Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Gold nanoparticles catalyzed intramolecular C-S bond formation/ C-H bond functionalization/Cyclization Cascades

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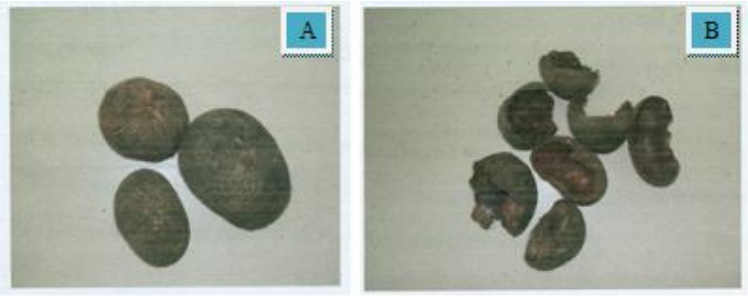


Fig. 1(A) *Kayea assamica* fruit (Before drying) **(B)** *Kayea assamica* fruit peel (After drying)

Preparation of the fruit extract

Kayea assamica (sia nahor) fruits were used to make the aqueous extract. *K. assamica* fruit (Fig. 1A) weighing 5g were thoroughly washed in distilled water, cut into pieces and dried. After removal the peel (Fig. 1B) the dried were crushed into 100 ml sterile distilled water and filtered throughWhatman No.1 filter paper (pore size 25 µm). The filtrate was further filtered through 0.6 µm sized filters.

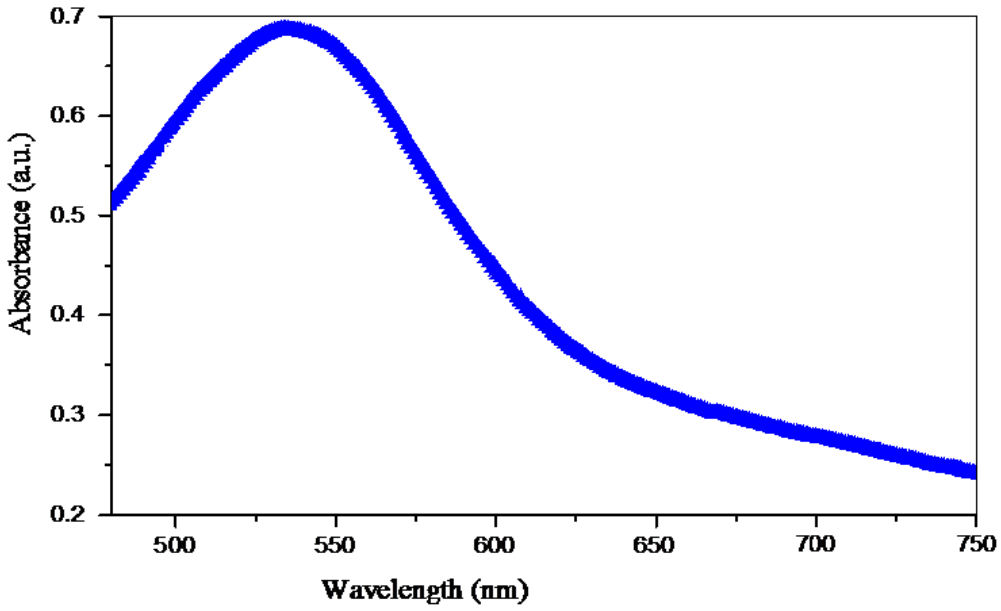


Fig.6 UV–vis absorption spectra of Au-nano particles

Typical procedure

General

Gold (III) chloride hydrate ($HAuCl_4.xH_2O$) 99.99% metal basis purchased from Sigma Aldrich. *Kayea assamica* fruits was collected from Lakhimpur, Assam, INDIA in the month of June–August 2013 and gently washed to remove dust. Melting points were recorded on a Reico melting point apparatus and were uncorrected. The UV–vis absorption spectrum was recorded on a Cary 100 Bio spectrophotometer (λ-max in nm) equipped with 1cm quartz cell. ^1H and ^{13}C Nuclear Magnetic Resonance spectra of pure compounds were acquired at 400 and 100 MHz respectively. All NMR samples were recorded in deuterated chloroform. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Elemental analyses were performed on a Flash 2000 Thermo Scientific instrument at NIT Silchar. The TEM characterizations were carried out at model no. CM-12 Philips TEM (IIT Kharagpur).

N-Phenylbenzo[d]thiazol-2-amine (2a): Yield 203 mg (90%). White solid, m.p. 160-161 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.60-7.53 (m, 2H), 7.46-7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 151.0, 137.2, 131.3, 129.4, 128.9, 127.8, 127.4, 126.9, 124.1, 118.9; HRMS (ESI): MH^+Calcd for $C_{13}H_{10}N_2S$ 226.0564; Found 226.0563. Anal.Calcd for $C_{13}H_{10}N_2S$: C, 69.00; H, 4.45; N, 12.38. Found: C, 69.01; H, 4.45; N, 12.40.

6-methyl-N-p-tolylbenzo[d]thiazol-2-amine (2b): Yield 243 mg (96%). White solid, m.p. 227-228 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.53-7.35 (m, 2H), 7.32-7.23 (m, 3H), 2.56 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 155.2, 133.8, 132.1, 130.0, 129.2, 128.6, 127.6, 127.3, 123.5, 119.6, 25.5, 24.1.Anal.Calcd for $C_{15}H_{14}N_2S$: C, 70.83; H, 5.55; N, 11.01. Found: C, 70.88; H, 5.45; N, 11.00.

6-chloro-N-(4-chlorophenyl)[d]thiazol-2-amine (2c): Yield 264 mg (90%). White solid, m.p. 176-177^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.82 (s,1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.31-7.23 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2,

150.4, 145.2, 137.5, 133.8, 133.6, 130.5, 127.4, 125.9, 125.7, 119.2; Anal.Calcd for $C_{13}H_8Cl_2N_2S$: C, 52.89; H, 2.73; N, 9.49. Found: C, 52.87; H, 2.77; N, 9.66.

6-bromo-N-(4-bromophenyl)[d]thiazol-2-amine (2d): Yield 330 mg (86%). White solid, m.p. 187-188^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.77-7.62 (m, 3H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 149.1, 137.0, 134.9, 134.5, 131.8, 131.2, 127.2, 127.0, 126.4, 120.1; HRMS (ESI): MH $^+$Calcd for $C_{13}H_8Br_2N_2S$ 381.8774; found 381.8770. Anal.Calcd for $C_{13}H_8Br_2N_2S$: C, 40.65; H, 2.10; N, 7.29. Found: C, 40.59; H, 2.15; N, 7.30.

6-iodo-N-(4-iodophenyl)[d]thiazol-2-amine (2e): Yield 406 mg (85%). White solid, m.p. 213-214 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 9.03(s, 1H), 9.03 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 151.5, 134.1, 133.8, 131.4, 130.0, 127.6, 126.2, 125.7, 125.0, 119.3; Anal. Calcd for $C_{13}H_8I_2N_2S$: C, 32.66; H, 1.69; N, 5.86. Found: C, 32.71; H, 1.71; N, 5.82.

N-p-tolylbenzo[d]thiazol-2-amine (2f): Yield 216 mg (90%). White solid, m.p. 178-179 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 152.2, 137.3, 134.2, 131.8, 129.2, 127.0, 125.7, 121.9, 120.5, 118.7, 21.43; Anal.Calcd for $C_{14}H_{12}N_2S$: C, 69.97; H, 5.03; N, 11.66. Found: C, 69.95; H, 5.07; N, 11.69.

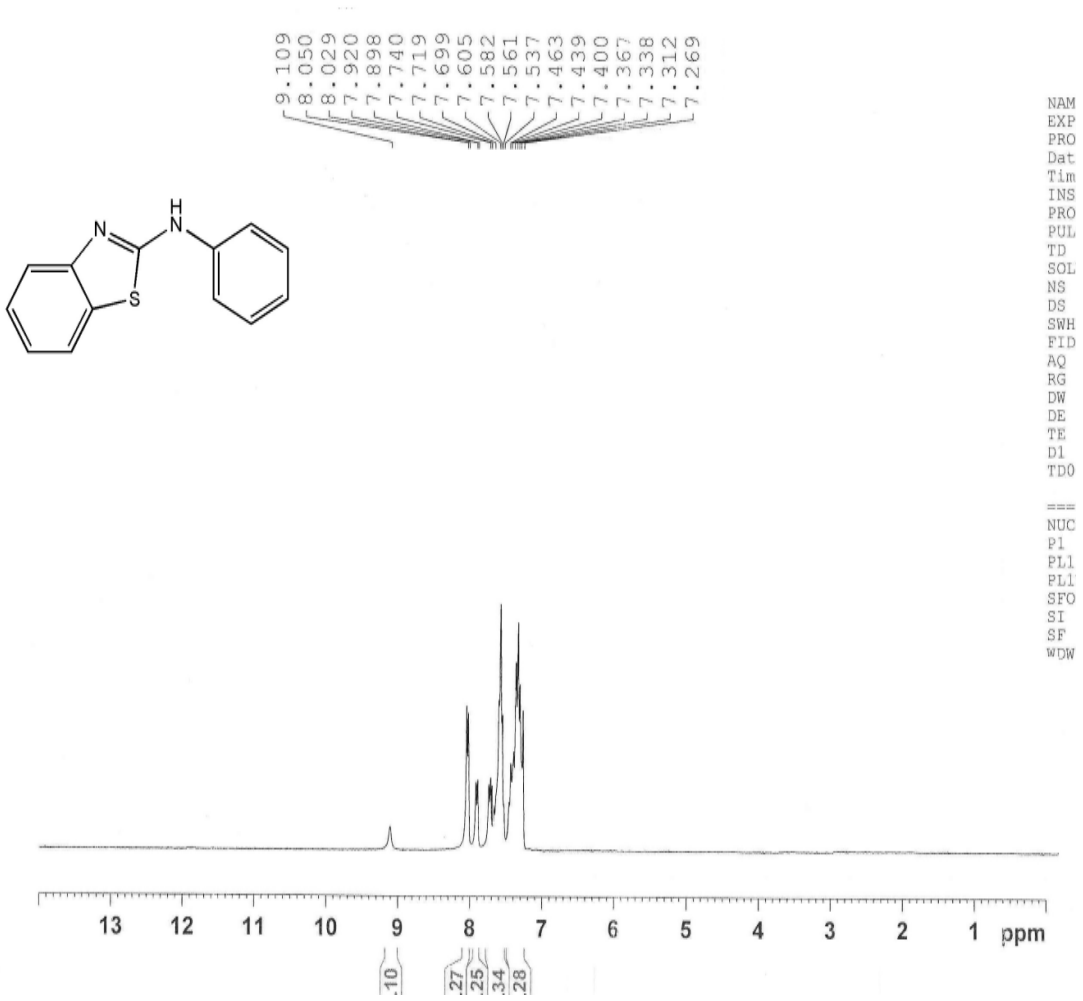
N-(4-chlorophenyl)benzo[d]thiazol-2-amine (2g): Yield 202 mg (78%). White solid, m.p. 202-209 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H),7.09 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 146.2, 133.1, 131.9, 131.3, 130.8, 128.8, 126.4 124.1, 121.4, 119.5 Anal. Calcd for $C_{13}H_9ClN_2S$: C, 59.88; H, 3.48; N, 10.74. Found: C, 59.91; H, 3.45; N, 10.71.

4-(6-Nitrobenzo[*d*]thiazol-2-yl)morpholine (2k):Yield 199 mg (75%). Yellow solid, m.p. 206-208^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 2.2 Hz, 1H),8.19 (dd, *J* = 9.2, 2.2 Hz, 1H),7.45 (d, *J* = 9.2 Hz, 1H), 3.90 (t, *J* = 5.2 Hz, 4H),3.66 (t, *J* = 5.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 157.6, 141.8, 130.7, 122.6, 118.2, 116.8, 66.3, 48.7. Anal.Calcd for $C_{11}H_{11}N_3O_3S$: C, 49.80; H, 4.18; N, 15.84. Found: C, 48.95; H, 4.17; N, 15.88.

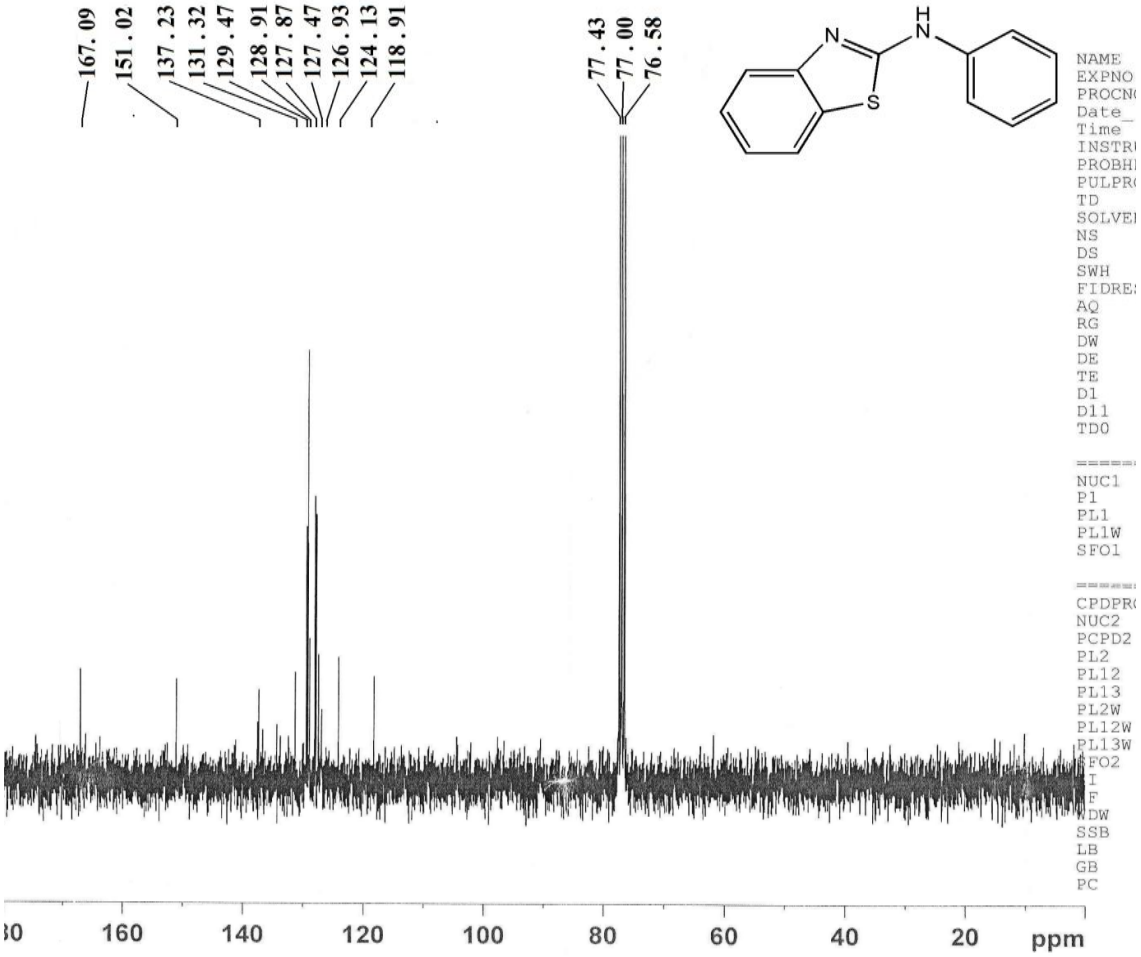
4-(6-Methoxybenzo[*d*]thiazol-2-yl)morpholine (2l):Yield 238 mg (95%). Off white solid, m.p. 137-139^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 9.3 Hz, 1H), 7.16 (d, *J* = 2.6 Hz, 1H), 6.94 (dd, *J* = 2.6, 2.5 Hz, 1H),3.97 (t, *J* = 5.4 Hz, 4H), 3.86 (s,3H),3.55 (t, *J* = 5.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 155.4, 146.6, 131.8, 119.4, 113.1, 105.1, 67.1, 55.2, 48.2. Anal.Calcd for $C_{12}H_{14}N_2O_2S$: C, 57.58; H, 5.64; N, 11.19. Found: C, 57.63; H, 5.69; N, 11.34.

2-Morpholinobenzo[d]thiazole-6-carbonitrile (2m): Yield 196 mg (80%). White solid, m.p. 173-175 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.43 (s, 2H),3.75 (t, *J* = 4.5 Hz, 4H), 3.49 (t, *J* = 4.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 162.3, 155.4, 133.5, 130.1, 125.3, 119.2, 103.9, 68.8, 48.3 . Anal.Calcd for $C_{12}H_{11}N_3OS$: C, 58.76; H, 4.52; N, 17.13. Found: C, 58.79; H, 4.58; N, 17.18.

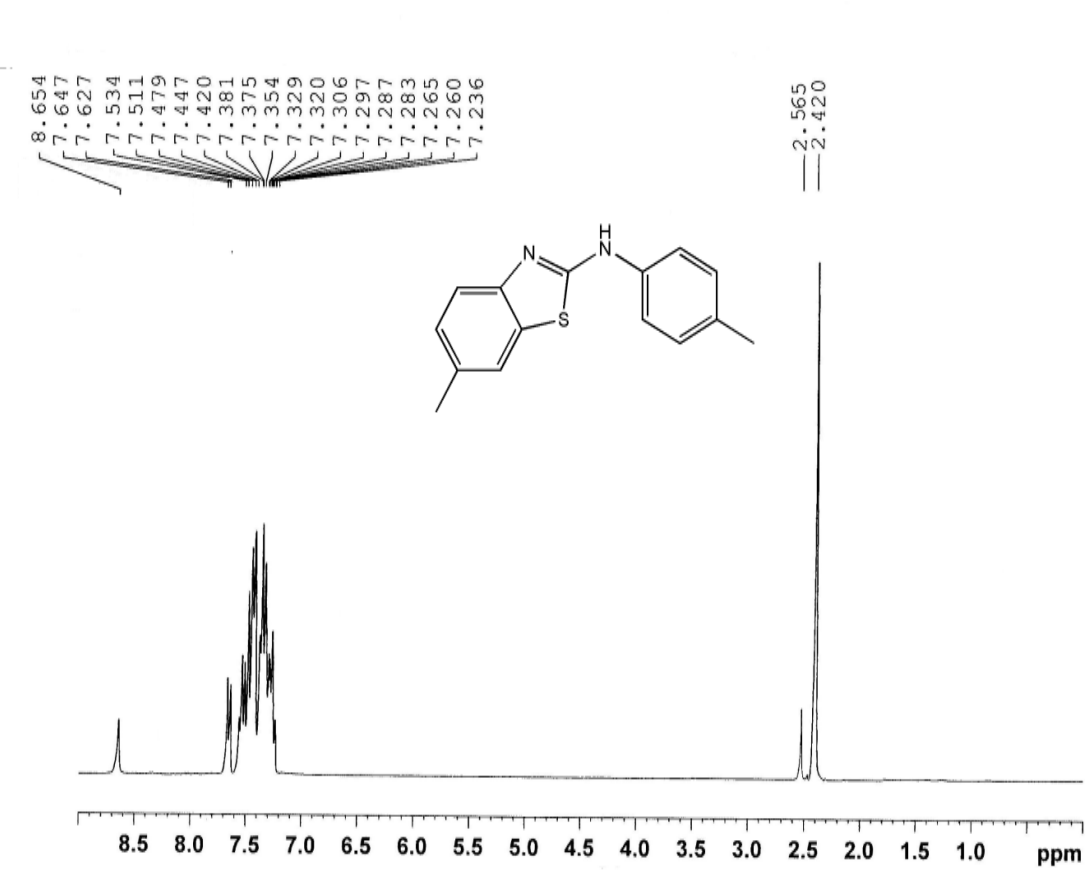
^{1}H NMR (400 MHz, $CDCl_3$) of compound 2a



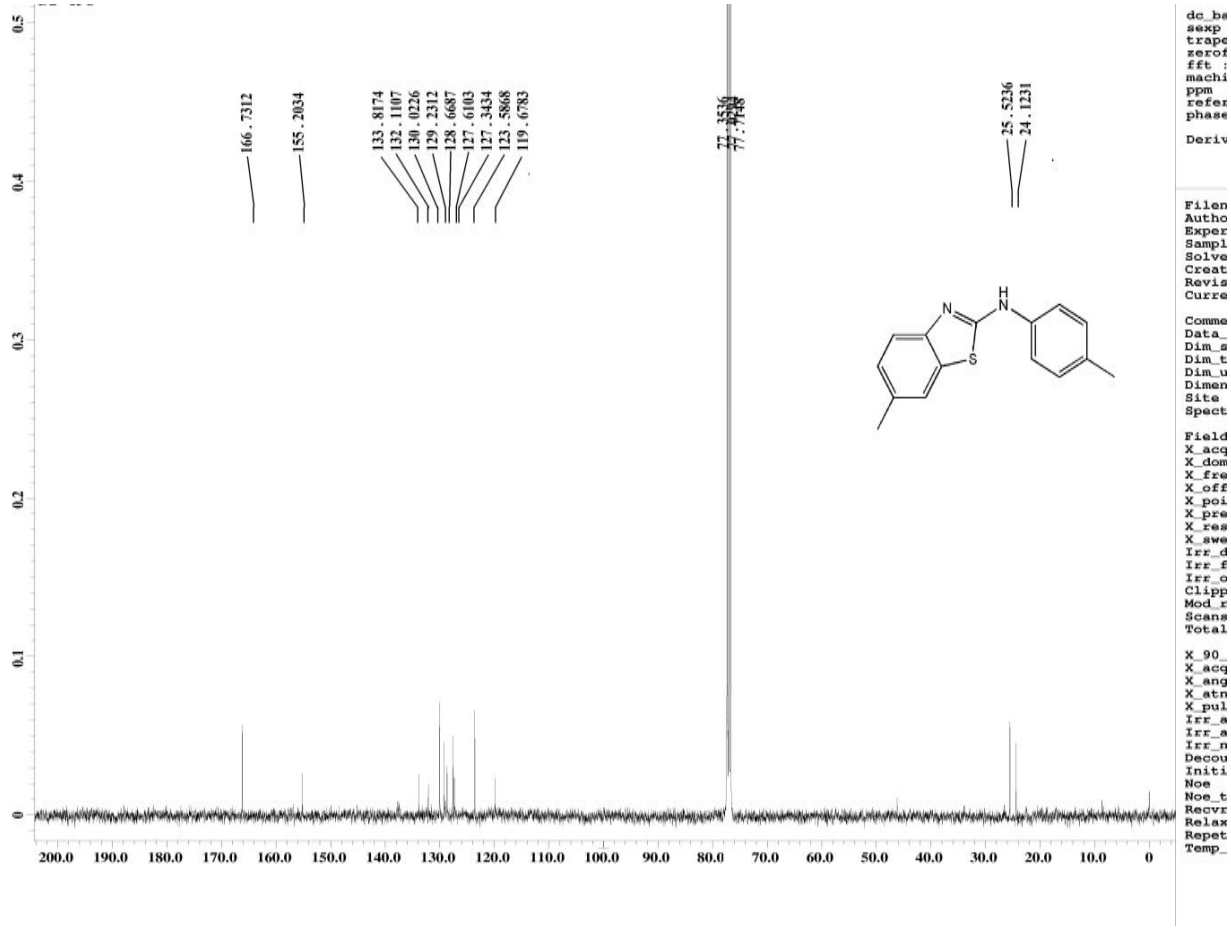
^{13}C NMR (400 MHz, $CDCl_3$) of compound 2a



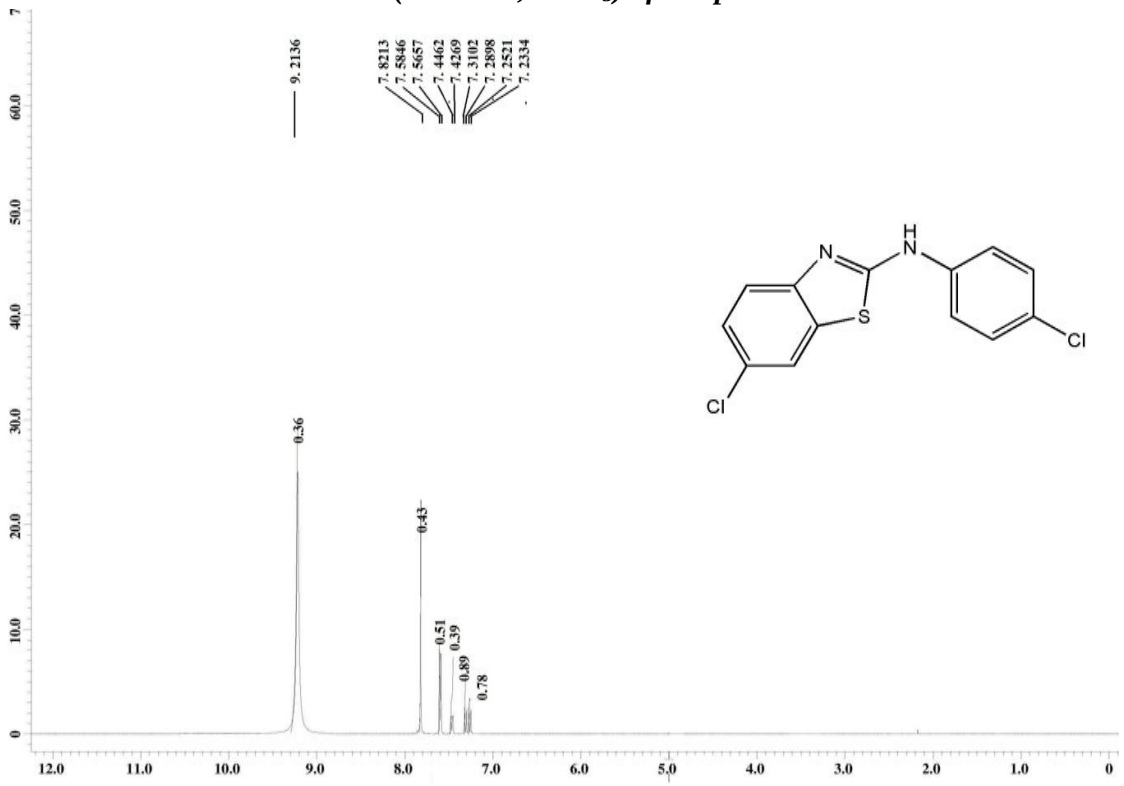
^{1}H NMR (400 MHz, $CDCl_3$) of compound 2b



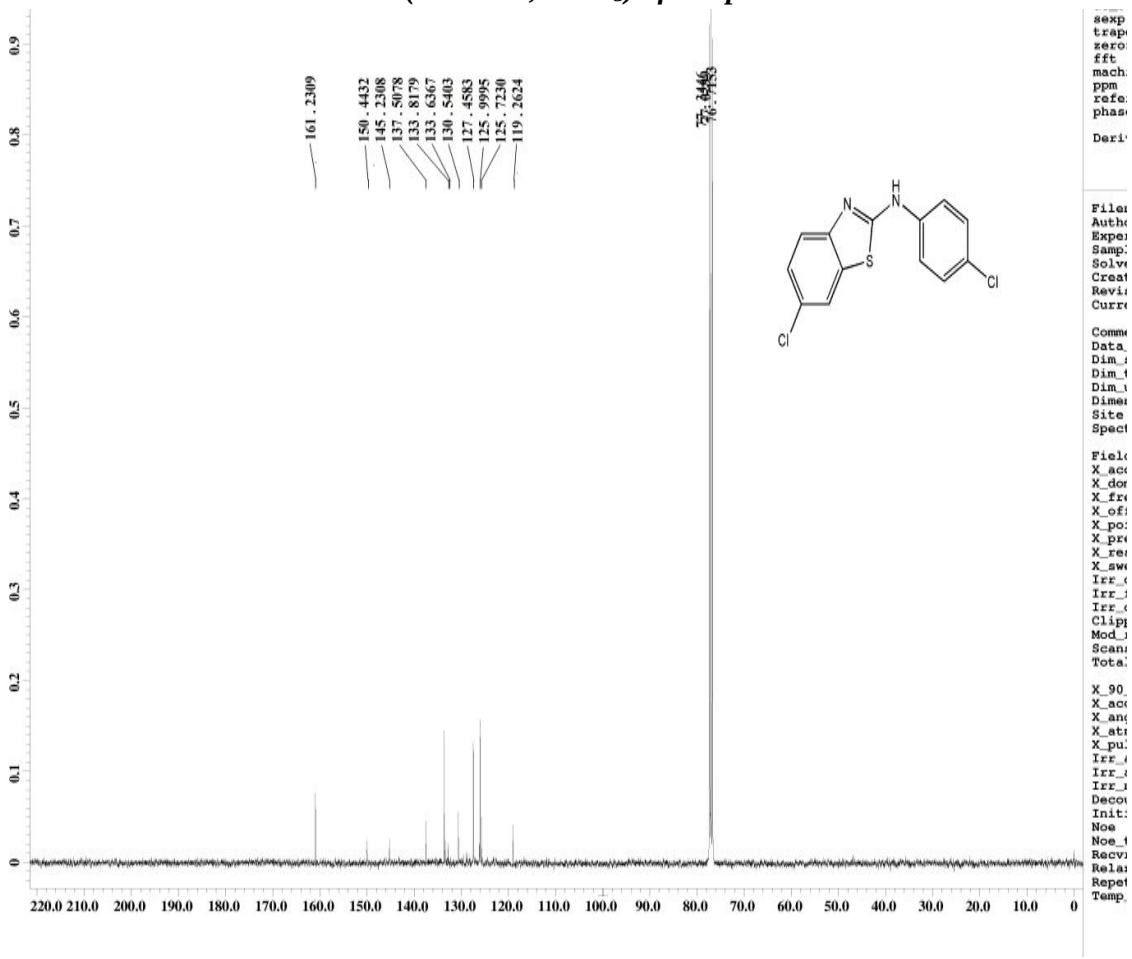
^{13}C NMR (400 MHz, $CDCl_3$) of compound 2b



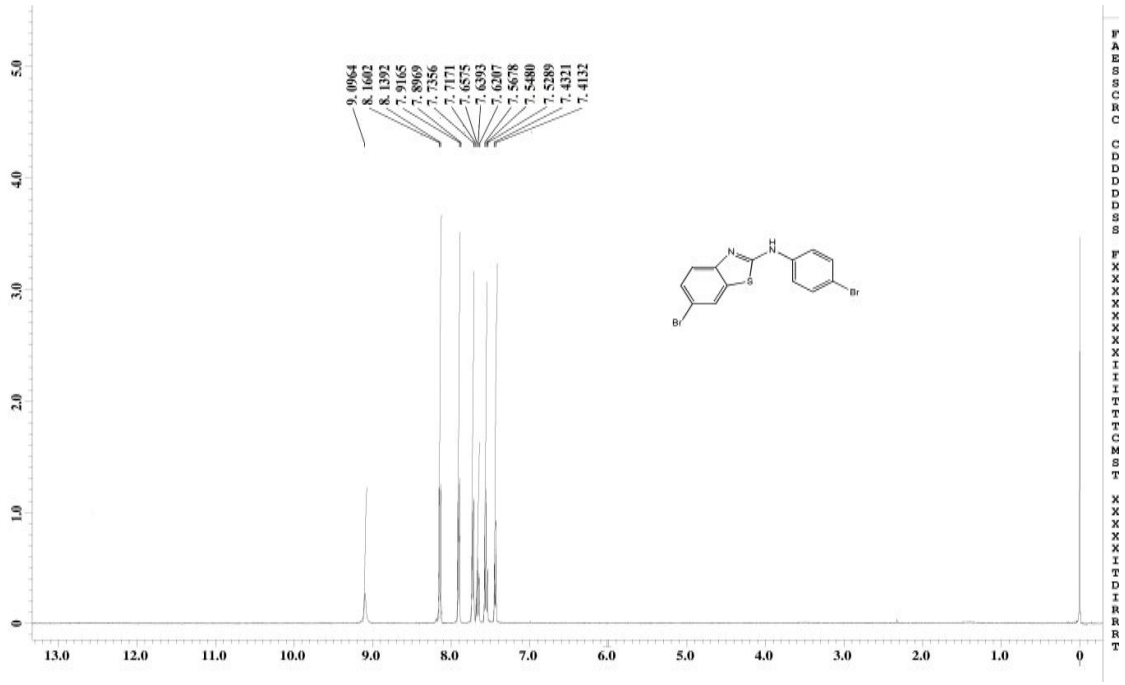
^{1}H NMR (400 MHz, $CDCl_3$) of compound 2c



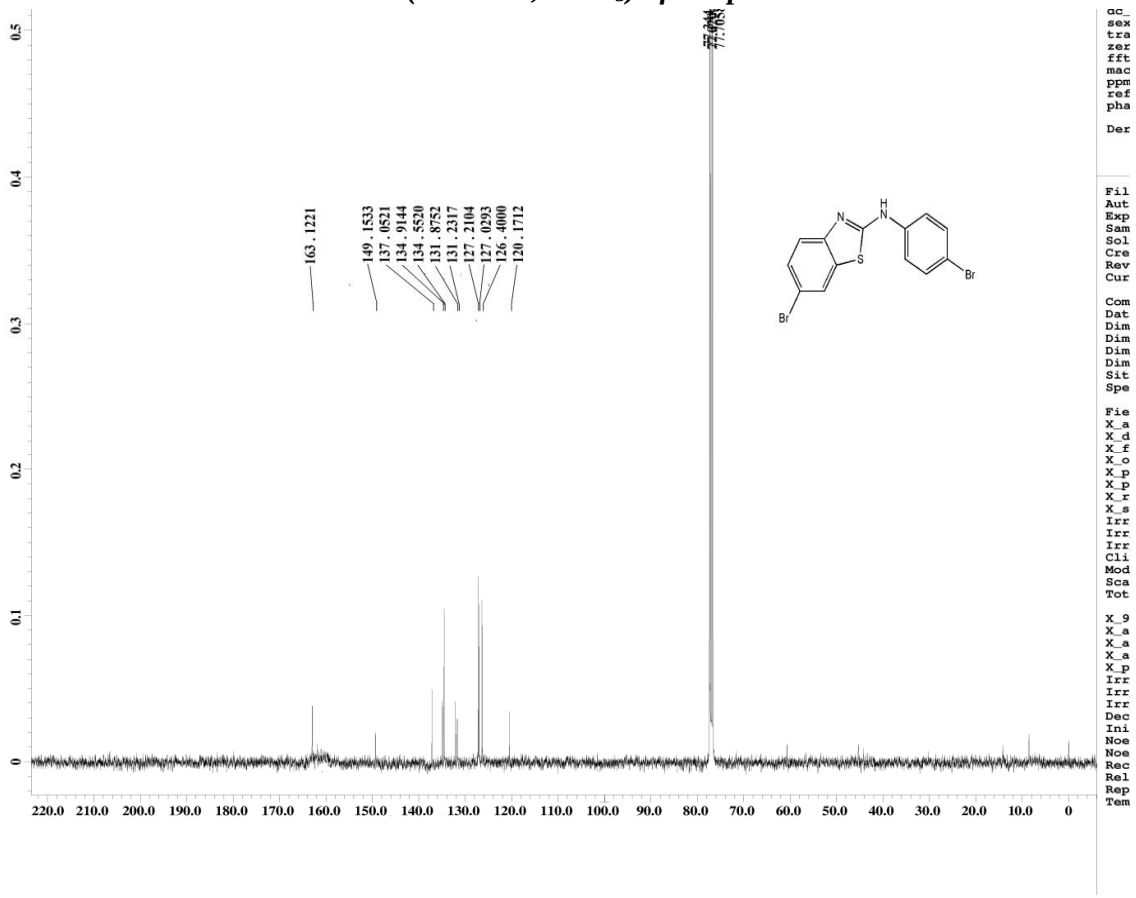
^{13}C NMR (400 MHz, $CDCl_3$) of compound 2c



^{1}H NMR (400 MHz, $CDCl_3$) of compound 2d

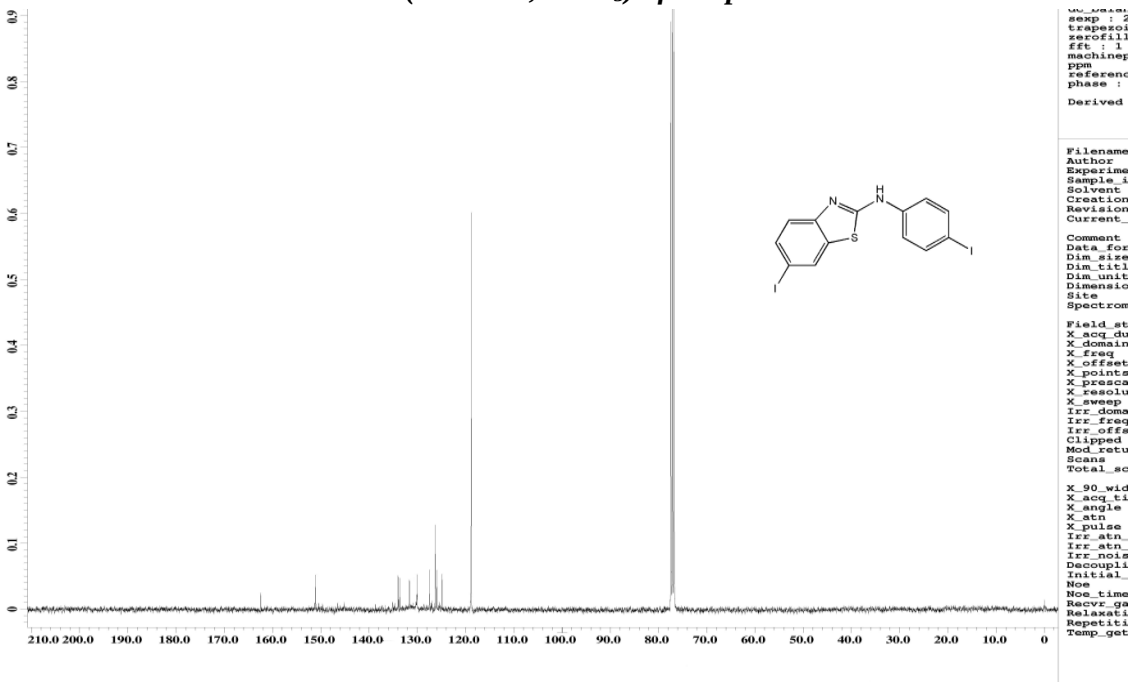


^{13}C NMR (400 MHz, $CDCl_3$) of compound 2d

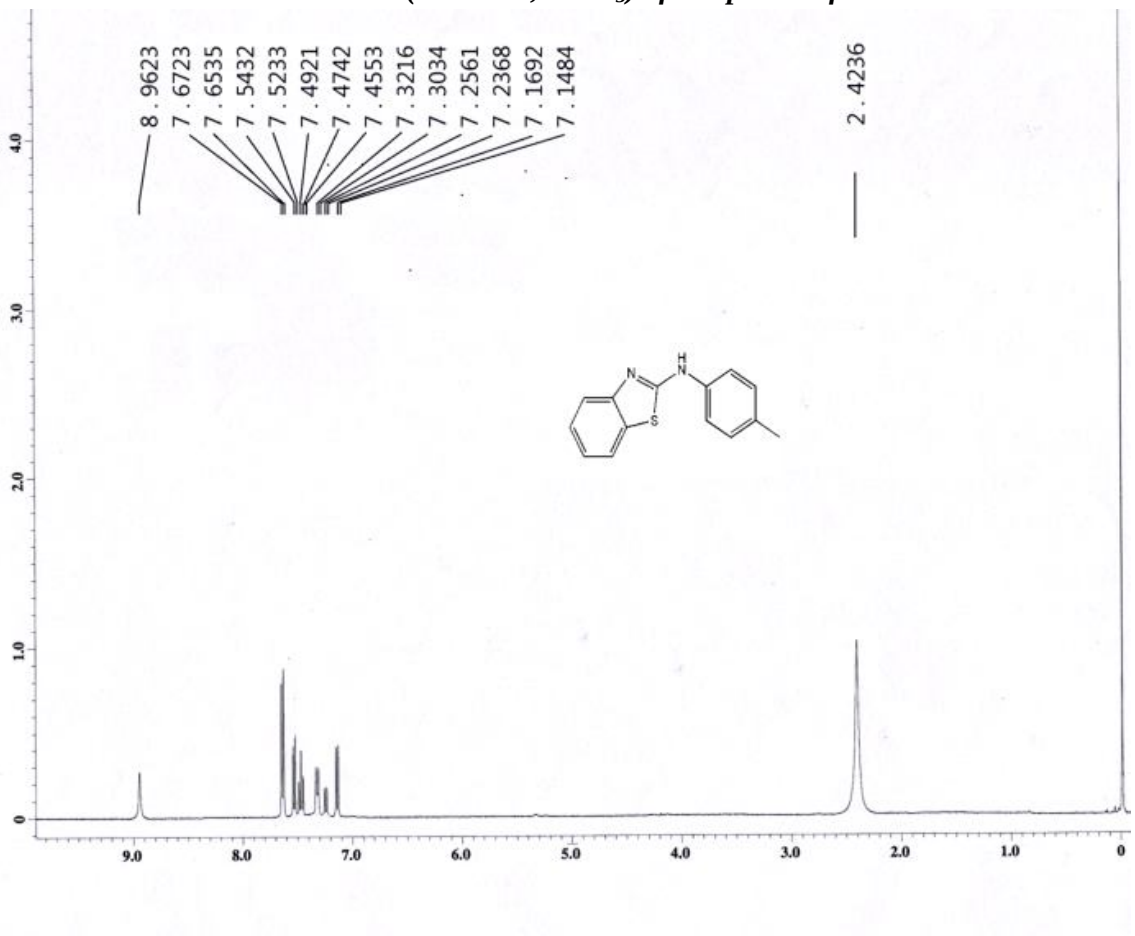


^{1}H NMR (400 MHz, $CDCl_3$) of compound 2e

^{13}C NMR (400 MHz, $CDCl_3$) of compound 2e



^{1}H NMR (400 MHz, $CDCl_3$) of compound 2f



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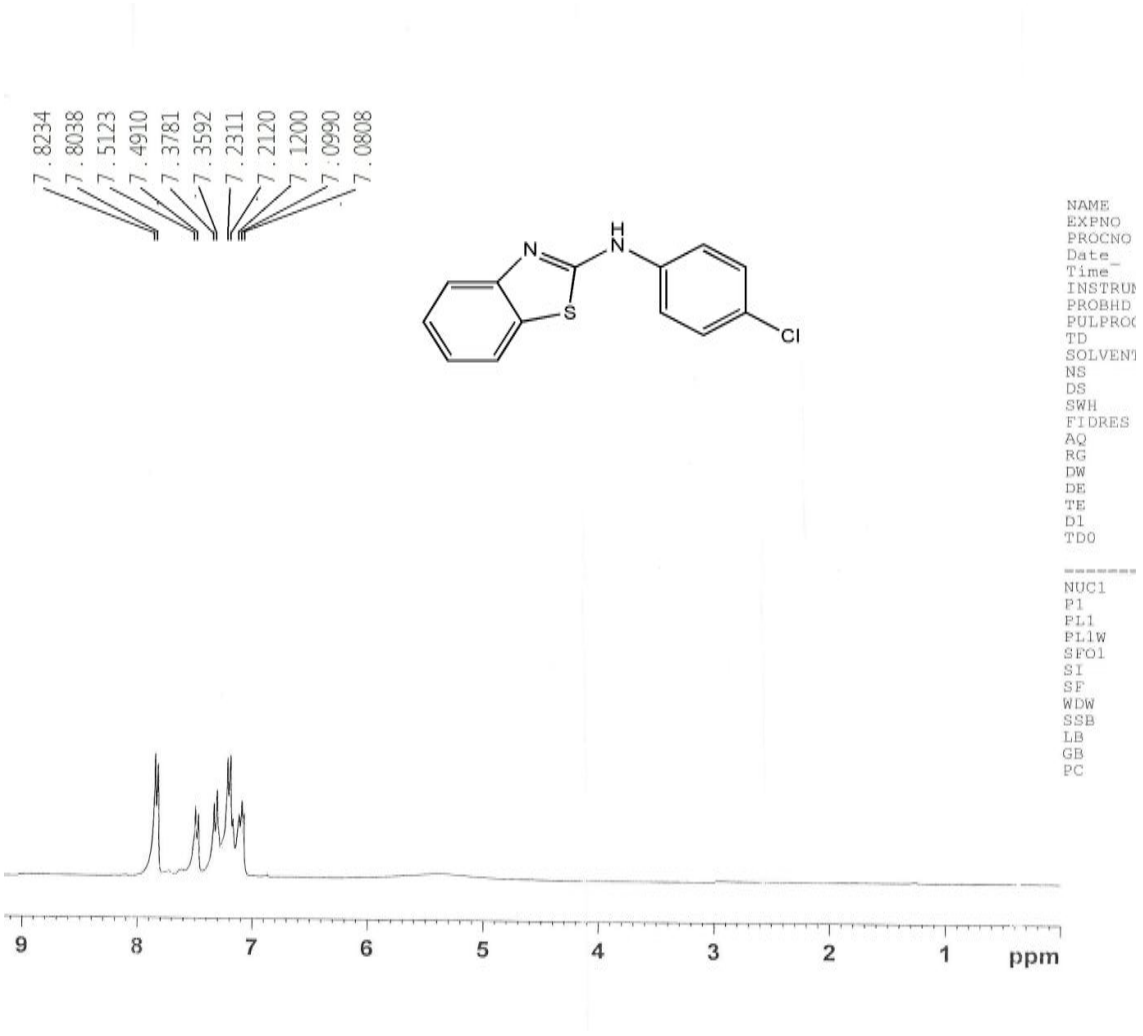
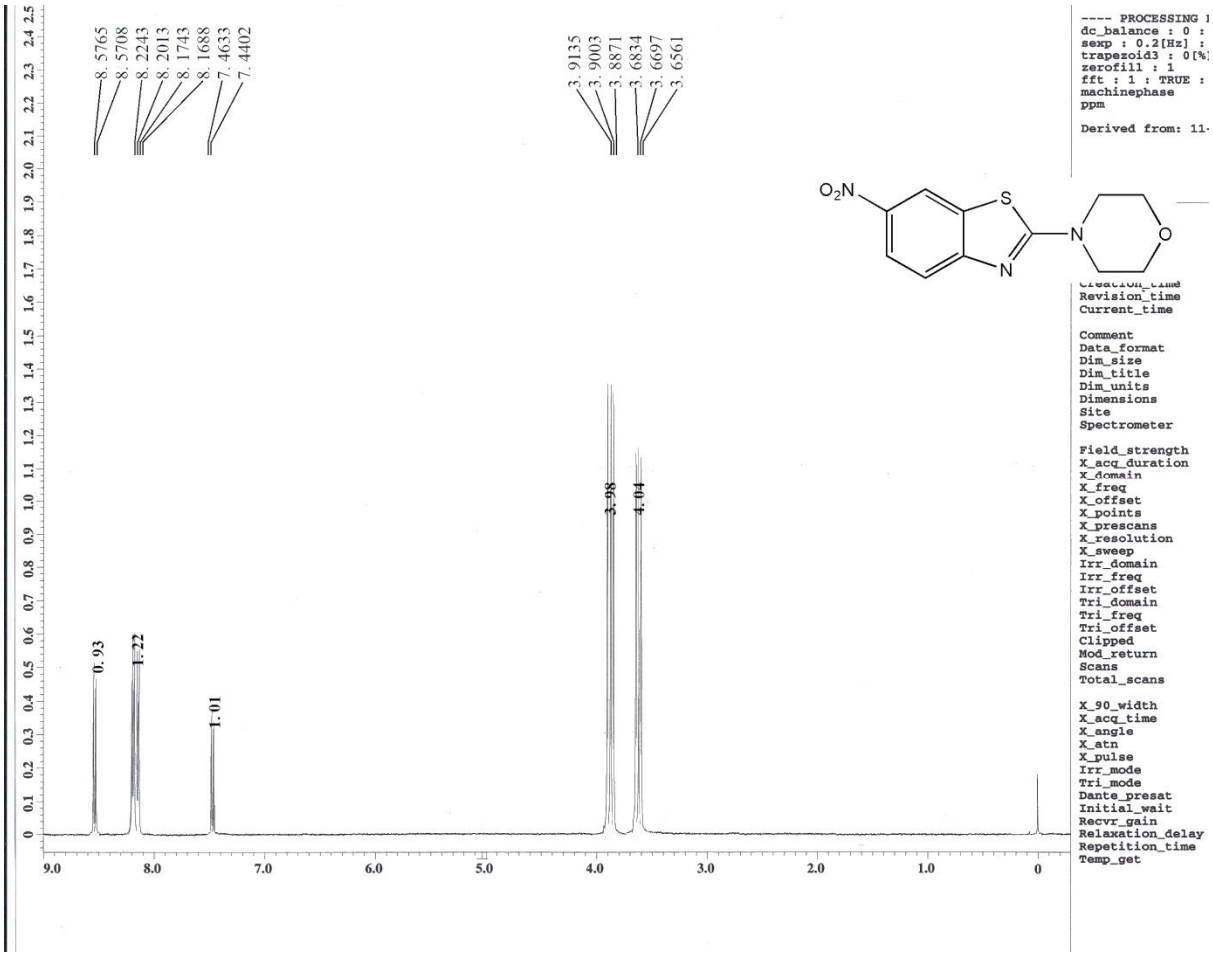


^{1}H NMR (400 MHz, $CDCl_3$) of compound 2k



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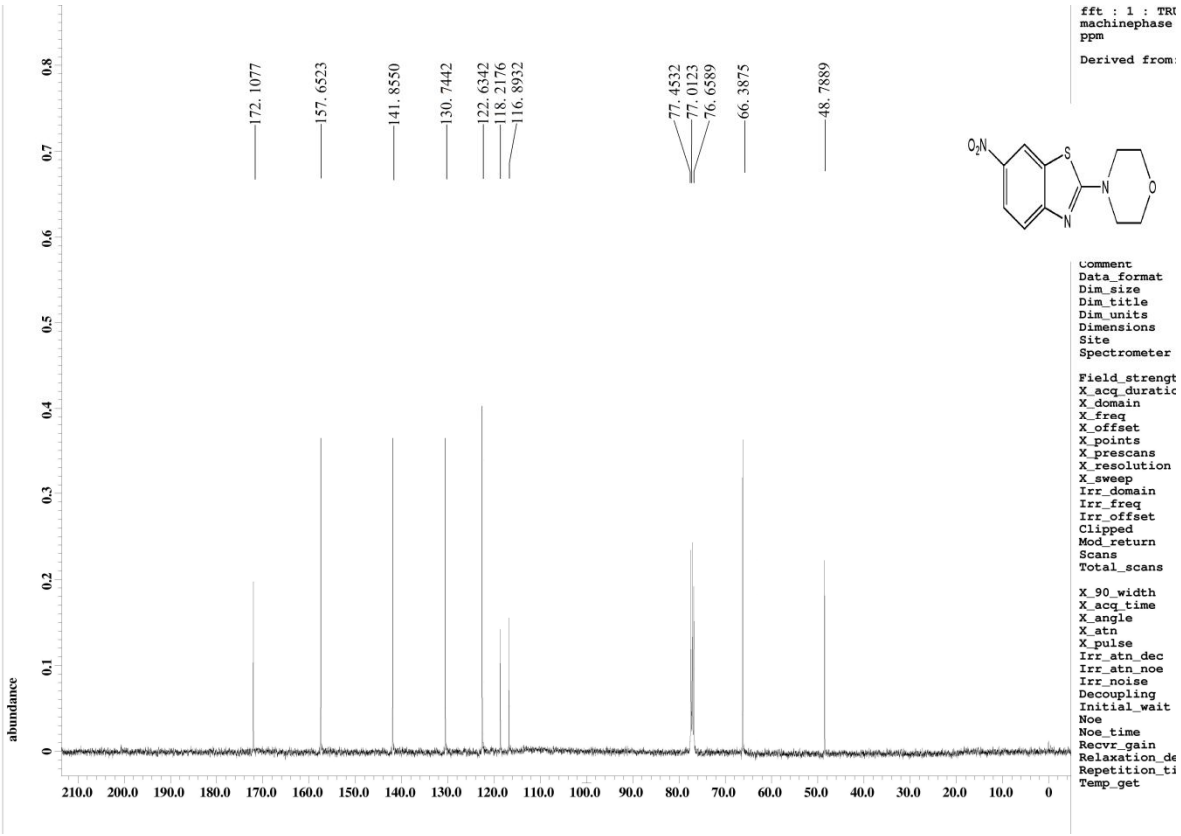

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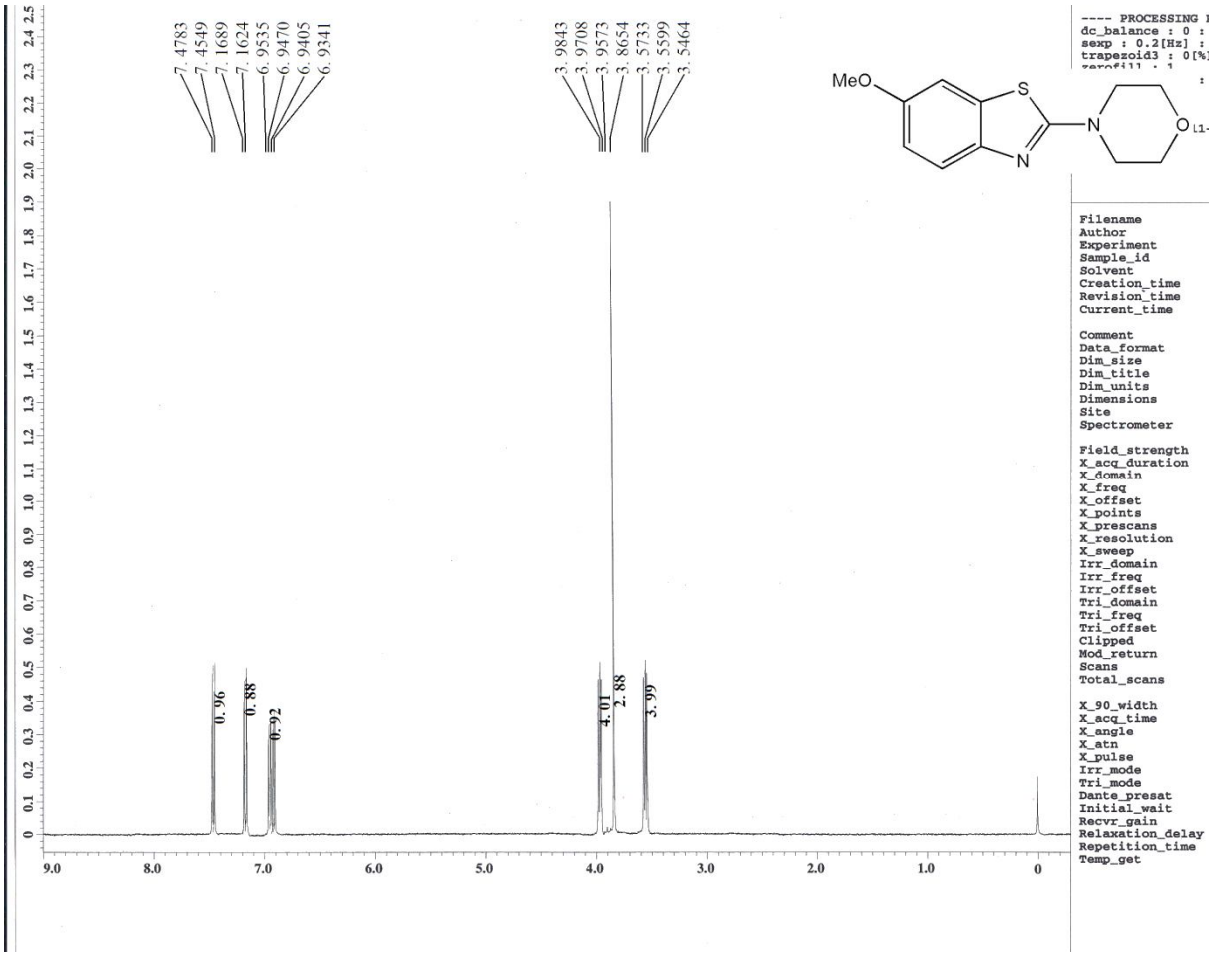

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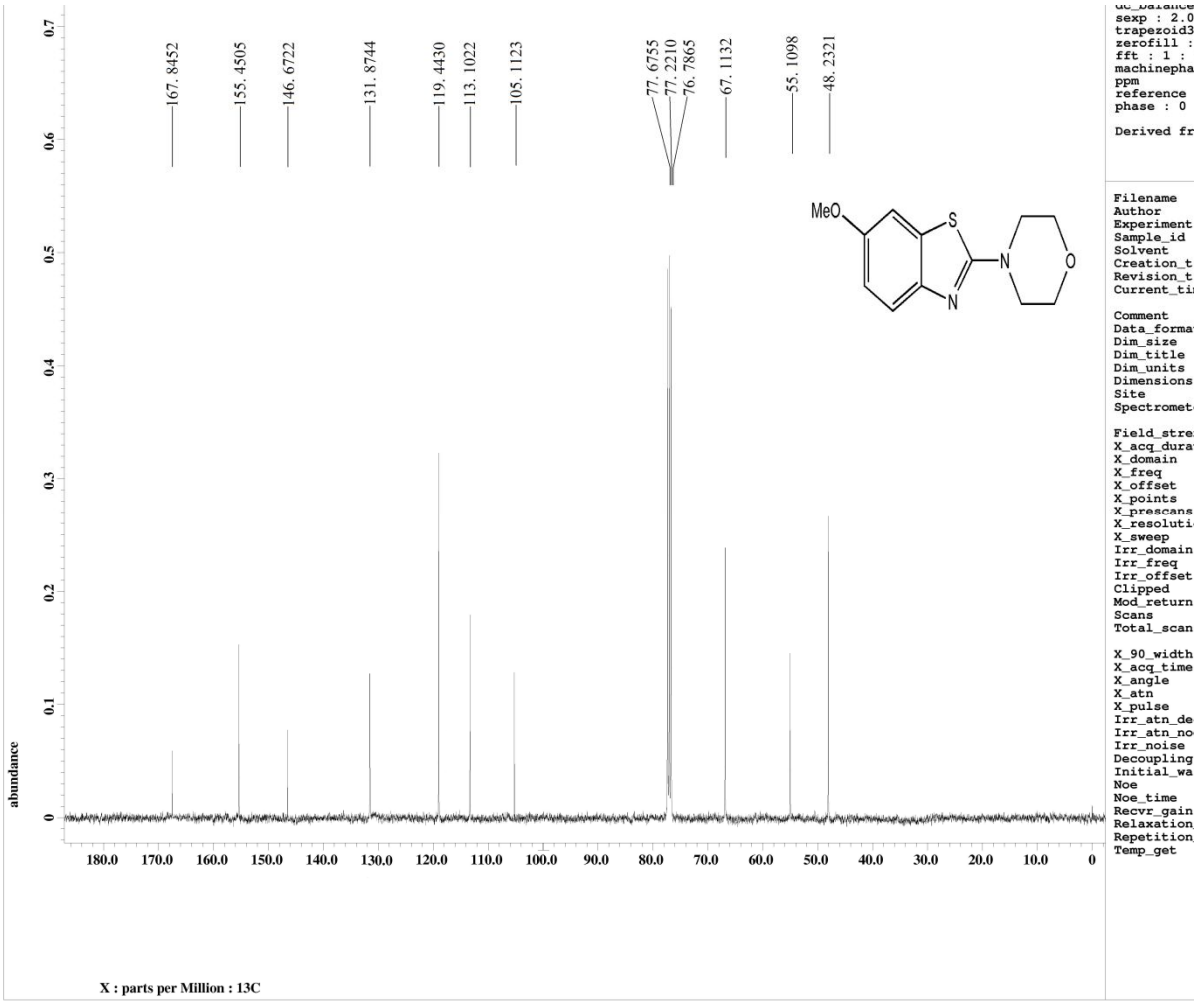
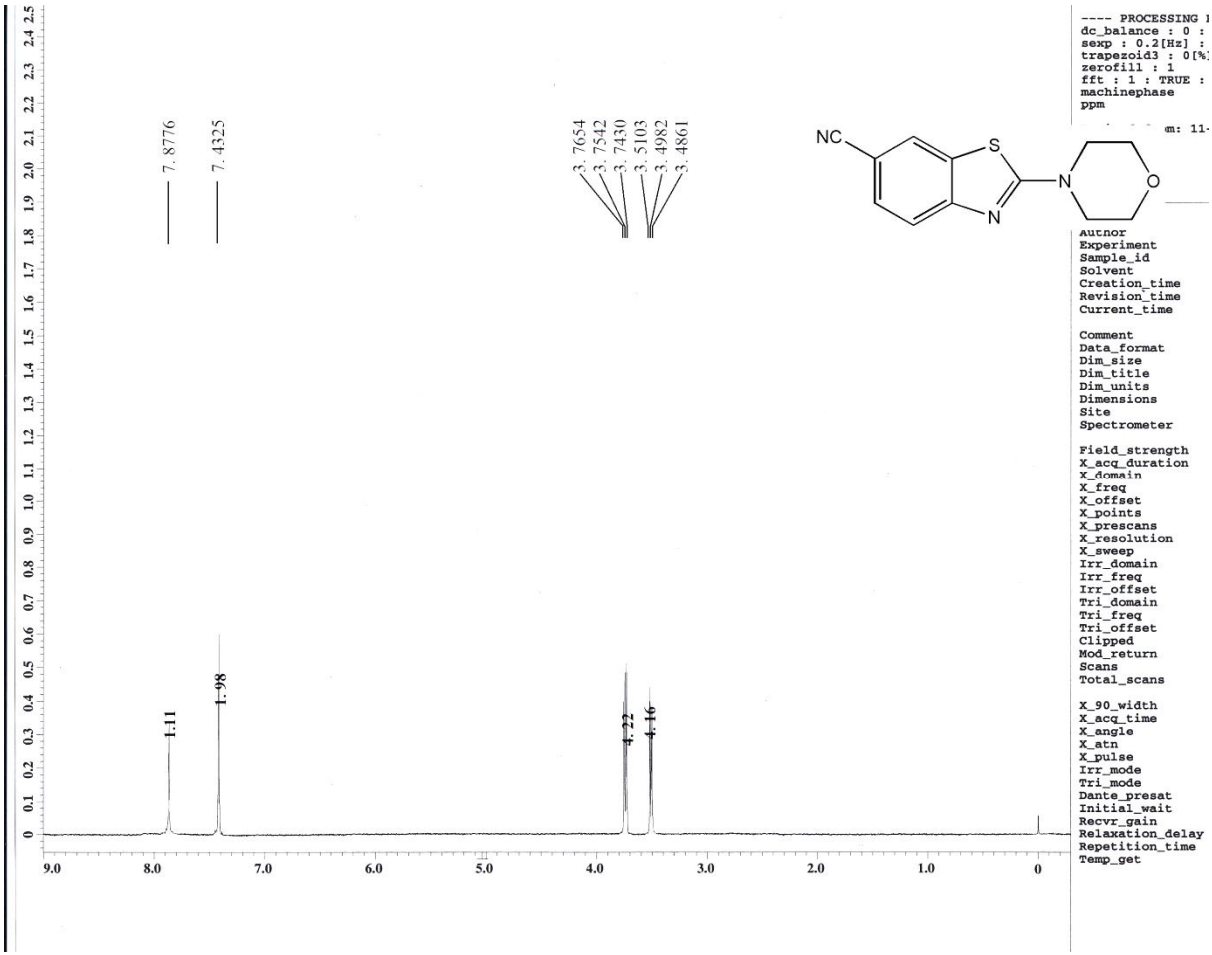


^{1}H NMR (400 MHz, $CDCl_3$) of compound 2m



^{13}C NMR (400 MHz, $CDCl_3$) of compound 2m