CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Synthesis of Extended Triphenylenes by Palladium-Catalyzed [2+2+2] Cycloaddition of Triphenylynes

Carmen Romero, Diego Peña*, Dolores Pérez*, and Enrique Guitián

CONTENTS

General methods: All reactions were carried out under argon using oven-dried glassware. Solvents were dried by distillation from a drying agent: THF from Na/benzophenone; toluene and benzene from Na; CH_3CN and CH_2Cl_2 from CaH_2. TMSCl, *i*-Pr_2NEt, *i*-Pr_2NH, TMEDA and *t*-$BuNH_2$ were distilled from CaH_2 prior to use. 2-Trimethylsilylphenyl triflate (**1**),[1] 1,1':2',1''-terphenyl-4'-ol (3,4-diphenylphenol, **8**)[2] and $Pd(PPh_3)_4$[3] were prepared following published procedures. Commercial reagents were purchased from ABCR GmbH, Aldrich Chemical Co., or Strem Chemicals Inc., and were used without further purification, except that resorcinol monoacetate (**10**) was purified by column chromatography before use. *n*-BuLi and Bu_4NF (TBAF) were used in solution in hexane (2.40 M) and THF (1 M), respectively. TLC was performed on Merck silica gel 60 F_{254}; chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). ^1H and ^{13}C NMR spectra were recorded at 250.13 and 62.83 MHz (Bruker DPX-250 instrument) or 300 and 75 MHz (Varian Mercury-300 instrument), respectively. High- or low-temperature NMR spectra were recorded on either a Bruker AMX-500 or a Varian Inova-750 instrument. Low-resolution electron impact mass spectra (EI-LRMS) were determined at 70 eV on a HP-5988A instrument. High-resolution mass spectra (HRMS) and FAB (positive FAB in 3-nitrobenzyl alcohol) were obtained on a Micromass Autospec spectrometer. MALDI-TOF spectra were determined on a Bruker Autoflex instrument. IR spectra were recorded on a Mattson Cygnus 100 spectrophotometer. Melting points were measured on a Gallenkamp instrument. UV/Vis spectra were obtained on a Varian Cary 100 Bio or a Jasco V-530 spectrophotometers.

Synthesis of aryne precursor 7a

5'-Bromo-1,1':2',1''-terphenyl-4'-ol (2-bromo-4,5-diphenylphenol): A solution of Br_2 (160 μL, 3.12 mmol) in toluene (1.6 mL) was added dropwise to a solution of *t*-$BuNH_2$ (110 μL, 1.05 mmol) in toluene (8.0 mL) at -20°C. After addition was complete, the mixture was stirred at room temperature for 10 min. Then, a solution of 1,1':2',1''-terphenyl-4'-ol[2] (3,4-diphenylphenol, **8**, 640 mg, 2.60 mmol) in toluene (2.0 mL) was added dropwise at -78°C, and the resulting mixture was stirred overnight at room temperature. Then, H_2O (10 mL) was added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was

purified by column chromatography (SiO_2; 2:3 CH_2Cl_2/hexane), affording 5'-bromo-1,1':2',1''-terphenyl-4'-ol (682 mg, 81%) as a white solid: m.p. 88-90°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.75 (s, 1H), 7.49-7.27 (m, 11H), 5.75 (s, 1H) ppm; ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 151.2 (C), 141.6 (C), 140.0 (C), 139.7 (C), 134.5 (C), 133.5 (CH), 129.6 (2CH), 129.5 (2CH), 127.9 (4CH), 126.8 (CH), 126.5 (CH), 117.7 (CH), 109.0 (C) ppm; MS (EI), *m/z* (%): 326 (73), 324 (77); HRMS (EI) for $C_{18}H_{13}{}^{79}BrO$, calcd: 324.0150, found: 324.0143; HRMS (EI) for $C_{18}H_{13}{}^{81}BrO$, calcd: 326.0129, found: 326.0133.

3-Bromo-2-triphenylenol (9): A solution of 5'-bromo-1,1':2',1''-terphenyl-4'-ol (449 mg, 1.38 mmol) in CS_2 (60 mL) was added to a suspension of $AlCl_3$ (4.57 g, 34.5 mmol) and $CuCl_2$ (4.27 g, 31.7 mmol) in CS_2 (400 mL) at room temperature. The mixture was stirred at room temperature for 5 h and then poured on 10% aqueous HCl solution (200 mL). The phases were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2, hexane was added, and the resulting precipitate was filtered, affording **9** (380 mg, 85%) as a white solid: m.p. 135-140°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 8.63-8.50 (m, 2H), 8.49-8.40 (m, 2H), 8.19 (s, 1H), 7.70-7.60 (m, 4H), 5.75 (s, 1H) ppm; ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 151.1 (C), 131.2 (C), 130.1 (C), 129.0 (C), 128.8 (C), 128.7 (C), 127.7 (CH), 127.4 (CH), 127.3 (CH), 127.1 (CH), 126.9 (CH), 123.4 (CH), 123.3 (2 CH), 122.7 (CH), 114.8 (C), 111.4 (C), 109.0 (CH) ppm; MS (EI), *m/z* (%): 324 (93), 322 (90); HRMS (EI) for $C_{18}H_{11}{}^{79}BrO$, calcd: 321.9993, found: 321.9989; HRMS (EI) for $C_{18}H_{11}{}^{81}BrO$, calcd: 323.9973, found: 323.9970; UV/Vis (CH_2Cl_2), λ_{max} (ε): 351 (5600), 335 (6000), 290 (sh, 14800), 264 (44000), 256 (sh, 33200 mol^{-1} dm^3 cm^{-1}) nm.

3-(Trimethylsilyl)triphenylenyl 2-trifluoromethanesulfonate (7a): A solution of 3-bromo-2-triphenylenol (**9**, 205 mg, 0.64 mmol) and HMDS (140 µL, 0.66 mmol) in THF (2.0 mL) was refluxed for 1 h. The solvent was evaporated under reduced pressure, and the residue was subjected to vacuum to remove excess NH_3 and unreacted HMDS. ^{1}H NMR of the crude residue showed quantitative formation of the corresponding silyl ether. This crude product was dissolved in THF (4.0 mL), and the solution was cooled to -100°C (external temperature). *n*-BuLi (270 µL, 2.59 M, 0.70 mmol) was added dropwise and the reaction mixture was stirred for 30 min while the temperature reached -80°C. The mixture was again cooled to -100°C, Tf_2O (130 µL, 0.77 mmol) was added

dropwise and stirring was kept up for 30 min while the temperature returned to -80°C. Then, saturated aqueous $NaHCO_3$ (2 mL) was added at low temperature, the phases were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 1:2 CH_2Cl_2/hexane), affording **7a** (182 mg, 64%) as a white solid: m.p. 133-135°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.81 (s, 1H), 8.68-8.60 (m, 3H), 8.56 (s, 1H), 8.49 (d, *J* = 9.4 Hz, 1H), 7.74-7.69 (m, 4H), 0.53 (s, 9H) ppm; ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 154.3 (C), 132.3 (C), 131.9 (CH), 131.1 (C), 130.4 (C), 129.9 (C), 128.7 (C), 128.5 (C), 128.4 (CH), 128.3 (C), 127.8 (CH), 127.6 (2 CH), 127.2 (CH), 123.5 (CH), 123.4 (CH), 123.3 (CH), 118.6 (q, *J* = 321 Hz, CF_3), 113.4 (CH), -0.6 (TMS) ppm; MS (EI), *m/z* (%): 448 (83), 433 (65); HRMS (EI) for $C_{22}H_{19}F_3O_3SSi$, calcd: 448.0776, found: 448.0774; IR (KBr): 1212, 1144, 921, 840, 752 cm^{-1}; UV/Vis (CH_2Cl_2), λ_{max} (ε): 308 (11900), 287 (22700), 262 (69200), 255 (sh, 49000 mol^{-1} dm^3 cm^{-1}) nm.

Synthesis of aryne precursor 7b

4-Bromo-3-hydroxyphenyl acetate:[4] *i*-Pr_2NH (410 µL, 2.95 mmol) was added to a solution of resorcinol monoacetate (**10**, 4.49 g, 29.54 mmol) in CH_2Cl_2 (210 mL). NBS (6.05 g, 33.97 mmol) was added in one portion at -100°C, and the resulting mixture was stirred for 14 h while the temperature reached 20°C. Then, 10% aqueous HCl (150 mL) was added, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, and the resulting residue was purified by column chromatography (SiO_2; 1:1 to 3:1 CH_2Cl_2/hexane), affording 4-bromo-3-hydroxyphenyl acetate (3.60 g, 53%) as a yellowish oil: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.7 Hz, 1H), 6.79 (d, *J* = 2.6 Hz, 1H), 6.62 (dd, *J* = 8.7, 2.6 Hz, 1H), 5.61 (br s, 1H), 2.29 (s, 3H) ppm; ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 169.5 (C), 153.0 (C), 150.7 (C), 132.3 (CH), 114.9 (CH), 109.8 (CH), 106.9 (C), 21.0 (CH_3) ppm; MS (EI), *m/z* (%): 232 (11), 230 (11); HRMS (EI) for $C_8H_7{}^{79}BrO_3$, calcd: 229.9579, found: 229.9584; HRMS (EI) for $C_8H_7{}^{81}BrO_3$, calcd: 231.9558, found: 231.9565.

5-Acetoxy-2-bromophenyl trifluoromethanesulfonate (11): Tf_2O (2.25 mL, 13.42 mmol) was added dropwise to a solution of 4-bromo-3-hydroxyphenyl acetate (1.35 g, 5.84 mmol) and *i*-Pr_2NEt (1.17 mL, 6.71 mmol) in CH_2Cl_2 (11 mL) at 0°C, and this reaction mixture was stirred at room temperature for 80 min. Then, cold 5% aqueous

$NaHCO_3$ (10 mL) was slowly added and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. and the resulting residue was purified by column chromatography (SiO_2; 1:1 CH_2Cl_2/ hexane), affording **11** (1.95 g, 92%) as a yellowish oil: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.8 Hz, 1H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.08 (dd, *J* = 8.8, 2.5 Hz, 1H), 2.32 (s, 3H) ppm; ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 168.4 (C), 150.3 (C), 146.8 (C), 134.2 (CH), 122.9 (CH), 118.6 (q, *J* = 321 Hz, CF_3), 117.0 (CH), 112.5 (C), 21.0 (CH_3) ppm; MS (EI), *m/z* (%): 364 (12), 362 (9); HRMS (EI) for $C_9H_6{}^{79}BrF_3O_5S$, calcd: 361.9071, found: 361.9084; HRMS (EI) for $C_9H_6{}^{81}BrF_3O_5S$, calcd: 363.9051, found: 363.9059.

4-Bromo-1,2-bis(hexyloxy)benzene:[5] SiO_2 (9.00 g) and NBS (3.36 g, 18.86 mmol) were added to a solution of 1,2-bis(hexyloxy)benzene (4.99 g, 17.92 mmol) in CH_2Cl_2 (180 mL). After vigorous stirring at room temperature for 8 h, this mixture was filtered to remove SiO_2, concentrated under reduced pressure to approx. 50 mL, and washed with saturated aqueous $Na_2S_2O_5$ (50 mL). The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography (SiO_2; 1:1 CH_2Cl_2/hexane), affording 4-bromo-1,2-bis(hexyloxy)benzene (6.39 g, 100%) as a colourless oil: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.99 (d, *J* = 9.0 Hz, 1H), 6.97 (s, 1H), 6.73 (d, *J* = 9.0 Hz, 1H), 3.98-3.92 (m, 4H), 1.84-1.74 (m, 4H), 1.48-1.27 (m, 12H), 0.93-0.87 (m, 6H); MS (EI), *m/z* (%): 358 (18), 356 (18).

3,4-Bis(hexyloxy)-1-phenylboronic acid (13):[6] *n*-BuLi (8.20 mL, 2.40 M, 19.71 mmol) was added dropwise to a solution of 4-bromo-1,2-bis(hexyloxy)benzene (6.39 g, 17.90 mmol) in THF (90 mL), and the mixture was stirred at -80°C for 1 h. Then, $B(OMe)_3$ (10.14 mL, 90.50 mmol) was added and the mixture was allowed to reach room temperature while stirring overnight, after which a further 10% aqueous HCl (100 mL) was added and stirring was kept up for 30 min. The phases were separated and the aqueous layer was extracted with AcOEt. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to obtain a pale yellow solid, which was washed with hexane (100 mL) and filtered, affording a mixture of the boronic acid **13** and the corresponding boroxine, the cyclic anhydride trimer [$(ArBO)_3$]. Heating this mixture at 50^{o}C under reduced pressure for 18 h completed the

dehydration of the boronic acid, affording the boroxine derived from **13** (3.98 g, 73 %) as a white solid: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.1 Hz, 3H), 7.70 (s, 3H), 7.00 (d, *J* = 8.1 Hz, 3H), 4.17-4.07 (m, 12H), 1.91-1.83 (m, 12H), 1.55-1.37 (m, 36H), 0.96-0.93 (m, 18H).

3,3'',4,4''-Tetrakis(hexyloxy)-1,1':2',1''-terphenyl-4'-ol (14): An aqueous Na_2CO_3 solution (2%, 200 mL) was added to a mixture of triflate **11** (3.51 g, 9.67 mmol), $Pd(PPh_3)_4$ (1.12 g, 0.97 mmol) and the boroxine derived from boronic acid **13** (11.5 g, 12.57 mmol) in THF (65 mL). After stirring at 85^{o}C for 48 h, this mixture was cooled to room temperature and the phases were separated. The aqueous phase was acidified to pH 1 by careful addition of 10% aqueous HCl solution, and was then extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude was dissolved in THF (150 mL), a mixture of saturated $NaHCO_3$ and MeOH (1:1, 150 mL) was added, and this mixture was stirred at 85°C for 12 h, after which the phases were separated and the aqueous layer was carefully acidified to pH 1 with 10% aqueous HCl and extracted with AcOEt. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 1:4 AcOEt/hexane), affording **14** (5.31 g, 85%): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.17 (m, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.73 (s, 1H), 6.68-6.57 (m, 4H), 6.50 (s, 1H), 6.48 (s, 1H), 5.80 (br s, 1H), 3.86 (t, *J* = 6.7 Hz, 4H), 3.63-3.56 (m, 4H), 1.73-1.63 (m, 4H), 1.56-1.48 (m, 4H), 1.39-1.16 (m, 24H), 0.83-0.78 (m, 12H) ppm; ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 155.0 (C), 148.1 (2C), 147.6 (C), 147.4 (C), 141.4 (C), 134.3 (2C), 132.6 (C), 131.5 (CH), 121.9 (2CH), 117.0 (CH), 116.0 (CH), 115.7 (CH), 114.1 (CH), 113.2 (2CH), 69.3 (CH_2), 69.2 (CH_2), 69.0 ($2CH_2$), 31.6 ($2CH_2$), 31.5 ($2CH_2$), 29.22 (CH_2). 29.20 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 25.7 ($2CH_2$), 25.6 ($2CH_2$), 22.6 ($4CH_2$), 14.0 ($4CH_3$) ppm; MS (EI), *m/z* (%): 646 (100); HRMS (EI) for $C_{42}H_{62}O_5$, calcd: 646.4597, found: 646.4592.

5'-Bromo-3,3'',4,4''-tetrakis(hexyloxy)-1,1':2',1''-terphenyl-4'-ol: SiO_2 (4.08 g) and NBS (1.73 g, 9.72 mmol) were each added in one portion to a solution of **14** (5.27 g, 8.16 mmol) in CH_2Cl_2 (140 mL), and this mixture was vigorously stirred at room temperature for 6 h, after which it was filtered and washed with saturated aqueous $Na_2S_2O_5$ (100 mL). The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under

reduced pressure. The residue was purified by column chromatography (SiO_2; 2:1 CH_2Cl_2/hexane), affording 5'-bromo-3,3",4,4"-tetrakis(hexyloxy)-1,1':2',1"-terphenyl-4'-ol (3.77 g, 64%): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.50 (s, 1H), 7.06 (s, 1H), 6.76-6.60 (m, 4H), 6.56 (d, *J* = 8.8 Hz, 2H), 5.66 (s, 1H), 3.94 (t, *J* = 6.5 Hz, 4H), 3.72-3.66 (m, 4H), 1.85-1.74 (m, 4H), 1.69-1.60 (m, 4H), 1.48-1.26 (m, 24H), 0.93-0.88 (m, 12H) ppm; ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 151.2 (C), 148.3 (C), 148.1 (2C), 147.9 (C), 141.4 (C), 134.4 (C), 133.3 (CH), 133.1 (C), 132.9 (C), 121.8 (CH), 121.7 (CH), 117.5 (CH), 115.8 (CH), 115.5 (CH), 113.3 (CH), 113.1 (CH), 108.5 (C), 69.15 ($2CH_2$), 69.06 ($2CH_2$), 31.6 ($4CH_2$), 29.2 ($2CH_2$), 29.0 ($2CH_2$), 25.7 ($4CH_2$), 22.6 ($4CH_2$), 14.0 ($4CH_3$) ppm; MS (EI), *m/z* (%): 726 (100), 724 (90); HRMS (EI) for $C_{42}H_{61}{}^{79}BrO_5$, calcd: 724.3702, found: 724.3684; HRMS (EI) for $C_{42}H_{61}{}^{81}BrO_5$, calcd: 726.3682, found: 726.3667.

3-Bromo-6,7,10,11-tetrakis(hexyloxy)-2-triphenylenol (15): A solution of 5'-bromo-3,3",4,4"-tetrakis(hexyloxy)-1,1':2',1"-terphenyl-4'-ol (1.71 g, 2.37 mmol) in CH_2Cl_2 (200 mL) was added to a suspension of anhydrous $FeCl_3$ (1.14 g, 7.10 mmol) in CH_2Cl_2 (80 mL). This mixture was vigorously stirred at room temperature for 25 min, MeOH (150 mL) was added, and stirring was kept up for a further 60 min. The solvent was removed under reduced pressure and the crude was purified by column chromatography (SiO_2; 2:1 CH_2Cl_2/hexane), affording a yellowish solid. This solid was washed with MeOH (50 mL), obtaining **15** (1.64 g, 96%) as a white solid: m.p. 127-129ºC: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 8.00 (s, 1H), 7.80 (s, 1H), 7.76 (s, 2H), 7.74 (s, 1H), 5.71 (s, 1H), 4.25-4.15 (m, 8H), 2.00-1.87 (m, 8H), 1.58-1.56 (m, 8H), 1.40-1.29 (m, 16H), 0.96-0.86 (m, 12H) ppm; ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 150.1 (C), 149.8 (C), 149.2 (C), 149.1 (C), 149.0 (C), 130.3 (C), 126.5 (CH), 124.42 (C), 124.39 (C), 123.3 (C), 122.5 (2C), 110.1 (C), 108.5 (CH), 107.1 (CH), 106.8 (CH), 106.6 (CH), 106.2 (CH), 69.7 (CH_2), 69.6 (CH_2), 69.3 (CH_2), 69.2 (CH_2), 31.7 ($4CH_2$), 29.7 (CH_2), 29.32 ($2CH_2$), 29.26 (CH_2), 25.8 ($4CH_2$), 22.6 ($4CH_2$), 14.0 ($4CH_3$) ppm; MS (EI), *m/z* (%): 724 (16), 722 (5); HRMS (EI) for $C_{42}H_{59}{}^{79}BrO_5$, calcd: 722.3546, found: 722.3516; HRMS (EI) for $C_{42}H_{59}{}^{81}BrO_5$, calcd: 724.3525, found: 724.3519; UV/Vis (CH_2Cl_2), λ_{max} (ε): 310 (16400), 278 (55800), 270 (sh, 51400 mol^{-1} dm^3 cm^{-1}) nm.

6,7,10,11-Tetrakis(hexyloxy)-3-(trimethylsilyl)-2-triphenylenol (16): A solution of **15** (0.564 g, 0.78 mmol) and HMDS (0.180 mL, 0.86 mmol) in THF (6 mL) was refluxed for 60 min. The solvent was evaporated under reduced pressure and the residue

was subjected to vacuum to remove excess NH_3 and unreacted HMDS. The quantitative formation of the corresponding silyl ether was verified by ^{1}H NMR spectroscopy. *n*-BuLi (0.66 mL, 2.36 M, 1.56 mmol) was added dropwise to a solution of the crude silyl ether and TMEDA (59 µL, 0.39 mmol) in THF (7.5 mL) at -100°C, and this mixture was stirred for 70 min while the temperature reached -30°C. TMSCl (0.320 mL, 2.50 mmol) was added, stirring was continued at room temperature for 30 min, aqueous HCl solution (5%, 4 mL) was added, and after a further 2 h stirring at room temperature the phases were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 1:3 Et_2O/hexane), affording **16** (0.452 g, 81%) as a yellow solid: m.p. 68-70^{o}C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.50 (s, 1H), 8.02 (s, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 7.76 (s, 1H), 7.72 (s, 1H), 6.10 (s, 1H), 4.29-4.18 (m, 6H), 3.88 (t, *J* = 6.1 Hz, 2H), 1.99-1.87 (m, 6H), 1.58-1.52 (m, 8H), 1.44-1.32 (m, 12H), 1.27-1.10 (m, 6H), 0.96-0.86 (m, 9H), 0.81 (t, *J* = 6.5 Hz, 3H), 0.48 (s, 9H) ppm; ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 159.4 (C), 149.3 (C), 149.0 (C), 148.6 (C), 148.5 (C), 131.4 (C), 130.5 (CH), 125.7 (C), 124.6 (C), 124.3 (C), 123.1 (C), 122.8 (C), 122.2 (C), 107.3 (CH), 106.8 (CH), 106.6 (2CH), 106.4 (CH), 69.8 (CH_2), 69.6 (CH_2), 69.4 (CH_2), 69.1 (CH_2), 31.64 ($2CH_2$), 31.59 (CH_2), 31.51 (CH_2), 29.3 (CH_2), 29.2 ($2CH_2$), 29.0 (CH_2), 25.83 ($3CH_2$), 25.77 (CH_2), 22.6 ($3CH_2$), 22.5 (CH_2), 14.0 ($4CH_2$), -0.8 (TMS) ppm; MS (FAB^+), *m/z* (%): 716 (100); HRMS (FAB^+) for $C_{45}H_{68}O_5Si$, calcd: 716.4836, found: 716.4820; UV/Vis (CH_2Cl_2), λ_{max} (ε): 310 (9200), 279 (25900), 271 (sh, 23000 mol^{-1} dm^3 cm^{-1}) nm.

6,7,10,11-Tetrakis(hexyloxy)-3-(trimethylsilyl)triphenylenyl 2-trifluoromethane-sulfonate (7b): Tf_2O (0.160 mL, 0.98 mmol) was added dropwise to a solution of compound **16** (0.573 g, 0.80 mmol) and pyridine (0.120 mL, 1.44 mmol) in CH_2Cl_2 (8 mL) at 0°C, and this mixture was stirred at room temperature for 30 min. Cold 5% aqueous $NaHCO_3$ (10 mL) was added slowly, stirring was continued for 15 min, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with 5% aqueous HCl (10 mL), the phases were separated and the aqueous layer was again extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2; 1:3 Et_2O/hexane), affording **7b** (0.675 g, 100%) as a yellowish solid: m.p. 80-84ºC; ^{1}H NMR (250 MHz, $CDCl_3$): δ

= 8.59 (s, 1H), 8.35 (s, 1H), 7.98 (s, 1H), 7.81 (s, 3H), 4.28-4.21 (m, 8H), 2.02-1.91 (m, 8H), 1.62-1.54 (m, 8H), 1.48-1.39 (m, 16H), 0.94 (t, J = 6.8 Hz, 12H), 0.5 (s, 9H) ppm; ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 153.4 (C), 150.3 (C), 150.0 (C), 149.1 (2C), 131.3 (CH), 131.1 (C), 129.1 (C), 127.3 (C), 124.8 (C), 124.4 (C), 122.4 (C), 122.3 (C), 118.7 (q, J = 320 Hz, CF_3), 112.8 (CH), 106.9 (CH), 106.6 (CH), 106.5 (2CH), 69.4 ($3CH_2$), 69.1 (CH_2), 31.7 ($4CH_2$), 29.3 ($3CH_2$), 29.2 (CH_2), 25.8 ($4CH_2$), 22.6 ($4CH_2$), 14.0 ($4CH_3$), -0.7 (TMS) ppm; MS (FAB^+), *m/z* (%): 848 (100); HRMS (FAB^+) for $C_{46}H_{67}F_3O_7SSi$, calcd: 848.4329, found: 848.4293; IR (CsI): 2929, 2858, 1264, 842 cm^{-1}; UV/Vis (CH_2Cl_2), λ_{max} (ε): 307 (34100), 280 (106600), 271 (sh, 76900 mol^{-1} dm^3 cm^{-1}) nm.

References

[1] D. Peña, A. Cobas, D. Pérez, E. Guitián, *Synthesis* **2002**, 1454.

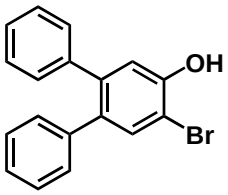
[2] A. Kawamoto, H. Uda, N. Harada, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3279.

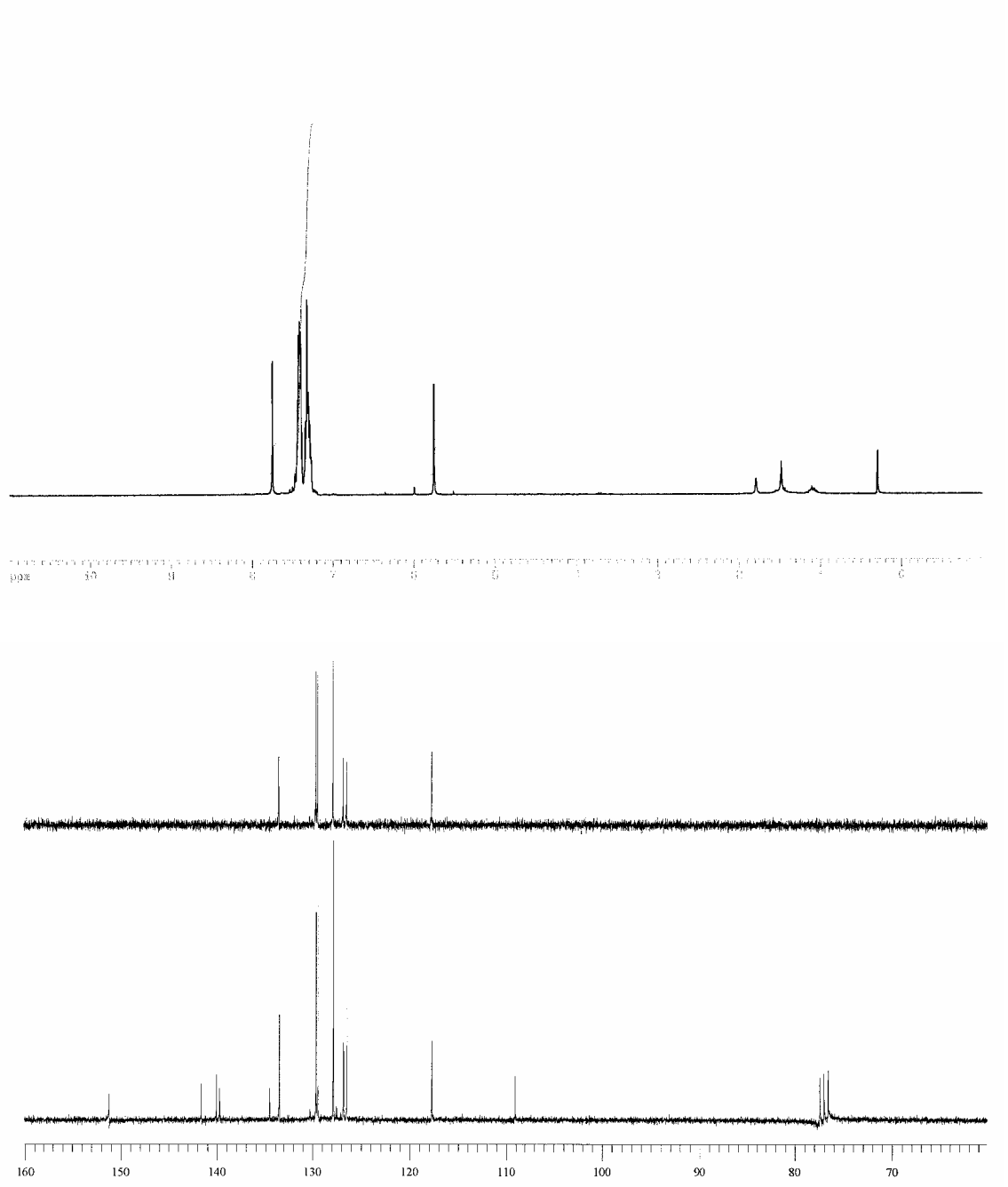
[3] L. S. Hegedus, *Palladium in Organic Synthesis*, in *Organometallics in Synthesis: A Manual* (Ed.: M. Schlosser), John Wiley & Sons, New York, **1994**.

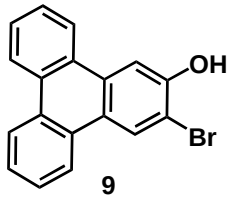
[4] G. Nicolosi, M. Piatelli, C. Sanfilippo, *Tetrahedron* **1993**, *49*, 3143.

[5] H. Konishi, K. Aritomi, T. Okano, J. Kiji, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 591.

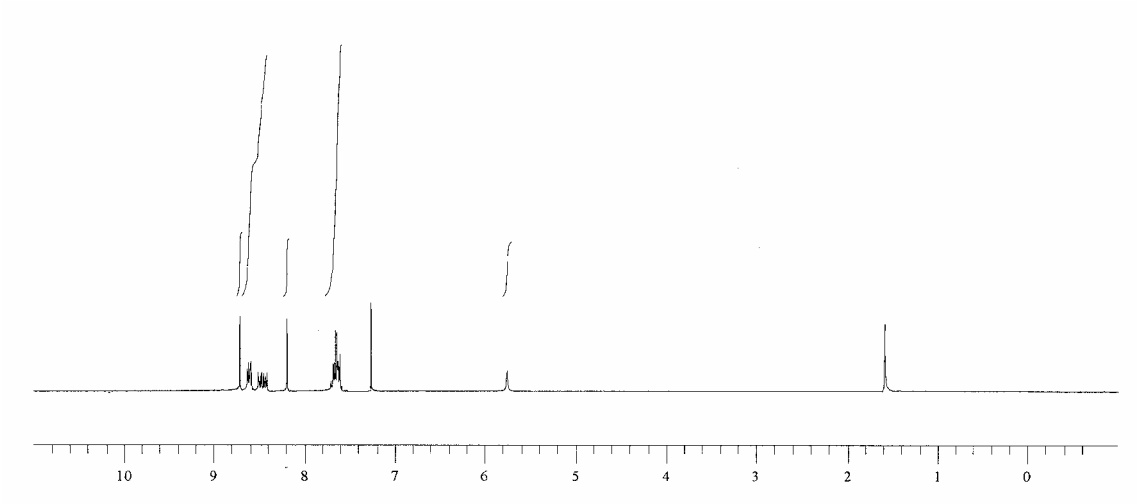
[6] H. Meier, B. Rose, *J. prakt. Chem.* **1998**, *340*, 536.

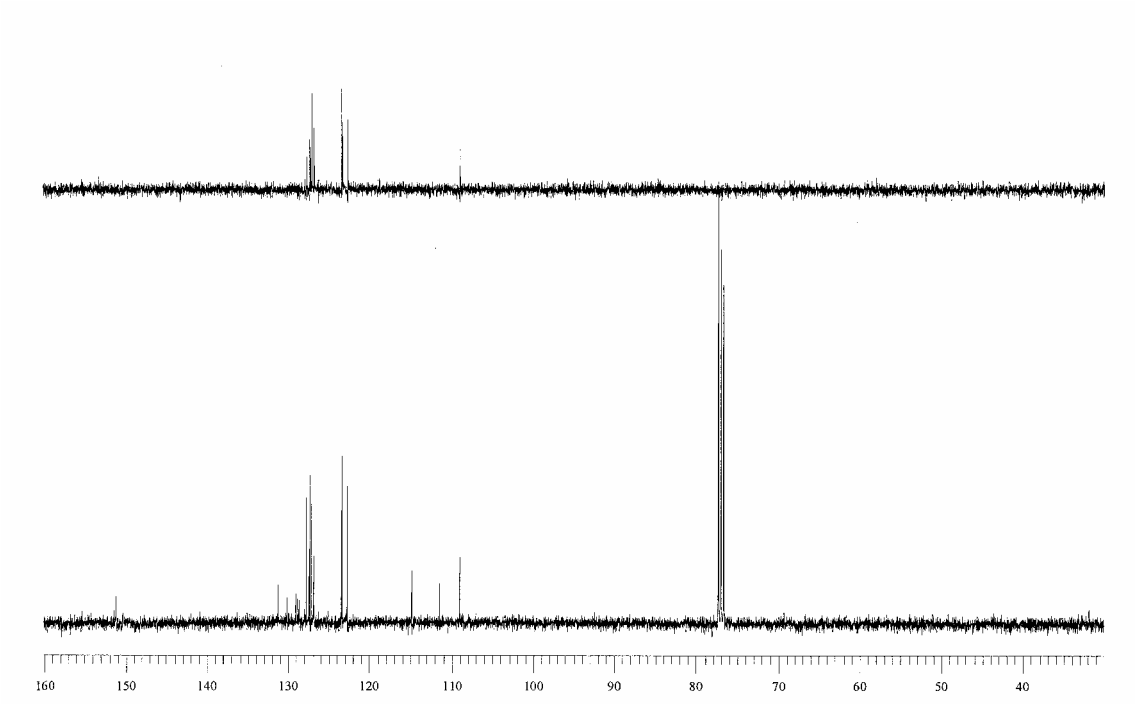

OH
Br

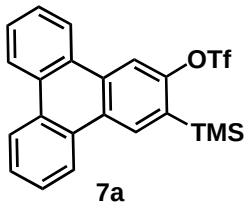

160
150
140
130
120
110
100
90
80
70



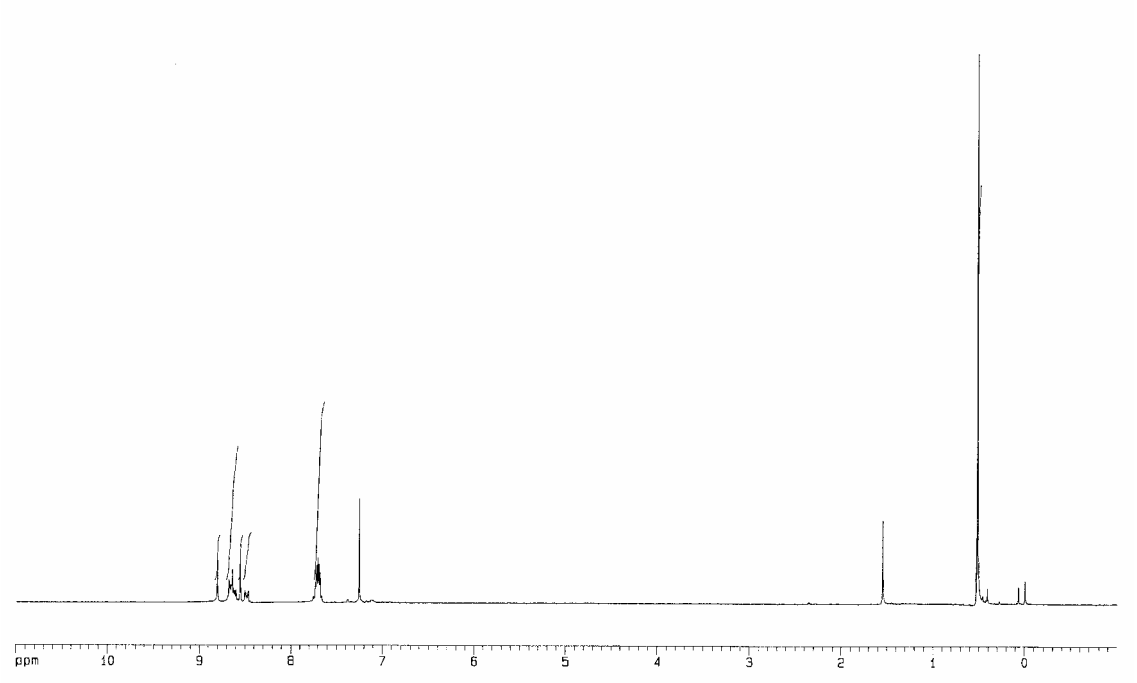
9

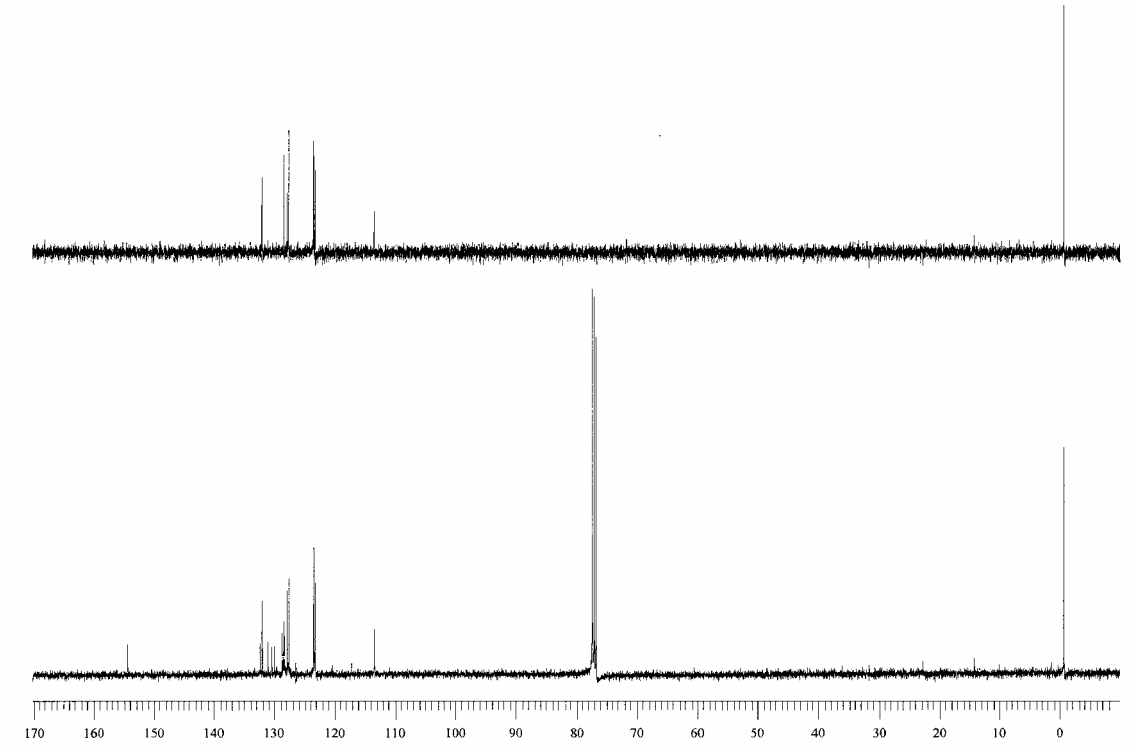


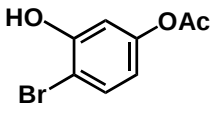


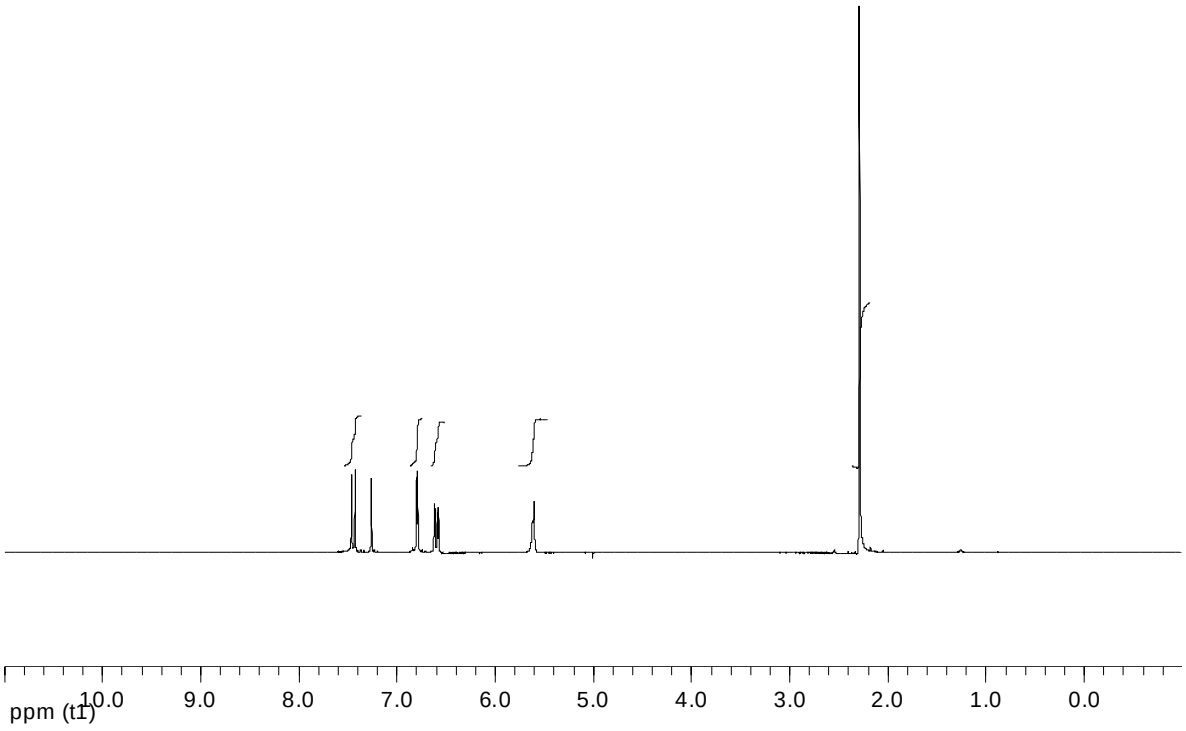

OTf
TMS

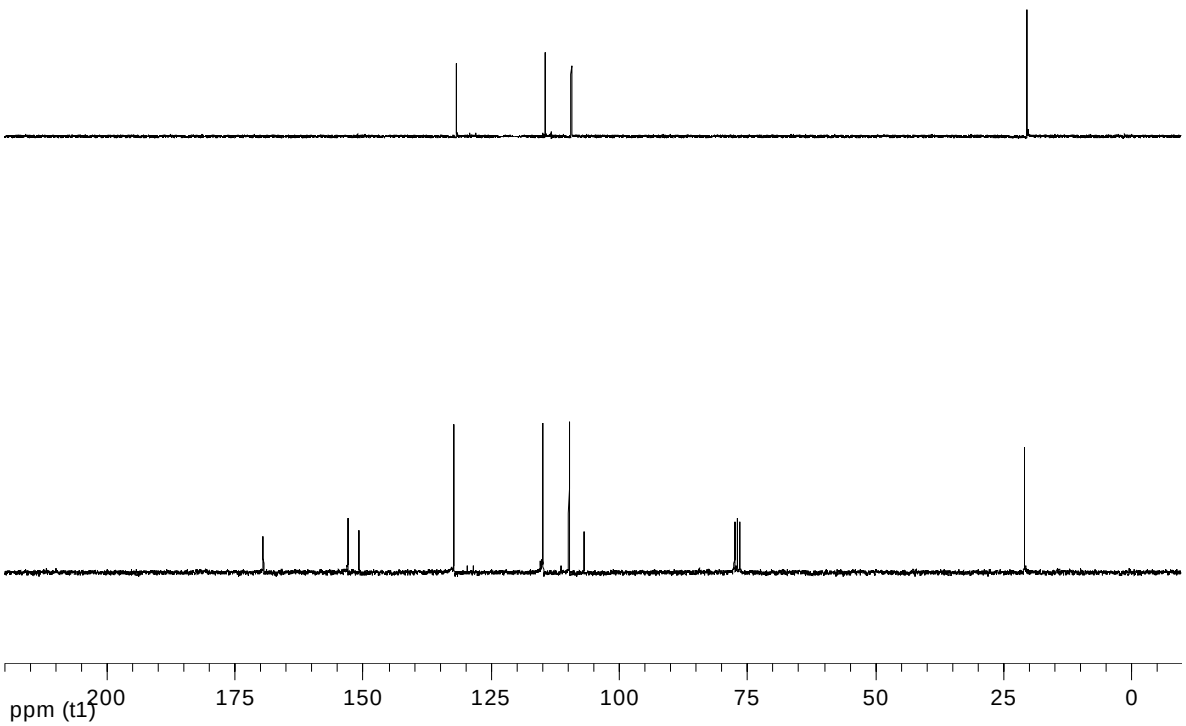
7a

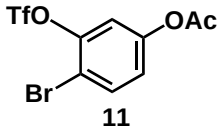

ppm
10
9
8
7
6
5
4
3
2
1
0


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

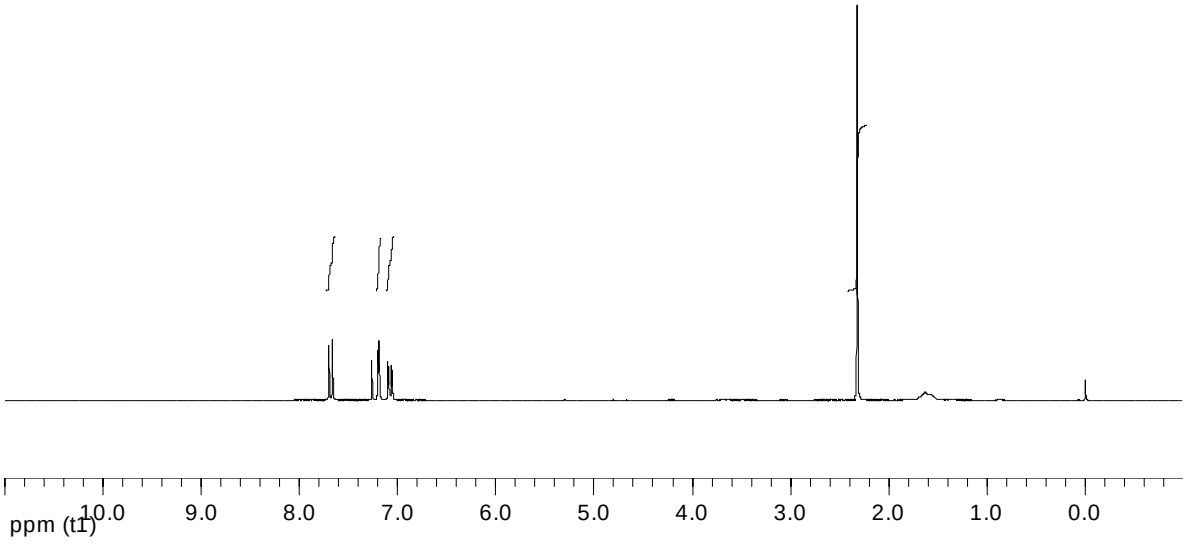

HO
OAc
Br

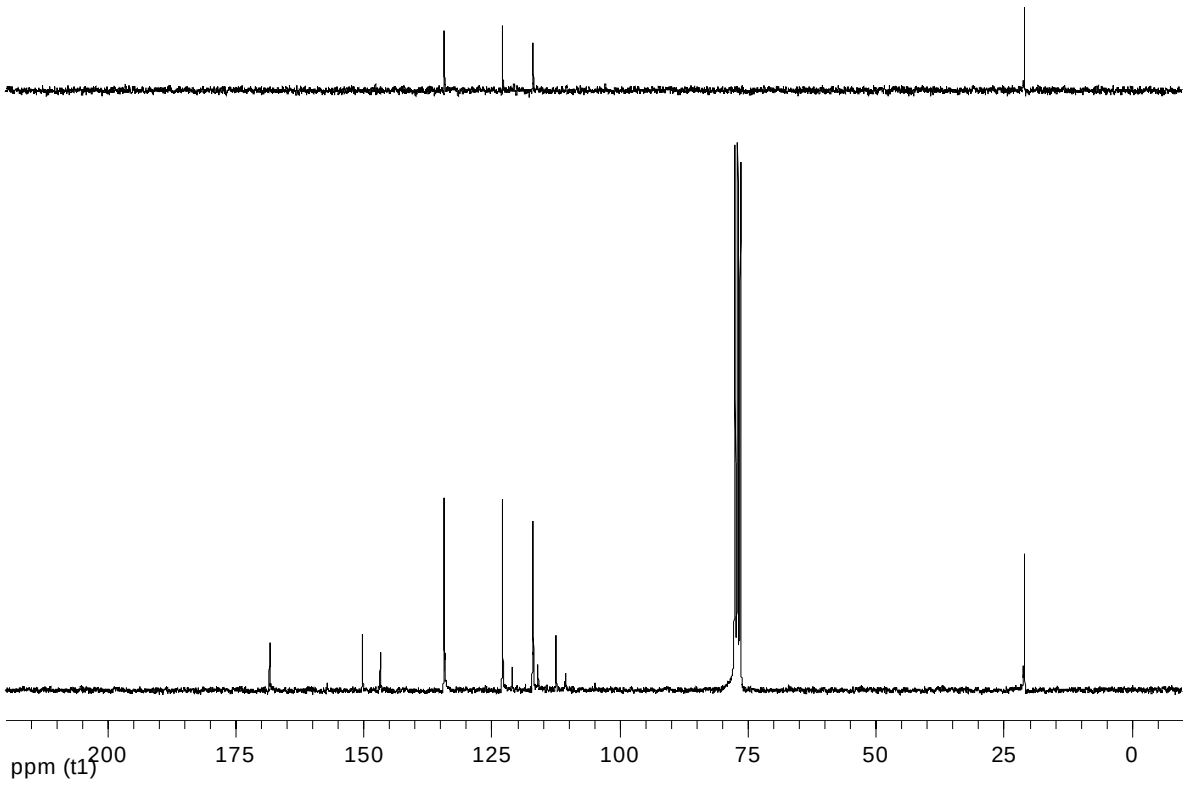

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

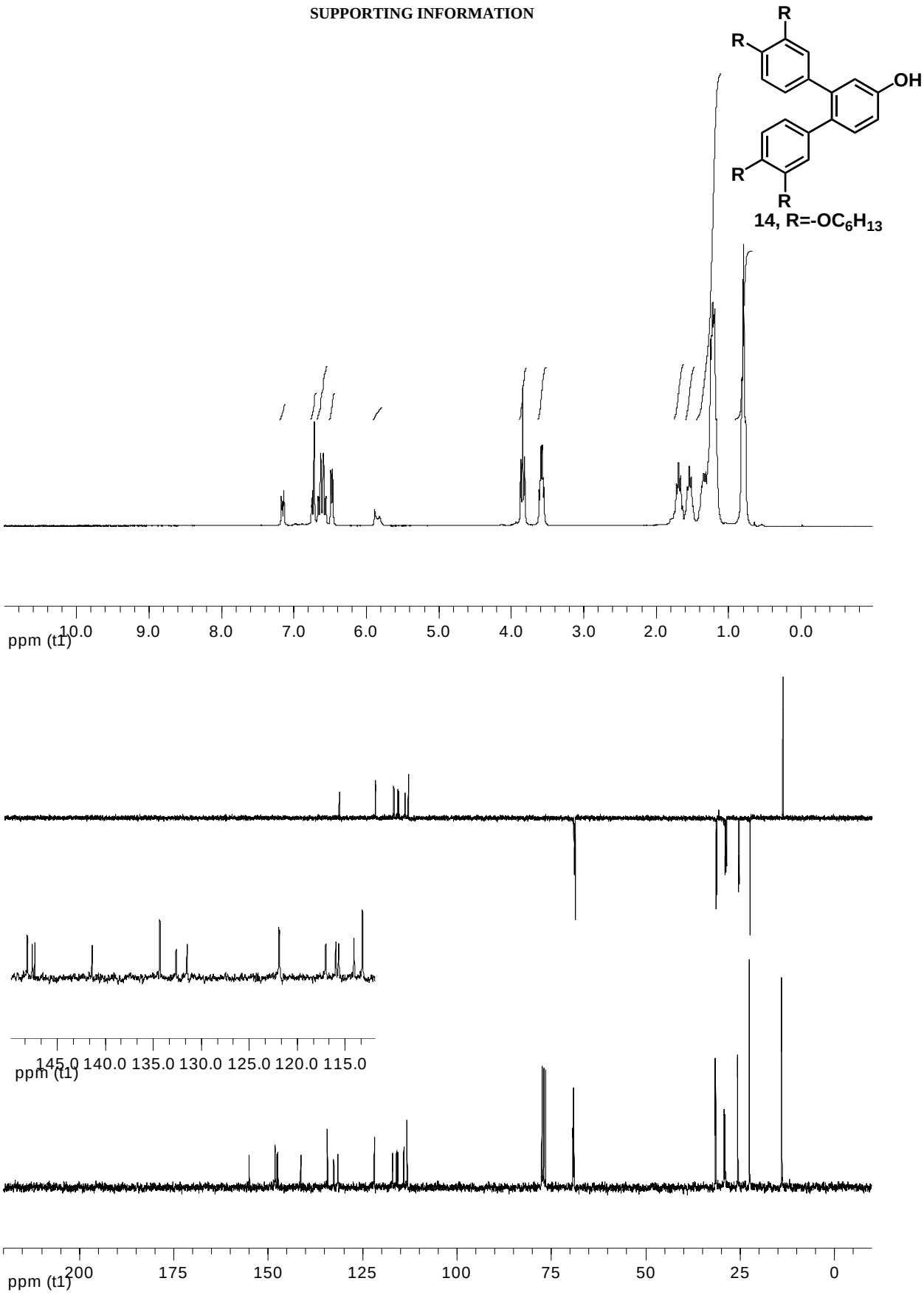

200
175
150
125
100
75
50
25
0
ppm (t1)

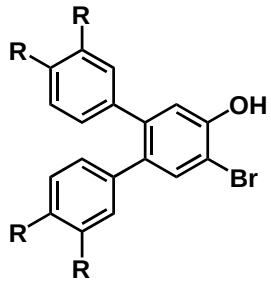

TfO
OAc
Br

11

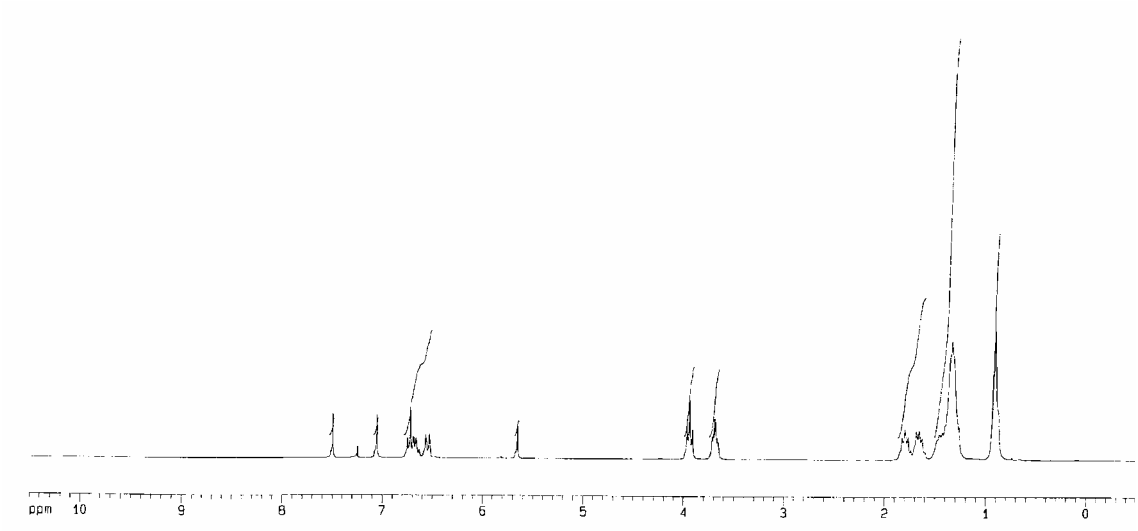

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

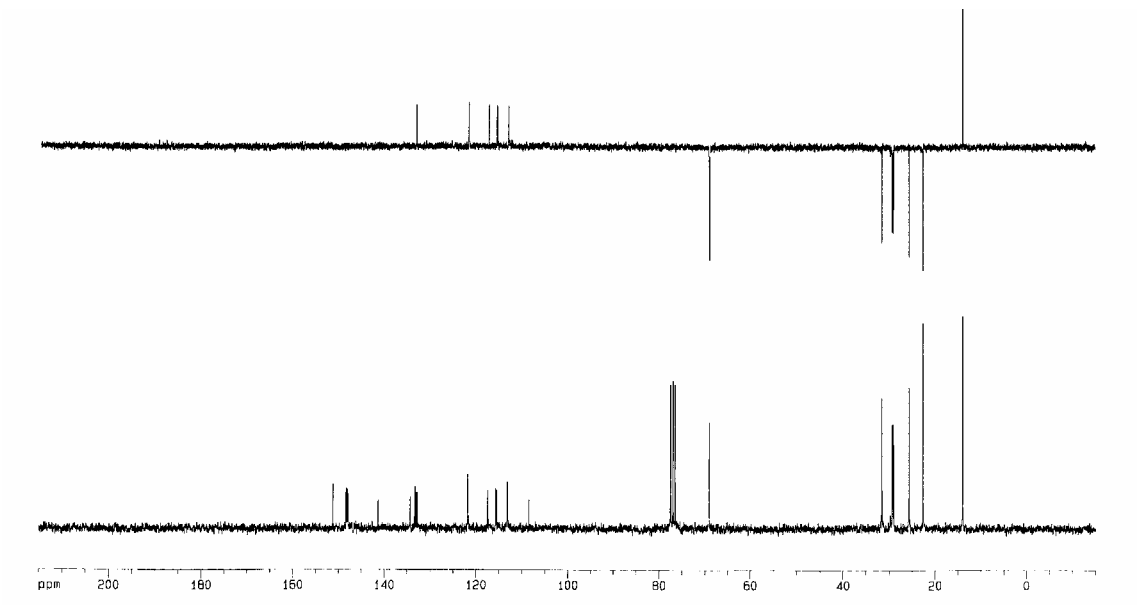

200
175
150
125
100
75
50
25
0
ppm (t1)

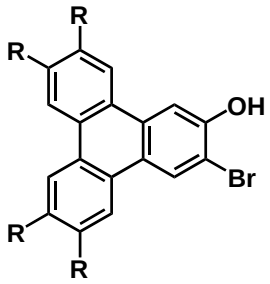

R
R
OH
R
R
14, R=-OC6H13
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
145.0 140.0 135.0 130.0 125.0 120.0 115.0
ppm (t1)
200
175
150
125
100
75
50
25
0
ppm (t1)


R
R
OH
Br
R
R

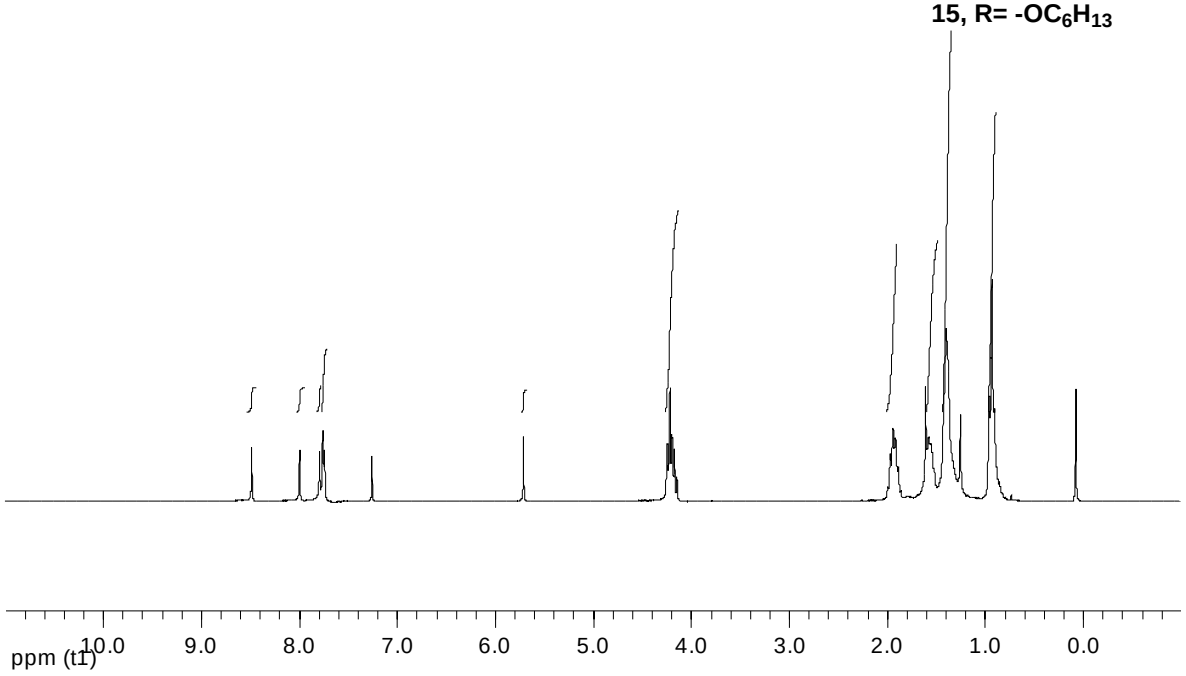
R= -OC_6H_{13}

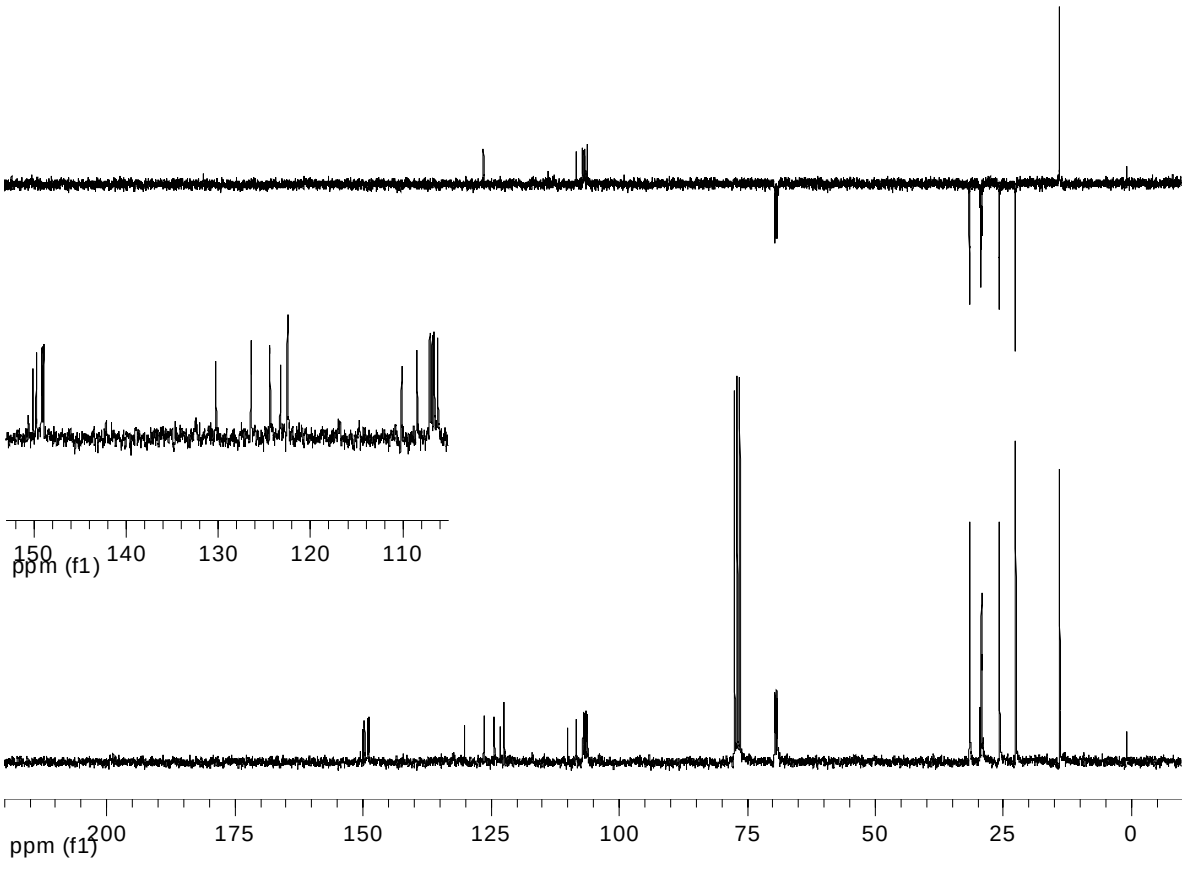

ppm 10 9 8 7 6 5 4 3 2 1 0

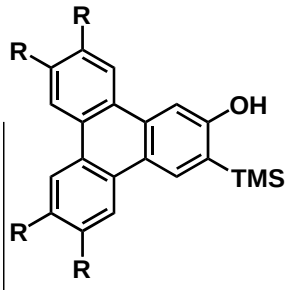

ppm 200 180 160 140 120 100 80 60 40 20 0


R
R
OH
Br
R
R

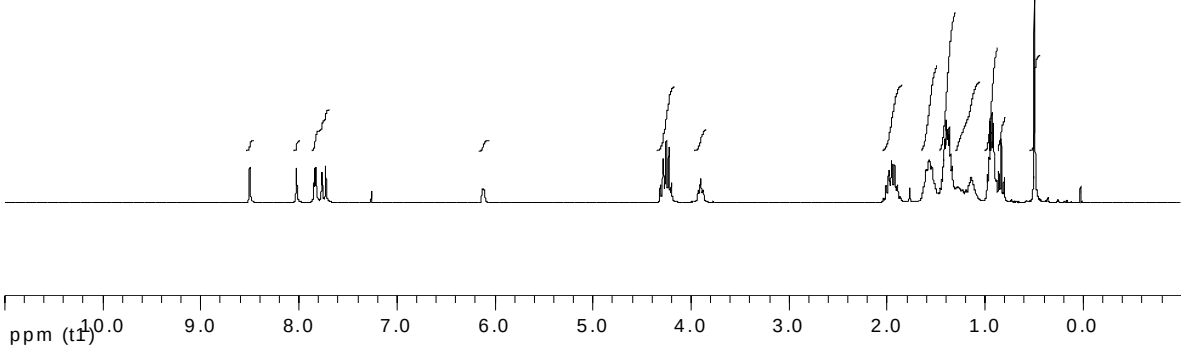
15, R= -OC_6H_{13}

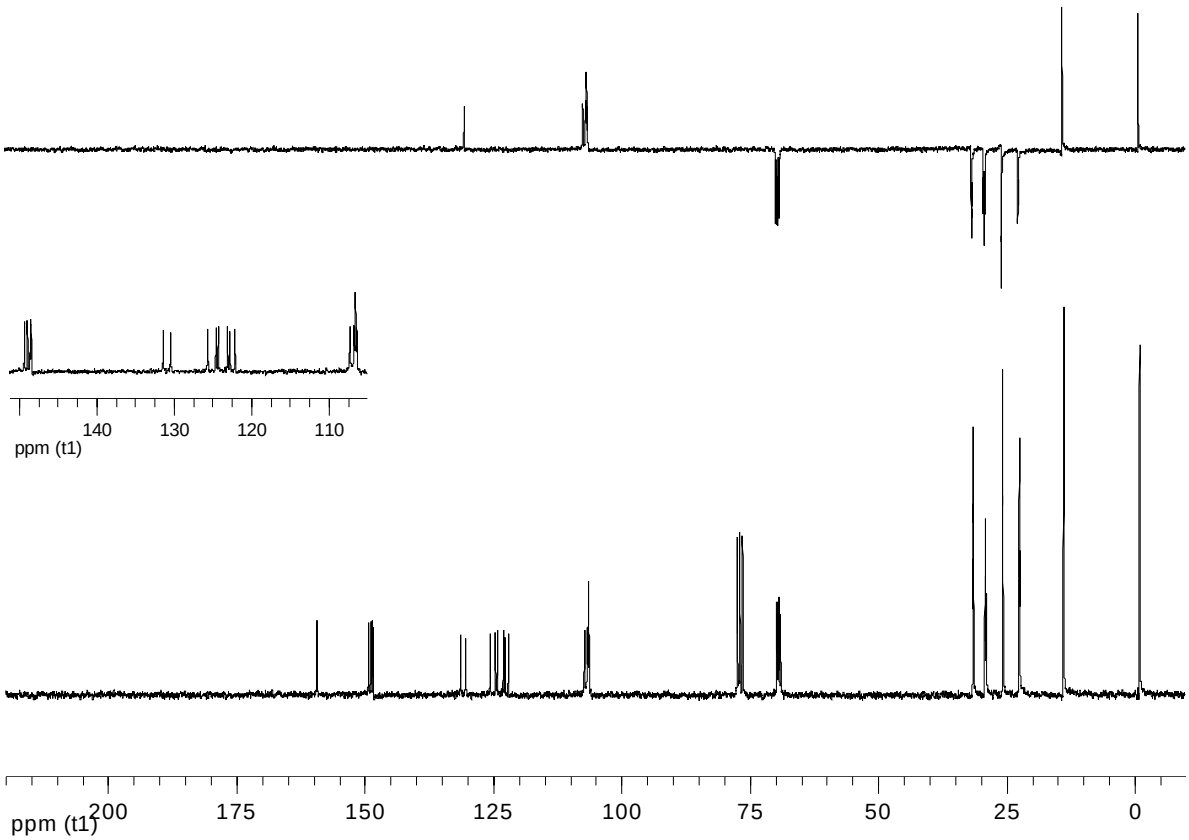

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

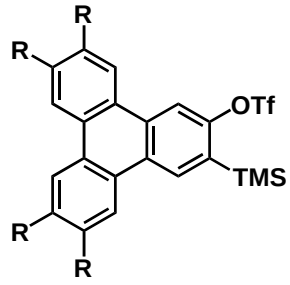

150
140
130
120
110
ppm (f1)
200
175
150
125
100
75
50
25
0
ppm (f1)


R
R
OH
TMS
R
R

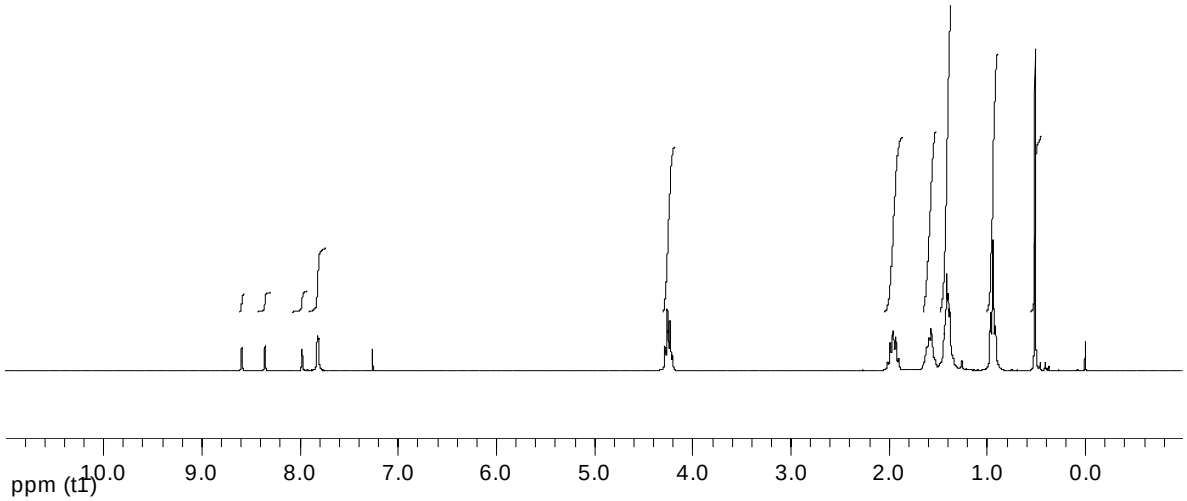
16, R= -OC_6H_{13}

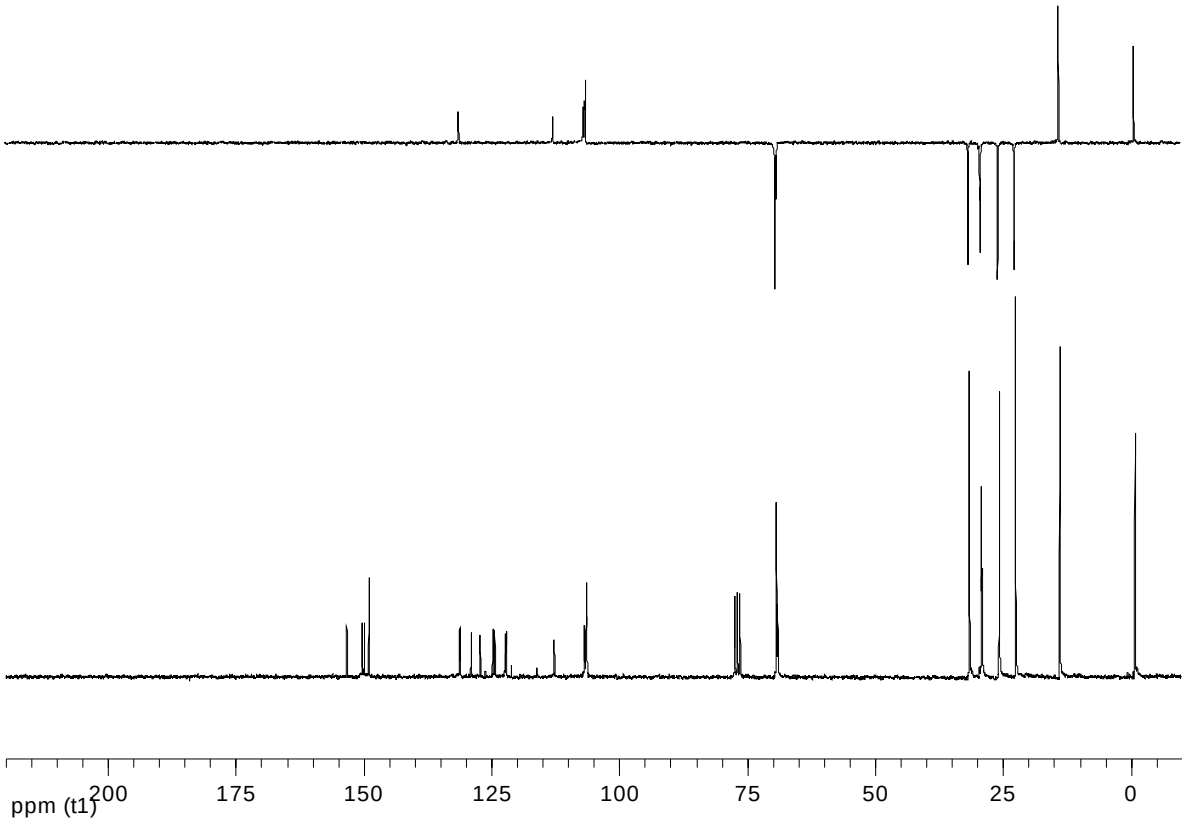

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

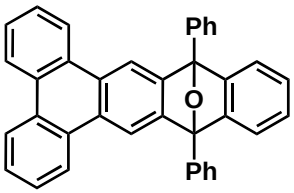

140
130
120
110
ppm (t1)
200
175
150
125
100
75
50
25
0
ppm (t1)


R
R
OTf
TMS
R
R

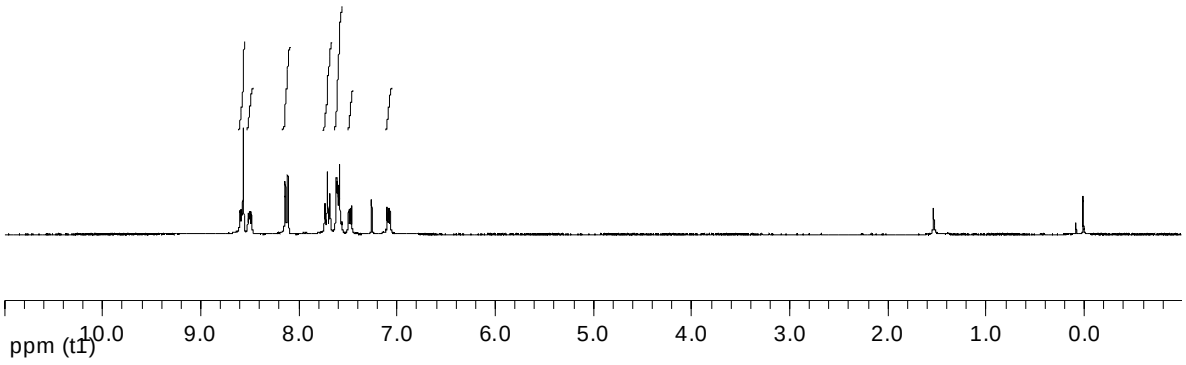
7b, R= -OC_6H_{13}

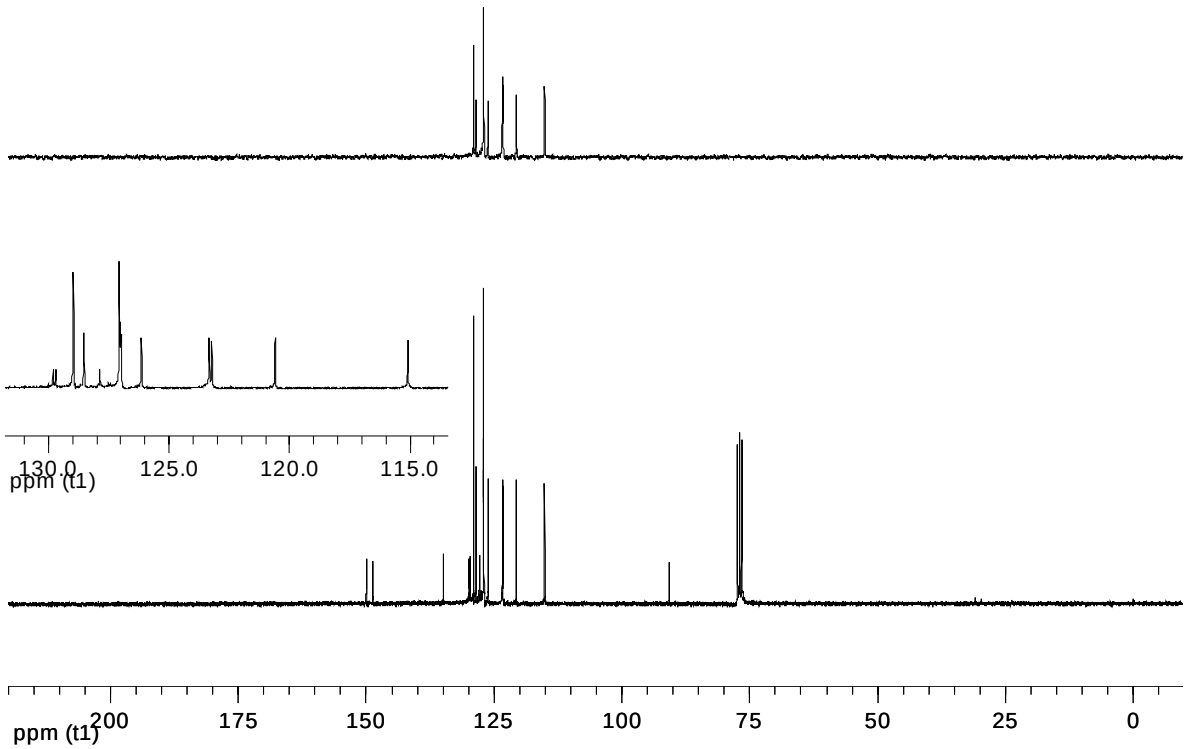

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

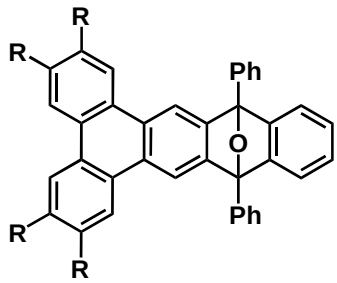

200
175
150
125
100
75
50
25
0
ppm (t1)


Ph
O
Ph

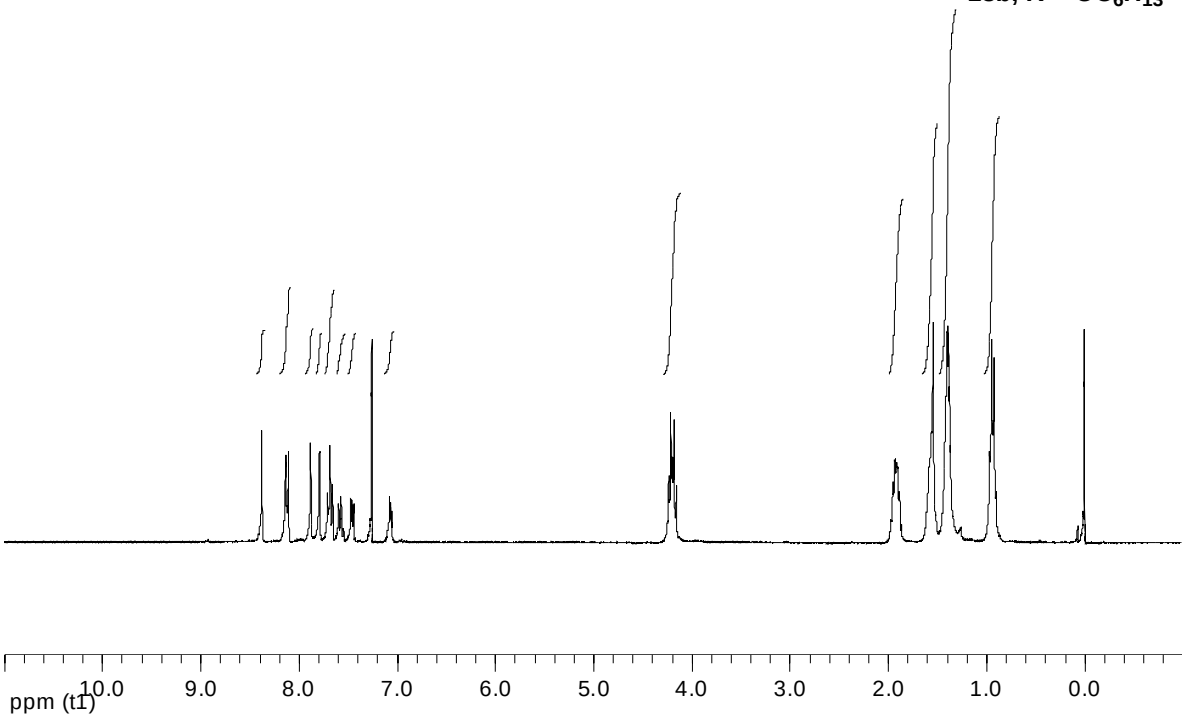
18a

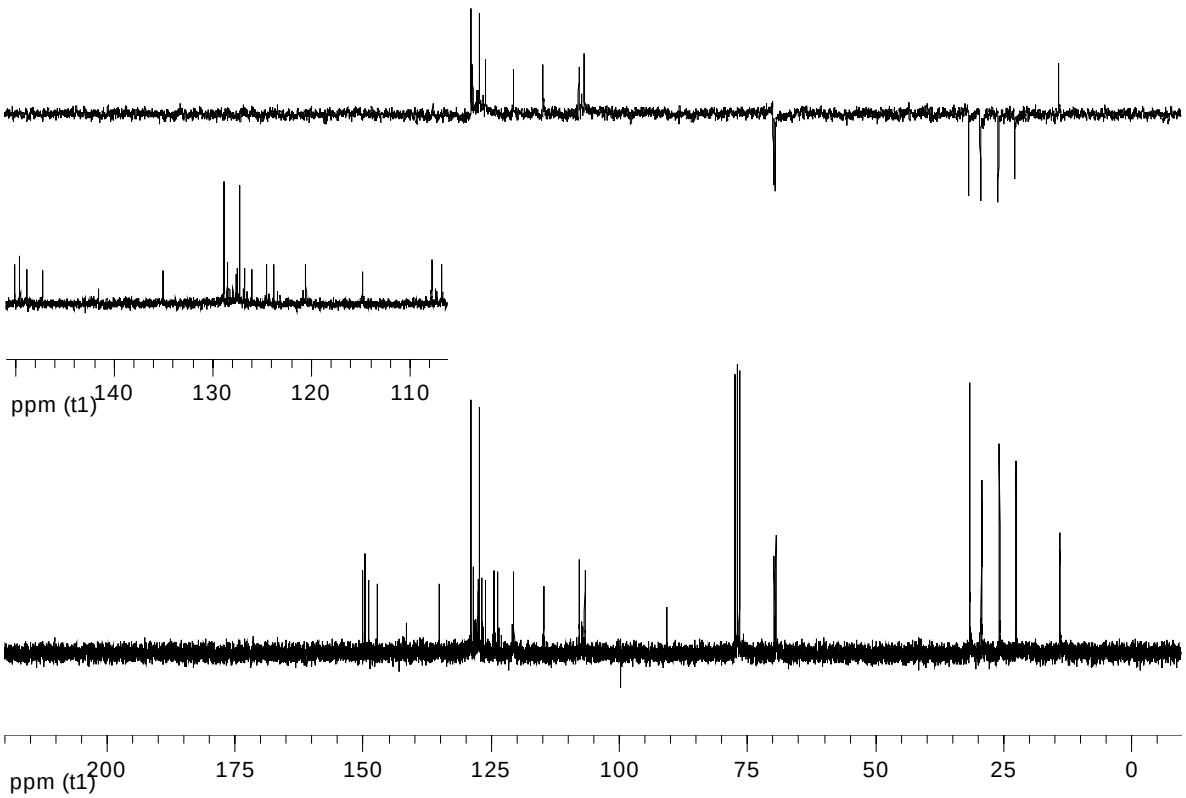

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


130.0
125.0
120.0
115.0
ppm (t1)
200
175
150
125
100
75
50
25
0
ppm (t1)

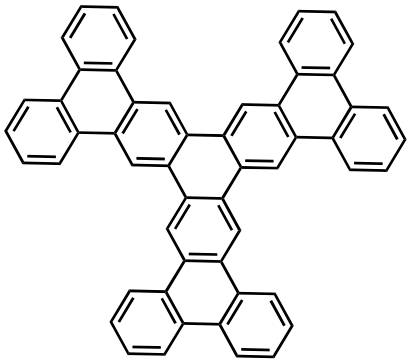


18b, R= -OC_6H_{13}

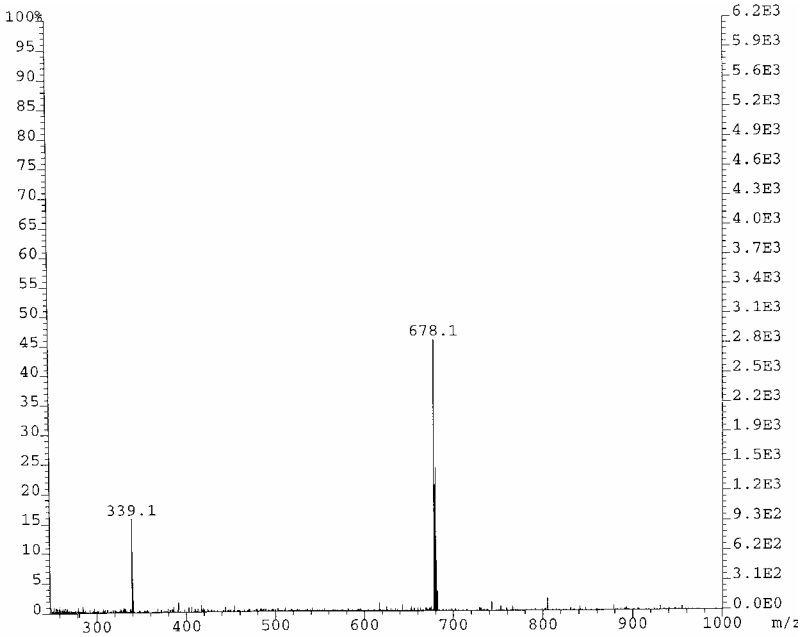


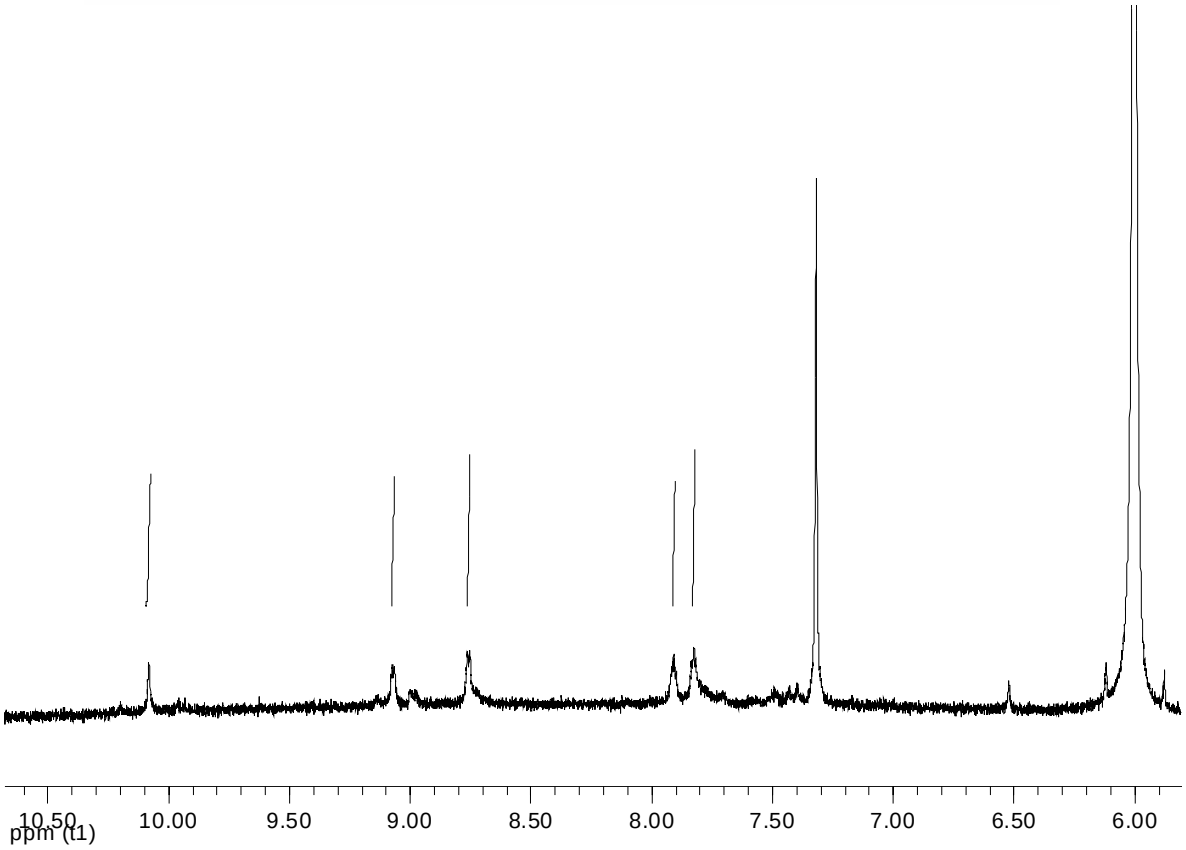


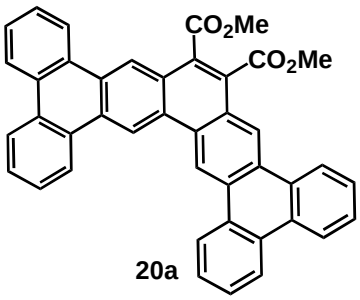
- During ^{13}C-NMR characterization decomposition of compound **18b** in $CDCl_3$ was observed.



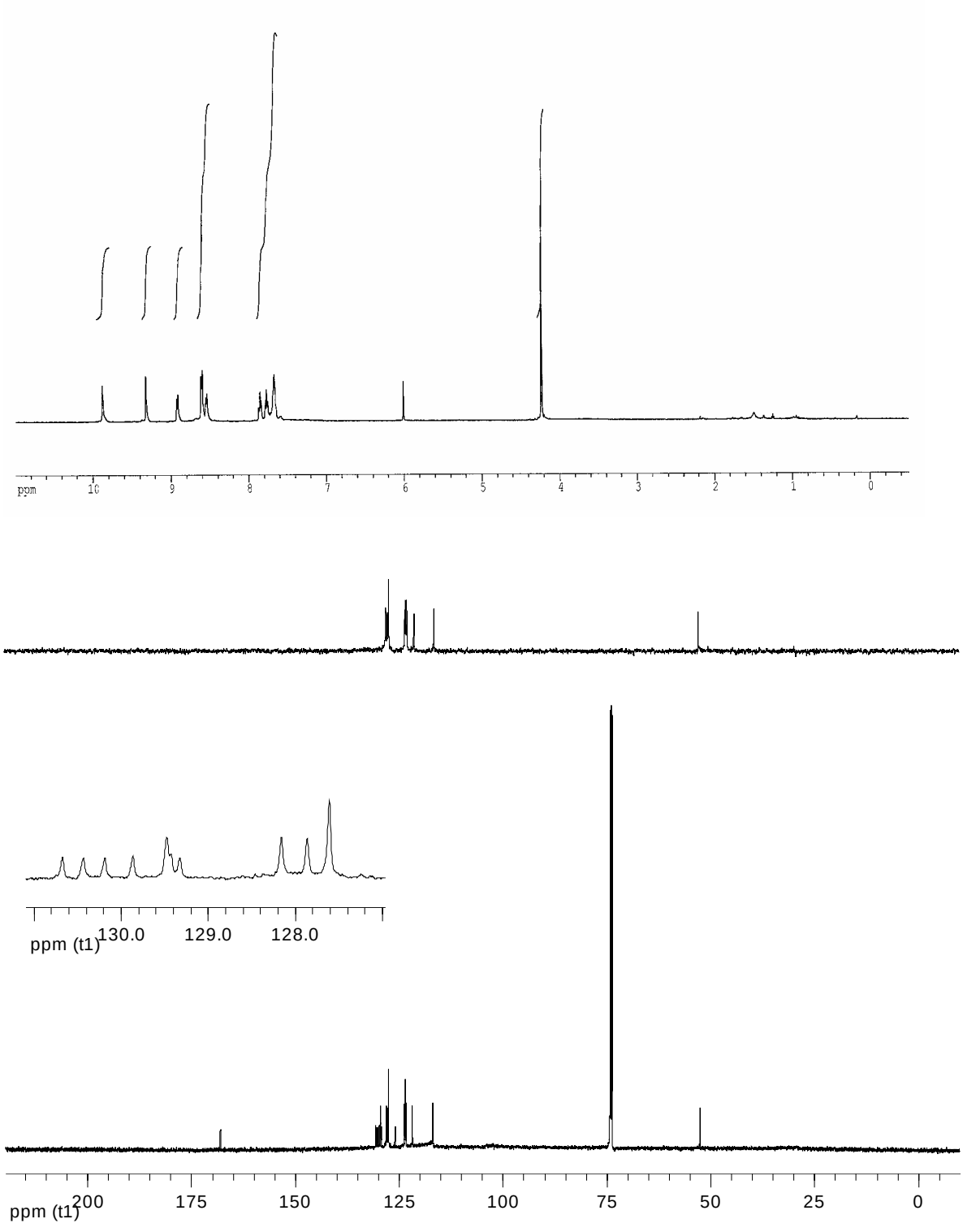
19a

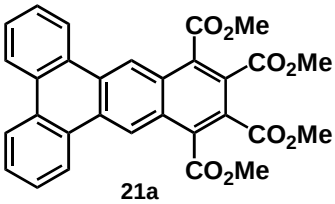

100%
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
678.1
339.1
300
400
500
600
700
800
900
1000
m/z
6.2E3
5.9E3
5.6E3
5.2E3
4.9E3
4.6E3
4.3E3
4.0E3
3.7E3
3.4E3
3.1E3
2.8E3
2.5E3
2.2E3
1.9E3
1.5E3
1.2E3
9.3E2
6.2E2
3.1E2
0.0E0


10.50
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
ppm (t1)

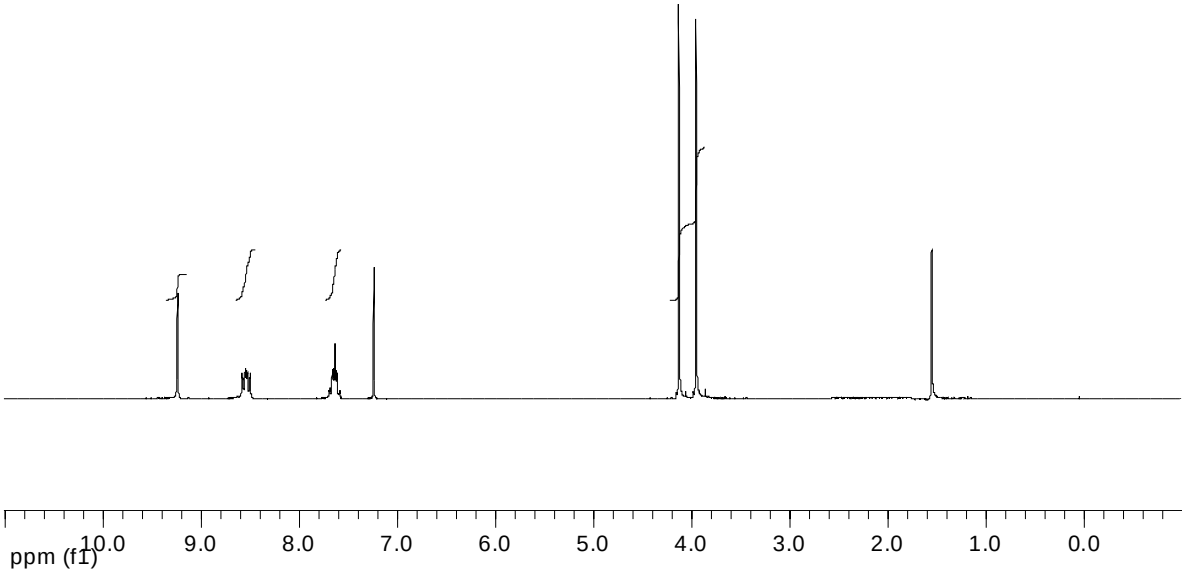

CO2Me
CO2Me

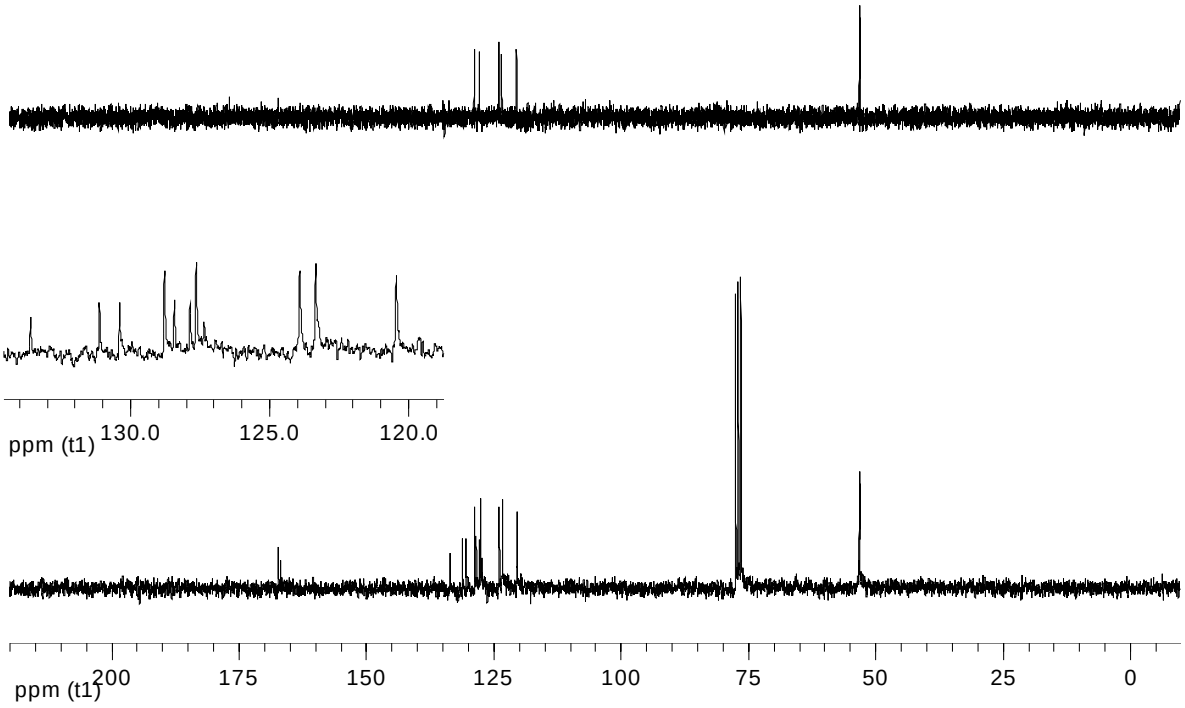
20a

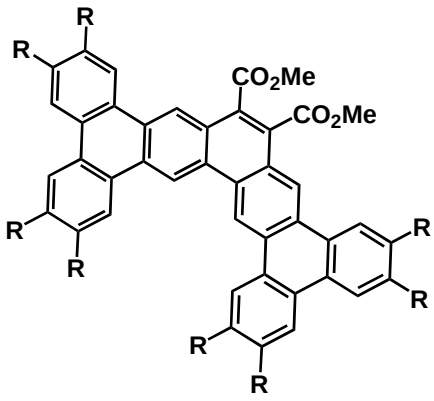

ppm
10
9
8
7
6
5
4
3
2
1
0
ppm (t1)
130.0
129.0
128.0
ppm (t1)
200
175
150
125
100
75
50
25
0


CO2Me
CO2Me
CO2Me
CO2Me

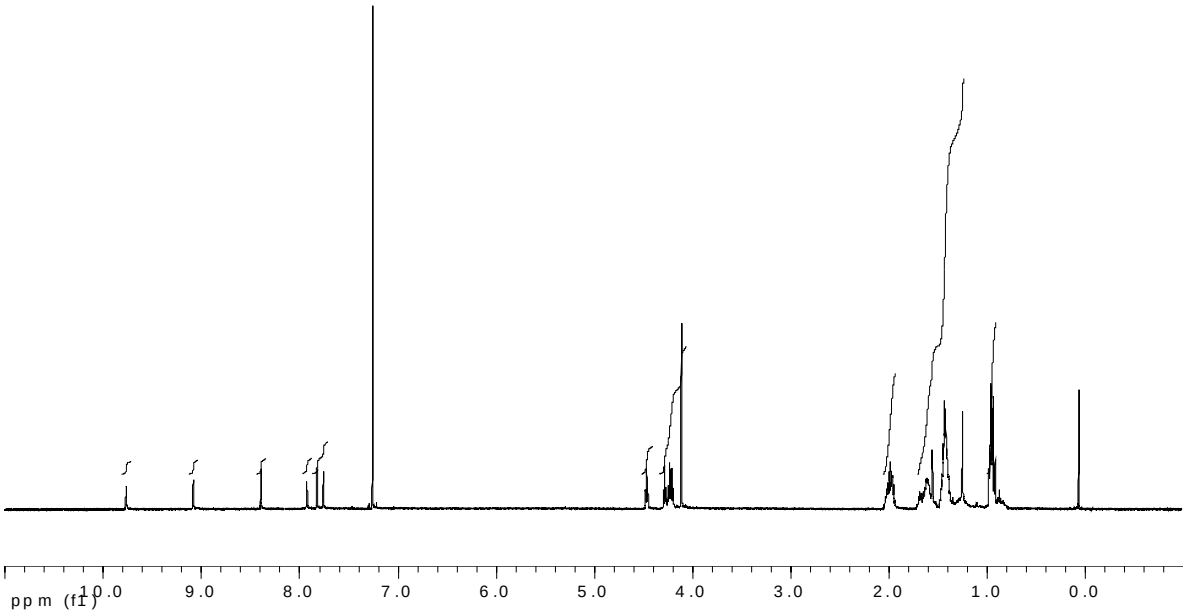
21a

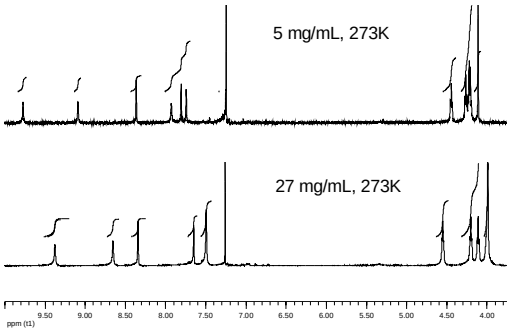

ppm (f1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


ppm (t1)
130.0
125.0
120.0
ppm (t1)
200
175
150
125
100
75
50
25
0

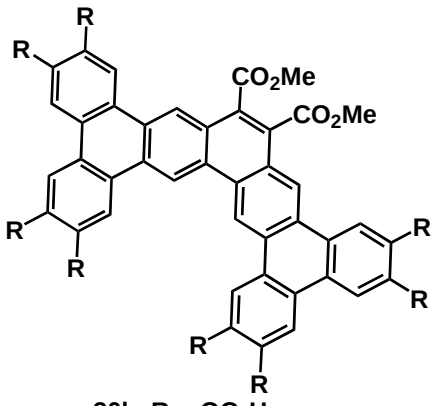


20b, R= -OC_6H_{13}

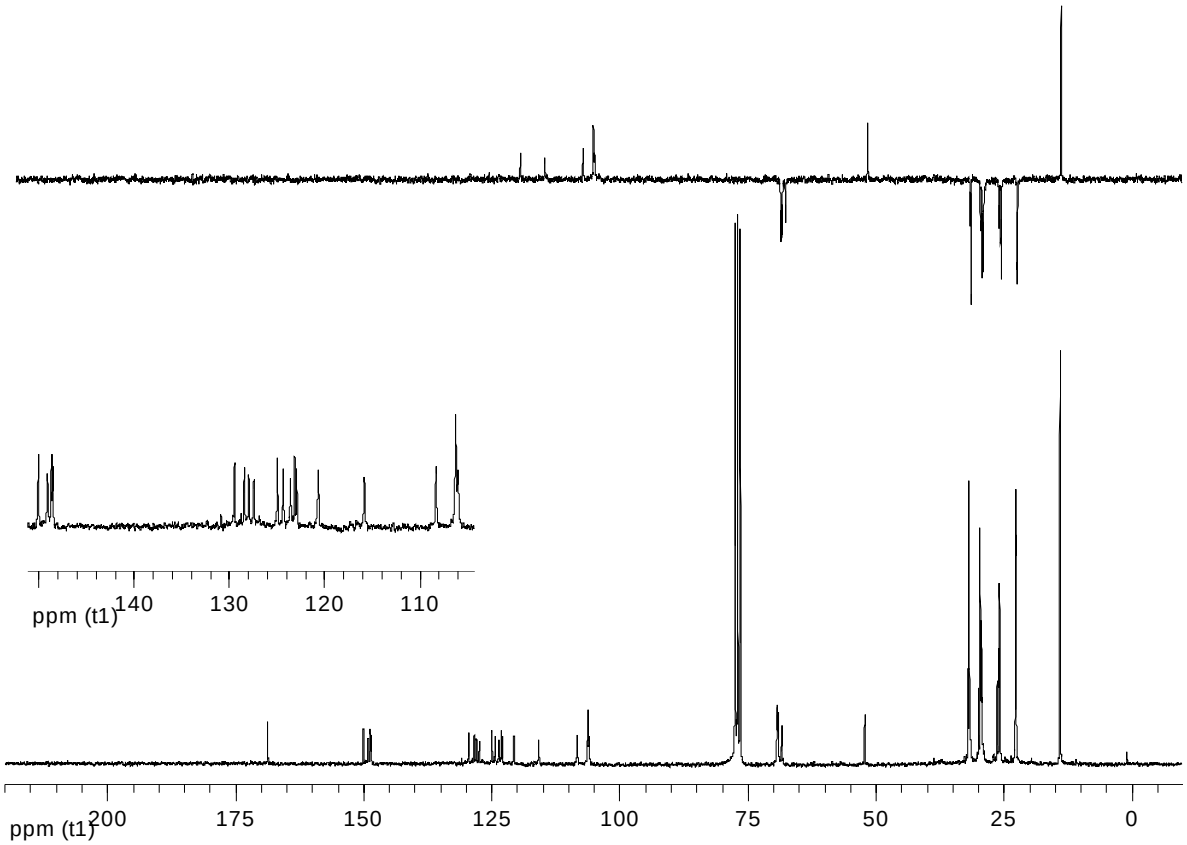


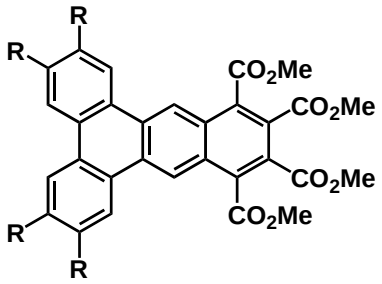


Concentration dependence of the ^{1}H-NMR spectrum of compound **20b** in $CDCl_3$.

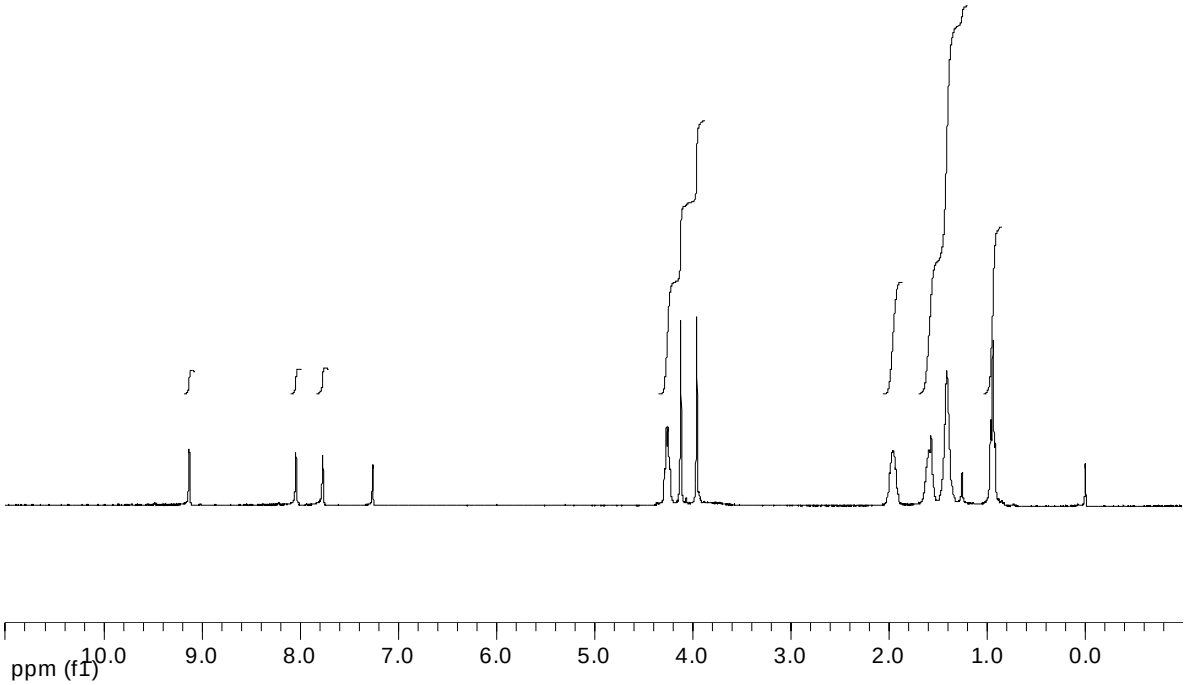

R
R
CO2Me
CO2Me
R
R
R
R
R
R

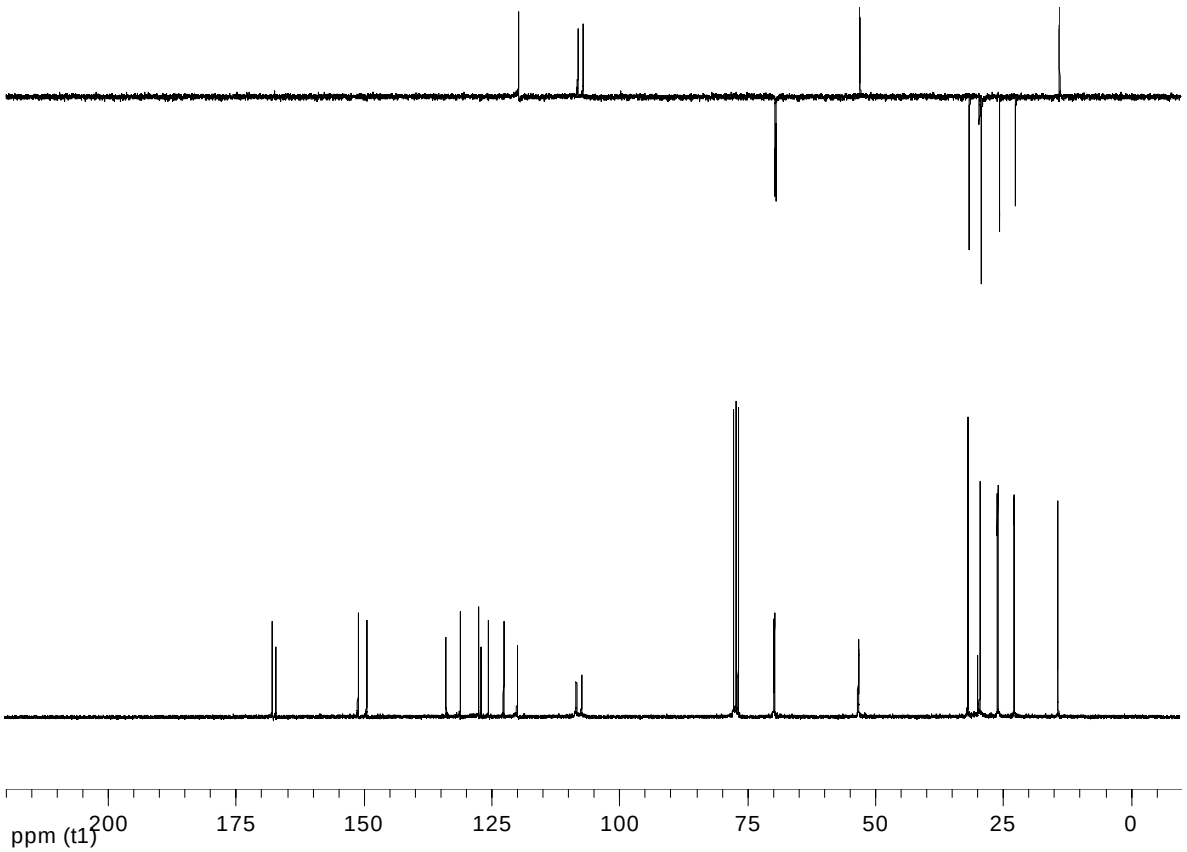
20b, R= -OC_6H_{13}

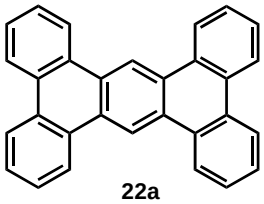

ppm (t1)
140
130
120
110
ppm (t1)
200
175
150
125
100
75
50
25
0


R
R
CO2Me
CO2Me
CO2Me
CO2Me
R
R

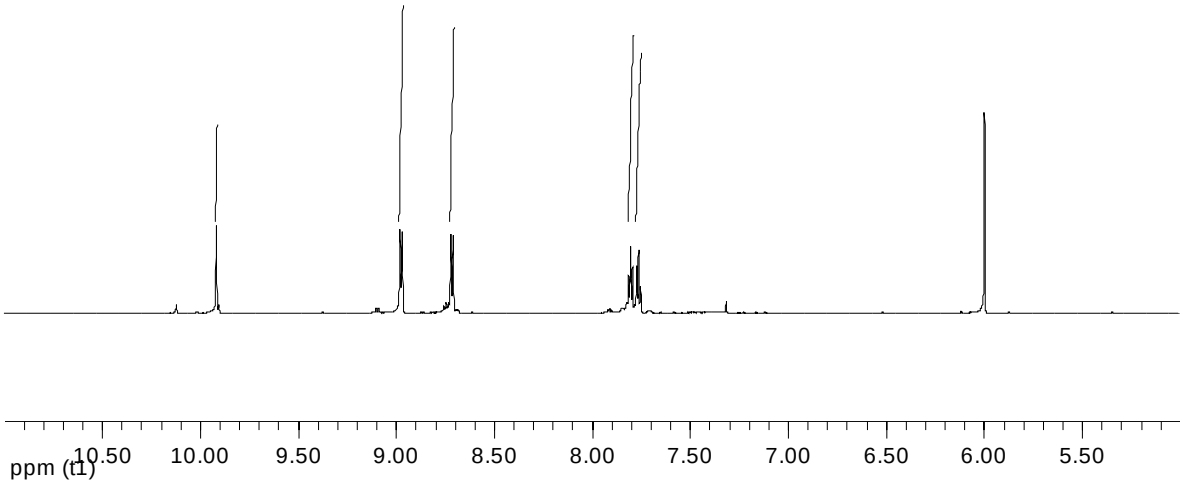
21b, R= -OC_6H_{13}

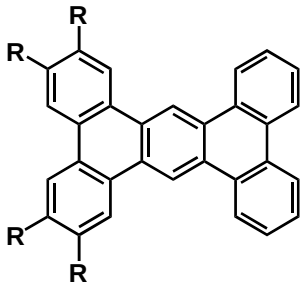

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


200
175
150
125
100
75
50
25
0
ppm (t1)

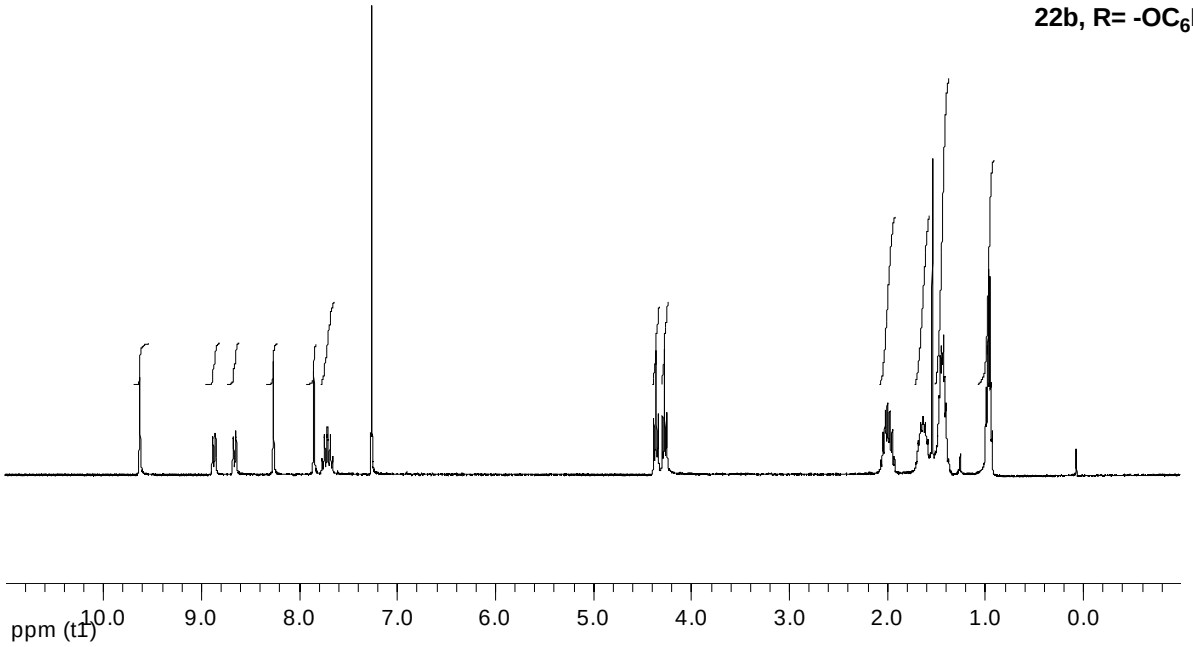


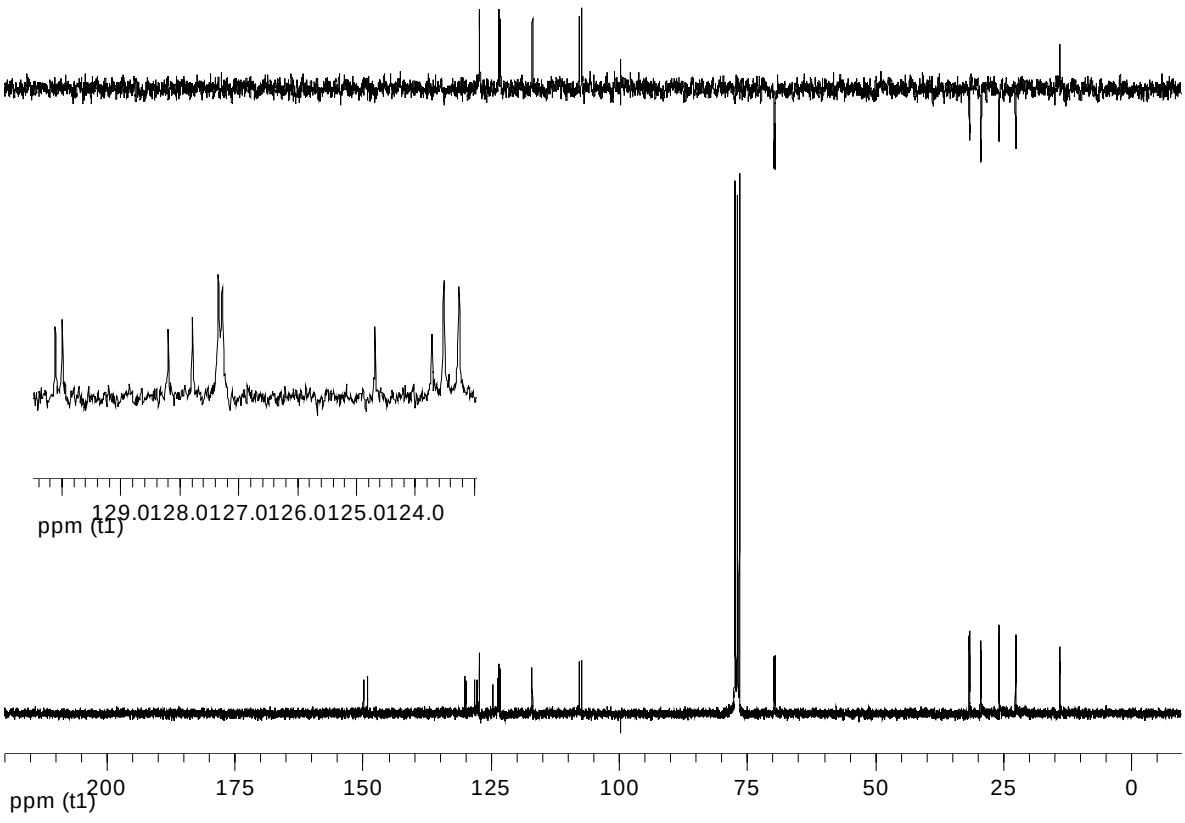
22a

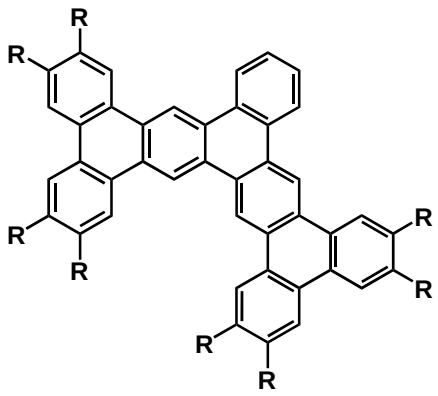



R
R
R
R

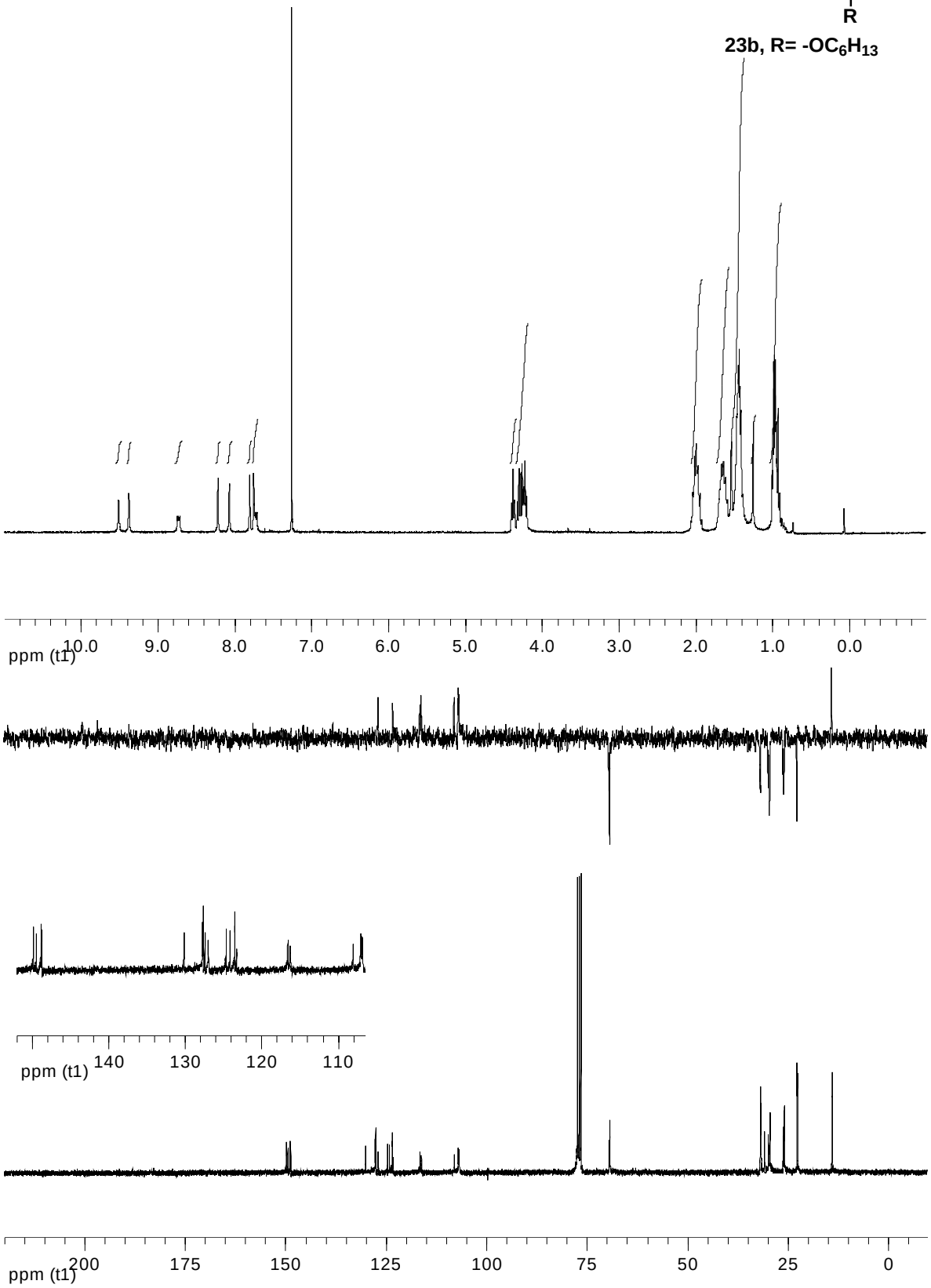
22b, R= -OC_6H_{13}


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


129.0128.0127.0126.0125.0124.0
ppm (t1)
200
175
150
125
100
75
50
25
0
ppm (t1)


R
R
R
R
R
R
R
R

23b, R= -OC_6H_{13}


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
140
130
120
110
ppm (t1)
200
175
150
125
100
75
50
25
0
ppm (t1)