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4*H*-1,2,6-Thiadiazin-4-one-containing small molecule donors and additive effects on their performance in solution-processed organic solar cells

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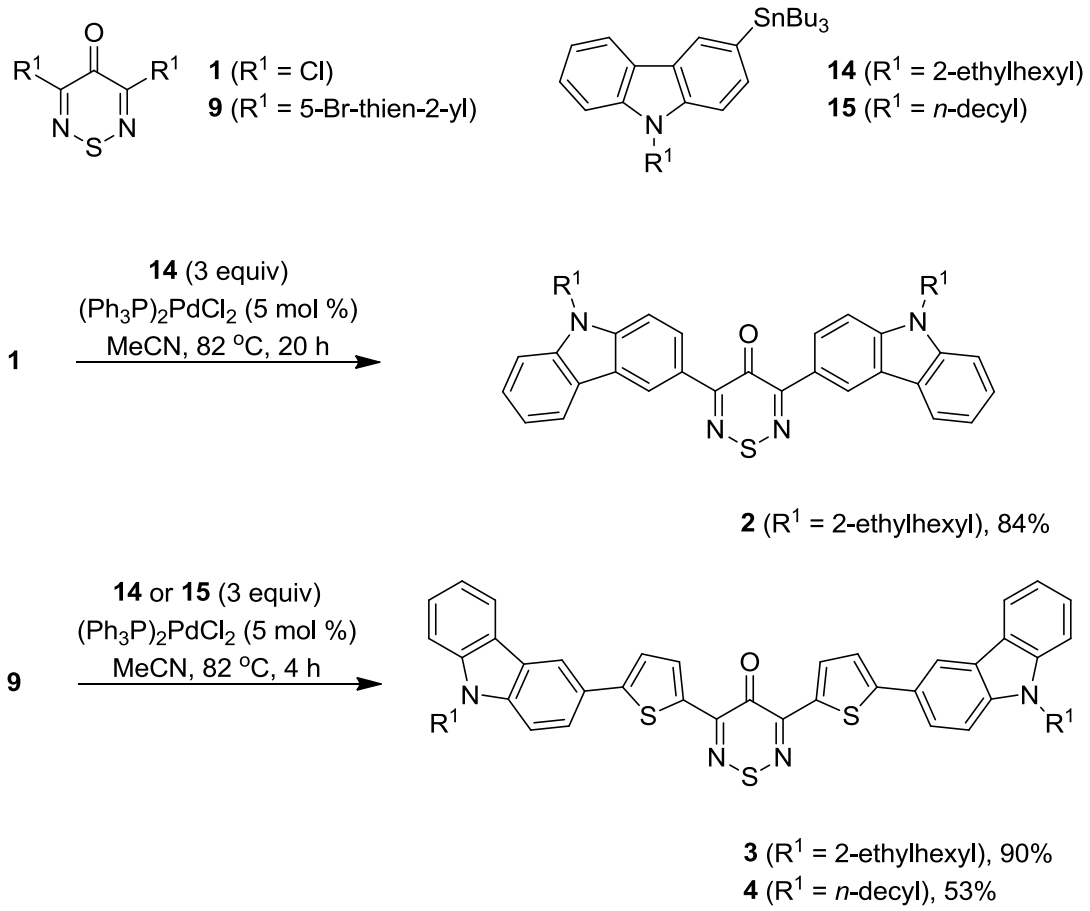
Appendix

1. Synthesis and structural characterization of molecules

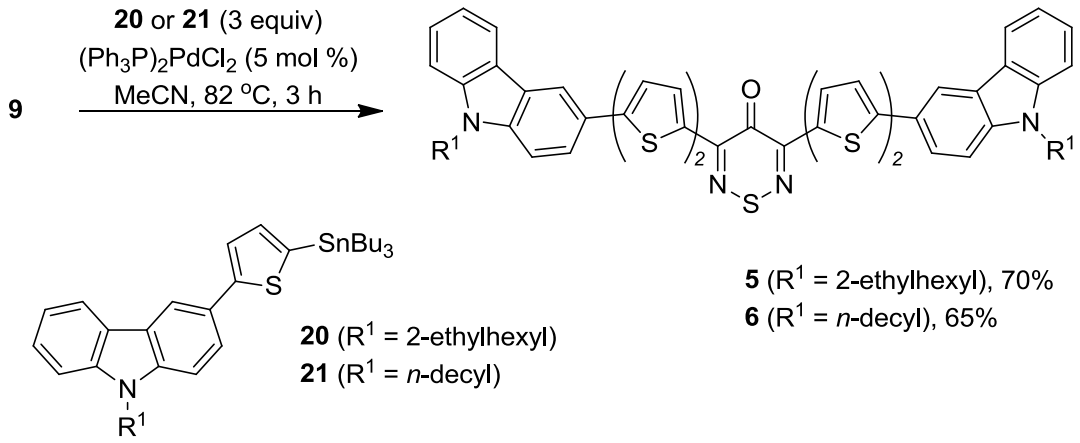
The synthesis of the D-A-D small molecules started from 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**), that can be readily prepared in two steps from dichloromalononitrile and SCl_2 in multigram quantities,[1] and is a versatile building block that can participate in a range of palladium catalyzed C-C coupling reactions such as Stille and Suzuki-Miyaura couplings to give various 3,5-di(het)aryl substituted systems.[2,3]

As such, the Stille reaction of dichlorothiadiazinone **1** with 9-(2-ethylhexyl)-3-(tributylstannyl)-9*H*-carbazole (**14**), prepared using standard methods (see section 2.2),[4-6] gave the first analogue **2** (R^1 = 2-ethylhexyl, n = 0) in 84% yield, while the analogous Stille coupling reactions between 3,5-bis(5-bromothien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**9**)[2] and either 9-(2-ethylhexyl)-3-(tributylstannyl)-9*H*-carbazole (**14**) or 9-decyl-3-(tributylstannyl)-9*H*-carbazole (**15**) gave the D-A-D analogues **3** (R^1 = 2-ethyl-hexyl, R^2 = H, n = 1), and **4** (R^1 = *n*-decyl, R^2 = H, n = 1) in 90 and 53% yields, respectively (Scheme S1).



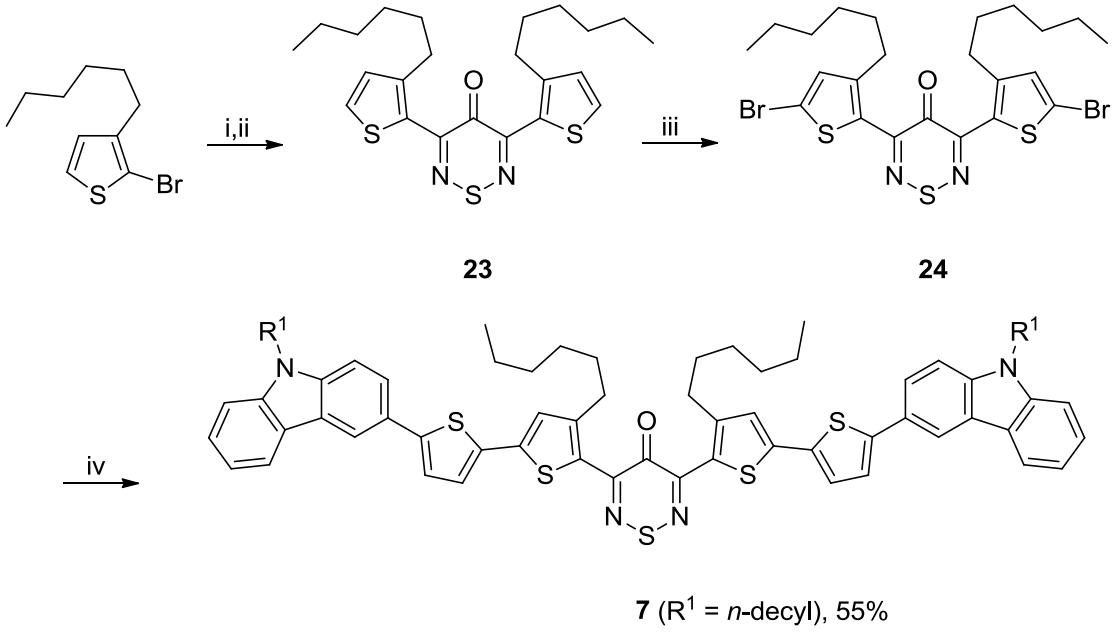
Scheme S1 Synthesis of thiadiazinones **2**, **3** and **4**.

To access compounds with extended π conjugation we targeted small molecule D-A-Ds bearing additional thienyl groups between the carbazole and thiadiazine moieties. To achieve this goal, we first prepared the 9-alkyl-3-[5-(tri-*n*-butyl-stannyl)thien-2-yl]-9*H*-carbazoles **20** (R^1 = 2-ethylhexyl) and **21** (R^1 = *n*-decyl) in a 5-steps sequence that involved standard synthetic methods (see section 2.3). Subsequent Stille coupling of the synthesised organostannanes **20** and **21** with bromothiophene **9** gave thiadiazinones **5** and **6** in good yields (65-70%, Scheme S2). Similar 9-alkyl-3-[5-(tri-alkylstannyl)thien-2-yl]-9*H*-carbazole reagents have been used recently in Stille coupling reactions.[7,8]



Scheme S2 Synthesis of thiadiazinones **5** and **6**.

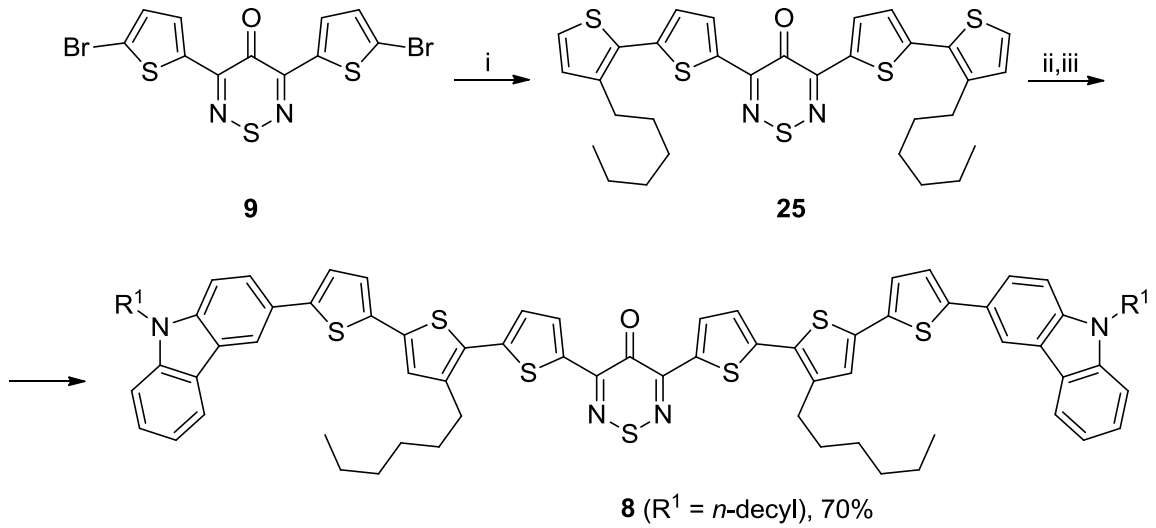
A lengthier synthesis was needed for the D-A-D analogue **7** which was a 3,5-bis(3-*n*-hexylthien-2-yl)-4*H*-1,2,6-thiadiazin-4-one analogue of the D-A-D **6**. This required the synthesis of 3,5-bis(5-bromo-3-*n*-hexylthien-2-yl)-4*H*-1,2,6-thiadia-zin-4-one (**24**) using standard methodology (see section 2.5) which was then coupled with 9-*n*-decyl-3-[5-(tri-*n*-butylstannyl)thien-2-yl]-9*H*-carbazole **21** *via* a Stille reaction to give the D-A-D **7** as a purple powder in 55% (Scheme S3).



Scheme S3 *Reagents and conditions:* i) *n*-BuLi (1.2 equiv), THF, -78 °C, then *n*-Bu_3SnCl (1.2 equiv), 16 h, 95%; ii) **1** (0.5 equiv), $(Ph_3P)_2PdCl_2$ (5 mol %), MeCN, 82 °C, 4 h, 96%;

iii) NBS (2.1 equiv), DMF, 20 °C, 2 d, 92%; iv) **21** (3 equiv), $(Ph_3P)_2PdCl_2$ (5 mol %), PhMe, 110 °C, 8 h, 55%.

The synthesis of the largest π-extended D-A-D **8**, which contained *n*-hexyl substituted terthienyl units between the carbazole and thiadiazine moieties, required access to 3,5-bis[3'-hexyl-(2,2'-bithien)-5-yl]-4*H*-1,2,6-thiadiazin-4-one (**26**) which was prepared in three steps from the di(bromothienyl)thiadiazinone **9**. Subsequent bromination of the peripheral thienyl groups and Stille coupling with the 9-(*n*-decyl)carbazole tin reagent **21** gave the desired D-A-D **8** as a purple powder in 70% yield (Scheme S4).



Scheme S4 *Reagents and conditions:* i) 3-Hexylthiophene-2-boronic acid pinacol ester (2.2 equiv), $(Ph_3P)_2PdCl_2$ (5 mol %), Cs_2CO_3 (2.2 equiv), PhMe, sealed tube, 120 °C, 1 d, 98%; ii) NBS (2.1 equiv), DMF/THF (4:1), 20 °C, 16 h, 99%; iii) **21** (3 equiv), $(Ph_3P)_2PdCl_2$ (10 mol %), PhMe, 110 °C, 20 h, 70%.

The above D-A-Ds were characterised using standard methods used for small organic molecules, which included ^1H and ^{13}C NMR spectroscopy (see Appendix) and elemental analysis to confirm bulk purity. All the compounds were readily soluble in common organic solvents such as THF, chloroform, dichloromethane, etc.

2. Experimental Procedures

2.1 General experimental procedures

All chemicals were commercially available, except for 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**)[1] and 3,5-bis(5-bromothien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**9**),[2] which were prepared according to literature procedures. *N*-bromosuccinimide (NBS) was recrystallised from water. Acetonitrile and toluene were distilled over CaH_2 before use. Tetrahydrofuran (THF) used in stannylation reactions was distilled over sodium and benzophenone. Reactions were protected from moisture with $CaCl_2$ drying tubes or an Ar atmosphere. Anhydrous Na_2SO_4 was used for drying organic extracts and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by thin layer chromatography (TLC) using commercial glass backed TLC plates (Merck Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm).[9] Melting points were determined using a PolyTherm-A, Wagner & Munz, Koefler-Hotstage Microscope apparatus or were determined using a TA Instruments DSC Q1000 with samples hermetically sealed in aluminium pans under an argon atmosphere; using heating rates of 5 °C/min (DSC mp listed by *onset* and *peak* values). Solvents used for recrystallization are indicated after the melting point. UV-visible spectra of solutions were obtained using a Perkin-Elmer Lambda-25 UV-vis spectrophotometer and inflections are identified by the abbreviation "inf". IR spectra were recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer with Pike *Miracle* Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w, respectively. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 machine (at 500 and 125 MHz, respectively). Deuterated solvents were used for homonuclear lock and the signals are

referenced to the deuterated solvent peaks. MALDI-TOF MS was conducted on a Bruker Autoflex III Smartbeam instrument.

2.2. Preparation of carbazole starting materials

2.2.1. N-Alkylation of 9*H*-carbazoles (based on the method of Bu *et al.*,[4])

*2.2.1.1. 9-(2-Ethylhexyl)-9*H*-carbazole (**10**). (Typical procedure)*: To a mixture of tetra-*n*-butylammonium bromide (TBAB) (80 mg, 0.25 mmol), and aqueous 50% NaOH (3 mL) was added a solution of 9*H*-carbazole (1.0 g, 6.0 mmol) and 3-(bromomethyl)heptane (3.47 g, 18 mmol) in PhH (10 mL). The mixture was heated at reflux for 7 h, allowed to cool to *ca.* 20 °C and then poured into water (25 mL). The organic components were extracted with dichloromethane (3 × 25 mL). The organic phase was washed with water (20 mL) and dried (Na_2SO_4). The solvent was then evaporated under vacuum and the residue was distilled (*ca.* 160 °C and 60 mbar) on a Kugelrohr apparatus to remove unreacted 3-(bromomethyl)-heptane, to afford the title compound **10** (1.54 g, 92%) as a colorless oil; R_f 0.31 (*n*-hexane); ν_{max}/cm^{-1} 3053w (Ar CH), 2957w, 2928w, 2872w and 2859w (alkyl CH), 1628w, 1597m, 1483s, 1462s, 1452s, 1379w, 1342m, 1325s, 1246w, 1219m, 1204m, 1153m, 1121m, 1024w, 1003w, 841w; δ_H(500 MHz; $CDCl_3$) 8.12 (2H, d, *J* 7.7, Ar *H*), 7.49-7.45 (2H, m, Ar *H*), 7.40 (2H, d, *J* 8.2, Ar *H*), 7.26-7.20 (2H, m, Ar *H*), 4.18 (2H, dd, *J* 7.1, 5.6, CH_2), 2.10-2.03 (1H, m, C*H*), 1.40-1.21 (8H, m, CH_2), 0.92 (3H, t, *J* 7.4, CH_3), 0.88 (3H, t, *J* 7.4, CH_3); δ_C(125 MHz; $CDCl_3$) 140.9 (s), 125.5 (d), 122.7 (s), 120.2 (d), 118.6 (d), 108.9 (d), 47.4 (t), 39.4 (d), 31.0 (t), 28.8 (t), 24.4 (t), 23.0 (t), 14.0 (q), 10.9 (q); identical to an authentic sample.[10]

*2.2.1.2. 9-*n*-Decyl-9*H*-carbazole (**11**).* Similar treatment of 9*H*-carbazole (1.0 g, 6.0 mmol) with 1-bromodecane (3.98 g, 18 mmol) in PhH (10 mL) gave the title compound

11 (1.57 g, 85%) as a colorless oil; R_f 0.45 (*n*-hexane/DCM, 9:1); ν_{max}/cm^{-1} 3053w and 3022w (Ar CH), 2953w, 2924w, 2870w and 2853w (alkyl CH), 1628w, 1597m, 1485s, 1464s, 1452s, 1418w, 1378w, 1346m, 1333m, 1325s, 1256w, 1234w, 1229w, 1219w, 1192w, 1152m, 1128w, 1121m, 1067w, 1024w, 1016w, 1003w, 955w, 926w, 903w, 880w, 779w, 748s; δ_H(500 MHz; $CDCl_3$) 8.14 (2H, d, *J* 7.7, Ar *H*), 7.50 (2H, ddd, *J* 8.1, 8.1, 0.9, Ar *H*), 7.43 (2H, d, *J* 8.1, Ar *H*), 7.26 (2H, dd, *J* 7.3, 7.3, Ar *H*), 4.32 (2H, t, *J* 7.3, C*H*$_2$), 1.93-1.87 (2H, m, C*H*$_2$), 1.43-1.28 (14H, m, C*H*$_2$), 0.92 (3H, t, *J* 6.8, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) 140.4 (s), 125.5 (d), 122.8 (s), 120.3 (d), 118.7 (d), 108.6 (d), 43.1 (t), 31.8 (t), 29.52 (t), 29.49 (t), 29.4 (t), 29.3 (t), 28.9 (t), 27.3 (t), 22.7 (t), 14.1 (q); identical to an authentic sample.[11]

2.2.2. Bromination of 9-alkyl-9*H*-carbazoles (based on the method of Promarak *et al.*[5])

*2.1.2.1. 3-Bromo-9-(2-ethylhexyl)-9H-carbazole (**12**)* (Typical procedure): A solution of 9-(2-ethylhexyl)-9*H*-carbazole (**10**) (1.00 g, 3.58 mmol) in THF (10 mL) was cooled to *ca.* 0 °C and then NBS (638 mg, 3.58 mmol) was added in four portions over 30 min and the solution stirred for a further 30 min at this temperature. Then H_2O (20 mL) was added and the mixture was extracted with DCM (2 × 20 mL), dried (Na_2SO_4), filtered and the solvent evaporated. To the residue was added *n*-pentane (20 mL) and the mixture filtered to remove any remaining succinimide, to afford the title compound **12** (1.29 g, 95%) as a colorless oil (82% purity by ^{1}H NMR), which was used for the next step without further purification: R_f 0.38 (*n*-hexane); (found: C, 66.92; H, 6.89; N, 4.00. $C_{20}H_{24}BrN$ requires C, 67.04; H, 6.75; N, 3.91%); λ_{max}(DCM)/nm 239 (log ε 3.57), 247 inf (3.42), 267 (3.37), 298 (3.08), 335 (2.37), 352 (2.42); ν_{max}/cm^{-1} 3091w and 3009w (Ar CH), 2957w, 2928w, 2872w and 2857w (alkyl CH), 1626w, 1595w, 1487m, 1474s,

1460s, 1445s, 1379w, 1342m, 1331m, 1317m, 1286w, 1273m, 1244w, 1217m, 1204m, 1153m, 1142m, 1124w, 1053m, 1022m, 1009w, 963w, 926w, 870m, 831w, 806s, 795s, 758s, 744s; δ_H(500 MHz; $CDCl_3$) 8.22 (1H, s, Ar *H*), 8.06 (1H, d, *J* 7.8, Ar *H*), 7.55-7.50 (2H, m, Ar *H*), 7.43-7.38 (1H, m, Ar *H*), 7.27-7.21 (2H, m, Ar *H*), 4.15 (2H, dd, *J* 6.9, 4.1, C*H*$_2$), 2.07-1.99 (1H, m, C*H*), 1.40-1.21 (8H, m, C*H*$_2$), 0.93 (3H, t, *J* 7.3, C*H*$_3$), 0.88 (3H, t, *J* 7.0, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) 141.1 (s), 139.5 (s), 128.1 (d), 126.2 (d), 124.4 (s), 122.9 (d), 121.7 (s), 120.4 (d), 119.1 (d), 111.5 (s), 110.4 (d), 109.2 (d), 47.4 (t), 39.3 (d), 30.9 (t), 28.8 (t), 24.4 (t), 23.0 (t), 14.0 (q), 10.9 (q); *m*/*z* (MALDI-TOF) 359 (M^++2, 4%), 357 (M^+, 10), 279 (51); identical to that reported.[12] The crude product was isolated as an inseparable mixture containing the starting 9-(2-ethylhexyl)-9*H*-carbazole (**10**) (~10%) and overbrominated 3,6-dibromo-9-(2-ethylhexyl)-9*H*-carbazole (~8%) (by ^{1}H NMR):[13] 9-(2-ethylhexyl)-9*H*-carbazole (**10**): δ_H(500 MHz; $CDCl_3$) 8.13 (2H, d, *J* 7.7, Ar *H*) and δ_C(125 MHz; $CDCl_3$) 125.5 (d), 120.2 (d), 118.6 (d), 108.9 (d); 3,6-dibromo-9-(2-ethylhexyl)-9*H*-carbazole: δ_H(500 MHz; $CDCl_3$) 8.16 (2H, s, Ar *H*) and δ_C(125 MHz; $CDCl_3$) 128.9 (d), 123.1 (d), 111.9 (s), 110.6 (d).

*2.2.2.1. 3-Bromo-9-*n*-decyl-9*H*-carbazole (**13**).* Similar treatment of 9-*n*-decyl-9*H*-carbazole (**11**) (1.10 g, 3.57 mmol) in THF (10 mL) at *ca*. 0 ^{o}C with NBS (636 mg, 3.57 mmol) gave the *title compound* **13** (1.42 g, 86%) as a colorless oil (83% purity by ^{1}H NMR), which can be used for the next step without further purification: R_f 0.43 (*n*-hexane); (found: C, 68.42; H, 7.37; N, 3.59. $C_{22}H_{28}BrN$ requires C, 68.39; H, 7.30; N, 3.63%); λ_{max}(DCM)/nm 240 (log ε 3.60), 247 inf (3.44), 267 (3.40), 298 (3.10), 336 (2.43), 356 (2.52); ν_{max}/cm^{-1} 3057w (Ar CH), 2953m, 2924m and 2853m (alkyl CH), 1628w, 1595w, 1487m, 1474s, 1462s, 1445m, 1379w, 1346m, 1331m, 1317m, 1273m, 1234m, 1227m, 1153m, 1144w, 1125w, 1055m, 1022m, 1009w, 924w, 870m, 795s,

745s; δ_H(500 MHz; $CDCl_3$) 8.20 (1H, s, Ar *H*), 8.05 (1H, d, *J* 7.7, Ar *H*), 7.55-7.45 (2H, m, Ar *H*), 7.42-7.39 (1H, m, Ar *H*), 7.27 (1H, d, *J* 8.6, Ar *H*), 7.26-7.23 (1H, m, Ar *H*), 4.31-4.25 (2H, m, CH_2), 1.90-1.79 (2H, m, CH_2), 1.39-1.20 (14H, m, CH_2), 0.89-0.86 (3H, m, CH_3); δ_C(125 MHz; $CDCl_3$) 140.7 (s), 139.0 (s), 128.2 (d), 126.3 (d), 124.5 (s), 123.0 (d), 121.8 (s), 120.5 (d), 119.1 (d), 111.5 (s), 110.1 (d), 108.9 (d), 43.2 (t), 31.8 (t), 29.48 (t), 29.46 (t), 29.4 (t), 29.2 (t), 28.9 (t), 27.3 (t), 22.6 (t), 14.1 (q); *m*/*z* (MALDI-TOF) 387 (M^++2, 34%), 385 (M^+, 37), 371 (31), 358 (43), 306 (70), 261 (100), 259 (98). The crude product was isolated as an inseparable mixture containing tentatively the starting 9-*n*-decyl-9*H*-carbazole (**11**) (~7%) and overbrominated 3,6-dibromo-9-*n*-decyl-9*H*-carbazole (~10%) (by ^{1}H NMR):[14] 9-*n*-decyl-9*H*-carbazole (**11**): δ_H(500 MHz; $CDCl_3$) 8.11 (2H, d, *J* 7.7, Ar *H*) and δ_C(125 MHz; $CDCl_3$) 125.5 (d), 120.3 (d), 118.6 (d), 108.6 (d); 3,6-dibromo-9-*n*-decyl-9*H*-carbazole: δ_H(500 MHz; $CDCl_3$) 8.15 (2H, d, *J* 1.6, Ar *H*) and δ_C(125 MHz; $CDCl_3$) 139.3 (s), 129.0 (d), 123.4 (s), 123.2 (d), 111.9 (d), 110.4 (d).

2.2.3. Stannylation of 9-alkyl-3-bromo-9*H*-carbazoles (based on the method of Jäkle *et al.*,[6]).

2.2.3.1. 9-(2-Ethylhexyl)-3-(tri-n-*butylstannyl)-9*H*-carbazole (**14**). (Typical procedure):* To a stirred solution of crude 3-bromo-9-(2-ethylhexyl)-9*H*-carbazole (**12**) (1.0 g, 2.28 mmol) in THF (10 mL) at *ca.* -78 ºC was added dropwise a solution of *n*-BuLi (2.5 M in *n*-hexane; 1.0 mL, 2.51 mmol). After the addition, the reaction mixture was stirred at *ca.* -78 ºC for 30 min and then allowed to warm to *ca.* 20 ºC over 30 min. Then the mixture was cooled to *ca.* -78 ºC, and *n*-Bu_3SnCl (0.68 mL, 2.51 mmol) was added in one portion. Next, the cooling bath was removed and the mixture was stirred at *ca.* 20 ºC for 16 h. The reaction mixture was then quenched by adding saturated NH_4Cl (10 mL) and extracted with *t*-BuOMe (3 × 10 mL). The combined organic layer was then washed with

brine (10 mL) and dried (Na_2SO_4). After filtration, the solvent was removed under vacuum to afford the *title compound* **14** (1.29 g, 73%) as a yellow oil (73% purity by ^{1}H NMR), which was used for the next step without further purification: R_f 0.32 (*n*-hexane); λ_{max}(DCM)/nm 238 (log ε 3.63), 266 (3.48), 296 (3.15), 329 (2.44), 345 (2.50); ν_{max}/cm^{-1} 3050w (Ar CH), 2957m, 2924m, 2872m and 2855m (alkyl CH), 1599w, 1433m, 1464m, 1452m, 1416w, 1377w, 1342w, 1325w, 1292w, 1252w, 1220w, 1204w, 1180w, 1153w, 1121w, 1074w, 1024w, 1003w, 961w, 878w, 866w, 843w, 770w, 748s; δ_H(500 MHz; $CDCl_3$) 8.23 (1H, s, Ar *H*), 8.17 (1H, d, *J* 7.7, Ar *H*), 7.57 (2H, d, *J* 8.0, Ar *H*), 7.50-7.47 (1H, m, Ar *H*), 7.45-7.41 (2H, m, Ar *H*), 7.27 (1H, t, *J* 7.9, Ar *H*), 4.21-4.10 (2H, m, CH_2), 2.15-2.05 (1H, m, C*H*), 1.71-1.56 (6H, m, CH_2), 1.45-1.30 (14H, m, CH_2), 1.27-1.10 (6H, m, CH_2), 0.99-0.90 (15H, m, CH_3); δ_C(125 MHz; $CDCl_3$) 141.1 (s), 140.6 (s), 133.2 (d), 129.3 (s), 128.1 (d), 125.4 (d), 123.1 (s), 122.6 (s), 120.2 (d), 118.6 (d), 108.91 (d), 108.89 (d), 47.3 (t), 39.4 (d), 31.0 (t), 29.2 (t), 28.8 (t), 27.4 (t), 24.4 (t), 23.1 (t), 14.0 (q), 13.7 (q), 10.9 (q), 9.8 (t); *m*/*z* (MALDI-TOF) 570 (M^++1, 62%), 556 (29), 512 (26), 348 (100), 279 (37). The crude product was isolated as an inseparable mixture containing protodebrominated 9-(2-ethylhexyl)-9*H*-carbazole (**10**) (~16%), *n*-Bu_3SnCl (~11%) and other unknown minor impurities: 9-(2-ethylhexyl)-9*H*-carbazole (**10**): δ_H(500 MHz; $CDCl_3$) 8.14 (2H, d, *J* 7.7, Ar *H*) and δ_C(125 MHz; $CDCl_3$) 140.9 (s), 125.5 (d), 122.8 (s), 120.1 (d), 108.8 (d); *n*-Bu_3SnCl: δ_H(500 MHz; $CDCl_3$) 1.71-1.56 (6H, m, CH_2), 1.45-1.30 (12H, m, CH_2), 0.92 (9H, t, *J* 7.1, CH_3) and δ_C(125 MHz; $CDCl_3$) 27.8 (t), 26.8 (t), 17.5 (t), 13.6 (q).

2.2.3.1. 9-n-*Decyl-3-(tri*-n-*butylstannyl)-9*H-*carbazole (**15**).* Similar treatment of crude 3-bromo-9-*n*-decyl-9*H*-carbazole (**13**) (1.00 g, 2.59 mmol) in THF (10 mL) with *n*-BuLi (2.5 M in *n*-hexane; 1.14 mL, 2.85 mmol) and *n*-Bu_3SnCl (0.77 mL, 2.85 mmol) gave the

title compound **15** (1.80 g, 84%) as a yellow oil (82% purity by ^{1}H NMR), which was used in the next step without further purification: R_f 0.46 (*n*-hexane); λ_{max}(DCM)/nm 236 (log ε 3.46), 266 (3.29), 294 (3.01), 329 (2.34), 344 (2.38); ν_{max}/cm^{-1} 3053w (Ar CH), 2955s, 2924s, 2870m and 2852m (alkyl CH), 1591w, 1558w, 1485m, 1464s, 1452s, 1416w, 1377m, 1346m, 1325m, 1292w, 1269w, 1240w, 1153m, 1121w, 1074w, 1049w, 1022w, 1003w, 961w, 876w, 843w, 797w, 770w, 748s; δ_H(500 MHz; $CDCl_3$) 8.18 (1H, s, Ar *H*), 8.11 (1H, d, *J* 7.9, Ar *H*), 7.53-7.43 (2H, m, Ar *H*), 7.41-7.38 (2H, m, Ar *H*), 7.23 (1H, t, *J* 7.8, Ar *H*), 4.32-4.27 (2H, m, CH_2), 1.90-1.84 (2H, m, CH_2), 1.68-1.57 (6H, m, CH_2), 1.39-1.25 (24H, m, CH_2), 1.42-1.10 (2H, m, CH_2), 0.95-0.89 (12H, m, CH_3); δ_C(125 MHz; $CDCl_3$) 140.6 (s), 140.1 (s), 133.2 (d), 129.3 (s), 128.2 (d), 125.4 (d), 123.1 (s), 122.6 (s), 120.2 (d), 118.7 (d), 108.62 (d), 108.52 (d), 43.0 (t), 31.8 (t), 29.52 (t), 29.49 (t), 29.4 (t), 29.2 (t), 29.0 (t), 27.4 (t), 27.3 (t), 22.6 (t), 17.5 (t), 14.1 (q), 13.7 (q), 9.76 (t); *m*/*z* (MALDI-TOF) 597 (M^+, 28%), 596 (84), 540 (100), 484 (19). The crude product was isolated as an inseparable mixture containing *n*-Bu_3SnCl (~10%), 9-*n*-decyl-9*H*-carbazole (**11**) (~8%) and other unidentified minor impurities: 9-*n*-decyl-9*H*-carbazole (**11**): δ_H(500 MHz; $CDCl_3$) 8.13 (2H, d, *J* 8.0, Ar *H*), 7.31 (2H, d, *J* 8.9, Ar *H*) and δ_C(125 MHz; $CDCl_3$) 140.4 (s), 125.5 (d), 122.8 (s), 120.3 (d), 108.59 (d), 43.05 (t), 29.25 (t), 28.9 (t); *n*-Bu_3SnCl: δ_H(500 MHz; $CDCl_3$) 1.68-1.57 (6H, m, CH_2), 1.39-1.25 (12H, m, CH_2), 0.95-0.89 (9H, m, CH_3) and δ_C(125 MHz; $CDCl_3$) 27.8 (t), 26.8 (t), 17.5 (t), 13.6 (q).

2.3. Preparation of 9-alkyl-3-thien-2-yl-9*H*-carbazole starting materials and 3-*n*-hexyl-2-(tri-*n*-butylstannyl)thiophene

2.3.1. Thienylation of 9-alkyl-3-bromo-9*H*-carbazoles

*2.3.1.1. 9-(2-Ethylhexyl)-3-(thien-2-yl)-9*H*-carbazole (**16**). (Typical procedure):* To a stirred solution of 3-bromo-9-(2-ethylhexyl)-9*H*-carbazole (**12**) (358 mg, 1.00 mmol) in

PhMe (4 mL) at *ca*. 20 °C, was added 2-(tri-*n*-butylstannyl)thiophene (933 mg, 2.50 mmol) and $Pd(Ph_3P)_2Cl_2$ (10.5 mg, 0.015 mmol). The solution was then deareated by bubbling into the reaction mixture Ar gas for 10 min. The reaction mixture was then heated at reflux under Ar, until no starting material remained (TLC, 6 h). On cooling to *ca.* 20 °C the reaction mixture was adsorbed onto silica and chromatographed (*n*-hexane/DCM, 9:1) to give the *title compound* **16** (181 mg, 75%) as a colorless oil: R_f 0.45 (*n*-hexane); (found: C, 79.68; H, 7.50; N, 4.01. $C_{24}H_{27}NS$ requires C, 79.73; H, 7.53; N, 3.87%); λ_{max}(DCM)/nm 240 (log ε 3.40), 260 inf (3.12), 305 (3.38), 327 inf (3.17); ν_{max}/cm^{-1} 3055w (Ar CH), 2957m, 2928m, 2872m and 2857m (alkyl CH), 1628w, 1599m, 1489m, 1477m, 1468s, 1437m, 1429m, 1379m, 1331m, 1294m, 1280m, 1258m, 1219m, 1205m, 1155m, 1125w, 1080w, 1065w, 1049w, 1024w, 1011w, 964w, 908m, 880m, 851m, 799s, 766m, 745s, 727s; δ_H(500 MHz; $CDCl_3$) 8.33 (1H, s, Ar *H*), 8.14 (1H, d, *J* 7.7, Ar *H*), 7.73 (1H, dd, *J* 8.5, 1.8, Ar *H*), 7.50-7.45 (1H, m, Ar *H*), 7.41-7.36 (2H, m, Ar *H*), 7.36-7.33 (1H, m, Ar *H*), 7.28-7.22 (2H, m, Ar *H*), 7.14-7.10 (1H, m, Ar *H*), 4.21-4.13 (2H, m, C*H*$_2$), 2.12-2.04 (1H, m, C*H*), 1.42-1.20 (8H, m, C*H*$_2$), 0.93 (3H, t, *J* 7.5, C*H*$_3$), 0.88 (3H, t, *J* 7.1, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) 145.8 (s), 141.4 (s), 140.5 (s), 128.0 (d), 125.9 (d), 125.6 (s), 124.2 (d), 123.6 (d), 123.2 (s), 122.7 (s), 122.0 (d), 120.4 (d), 119.0 (d), 117.8 (d), 109.2 (d), 109.15 (d), 47.5 (t), 39.4 (d), 31.0 (t), 28.8 (t), 24.4 (t), 23.0 (t), 14.0 (q), 10.9 (q); *m*/*z* (MALDI-TOF) 362 (M^++1, 25%), 361 (M^+, 100).

2.3.1.2. 9-n-*Decyl-3-(thien-2-yl)-9*H-*carbazole (**17**).* Similar treatment of 3-bromo-9-*n*-decyl-9*H*-carbazole (**13**) (386 mg, 1.00 mmol) in PhMe (4 mL) with 2-(tri-*n*-butylstannyl)thiophene (933 mg, 2.50 mmol) and $Pd(Ph_3P)_2Cl_2$ (10.5 mg, 0.015 mmol) gave on chromatography (*n*-hexane/DCM, 9:1) the *title compound* **17** (331 mg, 85%) as a colorless oil: R_f 0.46 (*n*-hexane/DCM, 9:1); (found: C, 80.07; H, 8.04; N, 3.58. $C_{26}H_{31}NS$

requires C, 80.15; H, 8.02; N, 3.60%); λ_{max}(DCM)/nm 240 (log ε 3.65), 258 inf (3.44), 298 (3.66), 319 inf (3.34); ν_{max}/cm^{-1} 3049w (Ar CH), 2953m, 2924m and 2853m (alkyl CH), 1684w, 1653w, 1628w, 1599w, 1558w, 1489m, 1477m, 1468m, 1439m, 1429m, 1383w, 1346m, 1331m, 1294m, 1281m, 1236m, 1225m, 1153m, 1124w, 1080w, 1047w, 1024w, 964w, 926w, 878m, 851m, 822w, 799s, 766m, 745s, 727s; δ_H(500 MHz; $CDCl_3$) 8.38-8.32 (1H, m, Ar *H*), 8.19-8.15 (1H, m, Ar *H*), 7.79-7.73 (1H, m, Ar *H*), 7.54-7.46 (1H, m, Ar *H*), 7.43-7.38 (3H, m, Ar *H*), 7.29-7.26 (2H, m, Ar *H*), 7.18-7.12 (1H, m, Ar *H*), 4.32-4.25 (2H, m, CH_2), 1.92-1.83 (2H, m, CH_2), 1.45-1.20 (14H, m, CH_2), 0.96-0.88 (3H, m, CH_3); δ_C(125 MHz; $CDCl_3$) 145.8 (s), 140.9 (s), 140.0 (s), 127.9 (d), 125.9 (d), 125.6 (s), 124.2 (d), 123.6 (d), 123.2 (s), 122.8 (s), 122.0 (d), 120.5 (d), 119.0 (d), 117.7 (d), 108.9 (d), 108.85 (d), 43.2 (t), 31.8 (t), 29.49 (t), 29.46 (t), 29.4 (t), 29.2 (t), 29.0 (t), 27.3 (t), 22.6 (t), 14.1 (q); *m*/*z* (MALDI-TOF) 390 (M^++1, 26%), 389 (M^+, 59), 262 (100).

2.3.2. Bromination of 9-alkyl-3-(thien-2-yl)-9*H*-carbazoles

*2.3.2.1. 3-(5-Bromothien-2-yl)-9-(2-ethylhexyl)-9*H*-carbazole (**18**). (Typical procedure):* A solution of 9-(2-ethylhexyl)-3-(thien-2-yl)-9*H*-carbazole (**16**) (363 mg, 1.00 mmol) in THF (20 mL) was cooled to *ca.* 0 °C and then NBS (178 mg, 1.00 mmol) was added in four portions over 30 min and the solution stirred for a further 30 min at this temperature. Then H_2O (20 mL) was added and the mixture was extracted with Et_2O (2 × 20 mL), dried (Na_2SO_4), filtered and the solvent evaporated. Then crude product was purified by short dry-flash chromatography (*n*-hexane) to give the *title compound* **18** (407 mg, 92%) as a colorless oil: R_f 0.29 (*n*-hexane); (found: C, 65.36; H, 6.07; N, 3.39. $C_{24}H_{26}BrNS$ requires C, 65.45; H, 5.95; N, 3.18%); λ_{max}(DCM)/nm 242 (log ε 3.55), 258 inf (3.35), 300 (3.60), 320 inf (3.29); ν_{max}/cm^{-1} 3051w (Ar CH), 2957m, 2928m and 2870w (alkyl CH), 1628w, 1599m, 1481m, 1468m, 1435m, 1379m, 1346m, 1325m,

1290w, 1271w, 1256w, 1248w, 1219m, 1204m, 1155m, 1124w, 1064w, 1059w, 1024w, 1011w, 982w, 955w, 947w, 878w, 788s, 766w, 745s, 725m; δ_H(500 MHz; $CDCl_3$) 8.22 (1H, d, *J* 1.8, Ar *H*), 8.12 (1H, d, *J* 7.7, Ar *H*), 7.61 (1H, dd, *J* 8.5, 1.8, Ar *H*), 7.51-7.47 (1H, m, Ar *H*), 7.40 (1H, d, *J* 8.2, Ar *H*), 7.37 (1H, d, *J* 8.5, Ar *H*), 7.28-7.25 (1H, m, Ar *H*), 7.06 (2H, dd, *J* 9.7, 3.8, Ar *H*), 4.20-4.11 (2H, m, C*H*$_2$), 2.11-2.03 (1H, m, C*H*), 1.46-1.24 (8H, m, C*H*$_2$), 0.93 (3H, t, *J* 7.5, C*H*$_3$), 0.89 (3H, t, *J* 7.1, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) 147.4 (s), 141.4 (s), 140.6 (s), 130.8 (d), 126.0 (d), 124.8 (s), 123.8 (d), 123.2 (s), 122.6 (s), 122.0 (d), 120.4 (d), 119.1 (d), 117.5 (d), 109.7 (s), 109.3 (d), 109.2 (d), 47.5 (t), 39.4 (d), 31.0 (t), 28.8 (t), 24.4 (t), 23.0 (t), 14.0 (q), 10.9 (q); *m*/*z* (MALDI-TOF) 441 (M^++2, 85%), 439 (M^+, 89), 342 (100), 340 (99).

*2.3.2.2. 3-(5-Bromothien-2-yl)-9-*n*-decyl-9*H*-carbazole (**19**).* Similar treatment of 9-*n*-decyl-3-(thien-2-yl)-9*H*-carbazole (**17**) (390 mg, 1.00 mmol) with NBS (178 mg, 1.00 mmol) gave the *title compound* **19** (464 mg, 99%) as a colorless oil: R_f 0.46 (*n*-hexane); (found: C, 66.50; H, 6.61; N, 3.07. $C_{26}H_{30}BrNS$ requires C, 66.66; H, 6.45; N, 2.99%); λ_{max}(DCM)/nm 241 (log ε 3.43), 305 (3.46), 325 inf (3.24); ν_{max}/cm^{-1} 3049w (Ar CH), 2953m, 2924m and 2853w (alkyl CH), 1628w, 1599m, 1559w, 1481s, 1468s, 1452m, 1441m, 1435m, 1385m, 1350m, 1327m, 1290m, 1271m, 1242m, 1217m, 1196w, 1153m, 1125w, 1057w, 1022w, 1011w, 982m, 955w, 949w, 926w, 878w, 766s, 745s, 727s; δ_H(500 MHz; $CDCl_3$) 8.22 (1H, s, Ar *H*), 8.14-8.10 (1H, m, Ar *H*), 7.65-7.59 (1H, m, Ar *H*), 7.50-7.42 (1H, m, Ar *H*), 7.40-7.33 (2H, m, Ar *H*), 7.27-7.22 (1H, m, Ar *H*), 7.09-7.02 (2H, m, Ar *H*), 4.31-4.22 (2H, m, C*H*$_2$), 1.91-1.82 (2H, m, C*H*$_2$), 1.40-1.20 (14H, m, C*H*$_2$), 0.91-0.83 (3H, m, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) 147.4 (s), 140.9 (s), 140.1 (s), 130.8 (d), 126.1 (d), 124.8 (s), 123.85 (d), 123.25 (s), 122.6 (s), 122.05 (d), 120.5 (d), 119.1 (d), 117.6 (d), 109.7 (s), 109.1 (d), 108.9 (d), 43.2 (t), 31.8 (t), 29.50 (t), 29.47 (t), 29.4

(t), 29.2 (t), 29.0 (t), 27.3 (t), 22.6 (t), 14.1 (q); *m*/*z* (MALDI-TOF) 469 (M^++2, 100%), 467 (M^+, 90). The product contained an inseparable minor unidentified impurity and was used in the next step without further purification.

2.3.3. Stannylation of 9-alkyl-3-(5-bromothien-2-yl)-9*H*-carbazoles and 2-bromo-3-*n*-hexylthiophene

2.2.3.1. 9-(2-Ethylhexyl)-3-[5-(tri-n-*butylstannyl)thien-2-yl]-9*H-*carbazole (**20**). (Typical procedure).* To a stirred solution of 3-(5-bromothien-2-yl)-9-(2-ethylhexyl)-9*H*-carbazole (**18**) (1.00 g, 2.27 mmol) in THF (10 ml) at -78 °C was added dropwise a solution of *n*-BuLi (2.5 M in *n*-hexane; 1.0 mL, 2.51 mmol). After the addition, the reaction mixture was stirred at -78 °C for 30 min and then warmed to room temperature over 30 min. Then the mixture was cooled to -78 °C, and *n*-Bu_3SnCl (0.68 mL, 2.51 mmol) was added in one portion. Next, the cold bath was removed and the mixture was stirred at room temperature for 16h. The reaction mixture was then quenched by adding a saturated solution of NH_4Cl (10 mL) and extracted with *t*-BuOMe (3 × 10 mL). The combined organic layer was then washed with brine (10 mL) and dried (Na_2SO_4). After filtration, the solvent was removed by evaporation to afford the *title compound* **20** (0.83 g, 63%) as a yellow oil (77% purity by ^{1}H NMR), which can be used for the next step without further purification: R_f 0.38 (*n*-hexane); λ_{max}(DCM)/nm 240 (log ε 3.53), 259 inf (3.31), 299 (3.54), 317 inf (3.31); ν_{max}/cm^{-1} 3055w (Ar CH), 2955s, 2926s, 2870m and 2855m (alkyl CH), 1599w, 1559m, 1522m, 1491m, 1464s, 1420m, 1368m, 1348m, 1294w, 1283w, 1263w, 1248w, 1217m, 1206m, 1153m, 1125w, 1072m, 1047w, 1024w, 961m, 930m, 878m, 833m, 793s, 768m, 745s; δ_H(500 MHz; $CDCl_3$) 8.33 (1H, dd, *J* 6.2, 1.5, Ar *H*), 8.14 (1H, d, *J* 7.7, Ar *H*), 7.74 (1H, ddd, *J* 7.6, 7.6, 1.7, Ar *H*), 7.49-7.44 (2H, m, Ar *H*), 7.41-7.36 (2H, m, Ar *H*), 7.25-7.23 (1H, m, Ar *H*), 7.18

(1H, d, *J* 3.3, Ar *H*), 4.22-4.12 (2H, m, CH_2), 2.12-2.04 (1H, m, C*H*), 1.65-1.59 (6H, m, CH_2), 1.44-1.25 (14H, m, CH_2), 1.20-1.09 (6H, m, CH_2), 0.96-0.95 (15H, m, CH_3); δ_C(125 MHz; $CDCl_3$) 151.4 (s), 141.3 (s), 140.3 (s), 136.5 (d), 135.2 (s), 125.8 (d), 125.6 (s), 124.3 (d), 123.3 (d), 123.15 (s), 122.9 (s), 120.2 (d), 118.9 (d), 117.7 (d), 109.13 (d), 108.9 (d), 47.5 (t), 39.4 (d), 31.0 (t), 29.0 (t), 28.8 (t), 27.3 (t), 24.4 (t), 23.0 (t), 14.0 (q), 13.7 (q), 10.9 (q), 10.8 (t); *m*/*z* (MALDI-TOF) 651 (M^+, 20%), 649 (15), 594 (100), 480 (5), 361 (19). The crude product was isolated as an inseparable mixture containing the hydrodebrominated 9-(2-ethylhexyl)-3-(thien-2-yl)-9*H*-carbazole (**16**) (~23%) and other minor impurities: 9-(2-ethylhexyl)-3-(thien-2-yl)-9*H*-carbazole (**16**): 7.11 (1H, dd, *J* 5.0, 3.5, C*H*) and δ_C(125 MHz; $CDCl_3$) 145.8 (s), 141.4 (s), 140.5 (s), 128.0 (d), 125.9 (d), 124.25 (d), 123.6 (d), 123.2 (s), 122.7 (s), 122.0 (d), 120.4 (d), 119.0 (d), 117.8 (d), 109.22 (d), 109.09 (d).

2.3.3.2. 9-n-*Decyl-3-[5-(tri*-n-*butylstannyl)thien-2-yl]-9*H-*carbazole (**21**)*. Similar treatment of 3-(5-bromothien-2-yl)-9-*n*-decyl-9*H*-carbazole (**19**) (1.00 g, 2.13 mmol) with *n*-BuLi (2.5 M in *n*-hexane; 0.94 mL, 2.36 mmol) and *n*-Bu_3SnCl (0.64 mL, 2.36 mmol) gave the *title compound* **21** (1.54 g, 97%) as a yellow oil (91% purity by ^{1}H NMR), which can be used for the next step without further purification: R_f 0.34 (*n*-hexane); λ_{max}(DCM)/nm 239 (log ε 3.40), 300 (3.45), 318 inf (3.22); ν_{max}/cm^{-1} 3055w (Ar CH), 2955s, 2924s, 2870m and 2853m (alkyl CH), 1599w, 1558m, 1522m, 1491m, 1477s, 1468s, 1429m, 1375m, 1348m, 1331m, 1292m, 1283w, 1242w, 1223w, 1198w, 1153m, 1125w, 1074m, 1049w, 1022w, 982w, 961w, 878m, 853w, 831w, 799s, 767m, 745s, 727s; δ_H(500 MHz; $CDCl_3$) 8.34 (1H, s, Ar *H*), 8.14 (1H, d, *J* 7.9, Ar *H*), 7.76-7.68 (1H, m, Ar *H*), 7.49-7.46 (2H, m, Ar *H*), 7.42-7.38 (2H, m, Ar *H*), 7.25-7.23 (1H, m, Ar *H*), 7.17-7.16 (1H, m, Ar *H*), 4.32-4.26 (2H, m, CH_2), 1.91-1.84 (2H, m, CH_2), 1.66-1.60 (4H,

m, C*H*$_2$), 1.51-1.44 (4H, m, C*H*$_2$), 1.41-1.25 (20H, m, C*H*$_2$), 1.18-1.14 (4H, m, C*H*$_2$), 0.95-0.86 (12H, m, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) 151.4 (s), 140.9 (s), 139.9 (s), 136.5 (d), 135.2 (s), 125.9 (s), 125.8 (d), 124.32 (d), 123.3 (d), 123.2 (s), 122.9 (s), 120.5 (d), 118.9 (d), 117.8 (d), 108.84 (d), 108.81 (d), 43.2 (t), 31.8 (t), 29.51 (t), 29.48 (t), 29.4 (t), 29.26 (t), 29.25 (t), 29.0 (t), 27.4 (t), 27.3 (t), 22.7 (t), 13.71 (q), 13.68 (q), 10.8 (t); *m*/*z* (MALDI-TOF) 679 (M^+, 34%), 678 (M^+-1, 20), 677 (30), 622 (100), 510 (8), 389 (19). The crude product was isolated as an inseparable mixture containing the hydrodebrominated 9-*n*-decyl-3-(thien-2-yl)-9*H*-carbazole (**17**) (~9%) and other minor impurities: 9-*n*-decyl-3-(thien-2-yl)-9*H*-carbazole (**17**): δ_H(500 MHz; $CDCl_3$) 8.21 (1H, m, Ar *H*) and δ_C(125 MHz; $CDCl_3$) 127.9 (d), 124.27 (d), 123.6 (d), 122.0 (d), 118.95 (d), 117.7 (d), 108.9 (d).

2.3.3.3. 3-n-*Hexyl-2-(tri*-n-*butylstannyl)thiophene (**22**).* Similar treatment of 2-bromo-3-*n*-hexylthiophene (0.40 mL, 2.00 mmol) with *n*-BuLi (2.5 M in *n*-hexane; 0.96 mL, 2.40 mmol) and *n*-Bu_3SnCl (0.65 mL, 2.40 mmol) gave the *title compound* **22** (1.08 g, 76%) as a yellow oil (64% purity by ^{1}H NMR), which was an inseparable mixture with *n*-Bu_3SnCl and was used for the next step without further purification: R_f 0.82 (*n*-hexane); λ_{max}(DCM)/nm 241 (log ε 3.91); ν_{max}/cm^{-1} 3060w (Ar CH), 2955s, 2926s, 2870m and 2855m (alkyl CH), 1510w, 1464m, 1418w, 1393w, 1377m, 1364w, 1341w, 1292w, 1258w, 1250w, 1219w, 1180w, 1153w, 1074m, 1047w, 1022w, 1001w, 961m, 874m, 866m, 829m, 772m; δ_H(500 MHz; $CDCl_3$) 7.53 (1H, d, *J* 4.5, Ar *H*), 7.10 (1H, d, *J* 3.2, Ar *H*), 2.60 (2H, t, *J* 7.1, C*H*$_2$), 1.68-1.52 (8H, m, C*H*$_2$), 1.39-1.29 (12H, m, C*H*$_2$), 1.14-1.10 (6H, m, C*H*$_2$), 0.99-0.89 (12H, m, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) 150.7 (s), 130.8 (s), 130.6 (d), 129.1 (d), 32.9 (t), 32.2 (t), 31.8 (t), 29.4 (t), 29.04 (t), 27.3 (t), 22.6 (t), 14.1 (q), 13.6 (q), 10.9 (t); *m*/*z* (MALDI-TOF) 459 (M^++1, 100%), 458 (M^+, 24), 401 (100), 345 (17). *n*-Bu_3SnCl:

δ_H(500 MHz; $CDCl_3$) 1.68-1.52 (6H, m, CH_2), 1.39-1.29 (12H, m, CH_2), 0.99-0.89 (9H, m, CH_3) and δ_C(125 MHz; $CDCl_3$) 27.8 (t), 26.8 (t), 17.5 (t), 13.6 (q).

2.4. Synthesis of thiadiazinone small molecule donors *via* Stille coupling reactions.

*2.4.1. 3,5-Bis[9-(2-ethylhexyl)-9*H*-carbazol-3-yl]-4*H*-1,2,6-thiadiazin-4-one (**2**). (Typical procedure).* To a stirred solution of 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**) (37 mg, 0.20 mmol) in MeCN (1 mL) at *ca*. 20 °C, was added 9-(2-ethylhexyl)-3-(tri-*n*-butylstannyl)-9*H*-carbazole (**14**) (341 mg, 0.60 mmol) and $Pd(Ph_3P)_2Cl_2$ (4 mg, 0.01 mmol). The solution was then deareated by bubbling Ar gas into the reaction mixture for 10 min and then the mixture was heated at reflux under Ar, until no starting material remained (TLC, 20 h). On cooling to *ca.* 20 °C the reaction mixture was adsorbed onto silica and chromatographed (*n*-hexane/DCM, 1:1) to give the *title compound* **2** (113 mg, 84%) as an orange viscous oil: R_f 0.28 (*n*-hexane/DCM, 8:2); (found: 77.10; H, 7.41; N, 8.24. $C_{43}H_{48}N_4OS$ requires C, 77.21; H, 7.23; N, 8.38%); λ_{max}(DCM)/nm 236 (log ε 3.99), 258 inf (3.68), 289 (3.79), 332 (3.40), 350 (3.40), 383 inf (3.51), 419 (3.66); ν_{max}/cm^{-1} 3056w (Ar CH), 2957m, 2928m, 2872m and 2957m (alkyl CH), 1626m, 1595m, 1491m, 1483m, 1464s, 1452s, 1431m, 1379m, 1339s, 1325s, 1281m, 1246m, 1221m, 1206m, 1155s, 1126s, 1070w, 1024w, 1001w, 961w, 904w, 877w, 844w, 818m, 785m, 767m, 747s; δ_H(500 MHz; $CDCl_3$) 9.16 (2H, d, *J* 1.6, Ar *H*), 8.39 (2H, dd, *J* 8.7, 1.7, Ar *H*), 8.21 (2H, d, *J* 7.7, Ar *H*), 7.50 (2H, dd, *J* 7.6, 7.6, Ar *H*), 7.47-7.42 (4H, m, Ar *H*), 7.29 (2H, dd, *J* 7.4, 7.4, Ar *H*), 4.25-4.16 (4H, m, CH_2), 2.13-2.06 (2H, m, C*H*), 1.44-1.25 (16H, m, CH_2), 0.93 (6H, t, *J* 7.4, CH_3), 0.88 (6H, t, *J* 7.2, CH_3); δ_C(125 MHz; $CDCl_3$) 166.5 (s), 160.2 (s), 142.4 (s), 141.4 (s), 126.8 (d), 126.0 (d), 125.9 (s), 123.3 (s), 122.6 (s), 122.1 (d), 120.7 (d), 119.6 (d), 109.3 (d), 108.6 (d), 47.6 (t), 39.4

(d), 31.0 (t), 28.8 (t), 24.4 (t), 23.0 (t), 14.0 (q), 10.9 (q); *m*/*z* (MALDI-TOF) 669 (M^++1, 25%), 668 (M^+, 17), 570 (89), 306 (100).

*2.4.2. 3,5-Bis{5-[9-(2-ethylhexyl)-9*H*-carbazol-3-yl]thien-2-yl}-4*H*-1,2,6-thiadiazin-4-one* (**3**). Similar treatment of 3,5-bis(5-bromothien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**9**) (87 mg, 0.20 mmol) in MeCN (1 mL) with 9-(2-ethylhexyl)-3-(tri-*n*-butylstannyl)-9*H*-carbazole (**14**) (341 mg, 0.60 mmol) and $Pd(Ph_3P)_2Cl_2$ (4 mg, 0.01 mmol) heated to reflux for 4 h gave on chromatography (*n*-hexane/DCM, 6:4) the *title compound* **3** (150 mg, 90%) as a red powder, (DSC) mp onset: 160.8 °C, peak max: 166.1 °C (from PhH/MeCN); R_f 0.60 (*n*-hexane/DCM, 6:4); (found: C, 73.61; H, 6.40; N, 6.80. $C_{51}H_{52}N_4OS_3$ requires C, 73.52; H, 6.29; N, 6.72%); λ_{max}(DCM)/nm 243 (log ε 3.51), 294 (3.11), 300 inf (3.74), 386 inf (3.75), 438 inf (3.88), 506 (3.80); ν_{max}/cm^{-1} 3055w and 3015w (Ar CH), 2957w, 2928w, 2870w and 2855w (alkyl CH), 1626w, 1599m, 1533w, 1481m, 1466m, 1441s, 1422s, 1379w, 1360m, 1333w, 1296w, 1279m, 1256w, 1248w, 1219m, 1203m, 1155m, 1124m, 1067m, 1044m, 1023w, 973w, 926w, 878w, 795s, 783m, 766w, 745s, 727m; δ_H(500 MHz; $CDCl_3$) 8.44-8.36 (2H, m, Ar *H*), 8.20-8.11 (4H, m, Ar *H*), 7.80-7.74 (2H, m, Ar *H*), 7.46-7.27 (10H, m, Ar *H*), 4.17-4.02 (4H, m, CH_2), 2.09-2.00 (2H, m, C*H*), 1.40-1.21 (16H, m, CH_2), 0.92 (6H, t, *J* 7.3, CH_3), 0.87 (6H, t, *J* 7.1, CH_3); δ_C(125 MHz; $CDCl_3$) 161.4 (s), 153.4 (s), 153.1 (s), 141.3 (s), 141.0 (s), 134.1 (s), 133.3 (d), 126.0 (d), 124.8 (s), 124.0 (d), 123.3 (s), 122.8 (s), 122.6 (d), 120.6 (d), 119.3 (d), 118.0 (d), 109.3 (d), 109.2 (d), 47.5 (t), 39.4 (d), 31.0 (t), 28.8 (t), 24.4 (t), 23.0 (t), 14.0 (q), 10.9 (q); *m*/*z* (MALDI-TOF) 833 (M^++1, 15%), 734 (18), 734 (69), 666 (17), 570 (21), 565 (70), 556 (82), 465 (100).

*2.4.3. 3,5-Bis[5-(9-*n*-decyl-9*H*-carbazol-3-yl)thien-2-yl]-4*H*-1,2,6-thiadiazin-4-one* (**4**). Similar treatment of 3,5-bis(5-bromothien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**9**) (87 mg,

0.20 mmol) in MeCN (1 mL) with 9-*n*-decyl-3-(tri-*n*-butylstannyl)-9*H*-carbazole (**15**) (406 mg, 0.60 mmol) and $Pd(Ph_3P)_2Cl_2$ (4 mg, 0.01 mmol) heated at reflux for 4 h gave on chromatography (*n*-hexane/DCM, 6:4) the *title compound* **4** (95 mg, 53%) as a red powder, mp 84-85 ^oC (from DCM/MeCN); R_f 0.80 (*n*-hexane/DCM, 6:4); (found: C, 74.16; H, 6.92; N, 6.36. $C_{55}H_{60}N_4OS_3$ requires C, 74.28; H, 6.80; N, 6.30%); λ_{max}(DCM)/nm 242 (log ε 3.52), 296 (3.39), 440 inf (3.18), 506 (3.44); ν_{max}/cm^{-1} 3047 (Ar CH), 2953w, 2922m and 2853w (alkyl CH), 1618m, 1597m, 1479m, 1468m, 1441s, 1425s, 1387m, 1375m, 1352m, 1327w, 1298w, 1281w, 1271w, 1227w, 1194w, 1155m, 1142w, 1124w, 1065w, 1049m, 1024w, 880w, 870w, 797s, 781m, 742s; δ_H(500 MHz; $CDCl_3$) 8.45 (2H, d, *J* 1.0, Ar *H*), 8.25 (2H, d, *J* 4.2, Ar *H*), 8.15 (2H, d, *J* 7.5, Ar *H*), 7.83 (2H, dd, *J* 8.4, 1.4, Ar *H*), 7.49 (2H, dd, *J* 7.6, 7.6, Ar *H*), 7.44-7.39 (6H, m, Ar *H*), 7.29-7.26 (2H, m, Ar *H*), 4.28 (4H, t, *J* 7.2, C*H*$_2$), 1.91-1.85 (4H, m, C*H*$_2$), 1.39-1.24 (28H, m, C*H*$_2$), 0.87 (6H, t, *J* 6.8, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) 161.6 (s), 153.6 (s), 153.2 (s), 140.9 (s), 140.6 (s), 134.1 (s), 133.4 (d), 126.1 (d), 124.8 (s), 124.1 (d), 123.4 (s), 122.8 (s), 122.7 (d), 120.6 (d), 119.3 (d), 118.2 (d), 109.1 (d), 109.0 (d), 43.2 (t), 31.8 (t), 29.52 (t), 29.50 (t), 29.4 (t), 29.3 (t), 29.0 (t), 27.3 (t), 22.7 (t), 14.1 (q); *m/z* (MALDI-TOF) 889 (M^++1, 6%), 888 (M^+, 23), 625 (22), 612 (13), 583 (26), 377 (100).

*2.4.4. 3,5-Bis{5'-[9-(2-ethylhexyl)-9*H*-carbazol-3-yl]-(2,2'-bithien)-5-yl}-4*H*-1,2,6-thiadiazin-4-one* (**5**). Similar treatment of 3,5-bis(5-bromothien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**9**) (44 mg, 0.10 mmol) in PhMe (1 mL) with 9-(2-ethylhexyl)-3-[5-(tri-*n*-butylstannyl)-thien-2-yl]-9*H*-carbazole (**20**) (196 mg, 0.30 mmol) and $Pd(Ph_3P)_2Cl_2$ (3.5 mg, 0.005 mmol) heated at reflux for 3 h gave on chromatography (*n*-hexane/DCM, 4:6) the *title compound* **5** (70 mg, 70%) as a purple powder, mp 164-165 ^oC (from DCM/MeCN); R_f 0.63 (*n*-hexane/DCM, 4:6); (found: C, 70.94; H, 5.71; N, 3.59.

$C_{59}H_{56}N_4OS_5$ requires C, 71.05; H, 5.66; N, 5.62%); λ_{max}(DCM)/nm 239 (log ε 4.66), 302 (4.40), 348 (4.34), 463 inf (4.34), 537 (4.58); ν_{max}/cm^{-1} 3063w (Ar CH), 2957w, 2930w, 2926w, 2870w and 2857w (alkyl CH), 1614m, 1597m, 1516w, 1489m, 1481m, 1467m, 1445s, 1429s, 1379m, 1348m, 1335m, 1294w, 1279w, 1258w, 1219m, 1206m, 1155m, 1125w, 1043m, 1024w, 964w, 872m, 808m, 791s, 783m, 764w, 745m; δ_H(500 MHz; $CDCl_3$) 8.23 (2H, d, *J* 1.5, Ar *H*), 8.10 (2H, d, *J* 7.6, Ar *H*), 8.05 (2H, d, *J* 4.0, Ar *H*), 7.65 (2H, dd, *J* 8.5, 1.6, Ar *H*), 7.46 (2H, dd, *J* 7.5, 7.5, Ar *H*), 7.36 (2H, d, *J* 8.1, Ar *H*), 7.32 (2H, d, *J* 8.5, Ar *H*), 7.29 (2H, d, *J* 3.7, Ar *H*), 7.24-7.22 (4H, m, Ar *H*), 7.16 (2H, d, *J* 4.0, Ar *H*), 4.14-4.05 (4H, m, C*H*$_2$), 2.07-2.02 (2H, m, C*H*), 1.41-1.23 (16H, m, C*H*$_2$), 0.91 (6H, t, *J* 7.4, C*H*$_3$), 0.87 (6H, t, *J* 7.1, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) one C (d) resonance missing 161.1 (s), 152.8 (s), 146.4 (s), 145.4 (s), 141.4 (s), 140.7 (s), 134.7 (s), 134.1 (s), 133.0 (d), 126.0 (d), 124.8 (s), 123.8 (d), 123.5 (d), 123.2 (s), 122.73 (d), 122.69 (s), 120.5 (d), 119.1 (d), 117.4 (d), 109.3 (d), 109.2 (d), 47.5 (t), 39.4 (d), 31.0 (t), 28.8 (t), 24.4 (t), 23.0 (t), 14.0 (q), 10.9 (q); *m*/*z* (MALDI-TOF) 997 (M^++1, 21%), 899 (100), 810 (18), 800 (77), 787 (18).

2.4.5. 3,5-Bis[5'-(9-n-*decyl-9*H-*carbazol-3-yl)-(2,2'-bithien)-5-yl]-4*H-*1,2,6-thiadiazin-4-one* (**6**). Similar treatment of 3,5-bis(5-bromothien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**9**) (44 mg, 0.10 mmol) in PhMe (1 mL) with 9-*n*-decyl-3-[5-(tri-*n*-butylstannyl)thien-2-yl]-9*H*-carbazole (**21**) (204 mg, 0.30 mmol) and $Pd(Ph_3P)_2Cl_2$ (3.5 mg, 0.005 mmol) heated at reflux for 3 h gave on chromatography (*n*-hexane/DCM, 4:6) the *title compound* **6** (68 mg, 65%) as a purple powder, mp 125-126 ^oC (from DCM/MeCN); R_f 0.75 (*n*-hexane/DCM, 1:1); (found: C, 71.92; H, 6.03; N, 5.46. $C_{63}H_{64}N_4OS_5$ requires C, 71.82; H, 6.12; N, 5.32%); λ_{max}(DCM)/nm 245 (log ε 4.86), 309 inf (4.61), 351 (4.55), 486 inf (4.62), 539 (4.77); ν_{max}/cm^{-1} 3063w (Ar CH), 2951w, 2924w and 2853w (alkyl CH),

1612m, 1601m, 1558m, 1506m, 1481m, 1468m, 1445s, 1425s, 1387m, 1348m, 1327m, 1294w, 1265w, 1244w, 1231m, 1153m, 1125w, 1045m, 872w, 789s, 779m, 742m; δ_H(500 MHz; $CDCl_3$) 8.25 (2H, s, Ar *H*), 8.11 (2H, d, *J* 7.7, Ar *H*), 8.08 (2H, d, *J* 4.0, Ar *H*), 7.66 (2H, d, *J* 8.4, Ar *H*), 7.47 (2H, dd, *J* 7.5, 7.5, Ar *H*), 7.38 (2H, d, *J* 8.2, Ar *H*), 7.35 (2H, d, *J* 8.5, Ar *H*), 7.30 (2H, d, *J* 3.5, Ar *H*), 7.26-7.23 (4H, m, Ar *H*), 7.18 (2H, d, *J* 4.0, Ar *H*), 4.25 (4H, t, *J* 7.2, CH_2), 1.88-1.83 (4H, m, C*H*), 1.37-1.24 (28H, m, CH_2), 0.87 (6H, t, *J* 6.6, CH_3); δ_C(125 MHz; $CDCl_3$) one C (d) resonance missing 161.2 (s), 152.8 (s), 146.4 (s), 145.4 (s), 140.9 (s), 140.2 (s), 134.7 (s), 134.1 (s), 133.0 (d), 126.0 (d), 124.9 (s), 123.8 (d), 123.5 (d), 123.3 (s), 122.8 (d), 122.7 (s), 120.5 (d), 119.1 (d), 117.5 (d), 109.0 (d), 108.9 (d), 43.2 (t), 31.8 (t), 29.52 (t), 29.50 (t), 29.4 (t), 29.3 (t), 29.0 (t), 27.3 (t), 22.7 (t), 14.1 (q); *m*/*z* (MALDI-TOF) 1052 (M^+, 27%), 926 (100), 812 (25), 799 (41), 786 (20), 496 (49), 369 (35).

2.5. Preparation of 3,5-Bis[5'-(9-*n*-decyl-9*H*-carbazol-3-yl)-4-*n*-hexyl-(2,2'-bithien)-5-yl]-4*H*-1,2,6-thiadiazin-4-one (**7**)

2.5.1. 3,5-Bis(3-n-*hexylthien-2-yl)-4*H-*1,2,6-thiadiazin-4-one (**23**).* To a stirred solution of 3,5-dichoro-4*H*-1,2,6-thiadiazin-4-one (**1**) (92 mg, 0.50 mmol) in MeCN (5 mL) at *ca*. 20 °C, was added crude 3-*n*-hexyl-2-(tri-*n*-butylstannyl)thiophene (**22**) (1.07 g, 1.50 mmol) and $Pd(Ph_3P)_2Cl_2$ (17.6 mg, 0.025 mmol). The solution was then deareated by bubbling Ar gas into the reaction mixture for 10 min and then the reaction was heated at reflux under Ar, until no starting material remained (TLC, 4 h). On cooling to *ca.* 20 °C the reaction mixture was adsorbed onto silica and chromatographed (*n*-hexane/DCM, 8:2) to give the *title compound* **23** (214 mg, 96%) as a yellow oil: R_f 0.30 (*n*-hexane/DCM, 8:2); (found: C, 61.69; H, 6.81; N, 6.19. $C_{23}H_{30}N_2OS_3$ requires C, 61.84; H, 6.77; N, 6.27%); λ_{max}(DCM)/nm 269 (log ε 4.08), 322 (3.89), 395 inf (4.35), 411 (4.38),

434 (4.24); ν_{max}/cm^{-1} 3097w and 3063w (Ar CH), 2985m, 2929m, 2868m and 2855m (alkyl CH), 1730w, 1643w, 1612s, 1533w, 1508m, 1466m, 1445s, 1406s, 1385s, 1341m, 1287w, 1260w, 1239w, 1177w, 1113w, 1086w, 1020w, 908w, 883w, 845m, 741s; δ_H(500 MHz; $CDCl_3$) 7.52 (2H, d, *J* 5.1, Ar *H*), 7.04 (2H, d, *J* 5.1, Ar *H*), 3.06 (4H, t, *J* 7.7, C*H*$_2$), 1.68-1.62 (4H, m, C*H*), 1.43-1.31 (12H, m, C*H*$_2$), 0.91 (6H, t, *J* 7.0, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) 162.0 (s), 154.9 (s), 149.2 (s), 131.1 (d), 130.1 (d), 126.9 (s), 31.7 (t), 31.1 (t), 30.0 (t), 29.4 (t), 22.6 (t), 14.1 (q); *m*/*z* (MALDI-TOF) 447 (M^++1, 24%), 445 (37), 242 (100), 195 (52).

*2.5.2. 3,5-Bis(5-bromo-3-*n*-hexylthien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**24**)*. To a stirred solution of 3,5-bis(3-*n*-hexylthien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**23**) (223 mg, 0.50 mmol) in DMF (2 mL) at *ca.* 20 °C was added in one portion NBS (187 mg, 1.05 mmol). The reaction mixture was stirred at this temperature until complete consumption of the starting material (TLC, 48 h). Then H_2O (20 mL) was added and the mixture was extracted with Et_2O (2 × 20 mL), dried (Na_2SO_4), filtered and the solvent evaporated. Dry-flash chromatography (*n*-hexane) of the residue gave the *title compound* **24** (278 mg, 92%) as yellow needles, mp 86-88 °C (from MeCN): R_f 0.33 (*n*-hexane); (found: C, 45.81; H, 4.76; N, 4.55. $C_{23}H_{28}Br_2N_2OS_3$ requires C, 45.70; H, 4.67; N, 4.63%); λ_{max}(DCM)/nm 272 (log ε 3.99), 406 inf (4.16), 428 (4.25), 454 (4.17); ν_{max}/cm^{-1} 2953w, 2924m and 2855w (alkyl CH), 1734w, 1684w, 1605m, 1537m, 1508m, 1466m, 1441m, 1363s, 1375m, 1260m, 1234m, 1179m, 1152m, 1026w, 984w, 941w, 833m, 783w, 748m, 741m; δ_H(500 MHz; $CDCl_3$) 7.02 (2H, s, Ar *H*), 3.03 (4H, t, *J* 7.8, C*H*$_2$), 1.65-1.59 (4H, m, C*H*$_2$), 1.42-1.30 (12H, m, C*H*$_2$), 0.91 (6H, t, *J* 6.9, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) 161.4 (s), 153.8 (s), 150.0 (s), 132.9 (d), 128.0 (s), 121.0 (s), 31.7 (t), 31.2 (t), 29.7 (t), 29.3 (t),

22.6 (t), 14.1 (q); *m*/*z* (MALDI-TOF) 605 (M^++3, 35%), 603 (M^++1, 43), 556 (10), 535 (58), 533 (100), 523 (46), 521 (52), 304 (40).

2.5.3. 3,5-Bis[5'-(9-n-*decyl-9*H-*carbazol-3-yl)-4*-n-*hexyl-(2,2'-bithien)-5-yl]-4*H-*1,2,6-thiadiazin-4-one (**7**)*. To a stirred solution of 3,5-bis(5-bromo-3-*n*-hexylthien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**24**) (60 mg, 0.10 mmol) in PhMe (1 mL) at *ca*. 20 °C, was added 9-decyl-3-[5-(tributylstannyl)thien-2-yl]-9*H*-carbazole (**21**) (204 mg, 0.30 mmol) and $Pd(Ph_3P)_2Cl_2$ (3.5 mg, 0.005 mmol). The solution was then deareated by bubbling Ar gas into the reaction mixture for 10 min and then the mixture was heated at reflux under Ar, until no starting material remained (TLC, 8 h). On cooling to *ca.* 20 °C the reaction mixture was adsorbed onto silica and chromatographed (*n*-hexane/DCM, 4:6) to give the *title compound* **7** (67 mg, 55%) as a purple powder, mp 74-76 °C (from MeCN): R_f 0.67 (*n*-hexane/DCM, 1:1); (found: C, 73.63; H, 7.31; N, 4.50. $C_{75}H_{88}N_4OS_5$ requires C, 73.72; H, 7.26; N, 4.59%); λ_{max}(DCM)/nm 245 (log ε 5.08), 308 (4.82), 366 (4.79), 455 inf (4.79), 528 (4.91); ν_{max}/cm^{-1} 3065w (Ar CH), 2953m, 2924m and 2853m (alkyl CH), 1612m, 1599m, 1491m, 1481m, 1468m, 1449m, 1406s, 1350m, 1294w, 1281w, 1235w, 1225w, 1153m, 1124w, 1090w, 1065w, 1022w, 881w, 849w, 831w, 791s, 745s; δ_H(500 MHz; $CDCl_3$) 8.32 (2H, d, *J* 1.7 Ar *H*), 8.13 (2H, d, *J* 7.7, Ar *H*), 7.73 (2H, dd, *J* 8.4, 1.8, Ar *H*), 7.49 (2H, dd, *J* 7.9, 7.9, Ar *H*), 7.41-7.38 (6H, m, Ar *H*), 7.29 (2H, d, *J* 7.8, Ar *H*), 7.27-7.24 (2H, m, Ar *H*), 7.15 (2H, s, Ar *H*), 4.29 (4H, t, *J* 6.9, CH_2), 3.06 (4H, t, *J* 7.9, CH_2), 1.91-1.85 (4H, m, C*H*), 1.72-1.66 (4H, m, CH_2), 1.46-1.24 (40H, m, CH_2), 0.94 (6H, t, *J* 7.0, CH_3), 0.88 (6H, t, *J* 6.8, CH_3); δ_C(125 MHz; $CDCl_3$) 161.9 (s), 153.8 (s), 150.6 (s), 146.1 (s), 142.7 (s), 140.9 (s), 140.2 (s), 135.0 (s), 126.3 (d), 126.0 (d), 125.9 (d), 125.2 (s), 125.1 (s), 123.9 (d), 123.3 (s), 122.9 (d), 122.8 (s), 120.5 (d), 119.1 (d), 117.6 (d), 109.1 (d), 108.9 (d), 43.2 (t), 31.9 (t), 31.8 (t), 31.7 (t), 29.8 (t), 29.52 (t), 29.50 (t), 29.48 (t), 29.4

(t), 29.3 (t), 29.0 (t), 27.3 (t), 22.68 (t), 22.65 (t), 14.16 (q), 14.10 (q); *m*/*z* (MALDI-TOF) 1222 (M^++1, 38%), 1221 (M^+, 9), 1138 (50), 613 (80), 581 (100), 556 (97), 524 (27).

2.6. Preparation of 3,5-Bis[5''-(9-*n*-decyl-9*H*-carbazol-3-yl)-3'-*n*-hexyl-(2,2':5',2''-terthien)-5-yl]-4*H*-1,2,6-thiadiazin-4-one (8)

2.6.1. 3,5-Bis[3'-n-*hexyl-(2,2'-bithien)-5-yl]-4*H-*1,2,6-thiadiazin-4-one (**25**)*. To a stirred solution of 3,5-bis(5-bromothien-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**9**) (44 mg, 0.10 mmol) in PhMe (0.5 mL) at *ca*. 20 °C, was added 3-*n*-hexylthiophene-2-boronic acid pinacol ester (66 μL, 0.22 mmol), followed by Cs_2CO_3 (72 mg, 0.22 mmol) and $Pd(Ph_3P)_4$ (5.8 mg, 0.005 mmol). The solution was then deareated by bubbling Ar gas into the reaction mixture for 10 min and then the mixture was heated at *ca.* 120 °C in a sealed tube under Ar, until no starting material remained (TLC, 24 h). On cooling to *ca.* 20 °C the reaction mixture was adsorbed onto silica and chromatographed (*n*-hexane/DCM, 8:2) to give the *title compound* **25** (60 mg, 98%) as orange plates, mp 72-73 °C (from *n*-pentane/0 °C): R_f 0.39 (*n*-hexane/DCM, 8:2); (found: C, 60.92; H, 5.72; N, 4.49. $C_{31}H_{34}N_2OS_5$ requires C, 60.94; H, 5.61; N, 4.59%); λ_{max}(DCM)/nm 294 (log ε 4.33), 440 inf (4.55), 484 (4.72); ν_{max}/cm^{-1} 3103w and 3061w (Ar CH), 2957w, 2926m and 2853w (alkyl CH), 1626m, 1508m, 1437s, 1375w, 1348w, 1314w, 1275w, 1240w, 1123w, 1080w, 1069m, 1049m, 880m, 831m, 804s, 779m, 743m; δ_H(500 MHz; $CDCl_3$) 8.22 (2H, s, Ar *H*), 7.23 (2H, d, *J* 5.2, Ar *H*), 7.19 (2H, dd, *J* 4.1, 1.1, Ar *H*), 6.97 (2H, d, *J* 5.1, Ar *H*), 2.85 (4H, t, *J* 7.7, C*H*), 1.71-1.65 (4H, m, CH_2), 1.44-1.29 (12H, m, CH_2), 0.89 (6H, t, *J* 7.0, CH_3); δ_C(125 MHz; $CDCl_3$) 161.4 (s), 153.3 (s), 144.4 (s), 141.0 (s), 135.7 (s), 132.7 (d), 130.41 (d), 130.37 (s), 126.2 (d), 124.9 (d), 31.7 (t), 30.4 (t), 29.6 (t), 29.2 (t), 22.6 (t), 14.1 (q); *m*/*z* (MALDI-TOF) 610 (M^+, 38%), 539 (100), 527 (32), 307 (63), 276 (62), 204 (18).

2.6.2. 3,5-Bis[5'-bromo-3'-n-*hexyl-(2,2'-bithien)-5-yl]-4*H-*1,2,6-thiadiazin-4-one (**26**).* To a stirred solution of 3,5-bis[3'-*n*-hexyl-(2,2'-bithien)-5-yl]-4*H*-1,2,6-thiadiazin-4-one (**25**) (61 mg, 0.10 mmol) in DMF/THF (4:1, 5 mL) at *ca*. 20 °C was added in one portion NBS (37 mg, 0.21 mmol). The mixture was stirred at this temperature until the starting material was consumed (TLC, 16 h). Then H_2O (20 mL) was added and the mixture extracted with Et_2O (2 × 20 mL), dried (Na_2SO_4), filtered and the solvent evaporated. Dry-flash chromatography (*n*-hexane/DCM, 9:1) of the residue gave the *title compound* **26** (76 mg, 99%) as a yellow powder, mp 102-104 °C (from MeCN): R_f 0.35 (*n*-hexane/DCM, 9:1); (found: C, 48.53; H, 4.12; N, 3.53. $C_{31}H_{32}Br_2N_2OS_5$ requires C, 48.43; H, 4.20; N, 3.64%); λ_{max}(DCM)/nm 295 (log ε 4.44), 484 (4.83); ν_{max}/cm^{-1} 3064w (Ar CH), 2953m, 2926m and 2855w (alkyl CH), 1624m, 1537w, 1508w, 1435s, 1375w, 1350m, 1314w, 1281w, 1231w, 1213w, 1065m, 1047m, 989w, 889w, 870w, 833m, 824m, 802m, 779m, 743w; δ_H(500 MHz; $CDCl_3$) 8.20 (2H, d, *J* 4.1, Ar *H*), 7.13 (2H, d, *J* 4.0, Ar *H*), 6.93 (2H, s, Ar *H*), 2.78 (4H, t, *J* 7.7, C*H*$_2$), 1.67-1.61 (4H, m, C*H*$_2$), 1.42-1.25 (12H, m, C*H*$_2$), 0.89 (6H, t, *J* 7.0, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) 161.3 (s), 153.3 (s), 143.0 (s), 141.6 (s), 136.0 (s), 133.1 (d), 132.7 (d), 131.8 (s), 126.5 (d), 111.9 (s), 31.6 (t), 31.3 (t), 29.5 (t), 29.1 (t), 22.6 (t), 14.1 (q); *m*/*z* (MALDI-TOF) 768 (M^++2, 46%), 766 (M^+, 32), 699 (86), 697 (100), 387 (47), 385 (41), 356 (30), 354 (32).

2.6.3. 3,5-Bis[5''-(9-n-*decyl-9*H-*carbazol-3-yl)-3'*-n-*hexyl-(2,2':5',2''-terthien)-5-yl]-4*H-*1,2,6-thiadiazin-4-one* (**8**). To a stirred solution of 3,5-bis[5'-bromo-3'-*n*-hexyl-(2,2'-bithien)-5-yl]-4*H*-1,2,6-thiadiazin-4-one (**26**) (77 mg, 0.10 mmol) in PhMe (1 mL) at *ca*. 20 °C, was added 9-*n*-decyl-3-[5-(tri-*n*-butylstannyl)thien-2-yl]-9*H*-carbazole (**21**) (204 mg, 0.30 mmol) and $Pd(Ph_3P)_2Cl_2$ (7 mg, 0.01 mmol). The solution was then deareated by bubbling Ar gas into the reaction mixture for 10 min and then the mixture was

heated at reflux under Ar, until no starting material remained (TLC, 20 h). On cooling to *ca.* 20 °C the reaction mixture was adsorbed onto silica and chromatographed (*n*-hexane/DCM, 1:1) to give the *title compound* **8** (97 mg, 70%) as a purple powder, mp 119-121 °C (from DCM/MeCN): R_f 0.58 (*n*-hexane/DCM, 1:1); (found: C, 71.79; H, 6.53; N, 3.93. $C_{83}H_{92}N_4OS_7$ requires C, 71.92; H, 6.69; N, 4.04%); λ_{max}(DCM)/nm 244 (log ε 4.92), 267 inf (4.73), 303 (4.63), 380 (4.72), 541 (4.83); ν_{max}/cm^{-1} 3065w (Ar CH), 2951m, 2924m and 2853m (alkyl CH), 1616m, 1601m, 1489m, 1468m, 1454m, 1422s, 1383m, 1352m, 1329w, 1294w, 1271w, 1242m, 1225m, 1213m, 1153m, 1125w, 1059m, 1024w, 878w, 856w, 824w, 814m, 804m, 789s, 764w, 741m; δ_H(500 MHz; $CDCl_3$) 8.32 (2H, d, *J* 1.4, Ar *H*), 8.27 (2H, d, *J* 4.1, Ar *H*), 8.14 (2H, d, *J* 7.8, Ar *H*), 7.72 (2H, dd, *J* 8.4, 1.6, Ar *H*), 7.50-7.47 (2H, m, Ar *H*), 7.42-7.40 (4H, dd, *J* 8.2, 4.1, Ar *H*), 7.27-7.24 (6H, m, Ar *H*), 7.20 (2H, d, *J* 3.7, Ar *H*), 7.09 (2H, s, Ar *H*), 4.31 (4H, t, *J* 7.1, C*H*$_2$), 2.88 (4H, t, *J* 7.8, C*H*), 1.89 (4H, quin, *J* 7.3, C*H*$_2$), 1.75 (4H, quin, *J* 7.5, C*H*$_2$), 1.51-1.24 (40H, m, C*H*$_2$), 0.93 (6H, t, *J* 6.9, C*H*$_3$), 0.87 (6H, t, *J* 6.6, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) one C (t) resonance missing 161.3 (s), 153.0 (s), 145.2 (s), 144.1 (s), 141.9 (s), 140.9 (s), 140.1 (s), 136.7 (s), 135.6 (s), 134.8 (s), 132.8 (d), 129.1 (s), 126.4 (d), 126.0 (d), 125.7 (d), 125.1 (s), 124.9 (d), 123.8 (d), 123.3 (s), 122.7 (s), 122.6 (d), 120.5 (d), 119.1 (d), 117.5 (d), 109.0 (d), 108.9 (d), 43.2 (t), 31.8 (t), 31.7 (t), 30.2 (t), 30.0 (t), 29.52 (t), 29.50 (t), 29.4 (t), 29.3 (t), 29.26 (t), 29.0 (t), 27.3 (t), 22.7 (t), 14.2 (q), 14.1 (q); *m*/*z* (MALDI-TOF) 1386 (M^++1, 2%), 1385 (M^+, 1), 662 (3), 535 (85), 463 (100), 451 (24), 394 (30).

3. Electrochemistry

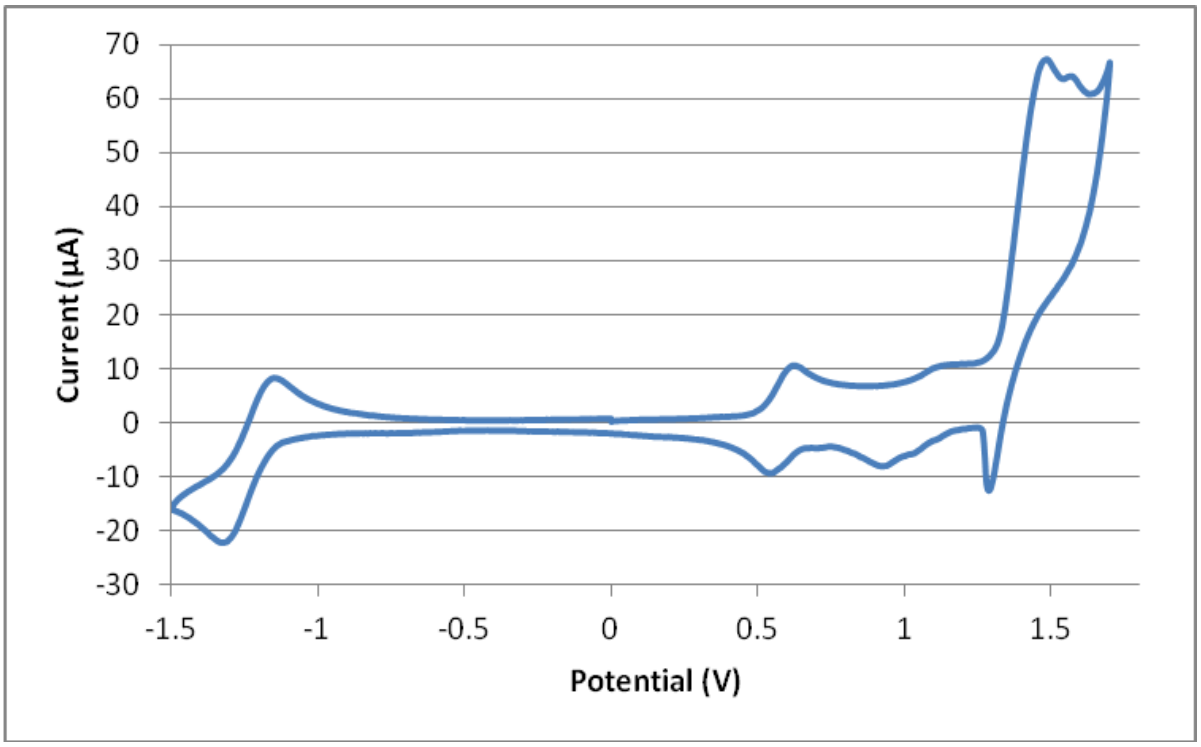
Electrochemistry studies were performed using a standard three-electrode cell under argon atmosphere. Prior to all measurements, the solutions were deaerated with Ar bubbling into the electrochemical cell for 15 min. Glassy carbon was used as working electrode and platinum wire as counter electrode. Ag/AgCl/KCl (1 M) was used as the reference electrode. Tetrabutylammonium tetrafluoroborate (n-Bu_4NBF_4, 99%) was used as the electrolyte (0.1 M) and was recrystallized from ethyl acetate and dried under vacuum at ca. 100 °C for 3 days before each experiment. Measurements were recorded using an EG&G Princeton Applied Research 263A potentiostat/galvanostat apparatus. The concentration of the small molecule studied was 1 mM in DCM. The scan rate for all CV runs was 50 mV/s. All results were calibrated using commercially available ferrocene (purified by sublimation) as an internal standard. To calculate HOMO/LUMO levels using the potentials obtained, the following equations were used:[15]

$$\begin{aligned} &EHOMO = -(E[ox \text{ vs. } Fc/Fc+] + 5.1)\ [eV] \\ &ELUMO = -(E[red \text{ vs. } Fc/Fc+] + 5.1)\ [eV] \end{aligned} \qquad (1)$$

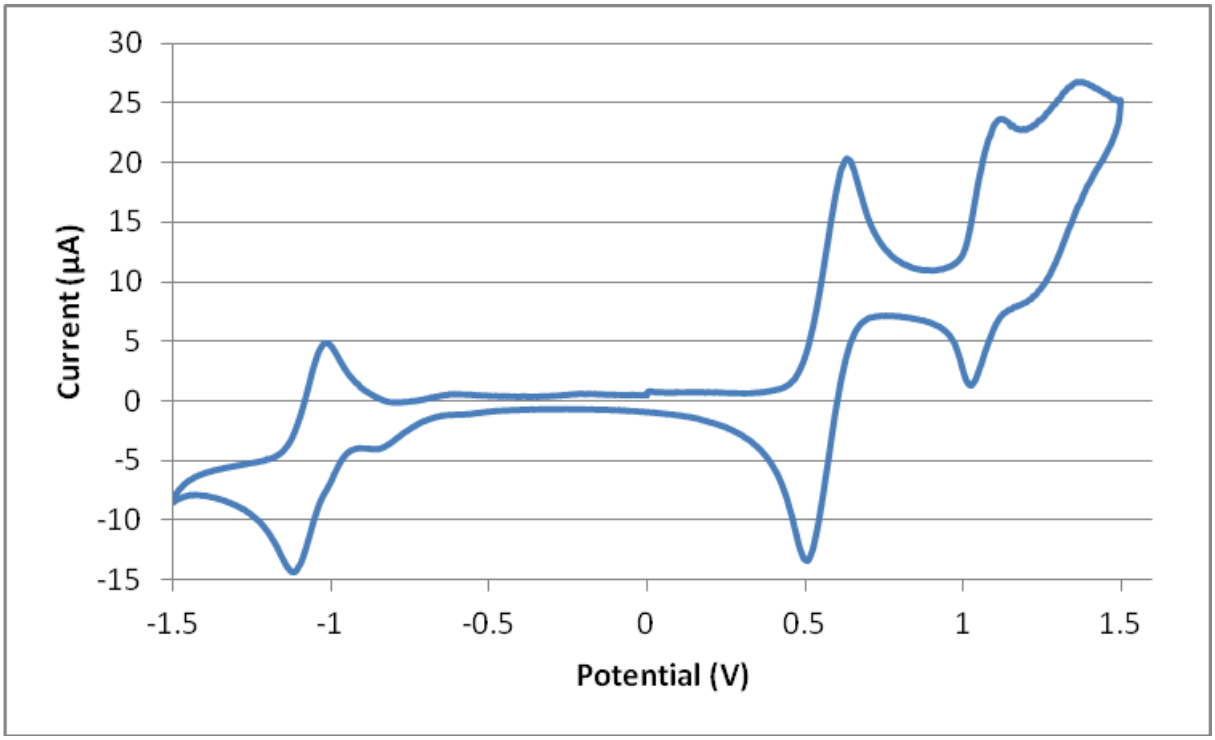
For HOMO–LUMO estimations, the peak onset was considered.

3.1 Cyclic voltammograms

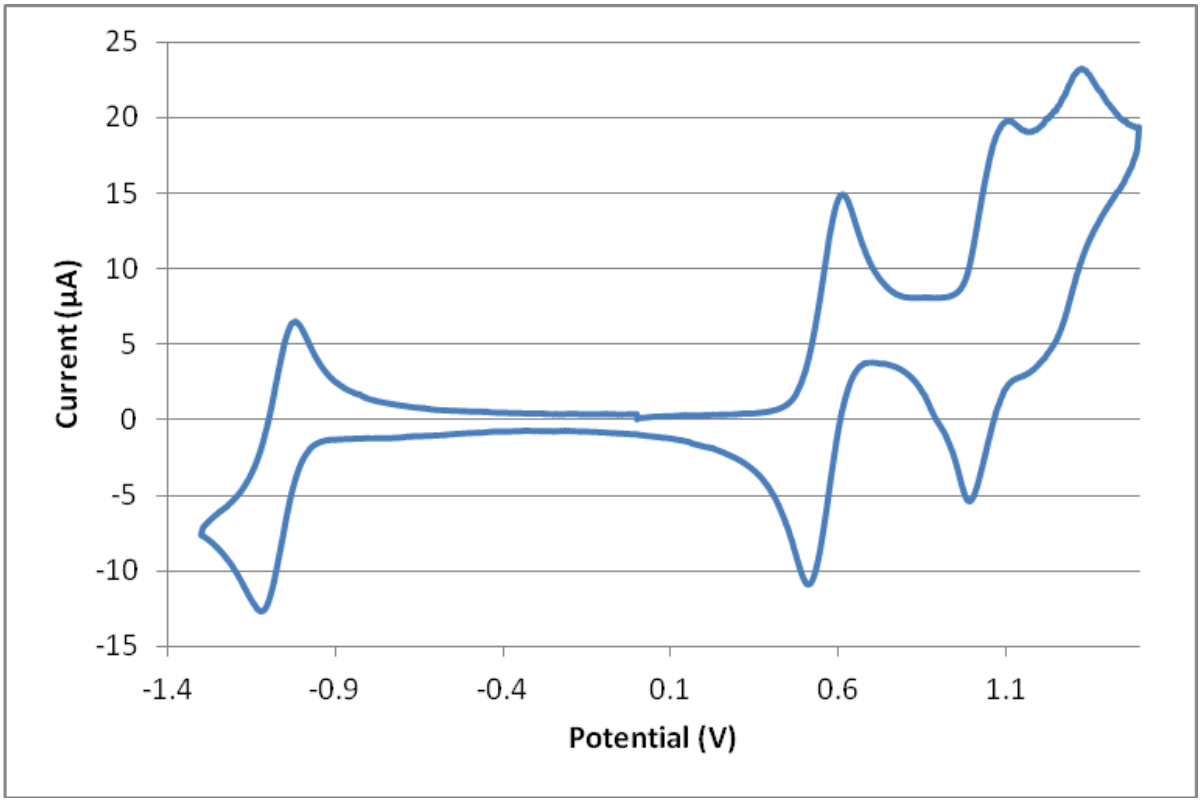
3.1.1 3,5-Bis[9-(2-ethylhexyl)-9H-carbazol-3-yl]-4H-1,2,6-thiadiazin-4-one (**2**)



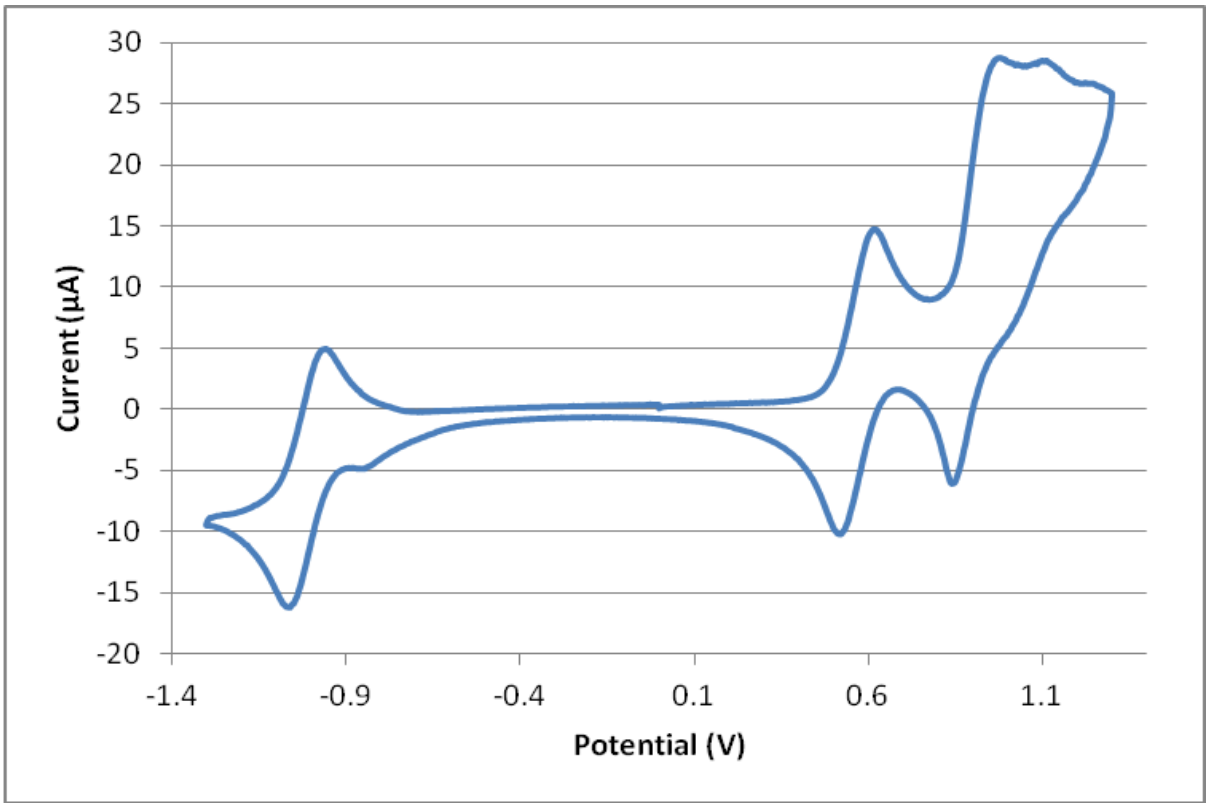
3.1.2. 3,5-Bis{5-[9-(2-ethylhexyl)-9H-carbazol-3-yl]thien-2-yl}-4H-1,2,6-thiadiazin-4-one (**3**)



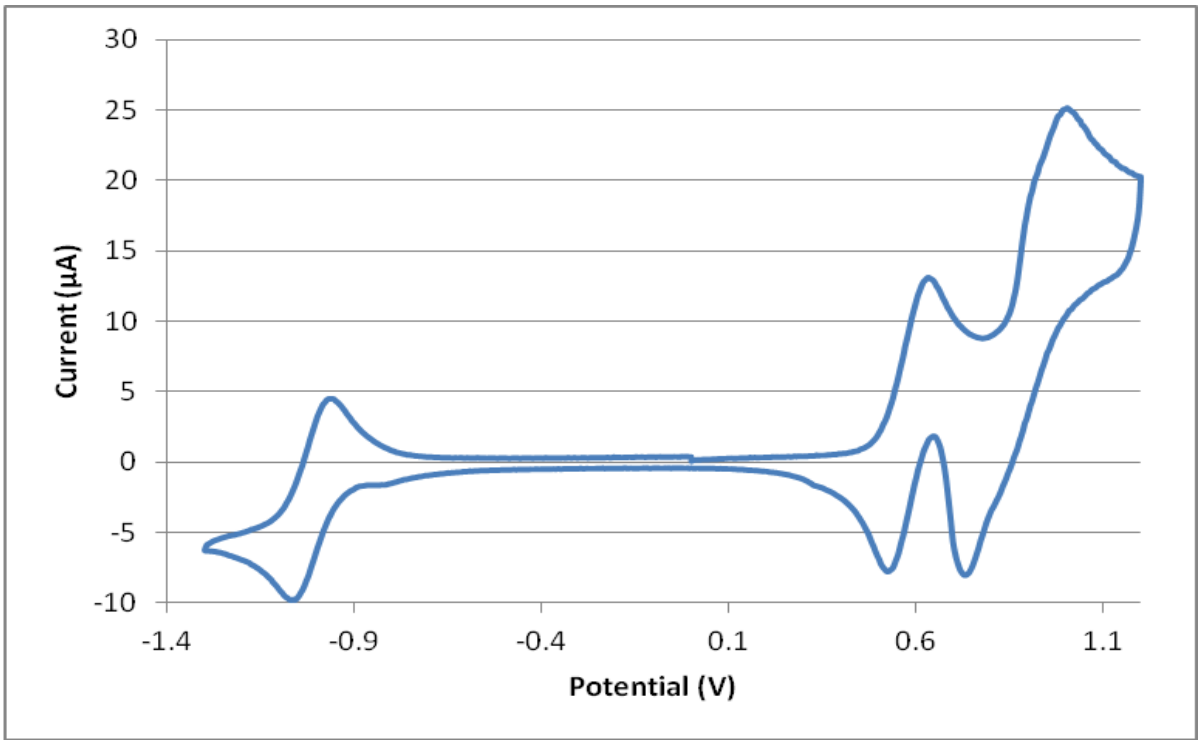
3.1.3. 3,5-Bis[5-(9-n-decyl-9H-carbazol-3-yl)thien-2-yl]-4H-1,2,6-thiadiazin-4-one (**4**)



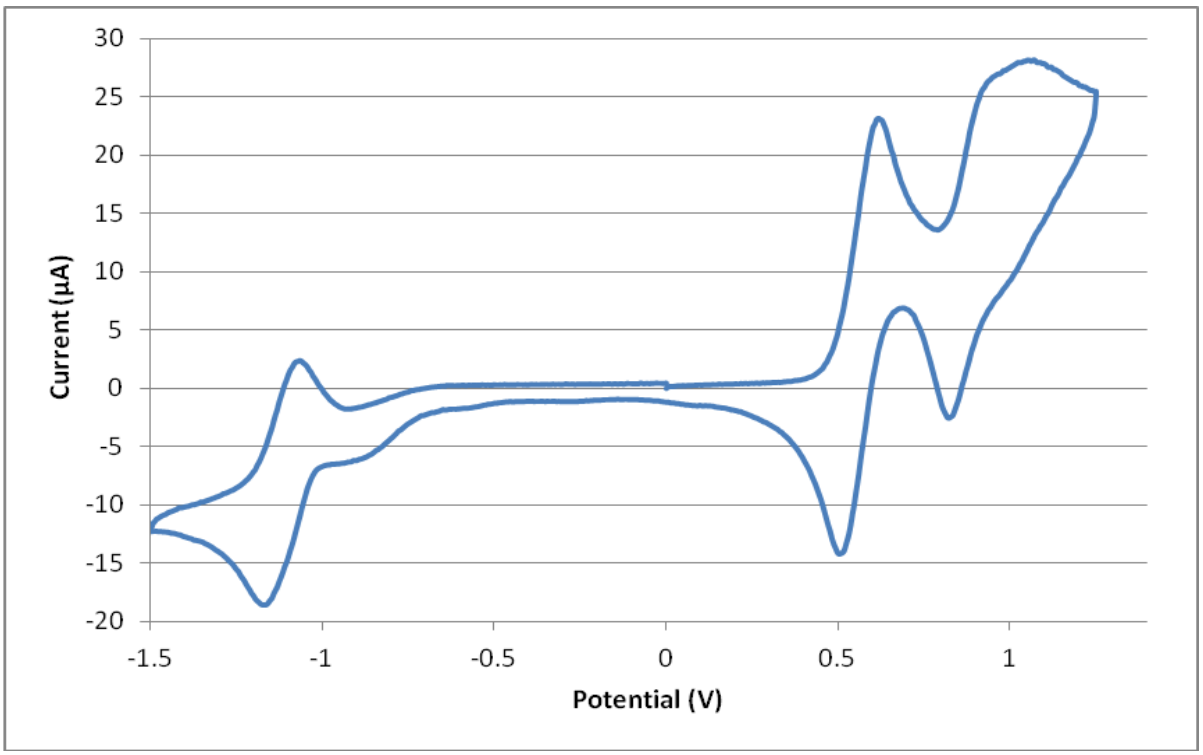
3.1.4. 3,5-Bis{5'-[9-(2-ethylhexyl)-9H-carbazol-3-yl]-(2,2'-bithien)-5-yl}-4H-1,2,6-thiadiazin-4-one (**5**)



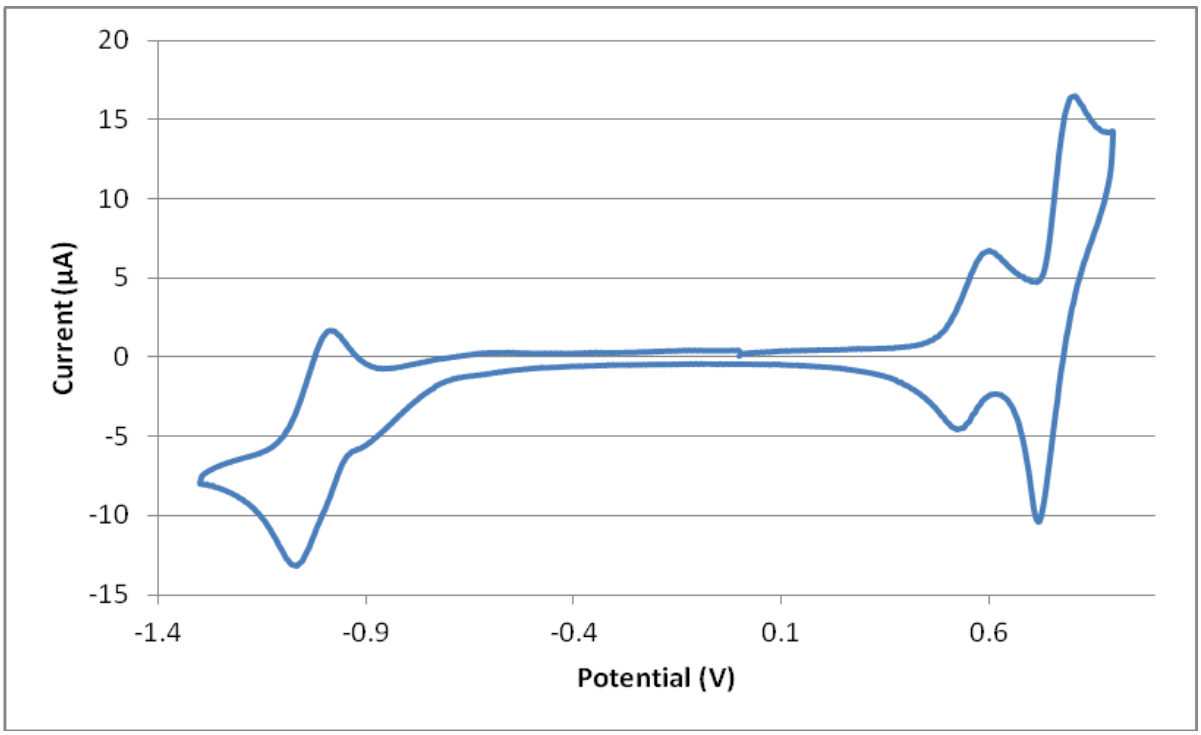
3.1.5. 3,5-Bis[5'-(9-n-decyl-9H-carbazol-3-yl)-(2,2'-bithien)-5-yl]-4H-1,2,6-thiadiazin-4-one (**6**)



3.1.6. 3,5-Bis[5'-(9-n-decyl-9H-carbazol-3-yl)-4-n-hexyl-(2,2'-bithien)-5-yl]-4H-1,2,6-thiadiazin-4-one (**7**).



3.1.7. 3,5-Bis[5''-(9-n-decyl-9H-carbazol-3-yl)-3'-n-hexyl-(2,2':5',2''-terthien)-5-yl]-4H-1,2,6-thiadiazin-4-one (**8**)



4. Full IUPAC names of materials referred to in main article

PTB7 – Poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl})

PCDTBT – Poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)], Poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]

Si-PCPDTBT – Poly[2,1,3-benzothiadiazole-4,7-diyl[4 ,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4, 5-b']dithiophene-2,6-diyl]]

P3HT – Poly(3-hexylthiophene-2,5-diyl)

$PC_{60}BM$ – [6,6]-Phenyl-C61-butyric acid methyl ester

$PC_{70}BM$ – [6,6]-Phenyl-C71-butyric acid methyl ester

ICBA – 1′,1′′,4′,4′′-Tetrahydro-di[1,4]methanonaphthaleno[1,2:2′,3′,56,60:2′′,3′′][5,6]fullerene-C60

5. Fabrication and characterization of organic solar cells

Photovoltaic devices were fabricated by doctor-blading on indium tin oxide (ITO)-covered glass substrates (Osram). These substrates were cleaned in toluene, water, acetone, and 2-propanol. After drying, the substrates were bladed with 40 nm PEDOT:PSS (HC Starck, PEDOT Al4083). Photovoltaic layers, consisting of each of the small molecules and PC70BM in 1:2 wt % ratios were dissolved in chlorobenzene with a total concentration of 20 mg/mL and bladed on top of the PEDOT:PSS layer. For the devices containing polydimethylsiloxane (PDMS, density 0.96 mg/mL) a small amount (0.1 mg/mL) was added to the active layer blend.[16] The best thicknesses of active layers for these blends are around 80-90 nm. Finally, a calcium/aluminium top electrode of 15/100 nm thickness was evaporated. The typical active area of the investigated devices was 10.4 mm2. The current-voltage characteristics of the solar cells were measured under AM1.5G irradiation on an OrielSol 1A Solar simulator (100 mW/cm^2).

The EQE was detected using a Cary 500 Scan UV-vis-NIR Spectrophotometer under monochromatic illumination, which was calibrated with a mono-crystalline silicon diode. AFM measurements were performed with a Nanosurf Easy Scan 2 in contact mode. Single carrier devices were fabricated and the dark current-voltage characteristics measured and analyzed in the space charge limited (SCL) regime.[17-19] The structure of hole only devices was glass/ITO/PEDOT:PSS/active layer/MoO3/Ag (100 nm). The reported mobility data are average values of six diodes of each pristine and blended films.

The field-effect mobility for the pristine materials and blends was determined in thin-film transistors (TFTs) using a bottom-gate, bottom-contact device structure. Heavily doped Si wafer with a 200 nm SiO_2 layer served as gate electrode and dielectric, respectively. The oxide surface was passivated using hexamethyldisilazane (HMDS).

Prior to the deposition of the semiconductor, the Au source and drain electrodes were functionalized with pentafluorobenzenethiol (PFBT) to increase the work function. All measurements were performed in nitrogen atmosphere using an Agilent B2902A parameter analyser. UV-visible spectra of films were measured using a UV-2700 spectrophotometer (Shimadzu).

Photoluminescence measurements were obtained using an FP-8300 spectrofluorometer (Jasco). The excitation wavelength corresponded to the peak absorption wavelengths obtained from the thin films. The emission of each film was normalized to its optical absorbance (optical density) to account for slight film thickness and concentration variations. The deposition of the active layer occurred on glass substrates using the same processing conditions as those used for solar cell device fabrication. The spectra of D-A-D **2**:$PC_{70}BM$ and pristine $PC_{70}BM$ contain a visible feature which is owed to a grating change in the instrument at 540 nm. Also visible is the emission contribution of the blank glass substrate in these spectra at ~520 and ~830 nm. This contribution, however, does not overlay the emission contributions from the active layers under study.

6. References

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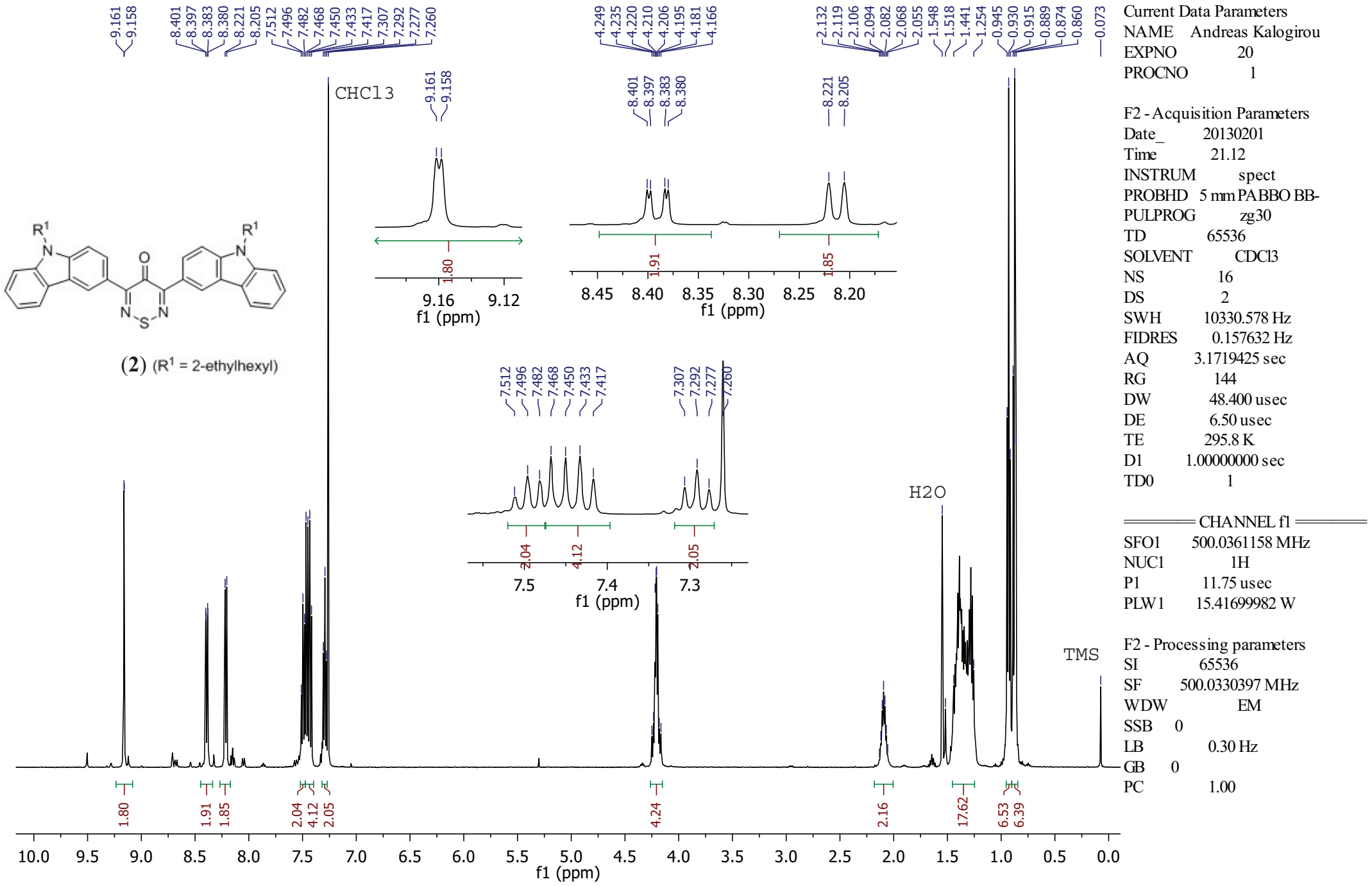
3,5-Bis(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)-4*H*-1,2,6-thiadiazin-4-one (**2**)



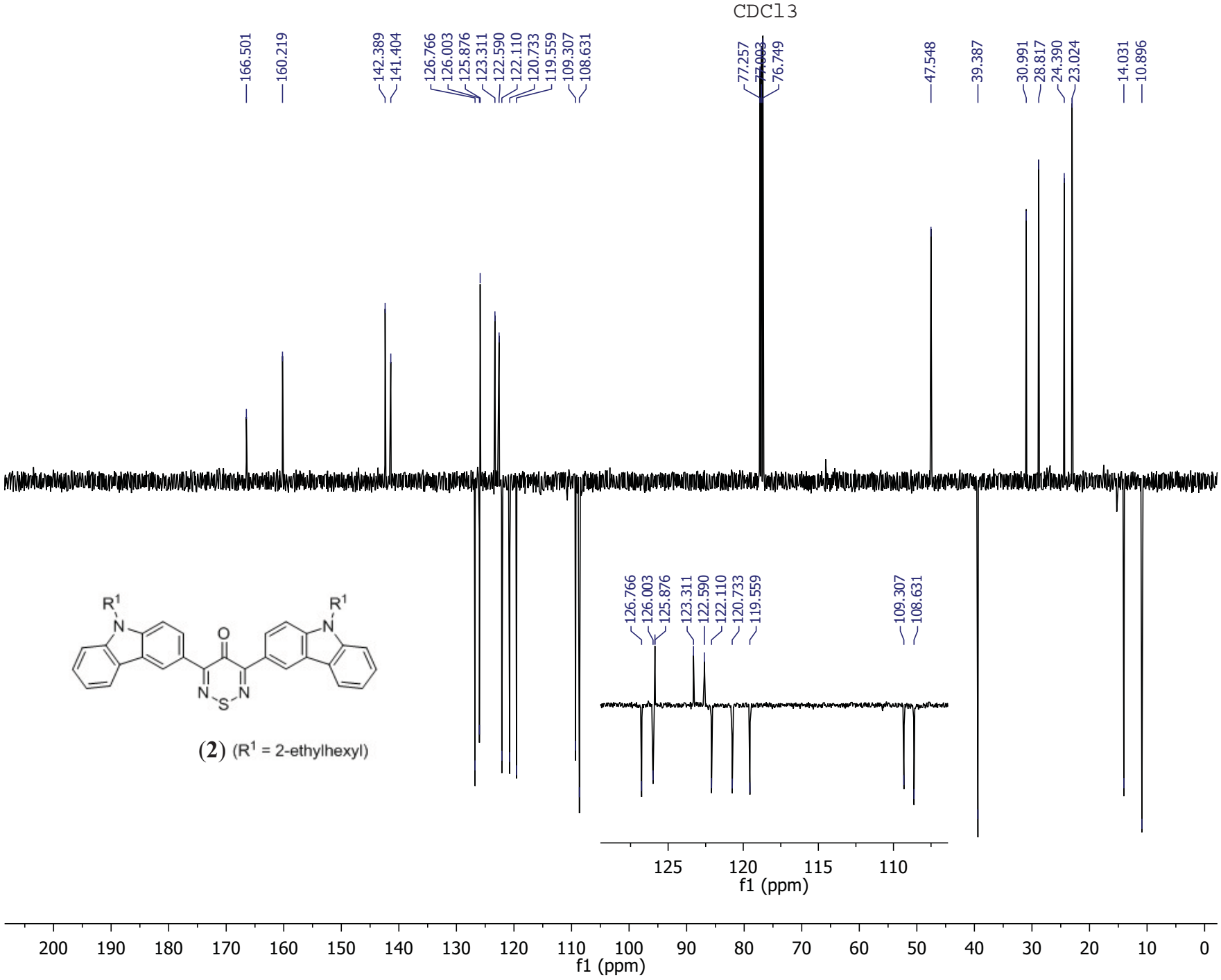
Current Data Parameters
NAME Andreas Kalogirou
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130201
Time 21.12
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 144
DW 48.400 usec
DE 6.50 usec
TE 295.8 K
D1 1.00000000 sec
TD0 1

CHANNEL f1
SFO1 500.0361158 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W

F2 - Processing parameters
SI 65536
SF 500.0330397 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

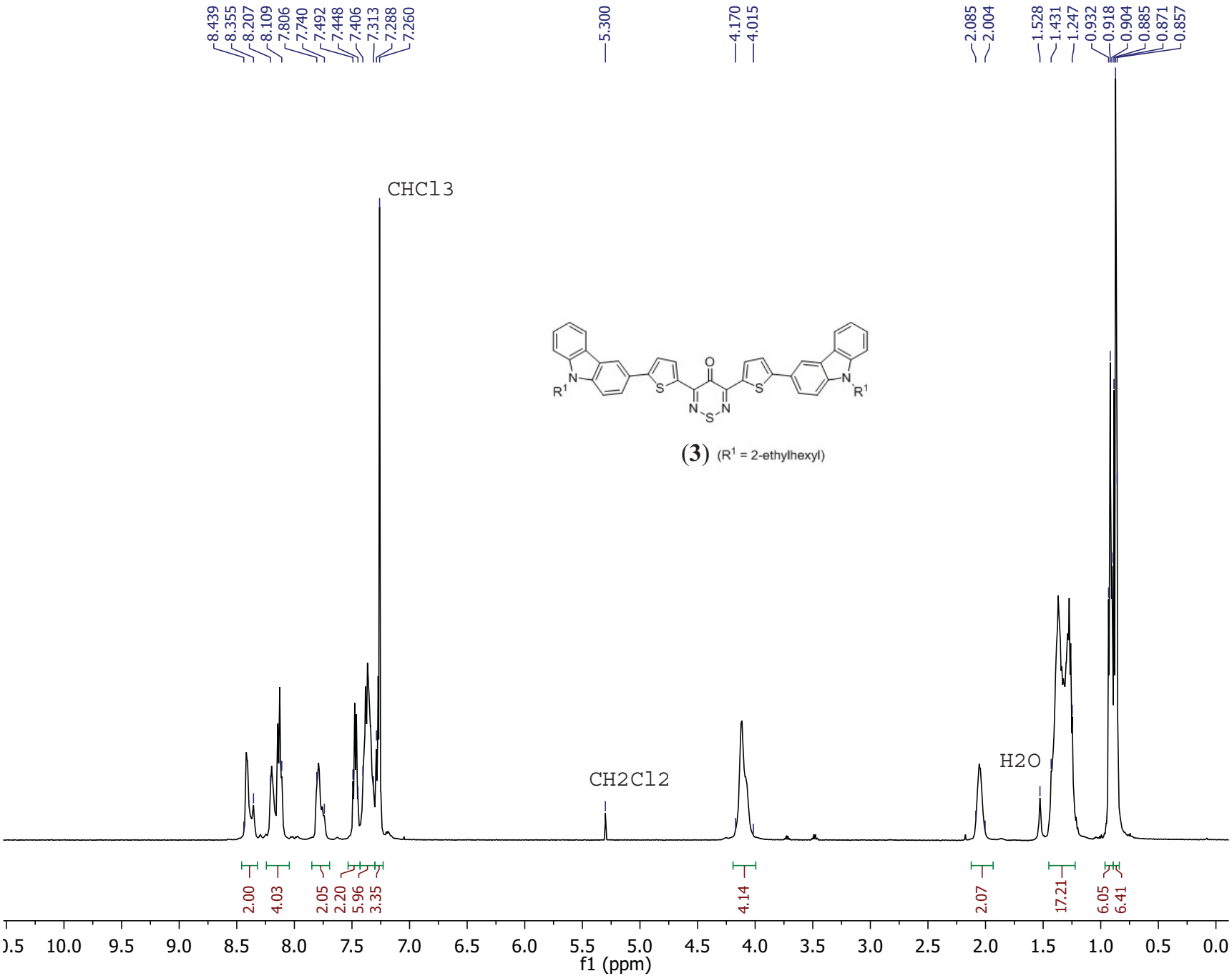
3,5-Bis(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)-4*H*-1,2,6-thiadiazin-4-one (**2**)



(**2**) (R^1 = 2-ethylhexyl)

Current Data Parameters
NAME Andreas Kalogirou
EXPNO 25
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130205
Time 18.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 400
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 297.0 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
CHANNEL f1
SFO1 125.7459782 MHz
NUC1 13C
P1 8.70 usec
P2 17.40 usec
PLW1 138.00000000 W
CHANNEL f2
SFO2 500.0350280 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.41699982 W
PLW12 0.33258000 W
F2 - Processing parameters
SI 32768
SF 125.7334094 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3,5-Bis(5-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)thiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**3**)



(**3**) (R^1 = 2-ethylhexyl)

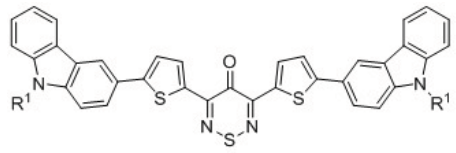
Current Data Parameters
NAME Andreas Kalogirou
EXPNO 34
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130209
Time 18.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 114
DW 48.400 usec
DE 6.50 usec
TE 295.8 K
D1 1.00000000 sec
TD0 1

CHANNEL f1
SFO1 500.0361158 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W

F2 - Processing parameters
SI 65536
SF 500.0330398 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

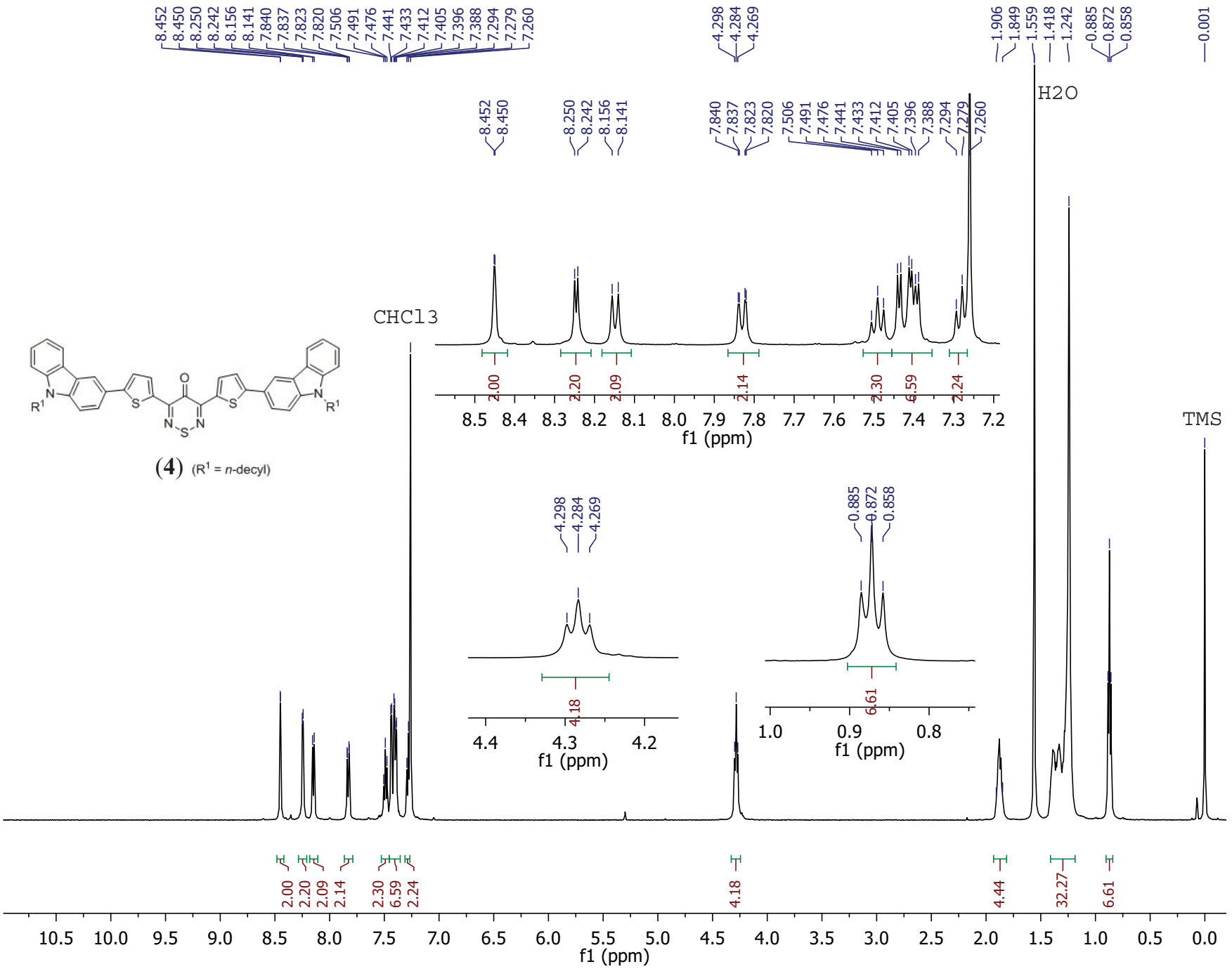
3,5-Bis(5-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)thiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**3**)



(**3**) (R^1 = 2-ethylhexyl)

Current Data Parameters
NAME Andreas Kalogirou
EXPNO 38
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130211
Time 15.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 2000
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 297.0 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
CHANNEL f1
SFO1 125.7459782 MHz
NUC1 13C
P1 8.70 usec
P2 17.40 usec
PLW1 138.00000000 W
CHANNEL f2
SFO2 500.0350280 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.41699982 W
PLW12 0.33258000 W
F2 - Processing parameters
SI 32768
SF 125.7334093 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3,5-Bis(5-(9-decyl-9*H*-carbazol-3-yl)thiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**4**)



(**4**) (R^1 = *n*-decyl)

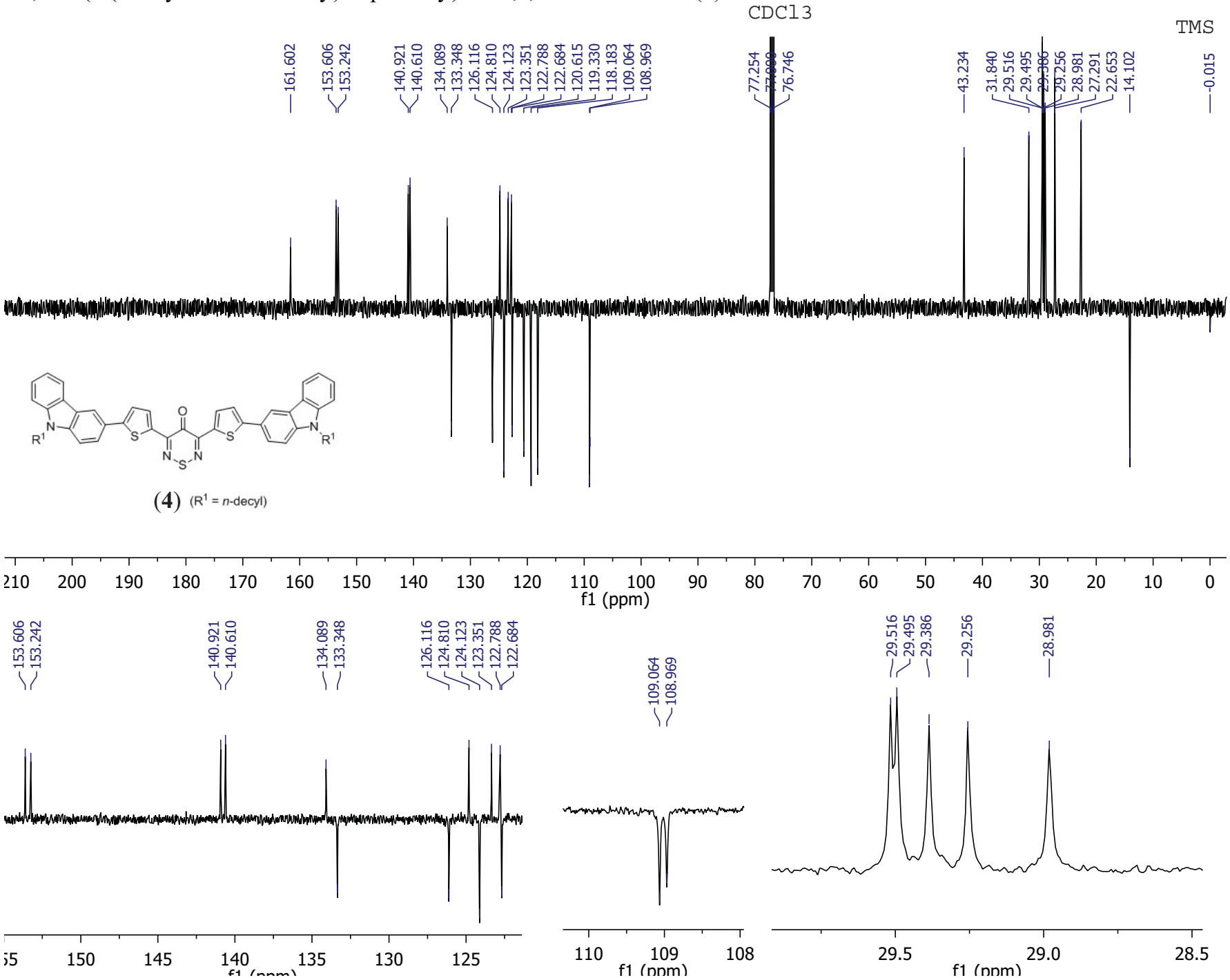
Current Data Parameters
NAME Andreas Kalogirou
EXPNO 229
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130611
Time 20.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 144
DW 48.400 usec
DE 6.50 usec
TE 295.8 K
D1 1.00000000 sec
TD0 1

CHANNEL f1
SFO1 500.0361158 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W

F2 - Processing parameters
SI 65536
SF 500.0330405 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

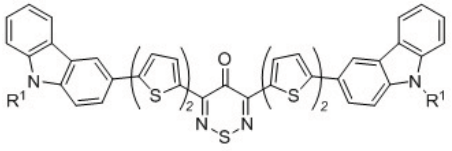
3,5-Bis(5-(9-decyl-9*H*-carbazol-3-yl)thiophen-2-yl)-4*H*-1,2,6-thiadiazin-4-one (**4**)



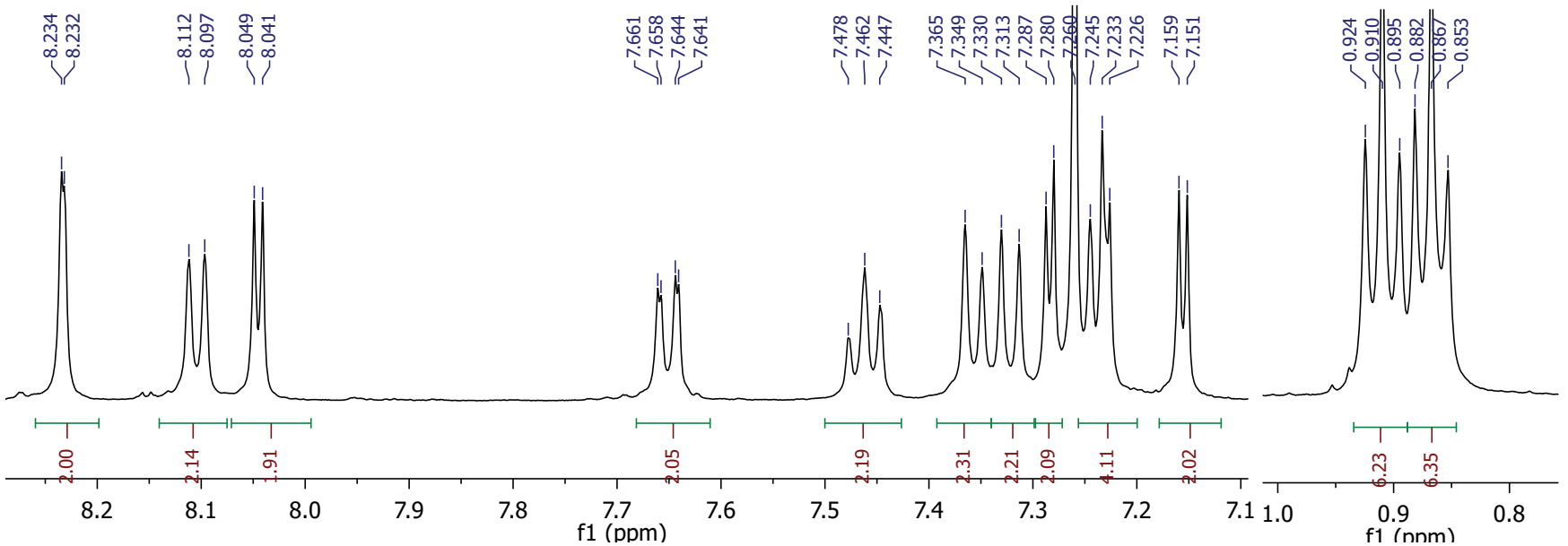
(**4**) (R^1 = *n*-decyl)

Current Data Parameters
NAME Andreas Kalogirou
EXPNO 230
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130612
Time 0.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 4000
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 1820
DW 16.800 usec
DE 6.50 usec
TE 296.6 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
CHANNEL f1
SFO1 125.7459782 MHz
NUC1 13C
P1 8.70 usec
P2 17.40 usec
PLW1 138.00000000 W
CHANNEL f2
SFO2 500.0350280 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.41699982 W
PLW12 0.33258000 W
F2 - Processing parameters
SI 32768
SF 125.7334083 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3,5-Bis(5'-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)-[2,2'-bithiophen]-5-yl)-4*H*-1,2,6-thiadiazin-4-one (**5**)



(**5**) (R^1 = 2-ethylhexyl)



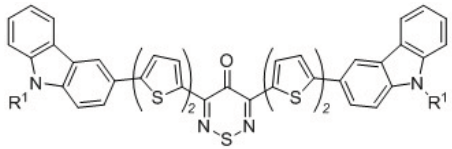
Current Data Parameters
NAME Andreas Kalogirou
EXPNO 338
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130814
Time 21.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 144
DW 48.400 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
TD0 1

CHANNEL f1
SFO1 500.0361158 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W

F2 - Processing parameters
SI 65536
SF 500.0330403 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

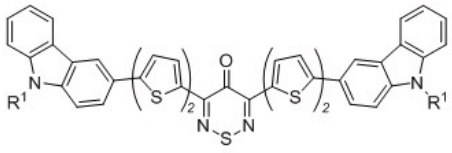
3,5-Bis(5'-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)-[2,2'-bithiophen]-5-yl)-4*H*-1,2,6-thiadiazin-4-one (**5**)



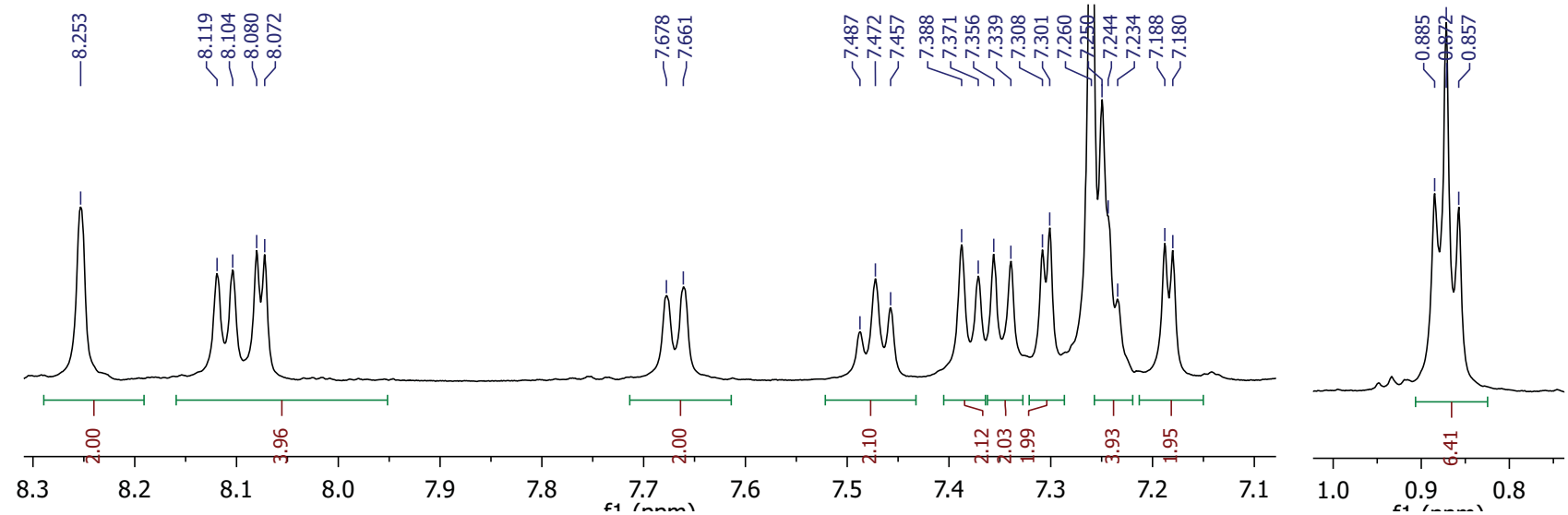
(**5**) (R^1 = 2-ethylhexyl)

Current Data Parameters
NAME Andreas Kalogirou
EXPNO 339
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130815
Time 1.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 5000
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 299.7 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
CHANNEL f1
SFO1 125.7459782 MHz
NUC1 13C
P1 8.70 usec
P2 17.40 usec
PLW1 138.00000000 W
CHANNEL f2
SFO2 500.0350280 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.41699982 W
PLW12 0.33258000 W
F2 - Processing parameters
SI 32768
SF 125.7334069 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3,5-Bis(5'-(9-decyl-9*H*-carbazol-3-yl)-[2,2'-bithiophen]-5-yl)-4*H*-1,2,6-thiadiazin-4-one (**6**)



(**6**) (R^1 = *n*-decyl)



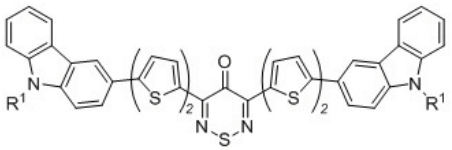
Current Data Parameters
NAME Andreas Kalogirou
EXPNO 381
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130914
Time 21.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 144
DW 48.400 usec
DE 6.50 usec
TE 295.7 K
D1 1.00000000 sec
TD0 1

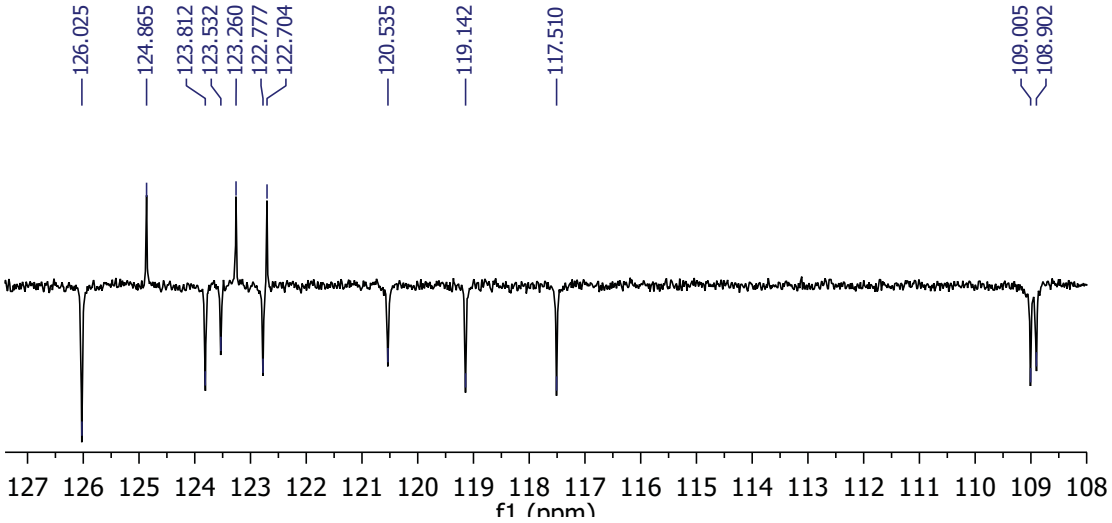
CHANNEL f1
SFO1 500.0361158 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W

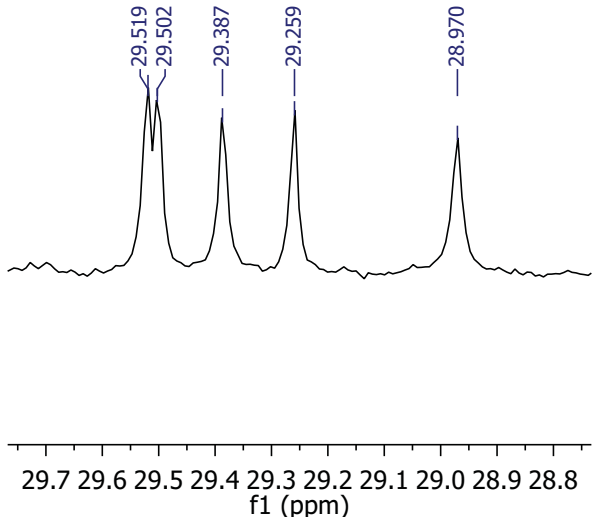
F2 - Processing parameters
SI 65536
SF 500.0330400 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

3,5-Bis(5'-(9-decyl-9*H*-carbazol-3-yl)-[2,2'-bithiophen]-5-yl)-4*H*-1,2,6-thiadiazin-4-one (**6**)



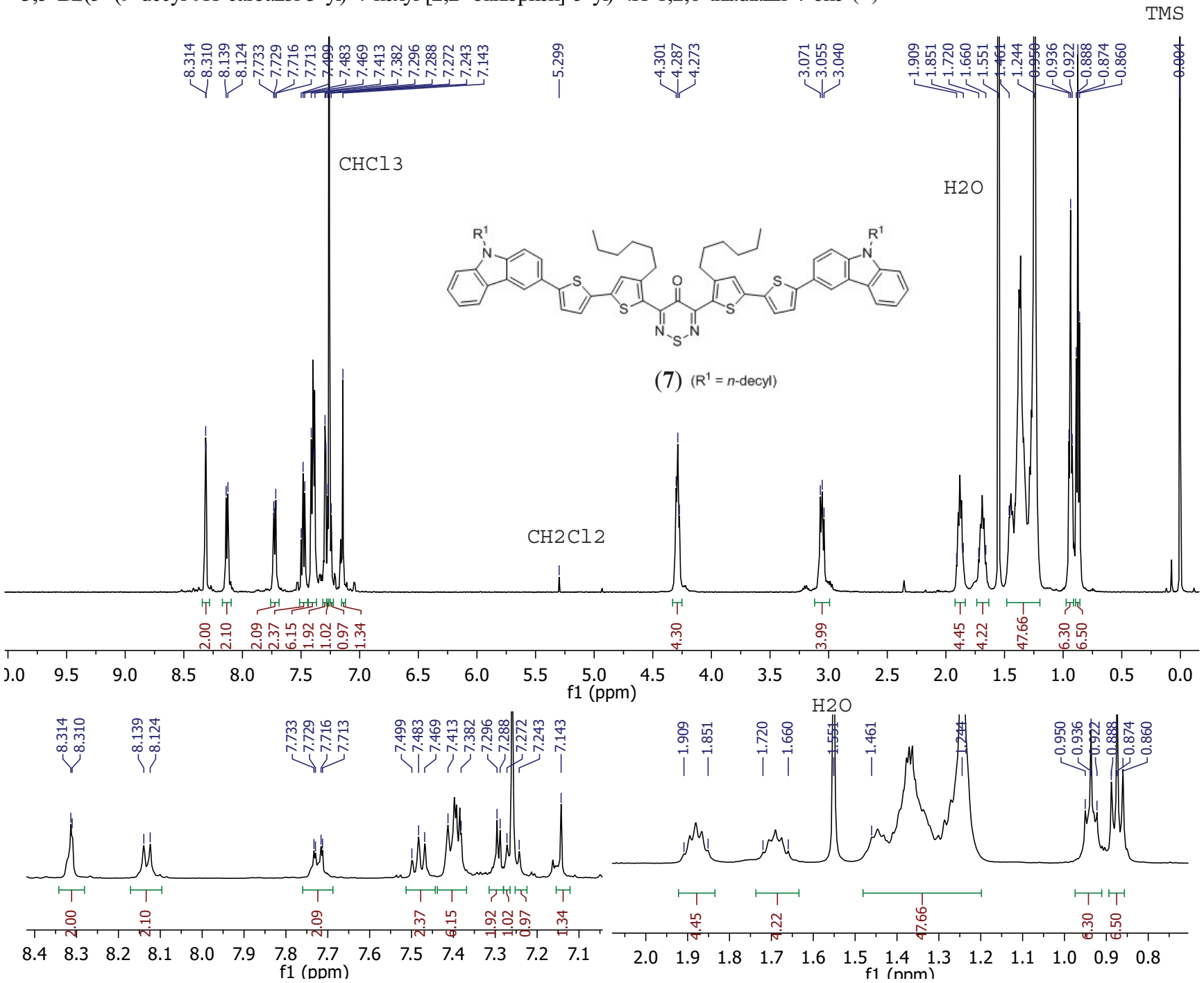
(**6**) (R^1 = *n*-decyl)





Current Data Parameters
NAME Andreas Kalogirou
EXPNO 382
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130915
Time 1.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 4500
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 1820
DW 16.800 usec
DE 6.50 usec
TE 297.1 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
CHANNEL f1
SFO1 125.7459782 MHz
NUC1 13C
P1 8.70 usec
P2 17.40 usec
PLW1 138.00000000 W
CHANNEL f2
SFO2 500.0350280 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.41699982 W
PLW12 0.33258000 W
F2 - Processing parameters
SI 32768
SF 125.7334080 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3,5-Bis(5'-(9-decyl-9*H*-carbazol-3-yl)-4-hexyl-[2,2'-bithiophen]-5-yl)-4*H*-1,2,6-thiadiazin-4-one (**7**)



(**7**) (R^1 = *n*-decyl)

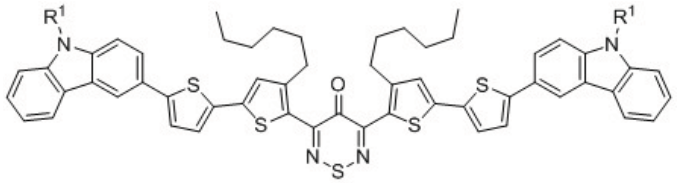
Current Data Parameters
NAME Andreas Kalogirou
EXPNO 419
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131021
Time 1.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 128
DW 48.400 usec
DE 6.50 usec
TE 298.4 K
D1 1.00000000 sec
TD0 1

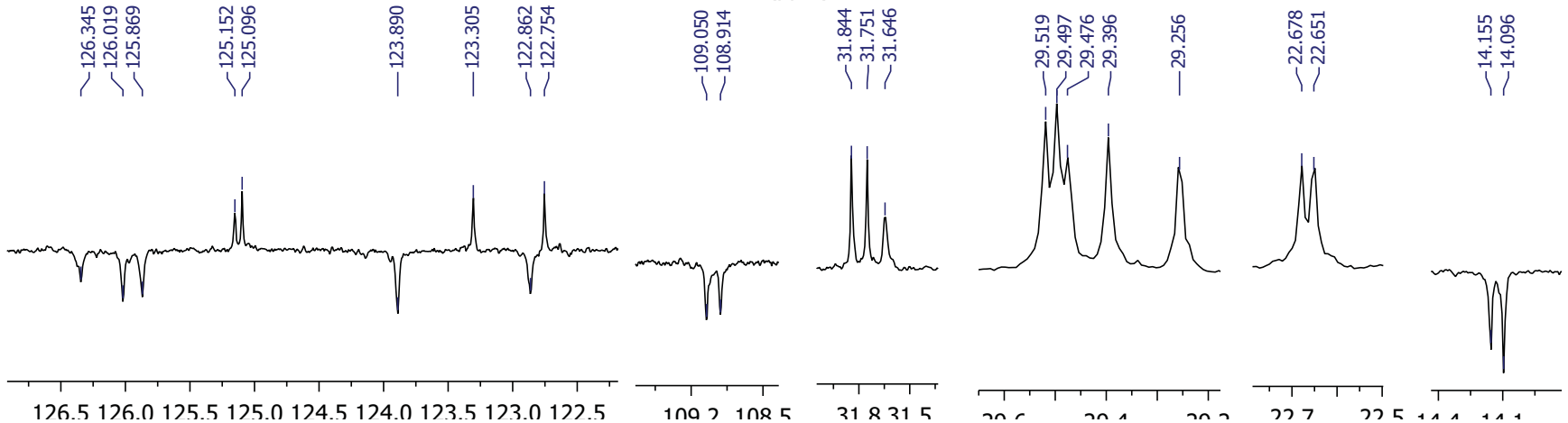
CHANNEL f1
SFO1 500.0361158 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W

F2 - Processing parameters
SI 65536
SF 500.0330401 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

3,5-Bis(5'-(9-decyl-9*H*-carbazol-3-yl)-4-hexyl-[2,2'-bithiophen]-5-yl)-4*H*-1,2,6-thiadiazin-4-one (**7**)

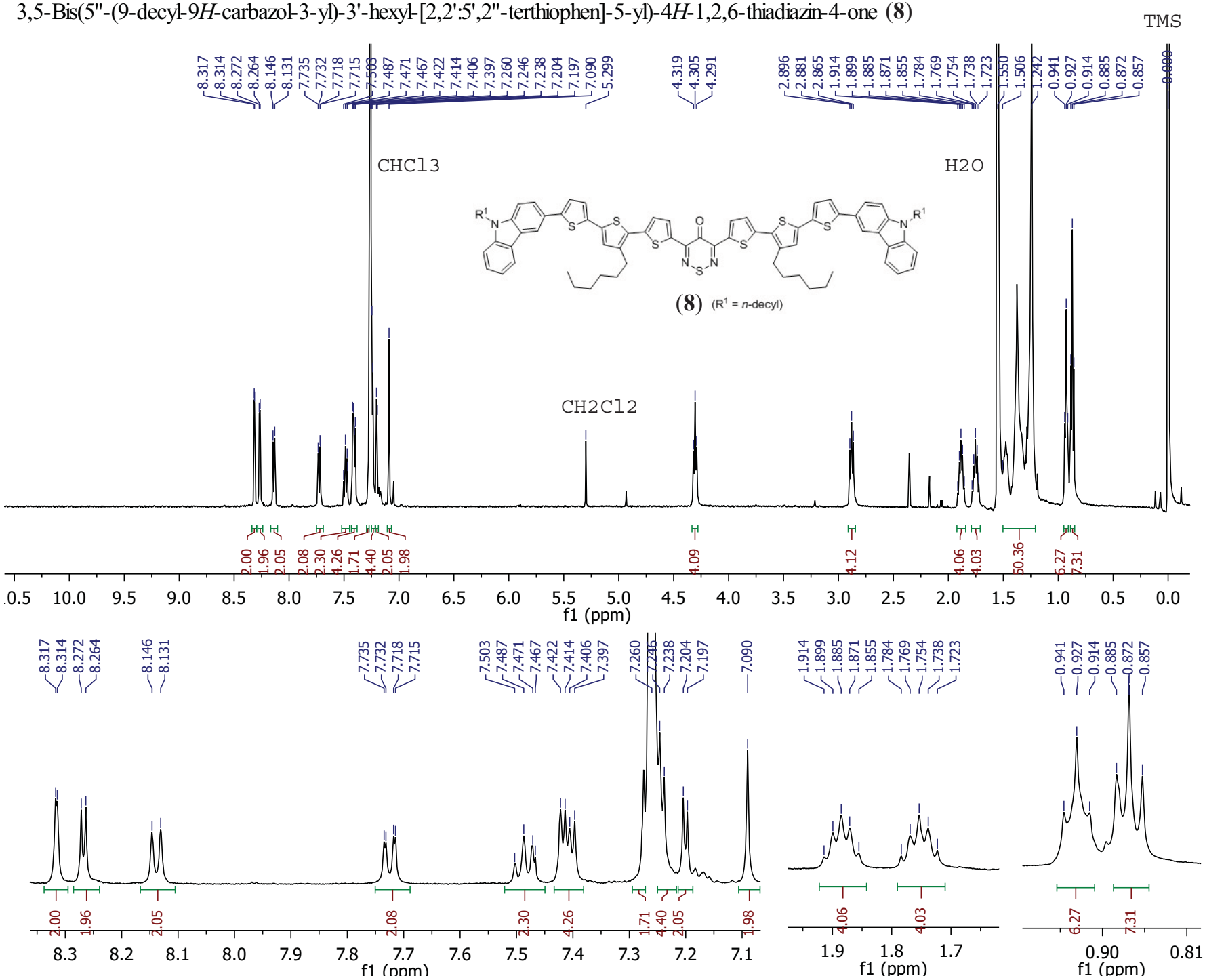


(**7**) (R^1 = *n*-decyl)



Current Data Parameters
NAME Andreas Kalogirou
EXPNO 420
PROCNO 1
F2 - Acquisition Parameters
Date_ 20131021
Time 5.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 5000
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 299.4 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
CHANNEL f1
SFO1 125.7459782 MHz
NUC1 13C
P1 8.70 usec
P2 17.40 usec
PLW1 138.00000000 W
CHANNEL f2
SFO2 500.0350280 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.41699982 W
PLW12 0.33258000 W
F2 - Processing parameters
SI 32768
SF 125.7334068 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

3,5-Bis(5"-(9-decyl-9*H*-carbazol-3-yl)-3'-hexyl-[2,2':5',2"-terthiophen]-5-yl)-4*H*-1,2,6-thiadiazin-4-one (**8**)



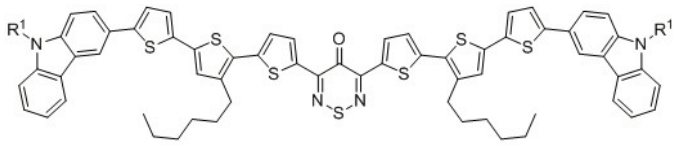
Current Data Parameters
NAME Andreas Kalogirou
EXPNO 443
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131031
Time 15.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 100
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 181
DW 48.400 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
TD0 1

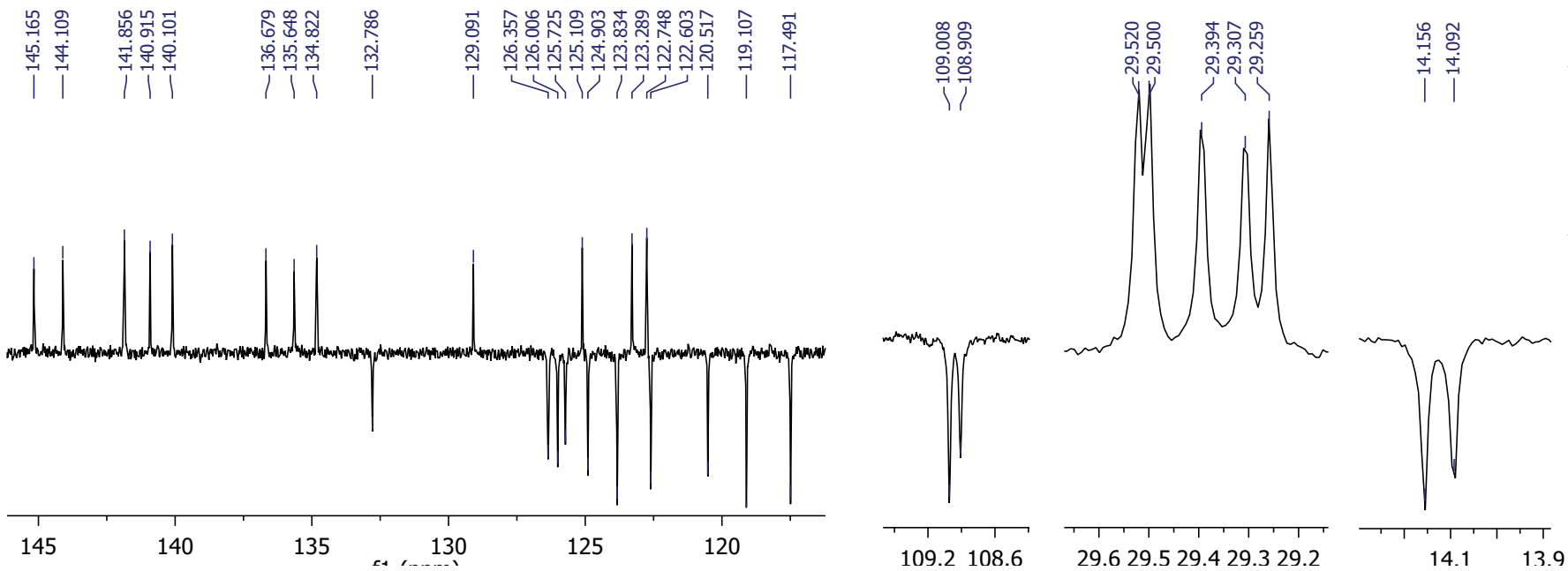
CHANNEL f1
SFO1 500.0361158 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W

F2 - Processing parameters
SI 65536
SF 500.0330396 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

3,5-Bis(5''-(9-decyl-9*H*-carbazol-3-yl)-3'-hexyl-[2,2':5',2''-terthiophen]-5-yl)-4*H*-1,2,6-thiadiazin-4-one (**8**)



(8) (R^1 = *n*-decyl)



Current Data Parameters
NAME Andreas Kalogirou
EXPNO 437
PROCNO 1
F2 - Acquisition Parameters
Date_ 20131030
Time 21.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 11500
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 1820
DW 16.800 usec
DE 6.50 usec
TE 298.9 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
D20 0.00689655 sec
TD0 1
CHANNEL f1
SFO1 125.7459782 MHz
NUC1 13C
P1 8.70 usec
P2 17.40 usec
PLW1 138.00000000 W
CHANNEL f2
SFO2 500.0350280 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 15.41699982 W
PLW12 0.33258000 W
F2 - Processing parameters
SI 32768
SF 125.7334060 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40