Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

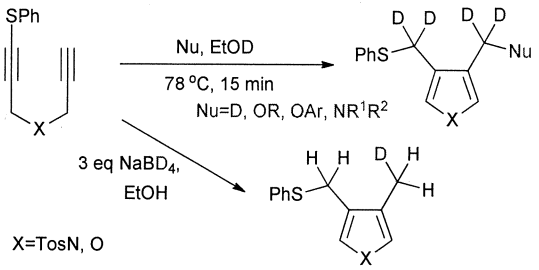
Supporting Information

Deuterative Cyclization of Sulfanyl 1,6-Diynes: Complete and Mono Deuteration of Functional Groups on Heterocycles

Yukiteru Ito and Mitsuhiro Yoshimatsu*

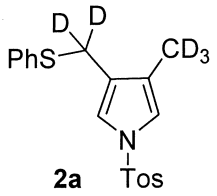
Department of Chemistry, Faculty of Education, Gifu University, Yanagido 1-1, Gifu 501-1193, Japan.

E-mail: yoshimae@gifu-u.ac.jp



1. Experimental section

Melting points were determined on a J-Science Lab. Micro melting point apparatus and uncorrected. Elemental analyses were performed at the Center of Instrumentation of Gifu University. ^{1}H and ^{13}C NMR spectra were determined with JEOL ECA600 (600 MHz) spectrometer at Gifu University. Chemical shifts are expressed in parts per million (ppm) with respected to tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet. IR spectra were determined on a JASCO FT-IR 460-Plus infrared spectrometer and are expressed in reciprocal centimeters. EI mass spectra (MS) were obtained using JEOL MS-700 spectrmeter with direct-insertion probe at 70 eV. All high-resolution mass determinations were obtained on the JMSD300 JMS2000 on line system. 4-Methyl-N-[3-(phenylsulfanyl)-2-prop-1-yl]-N-2-propyn-1-ylbenzenesulfonamide (**1**),[12a] 4-methyl-*N*-(2-pentyn-1-yl)-*N*-[3-(phenylthio)-2-propyn-1-yl]benzenesulfonamide, 4-methyl-*N*-(3-phenyl-2-propyn-1-yl)-*N*-[3-(phenylthio)-2-propyn-1-yl]benzenesulfonamide,[12b] were prepared according to our previous reports.

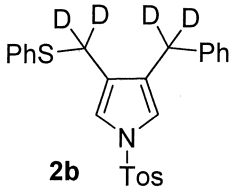


2a

Typical Procedure for Complete Deuterative Cyclization of 1,6-Diynes.

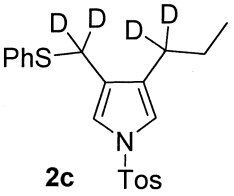
To a EtOD (1.0 mL) solution of sodium borodeuteride (17.7 mg, 0.42 mmol) and DBU (64.2 mg, 0.42 mmol) was added 4-methyl-*N*-[3-(phenylthio)-2-propyn-1-yl]-*N*-(2-propyn-1-yl)benzenesulfonamide (**1**) (50 mg, 0.14 mmol) under an Ar atomosphere. The reaction mixture was refluxed for 15 min. The cooled mixture was poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-*n*-hexane (15:1) to give 4-(methyl-d_3)-3-(phenylsulfanylmethyl-d_2)-1-(4-methylphenylsulfonyl)-*1H*-pyrrole (**2a**) (38.0 mg, 75 %) as white powders.

mp 69-70 °C, IR (KBr, cm^{-1}) 2924, 2853, 1596, 1583, 1518, 1480, 1439, 1368, 1308, 1188, 1174, 1093, 1075, 1058, 792, 703, 671, 582, 539; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.97 (0.08H, brs, CHD_2), 2.39 (3H, s, Me), 3.81 (0.08H, brs, CHD), 6.83 (1H, brs, ArH), 6.86 (1H, brs, ArH), 7.17-7.27 (7H, m, ArH), 7.60 (2H, d, J = 8.1 Hz, ArH); ^{2}H NMR (92 MHz, $CDCl_3$) δ 1.98 (brs), 3.82 (brs); The H/D ratio of determined by the intensities of the methylene or methyl protons of the product in the ^{1}H NMR spectra. ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6 (q), 118.4 (d), 119.4 (d), 126.5 (d), 123.9 (s), 119.3 (s), 126.7 (d×2), 128.7 (d×2), 129.8 (d×2), 130.4 (d×2), 135.8 (s), 136.1 (s), 144.6 (s); MS *m/z* 362 (M^+), 253 (M^+-SPh). High resolution mass calcd for $C_{19}H_{14}D_5NO_2S_2$: 362.1171, found *m/z* 362.1072.



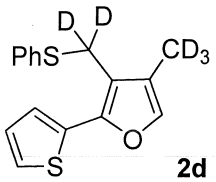
2b

4-(Phenylmethyl-d_2)-3-(phenylsulfanylmethyl-d_2)-1-(4-methylphenylsulfonyl)-*1H*-pyrrole (2b): Yield 52%, white powders, mp 108-109 °C, IR (KBr, cm^{-1}) 2924, 2853, 1597, 1495, 1480, 1370, 1307, 1188, 1173, 1092, 1070, 1026, 812, 738, 703, 673, 584, 539; ^1H NMR (600 MHz, $CDCl_3$) δ 2.41 (3H, s, Me), 3.67 (0.11H, brs, CHD), 3.75 (0.11H, brs, CHD), 6.78 (1H, d, J = 2.3 Hz, ArH), 6.90 (1H, d, J = 2.3 Hz, ArH), 7.10-7.26 (12H, m, ArH), 7.59 (2H, d, J = 8.6 Hz, ArH); ^2H NMR (92 MHz, $CDCl_3$) δ 3.68 (brs), 3.75 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6 (q), 119.2 (d), 120.0 (d), 123.9 (s), 126.3 (d), 126.4 (d), 126.7 (d×2), 127.6 (s), 128.4 (d×2), 128.6 (d×2), 128.7 (d×2), 129.9 (d×2), 130.2 (d×2), 135.6 (s), 136.0 (s), 139.2 (s), 144.7 (s); MS *m/z* 437 (M^+), 328 (M^+-SPh). High resolution mass calcd for $C_{25}H_{19}D_4NO_2S_2$: 437.1421, found *m/z* 437.1348.



2c

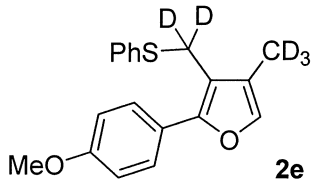
4-(Propyl-1,1-d_2)-3-(phenylsulfanylmethyl-d_2)-1-(4-methylphenylsulfonyl)-*1H*-pyrrole (2c): Yield 32%, white powders, mp 93-94 °C, IR (KBr, cm^{-1}) 3141, 2959, 2928, 2871, 1712, 1596, 1583, 1481, 1439, 1364, 1308, 1188, 1170, 1092, 1068, 980, 815, 741, 675, 585, 539; ^1H NMR (600 MHz, $CDCl_3$) δ 0.92 (3H, t, J = 7.3 Hz, Me), 1.56 (2H, t, J = 7.3 Hz, CH_2), 2.34 (0.10H, t, J = 7.3 Hz, CHD), 2.41 (3H, s, Me), 3.82 (0.10H, brs, CHD), 6.84 (1H, d, J = 2.7 Hz, ArH), 6.87 (1H, d, J = 2.3 Hz, ArH), 7.17-7.23 (7H, m, ArH), 7.61 (2H, d, J = 8.6 Hz, ArH); ^2H NMR (92 MHz, $CDCl_3$) δ 2.33 (brs), 3.82 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9 (q), 21.6 (q), 22.1 (t), 117.8 (d), 119.4 (d), 123.8 (s), 126.4 (d), 126.6 (d×2), 128.7 (d×2), 129.8 (d×2), 130.2 (d×2), 133.2 (s), 135.8 (s), 136.0 (s), 144.6 (s); MS *m/z* 389 (M^+), 280 (M^+-SPh). High resolution mass calcd for $C_{21}H_{19}D_4NO_2S_2$: 389.1421, found *m/z* 389.1415.



2d

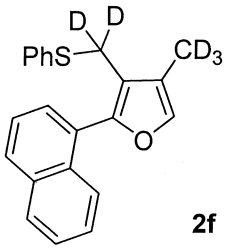
2-[4-(Methyl-d_3)-3-(phenylsulfanylmethyl-d_2)furan-2-yl]thiophene (2d): Yield 50%, yellow oil, IR (KBr, cm^{-1}) 2925, 1772, 1685, 1646, 1583, 1480, 1438, 1410, 1353, 1331, 1237, 1224, 1173, 1123, 1092, 1025, 997, 957, 849, 738, 691; ^1H NMR (600 MHz, $CDCl_3$) δ 1.95 (0.15H, brs, CHD_2), 4.10 (0.14H, brs, CHD), 7.04 (1H, dd, J = 4.2 and

4.8 Hz, ArH), 7.16 (1H, brs, ArH), 7.21-7.28 (5H, m, ArH), 7.38 (2H, d, J = 7.6 Hz, ArH); ^{2}H NMR (92 MHz, $CDCl_3$) δ 1.96 (brs), 4.11 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 116.1 (s), 122.1 (s), 123.8 (d), 124.8 (d), 126.7 (d), 127.4 (d), 128.9 (d×2), 130.8 (d×2), 132.9 (s), 136.0 (s), 138.1 (d), 146.7 (s); MS *m/z* 291 (M^+), 182 (M^+-SPh). High resolution mass calcd for $C_{16}H_9D_5OS_2$: 291.0800, found *m/z* 291.0705.



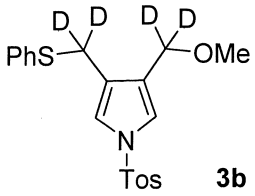
2e

4-Methoxy-[4-(methyl-d_3)-3-(phenylsulfanylmethyl-d_2)furan-2-yl]benzene (2e): yellow oil, Yield 41%, IR (KBr, cm^{-1}) 2956, 2931, 2839, 1765, 1654, 1609, 1583, 1513, 1480, 1464, 1440, 1334, 1304, 1255, 1179, 1123, 1032, 942, 838, 740, 691; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.00 (0.06H, brs, CHD_2), 3.83 (3H, s, Me), 4.07 (0.06H, brs, CHD), 6.93 (2H, brd, J = 9.0 Hz, ArH), 7.21 (2H, t, J = 7.6 Hz, ArH), 7.28 (2H, t, J = 7.5 Hz, ArH), 7.37 (2H, d, J = 7.5 Hz, ArH), 7.56 (2H, d, J = 9.0 Hz, ArH); ^{2}H NMR (92 MHz, $CDCl_3$) δ 2.01 (brs), 4.08 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.3 (q), 114.1 (d×2), 114.6 (s), 121.9 (s), 123.9 (s), 126.4 (d), 127.5 (d×2), 128.9 (d×2), 129.9 (d×2), 136.6 (s), 137.8 (d), 151.1 (s), 159.1 (s); MS *m/z* 315 (M^+), 206 (M^+-SPh). High resolution mass calcd for $C_{19}H_{13}D_5O_2S$: 315.1341, found *m/z* 315.1310.



2f

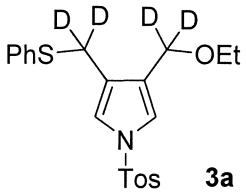
1-[4-(Methyl-d_3)-3-(phenylsulfanylmethyl-d_2)furan-2-yl]naphthalene (2f): Yield 63%, yellow oil, IR (KBr, cm^{-1}) 3057, 2925, 2851, 1712, 1584, 1555, 1507, 1480, 1439, 1380, 1297, 1216, 1172, 1136, 1107, 1024, 961, 931, 864, 802, 777, 736, 690, 663; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.15 (0.07H, brs, CHD_2), 3.95 (0.05H, brs, CHD_2), 7.06-7.08 (3H, m, ArH), 7.17-7.18 (2H, m, ArH), 7.36 (1H, s, ArH), 7.42-7.50 (4H, m, ArH), 7.86 (3H, d, J = 8.0 Hz, ArH); ^{2}H NMR (92 MHz, $CDCl_3$) δ 2.16 (brs), 3.97 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 118.4 (s), 121.4 (s), 125.1 (d), 126.0 (d), 126.1 (d), 126.2 (d), 126.4 (d), 128.0 (d), 280.0 (s), 128.2 (d), 128.7 (d×2), 129.1 (d), 130.1 (d×2), 132.1 (s), 133.8 (s), 136.1 (s), 139.1 (d), 151.2 (s); MS *m/z* 335 (M^+), 226 (M^+-SPh). High resolution mass calcd for $C_{22}H_{13}D_5OS$: 335.1392, found *m/z* 335.1374.



3b

Typical Procedure for Alkoxide-mediated Cyclization of 1,6-Diynes. To a mixture of MeOD (1.0 mL) and 1,4-dioxane (0.10 mL) of 4-methyl-*N*-[3-(phenylthio)-2-propyn-1-yl]-*N*-(2-propyn-1-yl)benzenesulfonamide (**1**) (50 mg, 0.14 mmol) was added 1M-MeONa (1.0 mL, 1.0 mmol) under an Ar atmosphere. The reaction mixture was stirred for 2 h at room temperature and poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-*n*-hexane (1:10) to give 4-(methoxymethyl-d_2)-3-(phenylsulfanylmethyl-d_2)-1-(4-methylphenylsulfonyl)-*1H*-pyrrole (**3b**) (41.1 mg, 75 %) as white powders.

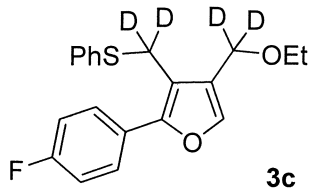
mp 67-68 °C, IR (KBr, cm^{-1}) 3144, 2975, 2925, 2915, 1595, 1583, 1515, 1482, 1459, 1439, 1369, 1311, 1222, 1189, 1172, 1127, 1092, 1072, 1055, 965, 816, 742, 675, 586, 540; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.40 (3H, s, Me), 3.29 (3H, s, Me), 3.90 (0.04H, brs, CHD), 4.29 (0.04H, brs, CHD), 6.91 (1H, brs, ArH), 7.04 (1H, brs, ArH), 7.15-7.25 (7H, m, ArH), 7.63 (2H, d, J = 8.0 Hz, ArH); ^{2}H NMR (92 MHz, $CDCl_3$) δ 3.91 (brs), 4.30 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6 (q), 57.8 (q), 119.8 (d), 120.0 (d), 123.7 (s), 124.7 (s), 126.4 (d), 126.8 (d×2), 128.7 (d×2), 129.9 (d×2), 130.3 (d×2), 135.8 (s), 135.9 (s), 144.9 (s); MS *m/z* 391 (M^+), 282 (M^+-SPh). High resolution mass calcd for $C_{20}H_{17}D_4NO_3S_2$: 391.1214, found *m/z* 391.1135.



3a

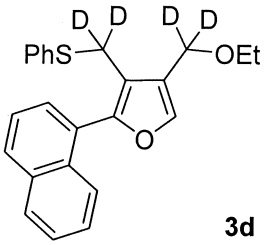
4-(Ethoxymethyl-d_2)-3-(phenylsulfanylmethyl-d_2)-1-(4-methylphenylsulfonyl)-*1H*-pyrrole (3a): Yield 56%, white powders, mp 74-75 °C, IR (KBr, cm^{-1}) 3134, 3059, 2974, 2926, 2868, 1596, 1519, 1480, 1439, 1371, 1308, 1173, 1092, 1059, 968, 813, 741, 673, 585, 539; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.19 (3H, t, J = 6.8 Hz, Me), 2.40 (3H, s, Me), 3.45-3.49 (2H, m, CH_2), 3.92 (0.04H, brs, CHD), 4.34 (0.04H, brs, CHD), 6.91 (1H, d, J = 2.3 Hz, ArH), 7.04 (1H, d, J = 2.3 Hz, ArH), 7.17-7.25 (7H, m, ArH), 7.63 (2H, d, J = 8.6 Hz, ArH); ^{2}H NMR (92 MHz, $CDCl_3$) δ 3.92 (brs), 4.35 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.1 (q), 21.6 (q), 65.7 (t), 119.6 (d), 119.9 (d), 123.8 (s), 125.0 (s), 126.4 (d), 126.8 (d×2), 128.7 (d×2), 129.9 (d×2), 130.3 (d×2), 135.8 (s), 135.9 (s), 144.9 (s); MS *m/z* 405 (M^+), 296

(M^+-SPh). High resolution mass could not be measured because the molecular ion peak m/z 405 was observed at the same chemical shift of PFK.



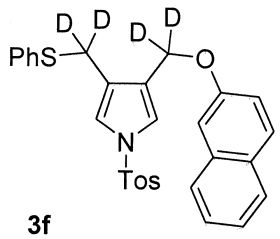
3c

4-Fluoro-[4-(ethoxymethyl-d_2)-3-(phenylsulfanylmethyl-d_2)furan-2-yl]benzene (3c): Yield 46%, yellow oil, IR (KBr, cm^{-1}) 2959, 2926, 2870, 1596, 1481, 1439, 1229, 1159, 1134, 1100, 1071, 1026, 947, 838, 814, 739, 690; ^1H NMR (600 MHz, $CDCl_3$) δ 1.22 (3H, t, J = 6.9 Hz, Me), 3.51-3.55 (2H, m, CH_2), 4.16 (0.04H, brs, CHD), 4.39 (0.04H, brs, CHD), 7.07 (2H, t, J = 8.9 Hz, ArH), 7.21 (1H, t, J = 7.6 Hz, ArH), 7.27 (2H, t, J = 7.5 Hz, ArH), 7.35 (2H, d, J = 7.5 Hz, ArH), 7.40 (1H, s, ArH), 7.54-7.56 (2H, m, ArH); ^2H NMR (92 MHz, $CDCl_3$) δ 4.12 (brs), 4.40 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.2 (q), 65.7 (t), 115.3 (s), 115.6 (d), 115.7 (d), 123.9 (s), 126.6 (d), 126.9 (s), 128.0 (d), 128.1 (d), 128.9 (d×2), 130.4 (d×2), 136.1 (s), 140.0 (d), 151.0 (s), 162.3 (s, J = 248.6 Hz); MS *m/z* 346 (M^+), 237 (M^+-SPh). High resolution mass calcd for $C_{20}H_{15}D_4FO_2S$: 346.1341, found *m/z* 346.1361.



3d

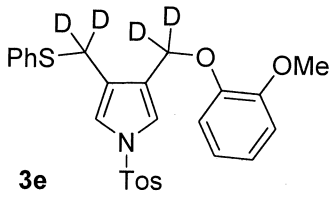
1-[4-(Ethoxymethyl-d_2)-3-(phenylsulfanylmethyl-d_2)furan-2-yl]naphthalene (3d): Yield 66%, yellow oil, IR (KBr, cm^{-1}) 2973, 2925, 2864, 1583, 1557, 1480, 1439, 1394, 1101, 1024, 963, 931, 802, 777, 739, 690; ^1H NMR (600 MHz, $CDCl_3$) δ 1.27 (3H, t, J = 6.9 Hz, Me), 3.61 (2H, q, J = 6.9 Hz, CH_2), 4.04 (0.04H, brs, CHD), 4.57 (0.04H, brs, CHD), 7.05 (3H, t, J = 2.8 Hz, ArH), 7.14-7.16 (2H, m, ArH), 7.39 (1H, d, J = 8.9 Hz, ArH), 7.44 (2H, d, J = 8.9 Hz, ArH), 7.48 (1H, t, J = 6.9 Hz, ArH), 7.55 (1H, s, ArH), 7.83 (1H, d, J = 8.2 Hz, ArH), 7.86 (2H, d, J = 8.3 Hz, ArH); ^2H NMR (92 MHz, $CDCl_3$) δ 4.07 (brs), 4.59 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.3 (q), 66.0 (t), 117.9 (s), 123.4 (s), 125.1 (d), 126.0 (d×2), 126.2 (d), 126.5 (d), 127.6 (s), 128.2 (d), 128.2 (d), 128.6 (d×2), 129.3 (d), 130.1 (d×2), 132.1 (s), 133.7 (s), 136.0 (s), 140.6 (d), 151.8 (s); MS *m/z* 378 (M^+), 269 (M^+-SPh). High resolution mass calcd for $C_{24}H_{18}D_4O_2S$: 378.1591, found *m/z* 378.1557.



3f

Typical Procedure for Sodium Naphthol-Mediated Cyclization of 1,6-Diyne. To a THF (0.40 mL) solution of 2-naphthol (101.4 mg, 0.70 mmol) was added sodium hydride (28.1 mg, 0.70 mmol) at 0 °C. EtOD (0.40 mL) was added to the reaction mixture. The whole was stirred for 10 min at room temperature. To the mixture was added a EtOD (0.60 mL) solution of 4-methyl-*N*-[3-(phenylthio)-2-propyn-1-yl]-*N*-(2-propyn-1-yl)benzenesulfonamide (**1**) (50 mg, 0.14 mmol) under an Ar atmosphere. The reaction mixture was stirred for 30 min at 75 °C. The work-up procedure gave 4-(2-naphthoxymethyl-d_2)-3-(phenylsulfanylmethyl-d_2)-1-(4-methylphenylsulfonyl)-*1H*-pyrrole (**3f**) (33 mg, 46 %) as white powders.

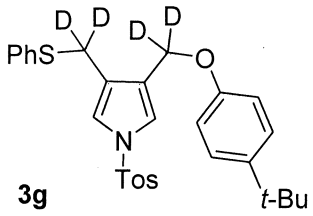
mp 109-110 °C, IR (KBr, cm^{-1}) 3133, 3058, 2924, 2854, 1629, 1599, 1509, 1467, 1439, 1371, 1315, 1258, 1217, 1173, 1120, 1092, 1069, 1026, 837, 812, 746, 672, 585, 539, 539, 672; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.37 (3H, s, Me), 3.96 (0.07H, brs, CHD), 5.03 (0.08H, brs, CHD), 6.94 (1H, brs, ArH), 7.13-7.22 (10H, m, ArH), 7.34 (1H, t, J = 6.9 Hz, ArH), 7.43 (1H, t, J = 6.8 Hz, ArH), 7.60 (2H, d, J = 8.3 Hz, ArH), 7.69 (1H, d, J = 8.3 Hz, ArH), 7.72 (1H, d, J = 8.9 Hz, ArH), 7.76 (1H, d, J = 8.3 Hz, ArH); ^{2}H NMR ($CDCl_3$) δ 3.96 (brs), 5.04 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6 (q), 107.2 (d), 118.8 (d), 120.1 (d), 120.2 (d), 123.4 (s), 123.6 (s), 123.8 (d), 126.4 (d), 126.6 (d), 126.8 (d×2), 127.6 (d), 128.8 (d×2), 129.1 (s), 129.4 (d), 129.9 (d×2), 130.6 (d×2), 134.4 (s), 135.4 (s), 135.7 (s), 145.0 (s), 156.3 (s); MS *m/z* 503 (M^+), 394 (M^+-SPh), 360 (M^+-naphthoxy). High resolution mass calcd for $C_{29}H_{21}D_4NO_3S_2$: 503.1527, found *m/z* 503.1432.



3e

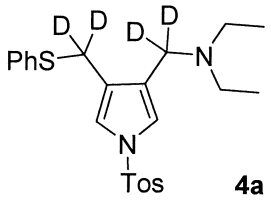
4-(2-Methoxyphenoxymethyl-d_2)-3-(phenylsulfanylmethyl-d_2)-1-(4-methylphenylsulfonyl)-*1H*-pyrrole (3e): Yield 45%, yellow oil, IR (KBr, cm^{-1}) 3132, 3062, 2924, 2836, 1593, 1503, 1481, 1456, 1439, 1371, 1309, 1256, 1226, 1174, 1124, 1092, 1067, 1027, 970, 812, 742, 674, 585, 539; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.41 (3H, s, Me), 3.80 (3H, s, Me), 4.00 (0.08H, brs, CHD), 4.96 (0.09H, brs, CHD), 6.82-6.89 (3H, m, ArH), 6.92-6.95 (2H, d, J = 2.0 Hz, ArH), 7.12-7.25 (8H, m, ArH), 7.60 (2H, d, J = 8.2 Hz, ArH); ^{2}H NMR (92 MHz, $CDCl_3$) δ 4.01 (brs), 4.98 (brs);

^{13}C NMR (150 MHz, $CDCl_3$) δ 21.7 (q), 55.8 (q), 111.9 (d), 115.0 (d), 120.1 (d), 120.3 (d), 120.8 (d), 122.0 (d), 123.8 (s), 123.9 (s), 126.5 (d), 126.9 (d×2), 128.8 (d×2), 130.1 (d×2), 130.4 (d×2), 135.7 (s), 135.9 (s), 145.0 (s), 147.8 (s), 150.1 (s); MS *m/z* 483 (M^+), 360 (M^+-2-methoxyphenoxy), 251 (M^+-SPh-2-methoxyphenoxy), 205 (M^+-Tos-2-methoxyphenoxy). High resolution mass calcd for $C_{26}H_{21}D_4NO_4S_2$: 483.1476, found *m/z* 483.1403.



3g

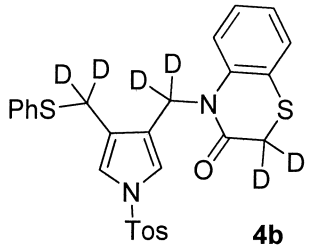
4-(4-*t*-Butylphenoxymethyl-d_2)-3-(phenylsulfanylmethyl-d_2)-1-(4-methylphenylsulfonyl)-*1H*-pyrrole (3g): Yield 56%, yellow oil, IR (KBr, cm^{-1}) 2961, 2868, 1607, 1597, 1582, 1511, 1480, 1439, 1372, 1293, 1247, 1188, 1071, 1026, 971, 829, 812, 739, 703, 671, 585, 553, 539; ^1H NMR (600 MHz, $CDCl_3$) δ 1.31 (9H, s, Me×3), 2.41 (3H, s, Me), 3.92 (0.11H, brs, CHD), 4.88 (0.11H, brs, CHD), 6.85 (2H, brd, J = 8.9 Hz, ArH), 6.93 (1H, d, J = 2.1 Hz, ArH), 7.13-7.29 (11H, m, ArH), 7.63 (1H, d, J = 8.2 Hz, ArH); ^2H NMR (92 MHz, $CDCl_3$) δ 3.93 (brs), 4.90 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6 (q), 31.5 (q×3), 34.1 (s), 114.2 (d×2), 120.1 (d), 123.7 (s), 123.7 (s), 126.2 (d×2), 126.5 (d), 126.8 (d×2), 128.7 (d×2), 130.0 (d×2), 130.5 (d×2), 135.5 (s), 135.8 (s), 143.8 (s), 145.0 (s), 156.2 (s); MS *m/z* 509 (M^+), 360 (M^+-4-*t*-butylphenoxy). High resolution mass calcd for $C_{29}H_{27}D_4NO_3S_2$: 509.1996, found *m/z* 509.1973.



4a

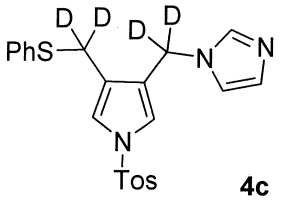
Typical Procedure for Diethylamination of 1,6-Diyne. To a mixture of diethylamine-d_1 (51.4 mg, 0.70 mmol),[14] DMSO (0.50 mL) and D_2O (3 drops) was added 4-methyl-*N*-[3-(phenylthio)-2-propyn-1-yl]-*N*-2-propyn-1-ylbenzenesulfonamide (**1**) (50 mg, 0.14 mmol) bis(hexafluoroacetylacetonato)nickel(II)hydrate (6.7 mg, 0.014 mmol) 、bis(triphenylphosphine)palladium(II)dichloride (9.9 mg, 0.014 mmol) and DBU (21.4 mg, 0.14 mmol) under an Ar atmosphere. The whole was stirred for 1 h. The work-up procedure gave 4-(diethylaminomethyl-d_2)-3-(phenylsulfanylmethyl-d_2)-1-(4-methylphenylsulfonyl)pyrrole (**4a**) (40.4 mg, 66 %) as a yellow oil.

IR (KBr, cm^{-1}) 2968, 2930, 2871, 2801, 1597, 1480, 1439, 1371, 1308, 1188, 1173, 1092, 1068; ^1H NMR (600 MHz, $CDCl_3$) δ 0.96 (6H, t, J = 7.5 Hz, Me×2), 2.40 (3H, s, Me), 2.40-2.44 (4H, m, CH_2×2), 3.35 (0.30H, brs, CHD), 3.98 (0.30H, brs, CHD), 6.89 (1H, d, J = 2.1 Hz, ArH), 6.95 (1H, d, J = 2.8 Hz, ArH), 7.14-7.23 (7H, m, ArH), 7.69 (2H, d, J = 8.9 Hz, ArH); ^2H NMR (92 MHz, $CDCl_3$) δ 3.36 (brs), 3.98 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.7 (q×2), 21.6 (q), 46.6 (t×2), 119.8 (d), 119.9 (d), 124.7 (s), 126.1 (d), 126.4 (s), 126.6 (d×2), 128.6 (d×2), 129.8 (d×2), 129.9 (d×2), 136.1 (s), 136.1 (s), 144.6 (s); MS *m/z* 432 (M^+), 277 (M^+-Tos). High resolution mass calcd for $C_{23}H_{24}D_4N_2O_2S_2$: 432.1843, found *m/z* 432.1220.



4b

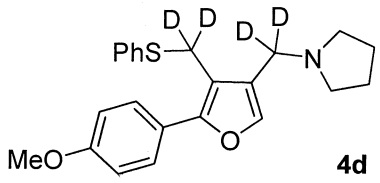
4-[[4-(Phenylsulfanylmethyl-d_2)-1-(4-methylphenylsulfonyl)-*1H*-pyrrol-3-yl]methyl-d_2]-*4H*-1,4-benzothiazin-3(*4H*)one-2,2-d_2 (4b): Yield 96%, a yellow oil, IR (KBr, cm^{-1}) 3131, 3061, 2924, 2855, 1710, 1666, 1585, 1519, 1479, 1445, 1368, 1308, 1279, 1189, 1173, 1092, 1068, 812, 755, 703, 672, 584, 539; ^1H NMR (600 MHz, $CDCl_3$) δ 2.40 (3H, s, Me), 3.43 (0.35H, brs, CHD), 3.44 (0.10H, brs, CH_2), 3.86 (0.16H, brs, CHD), 5.06 (0.16H, brs, CHD), 6.81-6.82 (2H, m, ArH), 6.97-7.01 (2H, m, ArH), 7.08 (1H, J = 7.5 Hz, ArH), 7.16-7.19 (7H, m, ArH), 7.34 (1H, d, J = 7.5 Hz, ArH), 7.47 (2H, d, J = 8.3 Hz, ArH); ^2H NMR (92 MHz, $CDCl_3$) δ 3.44 (brs), 3.87 (brs), 5.07 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 121.6 (q), 118.4 (d), 119.3 (d), 120.0 (d), 122.7 (s), 123.5 (s), 123.5 (d), 123.9 (s), 126.5 (d×2), 126.6 (d), 127.0 (d), 128.3 (d), 128.7 (d×2), 129.8 (d×2), 130.4 (d×2), 135.1 (s), 135.6 (s), 138.9 (s), 144.7 (s), 165.1 (s); MS *m/z* 526 (M^+), 417 (M^+-SPh). High resolution mass calcd for $C_{27}H_{18}D_6N_2O_3S_3$: 526.1325, found *m/z* 526.1331.



4c

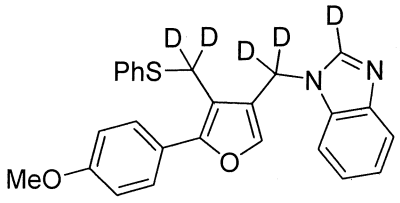
4-(*N*-Imidazoylmethyl-d_2)-3-(phenylsulfanylmethyl-d_2)-1-(4-methylphenylsulfonyl)-*1H*-pyrrole (4c): Yield 67%, IR (KBr, cm^{-1}) 3129, 3060, 2925, 1708, 1596, 1500, 1481, 1439, 1371, 1309, 1227, 1189, 1174, 1092, 1070, 1001, 970, 814, 742, 672, 585, 539; ^1H NMR (600 MHz, $CDCl_3$) δ 2.43 (3H, s, Me), 3.61 (0.20H, brs, CHD), 4.97 (0.20H, brs, CHD), 6.84 (1H, brs, ArH), 6.90 (1H, d, J = 2.1 Hz, ArH), 6.97 (1H, d, J = 2.8 Hz, ArH), 7.04 (1H, s, ArH),

7.17-7.20 (5H, m, ArH), 7.28 (2H, d, J = 8.3 Hz, ArH), 7.43 (1H, s, ArH), 7.62 (2H, d, J = 8.2 Hz, ArH); ^{2}H NMR (92 MHz, $CDCl_3$) δ 3.61 (brs), 4.97 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6 (q), 118.9 (s), 119.9 (d), 120.6 (d), 122.5 (s), 122.9 (s), 126.8 (d×2), 126.9 (d), 128.8 (d×2), 129.6 (d), 130.1 (d×2), 130.8 (d×2), 134.7 (s), 135.4 (d), 137.0 (s), 145.3 (s); MS *m/z* 427 (M^+), 318 (M^+-SPh). High resolution mass calcd for $C_{22}H_{17}D_4N_3O_2S_2$: 427.1326, found *m/z* 427.1256.



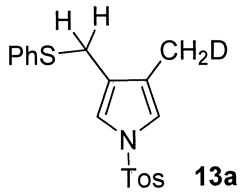
4d

1-[2-(*p*-Methoxyphenyl)-3-(phenylsulfanylmethyl-d_2)furan-4-methyl-d_2]-*1H*-pyrrlidine (4d): Yield 70%, a yellow oil, IR (KBr, cm^{-1}) 2958, 2956, 2854, 2785, 1668, 1606, 1577, 1552, 1506, 1480, 1460, 1439, 1305, 1252, 1179, 1136, 1033, 945, 835, 757, 741, 691; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.78 (4H, brs, CH_2×2), 3.96 (4H, brs, CH_2×2), 3.51 (0.20H, brs, CHD), 3.82 (3H, s, Me), 4.21 (0.20H, brs, CHD), 6.72 (2H, dd, J = 2.1and 6.9 Hz, ArH), 7.20 (1H, t, J = 6.9 Hz, rH), 7.27 (2H, t, J = 5.5 Hz, ArH), 7.36 (1H, s, furyl H), 7.37 (2H, d, J = 7.6 Hz, ArH), 7.55 (2H, d, J = 9.0 Hz, ArH); ^{2}H NMR (92 MHz, $CDCl_3$) δ 3.51 (brs), 4.23 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.5 (t×2), 54.2 (t×2), 55.3 (q), 114.1 (d×2), 114.3 (s), 123.7 (s), 126.3 (d), 127.6 (d×2), 128.8 (d×2), 129.9 (d×2), 136.7 (s), 139.1 (d), 151.3 (s), 159.1 (s); MS *m/z* 383 (M^+), 274 (M^+-SPh). High resolution mass calcd for $C_{23}H_{21}D_4NO_2S$: 383.1857, found *m/z* 383.1792.



4f

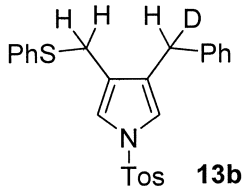
1-[2-(*p*-Methoxyphenyl)-3-(phenylsulfanylmethyl-d_2)furan-4-methyl-d_2]-*1H*-benzimidazole (4f): Yield 70%, yellow oil, IR (KBr, cm^{-1}) 3056, 2929, 2837, 1614, 1580, 1506, 1481, 1457, 1320, 1306, 1279, 1253, 1178, 1030, 942, 836, 745, 691; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.82 (3H, s, Me), 3.88 (0.11H, brs, CHD), 5.23 (0.11H, brs, CHD), 6.92 (2H, brd, J = 9.0 Hz, ArH), 7.21-7.30 (8H, m, ArH), 7.41 (2H, d, J = 6.9 Hz, ArH), 7.47 (2H, d, J = 8.9 Hz, ArH), 7.82 (1H, d, J = 7.6 Hz, ArH), 7.93 (0.23H, s, ArH); ^{2}H NMR (92 MHz, $CDCl_3$) δ 3.89 (brs), 5.24 (brs), 7.97 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.3 (q), 109.9 (d), 131.1 (s), 114.2 (d×2), 120.4 (d), 121.5 (s), 122.3 (d), 122.7 (s), 123.0 (d), 127.0 (d), 127.9 (d×2), 129.0 (d×2), 130.5 (d×2), 133.8 (s), 135.3 (s), 139.6 (d), 142.9 (s), 143.9 (s), 153.0 (s), 159.6 (s); MS *m/z* 431 (M^+), 322 (M^+-SPh). High resolution mass could not be measured because the molecular ion peak m/z 431 was observed at the same chemical shift of PFK.



13a

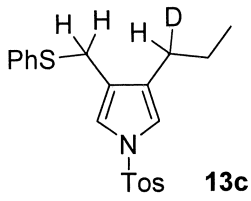
Typical Procedure for Monodeuteration-Cyclization of 1,6-Diyne. To a EtOH (1.0 mL) solution of DBU (64.2 mg, 0.42 mmol) and sodium borodeuteride (17.7 mg, 0.42 mmol) was added 4-methyl-*N*-[3-(phenylthio)-2-propyn-1-yl]-*N*-(2-propyn-1-yl)benzenesulfonamide (**1**) (50 mg, 0.14 mmol) under an Ar atmosphere. The reaction mixture was stirred under reflux condition for 15 min. The work-up procedure gave 4-(methyl-d_1)-3-(phenylsulfanylmethyl)-1-(4-methylphenylsulfonyl)-*1H*-pyrrole (**13a**) (33.0 mg, 65 %) as white powders.

White powders, mp 69-70 °C, IR (KBr, cm^{-1}) 3133, 3059, 2923, 1596, 1584, 1519, 1480, 1439, 1368, 1309, 1188, 1173, 1093, 1065, 813, 796, 741, 703, 673, 584, 539; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.98 (1.96H, brs, CH_2D), 2.40 (3H, s, Me), 3.82 (2H, s, CH_2), 6.83 (1H, brs, ArH), 6.86 (1H, brs, ArH), 7.16-7.25 (7H, m, ArH), 7.61 (2H, dd, J = 8.6 Hz, ArH); ^{2}H NMR (92 MHz, $CDCl_3$) δ 2.01 (brt, J = 2.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 9.84 (t, J= 20.2 Hz), 21.6 (q), 29.6 (t), 118.3 (d), 119.3 (d), 123.9 (s), 124.3 (s), 126.5 (d), 126.6 (d×2), 128.7 (d×2), 129.8 (d×2), 130.4 (d×2), 135.7 (s), 136.0 (s), 144.6 (s); MS *m/z* 358 (M^+), 249 (M^+-SPh). High resolution mass calcd for $C_{19}H_{18}DNO_2S_2$: 358.0920, found *m/z* 358.0840.



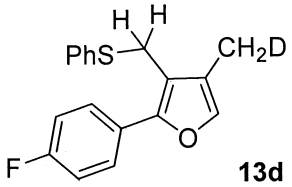
13b

4-(Phenylmethyl-d_1)-3-(phenylsulfanylmethyl)-1-(4-methylphenylsulfonyl)-*1H*-pyrrole (13b): Yield 39%, white powders, mp 108-109 °C, IR (KBr, cm^{-1}) 3142, 3056, 3026,2924, 2852, 1597, 1583, 1495, 1481, 1439, 1362, 1308, 1188, 1171, 1092, 1065, 812, 737, 677, 585, 539; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.41 (3H, s, Me), 3.69 (2H, s, CH_2), 3.75 (0.93H, brs, CHD), 6.78 (1H, brs, ArH), 6.90 (1H, brs, ArH), 7.11 (2H, d, J = 7.5 Hz, ArH), 7.17-7.21 (5H, m, ArH), 7.24-7.27 (4H, m, ArH), 7.59 (2H, brd, J = 8.2 Hz, ArH); ^{2}H NMR (92 MHz, $CDCl_3$) δ 3.78 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6 (q), 29.6 (t), 31.2 (t, J = 20.3 Hz), 119.3 (d), 120.0 (d), 124.1 (s), 126.3 (d), 126.4 (d), 126.7 (d×2), 127.7 (s), 128.4 (d×2), 128.6 (d×2), 128.7 (d×2), 129.9 (d×2), 130.3 (d×2), 135.7 (s), 136.0 (s), 139.2 (s), 144.7 (s); MS *m/z* 434 (M^+), 325 (M^+-SPh). High resolution mass calcd for $C_{25}H_{22}DNO_2S_2$: 434.1223, found *m/z* 434.1172.



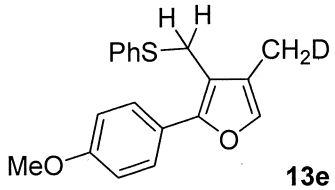
13c

4-(Propyl-1-d_1)-3-(phenylsulfanylmethy)-1-(4-methylphenylsulfonyl)-*1H*-pyrrole (13c): Yield 40%, white powders, mp 93-94 °C, IR (KBr, cm^{-1}) 2959, 2927, 2871, 1596, 1583, 1515, 1481, 1309, 1240, 1215, 1188, 1171, 1092, 1068, 815, 742, 675, 586, 540; ^1H NMR (600 MHz, $CDCl_3$) δ 0.92 (3H, t, J = 7.3 Hz, Me), 1.56 (2H, t, J = 7.3 Hz, CH_2), 2.34 (0.99H, t, J = 6.8 Hz, CHD), 2.41 (3H, s, Me), 3.83 (2H, s, CH_2), 6.84 (1H, d, J = 2.3 Hz, ArH), 6.87 (1H, d, J = 2.3 Hz, ArH), 7.17-7.23 (7H, m, ArH), 7.61 (2H, d, J = 8.2 Hz, ArH); ^2H NMR (92 MHz, $CDCl_3$) δ 2.36 (brs); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9 (q), 21.6 (q), 22.2 (t), 22.7 (d, J = 19.2 Hz), 29.6 (t), 117.8 (d), 119.4 (d), 123.9 (s), 126.4 (d), 126.6 (d×2), 128.7 (d×2), 129.8 (d×2), 130.2 (d×2), 133.2 (s), 135.8 (s), 136.0 (s), 144.6 (s); MS *m/z* 386 (M^+), 277 (M^+-SPh). High resolution mass calcd for $C_{21}H_{22}DNO_2S_2$: 386.1233, found *m/z* 386.1181.



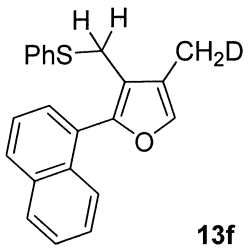
13d

4-Fluoro-[4-(methyl-d_1)-3-(phenylsulfanylmethyl)furan-2-yl]benzene (13d): Yield 63%, yellow oil, IR (KBr, cm^{-1}) 3075, 2926, 2853, 1769, 1659, 1604, 1509, 1480, 1440, 1412, 1342, 1303, 1162, 1087, 1024, 960, 840, 745, 691; ^1H NMR (600 MHz, $CDCl_3$) δ 2.02 (1.96H, brs, CH_2D), 4.07 (2H, s, CH_2), 7.07 (2H, brt, J = 8.2 Hz, ArH), 7.22 (2H, t, J = 7.5 Hz, ArH), 7.28 (2H, t, J = 7.5 Hz, ArH) , 7.37 (2H, dd, J = 1.3 and 8.3 Hz, ArH) , 7.56-7.59 (2H, m, ArH); ^2H NMR (92 MHz, $CDCl_3$) δ 2.05 (brt, J = 2.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 7.8 (t, J = 20.4 Hz), 29.2 (t), 115.6 (d), 115.7 (d), 115.9 (s), 122.2 (s), 126.7 (d), 127.3 (s), 127.8 (d), 127.9 (d), 128.9 (d×2), 130.3 (d×2), 136.2 (s), 138.4 (d), 150.2 (s), 162.2 (d, J = 248.5 Hz); MS *m/z* 299 (M^+), 190 (M^+-SPh). High resolution mass calcd for $C_{18}H_{14}DFOS$: 299.0890, found *m/z* 299.0836.



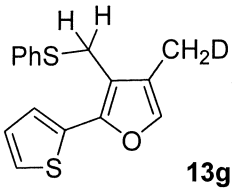
13e

4-Methoxy-[4-(methyl-d_1)-3-(phenylsulfanylmethyl)furan-2-yl]benzene (13e): Yield 43%, yellow oil, IR (KBr, cm^{-1}) 2930, 2838, 1766, 1608, 1583, 1509, 1480, 1464, 1440, 1305, 1027, 951, 836, 740, 691; ^1H NMR (600 MHz, $CDCl_3$) δ 2.01 (1.96H, brs, CH_2D), 3.82 (3H, s, Me), 4.09 (2H, s, CH_2), 6.93 (2H, d, J = 8.7 Hz, ArH), 7.21 (2H, t, J = 7.3 Hz), 7.29 (2H, d, J= 7.4 Hz, ArH), 7.37 (2H, d, J= 6.9 Hz, ArH), 7.56 (2H, d, J= 9.2 Hz, ArH); ^2H NMR (92 MHz, $CDCl_3$) δ 2.04 (brt, J= 2.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 7.8 (t, J= 20.4 Hz), 29.1 (t), 55.3 (q), 114.1 (d×2), 114.7 (s), 122.0 (s), 123.9 (s), 126.4 (d), 127.4 (d×2), 128.9 (d×2), 129.8 (d×2), 136.6 (s), 137.8 (d), 151.1 (s), 159.0 (s); MS *m/z* 311 (M^+), 202 (M^+-SPh). High resolution mass calcd for $C_{19}H_{17}DO_2S$: 311.1090, found *m/z* 311.1095.



13f

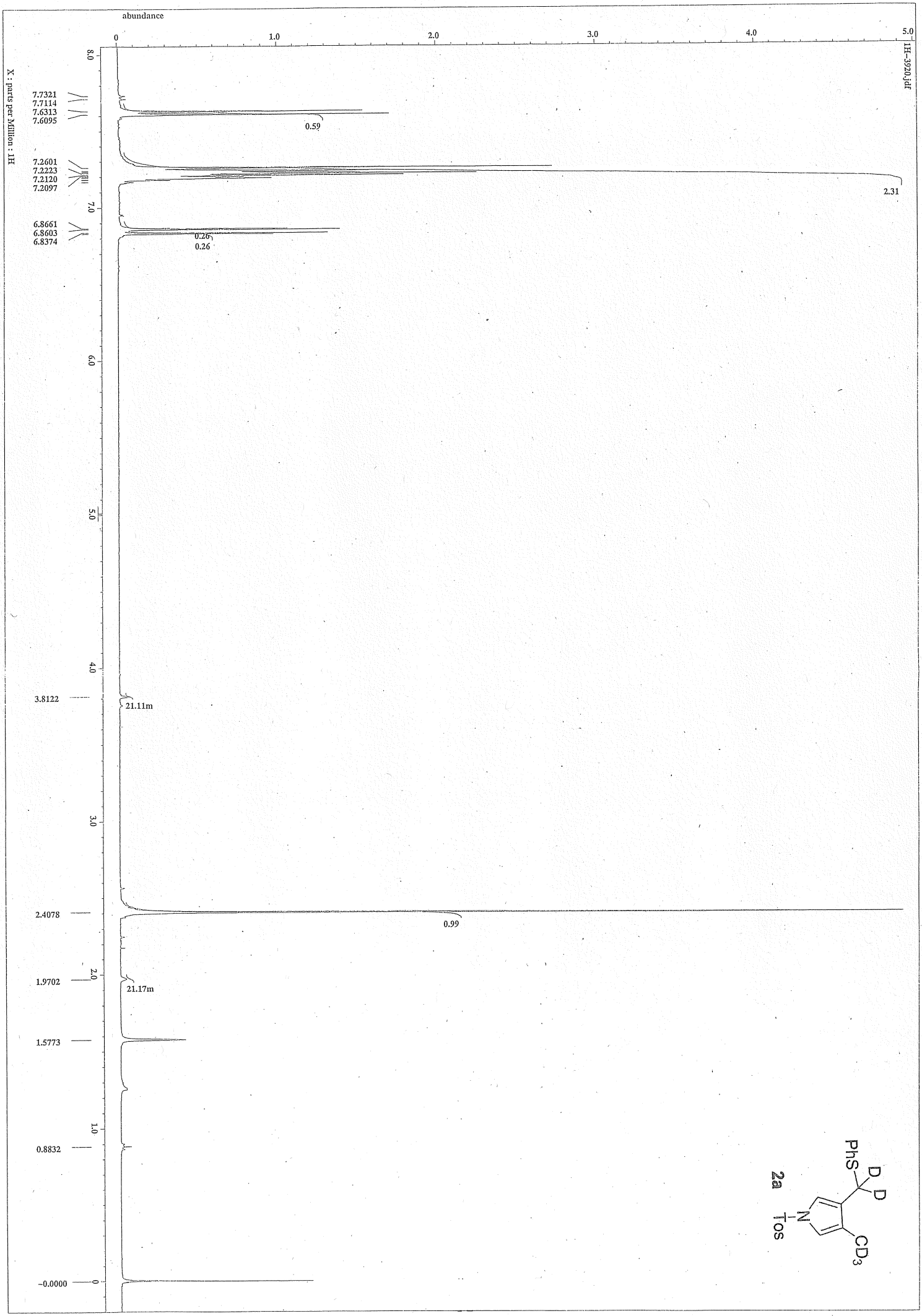
1-[4-(Methyl-d_1)-3-(phenylsulfanylmethyl)furan-2-yl]naphthalene (13f): Yield 56%, yellow oil, IR (KBr, cm^{-1}) 3056, 2925, 1769, 1710, 1583, 1509, 1480, 1439, 1388, 1340, 1253, 1232, 1176, 1135, 1102, 1090, 1067, 1024, 997, 936, 803, 778, 701, 691; ^1H NMR (600 MHz, $CDCl_3$) δ 2.17 (1. 96H, brs, CH_2D), 3.97 (2H, s, CH_2), 7.07-7.09 (3H, m, ArH), 7.18 (2H, dd, J = 2.0 and 6.2 Hz, ArH), 7.37 (1H, s, furyl H) , 7.42-7.50 (4H, m, ArH) , 7.86 (3H, dd, J = 2.0 and 5.5 Hz, ArH); ^2H NMR (92 MHz, $CDCl_3$) δ 2.22 (brt, J = 2.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 8.3 (t, J = 20.2 Hz), 29.0 (t), 118.5 (s), 125.1 (d), 126.0 (d), 126.1 (d), 126.3 (d), 126.4 (d), 128.0 (d), 128.0 (s), 128.2 (d), 128.7 (d×2), 129.2 (d), 130.1 (d×2), 132.1 (s), 133.8 (s), 136.1 (s), 139.1 (d), 151.2 (s); MS *m/z* 331 (M^+), 222 (M^+-SPh). High resolution mass could not be measured because the molecular ion peak m/z 331 was observed at the same chemical shift as PFK.



13g

2-[4-(Methyl-d_1)-3-(phenylsulfanylmethyl)furan-2-yl]thiophene (13g): Yield 69%, yellow oil, IR (KBr, cm^{-1}) 3106, 3075, 2926, 2853, 1772, 1655, 1583, 1480, 1439, 1442, 1353, 1238, 1050, 1023, 950, 849, 741, 692; ^1H NMR (600 MHz, $CDCl_3$) δ 1.96 (1.76H, brs, CH_2D), 4.11 (2H, brs, CH_2), 7.03 (1H, dd, J = 1.4 and 3.4 Hz, ArH), 7.15 (1H, brs, ArH), 7.19-7.28 (5H, m, ArH), 7.38 (2H, d, J = 6.9 Hz, ArH); ^2H NMR (92 MHz, $CDCl_3$) δ 1.99 (brt, J = 2.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 7.8 (t, J = 20.2 Hz), 29.1 (t), 116.2 (s), 122.2 (s), 123.8 (d), 124.8 (d), 126.7 (d),

127.4 (d), 128.9 (d×2), 130.8 (d×2), 132.8 (s), 136.1 (s), 138.1 (d), 146.7 (s); MS *m/z* 287 (M^+), 178 (M^+-SPh). High resolution mass calcd for $C_{16}H_{13}DOS_2$: 287.0549, found *m/z* 287.0539.


abundance
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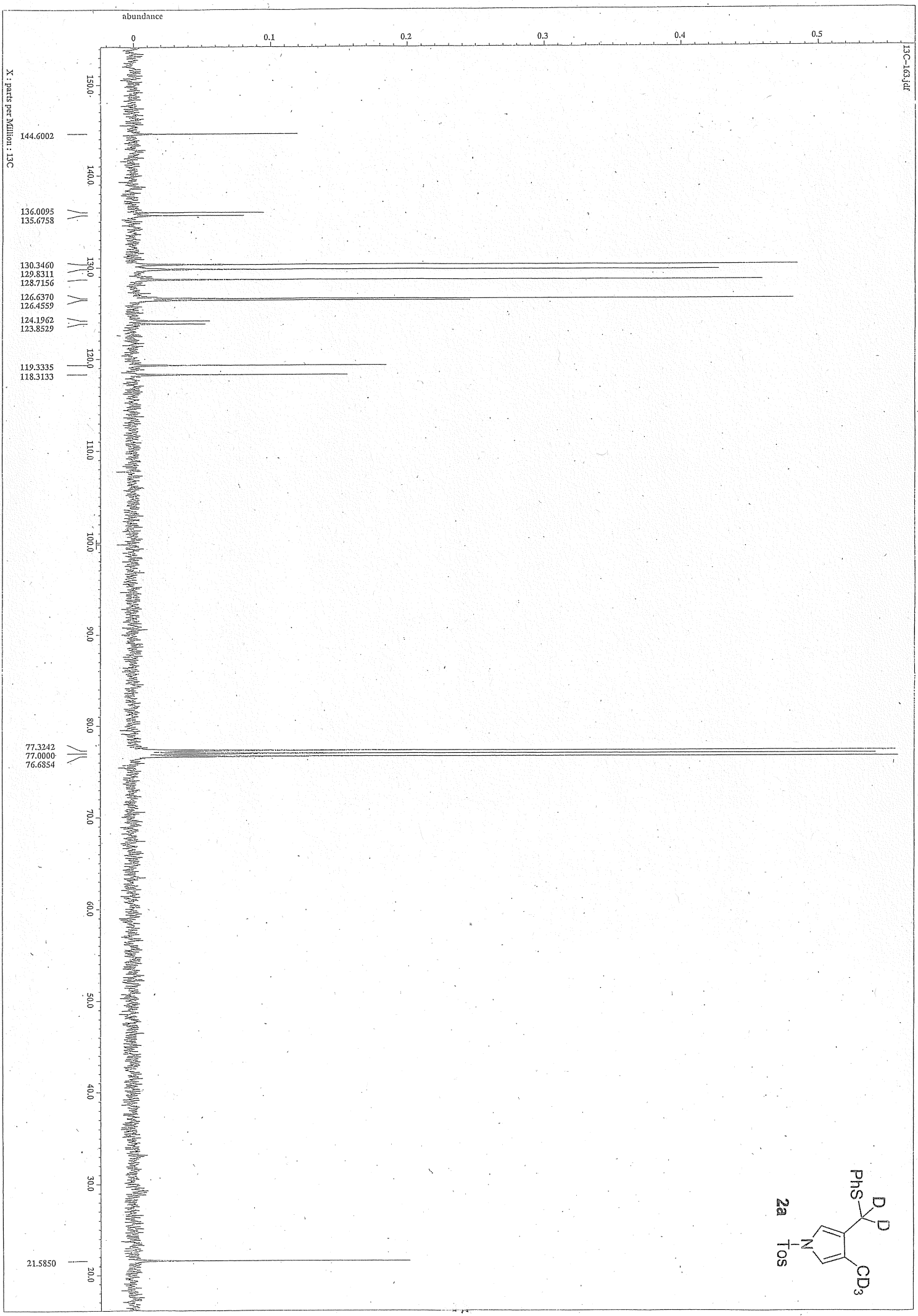
2.0
3.0
4.0
5.0
1H-3920.jdf
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.7321
7.7114
7.6313
7.6095
0.59
7.2601
7.2223
7.2120
7.2097
2.31
6.8661
6.8603
6.8374
0.26
0.26
3.8122
21.11m
2.4078
0.99
1.9702
21.17m
1.5773
0.8832
-0.0000
2a
PhS
D
D
N
Tos
CD3


abundance
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0.1
0.2
0.3
0.4
0.5
13C-163.jdf
X : parts per Million : 13C
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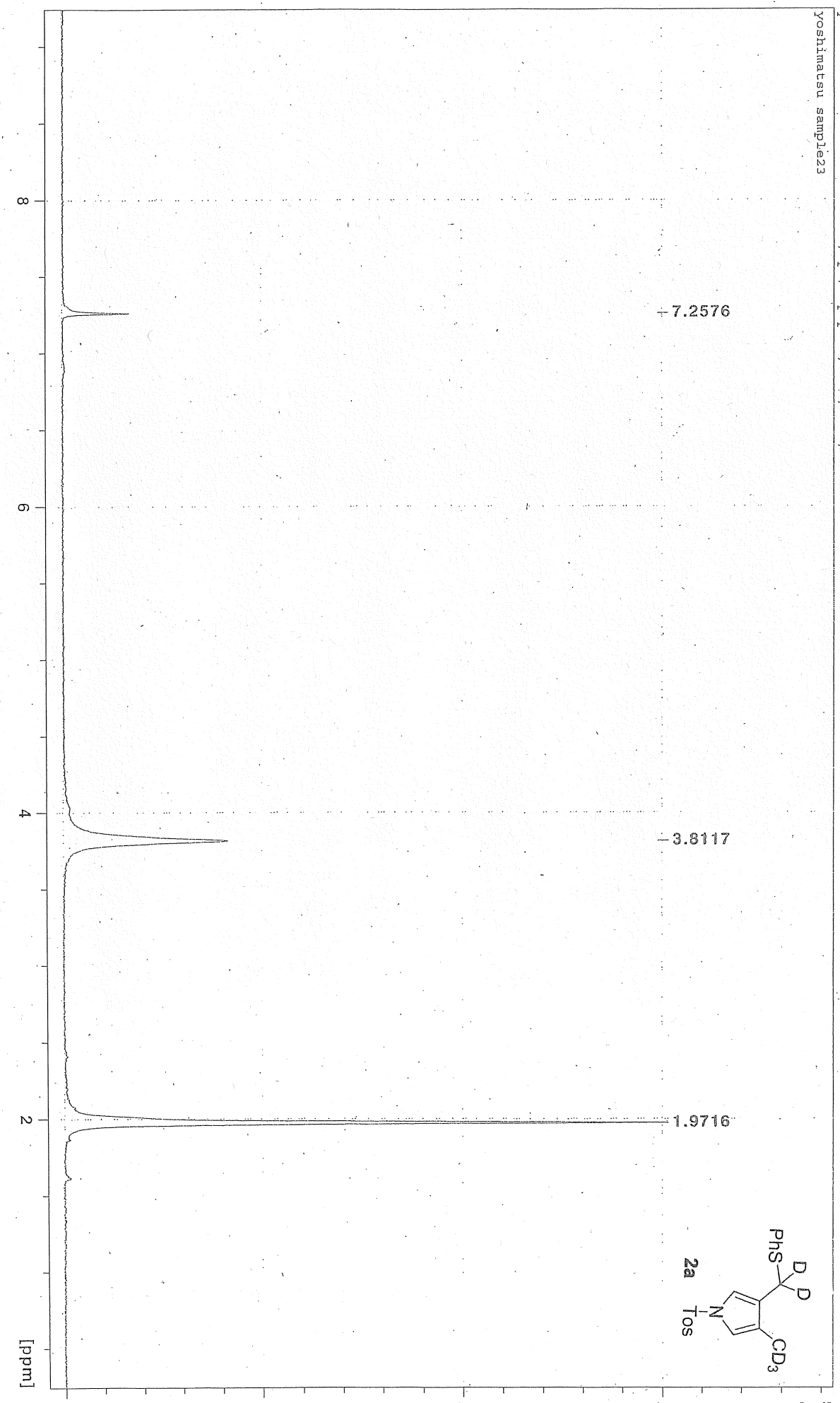
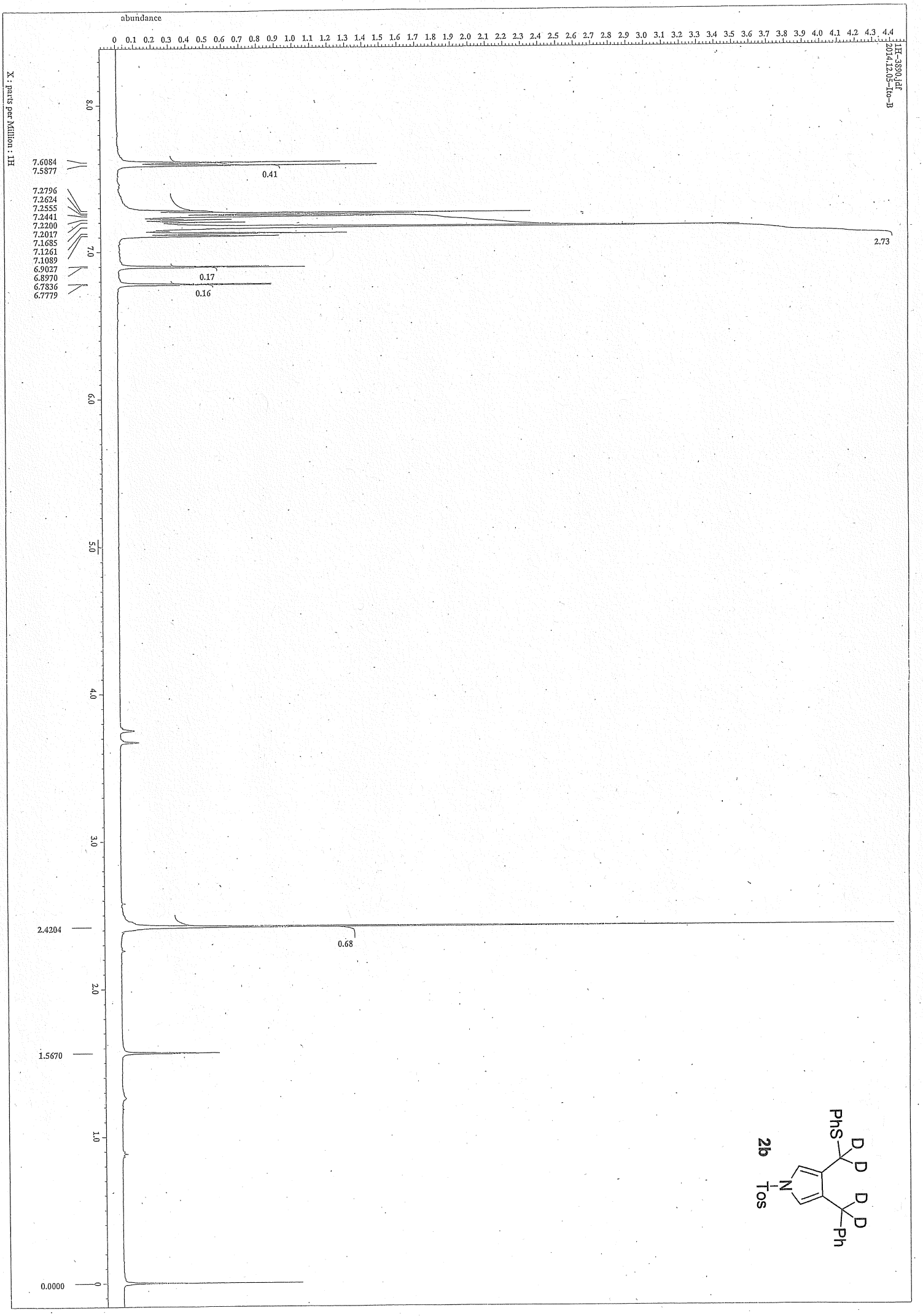
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
144.6002
136.0095
135.6758
130.3460
129.8311
128.7156
126.6370
126.4559
124.1962
123.8529
119.3335
118.3133
77.3242
77.0000
76.6854
21.5850
D
D
PhS
N
Tos
CD3
2a


yoshimatsu20141212d 232 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample23
7.2576
3.8117
1.9716
PhS
D D
N
Tos
CD3
2a
8
6
4
2
[ppm]
0
5
10
15
[rel]


abundance
X : parts per Million : 1H
1H-3890.jdf
2014.12.05-1to-B
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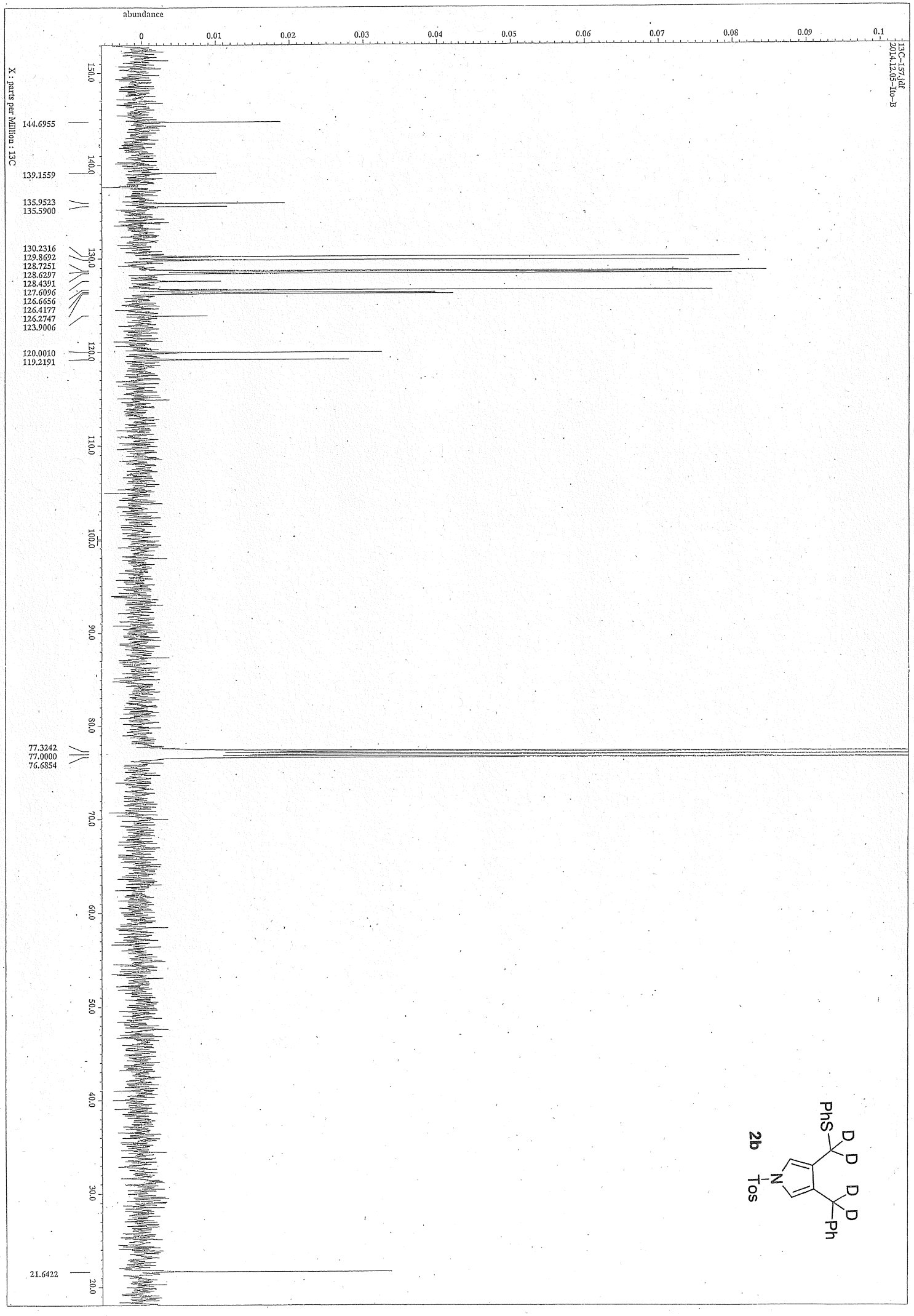
7.5877
7.2796
7.2624
7.2555
7.2441
7.2200
7.2017
7.1685
7.1261
7.1089
6.9027
6.8970
6.7836
6.7779
2.4204
1.5670
0.0000
0.41
2.73
0.17
0.16
0.68
PhS
D D
D D
Ph
N
Tos
2b


abundance
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0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
13C-157.jdf
2014.12.05-Ito-B
X : parts per Million : 13C
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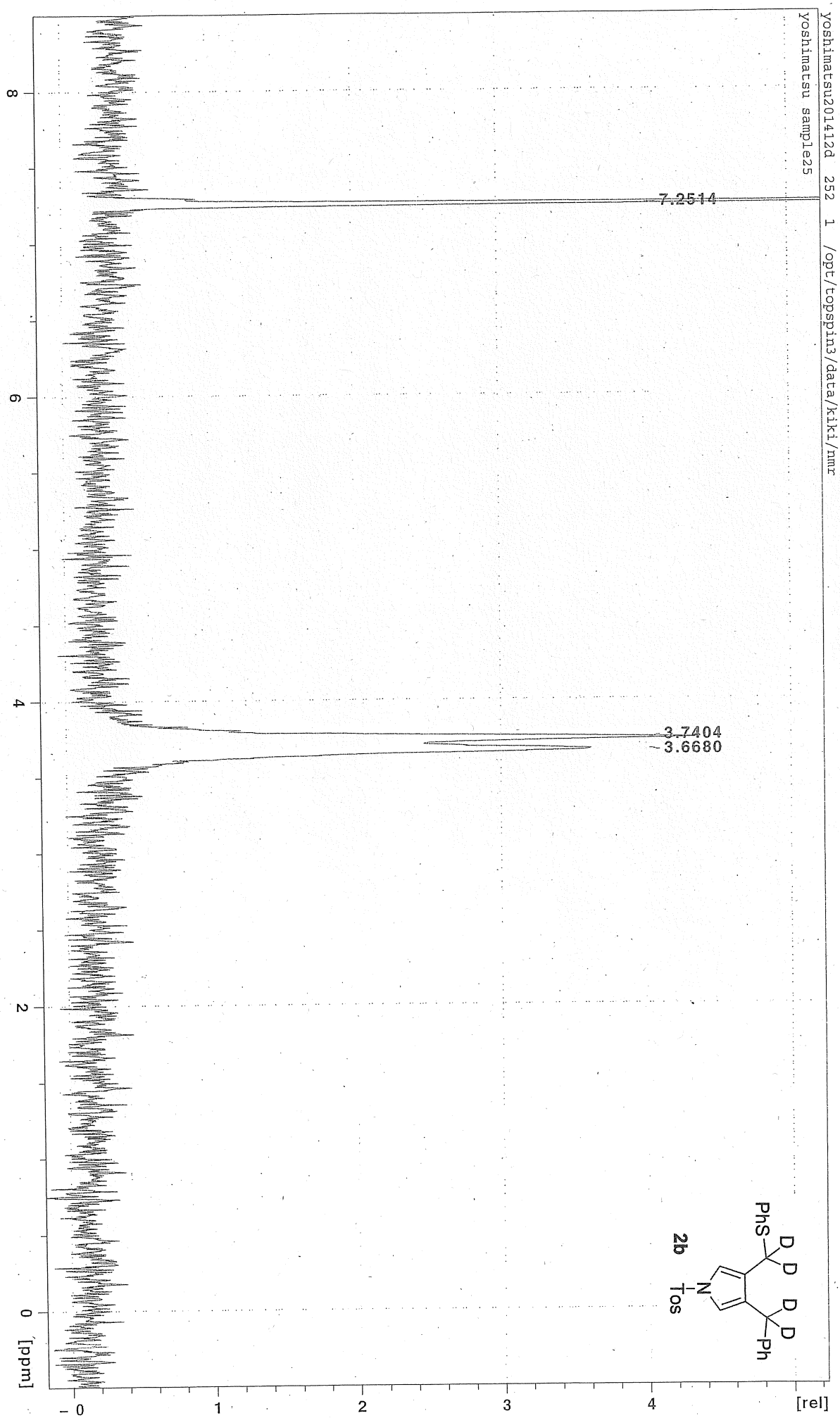
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
144.6955
139.1559
135.9523
135.5900
130.2316
129.8692
128.7251
128.6297
128.4391
127.6096
126.6656
126.4177
126.2747
123.9006
120.0010
119.2191
77.3242
77.0000
76.6854
21.6422
PhS
D D
D D
Ph
N
Tos
2b


yoshimatsu201412d 252 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample25
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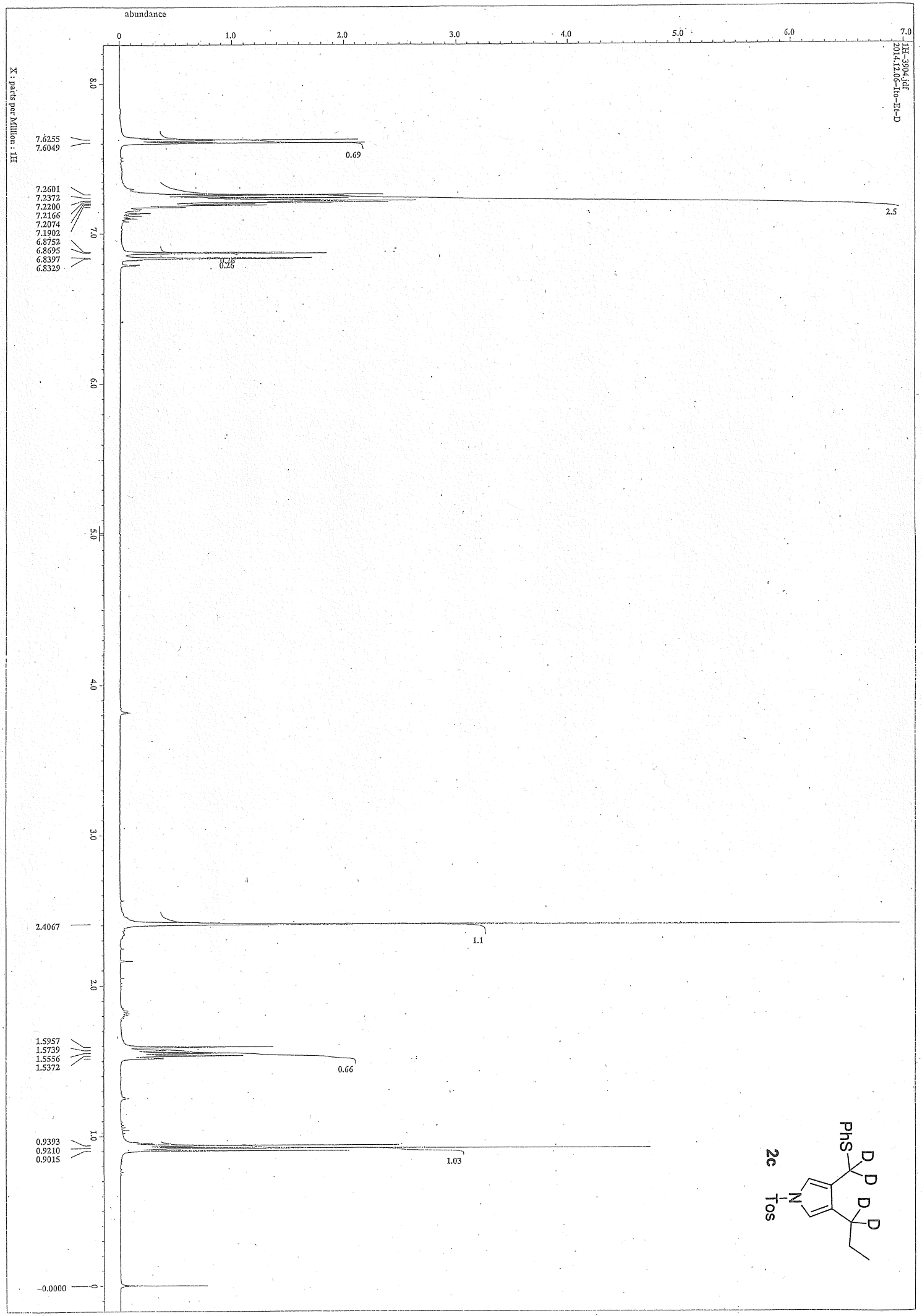
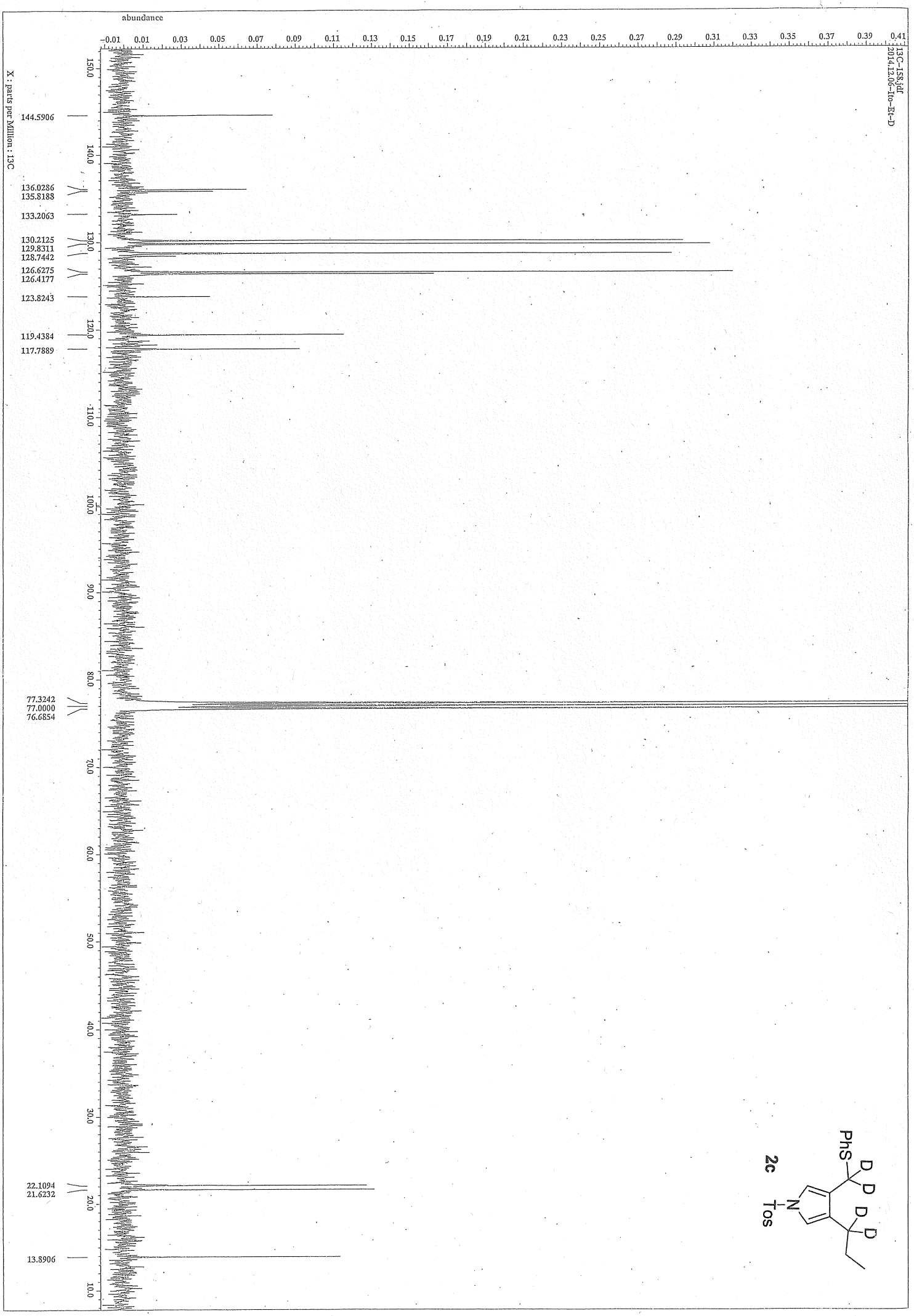
3.6680
8
6
4
2
0 [ppm]
– 0
1
2
3
4
[rel]
PhS
D D
D D
Ph
N
Tos
2b


abundance
X : parts per Million : 1H
JH-3904.jdf
2014.12.06-Ito-1D-D
7.6255
7.6049
7.2601
7.2372
7.2200
7.2166
7.2074
7.1902
6.8752
6.8695
6.8397
6.8329
2.4067
1.5957
1.5739
1.5556
1.5372
0.9393
0.9210
0.9015
−0.0000
0.69
2.5
0.26
0.26
1.1
0.66
1.03
2c
PhS
D
D
D
D
N
Tos


abundance
X : parts per Million : 13C
13C-158.jdf
2014.12.06-Ito-Et-D
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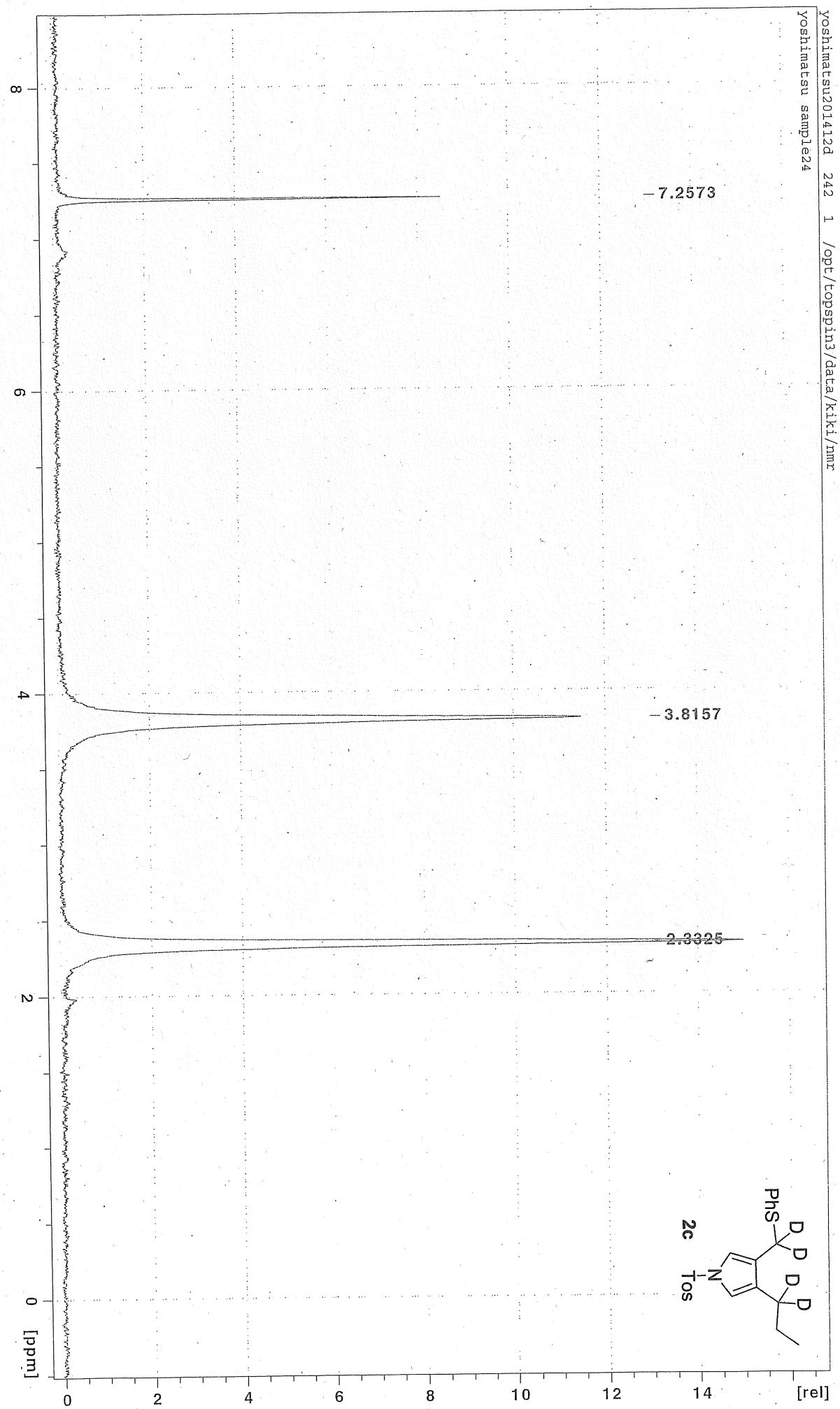
136.0286
135.8188
133.2063
130.2125
129.8311
128.7442
126.6275
126.4177
123.8243
119.4384
117.7889
77.3242
77.0000
76.6854
22.1094
21.6232
13.8906
PhS
D
D
D
D
N
Tos
2c


yoshimatsu201412d 242 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample24
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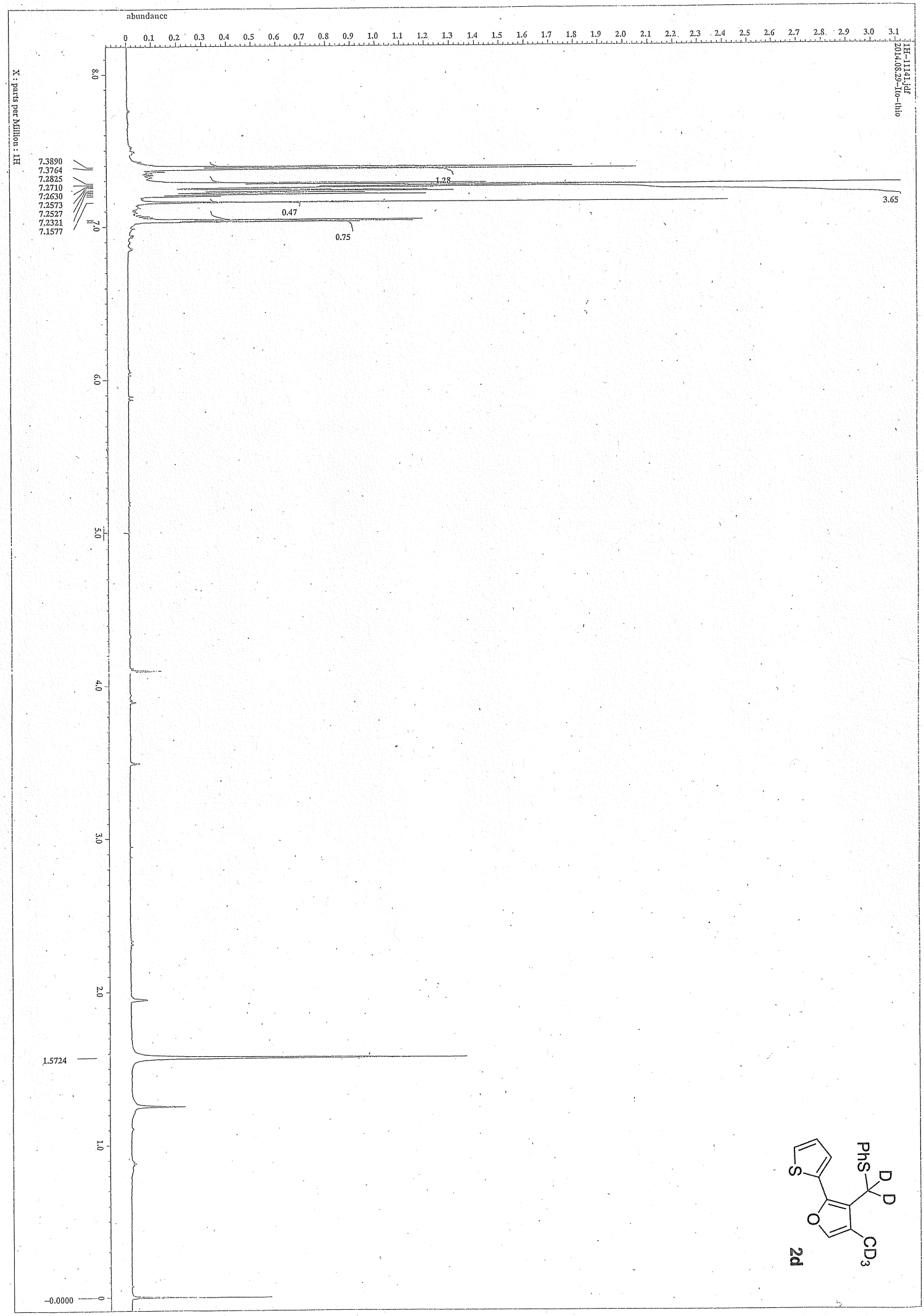
2.3325
PhS
D
D
D
D
N
Tos
2c
[ppm]
[rel]


abundance
X : parts per Million : 1H
1H-1114.jdf
2014.08.29-Ito-thio
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7.3764
7.2825
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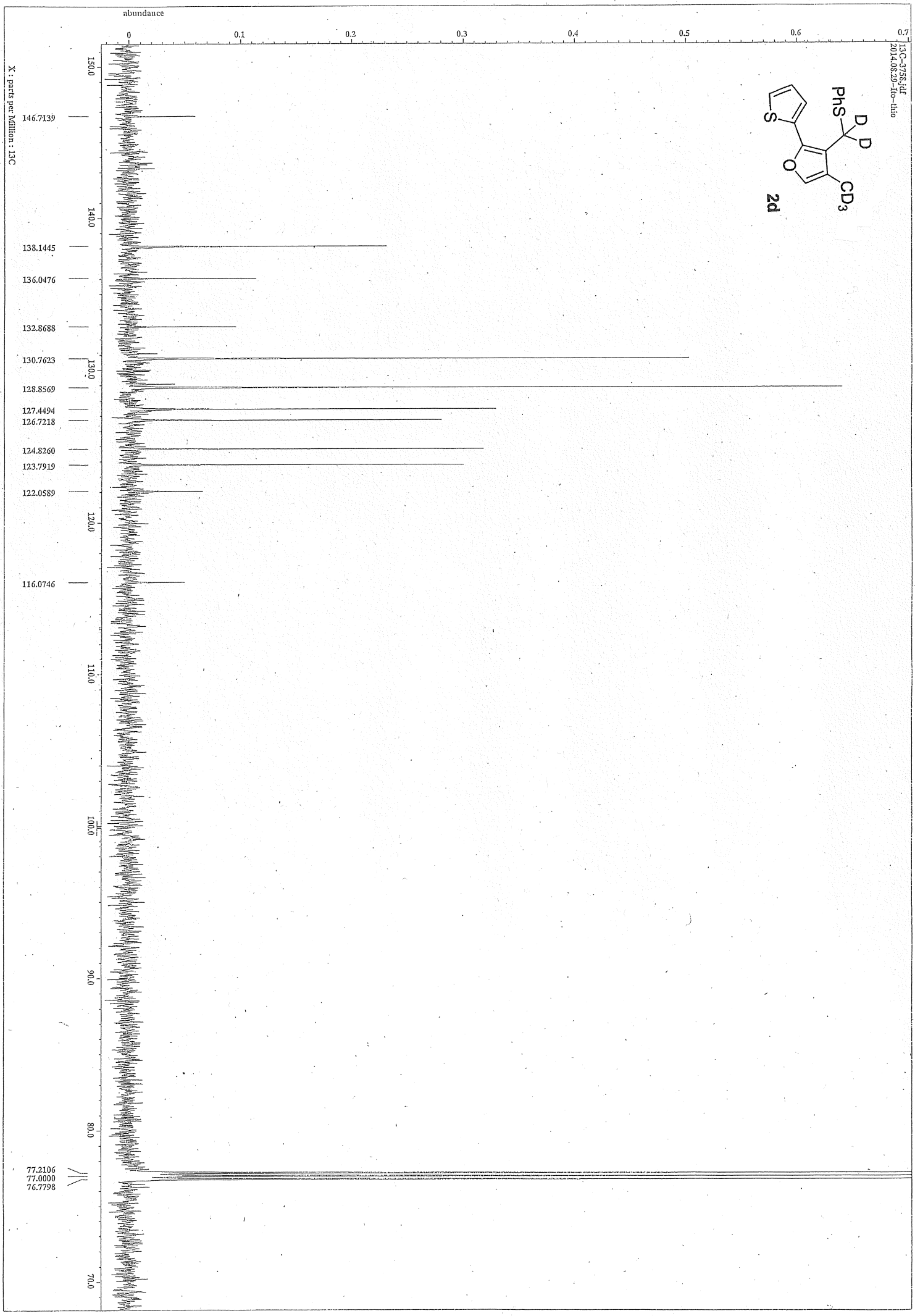
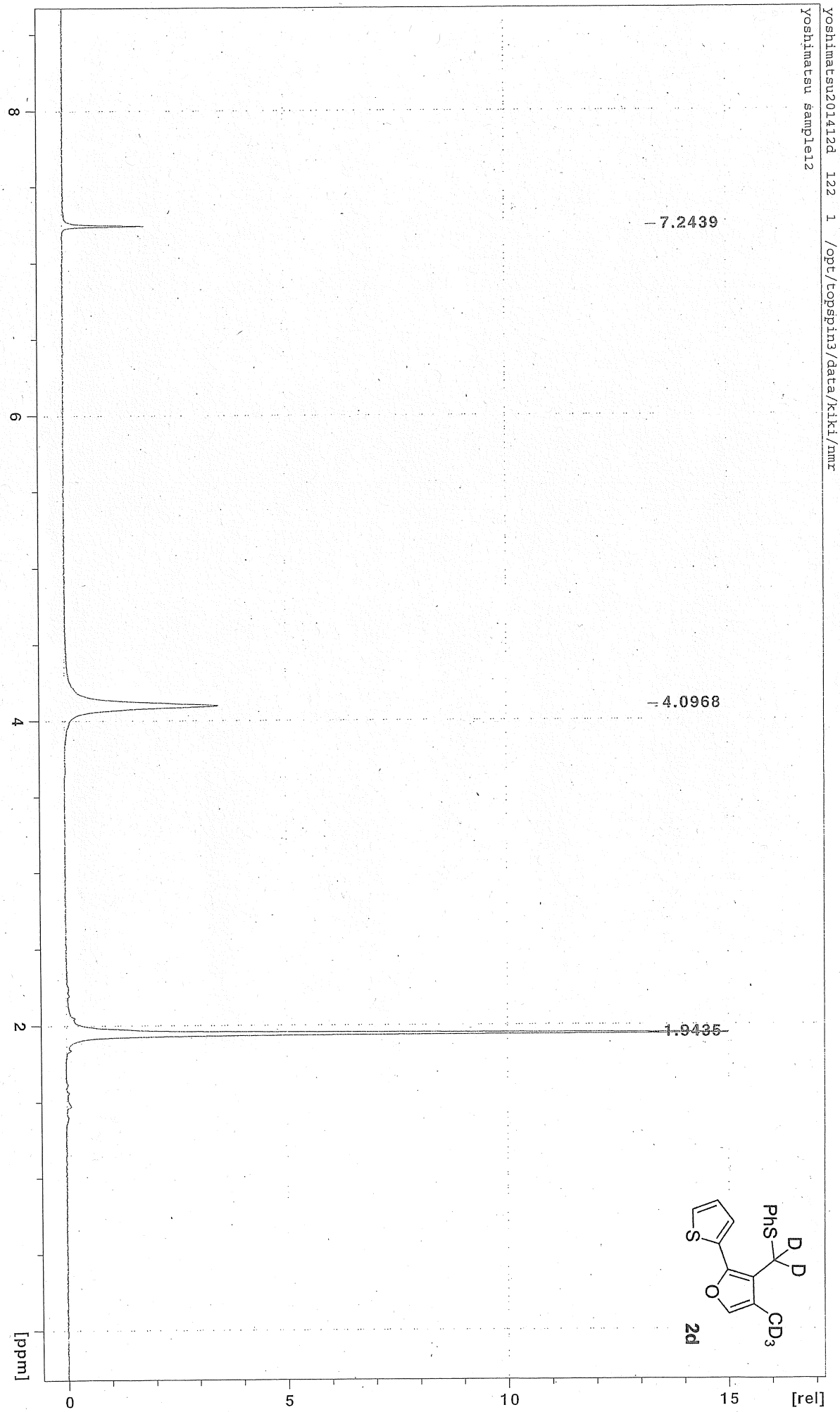
7.2630
7.2573
7.2527
7.2321
7.1577
1.28
3.65
0.47
0.75
1.5724
-0.0000
S
O
PhS
D
D
CD3
2d


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
X : parts per Million : 13C
13C-3758.jdf
2014.08.29-ito-thio
146.7139
138.1445
136.0476
132.8688
130.7623
128.8569
127.4494
126.7218
124.8260
123.7919
122.0589
116.0746
77.2106
77.0000
76.7798
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
PhS
D
D
S
O
CD3
2d


yoshimatsu20141124d 122 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample12
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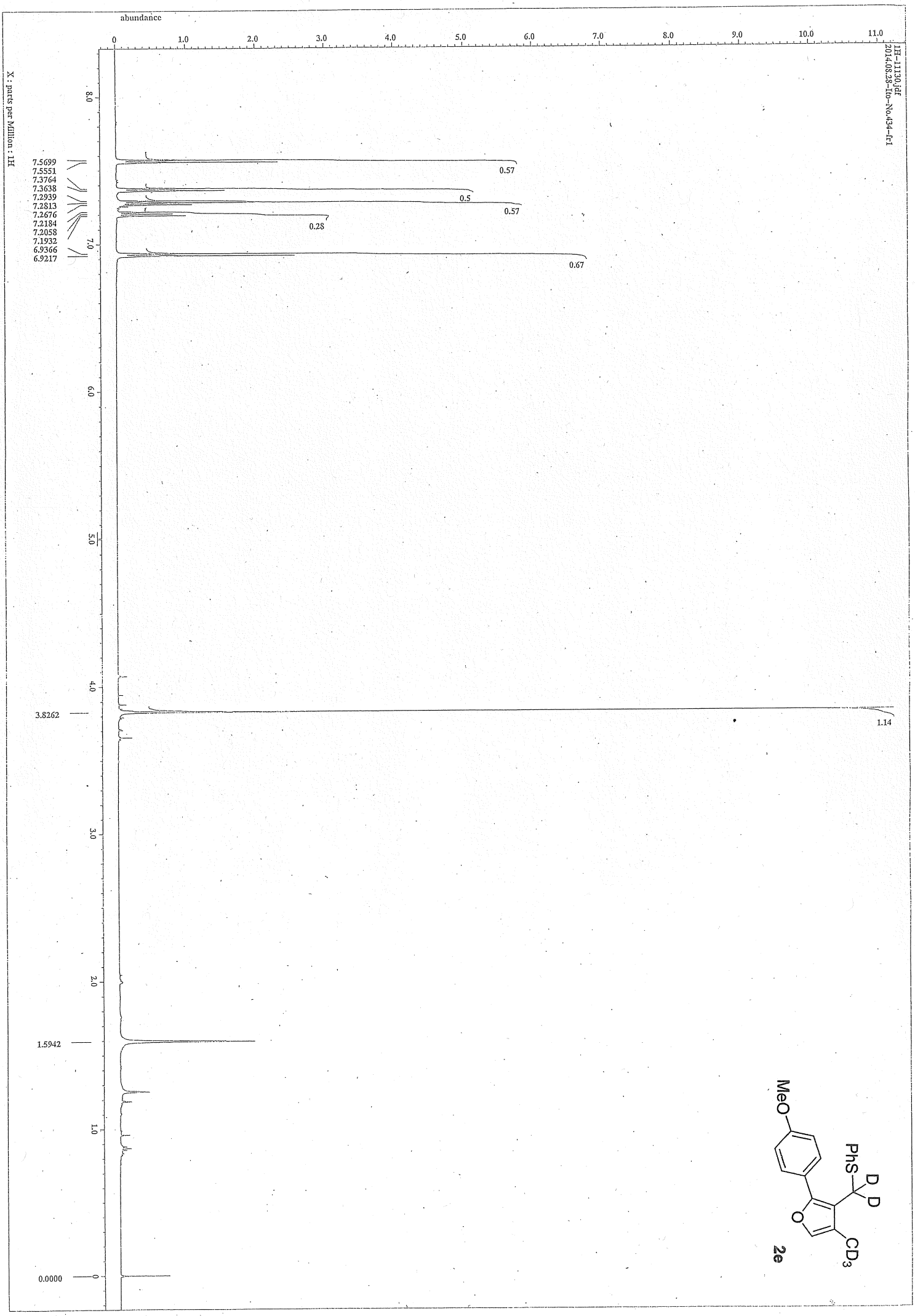
4.0968
1.9435
8
6
4
2
[ppm]
0
5
10
15
[rel]
S
O
PhS
D
D
CD3
2d


abundance
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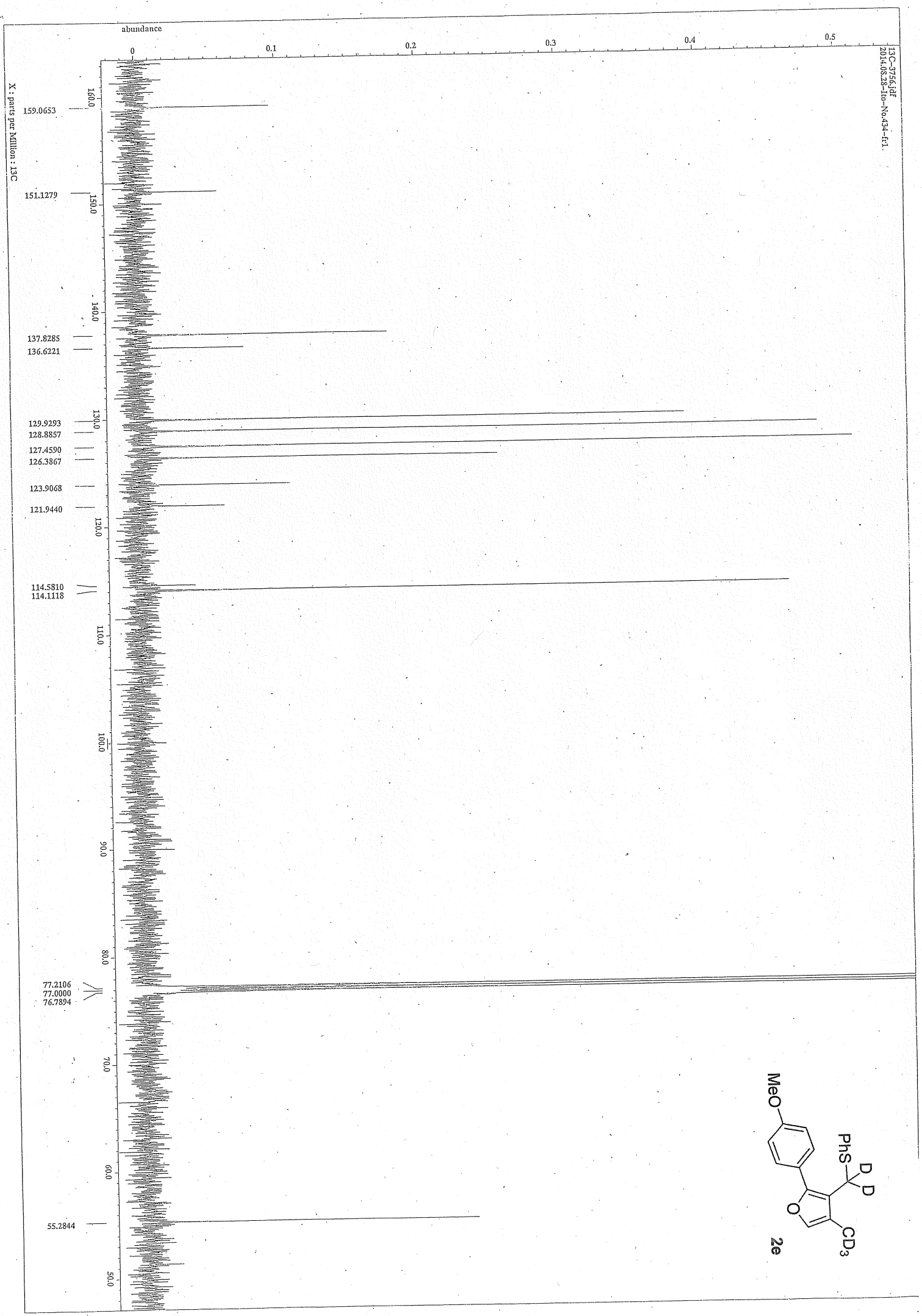
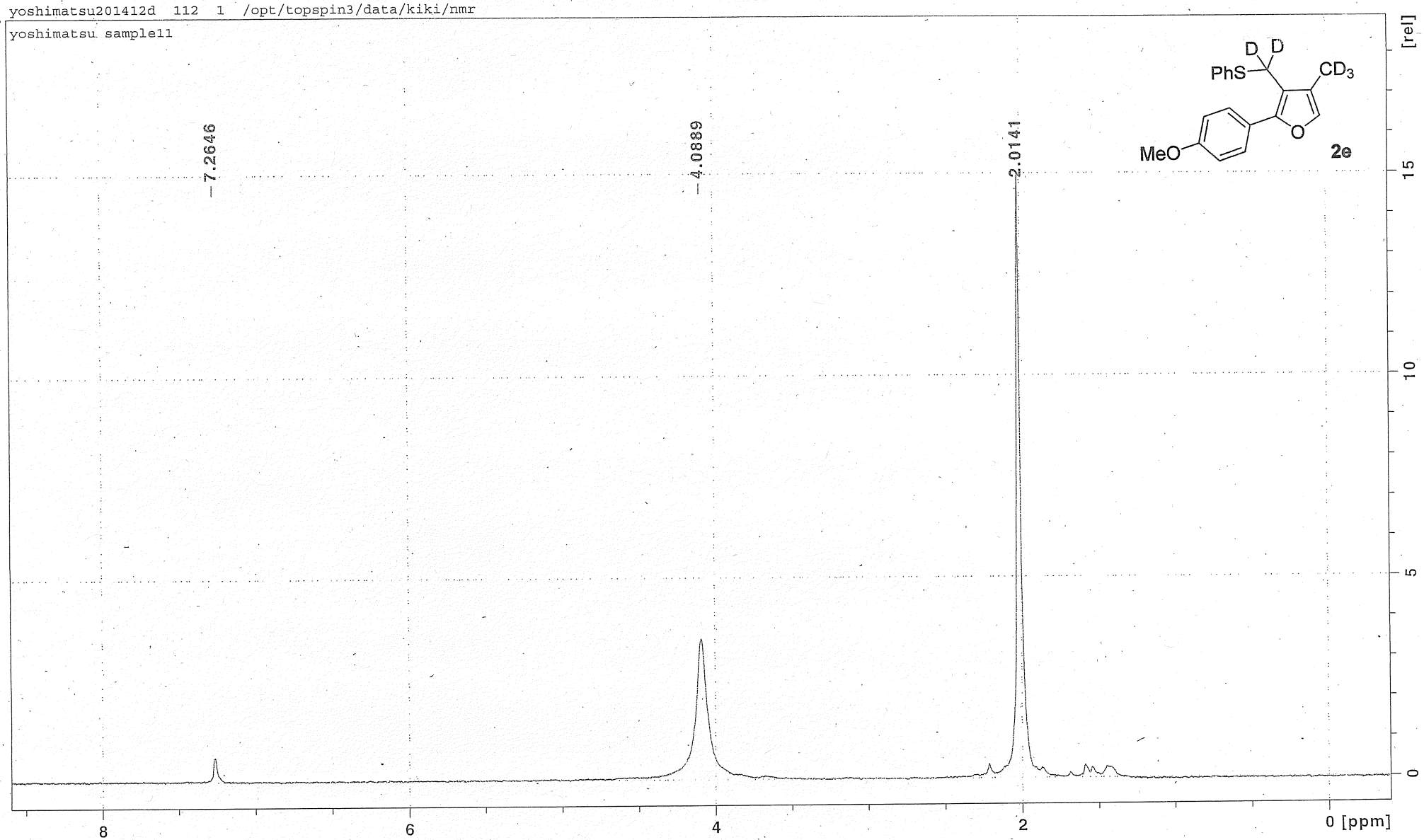
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
1H-11130.jdf
2014.08.28-Ito-No.434-fr1
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.5699
7.5551
7.3764
7.3638
7.2939
7.2813
7.2676
7.2184
7.2058
7.1932
6.9366
6.9217
3.8262
1.5942
0.0000
0.57
0.5
0.57
0.28
0.67
1.14
MeO
PhS
D D
O
CD3
2e


abundance
0
0.1
0.2
0.3
0.4
0.5
13C-3756.jdf
2014.08.28-1to-No.434-fr1.
X : parts per Million : 13C
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
159.0653
151.1279
137.8285
136.6221
129.9293
128.8857
127.4590
126.3867
123.9068
121.9440
114.5810
114.1118
77.2106
77.0000
76.7894
55.2844
MeO
PhS
D
D
O
CD3
2e


yoshimatsu201412d 112 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample11
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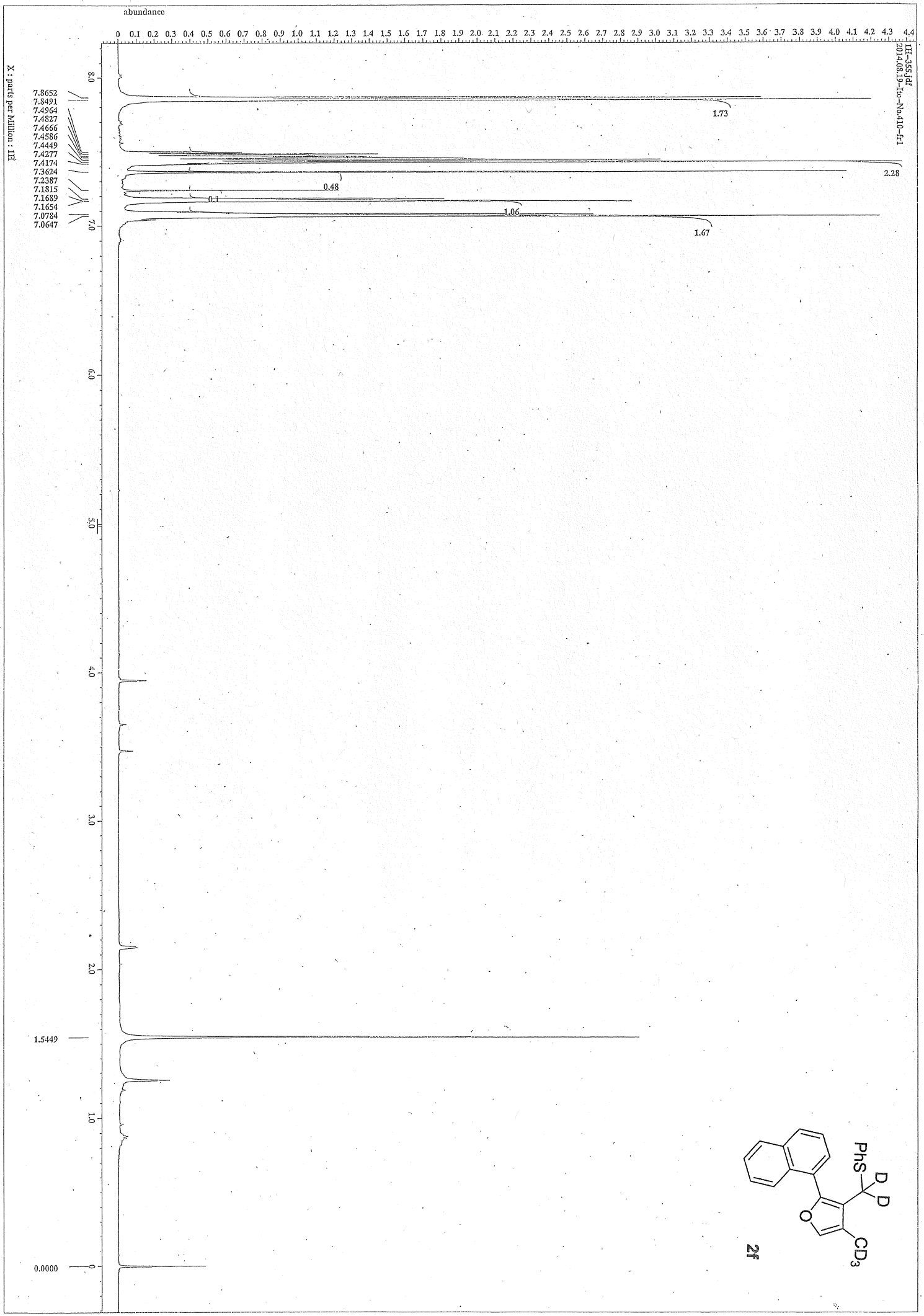
2.0141
D D
PhS
CD3
MeO
O
2e
[rel]
15
10
5
0
8
6
4
2
0 [ppm]


abundance
X : parts per Million : 1H
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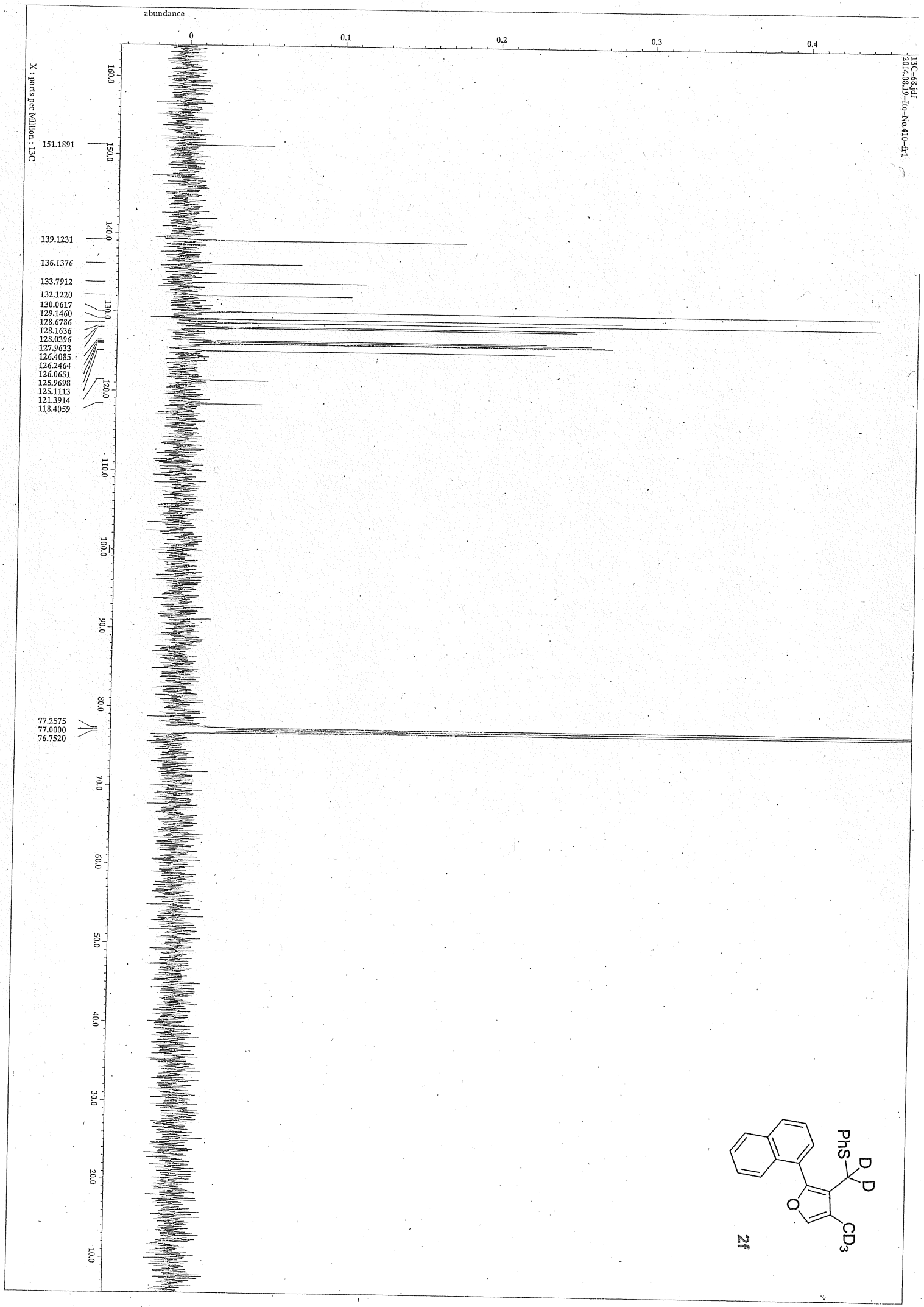
7.4964
7.4827
7.4666
7.4586
7.4449
7.4277
7.4174
7.3624
7.2387
7.1815
7.1689
7.1654
7.0784
7.0647
1.5449
0.0000
1.73
2.28
0.48
0.1
1.06
1.67
2H-355.jdf
2014.08.19-Iu-No.410-fr1
D D
PhS
O
CD3
2f


abundance
0
0.1
0.2
0.3
0.4
X : parts per Million : 13C
13C-68.jdf
2014.08.19-Ito-No.410-fr1
151.1891
139.1231
136.1376
133.7912
132.1220
130.0617
129.1460
128.6786
128.1636
128.0396
127.9633
126.4085
126.2464
126.0651
125.9698
125.1113
121.3914
118.4059
77.2575
77.0000
76.7520
160.0
150.0
140.0
130.0
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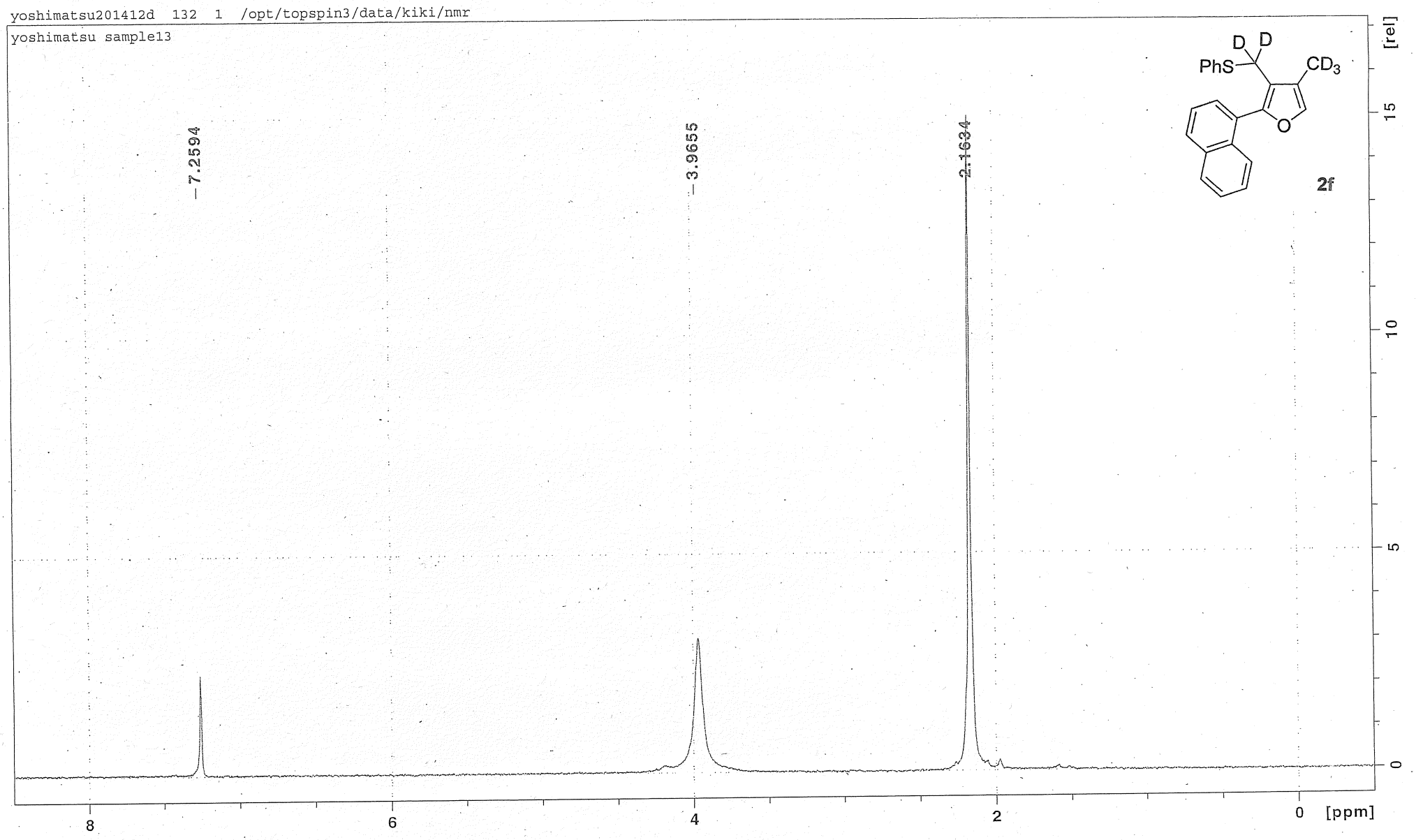
20.0
10.0
PhS
D D
O
CD3
2f


yoshimatsu201412d 132 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample13
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3.9655
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D D
PhS
CD3
O
2f
[rel]
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5
0
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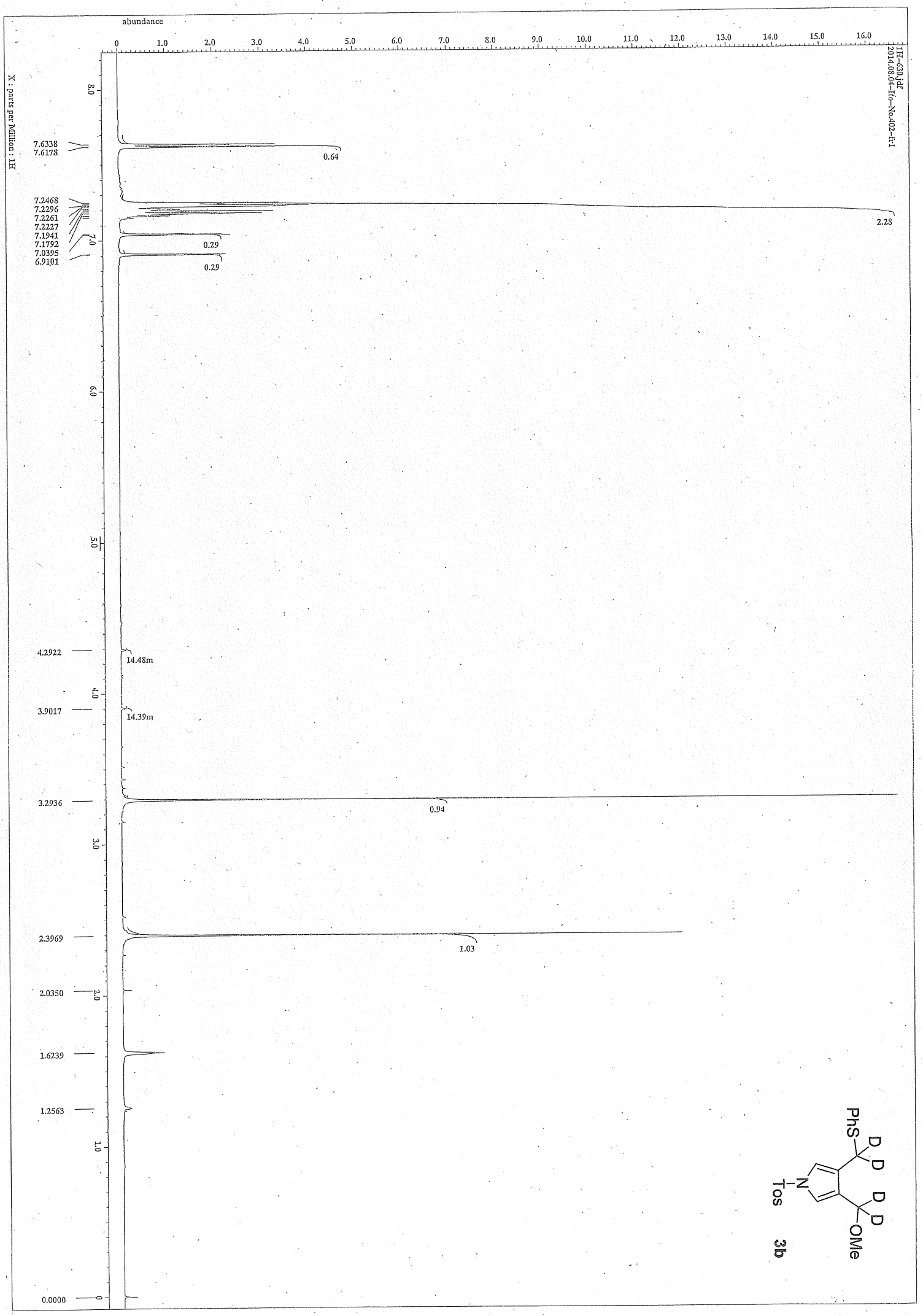
6
4
2
0
[ppm]


abundance
X : parts per Million : H
1H-630.idf
2014.08.04-Ito-No.402-fr1
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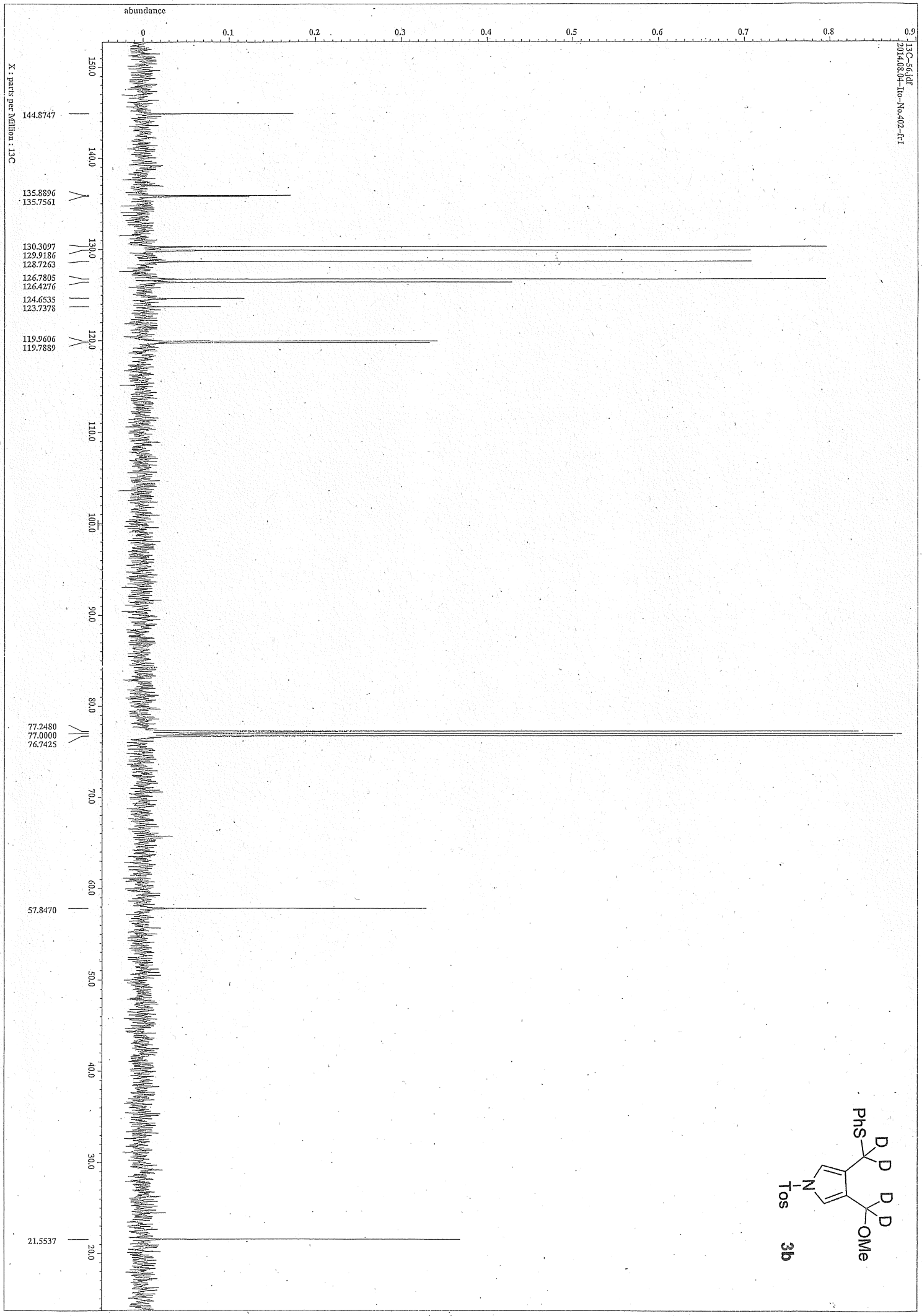
7.2468
7.2296
7.2261
7.2227
7.1941
7.1792
7.0395
6.9101
0.29
0.29
2.28
4.2922
14.48m
3.9017
14.39m
3.2936
0.94
2.3969
1.03
2.0350
1.6239
1.2563
0.0000
PhS
D D
N
Tos
D D
OMe
3b


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
13C-56.jdf
2014.08.04-Ito-No.402-fr1
X : parts per Million : 13C
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
144.8747
135.8896
135.7561
130.3097
129.9186
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126.7805
126.4276
124.6535
123.7378
119.9606
119.7889
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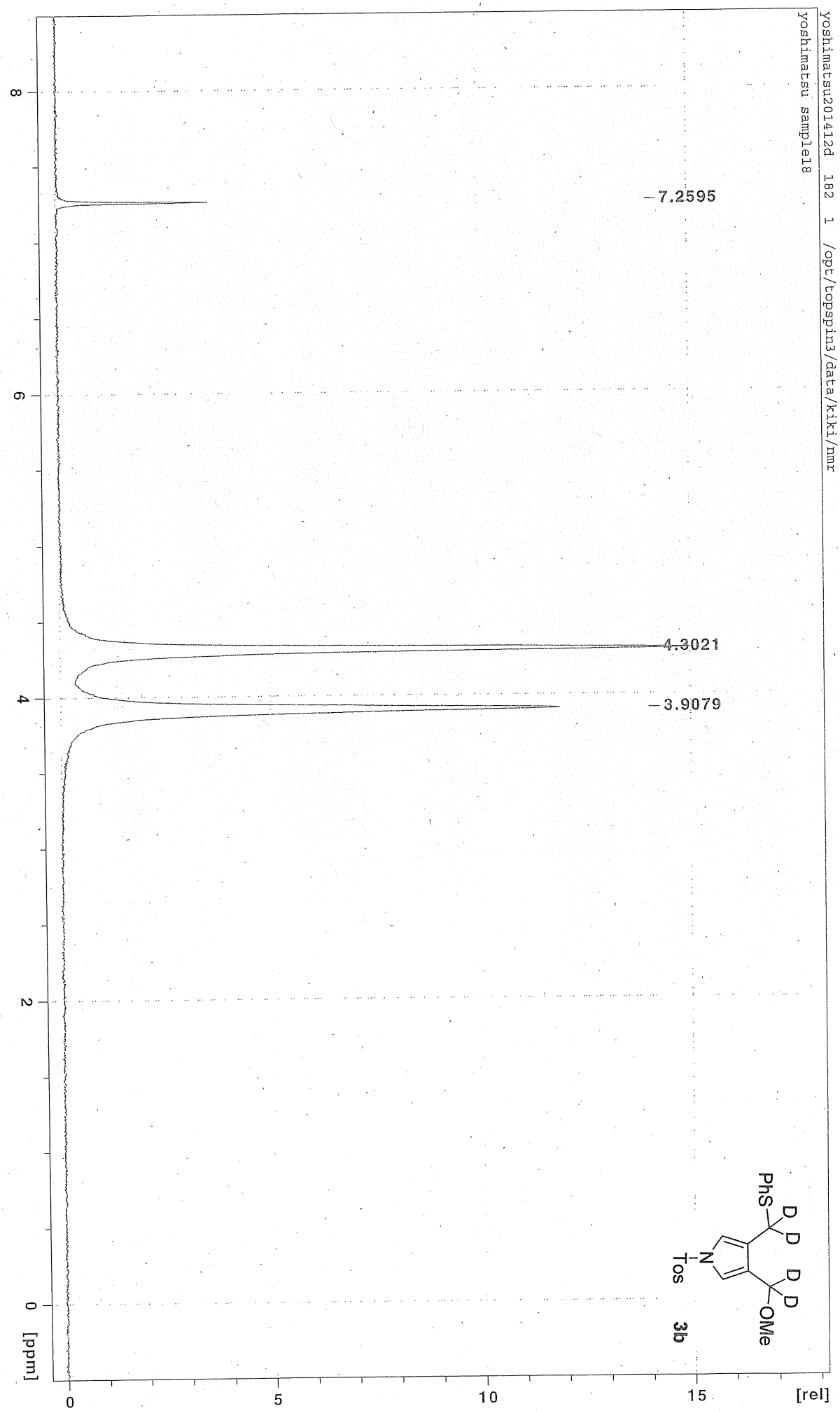
77.0000
76.7425
57.8470
21.5537
PhS
D D
D D
OMe
N
Tos
3b


yoshimatsu201412d 182 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample18
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8
6
4
2
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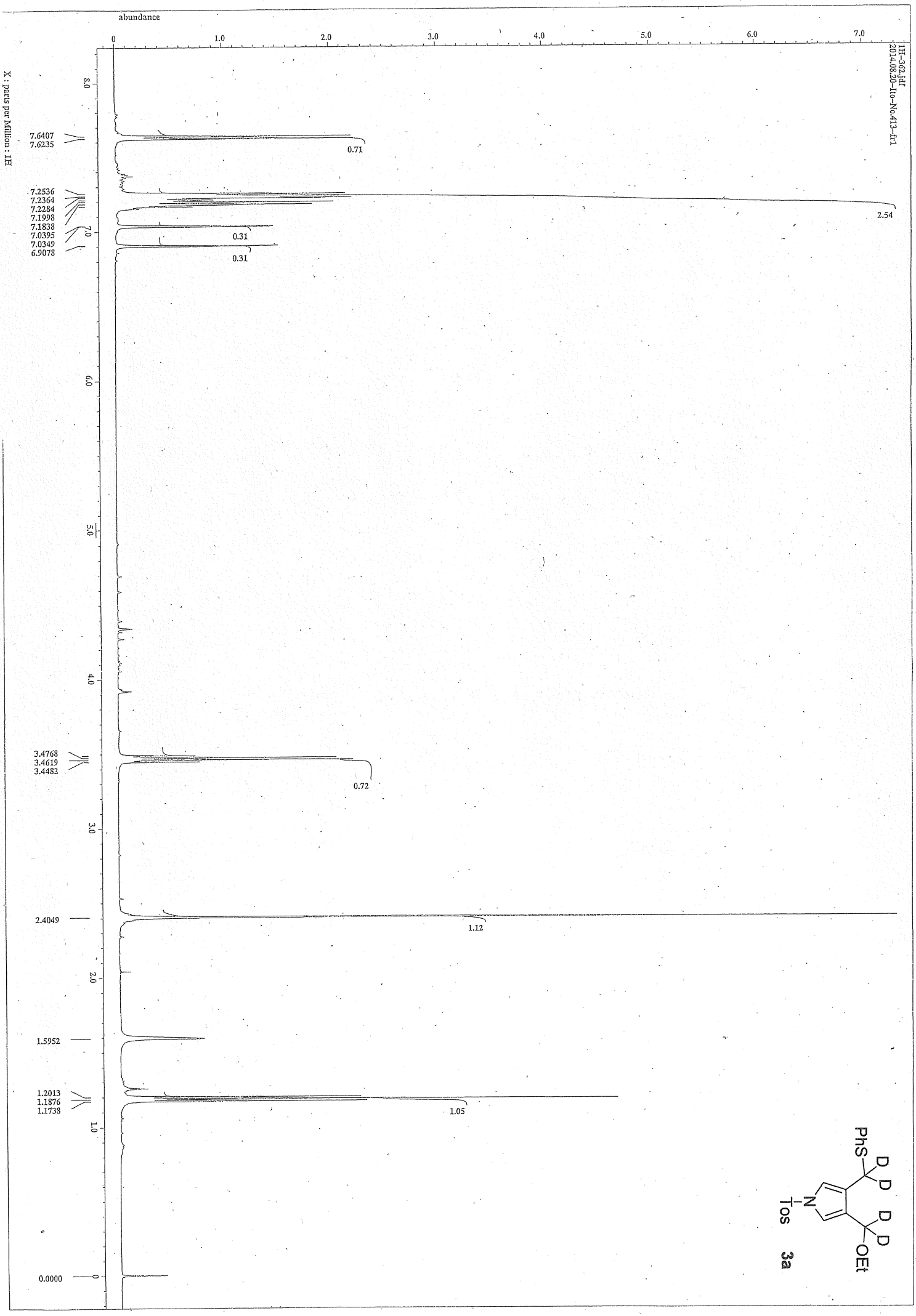
[ppm]
0
5
10
15
[rel]
PhS
D D
D D
OMe
N
Tos
3b


abundance
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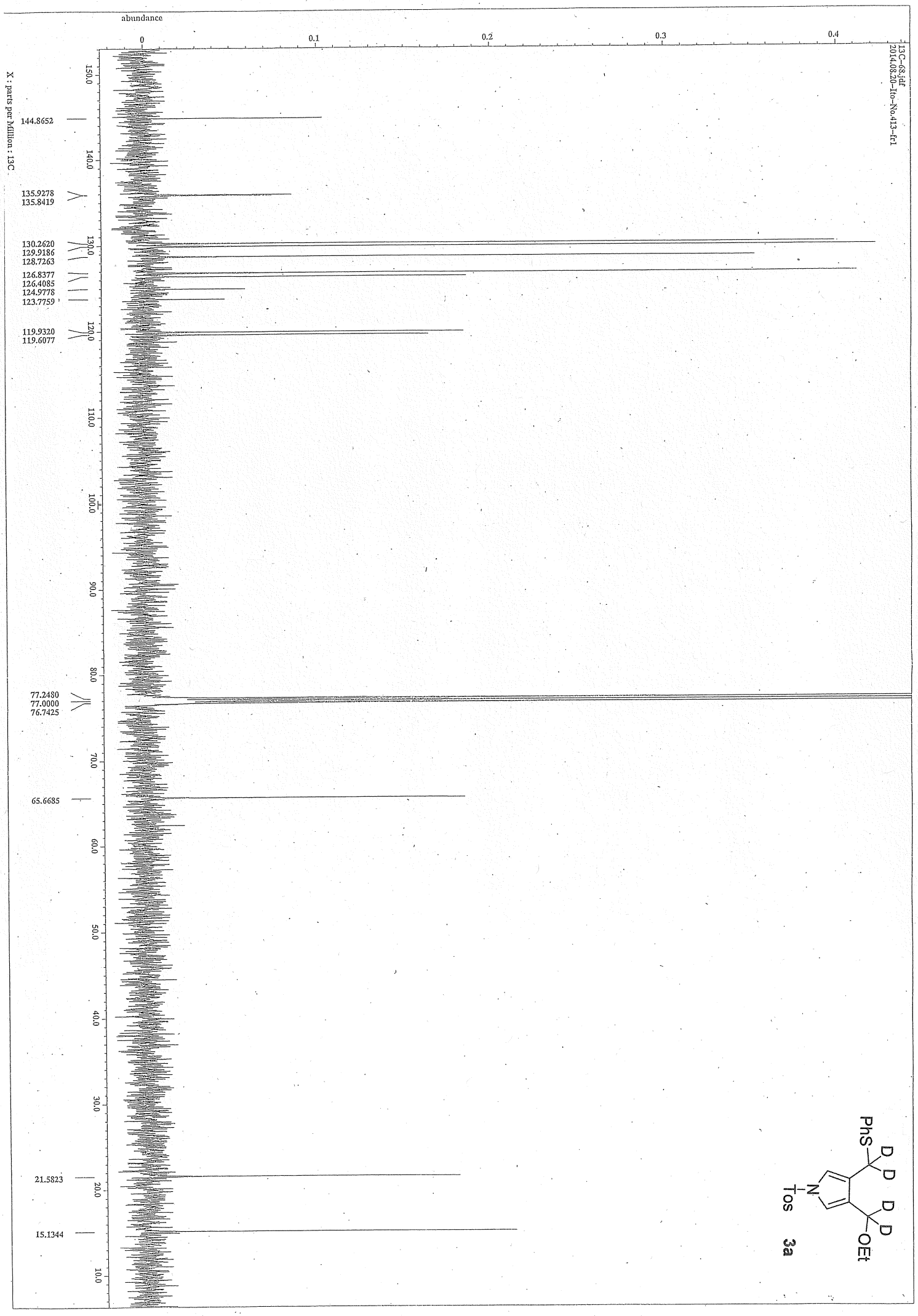
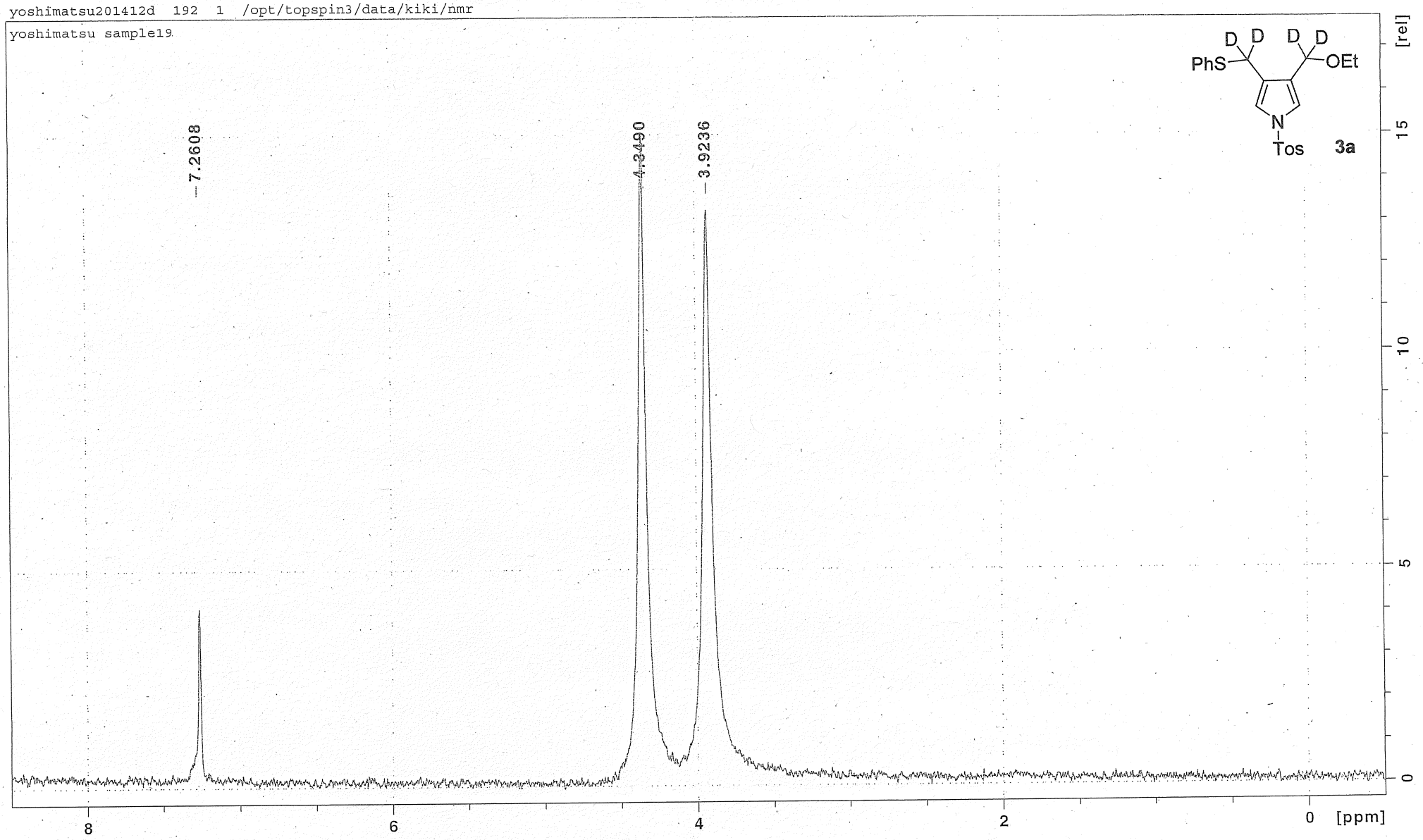
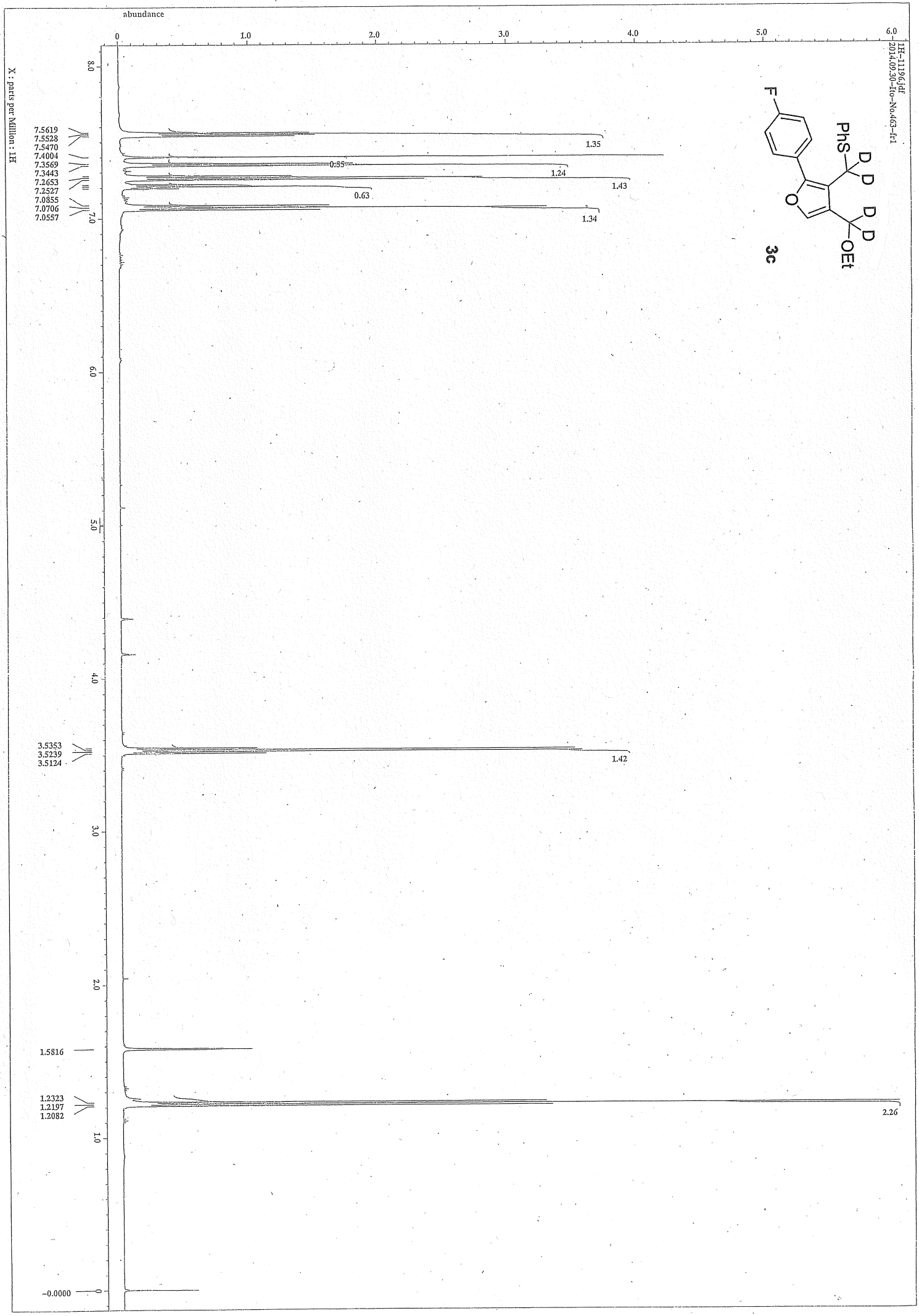
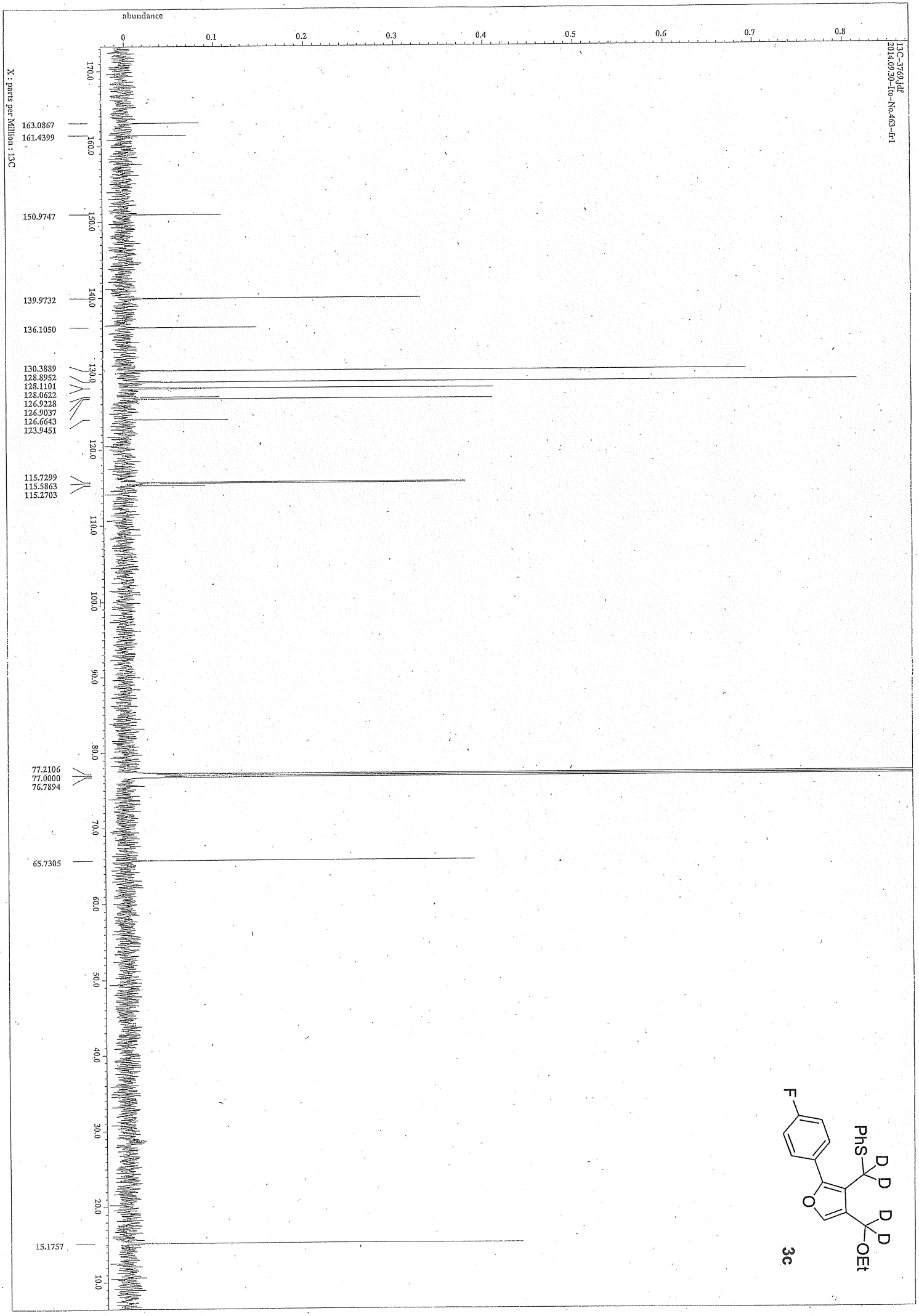
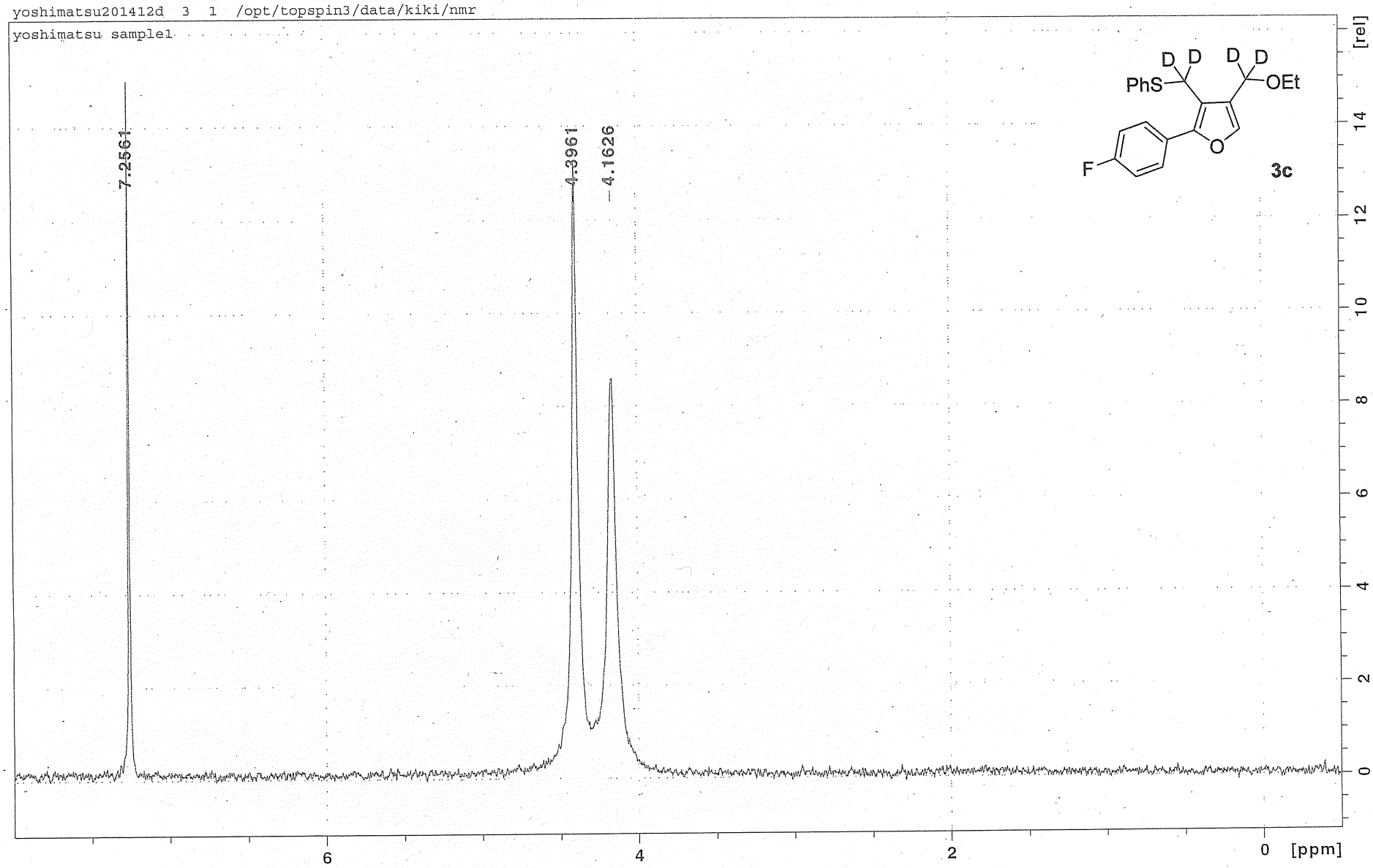
4.0
5.0
6.0
7.0
1H-362.jdf
2014.08.20-1to-No.413-fr1
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.6407
7.6235
0.71
7.2536
7.2364
7.2284
7.1998
7.1838
7.0395
7.0349
6.9078
2.54
0.31
0.31
3.4768
3.4619
3.4482
0.72
2.4049
1.12
1.5952
1.2013
1.1876
1.1738
1.05
0.0000
PhS
D
D
D
D
OEt
N
Tos
3a

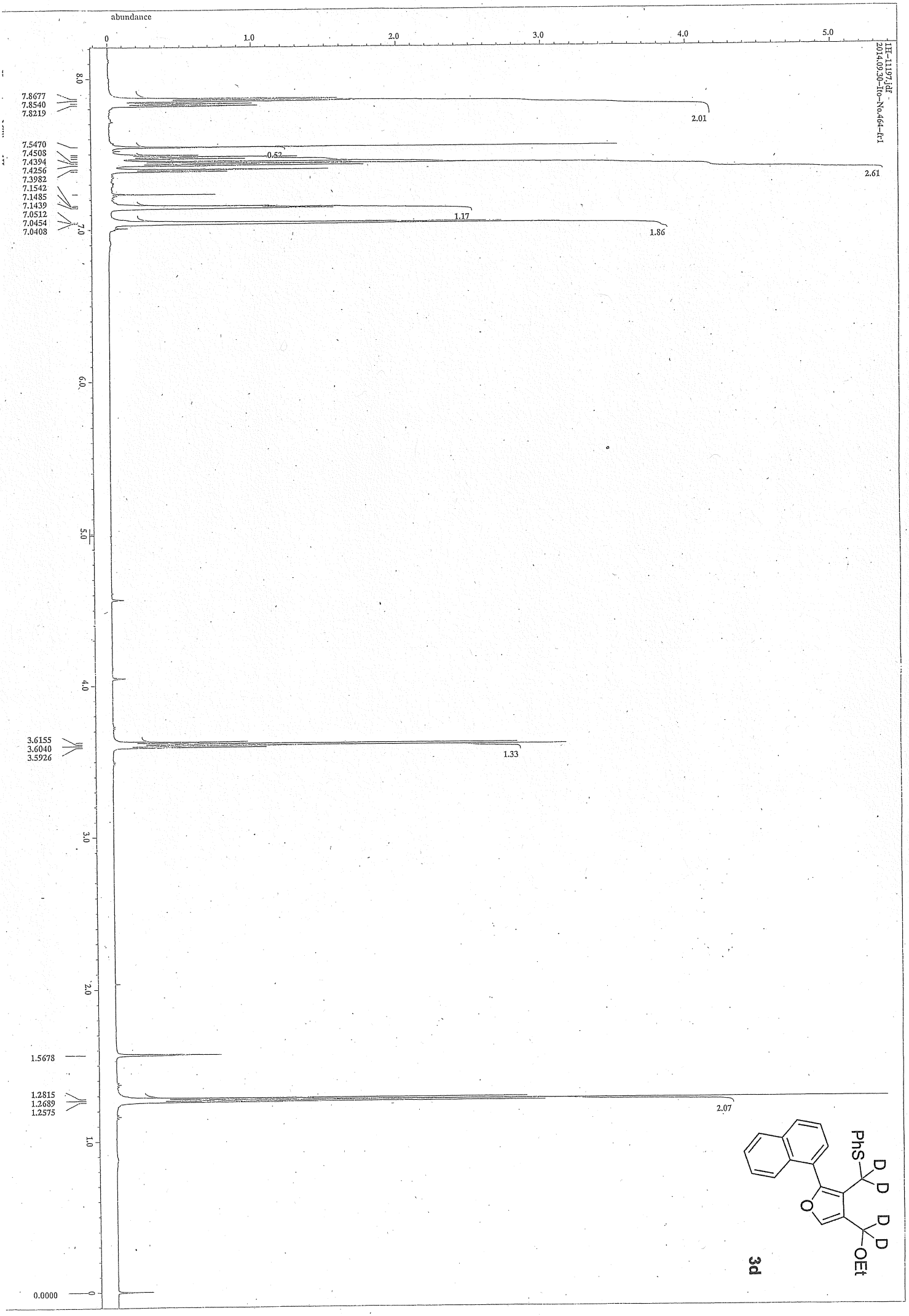

abundance
0
0.1
0.2
0.3
0.4
X : parts per Million : 13C
13C-68.jdf
2014.08.20-Ito-No.413-fr1
144.8652
135.9278
135.8419
130.2620
129.9186
128.7263
126.8377
126.4085
124.9778
123.7759
119.9320
119.6077
77.2480
77.0000
76.7425
65.6685
21.5823
15.1344
PhS
D D
D D
OEt
N
Tos
3a

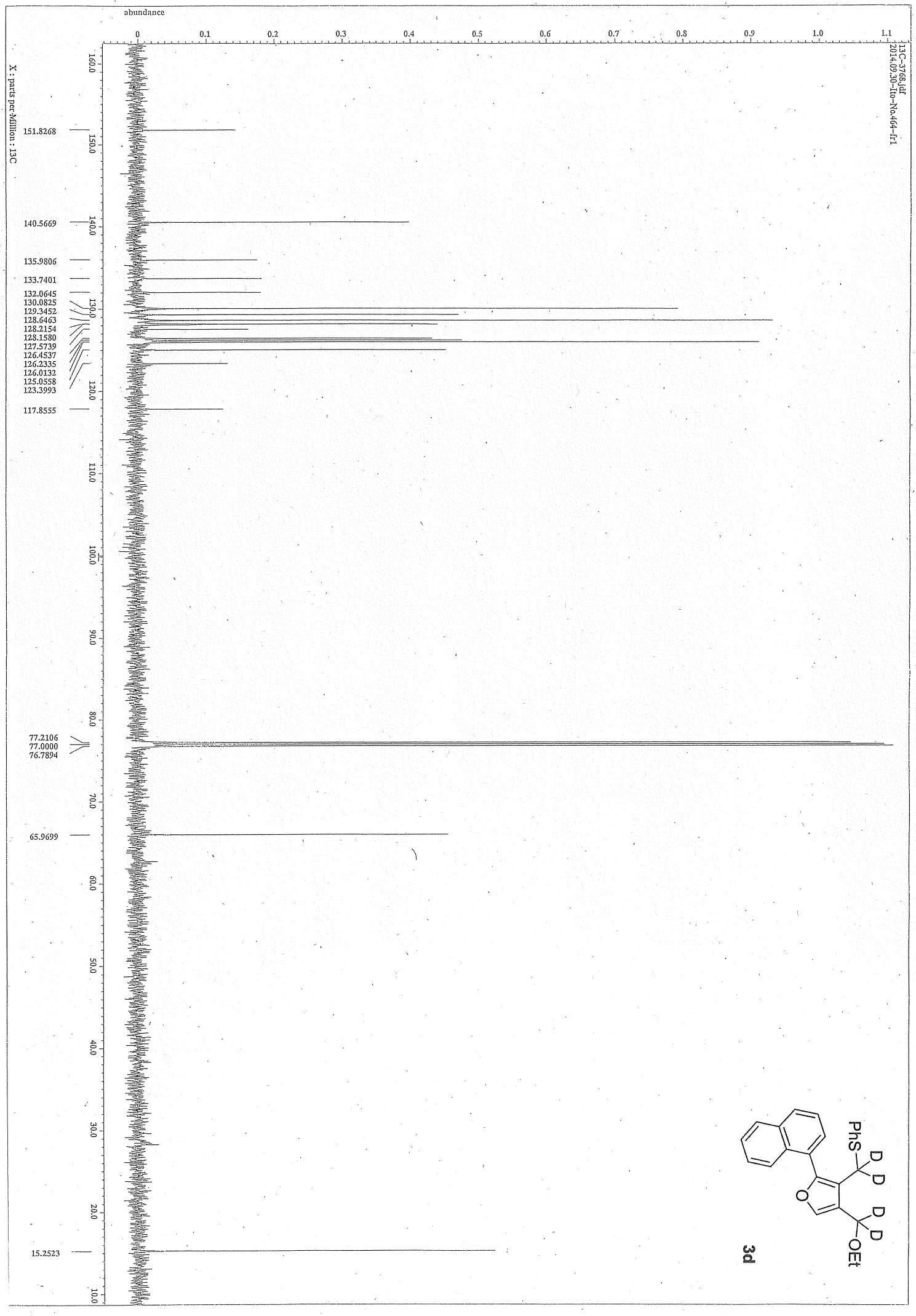

yoshimatsu201412d 192 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample19
7.2608
4.3490
3.9236
D D D D
PhS
OEt
N
Tos
3a
[rel]
15
10
5
0
8
6
4
2
0
[ppm]

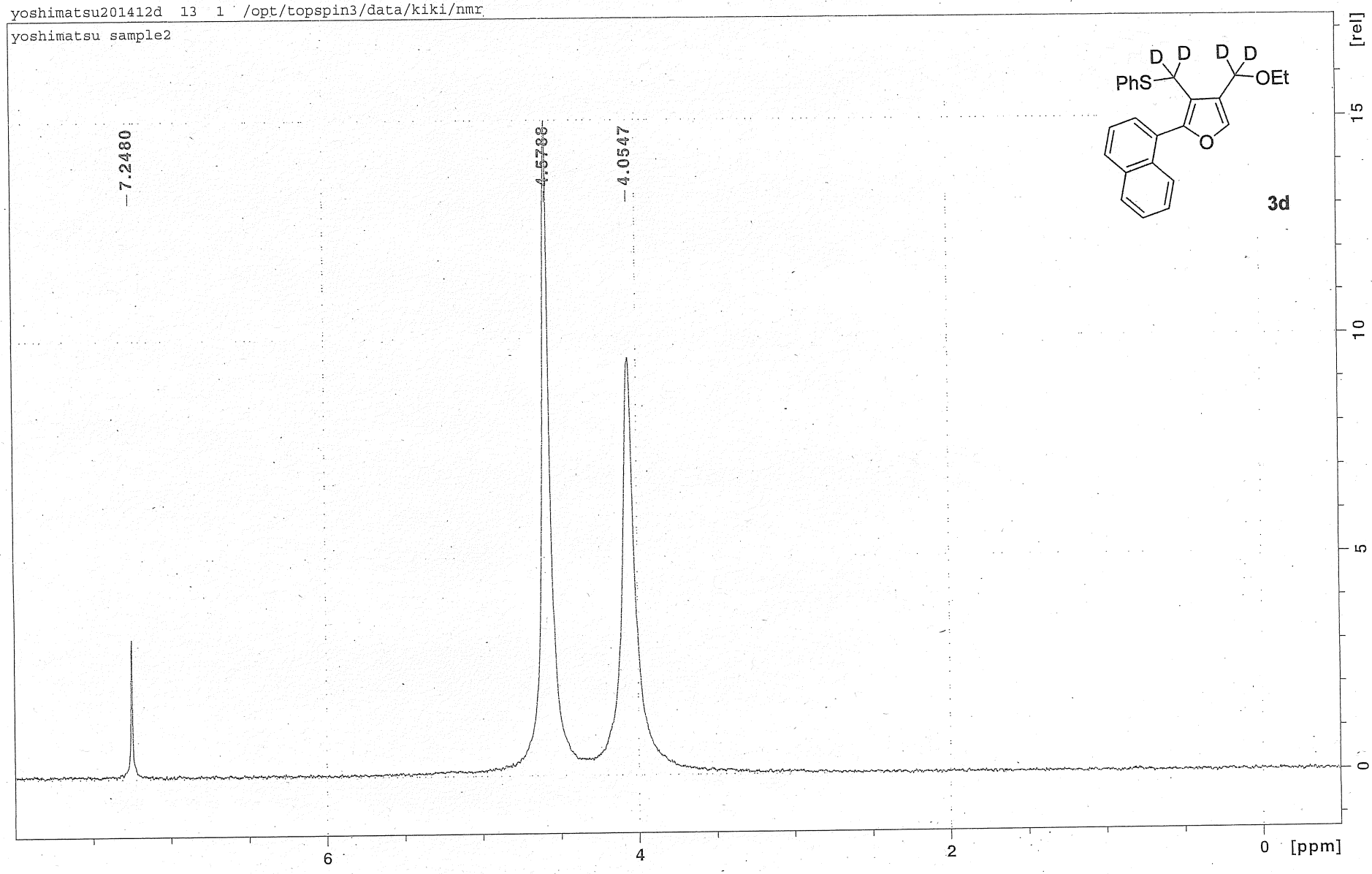

abundance
X : parts per Million : 1H
1H-11196.jdf
2014.09.30-Ito-No.463-1r1
7.5619
7.5528
7.5470
7.4004
7.3569
7.3443
7.2653
7.2527
7.0855
7.0706
7.0557
3.5353
3.5239
3.5124
1.5816
1.2323
1.2197
1.2082
−0.0000
1.35
0.55
1.24
1.43
0.63
1.34
1.42
2.26
F
PhS
D D
D D
O
OEt
3c

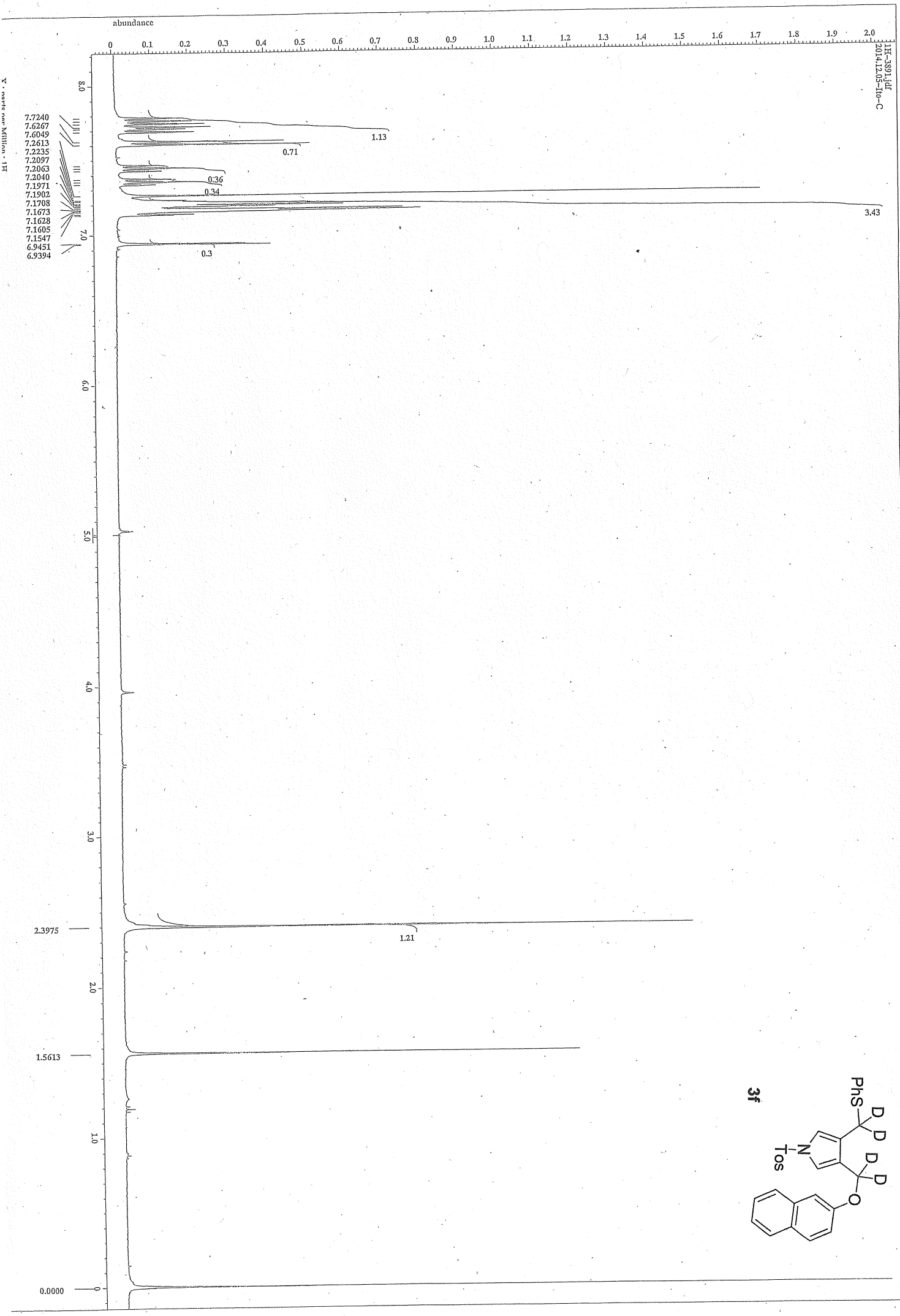

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
13C-3769.jdf
2014.09.30-to-No.463-fr1
X : parts per Million : 13C
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
163.0867
161.4399
150.9747
139.9732
136.1050
130.3889
128.8952
128.1101
128.0622
126.9228
126.9037
126.6643
123.9451
115.7299
115.5863
115.2703
77.2106
77.0000
76.7894
65.7305
15.1757
F
O
PhS
D
D
D
D
OEt
3c

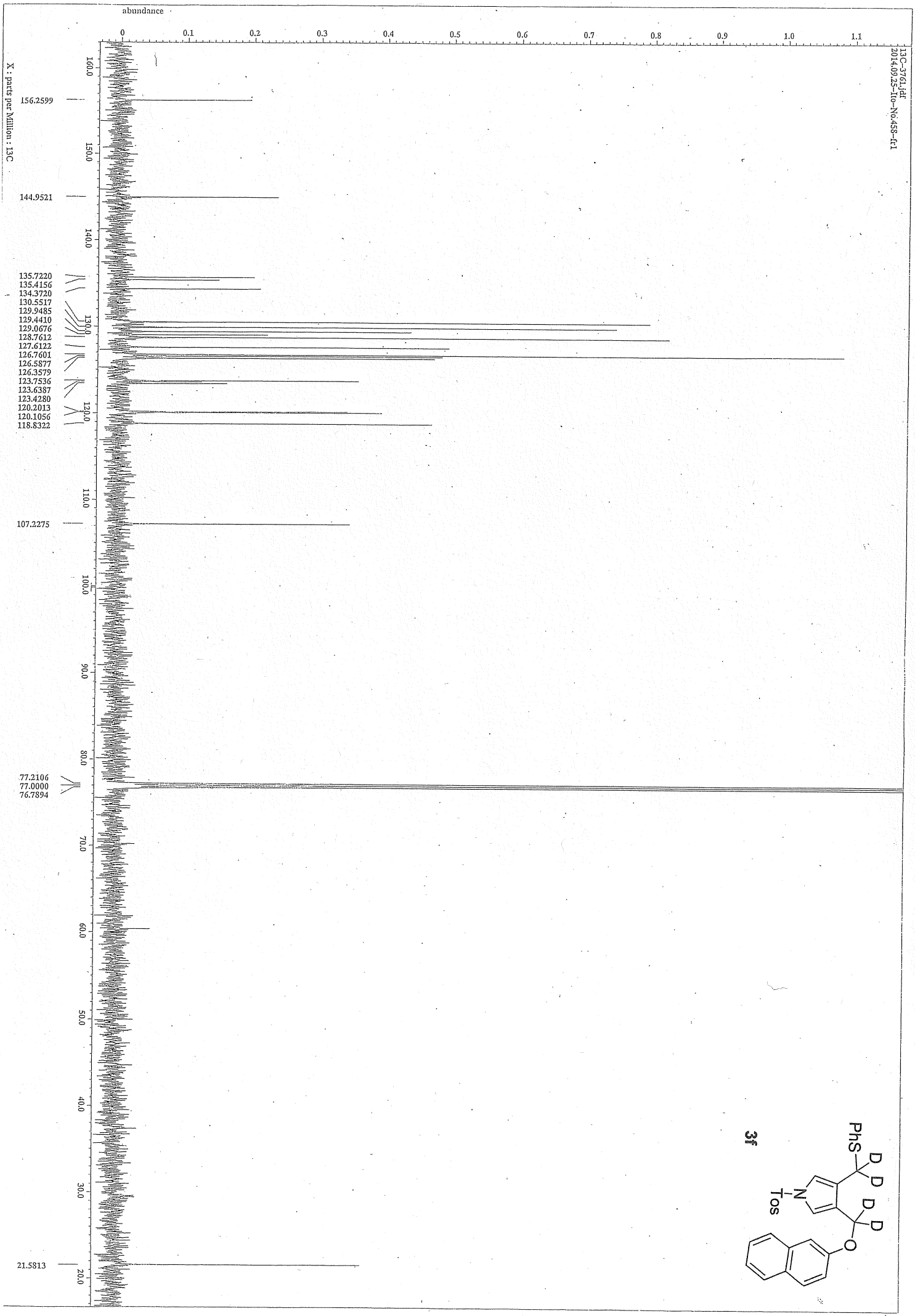

yoshimatsu201412d 3 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample1
7.2561
4.3961
4.1626
D D D D
PhS
OEt
O
F
3c
[rel]
0
2
4
6
8
10
12
14
6
4
2
0
[ppm]

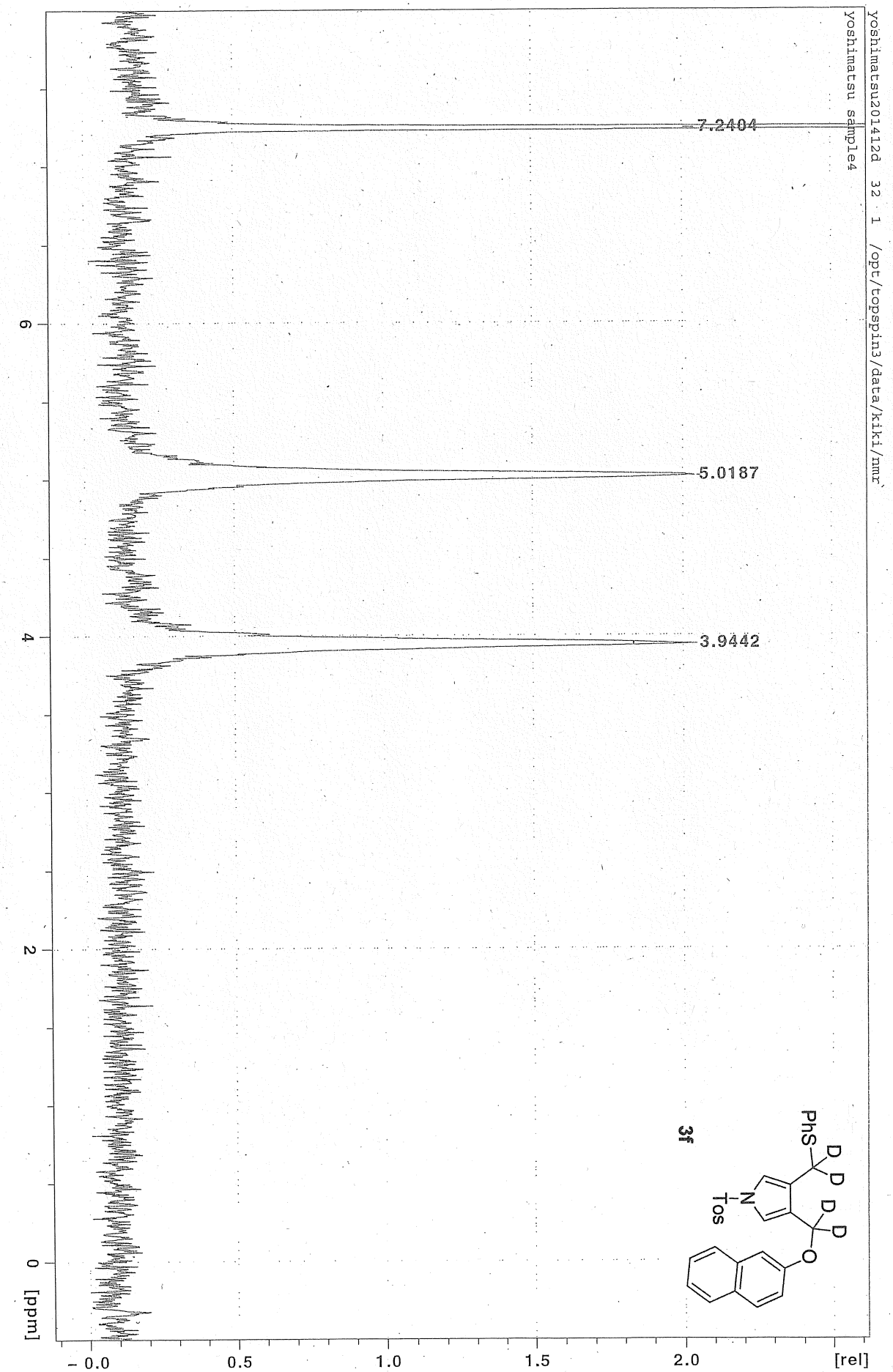

abundance
0
1.0
2.0
3.0
4.0
5.0
IH-11197.jdf
2014.09.30-Ito-No.464-Fr1
7.8677
7.8540
7.8219
7.5470
7.4508
7.4394
7.4256
7.3982
7.1542
7.1485
7.1439
7.0512
7.0454
7.0408
3.6155
3.6040
3.5926
1.5678
1.2815
1.2689
1.2575
0.0000
2.01
0.52
2.61
1.17
1.86
1.33
2.07
PhS
D D
O
D D
OEt
3d

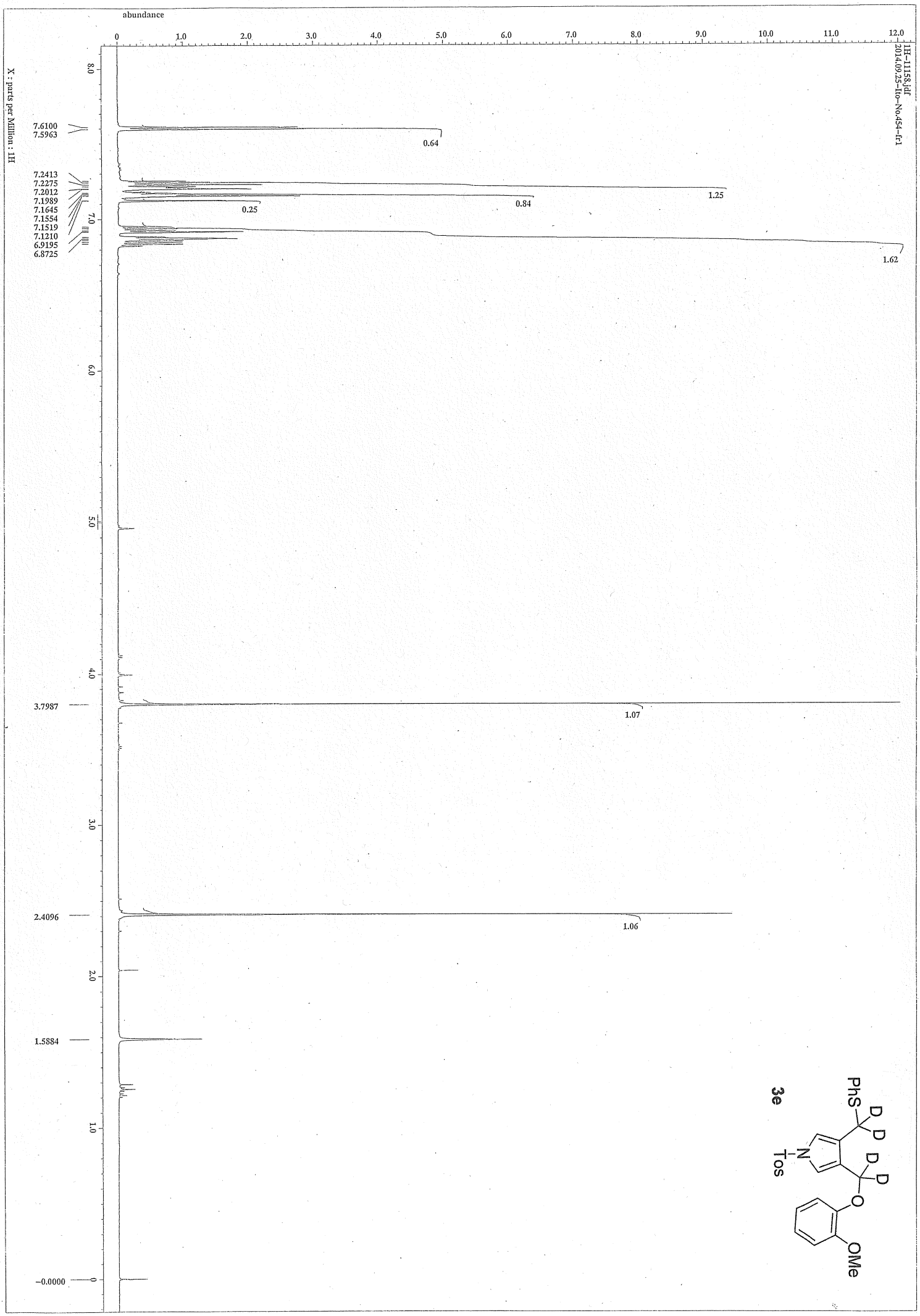

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
13C-3768.jdf
2014.09.30-Ito-No.464-fr1
X : parts per Million : 13C
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
151.8268
140.5669
135.9806
133.7401
132.0645
130.0825
129.3452
128.6463
128.2154
128.1580
127.5739
126.4537
126.2335
126.0132
125.0558
123.3993
117.8555
77.2106
77.0000
76.7894
65.9699
15.2523
PhS
D D
D D
OEt
O
3d

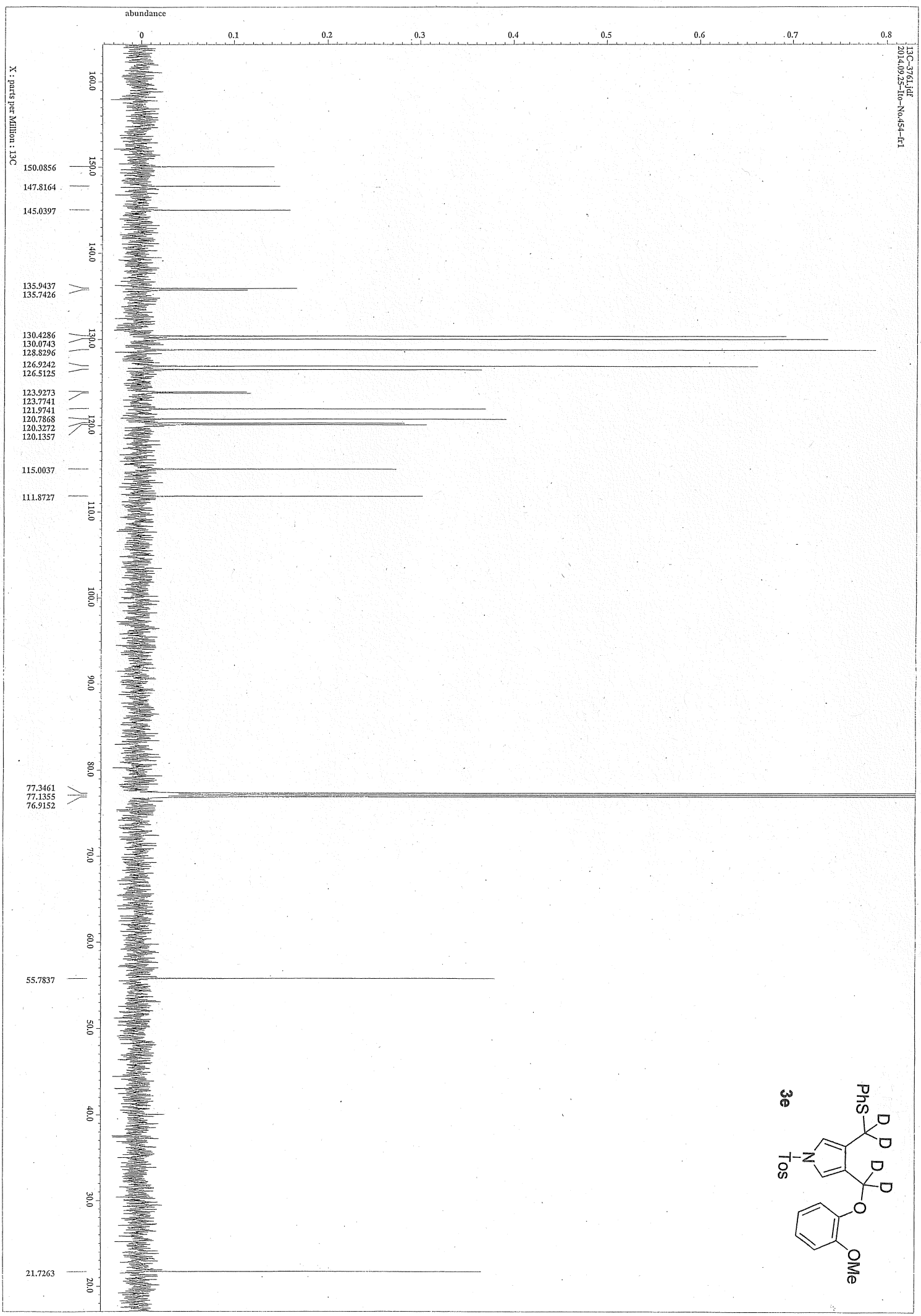

yoshimatsu201412d 13 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample2
7.2480
4.5708
4.0547
D D D D
PhS
OEt
O
3d
[rel]
15
10
5
0
6
4
2
0 [ppm]

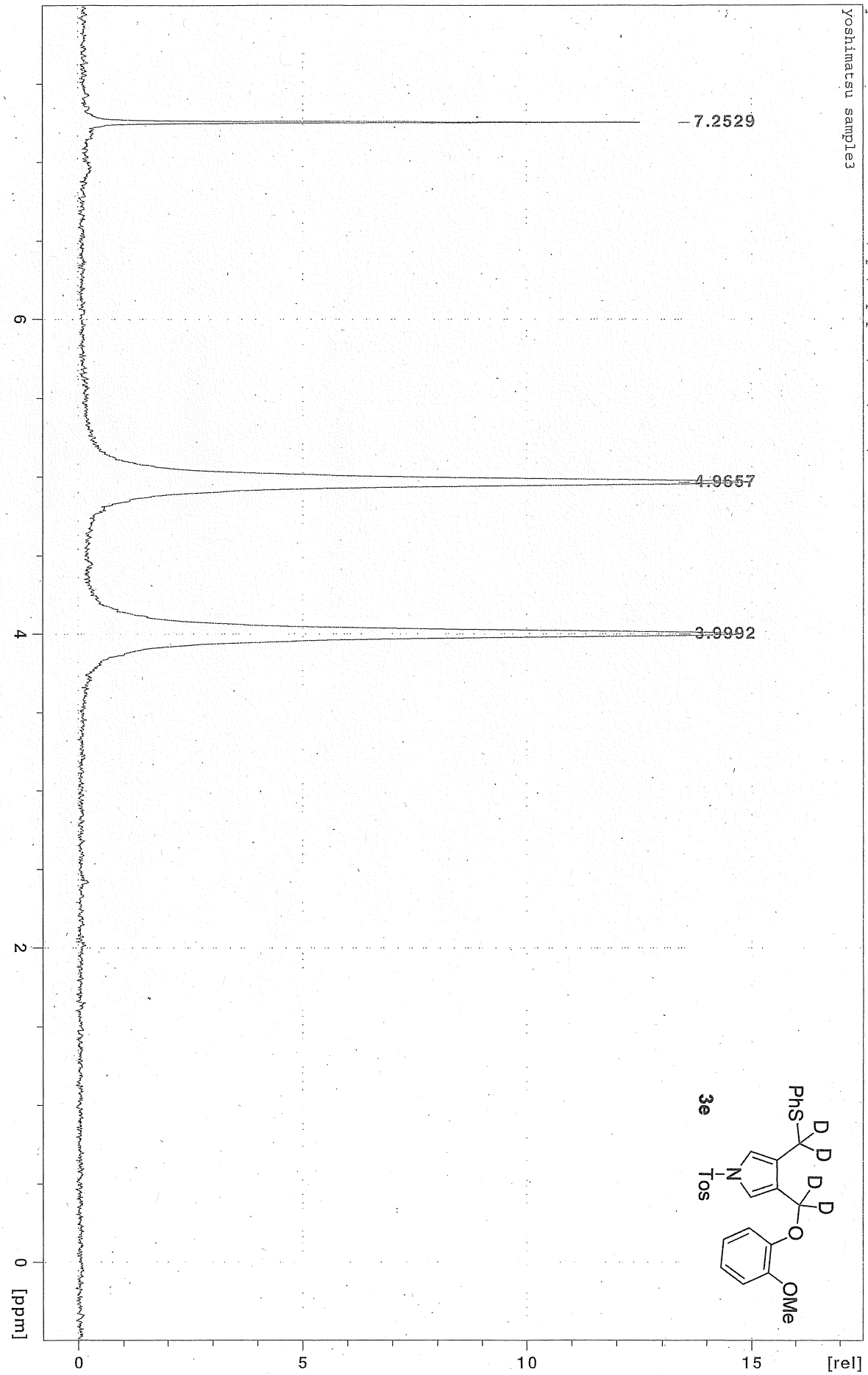

abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0
JJH-3891.jdf
2014.12.05-Ito-C
X - norte non-Million - 1H
7.7240
7.6267
7.6049
7.2613
7.2235
7.2097
7.2063
7.2040
7.1971
7.1902
7.1708
7.1673
7.1628
7.1605
7.1547
6.9451
6.9394
1.13
0.71
0.36
0.34
3.43
0.3
1.21
2.3975
1.5613
0.0000
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
3f
PhS
D D
N
Tos
D D
O

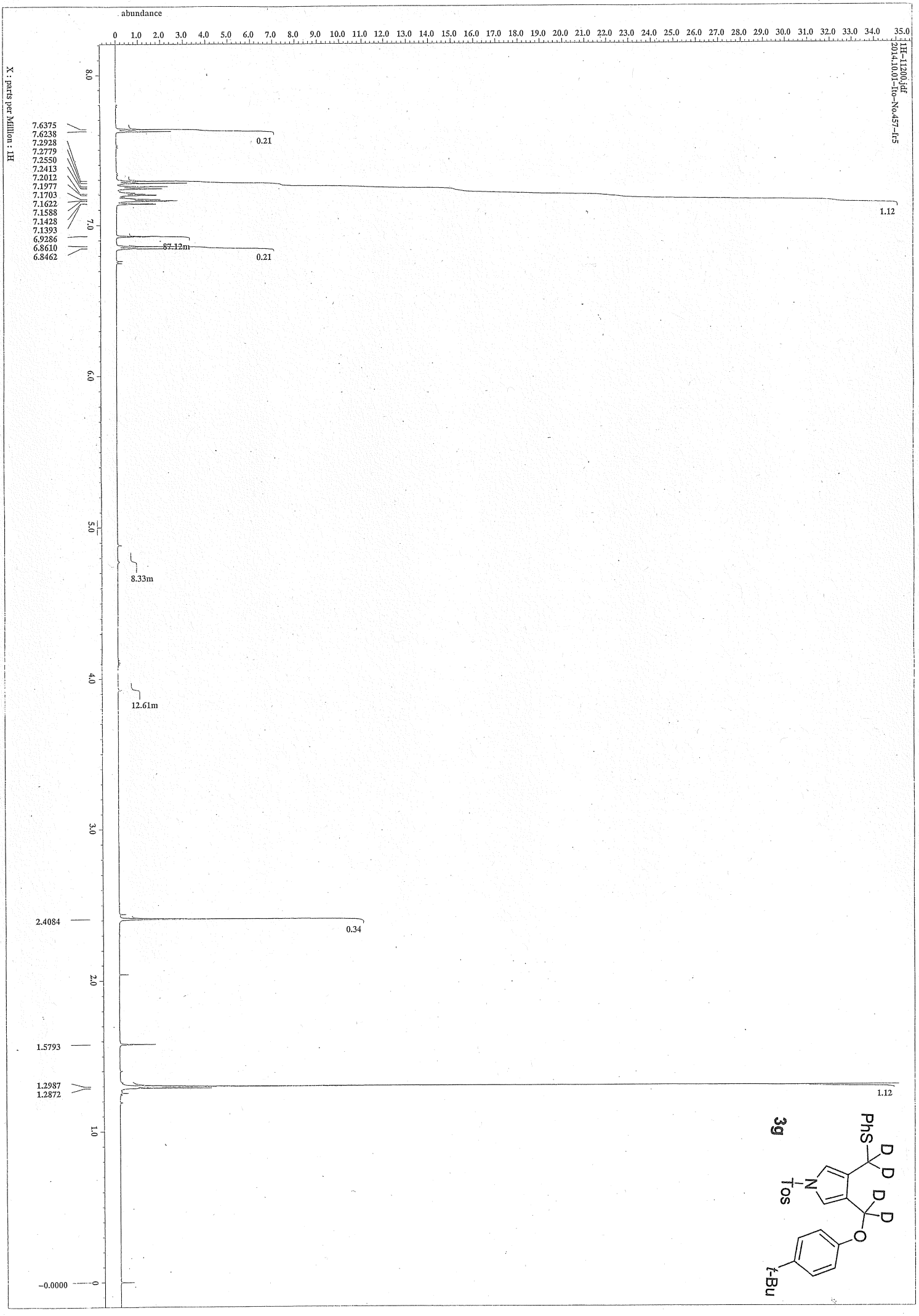

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
X : parts per Million : 13C
13C-376J.jdf
2014.09.25-To-No.458-fr1
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
156.2599
144.9521
135.7220
135.4156
134.3720
130.5517
129.9485
129.4410
129.0676
128.7612
127.6122
126.7601
126.5877
126.3579
123.7536
123.6387
123.4280
120.2013
120.1056
118.8322
107.2275
77.2106
77.0000
76.7894
21.5813
3f
PhS
D D
D D
N
Tos
O

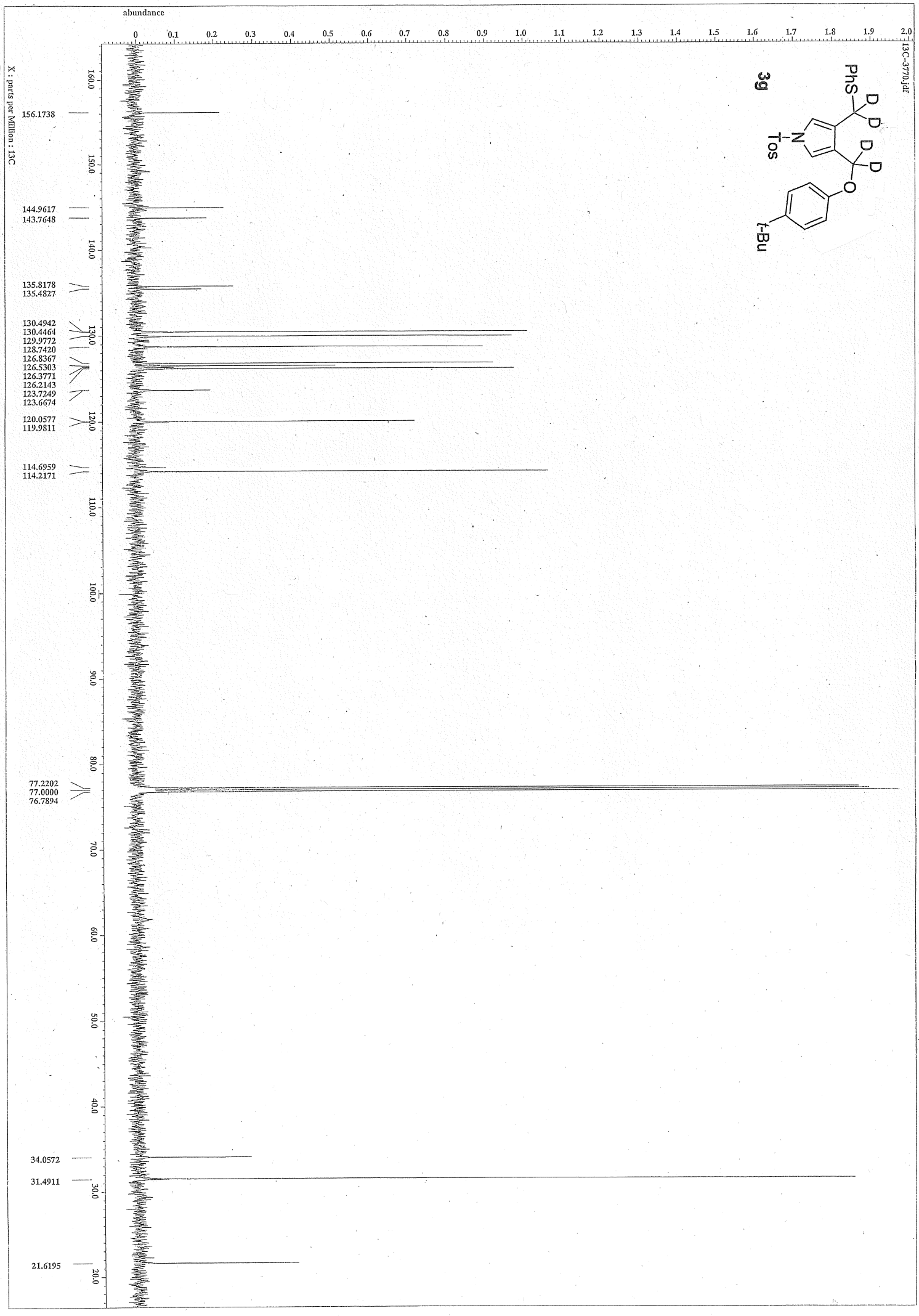

yoshimatsu2014l2d 32 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample4
7.2404
5.0187
3.9442
3f
PhS
D D
D D
N
Tos
O
6
4
2
0 [ppm]
– 0.0
0.5
1.0
1.5
2.0
[rel]

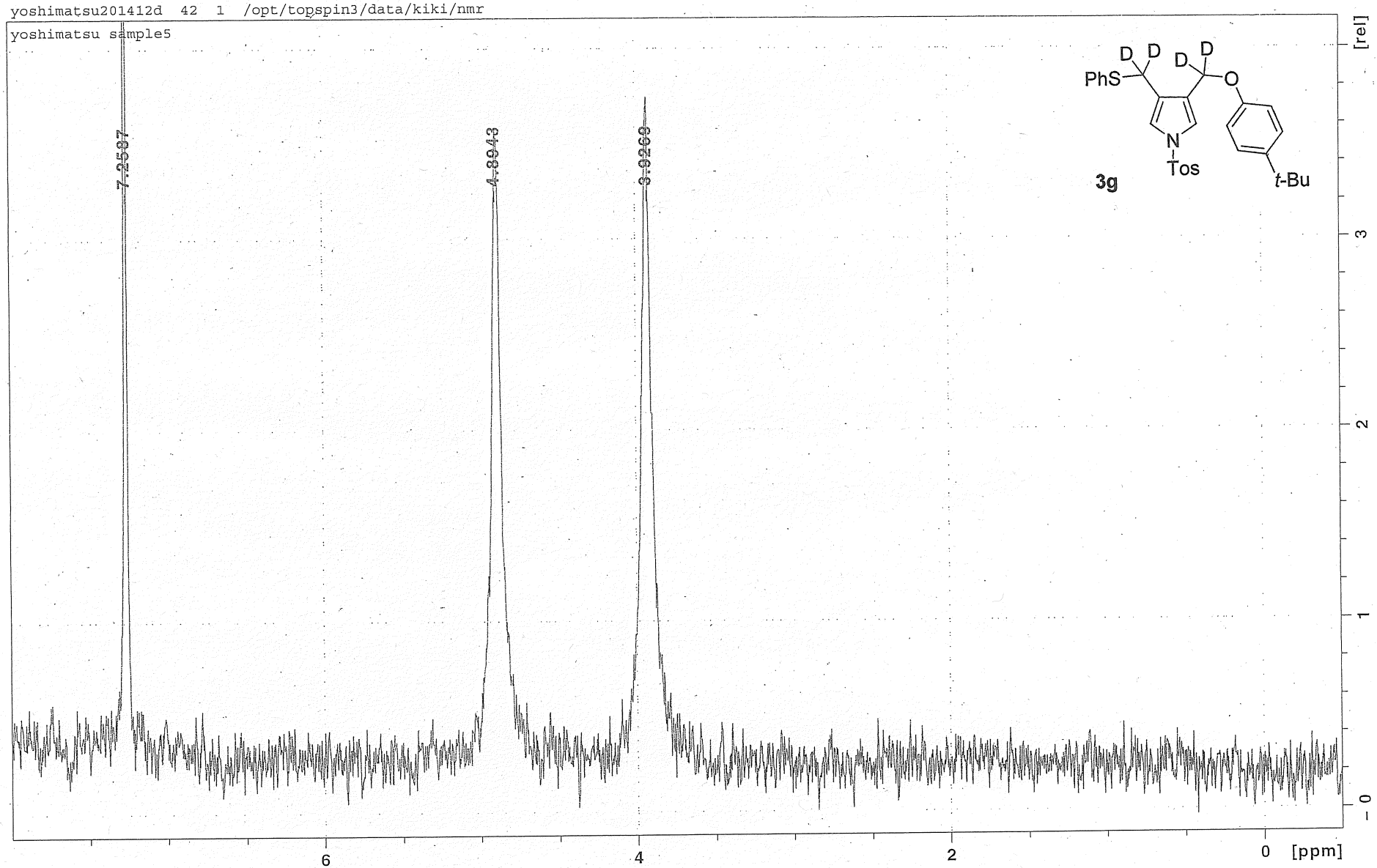

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
1H-111158.idf
2014.09.25-Ito-No.454-fr1
X : parts per Million : 1H
7.6100
7.5963
7.2413
7.2275
7.2012
7.1989
7.1645
7.1554
7.1519
7.1210
6.9195
6.8725
3.7987
2.4096
1.5884
−0.0000
0.64
0.25
0.84
1.25
1.62
1.07
1.06
3e
PhS
D D
D D
N
Tos
O
OMe

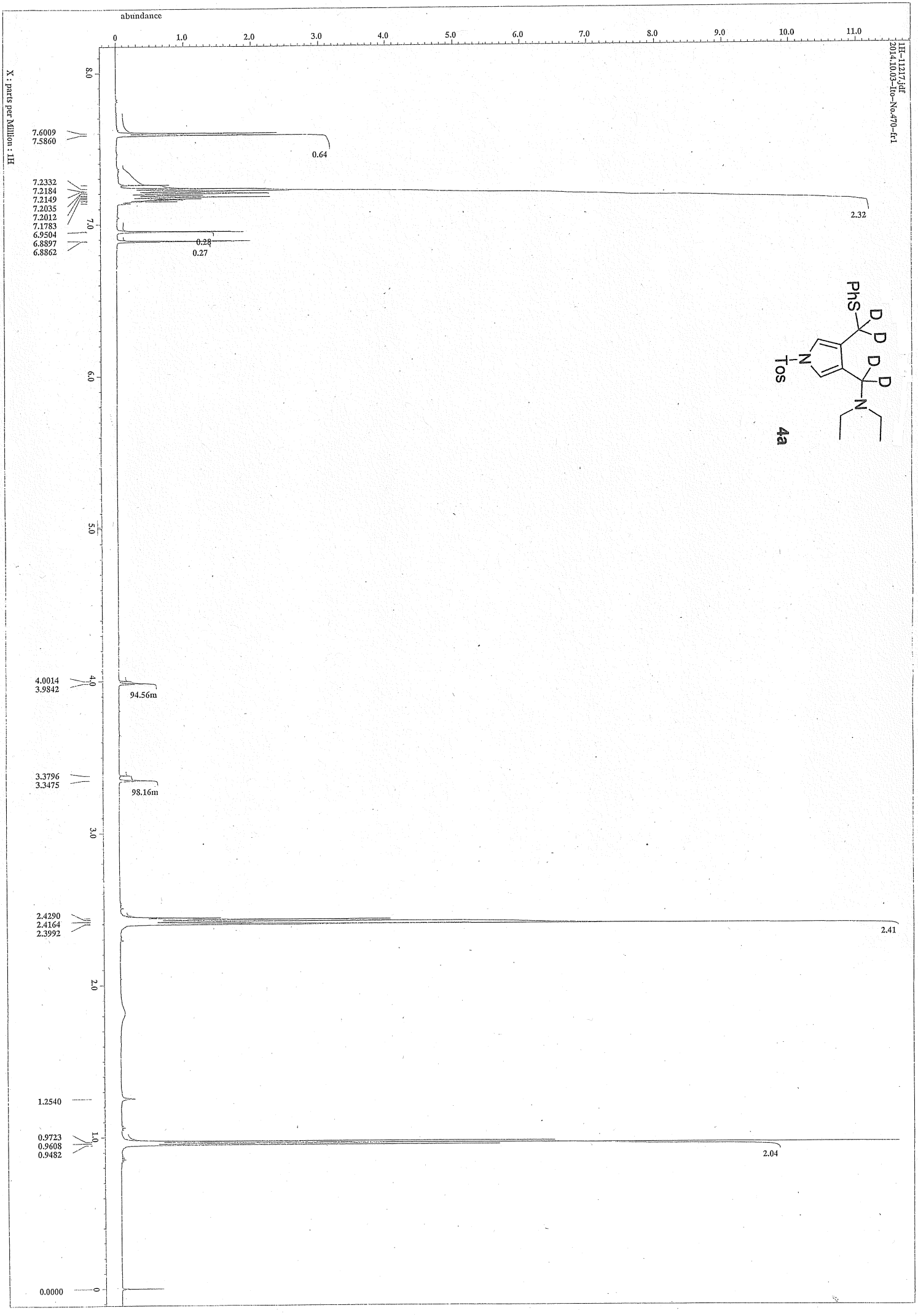

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
13C-3761.jdf
2014.09.25-Ito-No.454-fr1
X : parts per Million : 13C
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
150.0856
147.8164
145.0397
135.9437
135.7426
130.4286
130.0743
128.8296
126.9242
126.5125
123.9273
123.7741
121.9741
120.7868
120.3272
120.1357
115.0037
111.8727
77.3461
77.1355
76.9152
55.7837
21.7263
3e
PhS
D
D
N
Tos
D
D
O
OMe

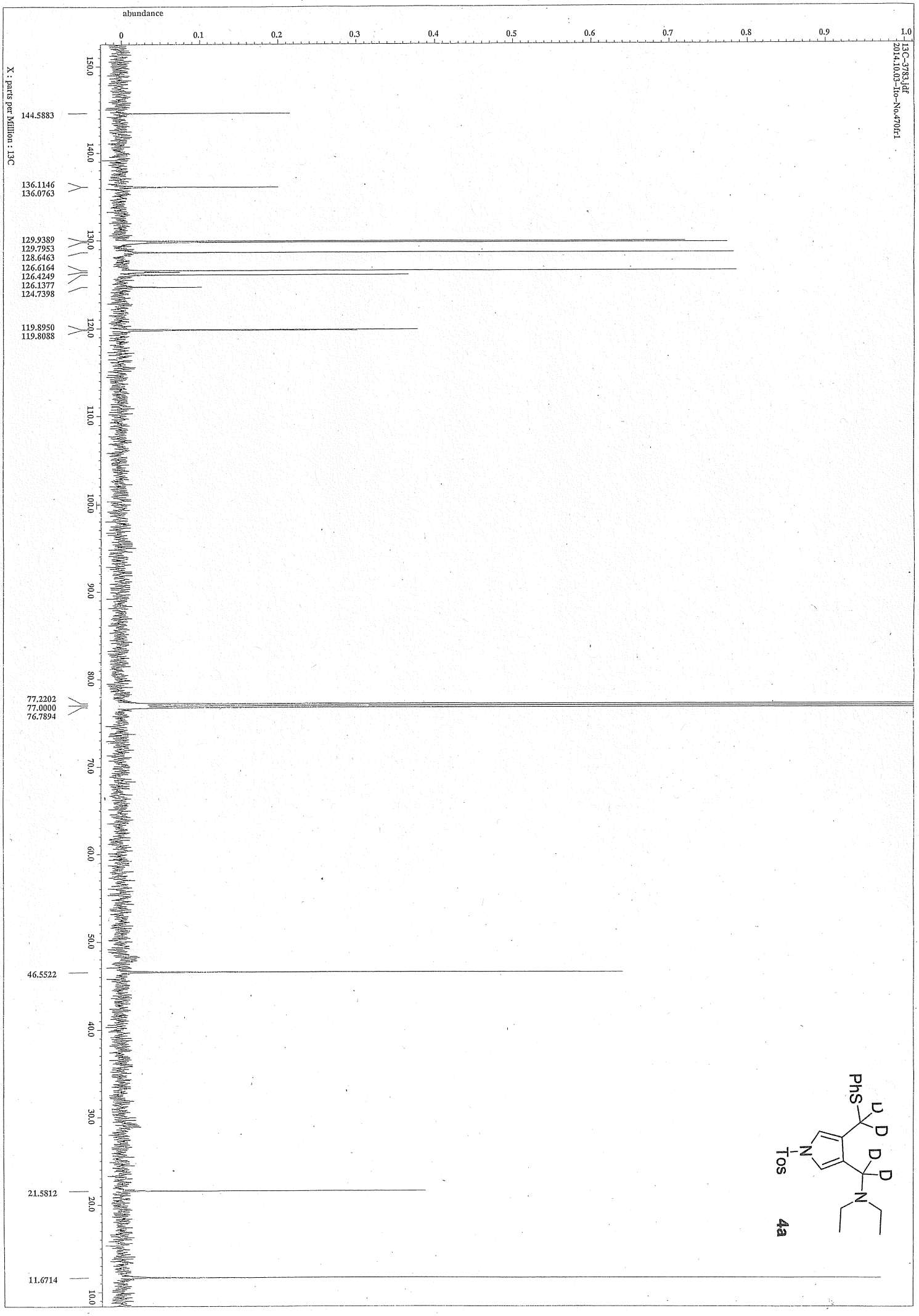

yoshimatsu2014120 22 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample3
7.2529
4.9657
3.9992
PhS
D D
D D
O
OMe
N
Tos
3e
0
2
4
6
[ppm]
0
5
10
15
[rel]

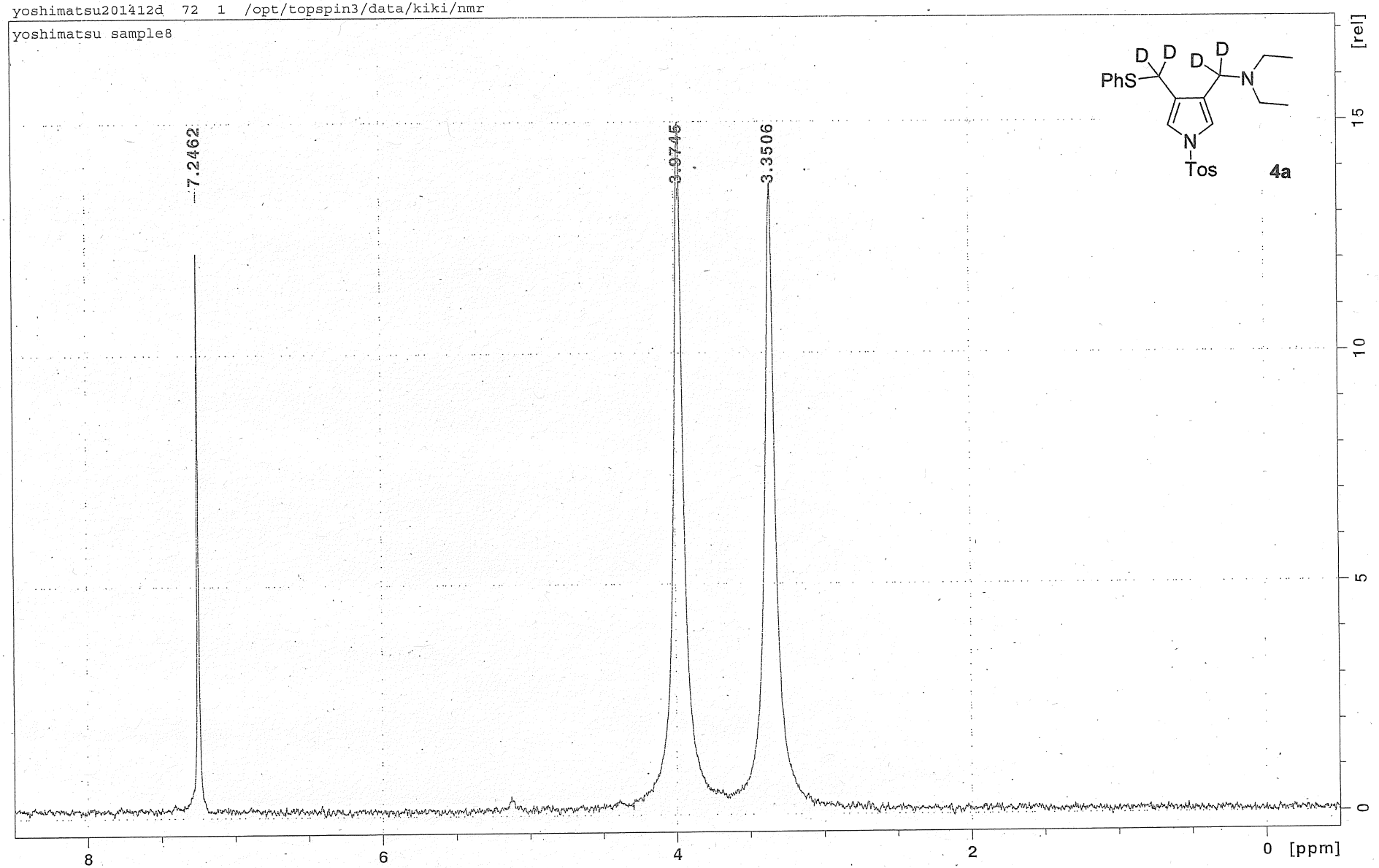

abundance
1H-11200.idf
2014.10.01-Ito-No.457-fr5
X : parts per Million : 1H
7.6375
7.6238
7.2928
7.2779
7.2550
7.2413
7.2012
7.1977
7.1703
7.1622
7.1588
7.1428
7.1393
6.9286
6.8610
6.8462
0.21
1.12
87.12m
0.21
8.33m
12.61m
2.4084
0.34
1.5793
1.2987
1.2872
1.12
3g
PhS
D D
D D
N
Tos
O
t-Bu

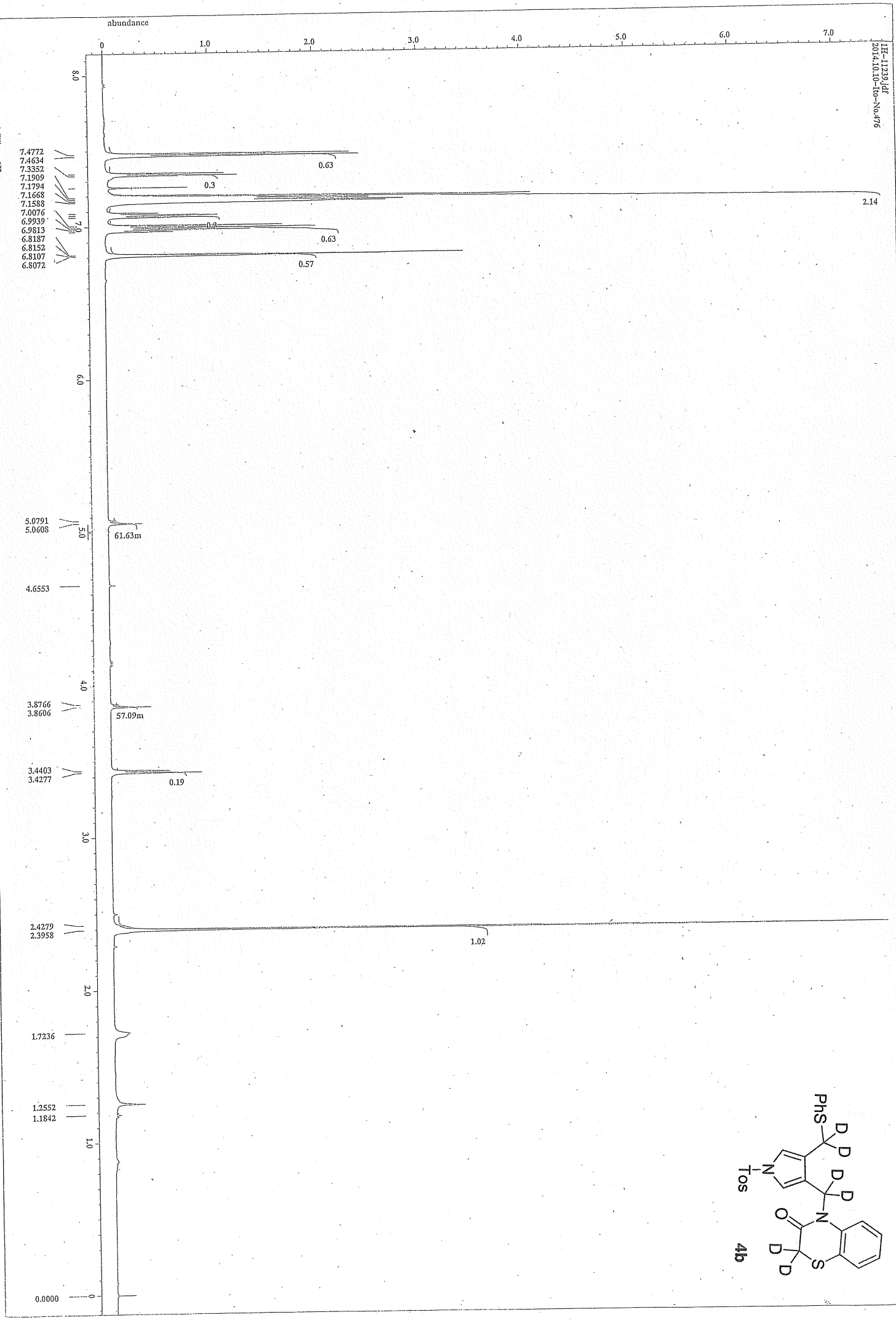

abundance
X : parts per Million : 13C
13C-3770.jdf
3g
PhS
D D
D D
N
Tos
O
t-Bu
156.1738
144.9617
143.7648
135.8178
135.4827
130.4942
130.4464
129.9772
128.7420
126.8367
126.5303
126.3771
126.2143
123.7249
123.6674
120.0577
119.9811
114.6959
114.2171
77.2202
77.0000
76.7894
34.0572
31.4911
21.6195

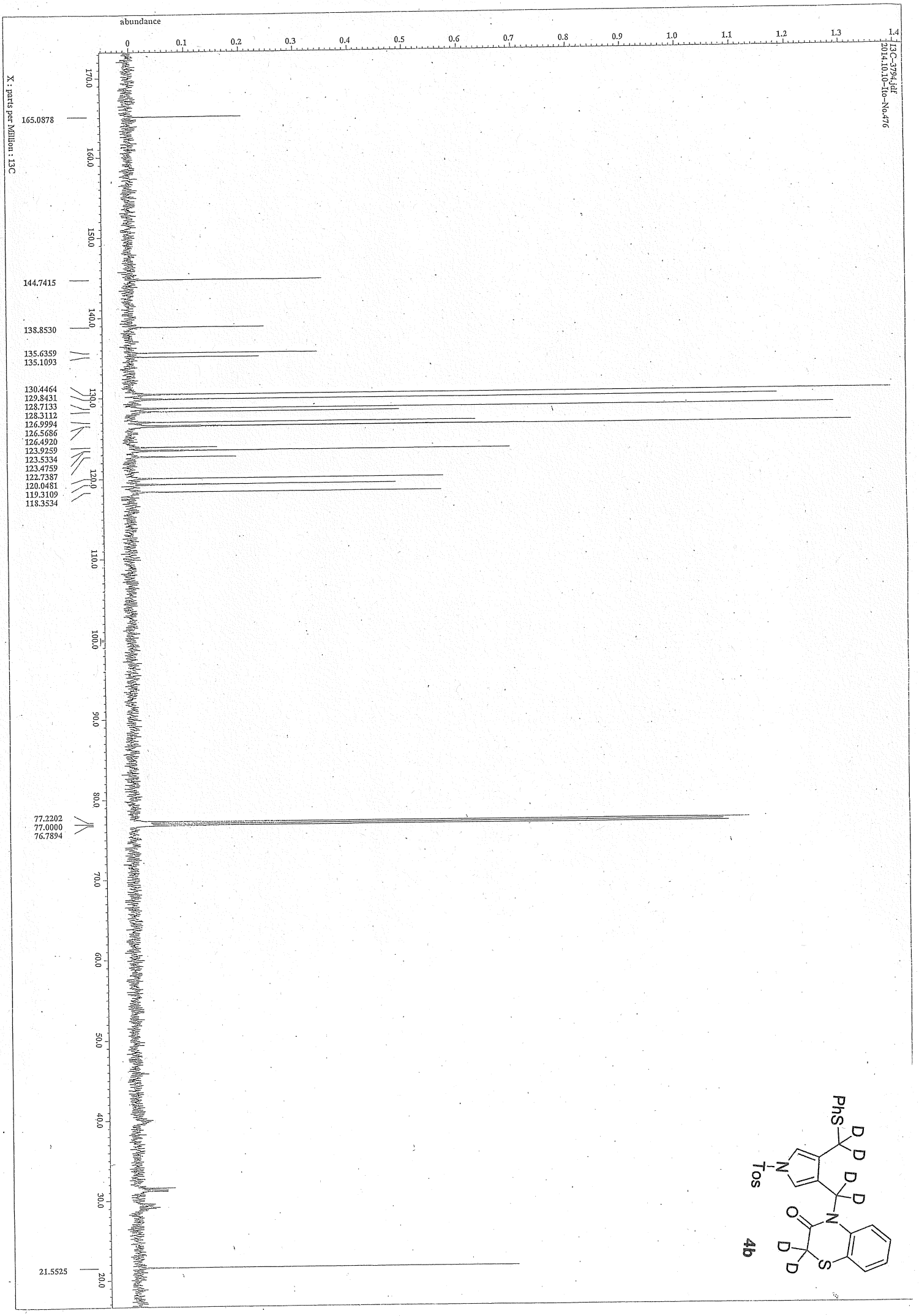

yoshimatsu201412d 42 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample5
7.2597
4.8943
3.9269
D D D D
PhS
O
N
Tos
t-Bu
3g
[rel]
3
2
1
0
6
4
2
0
[ppm]

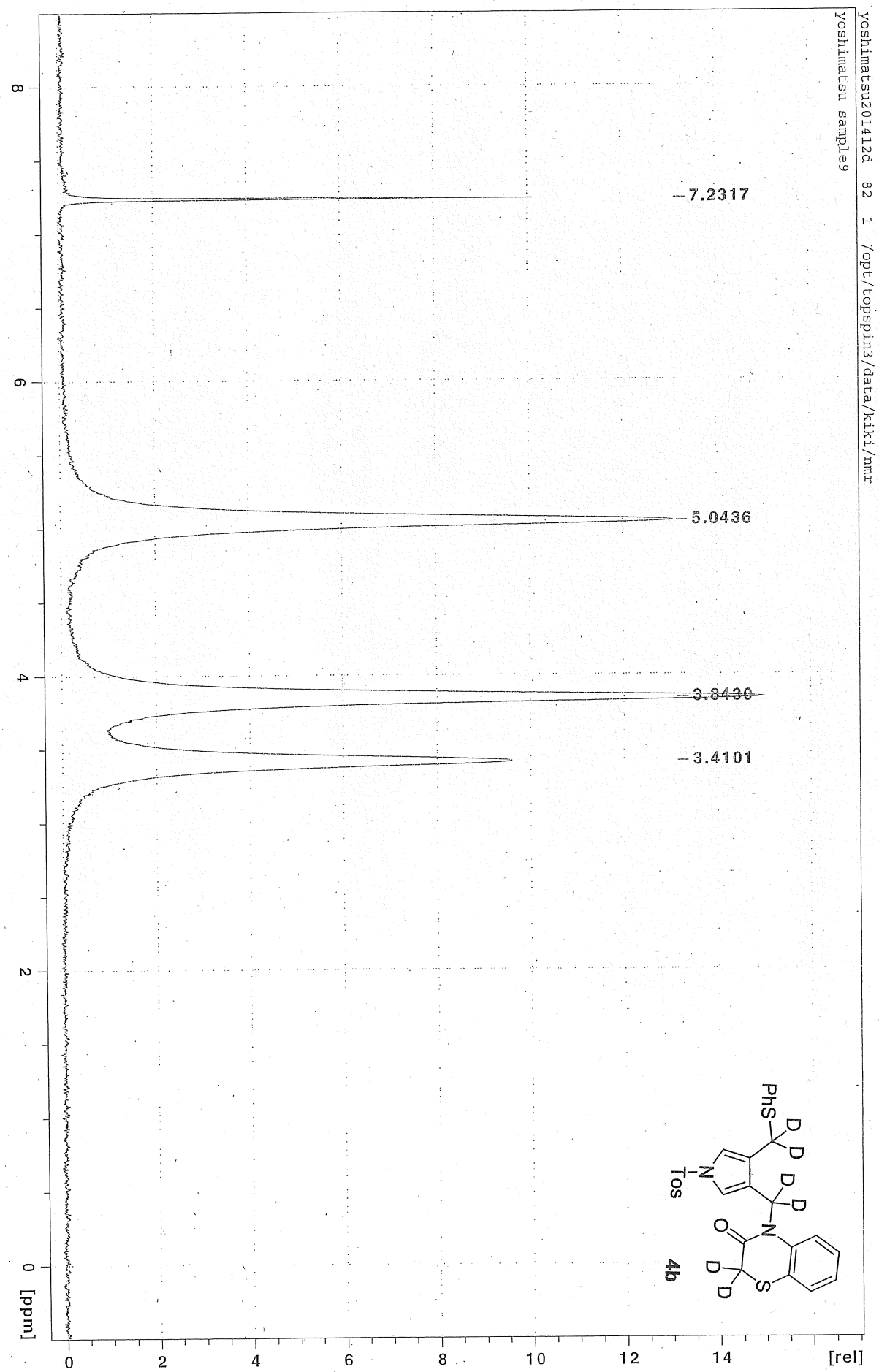

abundance
X : parts per Million : 1H
1H-11217.jdf
2014.10.03-Ito-No.470-fr1
7.6009
7.5860
0.64
7.2332
7.2184
7.2149
7.2035
7.2012
7.1783
6.9504
6.8897
6.8862
0.28
0.27
2.32
PhS
D D
N
Tos
D D
N
4a
4.0014
3.9842
94.56m
3.3796
3.3475
98.16m
2.4290
2.4164
2.3992
2.41
1.2540
0.9723
0.9608
0.9482
2.04
0.0000

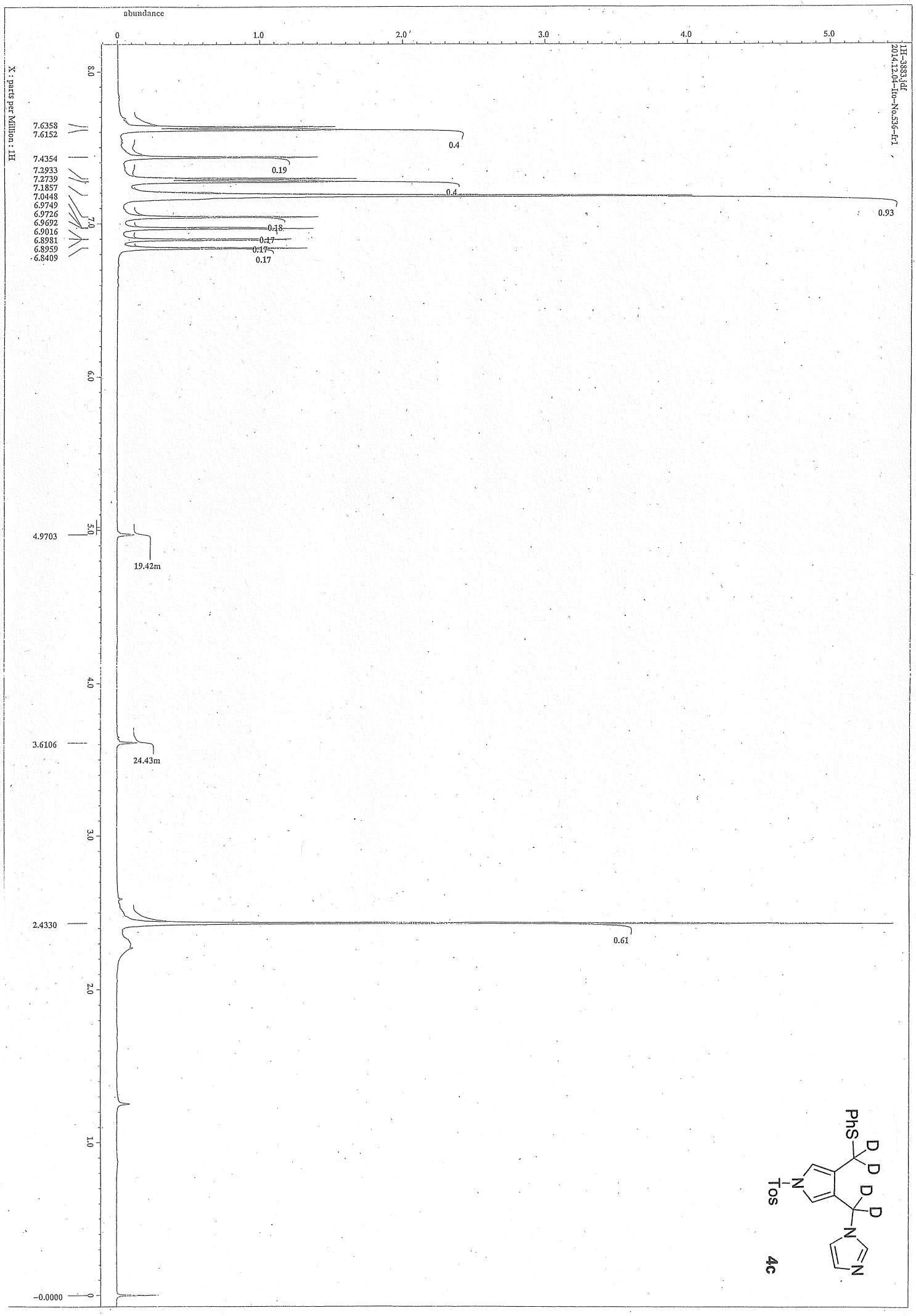

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
13C-3783.jdf
2014.10.03-Ito-No.470f1
X : parts per Million : 13C
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
144.5883
136.1146
136.0763
129.9389
129.7953
128.6463
126.6164
126.4249
126.1377
124.7398
119.8950
119.8088
77.2202
77.0000
76.7894
46.5522
21.5812
11.6714
PhS
D
D
D
N
Tos
N
4a

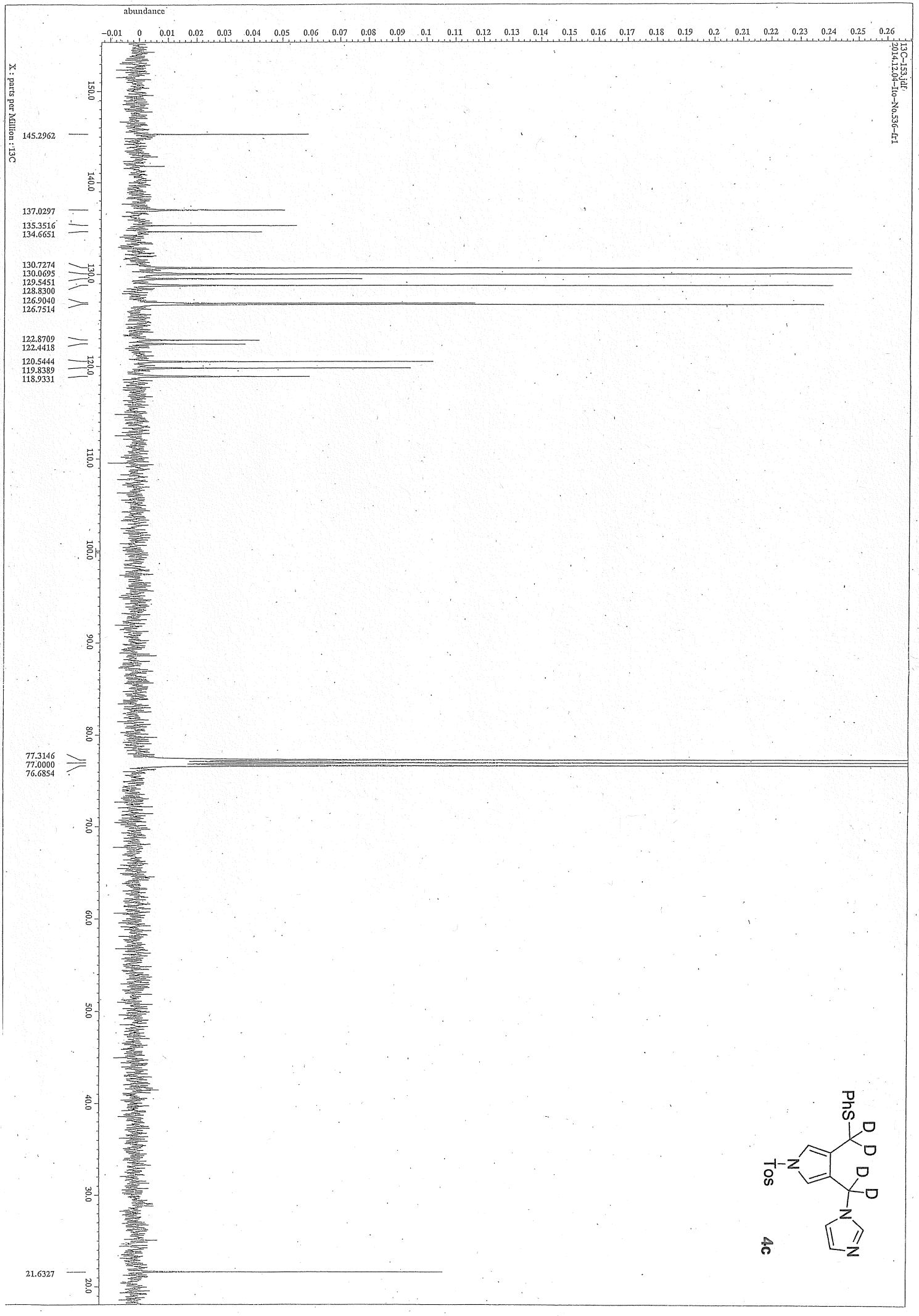

yoshimatsu201412d 72 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample8
7.2462
3.3745
3.3506
D D D D
PhS
N
N
Tos
4a
[rel]
15
10
5
0
8
6
4
2
0 [ppm]

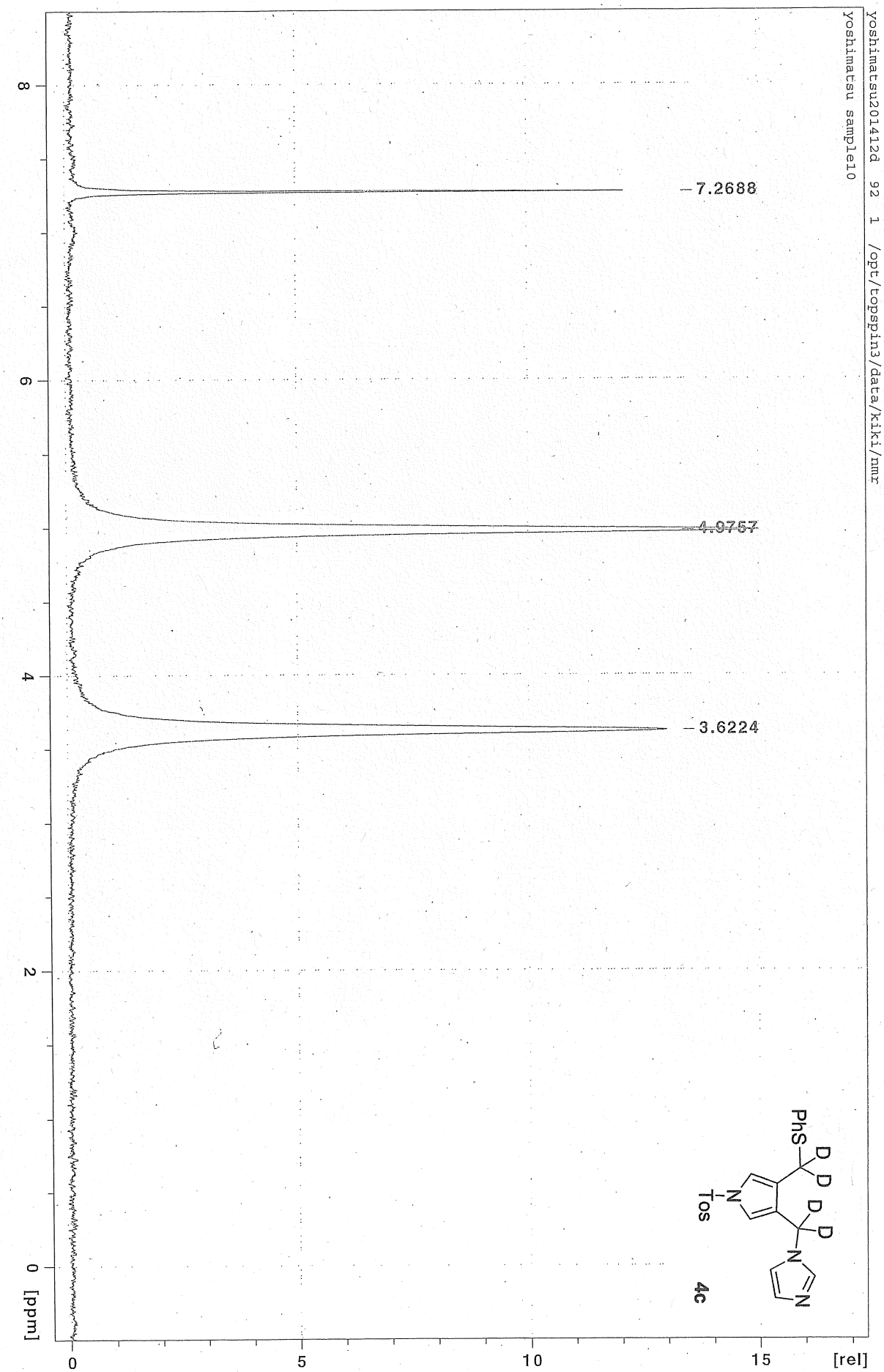

abundance
X : parts per Million : 1H
1H-11239.jdf
2014.10.10-1to-No.476
7.4772
7.4634
7.3352
7.1909
7.1794
7.1668
7.1588
7.0076
6.9939
6.9813
6.8187
6.8152
6.8107
6.8072
0.63
0.3
2.14
0.9
0.63
0.57
5.0791
5.0608
61.63m
4.6553
3.8766
3.8606
57.09m
3.4403
3.4277
0.19
2.4279
2.3958
1.02
1.7236
1.2552
1.1842
0.0000
PhS
D D
N
Tos
D D
N
O
D D
S
4b

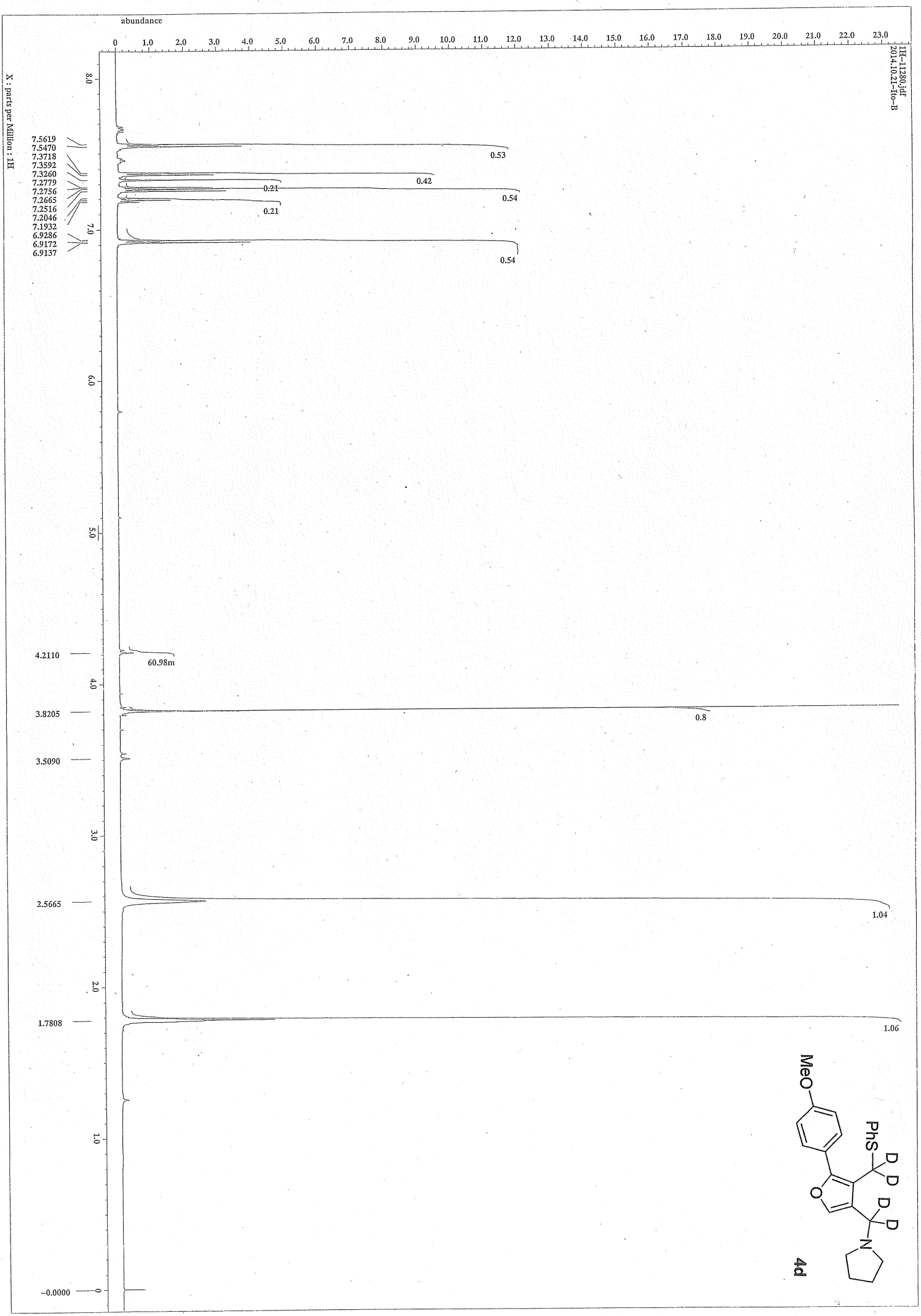

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
13C-3794.jdf
2014.10.10-Ito-No.476
X : parts per Million : 13C
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
165.0878
144.7415
138.8530
135.6359
135.1093
130.4464
129.8431
128.7133
128.3112
126.9994
126.5686
126.4920
123.9259
123.5334
123.4759
122.7387
120.0481
119.3109
118.3534
77.2202
77.0000
76.7894
21.5525
PhS
D
D
D
D
N
Tos
O
N
S
D
D
4b

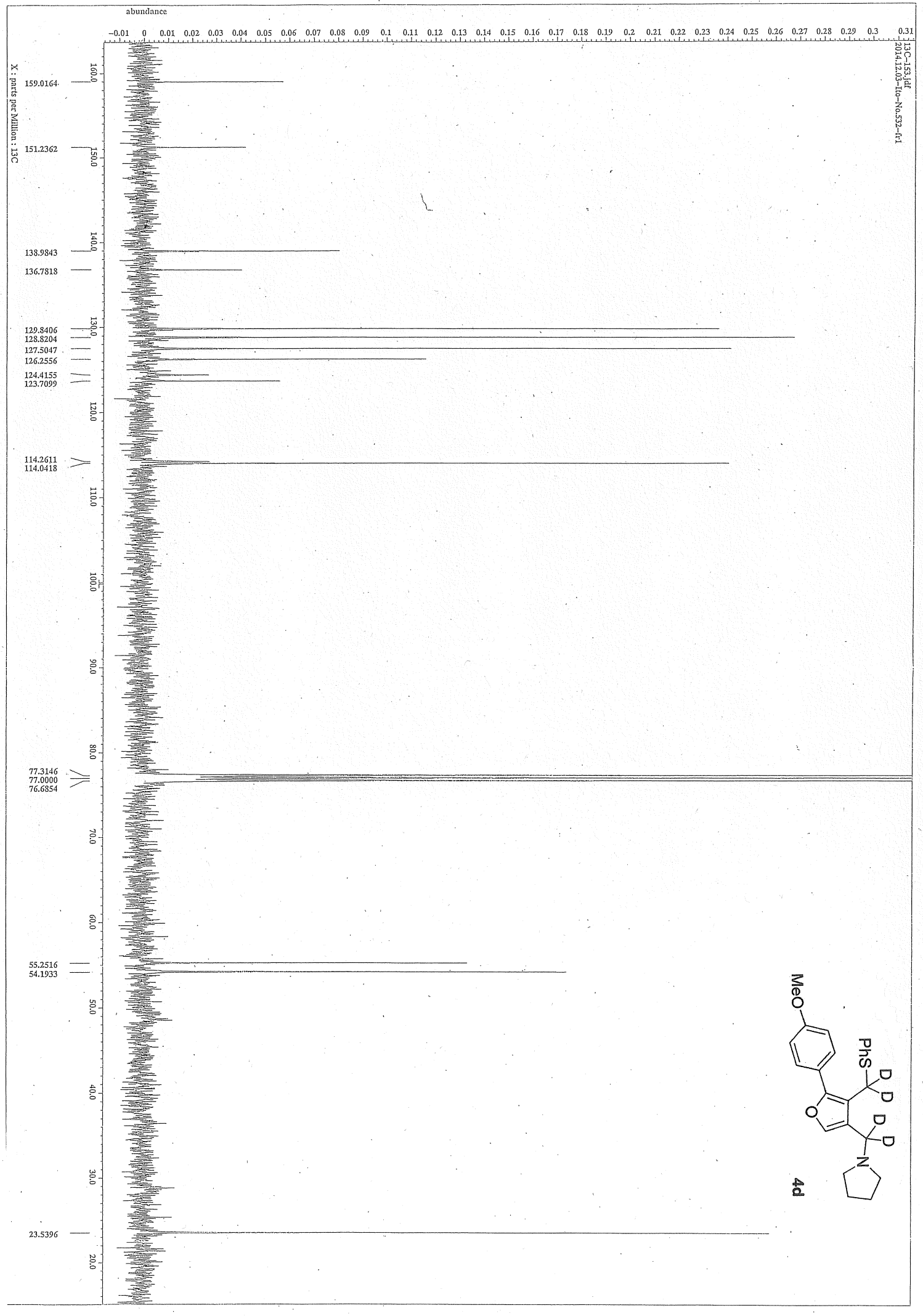

yoshimatsu20141204 82 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample9
7.2317
5.0436
3.8430
3.4101
PhS
D D
D D
N
Tos
O
N
D D
S
4b
0 [ppm]
0 2 4 6 8 10 12 14 [rel]

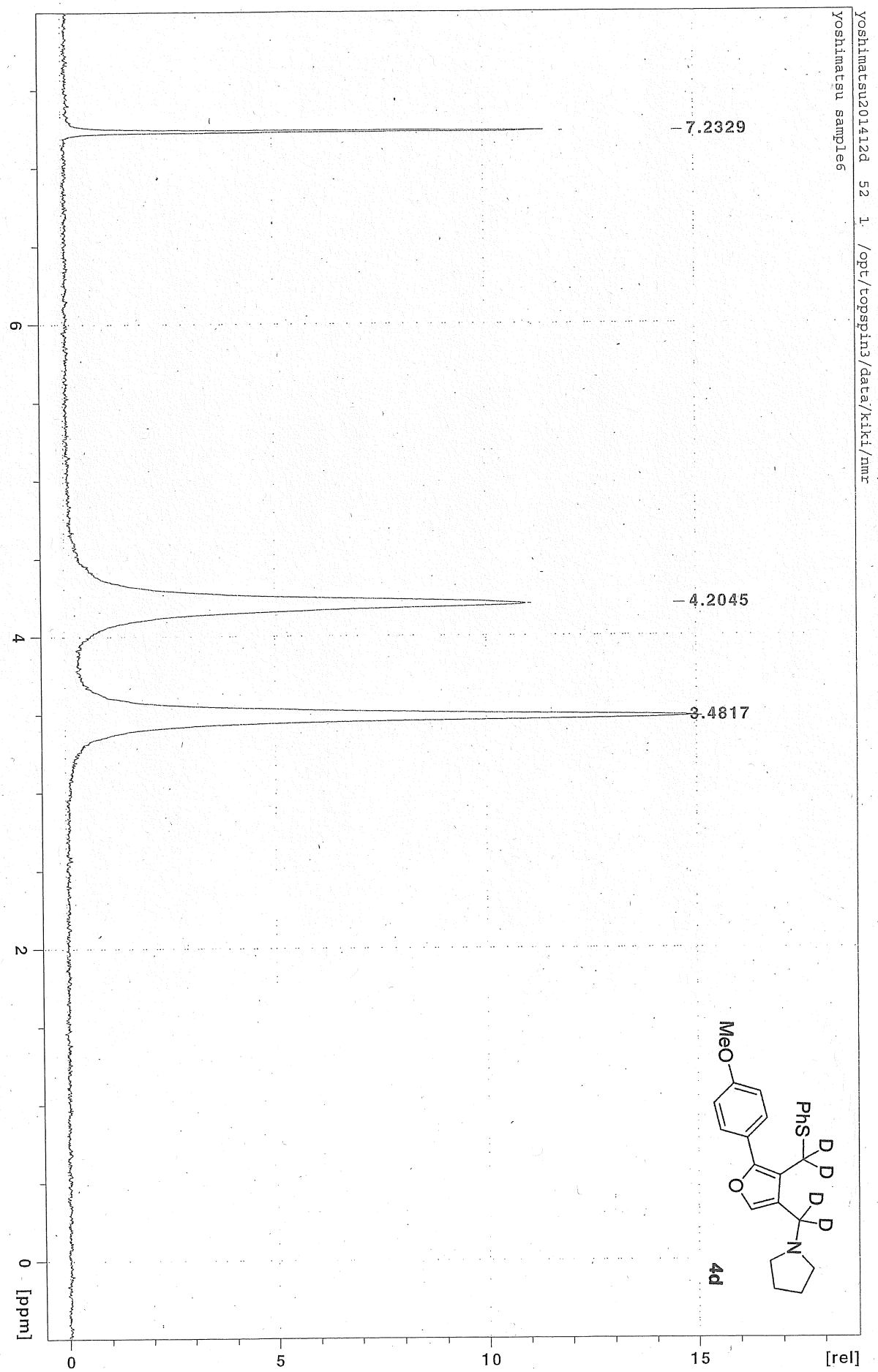

abundance
0
1.0
2.0
3.0
4.0
5.0
1H-3883.jdf
2014.12.04-Ito-No.536-fr1
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.6358
7.6152
7.4354
7.2933
7.2739
7.1857
7.0448
6.9749
6.9726
6.9692
6.9016
6.8981
6.8959
6.8409
0.4
0.19
0.4
0.93
0.18
0.17
0.17
0.17
4.9703
19.42m
3.6106
24.43m
2.4330
0.61
−0.0000
PhS
D D
D D
N
Tos
N
N
4c

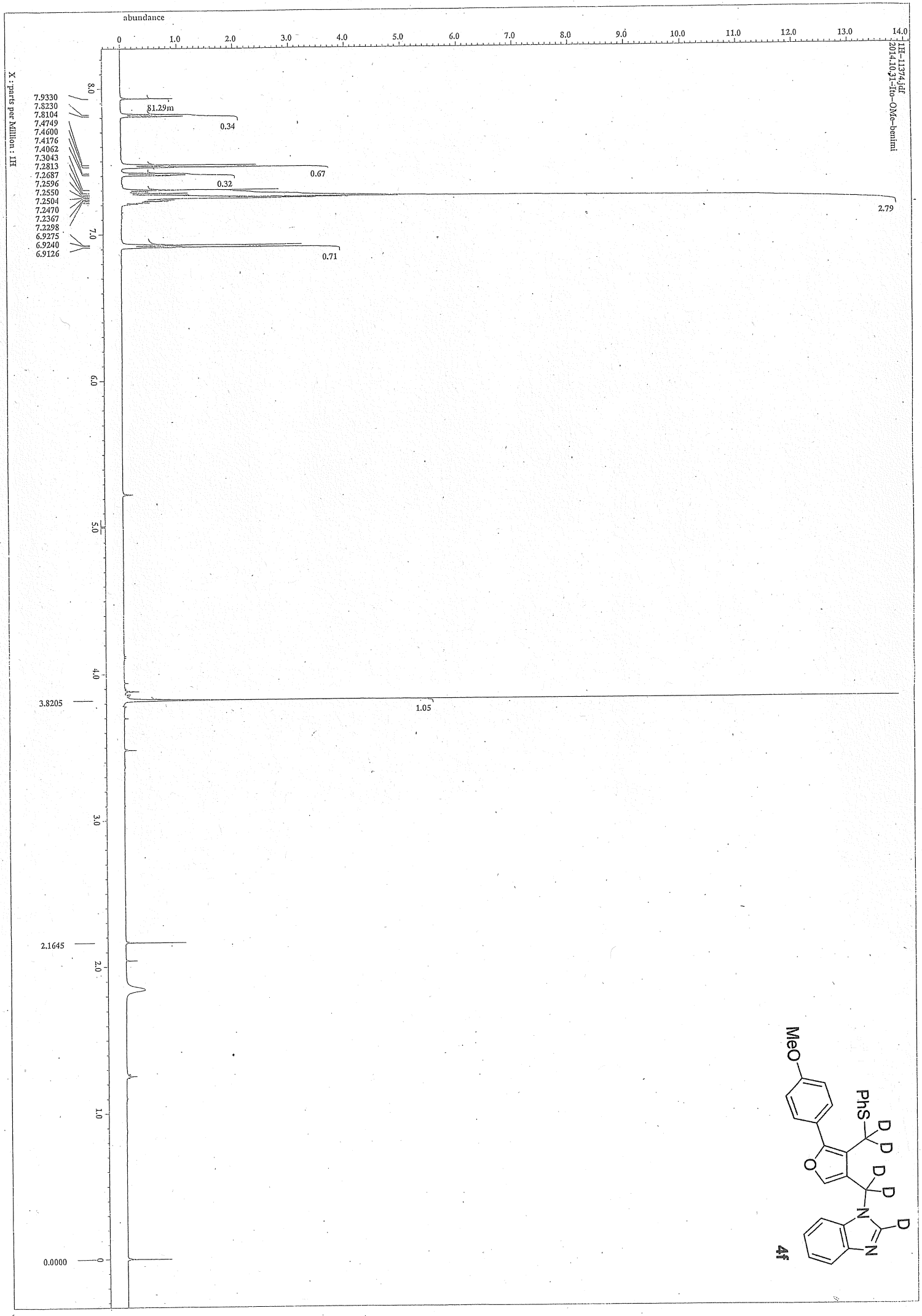

abundance
X : parts per Million : 13C
13C-153.jdf
2014.12.04-Ito-No.536-fr1
145.2962
137.0297
135.3516
134.6651
130.7274
130.0695
129.5451
128.8300
126.9040
126.7514
122.8709
122.4418
120.5444
119.8389
118.9331
77.3146
77.0000
76.6854
21.6327
PhS
D D
D D
N
Tos
N
N
4c

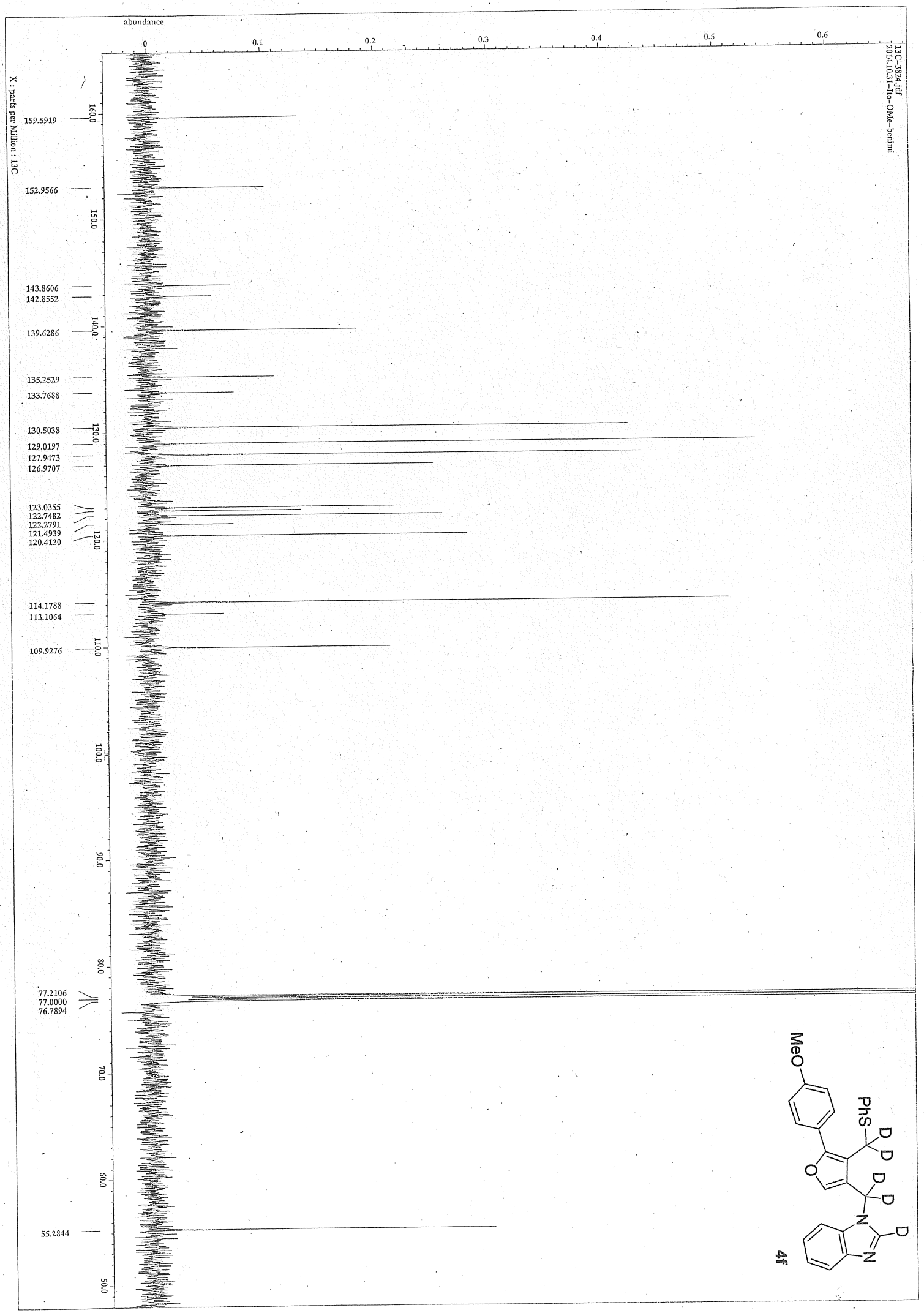

yoshimatsu201412d 92 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample10
7.2688
4.0757
3.6224
PhS
D D
D D
N
Tos
N
N
4c
8
6
4
2
0 [ppm]
0
5
10
15
[rel]

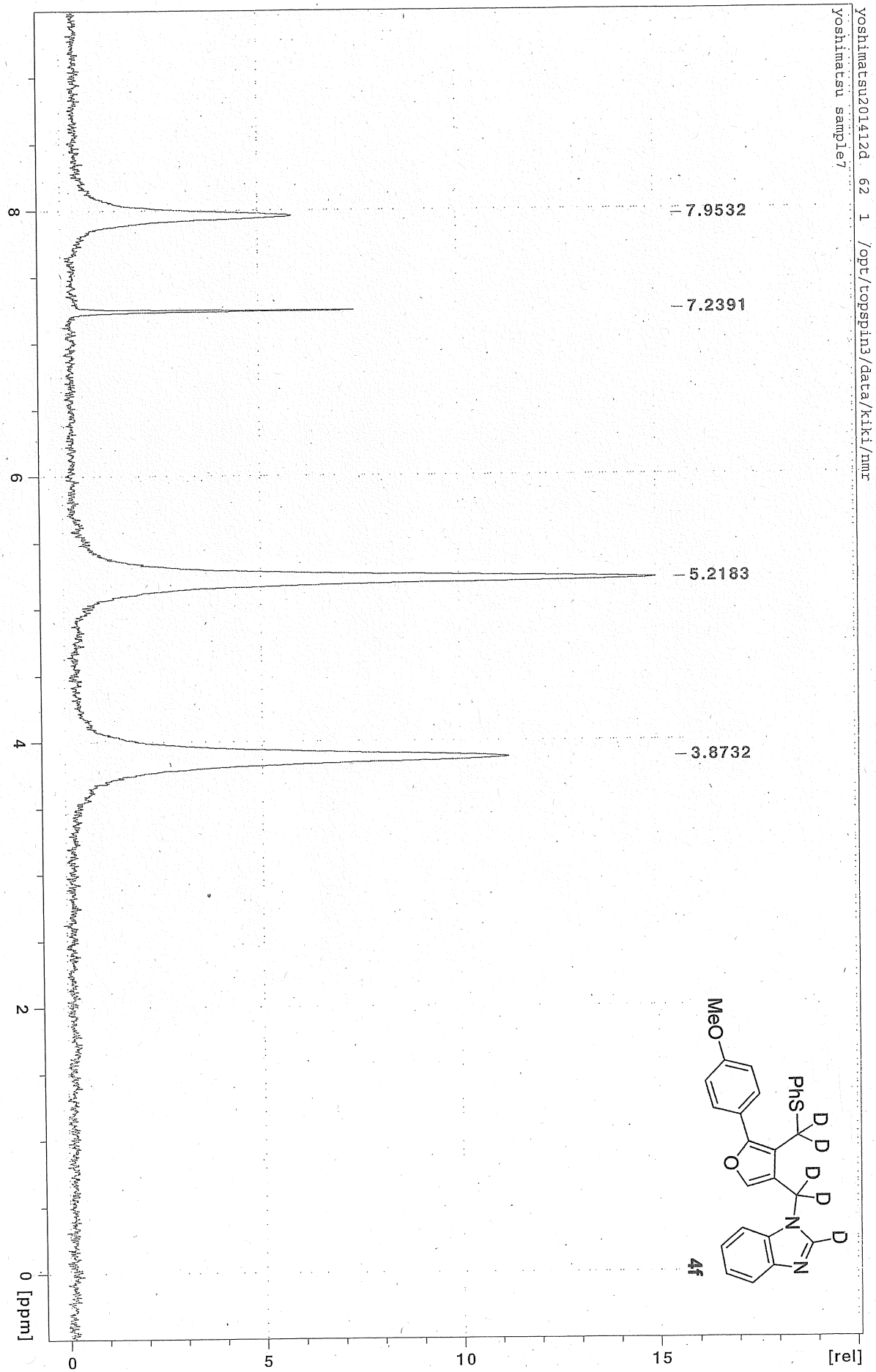

abundance
1H-11280.jdf
2014.10.21-Ito-B
X : parts per Million : 1H
7.5619
7.5470
7.3718
7.3592
7.3260
7.2779
7.2756
7.2665
7.2516
7.2046
7.1932
6.9286
6.9172
6.9137
4.2110
3.8205
3.5090
2.5665
1.7808
-0.0000
0.53
0.42
0.21
0.54
0.21
0.54
60.98m
0.8
1.04
1.06
MeO
PhS
D D
D D
O
N
4d

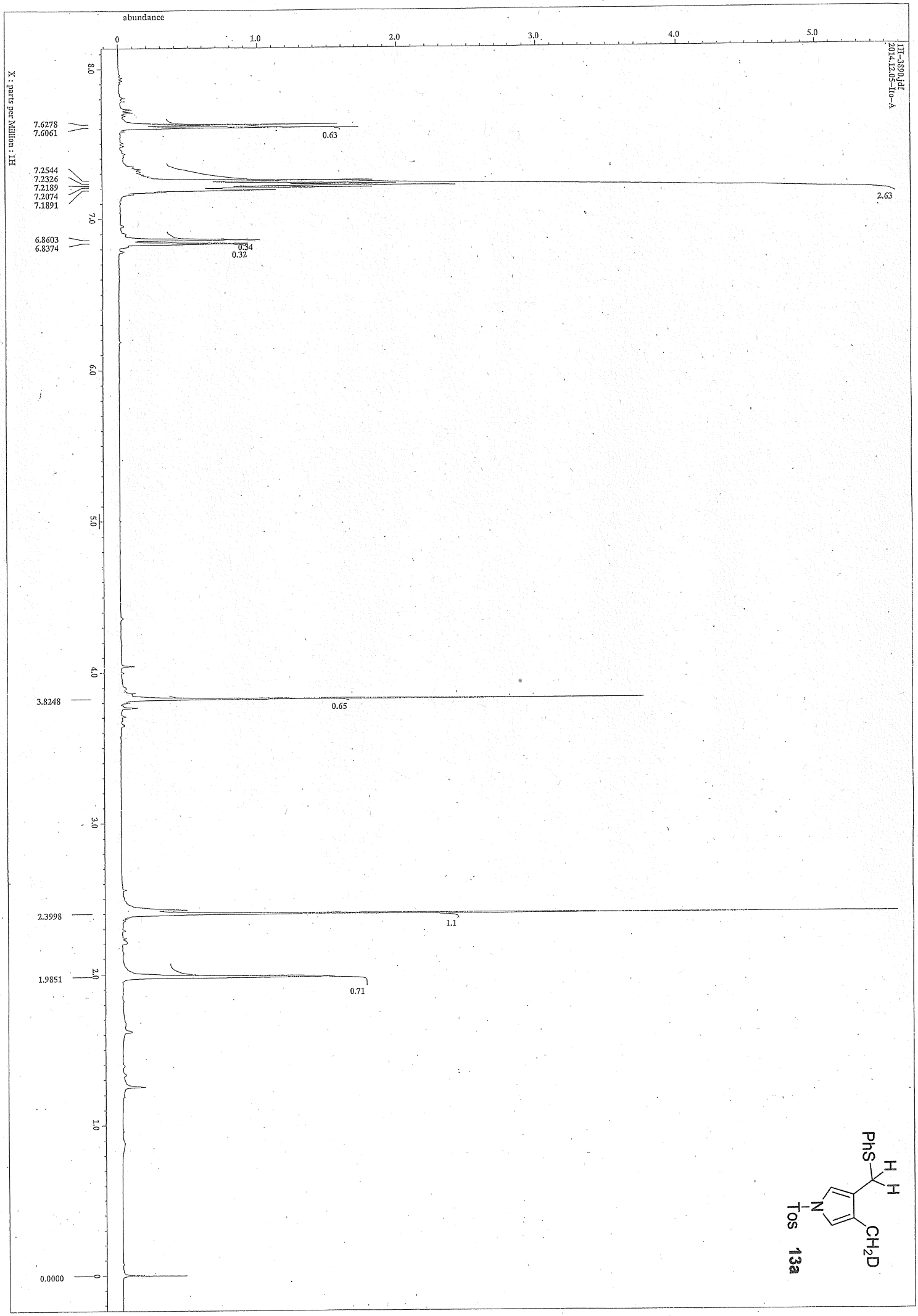

abundance
X : parts per Million : 13C
13C-153.jdf
2014.12.03-Ito-No.532-fr1
159.0164
151.2362
138.9843
136.7818
129.8406
128.8204
127.5047
126.2556
124.4155
123.7099
114.2611
114.0418
77.3146
77.0000
76.6854
55.2516
54.1933
23.5396
MeO
PhS
D D
D D
O
N
4d

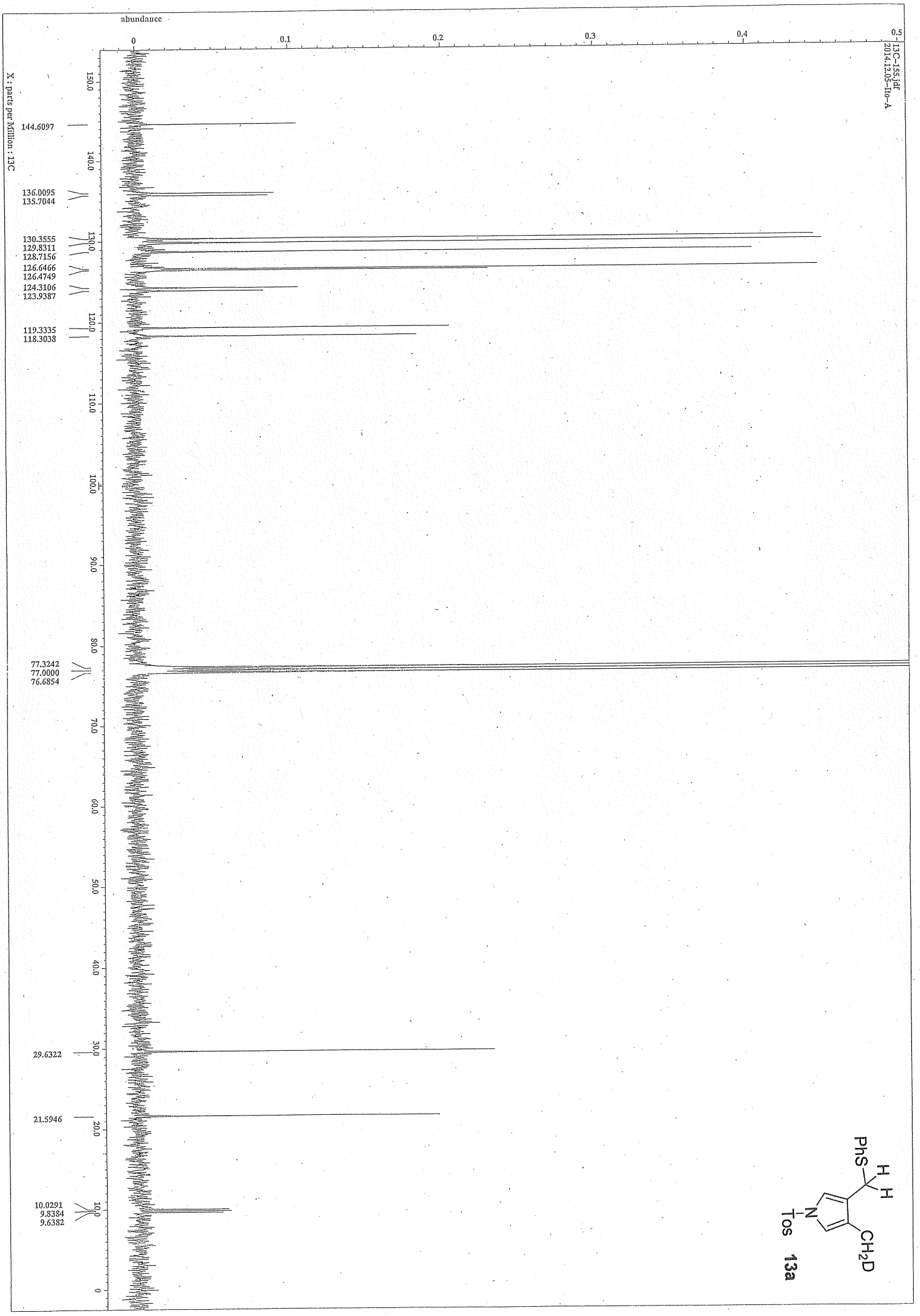

yoshimatsu20141 2d 52 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample6
7.2329
4.2045
3.4817
MeO
PhS
D D
D D
O
N
4d
0
2
4
6
[ppm]
0
5
10
15
[rel]

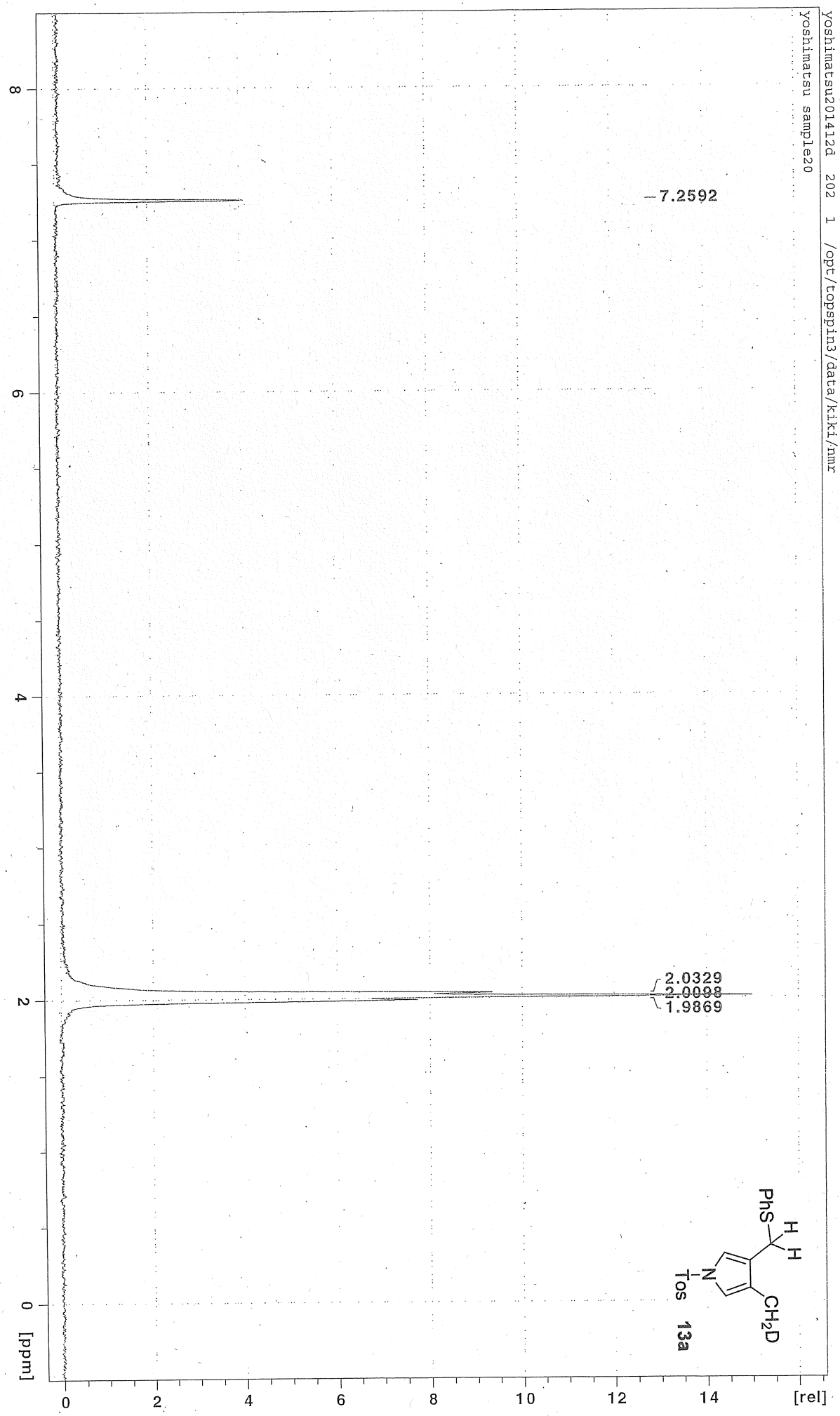

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
1H-11374.jdf
2014.10.31-1to-OMe-benimi
X : parts per Million : 1H
7.9330
7.8230
7.8104
7.4749
7.4600
7.4176
7.4062
7.3043
7.2813
7.2687
7.2596
7.2550
7.2504
7.2470
7.2367
7.2298
6.9275
6.9240
6.9126
81.29m
0.34
0.67
0.32
2.79
0.71
1.05
3.8205
2.1645
0.0000
MeO
PhS
D
D
D
D
D
O
N
N
4f

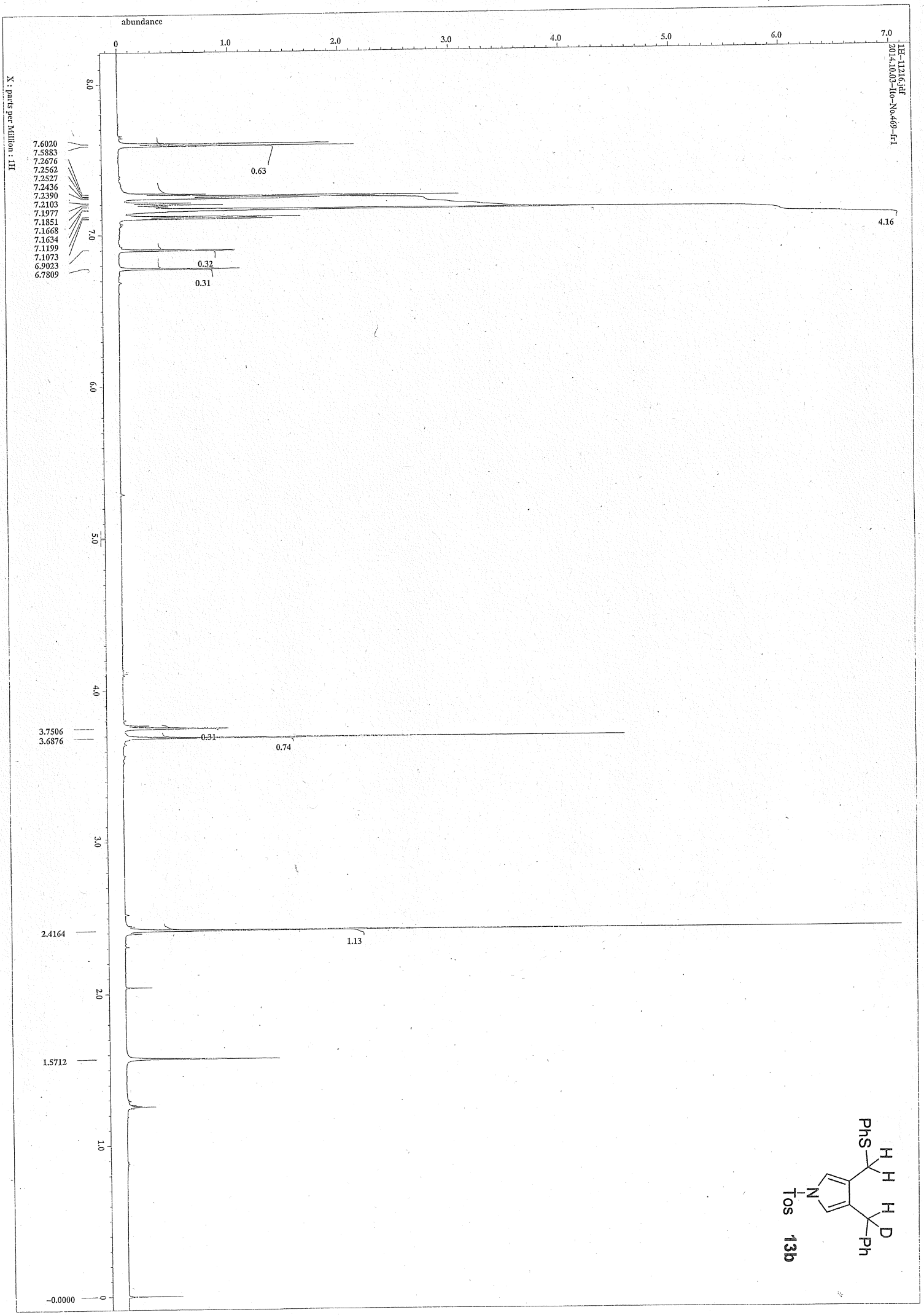

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
13C-3824.jdf
2014.10.31-Ito-OMe-benimi
X : parts per Million : 13C
159.5919
152.9566
143.8606
142.8552
139.6286
135.2529
133.7688
130.5038
129.0197
127.9473
126.9707
123.0355
122.7482
122.2791
121.4939
120.4120
114.1788
113.1064
109.9276
77.2106
77.0000
76.7894
55.2844
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
MeO
PhS
D
D
D
D
D
O
N
N
4f

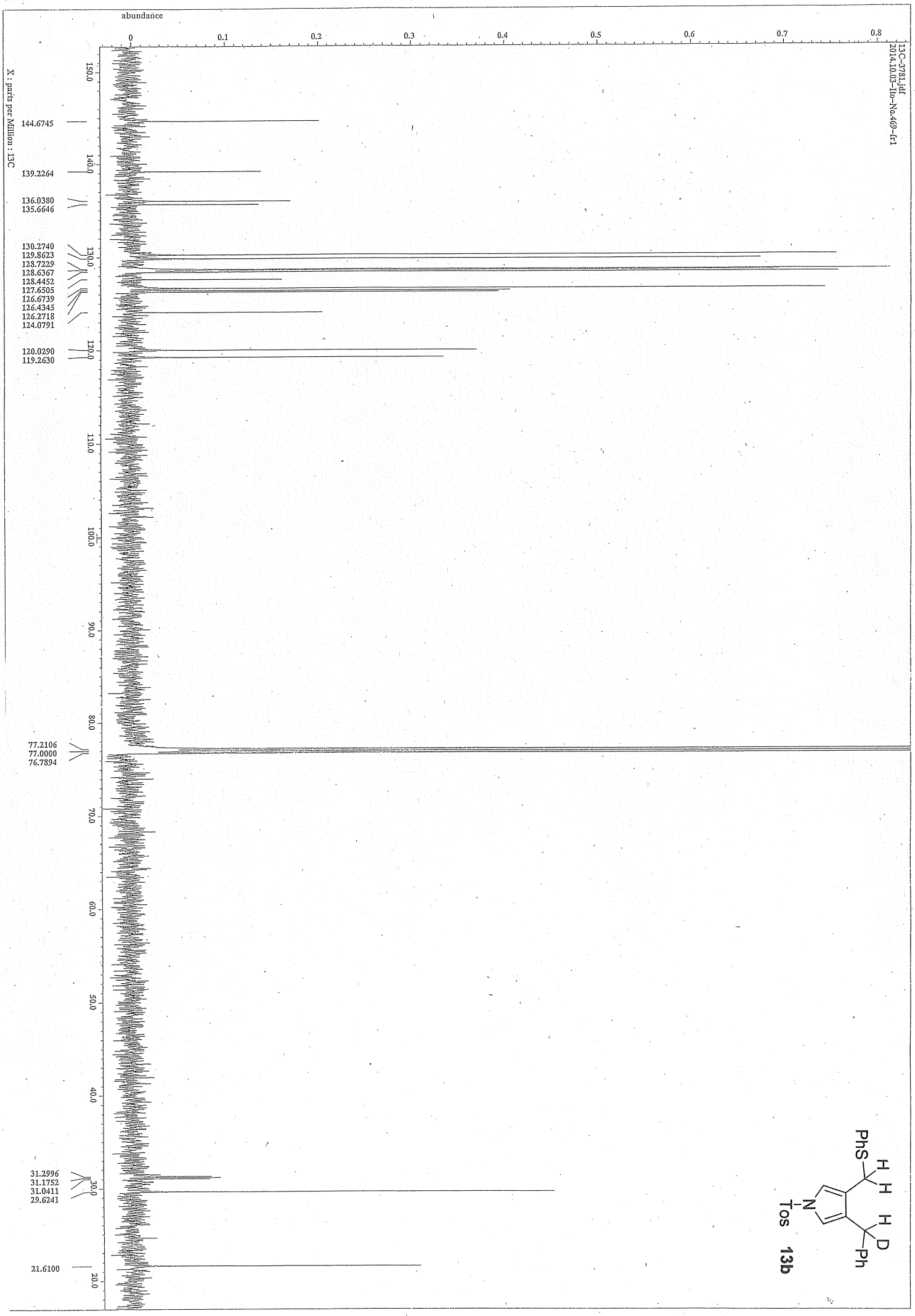

yoshimatsu2014i2d 62 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample7
7.9532
7.2391
5.2183
3.8732
MeO
PhS
D D
D D
D
N
N
O
4f
8
6
4
2
0 [ppm]
0
5
10
15
[rel]

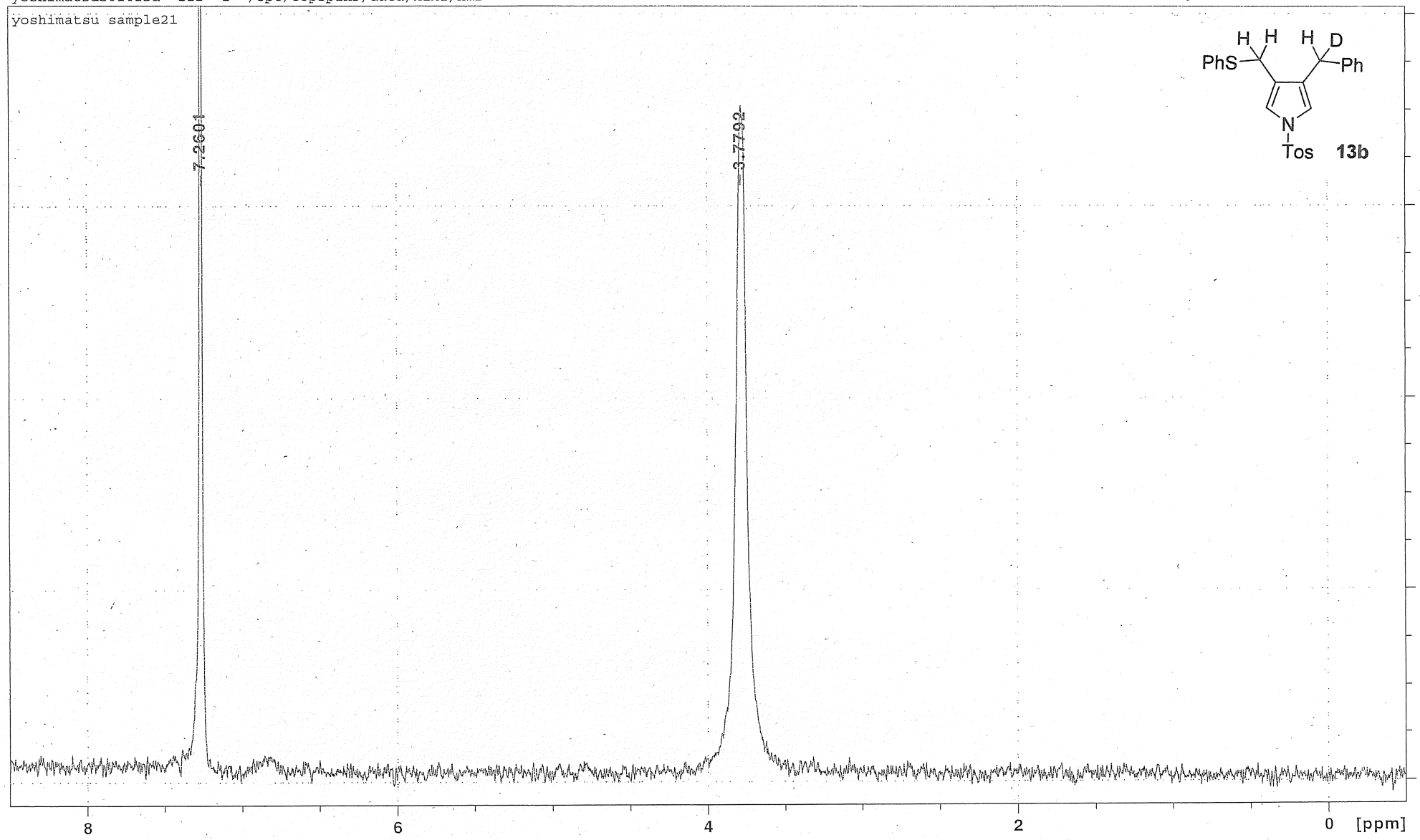

abundance
0
1.0
2.0
3.0
4.0
5.0
1H-3890.jdf
2014.12.05-1to-A
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.6278
7.6061
0.63
7.2544
7.2326
7.2189
7.2074
7.1891
2.63
6.8603
6.8374
0.34
0.32
3.8248
0.65
2.3998
1.1
1.9851
0.71
0.0000
PhS
H
H
N
Tos
CH2D
13a

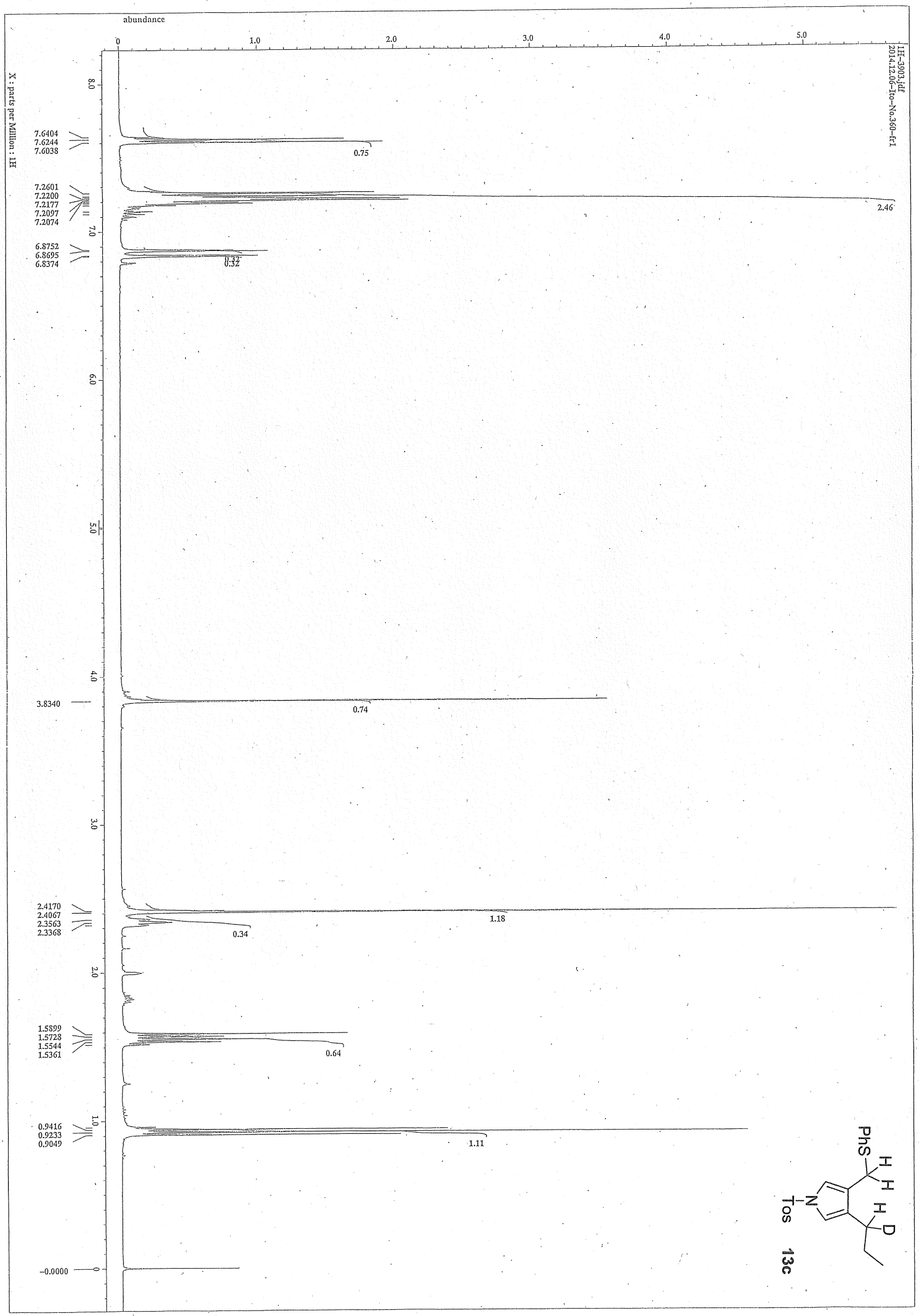

abundance
0
0.1
0.2
0.3
0.4
0.5
13C-155.jdf
2014.12.05-Ito-A
X : parts per Million : 13C
144.6097
136.0095
135.7044
130.3555
129.8311
128.7156
126.6466
126.4749
124.3106
123.9387
119.3335
118.3038
77.3242
77.0000
76.6854
29.6322
21.5946
10.0291
9.8384
9.6382
PhS
H H
N
Tos
CH2D
13a

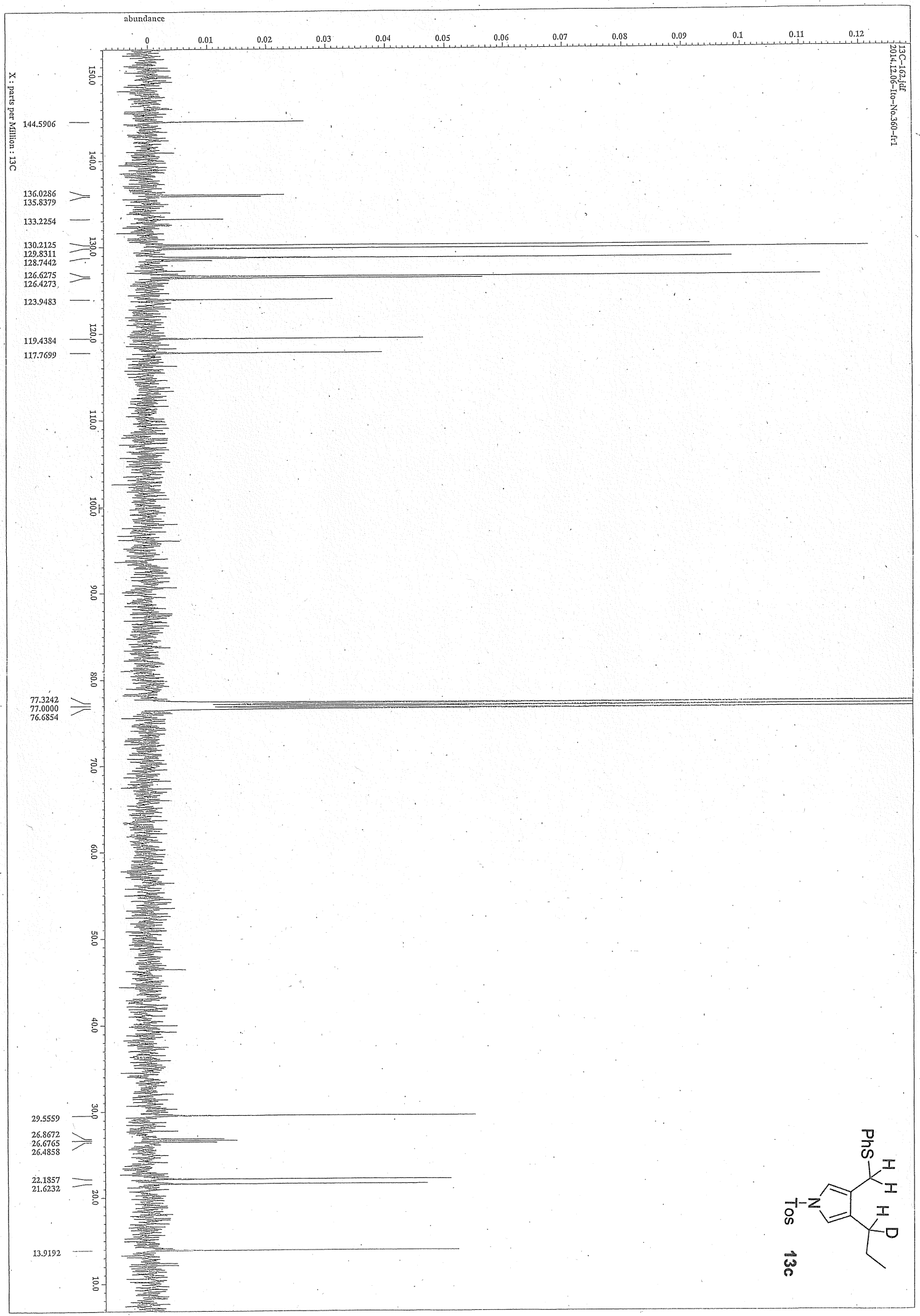

yoshimatsu201412d 202 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample20
7.2592
2.0329
2.0008
1.9869
PhS
H H
N
Tos
CH2D
13a
8
6
4
2
0 [ppm]
0
2
4
6
8
10
12
14
[rel]

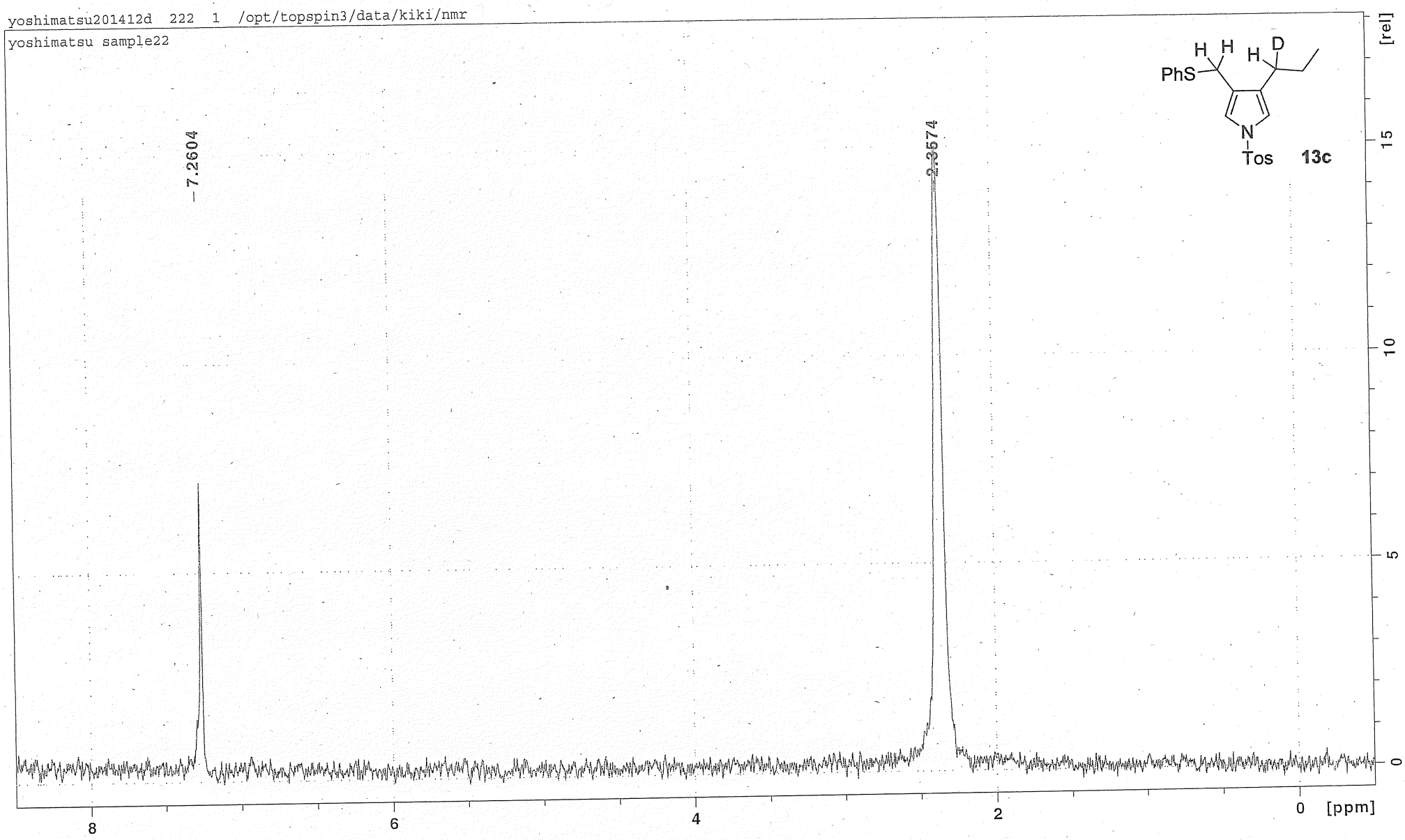

abundance
X : parts per Million : 1H
1H-11216.idf
2014.10.03-Ito-No.469-fr.1
7.6020
7.5883
7.2676
7.2562
7.2527
7.2436
7.2390
7.2103
7.1977
7.1851
7.1668
7.1634
7.1199
7.1073
6.9023
6.7809
3.7506
3.6876
2.4164
1.5712
-0.0000
0.63
4.16
0.32
0.31
0.31
0.74
1.13
PhS
H H
H D
N
Tos
Ph
13b

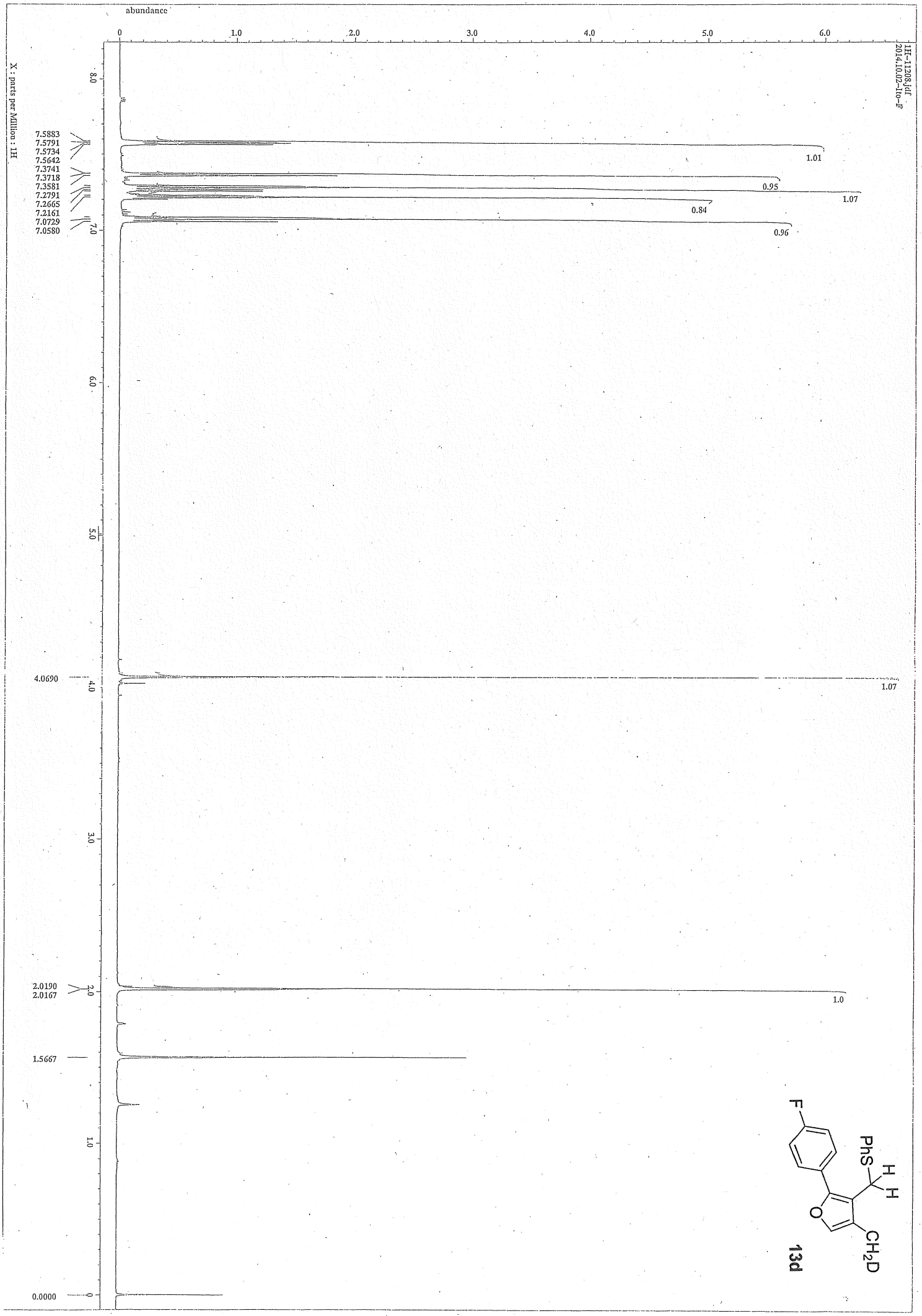

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
13C-3781.jdf
2014.10.03-Ito-No.469-fr1
X : parts per Million : 13C
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
144.6745
139.2264
136.0380
135.6646
130.2740
129.8623
128.7229
128.6367
128.4452
127.6505
126.6739
126.4345
126.2718
124.0791
120.0290
119.2630
77.2106
77.0000
76.7894
31.2996
31.1752
31.0411
29.6241
21.6100
PhS
H
H
H
D
Ph
N
Tos
13b

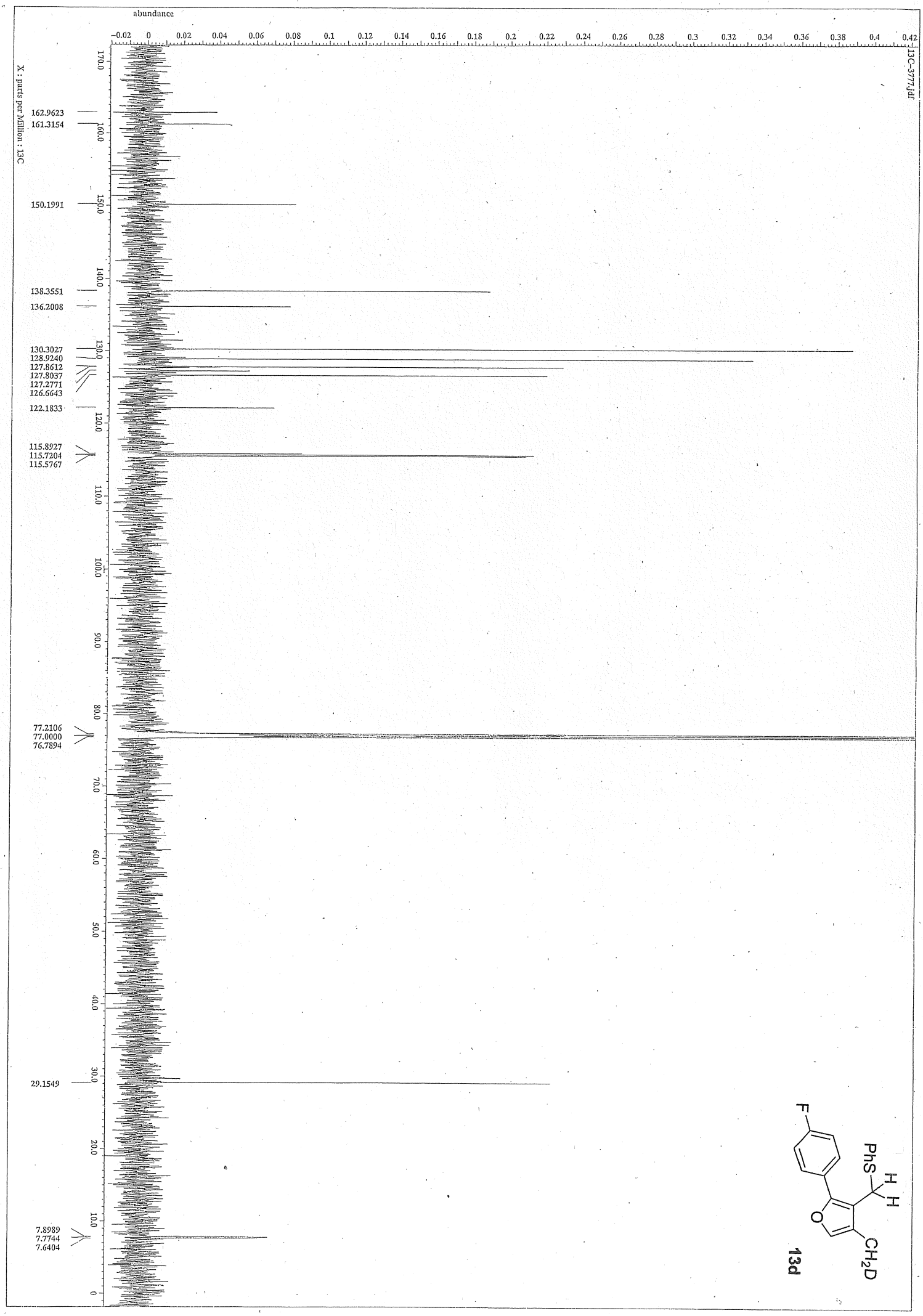

yoshimatsu201412d 212 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample21
7.2601
3.7792
H H H D
PhS
Ph
N
Tos
13b
[rel]
0
2
4
6
8
6
4
2
0
[ppm]

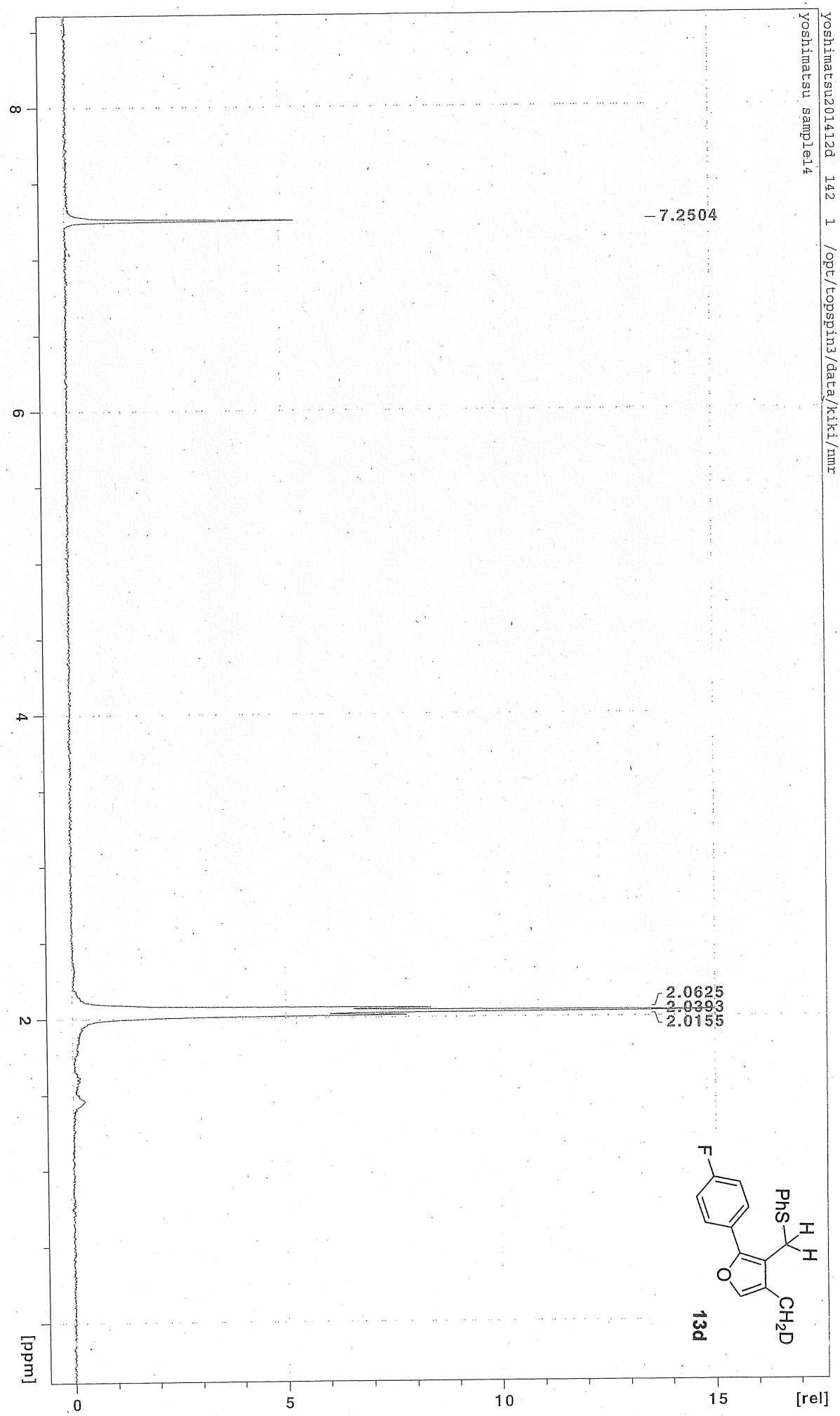

abundance
X : parts per Million : 1H
1H-3903.jdf
2014.12.06-Ito-No.360-fr.1
7.6404
7.6244
7.6038
7.2601
7.2200
7.2177
7.2097
7.2074
6.8752
6.8695
6.8374
3.8340
2.4170
2.4067
2.3563
2.3368
1.5899
1.5728
1.5544
1.5361
0.9416
0.9233
0.9049
-0.0000
0.75
2.46
0.32
0.74
1.18
0.34
0.64
1.11
PhS
H
H
H
D
N
Tos
13c

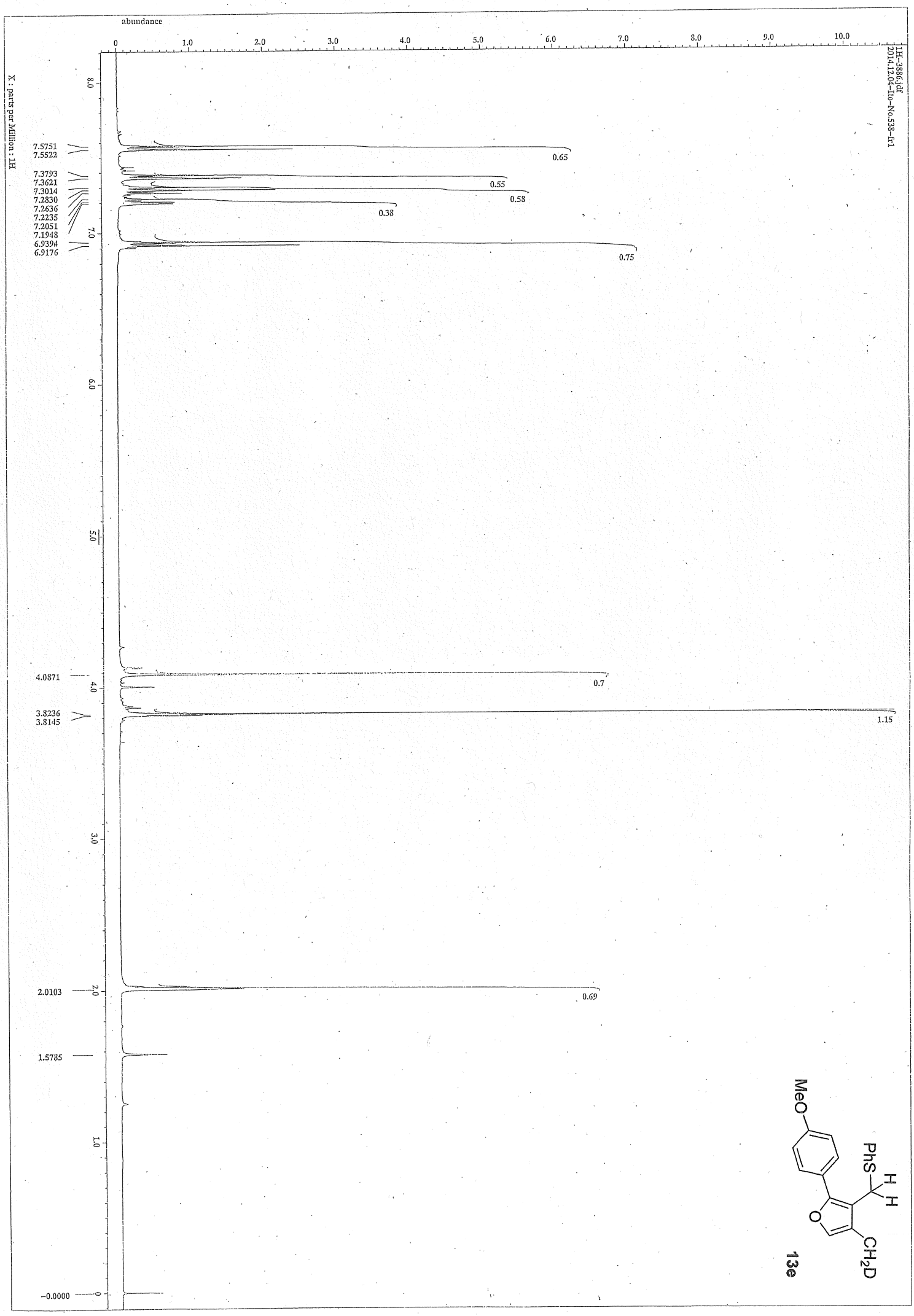

abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
13C-162.jdf
2014.12.06-Ito-No.360-fr1
X : parts per Million : 13C
144.5906
136.0286
135.8379
133.2254
130.2125
129.8311
128.7442
126.6275
126.4273
123.9483
119.4384
117.7699
77.3242
77.0000
76.6854
29.5559
26.8672
26.6765
26.4858
22.1857
21.6232
13.9192
PhS
H
H
H
D
N
Tos
13c

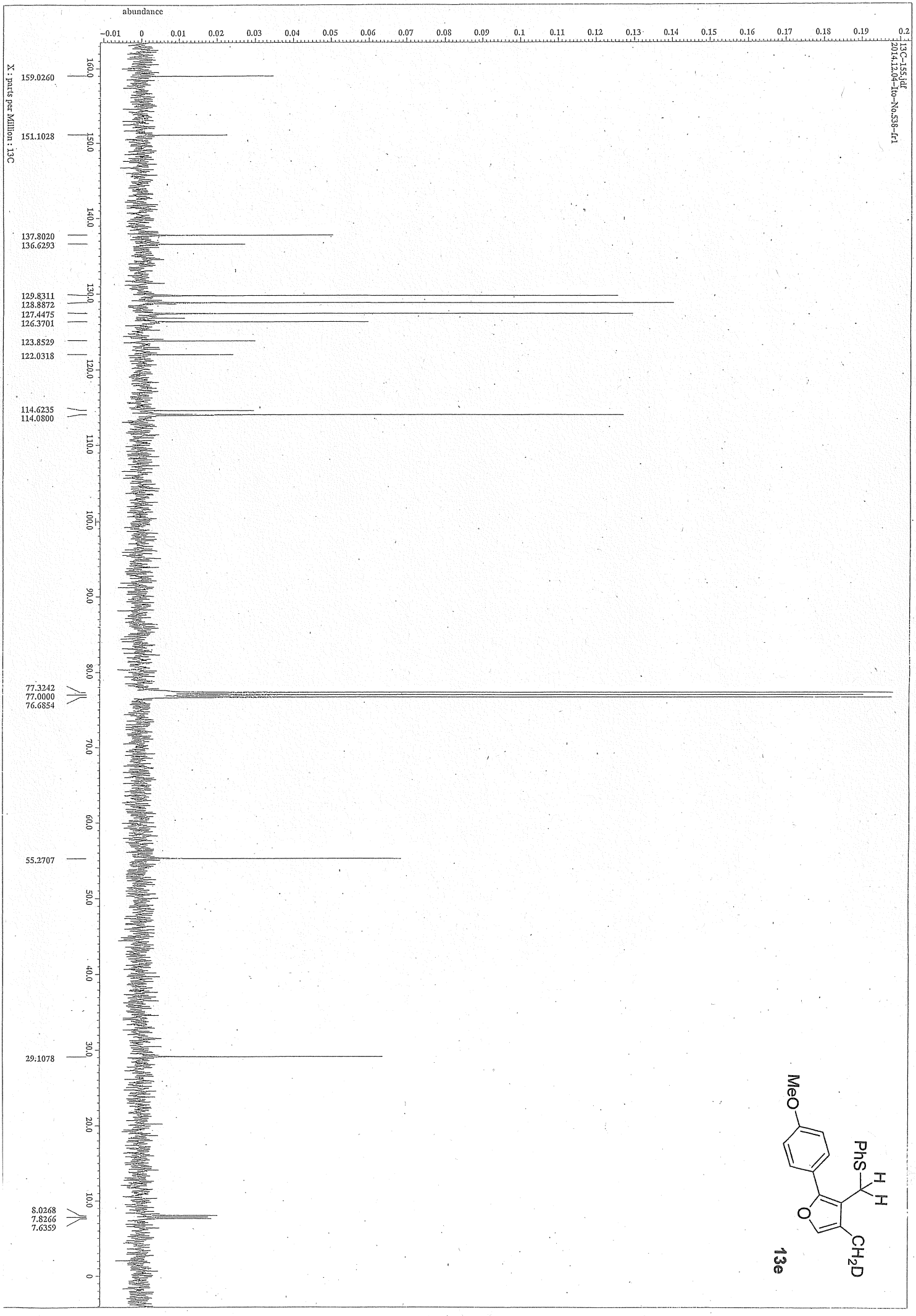

yoshimatsu201412d 222 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample22
7.2604
2.3574
H H H D
PhS
N
Tos
13c
[rel]
15
10
5
0
8
6
4
2
0
[ppm]

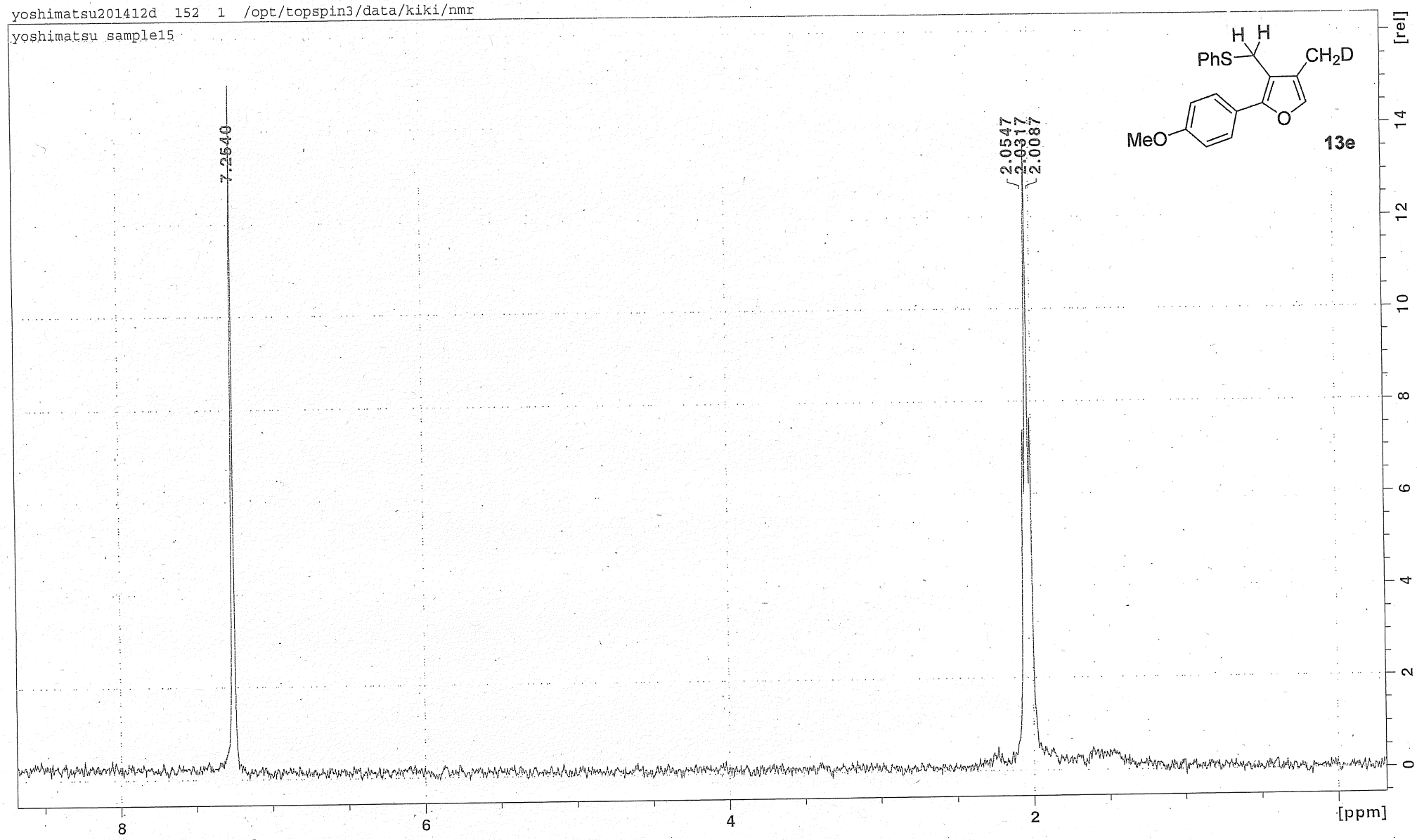

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
1H-11208.jdf
2014.10.02-1to-F
X : parts per Million : 1H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.5883
7.5791
7.5734
7.5642
7.3741
7.3718
7.3581
7.2791
7.2665
7.2161
7.0729
7.0580
1.01
0.95
1.07
0.84
0.96
4.0690
1.07
2.0190
2.0167
1.0
1.5667
F
PhS
H
H
O
CH2D
13d

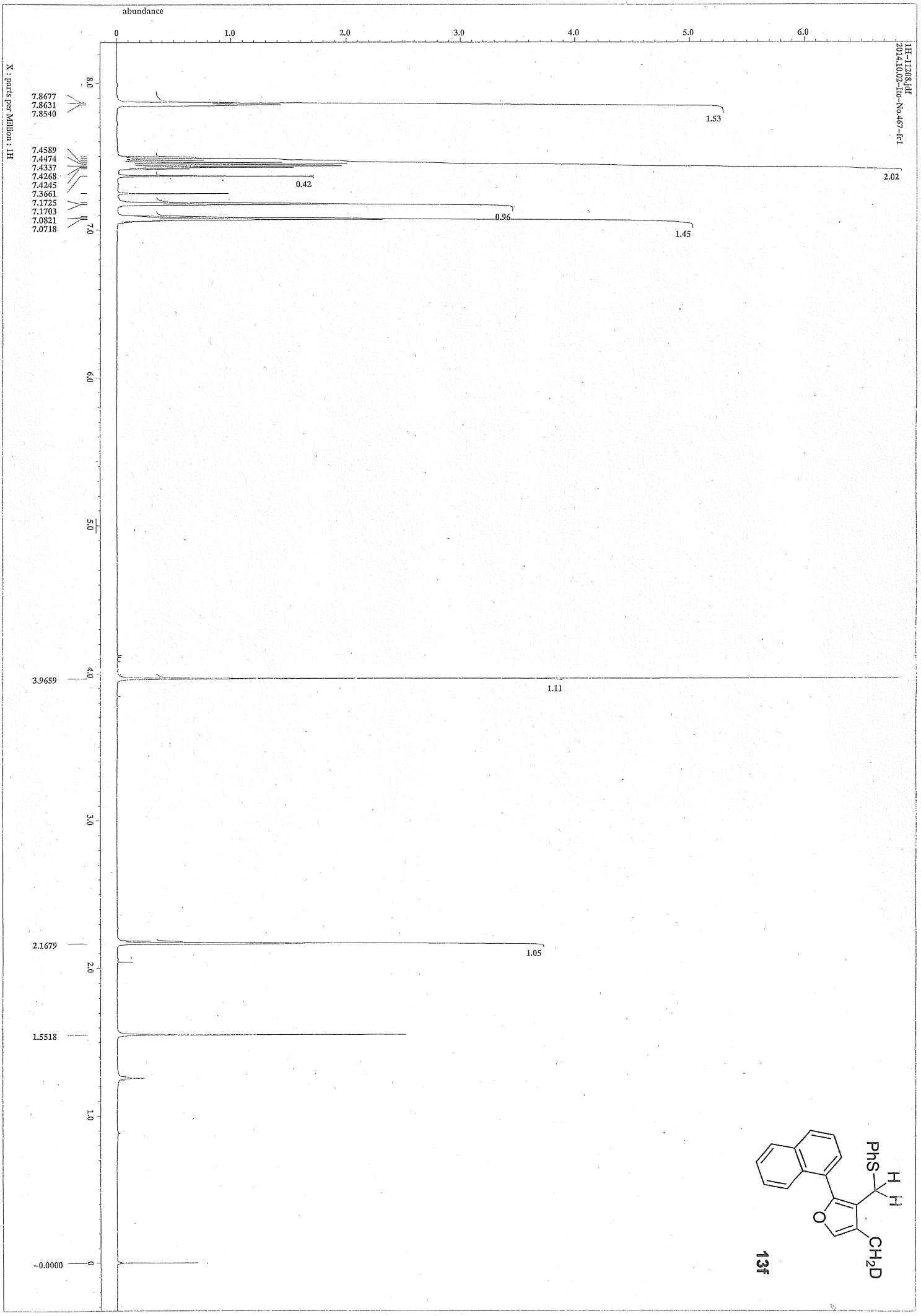

abundance
X : parts per Million : 13C
13C-3777.jdf
162.9623
161.3154
150.1991
138.3551
136.2008
130.3027
128.9240
127.8612
127.8037
127.2771
126.6643
122.1833
115.8927
115.7204
115.5767
77.2106
77.0000
76.7894
29.1549
7.8989
7.7744
7.6404
F
PhS
H
H
O
CH2D
13d

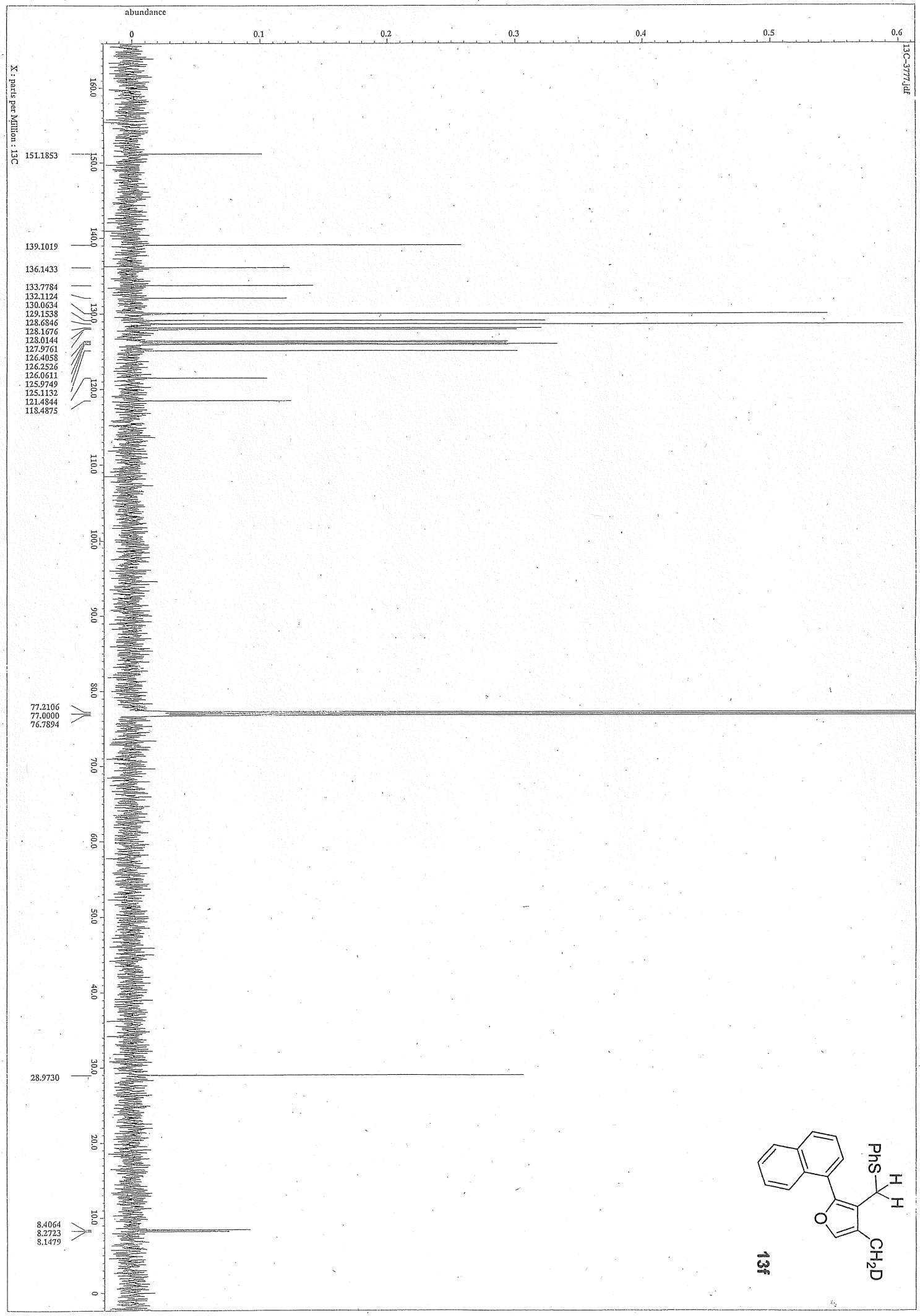

yoshimatsu20141204 142 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample14
7.2504
2.0625
2.0393
2.0155
F
PhS
H
H
O
CH2D
13d
8
6
4
2
[ppm]
0
5
10
15
[rel]

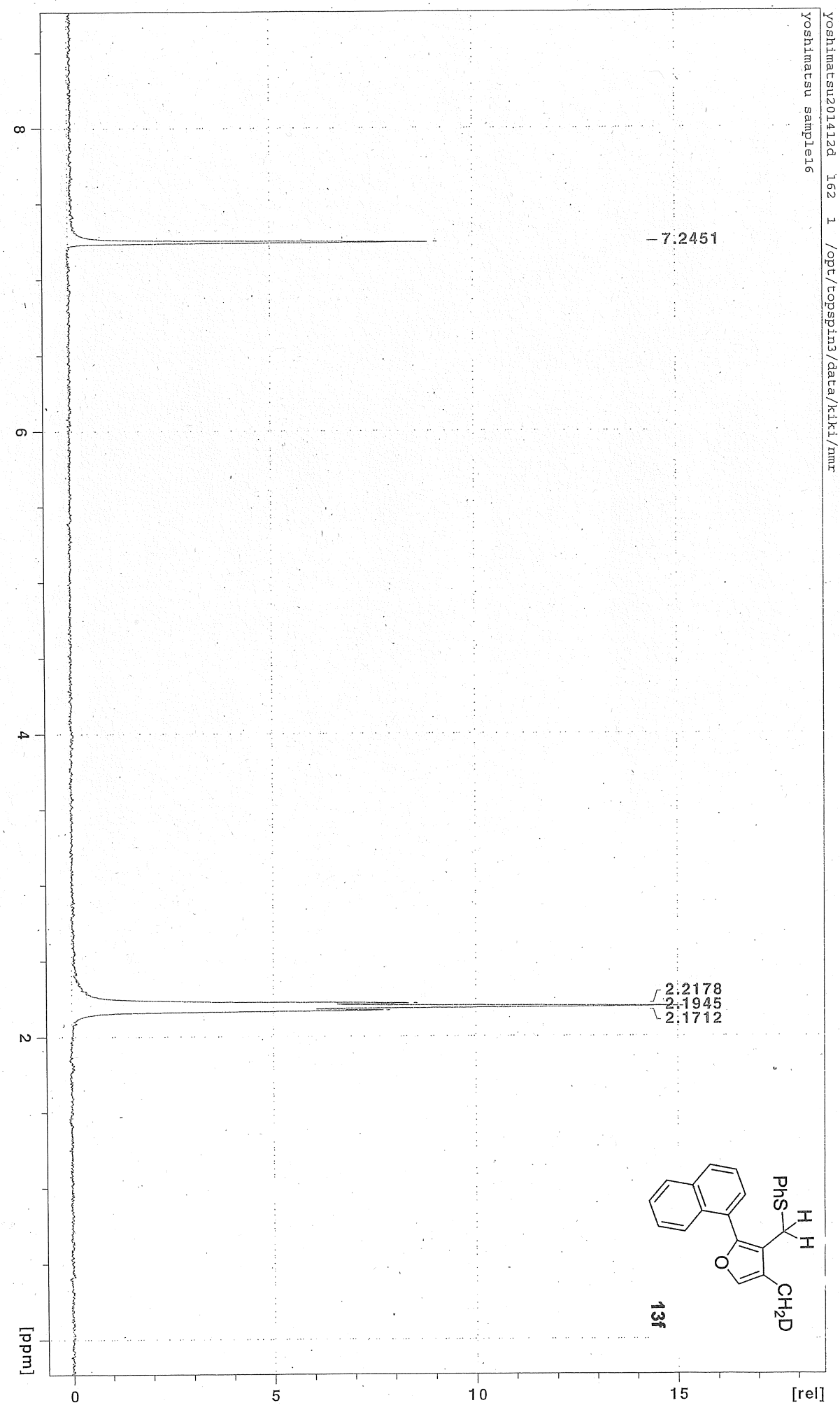

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
1H-3886.jdf
2014.12.04-Ito-No.538-fr1
X : parts per Million : 1H
7.5751
7.5522
7.3793
7.3621
7.3014
7.2830
7.2636
7.2235
7.2051
7.1948
6.9394
6.9176
4.0871
3.8236
3.8145
2.0103
1.5785
−0.0000
0.65
0.55
0.58
0.38
0.75
0.7
1.15
0.69
MeO
PhS
H H
O
CH2D
13e

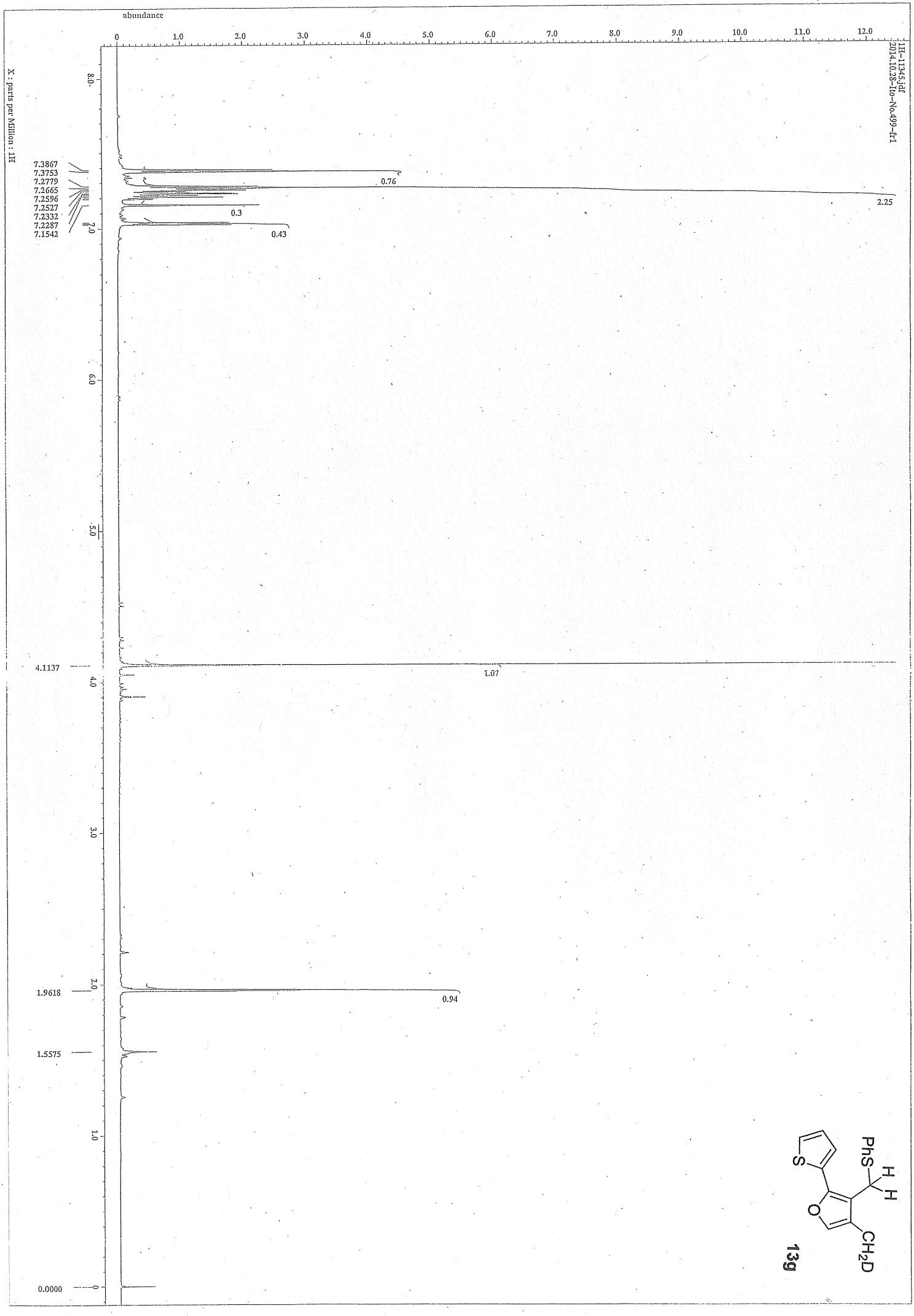

abundance
X : parts per Million : 13C
13C-155.1df
2014.12.04-1to-No.538-fr1
159.0260
151.1028
137.8020
136.6293
129.8311
128.8872
127.4475
126.3701
123.8529
122.0318
114.6235
114.0800
77.3242
77.0000
76.6854
55.2707
29.1078
8.0268
7.8266
7.6359
MeO
PhS
H H
O
CH2D
13e

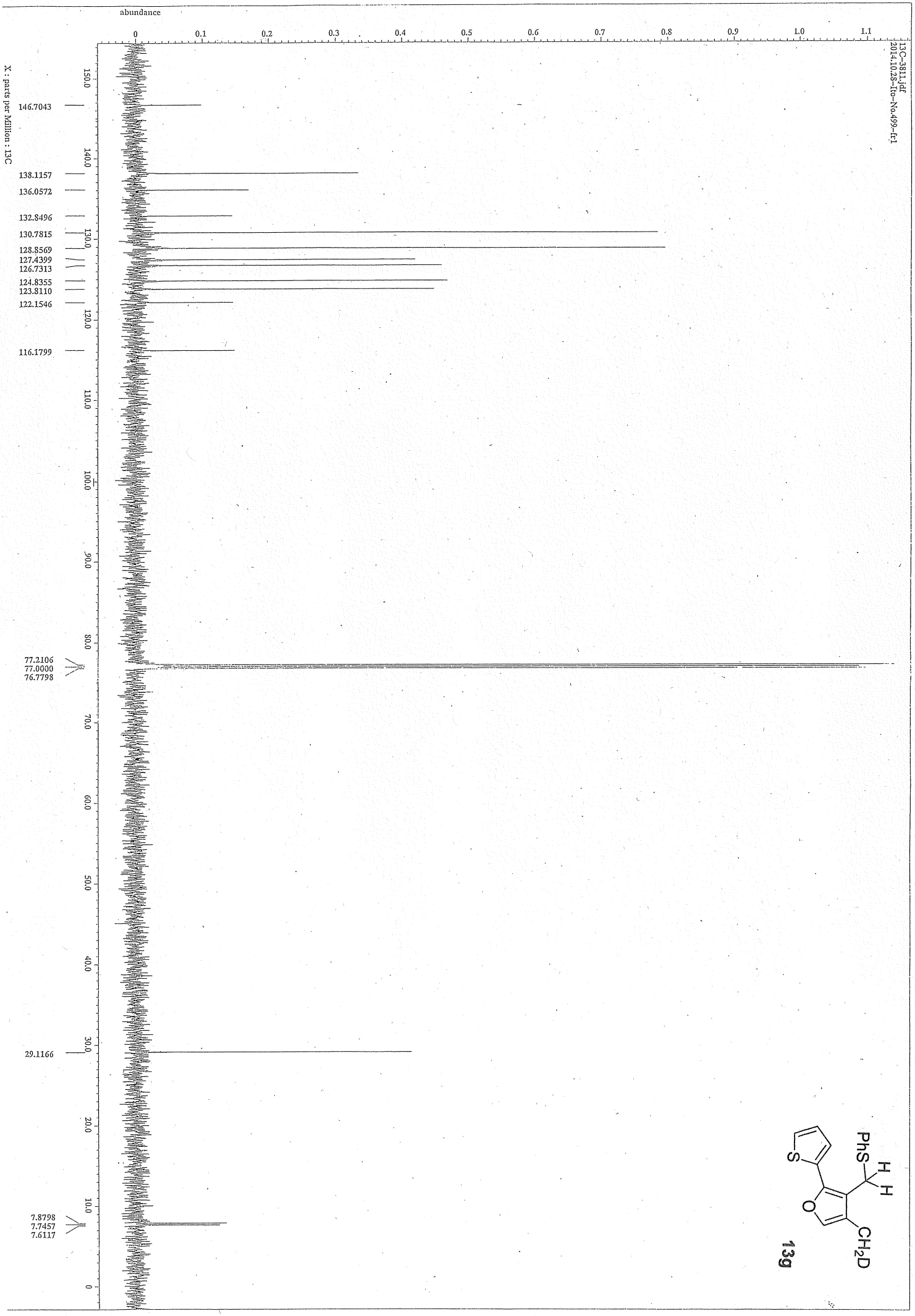

yoshimatsu201412d 152 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample15
7.2540
2.0547
2.0317
2.0087
H H
PhS
CH2D
O
MeO
13e
[rel]
0
2
4
6
8
10
12
14
8
6
4
2
[ppm]

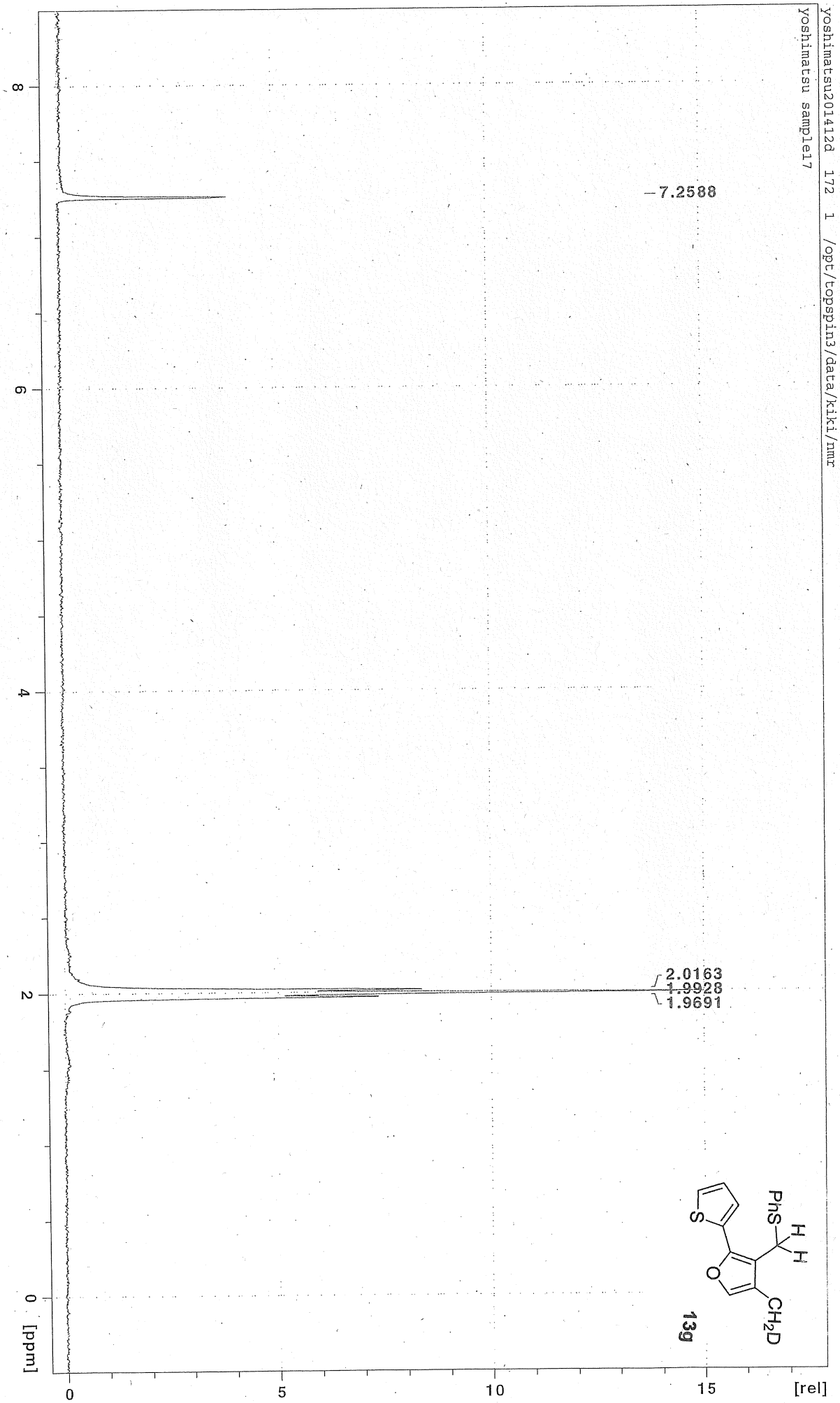

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
1H-11208.jdf
2014.10.02-1to-No.467-fr1
X : parts per Million : 1H
7.8677
7.8631
7.8540
7.4589
7.4474
7.4337
7.4268
7.4245
7.3661
7.1725
7.1703
7.0821
7.0718
1.53
2.02
0.42
0.96
1.45
3.9659
1.11
2.1679
1.05
1.5518
-0.0000
PhS
H
H
O
CH2D
13f


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
13C-3777.jdf
X : parts per Million : 13C
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
151.1853
139.1019
136.1433
133.7784
132.1124
130.0634
129.1538
128.6846
128.1676
128.0144
127.9761
126.4058
126.2526
126.0611
125.9749
125.1132
121.4844
118.4875
77.2106
77.0000
76.7894
28.9730
8.4064
8.2723
8.1479
PhS
H
H
O
CH2D
13f


yoshimatsu20141204 162 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample16
7.2451
2.2178
2.1945
2.1712
PhS
H
H
O
CH2D
13f
8
6
4
2
[ppm]
0
5
10
15
[rel]


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
1H-113455.jdf
2014.10.28-Ito-No.499-Fr1
X : parts per Million : 1H
7.3867
7.3753
7.2779
7.2665
7.2596
7.2527
7.2332
7.2287
7.1542
0.76
2.25
0.3
0.43
4.1137
1.07
1.9618
0.94
1.5575
0.0000
PhS
H H
S
O
CH2D
13g


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
13C-3811.jdf
2014.10.28-Ito-No.499-fr1
X : parts per Million : 13C
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
146.7043
138.1157
136.0572
132.8496
130.7815
128.8569
127.4399
126.7313
124.8355
123.8110
122.1546
116.1799
77.2106
77.0000
76.7798
29.1166
7.8798
7.7457
7.6117
S
O
H
H
PhS
CH2D
13g


yoshimatsu201412d 172 1 /opt/topspin3/data/kiki/nmr
yoshimatsu sample17
7.2588
2.0163
1.9928
1.9691
PhS
H H
S
O
CH2D
13g
8
6
4
2
0
[ppm]
0
5
10
15
[rel]