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Supporting Information

TBATB mediated debenzylative cross-coupling of aryl benzyl sulfides with electron rich compounds: Synthesis of diaryl sulfides

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1. Experimental Section

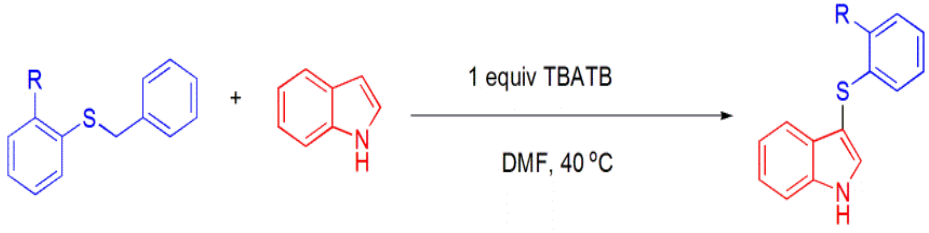
All solvents and chemicals were purchased from Sigma Aldrich and used without further purification. ^{1}H and ^{13}C Nuclear Magnetic Resonance spectra of pure compounds were acquired at 400 and 100 MHz respectively. All NMR samples were recorded in deuterated chloroform. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Mass spectra were recorded using WATER MS system, Q-tof premier and data analyzed using Mass Lynx 4.1. Elemental analyses were performed on a Flash 2000 Thermo Scientific instrument at NIT Silchar. Infrared spectra were recorded on a FTIR spectrometer. Solid samples were examined as a thin film between KBr salt plates.

2. General procedure for coupling of arylbenylsulfide with NuH

A mixture of arylbenzylsulfide **1** (0.5 mmol), **NuH** (0.5 mmol) and TBATB (0.5 mmol) in DMF (2 ml) were stirred at 40 ^{o}C for 24h under open atmosphere. After the completion of the reaction (monitored by TLC) the solvent was removed under vacuum, added water (3 mL) and extracted with diethylether (3x10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified on a silica gel column using hexane/ EtOAc to get the pure product **3**.

3. General procedure for reaction of arylbenzylsulfide (1) with indole (2a)

A mixture of arylbenzylsulfide **1** (0.5 mmol), indole (0.5 mmol) and TBATB (0.5 mmol) in DMF (2 ml) were stirred at 40 ^{o}C for specified time. The progress of the reaction was monitored by TLC. After the reaction the solvent was removed under vacuum, added water (3 mL) and extracted with diethylether (3x10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified on a silica gel column using hexane/ EtOAc to get the pure product. The maximum isolated yields (%) of **3c, 3g, 3m** were found as 81, 77 and 31 respectively (**Fig. 1**).



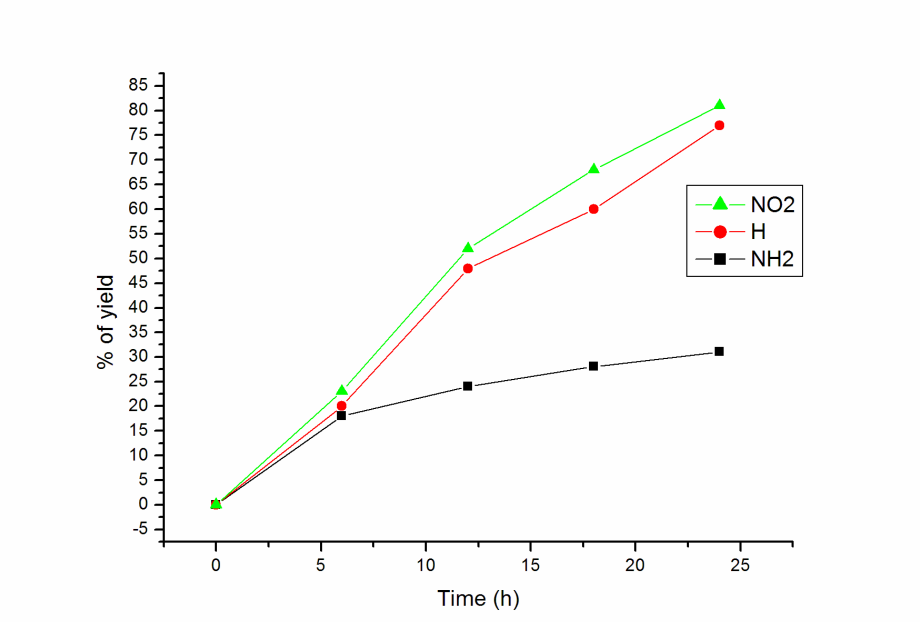


Fig. 1

Entry	Reaction time [h]	R=NO_2 **(3c)** yield [%][a]	R=H **(3g)** yield [%][a]	R=NH_2 **(3m)** yield [%][a]
1	0-5 (min)	0	0	0
2	6	23	20	18
3	12	52	48	24
4	18	68	60	28
5	24	81	77	31

[a]Yields of isolated product after chromatographic purification unless otherwise noted.

Benzylbromide (C)

Yield: 14% (30 mg, colorless liquid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.71 (m, 2H, ArH), 7.55-7.52 (m, 2H, ArH), 7.34-7.27 (m, 1H, ArH), 4.53(s, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.5, 129.7, 128.6, 126.8, 6.0.

1-(2-nitrophenylthio) napthalen-2-ol (3a)

Yield: 87% (258 mg, yellow solid); m.p. 170-171 ^{o}C. IR (KBr) (ν_{max}/cm^{-1}): 3435, 2905, 2845, 1588, 1545, 1497, 1335, 1055, 940, 865, 746, 689; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.9 Hz, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.97-7.86 (m, 6H), 7.23 (s, 1H) 6.84 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 156.3, 155.3, 153.1, 148.6, 143.5, 138.4, 136.7, 130.2, 129.1, 128.5, 127.2, 118.6, 117.4, 115.0; HRMS (ESI) : M^+ Calcd for $C_{16}H_{11}NO_3S$ 297.0460, found 297.0463. Anal. Calcd for $C_{16}H_{11}NO_3S$: C, 64.63; H, 3.73; N, 4.71. Found: C, 64.58; H, 3.91; N, 4.88.

4-(2-nitrophenylthio) napthalen-1-ol (3b)

Yield: 83% (246 mg, yellow liquid). IR (KBr) (ν_{max}/cm^{-1}): 3325, 2934, 2866, 1614, 1578, 1492, 1378, 1326, 1278, 906, 742, 715, 678; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29-8.21 (m, 4H), 8.14-8.07 (m, 4H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 156.0, 152.0, 151.8, 149.9, 149.2, 146.4, 141.5, 139.8, 138.3, 135.3, 134.8,129.1 120.1, 119.2, 116.4; HRMS (ESI) : M^+ Calcd for $C_{16}H_{11}NO_3S$ 297.0460, found 297.0462. Anal. Calcd for $C_{16}H_{11}NO_3S$: C, 64.63; H, 3.73; N, 4.71. Found: C, 64.77; H, 3.69; N, 4.93.

3-(2-nitrophenylthio)-1*H*-indole (3c)

Yield: 81% (225 mg, yellow solid); m.p. 188-190 ^{o}C. IR (KBr) (ν_{max}/cm^{-1}): 3423, 2925, 1578, 1507, 1335, 1067.7, 839, 726; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.57-7.36 (m, 6H), 7.31-7.25 (m, 3H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.8 Hz,

1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 134.8, 134.6, 127.7, 127.2, 126.4, 126.1, 125.1, 124.9, 121.9, 120.1, 112.1, 108.5, 103.9; HRMS (ESI) : M^+ Calcd for $C_{14}H_{10}N_2O_2S$ 270.0463, found 270.0457. Anal. Calcd for $C_{14}H_{10}N_2O_2S$: C, 62.21; H, 3.73; N, 10.36. Found: C, 62.38; H, 3.98; N, 10.57.

4-(2-nitrophenylthio) phenol (3d)

Yield: 81% (201 mg, yellow liquid). IR (KBr) (ν_{max}/cm^{-1}): 3431, 2924, 2856, 1509, 1331, 1269, 1110, 1040, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8 Hz, 2 H), 7.98 (d, *J* = 7.68 Hz, 2H), 7.60 (d, *J* = 7.52 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 9.2 Hz, 1H), 6.71 (d, *J* = 7 Hz, 1H), 6.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 146.1, 135.0, 134.6, 127.3, 127.1, 126.5, 119.7, 117.8; HRMS (ESI) : M^+ Calcd for $C_{12}H_9NO_3S$ 247.0303, found 247.0307. Anal. Calcd for $C_{12}H_9NO_3S$: C, 58.29; H, 3.67; N, 5.66. Found: C, 58.25; H, 3.78; N, 5.81.

3-(Phenylthio)-*1H*-indole (3g)

Yield: 77% (173 mg, white solid), m.p. 150-151 ^{o}C.

1-(4-nitrophenylthio) napthalen-2-ol (3i)

Yield: 74% (219 mg, yellow solid); m.p. 157-158 ^{o}C. IR (KBr) (ν_{max}/cm^{-1}): 3420, 2925, 1505, 1334, 1038, 727, 679; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 7.3 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.7 (d, *J* = 7.4 Hz, 1H), 7.69-7.58 (m, 3H), 7.27 (s, 1H), 6.75 (d, *J* = 7.2 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 146.1, 134.7, 134.3, 129.0, 129.1, 127.3, 127.1, 126.6, 123.7, 117.8, 109.5; Anal. Calcd for $C_{16}H_{11}NO_3S$: C, 64.63; H, 3.73; N, 4.71. found: C, 64.67; H, 3.67; N, 5.07.

4-(4-nitrophenylthio) napthalen-1-ol (3j)

Yield: 61% (181 mg, yellow liquid). IR (KBr) (ν_{max}/cm^{-1}): 3314, 2927, 2877, 1634, 1543,1499, 1324, 1234, 888, 732, 665; NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.95-7.82 (m, 5H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.50 (d, J = 7.5 Hz, 2H), 7.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 141.4, 137.3, 136.8, 136.6, 133.5, 130.4, 129.7, 119.6; Anal. Calcd for $C_{16}H_{11}NO_3S$: C, 64.63; H, 3.73; N, 4.71. Found: C, 64.44; H, 3.85; N, 4.77.

4-(4-nitrophenylthio) phenol (3k)

Yield: 61% (150 mg, yellow liquid). IR (KBr) (ν_{max}/cm^{-1}): 3418, 2923, 1507, 1333, 1033, 722; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.2,1 H), 7.97-7.88 (m, 2H), 7.75-7.71 (m, 1H), 7.64 (d, *J* = 7.28 Hz, 1H), 6.88-6.78 (m, 2H), 6.73 (d, *J* = 7.84 Hz, 1H), 6.67 (s, 1H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 162.1, 153.4, 150.8, 150.5, 141.5, 137.7, 134.8, 131.5; HRMS (ESI) : M^+ Calcd for $C_{12}H_9NO_3S$ 247.0303, found 247.0304. Anal. Calcd for $C_{12}H_9NO_3S$: C, 58.29; H, 3.67; N, 5.66. Found: C, 57.94; H, 3.59; N, 5.76.

1-(4-chlorophenylthio) napthalen-2-ol (3l)

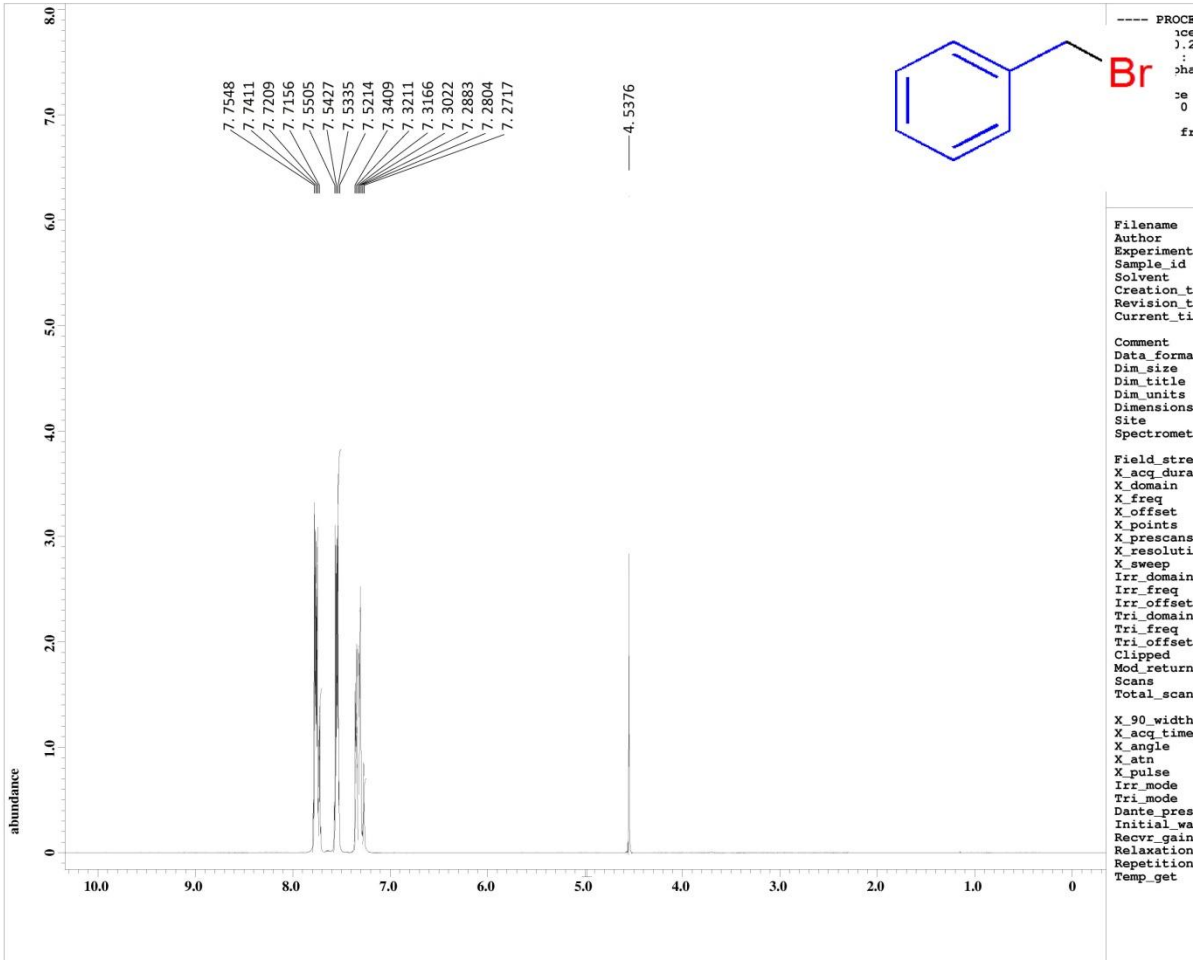
Yield: 67% (192 mg, yellow solid); m.p. 105-106^oC.

4-(4-chlorophenylthio) napthalen-1-ol (3o)

Yield: 65% (186 mg, yellow liquid). IR (KBr) (ν_{max}/cm^{-1}): 3356, 2926, 2866, 1601, 1533, 1465, 1310, 1139, 1066, 906, 876, 714, 688; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.3 Hz, 1H), 8.02-7.91 (m, 7H), 7.63 (d, *J* = 8 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 137.9, 135.1, 133.8, 128.9, 127.5, 125.3, 123.7, 120.8. HRMS (ESI): M^+ Calcd for $C_{16}H_{11}ClOS$ 286.0219, found 286.0218. Anal. Calcd for $C_{16}H_{11}ClOS$: C, 67.01; H, 3.87. Found: C, 67.15; H, 3.95.

4-(4-chlorophenylthio) phenol (3p)

Yield: 75% (177 mg, colorless liquid). IR (KBr) (ν_{max}/cm^{-1}): 3429, 2921, 2857, 1638, 1245, 1065, 761; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.48 (m, 6H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 135.1, 134.6, 127.3, 127.1, 126.5, 120.3. HRMS (ESI): M^+ Calcd for $C_{12}H_9ClOS$ 236.0063, found 236.0061. Anal. Calcd for $C_{12}H_9ClOS$: C, 60.89; H, 3.83. Found: C, 60.76; H, 3.92.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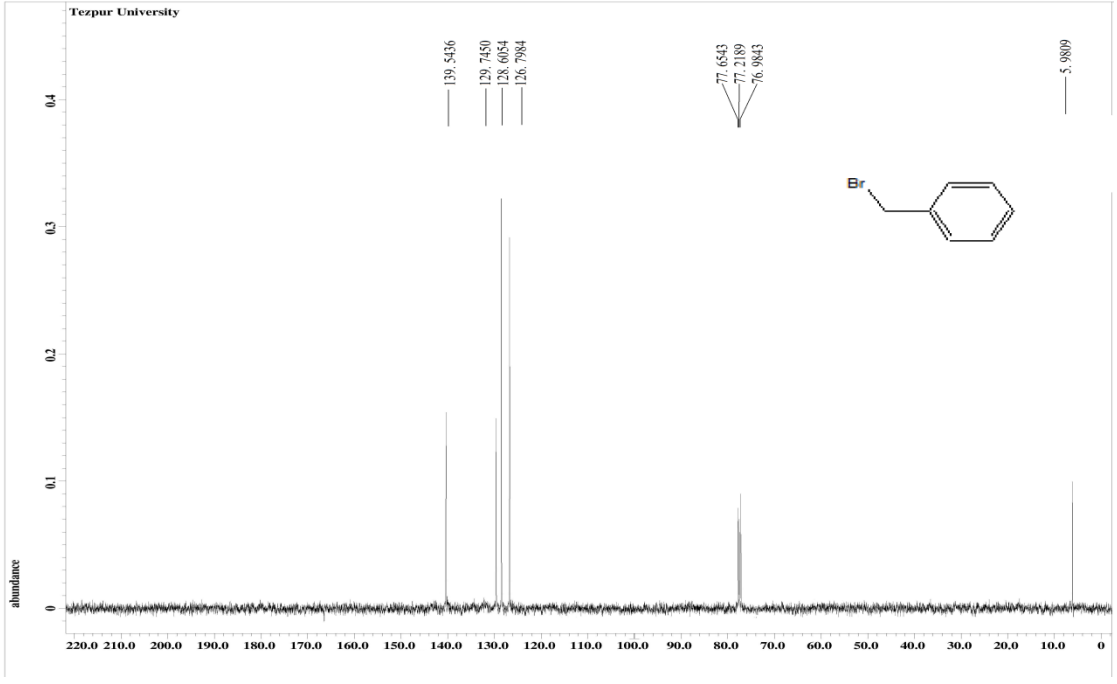
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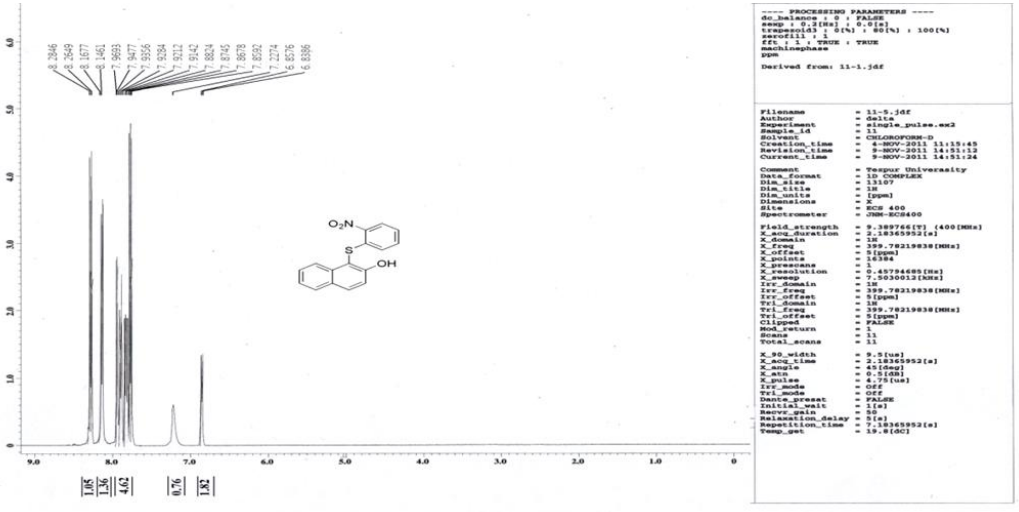
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3a:



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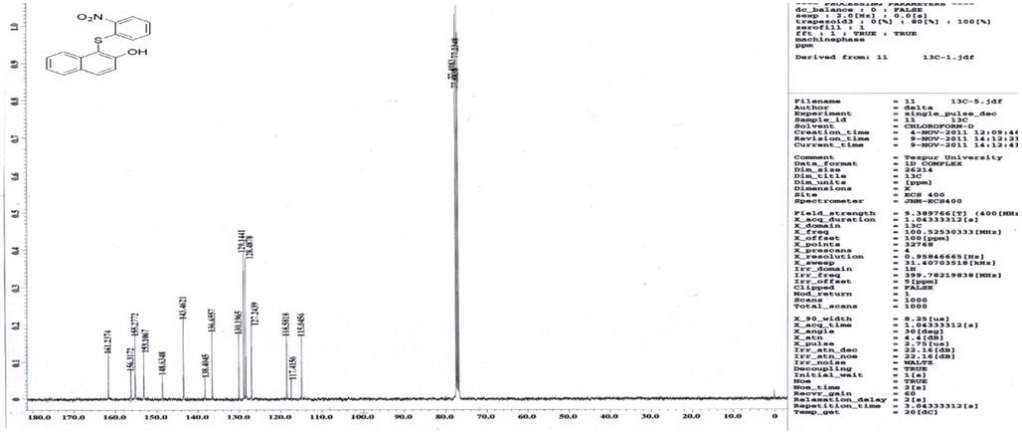
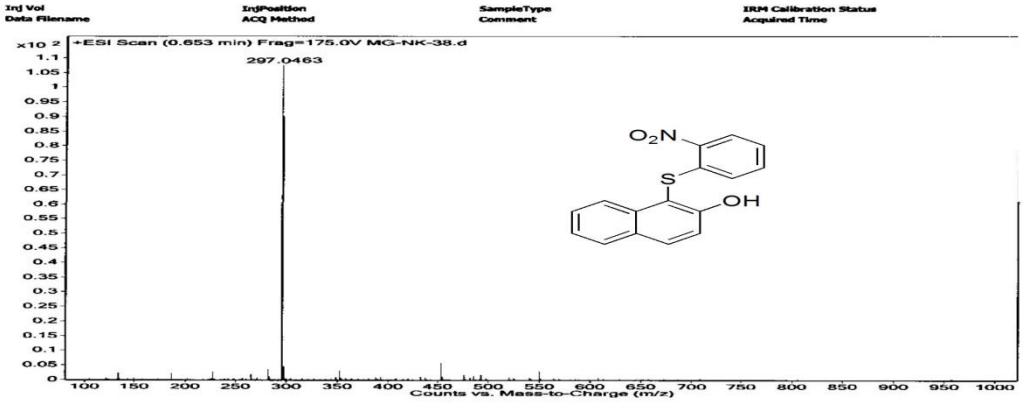


MASS SPECTRA of compound 3a:



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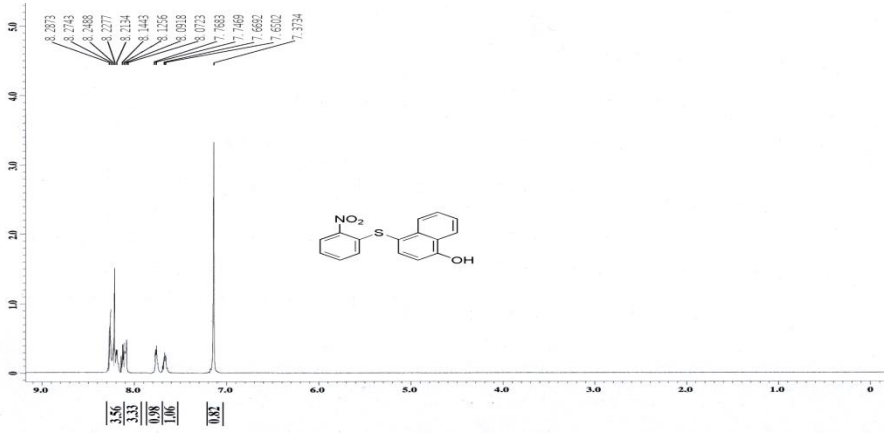

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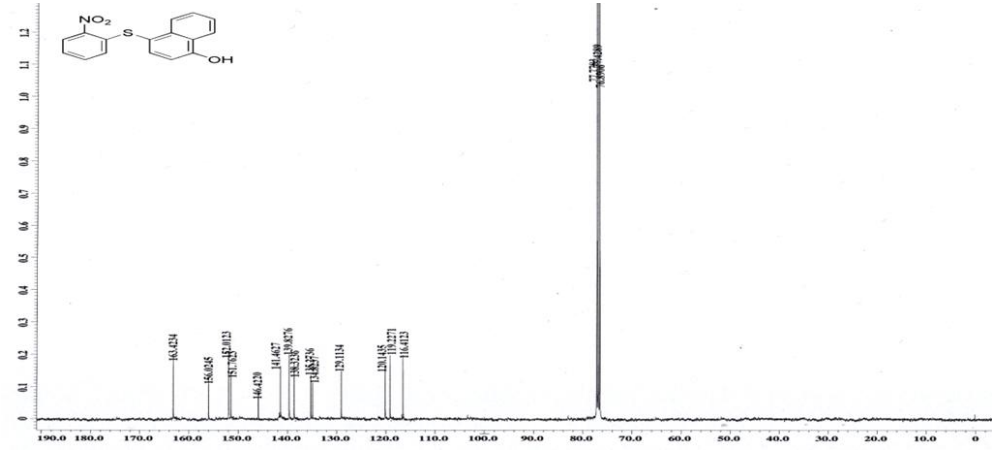

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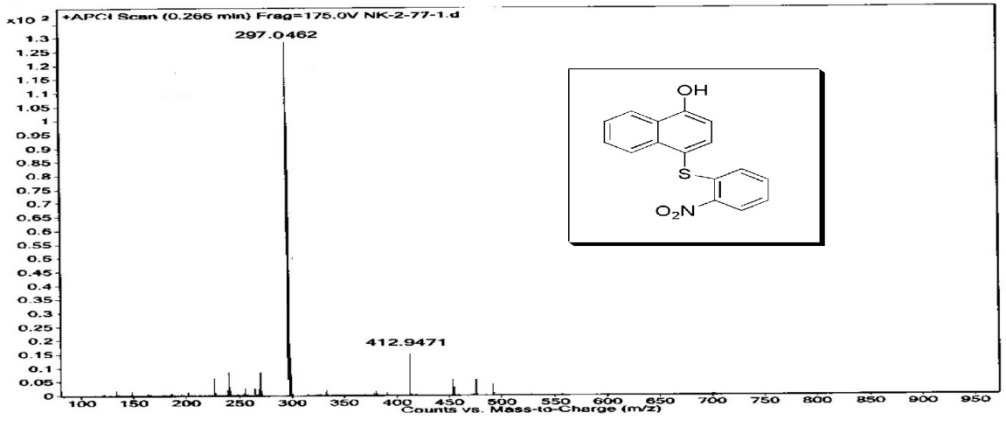

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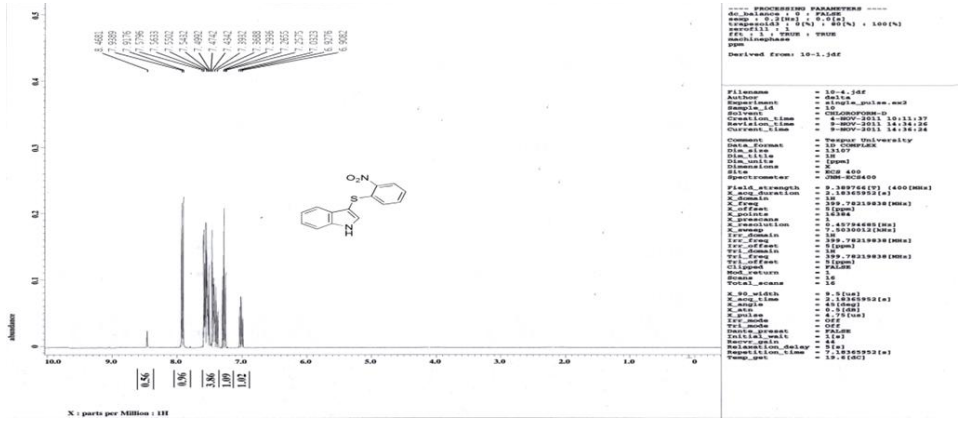

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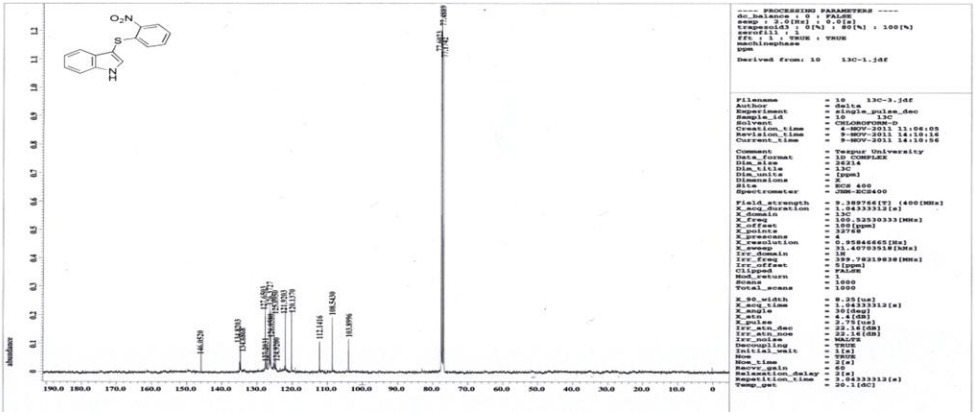
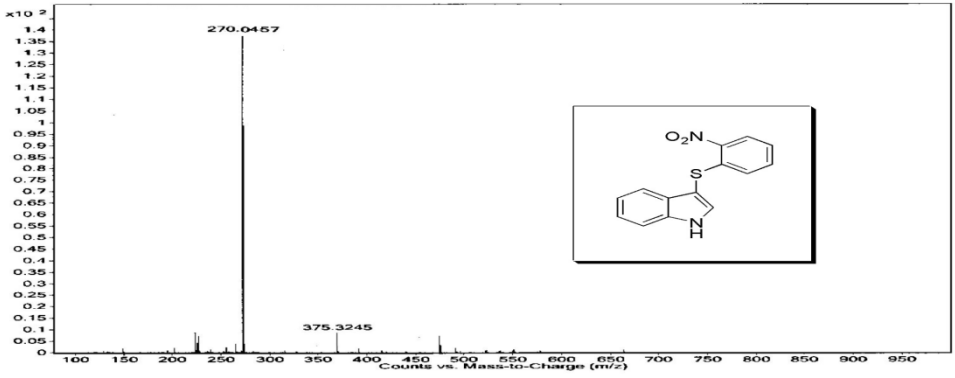


MASS SPECTRA of compound 3c:



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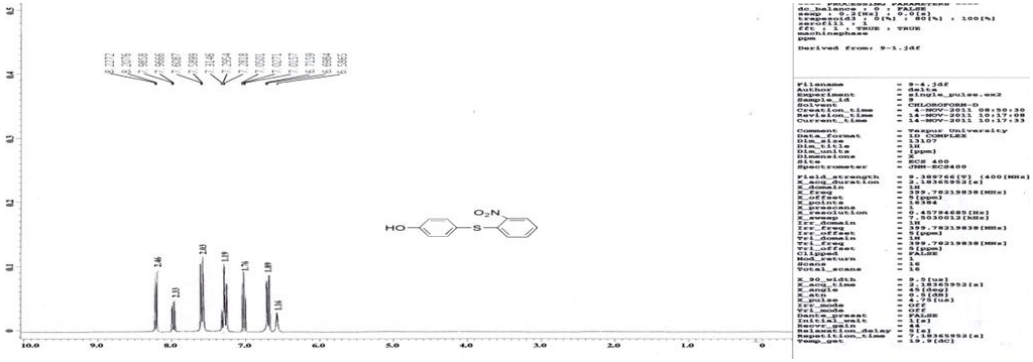

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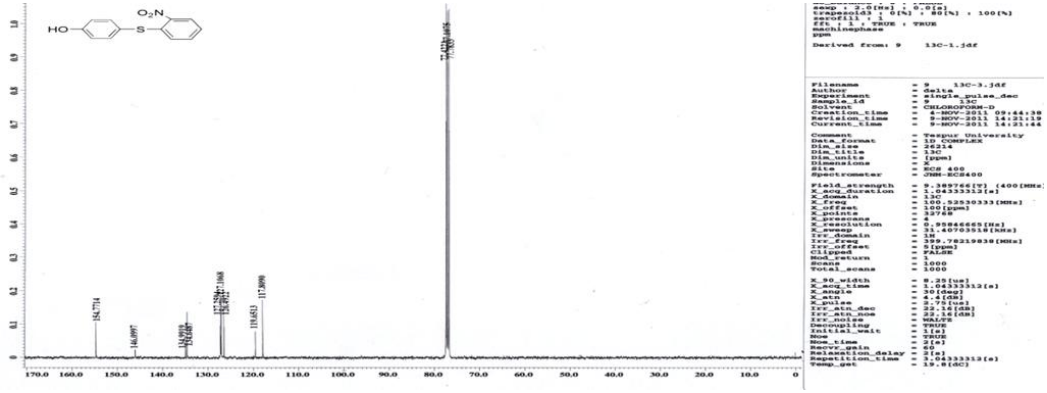

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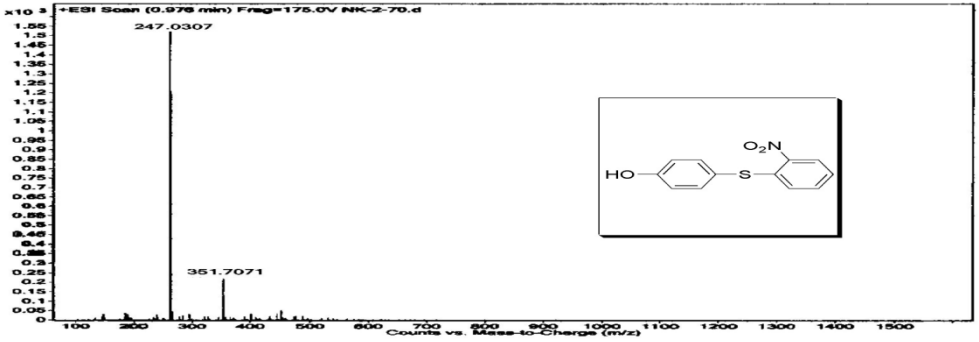

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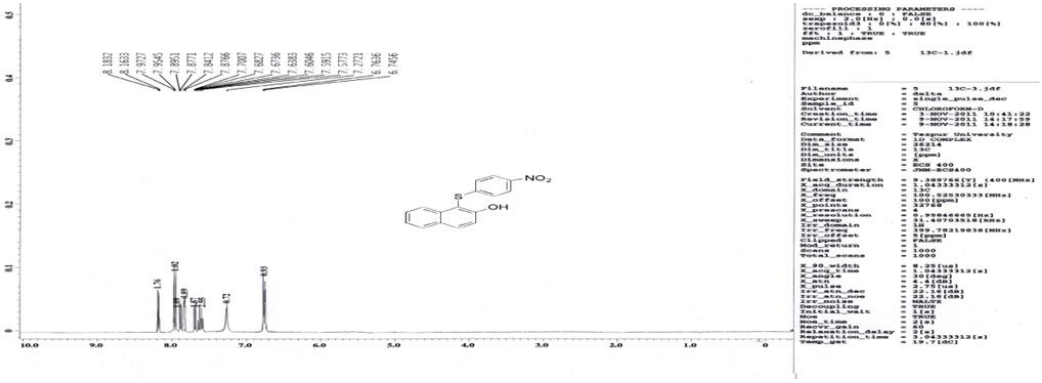

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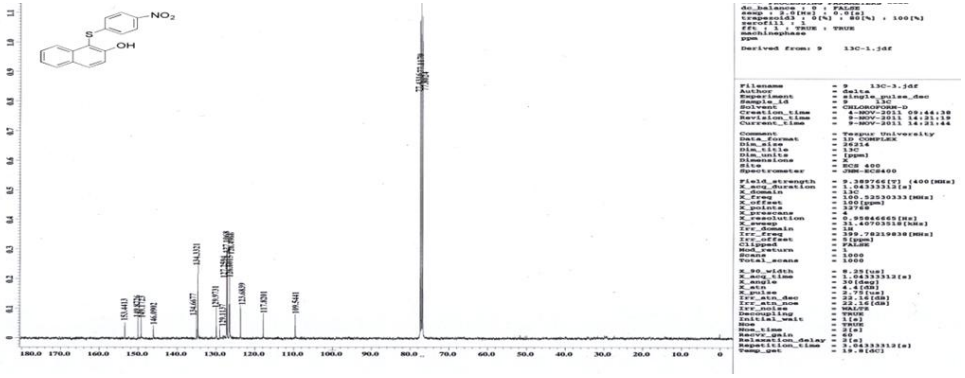

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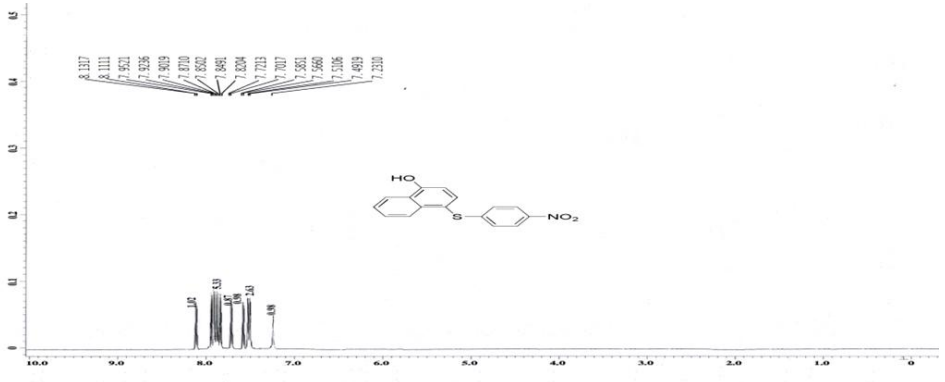
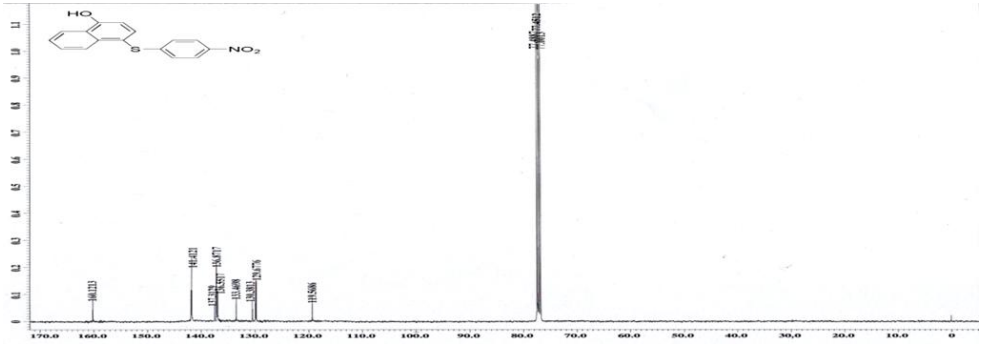


^{13}C NMR (100 MHz, $CDCl_3$) of compound 3j:



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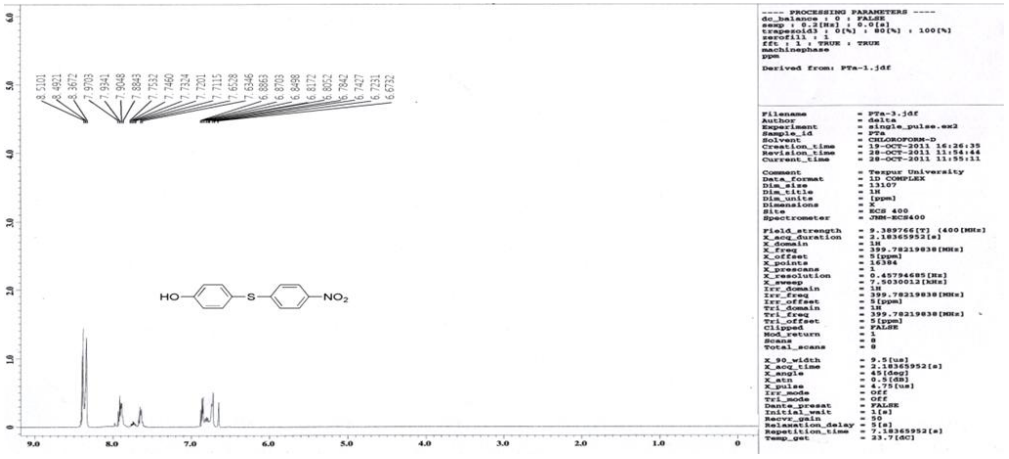
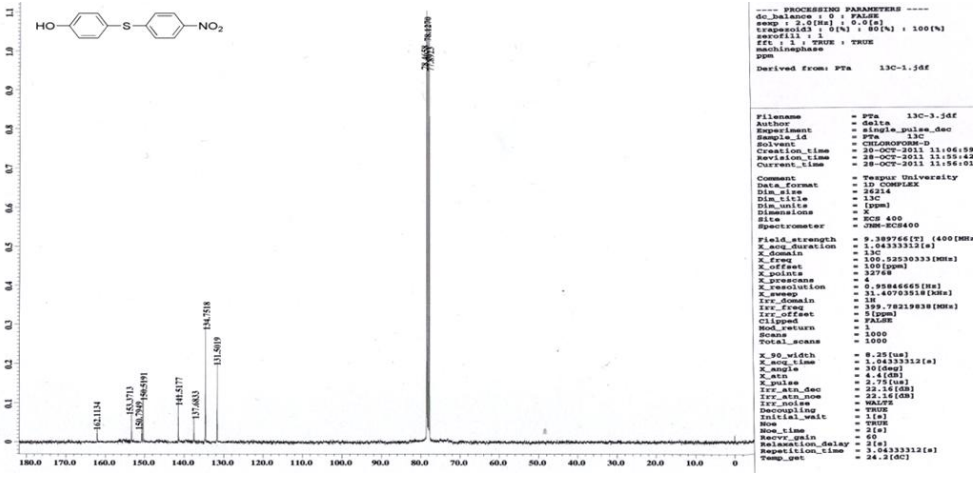
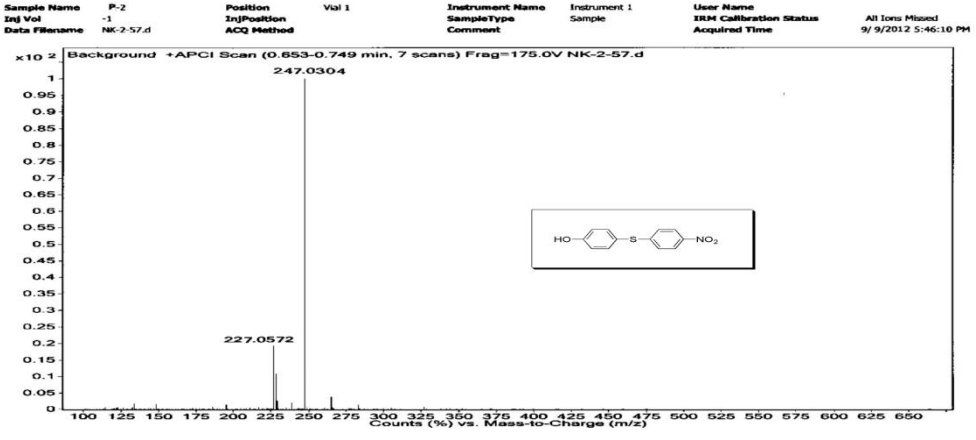


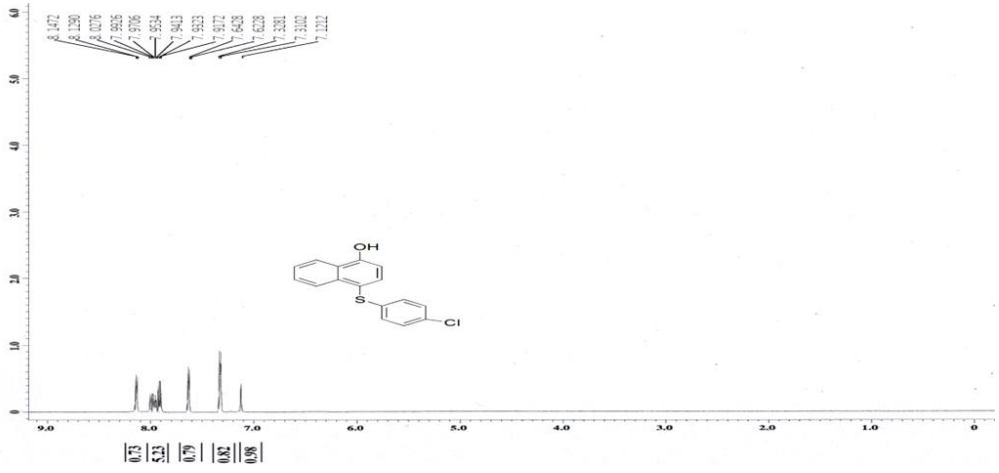
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3k:



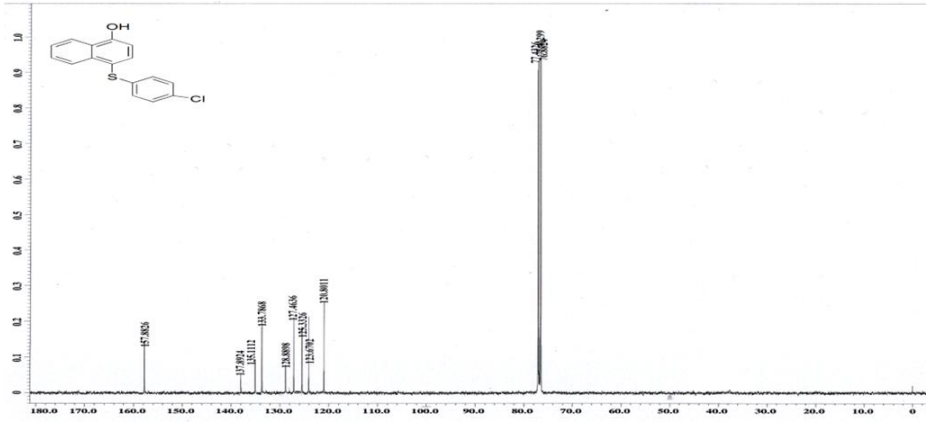
MASS SPECTRA of compound 3k:



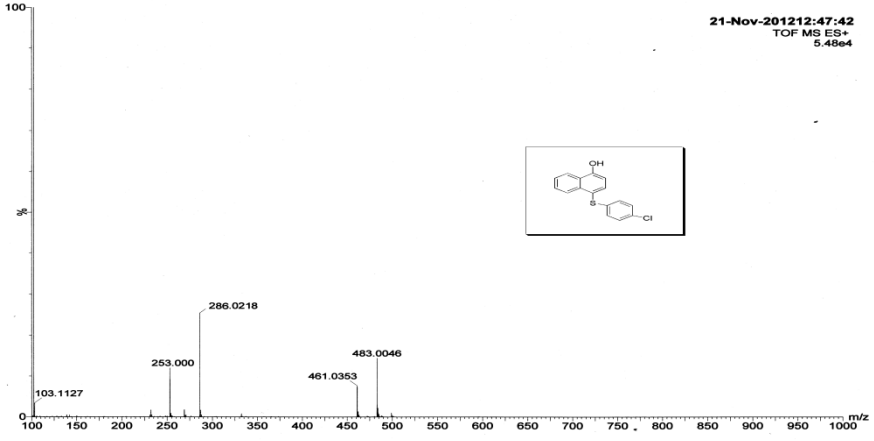
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3o:



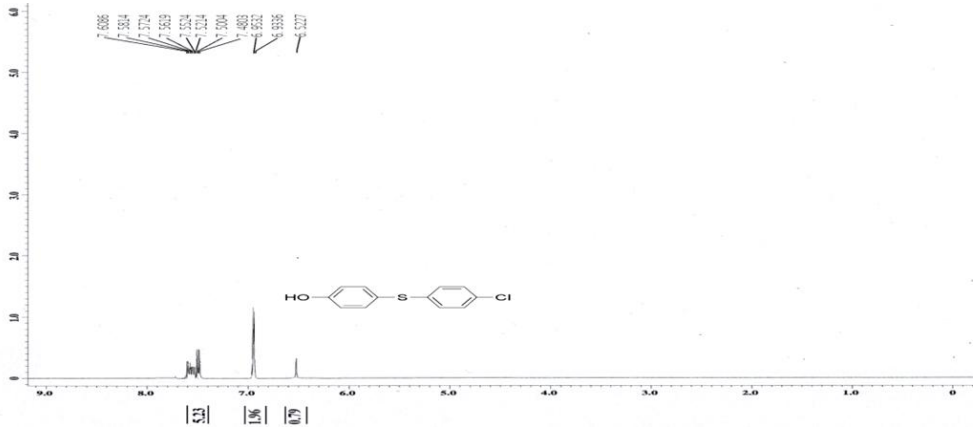
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3o:



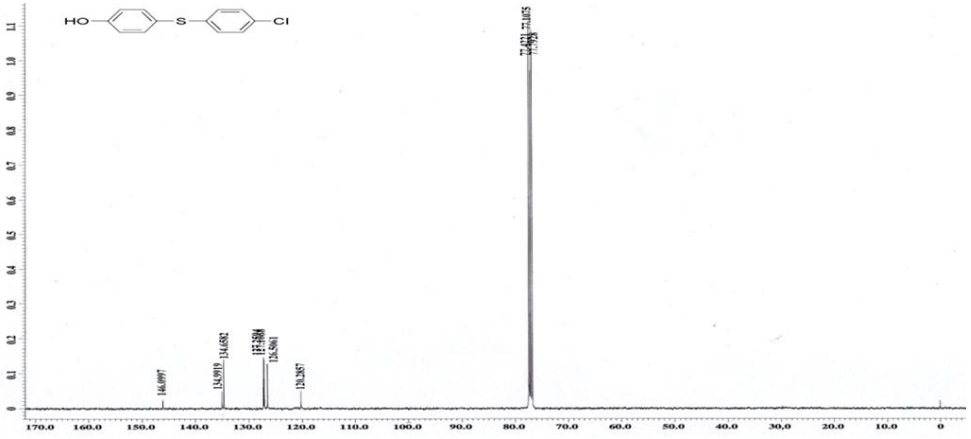
MASS SPECTRA of compound 3o:



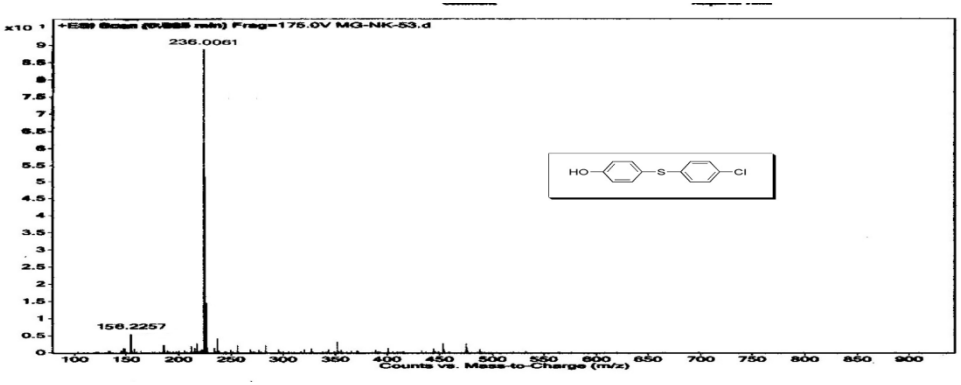
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3p:



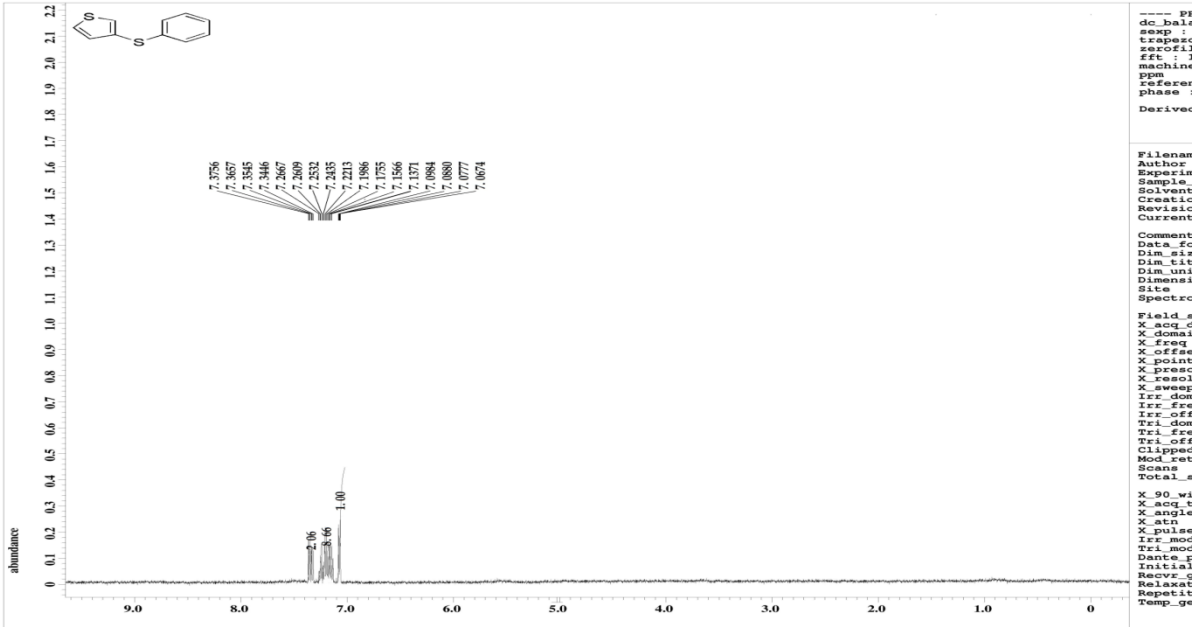
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3p:



MASS SPECTRA of compound 3p:



^{1}H NMR (400 MHz, $CDCl_3$) of compound 6a:



^{13}C NMR (100 MHz, $CDCl_3$) of compound 6a