α-Sulfanyl and α-Selanyl Propadienyl Cations: Regioselective Generations and Cycloadditions with Thioamides and Selemides Controlled by $MeNO_2$-H_2O System

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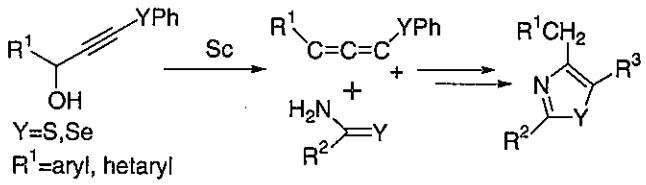


Preparations of 2-Phenylthiazole (2a-u)

Preparations of 4-(4-Methoxybenzyl)-2-phenyl-5-(phenylsulfanyl)thiazole (2a), Method B: To a nitromethane (0.5 ml)-water (0.05 ml) solution of 1-(*p*-methoxyphenyl)-3-(phenylsulfanyl)prop-2-yn-1-ol (**1a**) (50 mg, 0.18 mmol) was added thiobenzamide (50 mg, 0.37 mmol) and tetrabutylammonium hydrogen sulfate (6 mg, 0.018 mmol). Then scandium triflate (4 mg, 0.009 mmol) was added to a mixture. The whole was stirred under a reflux condition for 10 min and poured into a saturated $NaHCO_3$ (50 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-*n*-hexane (1:20) to give the title compound **2a** (65 mg, 93) as a yellow oil.

2a: IR (KBr, cm^{-1}) ν 3063, 3031, 2999, 2951, 2930, 2909, 2832, 1610, 1582, 1510, 1478, 1454, 1440, 1427, 1301, 1245, 1175, 1107, 1082, 1070, 1036, 1001, 985, 847, 817, 763, 741, 687, 661, 620; ^1H NMR (600 MHz, $CDCl_3$) δ 3.75 (3H, s, OMe), 4.19 (2H, s, CH_2), 6.77 (2H, d, *J*=9 Hz, ArH), 7.14-7.17 (3H, m, ArH), 7.22-7.24 (4H, m, ArH), 7.40-7.41 (3H, m, ArH), 7.90-7.91 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.7 (t), 55.2 (q), 113.7 (dx2), 120.9 (s), 126.2 (d), 126.5 (dx2), 127.1 (dx2), 128.9 (dx2), 129.1 (dx2), 129.9 (dx2), 130.4 (d), 131.1 (s), 133.4 (s), 137.3 (s), 158.0 (s), 162.3 (s), 170.5 (s); MS *m/z* 389 (M^+),

374 (M^+-Me), 312 (M^+-Ph), 280 (M^+-PhS). Anal. Calcd for $C_{23}H_{16}NOS_2$: C, 70.92; H, 4.92; N, 3.60. Found: C, 70.79; H, 4.98; N, 3.60.

4-Benzyl-2-phenyl-4-(phenylsulfanyl)thiazole (2b): a yellow oil, IR (KBr, cm^{-1}) ν 3060, 3028, 2921, 1607, 1581, 1504, 1490, 1478, 1454, 1439, 1427, 1375, 1315, 1219, 1178, 1156, 1072, 1053, 1024, 1001, 986, 916, 820, 762, 739, 723, 687, 663, 621; ^1H NMR (600 MHz, $CDCl_3$) δ 4.25 (2H, s, CH_2), 7.12-7.23 (8H, m, ArH), 7.31 (2H, d, *J*=7 Hz, ArH), 7.37-7.38 (3H, m, ArH), 7.88-7.90 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.5 (t), 121.3 (s), 126.2 (d), 126.3 (d), 126.5 (dx2), 127.2 (dx2), 128.3 (dx2), 128.8 (dx2), 128.9 (dx2), 129.1 (dx2), 130.4 (d), 133.4 (s), 137.2 (s), 138.9 (s), 161.8 (s), 170.4 (s); MS *m/z* 359 (M^+), 282 (M^+-Ph), 250 (M^+-PhS). Anal. Calcd for $C_{22}H_{17}NS_2$: C, 73.50; H, 4.77; N, 3.90. Found: C, 73.46; H, 4.83; N, 3.84.

4-(4-Chlorobenzyl)-2-phenyl-5-(phenylsulfanyl)-thiazole (2c): a yellow oil, IR (KBr, cm^{-1}) ν 3060, 2924, 1736, 1713, 1581, 1490, 1454, 1429, 1359, 1314, 1233, 1219, 1178, 1091, 1051, 1016, 1001, 986, 915, 846, 801, 762, 741, 710, 688, 667, 619; ^1H NMR (600 MHz, $CDCl_3$) δ 4.17 (2H, s, CH_2), 7.08-7.18 (9H, m, ArH), 7.31-7.32 (3H, m, ArH), 7.85-7.86 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.8 (t), 121.3 (s), 126.2 (d), 126.3 (dx2), 127.0 (dx2), 128.3 (dx2), 128.8 (dx2), 129.0 (dx2), 130.2 (dx2), 130.4 (d), 131.9 (s), 133.2 (s), 136.9 (s), 137.2 (s), 161.2 (s), 170.5 (s); MS *m/z* 393 (M^+), 316 (M^+-Ph), 284 (M^+-SPh). Anal. Calcd for $C_{22}H_{16}ClNS_2$: C, 67.08; H, 4.09; N, 3.56. Found: C, 67.25; H, 4.06; N, 3.54.

4-(4-Fluorobenzyl)-2-phenyl-5-(phenylsulfanyl)-thiazole (2d): a yellow oil, IR (KBr, cm^{-1}) ν 3060, 2922, 1602, 1581, 1508, 1489, 1478, 1454, 1440, 1427, 1222, 1157, 1052, 1023, 986, 853, 835, 822, 778, 763, 739, 668, 661, 620; ^1H NMR (600 MHz, $CDCl_3$) δ 4.20 (2H, s, CH_2), 6.88 (2H, d, *J*=8 Hz, ArH), 7.13 (2H, d, *J*=8 Hz, ArH), 7.14-7.16 (1H, m, ArH), 7.19-7.26 (4H, m, ArH), 7.39-7.40 (3H, m, ArH), 7.88-7.90 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.7 (t), 114.9 (d), 115.1 (d), 121.2 (s), 126.3 (dx2), 126.5 (dx2), 127.1 (dx2), 128.9 (dx2), 129.1 (dx2), 130.3 (d), 130.4 (d), 130.5 (d), 133.32 (s), 137.1 (s), 161.5 (d, *J*=244 Hz), 161.7 (s), 170.6 (s); MS *m/z* 377 (M^+), 300 (M^+-Ph), 268 (M^+-PhS). Anal. Calcd for $C_{22}H_{16}NFS_2$: C, 67.00; H, 4.27; N, 3.71. Found: C, 69.86; H, 4.29; N, 3.69.

4-(4-Bromobenzyl)-2-phenyl-5-(phenylsulfanyl)-thiazole (2e): white powder, from CH_2Cl_2-*n*-hexane, mp 72-73 °C, IR (KBr, cm^{-1}) ν 2923, 1581, 1504, 1487, 1454, 1439, 1428, 1071, 1052, 1024, 1012, 796, 763, 739, 687, 665, 475; ^1H NMR (600 MHz, $CDCl_3$) δ 4.09 (2H, s, CH_2), 7.02-7.07 (5H, m, ArH), 7.11-7.14 (2H, m, ArH), 7.23 (2H, d, *J*=8 Hz, ArH), 7.30 (3H, t, *J*=3 Hz, ArH), 7.79-7.80 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.0 (t), 120.1 (s), 121.4 (s), 126.4 (d), 126.4 (dx2), 127.1 (dx2), 128.9 (dx2), 129.1 (dx2), 130.5 (d), 130.7 (dx2), 131.3 (dx2), 133.3 (s), 137.0 (s), 137.8 (s), 161.1 (s), 170.6 (s); MS *m/z* 437 (M^+), 358 (M^+-Br), 360 (M^+-Ph), 328 (M^+-PhS). Anal. Calcd for $C_{22}H_{16}BrNS_2$: C, 60.27; H, 3.68; N, 3.20. Found: C, 59.99; H, 3.72; N, 3.16.

4-(1-Naphthylmethyl)-2-phenyl-5-(phenylsulfanyl)-thiazole (2f): pale yellow powders, from CH_2Cl_2-*n*-hexane, mp 94-96 °C, IR (KBr, cm^{-1}) ν 3060, 2925, 2852, 2384, 1713, 1597, 1580, 1509, 1479, 1455, 1439, 1219, 1146, 1025, 975, 783, 763, 740, 689, 634; ^1H NMR (600 MHz, $CDCl_3$) δ 4.60 (2H, s, CH_2), 7.03-7.12 (5H, m, ArH), 7.22-7.38 (7H, m, ArH), 7.60 (1H, d, *J*=8 Hz, ArH), 7.71-7.76 (3H, m, ArH), 8.27 (1H, d, *J*=8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.0 (t), 121.8 (s), 124.5 (d), 125.5 (dx2), 125.8 (d), 126.3 (d), 126.4 (dx2), 127.1 (d), 127.1 (d), 127.3 (dx2), 128.5 (d), 128.9 (dx2), 129.1 (dx2), 130.4 (d), 132.1 (s), 133.4 (s), 133.8 (s), 135.1 (s), 137.1 (s), 161.2 (s), 170.3 (s); MS *m/z* 409 (M^+), 332 (M^+-Ph), 300 (M^+-PhS). Anal. Calcd for $C_{26}H_{19}NS_2$: C, 76.25; H, 4.68; N, 3.42. Found: C, 76.18; H, 4.63; N, 3.41..

2-Phenyl-5-(phenylsulfanyl)-4-(2-thienylmethyl)-thiazole (2g): white prisms, from CH_2Cl_2-*n*-hexane, mp 63-64 °C, IR (KBr, cm^{-1}) ν 3104, 3064, 2914, 2901, 2852, 1713, 1579, 1579, 1504, 1491, 1476, 1454, 1439, 1419, 1359, 1308, 1284, 1237, 1177, 1156, 1120, 1075, 1050, 1026, 1000, 985, 923, 903, 849, 830, 763, 744, 687, 659, 625; ^1H NMR (600 MHz, $CDCl_3$) δ 4.43 (2H, s, CH_2), 6.87 (2H, d, *J*=3 Hz, ArH), 7.10-7.25 (5H, m, ArH), 7.39-7.41 (3H, m, ArH), 7.90-7.93 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.0 (t), 121.6 (s), 124.1 (d), 125.6 (d), 126.4 (d), 126.5 (dx2), 126.6 (d), 127.3 (dx2), 128.9 (dx2), 129.1 (dx2), 130.5 (d), 133.3 (s), 137.0 (s), 141.0 (s), 160.7 (s), 170.6 (s); MS *m/z* 365 (M^+), 280 (M^+-thienyl), 256 (M^+-PhS). Anal. Calcd for $C_{20}H_{14}NS_3$: C, 65.90; H, 3.87; N, 3.84. Found: C, 65.75; H, 4.20; N, 3.80.

4-(*p*-Methoxybenzyl)-2-methyl-5-(phenylsulfanyl)-thiazole (3a): a yellow oil, IR (KBr, cm^{-1}) ν 3059, 2999, 2833, 1610, 1582, 1510, 1478, 1440, 1301, 1246, 1177, 1035, 818, 771, 740, 689, 587; ^1H NMR (600 MHz, $CDCl_3$) δ 2.65 (3H, s, Me), 3.74 (3H, s, OMe), 4.10 (2H, s, CH_2), 6.76 (2H, d, *J*=9 Hz, ArH), 7.11 (2H, m, ArH), 7.14-7.16 (3H, m, ArH), 7.21-7.24 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.8 (q), 34.5 (t), 55.2 (q), 113.8 (dx2), 119.9 (s), 126.1 (d), 126.9 (dx2), 129.0 (dx2), 129.8 (dx2), 131.0 (s), 137.4 (s), 158.0 (s), 161.3 (s), 169.5 (s); MS *m/z* 327 (M^+), 312 (M^+-Me). Anal. Calcd for $C_{18}H_{17}NOS_2$: C, 66.02; H, 5.85; N, 4.28. Found: C, 65.79; H, 5.76; N, 4.26.

4-(4-Fluorobenzyl)-2-methyl-5-(phenylsulfanyl)-thiazole (3d): a yellow oil, IR (KBr, cm^{-1}) ν 2925, 2853, 2359, 1715, 1601, 1582, 1508, 1478, 1440, 1362, 1221, 1180, 1157, 1091, 1024, 840, 777, 740, 690; ^1H NMR (600 MHz, $CDCl_3$) δ 2.67 (3H, s, Me), 4.13 (2H, s, CH_2), 6.89 (2H, t, *J*=9 Hz, ArH), 7.09 (2H, d, *J*=7 Hz, ArH), 7.16-7.23 (3H, m, ArH), 7.25 (2H, d, *J*=8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.8 (q), 34.6 (t), 115.0 (d), 115.1 (d), 120.4 (s), 126.2 (d), 127.0 (dx2), 129.7 (dx2), 130.2 (d),

130.3 (d), 134.5 (s), 137.2 (s), 160.6 (s), 161.5 (d, *J*=245 Hz), 169.7 (s); MS *m/z* 315 (M^+), 238 (M^+-Ph), 206 (M^+-PhS). Anal. Calcd for $C_{17}H_{14}FNS_2$: C, 64.73; H, 4.47; N, 4.44. Found: C, 64.56; H, 4.49; N, 4.28.

2-Methyl-5-(phenylsulfanyl)-4-(2-thienylmethyl)-thiazole and 2-Methyl-5-(2-thienylmethyl)-4-(phenylsulfanyl)thiazole (3g): a yellow oil, ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.63 (s, Me), 2.67 (s, Me), 4.35 (s, CH_2), 4.40 (s, CH_2), 6.82 (d, *J*=3 Hz, ArH), 6.86 (dd, *J*=3 and 5 Hz, ArH), 7.06-7.35 (m, ArH); MS *m/z* 303 (M^+); high-resolution mass calcd for $C_{15}H_{13}NS_3$: 303.0208, found *m/z* 303.0139.

2-Methyl-4-(2-thienylmethyl)-5-(phenylsulfanyl)-thiazole (3g): a yellow oil, IR (KBr, cm^{-1}) ν 3070, 2917, 2364, 1581, 1507, 1478, 1439, 1373, 1299, 1249, 1178, 1078, 1052, 1024, 851, 739, 689, 630, 601; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.66 (3H, s, Me), 4.35 (2H, s, CH_2), 6.81 (1H, d, *J*=3 Hz, ArH), 6.85 (1H, dd, *J*=3 and 5 Hz, ArH), 7.08-7.10 (1H, m, ArH), 7.12-7.16 (3H, m, ArH), 7.22-7.36 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.8 (q), 29.8 (t), 120.7 (s), 124.0 (d), 125.5 (d), 126.2 (d), 126.6 (d), 127.1 (dx2), 129.0 (dx2), 137.1 (s), 141.1 (s), 159.7 (s), 169.7 (s); MS *m/z* 303 (M^+), 194 (M^+-PhS); high-resolution mass calcd for $C_{15}H_{13}S_3$: 303.0208, found *m/z* 303.0189.

4-(4-Methoxybenzyl)-2-phenyl-5-(phenylselanyl)-thiazole: white prisms, from CH_2Cl_2-*n*-hexane, mp 84-86 °C, IR (KBr, cm^{-1}) ν 2952, 2926, 2832, 1610, 1577, 1510, 1487, 1476, 1454, 1438, 1427, 1302, 1245, 1177, 1034, 1021, 999, 978, 848, 818, 763, 737, 688; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.74 (3H, s, MeO), 4.24 (2H, s, CH_2), 6.77 (2H, d, *J*=8 Hz, ArH), 7.19-7.24 (5H, m, ArH), 7.27-7.30 (2H, m, ArH), 7.38-7.40 (3H, m, ArH), 7.88-7.91 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.5 (t), 55.2 (q), 113.7 (dx2), 114.1 (s), 126.5 (dx2), 126.9 (d), 128.9 (dx2), 129.3 (dx2), 129.8 (dx2), 130.1 (dx2), 130.3 (d), 131.4 (s), 132.3 (s), 133.4 (s), 158.0 (s), 162.2 (s), 171.6 (s); MS *m/z* 437 (M^+), 422 (M^+-Me), 360 (M^+-Ph), 280 (M^+-PhSe). $C_{23}H_{19}NOSSe$: C, 63.30; H, 4.39; N, 3.21. Found: C, 63.09; H, 4.44; N, 3.21.

Preparation of 4-(4-Methoxybenzyl)-2-phenylthiazole (5a), Typical Procedure. A MeLi (5.1 ml, 5.70 mmol, 1M ether solution) was added dropwise to a THF (10 ml) solution of 4-(4-methoxybenzyl)-2-phenyl-5-(phenylselanyl)thiazole (0.50 g, 1.20 mmol) at -78 °C under an Ar atmosphere. The reaction mixture was stirred for 10 min and poured into water. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dired over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (1:20) to give **5a** (quant) as white powders. **5a**: from CH_2Cl_2-*n*-hexane, mp 51 °C, IR (KBr, cm^{-1}) ν 3111, 3042, 2997, 2964, 2933, 2902, 2835, 1958, 1901, 1764, 1608, 1583, 1510, 1455, 1430, 1313, 1297, 1246, 1178, 1123, 1110, 1073, 1034, 1000, 920, 872, 836, 819, 765, 734, 689, 663, 645, 634; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.79 (3H, s, OMe), 4.13 (2H, s, CH_2), 6.71 (1H, s, olefinic H), 6.87 (2H, d, *J*=8 Hz, ArH), 7.23-7.25 (2H, m, ArH), 7.37-7.43 (3H, m, ArH), 7.93 (2H, d, *J*=6 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 37.1 (t), 55.2 (q), 113.9 (d×2), 114.1 (d), 126.5 (d×2), 128.8 (d×2), 129.8 (d), 130.1 (d×2), 131.1 (s), 133.7 (s), 158.0 (s), 158.2 (s), 167.9 (s); MS *m/z* 281 (M^+), 266 (M^+-Me). Anal. Calcd for $C_{17}H_{15}NOS$: C, 72.57; H, 5.37; N, 4.98. Found: C, 72.14; H, 5.45; N, 4.90.

4-Benzyl-2-phenyl-5-(phenylselanyl)thiazole: white powder, from CH_2Cl_2-*n*-hexane, mp 73 °C; IR (KBr, cm^{-1}) ν 3057, 3028, 2905, 2358, 1956, 1598, 1575, 1484, 1450, 1438, 1418, 1334, 1300, 1226, 1172, 1073, 1021, 998, 977, 920, 891, 842, 763, 741, 727, 706, 688, 656, 623; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.30 (2H, s, CH_2), 7.15-7.18 (1H, m, ArH), 7.20-7.22 (3H, m, ArH), 7.23 (1H, m, ArH), 7.25-7.26 (1H, m, ArH), 7.29-7.31 (4H, m, ArH), 7.40-7.41 (3H, m, ArH), 7.90-7.92 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 36.4 (t), 114.4 (s), 126.1 (d), 126.5 (d×2), 127.0 (d), 128.3 (d×2), 128.9 (d×2), 128.9 (d×2),129.3, 130.1 (d×2), 130.3 (d), 132.2 (s), 133.3 (s), 139.2 (s), 161.7 (s), 171.6 (s); MS *m/z* 407 (M^+), 330 (M^+-Ph), 250 (M^+-PhSe); Anal. Calcd for $C_{22}H_{17}NSSe$: C, 65.02; H, 4.22; N, 3.45. Found: C, 64.73; H, 4.29; N, 3.43.

4-Benzyl-2-phenylthiazole (5b): a yellow oil; IR (KBr, cm^{-1}) ν 3060, 3027, 2908, 2360, 1602, 1514, 1496, 1457, 1435, 1310, 1232, 1073, 1030, 1002, 933, 762, 720, 689, 609; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.19 (2H, s, CH_2), 6.73 (1H, s, olefinic H), 7.24-7.26 (1H, m, ArH), 7.33 (4H, m, ArH), 7.38-7.43 (3H, m, ArH), 7.94 (2H, d, *J* = 8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 38.0 (t), 114.3 (d), 126.4 (d), 126.5 (d×2), 128.5 (d×2), 128.9 (d×2), 129.1 (d×2), 129.8 (d), 133.7 (s), 139.0 (s), 157.5 (s), 167.9 (s); MS *m/z* 251 (M^+). Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57. Found: C, 76.16; H, 5.29; N, 5.56.

4-(4-Chlorobenzyl)-2-phenyl-5-(phenylselanyl)-thiazole: white powders, from CH_2Cl_2-*n*-hexane, mp 85 °C, IR (KBr, cm^{-1}) ν 3066, 3029, 2918, 1595, 1576, 1505, 1488, 1453, 1437, 1421, 1404, 1311, 1294, 1232, 1173, 1158, 1089, 1065, 1020, 1000, 975, 914, 841, 799, 762, 740, 713, 685, 663, 635, 611; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.25 (2H, s, CH_2), 7.16 (2H, d, *J*=8 Hz, ArH), 7.19-7.27 (7H, m, ArH), 7.39-7.42 (3H, m, ArH), 7.88-7.90 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.7 (t), 114.5 (s), 126.5 (dx2), 127.1 (d), 128.3 (dx2), 128.9 (dx2), 129.4 (dx2), 130.0 (dx2), 130.2 (dx2), 130.4 (d), 131.9 (s), 132.1 (s), 133.2 (s), 137.6 (s), 161.2 (s), 171.8 (s); MS *m/z* 441 (M^+), 364 (M^+-Ph), 284 (M^+-PhSe). Anal. Calcd for $C_{22}H_{16}ClNSSe$: C, 59.94; H, 3.66; N, 3.18. Found: C, 59.62; H, 3.89; N, 3.13.

4-(4-Chlorobenzyl)-2-phenylthiazole (5c): a yellow oil; IR (KBr, cm^{-1}) ν 3108, 3061, 2911, 1597, 1577, 1513, 1491, 1459, 1433, 1406, 1330, 1309, 1232, 1177, 1131, 1090, 1030, 1015, 1001, 931, 916, 843, 800, 763, 728, 689,

663, 640, 604; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.14 (2H, s, CH_2), 6.75 (1H, s, olefinic H), 7.25 (2H, dd, *J*=1 and 9 Hz, ArH), 7.28 (2H, d, *J*=9 Hz, ArH), 7.40-7.43 (3H, m, ArH), 7.92 (2H, dd, *J*=2 and 8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 37.3 (t), 114.4 (d), 126.5 (d×2), 128.6 (d×2), 128.9 (d×2), 129.9 (d), 130.4 (d×2), 132.2 (s), 133.6 (s), 137.5 (s), 156.8 (s), 168.1 (s); MS *m/z* 285 (M^+), 250 (M^+-Cl); Anal. Calcd for $C_{16}H_{12}ClNS$: C, 67.24; H, 4.23; N, 4.90. Found: C, 67.54; H, 4.48; N, 4.87.

4-(4-Bromobenzyl)-2-phenyl-5-(phenylselanyl)-thiazole: white powders, from CH_2Cl_2-*n*-hexane, mp 88 °C; IR (KBr, cm^{-1}) ν 3061, 2911, 2357, 1954, 1888, 1800, 1748, 1683, 1650, 1575, 1540, 1487, 1450, 1437, 1419, 1403, 1313, 1227, 1197, 1176, 1098, 1068, 1022, 1010, 999, 977, 919, 838, 801, 763, 741, 712, 687, 662, 623; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.23 (2H, s, CH_2), 7.14 (2H, d, *J*=8 Hz, ArH), 7.20-7.21 (3H, m, ArH), 7.24-7.26 (2H, m, ArH), 7.32 (2H, d, *J*=8 Hz, ArH), 7.40-7.41 (3H, m, ArH), 7.89-7.90 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.8 (t), 114.6 (s), 120.1 (s), 126.5 (d×2), 127.1 (d), 128.9 (d×2), 129.4 (d×2), 130.1 (d×2), 130.4 (d), 130.7 (d×2), 131.3 (d×2), 132.1 (s), 133.2 (s), 138.1 (s), 161.1 (s), 171.8 (s); MS *m/z* 485 (M^+), 406 (M^+-Br), 328 (M^+-PhSe); Anal. Calcd for $C_{22}H_{16}BrNSSe$: C, 54.45; H, 3.32; N, 2.89. Found: C, 54.46; H, 3.49; N, 2.91.

4-(4-Bromobenzyl)-2-phenylthiazole (5d): white plates, from CH_2Cl_2-*n*-hexane, mp 65 °C, IR (KBr, cm^{-1}) ν 3080, 2919, 2832, 2358, 2332, 1959, 1903, 1587, 1576, 1508, 1485, 1457, 1430, 1403, 1310, 1233, 1196, 1160, 1101, 1070, 1031, 1002, 933, 915, 847, 816, 797, 768, 740, 688, 653, 620; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.13 (2H, s, CH_2), 6.76 (1H, s, olefinic H), 7.20 (2H, d, *J*=8 Hz, ArH), 7.39-7.42 (3H, m, ArH), 7.43 (2H, d, *J*=8 Hz, ArH), 7.92 (2H, dd, *J*=1 and 7 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 37.4 (t), 114.5 (d), 120.3 (s), 126.5 (d×2), 128.9 (d×2), 123.0 (d), 130.8 (d×2), 131.6 (d×2), 133.6 (s), 138.0 (s), 156.6 (s), 168.1 (s); MS *m/z* 329 (M^+), 250 (M^+-Br); Anal. Calcd for $C_{16}H_{12}BrNS$: C, 58.19; H, 3.66; N, 4.24. Found: C, 58.19; H, 3.80; N, 4.20.

4-(1-Naphthylmethyl)-2-phenyl-5-(phenylselanyl)-thiazole: white powders, from CH_2Cl_2-*n*-hexane, mp 105-107 °C, IR (KBr, cm^{-1}) ν 3058, 1577, 1477, 1438, 1397, 1234, 1020, 781,763, 734, 687; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.73 (2H, s, CH_2), 7.17-7.18 (3H, m, ArH), 7.29-7.35 (7H, m, ArH), 7.43-7.47 (2H, m, ArH), 7.69 (1H,d, *J*=8 Hz, ArH), 7.80-7.86 (3H, m, ArH), 8.34 (1H, d, *J*=8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.7 (t), 115.0 (s), 124.5 (d), 125.4 (dx2), 125.7 (d), 126.4 (dx2), 126.9 (d), 127.0 (d), 127.1 (d), 128.5 (d), 128.8 (dx2), 129.3 (dx2), 130.2 (d), 130.3 (dx2), 132.0 (s), 132.1 (s), 133.3 (s), 133.8 (s), 135.3 (s), 161.0 (s), 171.4 (s); MS *m/z* 457 (M^+), 300 (M^+-PhSe). Anal. Calcd for $C_{26}H_{19}NSSe$: C, 68.41; H, 4.20; N, 3.07. Found: C, 68.44; H, 5.35; N, 3.06.

4-(1-Naphthylmethyl)-2-phenylthiazole (5e): white powders, from CH_2Cl_2-*n*-hexane, mp 59 °C, IR (KBr, cm^{-1}) ν 3114, 3066, 2904, 2842, 2356, 2334, 2257, 1943, 1874, 1827, 1808, 1748, 1731, 1680, 1648, 1595, 1554, 1537, 1506, 1455, 1395, 1336, 1308, 1267, 1236, 1165, 1125, 1099, 1071, 1020, 996, 947, 912, 865, 776, 758, 685, 641, 606; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.65 (2H, s, CH_2), 6.50 (1H, s, olefinic H), 7.38-7.48 (7H, m, ArH), 7.78-7.80 (1H, m, ArH), 7.86-7.87 (1H, m, ArH), 7.95-7.96 (2H, brd, *J* = 7 Hz, ArH), 8.03-8.04 (1H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.7 (t), 114.7 (d), 124.4 (d), 125.6 (d×2), 126.0 (d), 126.5 (d×2), 127.4 (d), 127.5 (d), 128.6 (d), 128.9 (d×2), 129.9 (d), 132.0 (s), 133.7 (s), 133.9 (s), 135.0 (s), 157.2 (s), 167.7 (s); MS *m/z* 301 (M^+); Anal. Calcd for $C_{20}H_{15}NS$: C, 79.70; H, 5.02; N, 4.65. Found: C, 79.38; H, 5.17; N, 4.56.

2-Phenyl-5-(phenylselanyl)-4-(2-thienylmethyl)-thiazole: yellow powders, from CH_2Cl_2-*n*-hexane, mp 80-82 °C, IR (KBr, cm^{-1}) ν 3060, 2922, 1554, 1505, 1489, 1476, 1454, 1437, 1437, 1420, 1314, 1298, 1230, 1071, 1020, 999, 979, 850, 824, 762, 735, 688, 622; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.47 (2H, s, CH_2), 6.85-6.86 (2H, m, ArH), 7.10 (1H, dd, *J*=5 and 1 Hz, ArH), 7.19-7.22 (3H, m, ArH), 7.30-7.31 (2H, m, ArH), 7.38-7.42 (3H, m, ArH), 7.90-7.91 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.9 (t), 114.6 (s), 124.0 (d), 125.4 (d), 126.4 (dx2), 126.5 (d), 127.0 (d), 128.8 (dx2), 129.3 (dx2), 130.2 (dx2), 130.3 (d), 132.0 (s), 133.2 (s), 141.4 (s), 160.6 (s), 171.7 (s); MS *m/z* 413 (M^+), 328 (M^+-thienyl), 256 (M^+-PhSe). Anal. Calcd for $C_{20}H_{15}NS_2Se$: C, 58.25; H, 3.67; N, 3.40. Found: C, 57.94; H, 3.78; N, 3.34.

2-Phenyl-4-(2-thienylmethyl)thiazole (5f): a yellow oil, IR (KBr, cm^{-1}) ν 3104, 3062, 2903, 1598, 1514, 1498, 1459, 1435, 1327, 1309, 1231, 1179, 1131, 1073, 1037, 1001, 932, 916, 850, 827, 764, 689, 643, 616; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.38 (2H, s, CH_2), 6.90 (1H, s, olefinic H), 6.95-6.97 (2H, m, ArH), 7.18 (1H, dd, *J*=1 and 5 Hz, ArH), 7.40-7.44 (3H, m, ArH), 7.94 (2H, dd, *J*=2 and 7 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.1 (t), 114.5 (d), 124.2 (d), 125.8 (d), 126.5 (d×2), 126.8 (d), 128.9 (d×2), 129.9 (d), 133.6 (s), 141.2 (s), 156.4 (s), 168.0 (s); MS *m/z* 257 (M^+), 180 (M^+-Ph). Anal. Calcd for $C_{14}H_{11}NS_2$: C, 65.34; H, 4.31; N, 5.44. Found: C, 65.37; H, 4.54; N, 5.43.

4-(3,4-Dimethoxybenzyl)-2-phenyl-5-(phenylselanyl)-thiazole: white prisms, from CH_2Cl_2-*n*-hexane, mp 98 °C; IR (KBr, cm^{-1}) ν 3058, 3005, 2965, 2934, 2903, 2837, 1607, 1586, 1576, 1516, 1493, 1477, 1464, 1452, 1419, 1349, 1281, 1183, 1147, 1133, 1071, 1023, 979, 917, 896, 845, 796, 763, 741, 688, 623; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.74 (3H, s, OMe), 3.82 (3H, s, OMe), 4.24 (2H, s, CH_2), 6.73 (1H, d, *J*=8 Hz, ArH), 6.85 (1H, d, *J*=8 Hz, ArH), 6.87 (1H, s, ArH), 7.19-7.20 (3H, m, ArH), 7.28 (2H, m, ArH), 7.40-7.41 (3H, m, ArH), 7.90-7.91 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.9 (t), 55.6 (q), 55.8 (q), 111.1 (d), 112.2 (d), 113.9 (s), 120.9 (d), 126.4 (d×2), 126.9 (d), 128.9 (d×2), 129.3 (d×2), 129.9 (d×2), 130.3 (d), 131.8 (s), 132.3 (s), 133.3 (s), 147.4 (s), 148.7 (s), 162.1

(s), 171.7 (s); MS *m/z* 467 (M^+), 405 (M^+-2MeO), 390 (M^+-Ph), 310 (M^+-PhSe). Anal. Calcd for $C_{24}H_{21}NO_2SSe$: C, 61.80; H, 4.57; N, 3.00. Found: C, 61.70; H, 4.62; N, 2.99.

4-(3,4-Dimethoxybenzyl)-2-phenylthiazole (5g): a yellow oil; IR (KBr, cm^{-1}) ν 3105, 3060, 2997, 2932, 2832, 2359, 1590, 1514, 1460, 1332, 1260, 1234, 1189, 1155, 1139, 1074, 1029, 1001, 952, 916, 851, 810, 764, 690, 648, 628; ^1H NMR (600 MHz, $CDCl_3$) δ 3.87 (6H, s, OMe×2), 4.13 (2H, s, CH_2), 6.74 (1H, s, olefinic H), 6.83 (1H, d, *J* = 8 Hz, ArH), 6.86 (1H, dd, *J* = 2 and 9 Hz, ArH), 6.89 (1H, d, *J* = 2 Hz, ArH), 7.38-7.43 (3H, m, ArH), 7.93-7.95 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 37.6 (t), 55.8 (q), 55.8 (q), 111.1 (d), 112.3 (d), 114.2 (d), 121.0 (d), 126.4 (d×2), 128.8 (d×2), 129.8 (d), 131.5 (s), 133.7 (s), 147.6 (s), 148.9 (s), 157.8 (s), 167.9 (s); MS *m/z* 311 (M^+), 296 (M^+-Me), 280 (M^+-MeO); high resolution mass calcd for $C_{18}H_{17}NO_2S$: 311.0980, found m/z 311.0913.

4-(3,4-Methylenedioxyphenylmethyl)-2-phenyl-5-(phenylselanyl)thiazole: white prisms, from CH_2Cl_2-*n*-hexane, mp 86-88 °C, IR ν 1577, 1501, 1487, 1441, 1245, 1184, 1039, 1021, 929, 808, 777, 763, 737, 688; ^1H NMR (600 MHz, $CDCl_3$) δ 4.20 (2H, s, CH_2), 5.86 (2H, s, CH_2), 6.65 (1H, d, *J*=8 Hz, ArH), 6.73 (1H, dd, *J*=8 and 1 Hz, ArH), 6.82 (1H, d, *J*=1 Hz, ArH), 7.19-7.23 (3H, m, ArH), 7.27-7.29 (2H, m, ArH), 7.38-7.41 (3H, m, ArH), 7.89-7.91 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 36.0 (t), 100.7 (t), 108.0 (d), 109.5 (d), 114.2 (s), 121.8 (d), 126.5 (dx2), 127.0 (d), 128.9 (dx2), 129.3 (dx2), 130.0 (dx2), 130.3 (d), 132.2 (s), 132.9 (s), 133.3 (s), 145.8 (s), 147.4 (s), 161.8 (s), 171.7 (s); MS *m/z* 451 (M^+), 374 (M^+-Ph), 295 (M^+-PhSe). Anal. Calcd for $C_{23}H_{17}NO_2SSe$: C, 61.33; H, 3.80; N, 3.11. Found: C, 61.20; H, 3.96; N, 3.10.

4-(1,3-Benzodioxol-5-ylmethyl)-2-phenylthiazole (5h): a yellow oil; IR (KBr, cm^{-1}) ν 3108, 3061, 3014, 2890, 2774, 1607, 1501, 1488, 1458, 1442, 1360, 1323, 1245, 1186, 1127, 1096, 1074, 1039, 1001, 928, 869, 808, 779, 763, 689, 652, 627; ^1H NMR (600 MHz, $CDCl_3$) δ 4.09 (2H, s, CH_2), 5.92 (2H, s, CH_2), 6.76-6.78 (3H, m, ArH), 6.82 (1H, s, olefinic H), 7.38-7.43 (3H, m, ArH), 7.92-7.93 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 37.7 (t), 100.8 (t), 108.2 (d), 109.6 (d), 114.2 (d), 121.9 (d), 126.5 (d×2), 128.8 (d×2), 129.8 (d), 132.8 (s), 133.7 (s), 146.1 (s), 147.7 (s), 157.6 (s), 167.9 (s); MS *m/z* 295 (M^+). Anal. Calcd for $C_{17}H_{13}NO_2S$: C, 69.13; H, 4.44; N, 4.74. Found: C, 69.06; H, 4.63; N, 4.66.

2-Phenyl-5-(phenylselanyl)-4-(2,4,6-trimethylbenzyl)thiazole: pale yellow powders, from CH_2Cl_2-*n*-hexane, mp 119 °C, IR ν 2917, 1714, 1577, 1480, 1439, 1020, 850, 760, 738, 714, 688, 672, 620; ^1H NMR (600 MHz, $CDCl_3$) δ 2.15 (3H, s, Me), 2.30 (6H, s, Mex2), 4.09 (2H, s, CH_2), 6.75 (2H, s, ArH), 7.10-7.17 (3H, m, ArH), 7.22-7.29 (5H, m, ArH), 7.69-7.71 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.8 (qx2), 20.9 (q), 30.4 (t), 113.3 (s), 126.3 (dx2), 127.0 (d), 128.7 (dx2), 128.8 (dx2), 129.3 (dx2), 130.1 (d), 130.2 (dx2), 132.3 (s), 133.1 (s), 133.4 (s), 135.6 (s), 137.2 (sx2), 160.5 (s), 170.9 (s); MS *m/z* 449 (M^+), 434 (M^+-Me), 371 (M^+-Ph), 292 (M^+-PhSe). Anal. Calcd for $C_{25}H_{23}NSSe$:C, 66.95; H, 5.17; N, 3.12. Found: C, 66.73; H, 5.18; N, 3.09.

2-Phenyl-4-(2,4,6-trimethylbenzyl)thiazole (5i): a yellow oil; IR (KBr, cm^{-1}) ν 3107, 3061, 3004, 2943, 2916, 2858, 2731, 1950, 1731, 1612, 1578, 1512, 1496, 1484, 1459, 1376, 1332, 1073, 1252, 1230, 1177, 1126, 1073, 1030, 997, 931, 913, 851, 799, 763, 735, 689, 663, 644, 608, 572, 539, 512, 458, 444, 415; ^1H NMR (600 MHz, $CDCl_3$) δ 2.29 (3H, s, Me), 2.29 (6H, s, Me×2), 4.18 (2H, s, CH_2), 6.40 (1H, s, olefinic H), 6.90 (2H, s, ArH), 7.39-7.43 (3H, m, ArH), 7.93-7.95 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.9 (q×2), 20.9 (q), 31.8 (t), 113.1 (d), 126.4 (d×2), 128.8 (d×2), 128.9 (d×2), 129.8 (d), 132.5 (s), 133.8 (s), 135.9 (s), 136.8 (s×2), 156.8 (s), 167.8 (s); MS *m/z* 293 (M^+), 278 (M^+-Me). Anal. Calcd for $C_{19}H_{19}NS$: C, 77.77; H, 6.53; N, 4.77. Found: C, 77.33; H, 6.63; N, 4.67.

4-(4-Methoxybenzyl)-2-methyl-5-(phenylselanyl)-thiazole: a yellow oil, IR (KBr, cm^{-1}) ν 3055, 2996, 2951, 2929, 2832, 1609, 1577, 1509, 1475, 1462, 1438, 1301, 1245, 1176, 1104, 1066, 1034, 998, 817, 769, 735, 688, 666, 609; ^1H NMR (600 MHz, $CDCl_3$) δ 2.65 (3H, s, Me), 3.73 (3H, s, OMe), 4.15 (2H, s, CH_2), 6.75 (2H, d, *J*=8 Hz, ArH), 7.14 (2H, d, *J*=8 Hz, ArH), 7.18-7.19 (3H, m, ArH), 7.23-7.25 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.5 (q), 35.3 (t), 55.1 (q), 112.9 (s), 113.7 (d×2), 126.8 (d), 129.2 (d×2), 129.7 (d×2), 129.8 (d×2), 131.3 (s), 132.3 (s), 157.9 (s), 161.0 (s), 170.4 (s); MS *m/z* 375 (M^+), 360 (M^+-Me), 298 (M^+-Ph), 218 (M^+-PhSe). Anal. Calcd for $C_{18}H_{17}NOSSe$: C, 57.75; H, 4.58; N, 3.74. Found: C, 57.41; H, 4.57; N, 3.54.

4-(4-Methoxybenzyl)-2-methylthiazole (6a): white powders, from CH_2Cl_2-*n*-hexane, mp 53 °C, IR (KBr, cm^{-1}) ν 3106, 3031, 2997, 2913, 2834, 1611, 1584, 1511, 1463, 1439, 1374, 1301, 1245, 1179, 1126, 1107, 1034, 955, 818, 772, 736, 692, 661; ^1H NMR (600 MHz, $CDCl_3$) δ 2.67 (3H, s, Me), 3.77 (3H, s, OMe), 4.02 (2H, s, CH_2), 6.57 (1H, s, olefinic H), 6.84 (2H, d, *J* = 8 Hz, ArH), 7.18 (2H, d, *J* = 8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1 (q), 36.9 (t), 55.1 (q), 113.4 (d), 113.8 (d×2), 129.9 (d×2), 131.1 (s), 156.4 (s), 158.1 (s), 165.6 (s); MS *m/z* 219 (M^+), 204 (M^+-Me). Anal. Calcd for $C_{12}H_{13}NOS$: C, 65.72; H, 5.98; N, 6.39. Found: C, 65.52; H, 5.89; N, 6.33.

2-Methyl-5-(phenylselanyl)-4-(2-thienylmethyl)-thiazole: a red oil, IR (KBr, cm^{-1}) ν 3070, 2919, 1577, 1505, 1476, 1438, 1420, 1298, 1246, 1175, 1068, 1020, 999, 895, 850, 825, 759, 736, 689, 666, 613; ^1H NMR (600 MHz, $CDCl_3$) δ 2.70 (3H, s, Me), 4.40 (2H, s, CH_2), 6.82 (1H, d, *J*=3 Hz, ArH), 6.87 (1H, dd, *J*=8 and 7 Hz, ArH), 7.11 (1H, dd, *J*=1 and 6 Hz, ArH), 7.21-7.22 (3H, m, ArH), 7.27-7.29 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.4 (q), 30.6 (t), 113.5 (s), 123.9 (d), 125.3 (d), 126.5 (d), 126.8 (d), 129.2 (d×2), 129.9 (d×2), 132.0 (s), 141.4 (s),

159.5 (s), 170.5 (s); MS *m/z* 351 (M^+), 274 (M^+-Ph), 194 (M^+-PhSe). Anal. Calcd for $C_{15}H_{13}NS_2Se$: C, 51.42; H, 3.74; N, 4.00. Found: C, 51.74; H, 3.78; N, 3.84.

2-Methyl-4-(2-thienylmethyl)thiazole (6f): a brown oil; IR (KBr, cm^{-1}) ν 3104, 2919, 1521, 1473, 1438, 1372, 1321, 1243, 1181, 1127, 1073, 1038, 1003, 954, 850, 829, 694, 655, 605; ^1H NMR (600 MHz, $CDCl_3$) δ 2.68 (3H, s, Me), 4.27 (2H, s, CH_2), 6.75 (1H, s, olefinic H), 6.89 (1H, d, *J*=3 Hz, ArH), 6.93-6.94 (1H, m, ArH), 7.15 (1H, d, *J*=4 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1 (q), 31.9 (t), 113.9 (d), 125.6 (d), 126.8 (d), 127.3 (d), 141.4 (s), 154.9 (s), 165.9 (s); MS *m/z* 195 (M^+); high resolution mass calcd for $C_9H_9NO_2$: 195.0176. Found: 195.0102.

4-(4-Methoxybenzyl)-2-phenyl-5-(tributylstannyl)-selenazole: a yellow oil, IR (KBr, cm^{-1}) ν 2955, 2925, 2870, 2851, 1611, 1510, 1483, 1461, 1376, 1300, 1245, 1176, 1073, 1038, 999, 930, 809, 760, 689, 662; ^1H NMR (600 MHz, $CDCl_3$) δ 0.87 (9H, t, *J*=7 Hz, Mex3), 1.08-1.11 (6H, m, CH_2x3), 1.28-1.32 (6H, m, CH_2x3), 1.48-1.52 (6H, m, CH_2x3), 3.76 (3H, s, MeO), 4.11 (2H, s , CH_2), 6.80 (2H, d, *J*=8 Hz, ArH), 7.15 (2H, d, *J*=8 Hz, ArH), 7.36-7.37 (3H, m, ArH), 7.88 (2H, d, *J*=4 Hz, ArH); ^{13}C NMR(150 MHz, $CDCl_3$) δ 11.6 (tx3), 13.6 (qx3), 27.0 (tx3), 29.0 (tx3), 39.3 (t), 55.2 (q), 113.6 (dx2), 127.1 (dx2), 128.8 (dx2), 129.4 (dx2), 129.6 (d), 132.0 (s), 132.6 (s), 136.7 (s), 157.9 (s), 162.6 (s), 178.3 (s); MS *m/z* 560 (M^+ -Bu), 328 (M^+-$SnBu_3$), 251 (M^+-$SnBu_3$-Ph). Anal. Calcd for $C_{29}H_{41}NOSnSe$: C, 56.42; H, 6.69; N, 2.26. Found: C, 56.25; H, 6.65; N, 2.25.

4-(4-Methoxybenzyl)-2-phenyl-5-(tributylstannyl)-selenazole: a colorless oil, IR (KBr, cm^{-1}) ν 2955, 2925, 2870, 2851, 1611, 1510, 1483, 1461, 1376, 1300, 1245, 1176, 1073, 1038, 999, 930, 809, 760, 689, 662 ; ^1H NMR δ (600 MHz, $CDCl_3$) 0.87 (9H, t, *J*=7Hz Mex3), 1.08-1.11 (6H, m ,CH_2x3), 1.28-1.32 (6H, m , CH_2x3), 1.48-1.52 (6H, m , CH_2x3), 3.76 (3H, s, MeO), 4.11 (2H, s , CH_2), 6.80 (2H, d, *J*=8 Hz, ArH), 7.15 (2H, d, *J*=8 Hz, ArH), 7.36-7.37 (3H, m, ArH), 7.88 (2H, d, *J*=4 Hz, ArH); ^{13}C NMR (600 MHz, $CDCl_3$) δ 11.6 (tx3), 13.6 (qx3), 27.0 (tx3), 29.0 (tx3), 39.3 (t), 55.2 (q), 113.6 (dx2), 127.1 (dx2), 128.8 (dx2), 129.4 (dx2), 129.6 (d), 132.0 (s), 132.6 (s), 136.7 (s), 157.9 (s), 162.6 (s), 178.3 (s) ; MS *m/z* 560 (M^+, -Bu), 453 (M^+, -Bu, -C_7H_8O), 376 (M^+, -Bu, -Ph, -C_7H_8O), 328 (M^+, -$SnBu_3$), 251 (M^+, -$SnBu_3$, -Ph). Anal. Calcd for $C_{29}H_{41}NOSnSe$: C, 56.42; H, 6.69; N, 2.26. Found: C, 56.21; H, 6.65; N, 2.25.

4-(4-Methoxybenzyl)-2-phenylselenazole (7a): a yellow oil, IR (KBr, cm^{-1}) ν 3007, 2897, 2834, 2361, 2336, 1712, 1611, 1511, 1464, 1432, 1361, 1246, 1220, 1178, 1036, 982, 760, 691, 660, 637, 609: ^1H NMR (600 MHz,$CDCl_3$) δ 3.78 (3H, s, MeO), 4.11 (2H, s, CH_2), 6.86 (2H, d, *J*=8Hz, ArH), 7.27 (2H, d, *J*=8Hz, ArH), 7.28 (1H, s, olefinicH), 7.37-7.40 (3H, m, ArH), 7.87-7.88 (2H, m, ArH); ^{13}C NMR (600 MHz, $CDCl_3$) δ 38.1 (t), 55.2 (d), 113.9 (dx2), 119.2 (d), 127.0 (dx2), 128.9 (dx2), 130.0 (d), 130.1 (dx2), 131.2 (s), 136.4 (s), 158.1 (s), 158.4 (s), 174.2 (s); MS *m/z* 329 (M^+), 248 (M^+, -SeH), 348 (-MeOPh), 271 (-MeOPh, -Ph). Anal. Calcd for $C_{17}H_{15}NOSe$: C, 62.20; H, 4.66; N, 4.26. Found: C, 61.88; H, 4.65; N, 4.24.

4-(2-Thienylmethyl)-2-phenyl-5-(phenylselanyl)-selenazole: a yellow oil, IR (KBr, cm^{-1}) ν 3056, 1575, 1507, 1486, 1475, 1455, 1436 ,1420, 1288 ,1224, 1177, 1070, 1037, 1021 ,1005, 943, 916, 849, 824, 759, 734, 687, 666; ^1H NMR (600 MHz, $CDCl_3$) δ 4.47 (2H, s, CH_2), 6.87 (1H, d, *J*=1 Hz, ArH), 6.88 (1H, d, *J*=2 Hz, ArH), 7.12-7.13 (1H, m, ArH), 7.22-7.24 (3H, m, ArH), 7.36-7.40 (5H, m, ArH), 7.84-7.86 (2H, m, ArH); ^{13}C NMR(150 MHz, $CDCl_3$) δ 31.7 (t), 120.4 (s), 124.1 (d), 125.4 (d), 126.5 (d), 127.0 (dx2), 127.1 (d), 129.0 (dx2), 129.4 (dx2), 130.3 (dx2), 130.5 (d), 132.9 (s), 136.2 (s), 141.6 (s), 160.8 (s), 178.3 (s); MS *m/z* 461 (M^+), 384 (M^+-C_4H_4S), 304 (M^+-SePh). Anal. Calcd for $C_{20}H_{15}NSSe_2$: C, 52.29; H, 3.29; N, 3.04. Found: C, 52.06; H, 3.25; N, 3.02.

2-Phenyl-4-(2-thienylmethyl)-5-(tributylstannyl)-selenazole: a yellow oil, IR (KBr, cm^{-1}) ν 3064, 2955, 2924, 2869, 2854, 1513, 1483, 1462, 1438, 1422, 1375, 1340, 1290, 1271, 1229, 1175, 1073, 998, 960, 932, 874, 864, 851, 840, 815, 759, 688, 663, 314: ^1H NMR (600 MHz, $CDCl_3$) δ 0.88 (9H, t, *J*=8 Hz Mex3), 1.12-1.17 (6H, m, CH_2x3), 1.30-1.35 (6H, m, CH_2x3), 1.48-1.57 (6H, m, CH_2x3), 4.31 (2H, s, CH_3), 6.82 (1H, s, ArH) 7.11 (1H, d, *J*=8 Hz, ArH), 7.37-7.38 (3H, m, ArH), 7.90 (2H, brs, ArH); ^{13}C NMR (600 MHz, $CDCl_3$) δ 11.7 (tx3), 13.6 (qx3), 27.2 (tx3), 29.0 (tx3), 35.0 (t), 123.8 (d), 124.7 (d), 126.4 (d), 127.1 (dx2), 128.8 (dx2), 129.7 (d), 132.2 (s), 136.6 (s), 143.2 (s), 161.4 (s), 178.6 (s); MS *m/z* 536 (M^+-Bu), 433 (M^+-C_4H_4S-Ph), 319 (M^+-C_4H_4S-Ph-Bu_2) 304 (M^+-$SnBu_3$). Anal. Calcd for $C_{26}H_{37}NSSeSn$: C, 52.63; H, 6.28; N, 2.36. Found: C, 52.39; H, 6.17; N, 2.35.

4-(2-Thienyl)-2-phenylselenazole: (7f): a yellow oil, IR (KBr, cm^{-1}) ν 3093, 2923, 1516, 1494, 1464, 1438, 1296, 1232, 1179, 1104, 1073, 1034, 981, 906, 854, 826, 763, 693, 667, 613; ^1H NMR (600 MHz, $CDCl_3$) δ 2.29 (3H, s, CH_3), 4.37 (2H, s, CH_2), 6.95-6.96 (2H, m, ArH), 7.18 (1H, d, *J*=2 Hz, ArH), 7.40-7.41 (3H, m, ArH), 7.48 (1H, s, olefinic H), 7.88-7.90 (2H, m, ArH); ^{13}C NMR (600 MHz, $CDCl_3$) δ 33.1 (t), 119.6 (d), 124.2 (d), 125.7 (d), 126.8 (d), 127.0 (dx2), 128.9 (dx2), 130.1 (d), 136.3 (s), 141.5 (s), 156.8 (s), 174.4 (s); MS *m/z* 305 (M^+), 224 (M^+-SeH). Anal. Calcd for $C_{14}H_{21}NSSe$: C, 55.26; H, 3.64; N, 4.60. Found: C, 55.20; H, 3.61; N, 4.56.

2-Phenyl-4-(2,4,6-trimethylphenylmethyl)-5-(phenylselanyl)selenazole: IR (KBr, cm^{-1}) ν 2917, 1612, 1576, 1508, 1481, 1437, 1373, 1221, 1176, 1067, 1021, 998, 942, 850 ,759, 735, 688, 662; ^1H NMR (600 MHz, $CDCl_3$) δ 2.25 (3H, s, ArH), 2.42 (6H, s, Mex2), 4.15 (2H, s, CH_2), 6.85 (2H, s, CH_2), 7.23-7.35 (6H, m, ArH), 7.44 (2H, d, *J*=8 Hz, ArH), 7.70 (2H, d, *J*=8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.8 (qx2), 20.9 (q), 31.2 (t), 119.2 (s), 126.9 (dx2), 127.1 (d), 128.7 (dx2), 128.8 (dx2),

129.4 (dx2), 130.2 (d), 130.5 (dx2), 133.2 (s), 133.4 (s), 135.6 (s), 136.3 (s), 137.3 (sx2), 160.4 (s), 177.0 (s); MS *m/z* 497 (M^+), 482 (M^+-Me), 375 (M^+-C_9H_{11}), 340 (M^+-SePh), 221 (M^+-C_9H_{11}-SePh). Anal. Calcd for $C_{25}H_{23}NSe_2$: C, 60.61; H, 4.68; N, 2.83. Found: C, 60.36; H, 4.59; N, 2.81.

4-(2,4,6-Trimethylphenyl)-2-phenyl-5-(tributylstannyl)selenazole: a yellow oil, IR (KBr, cm^{-1}) ν 2956, 2923, 2870, 2853, 1715, 1511, 1482, 1461, 1375, 1219, 1074, 929, 851, 756, 689; ^1H NMR (600 MHz, $CDCl_3$) δ 0.91 (9H, t, *J*=7 Hz Mex3), 1.19-1.21 (6H, m, CH_2x3), 1.36-1.39 (6H, m, CH_2x3), 1.54-1.62 (6H, m, CH_2x3), 2.27 (2H, s, CH_3), 2.38 (6H, s, CH_3) 4.01 (2H, s, CH_2), 6.85 (2H, s, ArH), 7.29-7.30 (3H, m, ArH), 7.74 (2H, d, *J*=4 Hz, ArH); ^{13}C NMR (600 MHz, $CDCl_3$) δ 11.7 (tx3), 13.6 (qx3), 20.7 (qx2), 20.9 (q), 27.3 (tx3), 29.1 (tx3), 34.4 (t), 127.0 (dx2), 128.6 (dx2), 128.6 (dx2), 128.9 (d), 129.4 (d), 130.1 (s), 134.2 (s), 135.2 (s), 136.8 (s), 136.9 (sx2), 162.1 (s), 177.5 (s); MS *m/z* 572 (M^+-Bu), 340 (M^+-$SnBu_3$) 339 (M^+-C_9H_{12}-Bu_3). Anal. Calcd for $C_{28}H_{38}NClSeSn$: C, 59.16; H, 7.20; N, 2.22. Found: C, 58.93; H, 6.80; N, 2.31.

4-(2,4,6-Trimethylphenylmethyl)-2-phenylselenazole (7i): a yellow oil, IR (KBr, cm^{-1}) ν 2920, 2856, 1712, 1613, 1578, 1517, 1486, 1464, 1443, 1376, 1255, 1217, 1099, 1031, 979, 909, 852, 760, 729, 689, 667; ^1H NMR (600 MHz, $CDCl_3$) δ 2.29 (3H, s, CH_3), 4.18 (2H, s, CH_2), 6.90 (2H, s, ArH), 6.98 (1H, s, olefinic H), 7.40-7.41 (3H, m, ArH), 7.89 (2H, d, *J*=3 Hz, ArH); ^{13}C NMR (600 MHz, $CDCl_3$) δ 20.0 (qx2), 20.9 (q), 32.8 (t), 118.1 (d), 126.9 (dx2), 128.9 (dx2), 128.9 (dx2), 130.0 (d), 132.6 (s), 135.9 (s), 136.4 (s), 137.0 (sx2), 157.0 (s), 174.0 (s); MS *m/z* 341 (M^+), 339 (M^+-2H), 326 (M^+-Me), 222 (M^+-Me_3Ph), 219 (M^+-3xMe-Ph); high-resolution mass calcd for $C_{19}H_{19}NSe$: 341.0446, found *m/z* 341.681.

5-(4-Fluorobenzyl)-2-phenyl-4-(phenylsulfanyl)-selenazole: a yellow oil, IR ν 2359, 2342, 1601, 1581, 1508, 1485, 1455, 1438, 1221, 1157, 1024, 955, 821, 642, 760, 738, 688, 666; ^1H NMR (600 MHz, $CDCl_3$) δ 4.20 (2H, s, CH_2), 6.92 (2H, t, *J*=8 Hz, ArH), 7.17-7.26 (7H, m, ArH), 7.38-7.40 (3H, m, ArH), 7.82 (2H, d, *J*=8 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.5 (t), 114.9 (d), 115.1 (d), 126.4 (d), 126.9 (dx2), 127.3 (dx2), 127.4 (s), 129.0 (dx2), 129.1 (dx2), 130.4 (dx2), 130.4 (d), 130.6 (d), 134.8 (s), 136.2 (s), 138.0 (s), 161.3 (d, *J*=243 Hz), 162.0 (s); MS *m/z* 425 (M^+), 316 (M^+-PhS). Anal. Calcd for $C_{22}H_{16}NFSSe$: C, 62.26; H, 3.80; N, 3.30. Found: C, 61.98; H, 3.82; N, 3.27.

4-(4-Fluorobenzyl)-2-phenyl-5-(tributylstannyl)-selenazole: a yellow oil, IR (KBr, cm^{-1}) ν 2956, 2925, 2870, 2852, 1715, 1603, 1509, 1483, 1462, 1376, 1359, 1221, 1157, 1073, 1000, 930, 814, 759, 689, 661: ^1H NMR (600 MHz, $CDCl_3$) δ 0.82 (9H, t, *J*=7 Hz, Mex3), 1.08-1.11 (6H, m, CH_2x3), 1.28-1.32 (6H, m, CH_2x3), 1.48-1.53 (6H, m, CH_2x3), 4.13 (2H, s, CH_2), 6.93-6.96 (2H, m, ArH), 7.17-7.19 (3H, m, ArH), 7.36-7.37 (3H, m, ArH), 7.87 (2H, d, *J*=5 Hz, ArH); ^{13}C NMR (600 MHz, $CDCl_3$) δ 11.6 (tx3), 13.6 (qx3), 27.2 (tx3), 29.0 (tx3), 39.3 (t), 114.8 (d), 115.0 (d), 127.1 (dx2), 128.8 (dx2), 129.7 (d), 129.8 (d), 129.9 (d), 132.4 (s), 136.1 (s), 136.6 (s),161.4 (d, *J*=244 Hz), 161.9 (sx2), 178.6 (sx2) ; MS *m/z* 548 (M^+-Bu), 492 (M^+-Bu_2), 319 (M^+-Bu_2-Ph-C_6H_5F), 316 (M^+-$SnBu_3$) 211 (M^+-C_6H_5F-$SnBu_3$). Anal. Calcd for $C_{28}H_{38}NFSeSn$: C, 55.56; H, 6.32; N, 2.31. Found: C, 55.27; H, 6.29; N, 2.31.

4-(4-Fluorobenzyl)-2-phenylselenazole (7j): a yellow oil, IR (KBr, cm^{-1}) ν 3063, 2920, 2359, 2339, 1713, 1601, 1508, 1465, 1440, 1429, 1309, 1294, 1220, 1157, 1093, 1074, 1016, 981, 909, 855, 836, 825, 774, 760, 689, 668: ^1H NMR (600 MHz, $CDCl_3$) δ 4.14 (2H, s, CH_2), 6.99-7.02 (2H, m, ArH), 7.24-7.29 (2H, m, ArH), 7.32 (1H, s, olefinic H), 7.39-7.41 (3H, m, ArH), 7.86-7.88 (2H, m, ArH); ^{13}C NMR (600 MHz, $CDCl_3$) δ 38.2 (t), 115.2 (d), 115.3 (d), 119.4 (d), 127.0 (dx2), 128.9 (dx2), 130.5 (d), 130.6 (d), 134.9 (s), 131.3 (s), 157.6 (s), 161.6 (d, *J*=244 Hz), 174.5 (s); MS *m/z* 317 (M^+) 236 (M^+-SeH); high-resolution mass calcd for $C_{16}H_{12}FNSe$: 317.0118, found *m/z* 316.9975.

Preparation of 5-Benzyl-4-(1-naphtylmethyl)-2-phenylthiazole (13a), Typical procedure. Tributyltin hydride (1.66 g, 5.71 mmol) and azobisisobutyronitrile (94 mg, 0.57 mmol) were added to a toluene (5.0 ml) solution of 4-(naphthylmethyl)-2-phenyl-5-(phenylsulfanyl)thiazole (0.47 g, 1.1 mmol). The reaction mixture was refluxed for 40 min. The solvent was removed under reduced pressure. The compound was used without further purifications. Benzyl bromide (0.56 g, 3.30 mmol), cesium fluoride (0.33 g, 2.2 mmol) and tetrakis(triphenylphosphine)palladium (64 mg, 0.06 mmol) were added to a toluene (12 ml) solution of the trbutylstannane. The whole was heated under reflux condition for 1h and then poured into water (100 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-*n*-hexane to give the title compound (0.32 g, 77) as a yellow oil. **13a**: IR ν 3060, 2920, 2850, 2386, 2285, 1947, 1712, 1598, 1531, 1509, 1495, 1460, 1437, 1397, 1310, 1252, 1178, 1158, 1136, 1099, 1074, 1030, 1020, 1004, 965, 914, 791, 780, 762, 700, 690; ^1H NMR (600 MHz, $CDCl_3$) δ 4.01 (2H, s, CH_2), 4.61 (2H, s, CH_2), 7.08 (2H, d, *J*=8 Hz, ArH), 7.16-7.24 (4H, m, ArH), 7.31-7.34 (4H, m, ArH), 7.44-7.51 (2H, m, ArH), 7.70 (1H, d, *J*=8 Hz, ArH), 7.82-7.95 (4H, m, ArH), 8.25 (1H, d, *J*=8 Hz, ArH); ^{13}C NMR (600 MHz, $CDCl_3$) δ 32.5 (t), 32.9 (t), 124.1 (d), 125.5 (d), 125.6 (d), 125.9 (d), 126.1 (d), 126.2 (dx2), 126.7 (d), 127.1 (d), 128.3 (dx2), 128.6 (dx3), 128.7 (dx2), 129.5 (d), 132.1 (s), 133.5 (s), 133.8 (s), 133.8 (s), 135.3 (s), 139.5 (s), 151.1 (s), 164.9 (s); MS *m/z* 378 (M^+). Anal. Calcd for $C_{26}H_{19}NS$: C, 82.83; H, 5.41; N, 3.58. Found: C, 82.68; H, 5.37; N, 3.52.

4-(*p*-Fluorobenzyl)-2-phenyl-5-(tributylstannyl)-thiazole: quant, a yellow oil, ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.87 (9H, t, *J*=7 Hz, Mex3), 1.09-1.11 (6H, m, CH_2x3), 1.27-1.33 (6H, m, CH_2x3), 1.47-1.58 (6H, m, CH_2x3), 4.15 (2H, s, CH_2), 6.93-6.96 (2H, m, ArH), 7.17-7.19 (2H, m, ArH), 7.35-7.42 (3H, m, ArH), 7.94-7.96 (2H, m, ArH). The compound was used in the next step without further purifications.

5-Benzyl-4-(4-fluorobenzyl)-2-phenylthiazole (13b): white prisms, from CH_2Cl_2-*n*-hexane, mp 52-54 °C, IR ν 3064, 3028, 2918, 1601, 1535, 1508, 1459, 1438, 1222, 1156, 1092, 1074, 1016, 967, 913, 823, 762, 702, 690; ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.08 (2H, s, CH_2), 4.11 (2H, s, CH_2), 6.93-6.95 (2H, m, ArH), 7.13-7.14 (2H, m, ArH), 7.18-7.22 (3H, m, ArH), 7.26-7.28 (2H, m, ArH), 7.34-7.37 (3H, m, ArH), 7.85 (2H, m, ArH); ^{13}C NMR (600 MHz, $CDCl_3$) δ 32.4 (t), 34.5 (t), 115.0 (d), 115.2 (d), 126.2 (dx2), 126.8 (d), 128.3 (dx2), 128.7 (dx2), 128.8 (dx2), 129.6 (d), 123.0 (d), 130.0 (d), 132.6 (s), 133.8 (s), 135.1 (s), 139.5 (s), 151.7 (s), 160.6 (s), 162.2 (s), 165.1 (s); MS *m/z* 359 (M^+). Anal. Calcd for $C_{23}H_{18}NFS$: C, 76.85; H, 5.05; N, 3.90.

Preparation of 4-[1-(4-Methoxphenyl)ethyl]-2-phenyl-5-(1-phenylsulfanyl)thiazole (14a), Typical Procedure. *n*-BuLi (1.50 ml, 3.9 mmol, 2.6 M solution) was added dropwise to a THF (10 ml) solution of 4-(p-methoxybenzyl)-2-phenyl-5-(phenylsulfanyl)thiazole (0.50 g, 1.30 mmol) at -78 °C under an Ar atmosphere. Then, a THF (2.0 ml) solution of methyl iodide (1.80 g, 13 mmol) was added to the mixture. The whole was stirred for 10 min and poured into water (50 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (1:50) to give the title compound (0.46 g, 87%) as yellow powders. **14a**: from *n*-hexane, mp 58-61 °C, IR (KBr, cm^{-1}) ν 2962, 2927, 1610, 1582, 1511, 1478, 1460, 1440, 1264, 1245, 1177, 1036, 763, 739, 688; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.70 (3H, d, *J*=7 Hz, Me), 3.75 (3H, m, MeO), 6.77 (2H, q, *J*=7 Hz, CHMe), 6.77 (2H, d, *J*=7 Hz, ArH), 7.08-7.21 (5H, m, ArH), 7.33 (2H, d, *J*=9 Hz, ArH), 7.41-7.44 (2H, m, ArH), 7.94-7.96 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.0 (q), 38.4 (q), 55.2 (d), 113.6 (dx2), 119.3 (s), 126.1 (d), 126.5 (dx2), 126.9 (dx2), 128.7 (dx2), 128.9 (dx2), 129.0 (dx2), 130.3 (d), 133.7 (s), 136.8 (s), 137.5 (s), 158.0 (s), 166.5 (s), 170.4 (s); MS *m/z* 403 (M^+), 388 (M^+-Me), 326 (M^+-Ph), 294 (M^+-SPh). Anal. Calcd for $C_{24}H_{21}S_2NO$: C, 71.43; H, 5.25; N, 3.47. Found: C, 71.39; H, 5.30; N, 3.56.

4-[1-(4-Methoxyphenyl)-2-phenylethyl]-2-phenyl-5-(phenylsulfanyl)thiazole (14b): colorless prisms, from CH_2Cl_2-*n*-hexane, mp 94-96 °C, IR (KBr, cm^{-1}) ν 2926, 1609, 1582, 1510, 1488, 1477, 1455, 1440, 1250, 1178, 1036, 763, 740, 698, 688; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.29 (1H, dd, *J*=5 and 14 Hz, CH_2), 3.64 (1H, dd, *J*=10 and 14 Hz, CH_2), 3.75 (3H, s, MeO), 4.67 (1H, dd, *J*=5 and 10 Hz, CH), 6.74 (2H, d, *J*=8 Hz, ArH), 6.75-6.76 (2H, m, ArH), 7.07-7.17 (8H, m, ArH), 7.41 (2H, d, *J*=8Hz, ArH), 7.44-7,46 (3H, m, ArH), 7.99-8.01 (2H, m, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 42.7 (t), 46.6 (q), 55.8 (d), 113.7 (dx2), 121.2 (s), 125.9 (d), 125.9 (d), 126.5 (dx2), 127.1 (dx2), 128.1 (dx2), 128.9 (dx2), 128.9 (dx2), 129.1 (dx2), 129.2 (dx2), 130.3 (d), 133.8 (s), 135.3 (s), 137.2 (s), 140.4 (s), 158.1 (s), 164.2 (s), 170.1 (s); MS *m/z* 479 (M^+), 449 (M^+-Me), 388 (M^+-CH_2Ph), 370 (M^+ -SPh). Anal. Calcd for $C_{30}H_{25}NOS_2$: C, 75.12; H, 5.25; N, 2.92. Found: C, 74.89; H, 4.67; N, 2.88.

4-[1-(4-Fluorophenyl)ethyl]-2-phenyl-5-(phenylsulfanyl)thiazole (14c): a yellow oil, IR (KBr, cm^{-1}) ν 3061, 3027, 2923, 1603, 1583, 1507, 1478, 1454, 1440, 1223, 1158, 840, 764, 741, 687; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.30 (1H, dd, *J*=6 and 13 Hz, CH_2), 3.67 (1H, dd, *J*=10 and 13 Hz, CH_2), 4.69 (1H, dd, *J*=6 and 10Hz, CH), 6.75-6.76 (2H, t, *J*=3 Hz, ArH), 6.89-6.92 (2H, m, ArH), 7.05-7.06 (5H, m, ArH), 7.12-7.18 (3H, m, ArH), 7.42-7.43 (5H, m, ArH), 7.98-7.99 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 42.7 (t), 46.7 (d), 114.9 (d), 115.1 (d), 121.4 (s), 126.0 (d), 126.0 (d), 126.4 (dx2), 127.0 (dx2), 128.2 (dx2), 128.9 (dx2), 129.0 (dx2), 129.1 (dx2), 129.6 (d), 129.7 (d), 130.4 (d), 133.6 (s), 137.1 (s), 138.6 (s), 134.0 (s), 161.5 (d, *J*=245 Hz), 163.6 (s), 170.3 (s); MS *m/z* 467 (M^+), 376 (M^+-CH_2Ph), 358 (M^+-SPh); high-resolution mass calcd for $C_{29}H_{22}S_2FN$:467.1177, found *m/z* 467.1131.

Preparation of 4-[1-(4-Methoxyphenyl)ethyl]-2-phenylthiazole (15a), Typical Procedure. A toluene (1 ml) mixture of **14a** (70 mg, 0.17 mmol), tributyltin hydride (0.36 g, 1.4 mmol) and AIBN (24 mg, 0.14 mmol) were heated under reflux condition for 7h. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-*n*-hexane (1:50) to give 4-[1-(4-methoxyphenyl)ethyl]-2-phenyl-5-(tributylstannyl)thiazole (99 mg, quant) as a yellow oil. IR (KBr, cm^{-1}) ν 2956, 2926, 2871, 2852, 1611, 1510, 1480, 1463, 1303, 1245, 1177, 1074, 1038, 1008, 962, 830, 762, 689, 667, 602; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.87 (9H, t, *J*=7 Hz, Mex3), 1.10-1.14 (6H, m, Bu), 1.27-1.35 (6H, m, Bu), 1.44-1.53 (6H, m, Bu), 1.73 (3H, d, *J*=7 Hz, Me), 3.75 (3H, s, MeO), 4.06 (1H, q, *J*=7 Hz, CH), 6.81 (2H, d, *J*=9 Hz, ArH), 7.33-7.41 (5H, m, ArH), 8.00 (2H, d, *J*=9 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.1 (tx3), 13.6 (qx3), 23.9 (d), 27.2 (tx3), 28,7 (tx3), 43.2 (t), 55.2 (q), 113.5 (dx2), 123.1 (s), 126.5 (dx2), 128.5 (dx2), 128.7 (dx2), 129.2 (d), 134.3 (s), 138.3 (s), 157.8 (s), 167.4 (s), 172.1 (s); MS *m/z* 528 (M^+-Bu), 470 (M^+-2xBu). Anal. Calcd for $C_{30}H_{43}NOSSn$: C, 61.66; H, 7.42, N, 2.40. Found: C, 61.45; H, 7.44; N, 2.39. MeLi (0.45 ml, 0.50 mmol, 1.0 M ether solution) was added to: a THF (1.0 ml) solution of the above compound (56 mg, 0.10 mmol) at -72 °C under an Ar atmosphere. The reaction mixture was poured into water (50 ml). The organic layer

was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-*n*-hexane (1:30) to give a title compound (**15a**) (29 mg, quant) as a yellow oil. IR (KBr, cm^{-1}) ν 1611, 1511, 1497, 1462, 1439, 1302, 1247, 1178, 1035, 1002, 832, 766, 690; ^1H NMR (600 MHz, $CDCl_3$) δ 1.70 (3H, d, *J*=7 Hz, Me), 3.78 (3H, s, MeO), 4.31 (1H, q, *J*=7 Hz, CH), 6.75 (1H, s, CH), 6.86 (2H, dd, *J*=2 and 7 Hz, ArH), 7.26 (2H, dd, *J*=2 and 7 Hz, ArH), 7.38-7.42 (3H, m, ArH), 7.92-7.94 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.7 (q), 41.6 (d), 55.2 (q), 113.0 (d), 113.8 (dx2), 126.5 (dx2), 128.6 (dx2), 128.8 (dx2), 129.7 (d), 133.9 (s), 137.0 (s), 158.1 (s), 162.8 (s), 167.5 (s); MS *m/z* 295 (M^+), 280 (M^+-Me). Anal. Calcd for $C_{18}H_{17}SNO$: C,73.19, H,5.80; N,4.74. Found: C, 67.11; H,5.34; N,4.30.

4-[1-(4-Fluorophenyl)ethyl]-2-phenyl-5-(tributyl-stannyl)thiazole: a yellow oil, IR (KBr, cm^{-1}) ν 2957, 2926, 2871, 2852, 1716, 1602, 1508, 1480, 1463, 1430, 1376, 1223, 1158,1074, 1051, 1009, 962, 876, 835, 762, 739, 689, 667, 602; ^1H NMR (600 MHz, $CDCl_3$) δ 0.87 (9H, t, *J*=7 Hz, Mex3), 1.09-1.17 (6H, m, CH_2), 1.30-1.34 (6H, m, CH_2x3), 1.47-1.53 (6H, m, CH_2), 1.75 (3H, d, *J*=7 Hz, Me), 4.09 (1H, q, *J*=7 Hz, CH), 6.89-6.95 (2H, m, ArH), 7.33-7.40 (5H, m, ArH), 8.00 (2H, d, *J*=7 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.1 (tx3), 13.6 (qx3), 23.9 (q), 27.2 (tx3), 29.0 (tx3), 43.3 (d), 114.7 (d), 114.9 (d), 123.5 (s), 126.5 (dx2), 128.7 (dx2), 129.0 (dx2), 129.3 (d), 134.2 (s), 141.7 (s), 161.3 (d, *J*=244 Hz), 165.8 (s), 172.8 (s); MS *m/z* 516 (M^+-Bu), 458 (M^+-Bux2). Anal. Calcd for $C_{29}H_{40}NFSSn$: C, 60.85; H, 7.04; N, 2.45. Found: C, 60.91; H, 6.68; N, 2.51.

4-[1-(4-Fluorophenyl)ethyl]-2-phenylthiazole (15b): a yellow oil, IR (KBr, cm^{-1}) ν 3063, 2970, 2930, 2872, 1603, 1508, 1461, 1437, 1223, 1159, 1052, 1003, 979, 915, 836, 766, 690, 609, 597, 548; ^1H NMR (600 MHz, $CDCl_3$) δ 1.70 (3H, d, *J*=8 Hz, Me), 4.31-4.34 (1H, q, *J*=8 Hz, CH), 6.77 (1H, s, ArH), 6.97-7.01 (2H, m, ArH), 7.28-7.30 (2H, m, ArH), 7.36-7.41 (3H, m, ArH), 7.91-7.93 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.7 (q), 41.5 (d), 113.1 (d), 115.0 (d), 115.2 (d), 126.5 (dx2), 128.8 (dx2), 129.0 (d), 129.1 (d), 129.8 (d), 133.8 (s), 140.5 (s), 161.4 (d, *J*=244 Hz), 162.1 (s), 167.7 (s); MS *m/z* 284 (M^+), 283, 269 (M^+-Me), 268 (M^+-Me); high-resolution mass calcd for $C_{17}H_{14}SNF$: 283.0831, found *m/z* 283.0828.

4-(3,4-Dimethoxybenzyl)-2-phenyl-5-(tributyl-stannyl)thiazole: a yellow oil, IR ν 2955, 2927, 2852, 1591, 1514, 1481, 1464, 1425, 1377, 1339, 1259, 1234, 1152, 1141, 1074, 1031, 964, 865, 805, 763, 690; ^1H NMR (600 MHz, $CDCl_3$) δ 0.87 (9H, t, *J*=7 Hz, Mex3), 1.10 (6H, t, *J*=7 Hz, CH_2x3), 1.28-1.34 (6H, m, CH_2x3), 1.47-1.54 (6H, m, CH_2x3), 3.84 (6H, s, Mex2), 4.12 (2H, s, CH2), 6.72 (1H, d, *J*=8 Hz, ArH), 6.76 (1H, d, *J*=8 Hz, ArH), 6.87 (1H, s, ArH), 7.35-7.41 (3H, m, ArH), 7.95-7.96 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.0 (tx3), 13.5 (qx3), 27.1 (tx3), 29.9 (tx3), 38.4 (t), 55.6 (q), 55.7 (q), 110.9 (d), 111.9 (d), 120.3 (d), 124.7 (s), 126.4 (dx2), 128.6 (dx2), 129.3 (d), 132.9 (s), 133.9 (s), 147.3 (s), 148.6 (s), 162.5 (s), 172.4 (s); MS *m/z* 544 (M^+-Bu). Anal. Calcd for $C_{30}H_{43}NO_2SSn$: C, 74.39; H, 5.46; N, 3.61. Found: C, 74.32; H, 5.51; N, 3.57.

4-(3,4-Dimethoxybenzyl)-2,5-diphenylthiazole (16a): white powders, from CH_2Cl_2-*n*-hexane, mp 116-118 °C, IR (KBr, cm^{-1}) ν 2926, 2853, 1591, 1514, 1484, 1460, 1262, 1235, 1152, 1140, 1030, 1013, 808, 762691; ^1H NMR (600 MHz, $CDCl_3$) δ 3.83 (3H, s, OMe), 3.84 (3H, s, OMe), 4.15 (2H, s, CH_2), 6.78 (2H, brs, ArH), 6.89 (1H, brs, ArH), 7.36-7.47 (8H, m, ArH), 7.95-7.96 (2H, m, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.0 (t), 55.7 (q), 55.9 (q), 111.2 (d), 111.3 (d), 120.4 (d), 126.3 (dx2), 128.1 (d), 128.7 (dx2), 128.9 (dx2), 129.4 (dx2), 129.8 (d), 131.9 (s), 132.4 (s), 133.7 (s), 147.4 (s), 148.8 (s), 151.2 (s), 165.5 (s); MS *m/z* 387 (M^+), 311 (M^+-Ph). Anal. Calcd for $C_{24}H_{21}NO_2S$: C, 74.39; H, 5.46; N, 3.61. Found: C, 74.31; H, 5.50; N, 3.58.

4-(3,4-Dimethoxybenzyl)-2-phenyl-5-(2-pyridyl)-thiazole (16b): white powders, from CH_2Cl_2-*n*-hexane, mp 100-102 °C, IR (KBr, cm^{-1}) ν 3060, 2999, 2929, 1583, 1514, 1462, 1434, 1259, 1234, 1151, 1139, 1028, 764; ^1H NMR (600 MHz, $CDCl_3$) δ 3.83 (3H, s, OMe), 3.84 (3H, s, OMe), 4.45 (2H, s, CH_2), 6.78 (1H, d, *J*=8 Hz, ArH), 6.83 (1H, dd, *J*=1 and 8 Hz, ArH), 6.96 (1H, d, *J*=1 Hz, ArH), 7.19 (1H, dd, *J*=5 and 8 Hz, ArH), 7.42-7.45 (3H, m, ArH), 7.51 (1H, d, *J*=8 Hz, ArH), 7.68 (1H, dt, *J*=2 and 7 Hz, ArH), 7.99-8.00 (2H, m, ArH), 8.66 (1H, dd, *J*=1 and 5 Hz, ArH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 35.9 (t), 55.8 (q), 55.8 (q), 111.2 (d), 112.0 (d), 120.4 (d), 122.0 (d), 122.0 (d), 126.5 (dx2), 128.9 (dx2), 130.1 (d), 131.7 (s), 133.6 (s), 134.2 (s), 136.7 (d), 147.5 (s), 148.9 (s), 149.7 (d), 151.3 (s), 152.8 (s), 166.8 (s); MS *m/z* 388 (M^+), 310 (M^+-C_5H_4N). Anal. Calcd for $C_{23}H_{20}N_2O_2S$: C, 71.11; H, 5.19; N, 7.21. Found: C, 70.95; H, 5.24; N, 7.18.

X-ray Structure Report

Experimental

Data Collection

A colorless needle crystal of $C_{22}H_{16}BrNSSe$ having approximate dimensions of 0.20 x 0.10 x 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation.

Indexing was performed from 3 oscillations that were exposed for 90 seconds. The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 17.7844(14) Å
b = 5.5924(4) Å β = 112.210(3)°
c = 21.3572(17) Å
V = 1966.5(3) Å^3

For Z = 4 and F.W. = 485.30, the calculated density is 1.639 g/cm^3. The systematic absences of:

h0l: l ± 2n
0k0: k ± 2n

uniquely determine the space group to be:

$P2_1/c$ (#14)

The data were collected at a temperature of 23 ± 1°C to a maximum 2θ value of 55.0°. A total of 44 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° step, at χ=45.0° and ϕ = 120.0°. The exposure rate was 60.0 [sec./°]. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° step, at χ=45.0° and ϕ = 270.0°. The exposure rate was 60.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 17245 reflections that were collected, 4475 were unique (R_{int} = 0.038).

The linear absorption coefficient, μ, for Mo-Kα radiation is 40.592 cm^{-1}. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[3] on F^2 was based on 17245 observed reflections and 251 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0466$$

$$wR2 = [\Sigma (w (Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2]^{1/2} = 0.1322$$

The standard deviation of an observation of unit weight[4] was 0.72. A Sheldrick weighting scheme was used. Plots of $\Sigma w (|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 4.03 and -5.73 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[8]. All calculations were performed using the CrystalStructure[9,10] crystallographic software package.

References

(1) SIR97: Altomare, A., Burla, M., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A., Polidori, G., and Spagna, R. (1999). J. Appl. Cryst., 32, 115-119.

(2) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least Squares function minimized:

$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

(4) Standard deviation of an observation of unit weight:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations
N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) CrystalStructure 3.8: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC (2000-2006). 9009 New Trails Dr. The Woodlands TX 77381 USA.

(10) CRYSTALS Issue 11: Carruthers, J.R., Rollett,J.S., Betteridge, P.W., Kinna, D., Pearce, L., Larsen, A., and Gabe, E. Chemical Crystallography Laboratory, Oxford, UK. (1999)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{22}H_{16}BrNSSe$
Formula Weight	485.30
Crystal Color, Habit	colorless, needle
Crystal Dimensions	0.20 X 0.10 X 0.10 mm
Crystal System	monoclinic
Lattice Type	Primitive
Indexing Images	3 oscillations @ 90.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 17.7844(14) Å b = 5.5924(4) Å c = 21.3572(17) Å β = 112.210(3) ° V = 1966.5(3) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.639 g/cm^3
F_{000}	960.00
μ(MoKα)	40.592 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Detector Aperture	280 mm x 256 mm
Data Images	44 exposures
ω oscillation Range (χ=45.0, ϕ=120.0)	130.0 - 190.0°
Exposure Rate	60.0 sec./°
ω oscillation Range (χ=45.0, ϕ=270.0)	0.0 - 160.0°
Exposure Rate	60.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 17245 Unique: 4475 (R_{int} = 0.038)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (Fo^2 - Fc^2)^2$
Least Squares Weights	$1/[0.0010Fo^2+3.0000\sigma(Fo^2)+0.5000]/(4Fo^2)$
$2\theta_{max}$ cutoff	55.0^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	17245
No. Variables	251
Reflection/Parameter Ratio	68.71
Residuals: R1 ($I>2.00\sigma(I)$)	0.0466
Residuals: R (All reflections)	0.1105
Residuals: wR2 (All reflections)	0.1322
Goodness of Fit Indicator	0.719
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	4.03 $e^-/Å^3$
Minimum peak in Final Diff. Map	-5.73 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Br(1)	0.48825(2)	0.79723(7)	0.93332(2)	8.243(11)
Se(1)	0.22016(2)	0.66225(4)	0.51325(2)	5.705(8)
S(1)	0.10418(4)	0.31664(11)	0.55104(3)	4.729(16)
N(1)	0.22114(12)	0.1347(3)	0.65128(10)	4.05(4)
C(1)	0.14215(15)	0.1249(3)	0.61923(12)	3.89(5)
C(2)	0.25529(15)	0.3009(4)	0.62172(13)	4.17(6)
C(3)	0.20111(16)	0.4178(4)	0.56739(13)	4.38(6)
C(4)	0.34614(15)	0.3310(4)	0.65025(13)	5.04(6)
C(5)	0.38034(14)	0.4430(3)	0.71984(13)	3.78(5)
C(6)	0.35273(15)	0.6634(3)	0.73171(14)	4.40(6)
C(7)	0.38407(17)	0.7690(4)	0.79493(16)	5.05(7)
C(8)	0.44413(17)	0.6521(4)	0.84668(15)	4.98(7)
C(9)	0.47324(15)	0.4339(4)	0.83654(14)	4.88(6)
C(10)	0.44091(15)	0.3319(3)	0.77272(14)	4.38(6)
C(11)	0.08943(14)	-0.0353(3)	0.63916(12)	3.93(5)
C(12)	0.00661(15)	0.0056(4)	0.61850(13)	4.96(6)
C(13)	-0.04157(17)	-0.1467(4)	0.63927(15)	5.82(7)
C(14)	-0.00639(18)	-0.3354(4)	0.68157(15)	5.79(8)
C(15)	0.07506(17)	-0.3791(4)	0.70222(14)	5.24(7)
C(16)	0.12285(16)	-0.2309(4)	0.68114(13)	4.58(6)
C(17)	0.24004(15)	0.4650(3)	0.44689(12)	4.12(6)
C(18)	0.21098(15)	0.5395(4)	0.38064(13)	4.56(6)
C(19)	0.22666(17)	0.4042(4)	0.33287(13)	5.42(7)
C(20)	0.27013(18)	0.1968(4)	0.35076(15)	5.65(8)
C(21)	0.29897(17)	0.1204(4)	0.41670(14)	5.31(7)
C(22)	0.28393(16)	0.2537(4)	0.46519(13)	4.92(6)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Atomic coordinates and B_{iso} involving hydrogens/B_{eq}

atom	x	y	z	B_{eq}
H(1)	0.3114	0.7426	0.6956	5.37
H(2)	0.3646	0.9195	0.8030	6.45
H(3)	0.5147	0.3558	0.8728	5.69
H(4)	0.4605	0.1814	0.7648	5.39
H(5)	-0.0171	0.1373	0.5897	5.79
H(6)	-0.0984	-0.1199	0.6247	6.97
H(7)	-0.0394	-0.4364	0.6964	7.07
H(8)	0.0984	-0.5107	0.7311	6.39
H(9)	0.1793	-0.2621	0.6947	5.58
H(10)	0.1809	0.6842	0.3685	5.34
H(11)	0.2070	0.4549	0.2870	6.60
H(12)	0.2805	0.1047	0.3175	7.16
H(13)	0.3295	-0.0234	0.4289	6.64
H(14)	0.3033	0.2022	0.5110	6.09
H(15)	0.3701	0.1776	0.6530	6.28
H(16)	0.3605	0.4289	0.6202	6.24

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	0.1049(3)	0.1285(3)	0.0866(2)	-0.0387(2)	0.0439(2)	-0.0364(2)
Se(1)	0.1033(2)	0.05383(15)	0.0743(2)	0.00456(15)		0.0502(2)
	0.00369(13)					
S(1)	0.0546(4)	0.0698(4)	0.0537(4)	0.0070(3)	0.0188(3)	0.0024(3)
N(1)	0.0469(13)	0.0616(11)	0.0507(12)	-0.0020(9)	0.0243(11)	-0.0004(9)
C(1)	0.0418(15)	0.0599(14)	0.0468(14)	0.0011(11)	0.0176(12)	-0.0076(11)
C(2)	0.0477(15)	0.0644(15)	0.0518(16)	-0.0004(12)	0.0250(13)	-0.0065(12)
C(3)	0.0583(17)	0.0600(13)	0.0543(16)	0.0033(12)	0.0285(14)	-0.0004(12)
C(4)	0.0503(16)	0.0804(17)	0.0674(18)	-0.0027(13)	0.0298(14)	0.0018(14)
C(5)	0.0358(13)	0.0522(13)	0.0601(16)	-0.0020(11)	0.0233(13)	0.0041(12)
C(6)	0.0430(15)	0.0518(13)	0.0755(19)	0.0049(11)	0.0261(15)	0.0114(13)
C(7)	0.0592(18)	0.0486(13)	0.096(2)	-0.0018(13)	0.0432(18)	-0.0020(14)
C(8)	0.0566(18)	0.0624(15)	0.080(2)	-0.0135(14)	0.0371(17)	-0.0119(14)
C(9)	0.0464(16)	0.0676(16)	0.0659(19)	-0.0012(13)	0.0148(15)	0.0141(14)
C(10)	0.0483(16)	0.0474(12)	0.0747(19)	0.0024(11)	0.0279(15)	0.0065(13)
C(11)	0.0465(15)	0.0557(13)	0.0493(15)	-0.0022(11)	0.0204(13)	-0.0129(11)
C(12)	0.0450(16)	0.0673(16)	0.0711(19)	-0.0016(13)	0.0164(15)	-0.0000(13)
C(13)	0.0418(17)	0.0853(19)	0.093(2)	-0.0080(15)	0.0247(16)	-0.0034(16)
C(14)	0.067(2)	0.0698(17)	0.086(2)	-0.0148(15)	0.0330(18)	-0.0046(15)
C(15)	0.0615(18)	0.0630(16)	0.078(2)	-0.0030(14)	0.0305(17)	0.0014(13)
C(16)	0.0488(16)	0.0622(14)	0.0661(18)	0.0023(12)	0.0251(15)	-0.0021(13)
C(17)	0.0541(16)	0.0526(13)	0.0541(16)	-0.0014(12)	0.0251(14)	0.0072(11)
C(18)	0.0557(17)	0.0580(14)	0.0566(17)	-0.0038(12)	0.0180(14)	0.0095(12)
C(19)	0.0689(19)	0.0882(18)	0.0522(17)	-0.0116(16)	0.0264(16)	0.0025(14)
C(20)	0.065(2)	0.0878(19)	0.074(2)	-0.0087(16)	0.0407(17)	-0.0145(16)
C(21)	0.070(2)	0.0684(16)	0.071(2)	0.0076(14)	0.0363(17)	-0.0000(14)
C(22)	0.0686(19)	0.0640(14)	0.0603(18)	0.0023(14)	0.0312(16)	0.0070(13)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
Br(1)	C(8)	1.898(2)	Se(1)	C(3)	1.902(2)
Se(1)	C(17)	1.931(2)	S(1)	C(1)	1.727(2)
S(1)	C(3)	1.720(2)	N(1)	C(1)	1.311(3)
N(1)	C(2)	1.386(3)	C(1)	C(11)	1.471(3)
C(2)	C(3)	1.362(3)	C(2)	C(4)	1.505(3)
C(4)	C(5)	1.513(3)	C(5)	C(6)	1.385(3)
C(5)	C(10)	1.379(3)	C(6)	C(7)	1.383(3)
C(7)	C(8)	1.378(3)	C(8)	C(9)	1.374(3)
C(9)	C(10)	1.386(3)	C(11)	C(12)	1.388(3)
C(11)	C(16)	1.396(3)	C(12)	C(13)	1.394(4)
C(13)	C(14)	1.377(3)	C(14)	C(15)	1.367(4)
C(15)	C(16)	1.379(4)	C(17)	C(18)	1.375(3)
C(17)	C(22)	1.388(3)	C(18)	C(19)	1.381(4)
C(19)	C(20)	1.366(3)	C(20)	C(21)	1.372(4)
C(21)	C(22)	1.382(4)			

Table 5. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
C(4)	H(15)	0.950	C(4)	H(16)	0.950
C(6)	H(1)	0.950	C(7)	H(2)	0.950
C(9)	H(3)	0.950	C(10)	H(4)	0.950
C(12)	H(5)	0.950	C(13)	H(6)	0.950
C(14)	H(7)	0.950	C(15)	H(8)	0.950
C(16)	H(9)	0.950	C(18)	H(10)	0.950
C(19)	H(11)	0.950	C(20)	H(12)	0.950
C(21)	H(13)	0.950	C(22)	H(14)	0.950

Table 6. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C(3)	Se(1)	C(17)	99.19(11)	C(1)	S(1)	C(3)	89.46(12)
C(1)	N(1)	C(2)	110.98(18)	S(1)	C(1)	N(1)	114.48(19)
S(1)	C(1)	C(11)	122.22(16)	N(1)	C(1)	C(11)	123.30(19)
N(1)	C(2)	C(3)	114.8(2)	N(1)	C(2)	C(4)	118.59(19)
C(3)	C(2)	C(4)	126.6(2)	Se(1)	C(3)	S(1)	120.54(12)
Se(1)	C(3)	C(2)	129.1(2)	S(1)	C(3)	C(2)	110.3(2)
C(2)	C(4)	C(5)	114.5(2)	C(4)	C(5)	C(6)	120.64(19)
C(4)	C(5)	C(10)	121.2(2)	C(6)	C(5)	C(10)	118.2(2)
C(5)	C(6)	C(7)	121.3(2)	C(6)	C(7)	C(8)	119.0(2)
Br(1)	C(8)	C(7)	119.2(2)	Br(1)	C(8)	C(9)	119.47(18)
C(7)	C(8)	C(9)	121.3(2)	C(8)	C(9)	C(10)	118.6(2)
C(5)	C(10)	C(9)	121.7(2)	C(1)	C(11)	C(12)	121.6(2)
C(1)	C(11)	C(16)	120.0(2)	C(12)	C(11)	C(16)	118.5(2)
C(11)	C(12)	C(13)	120.3(2)	C(12)	C(13)	C(14)	119.7(2)
C(13)	C(14)	C(15)	120.8(3)	C(14)	C(15)	C(16)	119.7(2)
C(11)	C(16)	C(15)	121.0(2)	Se(1)	C(17)	C(18)	118.72(17)
Se(1)	C(17)	C(22)	121.26(19)	C(18)	C(17)	C(22)	120.0(2)
C(17)	C(18)	C(19)	119.5(2)	C(18)	C(19)	C(20)	120.6(2)
C(19)	C(20)	C(21)	120.2(2)	C(20)	C(21)	C(22)	119.9(2)
C(17)	C(22)	C(21)	119.7(2)				

Table 7. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
C(2)	C(4)	H(15)	108.2	C(2)	C(4)	H(16)	108.2
C(5)	C(4)	H(15)	108.0	C(5)	C(4)	H(16)	108.4
H(15)	C(4)	H(16)	109.5	C(5)	C(6)	H(1)	119.0
C(7)	C(6)	H(1)	119.7	C(6)	C(7)	H(2)	121.0
C(8)	C(7)	H(2)	120.1	C(8)	C(9)	H(3)	120.2
C(10)	C(9)	H(3)	121.2	C(5)	C(10)	H(4)	118.6
C(9)	C(10)	H(4)	119.7	C(11)	C(12)	H(5)	119.4
C(13)	C(12)	H(5)	120.3	C(12)	C(13)	H(6)	120.3
C(14)	C(13)	H(6)	119.9	C(13)	C(14)	H(7)	119.3
C(15)	C(14)	H(7)	119.9	C(14)	C(15)	H(8)	119.9
C(16)	C(15)	H(8)	120.4	C(11)	C(16)	H(9)	119.0
C(15)	C(16)	H(9)	120.0	C(17)	C(18)	H(10)	119.6
C(19)	C(18)	H(10)	121.0	C(18)	C(19)	H(11)	119.9
C(20)	C(19)	H(11)	119.4	C(19)	C(20)	H(12)	120.0
C(21)	C(20)	H(12)	119.7	C(20)	C(21)	H(13)	119.9
C(22)	C(21)	H(13)	120.2	C(17)	C(22)	H(14)	119.7
C(21)	C(22)	H(14)	120.6				

Table 8. Torsion Angles(°)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C(3)	Se(1)	C(17)	C(18)	142.1(2)	C(3)	Se(1)	C(17)	C(22)	-39.0(2)
C(17)	Se(1)	C(3)	S(1)	-91.99(17)	C(17)	Se(1)	C(3)	C(2)	88.8(2)
C(1)	S(1)	C(3)	Se(1)	-178.64(17)	C(1)	S(1)	C(3)	C(2)	0.7(2)
C(3)	S(1)	C(1)	N(1)	-0.5(2)	C(3)	S(1)	C(1)	C(11)	179.5(2)
C(1)	N(1)	C(2)	C(3)	0.5(3)	C(1)	N(1)	C(2)	C(4)	-177.9(2)
C(2)	N(1)	C(1)	S(1)	0.0(2)	C(2)	N(1)	C(1)	C(11)	-179.9(2)
S(1)	C(1)	C(11)	C(12)	-19.5(3)	S(1)	C(1)	C(11)	C(16)	162.0(2)
N(1)	C(1)	C(11)	C(12)	160.4(2)	N(1)	C(1)	C(11)	C(16)	-18.0(3)
N(1)	C(2)	C(3)	Se(1)	178.42(19)	N(1)	C(2)	C(3)	S(1)	-0.9(3)
N(1)	C(2)	C(4)	C(5)	-69.0(2)	C(3)	C(2)	C(4)	C(5)	112.8(3)
C(4)	C(2)	C(3)	Se(1)	-3.3(4)	C(4)	C(2)	C(3)	S(1)	177.4(2)
C(2)	C(4)	C(5)	C(6)	-55.9(3)	C(2)	C(4)	C(5)	C(10)	125.6(2)
C(4)	C(5)	C(6)	C(7)	-179.3(2)	C(4)	C(5)	C(10)	C(9)	179.4(2)
C(6)	C(5)	C(10)	C(9)	0.8(4)	C(10)	C(5)	C(6)	C(7)	-0.7(4)
C(5)	C(6)	C(7)	C(8)	0.3(4)	C(6)	C(7)	C(8)	Br(1)	179.4(2)
C(6)	C(7)	C(8)	C(9)	0.1(3)	Br(1)	C(8)	C(9)	C(10)	-179.3(2)
C(7)	C(8)	C(9)	C(10)	-0.0(4)	C(8)	C(9)	C(10)	C(5)	-0.5(4)
C(1)	C(11)	C(12)	C(13)	-178.7(2)	C(1)	C(11)	C(16)	C(15)	177.9(2)
C(12)	C(11)	C(16)	C(15)	-0.6(3)	C(16)	C(11)	C(12)	C(13)	-0.3(3)
C(11)	C(12)	C(13)	C(14)	1.3(4)	C(12)	C(13)	C(14)	C(15)	-1.6(4)
C(13)	C(14)	C(15)	C(16)	0.8(4)	C(14)	C(15)	C(16)	C(11)	0.3(4)
Se(1)	C(17)	C(18)	C(19)	178.1(2)	Se(1)	C(17)	C(22)	C(21)	-178.2(2)
C(18)	C(17)	C(22)	C(21)	0.7(3)	C(22)	C(17)	C(18)	C(19)	-0.8(3)
C(17)	C(18)	C(19)	C(20)	0.5(4)	C(18)	C(19)	C(20)	C(21)	-0.1(3)
C(19)	C(20)	C(21)	C(22)	0.1(3)	C(20)	C(21)	C(22)	C(17)	-0.3(4)

The sign is positive if when looking from atom 2 to atom 3 a clock-wise motion of atom 1 would superimpose it on atom 4.

Table 10. Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
Br(1)	H(3)[1)]	3.480	Br(1)	H(13)[2)]	3.182
Br(1)	H(14)[3)]	3.479	Br(1)	H(16)[3)]	3.377
Se(1)	H(13)[1)]	3.572	Se(1)	H(14)[1)]	3.371
N(1)	H(1)[4)]	2.671	N(1)	H(2)[4)]	3.493
N(1)	H(11)[2)]	3.045	C(1)	H(1)[4)]	3.547
C(1)	H(8)[1)]	3.446	C(1)	H(11)[2)]	3.354
C(2)	H(1)[4)]	3.471	C(2)	H(9)[1)]	3.438
C(3)	H(9)[1)]	3.399	C(4)	H(1)[4)]	3.550
C(5)	H(2)[4)]	3.489	C(5)	H(4)[3)]	3.033
C(5)	H(12)[2)]	3.221	C(6)	H(4)[1)]	3.397
C(6)	H(4)[3)]	3.296	C(6)	H(9)[1)]	2.910
C(6)	H(12)[2)]	3.006	C(6)	H(15)[1)]	3.403
C(7)	H(4)[1)]	2.870	C(7)	H(4)[3)]	3.490
C(7)	H(9)[1)]	3.461	C(7)	H(11)[5)]	3.454
C(7)	H(12)[2)]	2.944	C(8)	H(4)[1)]	3.506
C(8)	H(4)[3)]	3.410	C(8)	H(12)[2)]	3.090
C(8)	H(13)[2)]	3.236	C(8)	H(15)[3)]	3.304
C(9)	H(2)[4)]	3.387	C(9)	H(4)[3)]	3.150
C(9)	H(12)[2)]	3.303	C(9)	H(15)[3)]	3.033
C(10)	H(2)[4)]	2.870	C(10)	H(4)[3)]	2.933
C(10)	H(12)[2)]	3.353	C(11)	H(8)[1)]	3.501
C(11)	H(11)[2)]	3.091	C(12)	H(8)[1)]	3.578
C(13)	H(7)[6)]	3.458	C(13)	H(8)[6)]	3.373
C(13)	H(10)[7)]	3.543	C(14)	H(5)[4)]	3.508
C(14)	H(7)[6)]	3.291	C(14)	H(8)[6)]	3.429
C(14)	H(10)[8)]	3.475	C(15)	H(5)[4)]	3.578
C(15)	H(7)[6)]	3.502	C(15)	H(10)[2)]	3.505
C(15)	H(11)[2)]	3.346	C(16)	H(1)[4)]	3.252
C(16)	H(11)[2)]	2.679	C(17)	H(6)[8)]	3.082
C(17)	H(13)[1)]	3.365	C(18)	H(6)[8)]	3.059
C(18)	H(7)[8)]	2.926	C(18)	H(13)[1)]	3.136
C(19)	H(2)[9)]	2.930	C(19)	H(6)[8)]	3.181
C(19)	H(7)[8)]	3.154	C(19)	H(8)[10)]	3.319
C(19)	H(9)[11)]	3.397	C(20)	H(2)[9)]	3.125
C(20)	H(6)[8)]	3.316	C(20)	H(8)[10)]	3.322
C(20)	H(10)[4)]	3.366	C(21)	H(6)[8)]	3.335
C(21)	H(10)[4)]	3.128	C(22)	H(6)[8)]	3.216

Table 10. Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H(1)	N(1)[1)]	2.671	H(1)	C(1)[1)]	3.547
H(1)	C(2)[1)]	3.471	H(1)	C(4)[1)]	3.550
H(1)	C(16)[1)]	3.252	H(1)	H(4)[1)]	3.503
H(1)	H(9)[1)]	2.342	H(1)	H(11)[5)]	3.587
H(1)	H(12)[2)]	3.454	H(1)	H(15)[1)]	2.925
H(2)	N(1)[1)]	3.493	H(2)	C(5)[1)]	3.489
H(2)	C(9)[1)]	3.387	H(2)	C(10)[1)]	2.870
H(2)	C(19)[5)]	2.930	H(2)	C(20)[5)]	3.125
H(2)	H(3)[1)]	3.506	H(2)	H(4)[1)]	2.601
H(2)	H(9)[1)]	3.387	H(2)	H(11)[5)]	2.783
H(2)	H(12)[2)]	3.359	H(2)	H(12)[5)]	3.125
H(2)	H(15)[1)]	3.547	H(3)	Br(1)[4)]	3.480
H(3)	H(2)[4)]	3.506	H(3)	H(15)[3)]	2.931
H(3)	H(16)[12)]	3.224	H(4)	C(5)[12)]	3.033
H(4)	C(6)[4)]	3.397	H(4)	C(6)[12)]	3.296
H(4)	C(7)[4)]	2.870	H(4)	C(7)[12)]	3.490
H(4)	C(8)[4)]	3.506	H(4)	C(8)[12)]	3.410
H(4)	C(9)[12)]	3.150	H(4)	C(10)[12)]	2.933
H(4)	H(1)[4)]	3.503	H(4)	H(2)[4)]	2.601
H(4)	H(4)[12)]	3.297	H(4)	H(4)[3)]	3.297
H(4)	H(16)[12)]	3.500	H(5)	C(14)[1)]	3.508
H(5)	C(15)[1)]	3.578	H(5)	H(7)[1)]	3.423
H(5)	H(8)[1)]	3.540	H(5)	H(10)[7)]	3.501
H(6)	C(17)[8)]	3.082	H(6)	C(18)[8)]	3.059
H(6)	C(19)[8)]	3.181	H(6)	C(20)[8)]	3.316
H(6)	C(21)[8)]	3.335	H(6)	C(22)[8)]	3.216
H(6)	H(8)[6)]	3.139	H(6)	H(10)[8)]	3.507
H(6)	H(10)[7)]	2.877	H(7)	C(13)[13)]	3.458
H(7)	C(14)[13)]	3.291	H(7)	C(15)[13)]	3.502
H(7)	C(18)[8)]	2.926	H(7)	C(19)[8)]	3.154
H(7)	H(5)[4)]	3.423	H(7)	H(7)[13)]	3.550
H(7)	H(7)[6)]	3.550	H(7)	H(8)[6)]	3.224
H(7)	H(10)[8)]	2.746	H(7)	H(11)[8)]	3.134
H(8)	C(1)[4)]	3.446	H(8)	C(11)[4)]	3.501
H(8)	C(12)[4)]	3.578	H(8)	C(13)[13)]	3.373
H(8)	C(14)[13)]	3.429	H(8)	C(19)[14)]	3.319
H(8)	C(20)[14)]	3.322	H(8)	H(5)[4)]	3.540

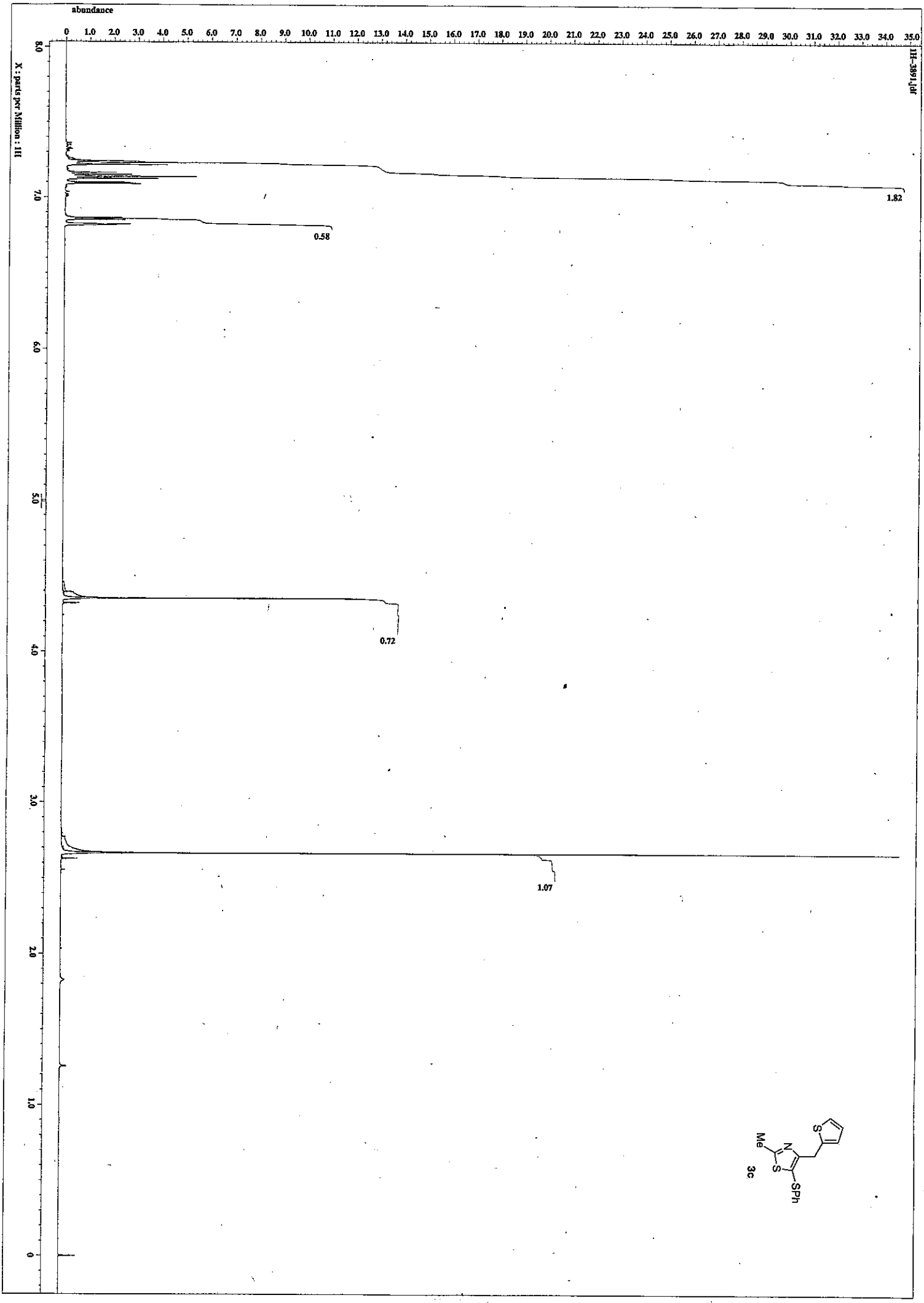
Table 10. Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H(8)	H(6)[13)]	3.139	H(8)	H(7)[13)]	3.224
H(8)	H(10)[2)]	3.292	H(8)	H(11)[14)]	3.095
H(8)	H(12)[14)]	3.106	H(9)	C(2)[4)]	3.438
H(9)	C(3)[4)]	3.399	H(9)	C(6)[4)]	2.910
H(9)	C(7)[4)]	3.461	H(9)	C(19)[2)]	3.397
H(9)	H(1)[4)]	2.342	H(9)	H(2)[4)]	3.387
H(9)	H(11)[2)]	2.519	H(9)	H(12)[14)]	3.197
H(10)	C(13)[7)]	3.543	H(10)	C(14)[8)]	3.475
H(10)	C(15)[11)]	3.505	H(10)	C(20)[1)]	3.366
H(10)	C(21)[1)]	3.128	H(10)	H(5)[7)]	3.501
H(10)	H(6)[8)]	3.507	H(10)	H(6)[7)]	2.877
H(10)	H(7)[8)]	2.746	H(10)	H(8)[11)]	3.292
H(10)	H(12)[1)]	3.363	H(10)	H(13)[1)]	2.957
H(11)	N(1)[11)]	3.045	H(11)	C(1)[11)]	3.354
H(11)	C(7)[9)]	3.454	H(11)	C(11)[11)]	3.091
H(11)	C(15)[11)]	3.346	H(11)	C(16)[11)]	2.679
H(11)	H(1)[9)]	3.587	H(11)	H(2)[9)]	2.783
H(11)	H(7)[8)]	3.134	H(11)	H(8)[10)]	3.095
H(11)	H(9)[11)]	2.519	H(12)	C(5)[11)]	3.221
H(12)	C(6)[11)]	3.006	H(12)	C(7)[11)]	2.944
H(12)	C(8)[11)]	3.090	H(12)	C(9)[11)]	3.303
H(12)	C(10)[11)]	3.353	H(12)	H(1)[11)]	3.454
H(12)	H(2)[11)]	3.359	H(12)	H(2)[9)]	3.125
H(12)	H(8)[10)]	3.106	H(12)	H(9)[10)]	3.197
H(12)	H(10)[4)]	3.363	H(13)	Br(1)[11)]	3.182
H(13)	Se(1)[4)]	3.572	H(13)	C(8)[11)]	3.236
H(13)	C(17)[4)]	3.365	H(13)	C(18)[4)]	3.136
H(13)	H(10)[4)]	2.957	H(14)	Br(1)[12)]	3.479
H(14)	Se(1)[4)]	3.371	H(15)	C(6)[4)]	3.403
H(15)	C(8)[12)]	3.304	H(15)	C(9)[12)]	3.033
H(15)	H(1)[4)]	2.925	H(15)	H(2)[4)]	3.547
H(15)	H(3)[12)]	2.931	H(16)	Br(1)[12)]	3.377
H(16)	H(3)[3)]	3.224	H(16)	H(4)[3)]	3.500

Symmetry Operators:

(1) X,Y+1,Z
(2) X,-Y+1/2,Z+1/2
(3) -X+1,Y+1/2,-Z+1/2+1
(4) X,Y-1,Z
(5) X,-Y+1/2+1,Z+1/2
(6) -X,Y+1/2,-Z+1/2+1
(7) -X,-Y+1,-Z+1
(8) -X,-Y,-Z+1
(9) X,-Y+1/2+1,Z+1/2-1
(10) X,-Y+1/2-1,Z+1/2-1
(11) X,-Y+1/2,Z+1/2-1
(12) -X+1,Y+1/2-1,-Z+1/2+1
(13) -X,Y+1/2-1,-Z+1/2+1
(14) X,-Y+1/2-1,Z+1/2

Copies for ^{1}H and ^{13}C NMR Spectral Data of ***3c, 5g, 6b, 7b, 7d, 14c*** *and* ***15b***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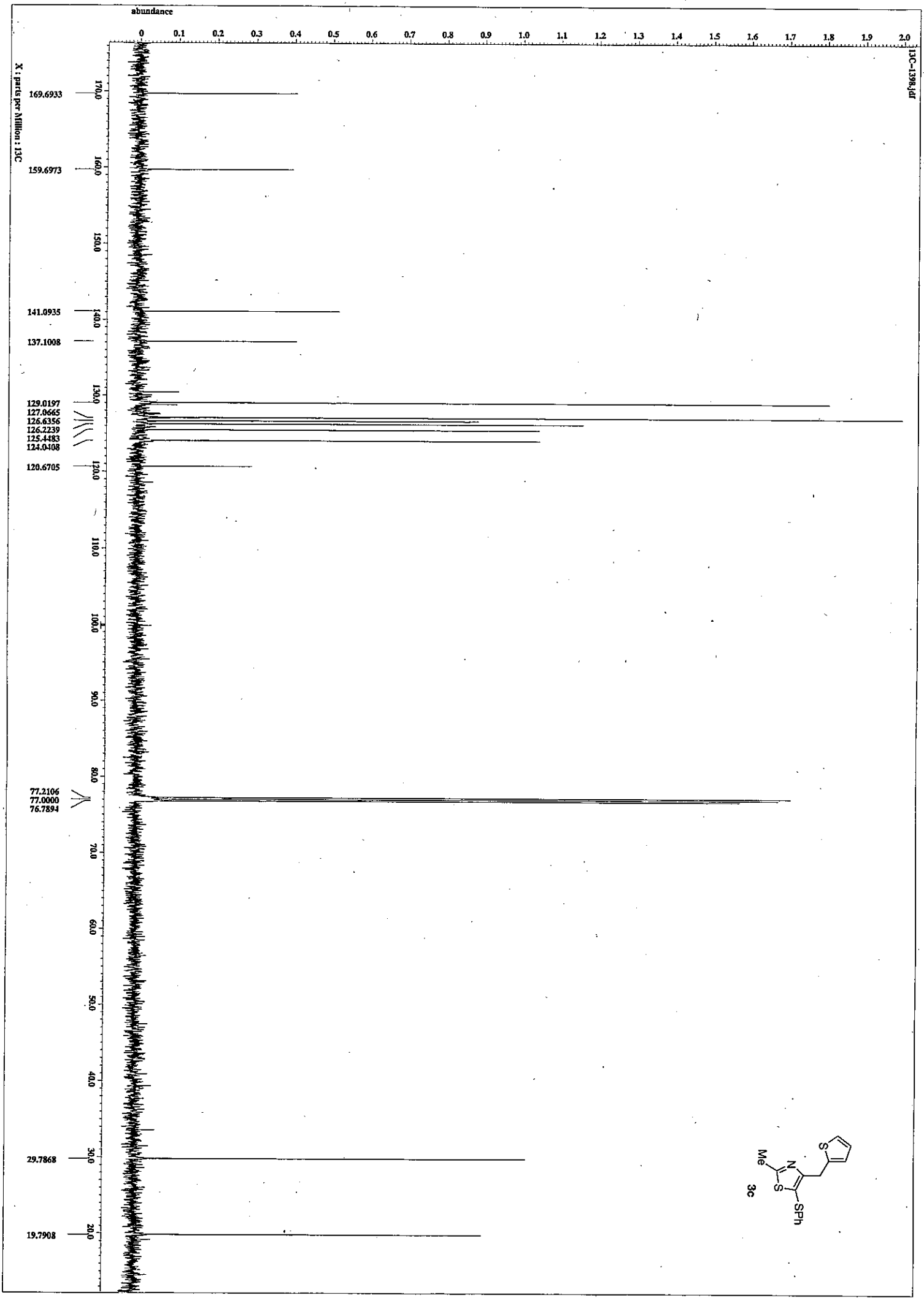
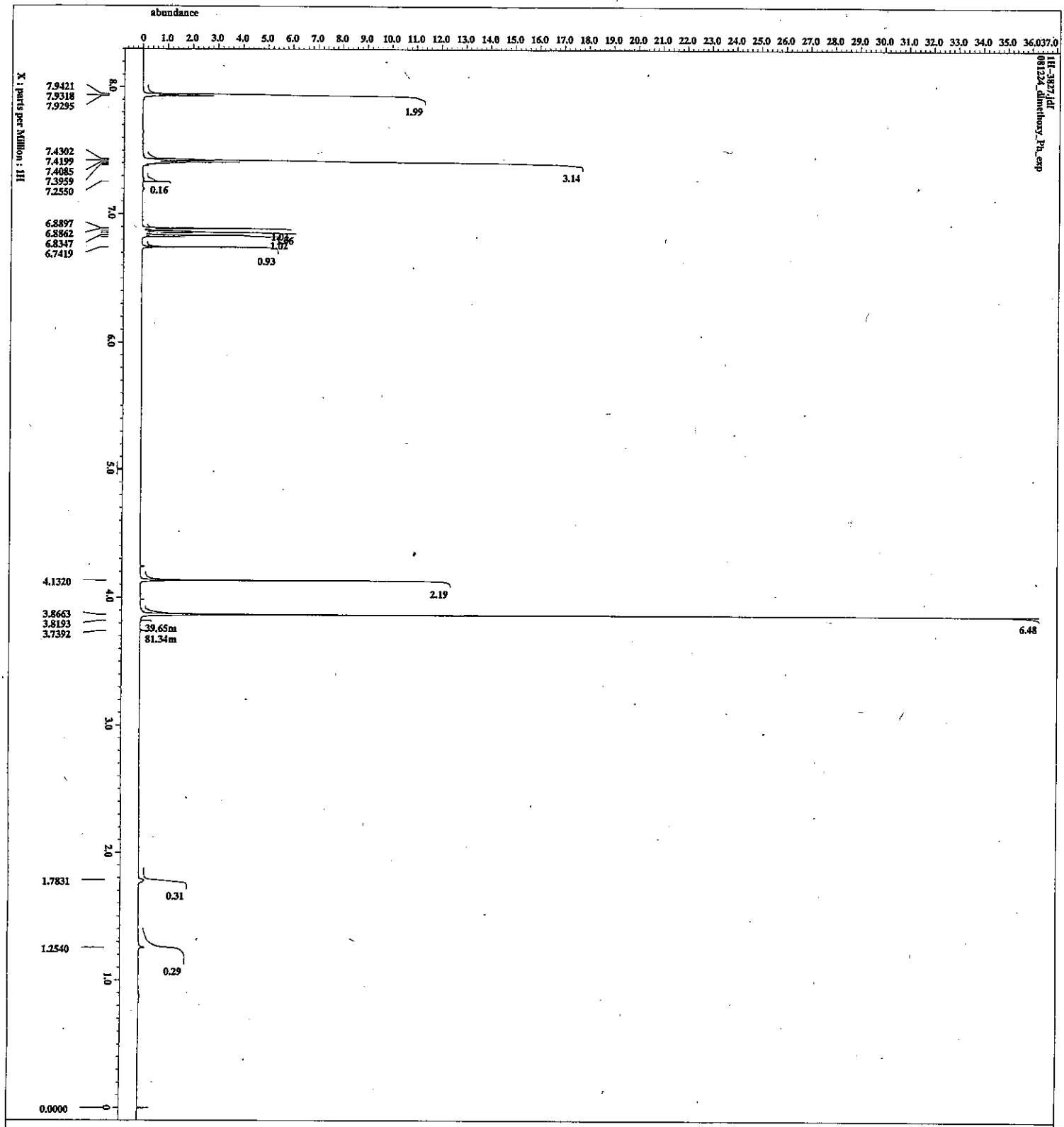
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0 24.0 25.0 26.0 27.0 28.0 29.0 30.0 31.0 32.0 33.0 34.0 35.0
HH-3891.jdf
X : parts per Million : 1H
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
0.58
1.82
0.72
1.07
Me
S
N
S
SPh
3c


abundance
X : parts per Million : 13C
13C-1398.jdf
169.6933
159.6973
141.0935
137.1008
129.0197
127.0665
126.6356
126.2239
125.4483
124.0408
120.6705
77.2106
77.0000
76.7894
29.7868
19.7908
Me
N
S
S
SPh
3c

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Filename                = 1H-3827.jdf
Author                  = delta
Experiment              = simple_pulse.exp2
Sample_id               = BF7191137
Solvent                 = CHLOROFORM-D
Creation_time           = 24-DEC-2008 19:27:14
Revision_time           = 24-DEC-2008 20:01:26
Current_time            = 24-DEC-2008 20:01:40

Comment                 = 081224_dimethoxy_Ph_e
Data_format             = 1D COMPLEX
Dim_size                = 131072
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 600
Spectrometer            = DELTA2_NMR

Field_strength          = 14.093639288[T] (600[M
X_acq_duration          = 1.4548992[s]
X_domain                = 1H
X_freq                  = 600.1723046[MHz]
X_offset                = 5[ppm]
X_points                = 16384
X_prescans              = 1
X_resolution            = 0.68733284[Hz]
X_sweep                 = 11.26126126[kHz]
Irr_domain              = 1H
Irr_freq                = 600.1723046[MHz]
Irr_offset              = 5[ppm]
Tri_domain              = 1H
Tri_freq                = 600.1723046[MHz]
Tri_offset              = 5[ppm]
Clipped                 = FALSE
Mod_return              = 1
Scans                   = 4
Total_scans             = 4

X_90_width              = 12.5[us]
X_acq_time              = 1.4548992[s]
X_angle                 = 45[deg]
X_atn                   = 2.2[dB]
X_pulse                 = 6.25[us]
Irr_mode                = Off
Tri_mode                = Off
Decpl_present           = FALSE
Initial_wait            = 1[s]
Recyc_grain             = 1
Relaxation_delay        = 2[s]
Repetition_time         = 3.4568992[s]
Temp_set                = 20.2[dC]
Spin_action             = SPIN ON
Spin_state              = SPIN ON
Spin_actual             = SPIN ON
Spin_set                = 15[Hz]
Spin_gas_source         = AIR
Sample_action           = LOADED
Sample_state            = LOAD
Sample_status           = LOADED
Changer_sample          = 0
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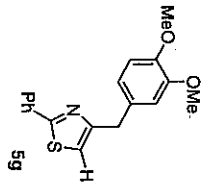
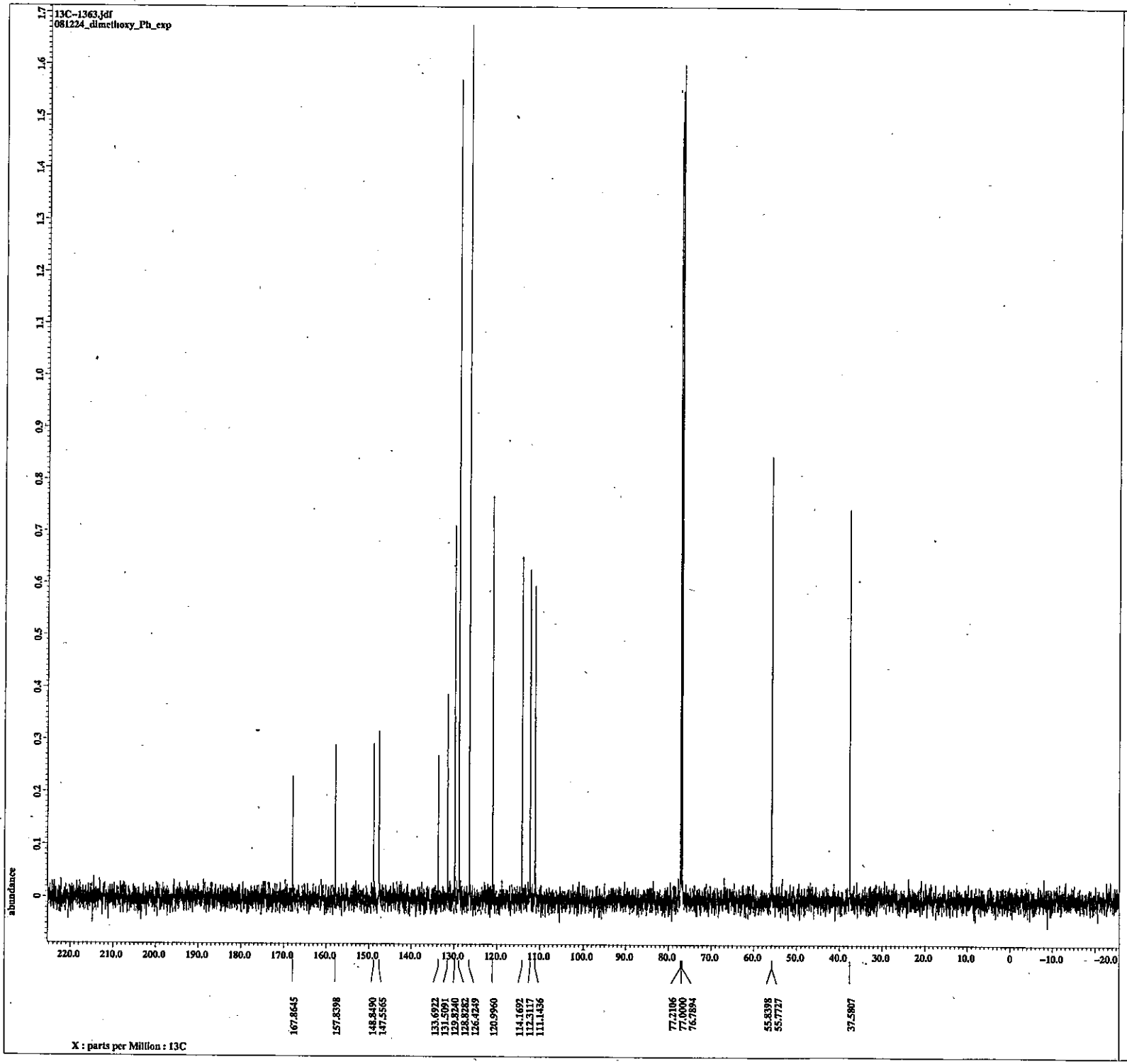
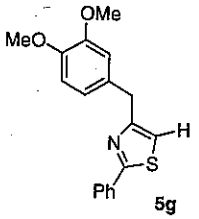


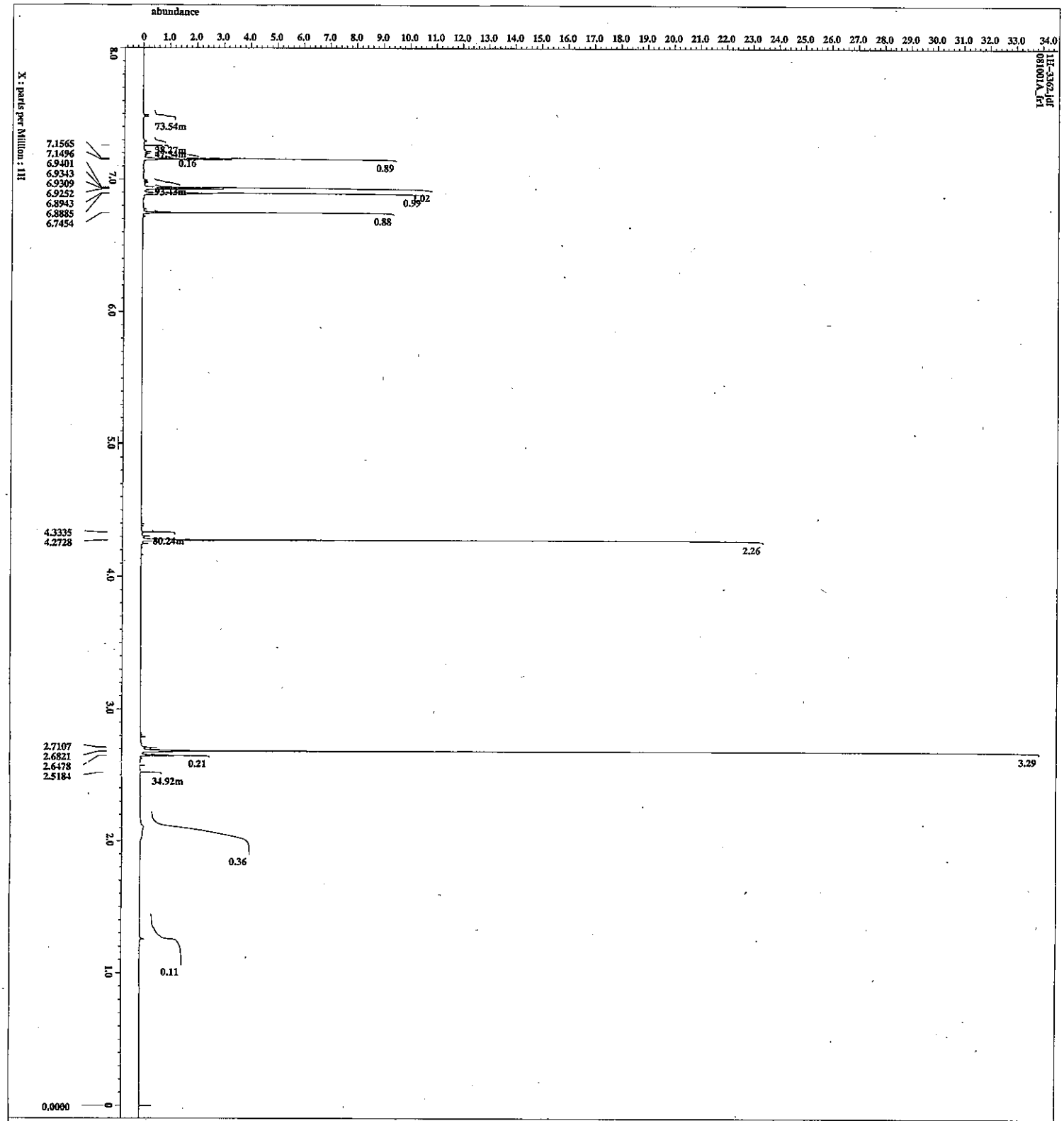
5g



Filename	= 13C-1363.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#719613
Solvent	= CHLOROFORM-D
Creation_time	= 24-DEC-2008 19:32:27
Revision_time	= 24-DEC-2008 20:04:56
Current_time	= 24-DEC-2008 20:05:00
Comment	= 081224_dimethoxy_Ph_e
Data_format	= 1D COMPLEX
Dim_size	= 26214
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= NCA 600
Spectrometer	= DELTA2_NMR
Field_strength	= 14.09636928[T] (600[M
X_acq_duration	= 0.69206016[s]
X_domain	= 13C
X_freq	= 150.91343039[MHz]
X_offset	= 100[ppm]
X_points	= 32768
X_prescans	= 4
X_resolution	= 1.44496109[Hz]
X_sweep	= 47.34848485[kHz]
Irr_domain	= 1H
Irr_freq	= 600.1723046[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 52
Total_scans	= 52
X_90_width	= 11.25[us]
X_acq_time	= 0.69206016[s]
X_angle	= 30[deg]
X_atn	= 6.2[dB]
X_pulse	= 3.75[us]
Irr_atn_dec	= 17.878[dB]
Irr_atn_noe	= 17.878[dB]
Irr_noise	= WALTZ
Decoupling	= TRUE
Initial_wait	= 1[s]
Noe	= TRUE
Noe_time	= 2[s]
Recvr_gain	= 58
Relaxation_delay	= 2[s]
Repetition_time	= 2.69206016[s]
Temp_get	= 20.9[dC]
Spin_action	= SPIN ON
Spin_state	= SPIN ON
Spin_status	= SPIN ON
Spin_set	= 14[Hz]
Spin_set	= 15[Hz]
Spin_gas_source	= AIR
Sample_action	= LOADED
Sample_state	= LOAD
Sample_status	= LOADED
Changer_sample	= 0



5g




```
Filename                = 1H-3362.jdf
Author                  = delta
Experiment              = single_pulse.exp
Sample_id               = 8873441G
Solvent                 = CHLOROFORM-D
Creation_time           = 1-OCT-2008 19:55:58
Revision_time           = 1-OCT-2008 20:27:19
Current_time            = 1-OCT-2008 20:27:39

Comment                 = 081001A_fr1
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Site                    = X
Spectrometer            = ECA 600
Spectrometer            = DELTA2_NMR

Field_strength          = 14.0963592B[T] (600[M
X_acq_duration          = 1.4548992[s]
X_domain                = 1H
X_freq                  = 600.1723046[MHz]
X_offset                = 5[ppm]
X_points                = 16384
X_prescans              = 1
X_resolution            = 0.687332B4[Hz]
X_sweep                 = 11.2613626[kHz]
Irr_domain              = 1H
Irr_freq                = 600.1723046[MHz]
Irr_offset              = 5[ppm]
Tri_domain              = 1H
Tri_freq                = 600.1723046[MHz]
Tri_offset              = 5[ppm]
Clipped                 = FALSE
Wrap_return             = 4
Scans                   = 4
Total_scans             = 4

X_90_width              = 12.5[us]
X_acq_time              = 1.4548992[s]
X_atn                   = 45[dB]
X_pulse                 = 2.25[us]
Irr_atn                 = 6.25[dB]
Irr_mode                = Off
Tri_mode                = Off
Dante_presat            = FALSE
Initial_wait            = 1[s]
Recyc_gain              = 1
Relaxation_delay        = 3[s]
Repetition_time         = 24.1548992[s]
Spin_action             = SPIN ON
Spin_state              = SPIN ON
Spin_status             = SPIN ON
Spin_set                = 16[Hz]
Spin_set                = 15[Hz]
Spin_gas_source         = AIR
Sample_action           = LOADED
Sample_state            = LOAD
Sample_status           = LOADED
Changer_sample          = 0
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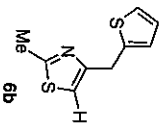
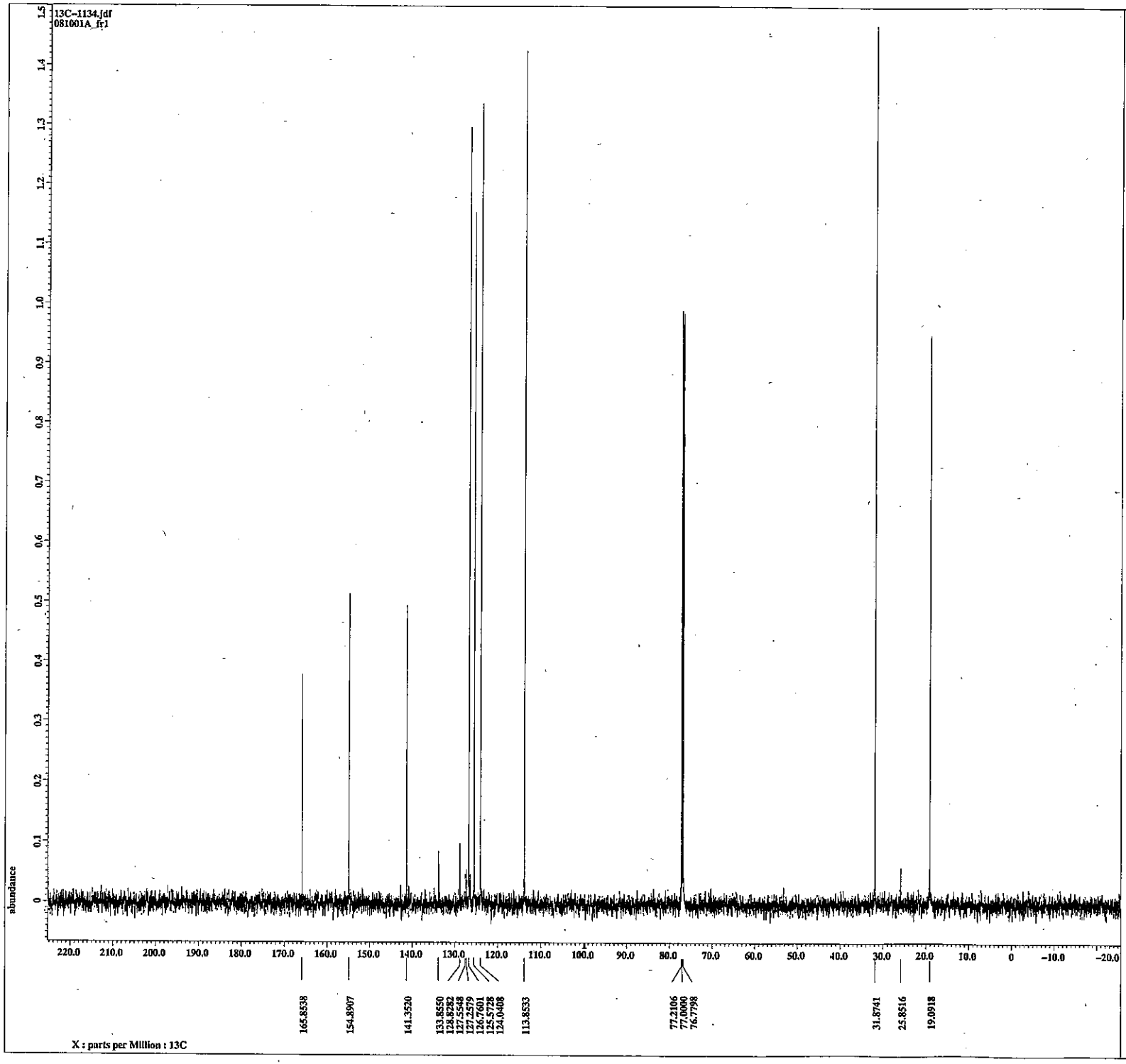


6b

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Filename          = 13C-1134.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = S#734935
Solvent           = CHLOROFORM-D
Creation_time     =  1-OCT-2008 20:03:25
Revision_time     =  1-OCT-2008 20:32:49
Current_time      =  1-OCT-2008 20:32:53

Comment           = 081001A_fr1
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 600
Spectrometer      = DELTA2_NMR

Field_strength    = 14.09636928[T] (600[M
X_acq_duration    = 0.69206016[s]
X_domain          = 13C
X_freq            = 150.91343039[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.44496109[Hz]
X_sweep           = 47.34848485[kHz]
Irr_domain        = 1H
Irr_freq          = 600.1723046[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 104
Total_scans       = 104

X_90_width        = 11.25[us]
X_acq_time        = 0.69206016[s]
X_angle           = 30[deg]
X_atn             = 6.2[dB]
X_pulse           = 3.75[us]
Irr_atn_dec       = 17.878[dB]
Irr_atn_noe       = 17.878[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 58
Relaxation_delay  = 2[s]
Repetition_time   = 2.69206016[s]
Temp_get          = 24.8[dC]
Spin_action       = SPIN ON
Spin_state        = SPIN ON
Spin_status       = SPIN ON
Spin_set          = 16[Hz]
Spin_set          = 15[Hz]
Spin_gas_source   = AIR
Sample_action     = LOADED
Sample_state      = LOAD
Sample_status     = LOADED
Changer_sample    = 0
```
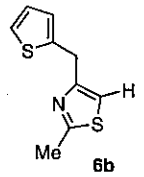
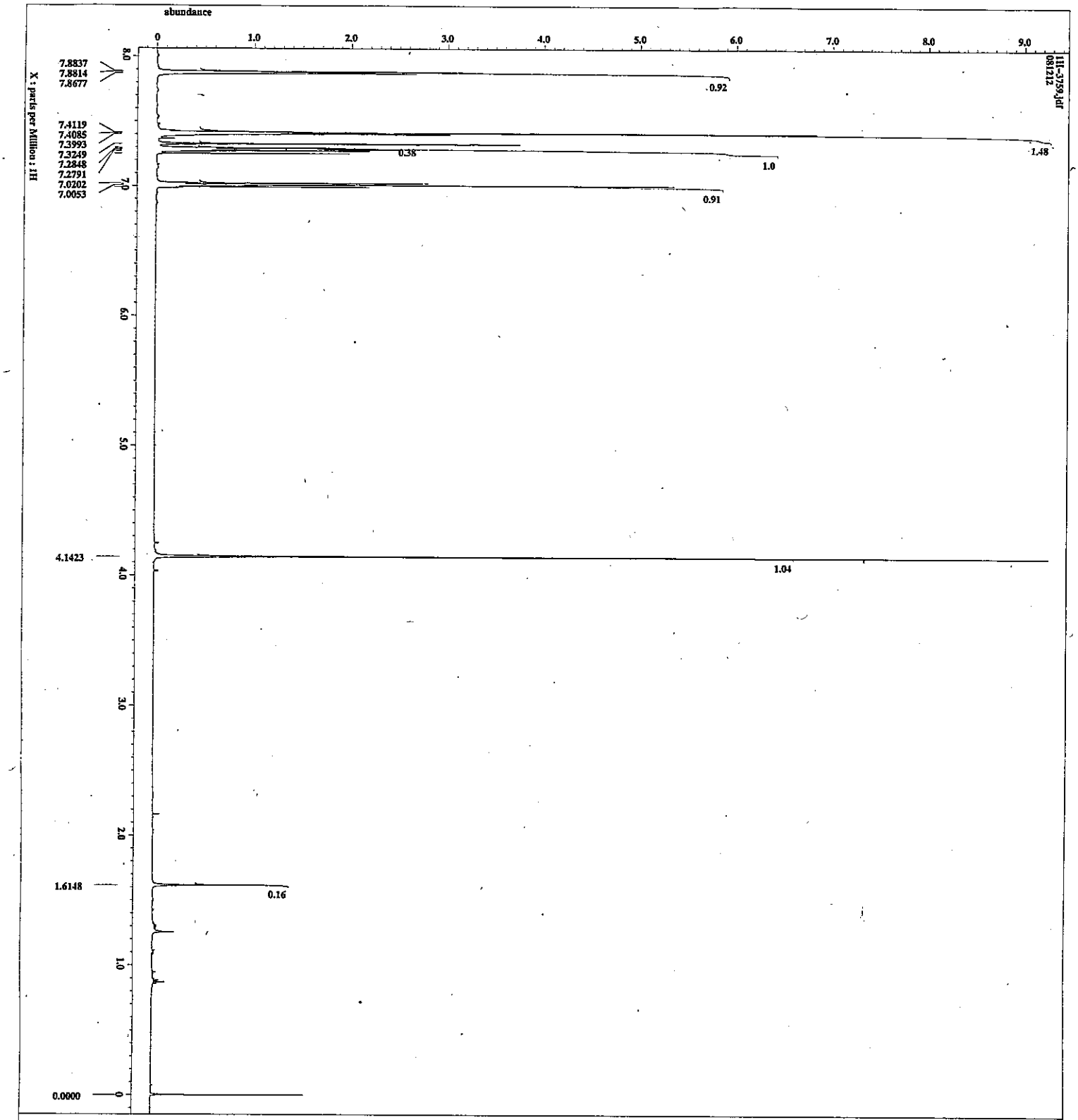



6b

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Filename                = 1H-3759.jdf
Author                  = data
Experiment              = single_pulse.exp
Sample_id               = BF709941
Solvent                 = CHLOROFORM-D
Creation_time           = 12-DEC-2008 19:10:33
Revision_time           = 12-DEC-2008 19:43:40
Current_time            = 12-DEC-2008 19:43:50

Comment                 = 081212
Data_format             = 1D COMPLEX
Dim_size                = 131107
Dim_title               = 1H
Dim_units               = [ppm]
Site                    = X
Spectrometer            = ECA 600
Dimensions              = DEFAS_NMR

Field_strength          = 14.093636928[T] (600[M
X_acq_duration          = 1.4548992[s]
X_domain                = 1H
X_freq                  = 600.1723046[MHz]
X_offset                = 5[ppm]
X_points                = 16384
X_prescans              = 1
X_resolution            = 0.68733284[Hz]
X_sweep                 = 11.2626126[kHz]
Irr_domain              = 1H
Irr_freq                = 600.1723046[MHz]
Irr_offset              = 5[ppm]
Tri_domain              = 1H
Tri_freq                = 600.1723046[MHz]
Tri_offset              = 5[ppm]
Clipped                 = FALSE
Mod_creturn             = 1
Scans                   = 4
Total_scans             = 4

X_90_width              = 12.5[us]
X_acq_time              = 1.4548992[s]
X_angle                 = 45[deg]
X_atn                   = 2.25[dB]
X_pulse                 = 6.25[us]
Irr_mode                = Off
Tri_mode                = Off
Decpwr_preset           = FALSE
Initial_wait            = 1[s]
Recvr_gain              = 42
Relaxation_delay        = 2[s]
Repetition_time         = 3.4548992[s]
Temp_get                = 23.2[dC]
Spin_action             = SPIN ON
Spin_state              = SPIN ON
Spin_status             = SPIN ON
Spin_set                = 15[Hz]
Spin_act                = 15[Hz]
Spin_gas_source         = AIR
Sample_action           = LOADED
Sample_state            = LOAD
Sample_status           = LOADED
Changer_sample          = 0
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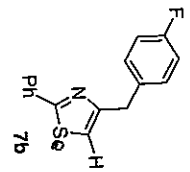
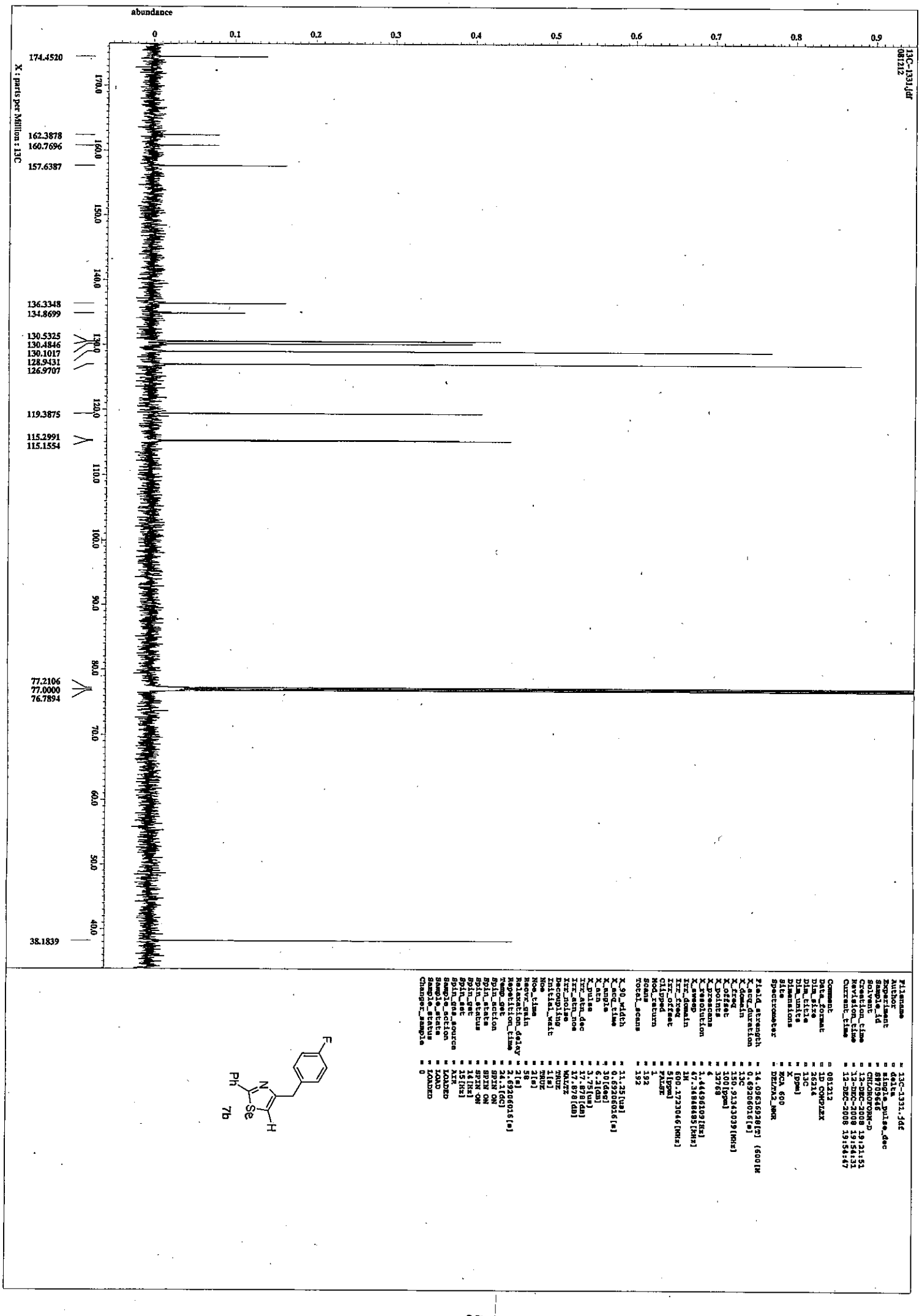
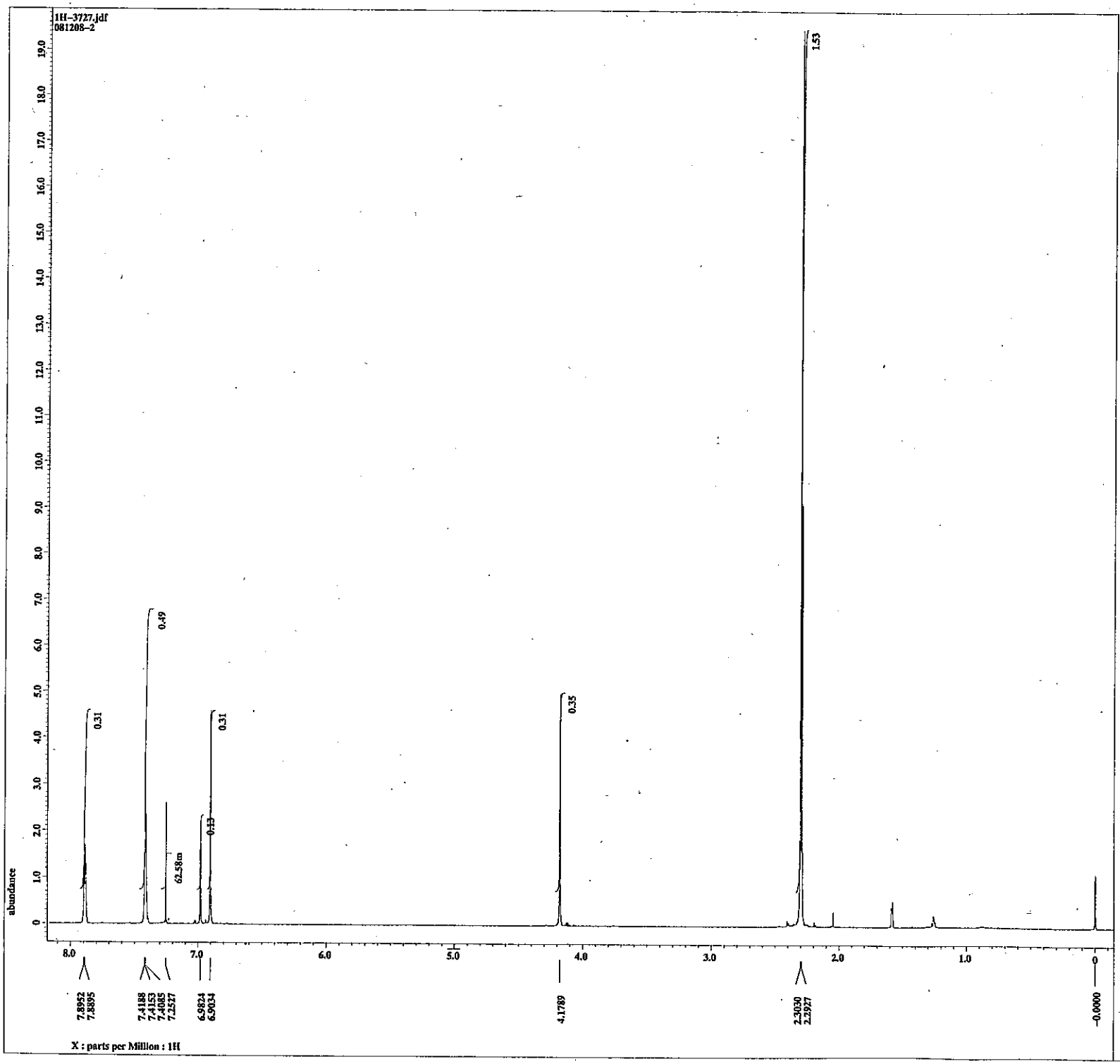
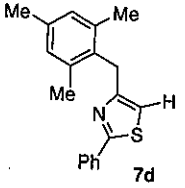


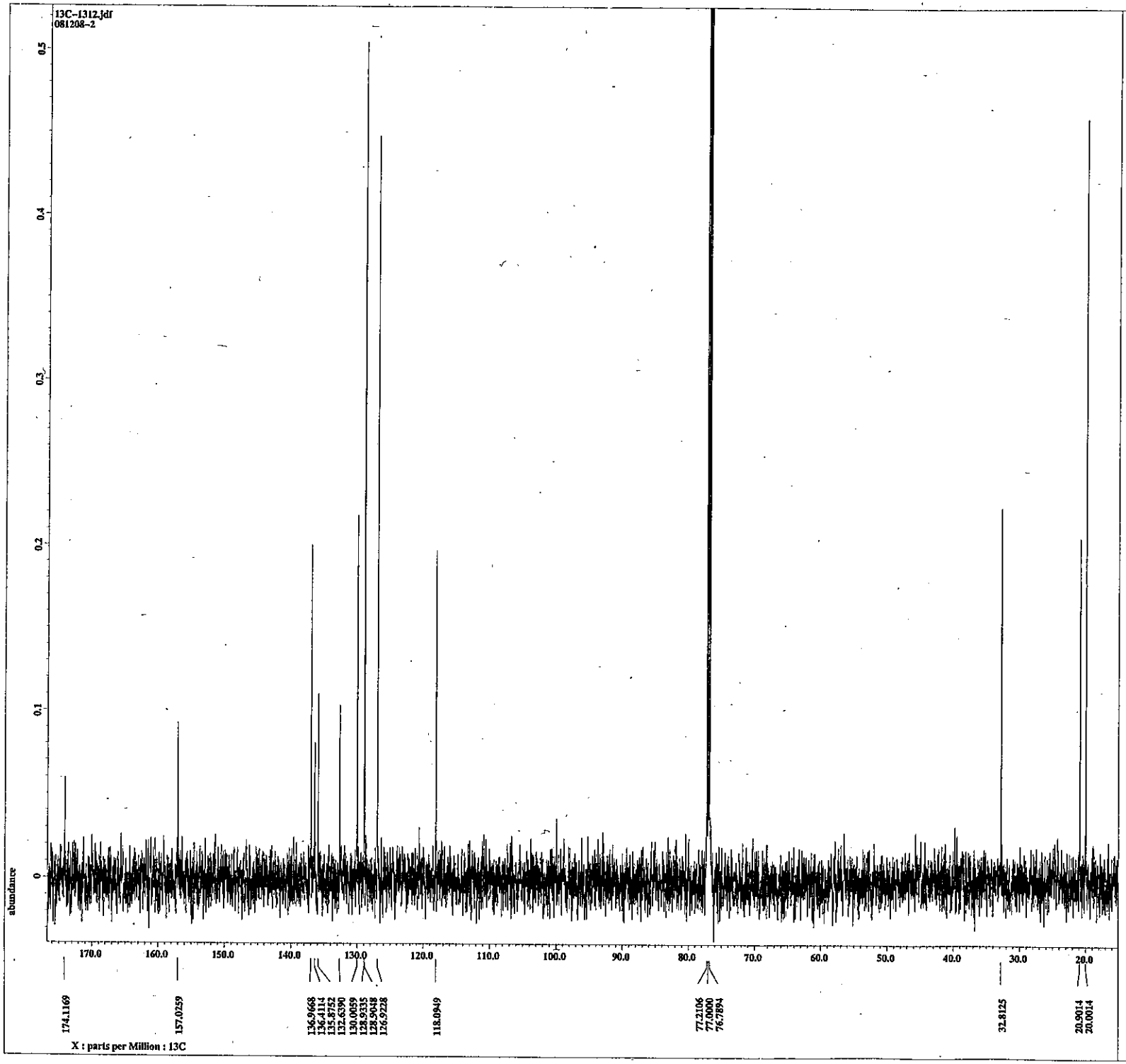

abundance
X : parts per Million : 13C
174.4520
162.3878
160.7696
157.6387
136.3348
134.8699
130.5325
130.4846
130.1017
128.9431
126.9707
119.3875
115.2991
115.1554
77.2106
77.0000
76.7894
38.1839
13C-1331.jdf
081212
Filename = 13C-1331.jdf
Author = data
Experiment = single_pulse_dec
Sample_id = SH709646
Solvent = CHLOROFORM-D
Creation_time = 12-DEC-2008 19:21:51
Revision_time = 12-DEC-2008 19:54:31
Current_time = 12-DEC-2008 19:54:47
Comment = 081212
Data_format = 1D COMPLEX
Dim_size = 16214
Dim_title = 13C
Dim_units = [ppm]
Site = WCA 600
Spectrometer = DEZRA2_NMR
Field_strength = 14.09636930[T] (600[M
X_acq_duration = 0.69206016[s]
X_domain = 13C
X_freq = 150.91343039[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.44496109[Hz]
X_sweep = 17.36868895[kHz]
X_sweep_domain = 600.17233046[MHz]
Irr_freq = 5[ppm]
Irr_offset = FALSE
clipped = 1
Mod_return = 192
scans = 192
total_scans = 192
X_90_width = 11.25[us]
X_acq_time = 0.69206016[s]
X_angle = 30[deg]
X_atn = 6.21[dB]
X_pulse = 1.75[us]
Irr_Atn_dec = 17.87[dB]
Irr_Atn_non = 47.87[dB]
Decoupling = WALTZ
Initial_wait = 1[s]
Mode = PNDZ
Nos_time = 2[s]
Recyc_grain = 58
Relaxation_delay = 2[s]
Repetition_time = 2.69206016[s]
Temp_get = 24.1[dC]
Spin_action = SPIN ON
Spin_state = SPIN ON
Spin_set = 161[Hz]
Spin_set = 151[Hz]
Spin_gas_source = AIR
Spin_sample = LOADED
Sample_action = LOAD
Sample_status = LOADED
Changer_sample = 0
F
Ph
N
Se
H
7b



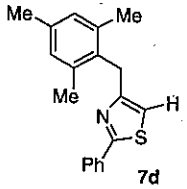

```
Filename          = 1H-3727.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = ##755291
Solvent           = CHLOROFORM-D
Creation_time     =  8-DEC-2008 20:27:52
Revision_time     =  8-DEC-2008 21:00:47
Current_time      =  8-DEC-2008 21:00:59

Comment           = 081208-2
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA 600
Spectrometer      = DELTA2_NMR

Field_strength    = 14.09636928[T] (600[M
X_acq_duration    = 1.4548992[s]
X_domain          = 1H
X_freq            = 600.1723046[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.68733284[Hz]
X_sweep           = 11.26126126[kHz]
Irr_domain        = 1H
Irr_freq          = 600.1723046[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 600.1723046[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 4
Total_scans       = 4

X_90_width        = 12.5[us]
X_acq_time        = 1.4548992[s]
X_angle           = 45[deg]
X_atn             = 2.2[dB]
X_pulse           = 6.25[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 44
Relaxation_delay  = 2[s]
Repetition_time   = 3.4548992[s]
Temp_get          = 19.9[dC]
Spin_action       = SPIN ON
Spin_state        = SPIN ON
Spin_status       = SPIN ON
Spin_get          = 13[Hz]
Spin_set          = 15[Hz]
Spin_gas_source   = AIR
Sample_action     = LOADED
Sample_state      = LOAD
Sample_status     = LOADED
Changer_sample    = 0
```



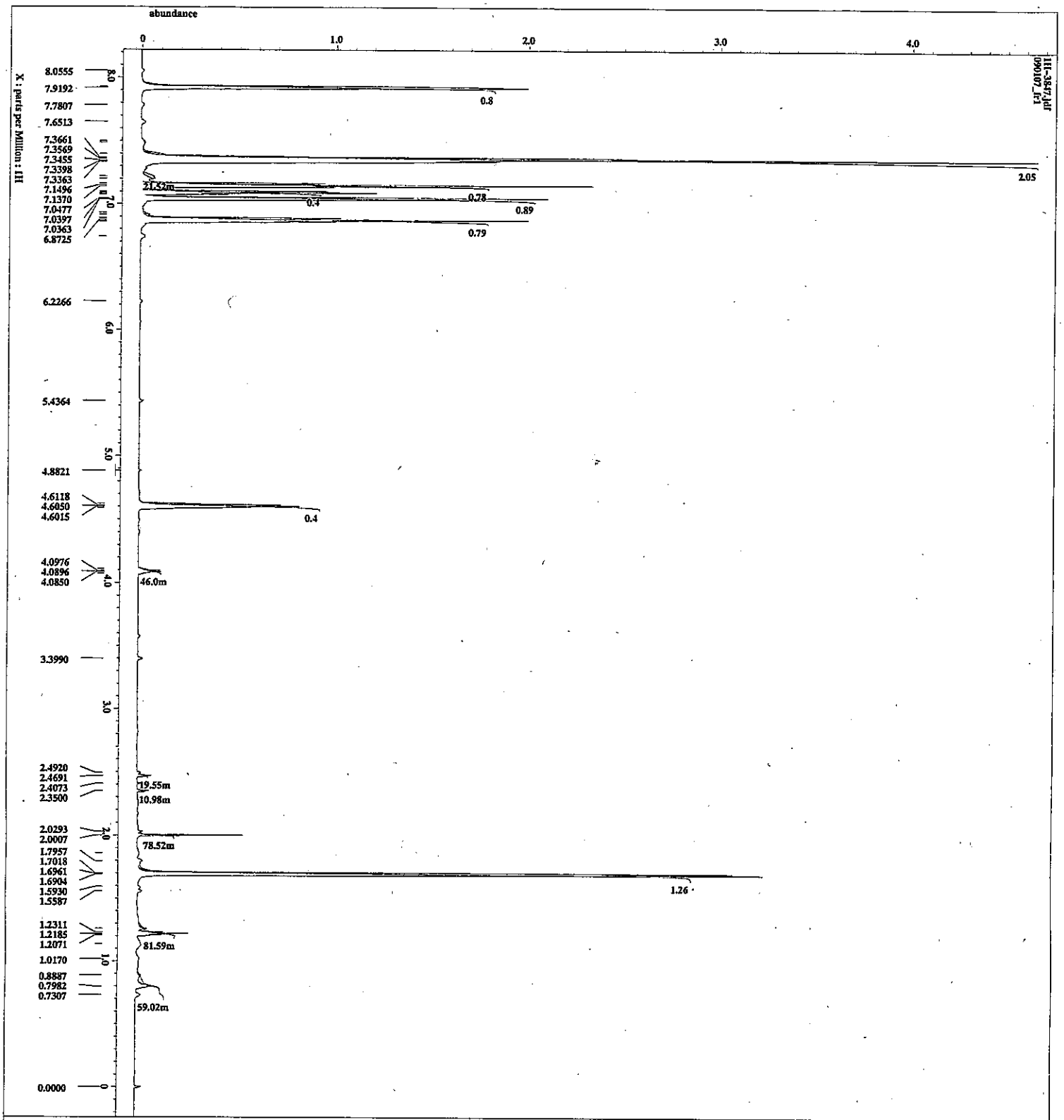
7d



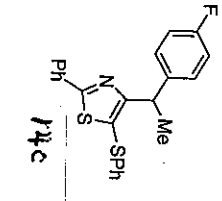
Filename	= 13C-1312.jdf
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= S#756121
Solvent	= CHLOROFORM-D
Creation_time	= 8-DEC-2008 20:35:30
Revision_time	= 8-DEC-2008 21:08:01
Current_time	= 8-DEC-2008 21:09:22
Comment	= 081208-2
Data_format	= 1D COMPLEX
Dim_size	= 26214
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= ECA 600
Spectrometer	= DELTA2_NMR
Field_strength	= 14.09636928[T] (600[M
X_acq_duration	= 0.69206016[s]
X_domain	= 13C
X_freq	= 150.91343039[MHz]
X_offset	= 100[ppm]
X_points	= 32768
X_prescans	= 4
X_resolution	= 1.44496109[Hz]
X_sweep	= 47.34848485[kHz]
Irr_domain	= 1H
Irr_freq	= 600.1723046[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 102
Total_scans	= 102
X_90_width	= 11.25[us]
X_acq_time	= 0.69206016[s]
X_angle	= 30[deg]
X_atn	= 6.2[dB]
X_pulse	= 3.75[us]
Irr_atn_dec	= 17.878[dB]
Irr_atn_noe	= 17.878[dB]
Irr_noise	= WALTZ
Decoupling	= TRUE
Initial_wait	= 1[s]
Noe	= TRUE
Noe_time	= 2[s]
Recvr_gain	= 58
Relaxation_delay	= 2[s]
Repetition_time	= 2.69206016[s]
Temp_get	= 20.8[dC]
Spin_action	= SPIN ON
Spin_state	= SPIN ON
Spin_status	= SPIN ON
Spin_set	= 15[Hz]
Spin_set	= 15[Hz]
Spin_gas_source	= AIR
Sample_action	= LOADED
Sample_state	= LOAD
Sample_status	= LOADED
Changer_sample	= 0



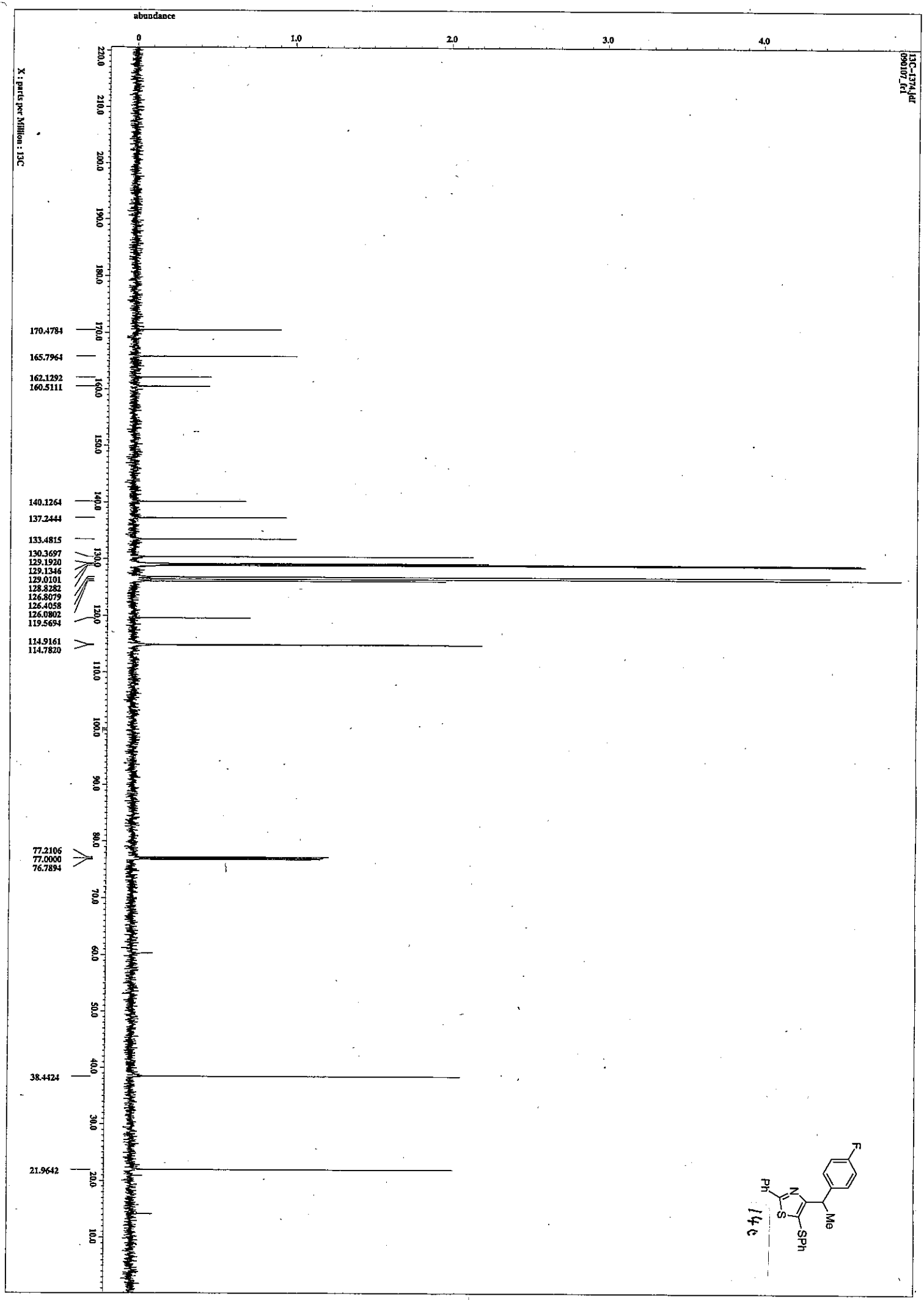
7d

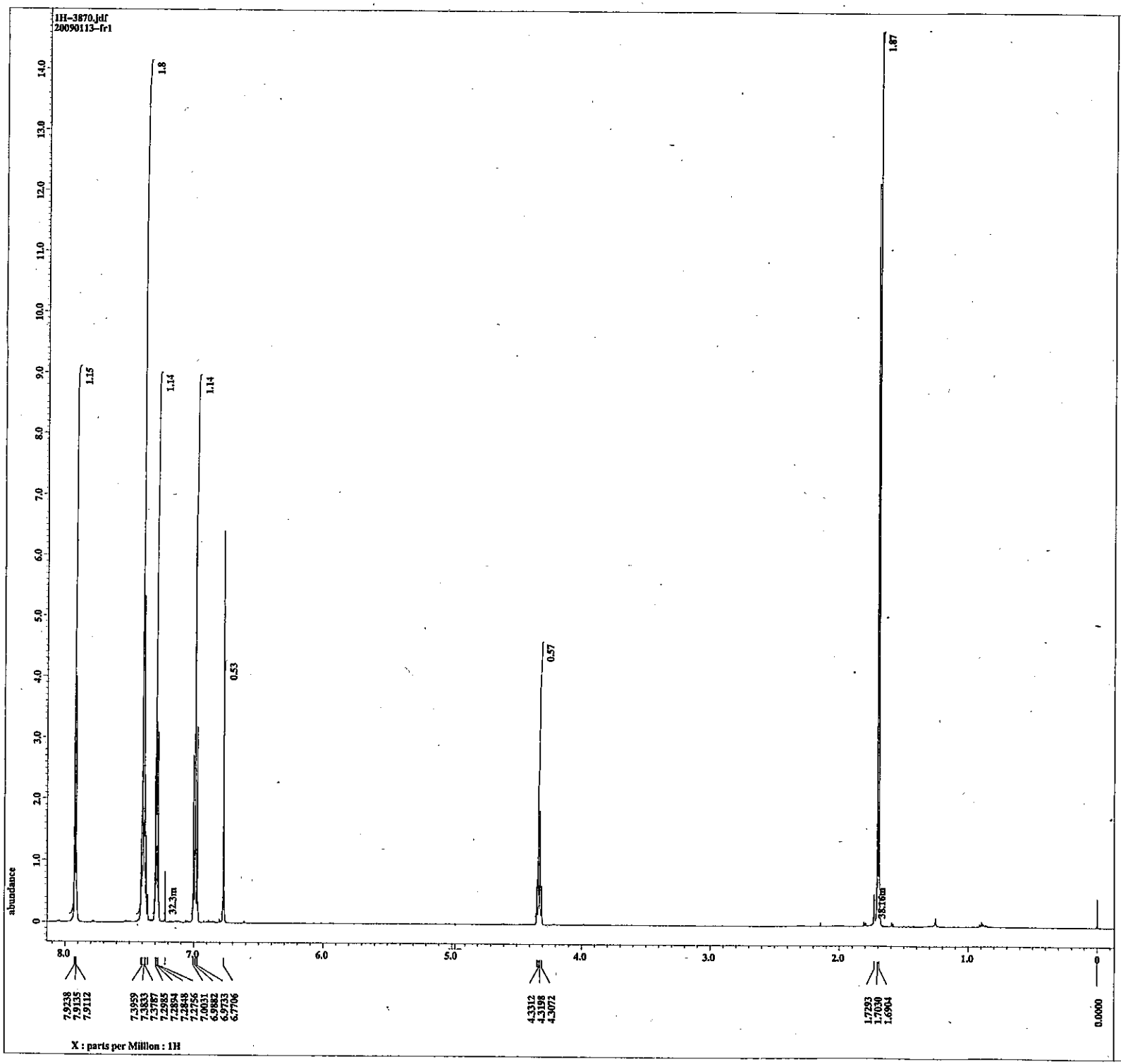



```
Filename                = 1H-3847.jdf
Author                  = data
Experiment              = single_pulse.exp
Sample_id               = 88723953
Solvent                 = CHLOROFORM-D
Creation_time           = 7-JAN-2009 19:33:20
Revision_time           = 7-JAN-2009 20:09:42
Current_time            = 7-JAN-2009 20:09:55

Comment                 = 090107_fr1
Data_format             = 1D COMPLEX
Dim_size                = 13107
Dim_title               = 1H
Dim_units               = [ppm]
Dimensions              = X
Site                    = ECA 600
Spectrometer            = DELTA2_NMR

Field_strength          = 14.093692928[T] (600[M
X_acq_duration          = 1.4548992[s]
X_domain                = 1H
X_freq                  = 600.1723046[MHz]
X_offset                = 5[ppm]
X_points                = 16384
X_prescans              = 1
X_resolution            = 0.687332384[Hz]
X_sweep                 = 11.261261261[kHz]
Irr_domain              = 1H
Irr_freq                = 600.1723046[MHz]
Irr_offset              = 5[ppm]
Tri_domain              = 1H
Tri_freq                = 600.1723046[MHz]
Tri_offset              = 5[ppm]
Clipped                 = FALSE
Mod_freturn             = 1
Scans                   = 4
Total_scans             = 4

X_90_width              = 12.5[us]
X_acq_time              = 1.4548992[s]
X_atn                   = 45[dBq]
X_angle                 = 2.2[dB]
X_pulse                 = 6.25[us]
Irr_mode                = Off
Tri_mode                = Off
Decim_present           = FALSE
Initial_wait            = 1[s]
Recvr_gain              = 26
Relaxation_delay        = 1[s]
Repetition_time         = 2.4548992[s]
Temp_action             = Equil(abs)
Temp_set                = 25.0[C]
Spin_state              = SPIN ON
Spin_status             = SPIN ON
Spin_set                = 15[Hz]
Spin_act                = 15[Hz]
Spin_gas_source         = AIR
Sample_action           = LOADED
Sample_state            = LOAD
Sample_status           = LOADED
Changer_sample          = 0
```



1tc


abundance
0
1.0
2.0
3.0
4.0
X : parts per Million : 13C
13C-1374.jdf
(090107_fr1
170.4784
165.7964
162.1292
160.5111
140.1264
137.2444
133.4815
130.3697
129.1920
129.1346
129.0101
128.8282
126.8079
126.4058
126.0802
119.5694
114.9161
114.7820
77.2106
77.0000
76.7894
38.4424
21.9642
F
Ph
N
S
Me
SPh
14c

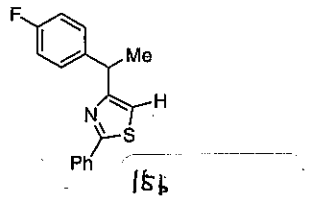


Filename = 1H-3870.jdf
Author = delta
Experiment = single_pulse.ex2
Sample_id = S#681344
Solvent = CHLOROFORM-D
Creation_time = 13-JAN-2009 18:23:53
Revision_time = 13-JAN-2009 18:58:37
Current_time = 13-JAN-2009 18:58:46

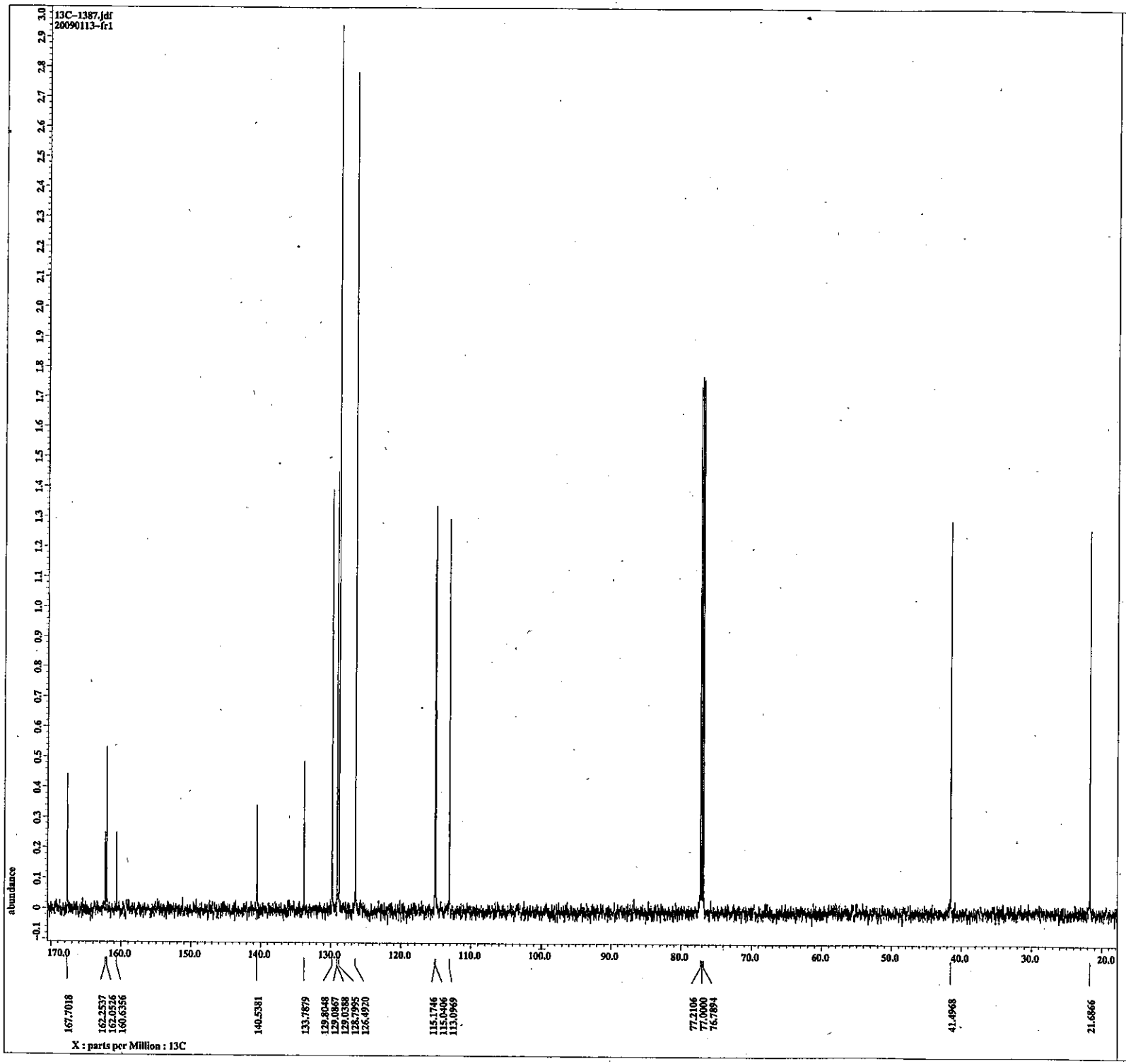
Comment = 20090113-fr1
Data_format = 1D COMPLEX
Dim_size = 13107
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = DELTA2_NMR

Field_strength = 14.09636928[T] (600[M
X_acq_duration = 1.4548992[s]
X_domain = 1H
X_freq = 600.1723046[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 1
X_resolution = 0.68733284[Hz]
X_sweep = 11.26126126[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 600.1723046[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 4
Total_scans = 4

X_90_width = 12.5[us]
X_acq_time = 1.4548992[s]
X_angle = 45[deg]
X_atn = 2.2[dB]
X_pulse = 6.25[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 34
Relaxation_delay = 2[s]
Repetition_time = 3.4548992[s]
Temp_get = 21.3[dC]
Spin_action = SPIN ON
Spin_state = SPIN ON
Spin_status = SPIN ON
Spin_get = 15[Hz]
Spin_set = 15[Hz]
Spin_gas_source = AIR
Sample_action = LOADED
Sample_state = LOAD
Sample_status = LOADED
Changer_sample = 0



42

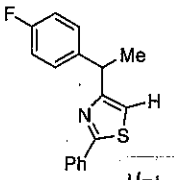


Filename = 13C-1387.jdf
Author = delta
Experiment = single_pulse_dec
Sample_id = SS681850
Solvent = CHLOROFORM-D
Creation_time = 13-JAN-2009 18:30:01
Revision_time = 13-JAN-2009 19:02:54
Current_time = 13-JAN-2009 19:06:03

Comment = 20090113-fr1
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA 600
Spectrometer = DELTA2_NMR

Field_strength = 14.09636928[T] (600[M
X_acq_duration = 0.69206016[s]
X_domain = 13C
X_freq = 150.91343039[MHz]
X_offset = 100[ppm]
X_points = 32760
X_prescans = 4
X_resolution = 1.44496109[Hz]
X_sweep = 47.34848485[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 52
Total_scans = 52

X_90_width = 11.25[us]
X_acq_time = 0.69206016[s]
X_angle = 30[deg]
X_atn = 6.2[dB]
X_pulse = 3.75[us]
Irr_atn_dec = 17.878[dB]
Irr_atn_noe = 17.878[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 58
Relaxation_delay = 2[s]
Repetition_time = 2.69206016[s]
Temp_get = 22[dC]
Spin_action = SPIN ON
Spin_state = SPIN ON
Spin_status = SPIN ON
Spin_get = 14[Hz]
Spin_set = 15[Hz]
Spin_gas_source = AIR
Sample_action = LOADED
Sample_state = LOAD
Sample_status = LOADED
Changer_sample = 0



15b