Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

This journal is © The Royal Society of Chemistry 2014

Convenient Access to Readily Soluble Symmetrical Dialkyl-substituted α-Oligofurans

Edward E. Korshin,*[a] Gregory M. Leitus[b] and Michael Bendikov[†a]

[a] *Department of Organic Chemistry, Weizmann Institute of Science, Rehovot 76100, Israel*

E-mails: edward.korshin@weizmann.ac.il; edward.korshin@gmail.com

[b] *Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel*

[†] Deceased July 2, 2013.

Experimental Details

General Methods: ^{1}H and ^{13}C{^{1}H}/DEPT NMR spectra were recorded in $CDCl_3$ or C_6D_6 solutions on a Bruker Avance-500, Bruker AMX-400 or Bruker Avance-300 spectrometers at ambient temperature. The reported ^{1}H NMR chemical shifts (δ) were referenced to the residual solvent peaks whereas ^{13}C chemical shifts were referenced to the central signal of the deuterated solvent;[1] δ values are expressed in ppm relative to TMS (0 ppm). Absolute values of the coupling constants (J) are expressed in Hertz (Hz). The spectra were interpreted according to the first-order analysis. Abbreviations used in the description of NMR data are as follows: br, broad (or broadened); sym, symmetrical; s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet. IR spectra were obtained with a Nicolet-6700 FT-IR instrument in $CHCl_3$ films. UV/Vis spectra were recorded using a Varian Cary 100 spectrophotometer in the double-beam transmission mode (200–800 nm). Steady state fluorescence measurements were performed on a Varian Cary Eclipse fluorimeter. Field desorption (FD) ionization high-resolution mass spectra (HRMS) were recorded on a Waters Micromass GCT Premier mass spectrometer. Electrospray ionization (ESI) low-resolution GC-MS spectra were measured on a Micromass Platform LCZ-4000. Melting points were measured with a TA Q200 Differential Scanning Calorimeter and were corrected. Column flash chromatography (FC) was performed on silica gel 60 (230-400 mesh ASTM) from Merck or on Florisil (100-200 mesh) from Fluka. TLC analysis was performed on Merck silica gel 60 F_{254} plates with UV detection and subsequent charring with alkaline $KMnO_4$ solution or with iodine/SiO_2.

All the reactions were conducted under a positive pressure of dry argon. THF, diethyl ether and toluene were distilled under nitrogen from blue Na/benzophenone ketyl immediately prior to use. HMPA was distilled in vacuum from CaH_2 lumps and was stored under argon over the same drying agent. *n*-Heptyl bromide, *n*-heptyl iodide, 3-furanaldehyde (**2**) and 3-bromofuran (**5**) were used being freshly distilled in vacuum. *n*-Hexyltriphenylphosphonium bromide (**6**),[2] 3-(1,3-dioxolan-2-yl)furan (**9**),[3] 2-tributylstannyl-3-(1,3-dioxolan-2-yl)furan (**10**),[4] 5-tributylstannyl-2,2′-bifuran (**22**),[5] 5-tributylstannyl-2,2′:5′,2″-terfuran (**23**),[5] α-bifuran **26** (n = 1),[6] and α-terfuran **26** (n = 2) were prepared according to the reported procedures.[7] Other commercially available reagents and anhydrous solvents were used as received.

3-*n*-Heptylfuran (3).[8]

a) Synthesis of 3 through Kumada-Corriu cross-coupling of 3-bromofuran (5). To magnesium turnings (340 mg, 14.0 mmol) in dry diethyl ether (15 mL) a solution of *n*-heptyl bromide (2.51 g, 14.0 mmol) in ether (20 mL) was added dropwise to maintain a mild reflux. After completion of the addition the mixture was refluxed for an additional 1 h. Thus generated ethereal solution of *n*-heptylmagnesium bromide was slowly cannulated to a cooled (0 ^{o}C) deep-red suspension of 3-bromofuran (**5**) (1.47 g, 10.0 mmol) and (dppp)$NiCl_2$ (271 mg, 0.5 mmol, 5 mol-%) in ether. The reaction mixture was mildly refluxed for 16 h, cooled to 0 ^{o}C and quenched by a slow addition of 1M aq. solution of NH_4Cl (50 mL). After stirring for 30 min at r.t., the resulting mixture was transferred into a separating funnel, diluted with additional ether (50 mL), pentane (50 mL) and 1M aqueous NH_4Cl solution (50 mL). The organic layer was separated, washed with aq. satd. $NaHCO_3$ (50 mL), brine (30 mL), and dried over $MgSO_4$. Filtration, evaporation at 150 Torr followed by FC on silica gel (pentane) afforded the title product **3** (335 mg, 20%). When for the same cross-coupling 5 mol-% (dppe)$NiCl_2$ was used as a catalyst instead of (dppp)$NiCl_2$, the product **3** was isolated in 24% yield.

b) Synthesis of 3 through halogen-lithium exchange in 3-bromofuran (5) followed by alkylation of 3-lithiofuran. To a cold (-78 ^{o}C) solution of 3-bromofuran (**5**) (3.30 g, 22.5 mmol) in dry THF (15 mL) a solution of *n*-BuLi (14.8 mL of 1.6 M solution in hexane, 23.7 mmol) was added dropwise over 25 min. The reaction mixture was stirred for 1 h at -78 ^{o}C. At that time, a solution of *n*-heptyl iodide (5.28 g, 29.5 mmol) in THF (10 mL) and HMPA (10 mL) was added dropwise. The reaction mixture was stirred at -60 ^{o}C for 14 h and quenched by a cautious addition of acetic acid (15 mL) in ether (50 mL). After warming of the resulting mixture to r.t., it was diluted with water (150 mL) and extracted with ether (3 x 100 mL). The combined organic extract was washed with water (2 x 50 mL), satd. $NaHCO_3$ (50 mL), brine (30 mL), and dried over $MgSO_4$. The solution was filtered, accurately evaporated, and the residue was subjected to FC on silica gel (pentane) to give **3** (1.002 g, 27%).

c) Synthesis of 3 through the Wittig olefination of furan-3-carbaldehyde (2) followed by hydrogenation. *(i) Preparation of E/Z-3-(n-hept-1-ene-1-yl)furan (**7**):* To a well-stirred suspension of *n*-hexyltriphenylphosphonium bromide (**6**) (6.75 g, 15.8 mmol, 1.5 equiv.) in dry THF (40 mL) at -78 ^{o}C was added LDA (8.0 mL of 2M soln in THF-heptane-ethylbenzene). The reaction mixture was allowed to warm to ambient temperature over1.5 h, stirred for 30 min and cooled to -78 ^{o}C. A solution of the aldehyde **2** (1.008 g, 10.50 mmol) in THF (10 mL) was added. The reaction mixture was allowed to warm to ambient temperature and stirred for 14 h.

The reaction mixture was cooled to 0 ^{o}C and quenched by addition of satd. solution NH_4Cl (25 mL). The resulted mixture was diluted with water (150 mL) and extracted with ether (2 x 150 mL). The combined ethereal extract was washed with satd. solution NH_4Cl (50 mL), water (2 x 50 mL), brine (50 mL), dried over Na_2SO_4. Filtration, evaporation at 150 Torr followed by FC on silica gel (pentane) gave 1.61 g of a colorless liquid (R_f 0.46 in hexane), consisted of *E/Z*-3-(hept-1-en-1-yl)furan (**7**) (*E-/Z- ca.* 1:2) and ethylbenzene in molar ratio of 5:2 (according to ^{1}H NMR spectra). ^{1}H NMR ($CDCl_3$, 300 MHz) for **7**: δ 7.40 (dd, $^3J = {}^4J$ = 1.5 Hz, 1H, *Z*-H-5), 7.31 (m, 0.5H, *E*-H-5), 7.23 (br s, 1H, *Z*-H-2), 6.53 (m, 0.5H, *E*-H-4), 6.47 (m, 1H, *Z*-H-4), 6.24 (br d, ^3J = 15.8 Hz, 0.5H, *E*-$C_{Fur}CH$=), 6.16 (br d, ^3J = 11.4 Hz, 1H, *Z*-$C_{Fur}CH$=), 5.96 (dt, ^3J = 15.8 Hz, ^3J = 6.9 Hz, 0.5H, *E*-CH=C*H*CH_2), 5.60 (dt, ^3J = 11.4 Hz, ^3J = 7.0 Hz, 1H, *Z*-CH=C*H*CH_2), 2.28 (dtd, $^3J = {}^3J$ = 7.0 Hz, ^4J = 1.6 Hz, 2H, *Z*-CH=CH-CH_2-CH_2), 2.17 (br td, $^3J = {}^3J$ = 6.9 Hz, 1H, *E*-CH=CH-CH_2-CH_2), 1.54-1.42 (m, 3H, *E*+*Z*-CH_2), 1.41-1.30 (m, 6H, 2 CH_2), 0.92 (t, 4.5H, ^3J = 6.8 Hz, CH_3). ^{13}C/DEPT NMR ($CDCl_3$, 75.5 MHz): δ 143.24 (*E*-CH-5), 142.58 (*Z*-CH-5), 140.72 (*Z*-CH-2), 139.26 (*E*-CH-2), 122.62 (C^3), 119.14 (*E*-$C_{Fur}C$H=), 118.51 (*Z*-$C_{Fur}C$H=), 110.96 (*Z*-CH-4), 107.50 (*E*-CH-4), 31.63 (*Z*-CH_2), 31.41 (*E*-CH_2), 29.23 (*Z*-CH_2), 29.20 (*Z*-CH_2), 29.05 (*E*-CH_2), 28.86 (*E*-CH_2), 22.56 (CH_2), 14.05 (CH_3). GC-MS (ESI): *m/z* (%) 164.1 (100%) $[M]^+$.

*(ii) Hydrogen transfer hydrogenation of E/Z-3-(n-hept-1-ene-1-yl)furan (**7**).* A mixture of the prepared in the previous step **7**, ammonium formate (1.72 g, 27.3 mmol) and 5% Pd/C (115 mg, 0.125 mmol of Pd) in MeOH (60 mL) was gently refluxed for 2 h (TLC monitoring). The reaction mixture was diluted with ether (300 mL) and filtered. Water (150 mL) was added to the filtrate; the ethereal layer was separated, washed with additional water (2 x 50 mL), brine (50 mL), and dried over $MgSO_4$. Filtration, evaporation, and FC of the oily residue (silica gel, pentane) gave the title product **3** (1.147 g, 66% in two steps) as a colorless mobile liquid, R_f 0.50 (hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34 (dd, $^3J = {}^4J$ = 1.6 Hz, 1H, H-5), 7.20 (br s, 1H, H-2), 6.27 (br s, 1H, H-4), 2.40 (br t, ^3J = 7.5 Hz, 2H, $C_{Fur}CH_2$), 1.59-1.51 (m, 2H, CH_2), 1.36-1.24 (m, 8H, 4 CH_2), 0.88 (t, ^3J = 6.9 Hz, 3H, CH_3). ^{13}C/DEPT NMR ($CDCl_3$, 75.5 MHz): δ 142.55 (CH-5), 138.69 (CH-2), 125.34 (C-3), 110.03 (CH-4), 31.81 (CH_2), 30.01 (CH_2), 29.25 (CH_2), 29.10 (CH_2), 24.74 (CH_2), 22.65 (CH_2), 14.09 (CH_3). GC-MS (ESI): *m/z* (%) 166.1 (100%) $[M]^+$.

2-Iodo-3-(1,3-dioxolan-2-yl)furan (11). To a cold (0 ^{o}C) solution of 3-(1,3-dioxolan-2-yl)furan (**9**) (1.269 g, 9.06 mmol) in dry ether (12 mL) a solution of *n*-BuLi (6.2 mL of 1.6M solution in hexane, 9.92 mmol, 1.1 equiv) was added over 5 min. The reaction mixture was stirred for additional 30 min at 0 ^{o}C, for 2 h at ambient temperature and cooled to -78 ^{o}C. A solution of iodine (2.512 g, 9.92 mmol, 1.1 equiv) in dry THF (20 mL) was added dropwise upon shaking of the reaction flask. The reaction mixture was allowed to warm to r.t. over 2 h, and was stirred at r.t. for 3 h. The mixture was poured into 10% aqueous solution $Na_2S_2O_3$ (150 mL) and extracted with EtOAc-hexane (1:1, 2 x 100 mL). The organic extract was washed with additional 10% $Na_2S_2O_3$ (50 mL), water (50 mL), brine (50 mL) and dried over Na_2SO_4. Filtration followed by evaporation afforded an oily residue, which was subjected to FC on silica gel (dichloromethane/benzene/hexane, 4:3:8) to recover the starting **9** (70 mg, 5.5%) and to give the title iodide **11** (1.295 g, 57% based on the consumed **9**) as a yellowish oil, R_f 0.18 (dichloromethane-benzene-hexane = 4 : 3 : 8). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, ^{3}J = 2.0 Hz, 1H, H-5), 6.47 (d, ^{3}J = 2.0 Hz, 1H, H-4), 5.62 (br s, 1H, O-HC-O), 4.16-3.96 (sym m, 4H, OCH_2CH_2O). ^{13}C/DEPT NMR ($CDCl_3$, 100.6 MHz): δ 148.15 (CH-5), 128.54 (C-3), 110.54 (CH-4), 99.30 (O-CH-O), 90.64 (C-2), 65.27 (2 CH_2O). HRMS (FD): calcd. for $C_7H_7IO_3$ $[M]^+$ 265.9440; found 265.9434.

3,3'-Di(1,3-dioxolan-2-yl)-2,2'-bifuran (12) and 3'-(1,3-dioxolan-2-yl)-[2,2'-bifuran]-3-carbaldehyde (13).

a) Synthesis through the Stille cross-coupling of 2-iodofuran 11 with 2-tributylstannylfuran (10). A mixture of 2- iodofuran **11** (332 mg, 1.25 mmol), 2-stannylfuran **10** (782 mg, 1.82 mmol, 1.45 equiv.) and $(Ph_3P)_4Pd$ (72 mg, 0.062 mmol, 5mol-%) in dry toluene (8 mL) was refluxed for 8 h. The resulted mixture was evaporated, and the residue was subjected to sequential FC on silica gel (gradient elution, from hexane to 40% EtOAc/hexane) to give the acetal-dimer **12** (187 mg, 54%).

b) Synthesis through the Ullmann homocoupling of 2-iodofuran 11. A heterogeneous mixture of **11** (118 mg, 0.443 mmol), $(dppp)NiCl_2$ (73 mg, 0.0135 mmol, 30 mol-%), potassium iodide (150 mg, 0.90 mmol, 2 equiv.) and zinc powder (116 mg, 1.774 mmol, 4 equiv.) in dry HMPA (2.0 mL) was heated at 100-110 ^{o}C for 14 h. The reaction mixture was poured in water (40 mL) and extracted with 40% EtOAc/hexane (2 x 40 mL). The extract was washed with additional water (20 mL), brine (20 mL) and dried over $MgSO_4$. The solution was filtered, evaporated and subjected to FC on silica gel (gradient elution, from 5% to 40% EtOAc/hexane) to give the less

polar aldehyde-acetal dimer **13** (3.5 mg, 6%) and the more polar acetal-dimer **12** (12.5 mg, 20%).

Acetal-dimer 12. A colorless solid; m.p. 120-121 ^{o}C; R_f 0.26 (EtOAc-hexane = 2 : 3). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.44 (d, ^{3}J = 2.0 Hz, 2H, H-5,5'), 6.60 (d, ^{3}J = 2.0 Hz, 2H, H-4,4'), 6.20 (s, 2H, 2 O-HC-O), 4.18-3.98 (sym m, 8H, 2 OCH_2CH_2O). ^{13}C/DEPT NMR ($CDCl_3$, 125.8 MHz): δ 143.57 (C-2,2'), 142.58 (CH-5,5'), 121.12 (C-3,3'), 110.04 (CH-4,4'), 97.63 (2 O-CH-O), 65.30 (4 CH_2O) ppm. The assignment was supported by COSY, HSQC and HMBC NMR experiments. HRMS (FD): calcd. for $C_{14}H_{14}O_6$ $[M]^+$ 278.0790; found 278.0797.

Aldehyde-acetal dimer 13. A yellowish solid; m.p. 89-91 ^{o}C, R_f 0.30 (EtOAc-hexane = 2 : 3). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.41 (br s, 1H, HC=O), 7.54 (br d, ^{3}J = 1.8 Hz, 1H, H-5'), 7.44 (dd, ^{3}J = 2.0 Hz, ^{5}J = 0.8 Hz, 1H, H-5), 6.88 (br d, ^{3}J = 2.0 Hz, 1H, H-4), 6.70 (br d, ^{3}J = 1.8 Hz, 1H, H-4'), 6.29 (s, 1H, O-HC-O), 4.20-4.02 (sym m, 4H, OCH_2CH_2O). ^{13}C/DEPT NMR ($CDCl_3$, 125.8 MHz): δ 186.13 (CH=O), 151.23 (C-2), 144.23 (CH-5'), 143.20 (CH-5), 142.85 (C-2'), 124.58 (C-3'), 124.10 (C-3), 110.99 (CH-4'), 108.81 (CH-4), 97.25 (O-CH-O), 65.47 (2 CH_2O). The assignment was supported by COSY, HSQC and HMBC NMR experiments. IR (CH_2Cl_2): ν 3157 (w), 3131 (w), 3060 (w), 2959 (m), 2929 (w), 2891 (m), 1673 (vs) (C=O), 1481 (m, br), 1397 (m), 1172 (s), 1116 (s, br), 1077 (s), 1033 (s), 888 (s) cm^{-1}. HRMS (FD): calcd. for $C_{12}H_{10}O_5$ $[M]^+$ 234.0528; found 234.0534.

5,5'''-Dibromo-3'',4'-di-*n*-heptyl-2,2':5',2'':5'',2'''-quaterfuran (19).

To a solution of quaterfuran **17** (223 mg, 0.482 mmol) in benzene (4 mL) and CH_2Cl_2 (1 mL) solid NBS (175 mg, 0.983 mmol, 2.04 equiv.) was added in one portion. The reaction mixture was stirred at r.t. for 2 h being protected from a direct light. At that time, TLC showed complete consumption of the starting **17** and formation of the less polar dibromide **19**. Subsequent work up as in the synthesis of dibromobifuran **15** and FC on silica gel (hexane) afforded the title dibromoquaterfuran **19** (172 mg, 58%) as unstable yellow-orange solid; R_f 0.35 (hexane). ^{1}H NMR (C_6D_6, 500 MHz): δ 6.40 (s, 2H, H-3',4''), 6.27 (d, ^{3}J = 3.4 Hz, 2H), 5.96 (d, ^{3}J = 3.4 Hz, 2H), 2.69 (t, ^{3}J = 7.6 Hz, 4H, 2 CH_2C_{Fur}), 1.58 (br tt, $^{3}J \approx {}^{3}J$ = 7.4 Hz, 4H, 2 CH_2-CH_2C_{Fur}), 1.39-1.33 (sym. m, 4H, 2 CH_2), 1.32-1.19 (m, 12H, 6 CH_2), 0.89 (t, ^{3}J = 7.0 Hz, 6H, 2 CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ = 148.83 (2 C), 144.23 (2 C), 142.17 (2 C), 125.28 (2 C), 121.78 (2 CH), 113.52 (2 CH), 32.26 (2 CH_2), 30.49 (2 CH_2), 29.83 (2 CH_2), 29.71 (2 CH_2), 25.52 (2 CH_2),

23.05 (2 CH_2), 14.32 (2 CH_3). HRMS (FD): calcd. for $C_{30}H_{36}{}^{79}Br^{81}BrO_4$ $[M]^+$ 620.0960; found 620.0952 (correct isotope pattern).

Preparation of 3''',4''-di-*n*-heptyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':sexifuran (20) through the Stille cross-coupling of dibromoquaterfuran 19. A solution of the dibromide **19** in benzene (3 mL) and CH_2Cl_2 (1 mL) was generated from the quaterfuran **17** (167 mg, 0.361 mmol) and NBS (131 mg, 0.735 mmol, 2.04 equiv.) as described above. Dry toluene (5 mL) and 2-tributylstannylfuran (**16**) (775 mg, 2.17 mmol, 6.0 equiv.) were added, and the solution was concentrated in vacuo at r.t. to *ca.* 5-6 mL volume. The concentrate was thoroughly flashed with argon, and $(Ph_3P)_4Pd$ (42 mg, 0.0365 mmol, 10 mol%) was added. The reaction mixture was gently refluxed for 12 h and evaporated. Sequential FC on silica gel (gradient elution, from hexane to 3% EtOAc in hexane) followed by FC on Et_3N-pretreated silica gel (hexane) afforded the sexifuran **20** (25 mg, 12% in two steps from **17**).

Diheptyl sexifuran 20. A yellow solid; m.p. 109-110 ^oC; R_f 0.25 (benzene-hexane = 1 : 10). ^1H NMR (C_6D_6, 400 MHz): δ 7.02 (dd, ^3J = 1.8 Hz, ^4J = 0.5 Hz, 2H, H-5,5''''), 6.60 (s, 2H, H-3'',4'''), 6.57 (br d, ^3J = 3.4 Hz, 2H, H-3,3''''), 6.56 (d, ^3J = 3.5 Hz, 2H, H-3''',4'), 6.54 (d, ^3J = 3.5 Hz, 2H, H-3',4''''),6.09 (dd, ^3J = 3.4 Hz, ^3J = 1.8 Hz, 2H, H-4,4''''), 2.81 (t, ^3J = 7.6 Hz, 4H, CH_2C_{Fur}), 1.66 (br tt, $^3J \approx {}^3J$ = 7.4 Hz, 4H, C*H*$_2$-CH_2C_{Fur}), 1.44-1.38 (sym m, 4H, 2 CH_2), 1.34-1.20 (m, 12H, 6 CH_2), 0.87 (t, ^3J = 6.9 Hz, 6H, 2 CH_3). ^{13}C/DEPT NMR (C_6D_6, 100.6 MHz): δ 146.84 (C-2,2''''), 146.41 (2 C), 146.30 (2 C), 145.02 (C-2'',5'''), 142.45 (C-2''',5''), 142.19 (CH-5,5''''), 125.29 (C-3''',4''), 111.72 (CH-4,4''''), 109.65 (CH-3'',4'''), 107.56 (CH-3',4''''), 107.27 (CH-3''',4'), 105.77 (CH-3,3''''), 32.21 (2 CH_2), 30.61 (2 *C*H_2-CH_2C_{Fur}), 29.86 (2 CH_2), 29.58 (2 CH_2), 25.70 (2 *C*H_2C_{Fur}), 23.04 (2 CH_2), 14.28 (2 CH_3). The assignment was supported by COSY, HSQC and HMBC NMR experiments. UV/Vis (1,4-dioxane): λ_{abs} 406, 448 (sh) nm. Fluorescense spectrum (1,4-dioxane): λ_{em} 446, 475 nm. HRMS (FD): calcd. for $C_{38}H_{42}O_6$ $[M]^+$ 594.2981; found 594.2971.

Single crystal X-ray study.[9]

Crystal data for 4. $C_{10}H_6O_4$, colorless, 0.04x0.06x0.08 mm^3, monoclinic, $P2_1/c$ (No.14), a= 6.1142(12) Å, b= 12.283(3) Å, c= 5.6061(11) Å, β=107.70(3)^o from 20 degrees of data, T=120(2) K, V= 401.09(16) $Å^3$, Z=2, *F*w=190.15 g/mol, *D*c=1.574 g/cm^3, μ=0.124 mm^{-1}. The suitable for single crystal X-ray study sample was prepared by recrystallization from EtOAc-hexane.

X-Ray data collection and processing. X-ray diffraction data for suitable single crystals of **4** were collected on a Bruker Appex2 KappaCCD diffractometer, MoKα (λ=0.71073Å), graphite monochromator, 8956 reflections collected, -8≤h≤8, -16≤k≤16, -7≤l≤7, frame scan width = 0.5°, scan speed 1.0° per 60 sec, typical peak mosaicity 0.53°, 2073 independent reflections (R-int =0.0200). The data were processed with APEX2.

Solution and refinement. Structure was solved by direct methods with SHELXS. Full matrix least-squares refinement is based on F^2 with SHELXL-97. 76 Parameters with 0 restraints, final R_1= 0.0308 (based on F^2) for data with I>2σ(I), R_1= 0.0334 on 987 reflections, goodness-of-fit on F^2 = 1.069, largest electron density peak = 0.367 e/$Å^{-3}$, deepest hole = -0.186 e/$Å^{-3}$.

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
O(1)	3591(1)	6282(1)	-9(1)	19(1)
O(2)	2068(1)	3478(1)	4621(1)	25(1)
C(2)	4196(1)	5225(1)	571(2)	16(1)
C(3)	3078(1)	4826(1)	2180(2)	16(1)
C(4)	1708(2)	5708(1)	2624(2)	18(1)
C(5)	2067(2)	6556(1)	1267(2)	20(1)
C(6)	3148(2)	3729(1)	3202(2)	19(1)

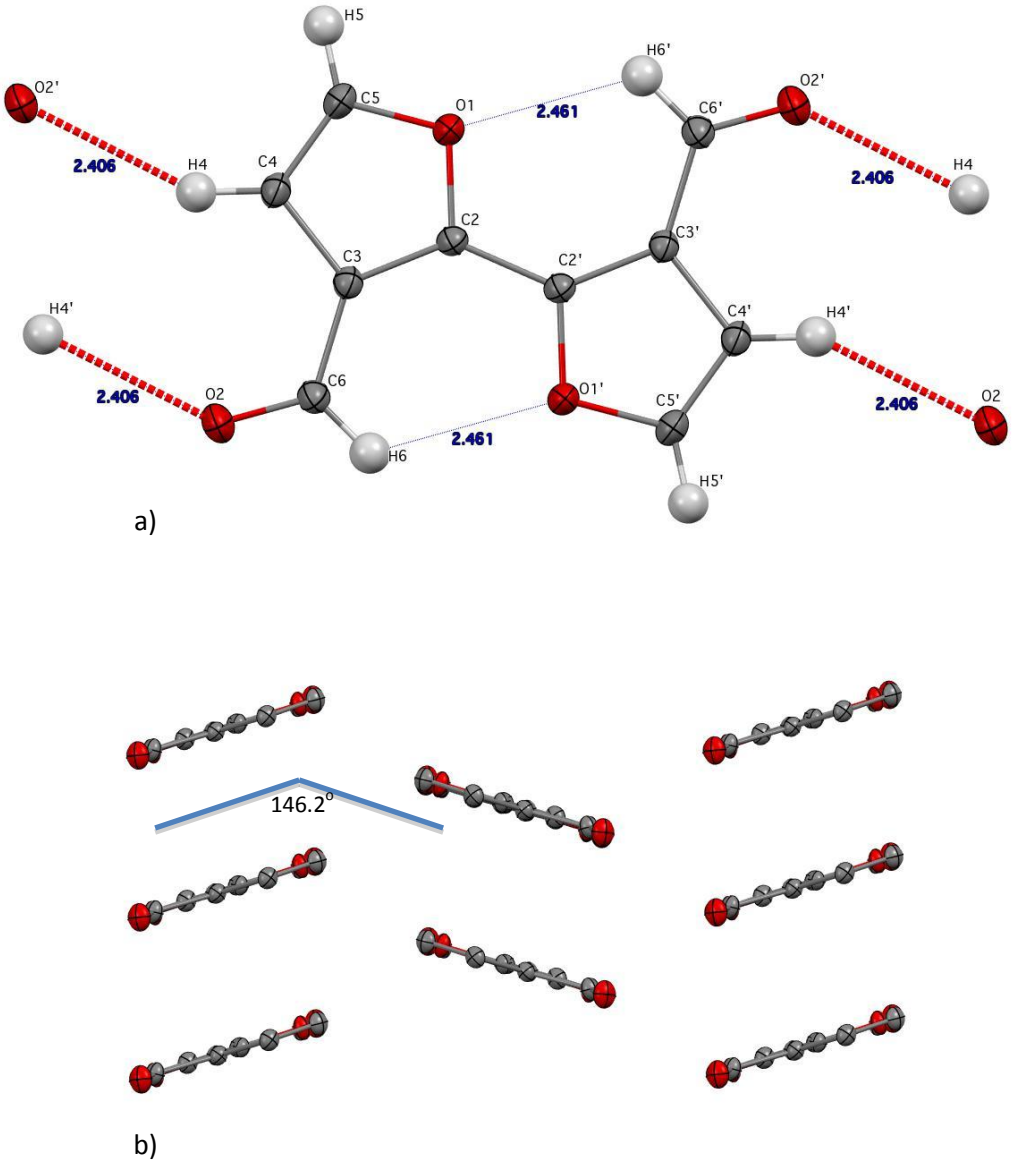


Figure S1. (a) Crystal structure (ellipsoid presentation at 50% of probability) of 2,2′-bifuran-3,3′-dicarbaldehyde (**4**) molecule.[9] Hydrogen bonds are shown: intramolecular O1···H6 bond 2.4612(5) Å and intermolecular O2···H4′ bond 2.4061(5) Å. The O2···H4′ and O2′···H4 intermolecular bonds combine molecules **4** in infinite plane chains lying in planes (111) and (1-11). (b) Herringbone-type packing of molecule **4** chains (view along the [1 0 -1] direction).

Table 2. Bond lengths [Å] and angles [deg].

O(1)–C(2)	1.3616(11)	C(2)–O(1)–C(5)	106.63(7)
O(1)–C(5)	1.3779(11)	O(1)–C(2)–C(3)	110.04(7)
O(2)–C(6)	1.2174(11)	O(1)–C(2)–C(2′)	115.66(9)
C(2)–C(3)	1.3767(11)	C(3)–C(2)–C(2′)	134.30(10)
C(2)–C(2′)	1.4375(16)	C(2)–C(3)–C(4)	106.09(8)
C(3)–C(4)	1.4362(12)	C(2)–C(3)–C(6)	128.63(8)
C(3)–C(6)	1.4602(12)	C(4)–C(3)–C(6)	125.24(8)
C(4)–C(5)	1.3464(13)	C(5)–C(4)–C(3)	106.35(8)
C(4)–H(4)	0.978(14)	C(5)–C(4)–H(4)	127.0(8)
C(5)–H(5)	0.950(13)	C(3)–C(4)–H(4)	126.6(8)
C(6)–H(6)	0.973(14)	C(4)–C(5)–O(1)	110.88(8)
		C(4)–C(5)–H(5)	132.4(8)
		O(1)–C(5)–H(5)	116.7(8)
		O(2)–C(6)–C(3)	122.18(8)
		O(2)–C(6)–H(6)	119.5(8)
		C(3)–C(6)–H(6)	118.3(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z.

Table 3. Anisotropic displacement parameters (A^2 x 10^3). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

Atom	U11	U22	U33	U23	U13	U12
O(1)	23(1)	16(1)	22(1)	2(1)	12(1)	3(1)
O(2)	29(1)	24(1)	30(1)	3(1)	18(1)	-2(1)
C(2)	17(1)	14(1)	16(1)	-1(1)	6(1)	0(1)
C(3)	16(1)	16(1)	16(1)	-2(1)	7(1)	-1(1)
C(4)	18(1)	19(1)	20(1)	-3(1)	9(1)	0(1)
C(5)	21(1)	19(1)	22(1)	-2(1)	10(1)	3(1)
C(6)	21(1)	17(1)	21(1)	-1(1)	10(1)	-2(1)

Table 4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

Atom	x	y	z	U(eq)
H(4)	680(20)	5686(11)	3660(20)	26(3)
H(5)	1420(20)	7264(11)	980(20)	26(3)
H(6)	4090(20)	3184(12)	2720(20)	27(3)

References and Notes

1 E. Pretsch, J. Seibl, W. Simon and T. Clerc, *Tables of Spectral Data for Structure Determination of Organic Compounds*, Springer-Verlag, Berlin, 1989.

2 C. W. Jefford, K. Sienkiewicz and S. R. Tornton, *Helv. Chim. Acta*, 1995, **78**, 1511-1524.

3 G. D. Hartman, W. Halczenko, J. D. Prugh and T. M. Williams, *J. Heterocycl. Chem.*, 1990, **27**, 679-682.

4 S. Gronowitz and G. Timari, *J. Heterocycl. Chem.*, 1990, **27**, 1159-1160.

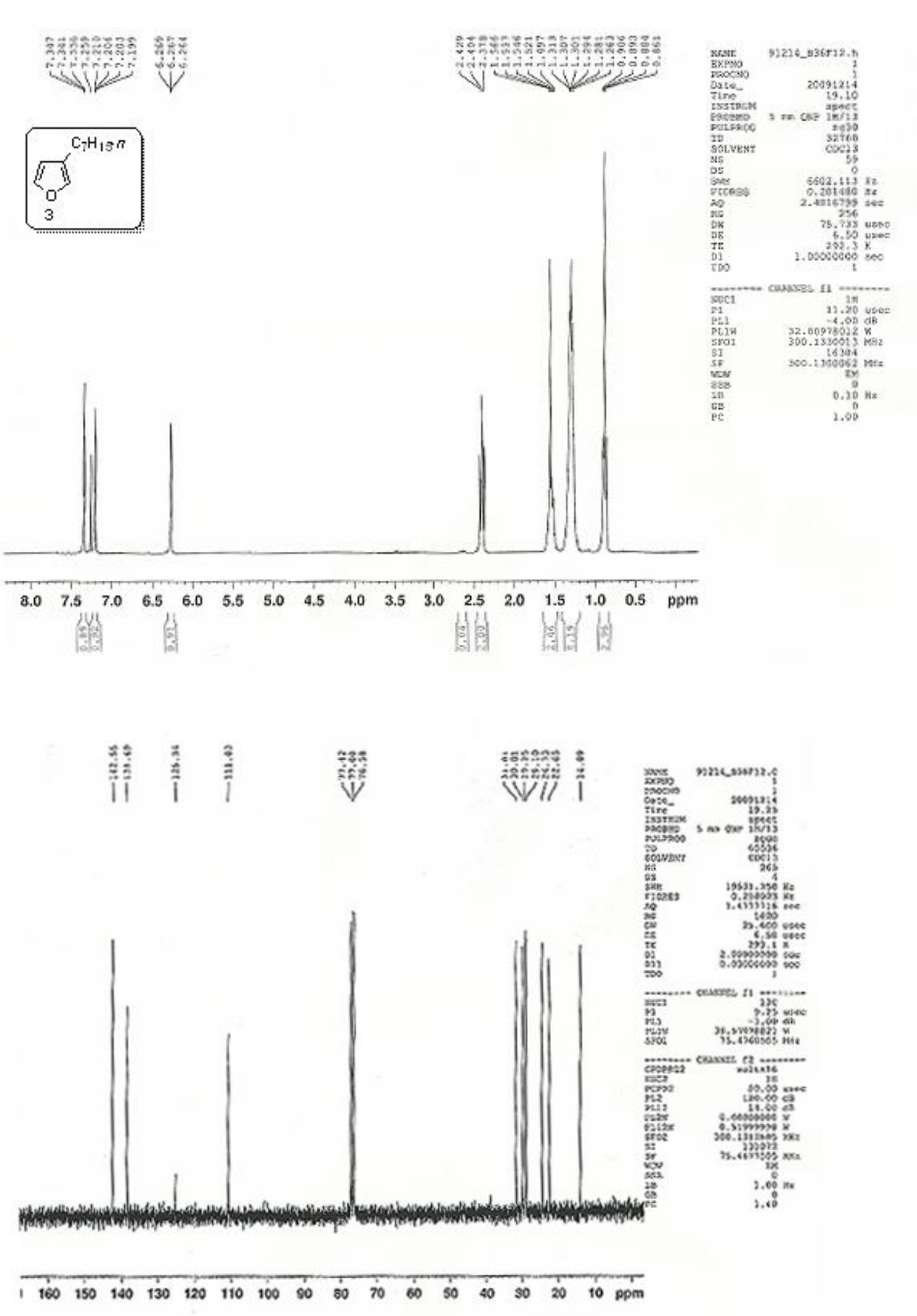
5 O. Gidron, Y. Diskin-Posner and M. Bendikov, *J. Am. Chem. Soc.*, 2010, **132**, 2148-2150.

6 T. Kauffmann and H. Lexy, *Chem. Ber.*, 1981, **114**, 3667-3673.

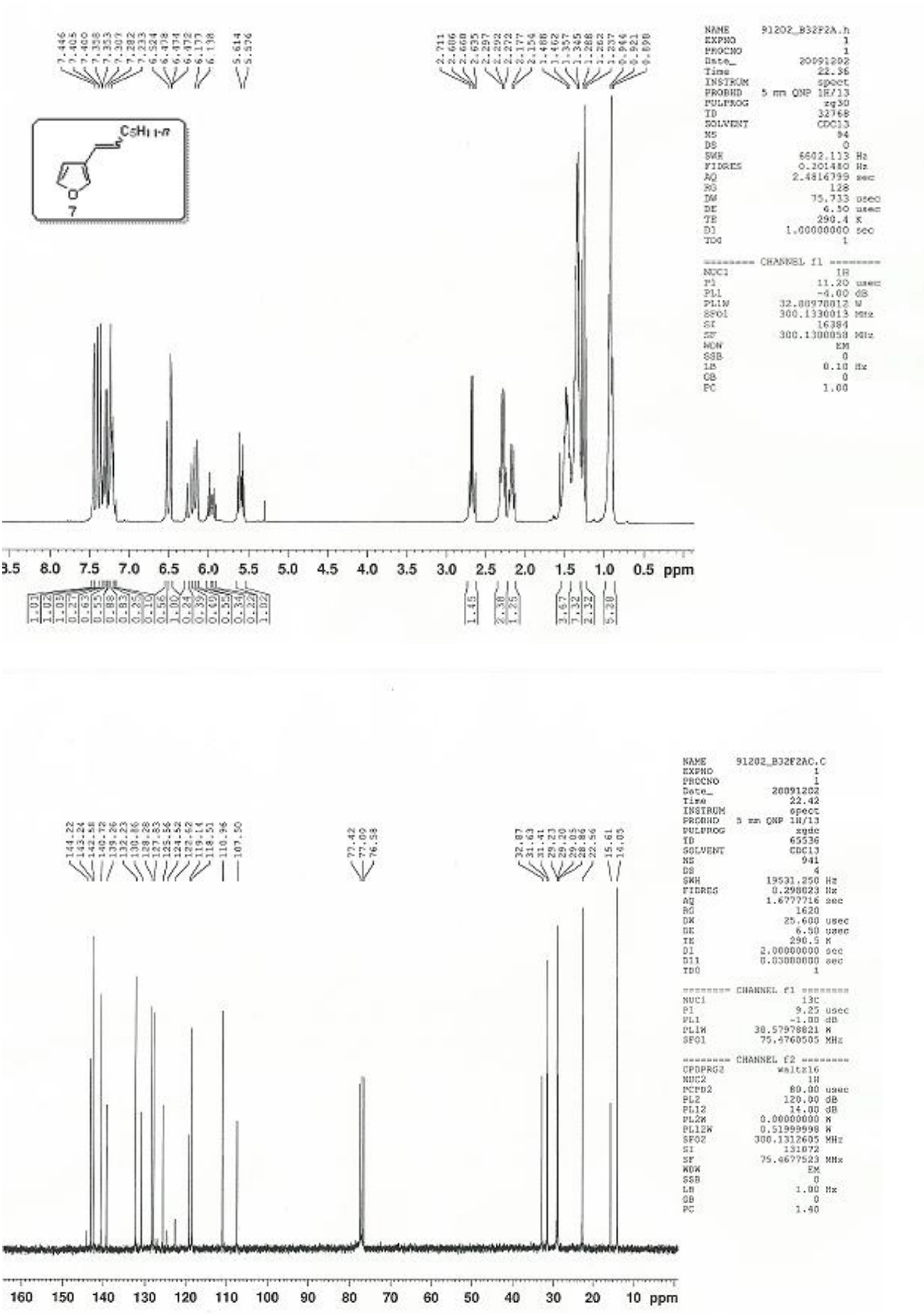
7 H. Ishida, K. Yui, Y. Aso, T. Otsubo and F. Ogura, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2828-2835.

8 D. Craig and C. J. Etheridge, *Tetrahedron*, 1996, **52**, 15289-15310.

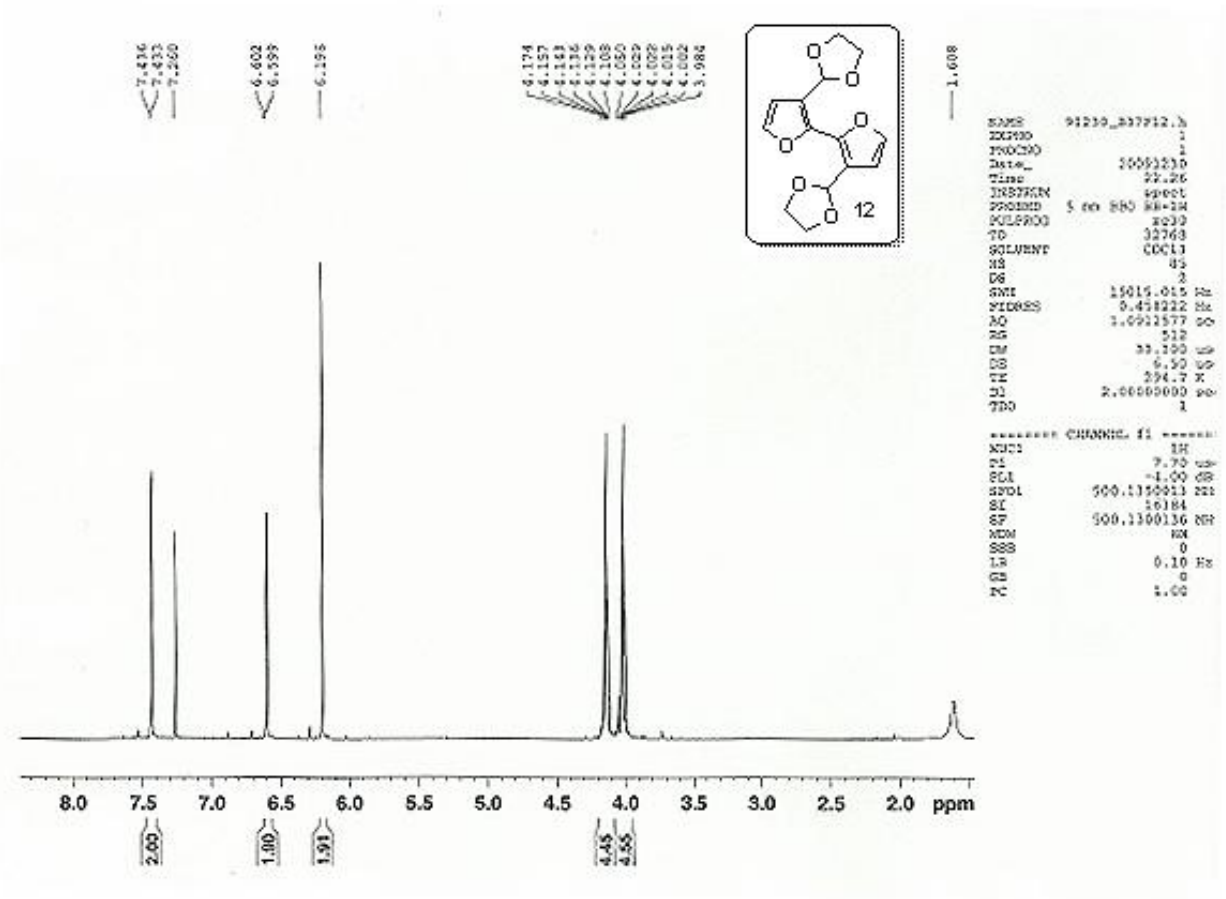
9 CCDC-970220 for 2,2′-bifuran-3,3′-dicarbaldehyde (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

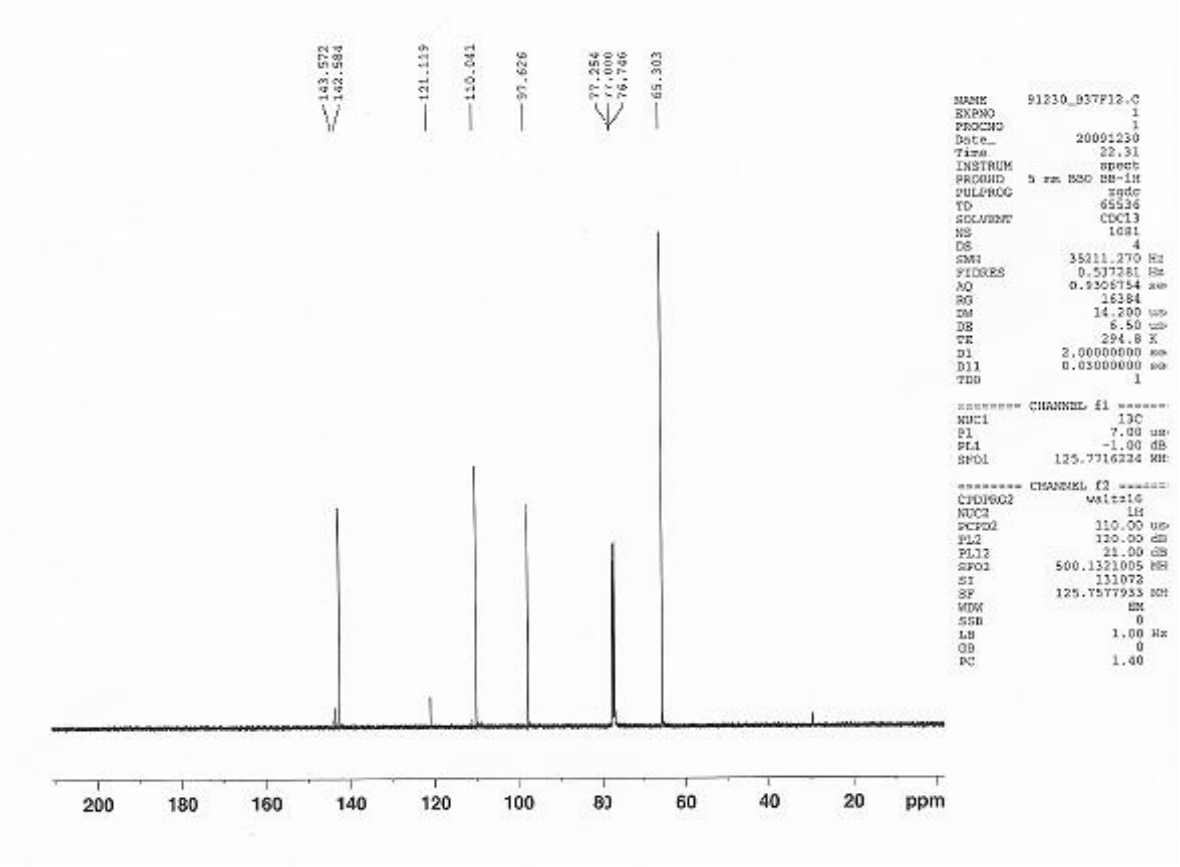


^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra of 3-*n*-heptylfuran (**3**) in $CDCl_3$.

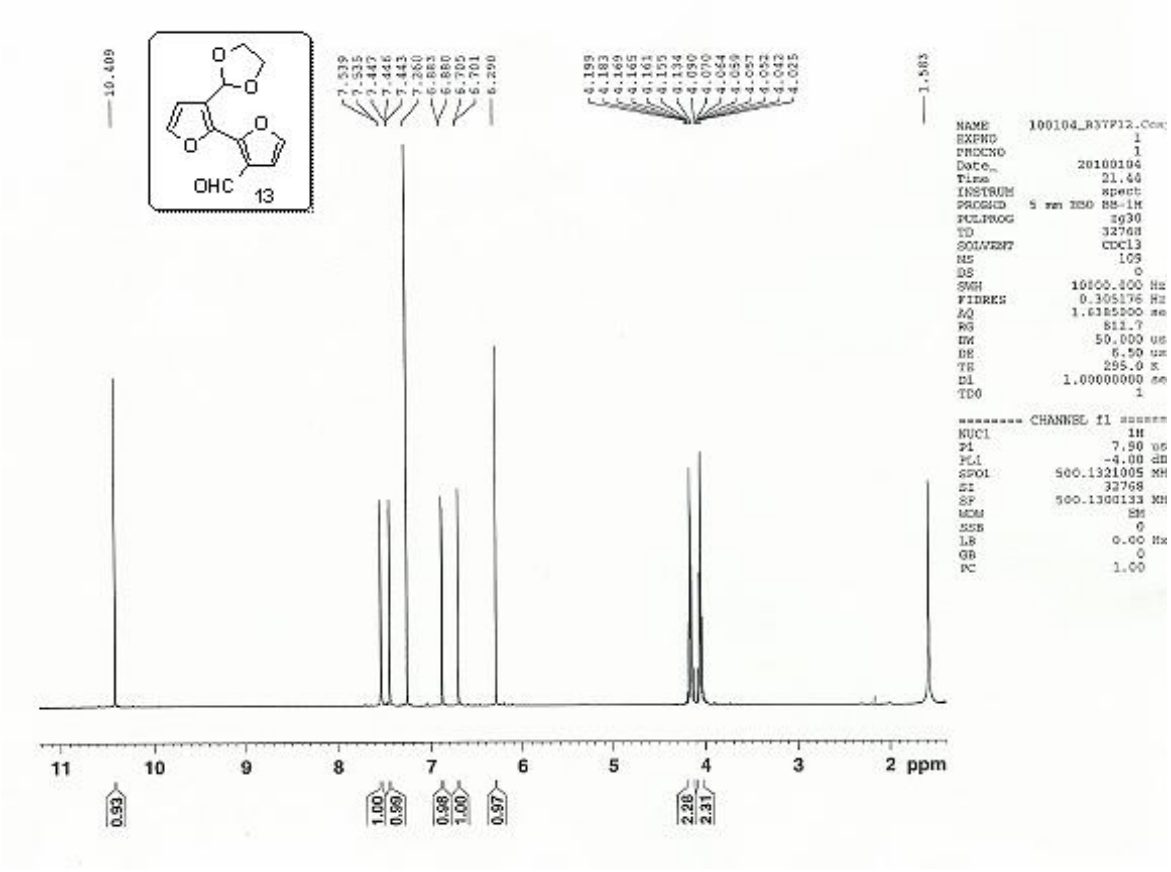


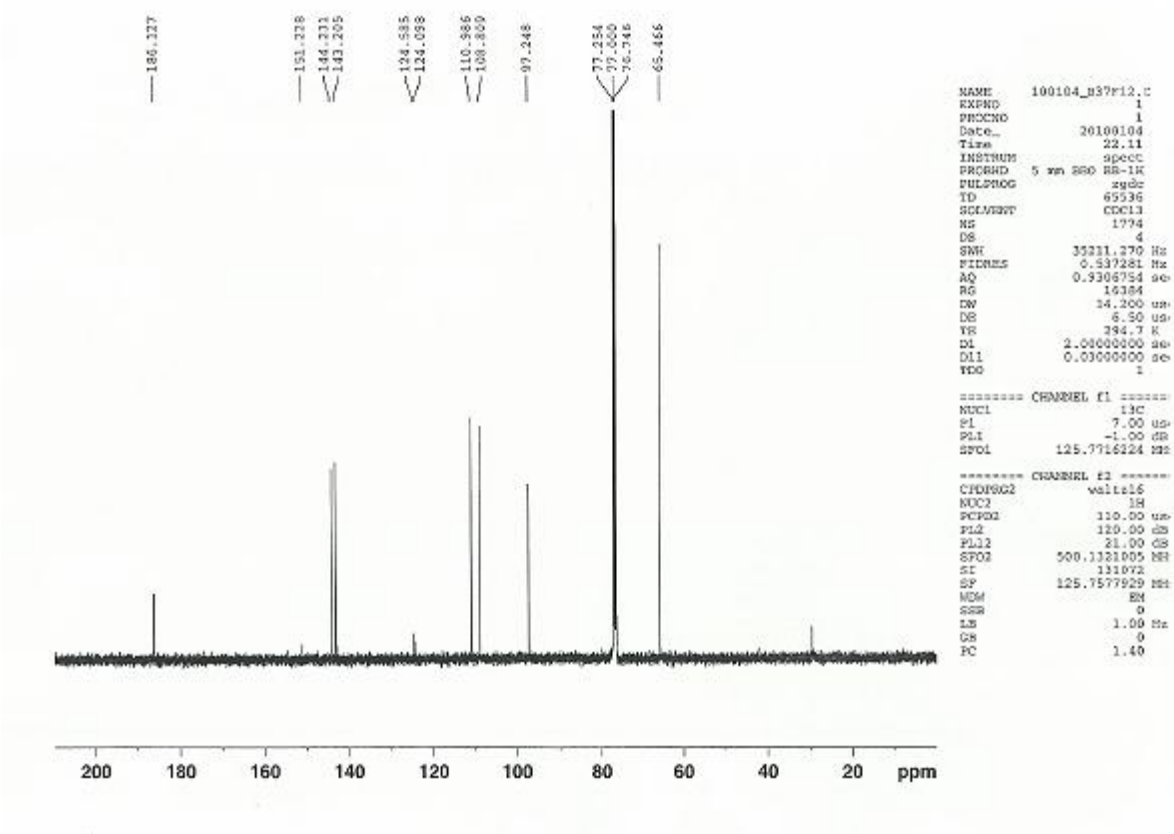
^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra of *E/Z*-3-(*n*-hept-1-ene-1-yl)furan (**7**) (*E/Z ca.* 1:2, the mixture contains *ca.* 28 mol% of ethylbenzene) in $CDCl_3$.



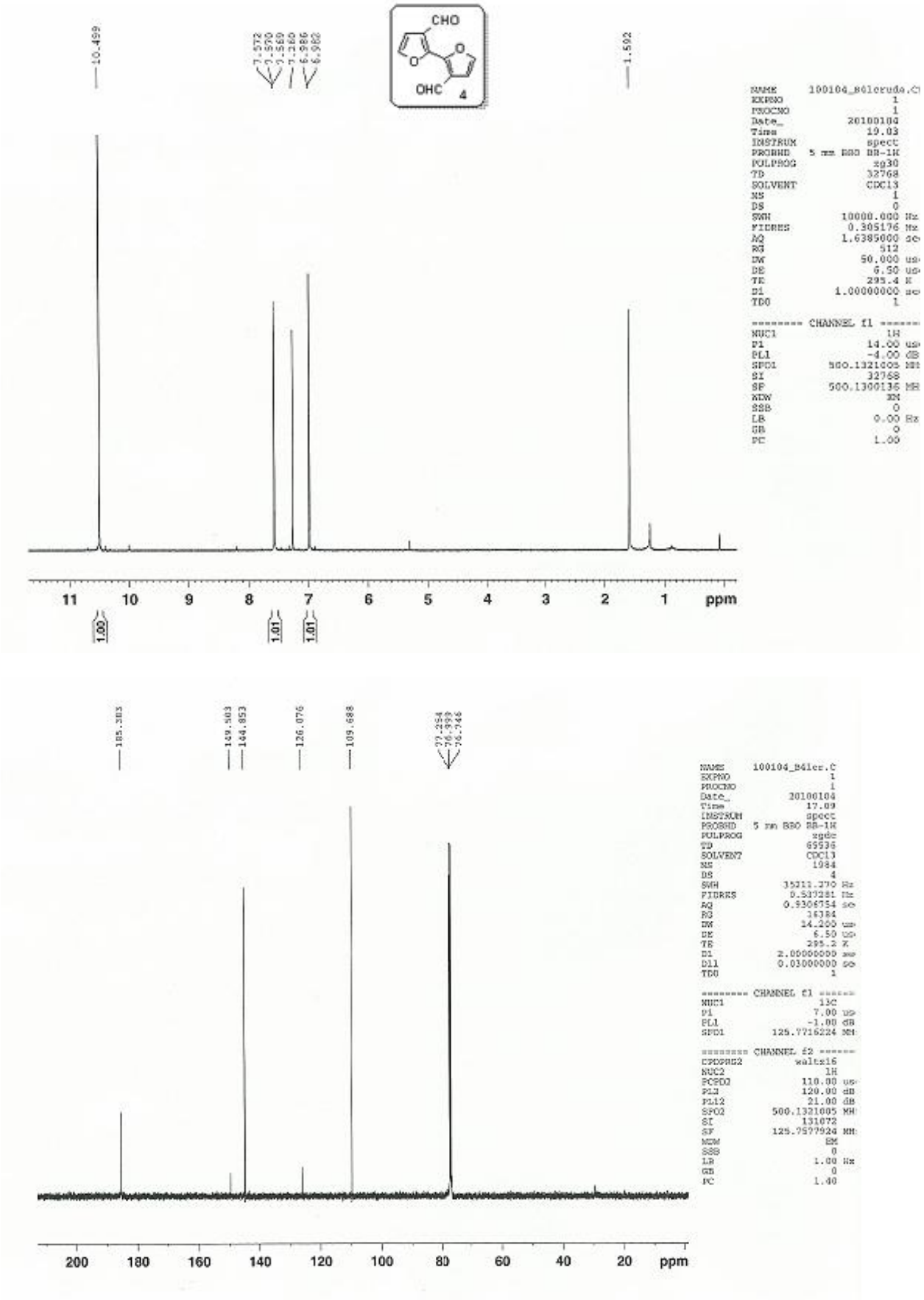


^{1}H NMR (500 MHz) and ^{13}C NMR (125.8 MHz) spectra of 3,3'-di(1,3-dioxolan-2-yl)-2,2'-bifuran (**12**) in $CDCl_3$.

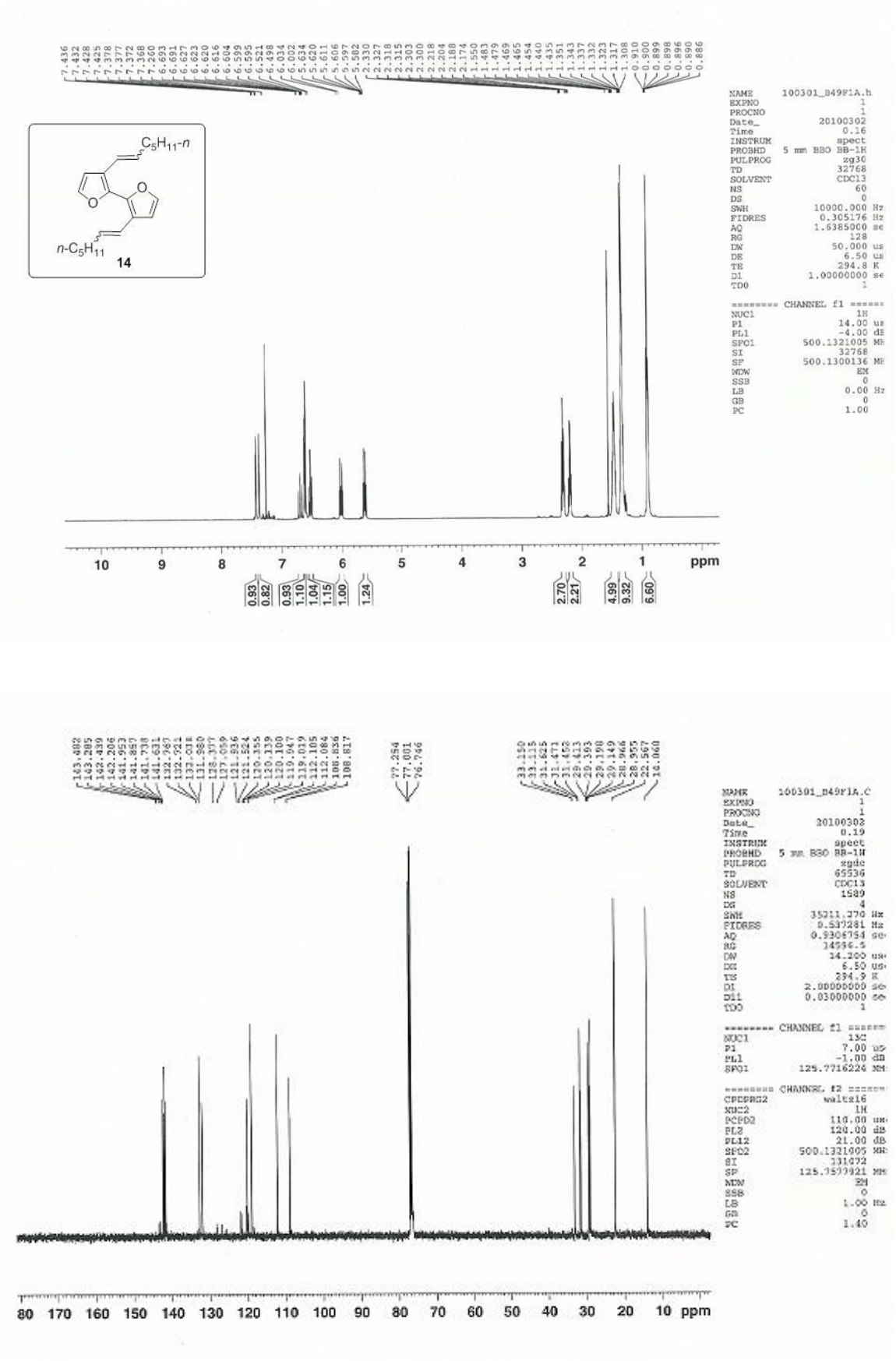




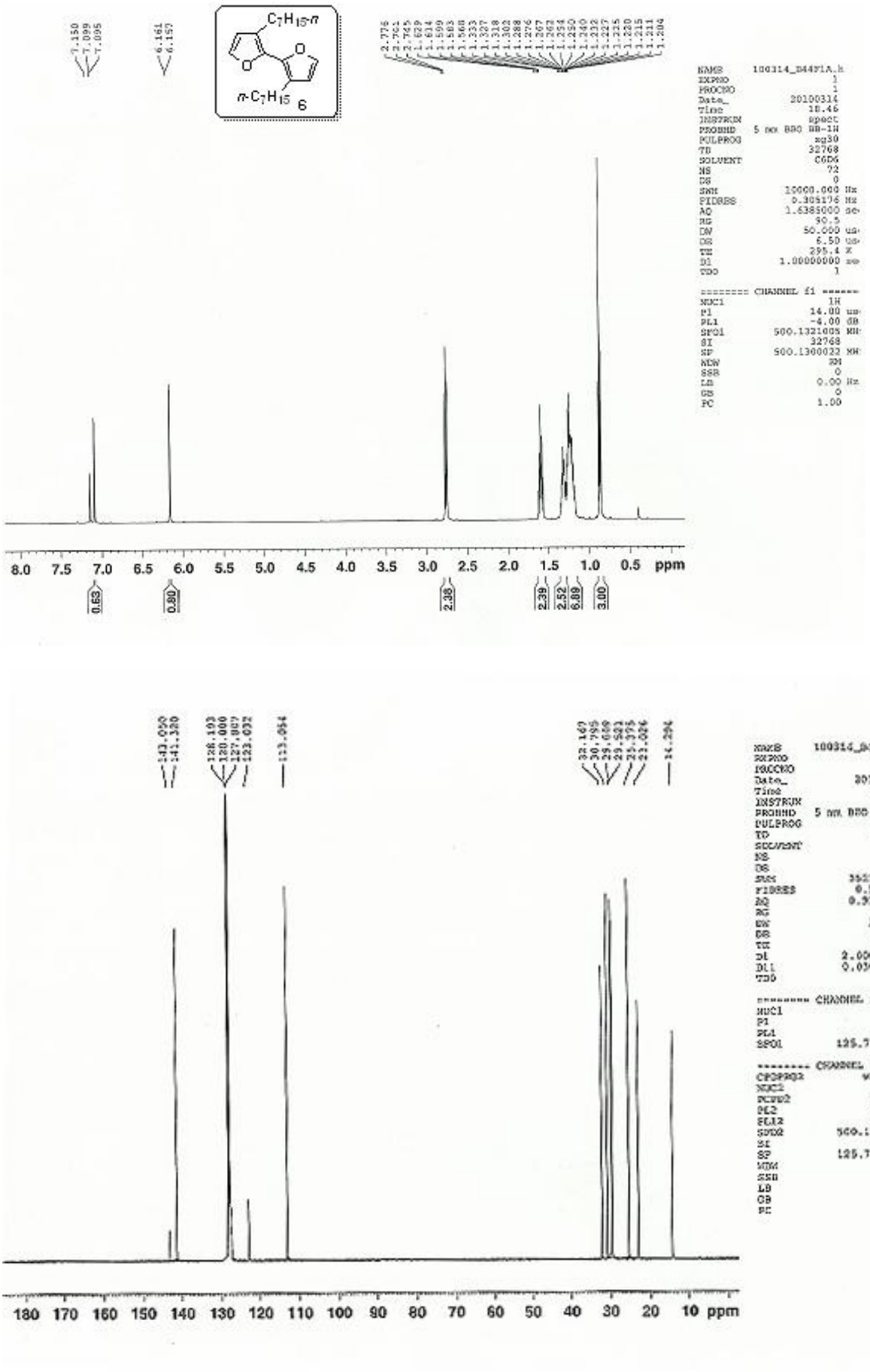
^{1}H NMR (500 MHz) and ^{13}C NMR (125.8 MHz) spectra of 3'-(1,3-dioxolan-2-yl)-2,2'-bifuran-3-carbaldehyde (**13**) in $CDCl_3$.



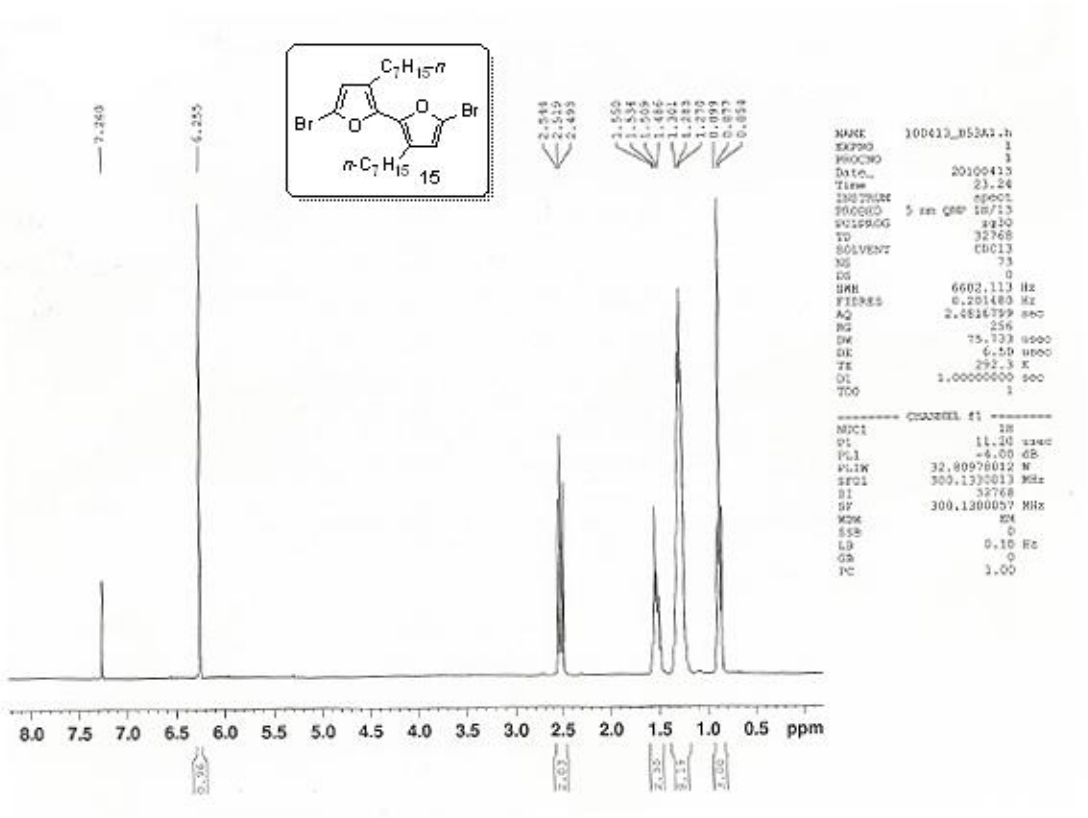
^{1}H NMR (500 MHz) and ^{13}C NMR (125.8 MHz) spectra of 2,2'-bifuran-3,3'-dicarbaldehyde (**4**) in $CDCl_3$.

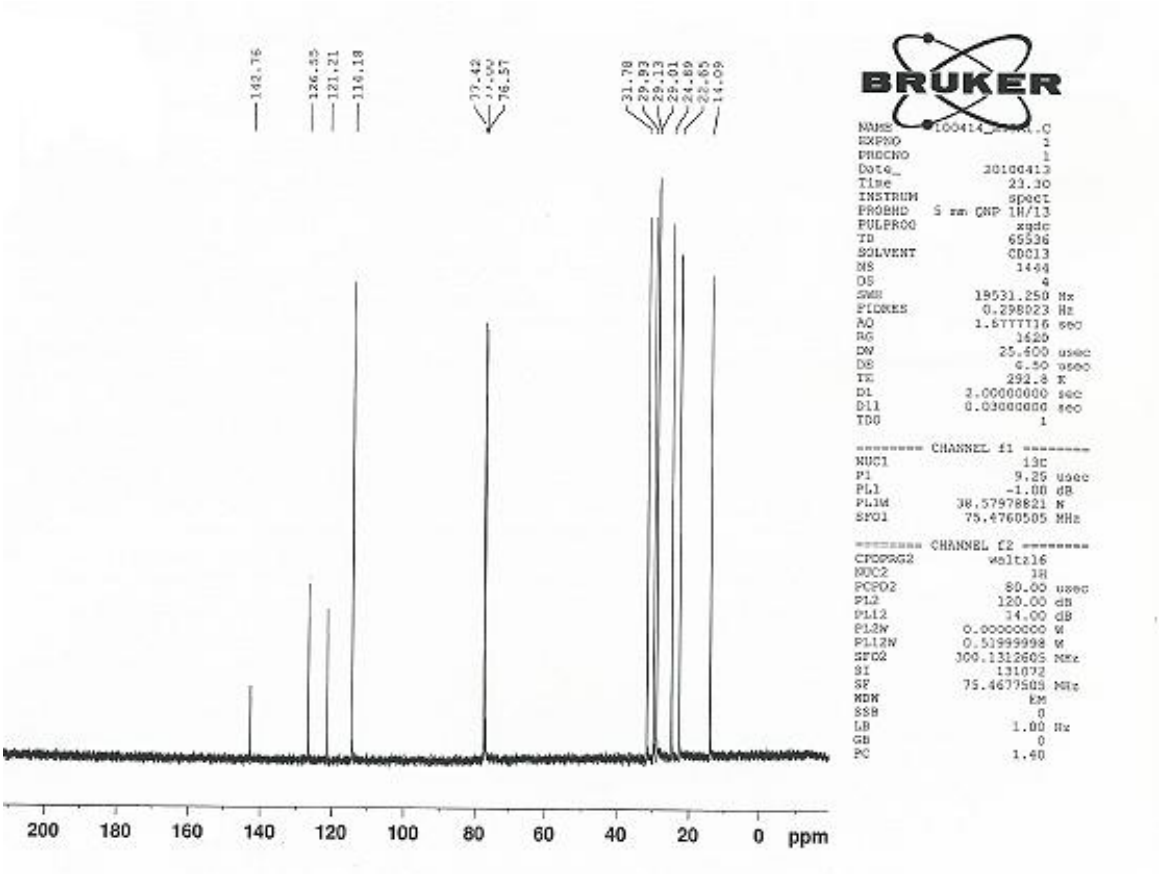


^{1}H NMR (500 MHz) and ^{13}C NMR (125.8 MHz) spectra of *E/Z*-3,3'-di-(*n*-hept-1-en-1-yl)-2,2'-bifuran (**14**) (a mixture of *E*- and *Z*-isomers *ca.* 45:55) in $CDCl_3$.

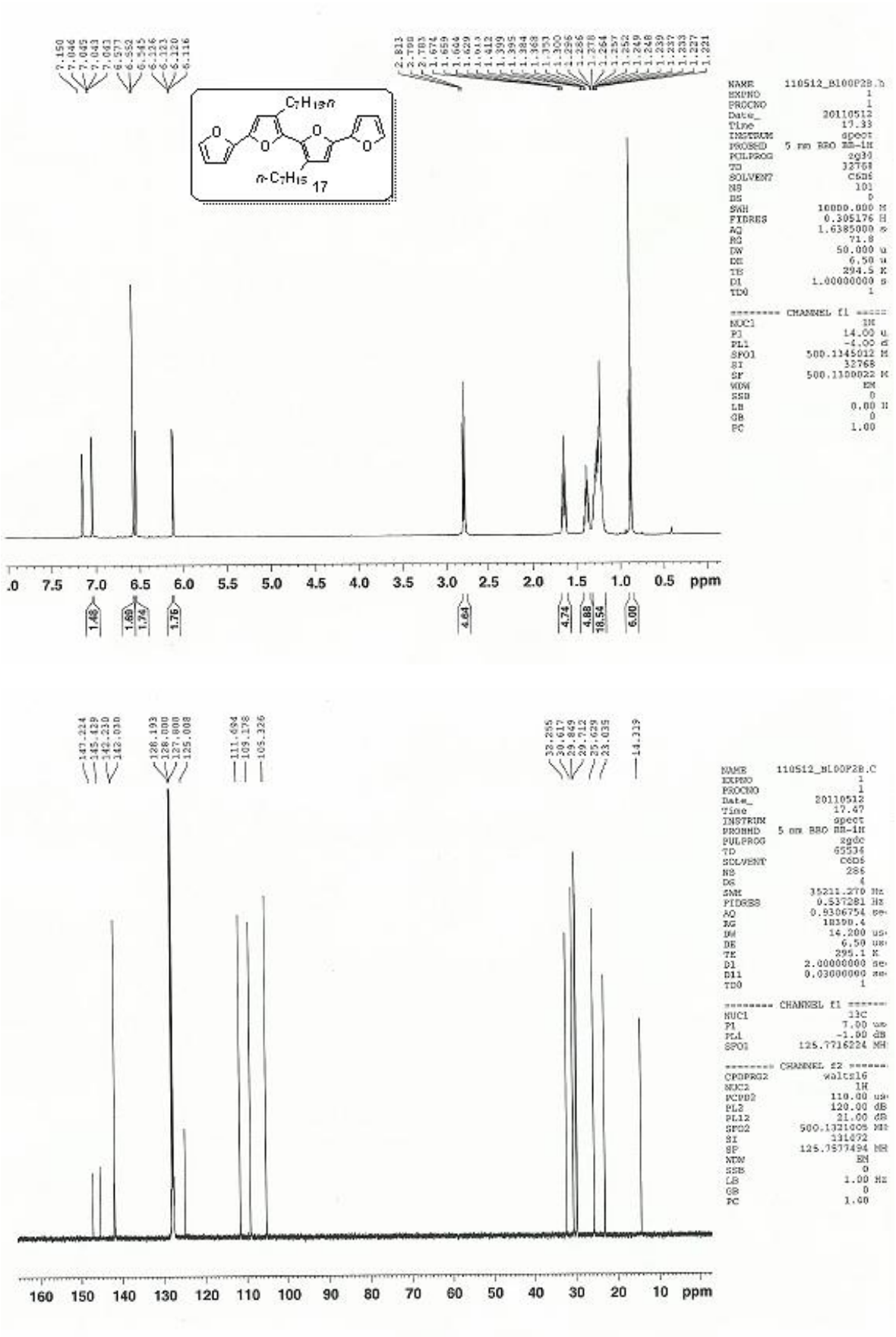


^{1}H NMR (500 MHz) and ^{13}C NMR (125.8 MHz) spectra of 3,3'-di-*n*-heptyl-2,2'-bifuran (**6**) in C_6D_6.

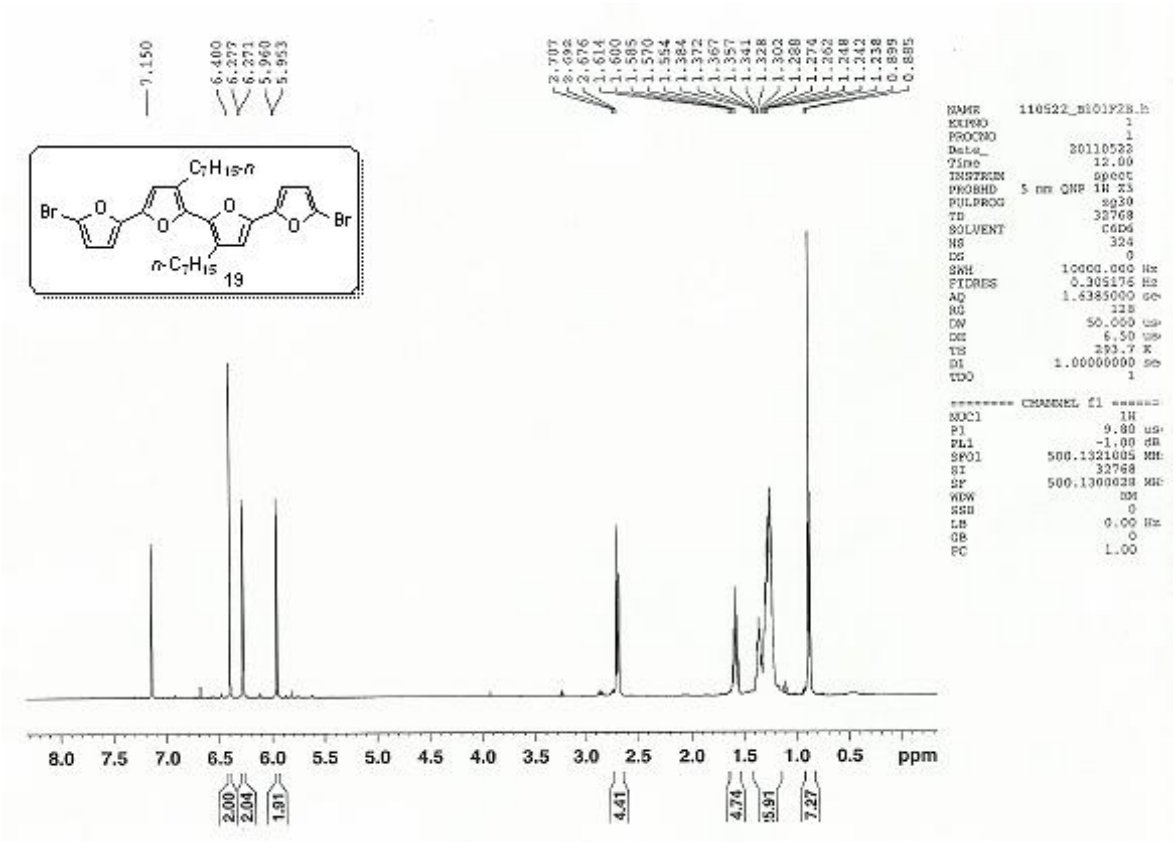


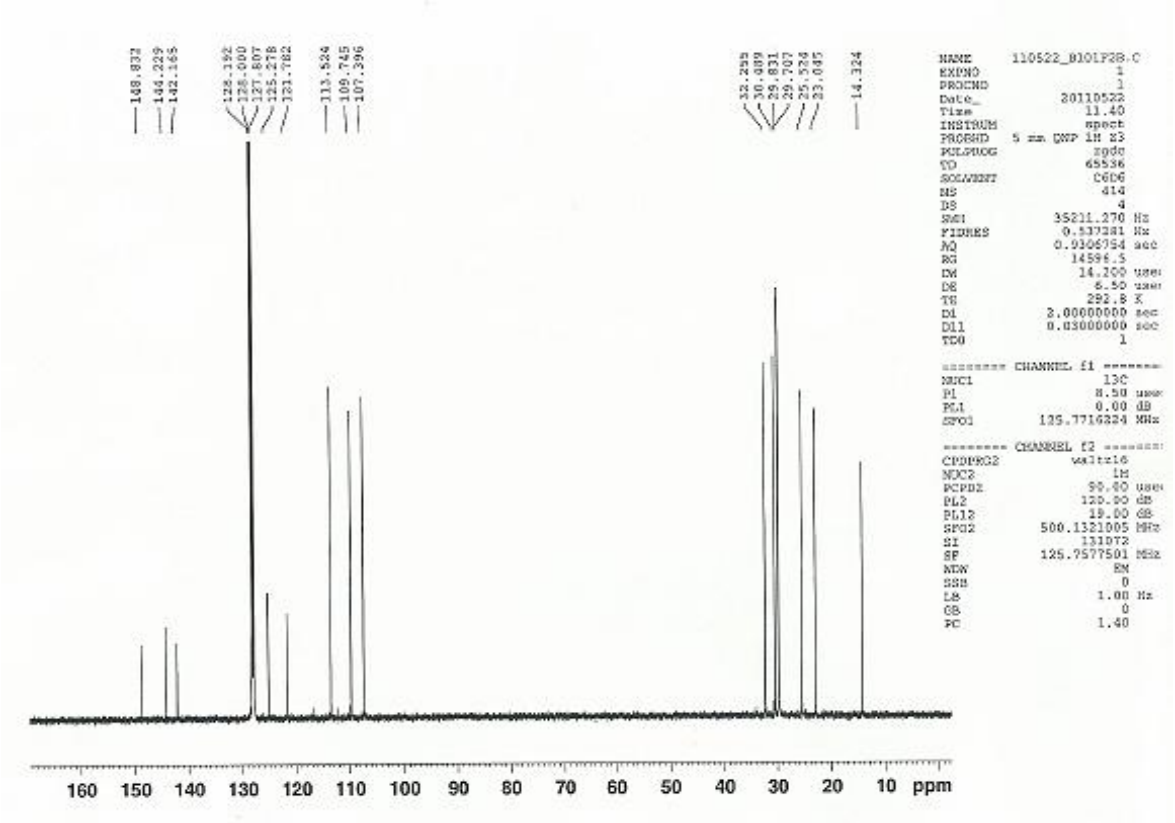


^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra of 5,5'-dibromo-3,3'-di-*n*-heptyl-2,2'-bifuran (**15**) in $CDCl_3$.



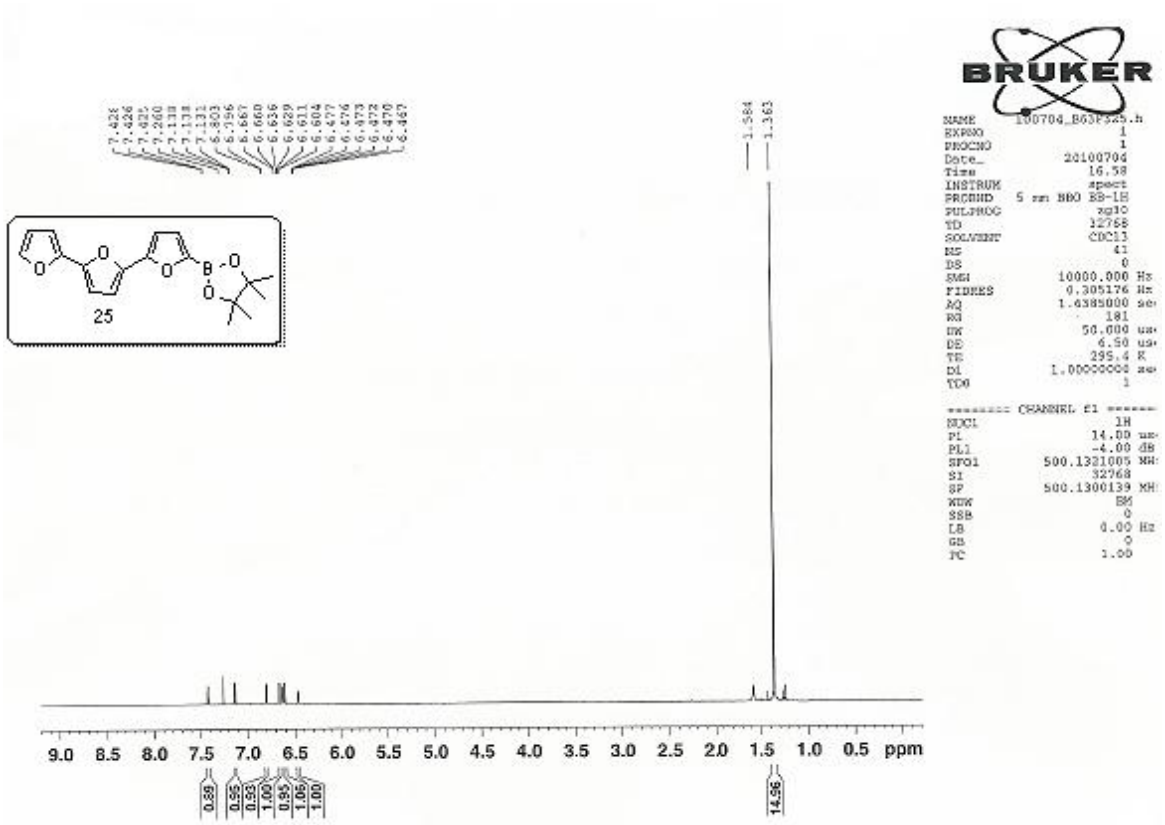
^{1}H NMR (500 MHz) and ^{13}C NMR (125.8 MHz) spectra of 3",4'-di-*n*-heptyl-2,2':5',2":5",2"'-quaterfuran (**17**) in C_6D_6.

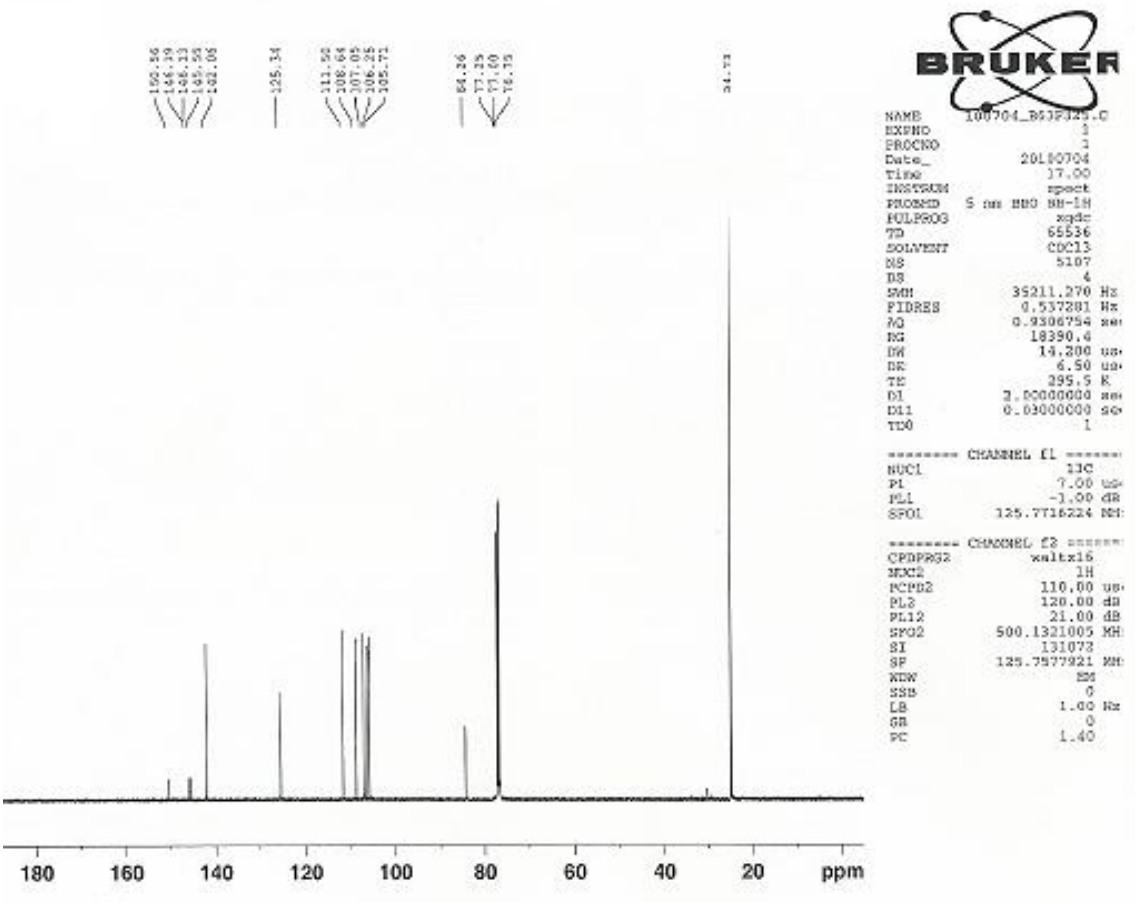




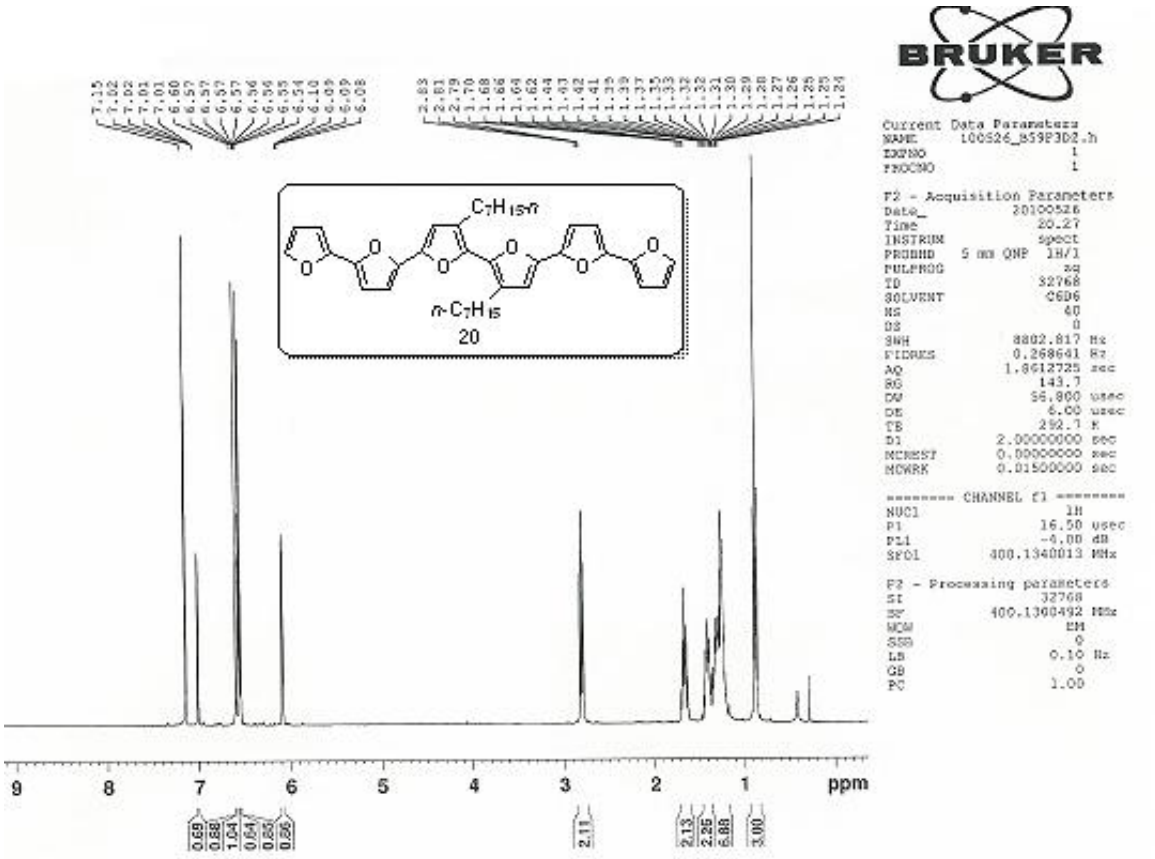
^{1}H NMR (500 MHz) and ^{13}C NMR (125.8 MHz) spectra of 5,5'''-dibromo-3'',4'-di-*n*-heptyl-2,2':5',2'':5'',2'''-quaterfuran (**19**) in C_6D_6.

^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra of 2-([2,2'-bifuran]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**24**) in $CDCl_3$.

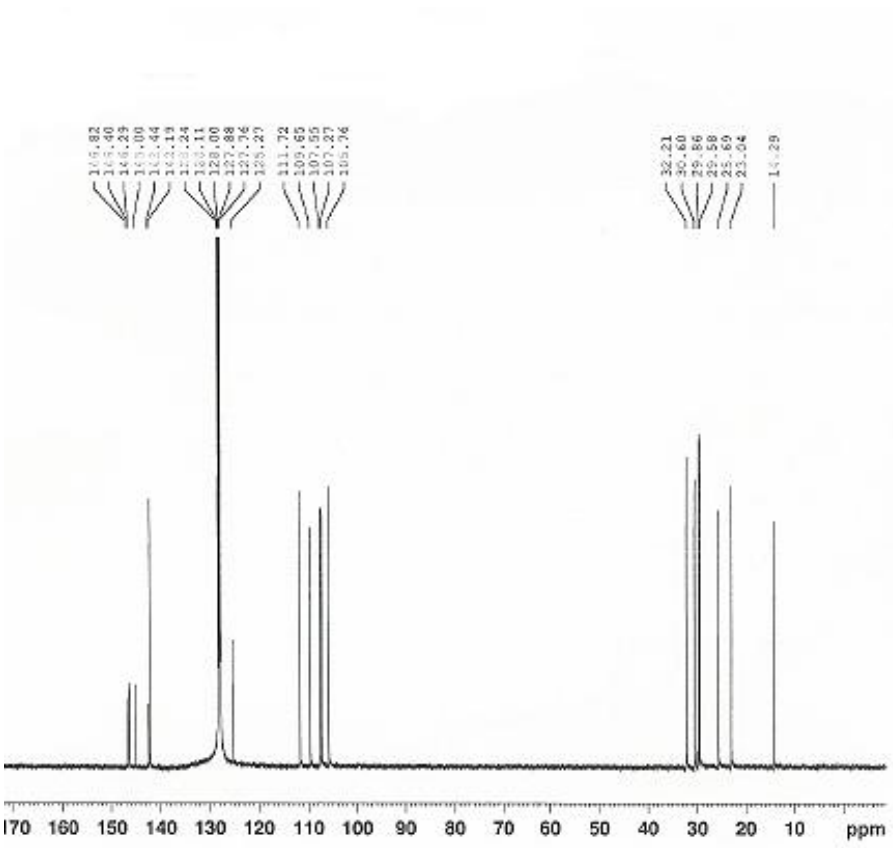




^{1}H NMR (500 MHz) and ^{13}C NMR (125.8 MHz) spectra of 2-([2,2':5',2"-terfuran]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**25**) in $CDCl_3$.

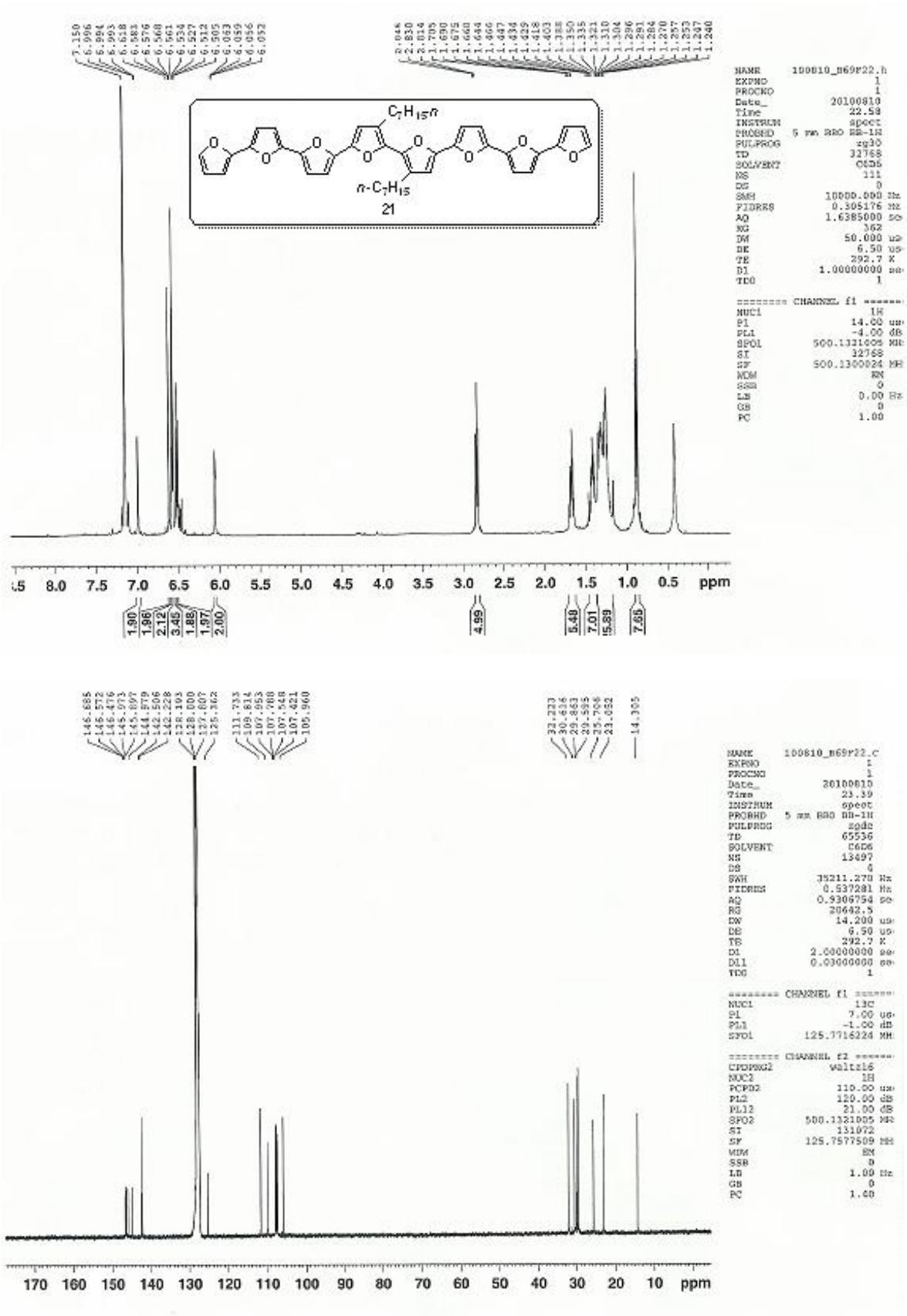



```
Current Data Parameters
NAME      100526_b59P3D2.h
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20100526
Time                  20.27
INSTRUM               spect
PROBHD    5 mm QNP  1H/1
PULPROG                 zg
TD                   32768
SOLVENT               C6D6
NS                      40
DS                       0
SWH               8802.817 Hz
FIDRES            0.268641 Hz
AQ                1.8612725 sec
RG                    143.7
DW                   56.800 usec
DE                    6.00 usec
TE                   292.7 K
D1                2.00000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    16.50 usec
PL1                   -4.00 dB
SFO1          400.1340013 MHz

F2 - Processing parameters
SI                       32768
SF                400.1300492 MHz
WDW                         EM
SSB                          0
LB                        0.10 Hz
GB                           0
PC                        1.00
```




```
Current Data Parameters
NAME      100526_b59P3D2.c
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20100526
Time                  20.30
INSTRUM               spect
PROBHD    5 mm QNP  1H/1
PULPROG               zgdc
TD                   65536
SOLVENT               C6D6
NS                     3631
DS                        2
SWH              28248.588 Hz
FIDRES            0.431039 Hz
AQ                1.1600372 sec
RG                      181
DW                   17.700 usec
DE                    6.00 usec
TE                   293.2 K
D1                2.00000000 sec
D11               0.03000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.00 usec
PL1                   -6.00 dB
SFO1          100.6243542 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                   120.00 dB
PL12                   12.00 dB
SFO2          400.1318050 MHz

F2 - Processing parameters
SI                      131072
SF                100.6127501 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra of 3''',4''-di-*n*-heptyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexifuran (**20**) in C_6D_6.



^{1}H NMR (500 MHz) and ^{13}C NMR (125.8 MHz) spectra of 3"",4"'-di-*n*-heptyl-2,2':5',2":5",2"':5"',2"":5"",2""':5""',2"""":5"""",2"""":5"""",2""""-octifuran (**21**) in C_6D_6.