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Highly and Catalytic Enantioselective Reaction of α -Sulfonyl Carbanions Using Chiral Bis(oxazoline)s

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General. All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silicagel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or p-anisaldehyde in ethanol/ heat. Column chromatography was carried out on a column packed with silicagel 60N spherical neutral size 63-210 μ m. The ^1H -NMR (200 MHz), ^{19}F -NMR (188 MHz), and ^{13}C -NMR (50.3 MHz) spectra for solution in CDCl_3 , were recorded on a Varian Gemini-200. Chemical shifts (δ) are expressed in ppm downfield from internal TMS or CHCl_3 . HPLC analyses were performed on a JASCO PU-2080 Plus or SHIMADZU LC-2010A HT using 4.6 x 250 mm CHIRALPAK AD-H or CHIRALCEL OJ-H or CHIRALCEL OD-H or CHIRALPAK AS-H column. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A. Optical rotations were measured on a HORIBA SEPA-300. Infrared spectra were recorded on a JASCO FT/IR-200 spectrometer.

1,2-Diphenyl-2-(methylsulfonyl)ethanol (2a): starting **1a** (21.0 mg, 0.123 mmol), product **2a** (6.5 mg, 19%), *syn-2a*: 10% ee, *anti-2a*: 1% ee. *syn-2a*; ^1H NMR δ 2.96 (s, 3H), 3.55 (d, J = 2.2 Hz, 1H), 4.40 (d, J = 9.8 Hz, 1H), 5.61 (dd, J = 2.2, 9.8 Hz, 1H), 7.15-7.27 (m, 10H); IR (KBr) 3473, 3051, 3010, 2934, 2360, 1494, 1454, 1411, 1287, 1200, 1135, 1051, 966, 916, 861, 841, 788, 751, 695 cm^{-1} ; EIMS m/z 276 (M^+ , 17), 170 (100), 105 (55), 91, (93), 77 (63); HPLC (CHIRALCEL OD-H hexane:*i*PrOH = 70:30, flow rate 0.5 ml/min), t_R 14.8 (major) and 18.6 (minor) min. *anti-2a*; ^1H NMR δ 2.71 (s, 3H), 3.91 (d, J = 2.7 Hz, 1H), 4.16 (d, J = 2.7 Hz, 1H), 6.01 (br, 1H), 7.21-7.41 (m, 10H); IR (KBr) 3452, 2921, 2853, 2356, 1496, 1454, 1297, 1218, 1193, 1136, 1060, 973, 818, 760, 700 cm^{-1} ; EIMS m/z 276 (M^+ , 14), 170 (83), 105 (30), 91 (100), 77, (71), 64 (35); HPLC (CHIRALCEL OD-H hexane:*i*PrOH = 80:20, flow rate 0.5 ml/min), t_R 21.7 (major) and 29.6 (minor) min

1,2-Diphenyl-2-[(2,2-dimethylethyl)sulfonyl]ethanol (2b): starting **1b** (24.2 mg, 0.114 mmol), product **2b** (25.8 mg, 71%), *syn-2b*: 29% ee, *anti-2b*: 21% ee. *syn-2b*; ^1H NMR δ 1.25 (s, 9H), 4.56 (d, J = 9.2 Hz, 1H) 5.06 (d, J = 1.3 Hz, 1H), 5.62 (dd, J = 1.3, 9.2 Hz, 1H), 7.06-7.27 (m, 10H); ^{13}C NMR δ 24.1, 63.5, 70.7, 74.6, 127.2, 127.7, 128.2, 128.3, 130.0, 131.7, 138.9; IR (KBr) 3478, 2979, 2916, 2360, 1558, 1495, 1455, 1399, 1274, 1241, 1199, 1099, 1037, 916, 782, 764, 701, 669, 625 cm^{-1} ; EIMS m/z 318 (M^+ , 1), 212 (27),

156 (61), 139 (29), 91 (24), 57 (100); HPLC (CHIRALPAK AD-H hexane:iPrOH = 80:20, flow rate 1.0 ml/min), t_R 16.7 (minor) and 22.5 (major) min. *anti-2b*; 1H NMR 1.25 (s, 9H), 3.55 (d, J = 3.6 Hz, 1H), 4.25 (d, J = 3.6 Hz, 1H), 6.13 (br, 1H), 7.15-7.32 (m, 10H); IR (KBr) 3434, 2933, 2362, 1558, 1493, 1455, 1365, 1280, 1214, 1107, 1059, 791, 761, 715, 700, 659 cm^{-1} ; EIMS m/z 318 (M^+ , 6), 212 (33), 156 (100), 107 (48), 105 (42), 91 (39), 57 (93); Anal. Calcd for $C_{18}H_{22}O_3S$: C, 67.90; H, 6.96. Found: C, 67.57; H, 7.29. HPLC (CHIRALPAK AD-H hexane:iPrOH = 90:10, flow rate 1.0 ml/min), t_R 17.1 (major) and 24.5 (minor) min.

1,2-Diphenyl-2-(phenylsulfonyl)ethanol (2c): starting **1c** (26.5 mg, 0.114 mmol), product **2c** (32.2 mg, 83%), *syn-2c*: 32% ee, *anti-2c*: 41% ee. *syn-2c*; 1H NMR δ 4.45 (d, J = 9.6 Hz, 1H), 4.53 (br, 1H) 5.76 (d, J = 9.6 Hz, 1H), 6.89-7.56 (m, 15H); ^{13}C NMR δ 73.9, 74.6, 127.2, 127.9, 128.3, 128.5, 128.7, 130.1, 130.5, 133.6, 137.3, 139.2; IR (KBr) 3480, 2927, 1507, 1455, 1290, 1139, 1085, 802, 756, 697 cm^{-1} ; EIMS m/z 338 (M^+ , 7), 232 (99), 197 (15), 105 (58), 91 (88), 77 (100); Anal. Calcd for $C_{20}H_{18}O_3S$: C, 70.98; H, 5.36. Found: C, 70.87; H, 5.37; HPLC (CHIRALCEL OD-H hexane:iPrOH = 70:30, flow rate 1.2 ml/min), t_R 10.0 (major) and 24.7 (minor) min. *anti-2c*; 1H NMR δ 3.48 (d, J = 2.7 Hz, 1H), 4.17 (d, J = 2.7 Hz, 1H), 6.02 (br, 1H), 7.04-7.66 (m, 15H); IR (KBr) 3477, 2976, 1495, 1455, 1274, 1198, 1100, 1037, 783, 764, 701 cm^{-1} ; EIMS m/z 338 (M^+ , 6), 232 (100), 197 (12), 91 (91), 77 (64). HPLC (CHIRALCEL OD-H hexane:iPrOH = 90:10, flow rate 0.6 ml/min), t_R 19.7 (major) and 24.0 (minor) min.

1,2-Diphenyl-2-(pentafluorophenylsulfonyl)ethanol (2d): starting **1d** (36.3 mg, 0.113 mmol), product **2d**: (34.4 mg, 71%), *syn-2d*: 23% ee, *anti-2d*: 14% ee. *syn-2d*; 1H NMR δ 2.88 (br, 1H), 4.72 (d, J = 9.9 Hz, 1H), 5.70 (d, J = 9.9 Hz, 1H), 7.13-7.34 (m, 10H); ^{13}C NMR δ 73.9, 74.6, 127.2, 127.9, 128.3, 128.5, 128.7, 130.1, 130.5, 133.6, 137.3, 139.2; ^{19}F NMR δ -158.2- -134.8 (m); IR (KBr) 3507, 2954, 1644, 1522, 1495, 1455, 1401, 1323, 1299, 1150, 1103, 1060, 987, 755, 715, 696, 659, 616 cm^{-1} ; EIMS m/z 428(M^+ , 3), 107 (100), 91 (48), 77 (37). Anal. Calcd for $C_{20}H_{13}F_5O_3S$: C, 56.08; H, 3.06. Found: C, 55.70; H, 3.44. HPLC (CHIRALCEL OD-H hexane:iPrOH = 95:5, flow rate 1.2 ml/min), t_R 17.3 (minor) and 28.5 (major) min. *anti-2d*; 1H NMR δ 3.48 (d, J = 2.7 Hz, 1H), 4.17 (d, J = 2.7 Hz, 1H), 6.02 (br, 1H), 7.04-7.66 (m, 15H); ^{19}F NMR δ -157.7- -133.9 (m); IR (KBr) 3540, 2922, 1646, 1522, 1494, 1456, 1397, 1337, 1294, 1148, 1100, 1026, 988, 765, 719, 703, 658, 611 cm^{-1} ; EIMS m/z 428 (M^+ , 3), 322 (6), 107 (100), 91 (52), 77 (34), 51 (10). HPLC (CHIRALCEL OD-H hexane: iPrOH = 95:5, flow rate 1.2 ml/min), t_R 26.0 (minor) and 34.1 (major) min

1,2-Diphenyl-2-(2-pyridylsulfonyl)ethanol (2e): starting **1e** (22.5 mg, 0.096 mmol), product **2e** (21.5 mg, 66%), *syn-2e*: 4% ee, *anti-2e*: 8% ee. *syn-2e*; ^1H NMR δ 4.04 (d, 1H, $J = 2.2$ Hz), 5.11 (d, 1H, $J = 9.8$ Hz), 5.73 (dd, 1H, $J = 2.2, 9.8$ Hz), 7.04-7.18 (m, 10H), 7.42-7.47 (m, 1H), 7.72-7.76 (m, 2H), 8.71-8.75 (m, 1H); IR (KBr) 3276, 3031, 2979, 1654, 1455, 1308, 1147, 1113, 982, 916, 761, 699, 648 cm^{-1} ; EIMS m/z 339 (M^+ , 3), 274 (10), 169 (27), 149 (58), 84 (37), 57 (100); HPLC(CHIRALCEL AD-H hexane: *i*PrOH = 85:15, flow rate 1.0 ml/min), t_R 37.3 (major) and 41.8 (minor) min. *anti-2e*; ^1H NMR δ 3.89 (d, $J = 2.6$ Hz, 1H), 4.88 (d, $J = 3.0$ Hz, 1H), 5.97 (t, $J = 2.7$ Hz, 1H), 7.06-7.35 (m, 10H), 7.41-7.48 (m, 1H), 7.74-7.70 (m, 2H), 8.70-8.73 (m, 1H); IR (KBr) 3467, 27924, 1578, 1453, 1312, 1160, 1109, 799, 701 cm^{-1} ; EIMS m/z 339 (M^+ , 15), 167 (18), 149 (36), 71 (39), 57 (100); HPLC(CHIRALPAK AD-H hexane: *i*PrOH = 85:15, flow rate 1.0 ml/min), t_R 25.2 (major) and 35.0 (minor) min.

1-(4-Methylphenyl)-2-phenyl-2-(trifluoromethylsulfonyl)ethanol (5): starting **1f** (24.0 mg, 0.107 mmol), product **5**: (25.9 mg, 70%), *syn-5*: 94% ee. *syn-5*; $[\alpha]_D^{26} +10.4$ (c 0.79, CHCl_3 , 94% ee); ^1H NMR δ 2.22 (s, 3H), 2.95 (br, 1H), 4.75 (d, $J = 9.9$ Hz, 1H), 5.56 (d, $J = 9.9$ Hz, 1H), 6.98-7.28 (m, 9H); ^{19}F NMR δ -73.3 (s); IR (KBr) 3572, 2925, 1613, 1517, 1493, 1455, 1352, 1261, 1195, 1106, 819, 794, 727, 697, 646, 618 cm^{-1} ; EIMS m/z 344 (M^+ , 1), 121 (100), 105 (14), 91 (12), 77 (25); Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{O}_3\text{S}$: C, 55.81; H, 4.39. Found: C, 55.62; H, 4.59. HPLC (CHIRALPAK AD-H $\times 2$ hexane/*i*PrOH = 95/5, flow rate 1.0 ml/min) t_R 37.8 (minor) and 44.5 (major) min.

1-(2-Methylphenyl)-2-phenyl-2-(trifluoromethylsulfonyl)ethanol (6): starting **1f** (20.2 mg, 0.0901 mmol), product **6** (17.7 mg, 57%), *syn-6*: 97% ee: *syn-6*. $[\alpha]_D^{20} -12.0$ (c 0.62, CHCl_3 , 97% ee); ^1H NMR δ 2.16 (s, 3H), 2.85 (br, 1H), 4.94 (d, $J = 10.0$ Hz, 1H), 5.85 (d, $J = 10.0$ Hz, 1H), 6.98-7.28 (m, 9H); ^{19}F NMR δ -73.2 (s); IR (neat) 3534, 3067, 2959, 1605, 1352, 1120, 1105, 760, 699 cm^{-1} ; EIMS m/z 344 (M^+ , 2), 121 (100), 105 (9), 91 (62), 71 (15), 65 (17). HPLC (CHIRALPAK OD-H hexane/*i*PrOH = 95/5, wave length 210 nm, flow rate 1.0 ml/min) t_R 14.2 (minor) and 17.7 (major) min.

1-(2,4-Dimethylphenyl)-2-phenyl-2-(trifluoromethylsulfonyl)ethanol (7): starting **1f** (21.5 mg, 0.0959 mmol), product **7** (14.1 mg, 41 %), *syn-7*: 98% ee. *syn-7*; $[\alpha]_D^{20} -1.1$ (c 1.19, CHCl_3 , 98% ee); ^1H NMR δ 2.11 (s, 3H), 2.19 (s, 3H), 2.78 (br, 1H), 4.93 (d, $J = 10.0$ Hz, 1H), 5.80 (d, $J = 10.0$ Hz, 1H), 7.02-7.31 (m, 8H); ^{19}F NMR δ -73.1 (s); IR (neat) 3436, 1615, 1496, 1353, 1201, 1106, 1040, 911, 736, 699, 648 cm^{-1} ;

EIMS m/z 358 (M^+ , 2), 135 (100), 107 (44), 91 (80), 77 (17), 65 (18); HPLC (CHIRALPAK OD-H hexane/*i*PrOH = 95/5, wave length 210 nm, flow rate 1.0 ml/min) t_R 12.3 (major) and 14.3 (minor) min.

1-(4-Methoxyphenyl)-2-phenyl-2-(trifluoromethylsulfonyl)ethanol (8): starting **1f** (23.3 mg, 0.104 mmol), product **8** (21.3 mg, 57%), *syn*-**8**: 98% ee. *syn*-**8**; $[\alpha]_D^{26} +15.4$ (*c* 0.33, CHCl₃, 98% ee); 1H NMR δ 2.95 (br, 1H), 3.70 (s, 3H), 4.73 (d, J = 10.0 Hz, 1H), 5.54 (d, J = 10.0 Hz, 1H), 6.65-7.35 (m, 9H); ^{19}F NMR δ -73.2; IR (KBr) 3572, 3479, 2927, 1455, 1352, 1195, 1106, 1046, 820, 794, 697, 646, 618 cm^{-1} ; EIMS m/z 360 (M^+ , 6), 210 (21), 137 (100), 109 (33), 91 (33), 77 (31); HPLC (CHIRALPAK AD-H hexane/*i*PrOH = 95/5, flow rate 1.0 ml/min) t_R 22.9 (minor) and 31.4 (major) min.

1-(4-Chlorophenyl)-2-phenyl-2-(trifluoromethylsulfonyl)ethanol (9): starting **1f** (23.3 mg, 0.104 mmol), product **9** (25.1 mg, 66%), *syn*-**9**: 84% ee. *syn*-**9**; $[\alpha]_D^{20} +10.8$ (*c* 0.78, CHCl₃, 84% ee); 1H NMR δ 3.19 (br, 1H), 4.69 (d, J = 9.6 Hz, 1H), 5.58 (d, J = 9.6 Hz, 1H), 7.00-7.30 (m, 9H); ^{13}C NMR δ 73.6, 75.0, 126.9, 128.0, 128.5, 128.9, 129.9, 130.1, 134.4, 136.9; ^{19}F NMR δ -73.3 (s); IR (KBr) 3526, 3066, 2945, 2358, 1596, 1492, 1455, 1334, 1296, 1194, 1102, 1079, 1014, 826, 735, 699, 685, 644, 619, 602 cm^{-1} ; EIMS m/z 364 (M^+ , 9), 165 (18), 141 (100), 113 (60), 91 (85), 77 (85); HPLC (CHIRALPAK AD-H hexane/*i*PrOH = 95/5, flow rate 1.0 ml/min) t_R 17.8 (minor) and 22.4 (major) min.

1-(2-Chlorophenyl)-2-phenyl-2-(trifluoromethylsulfonyl)ethanol (10): starting **1f** (22.4 mg, 0.100 mmol), product **10** (14.8 mg, 41%), *syn*-**10**: 82% ee. *syn*-**10**; $[\alpha]_D^{20} -20.7$ (*c* 0.54, CHCl₃, 82% ee); 1H NMR δ 3.16 (br, 1H), 5.03 (d, J = 9.4 Hz, 1H), 6.09 (d, J = 9.4 Hz, 1H), 7.06-7.41 (m, 9H); ^{19}F NMR δ -73.38 (s); IR (neat) 3537, 3332, 3032, 1661, 1562, 1358, 1200, 1107, 1035, 758, 699, 650 cm^{-1} ; EIMS m/z 364 (M^+ , 2), 141 (100), 139 (42), 105 (36), 91 (61), 77 (62); HPLC (CHIRALPAK AD-H hexane/*i*PrOH = 95/5, wave length 210 nm, flow rate 1.0 ml/min) t_R 22.5 (major) and 24.6 (minor) min.

1-(4-Fluorophenyl)-2-phenyl-2-(trifluoromethylsulfonyl)ethanol (11): starting **1f** (21.8 mg, 0.0972 mmol), product **11** (11.6 mg, 34%), *syn*-**11**: 92% ee. *syn*-**11**; $[\alpha]_D^{20} +5.23$ (*c* 0.28, CHCl₃, 92% ee); 1H NMR δ 2.96 (br, 1H), 4.71 (d, J = 10.0 Hz, 1H), 5.59 (d, J = 10.0 Hz, 1H), 6.84-7.28 (m, 9H); ^{19}F NMR δ -73.27 (s, CF₃-), -111.94 (m, -C₆H₄-F); IR (neat) 3530, 3059, 2981, 2890, 1661, 1605, 1511, 1355, 1203, 1107, 841, 782, 698, 649 cm^{-1} ; EIMS m/z 348 (M^+ , 2), 224 (6), 183 (8), 125 (100), 105 (20), 95 (52), 91 (98), 77 (32), 65 (44); HPLC (CHIRALPAK AD-H hexane/*i*PrOH = 95/5, wave length 210 nm, flow rate 1.0 ml/min) t_R 26.8 (minor) and 30.8 (major) min.

1-(1-Naphthyl)-2-phenyl-2-(trifluoromethylsulfonyl)ethanol (12): starting **1f** (23.6 mg, 0.105 mmol), product **12** (23.2 mg, 61%), *syn*-**12**: 96% ee. *syn*-**12**; $[\alpha]_{\text{D}}^{20} +19.6$ (*c* 0.96, CHCl₃, 96% ee); ¹H NMR δ 3.15 (br, 1H), 5.29 (d, *J* = 10.0 Hz, 1H), 6.22 (d, *J* = 9.8 Hz, 1H), 7.02-8.33 (m, 11H); ¹⁹F NMR δ -73.1 (s); IR (neat) 3536, 3065, 2976, 1683, 1513, 1456, 1354, 1199, 1107, 777, 698, 646 cm⁻¹; EIMS *m/z* 380 (M⁺, 3), 157 (100), 129 (48), 105 (14), 91 (86), 77 (15), 65 (21); HPLC (CHIRALPAK AD-H hexane/*i*PrOH = 95/5, wave length 210 nm, flow rate 1.0 ml/min) *t*_R 21.3 (major) and 22.6 (minor) min.

1-(2-Naphthyl)-2-phenyl-2-(trifluoromethylsulfonyl)ethanol (13): starting **1f** (22.8 mg, 0.102 mmol), product **13** (20.9 mg, 54%), *syn*-**13**: 96% ee. *syn*-**13**; $[\alpha]_{\text{D}}^{20} +4.3$ (*c* 0.72, CHCl₃, 90% ee); ¹H NMR δ 2.95 (br, 1H), 4.75 (d, *J* = 9.9 Hz, 1H), 5.56 (d, *J* = 9.9 Hz, 1H), 6.98-7.28 (m, 11H); ¹⁹F NMR δ -73.3; IR (KBr) 3527, 2941, 1683, 1507, 1456, 1356, 1218, 1203, 1104, 1046, 868, 837, 761, 695, 664, 630 cm⁻¹; EIMS *m/z* 380 (M⁺, 10), 185 (34), 127 (36), 91 (100); HPLC (CHIRALPAK AD-H $\times$ 2 hexane/*i*PrOH = 97/3, flow rate 2.0 ml/min) *t*_R 48.8 (minor) and 54.8 (major) min.

1-[2-(Furanyl)]-2-phenyl-2-(trifluoromethylsulfonyl)ethanol (14): starting **1f** (23.3 mg, 0.104 mmol), product **14** (11.7 mg, 35%), *syn*-**14**: 90% ee. *syn*-**14**; $[\alpha]_{\text{D}}^{20} -1.1$ (*c* 0.13, CHCl₃, 90% ee); ¹H NMR δ 3.05 (br, 1H), 5.04 (d, *J* = 9.8 Hz, 1H), 5.65 (d, *J* = 9.8 Hz, 1H), 6.09-6.14 (m, 3H), 7.21-7.37 (m, 5H); ¹⁹F NMR δ -73.3 (s); IR (KBr) 3435, 2953, 1497, 1456, 1346, 1199, 1109, 1015, 926, 809, 739, 697, 648 cm⁻¹; EIMS *m/z* 320 (M⁺, 1), 105 (19), 91 (100), 77 (18). HPLC (Daicel CHIRALPAK AD-H, hexane/*i*PrOH = 95/5, wave length 210 nm, flow rate 1.0 ml/min) *t*_R 20.5 (minor) and 30.7 (major) min.

[2-Phenyl-1-(2-thienyl)-2-(trifluoromethylsulfonyl)ethoxy]trimethylsilane (15): starting **1f** (20.1 mg, 0.0896 mmol), product **15** (23.1 mg, 63%), *syn*-**15**: 92% ee. *syn*-**15**; $[\alpha]_{\text{D}}^{20} -14.6$ (*c* 0.62, CHCl₃, 92% ee); ¹H NMR δ 0.09 (s, 9H), 4.75 (d, *J* = 9.8 Hz, 1H), 5.73 (d, *J* = 9.8 Hz, 1H), 6.53-6.54 (m, 1H), 6.65-6.69 (m, 1H), 7.10-7.30 (m, 6H); ¹⁹F NMR δ -72.8 (s); IR (neat) 3073, 2959, 2904, 1362, 1254, 1200, 1110, 887, 848, 754, 697 cm⁻¹; APCI-MS *m/z* 409 (M⁺, 16), 408 (24), 407 (100); HPLC (Daicel CHIRALPAK AD-H, hexane/*i*PrOH = 98/2, wave length 210 nm, flow rate 0.3 ml/min) *t*_R 13.9 (major) and 15.3 (minor) min.

1,4-Diphenyl-2-(trifluoromethylsulfonyl)-3-buten-2-ol (16): starting **1f** (20.7 mg, 0.0923 mmol), product **16**: (12.4 mg, 38%), *syn*-**16**: 97% ee. *syn*-**16**; $[\alpha]_{\text{D}}^{20} -10.4$ (*c* 0.37, CHCl₃, 97% ee); *syn*-**16**: ¹H NMR δ 2.83 (br, 1H), 4.62 (d, *J* = 8.8 Hz, 1H), 5.31 (dd, *J* = 7.4, 7.4 Hz, 1H), 5.88 (dd, *J* = 15.5, 6.4 Hz, 1H), 6.61 (d, *J* = 15.8 Hz, 1H), 7.11-7.47 (m, 10H); ¹⁹F NMR δ -73.7 (s); IR (neat) 3537, 3384, 3032, 2925, 1662, 1358,

1201, 1107, 968, 750, 697 cm^{-1} ; EIMS m/z 356 (M^+ , 1), 223 (3), 205 (6), 133 (36), 115 (9), 105 (15), 91 (100), 77 (21), 65 (15), 51 (16); HPLC (Daicel CHIRALPAK AD-H, hexane/*i*PrOH = 90/10, wave length 210 nm, flow rate 1.0 ml/min) t_R 12.4 (minor) and 19.7 (major) min:

1-Phenyl-2-(4-methylphenyl)-2-(trifluoromethylsulfonyl)ethanol (17) starting **1f** (23.8 mg, 0.0999 mmol), product **17** (20.8 mg, 60%), *syn*-**17**: 70% ee. *syn*-**17**; $[\alpha]_D^{20} +29.8$ (c 0.51, CHCl_3 , 70% ee); ^1H NMR δ 2.27 (s, 3H), 4.73 (d, $J = 9.8$ Hz, 1H), 5.57 (d, $J = 9.8$ Hz, 1H), 7.05-7.26 (m, 9H); ^{19}F NMR δ -73.2; IR (neat) 3546, 3034, 2925, 1455, 1348, 1185, 1058, 822, 772, 735, 698, 639, 607 cm^{-1} ; EIMS m/z 344 (M^+ , 2), 238 (2), 179 (1), 119 (9), 105 (100), 91 (15), 77 (50), 69 (21). HPLC (Daicel CHIRALPAK AD-H, hexane/*i*PrOH = 95/5, wave length 220 nm, flow rate 1.0 ml/min) t_R 13.8 (major) and 17.6 (minor) min.

1-Phenyl-2-(4-methoxyphenyl)-2-(trifluoromethanesulfonyl)ethanol (18) (starting **1f**: 23.9 mg, 0.0940 mmol; product **18**: 18.1 mg (53%), *syn*-**18**: 64% ee): *syn*-**18**; $[\alpha]_D^{20} +20.8$ (c 0.46, CHCl_3 , 64% ee); ^1H NMR δ 3.73 (s, 3H), 4.72 (d, $J = 9.8$ Hz, 1H), 5.54 (d, $J = 9.8$ Hz, 1H), 6.73-7.24 (m, 9H); ^{19}F NMR δ -73.2; IR (neat) 3524, 2976, 1610, 1514, 1457, 1352, 1260, 1184, 1031, 837, 700, 640, 607 cm^{-1} ; EIMS m/z 360 (M^+ , 2), 254 (25), 227 (13), 197 (15), 135 (34), 121 (78), 107 (100), 91 (39), 77 (61); HPLC (Daicel CHIRALPAK OJ-H, hexane/*i*PrOH = 90/10, wave length 210 nm, flow rate 1.5 ml/min) t_R 19.2 (major) and 24.6 (minor) min.

1-Phenyl-2-(4-chlorophenyl)-2-(trifluoromethylsulfonyl)ethanol (19) starting **1f** (23.0 mg, 0.0889 mmol), product **19** (20.7 mg, 64%), *syn*-**19**: 96% ee. *syn*-**19**; $[\alpha]_D^{20} +27.0$ (c 0.64, CHCl_3 , 96% ee); ^1H NMR δ 4.74 (d, $J = 10$ Hz, 1H), 5.54 (d, $J = 10$ Hz, 1H), 7.09-7.24 (m, 9H); ^{19}F NMR δ -73.1 (s); IR (neat) 3537, 2981, 2911, 1494, 1356, 1204, 1104, 1016, 840, 764, 742, 701, 633 cm^{-1} ; APCI-MS m/z 365 (M^+ , 46), 364 (22), 363 (100); HPLC (Daicel CHIRALPAK OD-H, hexane/*i*PrOH = 90/10, wave length 227 nm, flow rate 1.0 ml/min) t_R 10.0 (major) and 12.0 (minor) min.

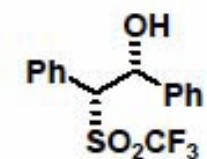
1,2-Diphenyl-2-(1,1,1,2,2,3,3,4,4-nonafluorobutylsulfonyl)ethanol (20) starting **1f** (25.6 mg, 0.0684 mmol), product **20** (12.6 mg, 38%), *syn*-**20**: 96% ee. *syn*-**20**; $[\alpha]_D^{20} -3.6$ (c 0.36, CHCl_3 , 96% ee); ^1H NMR δ 3.16 (br, 1H), 4.88 (d, $J = 9.4$ Hz, 1H), 5.59 (d, $J = 9.4$ Hz, 1H), 7.10-7.25 (m, 9H); ^{19}F NMR δ -80.5 (m, 3F), -107.7 (m, 2F), -120.2 (m, 2F), -125.2 (m, 2F); IR (neat) 3553, 3066, 2921, 1353, 1235, 1141, 1024, 740, 697, 619 cm^{-1} ; EIMS m/z 480 (M^+ , 1), 219 (3), 178 (3), 165 (3), 131 (3), 107 (76), 91 (100), 77 (32), 65

(19); HPLC (Daicel CHIRALPAK AD-H, hexane/*i*PrOH = 95/5, wave length 210 nm, flow rate 1.0 ml/min) t_R 10.2 (major) and 11.7 (minor) min.

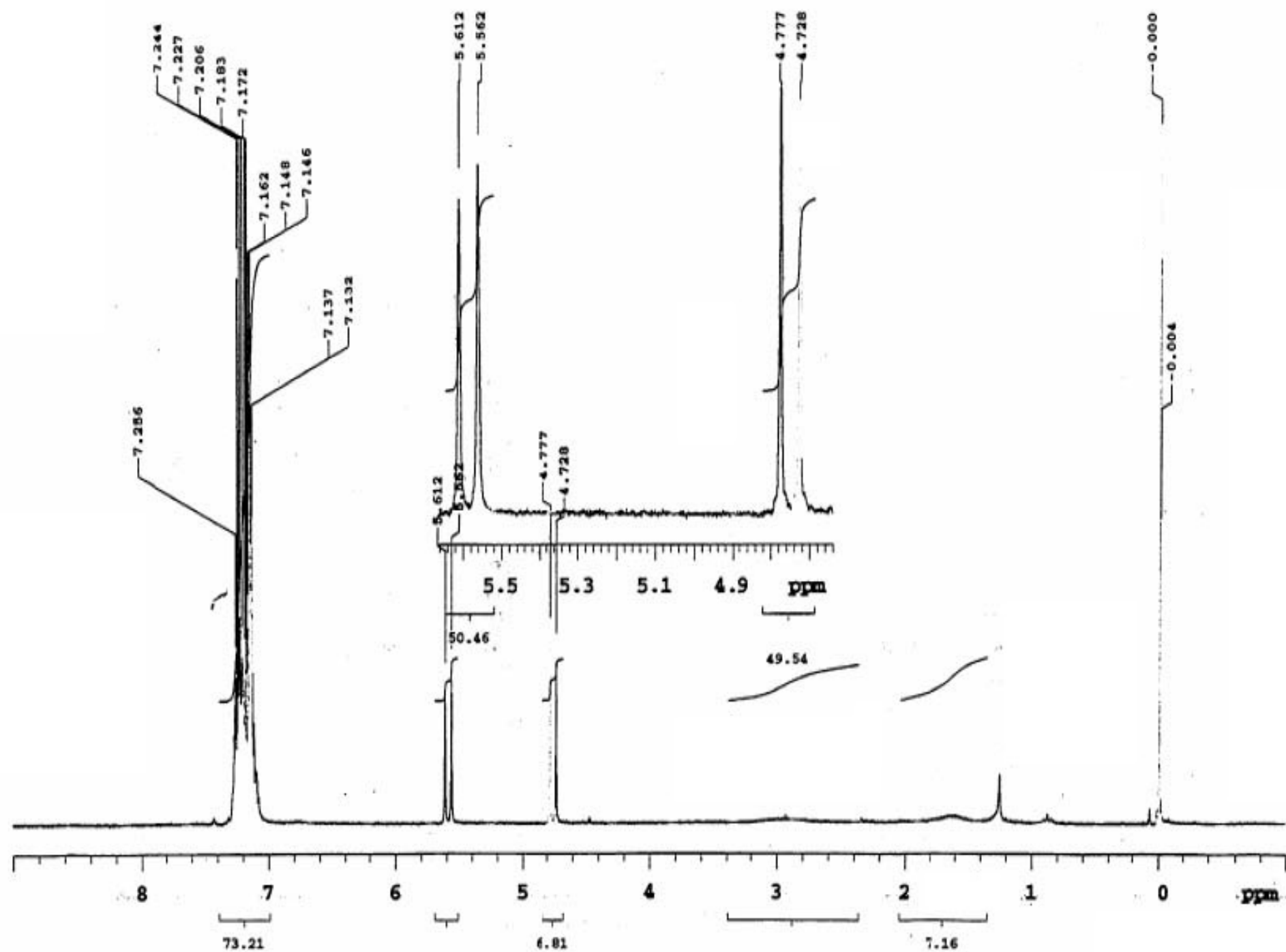
(*R*)-1-Fluoro-1-phenylmethyl trifluoromethyl sulfone (21): starting **1f** (26.3 mg, 0.117 mmol), product **21**: (14.0 mg, 50%), **21**: 99% ee. $[\alpha]_D^{20} +28.2$ (*c* 0.18, CHCl₃, 83% ee); ¹H NMR δ 6.42 (d, *J* = 47.6 Hz, 1H), 7.52-7.61 (m, 5H); ¹³C NMR δ 98.0, 102.5, 123.6, 128.3, 128.4, 129.0, 132.2; ¹⁹F NMR δ -73.5 (d, *J* = 8.4 Hz), -172.4 (dd, *J* = 8.4, 47.6 Hz); IR (KBr) 2970, 2923, 2852, 2358, 1496, 1457, 1373, 1313, 1293, 1207, 1123, 1051, 1027, 786, 724, 694 cm⁻¹; EIMS *m/z* 242 (M⁺, 3), 168 (10), 149 (15), 109 (100), 91 (48), 57 (80); HPLC (CHIRALCEL OB-H hexane/*i*PrOH = 98/2, flow rate 0.5 ml/min), t_R 13.0 (major) and 22.9 (minor) min.

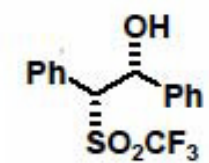
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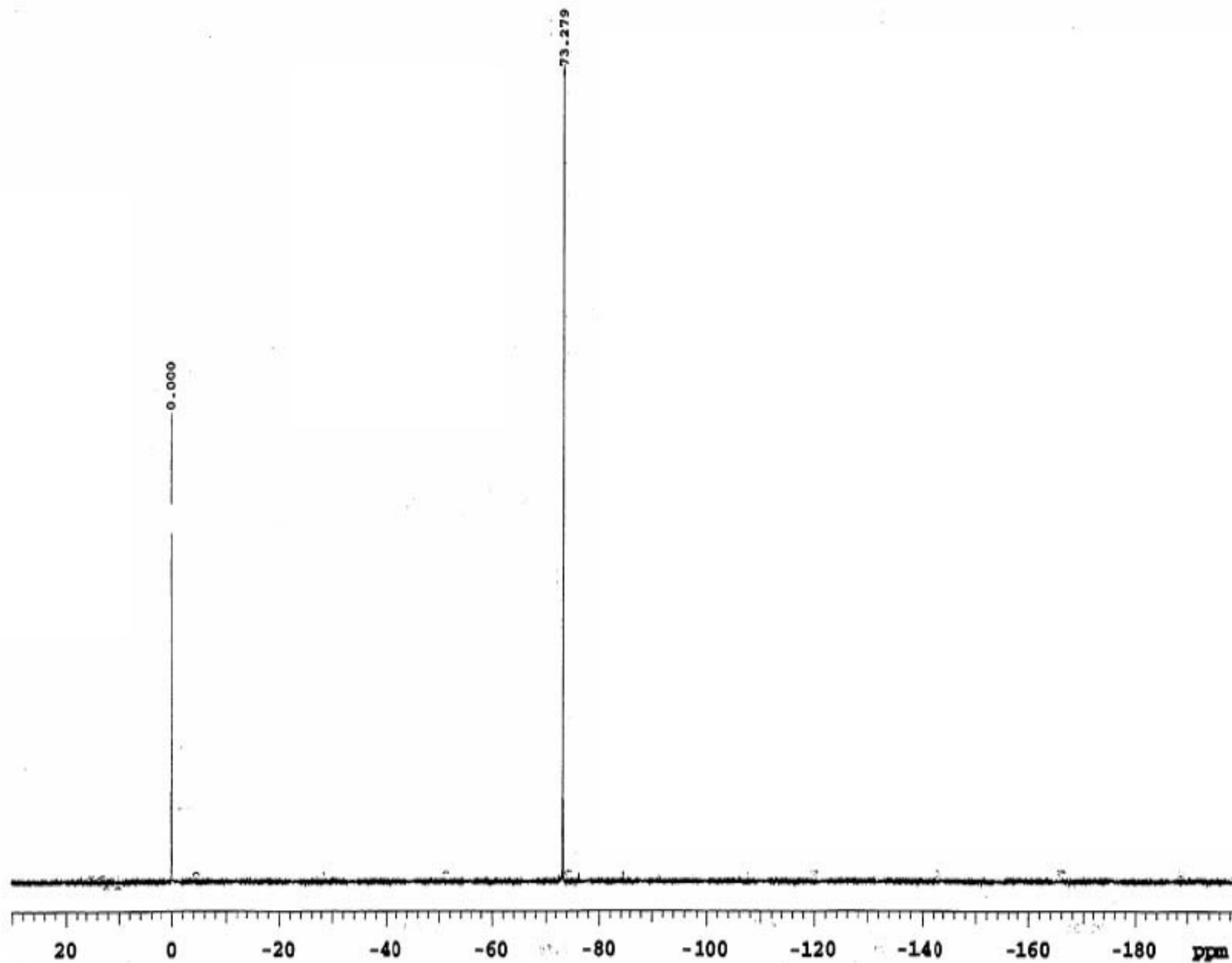


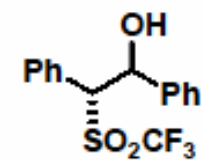
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¹H NMR



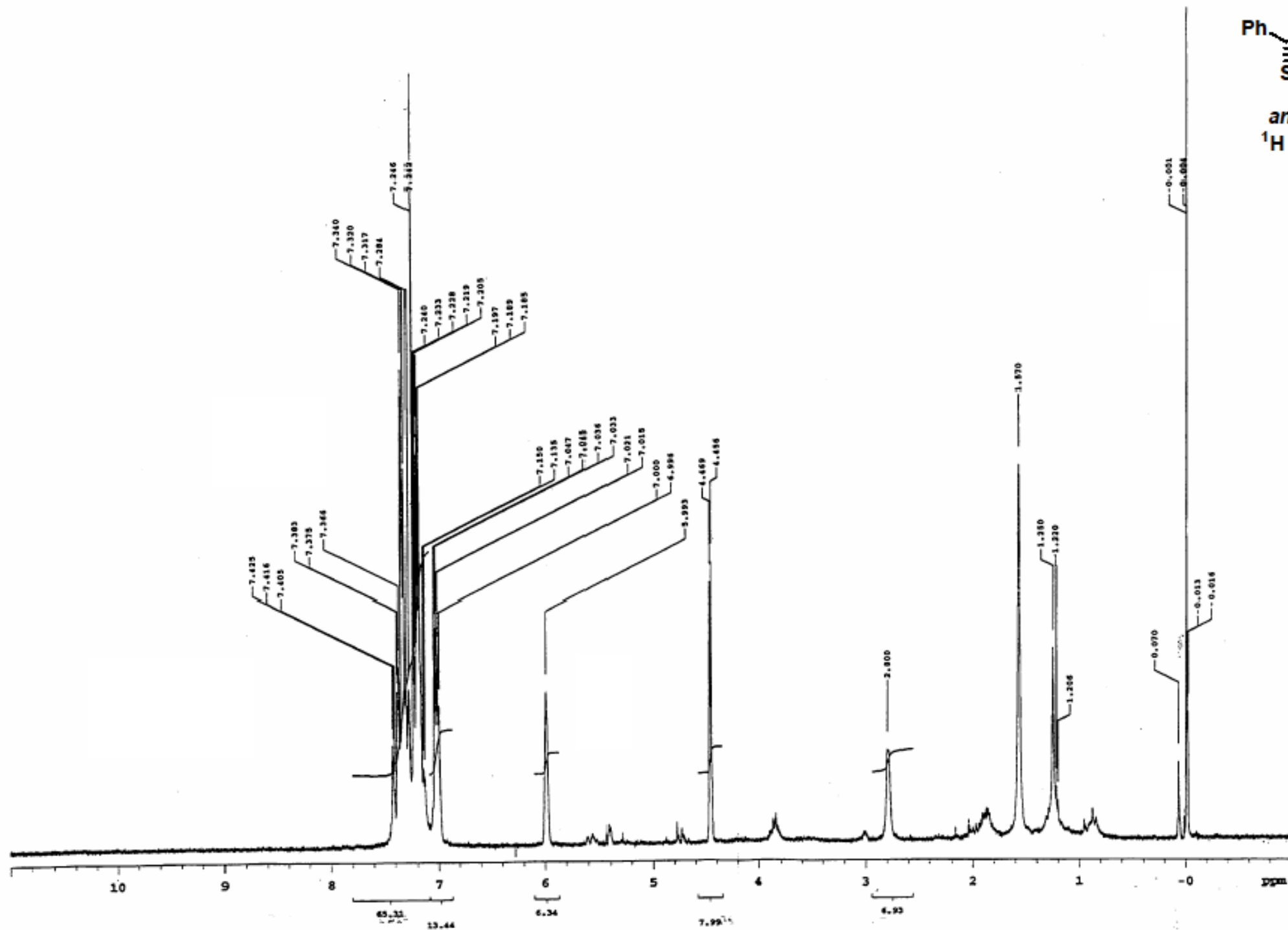


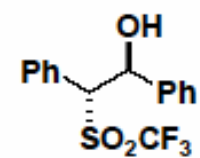
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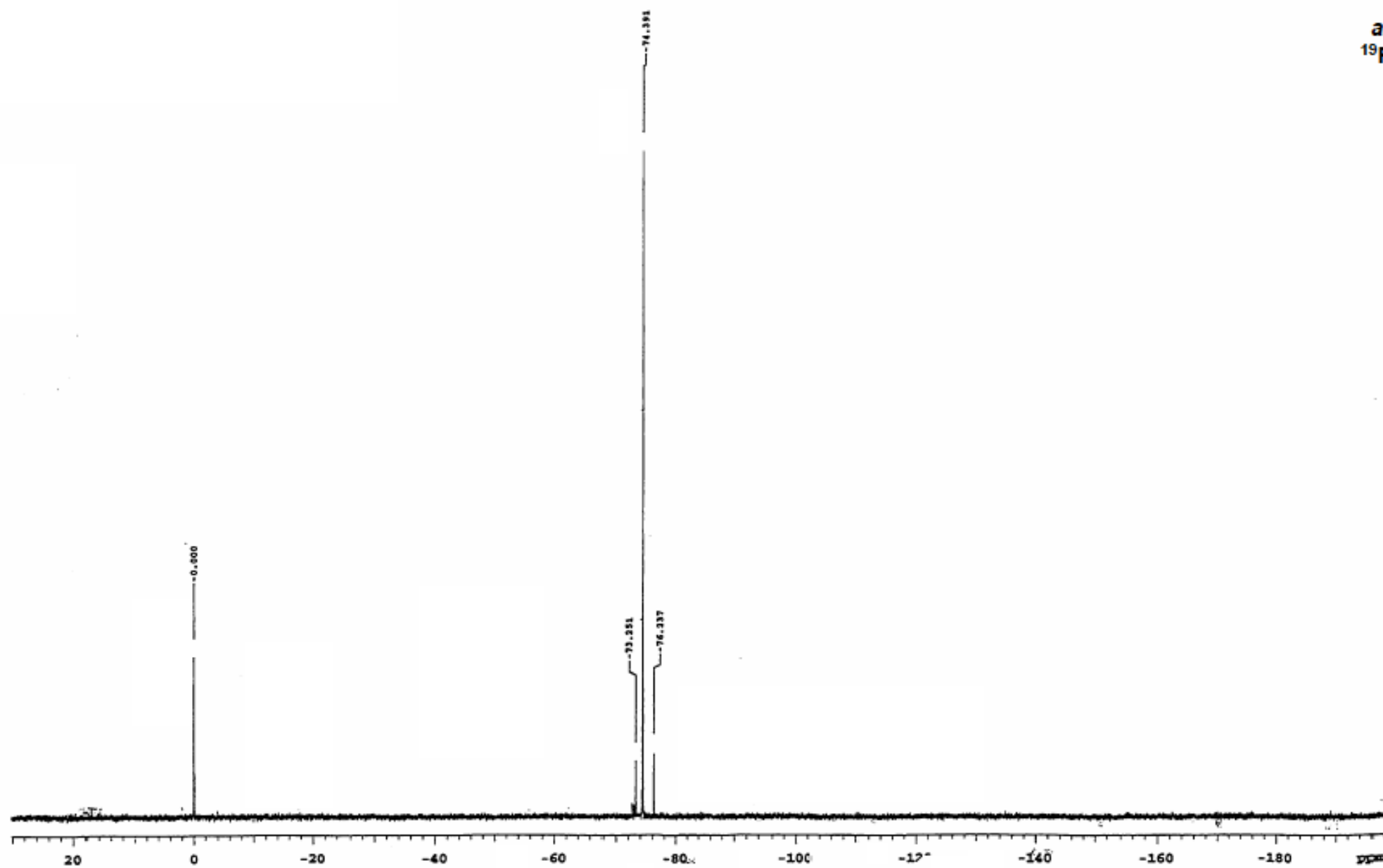


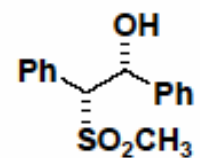
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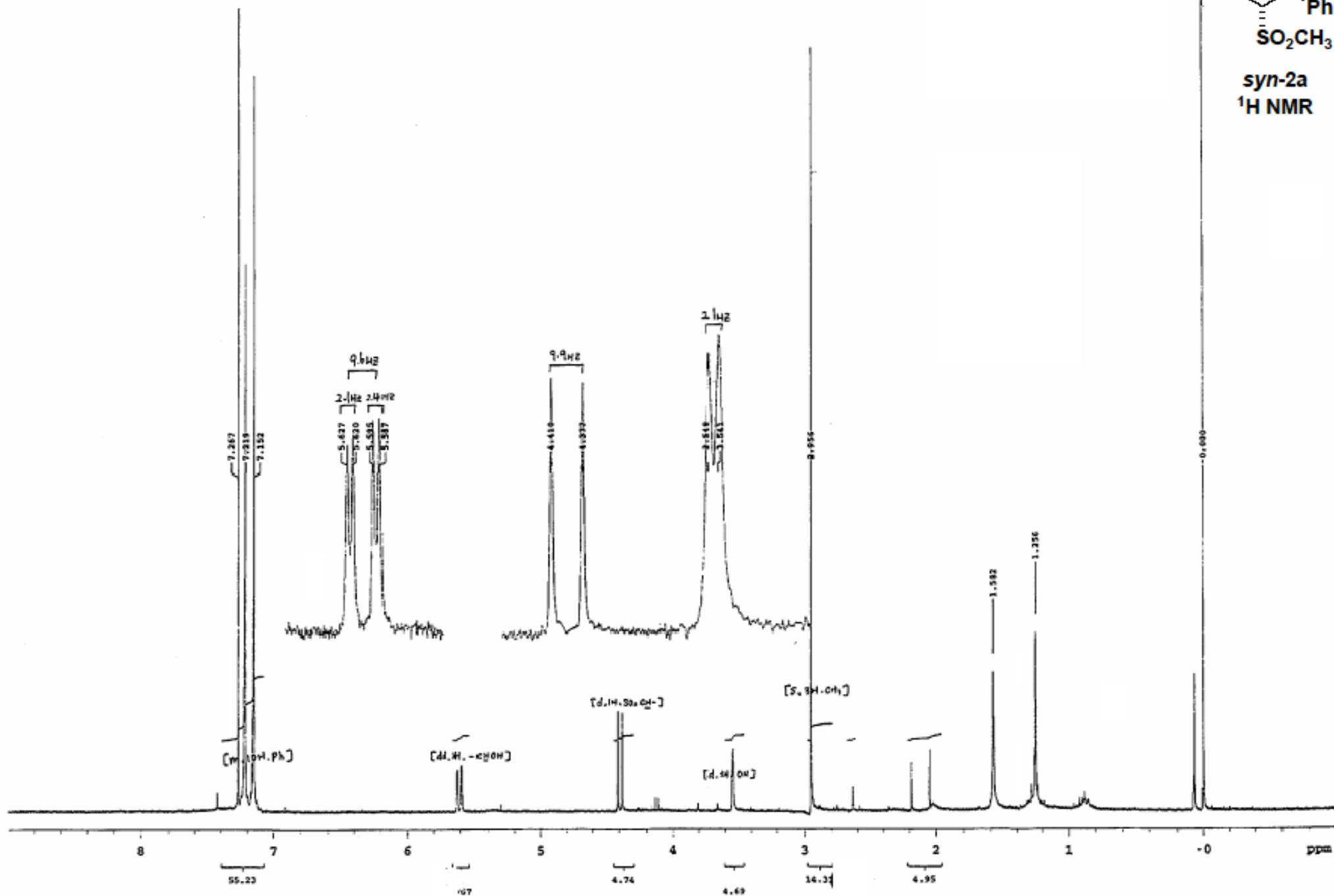


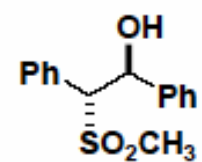
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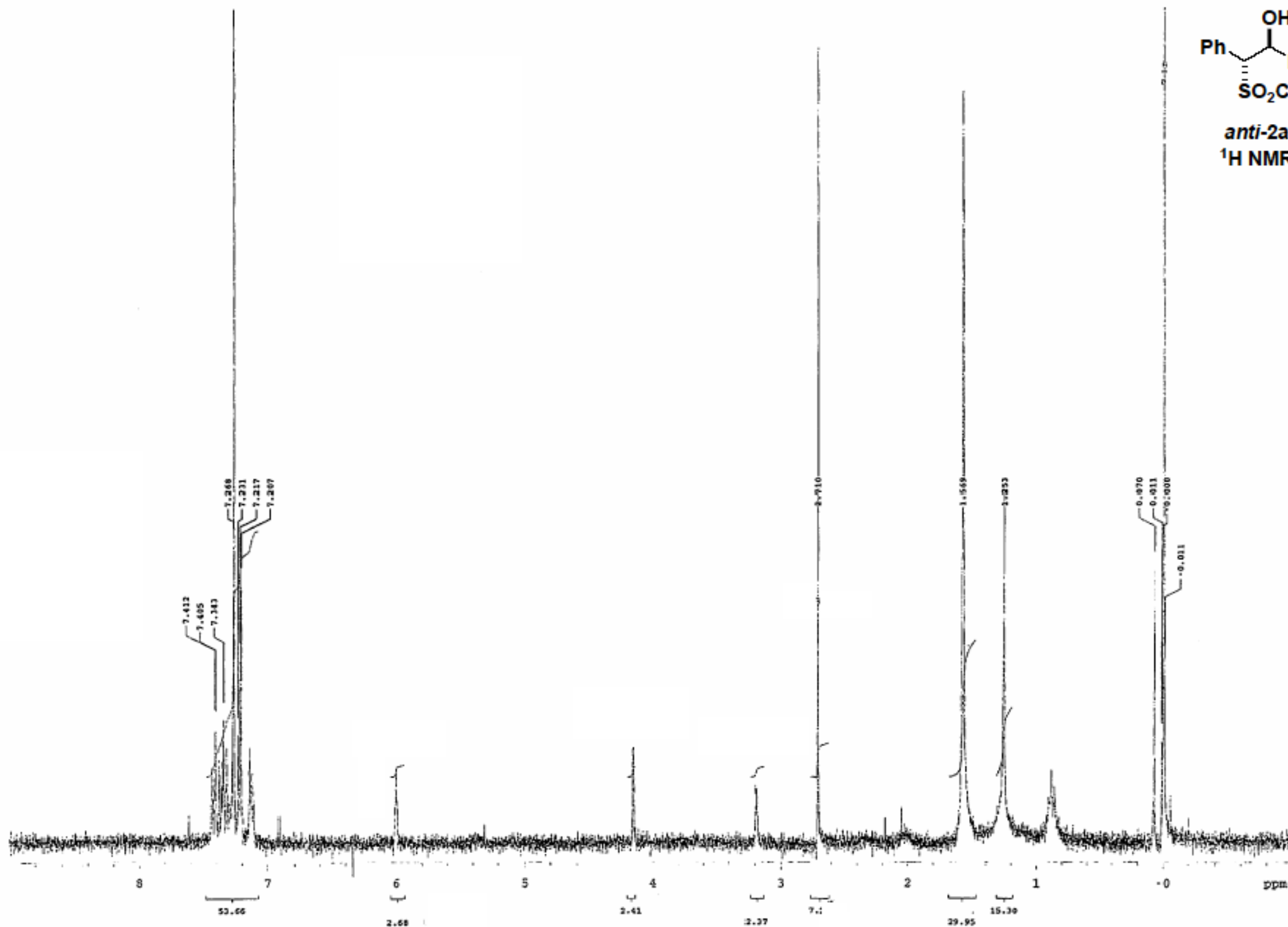


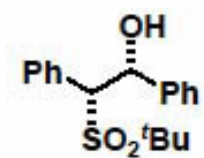
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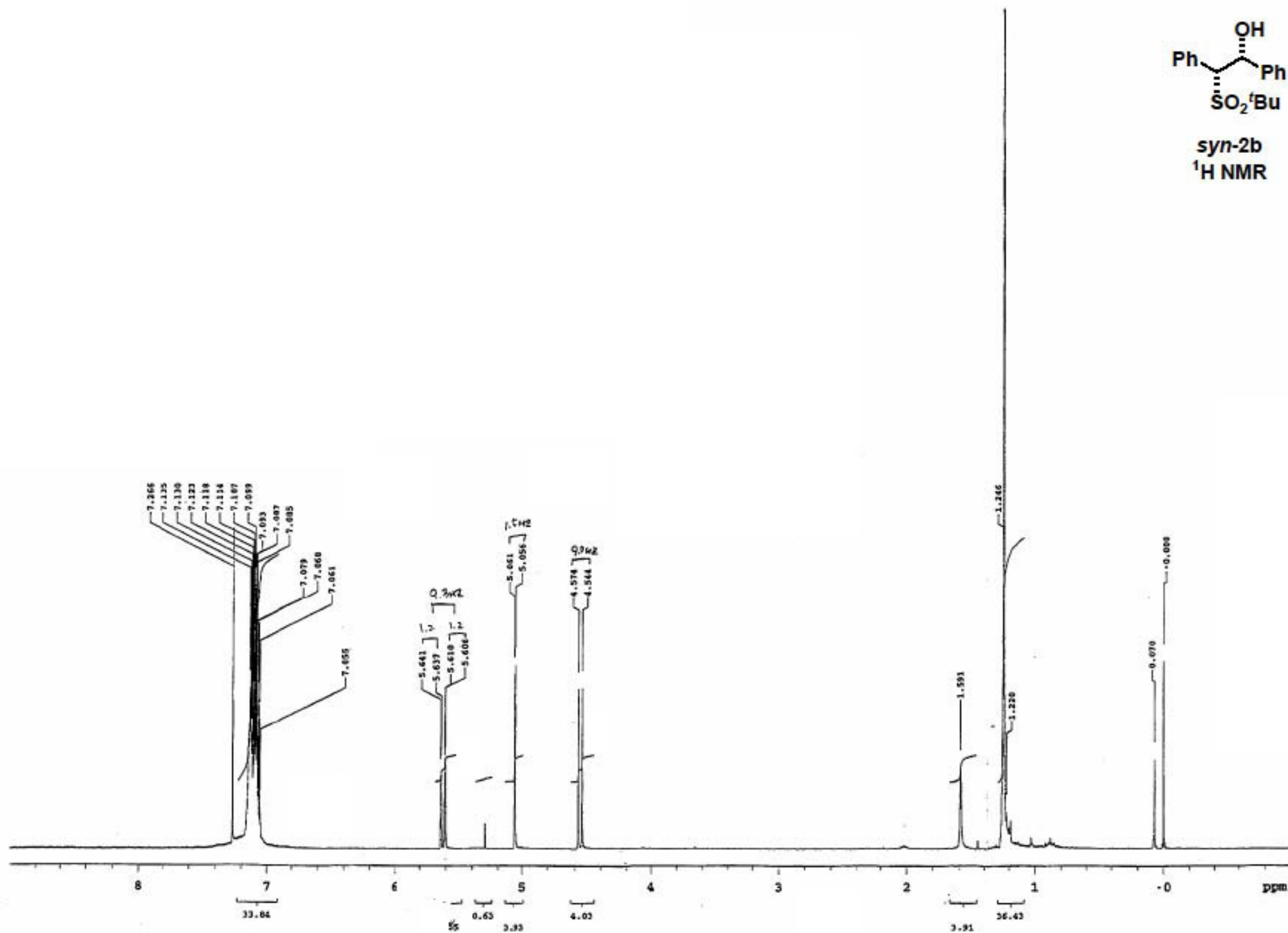


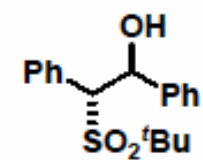
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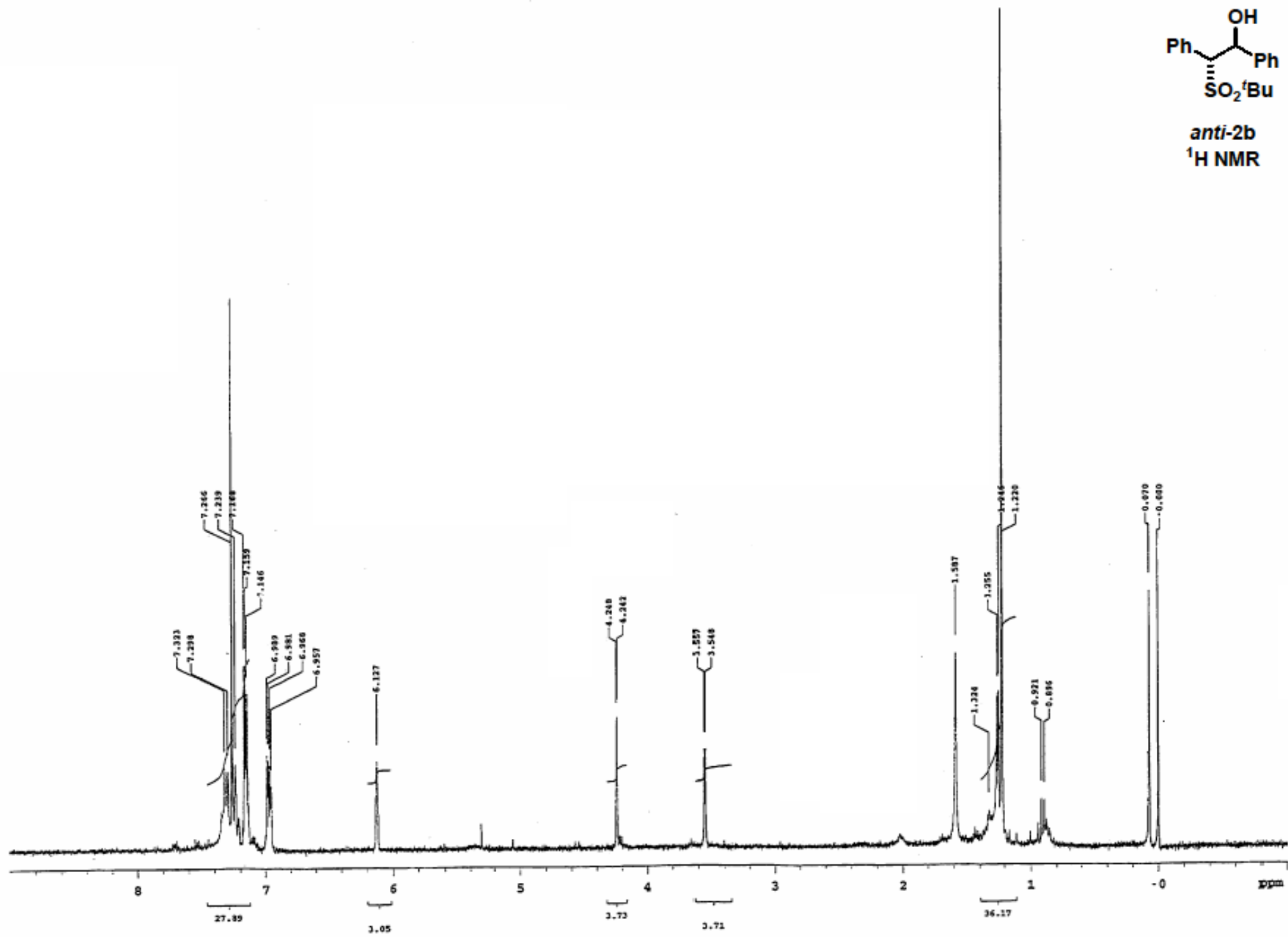


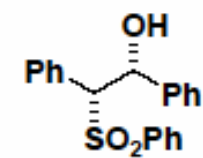
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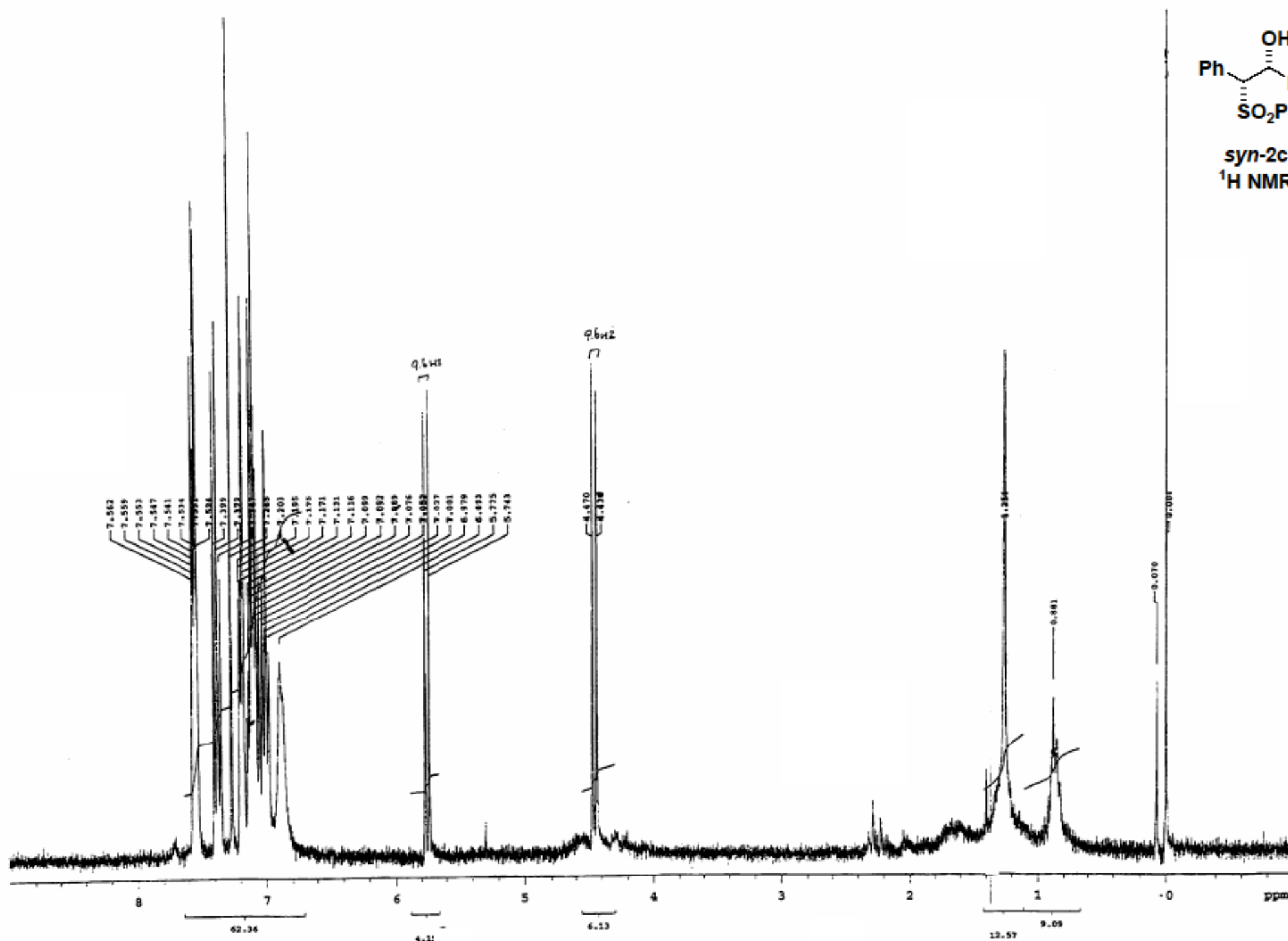


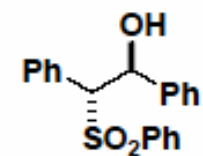
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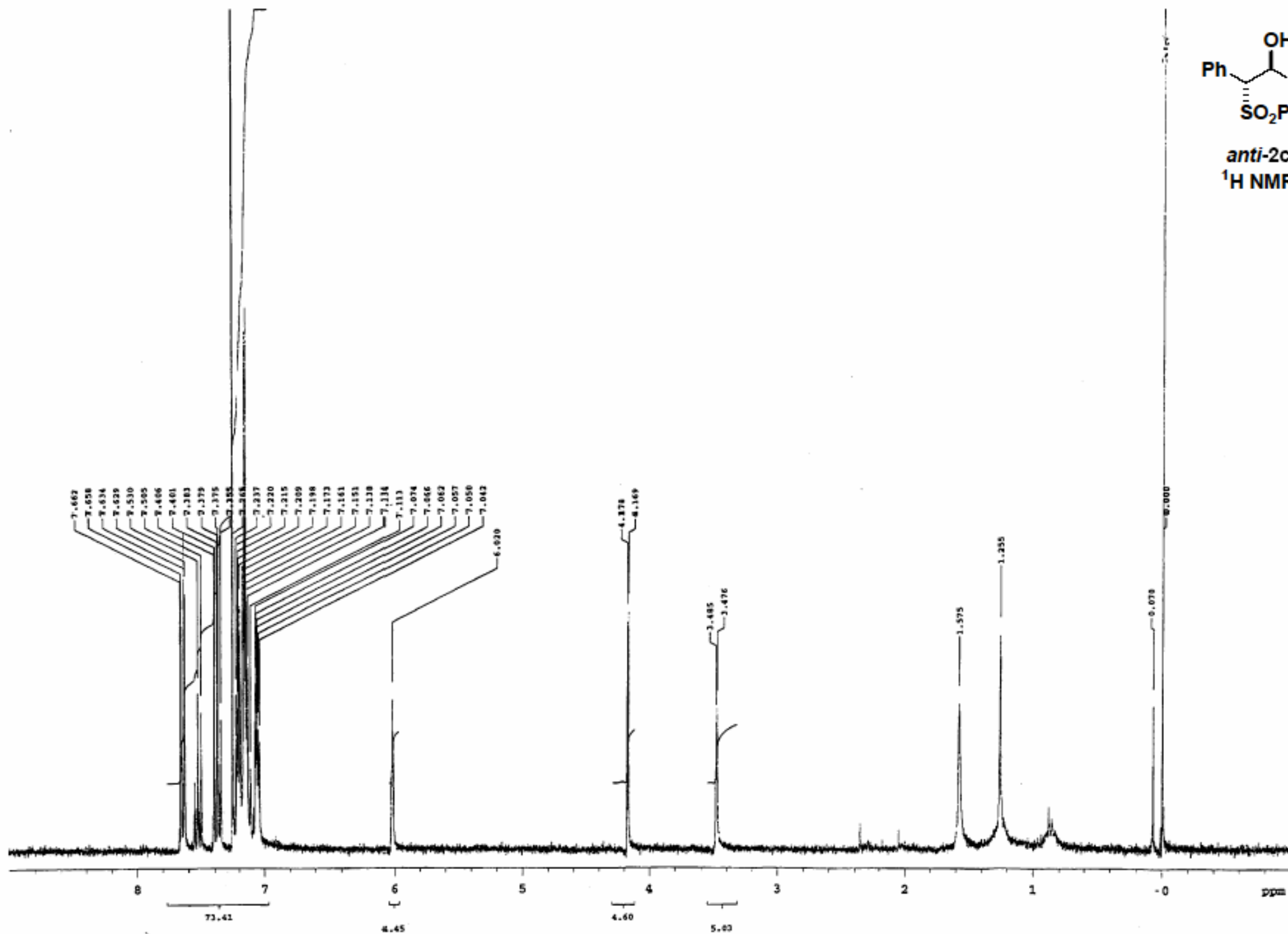


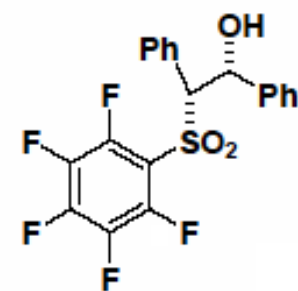
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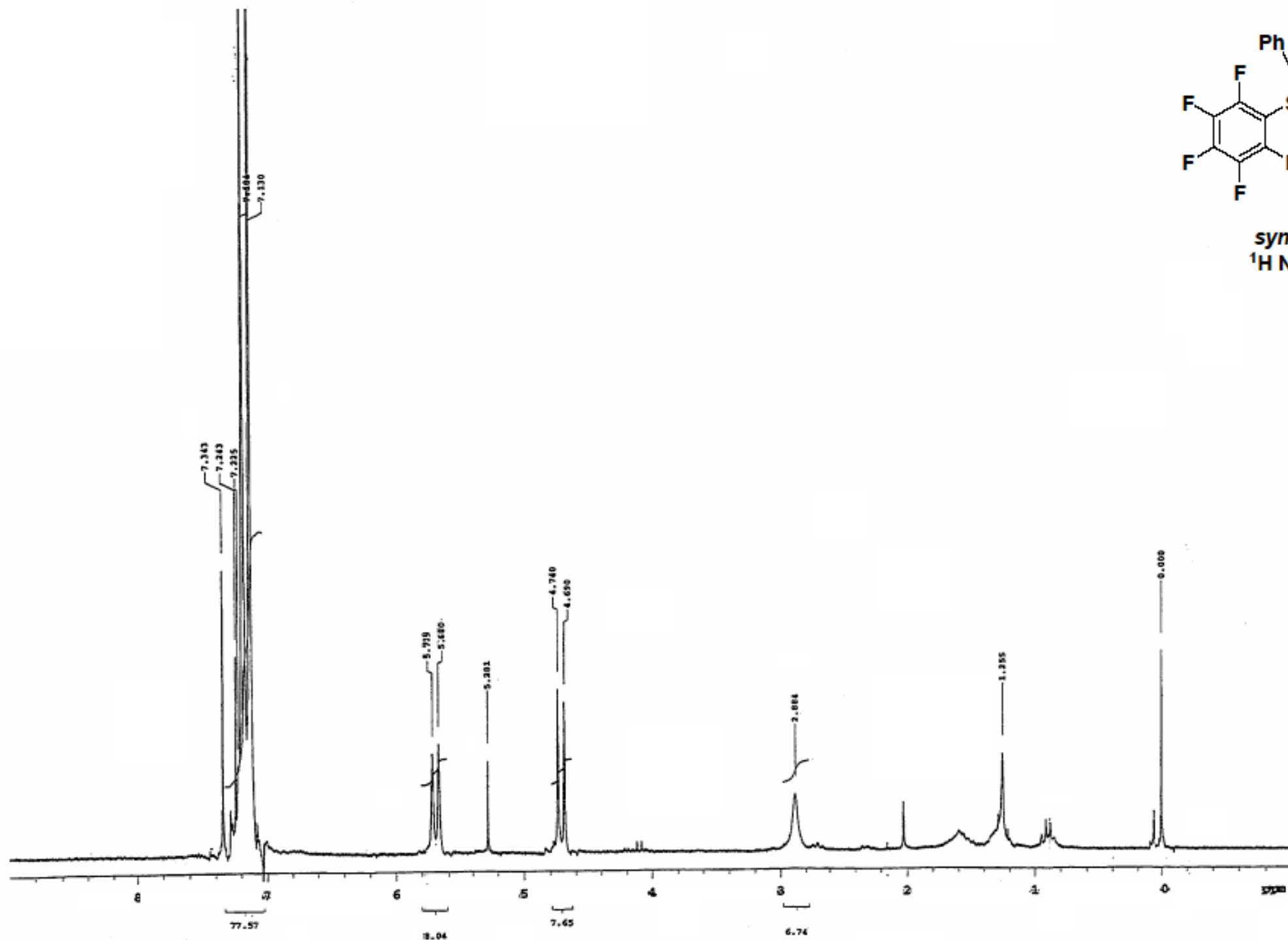


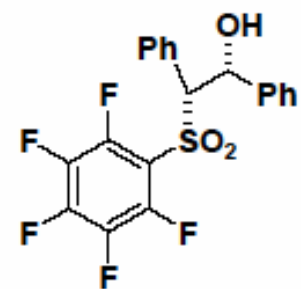
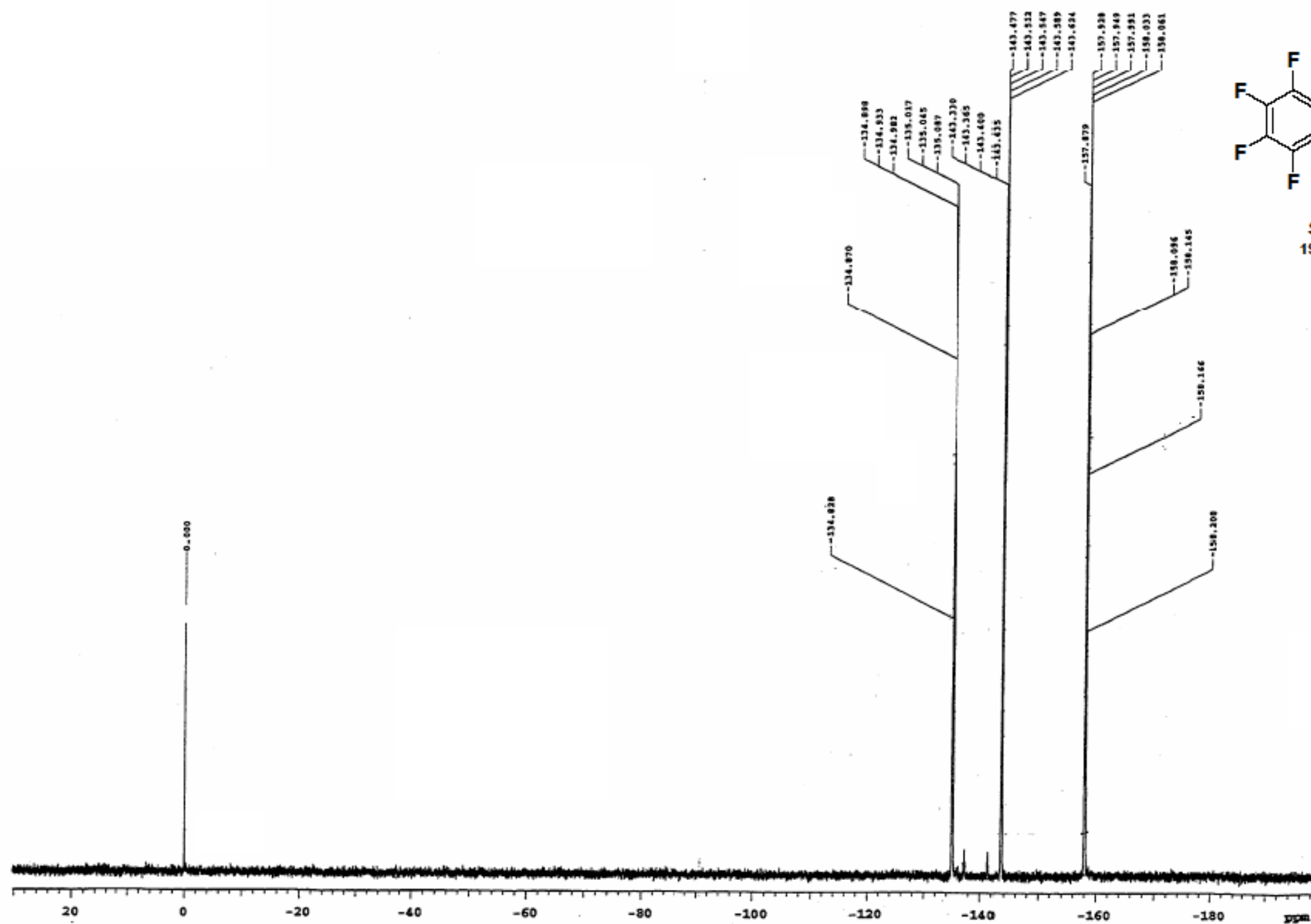
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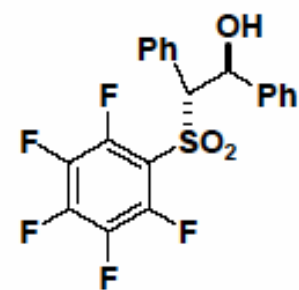
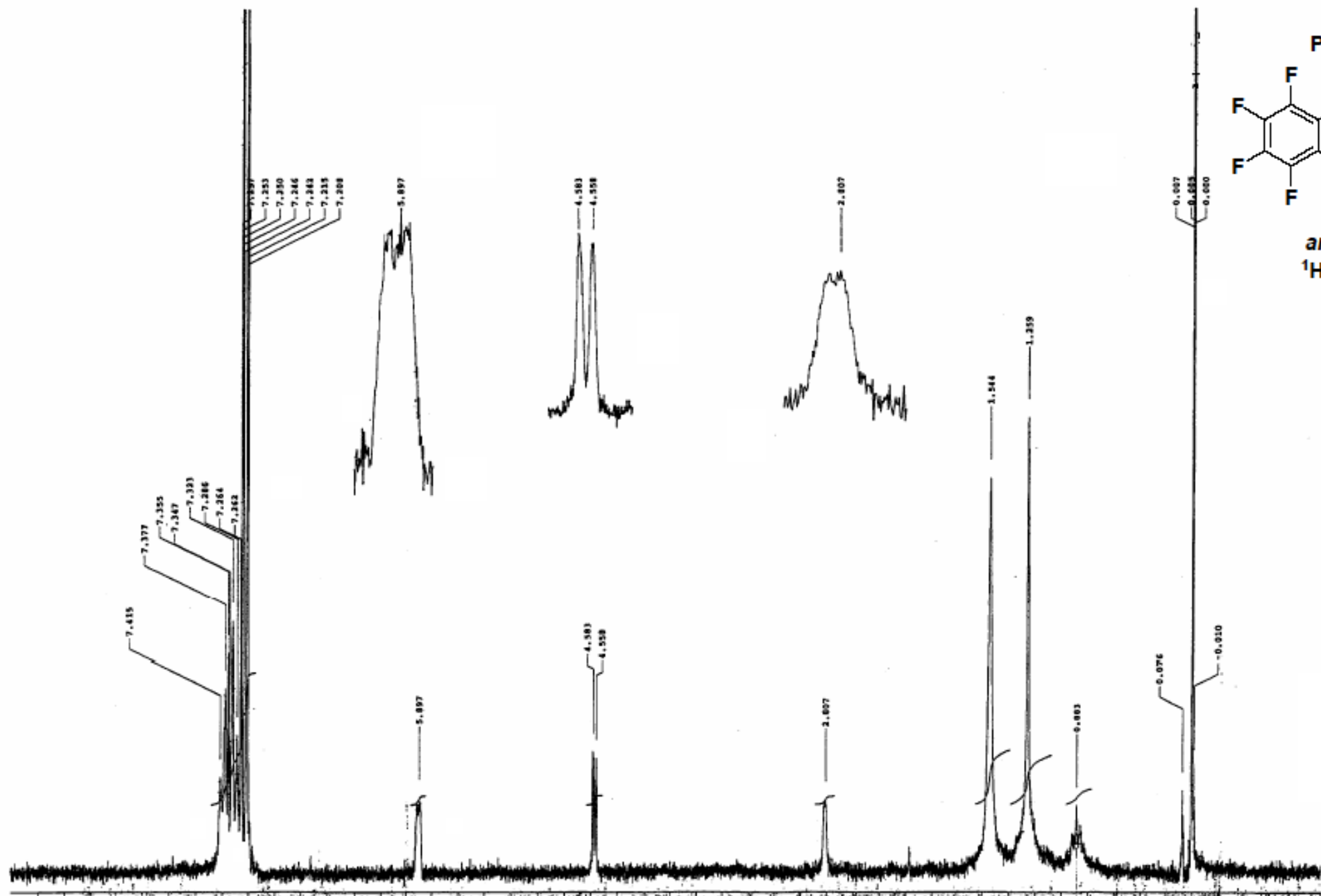


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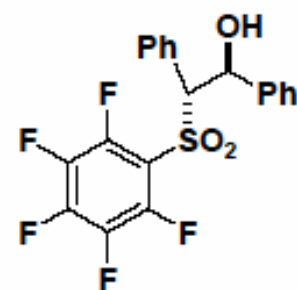




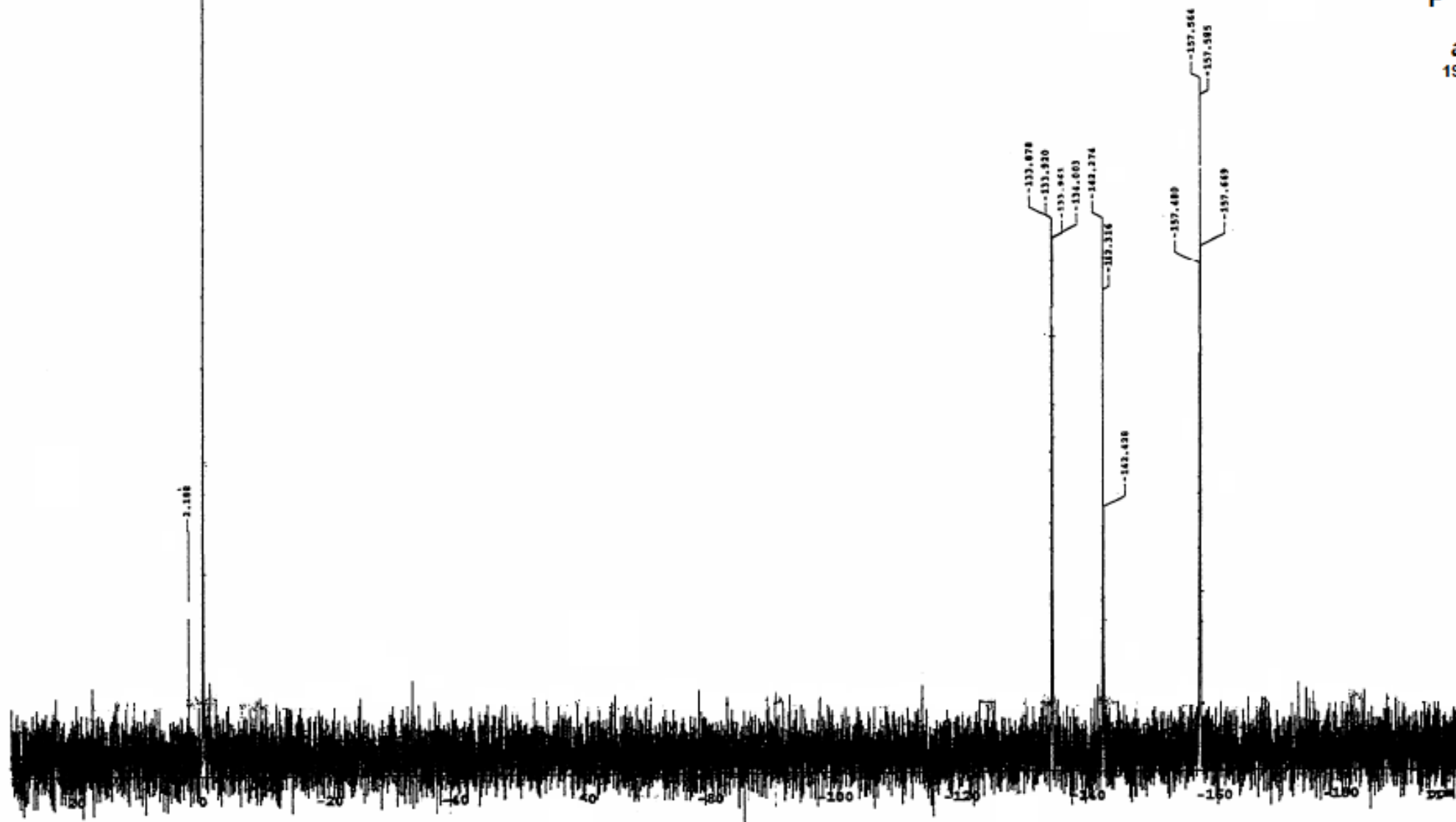
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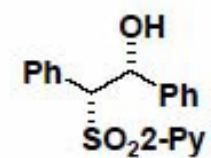


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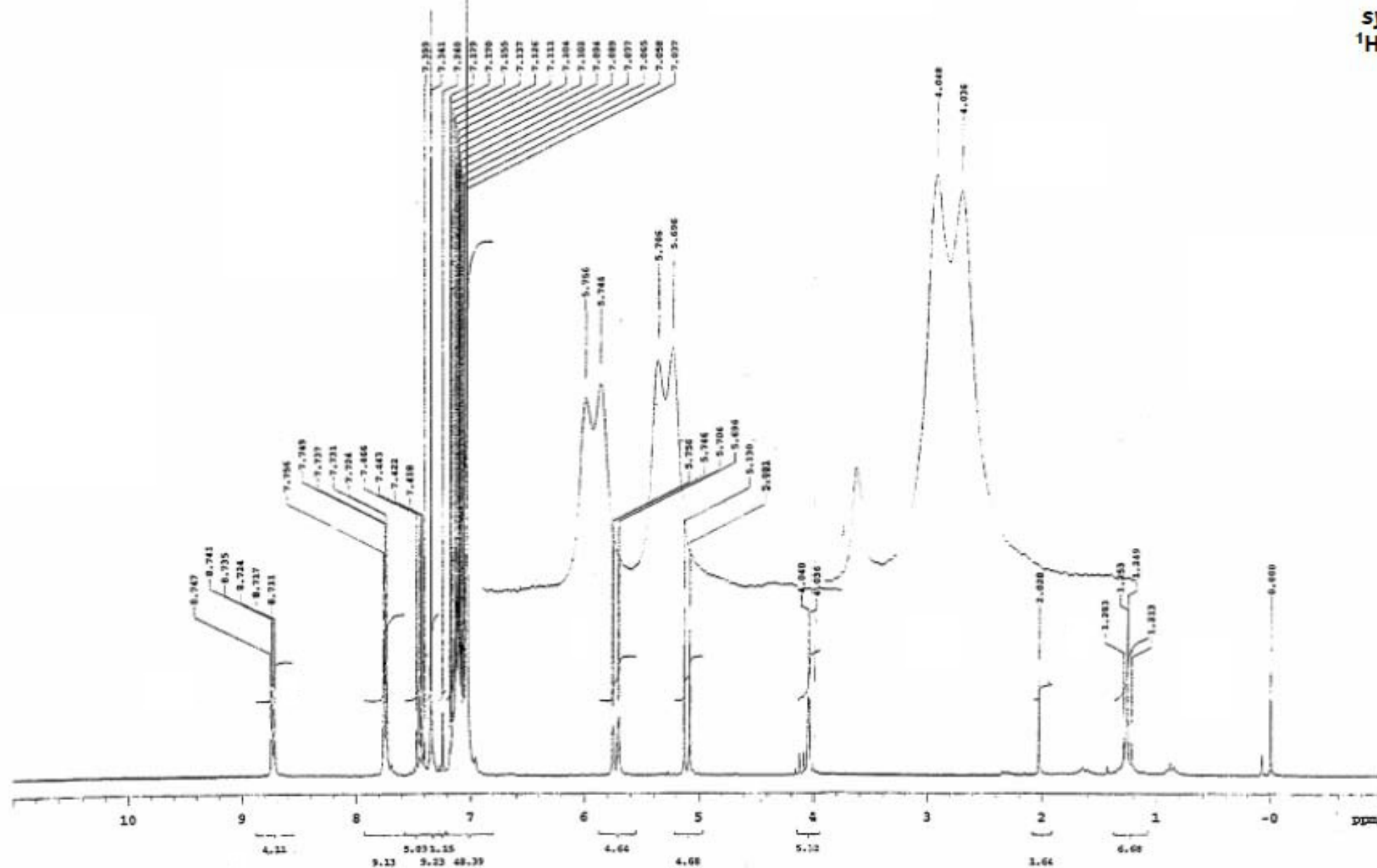


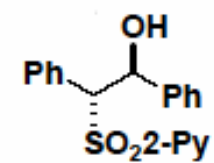
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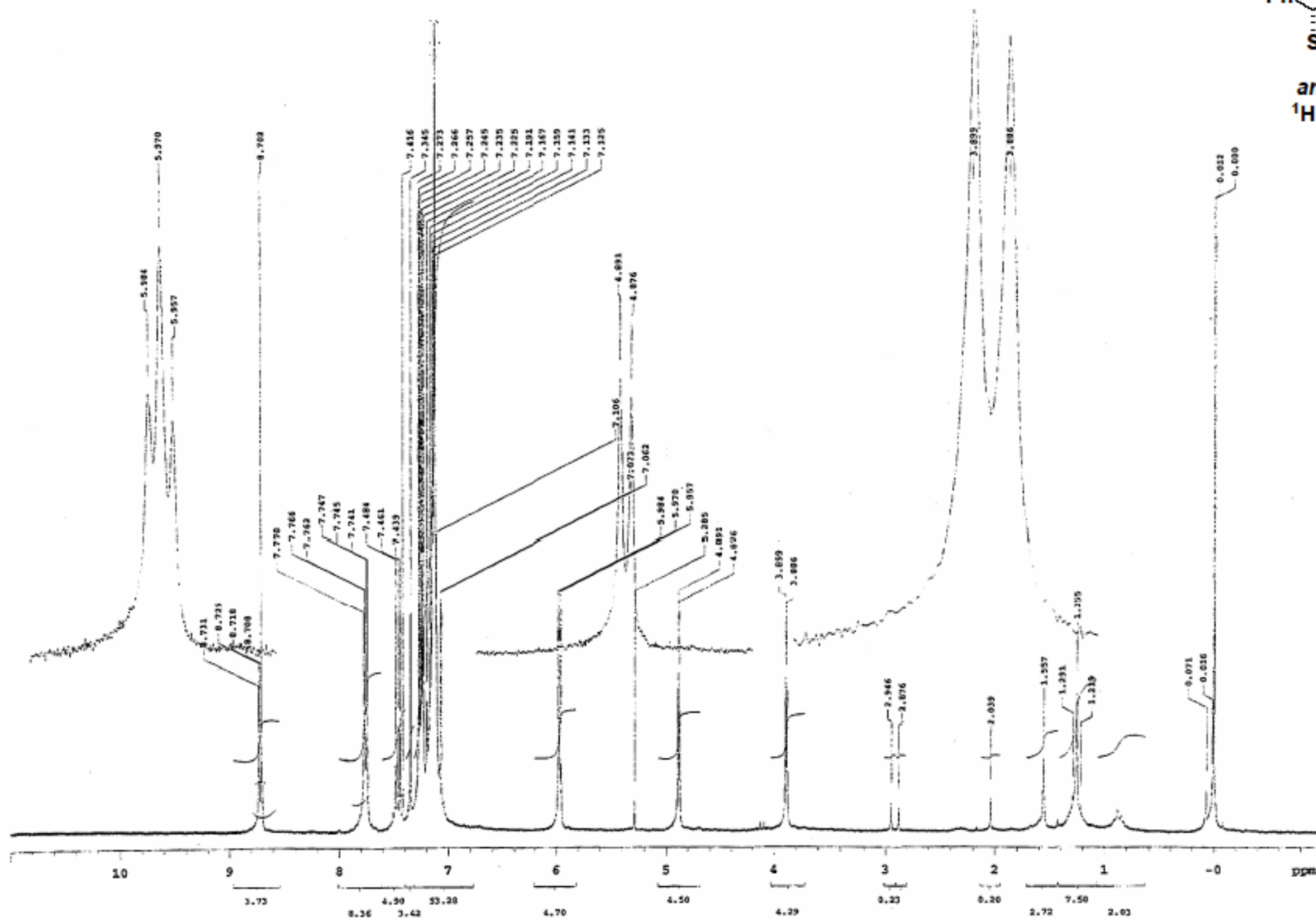


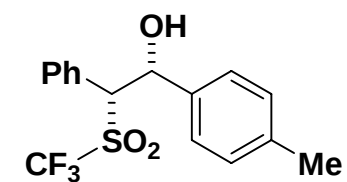
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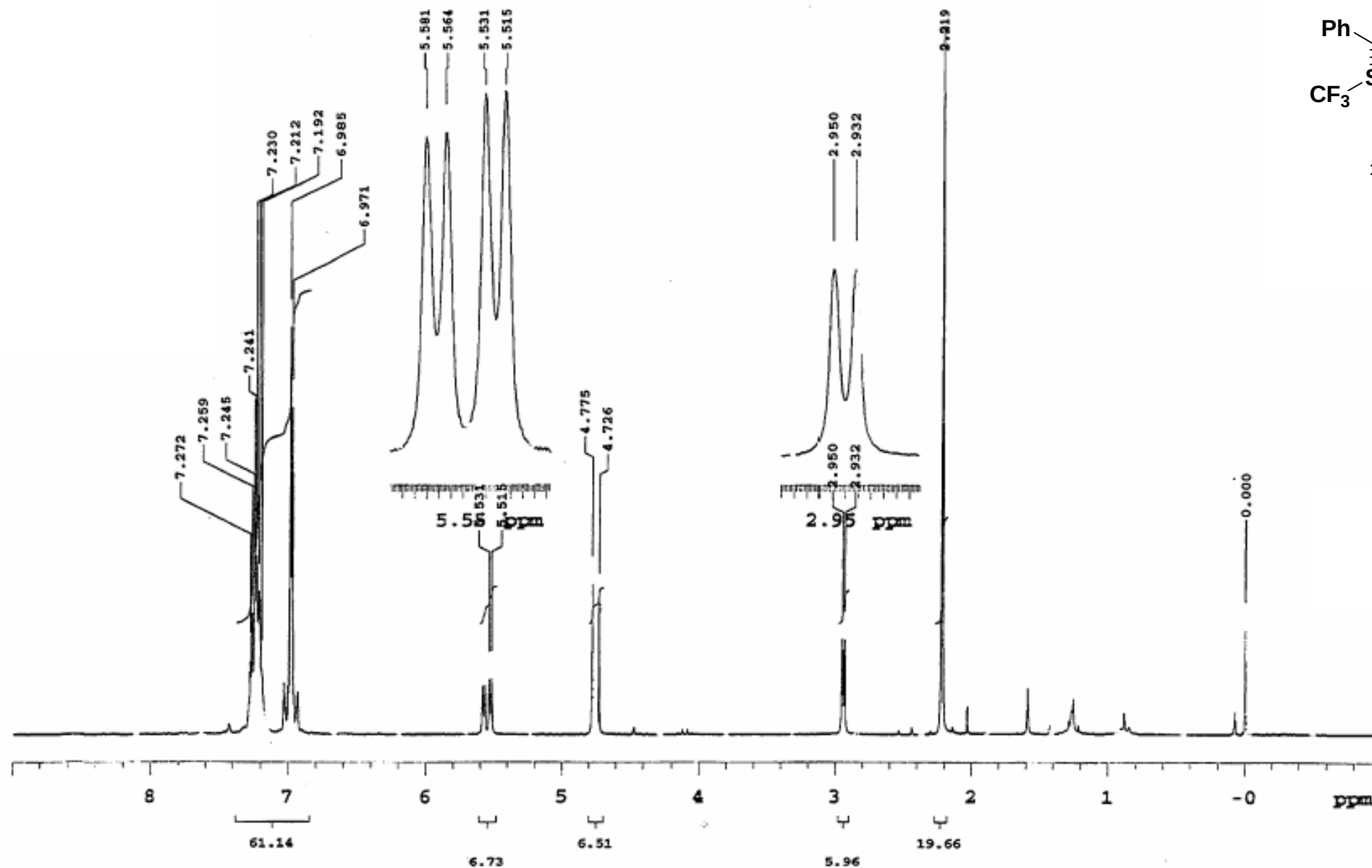


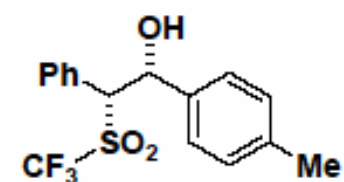
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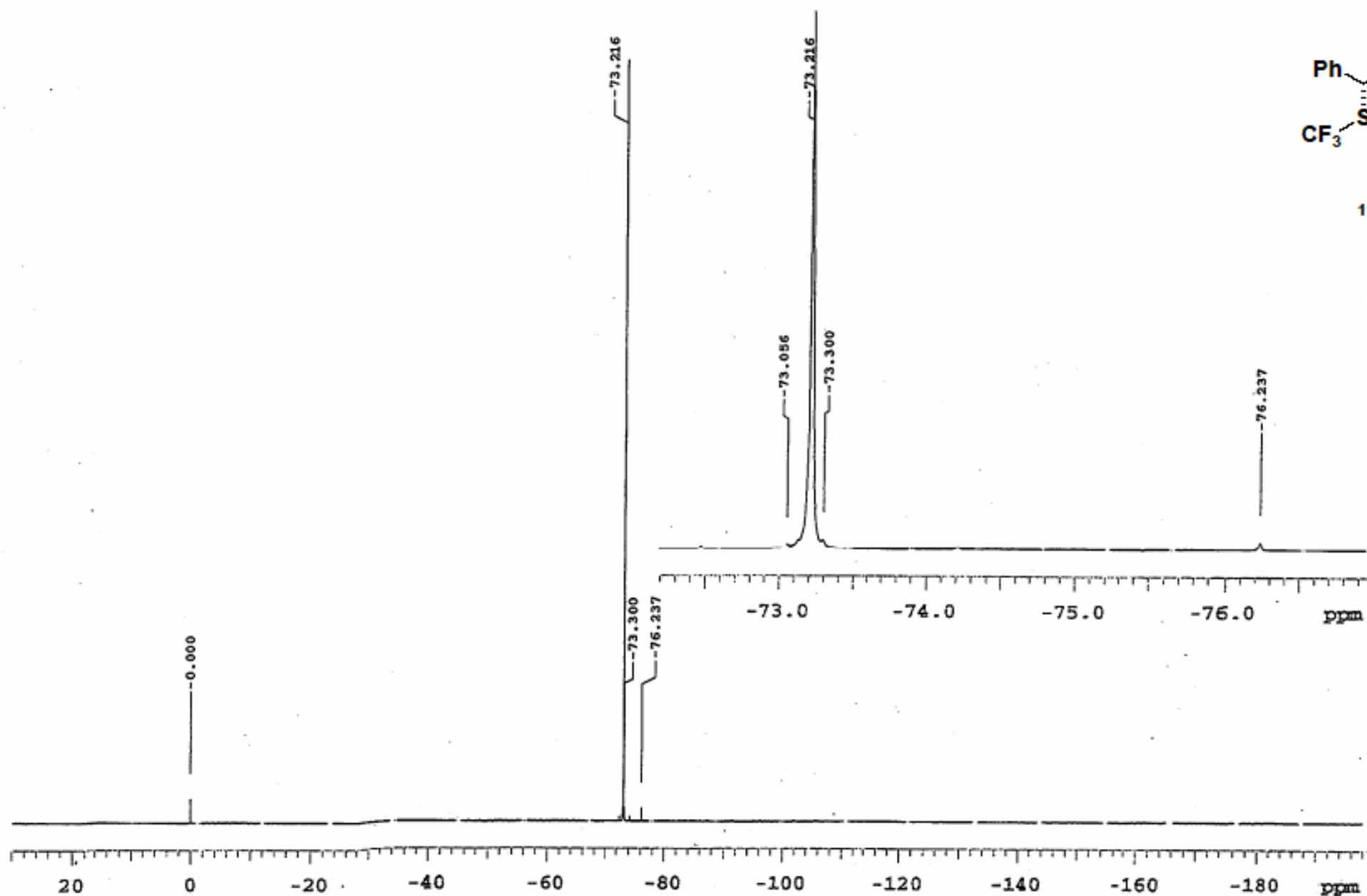


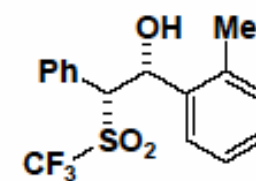
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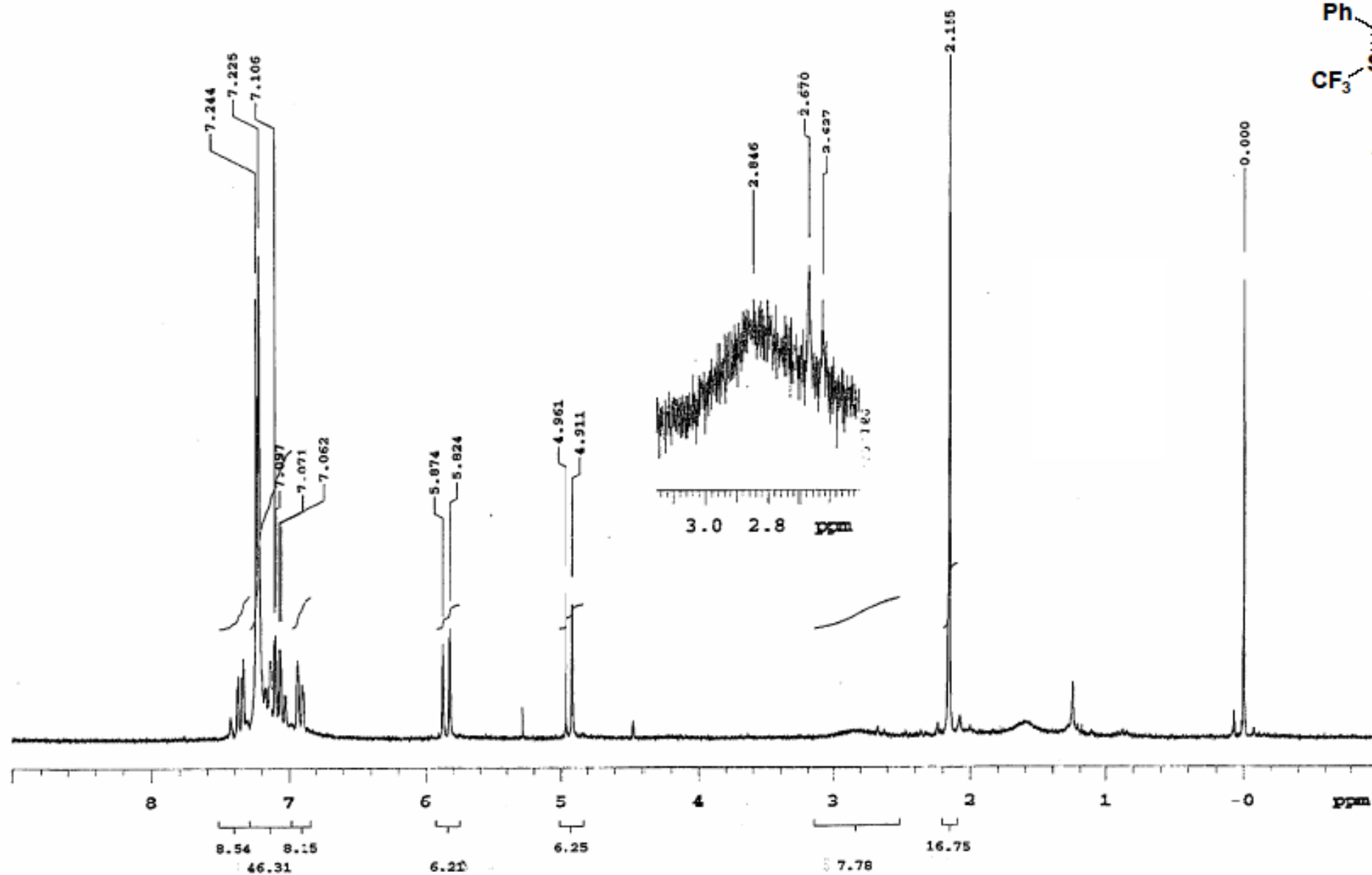


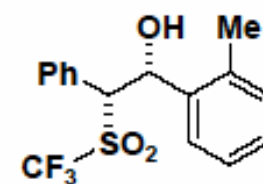
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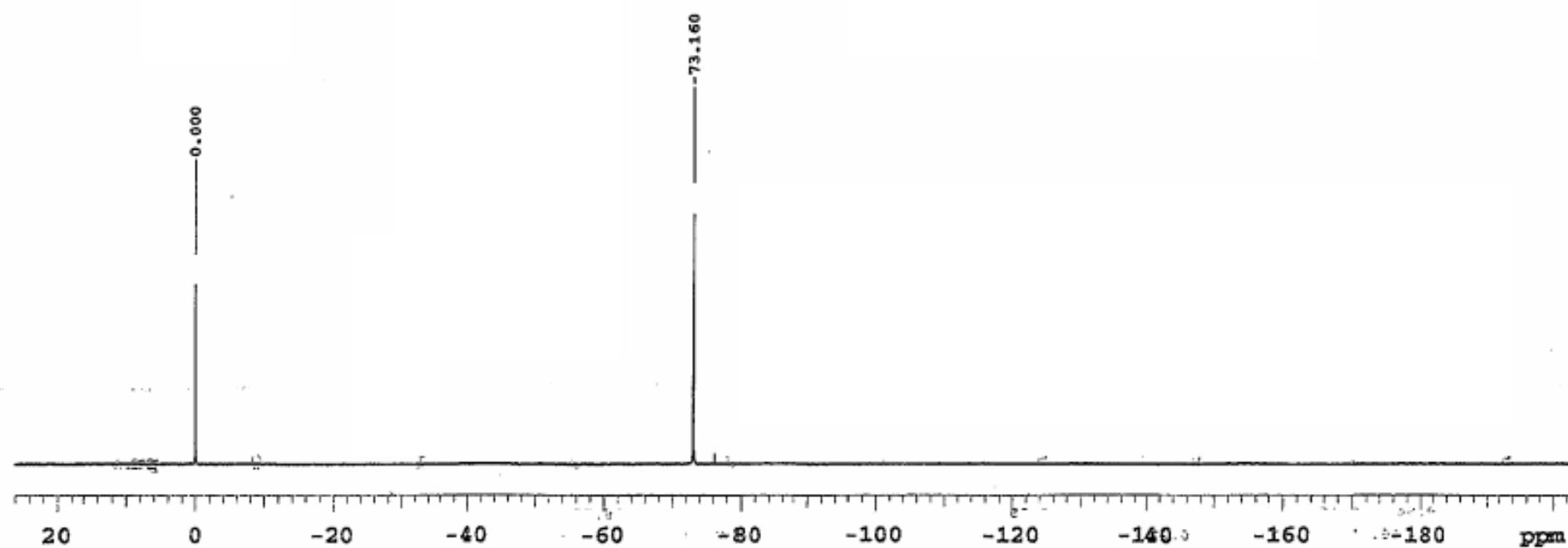


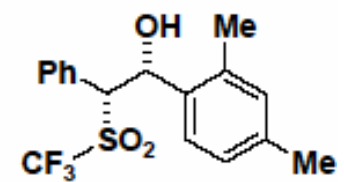
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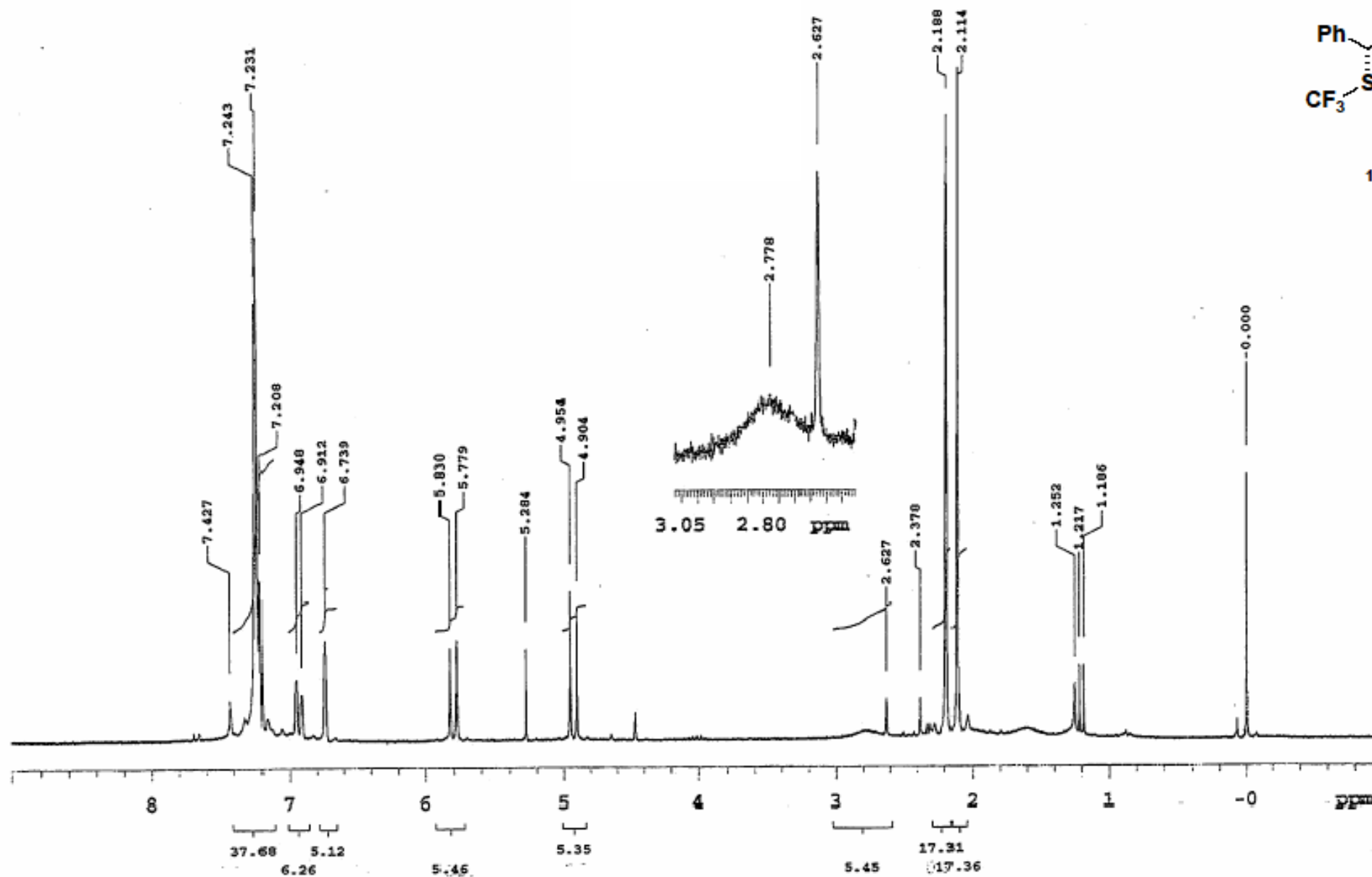


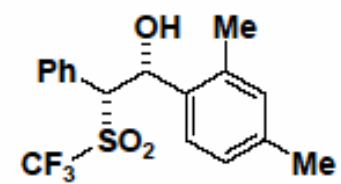
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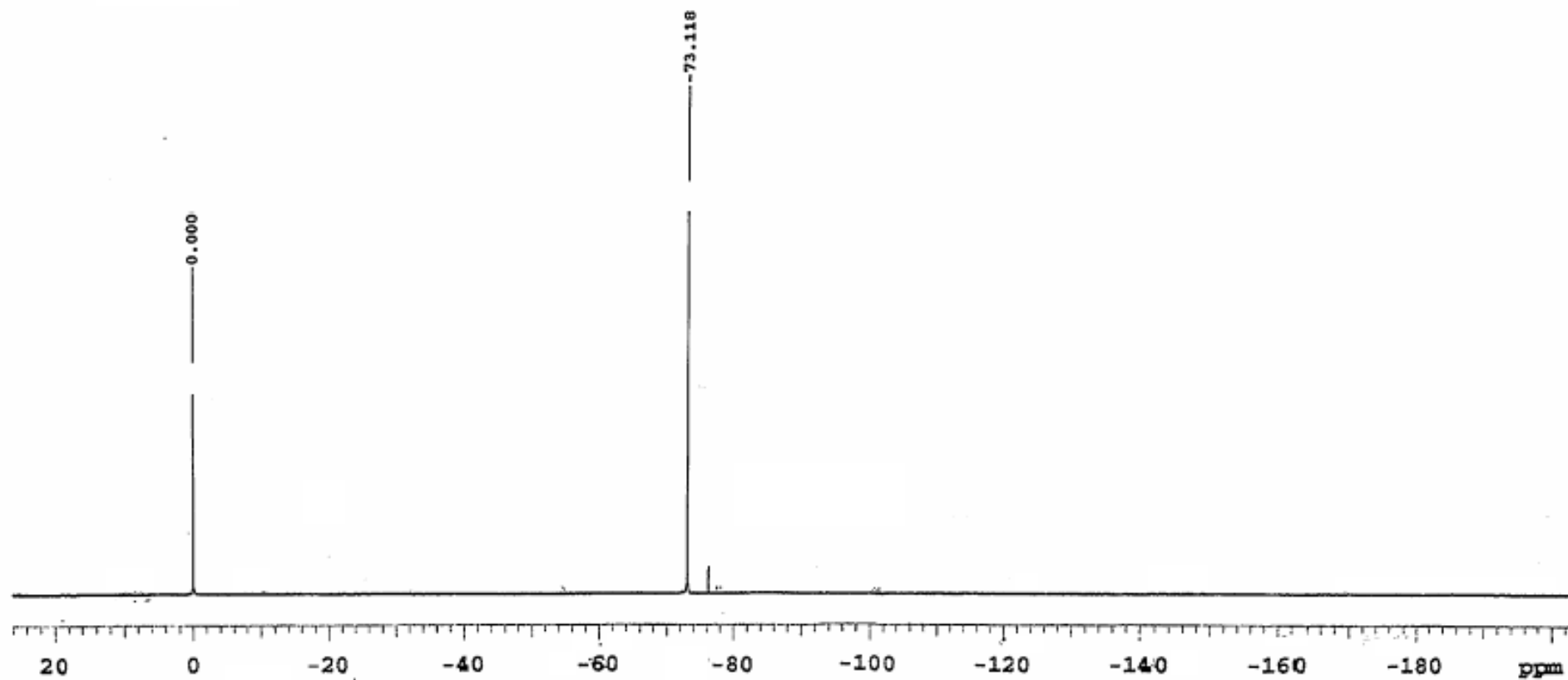


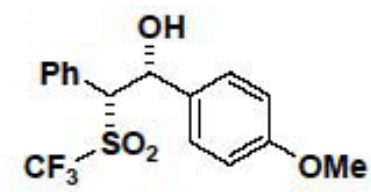
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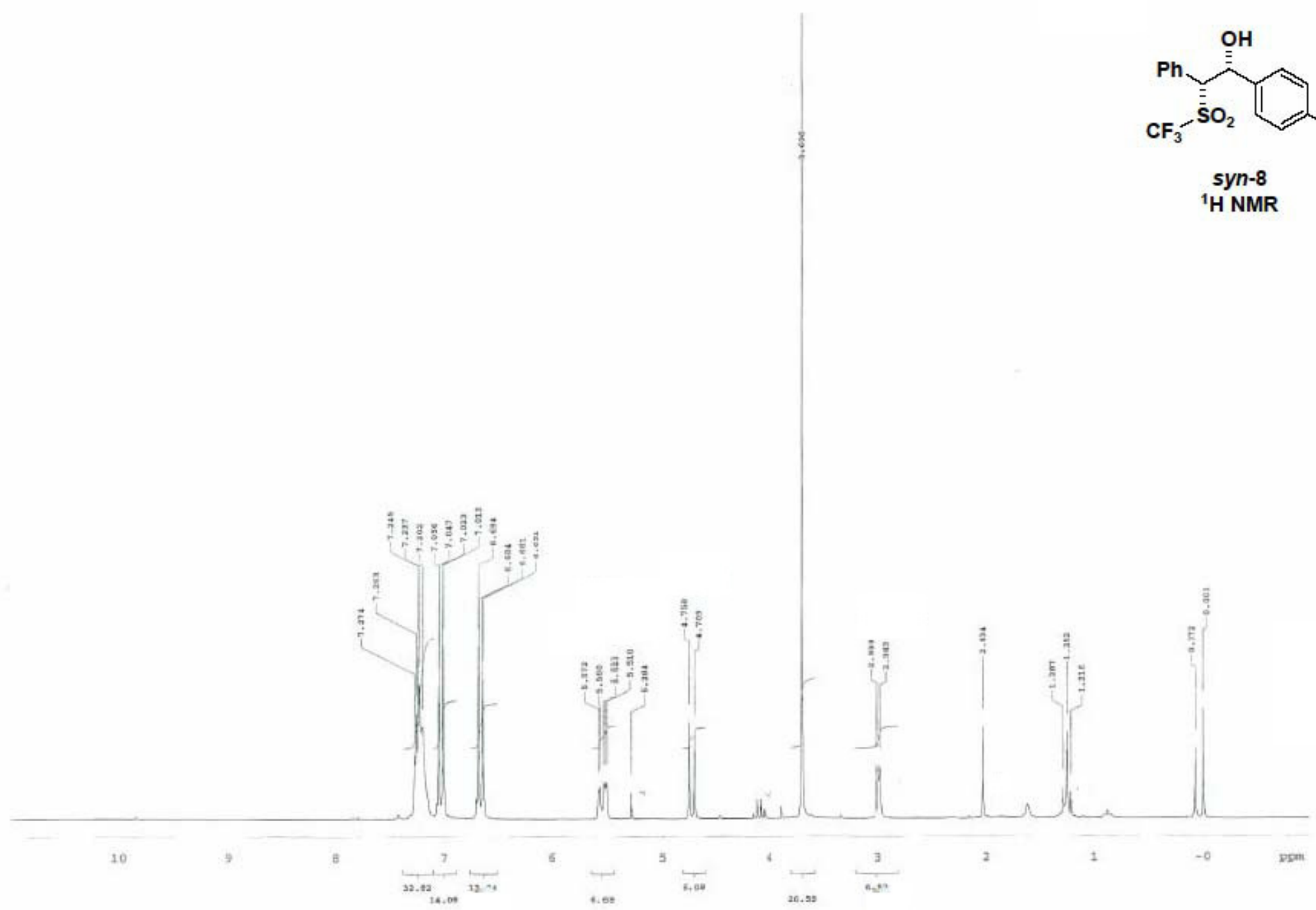


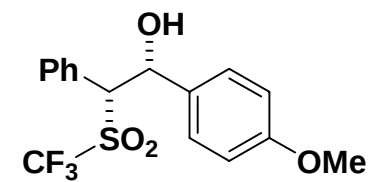
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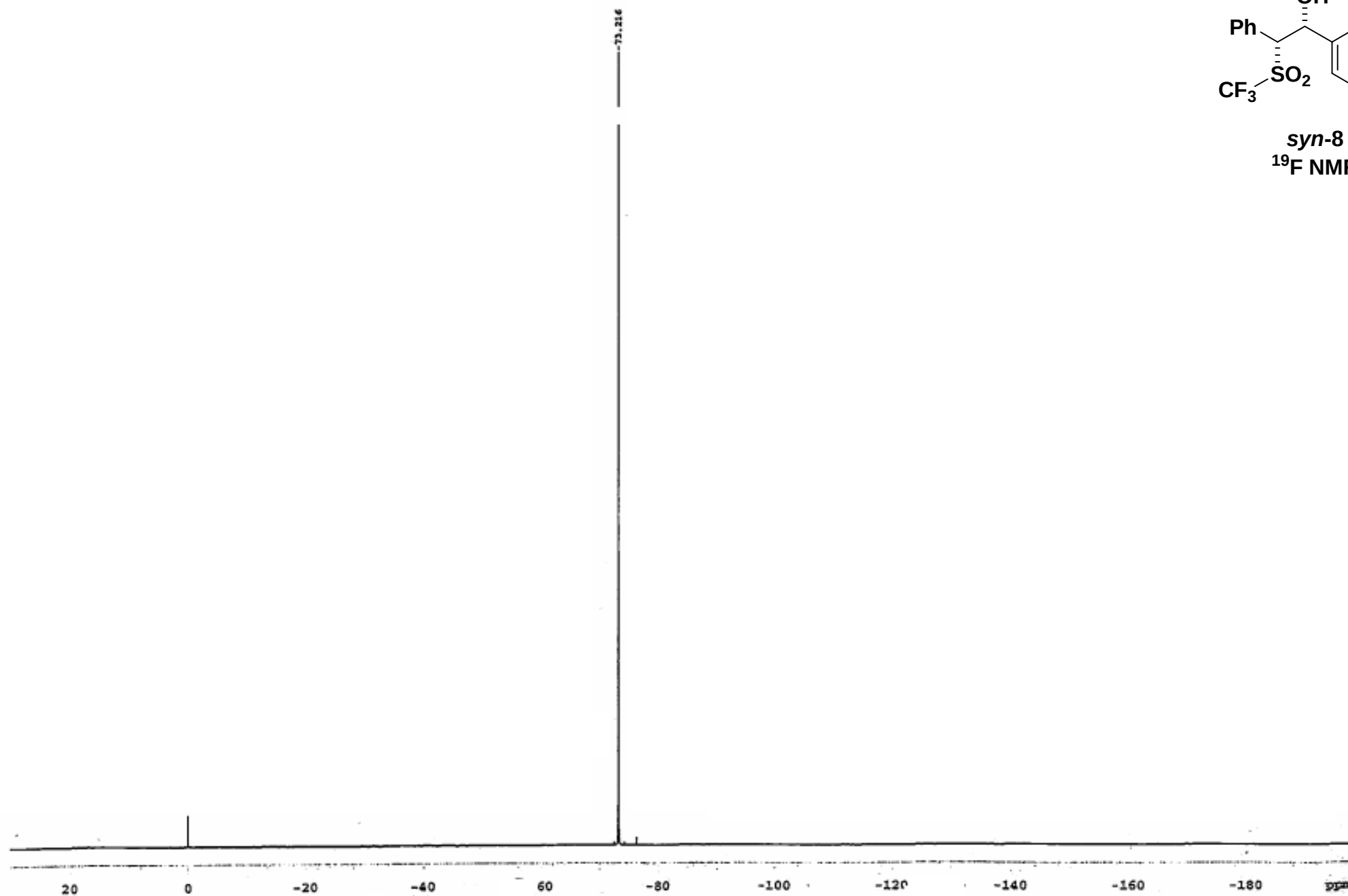


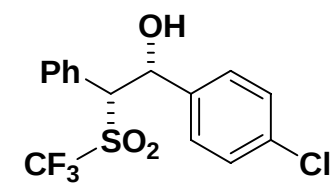
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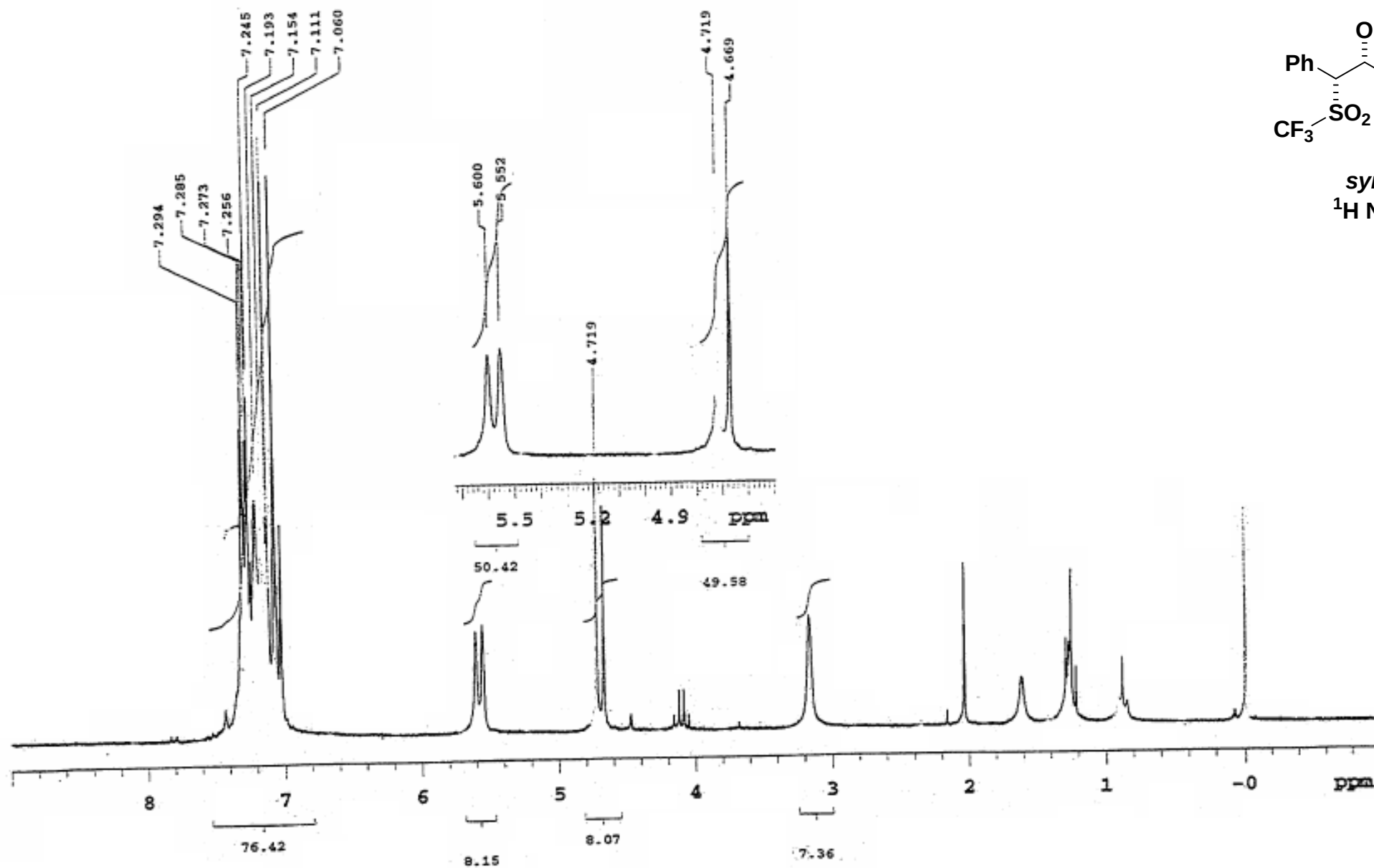


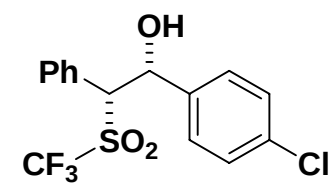
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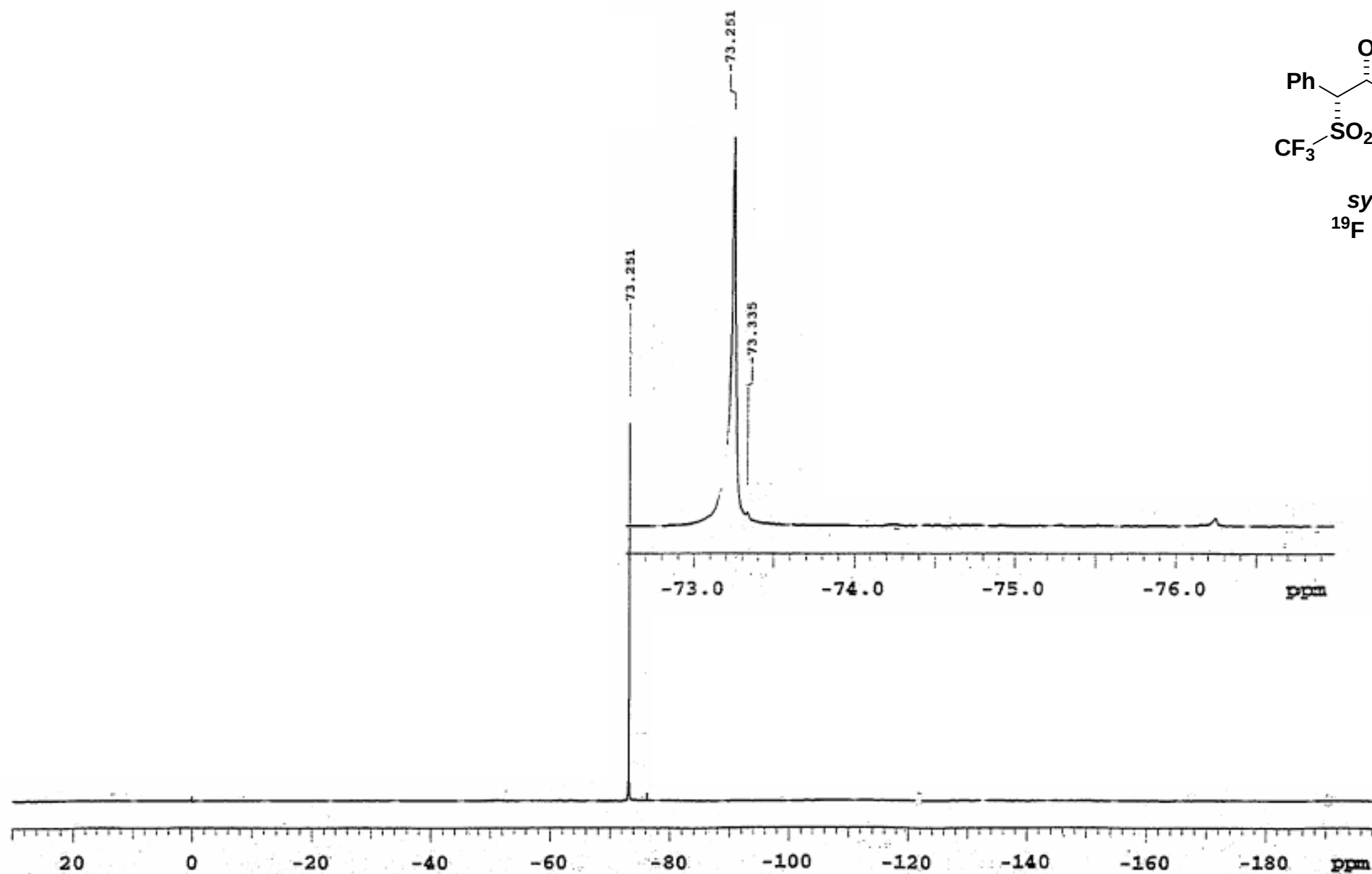


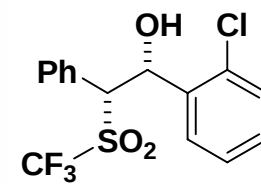
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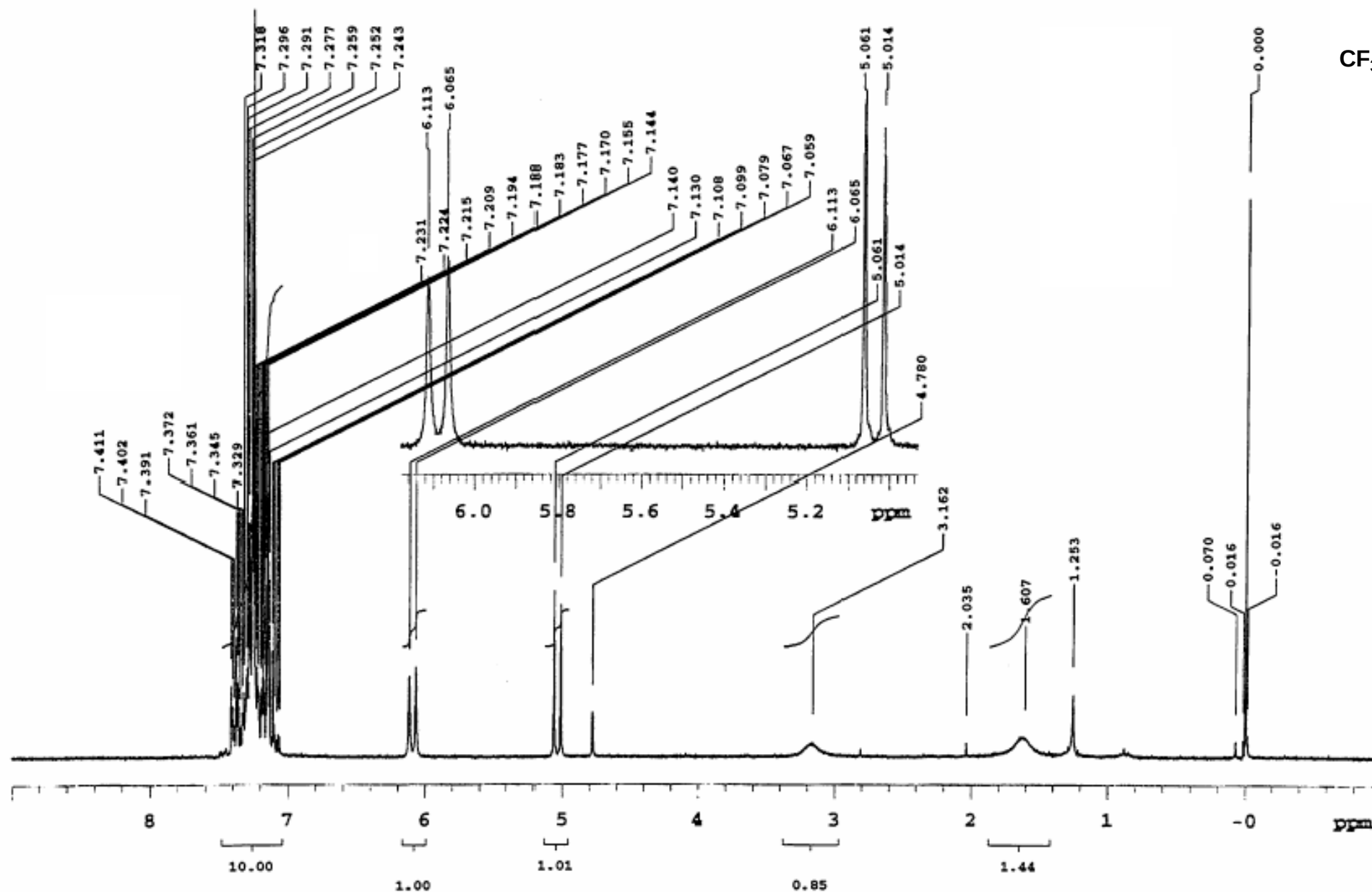


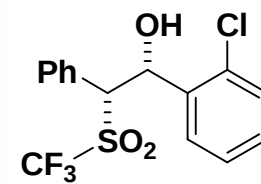
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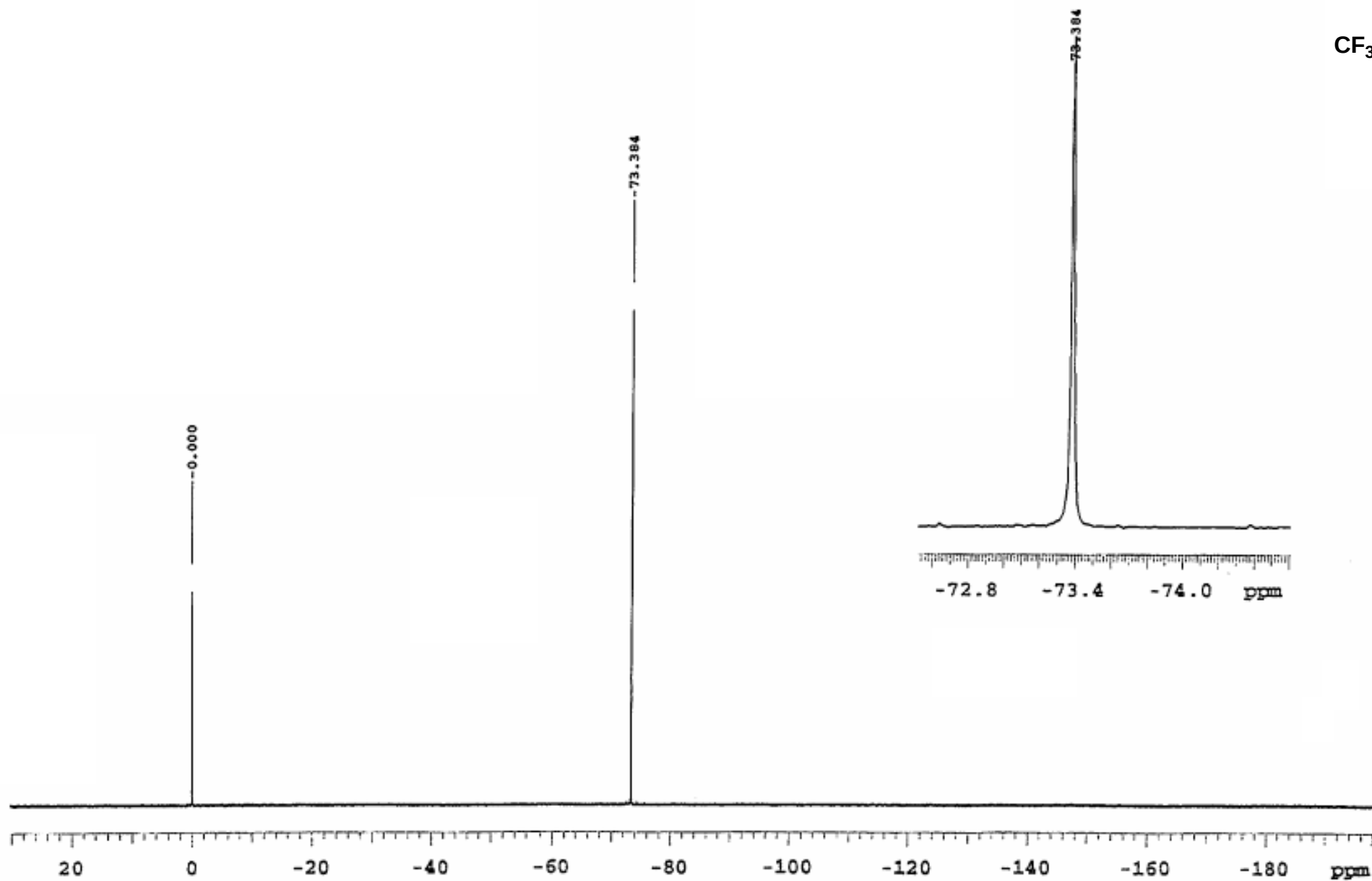


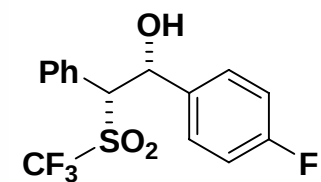
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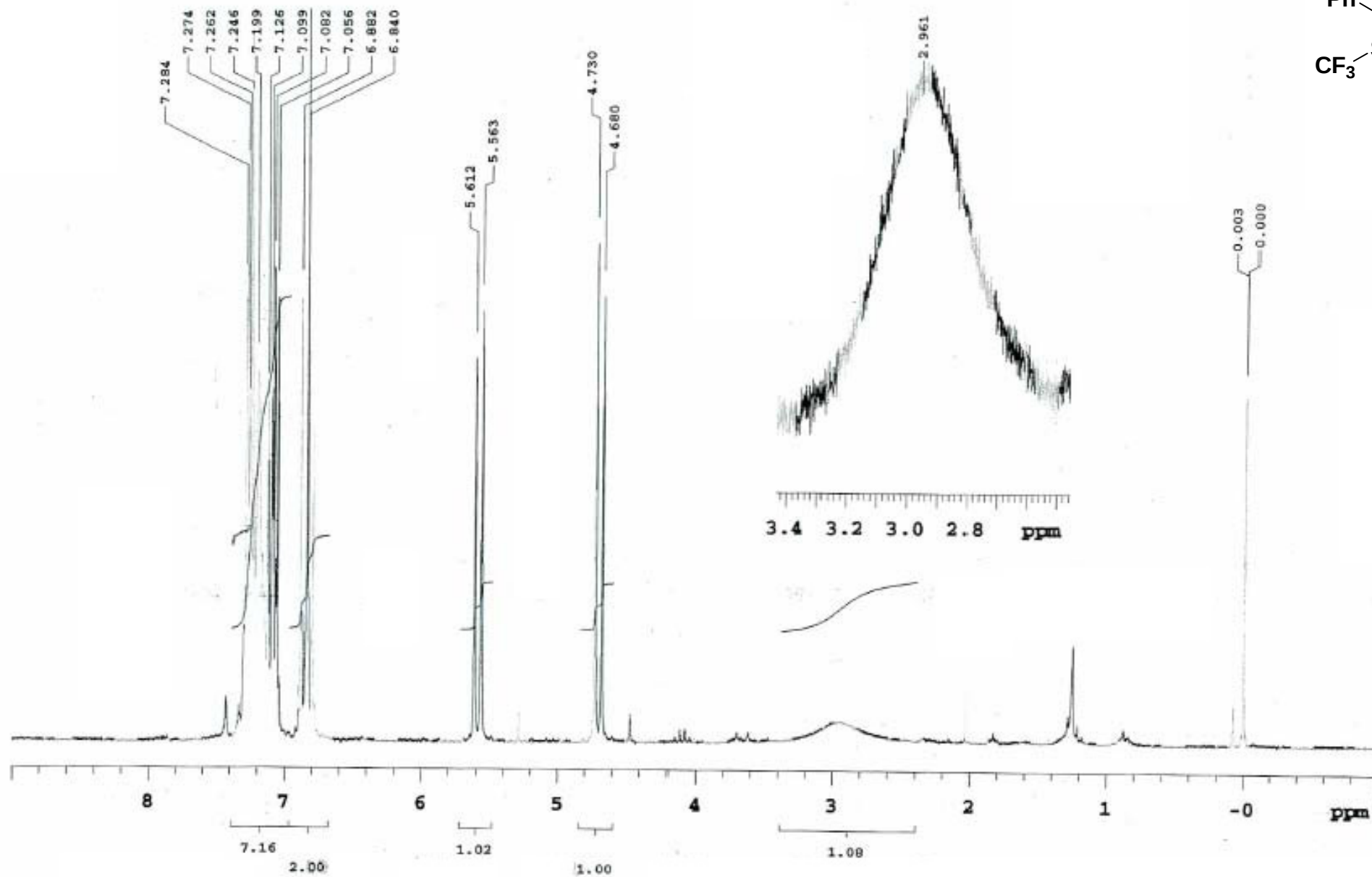


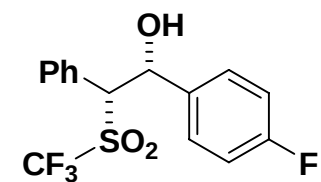
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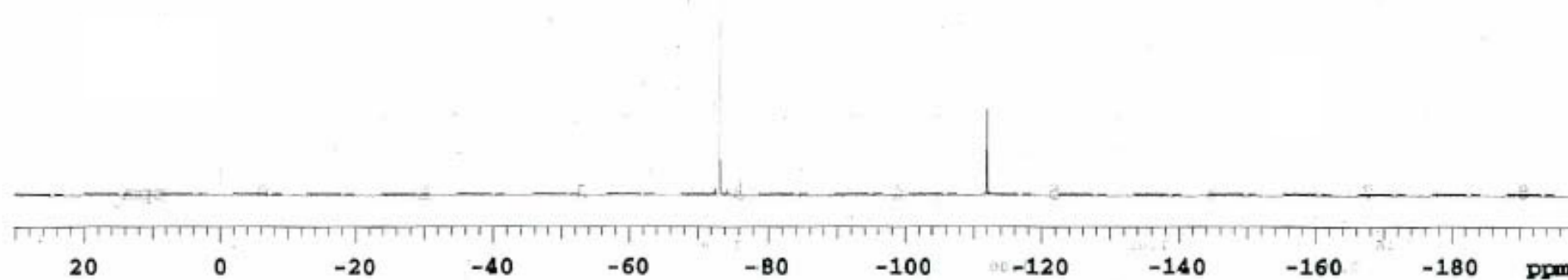
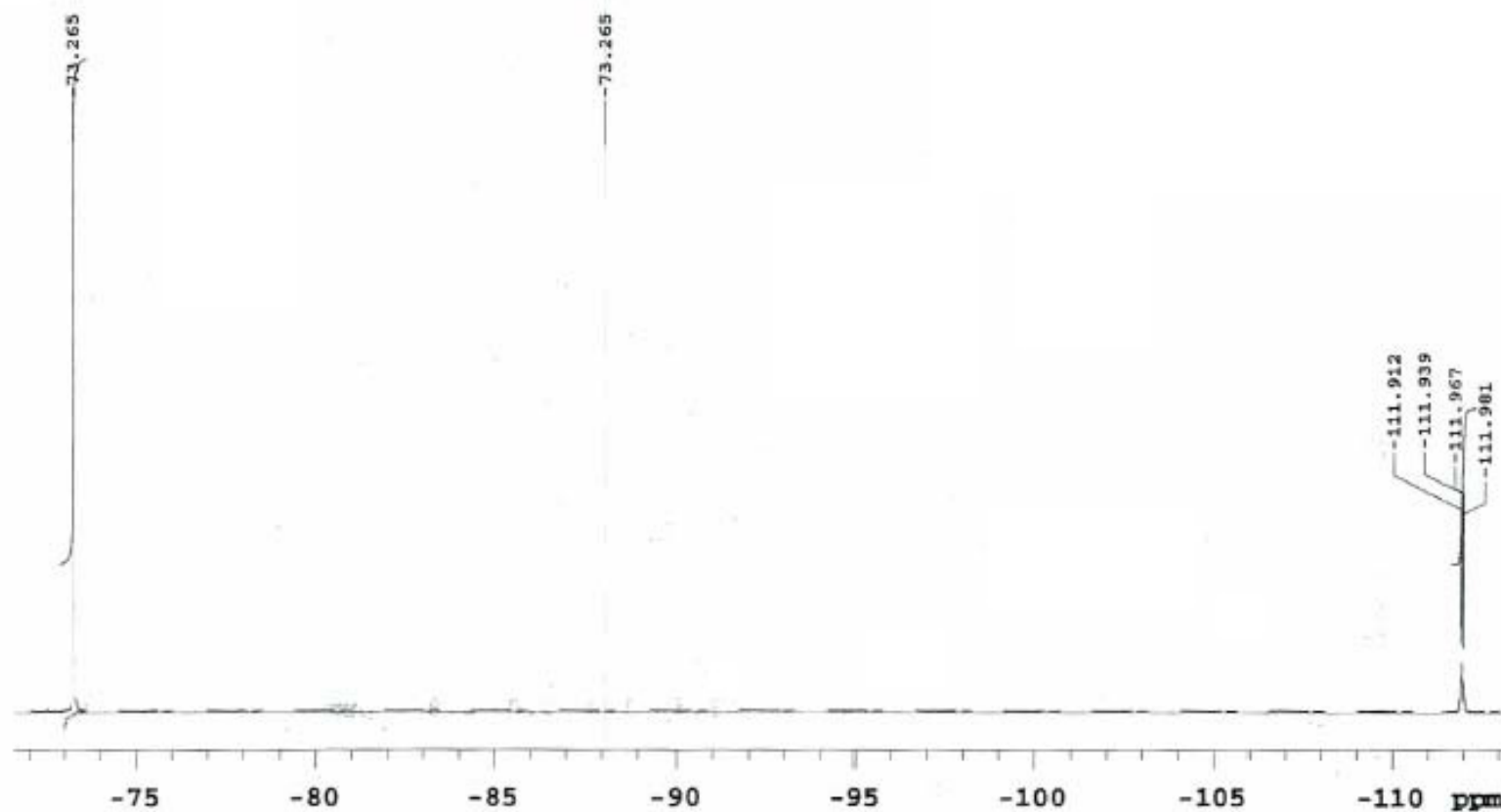


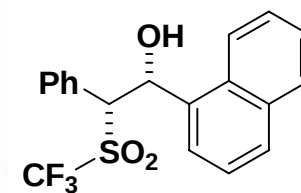
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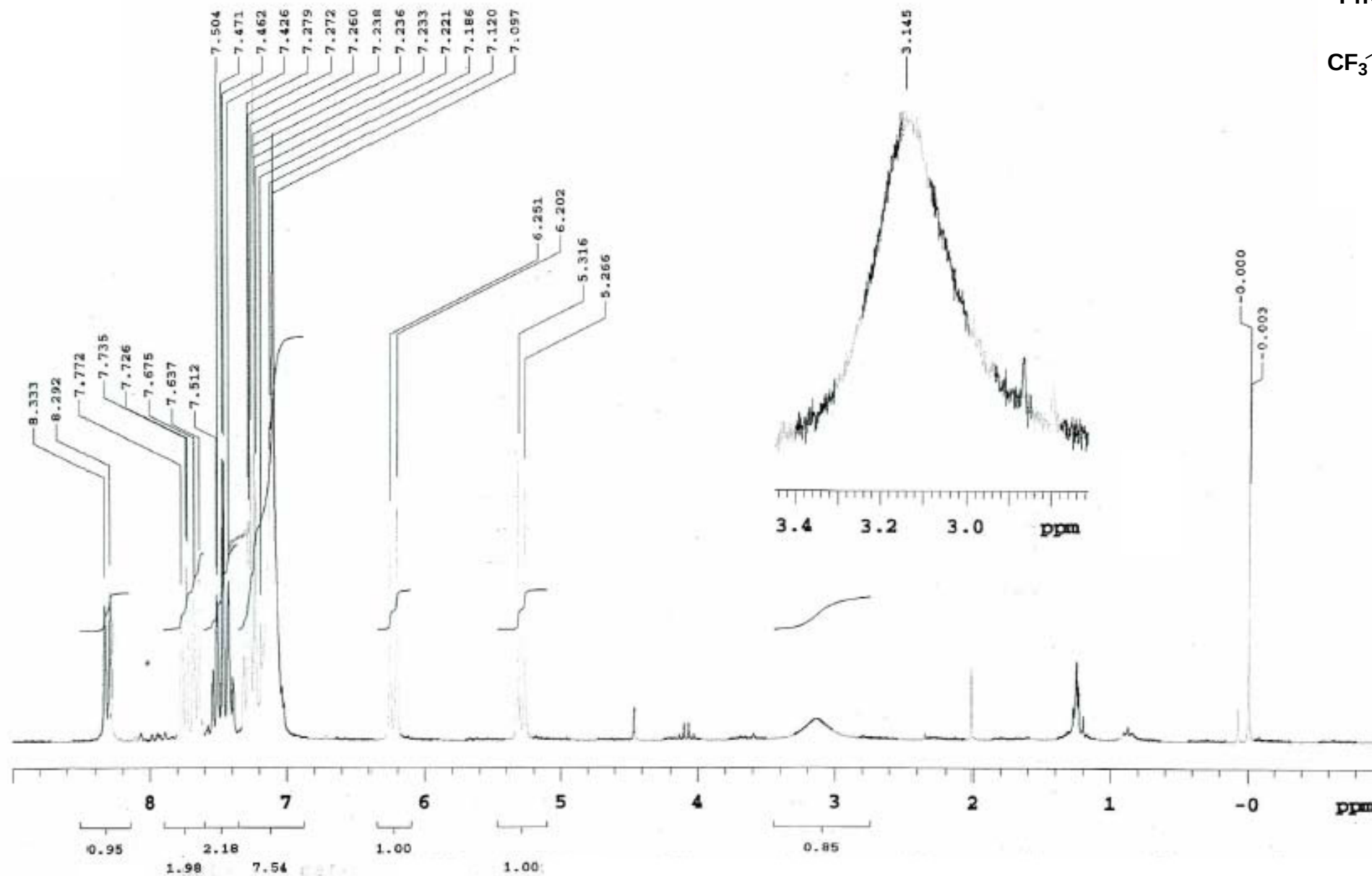


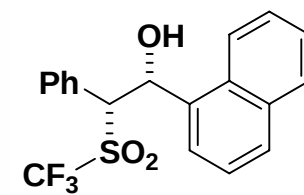
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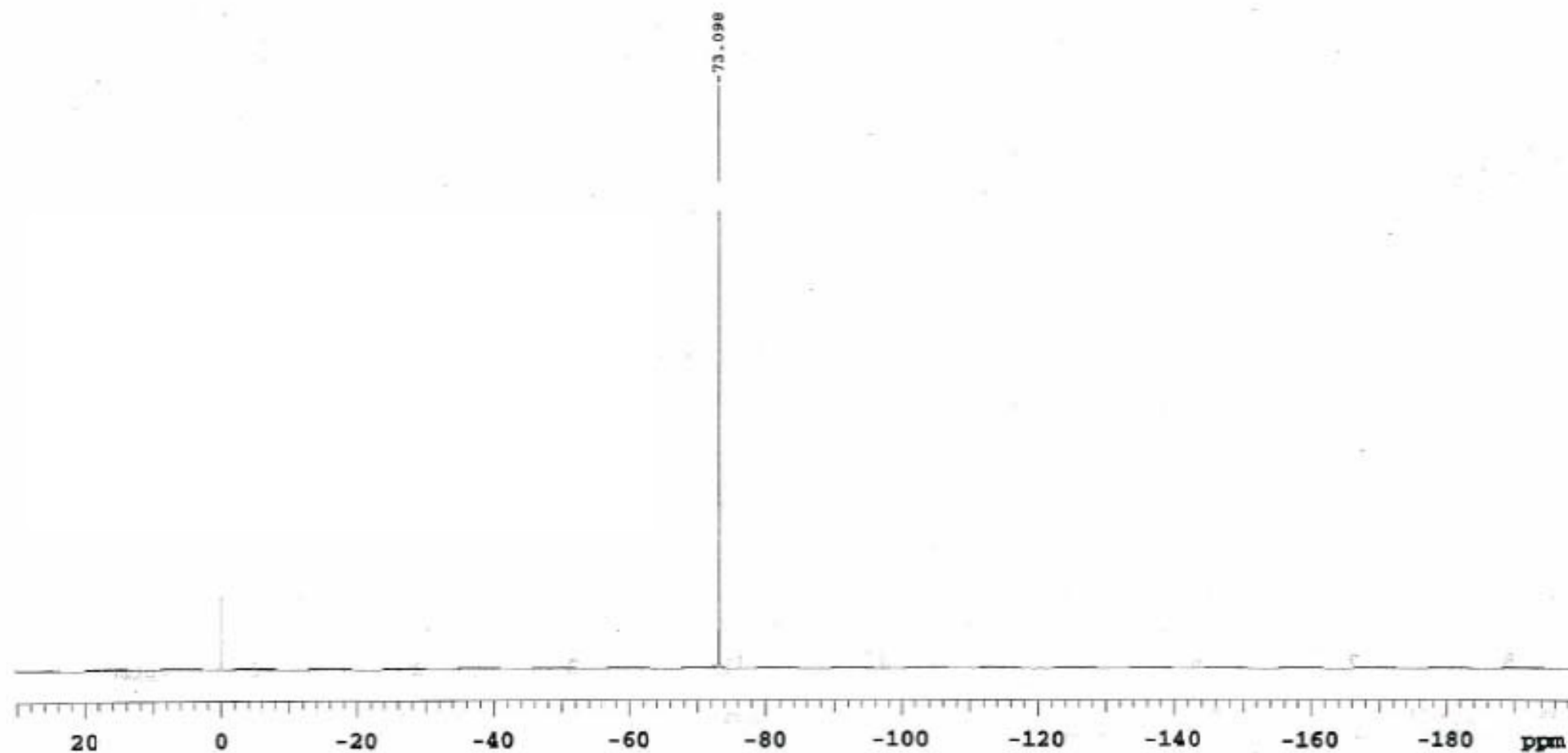


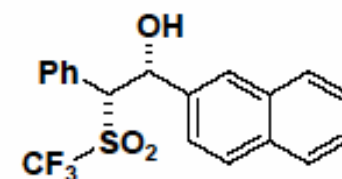
syn-12
¹H NMR



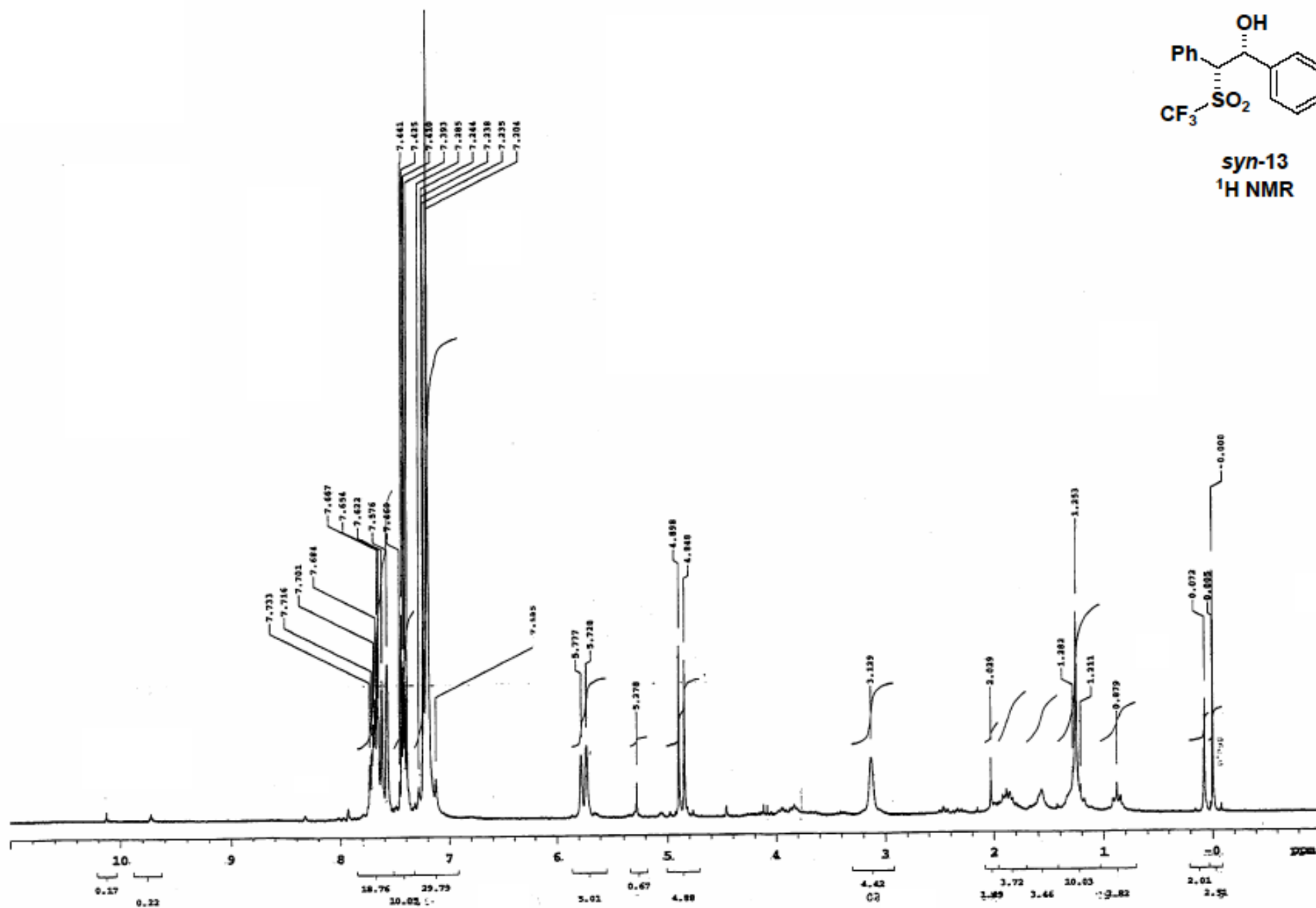


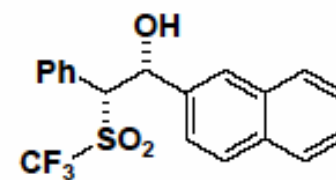
syn-12
¹⁹F NMR



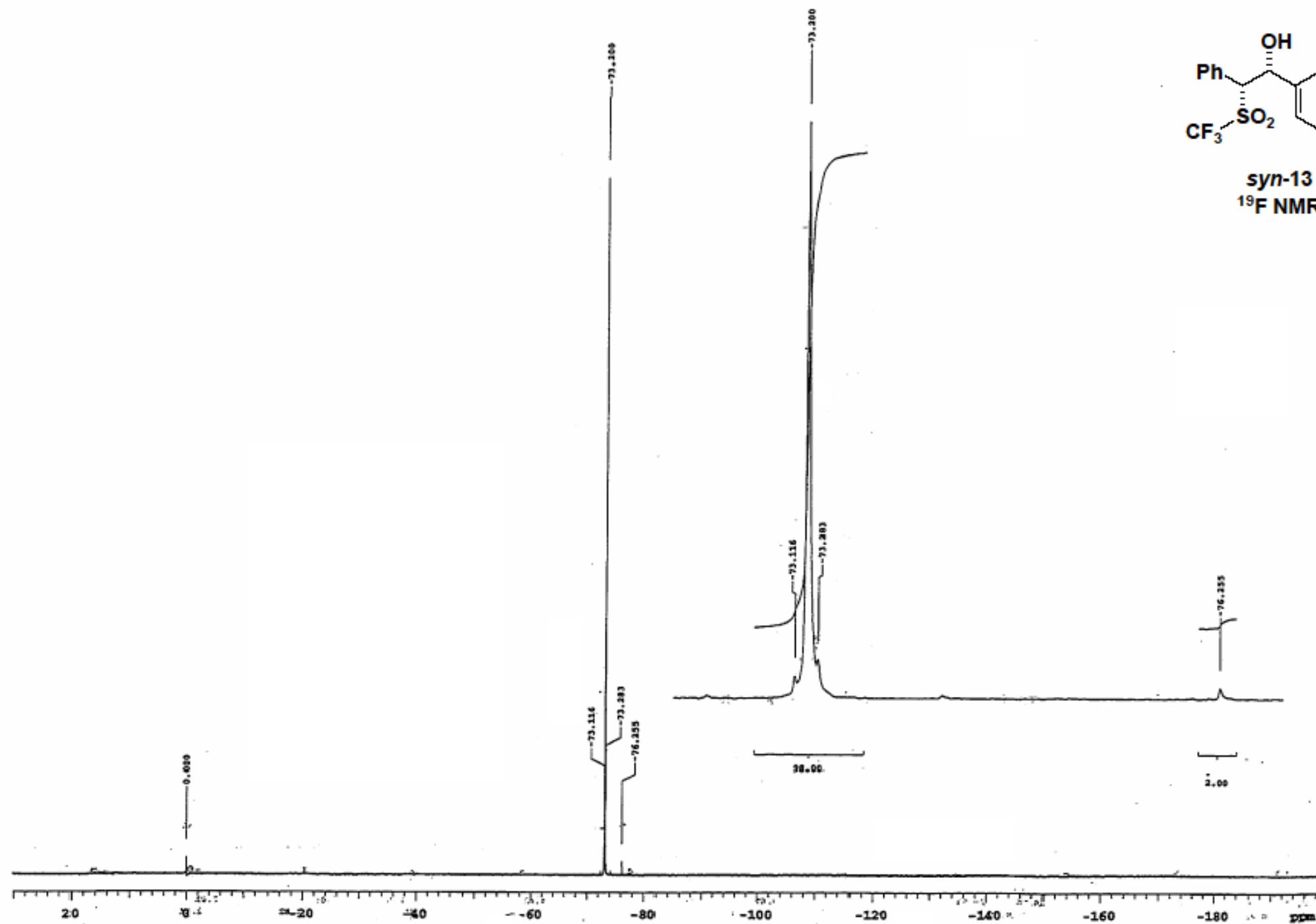


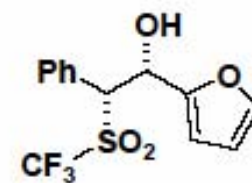
syn-13
¹H NMR



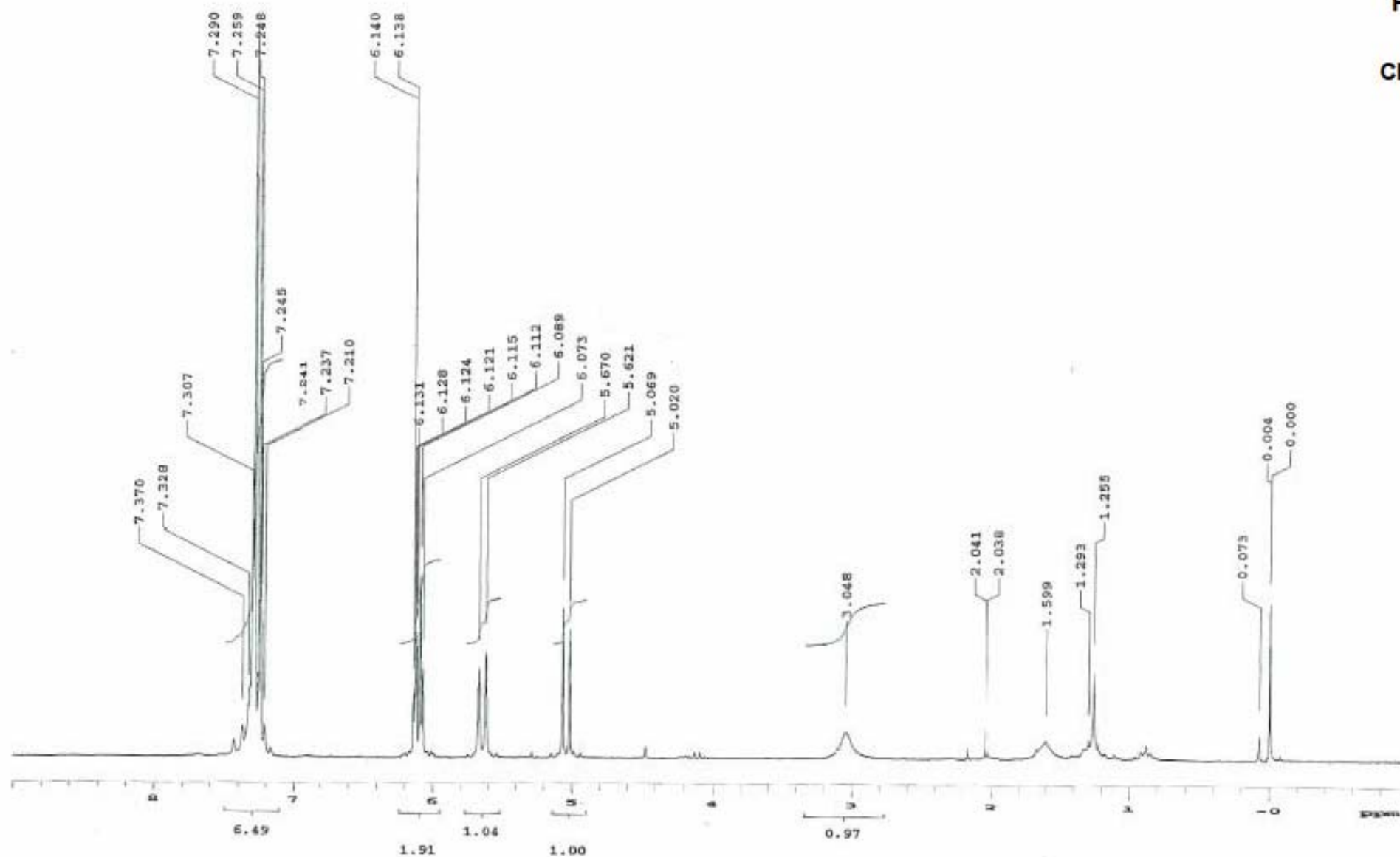


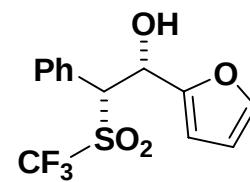
syn-13
¹⁹F NMR



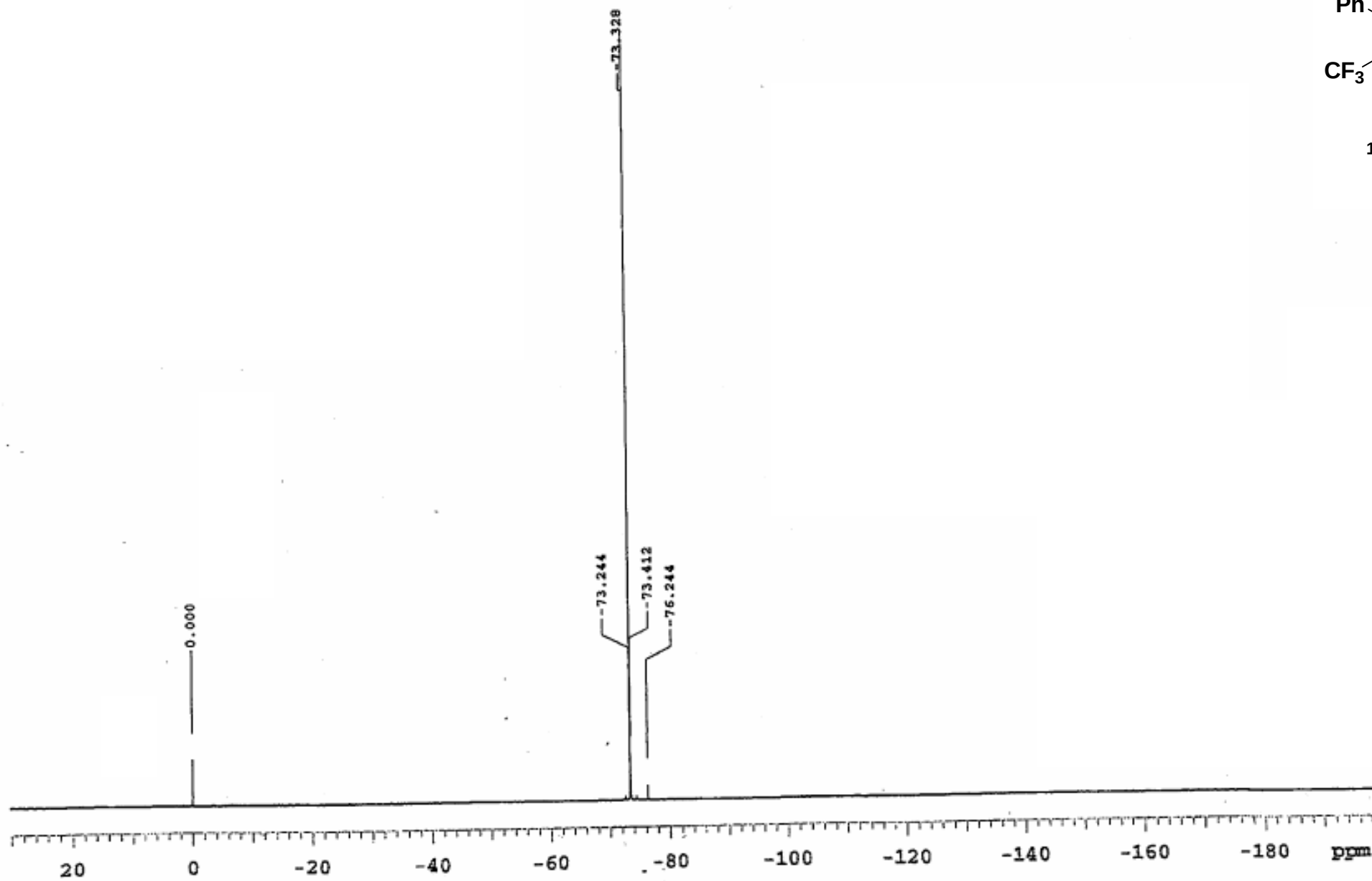


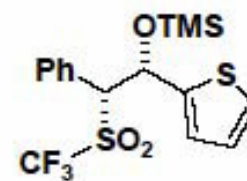
syn-14
¹H NMR



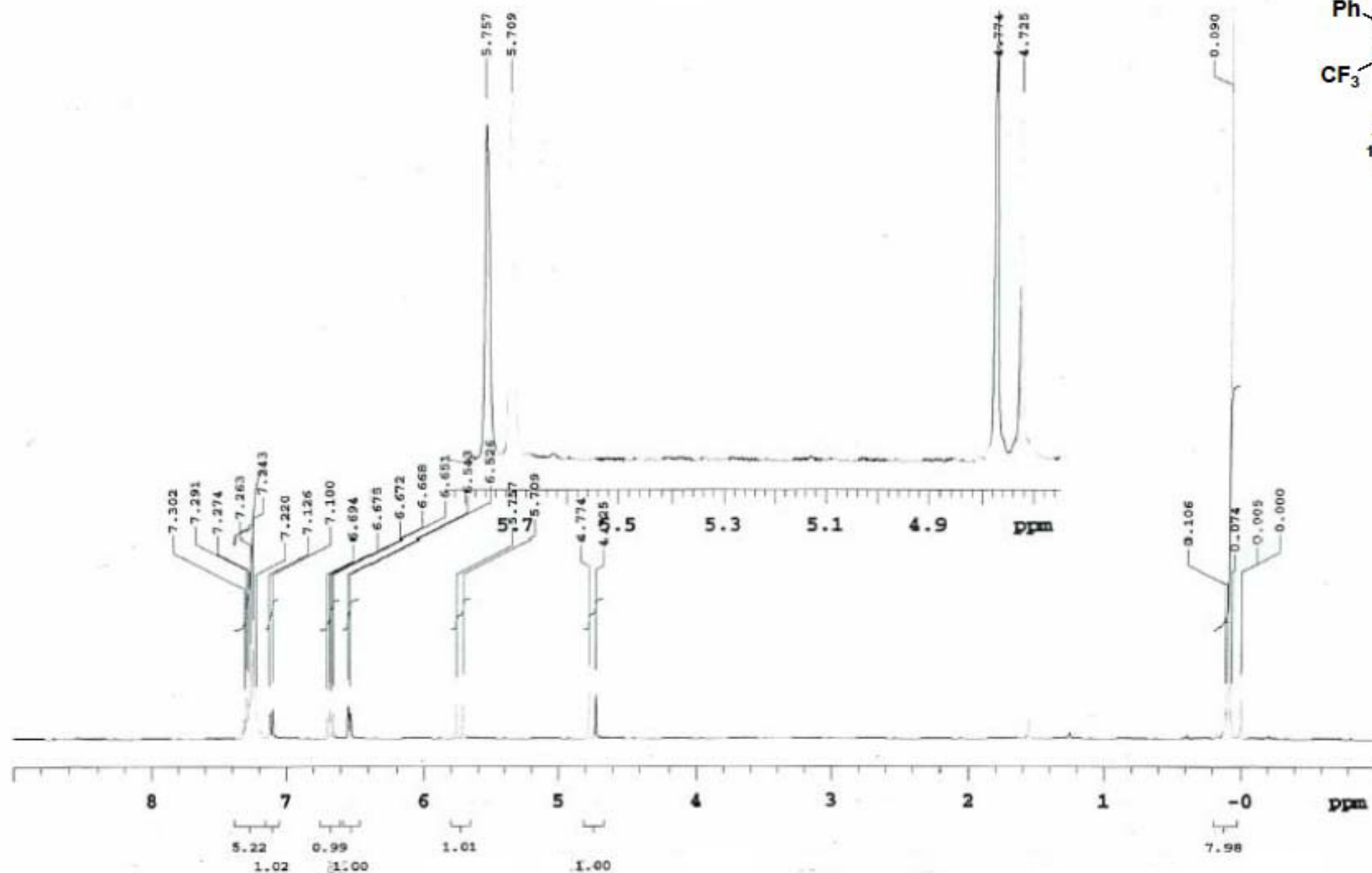


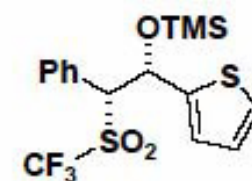
syn-14
 ^{19}F NMR



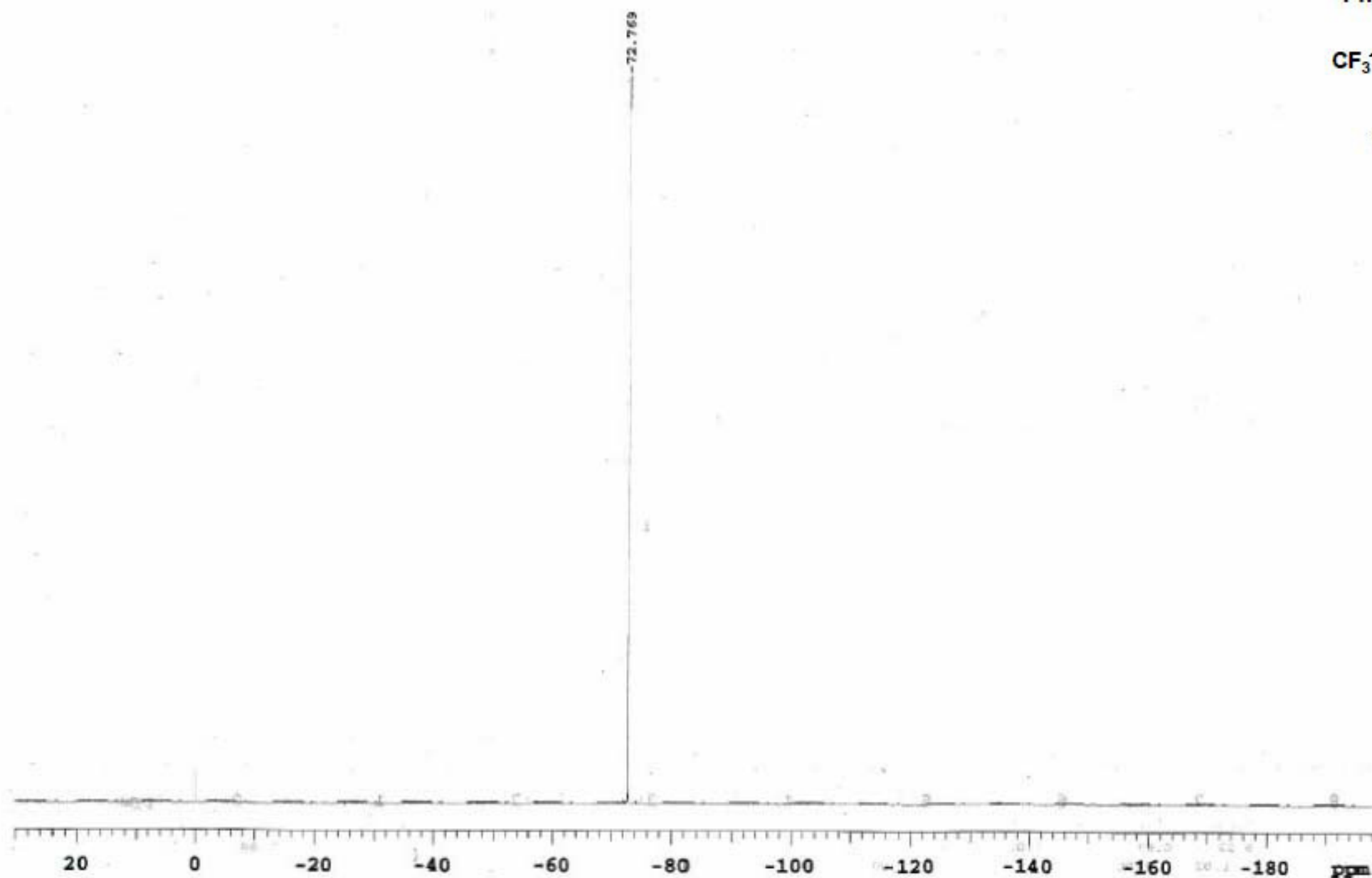


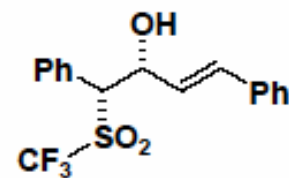
syn-15
¹H NMR



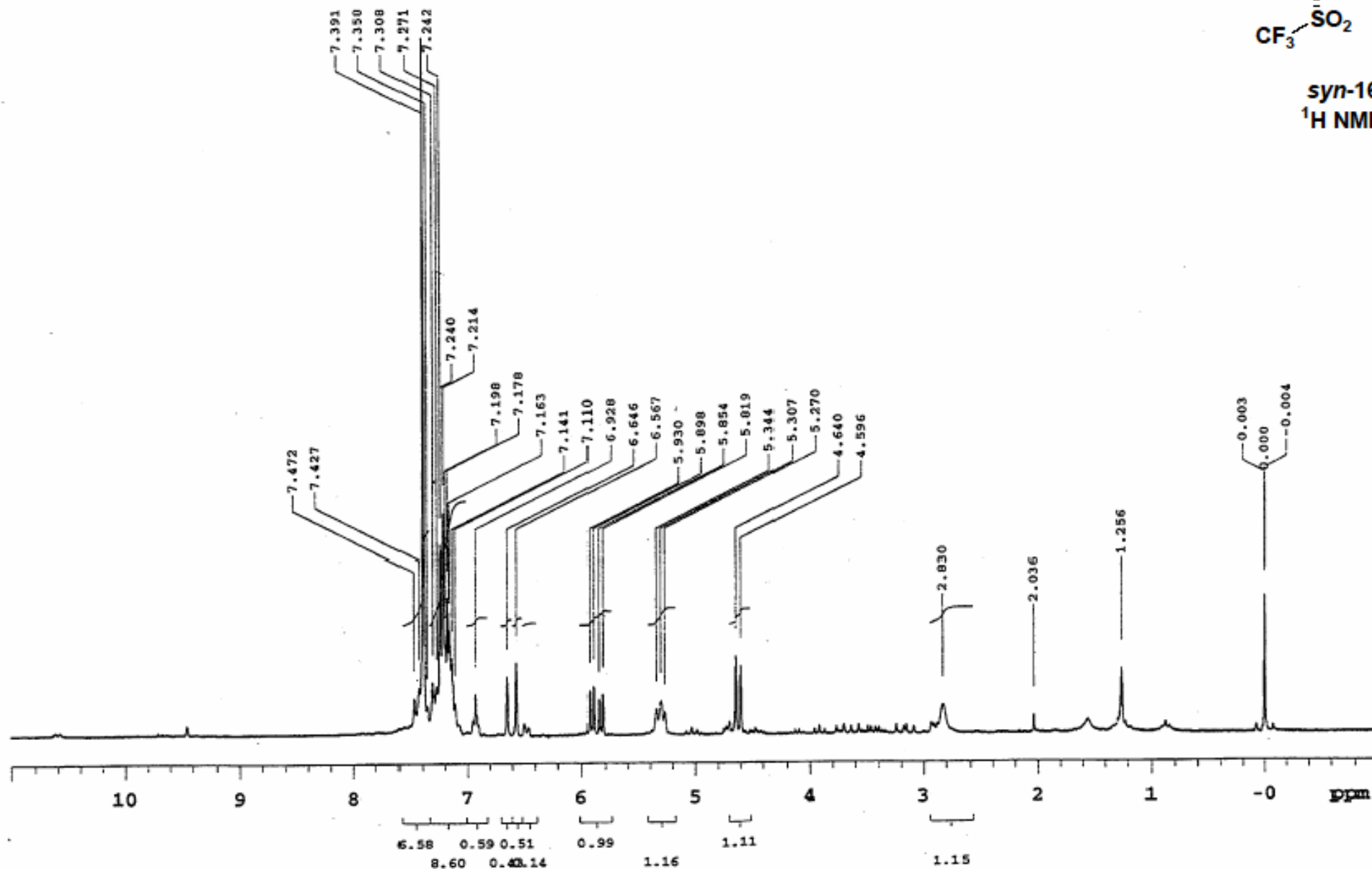


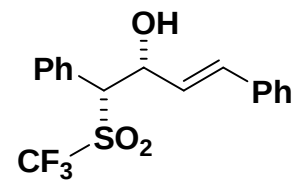
syn-15
 ^{19}F NMR



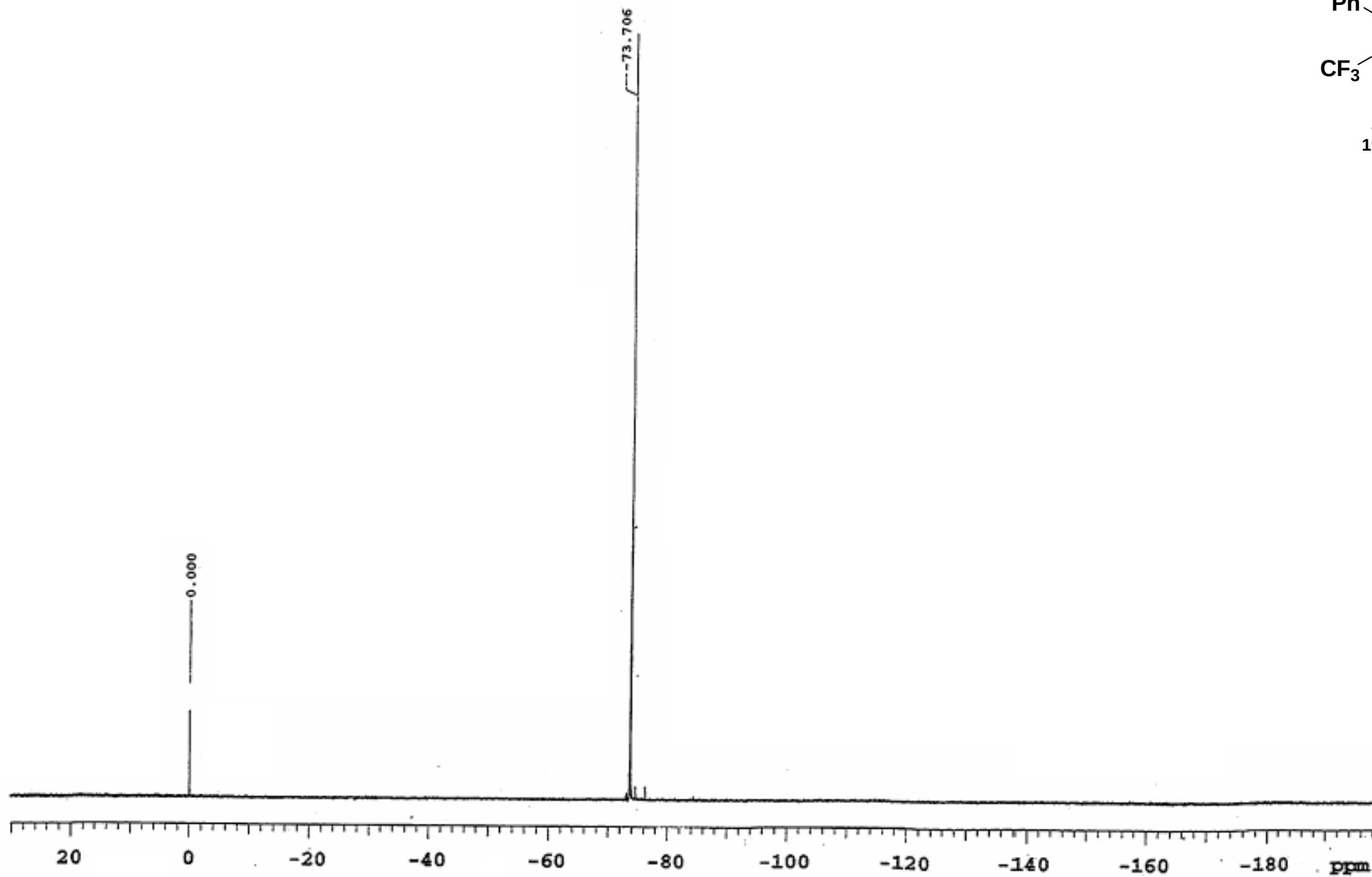


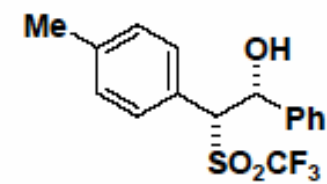
syn-16
¹H NMR



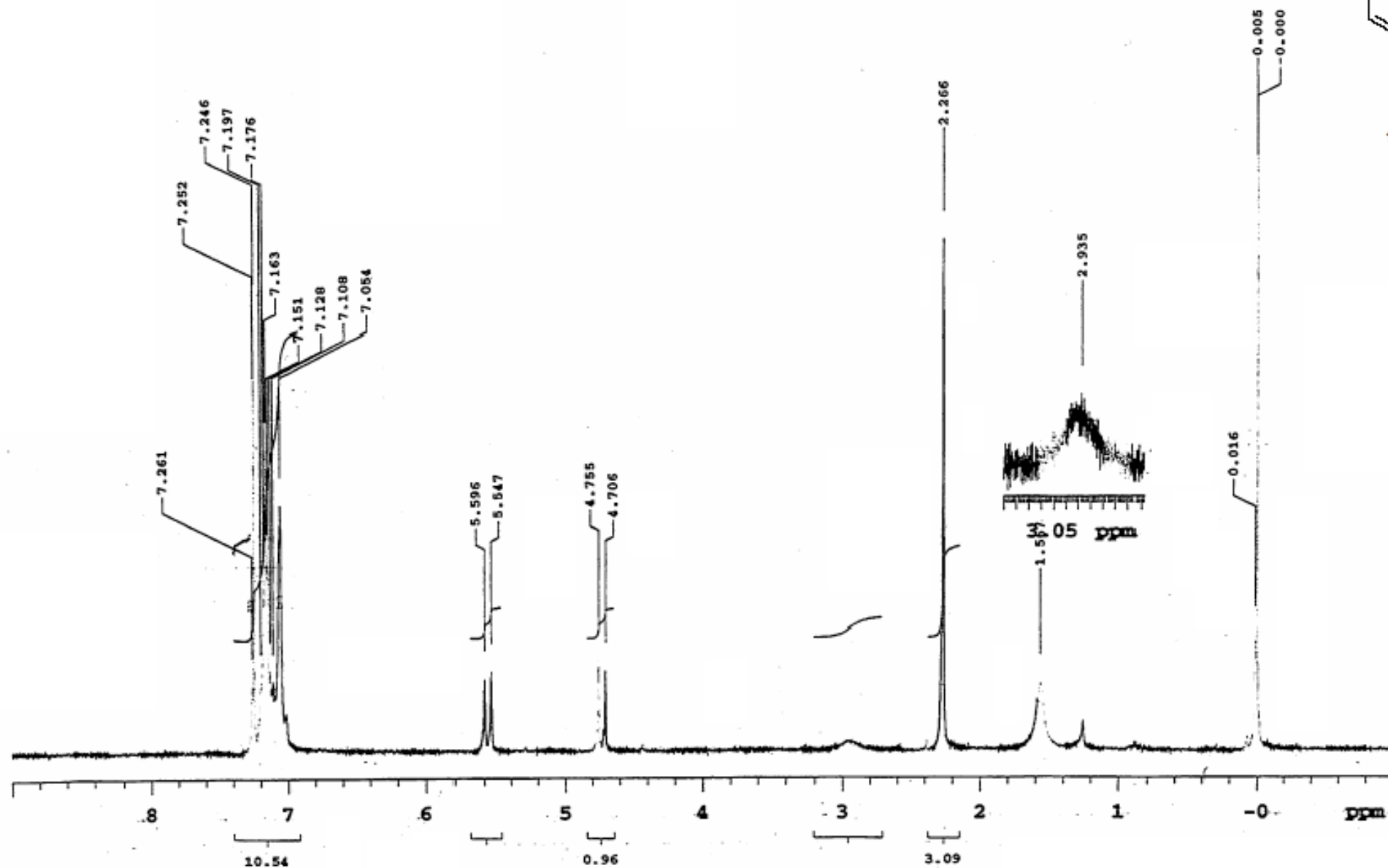


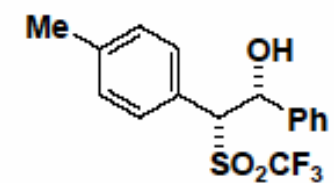
syn-16
 ^{19}F NMR



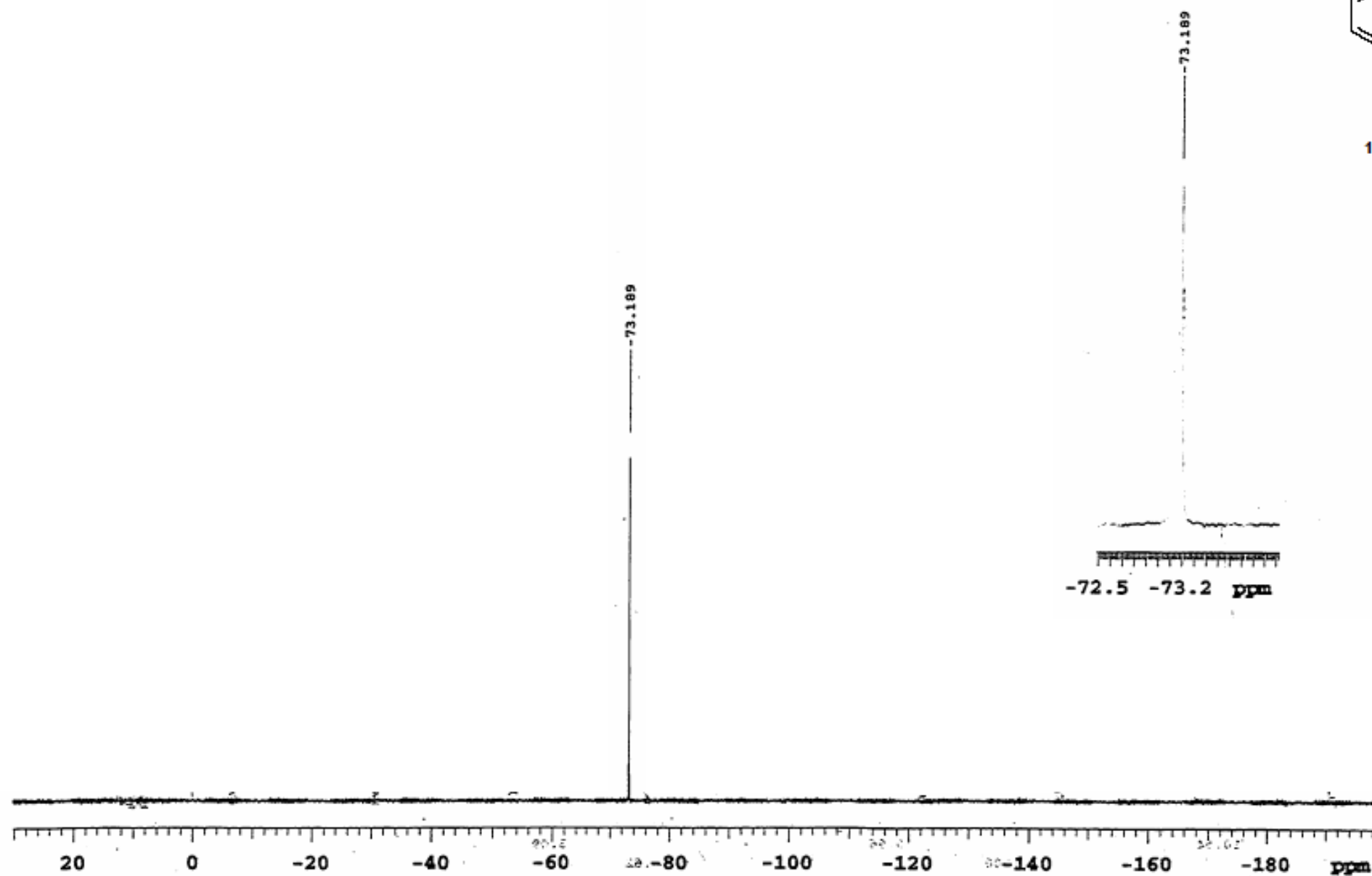


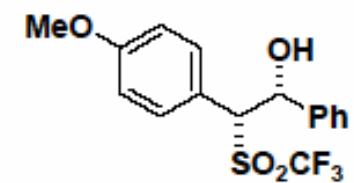
syn-17
¹H NMR



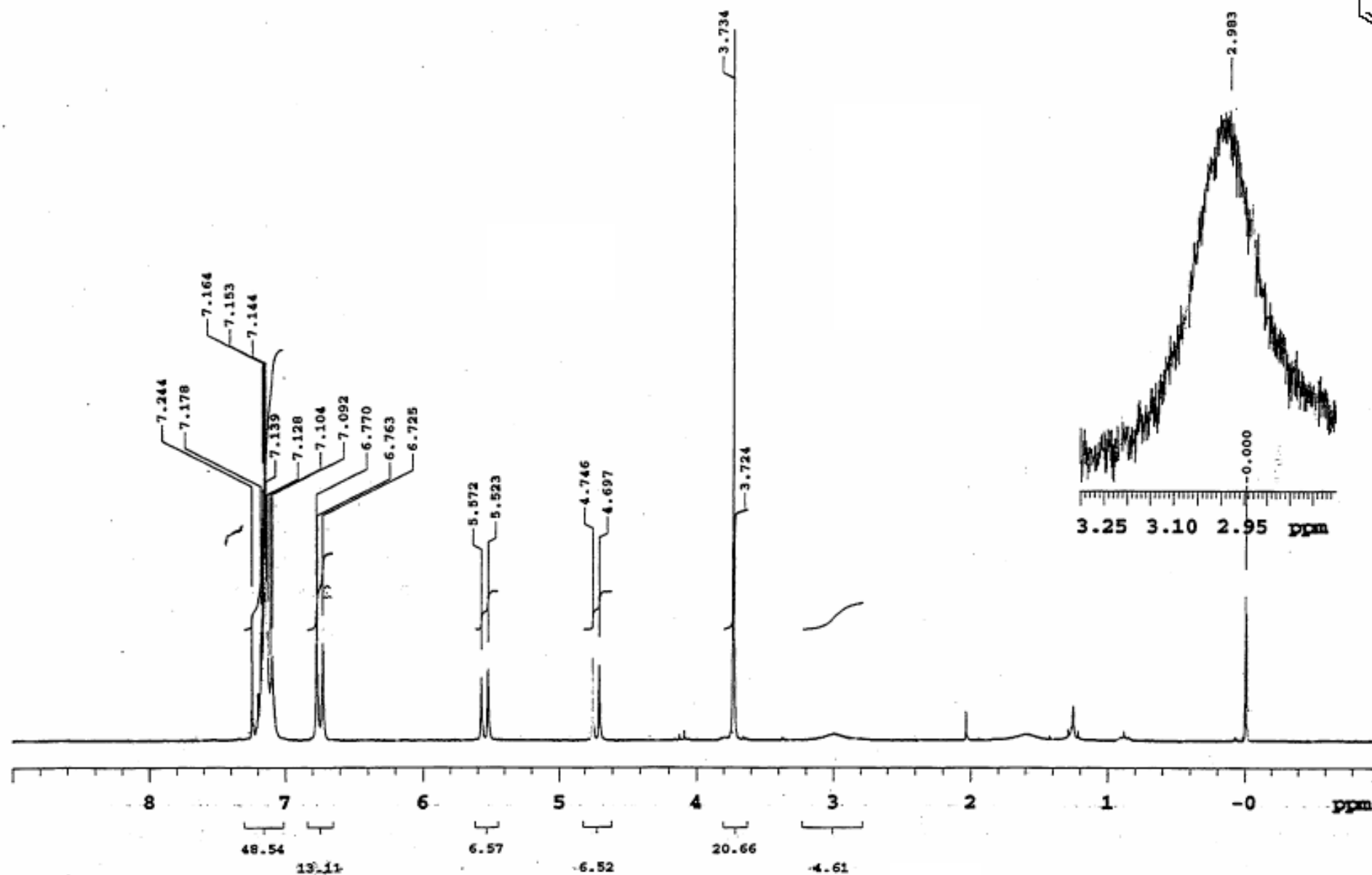


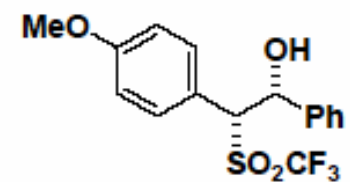
syn-17
 ^{19}F NMR



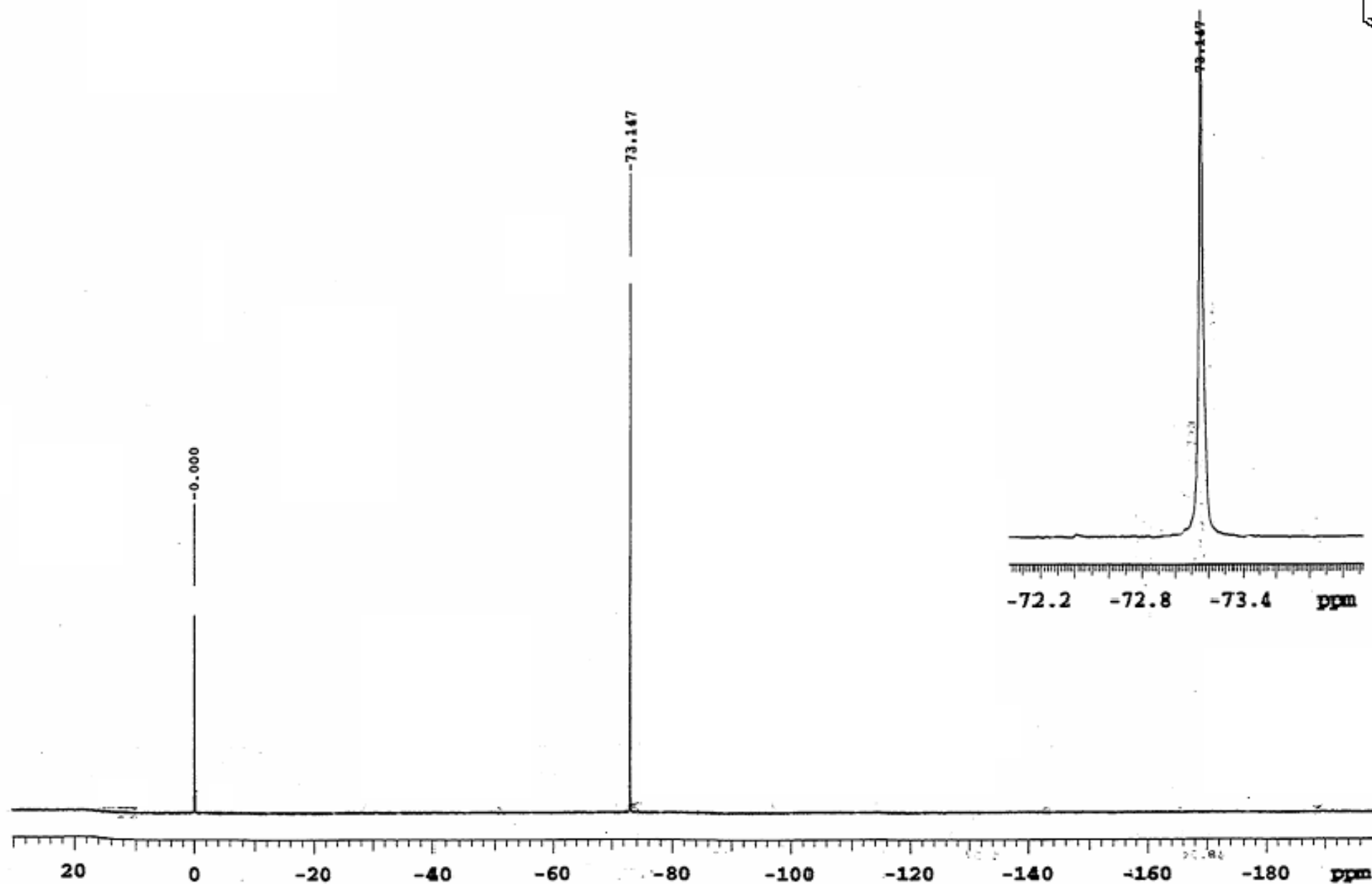


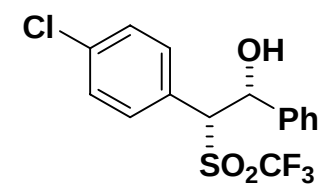
syn-18
¹H NMR



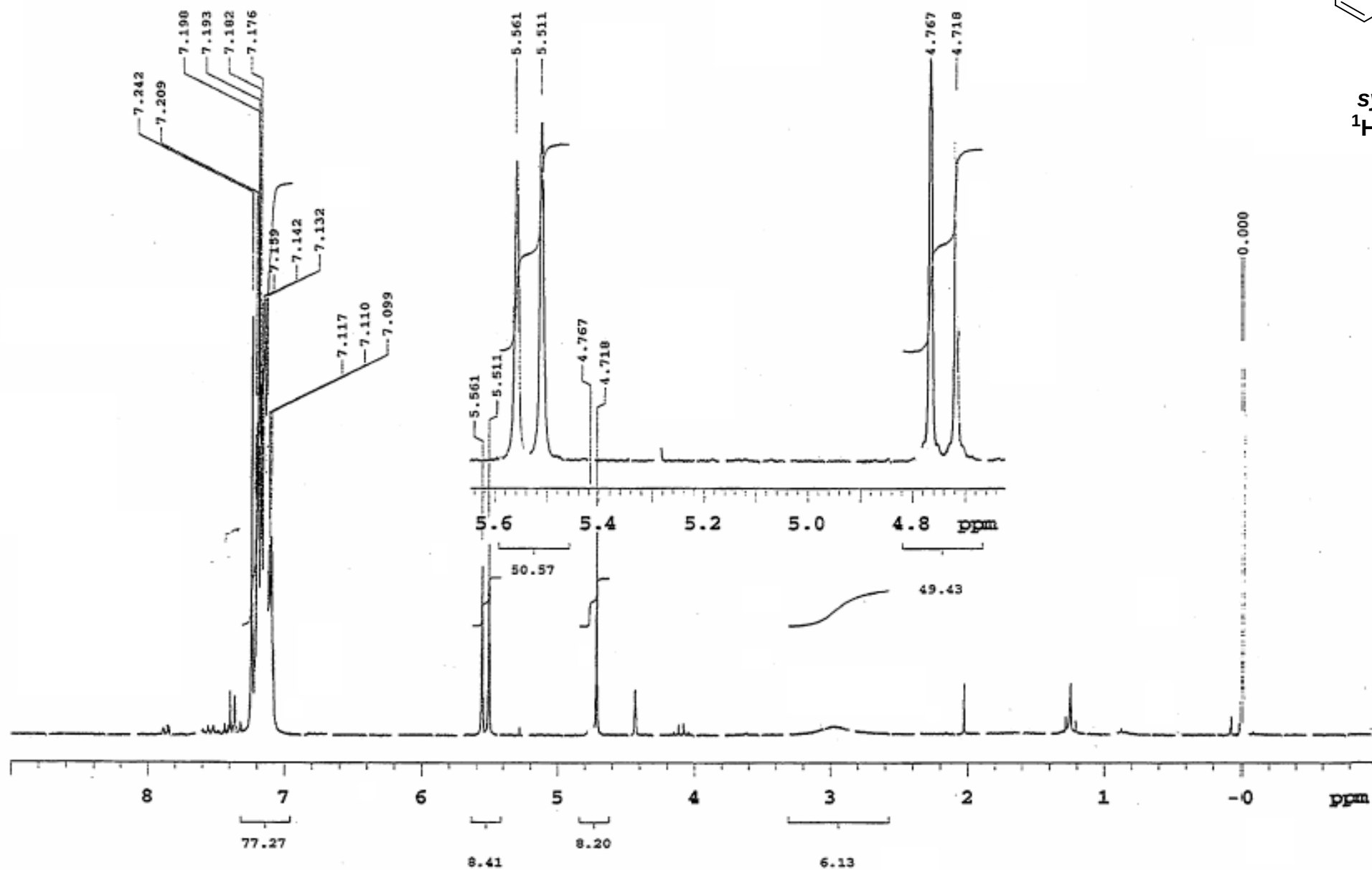


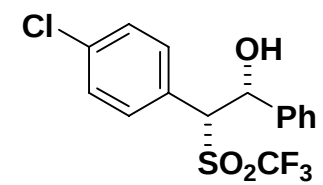
syn-18
 ^{19}F NMR



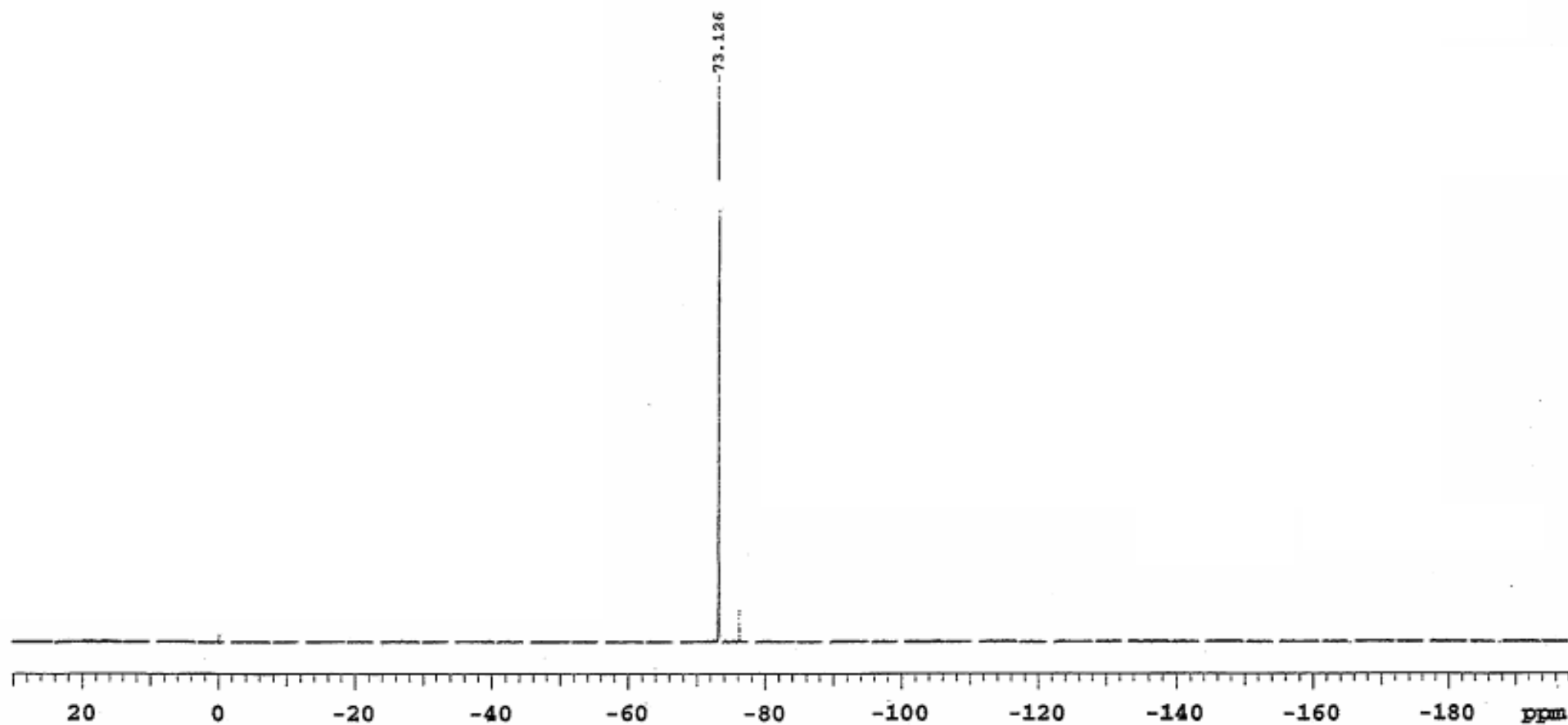


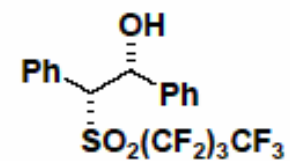
syn-19
¹H NMR



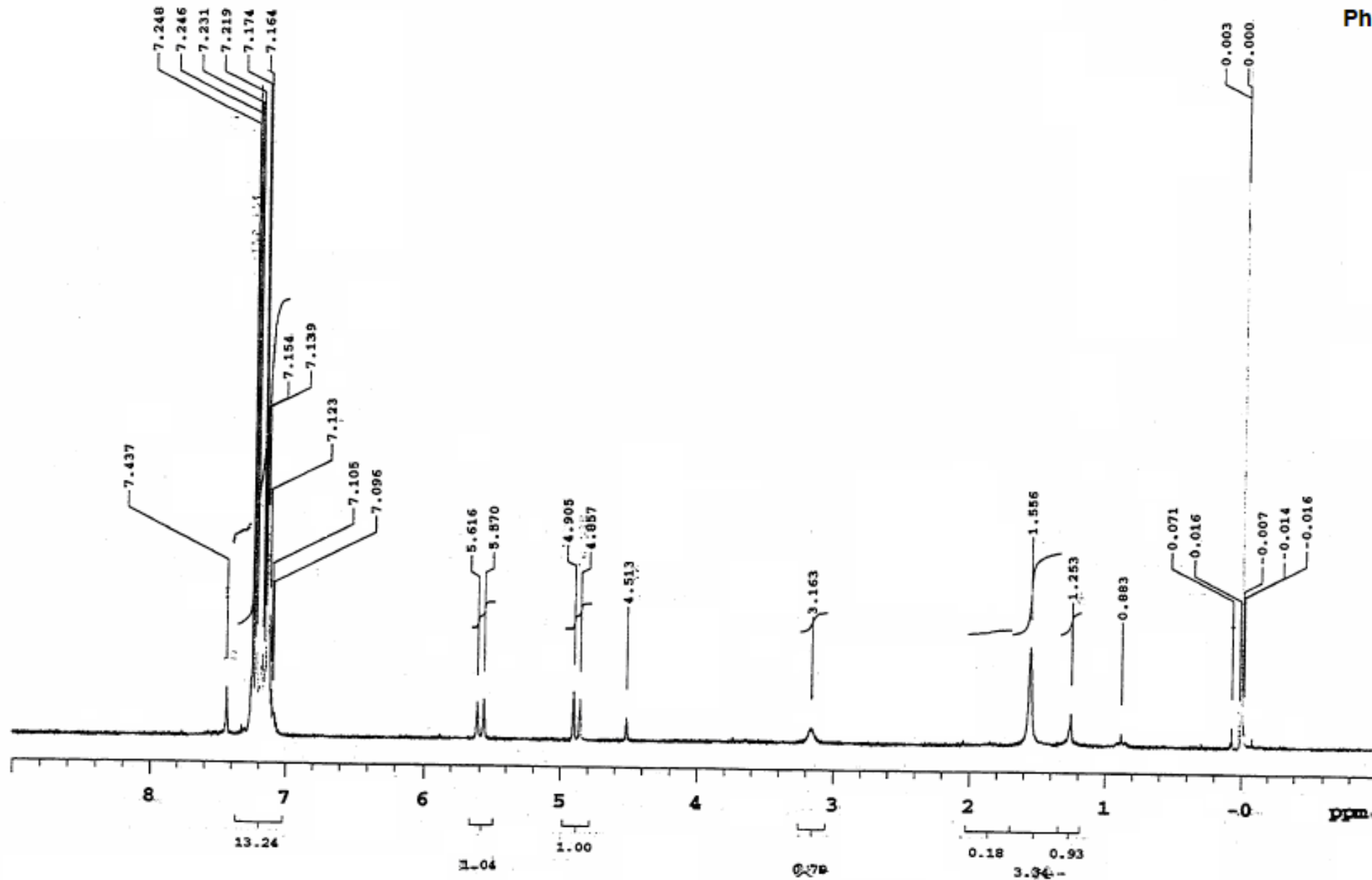


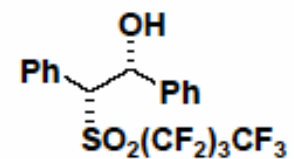
syn-19
 ^{19}F NMR



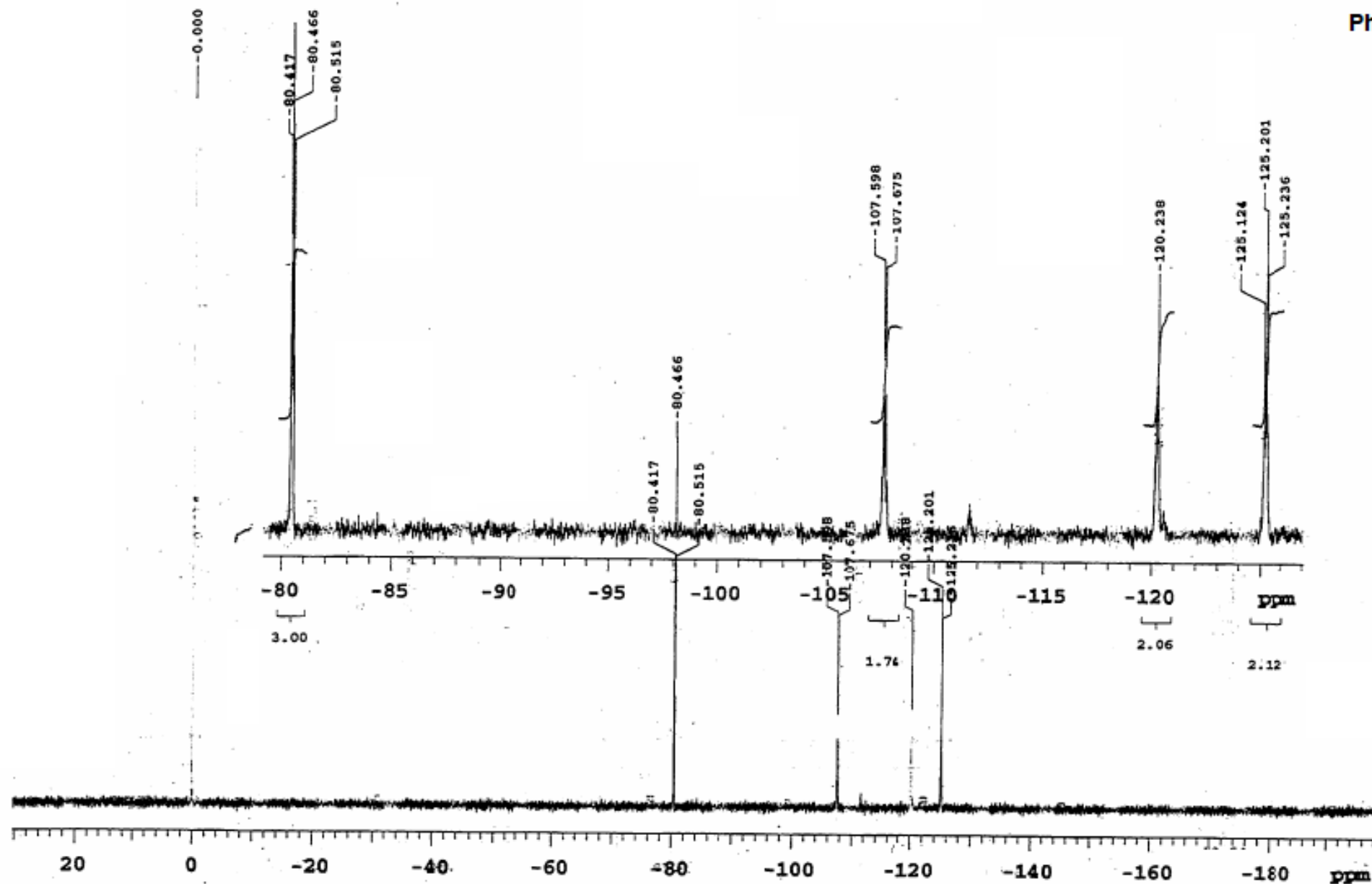


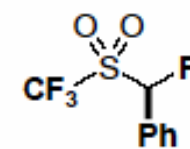
syn-20
¹H NMR



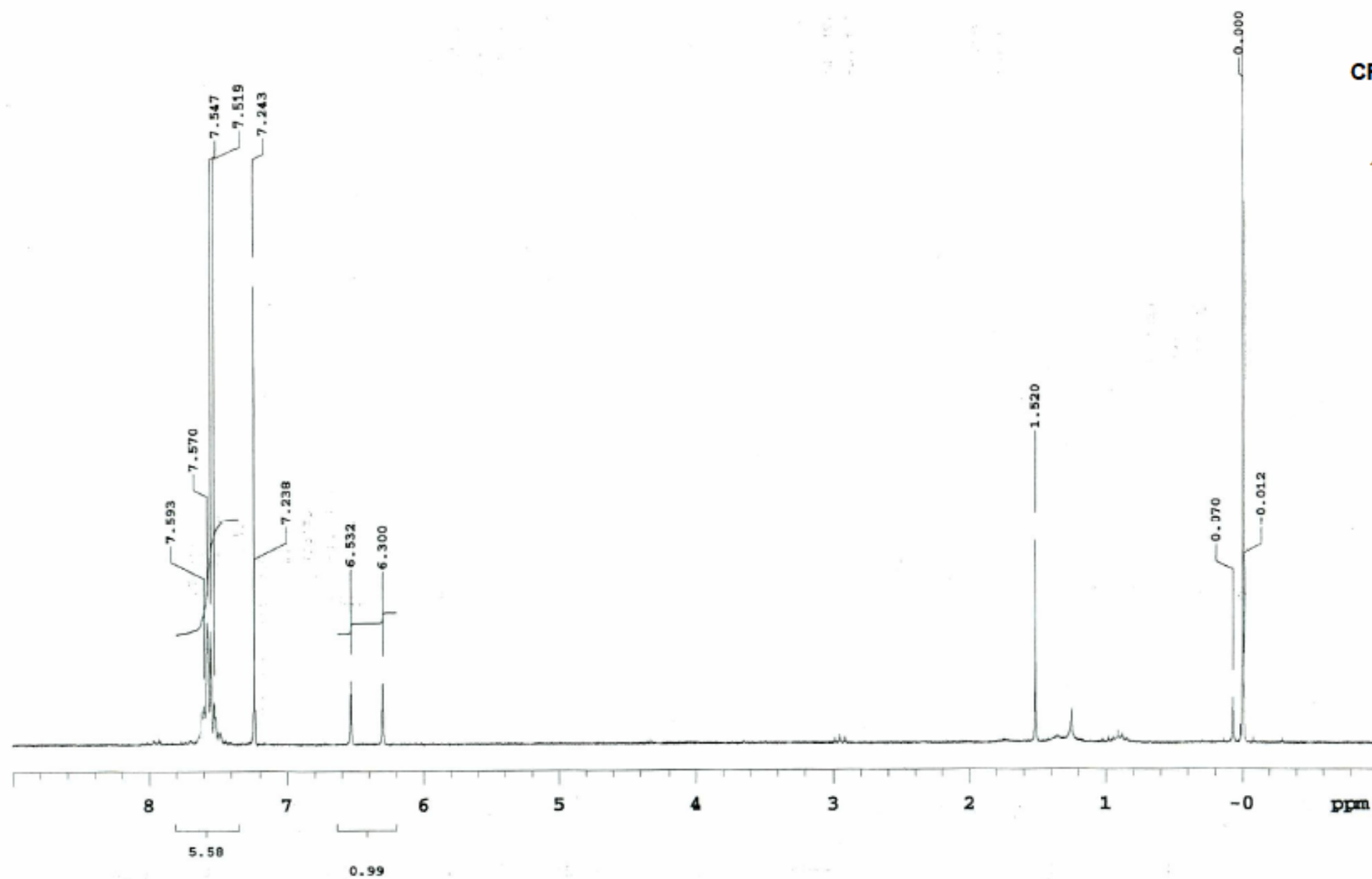


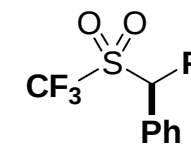
syn-20
¹⁹F NMR





21
 ^1H NMR





21
¹⁹F NMR

