Supplementary Material (ESI) for Chemical Communications

Supplementary information for transition-metal-catalyzed regioselective aroyl- and trifluoroacetylthiolation of alkynes using thioesters

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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) spectrometer. 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. All reactions were carried out under a N_2 atmosphere. All solvents were distilled before use. Thioesters **2a**-**j, 7b** were prepared by the reactions of the corresponding acid chlorides with thiols in the presence of pyridine in THF solution, and selenoester **2k** was prepared by the reaction of the benzoyl chloride with PhSeMgBr in THF solution. Thioesters **7a, c-f** were synthesized according to the literature (*J. Am. Chem. Soc.* **2000**, *122,* 11260.).

The Spectrum Data or Registry Number (RN) of Thio- and Selenoesters (2 and 7):

***p*-$CH_3C_6H_4C(O)SC_6H_4O$-*p*-CH_3 (2a): RN: 53271-44-6.**

***p*-$CH_3C_6H_4C(O)SC_6H_5$ (2b): RN: 21122-34-2.**

***p*-$CH_3C_6H_4C(O)SC_6H_4$-*p*-F (2c):** white solid; mp 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3 H), 7.10 (dd, J = 8.6, 2.9 Hz, 2 H), 7.23 (d, J = 8.3 Hz, 2 H), 7.44 (dd, J = 8.6, 5.1 Hz, 2 H), 7.89 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 116.3 (d, J = 22 Hz), 122.7 (d, J = 3.7 Hz), 128.4 (d, J = 189 Hz), 133.7, 137.0 (d, J = 8.7 Hz), 144.6, 162.2, 164.7, 189.4; IR (NaCl) 3066, 3044, 2926, 1695, 1667, 1604, 1590, 1574, 1491, 1434, 1409, 1390, 1318, 1293, 1228, 1218, 1206, 1179, 1157, 1124, 1116, 1096, 1013, 903, 850, 826, 811, 789, 718, 646, 624, 544, 499, 497, 430 cm^{-1}; mass spectrum (EI) m/z 246 (M^+, 1.1); HRMS calcd for $C_{14}H_{11}FOS$: 246.0515. Found: 246.0507.

***p*-$CH_3C_6H_4C(O)SC_6H_4$-*p*-NO_2 (2d): RN: 77750-05-1.**

$C_6H_5C(O)SC_6H_5$ (2e): RN: 884-09-3.

***p*-$FC_6H_4C(O)SC_6H_4$-*p*-CH_3 (2f): RN: 90172-74-0.**

3-$C_6H_4NC(O)SC_6H_4$-*p*-CH_3 (2g): RN: 52064-00-3.

2-$C_5H_3OC(O)SC_6H_4$-*p*-CH_3 (2h): RN: 17357-39-0.

***p*-$CH_3C_6H_4C(O)SCH_2C_6H_5$ (2i): RN: 17577-21-8.**

***t*-$C_4H_9C(O)SC_6H_4$-*p*-OCH_3 (2j): RN: 132381-65-8.**

$C_6H_5C(O)SeC_6H_5$ (2k): RN: 38447-68-6.

$F_3CC(O)SC_6H_4$-*p*-CH_3 (7a): RN: 75072-07-0.

$H_3CC(O)SC_6H_4$-*p*-CH_3 (7b): registry number 10436-83-6.

$Cl_3CC(O)SC_6H_4$-*p*-CH_3 (7c): registry number 56956-67-3.

$F_3CC(O)SC_6H_4$-*p*-OCH_3 (7d): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3 H), 7.00 (d, J = 6.8 Hz, 2 H), 7.36 (d, J = 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 115.5, 115.9 (c, $J_{C\text{-}F}$ = 290 Hz), 132.3, 136.1, 161.7, 184.2 (c, $J_{C\text{-}F}$ = 39.4 Hz); IR (NaCl) 2945, 2842, 1890, 1794, 1716, 1594, 1575, 1496, 1464, 1442, 1296, 1277, 1257, 1206, 1163, 1031, 937, 828, 742, 604 cm^{-1}; mass spectrum (EI) m/z 236 (M^+, 59); HRMS calcd for $C_9H_7F_3O_2S$: 236.0119. Found: 236.0097.

$F_3CC(O)SC_6H_5$ (7e): RN: 2378-04-3.

$F_3CC(O)SC_6H_4$-*p*-Cl (7f): RN: 181820-16-6.

$F_3CC(O)SCH_2C_6H_5$ (7g): RN: 714-05-6.

$F_3CC(O)S$-*n*-$C_{10}H_{21}$ (7h): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.1 Hz, 3 H), 1.26-1.39 (m, 14 H), 1.65 (tt, *J* = 7.6, 7.3 Hz, 2 H), 3.05 (t, *J* = 7.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.7, 28.6, 28.7, 29.0, 29.3, 29.4, 29.5, 31.9, 115.6 (c, $J_{C\text{-}F}$ = 289 Hz), 184.5 (c, $J_{C\text{-}F}$ = 39.4 Hz); IR (NaCl) 2927, 2856, 2362, 1709, 1468, 1283, 1205, 1165, 956, 744 cm^{-1}; mass spectrum (EI) m/z 270 (M^+, 0.28); HRMS calcd for $C_{12}H_{21}F_3OS$: 270.1265. Found: 270.1258.

Reaction of *p*-$CH_3C_6H_4C(O)SC_6H_4$-*p*-OCH_3 (2a) with 1-Octyne (1a) in the Presence of $Pd(dba)_2$/dppe (Entry 11 of Table 1, Entry 1 of Table 2): General Procedure of Palladium-Catalyzed Aroylthiolation of Alkynes Using Thioesters: Into a two-necked 3 mL reaction glass were added $Pd(dba)_2$ (28.8 mg, 0.05 mmol), dppe (23.9 mg, 0.06 mmol), **1a** (132 mg, 1.2 mmol) **2a** (258 mg, 1.0 mmol) and benzene (0.5 mL) under a N_2 atmosphere. After the solution was refluxed for 20 h, the resultant mixture was filtered through Celite, the solvent was evaporated, and the resultant crude product was dried *in vacuo*. *Z*-**4a** and *E*-**4a** were obtained in 30% (112 mg) and 48% (175 mg) yields by preparative TLC using hexane and ethyl acetate (40/1) as an eluent.

(*E*)-*p*-$CH_3C_6H_4C(O)C(H)$=C(*n*-C_6H_{13})SC_6H_4-*p*-OCH_3 (*E*-4a): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.1 Hz, 3 H), 1.30-1.34 (m, 4 H), 1.40-1.46 (m, 2 H), 1.68-1.75 (m, 2 H), 2.34 (s, 3 H), 2.89 (t, *J* = 7.8 Hz, 2 H), 3.87 (s, 3 H), 6.25 (s, 1 H), 6.98 (d, *J* = 8.9 Hz, 2 H), 7.14 (d, *J* = 8.1 Hz, 2 H), 7.47 (d, *J* = 8.9 Hz, 2 H), 7.55 (d, *J* = 8.1 Hz, 2 H); NOE experiment: Irradiation of the vinyl singlet at δ 6.25 resulted in a 17.0% enhancement of the signal at δ 7.55 (aryl doublet); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.4, 22.6, 29.3, 29.9, 31.6, 34.1, 55.4 114.5, 115.3, 120.6, 128.0, 129.0, 137.1, 137.2, 142.5, 160.9, 168.1, 187.1; IR (NaCl) 2955, 2927, 2856, 1645, 1606, 1592, 1568, 1556, 1493, 1462, 1440, 1361, 1290, 1250, 1210, 1181, 1051, 1032, 830, 818, 732 cm^{-1}; mass spectrum (EI) m/e 368 (M^+, 15); Anal. Calcd for $C_{23}H_{28}O_2S$: C, 74.96;

H, 7.66. Found: C, 74.74; H, 7.47.

(*Z*)-*p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4$-*p*-$OCH_3$ (*Z*-4a): yellow solid; mp 42.0-44.0 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.1 Hz, 3 H), 1.08-1.10 (m, 4 H), 1.14-1.25 (m, 2 H), 1.38-1.44 (m, 2 H), 2.23 (t, *J* = 7.6 Hz, 2 H), 2.40 (s, 3 H), 3.83 (s, 3 H), 6.90 (d, *J* = 8.3 Hz, 2 H), 7.01 (s, 1 H), 7.25 (d, *J* = 8.3 Hz, 2 H), 7.48 (d, *J* = 8.3 Hz, 2 H), 7.88 (d, *J* = 8.3 Hz, 2 H); NOE experiment: Irradiation of the vinyl singlet at δ 7.01 resulted in a 8.9 % enhancement of the signal at δ 2.23 (allyl triplet) and 17.5 % enhancement of the signal at δ 7.88 (aryl doublet); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 21.5, 22.4, 28.6, 29.9, 31.3, 37.0, 55.3, 114.5, 115.3, 122.1, 128.1, 129.1, 136.3, 137.2, 142.6, 160.6, 166.4, 188.2; IR (KBr) 2928, 2857, 1632, 1607, 1592, 1570, 1534, 1493, 1463, 1298, 1246, 1180, 1096, 1084, 911, 863, 831, 806, 733 cm^{-1}; mass spectrum (EI) m/e 368 (M^+, 25); HRMS calcd for $C_{23}H_{28}O_2S$: 368.1810. Found: 368.1817.

Other aroylthiolation products **4b**, **4c**, **4e-i** and **4k-4q** were synthesized by similar procedures.

(*E*)-*p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_5$ (*E*-4b) (Entry 2 of Table 2): yellow solid; 71.9-73.1 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3 H), 1.32-1.34 (m, 4 H), 1.40-1.46 (m, 2 H), 1.68-1.74 (m, 2 H), 2.34 (s, 3 H), 2.91 (t, *J* = 7.8 Hz, 2 H), 6.28 (s, 1 H), 7.13 (d, *J* = 8.4 Hz, 2 H), 7.45-7.47 (m, 3 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.56-7.58 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.5, 22.6, 29.3, 29.8, 31.6, 34.2, 115.2, 128.0, 129.0, 129.7, 129.8, 130.2, 135.6, 137.0, 142.6, 166.9, 187.1; IR (KBr) 2944, 2916, 2855, 1646, 1604, 1578, 1468, 1436, 1352, 1255, 1230, 1211, 1180, 1055, 821, 756, 734, 709, 692 cm^{-1}; mass spectrum (EI) m/e 338 (M^+, 16); HRMS calcd for $C_{22}H_{26}OS$: 338.1704. Found: 338.1711.

(*Z*)-*p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_5$ (*Z*-4b) (Entry 2 of Table 2): yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.2 Hz, 3 H), 1.05-1.20 (m, 6 H), 1.38-1.43 (m, 2 H), 2.25 (t, *J* = 7.8 Hz, 2 H), 2.41 (s, 3H), 7.03 (s, 1 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 7.36-7.42 (m, 3 H), 7.57-7.59 (m, 2 H), 7.89 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.6, 22.4, 28.6, 29. 9, 31.2, 37.2, 115.8, 128.1, 129.0, 129.2, 129.3, 131.5, 135.8, 136.2, 142.7, 165.1, 188.3; IR (NaCl) 2955, 2927, 2857, 1634, 1607, 1569, 1538, 1475, 1439, 1236, 1208, 1181, 1084, 1018, 863, 806, 788, 752, 704, 693 cm^{-1}; mass spectrum (EI) m/e 338 (M^+, 17); HRMS calcd for $C_{22}H_{26}OS$: 338.1704. Found: 338.1700.

(*E*)-*p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4$-*p*-F (*E*-4c) (Entry 3 of Table 2): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.1 Hz, 3 H), 1.30-1.34 (m, 4 H), 1.42-1.45 (m, 2 H), 1.67-1.73 (m, 2 H), 2.35 (s, 3 H), 2.89 (t, *J* = 7.8 Hz, 2 H), 6.22 (s, 1 H), 7.15-7.20 (m, 4 H), 7.52-7.58 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.5, 22.6, 29.3, 29.8, 31.6, 34.1, 115.1, 117.1 (d, $J_{C\text{-}F}$ = 22.0 Hz), 125.5 (d, $J_{C\text{-}F}$ = 2.4 Hz), 128.0, 129.1, 136.9, 137.8 (d, $J_{C\text{-}F}$ = 8.3 Hz), 142.8, 163.7 (d, $J_{C\text{-}F}$ = 250 Hz), 166.8, 187.2; IR (NaCl) 2956, 2928, 2856, 1652, 1607, 1590, 1568, 1558, 1490, 1466, 1362, 1233, 1181, 1156, 1051, 1015, 835, 817, 731cm^{-1}; mass spectrum (EI) m/e 356 (M^+, 8.1); HRMS calcd for $C_{22}H_{25}FOS$: 356.1610. Found: 356.1606.

(*Z*)-*p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4$-*p*-F (*Z*-4c) (Entry 3 of Table 2): yellow solid; mp 57-60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7.2 Hz, 3 H), 1.09-1.10 (m, 4 H), 1.17-1.22 (m, 2 H), 1.38-1.44 (m, 2 H), 2.22 (t, *J* = 7.8 Hz, 2 H), 2.42 (s, 3 H), 7.04 (s, 1 H), 7.07-7.11 (m, 2 H), 7.27 (d, *J* = 7.6 Hz, 2 H), 7.54-7.58 (m, 2 H), 7.89 (d, *J* = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.6, 22.4, 28.6, 29.8, 31.3, 37.1, 115.9, 116.2 (d, $J_{C\text{-}F}$ = 22.0 Hz), 126.9 (d, $J_{C\text{-}F}$ = 3.7 Hz), 128.1, 129.2, 136.0, 137.7 (d, $J_{C\text{-}F}$ = 8.3 Hz), 142.8, 163.5 (d, $J_{C\text{-}F}$ = 249 Hz), 164.7, 188.4; IR (KBr) 2952, 2925, 2856, 1628, 1606, 1534, 1484, 1236, 1224, 1183, 1082, 842, 808 cm^{-1}; mass spectrum (EI) m/e 356 (M^+, 9.3); HRMS calcd for $C_{22}H_{25}FOS$: 356.1610. Found: 356.1617.

(*E*)-$C_6H_5C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_5$ (*E*-4e) (Entry 5 of Table 2): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.0 Hz, 3 H), 1.31-1.35 (m, 4 H), 1.41-1.47 (m, 2 H), 1.69-1.77 (m, 2 H), 2.92 (t, *J* = 7.8 Hz, 2 H), 6.29 (s, 1 H), 7.31-7.35 (m, 2 H), 7.41-7.43 (m, 1 H), 7.45-7.49 (m, 3 H), 7.56-7.59 (m, 2 H), 7.61-7.63 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.3, 29.9, 31.6, 34.3, 114.9, 127.9, 128.3, 129.8, 129.9, 130.1, 132.0, 135.7, 139.6, 167.8, 187.3; IR (NaCl) 3060, 2955, 2927, 2856, 1651, 1597, 1557, 1466, 1440, 1362, 1229, 1179, 1047, 1024, 778, 751, 692, 643 cm^{-1}; mass spectrum (EI) m/e 324 (M^+, 25); Anal. Calcd for $C_{21}H_{24}OS$: C, 77.73; H, 7.46. Found: C, 77.59; H, 7.29.

(*Z*)-$C_6H_5C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_5$ (*Z*-4e) (Entry 5 of Table 2): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.2 Hz, 3 H), 1.06-1.20 (m, 6 H), 1.41-1.46 (m, 2 H), 2.26 (t, *J* = 7.8 Hz, 2 H), 7.05 (s, 1 H), 7.39-7.60 (m, 8 H), 7.99 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.3, 28.6, 29.9, 31.2, 37.3, 115.7, 128.0, 128.5, 129.0, 129.3, 131.3, 132.0, 135.7, 138.7, 165.9, 188.6; IR (NaCl) 3058, 2955, 2929, 2857, 1634, 1598, 1578, 1548, 1538, 1532, 1476, 1446, 1440, 1355, 1303, 1233, 1178, 1105, 1070, 1025, 1001, 859, 828, 774, 752, 704, 676 cm^{-1}; mass spectrum (EI) m/e 324 (M^+, 17); HRMS calcd for $C_{21}H_{24}OS$: 324.1548. Found. Found: 324.1540.

(*E*)-*p*-$FC_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4$-*p*-$CH_3$ (*E*-4f) (Entry 6 of Table 2): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.4 Hz, 3 H), 1.32-1.46 (m, 6 H), 1.68-1.75 (m, 2 H), 2.42 (s, 3 H), 2.89 (t, *J* = 7.8 Hz, 2 H), 6.23 (s, 1 H), 6.98-7.02 (m, 2 H), 7.28 (d, *J* = 7.8 Hz, 2 H), 7.44 (d, *J* = 7.8 Hz, 2 H), 7.63-7.66 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.4, 22.6, 29.3, 29.9, 31.6, 34.2, 114.2, 115.3 (d, $J_{C\text{-}F}$ = 21.5 Hz), 126.3, 130.3 (d, $J_{C\text{-}F}$ = 9.2 Hz), 130.6, 135.5, 135.9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 140.3, 165.0 (d, $J_{C\text{-}F}$ = 252 Hz), 168.7, 185.8; IR (NaCl): 2956, 2927, 2857, 1651, 1598, 1557, 1505, 1493, 1456, 1433, 1408, 1363, 1229, 1155, 1050, 1018, 829, 812 cm ^{1}; mass spectrum (EI) m/e 356 (M^+, 10); Anal. Calcd for $C_{22}H_{25}FOS$: C, 74.12; H, 7.07. Found: C, 74.13; H, 7.12.

(*Z*)-*p*-$FC_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4$-*p*-$CH_3$ (*Z*-4f) (Entry 6 of Table 2): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.2 Hz, 3 H), 1.05-1.21 (m, 6 H), 1.38-1.46 (m, 2 H), 2.25 (t, *J* = 7.8 Hz, 2 H), 2.39 (s, 3 H), 6.99 (s, 1 H), 7.11-7.16 (m, 2 H), 7.20 (d, *J* = 8.2 Hz, 2 H), 7.45 (d, *J* = 8.2 Hz, 2 H), 7.99-8.03 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.3, 22.4, 28.6, 30.0, 31.2, 37.2, 115.0, 115.5 (d, $J_{C\text{-}F}$ = 21.5 Hz), 127.6, 129.8, 130.4 (d, $J_{C\text{-}F}$ = 8.7 Hz), 135.1 (d, $J_{C\text{-}F}$ = 2.7 Hz), 135.6, 139.7, 165.1 (d, $J_{C\text{-}F}$ = 252 Hz), 167.2, 187.0; IR (NaCl) 2956, 2928, 2858, 1634, 1600, 1538, 1532, 1505, 1494, 1463, 1230, 1155, 1084, 1018, 867, 852, 812, 733 cm^{-1}; mass spectrum (EI) m/e 356 (M^+, 12); Anal. Calcd for $C_{22}H_{25}FOS$: C, 74.12; H, 7.07. Found: C, 74.02; H, 7.23.

(*E*)-3-$C_5H_4NC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}CH_3$ (*E*-4g) (Entry 7 of Table 2): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.6 Hz, 3 H), 1.34-1.47 (m, 6 H), 1.73 (dt, 2 H), 2.42 (s, 3 H), 2.94 (t, *J* = 7.8 Hz, 2 H), 6.23 (s, 1 H), 7.28-7.33 (m, 3 H), 7.44 (d, *J* = 7.8 Hz, 2 H), 8.01 (d, *J* = 7.8 Hz, 1 H), 8.64 (d, *J* = 3.9 Hz, 1 H), 8.74 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.4, 22.6, 29.3, 29.9, 31.5, 34.6, 113.2, 123.4, 125.9, 129.8, 130.7, 135.4, 135.5, 140.6, 149.1, 152.2, 171.2, 185.1; IR (NaCl) 3033, 2955, 2927, 2856, 1651, 1584, 1556, 1493, 1456, 1416, 1366, 1237, 1106, 1060, 1040, 1018, 849, 811, 732, 702, 662 cm ^{1}; mass spectrum (EI) m/e 339 (M^+, 20); Anal. Calcd for $C_{21}H_{25}NOS$: C, 74.29; H, 7.42; N, 4.13. Found: C, 74.07; H, 7.41; N, 4.16.

(*Z*)-3-$C_5H_4NC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}CH_3$ (*Z*-4g) (Entry 7 of Table 2): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, *J* = 8.9 Hz, 3 H), 1.05-1.21 (m, 6 H), 1.43 (dt, 2 H), 2.26 (t, *J* = 7.8 Hz, 2 H), 2.39 (s, 3 H), 7.01 (s, 1 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 7.40-7.47 (m, 3 H), 8.28 (d, *J* = 8.1 Hz, 1 H), 8.74 (d, *J* = 3.2 Hz, 1 H), 9.18 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 21.2, 22.3, 28.5, 29.9, 31.1, 37.2, 114.6, 123.5, 127.1, 129.8, 134.0, 135.4, 135.5, 139.8, 149.2, 152.3, 169.2, 186.6; IR (NaCl) 3020, 2955, 2927, 2857, 1634, 1585, 1569, 1530, 1493, 1456, 1416, 1249, 1088, 1019, 862, 812, 756, 704, 666, 620 cm ^{1}; mass spectrum (EI) m/e 339 (M^+, 20), 123 (100); Anal. Calcd for $C_{21}H_{25}NOS$: C, 74.29; H, 7.42; N, 4.13. Found: C, 74.01; H, 7.14; N, 4.13.

(*E*)-2-$C_4H_3OC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}CH_3$ (*E*-4h) (Entry 8 of Table 2): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 2 H), 1.30-1.34 (m, 4 H), 1.42-1.46 (m, 2 H), 1.66-1.72 (m, 2 H), 2.43 (s, 3 H), 2.93 (t, *J* = 7.7, 2 H), 6.18 (s, 1 H), 6.40-6.41 (m, 1 H), 6.77 (d, *J* = 3.7 Hz, 1 H), 7.28 (d, *J* = 7.7 Hz, 2 H), 7.42-7.44 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.3, 22.5, 29.2, 29.8, 31.5, 34.2, 111.9, 113.4, 115.6, 126.4, 130.5, 135.5, 140.3, 145.6, 154.3, 169.0, 175.6; IR (NaCl) 2955, 2927, 2856, 1643, 1572, 1492, 1467, 1432, 1394, 1353, 1262, 1165, 1156, 1088, 1056, 1017, 913, 884, 811, 756, 732, 694 cm^{-1}; mass spectrum (EI) m/e 328 (M^+, 30); Anal. Calcd for $C_{20}H_{24}O_2S$: C, 73.13; H, 7.36. Found: C, 72.89; H, 7.08.

(*Z*)-2-$C_4H_3OC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}CH_3$ (*Z*-4h) (Entry 8 of Table 2): yellow oil; ^{1}H NMR (400

MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.2 Hz, 3 H), 1.06-1.08 (m, 4 H), 1.15-1.19 (m, 2 H), 1.39-1.43 (m, 2 H), 2.22 (t, *J* = 7.8, 2 H), 2.38 (s, 3 H), 6.52-6.56 (m, 1 H), 6.92 (s, 1 H), 7.18-7.20 (m, 3 H), 7.44 (d, *J* = 8.1 Hz, 2 H), 7.55-7.56 (m, 1 H); NOE experiment: Irradiation of the vinyl singlet at δ 6.92 resulted in a 6.9 % enhancement of the signal at δ 2.22; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.3, 22.3, 28.5, 29.8, 31.2, 37.1, 112.3, 114.9, 115.6, 127.5, 129.8, 135.7, 139.6, 145.2, 154.1, 166.6, 177.3; IR (NaCl) 2955, 2928, 2858, 1633, 1574, 1538, 1493, 1470, 1258, 1157, 1101, 1010, 884, 813, 756 cm^{-1}; mass spectrum (EI) m/e 328 (M^+, 29); Anal. Calcd for $C_{20}H_{24}O_2S$: C, 73.13; H, 7.36. Found: C, 72.90; H, 6.97.

The structure of **4i** was tentatively assigned by ^{1}H NMR spectrum.

(*E*)-*p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SCH_2C_6H_5$ (*E*-4i) (Entry 9 of Table 2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (s, 1 H, vinyl proton).

(*Z*)-*p*-$CH_3C_6H_4C(O)C(H)=C(n\text{-}C_6H_{13})SCH_2C_6H_5$ (*Z*-4i) (Entry 9 of Table 2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 1 H, vinyl proton).

(*E*)-*p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_4Cl)SC_6H_4$-*p*-$OCH_3$ (*E*-4k) (Entry 11 of Table 2): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85-1.95 (m, 4 H), 2.35 (s, 3 H), 2.92 (t, *J* = 7.3 Hz, 2 H), 3.59 (t, *J* = 6.5 Hz, 2 H), 3.85 (s, 3 H), 6.29 (s, 1 H), 6.99 (d, *J* = 8.6 Hz, 2 H), 7.15 (d, *J* = 8.2 Hz, 2 H), 7.48 (d, *J* = 8.6 Hz, 2 H), 7.54 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21. 5, 27.1, 32.3, 33.0, 44.8, 55.4, 114.9, 115.3, 120.3, 128.0, 129.0, 136.9, 137.2, 142.7, 161.0, 166.9, 187.1; IR (NaCl) 2956, 2866, 2838, 1645, 1606, 1592, 1574, 1568, 1557, 1494, 1462, 1441, 1360, 1291, 1250, 1181, 1050, 1031, 830, 819, 734 cm^{-1}; mass spectrum (EI) m/e 374 (M^+, 24); Anal. Calcd for $C_{21}H_{23}ClO_2S$: C, 67.27; H, 6.18. Found: C, 67.08; H, 5.96.

(*Z*)-*p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_4Cl)SC_6H_4$-*p*-$OCH_3$ (*Z*-4k) (Entry 11 of Table 2): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58-1.61 (m, 4 H), 2.27 (t, *J* = 6.8 Hz, 2 H), 2.41 (s, 3 H), 3.38 (t, *J* = 5.7 Hz, 2 H), 3.84 (s, 3 H), 6.92 (d, *J* = 8. 6 Hz, 2 H), 7.02 (s, 1 H), 7.26 (d, *J* = 8.1 Hz, 2 H), 7.49 (d, *J* = 8.6 Hz, 2 H), 7.89 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 27.0, 31.7, 36.2, 44.4, 55.4, 114.7, 115.7, 121.9, 128.1, 129.2, 136.1, 137.2, 142.8, 160.7, 165.1, 188.2; IR (NaCl) 3002, 2956, 2866, 1632, 1607, 1591, 1570, 1538, 1493, 1461, 1441, 1288, 1246, 1208, 1180, 1174, 1104, 1074, 1030, 831, 806, 754, 734 cm^{-1}; mass spectrum (EI) m/e 374 (M^+, 23); Anal. Calcd for $C_{21}H_{23}ClO_2S$: C, 67.27; H, 6.18. Found: C, 67.26; H, 6.06.

(*E*)-*p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_3CN)SC_6H_4$-*p*-$OCH_3$ (*E*-4l) (Entry 12 of Table 2): yellow solid; mp 87.4-88.6 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.08-2.15 (m, 2 H), 2.35 (s, 3 H), 2.52 (t, *J* = 7.4 Hz, 2 H), 2.98 (t, *J* = 7.6 Hz, 2 H), 3.85 (s, 3 H), 6.34 (s), 7.01 (d, *J* = 8.8 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.48 (d, *J* = 8.8 Hz, 2 H), 7.53 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.8, 21.5, 25.5, 32.7, 55.4, 115.5, 115.7, 119.5, 119.7, 128.0, 129.1, 136.6, 137.1, 143.0, 161.2, 164.8, 187.1; IR (KBr) 1646, 1606, 1590, 1568, 1495, 1457, 1434, 1358, 1300, 1287, 1249, 1184, 1058, 1018, 835, 816, 797, 737, 705 cm^{-1}; mass spectrum (EI) m/e 351 (M^+, 29); Anal. Calcd for $C_{21}H_{21}NO_2S$: C, 71.76; H, 6.02; N, 3.99. Found: C, 71.72; H, 6.09; N, 4.00.

(*E*)-*p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_3CO_2CH_3)SC_6H_4$-*p*-$OCH_3$ (*E*-4m) (Entry 13 of Table 2): yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 2.07 (dt, 2 H), 2.33 (s, 3 H), 2.48 (t, *J* = 7.7 Hz, 3 H), 2.94 (t, *J* = 7.7 Hz, 2 H), 3.67 (s, 3 H), 3.84 (s, 3 H), 6.29 (s, 1 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 7.53 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 24.8, 32.9, 33.4, 51.4, 55.3, 115.1, 115.3, 120.2, 127.9, 129.0, 136.8, 137.1, 142.6, 161.0, 166.3, 173.6, 186.9; IR (NaCl) 2950, 1737, 1646, 1606, 1592, 1568, 1494, 1455, 1437, 1364, 1291, 1250, 1181, 1049, 1030, 831, 819, 733 cm^{-1}; mass spectrum (EI) m/e 384 (M^+, 17); Anal. Calcd for $C_{22}H_{24}O_4S$: C, 68.72; H, 6.29. Found: C, 68.68; H, 6.14.

(*Z*)-*p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_3CO_2CH_3)SC_6H_4$-*p*-$OCH_3$ (*Z*-4m) (Entry 13 of Table 2): orange solid; mp 85.0-87.9 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.75 (dt, 2 H), 2.16 (t, *J* = 7.3 Hz, 2 H), 2.30 (t, *J* = 7.3 Hz, 2 H), 2.41 (s, 3 H), 3.61 (s, 3 H), 3.84 (s, 3 H), 6.92 (d, *J* = 7.6 Hz, 2 H), 7.02 (s, 1 H), 7.26 (d, *J* = 8.2 Hz, 2 H), 7.48 (d, *J* = 7.6 Hz, 2 H), 7.89 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 24.8, 32.9, 36.0, 51.5, 55.4, 114.7, 116.0, 121.9, 128.1, 129.2, 136.1, 137.1, 142.8, 160.7, 164.4, 173.3, 188.2; IR (KBr) 1732, 1627, 1606, 1588, 1568, 1531, 1494, 1484, 1448, 1285, 1240, 1180, 1153, 1072, 1017, 845, 834, 809 cm^{-1}; mass spectrum (EI) m/e 384 (M^+, 21); HRMS calcd for $C_{22}H_{24}O_4S$: 384.1395. Found: 384.1393.

(*E*)-*p*-$CH_3C_6H_4C(O)C(H)=C(CH_2(c\text{-}C_5H_9))SC_6H_4$-*p*-$OCH_3$ (*E*-4n) (Entry 14 of Table 2): yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29-1.34 (m, 2 H), 1.52-1.56 (m, 2 H), 1.62-1.68 (m, 2 H), 1.83-1.87 (m, 2 H), 2.29-2.35 (m, 1 H), 2.33 (s, 3 H), 3.00 (d, J = 7.3 Hz, 2 H), 3.85 (s, 3 H), 6.24 (s, 1 H), 6.98 (d, J = 8.8 Hz, 2 H), 7.13 (d, J = 8.1 Hz, 2 H), 7.47 (d, J = 8.8 Hz, 2 H), 7.53 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 24.8, 32.4, 39.0, 40.5, 55.4, 115.1, 115.3, 120.8, 128.0, 129.0, 137.1, 137.2, 142.5, 160.9, 167.3, 187.3; IR (NaCl) 2951, 2866, 1647, 1606, 1592, 1560, 1493, 1462, 1440, 1407, 1360, 1290, 1250, 1210, 1181, 1104, 1050, 1032, 830, 819, 733 cm^{-1}; mass spectrum (EI) m/e 366 (M^+, 25); Anal. Calcd for $C_{23}H_{26}O_2S$: C, 75.37; H, 7.15. Found: C, 75.23; H, 7.28.

(*Z*)-*p*-$CH_3C_6H_4C(O)C(H)=C(CH_2(c\text{-}C_5H_9))SC_6H_4$-*p*-$OCH_3$ (*Z*-4n) (Entry 14 of Table 2): yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97-1.03 (m, 2 H), 1.43-1.64 (m, 6 H), 1.93-1.97 (m, 1 H), 2.24 (d, J = 6.8 Hz, 2 H), 2.41 (s, 3 H), 3.84 (s, 3 H), 6.90 (d, J = 8.5 Hz, 2 H), 7.01 (s, 1 H), 7.26 (d, J = 8.1 Hz, 2 H), 7.47 (d, J = 8.5 Hz, 2 H), 7.88 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 24.8, 32.2, 39.6, 42.9, 55.3, 114.5, 115.9, 122.3, 128.1, 129.1, 136.4, 137.2, 142.6, 160.5, 165.3, 188.2; IR (NaCl) 2951, 2866, 1632, 1607, 1592, 1571, 1537, 1494, 1462, 1453, 1441, 1288, 1246, 1207, 1180, 1101, 1082, 1031, 1018, 862, 830, 809, 799, 788, 755, 734 cm^{-1}; mass spectrum (EI) m/e 366 (M^+, 23); HRMS calcd for $C_{23}H_{26}O_2S$: 366.1654. Found: 366.1658.

(*E*)-*p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_2CH(CH_3)_2)SC_6H_4$-*p*-$OCH_3$ (*E*-4o) (Entry 15 of Table 2): yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, J = 6.3 Hz, 6 H), 1.58-1.73 (m, 3 H), 2.35 (s, 3 H), 2.90 (t, J = 6.8 Hz, 2 H), 3.86 (s, 3 H), 6.25 (s, 1 H), 6.99 (d, J = 8.8 Hz, 2 H), 7.14 (d, J = 7.9 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H), 7.55 (d, *J* = 7.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 22.4, 28.4, 32.2, 38.8, 55.4, 114.5, 115.3, 120.6, 128.0. 129.0, 137.1, 137.2, 142.5, 161.0, 168.4, 187.1; IR (NaCl) 3005, 2956, 2868, 1646, 1607, 1592, 1560, 1493, 1464, 1442, 1366, 1290, 1250, 1208, 1181, 1052, 1031, 1018, 830, 818, 759, 734 cm^{-1}; mass spectrum (EI) m/e 354 (M^+, 24); HRMS calcd for $C_{22}H_{26}O_2S$: 354.1654. Found: 354.1651.

(*Z*)-*p*-$CH_3C_6H_4C(O)C(H)=C((CH_2)_2CH(CH_3)_2)SC_6H_4$-*p*-$OCH_3$ (*Z*-4o) (Entry 15 of Table 2): yellow solid; mp 94.0-95.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.68 (d, *J* = 6.4 Hz, 6 H), 1.31-1.34 (m, 3 H), 2.25 (t, *J* = 7.7 Hz, 2 H), 2.41 (s, 3 H), 3.83 (s, 3 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 7.02 (s, 1 H), 7.25 (d, *J* = 7.9 Hz, 2 H), 7.49 (d, *J* = 8.8 Hz, 2 H), 7.89 (d, *J* = 7.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 22.1, 27.8, 35.2, 39.3, 55.4, 114.5, 115.3, 122.1, 128.1, 129.1, 136.3, 137.3, 142.6, 160.6, 166.8, 188.3; IR (KBr) 2957, 2868, 1632, 1606, 1590, 1570, 1534, 1492, 1464, 1442, 1296, 1239, 1181, 1171, 1098, 1086, 1027, 1016, 867, 830, 799, 789 cm^{-1}; mass spectrum (EI) m/e 354 (M^+, 26); Anal. Calcd for $C_{22}H_{26}O_2S$: C, 74.54; H, 7.39. Found: C, 74.38; H, 7.19.

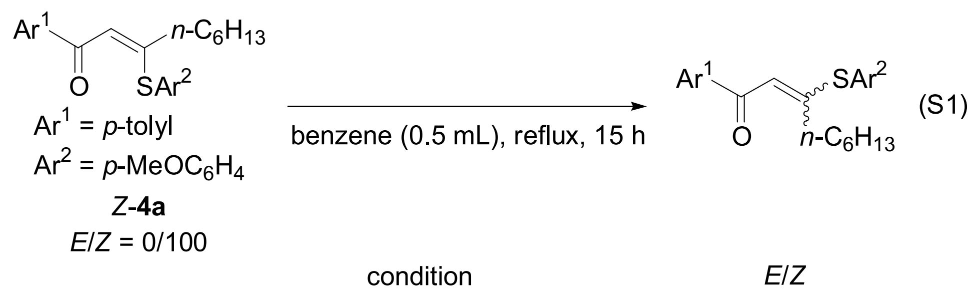
***p*-$CH_3C_6H_4C(O)C(H)=C(C_6H_5)SC_6H_4$-*p*-$OCH_3$ (4p, a mixture of stereoisomer) (Entry 16 of Table 2):** yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) *Z* isomer; δ 2.41 (s, 3 H), 3.68 (s, 3 H), 6.57 (d, *J* = 8.8 Hz, 2 H), 7.09-7.16 (m, 9 H), 7.25 (s, 1 H), 7.93 (d, *J* = 8.0 Hz, 2 H); *E* isomer; 2.33 (s, 3 H), 3.86 (s, 3 H), 6.28 (s, 1 H), 6.99 (d, *J* = 8.5 Hz, 2 H), other peaks overlap with those of *Z* isomer; ^{13}C NMR (100 MHz, $CDCl_3$) *Z* isomer; δ 21.6, 55.2, 113.9, 119.1, 123.4, 127.7, 128.2, 128.3, 128.9, 129.3, 136.0, 136.1, 138.9, 143.1, 159.5, 163.1, 188.3.; *E* isomer; δ 21.5, 55.4, 115.4, 117.4, 121.1, 128.1, 128.4, 128.5, 128.8, 129.0, 135.9, 137.1, 137.2, 142.9, 161.0, 161.1, 188.4; IR (KBr): 2929, 1626, 1605, 1591, 1570, 1560, 1526, 1492, 1460, 1443, 1406, 1333, 1302, 1291, 1245, 1174, 1106, 1030, 1017, 955, 830, 815, 770, 737, 703, 676 cm^{-1} ; mass spectrum (EI) m/e 360 (M^+, 38); (EI) m/e 360 (M^+, 38); Anal. Calcd for $C_{23}H_{20}O_2S$: C, 76.64; H, 5.59. Found: C, 76.48; H, 5.48.

The structure of ***Z*-4q** was tentatively determined by ^{1}H NMR spectrum (*vide infra*).

(*Z*)-$C_6H_5C(O)C(H){=}C(\textit{n}\text{-}C_6H_{13})SeC_6H_5$ (*Z*-4q) (Entry 17 of Table 2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 1 H, vinyl proton).

Reaction of *p*-$CH_3C_6H_4C(O)SC_6H_4$-*p*-OCH_3 (2a) with 1-Octyne (1a) in the Presence of $Pt(PPh_3)_4$ (Entry 18 of Table 1): Into a two-necked 3 mL reaction glass were added $Pt(PPh_3)_4$ (62.5 mg, 0.05 mmol), **2a** (254 mg, 0.983 mmol), **1a** (135 mg, 1.23 mmol) and toluene (0.5 mL) under a N_2 atmosphere. After the solution was refluxed for 13 h, the resultant mixture was filtered through Celite, the solvent was evaporated, and the resultant crude product was dried *in vacuo*. *Z*-**3a** and *E*-**4a** were obtained in 75% (255 mg) and 8% (30 mg) yield by preparative TLC using hexane and ethyl acetate (40/1) as an eluent.

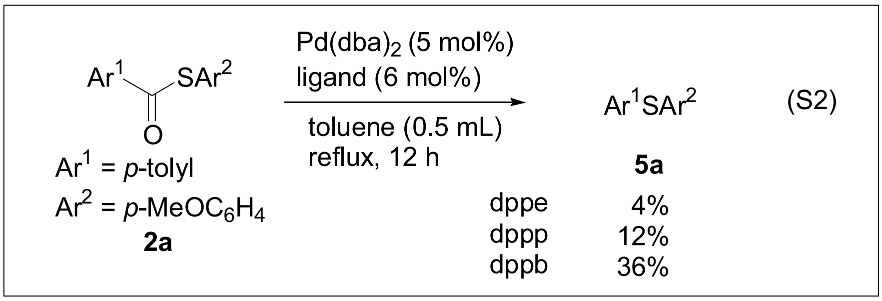
(*Z*)-*p*-$CH_3C_6H_4C(H){=}C(\textit{n}\text{-}C_6H_{13})SC_6H_4$-*p*-$OCH_3$ (*Z*-3a): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J = 7.0 Hz, 3 H), 1.19-1.27 (m, 6 H), 1.49-1.53 (m, 2 H), 2.16 (t, J = 7.4 Hz, 2 H), 2.34 (s, 3 H), 3.78 (s, 3 H), 6.61 (s, 1 H), 6.82 (d, J = 8.8 Hz, 2 H), 7.14 (d, J = 8.0 Hz, 2 H), 7.32 (d, J = 8.8 Hz, 2 H), 7.45 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.2, 22.5, 28.5, 28.8, 31.6, 37.6, 55.3, 114.4, 124.2, 128.6, 129.1, 129.2, 134.1, 134.2, 136.6, 136.9, 159.2; IR (NaCl) 2954, 2928, 2856, 1592, 1571, 1509, 1493, 1463, 1440, 1286, 1246, 1180, 1172, 1034, 827, 806 cm^{-1}; mass spectrum (EI) m/e 340 (M^+, 100). HRMS calcd for $C_{22}H_{28}OS$: 340.1861. Found: 340.1871.



condition	*E*/*Z*
none	0/100
Pd(dba)$_2$ (5 mol%), dppe (6 mol%)	0/100
1a (1.6 equiv.), Pd(dba)$_2$ (5 mol%), dppe (6 mol%)	61/39

***Z*-to-*E* Isomerization of *Z*-4a (eq S1) (Ref 16)**: Into a two-necked reaction glass were added Pd(dba)$_2$ (1.5 mg, 0.0026 mmol), dppe (1.2 mg, 0.0030 mmol), *Z*-**4a** (17 mg, 0.044 mmol), **1a** (8.9 mg, 0.081 mmol) and benzene (0.5 mL) under a N_2 atmosphere. After the solution was refluxed for 15 h, the reaction mixture was filtered through Celite, and the filtrate was evaporated and dried *in vacuo*. The products were analyzed by ^{1}H NMR spectroscopy.

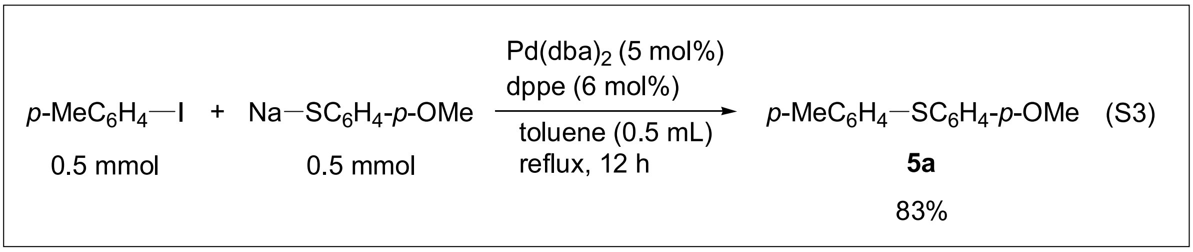
Z-to-*E* Isomerization of *Z*-**4a** occurred in the presence of catalytic amount of $Pd(dba)_2$ and dppe and 1.6 equiv amount of **1a**. These results indicated that **1a** is the crucial factor for the generation of active dppe ligated Palladium (0) complex.



Treatment of 2a in the Presence of Pd/dppe (eq S2) (Ref 18): Into a two-necked reaction glass were added $Pd(dba)_2$ (28.3 mg, 0.05 mmol), dppe (24.5 mg, 0.06 mmol), **2a** (262 mg, 1.01 mmol) and toluene (0.5 mL) under a N_2 atmosphere. After the solution was refluxed for 12 h, the reaction mixture was filtered through Celite, the solvent was evaporated and the resultant crude product was dried *in vacuo*. The products were analyzed by ^{1}H NMR spectroscopy.

Decarbonylation of **2a** using dppp and dppb ligands was similarly examined.

***p*-$CH_3C_6H_4SC_6H_4$-*p*-OCH_3 (5a): RN: 6013-47-4.**



Reaction of IC_6H_4-*p*-OCH_3 with $NaSC_6H_4$-*p*-OCH_3 in the Presence of Pd/dppe (eq S3) (Ref 18): Into a two-necked reaction glass were added $Pd(dba)_2$ (14.4 mg, 0.025 mmol), dppe (12.0 mg, 0.030 mmol), *p*-

MeC_6H_4I (109 mg, 0.500 mmol), $NaSC_6H_4OMe$-*p* (82 mg, 0.506 mmol) and toluene (0.5 mL) under a N_2 atmosphere. After the solution was refluxed for 12 h, the reaction mixture was filtered through Celite, the solvent was evaporated and the resultant crude product was dried *in vacuo*. The products were analyzed by ^1H NMR spectroscopy.

Reaction of $F_3CC(O)SC_6H_4$-*p*-CH_3 (7a) with 1-Octyne (1a) in the Presence of $Pt(PPh_3)_4$ (Entry 3 of Table 3, Entry 1 of Table 4): General Procedure of Platinum-Catalyzed Trifluoroacetylthiolation of Alkynes Using Thioesters: Into a two-necked 3 mL reaction glass were added $Pt(PPh_3)_4$ (31.1 mg, 0.025 mmol), **7a** (108 mg, 0.492 mmol), **1a** (82.0 mg, 0.74 mmol) and xylene (0.5 mL) under a N_2 atmosphere. After the solution was refluxed for 10 h, the reaction mixture was filtered through Celite, the solvent was evaporated and the resultant crude product was dried *in vacuo*. *Z*-**8a** and *E*-**8a** were obtained in 14% (23.2 mg) and 64% (106 mg) yields by preparative TLC using hexane as an eluent.

(*E*)-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4$-*p*-$CH_3$ (*E*-8a): pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 7.1 Hz, 3 H), 1.32-1.48 (m, 6 H), 1.66 (tt, 2 H), 2.42 (s, 3 H), 2.89 (t, J = 7.6 Hz, 2 H), 5.74 (s, 1 H), 7.29 (d, J = 8.1 Hz, 2 H), 7.37 (d, J = 8.1 Hz, 2 H); NOE experiment: Irradiation of the singlet of vinylic proton at δ 5.75 resulted in 2.7% enhancement of the signal at δ 7.37 (aryl doublet) and the triplet of allylic proton at δ 2.89 resulted in 0.58% enhancement of the signal at δ 7.37 (aryl doublet); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 22.0, 23.1, 29.8, 30.2, 32.0, 36.0, 108.5, 113.9 (q, $J_{C\text{-}F}$ = 291 Hz), 125.2, 131.5, 135.6, 141.8, 176.2 (q, $J_{C\text{-}F}$ = 33.5 Hz), 180.9; IR (NaCl) 2957, 2929, 2838, 1700, 1597, 1560, 1493, 1458, 1436, 1291, 1202, 1143, 1077, 1018, 842, 811, 725, 686 cm^{-1}; mass spectrum (EI) m/z 330 (M^+, 42); HRMS calcd for $C_{17}H_{21}F_3OS$ 330.1265, found 330.1270 Anal. Calcd for $C_{17}H_{21}F_3OS$: C, 61.80; H, 6.41. Found: C, 62.09; H, 6.69.

(*Z*)-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4$-*p*-$CH_3$ (*Z*-8a): yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, J = 6.8 Hz, 3 H), 1.05-1.12 (m, 6 H), 1.35-1.40 (m, 2 H), 2.25 (t, J = 7.8 Hz, 2 H), 2.40 (s, 1 H), 6.51 (s, 1 H), 7.23 (d, J = 7.8 Hz, 2 H), 7.41 (d, J = 7.8 Hz, 2 H); NOE experiment: Irradiation of the triplet of allylic proton at δ 2.25 resulted in 3.8% enhancement of the signal at δ 7.41 (aryl doublet) and 8.4% enhancement of the signal at δ 6.51 (vinylic singlet); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 21.3, 22.3, 28.5, 29.9, 31.1, 37.5, 110.2, 116.4 (q, J_{C-F} = 290 Hz), 125.7, 130.2, 135.4, 140.6, 177.3 (q, J_{C-F} = 34.4 Hz), 178.0; IR (NaCl) 2931, 2860, 2359, 1681, 1674, 1598, 1563, 1548, 1538, 1532, 1520, 1506, 1494, 1463, 1456, 1362, 1300, 1199, 1146, 1105, 1018, 864, 813, 729, 686 cm^{-1}; mass spectrum (EI) m/z 330 (M^+, 41); Anal. Calcd for $C_{17}H_{21}F_3OS$: C, 61.80; H, 6.41. Found: C, 62.02; H, 6.66.

Other trifluoroacetylthiolation products **8d-l** were synthesized by similar procedures.

(*E*)-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}OCH_3$ (*E*-8d) (Entry 2 of Table 4): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 6.6 Hz, 3 H), 1.33-1.46 (m, 6 H), 1.64 (tt, 2 H), 2.88 (t, *J* = 7.6 Hz, 2 H), 5.73 (s, 1 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 7.40 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.5, 29.3, 29.6, 31.4, 35.3, 55.4, 107.8, 115.6, 116.3 (q, J_{C-F} = 291 Hz), 118.7, 136.7, 161.5, 175.4 (q, J_{C-F} = 33.5 Hz), 180.9; IR (NaCl) 2958, 2930, 2858, 1697, 1593, 1560, 1553, 1496, 1465, 1441, 1292, 1254, 1202, 1174, 1143, 1106, 1077, 1031, 860, 831, 800, 726, 686 cm^{-1}; mass spectrum (EI) m/z 346 (M^+, 58); Anal. Calcd for $C_{17}H_{21}F_3O_2S$: C, 58.94; H, 6.11. Found: C, 58.88; H, 6.09.

(*Z*)-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}OCH_3$ (*Z*-8d) (Entry 2 of Table 4): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.1 Hz, 3 H), 1.08-1.19 (m, 6 H), 1.39 (b, 2 H), 2.24 (t, *J* = 7.8 Hz, 2 H), 3.85 (s, 3 H), 6.51 (s, 1 H), 6.95 (d, *J* = 8.6 Hz, 2 H), 7.44 (d, *J* = 78.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.3, 28.5, 29.9, 31.1, 37.5, 55.4, 110.1, 114.9, 116.4 (q, J_{C-F} = 289 Hz), 119.8, 137.0, 161.2, 177.2 (q, J_{C-F} = 33.9 Hz), 178.7; IR (NaCl) 2958, 2931, 2859, 1682, 1593, 1572, 1538, 1495, 1464, 1442, 1408, 1364, 1308, 1291, 1199, 1174, 1144, 1105, 1031, 864, 832, 729 cm^{-1}; mass spectrum (EI) m/z 346 (M^+, 69); Anal. Calcd for $C_{17}H_{21}F_3O_2S$: C, 58.94; H, 6.11. Found: C, 59.05; H, 6.02.

(*E*)-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_5$ (*E*-8e) (Entry 3 of Table 4): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 6.6 Hz, 3 H), 1.33-1.49 (m, 6 H), 1.66 (tt, 2 H), 2.90 (t, *J* = 7.8 Hz, 2 H), 5.72 (s, 1 H), 7.50 (b, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.5, 29.2, 29.6, 31.4, 35.4, 108.1, 116.2 (q, $J_{C\text{-}F}$ = 291 Hz), 128.1, 130.1, 130,8, 135.2, 175.5 (q, $J_{C\text{-}F}$ = 33.4 Hz), 179.7; IR (NaCl) 2958, 2930, 2859, 1699, 1560, 1477, 1442, 1291, 1203, 1143, 1077, 1024, 837, 750, 706, 685 cm^{-1}; mass spectrum (EI) m/z 316 (M^+, 26); Anal. Calcd for $C_{16}H_{19}F_3O_2S$: C, 60.74; H, 6.05. Found: C, 60.53; H, 6.05.

(*Z*)-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_5$ (*Z*-8e) (Entry 3 of Table 4): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, *J* = 6.7 Hz, 3 H), 1.05-1.17 (m, 6 H), 1.39 (m, 2 H), 2.25 (t, *J* = 7.6 Hz, 2 H), 6.53 (s, 1 H), 7.43-7.56 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.3, 28.6, 29.9, 31.1, 37.7, 110.5, 116.5 (q, $J_{C\text{-}F}$ = 292 Hz), 129.3, 129.5, 130,2, 135.6, 177.2, 177.4 (q, $J_{C\text{-}F}$ = 34.4 Hz); IR (NaCl) 2958, 2931, 2860, 1682, 1537, 1477, 1468, 1441, 1364, 1300, 1261, 1200, 1145, 1106, 1024, 862, 818, 752, 730, 706, 692 cm^{-1}; mass spectrum (EI) m/z 316 (M^+, 30); HRMS calcd for $C_{16}H_{19}F_3OS$: 316.1109. Found: 316.1112.

(*E*)-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}Cl$ (*E*-8f) (Entry 4 of Table 4): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 6.6 Hz, 3 H), 1.31-1.48 (m, 6 H), 1.68 (m, 2 H), 2.88 (t, *J* = 7.8 Hz, 2 H), 5.73 (s, 1 H), 7.44 (d, *J* = 8.6 Hz, 2 H), 7.48 (d, *J* = 8.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.2, 29.6, 31.4, 35.3, 108.3, 116.2 (q, $J_{C\text{-}F}$ = 291 Hz), 126.6, 130.5, 136.5, 137.4, 175.6 (q, $J_{C\text{-}F}$ = 33.5 Hz), 178.8; IR (NaCl) 2958, 2930, 2859, 1698, 1682, 1574, 1568, 1556, 1477, 1454, 1436, 1392, 1292, 1204, 1146, 1096, 1076, 1014, 859, 839, 825, 749, 726, 684 cm^{-1}; mass spectrum (EI) m/z 350 (M^+, 41); Anal. Calcd for $C_{16}H_{18}ClF_3OS$: C, 54.78; H, 5.17. Found: C, 54.68; H, 5.13.

(*Z*)-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SC_6H_4\text{-}p\text{-}Cl$ (*Z*-8f) (Entry 4 of Table 4): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7.3 Hz, 3 H), 1.07-1.43 (m, 8 H), 2.24 (t, *J* = 7.6 Hz, 2 H), 6.54 (s, 1 H), 7.42 (d, *J* = 8.3 Hz, 2 H), 7.49 (d, *J* = 8.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.3, 28.5, 29.7, 31.1, 37.6, 110.8, 116.3 (q, $J_{C\text{-}F}$ = 289 Hz), 127.7, 129.7, 136.8, 136.8, 176.1, 177.5 (q, $J_{C\text{-}F}$ = 34.4 Hz); IR (NaCl) 2958, 2931, 2859, 1682, 1574, 1538, 1476, 1389, 1364, 1296, 1201, 1176, 1146, 1107, 1093, 1014, 865, 824, 748, 728, 684 cm^{-1}; mass spectrum (EI) m/z 350 (M^+, 39); HRMS calcd for $C_{16}H_{18}ClF_3OS$: 350.0719. Found: 350.0714.

(*E*)-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})SCH_2C_6H_5$ (*E*-8g) (Entry 5 of Table 4): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3 H), 1.29-1.41 (m, 6 H), 1.57 (tt, 2 H), 2.83 (t, J = 7.8 Hz, 2 H), 4.09 (s, 2 H), 6.17 (s, 1 H), 7.30-7.37 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.5, 29.2, 29.7, 31.4, 36.2, 37.3, 106.9, 116.5 (q, $J_{C\text{-}F}$ = 291 Hz), 128.1, 128.9, 129.0, 133.6, 174.9 (q, $J_{C\text{-}F}$ = 32.3 Hz), 178.1; IR (NaCl) 2957, 2930, 2858, 1698, 1552, 1496, 1455, 1435, 1295, 1203, 1142, 1079, 822, 711, 696 cm^{-1}; mass spectrum (EI) m/z 330 (M$^+$, 2.2); Anal. Calcd for $C_{17}H_{21}F_3OS$: C, 61.80; H, 6.41. Found: C, 61.67; H, 6.42.

(*E*)-$F_3CC(O)C(H)=C(n\text{-}C_6H_{13})S\text{-}n\text{-}C_{10}H_{21}$ (*E*-8h) (Entry 6 of Table 4): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (b, 6 H), 1.27-1.42 (m, 20 H), 1.57 (tt, 2 H), 1.70 (tt, 2 H), 2.82-2.85 (m, 4 H), 6.01 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.1, 22.5, 22.7, 27.0, 28.9, 29.0, 29.2, 29.3, 29.4, 29.5, 29.8, 31.4, 31.9, 32.2, 36.6, 106.2, 116.6 (q, $J_{C\text{-}F}$ = 292 Hz), 174.7 (q, $J_{C\text{-}F}$ = 33.0 Hz), 179.3; IR (NaCl) 2957, 2927, 2856, 1698, 1556, 1467, 1434, 1293, 1201, 1143, 1079, 860, 824, 724, 693 cm^{-1}; mass spectrum (EI) m/z 380 (M$^+$, 8.5); Anal. Calcd for $C_{20}H_{35}F_3OS$: C, 63.12; H, 9.27. Found: C, 63.18; H, 9.23.

(*E*)-$F_3CC(O)C(H)=C((CH_2)_4Cl)SC_6H_5$ (*E*-8i) (Entry 7 of Table 4): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79-1.86 (tt, 2 H), 1.90-1.97 (tt, 2 H), 2.93 (t, J = 7.8 Hz, 2 H), 3.59 (t, J = 6.4 Hz, 2 H), 5.76 (s, 1 H), 7.5-7.54 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9, 32.1, 34.4, 44.4, 108.5, 116.1 (q, $J_{C\text{-}F}$ = 291 Hz), 127.8, 130.2, 130.9, 135.2, 175.6 (q, $J_{C\text{-}F}$ = 33.9 Hz), 178.5; IR (NaCl) 3063, 2957, 2868, 1698, 1556, 1477, 1442, 1292, 1203, 1143, 1077, 1024, 838, 750, 706, 686, cm^{-1}; mass spectrum (EI) m/z 322 (M$^+$, 45); Anal. Calcd for $C_{14}H_{14}ClF_3OS$: C, 52.10; H, 4.37. Found: C, 52.37; H, 4.41.

(*Z*)-$F_3CC(O)C(H)=C((CH_2)_4Cl)SC_6H_5$ (*Z*-8i) (Entry 7 of Table 4): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53-1.57 (m, 4 H), 2.29 (t, J = 7.2 Hz, 2 H), 3.34 (t, J = 6.0 Hz, 2 H), 6.54 (s, 1 H), 7.45-7.57 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0, 31.5, 36.8, 44.0, 110.7, 116.3 (q, $J_{C\text{-}F}$ = 289 Hz), 129.0, 129.6, 130.4, 135.5, 175.8, 177.4 (q, $J_{C\text{-}F}$ = 33.8 Hz); IR (NaCl) 3025, 2957, 2869, 1682, 1577, 1534, 1493, 1458, 1446, 1364, 1302, 1200, 1146, 1110, 1092, 1018, 863, 813, 729, 687, 654 cm^{-1}; mass spectrum (EI) m/z 322 (M^+, 54); HRMS calcd for $C_{17}H_{21}F_3OS$: 322.0406. Found: 322.0399.

(*E*)-$F_3CC(O)C(H)=C((CH_2)_3CN)SC_6H_5$ (*E*-8j) (Entry 8 of Table 4): pale yellow solid; mp 64-66 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (m, 2 H), 2.53 (t, J = 6.8 Hz, 2 H), 3.01 (t, J = 6.8 Hz, 2 H), 5.80 (s, 1 H), 7.53 (b, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0, 25.2, 34.0, 109.3, 116.1 (q, $J_{C\text{-}F}$ = 294 Hz), 118.9, 127.5, 130.4, 131.2, 135.2, 176.0 (q, $J_{C\text{-}F}$ = 34.4 Hz), 176.2; IR (NaCl) 3064, 2954, 2244, 1687, 1548, 1478, 1453, 1439, 1294, 1274, 1188, 1145, 1078, 1025, 999, 868, 854, 840, 766, 749, 708, 685, 574, 452 cm^{-1}; mass spectrum (EI) m/z 299 (M^+, 47); Anal. Calcd for $C_{14}H_{12}F_3NOS$: C, 56.18; H, 4.04; N, 4.68. Found: C, 56.18; H, 3.98; N, 4.73.

(*Z*)-$F_3CC(O)C(H)=C((CH_2)_3CN)SC_6H_5$ (*Z*-8j) (Entry 8 of Table 4): yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.73 (tt, J = 7.0, 7.8 Hz, 2 H), 2.16 (t, J = 7.0 Hz, 2 H), 2.45 (t, J = 7.8 Hz, 2 H), 6.56 (s, 1 H), 7.45-7.57 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7, 25.5, 36.4, 111.7, 116.5 (q, $J_{C\text{-}F}$ = 289 Hz), 118.5, 128.9, 130.1, 131.0, 135.7, 173.4, 177.8 (q, $J_{C\text{-}F}$ = 34.8 Hz); IR (NaCl) 3062, 2947, 2248, 1602, 1578, 1478, 1456, 1442, 1368, 1304, 1202, 1143, 1111, 1024, 1002, 865, 818, 754, 730, 706, 694 cm^{-1}; mass spectrum (EI) m/z 299 (M^+, 33); HRMS calcd for $C_{14}H_{12}F_3NOS$: 299.0592. Found: 299.0590.

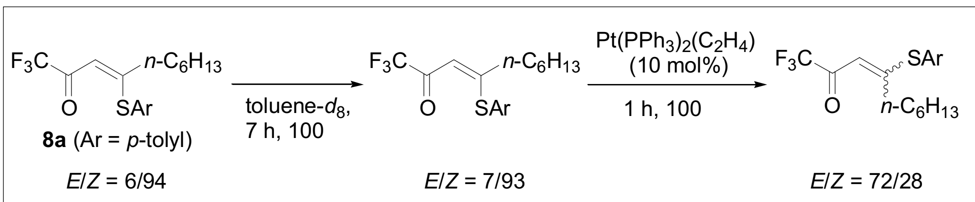
(*E*)-$F_3CC(O)C(H)=C((CH_2)_3CO_2CH_3)SC_6H_5$ (*E*-8k) (Entry 9 of Table 4): pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 2.01 (tt, 2 H), 2.48 (t, J = 7.6 Hz, 2 H), 2.96 (t, J = 7.8 Hz, 2 H), 3.70 (s, 3 H), 5.75 (s, 1 H), 7.50-7.54 (b, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 33.3, 34.2, 51.7, 108.7, 116.1 (q, $J_{C\text{-}F}$ = 291 Hz), 127.8, 130.2, 130.9, 135.2, 173.3, 175.6 (q, $J_{C\text{-}F}$ = 33.5 Hz), 178.0; IR (NaCl) 3063, 2953, 1738, 1732, 1698, 1565, 1556, 1477, 1441, 1368, 1293, 1255, 1204, 1142, 1076, 1024, 1000, 838, 752, 706, 689 cm^{-1}; mass spectrum (EI) m/z 332 (M^+, 13); Anal. Calcd for $C_{15}H_{15}F_3O_3S$: C, 54.21; H, 4.55. Found: C, 54.21; H, 4.49.

(*Z*)-$F_3CC(O)C(H)=C((CH_2)_3CO_2CH_3)SC_6H_5$ (*Z*-8k) (Entry 9 of Table 4): yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.72 (tt, 2 H), 2.11 (t, J = 7.2 Hz, 2 H), 2.32 (t, J = 7.8 Hz, 2 H), 3.60 (s, 3 H), 6.55 (s, 1 H), 7.42-

7.56 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 32.6, 36.5, 51.5, 110.8, 116.3 (q, $J_{C\text{-}F}$ = 289 Hz), 128.9, 129.5, 130.3, 135.4, 172.7, 175.3, 177.3 (q, $J_{C\text{-}F}$ = 34.4 Hz); IR (NaCl) 3062, 2953, 1738, 1682, 1538, 1478, 1440, 1366, 1300, 1254, 1201, 1146, 1111, 1091, 1024, 1001, 887, 856, 838, 820, 754, 730, 706, 693 cm^{-1}; mass spectrum (EI) m/z 332 (M^+, 16); Anal. Calcd for $C_{15}H_{15}F_3O_3S$: C, 54.21; H, 4.55. Found: C, 54.01; H, 4.55.

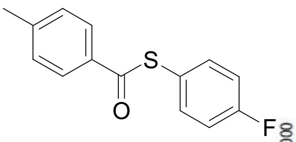
(*E*)-$F_3CC(O)C(H)=C(CH_2(c\text{-}C_5H_9))SC_6H_5$ (*E*-8l) (Entry 10 of Table 4): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (m 2 H), 1.55-1.69 (m, 4 H), 1.87 (m, 2 H), 2.21 (m, 1 H), 3.00 (d, *J* = 7.3 Hz, 2 H), 5.71 (s, 1 H), 7.51 (b, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 32. 5, 40.5, 40.5, 108.5, 116.3 (q, $J_{C\text{-}F}$ = 294 Hz), 128.4, 130.2, 130.8, 135.2, 175.7 (q, $J_{C\text{-}F}$ = 33.6 Hz), 179.2; IR (NaCl) 3063, 2953, 2869, 1808, 1556, 1476, 1441, 1296, 1201, 1142, 1077, 1024, 846, 837, 749, 707, 690 cm^{-1}; mass spectrum (EI) m/z 314 (M^+, 22); Anal. Calcd for $C_{16}H_{17}F_3OS$: C, 61.13; H, 5.45. Found: C, 60.94; H, 5.38.

(*Z*)-$F_3CC(O)C(H)=C(CH_2(c\text{-}C_5H_9))SC_6H_5$ (*Z*-8l) (Entry 10 of Table 4): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (m, 2 H), 1.47-1.57 (m, 6 H), 1.87 (m, 1 H), 2.27 (d, *J* = 7.1 Hz, 2 H), 6.54 (s, 1 H), 7.43-7.55 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 32.1, 39.8, 43.4, 110.9, 116.4 (q, $J_{C\text{-}F}$ = 300 Hz), 129.4, 130.1, 135.2, 135.6, 176.2, 177.2 (q, $J_{C\text{-}F}$ = 33.9 Hz); IR (NaCl) 3062, 2953, 2869, 1682, 1538, 1477, 1441, 1367, 1345, 1296, 1200, 1144, 1110, 1070, 1024, 1002, 863, 819, 752, 730, 706, 693 cm^{-1}; mass spectrum (EI) m/z 314 (M^+, 26); Anal. Calcd for $C_{16}H_{17}F_3OS$: C, 61.13; H, 5.45. Found: C, 61.28; H, 5.54.

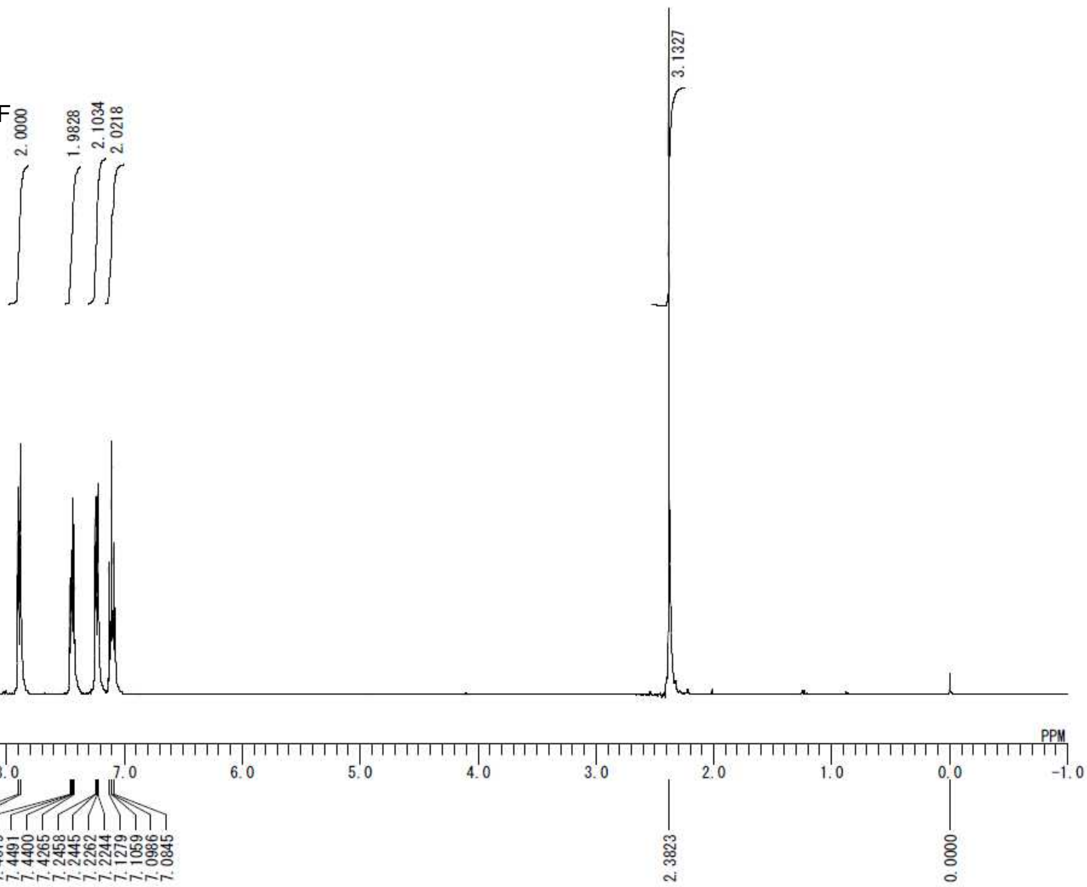


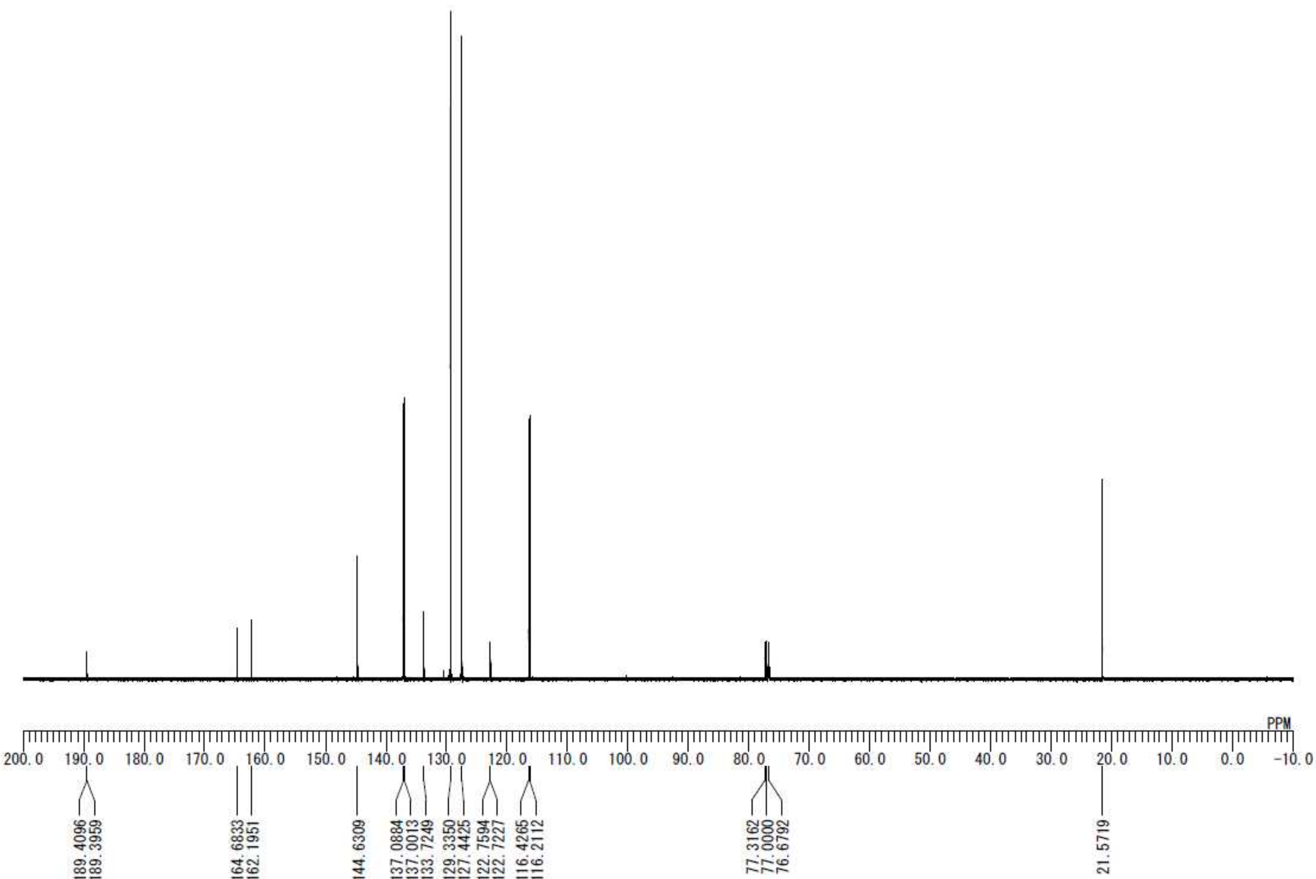
(S4)

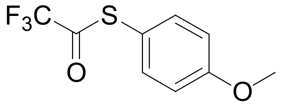
***Z*-to-*E* Isomerization of 8a in Toluene-d_8 (eq S4) (Ref 20):** Into a dry Pyrex NMR tube were added **8a** (*E*/*Z* = 6/94) (0.0506 mmol), 1,4-dioxane (0.0585 mmol as an internal standard) and 0.5 mL of toluene-d_8 under N_2 atmosphere. Then the sample was heated at 100 °C for 7 h; however, isomerization was hardly confirmed by ^{1}H NMR spectroscopy (*E*/*Z* = 7/93). Additional heating after the addition of $Pt(PPh_3)_2(C_2H_4)$ (0.006 mmol) resulted in the formation of *E*-**8a** (*E*/*Z* = 72/28).



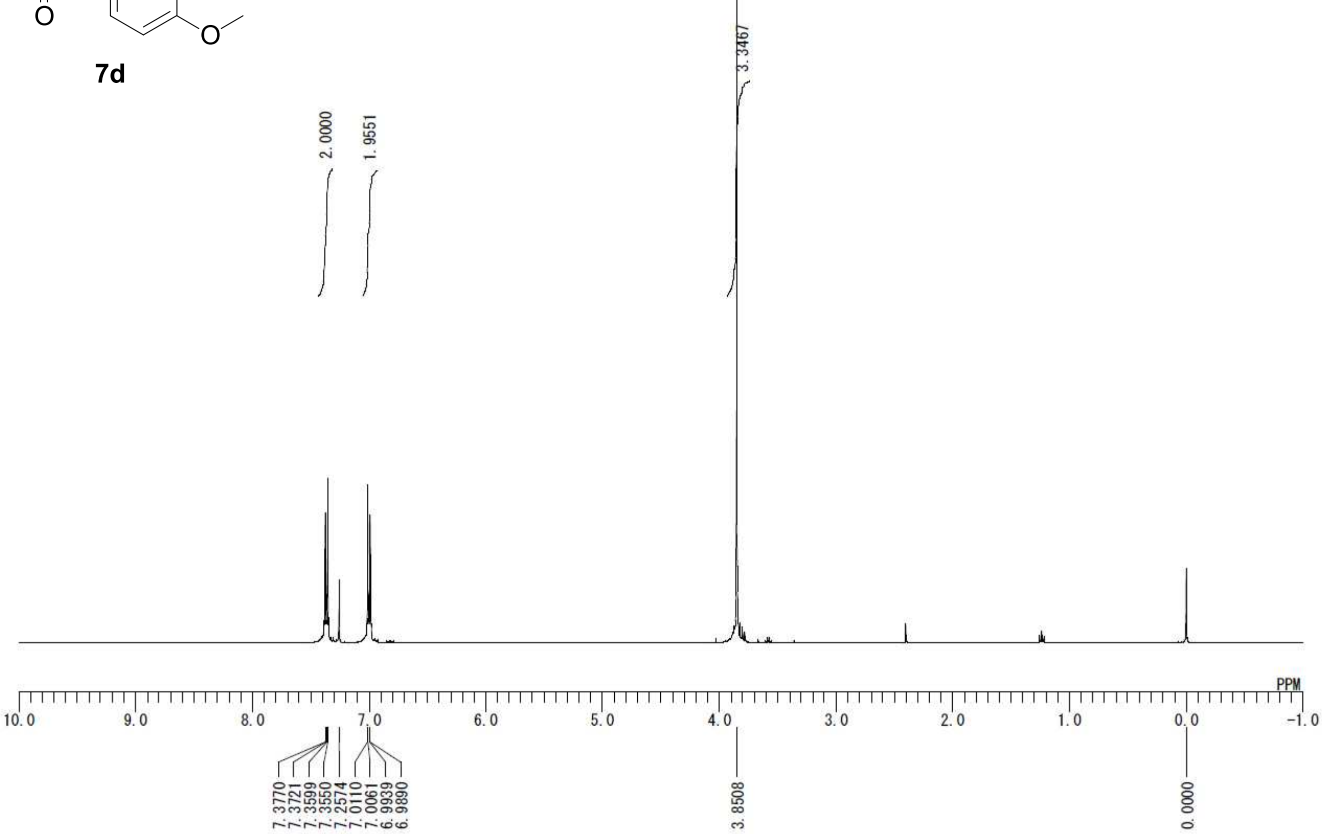
2c






F3C
S
O
O

7d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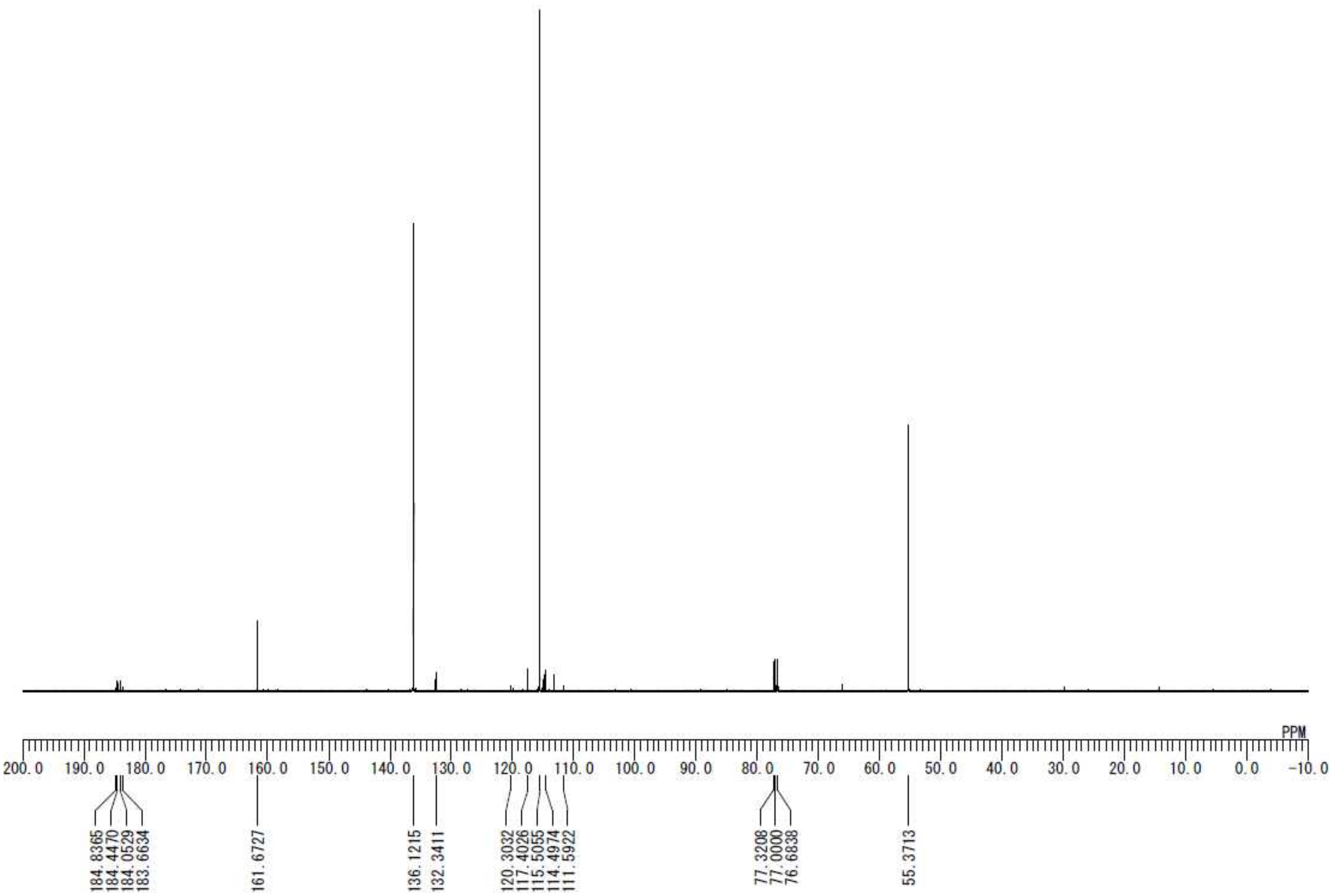
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70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
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184.0529
183.6634
161.6727
136.1215
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120.3032
117.4026
115.5055
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77.3208
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76.6838
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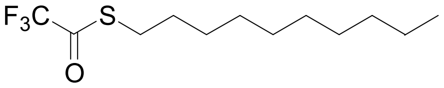
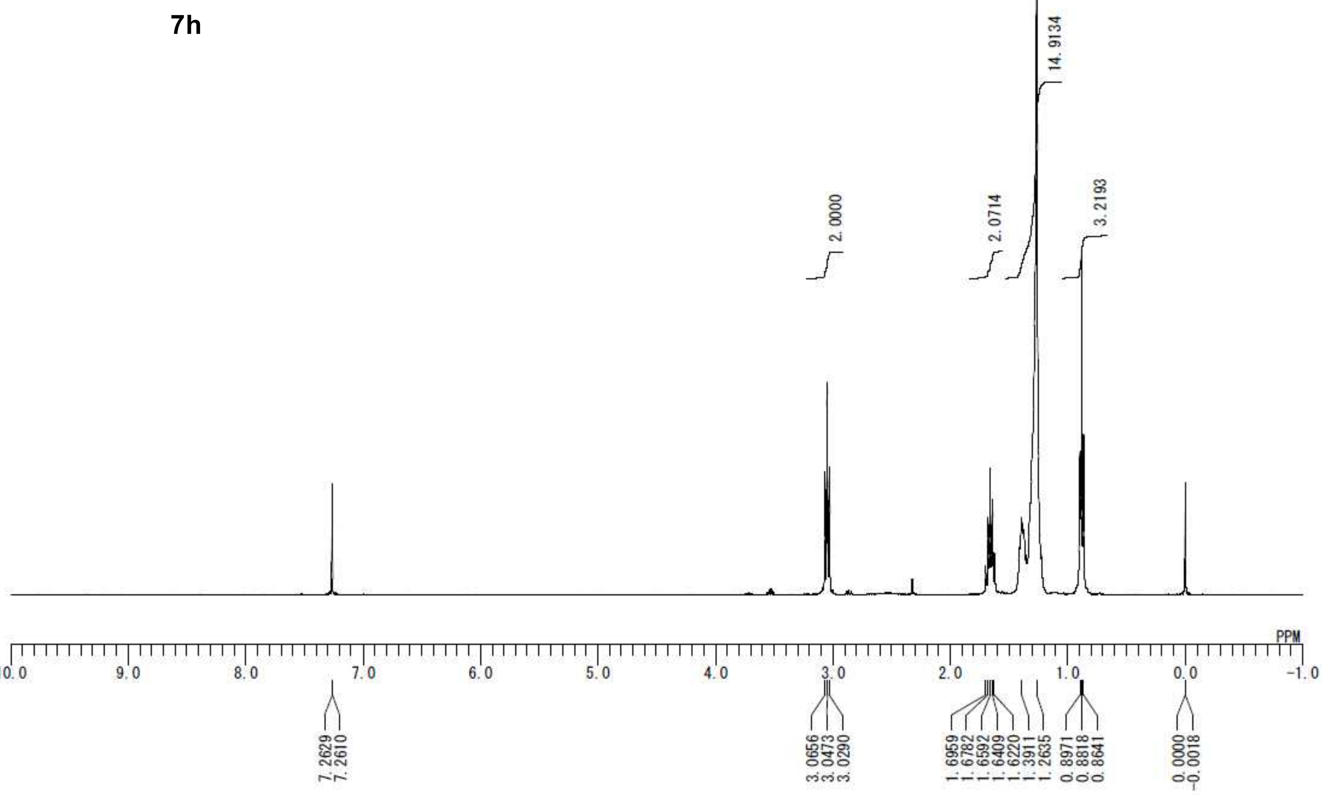
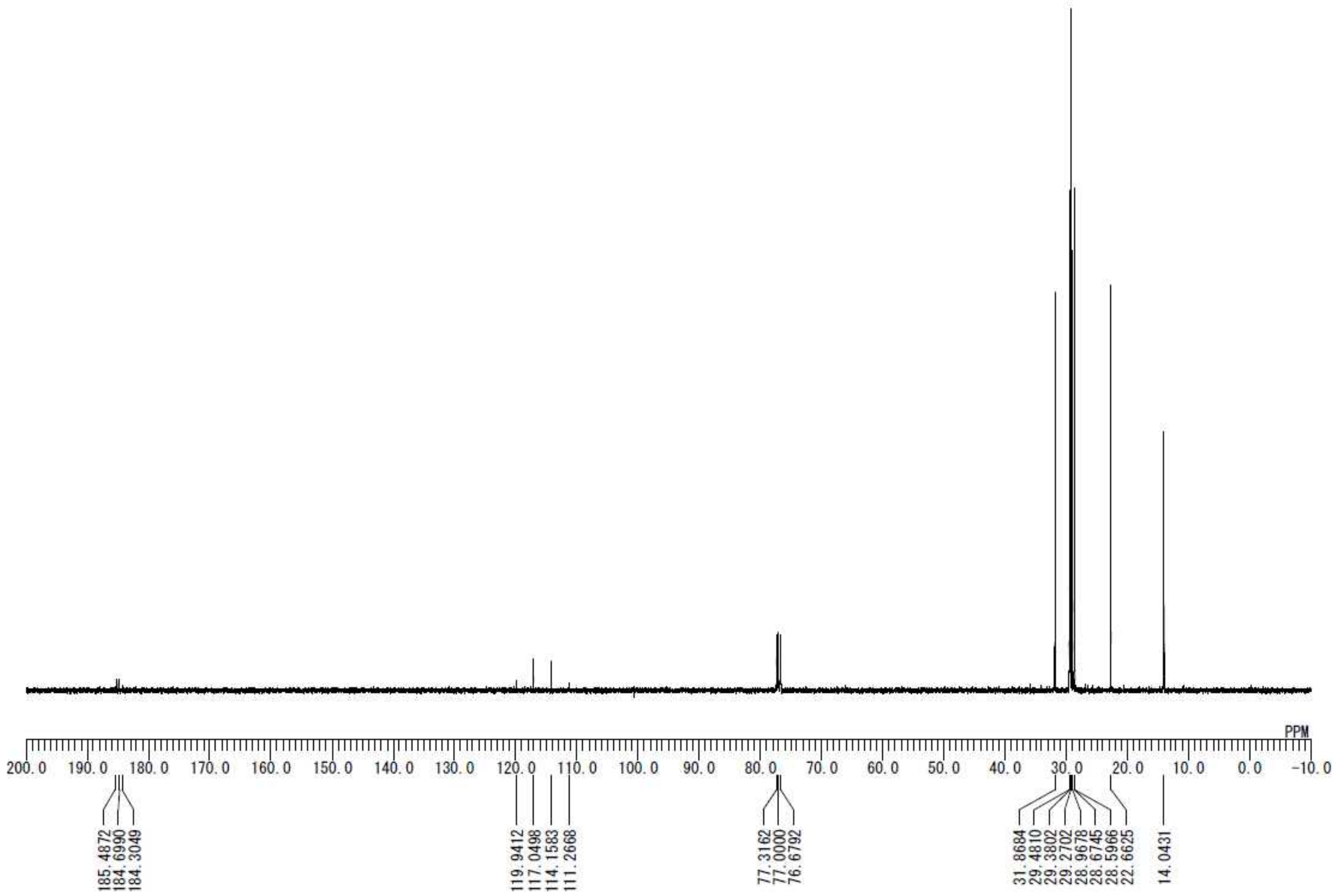
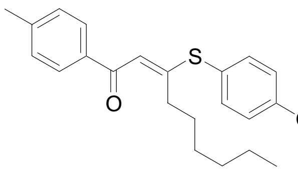


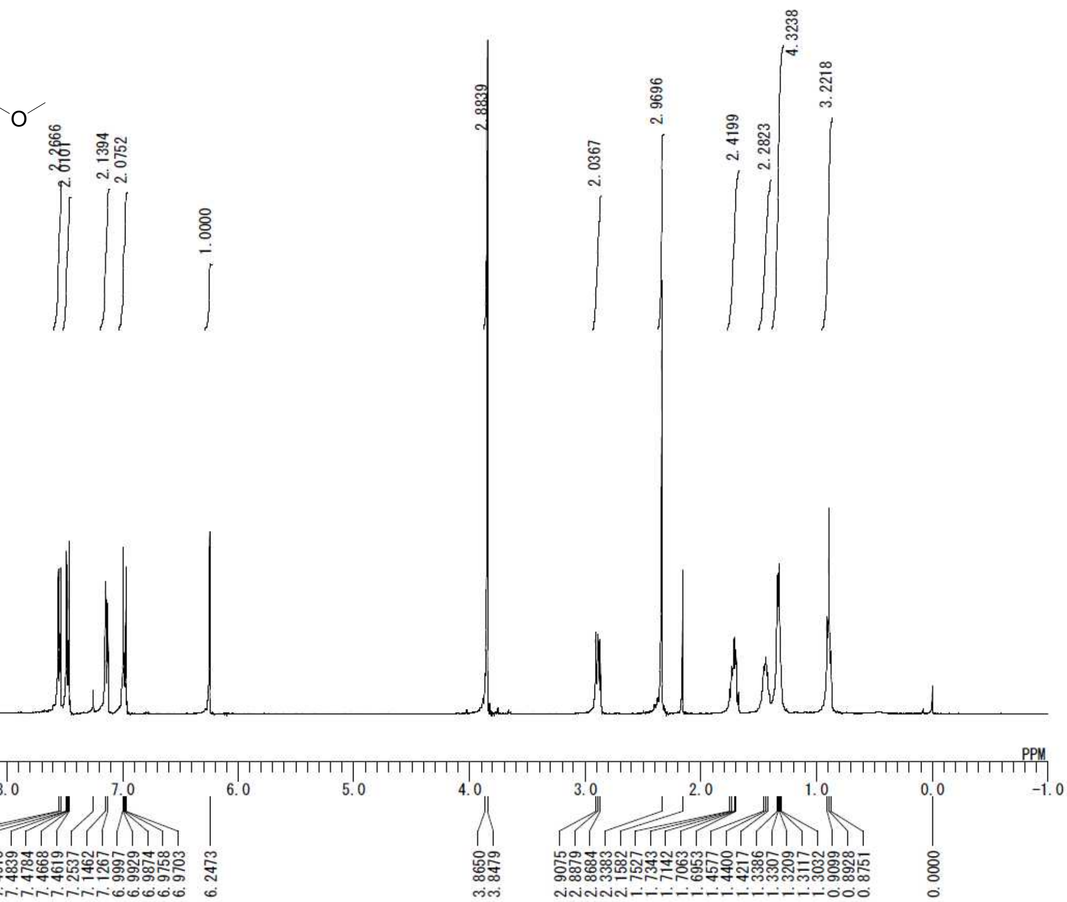
7h







E-**4a**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1.7142
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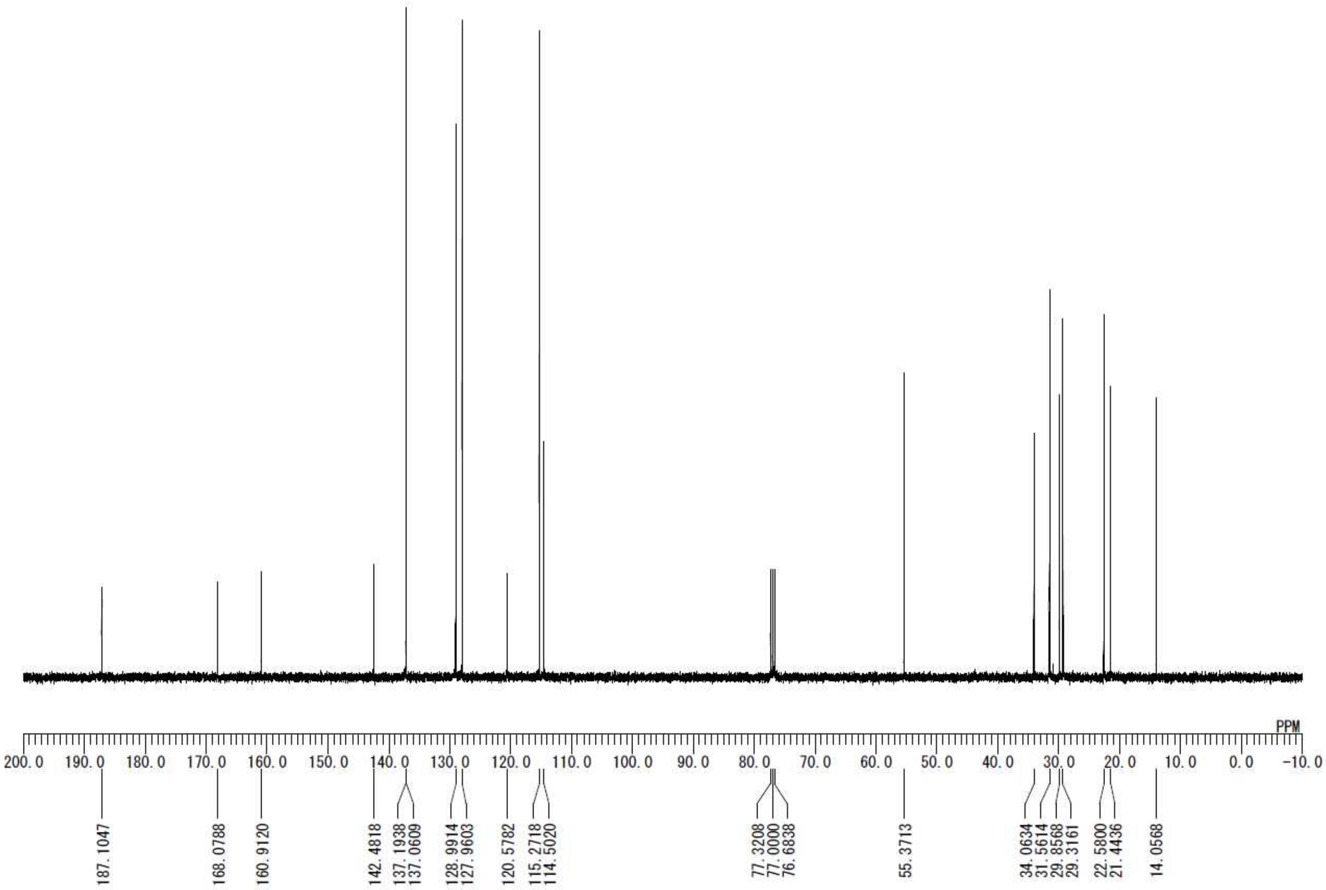
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142.4818
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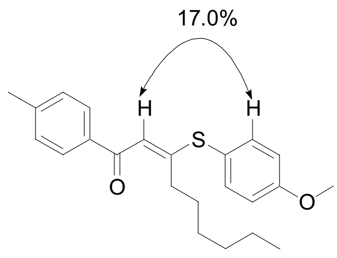
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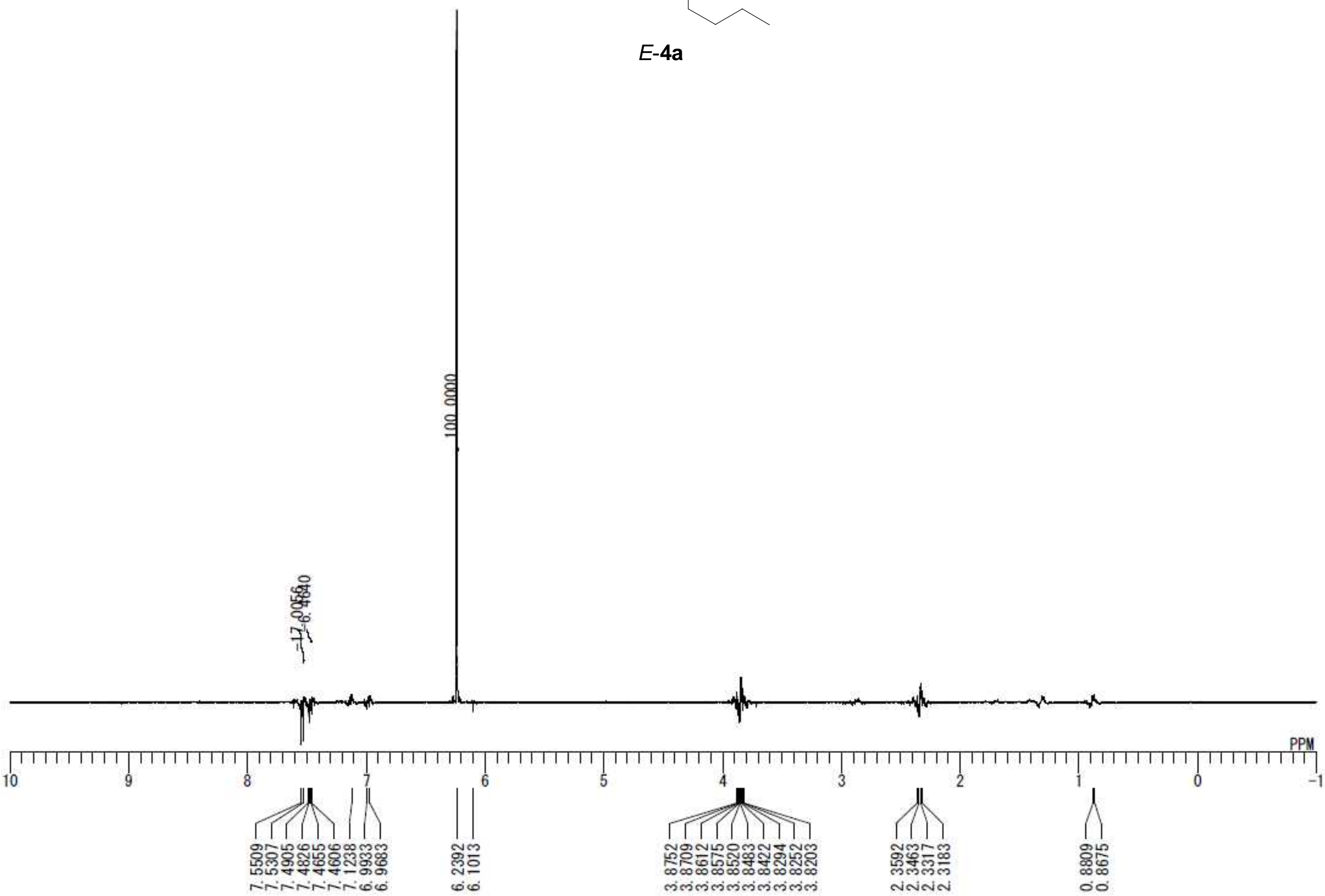
H
H
S
O
O

E-**4a**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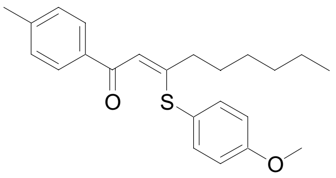

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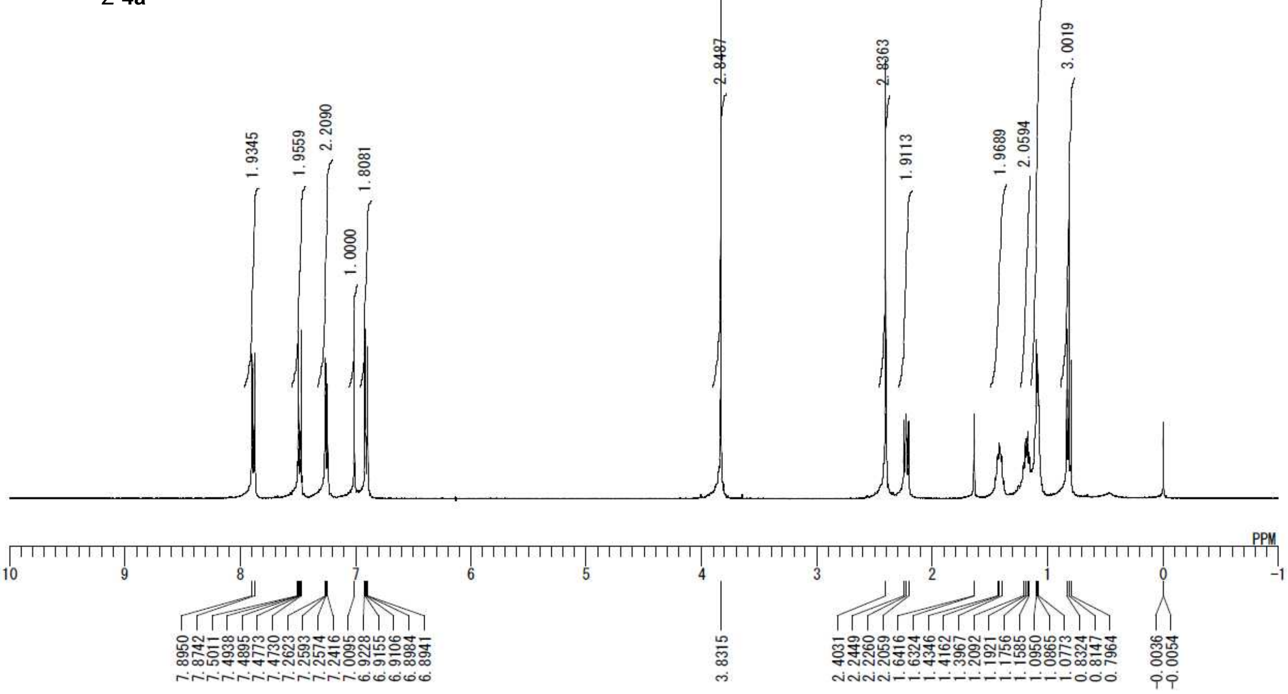

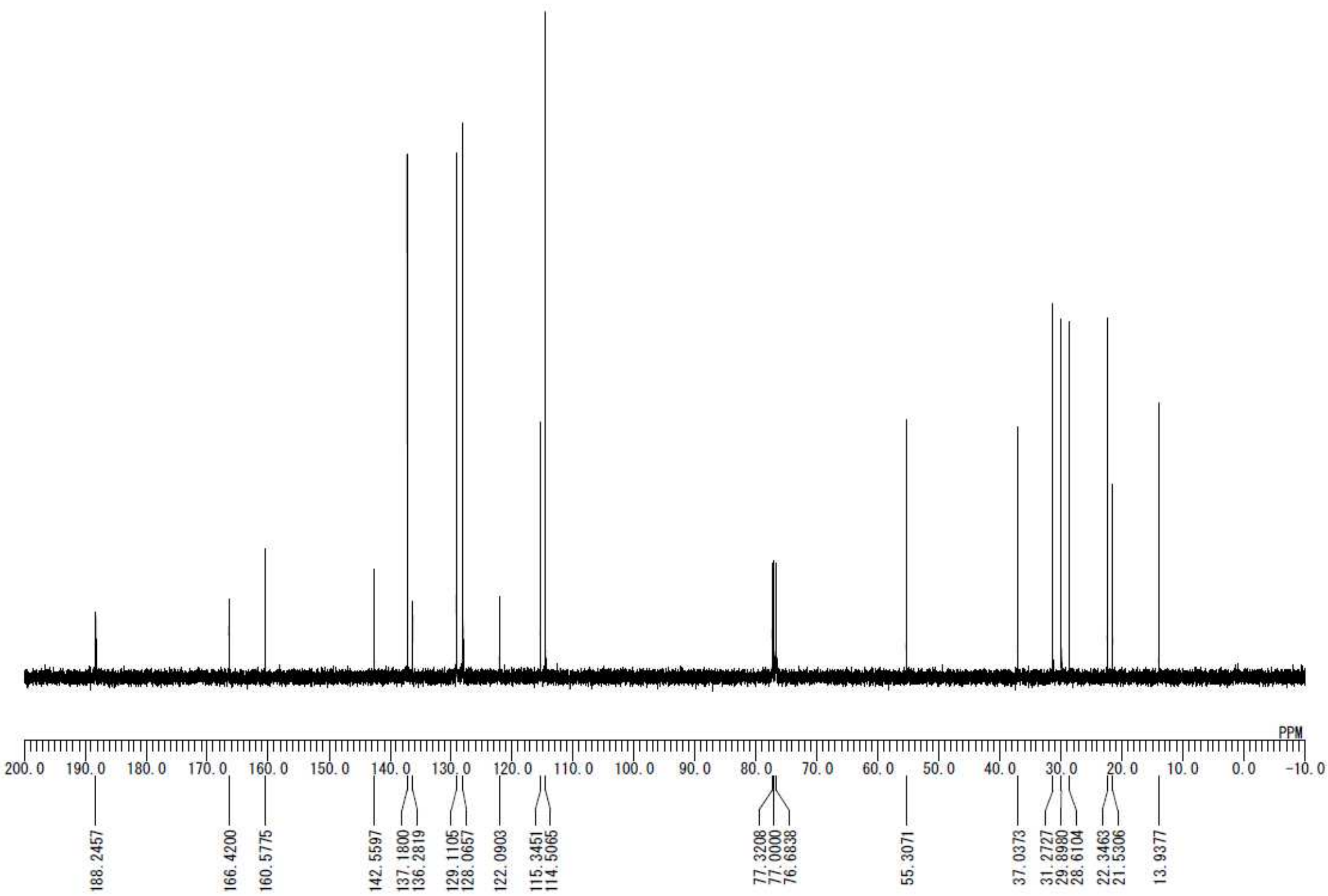

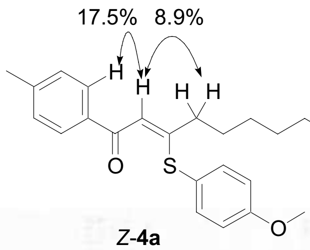
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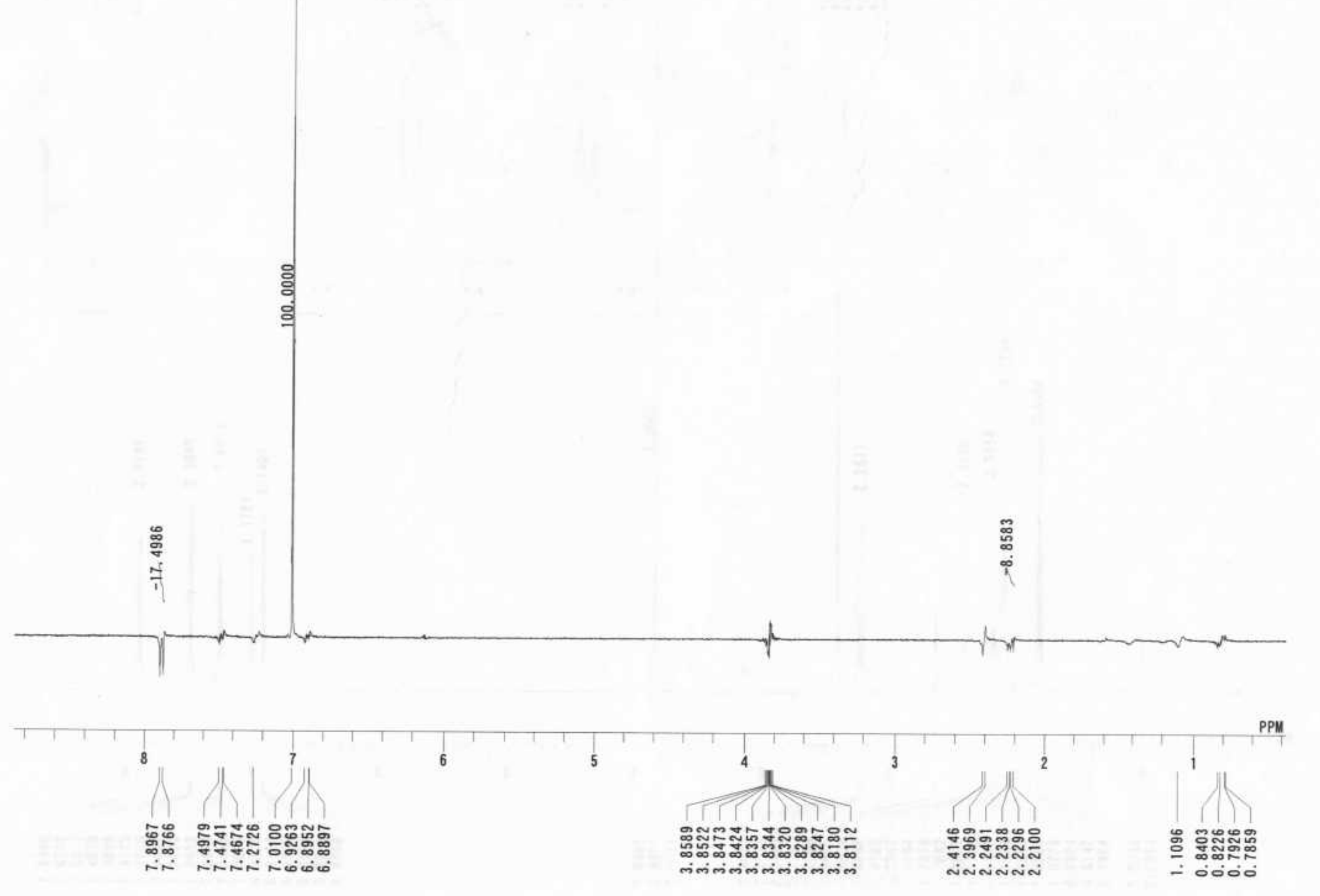
8.9%
H
H
H H
O
S
O

Z-**4a**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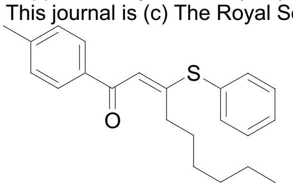
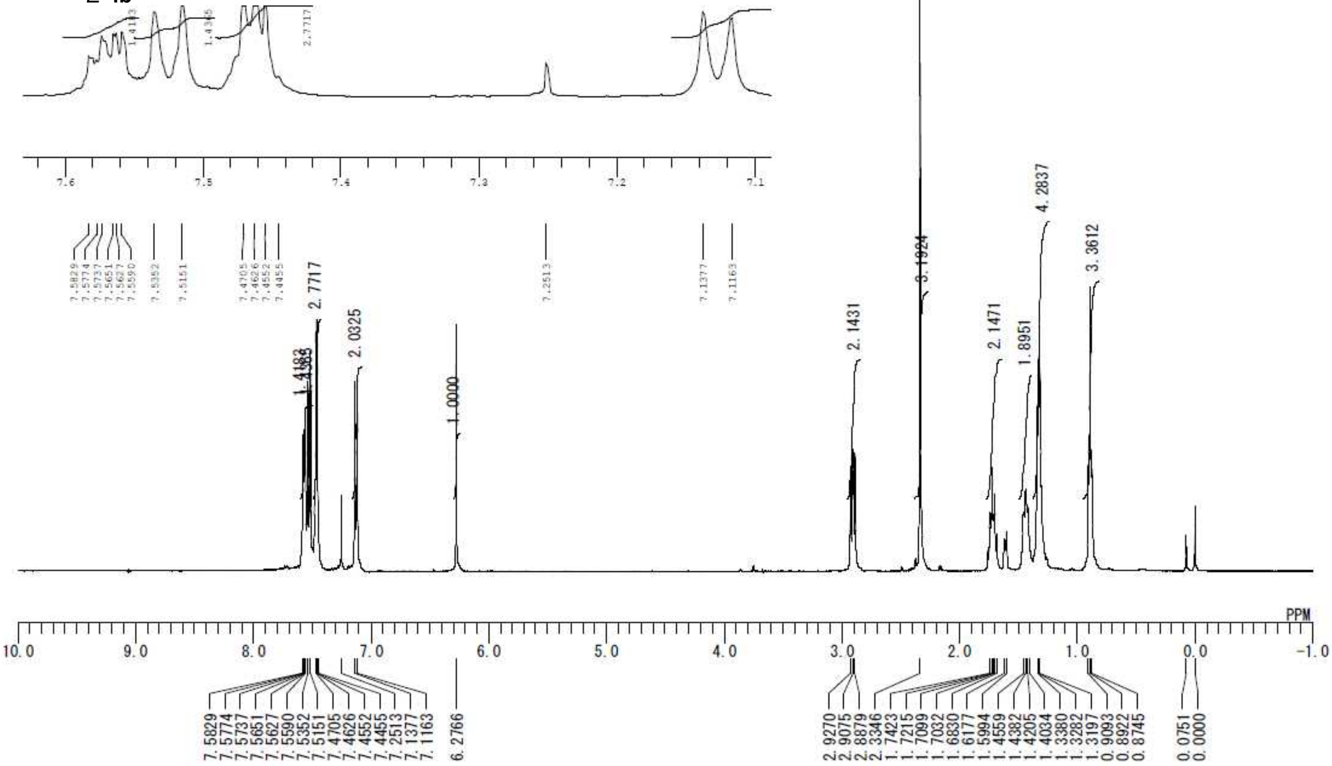

S
O

E-**4b**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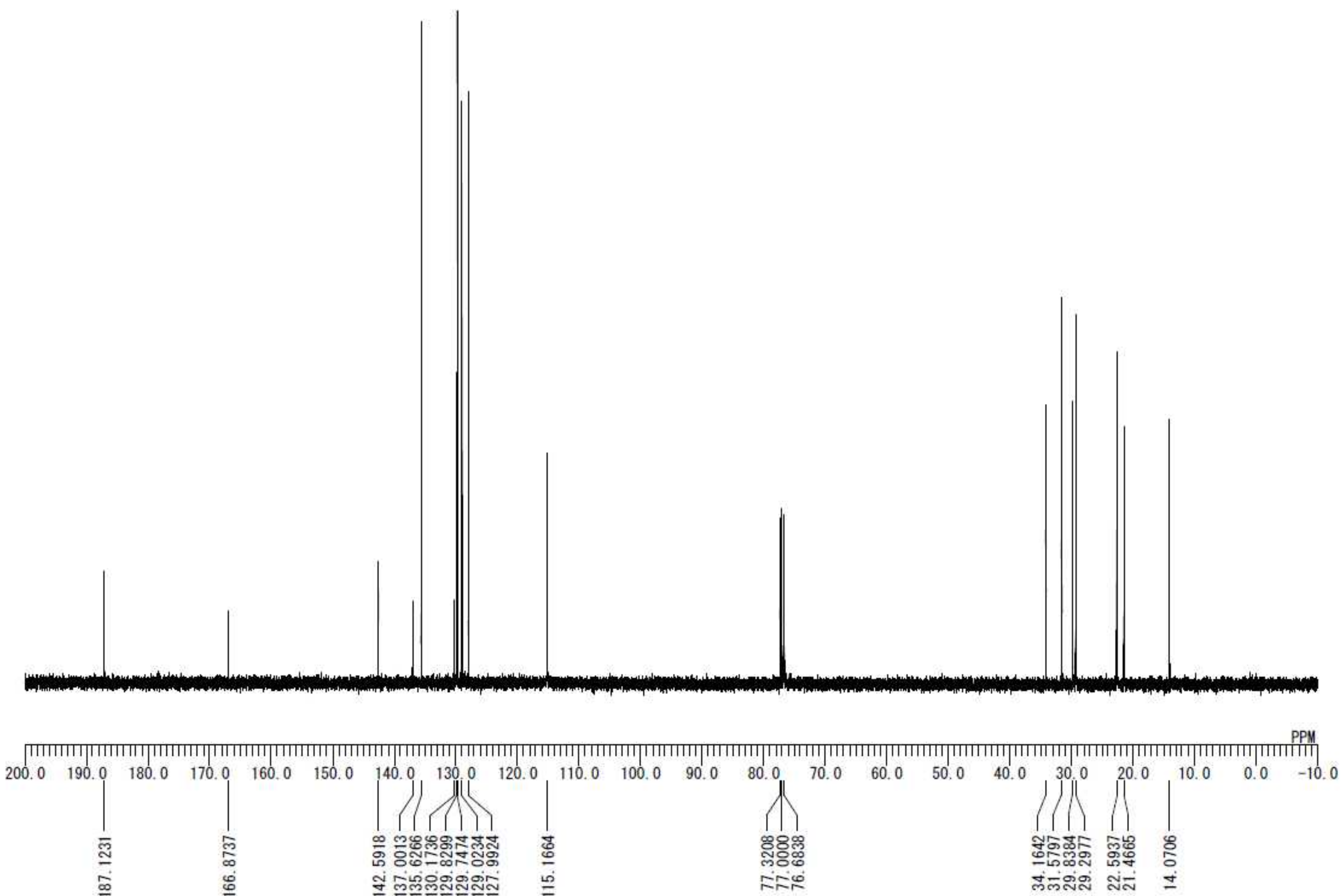
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30.0
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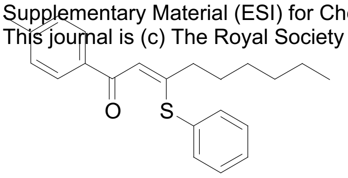
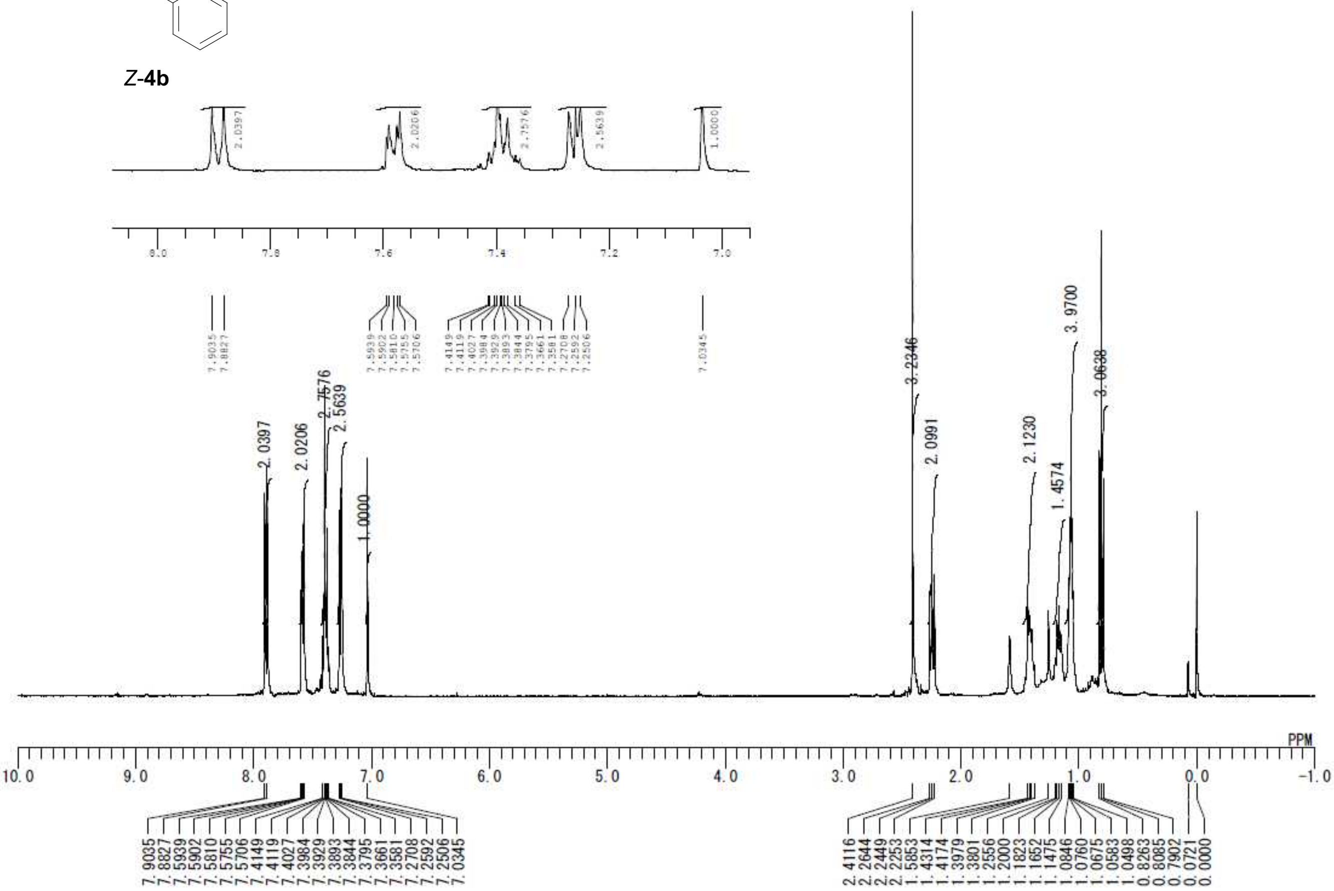

O
S

Z-**4b**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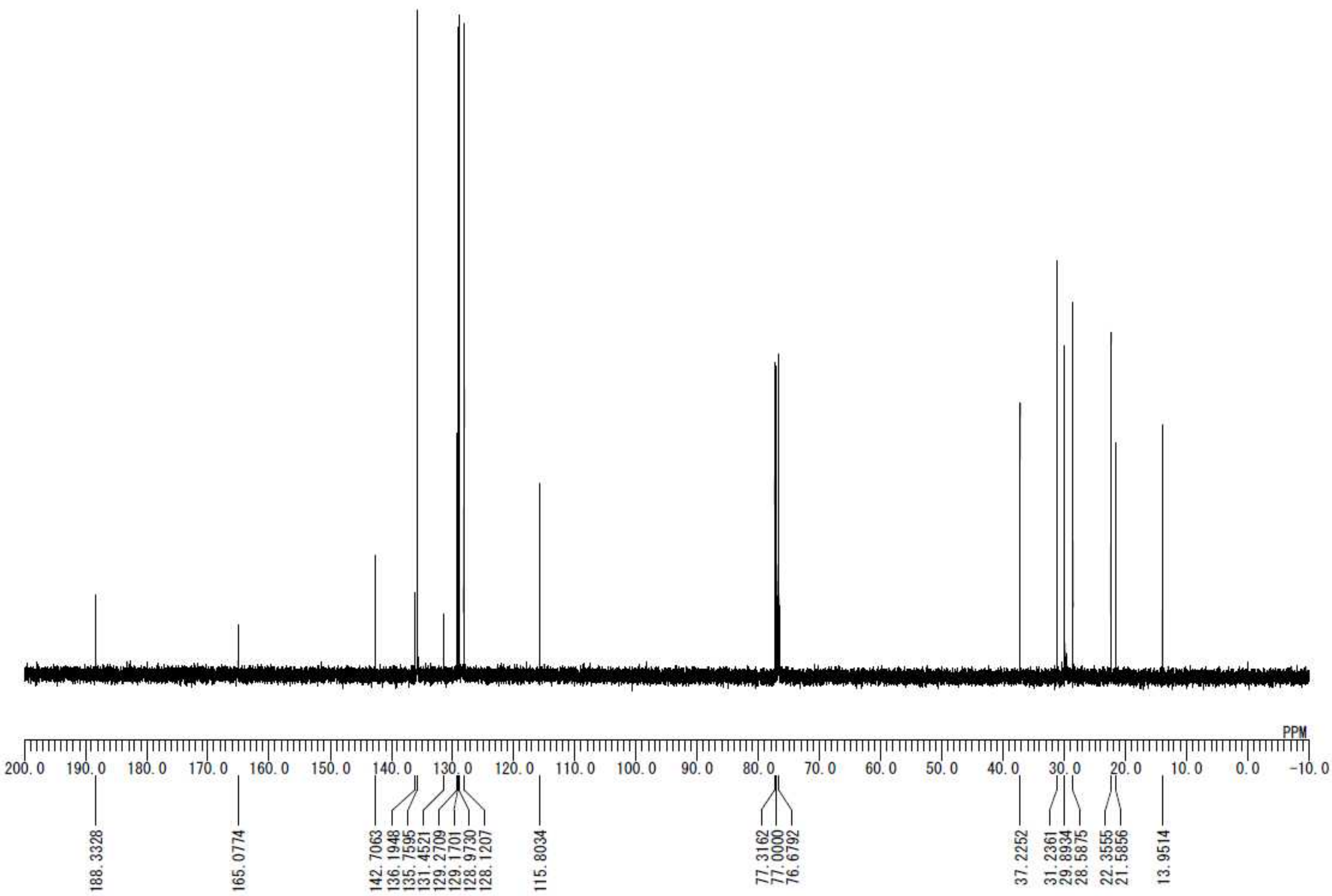
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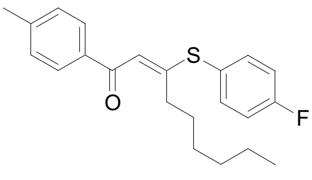

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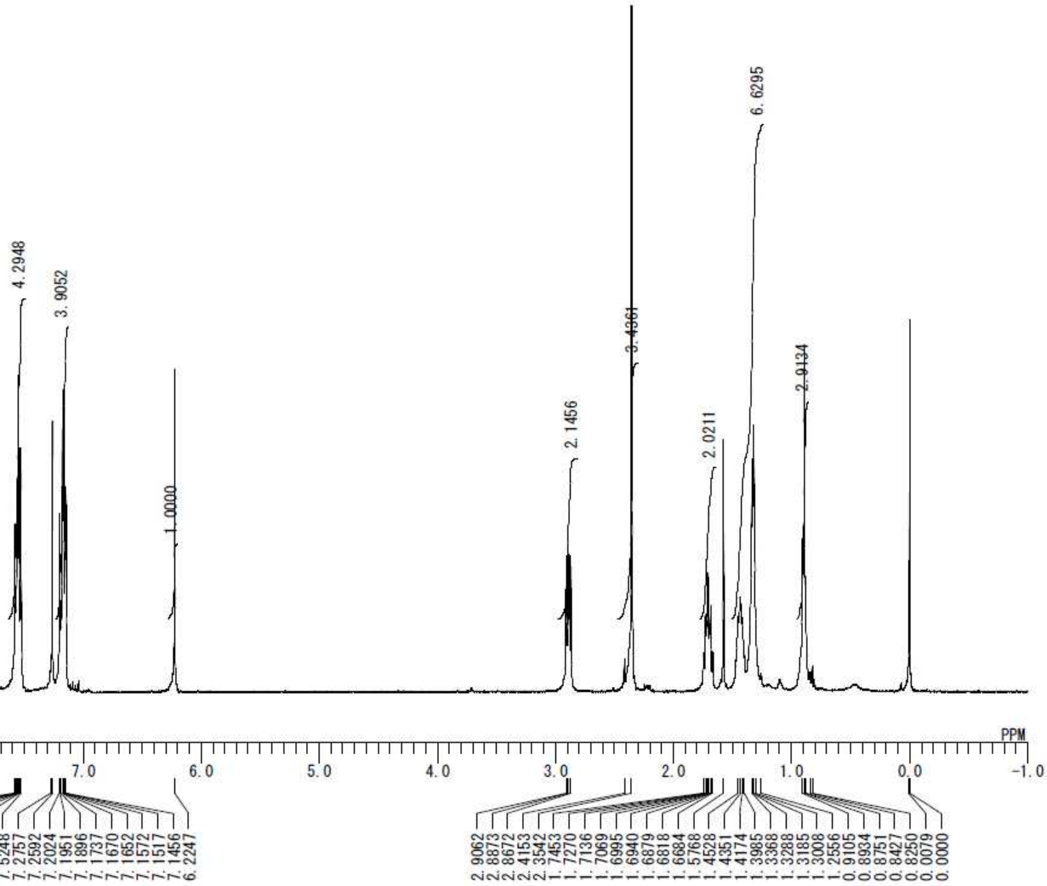

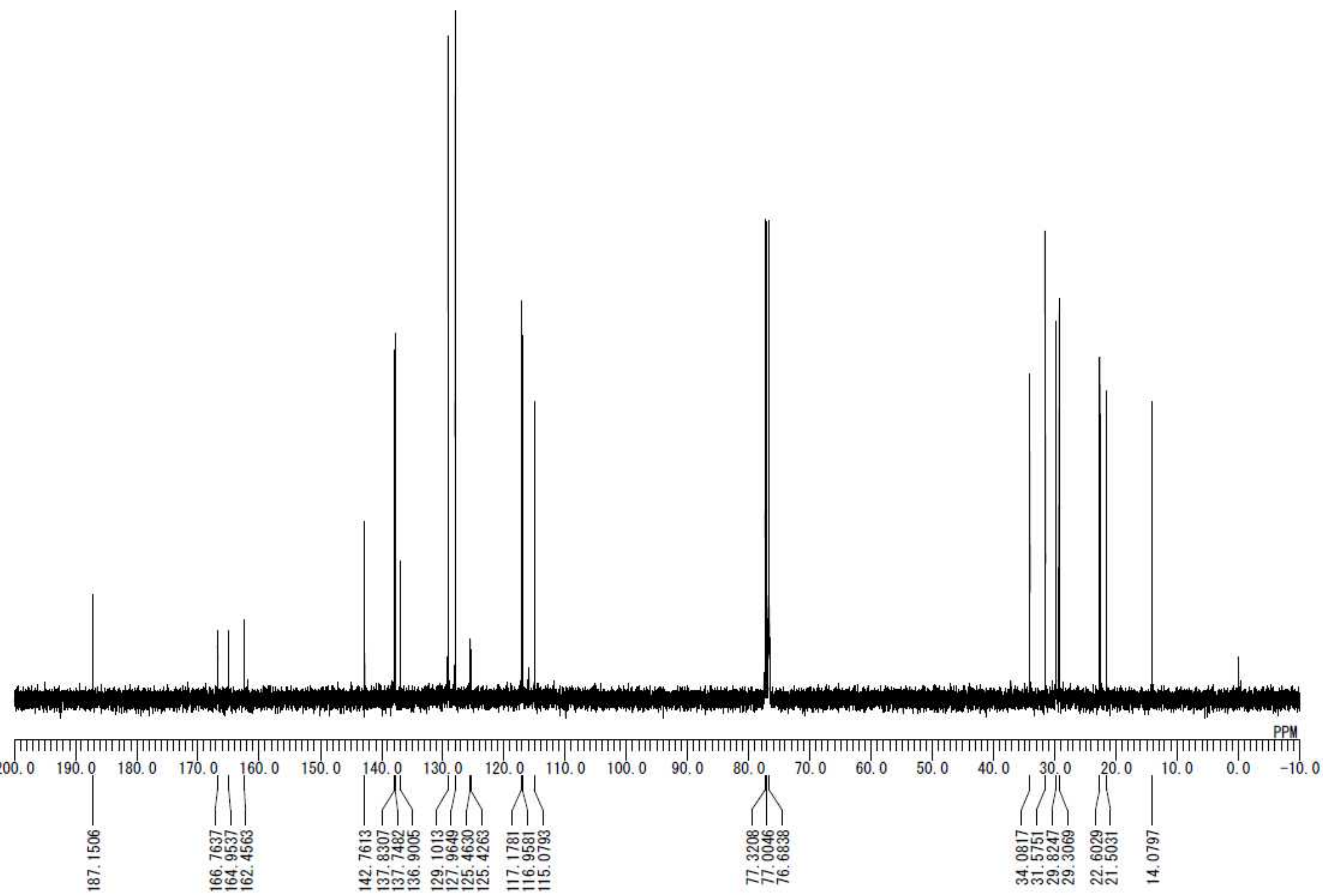

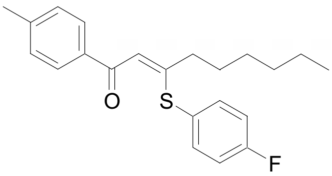

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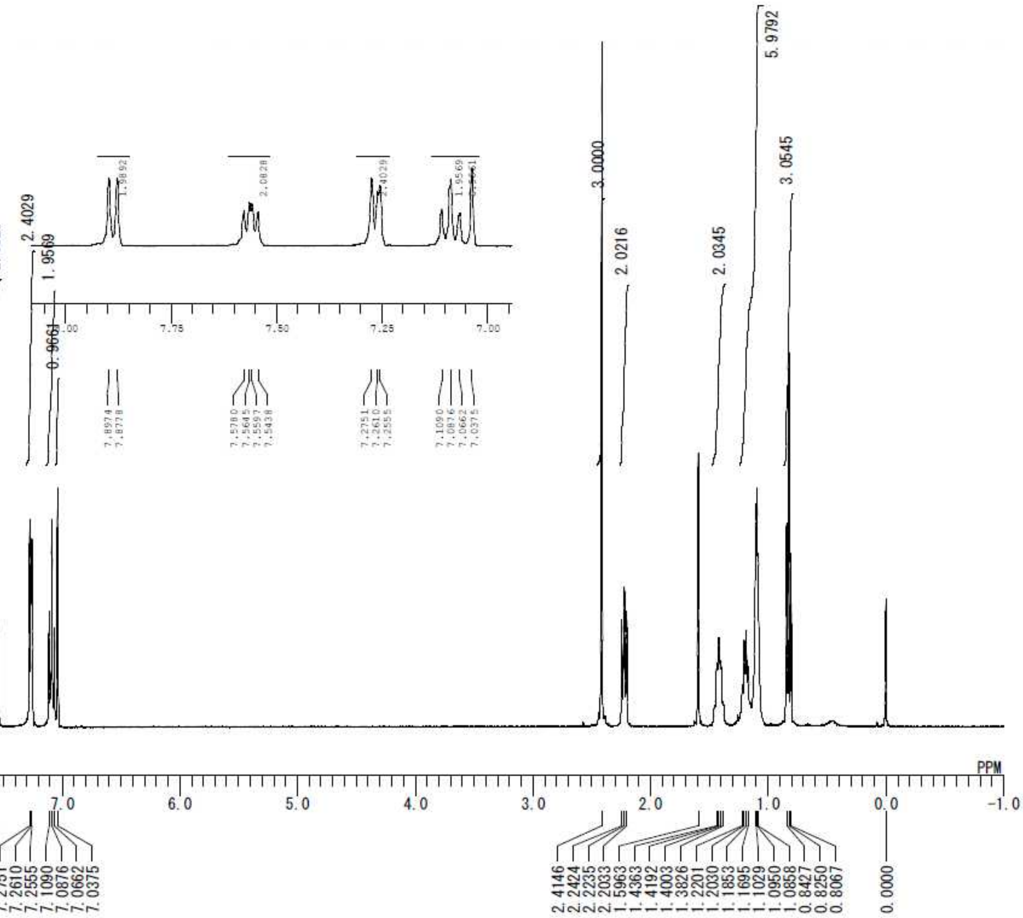

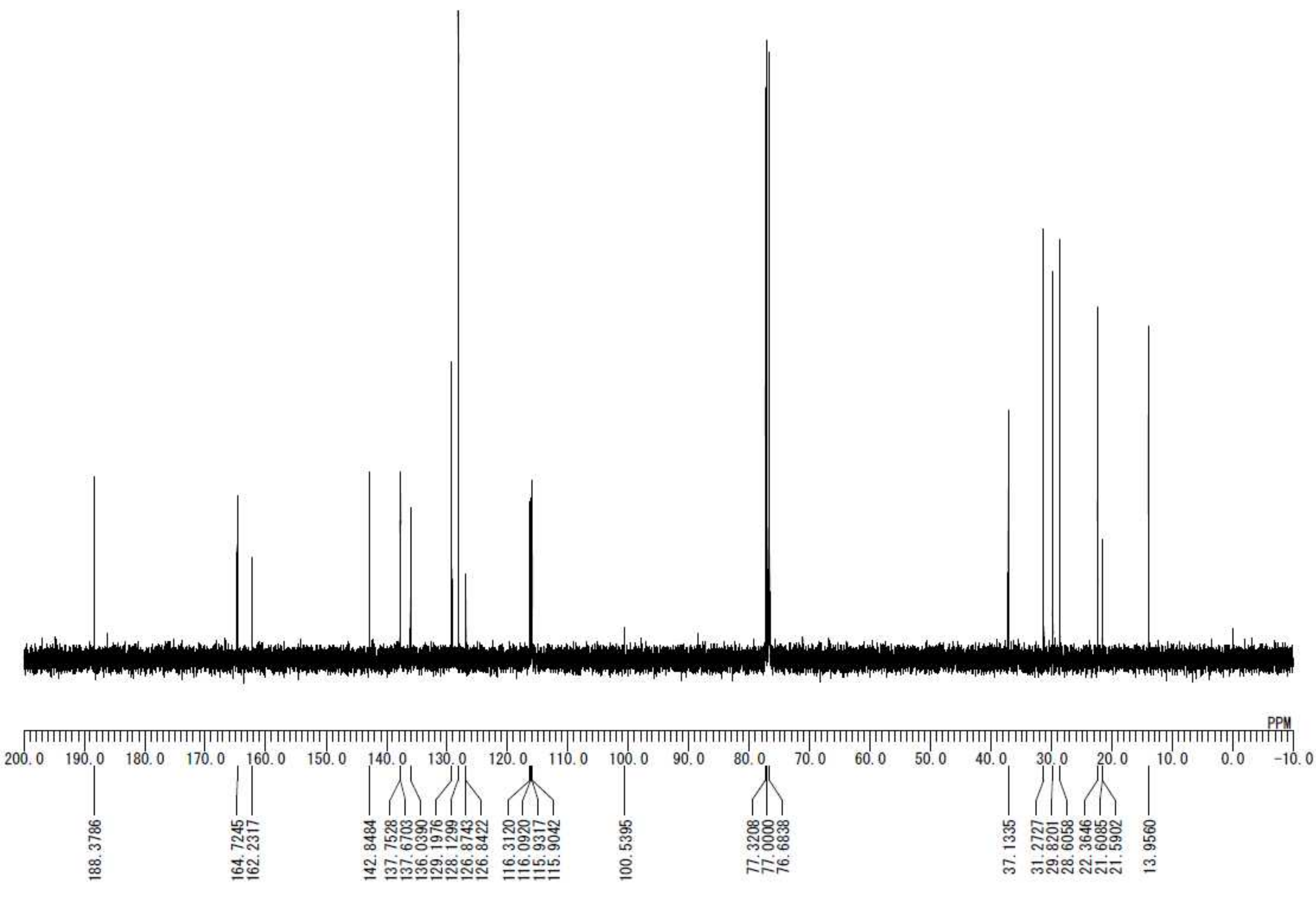

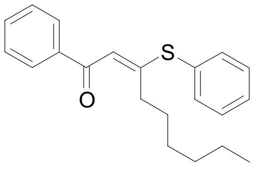

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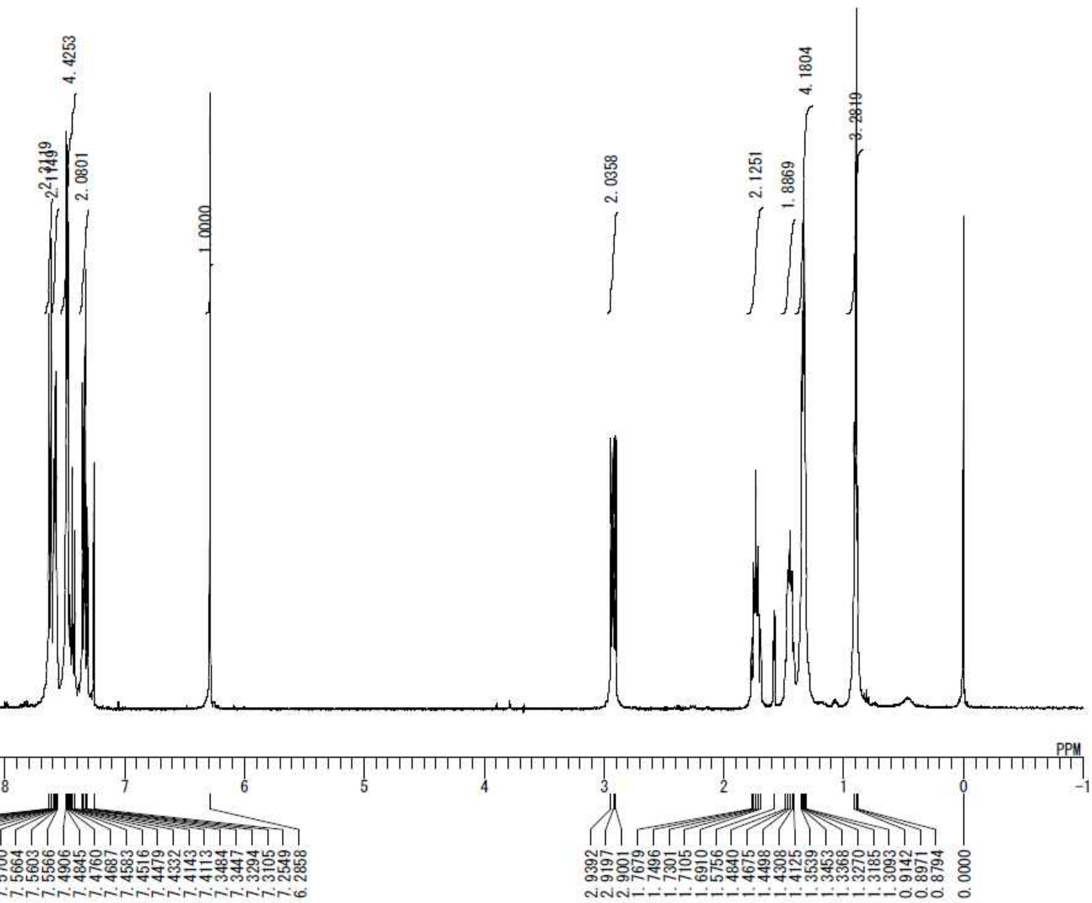

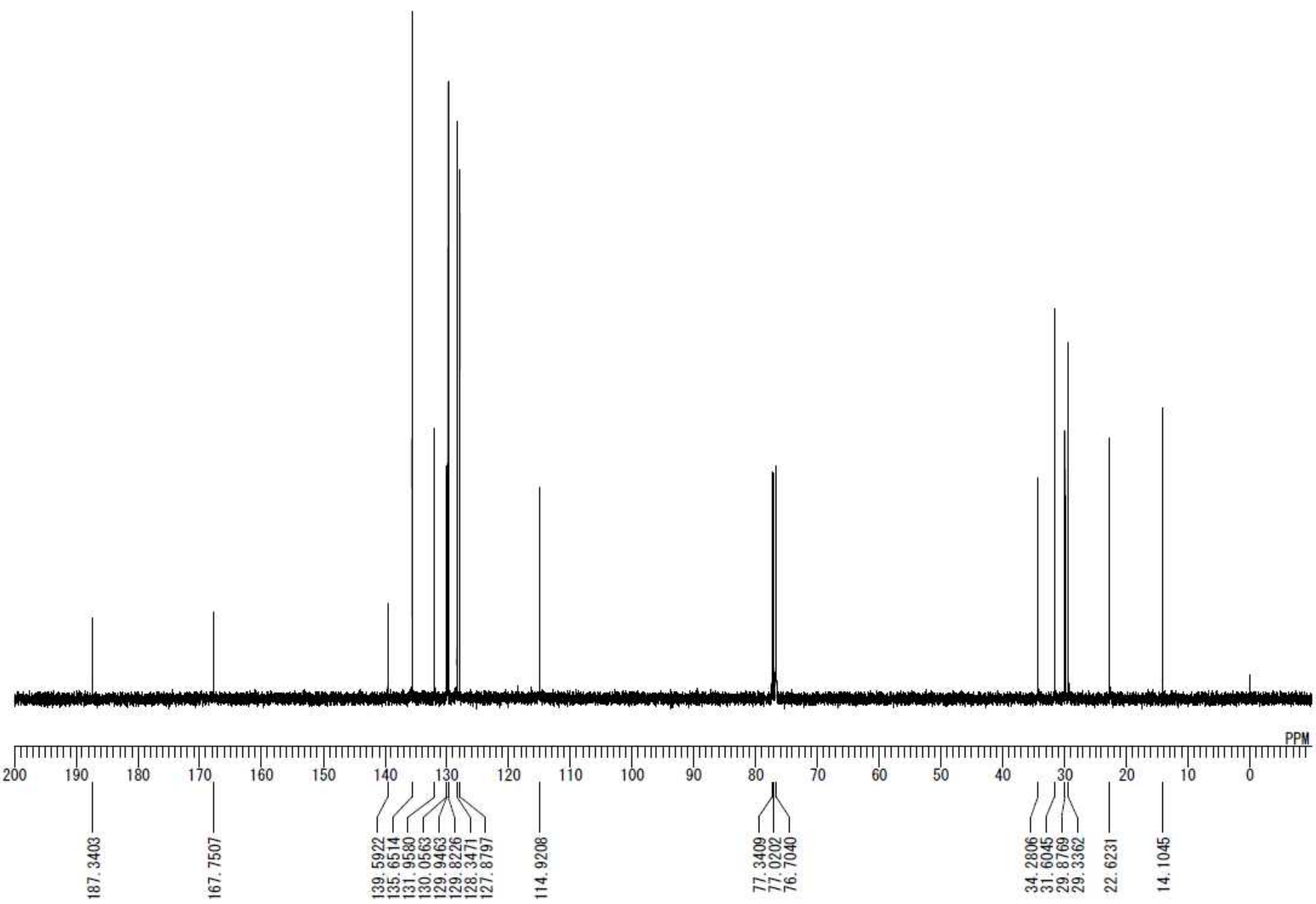

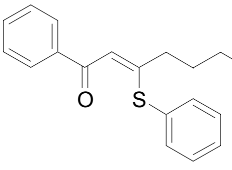

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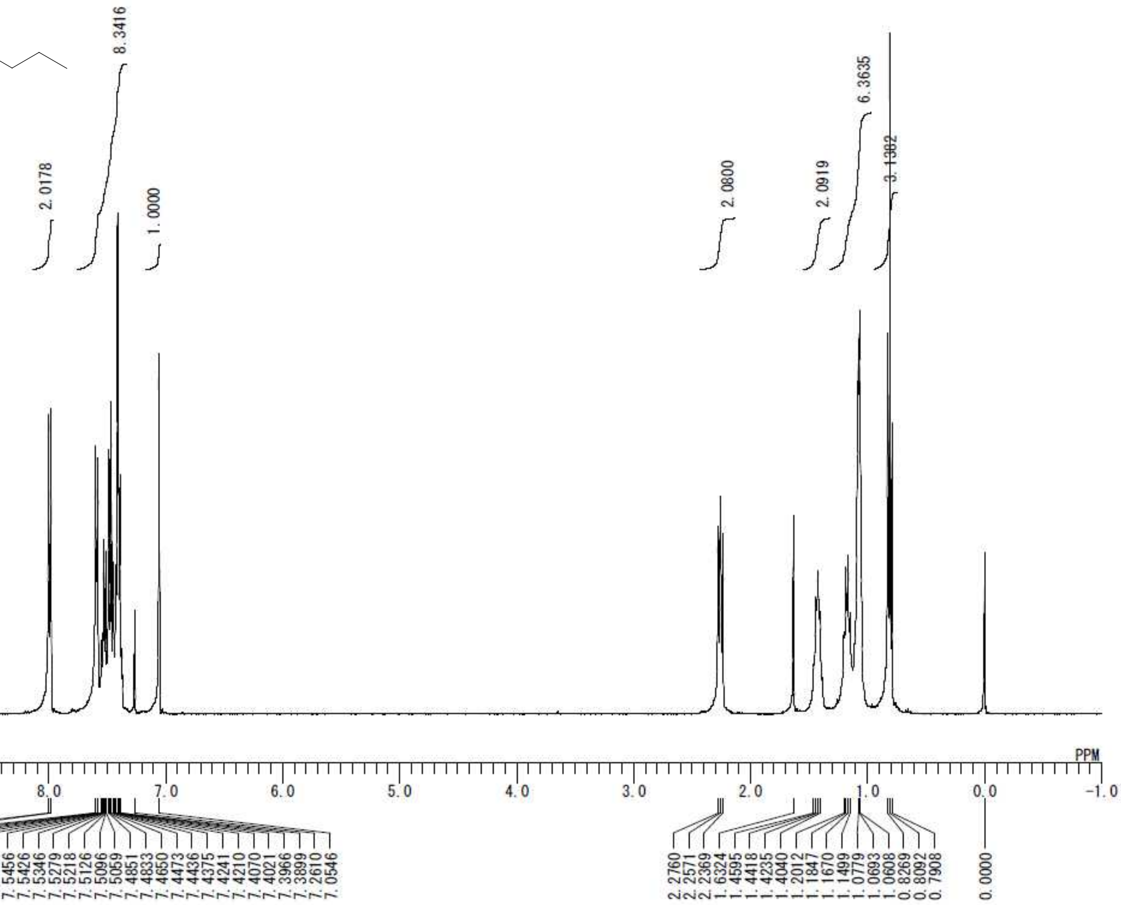

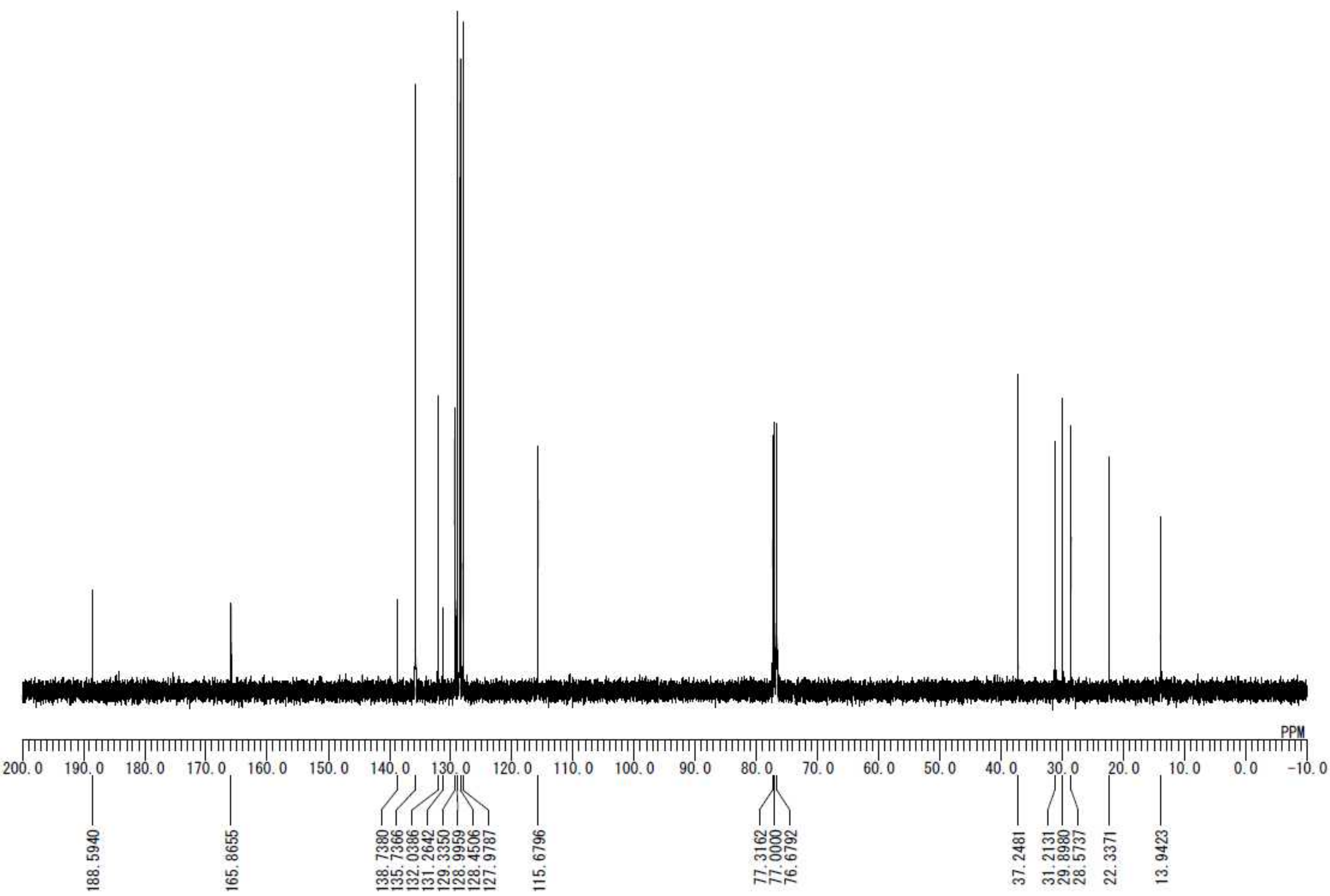

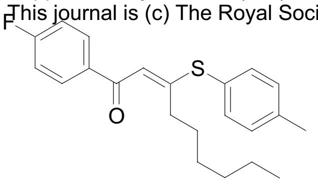

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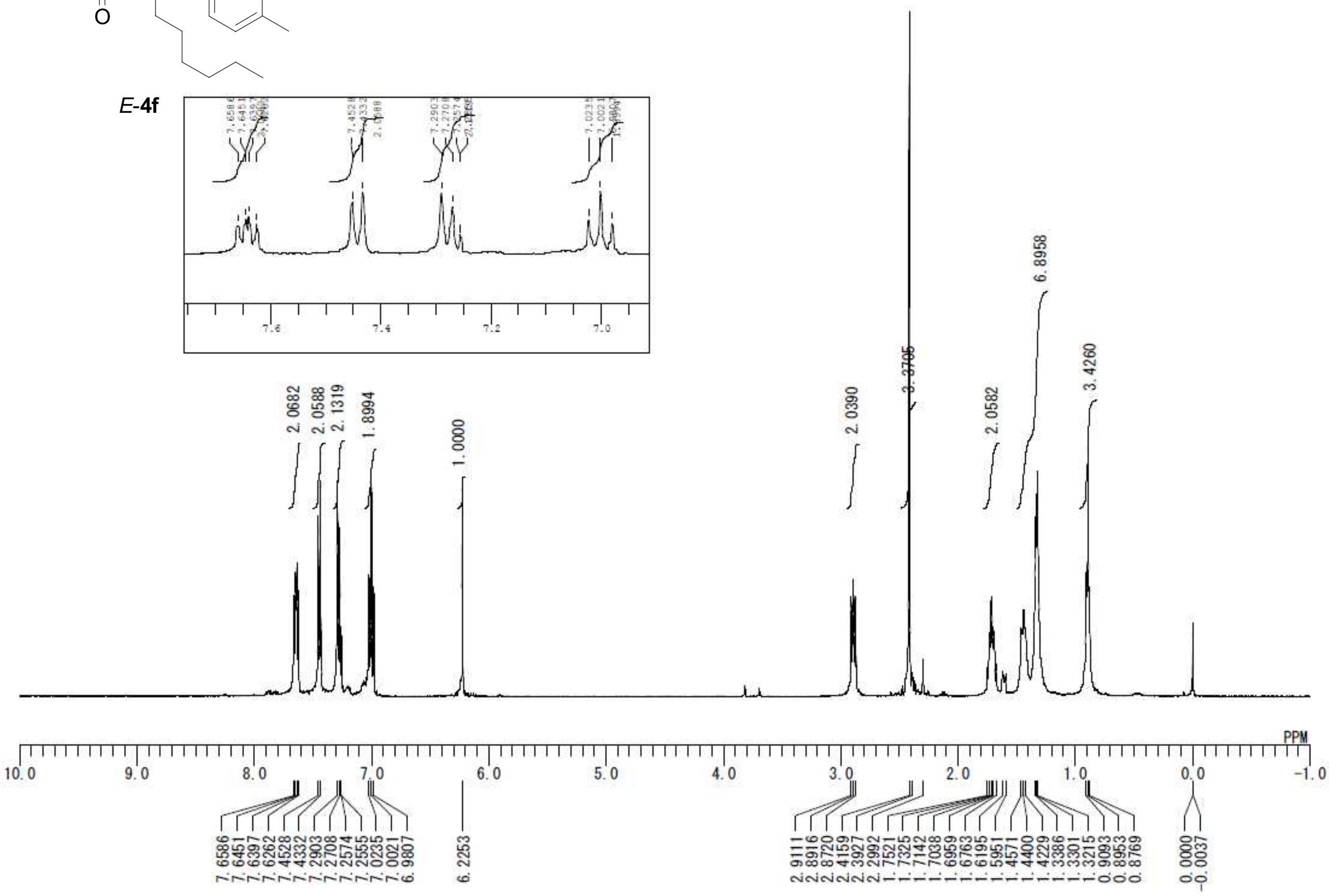
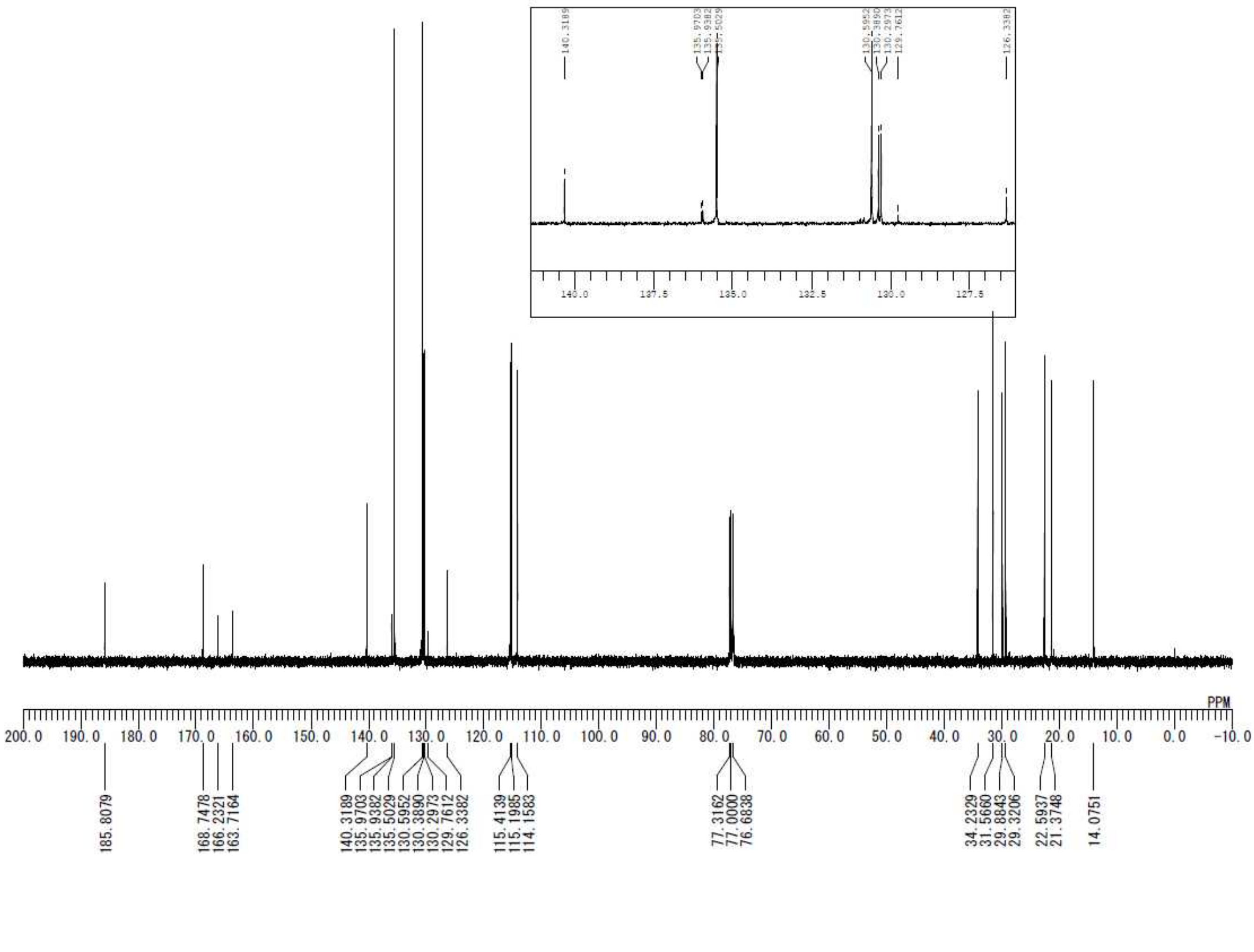
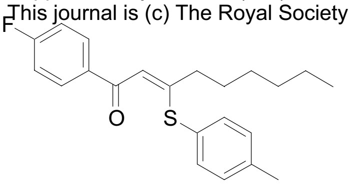
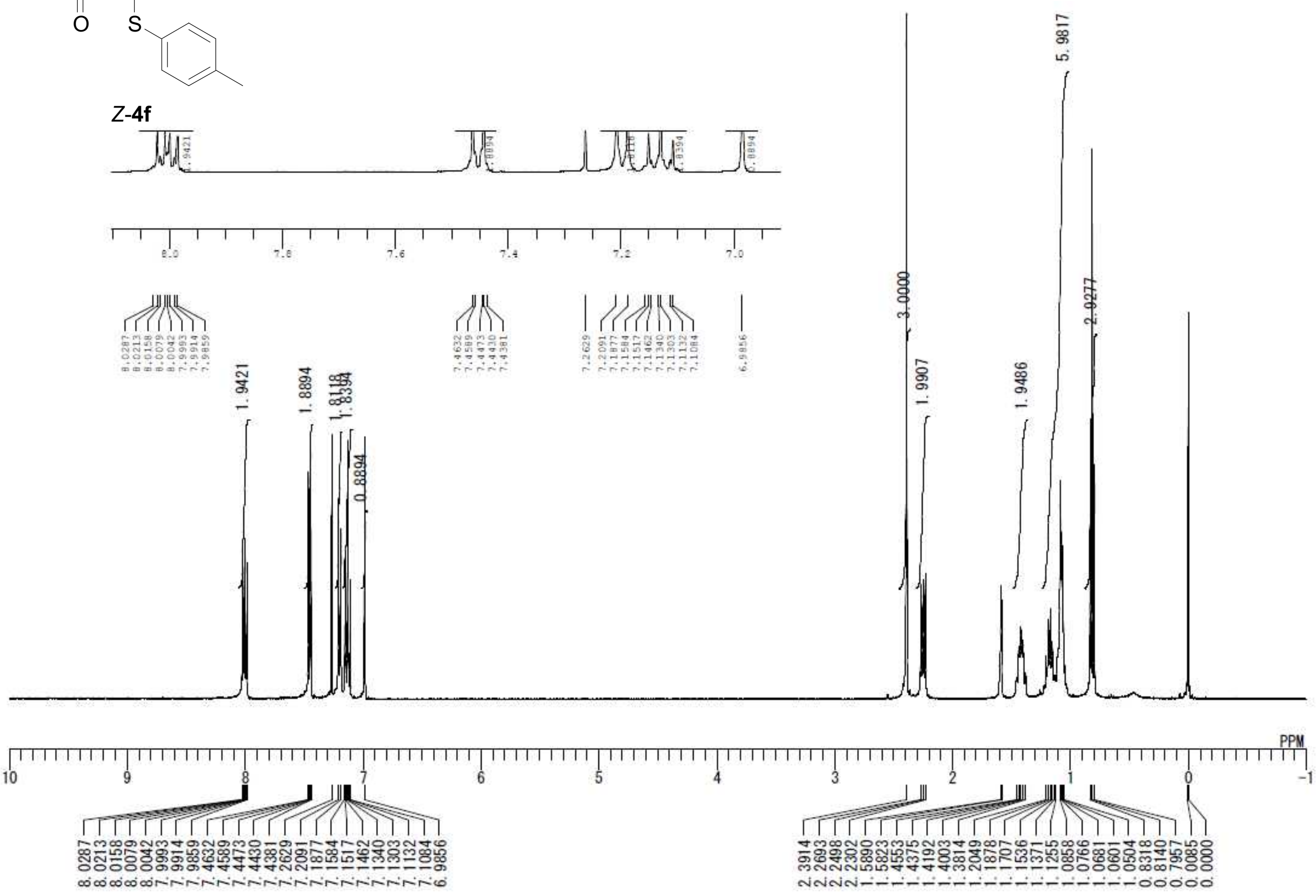





F
O
S

Z-**4f**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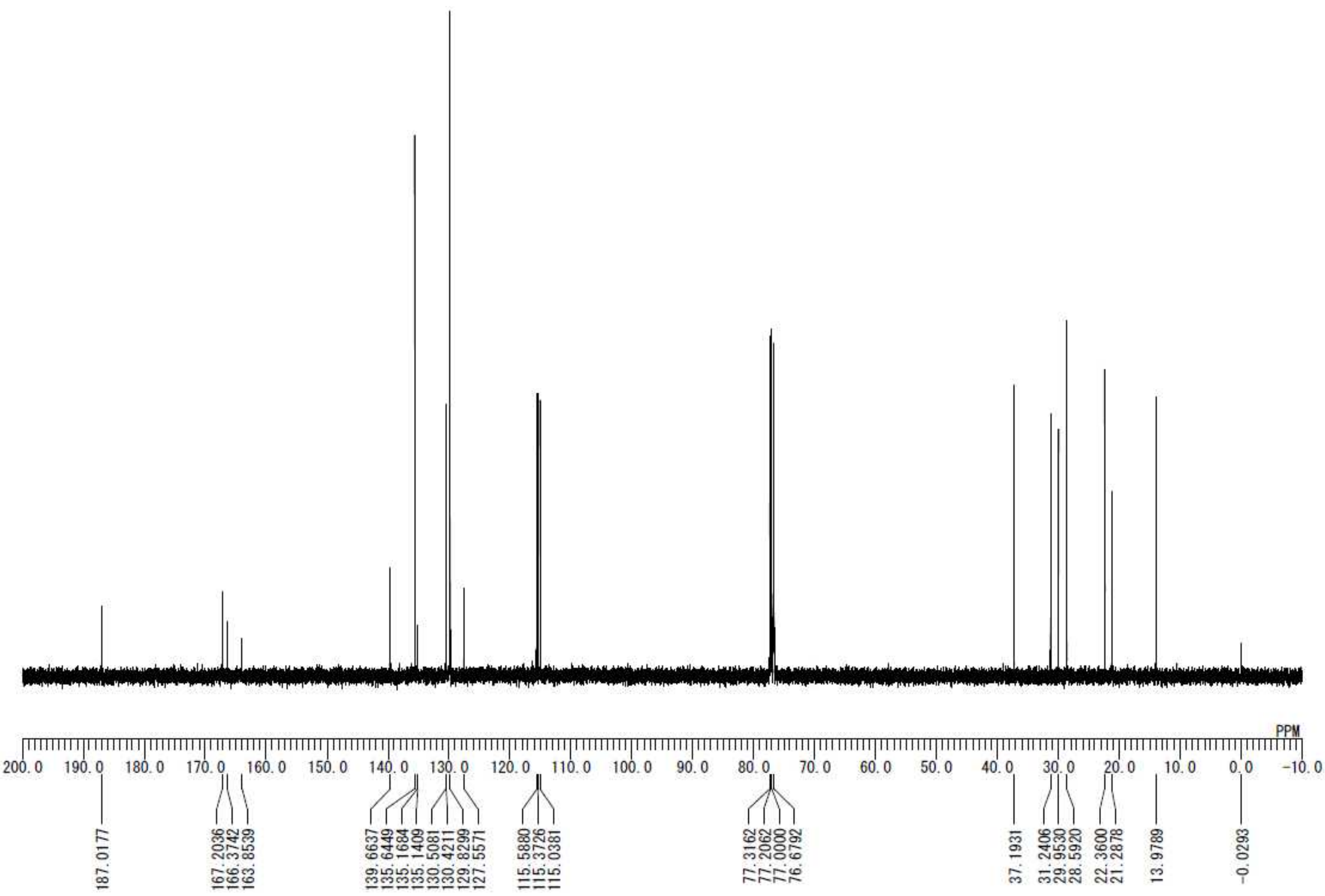
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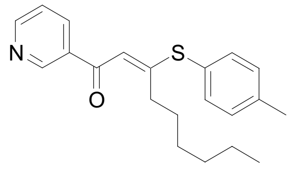
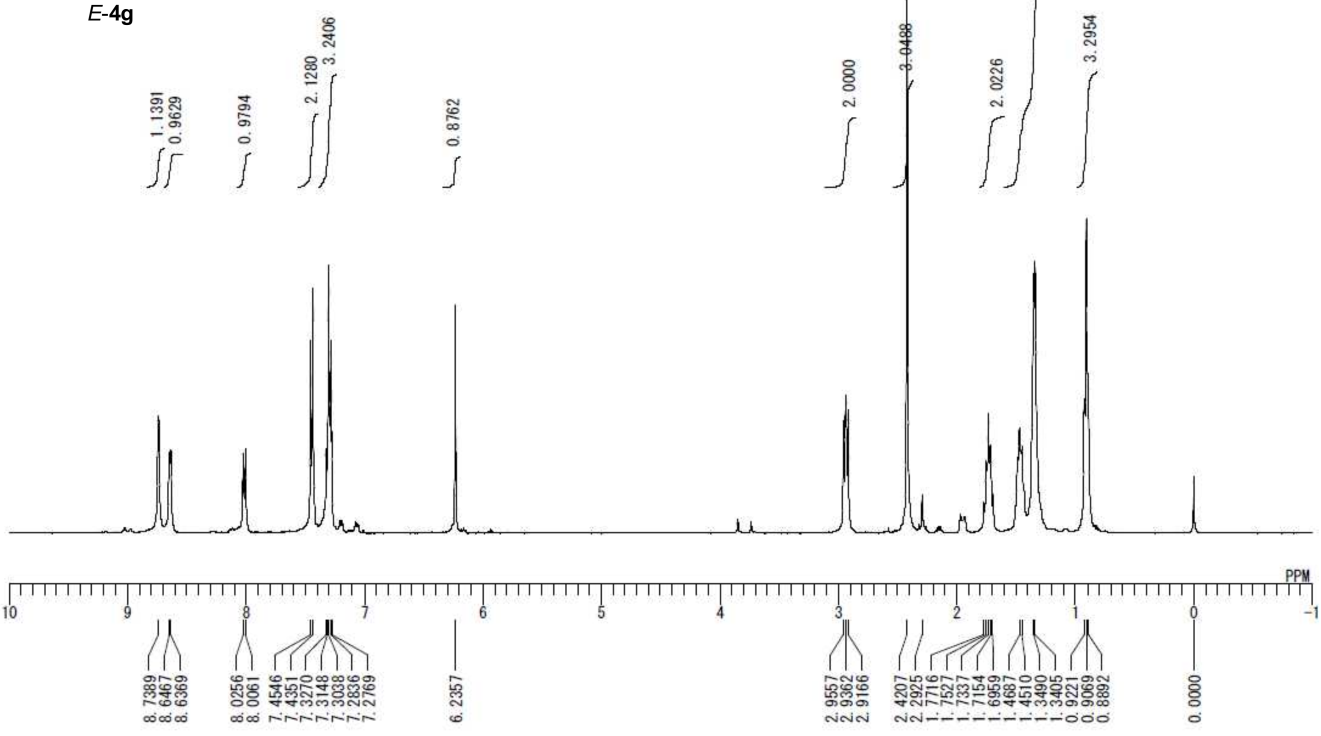
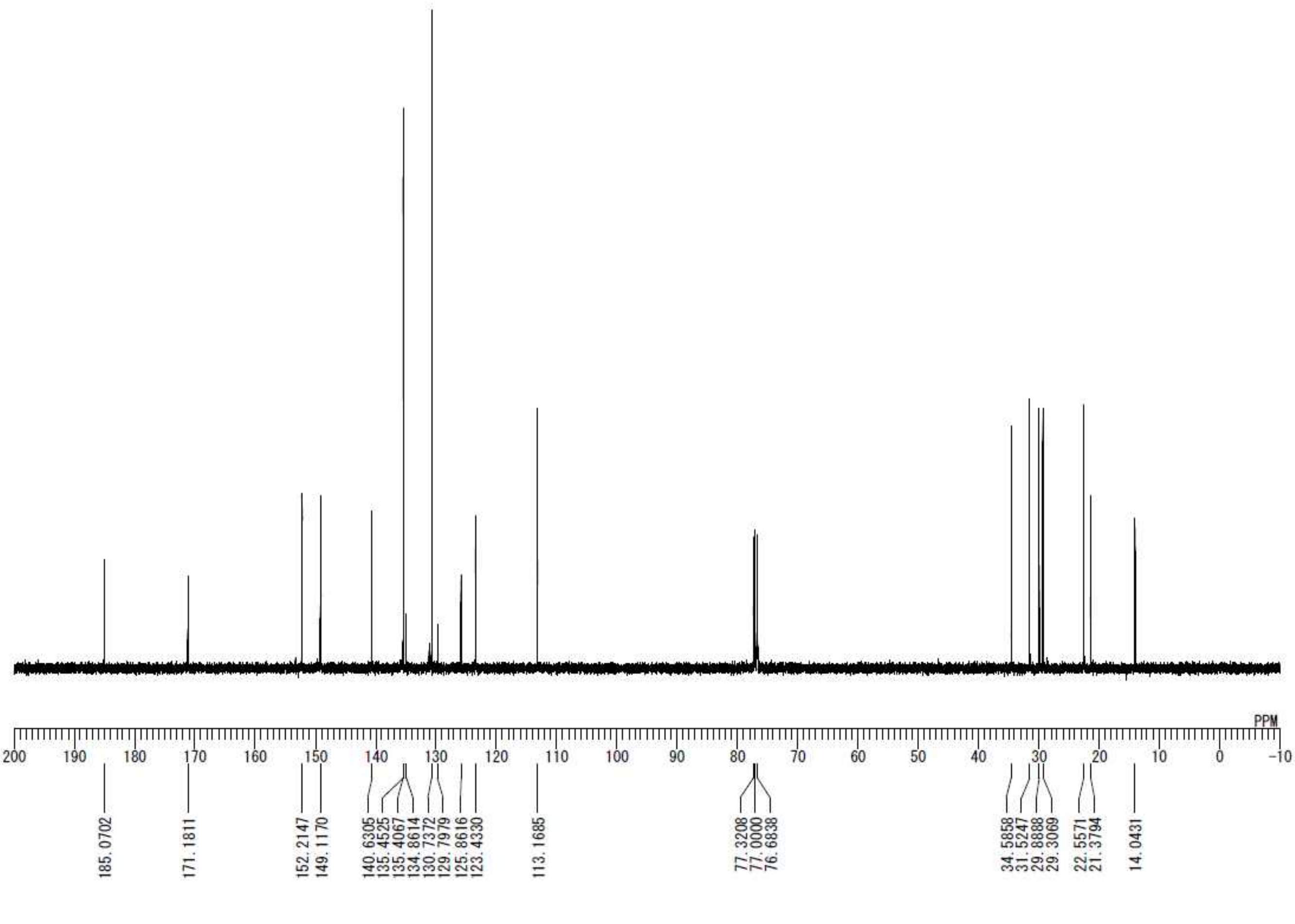
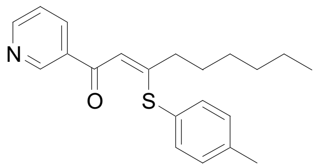


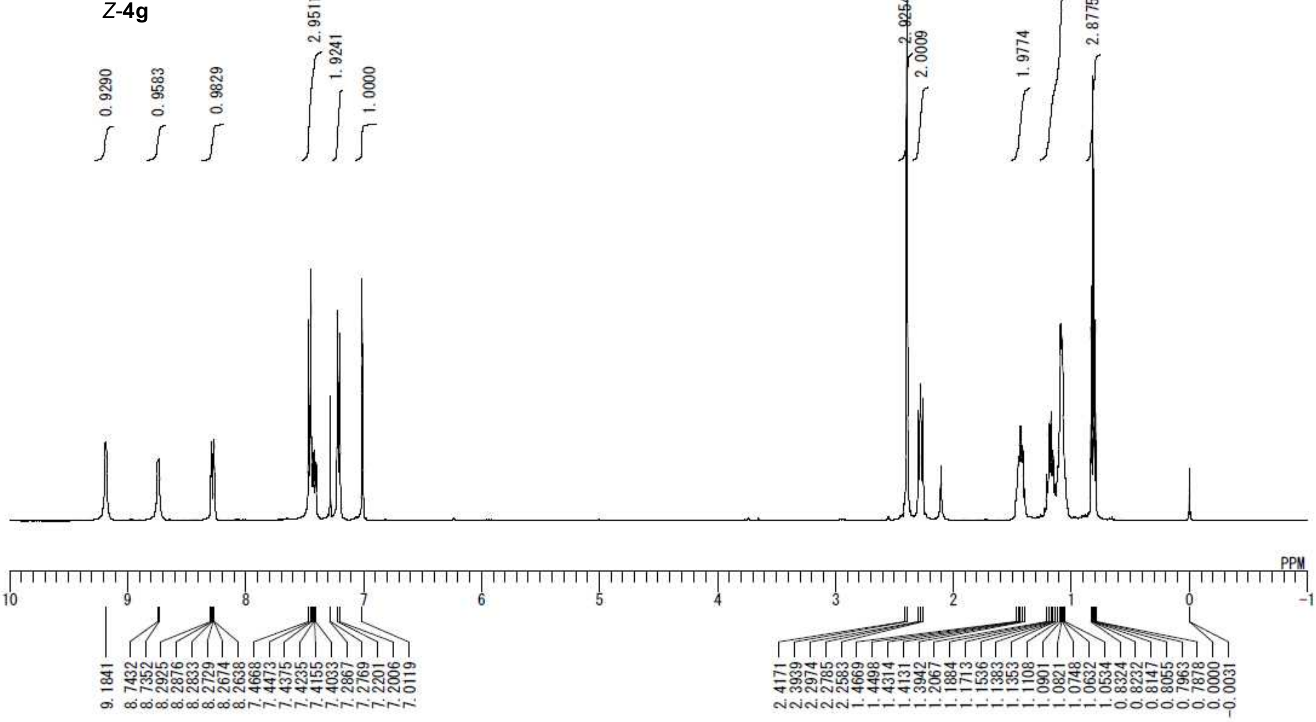
E-**4g**

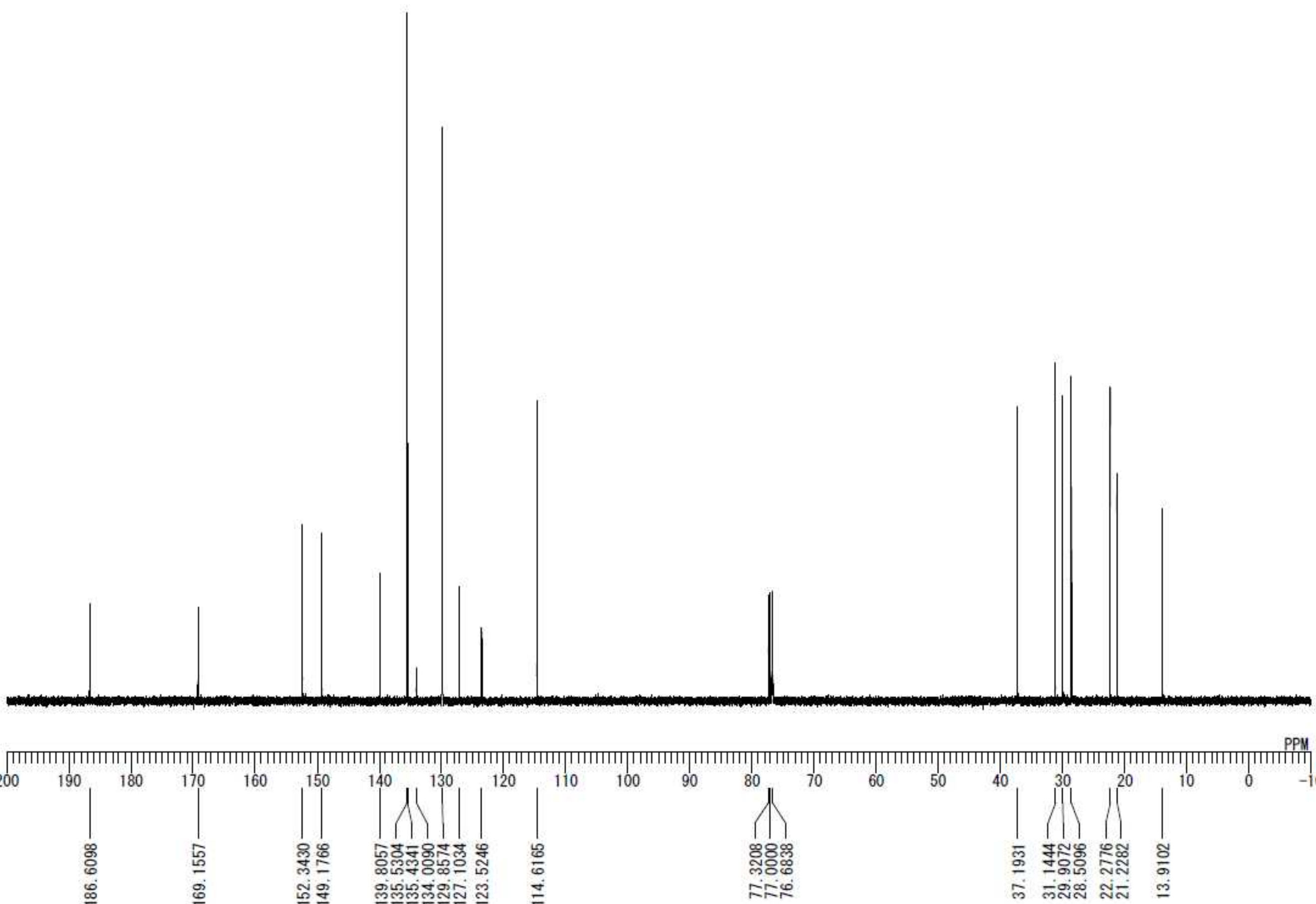


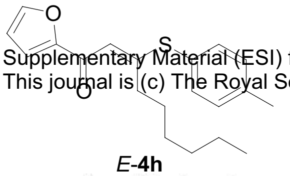




Z-**4g**







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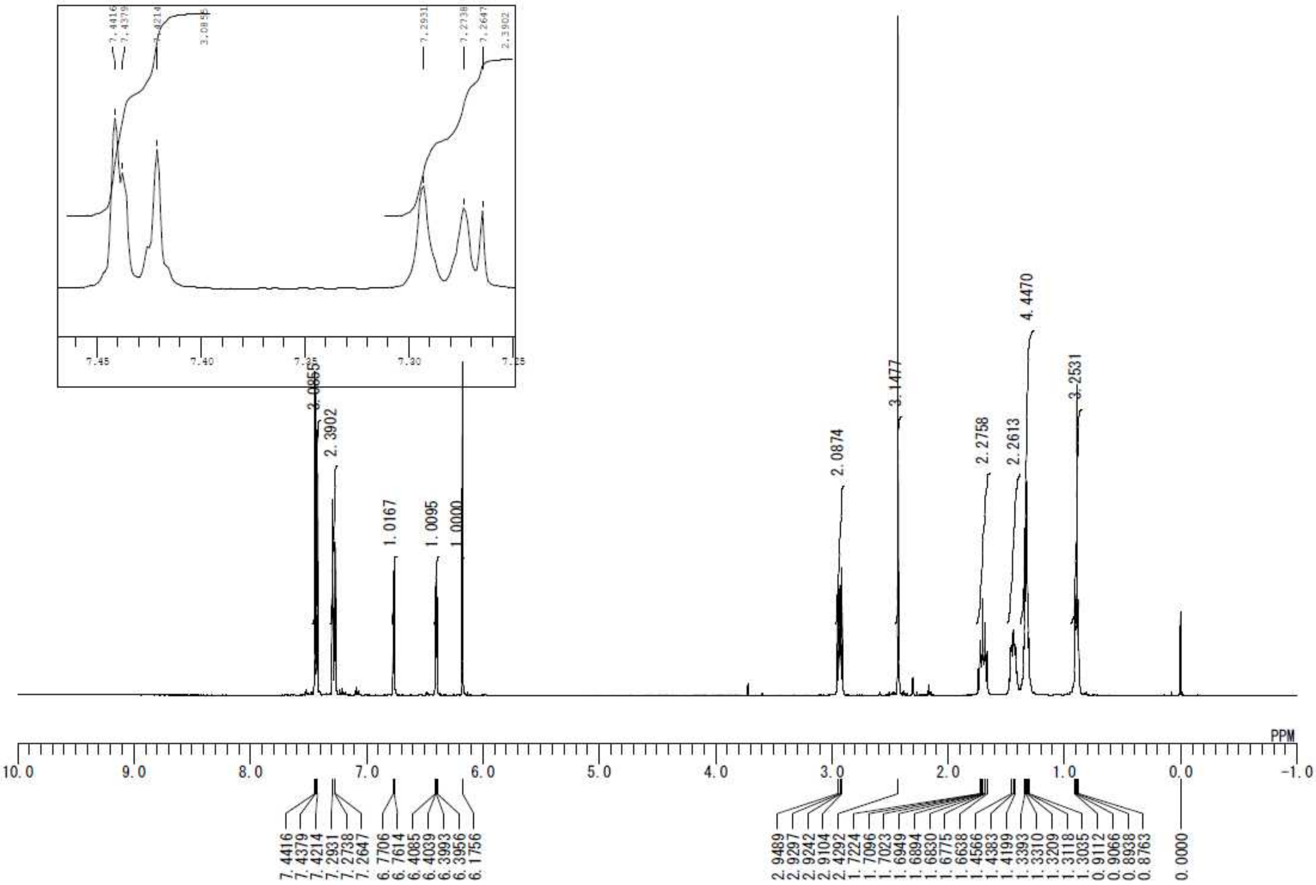
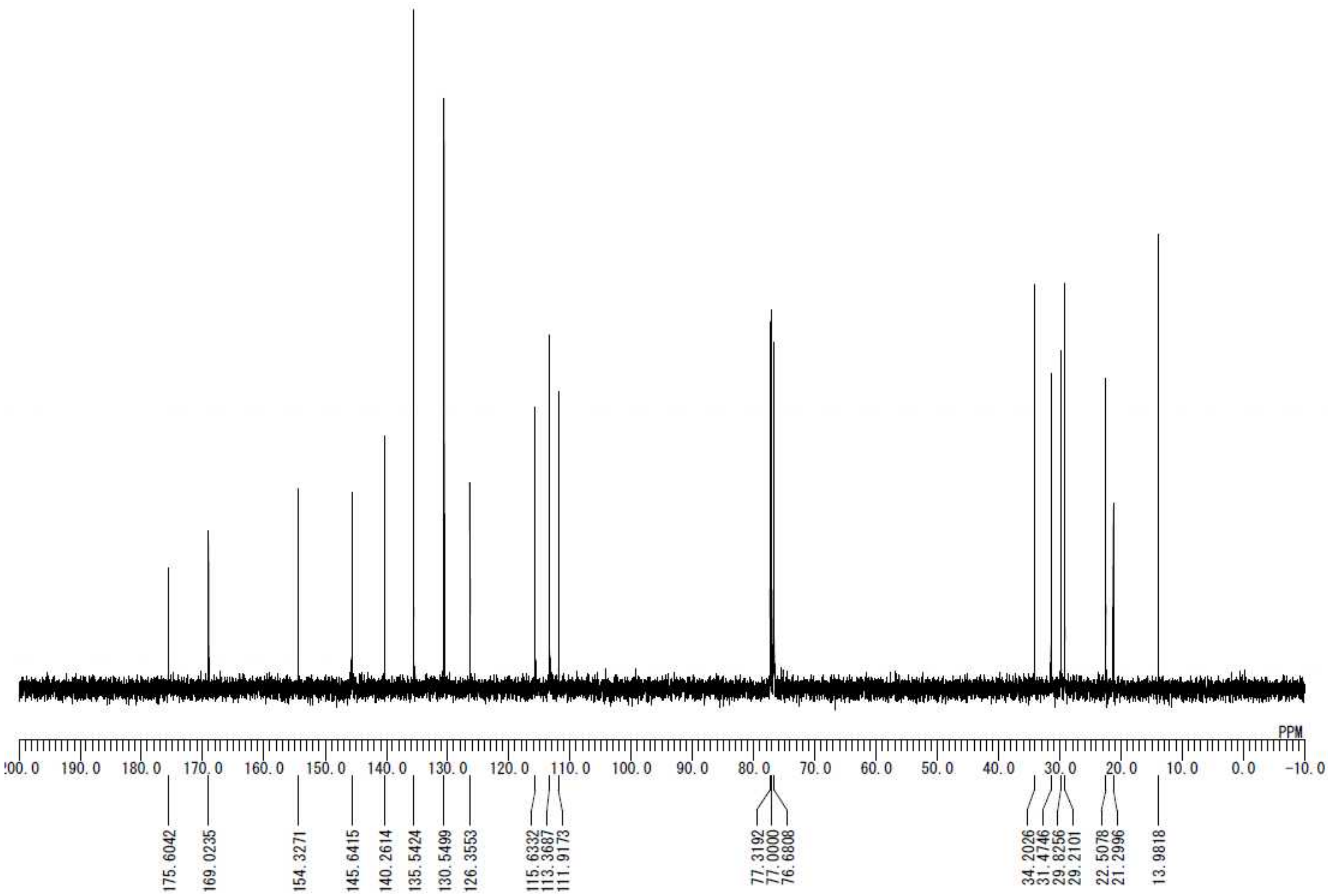
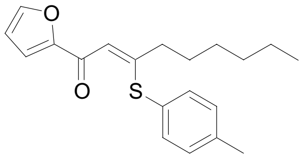
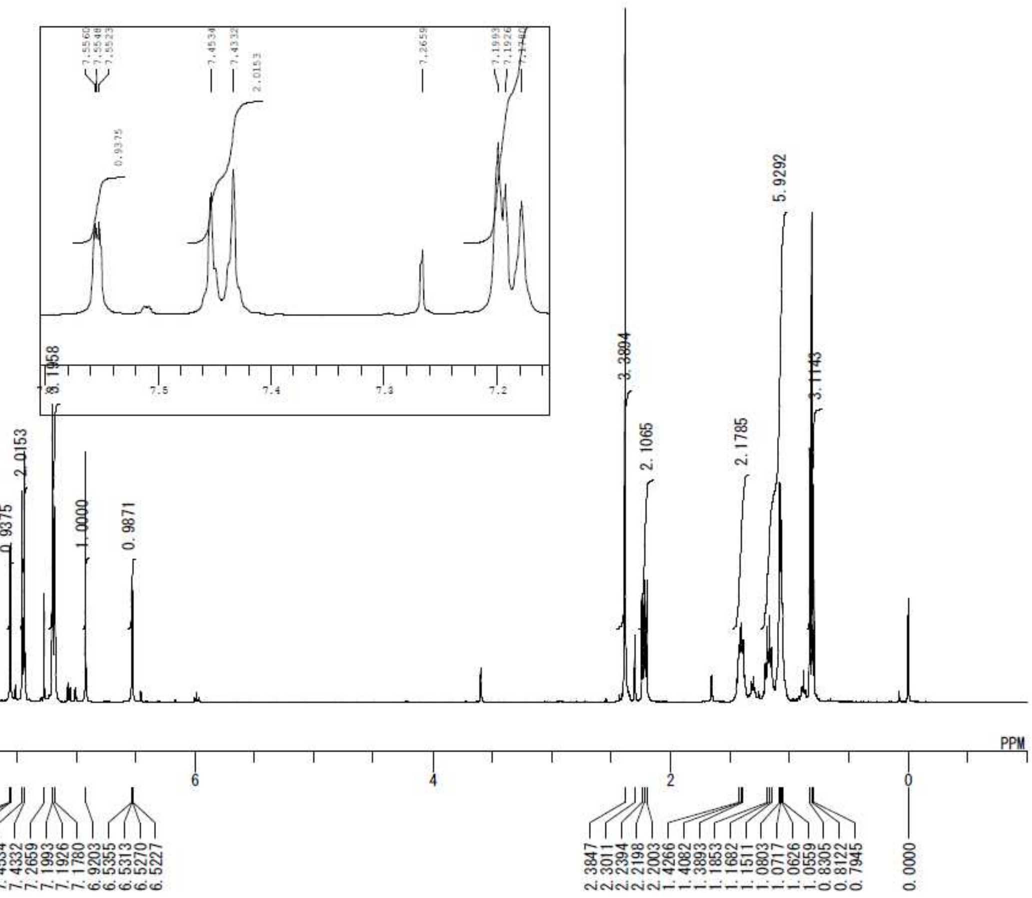
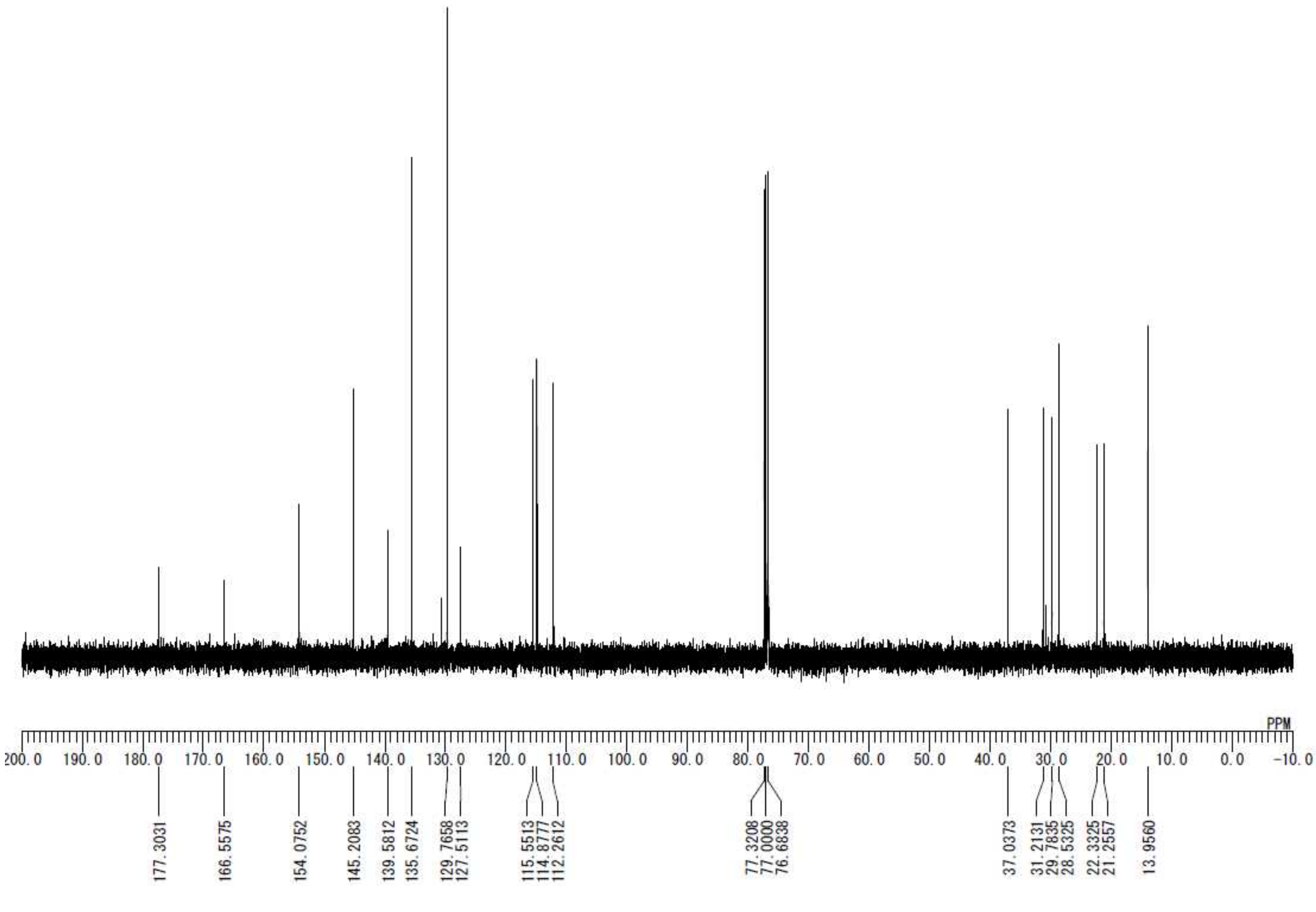


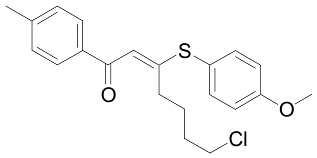




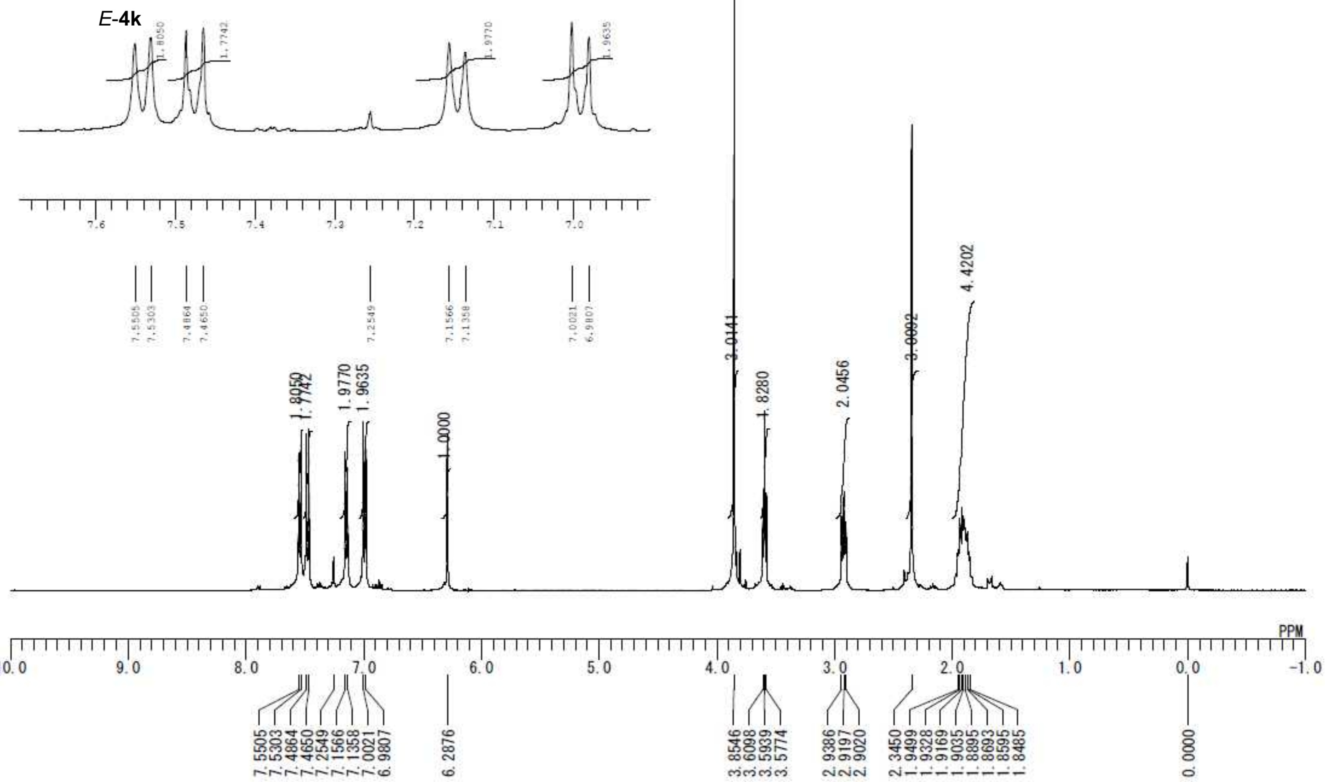
Z-**4h**

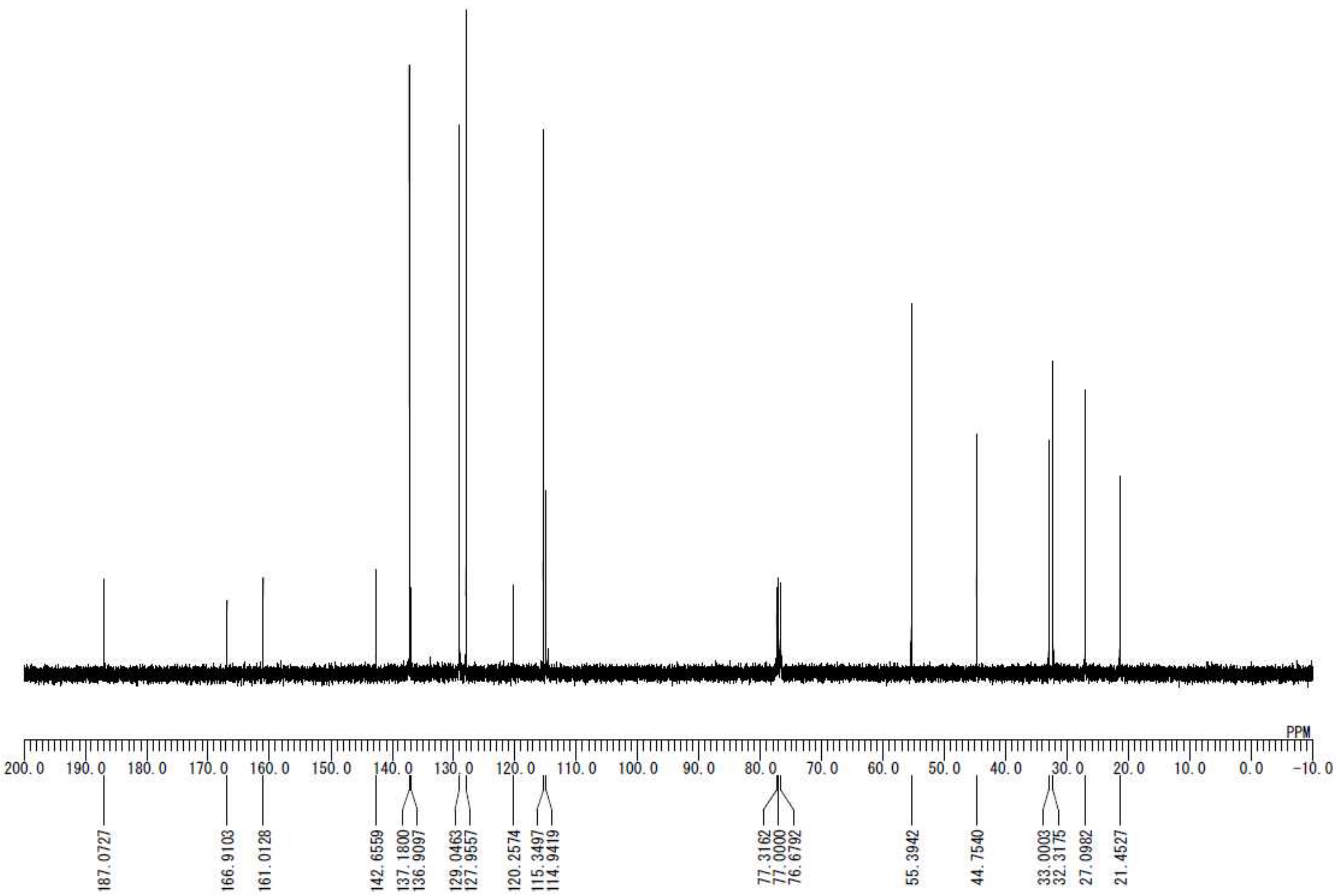


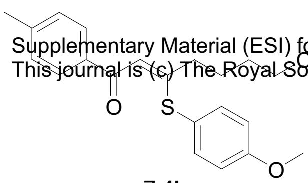




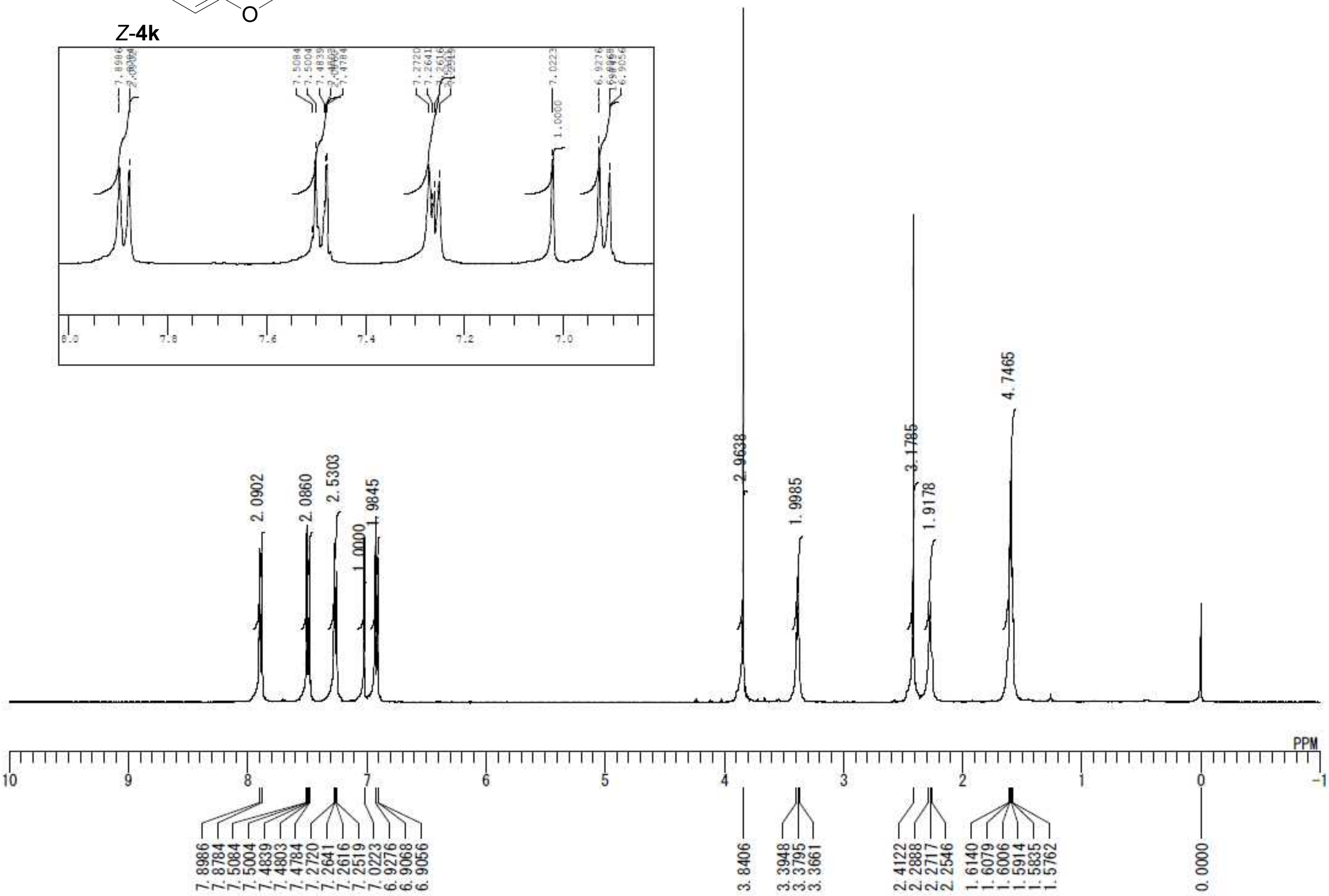
E-**4k**






O
S
Cl
O

Z-**4k**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1.9985
3.1785
1.9178
4.7465
PPM
10
9
8
7
6
5
4
3
2
1
0
-1
7.8986
7.8784
7.5084
7.5004
7.4839
7.4803
7.4784
7.2720
7.2641
7.2616
7.2519
7.0223
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6.9056
3.8406
3.3948
3.3795
3.3661
2.4122
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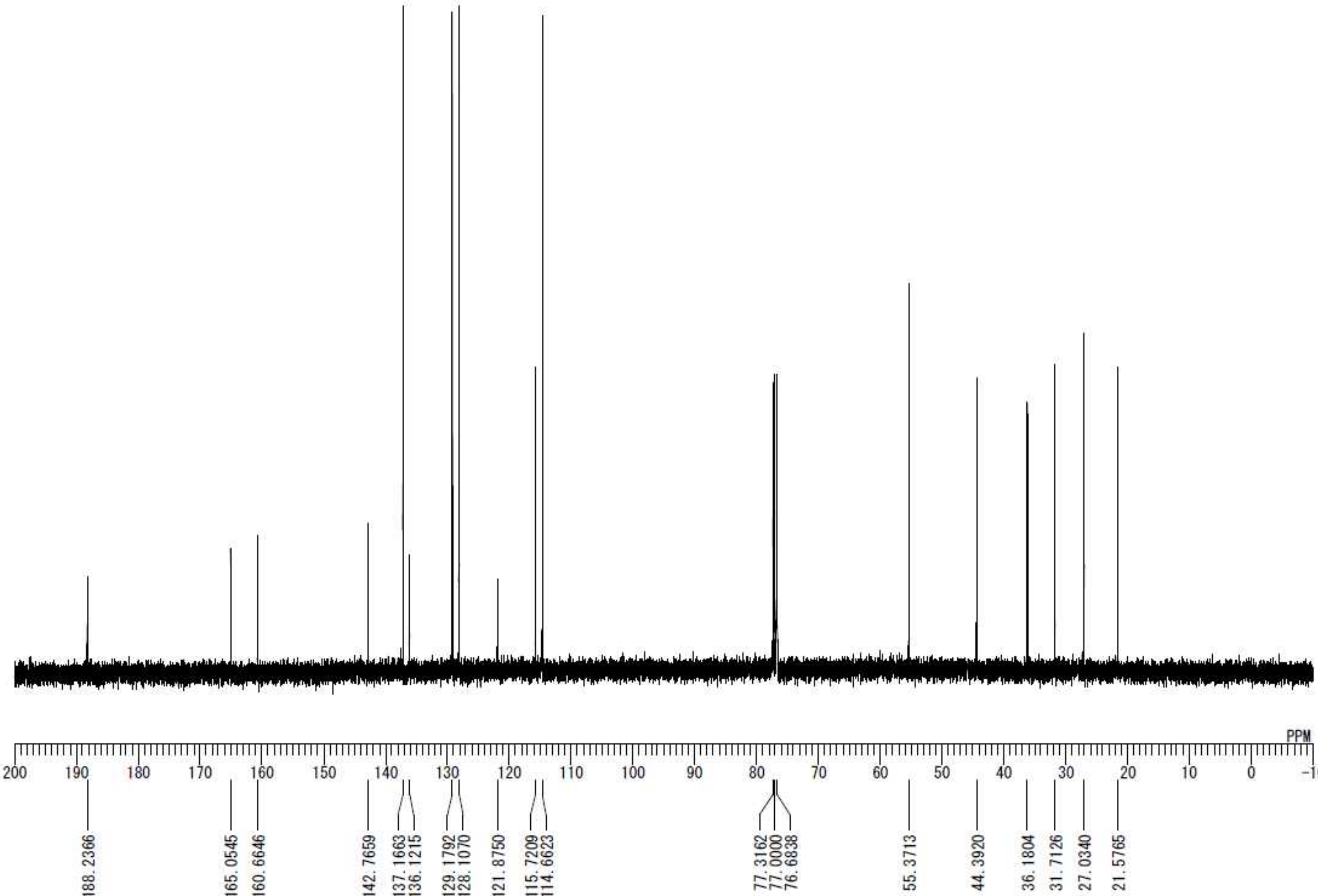
0.0000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130
120
110
100
90
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70
60
50
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30
20
10
0
-10
188.2366
165.0545
160.6646
142.7659
137.1663
136.1215
129.1792
128.1070
121.8750
115.7209
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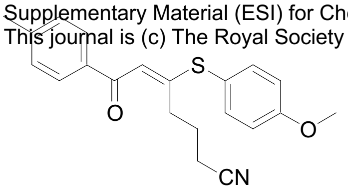
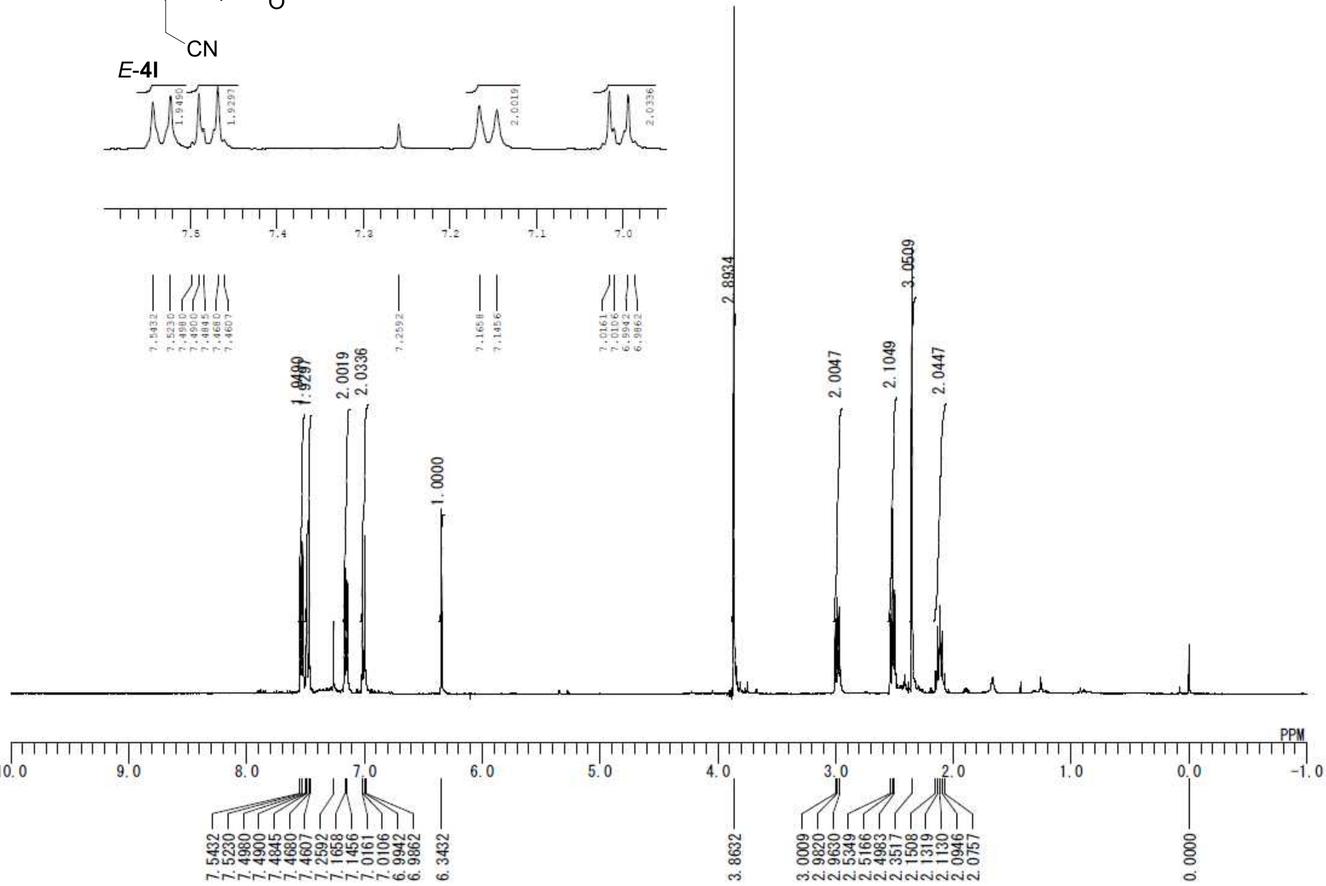
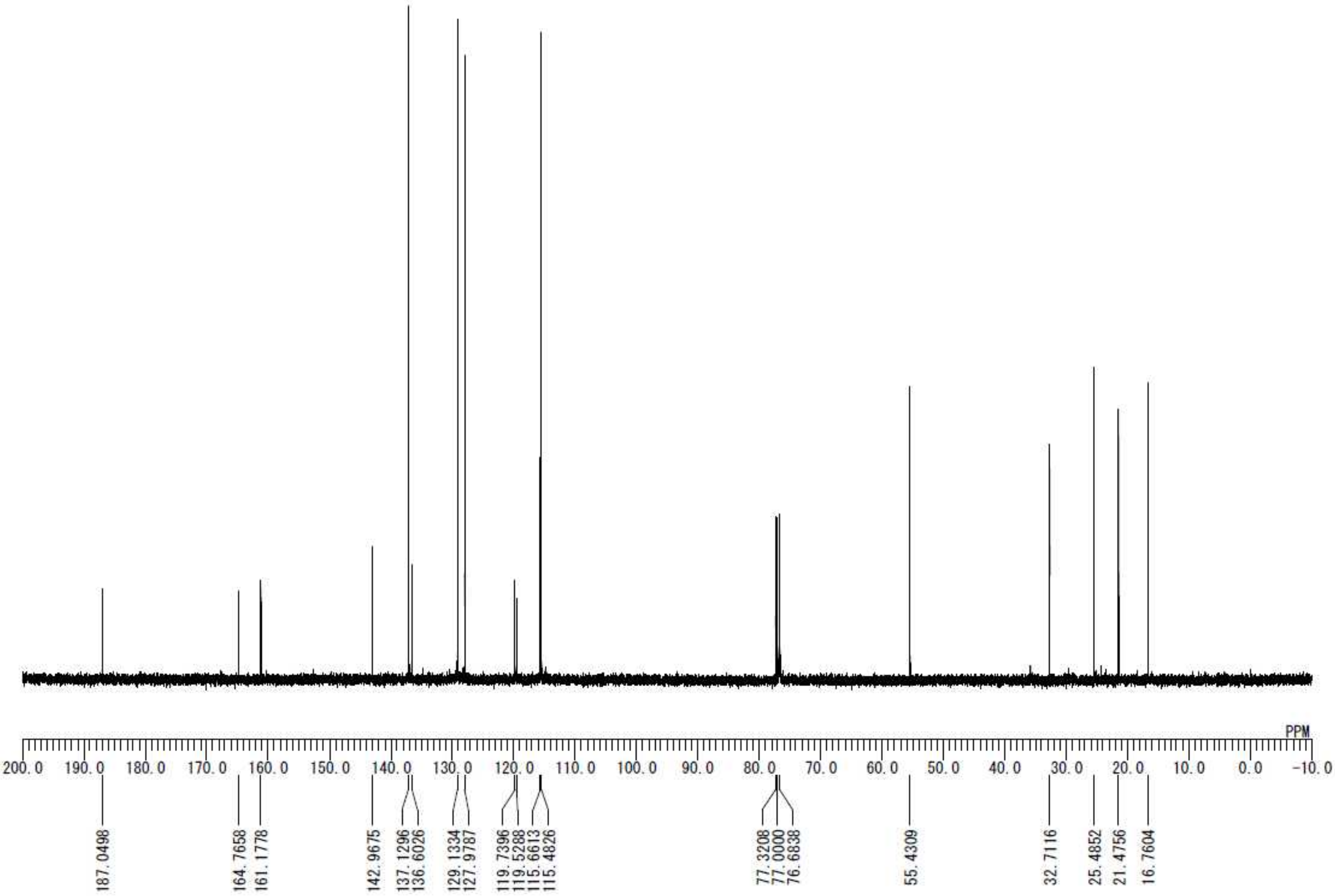
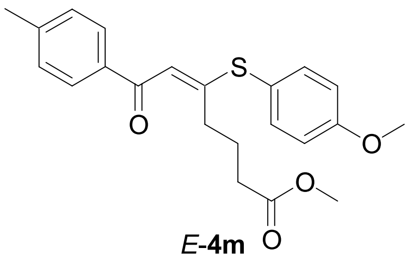
77.0000
76.6838
55.3713
44.3920
36.1804
31.7126
27.0340
21.5765



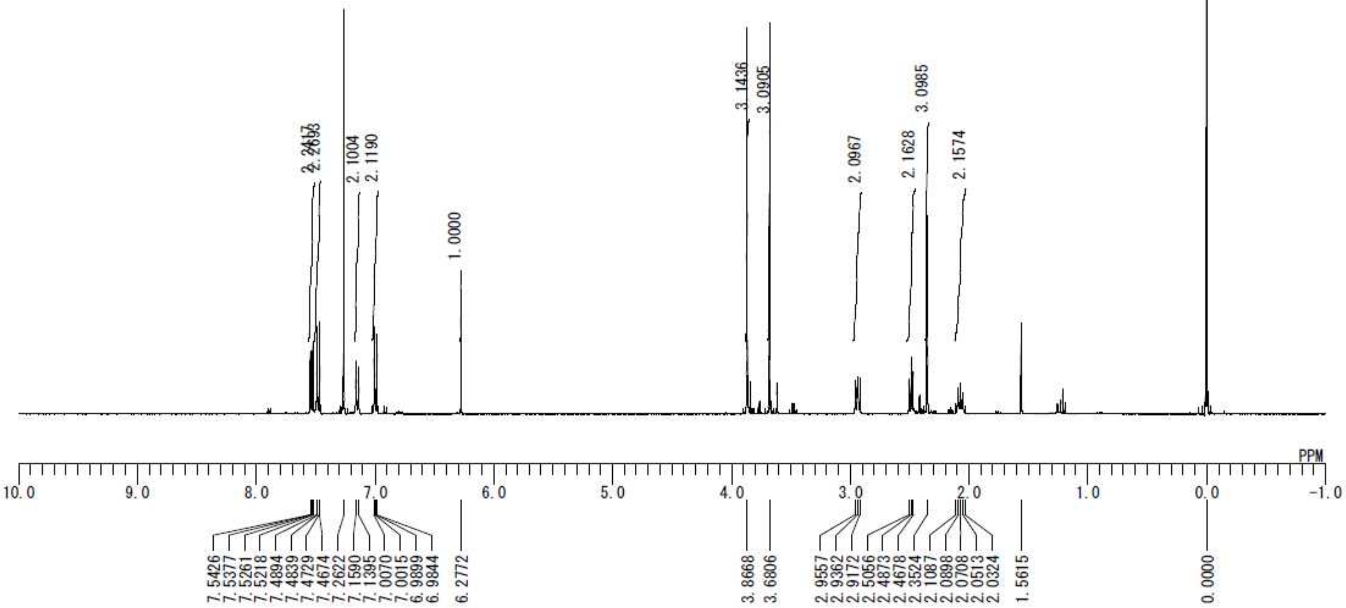
E-**4l**

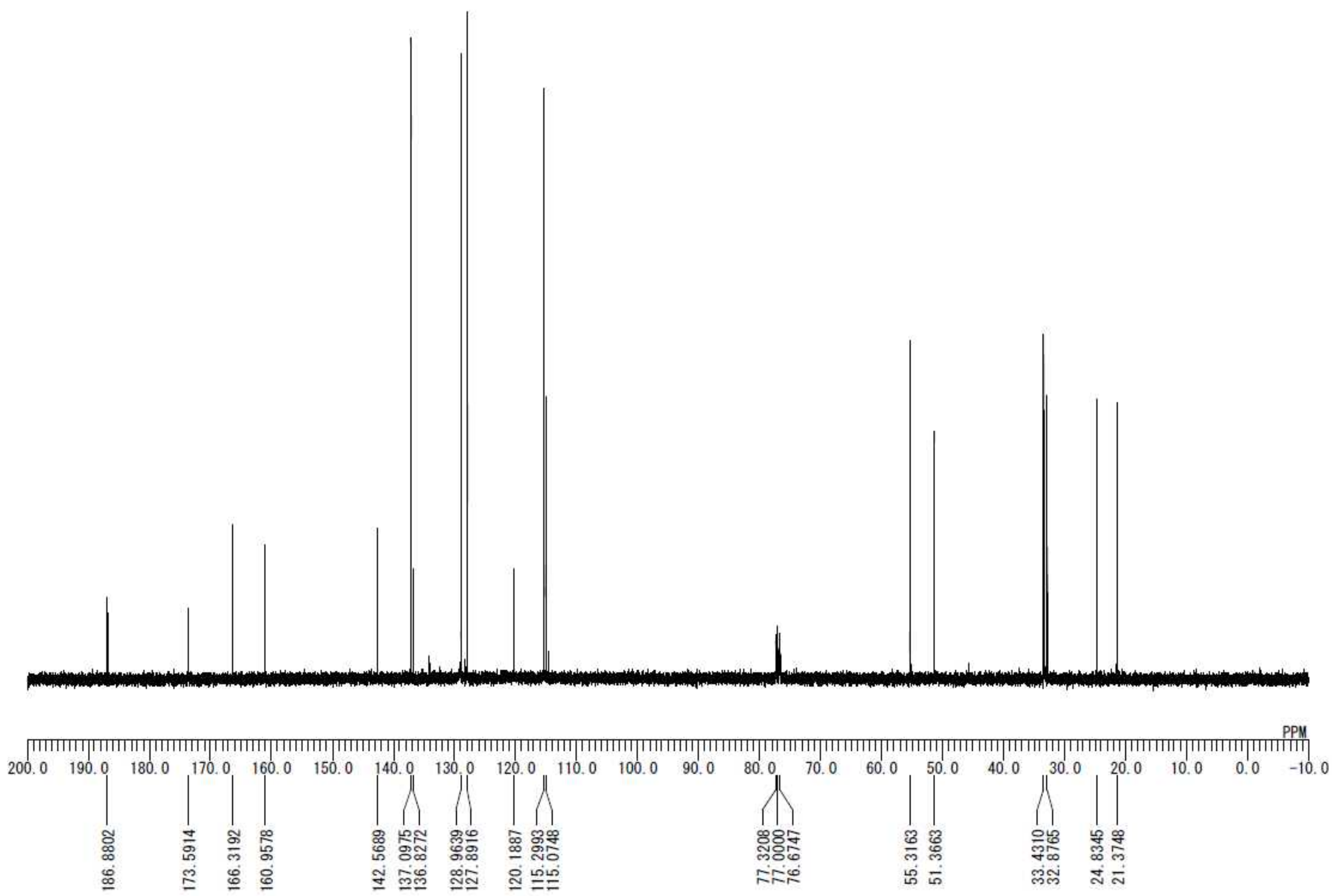


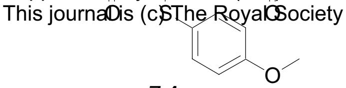




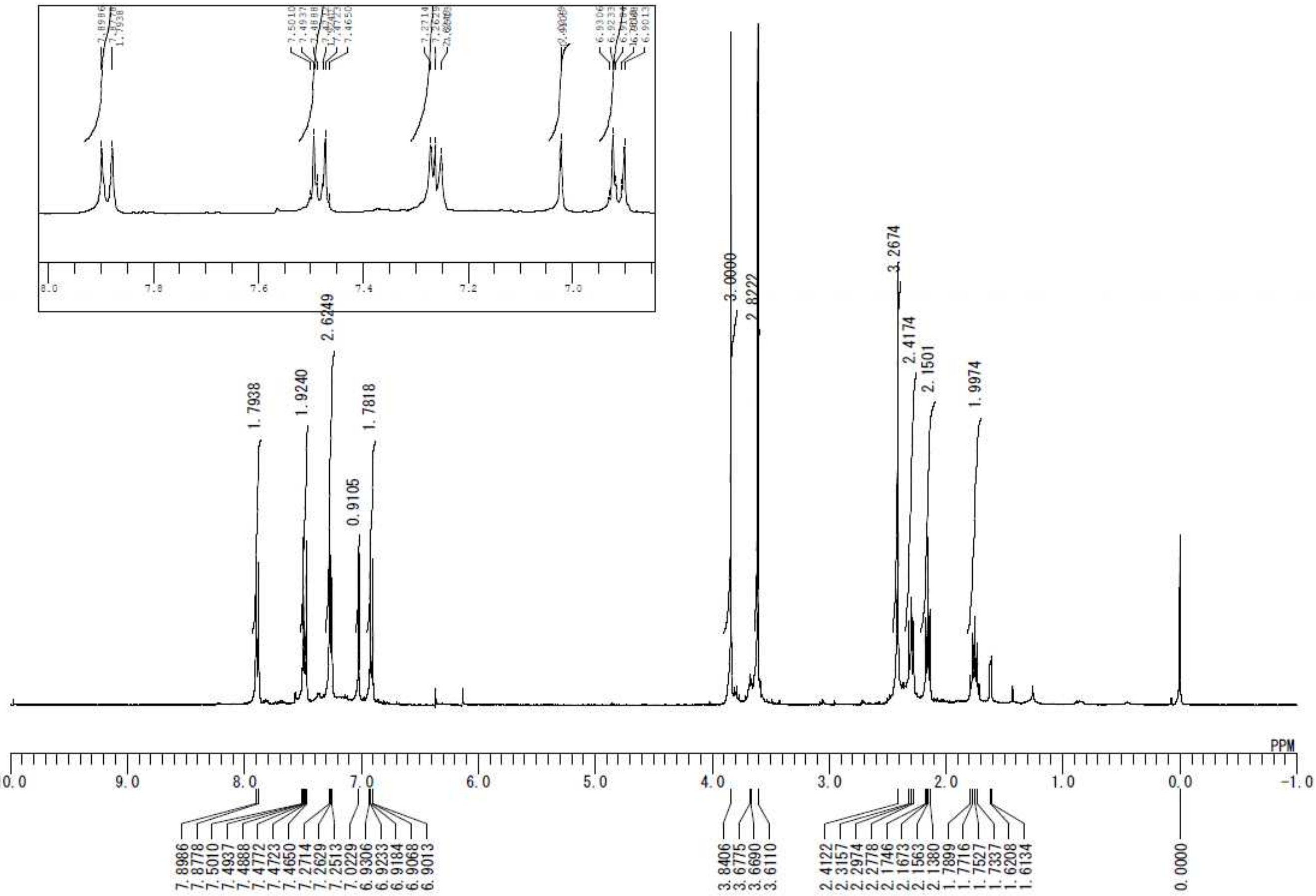
E-**4m**







Z-**4m**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2.6249
0.9105
1.7818
3.0000
2.8222
3.2674
2.4174
2.1501
1.9974
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.8986
7.8778
7.5010
7.4937
7.4888
7.4772
7.4723
7.4650
7.2714
7.2629
7.2513
7.0229
6.9306
6.9233
6.9184
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6.9013
3.8406
3.6775
3.6690
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2.1746
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1.7337
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1.6134
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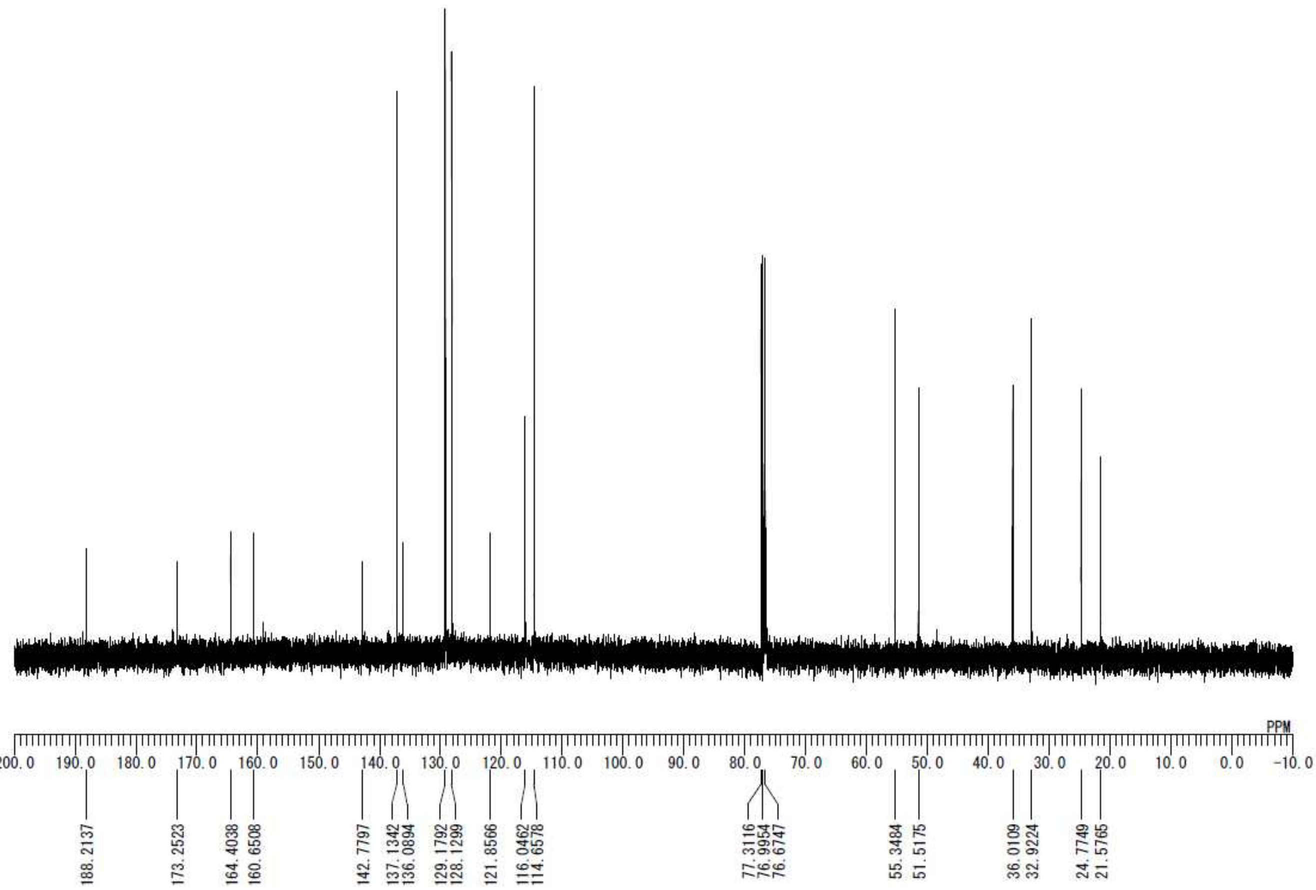
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140.0
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120.0
110.0
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80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
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173.2523
164.4038
160.6508
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137.1342
136.0894
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128.1299
121.8566
116.0462
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76.6747
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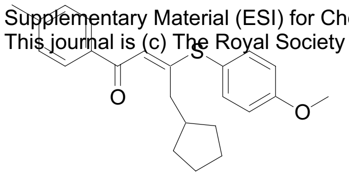
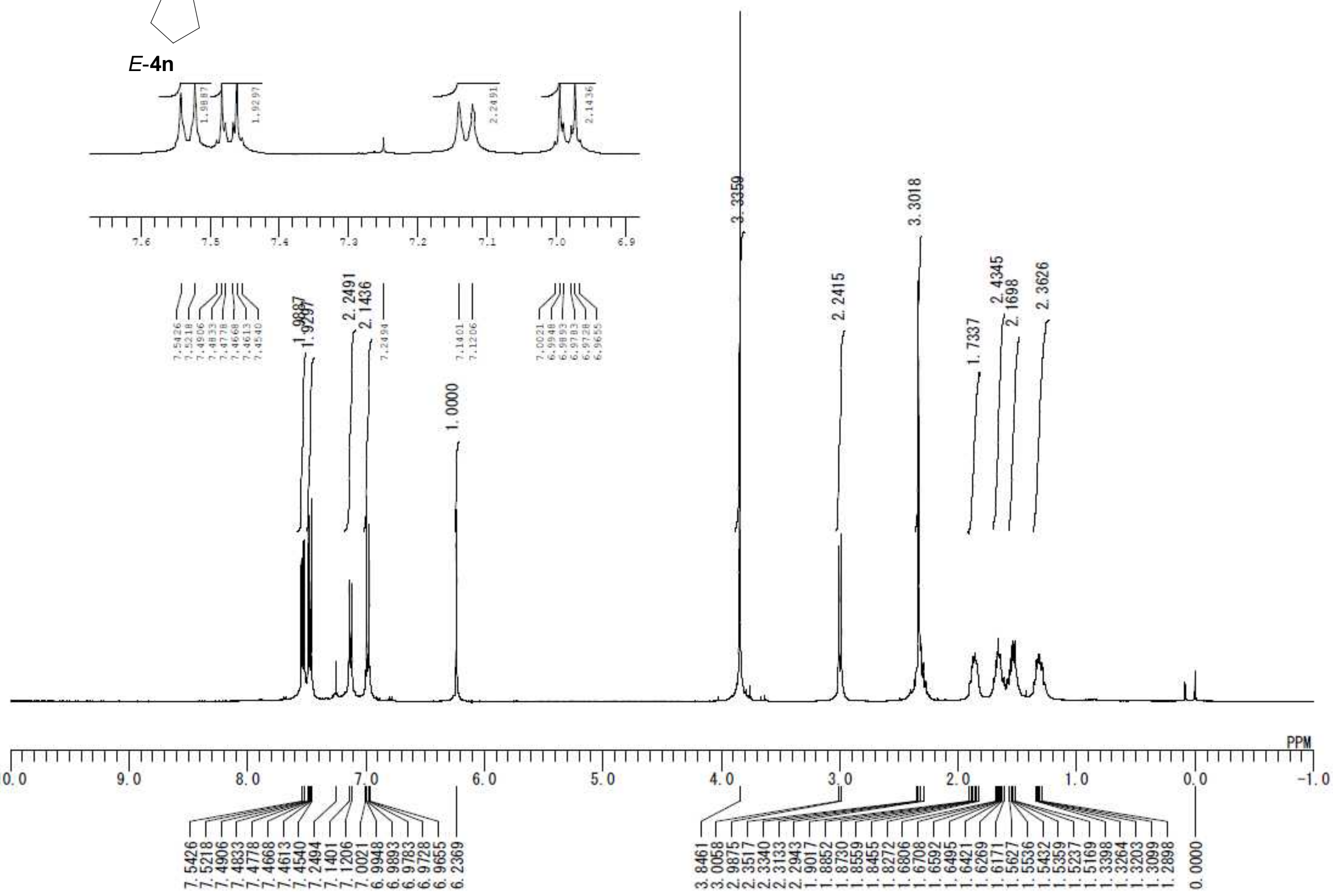
51.5175
36.0109
32.9224
24.7749
21.5765


S
O
O

E-**4n**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7.5218
7.4906
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7.4778
7.4668
7.4613
7.4540
7.2494
7.1401
7.1206
7.0021
6.9948
6.9893
6.9783
6.9728
6.9655
1.0000
3.3359
2.2415
3.3018
1.7337
2.4345
2.1698
2.3626
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
6.2369
3.8461
3.0058
2.9875
2.3517
2.3340
2.3133
2.2943
1.9017
1.8852
1.8730
1.8559
1.8455
1.8272
1.6806
1.6708
1.6592
1.6495
1.6421
1.6269
1.6171
1.5627
1.5536
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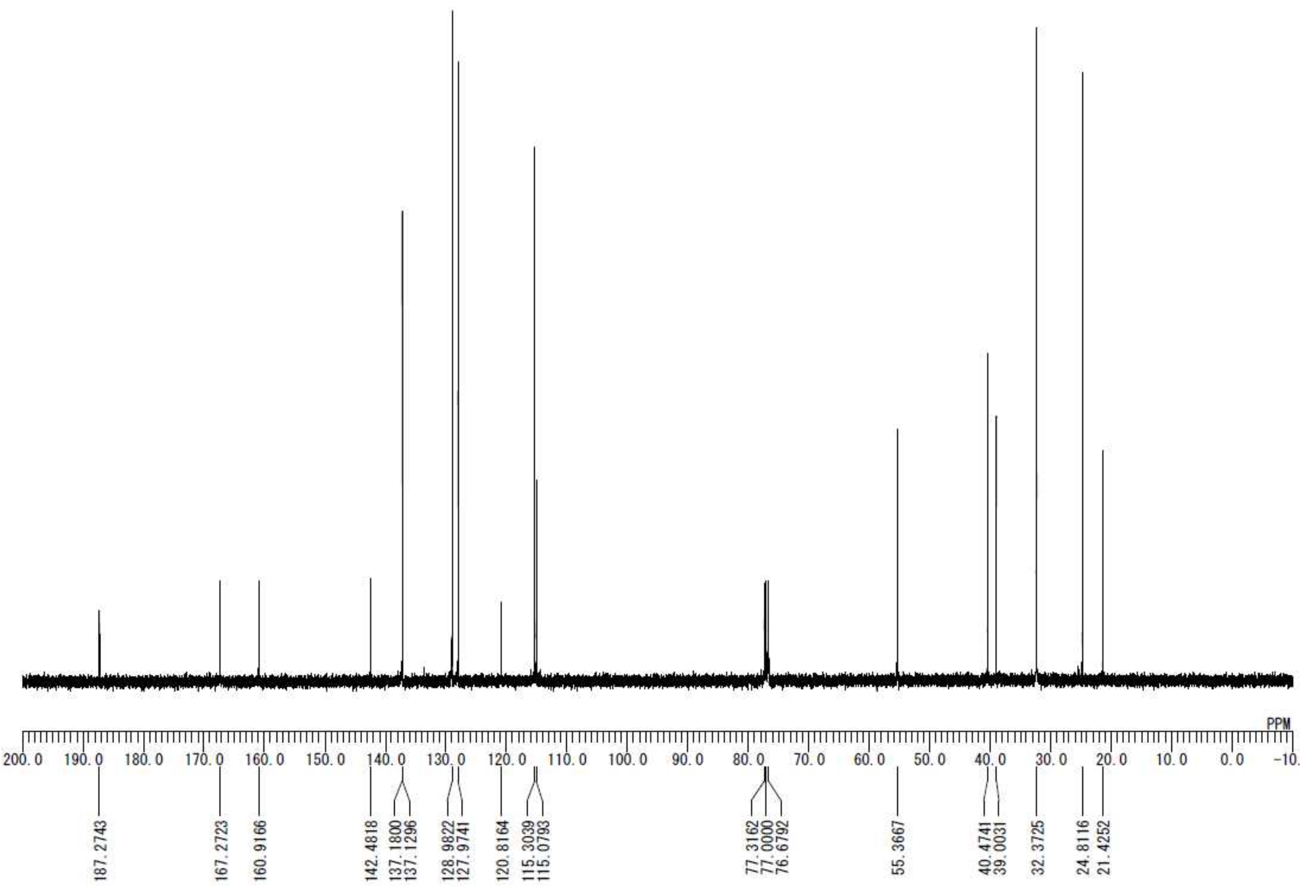
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150.0
140.0
130.0
120.0
110.0
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
187.2743
167.2723
160.9166
142.4818
137.1800
137.1296
128.9822
127.9741
120.8164
115.3039
115.0793
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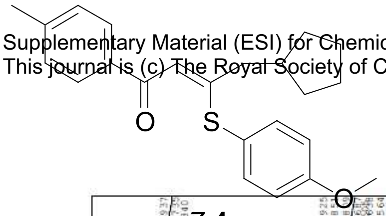
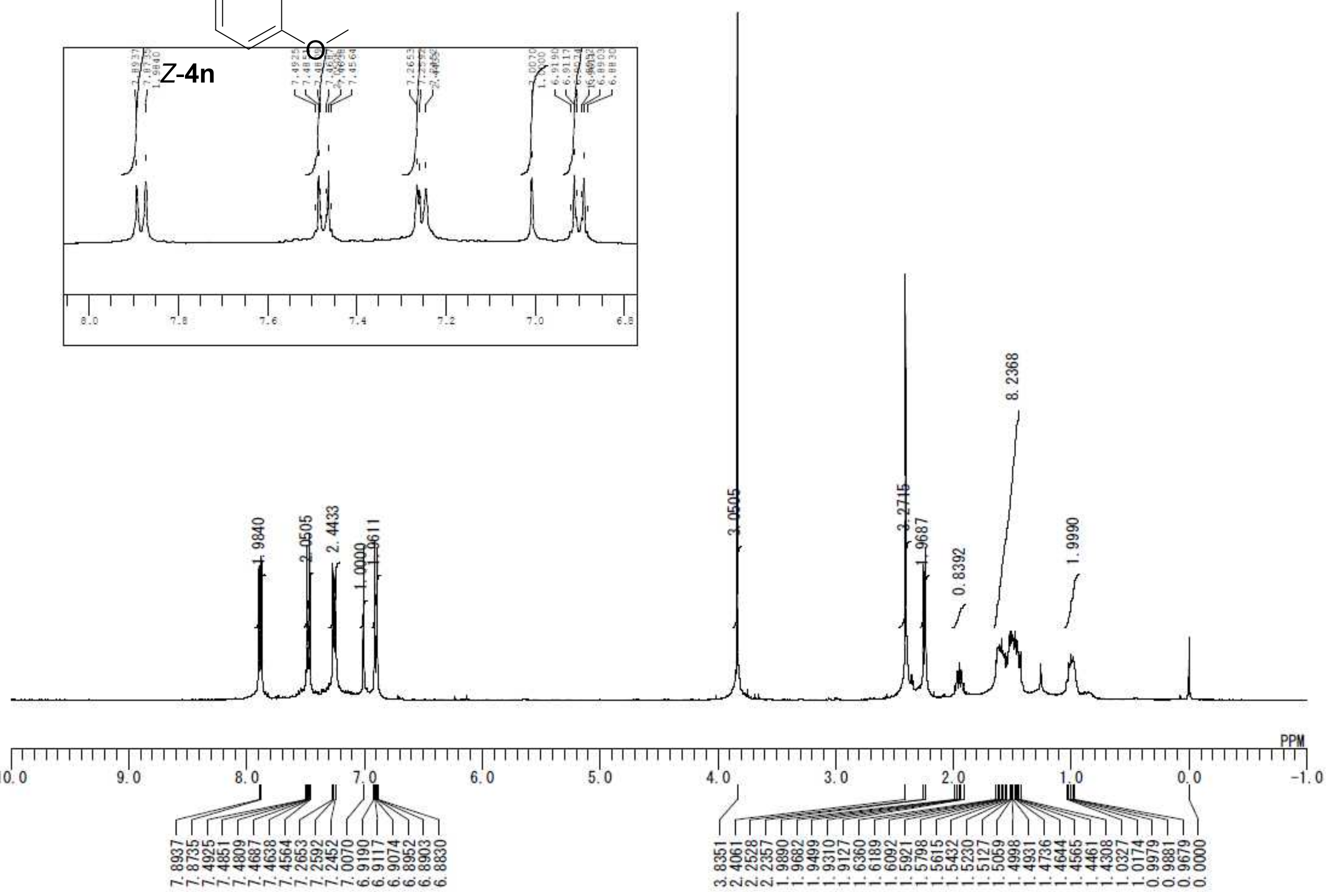
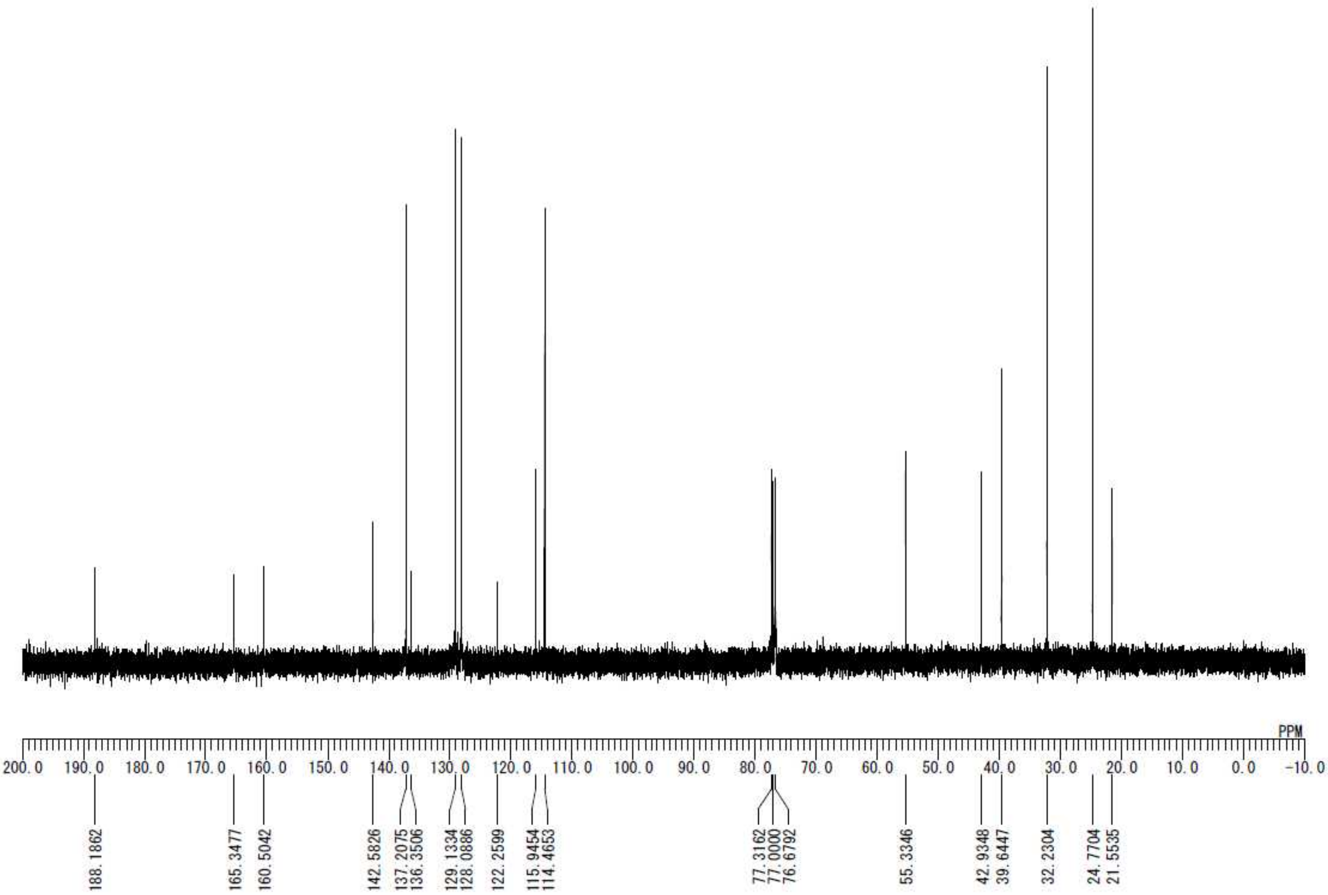
39.0031
32.3725
24.8116
21.4252

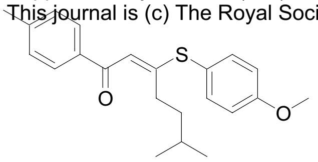
Supplementary Material (ESI) for Chemical Communications



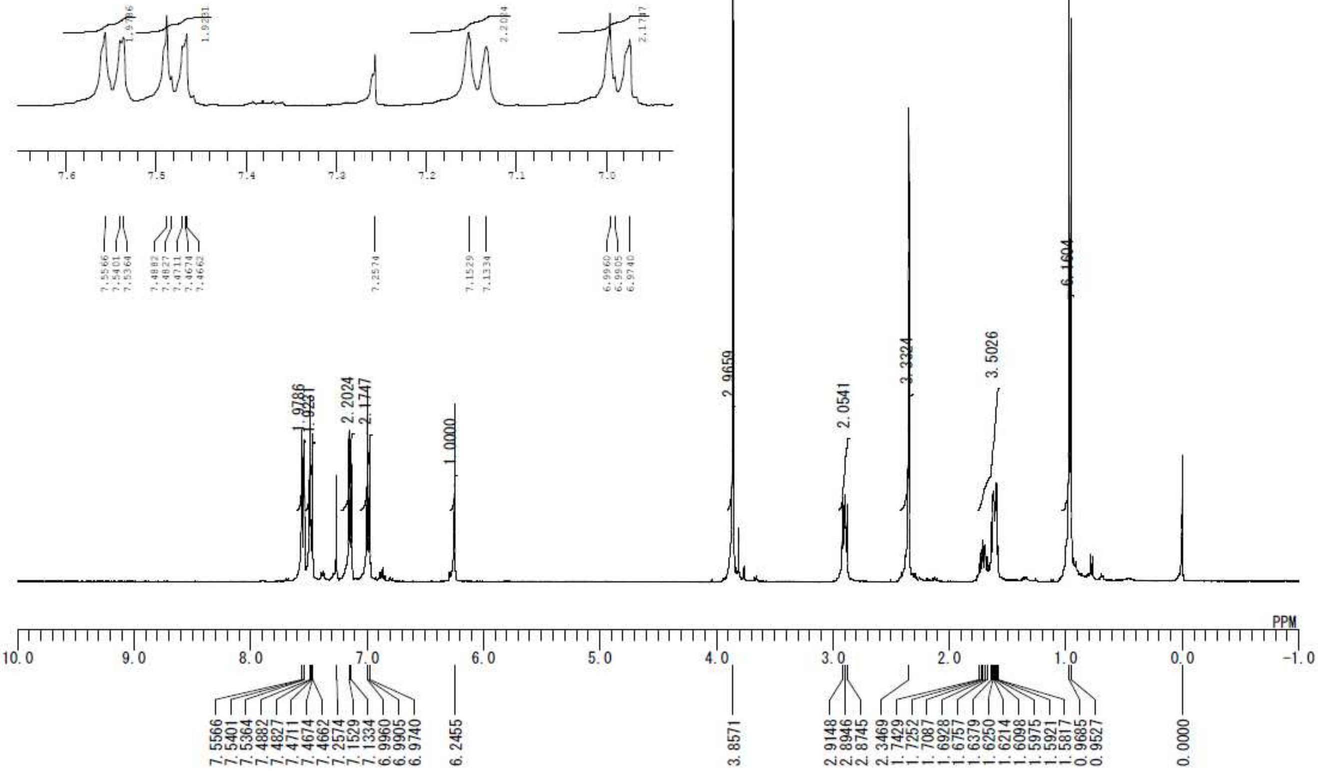
Z-**4n**






S
O
O

E-**4o**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2.9659
2.0541
3.3324
3.5026
6.1604
7.5566
7.5401
7.5364
7.4882
7.4827
7.4711
7.4674
7.4662
7.2574
7.1529
7.1334
6.9960
6.9905
6.9740
6.2455
3.8571
2.9148
2.8946
2.8745
2.3469
1.7429
1.7252
1.7087
1.6928
1.6757
1.6379
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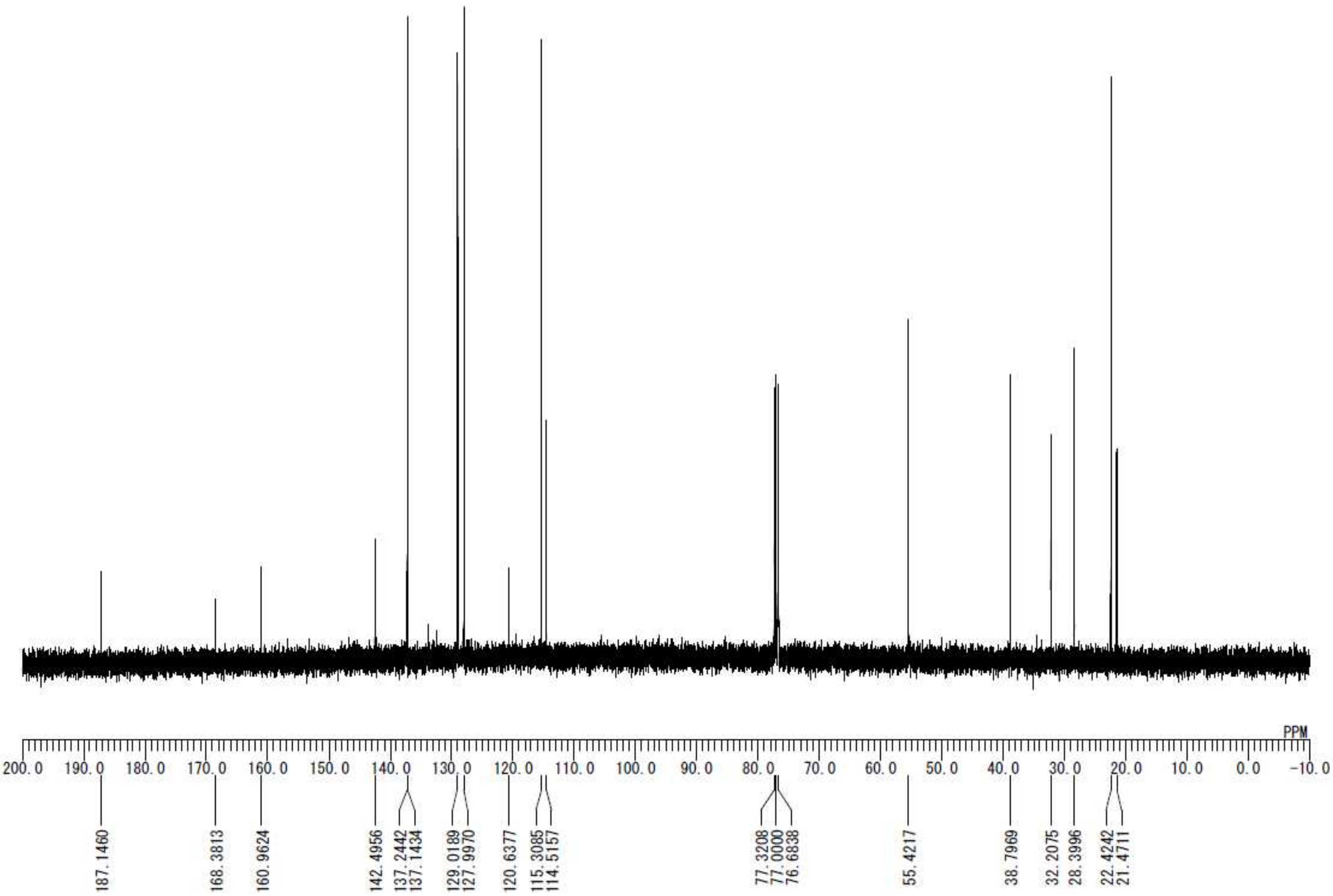
0.0000
PPM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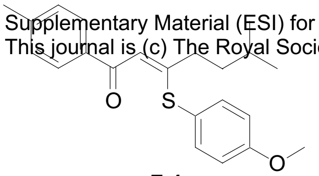
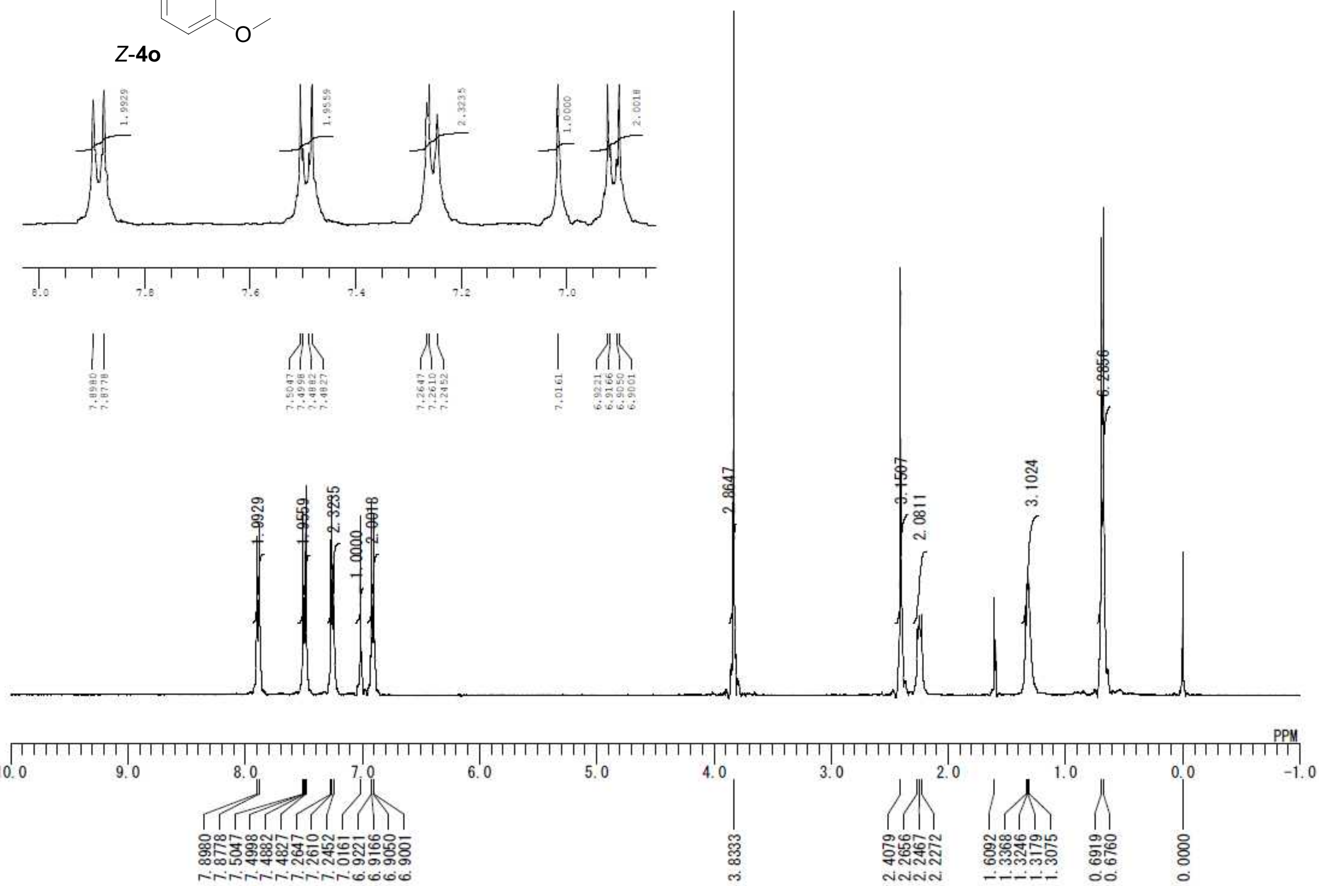
PPM


O
S
O

Z-**4o**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7.6
7.4
7.2
7.0
7.8980
7.8778
7.5047
7.4998
7.4882
7.4827
7.2647
7.2610
7.2452
7.0161
6.9221
6.9166
6.9050
6.9001
2.8647
3.1507
2.0811
3.1024
6.2856
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
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2.2656
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1.3075
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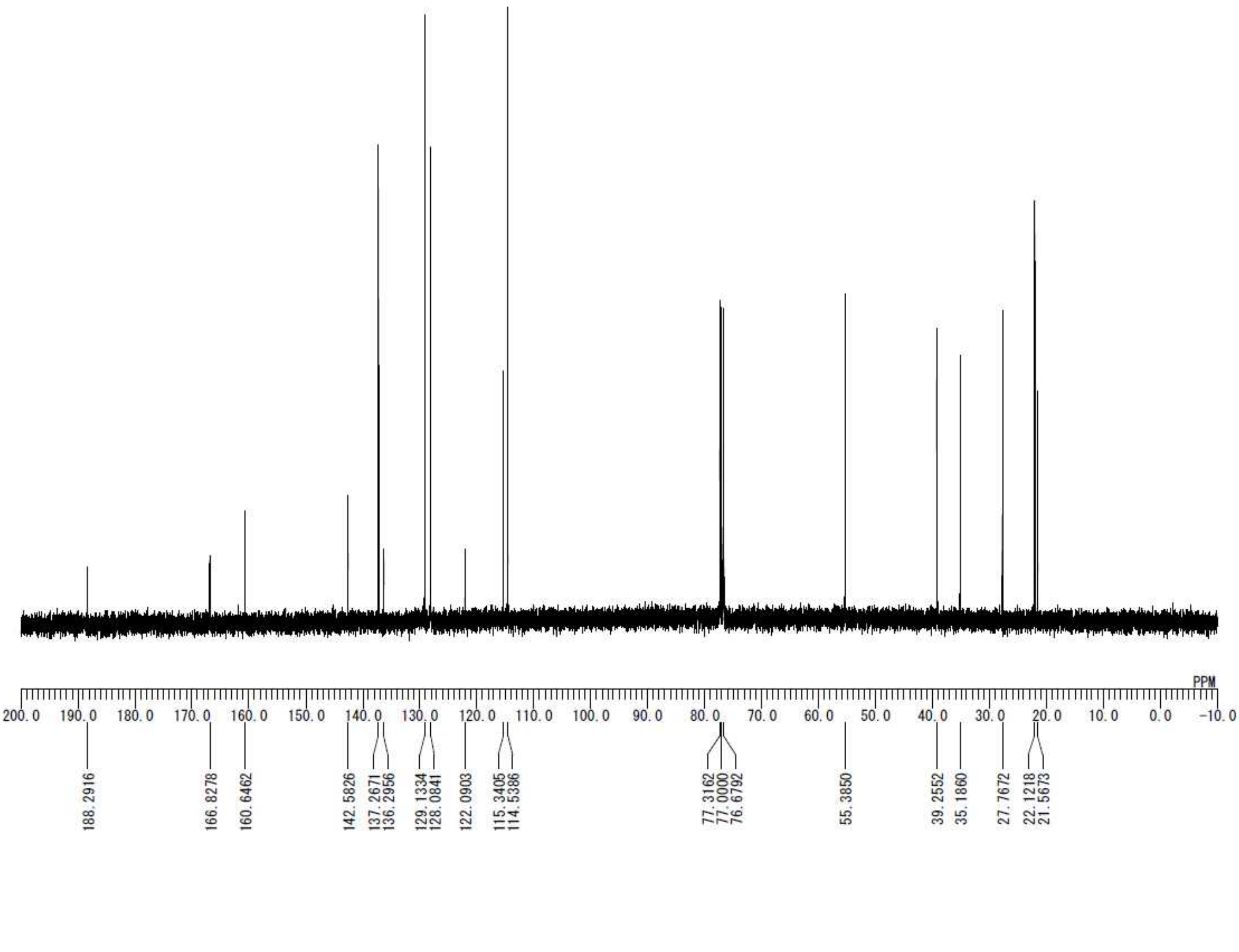
0.0000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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
188.2916
166.8278
160.6462
142.5826
137.2671
136.2956
129.1334
128.0841
122.0903
115.3405
114.5386
77.3162
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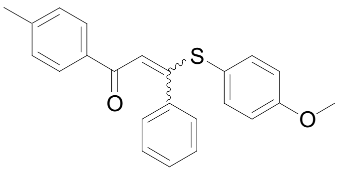
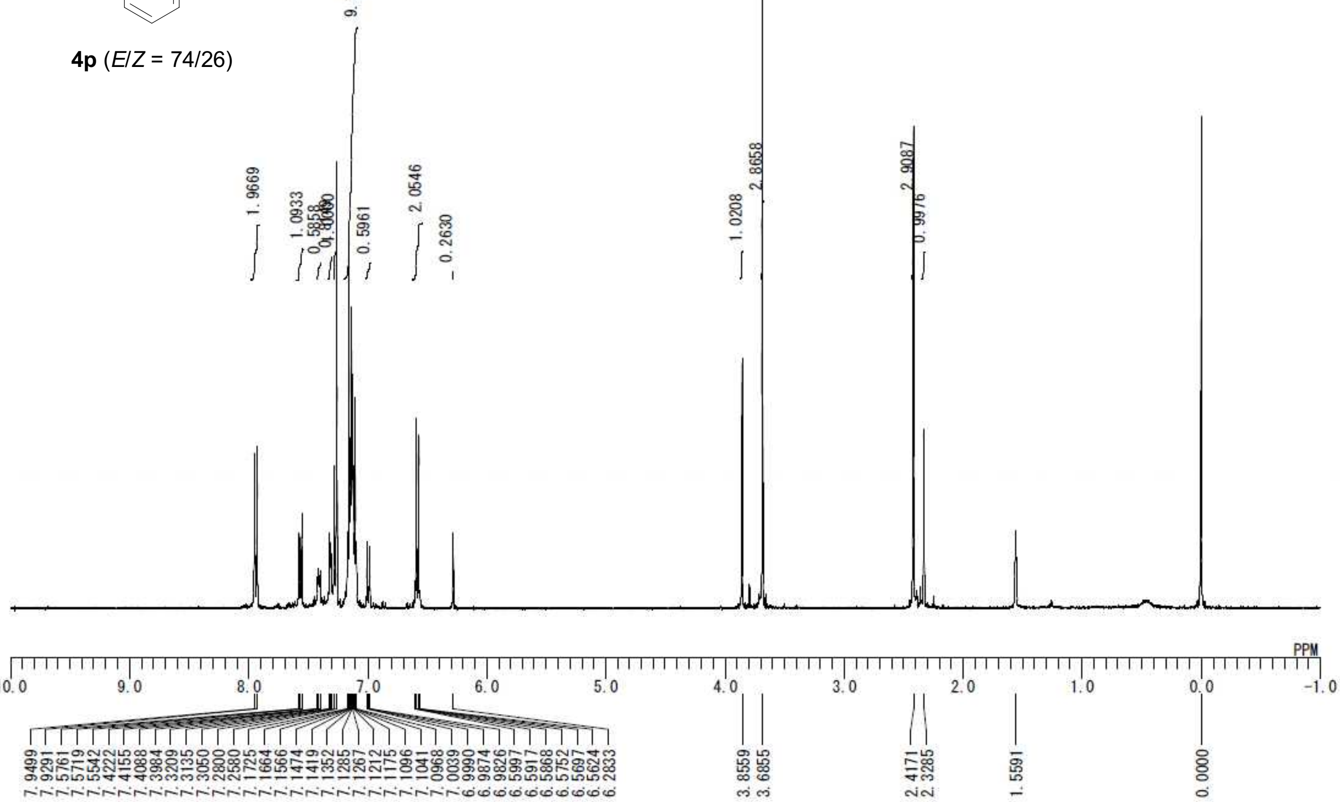
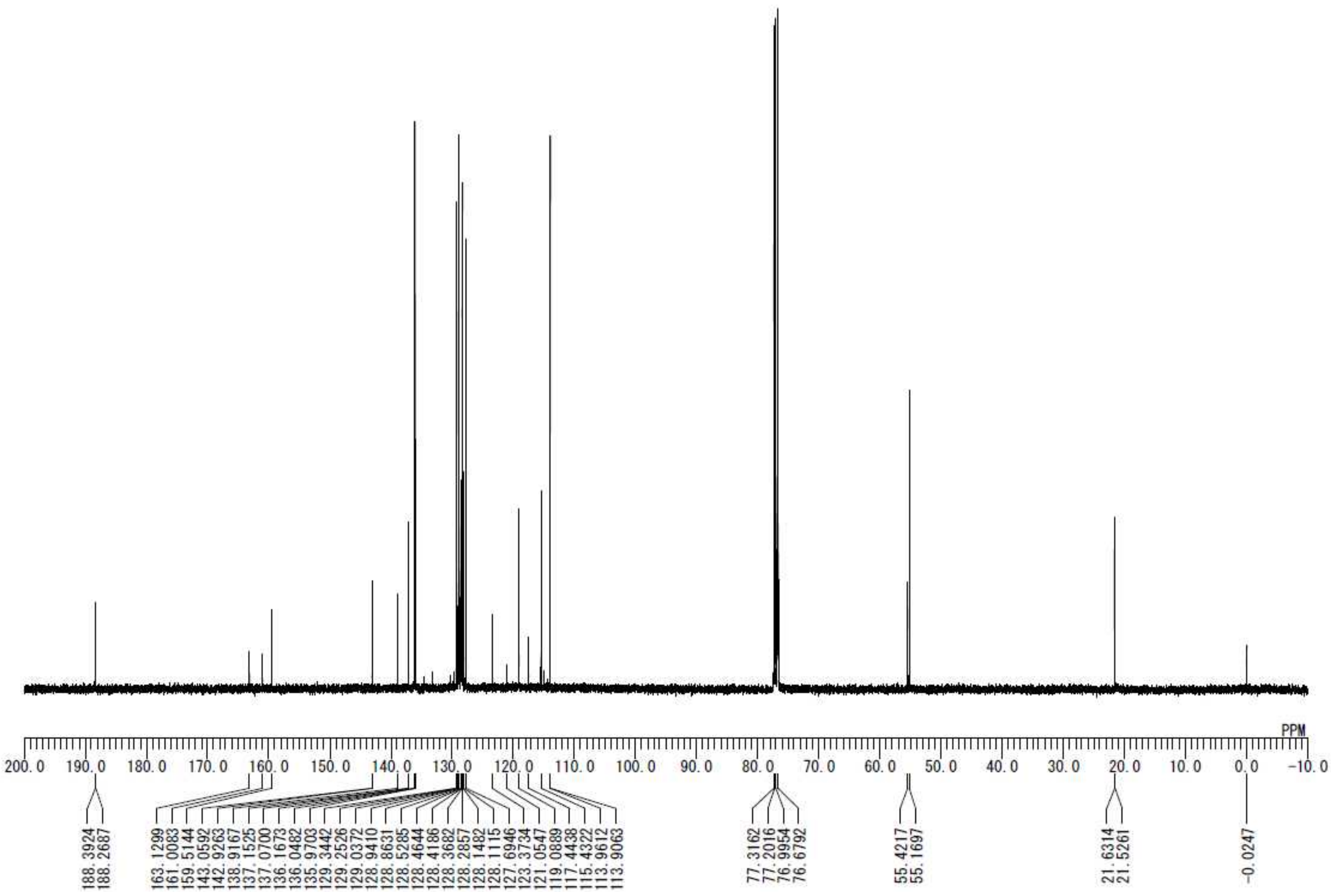
22.1218
21.5673

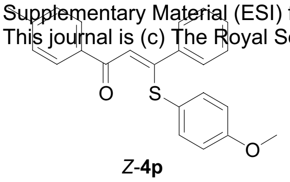
Supplementary Material (ESI) for Chemical Communications



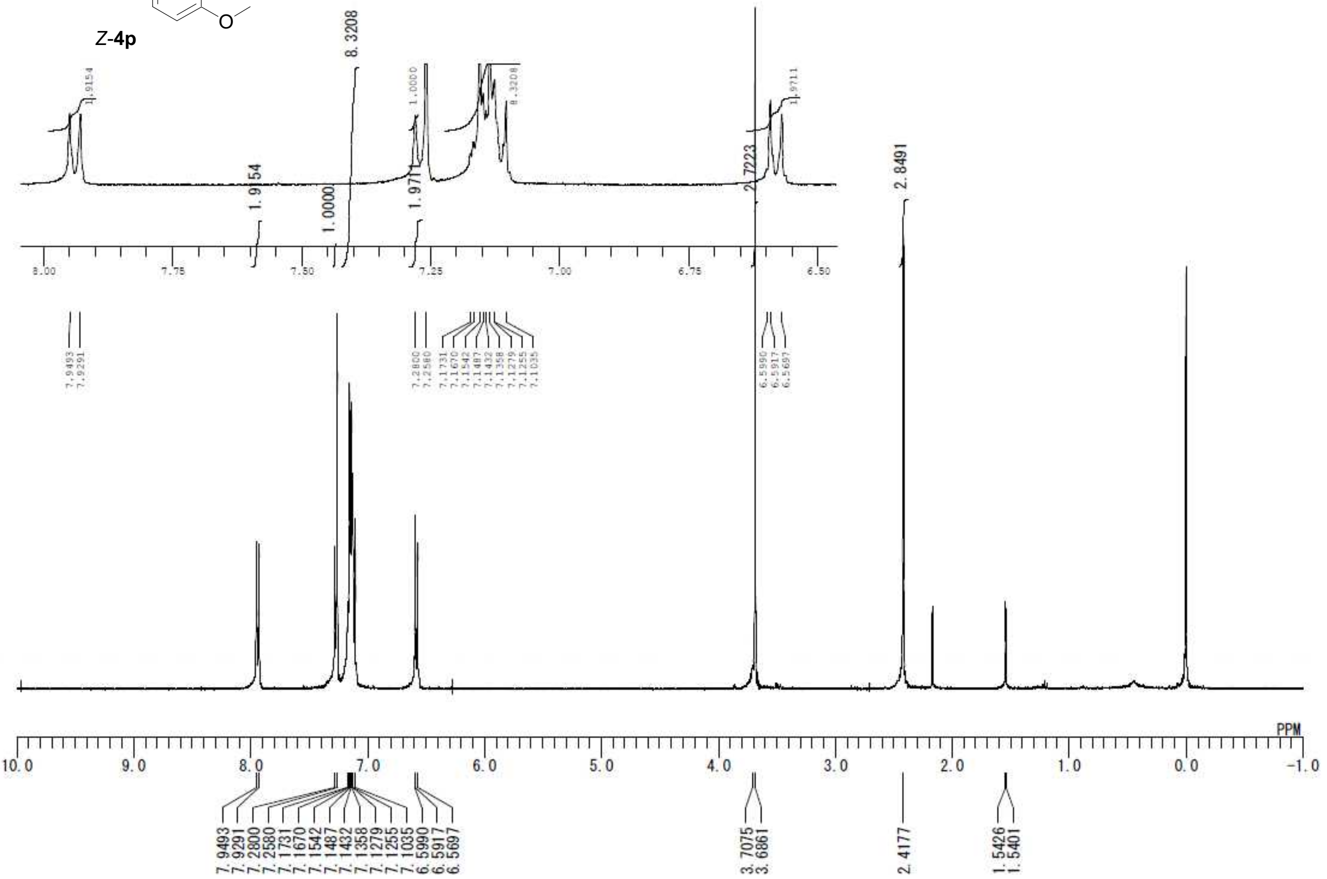
4p (*E*/*Z* = 74/26)






O
S
O

Z-**4p**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2.8491
PPM
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6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.9493
7.9291
7.2800
7.2580
7.1731
7.1670
7.1542
7.1487
7.1432
7.1358
7.1279
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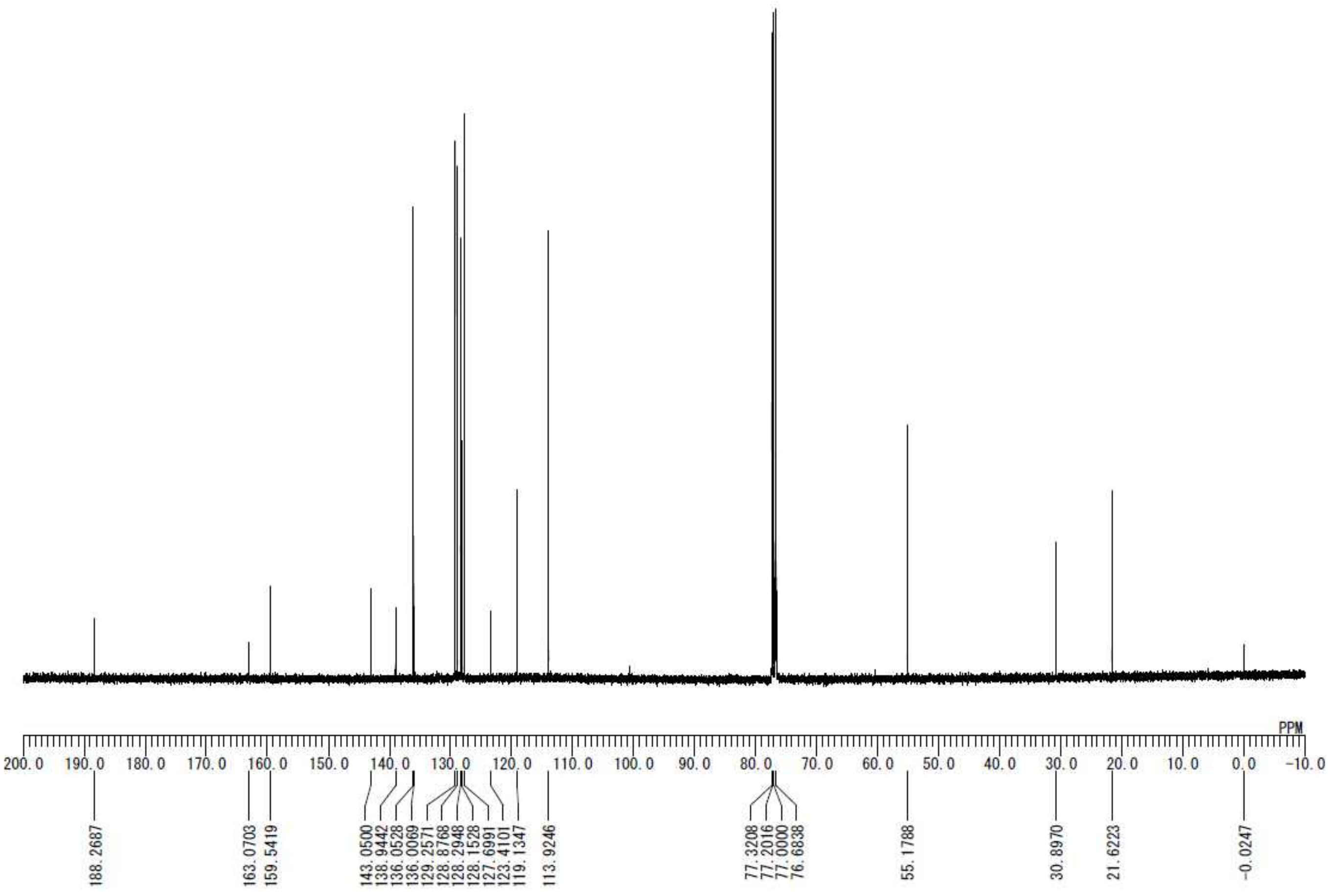
3.7075
3.6861
2.4177
1.5426
1.5401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120.0
110.0
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80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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163.0703
159.5419
143.0500
138.9442
136.0528
136.0069
129.2571
128.8768
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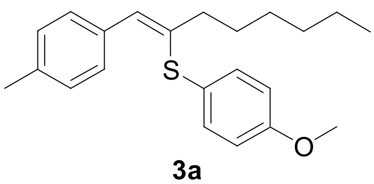
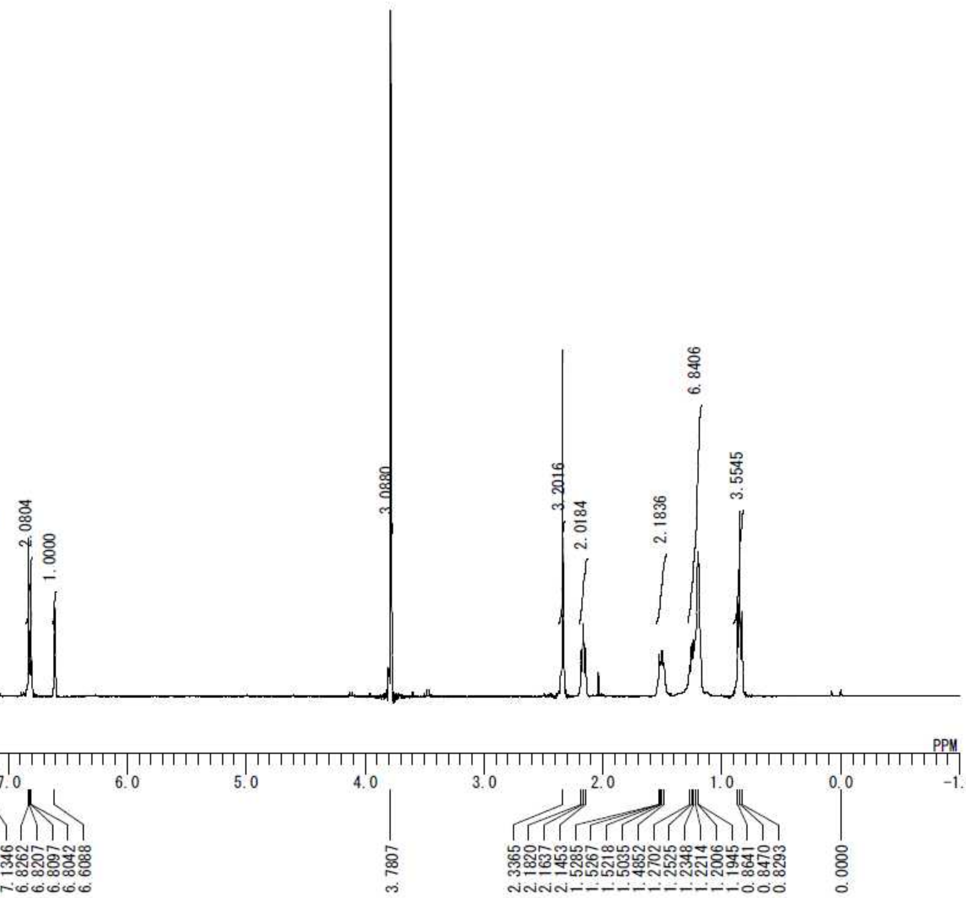
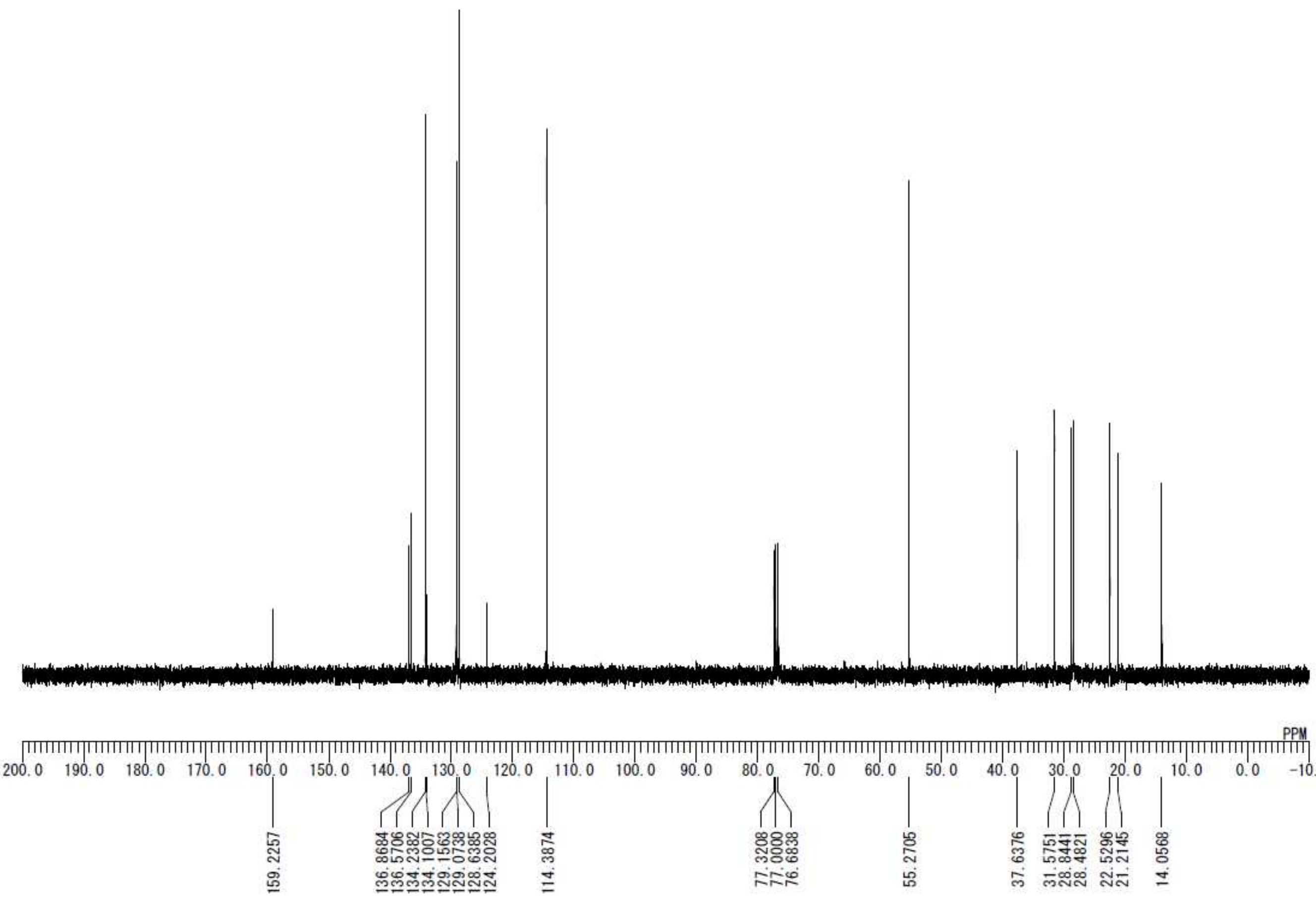
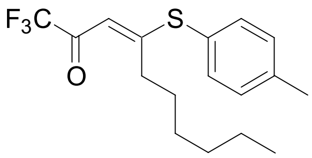


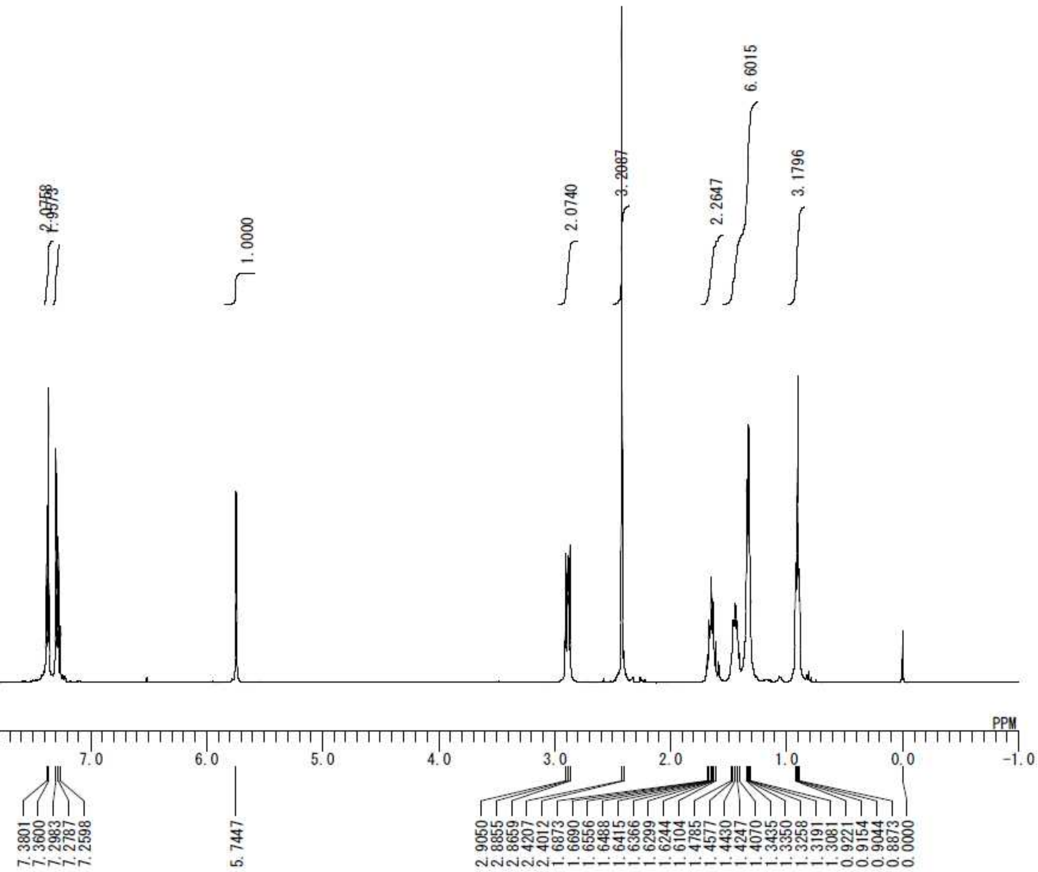
3a

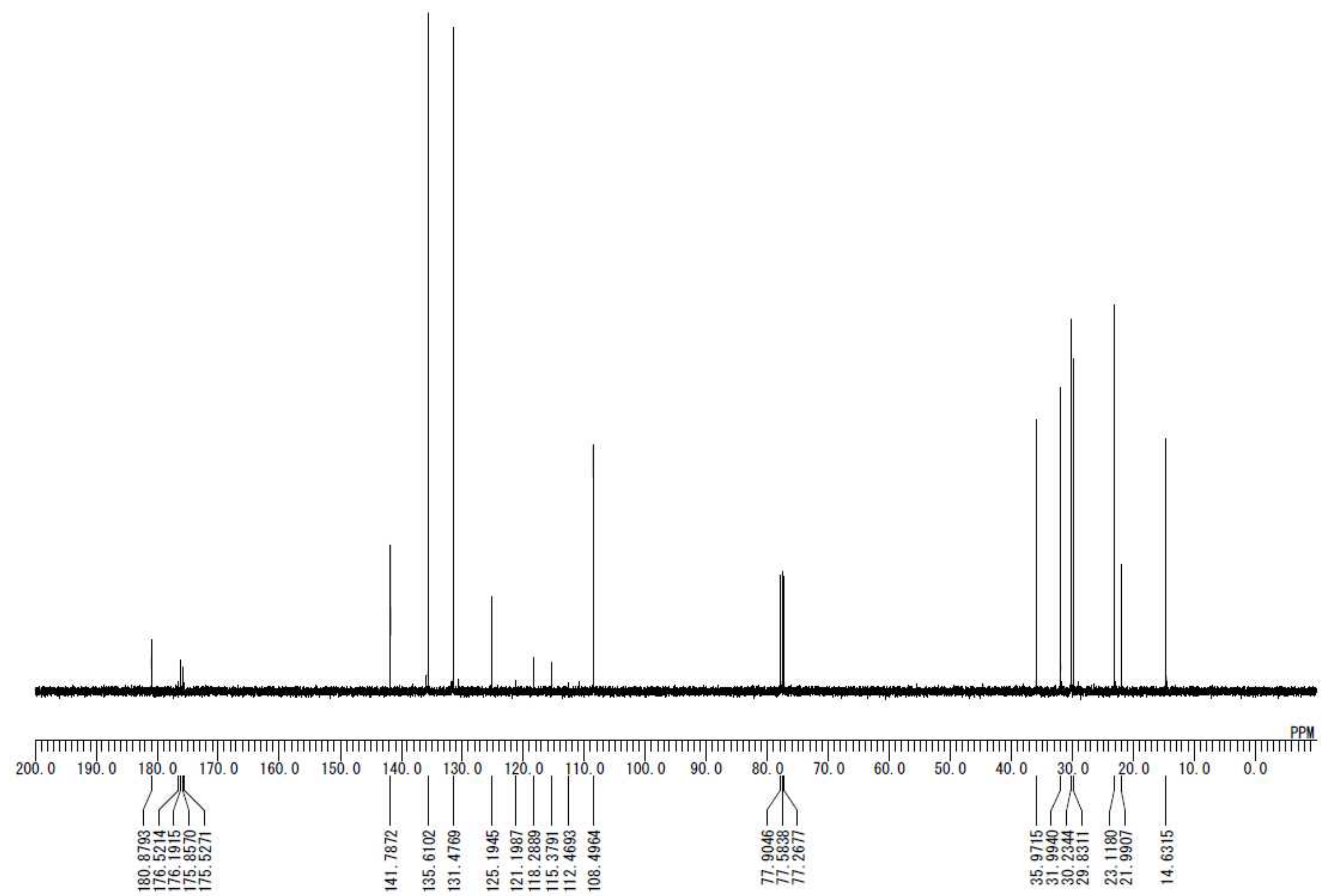


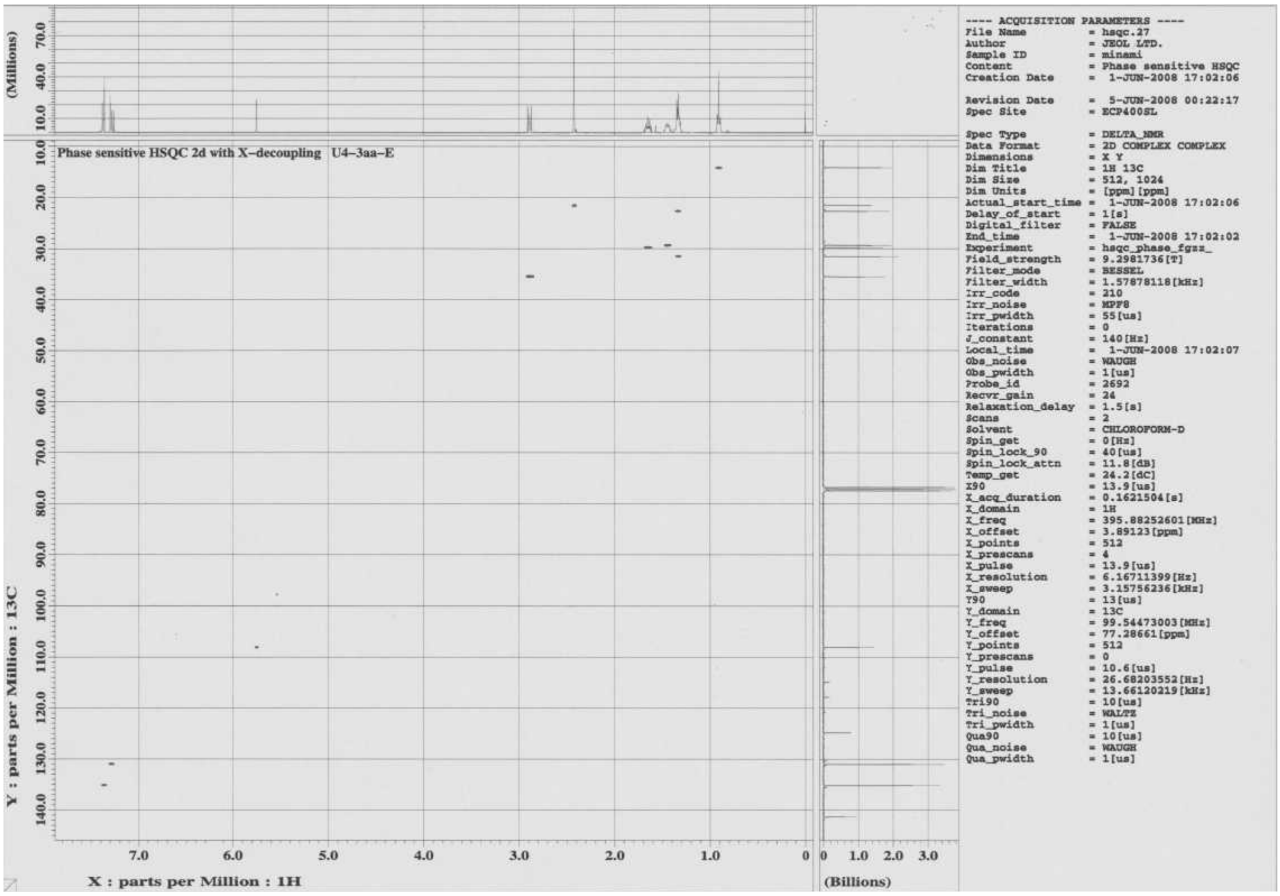


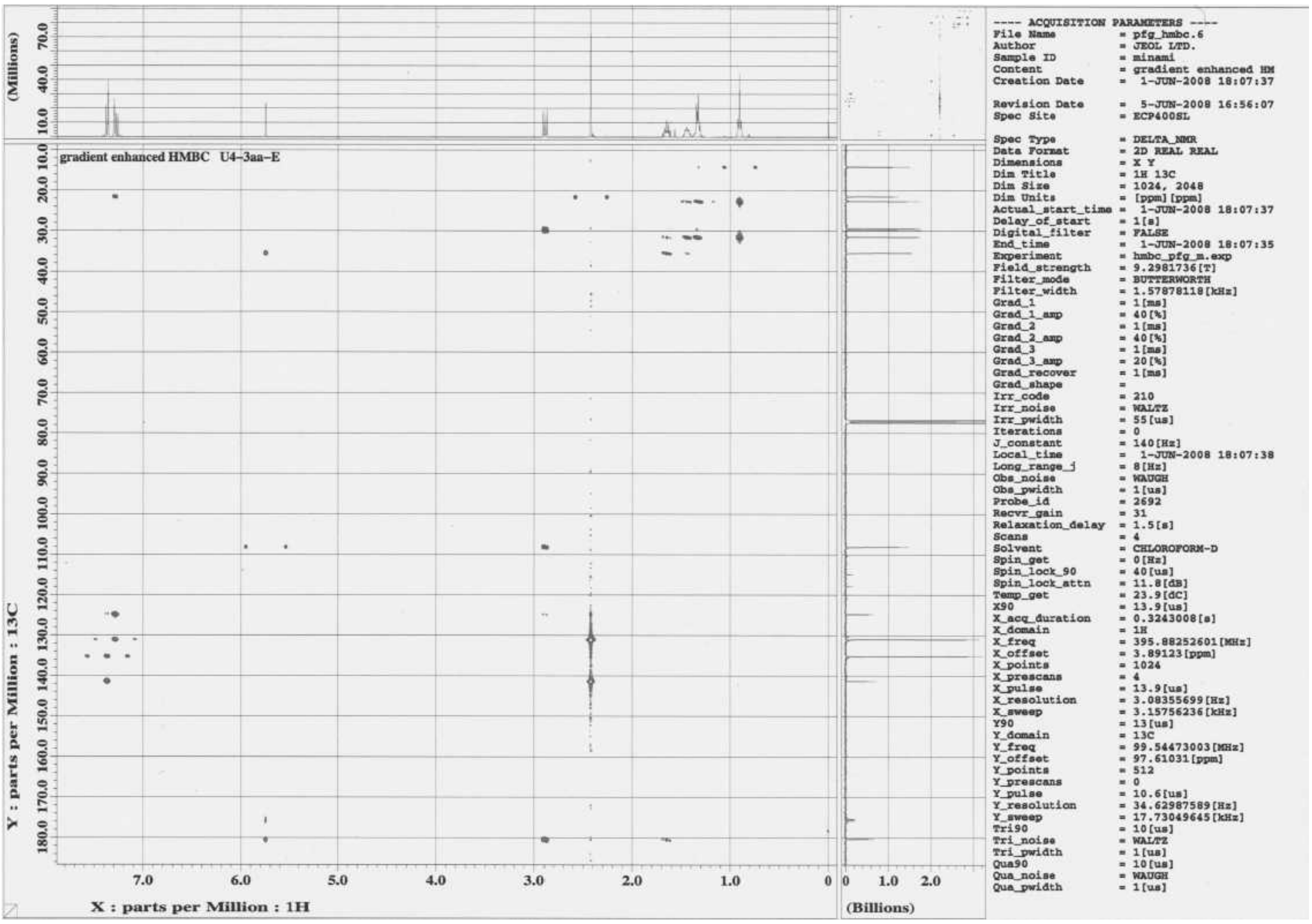


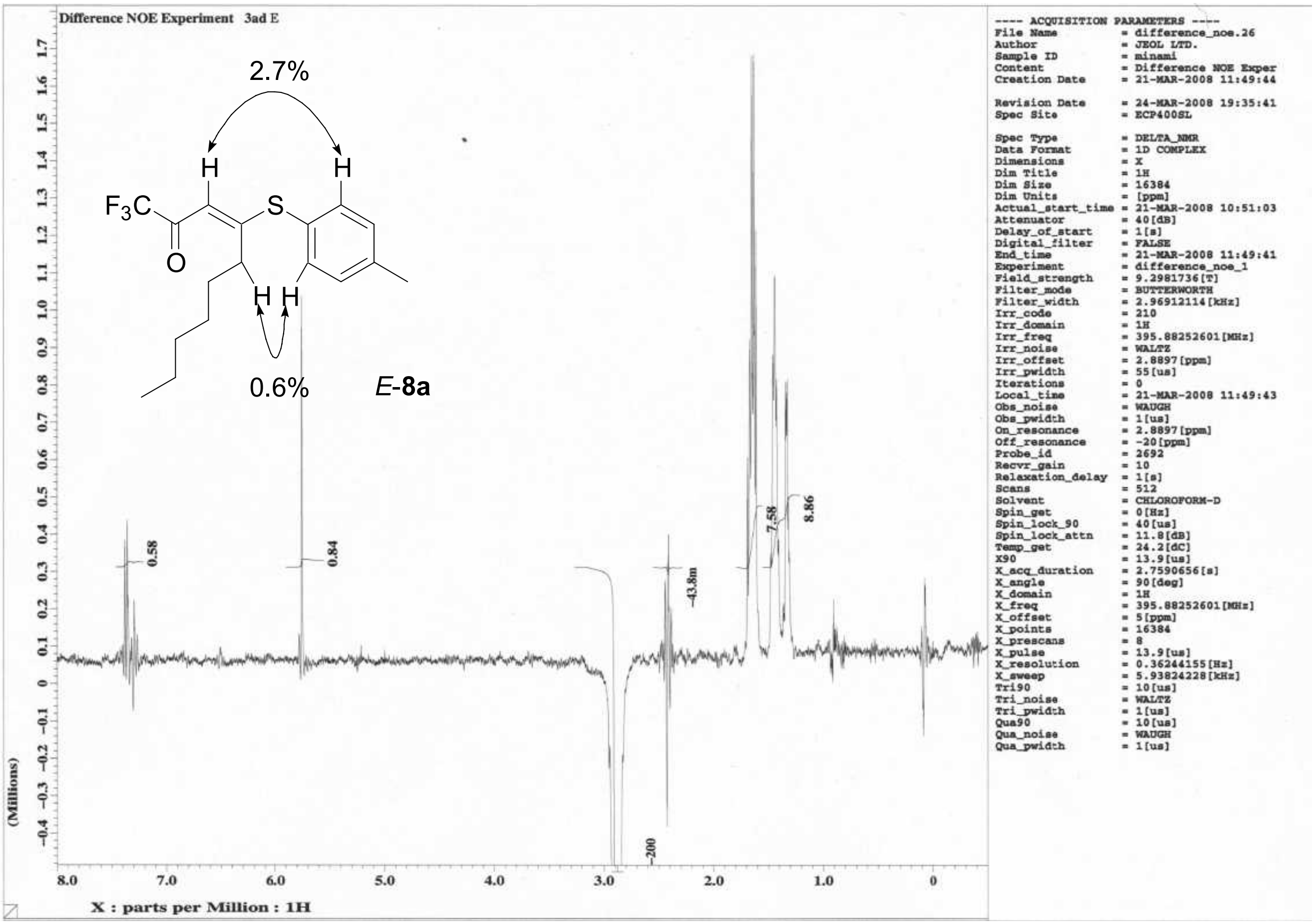
E-**8a**

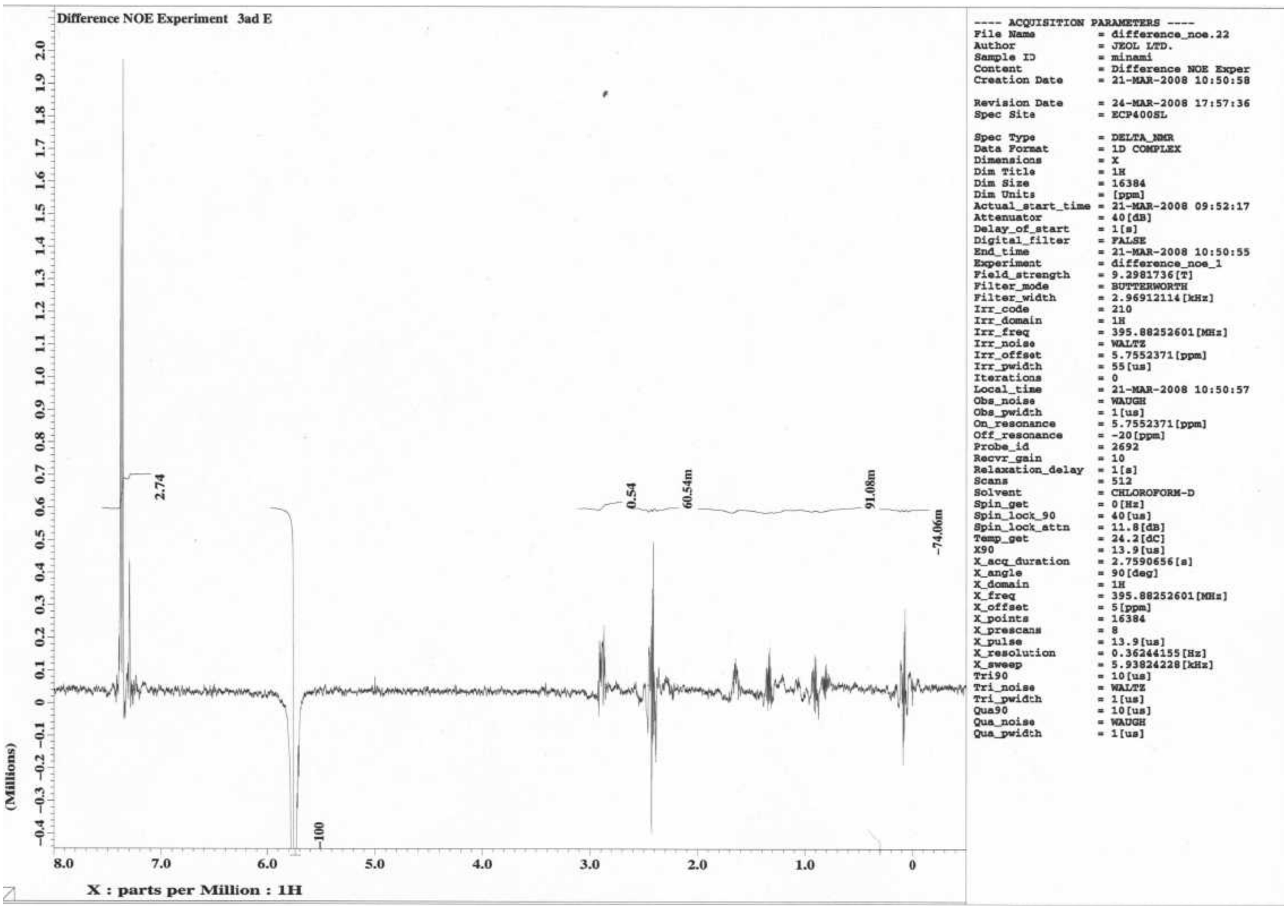


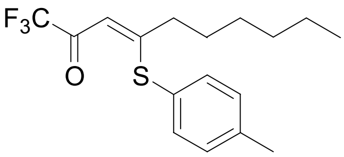



Phase sensitive HSQC 2d with X–decoupling U4–3aa–E
(Millions)
Y : parts per Million : 13C
X : parts per Million : 1H
(Billions)
---- ACQUISITION PARAMETERS ----
File Name = hsqc.27
Author = JEOL LTD.
Sample ID = minami
Content = Phase sensitive HSQC
Creation Date = 1-JUN-2008 17:02:06
Revision Date = 5-JUN-2008 00:22:17
Spec Site = ECP400SL
Spec Type = DELTA_NMR
Data Format = 2D COMPLEX COMPLEX
Dimensions = X Y
Dim Title = 1H 13C
Dim Size = 512, 1024
Dim Units = [ppm] [ppm]
Actual_start_time = 1-JUN-2008 17:02:06
Delay_of_start = 1[s]
Digital_filter = FALSE
End_time = 1-JUN-2008 17:02:02
Experiment = hsqc_phase_fgzz_
Field_strength = 9.2981736[T]
Filter_mode = BESSEL
Filter_width = 1.57878118[kHz]
Irr_code = 210
Irr_noise = MPF8
Irr_pwidth = 55[us]
Iterations = 0
J_constant = 140[Hz]
Local_time = 1-JUN-2008 17:02:07
Obs_noise = WAUGH
Obs_pwidth = 1[us]
Probe_id = 2692
Recvr_gain = 24
Relaxation_delay = 1.5[s]
Scans = 2
Solvent = CHLOROFORM-D
Spin_get = 0[Hz]
Spin_lock_90 = 40[us]
Spin_lock_attn = 11.8[dB]
Temp_get = 24.2[dC]
X90 = 13.9[us]
X_acq_duration = 0.1621504[s]
X_domain = 1H
X_freq = 395.88252601[MHz]
X_offset = 3.89123[ppm]
X_points = 512
X_prescans = 4
X_pulse = 13.9[us]
X_resolution = 6.16711399[Hz]
X_sweep = 3.15756236[kHz]
Y90 = 13[us]
Y_domain = 13C
Y_freq = 99.54473003[MHz]
Y_offset = 77.28661[ppm]
Y_points = 512
Y_prescans = 0
Y_pulse = 10.6[us]
Y_resolution = 26.68203552[Hz]
Y_sweep = 13.66120219[kHz]
Tri90 = 10[us]
Tri_noise = WALTZ
Tri_pwidth = 1[us]
Qua90 = 10[us]
Qua_noise = WAUGH
Qua_pwidth = 1[us]

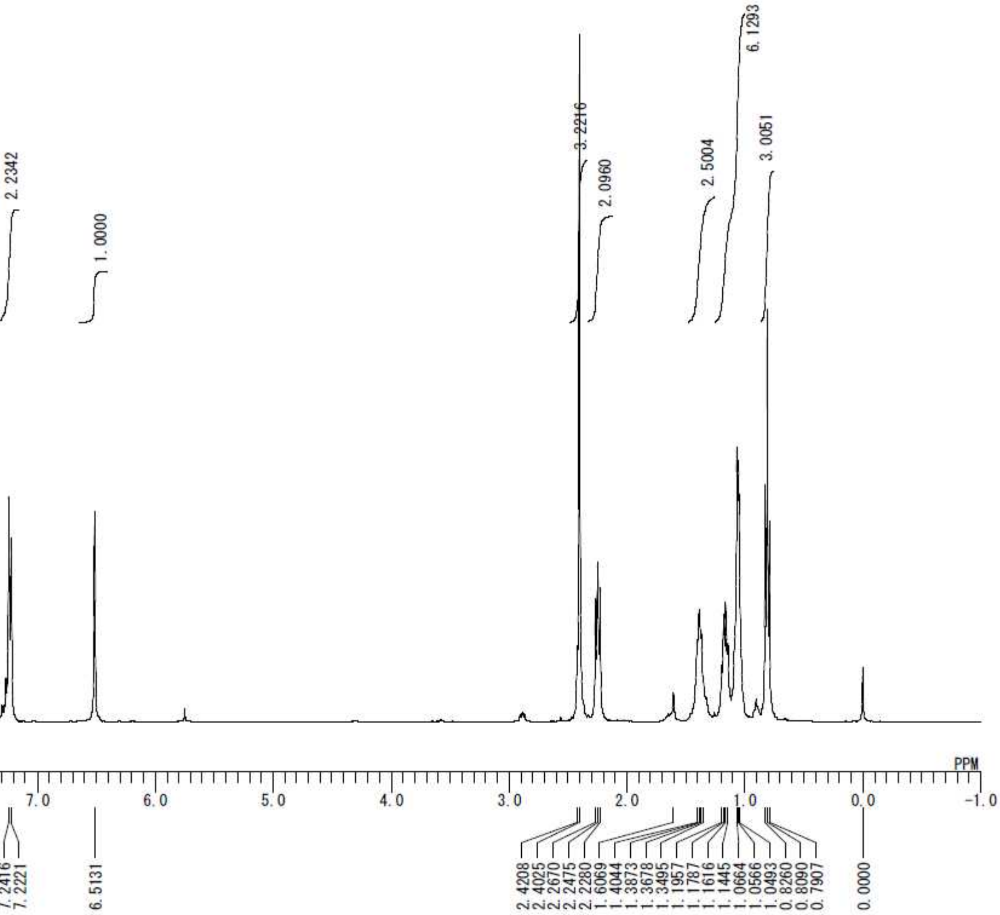

gradient enhanced HMBC U4–3aa–E
(Millions)
Y : parts per Million : 13C
X : parts per Million : 1H
(Billions)
---- ACQUISITION PARAMETERS ----
File Name = pfg_hmbc.6
Author = JEOL LTD.
Sample ID = minami
Content = gradient enhanced HM
Creation Date = 1-JUN-2008 18:07:37
Revision Date = 5-JUN-2008 16:56:07
Spec Site = ECP400SL
Spec Type = DELTA_NMR
Data Format = 2D REAL REAL
Dimensions = X Y
Dim Title = 1H 13C
Dim Size = 1024, 2048
Dim Units = [ppm] [ppm]
Actual_start_time = 1-JUN-2008 18:07:37
Delay_of_start = 1[s]
Digital_filter = FALSE
End_time = 1-JUN-2008 18:07:35
Experiment = hmbc_pfg_m.exp
Field_strength = 9.2981736[T]
Filter_mode = BUTTERWORTH
Filter_width = 1.57878118[kHz]
Grad_1 = 1[ms]
Grad_1_amp = 40[%]
Grad_2 = 1[ms]
Grad_2_amp = 40[%]
Grad_3 = 1[ms]
Grad_3_amp = 20[%]
Grad_recover = 1[ms]
Grad_shape =
Irr_code = 210
Irr_noise = WALTZ
Irr_pwidth = 55[us]
Iterations = 0
J_constant = 140[Hz]
Local_time = 1-JUN-2008 18:07:38
Long_range_j = 8[Hz]
Obs_noise = WAUGH
Obs_pwidth = 1[us]
Probe_id = 2692
Recvr_gain = 31
Relaxation_delay = 1.5[s]
Scans = 4
Solvent = CHLOROFORM-D
Spin_get = 0[Hz]
Spin_lock_90 = 40[us]
Spin_lock_attn = 11.8[dB]
Temp_get = 23.9[dC]
X90 = 13.9[us]
X_acq_duration = 0.3243008[s]
X_domain = 1H
X_freq = 395.88252601[MHz]
X_offset = 3.89123[ppm]
X_points = 1024
X_prescans = 4
X_pulse = 13.9[us]
X_resolution = 3.08355699[Hz]
X_sweep = 3.15756236[kHz]
Y90 = 13[us]
Y_domain = 13C
Y_freq = 99.54473003[MHz]
Y_offset = 97.61031[ppm]
Y_points = 512
Y_prescans = 0
Y_pulse = 10.6[us]
Y_resolution = 34.62987589[Hz]
Y_sweep = 17.73049645[kHz]
Tri90 = 10[us]
Tri_noise = WALTZ
Tri_pwidth = 1[us]
Qua90 = 10[us]
Qua_noise = WAUGH
Qua_pwidth = 1[us]

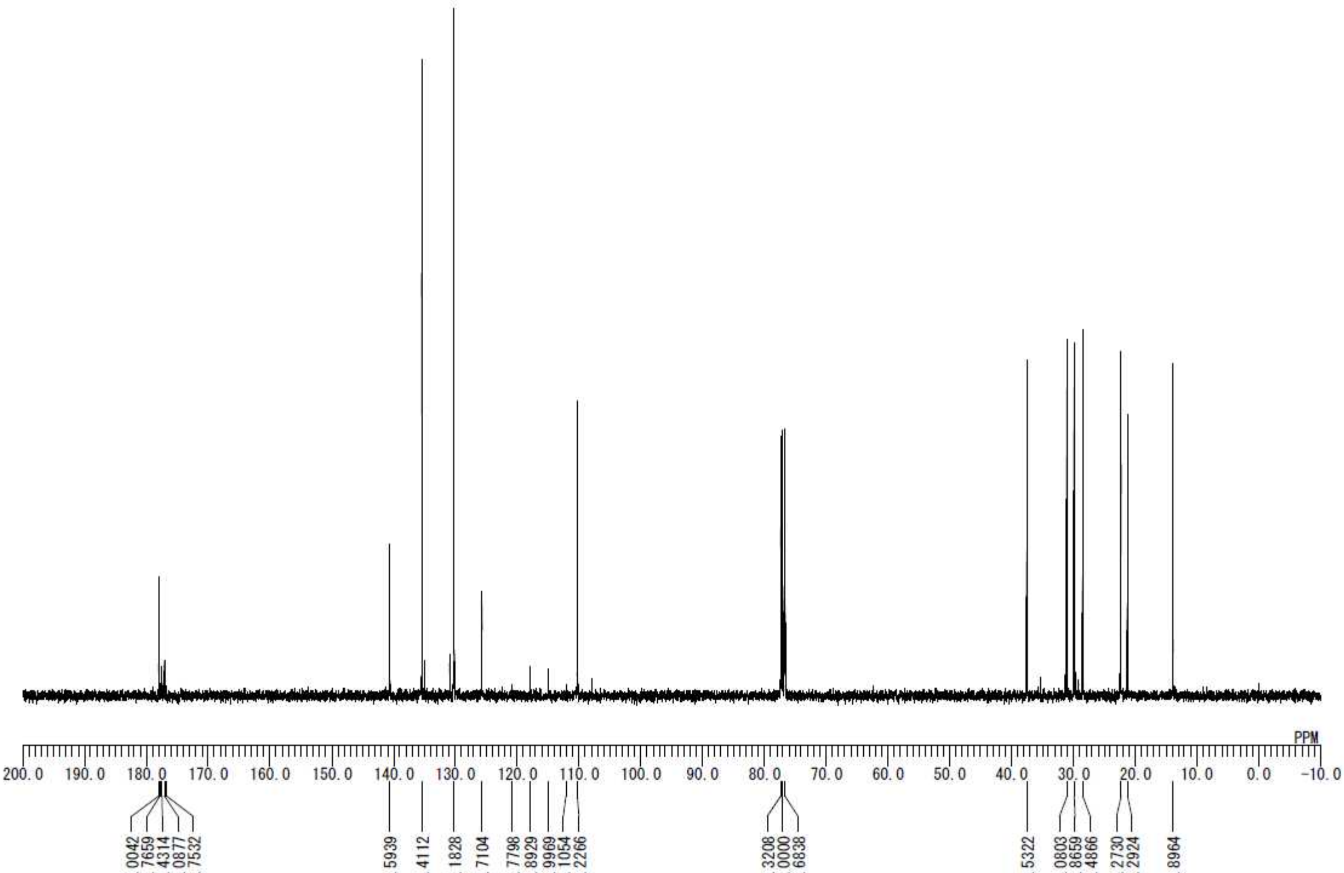

Difference NOE Experiment 3ad E
2.7%
0.6%
F3C
O
S
H
H
H H
E-8a
0.58
0.84
7.58
8.86
-43.8m
-200
X : parts per Million : 1H
(Millions)
---- ACQUISITION PARAMETERS ----
File Name = difference_noe.26
Author = JEOL LTD.
Sample ID = minami
Content = Difference NOE Exper
Creation Date = 21-MAR-2008 11:49:44
Revision Date = 24-MAR-2008 19:35:41
Spec Site = ECP400SL
Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 1H
Dim Size = 16384
Dim Units = [ppm]
Actual_start_time = 21-MAR-2008 10:51:03
Attenuator = 40[dB]
Delay_of_start = 1[s]
Digital_filter = FALSE
End_time = 21-MAR-2008 11:49:41
Experiment = difference_noe_1
Field_strength = 9.2981736[T]
Filter_mode = BUTTERWORTH
Filter_width = 2.96912114[kHz]
Irr_code = 210
Irr_domain = 1H
Irr_freq = 395.88252601[MHz]
Irr_noise = WALTZ
Irr_offset = 2.8897[ppm]
Irr_pwidth = 55[us]
Iterations = 0
Local_time = 21-MAR-2008 11:49:43
Obs_noise = WAUGH
Obs_pwidth = 1[us]
On_resonance = 2.8897[ppm]
Off_resonance = -20[ppm]
Probe_id = 2692
Recvr_gain = 10
Relaxation_delay = 1[s]
Scans = 512
Solvent = CHLOROFORM-D
Spin_get = 0[Hz]
Spin_lock_90 = 40[us]
Spin_lock_attn = 11.8[dB]
Temp_get = 24.2[dC]
X90 = 13.9[us]
X_acq_duration = 2.7590656[s]
X_angle = 90[deg]
X_domain = 1H
X_freq = 395.88252601[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 8
X_pulse = 13.9[us]
X_resolution = 0.36244155[Hz]
X_sweep = 5.93824228[kHz]
Tri90 = 10[us]
Tri_noise = WALTZ
Tri_pwidth = 1[us]
Qua90 = 10[us]
Qua_noise = WAUGH
Qua_pwidth = 1[us]


Difference NOE Experiment 3ad E
2.74
0.54
60.54m
91.08m
-74.06m
-100
X : parts per Million : 1H
(Millions)
---- ACQUISITION PARAMETERS ----
File Name = difference_noe.22
Author = JEOL LTD.
Sample ID = minami
Content = Difference NOE Exper
Creation Date = 21-MAR-2008 10:50:58
Revision Date = 24-MAR-2008 17:57:36
Spec Site = ECP400SL
Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 1H
Dim Size = 16384
Dim Units = [ppm]
Actual_start_time = 21-MAR-2008 09:52:17
Attenuator = 40[dB]
Delay_of_start = 1[s]
Digital_filter = FALSE
End_time = 21-MAR-2008 10:50:55
Experiment = difference_noe_1
Field_strength = 9.2981736[T]
Filter_mode = BUTTERWORTH
Filter_width = 2.96912114[kHz]
Irr_code = 210
Irr_domain = 1H
Irr_freq = 395.88252601[MHz]
Irr_noise = WALTZ
Irr_offset = 5.7552371[ppm]
Irr_pwidth = 55[us]
Iterations = 0
Local_time = 21-MAR-2008 10:50:57
Obs_noise = WAUGH
Obs_pwidth = 1[us]
On_resonance = 5.7552371[ppm]
Off_resonance = -20[ppm]
Probe_id = 2692
Recvr_gain = 10
Relaxation_delay = 1[s]
Scans = 512
Solvent = CHLOROFORM-D
Spin_get = 0[Hz]
Spin_lock_90 = 40[us]
Spin_lock_attn = 11.8[dB]
Temp_get = 24.2[dC]
X90 = 13.9[us]
X_acq_duration = 2.7590656[s]
X_angle = 90[deg]
X_domain = 1H
X_freq = 395.88252601[MHz]
X_offset = 5[ppm]
X_points = 16384
X_prescans = 8
X_pulse = 13.9[us]
X_resolution = 0.36244155[Hz]
X_sweep = 5.93824228[kHz]
Tri90 = 10[us]
Tri_noise = WALTZ
Tri_pwidth = 1[us]
Qua90 = 10[us]
Qua_noise = WAUGH
Qua_pwidth = 1[us]


F3C
O
S

Z-**8a**


2.1115
2.2342
1.0000
3.2216
2.0960
2.5004
6.1293
3.0051
PPM
0.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.4209
7.4014
7.2416
7.2221
6.5131
2.4208
2.4025
2.2670
2.2475
2.2280
1.6069
1.4044
1.3873
1.3678
1.3495
1.1957
1.1787
1.1616
1.1445
1.0664
1.0566
1.0493
0.8260
0.8090
0.7907
0.0000


PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
178.0042
177.7659
177.4314
177.0877
176.7532
140.5939
135.4112
130.1828
125.7104
120.7798
117.8929
114.9969
112.1054
110.2266
77.3208
77.0000
76.6838
37.5322
31.0803
29.8659
28.4866
22.2730
21.2924
13.8964

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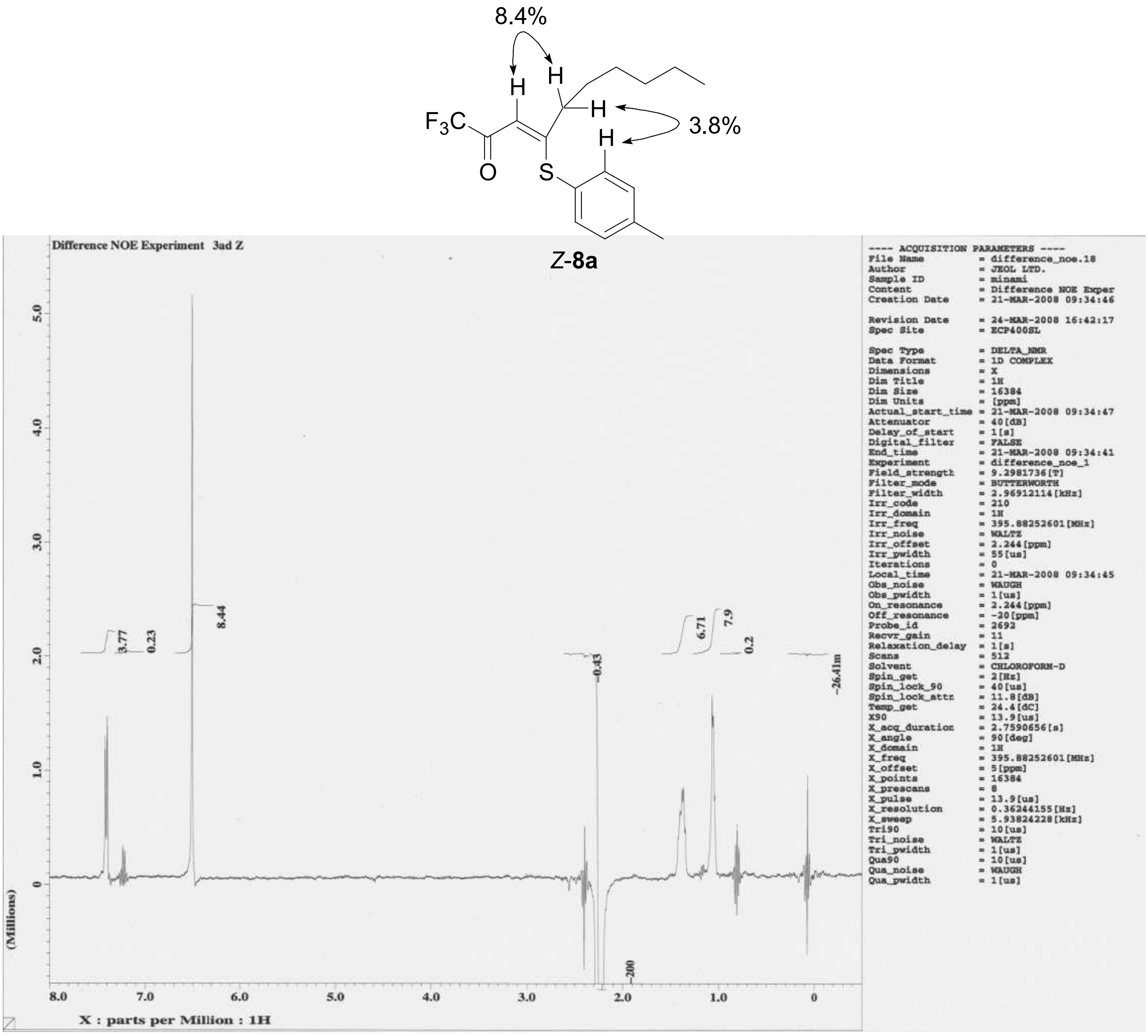

Z-**8a**

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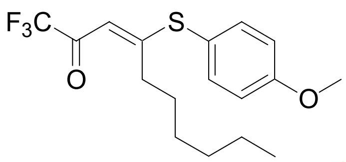
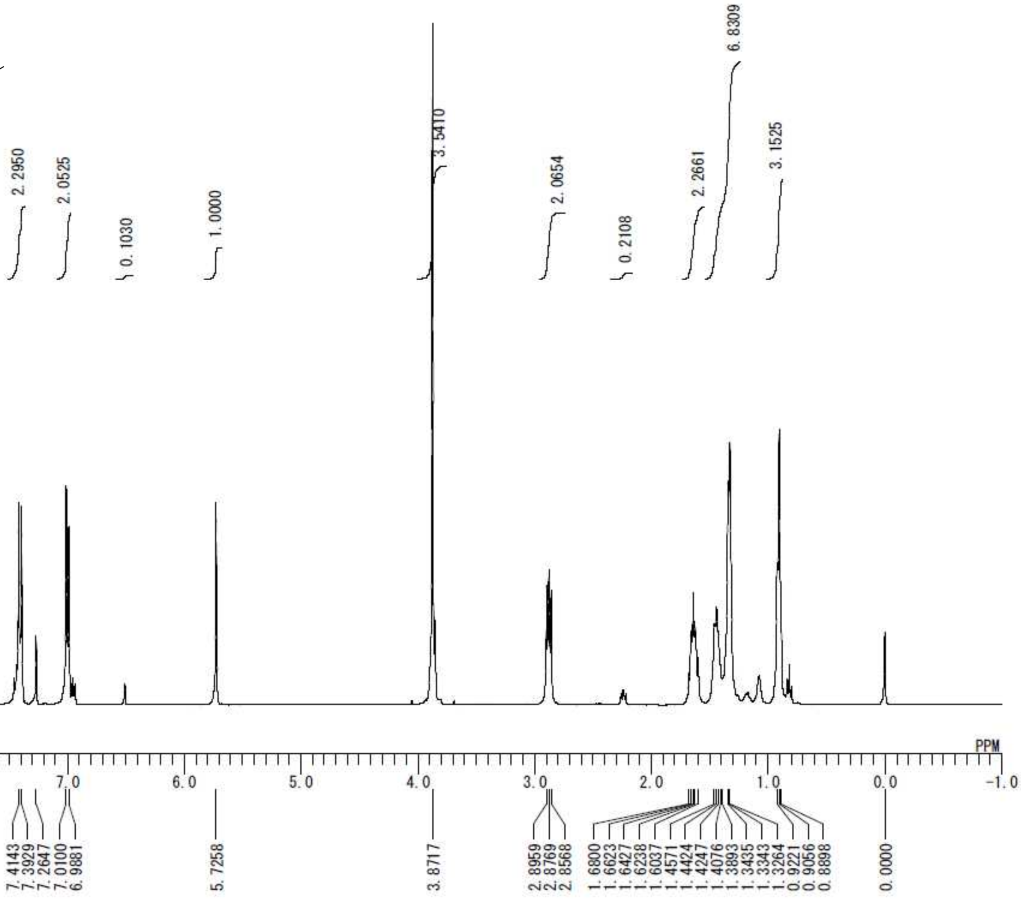
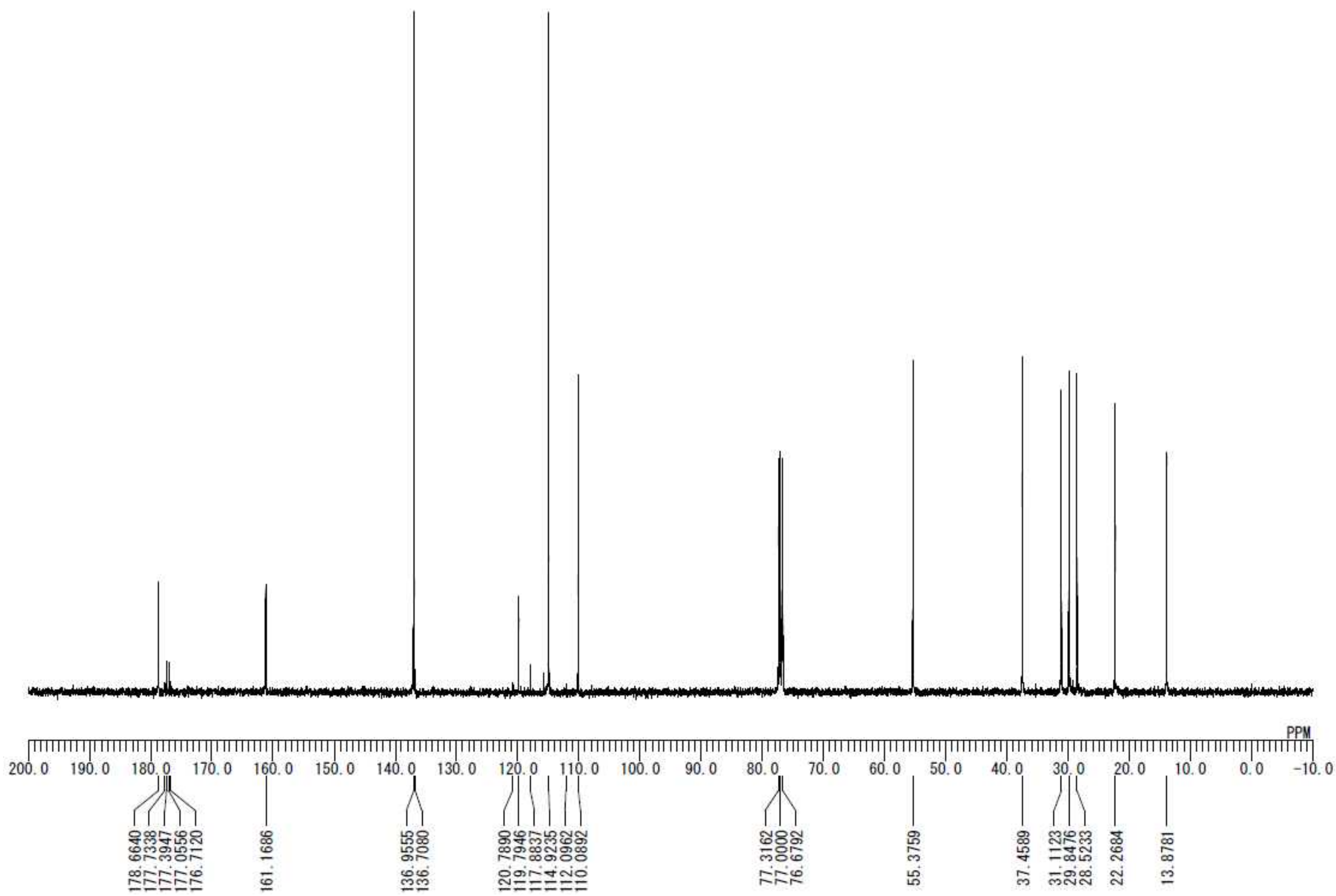
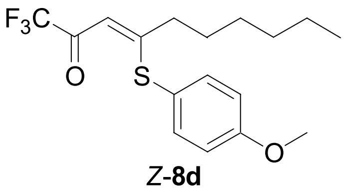


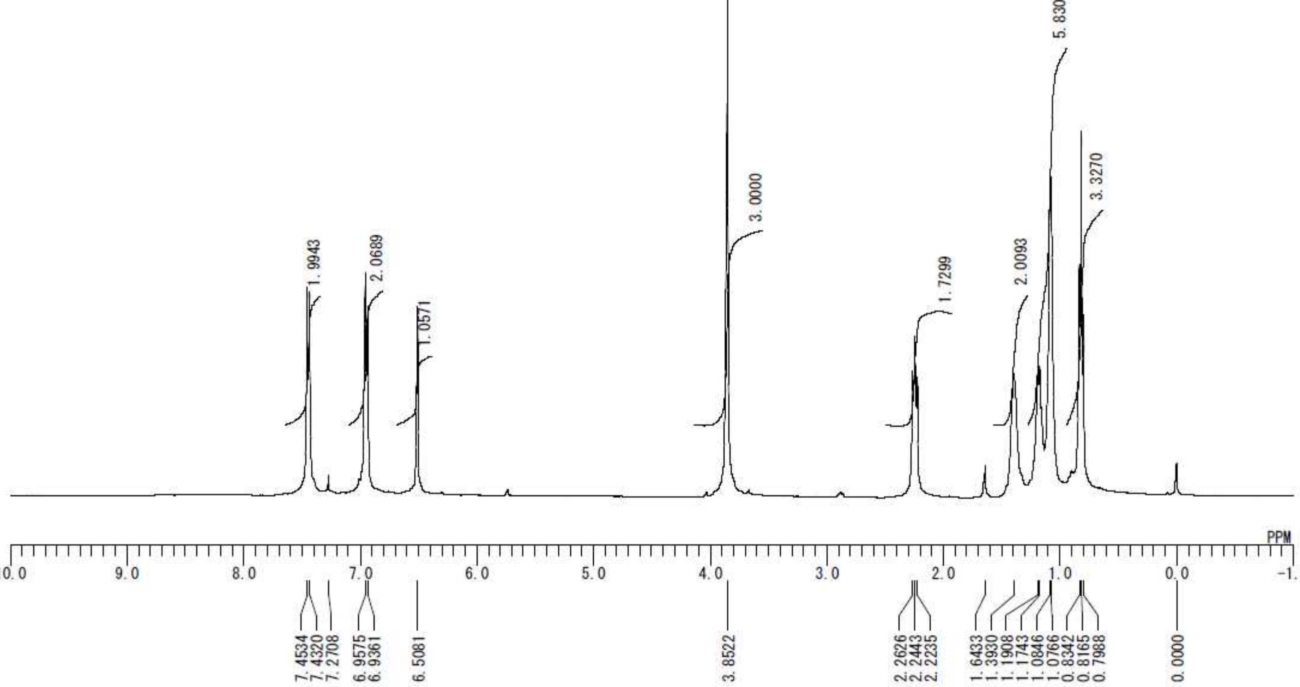
E-**8d**

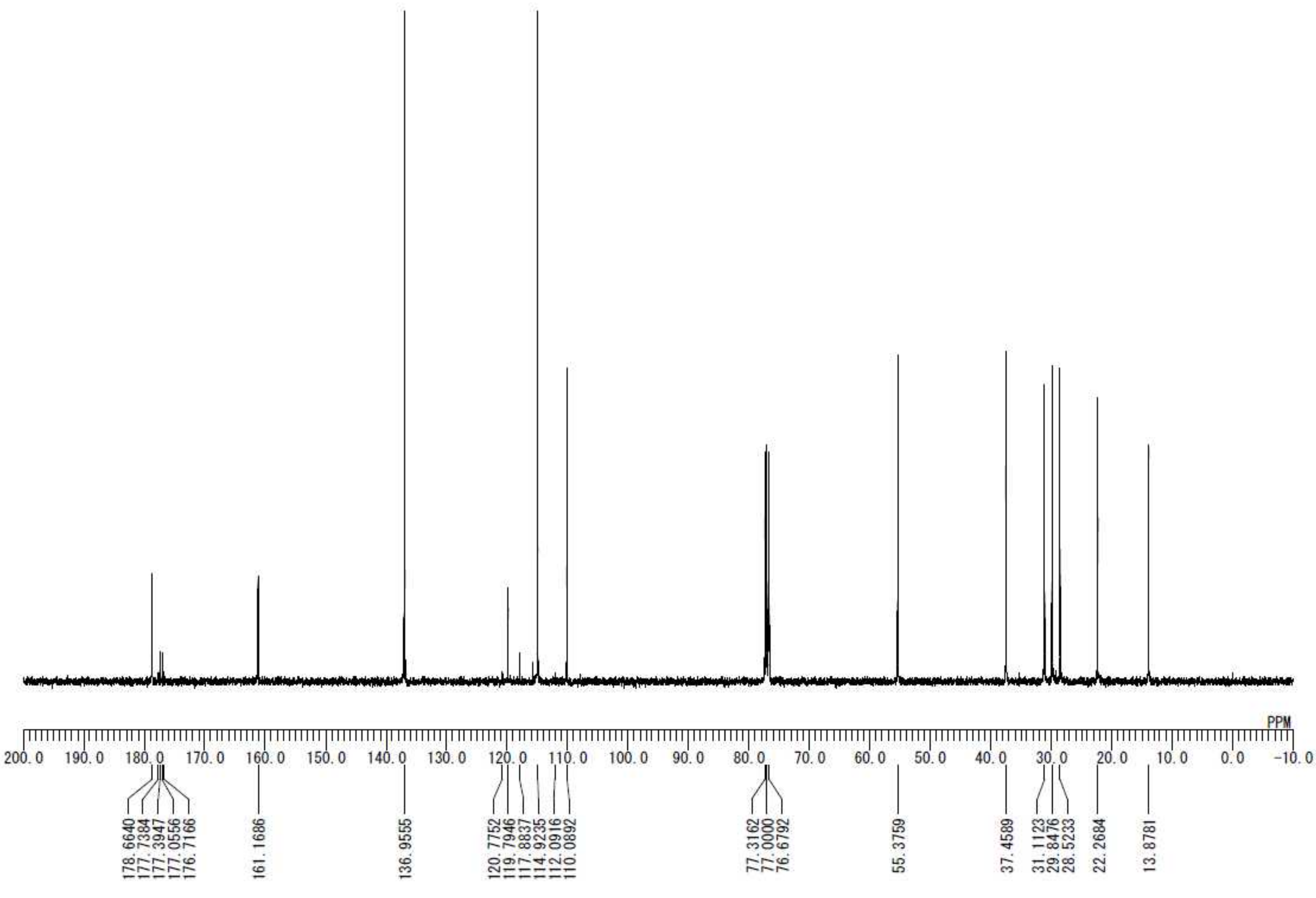





F3C
O
S
O

Z-**8d**


1.9943
2.0689
1.0571
3.0000
1.7299
2.0093
5.8305
3.3270
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.4534
7.4320
7.2708
6.9575
6.9361
6.5081
3.8522
2.2626
2.2443
2.2235
1.6433
1.3930
1.1908
1.1743
1.0846
1.0766
0.8342
0.8165
0.7988
0.0000


PPM
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
178.6640
177.7384
177.3947
177.0556
176.7166
161.1686
136.9555
120.7752
119.7946
117.8837
114.9235
112.0916
110.0892
77.3162
77.0000
76.6792
55.3759
37.4589
31.1123
29.8476
28.5233
22.2684
13.8781

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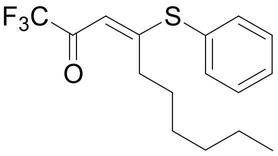
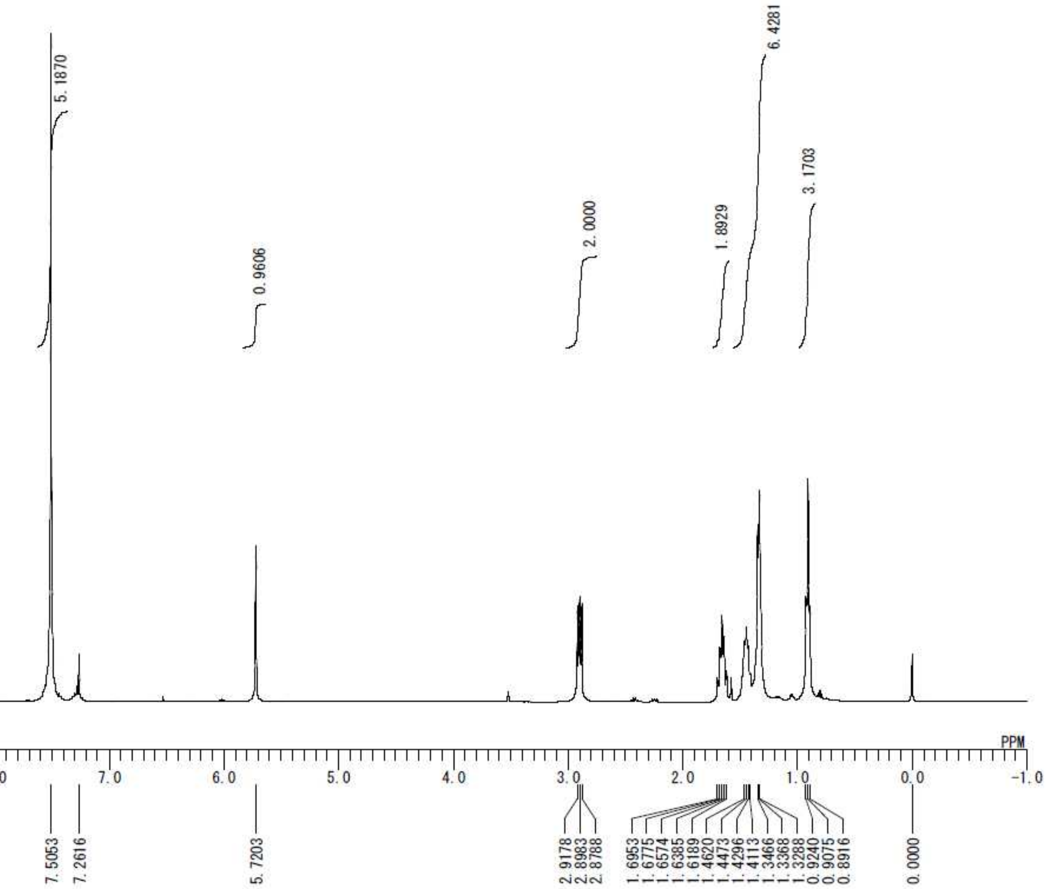
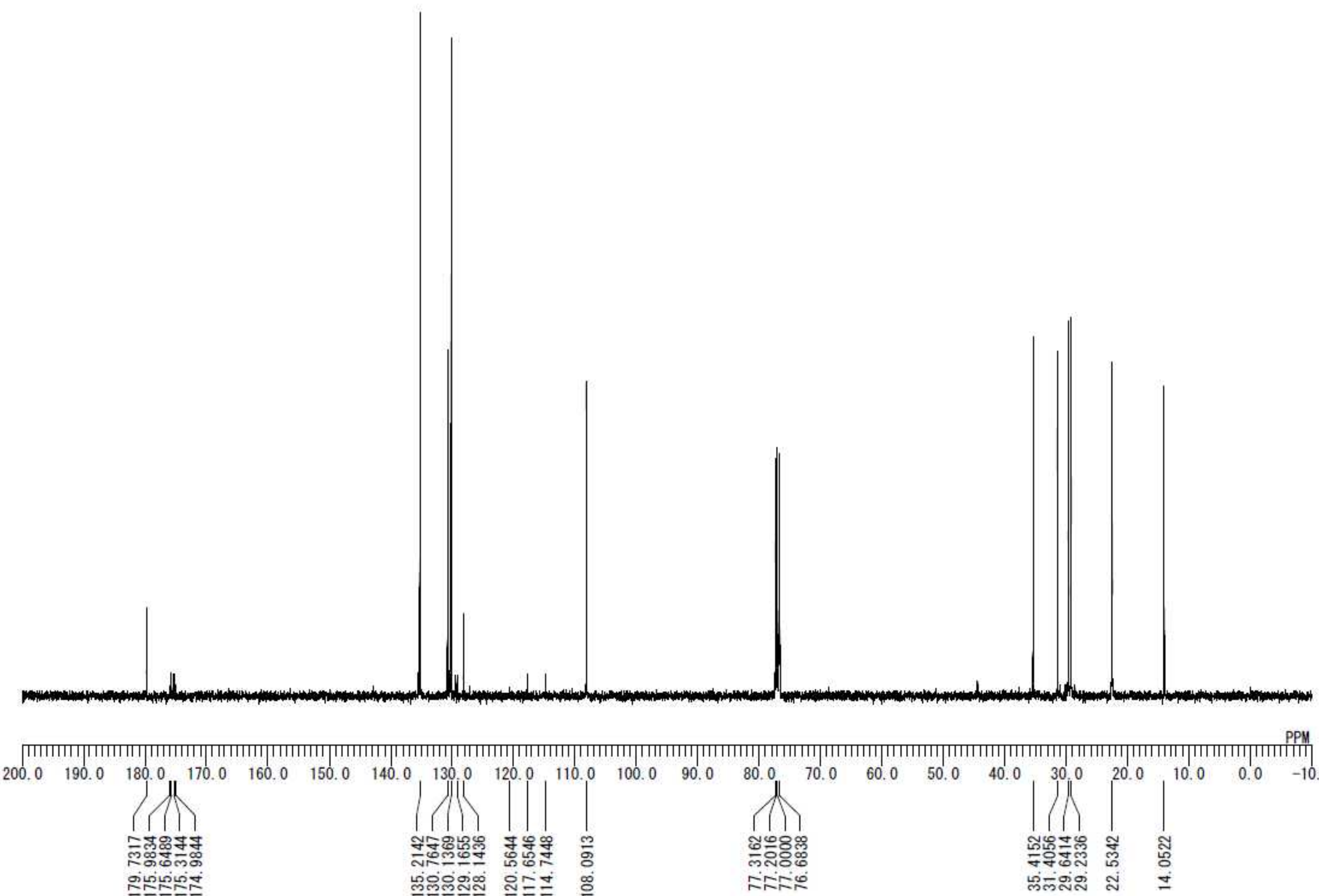
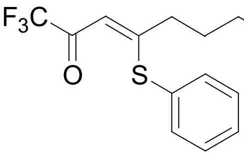


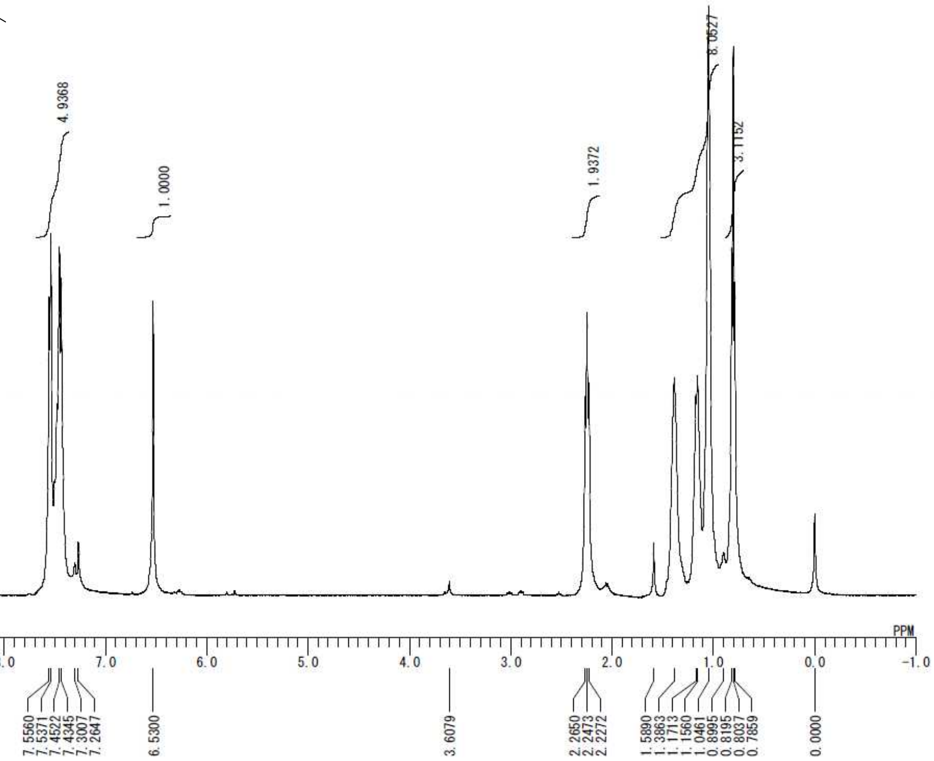
E-**8e**

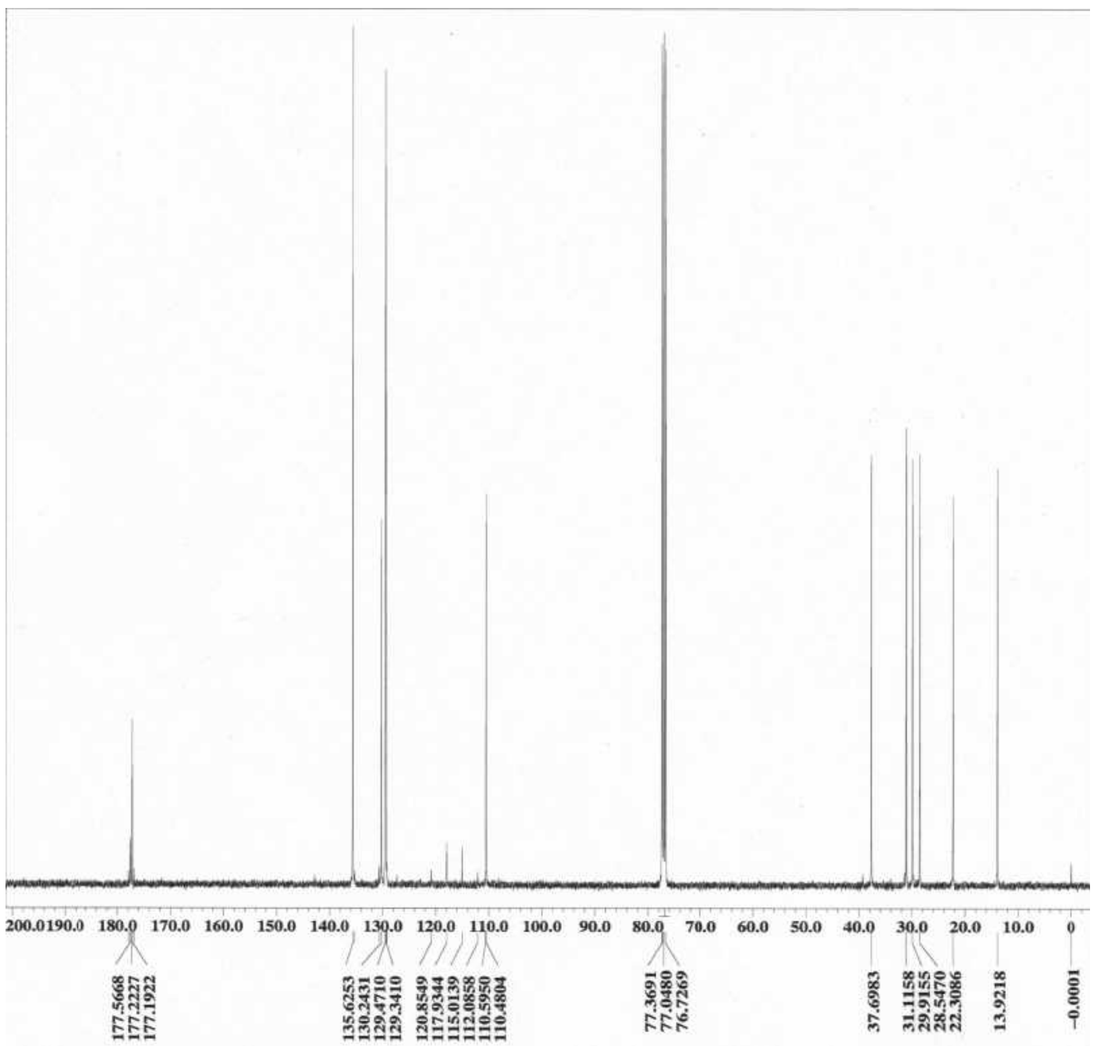






Z-**8e**


4.9368
1.0000
1.9372
8.0527
3.1152
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.5560
7.5371
7.4522
7.4345
7.3007
7.2647
6.5300
3.6079
2.2650
2.2473
2.2272
1.5890
1.3863
1.1713
1.1560
1.0461
0.8995
0.8195
0.8037
0.7859
0.0000


200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
177.5668
177.2227
177.1922
135.6253
130.2431
129.4710
129.3410
120.8549
117.9344
115.0139
112.0858
110.5950
110.4804
77.3691
77.0480
76.7269
37.6983
31.1158
29.9155
28.5470
22.3086
13.9218
-0.0001

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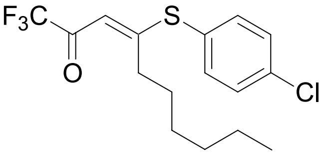
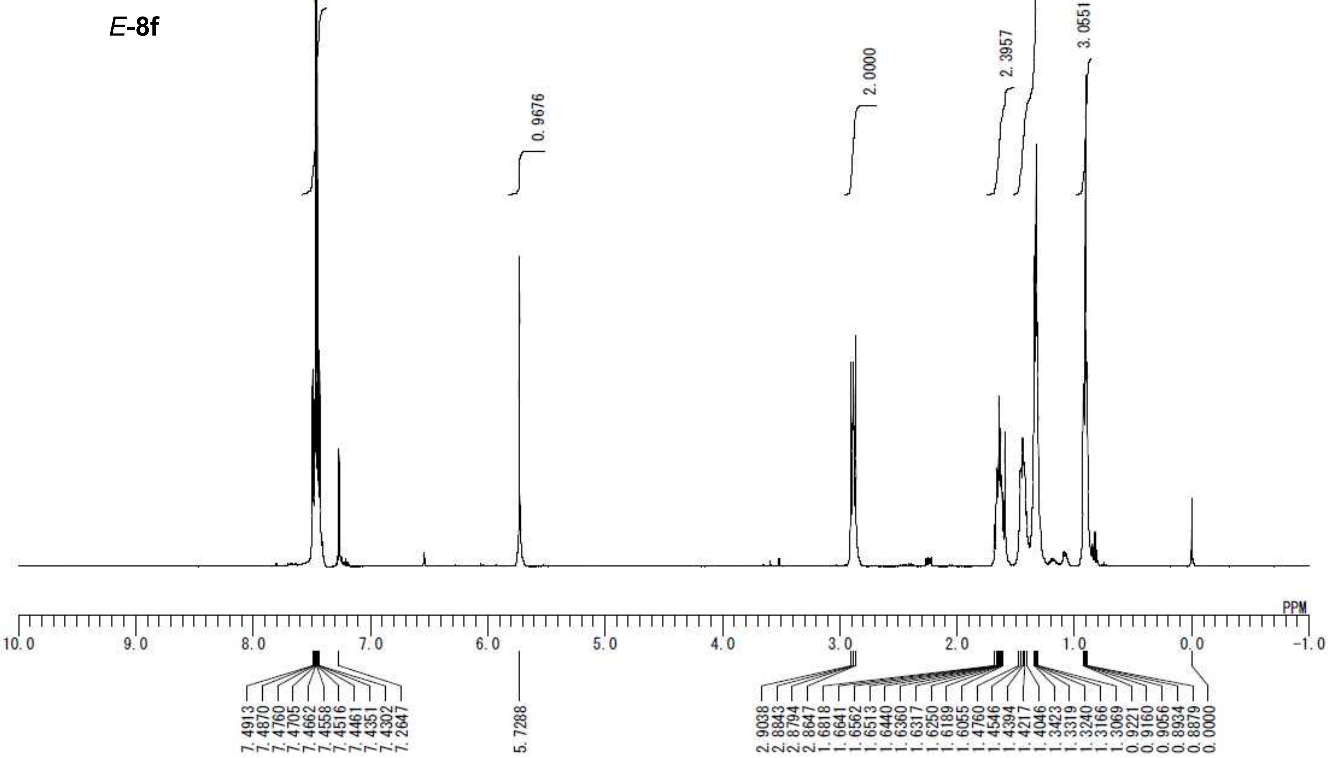
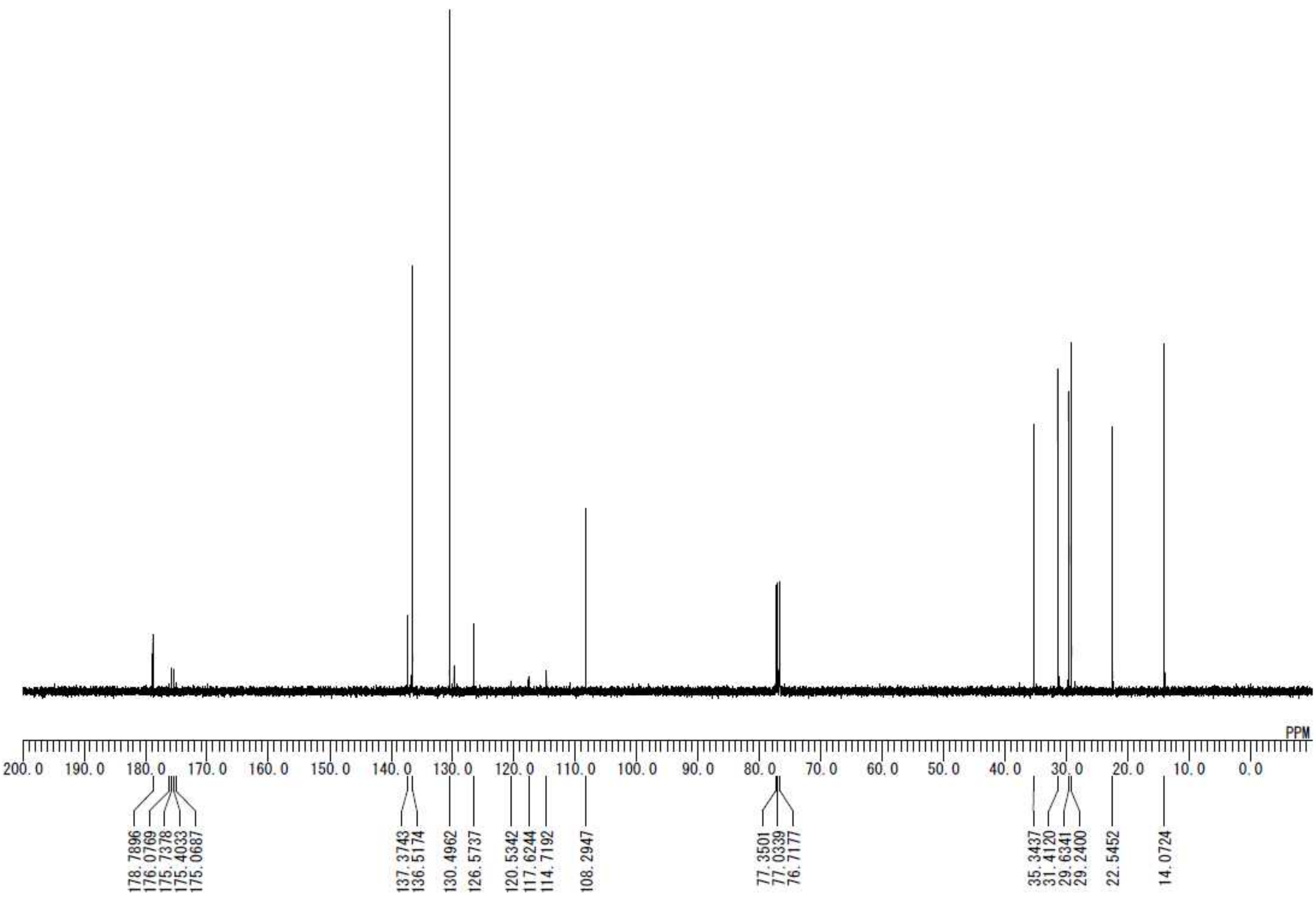


E-**8f**





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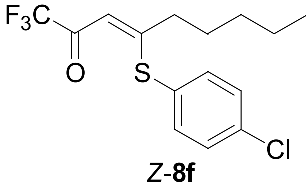
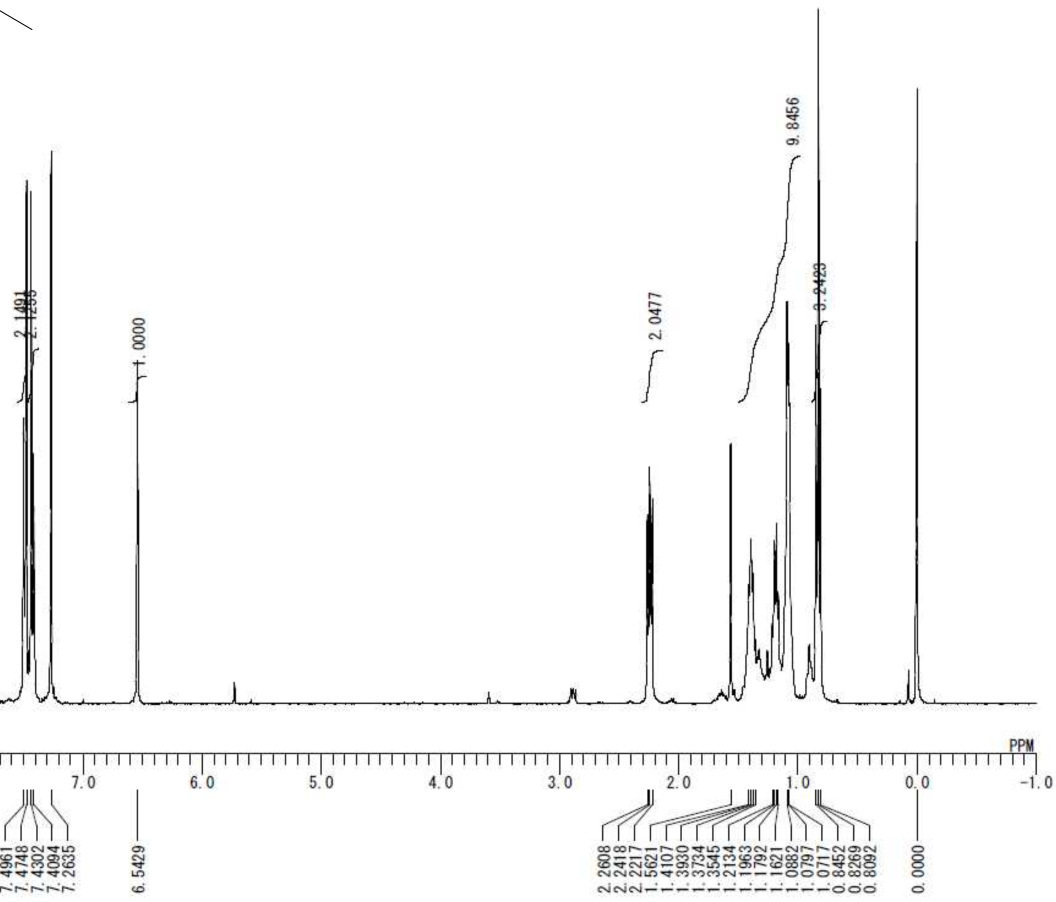
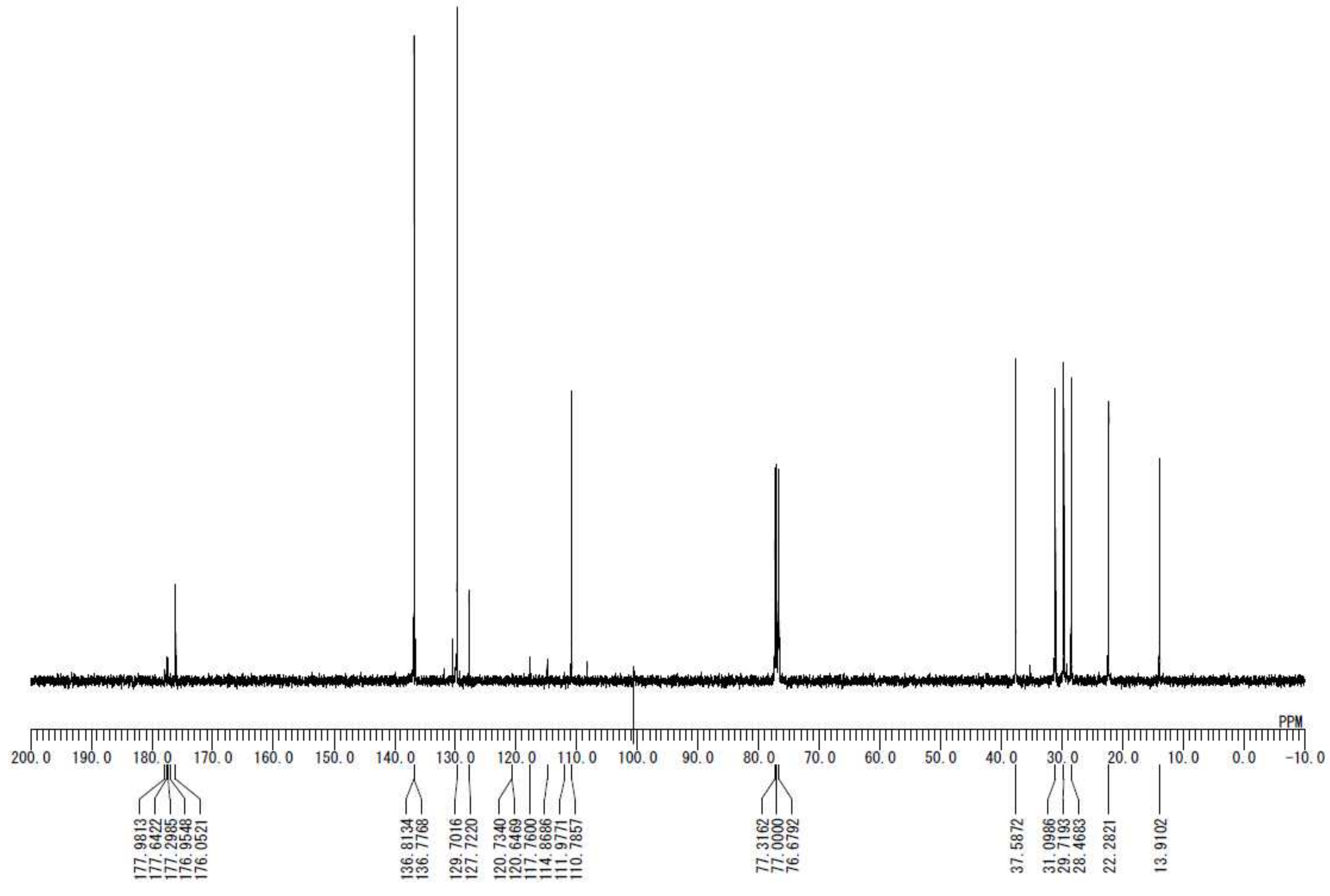
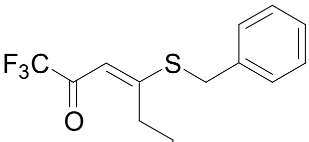


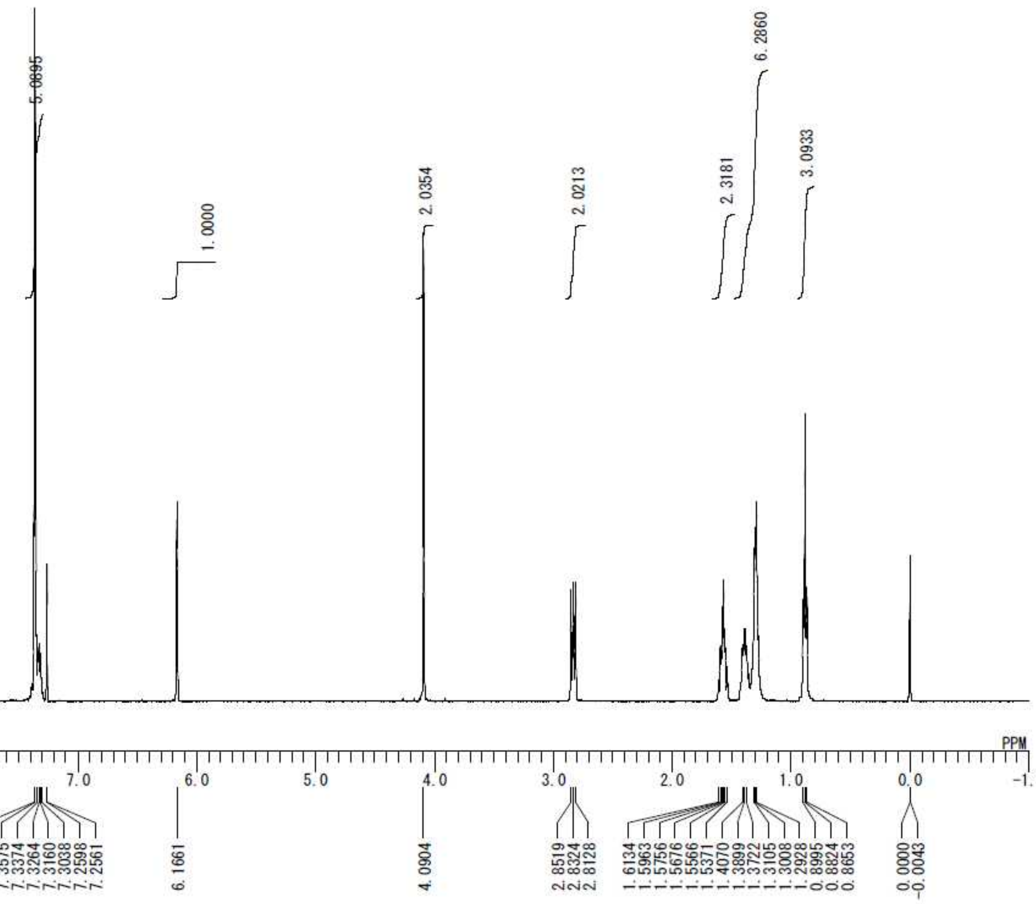
Z-**8f**

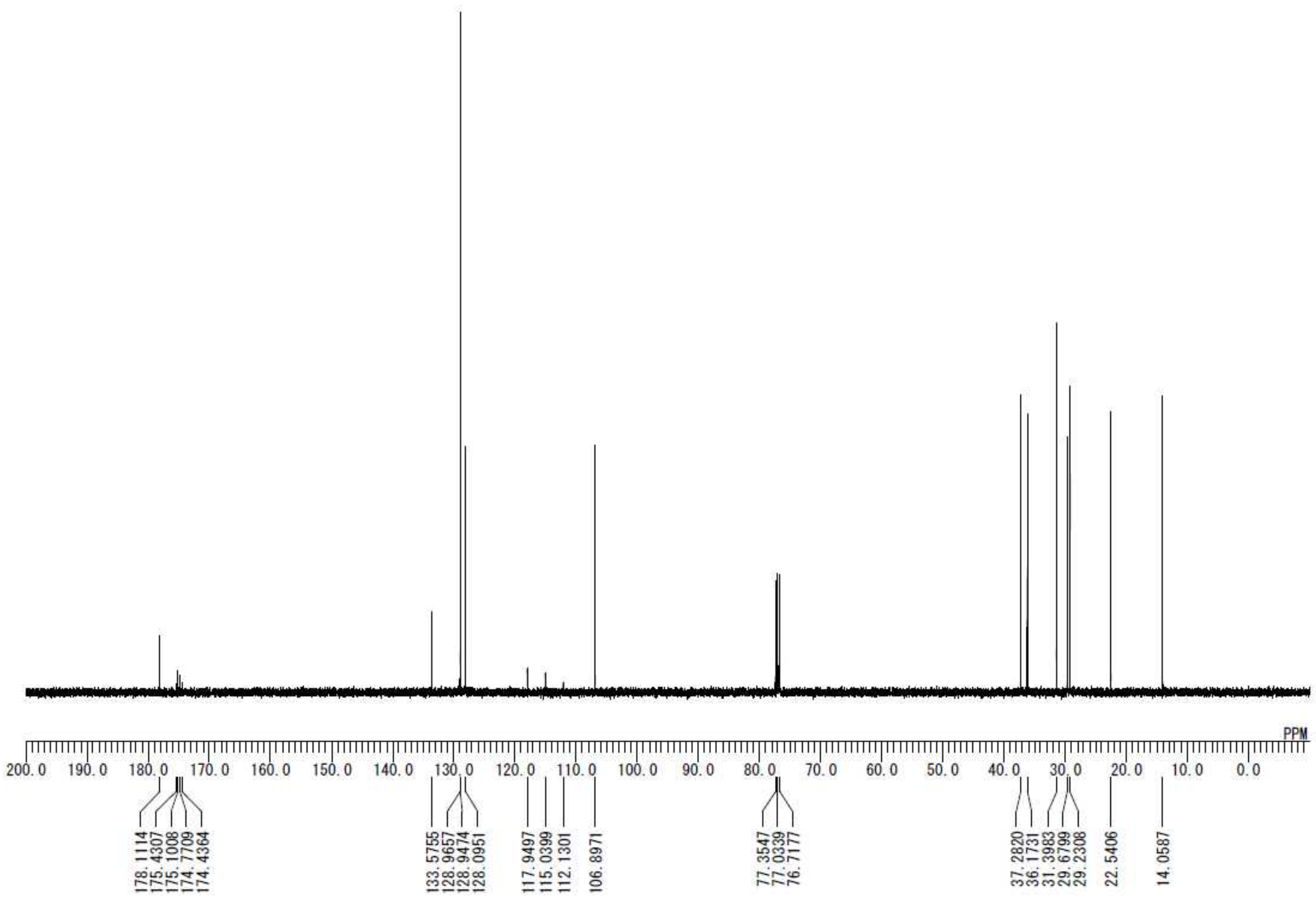


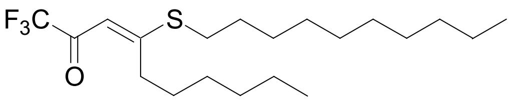




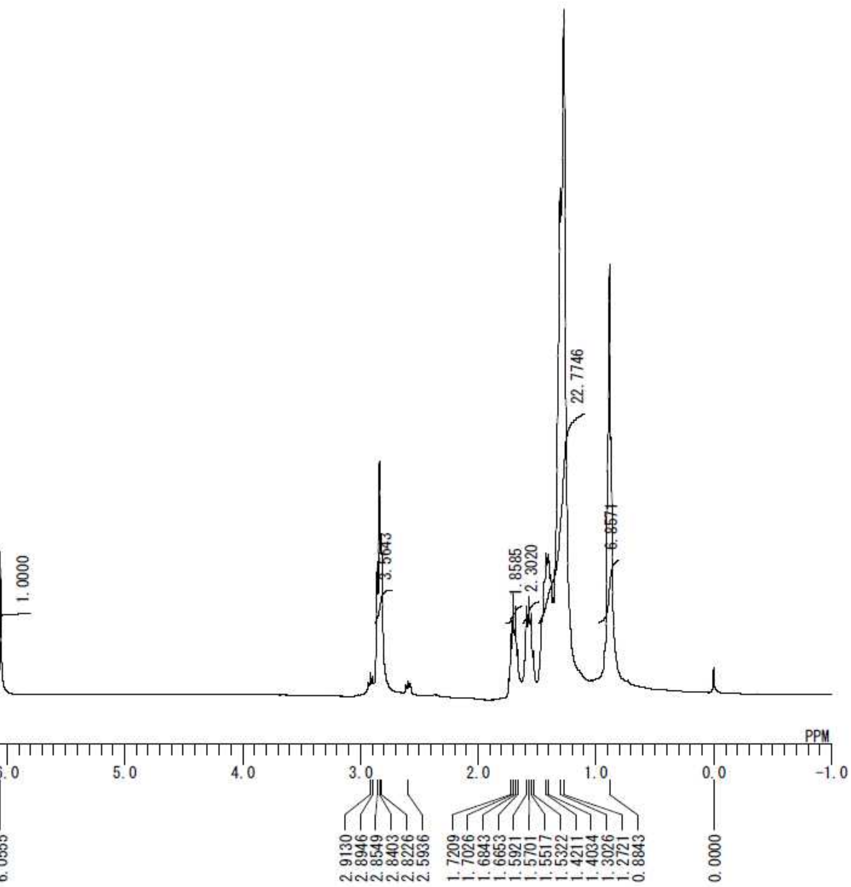
E-**8g**






F3C
S
O

E-**8h**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1.8585
2.3020
6.8571
1.0000
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.2665
6.4555
6.0555
2.9130
2.8946
2.8549
2.8403
2.8226
2.5936
1.7209
1.7026
1.6843
1.6653
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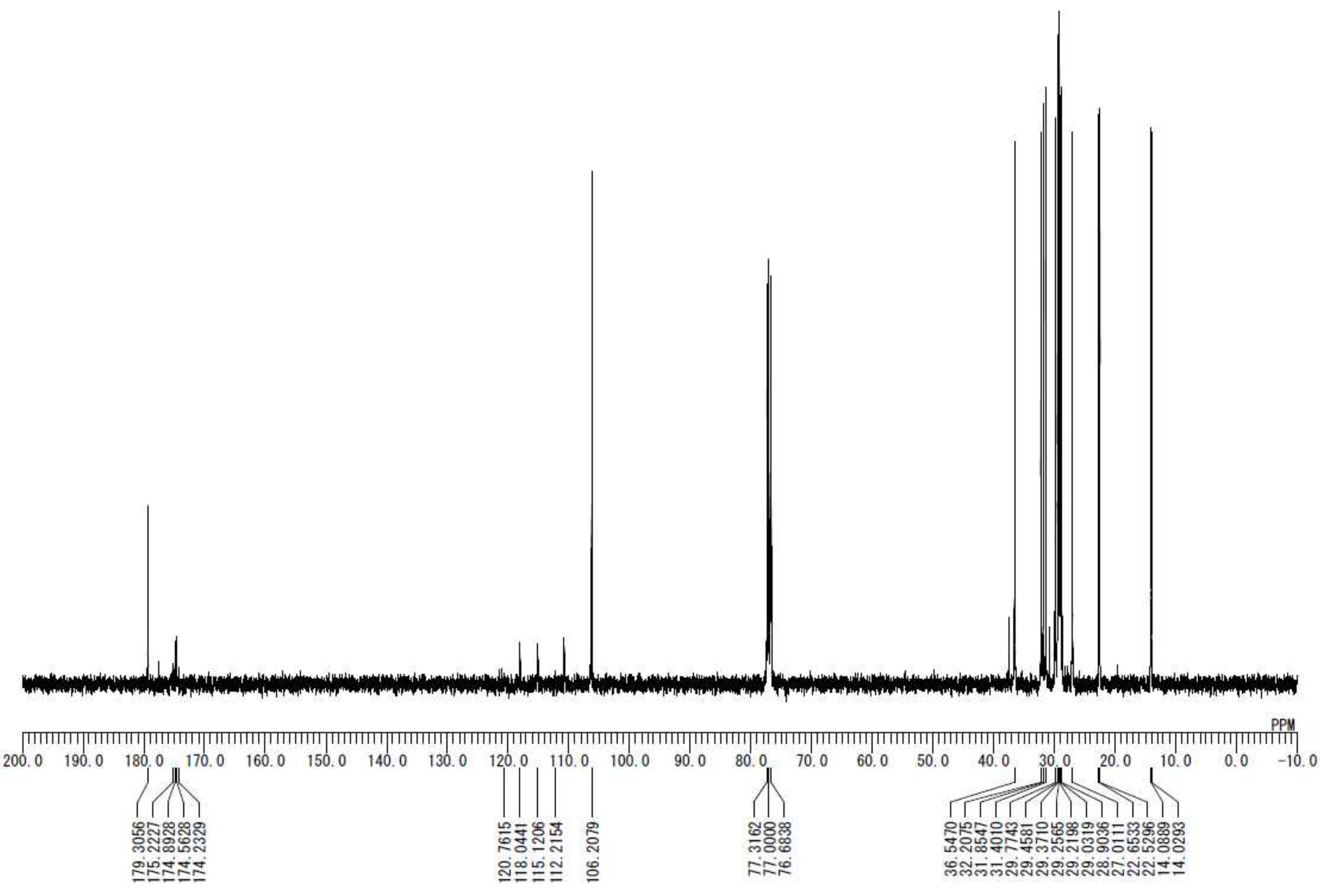
1.5517
1.5322
1.4211
1.4034
1.3026
1.2721
0.8843
0.0000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140.0
130.0
120.0
110.0
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
179.3056
175.2227
174.8928
174.5628
174.2329
120.7615
118.0441
115.1206
112.2154
106.2079
77.3162
77.0000
76.6838
36.5470
32.2075
31.8547
31.4010
29.7743
29.4581
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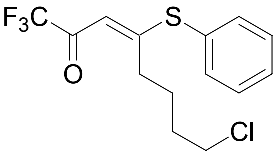
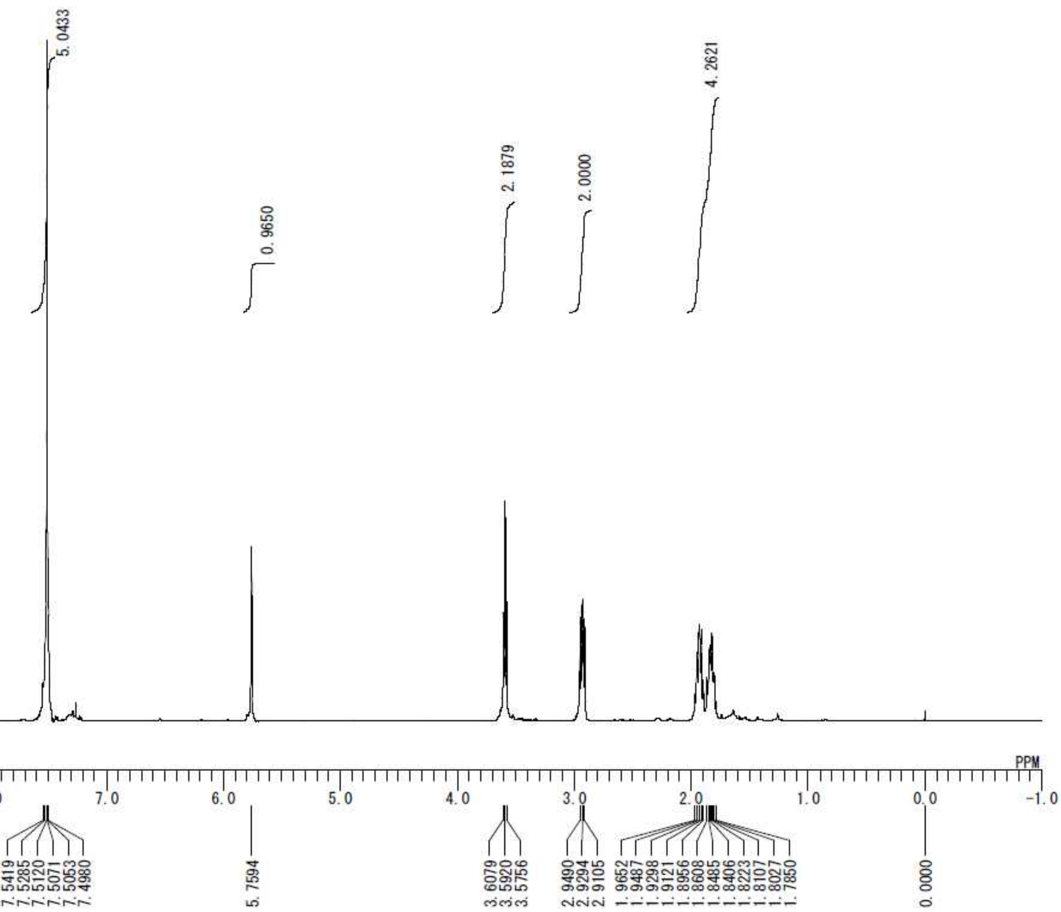
14.0293


F3C
S
O
Cl

E-**8i**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0.9650
2.1879
2.0000
4.2621
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.5419
7.5285
7.5120
7.5071
7.5053
7.4980
5.7594
3.6079
3.5920
3.5756
2.9490
2.9294
2.9105
1.9652
1.9487
1.9298
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1.8608
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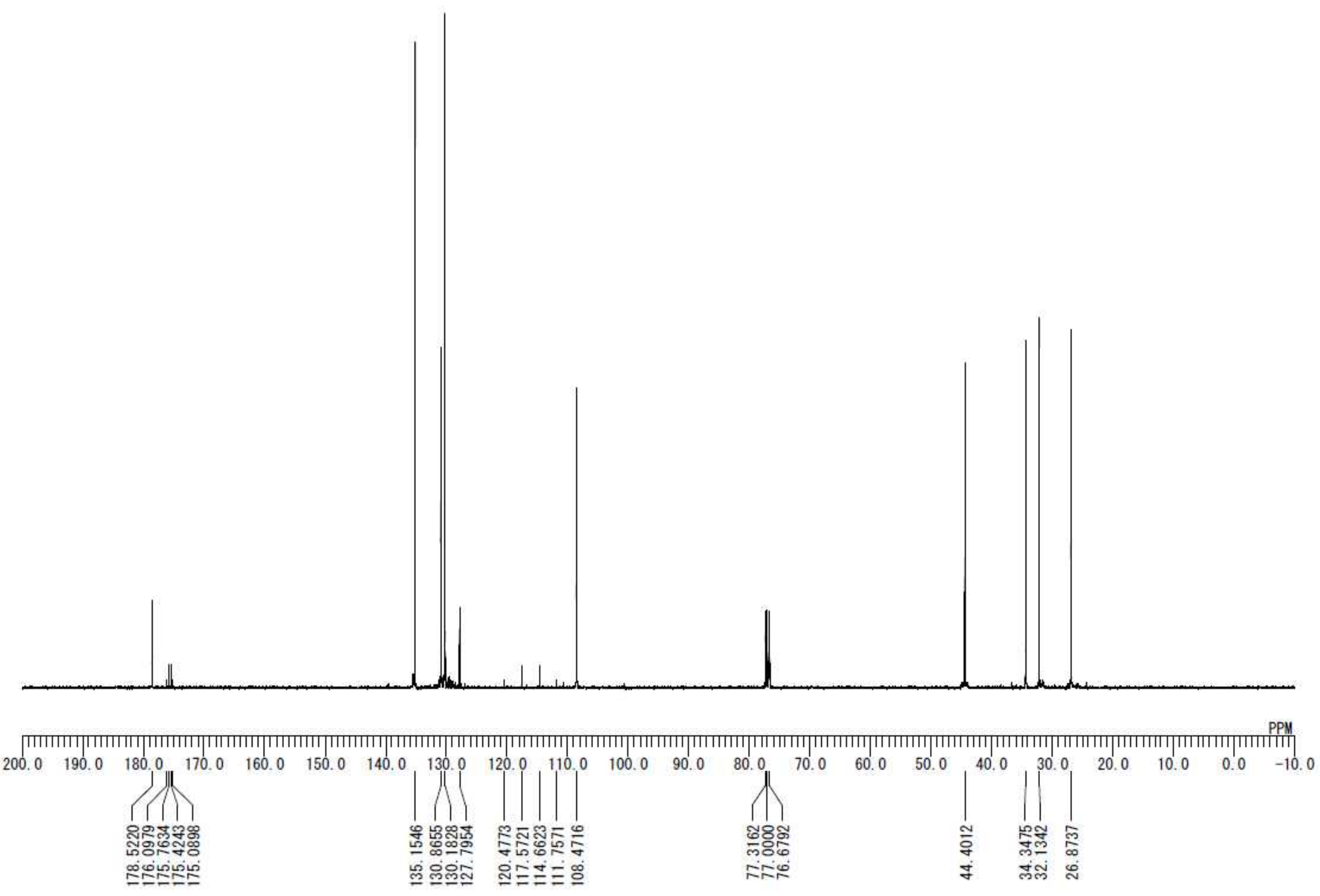
1.8406
1.8223
1.8107
1.8027
1.7850
0.0000


PPM
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
178.5220
176.0979
175.7634
175.4243
175.0898
135.1546
130.8655
130.1828
127.7954
120.4773
117.5721
114.6623
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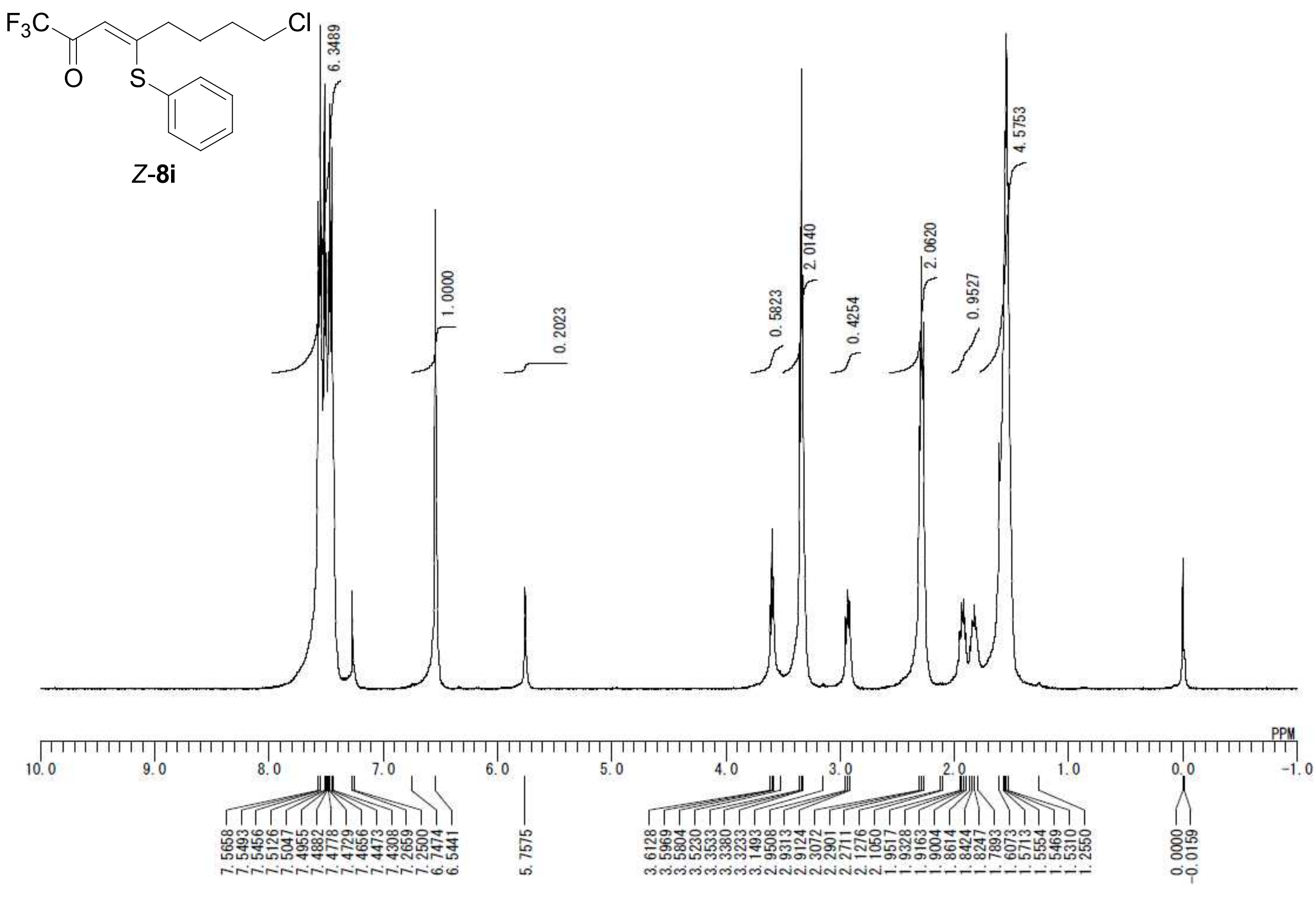
108.4716
77.3162
77.0000
76.6792
44.4012
34.3475
32.1342
26.8737


F3C
O
S
Cl
Z-8i
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0.5823
2.0140
0.4254
2.0620
0.9527
4.5753
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
7.5658
7.5493
7.5456
7.5126
7.5047
7.4955
7.4882
7.4778
7.4729
7.4656
7.4473
7.4308
7.2659
7.2500
6.7474
6.5441
5.7575
3.6128
3.5969
3.5804
3.5230
3.3533
3.3380
3.3233
3.1493
2.9508
2.9313
2.9124
2.3072
2.2901
2.2711
2.1276
2.1050
1.9517
1.9328
1.9163
1.9004
1.8614
1.8424
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1.6073
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1.5310
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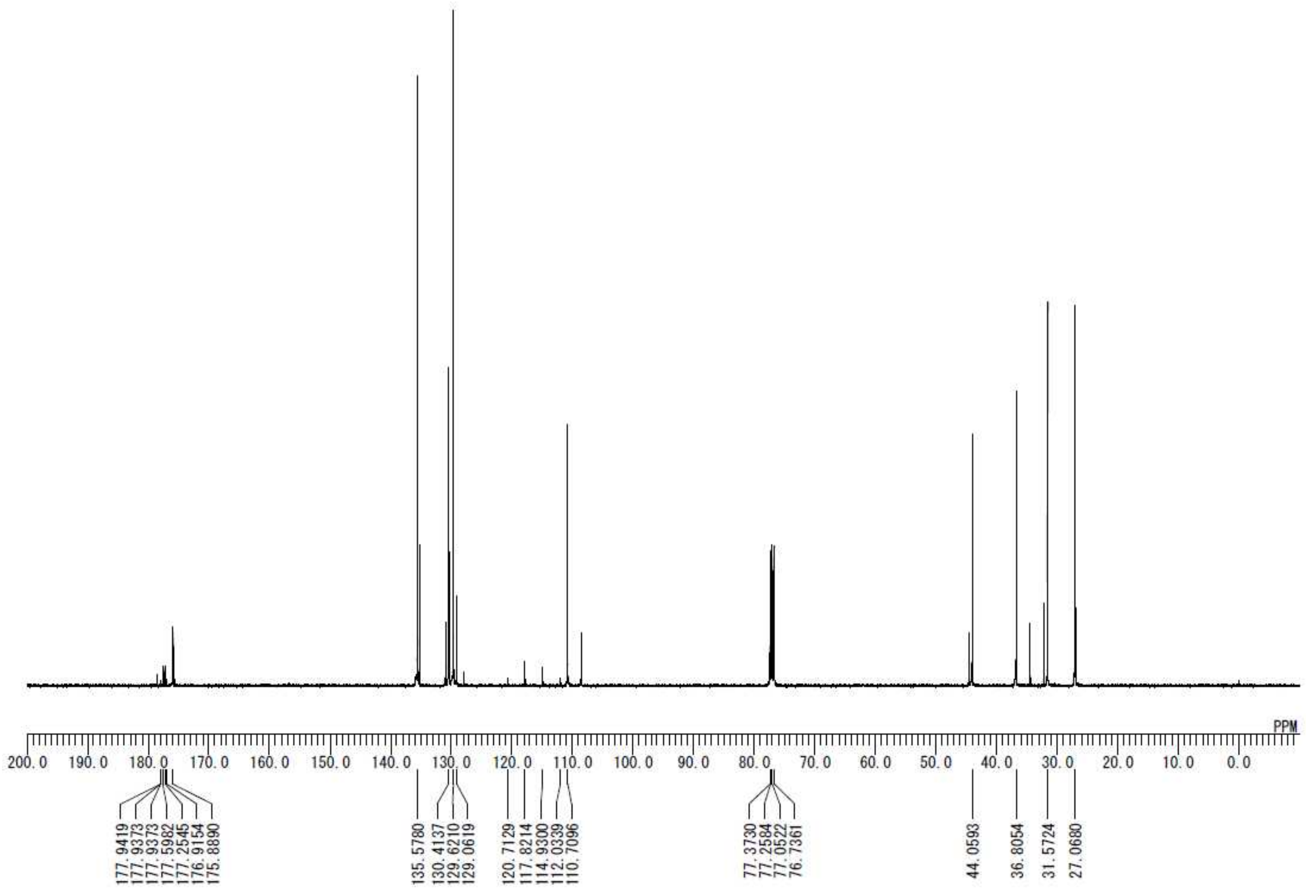
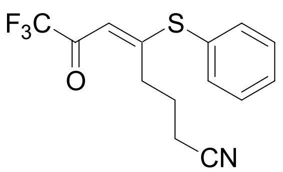
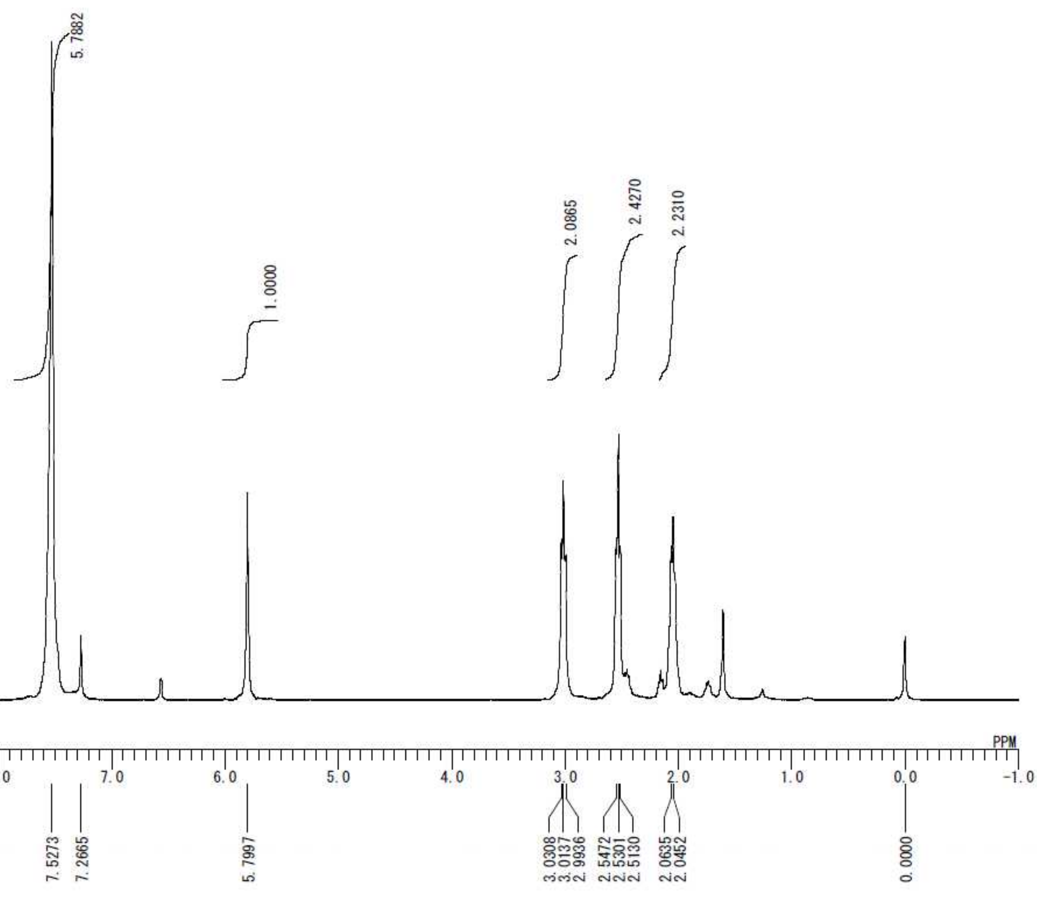
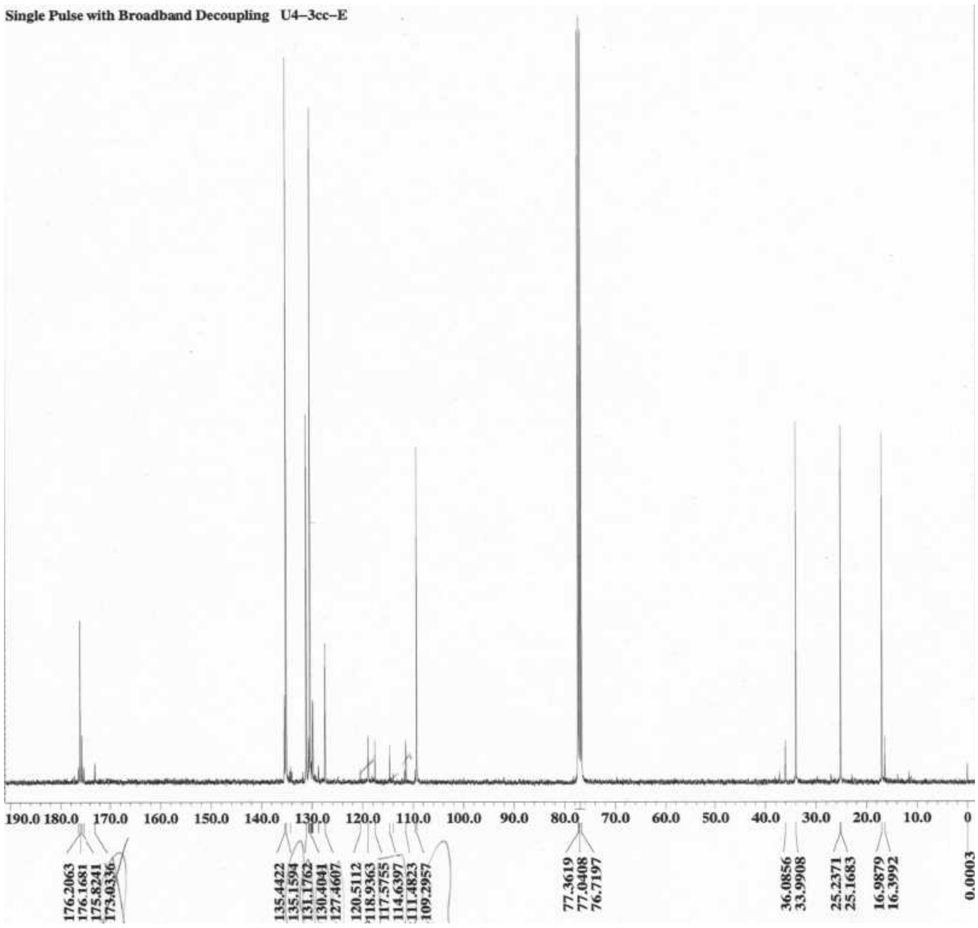
0.0000
-0.0159

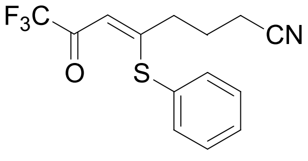




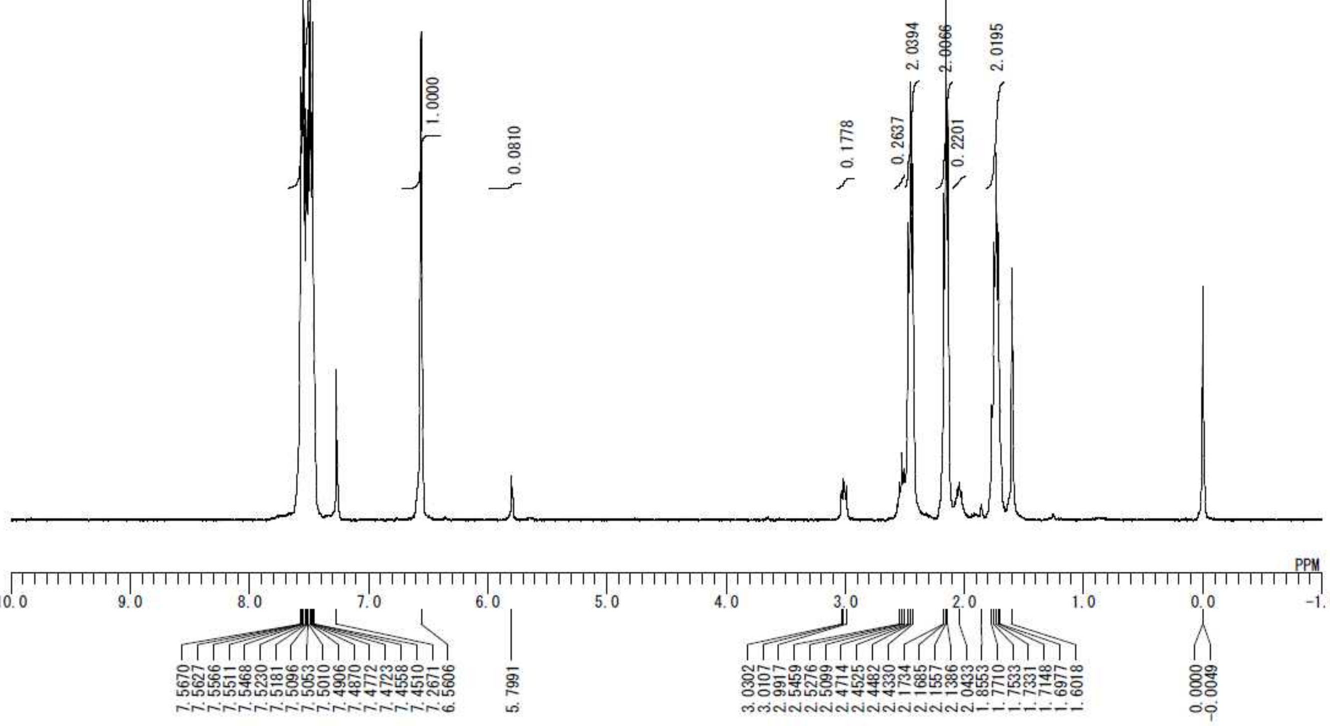
E-**8j**




Single Pulse with Broadband Decoupling U4-3cc-E
190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
176.2063
176.1681
175.8241
173.0336
135.4422
135.1594
131.1762
130.4041
127.4607
120.5112
118.9363
117.5755
114.6397
111.4823
109.2957
77.3619
77.0408
76.7197
36.0856
33.9908
25.2371
25.1683
16.9879
16.3992
0.0003


F3C
O
S
CN

Z-**8j**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0.1778
0.2637
2.0394
2.0066
0.2201
2.0195
PPM
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
7.5670
7.5627
7.5566
7.5511
7.5468
7.5230
7.5181
7.5096
7.5053
7.5010
7.4906
7.4870
7.4772
7.4723
7.4558
7.4510
7.2671
6.5606
5.7991
3.0302
3.0107
2.9917
2.5459
2.5276
2.5099
2.4714
2.4525
2.4482
2.4330
2.1734
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2.1557
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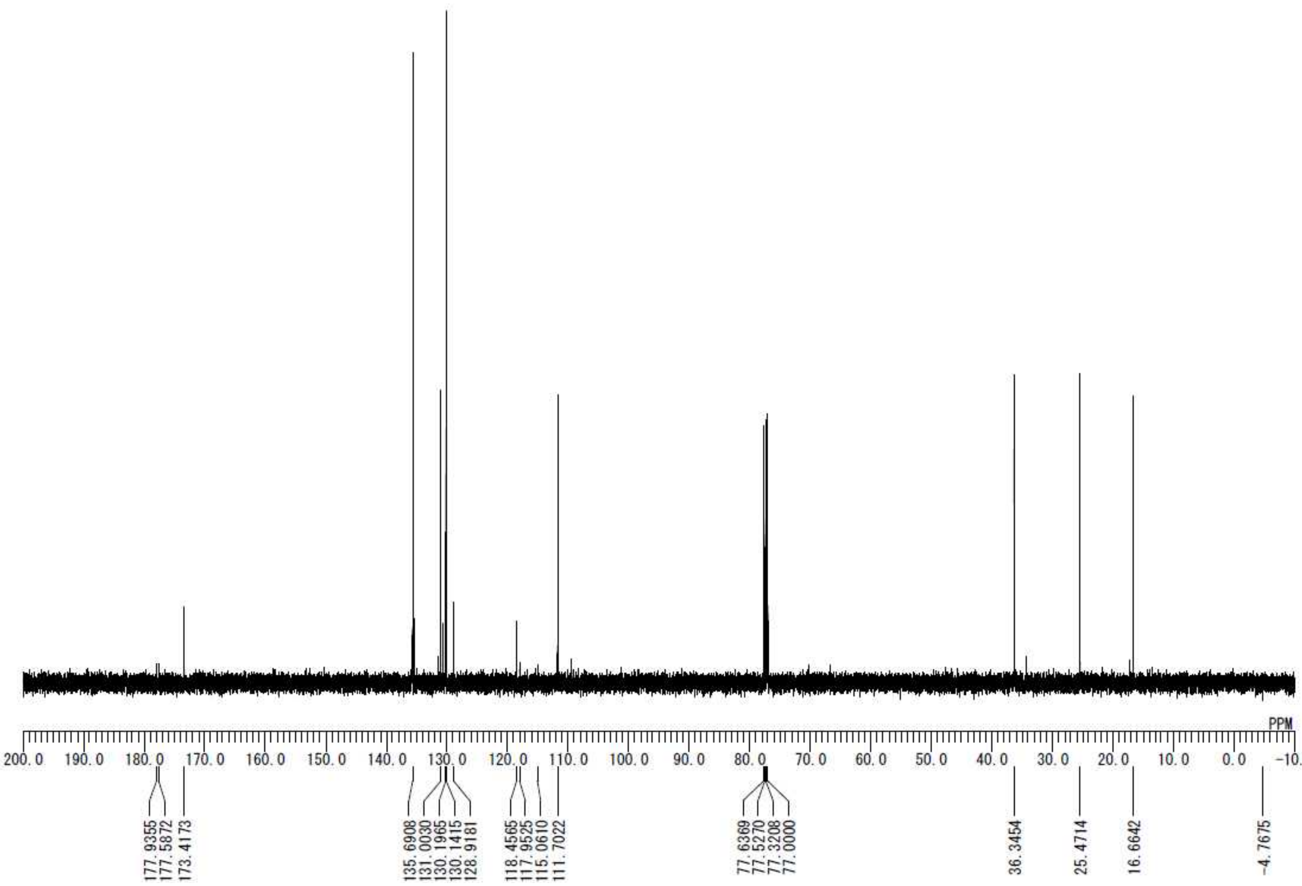
PPM
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160.0
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140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
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173.4173
135.6908
131.0030
130.1965
130.1415
128.9181
118.4565
117.9525
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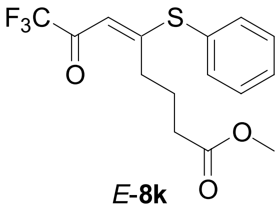
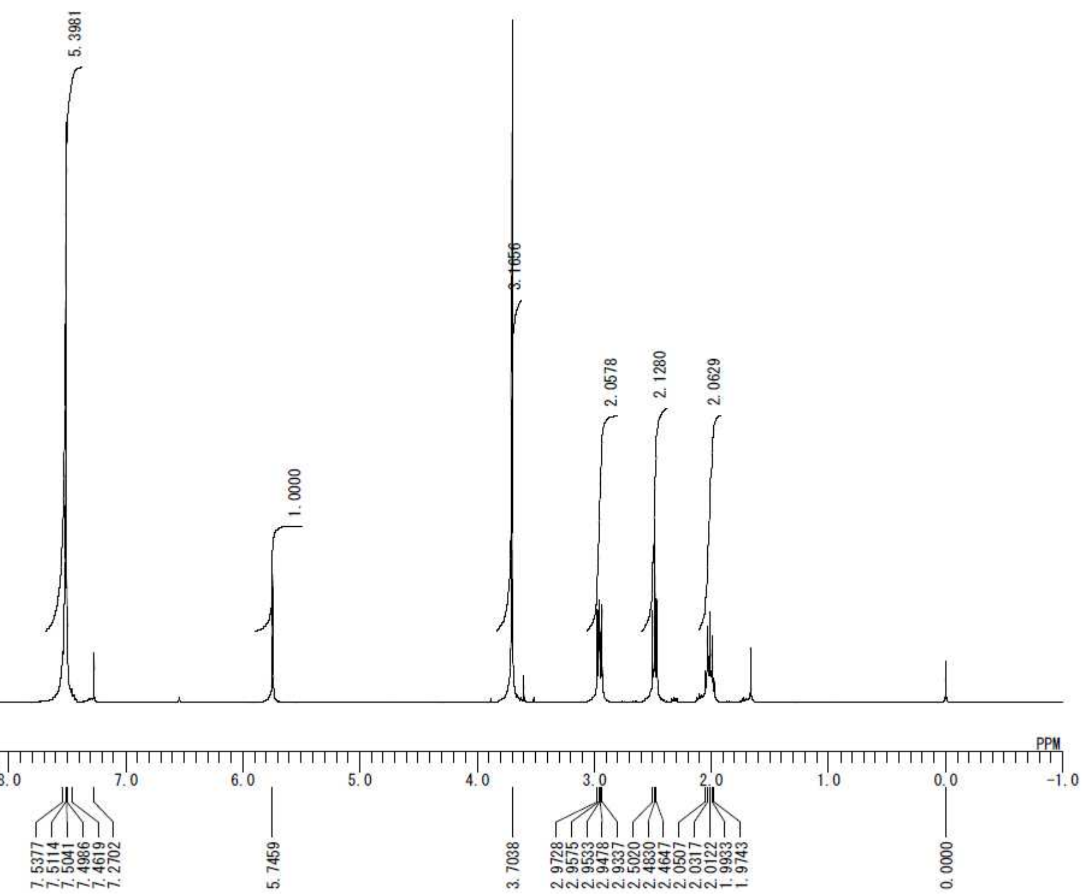
16.6642
-4.7675


F3C
O
S
O
O

E-**8k**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2.1280
2.0629
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
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7.5114
7.5041
7.4986
7.4619
7.2702
5.7459
3.7038
2.9728
2.9575
2.9533
2.9478
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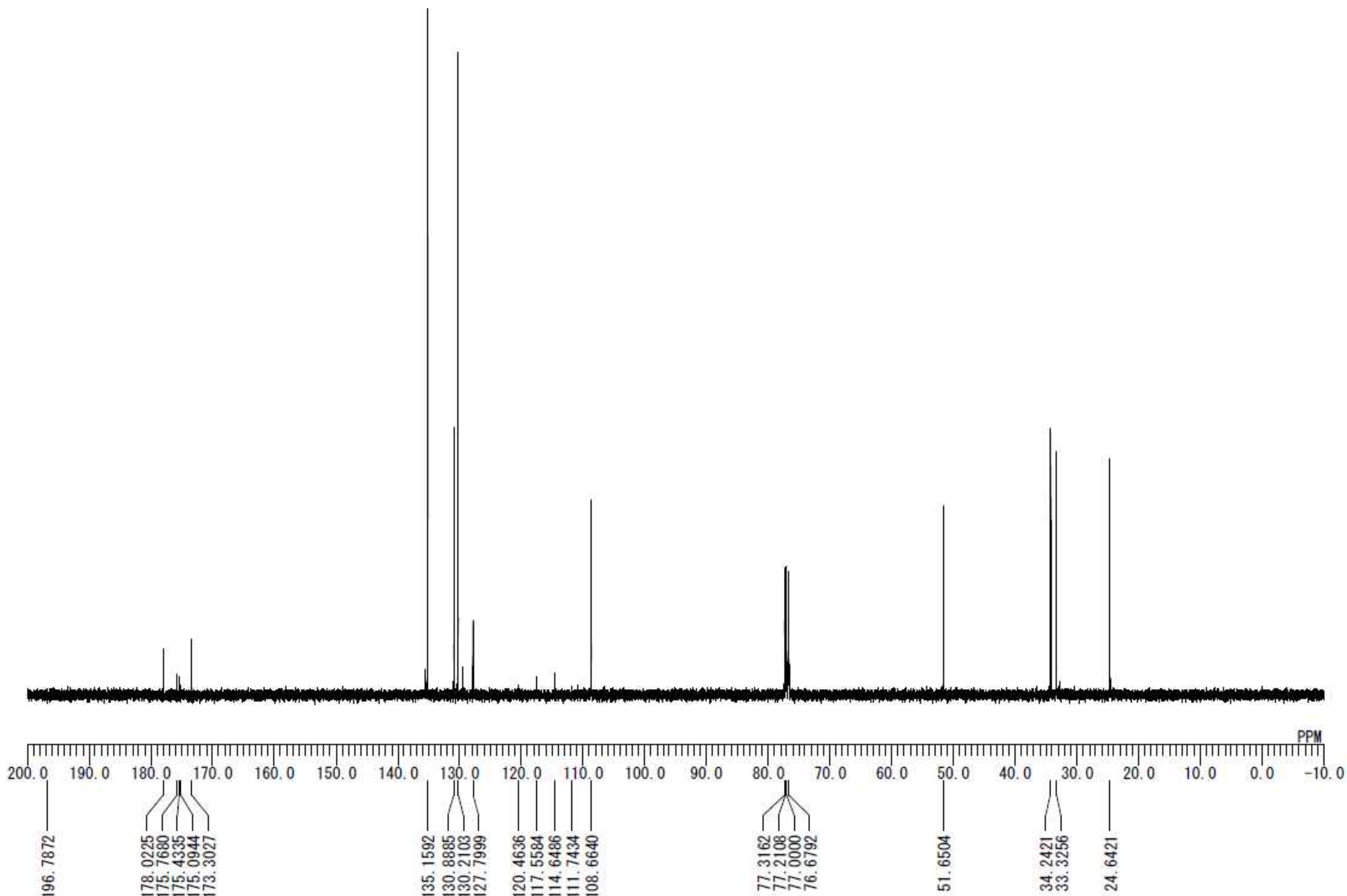
2.0122
1.9933
1.9743
0.0000


PPM
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180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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196.7872
178.0225
175.7680
175.4335
175.0944
173.3027
135.1592
130.8885
130.2103
127.7999
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117.5584
114.6486
111.7434
108.6640
77.3162
77.2108
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51.6504
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Supplementary Material (ESI) for Chemical Communications
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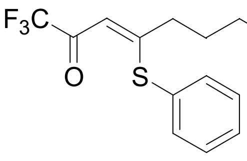
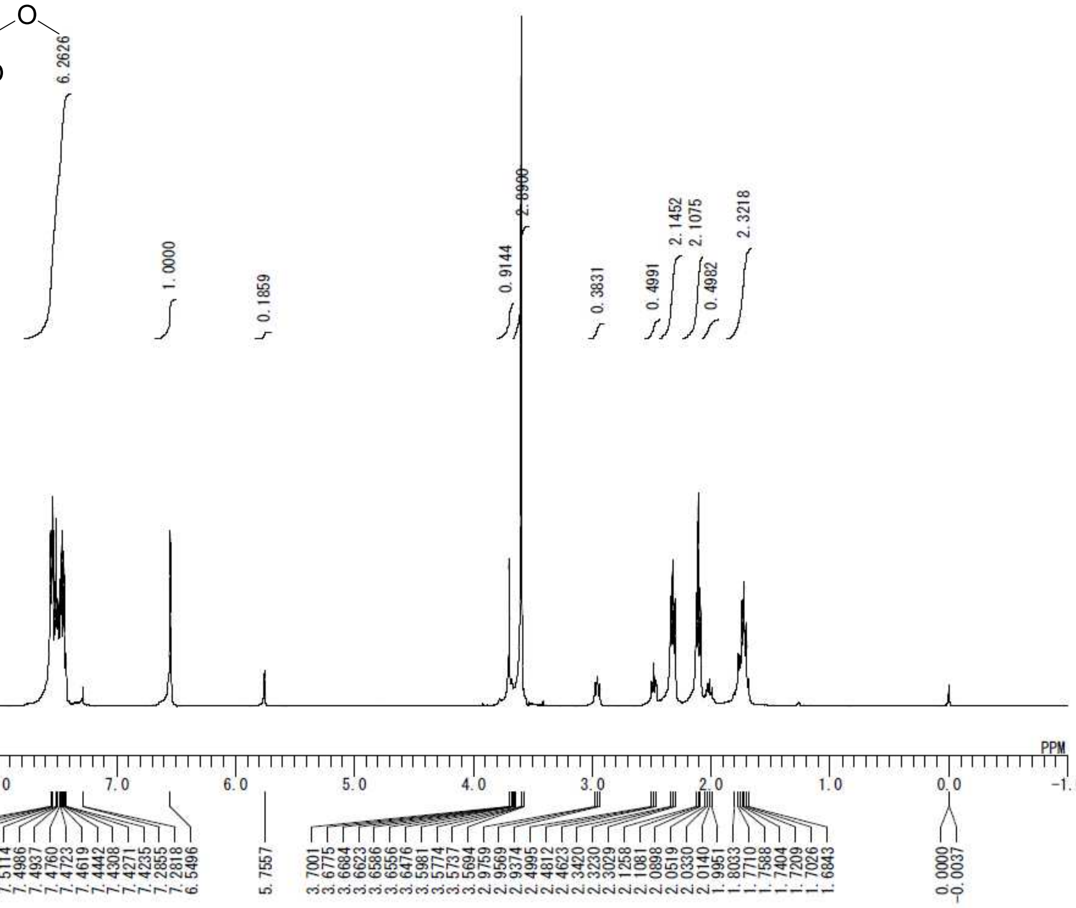
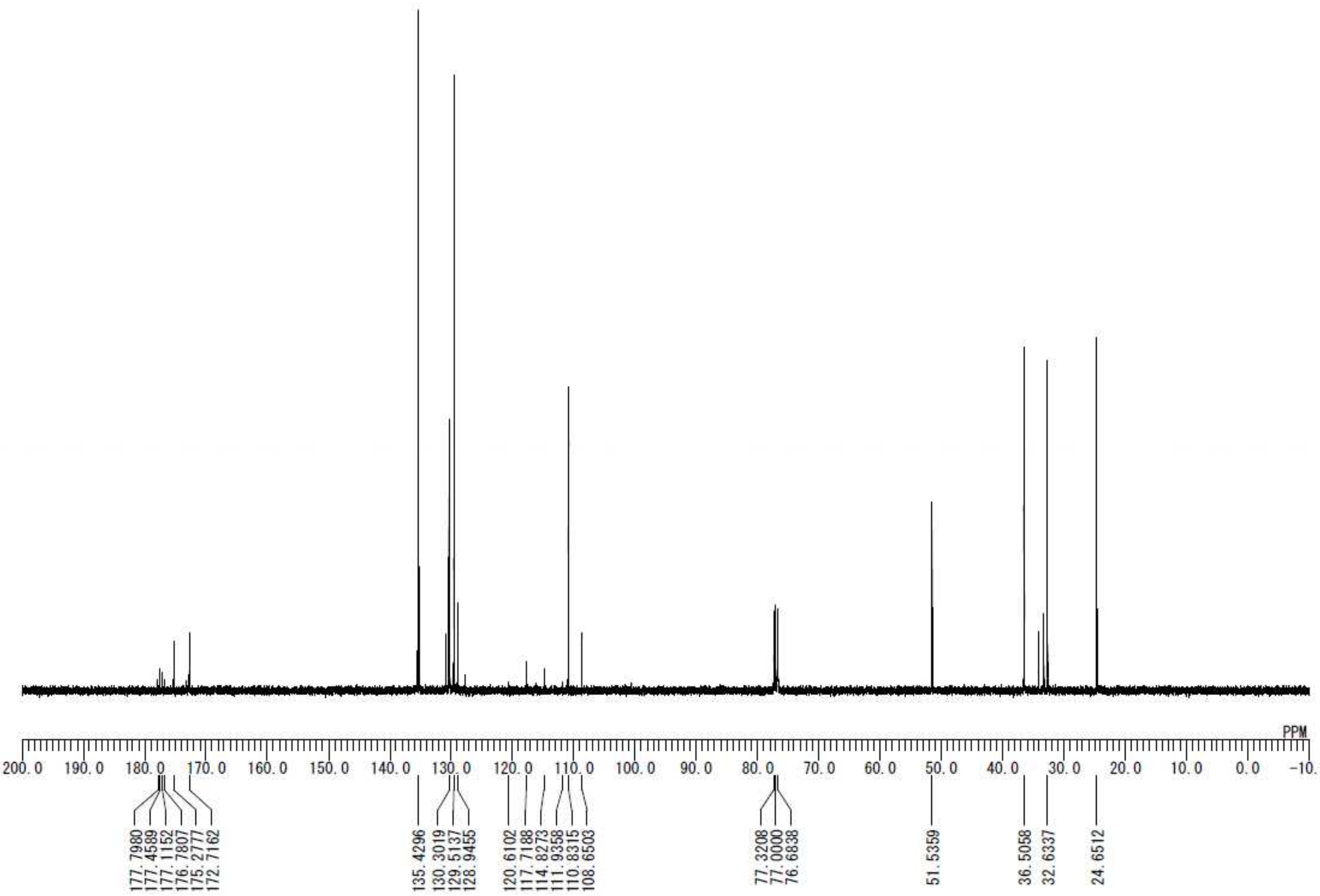
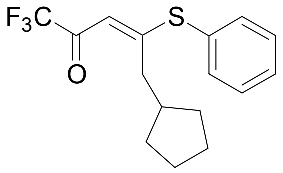


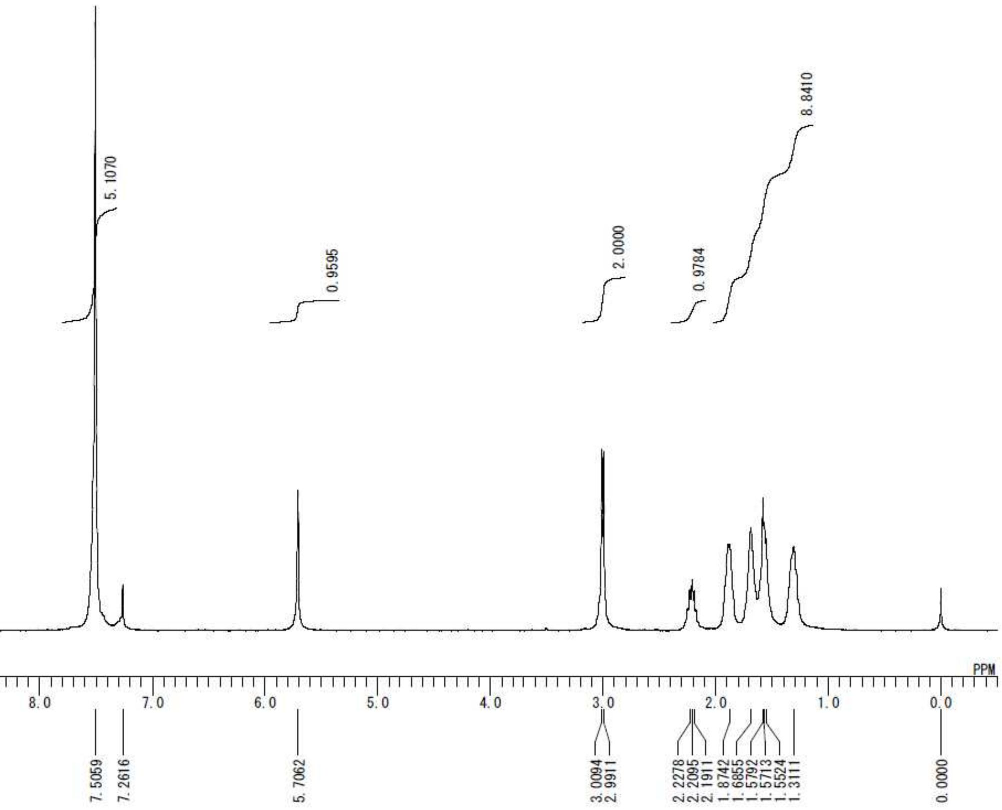
Z-**8k**






F3C
S
O

E-**8l**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PPM
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5.0
4.0
3.0
2.0
1.0
0.0
7.5059
7.2616
5.7062
3.0094
2.9911
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1.5713
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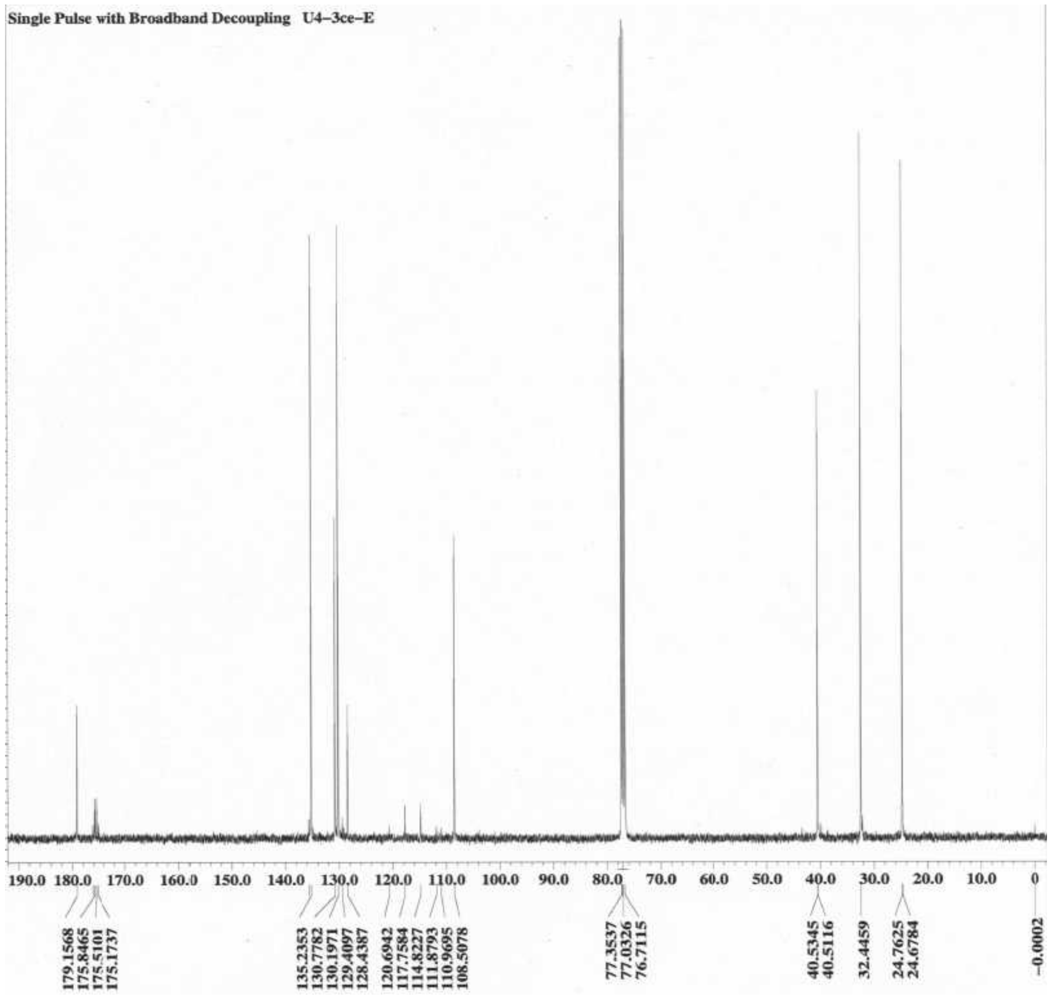
1.3111
0.0000


Single Pulse with Broadband Decoupling U4–3ce–E
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
179.1568
175.8465
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130.7782
130.1971
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128.4387
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117.7584
114.8227
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108.5078
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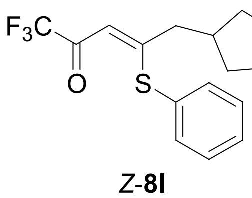

Z-**8l**