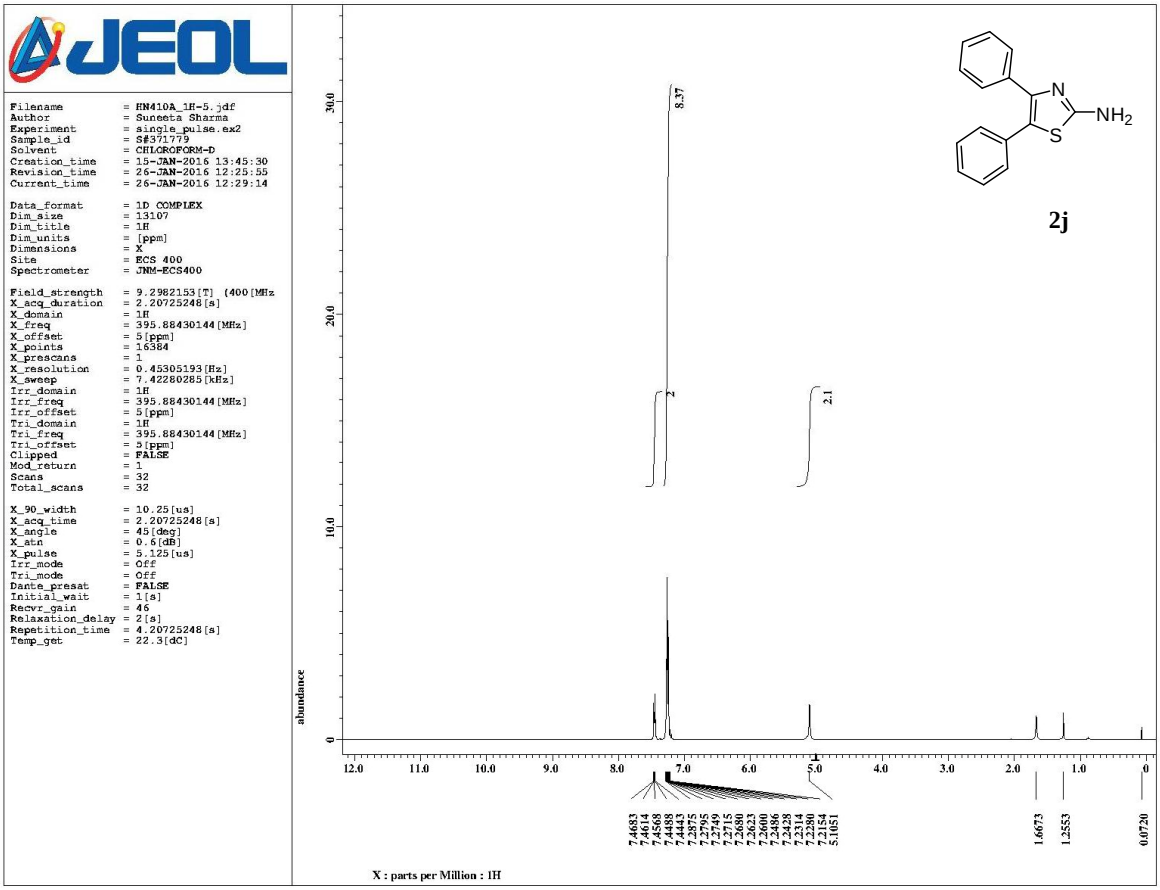

Figure S11. ^{1}H NMR spectrum of 2-amino-4,5-diphenylthiazole in $CDCl_3$.

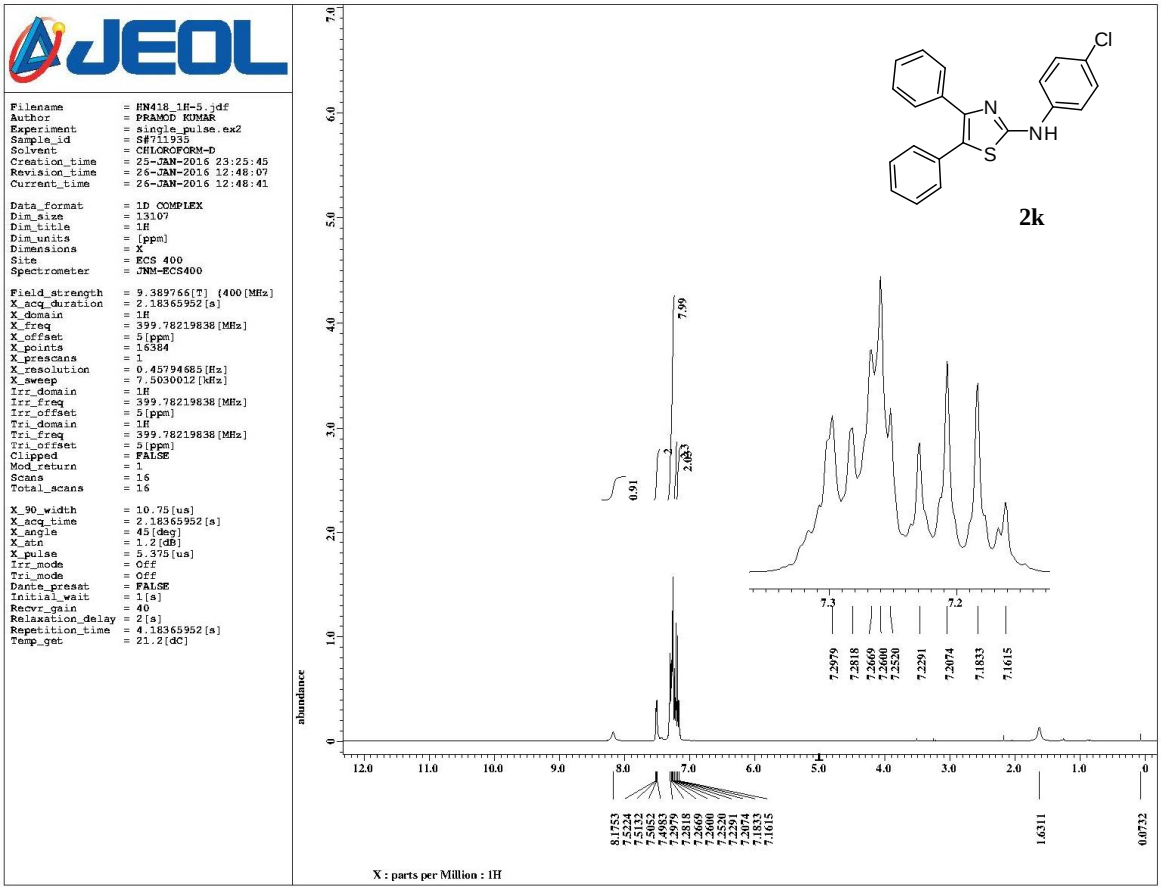

Figure S12. ^{1}H NMR spectrum of 2-(*p*-chlorophenyl)amino-4,5-diphenylthiazole in $CDCl_3$.

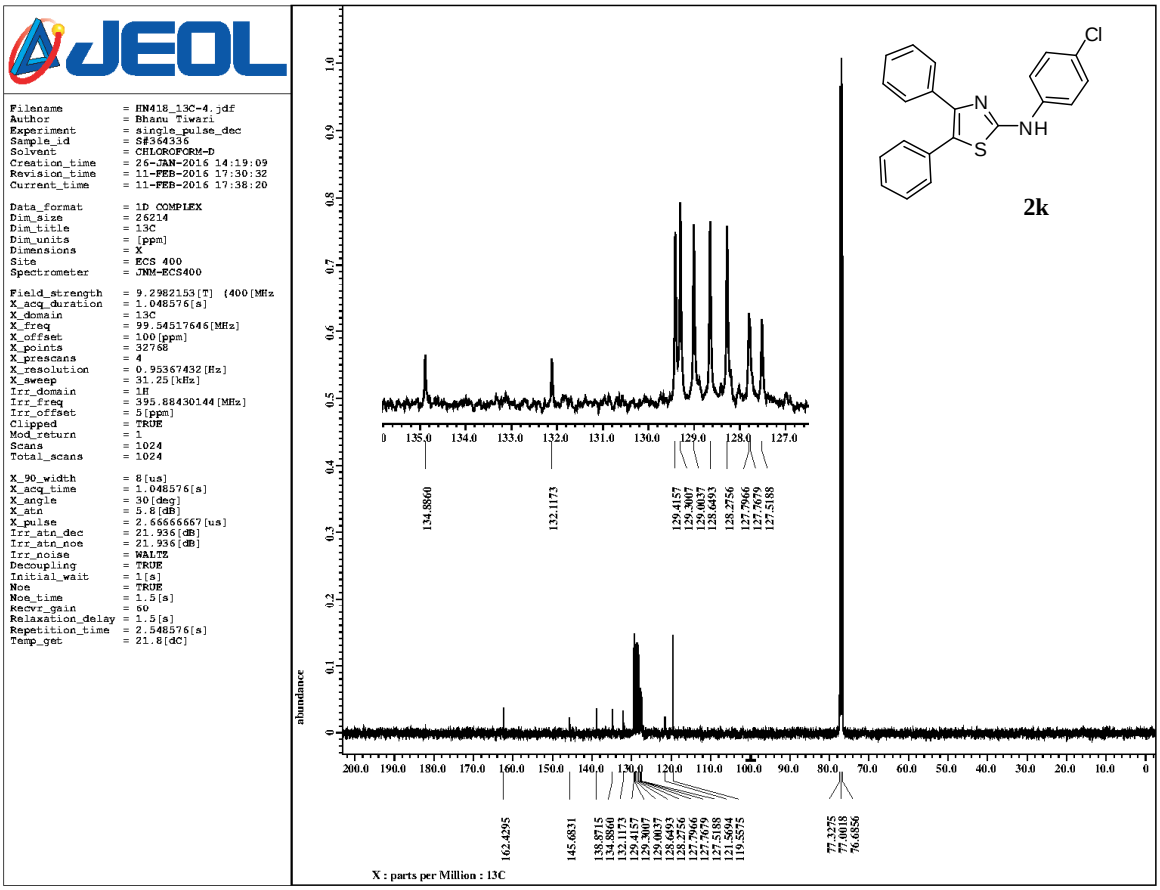

Figure S13. ^{13}C NMR spectrum of 2-(*p*-chlorophenyl)amino-4,5-diphenylthiazole in $CDCl_3$.

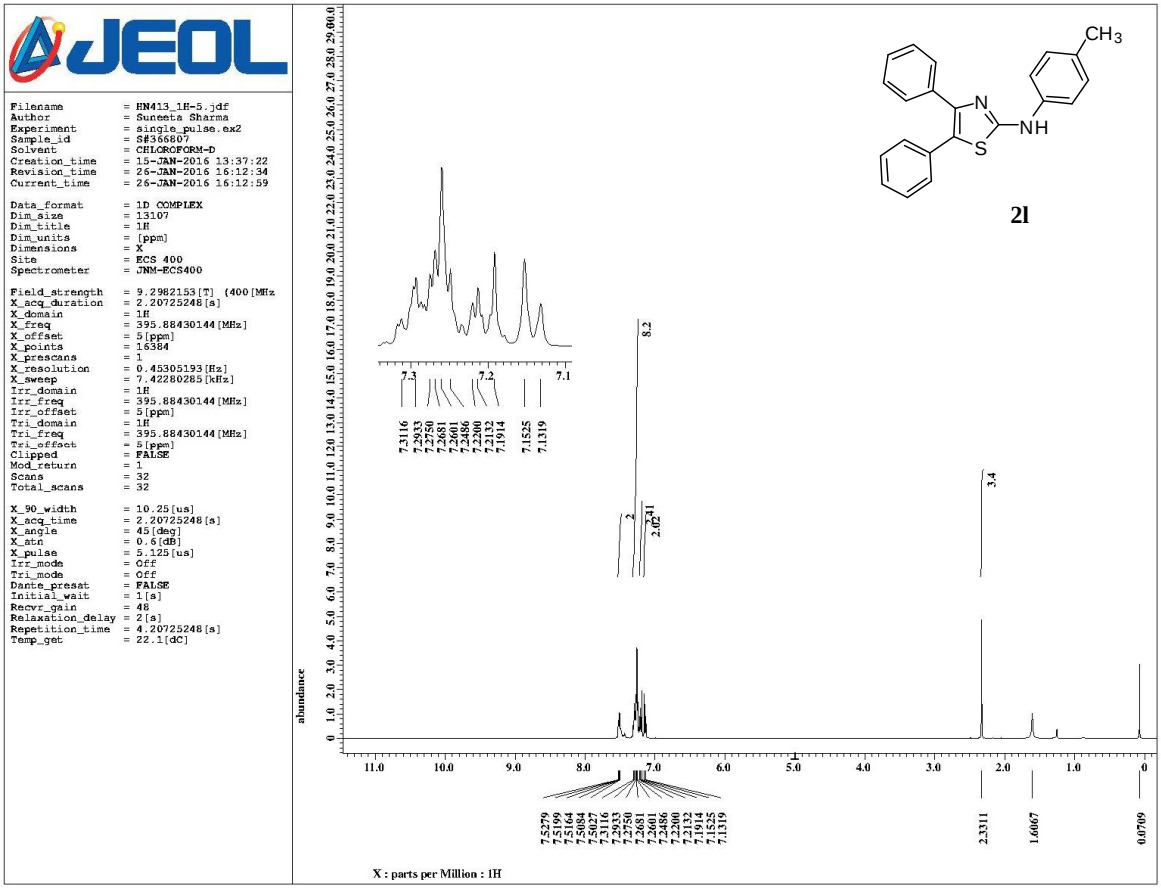

Figure S14. ^{1}H NMR spectrum of 4,5-diphenyl-2-(*p*-tolyl)aminothiazole in $CDCl_3$.

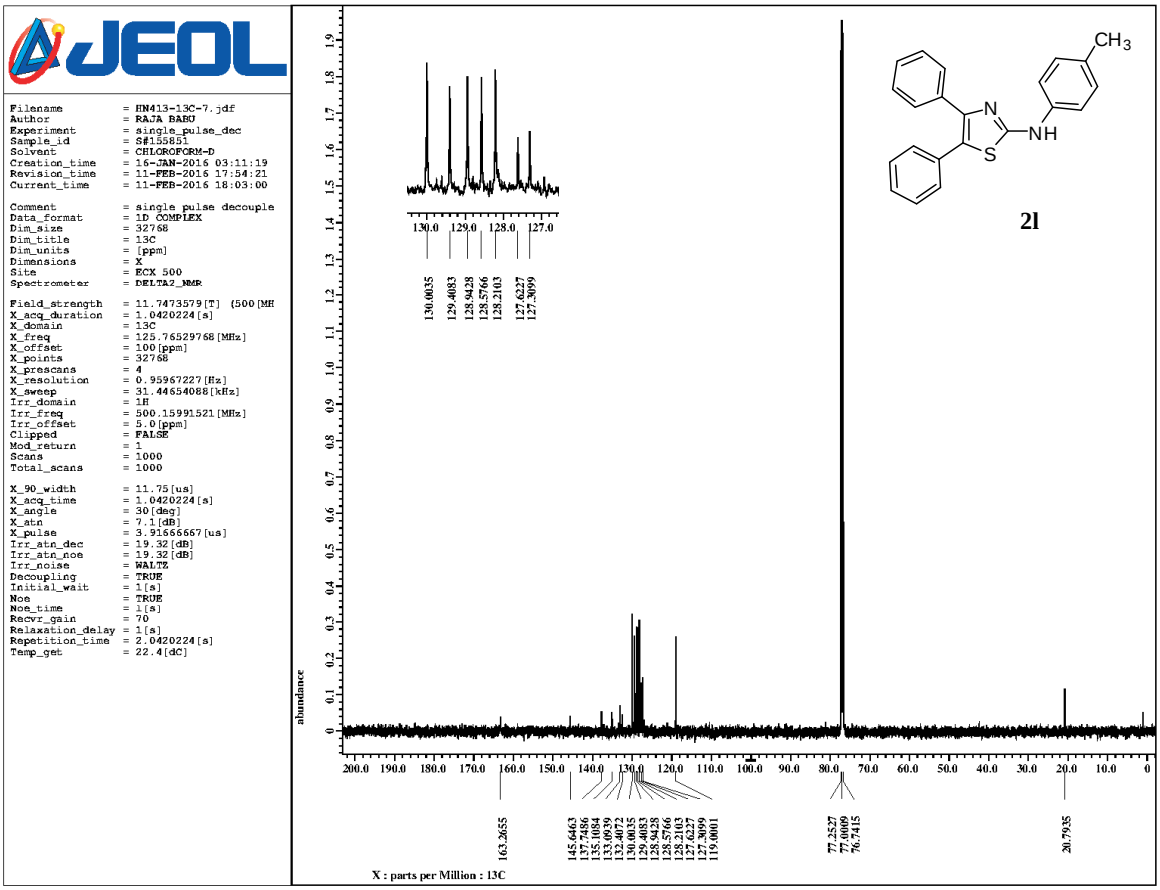

Figure S15. ^{13}C NMR spectrum of 4,5-diphenyl-2-(*p*-tolyl)aminothiazole in $CDCl_3$.

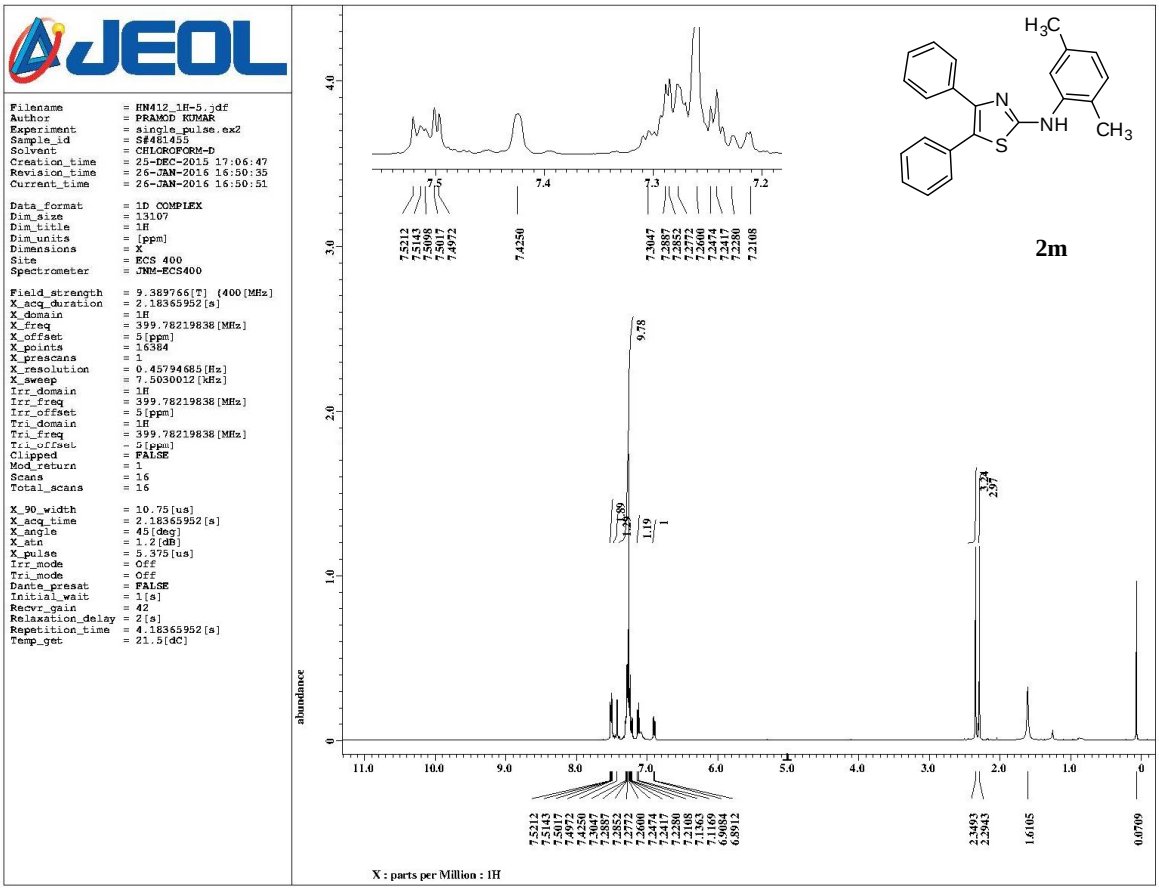

Figure S16. ^{1}H NMR spectrum of 2-(2,5-dimethylphenyl)amino-4,5-diphenylthiazole in $CDCl_3$.

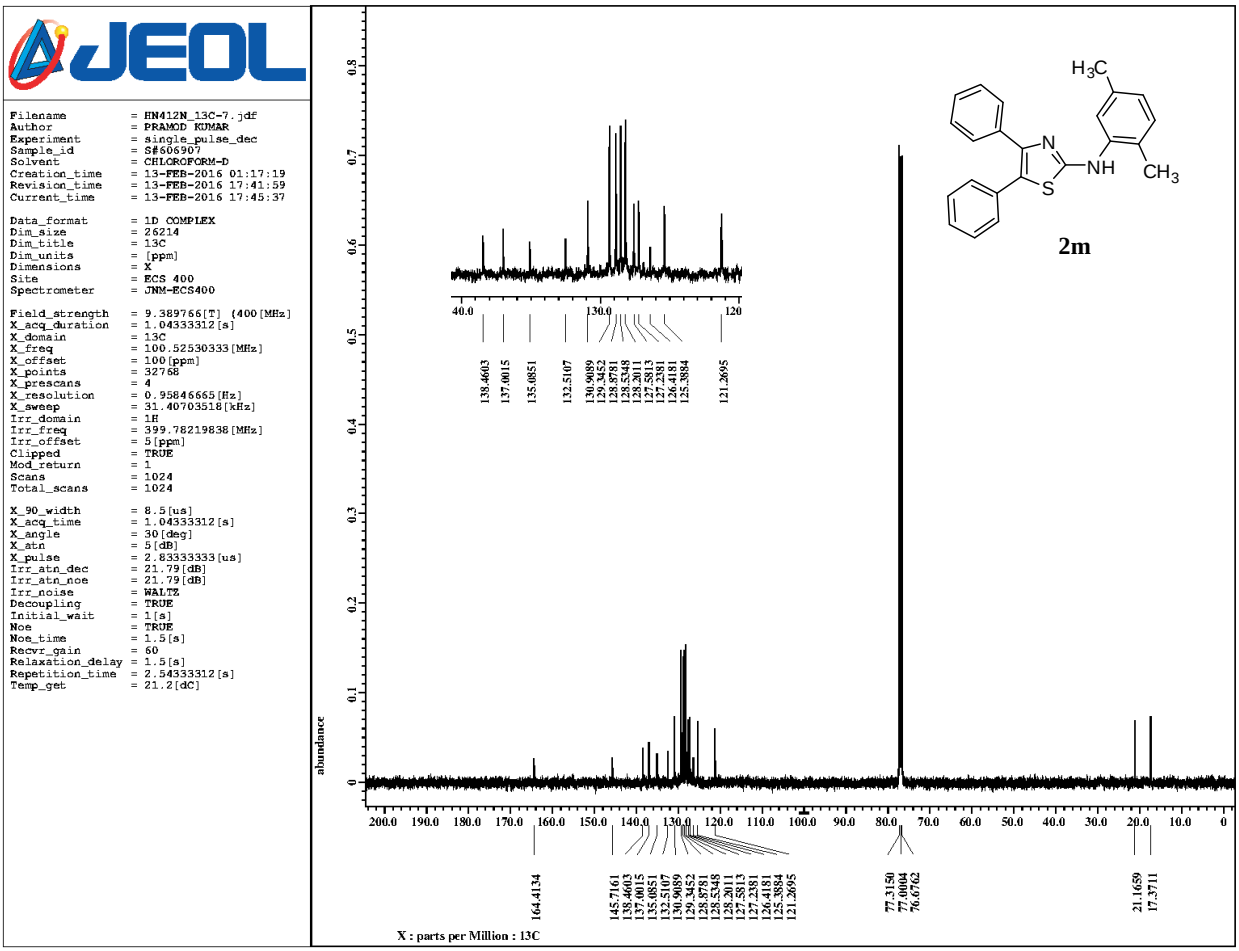

Figure S17. ^{13}C NMR spectrum of 2-(2,5-dimethylphenyl)amino-4,5-diphenylthiazole in $CDCl_3$.

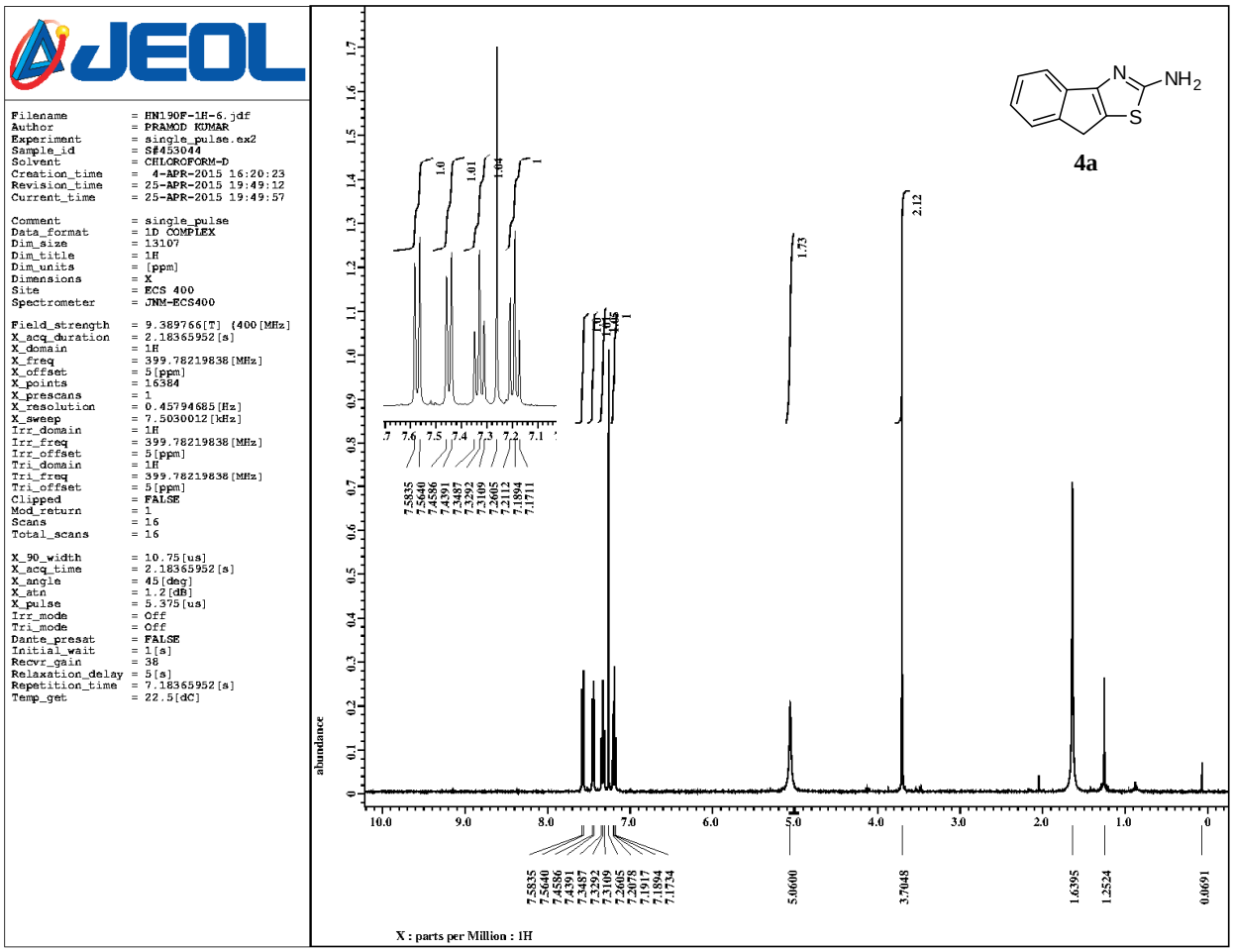

Figure S18. ^{1}H NMR spectrum of 2-amino-8*H*-indeno[1,2-*d*]thiazole in $CDCl_3$.

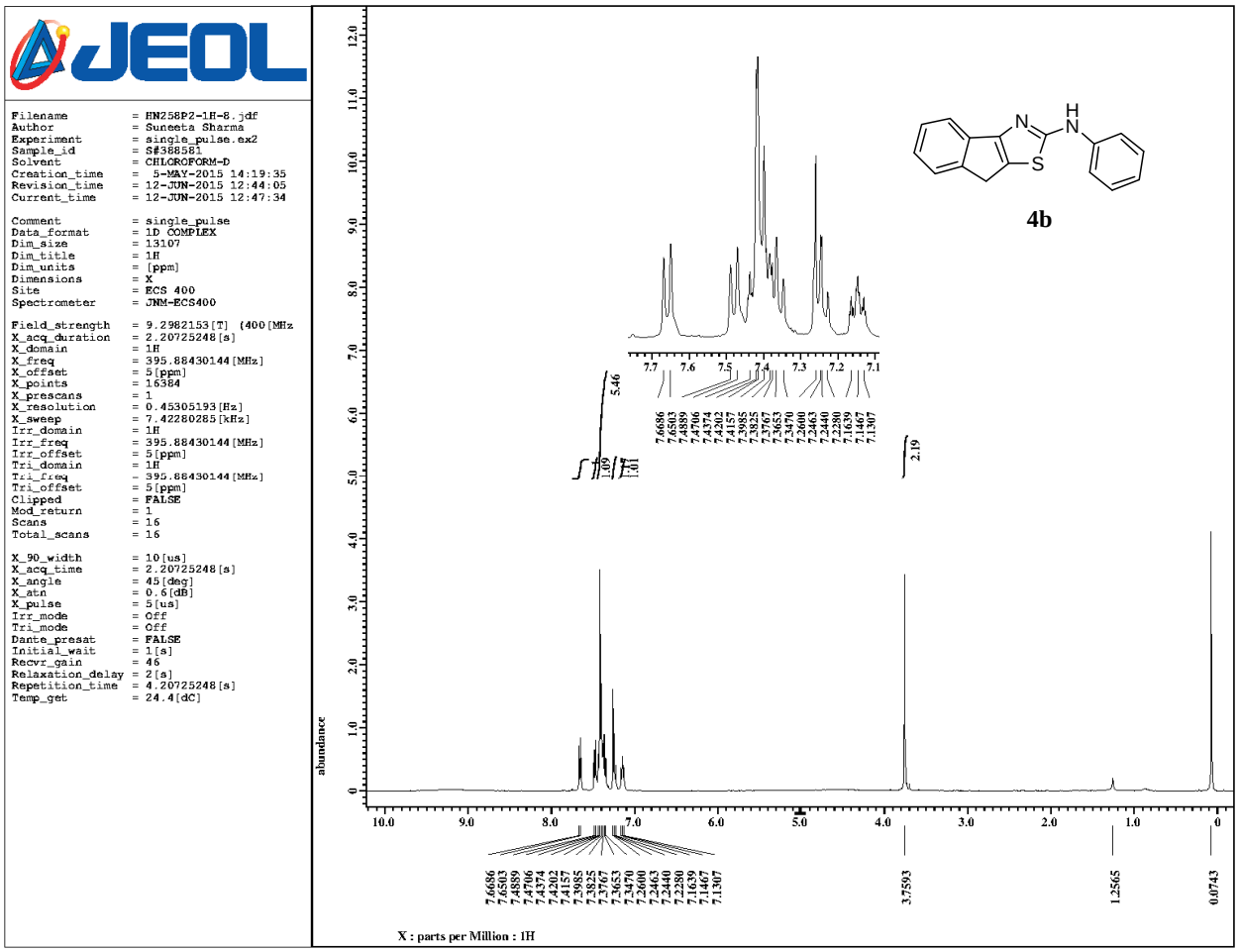

Figure S19. ^{1}H NMR spectrum of 2-phenylamino-8*H*-indeno[1,2-*d*]thiazole in $CDCl_3$.

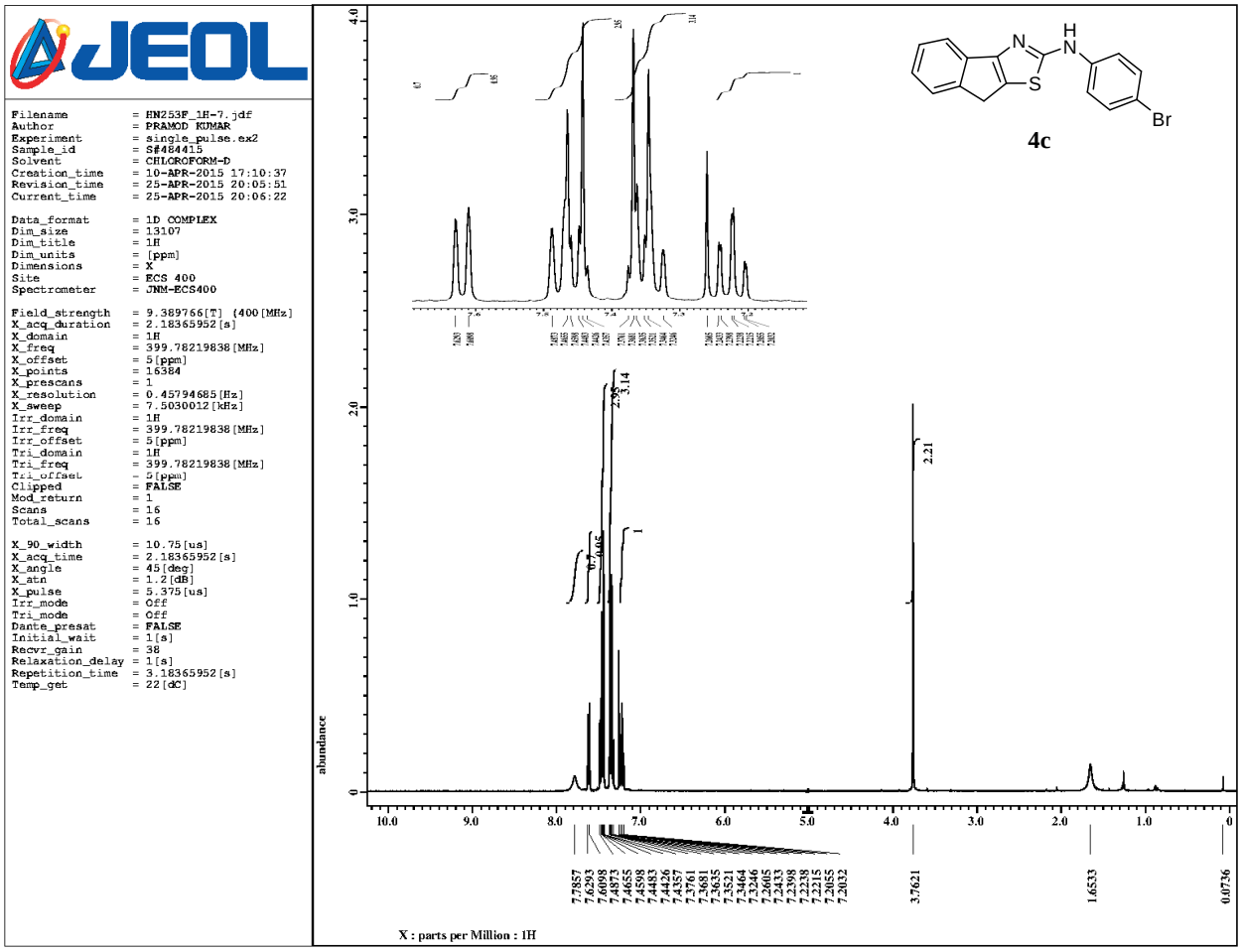

Figure S20. ^{1}H NMR spectrum of 2-(*p*-bromophenyl)amino-8*H*-indeno[1,2-*d*]thiazole in $CDCl_3$.

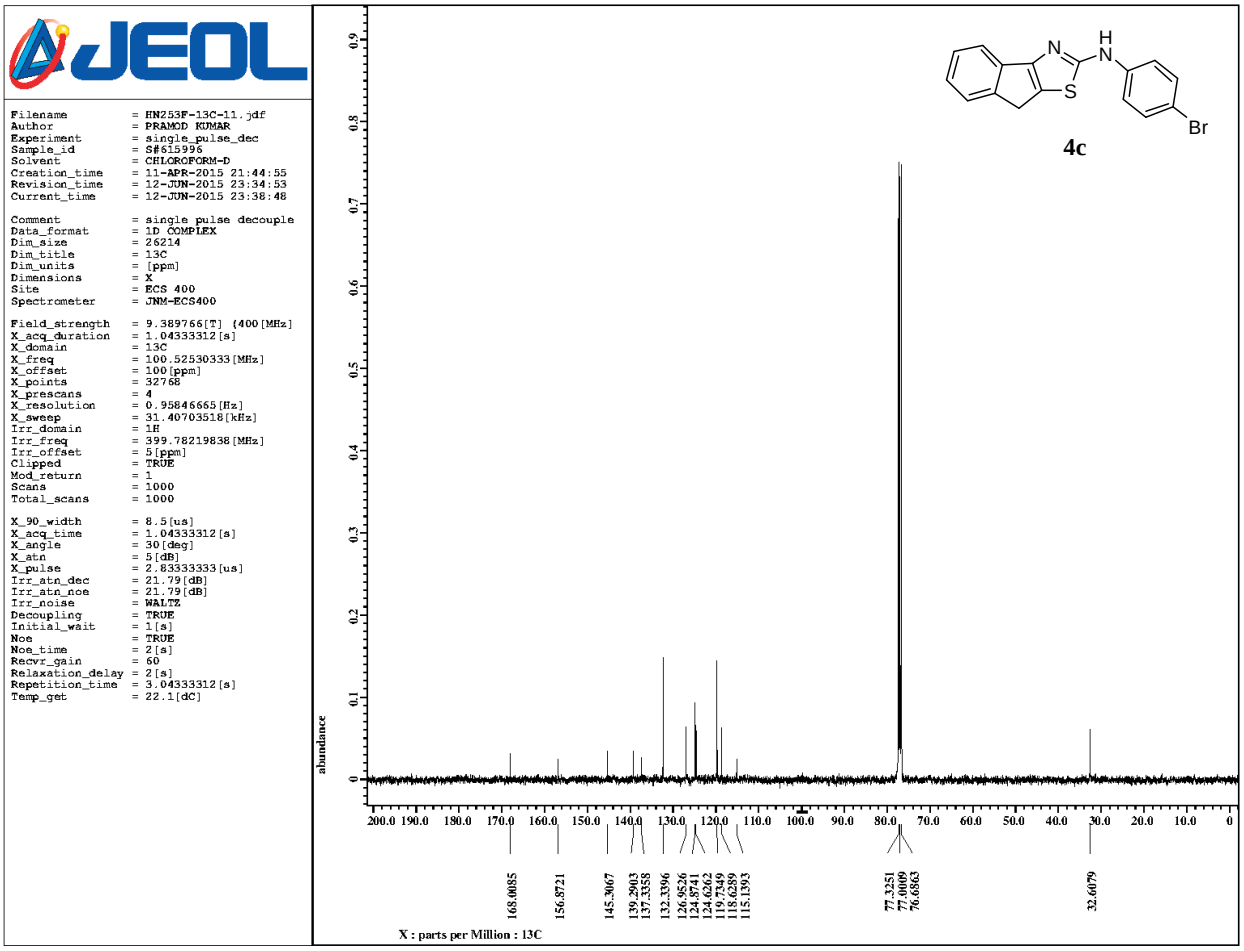

Figure S21. ^{13}C NMR spectrum of 2-(*p*-bromophenyl)amino-8*H*-indeno[1,2-*d*]thiazole in $CDCl_3$.

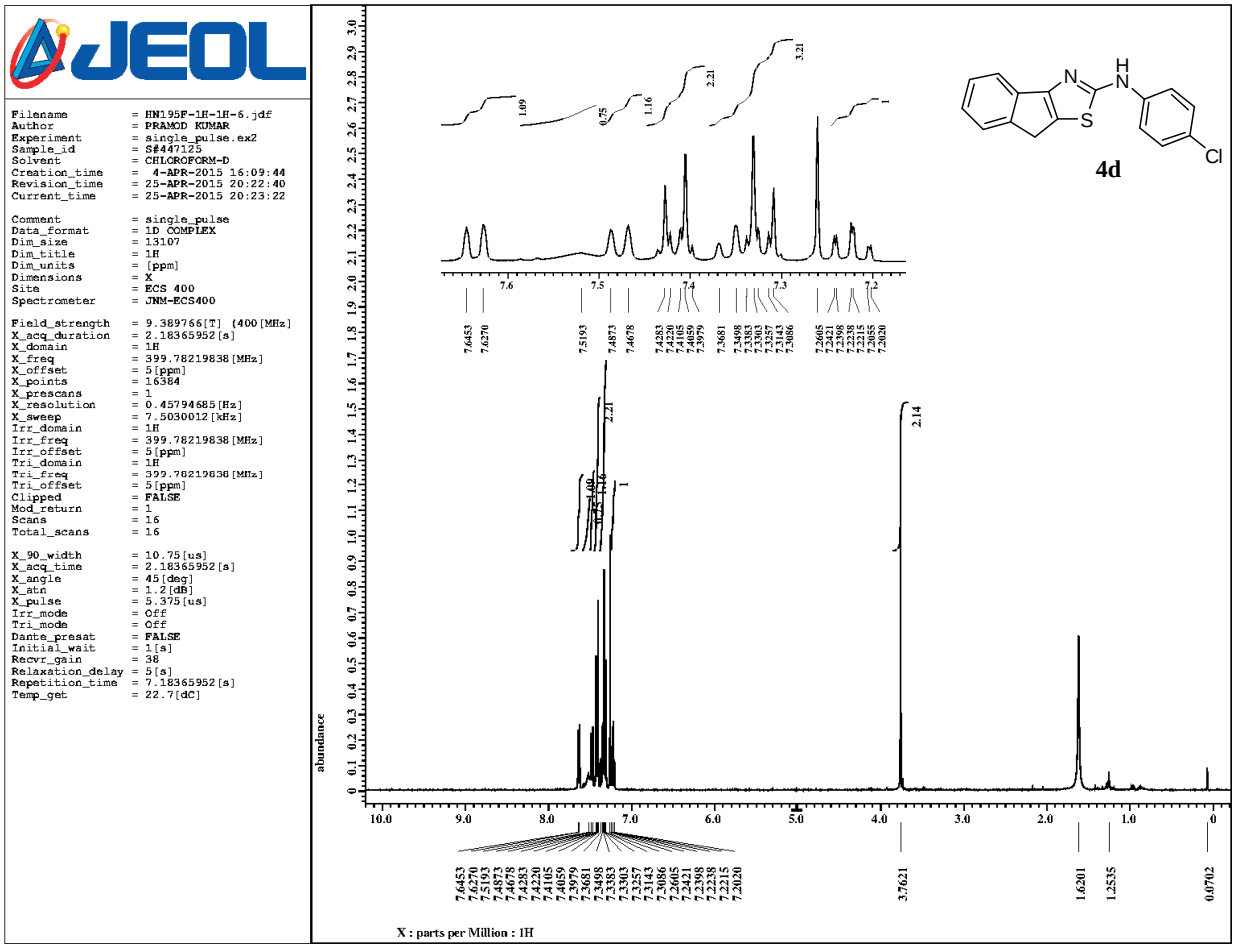

Figure S22. ^{1}H NMR spectrum of 2-(*p*-chlorophenyl)amino-8*H*-indeno[1,2-*d*]thiazole in $CDCl_3$.

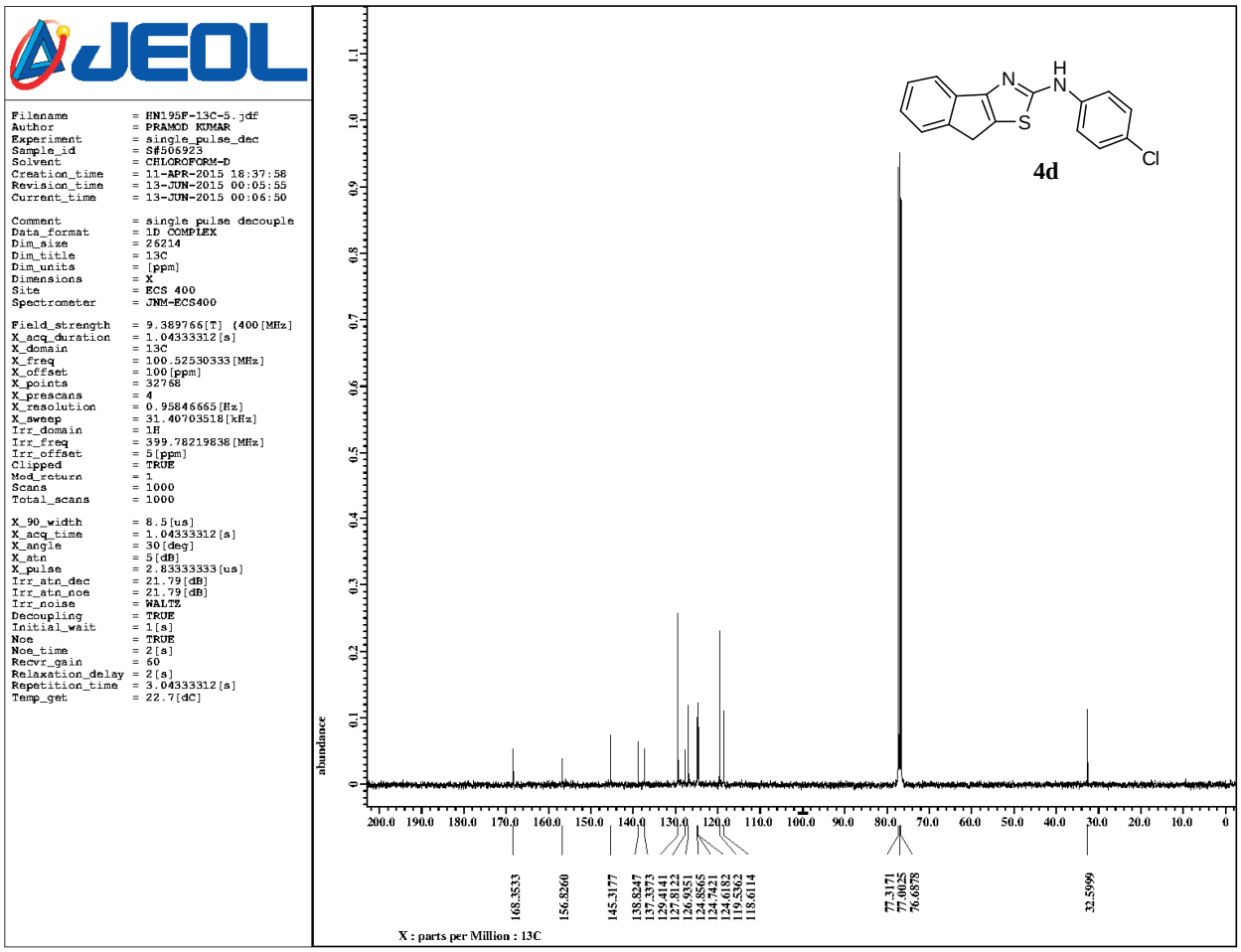

Figure S23. ^{13}C NMR spectrum of 2-(*p*-chlorophenyl)amino-8*H*-indeno[1,2-*d*]thiazole in $CDCl_3$.

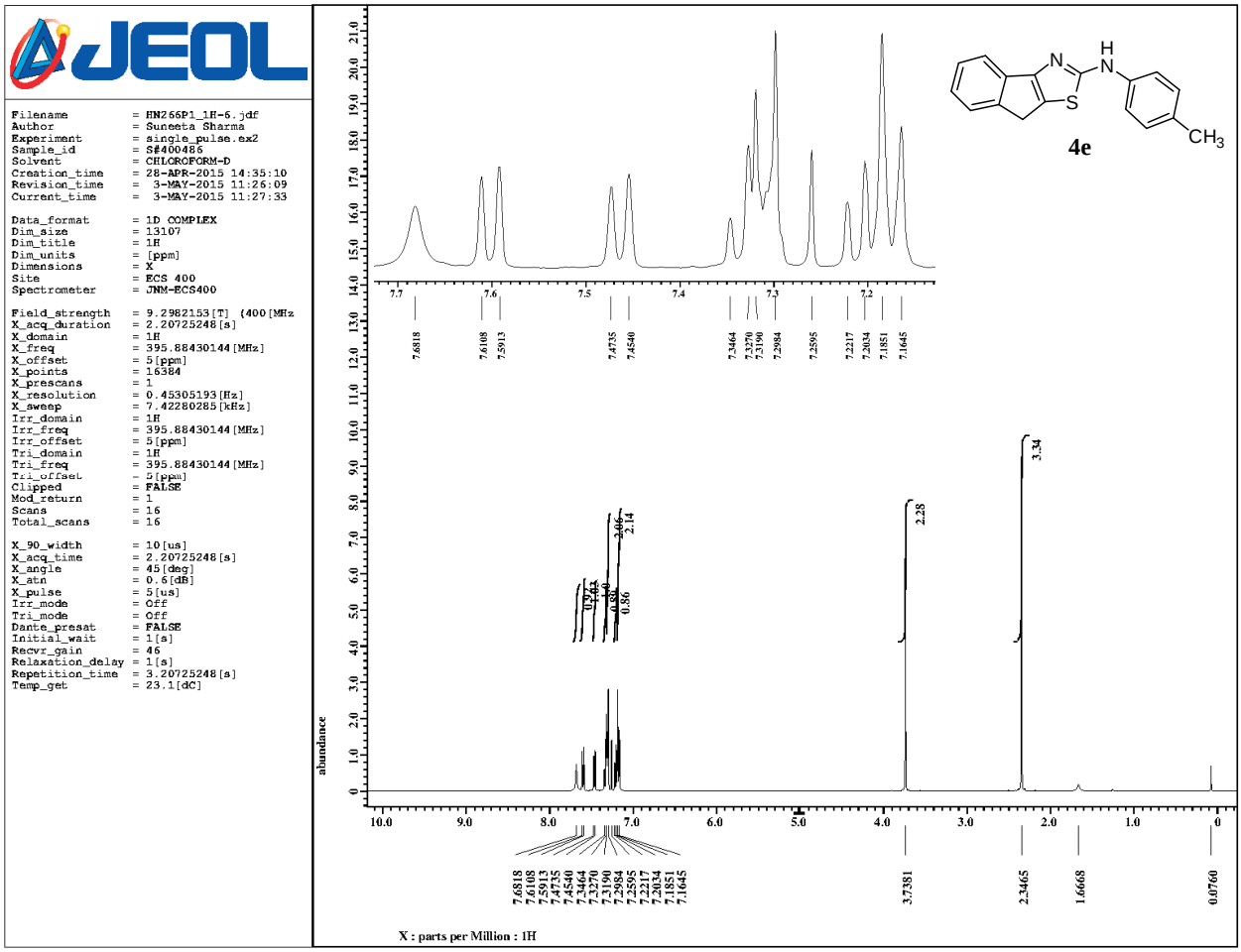

Figure S24. ^{1}H NMR spectrum of 2-(*p*-tolyl)amino-8*H*-indeno[1,2-*d*]thiazole in $CDCl_3$.

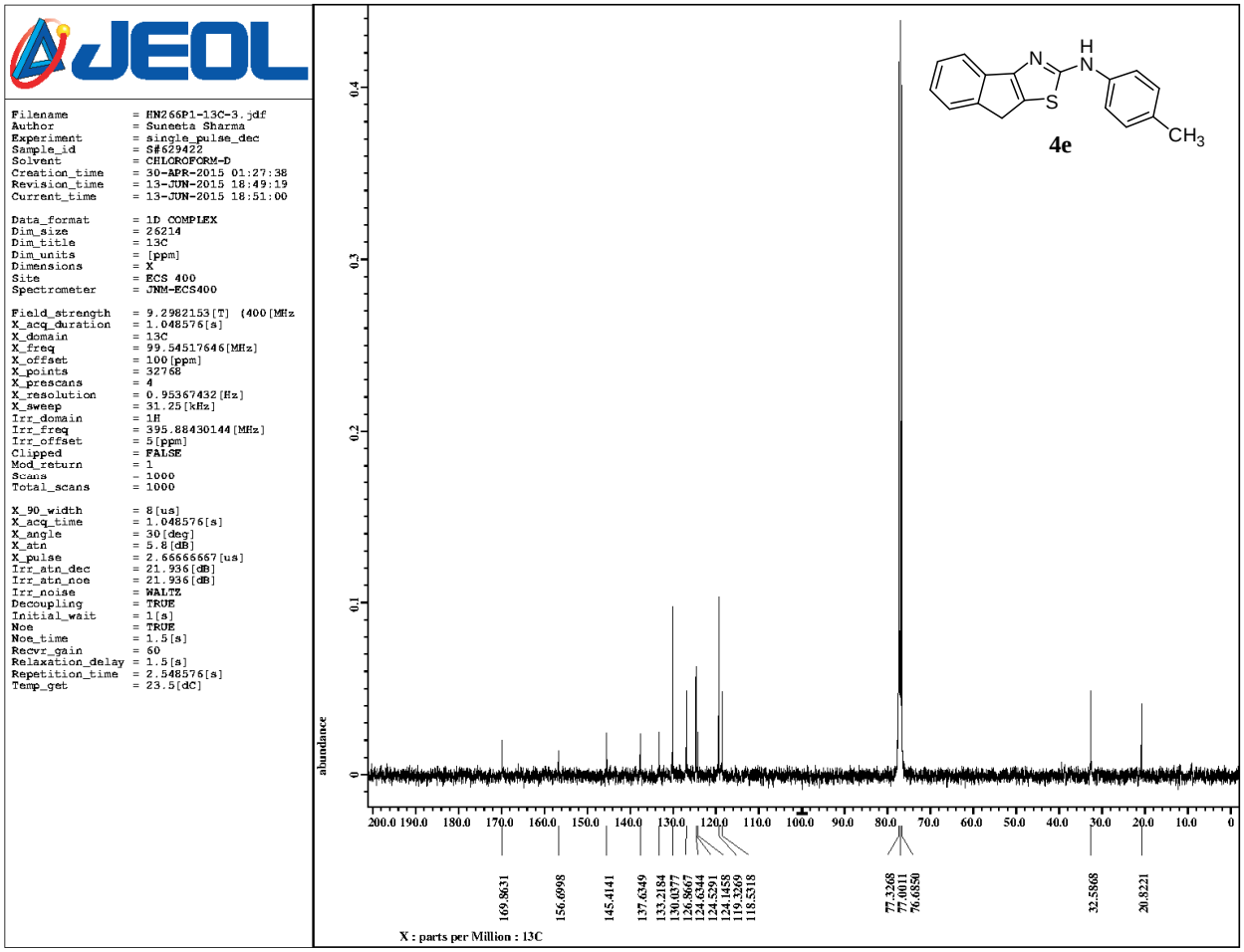

Figure S25. ^{13}C NMR spectrum of 2-(*p*-tolyl)amino-8*H*-indeno[1,2-*d*]thiazole in $CDCl_3$.

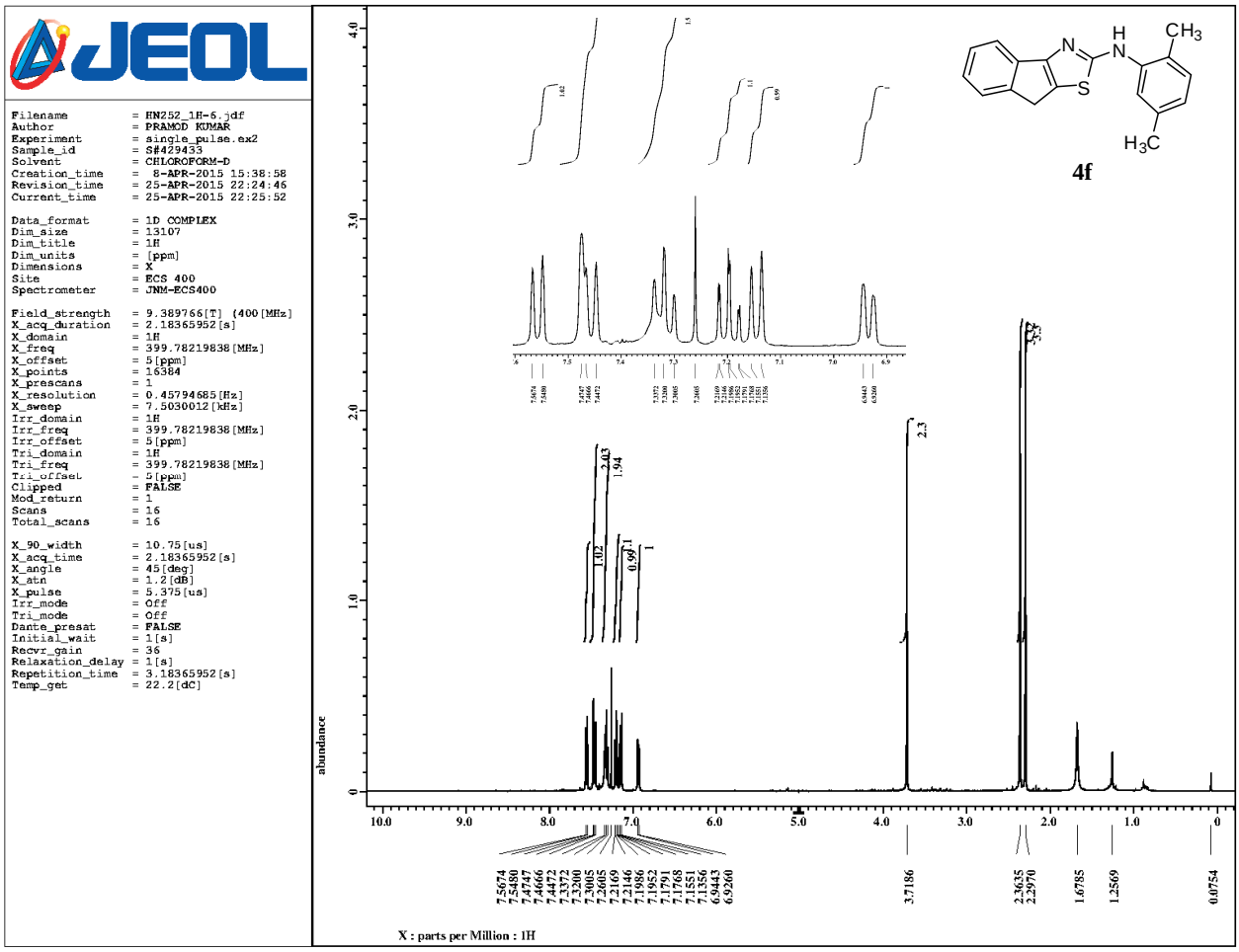

Figure S26. ^{1}H NMR spectrum of 2-(2,5-dimethylphenyl)amino-8*H*-indeno[1,2-*d*]thiazole in $CDCl_3$.

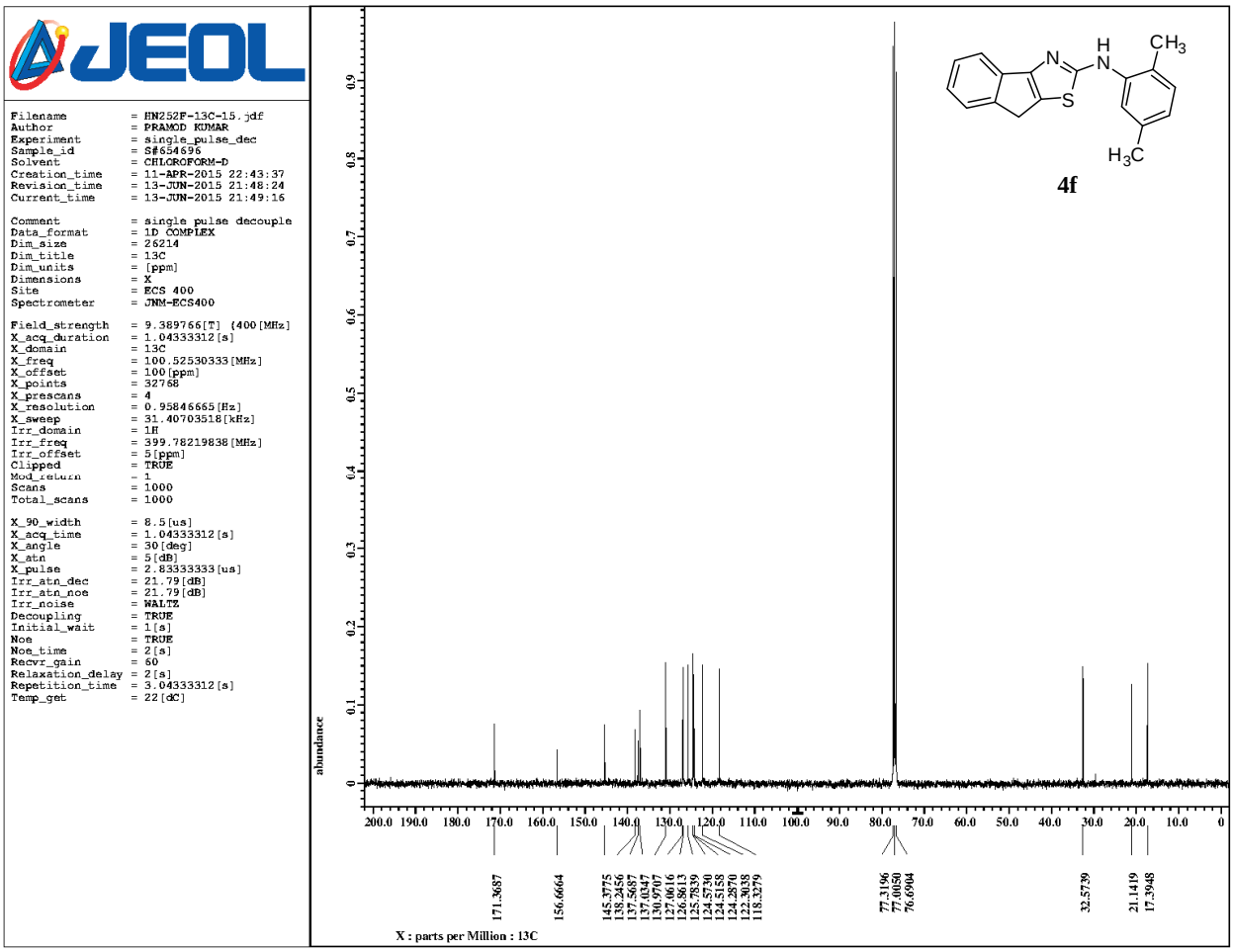

Figure S27. ^{13}C NMR spectrum of 2-(2,5-dimethylphenyl)amino-8*H*-indeno[1,2-*d*]thiazole in $CDCl_3$.

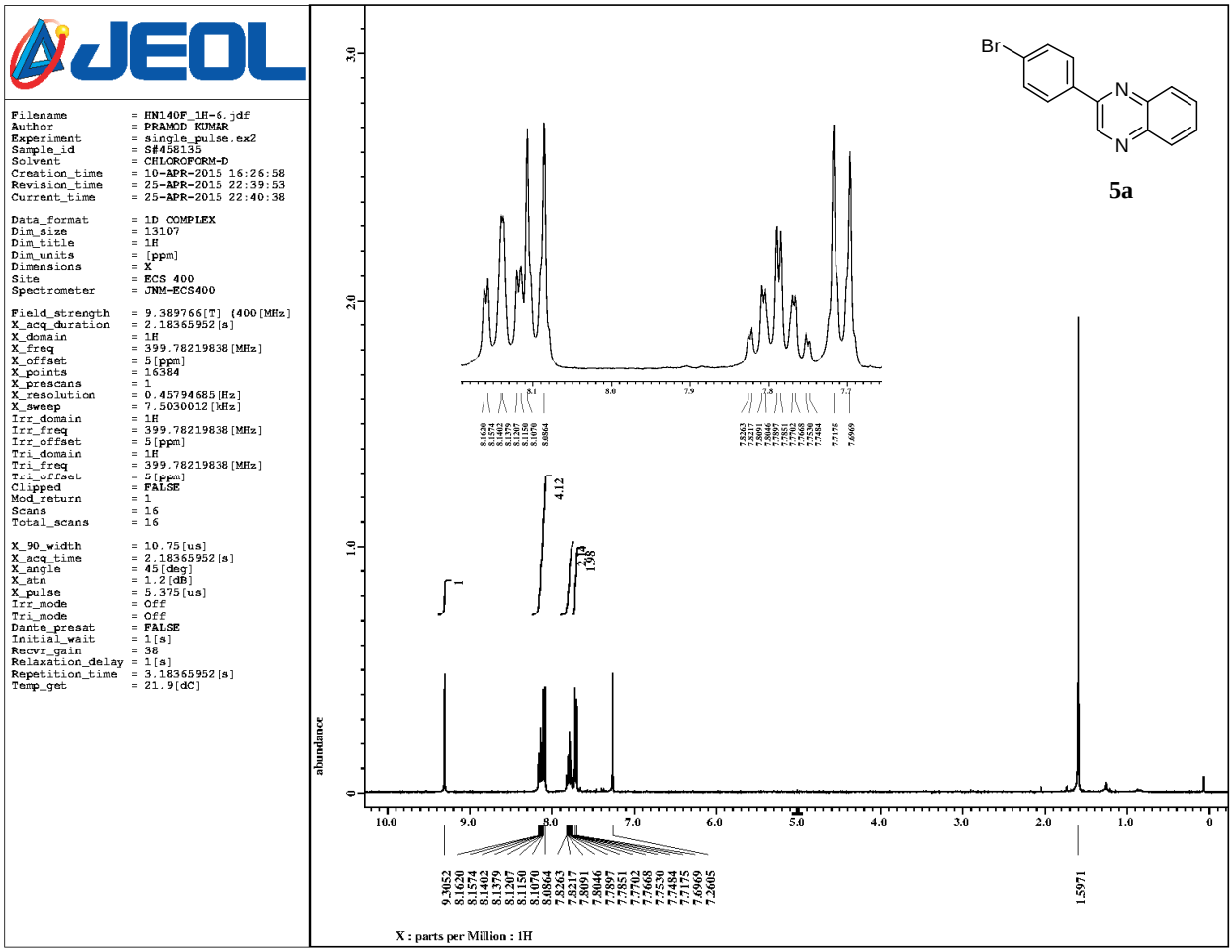

Figure S28. ^{1}H NMR spectrum of 2-(*p*-bromophenyl)quinoxaline in $CDCl_3$.

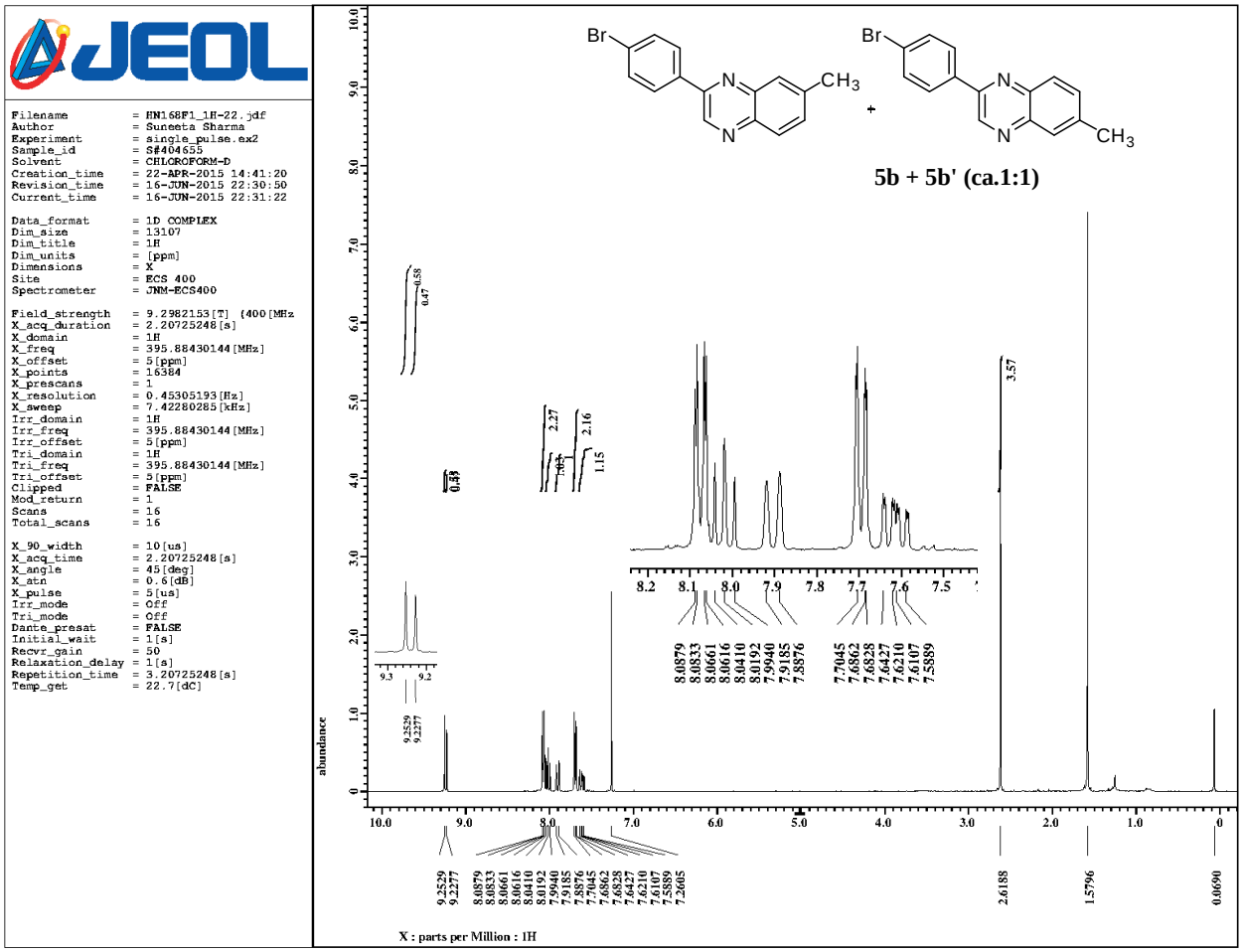

Figure S29. ^{1}H NMR spectrum of 2-(*p*-bromophenyl)-6/7-methylquinoxaline in $CDCl_3$.

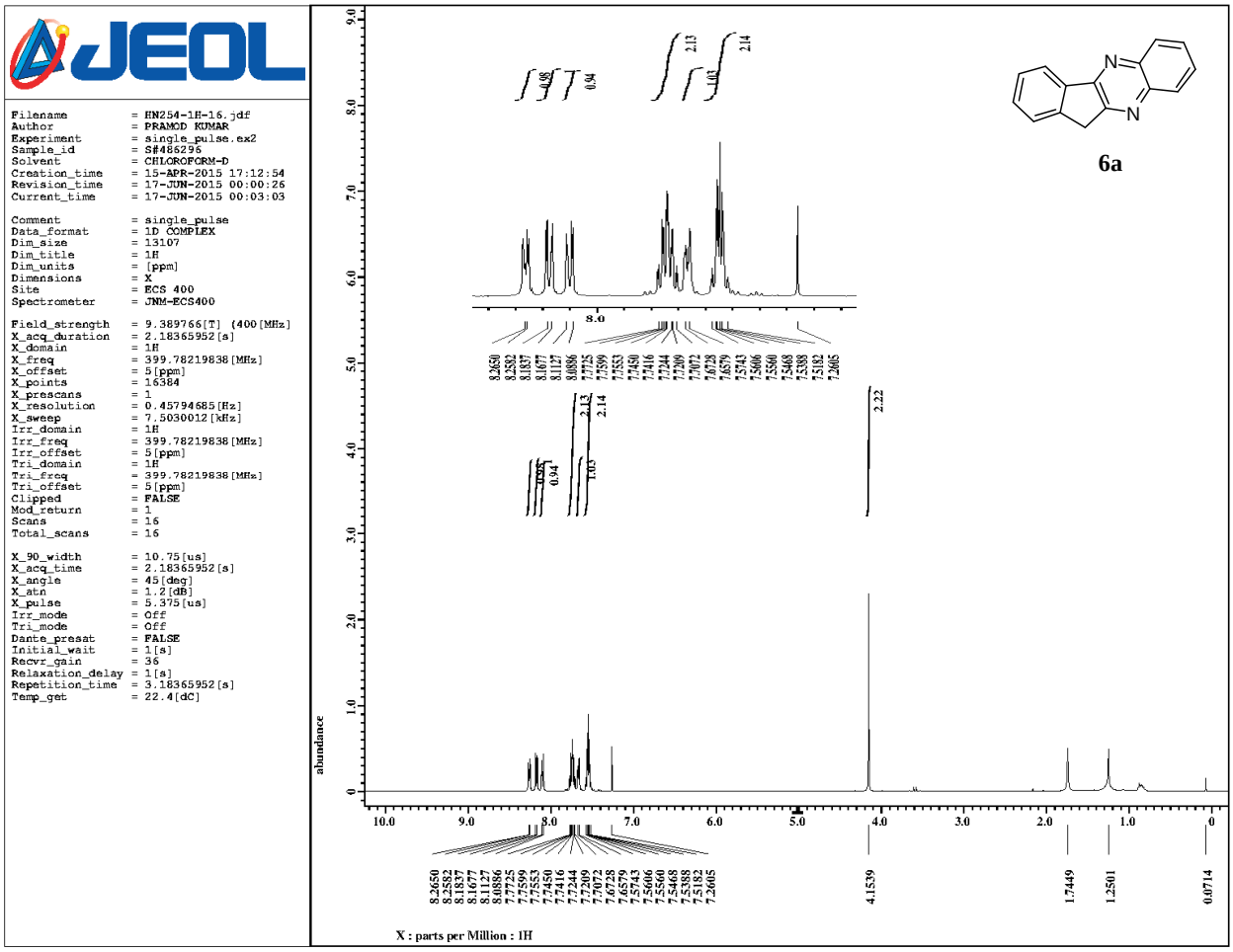

Figure S30. ^{1}H NMR spectrum of 11*H*-indeno[2,1-*b*]quinoxaline in $CDCl_3$.

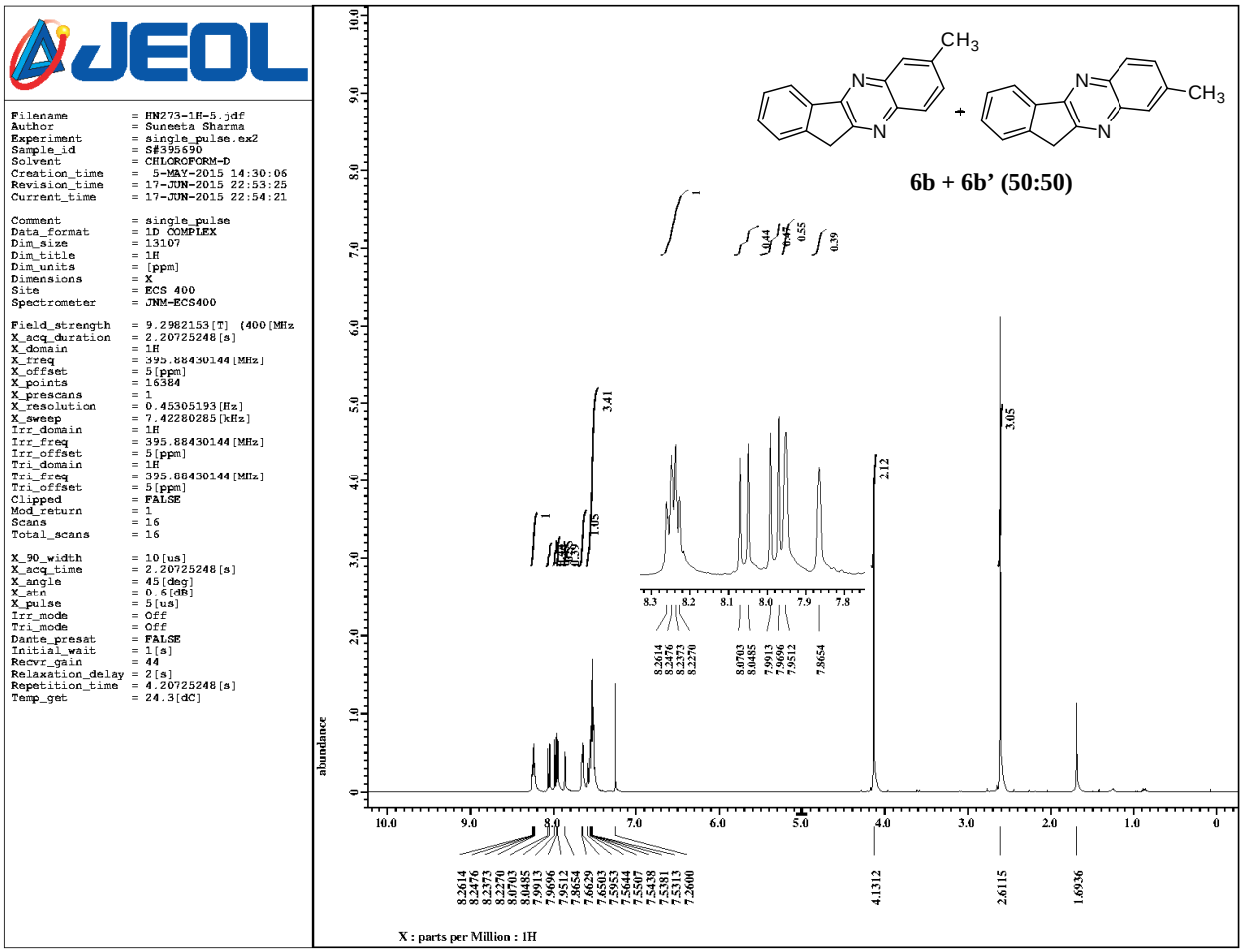

Figure S31. ^{1}H NMR spectrum of 7/8-methyl-11*H*-indeno[2,1-*b*]quinoxaline in $CDCl_3$.

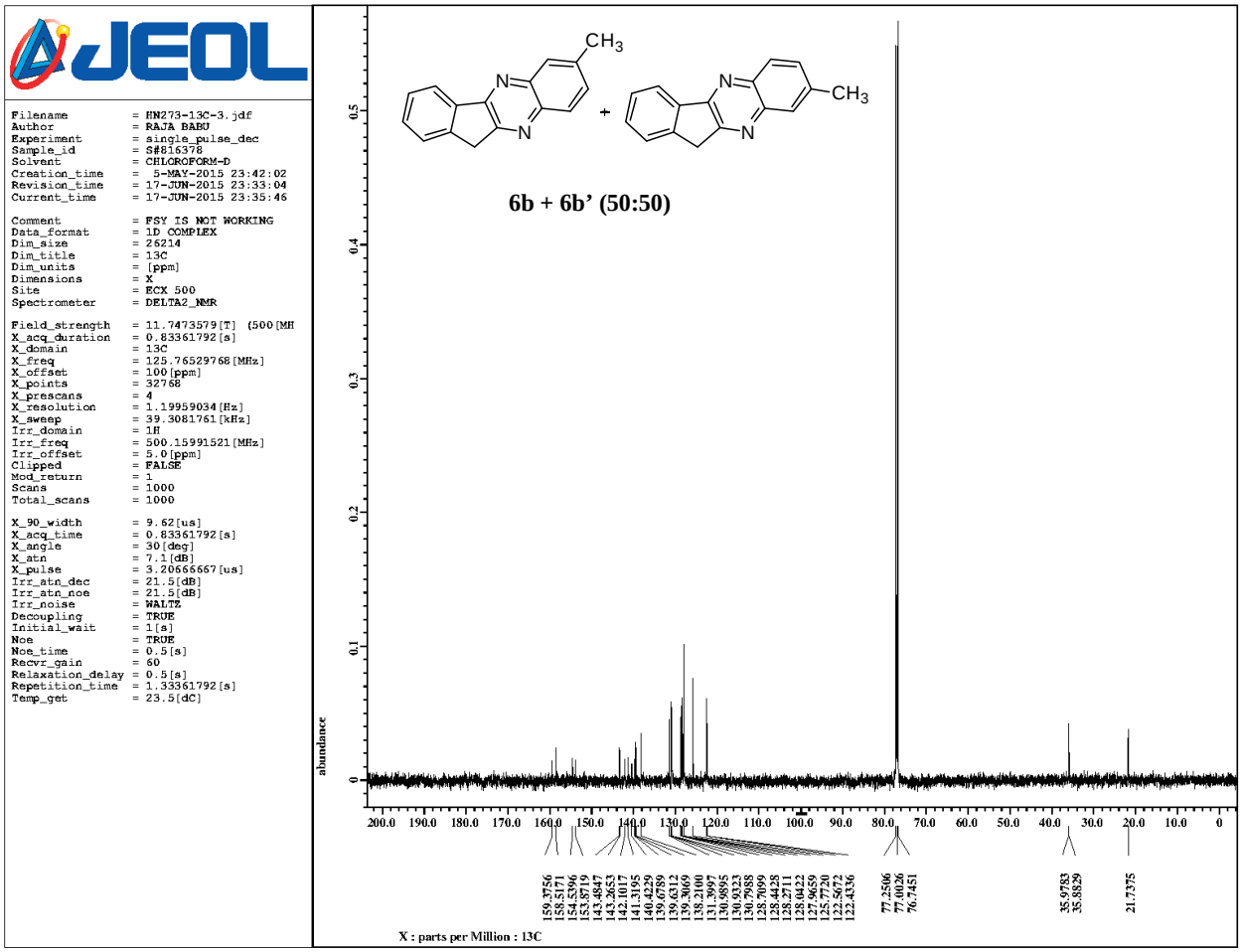

Figure S32. ^{13}C NMR spectrum of 7/8-methyl-11*H*-indeno[2,1-*b*]quinoxaline in $CDCl_3$.

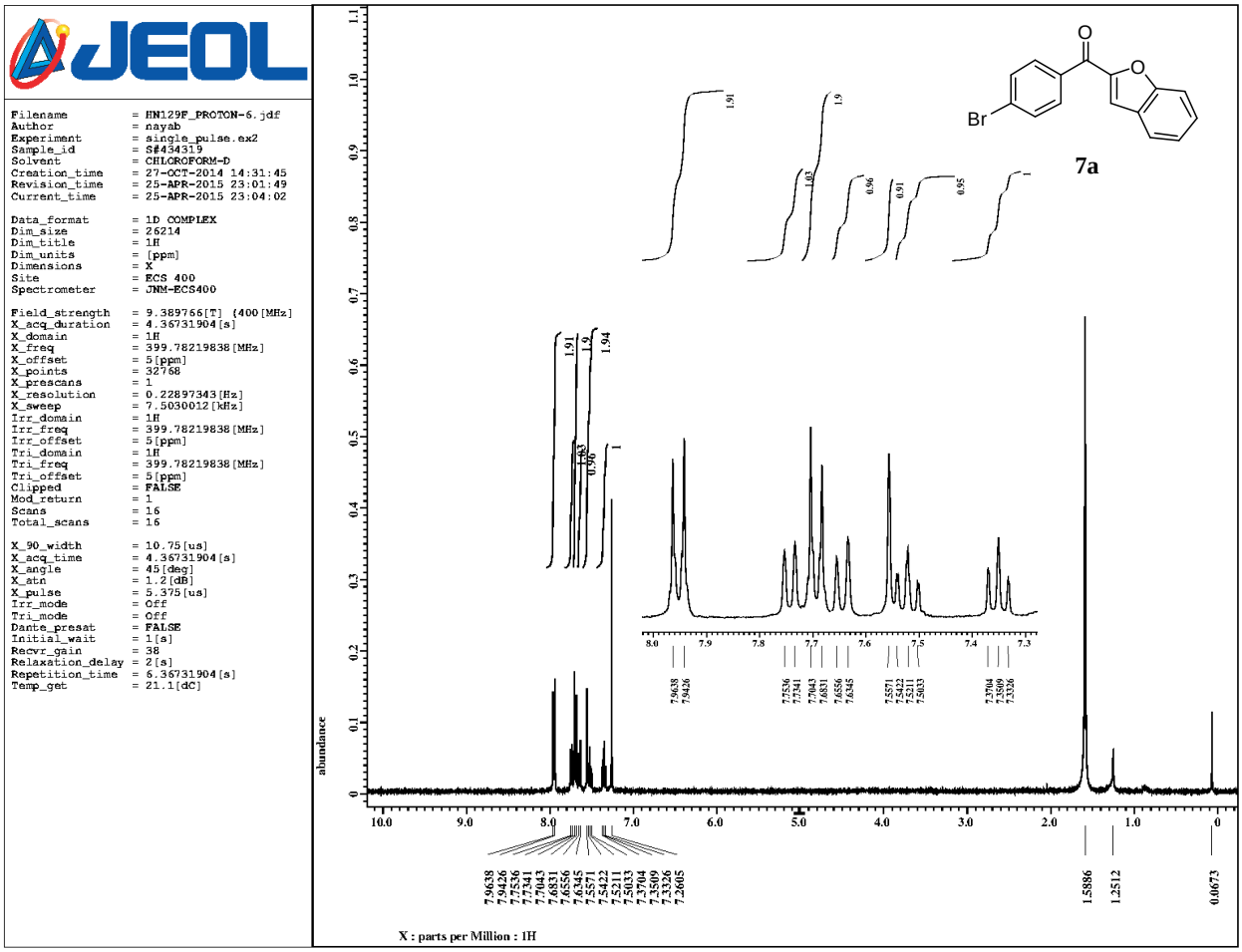

Figure S33. ^{1}H NMR spectrum of 2-benzofuranyl-(*p*-bromophenyl)methanone in $CDCl_3$.

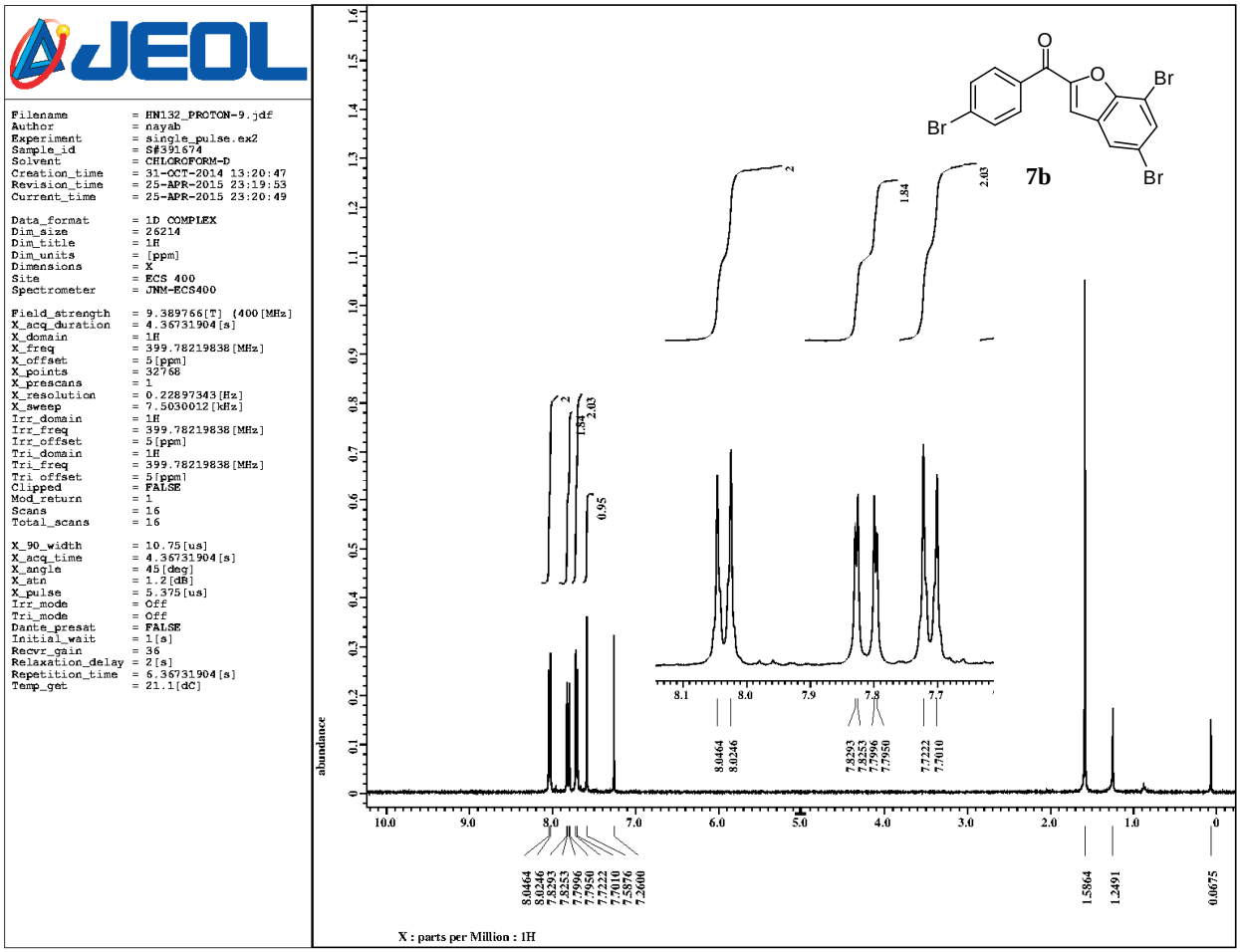

Figure S34. ^{1}H NMR spectrum of (*p*-bromophenyl)(5,7-dibromo-2-benzofuranyl)methanone in $CDCl_3$.