Supporting Information for:

Nickel-Catalyzed Alkenylation and Alkylation of Fluoroarenes via Activation of C–H Bond over C–F Bond

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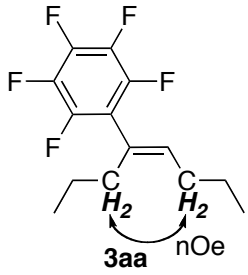
General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique or in a dry box under an argon atmosphere. Flash column chromatography was performed using Kanto Chemical silica gel (spherical, 40–50 μm). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating.

Apparatus. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR, and ^{19}F NMR) were recorded on a Varian Mercury 400 spectrometer spectrometer with Me_4Si or solvent resonance as the internal standard (^{1}H NMR, Me_4Si at 0 ppm or $CHCl_3$ at 7.26 ppm; ^{13}C NMR, Me_4Si at 0 ppm or $CDCl_3$ at 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, br = broad, m = multiplet), coupling constants (Hz), and integration. Fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded on or a Varian Mercury 300 spectrometer (282 MHz) spectrometer with $CFCl_3$ (0 ppm) as the internal standard. Melting points (mp) were determined using a YANAKO MP-500D. Elemental analyses were performed by Elemental Analysis Center of Kyoto University. High-resolution mass spectra were obtained with a JEOL JMS-700 (EI). Preparative recycling gel permeation chromatography (GPC) and preparative recycling silica gel chromatography were performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H (chloroform as an eluent) and JAIGEL-SIL or Nacalai tesque 5SL-II (hexane–ethyl acetate as an eluent). GC analysis was performed on a Shimadzu GC 2014 equipped with an ENV-1 column (Kanto Chemical, 30 m x 0.25 mm, pressure = 31.7 kPa, detector = FID, 290 °C) with helium gas as a carrier.

Chemicals. Unless otherwise noted, commercially available chemicals were distilled and degassed before use. $Ni(cod)_2$ was purchased from STREM and used without further purification. Anhydrous toluene was purchased from Kanto Chemical and degassed by purging vigorously with argon for 20 min and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.[1] 1,4-Bis(trimethylsilyl)-2-butyne (**2b**),[2] and 1-phenyl-1,3-butadiene (using cinnamaldehyde)[3] were prepared according to the respective literature procedure.

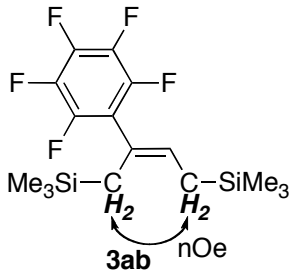
Nickel/$PCyp_3$-catalyzed alkenylation and alkylation of polyfluoroarenes. *A general procedure*. A polyfluoroarene (1.0–2.0 mmol) and an unsaturated compound (1.0–4.0 mmol) were added to a solution of $Ni(cod)_2$ (28 mg, 0.10 mmol) and $PCyp_3$ (24 mg, 0.10 mmol) in toluene (1.0 mL) in a dry box. After *n*-$C_{11}H_{24}$ (internal standard, 78 mg, 0.50 mmol) was added, the vial was taken outside the dry box and heated at the temperature for the time both specified in Tables 1 and 2 and Scheme 1. The resulting mixture was filtered through a silica gel pad, concentrated in vacuo, and purified by flash silica gel column chromatography to give the corresponding hydroarylation products in yields listed in Tables 1 and 2 and Scheme 1. In some cases, a mixture of mono- and dialkenylated

products and impurities (mainly tri- and oligomers of alkynes) were further separated by preparative recycling silica gel chromatography or GPC to determine the yields.



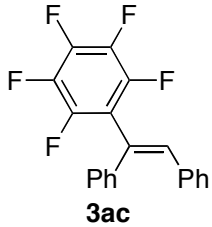
3aa

(*E*)-Pentafluoro(4-octen-4-yl)benzene (3aa). A colorless oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (t, *J* = 7.4 Hz, 1H), 2.35 (t, *J* = 7.6 Hz, 2H), 2.22 (q, *J* = 7.3 Hz, 2H), 1.48 (sext, *J* = 7.4 Hz, 2H), 1.29 (sext, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1 (dm, J_F = 244.9 Hz), 139.6 (dm, J_F = 252.6 Hz), 137.3 (dm, J_F = 252.6 Hz), 136.3, 126.3, 118.5–117.9 (m), 32.7, 30.3, 22.6, 21.5, 13.8 (The signals of the methyl groups are overlapping.); ^{19}F NMR (282 MHz, $CDCl_3$) δ –142.5 (dd, J_F = 24.8, 7.2 Hz, 2F), –158.1 (t, J_F = 20.5 Hz, 1F), –163.6 (td, J_F = 21.7, 8.1 Hz, 2F); IR (neat) 2963, 2928, 2874, 1518, 1493, 988; MS (EI, 70 eV) *m*/*z* (%) 278 (M^+, 24) 236 (16), 235 (100), 221 (16), 208 (73), 207 (78), 195 (11), 187 (30), 181 (79), 71 (15), 55 (15); Anal. Calcd for $C_{14}H_{15}F_5$: C, 60.43; H, 5.43. Found: C, 60.49; H, 5.67.



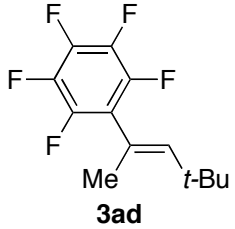
3ab

(*Z*)-[1,4-Bis(trimethylsilyl)-2-buten-2-yl]pentafluorobenzene (3ab). A yellow oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (t, *J* = 8.6 Hz, 1H), 1.84 (s, 2H), 1.61 (d, *J* = 8.6 Hz, 2H), 0.06 (s, 9H), –0.08 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0 (dm, J_F = 244.9 Hz), 139.3 (dm, J_F = 252.6 Hz), 137.3 (dm, J_F = 252.6 Hz), 129.9, 120.4, 120.3–118.7 (m), 21.8, 20.2, -1.2, –1.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ –142.6 (dd, J_F = 23.3, 6.2 Hz, 2F), –159.3 (t, J_F = 21.6 Hz, 1F), –164.3 (td, J_F = 22.5, 7.2 Hz, 2F); IR (neat) 2963, 2860, 1518, 1489, 1468, 1420, 1377, 1315, 1250, 1144, 1121, 1063, 988, 876, 858, 694 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 368 (M^++2, 21), 367 (M^++1, 56), 366 (M^+, 100), 263 (16), 259 (11), 200 (16), 183 (30), 182 (81), 177 (18), 163 (32), 151 (11), 143 (12), 102 (12), 81 (13), 77 (79), 75 (56), 74 (82), 73 (98), 72 (23), 59 (16), 58 (12); HMRS (EI) Calcd for $C_{16}H_{23}F_5Si_2$: M^+, 366.1258. Found: *m*/*z* 366.1240.



3ac

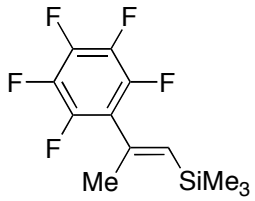
(*E*)-(1,2-Diphenylvinyl)pentafluorobenzene (3ac).[4] A yellow oil, R_f 0.60 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.15 (m, 8H), 7.14–7.08 (m, 2H), 6.76 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4 (dm, J_F = 247.2 Hz), 140.7 (dm, J_F = 254.1 Hz), 138.0, 137.4 (dm, J_F = 253.4 Hz), 135.4, 135.3, 129.4, 128.9, 128.6, 128.0, 128.88, 128.82, 127.3, 127.4, 118.7–118.0 (m), Signals for the phenyl groups are overlapping; ^{19}F NMR (282 MHz, $CDCl_3$) δ –141.5 (dd, J_F = 22.0, 8.2 Hz, 2F), –156.2 (t, J_F = 20.6 Hz, 1F), –162.7 (td, *J* = 22.0, 7.2 Hz, 2F); IR (neat) 3061, 3042, 3023, 1653, 1520, 1495, 1445, 1427, 1119, 1076, 1030, 983, 921, 880, 864, 795, 750, 735, 704, 561, 542 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 347 (M^++1, 27), 346 (M^+, 100), 331 (26), 325 (17), 324 (13), 306 (10), 179 (16), 178 (12); HMRS (EI) Calcd for $C_{20}H_{11}F_5$: M^+, 346.0781. Found: *m*/*z* 346.0781.



3ad

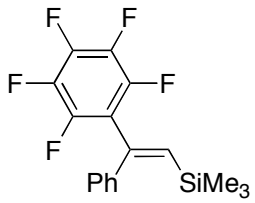
(*E*)-(4,4-Dimethyl-2-penten-2-yl)pentafluorobenzene (3ad). A yellow oil, R_f 0.60 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52–5.49 (m, 1H), 2.05–2.02 (m, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 143.8 (dm, J_F = 247.7 Hz), 139.5 (dm, J_F = 252.6 Hz), 137.3 (dm, J_F = 250.3 Hz), 120.9, 120.4, 120.0, 33.5, 30.6, 18.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.7 (dd, J_F = 22.7, 8.2 Hz, 2F), –158.7 (t, J_F = 20.6 Hz, 1F), –163.6 (td, *J* = 22.0, 7.5 Hz, 2F); IR (neat) 2963, 2872, 1651, 1520, 1487, 1385, 1366, 1314, 1163, 1076, 1038, 1017, 984, 943, 872, 845, 665 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 264 (M^+, 67), 250 (21), 249 (100), 221 (13), 207 (28), 195 (69), 187

(12), 181 (44); HMRS (EI) Calcd for $C_{13}H_{13}F_5$: M^+, 264.0937. Found: *m*/*z* 264.0928.



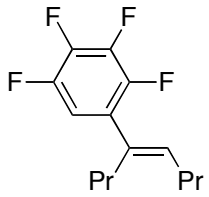
3ae

(*E*)-Pentafluoro[1-(trimethylsilyl)propen-2-yl]benzene (3ae). A green oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (s, 1H), 2.11 (s, 3H), 0.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2 (dm, J_F = 249.6 Hz), 139.6 (dm, J_F = 252.6 Hz), 137.8, 137.4, 137.3 (dm, J_F = 253.3 Hz), 121.8–121.1 (m), 22.4, –0.17; ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.4 (dd, J_F = 24.3, 6.8 Hz, 2F), –158.1 (t, J_F = 20.6 Hz, 1F), –163.3 (td, J_F = 23.0, 6.9 Hz, 2F); IR (neat) 2959, 1651, 1607, 1591, 1520, 1495, 1443, 1250, 1119, 1072, 1036, 988, 885, 866, 839, 762, 700 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 280 (M^+, 6), 267 (23), 266 (67), 265 (100), 225 (47), 187 (20), 183 (45), 182 (13), 181 (11), 170 (33), 169 (82), 165 (39), 164 (59), 163 (13), 159 (16), 151 (11), 149 (16), 145 (18), 143 (19), 133 (22), 125 (48), 119 (15), 115 (12), 99 (12), 81 (28), 78 (17), 77 (81), 75 (14), 73 (61), 59 (25); HMRS (EI) Calcd for $C_{11}H_{10}F_5Si$: M^+–Me, 265.0472. Found: *m*/*z* 265.0472.



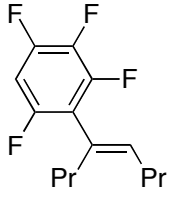
3af

(*E*)-Pentafluoro[2-phenyl-1-(trimethylsilyl)ethen-2-yl]benzene (3af). A yellow oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 3H), 7.27–7.21 (m, 2H), 6.06 (s, 1H), 0.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 143.5 (dm, J_F = 246.4 Hz), 142.0, 140.8, 140.0 (dm, J_F = 258.8 Hz), 137.3 (dm, J_F = 250.9 Hz), 128.2, 127.99, 127.93, 119.9, 119.5, –0.05; ^{19}F NMR (282 MHz, $CDCl_3$) δ –142.2 (dd, J_F = 22.7, 8.2 Hz, 2F), –157.0 (t, J_F = 20.6 Hz, 1F), –163.1 (td, J = 21.9, 8.2 Hz, 2F); IR (neat) 2959, 1593, 1520, 1495, 1250, 1175, 990, 945, 864, 843, 758, 700 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 343 (M^++1, 21), 342 (M^+, 84), 328 (26), 327 (100), 309 (11), 250 (25), 231 (14), 230 (12), 225 (13), 135 (15), 77 (14), 73 (21); Anal. Calcd for $C_{17}H_{13}F_5Si$: C, 59.64; H, 4.42. Found: C, 59.49; H, 4.37.



3ba

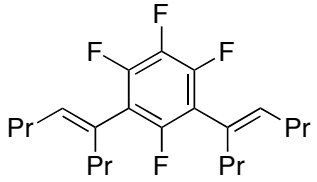
(*E*)-1,2,3,4-Tetrafluoro(4-octen-4-yl)benzene (3ba). A yellow oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85–6.75 (m, 1H), 5.53 (t, J = 7.3 Hz, 1H), 2.40 (t, J = 7.7 Hz, 2H), 2.18 (q, J = 7.3 Hz, 2H), 1.47 (sext, J = 7.5 Hz, 2H), 1.30 (sext, J = 7.3 Hz, 2H), 0.97 (t, J = 7.5 Hz, 3H), 0.87 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4 (dm, J_F = 246.4 Hz), 144.8 (dm, J_F = 242.4 Hz), 141.0 (dm, J_F = 252.6 Hz), 138.9 (dm, J_F = 251.8 Hz), 134.0, 133.5, 128.2–127.8 (m), 110.9 (dt, J_F = 19.2, 3.8 Hz), 32.3 (d, J_F = 2.3 Hz), 30.4, 22.8, 21.6, 13.94, 13.86; ^{19}F NMR (282 MHz, $CDCl_3$) δ –142.1——142.3 (m, 1F), –143.2——143.4 (m, 1F), –157.7 (t, J_F = 20.0 Hz, 1F), –160.1——160.4 (m, 1F); IR (neat) 2961, 2934, 2874, 1620, 1520, 1477, 1375, 1271, 1202, 1180, 1119, 1101, 1059, 1036, 1009, 966, 905, 862, 735, 712 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 261 (M^++1, 38), 260 (M^+, 89), 231 (27), 218 (70), 217 (100), 215 (13), 204 (14), 203 (61), 201 (25), 200 (23), 197 (21), 195 (10), 191 (38), 190 (89), 189 (90), 188 (11), 187 (52), 183 (29), 182 (36), 177 (57), 176 (29), 175 (42), 174 (27), 171 (11), 170 (17), 169 (73), 164 (32), 163 (83), 155 (17), 151 (33), 143 (12), 133 (15), 125 (14), 55 (58); Anal. Calcd for $C_{14}H_{15}F_5$: C, 64.61; H, 6.20. Found: C, 64.82; H, 6.40.



3ca

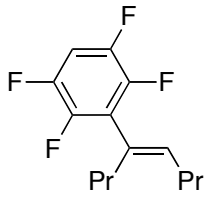
(*E*)-1,2,3,5-Tetrafluoro-4-(4-octen-4-yl)benzene (3ca). A yellow oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77–6.67 (m, 1H), 5.48 (t, J = 7.3 Hz, 1H), 2.34 (t, J = 7.6 Hz, 2H), 2.20 (q, J = 7.3 Hz, 2H), 1.48 (sext, J = 7.5 Hz, 2H), 1.30 (sext, J = 7.5 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4 (dm, J_F = 244.1 Hz), 149.0 (dm, J_F = 246.1 Hz), 148.9 (dm, J_F = 251.1 Hz), 137.0 (dm, J_F = 243.3 Hz), 135.3, 127.2, 118.6–118.0 (m), 100.2 (ddd, J_F = 29.7, 21.2, 3.8 Hz), 32.7, 30.2, 22.7, 21.5, 13.9, 13.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ –117.4 (t, J_F = 8.9 Hz,

1F), –134.9 (d, J_F = 22.0 Hz, 1F), –136.0––136.1 (m, 1F), –166.1––166.4 (m, 1F); IR (neat) 2964, 2937, 2874, 1641, 1514, 1501, 1460, 1377, 1285, 1148, 1121, 1051, 968, 876, 833 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 260 (M$^+$, 26), 218 (14), 217 (100), 203 (13), 190 (47), 189 (64), 177 (11), 175 (11), 169 (23), 163 (88), 55 (11); Anal. Calcd for $C_{14}H_{16}F_4$: C, 64.61; H, 6.20. Found: C, 64.64; H, 6.23.



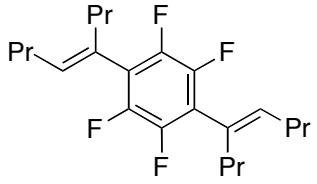
4ca

(*E,E*)-1,2,3,5-Tetrafluoro-4,6-di(4-octen-4-yl)benzene (4ca). A yellow oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (t, *J* = 7.3 Hz, 2H), 2.34 (t, *J* = 7.6 Hz, 4H), 2.20 (q, *J* = 7.3 Hz, 4H), 1.48 (sext, *J* = 7.3 Hz, 4H), 1.30 (sext, *J* = 7.5 Hz, 4H), 0.97 (t, *J* = 7.3 Hz, 6H), 0.89 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0 (dm, J_F = 241.8 Hz), 146.9 (dm, J_F = 245.6 Hz), 136.8 (dm, J_F = 247.9 Hz), 135.0, 127.5, 117.4 (t, J_F = 23.1 Hz), 32.8, 30.3, 22.7, 21.6, 13.91, 13.88; ^{19}F NMR (282 MHz, $CDCl_3$) δ –120.6 (d, J_F = 8.2 Hz, 1F), –138.7 (d, J_F = 22.0 Hz, 2F), –166.6 (td, J_F = 22.3, 11.3 Hz, 1F); IR (neat) 2964, 2872, 1630, 1474, 1377, 1057, 976, 891 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 370 (M$^+$, 23), 328 (24), 327 (100), 299 (12), 285 (22), 257 (10); Anal. Calcd for $C_{22}H_{30}F_4$: C, 71.32; H, 8.16. Found: C, 71.36; H, 8.08.



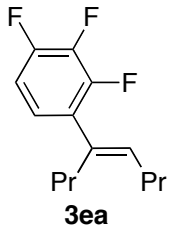
3da

(*E*)-1,2,4,5-Tetrafluoro-3-(4-octen-4-yl)benzene (3da). A yellow oil, R_f 0.60 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99–6.86 (m, 1H), 5.52 (t, *J* = 7.3 Hz, 1H), 2.38 (t, *J* = 7.7 Hz, 2H), 2.23 (q, *J* = 7.3 Hz, 2H), 1.49 (sext, *J* = 7.3 Hz, 2H), 1.31 (sext, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7 (dm, J_F = 247.1 Hz), 143.8 (dm, J_F = 236.0 Hz), 135.6, 127.3, 124.1 (t, J_F = 18.9 Hz), 103.7 (t, J_F = 22.6 Hz), 32.6, 30.2, 22.7, 21.6, 13.9, 13.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ –140.5––140.7 (m, 2F), –143.0––143.2 (m, 2F); IR (neat) 2924, 2855, 1643, 1607, 1493, 1285, 1171, 939, 899, 837, 714 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 260 (M$^+$, 37), 218 (18), 217 (100), 203 (17), 197 (11), 190 (69), 189 (70), 187 (11), 183 (12), 182 (16), 177 (13), 176 (12), 169 (47), 163 (64), 55 (19); HMRS (EI) Calcd for $C_{14}H_{16}F_4$: M$^+$, 260.1188. Found: *m/z* 260.1191.



4da

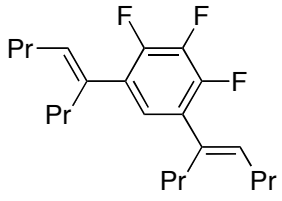
(*E,E*)-1,2,4,5-Tetrafluoro-3,6-di(4-octen-4-yl)benzene (4da). A yellow oil, R_f 0.60 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (t, *J* = 7.3 Hz, 2H), 2.38 (t, *J* = 7.5 Hz, 4H), 2.23 (q, *J* = 7.3 Hz, 4H), 1.48 (sext, *J* = 7.3 Hz, 4H), 1.33 (sext, *J* = 7.4 Hz, 4H), 0.97 (t, *J* = 7.3 Hz, 6H), 0.91 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8 (d, J_F = 246.1 Hz), 135.4, 127.5, 121.0–119.6 (m), 32.7, 30.3, 22.7, 21.6, 13.9, 13.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ –144.3 (s, 4F); IR (neat) 2976, 2880, 2835, 1470, 1454, 1377, 1308, 974, 897, 723 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 370 (M$^+$, 32), 328 (25), 327 (100), 299 (12), 285 (22), 231 (15), 211 (12); Anal. Calcd for $C_{22}H_{30}F_4$: C, 71.32; H, 8.16. Found: C, 71.13; H, 8.13.



3ea

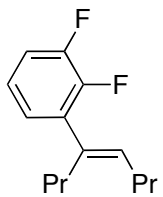
(*E*)-1,2,3-Trifluoro-4-(4-octen-4-yl)benzene (3ea). A yellow oil, R_f 0.60 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92–6.83 (m, 2H), 5.50 (t, *J* = 7.3 Hz, 1H), 2.40 (t, *J* = 7.6 Hz, 2H), 2.18 (q, *J* = 7.3 Hz, 2H), 1.49 (sext, *J* = 7.4 Hz, 2H), 1.29 (sext, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4 (dm, J_F = 248.8 Hz), 148.0 (dm, J_F = 251.9 Hz), 139.7 (dt, *J* = 251.0, 15.4 Hz), 134.3, 133.1, 129.4 (dd, *J* = 11.5, 3.0 Hz), 123.6, 123.2, 111.3 (dd, *J* = 16.9, 3.8 Hz), 32.4 (d, *J* = 2.3 Hz), 30.4, 22.9, 21.6, 14.0, 13.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ –137.5 (d, J_F = 25.4 Hz, 1F), –138.1 (d, J_F = 12.7 Hz, 1F), –161.7 (t, J_F = 19.1 Hz, 1F); IR (neat) 2924, 2855, 1607, 1508, 1464, 1310, 1273, 1231, 1182, 1038, 1016, 993, 808 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 242

(M^+, 33), 200 (14), 199 (100), 185 (11), 172 (38), 171 (66), 151 (15), 145 (50); Anal. Calcd for $C_{14}H_{17}F_3$: C, 69.40; H, 7.07. Found: C, 69.68; H, 7.22.



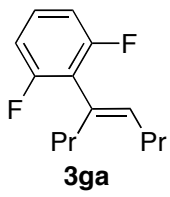
4ea

(*E,E*)-1,2,3-Trifluoro-4,6-di(4-octen-4-yl)benzene (4ea). A yellow oil, R_f 0.60 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (td, J = 7.8, 2.4 Hz, 1H), 5.51 (t, J = 7.3 Hz, 2H), 2.40 (t, J = 7.6 Hz, 4H), 2.17 (q, J = 7.3 Hz, 4H), 1.47 (sext, J = 7.3 Hz, 4H), 1.30 (sext, J = 7.4 Hz, 4H), 0.97 (t, J = 7.3 Hz, 6H), 0.87 (t, J = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0 (ddd, J_F = 248.4, 10.4, 3.0 Hz), 139.6 (dt, J_F = 249.5, 16.4 Hz), 134.4, 132.8, 128.1 (dd, J_F = 10.8, 5.4 Hz), 123.6 (dd, J_F = 3.9, 3.8 Hz), 32.5, 30.4, 22.9, 21.6, 14.0, 13.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ –140.3 (dd, J_F = 22.0, 8.2 Hz, 2F), –161.8 (t, J_F = 20.6 Hz); IR (neat) 2959, 2932, 2872, 1605, 1487, 1454, 1371, 1248, 1186, 1119, 1088, 1067, 1032, 974, 887, 739, 710 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 353 (M^++1, 19), 352 (M^+, 75), 310 (21), 309 (85), 267 (17), 241 (19), 183 (14), 111 (17), 55 (30); HMRS (EI) Calcd for $C_{22}H_{31}F_3$: M^+, 352.2378. Found: *m/z* 352.2366.



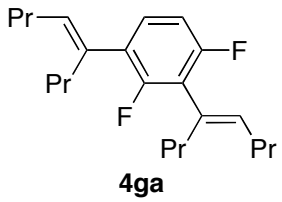
3fa

(*E*)-1,2-Difluoro-3-(4-octen-4-yl)benzene (3fa). A yellow oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06–6.88 (m, 3H), 5.54 (t, J = 7.3 Hz, 1H), 2.44 (t, J = 7.4 Hz, 2H), 2.19 (q, J = 7.3 Hz, 2H), 1.48 (sext, J = 7.4 Hz, 2H), 1.31 (sext, J = 7.4 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6 (dd, J_F = 248.1, 13.9 Hz), 147.9 (dd, J_F = 247.2, 12.7 Hz), 134.8 (d, J_F = 2.2 Hz), 134.1 (d, J_F = 11.5 Hz), 132.7 (d, J_F = 1.5 Hz), 125.0 (t, J_F = 3.5 Hz), 123.3 (dd, J_F = 6.9, 4.8 Hz), 114.9 (d, J_F = 17.8 Hz), 32.5 (d, J_F = 2.3 Hz), 30.4, 22.9, 21.6, 13.99, 13.95; ^{19}F NMR (282 MHz, $CDCl_3$) δ –139.4——139.6 (m, 1F), –142.1——142.4 (m, 1F); IR (neat) 2959, 2932, 2872, 1454, 1377, 1265, 1213, 1061, 972, 885, 820, 785, 727 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 224 (M^+, 36), 182 (15), 181 (100), 167 (11), 154 (32), 153 (55), 151 (10), 127 (35); HMRS (EI) Calcd for $C_{14}H_{18}F_2$: M^+, 224.1377. Found: *m/z* 224.1378.



3ga

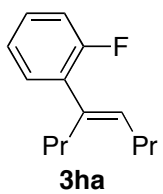
(*E*)-1,3-Difluoro-2-(4-octen-4-yl)benzene (3ga). A yellow oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.10 (m, 1H), 6.90–6.80 (m, 2H), 5.48 (t, J = 7.2 Hz, 1H), 2.39 (t, J = 7.5 Hz, 2H), 2.23 (q, J = 7.3 Hz, 2H), 1.49 (sext, J = 7.3 Hz, 2H), 1.32 (sext, J = 7.5 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H), 0.90 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (dd, J = 245.4, 8.4 Hz), 133.9, 128.5, 127.5 (t, J = 10.0 Hz), 120.9 (t, J = 21.1 Hz), 111.0 (dd, J = 24.2, 7.6 Hz), 32.9, 30.2, 22.8, 21.6, 14.0, 13.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ –113.9 (s, 2F); IR (neat) 2961, 2934, 2872, 1622, 1586, 1462, 1269, 1231, 995, 785, 729 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 225 (M^++1, 39), 224 (M^+, 88), 195 (19), 182 (73), 181 (100), 179 (16), 168 (20), 167 (70), 165 (31), 164 (27), 161 (10), 155 (24), 154 (83), 153 (89), 152 (13), 151 (62), 147 (13), 146 (26), 141 (67), 140 (40), 139 (54), 138 (37), 133 (60), 128 (45), 127 (89), 125 (11), 119 (42), 101 (18), 99 (12), 67 (16), 55 (46); HMRS (EI) Calcd for $C_{14}H_{19}F_2$: M^+, 224.1377. Found: *m/z* 224.1374.



4ga

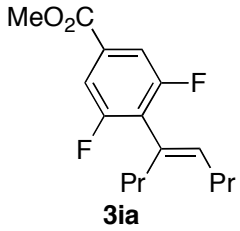
(*E,E*)-1,3-Difluoro-2,4-di(4-octen-4-yl)benzene (4ga). A yellow oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (td, J = 8.4, 6.4 Hz, 1H), 6.76 (td, J = 8.6, 1.5 Hz, 1H), 5.46 (td, J = 7.3, 2.1 Hz, 2H), 2.38 (quint, J = 7.3 Hz, 4H), 2.27–2.11 (m, 4H), 1.53–1.41 (m, 4H), 1.37–1.23 (m, 4H), 0.972 (t, J = 7.3, Hz, 3H), 0.968 (t, J = 7.3, Hz, 3H), 0.92–0.83 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 (dd, J_F = 244.8, 7.6 Hz), 157.0 (dd, J_F = 245.6, 7.9 Hz), 135.7, 133.6, 131.7, 128.9, 128.2 (dd, J_F = 9.3, 6.2 Hz), 127.6 (dd, J_F = 16.8, 3.8 Hz), 120.8 (dd, J_F = 22.3,

20.6 Hz), 110.2 (dd, J_F = 23.1, 3.8 Hz), 33.0, 32.6 (d, J_F = 3.1 Hz), 30.4, 30.2, 23.0, 22.8, 21.6, 14.03, 14.00, 13.9, Signals for the propyl groups are overlapping; ^{19}F NMR (282 MHz, $CDCl_3$) δ 115.3 (t, J_F = 7.8 Hz, 1F), –116.6 (dd, J_F = 15.5, 6.8 Hz, 1F); IR (neat) 2961, 2934, 1614, 1584, 1479, 1456, 1418, 1260, 1022, 986, 879, 813 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 335 (M^++1), 334 (M^+, 100), 305 (30), 293 (16), 292 (85), 291 (100), 277 (19), 264 (32), 263 (56), 251 (20), 250 (14), 249 (63), 238 (12), 237 (62), 235 (16), 223 (42), 222 (13), 221 (37), 207 (24), 196 (12), 195 (55), 194 (15), 193 (31), 191 (14), 183 (14), 181 (45), 179 (29), 178 (11), 177 (22), 175 (13), 173 (16), 171 (13), 170 (12), 167 (18), 166 (10), 165 (47), 164 (23), 159 (21), 153 (32), 151 (22), 147 (17), 146 (15), 141 (11), 133 (12), 127 (14), 111 (16), 70 (12), 69 (83), 67 (12), 55 (68), 53 (12); HMRS (EI) Calcd for $C_{22}H_{32}F_2$: M^+, 334.2472. Found: *m/z* 334.2489.



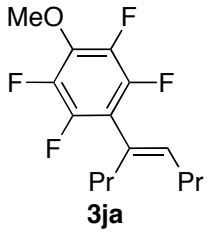
3ha

(*E*)-Fluoro-2-(4-octen-4-yl)benzene (3ha). A yellow oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.15 (m, 2H), 7.08–6.96 (m, 2H), 5.51 (t, *J* = 7.3 Hz, 1H), 2.45 (t, *J* = 7.5 Hz, 2H), 2.19 (q, *J* = 7.3 Hz, 2H), 1.48 (sext, *J* = 7.3 Hz, 2H), 1.31 (sext, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (d, J_F = 246.3 Hz), 136.0, 131.814, 131.810 (d, J_F = 14.6 Hz), 130.5 (d, J_F = 4.5 Hz), 127.8 (d, J_F = 8.4 Hz), 123.6 (d, J_F = 3.8 Hz), 115.3 (d, J_F = 23.1 Hz), 32.6 (d, J_F = 2.3 Hz), 30.4, 23.3, 21.6, 14.0, Signals for the methyl groups are overlapping; ^{19}F NMR (282 MHz, $CDCl_3$) δ –116.3 (s, 1F); IR (neat) 2959, 2931, 2872, 1613, 1576, 1487, 1451, 1379, 1258, 1221, 1206, 1091, 1034, 897, 824, 754 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 206 (M^+, 44), 164 (18), 163 (100), 149 (14), 136 (31), 135 (67), 133 (16), 109 (47); HMRS (EI) Calcd for $C_{14}H_{19}F$: M^+, 206.1471. Found: *m/z* 206.1477.



3ia

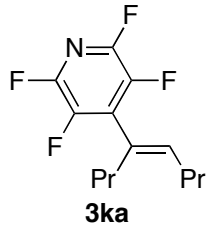
Methyl (*E*)-3,5-difluoro-4-(4-octen-4-yl)benzoate (3ia). A colorless oil, R_f 0.20 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.48 (m, 2H), 5.50 (t, *J* = 7.3 Hz, 1H), 3.92 (s, 3H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.22 (q, *J* = 7.3 Hz, 2H), 1.48 (sext, *J* = 7.3 Hz, 2H), 1.29 (sext, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 160.0 (dd, J_F = 248.0, 7.7 Hz), 134.8, 129.9 (t, J_F = 9.6 Hz), 128.0, 125.7 (t, J_F = 21.2 Hz), 112.4 (dd, J_F = 20.0, 8.5 Hz), 52.5, 32.6, 30.2, 22.7, 21.6, 13.89, 13.87; ^{19}F NMR (282 MHz, $CDCl_3$) δ –112.1 (s, 2F); IR (neat) 2961, 2934, 2874, 1732, 1566, 1435, 1421, 1379, 1331, 1232, 1188, 1105, 1086, 1030, 1003, 887, 770, 746 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 283 (M^++1, 47), 282 (M^+, 91), 253 (20), 252 (16), 251 (69), 241 (17), 240 (80), 239 (100), 226 (25), 225 (69), 213 (41), 212 (88), 211 (89), 209 (16), 200 (11), 199 (66), 198 (26), 197 (36), 193 (23), 186 (43), 185 (87), 181 (53), 180 (22), 179 (26), 177 (18), 167 (34), 166 (12), 165 (44), 164 (41), 157 (60), 153 (18), 152 (40), 151 (60), 146 (15), 145 (13), 141 (13), 138 (15), 133 (26), 127 (35), 126 (34), 125 (14), 67 (13), 59 (38), 55 (36); Anal. Calcd for $C_{15}H_{18}F_4O$: C, 68.07; H, 7.14. Found: C, 68.34; H, 7.17.



3ja

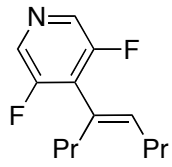
(*E*)-2,3,5,6-Tetrafluoro-4-(4-octen-4-yl)anisole (3ja). A colorless oil, R_f 0.20 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 (t, *J* = 7.3 Hz, 1H), 4.06 (s, 3H), 2.35 (t, *J* = 7.6 Hz, 2H), 2.21 (q, *J* = 7.3 Hz, 2H), 1.48 (sext, *J* = 7.3 Hz, 2H), 1.30 (sext, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3 (dm, J_F = 242.3 Hz), 140.7 (dm, J_F = 246.2 Hz), 136.6–136.2 (m), 135.6, 126.9, 116.8 (t, J_F = 19.7 Hz), 62.1, 32.8, 30.3, 22.7, 21.6, 13.9, 13.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ –144.3 (dd, J_F = 21.8, 8.6 Hz, 2F), –159.4 (dd, J_F = 24.0, 10.4 Hz, 2F); IR (neat) 2961, 2934, 2874, 1647, 1504, 1481, 1470, 1439, 1420, 1381, 1200, 1126, 1107, 1063, 1018, 984, 945, 903, 864 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 291 (M^++1, 40), 290 (M^+, 92), 261 (35),

248 (64), 247 (100), 233 (47), 231 (10), 221 (23), 220 (83), 219 (84), 217 (19), 215 (12), 207 (40), 206 (15), 205 (45), 204 (21), 200 (10), 199 (10), 194 (36), 193 (91), 189 (22), 188 (20), 187 (26), 185 (12), 176 (17), 175 (11), 169 (32), 163 (18), 162 (12), 161 (10), 157 (13), 151 (16), 143 (10), 81 (10), 67 (10), 55 (21); Anal. Calcd for $C_{15}H_{18}F_4O$: C, 62.06; H, 6.25. Found: C, 62.33; H, 6.53.



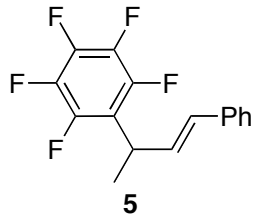
3ka

(*E*)-2,3,5,6-Tetrafluoro-4-(4-octen-4-yl)pyridine (3ka). A yellow oil, R_f 0.30 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 (t, J = 7.3 Hz, 1H), 2.43 (t, J = 7.6 Hz, 2H), 2.26 (q, J = 7.3 Hz, 2H), 1.50 (sext, J = 7.5 Hz, 2H), 1.32 (sext, J = 7.5 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4 (dm, J_F = 245.3 Hz), 139.6 (dm, J_F = 256.0 Hz), 137.6, 136.8–136.3 (m), 126.7, 31.9, 30.3, 22.5, 21.6, 13.8, 13.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ –92.1——92.5 (m, 2F), –143.9——144.1 (m, 2F); IR (neat) 2965, 2936, 2876, 1640, 1454, 1410, 1368, 1286, 1171, 1069, 961, 903, 878 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 261 (M^+, 47), 219 (37), 218 (32), 204 (18), 191 (100), 190 (35), 184 (12), 177 (18), 170 (35), 164 (16), 55 (12); HMRS (EI) Calcd for $C_{13}H_{15}F_4N$: M^+, 261.1141. Found: *m/z* 261.1146.



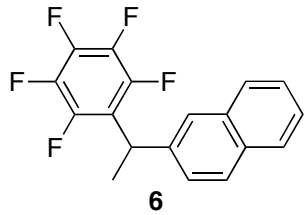
3la

(*E*)-3,5-Difluoro-4-(4-octen-4-yl)pyridine (3la). A yellow oil, R_f 0.20 (hexane–ethyl acetate = 19:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 2H), 5.57 (t, J = 7.3 Hz, 1H), 2.40 (t, J = 7.6 Hz, 2H), 2.22 (q, J = 7.3 Hz, 2H), 1.48 (sext, J = 7.5 Hz, 2H), 1.29 (sext, J = 7.5 Hz, 2H), 0.96 (t, J = 7.3 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7 (dd, J_F = 247.7, 3.4 Hz), 135.9, 133.9 (dd, J_F = 29.9, 6.1 Hz), 128.2 (t, J_F = 17.2 Hz), 126.6, 32.1, 30.2, 22.6, 21.5, 13.84, 13.79; ^{19}F NMR (282 MHz, $CDCl_3$) δ –129.1 (s, 2F); IR (neat) 2924, 2855, 1461, 1420, 1377, 1283, 1258, 1225, 1026, 874 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 226 (M^++1, 12), 225 (M^+, 79), 196 (15), 184 (10), 183 (67), 182 (100), 169 (17), 168 (46), 167 (11), 166 (17), 156 (18), 155 (95), 154 (90), 153 (28), 148 (13), 142 (59), 141 (36), 134 (23) 129 (10), 128 (48), 127 (71), 120 (11), 101 (13), 55 (54); Anal. Calcd for $C_{13}H_{17}F_2N$: C, 69.31; H, 7.61. Found: C, 69.46; H, 7.58.



5

(*E*)-(1-Phenyl-1-buten-3-yl)pentafluorobenzene (5). A colorless oil, R_f 0.20 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.18 (m, 5H), 6.48 (d, J = 15.7 Hz, 1H), 6.41 (ddt, J = 15.8, 6.7, 1.8 Hz, 1H), 4.09 (quint, J = 7.1 Hz, 1H), 1.56 (d, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7 (dm, J_F = 247.2 Hz), 139.5 (dm, J_F = 252.6 Hz), 137.5 (dm, J_F = 252.6 Hz), 136.5, 130.6, 130.2, 128.4, 127.5, 126.1, 118.5–118.1 (m), 33.4, 19.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ –143.3 (dd, J_F = 22.0, 8.5 Hz, 2F), –158.1 (t, J_F = 20.6 Hz, 1F), –162.9 (td, J_F = 22.0, 8.2 Hz, 2F); IR (neat) 3028, 2978, 1653, 1520, 1501, 1452, 1298, 1152, 1113, 1079, 1044, 968, 945 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 298 (M^+, 51), 284 (17), 283 (100), 263 (12), 181 (13), 91 (21); Anal. Calcd for $C_{16}H_{11}F_5$: C, 64.43; H, 3.72. Found: C, 64.68; H, 3.98.



6

2-(1-Pentafluorophenylethyl)naphthalene (6). A white solid, mp = 94.0–94.7 °C, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.73 (m, 4H), 7.51–7.41 (m, 2H), 7.37 (d, J = 7.6 Hz, 1H), 4.75 (q, J = 7.4 Hz, 1H), 1.87 (d, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9 (dm, J_F = 247.1 Hz), 139.6 (dm, J = 251.8 Hz), 139.3, 137.5 (dm, J_F = 251.8 Hz), 133.2, 132.2, 128.1, 127.7, 127.4, 126.1, 125.7, 125.5, 125.1, 119.1 (t, J_F = 17.0 Hz), 34.8, 18.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ –142.9 (d, J_F = 24.5 Hz, 2F), –157.6 (d, J_F = 36.4 Hz, 1F), –162.7 (d, J_F = 24.5 Hz, 2F); IR (KBr) 1518, 1418, 1071, 966, 909, 826,

750 cm^{-1}; MS (EI, 70 eV) *m/z* (%) 323 (M^+, 36), 322 (M^+, 97), 308 (40), 307 (100), 305 (12), 288 (26), 287 (84), 128 (17), 115 (10), 115 (12); HMRS (EI) Calcd for $C_{18}H_{11}F_5$: M^+, 322.0781. Found: *m/z* 322.0775.

Alkenylation of 1a with 2a using Ni(acac)$_2$ and [HPCyp$_3$]BF$_4$. Ni(acac)$_2$ (7.7 mg, 30 μmol), [HPCyp$_3$]BF$_4$ (9.8 mg, 30 μmol) and toluene (3.0 mL) were put in a 20 mL Schlenck tube. To the suspension was added a 1.08 M solution of $AlMe_3$ in hexane (0.11 mL, 0.12 mmol) dropwise, and then the resulting black suspension was stirred for an additional 5 min. **1a** (168 mg, 1.0 mmol) and **2a** (110 mg, 1.5 mmol) were added sequentially, and the mixture was stirred at 80 °C for 5 h before filtration through a silica gel pad. The filtrate was concentrated in vacuo, and the residue was purified on flash column chromatography on silica gel to afford **3aa** (0.24 g, 87%).

Deuterium crossover experiment. Ni(acac)$_2$ (2.6 mg, 10 μmol), PCyp$_3$ (2.4 mg, 10 μmol) and toluene (0.5 mL) were put in a 20 mL Schlenck tube. To the suspension was added a 1.08 M solution of $AlMe_3$ in hexane (22 μL, 24 μmol) dropwise, and then the resulting black suspension was stirred for an additional 5 min. **1a** (34 mg, 0.20 mmol) **1j**-d_1 (36 mg, 0.20 mmol, 95% deuteration), and **2a** (66 mg, 0.60 mmol) were added sequentially, and the mixture was stirred at 80 °C for 3 h before filtration through a silica gel pad. The filtrate was purified by flash silica gel column chromatography to give **3aa** (19.7 mg, 35%, 7% deuteration) and **3ja**-d_1 (22 mg, 38%, 88% deuteration).

References

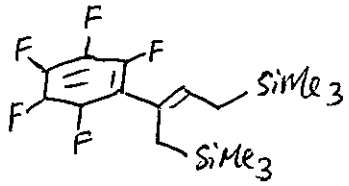
1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
2. Guijarro, A; Yus, M. *Tetrahedron* **1995**, *51*, 231.
3. Cole, K. P.; Hsung, R. P. *Org. Lett.* **2003**, *5*, 4843.
4. The corresponding (*Z*)-isomer is known, and its ^{1}H NMR spectra reported do not match those of **3ac**, see: Mattia, J.; Sikora, D. J.; Macomber, D. W.; Rausch, M. D.; Hickey, J. P.; Friesen, G. D.; Todd, L. J. *J. Organomet. Chem.* **1981**, *213*, 441.

8117-88-02-017-

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480251 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



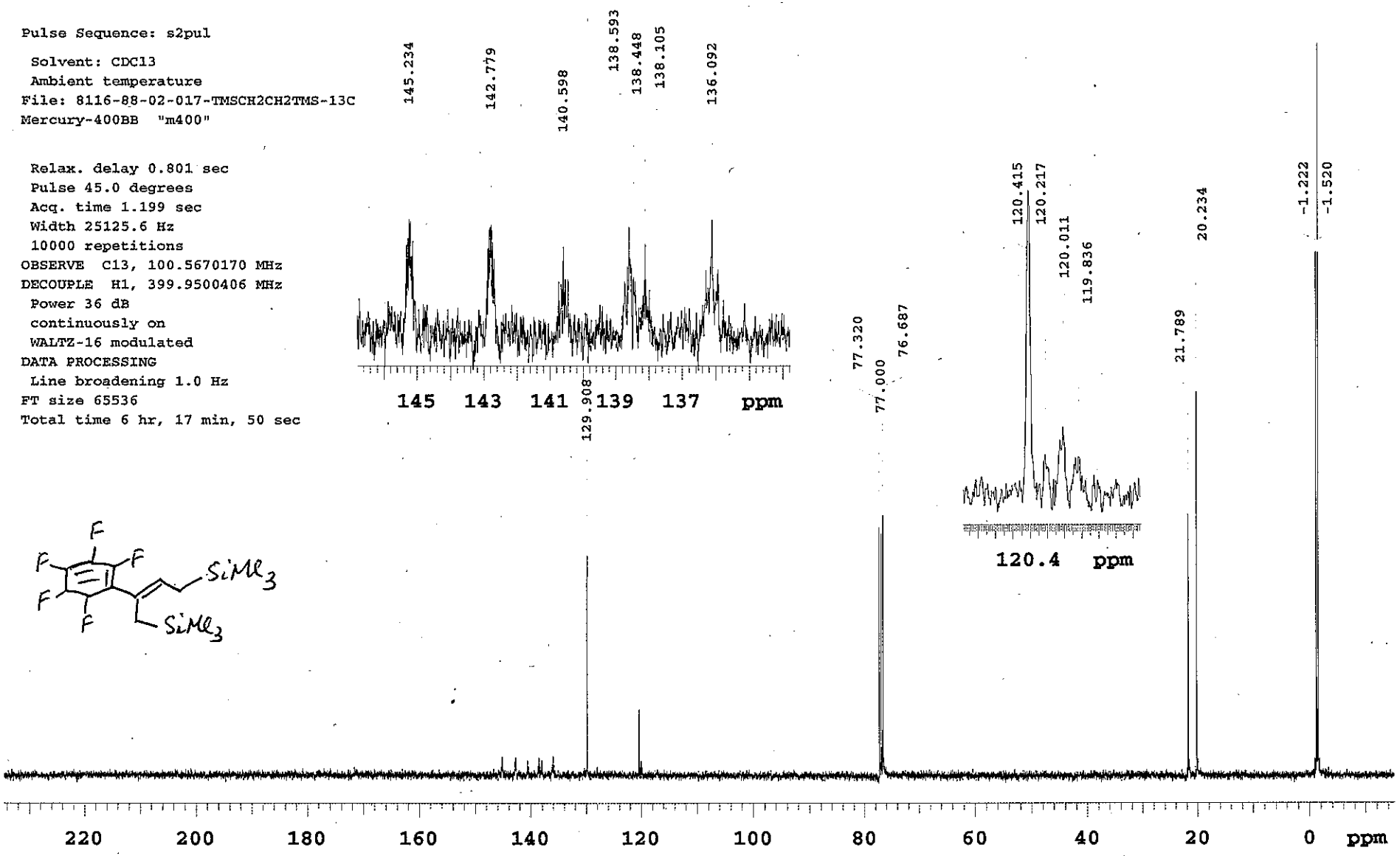
3ab

8117-88-02-017-

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8116-88-02-017-TMSCH2CH2TMS-13C
Mercury-400BB "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
10000 repetitions
OBSERVE C13, 100.5670170 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6 hr, 17 min, 50 sec

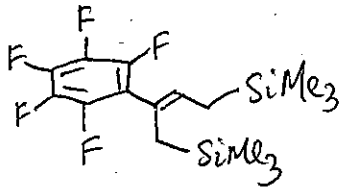


8110-88-02-017-GPC-fr3

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8110-02-017-TMSCH2CH2TMS
Mercury-300BB "m300"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 25380.7 Hz
52 repetitions
OBSERVE F19, 282.2476530 MHz
DATA PROCESSING
FT size 16384
Total time 1 hr, 4 min, 0 sec

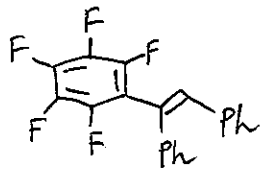


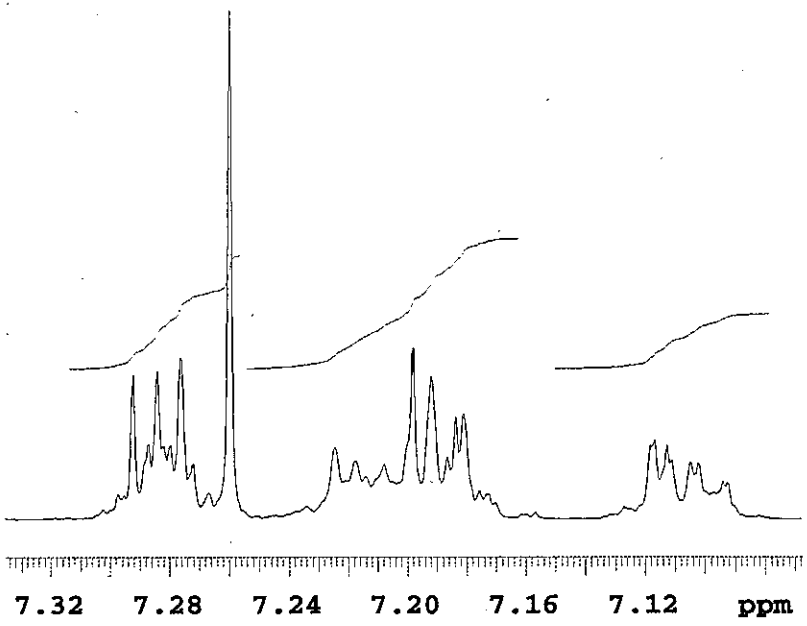
8903-88-5F-PhPh

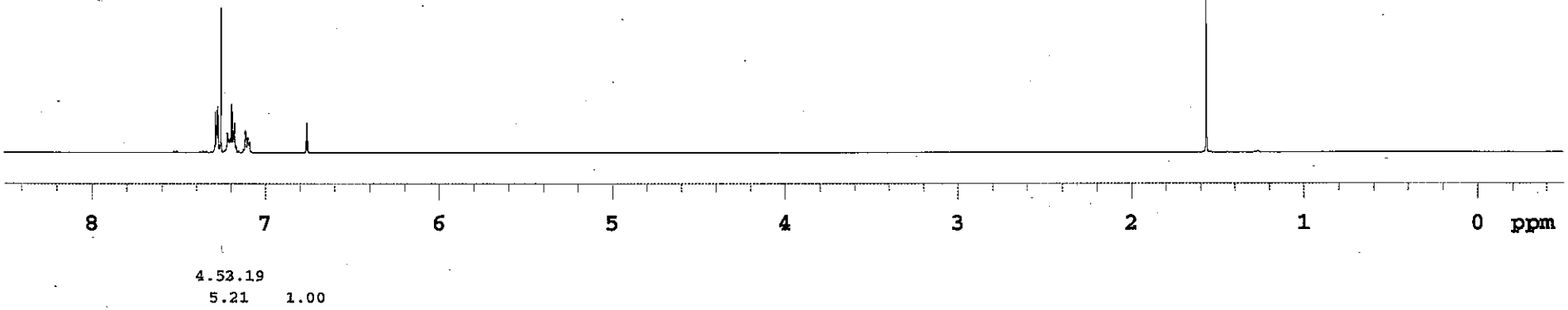
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480258 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec





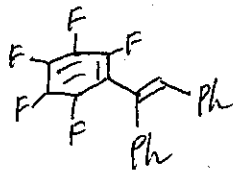


13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDC13
Ambient temperature
File: 8829-88-5F-PhPh-13C
Mercury-400BB "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
1708 repetitions
OBSERVE C13, 100.5669874 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 82662 hr, 26 min, 8 sec

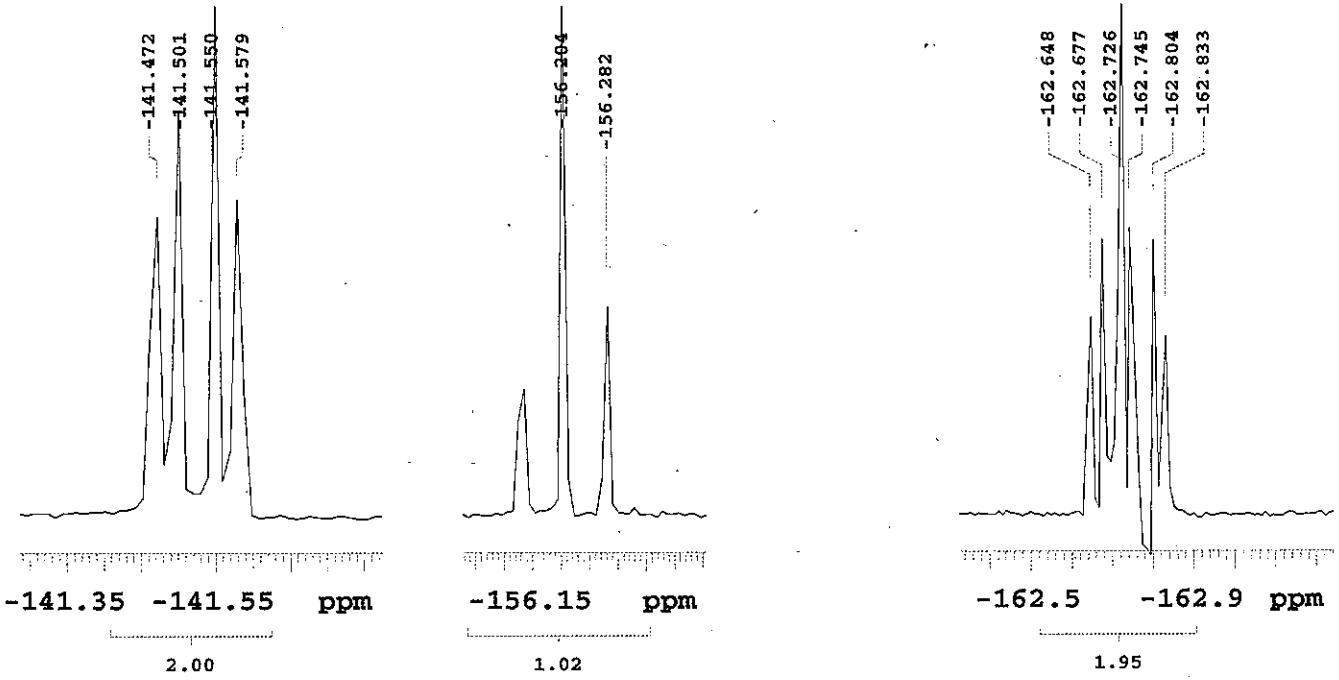


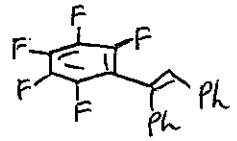
7Y26-88-01-193-column

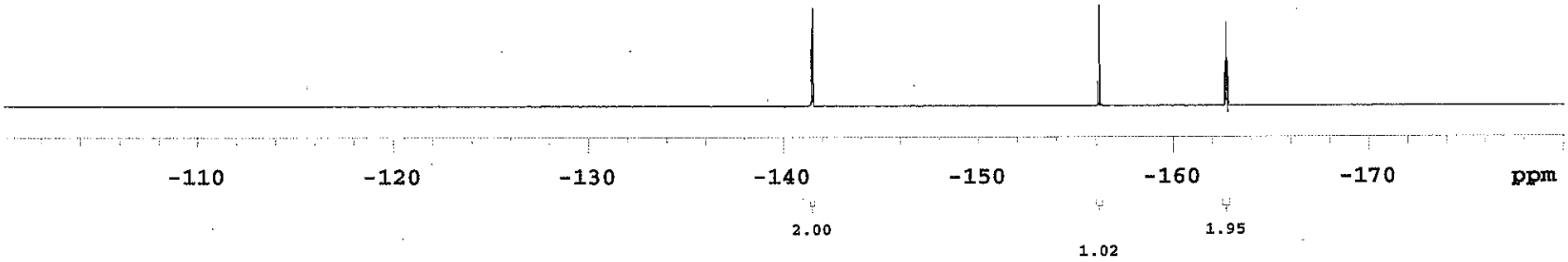
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 7Y26-01-193-5F-Ph-Ph
Mercury-300BB "m300"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 22573.4 Hz
64 repetitions
OBSERVE F19, 282.2474876 MHz
DATA PROCESSING
FT size 16384
Total time 6 min, 15 sec





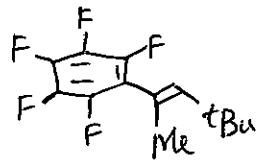


8804-88-01-200

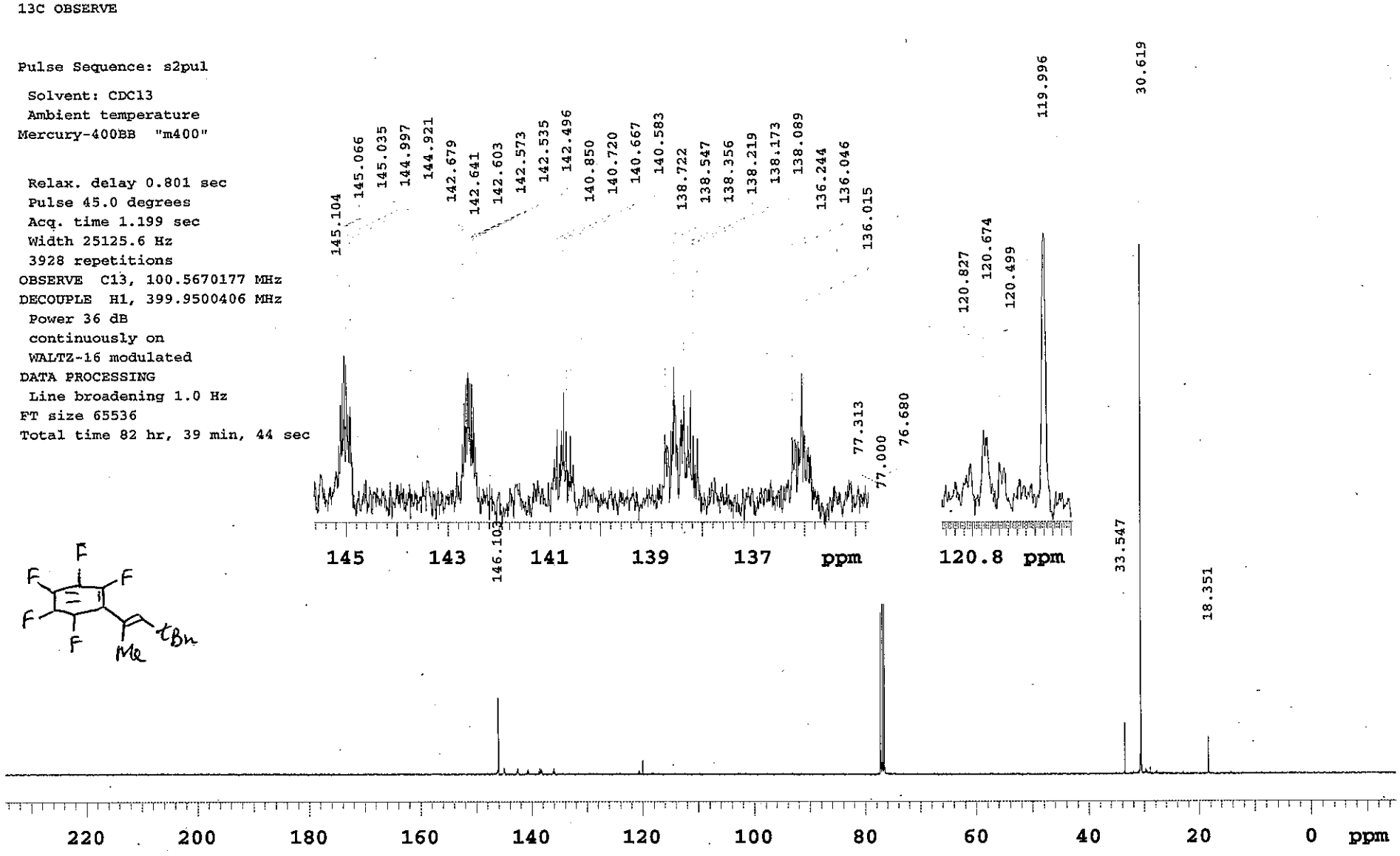
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480262 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



3ae

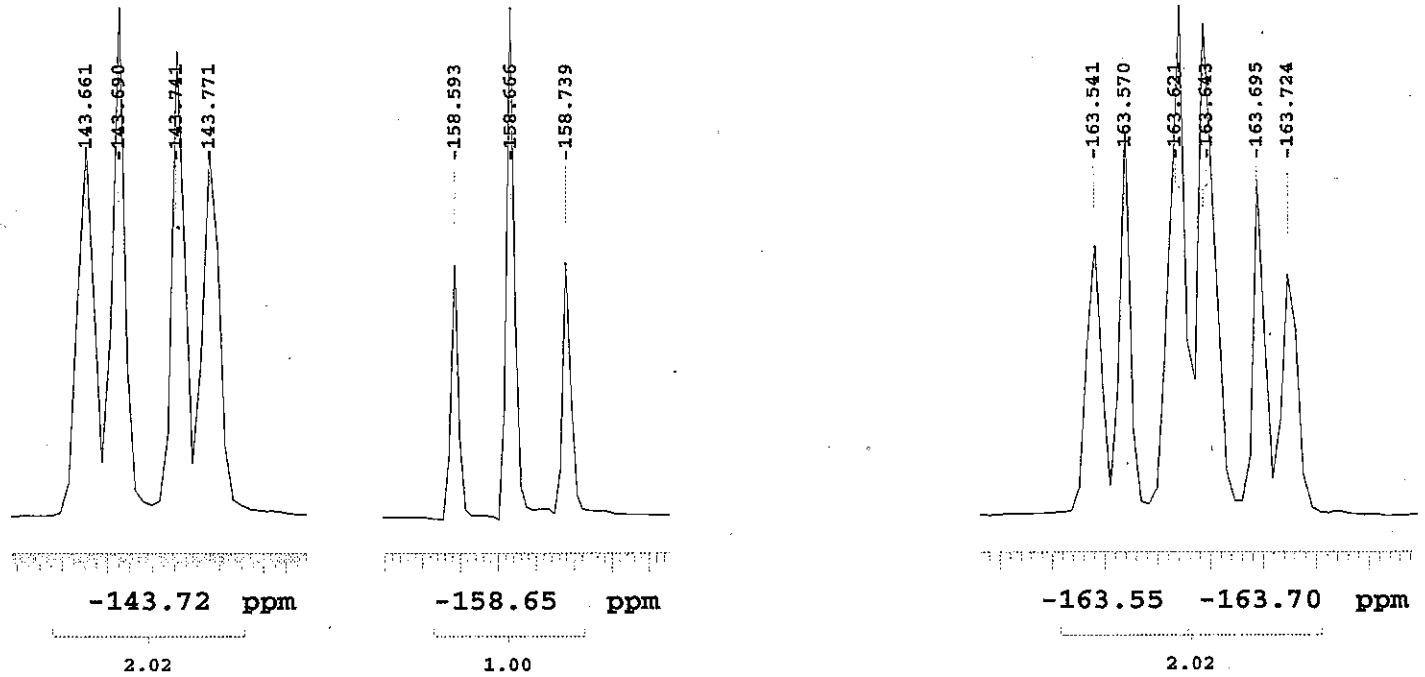

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"
Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
3928 repetitions
OBSERVE C13, 100.5670177 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 82 hr, 39 min, 44 sec
145.104
145.066
145.035
144.997
144.921
142.679
142.641
142.603
142.573
142.535
142.496
140.850
140.720
140.667
140.583
138.722
138.547
138.356
138.219
138.173
138.089
136.244
136.046
136.015
146.103
77.313
77.000
76.680
120.827
120.674
120.499
119.996
30.619
33.547
18.351
F
F
F
F
F
tBu
Me
145
143
141
139
137
ppm
120.8 ppm
220
200
180
160
140
120
100
80
60
40
20
0
ppm

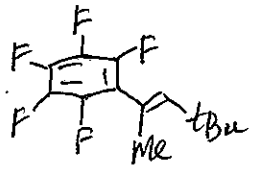
7Y29-88-01-200-column

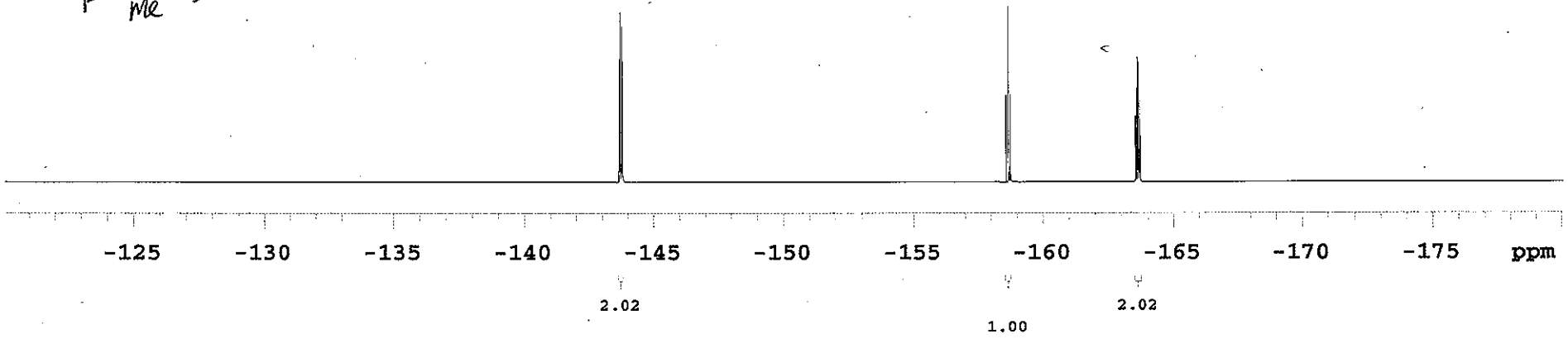
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 7Y29-01-200-5f-Tbu-Me
Mercury-300BB "m300"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 16949.2 Hz
100 repetitions
OBSERVE F19, 282.2474791 MHz
DATA PROCESSING
FT size 16384
Total time 5 min, 59 sec





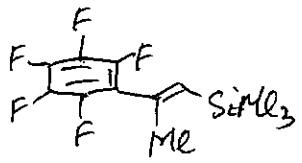


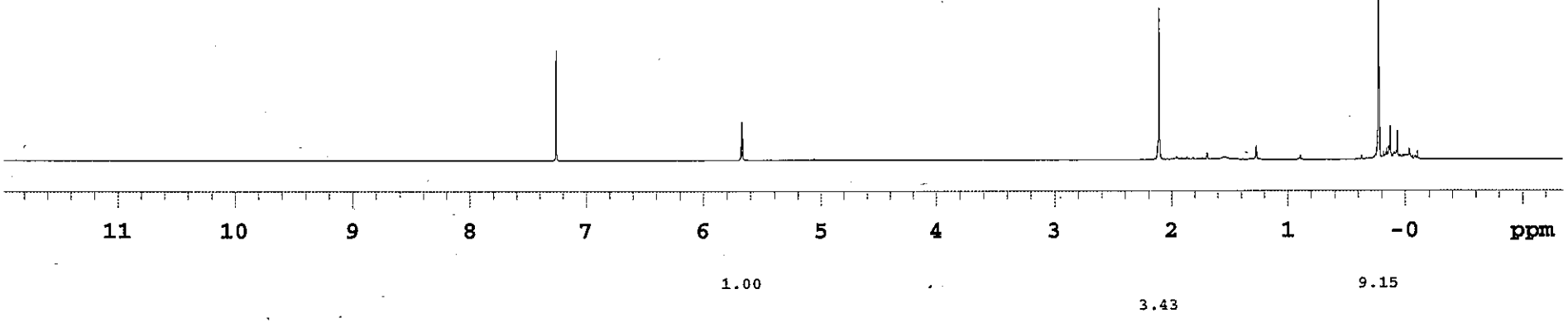
7Y20-88-01-190-column-monoPr

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 7y20-01-190-pentaf-Me-TMS7Y20-01-190-pentsf-Me-TMS
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480254 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



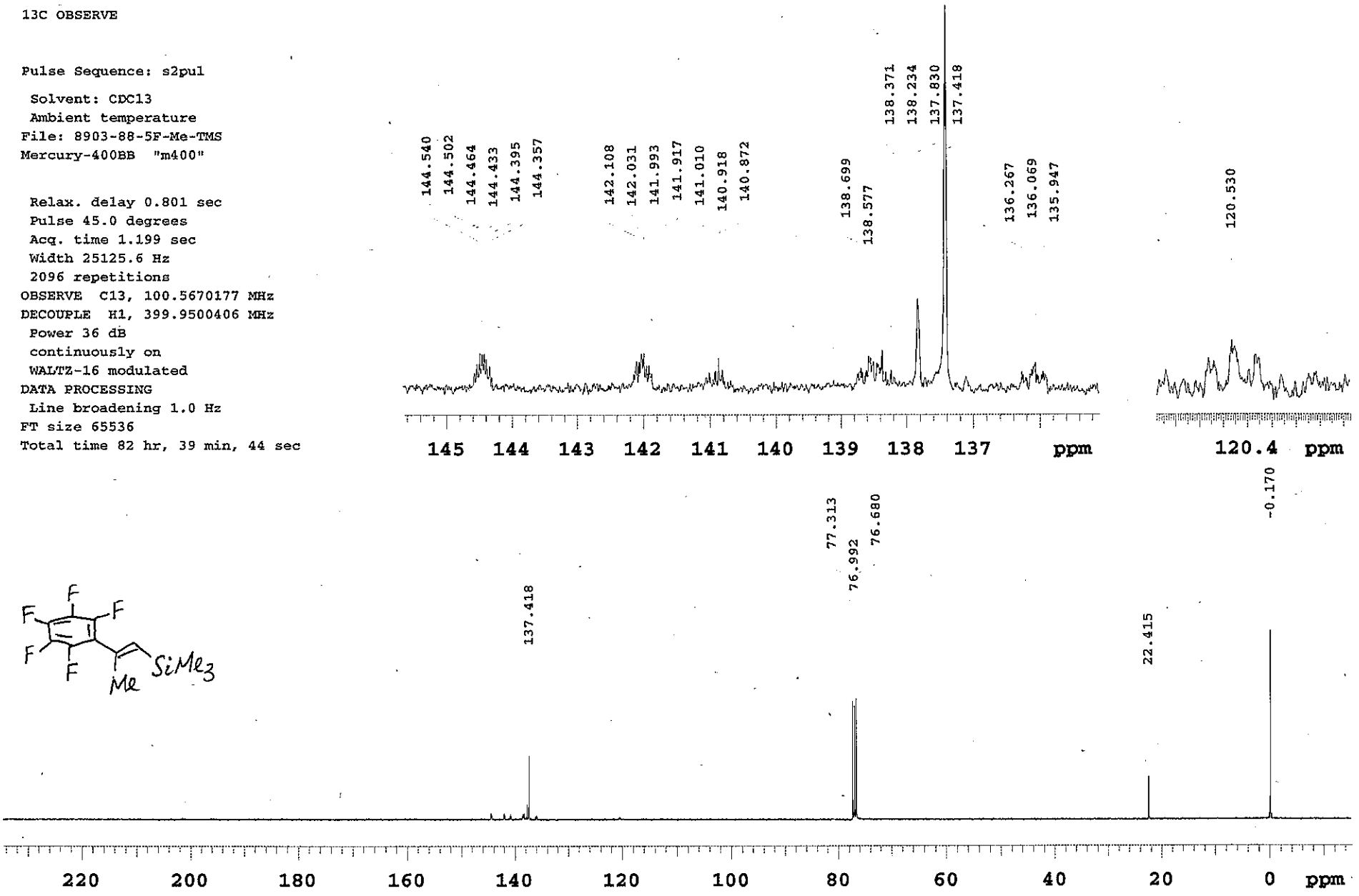


13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8903-88-5F-Me-TMS
Mercury-400BB "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
2096 repetitions
OBSERVE C13, 100.5670177 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 82 hr, 39 min, 44 sec

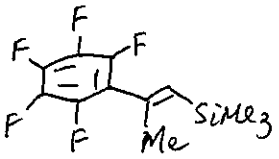


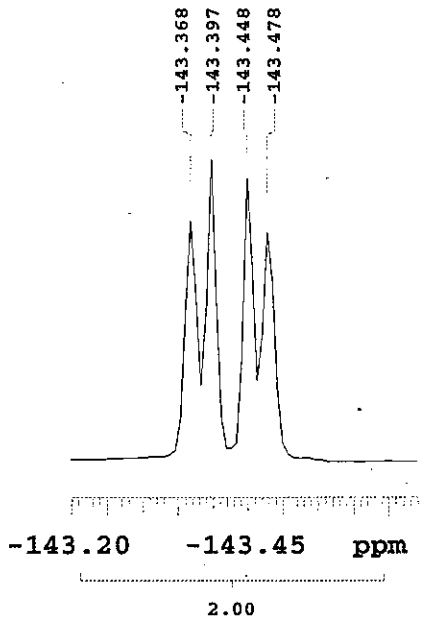
8830-88-5F-Me-TMS

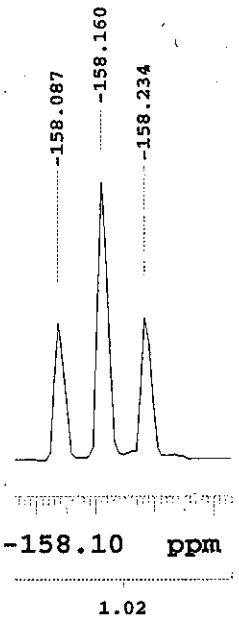
Pulse Sequence: s2pul

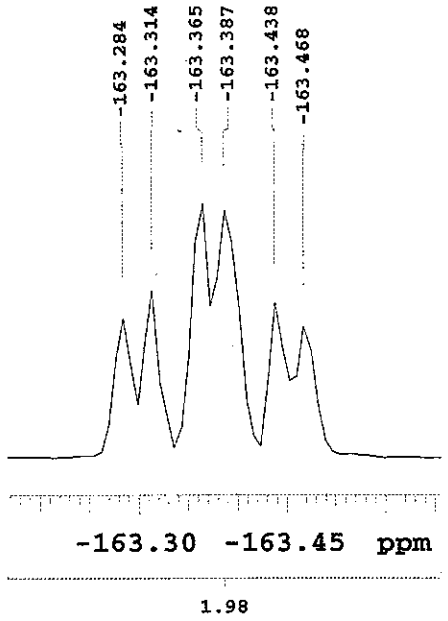
Solvent: CDCl3
Ambient temperature
Mercury-300BB "m300"

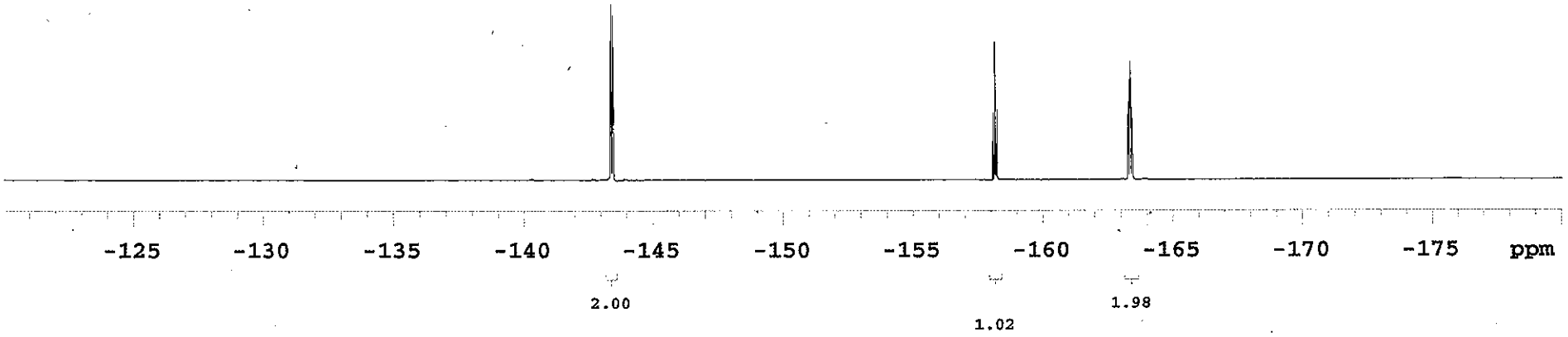
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 16949.2 Hz
84 repetitions
OBSERVE F19, 282.2474729 MHz
DATA PROCESSING
FT size 16384
Total time 1 hr, 9 min, 15 sec









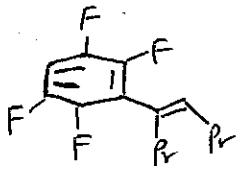


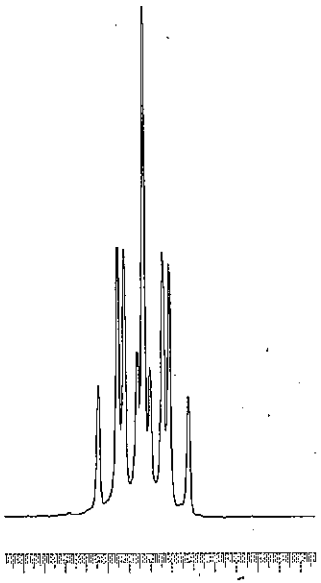
7X03-88-01-120-3d-1

Pulse Sequence: s2pul

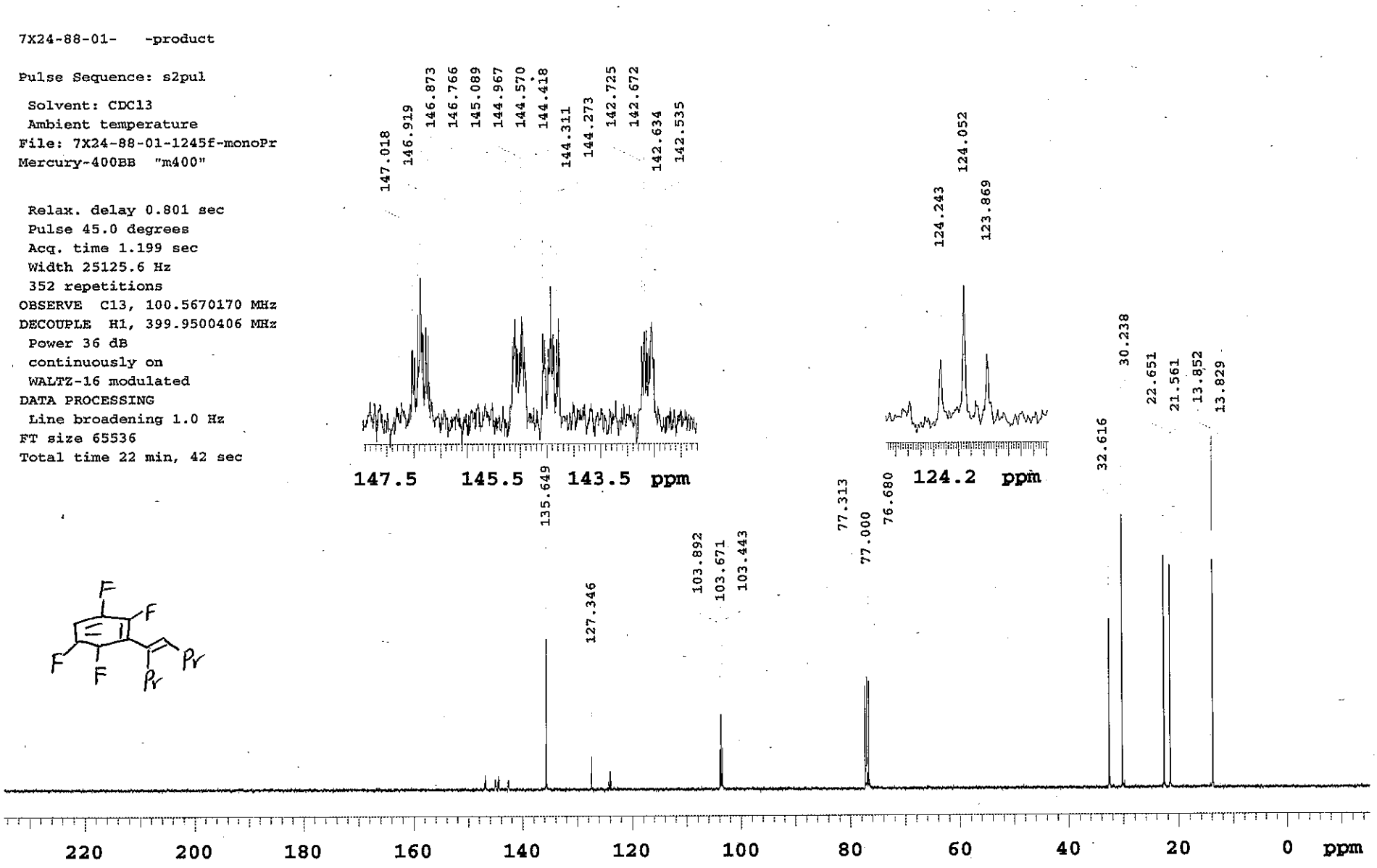
Solvent: CDCl3
Ambient temperature
File: 7X03-88-01-120-3d-1
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480253 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec





3da

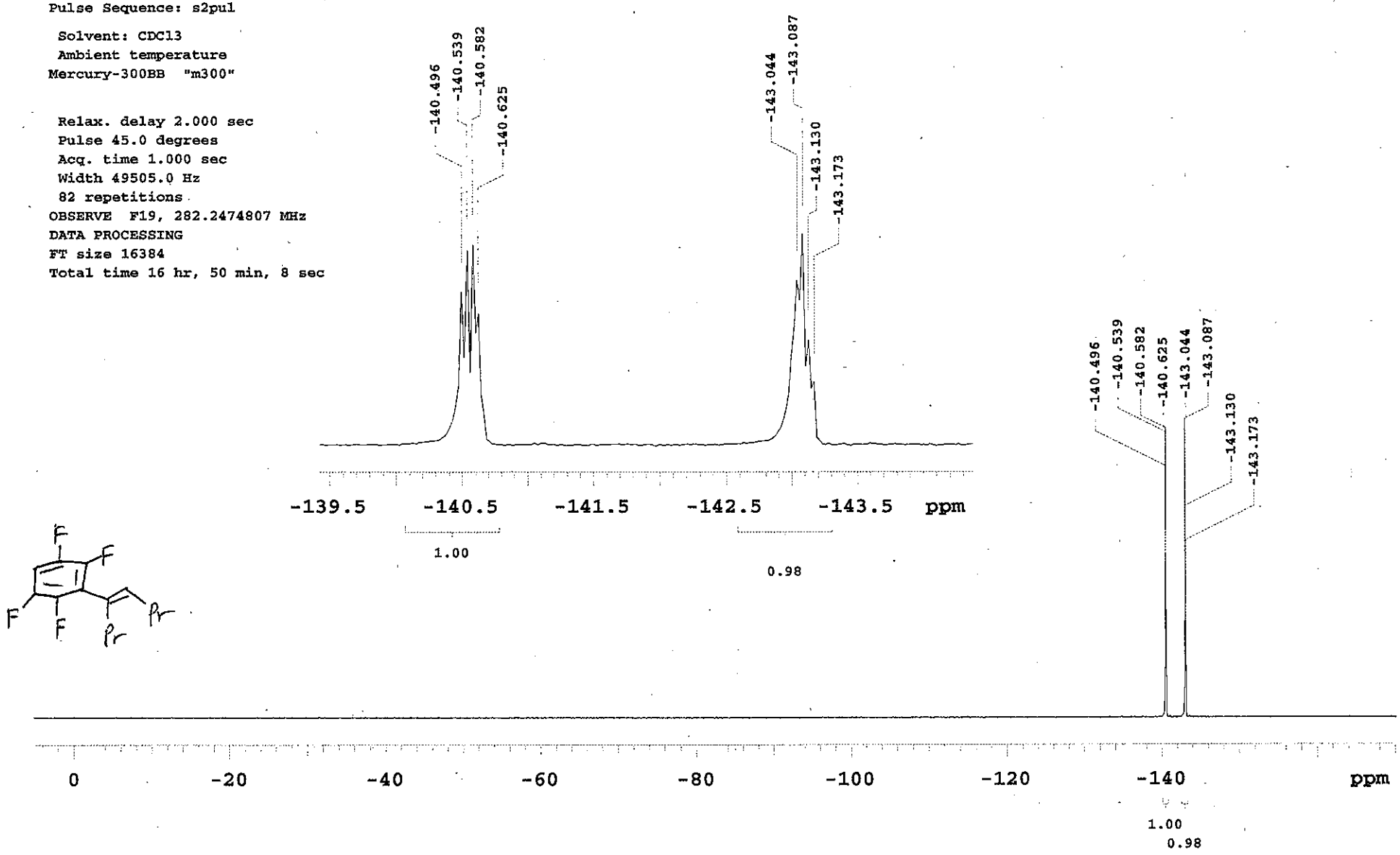

7X24-88-01- -product
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 7X24-88-01-1245f-monoPr
Mercury-400BB "m400"
Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
352 repetitions
OBSERVE C13, 100.5670170 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 22 min, 42 sec
147.018
146.919
146.873
146.766
145.089
144.967
144.570
144.418
144.311
144.273
142.725
142.672
142.634
142.535
147.5
145.5
143.5
ppm
124.243
124.052
123.869
124.2
ppm
135.649
127.346
103.892
103.671
103.443
77.313
77.000
76.680
32.616
30.238
22.651
21.561
13.852
13.829
F
F
F
F
Pr
Pr
220
200
180
160
140
120
100
80
60
40
20
0
ppm

8903-88-1245f_monoPrPr

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-300BB "m300"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 49505.0 Hz
82 repetitions
OBSERVE F19, 282.2474807 MHz
DATA PROCESSING
FT size 16384
Total time 16 hr, 50 min, 8 sec

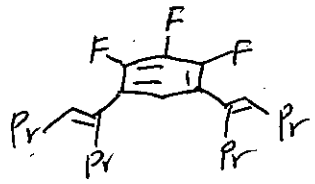


STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480254 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



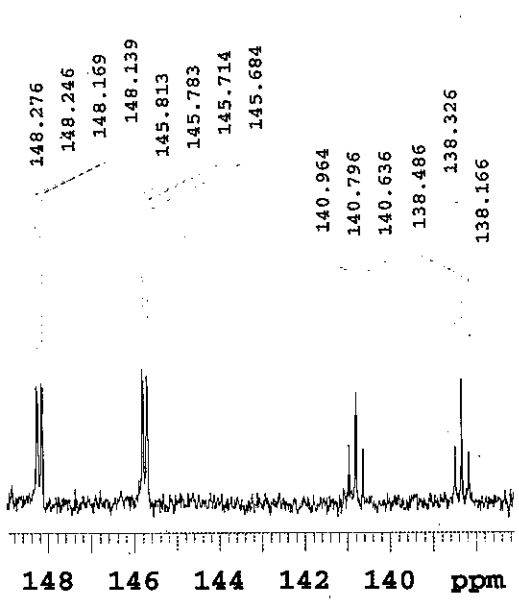
4ea

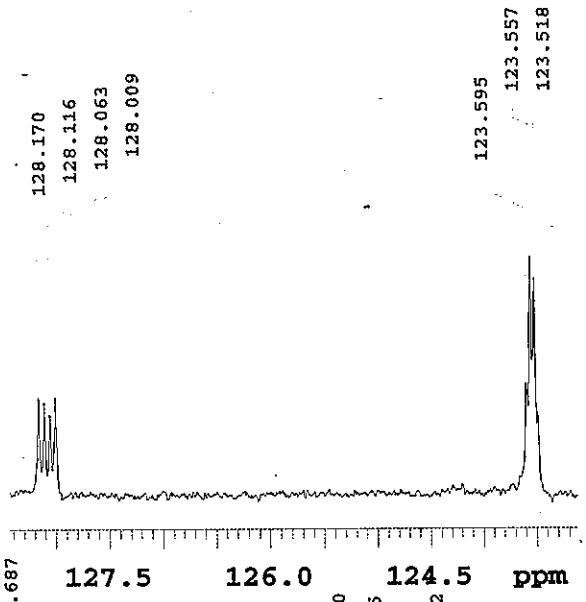
8822-88-02-123F-Di-PrPr

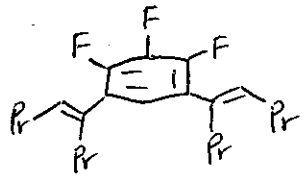
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8822-02-123F-DiPrPr
Mercury-400BB "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
11136 repetitions
OBSERVE C13, 100.5670185 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6297 hr, 29 min, 38 sec





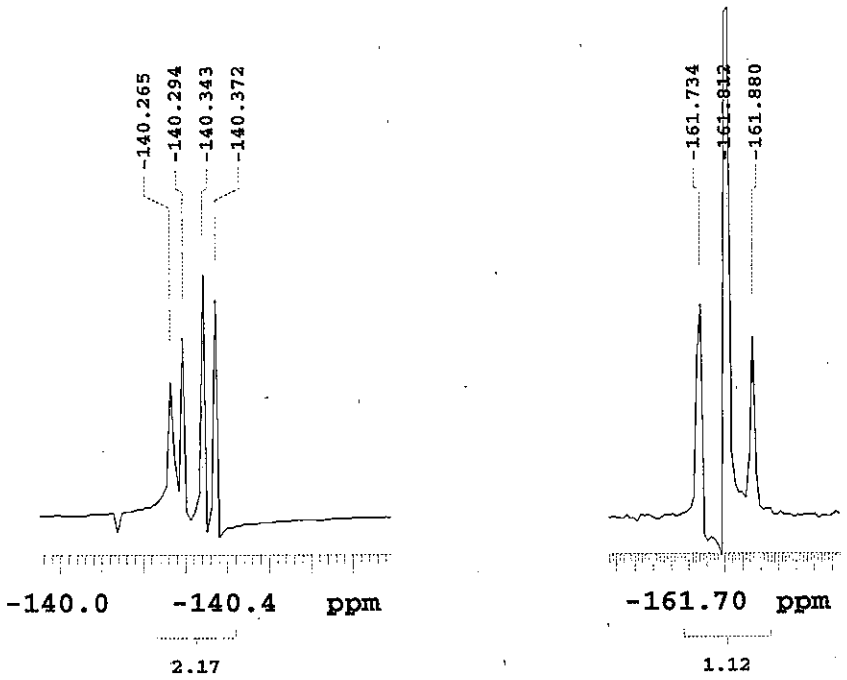


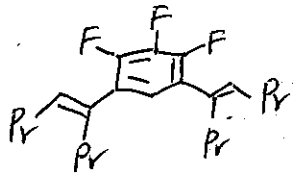
7Y01-88-01-164-GPC3-fr1

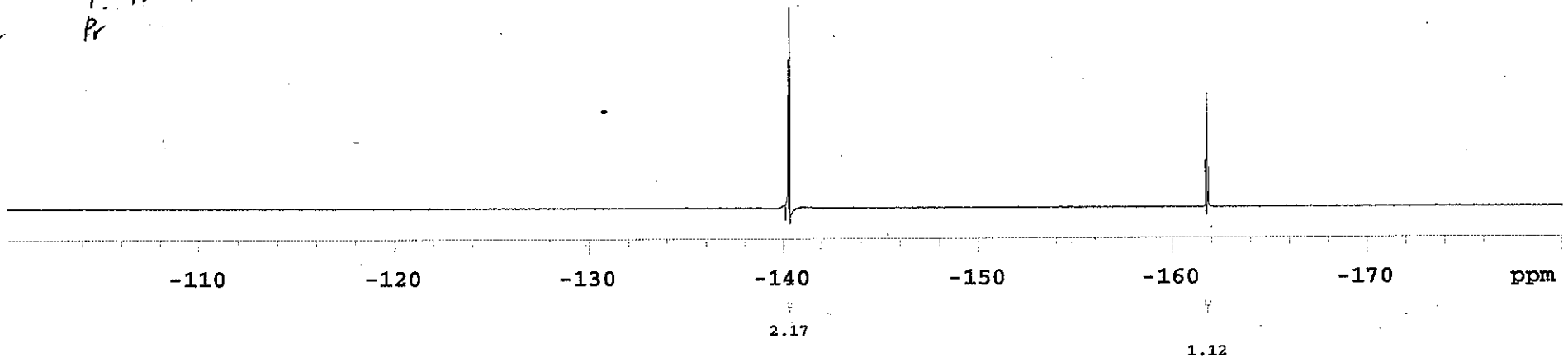
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 7Y01-01-164-123f-diPr
Mercury-300BB "m300"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 22573.4 Hz
20 repetitions
OBSERVE F19, 282.2474969 MHz
DATA PROCESSING
FT size 16384
Total time 1 min, 15 sec





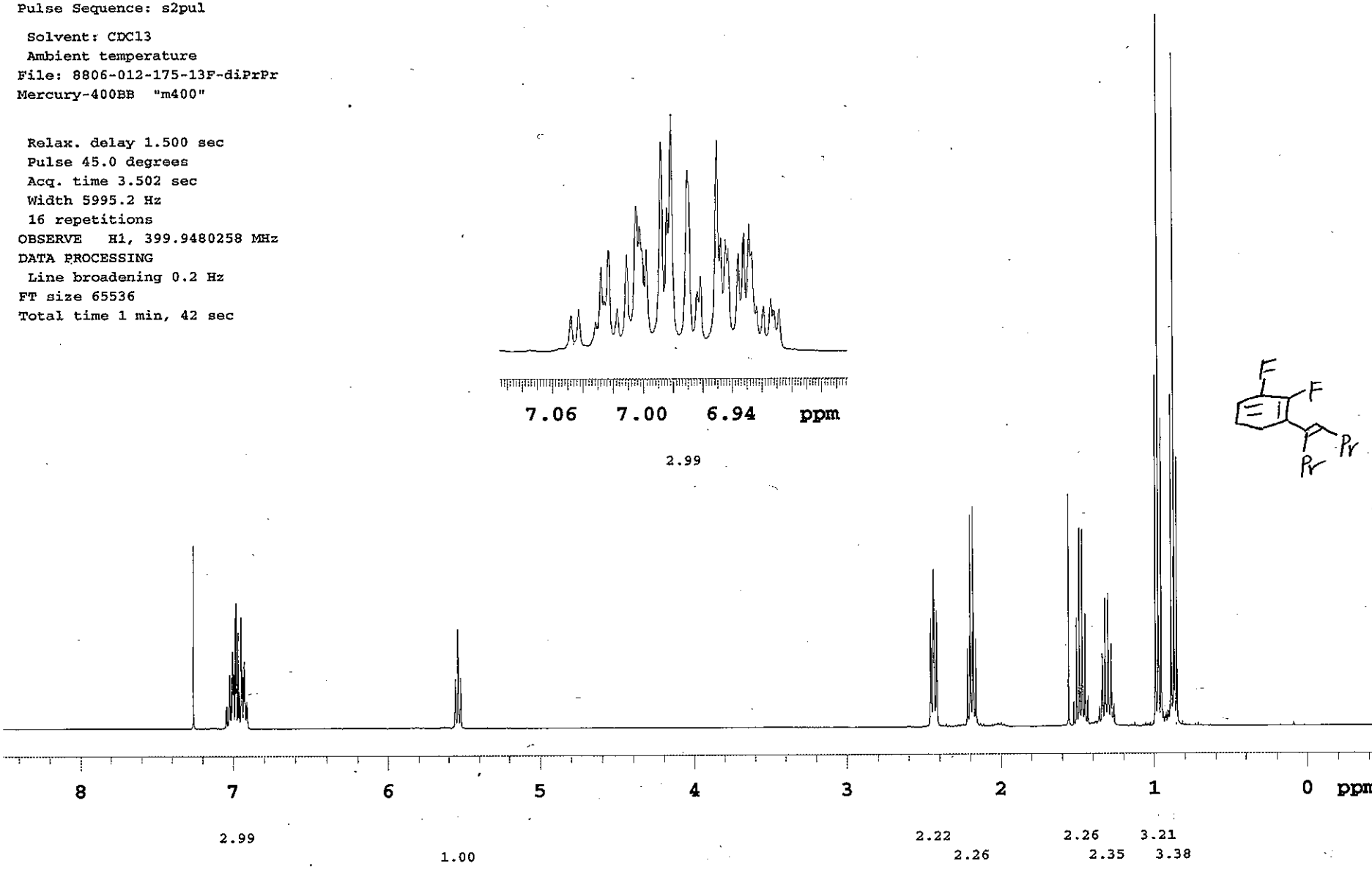


8806-88-01-175-

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8806-012-175-13F-diPrPr
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480258 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



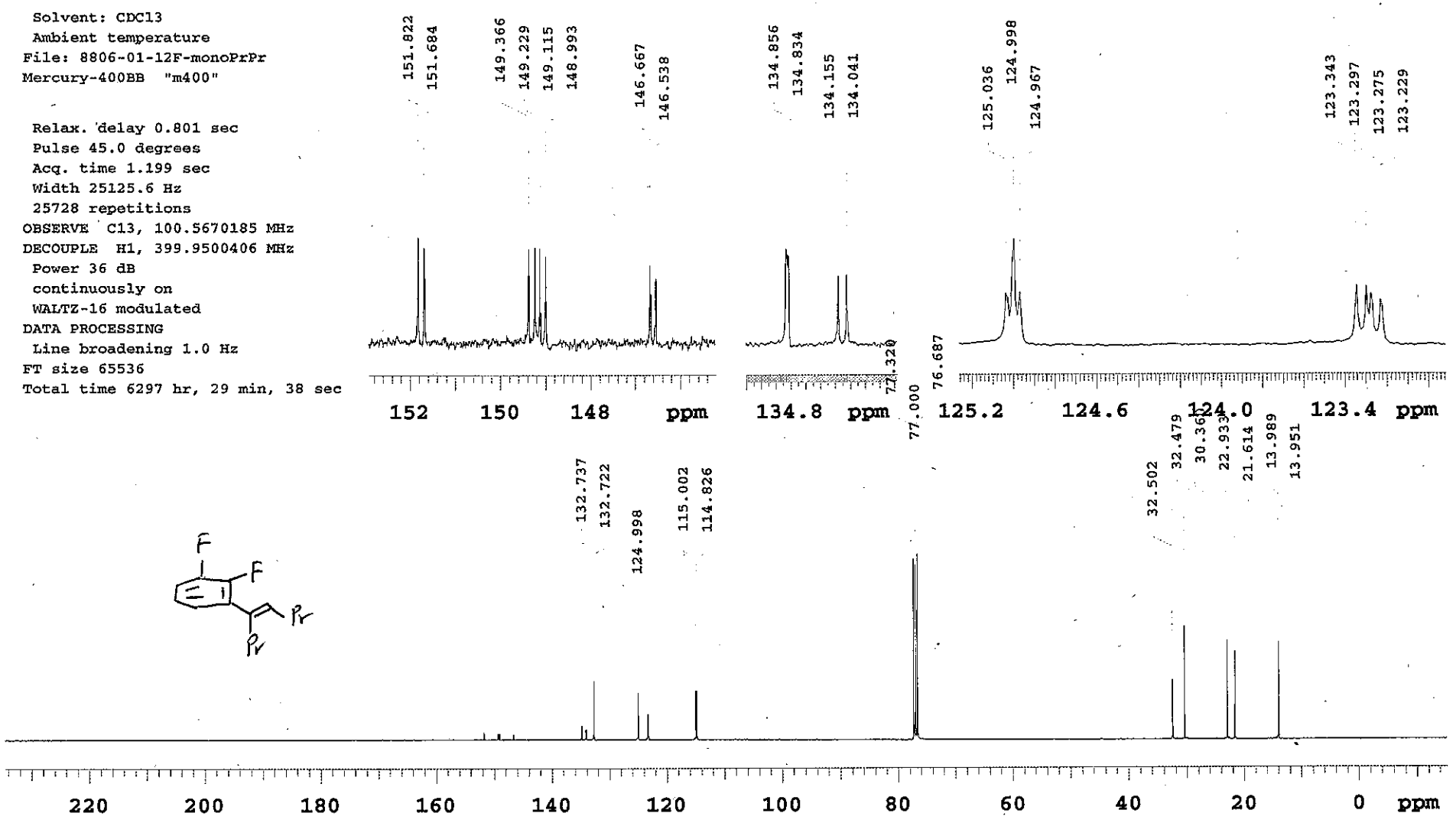
3fa

8806-88-01-12F-mpnoPr

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8806-01-12F-monoPrPr
Mercury-400BB "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
25728 repetitions
OBSERVE C13, 100.5670185 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6297 hr, 29 min, 38 sec

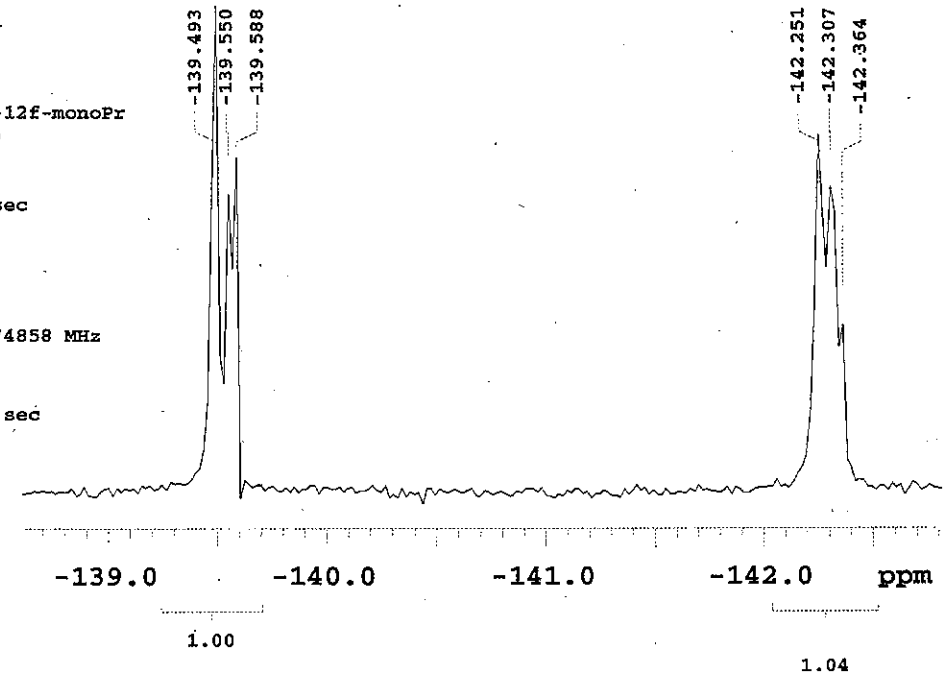


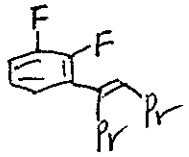
7Y09-88-01-175-GPC-fr2

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 7Y09-88-01-175-12f-monoPr
Mercury-300BB "m300"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 43668.1 Hz
24 repetitions
OBSERVE F19, 282.2474858 MHz
DATA PROCESSING
FT size 16384
Total time 1 min, 44 sec



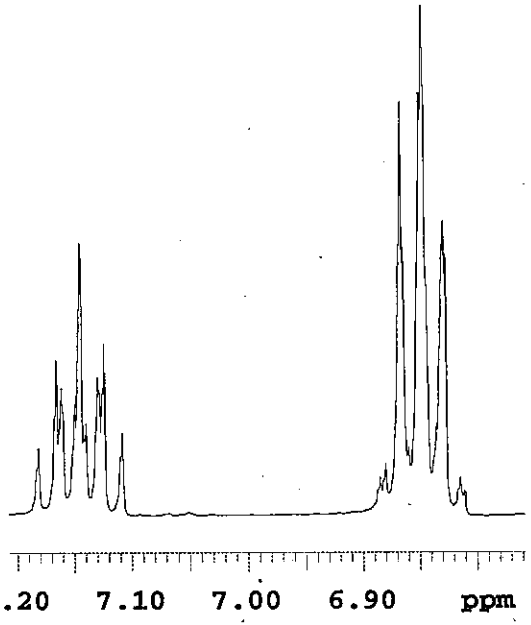


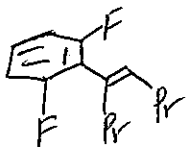
7Y20-88-01-174-gpc-fr5

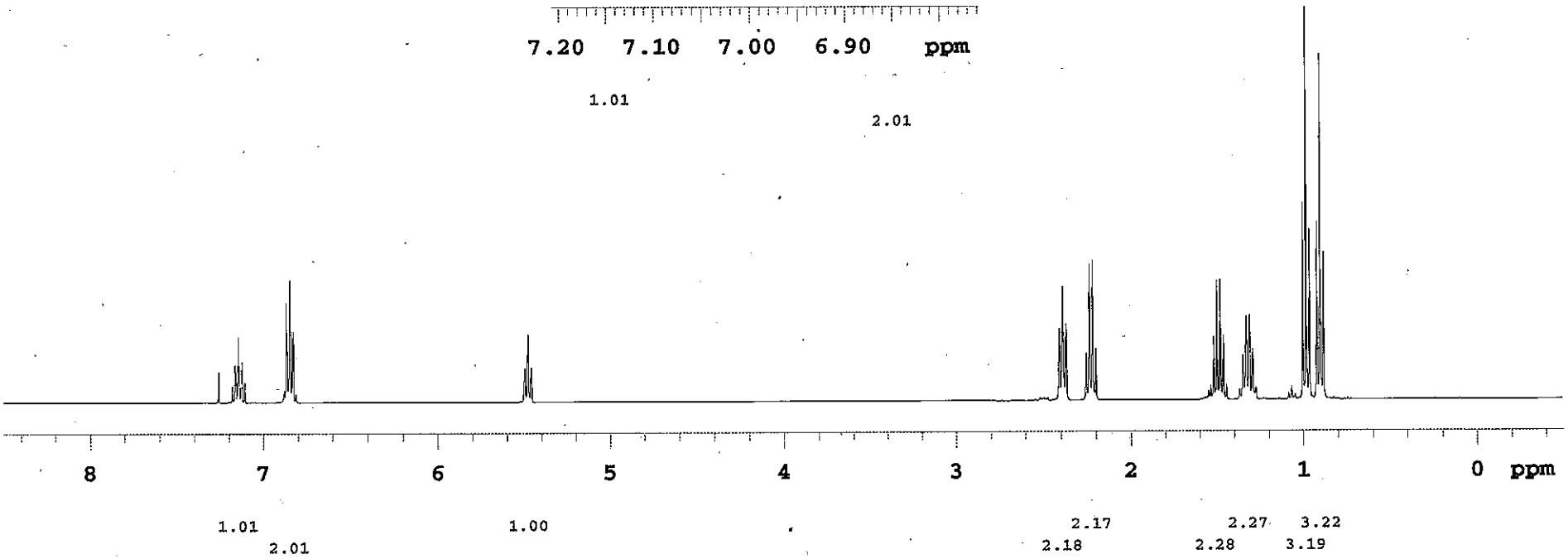
Pulse Sequence: s2pul

Solvent: CDC13
Ambient temperature
File: 7Y20-01-174-13f-monoPr
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480253 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec







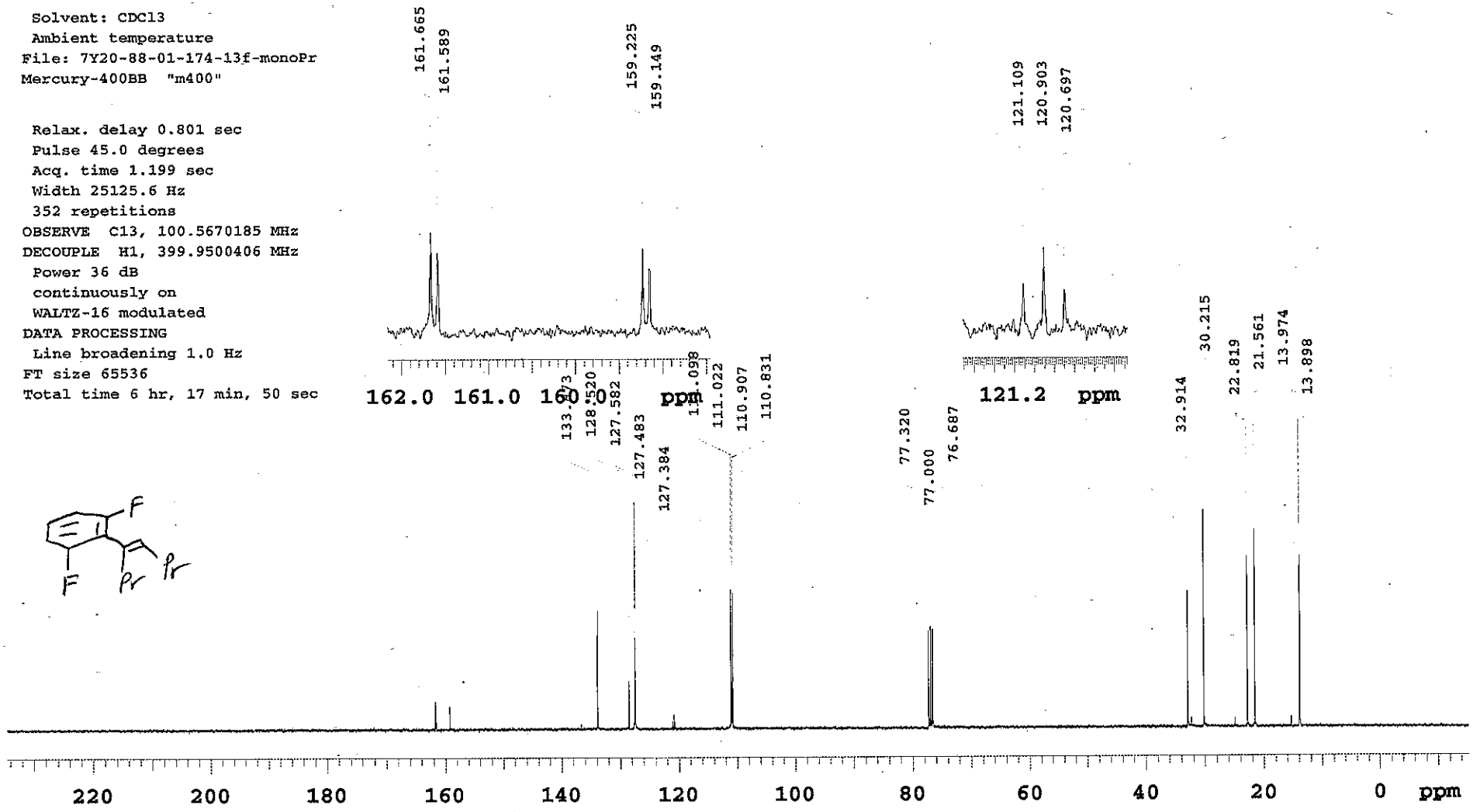
3fa

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 7Y20-88-01-174-13f-monoPr
Mercury-400BB "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
352 repetitions
OBSERVE C13, 100.5670185 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6 hr, 17 min, 50 sec

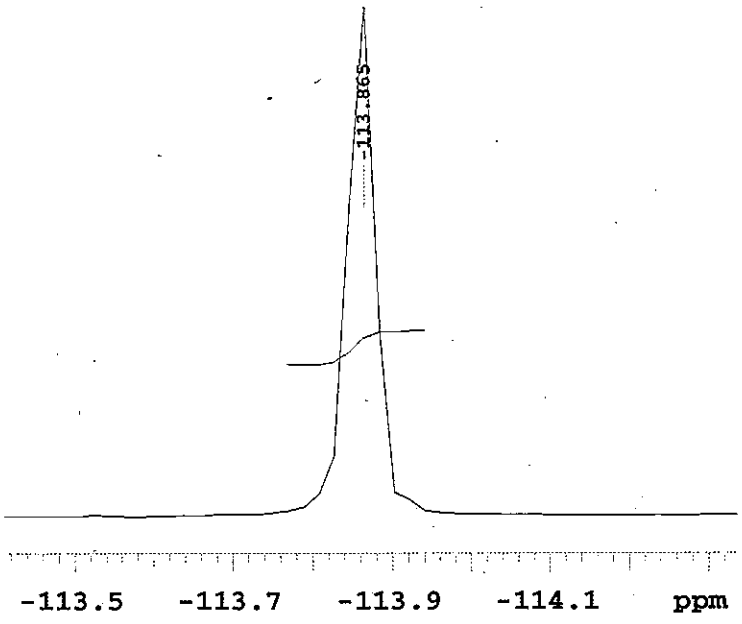


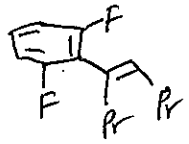
7Y10-88-01-174-GPC-fr5

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 7Y10-01-174-13f-monoPr
Mercury-300BB "m300"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 43668.1 Hz
24 repetitions
OBSERVE F19, 282.2474911 MHz
DATA PROCESSING
FT size 16384
Total time 1 min, 44 sec



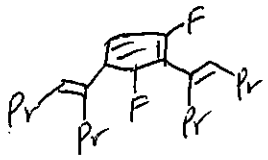


8808-88-01-175-GPC~fr3

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8809-88-01-175~13F-DiPrPr
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480258 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec

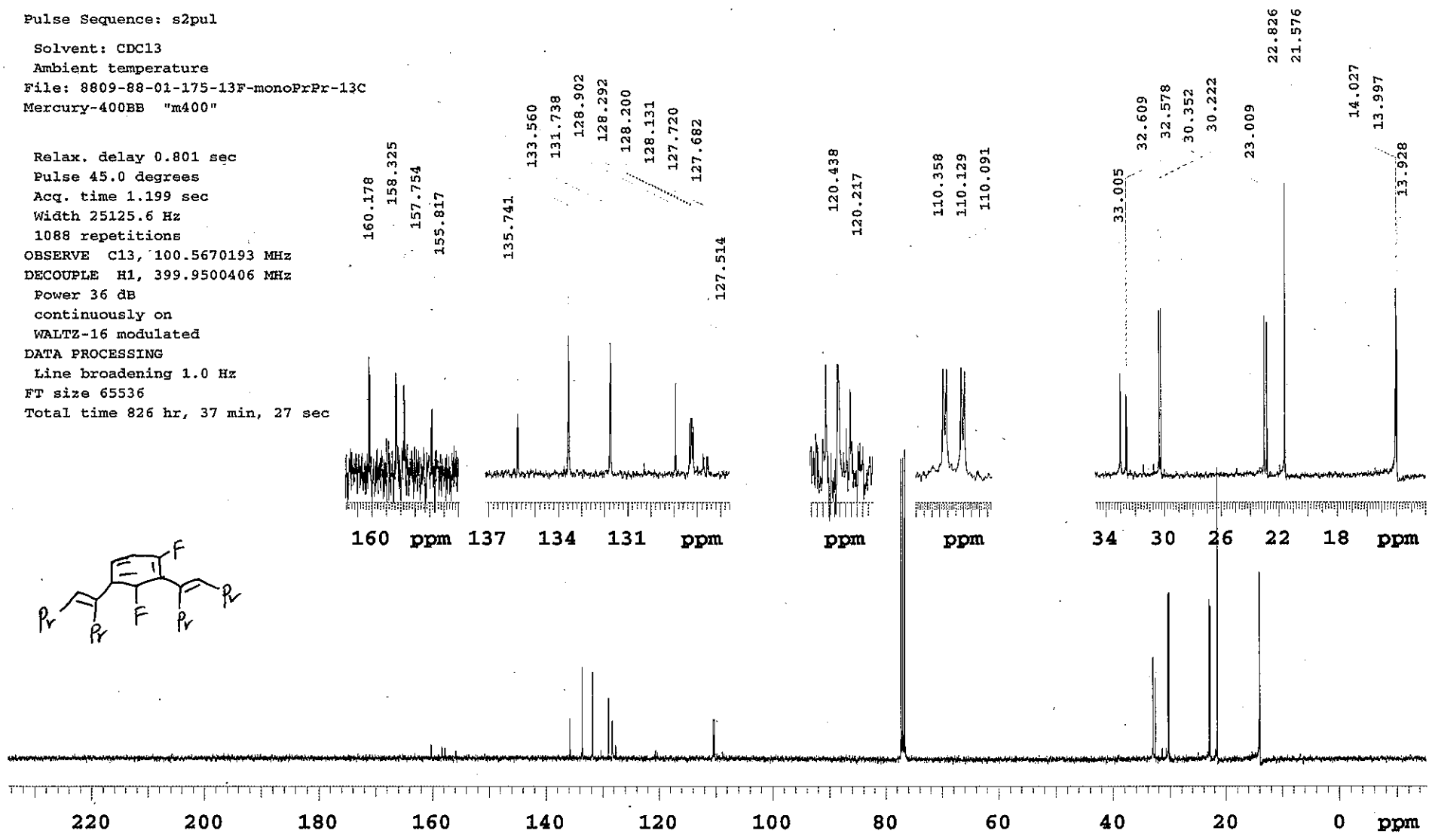


8808-88-01-175-GPC-fr3

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8809-88-01-175-13F-monoPrPr-13C
Mercury-400BB "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
1088 repetitions
OBSERVE C13, 100.5670193 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 826 hr, 37 min, 27 sec

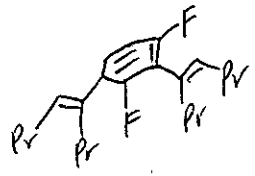


8808-88-01-175-GPC-fr3

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8809-88-01-17%-13F-DiPrPr
Mercury-300BB "m300"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 14104.4 Hz
44 repetitions
OBSERVE F19, 282.2474837 MHz
DATA PROCESSING
FT size 16384
Total time 11 hr, 5 min, 8 sec

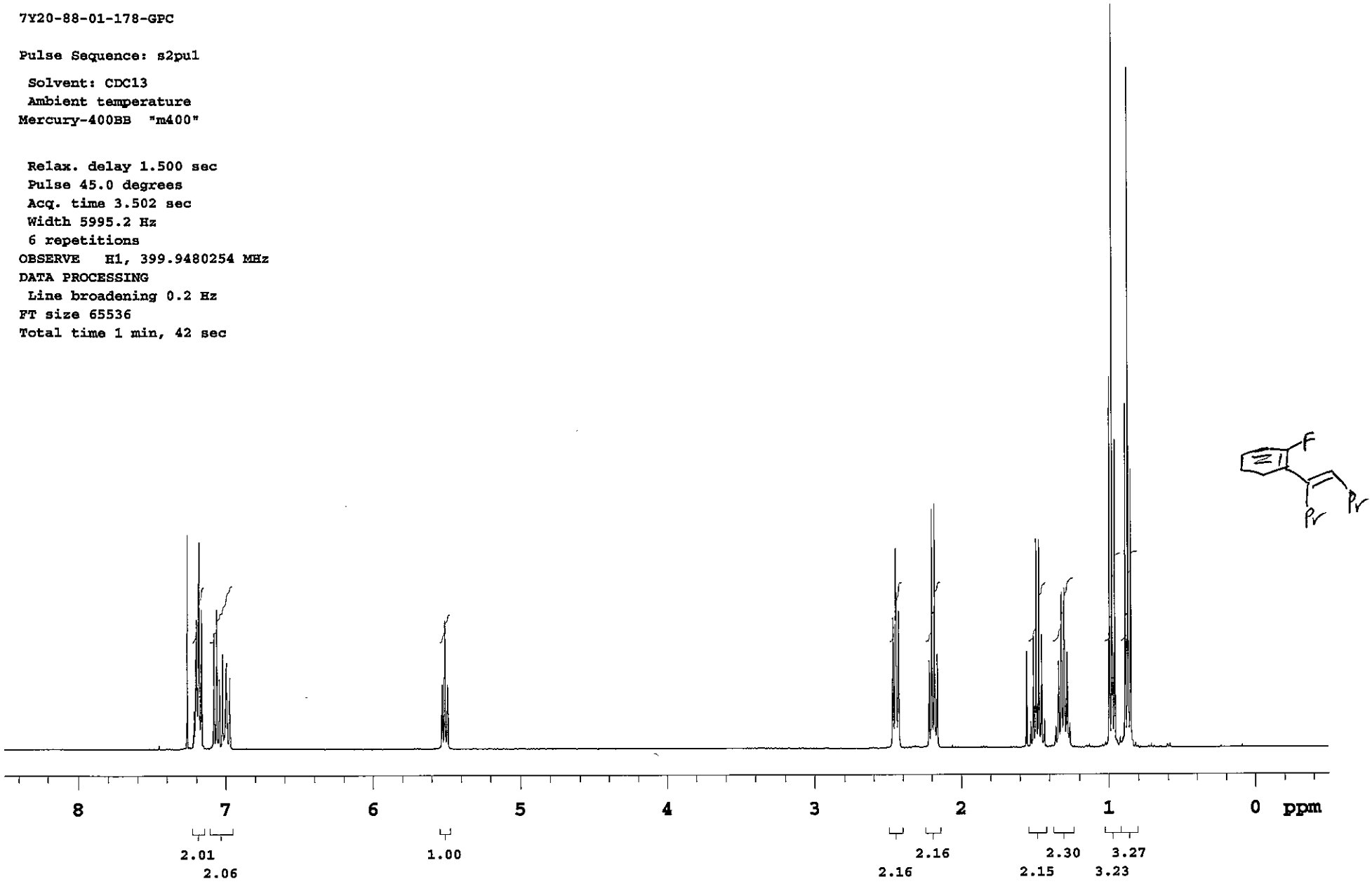


7Y20-88-01-178-GPC

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
6 repetitions
OBSERVE H1, 399.9480254 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



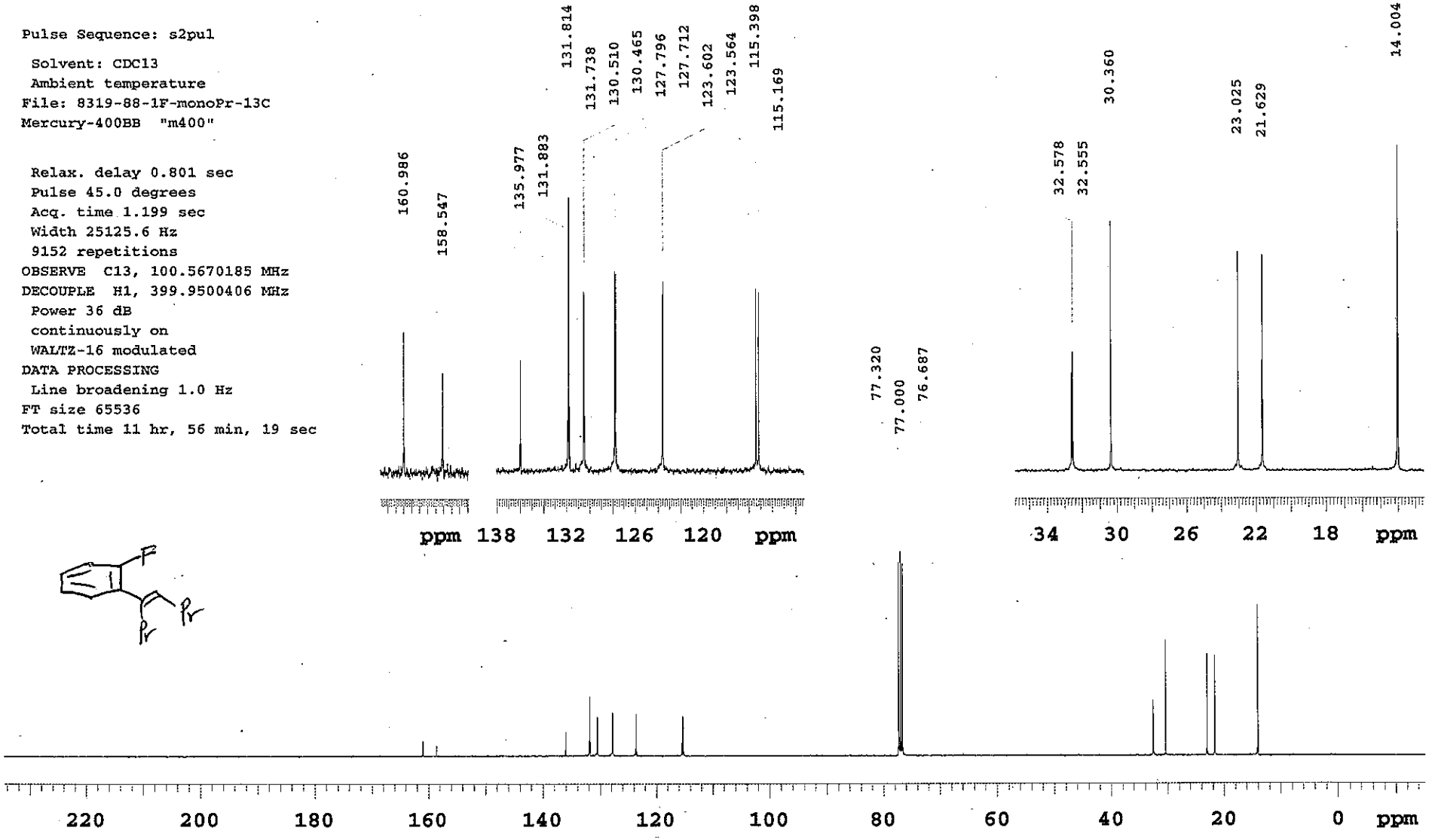
zha

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8319-88-1F-monoPr-13C
Mercury-400BB "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
9152 repetitions
OBSERVE C13, 100.5670185 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 11 hr, 56 min, 19 sec

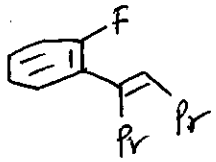


8903-88-02-185-column-fr2

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8903-88-1F-monoPrPr
Mercury-300BB "m300"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 14104.4 Hz
226 repetitions
OBSERVE F19, 282.2474872 MHz
DATA PROCESSING
FT size 16384
Total time 11 hr, 5 min, 8 sec

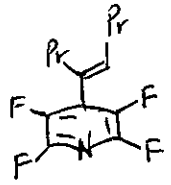


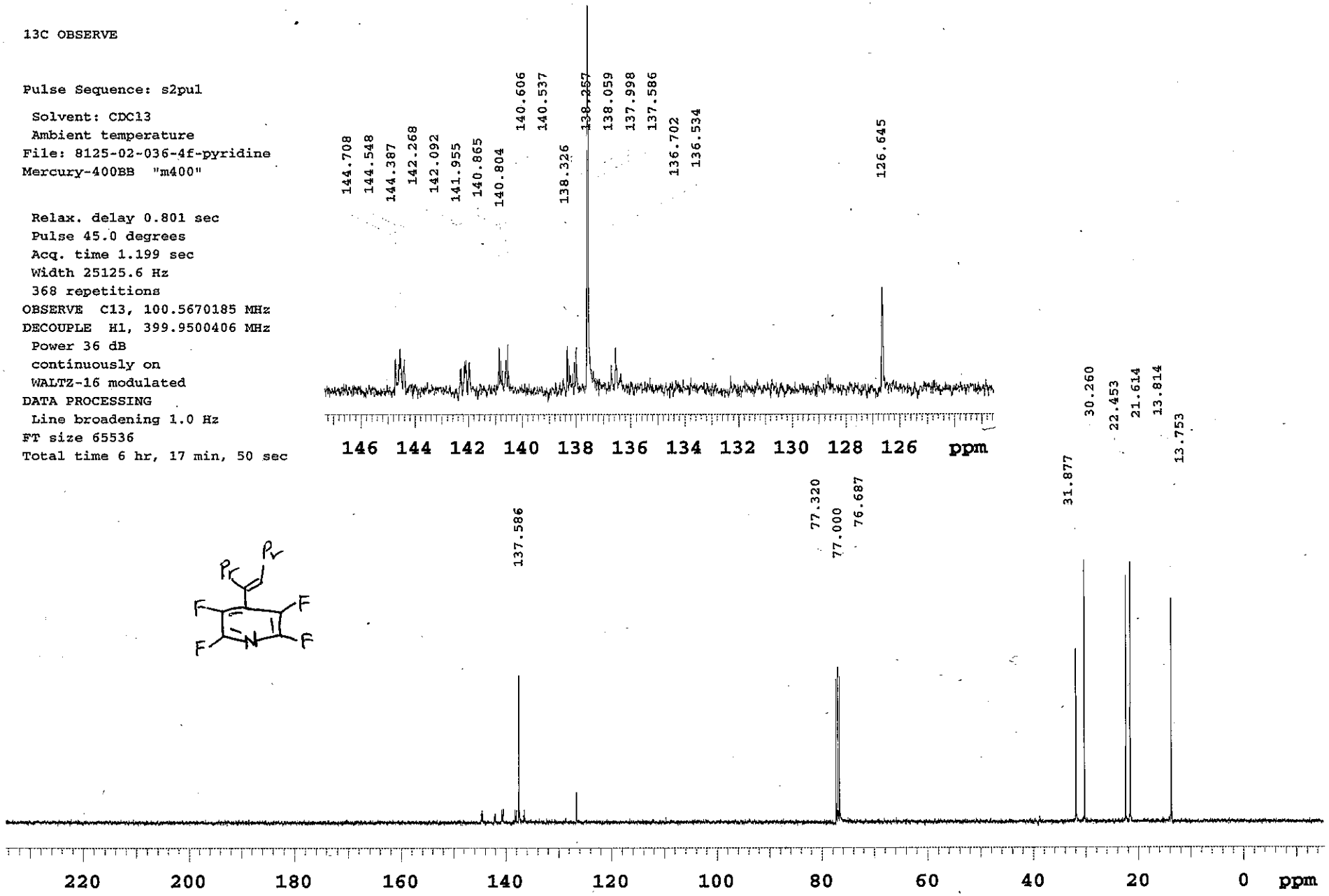
8324-88-02-067-1H

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480254 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



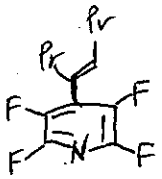

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 8125-02-036-4f-pyridine
Mercury-400BB "m400"
Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
368 repetitions
OBSERVE C13, 100.5670185 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6 hr, 17 min, 50 sec
144.708
144.548
144.387
142.268
142.092
141.955
140.865
140.804
140.606
140.537
138.326
138.267
138.059
137.998
137.586
136.702
136.534
126.645
146 144 142 140 138 136 134 132 130 128 126 ppm
137.586
77.320
77.000
76.687
31.877
30.260
22.453
21.614
13.814
13.753
220 200 180 160 140 120 100 80 60 40 20 0 ppm

8805-88-02-4F-pyridine

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8805-88-02-4F-pyridine-PrPr
Mercury-300BB "m300"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 22573.4 Hz
178 repetitions
OBSERVE F19, 282.2474877 MHz
DATA PROCESSING
FT size 16384
Total time 1 hr, 14 min, 45 sec

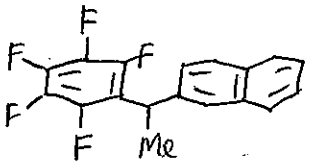


8627-88-02-141-column-fr1

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8627-02-141-5F-vinylnaphthalene
Mercury-400BB "m400"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 5995.2 Hz
16 repetitions
OBSERVE H1, 399.9480263 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 42 sec



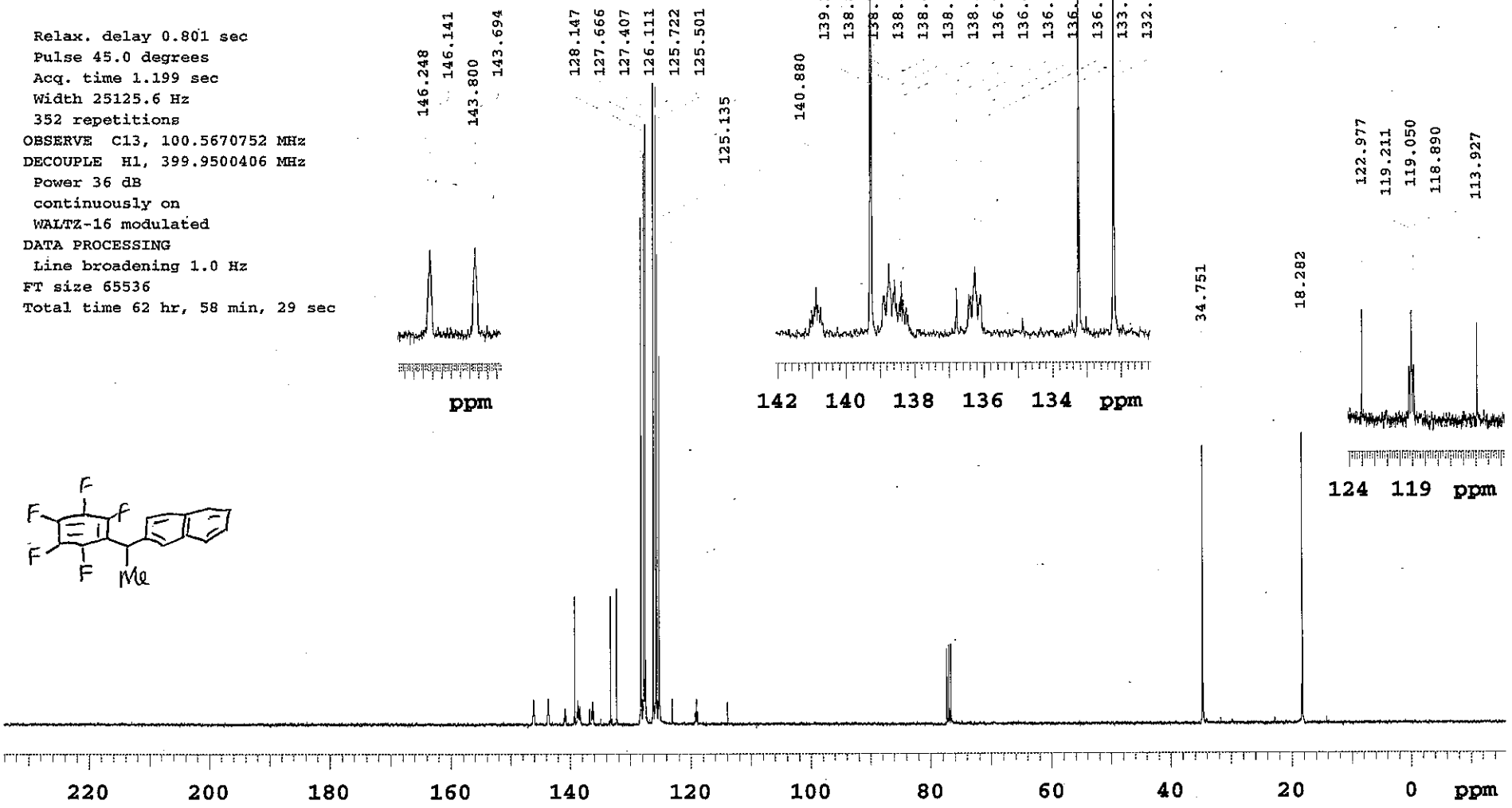
6

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDC13
Ambient temperature
File: 8627-02-141-5F-vinylnaphthalene-13C
Mercury-400BB "m400"

Relax. delay 0.801 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.6 Hz
352 repetitions
OBSERVE C13, 100.5670752 MHz
DECOUPLE H1, 399.9500406 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 62 hr, 58 min, 29 sec

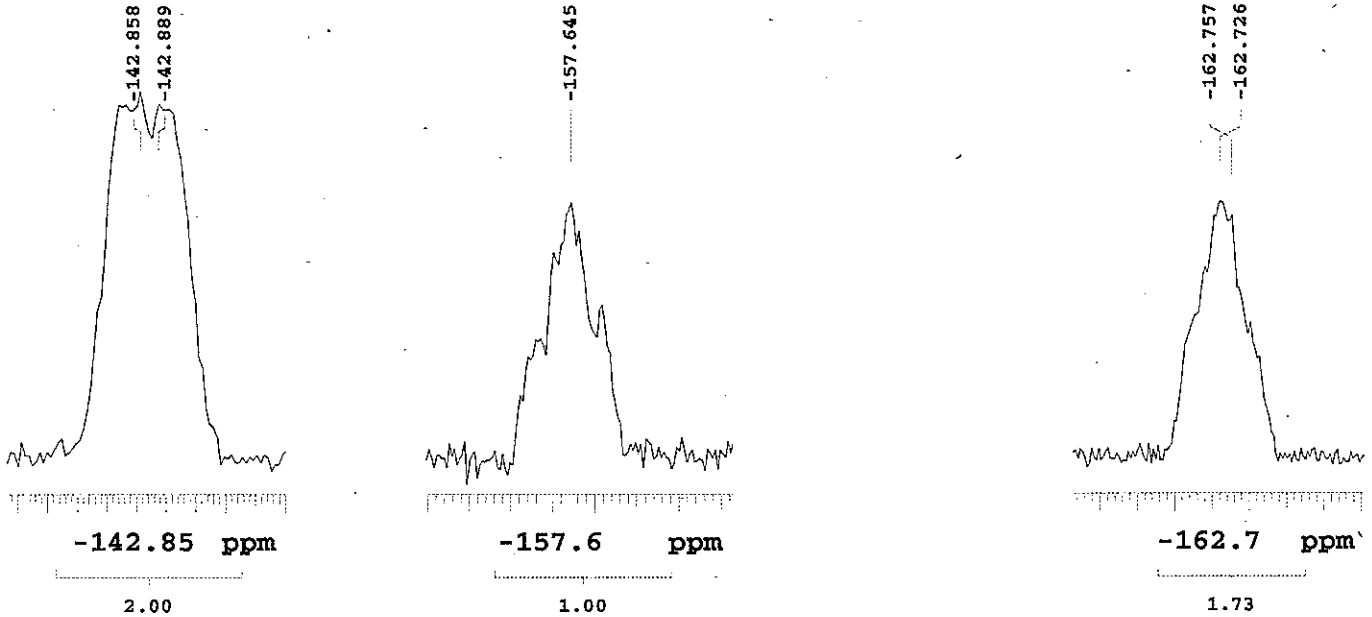


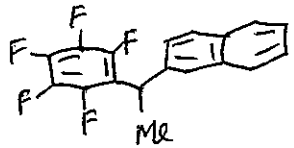
8627-88-02-141-column-fr1

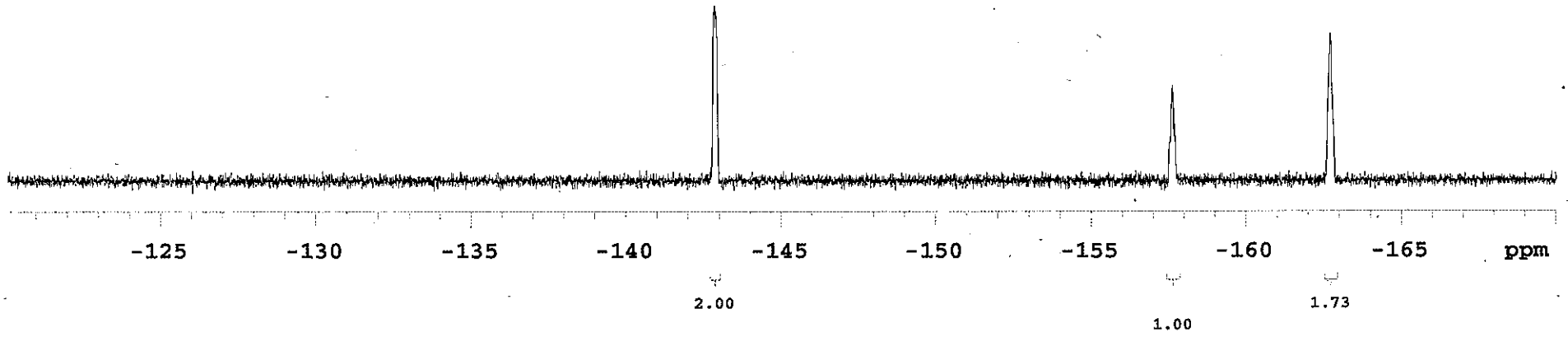
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: 8627-88-02-141-5F-vinylnaphthalene
Mercury-300BB "m300"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 14104.4 Hz
124 repetitions
OBSERVE F19, 282.2474836 MHz
DATA PROCESSING
FT size 16384
Total time 58 min, 30 sec



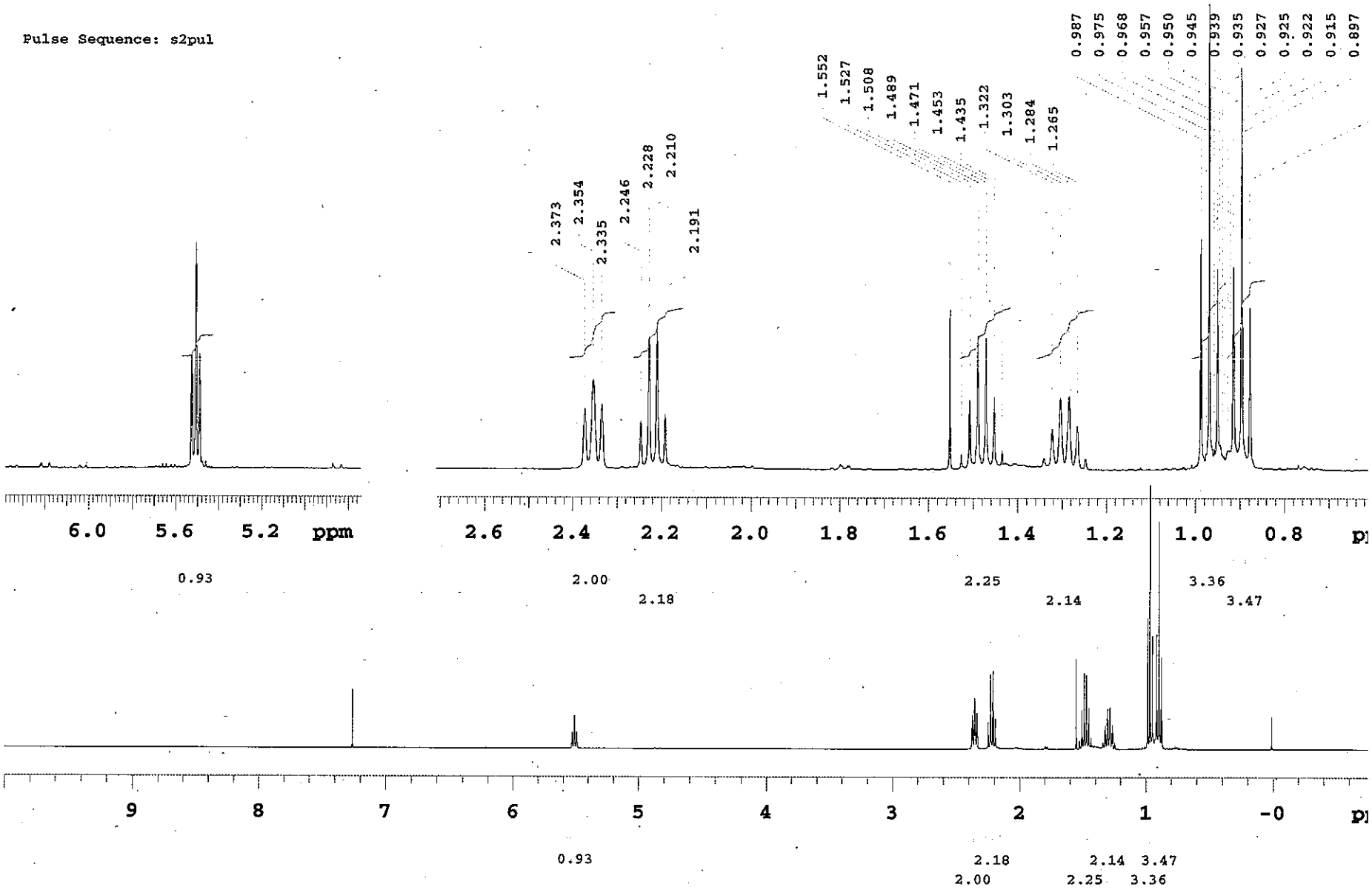


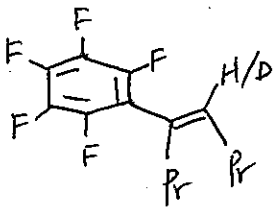


p151

STANDARD 1H OBSERVE

Pulse Sequence: s2pul





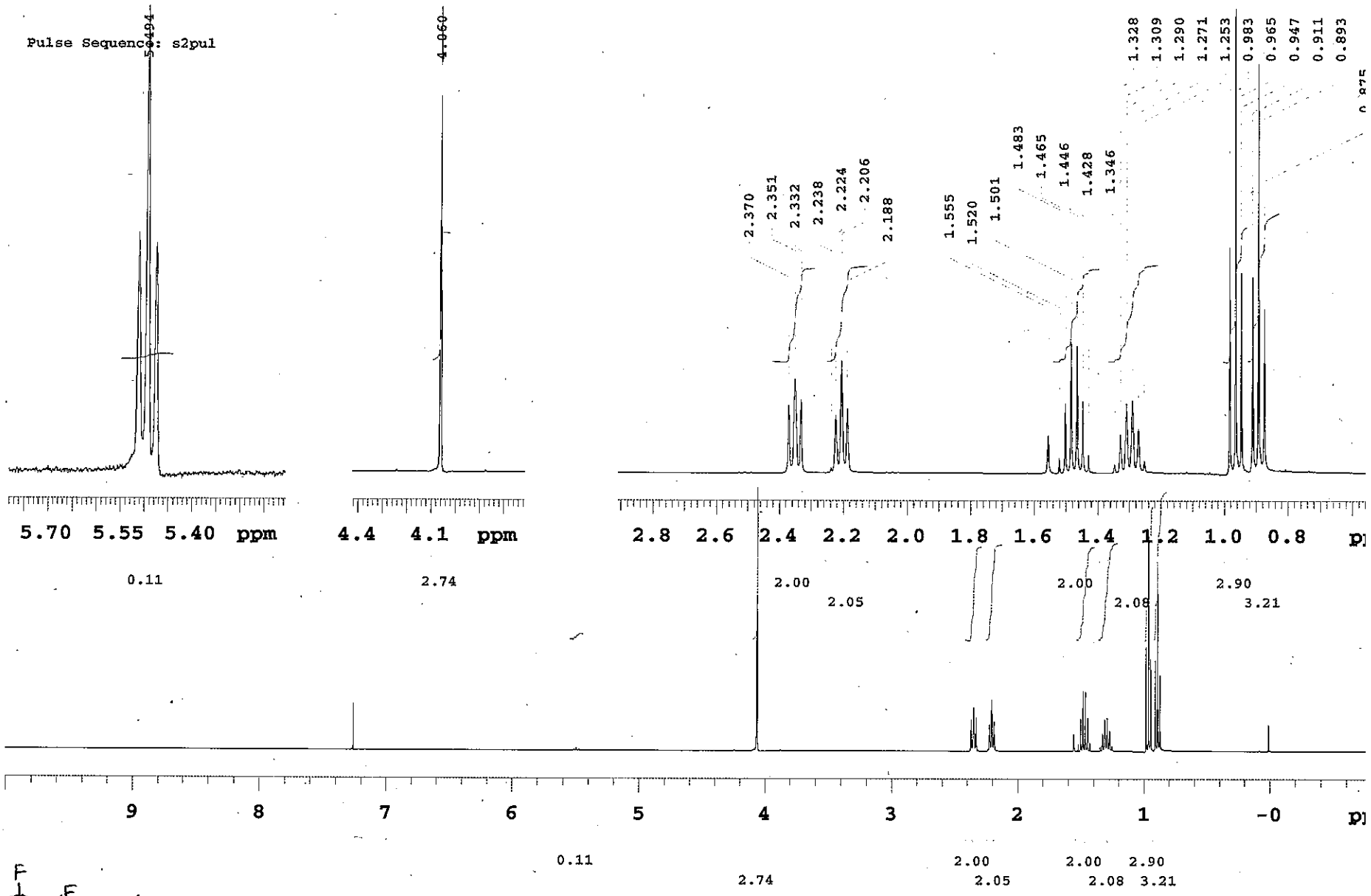
3aa, 7%D

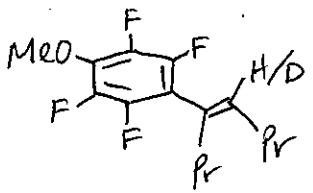
19.7 mg
35%.

p151

STANDARD 1H OBSERVE

Pulse Sequence: s2pul





3ja-d, 88% D

22.1 mg

38%