Supporting Information for

Selective Thienylation of Fluorinated Benzothiadiazoles and Benzotriazoles for Organic Photovoltaics

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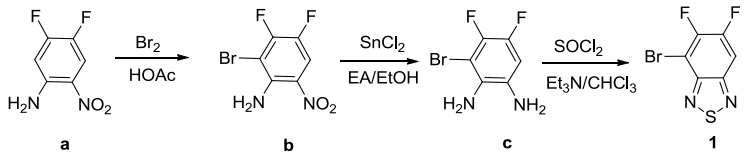
General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Agilent AM400 and AM500 spectrometer. ^{19}F NMR was recorded on a Agilent AM400 spectrometer ($CFCl_3$ as outside standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction.

Materials: All reagents were used as received from commercial sources. All reagents were weighed and handled in air, and refilled with an inert atmosphere of N_2 at room temperature. DMF and DMSO were distilled under reduced pressure from CaH_2. The DMSO was stored with the powder of 4 Å molecular sieves. Toluene and 1,4-Dioxane was distilled from sodium and benzophenone immediately before use.

Procedure for the preparation of compound 1.

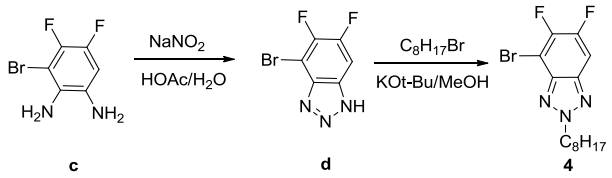


2-Bromo-3,4-difluoro-6-nitroaniline (b).[1] To a solution of 4,5-difluoro-2-nitroaniline (17.4 g, 100 mmol) in acetic acid (100 ml) was added bromine (32 g, 2 equiv) dropwise at 50- 56 °C, and stirred for 2.5 hours. The reaction mixture was poured into ice water (250 mL) and the resulting precipitate was collected by filtration and washed with water sufficiently then dried to give compound **b** (23.3 g, 92% yield) as a yellow solid.

3-Bromo-4,5-difluorobenzene-1,2-diamine (c).[2] To a solution of **b** (7.6 g, 30 mmol) and $SnCl_2{\cdot}2H_2O$ (34 g, 150 mmol) were dissolved in 70 mL ethyl acetate and 30 mL absolute ethanol under N_2. Then the mixture was heated at 75 °C with stirring for 3 h. The reaction mixture was then cooled to room temperature, and poured into 200 mL ice water. Aqueous saturated solution of $NaHCO_3$ was added to adjust the pH to 5. The residue was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue (5.6 g, 75%

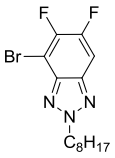
yield) was used for the next step without further purification.

4-Bromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (1). To a 500 mL three- necked round bottom flask were added **c** (5.6 g, 25 mmol), $CHC1_3$ (150 mL) and triethylamine (11.4 mL, 4 equiv). After stirring for 15 min, thionyl chloride ($SOCl_2$, 7.2 g, 2 equiv) was added dropwise and the mixture was heated to reflux for 5 h. The reaction mixture was then cooled to room temperature, and concentrated. The residue was extracted with CH_2Cl_2, washed with water and brine. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified with silica gel column chromatography (100% hexane) to give FBT **1** as a white solid (5.1 g, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (apparent t, J = 8.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.5 (dd, J = 19.9 Hz, 7.5 Hz, 1F), -125.7 (dd, J = 19.7 Hz, 8.8 Hz, 1F).



c d 4

4-Bromo-5,6-difluoro-1H-benzo[d][1,2,3]triazole (d). To a solution of HOAc (2.4 mL, 40 mmol) in 100 mL of H_2O was added compound **c** (4.66 g, 20 mmol). The reaction mixture was heated to 70 ^{o}C and stirred for 1 h. The reaction mixture was then cooled to room temperature, a solution of $NaNO_2$ (1.52 g) in 20 mL of H_2O was then added. The resulting reaction mixture was stirred for another 1 h at room temperature. The resulting precipitate was filtered to give compound **d** (3.51 g, 75% yield) without further purification.

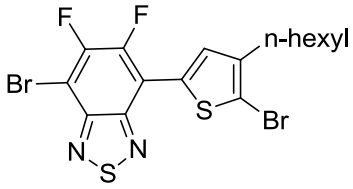


4-Bromo-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazole (4). To a solution of **d** (2.3 g, 10 mmol) in 50 mL of methanol were added *t*BuOK (1.15 g, 1.02 equiv) and $C_8H_{17}Br$ (1.95 g, 1.01 equiv) under N_2. The reaction mixture was then heated to reflux for 24 h. The reaction mixture was cooled to room temperature, and was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The product (1.20 g, 35% yield) was purified with silica gel chromatography(Petroleum ether(100%)) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J

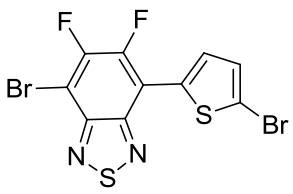
= 8.6 Hz, 7.0 Hz, 1H), 4.70 (t, *J* = 7.4 Hz, 2H), 2.10 (m, 2H), 1.40-1.15 (m, 10H) , 0.86 (t, *J* = 6.8 Hz, 3H) .^{19}F NMR (376 MHz, $CDCl_3$) -128.9 (dd, *J* = 19.2 Hz, 6.8 Hz, 1F), -129.7 (dd, *J* = 19.7 Hz, 8.8 Hz, 1F).

General Procedure for Selective Thienylation of FBT 1 with Thiophenes.

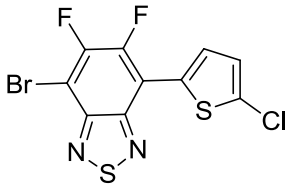
To a 25 mL of sealed tube were added $Pd(TFA)_2$ (2.5 mol %), Ag_2O (93 mg 2.0 equiv) and 4-bromo-5,6-difluorobenzo[c][1,2,5]thiadiazole **(1)** (50 mg, 1 equiv) under N_2, followed by DMSO (1 mL) with stirring. Thiophene **2** (0.4 mmol, 2 equiv) were then added subsequently. The reaction mixture was stirred at 80 ^{o}C (preheated oil bath). After stirring for 6 h, the reaction mixture was cooled to room temperature, filtered and diluted with dichloromethane, washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.



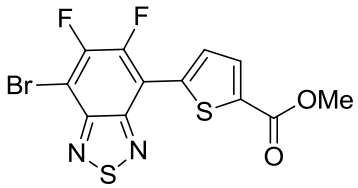
4-Bromo-7-(5-bromo-4-hexylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (3a). The product (80 mg, 81% yield) was purified with silica gel chromatography (Petroleum ether(100%)) as a yellow solid. m.p. 91 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.66 (m, 2H), 1.45-1.25 (m, 6H) , 0.90 (t, *J* = 7.0 Hz, 3H) .^{19}F NMR (376 MHz, $CDCl_3$) δ -120.2 (d, *J* = 18.4 Hz, 1F), -126.7 (d, *J* = 18.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0 (dd, *J* = 255.4 Hz, 19.8 Hz), 149.8(d, *J* = 5.3 Hz), 149.1 (dd, *J* = 261.5 Hz, 19.4 Hz), 147.4 (d, *J* = 8.9 Hz), 142.7, 132.2 (d, *J* = 9.9 Hz), 130.5 (m), 114.9 (d, *J* = 8.1 Hz), 112.6 (d, *J* = 11.5 Hz), 97.1 (d, *J* = 22.3 Hz), 31.6, 29.7, 29.5, 28.9, 22.6, 14.1. MS (EI): *m/z* (%) 496 (M^+), 366, 345, 252, 41(100). HRMS: Calculated for $C_{16}H_{14}N_2F_2S_2Br_2$: 493.8933; Found: 493.8930.



4-Bromo-7-(5-bromothiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (3b). The product (60 mg, 73% yield) was purified with silica gel chromatography (Petroleum ether(100%)) as a yellow solid. m.p. 155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 4.2 Hz, 1H), 7.20 (d, *J* = 4.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.1 (d, *J* = 19.2 Hz, 1F), -126.6 (d, *J* = 19.2 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2 (dd, *J* = 255.4 Hz, 20.0 Hz), 149.8(d, *J* = 5.5 Hz), 149.2 (dd, *J* = 261.8 Hz, 19.5 Hz), 147.4 (d, *J* = 8.4 Hz), 134.8 (d, *J* = 8.0 Hz), 130.8 (d, *J* = 10.3 Hz), 129.6 (m), 126.6, 112.4 (d, *J* = 11.9 Hz), 97.4 (d, *J* = 23.5 Hz). MS (EI): *m/z* (%) 414 (M^+), 312 (M^+), 310 (M^+), 40 (100). HRMS: Calculated for $C_{10}H_2N_2F_2S_2Br_2$: 409.7994; Found: 409.7991.

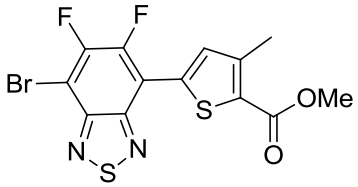


4-Bromo-7-(5-chlorothiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (3c). The product (54 mg, 74% yield) was purified with silica gel chromatography (Petroleum ether(100%)) as a yellow solid. m.p. 137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 4.0 Hz, 1H), 7.06 (dd, *J* = 4.0 Hz, 1.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.1 (d, *J* = 19.0 Hz, 1F), -126.8 (d, *J* = 19.0 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2 (dd, *J* = 255.5 Hz, 20.0 Hz), 149.8 (d, *J* = 5.4 Hz), 149.2 (dd, *J* = 261.7 Hz, 19.4 Hz), 147.4 (d, *J* = 8.5 Hz), 134.8 (d, *J* = 8.0 Hz), 130.8 (d, *J* = 10.3 Hz), 129.6 (m), 126.6, 112.4 (d, *J* = 12.6 Hz), 97.4 (d, *J* = 21.9 Hz). MS (EI): *m/z* (%) 368 (M^+,100), 366 (M^+), 332, 252. HRMS: Calculated for $C_{10}H_2N_2F_2S_2BrCl$: 365.8499; Found: 365.8496.

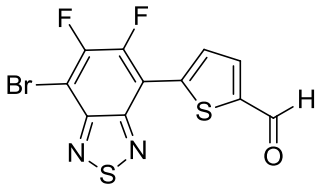


Methyl 5-(7-bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophene-2-carboxylate (3d). The product (59 mg, 76%) was purified with silica gel chromatography (Petroleum ether /Dichloromethane = 50:1) as a yellow solid. m.p. 154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 3.6 Hz, 1H), 7.90 (dd, *J* = 4.2 Hz, 1.0 Hz, 1H), 3.95 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.9 (d, *J* = 17.7 Hz, 1F), -124.6 (d, *J* = 17.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 152.2 (dd, *J* =

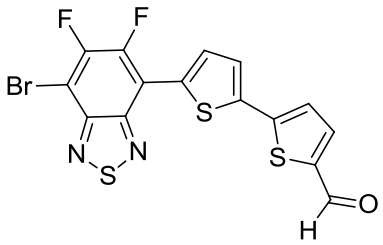
256.1 Hz, 19.8 Hz), 150.0 (dd, *J* = 264.0 Hz, 19.6 Hz), 149.8, 147.5 (d, *J* = 7.9 Hz), 137.0 (m), 136.0 (d, *J* = 6.2 Hz), 133.2, 131.4 (d, *J* = 9.5 Hz), 112.3 (d, *J* = 10.3 Hz), 98.9 (d, *J* = 21.6 Hz), 52.4. MS (EI): *m/z* (%) 392 (M^+), 390 (M^+), 361(100). HRMS: Calculated for $C_{12}H_5N_2O_2S_2F_2Br$: 389.8944; Found: 389.8942.



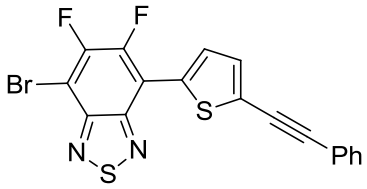
Methyl 5-(7-bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)-3-methylthiophene-2-carboxylate (3e). The product (68 mg, 84% yield) was purified by silica chromatography (Petroleum ether /Ethyl Acetate = 50:1) as a yellow solid. m.p. 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 3.92 (s, 3H), 2.64 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.0 (d, *J* = 18.2 Hz, 1F), -124.7 (d, *J* = 18.2 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 152.2 (dd, *J* = 255.8 Hz, 19.8 Hz), 150.0 (dd, *J* = 264.0 Hz, 19.6 Hz), 149.8, 147.5 (d, *J* = 7.9 Hz), 146.0, 145.1 (d, *J* = 5.0 Hz), 135.1 (d, *J* = 9.2 Hz), 134.2 (m), 129.2 (d, *J* = 6.2 Hz), 98.7 (d, *J* = 20.6 Hz), 52.0, 16.0. MS (EI): *m/z* (%) 406 (M^+), 404 (M^+), 375 (100), 346. HRMS: Calculated for $C_{13}H_7N_2O_2S_2F_2Br$: 403.9100; Found: 403.9104.



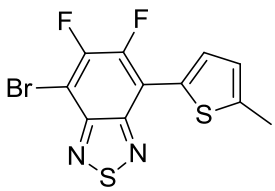
5-(7-Bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde (3f). The product (53 mg, 74% yield) was purified by silica chromatography (Petroleum ether /Ethyl Acetate = 50:1) as a yellow solid. m.p. 165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.32 (d, *J* = 4.0 Hz, 1H), 7.88 (dd, *J* = 4.0 Hz, 1.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.8 (d, *J* = 19.2 Hz, 1F), -123.5 (d, *J* = 19.2 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 152.2 (dd, *J* = 256.1 Hz, 19.8 Hz), 150.3 (dd, *J* = 264.9 Hz, 19.3 Hz), 149.8 (d, *J* = 5.1 Hz), 147.4 (d, *J* = 7.8 Hz), 145.4 (d, *J* = 5.5 Hz), 139.6 (m), 135.6, 131.7 (d, *J* = 9.4 Hz), 112.1, 99.8 (d, *J* = 21.5 Hz). MS (EI): *m/z* (%) 362 (M^+, 100), 360 (M^+, 100), 332, 289. HRMS: Calculated for $C_{11}H_3ON_2BrS_2F_2$: 359.8838; Found: 359.8834.



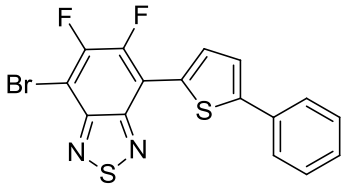
5'-(7-Bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)-[2,2'-bithiophene]-5-carbaldehyde (3g). The product (58 mg, 66% yield) was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1) as a yellow solid. m.p. 158 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.21 (d, *J* = 4.0 Hz, 1H), 7.72 (d, *J* = 4.0 Hz, 1H), 7.46 (dd, *J* = 4.0 Hz, 1.2 Hz, 1H) , 7.39 (d, *J* = 4.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.1 (d, *J* = 19.0 Hz, 1F), -125.5 (d, *J* = 19.0 Hz, 1F). MS (EI): *m/z* (%) 444 (M^+, 100), 442 (M^+, 100), 369. HRMS: Calculated for $C_{15}H_5ON_2BrS_3F_2$: 441.8715; Found: 441.8711.



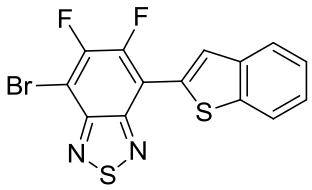
4-Bromo-5,6-difluoro-7-(5-(phenylethynyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (3h). The product (64 mg, 74% yield) was purified with silica gel chromatography (Petroleum ether(100%)) as a yellow solid. m.p. 166 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 4.0 Hz, 1H), 7.60-7.50 (m, 2H), 7.40-7.34 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.2 (d, *J* = 19.2 Hz, 1F), -126.2 (d, *J* = 19.2 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (dd, *J* = 255.4 Hz, 19.6 Hz), 149.8 (d, *J* = 5.5 Hz), 149.4 (dd, *J* = 262.8 Hz, 19.2 Hz), 147.6 (d, *J* = 8.5 Hz), 132.1, 131.46, 131.41 131.3, 128.8, 128.4, 127.3 (d, *J* = 7.3 Hz), 122.6, 112.7 (d, *J* = 11.6 Hz), 97.5 (d, *J* = 21.5 Hz), 96.1, 82.2. MS (EI): *m/z* (%) 435 (M^+), 434 (M^+, 100), 433 (M^+), 432 (M^+), 145. HRMS: Calculated for $C_{18}H_7N_2F_2S_2Br$: 431.9202; Found: 431.9201.



4-Bromo-5,6-difluoro-7-(5-methylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3i). The product (50 mg, 72% yield) was purified with silica gel chromatography (Petroleum ether(100%)) as a yellow solid. m.p. 155 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 4.0 Hz, 1H), 6.89 (dd, *J* = 2.4 Hz, 1.2 Hz 1H), 2.58 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.4 (d, *J* = 19.2 Hz, 1F), -127.7 (d, *J* = 19.2 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (dd, *J* = 255.0 Hz, 20.0 Hz), 149.8 (d, *J* = 5.6 Hz), 148.7 (dd, *J* = 260.2 Hz, 19.2 Hz), 147.8 (d, *J* = 8.6 Hz), 144.6 (d, *J* = 6.6 Hz), 131.7 (d, *J* = 8.9 Hz), 128.4 (m), 126.0, 113.6 (d, *J* = 12.4 Hz), 96.2 (d, *J* = 20.5 Hz), 15.3. MS (EI): *m/z* (%) 348 (M^+, 100), 347 (M^+), 346 (M^+). HRMS: Calculated for $C_{11}H_5N_2F_2S_2Br$: 345.9046; Found: 345.9045.

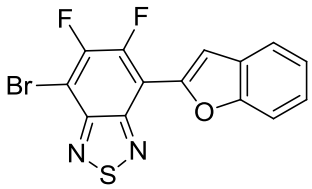


4-Bromo-5,6-difluoro-7-(5-phenylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3j). The product (69 mg, 84% yield) was purified with silica gel chromatography (Petroleum ether(100%)) as a yellow solid. m.p. 124 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 4.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.46-7.38 (m, 3H), 7.34 (t, *J* = 7.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.0 (d, *J* = 17.7 Hz, 1F), -127.4 (d, *J* = 17.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (dd, *J* = 255.2 Hz, 20.0 Hz), 149.9 (d, *J* = 5.2 Hz), 149.4 (dd, *J* = 261.3 Hz, 19.0 Hz), 148.2 (d, *J* = 6.6 Hz), 147.7 (d, *J* = 9.0 Hz), 133.6, 132.5 (d, *J* = 9.3 Hz), 130.1, 129.0, 128.3, 126.0, 123.5, 113.3 (d, *J* = 11.5 Hz), 96.7 (d, *J* = 23.3 Hz). MS (EI): *m/z* (%) 411 (M^+), 410 (M^+), 408 (M^+), 121, 83 (100). HRMS: Calculated for $C_{16}H_7N_2S_2BrF_2$: 407.9202; Found: 407.9197.

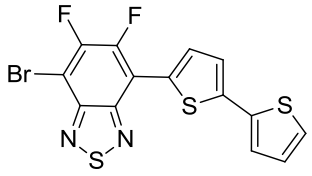


4-(Benzo[b]thiophen-2-yl)-7-bromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (3k). The product (66 mg, 86% yield) was purified with silica gel chromatography (Petroleum ether(100%)) as a yellow solid. m.p. 169 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.89 (m, 2H), 7.41 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.1 (d, *J* = 18.4 Hz, 1F), -125.3 (d, *J* = 18.4 Hz, 1F). ^{13}C NMR (100 MHz,

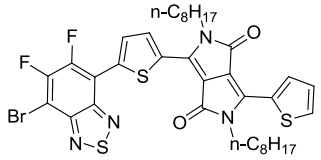
$CDCl_3$) δ 152.3 (dd, *J* = 255.6 Hz, 20.0 Hz), 150.1 (dd, *J* = 262.8 Hz, 19.2 Hz), 149.9 (d, *J* = 5.3 Hz), 148.0 (d, *J* = 8.1 Hz), 140.9 (d, *J* = 5.7 Hz), 139.0, 130.8 (m), 128.5 (d, *J* = 8.4 Hz), 125.8, 124.8, 124.5, 121.9, 113.4 (d, *J* = 11.7 Hz), 98.2 (d, *J* = 19.6 Hz). MS (EI): *m/z* (%) 385 (M^+), 384 (M^+, 100), 383 (M^+), 382 (M^+). HRMS: Calculated for $C_{14}H_5N_2F_2S_2Br$: 381.9041; Found: 381.9042.



4-(Benzofuran-2-yl)-7-bromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (3l). The product (39 mg, 53% yield) was purified with silica gel chromatography (Petroleum ether) as a yellow solid. m.p. 168 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.9 (d, *J* = 17.7 Hz, 1F), -125.8 (d, *J* = 17.7 Hz, 1F). MS (EI): *m/z* (%) 369 (M^+), 368 (M^+), 367 (M^+), 366 (M^+), 141(100). Anal.Calcd for $C_{14}H_5BrF_2N_2OS$: C, 45.80; H, 1.37; N, 7.63. Found C, 45.57; H, 1.24; N, 7.80.



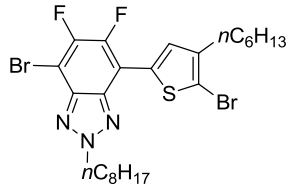
4-([2,2'-Bithiophen]-5-yl)-7-bromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (**3m**). 5 mol % of $Pd(TFA)_2$ was used**.** The product (34 mg, 40% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether (100%)). m.p. 165 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 4.0 Hz, 1H), 7.32 (d, *J* = 3.6 Hz, 1H), 7.30 (t, *J* = 5.2 Hz, 2H), 7.08 (dd, *J* = 5.2 Hz, 4.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.3 (d, *J* = 18.6 Hz, 1F), -126.7 (d, *J* = 18.6 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2 (dd, *J* = 255.0 Hz, 20.0 Hz), 150.0 (dd, *J* = 261.2 Hz, 19.2 Hz), 149.8, 147.7 (d, *J* = 8.3 Hz), 141.4 (d, *J* = 5.2 Hz), 136.6, 132.3 (d, *J* = 9.7 Hz), 129.6(m), 128.1, 125.5, 124.6, 124.0, 113.1 (d, *J* = 15.8 Hz), 96.8 (d, *J* = 23.4 Hz). MS (EI): *m/z* (%) 416 (M^+, 100), 415 (M^+), 414 (M^+). HRMS: Calculated for $C_{14}H_5BrN_2S_3F_2$: 413.8766; Found: 413.8763.



3-(5-(7-Bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2,5-dioctyl-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3n). The reaction was performed on a 0.1 mmol scale and was carried out with **1** (4 equiv), $Pd(TFA)_2$ (5 mol %), Ag_2O (4 equiv) and 1.5 mL DMSO in a Schlenk tube for 10 h at 80 ^oC. The product (52 mg, 68% yield) as a black solid was purified with silica gel chromatography (Petroleum ether /Dichloromethane = 20:1). m.p. 145 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 3.2 Hz, 1H), 8.95 (d, *J* = 3.6 Hz, 1H), 8.39 (d, *J* = 4.4 Hz, 1H), 7.64 (d, *J* = 4.8 Hz, 1H), 7.27 (d, *J* = 4.8 Hz, 1H), 4.14 (t, *J* = 7.8 Hz, 2H), 4.05 (t, *J* = 8.0 Hz, 2H), 1.90-1.60 (m, 4H), 1.50-1.25 (m, 20H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.85 (t, *J* = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.1 (d, *J* = 18.6 Hz, 1F), -124.0 (d, *J* = 18.6 Hz, 1F). MS (MALDI): *m/z* (%) 777.4 (M^+), 776.4 (M^+, 100), 775.4 (M^+), 774.4 (M^+), 773.4 (M^+), 772.4 (M^+). HRMS: Calculated for $C_{36}H_{39}N_4O_2F_2S_3Br$: 772.1384; Found: 772.1381.

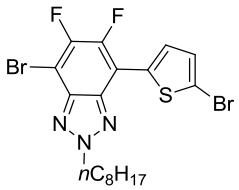
General procedure for the preparation of compounds 3o-3q:

To a 25 mL of sealed tube were added $Pd(OAc)_2$ (5 mol %), Ag_2O (93 mg, 2.0 equiv) under N_2, followed by DMSO (1 mL) with stirring. HOAc (12 uL, 1 equiv), 4-bromo-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazole (**4**) (0.2 mmol, 1 equiv) and thiophene (0.4 mmol, 2 equiv) were then added subsequently. The reaction mixture was stirred at 80 ^oC (preheated oil bath). After stirring for 8 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered, washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified with silica gel chromatography to provide pure product

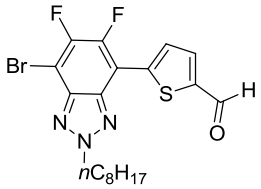


4-Bromo-7-(5-bromo-4-hexylthiophen-2-yl)-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazole (3o). The product (76 mg, 64% yield) was purified with silica gel chromatography (Petroleum ether(100%)) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 4.75 (t, *J* = 7.6 Hz, 2H),

2.64 (t, *J* = 7.6 Hz, 2H), 2.14 (m, 2H), 1.65 (m, 2H), 1.50-1.20 (m, 16H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.8 (d, *J* = 18.4 Hz, 1F), -132.4 (d, *J* = 18.4 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4 (dd, *J* = 247.8 Hz, 18.8 Hz), 146.5 (dd, *J* = 254.2 Hz, 18.2 Hz), 142.4, 139.6 (d, *J* = 5.5 Hz), 136.5 (d, *J* = 8.7 Hz), 131.2 (d, *J* = 7.0 Hz), 131.0 (dd, *J* = 5.8 Hz, 3.2 Hz), 113.4 (d, *J* = 9.2 Hz), 110.8 (d, *J* = 12.8 Hz), 93.9 (d, *J* = 22.6 Hz), 57.2, 31.7, 31.6, 30.0, 29.7, 29.5, 29.0, 28.9, 28.88, 26.5, 22.6, 22.59, 14.1, 14.0. MS (MALDI): *m/z* (%) 592.0 (M^+-H), 590.0 (M^+-H), 588.0 (M^+-H). HRMS: Calculated for $C_{24}H_{30}N_3F_2SBr_2$: 588.0490; Found: 588.0490.



4-Bromo-7-(5-bromothiophen-2-yl)-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazole (3p). The product (53 mg, 52% yield) was purified with silica gel chromatography (Petroleum ether(100%)) as yellow solid. m.p. 65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 4.0 Hz, 1H), 7.15 (dd, *J* = 4.0 Hz, 1.2 Hz, 1H), 4.75 (t, *J* = 7.4 Hz, 2H), 2.14 (m, 2H), 1.50-1.20 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -129.1 (d, *J* = 18.8 Hz, 1F), -132.5 (d, *J* = 18.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3 (dd, *J* = 259.0 Hz, 18.7 Hz), 146.8 (dd, *J* = 265.4 Hz, 18.8 Hz), 139.6 (d, *J* = 5.5 Hz), 136.4 (d, *J* = 8.6 Hz), 133.0 (dd, *J* = 6.0 Hz, 3.2 Hz), 130.6 (d, *J* = 6.8 Hz), 130.2, 116.2 (d, *J* = 9.3 Hz), 110.6 (d, *J* = 12.7 Hz), 94.3 (d, *J* = 22.9 Hz), 57.2, 31.7, 30.0, 29.0, 28.9, 26.5, 22.6, 14.0. MS (MALDI): *m/z* (%) 508.0(M^+-H), 507.0 (M^+-H), 506.0 (M^+-H), 504.0 (M-H). HRMS: Calculated for $C_{18}H_{18}N_3F_2SBr_2$: 503.9551; Found: 503.9561.

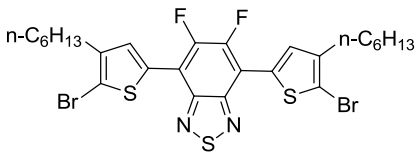


5-(7-Bromo-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazol-4-yl)thiophene-2-carbaldehyde (3q). The product (56 mg, 62% yield) was purified with silica gel chromatography (Petroleum ether/ Ethyl acetate(100:1)) as yellow solid. m.p. 71 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.28 (d, *J* =

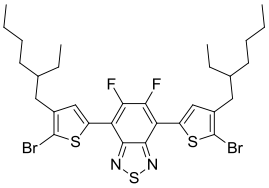
4.2 Hz, 1H), 7.83 (dd, *J* = 4.0 Hz, 1.6 Hz, 1H), 4.77 (t, *J* = 7.4 Hz, 2H), 2.15 (m, 2H), 1.45-1.20 (m, 10H), 0.85 (t, *J* = 6.6 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -128.7 (d, *J* = 19.7 Hz, 1F), -129.2 (d, *J* = 19.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.1, 149.0 (dd, *J* = 251.0 Hz, 15.1 Hz), 147.7 (dd, *J* = 256.9 Hz, 17.5 Hz), 144.5 (d, *J* = 6.8 Hz), 140.4 (m), 139.6 (d, *J* = 4.4 Hz), 136.5 (d, *J* = 8.2 Hz), 135.8, 130.8 (d, *J* = 7.1 Hz), 110.1 (d, *J* = 12.6 Hz), 96.8 (d, *J* = 22.5 Hz), 57.4, 31.6, 30.0, 29.0, 28.9, 26.4, 22.5, 14.0. MS (EI): *m/z* (%) 457 (M^+), 455 (M^+), 376, 208 (100). HRMS: Calculated for $C_{19}H_{20}ON_3S_2F_2Br$: 455.0479; Found: 455.0475.

General procedure for the preparation of compounds 6a and 6b

To a 25 mL of sealed tube were added $Pd(TFA)_2$ (5 mol %), Ag_2O (186 mg 4.0 equiv) and **5** (0.2 mmol, 1 equiv) under N_2, followed by DMSO (1 mL) with stirring. Thiophene (0.8 mmol, 4 equiv) was then added. The reaction mixture was stirred at 80 ^{o}C (preheated oil bath). After stirring for 10 h, the reaction mixture was cooled to room temperature, diluted with dichloromethane, filtered, washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified with silica gel chromatography (Petroleum ether (100%)) to provide pure product



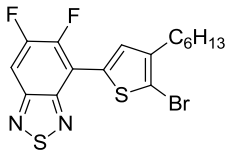
4,7-bis(5-bromo-4-hexylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (6a). The product (90 mg, 68%) was purified with silica gel chromatography (Petroleum ether(100%)) as a red solid. 17% of **7a** (14 mg) was also isolated. **6a:** m.p. 101.1 ^{o}C. This is known compound.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 2H), 2.65 (t, *J* = 7.6 Hz, 4H), 1.66 (m, 4H), 1.45-1.27 (m, 12H), 0.90 (t, *J* = 6.8 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.1 (s, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5 (dd, *J* = 259.1 Hz, 20.3 Hz), 148.1 (t, *J* = 4.1 Hz), 142.5, 131.5 (t, *J* = 4.8 Hz), 131.1, 114.4 (t, *J* = 3.6 Hz), 110.7 (m), 31.6, 29.7, 29.5, 29.0, 22.6, 14.1. MS (MALDI): *m/z* (%) 664.0 (M^+), 662.0 (M^+), 660.0 (M^+). HRMS: Calculated for $C_{26}H_{28}Br_2F_2N_2S_3$: 659.9749; Found: 659.9751.



4,4'-(5,5'-(5,6-difluorobenzo[c][1,2,5]thiadiazole-4,7-diyl)bis(3-hexylthiophene-5,2-diyl))bis(N,N-diphenylaniline) (6b). The product (95 mg, 66%) was purified with silica gel chromatography (Petroleum ether (100%)) as a red solid. This is known compound.[4] 11% of **7b** (10 mg) was also isolated. **6b**: m.p. 83 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 2H), 2.56 (d, *J* = 7.6 Hz, 4H), 1.69 (m, 2H), 1.45-1.25(m, 16H), 0.93(t, *J* = 7.8 Hz, 12H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.0 (s, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0 (dd, *J* = 258.9 Hz, 20.0 Hz), 148.1 (m), 141.6, 132.1 (t, *J* = 4.7 Hz), 131.0, 115.1 (t, *J* = 3.6 Hz), 110.7 (m), 39.9, 33.7, 32.4, 28.8, 25.7, 23.1, 14.2, 10.8.

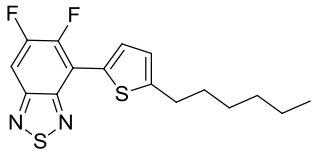
General procedure for the preparation of compounds 7a and **7c-e.**

To a 25 mL of sealed tube were added $Pd(TFA)_2$ (2.5 mol %), Ag_2O (2.0 equiv) and **5** (3.0 equiv) under N_2, followed by DMSO with stirring. Thiophene (1 equiv) was then added. The reaction mixture was stirred at 80 ^{o}C (preheated oil bath). After stirring for 10 h, the reaction mixture was cooled to room temperature, diluted with dichloromethane, filtered, washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified with silica gel chromatography to provide pure product



4-(5-Bromo-4-hexylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (7a). The reaction was performed on a 2 mmol scale in 6 mL DMSO. The product (590 mg, 71%) was purified with silica gel chromatography (Petroleum ether (100%)) as a yellow solid. 22% yield of 6**a** (147 mg) was also isolated. **7a**: m.p. 69 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.60 (dd, *J* = 9.0 Hz, 7.8 Hz, 1H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.66 (m, 2H), 1.45-1.27 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.1 (dd, *J* = 17.1 Hz, 8.8 Hz, 1F), -128.7 (dd, *J* = 16.9 Hz, 7.5 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (dd, *J* = 256.2 Hz, 18.8 Hz), 150.4 (d, *J* = 11.6 Hz), 149.1 (dd, *J* = 260.0 Hz, 19.3 Hz), 148.7 (d, *J* = 8.2 Hz), 142.5, 132.0 (d, *J* = 9.9 Hz), 131.0 (m), 114.4 (d, *J* = 8.3

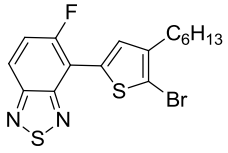
Hz), 113.3 (d, *J* = 11.2 Hz), 103.6 (d, *J* = 20.2 Hz), 31.6, 29.7, 29.5, 28.9, 22.6, 14.1. MS (EI): *m/z* (%) 418 (M^+), 416 (M^+), 267(100). HRMS: Calculated for $C_{16}H_{15}N_2F_2S_2Br$: 415.9828; Found: 415.9832.



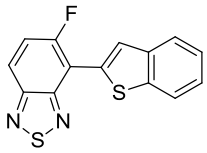
5,6-Difluoro-4-(5-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (7c). The reaction was performed on a 1.0 mmol scale in 2.5 mL of DMSO. The product (161 mg, 48% yield) was purified with silica gel chromatography (Petroleum ether (100%)) as a yellow oil. 4% yield of 6**c** (10 mg) was also isolated. **7c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.8 Hz, 1H), 7.49 (apparent t, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 2.8 Hz, 1H), 2.88 (t, *J* = 7.6 Hz, 2H), 1.75 (m, 2H), 1.50-1.25 (m, 6H) , 0.90 (t, *J* = 7.0 Hz, 3H) . ^{19}F NMR (376 MHz, $CDCl_3$) -127.3 (dd, *J* = 17.1 Hz, 8.8 Hz, 1F), -129.7 (dd, *J* = 16.9 Hz, 7.5 Hz, 1F). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4 (dd, *J* = 255.6 Hz, 19.0 Hz), 150.4 (d, *J* = 12.6 Hz), 150.1 (d, *J* = 5.3 Hz), 149.0 (d, *J* = 8.5 Hz), 148.5 (dd, *J* = 258.5 Hz, 19.1 Hz), 131.2, 128.6 (dd, *J* = 5.6 Hz, 3.6 Hz), 124.5, 114.2 (d, *J* = 13.0 Hz), 102.8 (d, *J* = 20.4 Hz), 31.5, 31.4, 30.0, 28.8, 22.5, 14.0. MS (EI): *m/z* (%) 338 (M^+), 267 (100), 141. HRMS: Calculated for $C_{16}H_{16}N_2S_2F_2$: 338.0723; Found: 338.0724.

General Procedure for the preparation of compounds 9a-d.

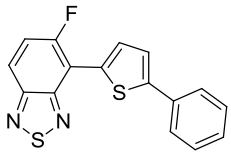
To a 25 mL of sealed tube were added $Pd(OAc)_2$ (5 mol %), AgOAc (133 mg 4.0 equiv), **8** (0.6 mmol, 3 equiv) under N_2, followed by DMSO (2 mL) with stirring. 2-Methylpyridine (30 uL 1.5equiv), and thiophene (0.2 mmol, 1 equiv) were then added. The reaction mixture was stirred at 80 ^{o}C (oil bath). After stirring for 9 h, the reaction mixture was cooled to room temperature, diluted with dichloromethane, filtered, washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified with silica gel chromatography (Petroleum ether (100%)) to provide pure product.



4-(5-Bromo-4-hexylthiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (9a). The product (34 mg, 42% yield) was purified with silica gel chromatography (Petroleum ether(100%)) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.85 (dd, *J* = 9.4 Hz, 5.0 Hz, 1H), 7.51 (dd, *J* = 11.4 Hz, 9.4 Hz, 1H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.66 (m, 2H), 1.45-1.30 (m, 6H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.3 (dd, *J* = 11.5 Hz, 4.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6 (d, *J* = 254.9 Hz), 152.5 (d, *J* = 10.4 Hz), 152.3, 142.2, 131.9 (d, *J* = 5.4 Hz), 131.2 (d, *J* = 8.9 Hz), 121.9 (d, *J* = 30.9 Hz), 120.0 (d, *J* = 10.9 Hz), 113.1 (d, *J* = 8.5 Hz), 112.2 (d, *J* = 14.6 Hz), 31.6, 29.8, 29.6, 28.9, 22.6, 14.1. MS (EI): *m/z* (%) 398 (M^+), 249 (100). HRMS: Calculated for $C_{16}H_{16}N_2FS_2Br$: 397.9922; Found: 397.9923.

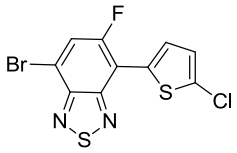


4-(Benzo[b]thiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (9b). The product (26 mg, 45% yield) was purified with silica gel chromatography (Petroleum ether(100%)) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.85 (dd, *J* = 9.0 Hz, 4.8 Hz, 1H), 7.92 (m, 2H), 7.59 (dd, *J* = 11.4 Hz, 9.0 Hz, 1H), 7.41 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.2 (dd, *J* = 11.6 Hz, 4.5 Hz, 1F). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 159.5 (d, *J* = 256.1 Hz), 153.1 (d, *J* = 9.9 Hz), 152.4, 140.6 (d, *J* = 6.1 Hz), 139.2, 132.3 (d, *J* = 5.4 Hz), 127.4 (d, *J* = 7.8 Hz), 125.1, 124.5, 124.2, 121.9 (d, *J* = 31.0 Hz), 121.8, 121.0 (d, *J* = 11.1 Hz), 112.8 (d, *J* = 14.8 Hz). MS (EI): *m/z* (%) 286 (M^+, 100), 109. HRMS: Calculated for $C_{14}H_7N_2FS_2$: 286.0035; Found: 286.0040.

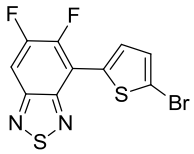


5-Fluoro-4-(5-phenylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (9c). The product (29 mg, 47% yield) was purified with silica gel chromatography (Petroleum ether(100%)) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 4.0 Hz, 1H), 7.85 (dd, *J* = 9.4 Hz, 4.6 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.54 (dd, *J* = 11.2 Hz, 9.2 Hz, 1H), 7.46-7.38 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.3 (dd, *J* = 11.6 Hz, 4.9 Hz, 1F). ^{13}C NMR (125 MHz, $CDCl_3$) δ

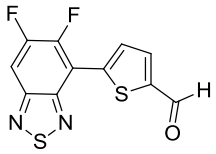
158.6 (d, *J* = 254.6 Hz), 152.8 (d, *J* = 10.2 Hz), 152.4, 146.6 (d, *J* = 6.9 Hz), 140.0, 131.6 (d, *J* = 5.6 Hz), 131.5 (d, *J* = 8.4 Hz), 128.9, 125.9, 123.3, 122.0, 121.8, 119.8 (d, *J* = 11.0 Hz), 112.8 (d, *J* = 14.9 Hz). MS (EI): *m/z* (%) 312 (M^+, 100), 121. HRMS: Calculated for $C_{16}H_9N_2FS_2$: 312.0191; Found: 312.0190.



7-Bromo-4-(5-chlorothiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (9d). The product (30 mg, 43% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether(100%)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 4.0 Hz, 1H), 7.80 (d, *J* = 11.2 Hz, 1H), 7.04 (dd, *J* = 4.4 Hz, 1.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.8 (d, *J* = 10.9 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1 (d, *J* = 257.1 Hz), 151.6 (d, *J* = 12.1 Hz), 151.0, 133.7 (d, *J* = 8.7 Hz), 130.5 (d, *J* = 5.8 Hz), 130.0 (d, *J* = 9.5 Hz), 126.5, 124.4 (d, *J* = 33.2 Hz), 112.2 (d, *J* = 12.6 Hz), 111.6 (d, *J* = 14.1 Hz). MS (EI): *m/z* (%) 398 (M^+), 249 (100). HRMS: Calculated for $C_{10}H_3N_2FS_2BrCl$: 347.8594; Found: 347.8596.



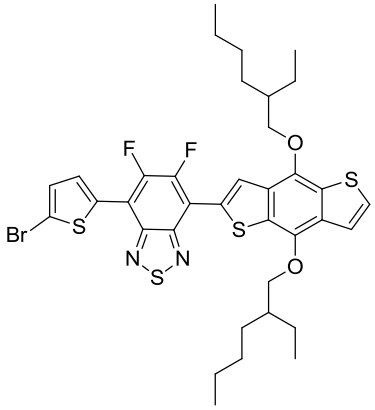
4-(5-Bromothiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (7d). The reaction was performed on a 4.0 mmol scale in 4 mL DMSO. The product (916 mg, 69%) was purified with silica gel chromatography (Petroleum ether (100%)) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 4.0 Hz, 1H), 7.64 (dd, *J* = 9.0 Hz, 7.4 Hz, 1H), 7.20 (dd, *J* = 4.2 Hz, 1.0 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.1 (dd, *J* = 12.6 Hz, 9.6 Hz, 1F), -128.5 (dd, *J* = 16.2 Hz, 6.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (dd, *J* = 256.4 Hz, 18.8 Hz), 150.4 (d, *J* = 12.5 Hz), 149.1 (dd, *J* = 260.2 Hz, 19.4 Hz), 148.7 (d, *J* = 8.3 Hz), 133.0 (m), 131.4 (d, *J* = 10.1 Hz), 130.2 (d, *J* = 0.9 Hz), 117.3 (d, *J* = 7.9 Hz), 113.1 (m), 104.0 (d, *J* = 21.2 Hz). MS (EI): *m/z* (%) 334 (M^+, 100) , 332 (M^+, 100), 253, 209. HRMS: Calculated for $C_{10}H_3N_2F_2S_2Br$: 331.8889; Found: 331.8893.



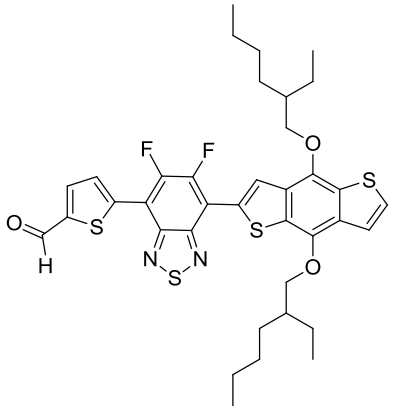
5-(5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde (7e). The reaction was performed on a 1 mmol scale in 3 mL DMSO. The product (130 mg, 46% yield) was purified with silica gel chromatography (Petroleum ether /Dichloromethane = 40:1) as a yellow solid. m.p. 157 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.34 (d, *J* = 4.0 Hz, 1H), 7.89 (dd, *J* = 3.6 Hz, 1.2 Hz, 1H), 7.77 (dd, *J* = 8.8 Hz, 7.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.3 (dd, *J* = 16.4 Hz, 8.1 Hz, 1F), -126.8 (dd, *J* = 16.9 Hz, 9.0 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 153.8 (dd, *J* = 257.2 Hz, 18.8 Hz), 150.5 (dd, *J* = 263.4 Hz, 19.4 Hz), 150.4 (d, *J* = 12.1 Hz), 148.7 (d, *J* = 7.4 Hz), 145.1 (d, *J* = 5.7 Hz), 140.2 (m), 135.5 (d, *J* = 7.9 Hz), 131.6 (d, *J* = 9.2 Hz), 112.8 (d, *J* = 10.6 Hz), 105.8 (d, *J* = 20.0 Hz). MS (EI): *m/z* (%) 282 (M^+, 100), 281, 209. HRMS: Calculated for $C_{11}H_4N_2F_2OS_2$: 281.9733; Found: 281.9738.

General procedure for the preparation of compounds 11 and 12.

To a 25 mL of sealed tube were added $Pd(TFA)_2$ (5 mol %), Ag_2O (93 mg 2.0 equiv), **7** (0.2 mmol, 1 equiv) under N_2, followed by DMSO (1 mL) with stirring. **10** (0.3 mmol, 1.5 equiv) was then added. The reaction mixture was stirred at 80 ^{o}C (preheated oil bath). After stirring for 7 h, the reaction mixture was cooled to room temperature, diluted with dichloromethane, filtered, washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified with silica gel chromatography to provide pure product.

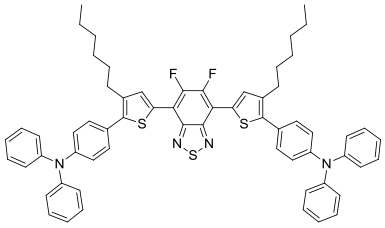


4-(4,8-Bis(octyloxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-7-(5-bromothiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (11). The product (86 mg, 55% yield) as a dark brown solid was purified with silica gel chromatography (Petroleum ether/dichloromethane = 40:1). m.p. 112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.89 (d, *J* = 3.6 Hz, 1H), 7.35 (dd, *J* = 13.0 Hz, 1.4Hz, 2H), 7.09 (d, *J* = 4.0 Hz, 1H), 4.21 (d, *J* = 4.0 Hz, 2H), 4.15 (d, *J* = 4.8 Hz, 2H), 1.90-1.35 (m, 18H), 1.09 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.99 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.3 (d, *J* = 14.8 Hz, 1F), -127.8 (d, *J* = 14.8 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4 (dd, *J* = 260.4 Hz, 19.8 Hz), 149.6 (dd, *J* = 257.8 Hz, 20.2 Hz), 148.5 (d, *J* = 12.0 Hz), 148.1 (d, *J* = 9.5 Hz), 145.2, 143.8, 133.2 (m), 132.6, 131.1 (d, *J* = 10.8 Hz), 130.9 130.8, 130.2 (d, *J* = 6.7 Hz), 130.1, 126.6, 124.6 (d, *J* = 9.2 Hz), 120.3, 117.3 (d, *J* = 8.1 Hz), 110.7 (d, *J* = 11.2 Hz), 111.6 (d, *J* = 11.4 Hz), 111.2 (d, *J* = 10.6 Hz), 75.9, 75.7, 40.73, 40.69, 30.6, 30.5, 29.3, 29.26, 23.9, 23.87, 23.2, 14.2, 11.5, 11.4. MS (MALDI): *m/z* (%) 780.1 (M^+), 779.1 (M^+), 778.1 (M^+), 776.1 (M^+), 553.9 (100). HRMS: Calculated for $C_{36}H_{39}N_2O_2F_2S_4Br$: 776.1040; Found: 776.1039.

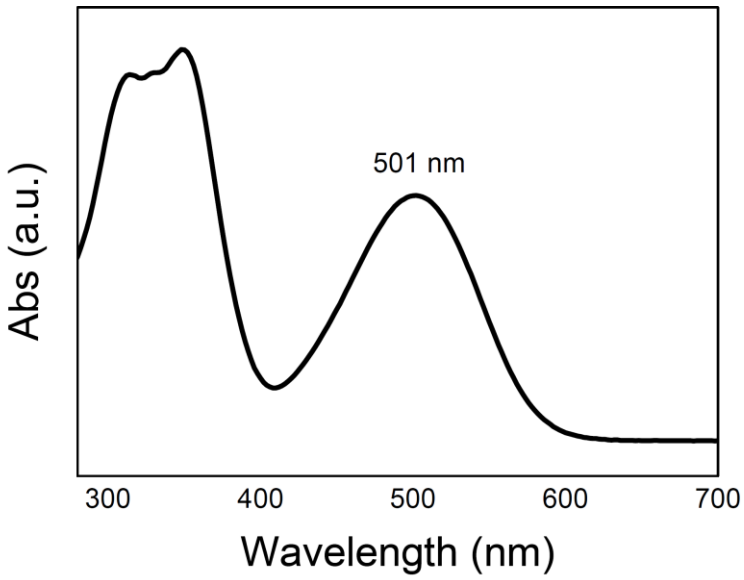


5-(7-(4,8-Bis(octyloxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde (12). The product (89 mg, 61% yield) as a dark brown solid was purified with silica gel chromatography (Petroleum ether/Dichloromethane=20:1). m.p. 164 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.68 (s, 1H), 8.25 (d, *J* = 4.2 Hz, 1H), 7.78 (d, *J* = 3.6 Hz, 1H), 7.36 (d, *J* = 4.2 Hz, 2H), 4.20 (d, *J* = 14.1 Hz, 4H), 1.90-1.30 (m, 18H), 1.09 (t, *J* = 7.5 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.98 (m, 6H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -124.4 (d, *J* = 14.7 Hz, 1F), -126.3 (d, *J* = 14.7 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0, 150.9 (dd, *J* = 261.7 Hz, 19.6 Hz), 150.0 (dd, *J* = 260.5 Hz, 19.1 Hz), 148.4 (d, *J* = 9.1 Hz), 148.2 (d, *J* = 8.4 Hz), 145.4, 144.6 (d, *J* = 5.9 Hz), 143.8, 140.3, 135.2, 132.8, 131.2 (d, *J* = 9.4 Hz), 130.7, 130.5, 130.3, 129.8, 126.9, 125.3 (d,

J = 9.4 Hz), 120.3, 113.2 (d, *J* = 10.9 Hz), 110.7 (d, *J* = 11.2 Hz), 75.9, 75.8, 40.7, 40.68, 30.6, 30.5, 29.3, 29.26, 23.9, 23.87, 23.2, 14.2, 11.5, 11.4. MS (MALDI): *m/z* (%) 728.2 (M^++H), 727.2 (M^++H). HRMS: Calculated for $C_{37}H_{40}N_2O_3F_2N_2S_4$: 726.1890; Found: 727.1946.



4,4'-(5,5'-(5,6-difluorobenzo[c][1,2,5]thiadiazole-4,7-diyl)bis(3-hexylthiophene-5,2-diyl))bis(N,N-diphenylaniline) (14). To a 25 mL of sealed tube were added **6a** (0.1 mmol, 1.0 equiv), (4-(diphenylamino)phenyl)boronic acid (73 mg, 2.5 equiv), $Pd(PPh_3)_4$ (2 mol %), K_2CO_3 (55 mg 4.0 equiv) under N_2, followed by DMF (2 mL), H_2O (400 uL) with stirring. The reaction mixture was stirred at 110 ^oC (oil bath). After stirring for 10 h, the reaction mixture was cooled to room temperature, diluted with dichloromethane, filtered, washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified with silica gel chromatography (Petroleum ether (100%)) to provide pure product (95 mg, 96%) as a red solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 2H), 7.40 (d, *J* = 8.8 Hz, 4H), 7.30 (t, *J* = 7.6 Hz, 8H), 7.20-7.10 (m, 12H), 7.06 (t, *J* = 7.2 Hz, 4H), 2.77 (t, *J* = 7.8 Hz, 4H), 1.71 (m, 4H), 1.45-1.25(m, 12H), 0.90(t, *J* = 5.8 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.6 (s, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7 (dd, *J* = 258.5 Hz, 20.2 Hz), 148.8 (t, *J* = 4.1 Hz), 147.4, 147.38, 141.7, 138.7, 133.5, 129.9, 129.3, 129.1, 127.7, 124.7, 123.2, 122.9, 111.2 (m), 31.6, 31.0, 29.2, 28.8, 22.6, 14.1. MS (MALDI): *m/z* (%) 993.4 (M^+), 992.4 (M^+), 991.4 (M^+), 990.4 (M^+, 100). HRMS: Calculated for $C_{62}H_{56}N_4F_2S_3$: 990.36297; Found: 990.3618.



Figue S1: UV-vis absorption spectra of **14** in chloroform.

References:

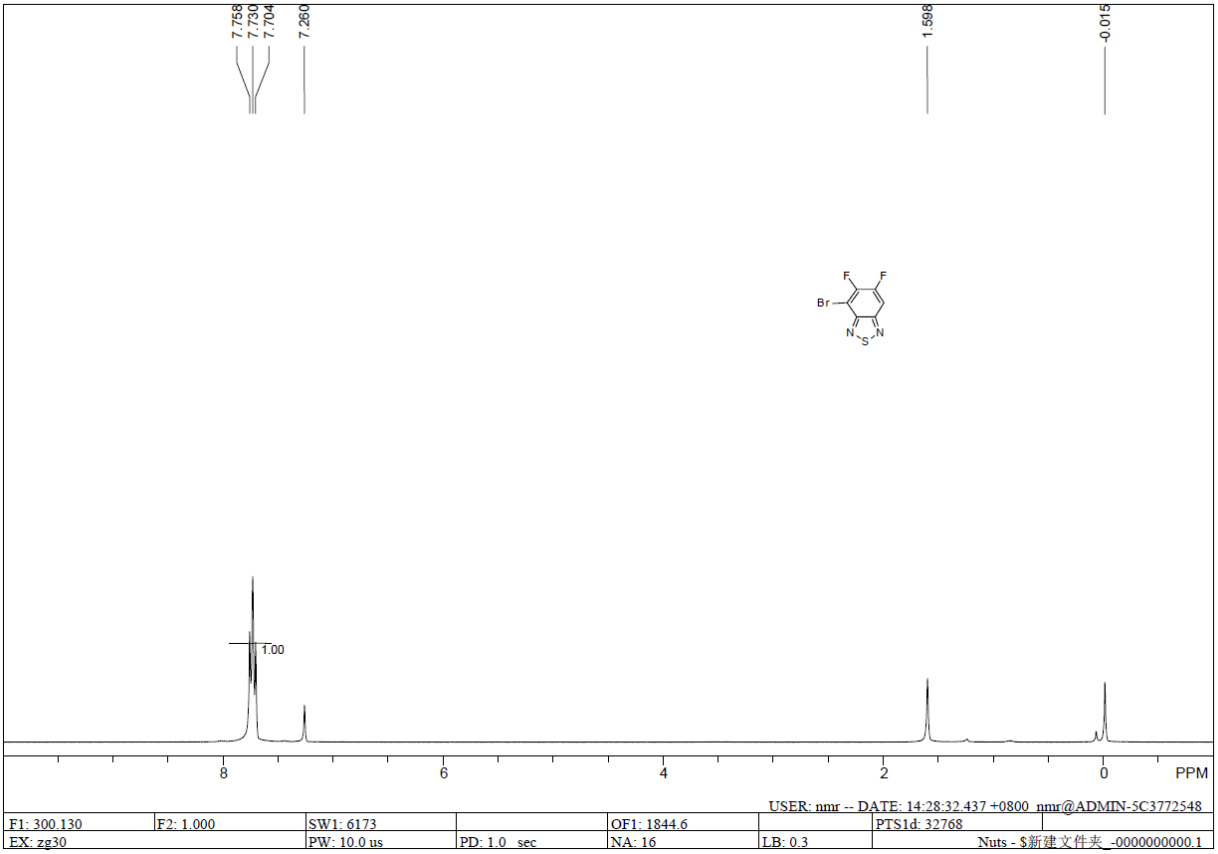
(1) a) Krikura, T.; Ishizaki, T.; Hirai, K.; Murayama, S.; Suzue, S. US Patent US4791225 A1, 1988.

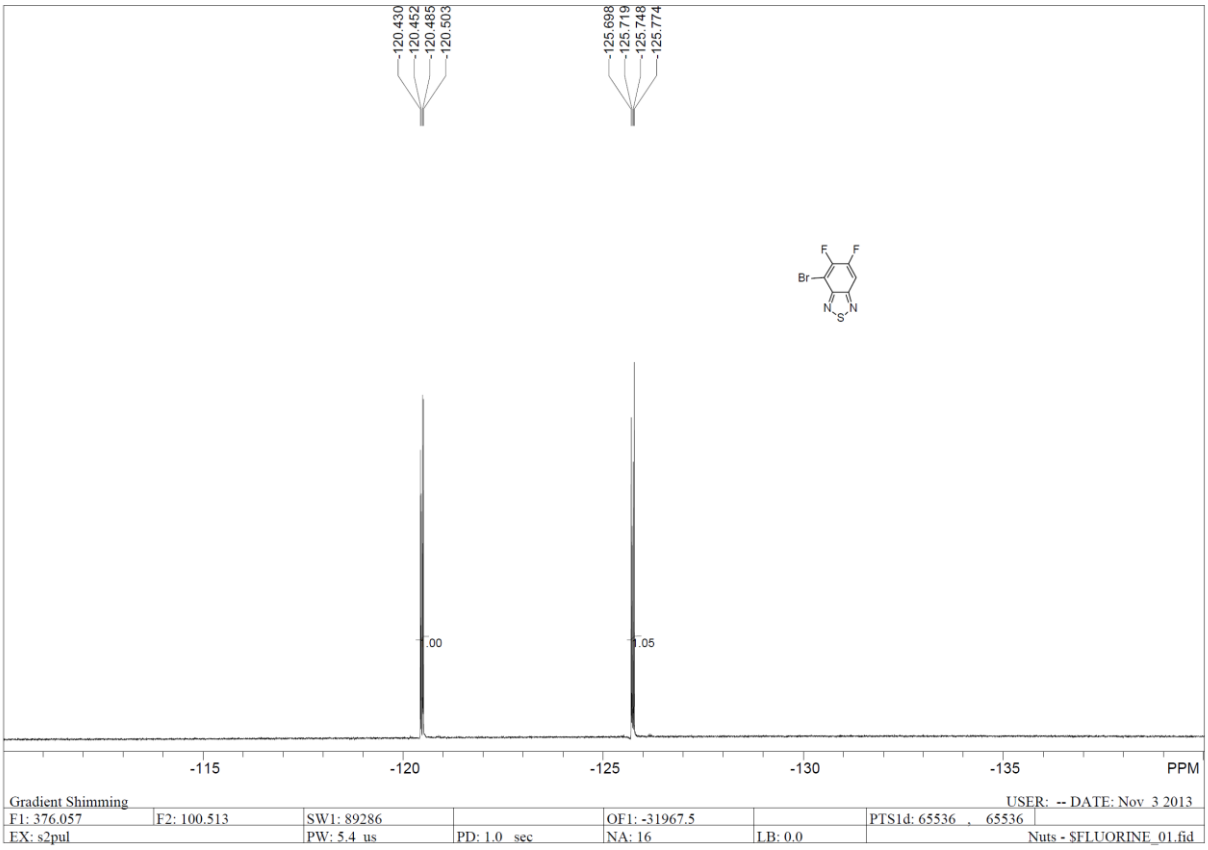
(2) Weber, E.; Keana, J. F. W. US5514680 A1, 1996.

(3) Wang, N.; Chen, Z.; Wei, W.; Jiang, Z. *J. Am. Chem. Soc.* **2013**, DOI: 10.1021/ja409881g.

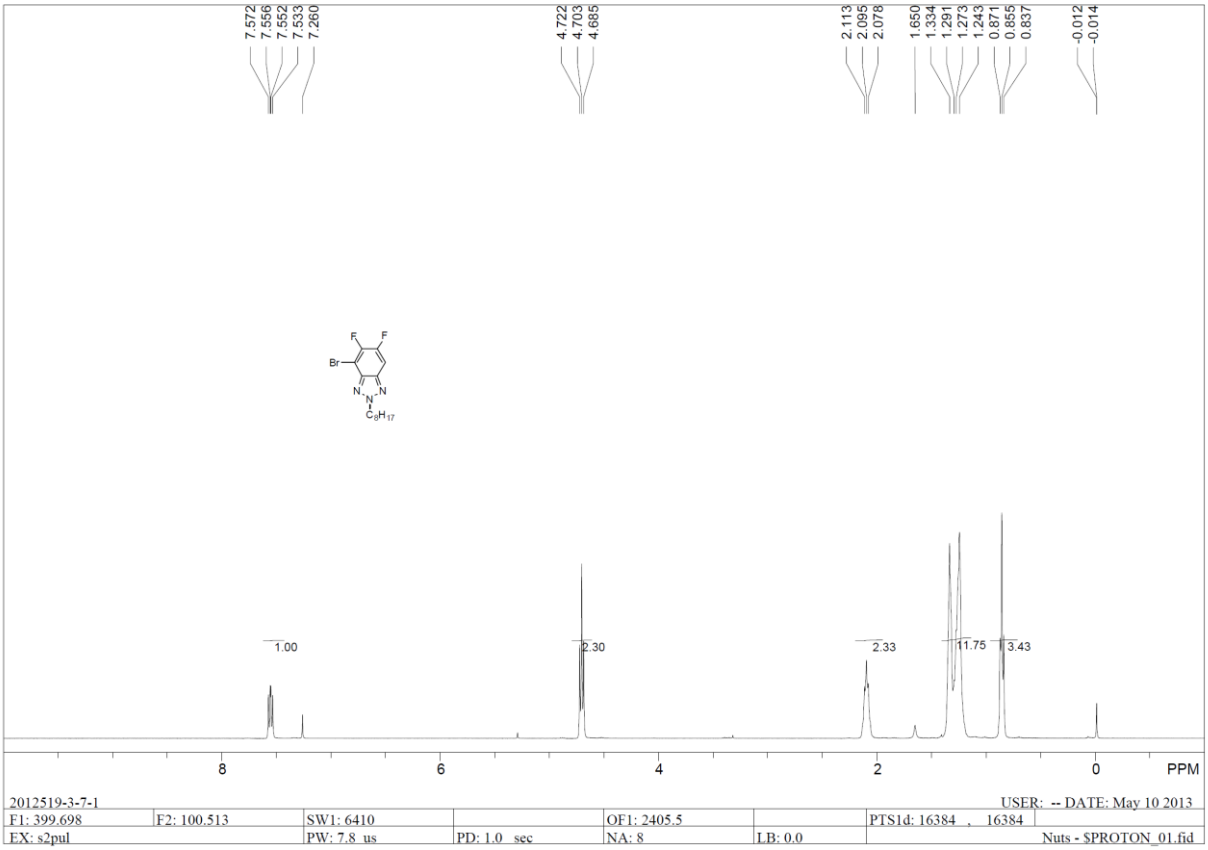
(4) Zhou, H; Stuart, A.C.; Price, S.C.; You, W; Yang, L; Liu, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 2995 – 2998.

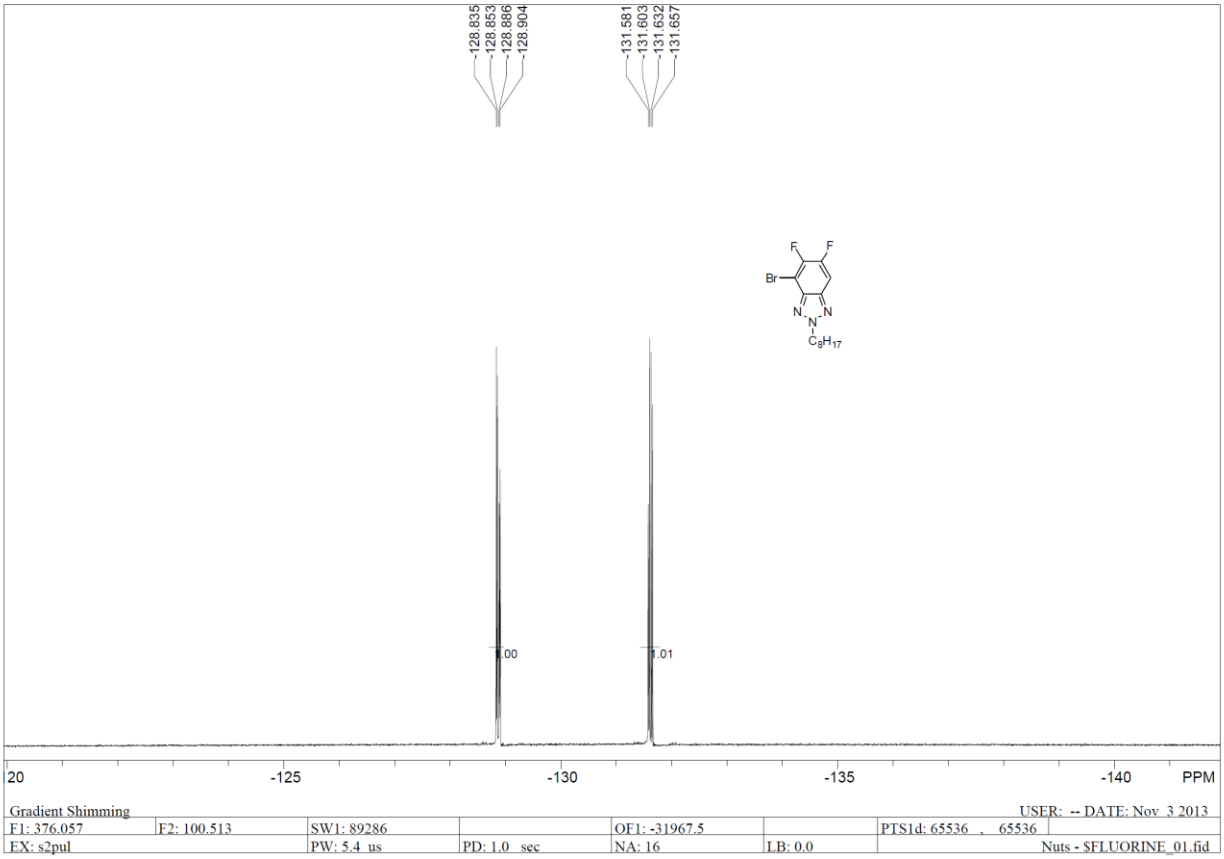
4-Bromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (1).



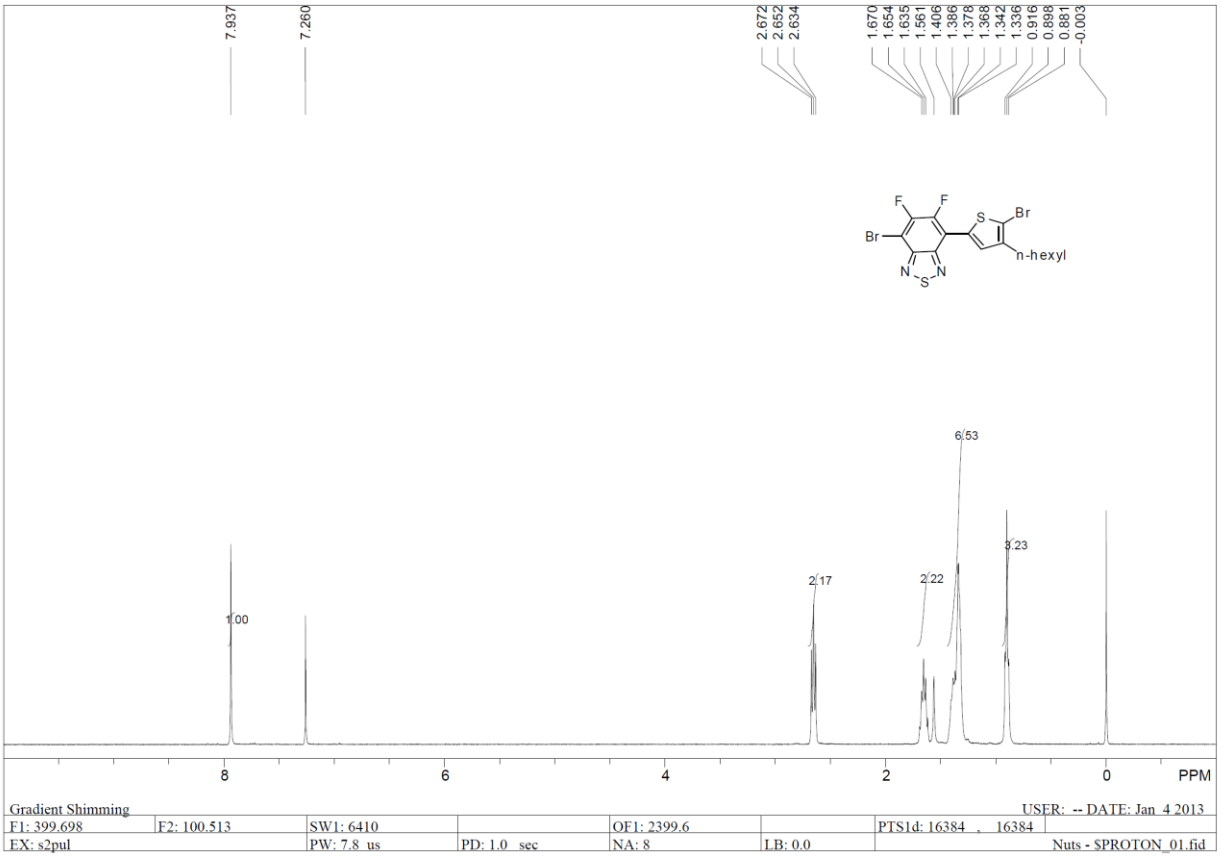


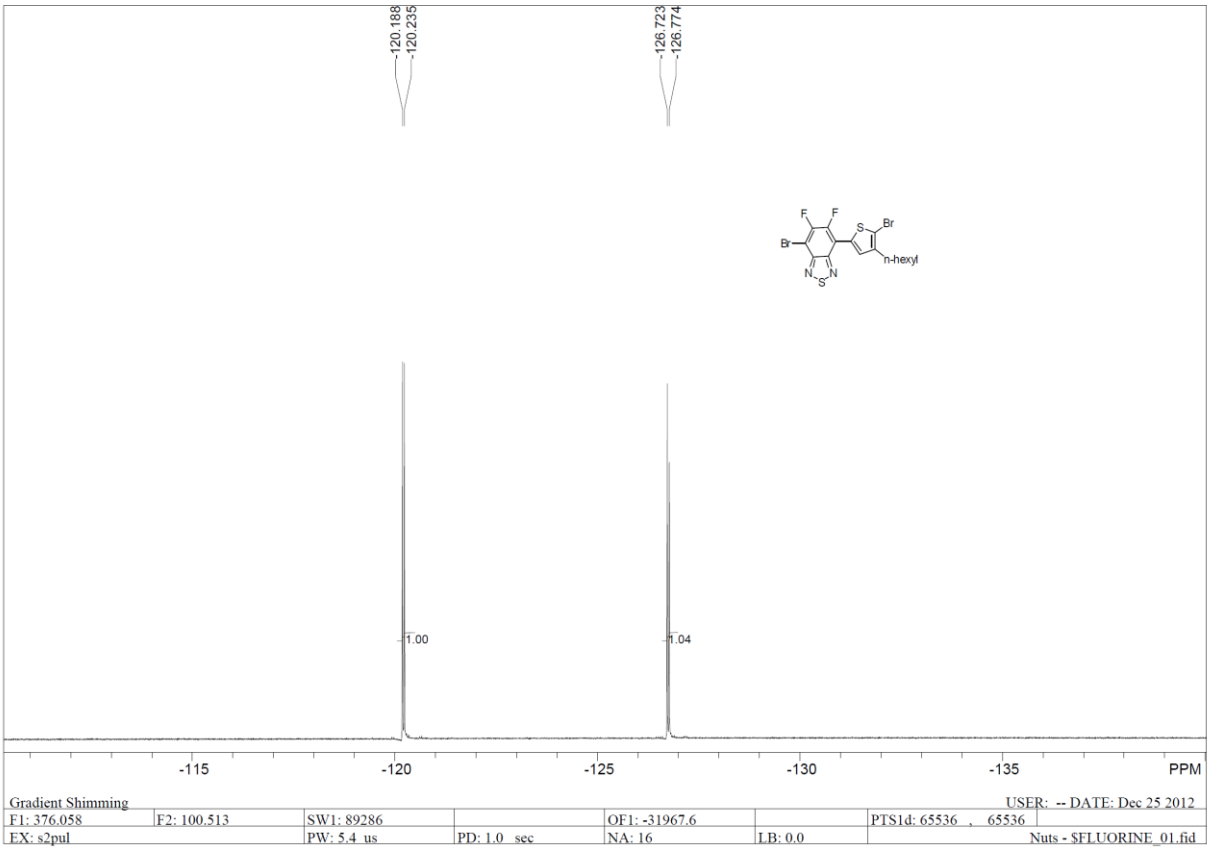
4-Bromo-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazole(4).

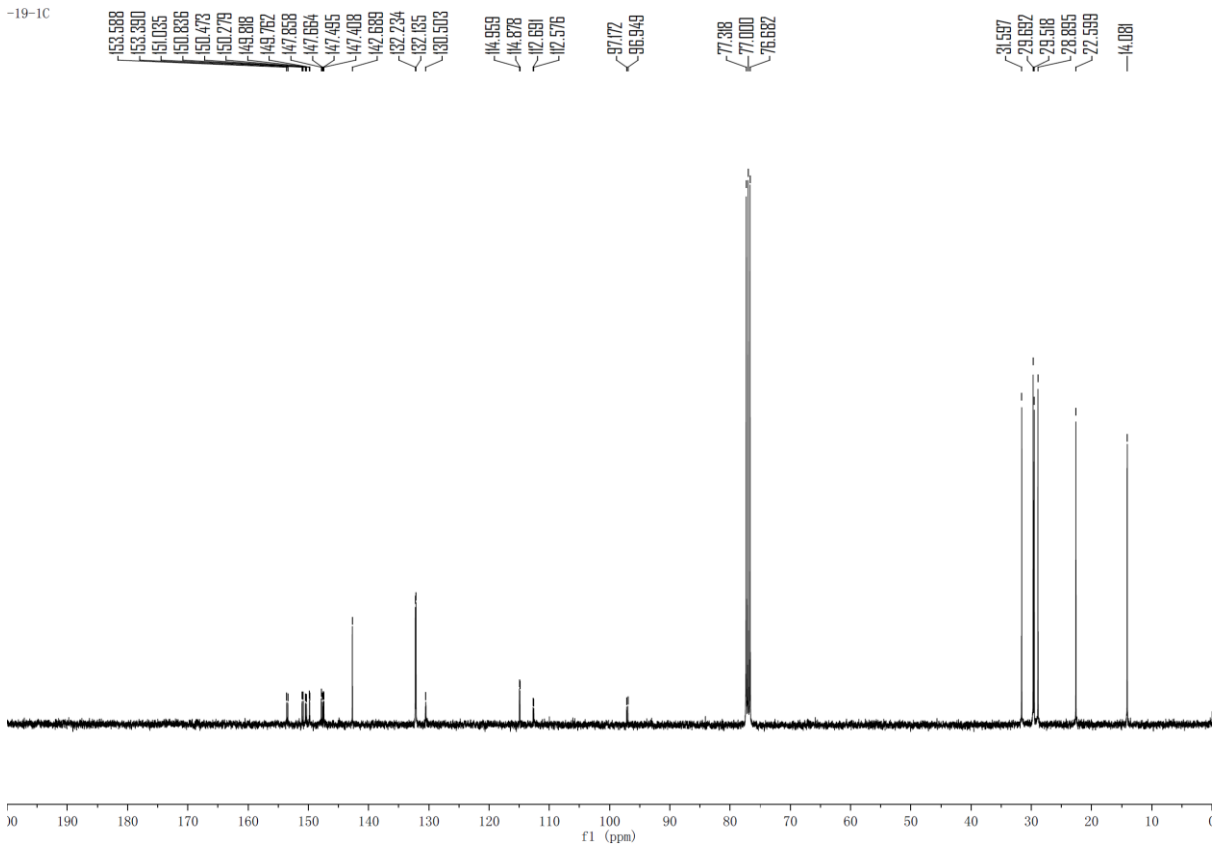




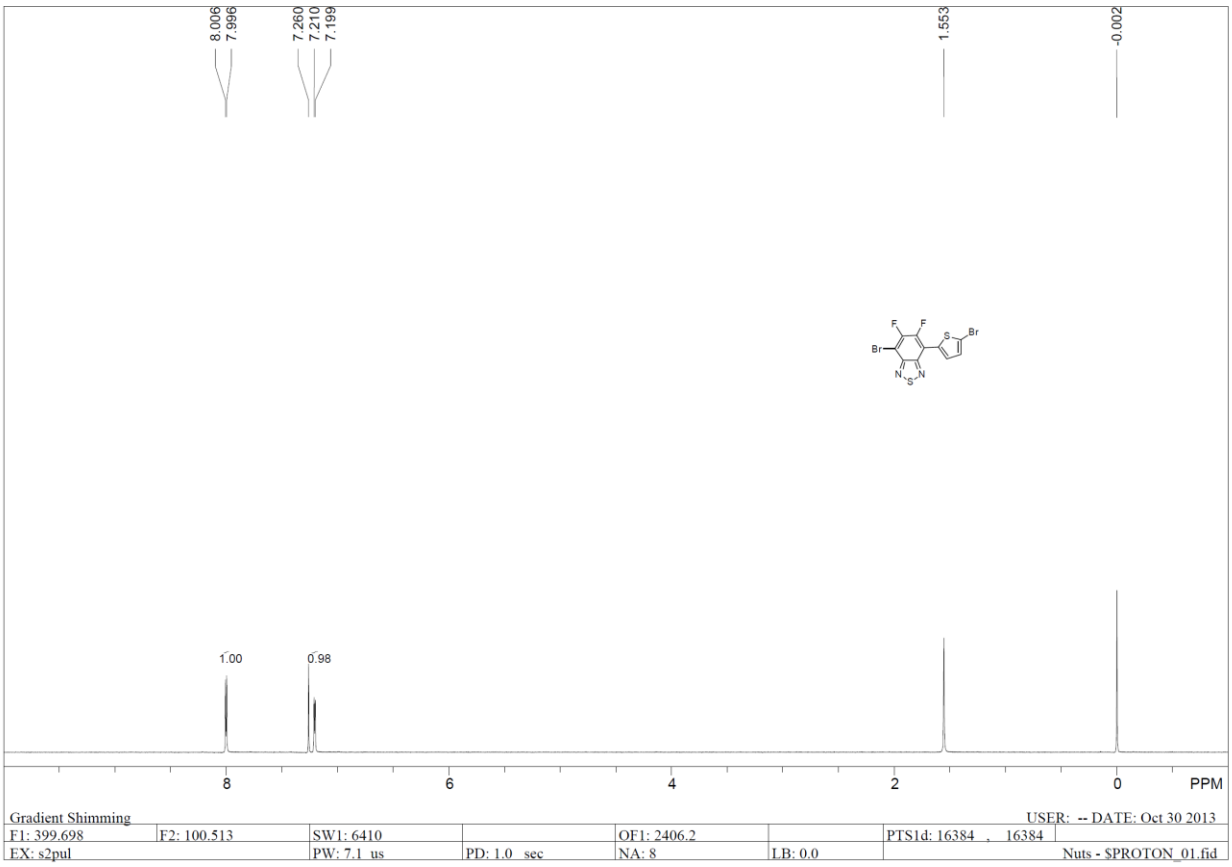
4-Bromo-7-(5-bromo-4-hexylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (3a).

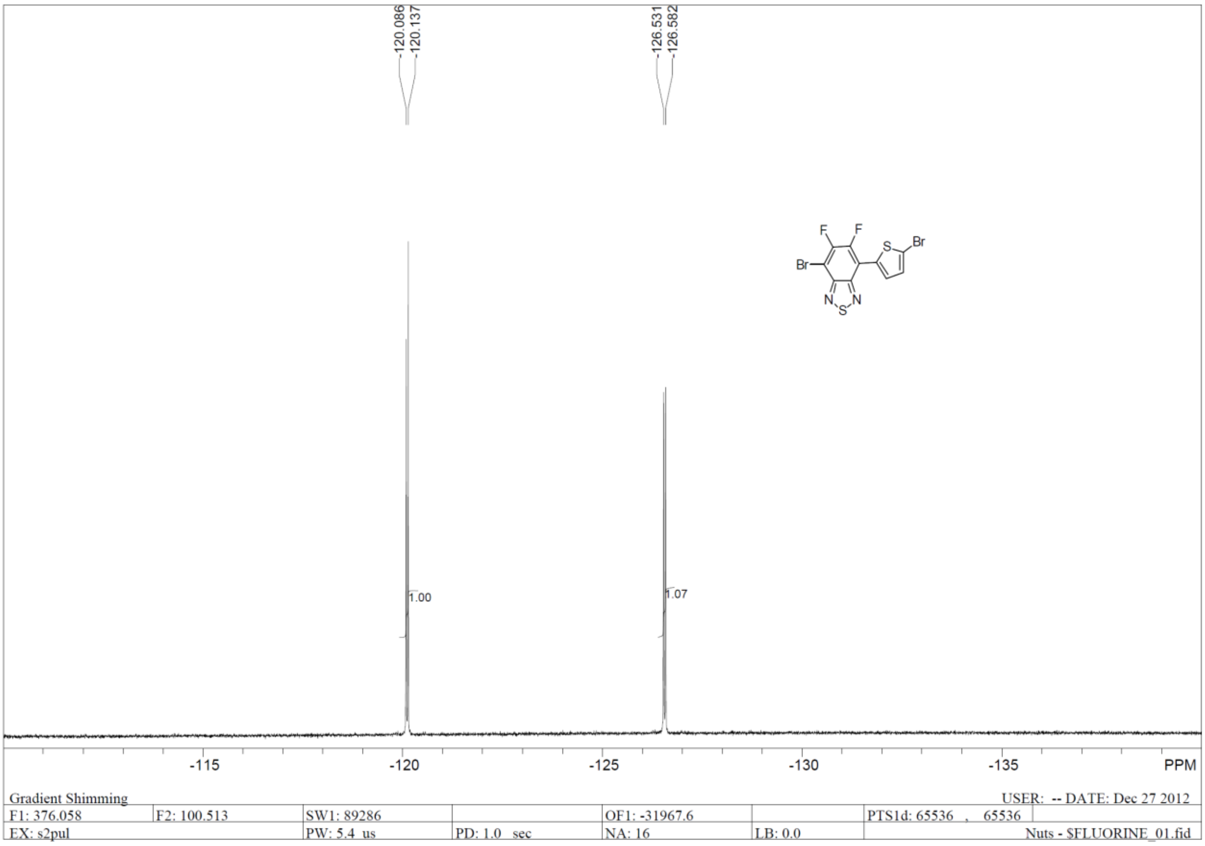






4-Bromo-7-(5-bromothiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (3b).

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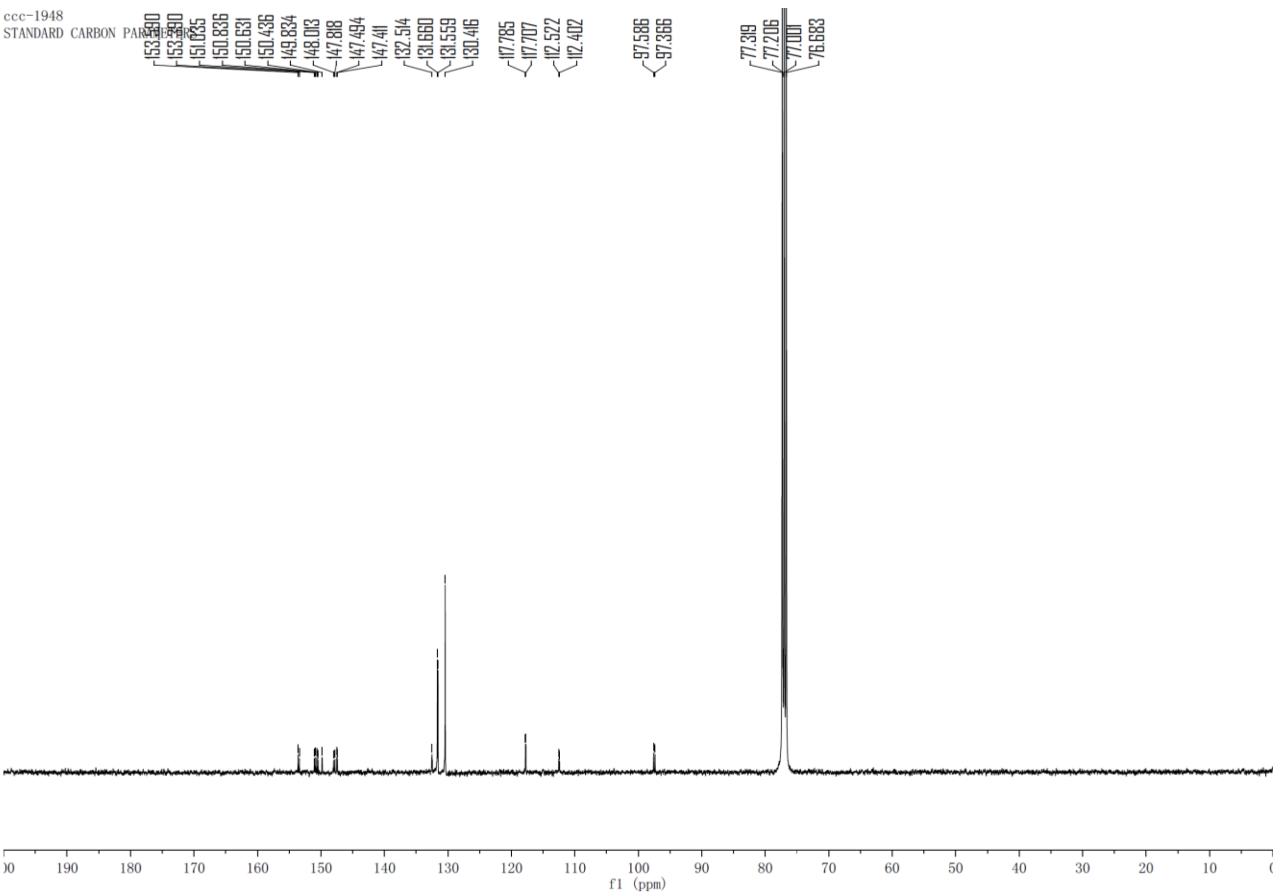
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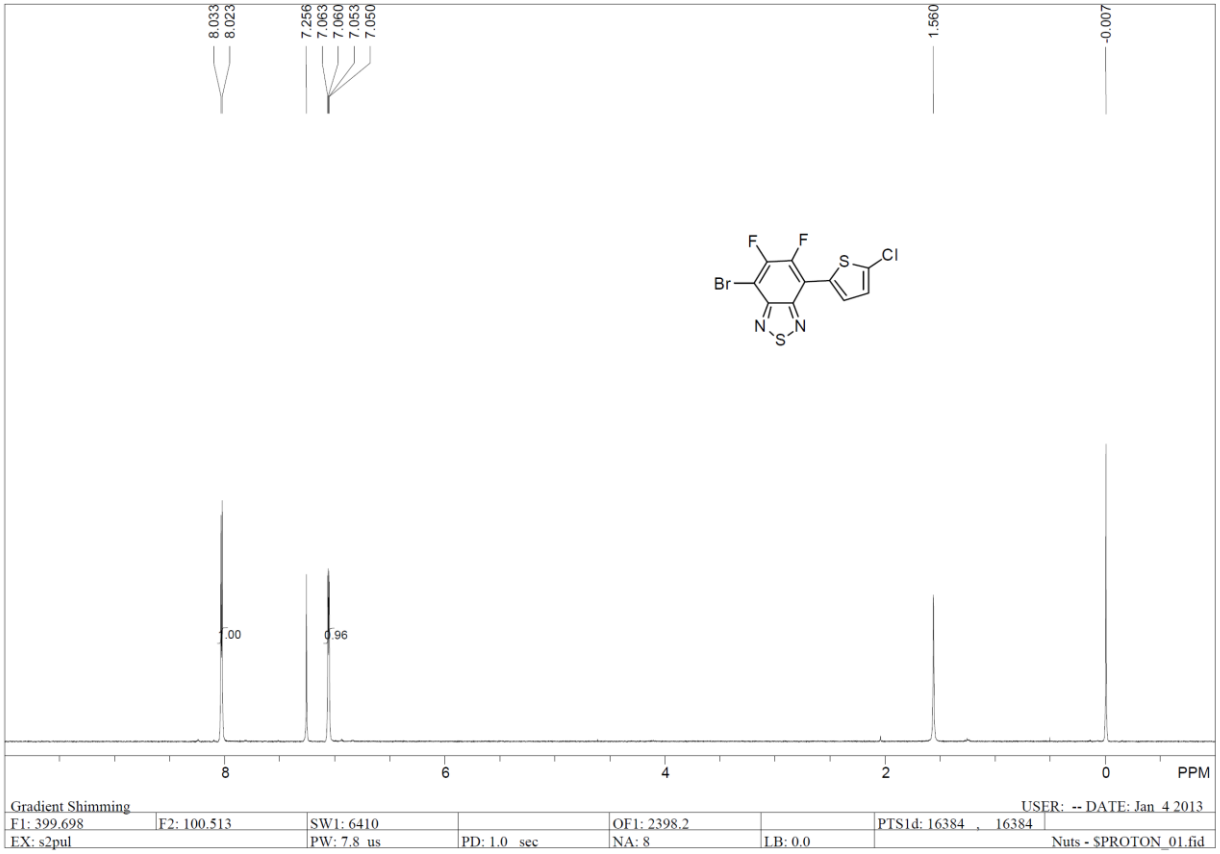
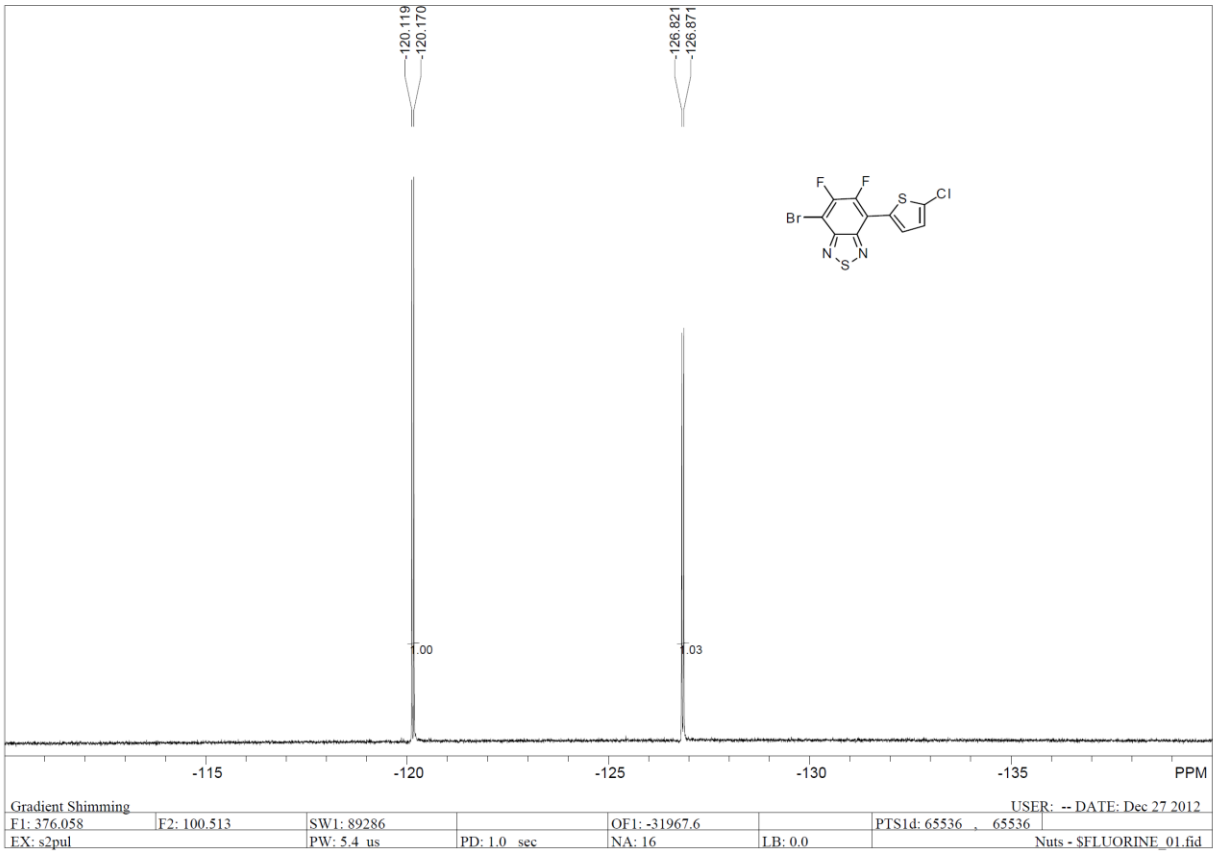
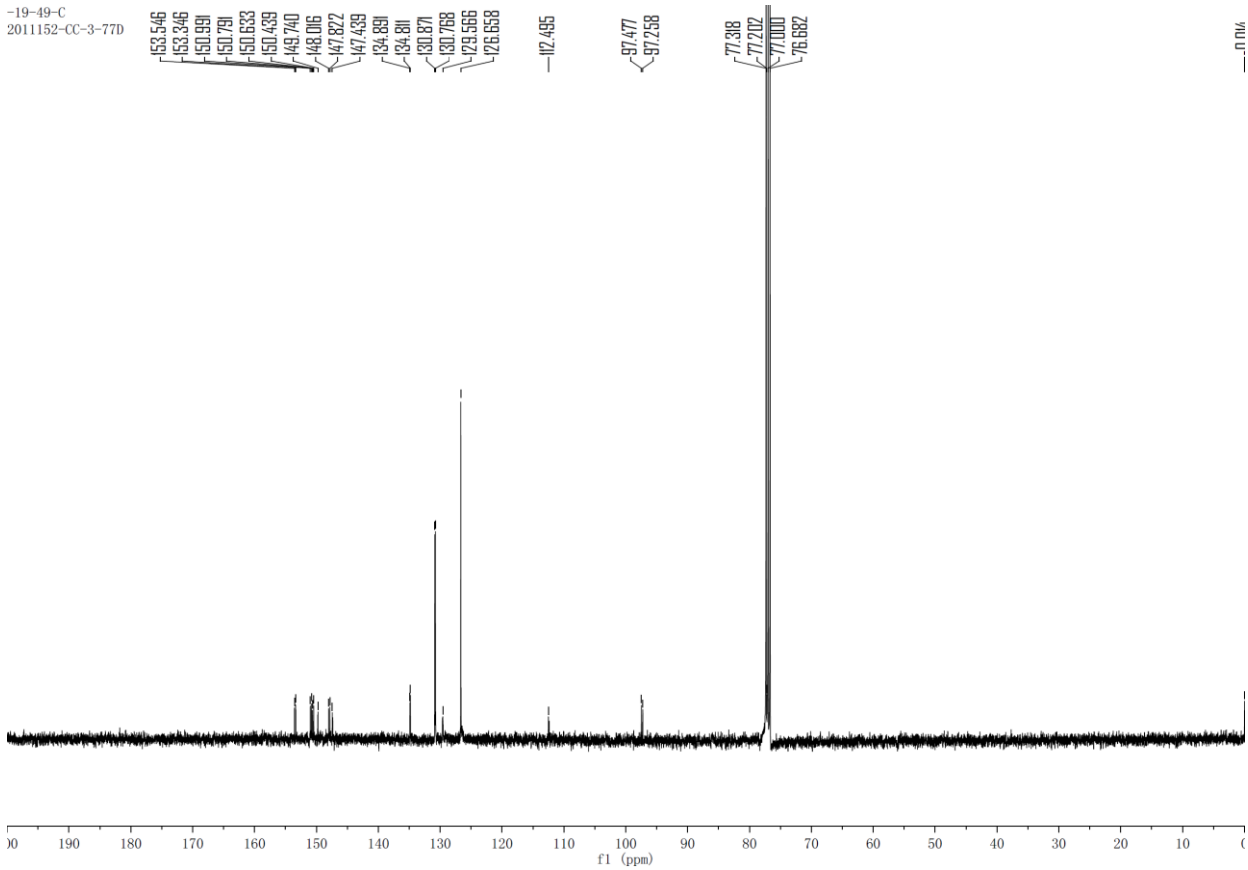
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

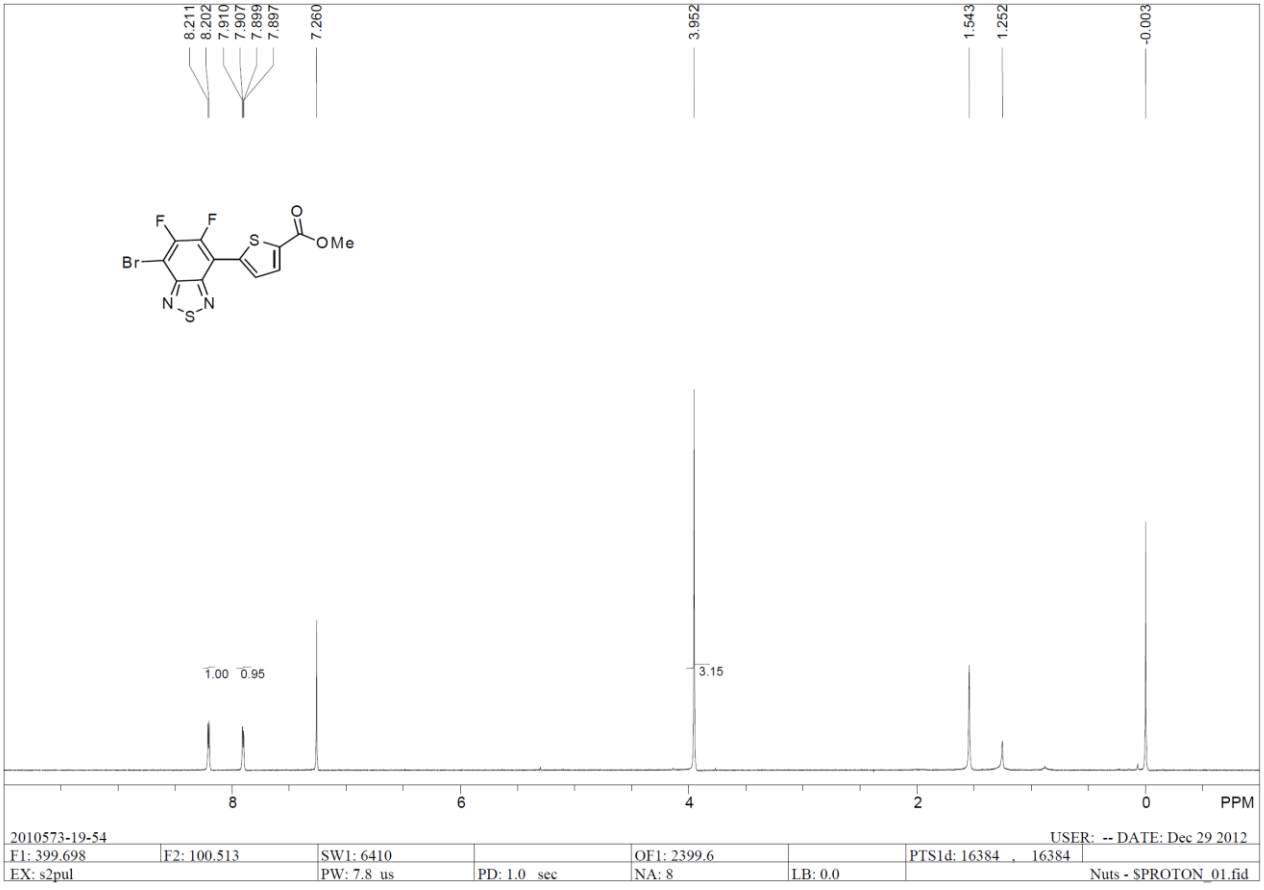
4-Bromo-7-(5-chlorothiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (3c).

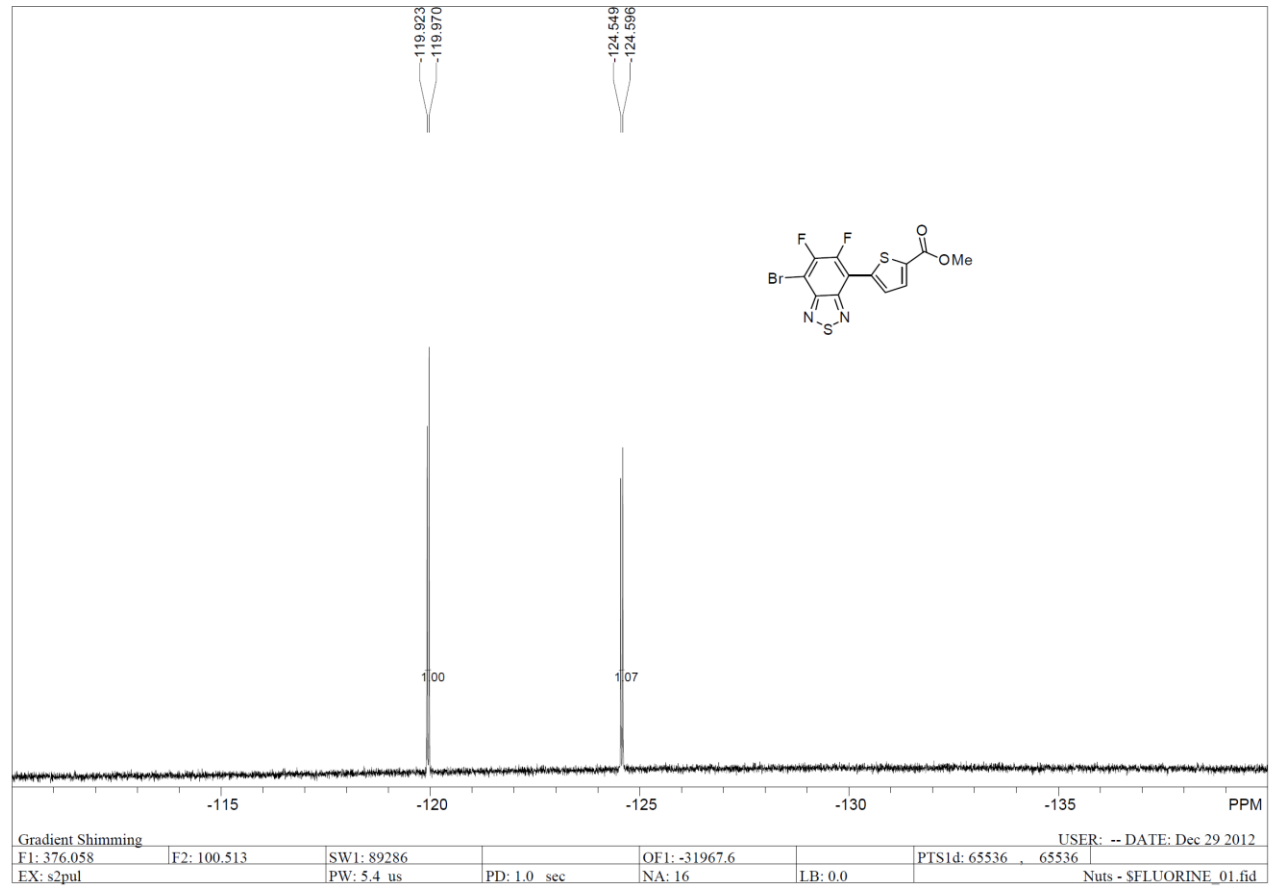


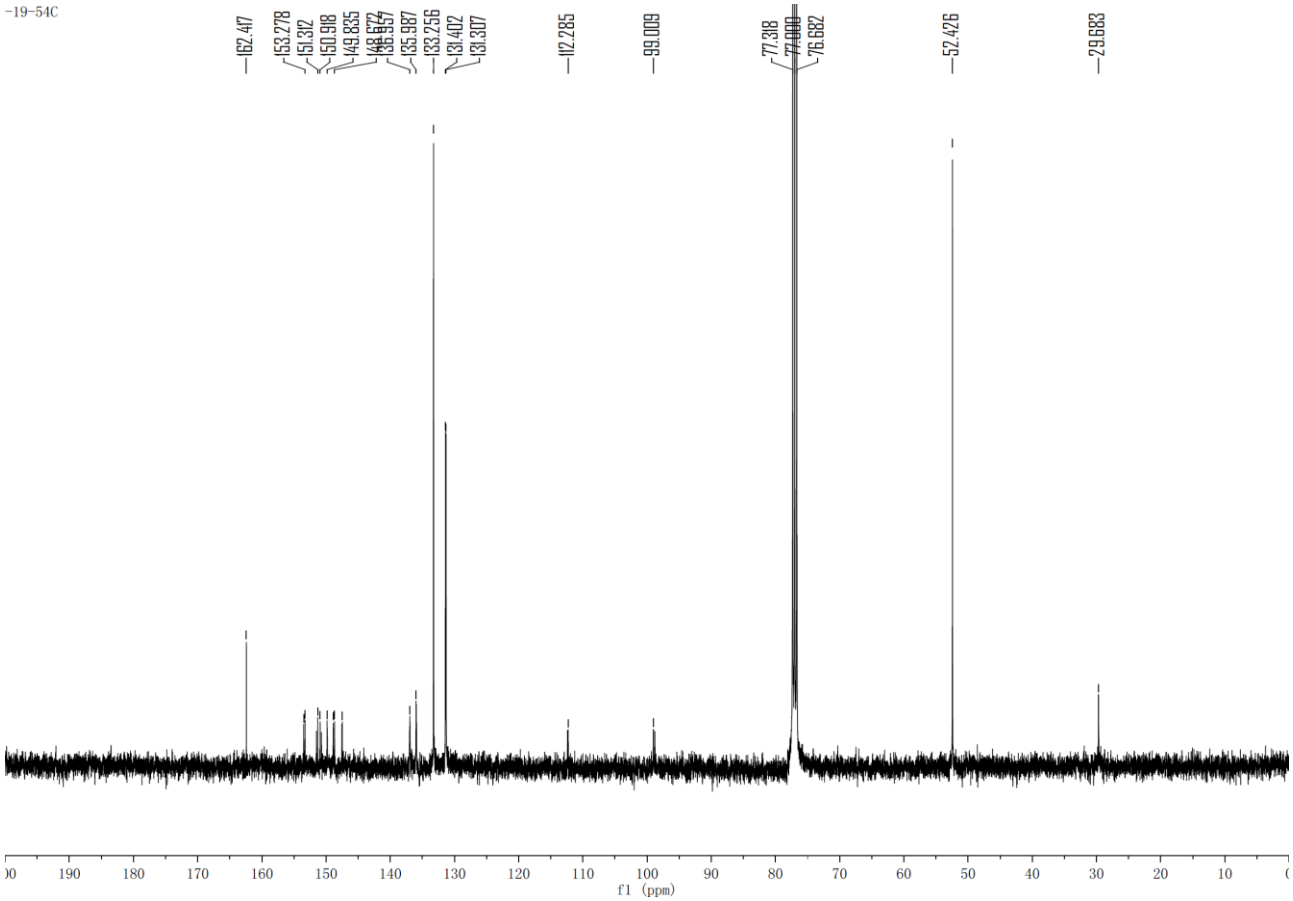




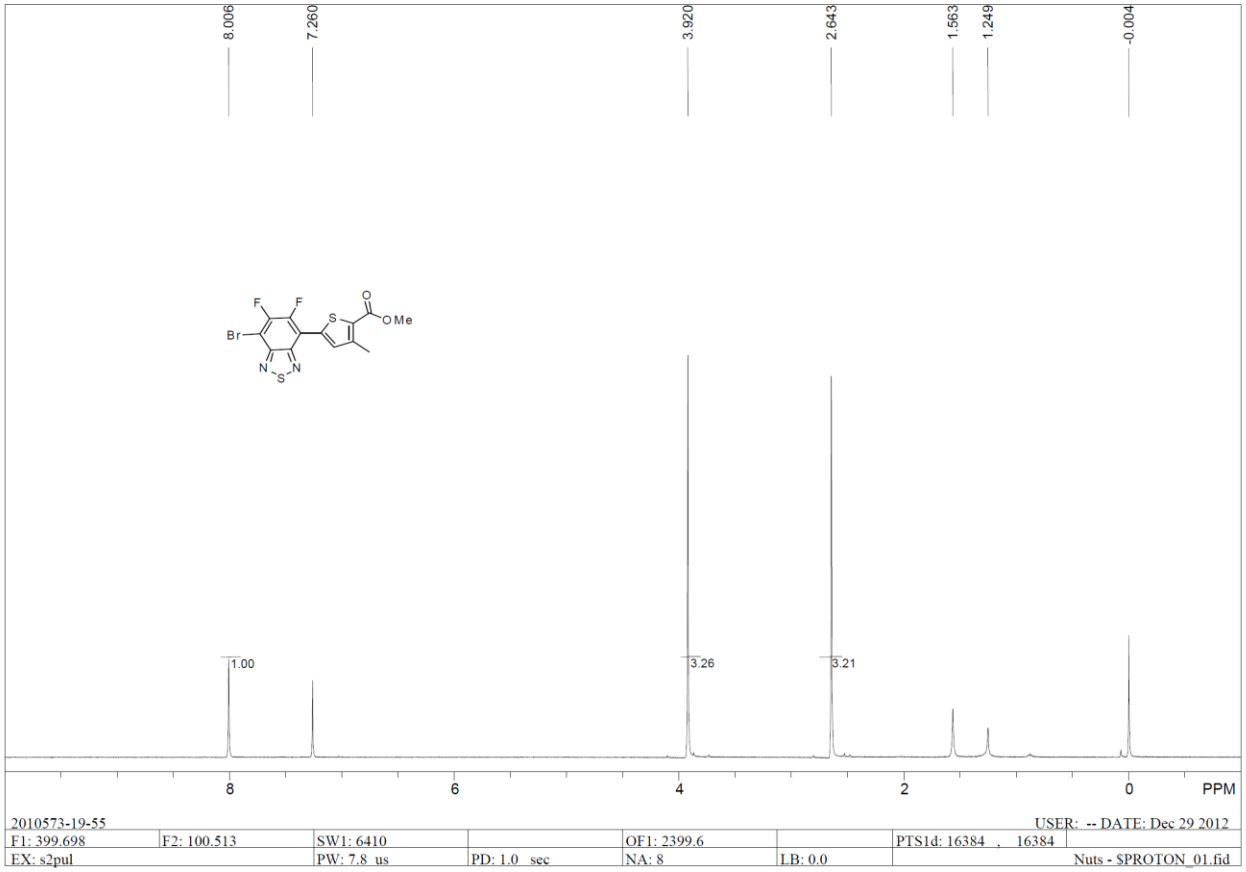
Methyl 5-(7-bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophene-2-carboxylate (3d).

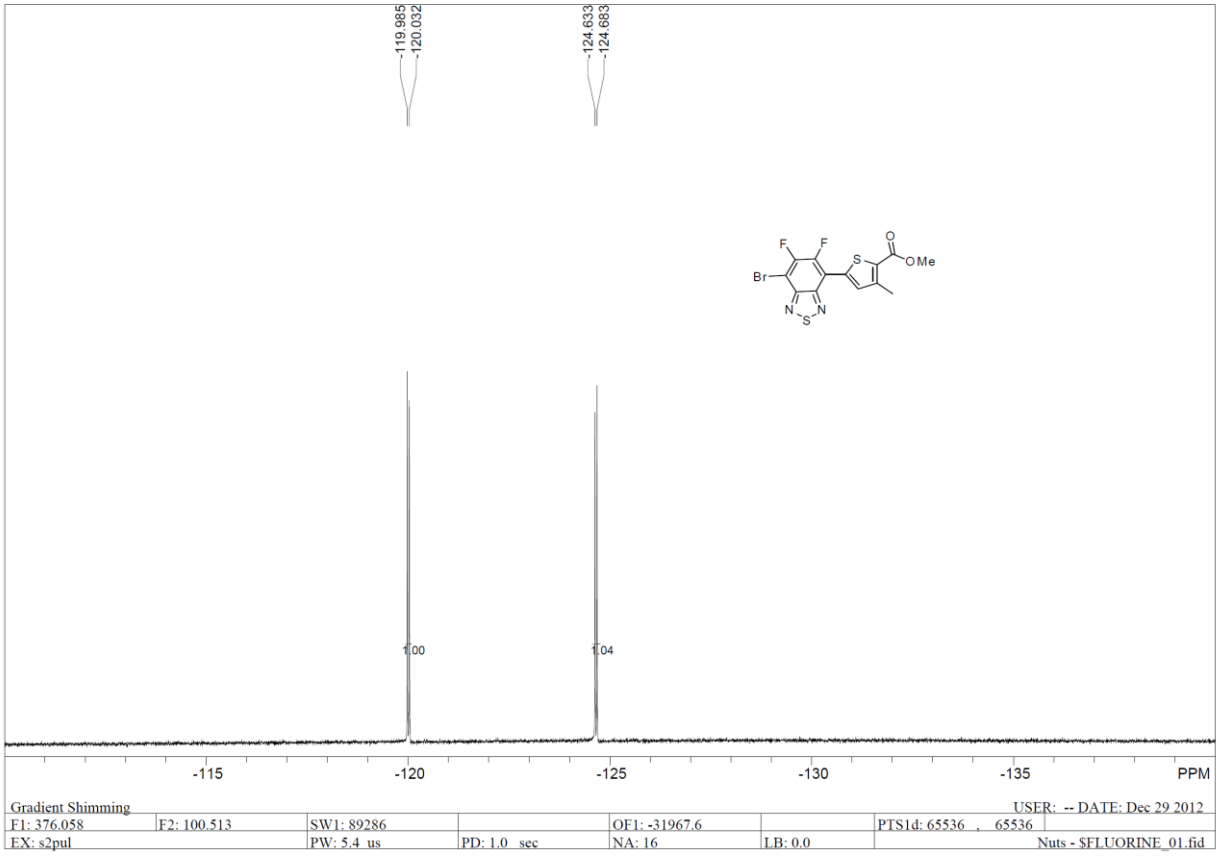


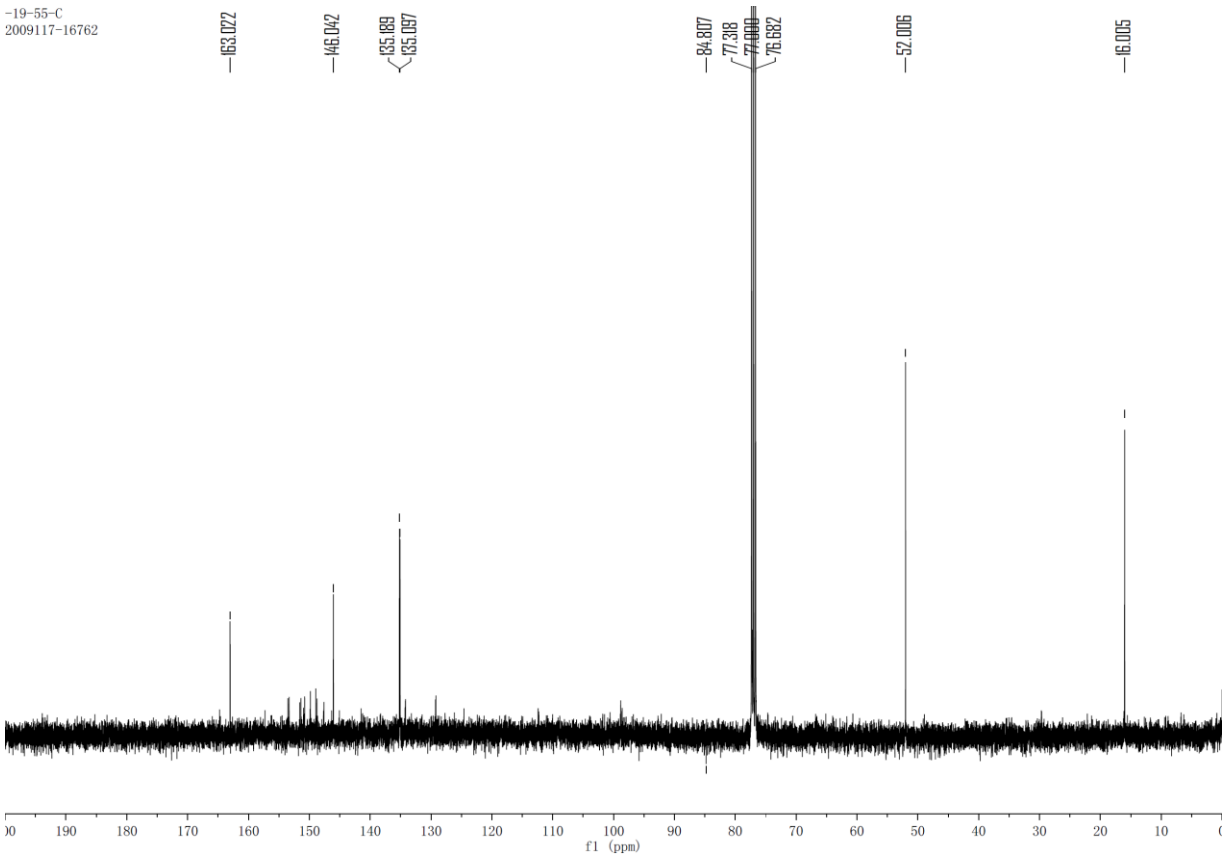

-119.923
-119.970
-124.549
-124.596
F
F
Br
S
O
OMe
N
S
N
1.00
1.07
-115
-120
-125
-130
-135
PPM
Gradient Shimming
USER: -- DATE: Dec 29 2012
F1: 376.058
F2: 100.513
SW1: 89286
OF1: -31967.6
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.4 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $FLUORINE_01.fid


-19-54C
162.417
153.278
151.312
150.918
149.835
148.677
136.557
135.987
133.256
131.402
131.307
112.285
99.009
77.318
77.000
76.682
52.426
29.683
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

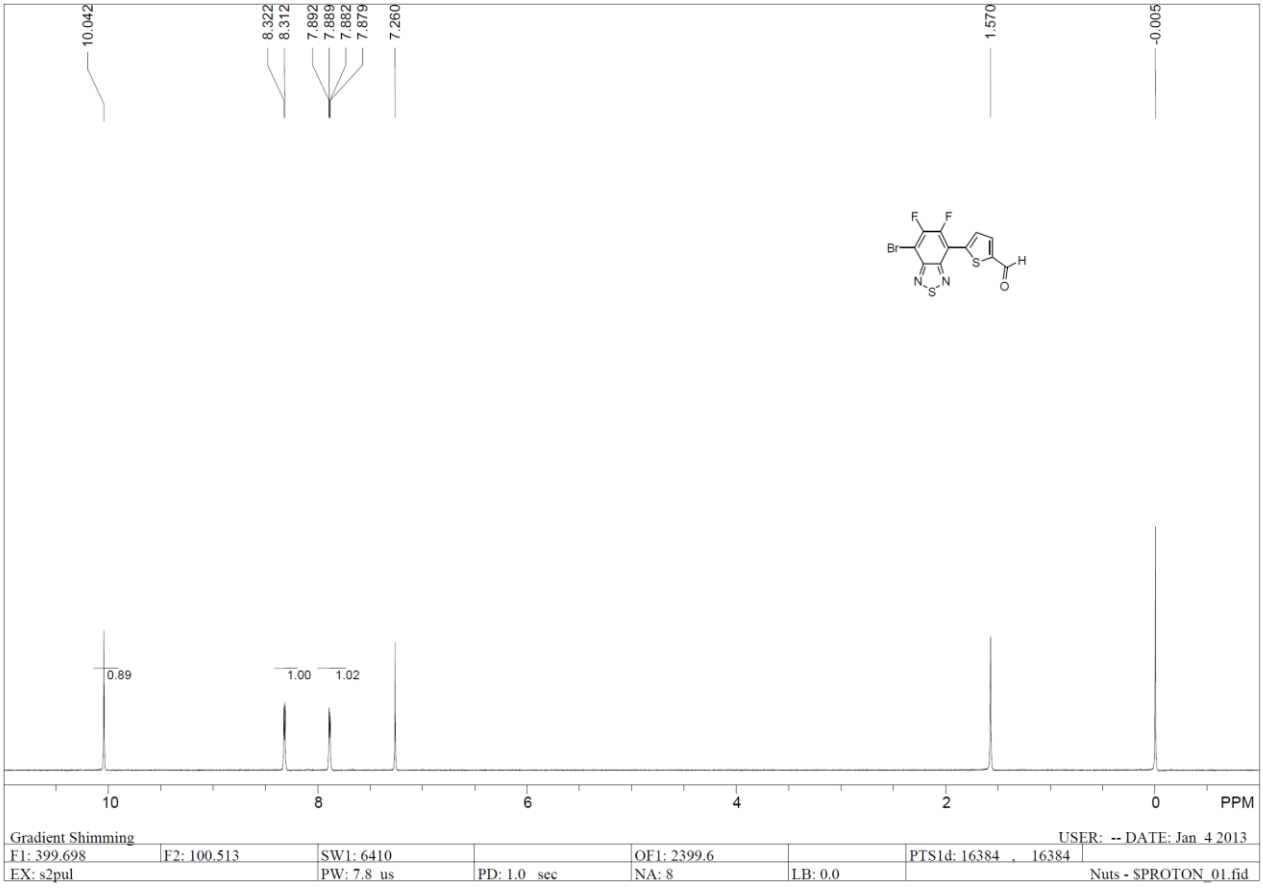
Methyl 5-(7-bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)-3-methylthiophene-2-carboxylate (3e).

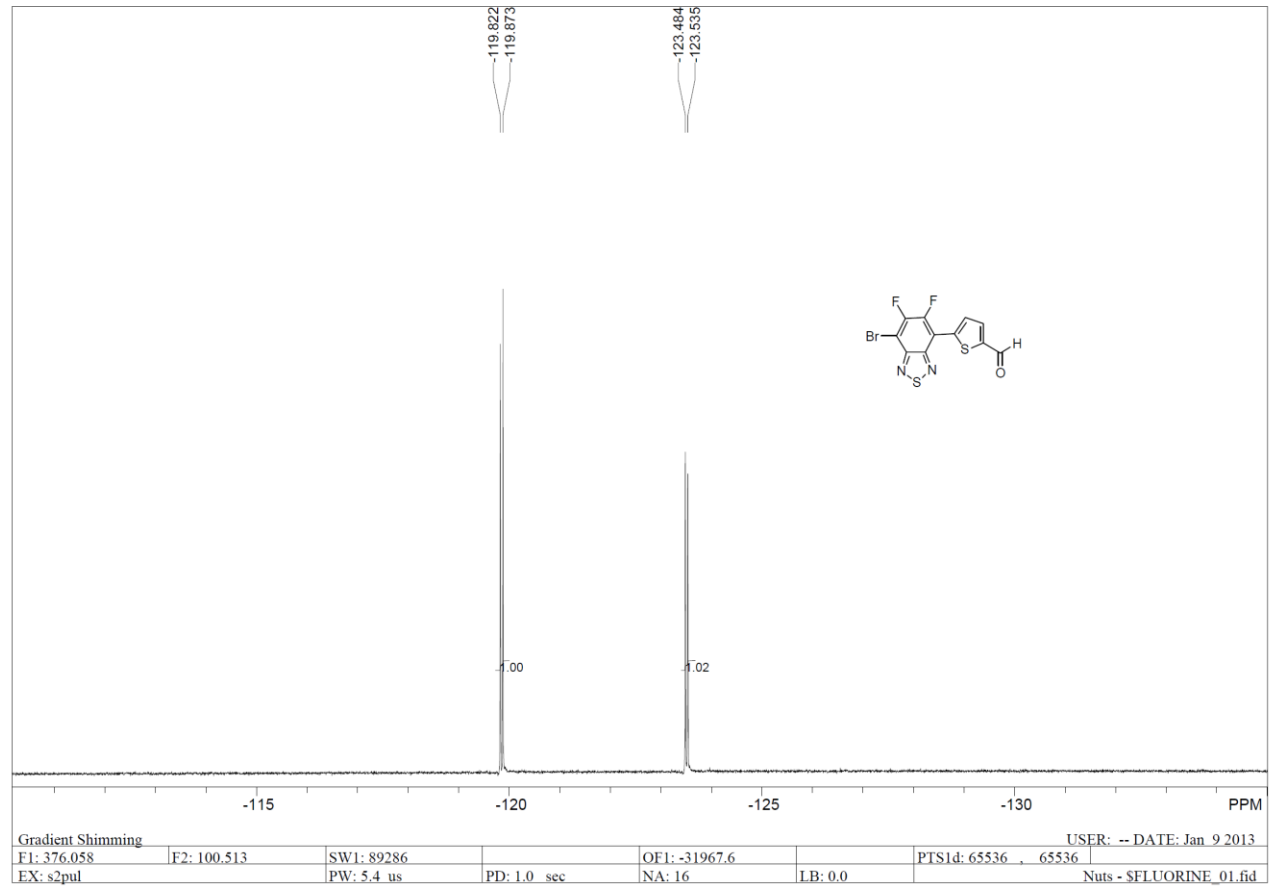


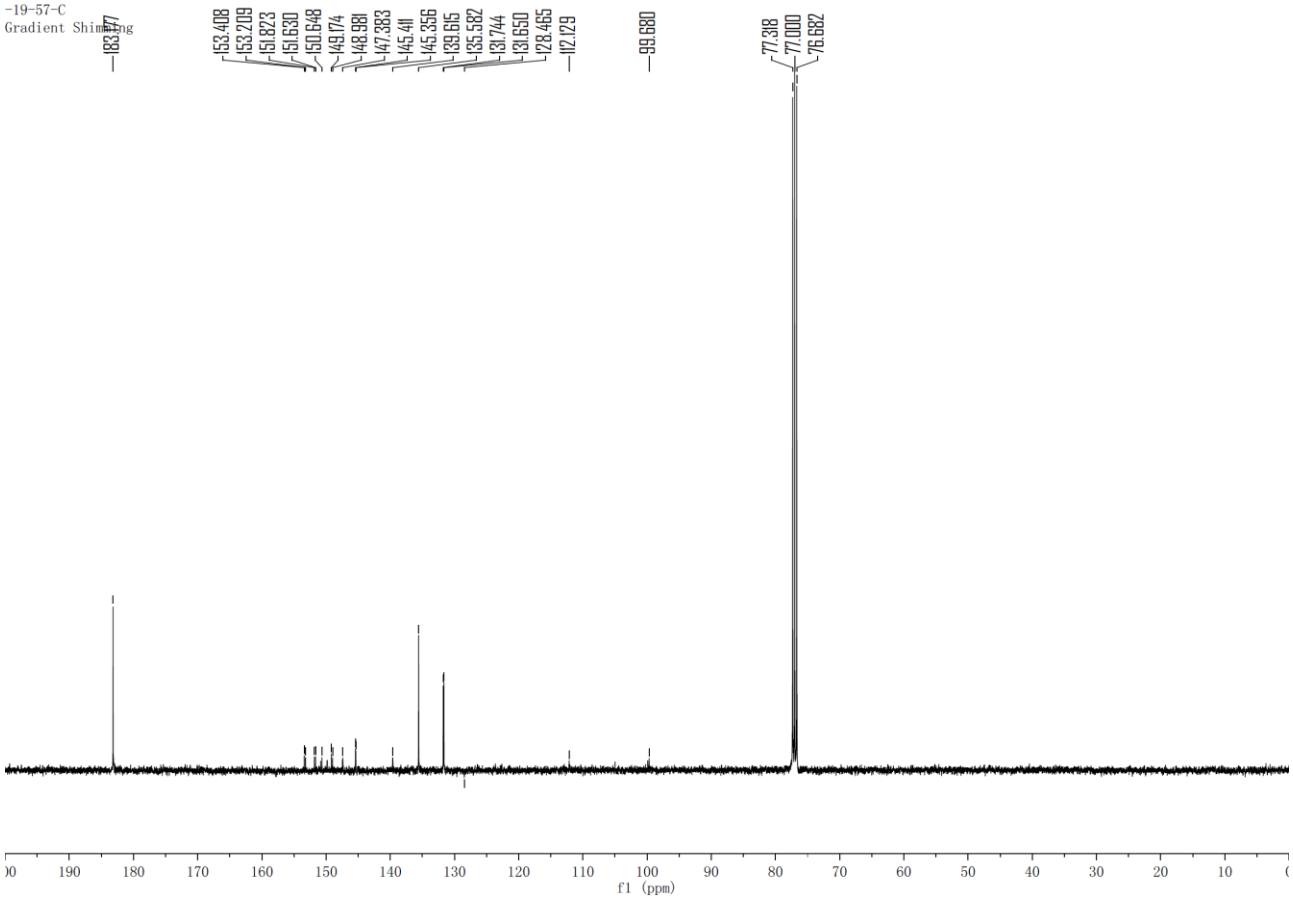




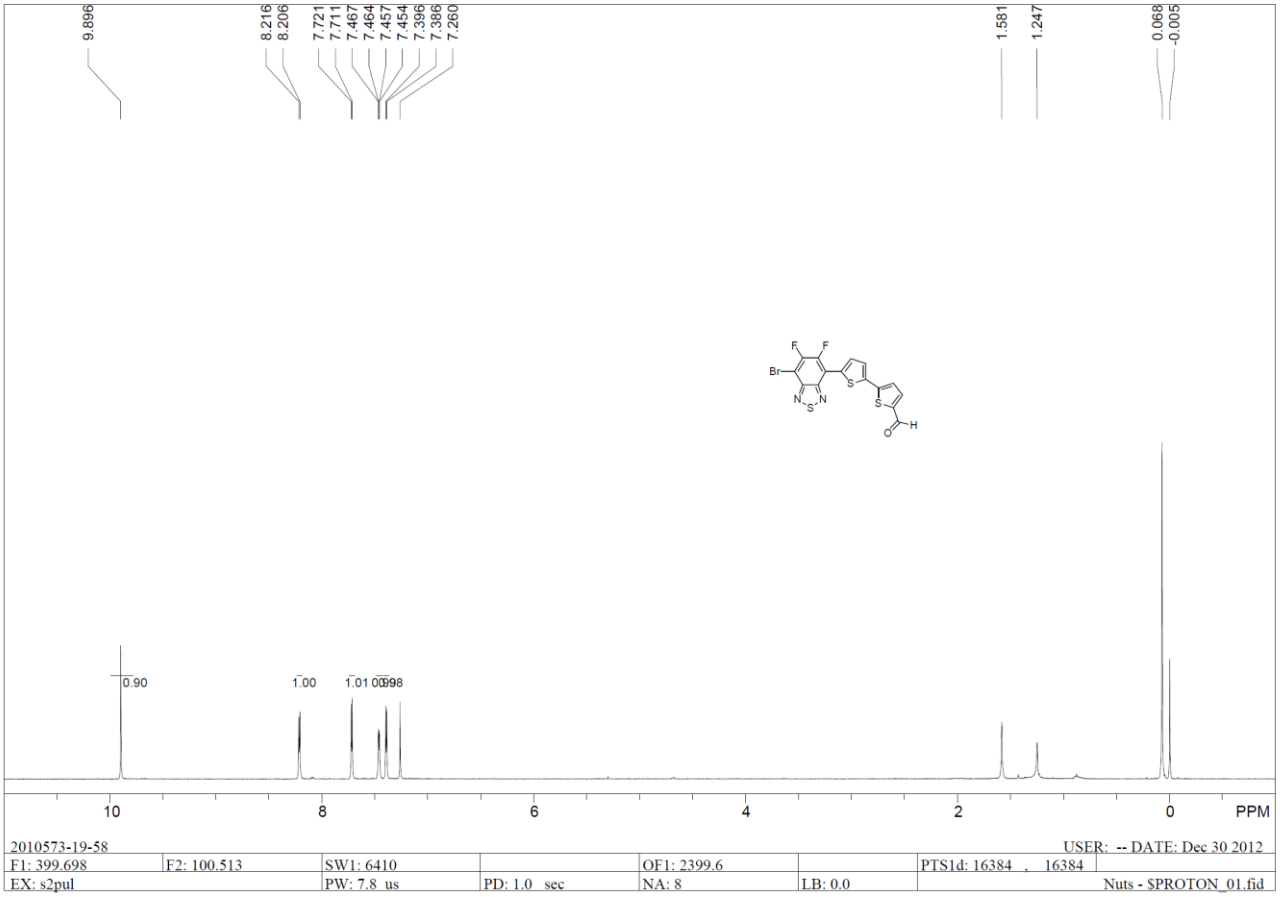
5-(7-Bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde (3f).

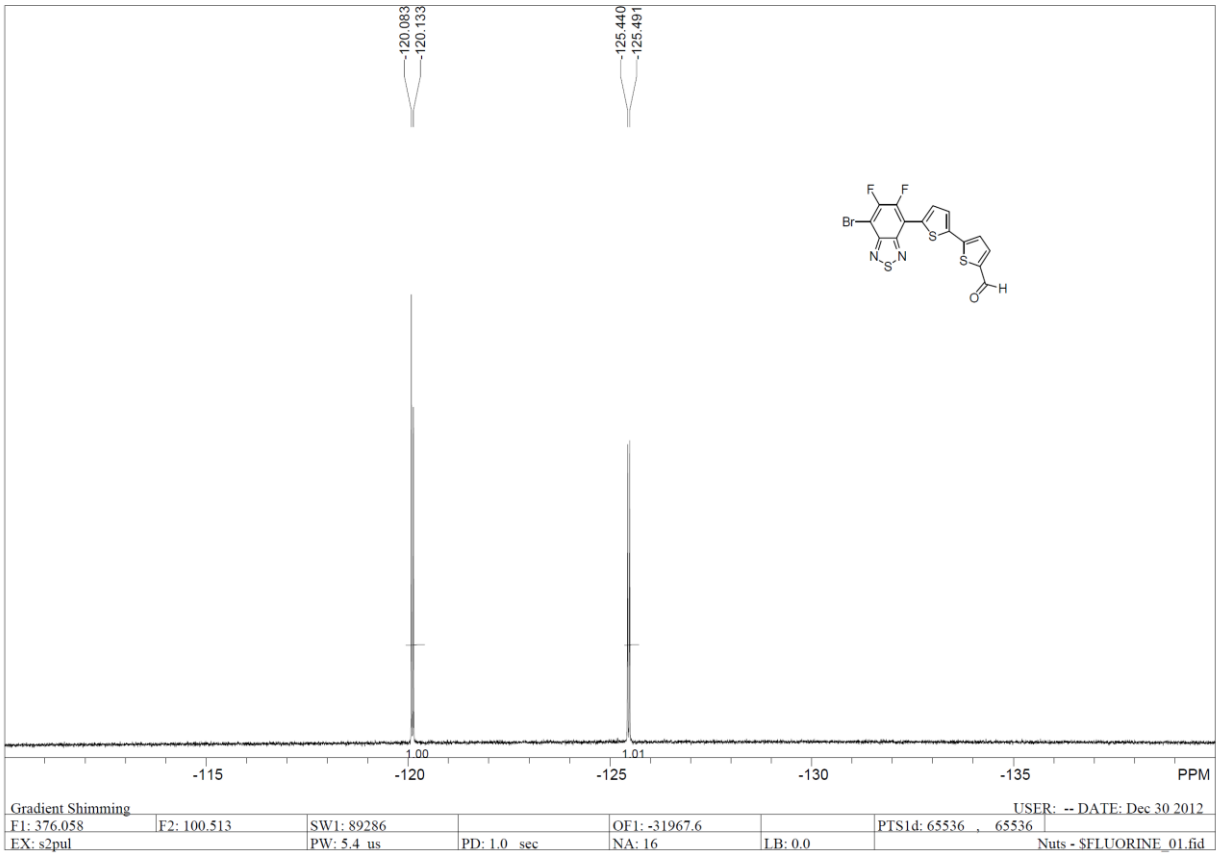



119.822
119.873
123.484
123.535
1.00
1.02
F
F
Br
S
H
O
N
S
N
-115
-120
-125
-130
PPM
Gradient Shimming
USER: -- DATE: Jan 9 2013
F1: 376.058
F2: 100.513
SW1: 89286
OF1: -31967.6
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.4 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $FLUORINE_01.fid

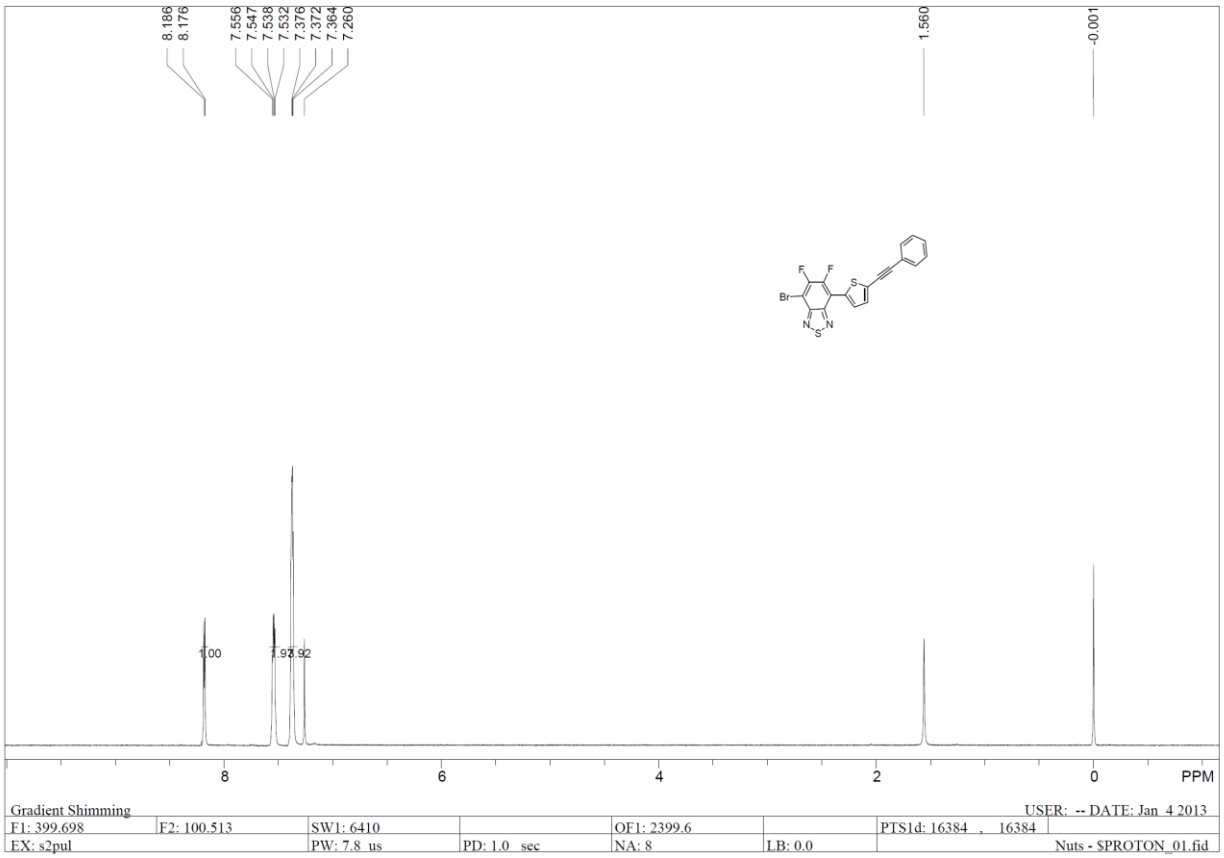

-19-57-C
Gradient Shimming
183.177
153.408
153.209
151.823
151.630
150.648
149.174
148.981
147.383
145.411
145.356
139.615
135.582
131.744
131.650
128.465
112.129
99.680
77.318
77.000
76.682
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

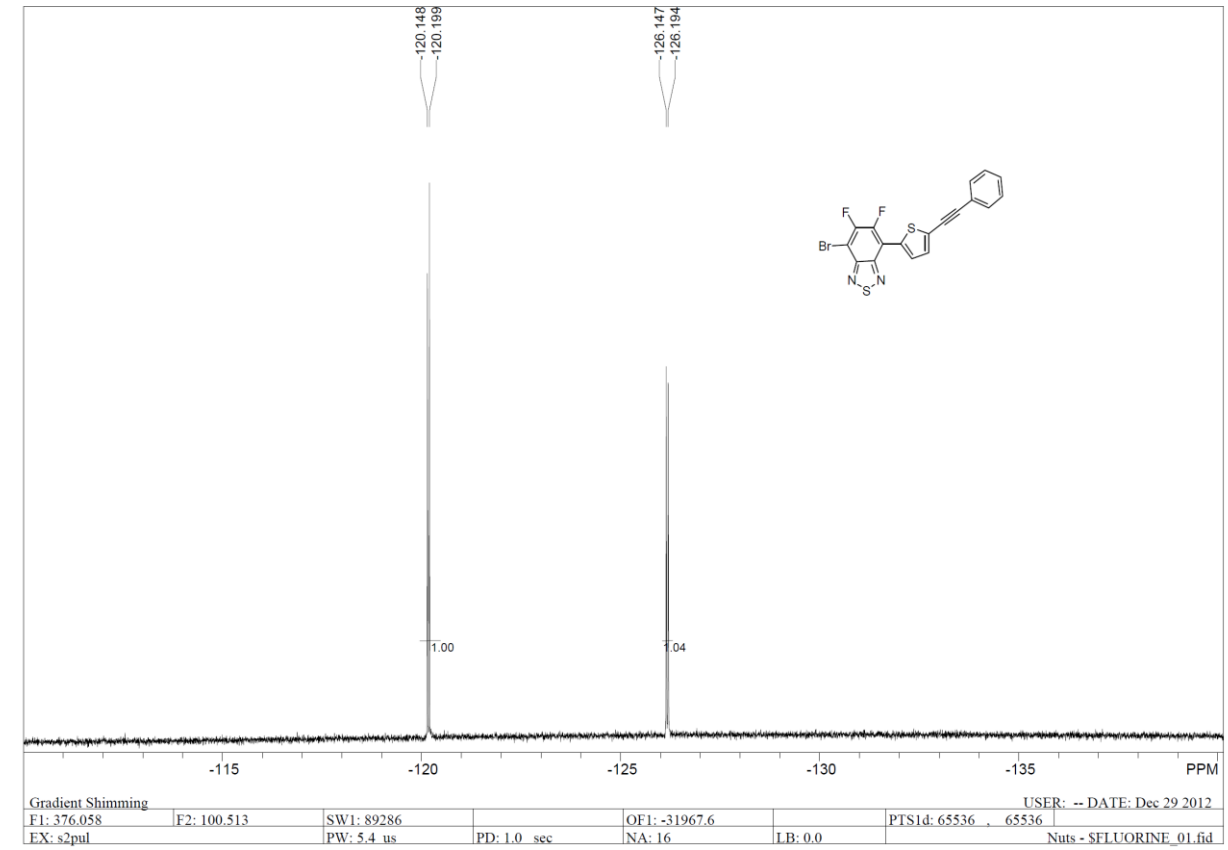
5'-(7-Bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)-[2,2'-bithiophene]-5-carbaldehyde (3g).

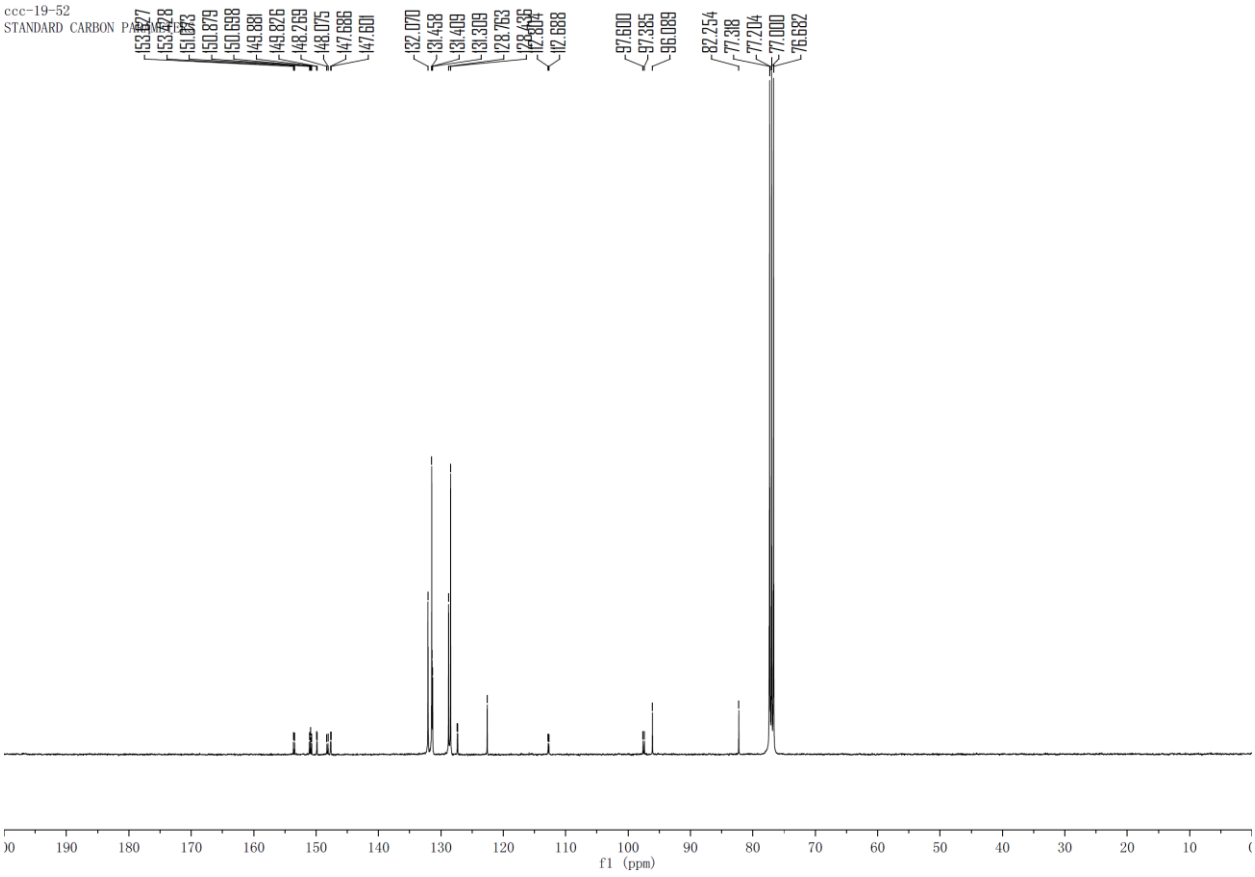




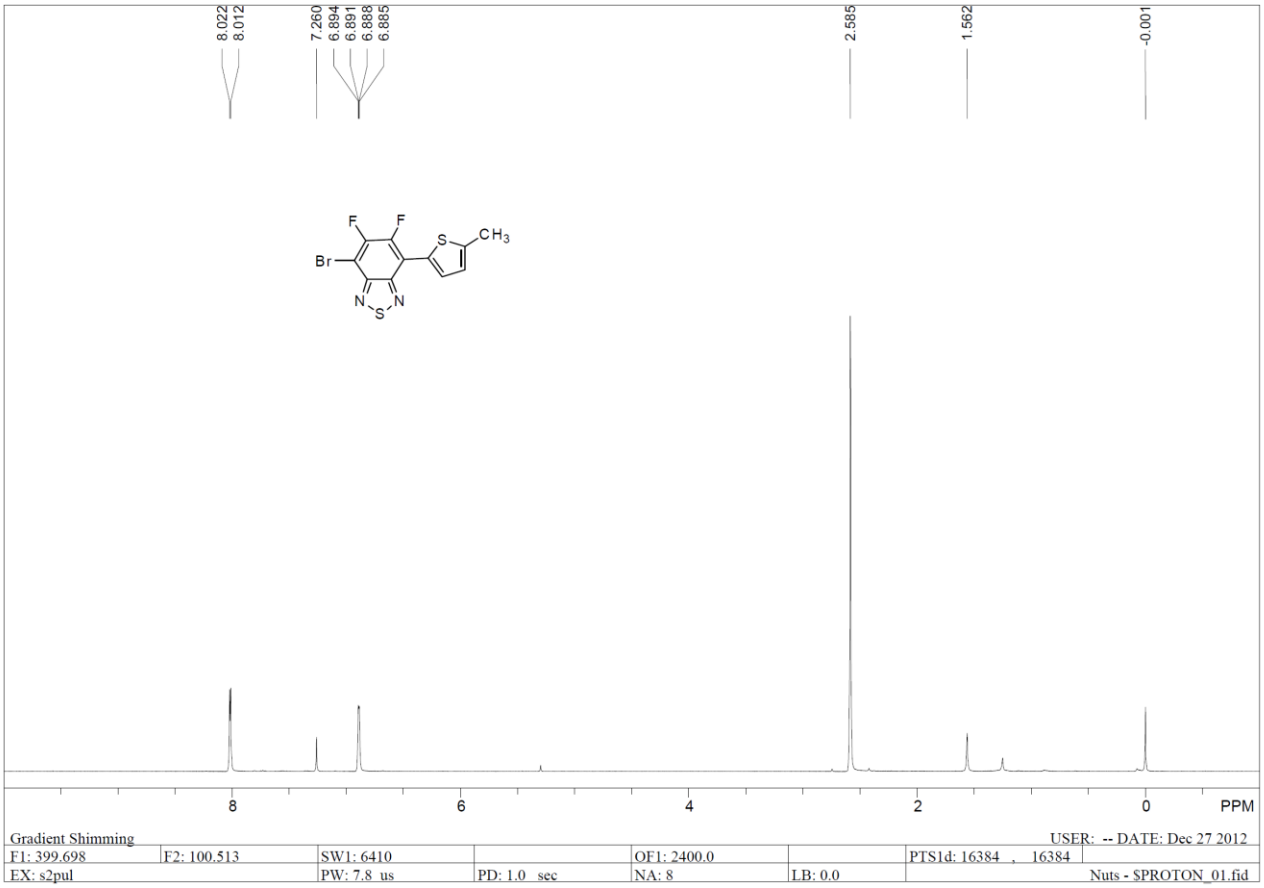
4-Bromo-5,6-difluoro-7-(5-(phenylethynyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (3h).

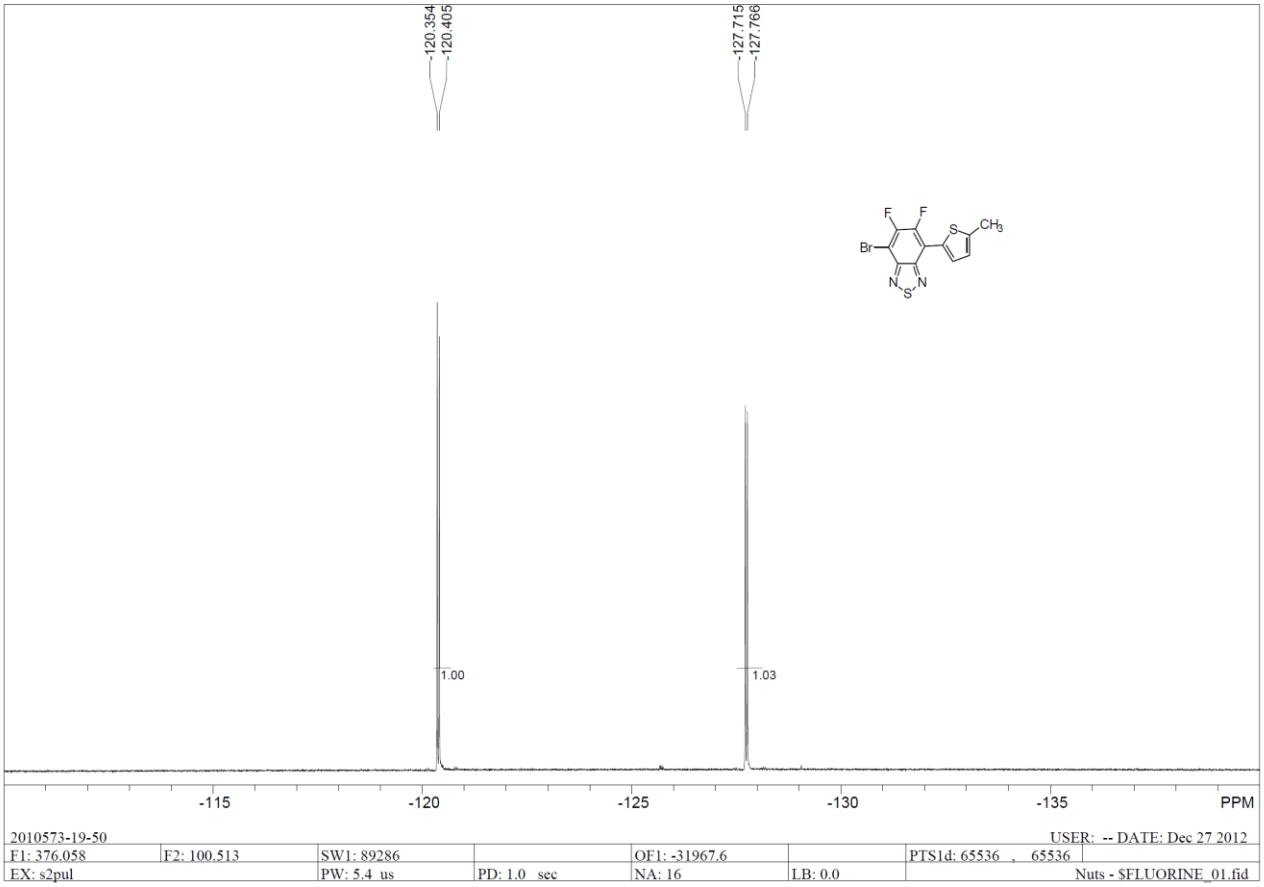


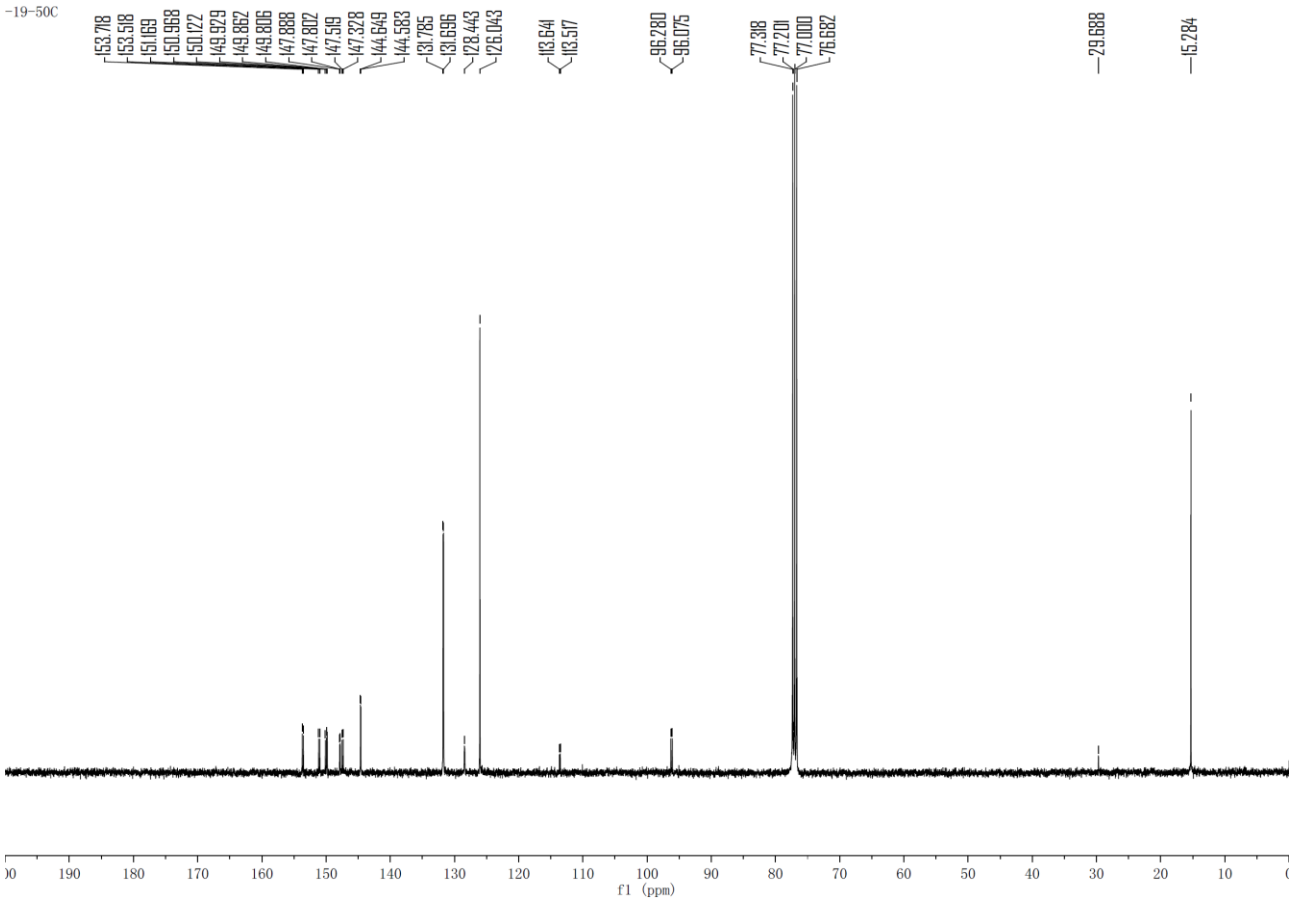




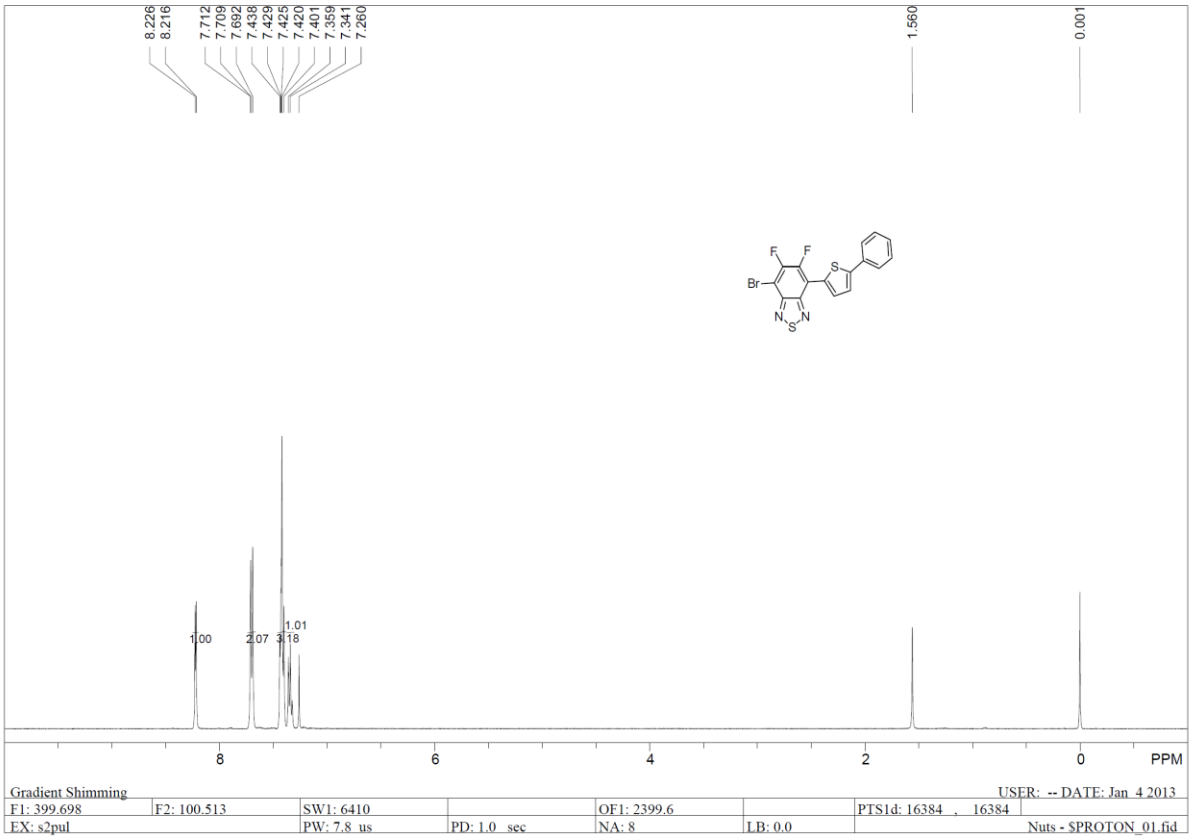
4-Bromo-5,6-difluoro-7-(5-methylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3i).

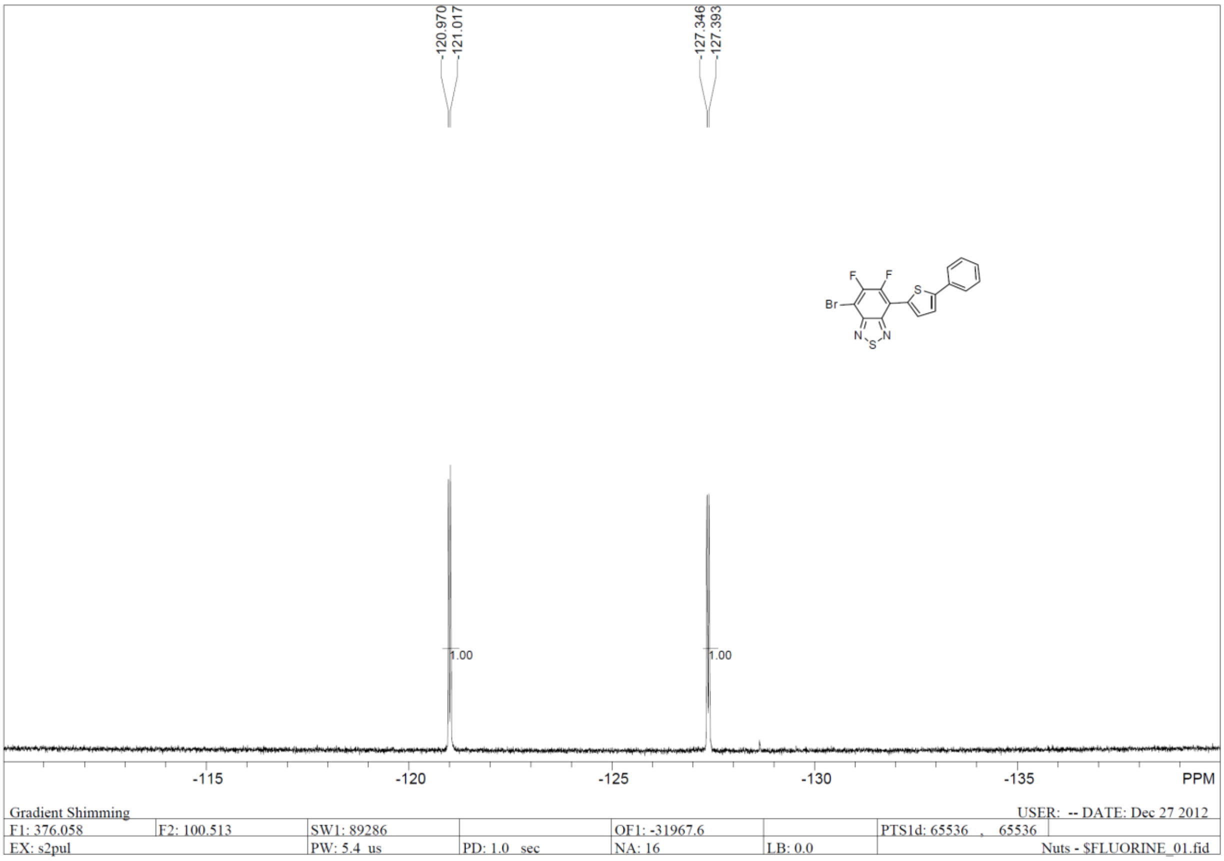

8.022
8.012
7.260
6.894
6.891
6.888
6.885
2.585
1.562
-0.001
F
F
Br
S
CH3
N
S
N
8
6
4
2
0
PPM
Gradient Shimming
USER: -- DATE: Dec 27 2012
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2400.0
PTS1d: 16384 , 16384
EX: s2pul
PW: 7.8 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $PROTON_01.fid

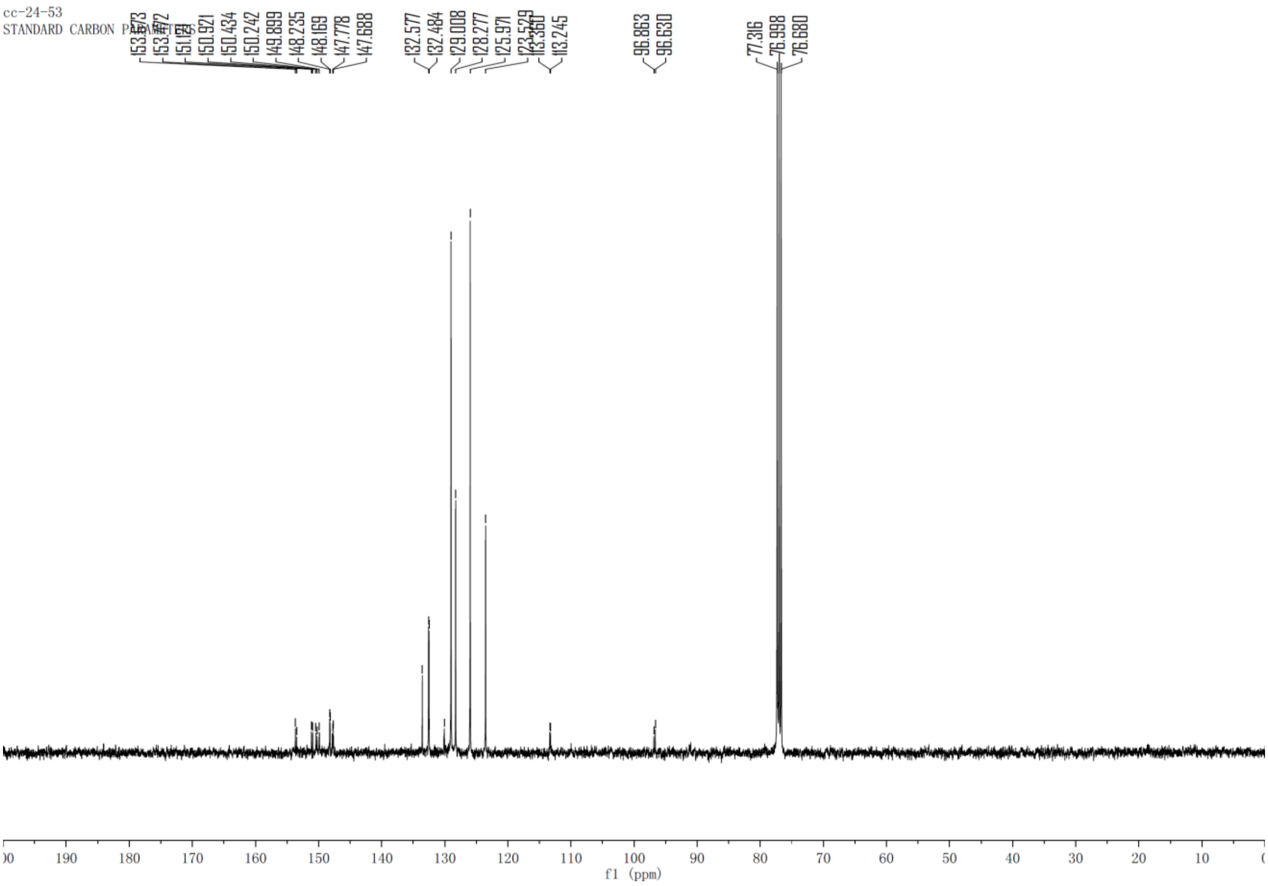

120.354
120.405
127.715
127.766
F
F
Br
S
CH3
N
S
N
1.00
1.03
-115
-120
-125
-130
-135
PPM
2010573-19-50
USER: -- DATE: Dec 27 2012
F1: 376.058
F2: 100.513
SW1: 89286
OF1: -31967.6
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.4 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $FLUORINE_01.fid



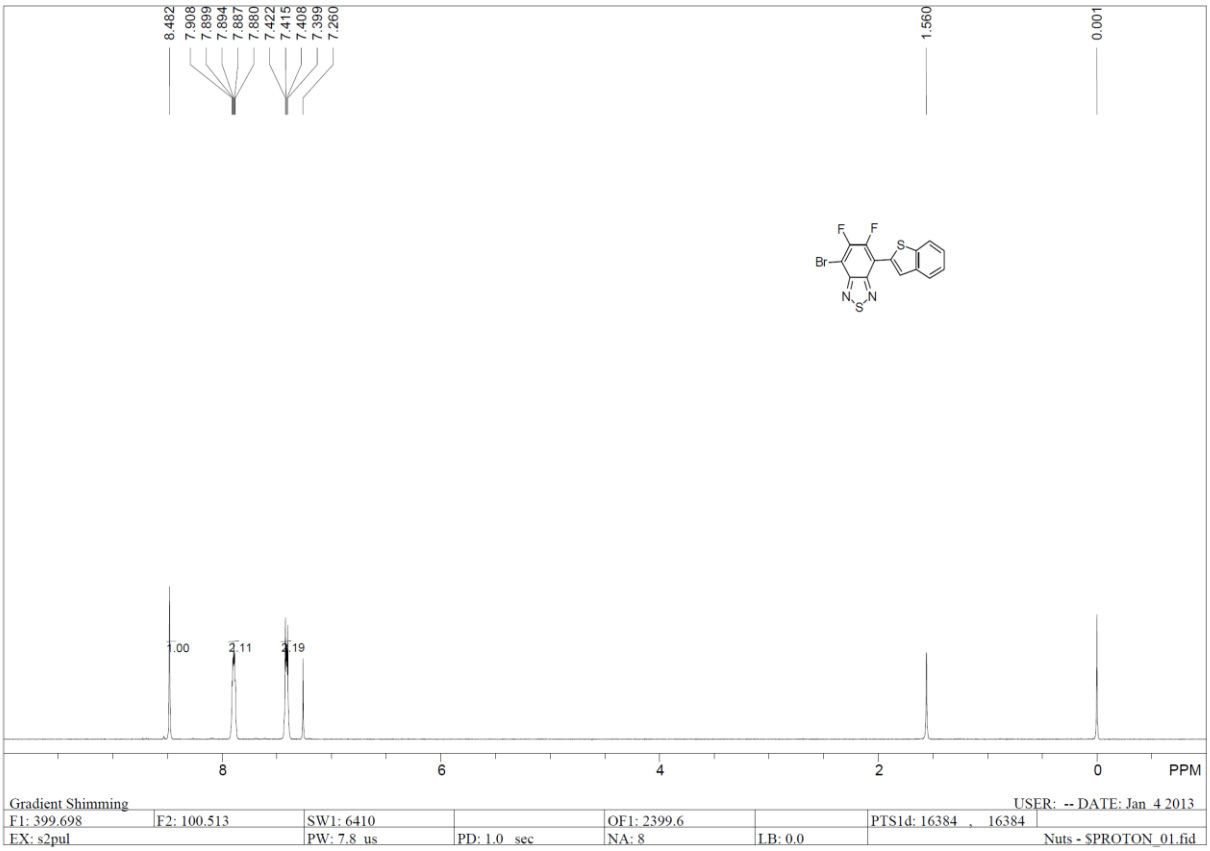
4-Bromo-5,6-difluoro-7-(5-phenylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3j).

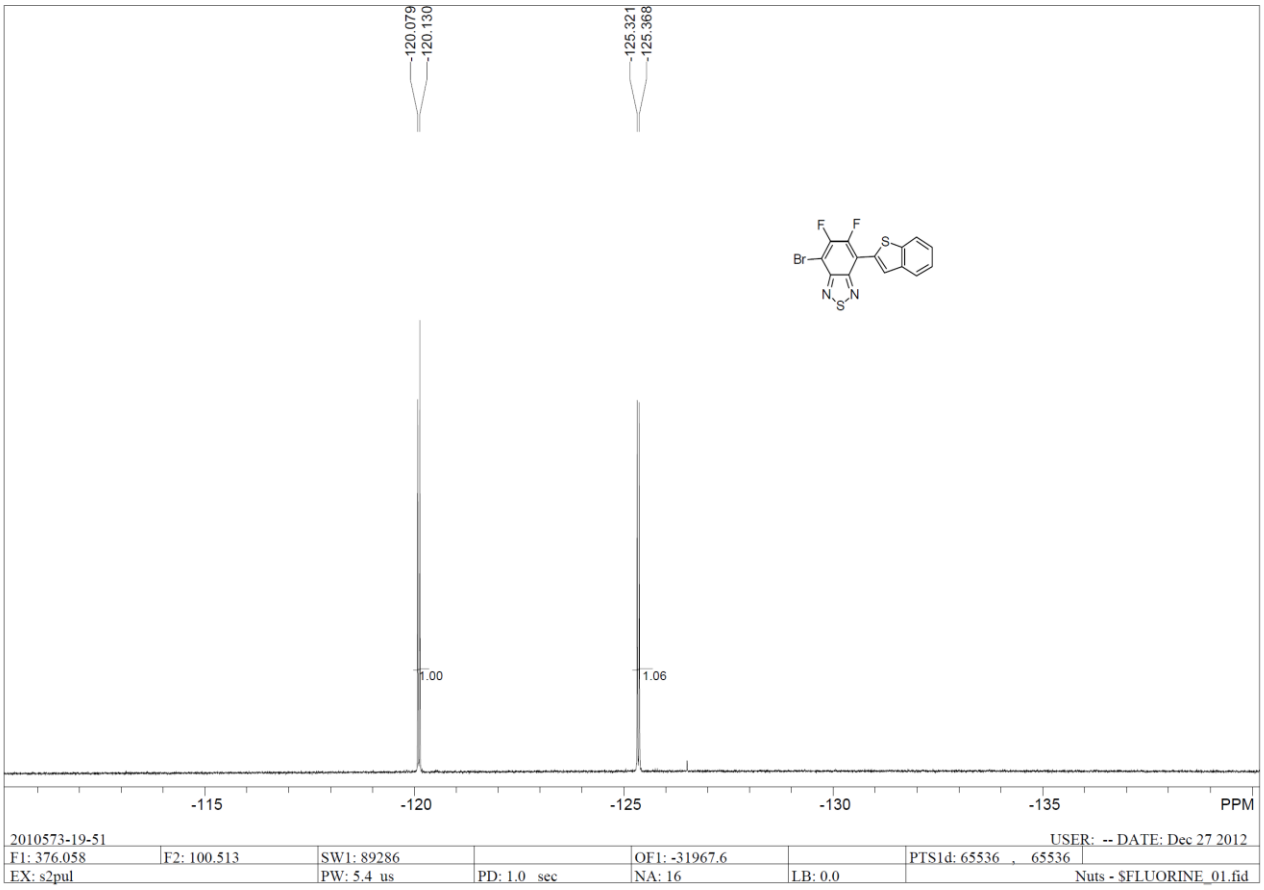


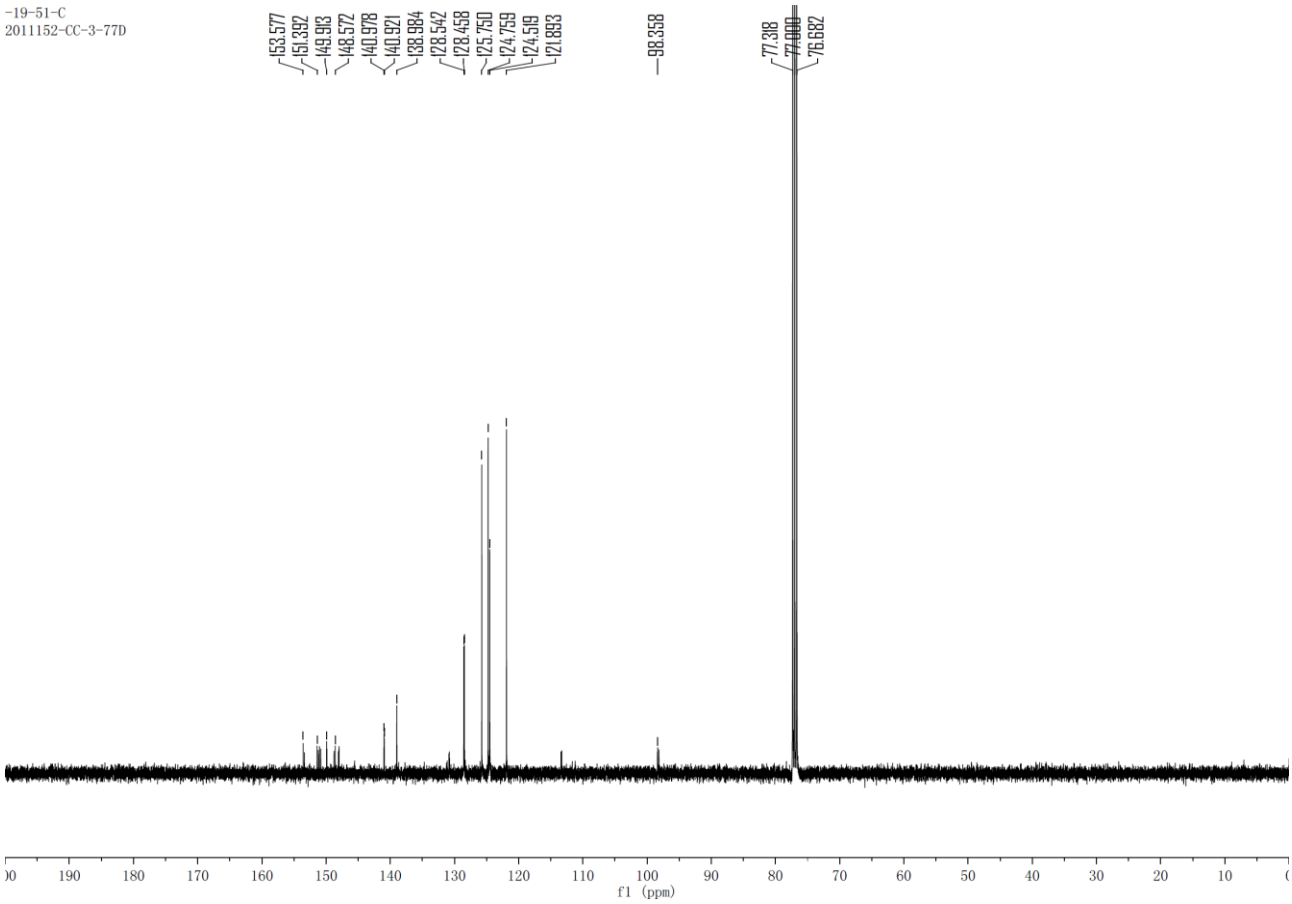

-120.970
-121.017
-127.346
-127.393
F
F
Br
S
N
S
N
1.00
1.00
-115
-120
-125
-130
-135
PPM
Gradient Shimming
USER: -- DATE: Dec 27 2012
F1: 376.058
F2: 100.513
SW1: 89286
OF1: -31967.6
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.4 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $FLUORINE_01.fid


cc-24-53
STANDARD CARBON PARAMETERS
150.921
150.434
150.242
149.899
148.235
148.169
147.778
147.688
132.577
132.484
129.008
128.277
125.971
123.529
113.245
96.863
96.630
77.316
76.998
76.680
f1 (ppm)

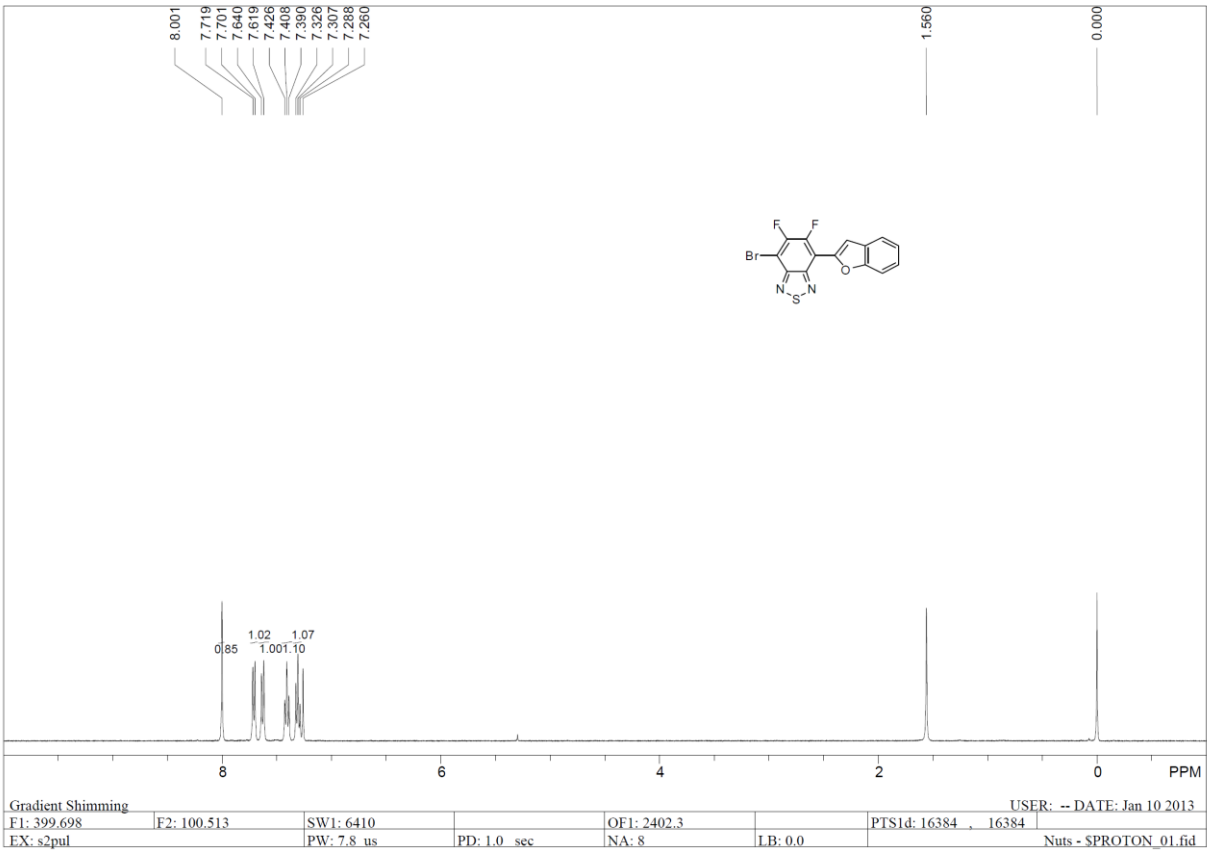
4-(Benzo[b]thiophen-2-yl)-7-bromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (3k).

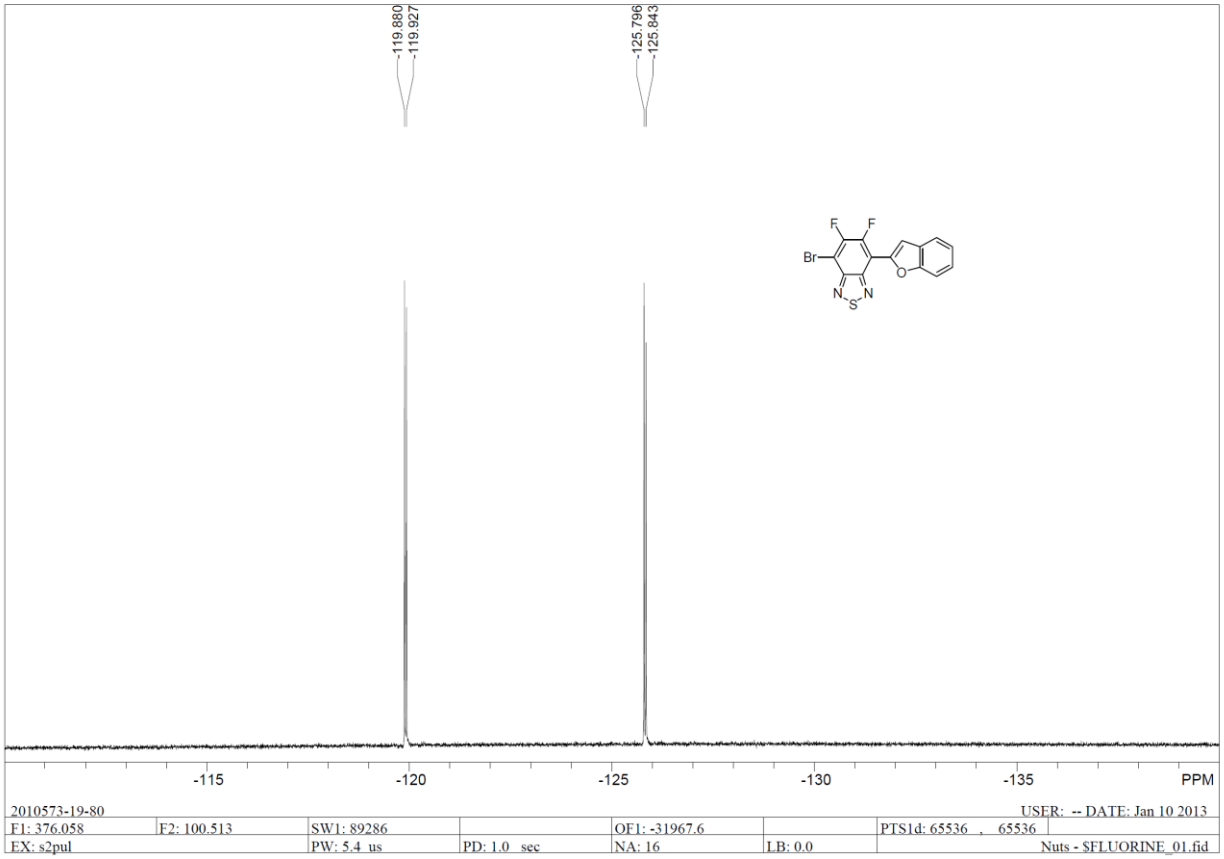




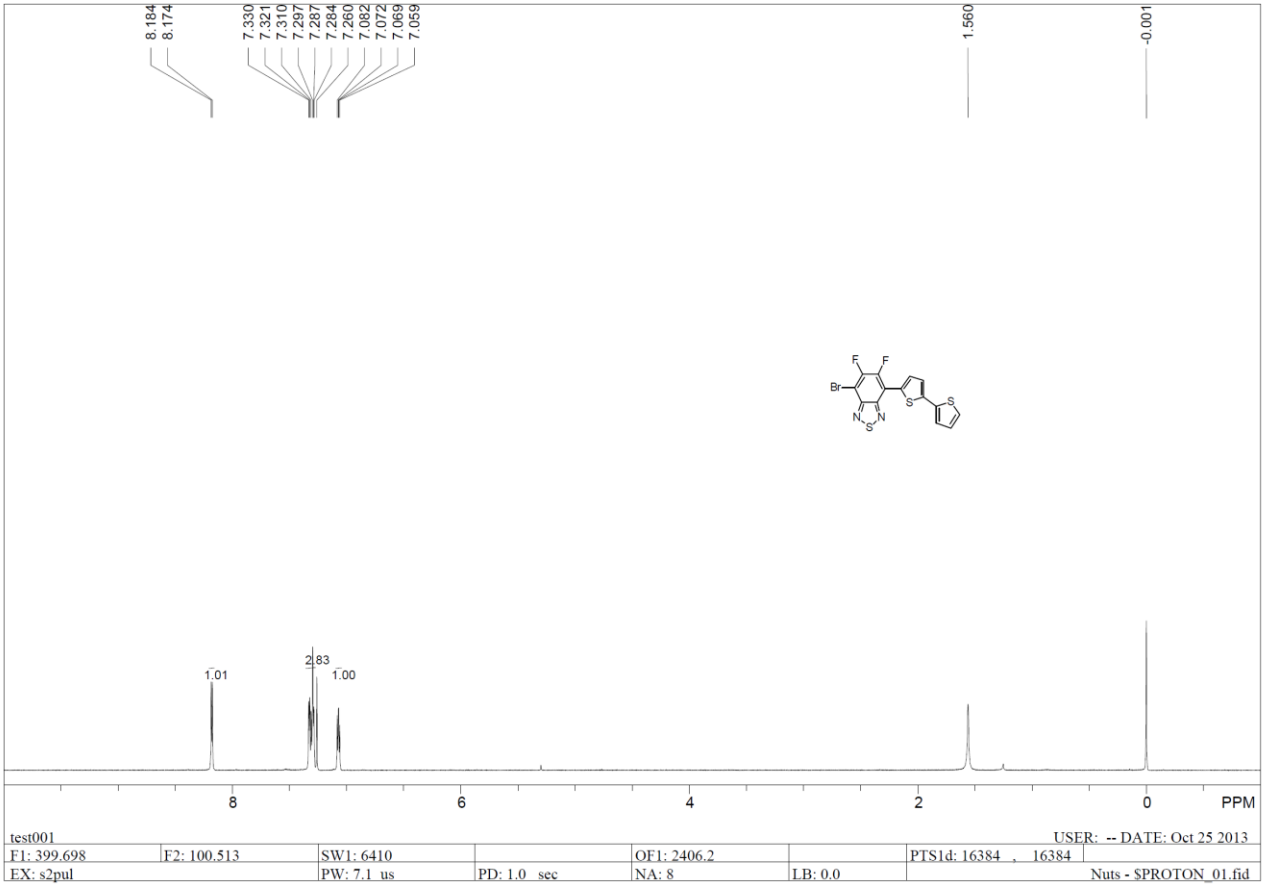


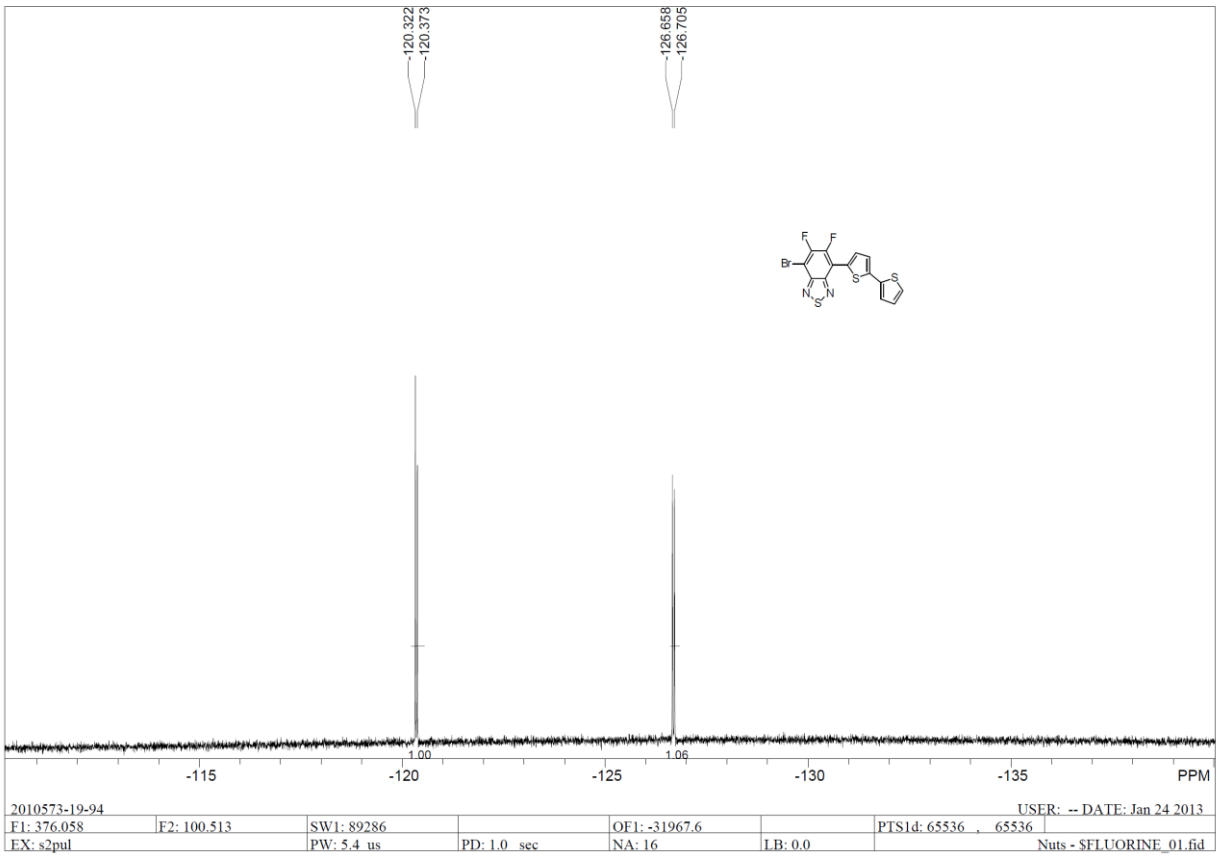
4-(Benzofuran-2-yl)-7-bromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (3l).

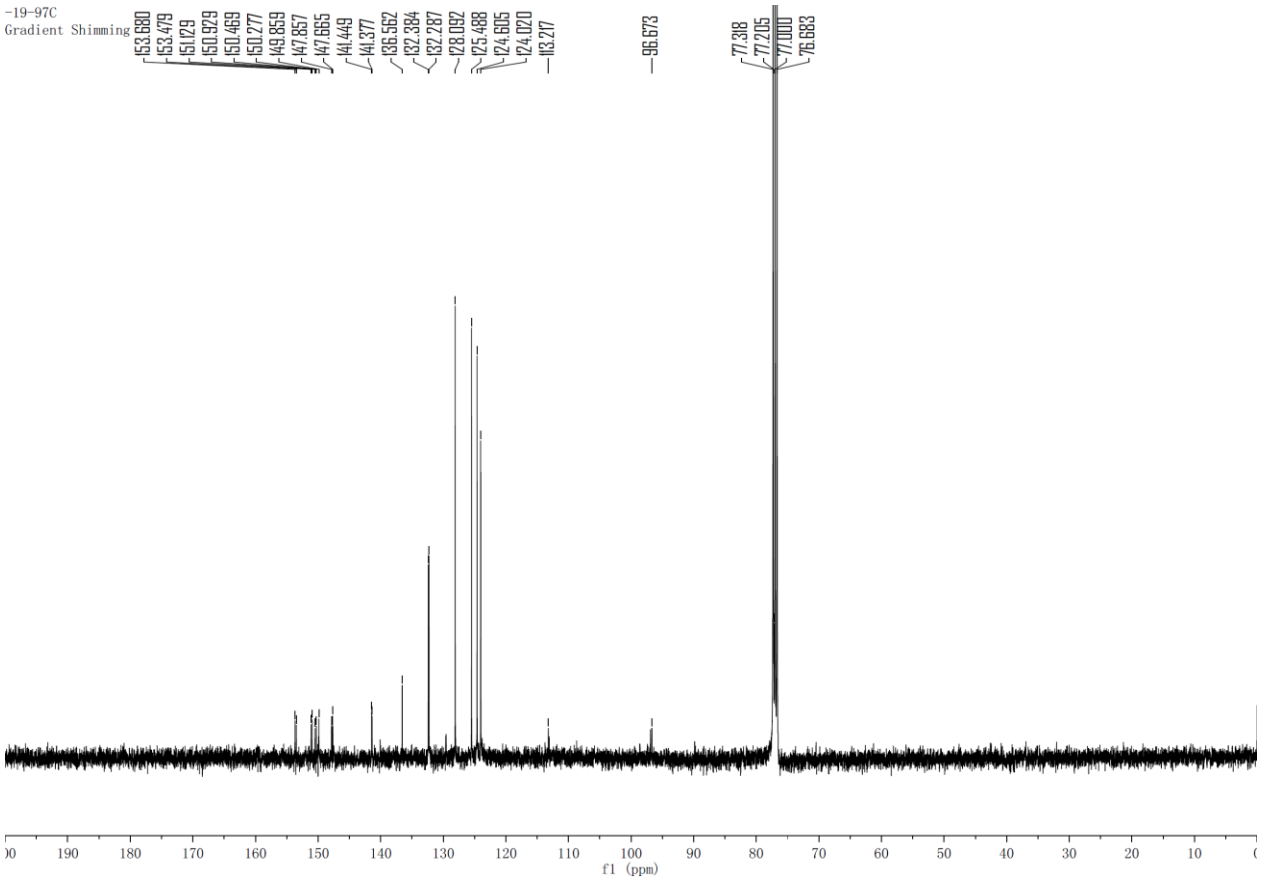




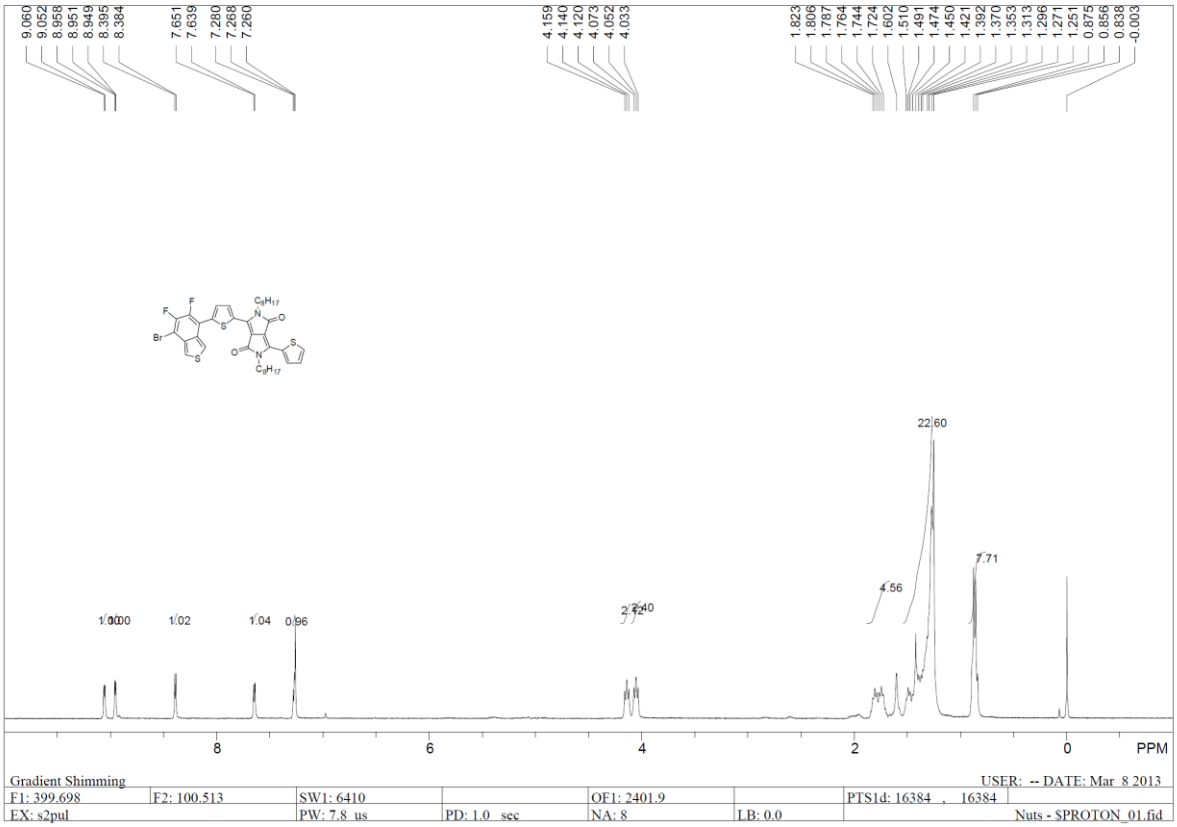
4-([2,2'-Bithiophen]-5-yl)-7-bromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (3m).

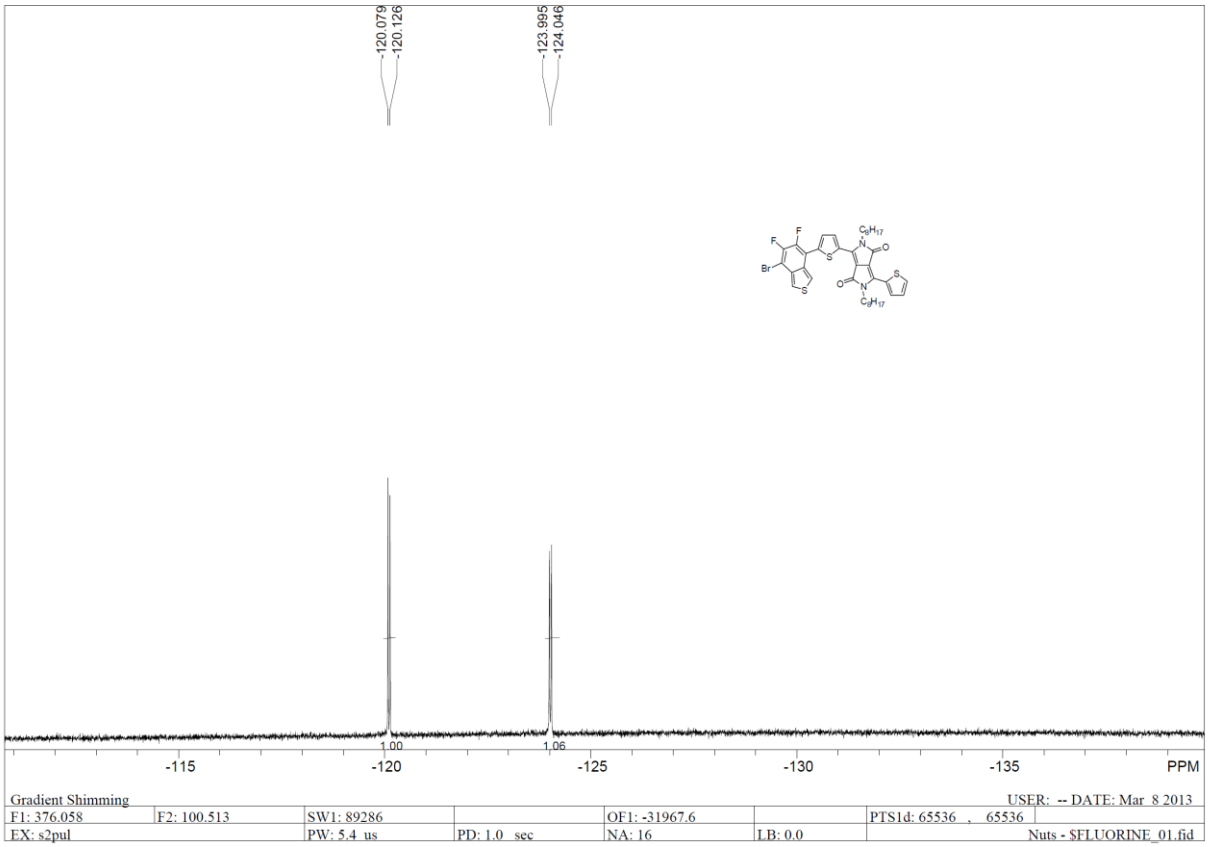

8.184
8.174
7.330
7.321
7.310
7.297
7.287
7.284
7.260
7.082
7.072
7.069
7.059
1.560
-0.001
F
F
Br
S
S
N
N
S
1.01
2.83
1.00
8
6
4
2
0
PPM
test001
USER: -- DATE: Oct 25 2013
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2406.2
PTS1d: 16384 , 16384
EX: s2pul
PW: 7.1 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $PROTON_01.fid


-120.322
-120.373
-126.658
-126.705
F
F
Br
S
S
N
N
S
1.00
1.06
-115
-120
-125
-130
-135
PPM
2010573-19-94
USER: -- DATE: Jan 24 2013
F1: 376.058
F2: 100.513
SW1: 89286
OF1: -31967.6
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.4 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $FLUORINE_01.fid

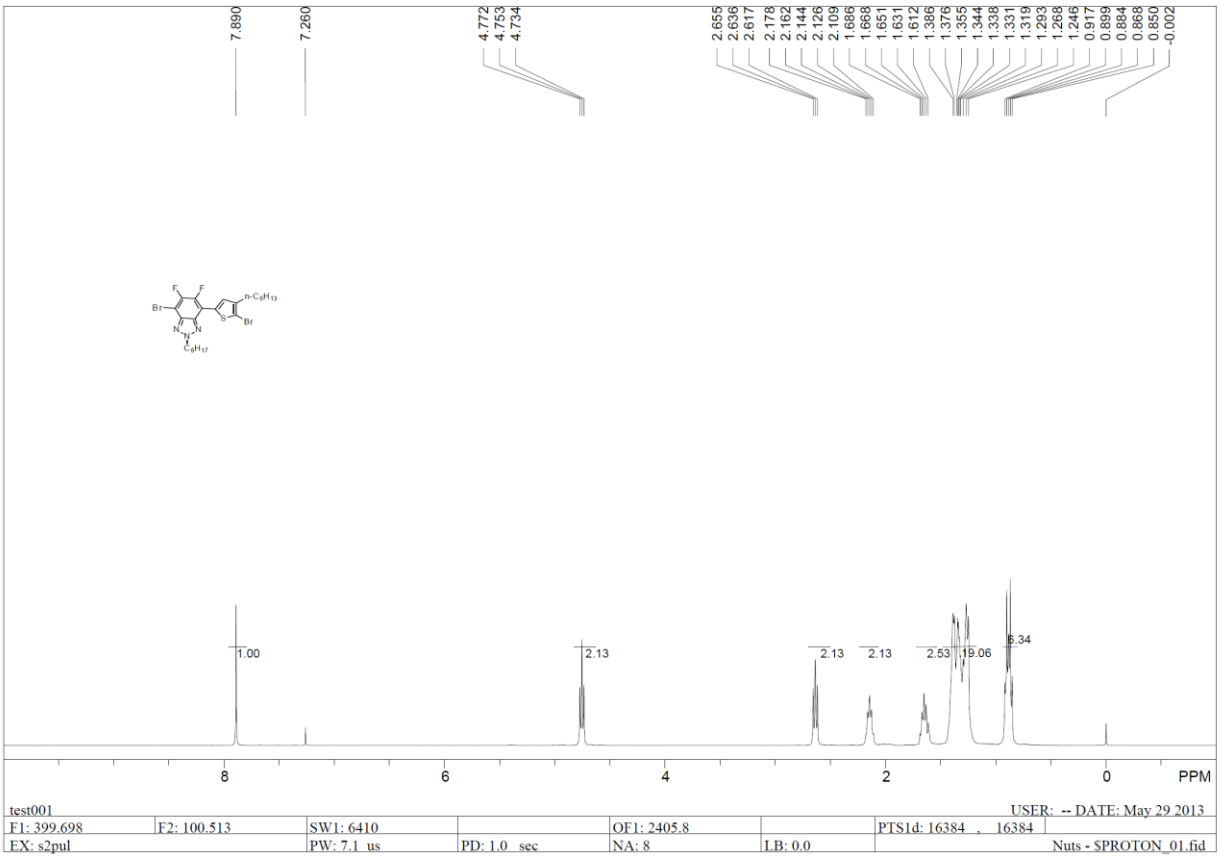


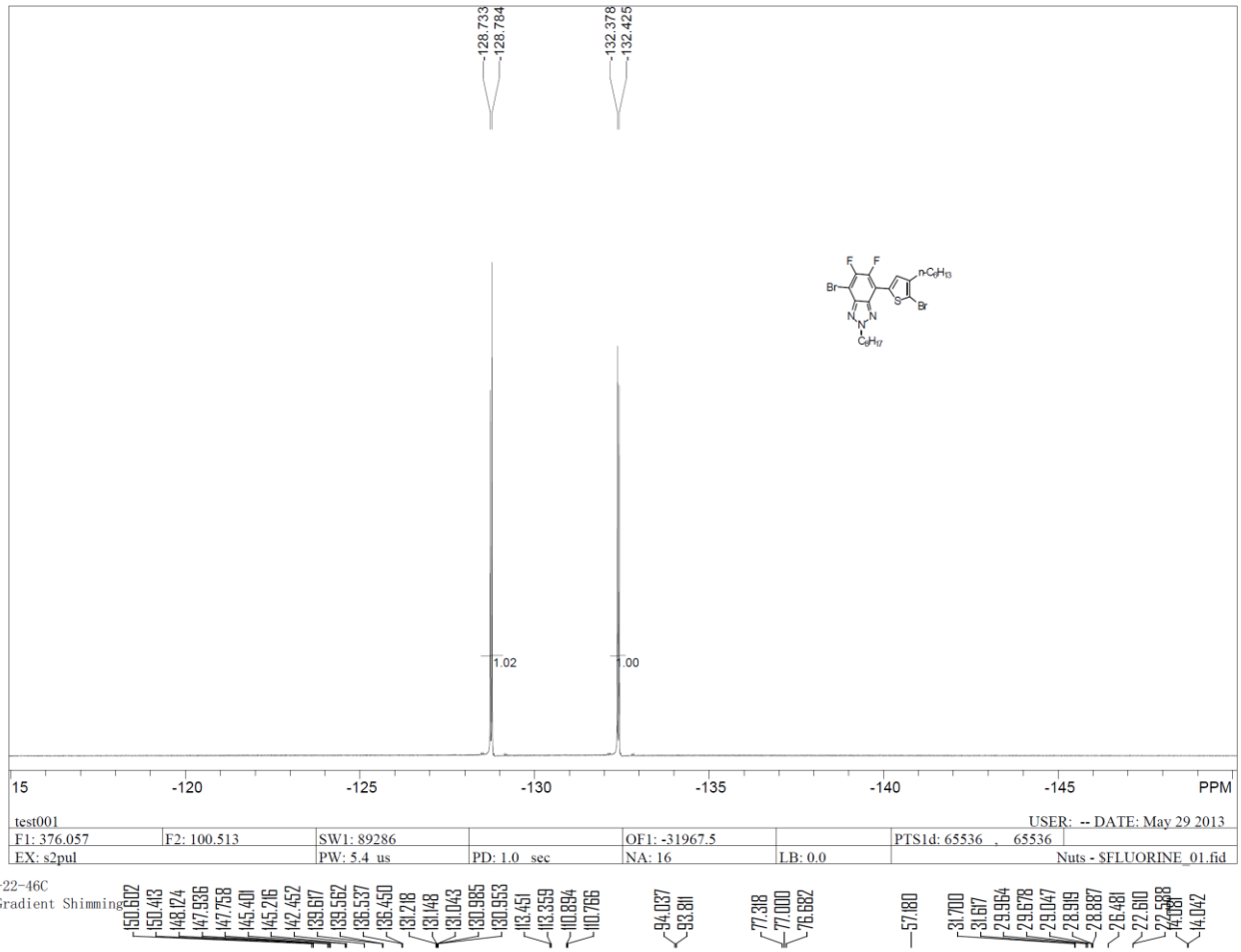
3-(5-(7-Bromo-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2,5-dioctyl-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3n).



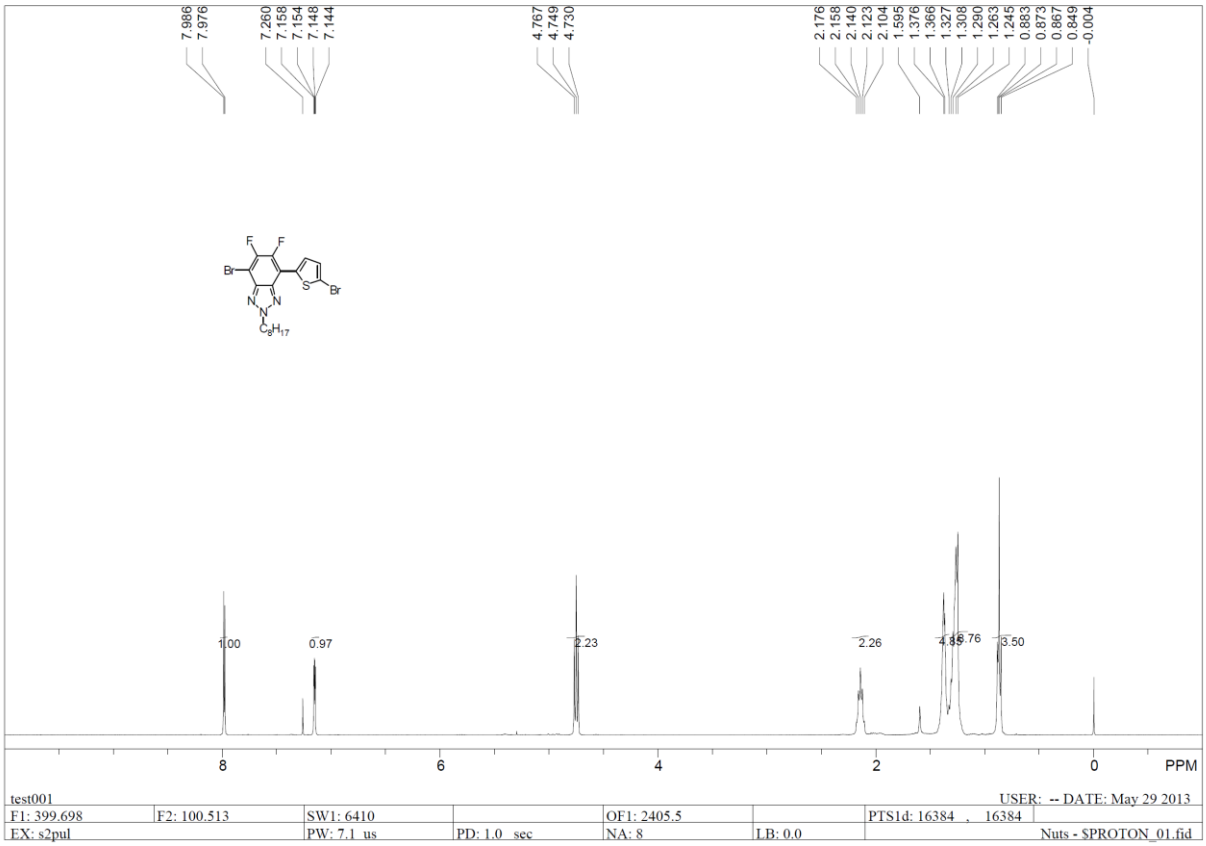


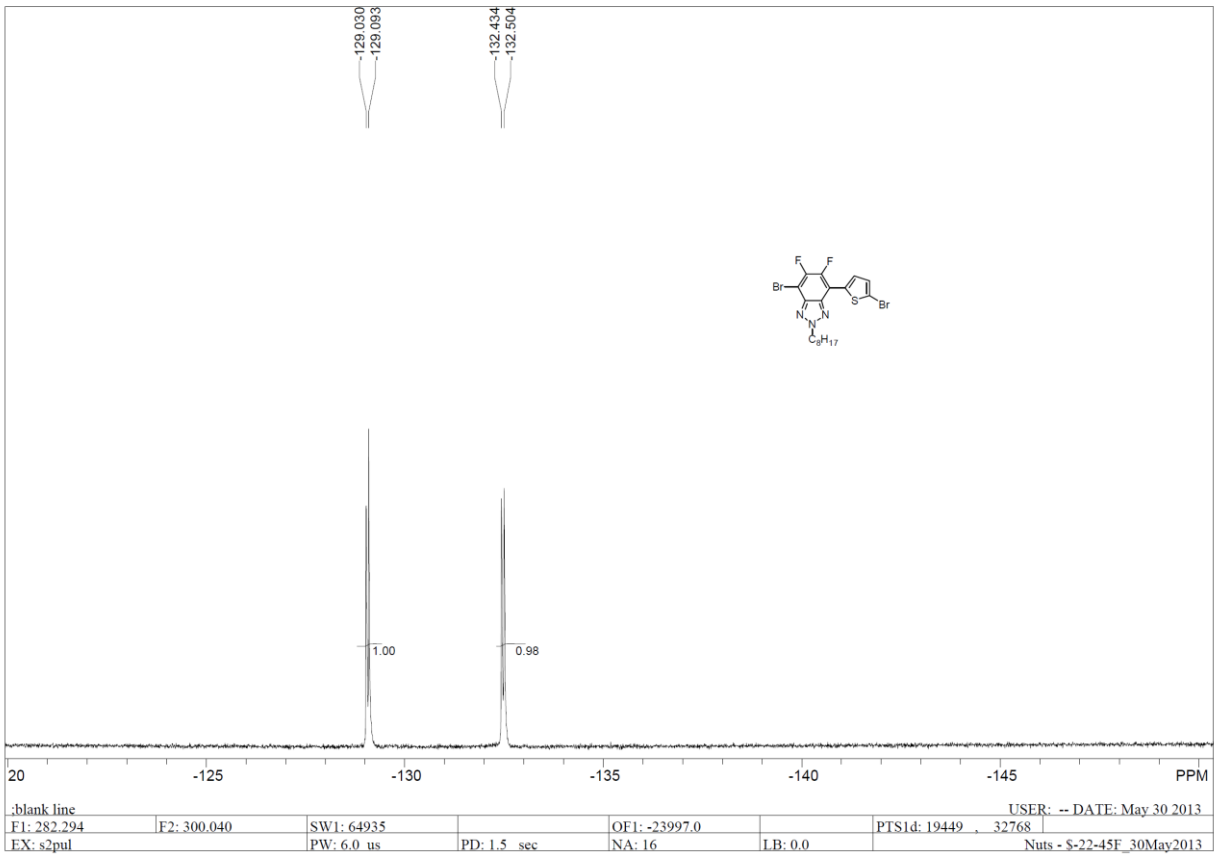
4-Bromo-7-(5-bromo-4-hexylthiophen-2-yl)-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazole (3o).

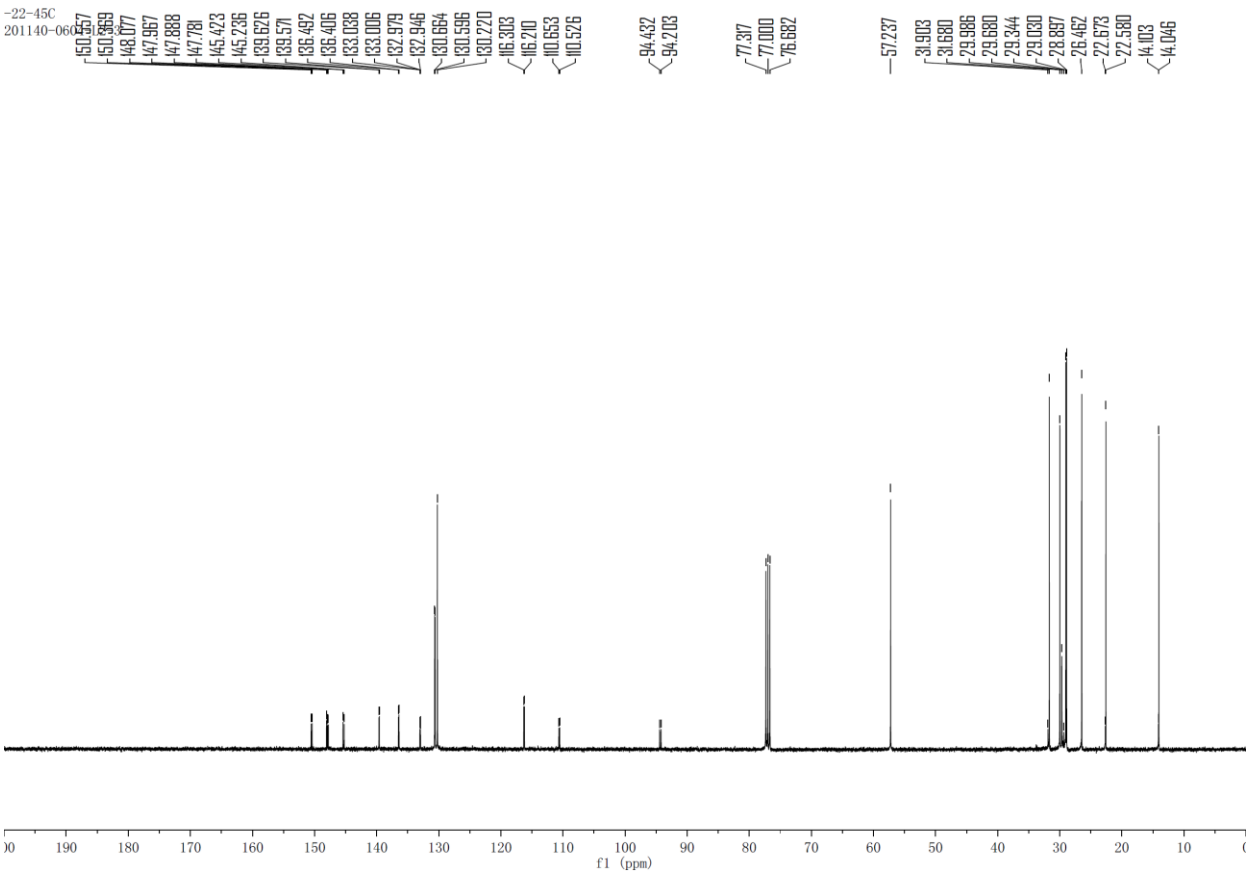



-128.733
-128.784
-132.378
-132.425
1.02
1.00
15
-120
-125
-130
-135
-140
-145
PPM
test001
USER: -- DATE: May 29 2013
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.4 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $FLUORINE_01.fid
-22-46C
Gradient Shimming
150.602
150.413
148.124
147.936
147.758
145.401
145.216
142.452
139.617
139.562
136.537
136.450
131.218
131.148
131.043
130.985
130.953
113.451
113.359
110.894
110.766
94.037
93.811
77.318
77.000
76.682
57.180
31.700
31.617
29.964
29.678
29.047
28.919
28.887
26.481
22.610
22.588
14.042
f1 (ppm)

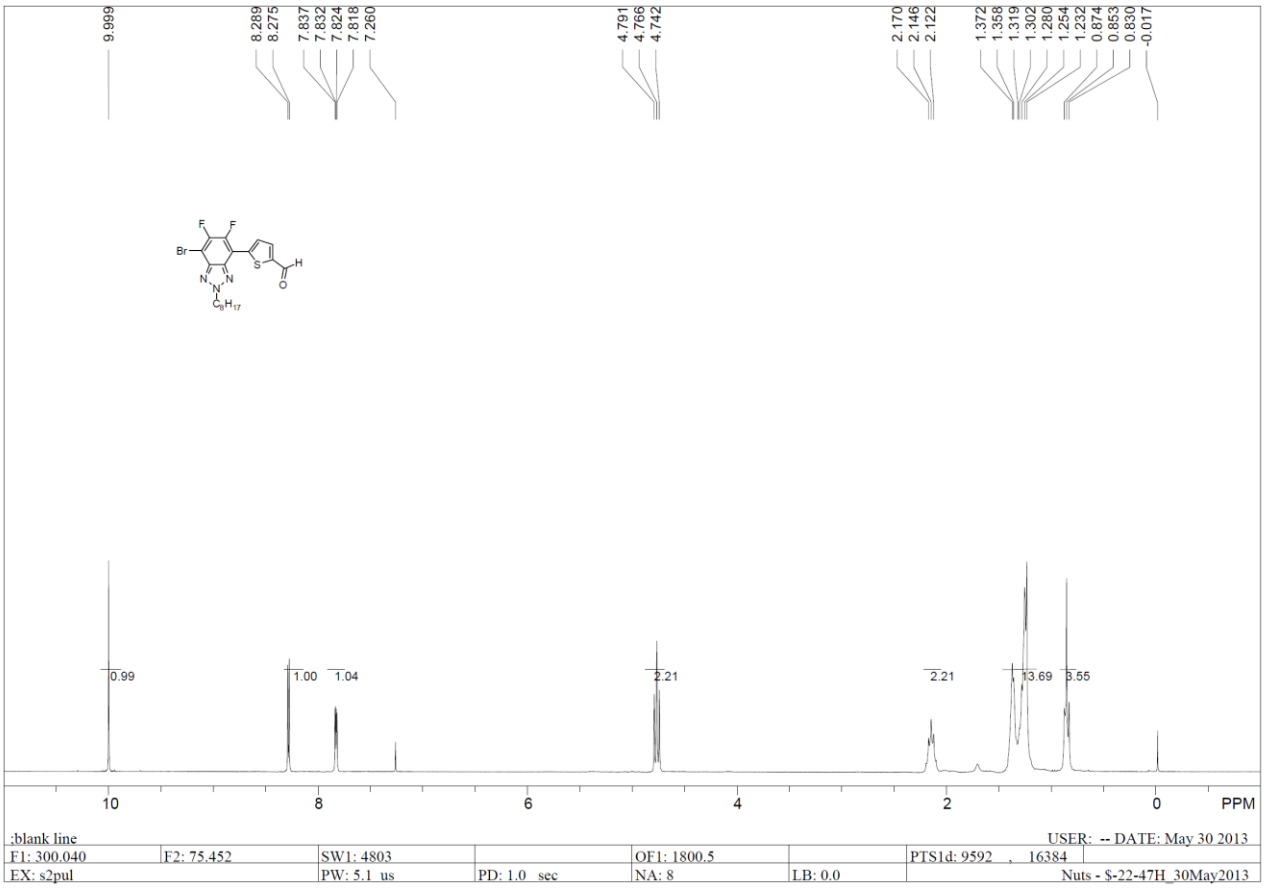
4-Bromo-7-(5-bromothiophen-2-yl)-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazole (3p).

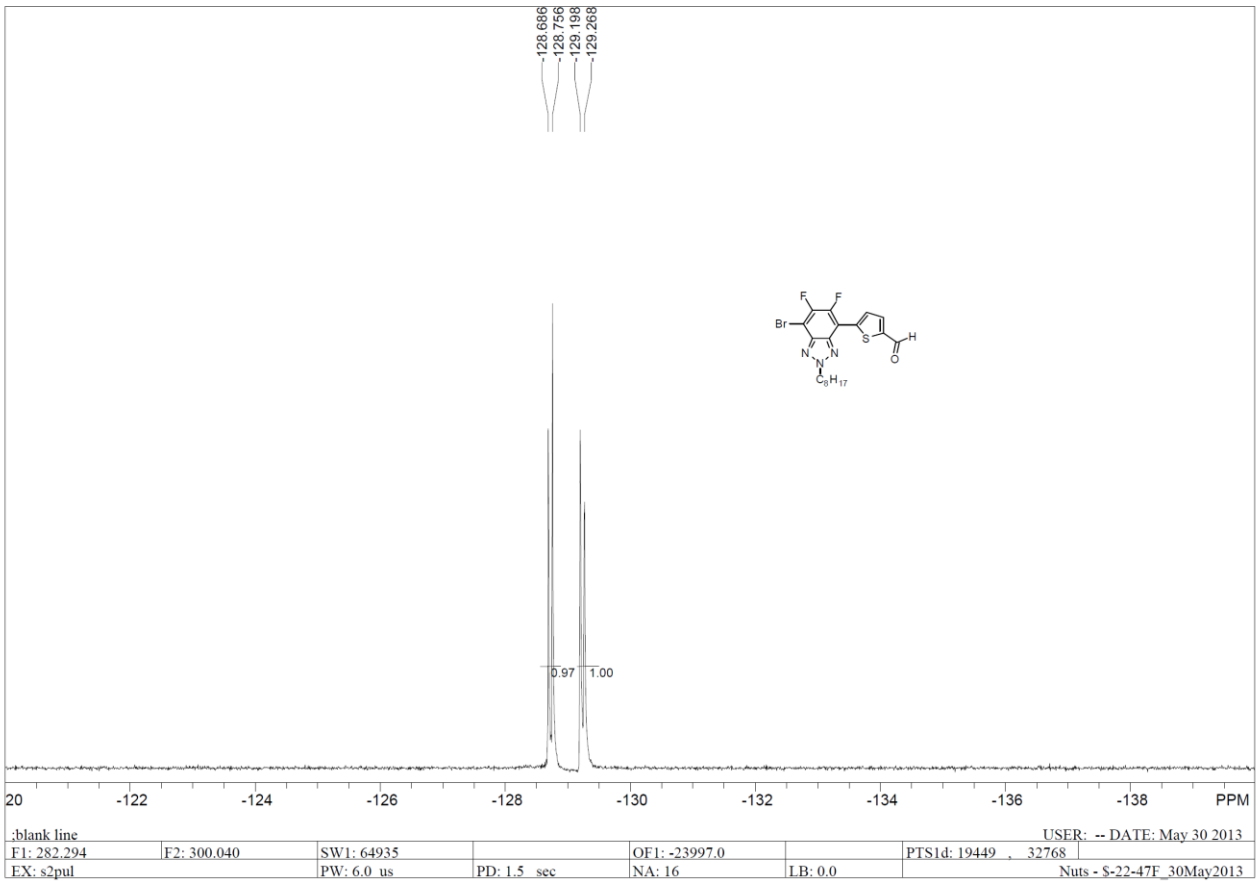


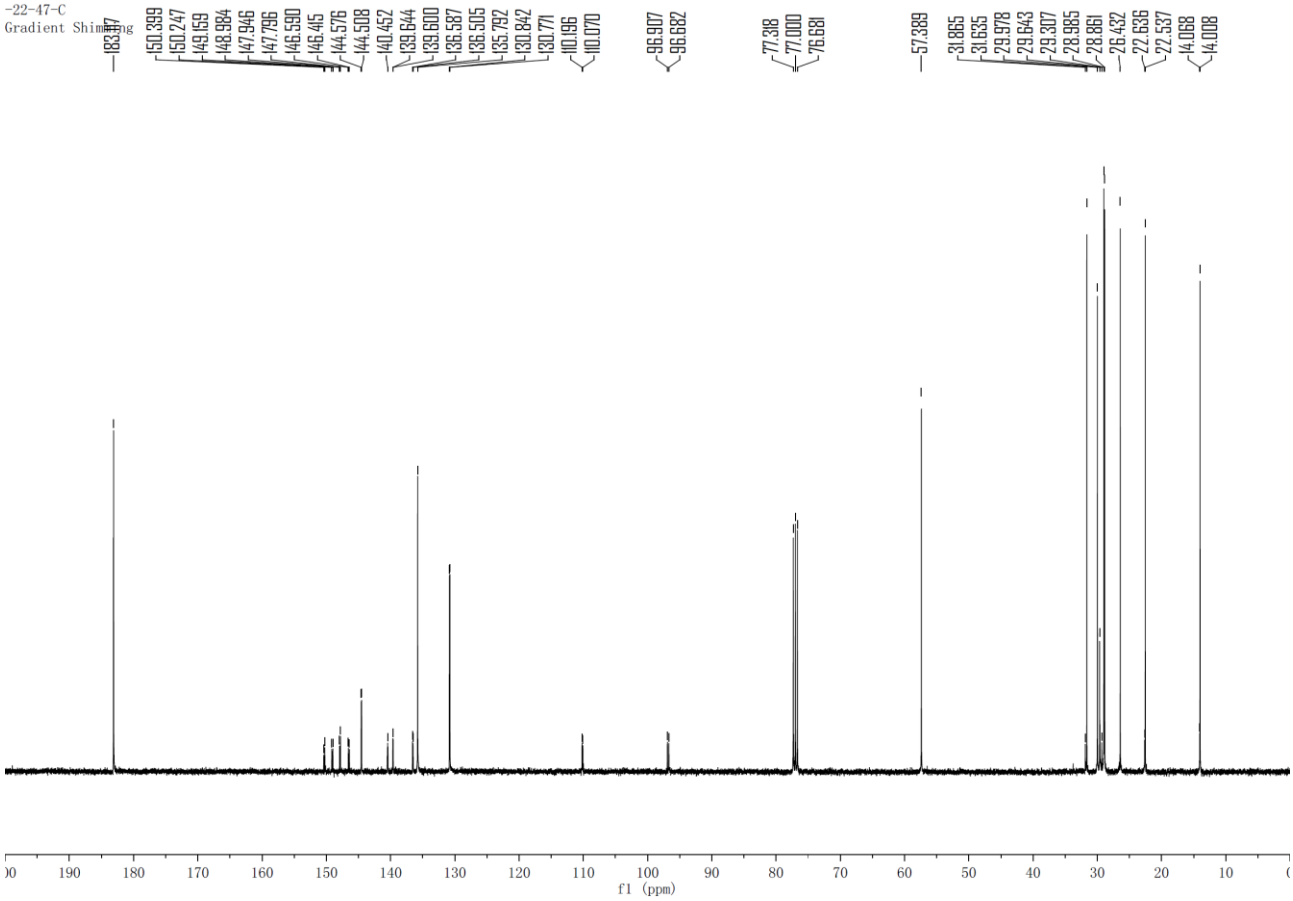




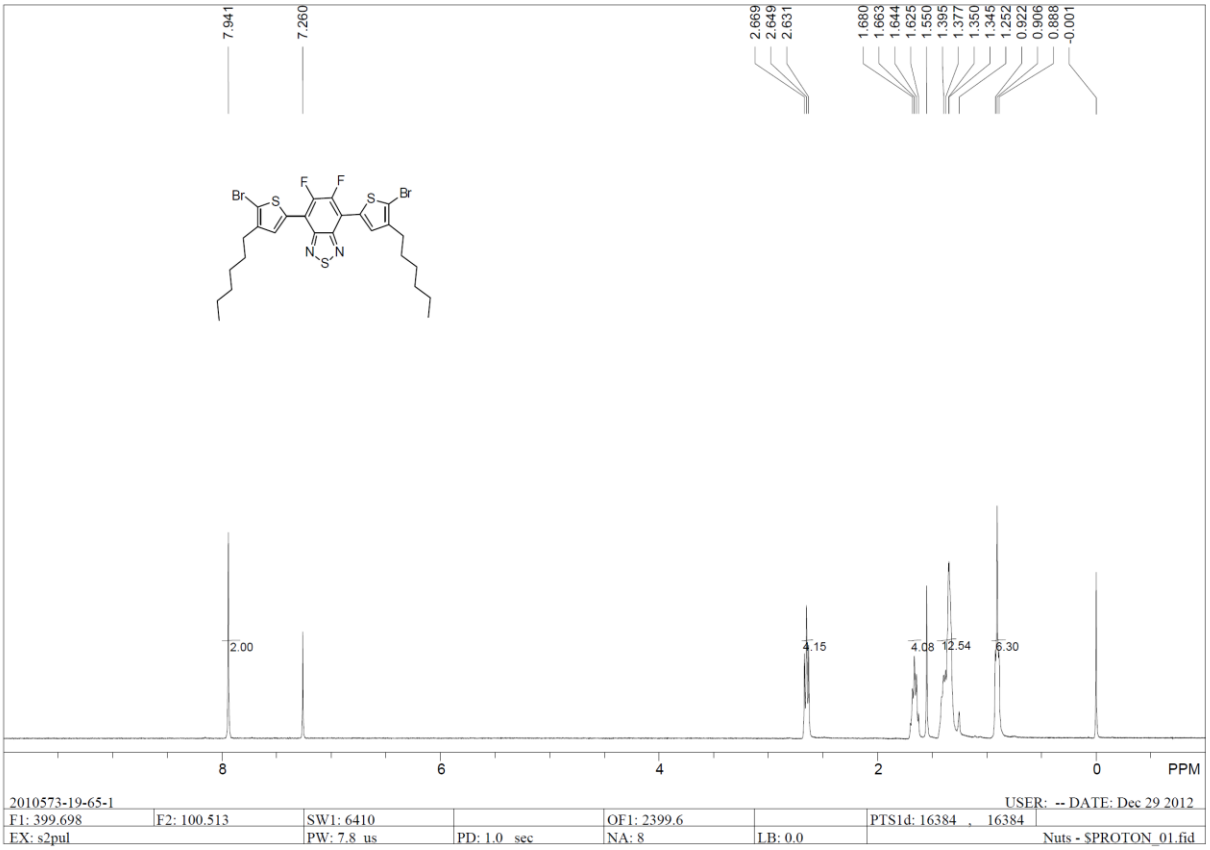
5-(7-Bromo-5,6-difluoro-2-octyl-2H-benzo[d][1,2,3]triazol-4-yl)thiophene-2-carbaldehyde(3q).

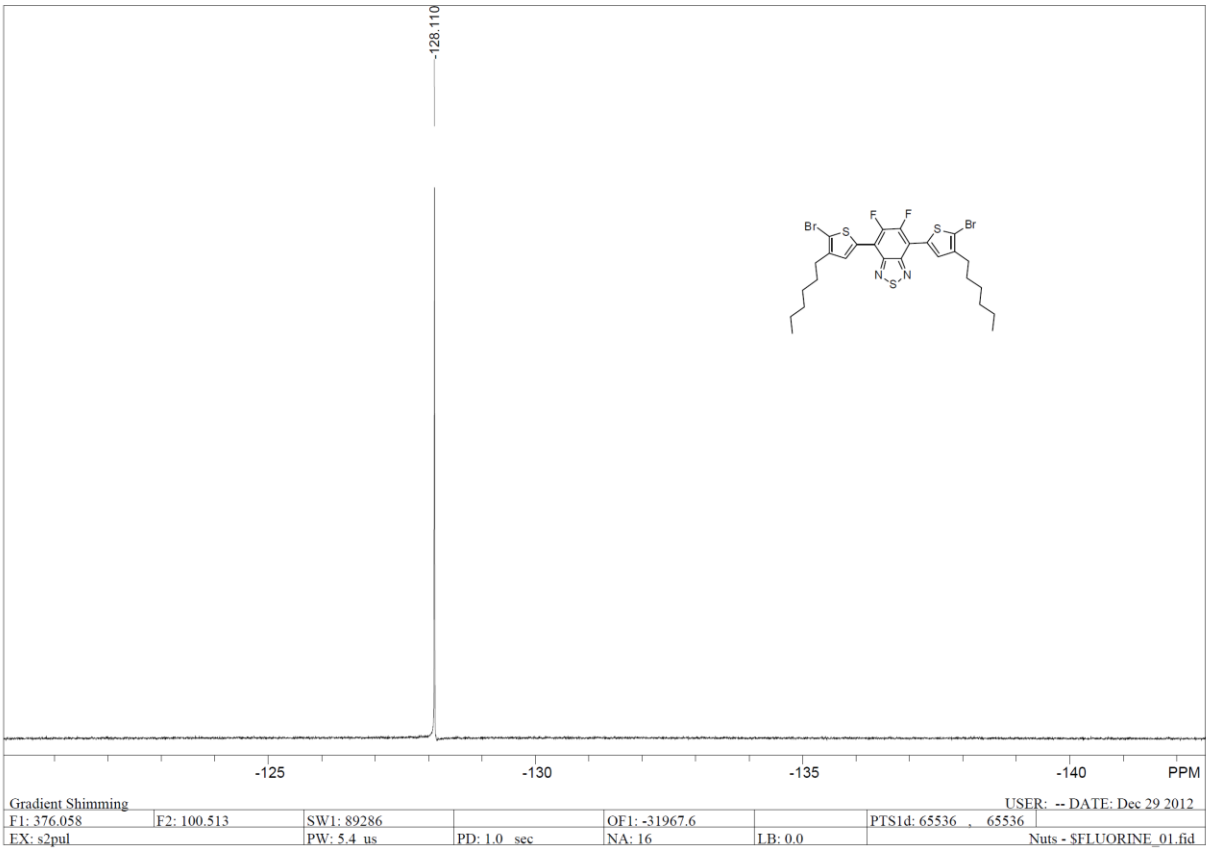


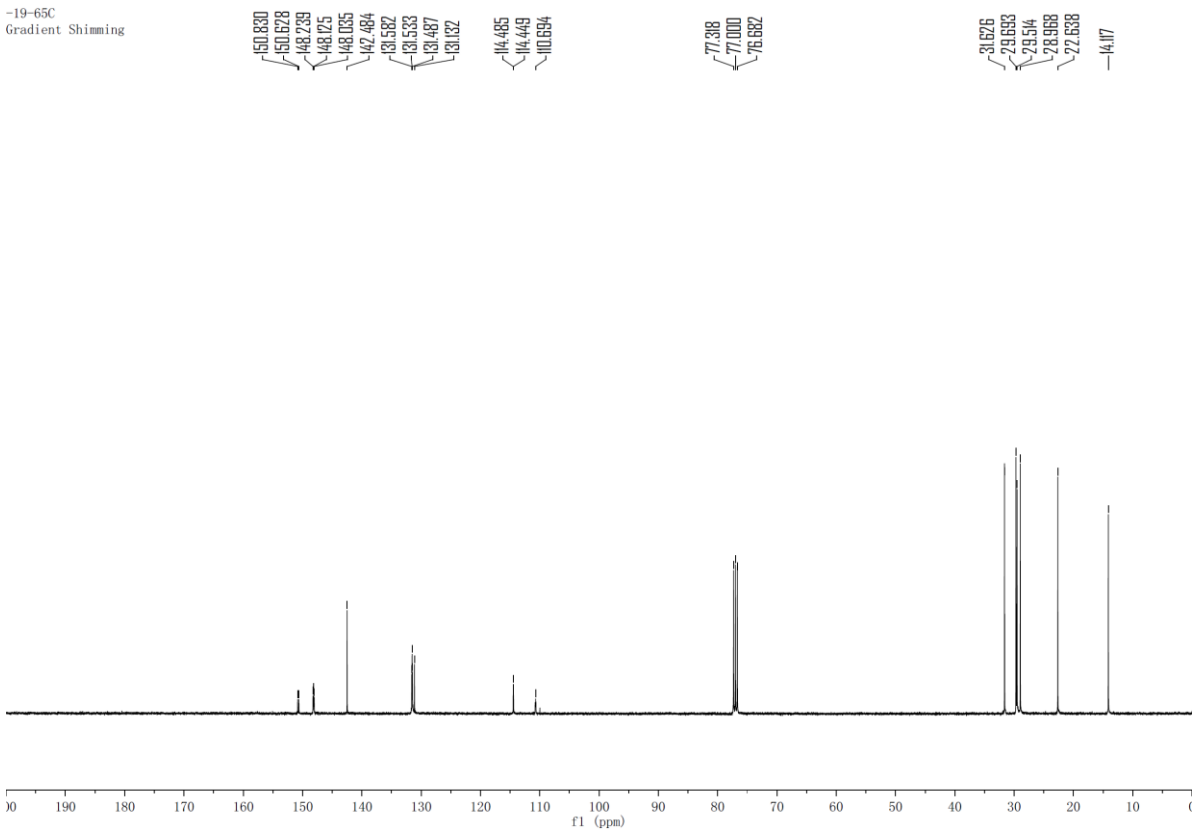

128.686
128.756
129.198
129.268
F
F
Br
S
H
O
N
N
N
C_8H_{17}
0.97
1.00
20
-122
-124
-126
-128
-130
-132
-134
-136
-138
PPM
;blank line
USER: -- DATE: May 30 2013
F1: 282.294
F2: 300.040
SW1: 64935
OF1: -23997.0
PTS1d: 19449 , 32768
EX: s2pul
PW: 6.0 us
PD: 1.5 sec
NA: 16
LB: 0.0
Nuts - $-22-47F_30May2013


-22-47-C
Gradient Shimming
183.377
150.399
150.247
149.159
148.984
147.946
147.796
146.590
146.445
144.576
144.508
140.452
139.644
139.600
136.587
136.505
135.792
130.842
130.771
110.196
110.070
96.907
96.682
77.318
77.000
76.681
57.389
31.865
31.635
29.978
29.643
29.307
28.985
28.881
26.432
22.636
22.537
14.068
14.008
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

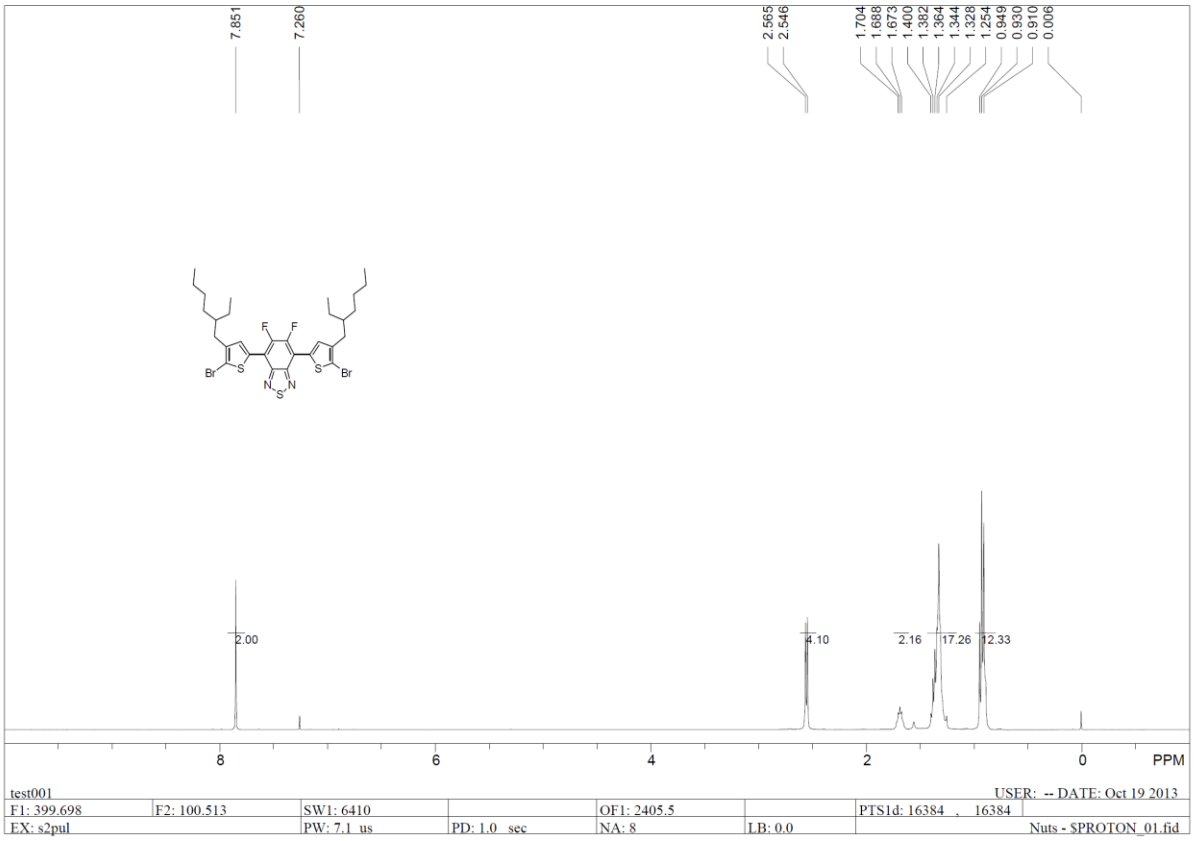
4,7-bis(5-bromo-4-hexylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (6a).

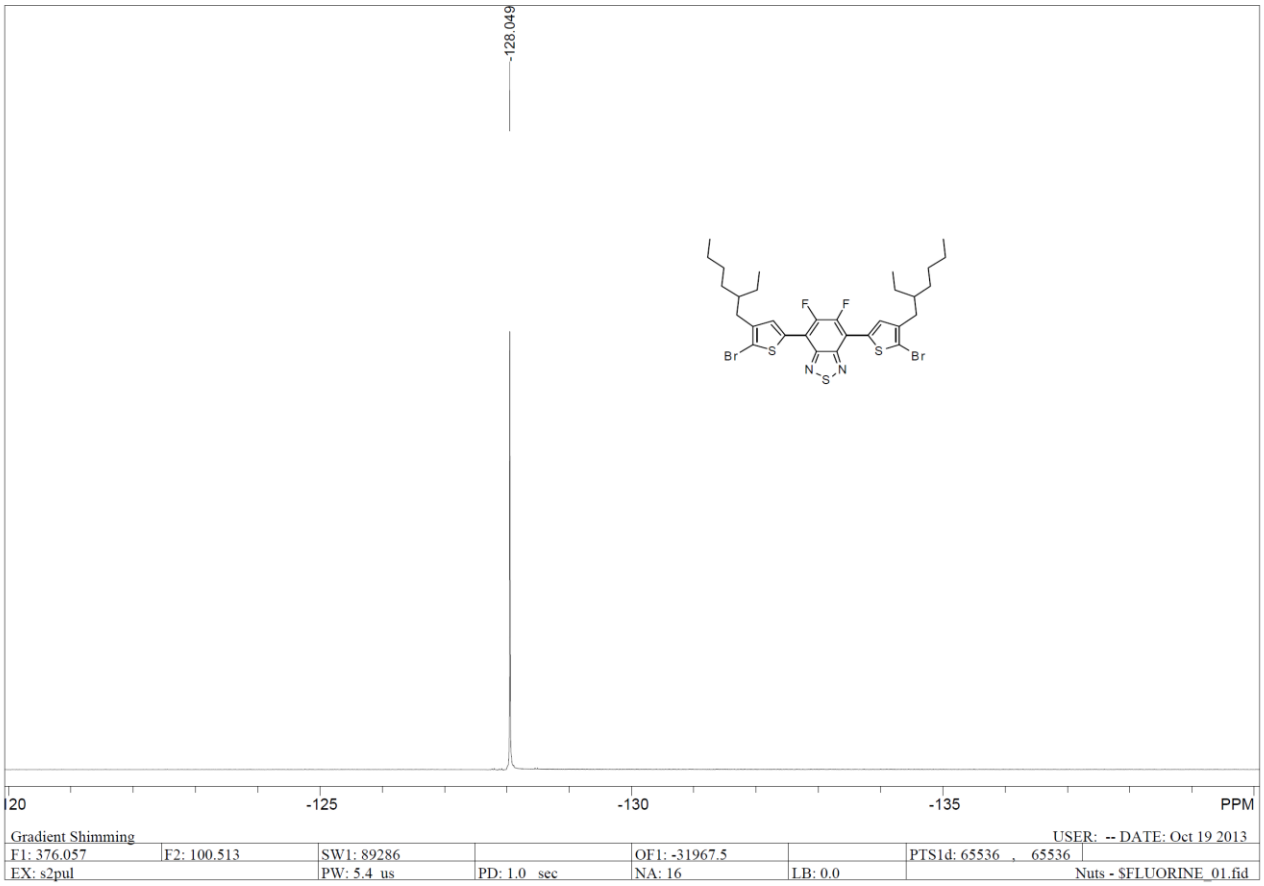






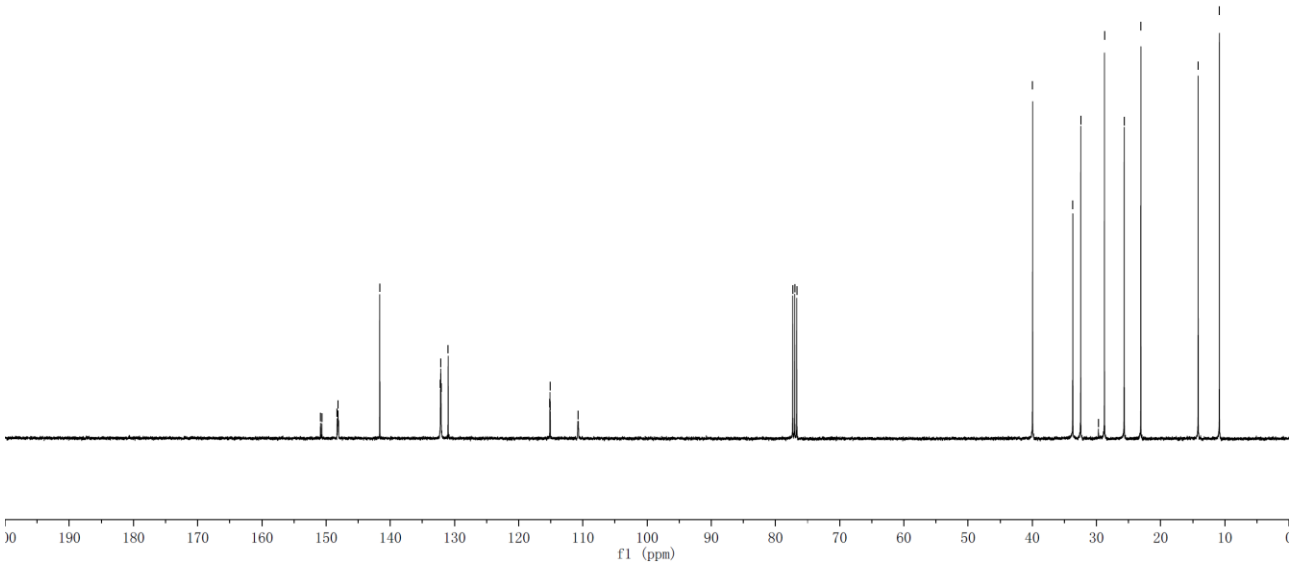
4,4'-(5,5'-(5,6-difluorobenzo[c][1,2,5]thiadiazole-4,7-diyl)bis(3-hexylthiophene-5,2-diyl))bis(N,N-diphenylanil ine) (6b).



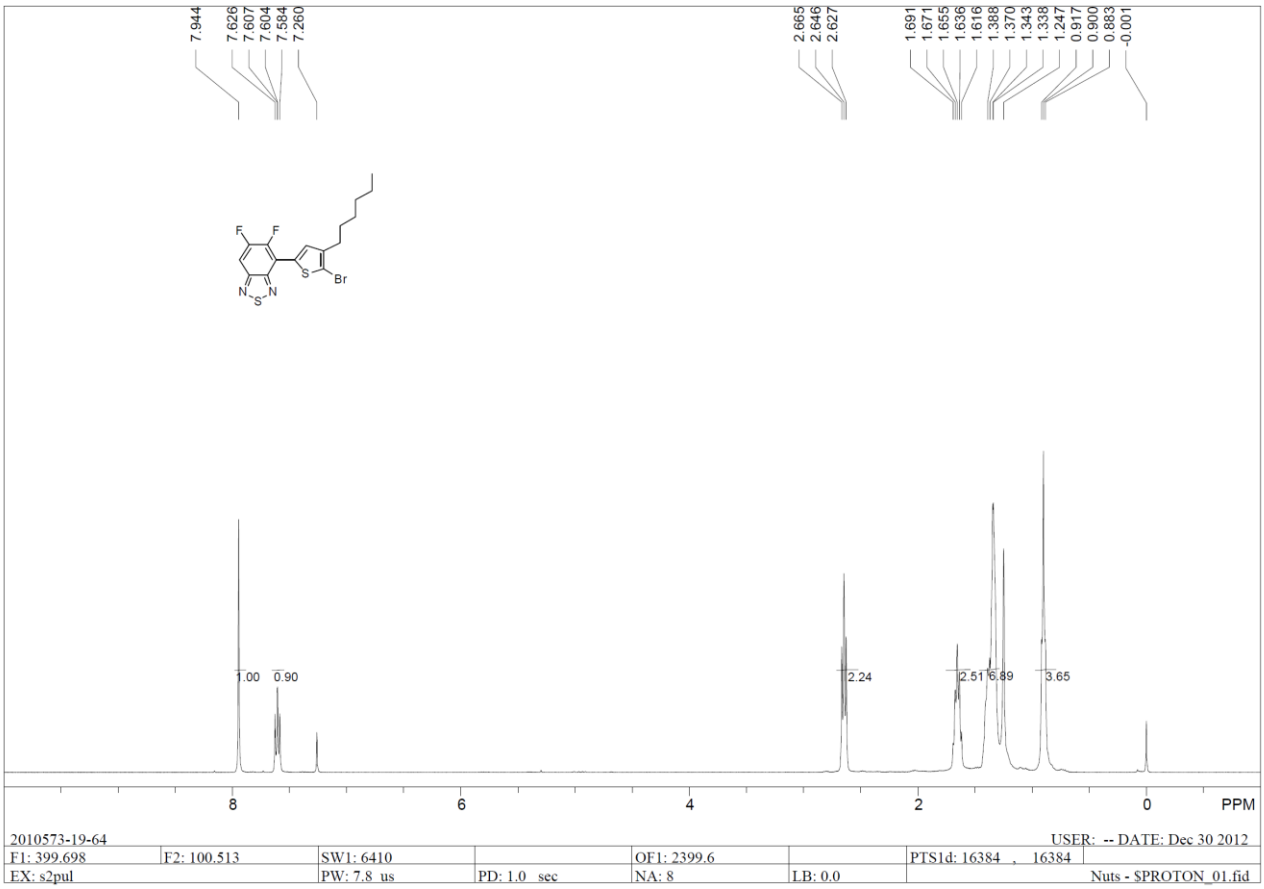


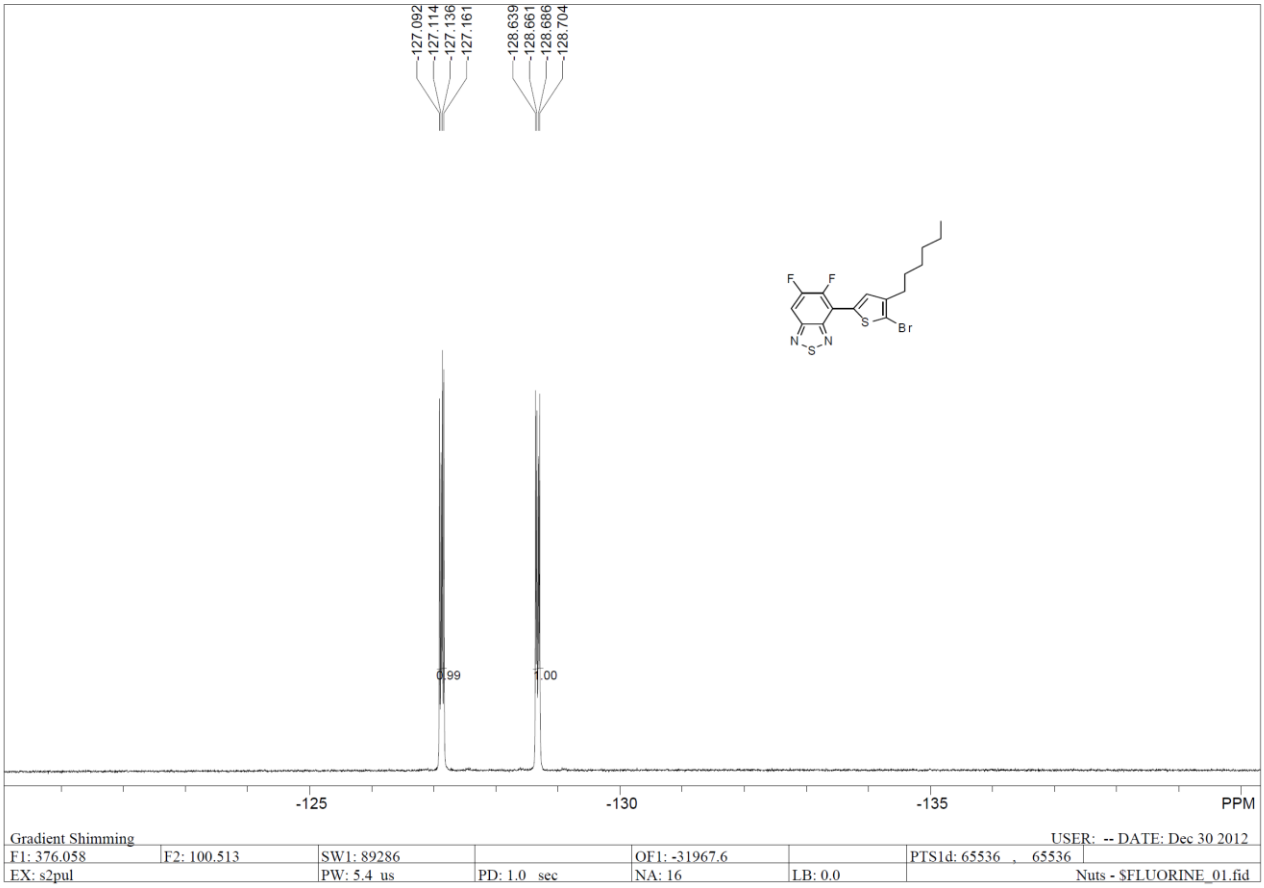
-24-54-1C

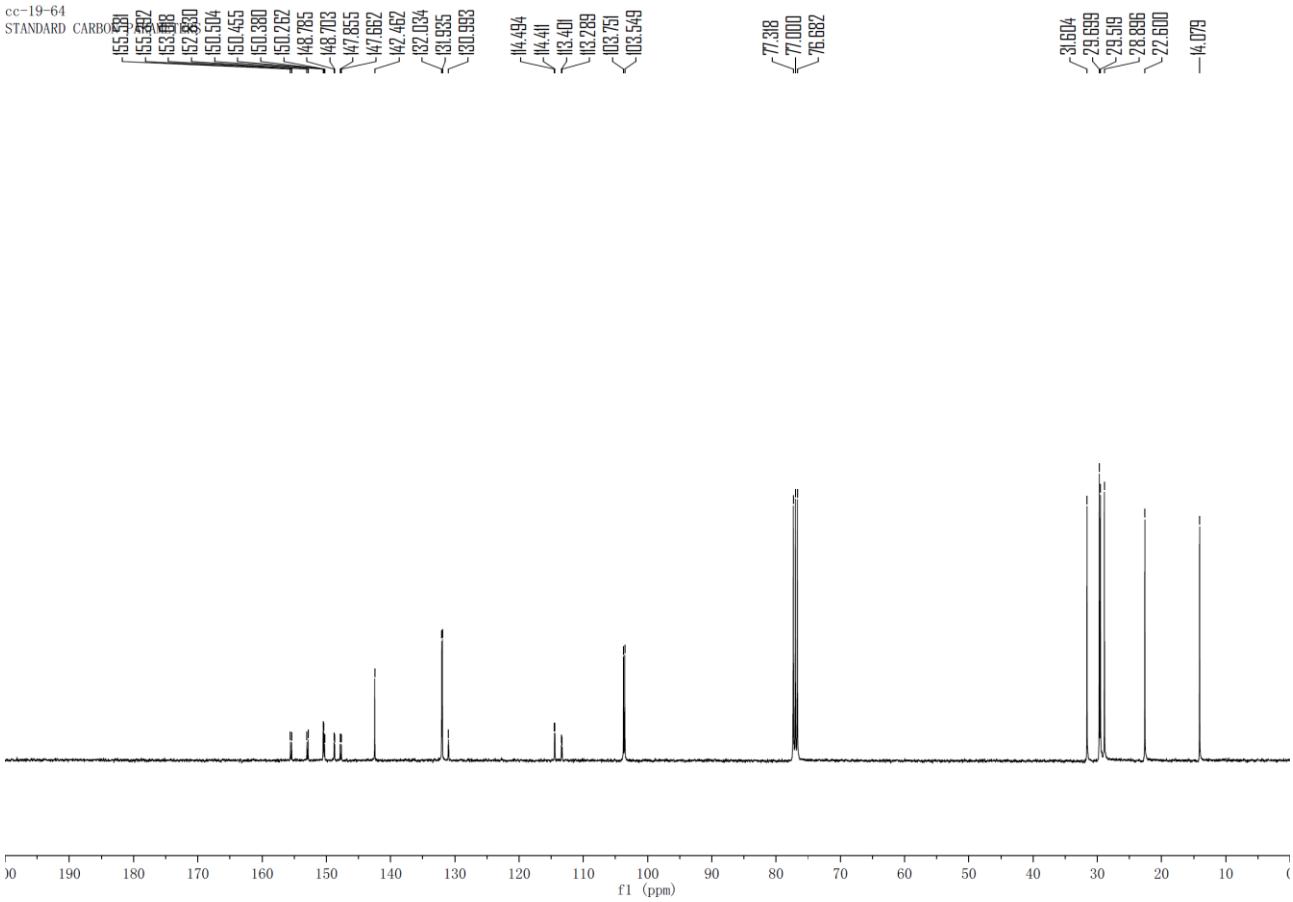
150.857
150.657
148.268
148.141
141.641
132.182
132.133
132.088
130.988
115.149
115.113
115.077
110.708
77.317
77.000
76.682
39.949
33.683
32.455
29.689
28.753
25.681
23.083
14.152
10.847



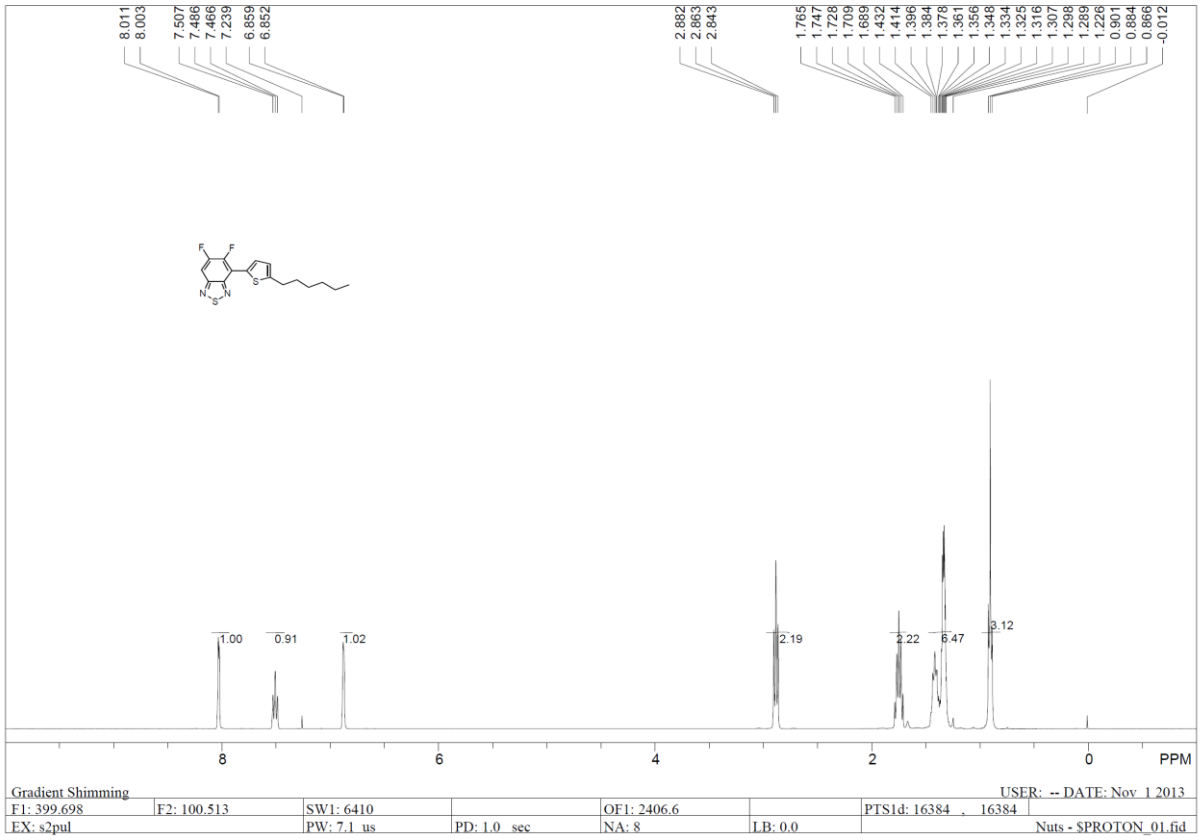
4-(5-Bromo-4-hexylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (7a).

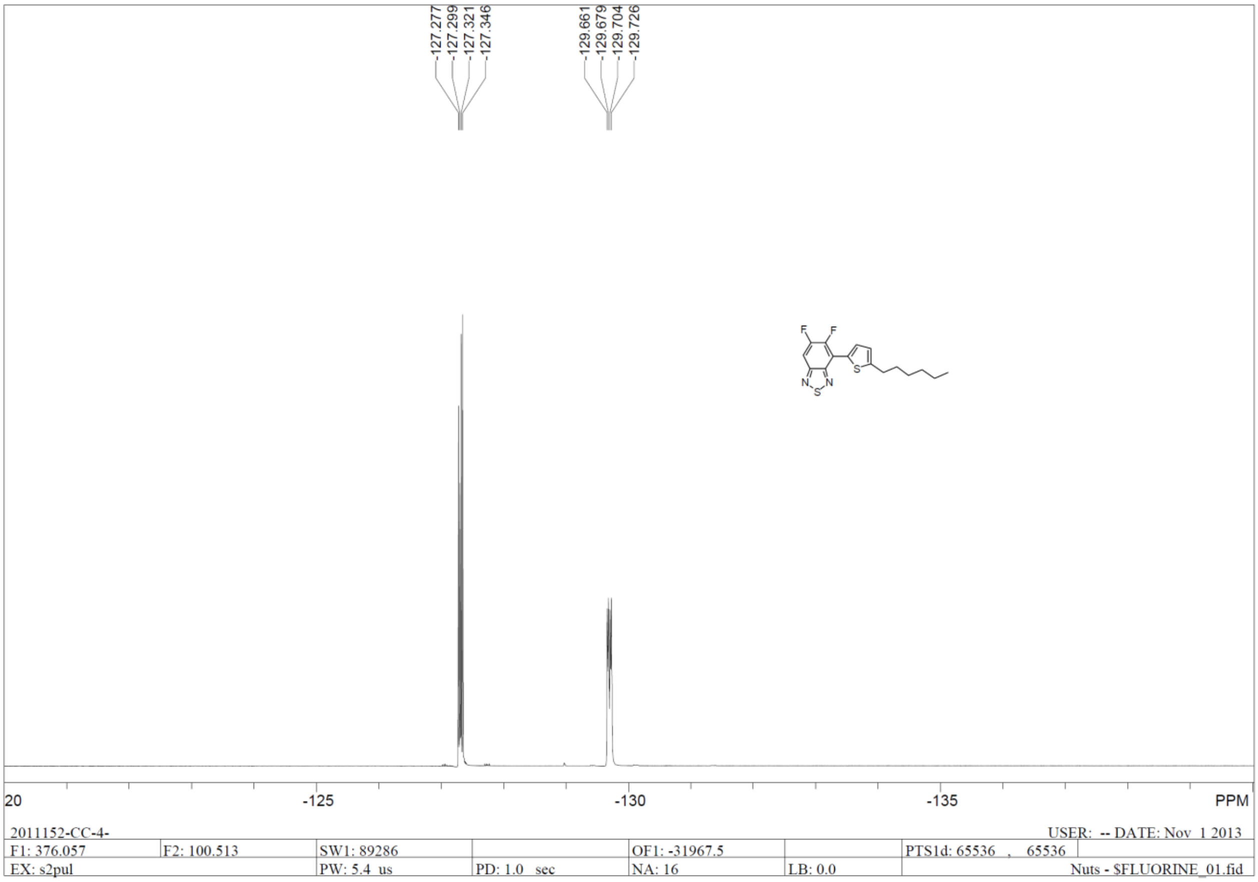


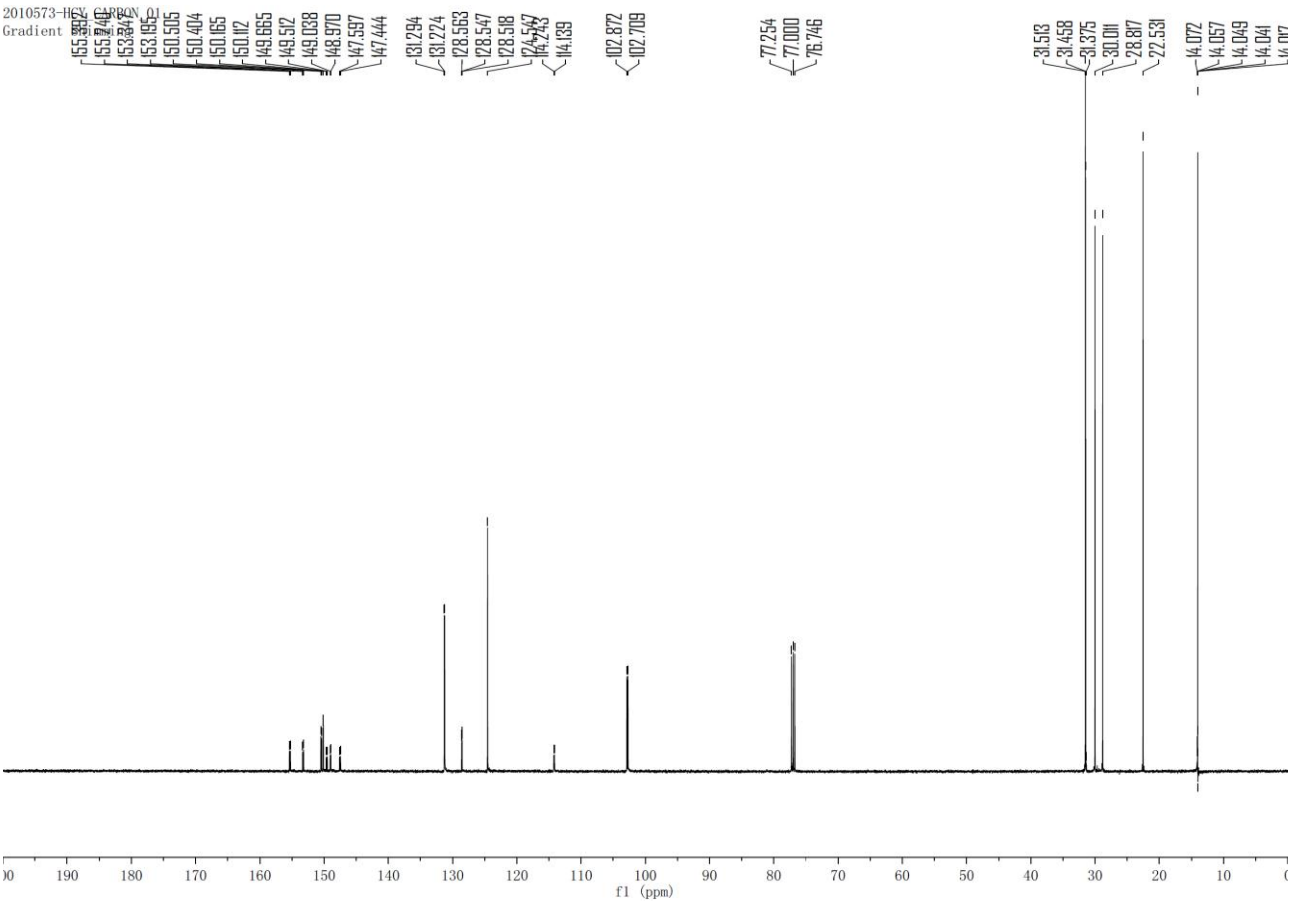




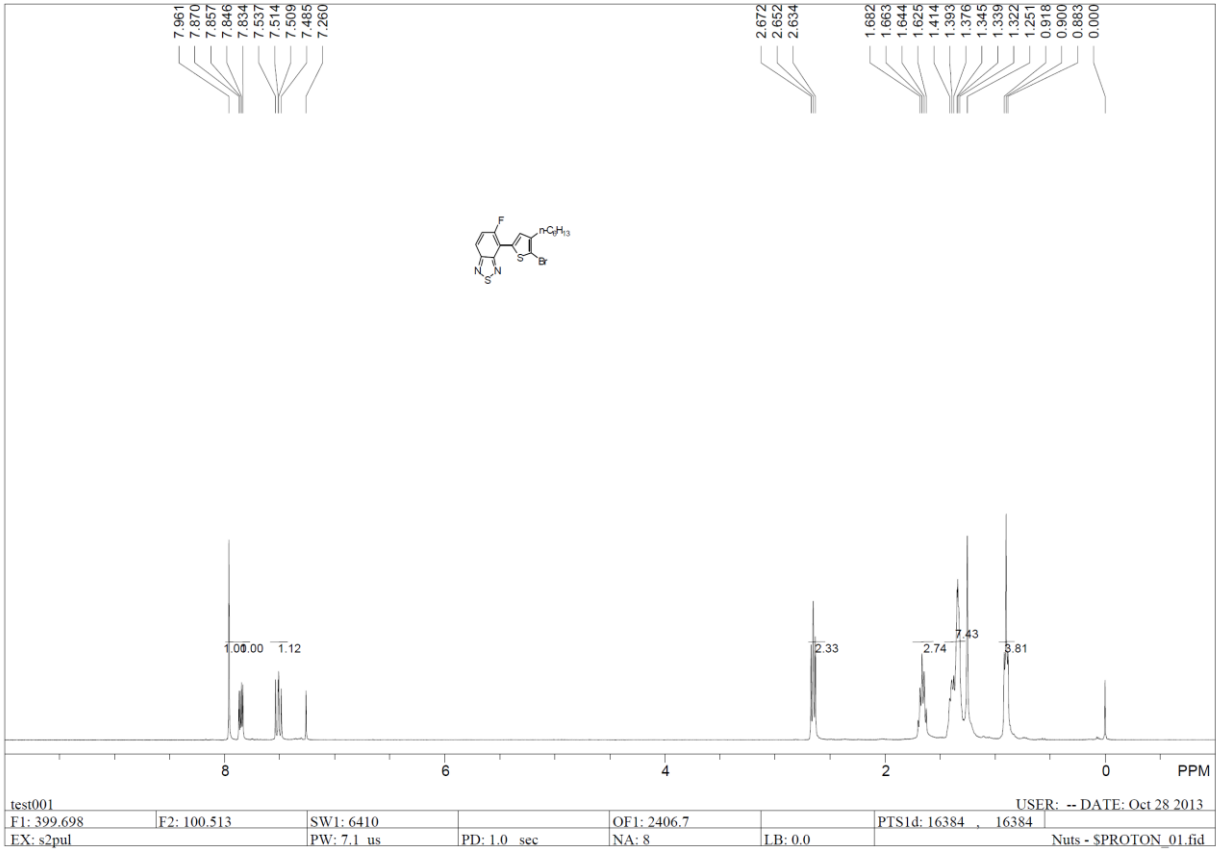
5,6-Difluoro-4-(5-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole(7c).

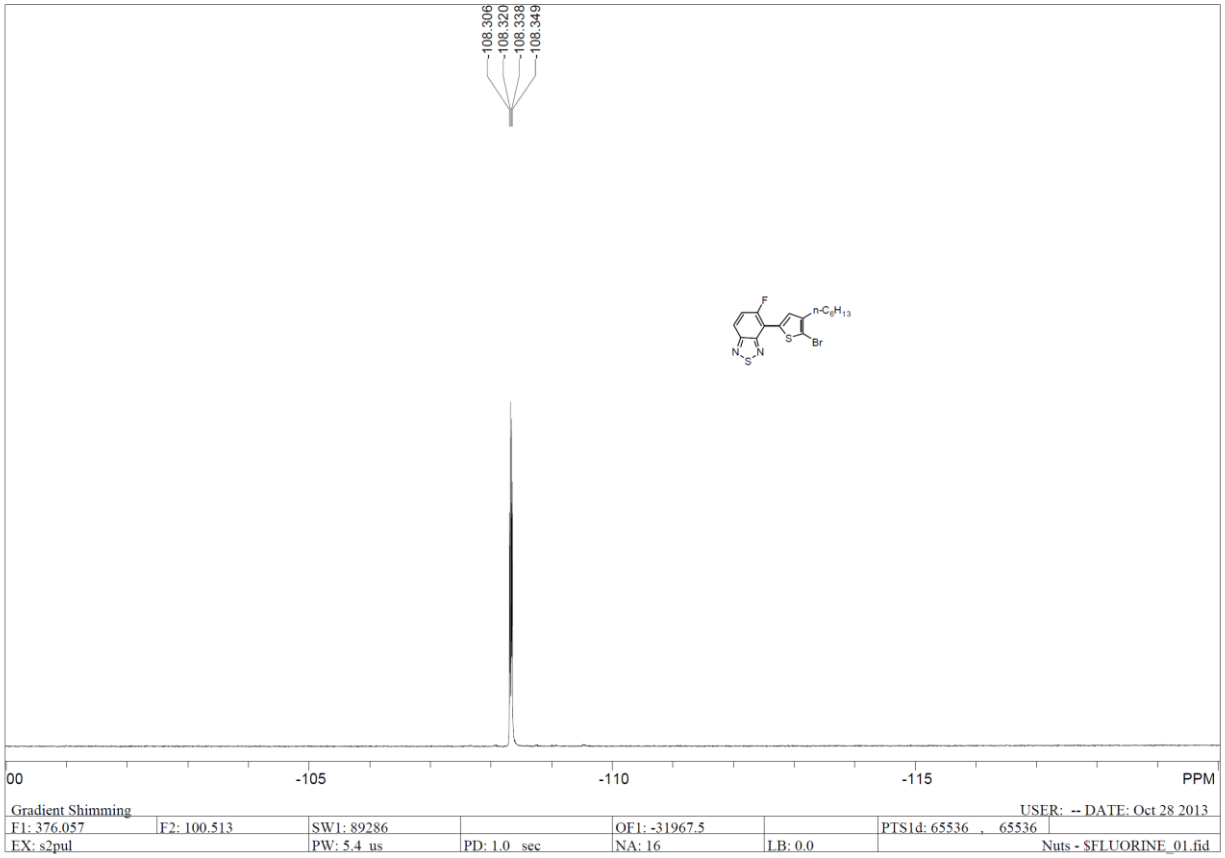


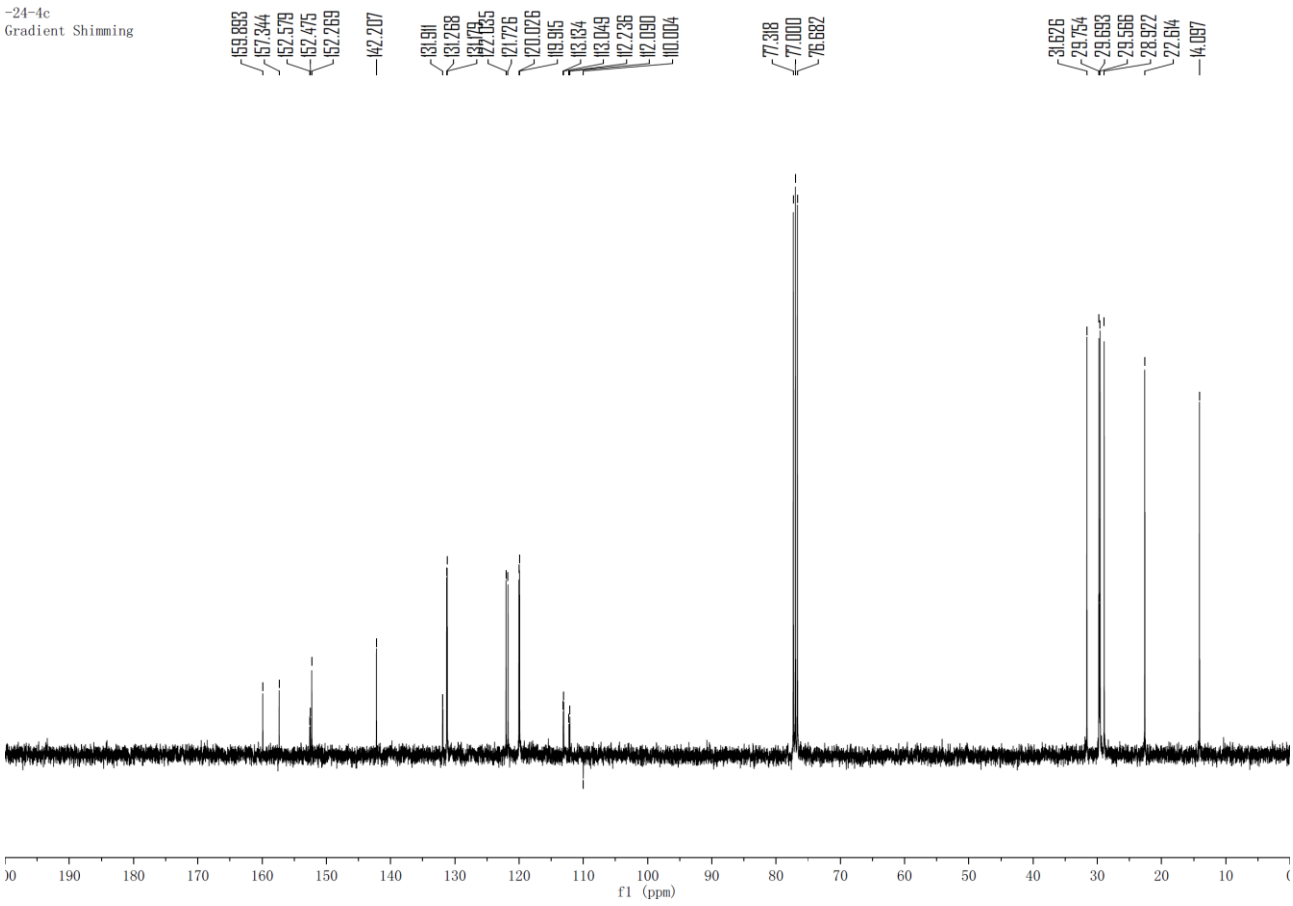

-127.277
-127.299
-127.321
-127.346
-129.661
-129.679
-129.704
-129.726
-125
-130
-135
PPM
2011152-CC-4-
USER: -- DATE: Nov 1 2013
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.4 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $FLUORINE_01.fid


153.195
150.505
150.404
150.165
150.112
149.665
149.512
149.038
148.970
147.597
147.444
131.294
131.224
128.563
128.547
128.518
114.243
114.139
102.872
102.709
77.254
77.000
76.746
31.513
31.458
31.375
30.011
28.817
22.531
14.072
14.057
14.049
14.041
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

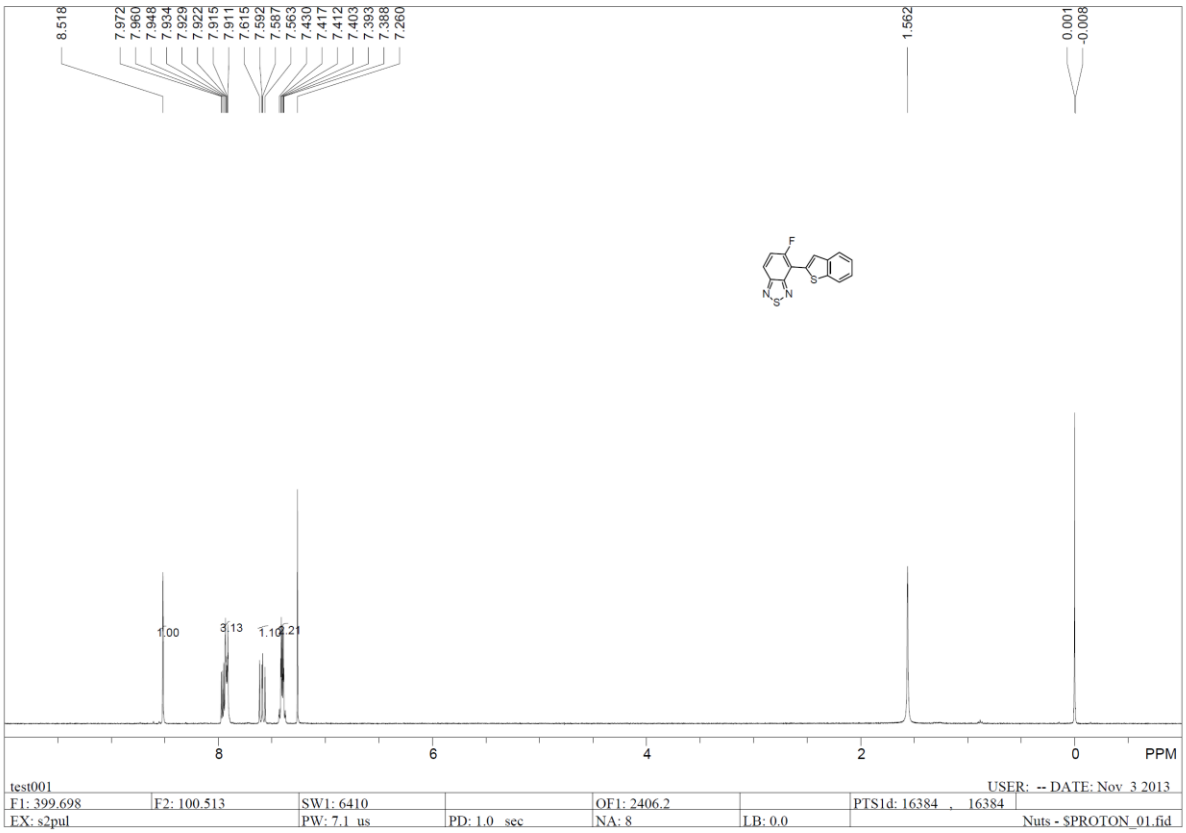
4-(5-Bromo-4-hexylthiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (9a).

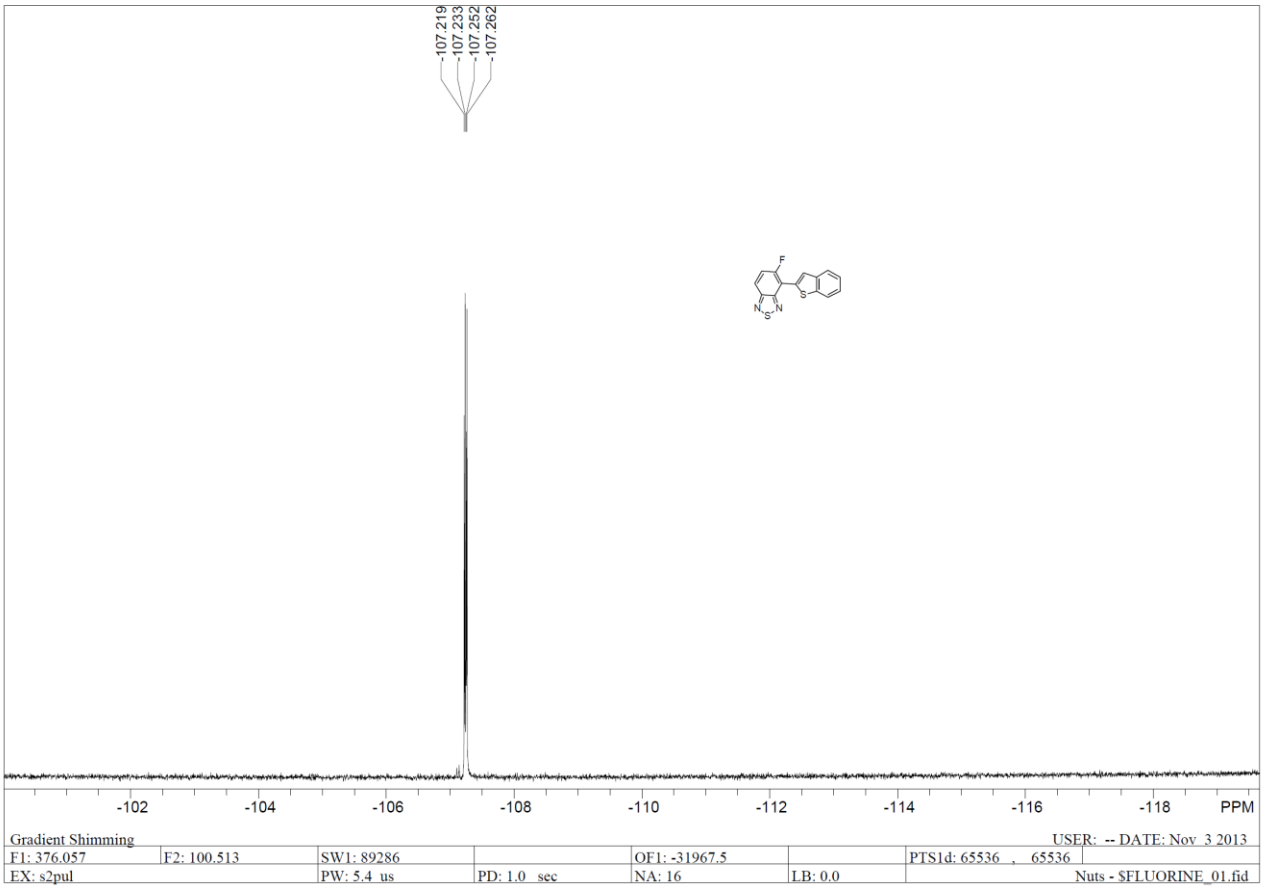


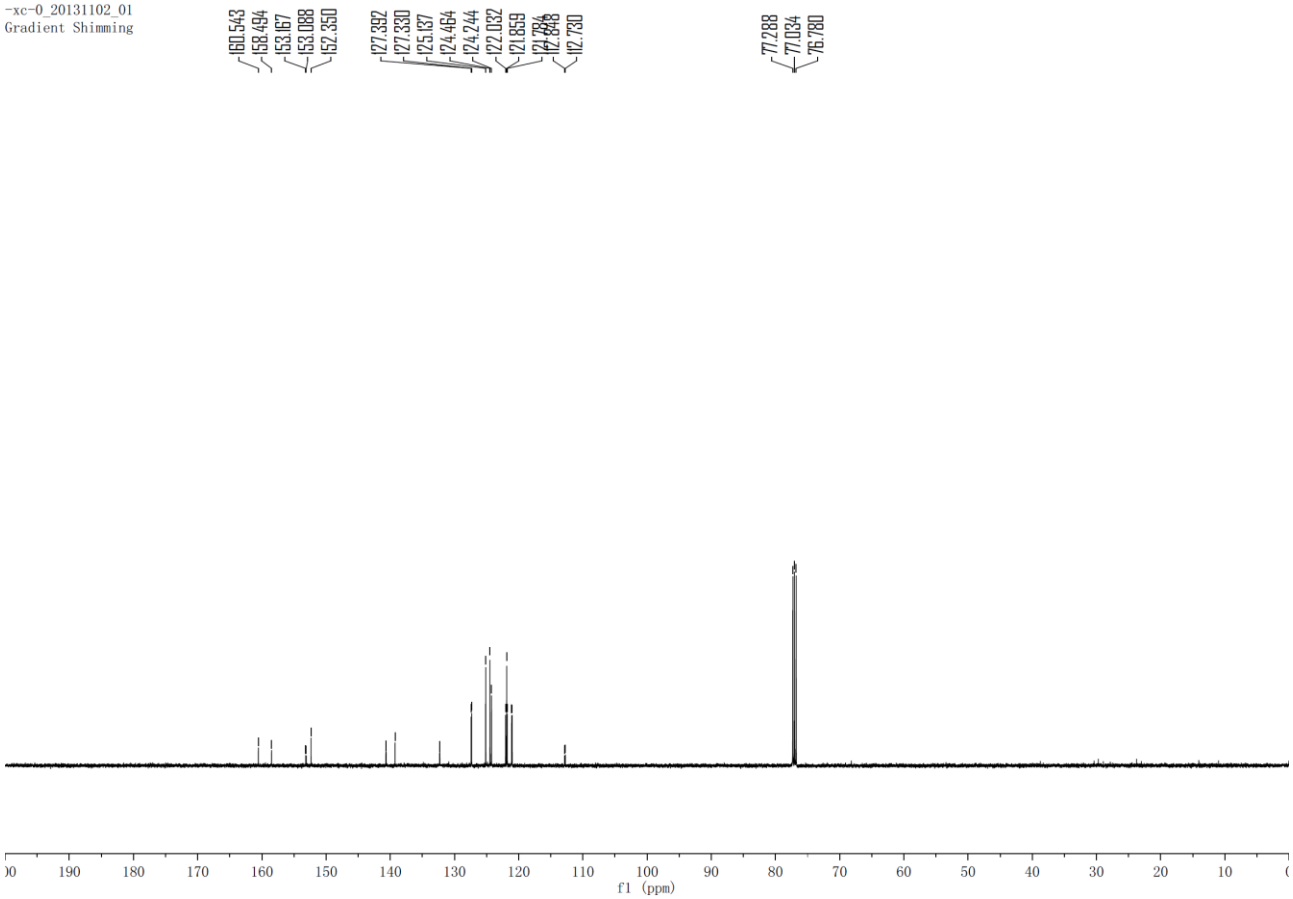




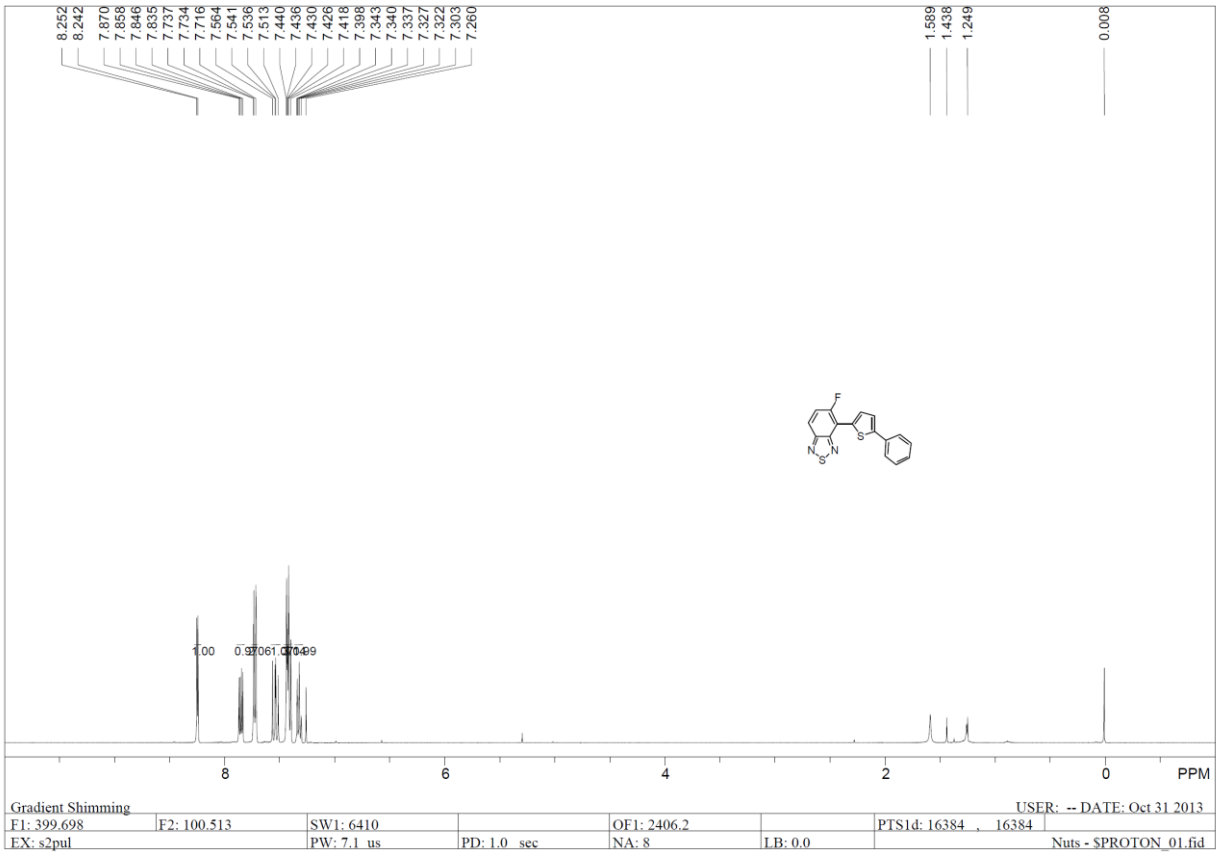
4-(Benzo[b]thiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (9b).

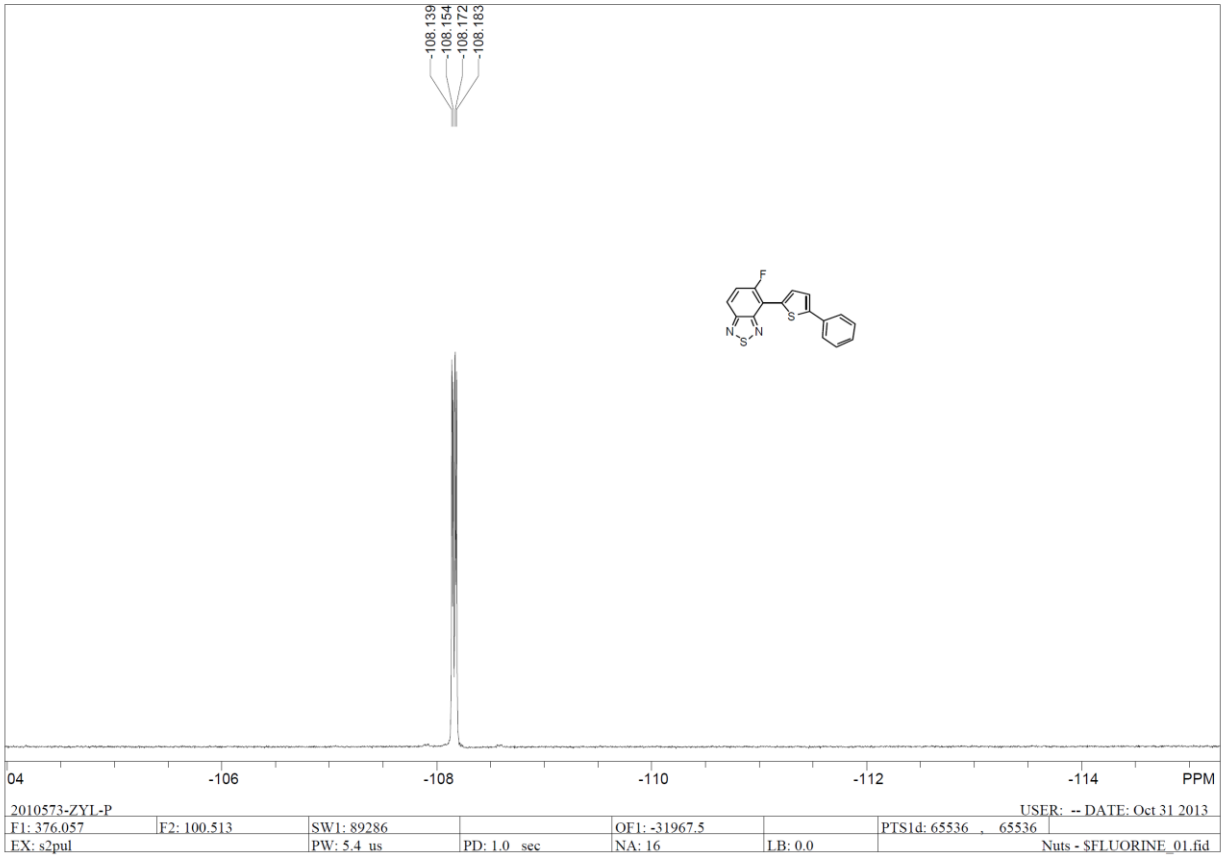


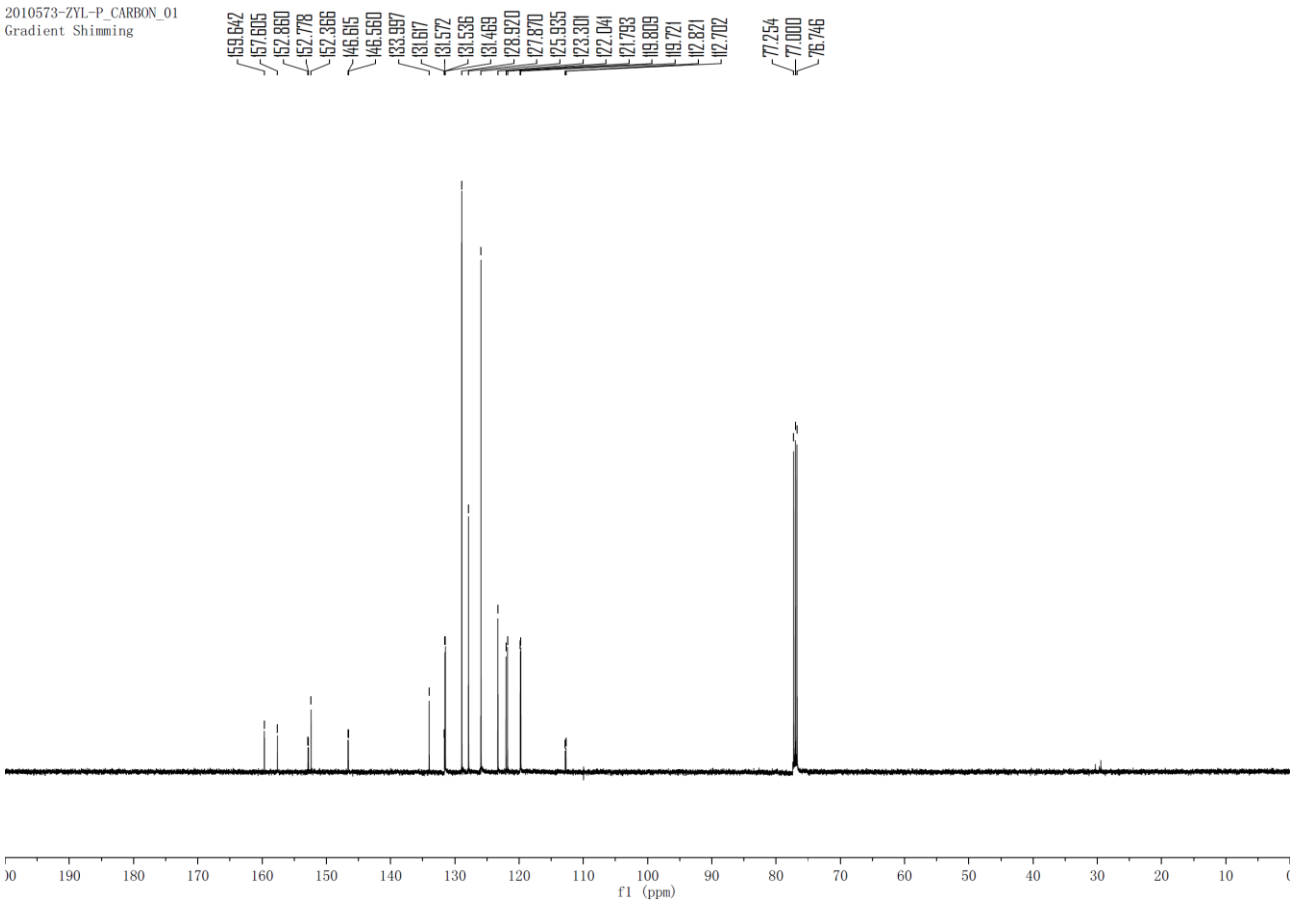

-107.219
-107.233
-107.252
-107.262
F
S
N
S
N
-102
-104
-106
-108
-110
-112
-114
-116
-118
PPM
Gradient Shimming
USER: -- DATE: Nov 3 2013
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.4 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $FLUORINE_01.fid


-xc-0_20131102_01
Gradient Shimming
160.543
158.494
153.167
153.088
152.350
127.392
127.330
125.137
124.464
124.244
122.032
121.859
77.288
77.034
76.780
f1 (ppm)

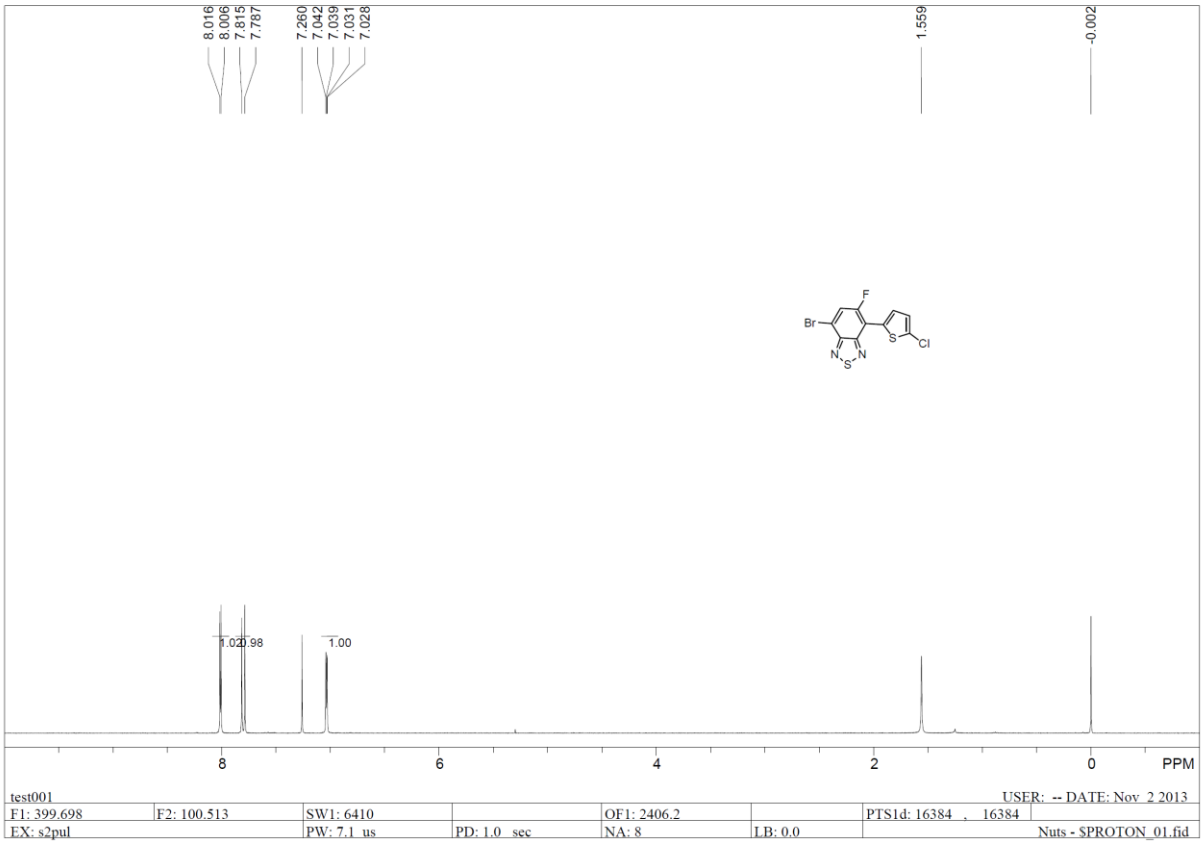
5-Fluoro-4-(5-phenylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (9c).

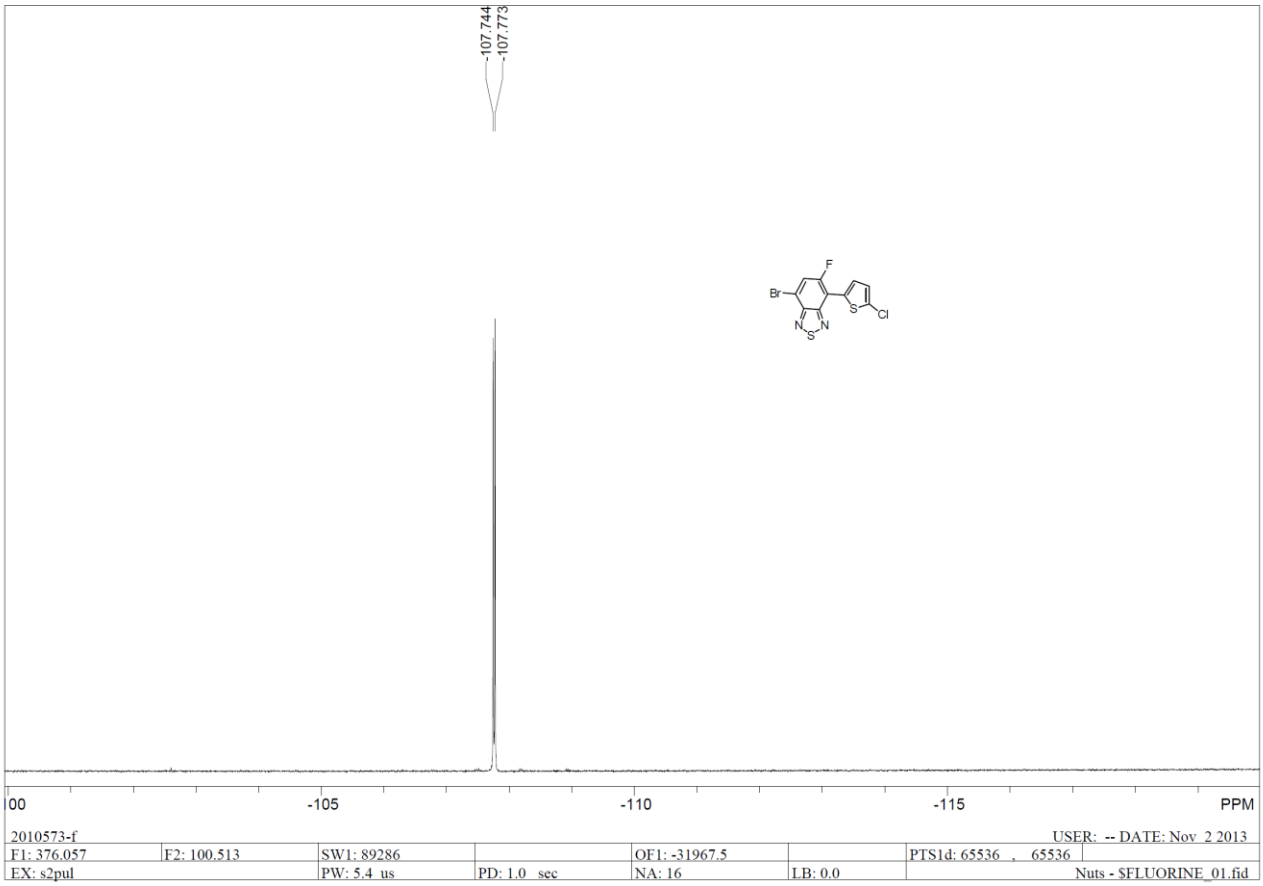


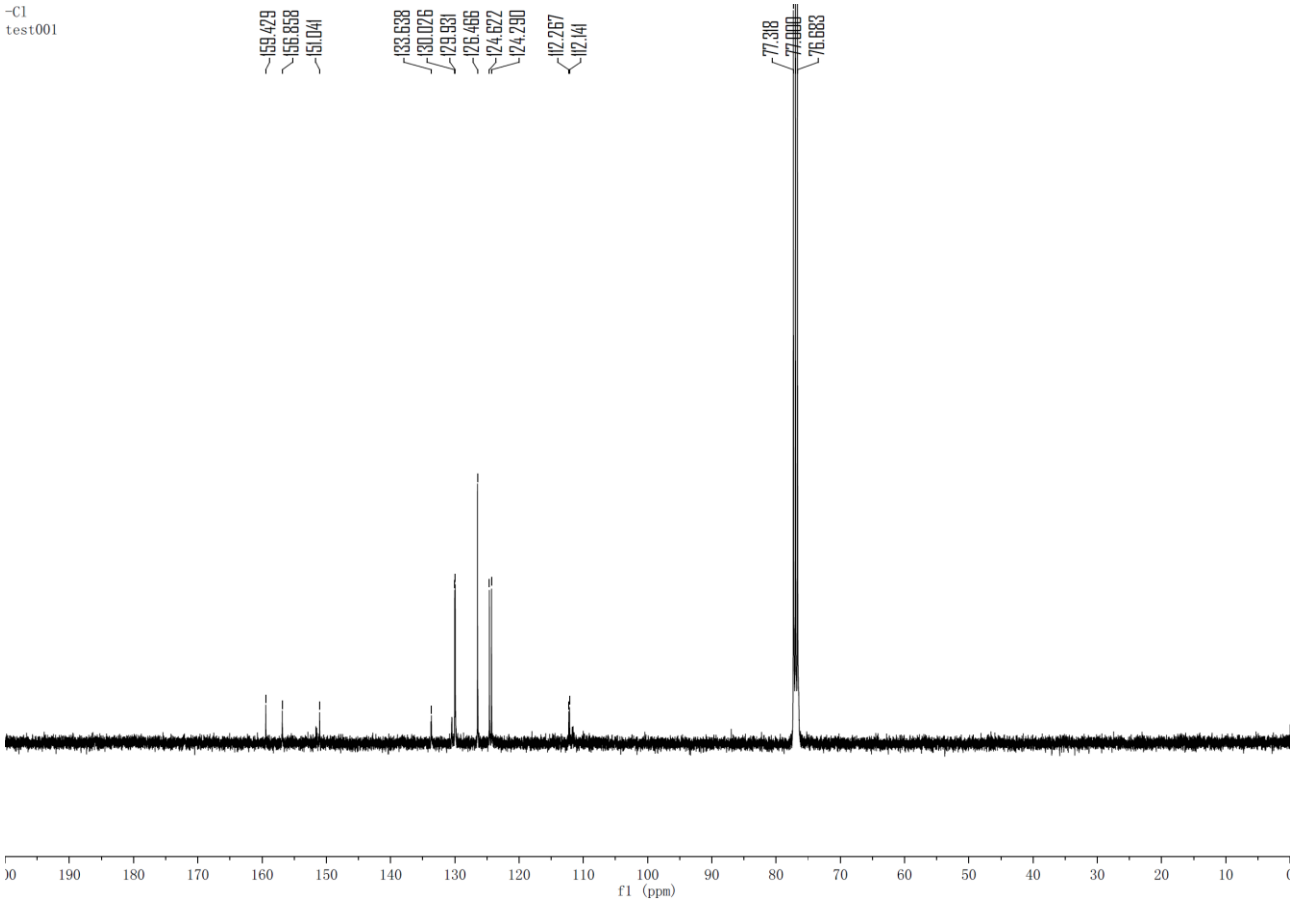




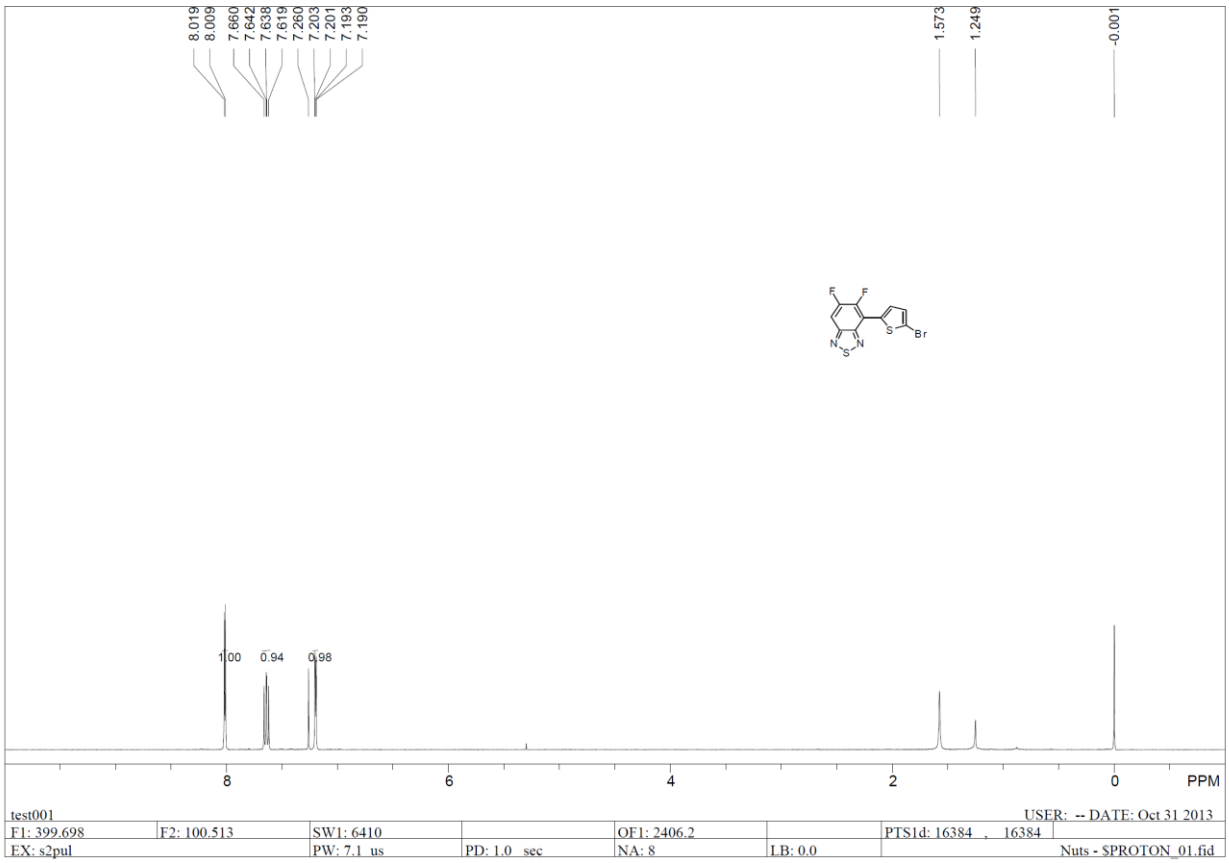
7-Bromo-4-(5-chlorothiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (9d).

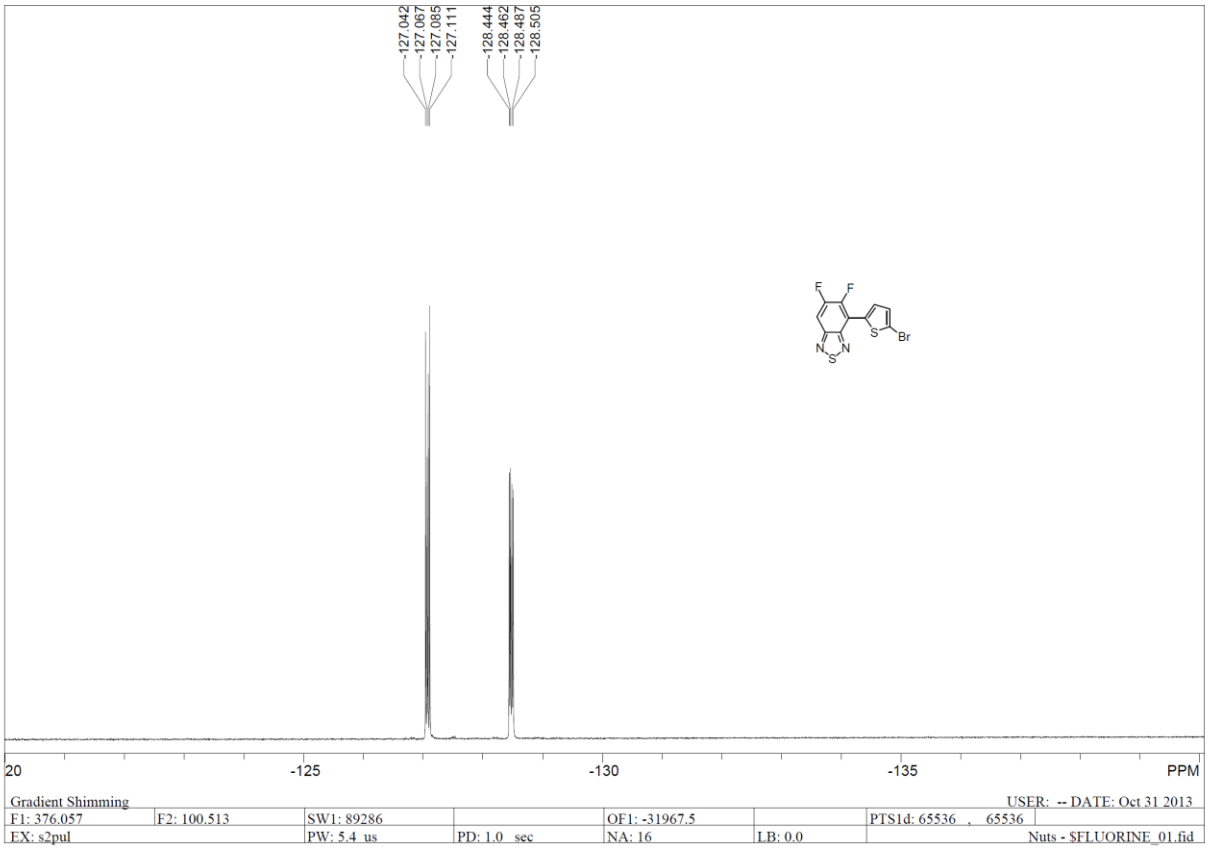


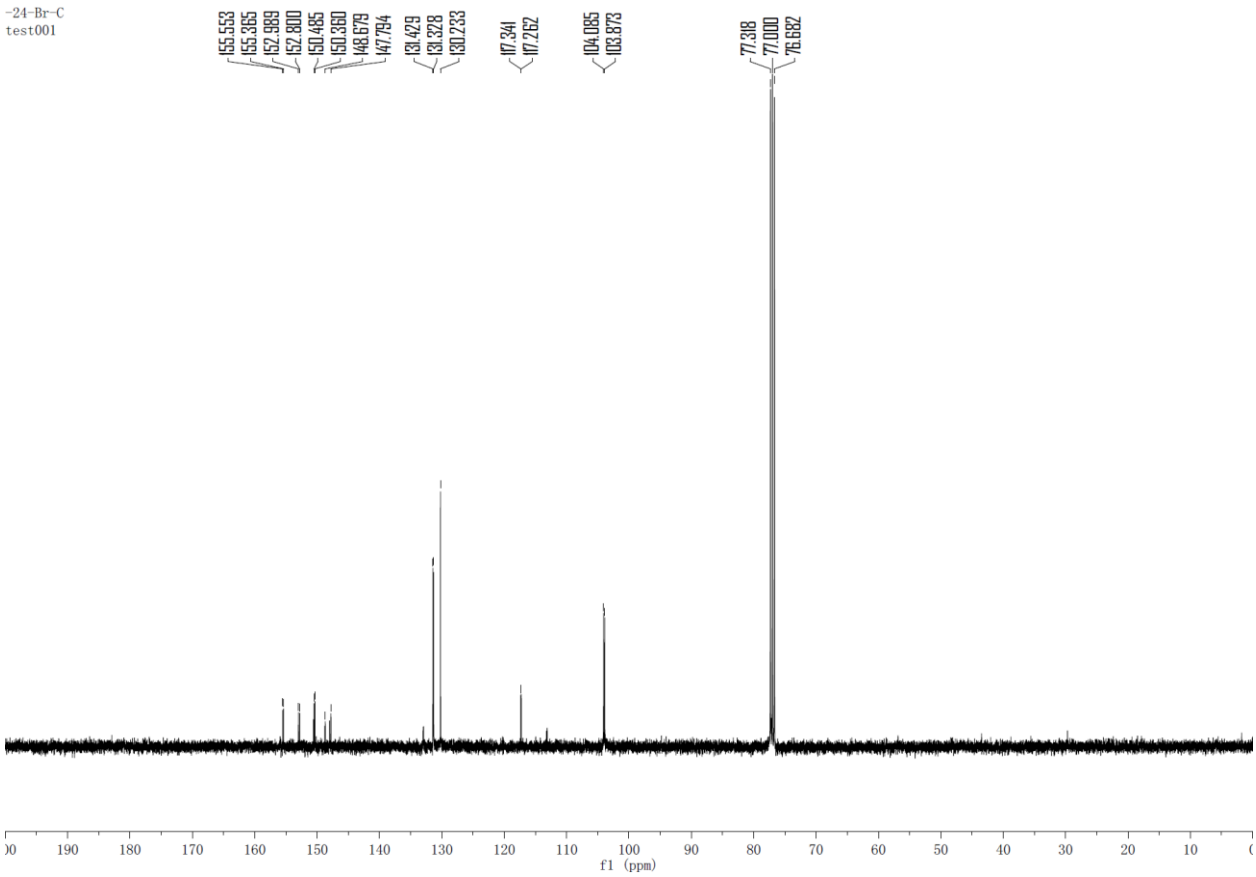

-107.744
-107.773
F
Br
S
Cl
N
N
S
00
-105
-110
-115
PPM
2010573-f
USER: -- DATE: Nov 2 2013
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.4 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $FLUORINE_01.fid


-Cl
test001
159.429
156.858
151.041
133.638
130.026
129.931
126.466
124.622
124.290
112.267
112.141
77.318
77.000
76.683
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

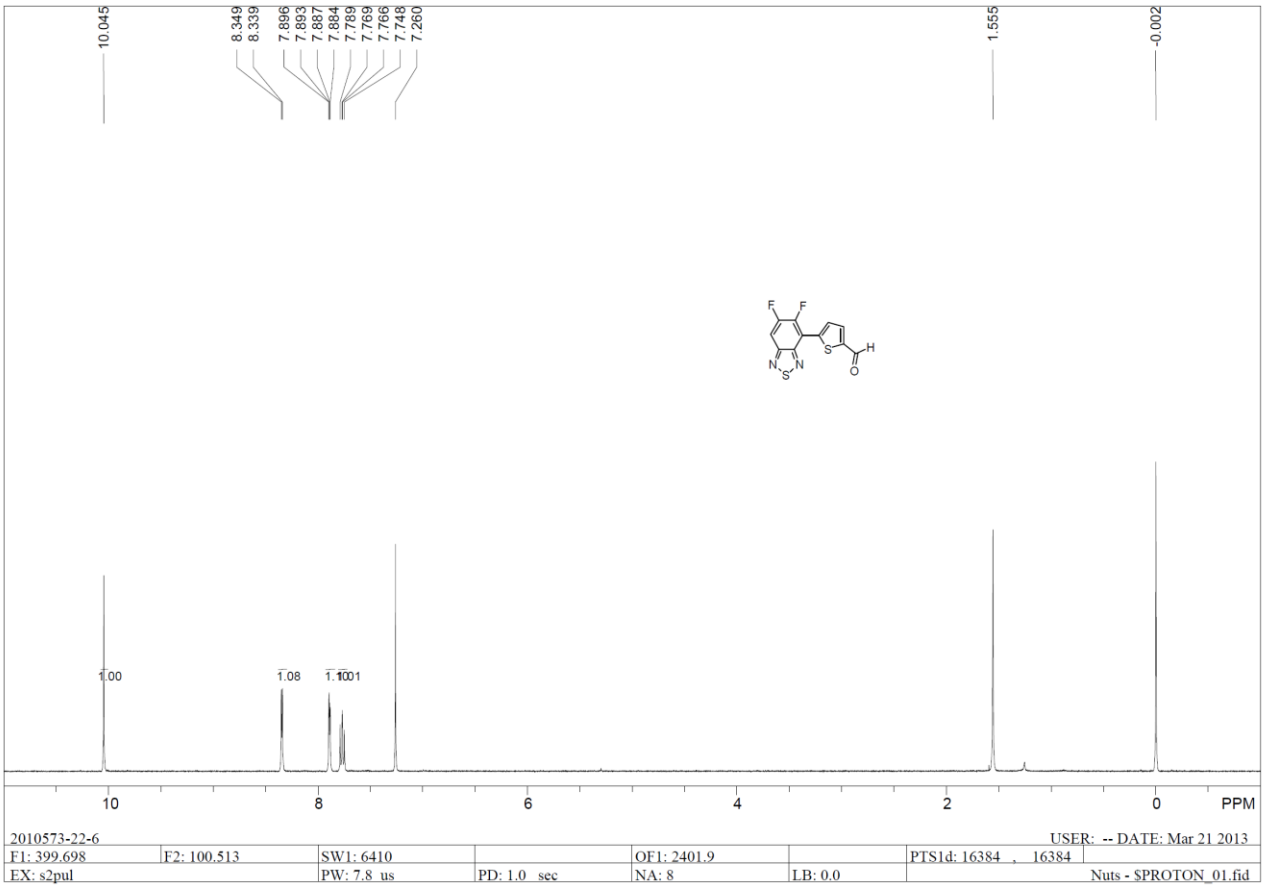
4-(5-Bromothiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (7d).

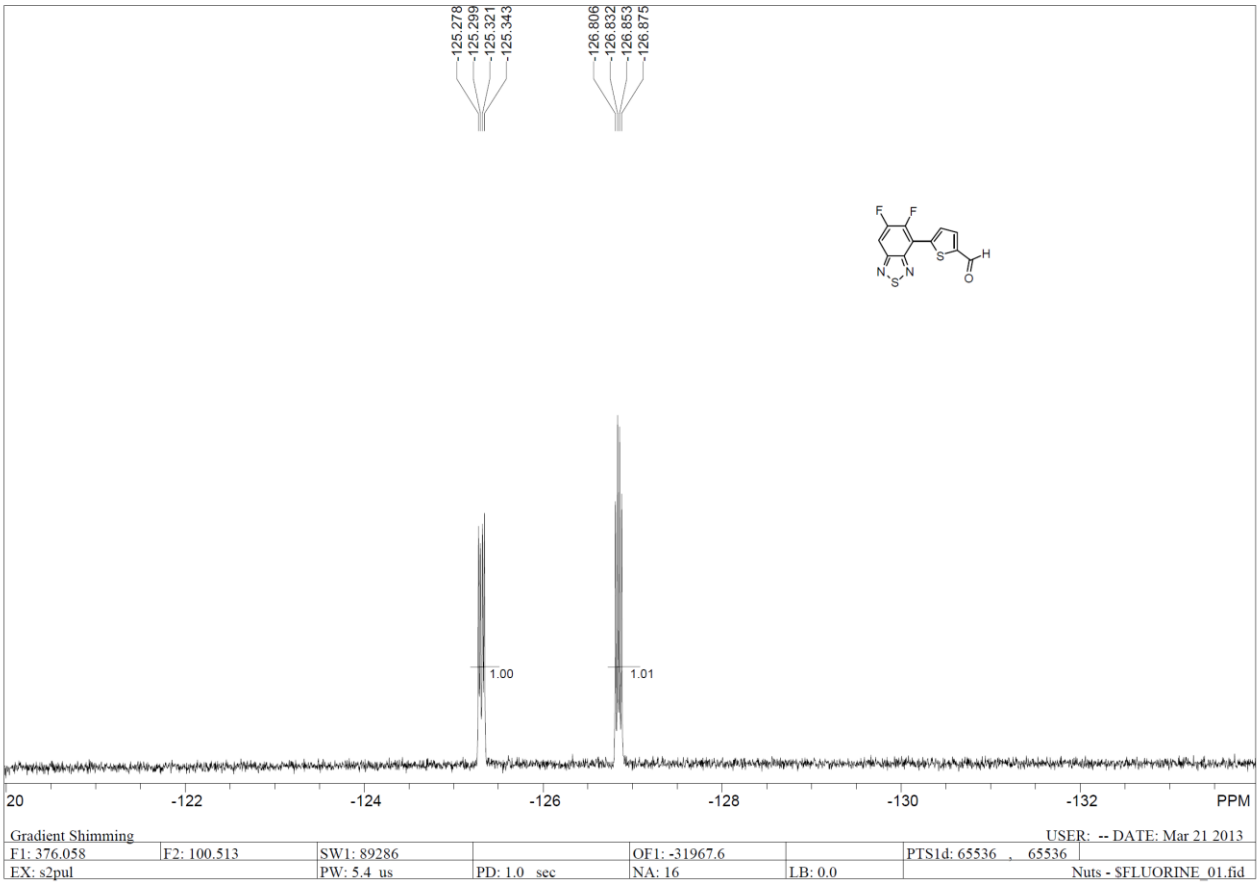


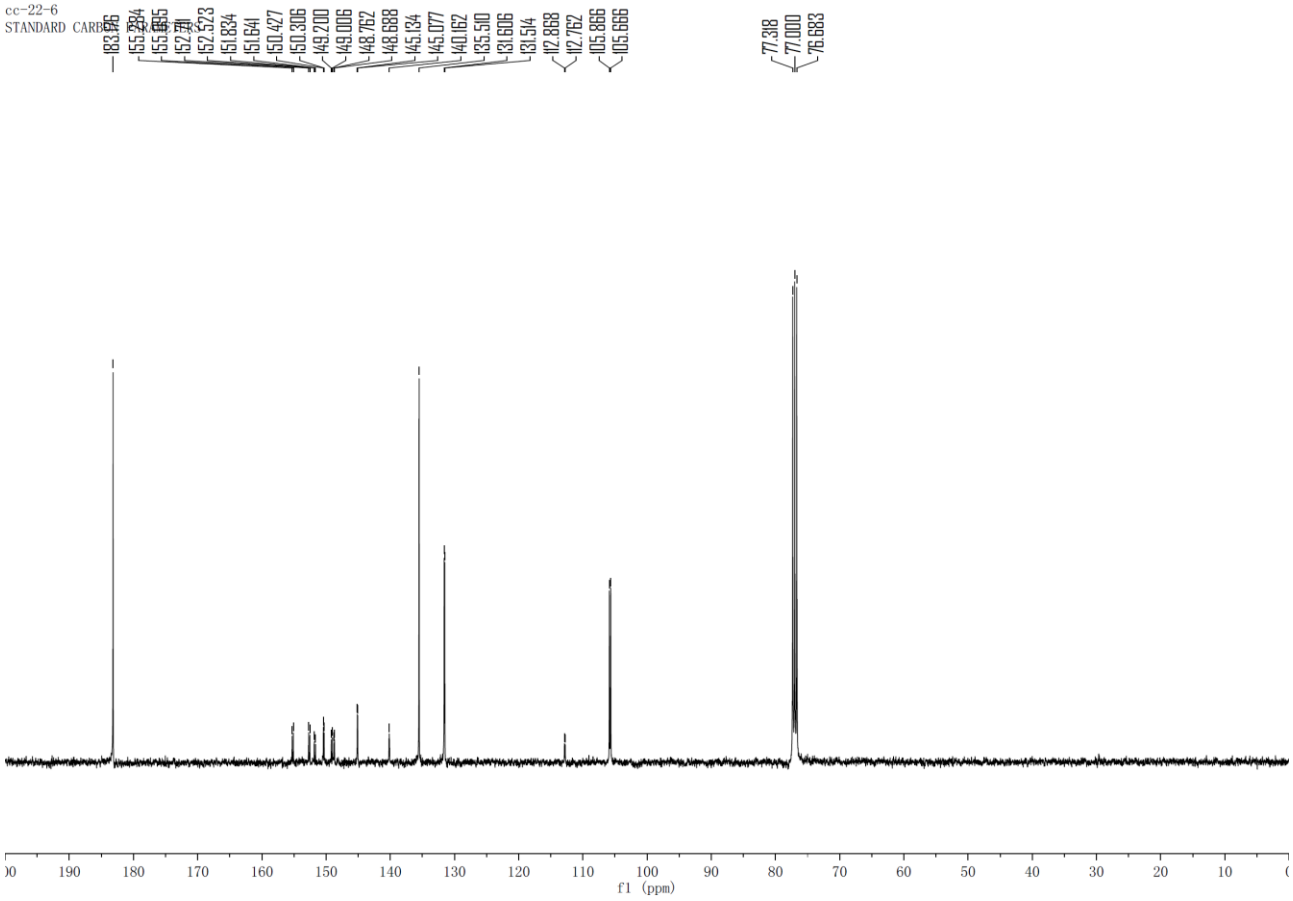




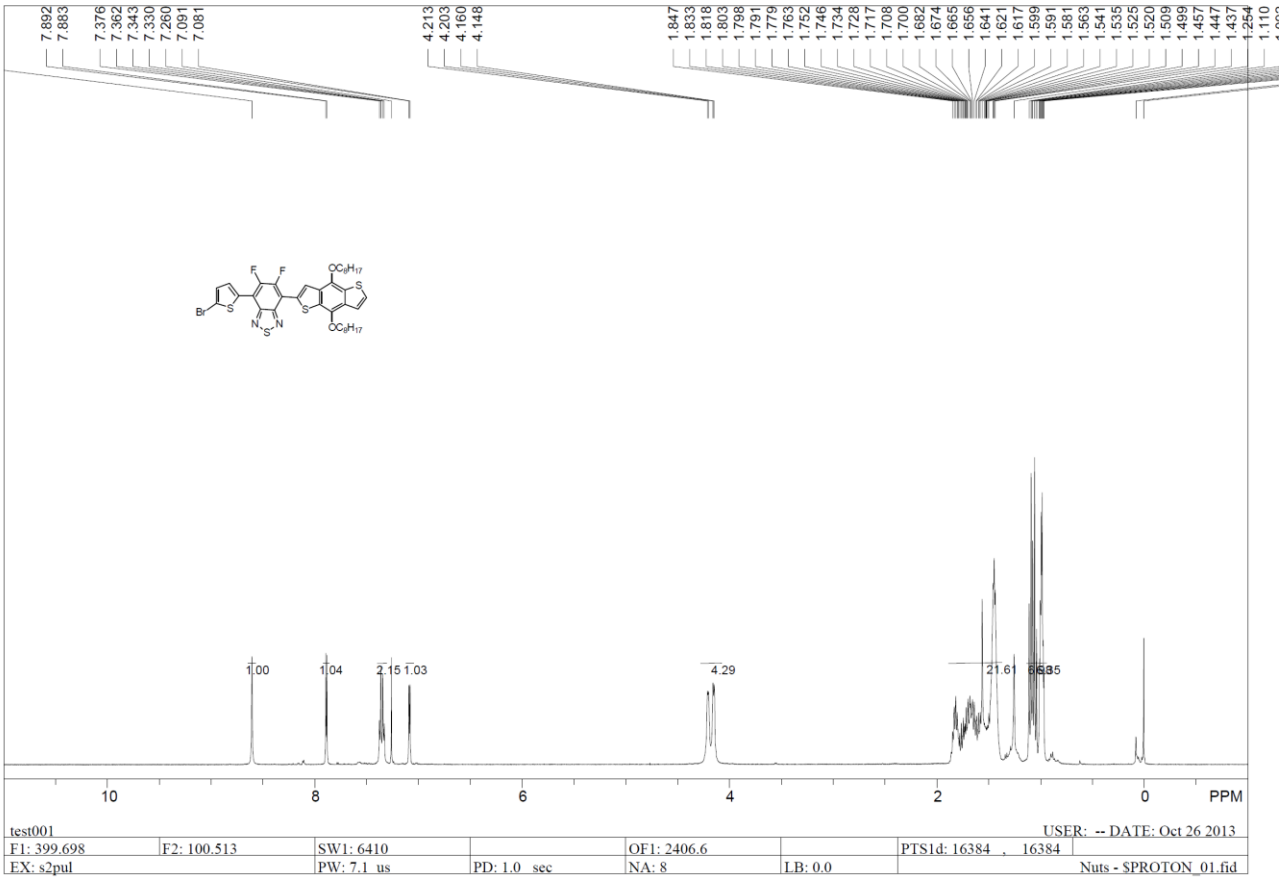
5-(5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde (7e).

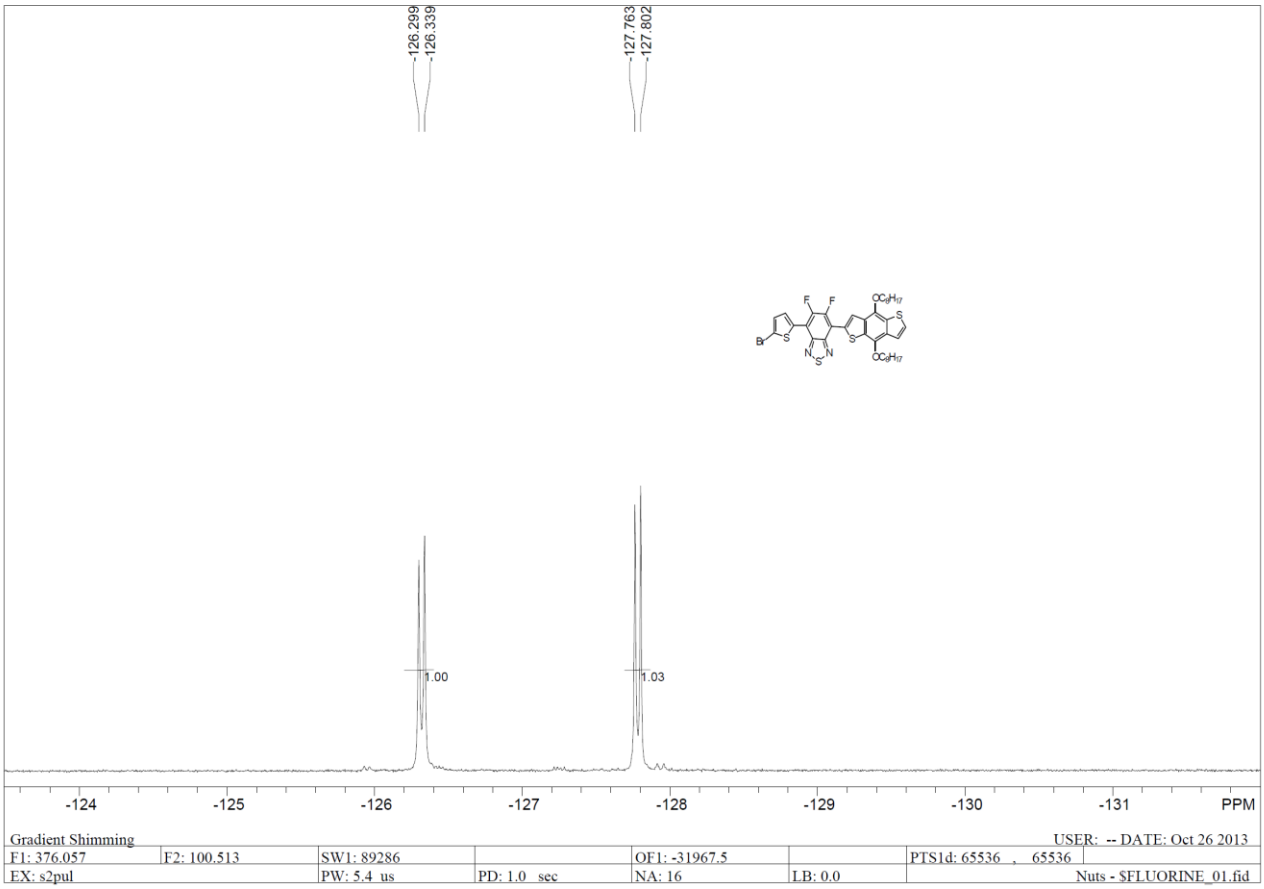


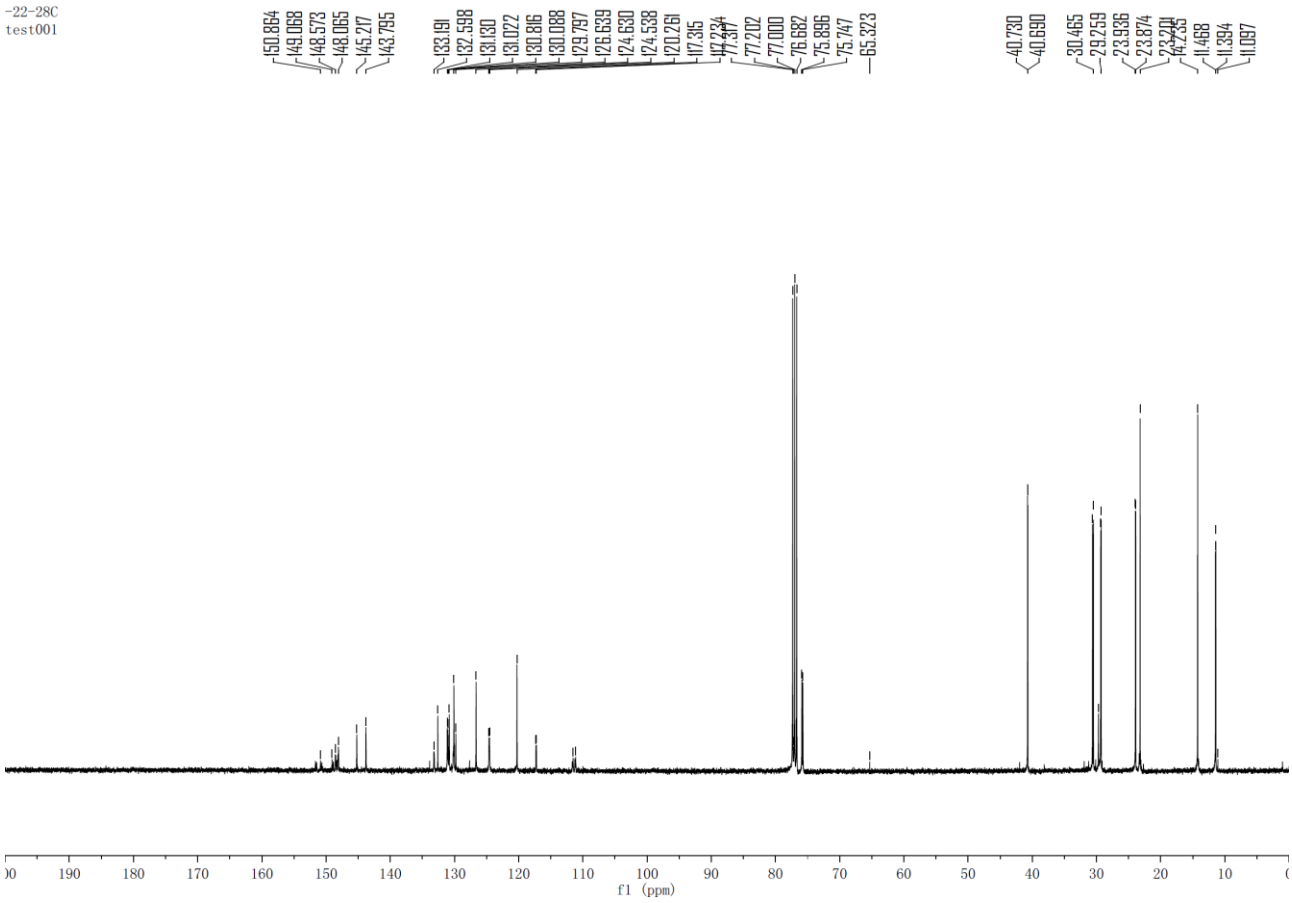

-125.278
-125.299
-125.321
-125.343
-126.806
-126.832
-126.853
-126.875
F
F
S
N
S
N
H
O
1.00
1.01
20
-122
-124
-126
-128
-130
-132
PPM
Gradient Shimming
USER: -- DATE: Mar 21 2013
F1: 376.058
F2: 100.513
SW1: 89286
OF1: -31967.6
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.4 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $FLUORINE_01.fid


cc-22-6
STANDARD CARBON
183.376
155.234
155.085
152.711
152.573
151.834
151.641
150.427
150.306
149.200
149.006
148.762
148.688
145.134
145.077
140.162
135.510
131.806
131.514
112.868
112.762
105.866
105.666
77.318
77.000
76.683
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

4-(4,8-Bis(octyloxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-7-(5-bromothiophen-2-yl)-5,6-difluorobenzo[c][1,2,5] thiadiazole (11).




-126.299
-126.339
-127.763
-127.802
1.00
1.03
-124
-125
-126
-127
-128
-129
-130
-131
PPM
Gradient Shimming
USER: -- DATE: Oct 26 2013
F1: 376.057
F2: 100.513
SW1: 89286
OF1: -31967.5
PTS1d: 65536 , 65536
EX: s2pul
PW: 5.4 us
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $FLUORINE_01.fid


-22-28C
test001
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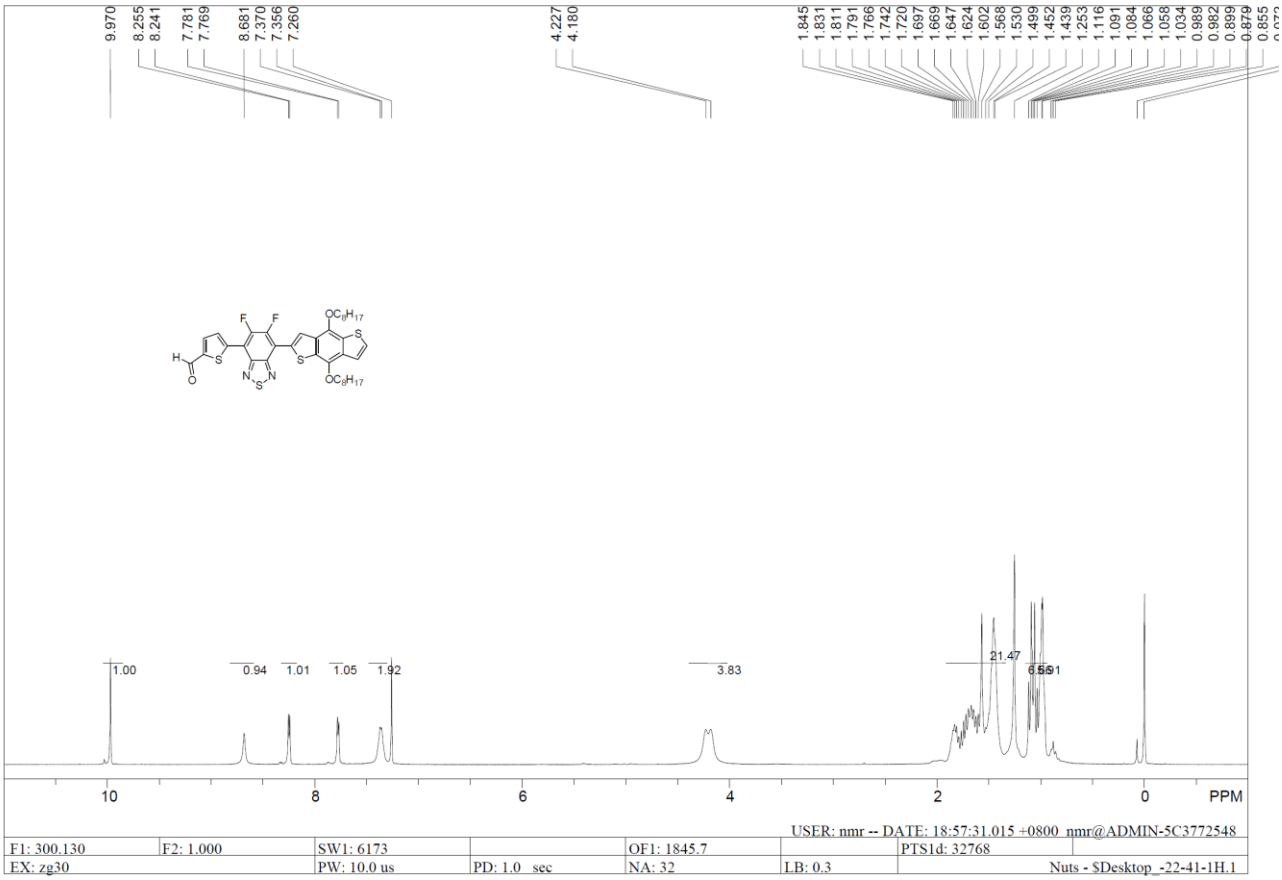
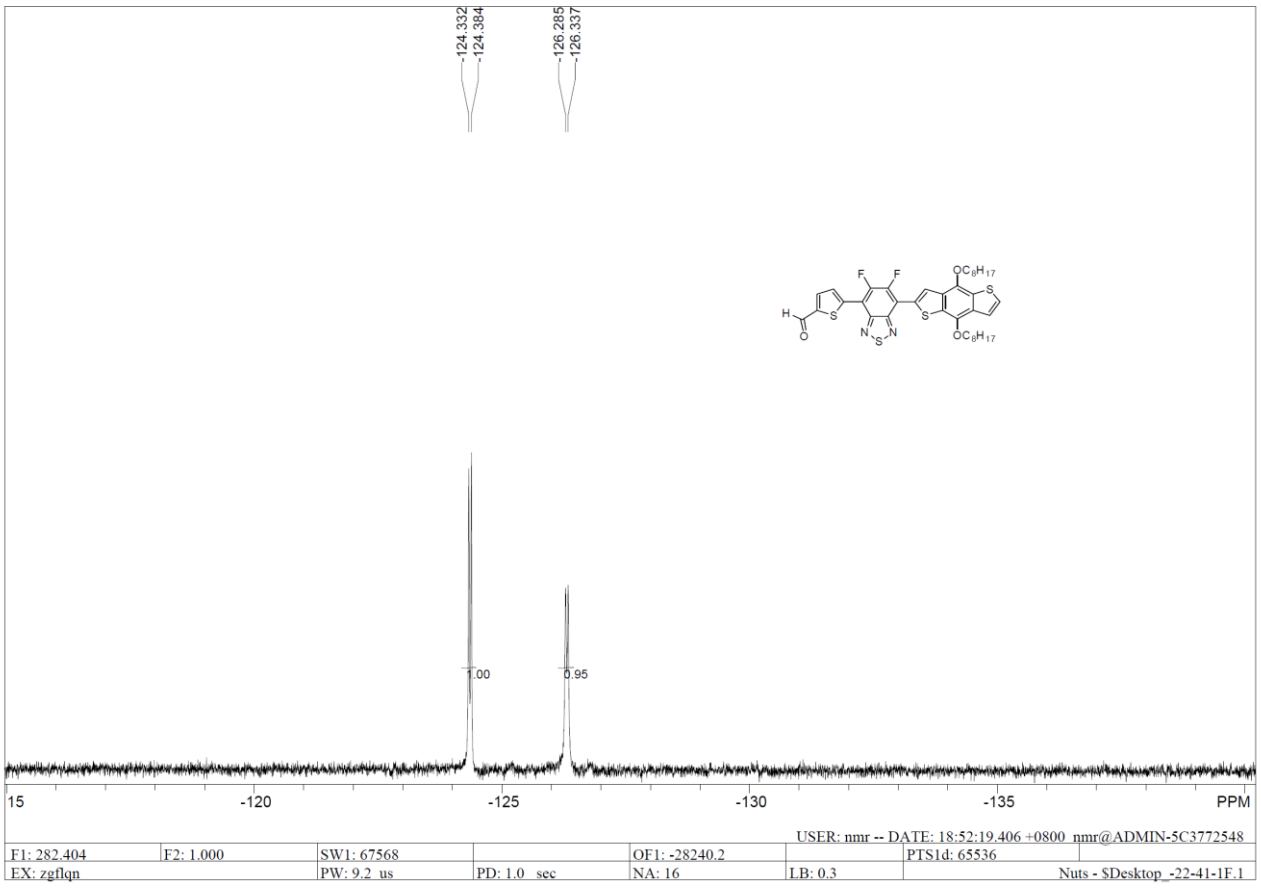
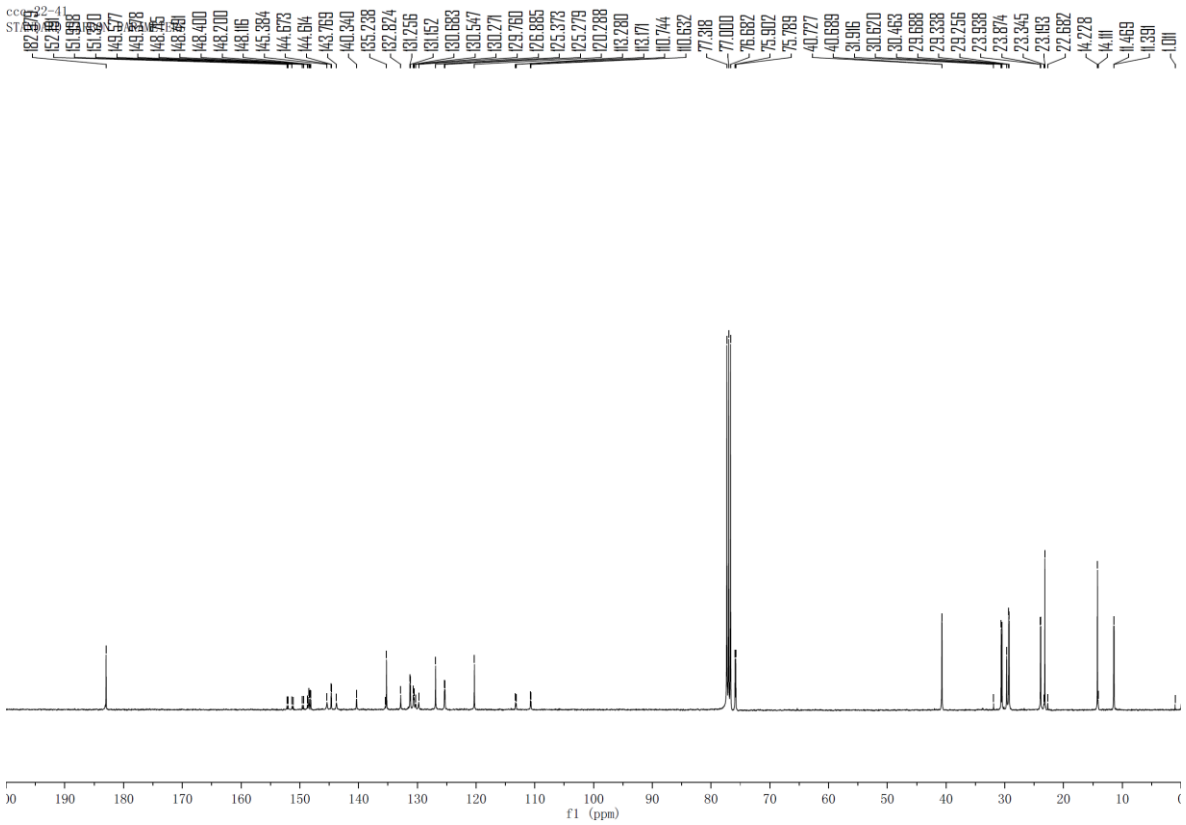
149.068
148.573
148.065
145.217
143.795
133.191
132.598
131.180
131.022
130.816
130.088
129.797
126.639
124.630
124.538
120.261
117.315
77.317
77.202
77.000
76.682
75.896
75.747
65.323
40.730
40.690
30.465
29.259
23.936
23.874
23.270
14.235
11.468
11.394
11.097
f1 (ppm)

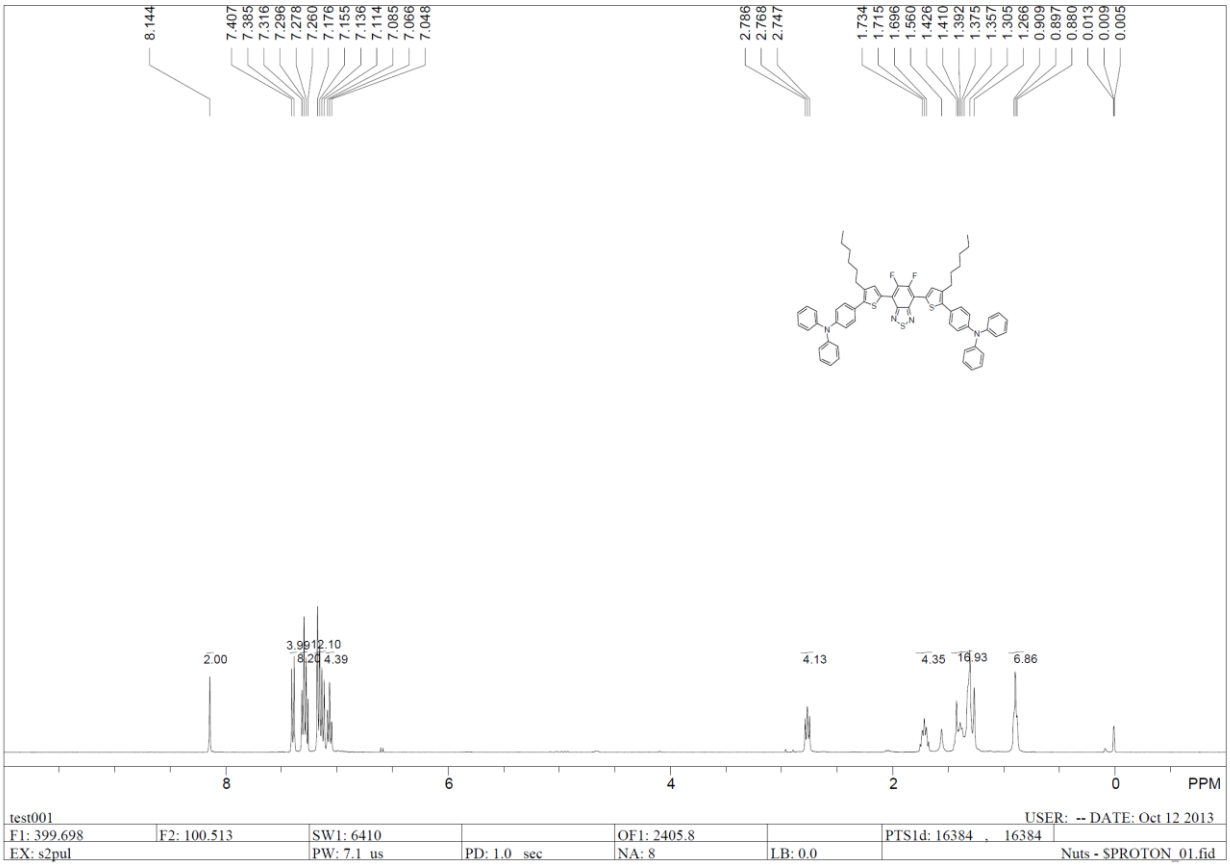
5-(7-(4,8-Bis(octyloxy)benzo[1,2-b:4,5-b']dithiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde (12).

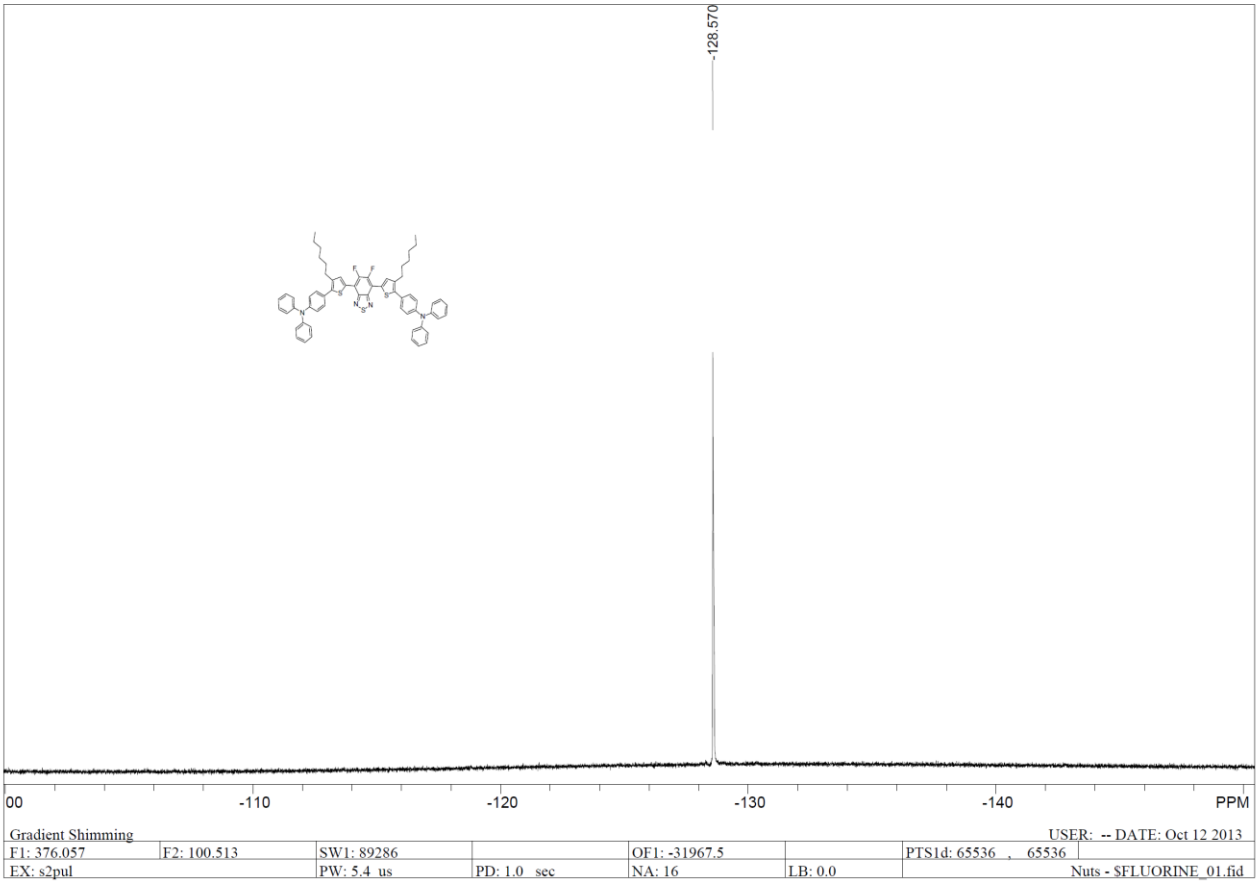






4,4'-(5,5'-(5,6-difluorobenzo[c][1,2,5]thiadiazole-4,7-diyl)bis(3-hexylthiophene-5,2-diyl))bis(N,N-diphenylanil ine) (14).

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OF1: -31967.5
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PW: 5.4 us
PD: 1.0 sec
NA: 16
LB: 0.0
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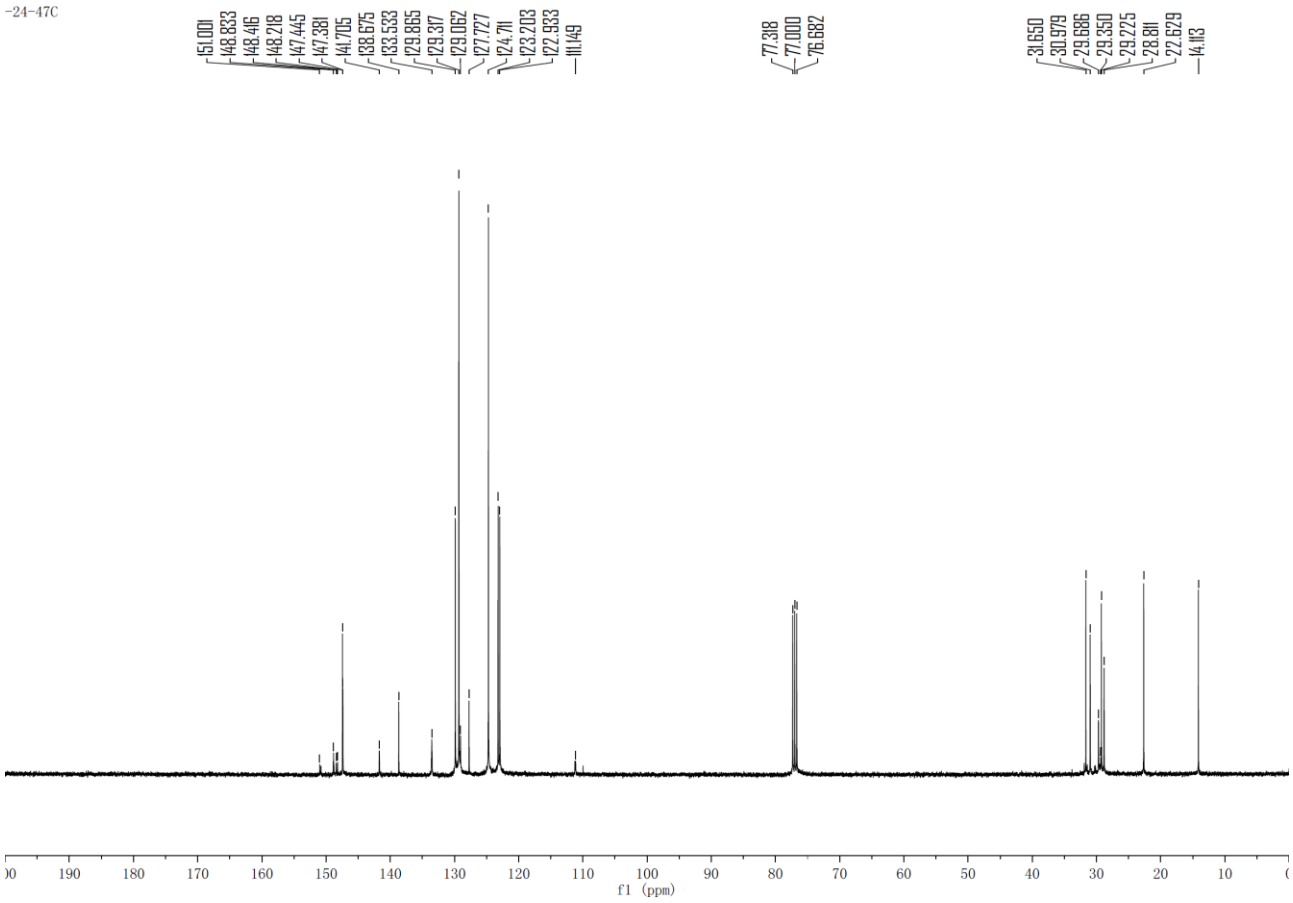
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122.933
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f1 (ppm)