Supporting Information for

One-Pot Syntheses of 2,3-Dihydrothiopyran-4-one Derivatives by Pd/Cu-Catalyzed Reactions of α,β-Unsaturated Thioesters with Propargyl Alcohols

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General Comments: ^{1}H and ^{13}C NMR spectra in $CDCl_3$, and DMF-d_8 solution were recorded with JEOL JNM-Alice 400 (400 MHz) spectrometers. The chemical shifts in the ^{1}H NMR spectra were recorded relative to Me_4Si as an internal standard and the chemical shifts in the ^{13}C NMR spectra were recorded relative to $CHCl_3$ (δ 77.0). The IR spectra was measured by a Perkin-Elmer Model 1600 spectrometer. Mass spectra (EI), High-resolution mass spectra (HRMS) and elemental analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Melting points were measured by a MPA100 Optimelt Automated Melting Point System. Preparative TLC was carried out using Wakogel B-5F silica gel. The X-ray crystal data of **3a** were collected using Rigaku RAXIS-RAPID Imaging Plate diffractometer. The ORTEP diagram was shown in 50% probability ellipsoid. All reactions were carried out under N_2 atmosphere. All solvents were distilled before use. Thioesters **1a-d**, **1f** were prepared from the reactions of the corresponding acid chlorides with thiols in the presence of pyridine in THF solution. Thioester **1e** was synthesized according to the literature (*Tetrahedron Lett.* **2001**, *42*, 1567).

The Spectrum Datas of thioesters:

H_2C=C(Me)C(O)$SC_6H_4NO_2$-p (1a); registry number 893445-27-7.

H_2C=C(*i*-Pr)C(O)$SC_6H_4NO_2$-*p* (1b); registry number 893445-29-9.

(*E*)-PhC(H)=CHC(O)$SC_6H_4NO_2$-*p* (1c); registry number 95390-11-7.

(*E*)-Me(H)C=C(Me)C(O)$SC_6H_4NO_2$-*p* (1d): an pale yellow solid; mp 77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (d, 3 H), 1.92 (s, 3 H), 6.98-7.04 (m, 1 H), 7.61 (d, 2 H, *J* = 8.8 Hz), 8.24 (d, 2 H, *J* = 8.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 12.4, 14.8, 123.9, 135.4, 136.7, 137.2, 138.5, 148.1, 189.3; IR (KBr) 3105, 2925, 2845, 1673, 1643, 1598, 1578, 1518, 1345, 1220, 1108, 1031, 981, 854, 742, 682, 662, 643 cm^{-1}; mass spectrum (EI) m/z 237 (M^+, 1.6); HRMS calcd for $C_{11}H_{11}OS$ 237.2760, found 237.0458.

H_2C=C(C_6H_4Me-*p*)C(O)SC_6H_4Me-*p* (1e): an pale yellow solid; mp 92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3 H), 2.38 (s, 3 H), 5.83 (s, 1 H), 6.24 (s, 1 H), 7.17 (d, 2 H, *J* = 8.1 Hz), 7.23 (d, 2 H, *J* = 8.3 Hz), 7.32-7.35 (m, 4 H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 21.5, 21.6, 122.7, 124.7, 128.4, 129.2, 130.3, 133.1, 134.8, 138.9, 139.9, 148.0, 192.5; IR (KBr) 3026, 2918, 1684, 1605, 1510, 1397, 1296, 1110, 963, 925, 824, 807, 750, 731, 554, 484 cm^{-1}; mass spectrum (EI) m/z 268 (M^+, 12); HRMS calcd for $C_{17}H_{16}OS$ 268.0922, found 268.0924.

(*E*)-PhC(H)=CHC(O)$SC_{10}H_{21}$-*n* (1f): an pale yellow solid; mp 41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3 H, *J* = 6.4 Hz), 1.26-1.40 (m, 15 H), 1.60-1.67 (m, 2 H), 3.01 (t, 2 H, *J* = 7.3 Hz), 6.71 (d, 1 H, *J* = 15.9 Hz), 7.38-7.39 (m, 3 H), 7.53-7.54 (m, 2 H), 7.60 (d, 2 H, *J* = 8.1 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 14.1, 14.2, 22.7, 28.9, 29.0, 29.2, 29.3, 29.6, 29.6, 31.9, 125.2, 128.4, 128.9, 130.4, 134.2, 140.1, 190.0; IR (KBr) 2922, 2848, 1656, 1611, 1468, 1448, 1332, 1302, 1035, 1012, 992, 890, 778, 754, 692, 578, 484, 462 cm^{-1}; mass spectrum (EI) m/z 304 (M^+, 12); HRMS calcd for $C_{19}H_{28}OS$ 304.1861, found 304.1863.

Pd/Cu-Catalyzed Reaction of CH_2=C(Me)C(O)S$C_6H_4NO_2$-*p* (1a) with HC≡CC(Me)$_2$OH (2a) in the presence of Et_3N and K_2CO_3 (run 3 of Table 1); General Procedure of Cyclization of α,β-Unsaturated Thioesters with Propargyl Alcohols: Into a two-neaked 3 mL reaction glass were added $PdCl_2$ (0.7 mg, 4 x 10^{-3} mmol), CuI (7.5 mg, 3.9 x 10^{-2} mmol), K_2CO_3 (6.1 mg, 4.4 x 10^{-2} mmol), **1a** (89.5 mg, 0.401 mmol), **2a** (50 μL, 0.52 mmol), Et_3N (60 μL, 0.43 mmol) and 0.5 mL of DMF under N_2 atmosphere. After the solution was stirred for 6 h at 80 ^oC, the reaction mixture was separated by preparative TLC using hexane and Et_2O (10/7) as an eluent (74.5 mg, 60%).

2,3-dihydro-3-methyl-6-(dimethyl-*p*-nitrophenoxy-methyl)-thiopyran-4-one (3a): an yellow solid; mp 111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (d, 3 H, *J* = 6.8 Hz), 1.72 (s, 6 H), 2.62-2.68 (m, 1 H), 3.02 (dd, 1 H, *J* = 13, 11 Hz), 3.19 (dd, 1 H, *J* = 13, 3.9 Hz), 6.28 (s, 1 H), 6.94 (d, 2 H, *J* = 9.3 Hz), 8.14 (d, 2 H, *J* = 9.3 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 14.30, 27.61, 28.34, 33.64, 39.53, 81.80, 118.0, 119.4, 125,2, 141.7, 160.3, 166.6, 196.6; IR (KBr) 2983, 2965, 2927, 1665, 1588, 1508, 1488, 1345, 1249, 1186, 1143, 949, 924, 867, 852, 752, 672 cm^{-1}; mass spectrum (EI) m/z 307 (M^+, 21); Anal. Calcd for $C_{15}H_{17}NO_4S$: C, 58.61; H, 5.57, N, 4.56, S, 10.43. Found: C, 58.32; H, 5.29, N, 4.53, S, 10.44. Other cyclic products **3b-3e**, **3g-3j** were similarly synthesized. Samples of **3d**, **3e**, **3i** and **3j** obtained after preparative TLC were a mixture of *threo* and *erythro*.

2,3-dihydro-3-methyl-6-(1'-*p*-nitrophenoxy-cyclopentyl)-thiopyran-4-one (3b): an yellow solid; mp 89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (d, 3 H, *J* = 5.2 Hz), 1.83 (m, 4 h), 2.17-2.25 (m, 4 H), 2.61-2.63 (m, 1 H), 2.98-3.18 (m, 2 H), 6.28 (s, 1 H), 6.88 (d, 2 H, *J* = 7.1 Hz), 8.13 (d, 2 H, *J* = 7.1 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 14.1, 24.2, 24.3, 33.6, 38.59, 39.56, 91.76, 117.2, 119.0, 125,3, 141.4, 160.2, 164.9, 196.6; IR (KBr) 3294, 2968, 2934, 2871, 1657, 1607, 1586, 1567, 1508, 1488, 1342, 1331, 1312, 1236, 1196, 1166, 1112, 982, 850, 838, 752, 694, 655, 631, 586 cm^{-1}; mass spectrum (EI) m/z 333 (M^+, 12); Anal. Calcd for $C_{17}H_{19}NO_4S$: C, 61.24; H, 5.74, N, 4.20. Found: C, 61.32; H, 5.46, N, 4.09.

2,3-dihydro-3-methyl-6-(1'-*p*-nitrophenoxy-cyclohexyl)-thiopyran-4-one (3c): an yellow solid; mp 105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (d, 3 H, *J* = 6.8 Hz), 1.56-1.79 (m, 8 H), 2.33 (t, 2 H, *J* = 13 Hz), 2.61-2.67 (m, 1 H), 3.01 (dd, 1 H, *J* = 13, 11 Hz), 3.17 (dd, 1 H, *J* = 13, 3.9 Hz), 6.30 (s, 1 H), 6.97

(d, 2 H, *J* = 9.0 Hz), 8.14 (d, 2 H, *J* = 9.0 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 14.36, 21.29, 25.10, 33.60, 34.36, 35.32, 39.63, 82.73, 117.7, 119.2, 125,2, 141.5, 159.9, 167.0, 196.5; IR (KBr) 3116, 3076, 2936, 2851, 1667, 1605, 1589, 1509, 1491, 1451, 1338, 1239, 1146, 1110, 954, 850, 751, 660, 496 cm^{-1}; mass spectrum (EI) m/z 347 (M^+, 39); HRMS calcd for $C_{18}H_{21}NO_4S$ 347.4297, found 347.1201. Anal. Calcd for $C_{18}H_{21}NO_4S$: C, 62.23; H, 6.09, N, 4.03. Found: C, 61.95; H, 5.91, N, 4.01.

2,3-dihydro-3-methyl-6-(methyl-phenyl-*p*-nitrophenoxy-methyl)-thiopyran-4-one (3d): The title compound was obtained as a mixture of inseparable diastereomers (51:49); an yellow solid; mp 111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (d, 1.5 H, *J* = 6.8 Hz), 1.23 (d, 1.5 H, *J* = 6.8 Hz),* 2.02 (s, 3 H), 2.59-2.65 (m, 1 H), 2.91-3.00 (m, 1 H), 3.02 (dd, 0.5 H, *J* = 13, 4.2 Hz), 3.13 (dd, 0.5 H, *J* = 13, 3.9 Hz),* 6.33 (s, 0.5 H), 6.44 (s, 0.5 H),* 6.89 (d, 2 H, *J* = 9.3 Hz), 7.37-7.43 (m, 3 H), 7.51 (d, 2 H, *J* = 7.6 Hz), 8.06(8.07) (d, 2 H, *J* = 9.3 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 14.21(14.25), 24.08(24.35), 33.92(33.94), 39.67(39.81), 85.04(85.14), 119.0(119.1), 120.3(120.5), 125,3, 125.9(125.9), 128.7(128.8), 128.9, 141.2(141.5), 142.3, 160.1, 167.3(167.3), 197.2; IR (KBr) 2973, 2932, 1668, 1606, 1590, 1509, 1490, 1446, 1344, 1244, 1169, 1112, 1069, 1032, 989, 921, 862, 850, 764, 751, 698, 676, 578, 494 cm^{-1}; mass spectrum (EI) m/z 369 (M^+, 4.0); Anal. Calcd for $C_{20}H_{19}NO_4S$: C, 65.02; H, 5.18, N, 3.79. Found: C, 64.74; H, 5.04, N, 3.65. * Minor diastereomer

2,3-dihydro-3-methyl-6-(*n*-pentyl-*p*-nitrophenoxy-methyl)-thiopyran-4-one (3e): The title compound was obtained as a mixture of inseparable diastereomers (51:49); an yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88-0.92 (m, 3 H), 1.19-1.22 (m, 3 H), 1.32-1.55 (m, 6 H), 1.90-2.02 (m, 2 H), 2.59-2.63 (m, 1 H), 2.97-3.07 (m, 1 H), 3.12-3.22 (m, 1 H), 4.71-4.77 (m, 1 H), 6.21 (s, 0.5 H),* 6.23 (s, 0.5 H), 6.94 (d, 1 H, *J* = 9.3 Hz),* 6.96 (d, 1 H, *J* = 9.3 Hz), 8.17 (d, 1 H, *J* = 9.3 Hz),* 8.18 (d, 1 H, *J* = 9.3 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 14.1, 14.4(14.4), 22.5, 25.1(25.2), 31.4(31.4), 33.4(33.7), 36.0(36.1), 39.8(40.2), 80.3(80.6), 115.2, 119.9(119.9), 125,7(125.7), 141.8(141.8), 161.2(161.3), 162.1, 196.0(196.1); IR (NaCl) 2995, 2930, 2860, 1666, 1609, 1591, 1514, 1494, 1456, 1344, 1252, 1174, 112, 1011, 846, 752, 689, 658 cm^{-1}; mass spectrum (EI) m/z 349 (M^+, 87); Anal. Calcd for $C_{18}H_{23}NO_4S$: C, 61.87; H, 6.63, N, 4.01. Found: C, 61.60; H, 6.46, N, 3.75. * Minor diastereomer

2,3-dihydro-3-isopropyl-6-(dimethyl-*p*-nitrophenoxy-methyl)-thiopyran-4-one (3g): an pale yellow solid; mp 127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (d, 3 H, *J* = 6.8 Hz), 0.97 (d, 2 H, *J* = 6.8 Hz), 1.71 (s, 6 H), 2.22-2.26 (m, 1 H), 2.35-2.43 (m, 1 H), 3.13 (dd, 1 H, *J* = 8.8, 3.4 Hz), 3.25 (dd, 1 H, *J* = 14, 3.6 Hz), 6.24 (s, 1 H), 6.93 (d, 2 H, *J* = 9.3 Hz), 8.13 (d, 2 H, *J* = 9.3 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 19.4, 20.3, 25.2, 27.7, 28.0, 28.9, 50.4, 81.8, 118.1, 119.9, 125,3, 141.9, 160.6, 166.3, 196.1; IR (KBr) 2957, 2360, 1660, 1586, 1507, 1489, 1340, 1247, 1139, 1110, 851, 752, 670 cm^{-1}; mass spectrum (EI) m/z 335 (M^+, 25); Anal. Calcd for $C_{17}H_{21}NO_4S$: C, 60.87; H, 6.31, N, 4.18. Found: C, 60.74; H, 6.12, N, 4.46.

2-phenyl-2,3-dihydro-6-(dimethyl-*p*-nitrophenoxy-methyl)-thiopyran-4-one (3h): an yellow solid; mp 92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (s, 6 H), 2.95 (dd, 1 H, *J* = 17, 3.4 Hz), 3.08 (dd, 1 H, *J* = 17, 13 Hz), 4.62 (dd, 1 H), 6.40 (s, 1 H), 6.91 (d, 2 H, *J* = 9.3 Hz), 7.34-7.37 (m, 5 H), 8.00 (d, 2 H, *J* = 9.3 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 27.4, 28.2, 43.6, 46.3, 81.8, 118.3, 120.0, 125.3, 127.4, 128.6, 128.9, 137.3, 141.9, 160.4, 167.3, 194.7; IR (KBr) 3066, 2990, 1659, 1606, 1590, 1565, 1506, 1489, 1454, 1384, 1340, 1296, 1257, 1137, 1108, 929, 891, 856, 751, 725, 698, 670, 495 cm^{-1}; mass spectrum (EI) m/z 369 (M^+, 21); Anal. Calcd for $C_{20}H_{19}NO_4S$: C, 65.02; H, 5.18, N, 3.79. Found: C, 65.09; H, 5.34, N, 3.73.

2,3-dihydro-2,3-dimethyl-6-(dimethyl-*p*-nitrophenoxy-methyl)-thiopyran-4-one (3i): The title compound was obtained as a mixture of inseparable diastereomers (55:45); an yellow solid; mp 84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, 1.4 H, *J* = 7.1 Hz),* 1.25 (d, 1.6 H, *J* = 7.1 Hz), 1.32 (d, 1.4 H, *J* = 7.1 Hz),* 1.42 (d, 1.6 H, *J* = 7.1 Hz), 1.71 (s, 6 H), 2.40-2.46 (m, 0.6 H), 2.67-2.70 (m, 0.4 H),* 3.22-3.28 (m, 0.6 H), 3.58-3.61 (m, 0.4 H),* 6.25 (s, 0.4 H),* 6.26 (s, 0.6 H), 6.94 (d, 0.9 H, *J* = 9.3 Hz),* 6.94 (d, 1.1 H, *J* = 9.3 Hz), 8.13 (d, 2 H, *J* = 9.3 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 9.89(15.2), 13.0(18.9), 27.6(27.9), 27.8(27.9), 41.5(44.8), 42.8(46.5), 81.7(81.7), 118.0(118.0), 118.6(118.8), 125.3, 141.8, 160.1, 164.8(165.8), 197.2(198.1); IR (KBr) 3092, 2988, 2931, 1664, 1607, 1587, 1514, 1489, 1445, 1344, 1251, 1222, 1198, 1185, 1141, 1113, 947, 930, 869, 851, 752, 670, 612, 548, 495 cm^{-1}; mass spectrum (EI) m/z 321 (M^+, 14); Anal. Calcd for $C_{16}H_{19}NO_4S$: C, 59.79; H, 5.96, N, 4.36. Found:

C, 59.51; H, 5.58, N, 4.21. * Minor diastereomer

2,3-dihydro-2,3-dimethyl-6-(1'-*p*-nitrophenoxy-cyclohexyl)-thiopyran-4-one (3j): The title compound was obtained as a mixture of inseparable diastereomers (72:28); an yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, 2.2 H, *J* = 7.1 Hz), 1.24 (d, 0.8 H, *J* = 7.1 Hz),* 1.32 (d, 2.2 H, *J* = 7.1 Hz), 1.42 (d, 0.8 H, *J* = 7.1 Hz),* 1.56-1.80 (m, 8 H), 2.32 (d, 2 H, *J* = 14 Hz), 2.41-2.48 (m, 0.3 H),* 2.67-2.68 (m, 0.7 H),* 3.21-3.25 (m, 0.3 H),* 3.56-3.58 (m, 0.7 H), 6.27 (s, 0.7 H), 6.28 (s, 0.3 H),* 6.96 (d, 1.4 H, *J* = 9.0 Hz), 6.97 (d, 0.6 H, *J* = 9.0 Hz),* 8.13 (d, 2 H, *J* = 9.3 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 9.97(15.3), 13.1(19.0), 21.2, 24.9, 34.5, 34,8, 34.9, 41.5(44.9), 42.8(46.6), 82.8(82.8), 118.0(117.9), 118.6(118.8), 125.4, 141.8, 160.3, 165.4(166.5), 197.3(198.2); IR (NaCl) 2937, 2862, 1660, 1606, 1590, 1514, 1492, 1448, 1341, 1299, 1262, 1241, 1147, 1112, 975, 958, 875, 849, 752, 693, 660 cm^{-1}; mass spectrum (EI) m/z 361 (M^+, 4.0); Anal. Calcd for $C_{19}H_{23}NO_4S$: C, 63.13; H, 6.41, N, 3.88. Found: C, 62.98; H, 6.19, N, 4.15. * Minor diastereomer

The Pd/Cu-catalyzed Reaction of 1a with 2a in DMF-d_7 (Figure 2): Into a dry Pyrex NMR tube were added $PdCl_2$ (4 x 10^{-3} mmol), CuI (4 x 10^{-2} mmol) and K_2CO_3 (4 x 10^{-2} mmol), **1a** (0.4 mmol), **2a** (0.52 mmol), NEt_3 (0.4 mmol), 1,4-dioxane (6.3 x 10^{-2} mmol) as an internal standard and 0.5 mL of DMF-d_7 under N_2 atmosphere. The reaction at 80 ^{o}C was monitored by ^{1}H NMR spectroscopy.

Synthesis of Authentic CH_2=C(Me)C(O)C≡CC(Me)$_2$(OH) (4a):[S1] Into a two-necked reaction vessel were added CH_2=C(Me)C(O)Cl (0.6 mL, 5.3 mmol) (0.6 mL, 5.3 mmol), **2a** (0.4 mL, 4.1 mmol), CuI (2.0 x 10^{-2} mmol), Et_3N (13 mL). After the solution was stirred for 44 h at 25 ^{o}C, the reaction mixture was filtrated through Celite and distilled. The compound **4a** was purified by HPLC (308 mg, 49%).

4a: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 (s, 6 H), 1.85 (s, 3 H), 2.91 (s, 1 H), 6.00 (s, 1 H), 6.38 (s, 1 H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 15.9, 30.6, 65.0, 78.9, 96.6, 131.3, 144.6, 180.1; mass spectrum (EI) m/z 152 (M^+, 3.0); HRMS calcd for $C_{15}H_{17}NO_4S$ 152.0837, found 152.0829.

Reaction of 4a with $HSC_6H_4NO_2$-*p* (6a) (eq 2): Into a two-neaked reaction vessel were added K_2CO_3 (4.4×10^{-2} mmol), **4a** (0.4 mmol), **6a** (0.4 mmol), Et_3N (60 μL, 0.43 mmol) and 0.5 mL of DMF under N_2 atmosphere. After the solution was stirred for 6 h at 80 ^oC, the reaction mixture was filtrated through Celite and distilled under reduced pressure.

Synthesis of Authentic CH_2=C(Me)C(O)C(H)=C(C(Me)$_2$(OH))$SC_6H_4NO_2$-*p* (5a): Into a two-necked reaction vessel were added $PdCl_2$ (4.5 mg, 0.025 mmol), CuI (45 mg, 0.24 mmol), K_2CO_3 (38 mg, 0.28 mmol), **1a** (536 mg, 2.40 mmol), **2a** (300 μL, 3.1 mmol), Et_3N (340 μL, 2.4 mmol), and 0.5 mL of DMF under N_2 atmosphere. After the solution was stirred for 40 min at 80 °C, the resultant mixture was filtrated through Celite and distilled under reduced pressure. The compound **5a** was isolated by preparative TLC using hexane/Et_2O/EtOH (10/7/1) as an eluent (291 mg, 39%).

5a: an yellow solid; mp 89 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.49 (s, 6 H), 1.74 (s, 3 H), 2.13 (s, 1 H), 5.86 (s, 1 H), 5.90 (s, 1 H), 7.36-7.39 (m, 3 H), 8.06 (d, 2 H, J_{H-H} = 8.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ 16.8, 29.2, 31.0, 75.2, 123.9, 127.6, 127.9, 132.9, 144.9, 145.6, 145.7, 148.2, 193.8; NOE experiment: Irradiation of the singlet of homoallylic proton at δ 1.49 resulted in 6.4% enhancement of the signal at δ 7.39 (internal vinyl singlet) and the singlet of terminal *trans*-vinyl proton at δ 5.90 resulted in 2.9% enhancement of the signal at δ 7.39 (internal vinyl singlet); IR (KBr) 3452, 3098, 2977, 1652, 1595, 1575, 1514, 1340, 1182, 1109, 1090, 977, 851, 744, 686, 534, 466 cm^{-1}; mass spectrum (EI) m/z 307 (M^+, 133); Anal. Calcd for $C_{15}H_{17}NO_4S$: C, 58.61; H, 5.57, N, 4.56. Found: C, 58.36; H, 5.32, N, 4.39.

Intramolecular cyclization of 5a (eq 3): Into a two-neaked reaction vessel were added CH_2=C(Me)C(O)-CH=C($SC_6H_4NO_2$-*p*)C(Me)$_2$(OH) (**5a**) (0.2 mmol), Et_3N (30 μL, 0.21 mmol) and 0.25 mL of DMF under N_2 atmosphere. After the solution was stirred for 6 h at 80 ^oC, the reaction mixture was filtrated through Celite, and distilled under reduced pressure.

ORTEP Diagram of 3a: Space group monoclinic, $P2_1/a$(#14) with a = 11.1771(4) Å, b = 14.9463(5) Å, c = 11.0961(6) Å, β = 1212.578(1) °, Z = 4, ρ = 1.307 g/cm^3, R = 0.074, and R_w = 0.184.

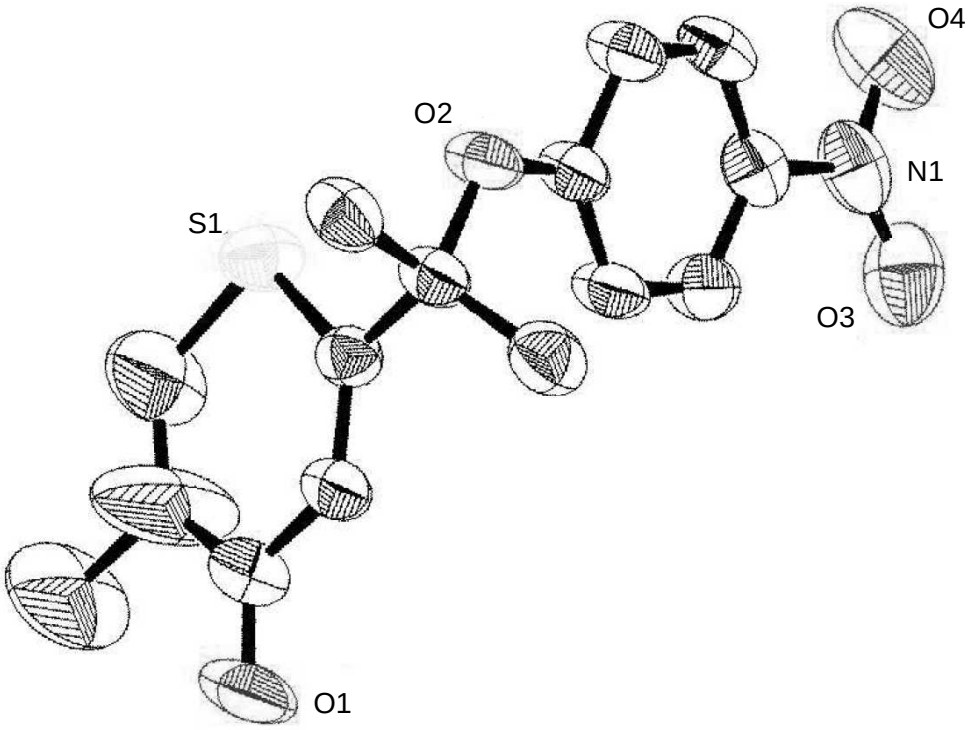
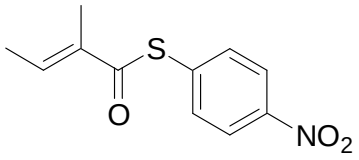


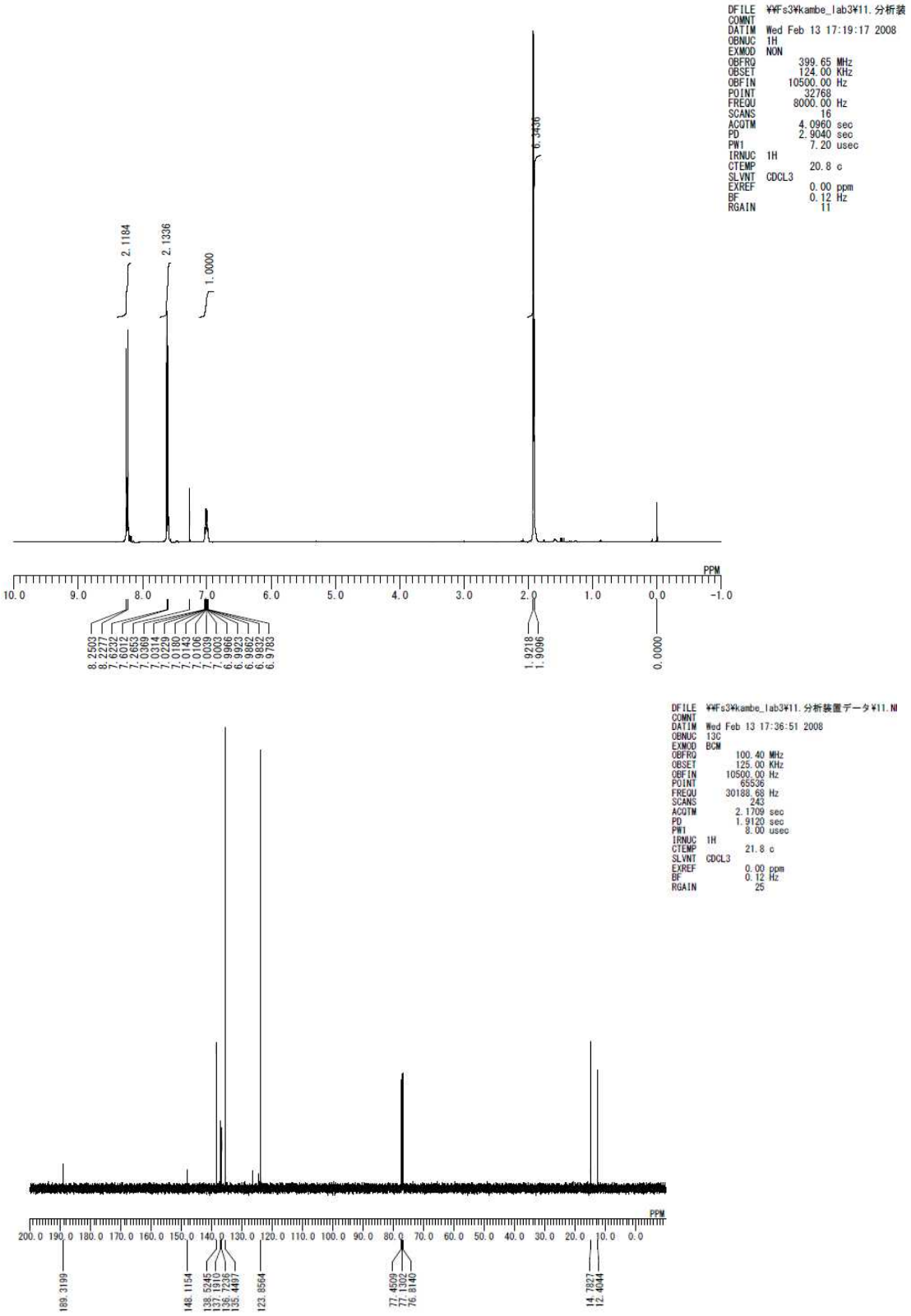
Figure 1S. Molecular structure of **3a**.

References

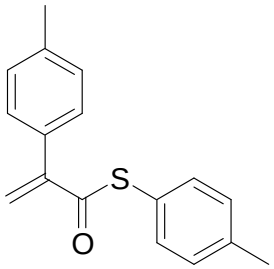
S1) Chowdhury, C.; Kundu, N. G. *Tetrahedron* **1999**, *55*, 7011.



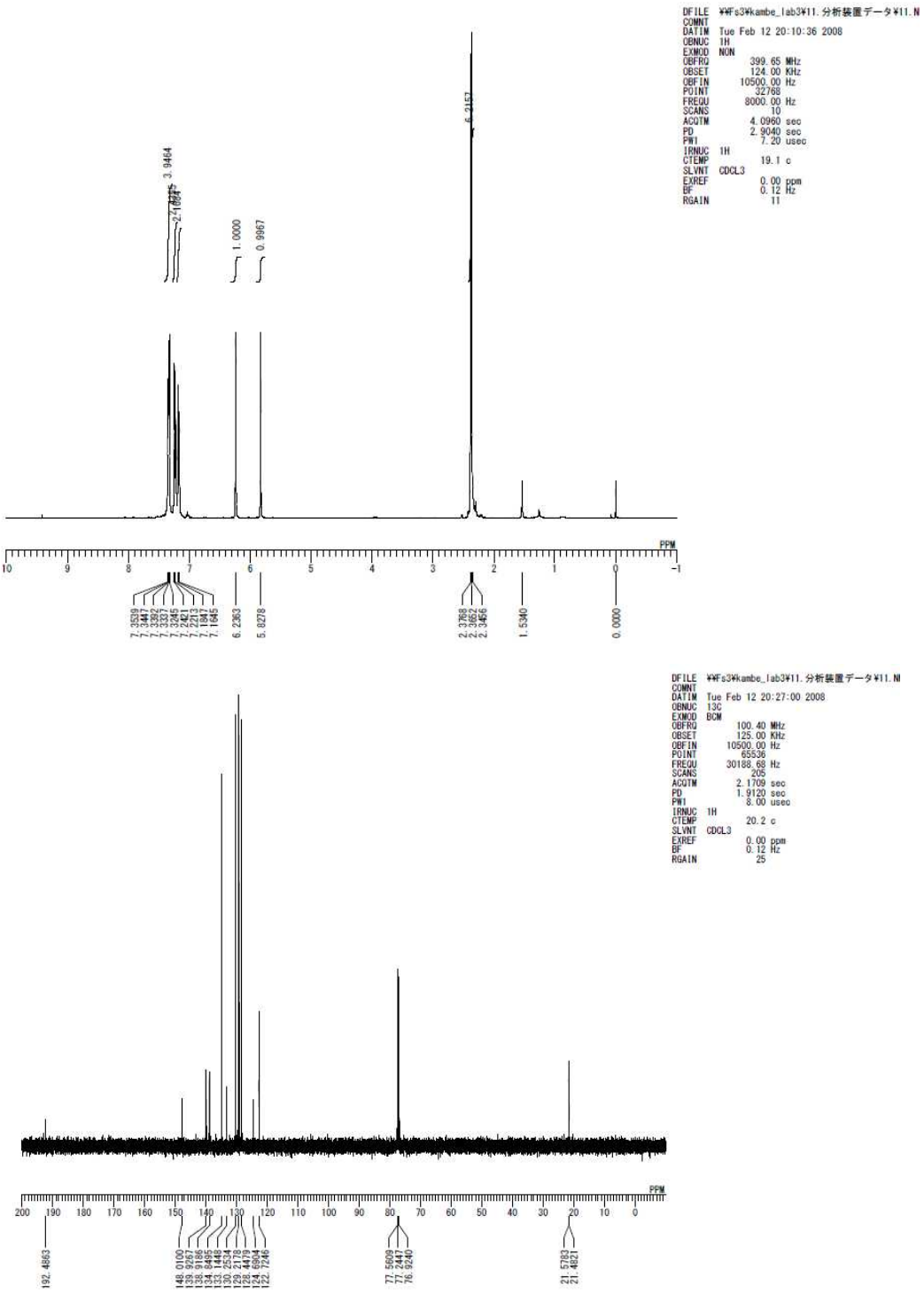
1d



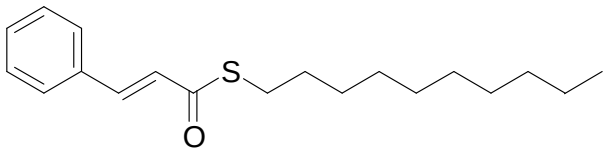
^{1}H and ^{13}C NMR spectrum for **1d**



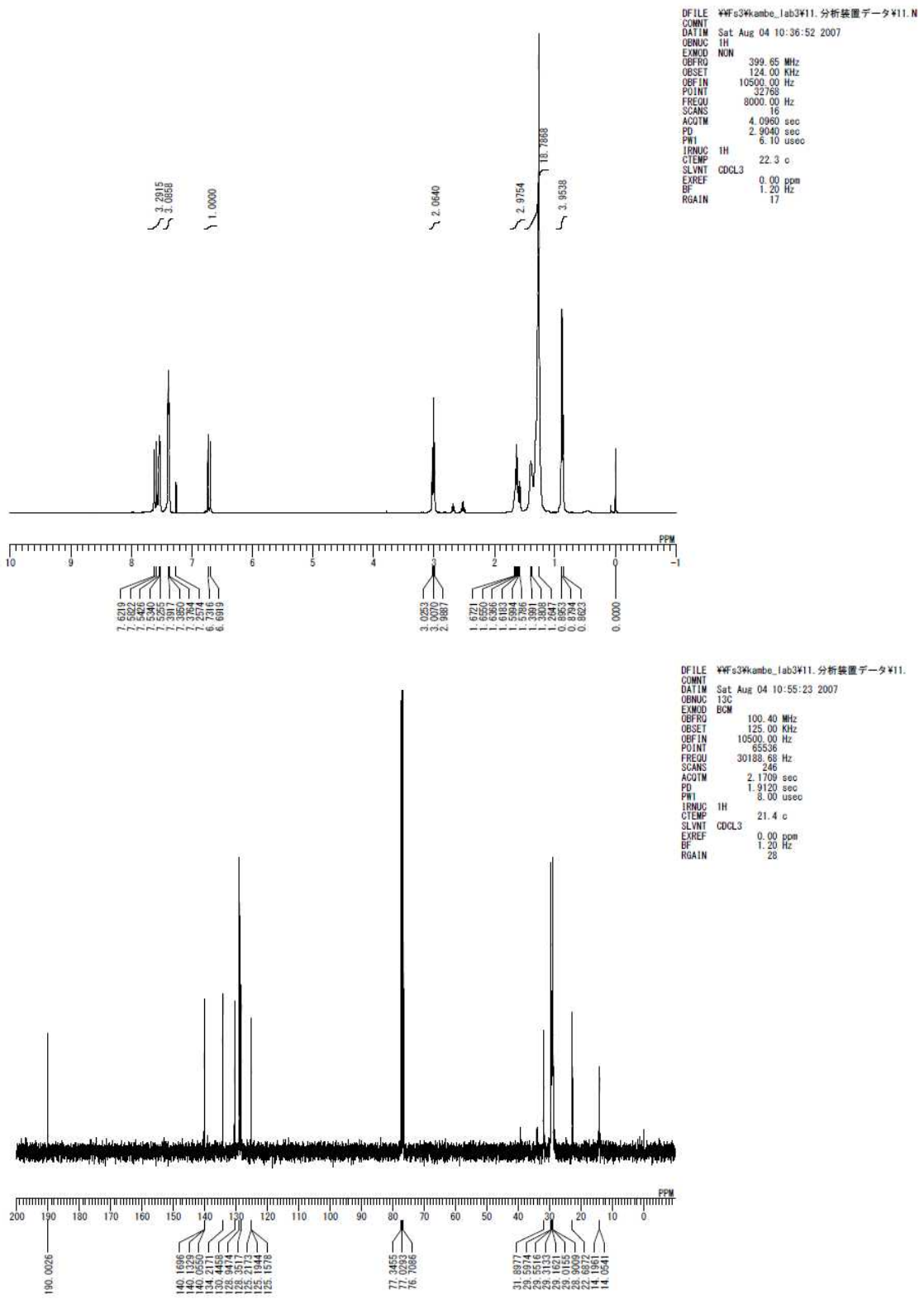
1e



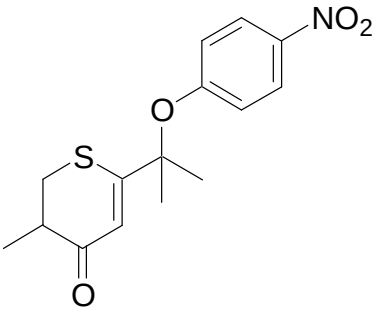
^{1}H and ^{13}C NMR spectrum for **1e**



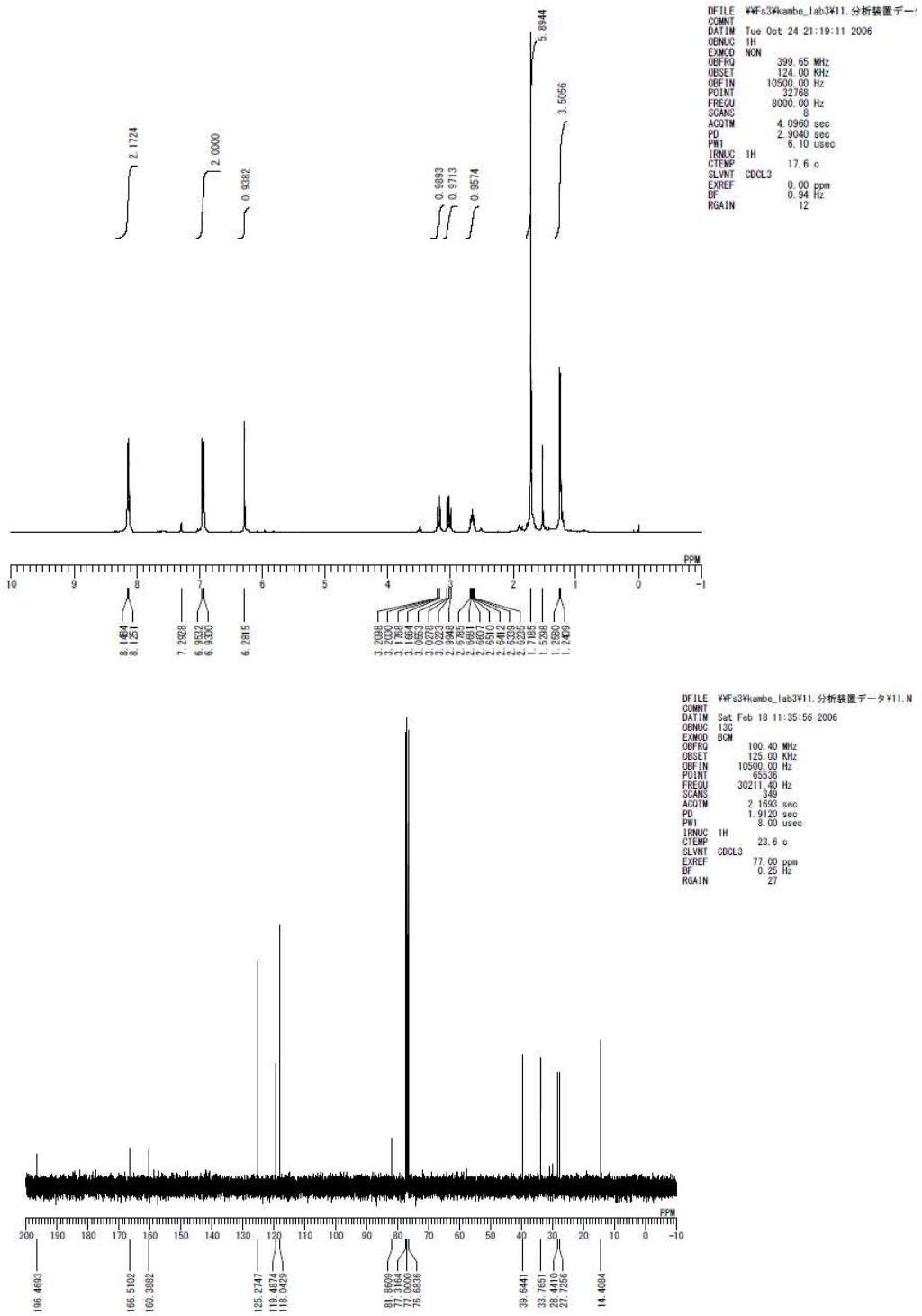
1f



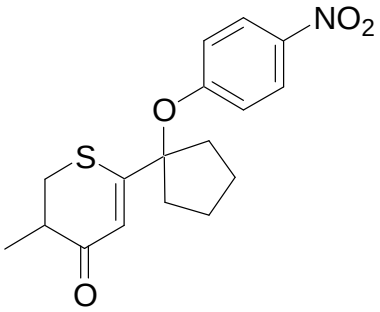
^{1}H and ^{13}C NMR spectrum for **1f**



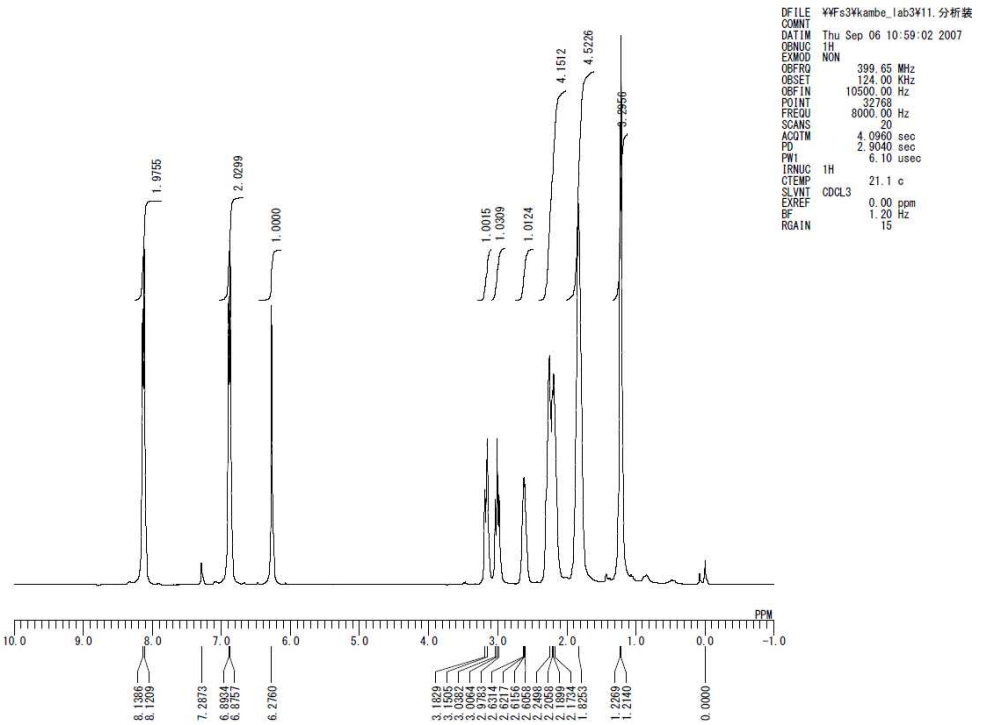
3a

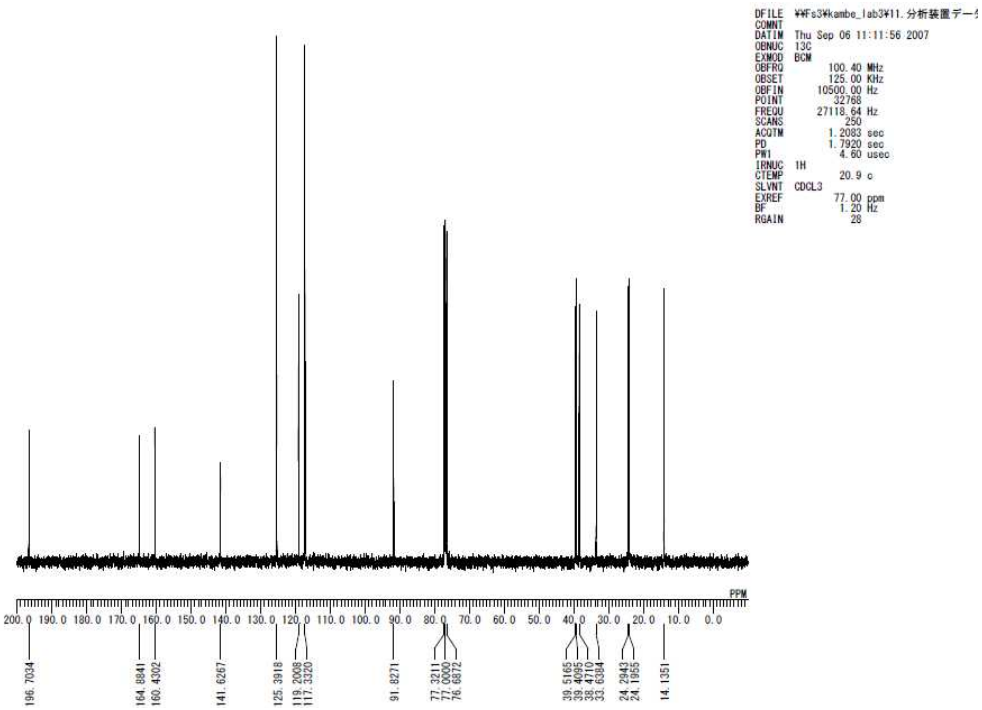


^{1}H and ^{13}C NMR spectrum for **3a**

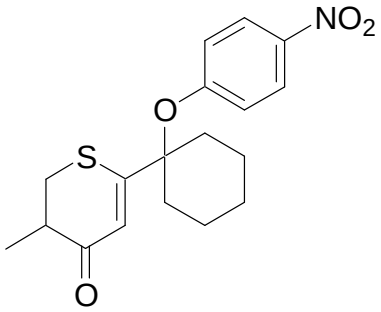


3b

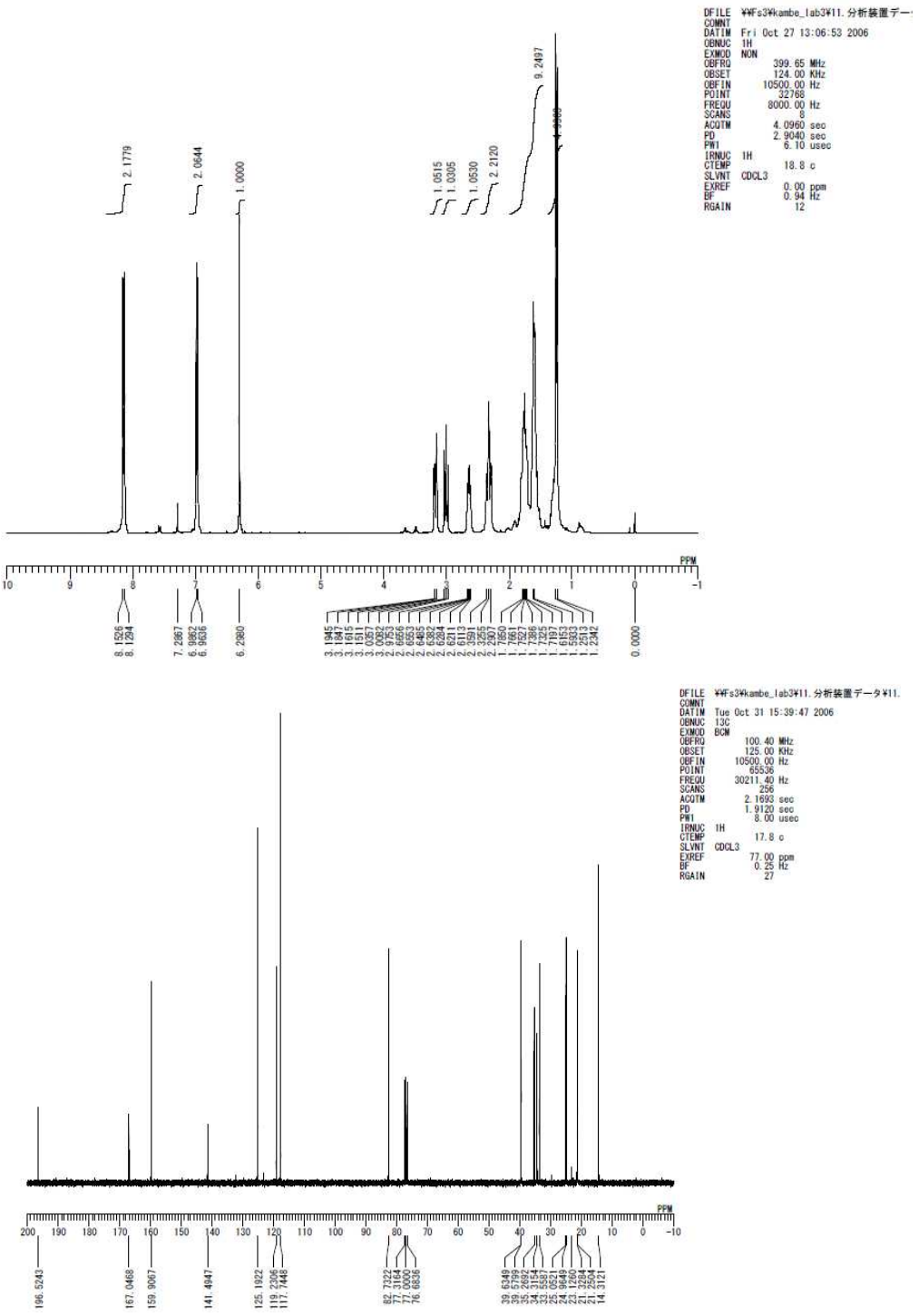




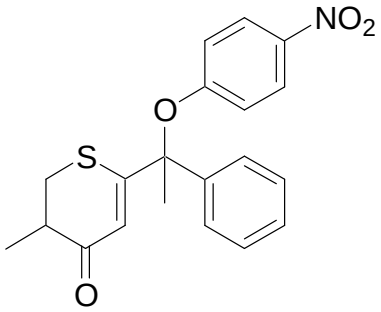
^{1}H and ^{13}C NMR spectrum for **3b**



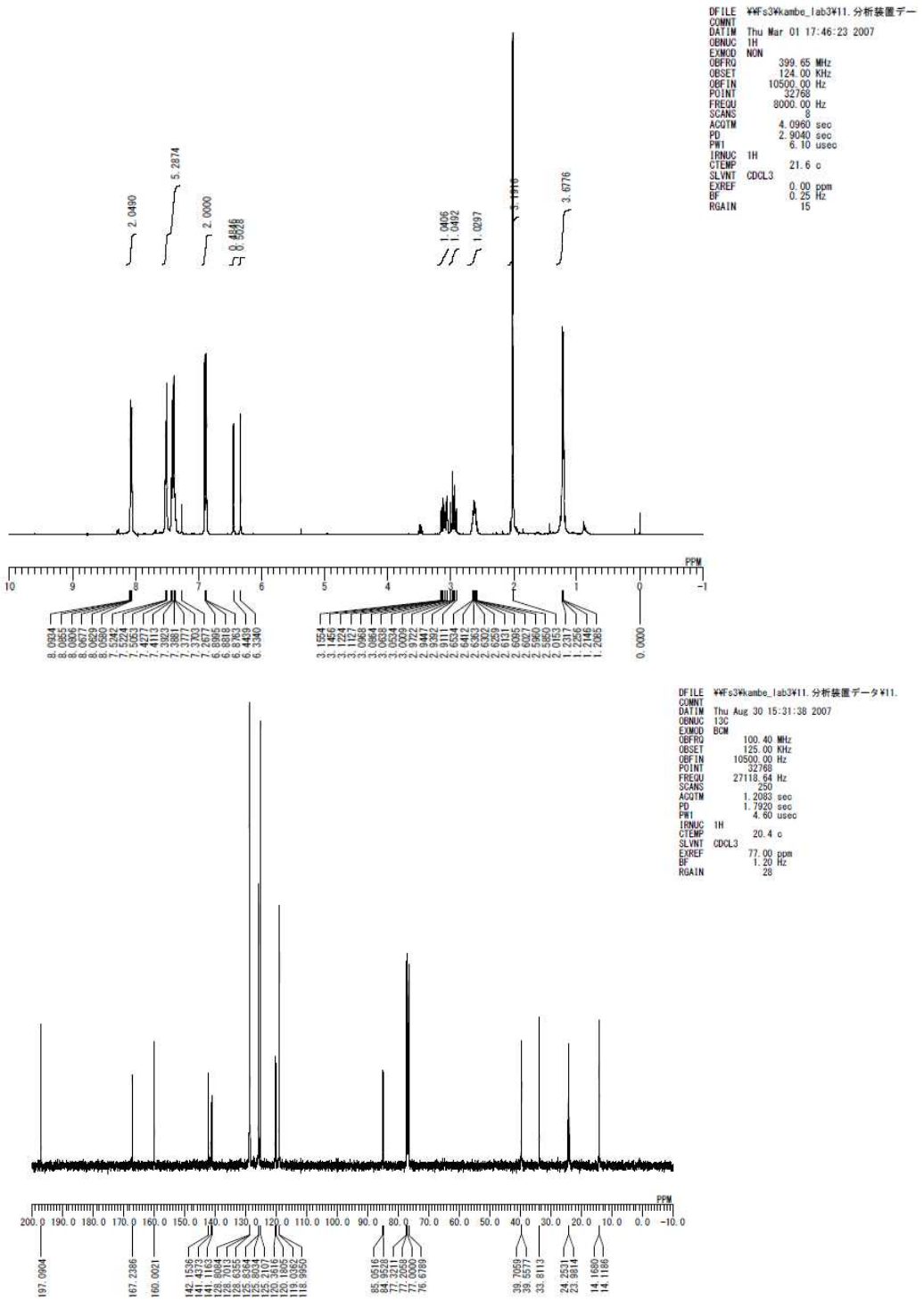
3c



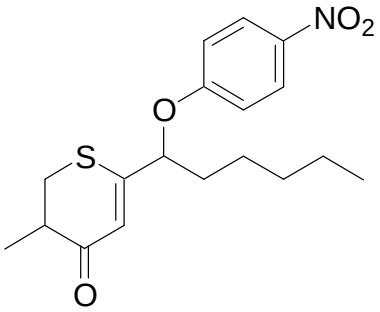
^{1}H and ^{13}C NMR spectrum for **3c**



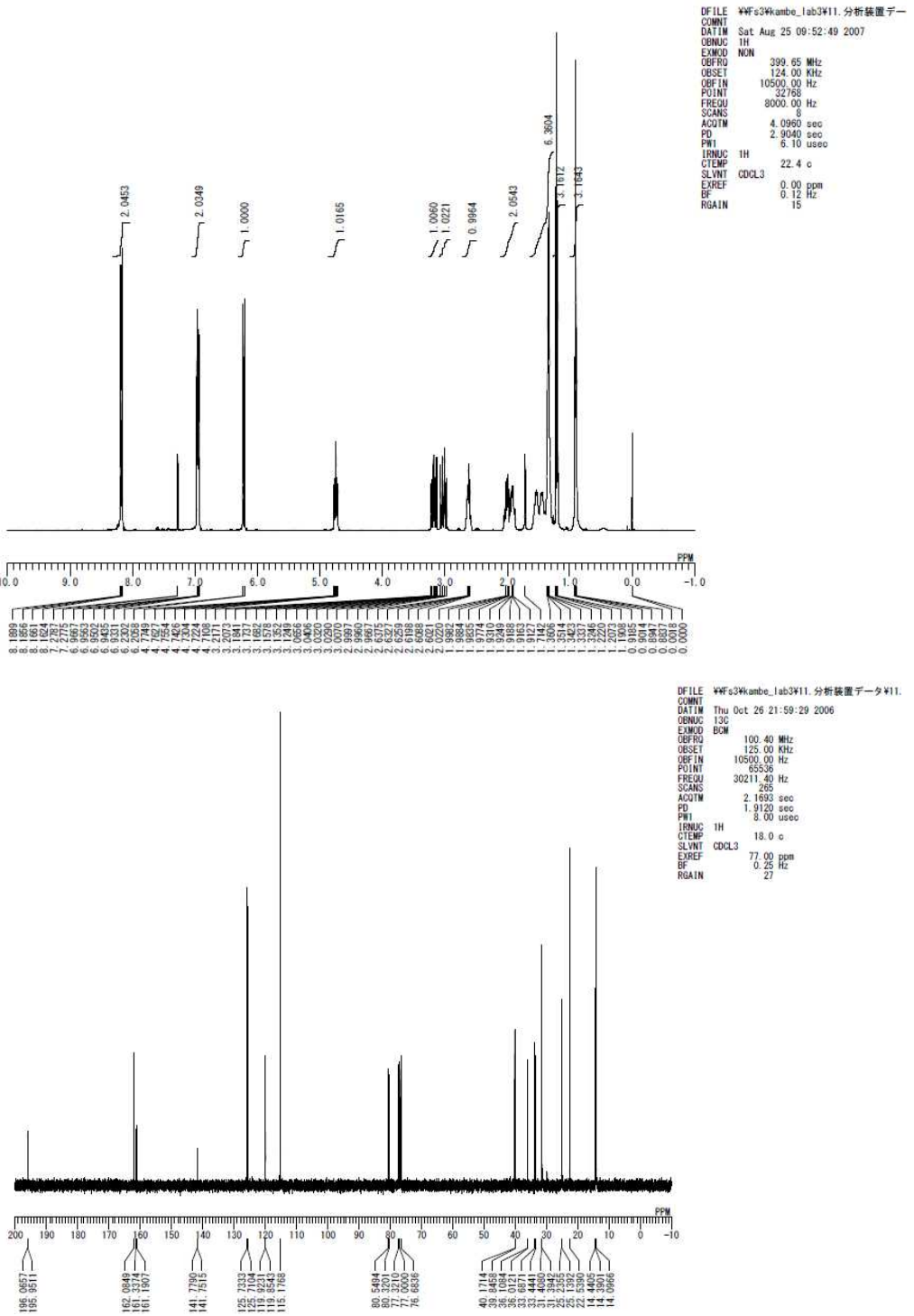
3d



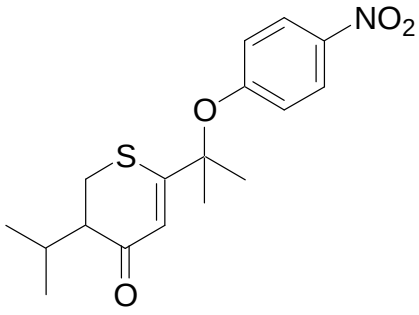
^{1}H and ^{13}C NMR spectrum for **3d**



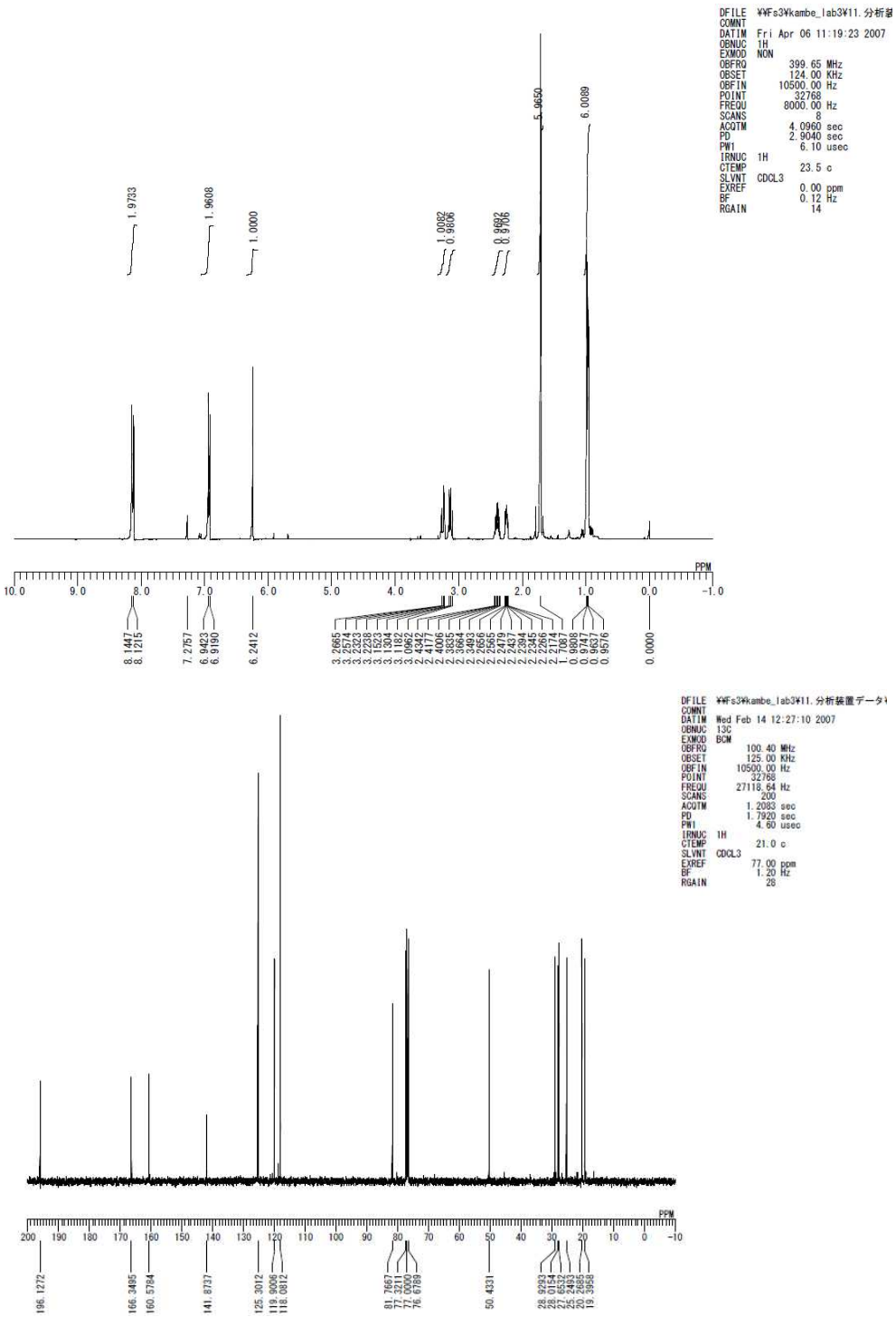
3e



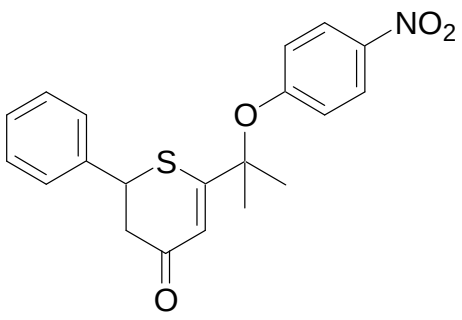
^{1}H and ^{13}C NMR spectrum for **3e**



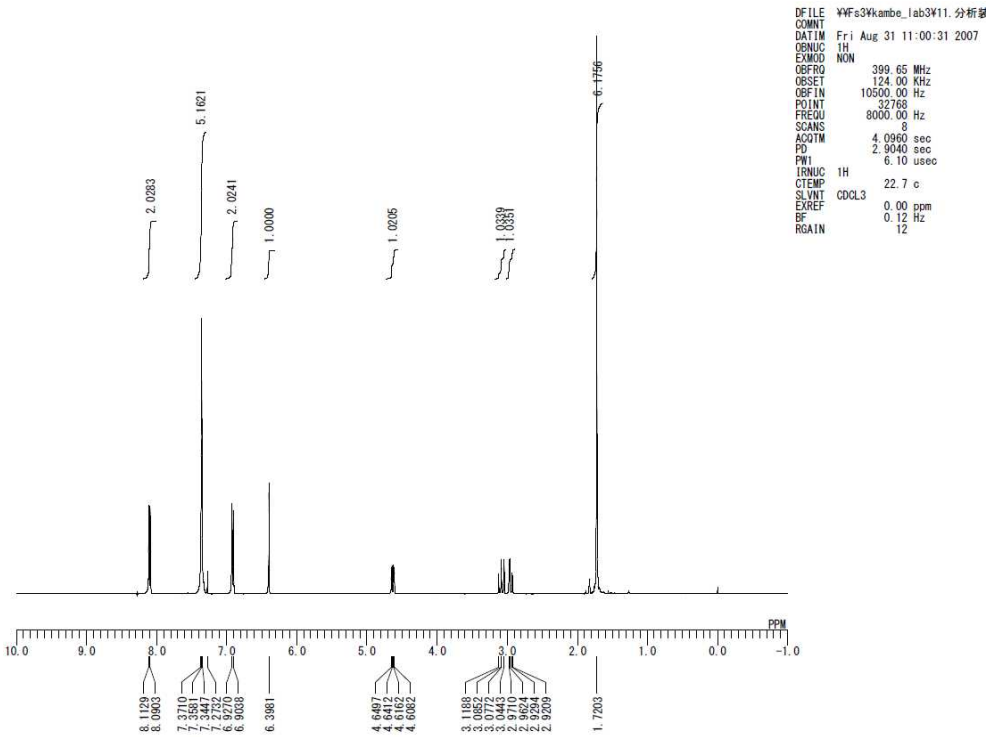
3g

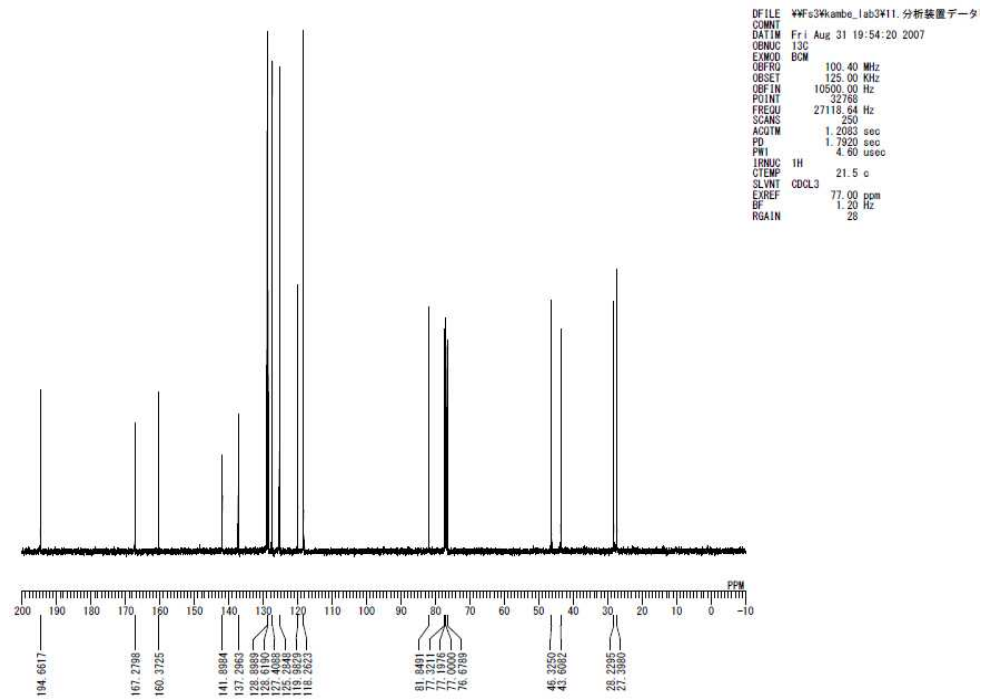


^{1}H and ^{13}C NMR spectrum for **3g**

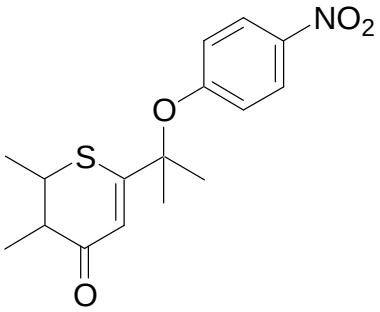


3h

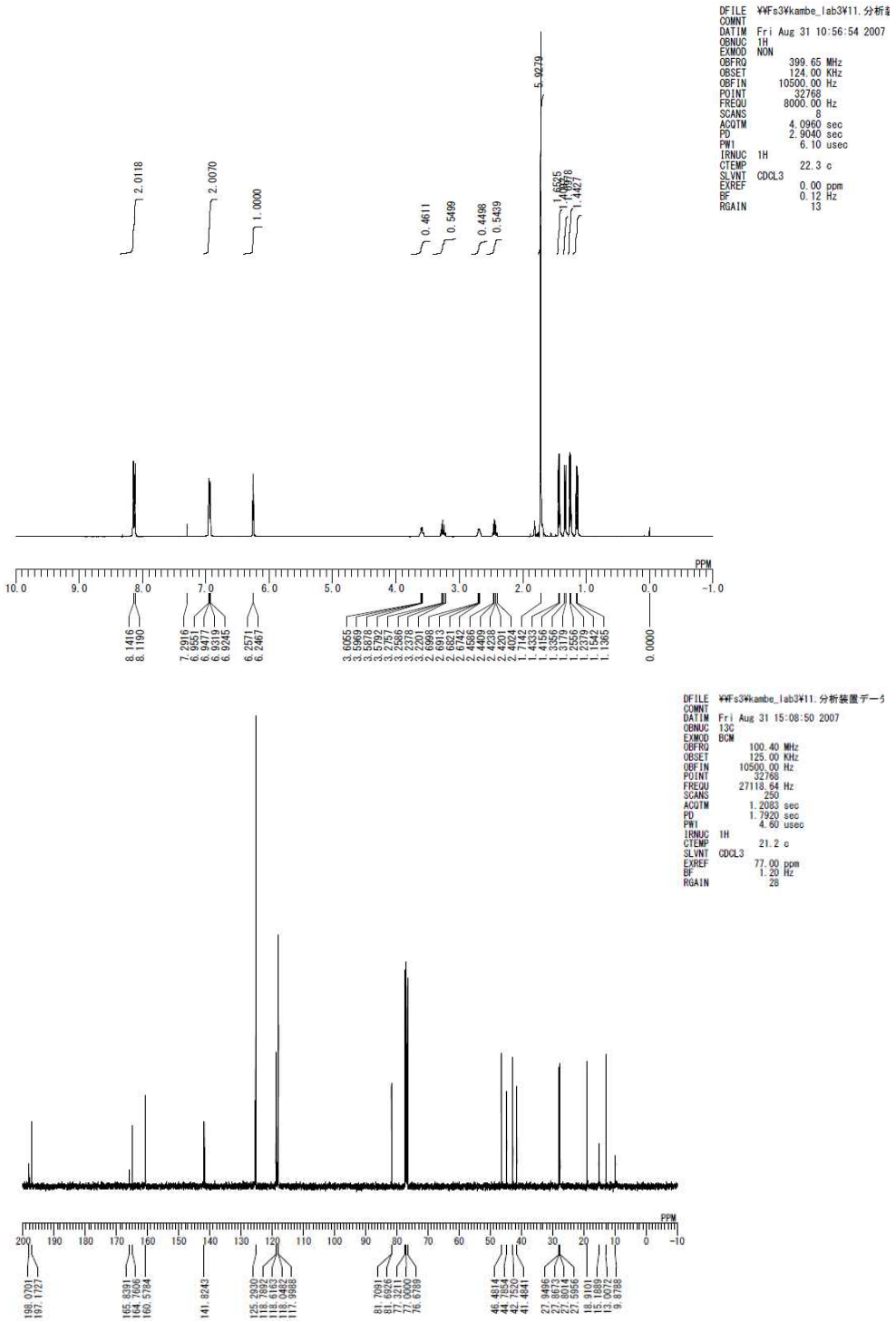




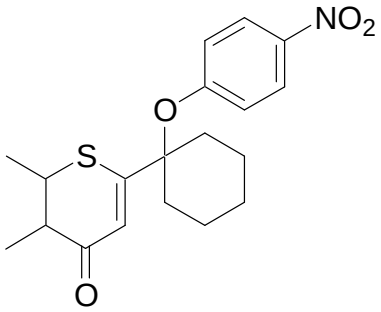
^{1}H and ^{13}C NMR spectrum for **3h**



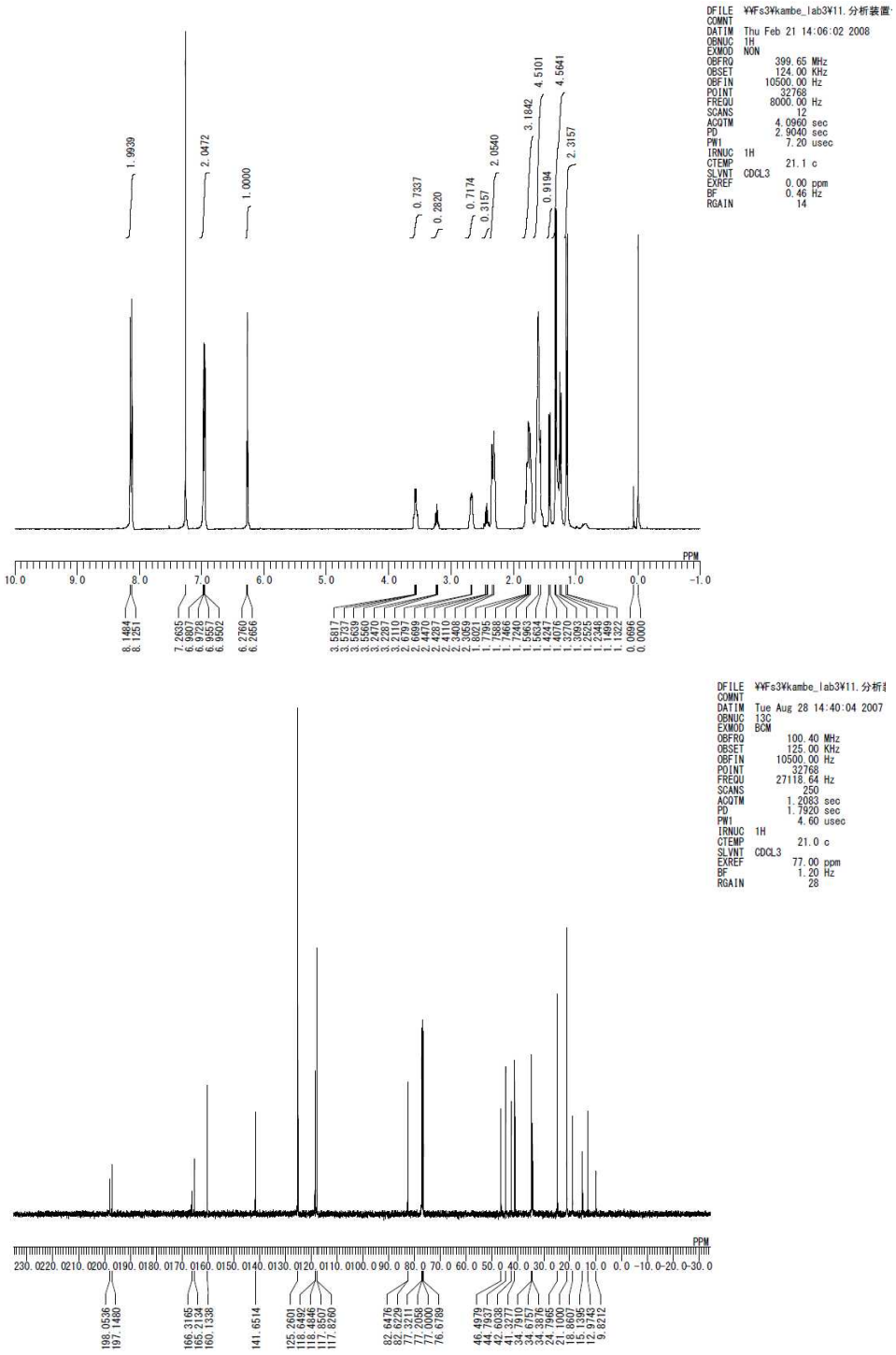
3i



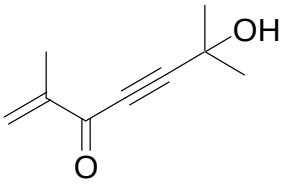
^{1}H and ^{13}C NMR spectrum for **3i**



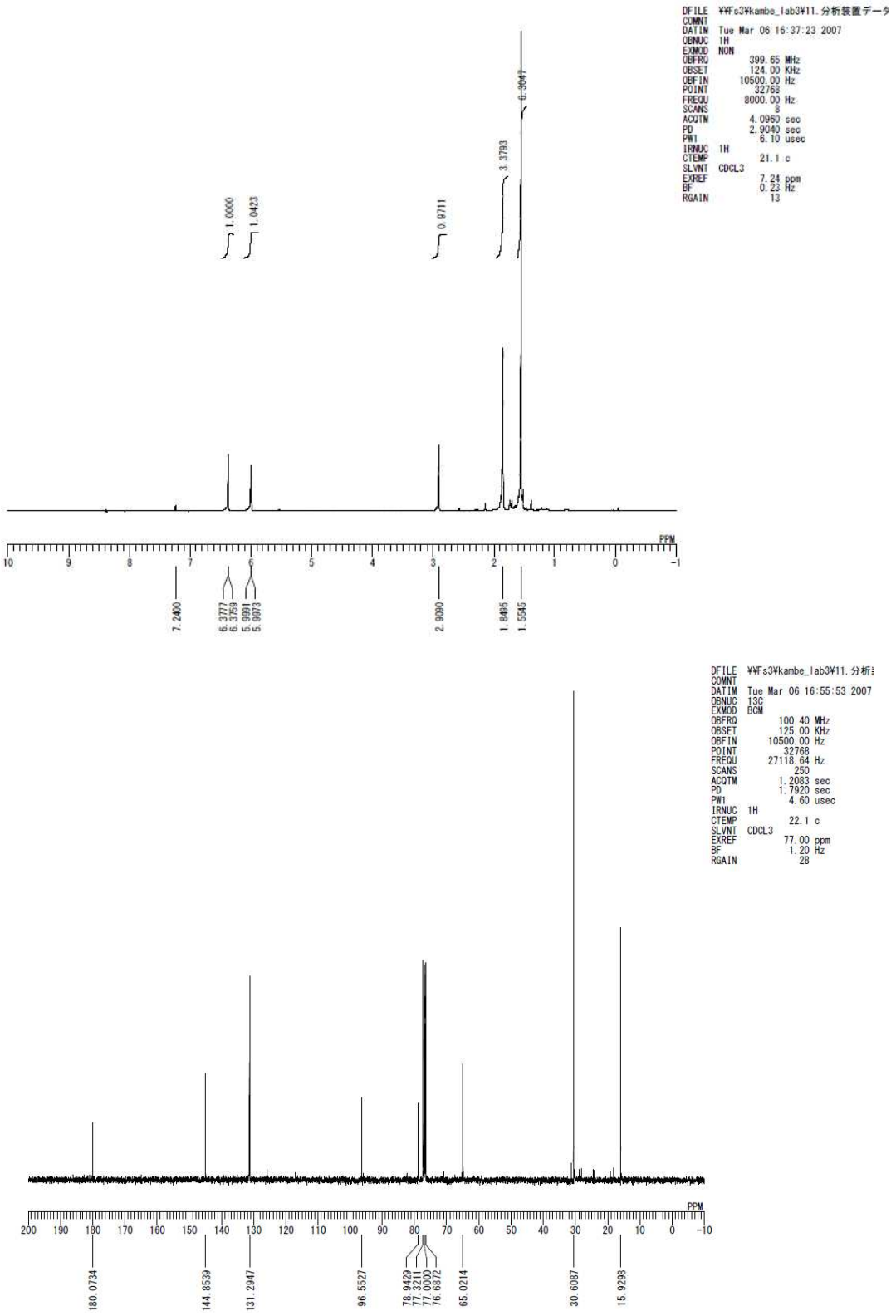
3j



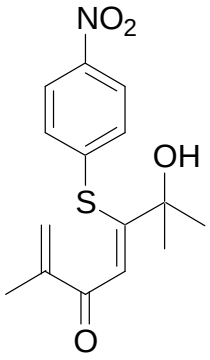
^{1}H and ^{13}C NMR spectrum for **3j**



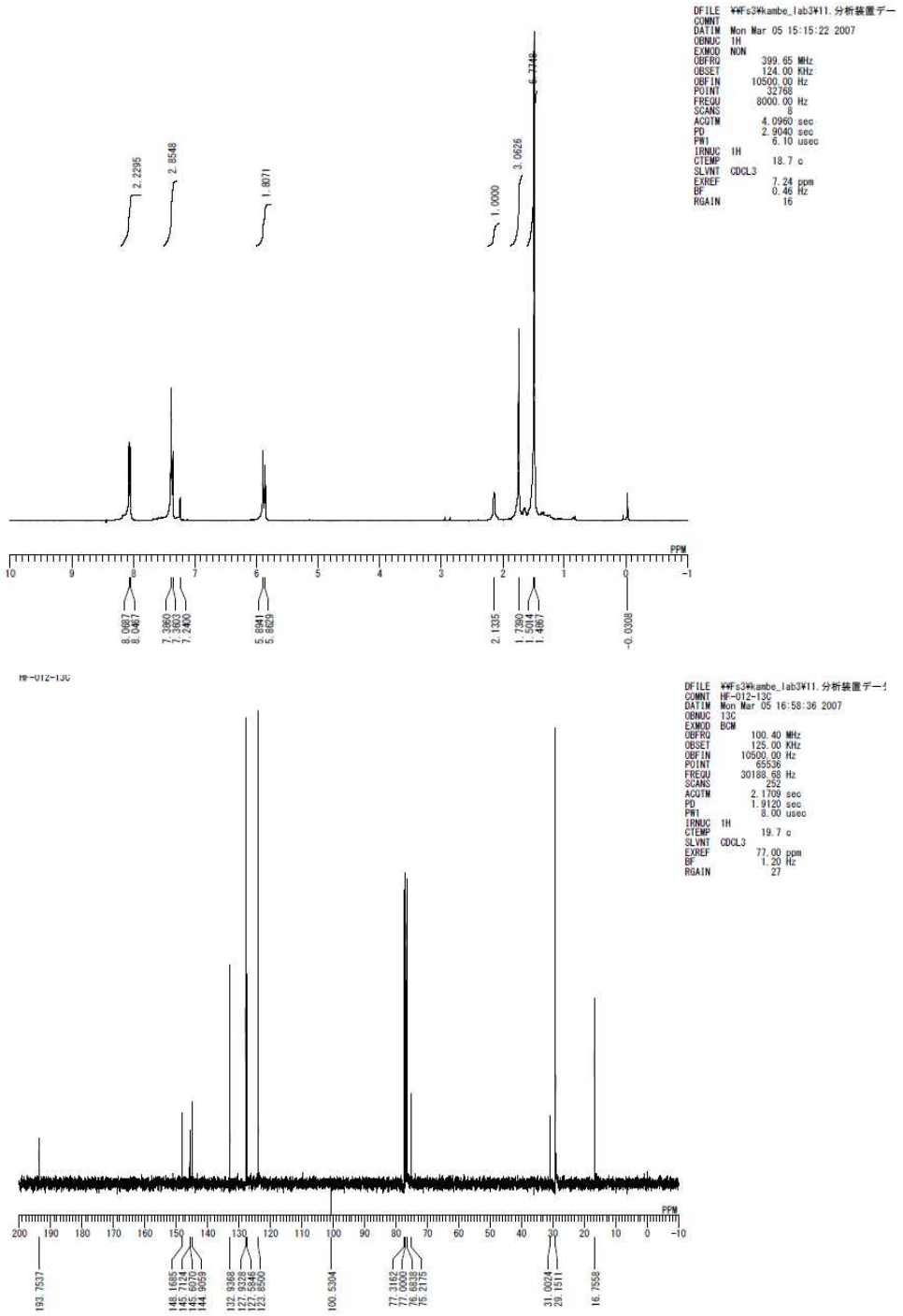
4a



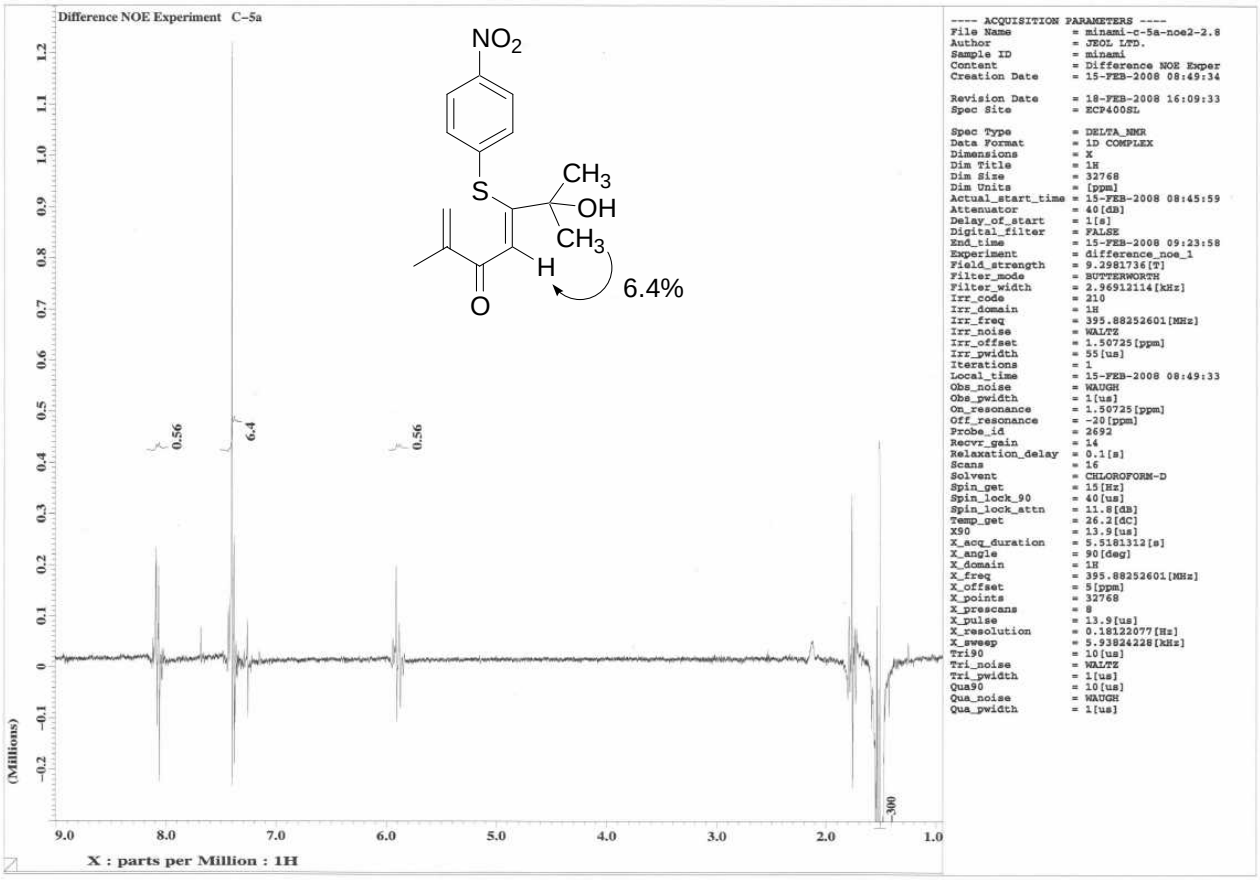
^{1}H and ^{13}C NMR spectrum for **4a**

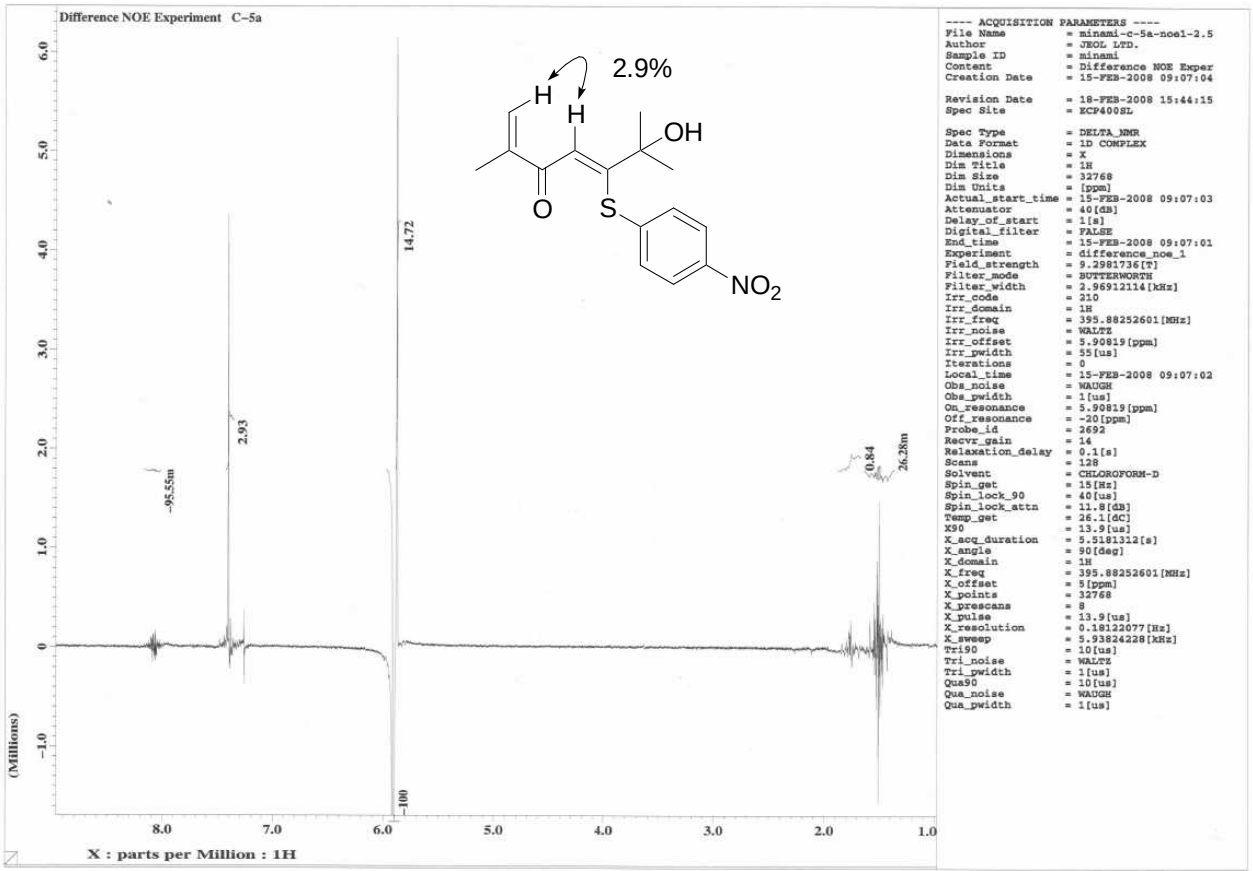


5a



^{1}H and ^{13}C NMR spectrum for **5a**





Difference NOE Experiment for **5a**