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Supporting Information

1-Phenyl-1,2,3,4,4-pentafluoro-1,3-butadiene (*E*-2a and *Z*-2a). Bp 55-58 °C (19 Torr). Analytical sample was purified by column chromatography on SiO_2 eluting with petroleum ether. Anal. Calcd for $C_{10}H_5F_5$: C, 54.56; H, 2.29. Found: C, 54.76; H, 2.24. MS (EI) *m/z* (relative intensity) [ion species]: 220 (69) $[M]^+$; 219 (19) $[M-1]^+$; 201 (19) $[M-F]^+$; 200 (37) $[M-HF]^+$; 170 (20) $[M-CF_2]^+$; 169 (62) $[M-CF_2H]^+$; 151 (100) $[M-CF_3]^+$; 75 (9) $[C_6H_3]^+$; 51 (10) $[CF_2H]^+$. λ_{max}, (nm) 261.8 ($\varepsilon = 0.88\times10^4$). IR ($cm^{-1}$): 1773 (s), 1687 (w), 1602 (vw). ^1H NMR (300 MHz) δ 7.4 (m, 3H, CHar), 7.69 (m, 2H, CHar).

1-(4-Tolyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (*E*-2b and *Z*-2b). Bp 49-52 °C (4 Torr). MS *m/z* 234 (47) $[M]^+$; 219 (100) $[M-CH_3]^+$; 213 (10) $[M-H_2F]^+$; 200 (9) $[M-CH_3F]^+$; 183 (9) $[M-CHF_2]^+$; 169 (66) $[M-CH_3-CF_2]^+$; 164 (17) $[M-CH_3-C_4H_9]^+$; 163 (19) $[M-CH_2F_3]^+$; 143 (5) $[M-CH_3C_6H_4]^+$; 133 (9); 116 (6); 99 (7); 91 (8, $C_7H_7^+$); 69 (9); 51 (7) $[CF_2H]^+$. IR 1776 (s), 1683 (m), 1612 (m). ^1H NMR (300 MHz) δ 2.42 (3H, CH_3), 7.28 (d, J = 9 Hz, 2H, CHar), 7.63 (d, J = 9 Hz, 2H, CHar).

1-(4-Methoxyphenyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (*E*-2c and *Z*-2c). Bp 85-88 °C (0.5 Torr). MS *m/z* 250 (100) $[M]^+$; 249 (21) $[M-1]^+$; 231 (41) $[M-F]^+$; 235 (7) $[M-CH_3]^+$; 230 (24) $[M-HF]^+$; 219 (43) $[M-CH_3O]^+$; 207 (16) $[C_9H_7OF_4]^+$; 200 (24) $[C_{10}H_4F_4]^+$; 187 (73) $[C_9H_6OF_3]^+$; 181 (35) $[M-CF_3]^+$; 169 (39) $[C_9H_4F_3]^+$; 157 (20) $[CH_3OC_6H_4CF_2]^+$; 156 (12) $[C_8H_3F_3]^+$; 138 (30) $[C_8H_7OF]^+$; 137 (16) $[C_8H_6OF]^+$; 81 (11) $[C_2F_3]^+$; 69 (12) $[CF_3]^+$; 51 (8) $[CF_2H]^+$. λ (nm), 276.9 ($\varepsilon = 2.13\times10^4$), 216.8 ($\varepsilon = 1.2\times10^4$). IR 1776 (s), 1682 (w), 1610 (s). ^1H NMR (300 MHz) δ 3.86 (3H, OCH_3), 6.97 (d, J = 8.5 Hz, 2H, CHar), 7.66 (d, J = 8.5 Hz, 2H, CHar).

1-(4-Cyclohexyloxyphenyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (*E*-2d and *Z*-2d). Purified by column chromatography on SiO_2 using heptane-benzene (8:1) eluent, R_F 0.72, colorless oil. MS *m/z* 319 (7) $[M+1]^+$; 318 (39) $[M]^+$; 236 (100) $[C_{10}H_5F_5O]^+$; 217 (36) $[HOC_6H_4C_4F_4]^+$; 216 (49) $[OC_6H_4C_4F_4]^+$; 188 (32) $[C_{13}H_{16}O]^+$; 187 (24) $[C_6H_{11}OC_6H_4C]^+$; 186 (18) $[C_{13}H_{14}O]^+$; 169 (26) $[C_9H_4F_3]^+$; 167 (57) $[C_{12}H_7O]^+$; 138 (18) $[C_8H_4F_2]^+$; 83 (89) $[C_6H_{11}]^+$; 81 (44) $[C_2F_3]^+$; 67 (56) $[C_5H_7]^+$; 55 (40) $[C_4H_7]^+$; 54 (21) $[C_4H_6]^+$; 53 (26) $[C_4H_5]^+$; 51 (9) $[CHF_2]^+$. λ_{max}, 281.8 ($\varepsilon = 2.43\times10^4$), 217.8 ($\varepsilon = 1.37\times10^4$). IR 1775 (m), 1682 (w), 1608 (s). ^1H NMR (300 MHz) δ 1.35-2.0 (m, 10H,

CH_2), 4.32 (tt, J = 8.9, 3.8 Hz, 1H, >CH-O), 6.95 (d, J = 8.9 Hz, 2H, CHar), 7.64 (d, J = 8.9 Hz, 2H, CHar).

1-(4-*N*,*N*-Dimethylaminophenyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (*E*-2e and *Z*-2e). Purified by column chromatography on SiO_2 using cyclohexane-benzene (1:1) eluent, R_F 0.69, mp 78 °C, yellow crystals. MS *m/z* 263 (100) $[M]^+$; 262 (38) $[M-1]^+$; 247 (7.5) $[M-CH_4]^+$; 244 (58) $[M-F]^+$; 243 (18) $[M-HF]^+$; 242 (20) $[M-H_2F]^+$; 228 (4.5) $[M-CH_4F]^+$; 219 (21) $[M-N(CH_3)_2]^+$; 212 (8) $[M-CHF_2]^+$; 200 (13) $[M-N(CH_3)_2F]^+$; 194 (7) $[M-CF_3]^+$; 178 (7) $[C_{10}H_6NF_2]^+$; 169 (37) $[C_9H_9NF]^+$; 151 (10) $[(CH_3)_2NC_6H_4CF]^+$; 132 (7.5) $[(CH_3)_2NC_6H_4C]^+$; 97 (14) $[C_6H_5F]^+$; 69 (8) $[CF_3]^+$. λ_{max}, 325 (ε = 2.6×10^4). IR 1775 (m), 1676 (w), 1610 (s). ^{1}H NMR (300 MHz) δ 3.03 (6H, NMe_2), 6.68 (d, J = 9 Hz, 2H, CHar), 7.59 (d, J = 9 Hz, 2H, CHar). ^{13}C {^{1}H} NMR δ 40.51, 112.07 (d, J = 2.4 Hz), 115.56 (dd, J = 23.8, 7.2 Hz), 120.80 (ddddd, C(3), J = 229.7, 51.4, 30.0, 25, 4.5 Hz), 128.17 (t, J = 8.3 Hz), 134.97 (ddddd, C(2), J = 231, 55.8, 24.7, 7, 4 Hz), 152.06 (d, J = 2 Hz), 152.38 (ddddd, C(1), J = 239, 42.3, 4.5, 2.5, 2.5 Hz), 154.00 (ddddd, C(4), J = 294, 284, 49, 6.8, 3 Hz).

1-(4-Bromophenyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (*E*-2f). (*Method B*). After vacuum column distillation fractions with different compositions were obtained. Fraction I, bp 84-86 °C (0.6 Torr) contained dibromobenzene (59 %) and **2f** as *E* isomer only (41 %, yield 11%). Analytical sample was purified by column chromatography on silicagel eluting with heptane, R_F 0.78. Fraction II, bp 160-185 °C (0.3 Torr) and the distillation residue contained 1,4-bis(4-bromophenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (**4a**) (1.5 g, 23 %). Anal. Calcd for $C_{10}H_4F_5Br$: C, 40.17; H, 1.35. Found: C, 40.35; H, 1.72. MS *m/z* 298, 300 (16) $[M]^+$; 247, 249 (3) $[M-CF_2H]^+$; 229, 231 (4) $[M-CF_3]^+$; 219 (100) $[M-Br]^+$; 200 (16) $[C_{10}H_4F_4]^+$; 169 (99) $[C_9H_4F_3]^+$; 150 (17) $[C_9H_4F_2]^+$; 149 (11) $[C_9H_3F_2]^+$; 93 (6) $[C_3F_3]^+$; 81 (6) $[C_2F_3]^+$; 75 (10) $[C_6H_3]^+$; 69 (6) $[CF_3]^+$; 50 (12) $[CF_2]^+$. λ_{max}, 272 ($\varepsilon = 2.25\times10^4$). IR 1770 (s), 1684 (w), 1590 (m). ^{1}H NMR (300 MHz) δ 7.62.

1-(4-Trifluoromethylphenyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (*E*-2g and *Z*-2g). This was prepared by *Method A*, yield 5 %, purity 58 % (*E*/*Z* = 87:13), Bp 62-65 °C (4 Torr); **2g** (9 % (*E*/*Z* = 91:9), purity 70 % by distillation) together with **4d** (yield 42 %) were also prepared by modified *Method B*: The solution of BuLi in hexane was added to 4-trifluoromethylbromobenzene (**1g**) in ether

at -70 °C.[22] The prepared ogranometallic was added by cannula in small portions to the solution of *F*-1,3-butadiene (1.2 equiv. in THF) at -70 °C for 30 min and stirred at -70 for 1.5h, allowed to warm to 0 °C and worked up as in method *A*. Analytical sample of **2g** was purified by column chromatography on SiO_2 eluting with petroleum ether. Anal. Calcd for $C_{11}H_4F_8$: C, 45.85; H, 1.40. Found: C, 46.25; H, 1.82. MS *m/z* 288 (15) $[M]^+$; 269 (14) $[M-F]^+$; 249 (8) $[M-HF-F]^+$; 237 (7); 219 (86) $[M-CF_3]^+$; 200 (14); 187 (11); 169 (100); 149 (7); 109 (5); 99 (10); 75 (9); 69 (20) $[CF_3]^+$. IR 1771 (m), 1734 (w), 1620 (w). λ_{max}, 270 ($\varepsilon = 1.85\times10^4$). ^{1}H NMR (300 MHz) δ 7.73 and 7.85 (AB system, 4H, J = 8.2 Hz).

(*E,E*)-1,4-Bis(4-trifluoromethylphenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (4d). This was separated from the distillation residue by crystallisation, Mp 111 °C (ethanol). Anal. Calcd for $C_{18}H_8F_{10}$: C, 52.19; H, 1.95. Found: C, 52.22; H, 2.35. MS *m/z* 414 (95) $[M]^+$; 395 (33) $[M-F]^+$; 345 (100) $[M-CF_3]^+$; 335 (42); 305 (41); 295 (44); 268 (74); 256 (53); 200 (39); 195 (41); 169 (23); 145 (45); 69 (52) $[CF_3]^+$. IR 1617 (w). ^{19}F NMR (470.3 MHz) δ -63.66 (6F), -142.61 and -157.75 (AA'XX' system, 4F). ^{1}H NMR (300 MHz) δ 7.75 and 7.90 (AB system, 4H, J = 8.5 Hz).

Tetrafluorobutadienylene-phenylene oligomers (*E,E*-3a-c) were prepared by the reaction of *p*-dibromobenzene (**1f**) (12 g, 0.05 mol) with Mg (2.4 g, 0.1 mol) in THF (50 mL) at 60 °C for 1.5 h, and further addition of *F*-1,3-butadiene (8 g, 0.05 mol) solution in THF (5 mL) (precooled by CO_2-ethanol mixture) at 5 °C. After being stirred for 2 h, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was worked up as in *Method A*. The insoluble deposit (0.6 g) was not analyzed. After rotary evaporation of the solvent, the remainder substance was crystallised from benzene-heptane mixture. By further fractional recrystallisation, different oligomers Br-$(C_6H_4C_4F_4)_n$-Br (**3a-c**) were obtained: **3a** ($n \approx$ 5-6, 0.1 g, 0.8 %, mp 99-131 °C, freon 113). Calcd for $(C_6H_4C_4F_4)_n$: C, 60.01; H, 2.02; F, 37.97. Found: C, 56.67; H, 2.47; F, 30.42; Br, 11.19. ^{19}F NMR (376.5 MHz) δ -158.8 (ddd, J = 130, 36, 13 Hz, ~2F), -157.5 (ddd, J = 129, 36, 13 Hz; ~2F), -153 to -160.5 (overlapping multiplets, ~6F), -144.3 (dm, J = 130 Hz, ~1F), -143.4 (ddd, J = 130, 33, 14 Hz, ~2F), -143.0 (dm, J = 130 Hz, ~2F), -142.3 (ddd, J = 130, 32, 13 Hz, ~2F), -140

(22) Trost, B. M.; Arndt, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 5288.

to -144 (overlapping multiplets, ~4F). ^{1}H NMR (400.1 MHz) δ 7.61, 7.64 (AB system, ~8H), 7.88 (s, ~4H), 7.4 - 7.88 (m, ~16H). **3b** (n ≈ 7-8, 0.15 g, 1.1 %, mp 144-163 °C, benzene). Found: C, 60.20; H, 2.47; F, 28.34; Br, 9.68. ^{19}F NMR and ^{1}H NMR data are similar to **3a** with higher intensity of broad multiplets. **3c** (n ≈ 10-11; 0.25 g, 2 %, mp >350 °C, insoluble in benzene). Found: C, 54.39; H, 2.37; F, 30.24; Br, 6.81.

(*E,E*)-1,4-Bis(4-bromophenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (4a). MS *m/z* 438, 436 (95), 434 $[M]^+$; 416 (2.5) $[M\text{-}HF]^+$; 357, 355 (65) $[M\text{-}Br]^+$; 307(18), 305 (18); 276 (100) $[M\text{-}Br_2]^+$; 256 (80) $[M\text{-}Br_2\text{-}HF]^+$; 225 (23); 207, 205 (21) $[BrC_6H_4CF_2]^+$; 200 (28) $[C_{10}H_4F_4]^+$; 138 (22) $[C_6H_4C_2F_2]^+$; 126 (16) $[C_6H_4CF_2]^+$; 107 (16) $[C_6H_4CF]^+$; 75 (21) $[C_6H_3]^+$; 51 (13) $[CHF_2]^+$.

(*E,E*) and (*E,Z*)-1,4-Bis(4-cyclohexyloxyphenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (4b). (*E,E*)-**4b**: MS *m/z* 476 (2) $[M+2]^+$; 475 (10) $[M+1]^+$; 474 (46) $[M]^+$; 392 (14) $[M\text{-}C_6H_{10}]^+$; 311 (19) $[M\text{-}C_6H_{10}\text{-}C_6H_9]^+$; 310 (100) $[M\text{-}C_6H_{10}\text{-}C_6H_{10}]^+$; 290 (14) $[M\text{-}C_6H_{10}\text{-}C_6H_{10}\text{-}HF]^+$; 261 (4) $[C_{16}H_{15}F_2O]^+$; 236 (6) $[C_{14}H_{14}F_2O]^+$; 217 (6) $[C_{10}H_5F_4O]^+$; 216 (7) $[C_{10}H_4F_4O]^+$; 186 (7) $[C_9H_5F_3O]^+$; 169 (3) $[C_9H_4F_3]^+$; 167 (3) $[C_9H_5F_2O]^+$; 143 (9) $[C_7H_5F_2O]^+$; 94 (9) $[C_6H_7O]^+$; 83 (15) $[C_2H_2F_3]^+$; 81(12) $[C_2F_3]^+$; 71 (10) $[C_5H_{11}]^+$; 69 (7) $[C_5H_9]^+$; 57 (12) $[C_4H_9]^+$; 55 (59) $[C_4H_7]^+$. IR 1634 (w), 1606 (s). (*E,Z*)-**4b**: ^{19}F NMR (75.4 MHz) δ -141.34 (ddd, F-1), -157.26 (ddd, F-2), -143.05 (ddd, F-3), -121.38 (ddd, F-4), J_{trans}(1-2) = 132.8, (1-3) 13.3, (1-4) 6.5, (2-3) 40.4, (2-4) 7, J_{cis} (3-4) = 18.5 Hz.

(*E*)-1-(4-Tolyl)-1,2,3-trifluoro-4-butylocta-1,3-diene (5c). MS *m/z* 310 (100) $[M]^+$; 290 (3) $[M\text{-}HF]^+$; 267 (15) $[M\text{-}C_3H_7]^+$; 253 (6) $[M\text{-}C_4H_9]^+$; 247 (6) $[M\text{-}C_3H_7]^+$; 225 (17) $[M\text{-}C_6H_{13}]^+$; 211 (44) $[M\text{-}C_7H_{15}]^+$; 205 (48) $[M\text{-}C_6H_{13}\text{-}HF]^+$; 191 (35) $[M\text{-}C_7H_{15}\text{-}HF]^+$; 183 (22); 164 (19); 161 (17); 141 (35) $[CH_3C_6H_4CF_2]^+$; 123 (21, $C_8H_8F^+$); 105 (16); 91 (8, $C_7H_7^+$). IR 2959 (s), 2929 (s), 2883 (s), 1665 (w), 1612 (w), 1514 (m), 1465 (s), 1380 (m), 1328 (w), 1277 (m), 1233 (m), 1210 (m), 1190 (m), 1137 (s), 1112 (s), 1065 (m), 820 (m). ^{19}F NMR (75.4 MHz) δ -121.56 (dd, 1F, F-3), -145.91 (dd, 1F, F-1), -151.44 (ddt, 1F, F-2), J_{FF}: (1-2) = 132, (2-3) = 35, (1-3) = 11, $^5J_{F(2)H}$ = 2.8 Hz. ^{1}H NMR (300 MHz) δ 0.88 (t, J = 7.3 Hz, 3H, CH_3), 0.94 (t, J = 7.1 Hz, 3H, CH_3), 1.22- 1.5 (m, 8H, CH_2), 2.06 (m, 2H, CH_2), 2.26 (m, 2H, CH_2), 2.39 (3H, Ar-C<u>H</u>$_3$), 7.25 (d, J = 8 Hz, 2H, CHar), 7.60 (d, J = 8 Hz, 2H, CHar).

(*E,E*)-1-(4-Tolyl)-1,2,3,4-tetrafluoroocta-1,3-diene (5a). GC/MS *m/z* 272 (77) $[M]^+$; 229 (100) $[M-C_3H_7]^+$; 215 (16) $[M-C_4H_9]^+$; 209 (48) $[M-C_3H_7-HF]^+$; 179 (30) $[M-HF-CH_4-C_4H_9]^+$; 164 (23) $[M-CHF_2-C_4H_9]^+$; 160 (23) $[M-2HF-CH_3-C_4H_9]^+$; 141 (9) $[C_7H_7CF_2]^+$; 133 (8); 119 (6) $[C_2F_2C_4H_9]^+$; 91 (5, $C_7H_7^+$); 65 (5, $C_2H_3F_2^+$) 51 (5, CHF_2^+). ^{19}F NMR (75.4 MHz) δ -144.27 (ddd, 1F, F-1), -159.64 (dddt, 1F, F-2), -165.15 (dddt, 1F, F-3), -135.4 (dddt, 1F, F-4); J_{FF}: (1-2) 122, (3-4) 126, (1-4) 26, (2-3) 33, (1-3) 9.5, (2-4) 10.4; J_{FH}: (4-H) 23, (3-H) 4.7, (2-H) 2.5 Hz. ^{1}H NMR (300 MHz) δ 0.96 (t, 3H, CH_3), 1.36- 1.66 (m, 4H, CH_2), 2.39 (3H, Ar-C$\underline{H}_3$), 2.52 (m, 2H, CH_2), 7.25 (d, J = 8 Hz, 2H, CHar), 7.61 (d, J = 8 Hz, 2H, Char).

(*Z,E*)-1-(4-Tolyl)-2,3,4-trifluoro-1-butylocta-1,3-diene (5b). ^{19}F NMR (75.4 MHz) δ -118.47 (ddt, 1F, F-2), -158.13 (ddm, 1F, F-3), -138.36 (ddt, 1F, F-4); J_{FF} (2-3) 37.2, (2-4) 13.3, (3-4) 132.3; J_{HF}: (4-H) 22.4, (2-H) 3.1 Hz. ^{1}H NMR (300 MHz) δ 0.79 (t, J = 7.1 Hz, 3H, CH_3), 0.87 (m, 3H, CH_3), 1.22- 1.36 (m, 8H, CH_2), 2.20 (dm, J = 23.1 Hz, 2H, CH_2), 2.33 (3H, Ar-C$\underline{H}_3$), 2.53 (m, 2H, CH_2), 6.98 (d, J = 8 Hz, 2H, CHar), 7.37 (d, J = 8.3 Hz, 2H, CHar).

(*E,E*)-1-(4-Tolyl)-4-phenyl-1,2,3,4-tetrafluoro-1,3-butadiene (6a). This was prepared from **1a** and **2b** (yield 19.6%, cryst. from methanol). Anal. Calcd for $C_{17}H_{12}F_4$: C, 69.86; H, 4.14. Found: C, 69.49; H, 4.08. IR 1668 (w), 1609 (w). ^{19}F NMR (376.5 MHz) ABXY system, δ -142.48 (m, 1F, F-1), -160.5 (m, 1F, F-2), -159.2 (m, 1F, F-3), -142.88 (m, 1F, F-4); J(1-2) ≈ (3-4) ≈ 128 Hz. ^{1}H NMR (300 MHz) δ 2.41 (3H, CH_3), 7.27 (d, J = 8 Hz, 2H, CHar), 7.46 (m, 3H, CHar), 7.66 (d, J = 8 Hz, 2H, CHar), 7.77 (dd, J = 8, 1 Hz, 2H, CHar).

(*E,E*)-1-(4-Methoxyphenyl)-4-phenyl-1,2,3,4-tetrafluoro-1,3-butadiene (6b). This was prepared from **1c** and **2a** (yield 35% based on **2a**, cryst. from methanol and ethanol). MS *m/z* 309 (6) $[M+1]^+$; 308 (29) $[M]^+$; 293 (15) $[M-CH_3]^+$; 288 (10) $[M-HF]^+$; 277 (5) $[M-CH_3O]^+$; 273 (4) $[M-HF-CH_3]^+$; 257 (8) $[M-HF-OCH_3]^+$; 214 (100) $[M-C_6H_3F]^+$; 200 (14) $[C_{10}H_4F_4]^+$; 199 (72) $[C_{10}H_3F_4]^+$; 139 (11) $[C_8H_8OF]^+$. ^{19}F NMR (376.5 MHz) δ -142.13 (ddd, 1F, F-1), -162.08 (ddd, 1F, F-2), -158.87 (ddd, 1F, F-3), -143.15 (ddd, 1F, F-4), J(1-2) = 129.5, (1-3) 12, (1-4) 31, (2-3) 36.2, (2-4) 11.5, (3-4) 130 Hz. ^{1}H NMR (300 MHz) δ 3.85 (3H, OCH_3), 6.96 (d, J = 8.5 Hz, 2H, CHar), 6.99 (m, 1H, CHar), 7.48 (d, J = 8.5 Hz, 2H, CHar), 7.46 (m, 2H, CHar), 7.75 (m, 2H, CHar).

(*E,E*)-1-(4-Methoxyphenyl)-4-(4-tolyl)-1,2,3,4-tetrafluoro-1,3-butadiene (6c). This was prepared from **1b** and **2c** (yield 25%, cryst. from methanol). MS 323 (20) $[M+1]^+$; 322 (100) $[M]^+$; 307 (24) $[M-CH_3]^+$; 302 (43) $[M-HF]^+$; 291 (12) $[M-CH_3O]^+$; 287 (13) $[M-HF-CH_3]^+$; 272 (18) $[M-HF-CH_3-CH_3]^+$; 256 (10) $[M-HF-CH_3-OCH_3]^+$; 231 (8) $[M-CH_3C_6H_4]^+$; 230 (10) $[M-CH_3C_6H_5]^+$; 214 (7) $[M-CH_3OC_6H_4]^+$; 161 (20) $[M/2]^+$; 141 (13) $[CH_3C_6H_4CF_2]^+$; 108 (10) $[C_7H_8O]^+$; 91 (13) $[C_7H_7]^+$; 81 (5) $[C_2F_3]^+$; 63 (13) $[C_2HF_2]^+$; 40 (10) $[H_2F_2]^+$. IR 1666 (m), 1643 (w), 1605 (s). ^{19}F NMR (75.4 MHz) ABXY system, δ -142.36 (m, 1F, F-1), -161.62 (m, 1F, F-2), -159.73 (m, 1F, F-3), -143.00 (m, 1F, F-4); *J* (1-2) = -129.9, (1-3) 12.1, (1-4) 30.9, (2-3) -36.7, (2-4) 12.6, (3-4) -130.2 Hz.[18] ^1H NMR (300 MHz) δ 2.42 (3H), 3.88 (3H), 6.99 (d, *J* = 9 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 7.66 (d, *J* = 8 Hz, 2H), 7.72 (d, *J* = 9 Hz, 2H).

(*E,E*)-1-(4-Cyclohexyloxyphenyl)-4-(4-tolyl)-1,2,3,4-tetrafluoro-1,3-butadiene (6d). This was prepared from **1b** and **2d** (yield 23%, cryst. from methanol). MS *m/z* 391 (10) $[M+1]^+$; 390 (41) $[M]^+$; 370 (2) $[M-HF]^+$; 308 (7) $[M-C_6H_{10}]^+$; 307 (20) $[M-C_6H_{11}]^+$; 293 (26) $[M-CH_3-C_6H_{10}]^+$; 288 (32) $[M-C_6H_{11}-F]^+$; 273 (8) $[M-F-CH_3-C_6H_{11}]^+$; 216 (12) $[C_{10}H_4F_4O]^+$; 143 (13) $[C_7H_5F_2O]^+$; 141 (8) $[C_8H_7F_2]^+$; 138 (8) $[C_8H_4F_2]^+$; 91 (8) $[C_7H_7]^+$; 83 (11) $[C_6H_{11}]^+$; 81 (10) $[C_6H_9]^+$; 55 (56) $[C_4H_7]^+$. IR 1664 (w), 1605 (s). ^{19}F NMR (376.5 MHz) δ -142.46 (ddd, F-1), -162.02 (ddd, F-2), -159.72 (ddd, F-3), -143.17 (ddd, F-4); *J* (1-2) = 129, (1-3) 11, (1-4) 31, (2-3) 37, (2-4) 11, (3-4) 129 Hz. ^1H NMR (400 MHz) δ 1.4- 2.0 (m, 10H, CH_2), 2.41 (3H, CH_3), 4.33 (tt, *J* = 8.9, 3.6 Hz, 1H, >CH-O), 6.96 (d, *J* = 9 Hz, 2H, CHar), 7.26 (d, *J* = 8.3 Hz, 2H, CHar), 7.65 (d, *J* = 8.3 Hz, 2H, CHar), 7.68 (d, *J* = 9 Hz, 2H, CHar).

(*E,E*), (*E,Z*), (*Z,E*)-1-(4-*N,N*-Dimethylaminophenyl)-4-(4-cyclohexyloxyphenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (6e). MS *m/z* 421 (5) $[M+2]^+$; 420 (25) $[M+1]^+$; 419 (100) $[M]^+$; 399 (1) $[M-HF]^+$; 381 (4) $[M-F-F]^+$; 338 (18) $[M-C_6H_9]^+$; 336 (72) $[M-C_6H_{11}]^+$; 317 (30) $[M-C_6H_{11}F]^+$; 299 (7) $[C_{18}H_{12}F_3N]^+$; 292 (14) $[M-C_6H_{11}-N(CH_3)_2]^+$; 273 (8) $[M-C_6H_{11}-N(CH_3)_2-F]^+$; 261 (15) $[C_{12}H_{11}F_4NO]^+$; 244 (7) $C_{12}H_{10}F_4N^+$; 225 (6) $[C_{12}H_{10}F_3N]^+$; 169 (6) $[C_9H_9F_2N]^+$; 143 (2) $[C_7H_5F_2O]^+$; 83 (8) $[C_6H_{11}]^+$; 57 (9) $[C_4H_9]^+$; 55 (37) $[C_4H_7]^+$. IR 1665 (w), 1645 (vw), 1608 (s). Other isomers (*E,Z* : *Z,E* = 4:3) remained in the mother liquor solution. **6e** (*E,Z* isomer): ^{19}F NMR (75.4 MHz) δ -141.7 (ddd, 1F, F-1), -159.78 (ddd, 1F, F-2), -142.05 (ddd, 1F, F-3), -121.65 (ddd, 1F, F-4), *J* (1-2)

= 134, (1-3) 15, (1-4) 8, (2-3) 39, (2-4) 7.5, (3-4) 21 Hz. **6e** (*Z,E* isomer): ^{19}F NMR (75.4 MHz) δ -122.85 (ddd, 1F, F-1), -145.43 (ddd, 1F, F-2), -156.73 (ddd, 1F, F-3), -142.1 (ddd, 1F, F-4), *J* (1-2) = 21, (1-3) 8, (1-4) 8, (2-3) 41, (2-4) 14, (3-4) 133 Hz.

1-(4-Bromophenyl)-4-(4-tolyl)-1,2,3,4-tetrafluoro-1,3-butadiene (*E,E*-6f). This was prepared by lithiation of **1f** with BuLi (see preparation of **2f** by *method B*) and further reaction with **2b** (19% yield, cryst. from methanol). Anal. Calcd for $C_{17}H_{11}F_4Br$: C, 55.01; H, 2.99. Found: C, 55.38; H, 3.22. MS *m/z* 372, 370 (100) $[M]^+$; 357, 355 (15) $[M\text{-}CH_3]^+$; 292 (9) $[M\text{-}Br+1]^+$; 291 (48) $[M\text{-}Br]^+$; 276 (28) $[M\text{-}Br\text{-}CH_3]^+$; 275 (12) $[M\text{-}HBr\text{-}CH_3]^+$; 272 (10) $[M\text{-}Br\text{-}F]^+$; 271 (32) $[M\text{-}Br\text{-}HF]^+$; 256 (54) $[M\text{-}Br\text{-}HF\text{-}CH_3]^+$; 255 (17) $[M\text{-}HBr\text{-}HF\text{-}CH_3]^+$; 251 (22) $[M\text{-}Br\text{-}2HF]^+$; 214 (18) $[C_{11}H_6F_4]^+$; 207, 205 (10) $[BrC_6H_4CF_2]^+$; 200 (14) $[C_{10}H_4F_4]^+$; 169 (10) $[C_9H_4F_3]^+$; 91 (20) $[C_7H_7]^+$; 65 (8) $[C_2H_3F_2]^+$; 51 (9) $[CHF_2]^+$. IR 1647 (w), 1626 (w), 1605 (w). ^{19}F NMR (75.4 MHz) ABXY system, δ -143.5 (m, 1F, F-1), -157.68 (m, 1F, F-2), -161.0 (m, 1F, F-3), -141.9 (m, 1F, F-4); *J* (1-2) ≈ 129, (3-4) ≈ 129 Hz. ^{1}H NMR (300 MHz) δ 2.42 (3H, CH_3), 7.28 (d, *J* = 8.5 Hz, 2H, CHar), 7.62 (m, 4H, CHar), 7.67 (d, *J* = 8.5 Hz, 2H, CHar).

(*E,E*)-1-(4-Cyclohexyloxyphenyl)-4-(4-bromophenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (6g). This was prepared from **1f** and **2d** (14% yield, dark yellow solid, cryst. from hexane). Anal. Calcd for $C_{22}H_{19}F_4BrO$: C, 58.04; H, 4.21. Found: C, 58.09; H, 4.21. MS *m/z* 456, 454 (69) $[M]^+$; 375 (16) $[M\text{-}Br]^+$; 374, 372 (89) $[M\text{-}C_6H_{10}]^+$; 354, 352 (22) $[M\text{-}HF\text{-}C_6H_{10}]^+$; 293 (100) $[M\text{-}C_6H_{10}\text{-}Br]^+$; 274 (26) $[M\text{-}F\text{-}Br\text{-}C_6H_{10}]^+$; 273 (58) $[M\text{-}HF\text{-}Br\text{-}C_6H_{10}]^+$; 256 (54) $[M\text{-}Br\text{-}HF\text{-}CH_3]^+$; 255 (16) $[C_{16}H_9F_2O]^+$; 245, 243 (47) $[C_{10}H_6BrF_2]^+$; 225 (46) $[C_{13}H_{15}F_2O]^+$; 216 (20) $[C_{10}H_4F_4O]^+$; 207, 205 (15) $[BrC_6H_4CF_2]^+$; 200 (9) $[C_{10}H_4F_4]^+$; 143 (14) $[HOC_6H_4CF_2]^+$; 83 (23) $[C_6H_{11}]^+$; 65 (10) $[C_2H_3F_2]^+$; 53 (6) $[C_4H_5]^+$. IR 1658 (w), 1604 (m). ^{19}F NMR (75.4 MHz) ABXY system, δ -141.58 (m, 1F, F-1), -162.89 (m, 1F, F-2), -157.27 (m, 1F, F-3), -143.84 (m, 1F, F-4), *J* (1-2) = -129.5, (1-3) 12.7, (1-4) 30.4, (2-3) -36.6, (2-4) 12.7, (3-4) -129.9 Hz[23] . ^{1}H NMR (300 MHz) δ 1.38-2.02 (m, 10H, $5CH_2$), 4.34 (m, 1H, CH), 6.97

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(23) Coupling constant values were obtained from simulated spectrum performed by "High resolution NMR spectra analysis" CALM version 2.00 (C) 1991 Resonance Co.

(d, J = 9 Hz, 2H, CHar), 7.60 and 7.63 (AB system, J = 9 Hz, 4H, CHar), 7.69 (d, J = 9 Hz, 2H, CHar).

(*E,E*)-1-(4-*N,N*-Dimethylaminophenyl)-4-(4-bromophenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (6h). This was prepared from **1f** and **2e** (29% yield, yellow crystals, cryst. from methanol). Mp 162 °C. Anal. Calcd for $C_{18}H_{14}BrF_4N$: C, 54.02; H, 3.53; N, 3.50. Found: C, 53.75; H, 3.64; N, 3.30. MS *m/z* 401, 399 (100) $[M]^+$; 381, 379 (16) $[M\text{-}HF]^+$; 380, 378 (20) $[M\text{-}H_2F]^+$; 356, 354 (4) $[M\text{-}N(CH_3)_2\text{-}1]^+$; 320 (8) $[M\text{-}Br]^+$; 301 (7) $[M\text{-}F\text{-}Br]^+$; 300 (7) $[M\text{-}HF\text{-}Br]^+$; 276 (22) $[M\text{-}Br\text{-}N(CH_3)_2]^+$; 256 (31) $[M\text{-}Br\text{-}HF\text{-}N(CH_3)_2]^+$; 244 (14) $[C_{12}H_{10}NF_4]^+$; 225 (8) $[C_{12}H_{10}NF_3]^+$; 200 (13) $[C_{10}H_4F_4]^+$; 169 (6) $[C_9H_4F_3]^+$; 119 (5) $[C_8H_9N]^+$; 107 (5) $[C_7H_4F]^+$; 51 (6) $[CHF_2]^+$. IR 1662 (w), 1603 (s). ^{19}F NMR (75.4 MHz) δ -142.19 (ddd, 1F, F-1), -165.43 (ddd, 1F, F-2), -156.53 (ddd, 1F, F-3), -144.58 (ddd, 1F, F-4); J (1-2) = 128, (1-3) 12.5, (1-4) 31, (2-3) 36.5, (2-4) 12.5, (3-4) 128 Hz. ^{1}H NMR (300 MHz) δ 3.03 (6H), 6.73 (d, J = 9 Hz, 2H), 7.6 (m, 6H).

(*E,E*)-1-(4-*N,N*-Dimethylaminophenyl)-4-(4-trifluoromethylphenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (6i). This was prepared from **1g** and **2e** (42 % yield, yellow crystals, from ethanol). Mp 181 °C. Anal. Calcd for $C_{19}H_{14}F_7N$: C, 58.62; H, 3.62; N, 3.60. Found: C, 58.28; H, 3.83; N, 3.53. IR 1663 (w), 1641 (w), 1604 (s). ^{19}F NMR (470.3 MHz) δ -63.54 (3F), -141.89 (ddd, 1F, J = 128.2, 33.6, 15.3 Hz), -145.27 (ddd, 1F, J = 131.2, 33.6, 15.3 Hz), -155.26 (ddd, 1F, J = 131.2, 36.6, 15.3 Hz), -166.43 (ddd, 1F, J = 128.2, 36.6, 15.3 Hz). ^{1}H NMR (300 MHz) δ 3.05 (6H), 6.74 (d, 2H, J = 8.8 Hz), 7.66 (d, 2H, J = 9.3 Hz), 7.71 and 7.88 (AB system, 4H, J = 8.2 Hz).

(*E,E,E*)-1-(4-Tolyl)-6-phenyl-1,2,3,4,5,6-hexafluoro-1,3,5-hexatriene (8a). This was prepared from **2a** and **7b** (33% yield, cryst. from methanol and recryst. from ethanol). MS *m/z* 355 (12) $[M+1]^+$; 354 (53) $[M]^+$; 339 (3) $[M\text{-}CH_3]^+$; 334 (4) $[M\text{-}HF]^+$; 319 (10) $[M\text{-}HF\text{-}CH_3]^+$; 177 (7) $[M/2]^+$; 141 (55) $[CH_3C_6H_4CF_2]^+$; 127 (42) $[C_6H_5CF_2]^+$; 119 (65) $[C_8H_4F]^+$; 91 (100) $[C_7H_7]^+$; 77 (15) $[C_6H_5]^+$; 65 (20) $[C_2H_3F_2]^+$; 63 (11) $[C_2HF_2]^+$; 51 (12) $[CHF_2]^+$. IR 1668 (m), 1608 (m). ^{19}F NMR (376.5 MHz) δ -140.80 (ddd, 2F, F-1), -163.81 (ddd, 1F, F-2), -149.21 (dddd, 2F, F-3), -149.81 (dddd, 1F, F-4), -162.63 (ddd, 1F, F-5), -141.02 (ddd, 1F, F-6); J (1-2) = 129, (1-3) 16, (1-4) 32, (2-3) 32; (2-4) 11, (3-4) 134, (3-5) 11, (3-6) 32, (4-5) 31, (4-6) 16, (5-6) 129 Hz. ^{1}H NMR (400 MHz) δ 2.39 (3H, CH_3), 7.28 (d, 2H, CHar), 7.47 (m, 3H, CHar), 7.66 (d, 2H, CHar), 7.76 (dd, J = 8, 2 Hz, 2H, CHar).

(*E,E,E*)-1-(4-Methoxyphenyl)-6-phenyl-1,2,3,4,5,6-hexafluoro-1,3,5-hexatriene (8b). This was prepared from **2c** and **7a** (yield 32.5%, cryst. from methanol). Anal. Calcd for $C_{19}H_{12}F_6O$: C, 61.63; H, 3.27. Found: C, 61.27; H, 3.43. MS *m/z* 371 (22) $[M+1]^+$; 370 (100) $[M]^+$; 350 (13) $[M-HF]^+$; 330 (4) $[M-2HF]^+$; 319 (11) $[M-HF-OCH_3]^+$; 261 (13) $[C_{12}H_3F_6]^+$; 256 (8) $[C_{13}H_8F_4O]^+$; 243 (17) $[C_{12}H_7F_4O]^+$; 231 (9) $[CH_3OC_6H_4C_4F_4]^+$; 200 (6) $[C_6H_4C_4F_4]^+$; 185 (20) $[M/2]^+$; 169 (9) $[C_9H_7F_2O]^+$; 157 (77) $[CH_3OC_6H_4CF_2]^+$; 127 (45) $[C_6H_5CF_2]^+$; 77 (8) $[C_6H_5]^+$; 63 (10) $[C_2HF_2]^+$; 51 (5) $[CHF_2]^+$. IR 1669 (m), 1604 (s). ^{19}F NMR (75.4 MHz) ABMNXY system, δ -140.35 (m, 2F, F-1), -165.42 (m, 1F, F-2), -148.68 (m, 2F, F-3), -150.35 (m, 1F, F-4), -162.45 (m, 1F, F-5), -141.1 (m, 1F, F-6); *J* (1-2) = 128, (3-4) 133, (5-6) 129 Hz. ^1H NMR (300 MHz) δ 3.91 (3H, OCH_3), 7.05 (d, *J* = 9 Hz, 2H, CHar), 7.5 (m, 3H, CHar), 7.75 (d, *J* = 9 Hz, 2H, CHar), 7.78 (m, 2H, CHar).

(*E,E,E*)-1-(4-Methoxyphenyl)-6-(4-tolyl)-1,2,3,4,5,6-hexafluoro-1,3,5-hexatriene (8c). This was prepared from **2c** and **7b** (yield 12%, cryst. from methanol). MS *m/z* 385 (1) $[M+1]^+$; 385 (4, M^+); 370 (1) $[M-CH_2]^+$; 364 (1) $[M-HF]^+$; 349 (0.5) $[M-HF-CH_3]^+$; 288 (88) $[C_{14}H_9F_5O]^+$; 268 (10) $[C_{14}H_8F_4O]^+$; 245 (100) $[C_{12}H_6F_5]^+$; 231 (32) $[CH_3OC_6H_4C_4F_4]^+$; 225 (22) $[C_{12}H_5F_4]^+$; 195 (24) $[C_{11}H_6F_3]^+$; 180 (18) $[C_{10}H_3F_3]^+$; 157 (20) $[CH_3OC_6H_4CF_2]^+$; 151 (12) $[C_9H_8FO]^+$; 139 (17) $[C_8H_5F_2]^+$; 108 (6) $[C_7H_8O]^+$; 63 (8) $[C_2HF_2]^+$; 55 (8) $[C_3F]^+$. IR 1672 (m), 1606 (s). ^{19}F NMR (75.4 MHz) ABMNXY system, δ -140.79 (m, 2F, F-1 and F-6), -165.22 (m, 1F, F-2), -149.62 (m, 2F, F-3 and F-4), -163.5 (m, 1F, F-5). ^1H NMR (300 MHz) δ 2.42 (3H, CH_3), 3.88 (3H, OCH_3), 6.99 (d, *J* = 9 Hz, 2H, CHar), 7.29 (d, *J* = 8 Hz, 2H, CHar), 7.66 (d, *J* = 8 Hz, 2H, CHar), 7.72 (d, *J* = 9 Hz, 2H, CHar).

(*E,E,E*)-1-(4-Cyclohexyloxyphenyl)-6-(4-tolyl)-1,2,3,4,5,6-hexafluoro-1,3,5-hexatriene (8d). MS *m/z* 452 (47) $[M]^+$; 370 (81) $[M-C_6H_{10}]^+$; 356 (9) $[M-C_6H_{10}-CH_2]^+$; 350 (10) $[M-C_6H_{10}-HF]^+$; 335 (9) $[M-C_6H_{10}-HF-CH_3]^+$; 330 (6) $[M-C_6H_{10}-2HF]^+$; 315 (7) $[M-C_6H_{10}-2HF-CH_3]^+$; 268 (43) $[C_{15}H_{15}F_3O]^+$; 238 (16) $[C_{13}H_6F_4]^+$; 215 (9) $[C_{11}H_7F_4]^+$; 143 (93) $[HOC_6H_4CF_2]^+$; 141 (68) $[CH_3C_6H_4CF_2]^+$; 83 (19) $[C_6H_{11}]^+$; 55 (100) $[C_4H_7]^+$. IR 1675 (m), 1637 (w), 1606 (s). ^{19}F NMR (376.5 MHz) δ -141.49 (ddd, 1F, F-1), -168.19 (ddd, 1F, F-2), -149.29 (dddd, 1F, F-3), -150.75 (dddd, 1F, F-4), -164.96 (ddd, 1F, F-5), -141.31 (ddd, 1F, F-6), *J* (1-2) = 127, (1-3) 15.5, (1-4) 31.5, (2-3) 35, (2-4) 14.5, (3-4) 134.5, (3-5) 14.5, (3-6) 31, (4-5) 34.5, (4-6)15, (5-6) 129 Hz.

(*E,E,E*) and (*E,Z,E*)-1-(4-*N,N*-Dimethylaminophenyl)-6-(4-cyclohexyloxyphenyl)-1,2,3,4,5,6-hexafluoro-1,3,5-hexatriene (8e). This was prepared from **2d** and **7c**. The crude semicrystalline product was washed with heptane. Purification of the crude product by column chromatography on silica eluting with heptane-benzene (2:1) gave yellow solid of **8e** as a mixture of major *E,E,E* and *E,Z,E* isomers (5:1). **8e** (*E,E,E* isomer, 13%, recryst. from hexane): Anal. Calcd for $C_{26}H_{25}F_6NO$: C, 64.86; H, 5.23; N, 2.91. Found: C, 64.60; H, 5.24; N, 2.84. MS *m/z* 482 (20) $[M+1]^+$; 481 (100) $[M]^+$; 461 (2) $[M-HF]^+$; 452 (1) $[M-C_2H_5]^+$; 399 (56) $[M-C_6H_{10}]^+$; 379 (24) $[M-C_6H_{10}-HF]^+$; 335 (4) $[M-C_6H_{10}-HF-N(CH_3)_2]^+$; 256 (8) $[C_{13}H_{10}F_4N]^+$; 244 (12) $[C_{12}H_{10}F_4N]^+$; 200 (18) $[C_{10}H_4F_4]^+$; 170 (28) $[C_9H_{10}F_2N]^+$; 143 (12) $[C_7H_5F_2O]^+$; 97 (9) $[C_6H_9O]^+$; 83 (17) $[C_6H_{11}]^+$; 71 (14) $[C_5H_{11}]^+$; 57 (48) $[C_4H_9]^+$; 55 (55) $[C_4H_7]^+$. IR 1665 (m), 1608 (s). ^{19}F NMR (376.5 MHz) δ -141.17 (ddd, F-1), -165.62 (ddd, F-2), -149.27 (dddd, F-3), -150.09 (dddd, F-4), -163.47 (ddd, F-5), -140.66 (ddd, F-6); *J* (1-2) = 128.5, (1-3) 15.5, (1-4) 32.5, (2-3) 32, (2-4) 12, (3-4) 134, (3-5) 12.3, (3-6) 32, (4-5) 32.5, (4-6) 15.5, (5-6) 129 Hz. ^1H NMR (300 MHz) δ 1.37- 2.0 (m, 10H), 3.01 (6H), 4.31 (m, 1H), 6.72 (d, *J* = 9 Hz, 2H), 6.9 (d, *J* = 9 Hz, 2H), 7.56 (d, *J* = 9 Hz, 2H), 7.58 (d, *J* = 9 Hz, 2H). **8e** (*E,Z,E* isomer): ^{19}F NMR (376.5 MHz, acetone-d_6) δ -139.92 (ddd, F-1), -166.65 (dd, F-2), -135.71 (dddd, F-3) -137.89 (dddd, F-4), -163.25 (dd, F-5), -140.54 (ddd, F-6); *J* (1-2) = 129, (1-3) 16.3, (1-4) 7.5, (2-3) 39, (3-4) ~15, (3-6) 7.7, (4-5) 38, (4-6) 16.7, (5-6) 128 Hz.

(*E,E*)-1-(4-Hydroxyphenyl)-4-(4-tolyl)-1,2,3,4-tetrafluoro-1,3-butadiene (9). IR 3591 (m) (O-H), 1669 (w), 1611 (s). ^{19}F NMR (75.4 MHz) ABXY system, δ -142.2 (m, 1F, F-1), -161.52 (m, 1F, F-2), -159.83 (m, 1F, F-3), -143.10 (m, 1F, F-4).

(*E,E*)-1-(4-Carboxyphenyl)-4-(4-cyclohexyloxyphenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (10a). Crystallised from benzene. Anal. Calcd for $C_{23}H_{20}F_4O_3$: C, 65.71; H, 4.80. Found: C, 65.60; H, 5.04. IR 2938, 2858, 2866, 2547, 1686, 1603, 1569, 1510, 1454, 1426, 1295, 1249, 1179, 1149, 1118, 1051, 1020, 968, 952, 892, 863, 836, 811, 763, 699, 642. ^{19}F NMR (75.4 MHz) δ -144.17 (ddd, F-1), -154.93 (ddd, F-2), -163.52 (ddd, F-3), -140.87 (ddd, F-4); *J* (1-2) = 128, (1-3) 13, (1-4) 32, (2-3) 37, (2-4) 13, (3-4) 129 Hz. ^1H NMR (300 MHz, acetone-d_6) δ 1.37- 2.0 (m, 10H), 4.51 (tt, *J* = 8, 3.7 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 8.21 (d, *J* = 8.3 Hz, 2H).

(*E,E*)-1-(4-*N,N*-Dimethylaminophenyl)-4-(4-carboxyphenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (10b). Mp 113 °C. (ethanol). IR ($CHCl_3$) 2954, 2928, 2859, 1727, 1667, 1651, 1610, 1527, 1447, 1368, 1276, 1140, 1057, 940, 821. ^{19}F NMR (75.4 MHz) ABXY system, δ -142.48 (m, F-1), -164.56 (m, F-2), -157.73 (m, F-3), -143.68 (m, F-4). *J* (1-2) = -128.7, (1-3) 12.6, (1-4) 30.8, (2-3) -37.3, (2-4) 13.0, (3-4) -130.8 Hz[18]. ^1H NMR (300 MHz) δ 3.03 (6H), 6.73 (d, *J* = 8.8 Hz), 7.41 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8 Hz, 2H).

(*E,E*)-1-(4-Formylphenyl)-4-(4-cyclohexyloxyphenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (11). Compound **6g** (120 mg, 0.264 mmol) was dissolved in 20 mL of dry ether, cooled to -75 °C and BuLi (0.3 mL, 1.7 M in hexane) was slowly added by syringe. The mixture was stirred for 1.5 h. Then 20.5 μL of DMF in 1 mL of ether was added, stirred for 1 h and allowed to warm to +15 °C. The reaction mixture was worked up with a 5% solution of HCl, extracted with ether, washed with a $NaHCO_3$ solution and with water. The ethereal layer was dried over $MgSO_4$. After evaporation of solvent, 70 mg (66 %) of **11** were isolated. IR 2937, 2857, 1704 (CH=O), 1674, 1605, 1570, 1510, 1451, 1373, 1311, 1278, 1256, 1214, 1179, 1144, 1114, 1077, 1047, 1021, 968, 912, 834, 767, 734. ^{19}F NMR (75.4 MHz) δ -144.07 (ddd, F-1), -154.41 (ddd, F-2), -163.68 (ddd, F-3), -140.07 (ddd, F-4); *J* (1-2) 129, (1-3) 13, (1-4) 32.5, (2-3) 36, (2-4) 13, (3-4) 128 Hz. ^1H NMR (300 MHz) δ 1.37- 2.02 (m, 10H), 4.34 (m, 1H), 6.97 (d, *J* = 9 Hz, 2H), 7.69 (d, *J* = 9 Hz, 2H), 7.92 and 7.95 (AB system, 4H).

(*E,E*)-1,4-Bis(4-methoxycarbonylphenyl)-1,2,3,4-tetrafluoro-1,3-butadiene (12). CH_2N_2 in 10 mL of ether was added to opaque mixture of **10c** (30 mg) in THF (10 mL). The mixture became transparent. After 20 min the solvent was removed by rotary evaporation and a pale yellow precipitate was purified by TLC on silicagel, eluting with $CHCl_3$ to obtain **12** (R_F 0.65, 14 mg, 43%) colorless precipitate, mp 179-180 °C (182-184 °C).[5] ^{19}F NMR (75.4 MHz) AA'XX' system, δ -142.26 (m, *J* ≈ 129 Hz), -157.12 (m, *J* ≈ 129 Hz). ^1H NMR (300 MHz) δ 3.96 (6H), 7.86 (d, *J* = 8.7 Hz, 4H), 8.14 (d, *J* = 8.6 Hz, 4H).

S1

Table 2. ^{19}F NMR Data of 1-Aryl-1,2,3,4,4-pentafluoro-1,3-butadienes (*E* and *Z* 2a-g).

Comp.		^{19}F NMR Chemical shifts [a]					Coupling constants J_{FF} (Hz)									
R		a	b	c	d	e	a-b	c-e	a-e	b-c	a-c	a-d	b-d	b-e	c-d	d-e
2a	*E*	-142.8	-159.63[b]	-181.0	-95.02[d]	-106.9	133	116	21.5	35.5	11	5.5	3	12.5	29	50.5
H	*Z*	-116.71[c]	-141.5	-175.43[b]	-93.0[d]	-107.5[b]	14.8	118	3	36	5	[e]	4.5	15	28	45.5
2b	*E*	-142.6	-160.53	-180.53	-95.57[d]	-107.39	133	116	21	35.4	11	5	3	12	30.5	50
CH_3	*Z*	-116.34[c]	-142.5[b]	-175.0	-93.5[d]	-107.6[b]	13.5	117	[e]	35.4	[e]	[e]	[e]	[e]	27	46.5
2c	*E*	-142.22	-162.11	-180.0	-95.78	-107.6	132	116	20	35.4	11	6	4	13	28.5	51
OCH_3	*Z*	-115.33[c]	-143.47	-174.77	-93.7	-107.77	16.5	118	2.8	33	6.5	3	5	16.5	28	46
2d	*E*	-142.22	-162.3	-179.87	-96.02	-107.79	133	116	21	35	10.5	6	4	13	28.5	51
OC_6H_{11}	*Z*	-115.39[c]	-143.55	-174.57	-93.87	-107.8	16	117	[e]	34	6.5	3	5	[e]	27.5	47
2e	*E*	-142.84	-164.59	-178.61	-96.88	-108.4	132	116	20	35	9	5	3.5	13	27	53
$N(CH_3)_2$	*Z*	-115.83[b]	-145.87	-173.79	-94.63	-108.1[b]	18	118	[e]	35.5	7	3	5	[e]	27	47
2f	*E*	-143.43	-158.3	-181.41	-94.43	-106.52	132	116	22	35	12	6	4	13	29.5	48
Br	*Z*	-117.51[b]	-140.08	-175.71	-92.36	-107.2	15.5	118	3	36	4	3	4	15.5	28.5	44
2g[f]	*E*	-144.06	-157.10	-182.33	-93.71	-105.87	132	116.0	23	36	12.2	6.0	5.5	12.5	27.5	49.5
CF_3	*Z*	-118.67[b]	-138.51	-176.44	-91.57	-106.87	17	118.8	3.5	36.4	5.5	4	3.5	15	28	43

[a] See Figure 1 for nuclei labelling; multiplicity of signals: dddd if not otherwise indicated; [b] ddd; [c] dm; [d] ddm; [e] unresolved constants; [f] δ (CF_3) = -63.71 ppm.

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Table 3. Parameters of Regression Equations 1 and 2: ^{19}F NMR Chemical Shifts of *p*-Substituted 1-Aryl-1,2,3,4,4-pentafluoro-1,3-butadienes (*E* and *Z* 2a-c,e-g) versus Hammet *p*-Substituent Constants σ_p[a].

Core[f]	Isomer	Nuclei[b]	δ°	ρ	*r*[c]	*s*[d]	*N*[e]
			δF (σ_p), equation 1				
p-C_6H_4-CF=CX-$\underline{F}_b$	*E*	b	-160.09	6.535	0.988	0.461	6
p-C_6H_4-CF=CX-$\underline{F}_b$	*Z*	b	-141.71	6.335	0.998	0.164	6
p-C_6H_4-CF=CF-CY-$\underline{F}_c$	*E*	c	-180.78	-3.090	0.989	0.210	6
p-C_6H_4-CF=CF-CY-$\underline{F}_c$	*Z*	c	-175.29	-2.192	0.991	0.128	6
p-C_6H_4-(CF=CF)$_2$-$\underline{F}_e$	*E*	e	-107.02	2.162	0.997	0.077	6
p-C_6H_4-(CF=CF)$_2$-$\underline{F}_d$	*E*	d	-95.11	2.709	0.998	0.084	6
p-C_6H_4-(CF=CF)$_2$-$\underline{F}_e$	*Z*	e	-107.46	1.055	0.998	0.030	6
p-C_6H_4-(CF=CF)$_2$-$\underline{F}_d$	*Z*	d	-93.01	2.625	0.998	0.074	6
			ΔδF (σ_p), equation 2				
p-C_6H_4-C$\underline{F}_a$=C$\underline{F}_b$-X	*E*	b-a	-17.05	7.793	0.994	0.390	6
p-C_6H_4-C$\underline{F}_a$=C$\underline{F}_b$-X	*Z*	b-a	-24.87	9.033	0.994	0.471	6
Ar-CF=CF-C$\underline{F}_c$=C$\underline{F}_e$F	*E*	e-c	73.76	5.252	0.994	0.256	6
Ar-CF=CF-C$\underline{F}_c$=C$\underline{F}_d$F	*E*	d-c	85.58	6.264	0.988	0.455	6
Ar-CF=CF-C$\underline{F}_c$=C$\underline{F}_e$F	*Z*	e-c	67.82	3.247	0.997	0.115	6
Ar-CF=CF-C$\underline{F}_c$=C$\underline{F}_d$F	*Z*	d-c	82.27	4.817	0.998	0.153	6

[a] The following values were used for σ_p Hammet substituent constants:[11] -CF_3, 0.53; -Br, 0.26; -CH_3, -0.14; -OCH_3, -0.28; -$N(CH_3)_2$, -0.63; [b] See Figure 1 for nuclei labelling; [c] Correlation coefficient; [d] Standard deviation; [e] Number of substituents in the regression analysis; [f] X: –CF=CF_2, Y: =CF_2.

S3

Table 4. The ρ_x/ρ_y Relationships for 1-Aryl-1,2,3,4,4-pentafluoro-1,3-butadienes (2a-c,e-g).

Isomer	ρ_b/ρ_e	ρ_b/ρ_d	ρ_{b-a}/ρ_{e-c}	ρ_{b-a}/ρ_{d-c}
E	3.02	2.41	1.48	1.24
Z	6.00	2.41	2.78	1.88

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Table 5. Absorbtion Maxima* of (*E,E*)-1,4-Diaryl-1,2,3,4-tetrafluoro-1,3-butadienes (6a-i, 10a,b, 4a-d) and (*E,E,E*)-1,6-Diaryl-1,2,3,4,5,6-hexafluoro-1,3,5-hexatrienes (8a-e)

R-C_6H_4-$(CF=CF)_n$-C_6H_4-R'

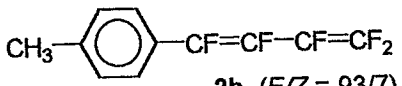
			λ_{max}, nm ($\varepsilon\times10^4$)	
	R	R'	n = 2	n = 3
6a, 8a	CH_3	H	296 (3.4)	315 (2.03)
6b, 8b	CH_3O	H	312 (2.1)	334 (4.3)
6c, 8c	CH_3O	CH_3	308 (3.3)	322 (3.7)
6d, 8d	$C_6H_{11}O$	CH_3	315 (3.25)	334 (3.8)
6e, 8e	$(CH_3)_2N$	OC_6H_{11}	348 (4.3)	372 (3.6)
6f	Br	CH_3	311 (3.5)	-
6g	$C_6H_{11}O$	Br	320 (4.2)	-
6h	$(CH_3)_2N$	Br	360 (3.7)	-
6i	$(CH_3)_2N$	CF_3	369 (3.45)	-
10a	HOOC	OC_6H_{11}	330 (2.8)	-
10b	HOOC	$N(CH_3)_2$	351 (2.4)	-
4a	Br	Br	313 (5.7)	-
4b	$C_6H_{11}O$	OC_6H_{11}	321 (4.19)	-
4c	CH_3	CH_3	304 (2.19)	-
4d	CF_3	CF_3	306 (3.02)	-

* Dioxane solution

As follows Figures 5-21 containing copies of ^{1}H NMR spectra for compounds, which identity and purity were established using spectroscopic data.

List of Figures: Figure 5: **2b**; Figure 6: **2c**; Figure 7: **2d**; Figure 8: **2e**; Figure 9: **5c**; Figure 10: **5a**; Figure 11: **5b**; Figure 12: **6b**; Figure 13: **6c**; Figure 14: **6d**; Figure 15: **6h**; Figure 16: **8a**; Figure 17: **8c**; Figure 18: **4a**; Figure 19: **9**; Figure 20: **10b**; Figure 21: **11**.

Figure 5: ^{1}H NMR spectrum of **2b.**



2b, (*E*/*Z* = 93/7)

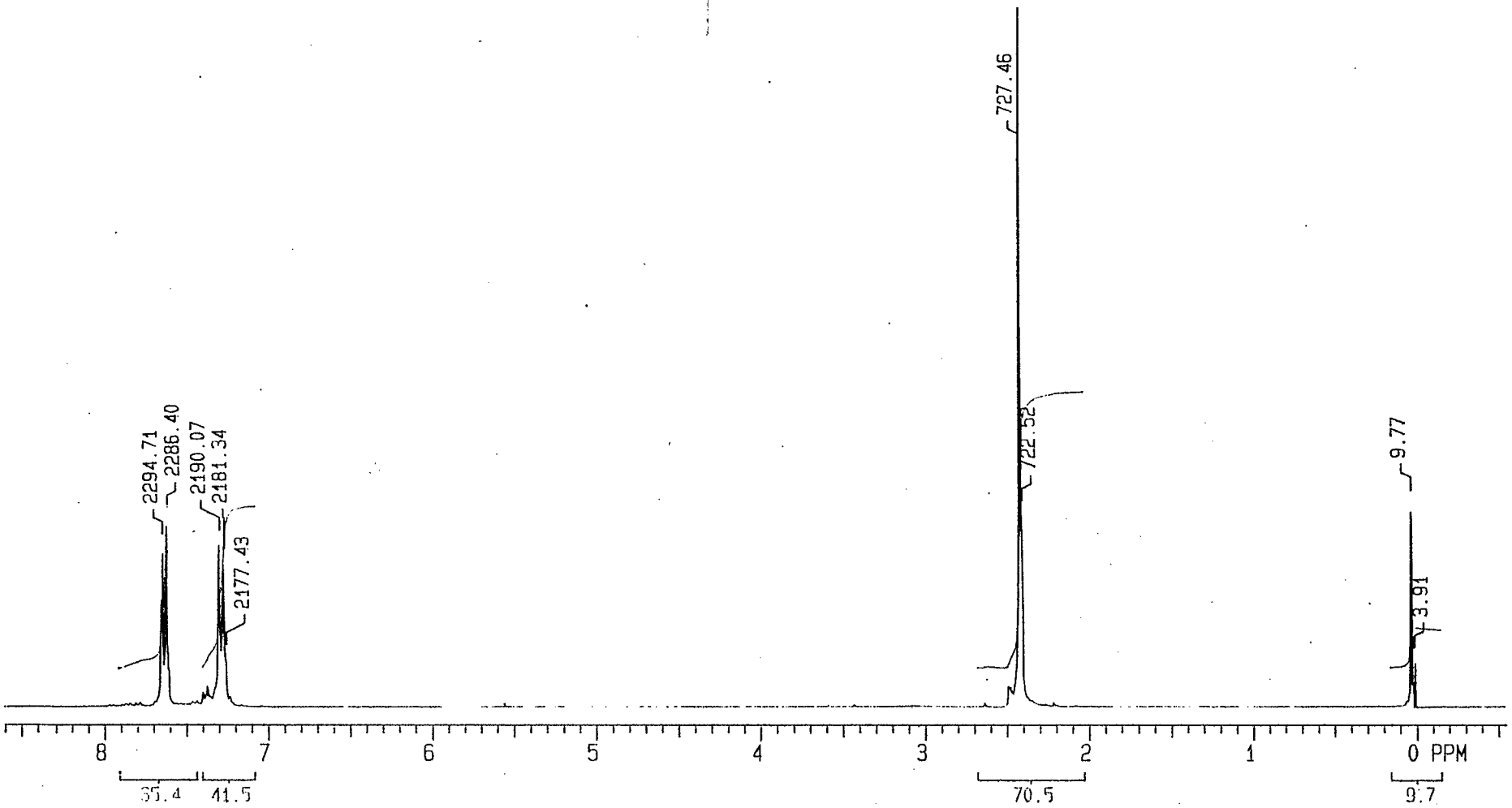
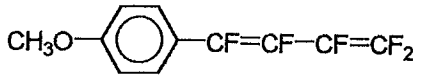
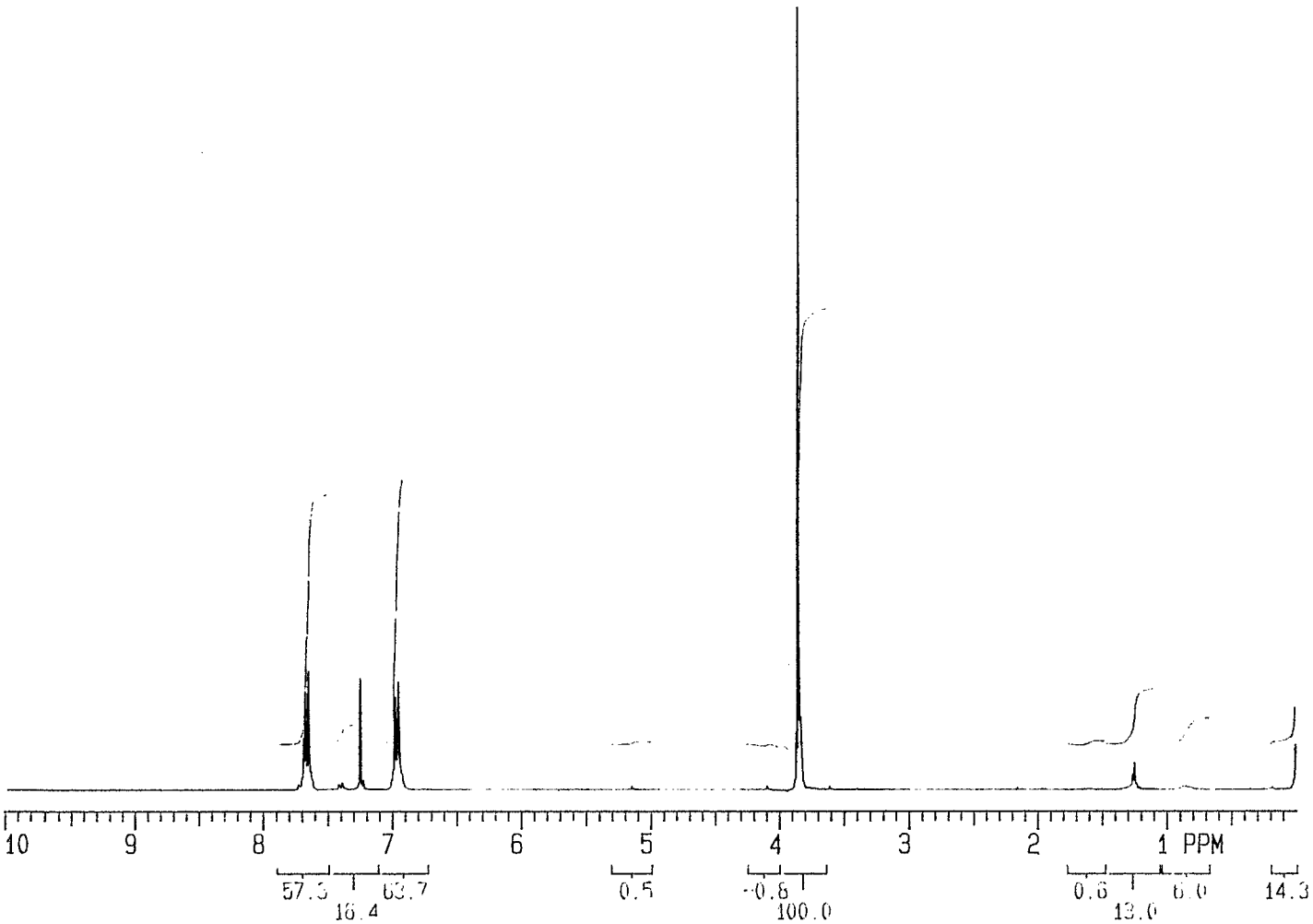


Figure 6: ^{1}H NMR spectrum of **2c.**



2c (*E*/*Z* = 77/23)



SZ-37

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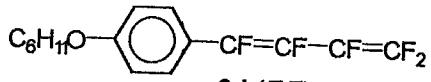
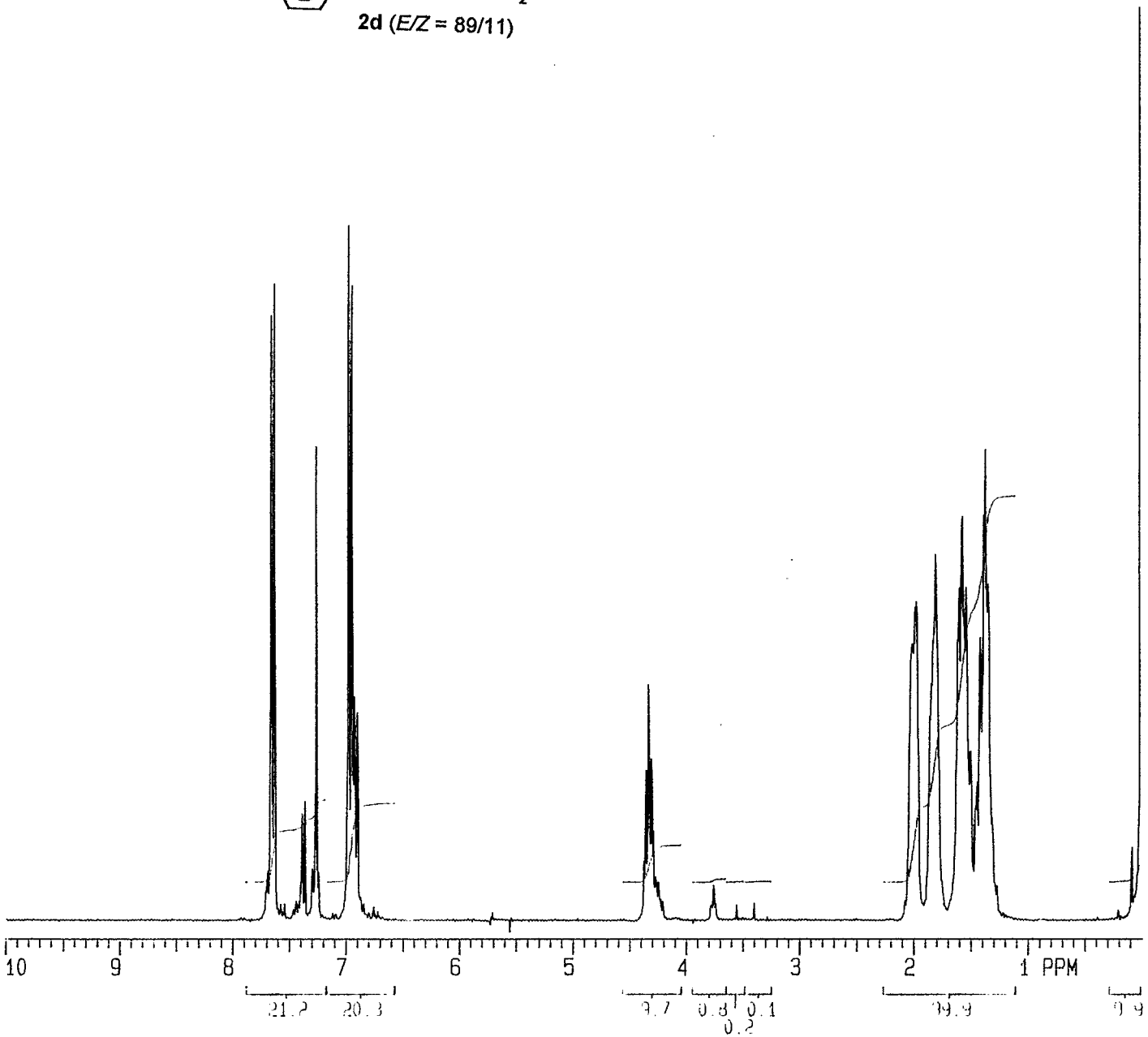
Figure 7: ^{1}H NMR spectrum of **2d.**



2d (*E*/*Z* = 89/11)



SZ-1952

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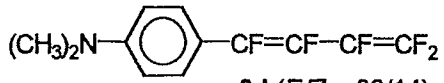
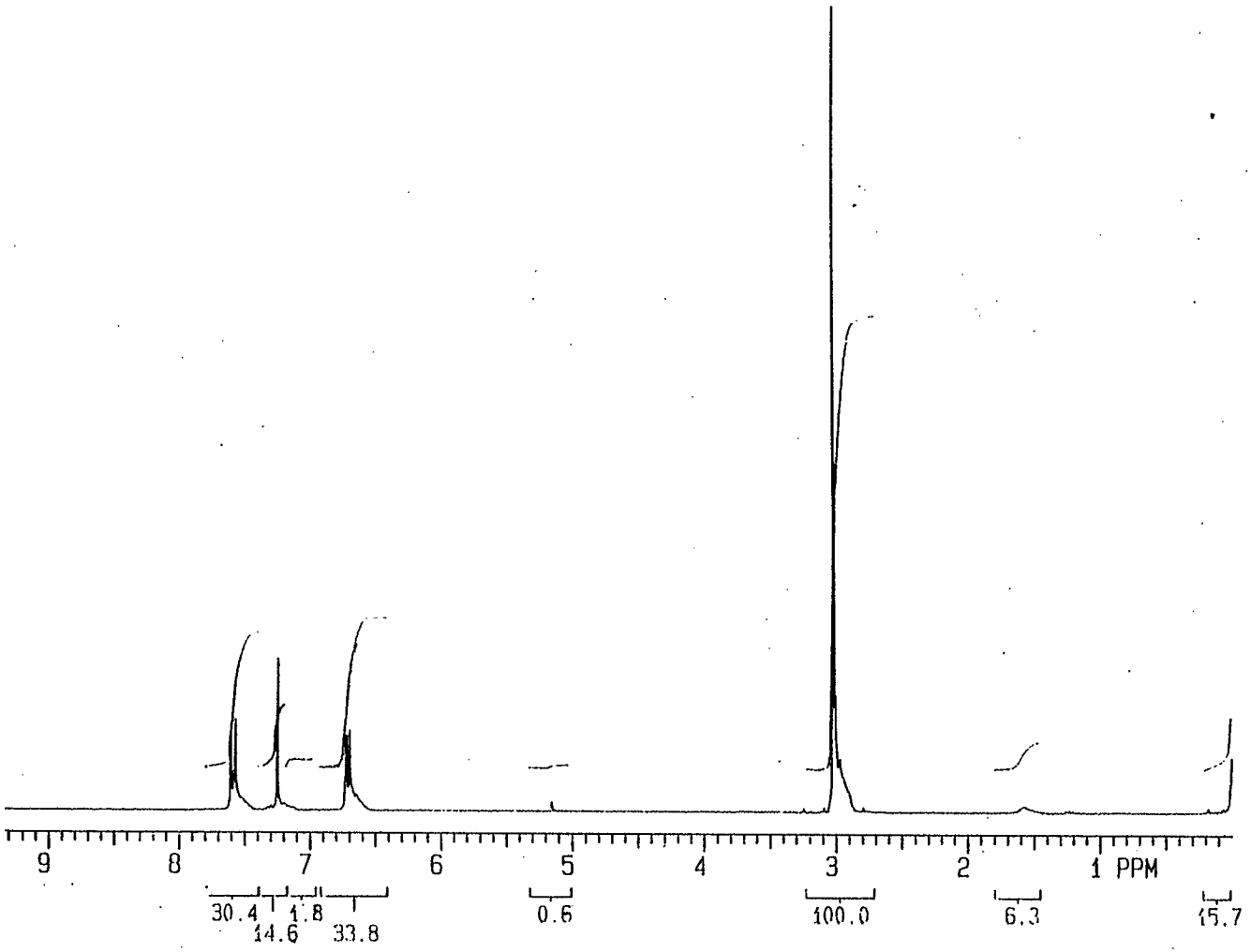
Figure 8: ^{1}H NMR spectrum of **2e.**



2d (*E*/*Z* = 86/14)



SZ-47

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NT	16		
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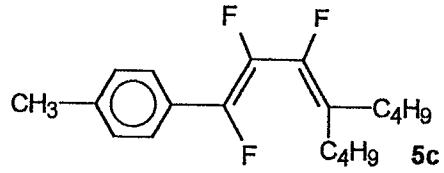
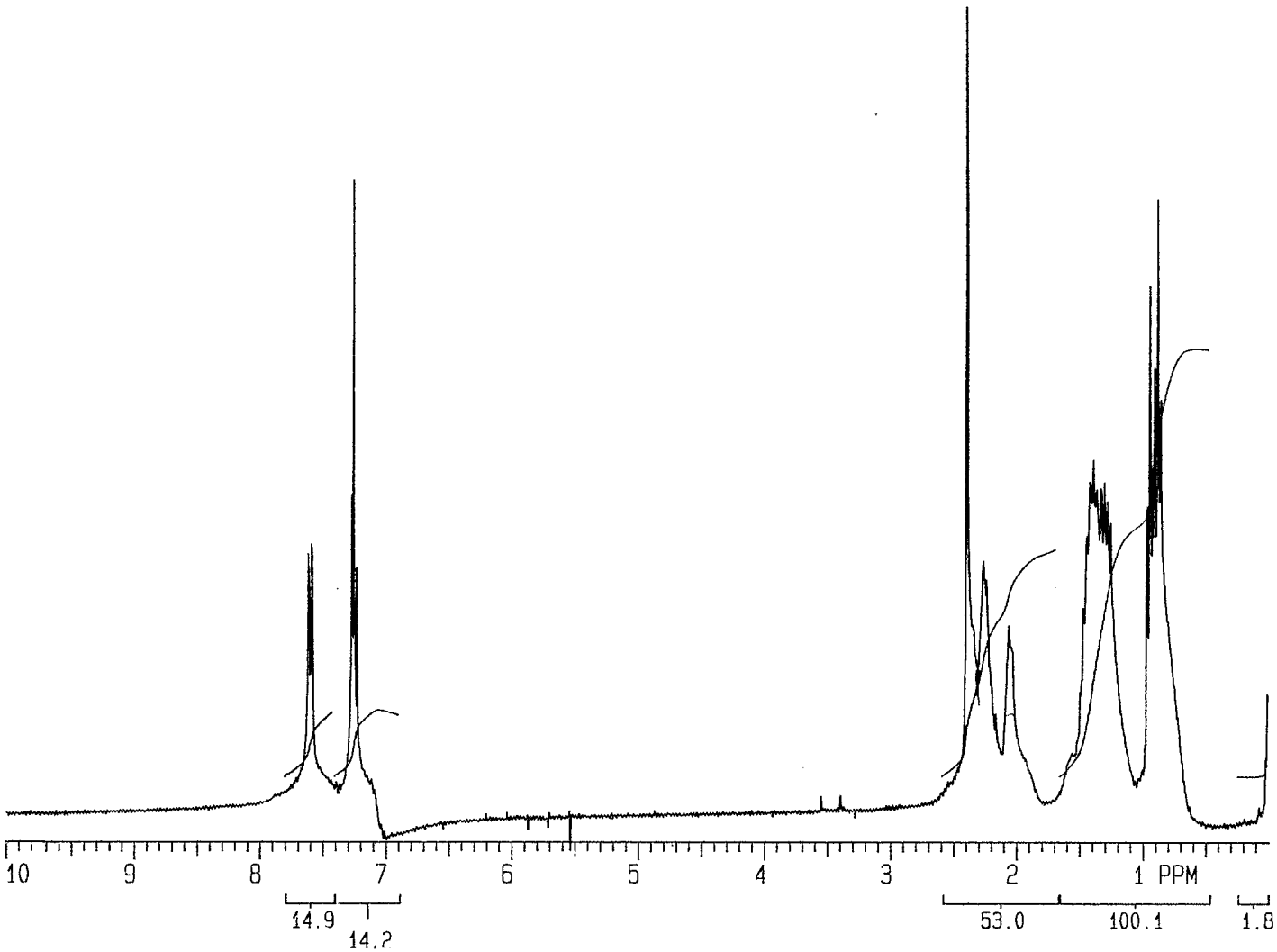
Figure 9: ^{1}H NMR spectrum of **5c.**



5c



C.116/3

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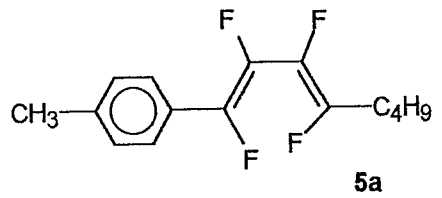
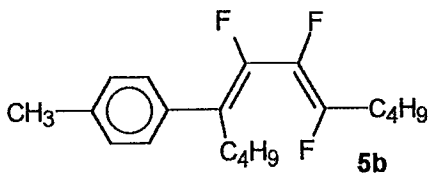
LOAD	N	INS	1.000
		AI	

Figure 10: ^{1}H NMR spectrum of **5a.**



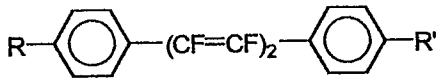
5a

Figure 11: ^{1}H NMR spectrum of **5b.**



5b

Figure 12: ^{1}H NMR spectrum of **6b**.



6b: R = OCH_3, R' = H

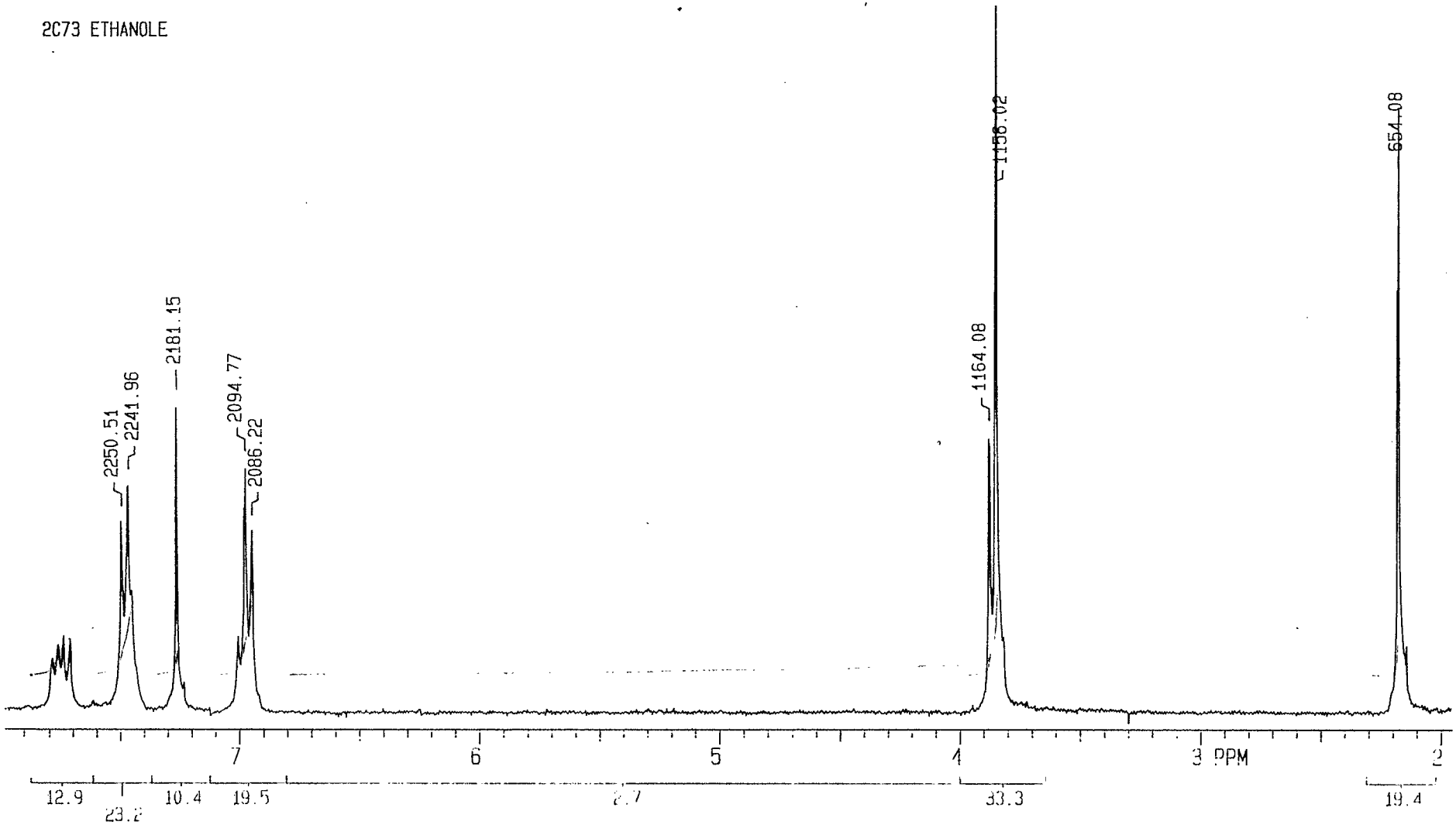
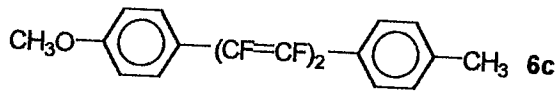
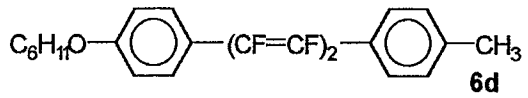


Figure 13: ^{1}H NMR spectrum of **6c.**

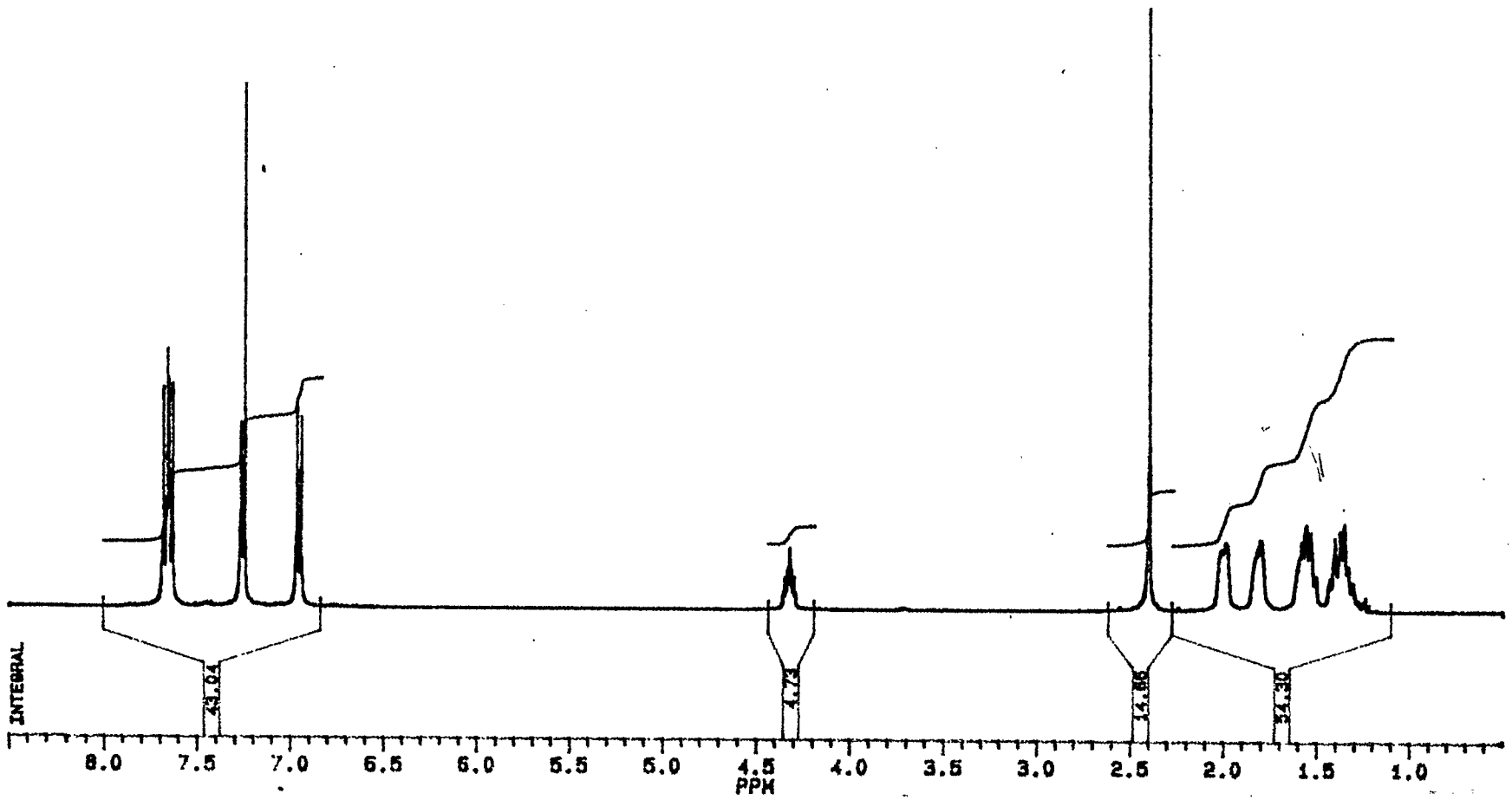


6c

Figure 14: ^{1}H NMR spectrum of **6d.**



6d



BRUKER

Z602.001
DATE 29-12-92

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SY 133.0
O1 6500.000
SI 65536
TD 65536
SW 6024.096
HZ/PT .184

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RG 80
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TE 297

FW 7600
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LB .200
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CX 23.00
CY 0.0
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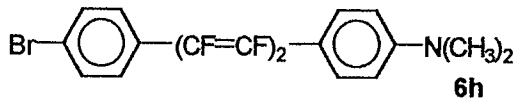
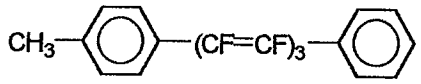
F2 .500P
HZ/CM 139.176
PPM/CM .348
SR 4397.41

Figure 15: ^{1}H NMR spectrum of **6h.**

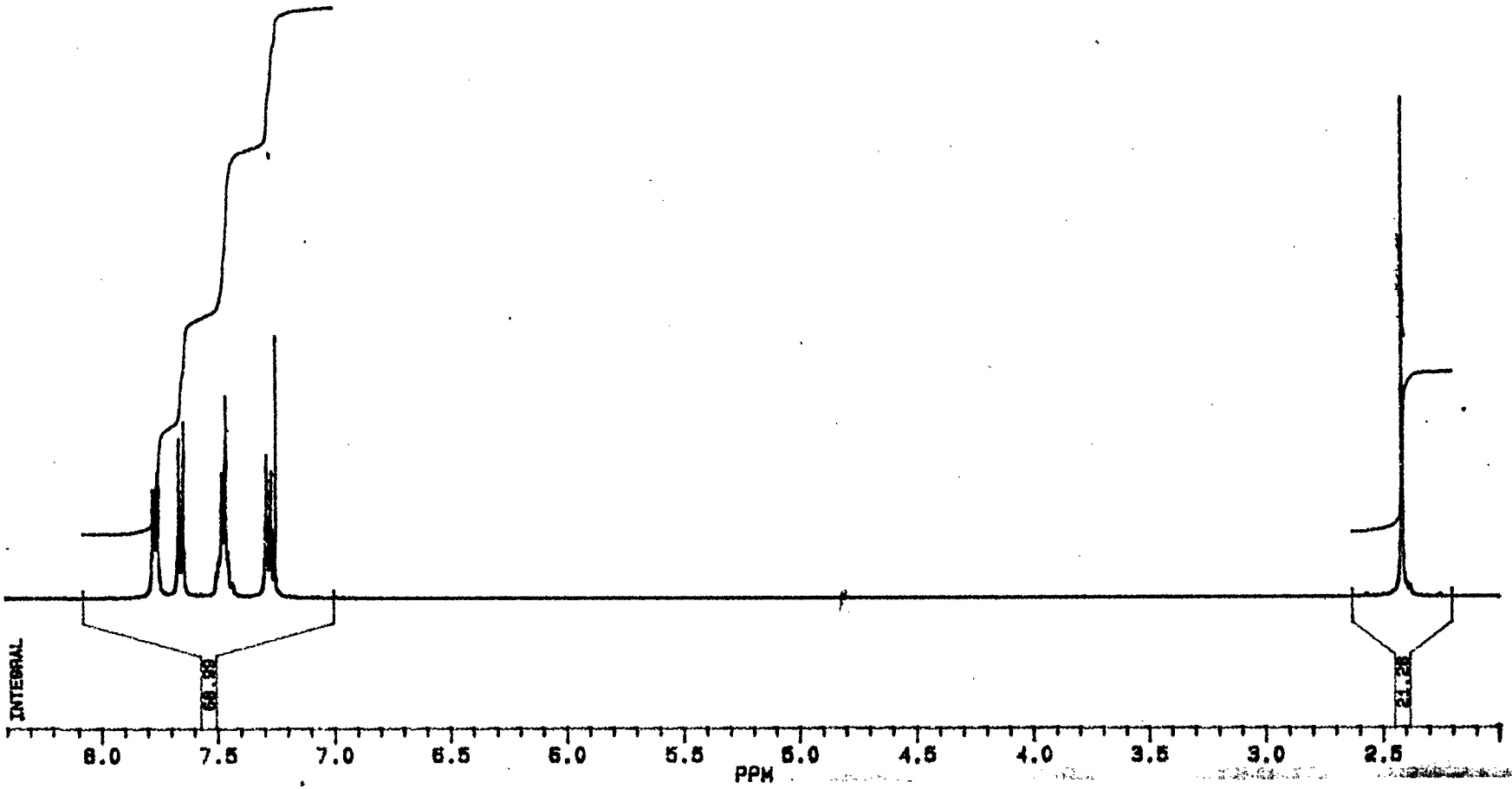


6h

Figure 16: ^{1}H NMR spectrum of **8a** (400.14 MHz).



8a



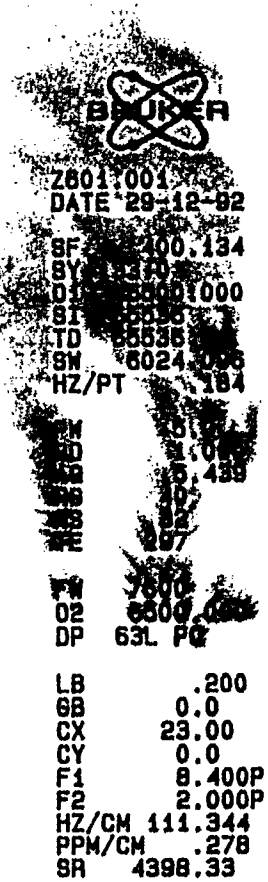
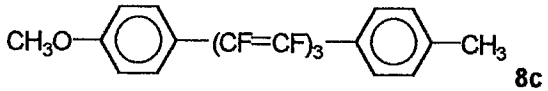
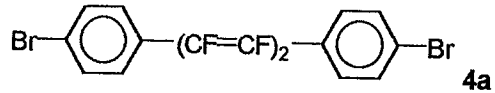


Figure 17: ^{1}H NMR spectrum of **8c.**

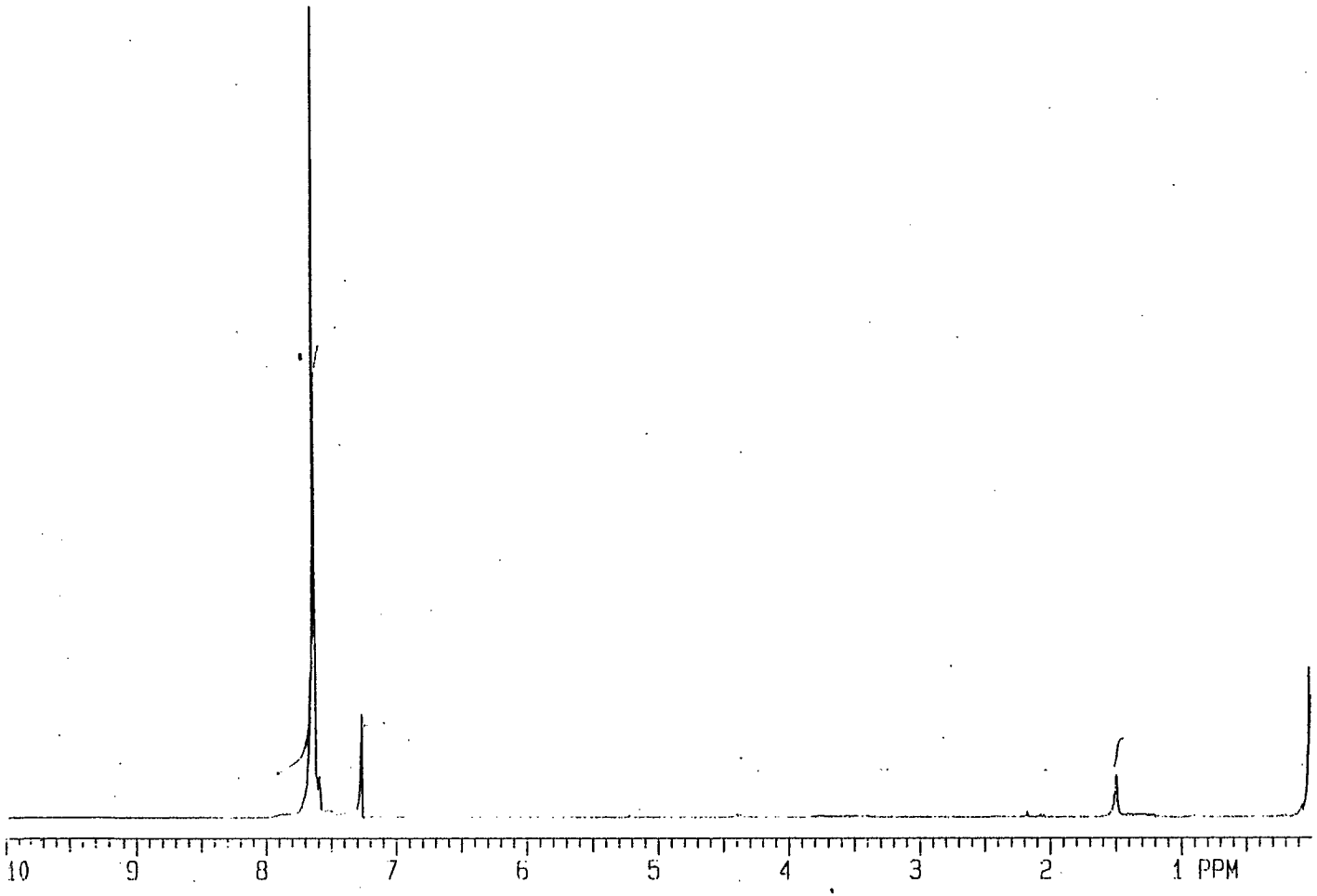


8c

Figure 18: ^{1}H NMR spectrum of **4a.**



4a



SZ-28

EXP1 PULSE SEQUENCE: S2PUL
DATE 02-11-93
SOLVENT CDCL3
FILE H

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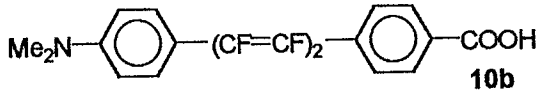
NP	16000	DHP	1.0
PW	7.4	DLP	1800
P1	0	HOMO	N
D1	0		
D2	0	PROCESSING	
TO	0	MATH	I
NT	16		
CT	16	DISPLAY	
PW90	20.0	SP	0
HB	2250	WP	3000.8
BS	64	VS	66
SS	0	SC	100
FL	N	WC	300
IN	Y	IS	455
DP	Y	RFL	534.7
ALOCK	A	RFP	0
WSHIM	E	TH	10
LOAD	N	INS	1.000
		AI	

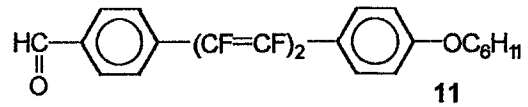
Figure 19: ^{1}H NMR spectrum of **9** (80 MHz).

Figure 20: ^{1}H NMR spectrum of **10b.**

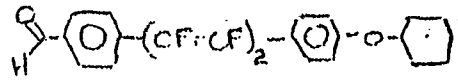


10b

Figure 21: ^{1}H NMR spectrum of **11.**



11



2C15'CRUDE (SZ-43)

EXP1 PULSE SEQUENCE: S2PUL
DATE 03-31-94
SOLVENT CDCL3
FILE H

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NP	16000	DHP	1.0
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D1	0		
D2	0	PROCESSING	
TO	0	MATH	I
NT	16		
CT	16	DISPLAY	
PW90	20.0	SP	0
FB	2250	WP	3000.8
BS	64	VS	581
SS	0	SC	100
IL	N	WC	300
IN	Y	IS	416
DP	Y	RFL	535.2
ALOCK	A	RFP	0
WSHIM	E	TH	10
LOAD	N	INS	1.000
		AI	