Electronic Supplementary Material (ESI) for New Journal of Chemistry.

$BF_3{\cdot}OEt_2$ Catalyzed S-H insertion reactions of α-diazo imidamides and enolizable thioamides under metal-free conditions

Supporting Information

CONTENTS

1. General information

Melting points were determined on a capillary melting point apparatus and uncorrected. IR spectra were recorded using ATR technique on a Bruker Alpha FT-IR spectrophotometer. All compounds were fully characterized. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded at 400 MHz using $CDCl_3$ in ppm (δ) related to tetramethylsilane (δ=0.00) as an internal standard and are reported as follows; chemical shift (ppm), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet dd = doublet of doublet, m = multiplet), coupling constant (*J*) values are given in parts per million and Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra were recorded at 100 MHz in $CDCl_3$. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the triplet at 77.7 ppm for $CDCl_3$. Carbon types were determined from ^{13}C NMR and DEPT experiments. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.7 ppm). High resolution mass analyses were performed using electrospray ionization (ESI) technique on a Thermo Exactive Orbitrap mass spectrometer. All solvents were purified by distillation following standard procedure. Thin layer chromatography was performed on silica or alumina plates and components visualized by observation under iodine/UV light at 254 nm. Column chromatography was performed on silica gel (100-200 mesh). All the reactions were conducted in oven-dried glassware with magnetic stirring. Reagents were added via syringes through septa. Indoles, NaN_3, TsCl, $BF_3{\cdot}OEt_2$, 2-mercaptobenzimidazoles, thiourea, thiosemicarbazones and other commercial chemicals were purchased from M/s Sigma Aldrich, Alfa Aesar and used as provided.

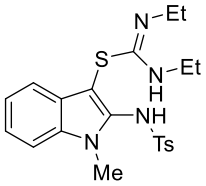
Experimental Section

2. General procedure for products 3, 6 and 8

To an oven-dried RB flask, a solution containing the appropriate 1 mmol of thiourea **2**, thiosemicarbazones **5** or mercaptobenzimidazole **7** in DCM was stirred for 5 min to obtain a homogeneous mixture and a drop of $BF_3.OEt_2$ was added and allowed to stir at room temperature. To this reaction mixture, a solution of 3-diazoindol-2-imine **1** (1.2 mmol) in DCM (4 mL) was added through syringe pump with the addition rate of 5mL/h at ambient temperature to afford until the reaction completed (monitored using TLC). After the completion of reaction, the solvent was removed under reduced pressure and diluted with ethyl acetate (10 mL) and

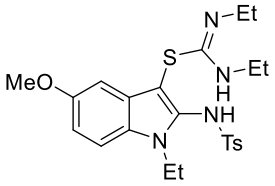
water (15 mL). The organic phase was separated and the aqueous layer washed with ethyl acetate (10 mL). Concentration of combined organic layers under reduced pressure afforded the crude product, which was purified by column chromatography using silica gel (100-200 mesh, EtOAc/hexane 30:70) to furnish carbamimidothioates **3a-i / 6a-k / 8a-f**.

3. Characterization data for products 3a-i



1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N′*-diethylcarbamimido thioate (3a)

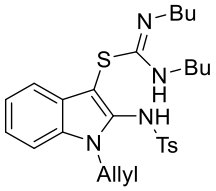
White solid; Yield: 84%; R_f = 0.24 (EtOAc/hexane = 3:1); m.p. 158-160 ºC; IR (neat): ν_{max} = 3254, 3176, 3047, 2978, 2929, 1623, 1494, 1370, 1233, 1125, 1091 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ= 8.94 (s, 1H), 7.76 (d, *J* = 8 Hz, 2H), 7.31-7.30 (m, 1H), 7.24-7.16 (m, 5H), 3.77 (br s, 2H), 3.47 (br s, 2H), 3.29 (s, 3H), 1.90 (br s, 1H), 2.42 (s, 3H), 1.46 (br s, 3H), 1.09 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.1, 153.0, 144.7, 140.2, 135.1, 129.0, 128.9, 125.7, 120.9, 120.7, 116.1, 109.1, 75.5, 39.7, 39.0, 29.2, 21.4, 15.0, 13.3 ppm; HRMS (ESI) Calcd for $C_{21}H_{26}N_4O_2S_2$ $[M+H]^+$; 431.1575, found: 431.1563.



1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl *N,N′*-diethylcarbamimidothioate (3b)

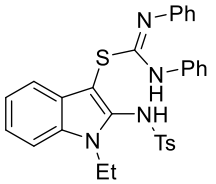
White solid; Yield: 93%; R_f = 0.31 (EtOAc/hexane = 3:1); m.p. 161-162 ºC; IR (neat): ν_{max} = 3253, 3175, 3040, 2979, 2930, 1623, 1483, 1380, 1218, 1125, 1089 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.86-8.77 (br s, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 7.2 Hz, 2H), 4.76 (br s, 1H), 3.95-3.94 (m, 2H), 3.86 (s, 3H), 3.67 (br s, 2H), 3.39 (br s, 2H), 2.40 (s, 3H), 1.40 (br s, 3H), 1.22 (t, *J* = 6.8 Hz, 3H), 1.05 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.1, 155.0, 152.7, 144.9, 140.1, 130.2, 129.0, 128.8, 125.5,

110.0, 109.0, 100.0, 74.8, 56.0, 39.7, 39.0, 37.4, 21.4, 15.0, 14.3, 13.3 ppm; HRMS (ESI) Calcd for $C_{23}H_{30}N_4O_3S_2$ $[M+H]^+$; 475.1837, found: 475.1834.



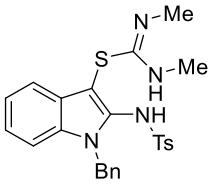
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-dibutylcarbamimido thioate (3c)

White solid; Yield: 90%; R_f = 0.31 (EtOAc/hexane = 3:1); m.p. 153-154 ºC; IR (neat): ν_{max} = 3258, 3169, 3045, 2928, 2869, 1626, 1495, 1372, 1224, 1125, 1091 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.74 (br s, 1H), 7.64 (d, *J* = 8 Hz, 2H), 7.13-6.99 (m, 6H), 5.59-5.50 (m, 1H), 4.93-4.80 (m, 3H), 4.44 (s, 2H), 3.53 (br s, 2H), 3.25 (br s, 2H), 2.30 (s, 3H), 1.68 (br s, 2H), 1.47-1.18 (m, 4H), 0.88-0.79 (m, 6H), 0.55 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.2, 152.4, 144.6, 140.2, 134.4, 133.5, 128.9, 128.9, 125.7, 120.8, 120.7, 116.3, 115.9, 109.9, 75.4, 45.0, 44.5, 43.5, 31.6, 29.8, 21.4, 19.9, 19.3, 13.6, 13.4 ppm; HRMS (ESI) Calcd for $C_{27}H_{36}N_4O_2S_2$ $[M+H]^+$; 513.2357, found: 513.2360.



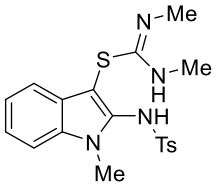
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-diphenylcarbamimido thioate (3d)

White solid; Yield: 84%; R_f = 0.27 (EtOAc/hexane = 3:1); m.p. 139-141 ºC; IR (neat): ν_{max} = 3249, 3204, 3041, 2975, 2927, 1619, 1570, 1494, 1365, 1217, 1120, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 7.2 Hz, 1H), 7.56-7.51 (m, 3H), 7.43-7.40 (m, 1H), 7.30-7.27 (m, 5H), 7.10-7.04 (m, 8H), 6.41 (br s, 1H), 4.54 (q, *J* = 7.2 Hz, 2H), 2.28 (s, 3H), 1.7 (br s, 1H), 1.51 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.9, 134.8, 129.9, 128.8, 127.6, 127.5, 124.1, 123.2, 121.9, 120.5, 119.5, 111.2, 94.1, 39.4, 21.7, 14.7 ppm; HRMS (ESI) Calcd for $C_{30}H_{28}N_4O_2S_2$ $[M+H]^+$; 541.1731, found: 541.1732.



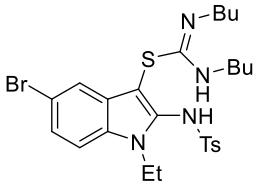
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N′*-dimethylcarbamimido thioate (3e)

White solid; Yield: 92%; R_f = 0.32 (EtOAc/hexane = 3:1); m.p. 152-153 ºC; IR (neat): ν_{max} = 3458, 3324, 3178, 3060, 2927, 1633, 1495, 1376, 1226, 1125, 1091 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8 Hz, 2H), 7.32-7.21 (m, 4H), 7.14-7.05 (m, 7H), 5.09 (s, 2H), 5.00 (br s, 1H), 3.35 (br s, 3H), 3.04 (br s, 3H), 2.37 (s, 3H), 1.94 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.3, 153.3, 144.4, 140.4, 137.6, 134.5, 129..4, 129.0, 128.4, 127.0, 126.9, 125.5, 121. 0, 120.9, 116.1, 110.0, 74.3, 46.1, 30.7, 30.6, 21.4 ppm; HRMS (ESI) Calcd for $C_{25}H_{26}N_4O_2S_2$ $[M+H]^+$; 479.1575; found: 479.1571.



1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N′*-dimethylcarbamimidothioate (3f)

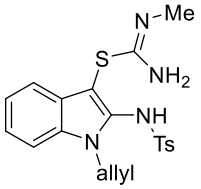
White solid; Yield: 93%; R_f = 0.34 (EtOAc/hexane = 3:1); m.p. 152-154 ºC; IR (neat): ν_{max} = 3458, 3324, 3178, 3060, 2927, 1633, 1495, 1376, 1226, 1125, 1091 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 8 Hz, 2H), 7.30-7.26 (m, 1H), 7.21-7.12 (m, 5H), 3.34 (br s, 3H), 3.25 (s, 3H), 3.00 (br s, 3H), 2.38 (s, 3H), 1.82 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.3, 153.1, 144.6, 140.4, 135.2, 129.1, 125.6, 121.0, 120.8, 116.3, 109.1, 75.7, 30.8, 29.2, 21.4 ppm; HRMS (ESI) Calcd for $C_{19}H_{22}N_4O_2S_2$ $[M+H]^+$; 403.1262 found: 403.1263.



1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1*H*-indol-3-yl *N,N′*-dibutylcarbamimidothioate (3g)

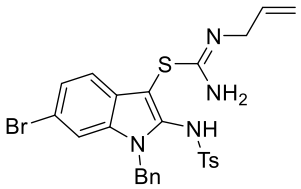
White solid; Yield: 96%; R_f = 0.24 (EtOAc/hexane = 3:1); m.p. 167-168 ºC; IR (neat): ν_{max} = 3458, 3324, 3178, 3060, 2927, 1633, 1495, 1376, 1226, 1125, 1091 cm^{-1}; ^1H NMR (400 MHz,

$CDCl_3$) δ = 8.84 (br s, 1H), 7.78 (d, *J* = 8 Hz, 2H), 7.31-7.30 (m, 1H), 7.24-7.19 (m, 3H), 7.08-7.06 (m, 1H), 6.88 (br s, 1H), 3.90-3.89 (m, 2H), 3.65 (br s, 2H), 3.35 (br s, 2H), 2.42 (s, 3H), 1.79 (br s, 2H), 1.44-1.35 (m, 4H), 1.11 (t, *J* = 7.2 Hz, 3H), 1.00 (br s, 6H), 0.69 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.3, 153.1, 144.7, 140.3, 134.7, 129.0, 128.3, 125.5, 123.4, 117.0, 113.7, 112.0, 74.9, 44.5, 43.6, 37.3, 31.7, 29.9, 21.4, 19.9, 19.4, 14.2, 13.7, 13.4 ppm; HRMS (ESI) Calcd for $C_{26}H_{35}{}^{81}BrN_4O_2S_2$ $[M+H]^+$; 581.1446, found: 581.1442.



1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N*,-methylcarbamimidothioate (3h)

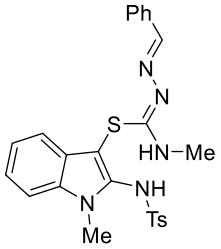
White solid; Yield: 67%; R_f = 0.21 (EtOAc/hexane = 3:1); m.p. 129-131 ºC; IR (neat): ν_{max} = 3383, 3054, 2925, 1648, 1496, 1374, 1224, 1125, 1089 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.0 (br s, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.42-7.30 (m, 1H), 7.21-7.16 (m, 5H), 5.50-5.43 (m, 1H), 4.92 (br s, 1H), 4.77-4.69 (m, 2H), 4.43 (br s, 2H), 3.19 (s, 3H), 3.03 (br s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.5, 150.0, 143.4, 140.8, 134.3, 133.1, 129.6, 129.1, 128.4, 125.8, 121.5, 121.2, 116.8, 116.1, 110.2, 78.7, 45.0, 30.2, 21.4; HRMS (ESI) Calcd for $C_{20}H_{22}N_4O_2S_2$ $[M+H]^+$ 415.1262, found. 415.1266.



1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]]-6-bromo-1*H*-indol-3-yl *N*,-allylcarbamimidothioate (3i)

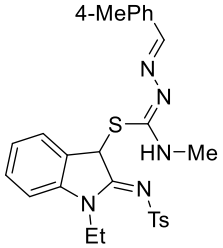
White solid; Yield: 68%; R_f = 0.21 (EtOAc/hexane = 3:1); m.p. 158-159 ºC; IR (neat): ν_{max} = 3383, 3212, 3060, 2924, 2857, 1644, 1496, 1377, 1225, 1125, 1088 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.29 (br s, 1H), 9.94 (br s, 1H), 7.62 (d, *J* = 8 Hz, 2H), 7.54 (s, 1H), 7.40-7.30 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 3H) 6.61 (d, *J* = 6.8 Hz, 2H), 6.38 (br s, 3H), 6.04-5.96 (m, 1H), 5.51-5.41 (m, 2H), 4.86 (s, 2H), 4.49 (br s, 1H), 4.13 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.2, 150.0, 143.0, 141.0, 137.2, 133.2, 130.9, 130.4, 129.1, 128.1, 127.4, 126.5,

125.7, 124.7, 119.8, 119.4, 114.9, 111.4, 46.4, 46.1, 41.0, 21.4 ppm; HRMS (ESI) Calcd for $C_{25}H_{24}{}^{81}BrN_4O_2S_2$ $[M+H]^+$; 571.0674, found 571.0614.



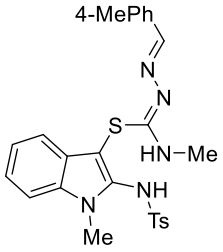
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6a)

White solid; Yield: 60%; R_f = 0.23 (EtOAc/hexane = 1:3); m.p. 130-131 ºC; IR (neat): ν_{max} = 3621, 3225, 3064, 2933, 1690, 1599, 1472, 1338, 1163, 1093, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 9.80 (br s, 1H), 7.76 (d= 8 Hz, 2H), 7.62-7.30 (m, 6H), 7.43-7.41 (m, 1H), 7.35-7.24 (m, 5H), 3.95 (s, 3H), 3.69 (s, 3H), 2.48 (s, 3H) 1.80 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.2, 153.2, 143.9, 137.1, 136.9, 134.9, 130.4, 129.5, 129.0, 128.5, 127.0, 126.7, 123.0, 121.1, 118.3, 110.6, 94.2, 32.2, 31.0, 21.7 ppm; HRMS (ESI) Calcd for $C_{25}H_{25}N_5O_2S_2$ $[M+H]^+$; 492.1483, found 492.1520.



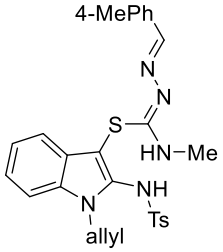
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6b)

White solid; Yield: 64%; R_f = 0.32 (EtOAc/hexane = 1:3); m.p. 149-152 ºC; IR (neat): ν_{max} = 3415, 3051, 2927, 1609, 1536, 1477, 1337, 1263, 1162, 1029, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.26 (s, 1H), 7.58-7.51 (m, 6H), 7.42-7.38(m, 1H), 7.25-7.24 (m, 6H), 4.58 (t, *J* = 4.4 Hz, 2H), 4.06 (br s, 1H), 2.77 (s, 3H), 2.46 (s, 6H), 1.55 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 151.9, 144.5, 139.6, 135.3, 134.9, 133..1, 129.7, 129.3, 128.1, 127.9, 127.3, 123.8, 121.6, 120.0, 111.1, 94.5, 39.5, 30.5, 21.8, 21.6, 14.7 ppm; HRMS (ESI) Calcd for $C_{27}H_{29}N_5O_2S_2$ $[M+H]^+$; 520.1840, found 520.1843.



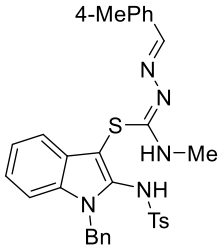
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6c)

White solid; Yield: 74%; R_f = 0.29 (EtOAc/hexane = 1:3); m.p. 142-143 ^oC; IR (neat): ν_{max} = 3415, 3224, 2924, 1538, 1403, 1338, 1257, 1163,1094, 1040, 813, 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.26 (s, 1H), 7.60-7.51 (m, 7H), 7.48-7.41(m, 2H), 7.30-7.23 (m, 6H), 5.34 (s, 1H), 4.00 (s, 3H), 2.76-2.75 (s, 3H), 2.49 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.9, 151.8, 144.6, 139.6, 136.1, 135.9, 134.7, 133.0, 129.6, 129.3, 127.9, 127.7, 127.2, 123.8, 121.9, 119.8, 110.6, 93.7, 53.5, 31.4, 30.5, 21.8, 21.6; HRMS (ESI) Calcd for $C_{26}H_{27}N_5O_2S_2$ $[M+H]^+$; 506.1684, found 506.1690.



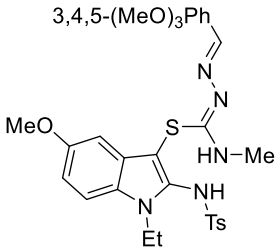
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6d)

White solid; Yield: 72%; R_f = 0.34 (EtOAc/hexane = 1:3); m.p. 139-140 ºC; IR (neat): ν_{max} 3415, 3223, 3050, 2926, 1608, 1536, 1476, 1387, 1337, 1162, 1093, 856, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.25 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.60-7.50 (m, 5H), 7.32-7.24 (m, 6H), 6.14-6.06 (m, 1H), 5.34-5.21 (m, 2H), 5.12-5.11 (m, 2H), 4.05 (br s, 1H), 2.76-2.75 (m, 3H), 2.48-2.44 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.7, 152.1, 144.6, 143.5, 139.7, 139.2, 135.5, 134.8, 133..4, 133.0, 129.7, 129.6, 129.3, 127.9, 127.3, 126.5, 123.9, 121.8, 119.9, 117.7, 111.7, 94.9, 47.3, 30.5, 21.6, 21.5; HRMS (ESI) Calcd for $C_{28}H_{29}N_5O_2S_2$ $[M+H]^+$; 532.1840, found 532.1836.



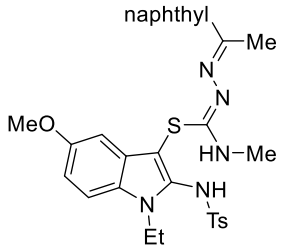
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6e)

White solid; Yield: 68%; R_f = 0.31 (EtOAc/hexane = 3:1); m.p. 142-143 ºC; IR (neat): ν_{max} 3415, 3051, 2927, 1536, 1337, 1263, 1162, 1093, 954, 814, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.30 (s, 1H), 7.65-7.60 (m, 4H), 7.37–7.27 (m, 11H), 7.15-7.14 (m, 2H), 5.75 (s, 2H), 4.0 (br s, 1H), 3.02 (br s, 1H), 2.75-2.74 (s, 3H), 2.49-2.47 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.1, 152.4, 144.8, 139.7, 136.8, 135.7, 135.5, 134.8, 133..0, 129.3, 128.8, 128.0, 127.9, 127.7, 127.4, 126.8, 124.2, 121.9, 119.9, 111.7, 95.7, 48.0, 30.5, 21.9, 21.6; HRMS (ESI) Calcd for $C_{32}H_{31}N_5O_2S_2$ $[M+H]^+$; 582.1997, found 582.1992.



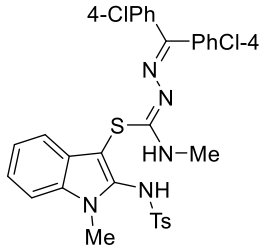
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(3,4,5-trimethoxyphenyl)methylidene]hydrazine-1-carboximidothioate (6f)

White solid; Yield: 76%; R_f = 0.32 (EtOAc/hexane = 3:1); m.p. 158-159 ºC; IR (neat): ν_{max} 3411, 3055, 2927, 1606, 1566, 1530, 1455, 1402, 1262, 1161, 1087, 733cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.22 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.38-7.36 (m, 1H), 7.20-7.18 (m, 4H), 7.01-7.00 (m, 4H), 4.46- 4.45 (m, 2H), 4.11 (br s, 1H), 3.95- 3.93 (9H), 3.84 (s,3H), 3.01 (s, 1H), 2.74 (s, 3H), 2.35 (s, 3H), 1.48 (*t*, 6.8Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.4, 155.7, 153.4, 151.6, 144.5, 139.6, 135.7, 135.1, 131.4, 129.6, 128.9, 127.6, 114.6, 112.0, 104.6, 100.7, 93.6, 61.0, 56.3, 55.9, 39.5, 30.4, 21.7, 14.8 ppm; HRMS (ESI) Calcd for $C_{30}H_{35}N_5O_6S_2$ $[M+H]^+$; 626.2107, found: 626.2110.



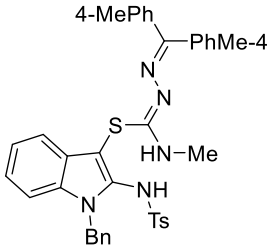
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-(1-(naphthalenyl)methylidene]hydrazine-1-carboximidothioate (6g)

White solid; Yield: 79%; R_f = 0.32 (EtOAc/hexane = 1:3); m.p. 163-164 ºC; ; IR (neat): ν_{max} 3417, 3214, 3055, 2982, 2938, 1731, 1539, 1484, 1378, 1241, 1161, 1089, 1037, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 6.8 Hz, 2H), 7.59 (d, *J* = 8 Hz, 1H), 7.48-7.40 (m, 7H), 7.23-7.20 (m, 2H), 7.04-7.00 (br s, 1H), 4.53 (q, *J* = 7.2 Hz, 2H), 4.02-4.01 (m, 1H), 3.84 (s, 3H), 3.00 (s, 1H), 2.80-2.78 (m, 3H), 2.48-2.41 (m, 6H), 1.53 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.4, 156.4, 155.6, 144.5 139.5, 135.0, 134.7, 129.6, 128.8, 128.7, 128.2, 127.9, 126.2, 114.6, 112.1, 100.7, 94.1, 55.9, 39.5, 30.5, 21.8, 14.8, 14.0 ppm. HRMS (ESI) Calcd for $C_{32}H_{33}N_5O_3S_2$ $[M+H]^+$; 601.2103, found 601.2098.



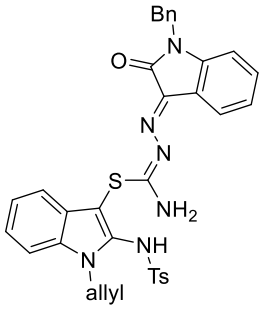
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl-*N*-methyl-2-[(di-*p*-chlorophenyl)methylidene]hydrazine-1-carboximidothioate (6h)

White solid; Yield: 57%; R_f = 0.29 (EtOAc/hexane = 1:3); m.p. 161-162 ºC; IR (neat): ν_{max} 3417, 3214, 3055, 2982, 2938, 1731, 1539, 1484, 1378, 1241, 1161, 1089, 1037, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.61 -7.56 (m, 6H), 7.49-7.47 (m, 2H), 7.40 (m, 7H), 7.30-7.22 (m, 6H), 7.00 (br s, 1H), 4.05-4.00 (m, 4H), 3.70 (br s, 1H), 3.04 (br s, 1H), 2.54-2.40 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2, 151.6, 144.6, 141.3, 136.7, 135.4, 135.2, 129.7, 127.7, 127.2, 124.6, 124.4, 123.5, 121.4, 119.2, 118.8, 110.6, 110.1, 91.5, 34.0, 31.0, 21.6,; HRMS (ESI) Calcd for $C_{31}H_{27}Cl_2N_5O_2S_2$ $[M+H]^+$; 636.1061, found 636.1060.



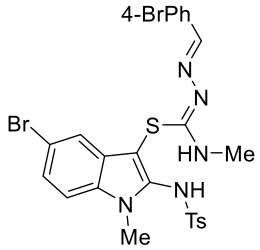
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl-*N*-phenyl-2-[(di-*p*-tolyl)methylidene]hydrazine-1-carboximidothioate (6i)

White solid; Yield: 46%; R_f = 0.31 (EtOAc/hexane = 1:3); m.p. 159-160 ºC; IR (neat): ν_{max} 3417, 3214, 3055, 2982, 2938, 1731, 1539, 1484, 1378, 1241, 1161, 1089, 1037, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.65 -7.63 (m, 6H), 7.44- 7.22 (m, 14H), 7.12 (m, 4H), 6.99-6.82 (m, 4H), 5.83 (s, 2H), 2.51- 2.48 (m, 6H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.1, 154.4, 145.0, 139.6, 138.0, 136.9, 136.0, 129.8, 129.6, 128.9, 128.8, 128.9, 127.9, 127.8, 126.7, 124.4, 122.2, 119.9, 118.2, 111.7, 95.4, 48.0, 25.3, 21.7, 21.5; HRMS (ESI) Calcd for $C_{44}H_{39}N_5O_2S_2$ $[M+H]^+$; 734.2623, found 734.2624.



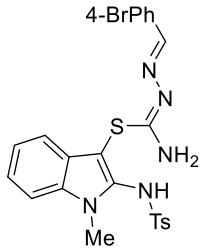
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-2[(1-benzyl-2-oxoindolin-3-ylidene)]hydrazine-1-carboximidothioate (6j)

Orange solid; Yield: 44%; R_f = 034 (EtOAc/hexane = 3:1); m.p. 133-134 ºC; IR (neat): ν_{max} 3265, 3131, 2924, 2855, 1696, 1608, 1535, 1467, 1358, 1262, 1138, 1086, 358 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.98 -7.92 (m, 3H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.41-7.33 (m, 7H), 7.30-7.22 (m, 5H), 7.19-7.15 (br s, 1H), 7.18 (s, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.06-5.99 (m, 1H), 5.26-5.20 (m, 2H), 5.08-5.06 (m, 4H), 2.43 (s, 3H), 1.88 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.4, 154.6, 142.9, 141.3, 136.4, 134.6, 134.6, 133.0, 132.1, 129.2, 129.1, 128.2, 127.4, 125.9, 123.7, 123.0, 122.8, 121.4, 119.1, 117.4, 117.3, 111.2, 110. 5, 47.6, 43.8, 21.4; HRMS (ESI) Calcd for $C_{34}H_{30}N_6O_3S_2$ $[M+H]^+$; 636.1932, found 636.1060.



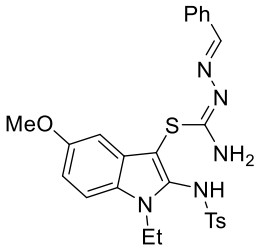
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-bromolphenyl)methylidene]hydrazine-1-carboximidothioate (6k)

White solid; Yield: 80%; yield. R_f = 0.31 (EtOAc/hexane = 3:1); m.p. 162-164 ºC; IR (neat): ν_{max} 3415, 3224, 2924, 1538, 1403, 1338, 1257, 1163,1094, 1040, 813, 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.24 (s, 1H), 7.72 (d, *J* = 1.2Hz, 1H), 7.60–7.58 (m, 5H), 7.49-7.47 (m, 1H), 7.41-7.38 (m, 1H), 7.30-7.25 (m, 3H), 4.54 (q, *J* = 7.2Hz, 1H), 4.00 (br s, 1H), 2.77 (d, *J* = 4.4 Hz, 3H), 2.48 (s, 3H), 1.53 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.9, 152.0, 144.6, 139.6, 135.3, 134.9, 133.1, 129.7, 129.2, 128.1, 127.9, 127.3, 123.8, 121.6, 120.0, 111.1, 39.5, 30.5, 21.6, 14.7; HRMS (ESI) Calcd for $C_{26}H_{25}{}^{81}BrN_5O_2S_2$ $[M+H]^+$; 663.9874, found 663.9871.



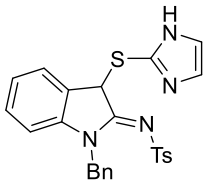
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-2[(4-bromophenyl)methylidene]hydrazine-1-carboximidothioate (6l)

White solid; Yield: 74%; R_f = 0.31 (EtOAc/hexane = 1:4); m.p. 160-161 ºC; IR (neat): ν_{max} 3224, 3053, 2942, 2805, 1534, 1487, 1385, 1335, 1234, 1159, 1092, 738cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.16 (s, 1H), 7.59-7.57 (m, 5H), 7.48-7.44 (m, 1H), 7.38-7.16 (m, 8H), 6.92 (s, 1H), 4.02 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2, 151.6, 144.6, 141.3, 135.7, 135.4, 135.2, 129.7, 127.6, 127.2, 124.6, 124.4, 123.5, 121.4, 119.2, 118.8, 110.6, 110.1, 91.5, 31.0, 21.6; HRMS (ESI) Calcd for $C_{24}H_{22}{}^{81}BrN_5O_2S_2$ $[M+H]^+$; 558.0456, found 558.0490.



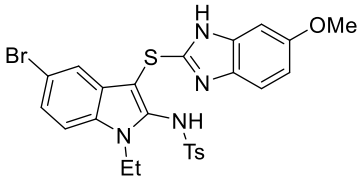
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl(2*E*)-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6m)

White solid; Yield: 76%; R_f = 0.39 (EtOAc/hexane = 3:1); m.p. 133-134 ºC; IR (neat): ν_{max} 3411, 3055, 2927, 1606, 1566, 1530, 1455, 1402, 1262, 1161, 1087, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.96-7.93 (m, 3H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.48—7.46 (m, 4H), 7.14 (d, *J* = 8Hz, 3H), 7.90-6.52 (m, 3H), 6.52 (s, 1H), 3.77 (s, 3H), 3.10 (q, *J* = 7.2 Hz, 2H) 2.40 (s, 3H), 1.30 (*t*, 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.0, 153.6, 143.3, 142.7, 138.1, 136.9, 133.2, 130.4, 129.1, 128.9, 128.4, 127.6, 126.1, 120.4, 119.6, 117.1, 115.3, 97.07, 55.5, 40.4, 30.4, 21.5, 14.9 ppm; HRMS (ESI) Calcd for $C_{26}H_{27}N_5O_3S_2$ $[M+H]^+$; 523.1588, found 523.1583.



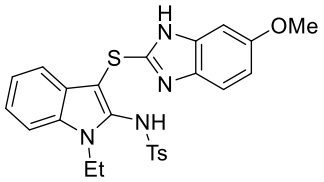
N-{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8a)

White solid; Yield: 87%; R_f = 0.32 (EtOAc/hexane = 1:4); m.p. 162-163 ºC; IR (neat): ν_{max} 3354, 3066, 2928, 1735, 1610, 1496, 1332, 1240, 1159, 1017 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.71-7.64 (m, 3H), 7.30-7.22 (m, 5H), 7.21-7.12 (m, 3H), 7.05-7.03 (m, 2H), 6.90 (s, 2H) 5.64 (s, 2H), 5.32 (s, 1H), 4.95 (br s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.7, 144.9, 142.1, 141.0, 139.9, 139.3, 134.3, 133.3, 132.4, 132.0, 131.4, 128.0, 125.7, 124.4, 115.8, 103.6, 51.9, 26.4 ppm; HRMS (ESI) Calcd for $C_{25}H_{22}N_4O_2S_2$ $[M+H]^+$; 475.1264, found 475.1259.



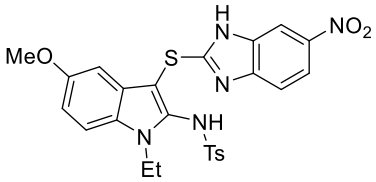
N-{1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-bromo-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8b)

White solid; Yield: 88%; R_f = 0.31 (EtOAc/hexane = 1:4); m.p. 166-167 ºC; IR (neat): ν_{max} 3063, 2930, 1601, 1443, 1391, 1334, 1158, 1119 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.45-7.42 (m, 1H), 7.31-7.30 (m, 3H), 7.21 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.16-7.14 (m, 2H), 6.87 (s, 1H), 6.79 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 2.33 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.3, 150.2, 144.2, 136.5, 135.9, 134.5, 129.5, 127.7, 127.6, 127.5, 123.4, 121.4, 119.2, 114.8, 111.9, 110.9, 97.0, 93.8 55.8, 39.1, 21.4, 14.7 ppm; HRMS (ESI) Calcd for $C_{25}H_{23}{}^{81}BrN_4O_3S_2$ $[M+H]^+$; 573.0452, found 573.0456.



N-{1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8c)

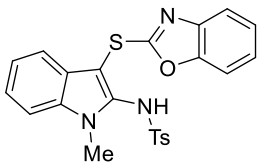
White solid; Yield: 81%; R_f = 0.31 (EtOAc/hexane = 1:4); m.p. 153-154 ºC; IR (neat): ν_{max} 3608, 3055, 2933, 2841, 1624, 1528, 1453, 1394, 1337, 1203, 1157, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8 Hz, 2H), 7.49-7.42 (m, 2H), 7.35-7.30 (m, 2H), 7.25-7.22 (m, 1H), 7.49-7.08 (m, 6H), 6.77-6.76 (m, 2H) 4.51 (q, *J* = 7.8 Hz, 2H), 3.78 (s, 3H), 2.22 (s, 3H), 1.49 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.3, 150.2, 144.2, 136.5, 135.9, 134.5, 129.5, 127.8, 127.6, 127.5, 123.4, 121.4, 119.2, 114.8, 111.9, 110.9, 97.0, 93.7, 55.8, 39.1, 21.4, 14.7 ppm; HRMS (ESI) Calcd for $C_{25}H_{24}N_4O_3S_2$ $[M+H]^+$; 493.1368, found: 493.1364.



N-{1-Ethyl-3-[(5-nitro-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-methoxy-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8d)

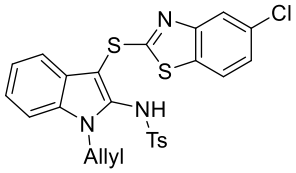
White solid; Yield: 77% R_f = 0.23 (EtOAc/hexane = 1:4); m.p. 179-181 ºC; IR (neat): ν_{max} 3592, 3231, 2927, 2850, 1521, 1482, 1416, 1334, 1218, 1162, 813 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.31 (s, 1H), 8.09 (dd, J_1 = 8.8 Hz, J_2 = 2 Hz, 2H), 7.64 (d, *J* = 8Hz, 2H), 7.42 (s, 1H), 7.38-7.35 (m, 1H), 7.30 (s, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.99-6.97 (m, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 2.28 (s, 3H), 2.03 (br s, 1H), 1.50 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ = 155.4, 144.1, 136.2, 135.2, 129.4, 129.4, 128.4, 127.4, 117.9, 114.0, 111.8 100.5, 55.8, 39.1, 21.4, 14.8 ppm; HRMS (ESI) Calcd for $C_{25}H_{23}N_5O_5S_2$ $[M+H]^+$; 538.1218, found 538.1218.



N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8e)

Red solid; Yield: 94%; R_f = 0.33 (EtOAc/hexane = 1:4); m.p. 148-149 ºC; IR (neat): ν_{max} 3224, 3053, 2942, 2805, 1534, 1487, 1385, 1335, 1234, 1159, 1092, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.16 (s, 1H), 7.59-7.55 (m, 4H), 7.47-7.45 (m, 1H), 7.39-7.35 (m, 2H), 7.31-7.22 (m, 3H), 7.18-7.16 (m, 2H), 4.02 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2, 151.6, 144.6, 141.3, 135.7, 135.4, 135.2, 129.7, 127.7, 127.2, 124.6, 124.4, 123.5, 121.4, 119.2, 118.7, 110.6, 110.1, 91.5, 31.0, 21.6; HRMS (ESI) Calcd for $C_{23}H_{19}N_3O_3S_2$ $[M+H]^+$; 450.0946, found 450.0942.



N-{1-Allyl-3-[(5-chloro-1H-benzo[d]thiazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8f)

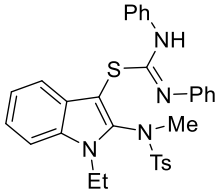
White solid; Yield: 89%; R_f = 0.34 (EtOAc/hexane = 1:4); m.p. 161-163 ºC; IR (neat): ν_{max} 3063, 2927, 2848, 1592, 1530, 1418, 1332, 1160, 1079, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.19 (s, 1H), 7.71. 7.66 (m, 3H), 7.54 (dd, J_1 = 20.4 Hz, J_2 = 8 Hz, 2H), 7.40-7.36 (m, 1H), 7.30-7.22 (m, 5H), 7.14 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 6.15-6.06 (m, 1H), 5.33 (d, J = 10.4 Hz, 1H), 5.18-5.11 (m, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.6, 154.6, 144.9, 135.5, 135.3, 135.0, 133.2, 132.9, 132.1, 129.8, 127.9, 126.8, 124.9, 124.4, 124.0, 122.1, 121.9, 121.4, 121.1, 119.5, 117.4, 111.7, 95.8, 46.9, 21.7 ppm; HRMS (ESI) Calcd for $C_{25}H_{20}ClN_3O_2S_3$ $[M+H]^+$; 528.0454, found 528.1229.

6. General procedure for the alkylation and acylation of carbimimidothioates 14a-c

To an oven-dried RB flask, a solution containing equimolar amount of the appropriate carbamimidothioate **3**/**8** and alkyl halide was stirred in DCM for 5 min to obtain a homogeneous

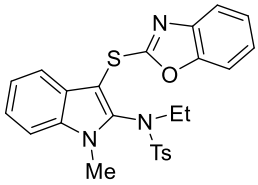
mixture, then a drop of DBU was added and allowed to stir at room temperature until the disappearance of the starting material (monitored using TLC). Similar procedure was followed for acylation in the presence of NaOH instead of DBU. After the completion of reaction, the solvent was removed under reduced pressure and diluted with ethyl acetate (10 mL) and water (15 mL). The organic phase was separated and the aqueous layer washed with ethyl acetate (10 mL). Concentration of combined organic layers under reduced pressure afforded the crude product, which was purified by column chromatography using silica gel (100-200 mesh, EtOAc/hexane 30:70) to furnish the corresponding carbamimidothioates **14a-c**.

7. Spectral data for products 14a-c



1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)methylamino]-1*H*-indol-3-yl *N,N'*-diphenylcarbamimidothioate (14a)

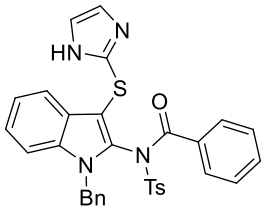
White solid; Yield: 58%; R_f = 0.71 (EtOAc/hexane = 1:3); m.p. 154-155 ºC; IR (neat): ν_{max} 3063, 2930, 1601, 1443, 1391, 1334, 1158, 1119 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.62-7.55 (m, 3H), 7.50-7.42 (m, 3H), 7.31-7.30 (m, 4H), 7.22-7.20 (m, 2H), 7.14-7.10 (m, 5H), 6.91 (s, 1H), 6.80 (s, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 2.33 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.0, 151.7, 144.4, 142.0, 137.5, 135.6, 135.2, 129.8, 127.8, 127.7, 124.4, 124.0, 123.9, 121.5, 119.7, 118.9, 110.7, 92.8, 47.4, 30.5, 21.7, 14.5 ppm; HRMS (ESI) Calcd for $C_{31}H_{30}N_4O_2S_2$ $[M+H]^+$; 555.1888 found, 555.1886.



N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-N-ethyl-4-methylbenzenesulfonamide (14b)

White solid; Yield: 64%; R_f = 0.77 (EtOAc/hexane = 1:3); m.p. 119-120 ºC; IR (neat): ν_{max} = 2978, 2937, 1980, 1775, 1619, 1570, 1494, 1364, 1247, 1130, 1123, 852, 634 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ =7.58 (d, *J* = 7.2 Hz, 1H), 7.51-7.45 (m, 3H), 7.40-7.35 (m, 1H), 7.30-7.27 (m, 1H), 7.22-7.15 (m, 6H), 4.16-4.07 (m, 1H), 3.92 (s, 3H), 3.69-3.60 (m, 1H), 2.38 (s, 3H),

1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.0, 151.7, 144.4, 142.0, 137.5, 135.6, 135.2, 129.8, 127.8, 127.7, 124.4, 124.0, 123.9, 121.5, 119.7, 118.9, 110.7, 92.8, 47.4, 30.5, 21.7, 14.5 ppm; HRMS (ESI) Calcd for $C_{25}H_{23}N_3O_3S_2$ $[M+H]^+$; 478.1259 found, 478.1259.



N-{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-N-benzenecarbonyl-4-methylbenzenesulfonamide (14c)

White solid; Yield: 70%; R_f = 0.38 (EtOAc/hexane = 1:3); m.p. 159-161 ºC; IR (neat): ν_{max} = 3249, 3204, 2975, 2927, 1788, 1619, 1570, 1494, 1365, 1217, 1120, 1093 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.98-7.90 (m, 2H), 7.88-7.86 (m, 2H), 7.63 (s, 1H), 7.54-7.46 (m, 6H), 7.33-7.24 (m, 6H), 7.09-7.07 (m, 1H), 6.86-6.78 (m, 2H), 4.34 (s, 2H), 4.20 (br s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.2, 154.6, 145.0, 135.4, 135.3, 135.0, 133.3, 133.1, 132.1, 129.8, 127.9, 126.9, 124.5, 124.0, 122.1, 121.9, 121.4, 121.2, 119.5, 117.4, 111.7, 95.8, 47.1, 21.6, 14.7 ppm; HRMS (ESI) Calcd for $C_{32}H_{26}N_4O_3S_2$ $[M+H]^+$; 579.1524 found, 579.1523.

4. Crystal data for product 6c

Crystal Data for 6c: (CCDC 2180196) $C_{26}H_{27}N_5O_2S_2$, M = 505.65, 0.212 x 0.143 x 0.115 mm, Triclinic, space group P -1 with a = 11.3439(9) Å, b = 11.8482(9) Å, c = 12.3204(9) Å, α = 97.380(3), β = 112.378(2), γ = 103.183(3), V = 1447.62(19) Å^3, T = 302.(2) K, R_1 = 0.0385, wR_2 = 0.1064 on observed data, z = 2, D_{calcd} = 1.236 mg cm^{-3}, $F(000)$ = 566, Absorption coefficient = 1.955 mm^{-1}, λ = 0.71073 Å, 7266 reflections were collected on a smart apex CCD single crystal diffractometer 9932 observed reflections ($I > 2\backslash s(I)$). The largest difference peak and hole = 1.914 and -0.485 eÅ^{-3}, respectively. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL–2014 software.

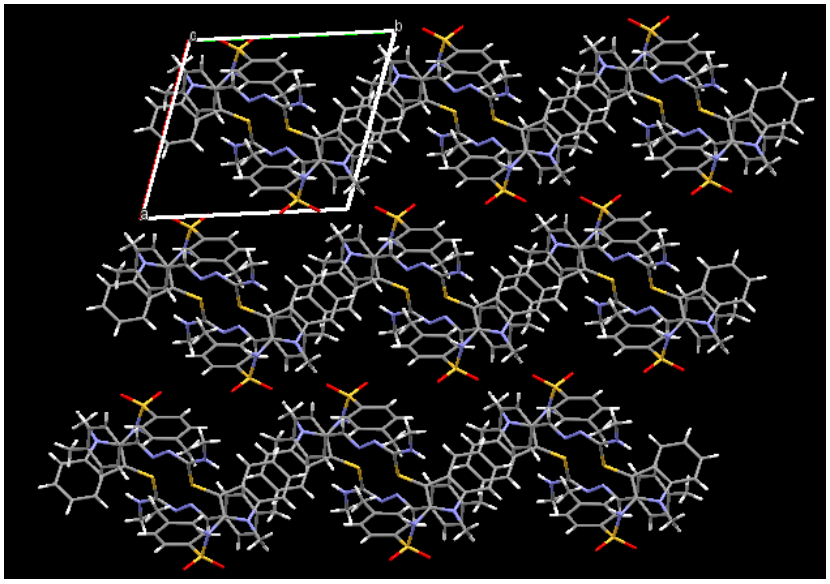


Figure 1. Partial crystal packing view of compound **6c** through *b*-axis

There is a C–H···π interaction that is described as given below:

C(20)-H(20)---Cg(1); H(20)---Cg(1) = 2.875 Å and < C(20)-H(20)---Cg(1); H(20)---Cg(1) = 155.65°

The molecules are arranged in three-dimensional network with the presence of a C–H···π interaction. The C–H···π interaction is shown below Figure 2

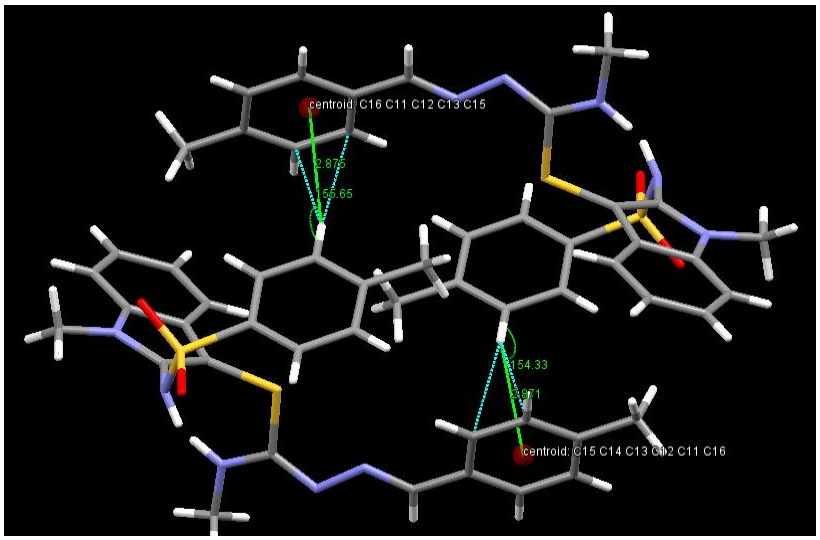
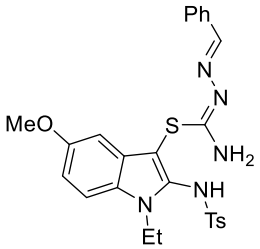


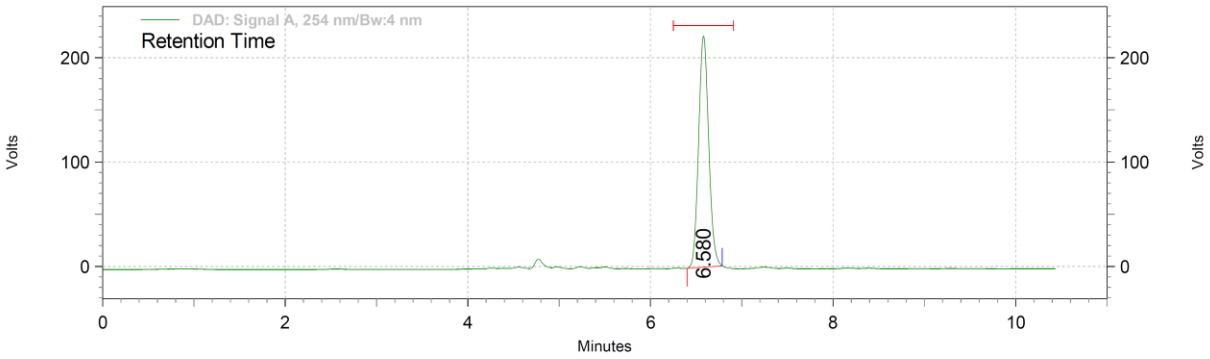
Figure 2. A partial packing view of **6c** showing C-H-π interactions in solid state arrangement

5. HPLC chromatogram for product 6m



Area % Report

Data File: D:\Ezchrom\hplc data\RFM-242_100ACN_0.6ML2019_abs_100ACN.met.rslt\369.dat
Method: D:\Ezchrom\Method\2019_abs_100ACN.met
Acquired: 08-Dec-21 1:51:22 PM (GMT +05:30)
Printed: 25-May-22 3:57:11 PM (GMT +05:30)



DAD: Signal A, 254 nm/Bw:4 nm
Results

Retention Time	Area	Area %	Height	Height %	**Name**
6.580	3562869	100.00	465039	100.00	**RFM-242**

Totals	3562869	100.00	465039	100.00	

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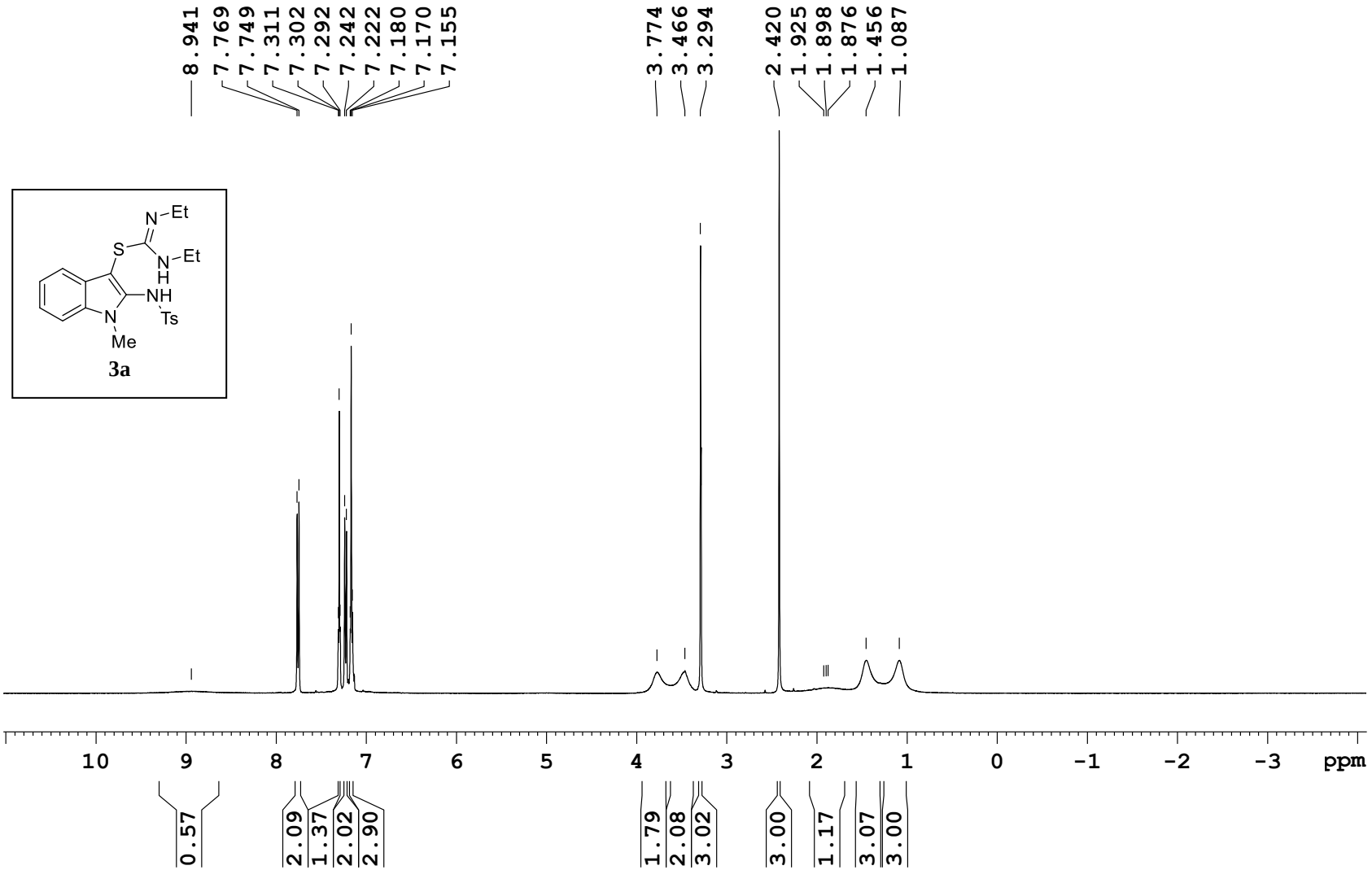
$BF_3 \cdot OEt_2$ Catalyzed S-H insertion reactions of α-diazo imidamides and enolizable thioamides under metal-free conditions

Supporting Information

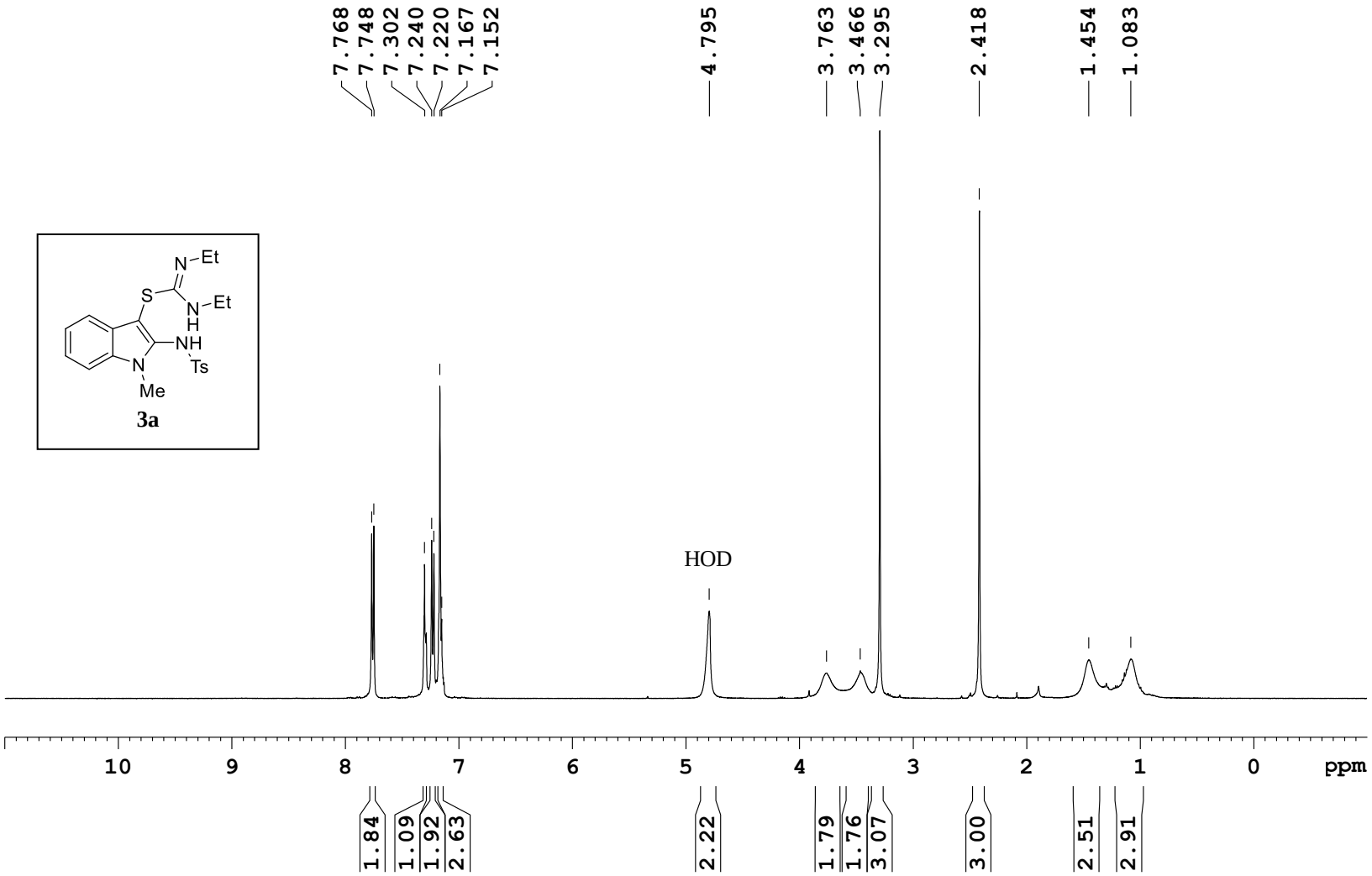
Copies of ^1H and ^{13}C NMR spectra

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N*,*N*'-diethylcarbamimidothioate (3a)



^{1}H NMR Spectrum of **3a**

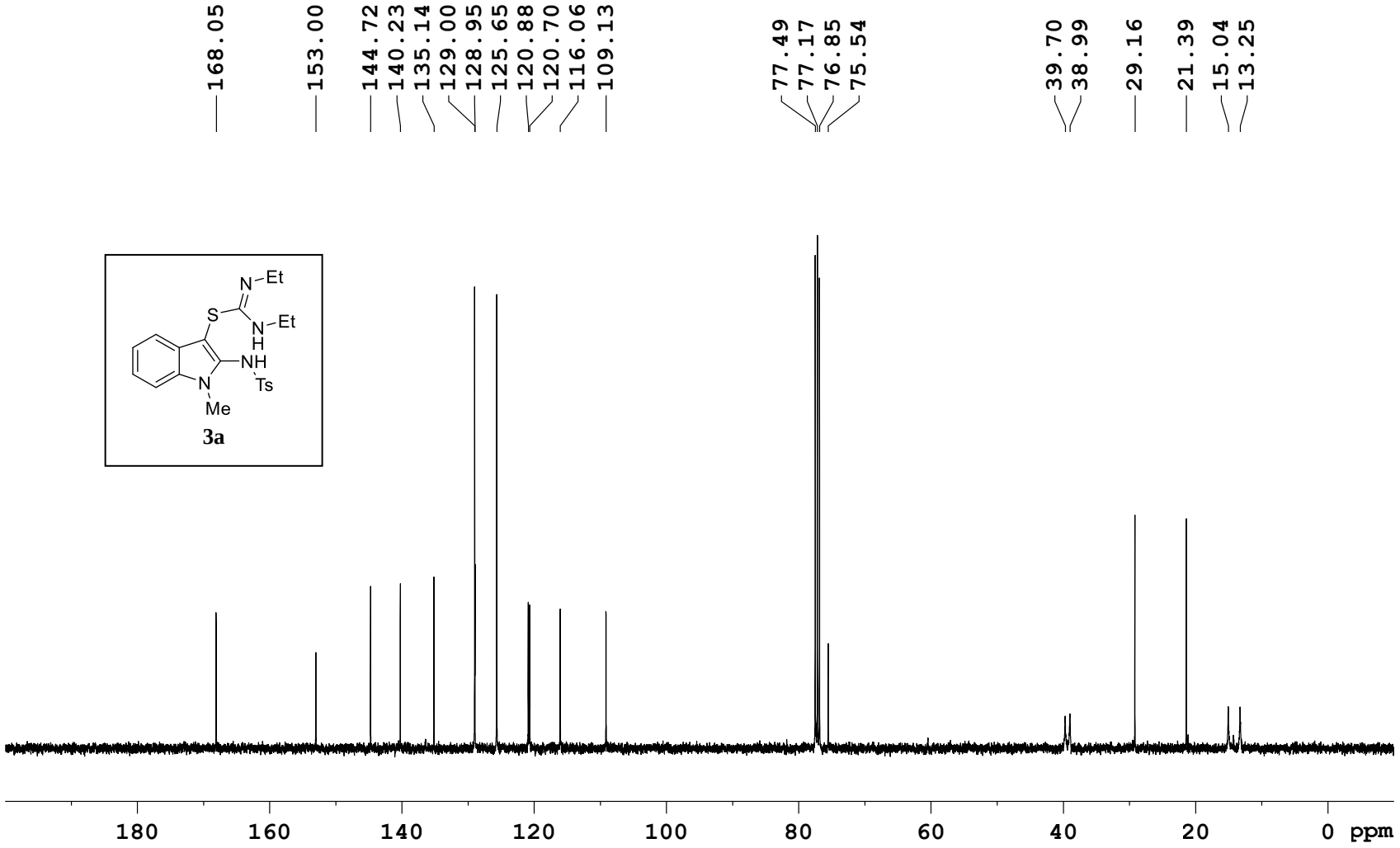
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N*,*N*'-diethylcarbamimidothioate (3a)



3a

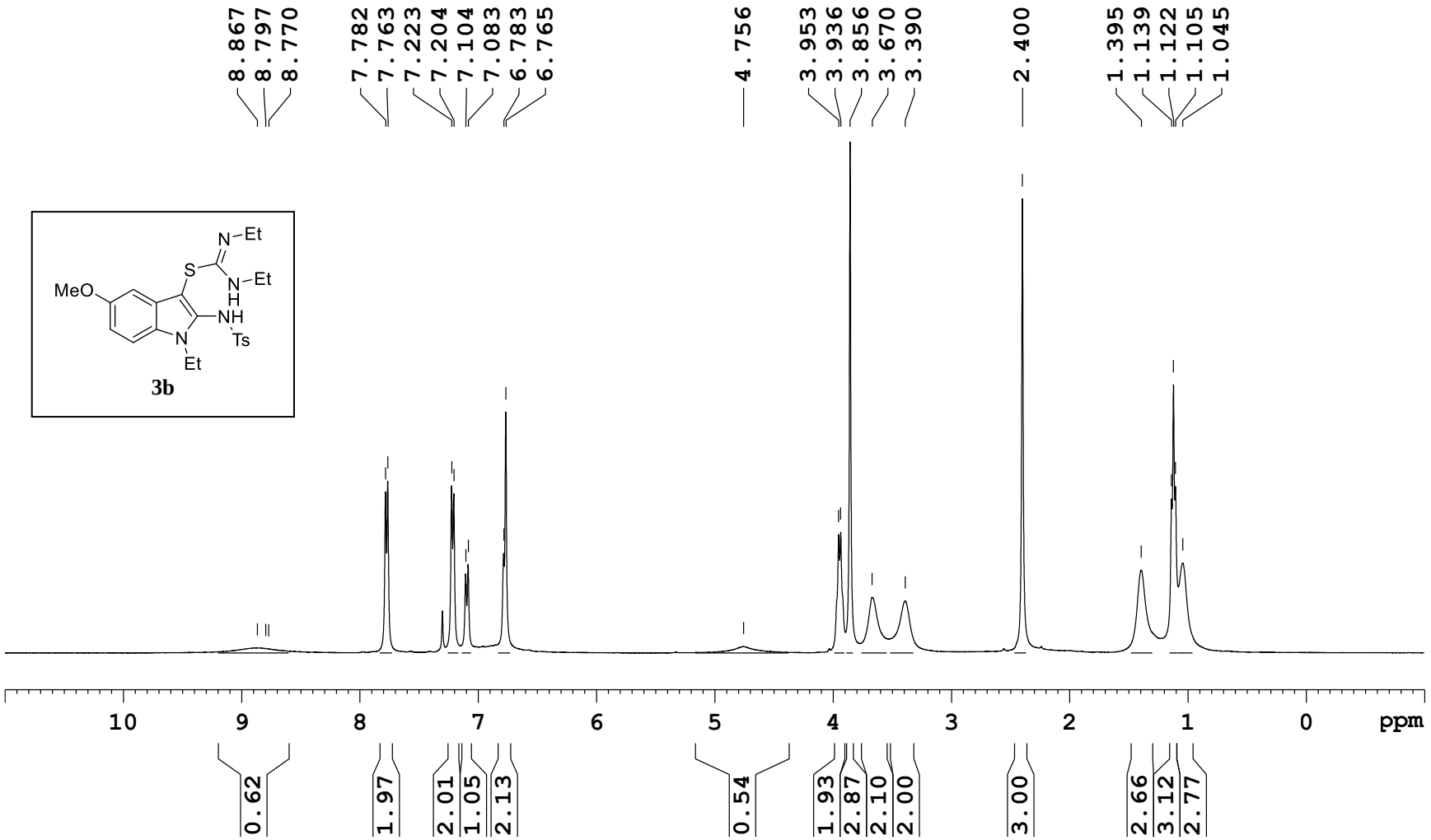
NMR Spectrum of **3a** after D_2O exchange experiment ($CDCl_3$, 400 MHz)

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N*,*N*'-diethylcarbamimidothioate (3a)



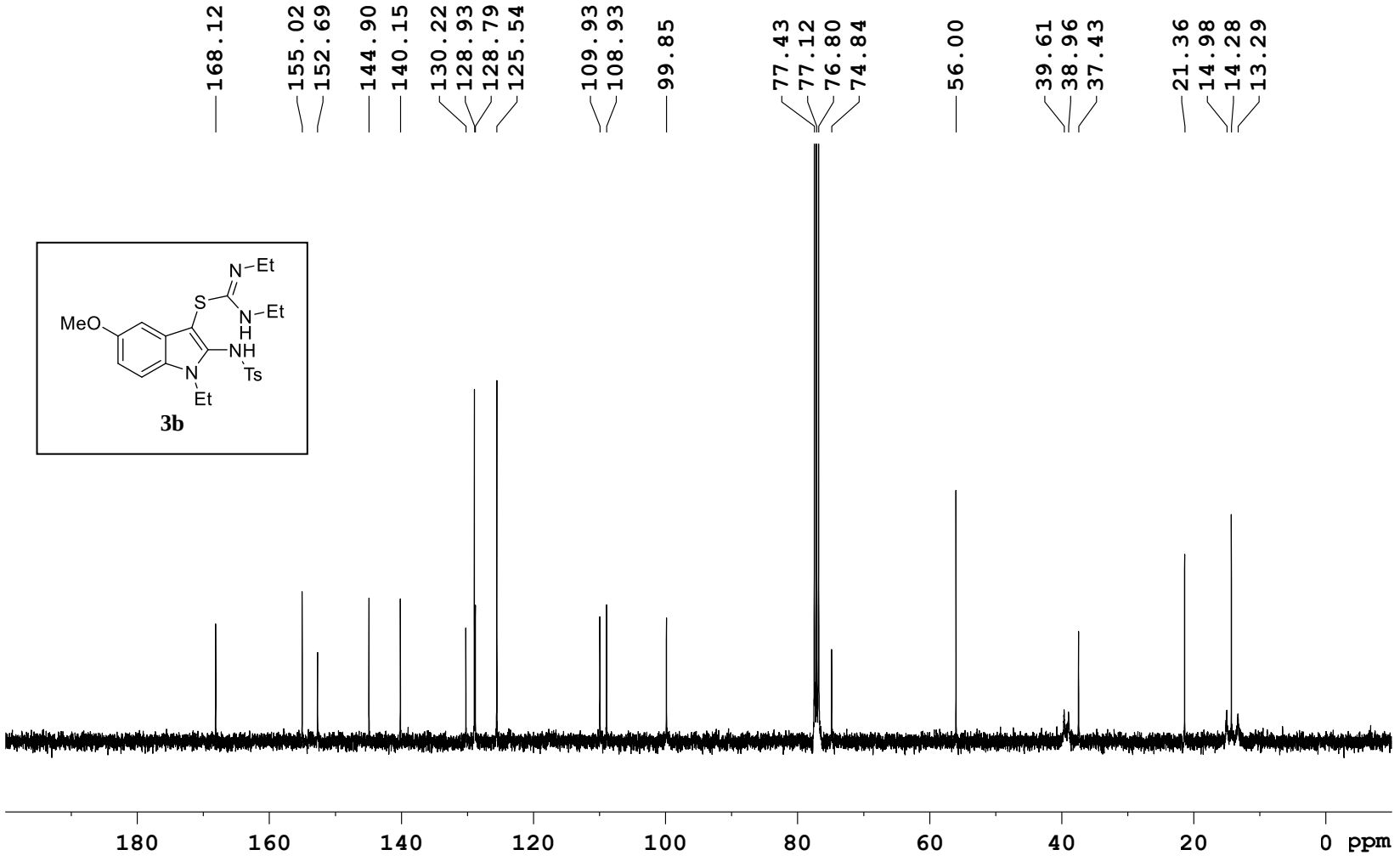
^{13}C NMR spectrum of **3a**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl *N,N'*-diethylcarbamimidothioate (3b)



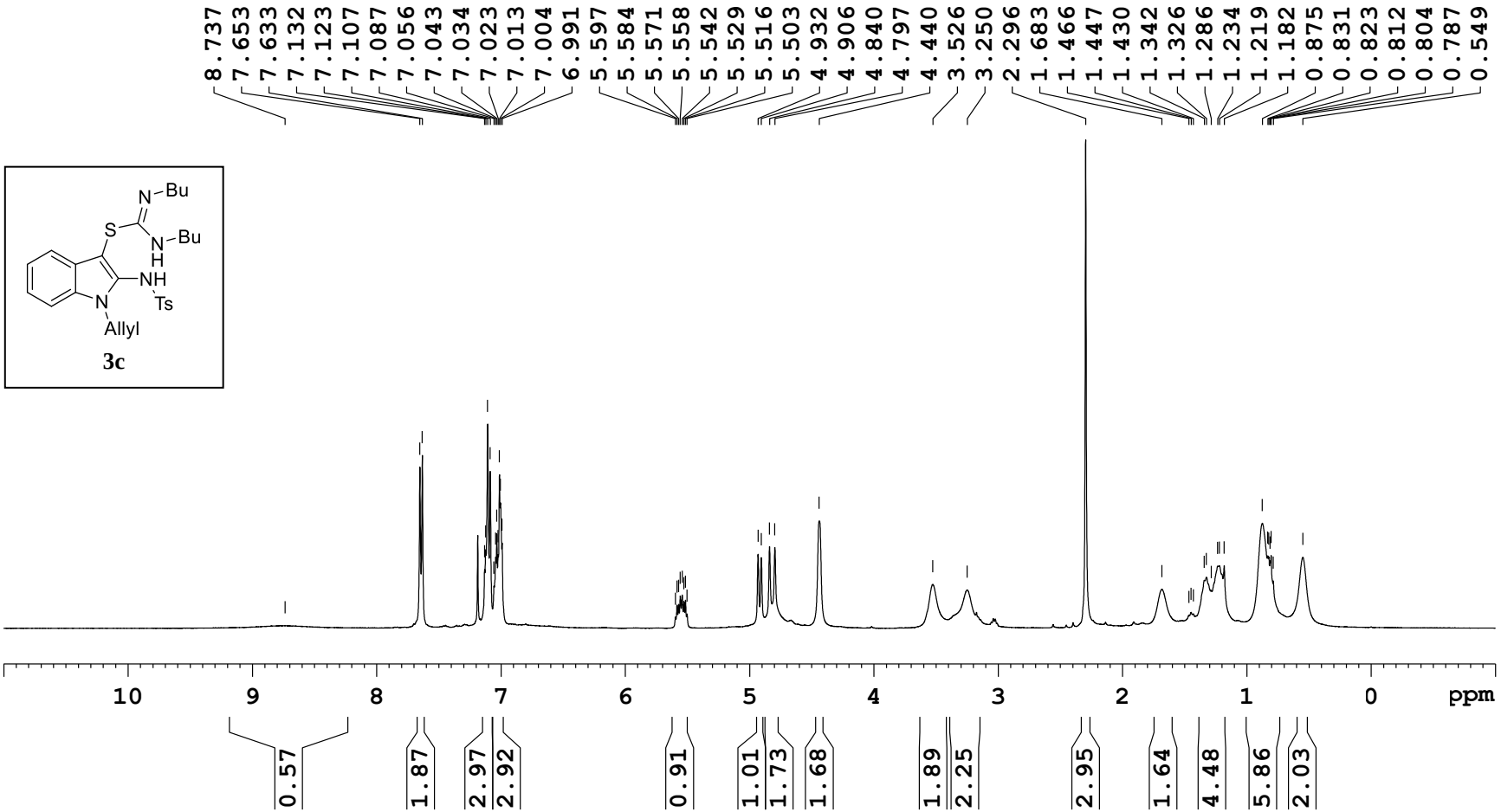
^{1}H NMR Spectrum of **3b**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl *N,N'*-diethylcarbamimidothioate (3b)



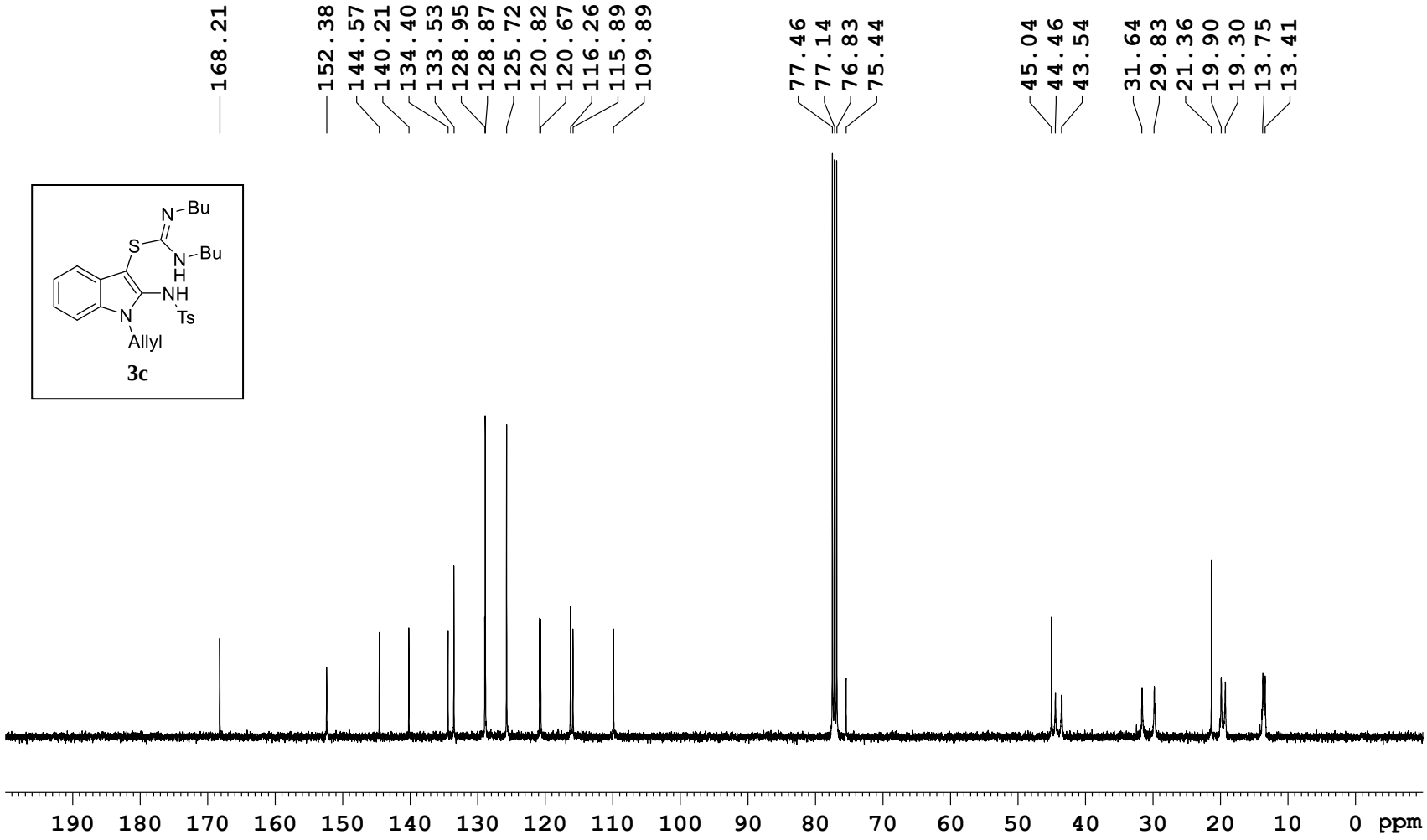
^{13}C NMR Spectrum of **3b**

1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-dibutylcarbamimidothioate (3c)



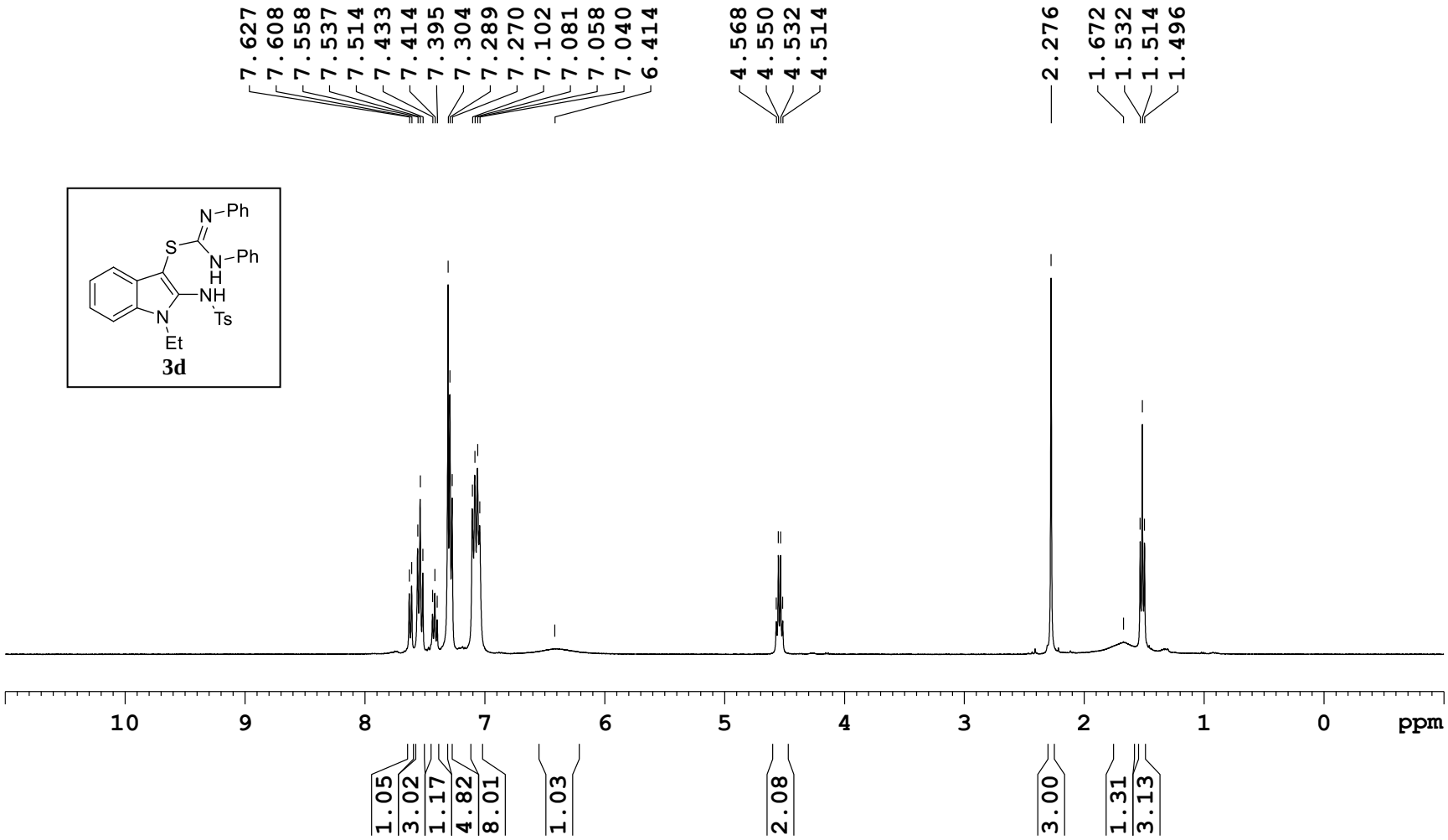
^{1}H NMR Spectrum of **3c**

1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-dibutylcarbamimidothioate (3c)



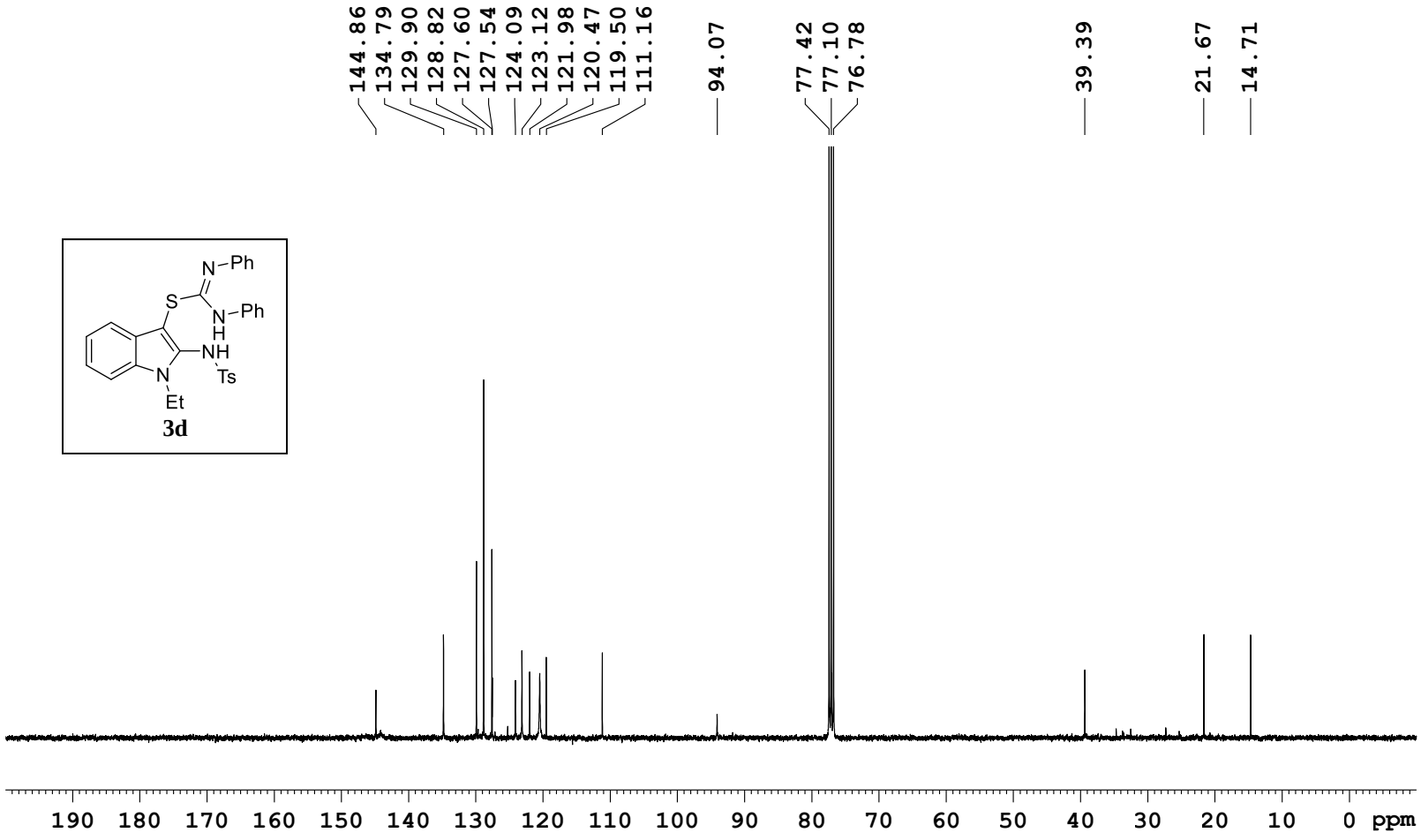
^{13}C NMR Spectrum of **3c**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-diphenylcarbamimidothioate (3d)



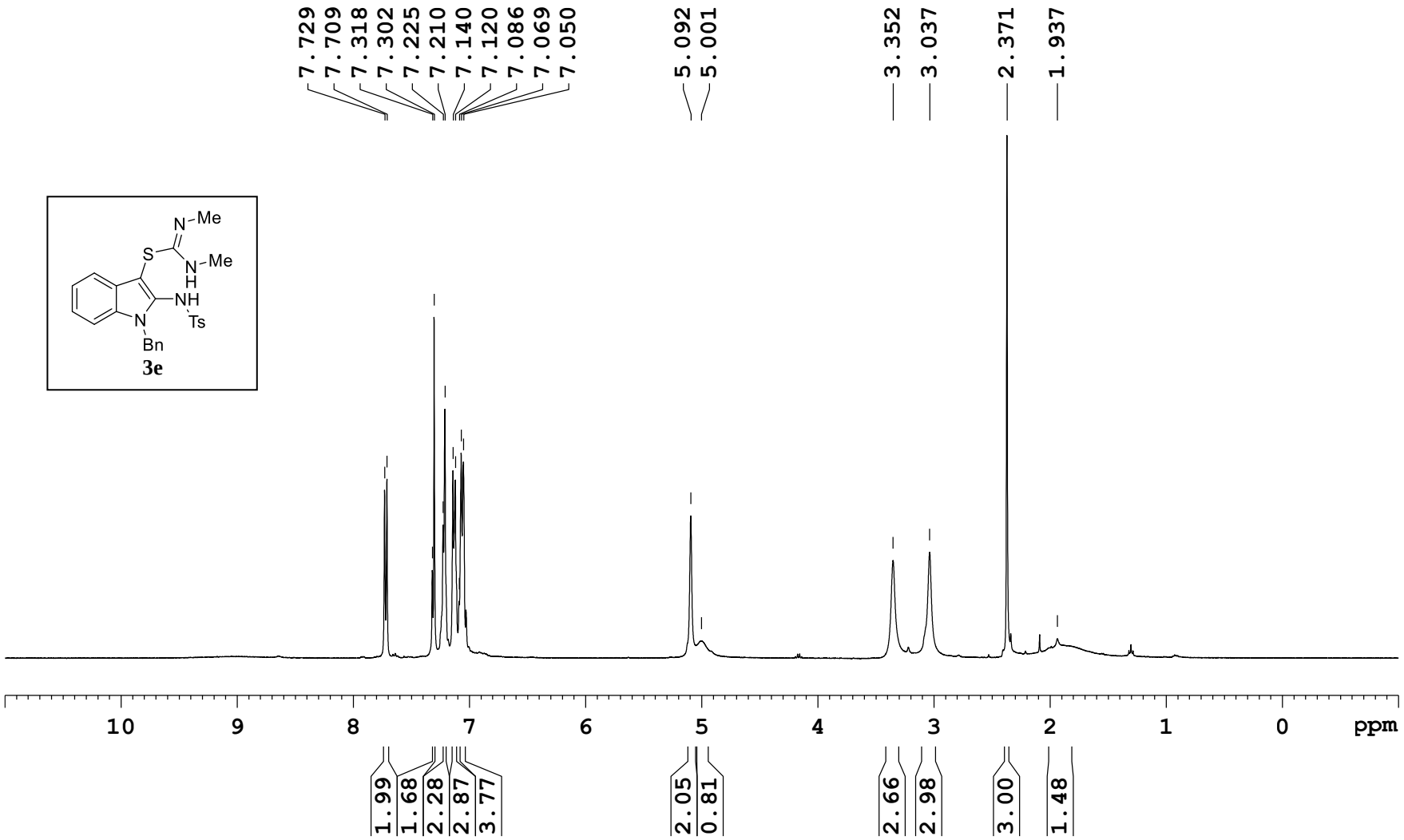
[1]H NMR Spectrum of **3d**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-diphenylcarbamimidothioate (3d)



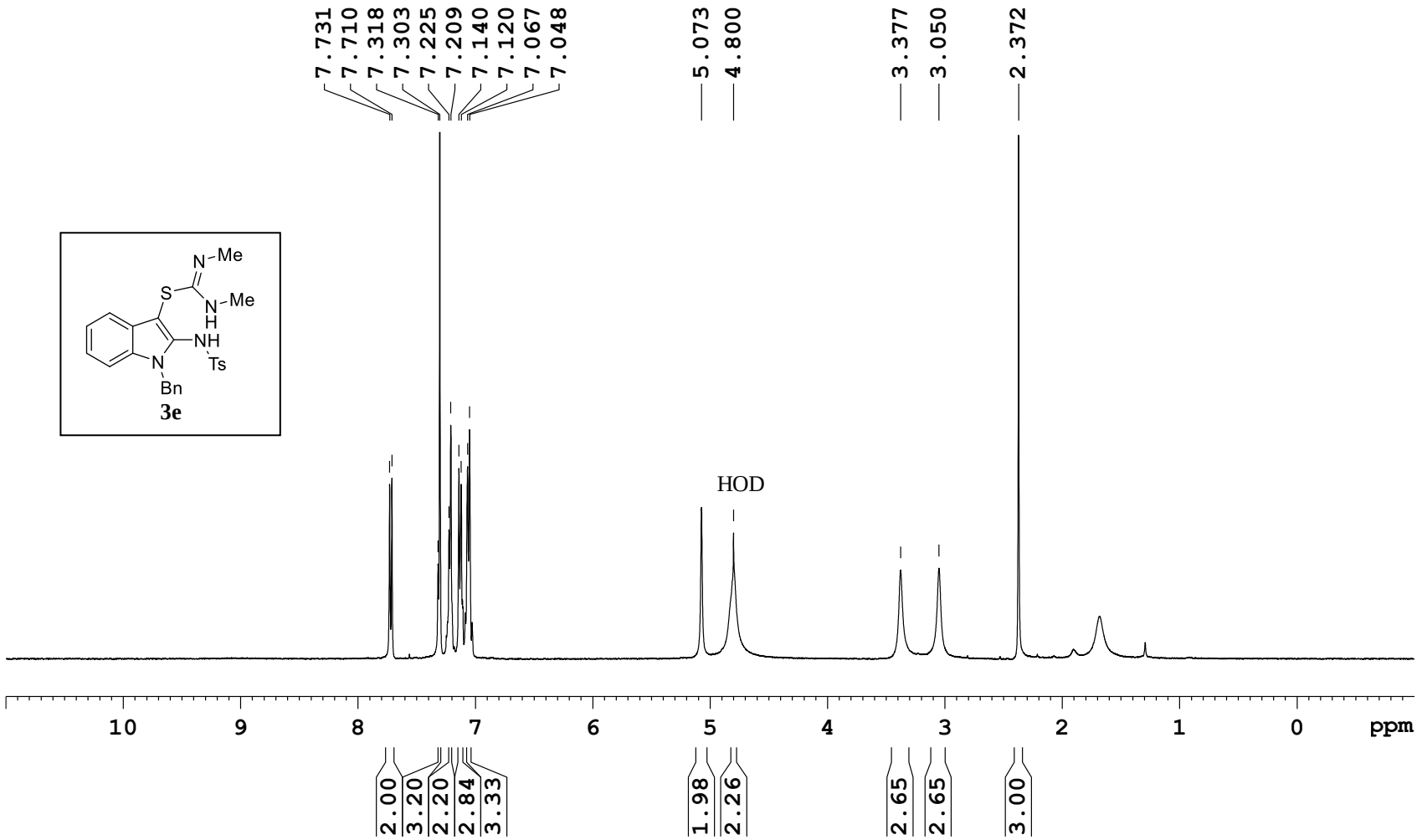
^{13}C NMR Spectrum of **3d**

1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-dimethylcarbamimidothioate (3e)



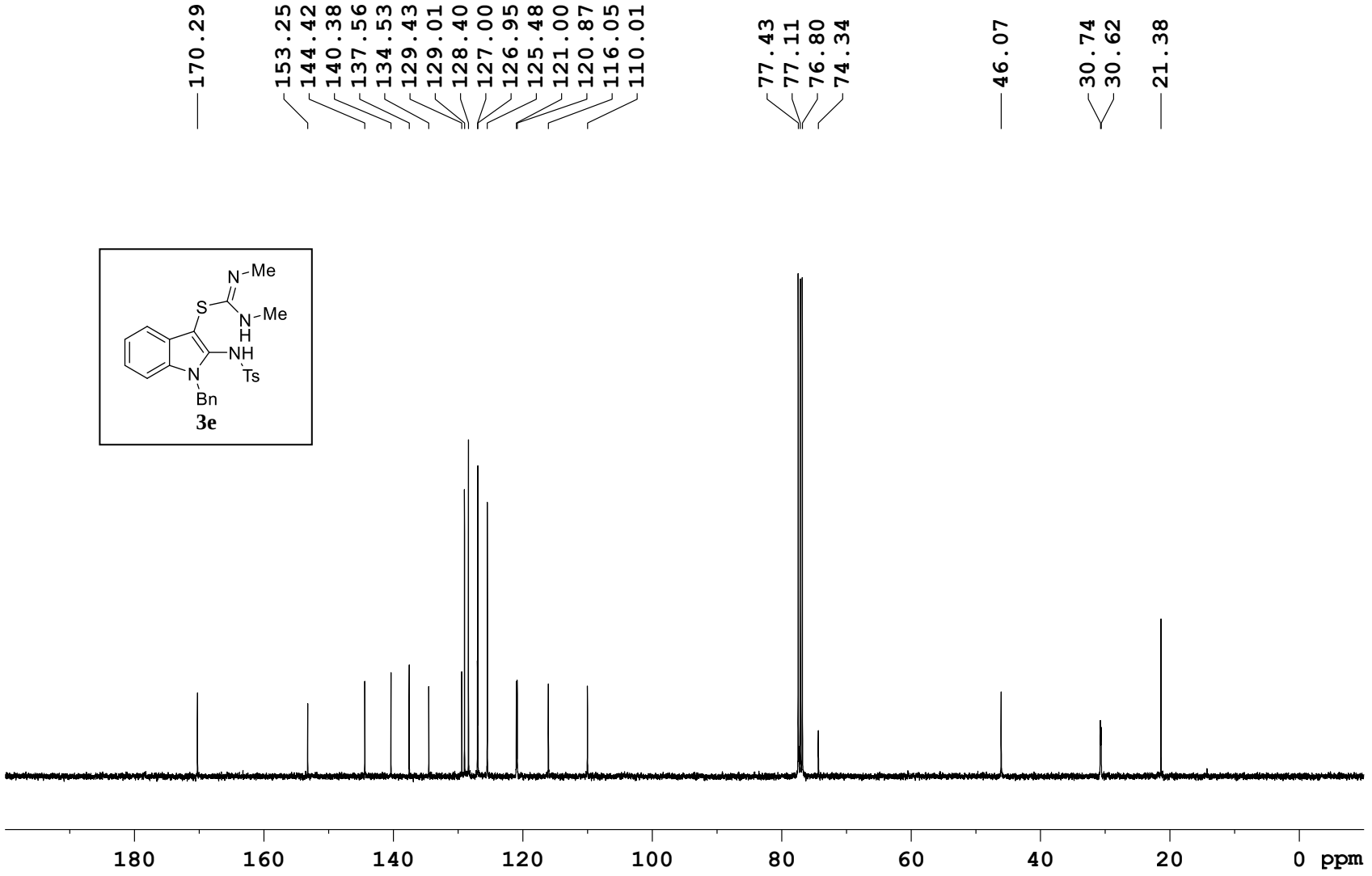
^{1}H NMR Spectrum of **3e**

1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-dimethylcarbamimidothioate (3e)



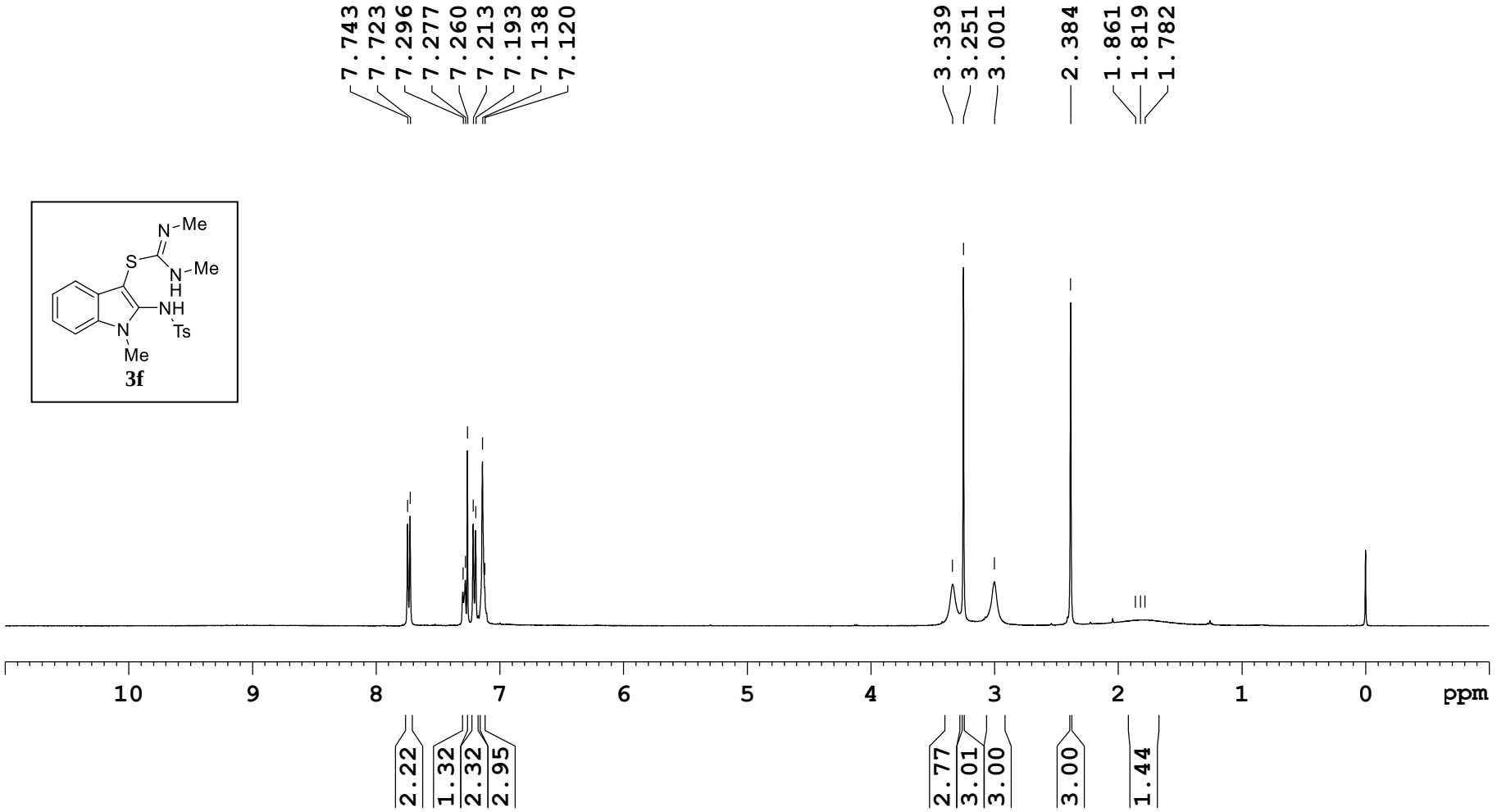
NMR spectrum of **3e** after D_2O exchange experiment ($CDCl_3$, 400 MHz)

1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-dimethylcarbamimidothioate (3e)



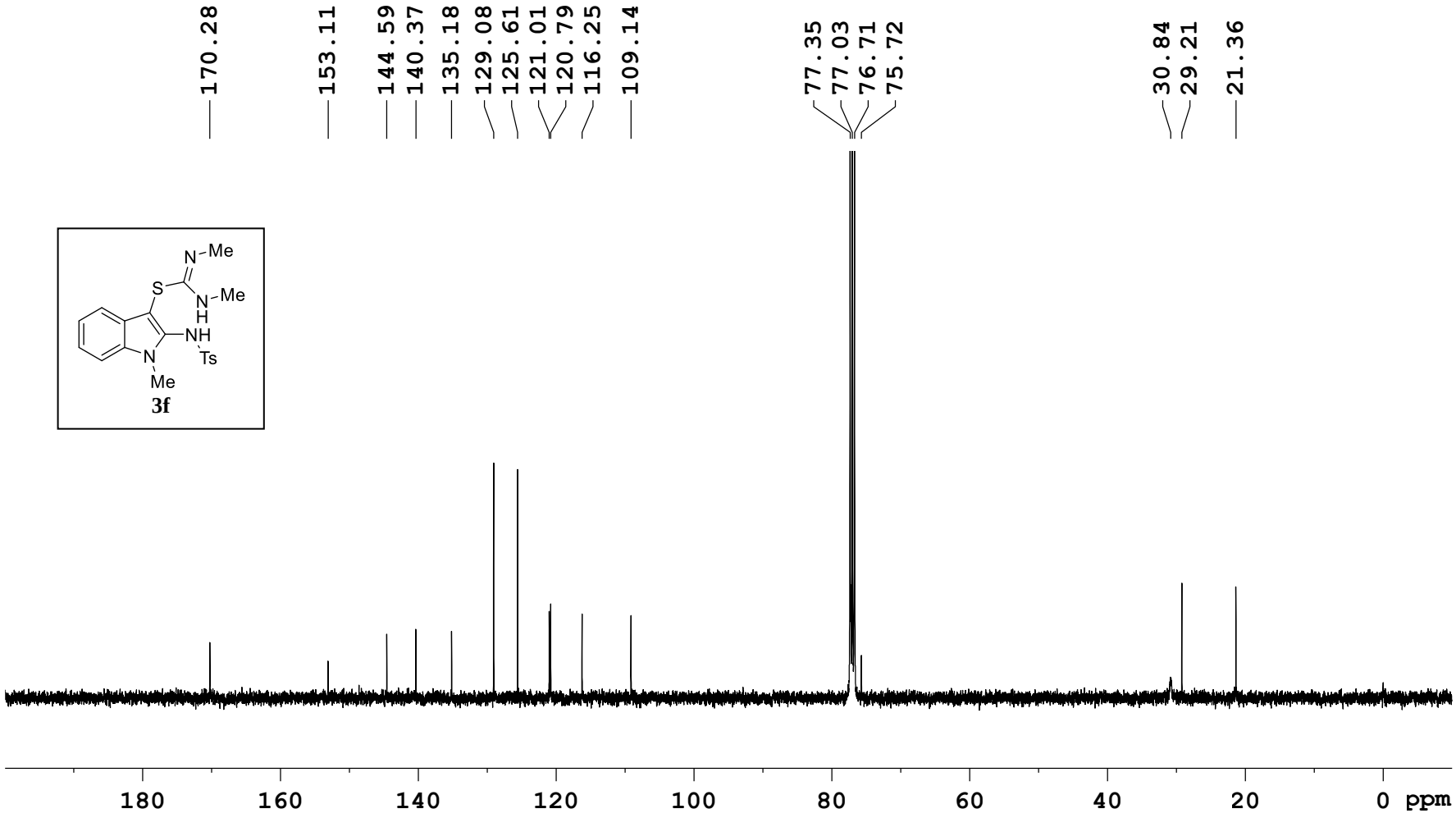
^{13}C NMR Spectrum of **3e**

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-dimethylcarbamimidothioate (3f)



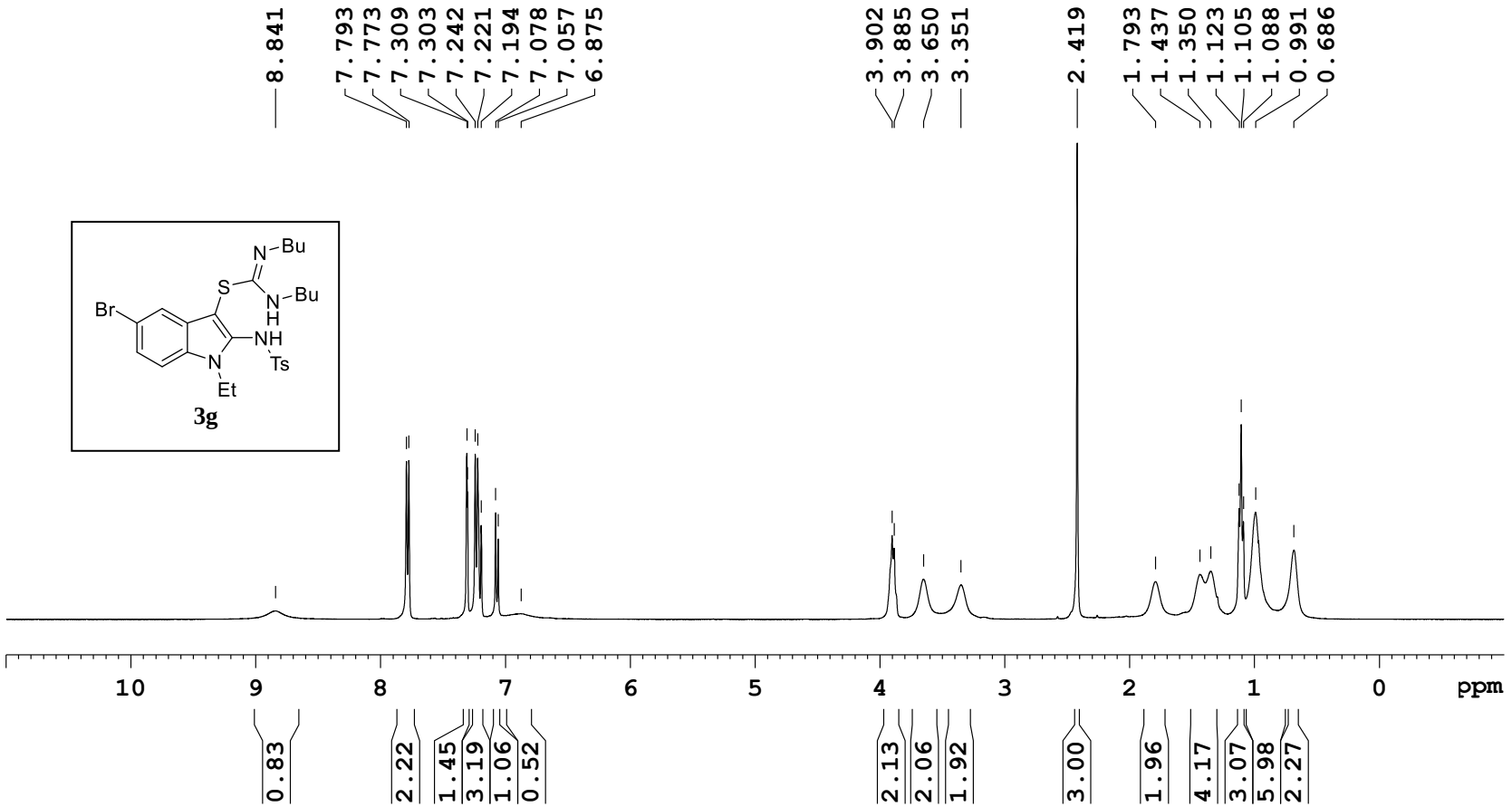
^{1}H NMR Spectrum of **3f**

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-dimethylcarbamimidothioate (3f)



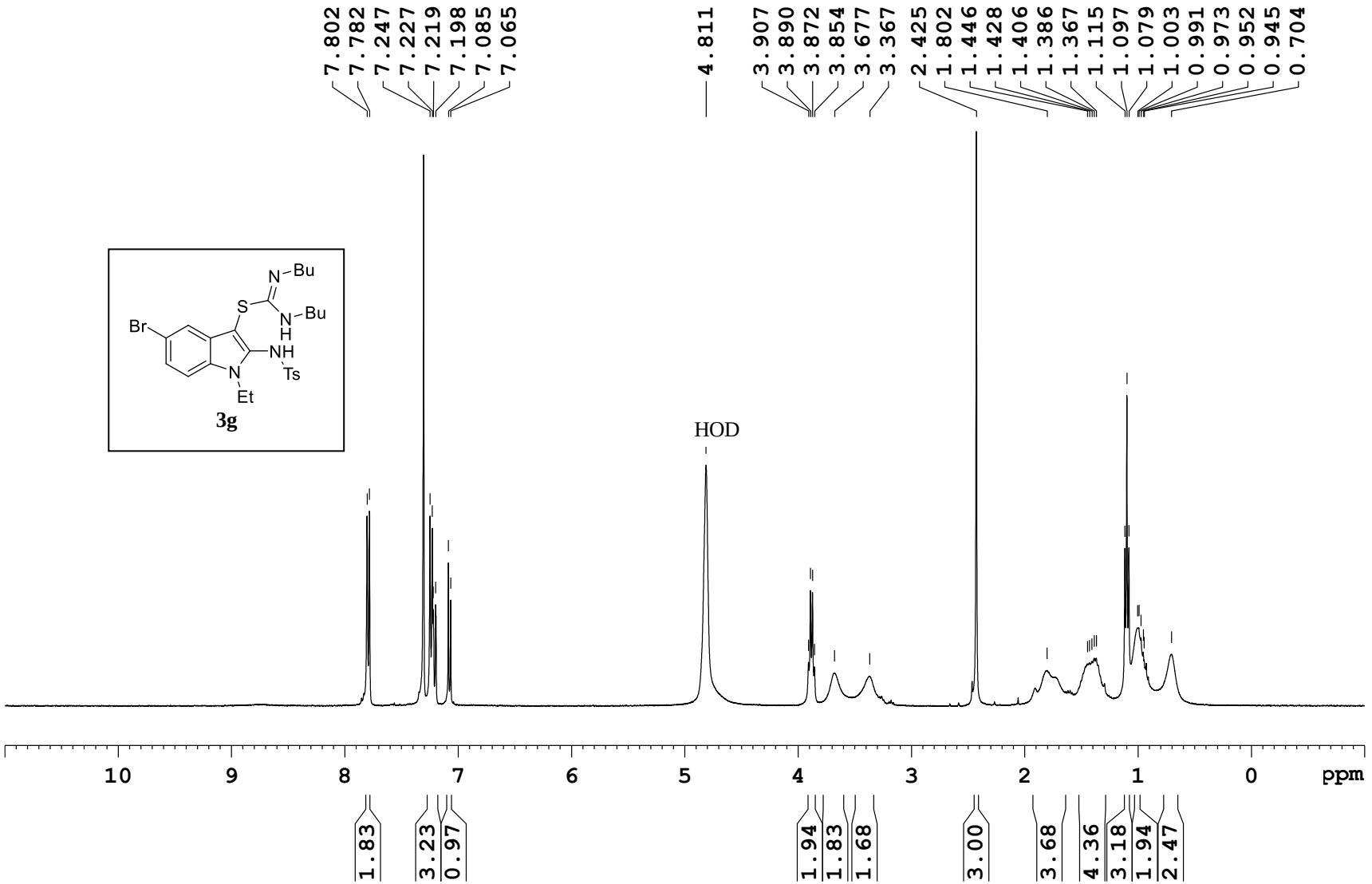
^{13}C NMR Spectrum of **3f**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1*H*-indol-3-yl N,N'-dibutylcarbamimidothioate (3g)



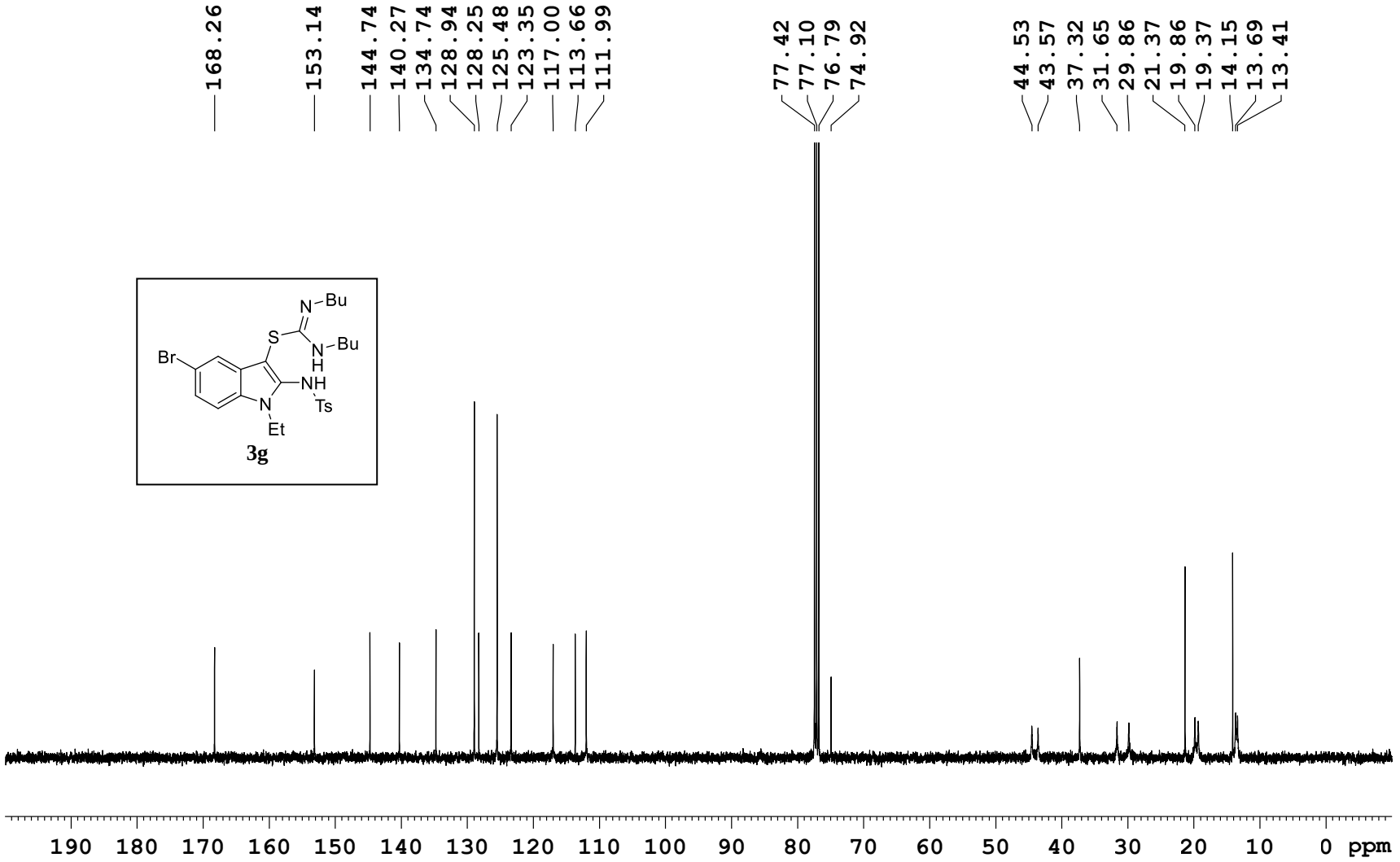
^{1}H NMR Spectrum of **3g**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1*H*-indol-3-yl N,N'-dibutylcarbamimidothioate (3g)



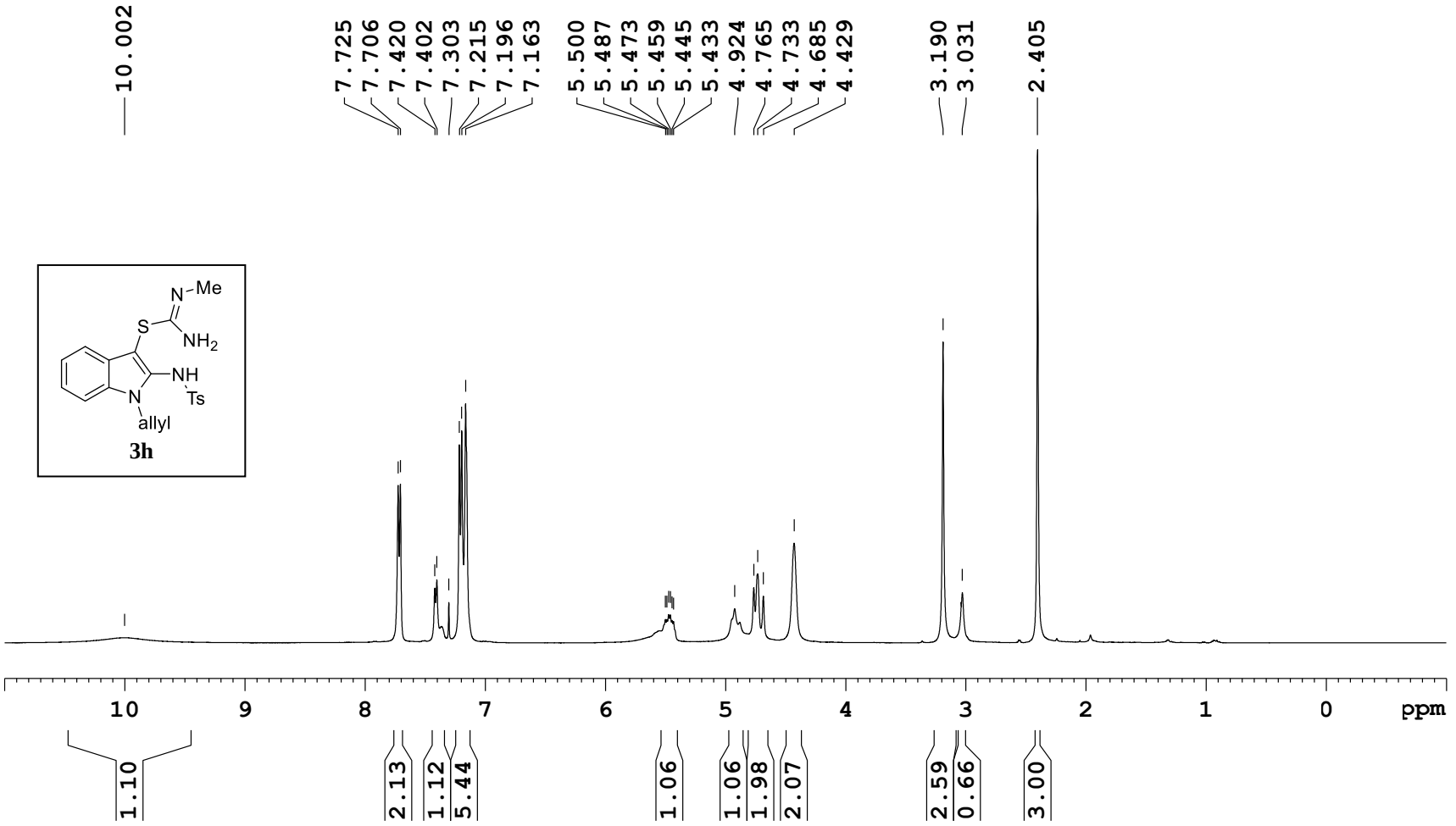
NMR spectrum of **3g** after D_2O exchange experiment ($CDCl_3$, 400 MHz)

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1*H*-indol-3-yl *N,N'*-dibutylcarbamimidothioate (3g)



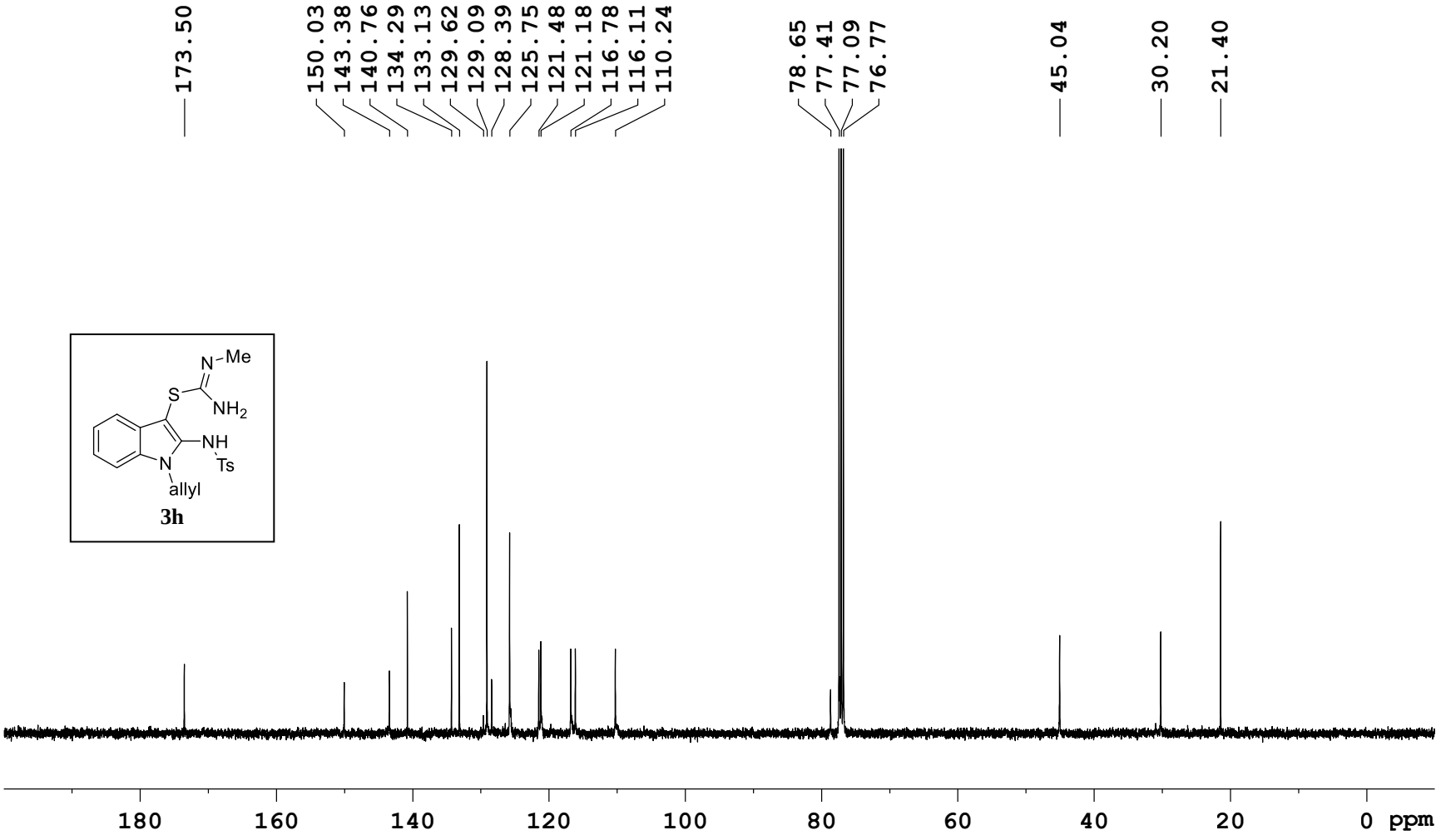
^{13}C NMR Spectrum of **3g**

1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N*-methylcarbamimidothioate (3h)



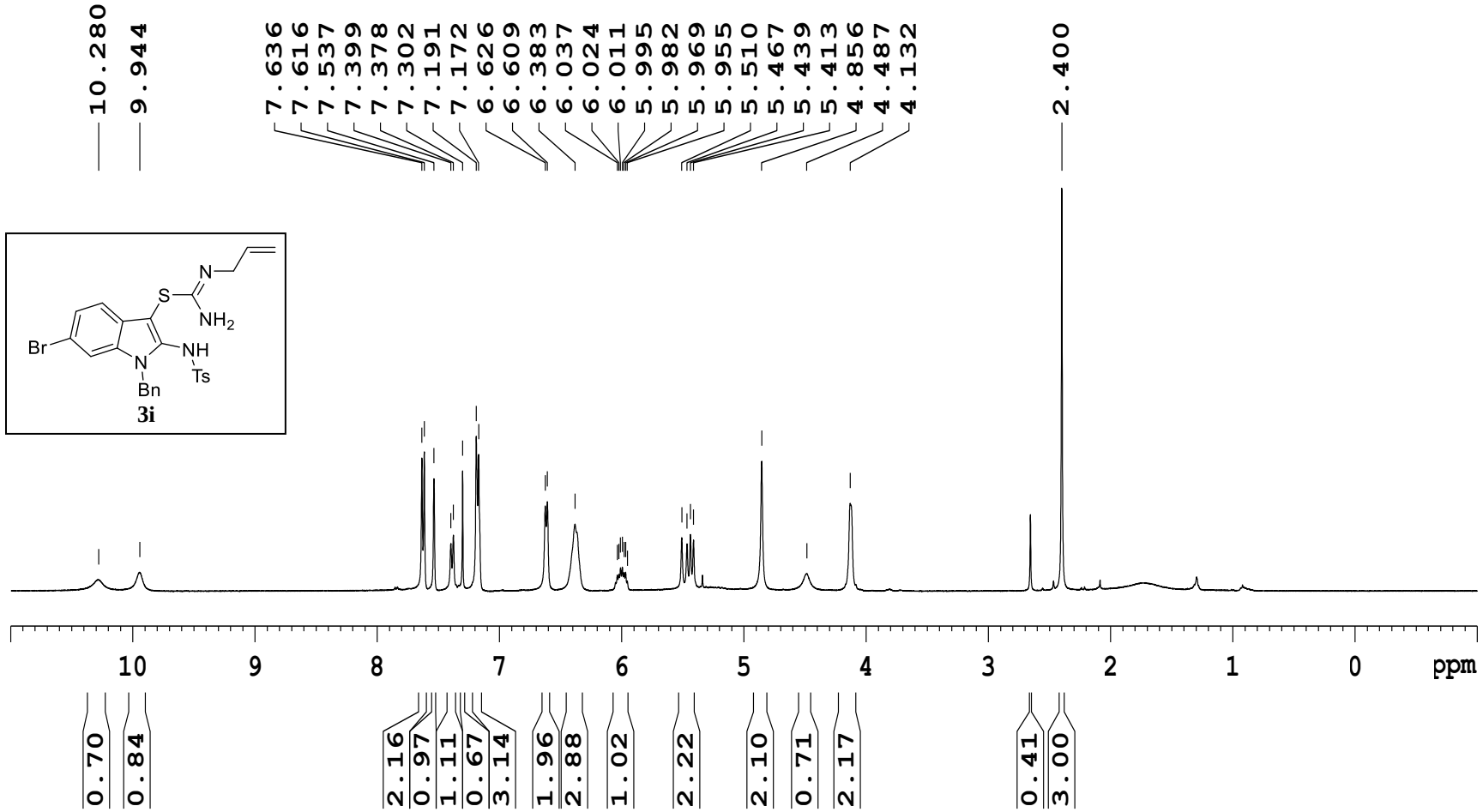
^{1}H NMR Spectrum of **3h**

1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N*-methylcarbamimidothioate (3h)



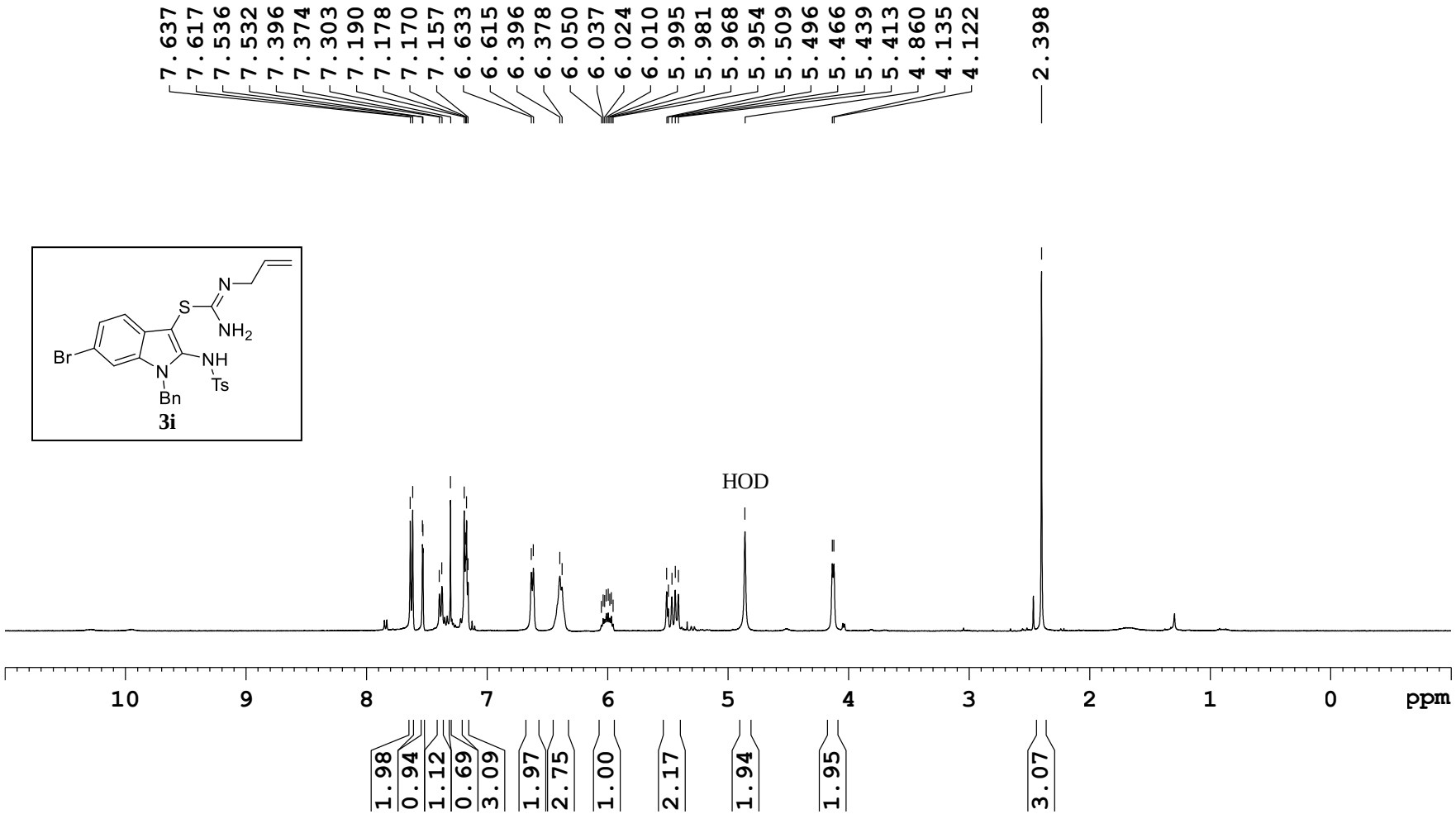
^{13}C NMR Spectrum of **3h**

1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]]-5-bromo-1*H*-indol-3-yl *N*-allylcarbamimidothioate (3i)



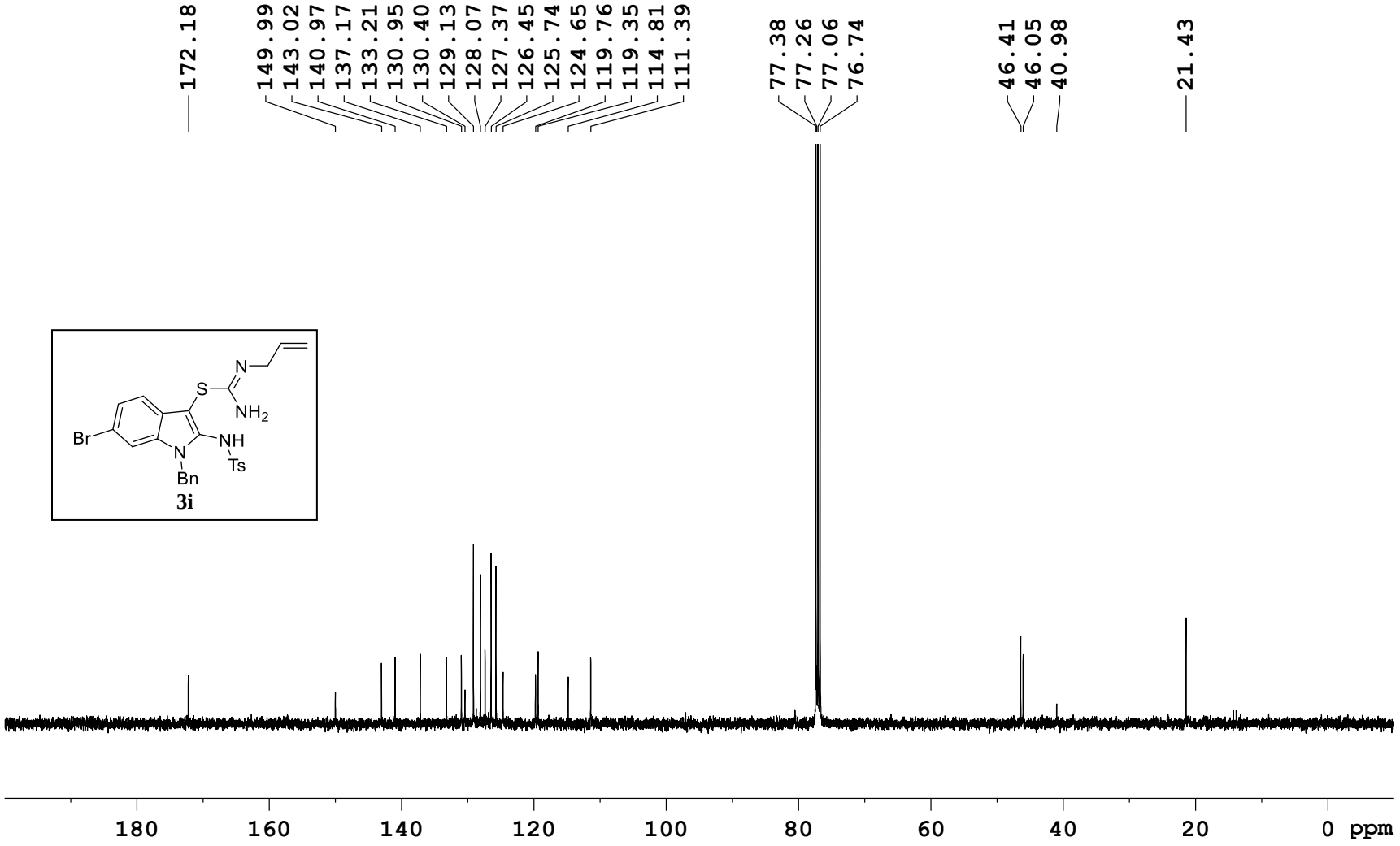
^{1}H NMR Spectrum of **3i**

1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]]-5-bromo-1*H*-indol-3-yl *N*-allylcarbamimidothioate (3i)



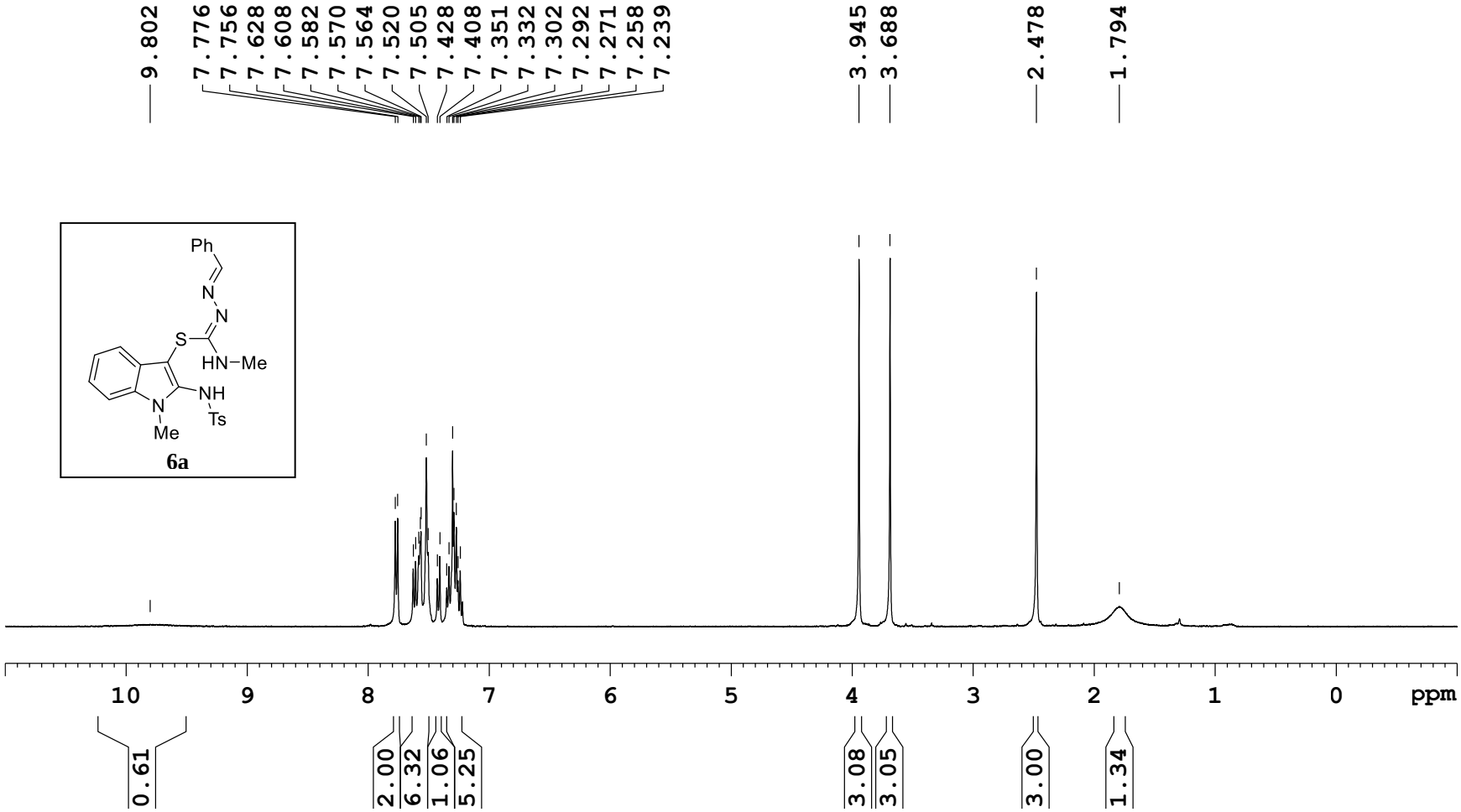
NMR Spectrum of **3i** after D_2O exchange experiment ($CDCl_3$, 400 MHz)

1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1*H*-indol-3-yl *N*-allylcarbamimidothioate (3i)



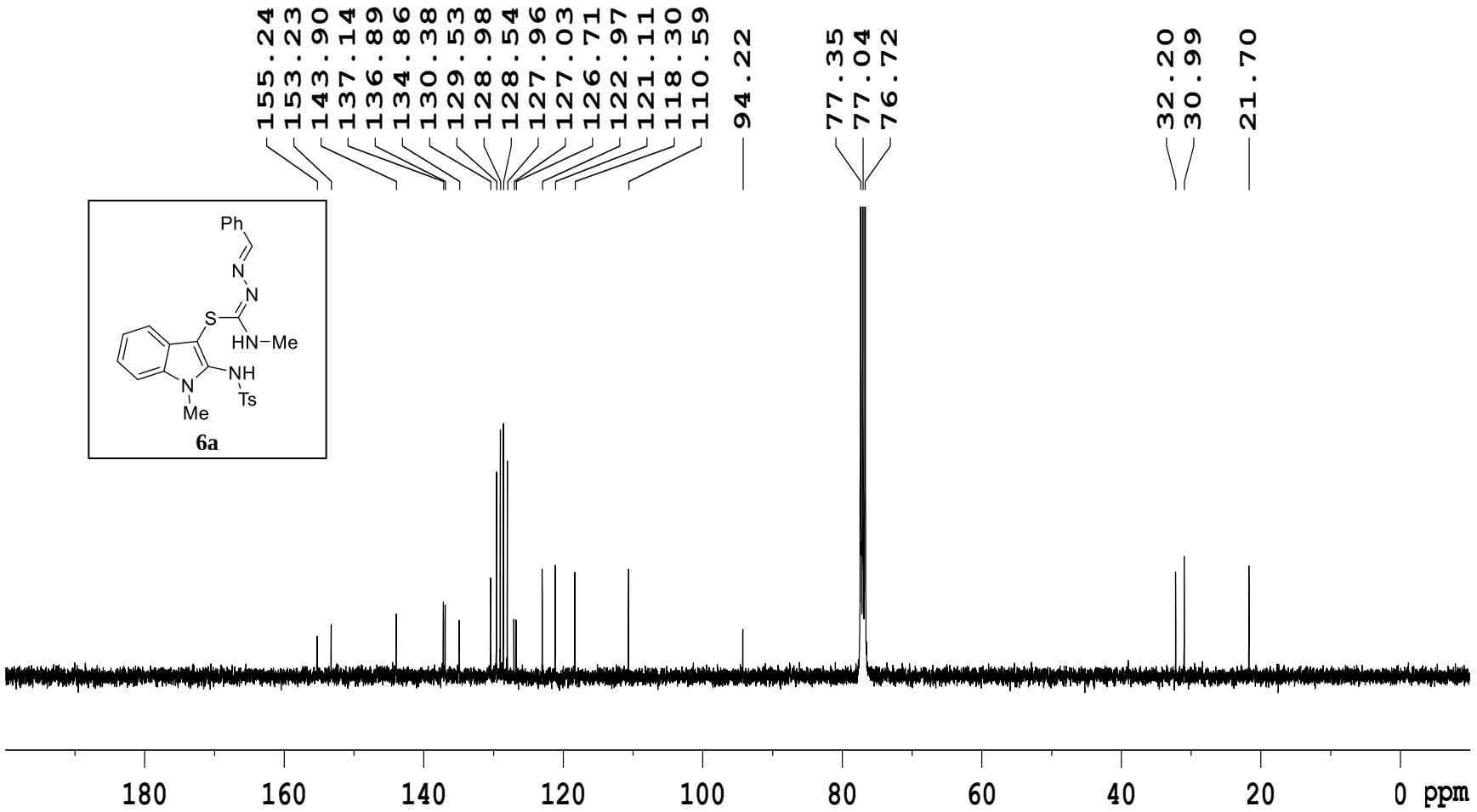
^{13}C NMR Spectrum of **3i**

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6a)



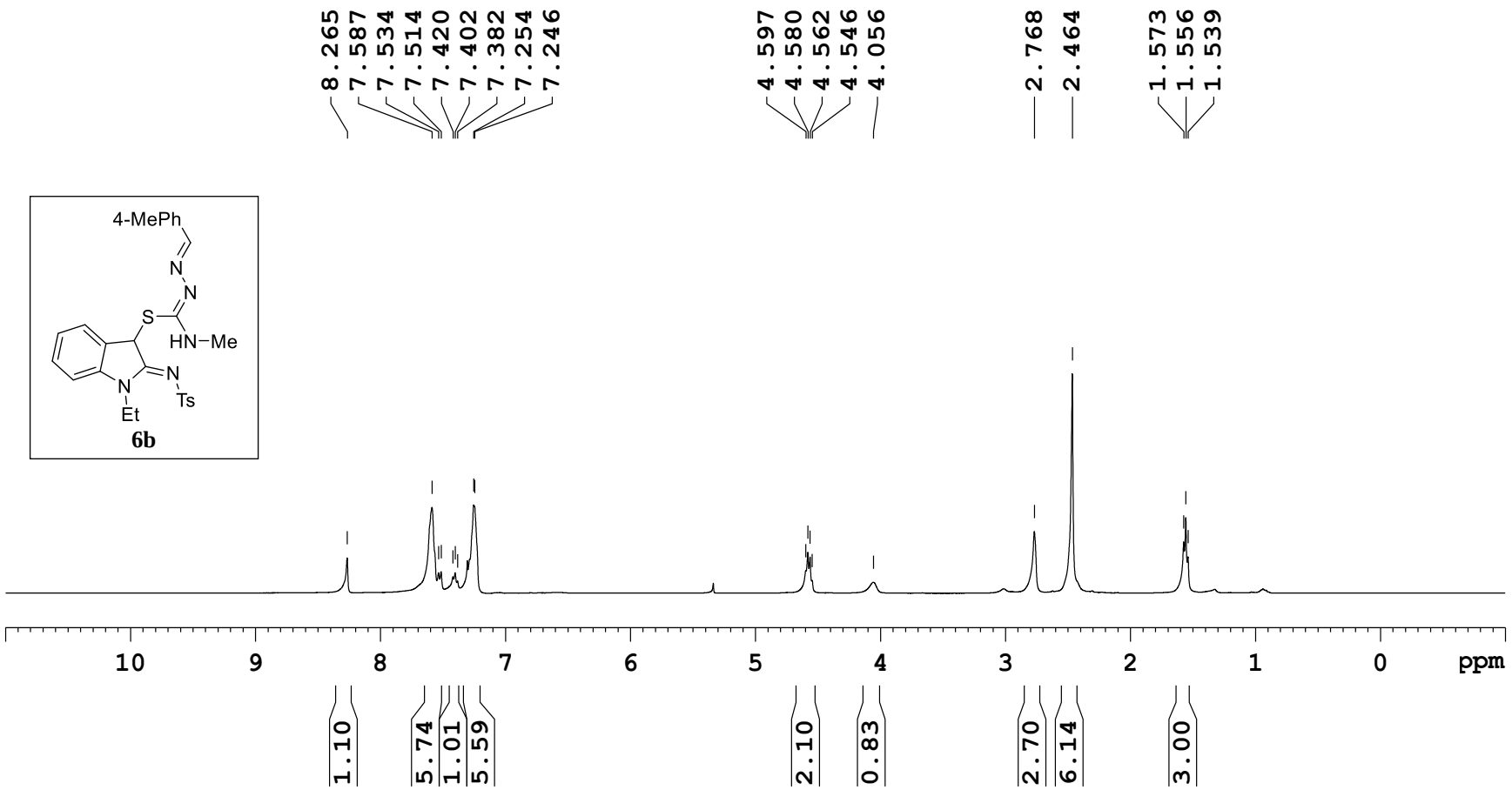
^{1}H NMR Spectrum of **6a**

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6a)



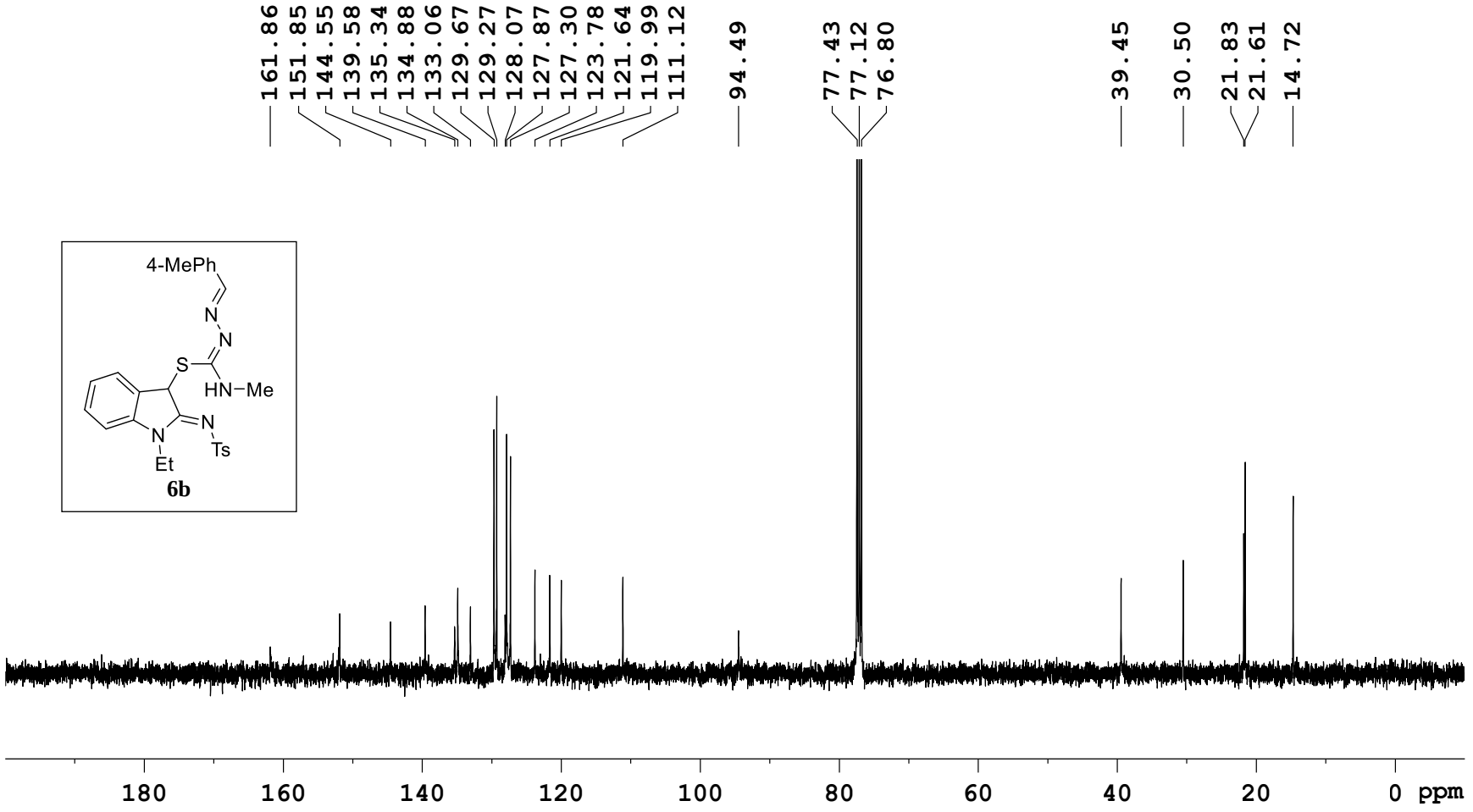
^{13}C NMR Spectrum of **6a**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6b)



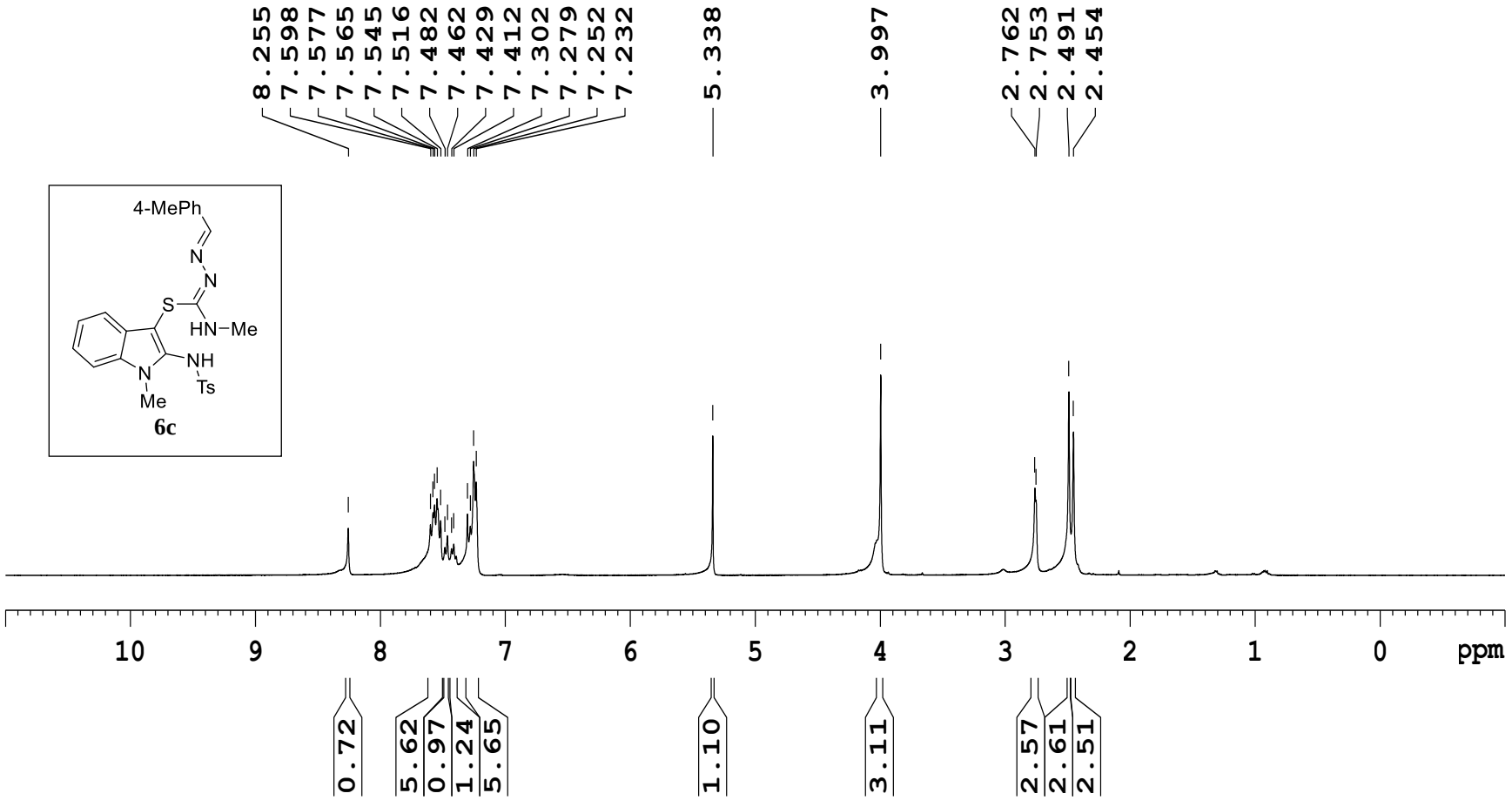
^{1}H NMR Spectrum of **6b**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6b)



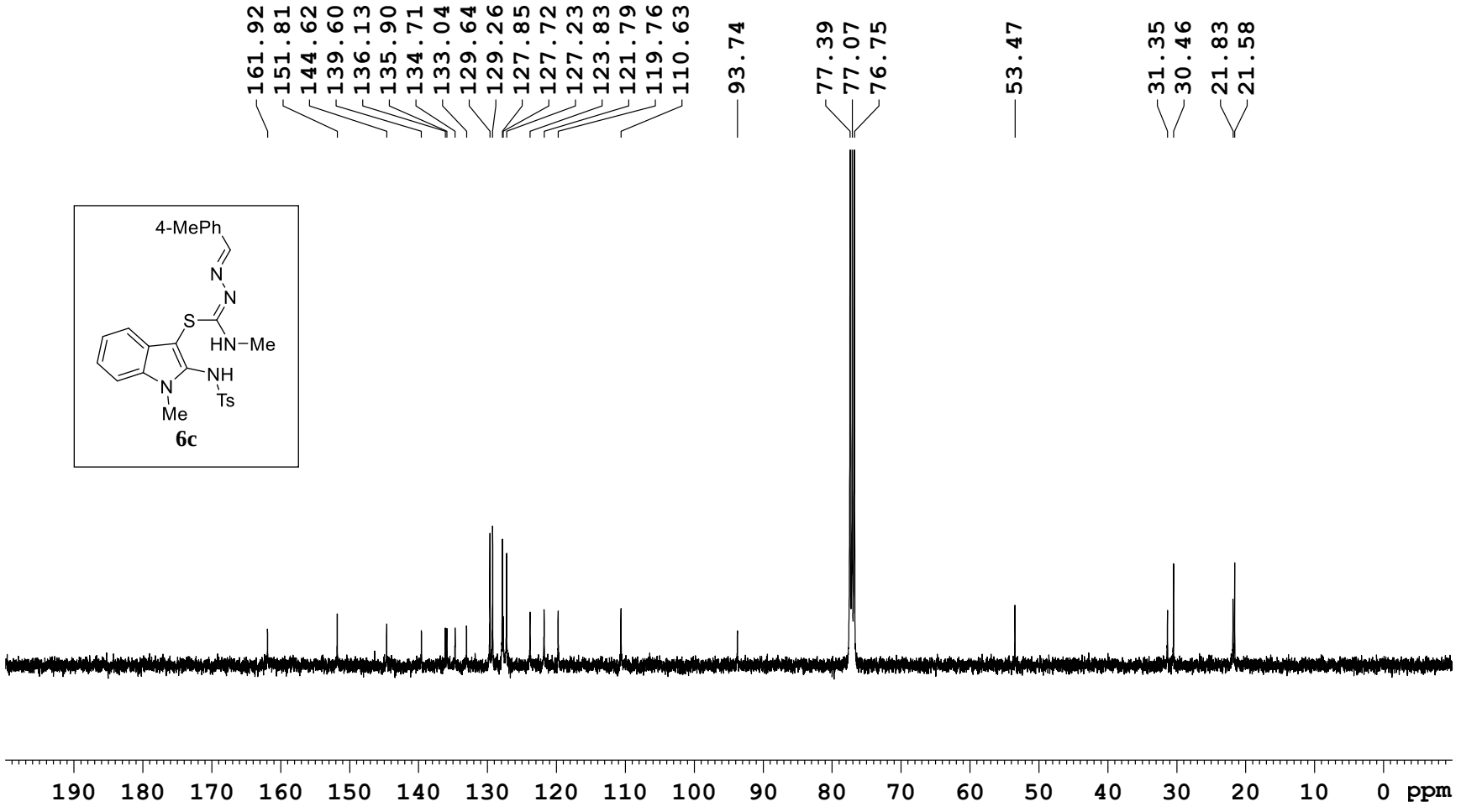
^{13}C NMR Spectrum of **6b**

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6c)



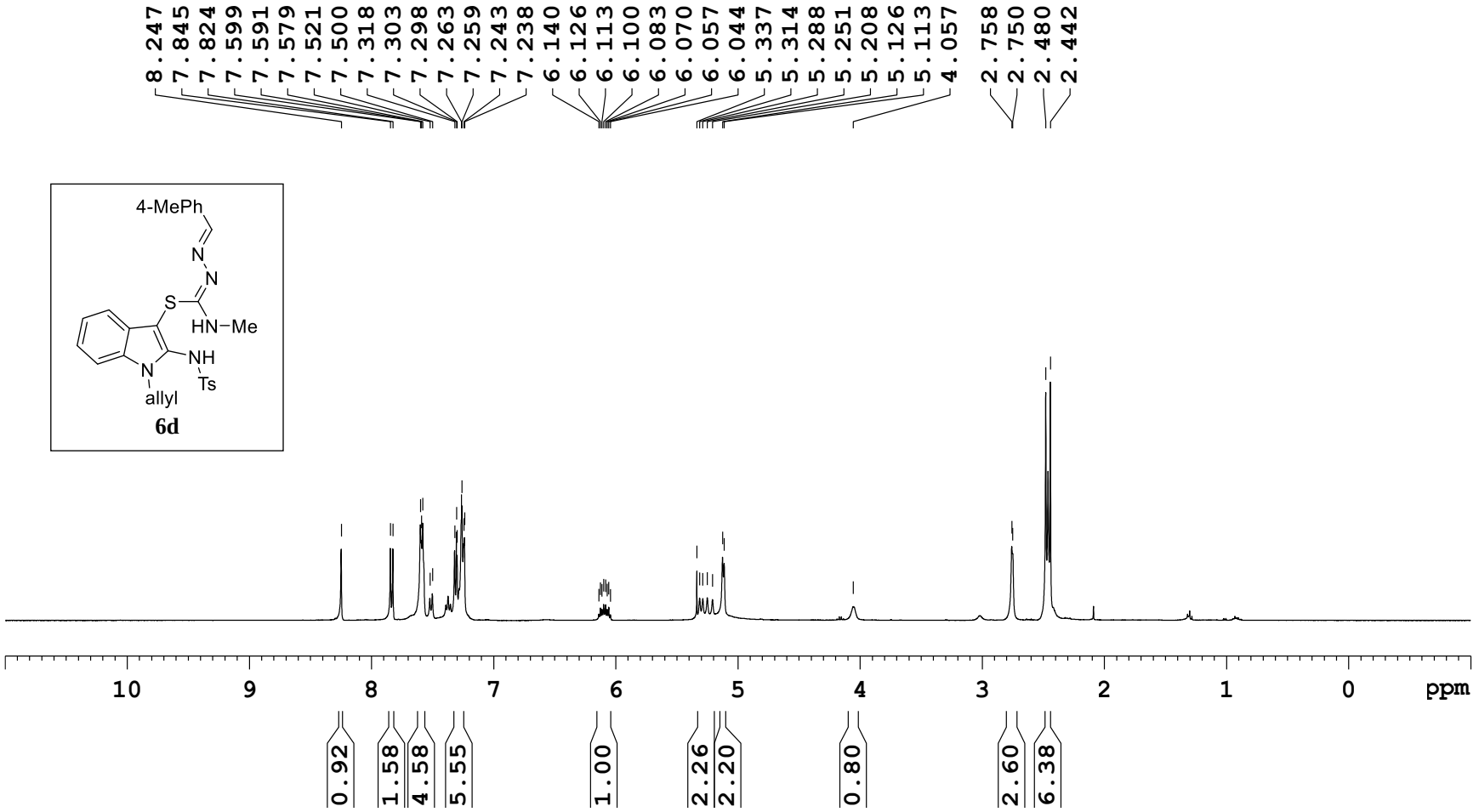
^{1}H NMR Spectrum of **6c**

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6c)



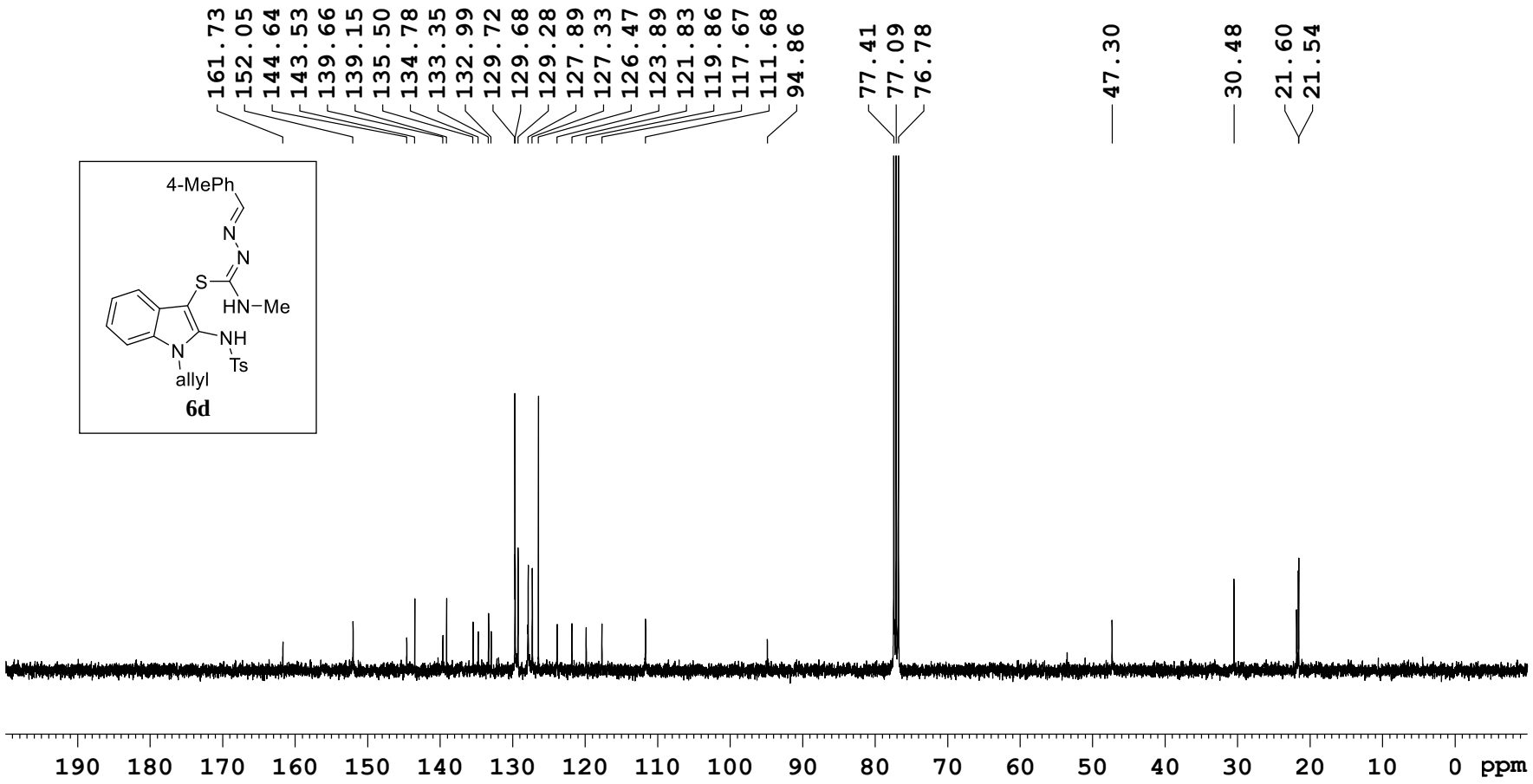
^{13}C NMR Spectrum of **6c**

1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6d)



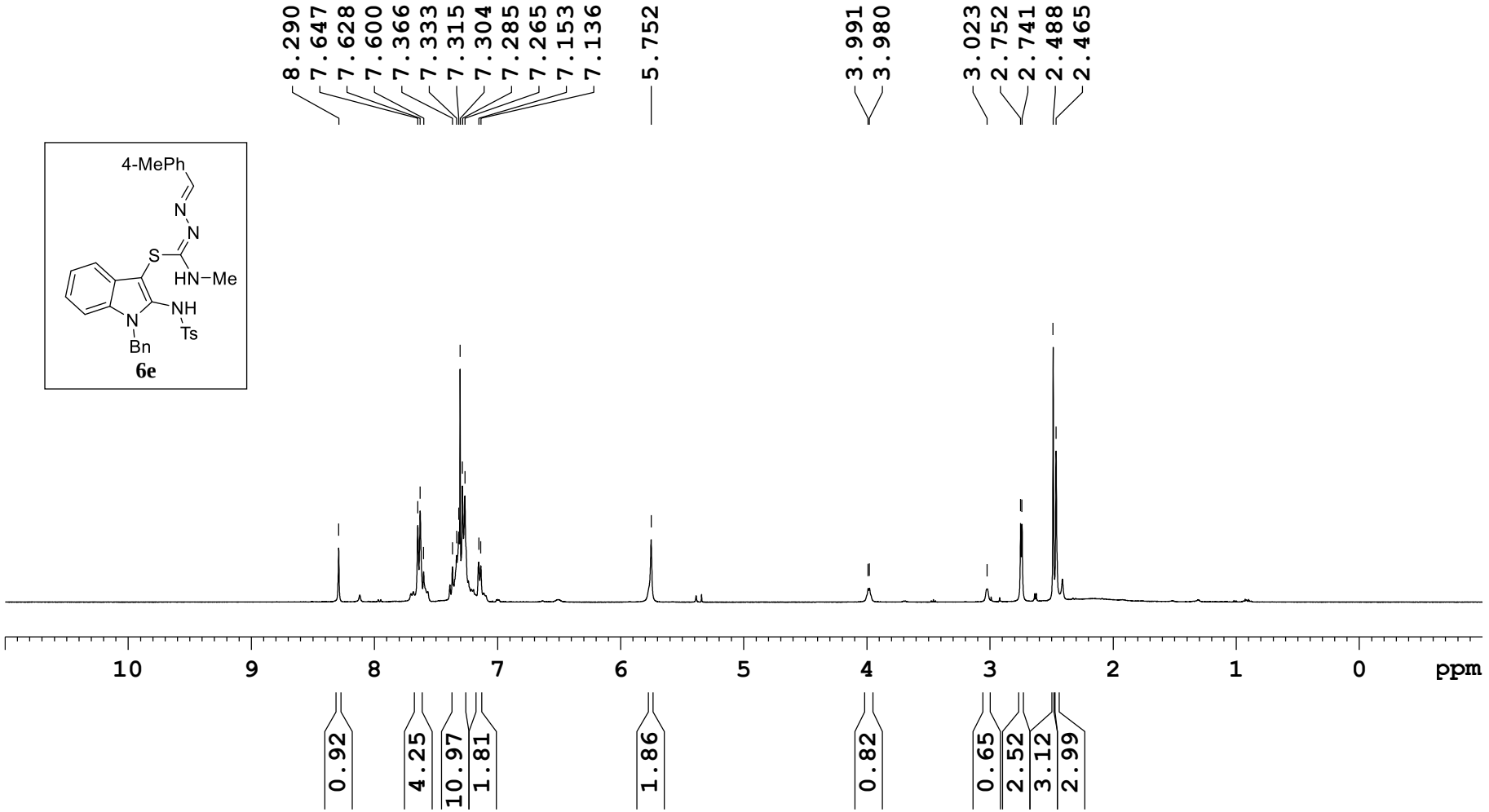
^{1}H NMR Spectrum of **6d**

1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6d)



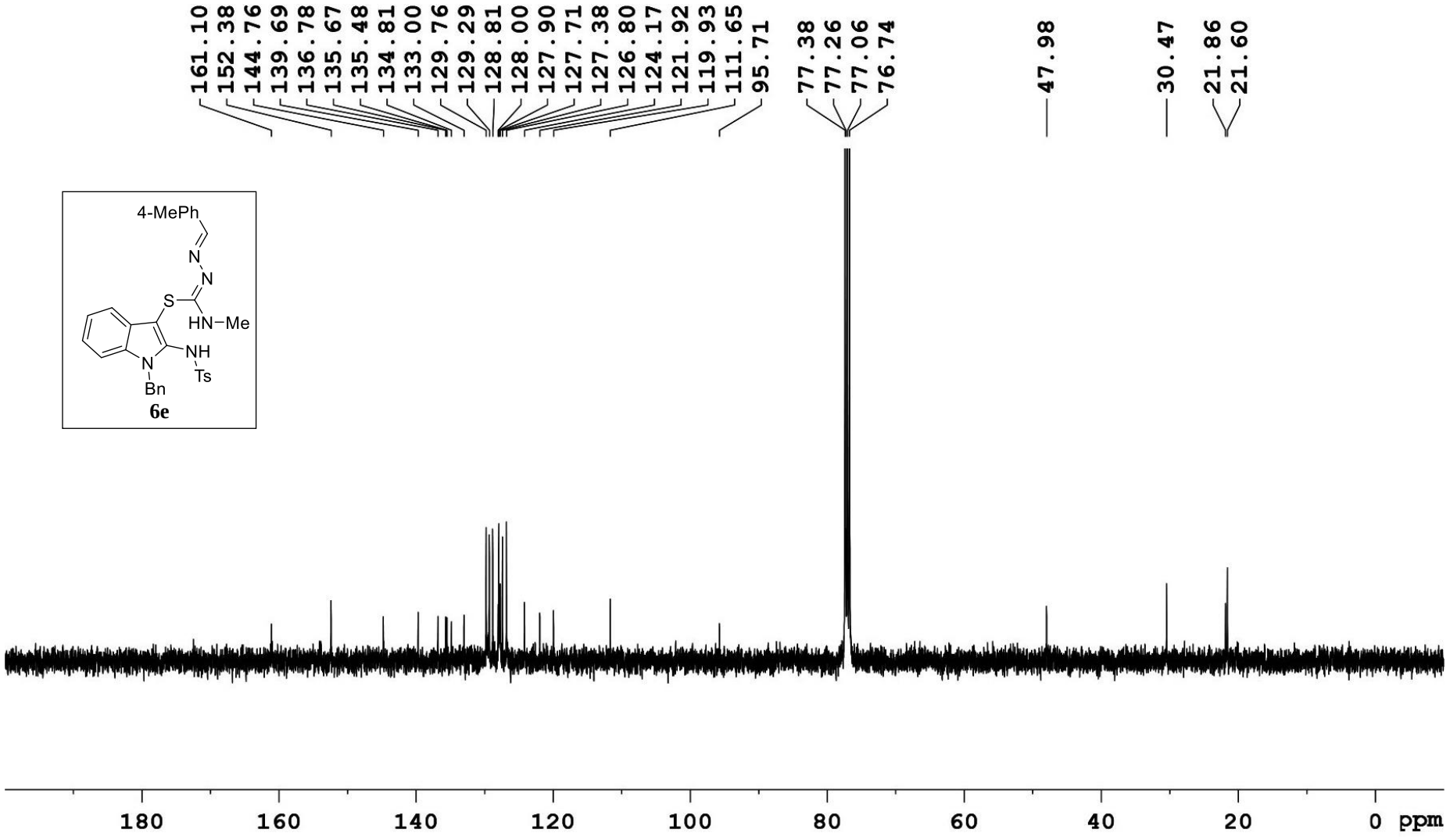
^{13}C NMR Spectrum of **6d**

1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6e)



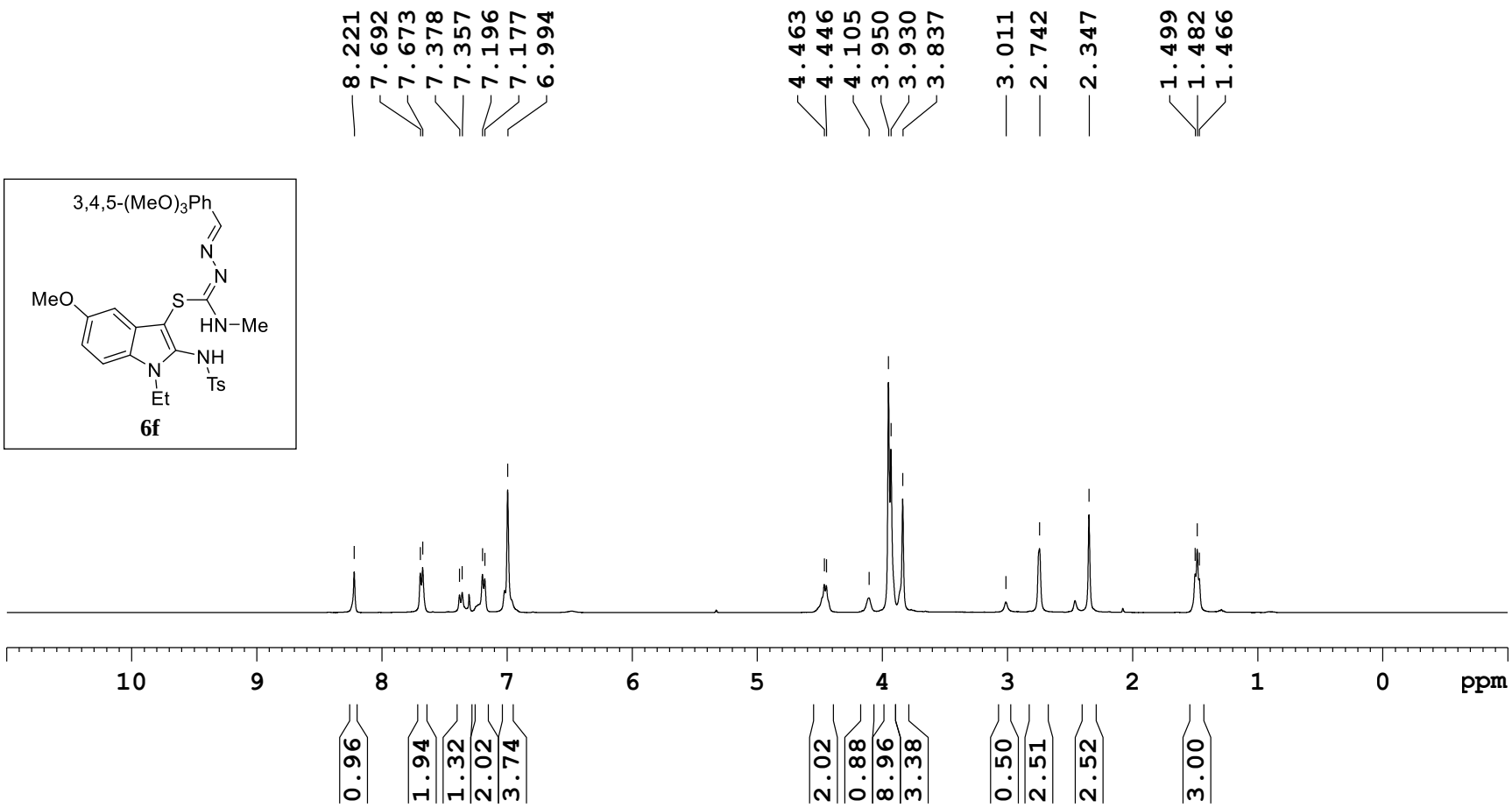
^{1}H NMR Spectrum of **6e**

1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6e)



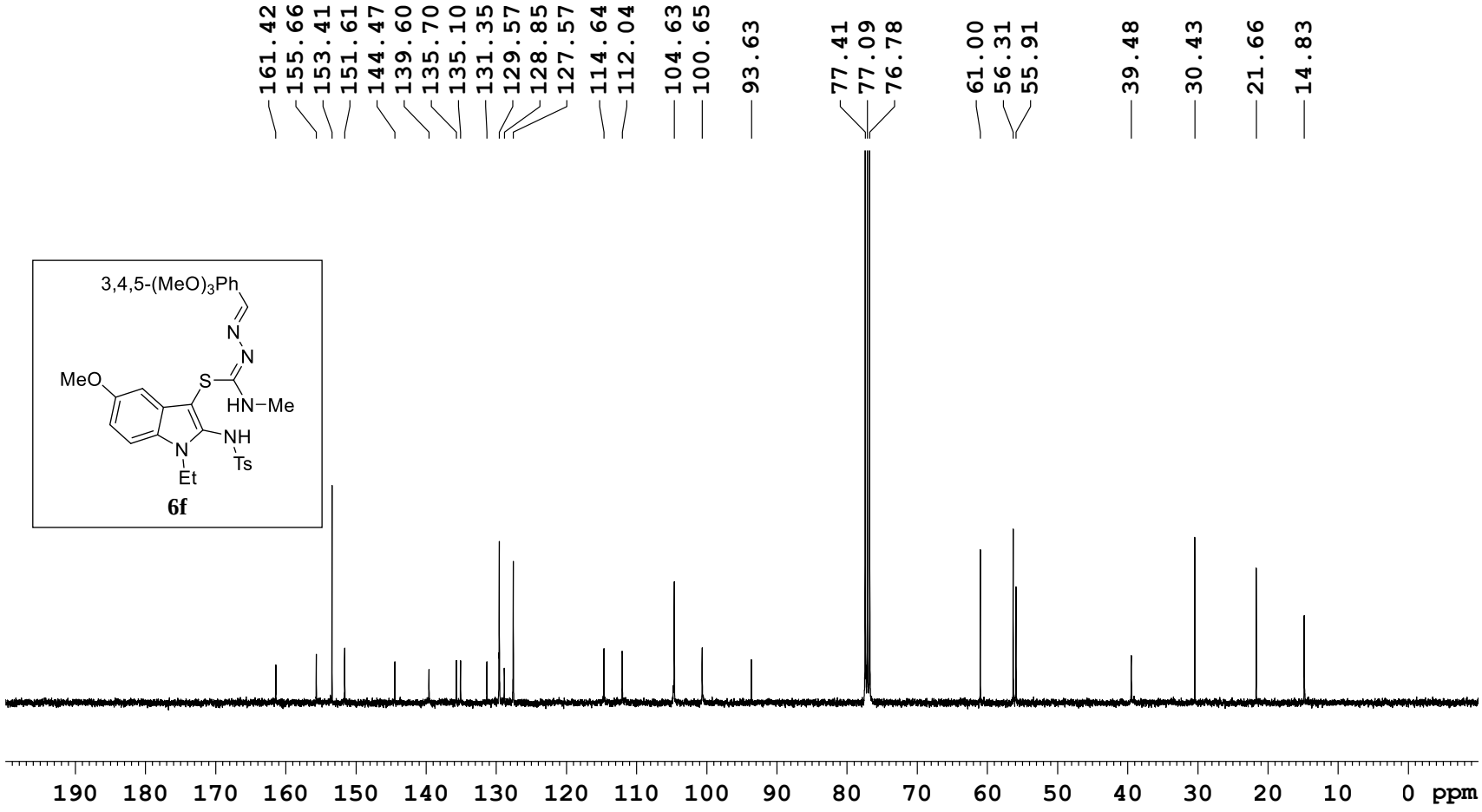
^{13}C NMR Spectrum of **6e**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(3,4,5-trimethoxyphenyl)methylidene]hydrazine-1-carboximidothioate (6f)



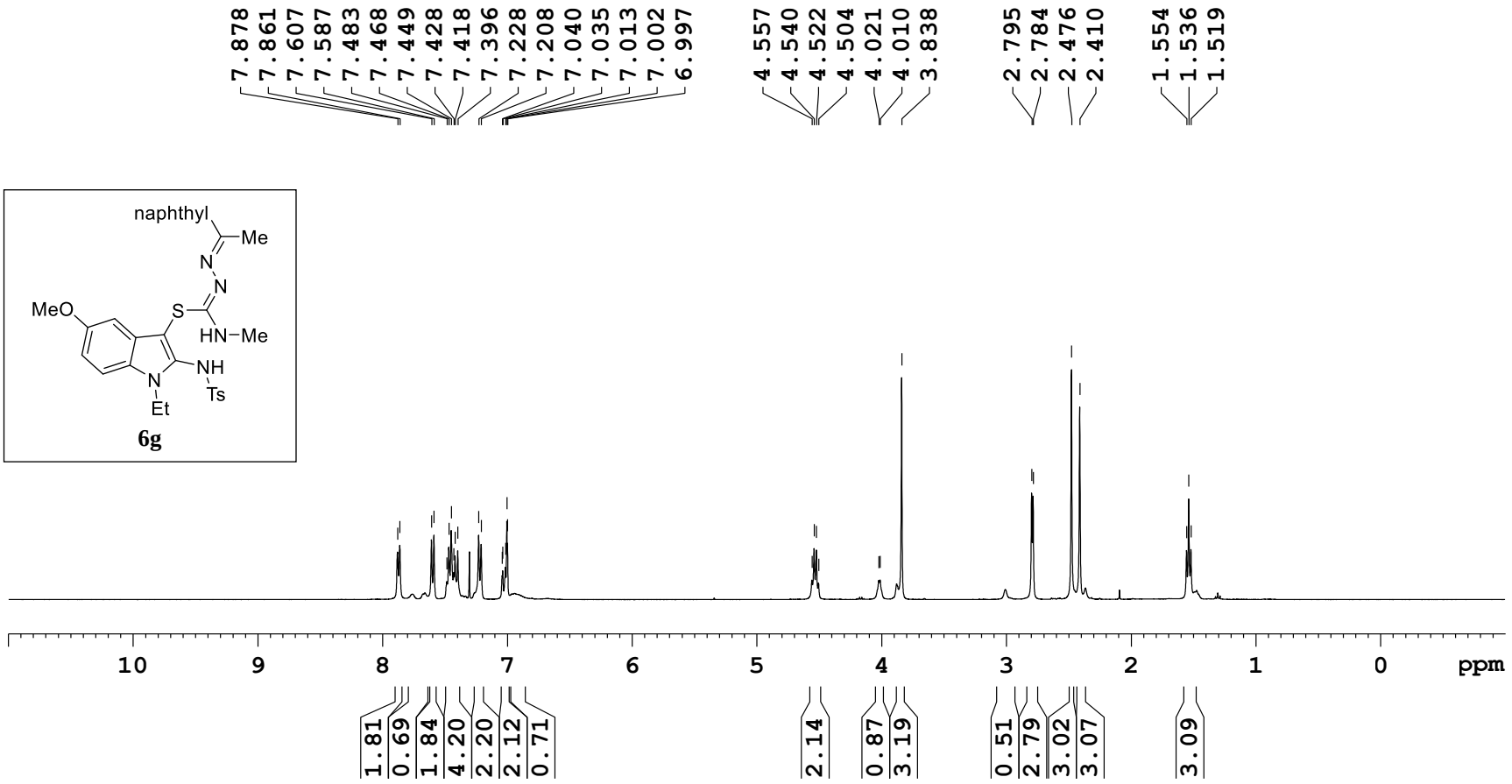
^{1}H NMR Spectrum of **6f**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(3,4,5-trimethoxyphenyl)methylidene]hydrazine-1-carboximidothioate (6f)



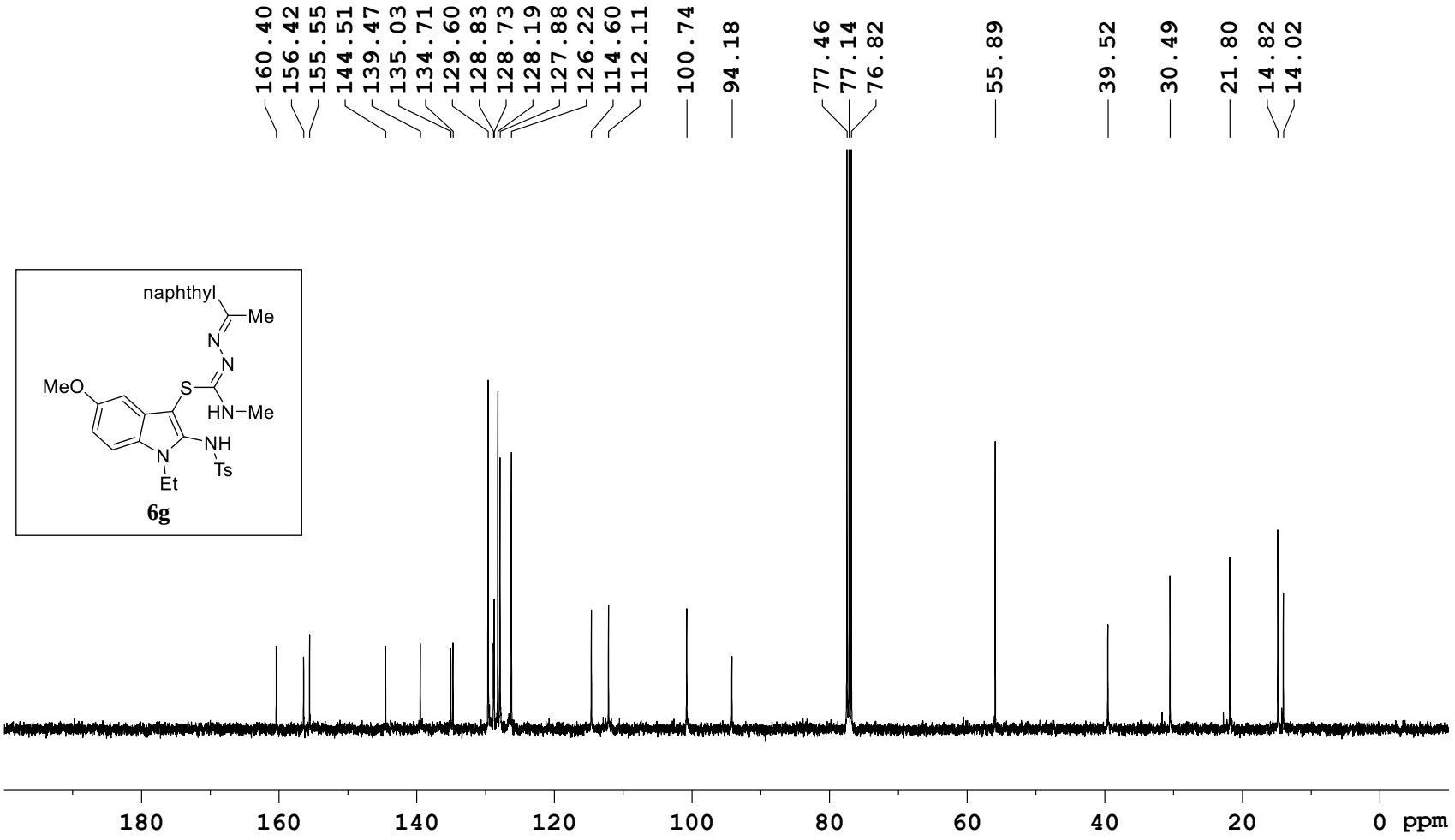
^{13}C NMR Spectrum of **6f**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-(1-(naphthalenyl)methylidene]hydrazine-1-carboximidothioate (6g)



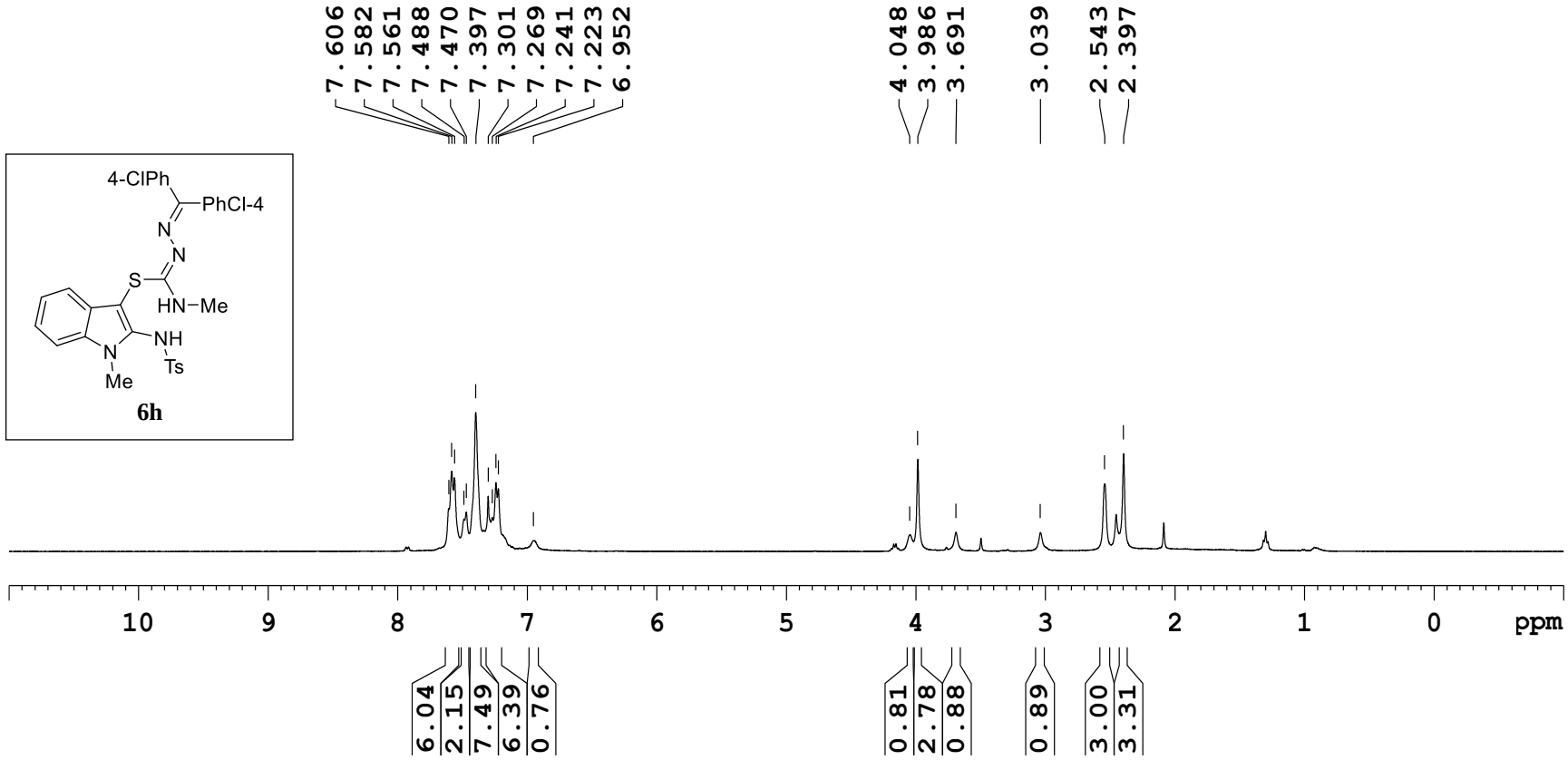
^{1}H NMR Spectrum of **6g**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-(1-(naphthalenyl)methylidene]hydrazine-1-carboximidothioate (6g)



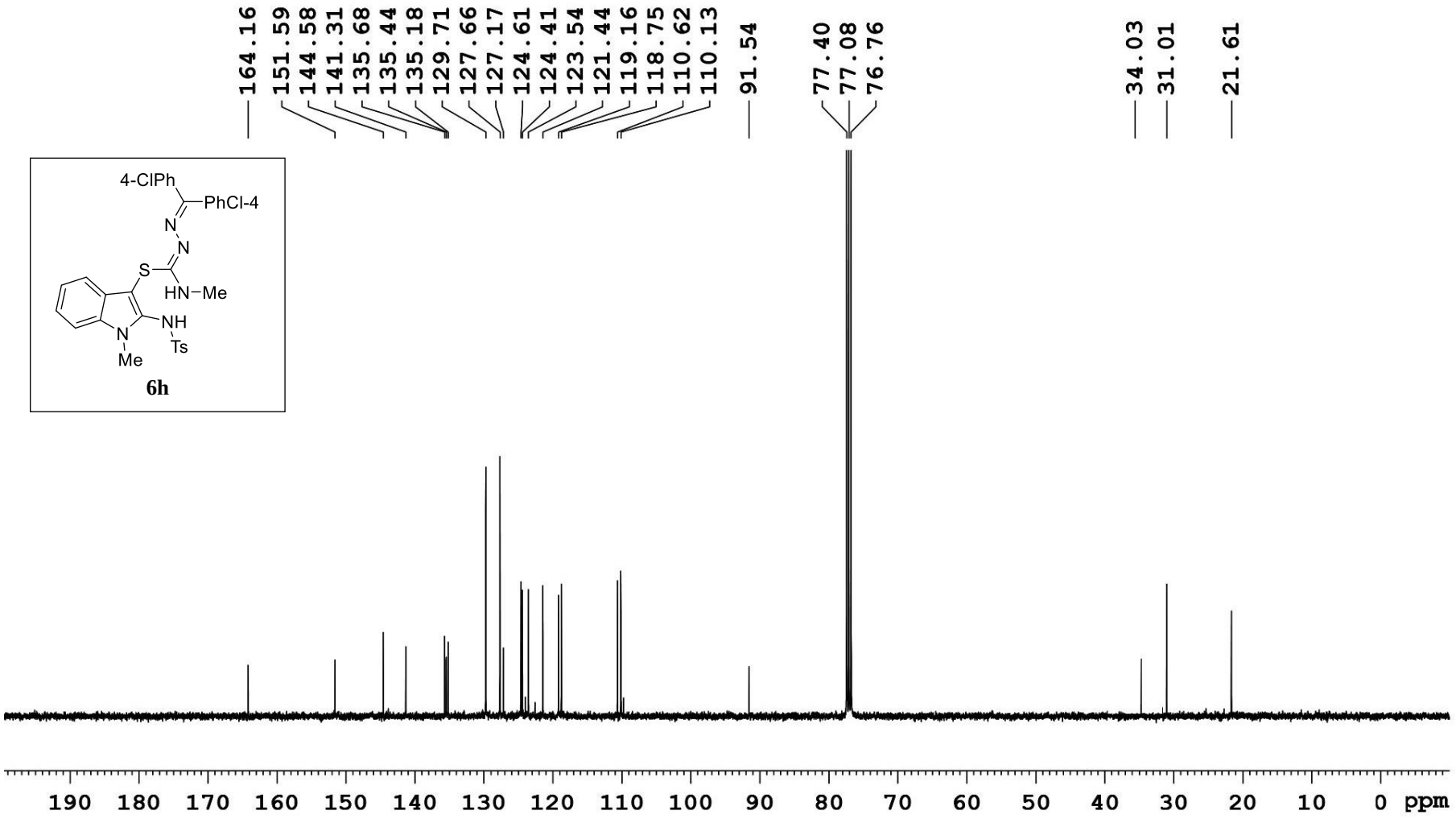
^{13}C NMR Spectrum of **6g**

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl-*N*-methyl-2-[(di-P-Chlorophenyl)methylidene]hydrazine-1-carboximidothioate (6h)



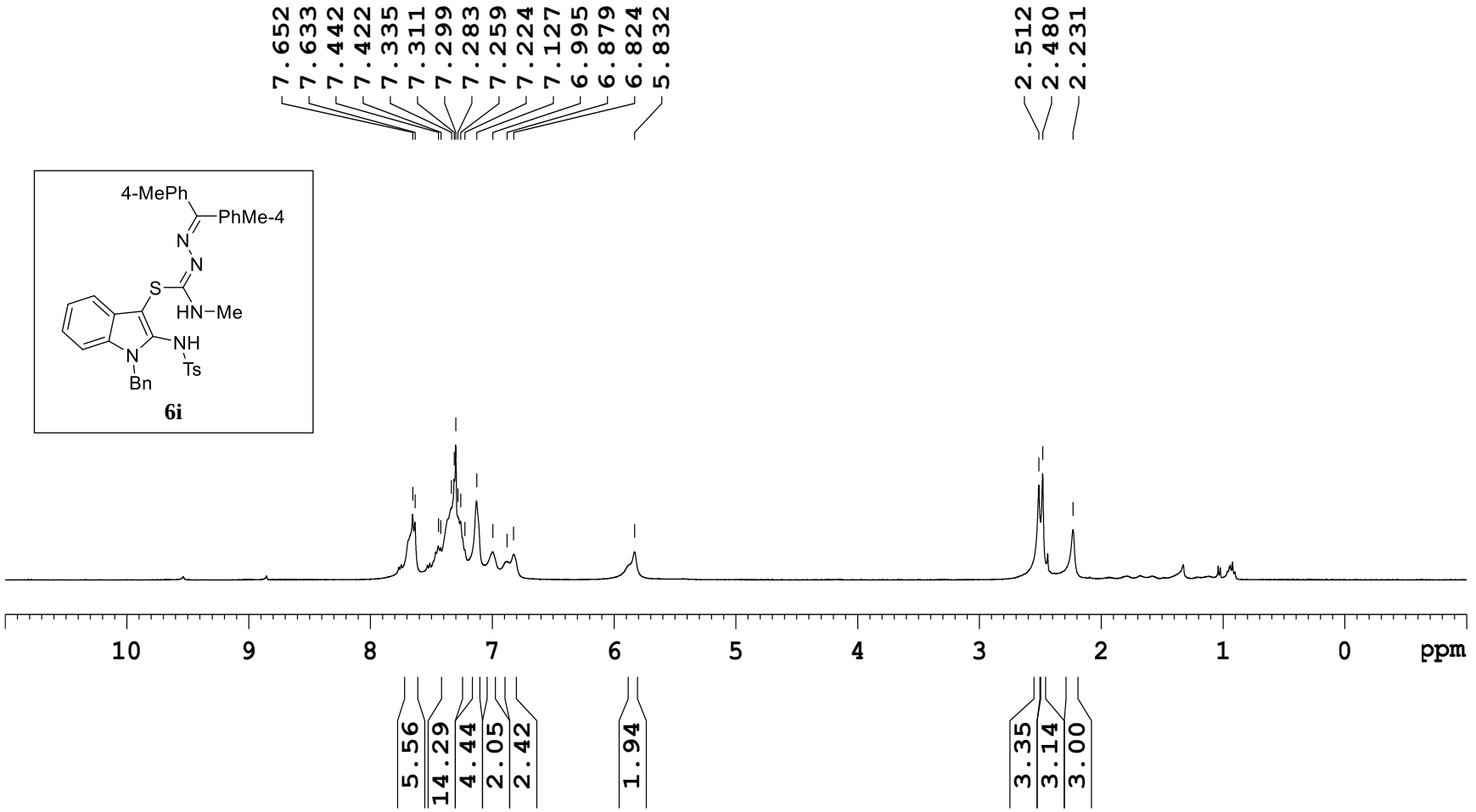
^{1}H NMR Spectrum of **6h**

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl-*N*-methyl-2-[(di-*p*-chlorophenyl)methylidene]hydrazine-1-carboximidothioate (6h)



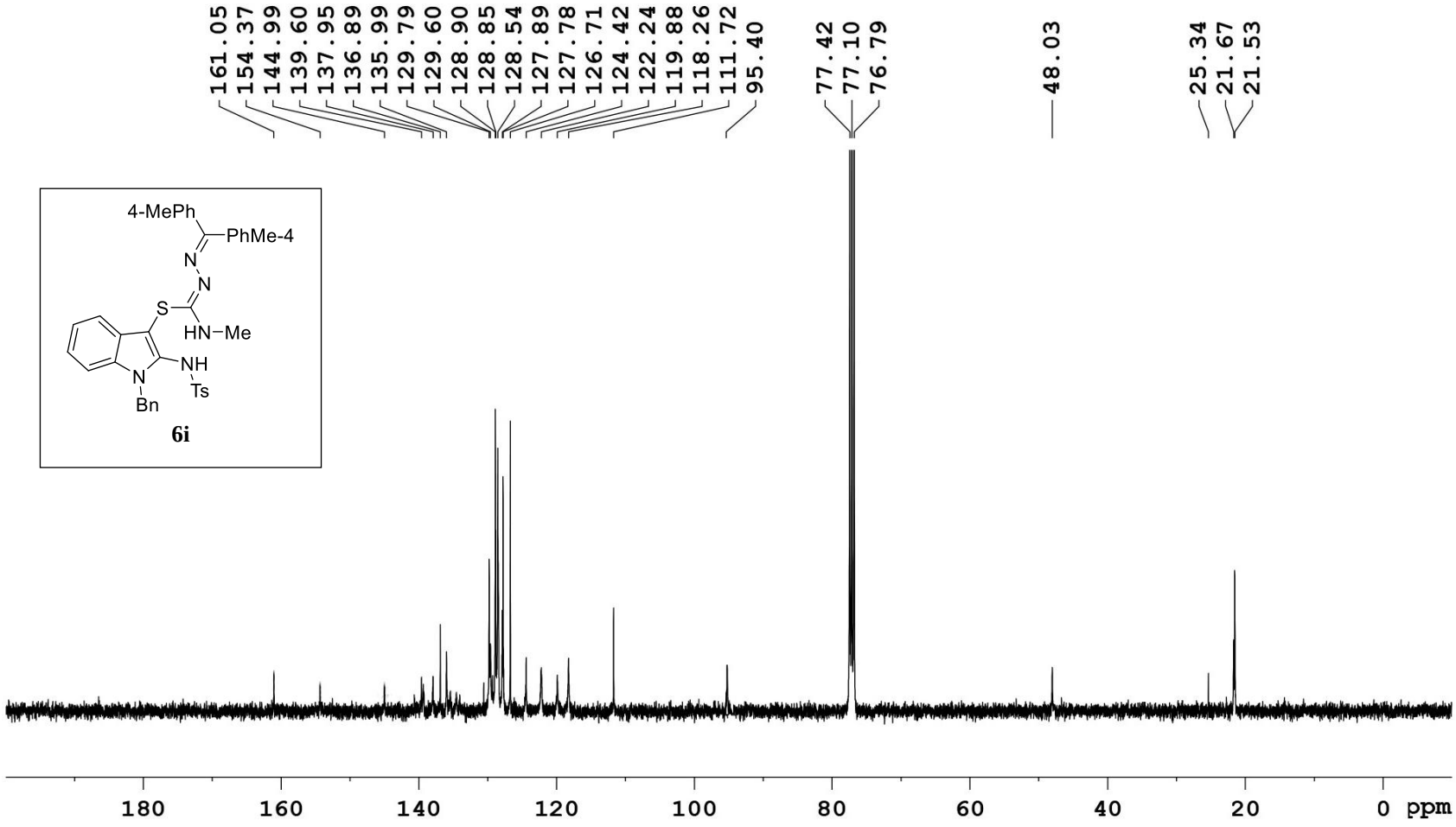
^{13}C NMR Spectrum of **6h**

1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl-*N*-phenyl-2-[(di-*p*-tolyl)methylidene]hydrazine-1-carboximidothioate (6i)



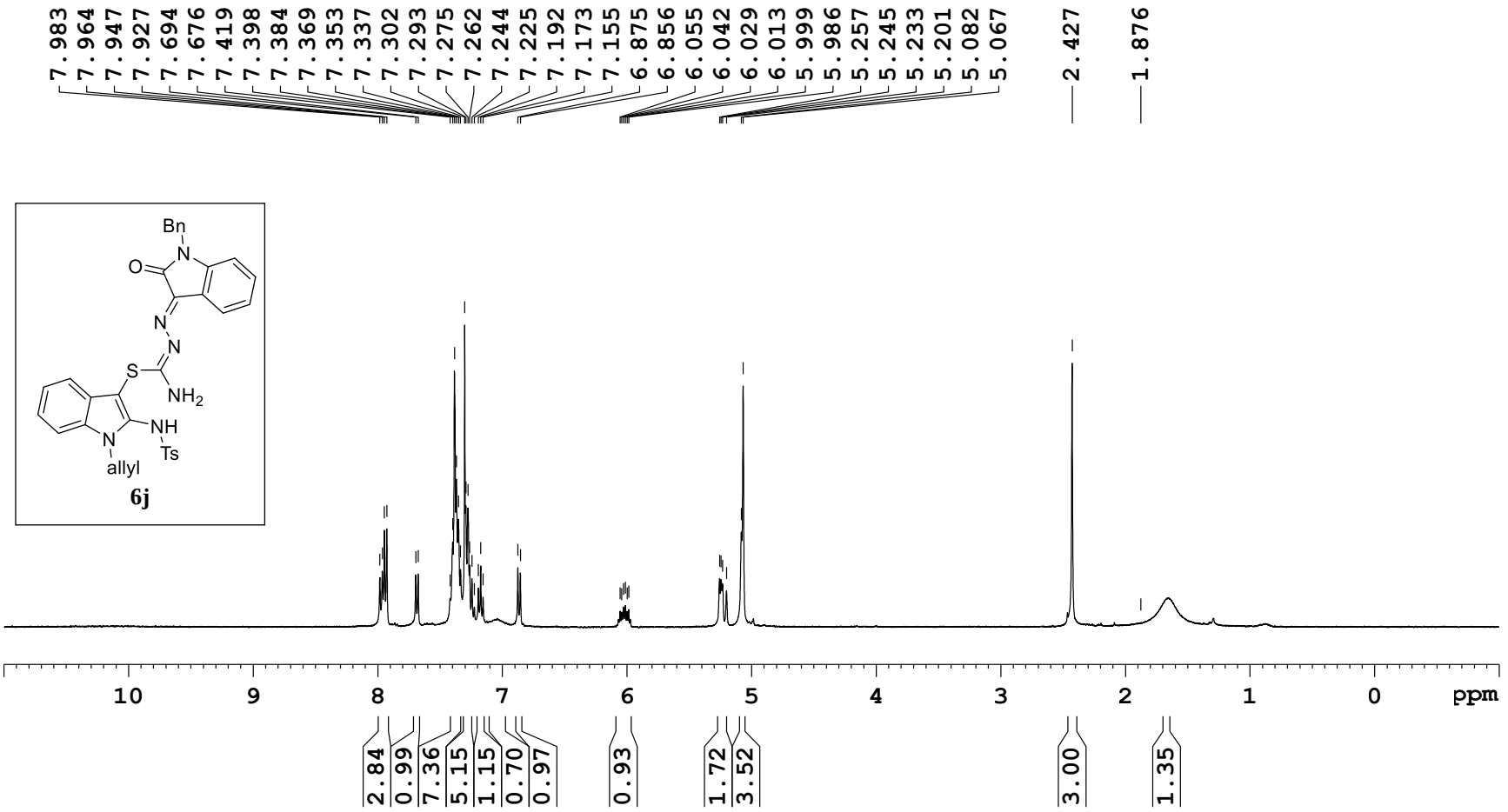
^{1}H NMR Spectrum of **6i**

1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl-N-phenyl-2-[(di-*p*-tolyl)methylidene]hydrazine-1-carboximidothioate (6i)



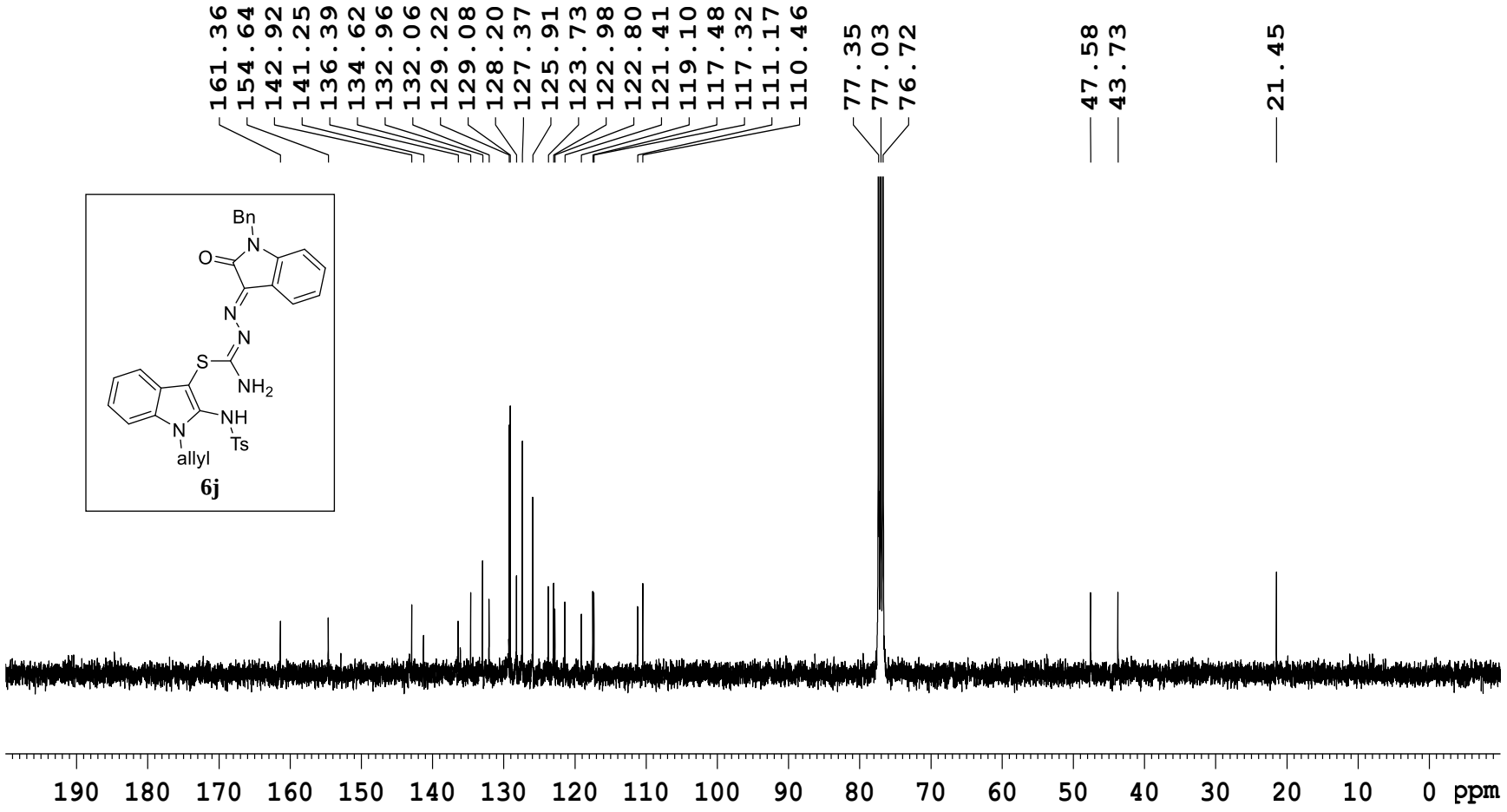
^{13}C NMR Spectrum of **6i**

1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-2[(1-benzyl-2-oxoindolin-3-ylidene)]hydrazine-1-carboximidothioate (6j)



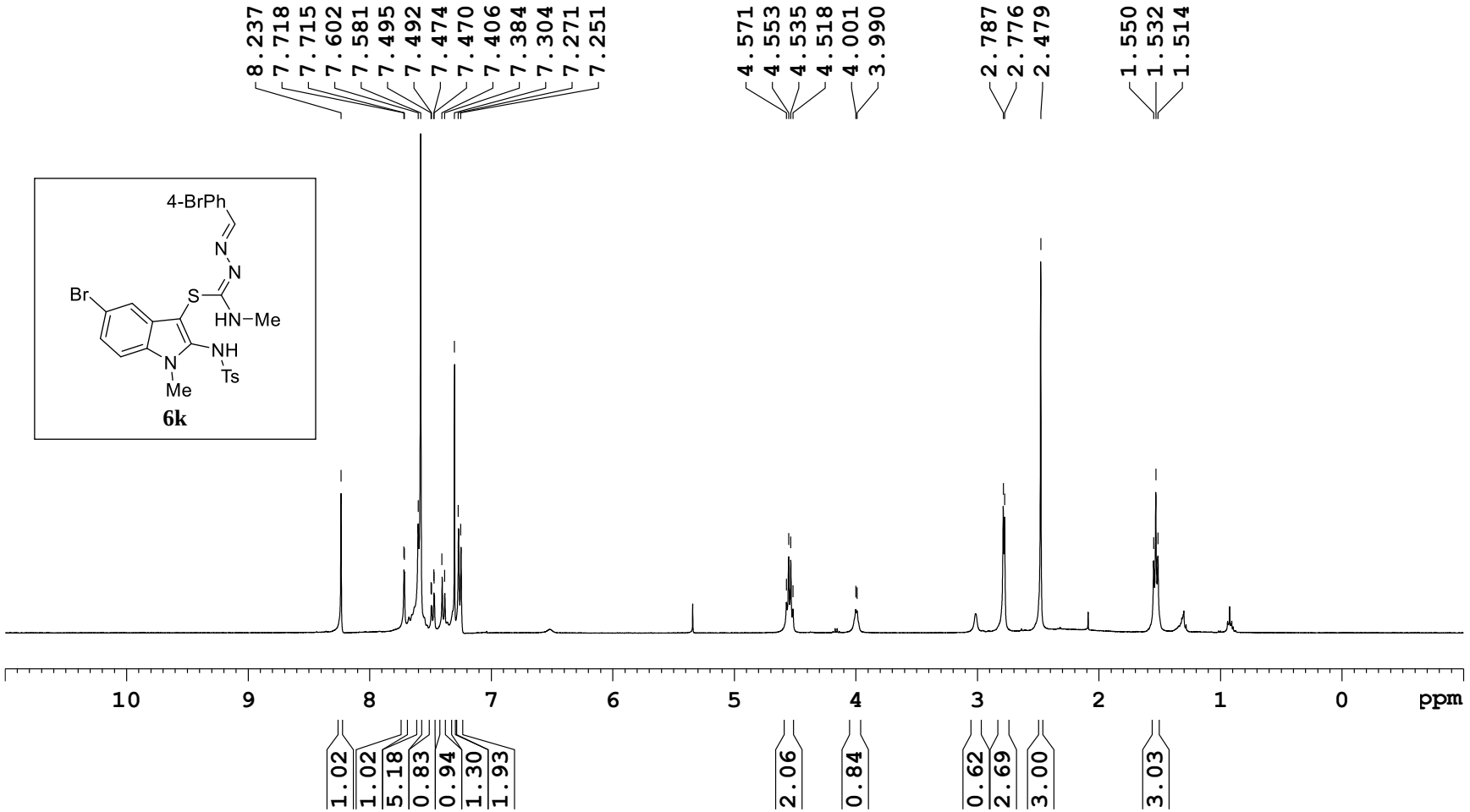
^{1}H NMR Spectrum of **6j**

1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-2[(1-benzyl-2-oxoindolin-3-ylidene)]hydrazine-1-carboximidothioate (6j)



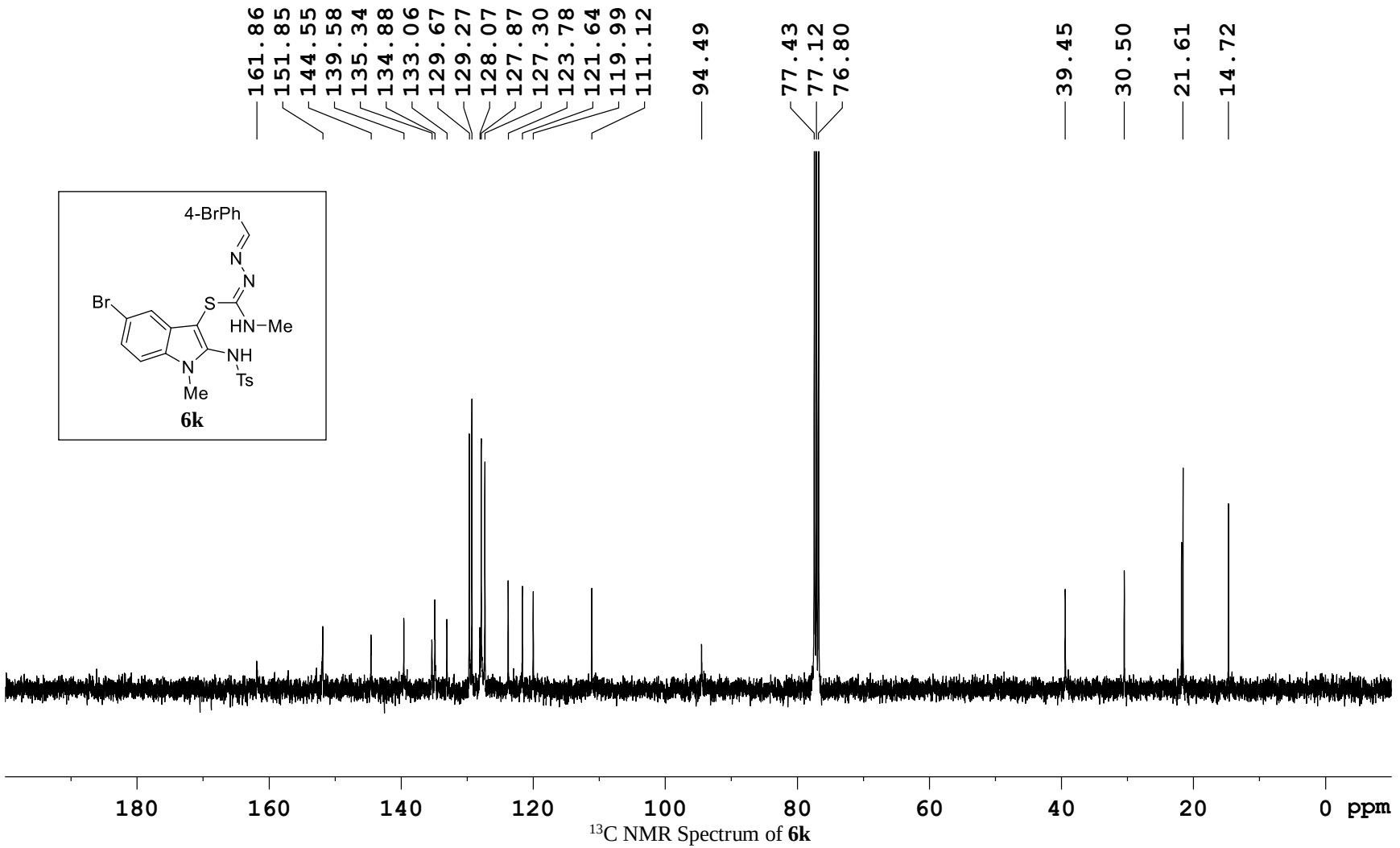
^{13}C NMR Spectrum of **6j**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-bromolphenyl)methylidene]hydrazine-1-carboximidothioate (6k)



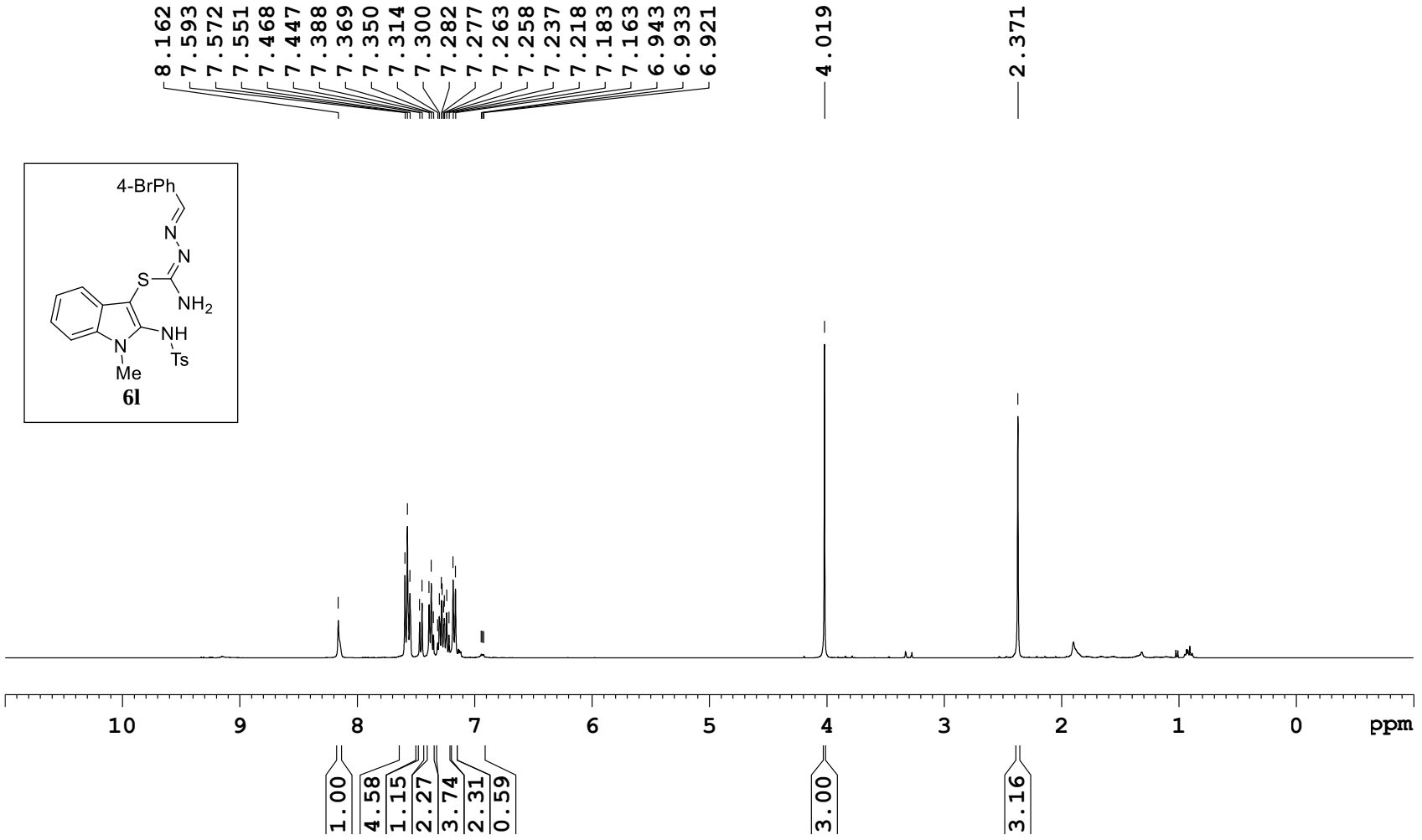
^{1}H NMR Spectrum of **6k**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-bromolphenyl)methylidene]hydrazine-1-carboximidothioate (6k)



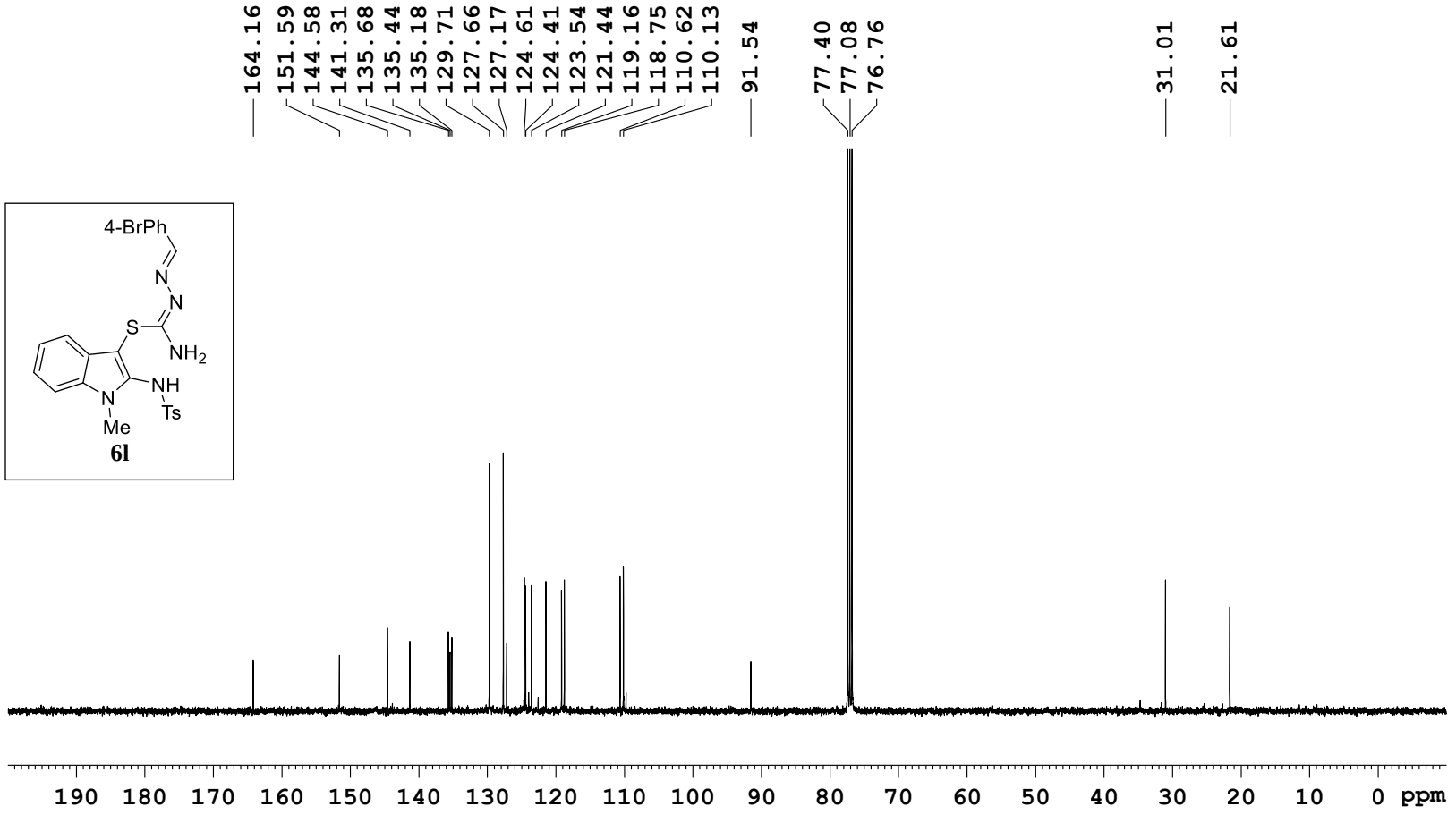
^{13}C NMR Spectrum of **6k**

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)--2[(4-bromophenyl)methylidene]hydrazine-1-carboximidothioate (6l)



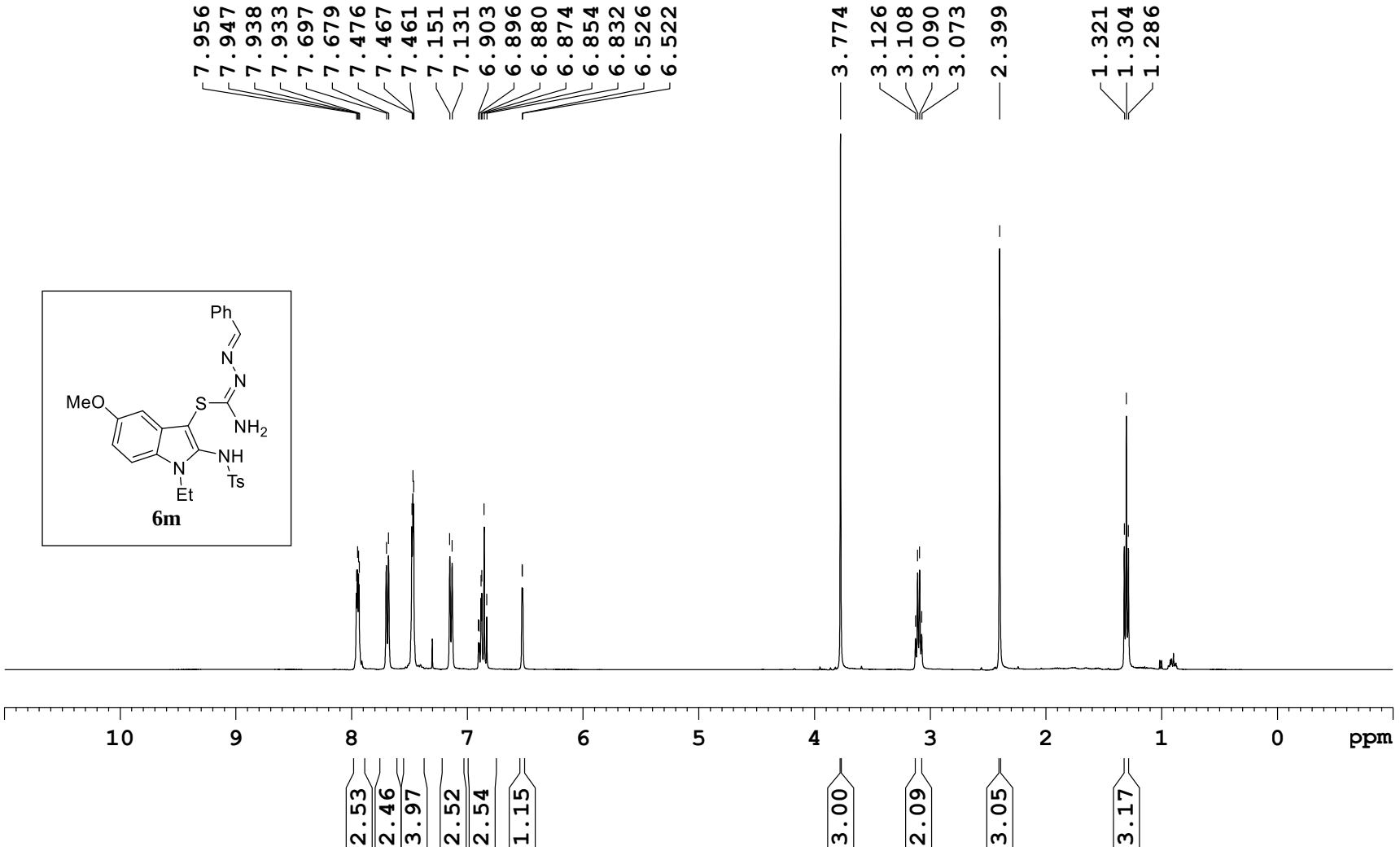
^{1}H NMR Spectrum of **6l**

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)--2[(4-bromophenyl)methylidene]hydrazine-1-carboximidothioate (6l)



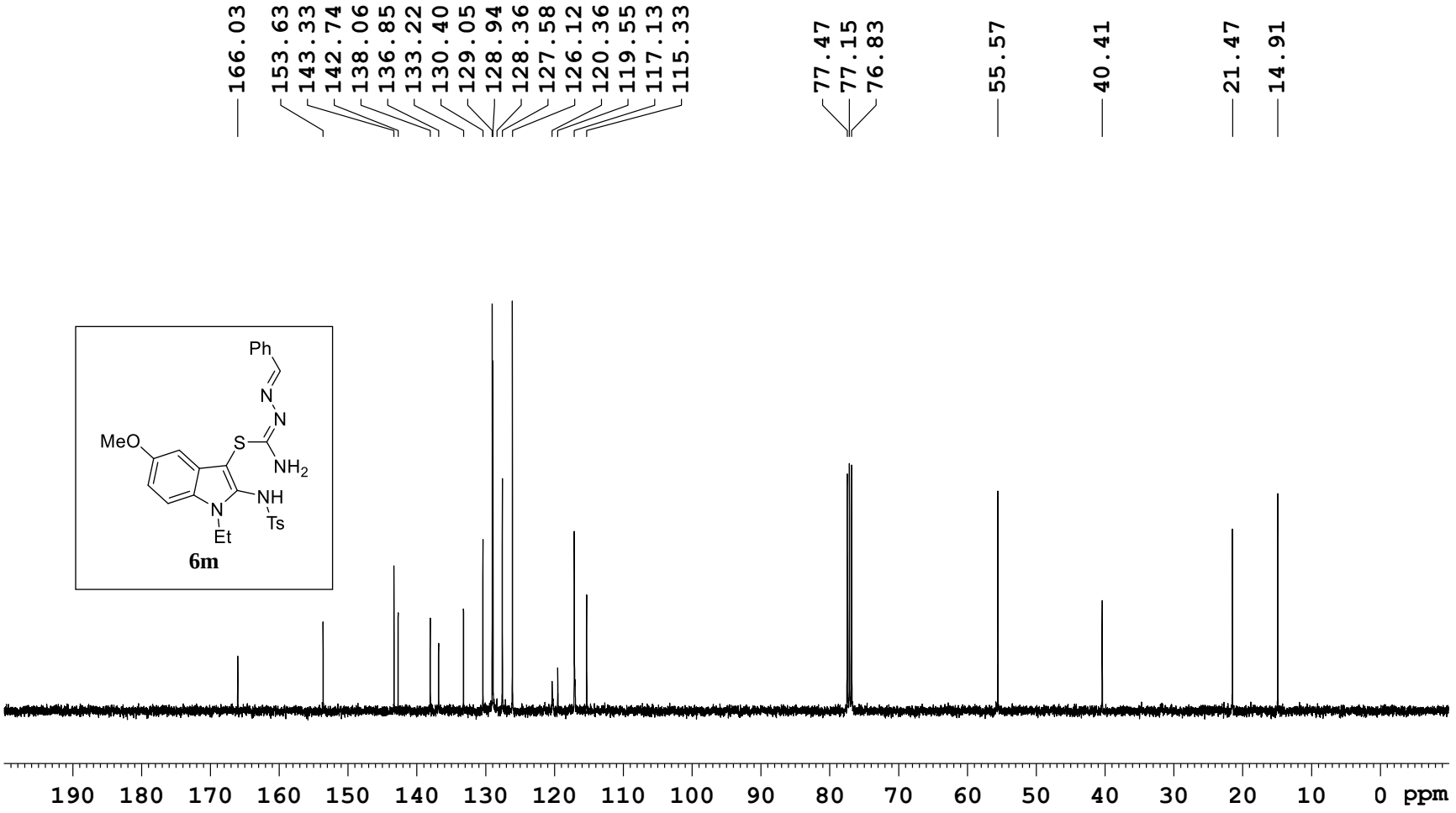
^{13}C NMR Spectrum of **6l**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl(2*E*)-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6m)



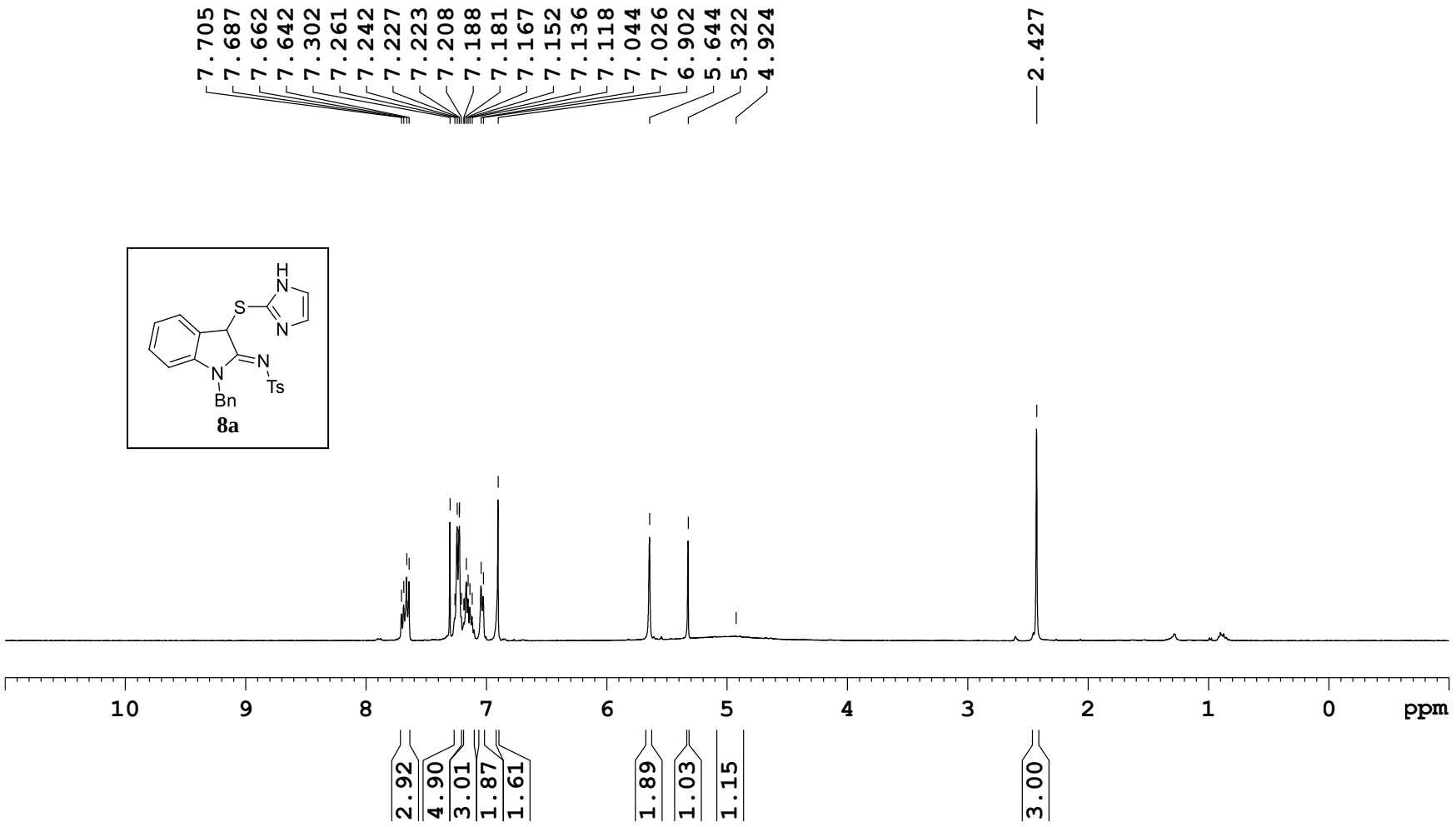
^{1}H NMR Spectrum of **6m**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl(2*E*)-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6m)



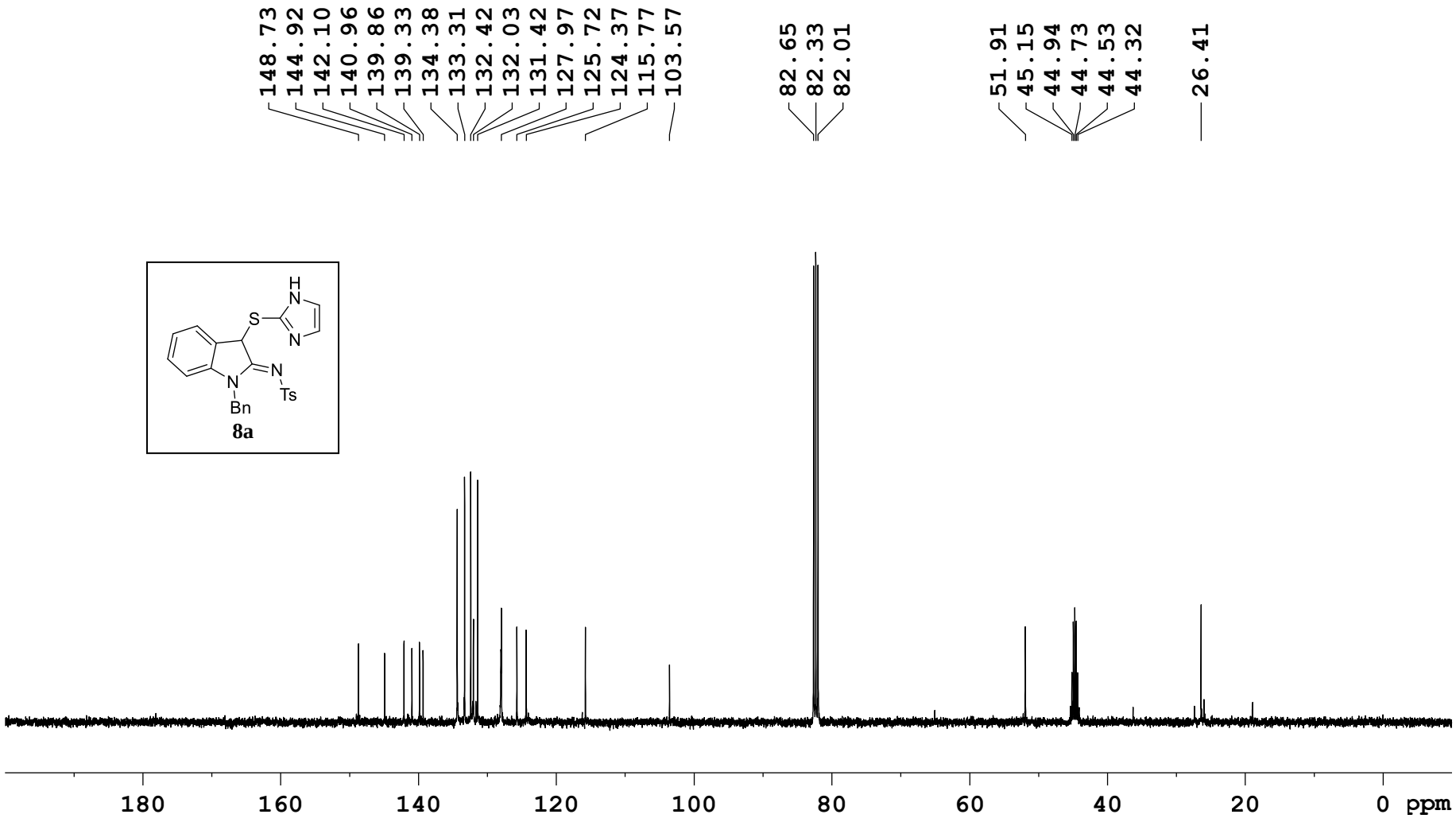
^{13}C NMR Spectrum of **6m**

N-{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1H-indol-2-yl}4-methylbenzenesulfonamide (8a)



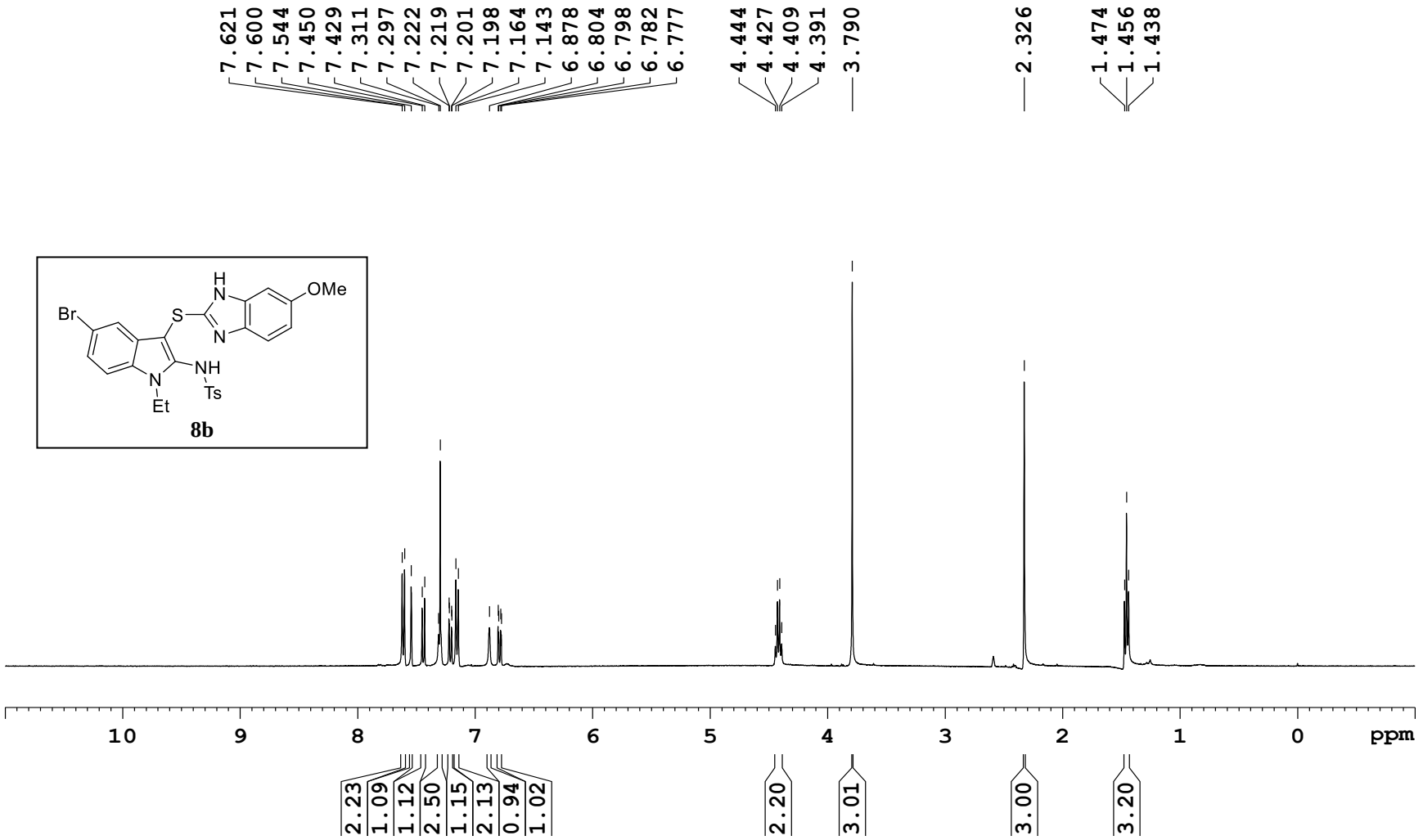
^{1}H NMR Spectrum of **8a**

N-{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8a)



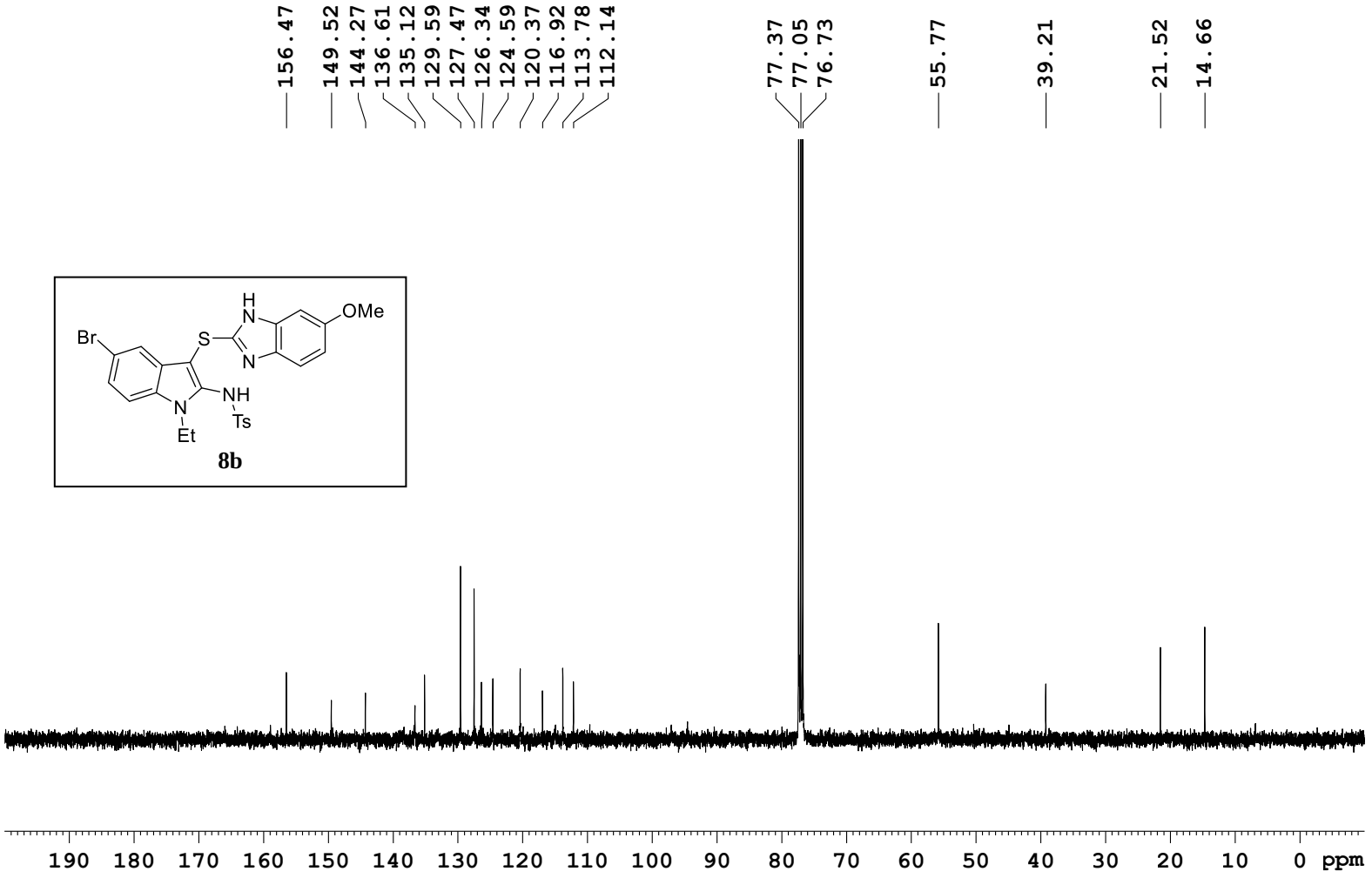
^{13}C NMR Spectrum of **8a**

N-{1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-bromo-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8b)



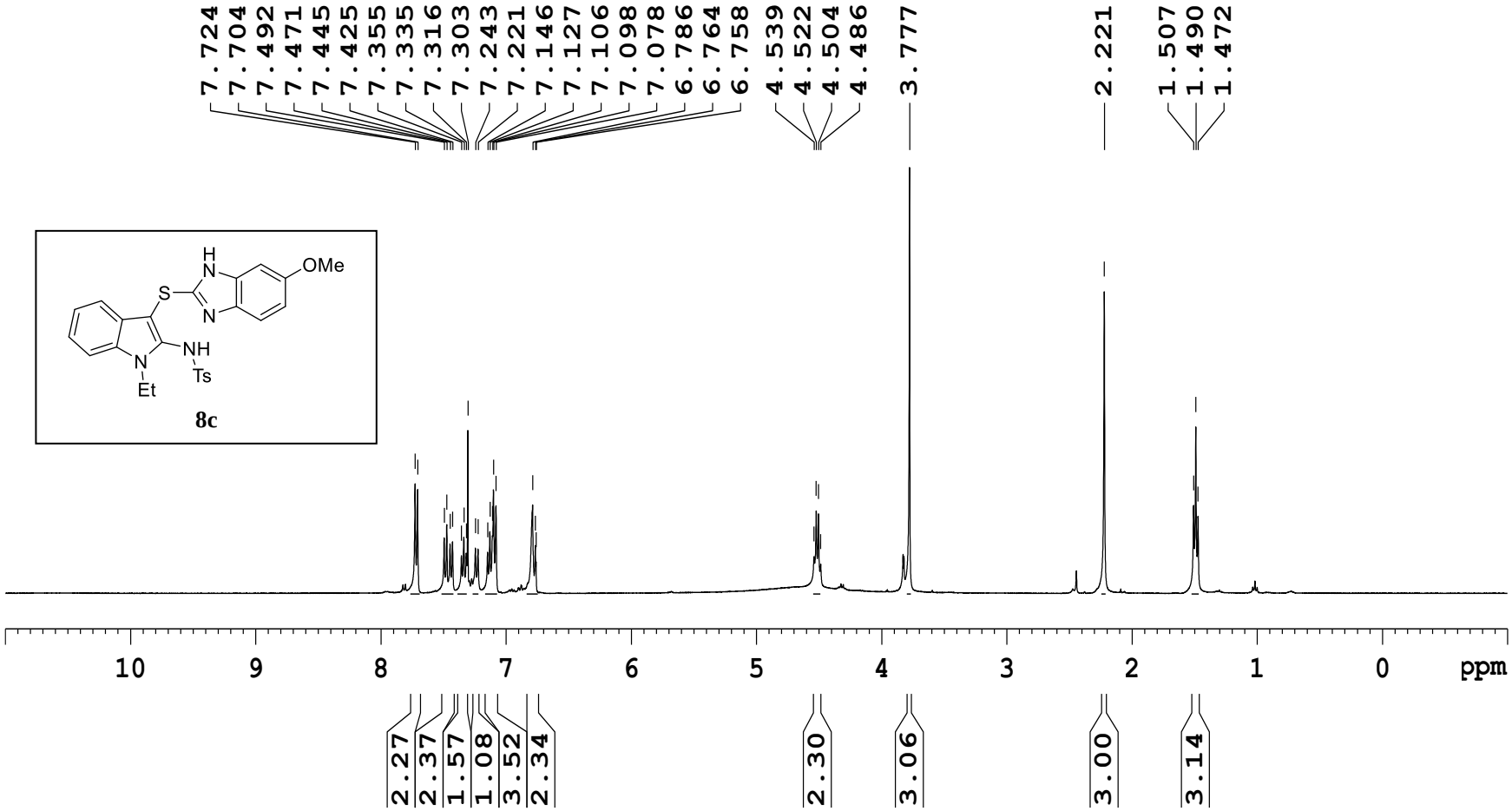
^{1}H NMR Spectrum of **8b**

N-{1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-bromo-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8b)



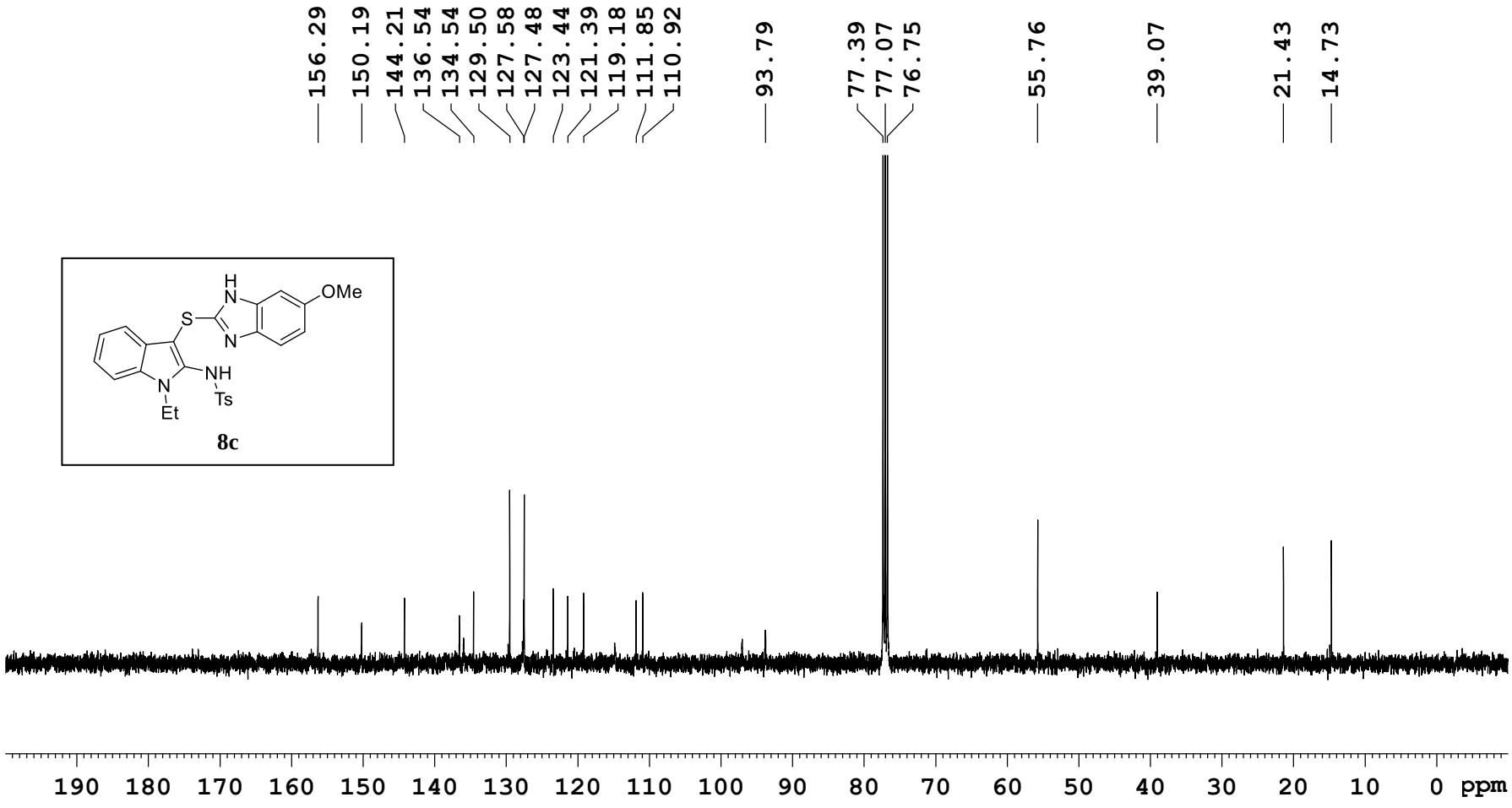
^{13}C NMR Spectrum of **8b**

N-{1-Ethyl-3-[(5-methoxy-1-H-benzo[d]imidazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8c)



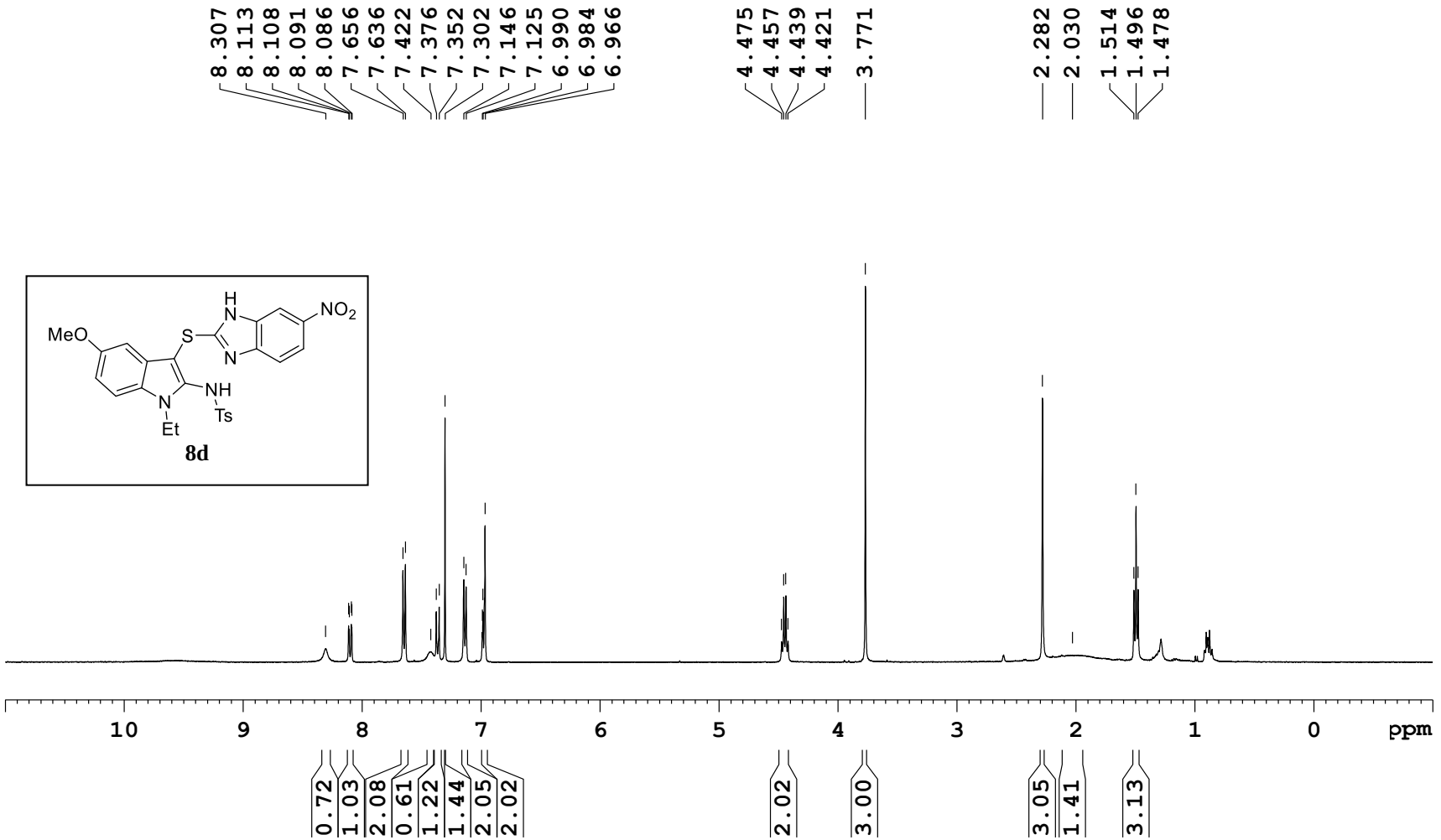
^{1}H NMR Spectrum of **8c**

N-{1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4 methylbenzenesulfonamide (8c)



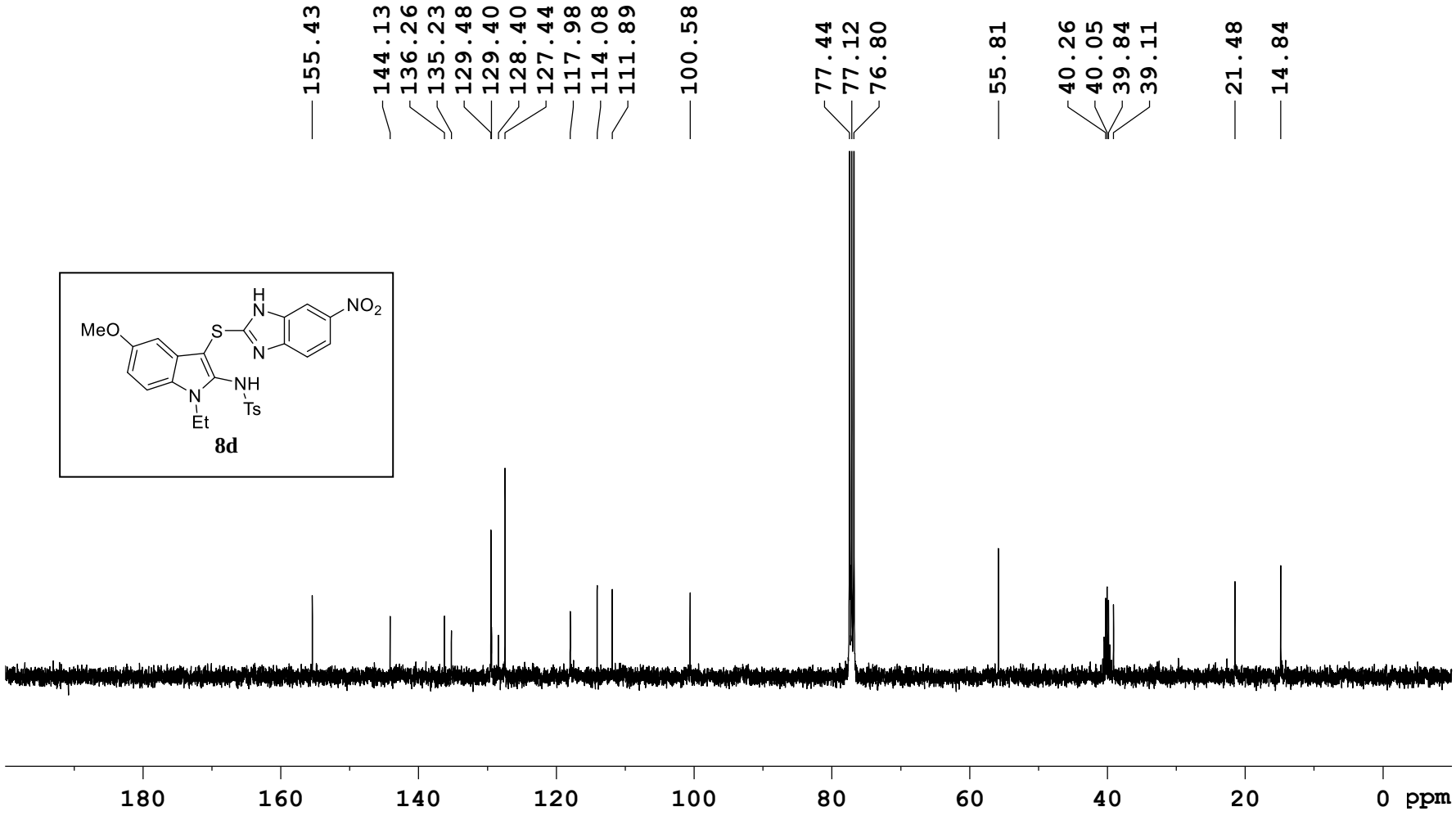
^{13}C NMR Spectrum of **8c**

N-{1-Ethyl-3-[(5-nitro-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-methoxy-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8d)



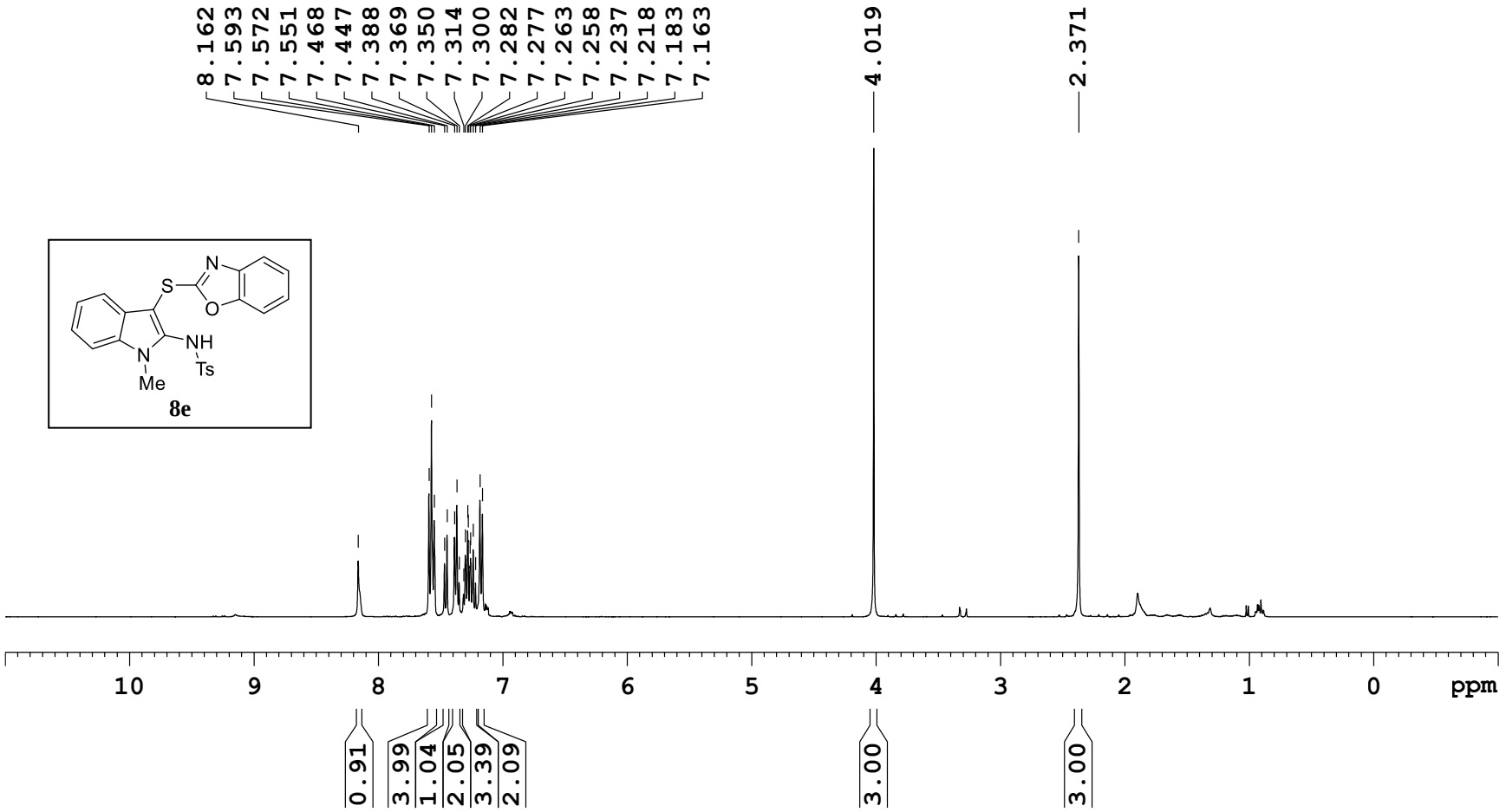
^{1}H NMR Spectrum of **8d**

N-{1-Ethyl-3-[(5-nitro-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-methoxy-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8d)



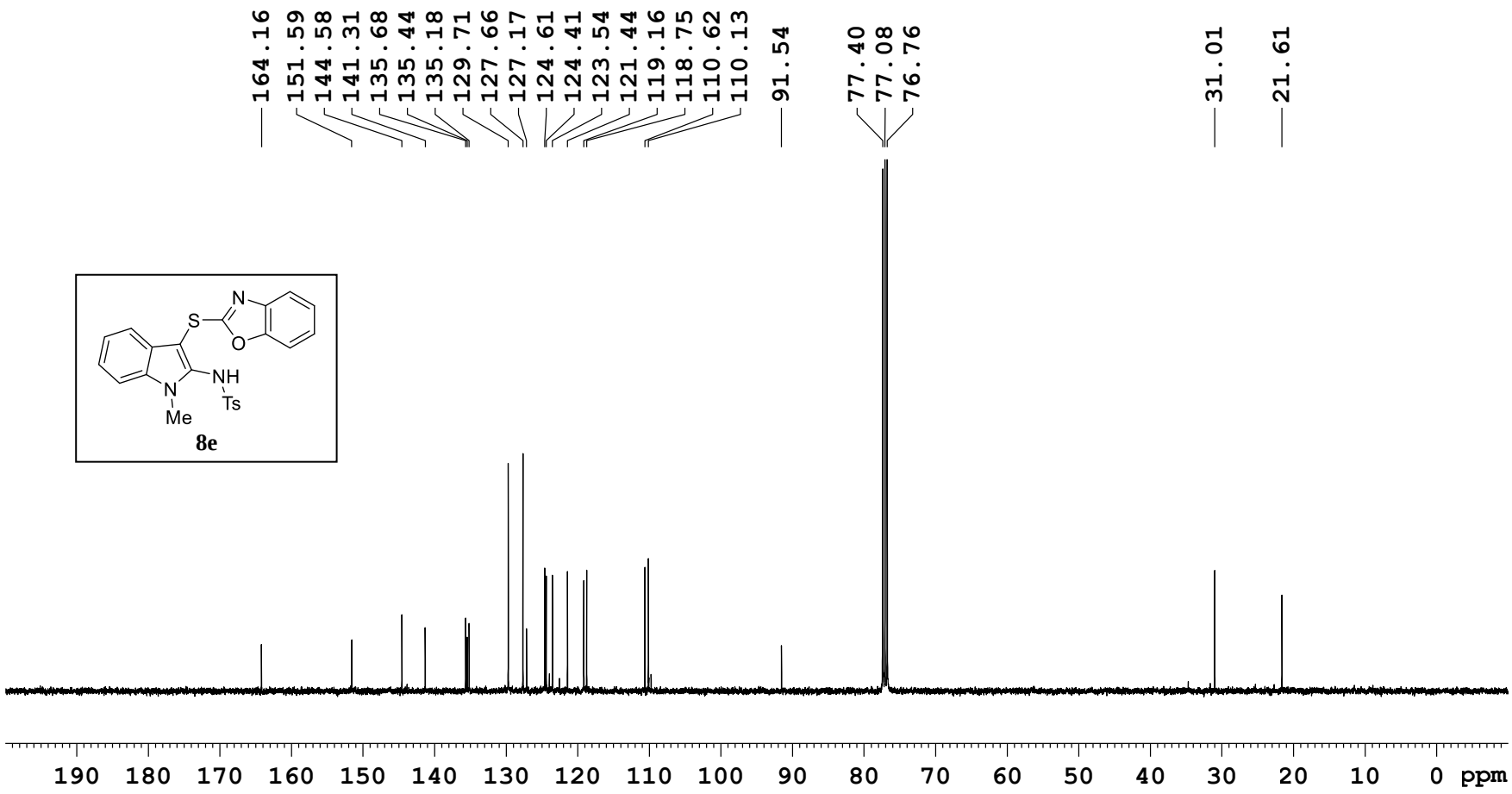
^{13}C NMR Spectrum for **8d**

N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8e)



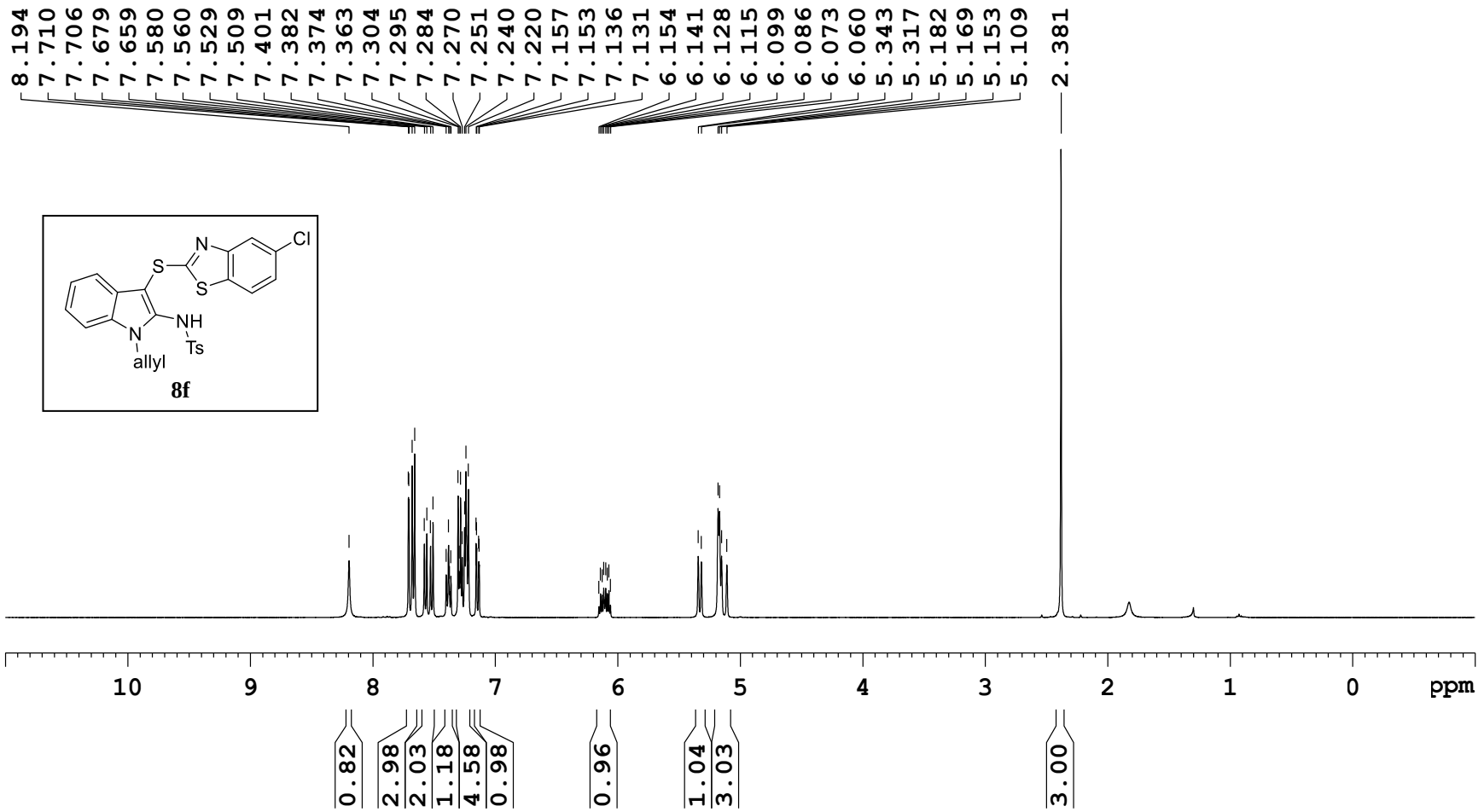
^{1}H NMR Spectrum of **8e**

N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8e)



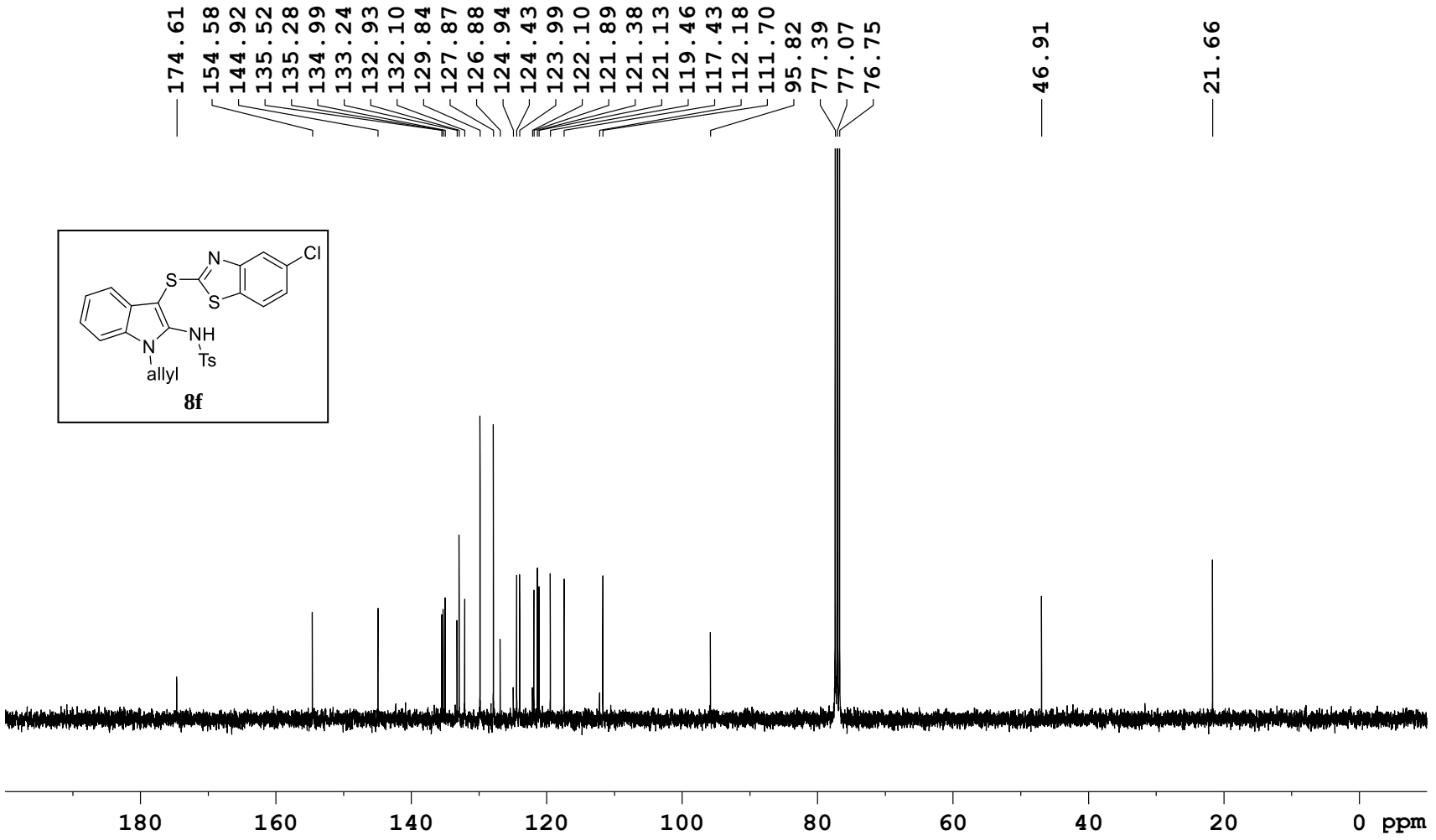
^{13}C NMR Spectrum of **8e**

N-{1-Allyl-3-[(5-chloro-1H-benzo[d]thiazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8f)



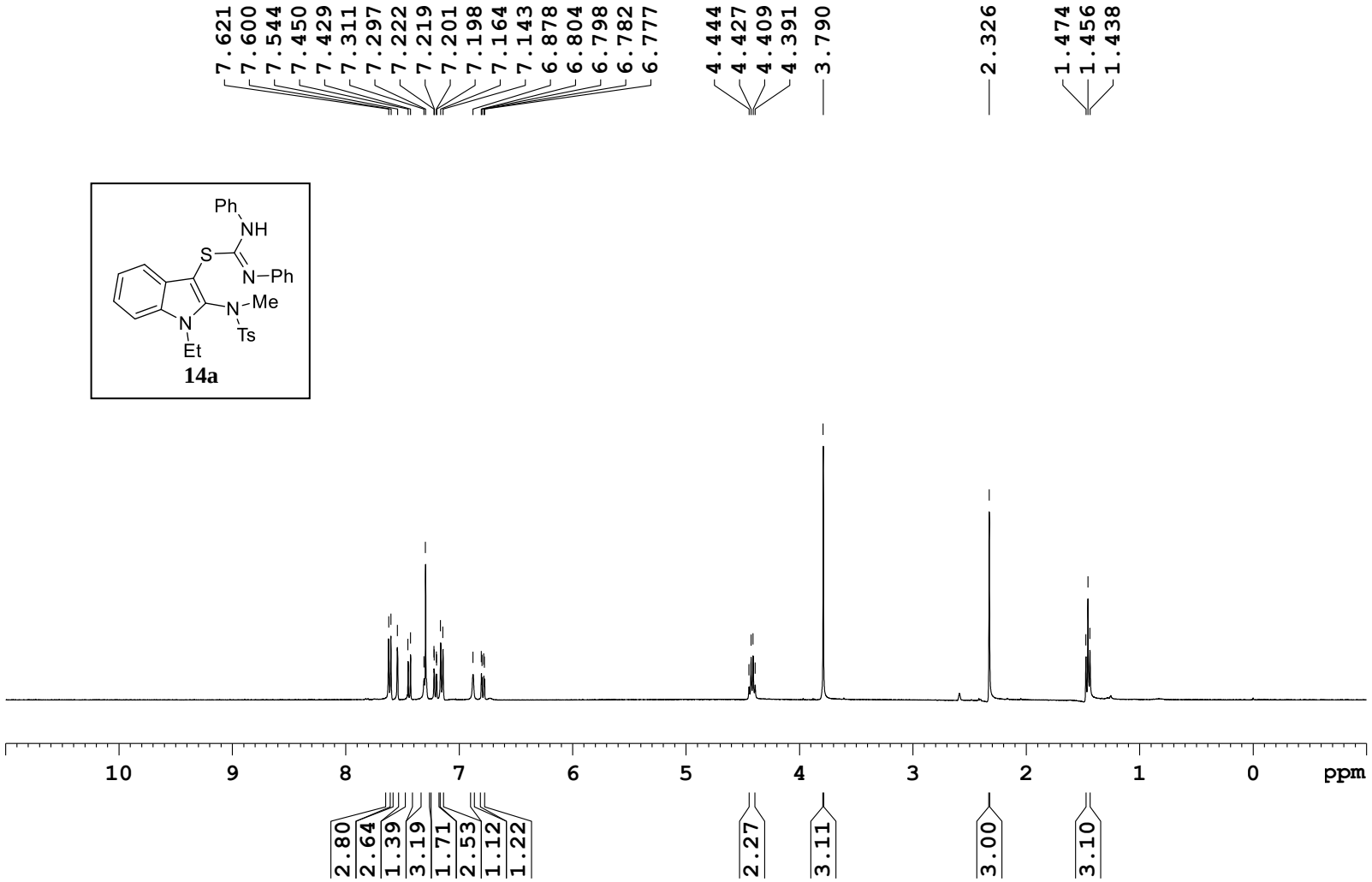
^{1}H NMR Spectrum of **8f**

N-{1-Allyl-3-[(5-chloro-1H-benzo[d]thiazol-2-yl)sulfanyl]-1H-indol-2-yl}-4-methylbenzenesulfonamide (8f)



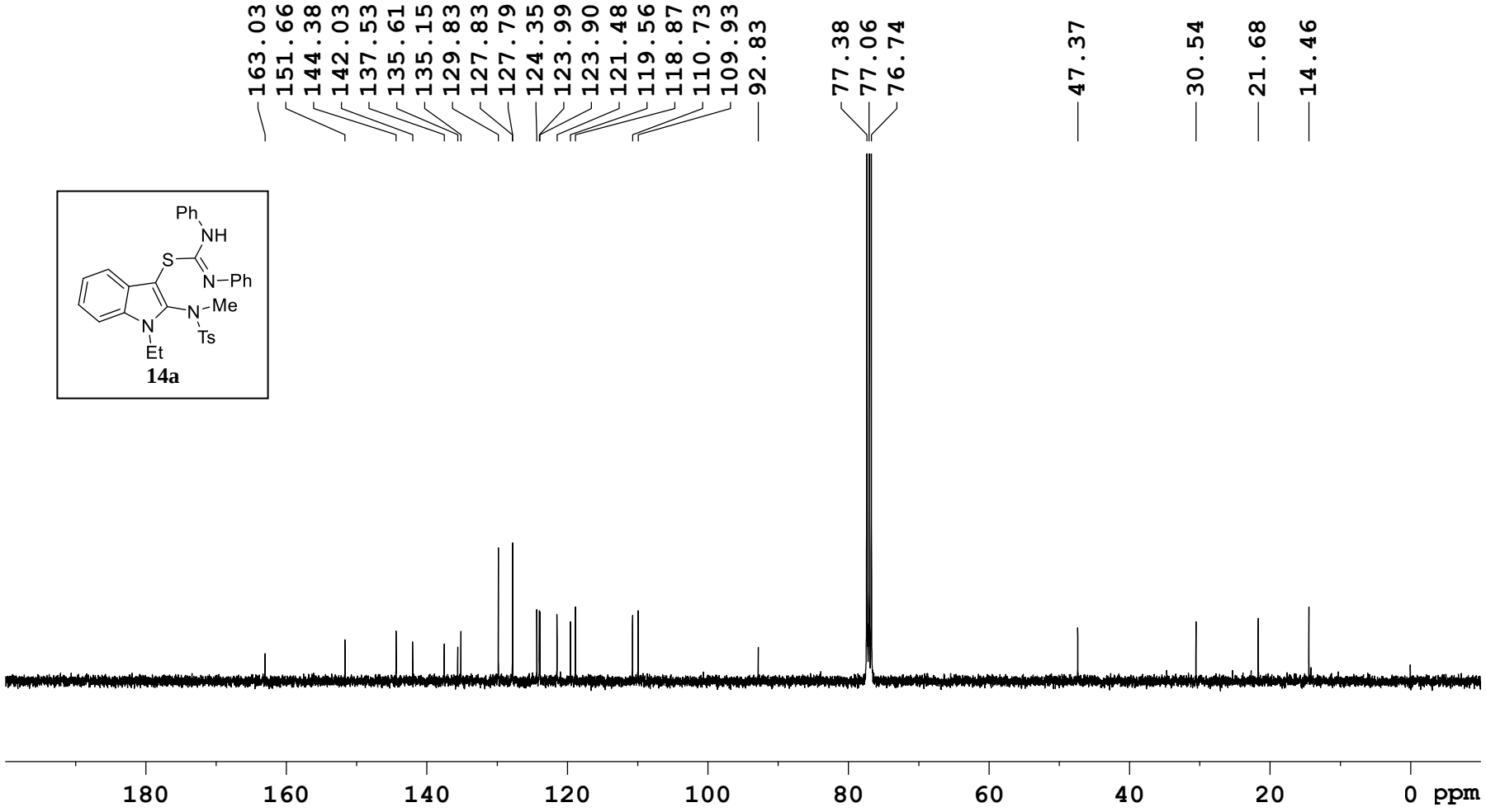
^{13}C NMR Spectrum of **8f**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)methylamino]-1*H*-indol-3-yl *N,N'*-diphenylcarbamimidothioate (14a)



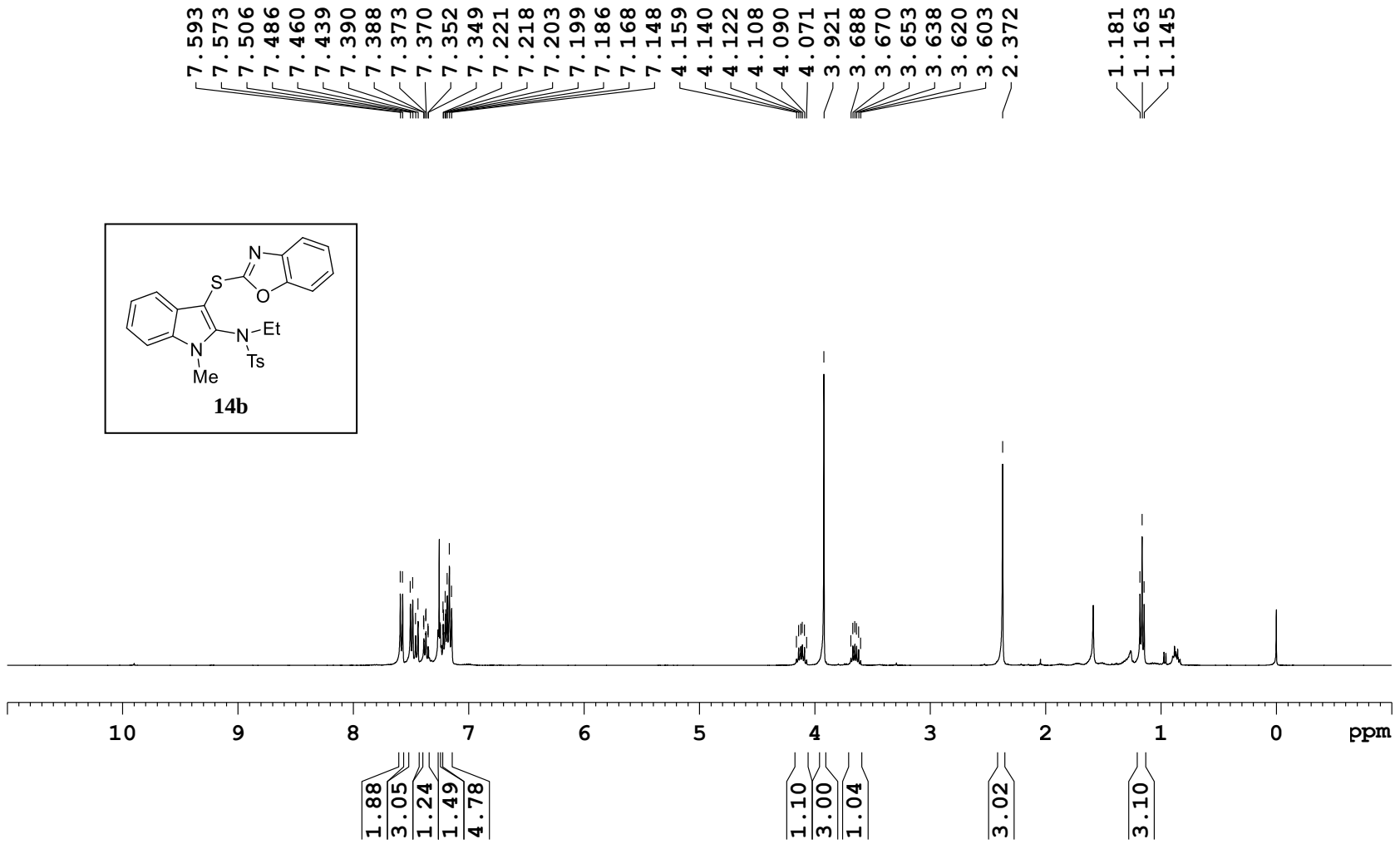
^{1}H NMR Spectrum of **14a**

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)methylamino]-1*H*-indol-3-yl *N,N'*-diphenylcarbamimidothioate (14a)



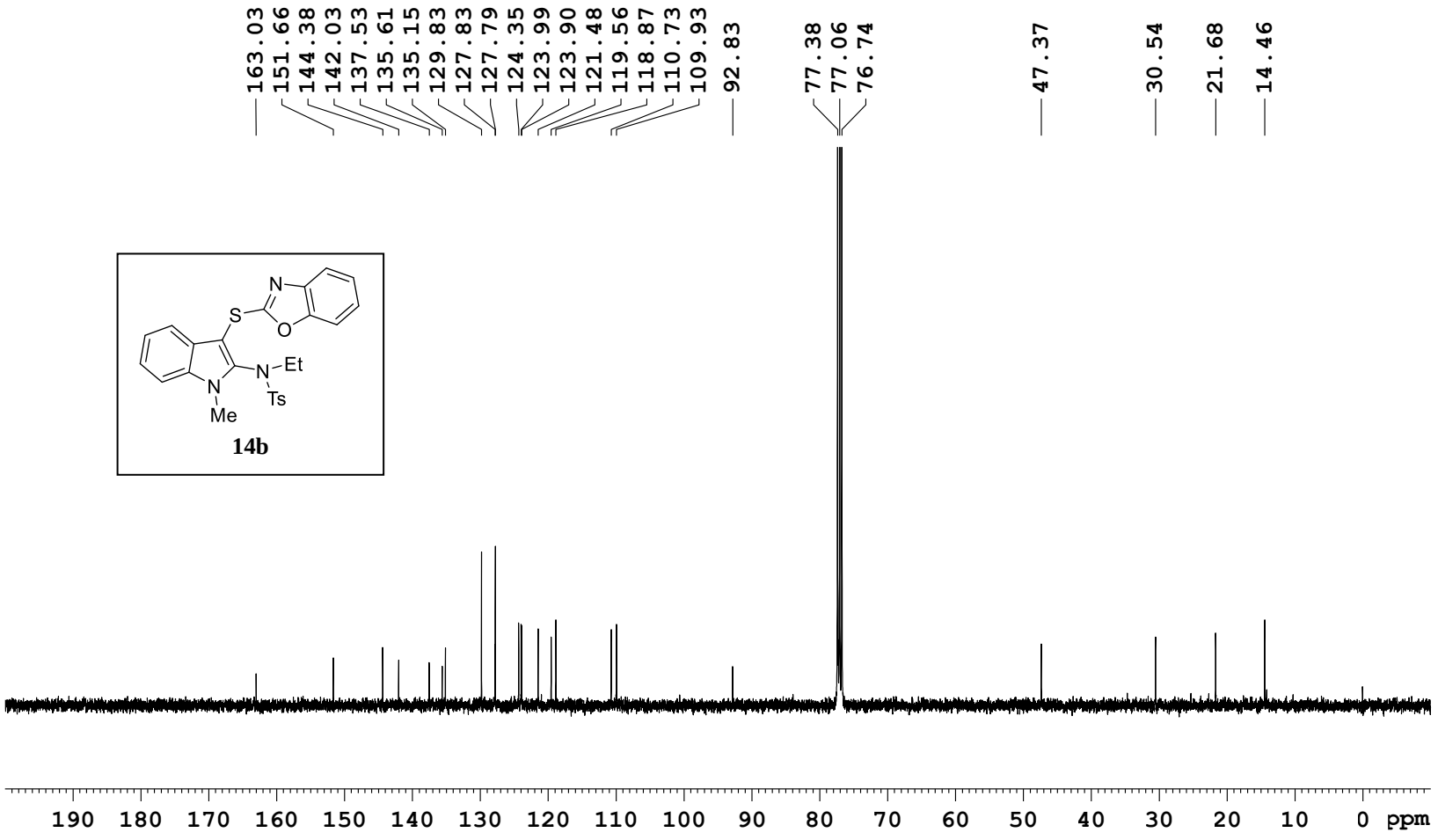
^{13}C NMR Spectrum of **14a**

N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-N-ethyl-4-methylbenzenesulfonamide (14b)



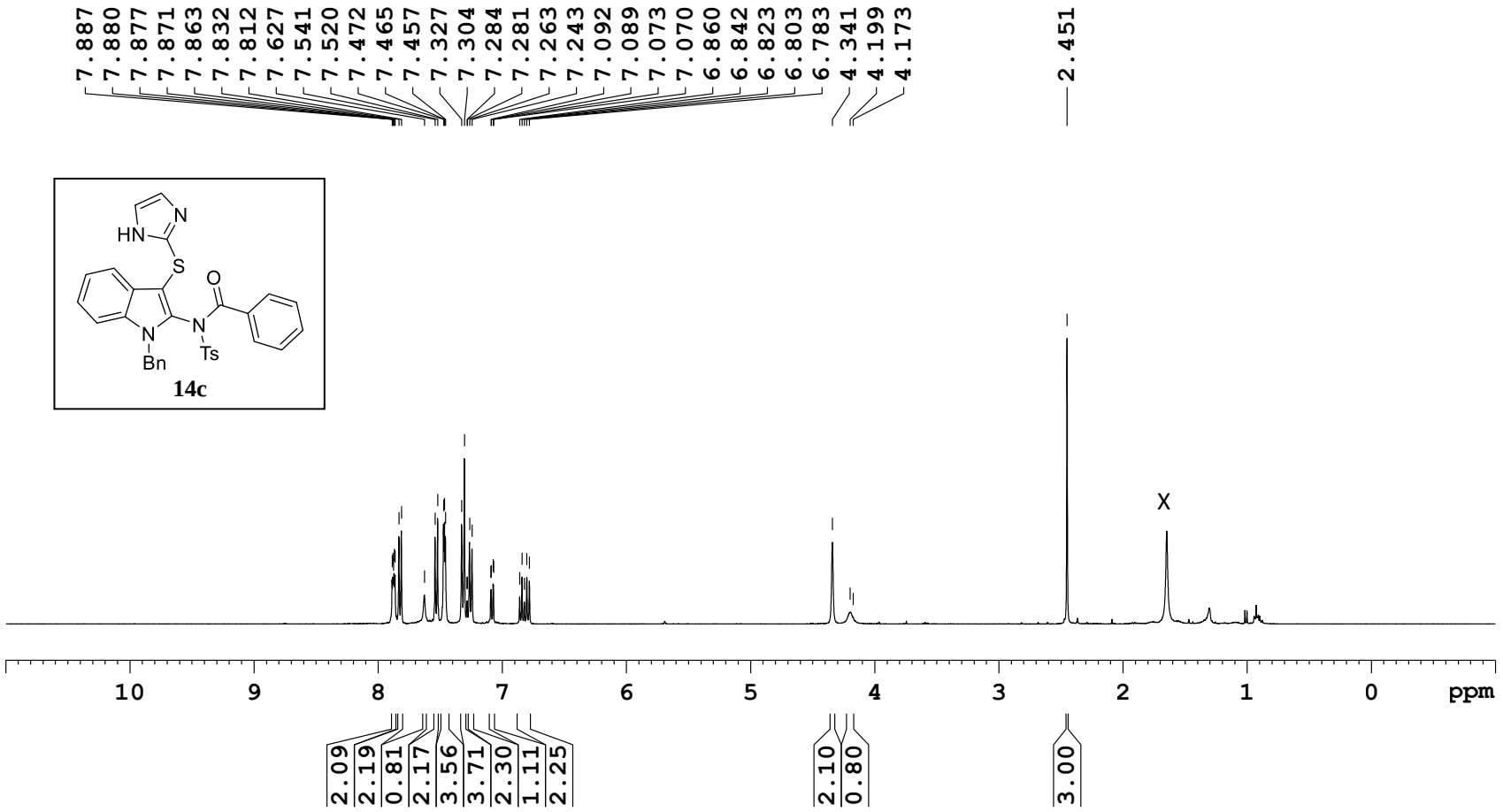
^{1}H NMR Spectrum of **14b**

N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-N-ethyl-4-methylbenzenesulfonamide (14b)



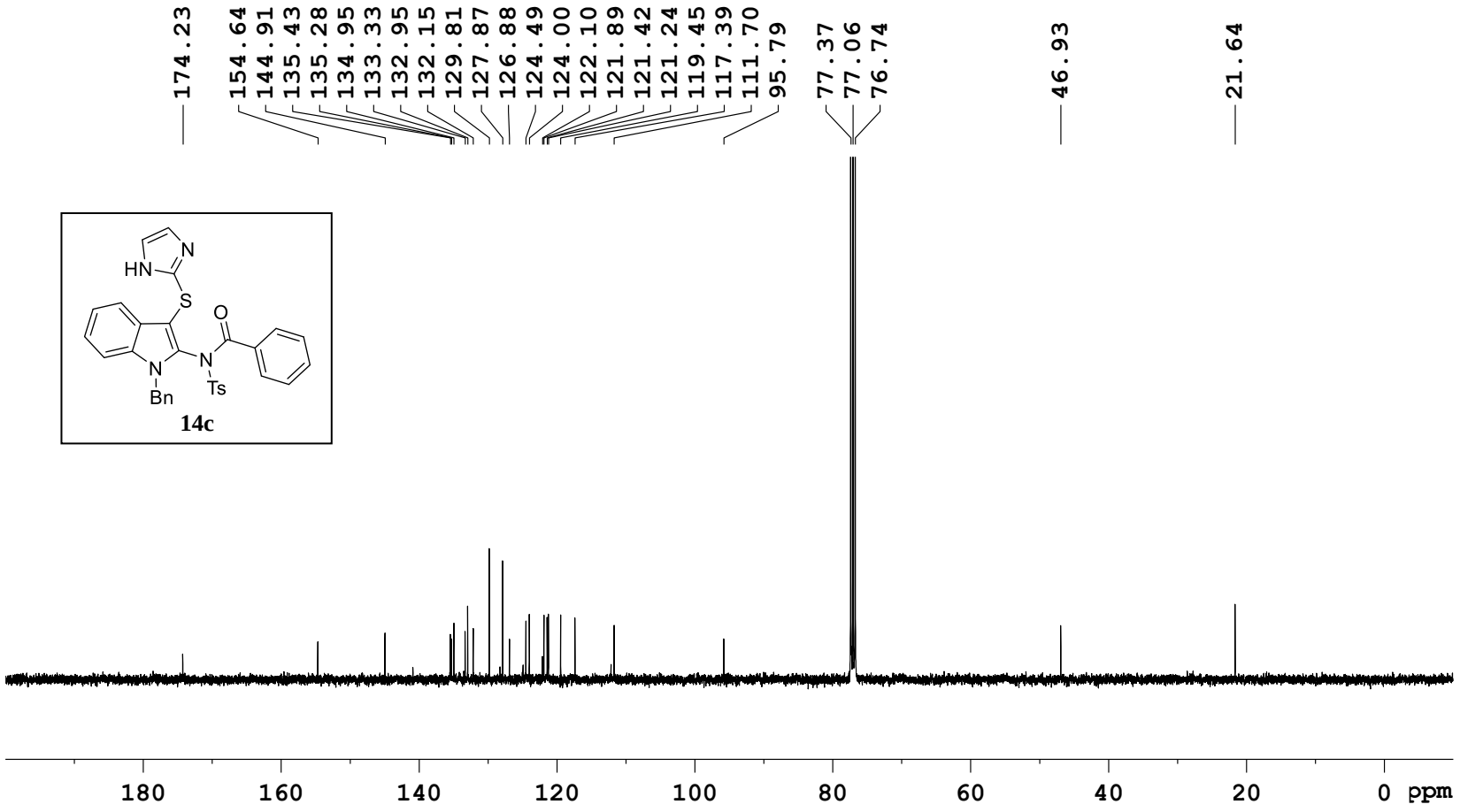
^{13}C NMR Spectrum of **14b**

N-{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-N-benzenecarbonyl-4-methylbenzenesulfonamide (14c)



^{1}H NMR Spectrum of **14c**

N-{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-N-benzenecarbonyl-4-methylbenzenesulfonamide (14c)



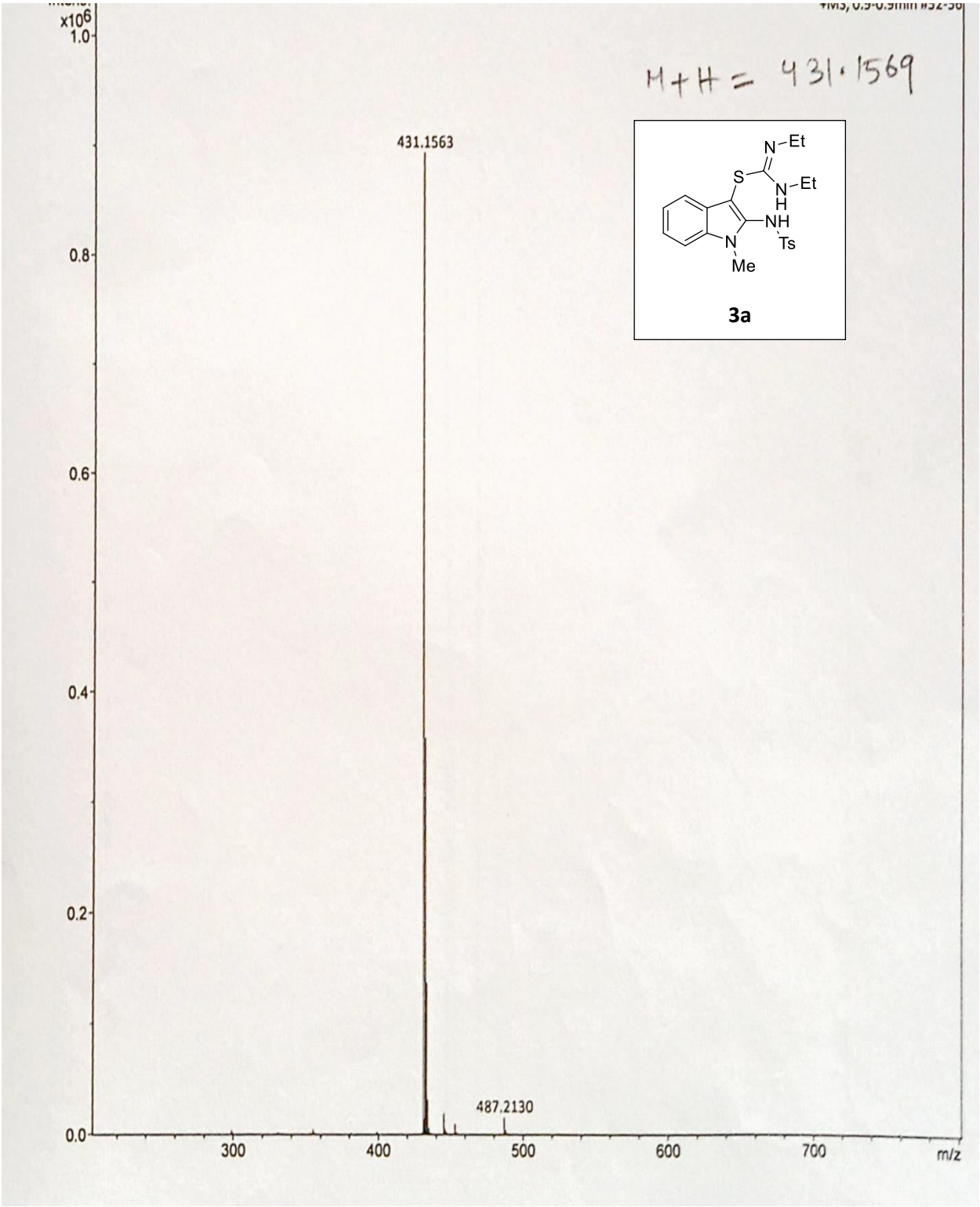
^{13}C NMR Spectrum of **14c**

$BF_3 \cdot OEt_2$Catalyzed S-H insertion reactions of α-diazoimidamides and enolizablethioamides under metal-free conditions

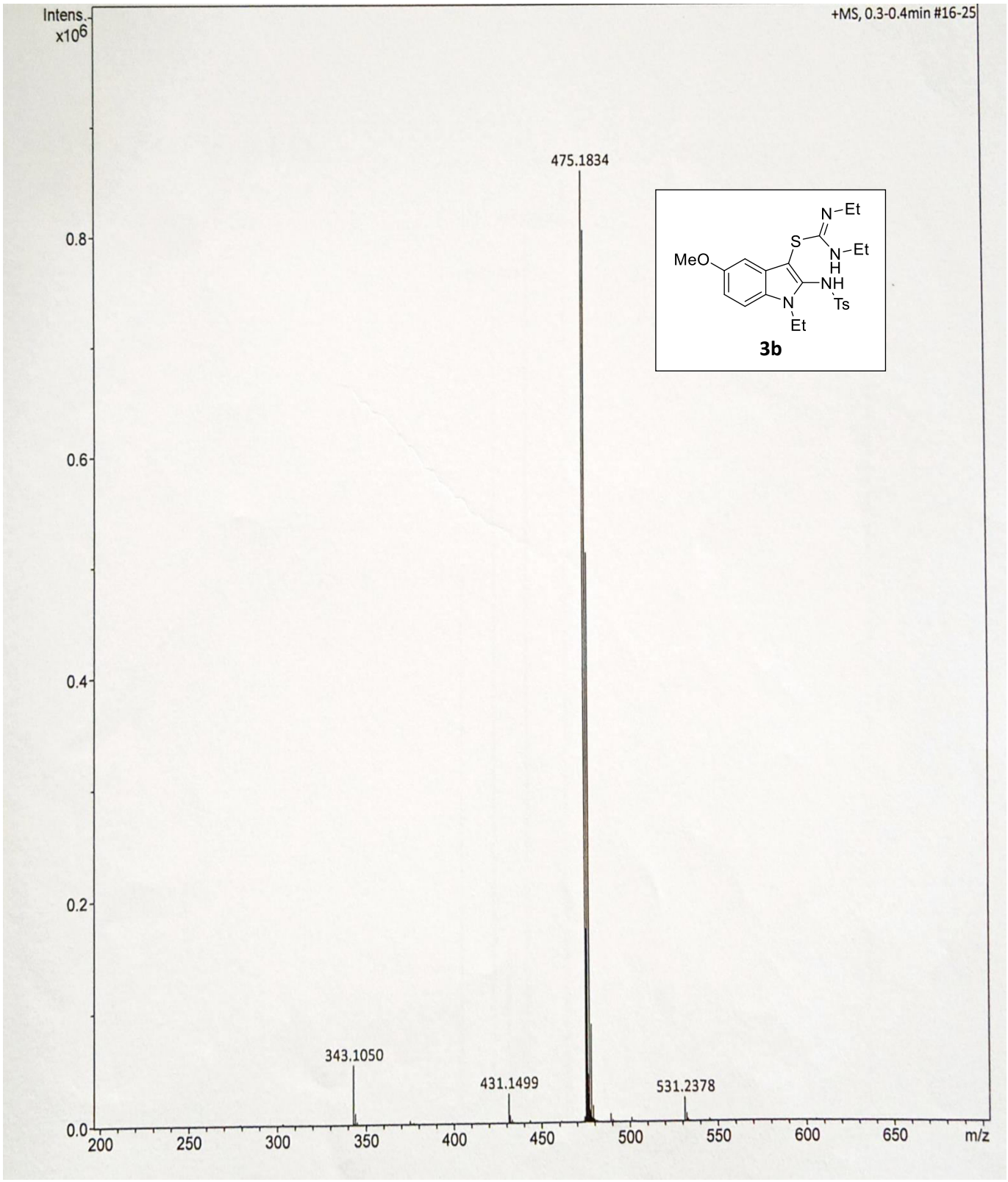
Supporting Information

HRMS spectra

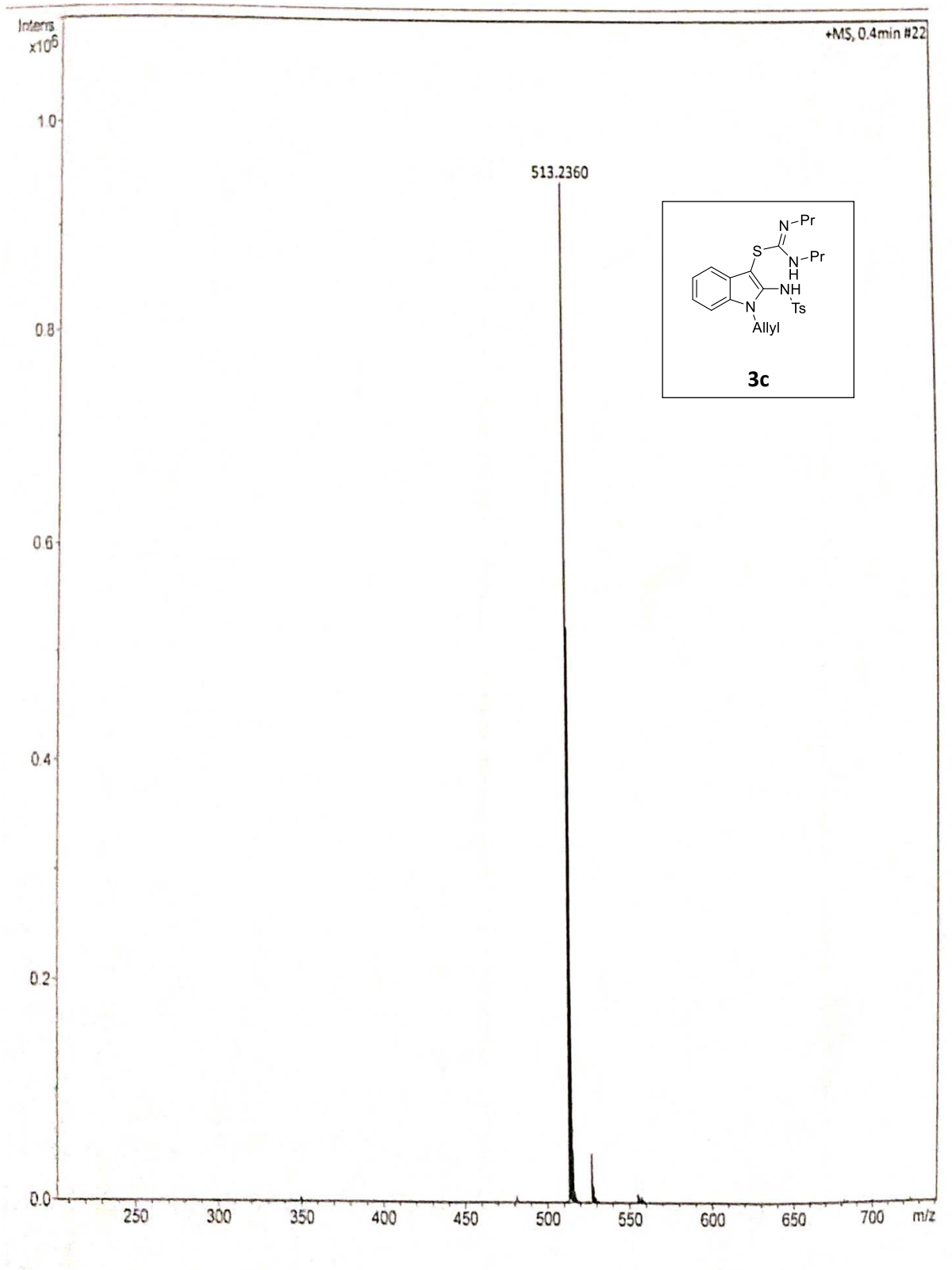
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-diethylcarbamimidothioate (3a)



1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl *N,N′*-diethylcarbamimidothioate (3b)

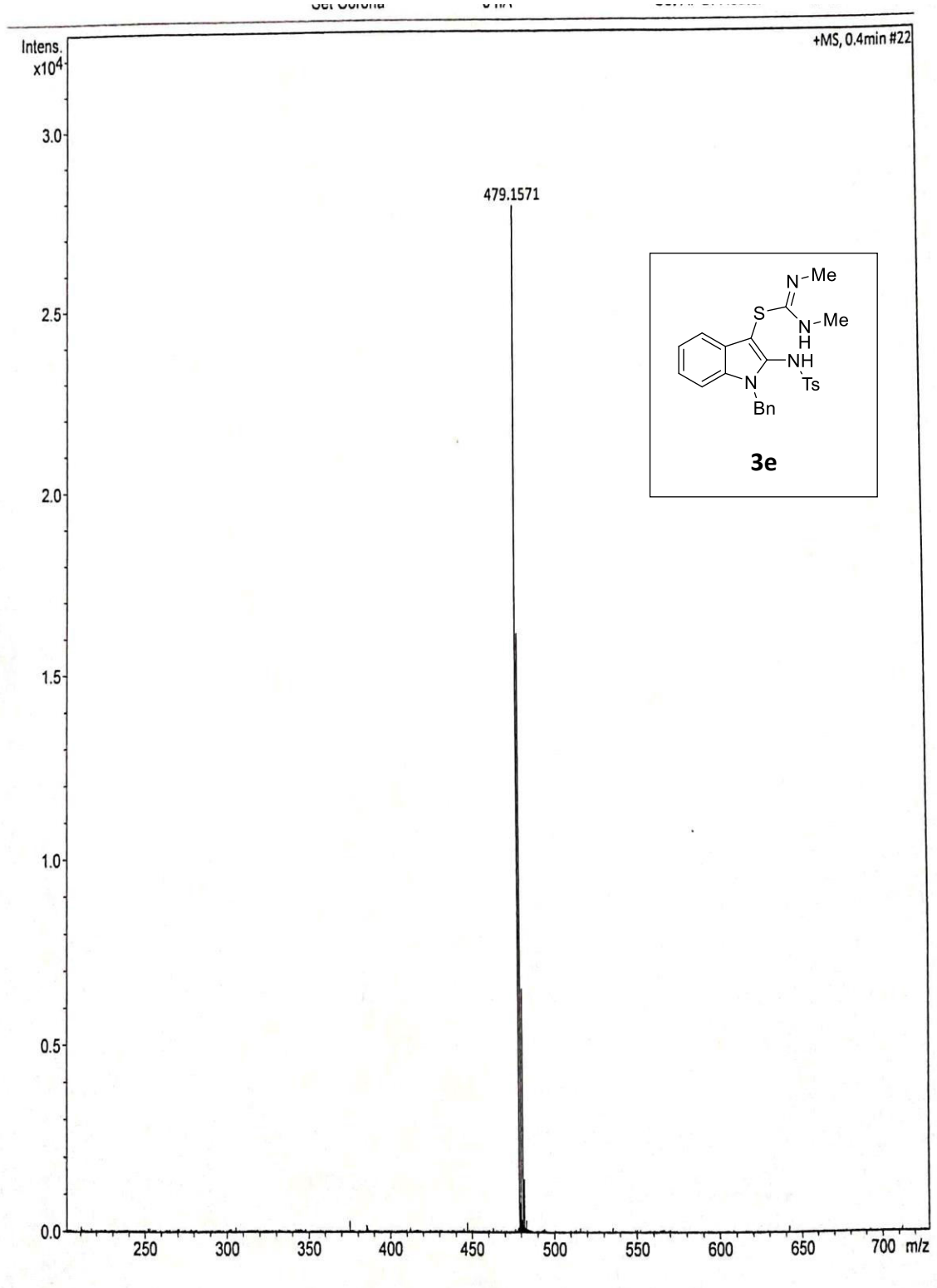


1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N′*-dibutylcarbamimido thioate (3c)

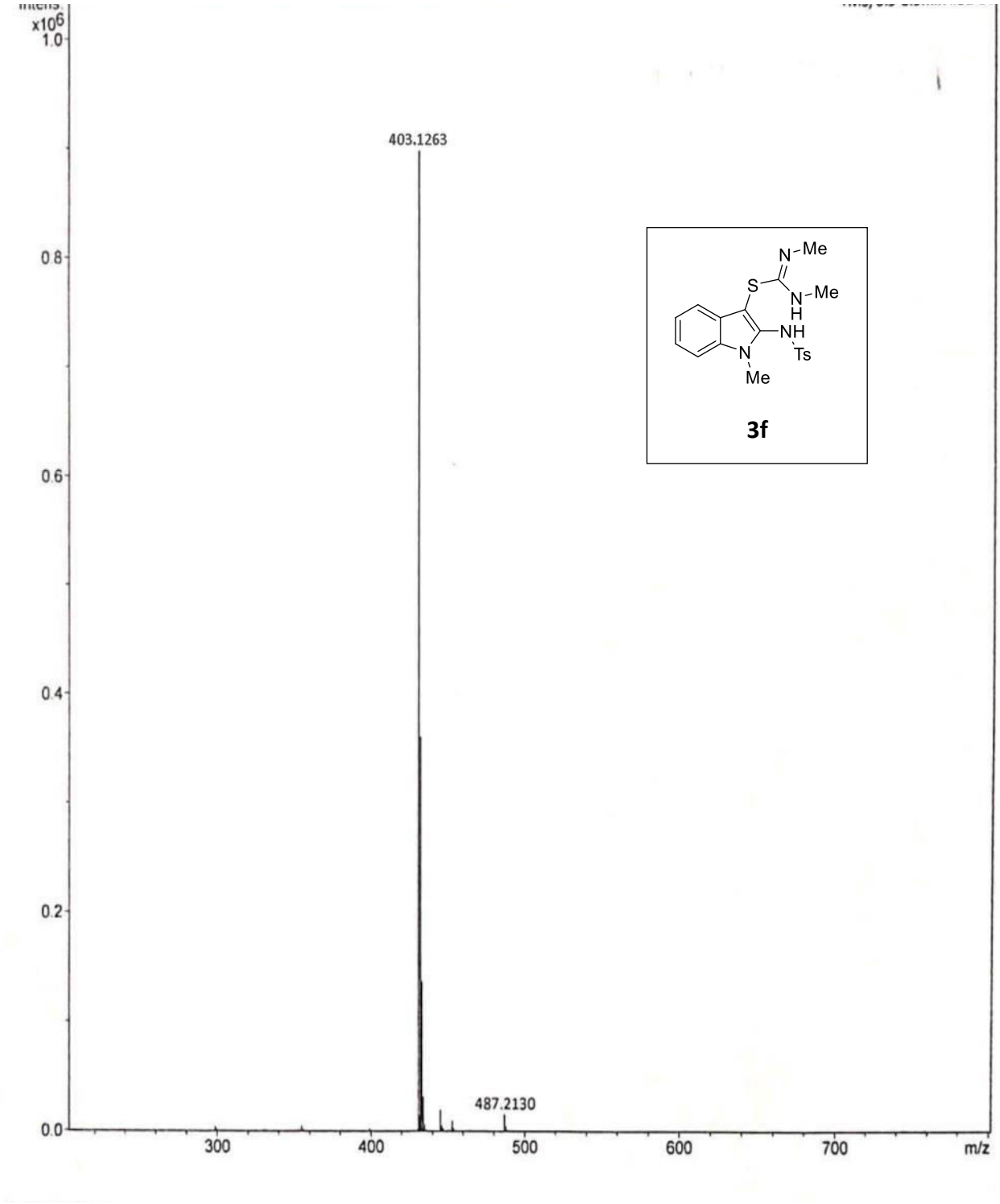


1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-diphenylcarbamimidothioate (3d)

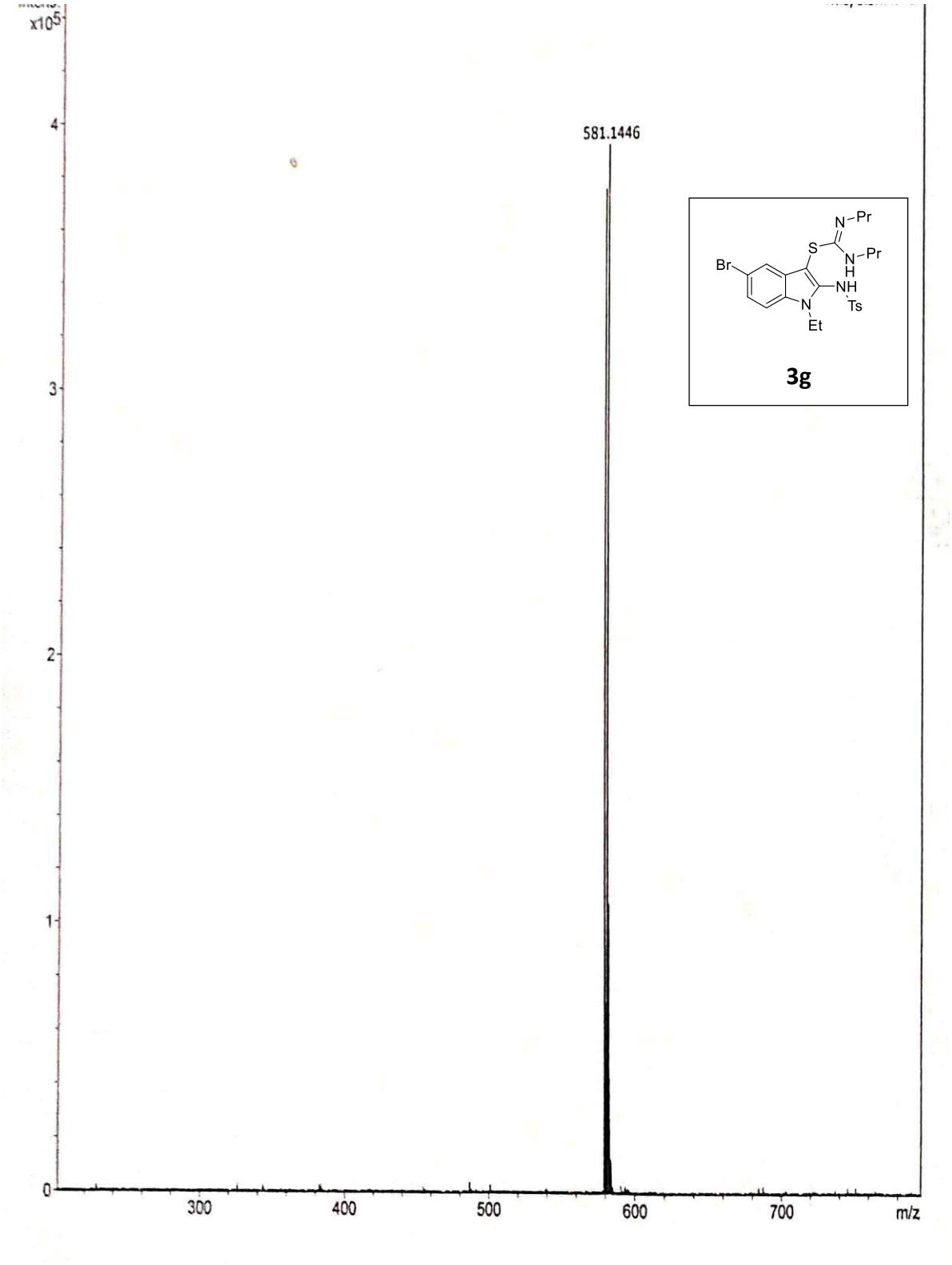
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N′*-dimethylcarbamimidothioate (3e)



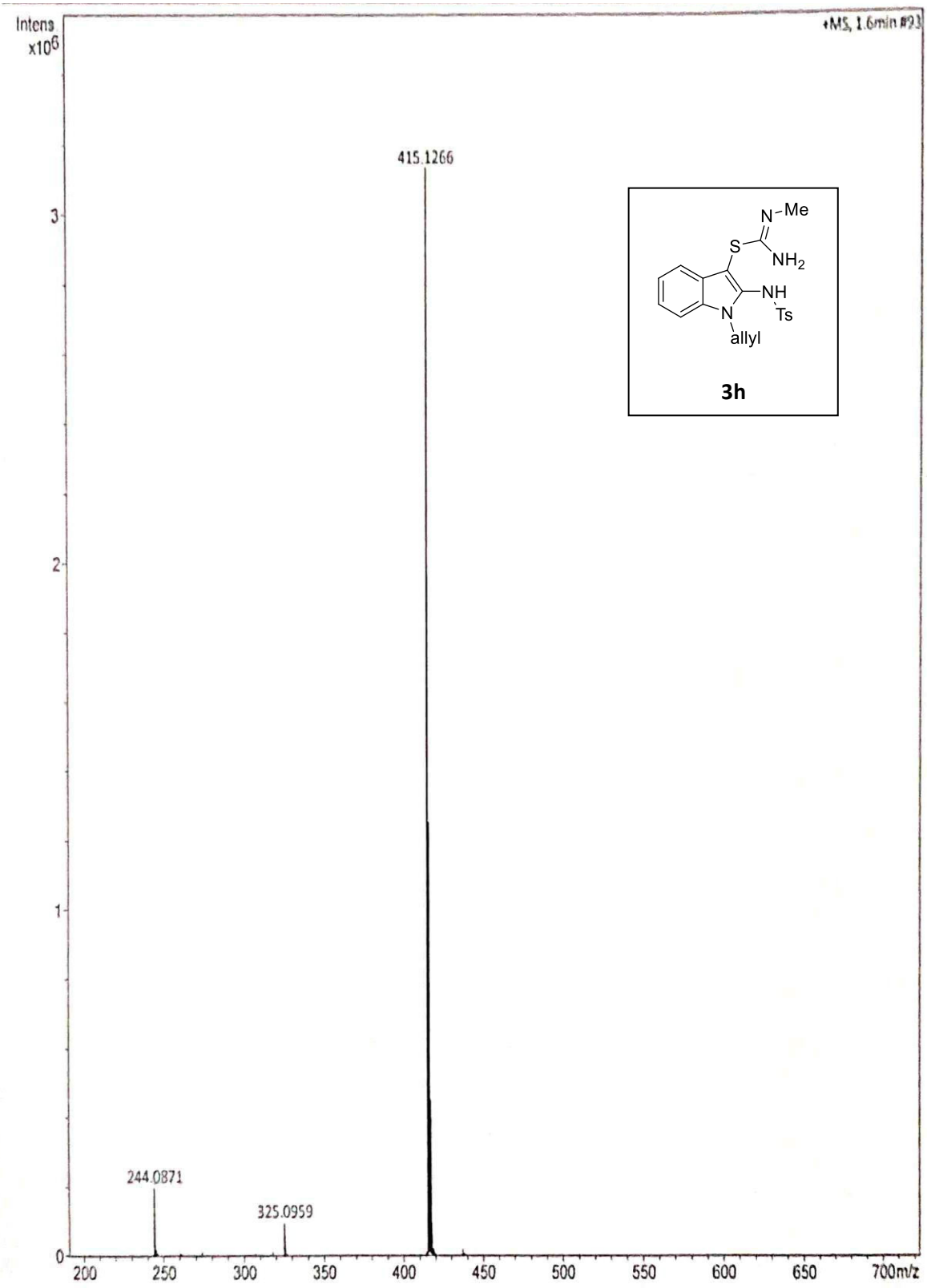
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N,N'*-dimethylcarbamimidothioate (3f)



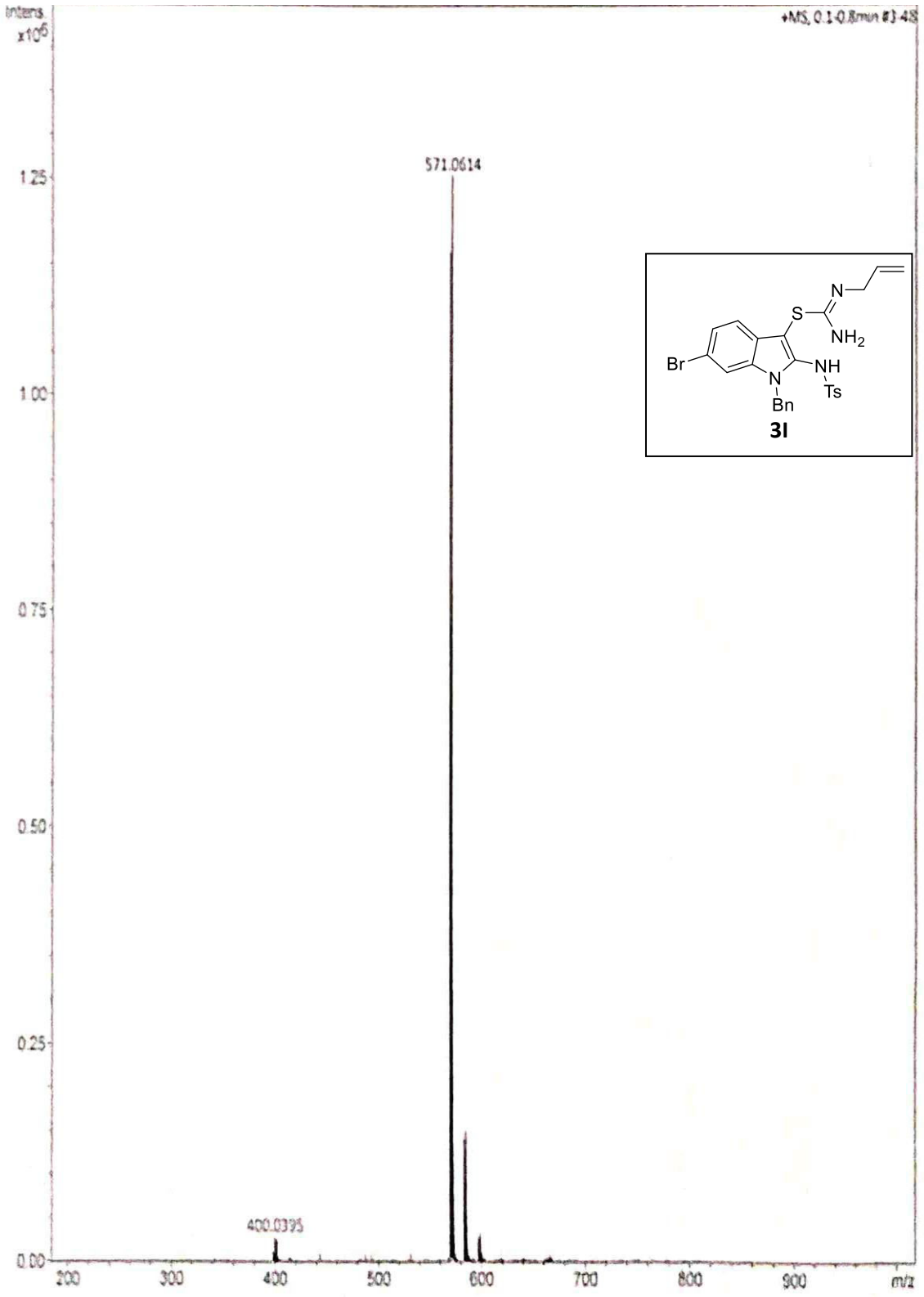
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1*H*-indol-3-yl *N,N′*-dibutylcarbamimidothioate (3g)



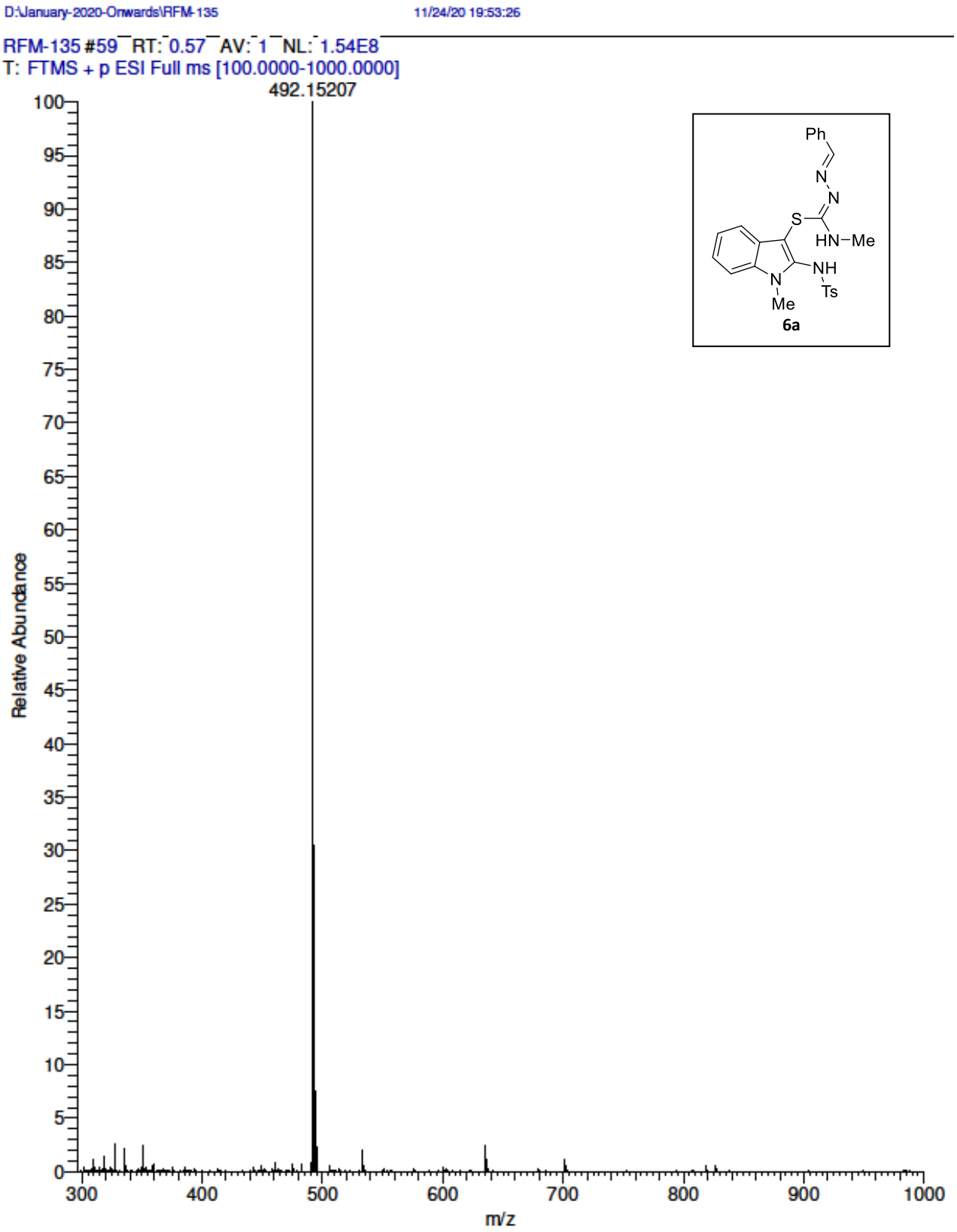
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl *N*,-methylcarbamimidothioate (3h)



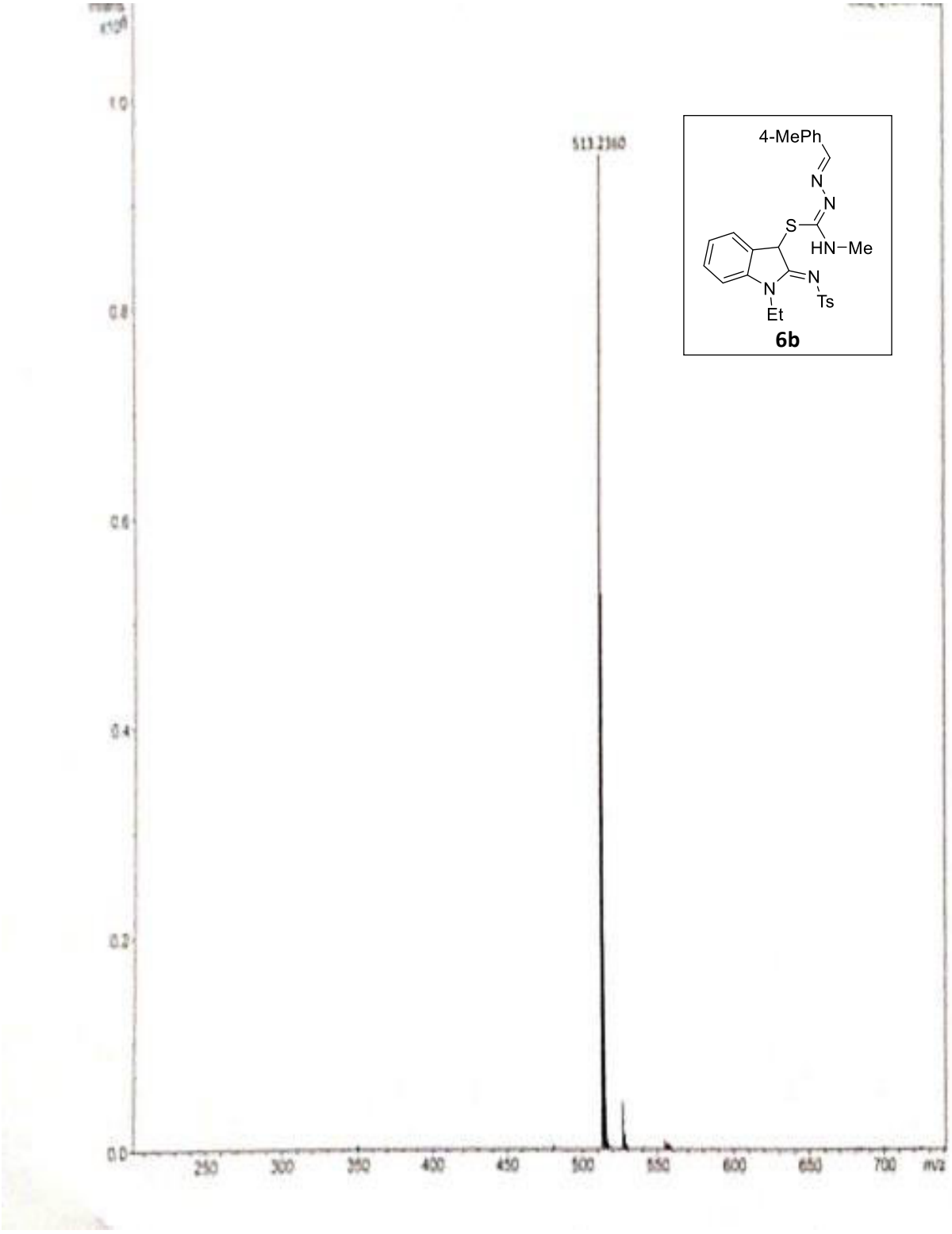
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]]-6-bromo-1*H*-indol-3-yl *N*,-allylcarbamimidothioate (3i)



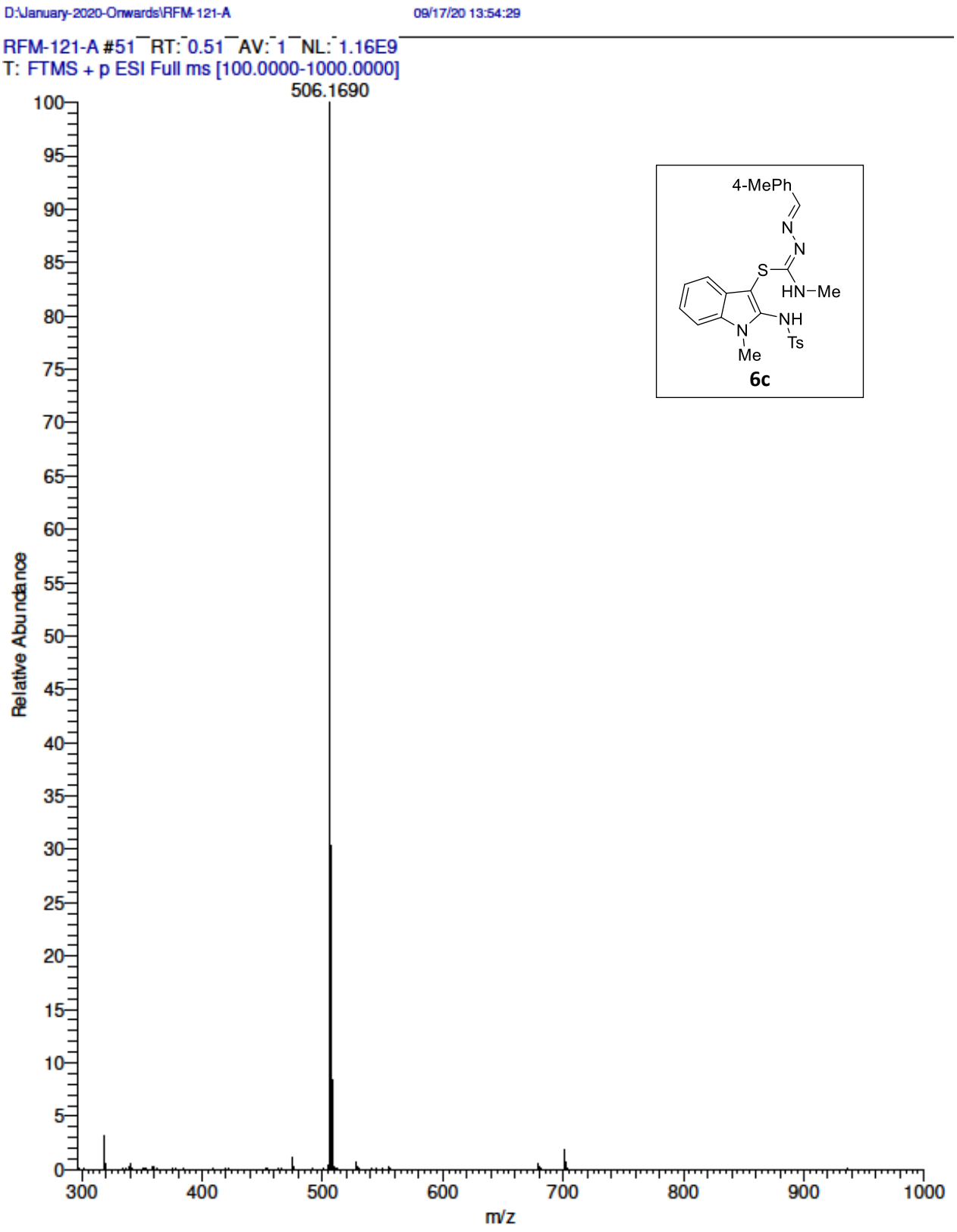
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6a)



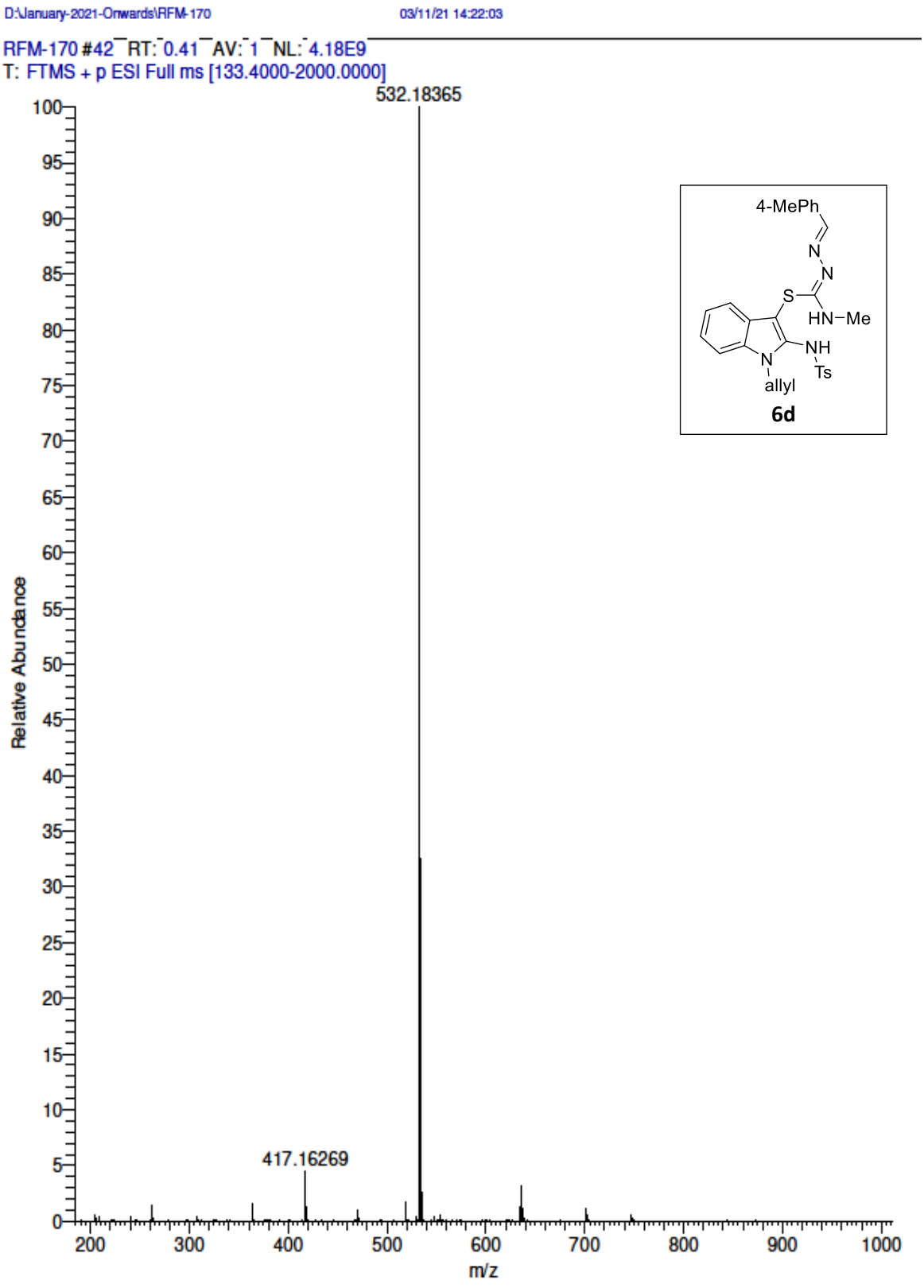
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6b)



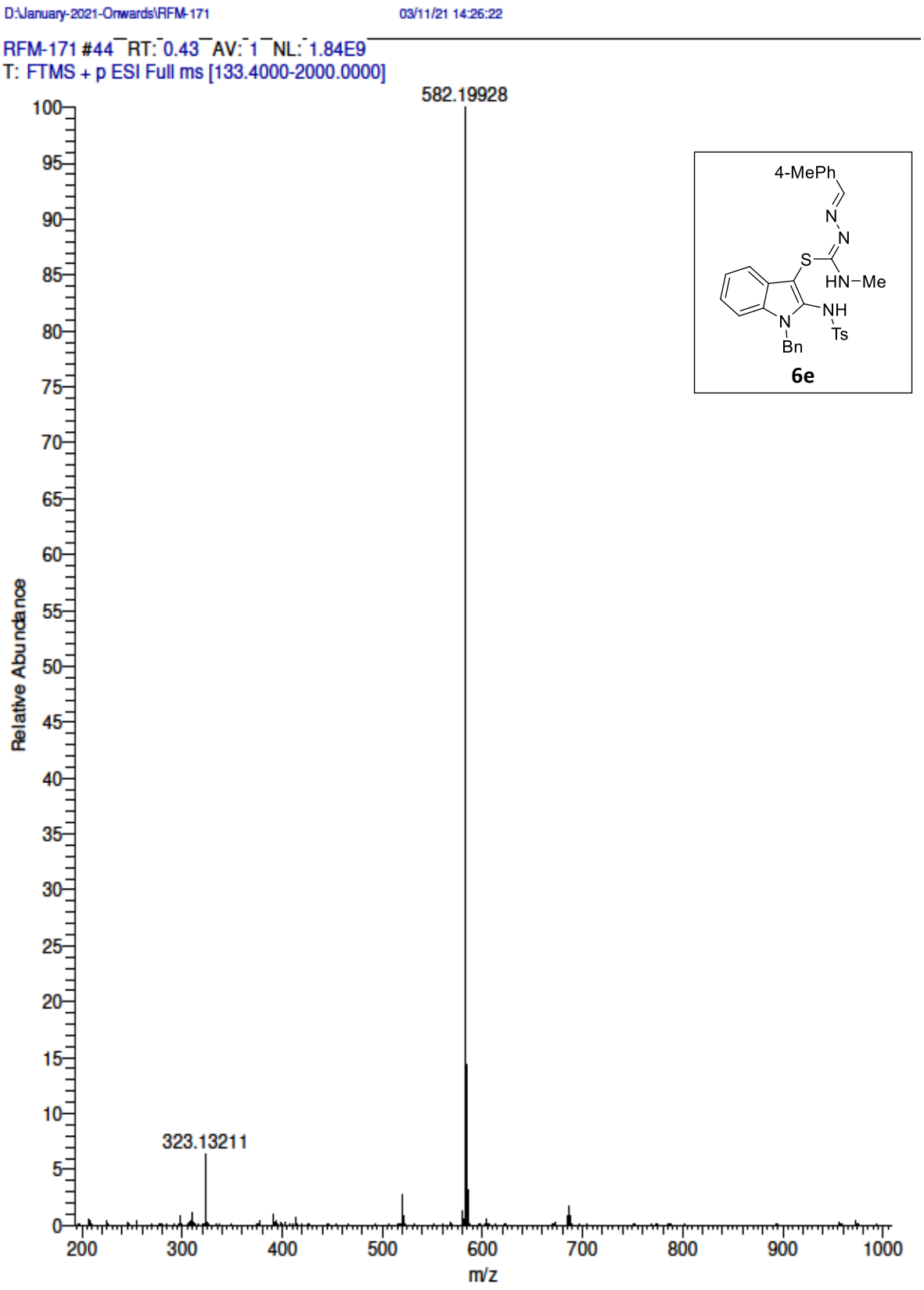
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6c)



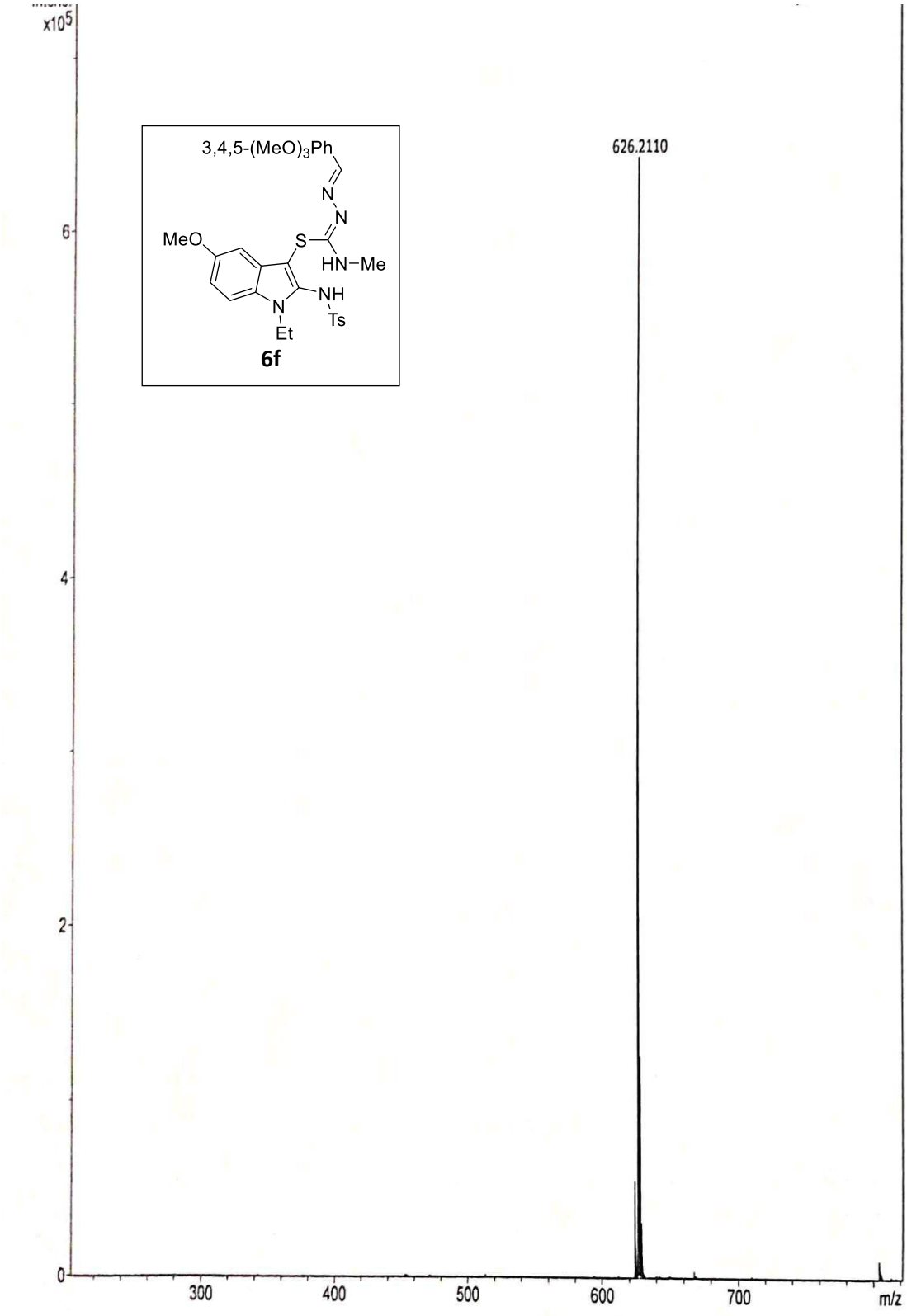
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6d)



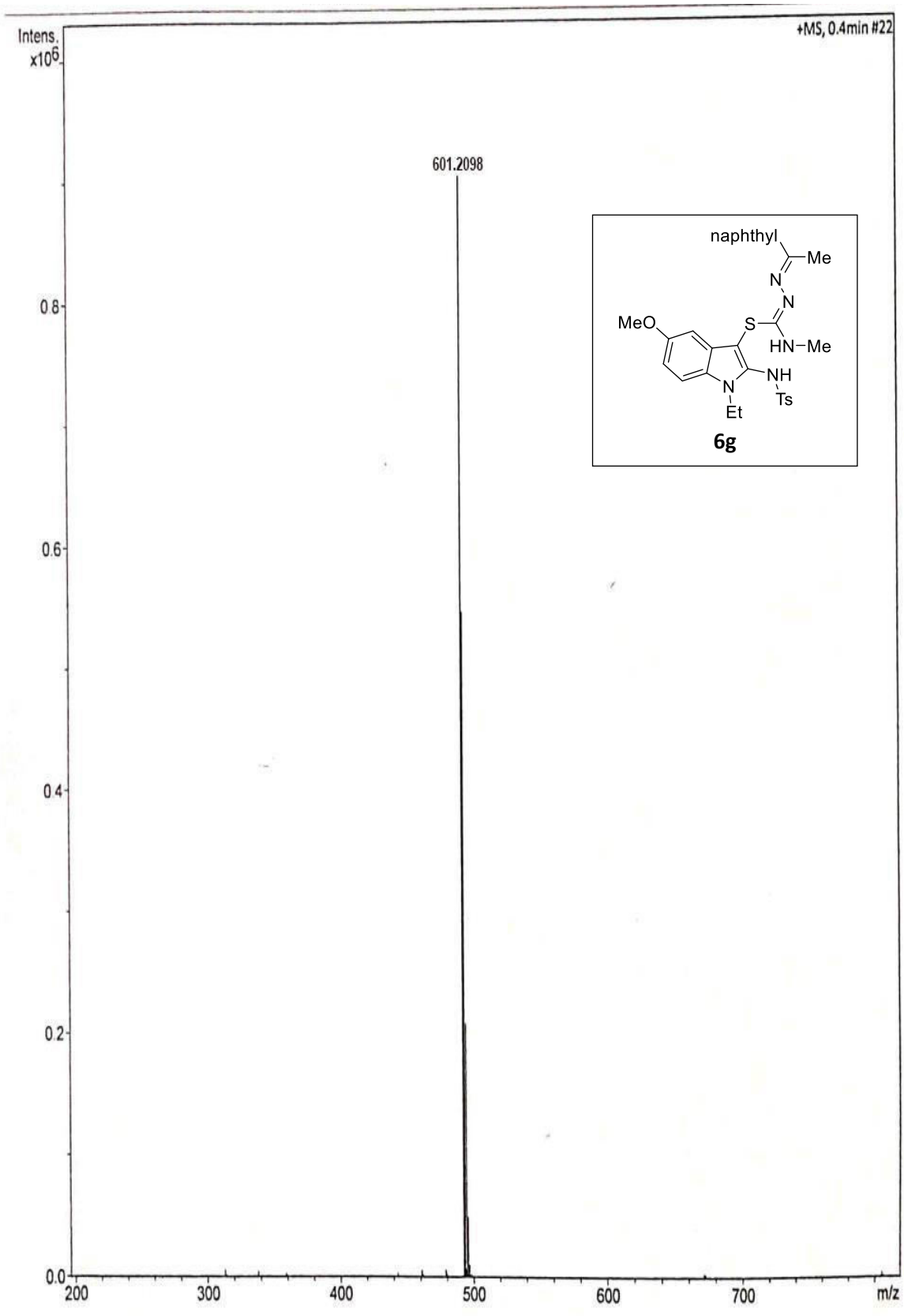
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6e)



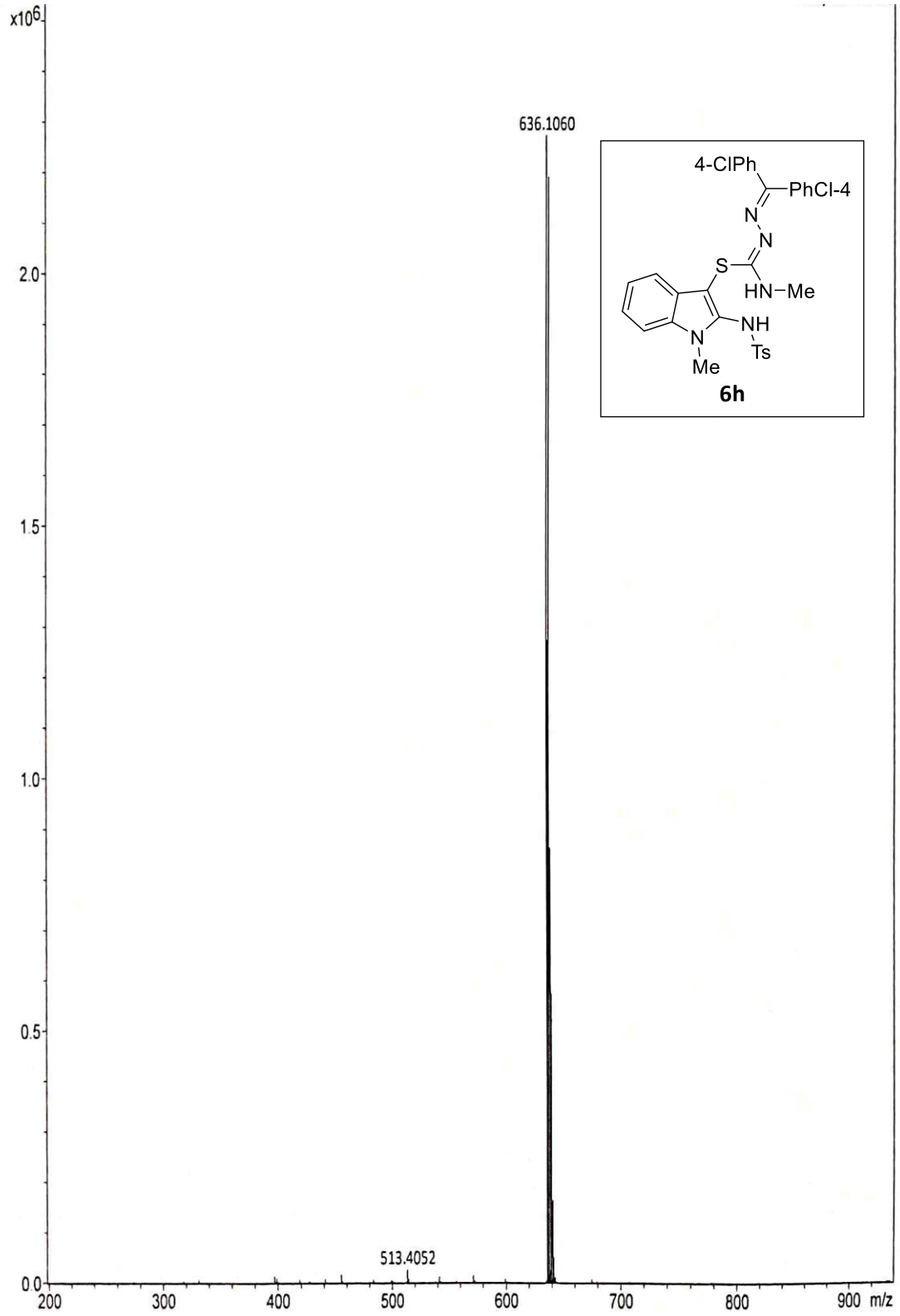
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(3,4,5-trimethoxyphenyl)methylidene]hydrazine-1-carboximidothioate (6f)



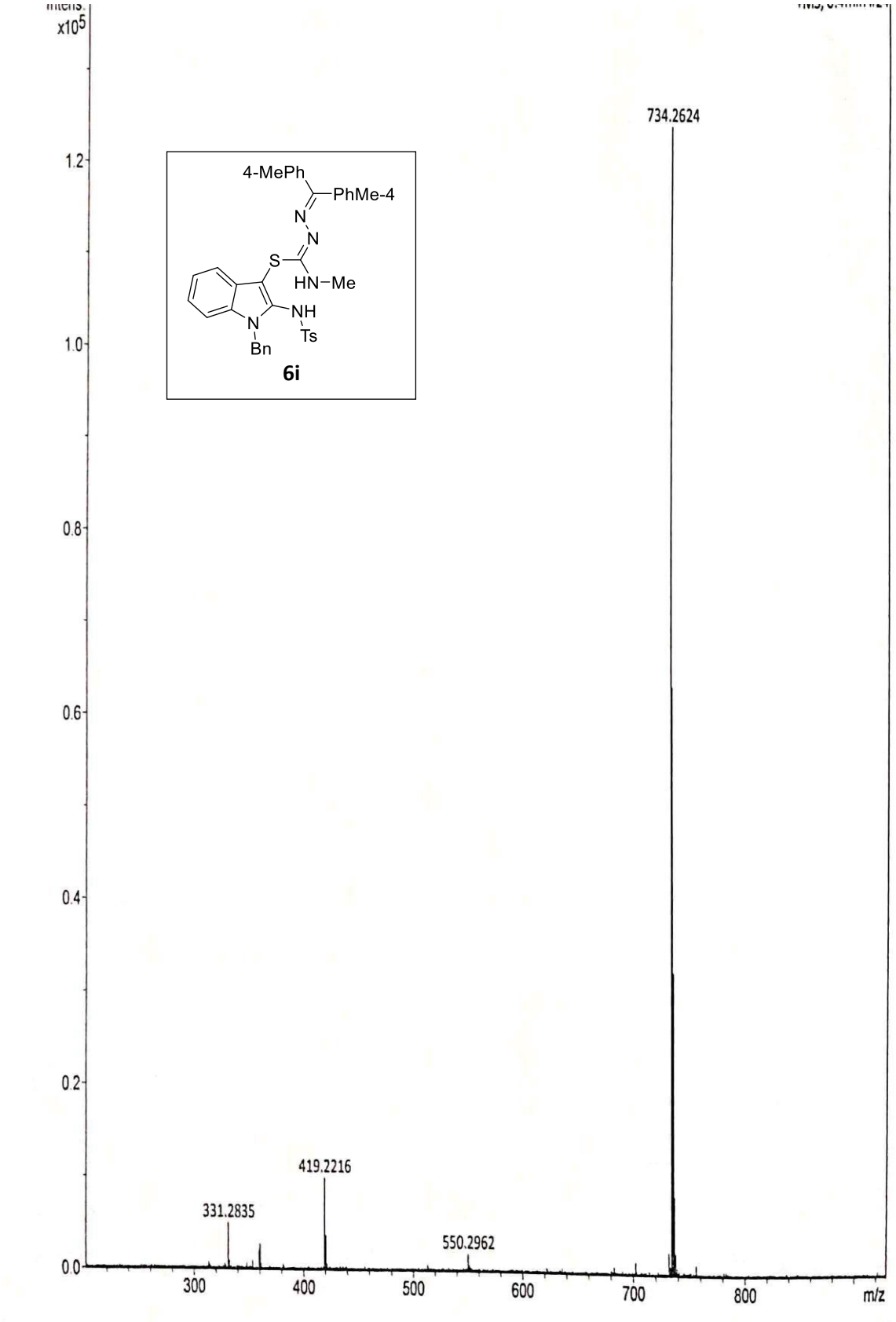
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-(1-(naphthalenyl)methylidene]hydrazine-1-carboximidothioate (6g)



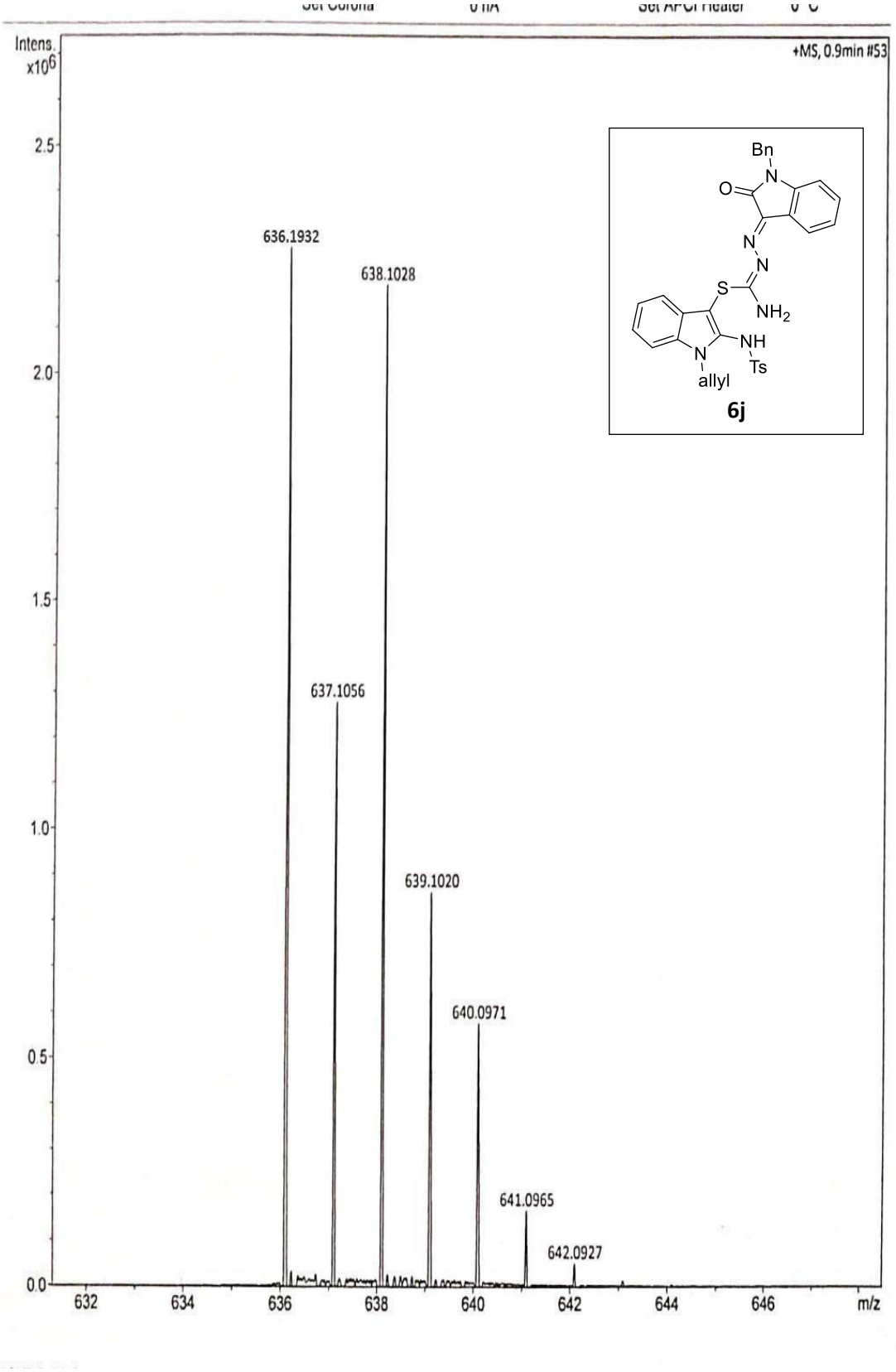
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl-*N*-methyl-2-[(di-*p*-chlorophenyl)methylidene]hydrazine-1-carboximidothioate (6h)



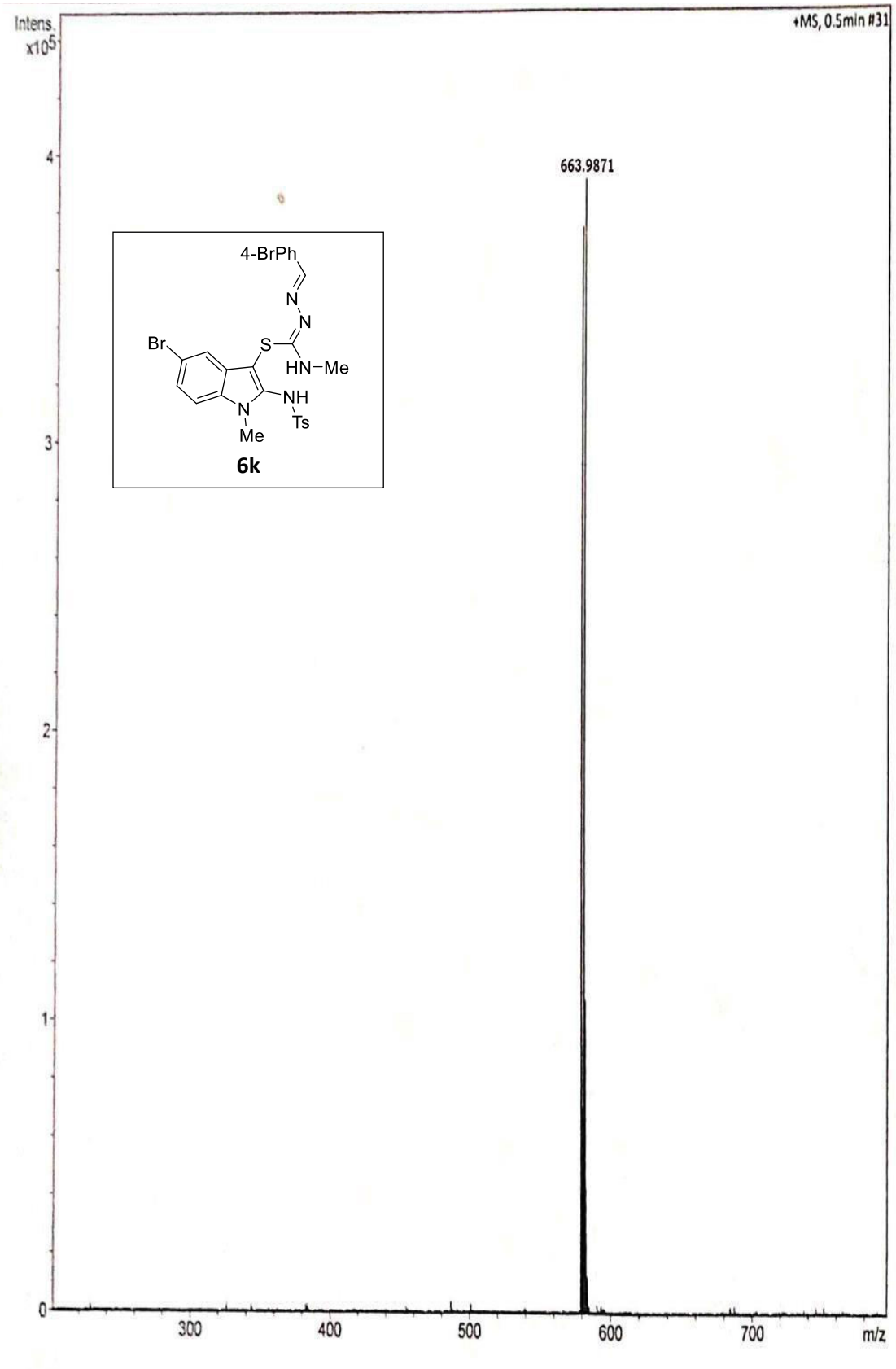
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl-*N*-phenyl-2-[(di-*p*-tolyl)methylidene]hydrazine-1-carboximidothioate (6i)



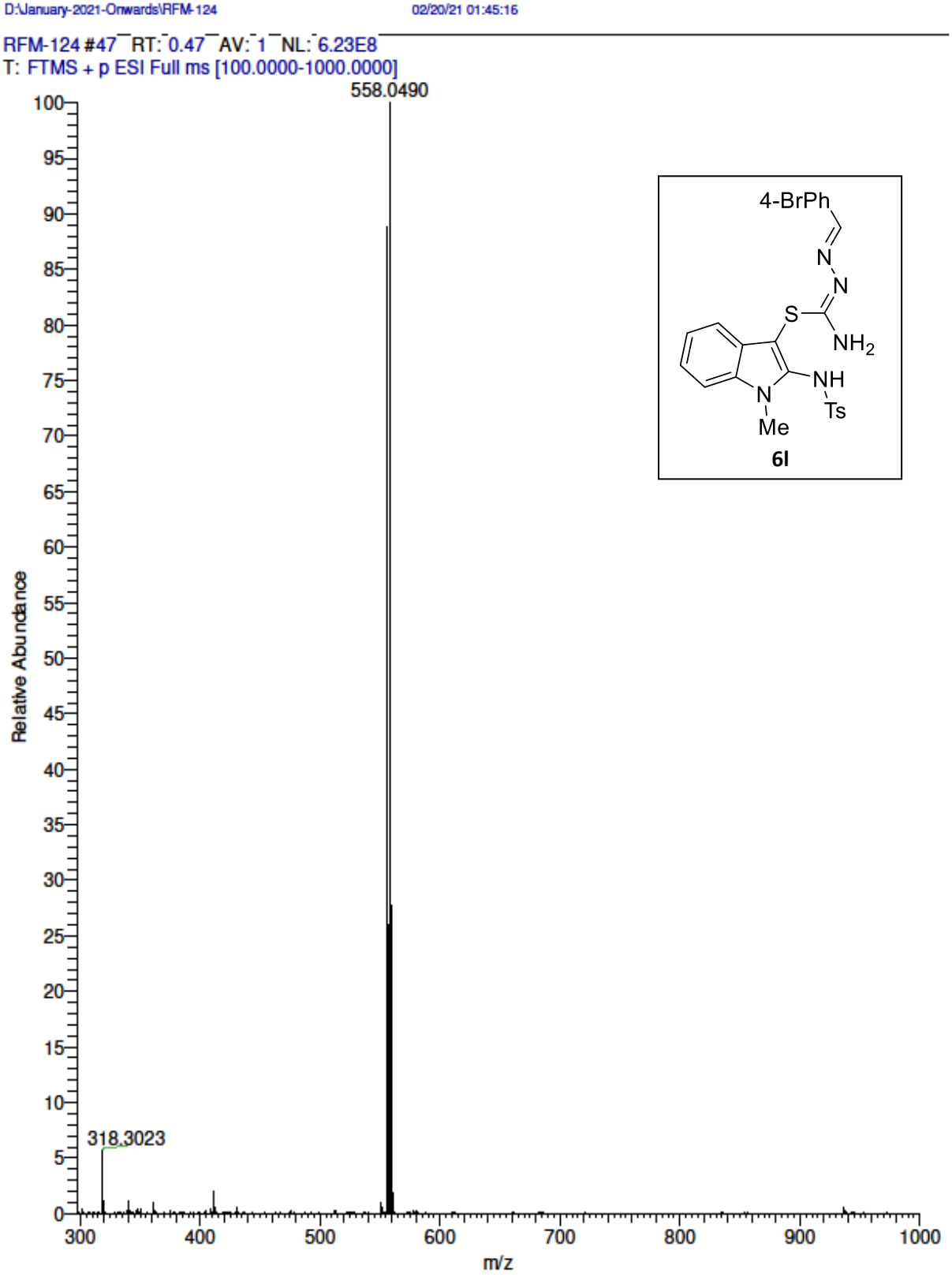
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-2[(1-benzyl-2-oxoindolin-3-ylidene)]hydrazine-1-carboximidothioate (6j)



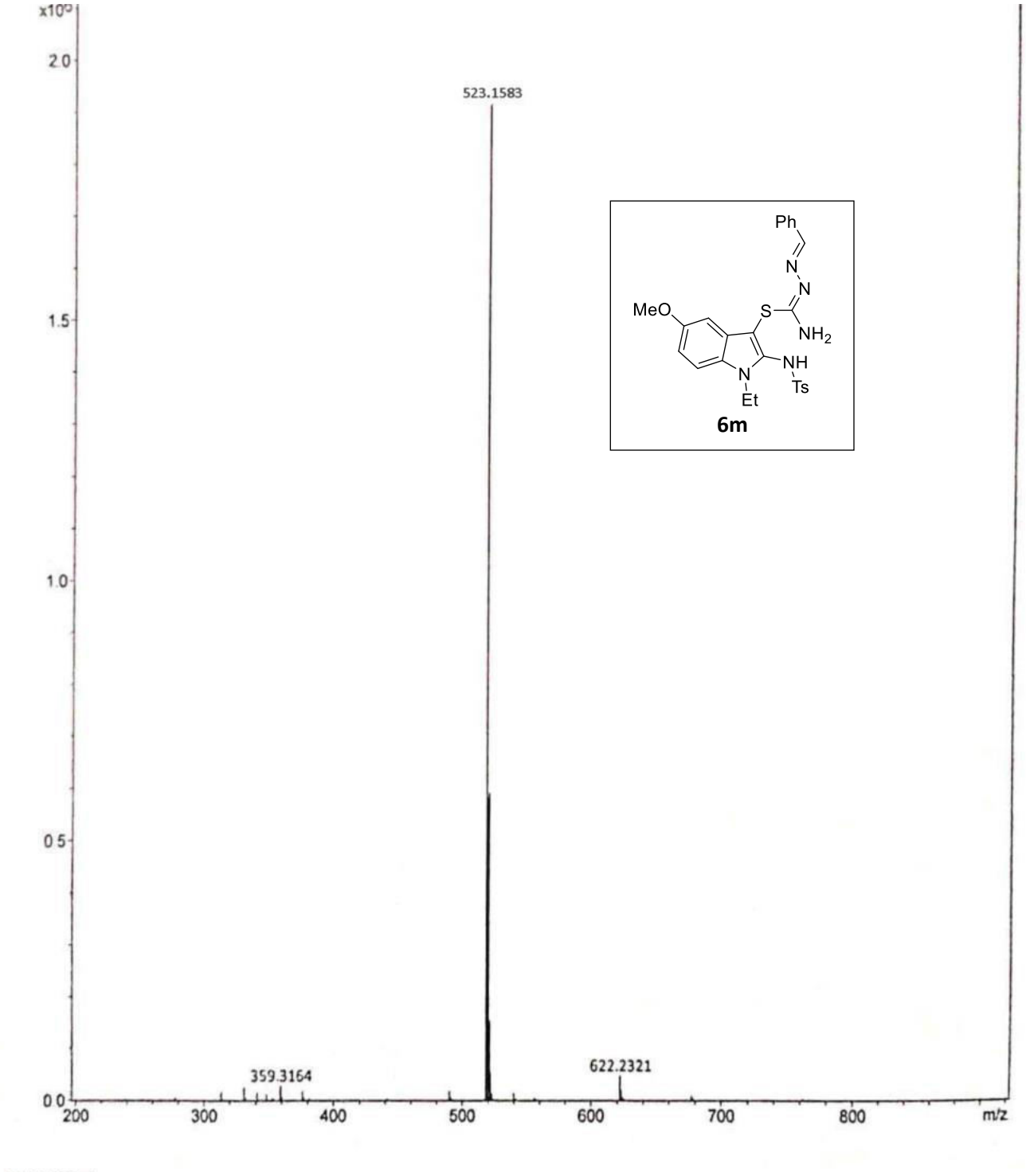
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1*H*-indol-3-yl(2*E*)-*N*-methyl-2-[(4-bromolphenyl)methylidene]hydrazine-1-carboximidothioate (6k)



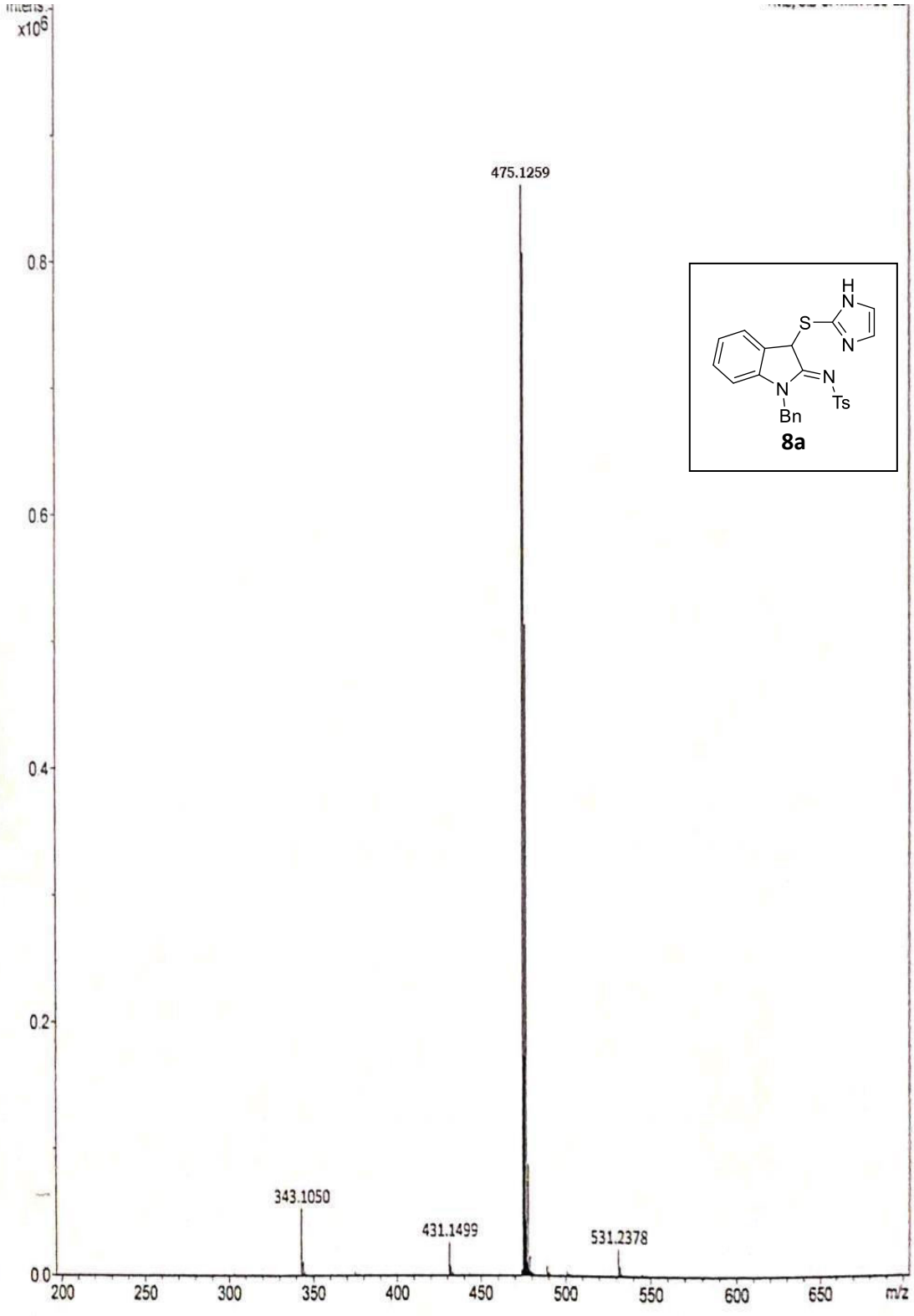
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1*H*-indol-3-yl(2*E*)-2[(4-bromophenyl)methylidene]hydrazine-1-carboximidothioate (6l)



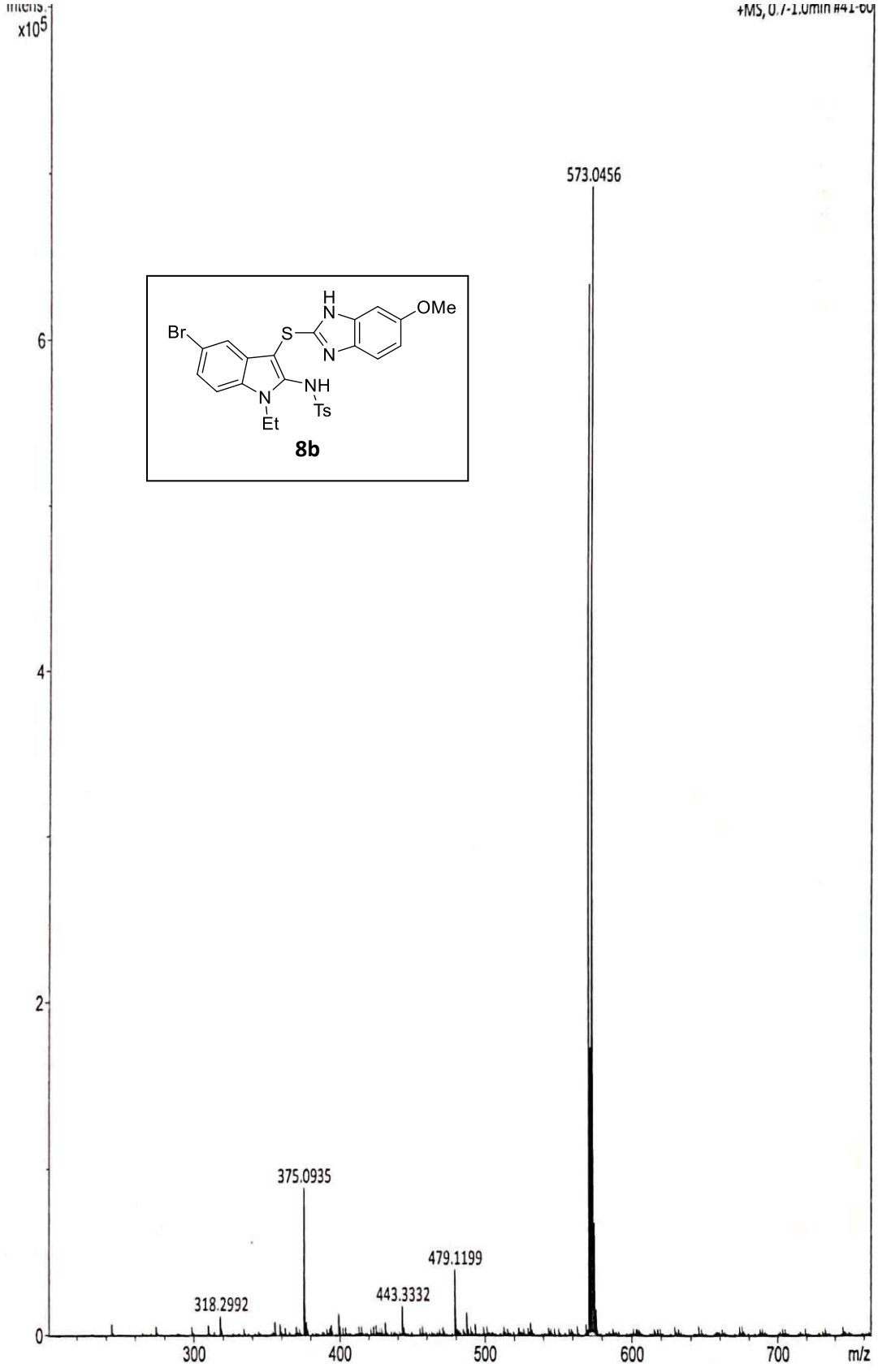
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1*H*-indol-3-yl(2*E*)-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6m)



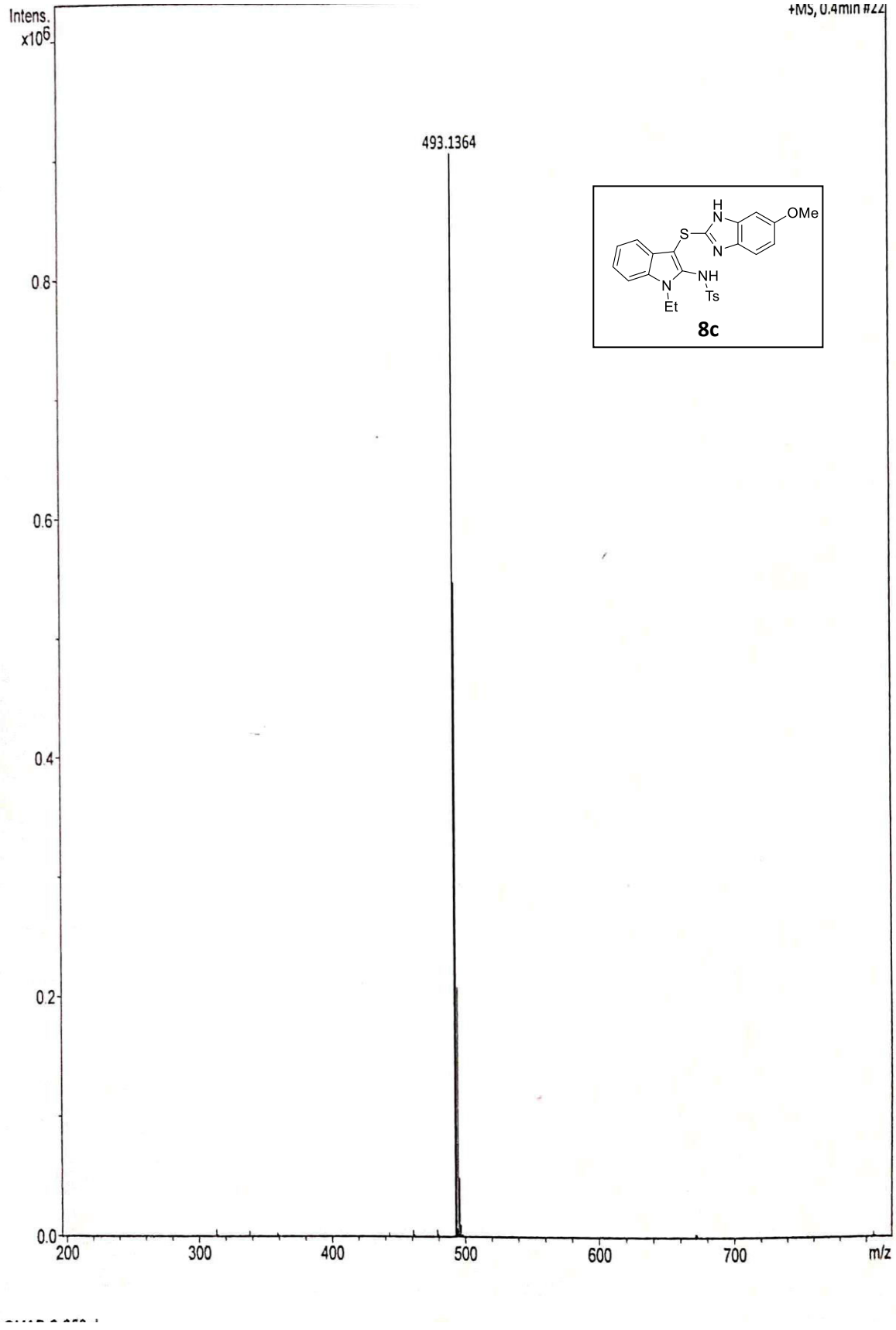
N-{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8a)



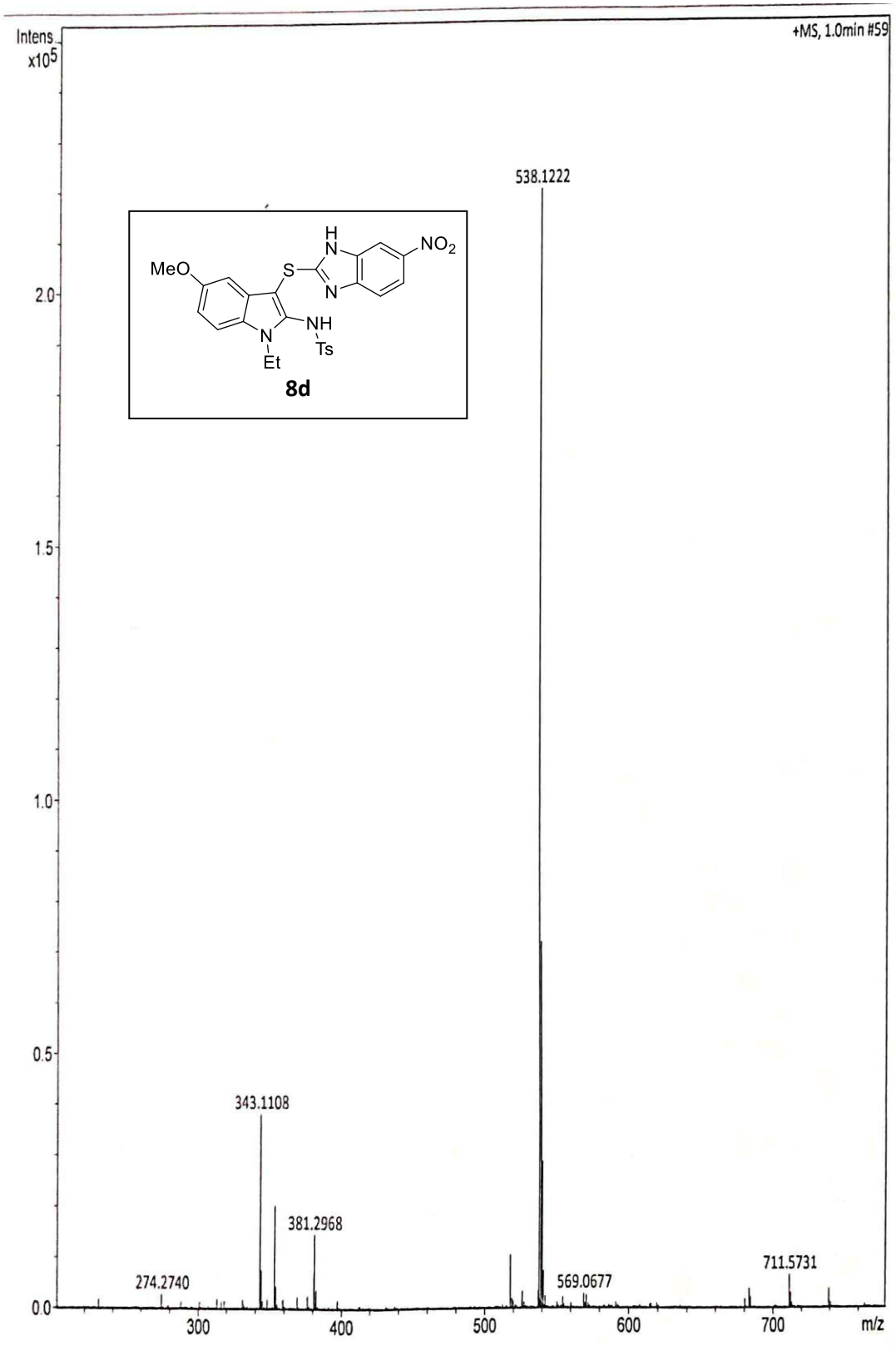
N-{1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-bromo-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8b)



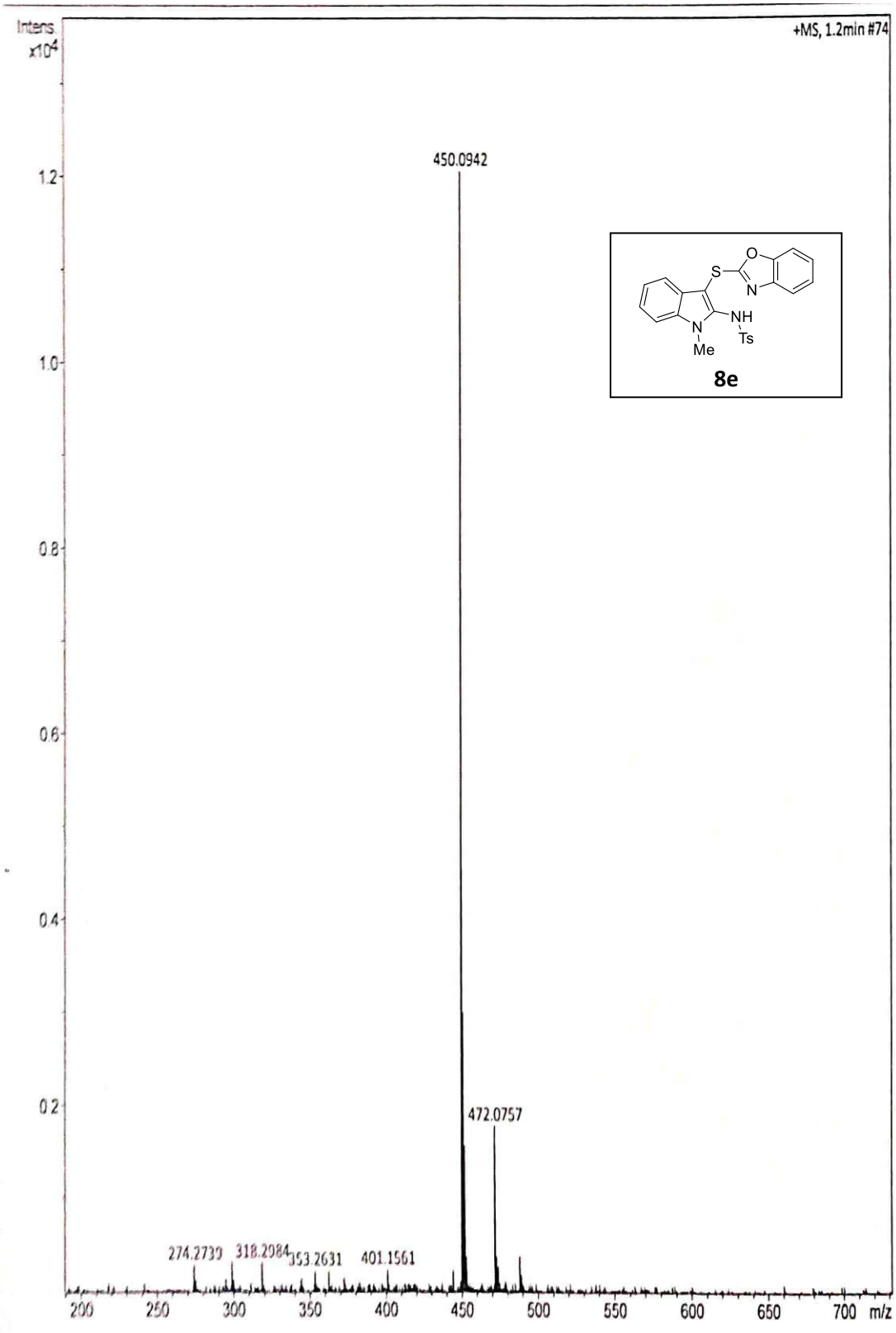
N-{1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8c)



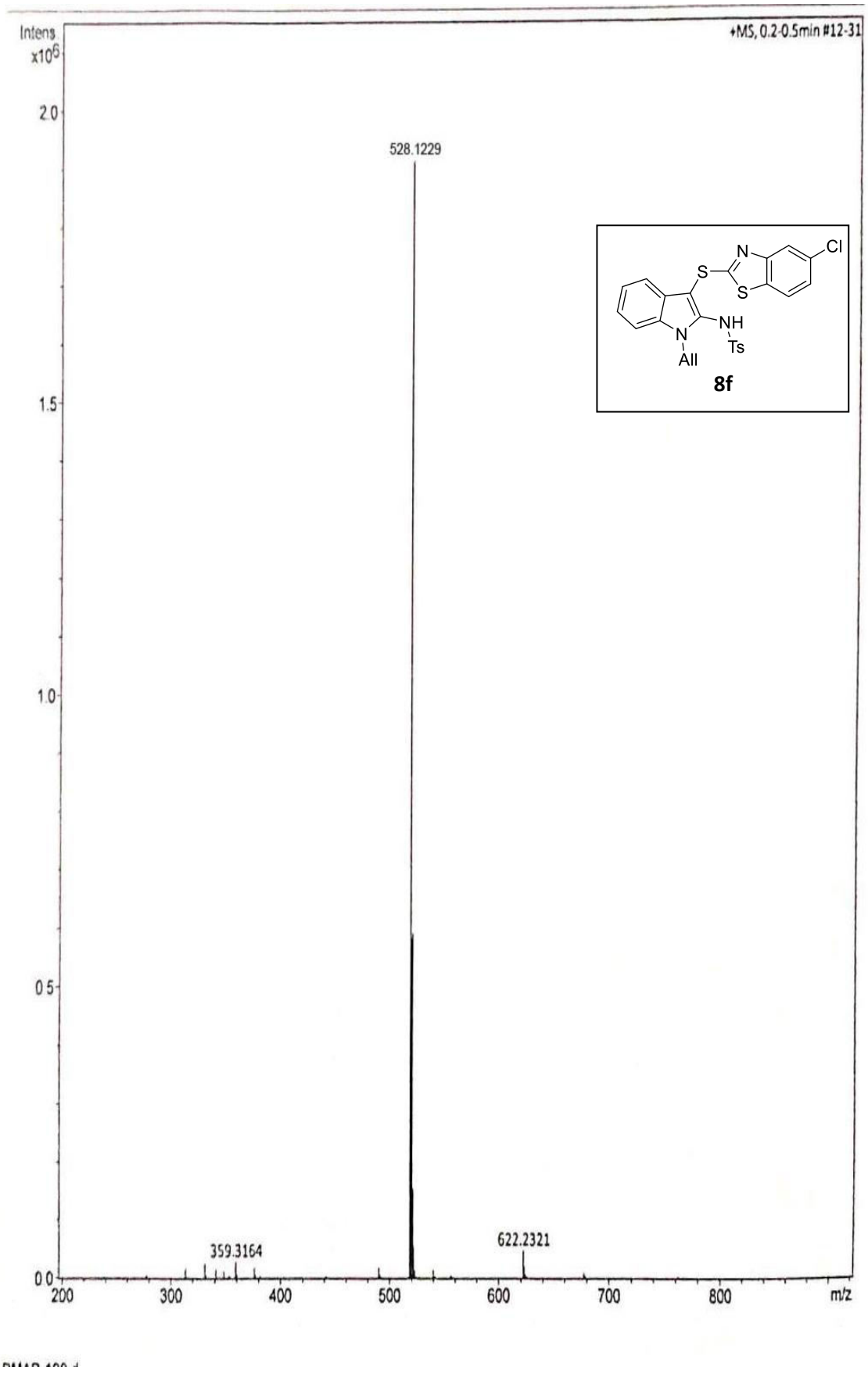
N-{1-Ethyl-3-[(5-nitro-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-methoxy-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8d)



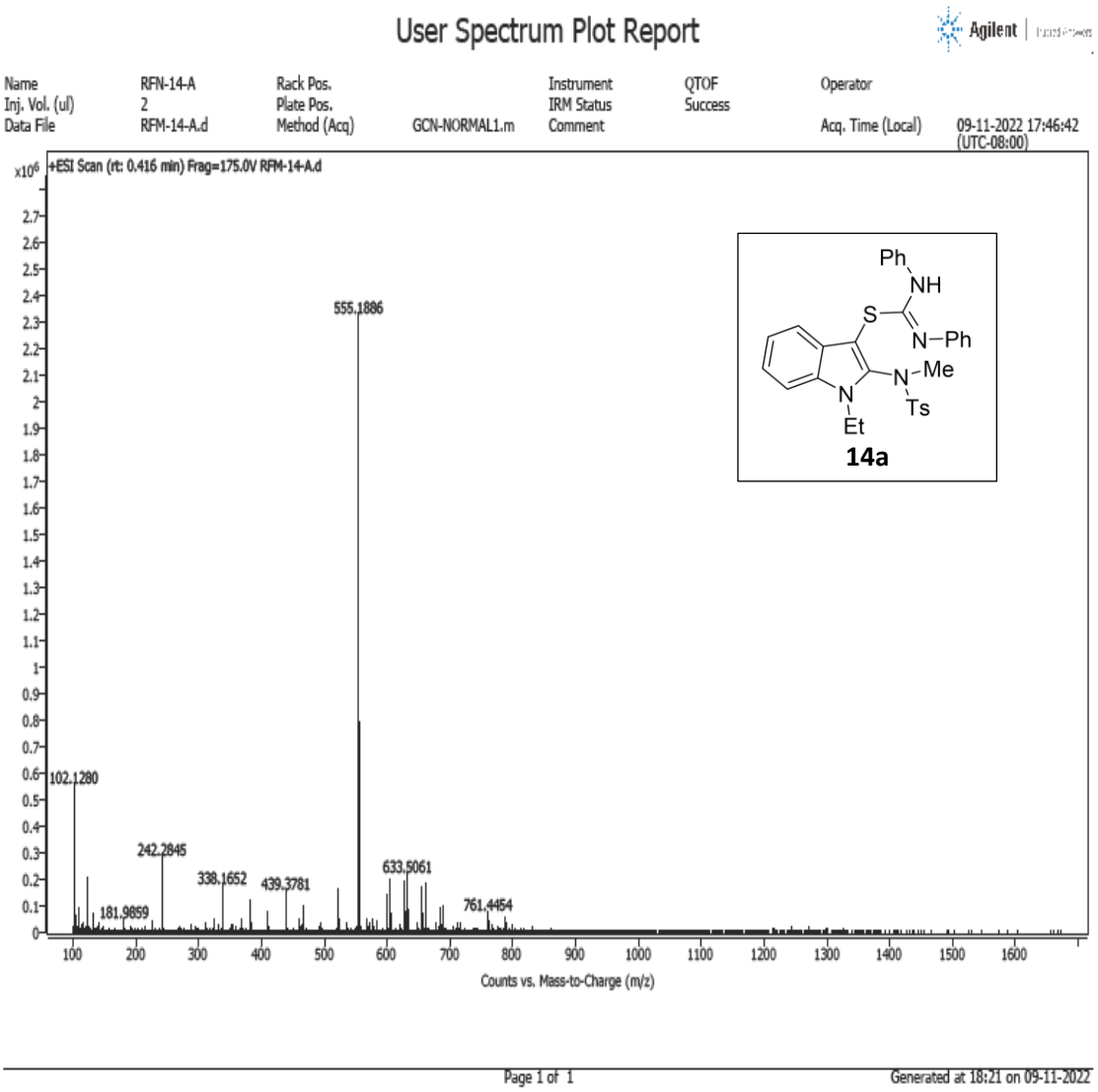
N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8e)



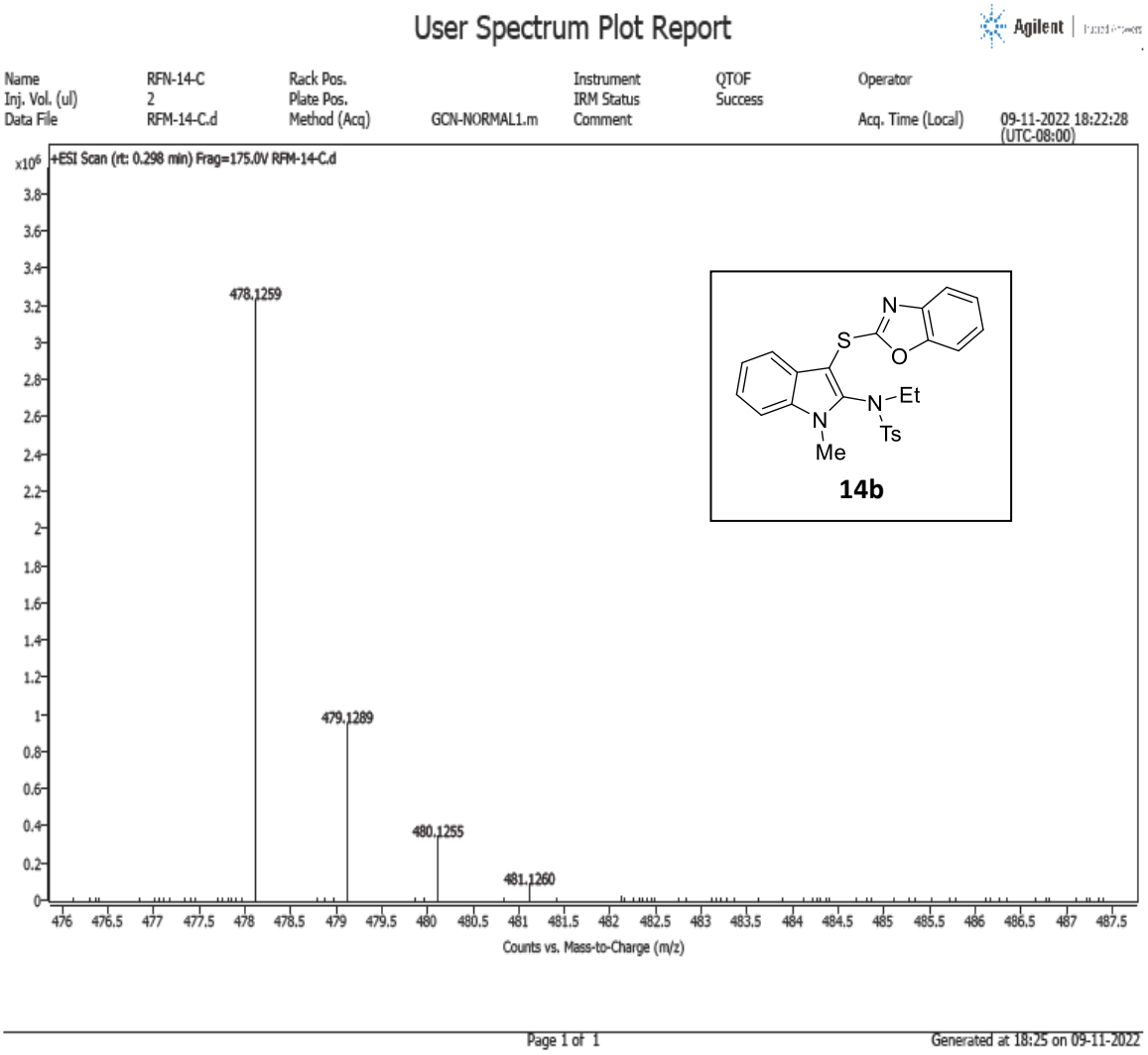
N-{1-Allyl-3-[(5-chloro-1H-benzo[d]thiazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-4-methylbenzenesulfonamide (8f)



1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)methylamino]-1*H*-indol-3-yl *N,N′*-diphenylcarbamimidothioate (14a)



N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-N-ethyl-4-methylbenzenesulfonamide (14b)



N-{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1*H*-indol-2-yl}-N-benzenecarbonyl-4-methylbenzenesulfonamide (14c)