The unprecedented ring transformation from thiazoline-spiro-thiophene to thieno[2,3-b]pyrazine involved in the reaction of 2-thiocarbamoyl thiazolium salts with dimethyl acetylenedicarboxylate

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Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR were recorded in the indicated solvents. The solvent THF was distilled from sodium benzophenone ketyl and dichloromethane was dried with phosphorus pentoxide and redistilled.

1. General procedure for the preparation of 2-thiocarbamoyl thiazolium inner salts 8

At −30 ^{o}C and under nitrogen atmosphere, NaH (4 mmol, 50% in mineral oil) was added to the suspension of *N*-alkyl thiazolium bromide or thiazolium chloride (3 mmol) in dry THF (50 mL), and the mixture was stirred for 0.5 h under the same conditions. To the resulting emulsion, the solution of aryl isothiocyanate (3 mmol) in THF (10 mL) was added dropwise, and the reaction mixture was then stirred for 8-10 h at −30 to −10 ^{o}C. After removal of the solvent under vacuum at room temperature, the residue was chromatographied on a neutral Al_2O_3 column eluting with a mixture of petroleum ether (30-60 ^{o}C) and acetone (from 3:1 to 1:1). The eluent was evaporated under vacuum below 40 ^{o}C to give 2-thiocarbamoyl thiazolium inner salts **8** in 64-95% yields.

3-Ethyl-2-(*p*-nitrophenyl)thiocarbamoyl thiazolium inner salt 8a: 95%, mp 148-149 ^{o}C, IR ν (cm^{-1}) 1591, 1581, 1560, 1503, 1330; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.27 (d, J = 8.9 Hz, 2H), 7.43 (d, J = 6.5 Hz, 2H), 7.31 (s, 1H), 5.00 (q, J =7.1 Hz, 2H), 2.60 (s, 3H), 1.62 (s, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 177.6, 170.8, 158.0, 145.2, 143.3, 124.7, 122.4, 119.5, 46.7, 14.9, 14.5. MS (TOF-ESI): 308 (M+1). Anal.Calcd for $C_{13}H_{13}N_3O_2S_2$: C 50.79, H 4.26, N 13.67. Found: C 50.82, H 4.44, N 13.30.

3-Butyl-2-(*p*-nitrophenyl)thiocarbamoyl thiazolium inner salt 8b: 92%, mp 110-111 ^{o}C, IR ν (cm^{-1}): 1584, 1570, 1521, 1496, 1328; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.27 (d, J = 8.8 Hz,

2H), 7.41 (d, *J* = 6.7 Hz, 2H), 7.31 (s, 1H), 4.94 (t, *J* =7.9 Hz, 2H), 2.59 (s, 3H), 1.92-1.98 (m, 2H), 1.44-1.52 (m, 2H), 1.00 (t, *J* =7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 177.4, 170.9, 158.2, 145.5, 143.2, 124.7, 122.2, 119.6, 50.9, 31.8, 20.0, 14.7, 13.6. MS (ESI): 336 (M+1). Anal.Calcd for $C_{15}H_{17}N_3O_2S_2$: C 53.71, H 5.11, N 12.53. Found: C 53.76, H 5.35, N 12.18.

3-Benzyl-2-(*p*-nitrophenyl)thiocarbamoyl thiazolium inner salt 8c: 80%, mp 141-142 ^{o}C, IR *v* (cm^{-1}) 1582, 1571, 1499, 1329; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.22 (d, *J* = 8.9 Hz, 2H), 7.37-7.44 (m, 3H), 7.25 (br, 2H), 7.30 (s, 1H), 7.26 (d, *J* = 6.8 Hz, 2H), 6.36 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 178.2, 170.8, 157.7, 146.5, 143.2, 132.7, 129.4, 128.8, 127.0, 124.6, 122.4, 119.7, 54.1, 15.0. MS (ESI): 370 (M+1). Anal.Calcd for $C_{18}H_{15}N_3O_2S_2$: C 58.52, H 4.09, N 11.37. Found: C 58.51, H 4.32, N 11.07.

3-(*p*-Methylbenzyl)-2-(*p*-nitrophenyl)thiocarbamoyl thiazolium inner salt 8d: 80%, mp 134-135 ^{o}C, IR *v* (cm^{-1}) 1581, 1567, 1498, 1328; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.22 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.28 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.31 (s, 2H), 2.42 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 178.2, 170.9, 157.8, 146.5, 143.3, 138.9, 130.0, 129.7, 127.1, 124.6, 122.4, 119.4, 54.0, 21.1, 15.0. MS (ESI): 384 (M+1). Anal.Calcd for $C_{19}H_{17}N_3O_2S_2$: C 59.51, H 4.47, N 10.96. Found: C 59.54, H 4.82, N 10.90.

3-(*p*-Bromobenzyl)-2-(*p*-nitrophenyl)thiocarbamoyl thiazolium inner salt 8e: 85%, mp 181-182 ^{o}C, IR *v* (cm^{-1}) 1583, 1566, 1514, 1499, 1326; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.25 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.35 (br, 2H), 7.29 (s, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.31 (br, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 178.5, 170.9, 157.1, 146.1, 143.5, 132.6, 131.6, 128.8, 124.7, 123.1, 122.5, 119.6, 53.5, 15.0. MS (ESI): 448 (M+1), 450. Anal.Calcd for $C_{18}H_{14}BrN_3O_2S_2$: C 48.22, H 3.15, N 9.37. Found: C 48.30, H 2.83, N 9.21.

3-Benzyl-2-phenylthiocarbamoyl thiazolium inner salt 8f: 88%, mp 172-173 ^{o}C, IR *v* (cm^{-1}) 1589, 1571, 1505; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.35-7.42 (m, 7H), 7.30-7.32 (m, 2H), 7.20 (s, 1H), 7.05-7.11 (m, 1H), 6.39 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ (ppm): 179.3, 167.9, 150.8, 145.9, 133.1, 129.3, 128.6, 128.5, 127.3, 124.0, 122.3, 118.9, 54.0, 15.0. MS (ESI): 325 (M+1). Anal.Calcd for $C_{18}H_{16}N_2S_2$: C 66.63, H 4.97, N 8.63. Found: C 66.65, H 4.80, N 8.58.

3-Benzyl-2-(*p*-methylphenyl)thiocarbamoyl thiazolium inner salt 8g: 73%, mp 168-169 ^{o}C, IR *v* (cm^{-1}) 1578, 1507, 1491; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.34-7.41 (m, 5H), 7.26-7.29 (m, 2H), 7.16 (d, *J* = 2.7 Hz, 2H), 7.14 (s, 1H), 6.38 (s, 2H), 2.35 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 179.2, 167.1, 148.4, 146.1, 133.5, 133.3, 129.1, 129.0, 128.5, 127.2, 122.4, 119.3, 53.9, 21.2, 14.9. MS (ESI): 339 (M+1). Anal.Calcd for $C_{19}H_{18}N_2S_2$: C 67.42, H 5.36, N 8.28. Found: C 67.52, H 5.51, N 8.21.

3-Benzyl-2-(*p*-fluorophenyl)thiocarbamoyl thiazolium inner salt 8h: 81%, mp 105-106 ^{o}C, IR *v* (cm^{-1}) 1574, 1506, 1493; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.47-7.51 (m, 2H), 7.37-7.39 (m, 3H), 7.27 (d, *J* = 6.8 Hz, 2H), 7.21 (s, 1H), 7.04 (d, *J* = 7.0 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 6.35

(s, 2H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 179.1, 167.7, 161.0, 157.8, 146.8, 146.2, 133.1, 129.2, 128.6, 127.1, 124.2, 124.1, 119.3, 115.1, 114.8, 54.0, 14.9. MS (ESI): 443 (M+1). Anal.Calcd for $C_{18}H_{15}FN_2S_2$: C 63.13, H 4.41, N 8.18. Found: C 63.37, H 4.60, N 8.11.

3-Benzyl-2-(*m*-nitrophenyl)thiocarbamoyl thiazolium inner salt 8i: 85%, mp 167-168 ^{o}C, IR *v* (cm^{-1}) 1571, 1516, 1499, 1349; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.16 (s, 1H), 7.92 (dt, *J* = 8.1, 1.2 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 8.1 Hz, 2H), 7.37-7.42 (m, 3H), 7.27 (d, *J* =8.1 Hz, 2H), 6.37 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 170.8, 148.6, 146.3, 132.8, 129.4, 129.0, 128.9, 128.8, 127.1, 119.2, 118.5, 117.6, 54.2, 15.0. MS (ESI): 370 (M+1). Anal. Calcd for $C_{18}H_{15}N_3O_2S_2$: C 58.52, H 4.09, N 11.37. Found: C 58.55, H 3.68, N 11.29.

3-Benzyl-2-(*p*-trifluoromethylphenyl)thiocarbamoyl thiazolium inner salt 8j: 89%, mp 122-123 ^{o}C, IR *v* (cm^{-1}) 1607, 1574, 1516, 1496, 1321; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.58 (d, *J* = 8.4 Hz, 2H), 7.34-7.44 (m, 5H), 7.24-7.28 (m, 3H), 6.37 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 178.6, 169.7, 154.5, 146.3, 132.9, 129.3, 128.7, 127.1, 126.4, 125.72, 125.67, 125.6, 125.3, 124.8, 122.8, 122.1, 119.5, 54.0, 14.9. MS (ESI): 393 (M+1). Anal.Calcd for $C_{19}H_{15}F_3N_2S_2$: C 58.15, H 3.85, N 7.14. Found: C 58.25, H 3.73, N 7.18.

3-Methylbenzyl-2-(*p*-fluorophenyl)thiocarbamoyl thiazolium inner salt 8k: 75%, mp 125-126 ^{o}C, IR *v* (cm^{-1}): 1575, 1508, 1493; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.51 (br, 2H), 7.18 (s, 5H), 7.03 (t, *J* = 8.8 Hz, 2H), 6.30 (s, 2H), 2.37 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 179.2, 167.8, 161.0, 157.8, 146.7, 146.0, 138.6, 130.0, 129.9, 127.2, 124.2, 124.1, 118.9, 115.1, 114.8, 53.9, 21.1, 15.0. MS (ESI): 357 (M+1). Anal.Calcd for $C_{19}H_{17}FN_2S_2$: C 64.02, H 4.81, N 7.86. Found: C 63.98, H 4.62, N 7.64.

3-Methylbenzyl-2-(*p*-trifluoromethylphenyl)thiocarbamoyl thiazolium inner salt 8l: 84%, mp 121-122 ^{o}C, IR *v* (cm^{-1}) 1606, 1573, 1515, 1494, 1321; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.59 (d, *J* = 8.3 Hz, 2H), 7.40 (brs, 2H), 7.23 (s, 1H), 7.20 (d, *J* = 8.9 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.30 (s, 2H), 2.40 (s, 3H) , 2.36 (s, 3H); ^{13}C NMR(75 MHz, $CDCl_3$) δ (ppm): 178.5, 169.8, 154.4, 146.2, 138.7, 129.9, 129.8, 127.2, 126.4, 125.74, 125.69, 125.6, 125.3, 122.9, 122.1, 119.2, 53.9, 21.1, 14.9. MS (ESI): 407 (M+1). Anal.Calcd for $C_{20}H_{17}F_3N_2S_2$: C 59.10, H 4.22, N 6.89. Found: C 59.27, H 4.22, N 6.79.

3-Bromobenzyl-2-(*p*-methylphenyl)thiocarbamoyl thiazolium inner salt 8m: 64%, mp 163-164 ^{o}C, IR *v* (cm^{-1}) 1575, 1503, 1484, 1475; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.51 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.0 Hz, 2H), 7.16-7.20 (m, 4H), 6.33 (s, 2H), 2.35 (s, 3H), 2.33 (s, 3H); ^{13}CNMR(75MHz, $CDCl_3$) δ (ppm): 179.5, 166.9, 148.0, 145.9, 133.8, 132.3, 129.1, 129.0, 122.7, 122.5, 119.4, 53.4, 21.1, 14.9. MS (ESI): 417 (M+1), 419. Anal.Calcd for $C_{19}H_{17}BrN_2S_2$: C 54.67, H 4.11, N 6.71. Found: C 54.25, H 3.83, N 6.30.

3-Bromobenzyl-2-(*p*-fluorophenyl)thiocarbamoyl thiazolium inner salt 8n: 82%, mp 132-133 ^{o}C, IR *v* (cm^{-1}) 1575, 1506, 1488; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.46-7.53 (m, 4H), 7.16-7.21 (m, 3H), 7.00-7.06 (m, 2H), 6.30 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 179.5, 167.5, 161.1, 157.9, 146.5, 145.9, 132.4, 132.1, 128.9, 124.3, 124.2, 122.8, 119.4,

115.1, 114.8, 53.4, 14.9. MS (ESI): 421 (M+1). Anal.Calcd for $C_{18}H_{14}BrFN_2S_2$: C 51.31, H 3.35, N 6.65. Found: C 51.36, H 3.59, N 6.67.

3-Bromobenzyl-2-(*m*-nitrophenyl)thiocarbamoyl thiazolium inner salt 8o: 78%, mp 162-163 ^oC, IR ν (cm^{-1}): 1567, 1514, 1501, 1486, 1343; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.22 (brs, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 7.2 Hz, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.49 (t, J = 8.1 Hz, 2H), 7.32 (s, 1H), 7.18 (d, J = 8.1 Hz, 2H), 6.32 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 170.8, 151.8, 148.6, 146.2, 132.6, 131.8, 129.1, 129.0, 128.8, 123.1, 119.6, 118.6, 117.5, 53.6, 15.0. MS (ESI): 448 (M+1). Anal.Calcd for $C_{18}H_{14}BrN_3O_2S_2$: C 48.22, H 3.15, N 9.37. Found: C 48.33, H 3.18, N 9.23.

3-Bromobenzyl-2-(*p*-trifluoromethylphenyl)thiocarbamoyl thiazolium inner salt 8p: 90%, mp 169-170 ^oC, IR ν (cm^{-1}) 1606, 1576, 1515, 1485, 1320; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.60 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.37 (brs, 2H), 7.27 (s, 1H), 7.18 (d, J = 8.2 Hz, 2H), 6.32 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 178.8, 169.6, 154.1, 146.1, 132.4, 131.9, 128.9, 125.8, 125.73, 125.70, 125.67, 125.4, 122.9, 122.2, 119.6, 53.5, 14.9. MS (ESI): 471 (M+1). Anal.Calcd for $C_{19}H_{14}BrF_3N_2S_2$: C 48.41, H 2.99, N 5.94. Found: C 48.65, H 2.96, N 5.78.

2. General procedure for the reaction of 2-thiocarbamoyl thiazolium salts 8 with DMAD.

A solution of dimethyl acetylenedicarboxylate (2.5 mmol) in dichloroethane (10 mL) was added dropwise to the 2-thiocarbamoyl thiazolium salts **8** (1 mmol) in dichloroethane (20 mL) while cooling in an ice-bath. The mixture was then stirred at 0 ^oC for 0.5 hour. After removal of the solvent under vacuum at room temperature, the residue was chromatographied on a neutral Al_2O_3 column eluting with a mixture of petroleum ether (30-60 ^oC) and ethyl acetate (from 3:1 to 1:1). The eluent was evaporated under vacuum below 40 ^oC, and the products **9** were isolated in 72-97% yields.

(*E*)-Dimethyl 1-ethyl-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-nitrophenyl)-1,4-dihydrothieno[2, 3-b]pyrazine-6,7-dicarboxylate 9a: 97%, mp 123-124 ^oC, IR ν (cm^{-1}) 1737, 1715, 1591; ^1H NMR (500 MHz, CD_3COCD_3) δ (ppm): 8.26 (d, J = 9.0 Hz, 2H), 7.46 (d, J = 9.1 Hz, 2H), 5.91 (s, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.63 (s, 3H), 3.59 (t, J = 7.0 Hz, 2H), 3.54 (s, 3H), 2.27 (s, 3H), 1.02 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.6, 165.5, 164.2, 161.5, 154.7, 152.3, 149.9, 143.3, 138.0, 137.3, 130.1, 126.1, 124.2, 118.2, 116.0, 106.6, 53.7, 53.1, 52.2, 44.1, 17.2, 14.8. MS (TOF-ESI): 592 (M+1). Anal.Calcd for $C_{25}H_{25}N_3O_{10}S_2$: C 50.75, H 4.26, N 7.10. Found: C 50.79, H 4.54, N 6.87.

(*E*)-Dimethyl 1-butyl-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-nitrophenyl)-1,4-dihydrothieno[2, 3-b]pyrazine-6,7-dicarboxylate 9b: 95%, mp 130-131 ^oC; IR ν (cm^{-1}) 1738, 1714, 1590; ^1H NMR (500 MHz, CD_3COCD_3) δ (ppm): 8.28 (d, J = 9.2 Hz, 2H), 7.46 (d, J = 9.2 Hz, 2H), 5.92 (s, 1H), 3.95 (s, 3H), 3.91 (s, 3H), 3.65 (s, 3H), 3.59 (t, J = 6.8 Hz, 2H), 3.54 (s, 3H), 2.31 (s, 3H), 1.41-1.44 (m, 2H), 1.05-1.09 (m, 2H), 0.64 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.6, 164.2, 161.5, 155.5, 152.6, 150.0, 143.1, 138.2, 136.8, 129.7, 126.1, 124.7, 117.4,

116.0, 105.1, 53.7, 53.15, 53.08, 52.2, 48.3, 32.4, 19.9, 17.1, 13.6. MS (MALDI-TOF): 619 (M^+). Anal.Calcd for $C_{27}H_{29}N_3O_{10}S_2$: C 52.33, H 4.72, N 6.78. Found: C 52.27, H 4.89, N 6.64.

(*E*)-Dimethyl 1-benzyl-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-nitrophenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9c: 82%, mp 161-162 ^oC; IR ν (cm^{-1}) 1735, 1718, 1708, 1590; ^1H NMR (500 MHz, CD_3COCD_3) δ (ppm): 8.21 (d, J = 9.1 Hz, 2H), 7.23 (d, J = 9.1 Hz, 2H), 7.10-7.13 (m, 5 H), 5.93 (s, 1H), 4.73 (s, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 3.66 (s, 3H), 3.59 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.4, 164.2, 161.4, 154.0, 151.6, 149.2, 143.6, 139.7, 137.8, 137.3, 130.7, 129.4, 128.6, 128.1, 125.9, 124.1, 119.0, 116.6, 110.3, 53.6, 53.5, 53.12, 53.07, 52.2, 17.6. MS (MALDI-TOF): 562 (M-Bn), 653 (M^+). Anal. Calcd for $C_{30}H_{27}N_3O_{10}S_2$: C 55.12, H 4.16, N 6.43. Found: C 55.14, H 4.37, N 6.37.

(*E*)-Dimethyl 1-(*p*-methylbenzyl)-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-nitrophenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9d: 85%, mp 142-142 ^oC; IR ν (cm^{-1}) 1737, 1715, 1708, 1588; ^1H NMR (500 MHz, CD_3COCD_3) δ (ppm): 8.19 (d, J = 9.1 Hz, 2H), 7.14 (d, J = 9.1 Hz, 2H), 6.95 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 7.8 Hz, 2H), 5.92 (s, 1H), 4.66 (s, 2H), 3.95 (s, 3H), 3.90 (s, 3H), 3.65 (s, 3H), 3.58 (s, 3H), 2.30 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.4, 164.2, 161.5, 154.1, 151.7, 149.1, 143.5, 140.1, 138.2, 137.4, 134.5, 130.9, 129.9, 128.2, 125.7, 124.2, 118.8, 116.6, 111.0, 53.7, 53.5, 53.1, 52.2, 20.9, 17.6. MS (MALDI-TOF): 562 (M-MeBn), 668 (M+1). Anal. Calcd for $C_{31}H_{29}N_3O_{10}S_2$: C 55.76, H 4.38, N 6.29. Found: C 55.82, H 4.74, N 6.10.

(*E*)-Dimethyl 1-(*p*-bromobenzyl)-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-nitrophenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9e: 80%, mp 155-156 ^oC; IR ν (cm^{-1}) 1735, 1723, 1706, 1589; ^1H NMR (500 MHz, CD_3COCD_3) δ (ppm): 8.20 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 5.92 (s, 1H), 4.68 (s, 2H), 3.96 (s, 3H), 3.91 (s, 3H), 3.65 (s, 3H), 3.57 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.4, 164.2, 161.4, 153.8, 151.3, 148.8, 143.6, 140.8, 137.0, 136.6, 132.4, 131.0, 130.4, 125.8, 124.4, 122.2, 118.7, 116.9, 112.4, 53.7, 53.3, 53.1, 52.2, 17.6. MS (MALDI-TOF): 562 (M-BrBn), 732 (M+1). Anal. Calcd for $C_{30}H_{26}BrN_3O_{10}S_2$: C 49.19, H 3.58, N 5.74. Found: C 49.22, H 3.95, N 5.49.

(*E*)-Dimethyl 1-benzyl-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-phenyl-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9f: 75%, mp 159-160 ^oC; IR ν (cm^{-1}) 1740, 1718, 1603; ^1H NMR (500 MHz, CD_3COCD_3) δ (ppm): 7.36-7.38 (m, 3H), 7.33 (t, J = 7.6 Hz, 2H), 7.22-7.28 (m, 3H), 6.78 (d, J = 7.9 Hz, 2H), 5.84 (s, 1H), 4.50 (s, 2H), 3.93 (s, 3H), 3.79 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.7, 165.3, 164.3, 161.6, 148.5, 148.0, 144.9, 144.4, 137.6, 132.6, 131.2, 130.1, 129.6, 129.5, 128.8, 127.5, 125.9, 118.2, 118.1, 116.2, 55.8, 53.3, 53.1, 52.5, 52.1, 18.1; MS (TOF-ESI): 609 (M+1), 631 ($M+Na^+$). Anal. Calcd for $C_{30}H_{28}N_2O_8S_2$: C 59.20, H 4.64, N 4.60. Found: C 59.18, H 4.65, N 4.42.

(*E*)-Dimethyl 1-benzyl-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-methylphenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9g: 72%, mp 107-108 °C; IR *v* (cm^{-1}) 1736, 1716, 1603; ^1H NMR (500 MHz, CD_3COCD_3) δ (ppm): 7.40-7.41 (m, 3H), 7.28 (d, *J* = 7.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.61 (d, *J* = 7.9 Hz, 2H), 5.84 (s, 1H), 4.46 (s, 2H), 3.93 (s, 3H), 3.78 (s, 3H), 3.70 (s, 3H), 3.68 (s, 3H), 2.31 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.7, 165.3, 164.3, 161.6, 149.1, 148.5, 143.5, 141.5, 137.9, 137.5, 132.9, 130.7, 130.2, 129.8, 129.5, 128.9, 126.6, 119.1, 117.3, 116.1, 56.2, 53.3, 53.1, 52.4, 52.1, 21.0, 18.2. MS (MALDI-TOF): 622.9 (M+1). Anal.Calcd for $C_{31}H_{30}N_2O_8S_2$: C 59.79, H 4.86, N 4.50. Found: C 59.84, H 4.36, N 4.25.

(*E*)-Dimethyl 1-benzyl-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-fluorophenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9h: 77%, mp 119-120 °C; IR *v* (cm^{-1}) 1740, 1720, 1605; ^1H NMR (500 MHz, CD_3COCD_3) δ (ppm): 7.40-7.44 (m, 3H), 7.28 (d, *J* = 6.5 Hz, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 6.73 (dd, *J* = 8.7, 4.8 Hz, 2H), 5.84 (s, 1H), 4.48 (s, 2H), 3.94 (s, 3H), 3.79 (s, 3H), 3.70 (s, 3H), 3.68 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.7, 165.3, 164.3, 161.6, 160.5, 148.5, 148.0, 144.1, 140.4, 137.4, 132.9, 130.7, 129.8, 129.6, 129.01, 128.98, 128.9, 118.8, 118.1, 117.0, 116.7, 116.5, 56.1, 53.4, 53.2, 52.6, 52.2, 18.2. MS (MALDI-TOF): 535 (M-Bn), 627 (M+1). Anal. Calcd for $C_{30}H_{27}FN_2O_8S_2$: C 57.50, H 4.34, N 4.47. Found: C 57.53, H 4.60, N 4.41.

(*E*)-Dimethyl 1-benzyl-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*m*-nitrophenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9i: 77%, mp 99-100 °C; IR *v* (cm^{-1}) 1741, 1727, 1712, 1613; ^1H NMR (500 MHz, CD_3COCD_3) δ (ppm): 8.01 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.65 (t, *J* = 2.2 Hz, 1H), 7.62 (t, *J* = 8.2 Hz, 1H), 7.37 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.18-7.21 (m, 5H), 5.89 (s, 1H), 4.62 (s, 2H), 3.94 (s, 3H), 3.86 (s, 3H), 3.66 (s, 3H), 3.63 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, CD_3COCD_3) δ (ppm): 164.6, 164.4, 163.3, 160.5, 149.4, 148.7, 147.5, 145.7, 142.6, 136.5, 133.9, 130.9, 130.5, 128.5, 128.0, 127.8, 127.7, 120.9, 119.1, 115.9, 115.8, 113.4, 53.8, 52.7, 52.3, 52.0, 51.3, 17.0. MS (MALDI-TOF): 562 (M-Bn), 653 (M^+). Anal. Calcd for $C_{30}H_{27}N_3O_{10}S_2$: C 55.12, H 4.16, N 6.43. Found: C 54.61, H 4.43, N 6.16.

(*E*)-Dimethyl 1-benzyl-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-trifluoromethylphenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9j: 82%, mp 102-103 °C; IR *v* (cm^{-1}) 1736, 1712, 1612; ^1H NMR (500 MHz, CD_3COCD_3) δ (ppm): 7.65 (d, *J* = 8.5 Hz, 2H), 7.19-7.23 (m, 3H), 7.16 (d, *J* = 7.1 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 5.89 (s, 1H), 4.64 (s, 2H), 3.93 (s, 3H), 3.86 (s, 3H), 3.66 (s, 3H), 3.63 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.5, 165.4, 164.3, 161.5, 150.7, 149.0, 148.9, 143.0, 137.6, 135.1, 131.4, 129.4, 128.7, 127.3, 127.2, 127.1, 126.5, 126.1, 122.1, 121.9, 116.5, 113.4, 54.3, 53.5, 53.1, 52.9, 52.2, 17.8. MS (MALDI-TOF): 585 (M-Bn), 677 (M+1). Anal.Calcd for $C_{31}H_{27}F_3N_2O_8S_2$: C 55.02, H 4.02, N 4.14. Found: C 55.02, H 4.21, N 3.98.

(*E*)-Dimethyl 1-(*p*-methylbenzyl)-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-fluorophenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9k: 72%, mp 109-110 ^{o}C; IR ν (cm^{-1}) 1743, 1737, 1720, 1602; ^{1}H NMR (500 MHz, CD_3COCD_3) δ (ppm): 7.22 (d, J = 7.5 Hz, 2H), 7.14 (d, J = 7.5 Hz, 2H), 7.07 (t, J = 8.6 Hz, 2H), 6.70-6.73 (m, 2H), 5.83 (s, 1H), 4.43 (s, 2H), 3.94 (s, 3H), 3.79 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 2.40 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (75 MHz,CD_3COCD_3) δ (ppm): 165.7, 165.3, 164.3, 163.7, 161.6, 148.6, 148.0, 144.1, 140.4, 138.7, 134.2, 133.0, 130.7, 130.1, 129.8, 129.0, 128.9 119.0, 118.0, 116.9, 116.6, 116.5, 55.9, 53.4, 53.2, 52.5, 52.2, 21.2, 18.2. MS (MALDI-TOF): 535 (M-MeBn), 641 (M+1). Anal. Calcd for $C_{31}H_{29}FN_2O_8S_2$: C 58.11, H 4.56, N 4.37. Found: C 58.04, H 4.71, N 3.86.

(*E*)-Dimethyl 1-(*p*-methylbenzyl)-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-trifluoromethylphenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9l: 81%, mp 105-106 ^{o}C; IR ν (cm^{-1}) 1736, 1712, 1612; ^{1}H NMR (500 MHz, CD_3COCD_3) δ (ppm): 7.63 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 5.88 (s, 1H), 4.57 (s, 2H), 3.94 (s, 3H), 3.86 (s, 3H), 3.66 (s, 3H), 3.62 (s, 3H), 2.24 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.5, 165.4, 164.3, 161.5, 150.9, 148.9, 143.3, 138.3, 135.2, 134.5, 131.6, 130.0, 129.7, 128.8, 127.11, 127.06, 126.3, 125.9, 121.9, 116.4, 113.9, 54.3, 53.6, 53.1, 52.9, 52.2, 21.0, 17.8. MS (MALDI-TOF): 585 (M-MeBn), 691 (M+1). Anal. Calcd for $C_{32}H_{29}F_3N_2O_8S_2$: C 55.64, H 4.23, N, 4.06. Found: C 55.62, H 4.59, N, 3.77.

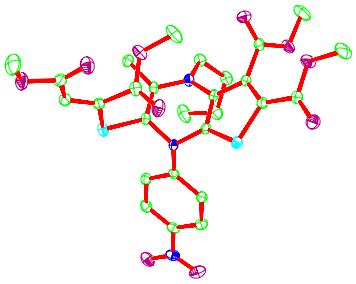
(*E*)-Dimethyl 1-(*p*-bromobenzyl)-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-methylphenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9m: 76%, mp 131-132 ^{o}C; IR ν (cm^{-1}) 1747, 1734, 1713, 1601; ^{1}H NMR (500 MHz, CD_3COCD_3) δ (ppm): 7.58 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.61 (d, J = 8.3 Hz, 2H), 5.83 (s, 1H), 4.44 (s, 2H), 3.93 (s, 3H), 3.78 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 2.33 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.7, 165.2, 164.3, 161.6, 149.4, 148.3, 143.1, 141.3, 138.0, 136.5, 133.0, 132.6, 131.9, 130.8, 129.7, 126.4 122.6, 119.9, 117.5, 116.4, 55.7, 53.3, 53.1, 52.5, 52.1, 21.0, 18.2. MS (MALDI-TOF): 531 (M-BrBn), 701 (M+1). Anal.Calcd for $C_{31}H_{29}BrN_2O_8S_2$: C 53.07, H 4.17, N 3.99. Found: C 53.04, H 4.40, N 3.94.

(*E*)-Dimethyl 1-(*p*-bromobenzyl)-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-fluorophenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9n: 82%, mp 110-111 ^{o}C; IR ν (cm^{-1}) 1748, 1736, 1715, 1601; ^{1}H NMR (500 MHz, CD_3COCD_3) δ (ppm): 7.59 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 7.12 (t, J = 8.6 Hz, 2H), 6.76-6.78 (m, 2H), 5.83 (s, 1H), 4.47 (s, 2H), 3.94 (s, 3H), 3.79 (s, 3H), 3.69 (s, 3H), 3.68 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.7, 165.3, 164.3, 161.6, 148.7, 147.9, 143.8, 140.2, 136.5, 132.9, 132.6, 131.9, 130.2, 128.7, 128.6, 122.6, 119.4, 118.2, 117.1, 116.8, 116.7, 55.5, 53.4, 53.2, 52.6, 52.2, 18.2. MS (MALDI-TOF): 535 (M-BrBn), 705 (M+1). Anal. Calcd for $C_{30}H_{26}BrFN_2O_8S_2$: C 51.07, H 3.71, N 3.97. Found: C 51.14, H 4.19, N 3.94.

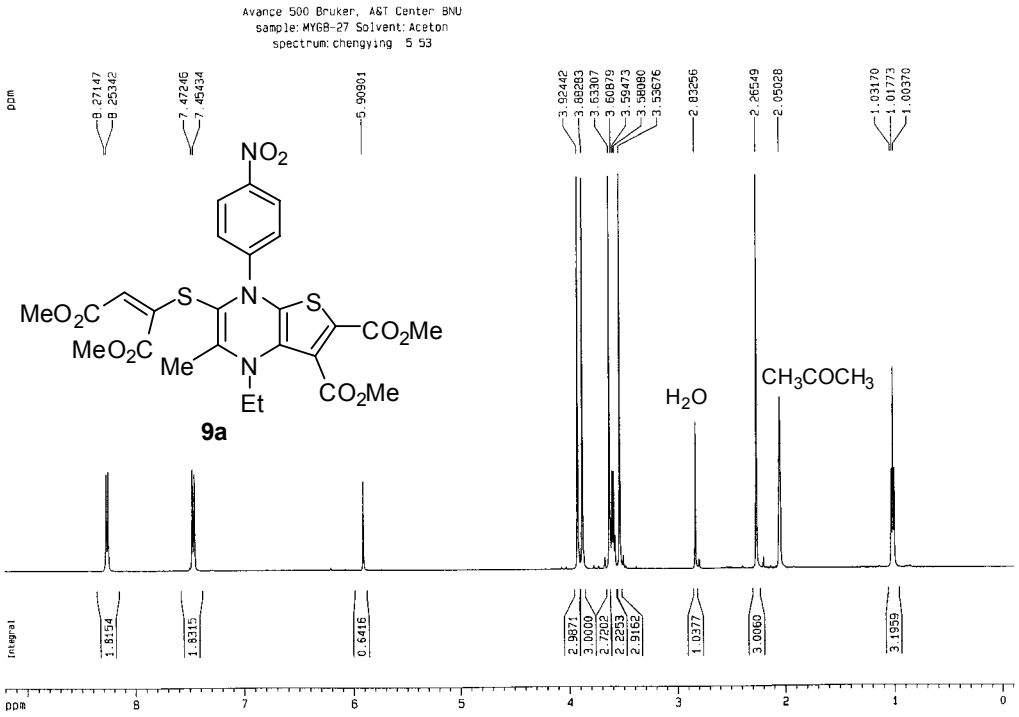
(*E*)-Dimethyl 1-(*p*-bromobenzyl)-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*m*-nitrophenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9o: 77%, mp 134-135 ^{o}C; IR ν (cm^{-1}) 1741, 1735, 1717, 1602; ^{1}H NMR (500 MHz, CD_3OD) δ (ppm): 8.00 (d, J = 7.9 Hz, 1H), 7.56 (s, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.30 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 1H), 7.00 (d, J = 7.8 Hz, 2H), 5.81 (s, 1H), 4.48 (s, 2H), 3.95 (s, 3H), 3.85 (s, 3H), 3.67 (s, 3H), 3.60 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, CD_3COCD_3) δ (ppm): 164.5, 164.4, 163.3, 160.5, 149.4, 148.6, 147.3, 145.4, 143.0, 135.6, 133.7, 131.5, 131.0, 130.5, 130.1, 127.1, 121.5, 121.1, 119.0, 116.2, 115.3, 114.5, 53.3, 52.7, 52.3, 52.1, 51.3, 17.1. MS (TOF-ESI): 732 (M+1)/734, 754 (M+Na^{+})/756. Anal. Calcd for $C_{30}H_{26}BrN_3O_{10}S_2$: C 49.19, H 3.58, N 5.74. Found: C 49.28, H 4.00, N 5.63.

(*E*)-Dimethyl 1-(*p*-bromobenzyl)-2-methyl-3-(1,2-dimethoxycarbonylvinylthio)-4-(*p*-trifluoromethylphenyl)-1,4-dihydrothieno[2,3-b]pyrazine-6,7-dicarboxylate 9p: 82%, mp 95-96 ^{o}C; IR ν (cm^{-1}): 1733, 1712, 1614; ^{1}H NMR (500 MHz, CD_3COCD_3) δ (ppm): 7.68 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.1 Hz, 4H), 5.89 (s, 1H), 4.61 (s, 2H), 3.94 (s, 3H), 3.86 (s, 3H), 3.66 (s, 3H), 3.62 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, CD_3COCD_3) δ (ppm): 165.5, 165.4, 164.2, 161.5, 150.3, 148.7, 143.8, 136.7, 134.6, 132.5, 131.6, 130.9, 127.3, 127.2, 126.2, 122.4, 122.0, 121.9, 116.7, 114.8, 54.0, 53.6, 53.1, 52.9, 52.2, 17.9. MS (MALDI-TOF): 585 (M-BrBn), 755 (M+1). Anal. Calcd for $C_{31}H_{26}BrF_3N_2O_8S_2$: C 49.28, H 3.47, N, 3.71. Found: C 49.25, H 3.74, N, 3.48.

3. Figure 1. Ortep drawing of X-ray structure of **9b** (50% probability was chosen for the ellipsoids).



4. The copies of NMR spectra of products 9.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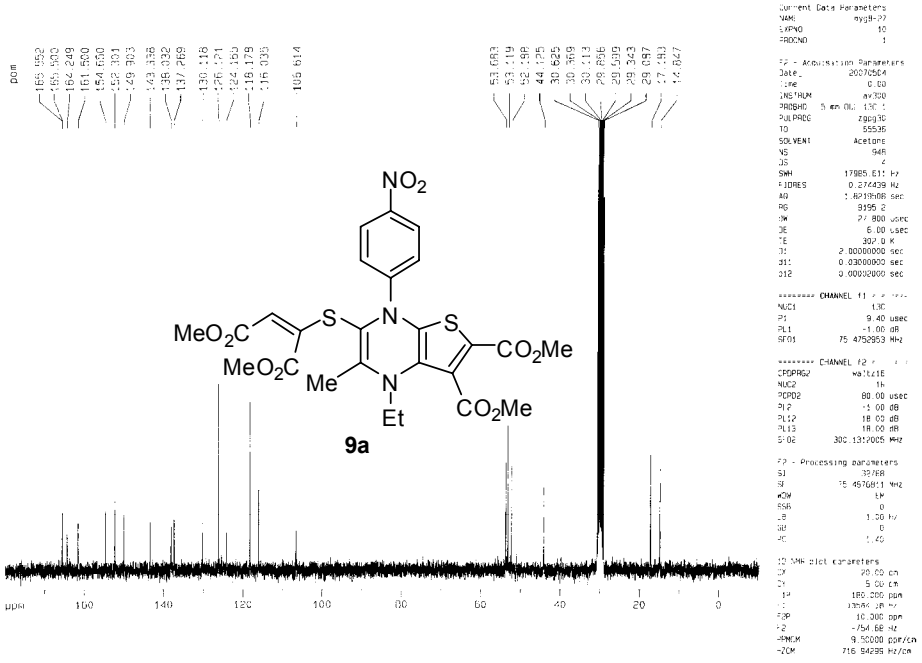
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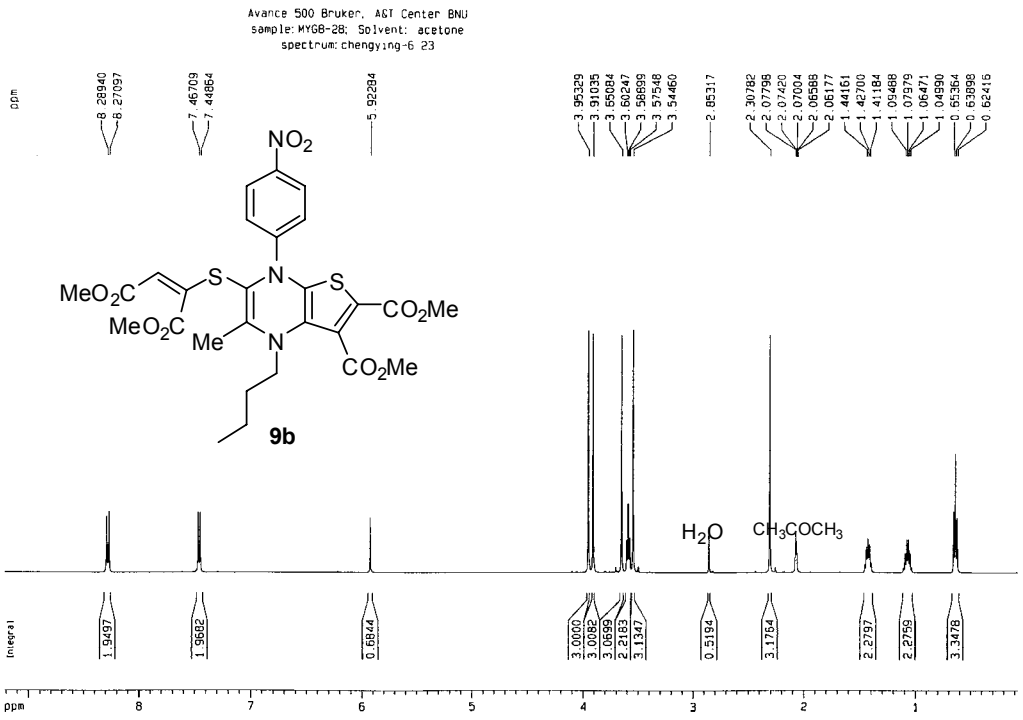
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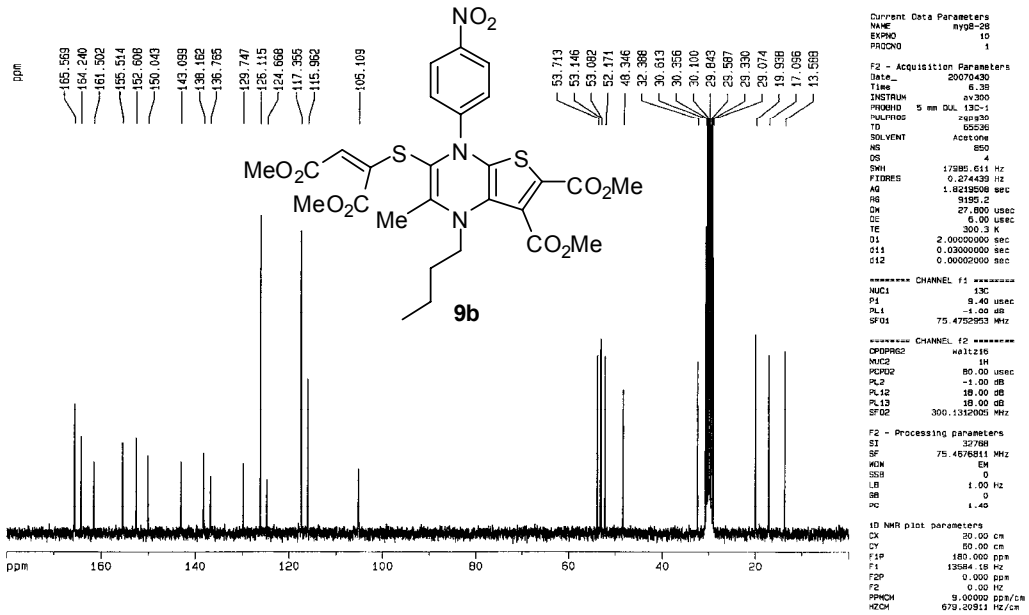
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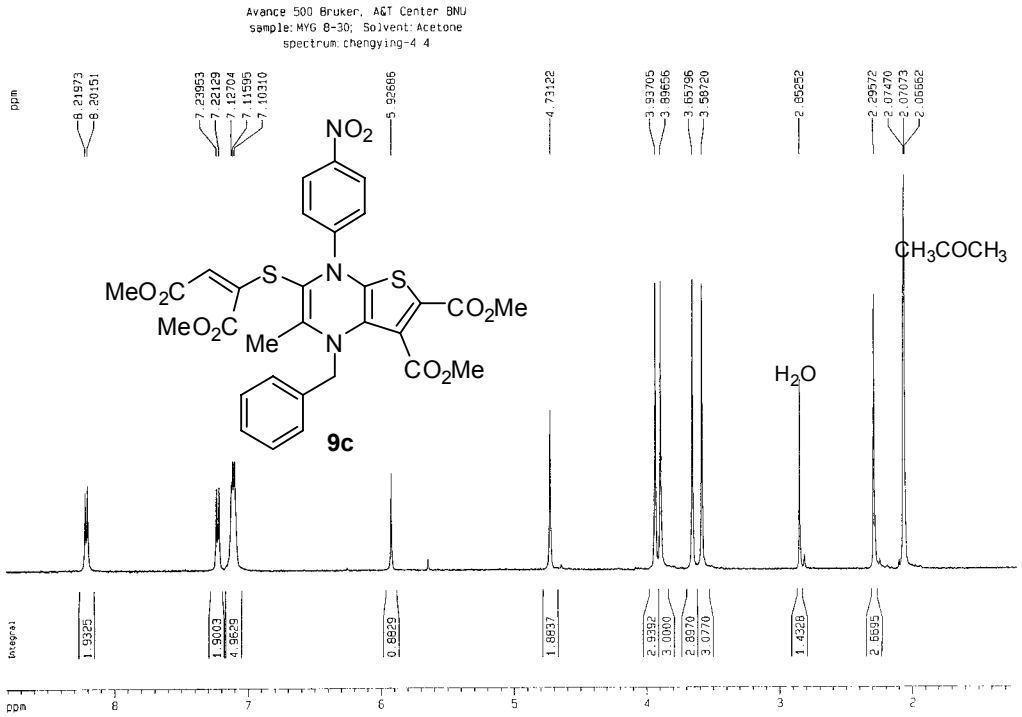
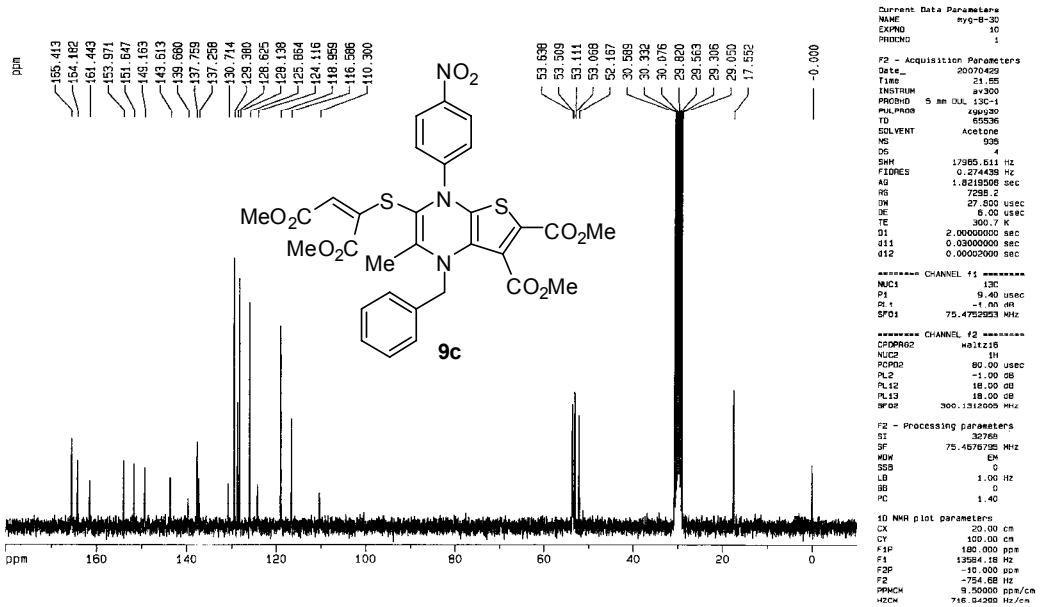
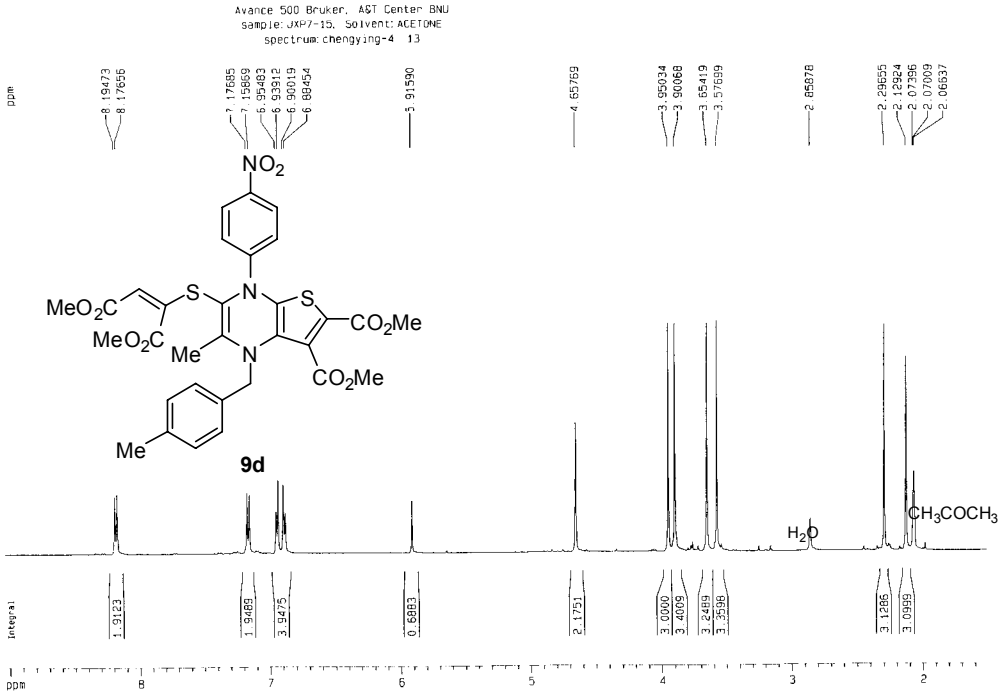
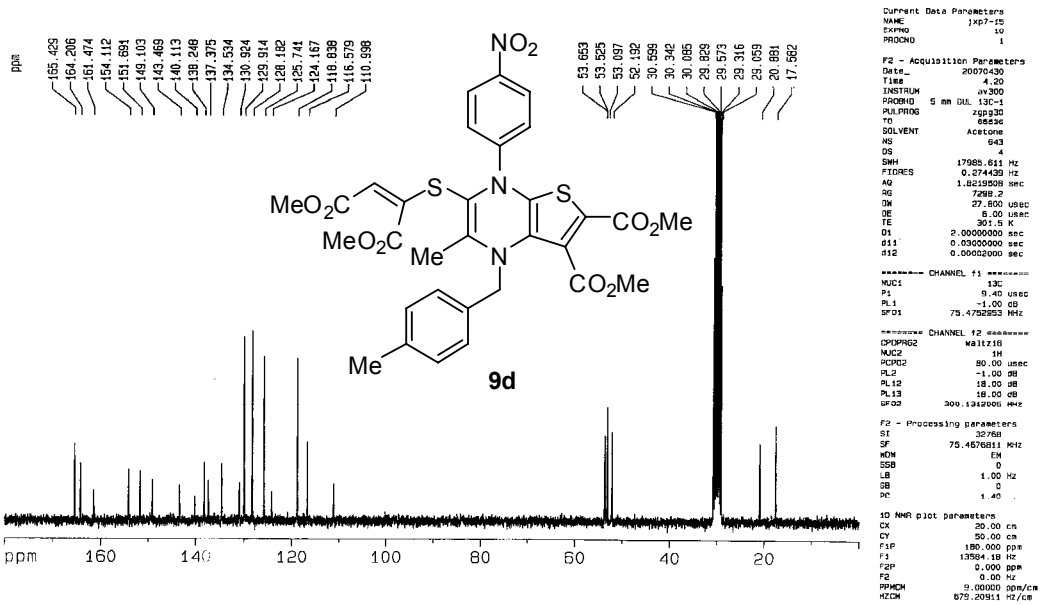
PPMCM 9.00000 ppm/cm
HZCM 679.20911 Hz/cm

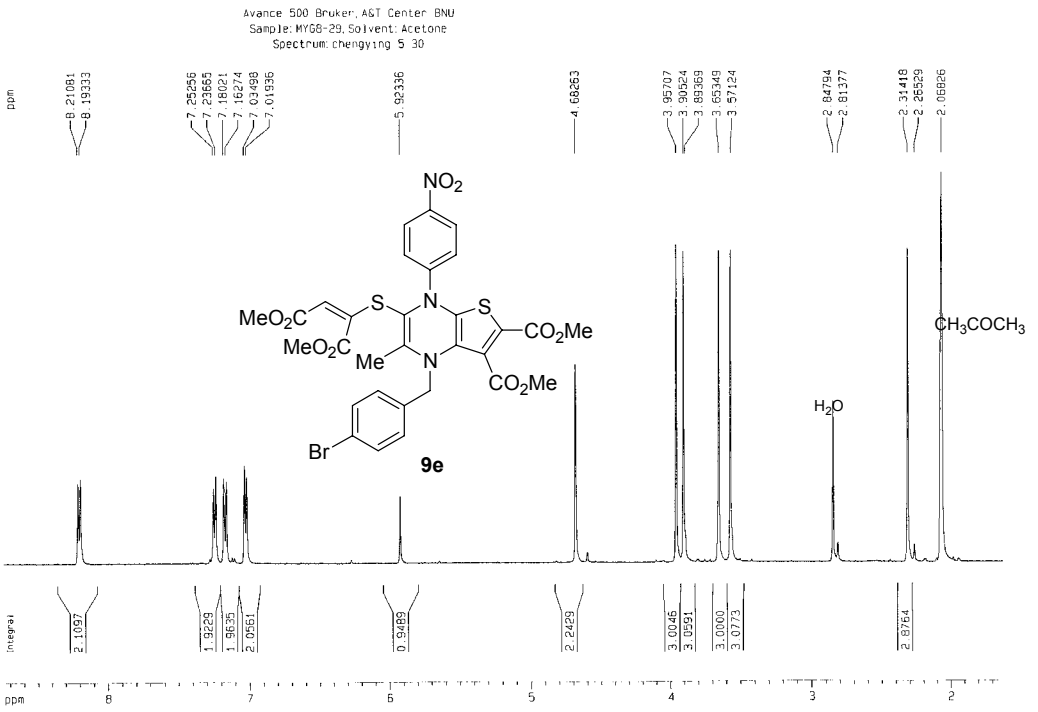


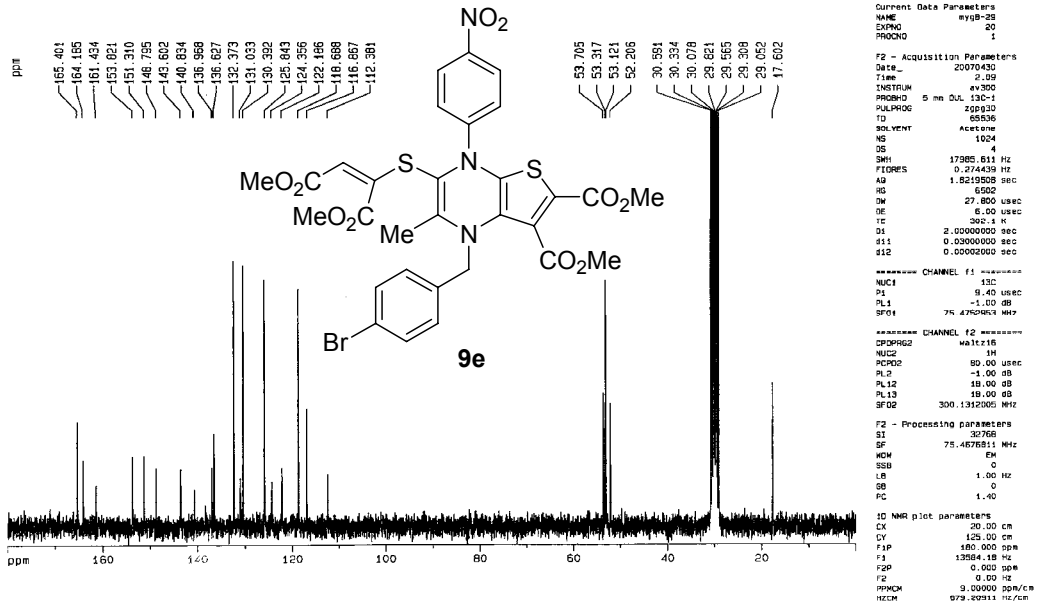



```
Current Data Parameters
NAME                  myg-8-30
EXPNO                       10
PROCNO                       1

F2 - Acquisition Parameters
Date_              20070429
Time                   21.55
INSTRUM                av300
PROBHD     5 mm DUL 13C-1
PULPROG             zgpg30
TD                       65536
SOLVENT              Acetone
NS                         936
DS                           4
SWH                17985.611 Hz
FIDRES                0.274439 Hz
AQ                    1.8219508 sec
RG                       7298.2
DW                       27.800 usec
DE                        6.00 usec
TE                       300.7 K
D1                    2.00000000 sec
d11                   0.03000000 sec
d12                   0.00002000 sec

======== CHANNEL f1 ========
NUC1                       13C
P1                        9.40 usec
PL1                      -1.00 dB
SFO1               75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    80.00 usec
PL2                      -1.00 dB
PL12                     18.00 dB
PL13                     18.00 dB
SFO2               300.1312005 MHz

F2 - Processing parameters
SI                         32768
SF                 75.4676795 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                       20.00 cm
CY                      100.00 cm
F1P                     180.000 ppm
F1                    13584.18 Hz
F2P                    -10.000 ppm
F2                     -754.68 Hz
PPMCM                  9.50000 ppm/cm
HZCM                 716.84209 Hz/cm
```

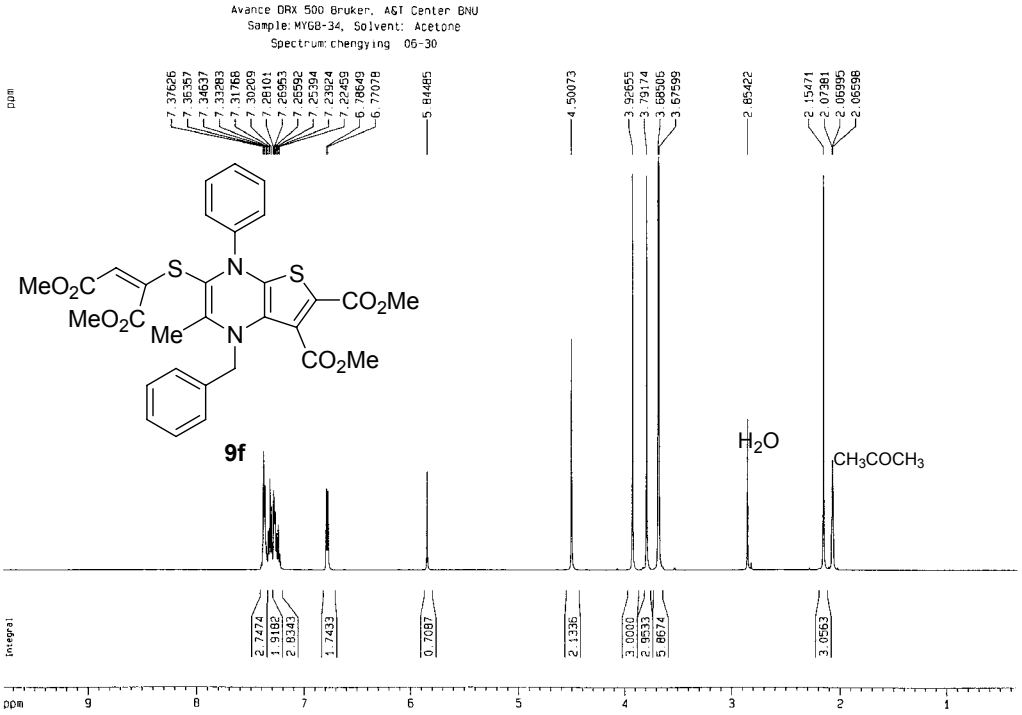

Avance 500 Bruker, A&T Center BNU
sample: JXP7-15, Solvent: ACETONE
spectrum: chengying-4 13
ppm
8.19473
8.17656
7.17685
7.15869
6.95483
6.93912
6.90019
6.88454
5.91590
4.65769
3.95034
3.90068
3.65419
3.57699
2.85878
2.29655
2.12924
2.07396
2.07009
2.06637
NO2
MeO2C
MeO2C
S
N
S
CO2Me
Me
N
CO2Me
Me
9d
H2O
CH3COCH3
Integral
1.9123
1.9488
3.9475
0.6883
2.1751
3.0000
3.4009
3.2489
3.3598
3.1286
3.0999
ppm
8
7
6
5
4
3
2

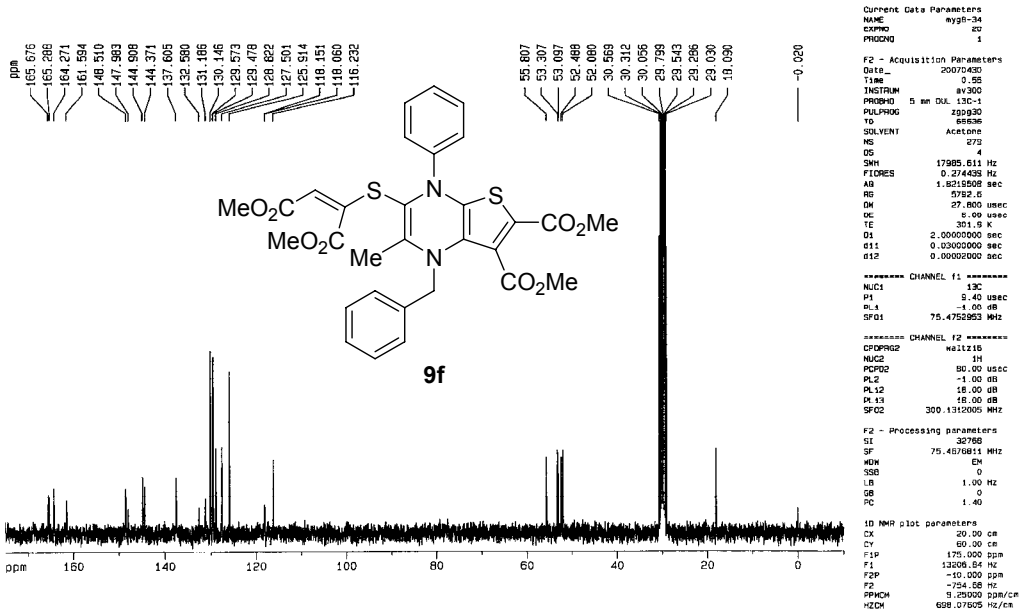

ppm
165.429
164.206
161.474
154.112
151.691
149.103
143.469
140.113
138.248
137.375
134.534
130.924
129.914
128.182
125.741
124.167
118.838
116.579
110.998
53.653
53.525
53.097
52.192
30.598
30.342
30.085
29.829
29.573
29.316
29.059
20.881
17.582
NO2
MeO2C
MeO2C
S
N
S
CO2Me
Me
N
CO2Me
Me
9d
ppm
160
140
120
100
80
60
40
20
Current Data Parameters
NAME jxp7-15
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070430
Time 4.20
INSTRUM av300
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 643
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 7298.2
DW 27.800 usec
DE 6.00 usec
TE 301.5 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.40 usec
PL1 -1.00 dB
SFO1 75.4752853 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 18.00 dB
PL13 18.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4676811 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 50.00 cm
F1P 180.000 ppm
F1 13584.18 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 9.00000 ppm/cm
HZCM 679.20911 Hz/cm

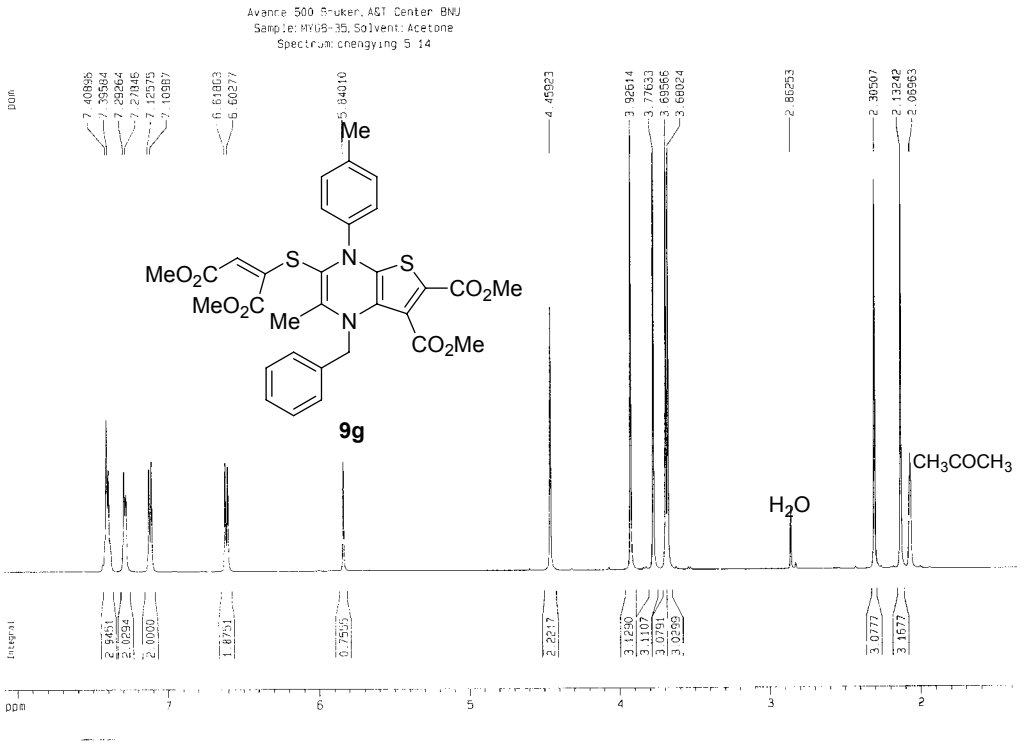


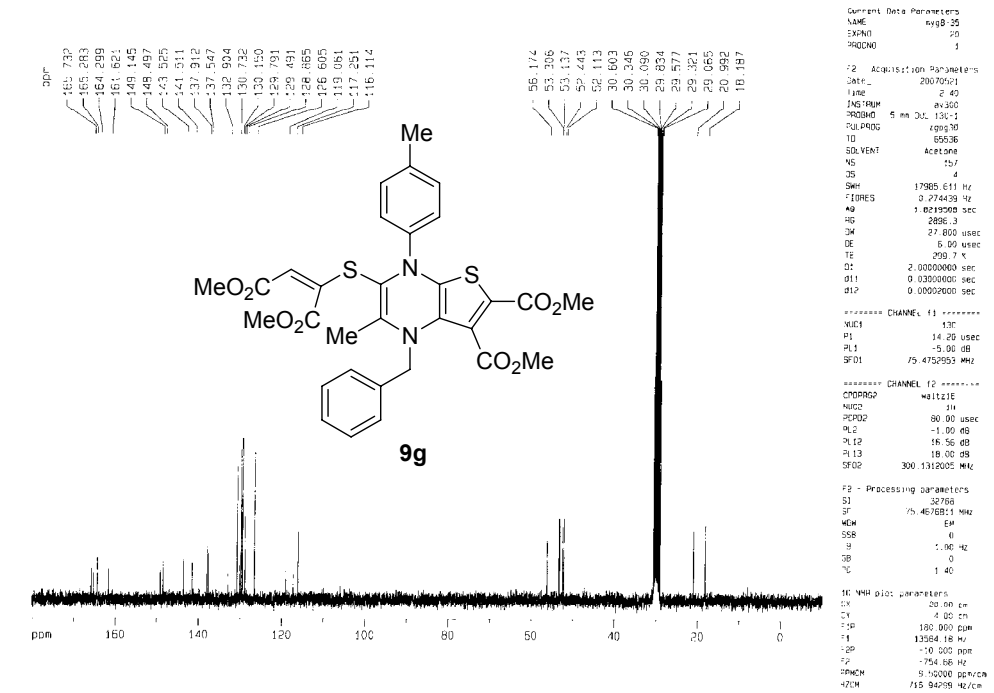


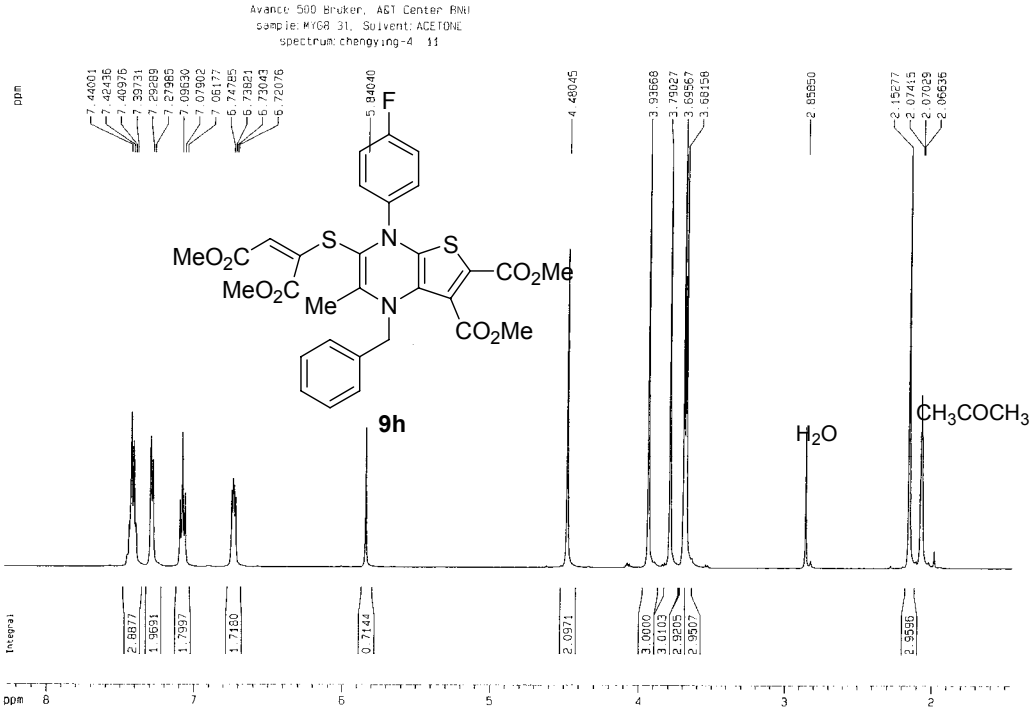

```
Current Data Parameters
NAME                  myg8-29
EXPNO                      20
PROCNO                      1

F2 - Acquisition Parameters
Date_              20070430
Time                   2.09
INSTRUM               av300
PROBHD   5 mm DUL 13C-1
PULPROG            zgpg30
TD                  65536
SOLVENT           Acetone
NS                     1024
DS                        4
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                1.8219508 sec
RG                     6502
DW                  27.800 usec
DE                   6.00 usec
TE                  302.1 K
D1                2.00000000 sec
d11               0.03000000 sec
d12               0.00002000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                      9.40 usec
PL1                    -1.00 dB
SF01             75.4750853 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                    -1.00 dB
PL12                   18.00 dB
PL13                   18.00 dB
SF02            300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF               75.4676811 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
CY                      125.00 cm
F1P                    180.000 ppm
F1                   13584.18 Hz
F2P                      0.000 ppm
F2                       0.00 Hz
PPMCM                 9.00000 ppm/cm
HZCM                979.20911 Hz/cm
```

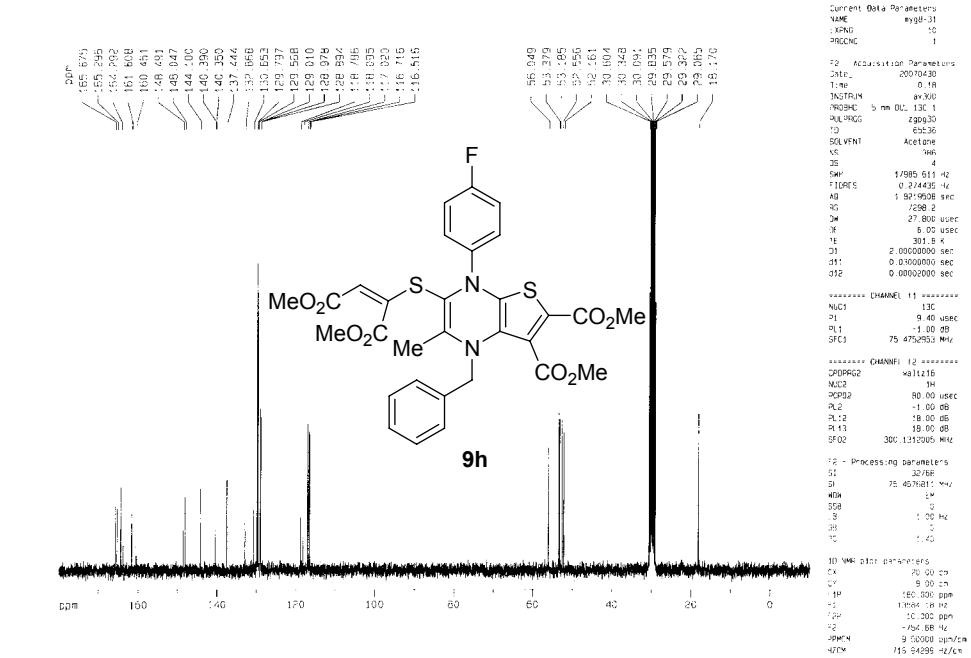

Avance DRX 500 Bruker. A&T Center BNU
Sample: MYGB-34, Solvent: Acetone
Spectrum: chengying 06-30
9f
H2O
CH3COCH3
Integral
ppm

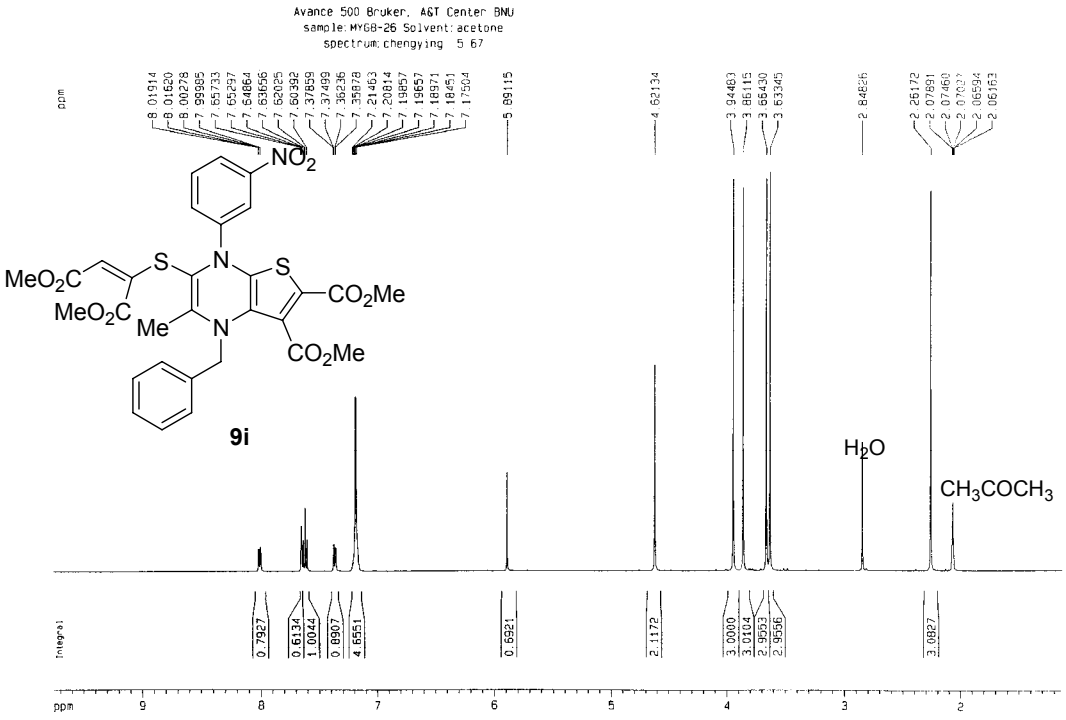

9f
ppm

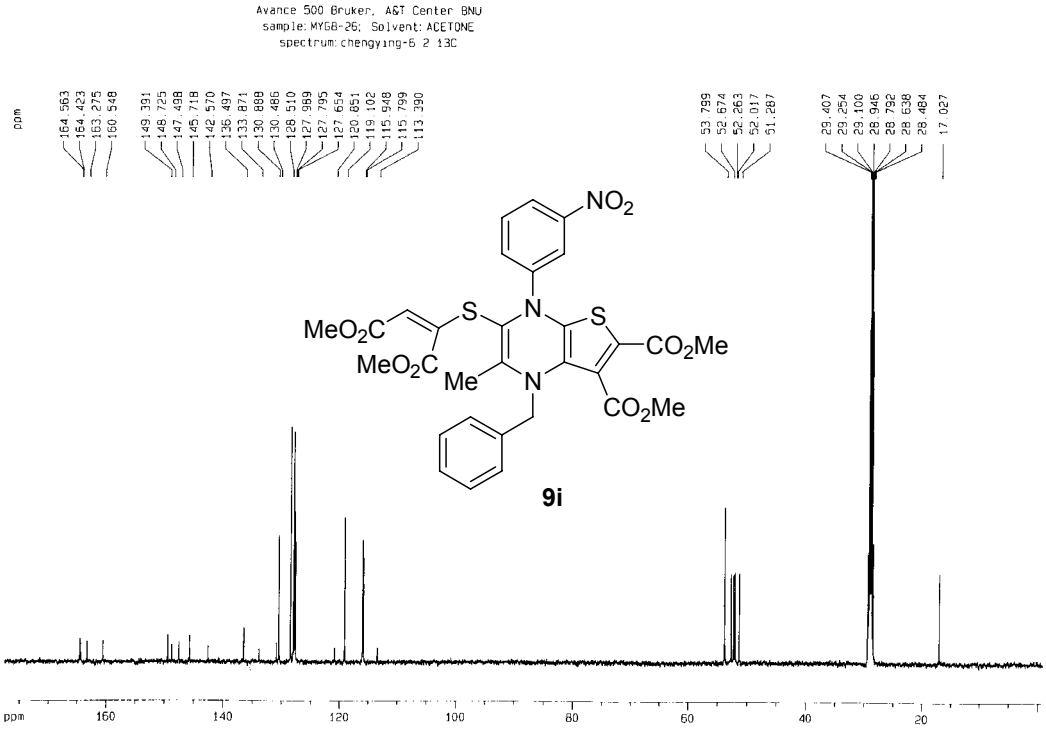

Avance 500 Bruker, AST Center BNU
Sample: MY08-35, Solvent: Acetone
Spectrum: chengying 5 14
Me
MeO2C
MeO2C
S
N
S
CO2Me
Me
N
CO2Me
9g
H2O
CH3COCH3
ppm

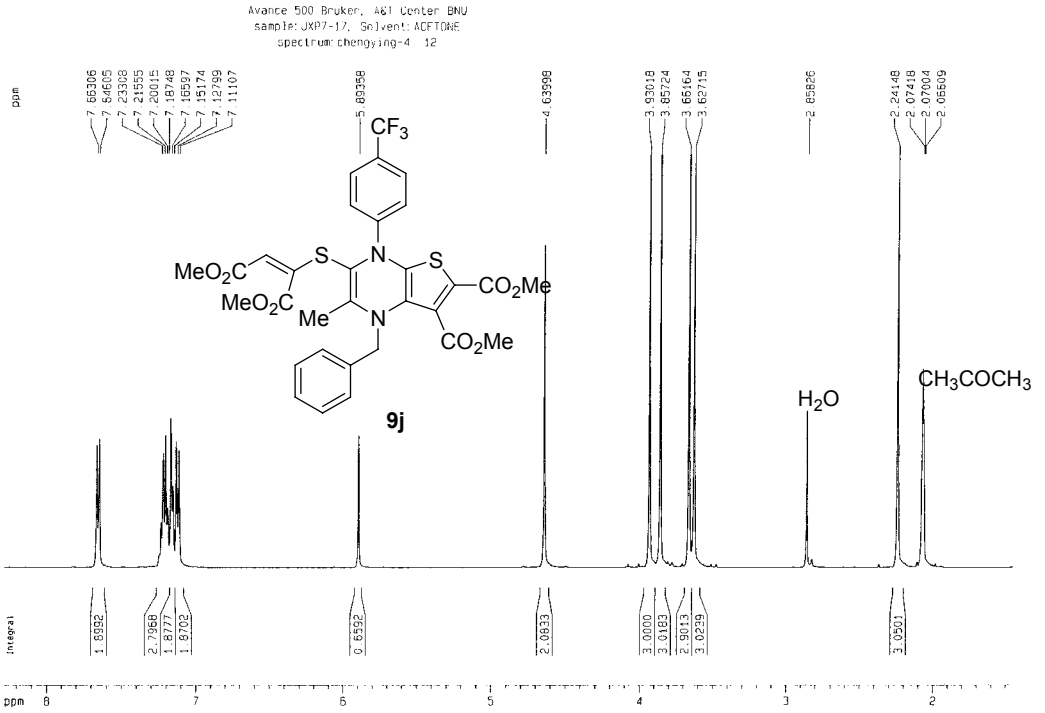

Me
MeO2C
MeO2C
S
N
S
CO2Me
Me
N
CO2Me
9g
ppm

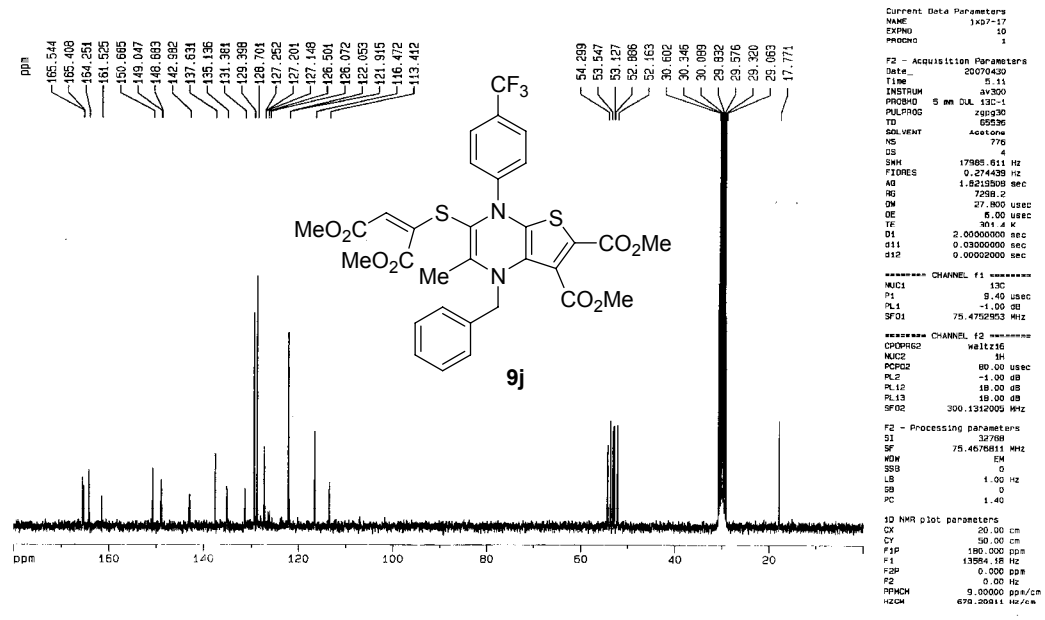

Avance 500 Bruker, A&T Center RNI
sample: MYG8 31, Solvent: ACETONE
spectrum: chengying-4 11
ppm
7.44001
7.42436
7.40976
7.39731
7.29289
7.27985
7.09630
7.07902
7.06177
6.74785
6.73821
6.73043
6.72076
5.84040
4.48045
3.93668
3.79027
3.69567
3.68158
2.85850
2.15277
2.07415
2.07029
2.05636
F
MeO2C
MeO2C
S
N
S
Me
N
CO2Me
CO2Me
9h
H2O
CH3COCH3
Integral
2.88777
1.96914
1.79977
1.71780
0.71444
2.09771
3.00004
3.01034
2.93205
2.95074
2.95961
ppm 8
7
6
5
4
3
2


F
MeO2C
MeO2C
S
N
S
Me
N
CO2Me
CO2Me
9h
ppm
160
140
120
100
80
60
40
20
0

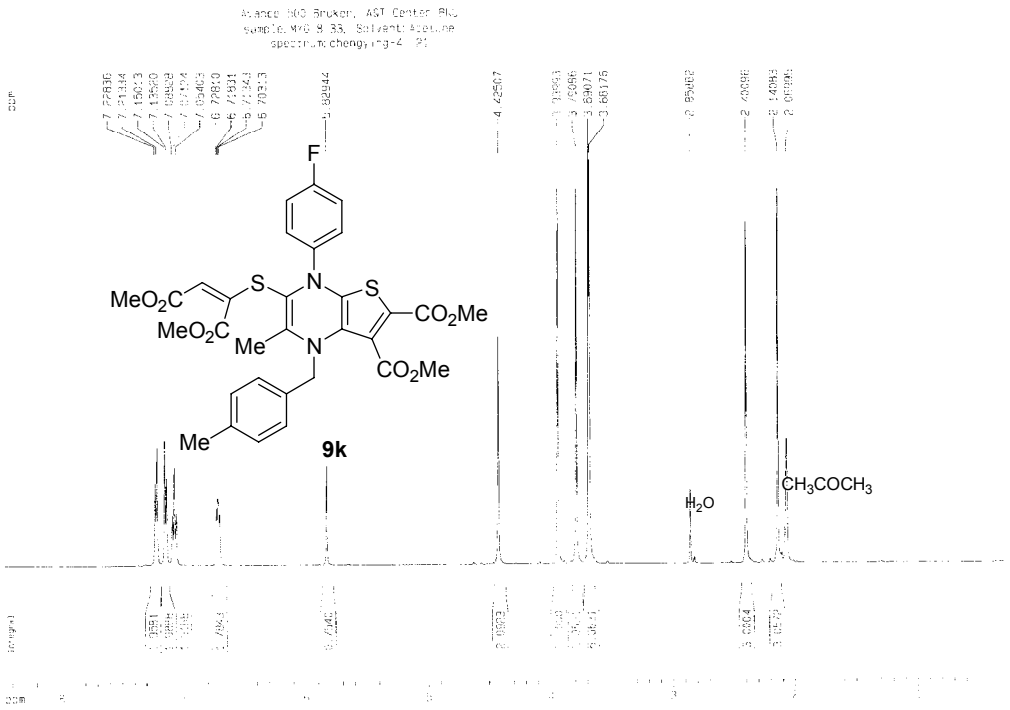

Avance 500 Bruker, A&T Center BNU
sample: MYG8-26 Solvent: acetone
spectrum: chengying 5 67
ppm
8.01914
8.01620
8.00278
7.99985
7.65733
7.65257
7.64864
7.63656
7.62025
7.60392
7.37859
7.37499
7.36236
7.35878
7.21463
7.20014
7.19857
7.19657
7.18971
7.18451
7.17504
5.89115
4.62134
3.94463
3.86115
3.66430
3.63345
2.84826
2.26172
2.07891
2.07460
2.06594
2.06163
NO2
MeO2C
MeO2C
S
N
S
CO2Me
Me
N
CO2Me
9i
H2O
CH3COCH3
Integral
0.7927
0.6134
1.0044
0.8907
4.6551
0.6821
2.1172
3.0000
3.0104
2.9953
2.9556
3.0827
ppm
9
8
7
6
5
4
3
2

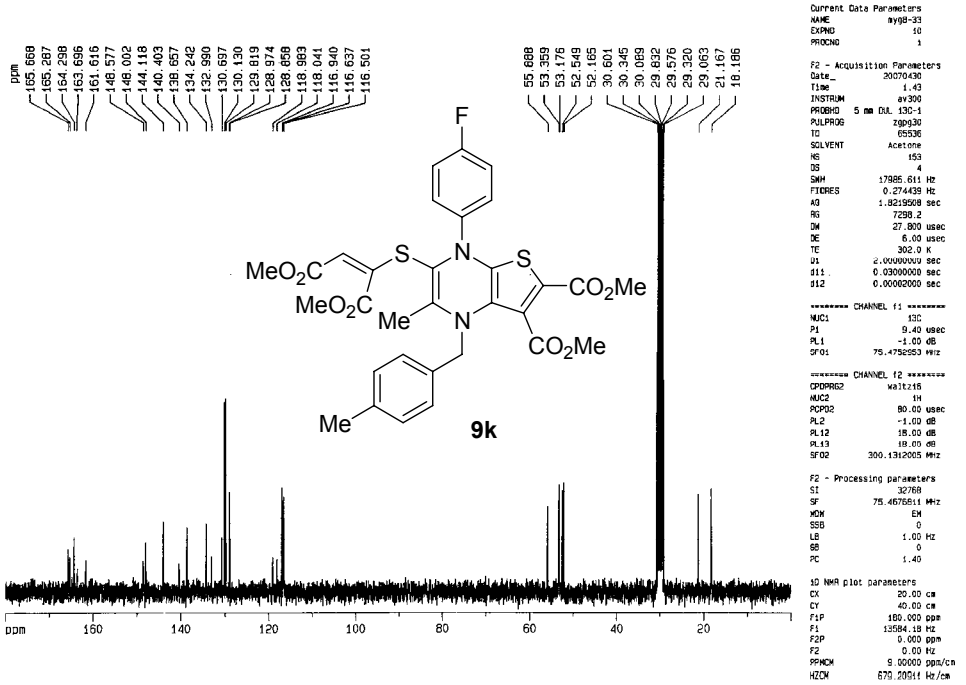

Avance 500 Bruker, A&T Center BNU
sample: MYG8-26; Solvent: ACETONE
spectrum: chengying-6 2 13C
ppm
164.563
164.423
163.275
160.548
149.391
148.725
147.498
145.718
142.570
136.497
133.871
130.889
130.486
128.510
127.989
127.795
127.654
120.851
119.102
115.548
115.799
113.390
53.799
52.674
52.263
52.017
51.287
29.407
29.254
29.100
28.946
28.792
28.638
28.484
17.027
NO2
MeO2C
MeO2C
S
N
S
CO2Me
Me
N
CO2Me
9i
ppm
160
140
120
100
80
60
40
20



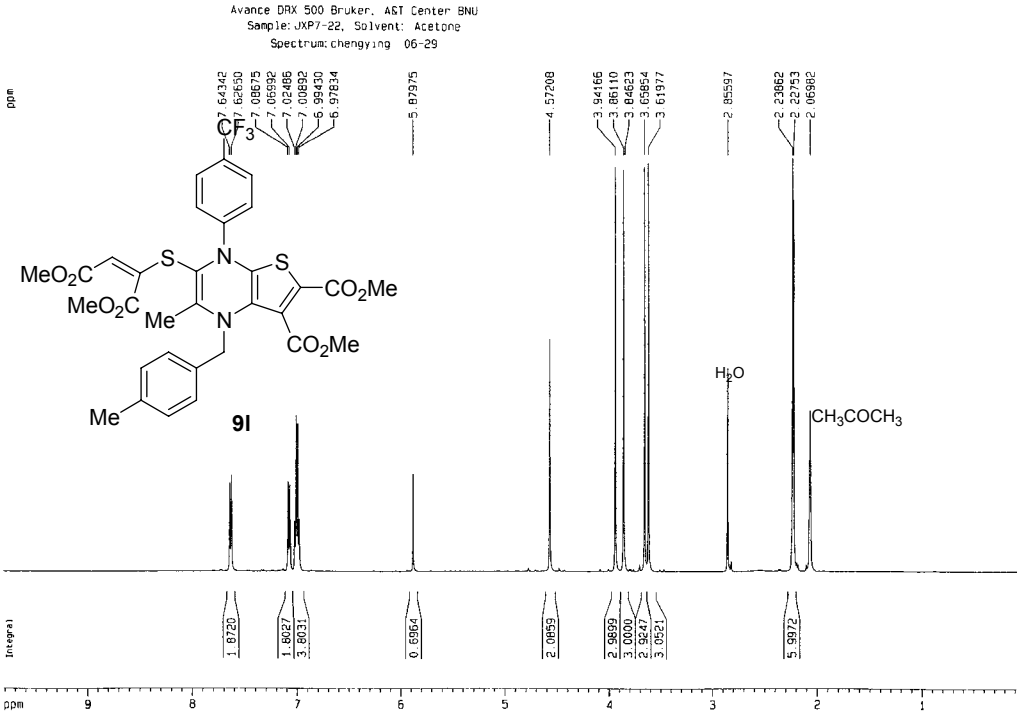


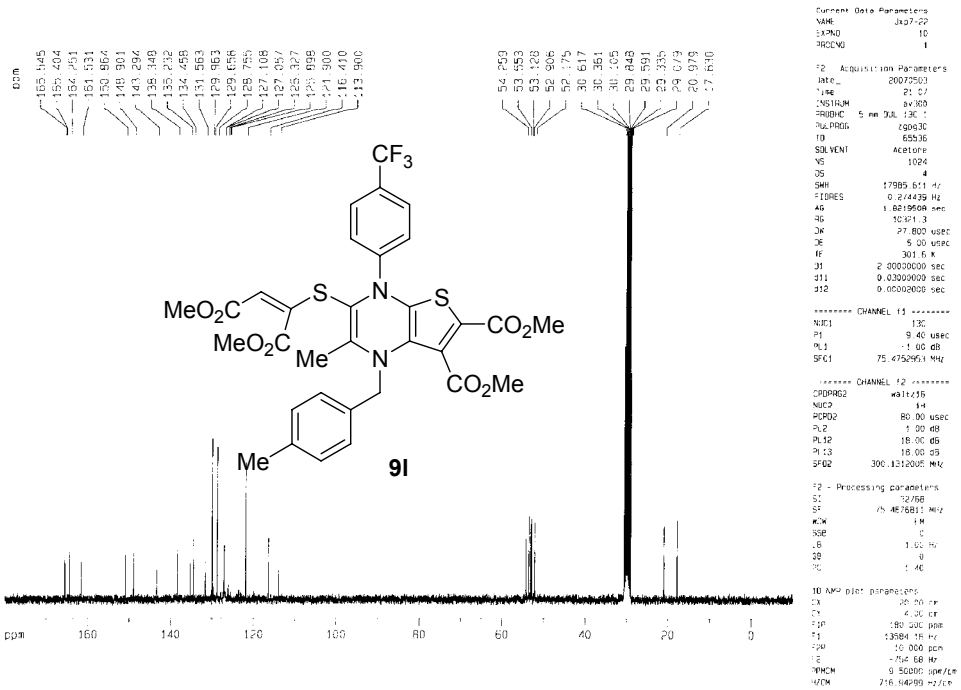

```
Current Data Parameters
NAME                  jxp7-17
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_              20070430
Time                    8.11
INSTRUM                av300
PROBHD    5 mm DUL 13C-1
PULPROG              zgpg30
TD                    65536
SOLVENT              Acetone
NS                       776
DS                         4
SWH                17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8213508 sec
RG                    7298.2
DW                   27.800 usec
DE                    6.00 usec
TE                   301.4 K
D1                 2.00000000 sec
d11                0.03000000 sec
d12                0.00002000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                      9.40 usec
PL1                    -1.00 dB
SFO1              75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                  80.00 usec
PL2                    -1.00 dB
PL12                   18.00 dB
PL13                   18.00 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                       32768
SF                75.4676811 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40

1D NMR plot parameters
CX                       20.00 cm
CY                       50.00 cm
F1P                     180.000 ppm
F1                    13584.18 Hz
F2P                       0.000 ppm
F2                        0.00 Hz
PPMCM                 9.00000 ppm/cm
HZCM                  679.20911 Hz/cm
```

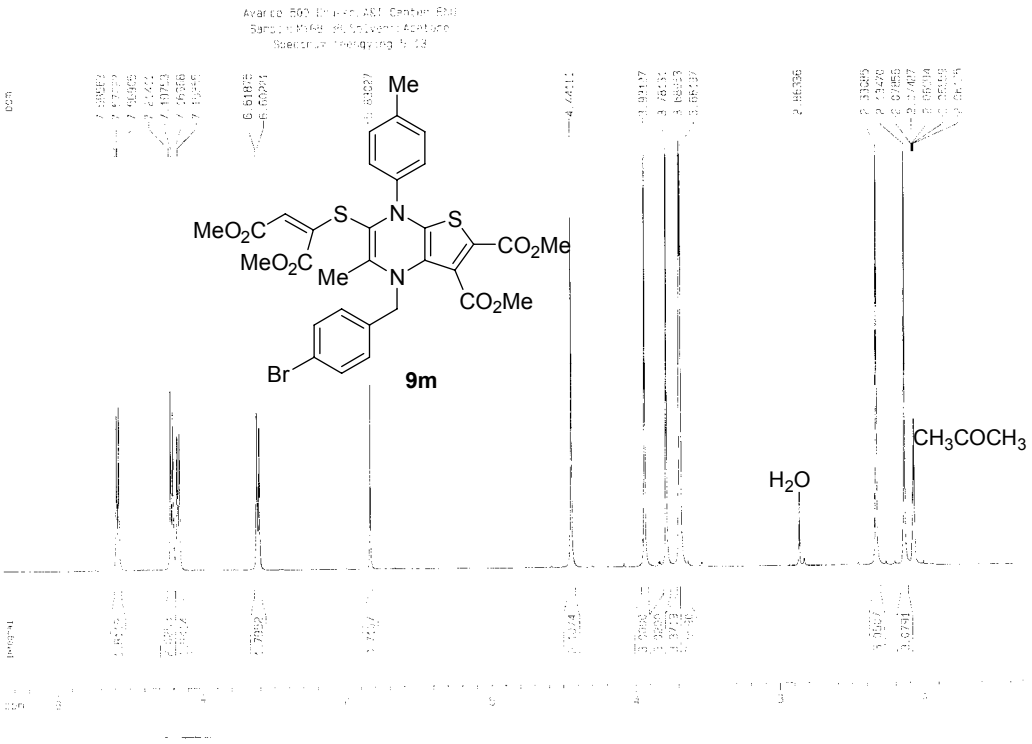


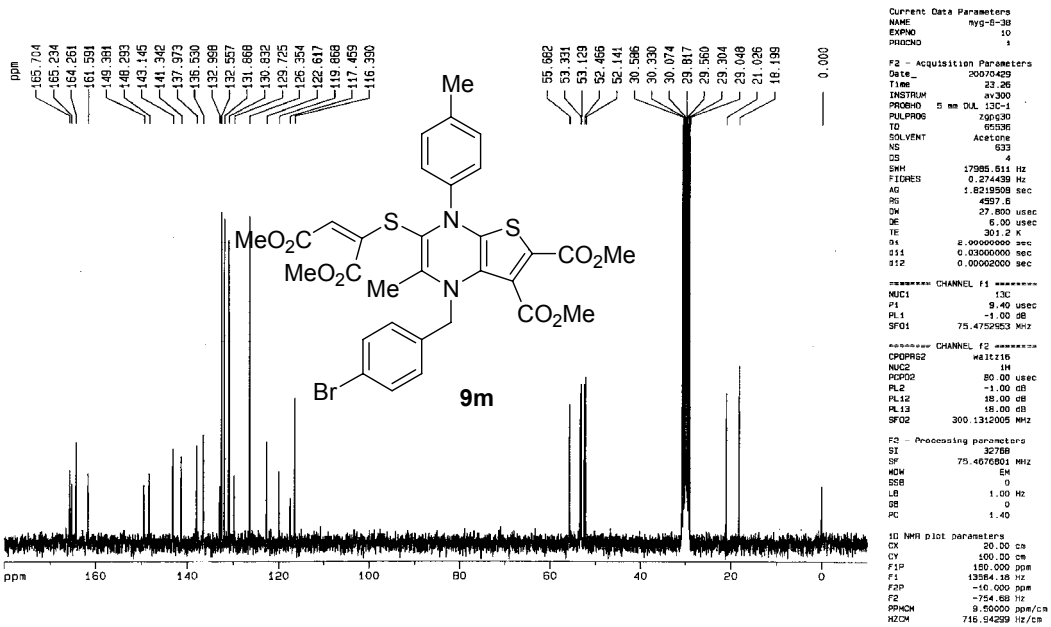



```
Current Data Parameters
NAME                  myg8-33
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_              20070430
Time                    1.43
INSTRUM                 av300
PROBHD   5 mm DUL 13C-1
PULPROG                 zgpg30
TD                      65536
SOLVENT                 Acetone
NS                        153
DS                          4
SWH                 17985.611 Hz
FIDRES                0.274439 Hz
AQ                    1.8219508 sec
RG                       7298.2
DW                       27.800 usec
DE                        6.00 usec
TE                       302.0 K
D1                    2.00000000 sec
d11                   0.03000000 sec
d12                   0.00002000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                        9.40 usec
PL1                      -1.00 dB
SFO1                75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                    80.00 usec
PL2                      -1.00 dB
PL12                     18.00 dB
PL13                     18.00 dB
SFO2               300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                  75.4676811 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                       20.00 cm
CY                       40.00 cm
F1P                     180.000 ppm
F1                    13584.18 Hz
F2P                      0.000 ppm
F2                       0.00 Hz
PPMCM                 9.00000 ppm/cm
HZCM                679.20911 Hz/cm
```

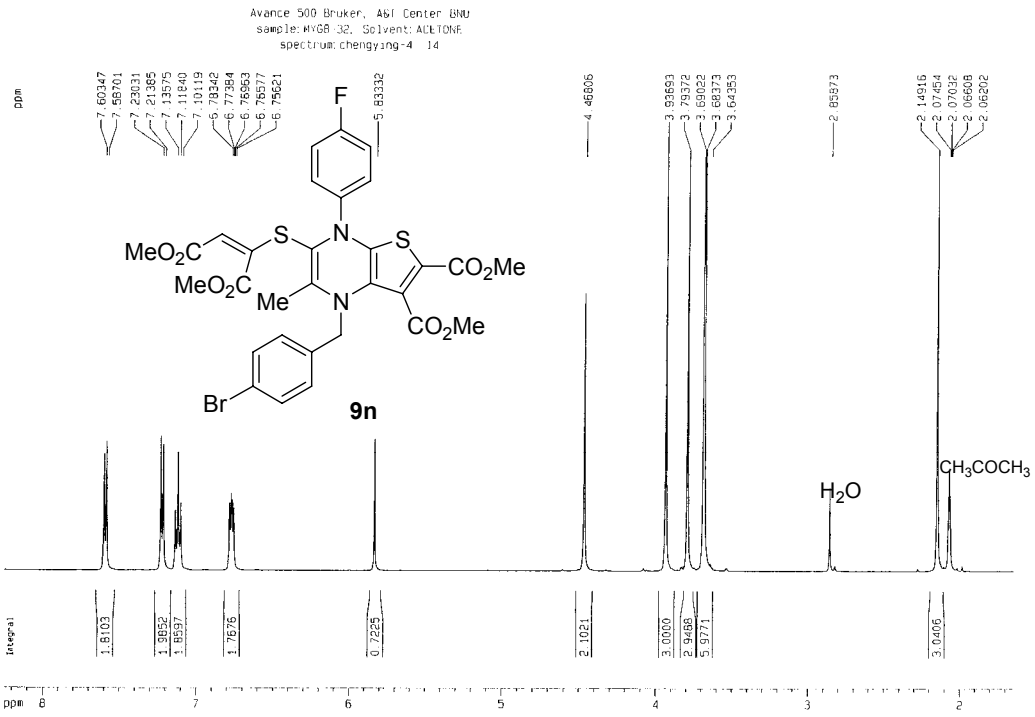

Avance DRX 500 Bruker, A&T Center BNU
Sample: JXP7-22, Solvent: Acetone
Spectrum: chengying 06-29
ppm
7.64342
7.62650
7.08675
7.06992
7.02486
7.00892
6.99430
6.97834
5.87975
4.57208
3.94166
3.86110
3.84623
3.65854
3.61977
2.85597
2.23862
2.22753
2.06982
CF3
MeO2C
MeO2C
S
N
S
CO2Me
Me
N
CO2Me
Me
9l
H2O
CH3COCH3
Integral
1.8720
1.8027
3.8031
0.6964
2.0859
2.9899
3.0000
2.9247
3.0521
5.9972
ppm

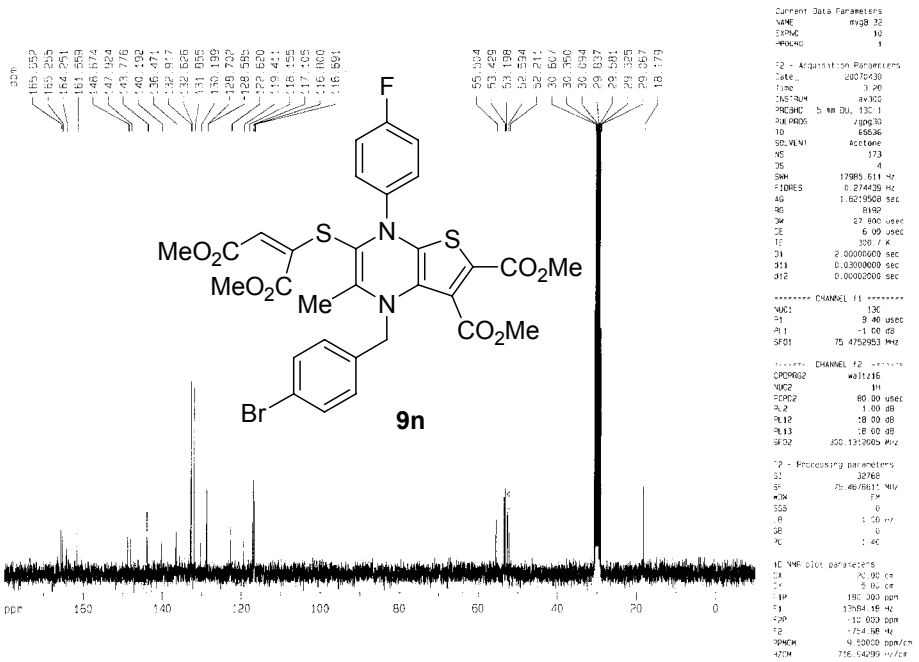

ppm
CF3
MeO2C
MeO2C
S
N
S
CO2Me
Me
N
CO2Me
Me
9l
ppm

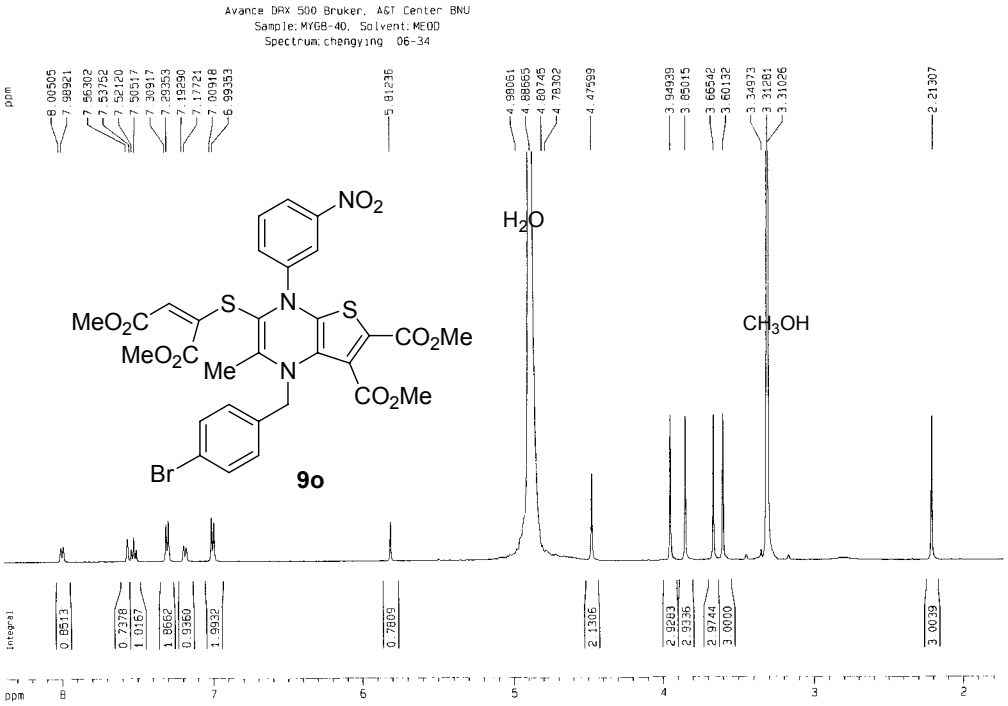


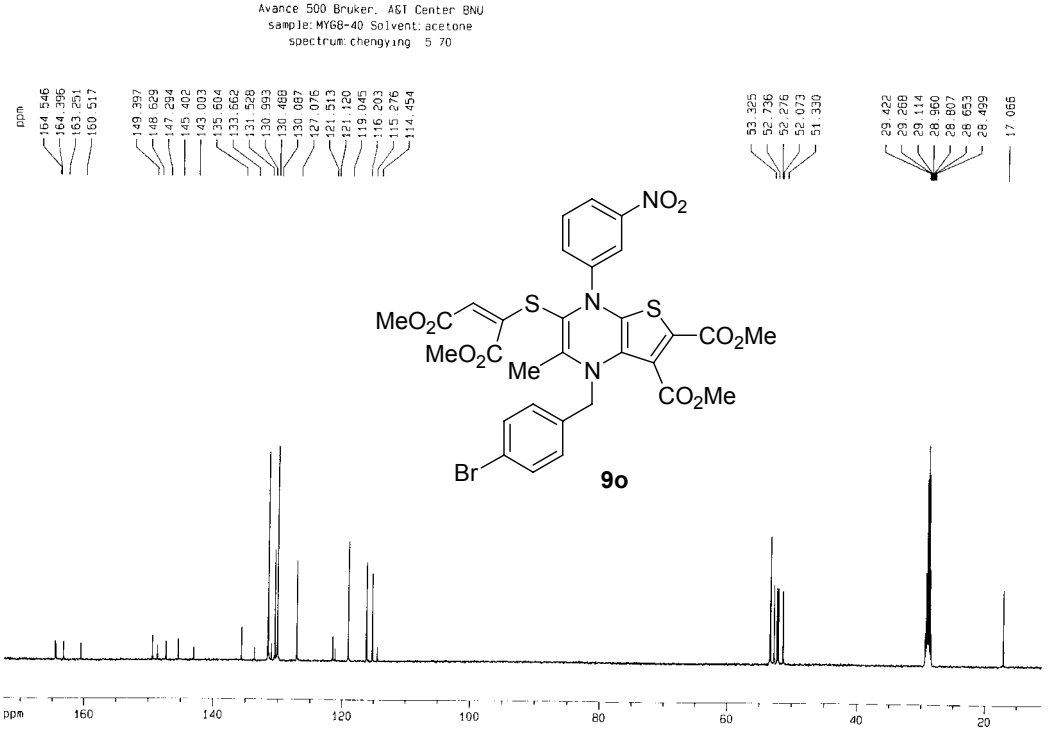


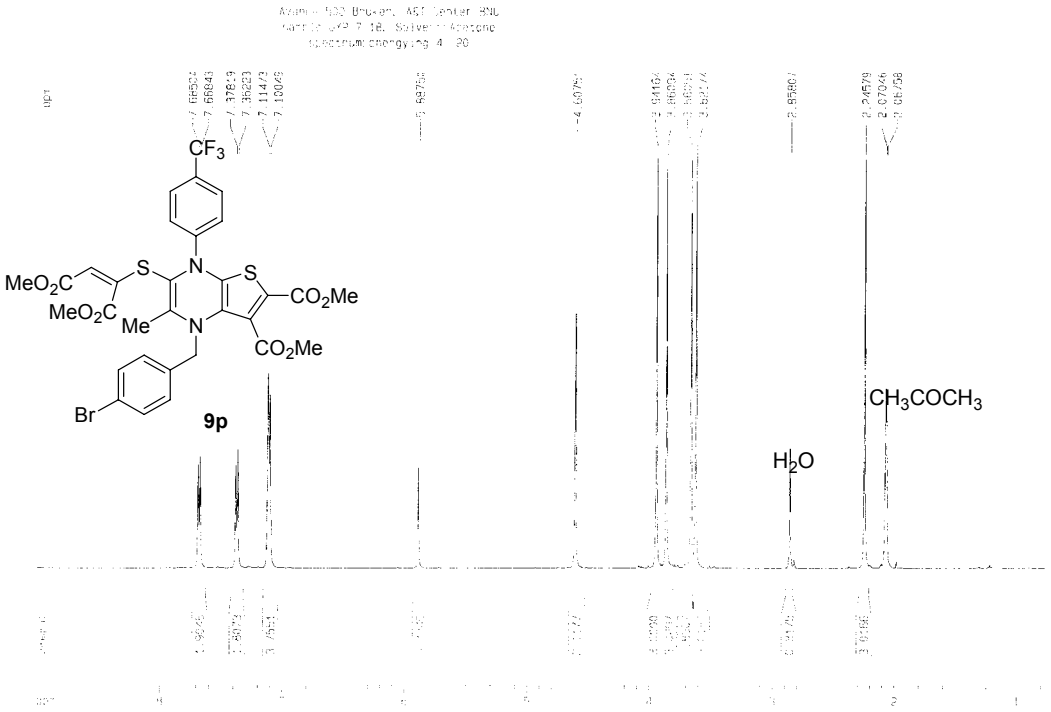

```
Current Data Parameters
NAME                  nyg-6-3B
EXPNO                       10
PROCNO                       1

F2 - Acquisition Parameters
Date_              20070429
Time                    23.26
INSTRUM                 av300
PROBHD   5 mm DUL 13C-1
PULPROG                 zgpg30
TD                       65536
SOLVENT                 Acetone
NS                          533
DS                            4
SWH                 17985.611 Hz
FIDRES                0.274439 Hz
AQ                    1.8219509 sec
RG                       4597.6
DW                      27.800 usec
DE                       6.00 usec
TE                      301.2 K
D1                    2.00000000 sec
D11                   0.03000000 sec
D12                   0.00002000 sec

======== CHANNEL f1 ========
NUC1                       13C
P1                        9.40 usec
PL1                      -1.00 dB
SF01                75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                    80.00 usec
PL2                      -1.00 dB
PL12                     18.00 dB
PL13                     18.00 dB
SF02               300.1312005 MHz

F2 - Processing parameters
SI                         32768
SF                  75.4676801 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                      20.00 cm
CY                     100.00 cm
F1P                   160.000 ppm
F1                  13584.18 Hz
F2P                   -10.000 ppm
F2                   -754.68 Hz
PPMCM                 9.50000 ppm/cm
HZCM                716.94299 Hz/cm
```

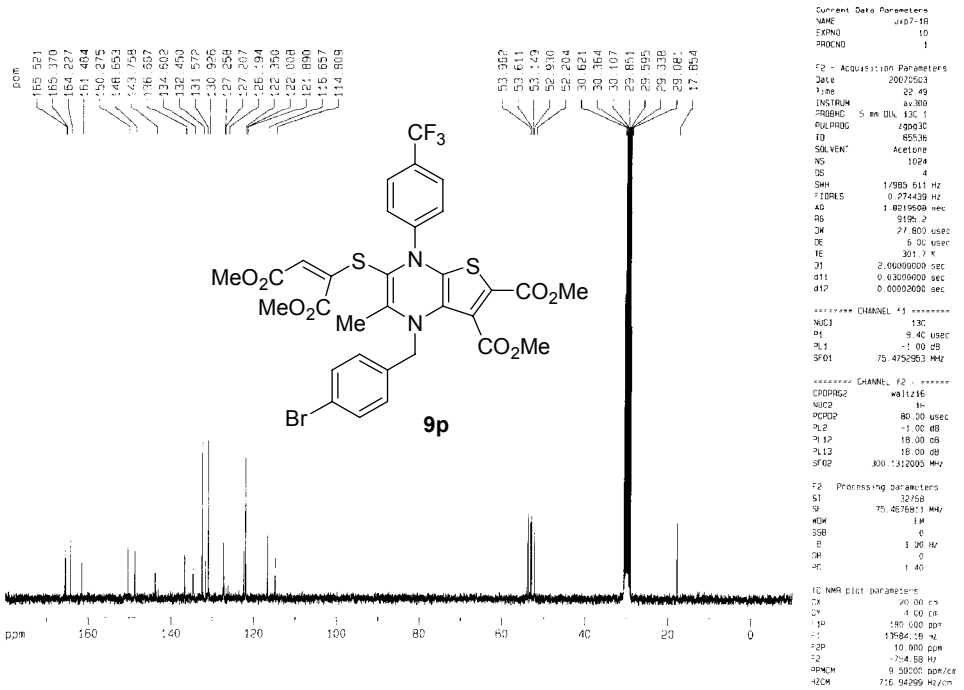

Avance 500 Bruker, A&T Center BNU
sample: MYGB-32, Solvent: ACETONE
spectrum: chengying-4 14
9n
H2O
CH3COCH3


9n


Avance DRX 500 Bruker, A&T Center BNU
Sample: MYG8-40, Solvent: MEOD
Spectrum: chengying 06-34
ppm
8.00505
7.98921
7.96302
7.53752
7.52120
7.50517
7.30917
7.28353
7.19290
7.17721
7.00918
6.99353
5.81236
4.98061
4.88665
4.80745
4.78302
4.47599
3.94939
3.85015
3.66542
3.60132
3.34973
3.31281
3.31026
2.21307
H2O
CH3OH
NO2
MeO2C
MeO2C
S
N
S
CO2Me
Me
N
CO2Me
Br
9o
integral
0.8513
0.7378
1.0167
1.8662
0.9360
1.9932
0.7809
2.1306
2.9263
2.9336
2.9744
3.0000
3.0039
ppm


Avance 500 Bruker, A&T Center BNU
sample: MYG8-40 Solvent: acetone
spectrum: chengying 5 70
ppm
164.546
164.396
163.251
160.517
149.397
148.629
147.294
145.402
143.003
135.604
133.662
131.528
130.993
130.488
130.087
127.076
121.513
121.120
119.045
116.293
115.276
114.454
53.325
52.736
52.276
52.073
51.330
29.422
29.268
29.114
28.960
28.807
28.653
28.499
17.066
NO2
MeO2C
MeO2C
S
N
S
CO2Me
Me
N
CO2Me
Br
9o
ppm


CF3
MeO2C
MeO2C
Me
S
N
S
N
CO2Me
CO2Me
Br
9p
H2O
CH3COCH3


CF3
MeO2C
MeO2C
Me
S
N
S
N
CO2Me
CO2Me
Br
9p
ppm
160
140
120
100
80
60
40
20
0