Supporting Information for

Pd-Catalyzed Oxidative Cross-Coupling Between Two Electron-Rich Heteroarenes

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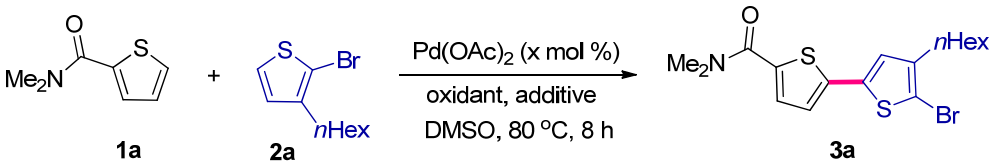
General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM300 and AM400 spectrometer. ^{19}F NMR was recorded on a Bruker AM300 spectrometer ($CFCl_3$ as outside standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (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. Toluene and 1,4-Dioxane was distilled from sodium and benzophenone immediately before use.

Screens for Pd-Catalyzed Oxidative Cross-Coupling of *N,N*-Dimethylthiophene-2-carboxamide 1a with 2-Bromo-3-hexylthiophene 2a (Table S1). To a 25 mL of Schlenck tube were added $Pd(OAc)_2$ (2.5 - 10 mol%), oxidant (1.5 - 3.0 equiv), *N*,*N*-dimethylthiophene-2-carboxamide **1a** (1.0 - 3.0 equiv) under N_2. Solvent (2 mL), additive (0-4.0 equiv), and 2-bromo-3-hexylthiophene **2a** (0.3 mmol-0.45 mmol, 1.0 – 1.5 equiv) were then added sequentially with stirring. The reaction mixture was stirred at 80 ^{o}C (oil bath). After stirring for 8 h, the reaction mixture was cooled to room temperature, purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 2:1) to give pure product.

Table S1. Pd-Catalyzed Oxidative Cross-Coupling of *N,N*-Dimethylthiophene-2-carboxamide 1a with 2-Bromo-3-hexylthiophene 2a.[a]

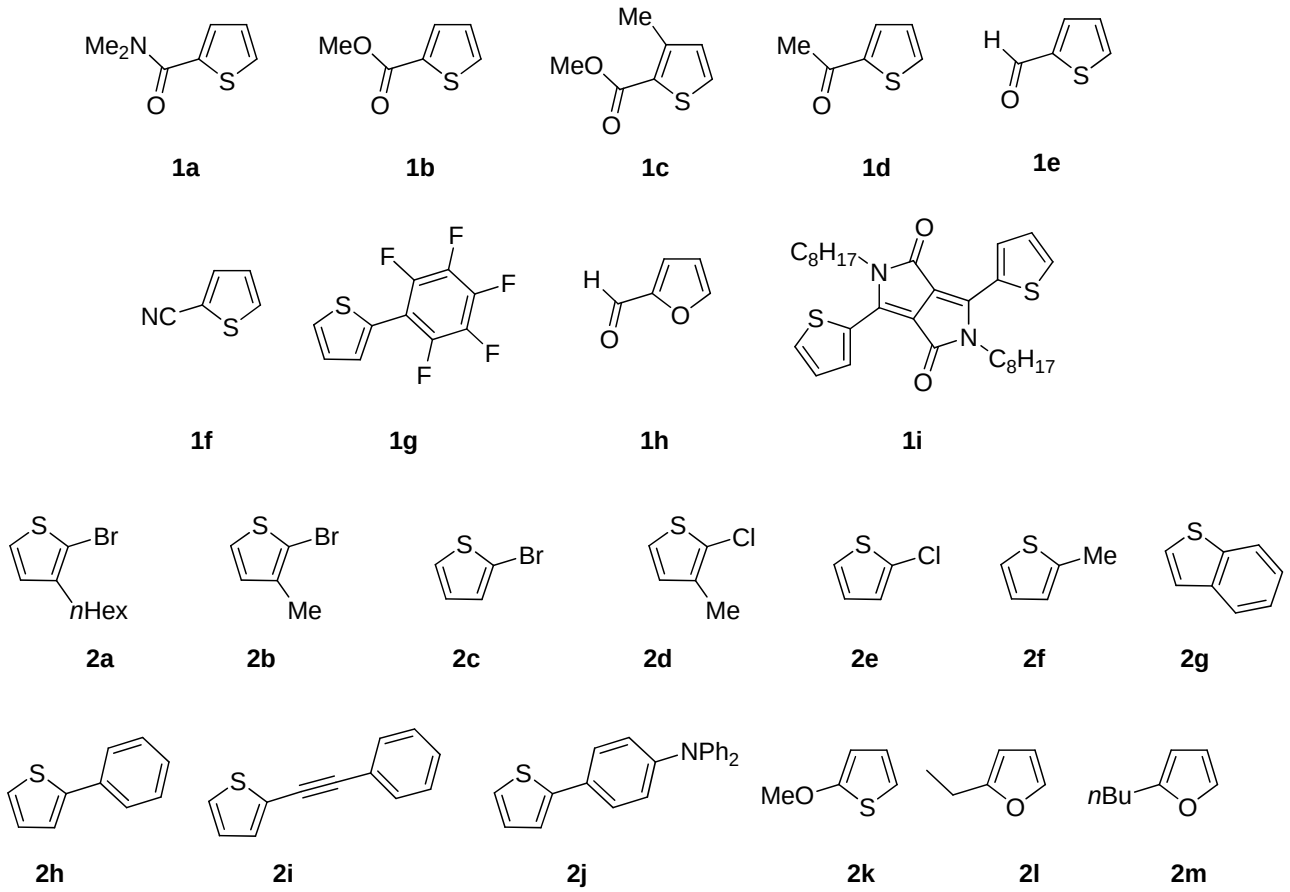


entry	1a/2a	x	oxidant (equiv)	solvent	additive (equiv)	yield[b]
1	1/1.5	10	AgOAc (3)	DMF		ND
2	1/1.5	10	AgOAc (3)	DCE		ND
3	1/1.5	10	AgOAc (3)	Dioxane		ND
4	1/1.5	10	AgOAc (3)	DMF/DMSO (V/V 5%)		8
5	1/1.5	10	AgOAc (3)	DMF/DMSO (V/V 1:1)		20
6	1/1.5	10	AgOAc (3)	DMSO		28
7	1/1.5	10	$Cu(OAc)_2$ (1.5)	DMSO		trace
8	1/1.5	10	$Cu(OAc)_2$ (1.5)	DMSO	K_2CO_3 (2)	trace
9	1/1.5	10	$Cu(OAc)_2$ (1.5)	DMSO	Cs_2CO_3 (2)	9
10	1/1.5	10	O_2 (1 atm)	DMSO	K_3PO_4 (3)	trace
11	1/1.5	10	O_2 (1 atm)	DMSO	Cs_2CO_3 (3)	trace
12	1/1.5	10	Ag_2CO_3 (1.5)	DMSO		24
13	1/1.5	10	Ag_2O (1.5)	DMSO	HOAc (0.5)	41
14	1/1.5	10	Ag_2O (1.5)	DMSO	PivOH (0.5)	39
15	1/1.5	10	Ag_2O (1.5)	DMSO	AdOH (0.5)	35
16	1/1.5	10	Ag_2O (1.5)	DMSO	$PhCO_2H$ (0.5)	42
17	2/1	10	Ag_2O (1.5)	DMSO	PhCOOH (0.5)	46
18	2/1	10	Ag_2O (3)	DMSO	PhCOOH (3)	60
19	3/1	10	Ag_2O (3)	DMSO	PhCOOH (3)	67
20	3/1	5	Ag_2O (3)	DMSO	PhCOOH (3)	72
21	3/1	2.5	Ag_2O (3)	DMSO	PhCOOH (3)	65
22	3/1	2.5	Ag_2O (3)	DMSO	*o*Ph-PhCOOH (3)	71
23	**3/1**	2.5	**Ag_2O (3)**	**DMSO**	***o*Ph-PhCOOH (2)**	**71**
24	3/1	2.5	Ag_2O (3)	DMSO	*o*Ph-PhCOOH (1)	58
25	3/1	2.5	Ag_2O (3)	DMSO	*o*Ph-PhCOOH (0.5)	56
26	3/1	2.5	Ag_2O (2)	DMSO	*o*Ph-PhCOOH (4)	48
27	3/1	2.5	Ag_2O (2)	DMSO	*o*Ph-PhCOOH (2)	57
28	3/1	2.5	Ag_2O (2.5)	DMSO	*o*Ph-PhCOOH (2)	63

29	2.5/1	2.5	Ag_2O (3)	DMSO	*o*Ph-PhCOOH (2)	61
30	2/1	2.5	Ag_2O (3)	DMSO	*o*Ph-PhCOOH (2)	53
31[c]	3/1	2.5	Ag_2O (3)	DMSO	*o*Ph-PhCOOH (2)	58

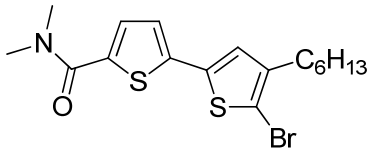
[a]Reaction conditions (unless otherwise specified): 0.3 mmol scale, Solvent (2 mL). [b]Isolated yield. [c]Reaction run at 90 °C.

Figure S1. Structures of Thiophenes and Furans

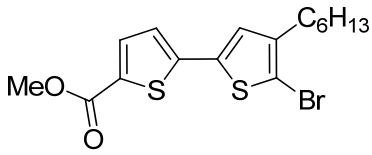


Typical Procedure for Pd-Catalyzed Oxidative Cross-Coupling between Two Thiophenes. To a 25 mL of Schlenck tube were added $Pd(OAc)_2$ (2.5 mol %), Ag_2O (208 mg 3.0 equiv) and [1,1'-biphenyl]-2-carboxylic acid (119 mg, 2.0 equiv) under N_2, followed by DMSO (2 mL) with stirring. Thiophene **1a** (0.9 mmol, 3 equiv) and thiophene **2a** (0.3 mmol, 1 equiv) were then added subsequently. The reaction mixture was stirred at 80 °C (oil bath). After stirring for 8 h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with 1 N HCl and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified with silica gel chromatography to provide pure product.

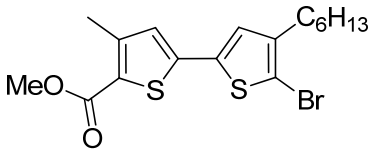
Note: For compounds **3a**, **3m, 3o-q**, the reaction was extracted with ethyl acetate, washed with 1 N NaOH, 1 N HCl and brine, dried over Na_2SO_4, filtered and concentrated.



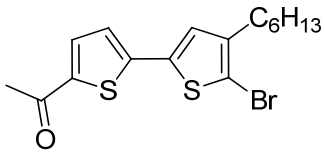
5'-Bromo-4'-hexyl-*N*,*N*-dimethyl-[2,2'-bithiophene]-5-carboxamide (3a). The product (85 mg, 71% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 2:1). m.p. 54 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 3.9 Hz, 1H), 7.00 (d, *J* = 3.9 Hz, 1H), 6.92 (s, 1H), 3.19 (s, 6H), 2.53 (t, *J* = 7.8 Hz, 2H), 1.57 (m, 2H), 1.32 (m, 6H), 0.89 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 163.7, 143.1, 140.2, 136.4, 135.7, 130.0, 125.4, 122.9, 108.8, 31.5, 29.5, 29.4, 28.8, 22.5, 14.0. IR (thin film): ν_{max} 3068, 1610 cm^{-1}. MS (EI): *m/z* (%) 401 (M^+), 399 (M^+), 274 (100), 243, 171. HRMS: Calculated for $C_{17}H_{22}NOS_2Br$: 399.0326; Found: 399.0331.



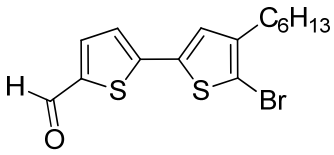
Methyl 5'-bromo-4'-hexyl-[2,2'-bithiophene]-5-carboxylate (3b). The product (81 mg, 70% yield) as a yellow liquid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material **1b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 3.9 Hz, 1H), 7.03 (d, *J* = 3.9 Hz, 1H), 6.95 (s, 1H), 3.88 (s, 3H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.57 (m, 2H), 1.32 (m, 6H), 0.89 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 162.3, 143.4, 143.3, 135.6, 134.1, 131.3, 125.8, 123.6, 109.7, 52.2, 31.5, 29.51, 29.47, 28.8, 22.5, 14.0. IR (thin film): ν_{max} 2952, 2927, 1716 cm^{-1}. MS (EI): *m/z* (%) 388 (M^+), 386 (M^+), 237 (100). HRMS: Calculated for $C_{16}H_{19}O_2S_2Br$: 386.0010; Found: 386.0008.



Methyl 5'-bromo-4'-hexyl-4-methyl-[2,2'-bithiophene]-5-carboxylate (3c). The product (77 mg, 64% yield) as a yellow liquid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material **1c**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.87 (s, 1H), 3.85 (s, 3H), 2.52 (t, *J* = 8.1 Hz, 2H), 2.51(s, 3H), 1.57 (m, 2H) , 1.31 (m, 6H), 0.89 (t, *J* = 6.4 Hz, 3H).^{13}C NMR (75.4 MHz, $CDCl_3$) δ 162.9, 147.1, 143.2, 140.5, 135.7, 127.5, 125.6, 124.4, 109.4, 51.7, 31.5, 29.44, 29.40, 28.8, 22.5, 16.0, 14.0. IR (thin film): ν_{max} 2953, 1713, 1466 cm^{-1}. MS (EI): *m/z* (%) 402 (M^+), 400 (M^+), 251, 43(100). HRMS: Calculated for $C_{17}H_{21}O_2S_2Br$: 400.0166; Found: 400.0161.

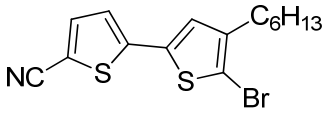


1-(5'-Bromo-4'-hexyl-[2,2'-bithiophen]-5-yl)ethanone (3d). 5% of $Pd(OAc)_2$ was used. The product (85 mg, 76%) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material **1d**. m.p. 69 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 3.9 Hz, 1H), δ 7.06 (d, *J* = 3.9 Hz, 1H), 6.99 (s, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.53 (s, 3H), 1.57 (m, 2H), 1.32 (m, 6H), 0.92 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 190.3, 145.0, 143.5, 142.4, 135.6, 133.2, 126.2, 123.9, 110.2, 31.5, 29.6, 29.5, 28.4, 26.5, 22.6, 14.1. IR (thin film): ν_{max} 2923, 1652 cm^{-1}. MS (EI): *m/z* (%) 372 (M^+), 370 (M^+), 221, 43(100). HRMS: Calculated for $C_{16}H_{19}OS_2Br$: 370.0061; Found: 370.0065.

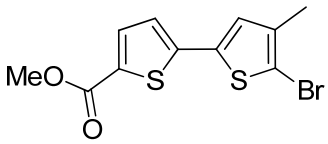


5'-Bromo-4'-hexyl-[2,2'-bithiophene]-5-carbaldehyde (3e). 5% of $Pd(OAc)_2$ was used. This compound is known.[2] The product (77 mg, 72% yield) as a yellow liquid was purified by silica chromatography (Petroleum ether /Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material **1e**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.64 (d, *J* = 4.0 Hz, 1H), δ 7.14

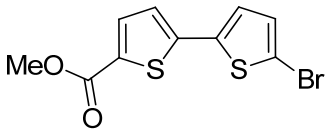
(d, *J* = 4.0 Hz, 1H), 7.03 (s, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.58 (m, 2H) , 1.32 (m, 6H), 0.89 (t, *J* = 6.2 Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 182.4, 146.2, 143.6, 141.6, 137.2, 135.3, 126.7, 124.0, 110.9, 31.5, 29.5, 29.4, 28.8, 22.5, 14.0. IR (thin film): ν_{max} 2954, 1664, 1460 cm^{-1}. MS (EI): *m/z* (%) 358 (M^+), 356 (M^+), 207 (100), 43. HRMS: Calculated for $C_{15}H_{17}OBrS_2$: 355.9904; Found: 355.9901.



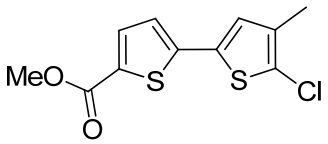
5'-Bromo-4'-hexyl-[2,2'-bithiophene]-5-carbonitrile (3f). The product (56 mg, 53%) as a yellow solid was purified by silica chromatography (Petroleum ether /Ethyl Acetate = 50:1). m.p. 49 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 4.0 Hz, 1H), δ 7.03 (d, *J* = 4.0 Hz, 1H), 6.96 (s, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.58 (m, 2H) , 1.32 (m, 6H), 0.90 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.8, 143.6, 138.2, 134.1, 126.6, 123.2, 114.0, 110.7, 107.5, 31.5, 29.52, 29.46, 28.8, 22.5, 14.0. IR (thin film): ν_{max} 2922, 2852, 2222, 1580, 1457 cm^{-1}. MS (EI): *m/z* (%) 355 (M^+), 353 (M^+), 204, 86, 84 (100). HRMS: Calculated for $C_{15}H_{16}NS_2Br$: 352.9908; Found: 352.9906



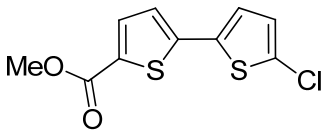
Methyl 5'-bromo-4'-methyl-[2,2'-bithiophene]-5-carboxylate (3g). The product (67 mg, 71% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1) and then distilled under vacuum to get rid of starting material **1b**. m.p. 90 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 3.8 Hz, 1H), 7.02 (d, *J* = 3.8 Hz, 1H), 6.95 (s, 1H), 3.88 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 143.2, 138.4, 135.4, 134.2, 131.3, 126.8, 123.7, 110.1, 52.2, 15.2. IR (thin film): ν_{max} 2921, 2850, 1717, 1470 cm^{-1}. MS (EI): *m/z* (%) 318 (M^+), 316 (M^+,100), 287, 285, 213. HRMS: Calculated for $C_{11}H_9O_2S_2Br$: 315.9227; Found: 315.9226.



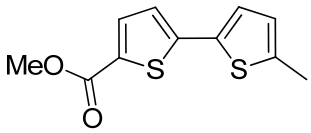
Methyl 5'-bromo-[2,2'-bithiophene]-5-carboxylate (3h). The product (55 mg, 62% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1) and then distillated under vacuum to get rid of starting material **1b**. This compound is known.[3] m.p. 108 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 3.9 Hz, 1H), 7.08 (d, *J* = 3.9 Hz, 1H), 7.02 (d, *J* = 3.9 Hz, 1H), 7.01 (d, *J* = 3.9 Hz, 1H), 3.89 (s, 3H).



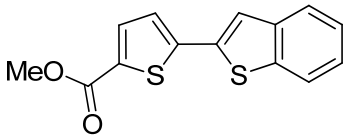
Methyl 5'-chloro-4'-methyl-[2,2'-bithiophene]-5-carboxylate (3i). The product (57 mg, 70% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1) and then distillated under vacuum to get rid of starting material **1b**. m.p. 86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 4.0 Hz, 1H), 6.92 (s, 3H), 3.87 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 143.3, 135.5, 134.1, 132.2, 131.3, 126.5, 125.5, 123.6, 52.2, 13.5. IR (thin film): ν_{max} 2924, 1708 cm^{-1}. MS (EI): *m/z* (%) 274 (M^+), 272 (M^+,100), 243, 241, 169. HRMS: Calculated for $C_{11}H_9O_2S_2Cl$: 271.9733; Found: 271.9738.



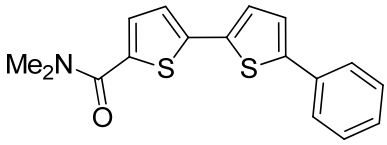
Methyl 5'-chloro-[2,2'-bithiophene]-5-carboxylate (3j). The product (48 mg, 61% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1) and then distillated under vacuum to get rid of starting material **1b**. This compound is known.[4] m.p. 87 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 3.9 Hz, 1H), 7.05 (d, *J* = 3.9 Hz, 1H), 7.03 (d, *J* = 3.9 Hz, 1H), 6.86 (d, *J* = 3.9 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 162.3, 143.0, 134.2, 131.6, 130.6, 127.2, 124.3, 123.9, 52.3. IR (thin film): ν_{max} 2919, 1717 cm^{-1}. MS (EI): *m/z* (%) 260 (M^+), 258 (M^+), 229, 227 (100), 155, 157. HRMS: Calculated for $C_{10}H_7O_2S_2Cl$: 257.9576; Found: 257.9578.



Methyl 5'-methyl-[2,2'-bithiophene]-5-carboxylate (3k). The product (38 mg, 53% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1) and then distillated under vacuum to get rid of starting material **1b**. This compound is known.[5] m.p. 106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 3.8 Hz, 1H), 7.07 (d, *J* = 3.6 Hz, 1H), 7.05 (d, *J* = 3.8 Hz, 1H), 6.69 (m, 1H), 3.88 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 162.6, 144.7, 141.2, 134.2, 133.9, 130.4, 126.3, 125.2, 123.1, 52.1, 15.4. IR (thin film): ν_{max} 2917, 1708 cm^{-1}. MS (EI): *m/z* (%) 238 (M^+, 100), 207, 179, 135. HRMS: Calculated for $C_{11}H_{10}O_2S_2$: 238.0122; Found: 238.0126.

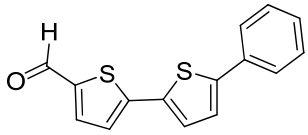


Methyl 5-(benzo[b]thiophen-2-yl)thiophene-2-carboxylate (3l). The product (49 mg, 60% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1) and then distillated under vacuum to get rid of starting material **1b**. This compound is known.[4] m.p. 139 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (m, 2H), 7.72 (d, *J* = 4.0 Hz, 1H), 7.49 (s, 1H), 7.35 (m, 2H), 7.24 (d, *J* = 4.0 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 162.4, 144.0, 140.0, 139.5, 135.9, 134.2, 132.3, 125.2, 125.1, 124.9, 123.9, 122.2, 121.4, 52.3. IR (thin film): ν_{max} 2918, 2849, 1716 cm^{-1}. MS (EI): *m/z* (%) 275 ($M^+ + H^+$), 274 (M^+, 100), 243, 171, 149. HRMS: Calculated for $C_{14}H_{10}O_2S_2$: 274.0122; Found: 274.0121.

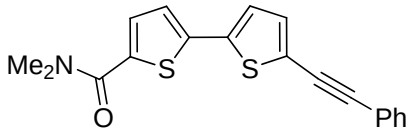


***N,N*-dimethyl-5'-phenyl-[2,2'-bithiophene]-5-carboxamide (3m)**. The product (60 mg, 64%) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 2:1). m.p. 172 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.32-7.21 (m, 4H), 7.12 (d, *J* = 3.6 Hz, 1H), 3.22(s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 163.8,

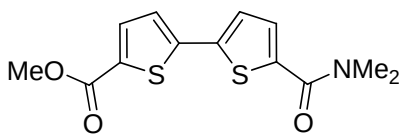
144.2, 140.8, 136.2, 135.5, 133.7, 130.2, 128.8, 127.7, 125.5, 123.8, 122.8. IR (thin film): ν_{max} 3108, 1601, 1407 cm^{-1}. MS (EI): *m/z* (%) 314 ($M^+ + H^+$), 313 (M^+), 269 (100), 197. HRMS: Calculated for $C_{17}H_{15}NOS_2$: 313.0595; Found: 313.0590.



5'-Phenyl-[2,2'-bithiophene]-5-carbaldehyde (3n). The product (53 mg, 65%) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1). m.p. 121 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 9.87 (s, 1H),7.69 (d, *J* = 3.9 Hz 1H), 7.62 (d, *J* = 6.9 Hz 2H), 7.42 (t, *J* = 7.0 Hz 2H), 7.35(d, *J* = 3.9 Hz 2H), 7.28 (t, *J* = 3.6 Hz, 2H).^{13}C NMR (75.4 MHz, $CDCl_3$) δ 182.4, 147.2, 146.1, 141.5, 137.4, 135.0, 133.4, 129.0, 128.2, 127.1, 125.8, 124.2, 124.0. MS (EI): *m/z* (%) 270 (M^+,100) 241, 197 . HRMS: Calculated for $C_{15}H_{10}OS_2$: 270.0173; Found: 270.0175.

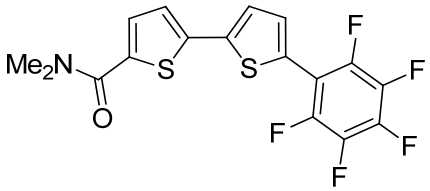


***N,N*-dimethyl-5'-(phenylethynyl)-[2,2'-bithiophene]-5-carboxamide (3o).** The product (53 mg, 52% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 2:1). m.p. 124 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (m, 2H), 7.36 (m, 3H), 7.28 (d, *J* = 3.6 Hz, 1H), 7.20 (d, *J* = 3.6 Hz, 1H), 7.15-7.10 (m, 2H), 3.21 (s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 163.6, 139.9, 137.6, 136.9, 132.8, 131.3, 130.0, 128.5, 128.3, 124.5, 123.4, 123.0, 122.5, 94.6, 82.3. IR (thin film): ν_{max} 3062, 2915, 2180, 1595 cm^{-1}. MS (EI): *m/z* (%) 338 ($M^+ + H^+$), 337 (M^+), 293, 221, 43 (100). HRMS: Calculated for $C_{19}H_{15}NOS_2$: 337.0595; Found: 337.0592.

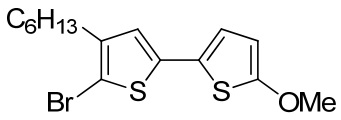


Methyl 5'-(dimethylcarbamoyl)-[2,2'-bithiophene]-5-carboxylate (3p). 3 equiv of **1a** was used. The product (61 mg, 69% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 2:1). m.p. 163 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 3.6

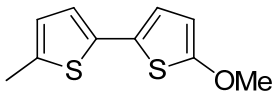
Hz, 1H), 7.28 (d, *J* = 3.6 Hz, 1H), 7.19 (dd, *J* = 3.6 Hz, 1.5 Hz, 2H), 3.90 (s, 3H), 3.20 (s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 163.5, 162.3, 142.9, 139.4, 138.1, 134.2, 132.3, 130.0, 124.8, 124.5, 52.2. IR (thin film): ν_{max} 2922, 1707, 1695 cm^{-1}. MS (EI): *m/z* (%) 295 (M^+), 251 (100), 179. HRMS: Calculated for $C_{13}H_{13}NO_3S_2$: 295.0337; Found: 295.0335.



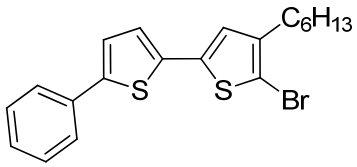
***N,N*-Dimethyl-5'-(perfluorophenyl)-[2,2'-bithiophene]-5-carboxamide (3q).** 3 equiv of **1a** was used. The product (72 mg, 60% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 2:1). m.p. 185 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 3.8 Hz, 1H), 7.26 (d, *J* = 3.8 Hz, 1H), 7.24 (d, *J* = 3.8 Hz, 1H), 7.13 (d, *J* = 3.8 Hz, 1H), 3.18 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 143.9 (dm, *J* = 251.6 Hz), 139.9 (dm, *J* = 257.0 Hz), 139.5, 139.0(t, *J* = 4.1 Hz), 138.0 (dm, *J* = 255.7 Hz), 137.5, 131.1(t, *J* = 5.4 Hz), 126.1 (m), 124.7, 123.9, 109.5(dt, *J* = 4.1,10.7 Hz), 37.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ -139.1 (m, 2F), -154.9 (m, 1F), -161.3 (m, 2F). IR (thin film): ν_{max} 2920, 1602, 1526, 1490 cm^{-1}. MS (EI): *m/z* (%) 403 (M^+), 359 (100), 287. HRMS: Calculated for $C_{17}H_{10}NOS_2F_5$: 403.0124; Found: 403.0127.



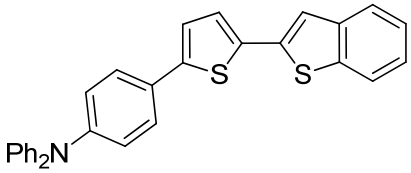
5-Bromo-4-hexyl-5'-methoxy-2,2'-bithiophene (3r). The reaction was run in a sealed tube with 3 equiv of **2j**. The product (60 mg, 56% yield) as a yellow liquid was purified with silica gel chromatography (Petroleum ether(100%)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.72 (d, *J* = 3.9 Hz, 1H), 6.69 (s, 1H), 6.10 (d, *J* = 3.9 Hz, 1H), 3.90 (s, 3H), 2.52 (t, *J* = 7.6 Hz, 2H), 1.58 (m, 2H) , 1.32 (m, 6H), 0.91 (t, *J* = 5.8 Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.6, 142.6, 137.4, 123.1, 123.0, 121.4, 106.1, 104.3, 60.2, 31.6, 29.6, 29.55, 28.9, 22.6, 14.1. IR (thin film): ν_{max} 2955, 1539, 1499 cm^{-1}. MS (EI): *m/z* (%) 360 ($M^+ + H^+$), 358 (M^+), 345, 343, 84 (100). HRMS: Calculated for $C_{15}H_{19}OBrS_2$: 358.0061; Found: 358.0057.



5-Methoxy-5'-methyl-2,2'-bithiophene (3s). The reaction was run in a sealed tube with 3 equiv of **2f**. The product (27 mg, 44% yield) as a yellow liquid was purified with silica gel chromatography (Petroleum ether(100%)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.80 (d, *J* = 3.2 Hz, 1H), 6.71(d, *J* = 4.0 Hz, 1H), 6.62 (d, *J* = 3.2 Hz, 1H), 6.10 (d, *J* = 4.0 Hz, 1H), 3.90 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.0, 138.0, 135.6, 125.6, 124.2, 122.1, 120.5, 104.2, 60.2, 15.3. IR (thin film): ν_{max} 2921, 2851, 1540, 1507 cm^{-1}. MS (EI): *m/z* (%) 211 ($M^+ + H^+$), 210 (M^+), 195 (100), 167. HRMS: Calculated for $C_{10}H_{10}OS_2$: 210.0173; Found: 210.0175.

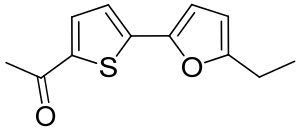


5-Bromo-4-hexyl-5'-phenyl-2,2'-bithiophene (3t). The product (80 mg, 66% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether(100%)) and then distilled under vacuum to get rid of starting material **2h**. m.p. 50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 3.2 Hz, 1H), 7.03 (d, *J* = 3.2 Hz, 1H), 6.87 (s, 1H), 2.53 (t, *J* = 7.2 Hz, 2H), 1.59 (m, 2H), 1.33 (m, 6H), 0.93 (s, 3H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 143.2, 142.9, 136.7, 135.9, 133.8, 128.9, 127.6, 125.5, 124.4, 124.2, 123.6, 107.6, 31.6, 29.6, 29.5, 28.9, 22.6, 14.1. MS (EI): *m/z* (%) 406 (M^+), 404 (M^+), 255 (100), 160. HRMS: Calculated for $C_{20}H_{21}S_2Br$: 404.0268; Found: 404.0267.

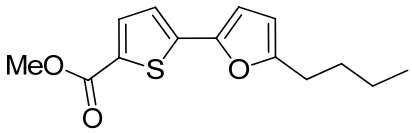


4-(5-(benzo[b]thiophen-2-yl)thiophen-2-yl)-N,N-diphenylaniline (3u). The product (73 mg, 53% yield) as a yellow solid was purified with silica gel chromatography (Petroleum ether: /Ethyl Acetate = 100:1). m.p. 196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.39 (s, 1H), 7.35-7.23 (m, 7H), 7.16-7.12 (m, 5H), 7.08-7.03

(m, 4H). ^{13}C NMR (150.8 MHz, $CDCl_3$) δ 147.5, 147.3, 144.3, 140.4, 138.9, 137.3, 135.6, 129.3, 127.7, 126.4, 126.0, 124.7, 124.6, 124.4, 123.4, 123.3, 123.2, 122.8, 122.0, 119.2. MS (EI): *m/z* (%) 459(M^+), 266, 105 (100). HRMS: Calculated for $C_{30}H_{21}NS_2$: 459.1115; Found: 459.1114

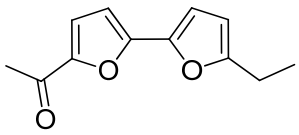


1-(5-(5-Ethylfuran-2-yl)thiophen-2-yl)ethanone (3v). To a 25 mL of sealed tube were added $Pd(TFA)_2$ (10 mol %), AgOAc (150 mg 3.0 equiv) and 1.10-phen (10.8 mg, 0.2 equiv) under N_2, followed by DMA (0.5 mL), DMSO (1.5 mL) with stirring. Thiophene **1e** (0.3 mmol, 1 equiv) and furan **2k** (0.9 mmol, 3 equiv) were then added subsequently. The reaction mixture was stirred at 100 ^{o}C (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 (Petroleum ether /Ethyl Acetate = 50:1) to provide pure product (33 mg, 50% yield) as a pale yellow solid. m.p. 55 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 3.9 Hz, 1H), 7.17 (d, *J* = 3.9 Hz, 1H), 6.59 (d, *J* = 3.3 Hz, 1H), 6.08 (d, *J* = 3.3 Hz, 1H), 2.70 (q, *J* = 7.5 Hz, 2H), 2.54 (s, 3H), 1.27 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 190.4, 159.1, 146.7, 142.2, 141.3, 133.3, 121.8, 109.0, 106.8, 26.5, 21.5, 12.0. IR (thin film): ν_{max} 1647 cm^{-1}. MS (EI): *m/z* (%) 220 (M^+), 205 (100). HRMS: Calculated for $C_{12}H_{12}O_2S$: 220.0558; Found: 220.0560.

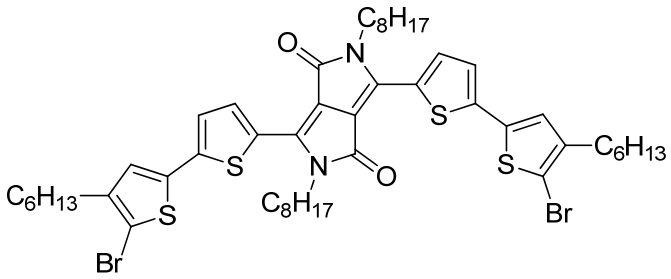


1-(5-(5-Ethylfuran-2-yl)thiophen-2-yl)ethanone (3w). To a 25 mL of sealed tube were added $Pd(TFA)_2$ (10 mol %), AgOAc (150 mg 3.0 equiv) and 1.10-phen (10.8 mg, 0.2 equiv) under N_2, followed by DMA (0.5 mL), DMSO (1.5 mL) with stirring. Thiophene **1b** (0.3 mmol, 1 equiv) and furan **2l** (0.9 mmol, 3 equiv) were then added subsequently. The reaction mixture was stirred at 100 ^{o}C (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 (Petroleum ether /Ethyl Acetate = 50:1) to provide pure product (39 mg, 49% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 4.0 Hz, 1H), 7.13 (d, *J* = 4.0 Hz, 1H), 6.54 (d, *J* = 3.2 Hz, 1H), 6.06 (d, *J* = 3.2 Hz, 1H), 3.88 (s, 3H), 2.66 (t, *J* = 7.8 Hz, 2H), 1.65 (m, 2H), 1.40 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 157.6, 146.7, 140.7, 134.1, 130.1, 121.5, 108.2, 107.3, 52.0, 30.0, 27.8, 22.2, 13.7.MS (EI): *m/z* (%) 264 (M^+), 221 (100). HRMS: Calculated for $C_{14}H_{16}O_3S$: 264.0820; Found: 264.0818.

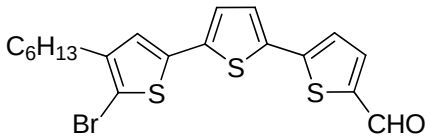


1-(5'-Ethyl-[2,2'-bifuran]-5-yl)ethanone (3x). The product (15 mg, 25% yield) as a pale yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1). m.p. 81 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, *J* = 3.9 Hz, 1H), 6.75 (d, *J* = 3.3 Hz, 1H), 6.59 (d, *J* = 3.9 Hz, 1H), 6.11 (d, *J* = 3.9 Hz, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 2.48 (s, 3H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 186.0, 159.6, 151.0, 150.4, 143.5, 119.7, 109.6, 106.6, 106.2, 25.9, 21.5, 12.0. IR (thin film): ν_{max} 2918, 1652, 1540 cm^{-1}. MS (EI): *m/z* (%) 204 (M^+), 189 (100), 133, 86, 84. HRMS: Calculated for $C_{12}H_{12}O_3$: 204.0786; Found: 204.0784.

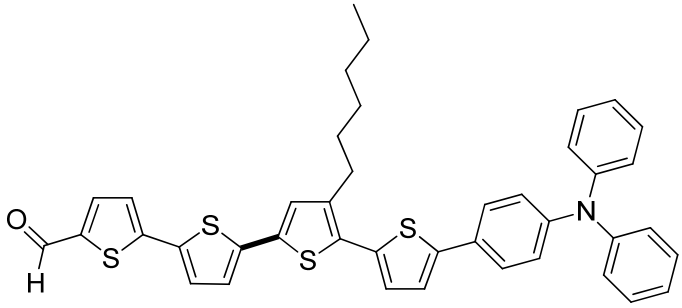


3,6-bis(5'-bromo-4'-hexyl-[2,2'-bithiophen]-5-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3y). The reaction was run on a 0.1 mmol scale in 3 mL DMSO and 5 mol % $Pd(OAc)_2$ was used. The product **3y** (42 mg, 41% yield) as a purple-black solid was purified with silica gel chromatography (Petroleum ether/dichloromethane = 8:1). m.p. 157 ^{o}C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (br, 2H), 7.19 (d, *J* = 3.6 Hz, 2H), 6.99 (br, 2H), 4.05 (t, *J* = 8.0 Hz, 4H), 2.55 (t, *J* = 7.6 Hz, 4H), 1.73 (m, 4H), 1.60 (m, 4H), 1.43-1.25 (m, 30H), 0.92-0.85 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.0, 143.5, 141.9, 138.8, 136.3, 135.5, 128.1, 125.8, 124.6, 110.0, 108.2, 42.2, 31.8,

31.6, 30.0, 29.7, 29.6, 29.20, 29.19, 28.9, 26.9, 22.7, 22.62, 22.60, 14.1. MS (MALDI): *m/z* (%) 1018 (M^+), 1017 (M^+), 1016 (M^+), 1014 (M^+), 1012 (M^+). HRMS (MALDI): Calculated for $C_{50}H_{66}O_2N_2S_4Br_2$: 1012.2368; Found: 1012.2362.

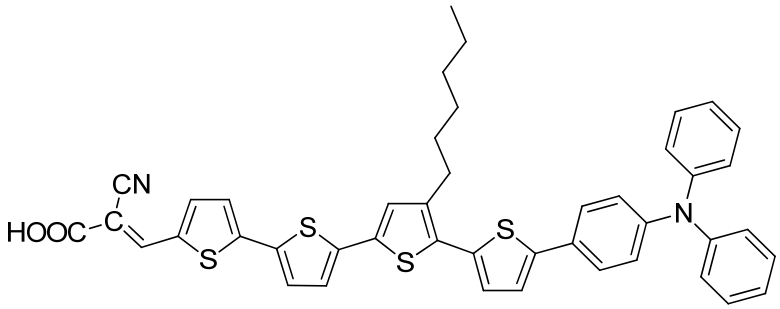


5''-Bromo-4''-hexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (5). 3 equiv of **2a** and 5 mol% of $Pd(OAc)_2$ were used. The product (93 mg, 71% yield (0.3 mmol scale); 534 mg, 68% yield (1.8 mmol scale in 5 mL DMSO)) as a yellow solid was purified with silica gel chromatography (Petroleum ether/ Ethyl Acetate = 50:1) and then distillated under vacuum to get rid of starting material **4**. This compound is known.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.65 (d, *J* = 3.8 Hz, 1H), δ 7.22 (d, *J* = 3.8 Hz, 1H), 7.20 (d, *J* = 3.8 Hz, 1H), δ 7.01 (d, *J* = 3.8 Hz, 1H), 6.89 (s, 1H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.58 (m, 2H), 1.33 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 182.3, 146.5, 143.2, 141.6, 138.3, 137.3, 135.7, 134.5, 126.8, 125.1, 124.4, 124.0, 108.8, 31.5, 29.54, 29.50, 28.8, 22.5, 14.0. IR (thin film): ν_{max} 2925, 2854, 1663, 1507, 1464, 1440 cm^{-1}. MS (EI): *m/z* (%) 440 (M^+), 438 (M^+), 289, 194, 57 (100). HRMS: Calculated for $C_{19}H_{19}OBrS_3$: 437.9781; Found: 437.9778.

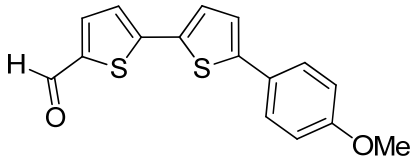


5'''-(4-(diphenylamino)phenyl)-4''-hexyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5-carbaldehyde (6). To a 25 mL of Schlenck tube were added $Pd(OAc)_2$ (6.0 mg, 5 mol%), PPh_3 (13.1 mg 10 mol%), K_2CO_3 (138 mg 2.0 equiv), **5** (220 mg, 1.0 equiv) and **2r** (250 mg, 1.5 equiv) under N_2. DMF (2.5 mL) was then added. The reaction mixture was stirred at 80 ^{o}C (oil bath). After stirring for 8 h, the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2, filtered, washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified with silica gel

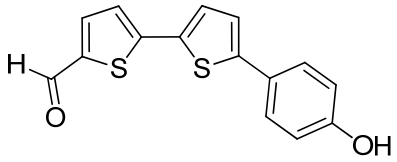
chromatography (Petroleum ether/ Ethyl Acetate = 50:1) to give pure product (253 mg, 74% yield) as a deep brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.63 (d, *J* = 4.0 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.28-7.23 (m, 5H), 7.19 (d, *J* = 4.0 Hz, 1H), 7.10-7.15 (m, 5H), 7.00-7.07 (m, 7H), 2.76 (br, 2H), 1.66 (m, 2H), 1.39 (m, 2H), 1.32 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.2, 147.34, 147.28, 146.7, 144.1, 141.4, 140.1, 138.9, 137.2, 134.1, 134.0, 133.5, 131.0, 129.2, 127.8, 127.3, 126.7, 126.3, 124.5, 124.2, 123.8, 123.4, 123.1, 122.5, 31.6, 30.4, 29.5, 29.2, 22.6, 14.1. MS (MALDI): *m/z* (%) 685.2 (M^+,100), 614.1, 581.1 HRMS: Calculated for $C_{41}H_{35}NOS_4$: 685.1601; Found: 685.1585.



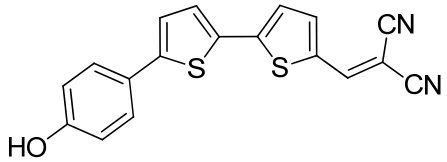
2-cyano-3-(5'''-(4-(diphenylamino)phenyl)-4''-hexyl-[2,2':5',2'':5'',2'''-quaterthiophen]-5-yl)acrylic (7). A solution of **6** (150 mg, 0.22 mml), 2-cyanoacetic acid (94 mg, 5.0 equiv) and ammonium acetate (51 mg, 3.0 equiv) in acetic acid (25 mL) was refluxed for 3 h in a flask. After cooled to room temperature, the reaction was quenched with water and extracted with CH_2Cl_2. The organic layer was washed with water, dried over Na_2SO_4. After filtration, the product (161 mg, 98% yield) was obtained as a dark brown solid. ^{1}H NMR (400 MHz, *d*6-DMSO) δ 13.70 (br, 1H), 8.43 (s, 1H), 7.91 (d, *J* = 4.4 Hz, 1H), 7.51-7.48 (m, 4H), 7.33-7.27 (m, 7H), 7.12 (d, *J* = 3.6 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 4H), 6.93 (d, *J* = 8.8 Hz, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 1.57 (m, 2H) , 1.32-1.25 (m, 6H), 0.83 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, *d*6-DMSO) δ 163.6, 147.0, 146.8, 146.2, 145.2, 143.3, 141.4, 140.2, 138.0, 134.0, 133.6, 133.2, 133.0, 130.2, 129.6, 128.1, 127.2, 127.1, 126.4, 125.4, 125.0, 124.4, 123.5, 123.4, 122.9, 116.6, 98.0, 31.1, 29.7, 29.0, 28.7, 22.1, 14.0. MS (MALDI): *m/z* (%) 752.2 (M^+,100),708.2, 681.1 HRMS: Calculated for $C_{44}H_{36}N_2O_2S_4$: 752.1660; Found: 752.1646.



5'-(4-Methoxyphenyl)-[2,2'-bithiophene]-5-carbaldehyde (9). 3 equiv of **1e** was used. The product (65 mg, 72%, 0.3 mmol scale) as a yellow solid was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 50:1). This compound is known.[6] ^{1}H NMR (300 MHz, *d6*-DMSO) δ 9.84 (s, 1H), 7.95 (d, *J* = 3.9 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 3.9 Hz, 1H), 7.48 (d, *J* = 3.9 Hz, 1H), 7.42 (d, *J* = 3.9 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 3.76 (s, 3H).



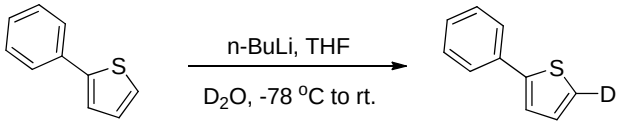
5'-(4-hydroxyphenyl)-[2,2'-bithiophene]-5-carbaldehyde (10). To a solution of compound **9** (77 mg, 0.26 mmol) in dichloromethane (10 mL) was added BBr_3 (4N in dichloromethane, 73 uL, 1.1 equiv) at 0 ^{o}C. After the reaction mixture was stirred for 4 h, additional BBr_3 (80 uL) was added. The reaction mixture was stirred overnight, and diluted with CH_2Cl_2. The resulting mixture was washed with water and concentrated. The residue was purified with silica gel chromatography (Petroleum ether/dichloromethane = 4:1) to give product **10** (62 mg, 84% yield) as a yellow solid. m.p. 229 ^{o}C. ^{1}H NMR (400 MHz, *d6*-DMSO) δ 9.85 (s, 1H), 9.81 (s, 1H), 7.97 (d, *J* = 3.6 Hz, 1H), 7.54 (d, *J* = 3.6 Hz, 1H), 7.52-7.48 (m, 3H), 7.36 (d, *J* = 3.6 Hz, 1H), 6.80 (d, *J* = 3.6 Hz, 2H). ^{13}C NMR (100 MHz, *d6*-DMSO) δ 183.8, 158.0, 145.9, 145.8, 140.8, 139.4, 132.6, 128.3, 127.0, 124.7, 123.9, 123.4, 116.0. MS (EI): *m/z* (%) 286 (M^+), 84, 66 (100). HRMS: Calculated for $C_{15}H_{10}O_2S_2$: 286.0122; Found: 286.0119.



2-((5'-(4-hydroxyphenyl)-[2,2'-bithiophen]-5-yl)methylene)malononitrile (11). To a solution of **10** (34 mg, 0.12 mmol) in dichloromethane (10 mL) were added piperidine (1 drop) and malononitrile (20 mg, 2.4 equiv) at room temperature. After the reaction mixture was stirred for 2 h. The reaction was diluted with CH_2Cl_2 and washed. The resulting mixture was concentrated and the

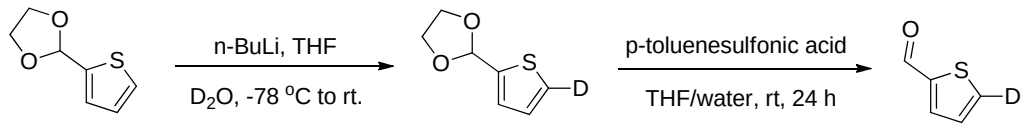
residue was purified with silica gel chromatography (Petroleum ether/dichloromethane = 2:1) to give product **11** (30 mg, 75% yield) as a dark-red solid. This compound is known.[8] m.p. 242-246 °C (lit.[8] 235-240 °C). ^{1}H NMR (400 MHz, *d*6-acetone) d 8.78 (s, 1H), 8.38 (s, 1H), 7.92 (d, *J* = 3.4 Hz, 1H), 7.62 (d, *J* = 3.4 Hz, 1H), 7.61 (dm, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 3.8 Hz, 1H), 7.40 (d, *J* = 3.8 Hz, 1H), 6.93 (dm, *J* = 7.8 Hz, 2H).

Kinetic isotope effect studies



2h *d*- **2h** > 99%

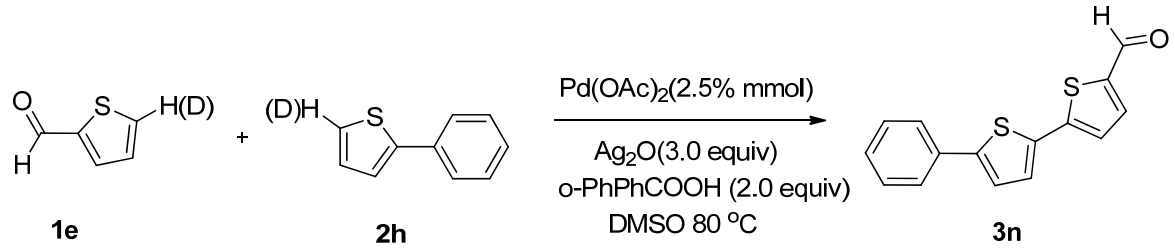
To an over-dried round bottom flask were added **2h** (10 mmol, 1.0 equiv), THF (20 mL) under N_2. The solution was cooled to -78 °C and *n*-BuLi (4.4 mL, 2.5 M in hexane, 1.1equiv) was added slowly. After stirring for 1 h, the reaction mixture was allowed to warm to room temperature and re-cool to -20 °C. D_2O (0.6 mL) was added slowly and the mixture was diluted with ethyl acetate, washed with water, dried over Na_2SO_4, filtered and concentrated. The product was purified with silica gel chromatography (100% petroleum ether) to give ***d*-2h** in >99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.8 Hz, 2 H), 7.39 (t, *J* = 6.8 Hz, 2 H), 7.32-7.28 (m, 2 H), 7.08 (d, *J* = 3.6 Hz, 1 H).



1-e' *d*-**1e'**, > 99% *d*-**1e**

Compound **1-e'** was prepared according to the literature.[7] Preparation of *d*-**1e'** is similar with *d*-**2h**. Compound *d*-**1e** was prepared by deprotection of *d*-**1e'** with p-toluenesulfonic acid (catalytic amount) in THF/water (4/1) in almost quantity yield (98%). *d*-**1e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1 H), 7.81 (d, *J* = 3.6 Hz, 1 H), 7.23 (d, *J* = 3.6 Hz, 1 H).

Kinetic isotope experiments.



1e **2h** **3n**

The initial rate measurements were carried out on a 0.3 mmol scale. The reactions were carried out according to standard procedure, stopped after the corresponding reaction time (10 min-120 min) and immediately cooled to room temperature. Then 100 uL internal standard (1,3,5-trimethoxybenzene in DMSO (0.1 mmol/mL)) was added. The yield was determined by GC. The obtained yields were plotted as concentration [**3n**] vs. time t (Figure S1). From the diagram, the following initial rates were calculated:

$K_H = 2.238 \times 10^{-4}$ mmol·mL^{-1}·min^{-1}

$K_{D(d\mathbf{1e\text{-}2h})} = 8.570 \times 10^{-5}$ mmol·mL^{-1}·min^{-1}

$K_{D(\mathbf{1e}\text{-}d\mathbf{2h})} = 5.454 \times 10^{-5}$ mmol·mL^{-1}·min^{-1}

Therefore, the $k_H/k_{D\ (d\mathbf{1e\text{-}2h})} = 2.6$; $k_H/k_{D\ (\mathbf{1e}\text{-}d\mathbf{2h})} = 4.1$

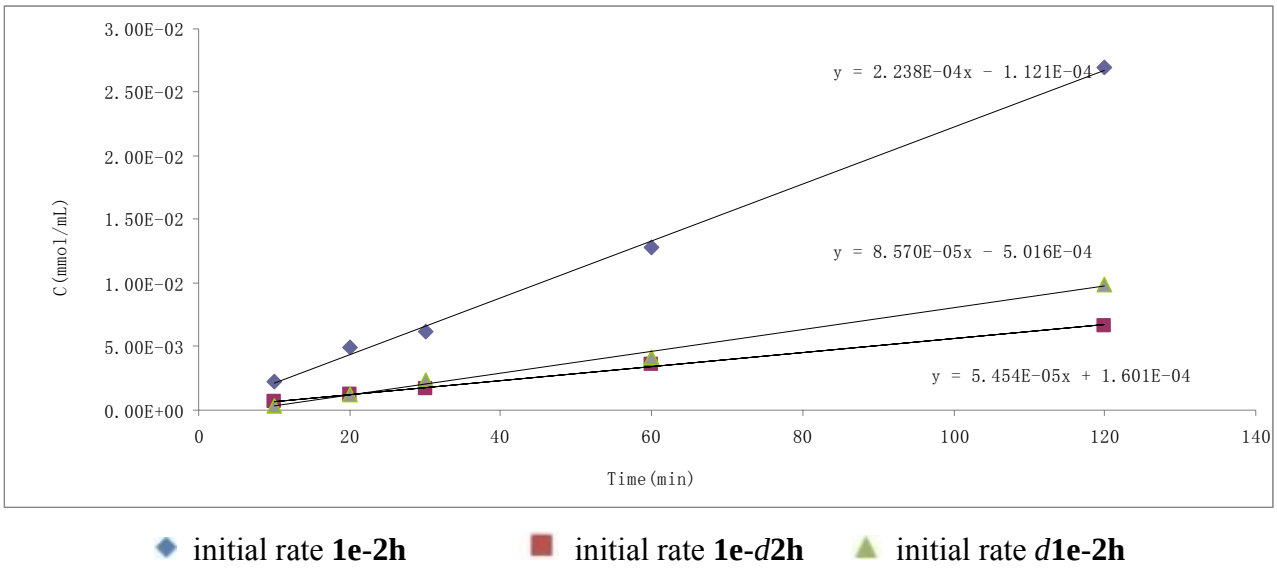


Figure S1. Initial rates of the standard reaction **1e-2h** (blue), **1e**-*d***2h** (red), and *d***1e-2h** (green).

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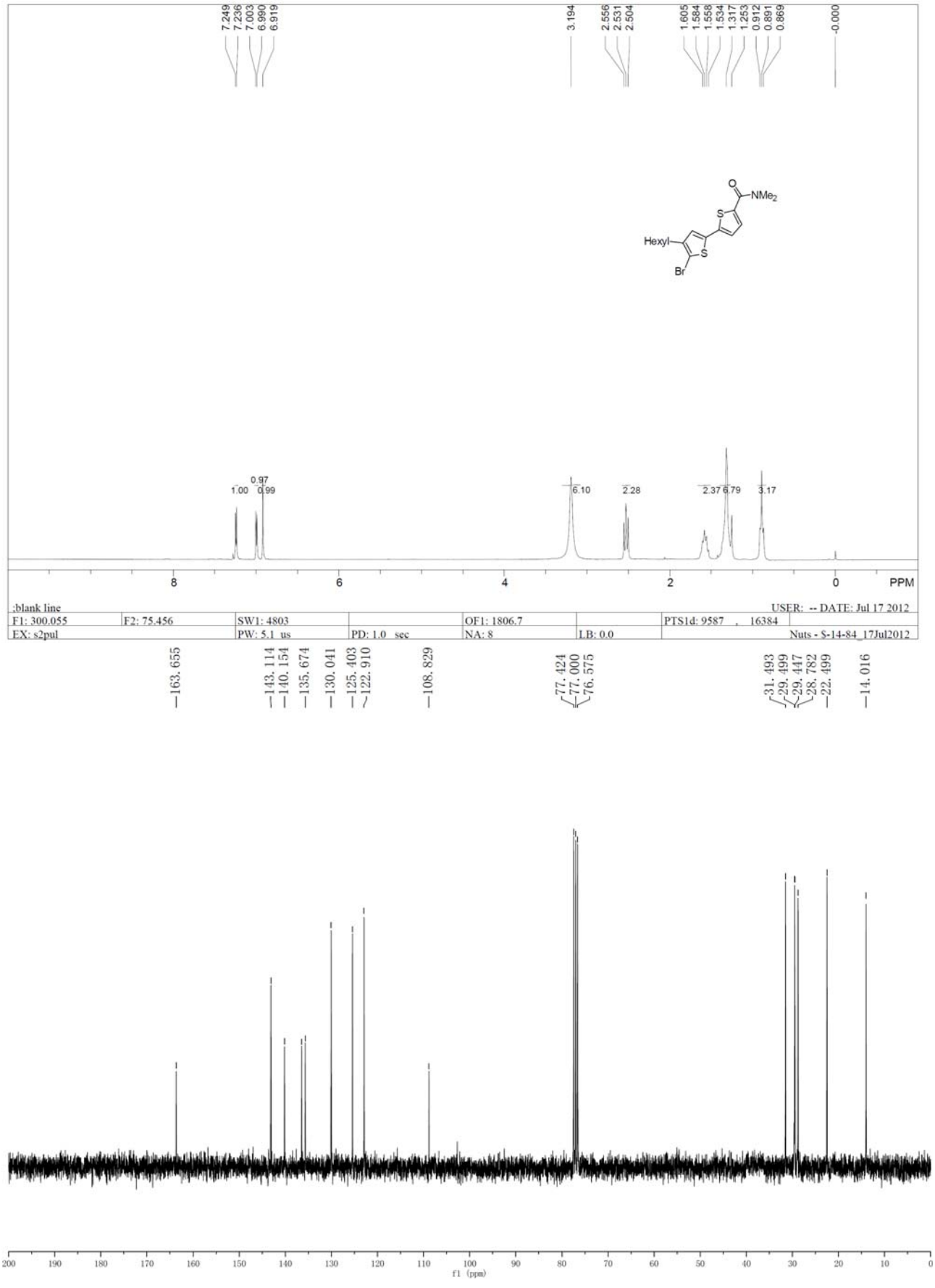
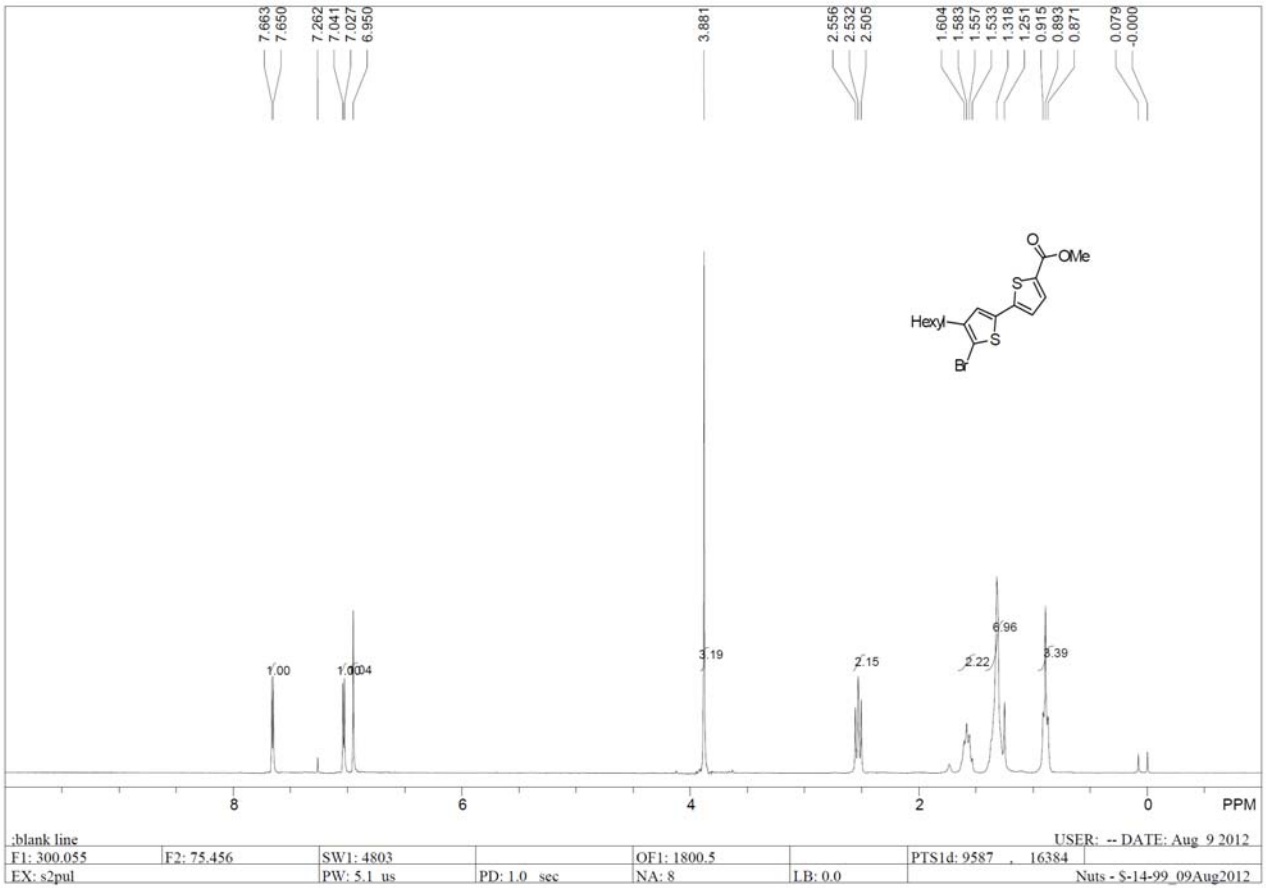
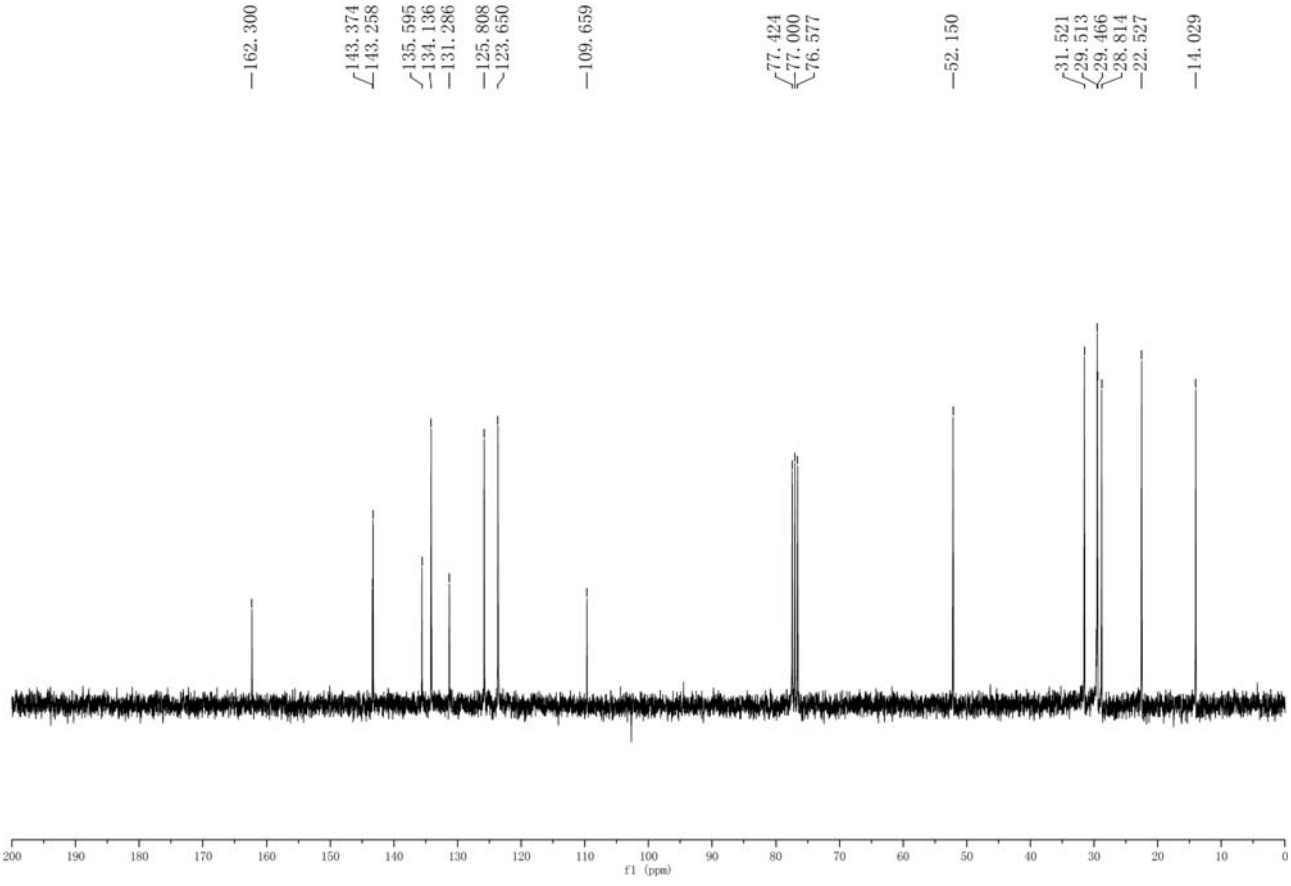
5'-Bromo-4'-hexyl-*N*,*N*-dimethyl-[2,2'-bithiophene]-5-carboxamide (3a).

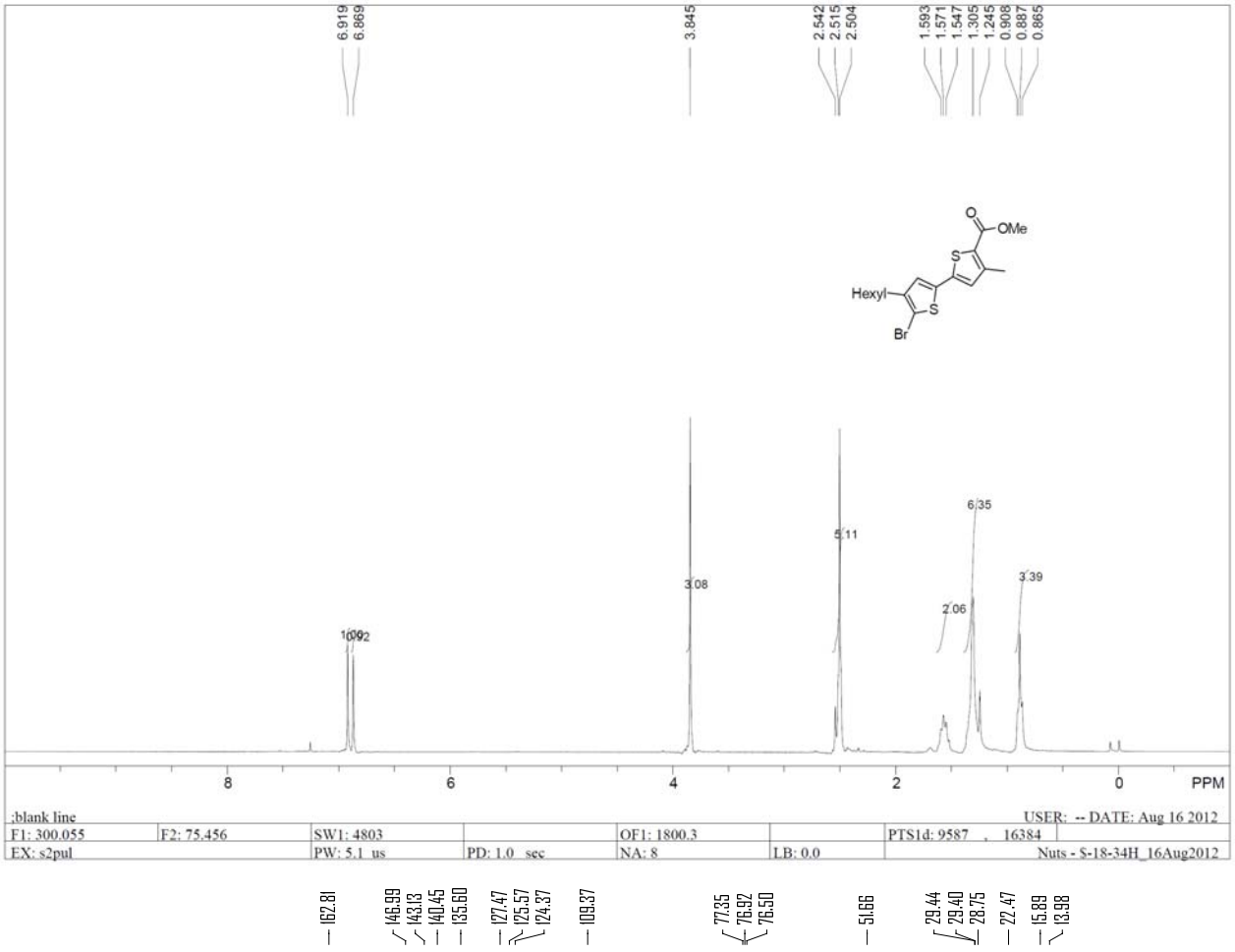


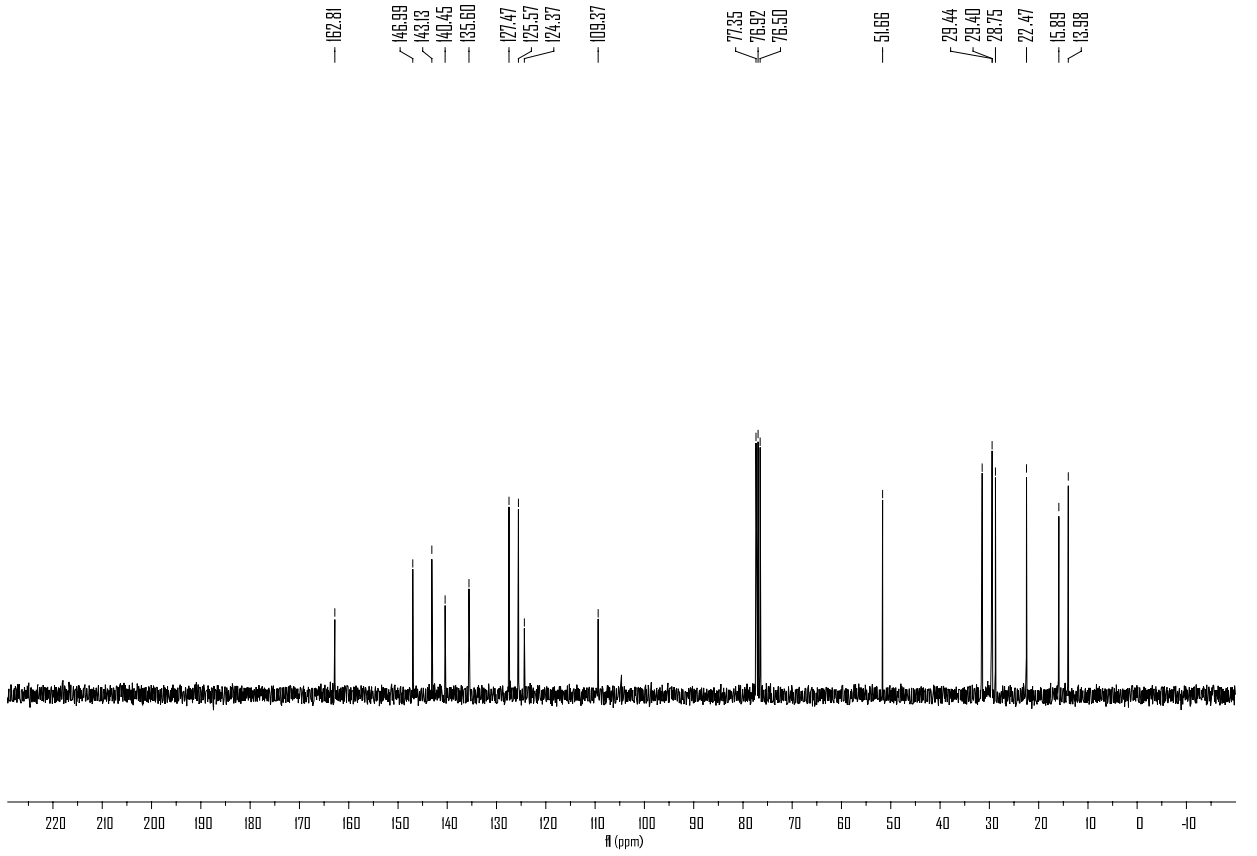
Methyl 5'-bromo-4'-hexyl-[2,2'-bithiophene]-5-carboxylate (3b).



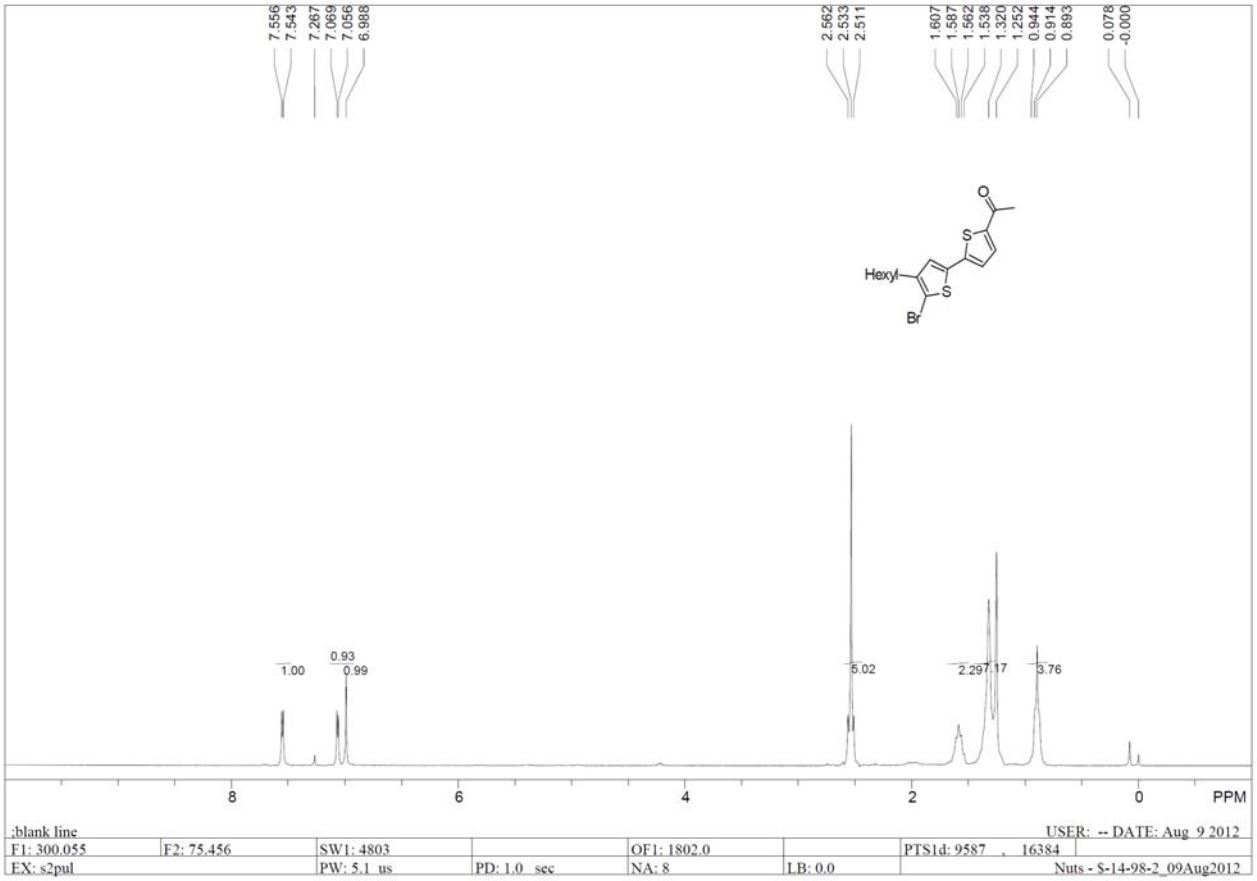


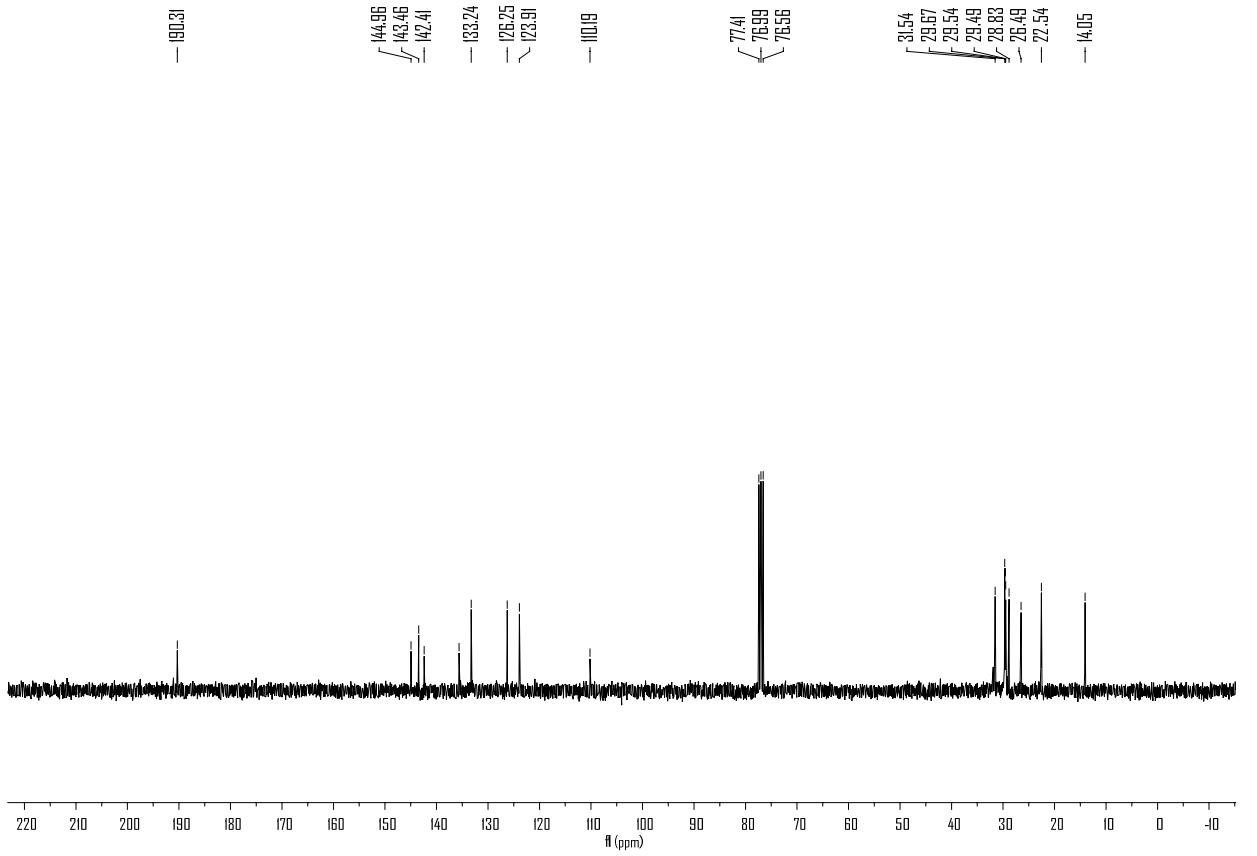
Methyl 5'-bromo-4'-hexyl-4-methyl-[2,2'-bithiophene]-5-carboxylate (3c).



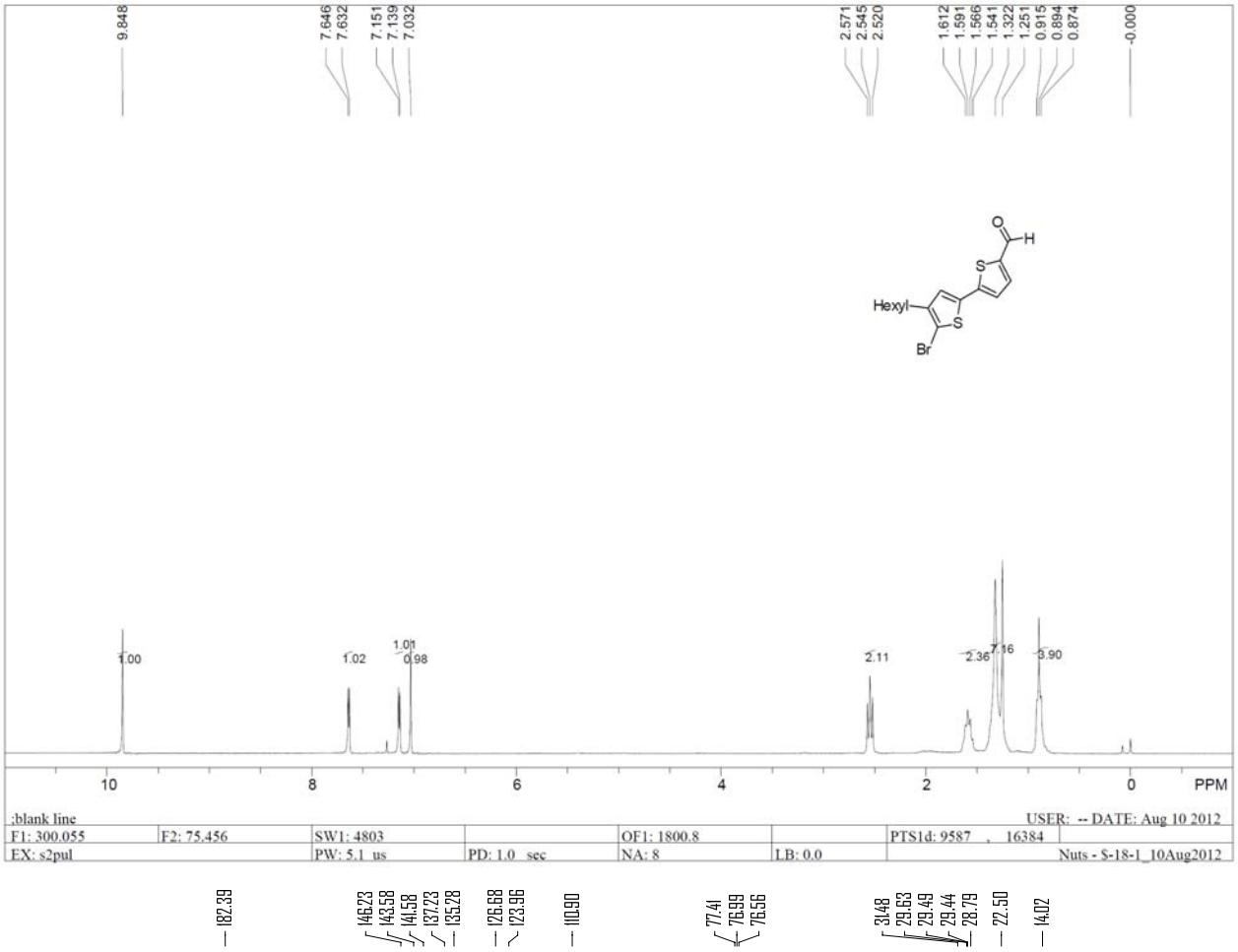


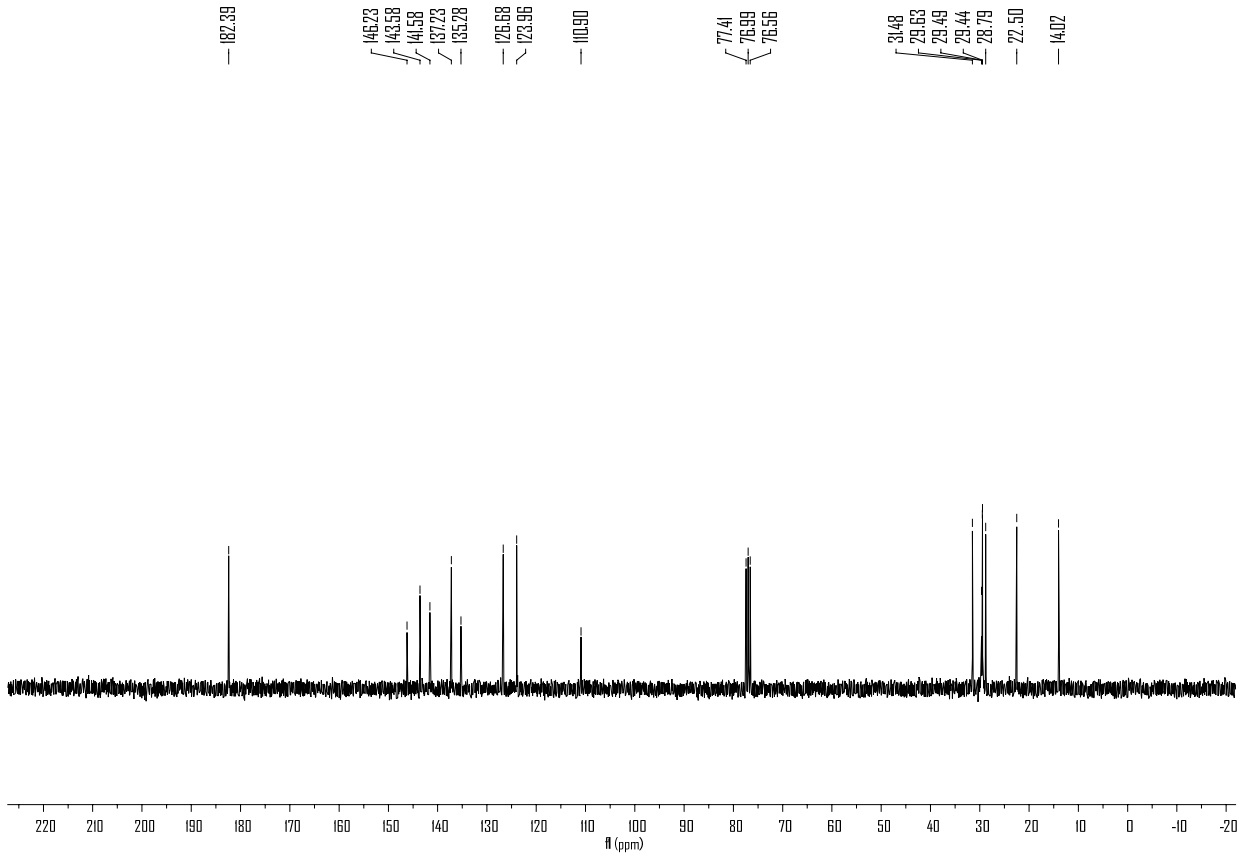
1-(5'-Bromo-4'-hexyl-[2,2'-bithiophen]-5-yl)ethanone (3d).



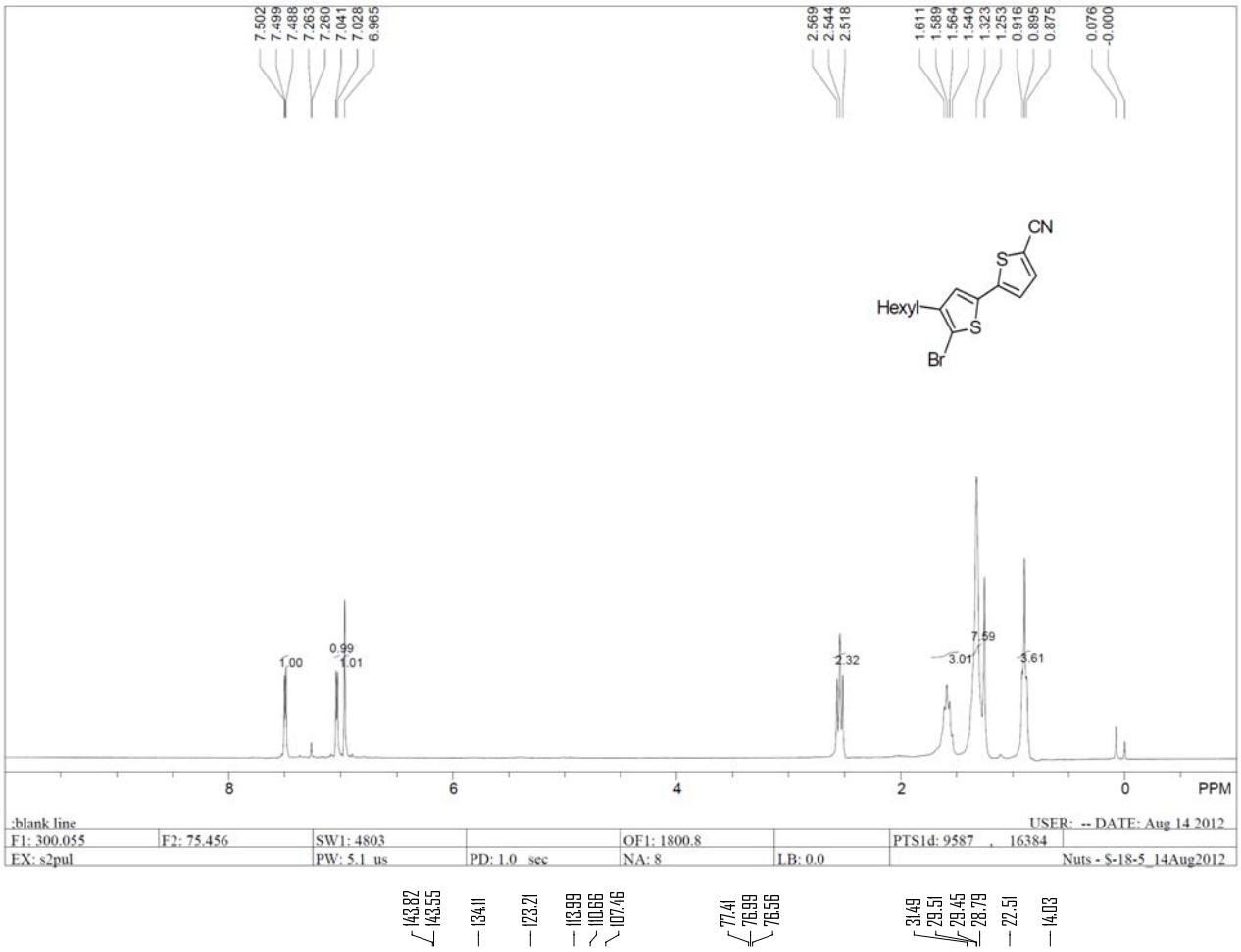


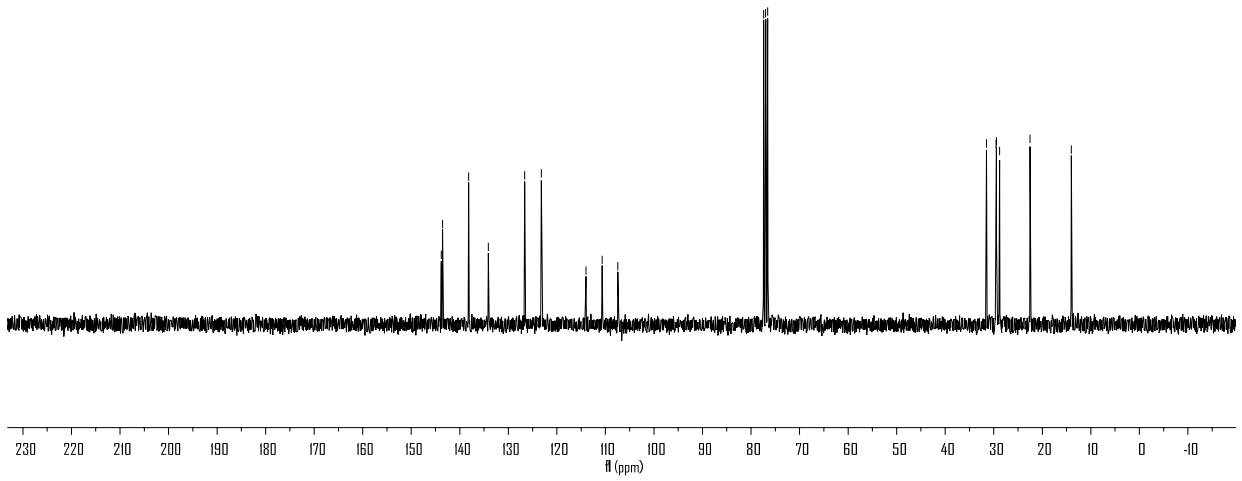
5'-Bromo-4'-hexyl-[2,2'-bithiophene]-5-carbaldehyde (3e).



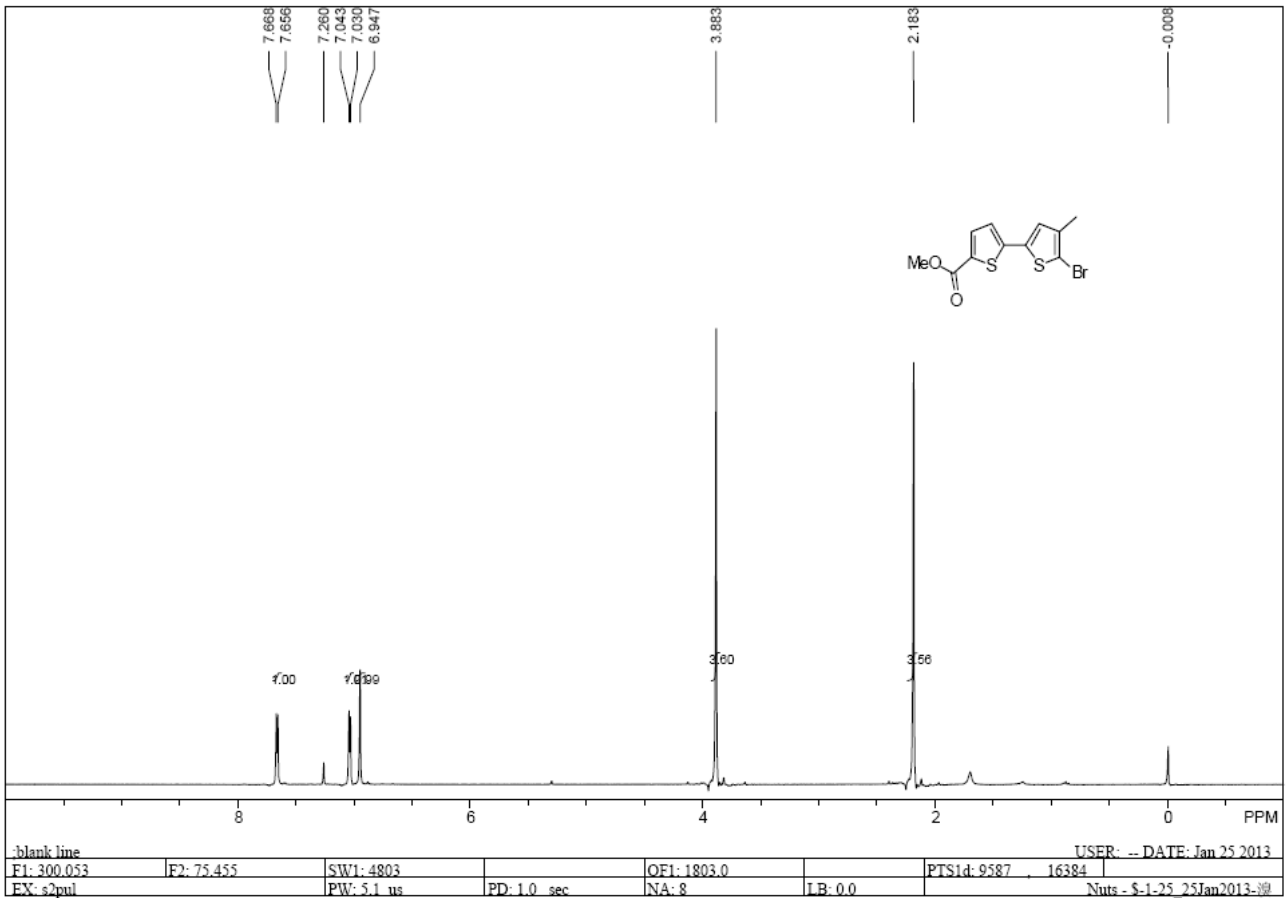


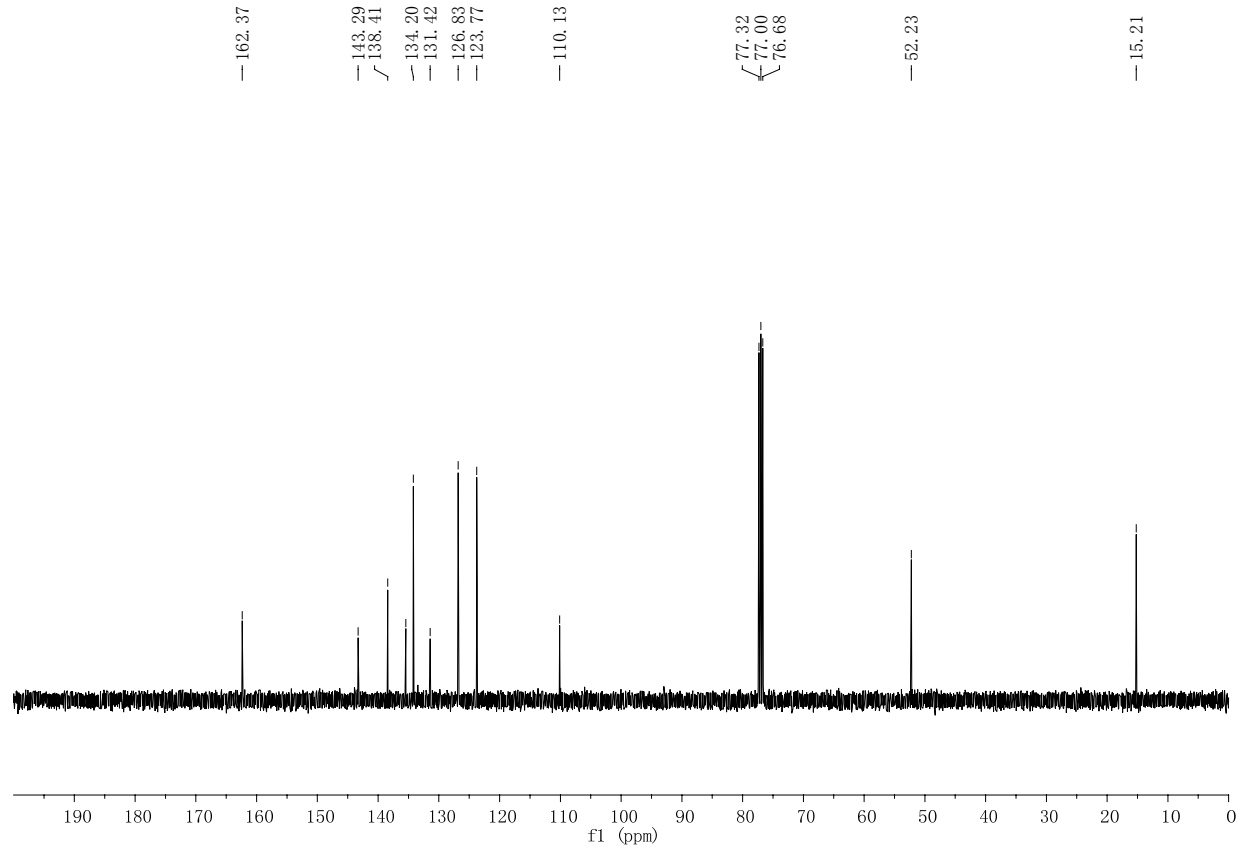
5'-Bromo-4'-hexyl-[2,2'-bithiophene]-5-carbonitrile (3f).



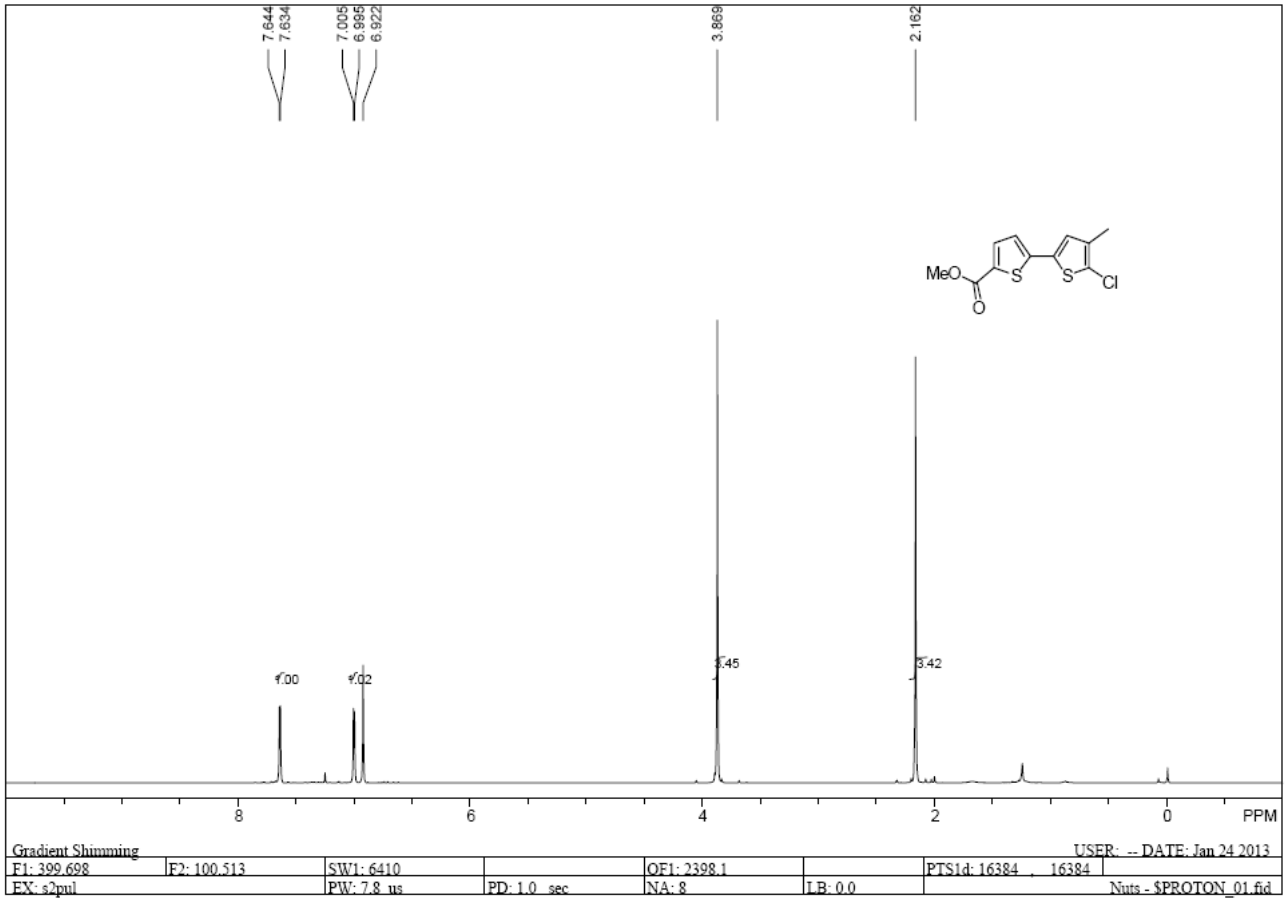


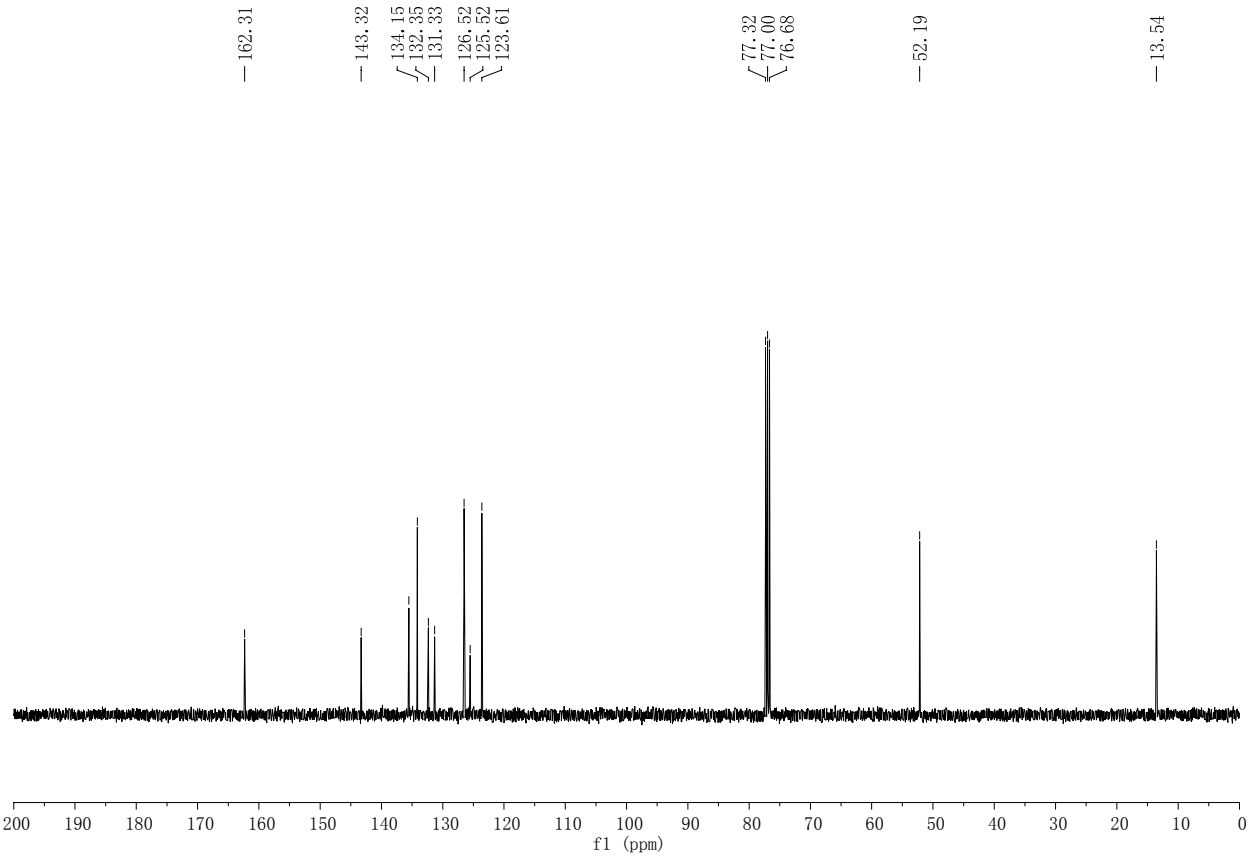
Methyl 5'-bromo-4'-methyl-[2,2'-bithiophene]-5-carboxylate (3g).



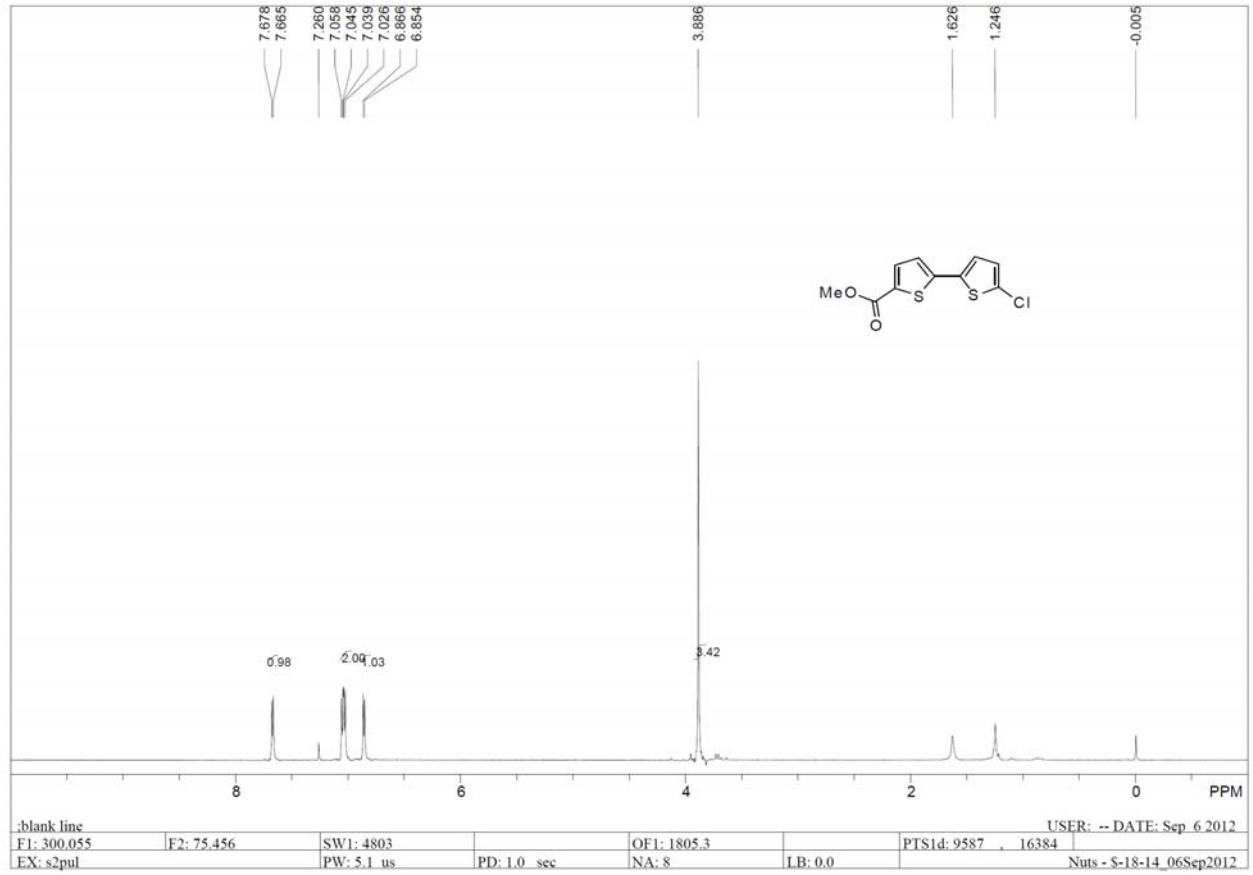


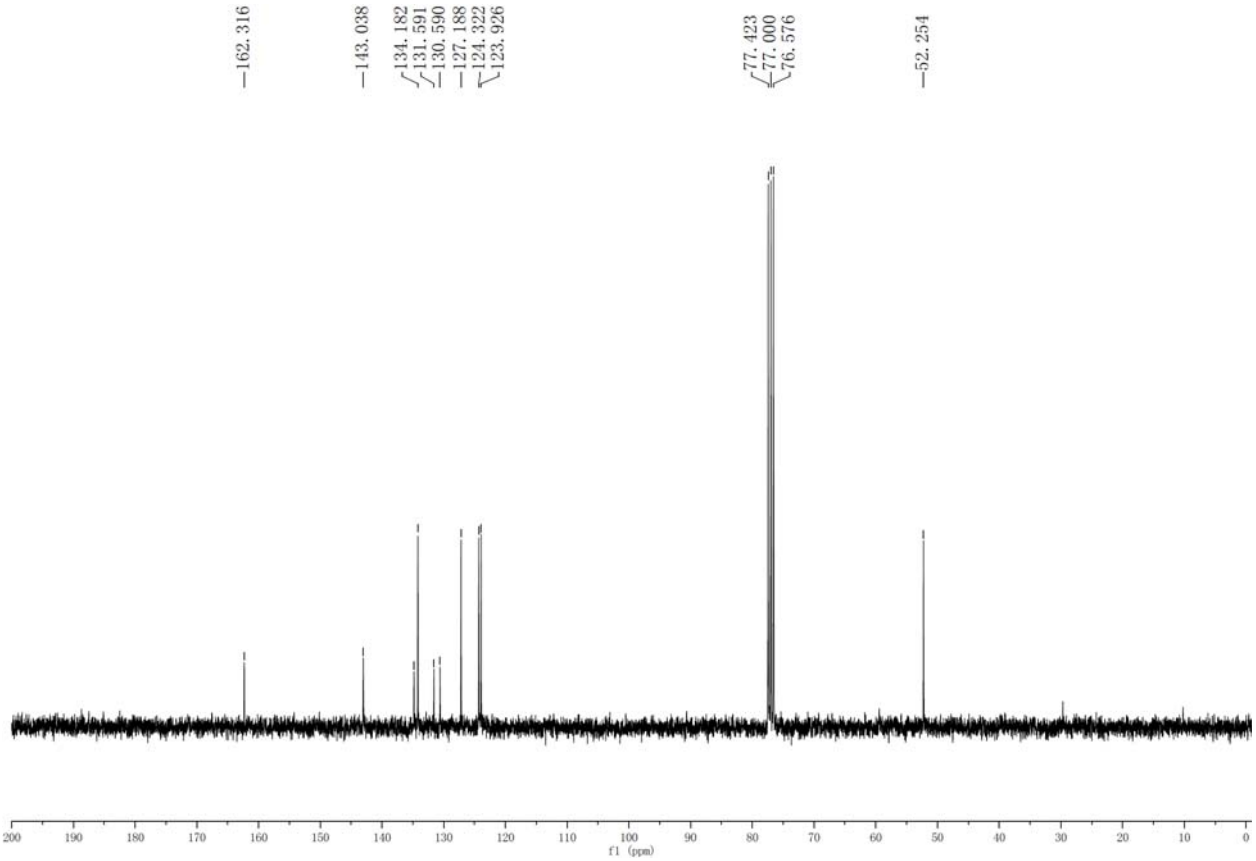
Methyl 5'-chloro-4'-methyl-[2,2'-bithiophene]-5-carboxylate (3i).



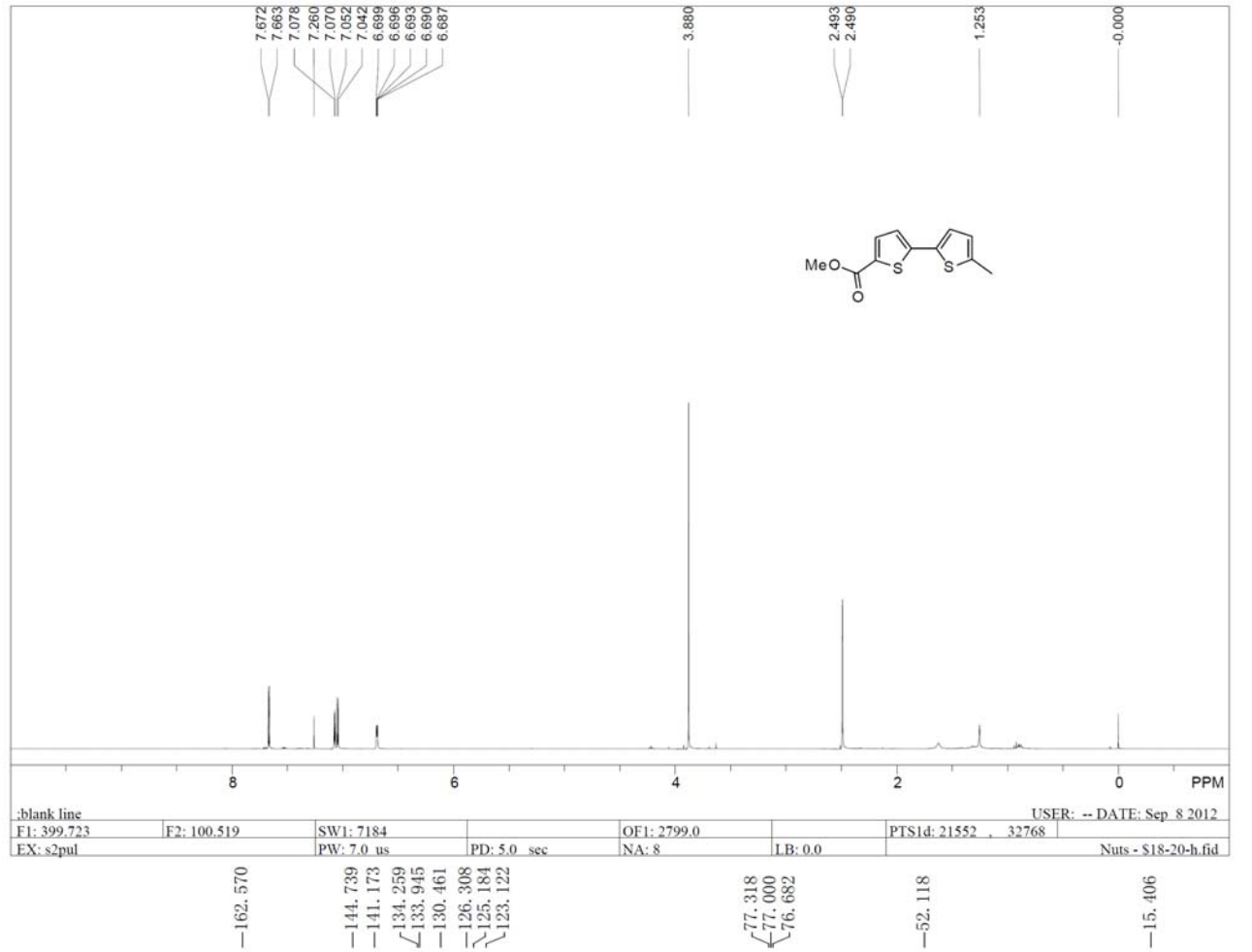


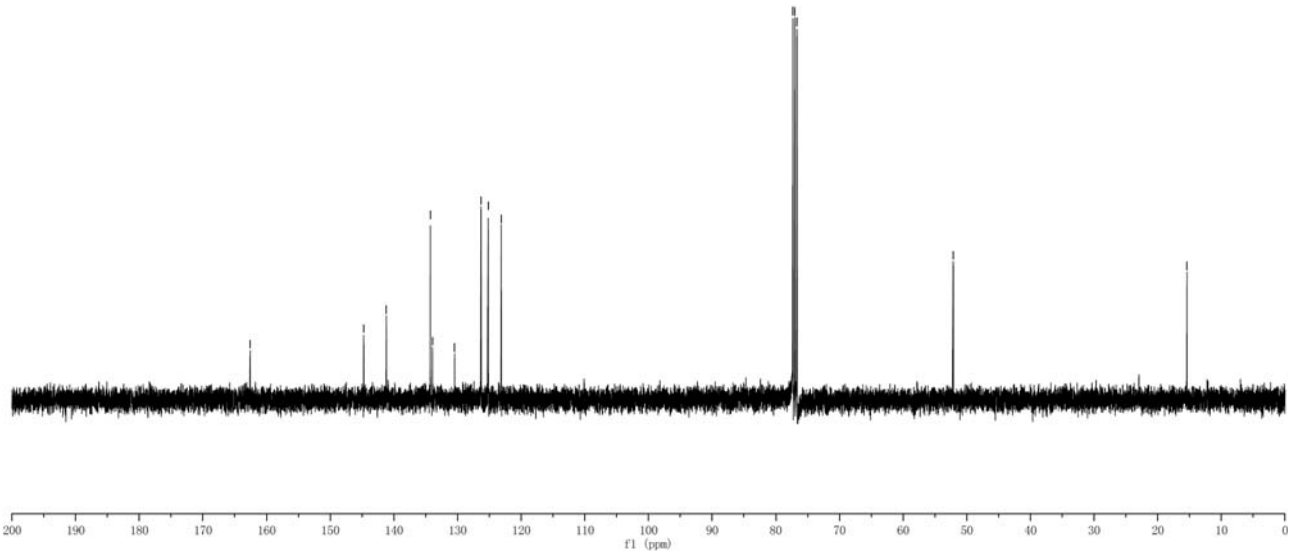
Methyl 5'-chloro-[2,2'-bithiophene]-5-carboxylate (3j).



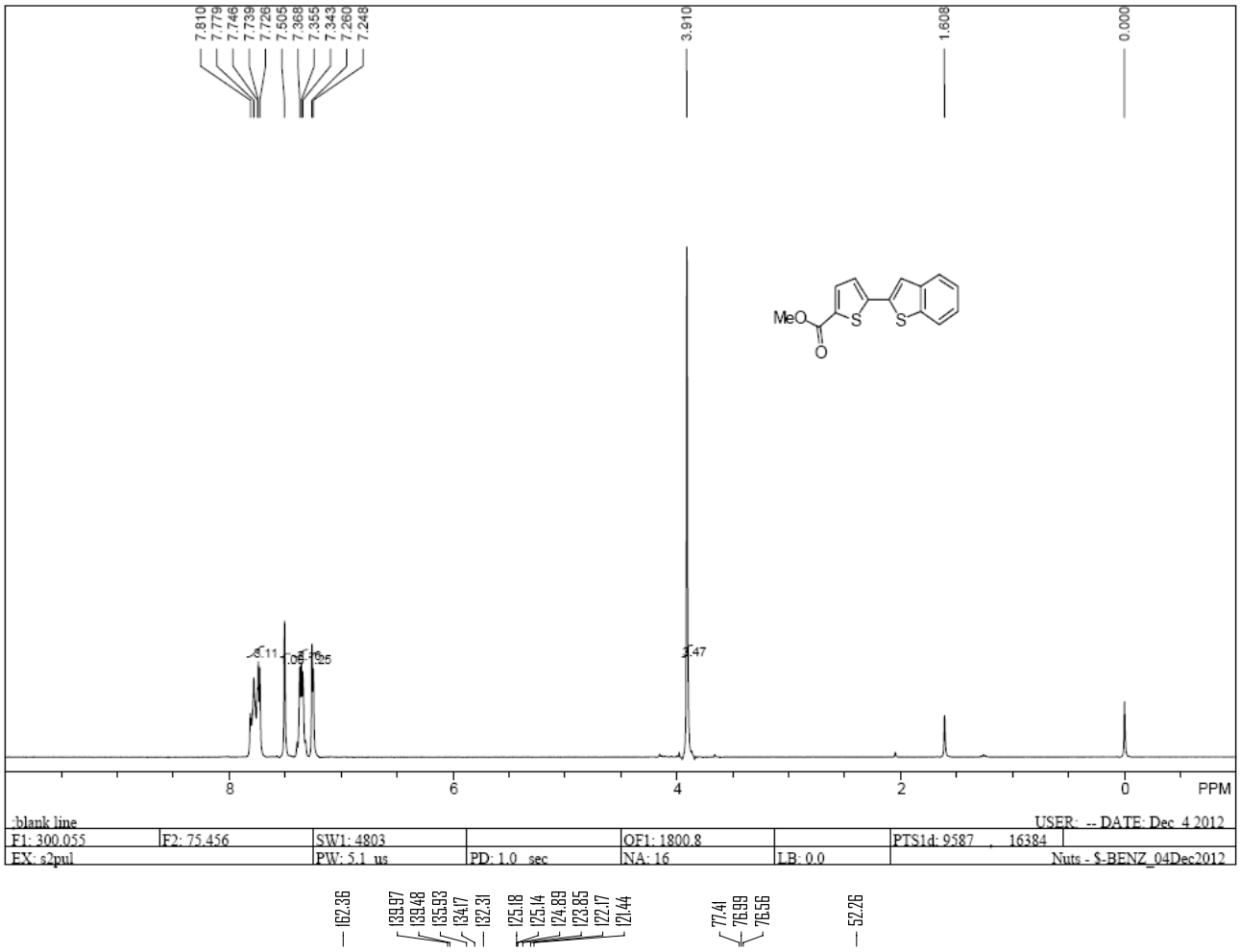


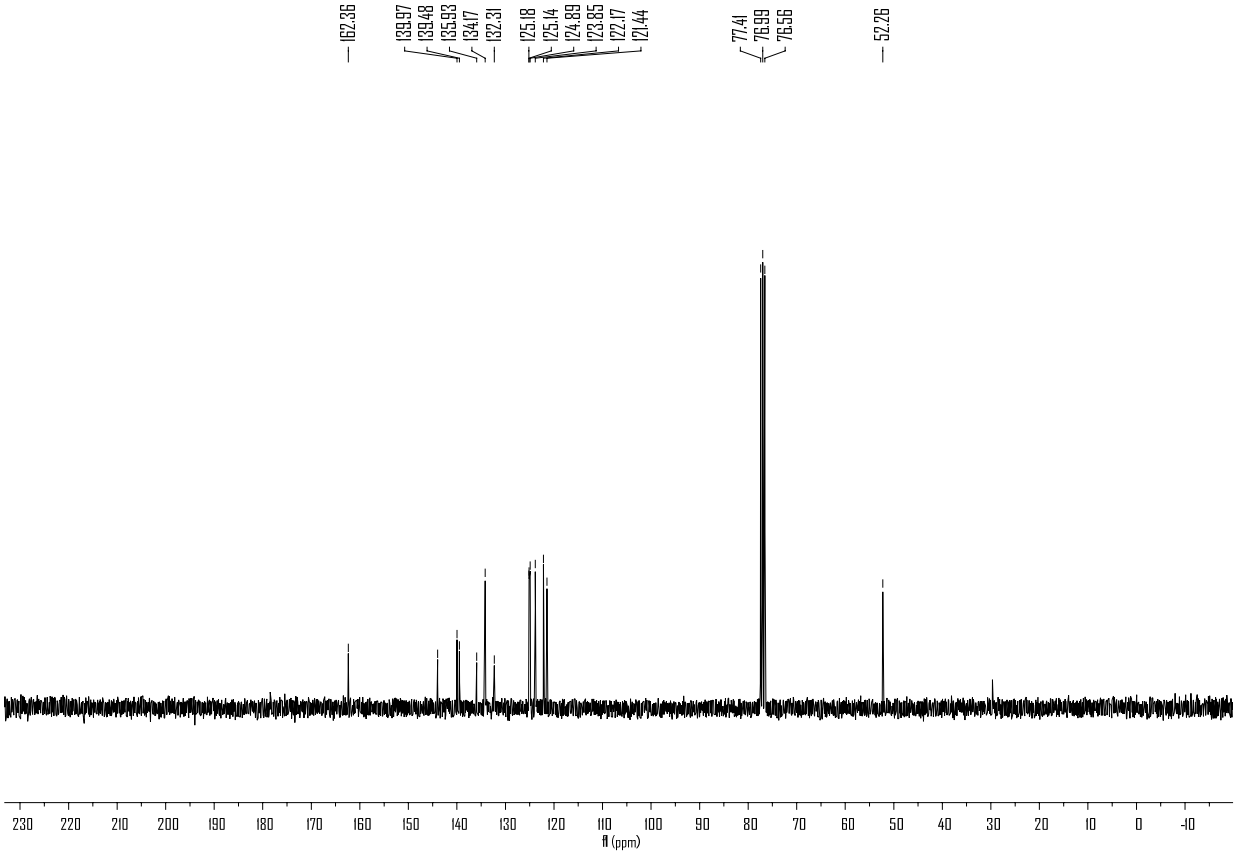
Methyl 5'-methyl-[2,2'-bithiophene]-5-carboxylate (3k).



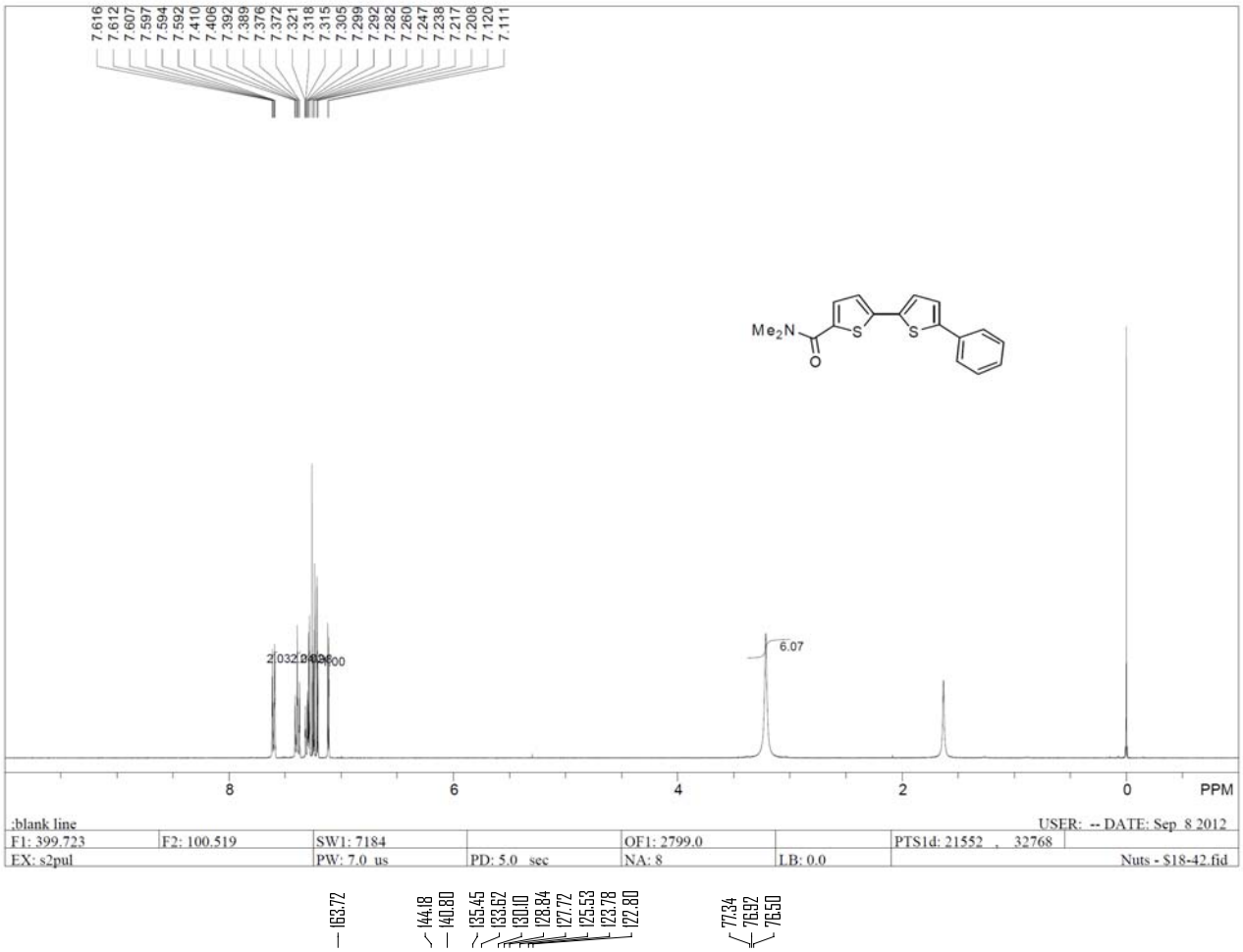


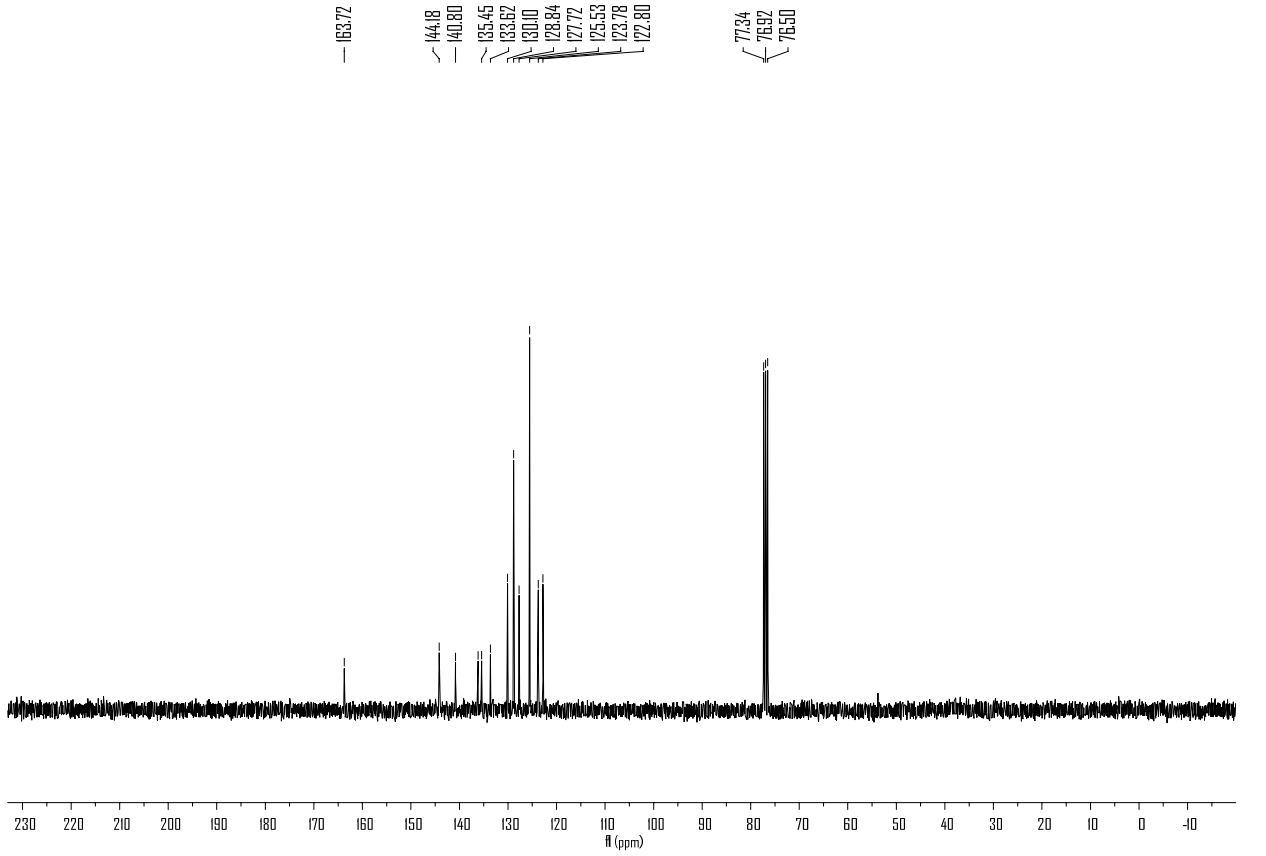
Methyl 5-(benzo[b]thiophen-2-yl)thiophene-2-carboxylate (3l).



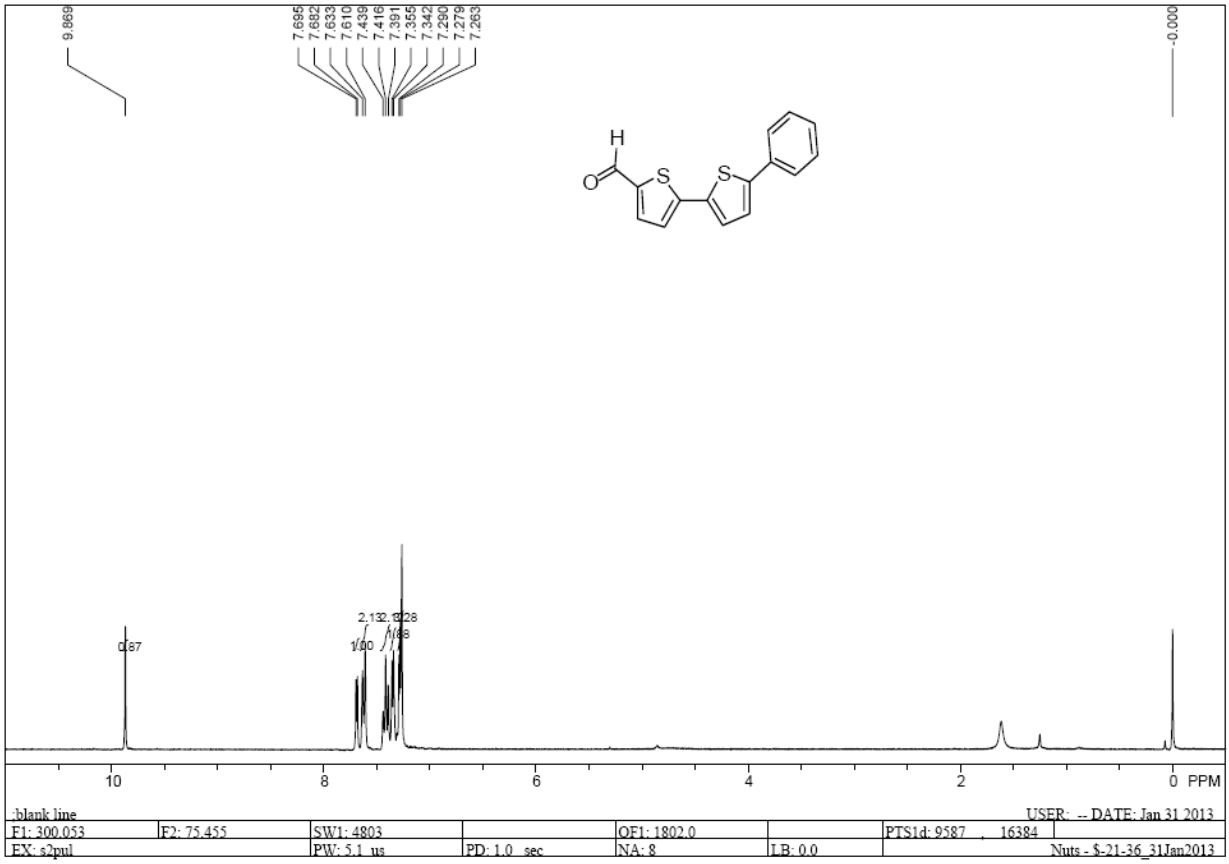


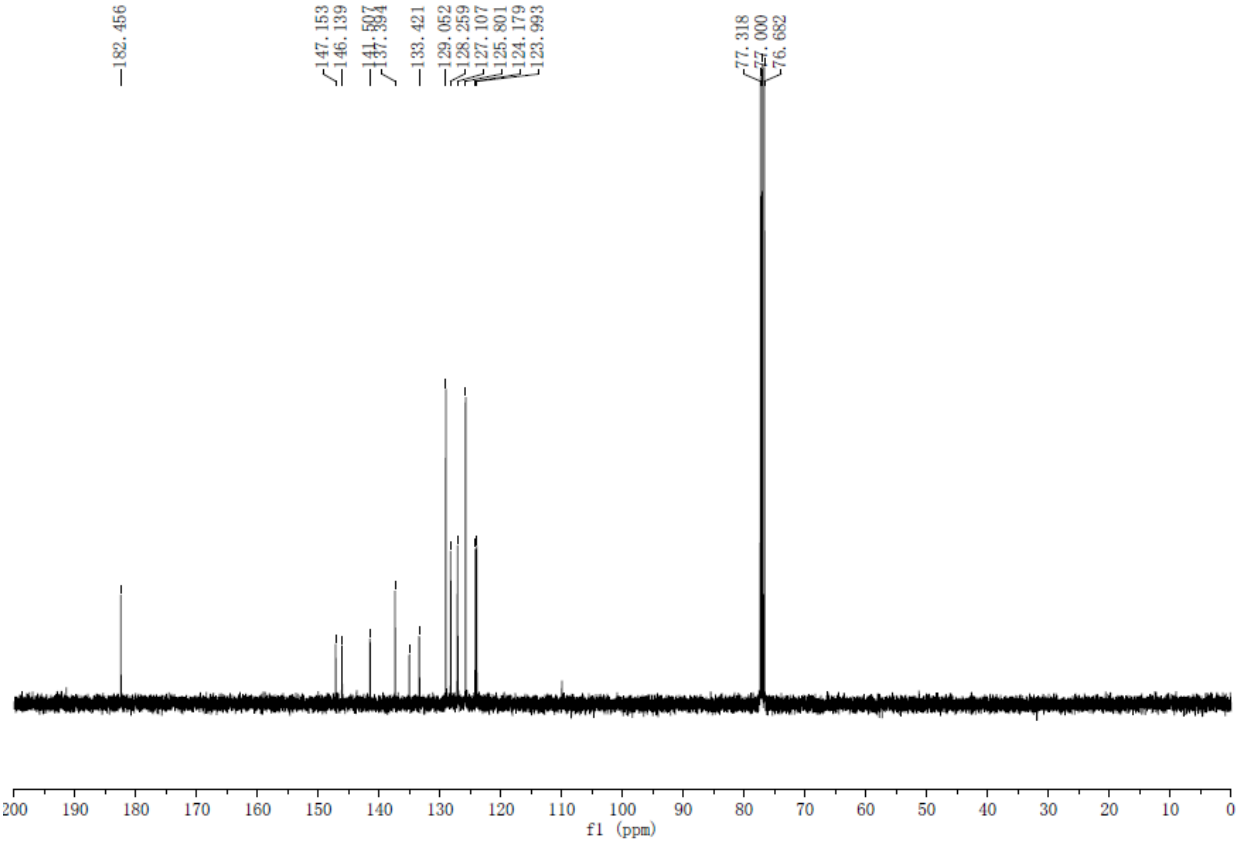
_N,N_-Dimethyl-5'-phenyl-[2,2'-bithiophene]-5-carboxamide (3m).



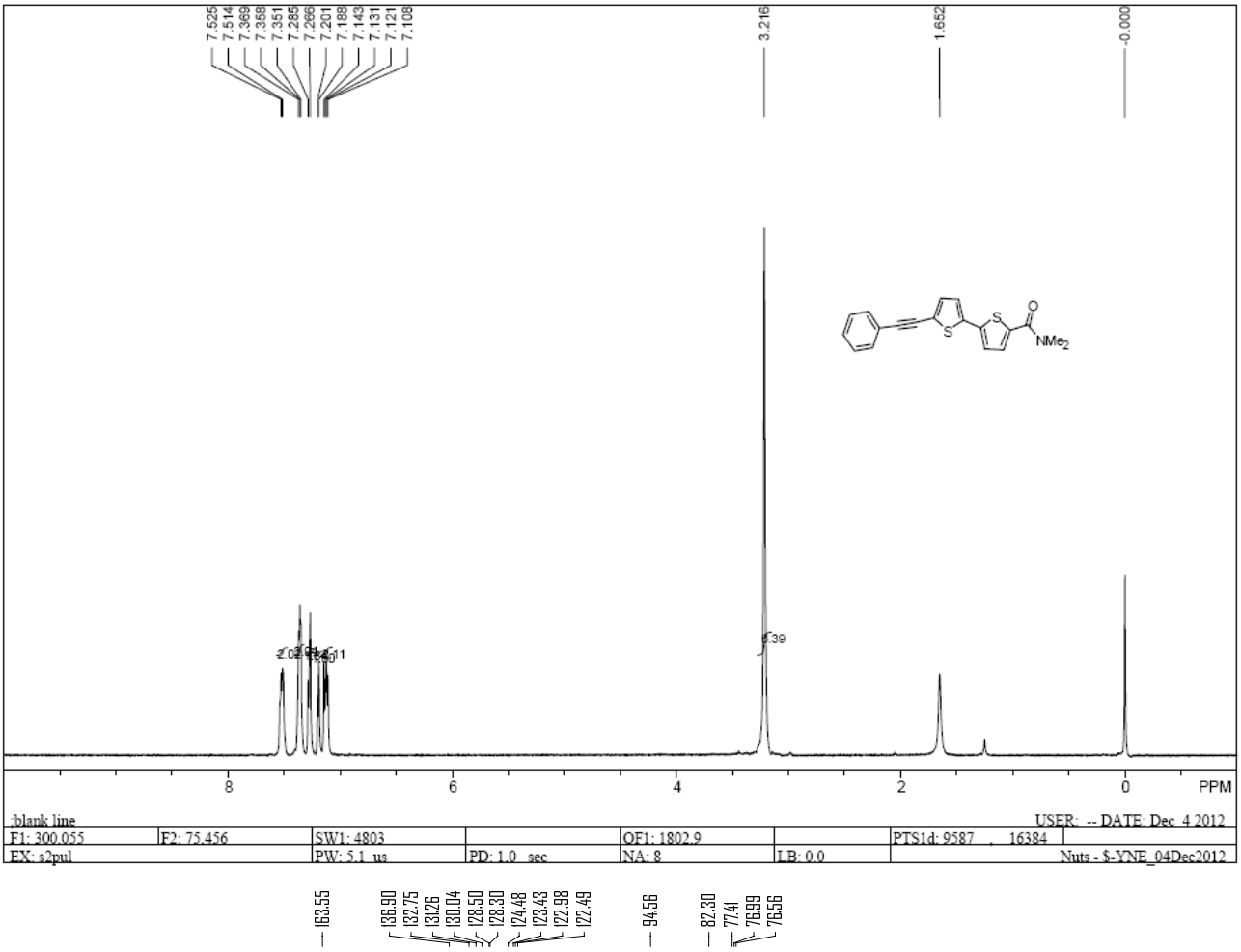


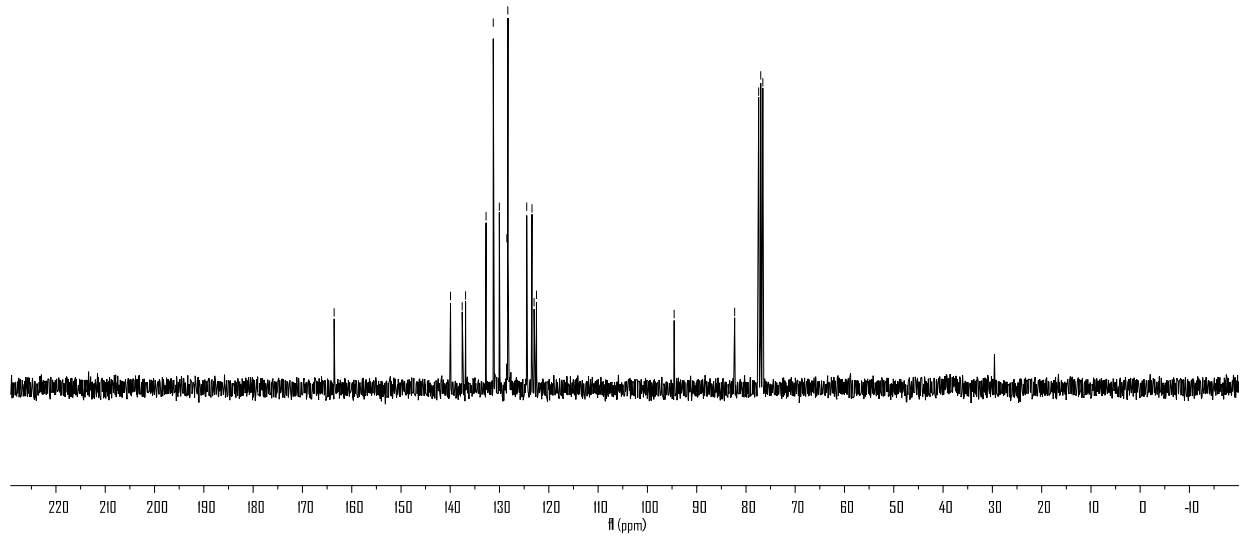
5'-Phenyl-[2,2'-bithiophene]-5-carbaldehyde (3n).



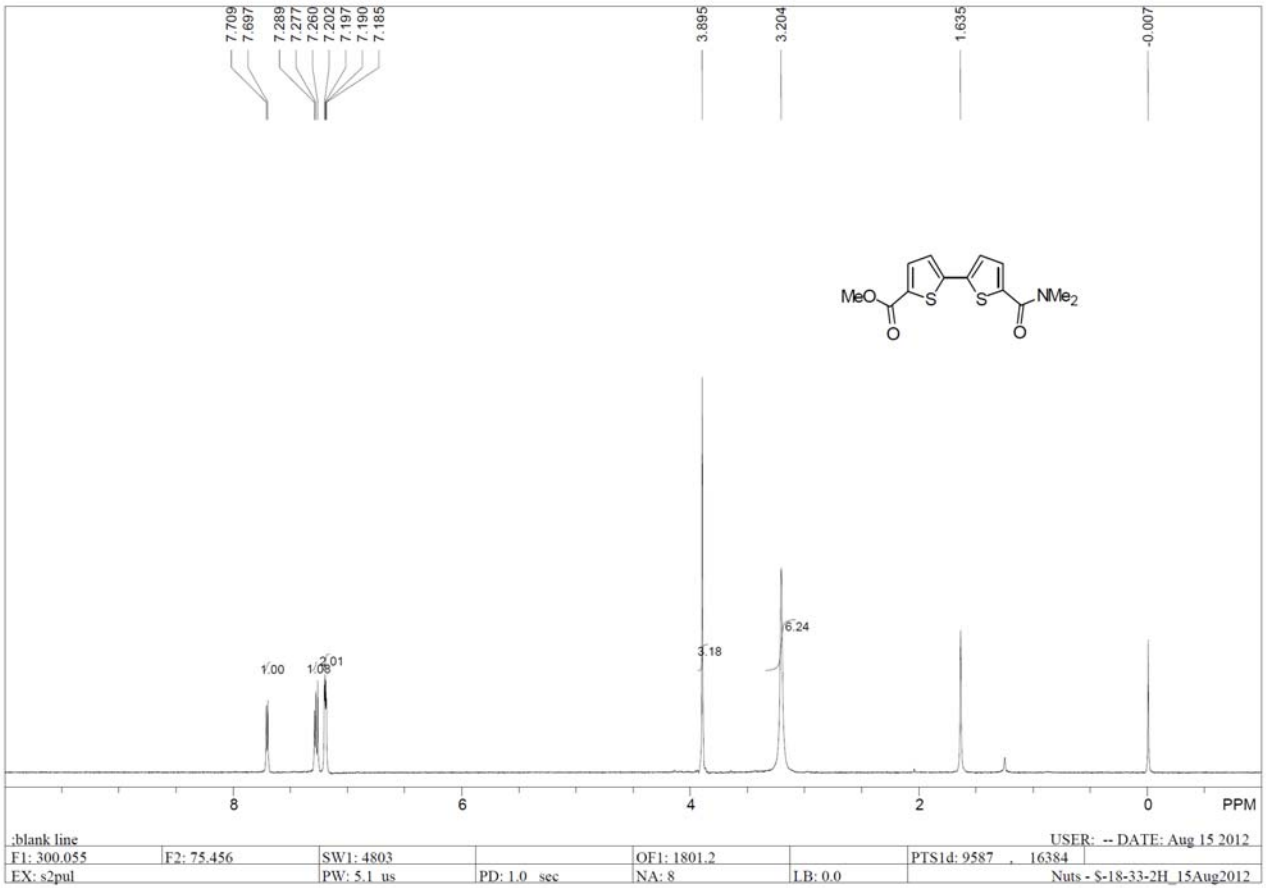


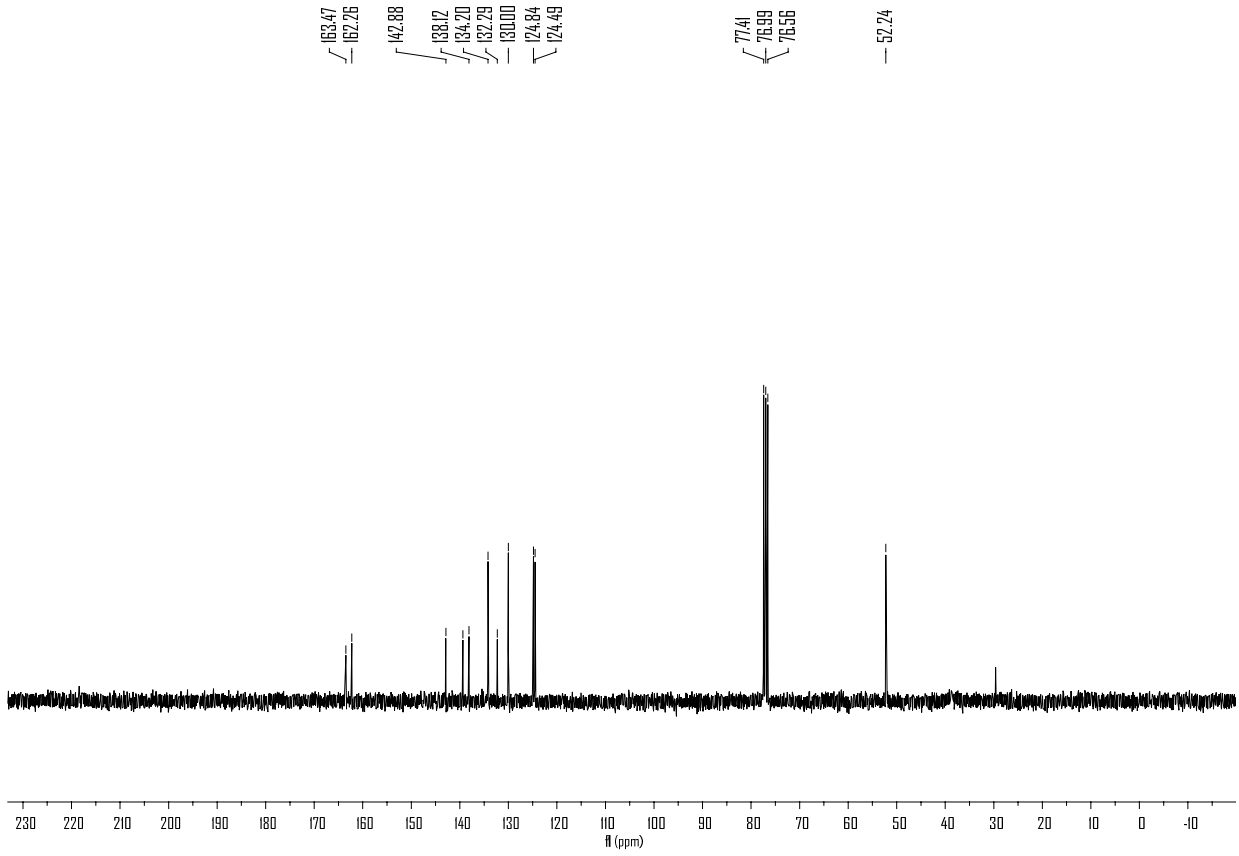
_N,N_-Dimethyl-5'-(phenylethynyl)-[2,2'-bithiophene]-5-carboxamide (3o).



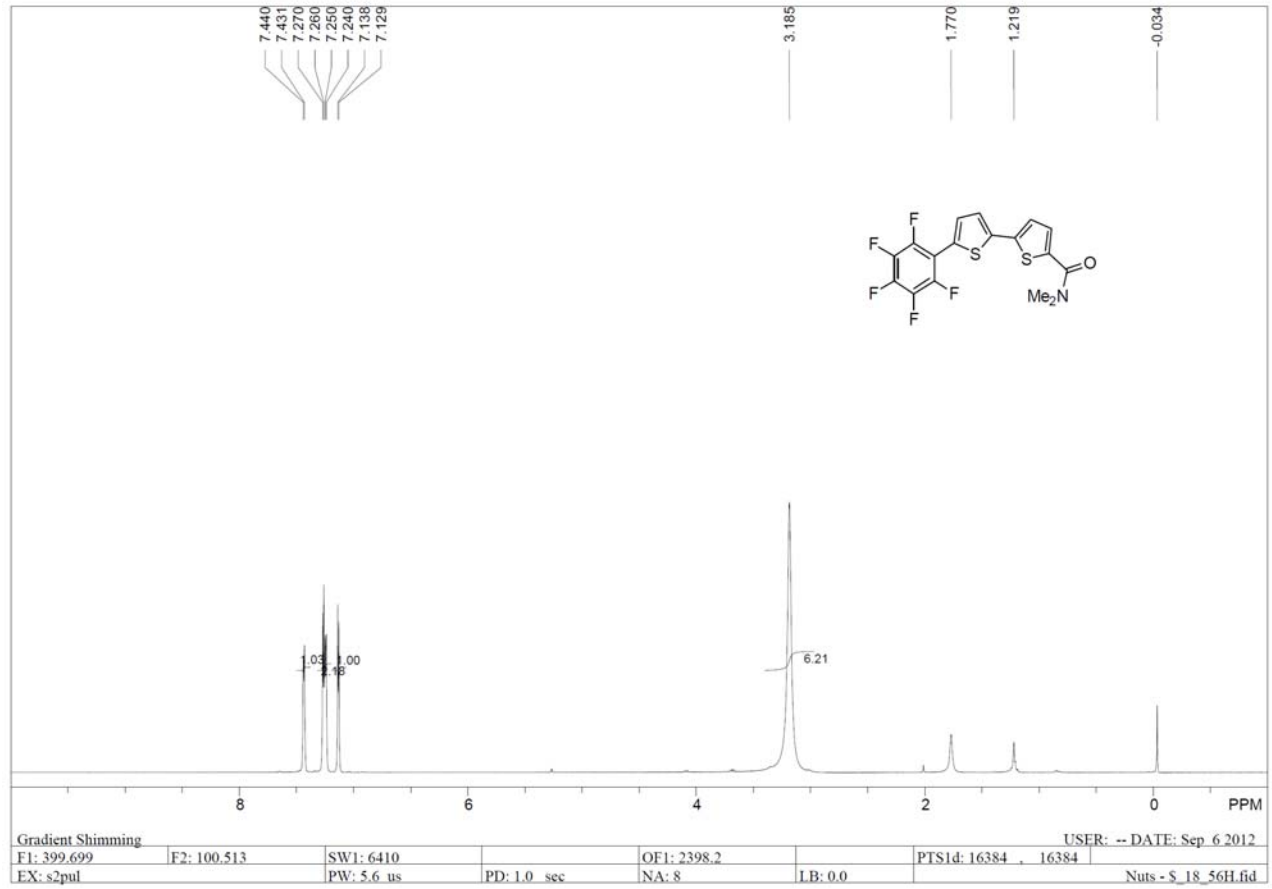


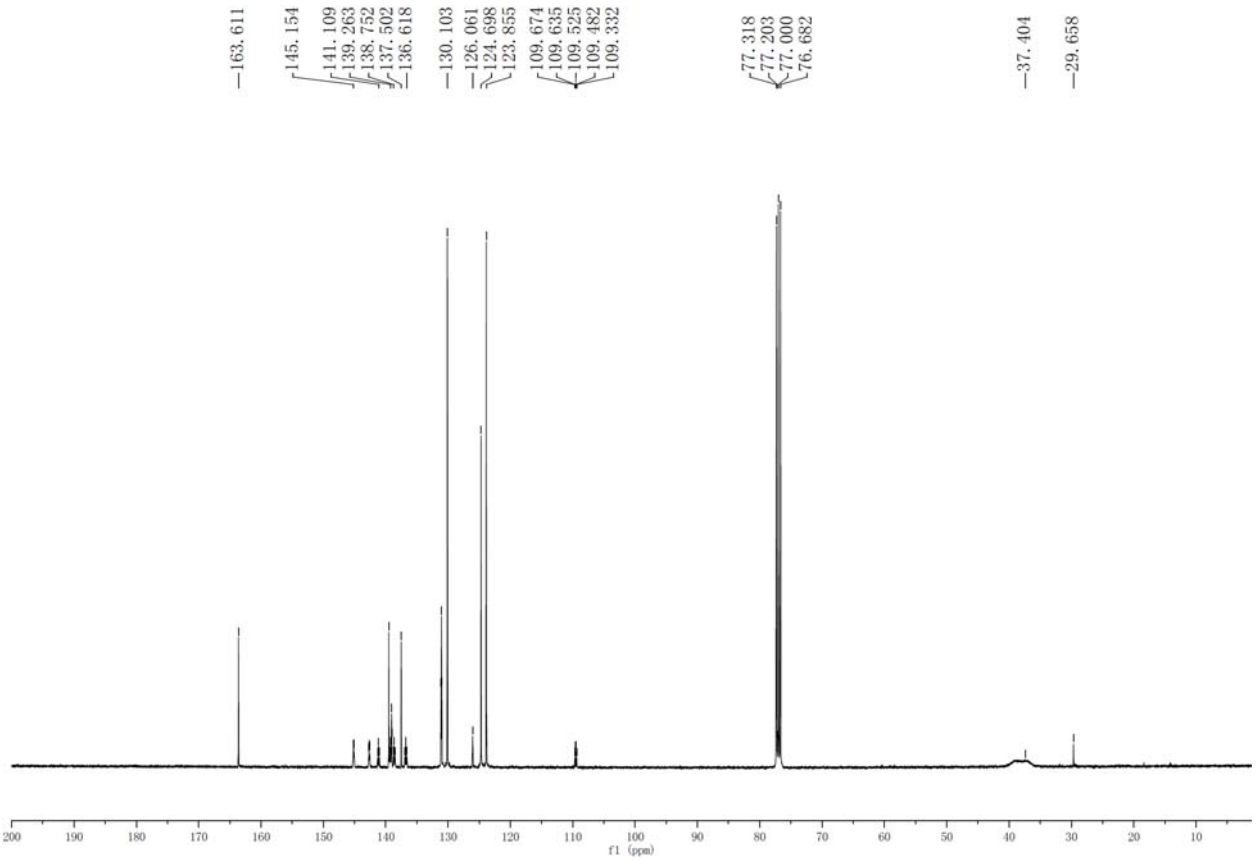
Methyl 5'-(dimethylcarbamoyl)-[2,2'-bithiophene]-5-carboxylate (3p).

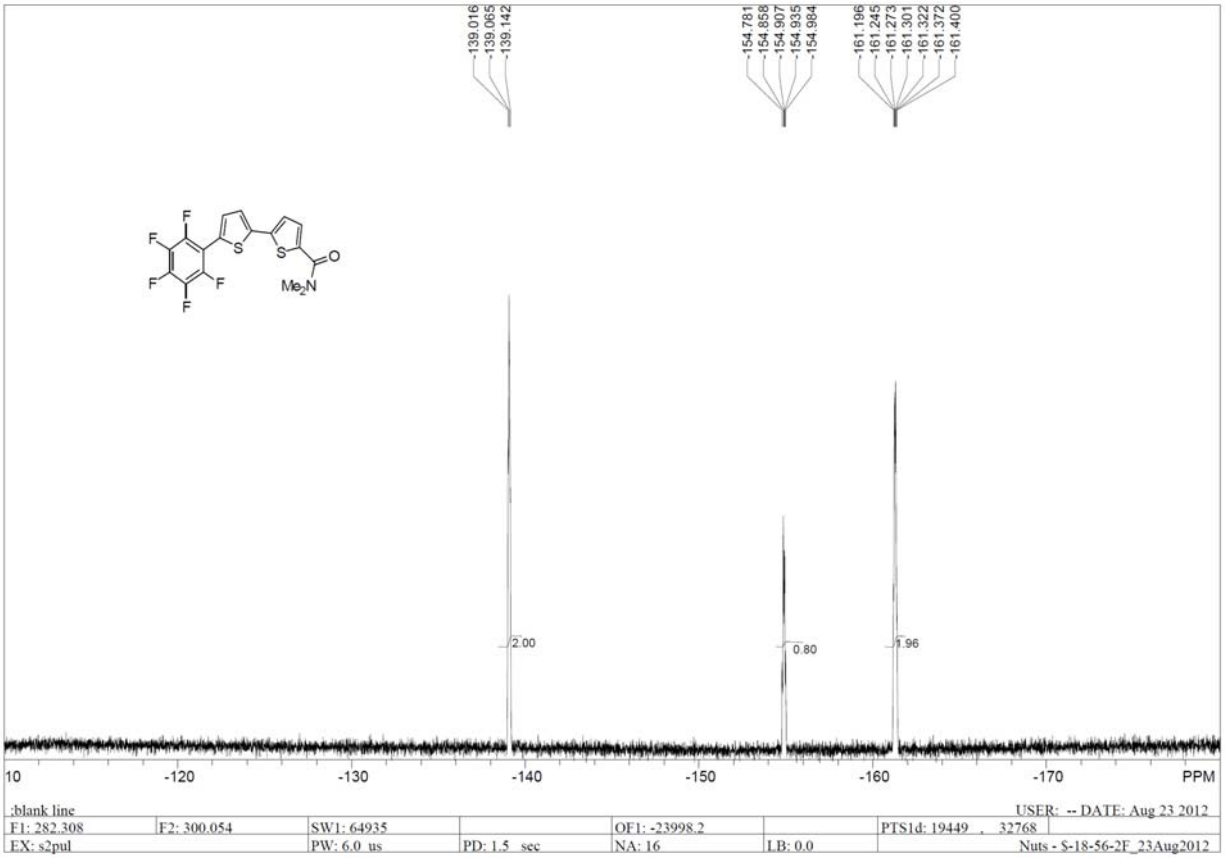




_N,N_-dimethyl-5'-(perfluorophenyl)-[2,2'-bithiophene]-5-carboxamide (3q).



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F
F
F
F
S
S
O
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PTS1d: 19449 , 32768
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PD: 1.5 sec
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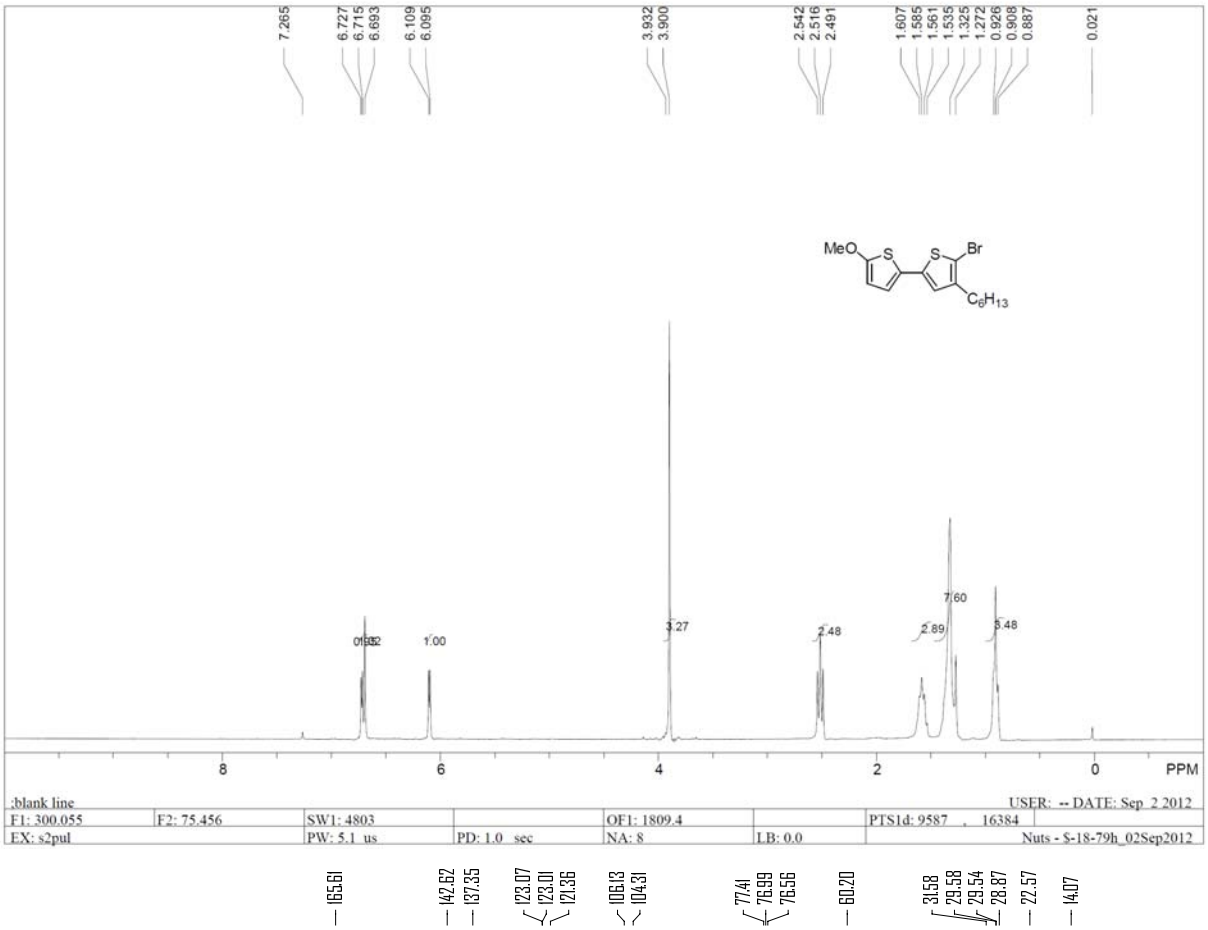
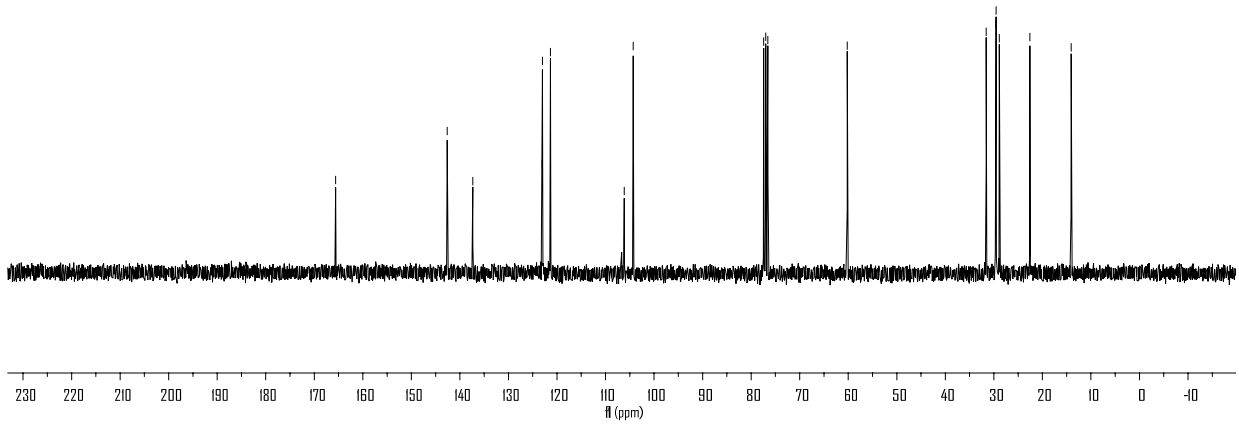
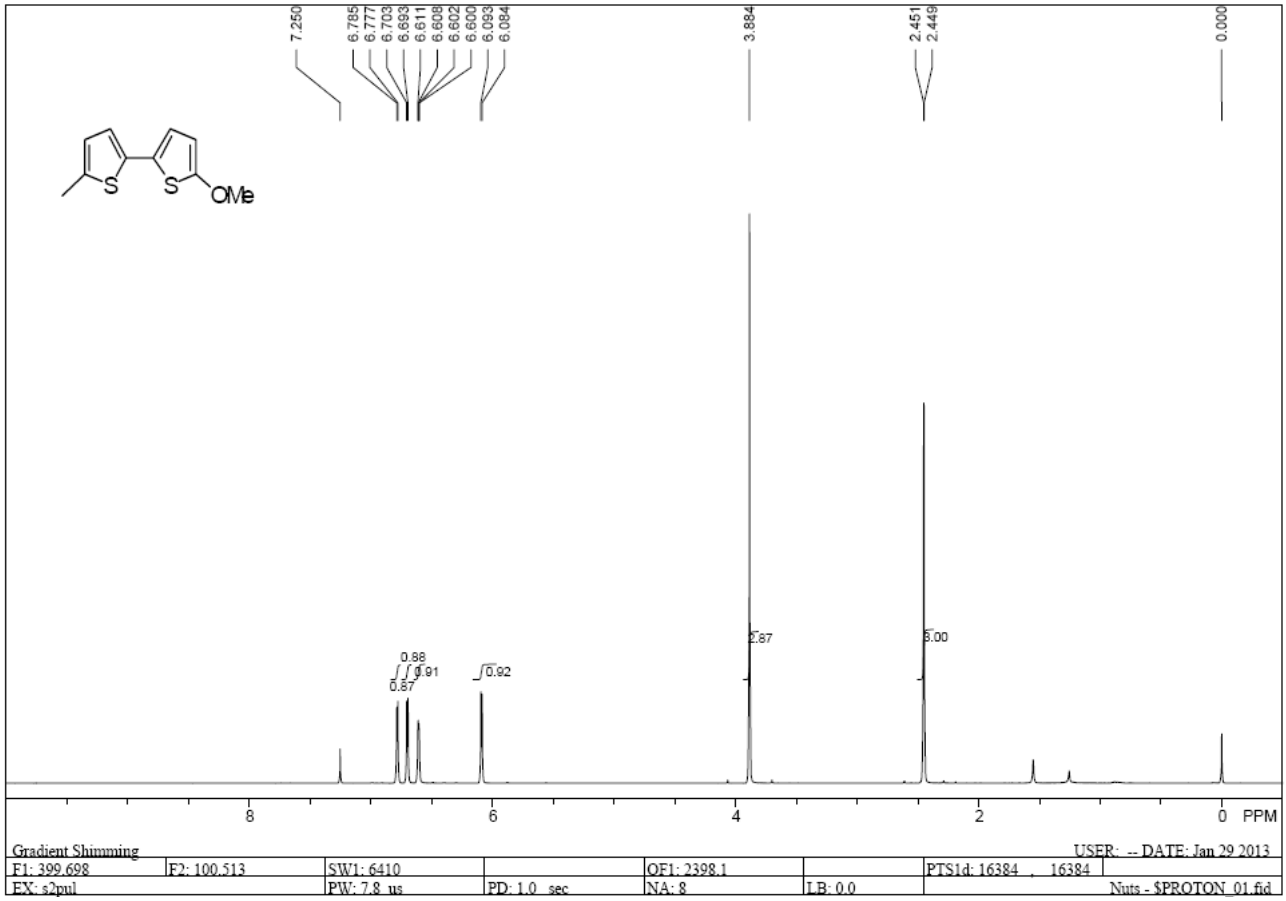
Nuts - $-18-56-2F_23Aug2012

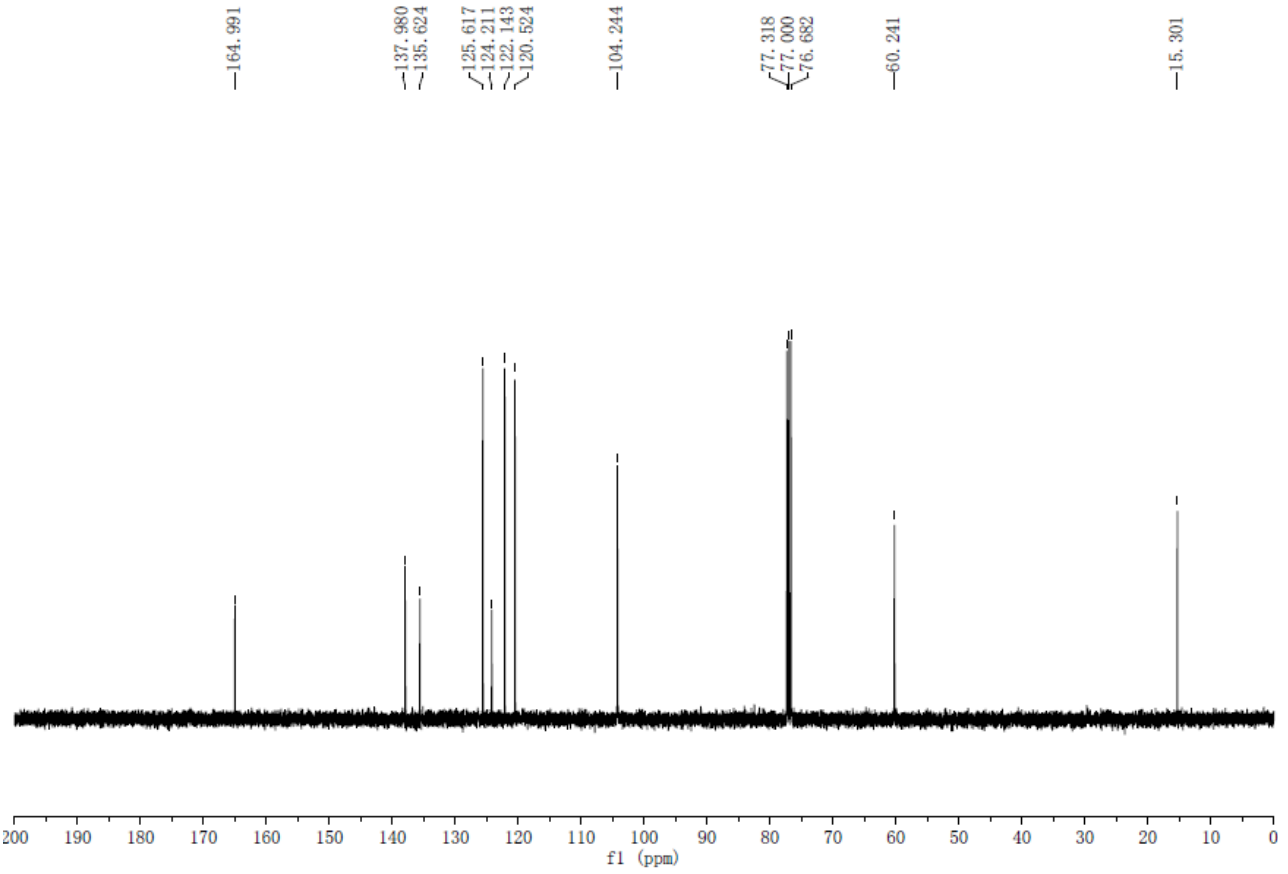
5-Bromo-4-hexyl-5'-methoxy-2,2'-bithiophene (3r).



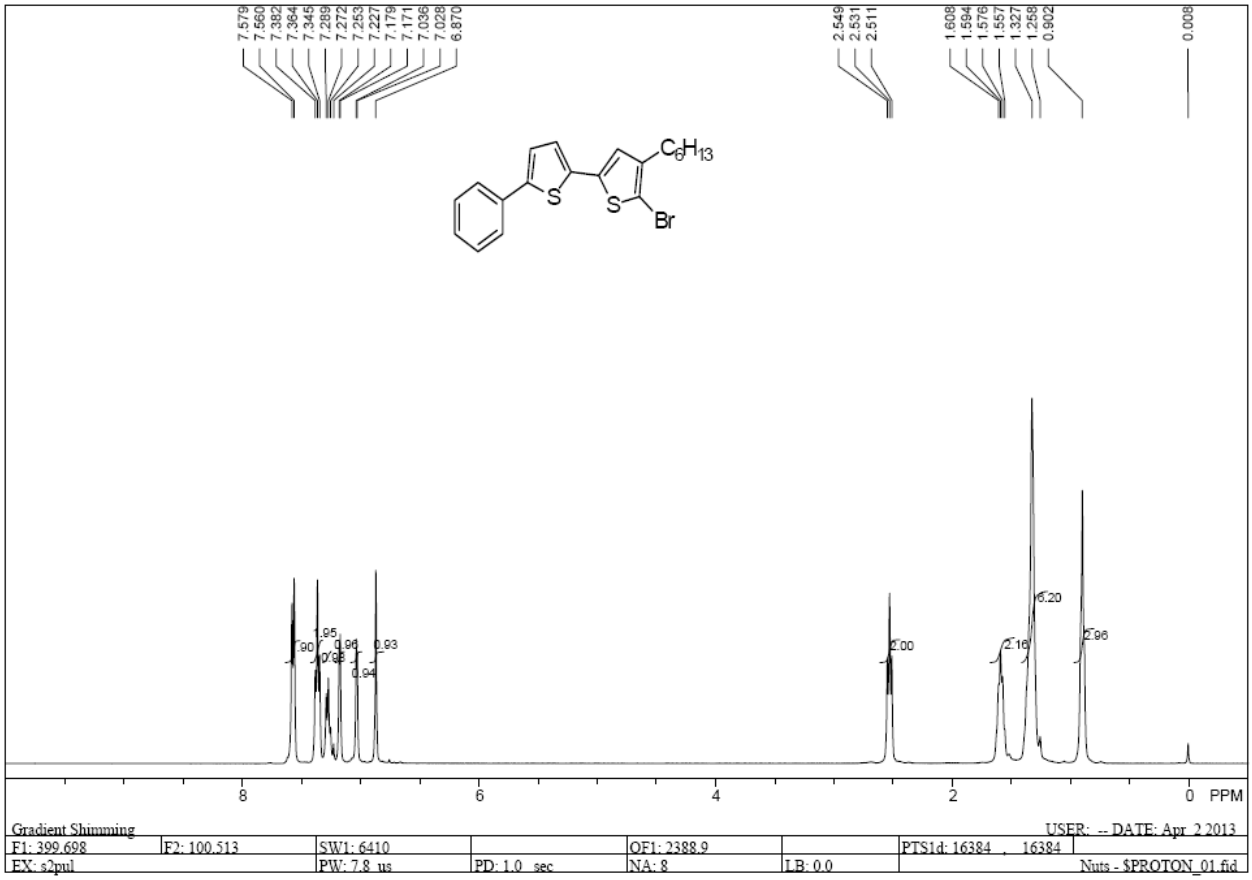


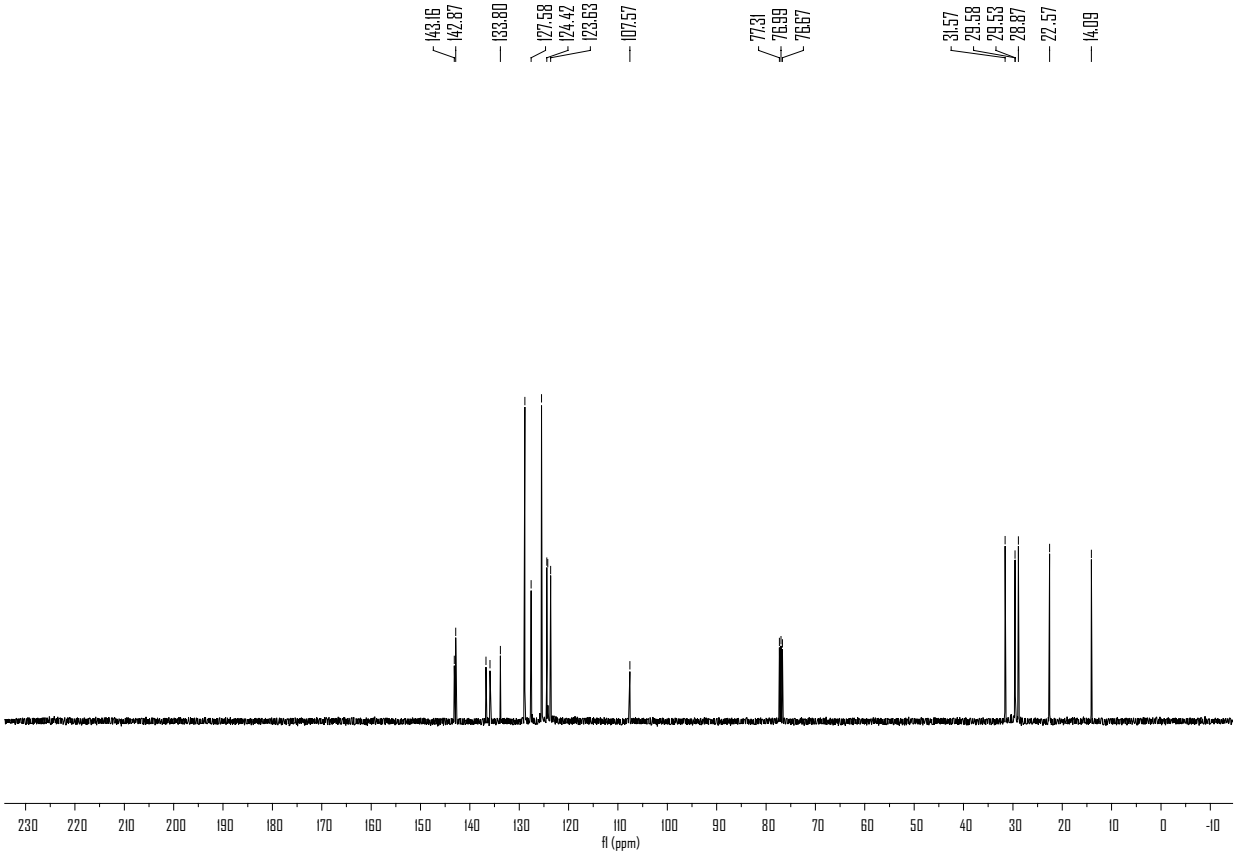
5-Methoxy-5'-methyl-2,2'-bithiophene (3s).



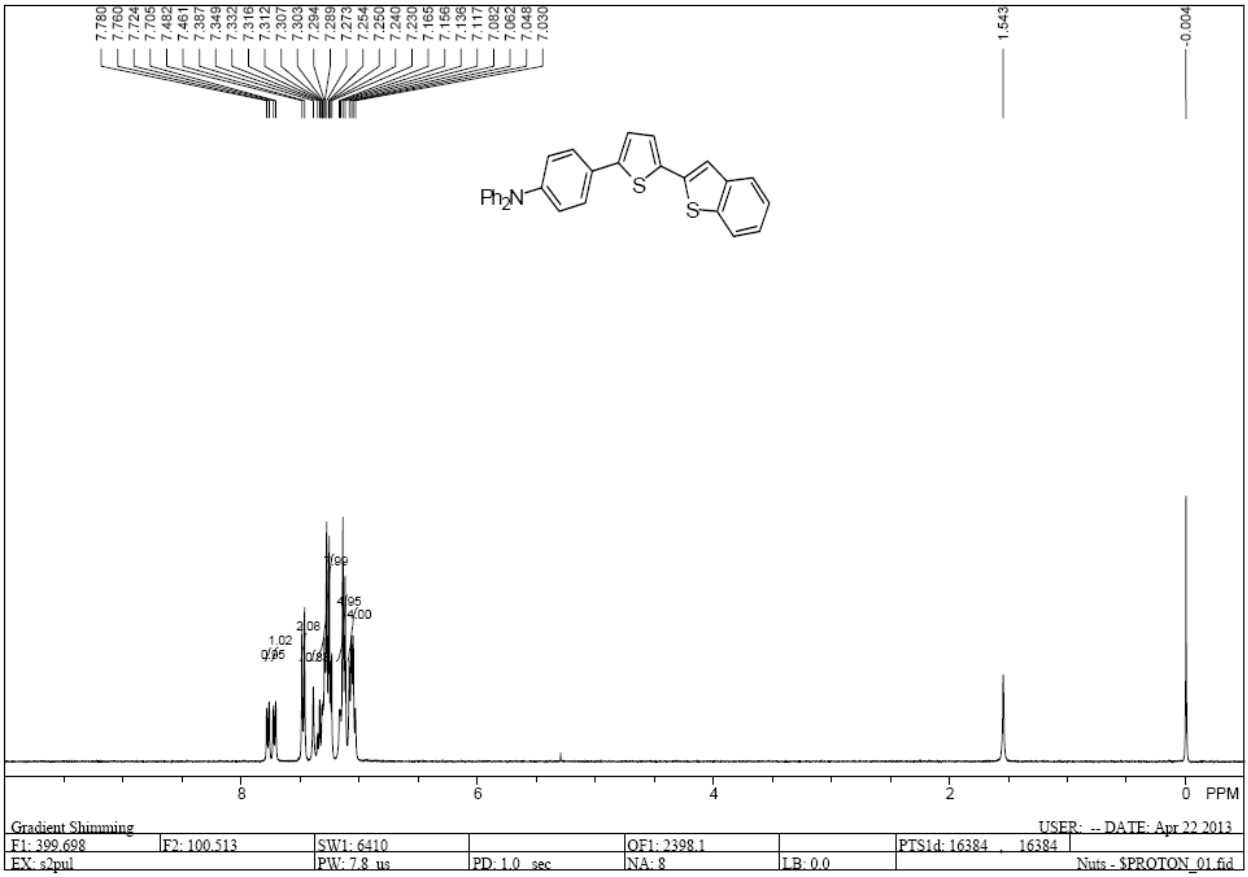


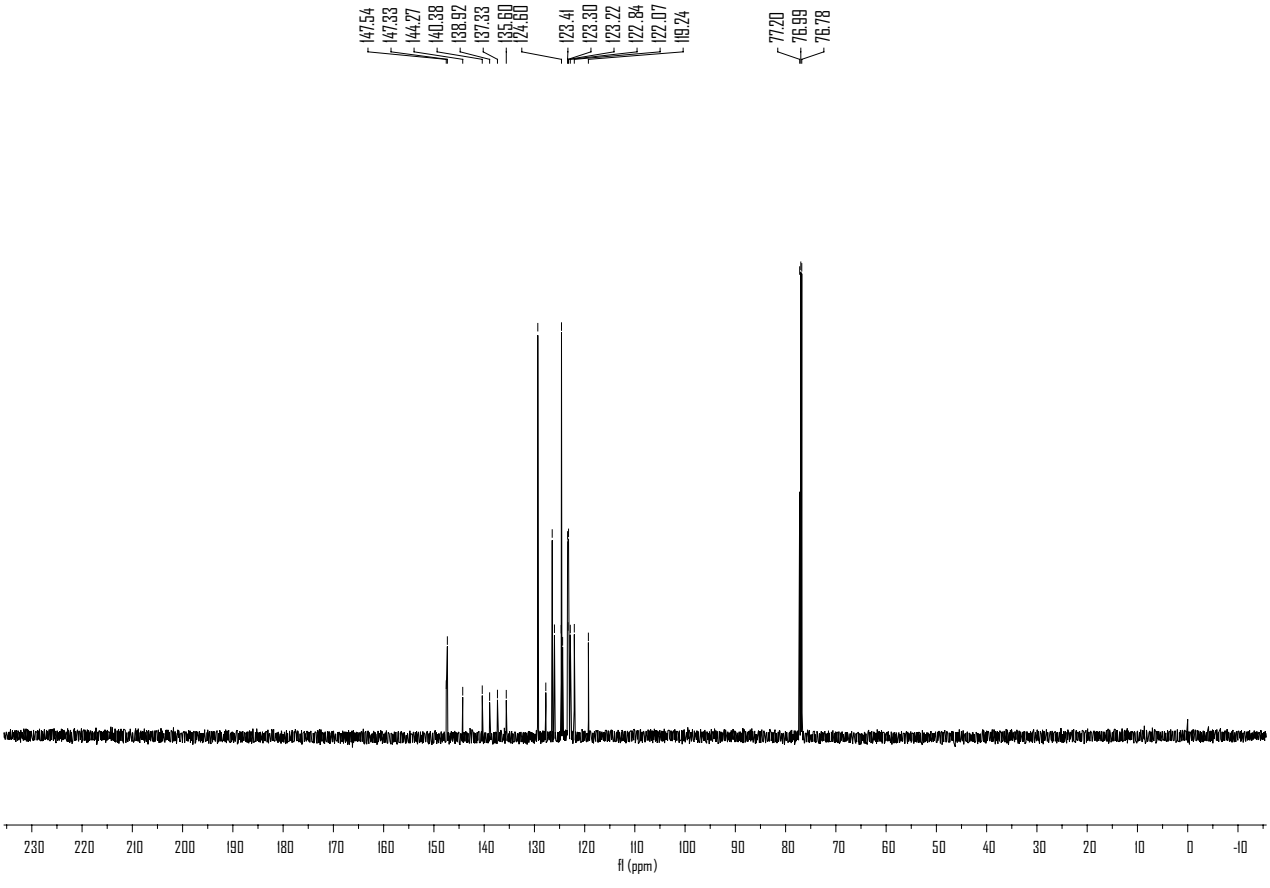
5-Bromo-4-hexyl-5'-phenyl-2,2'-bithiophene (3t)



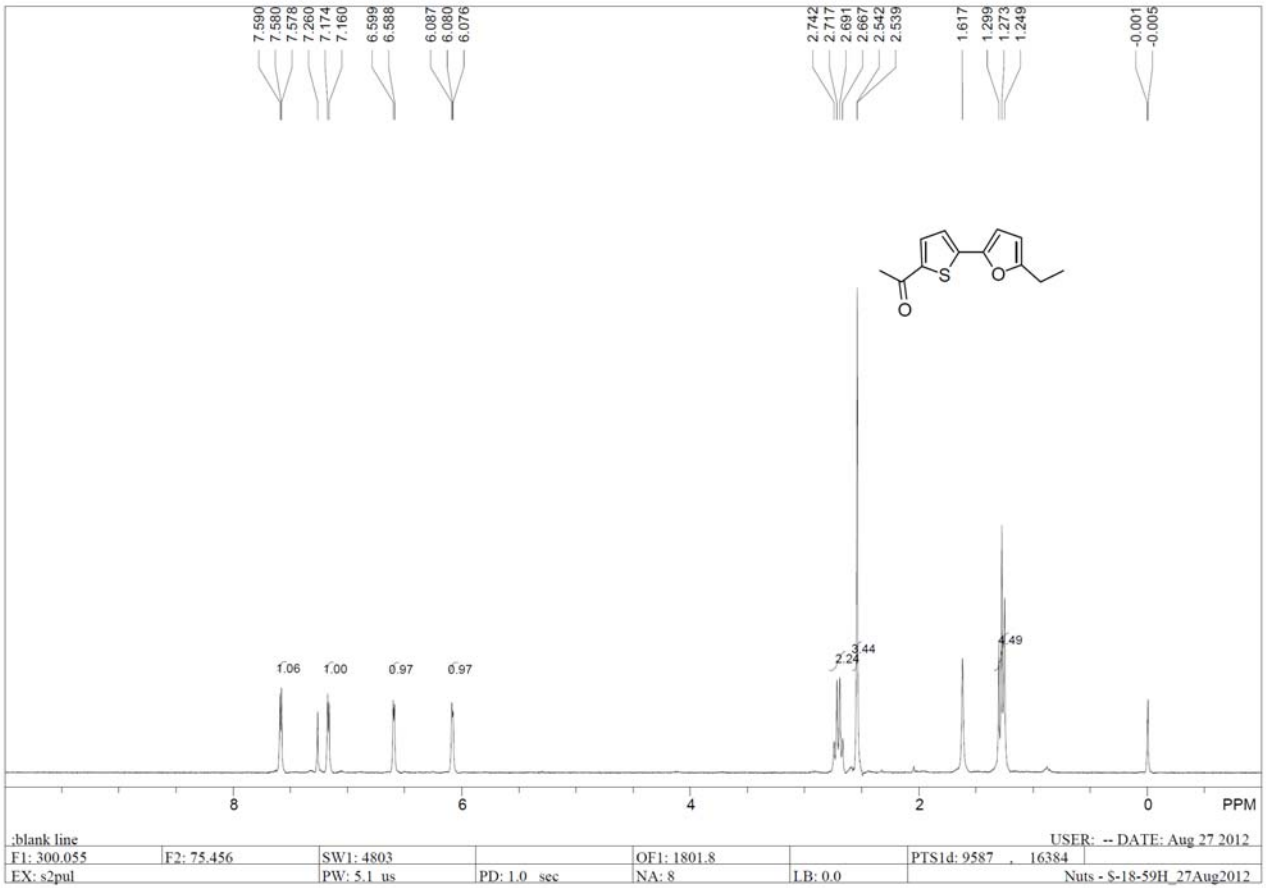


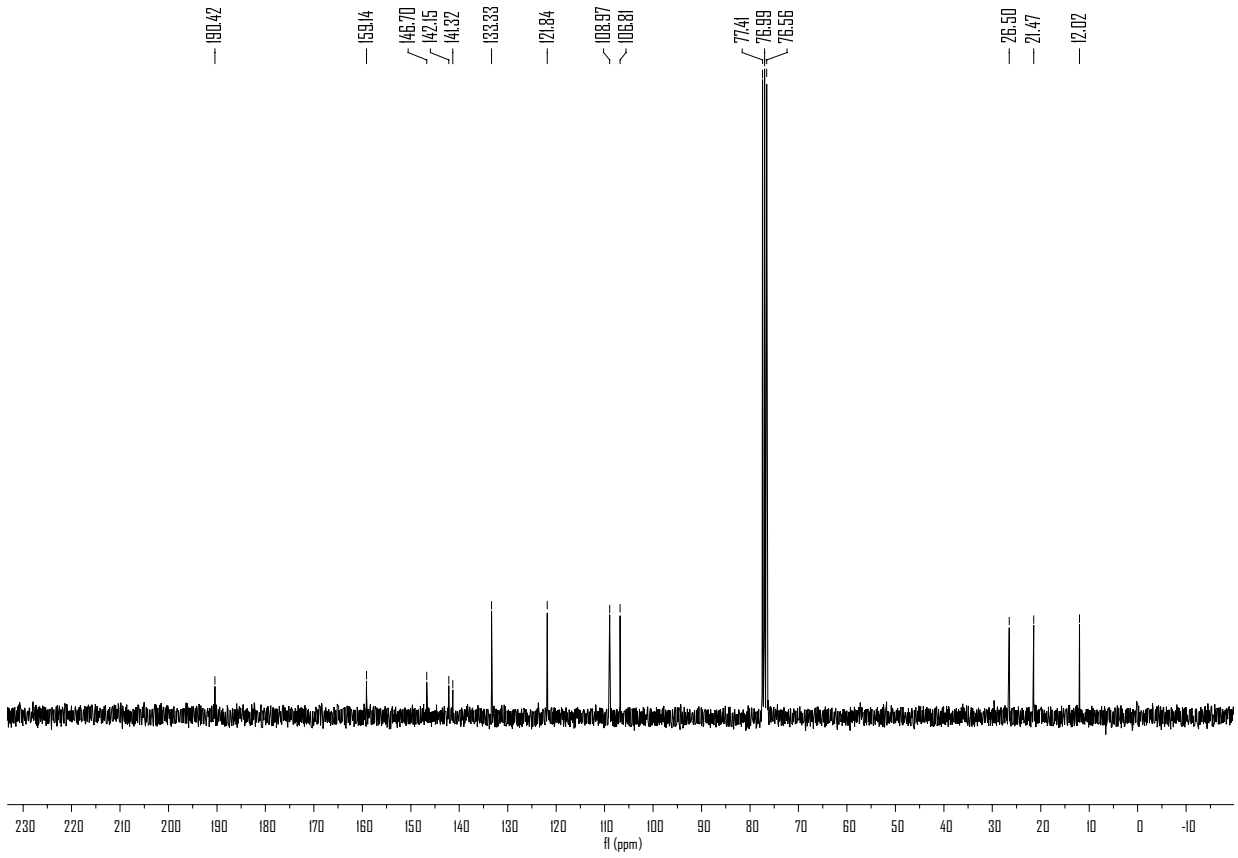
4-(5-(Benzo[b]thiophen-2-yl)thiophen-2-yl)-N,N-diphenylaniline(3u).



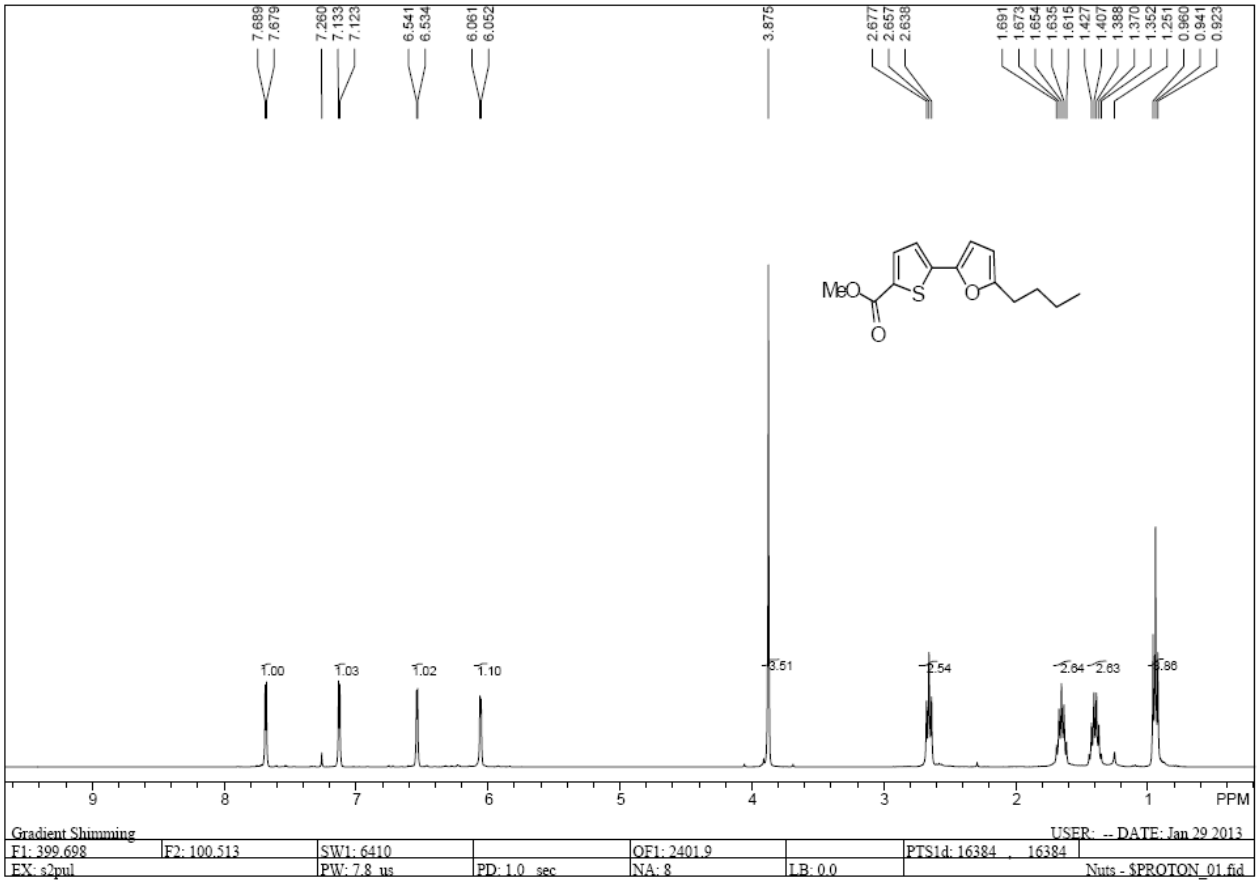


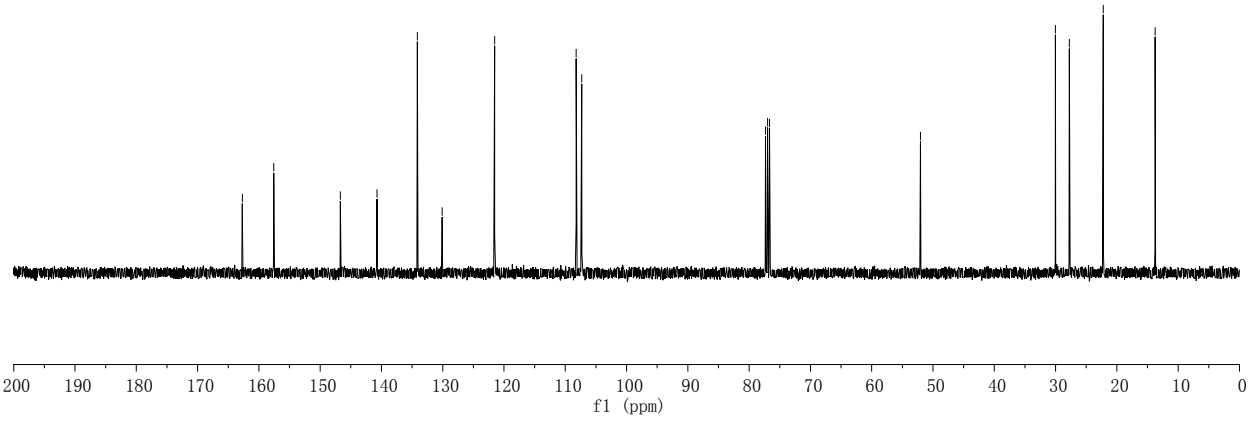
1-(5-(5-Ethylfuran-2-yl)thiophen-2-yl)ethanone (3v).



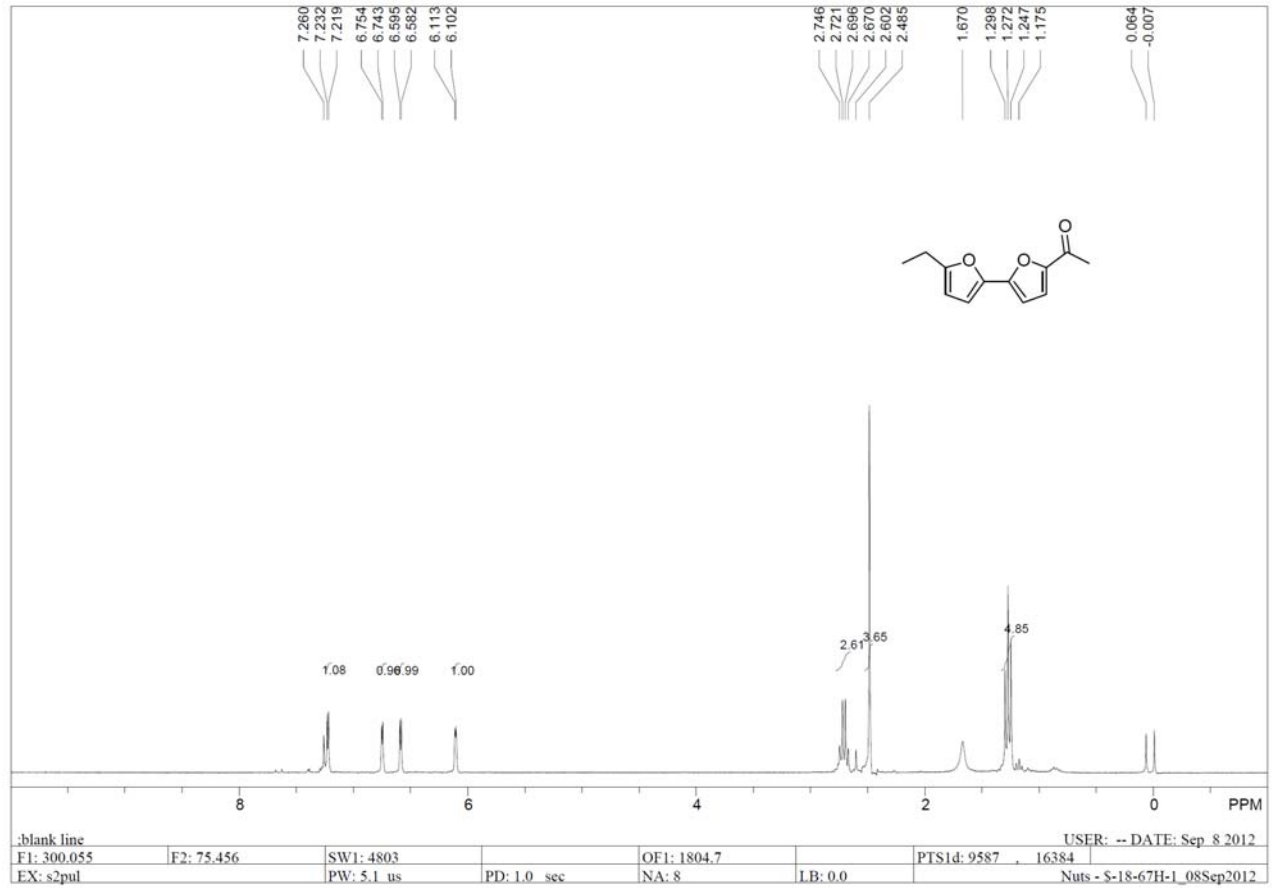


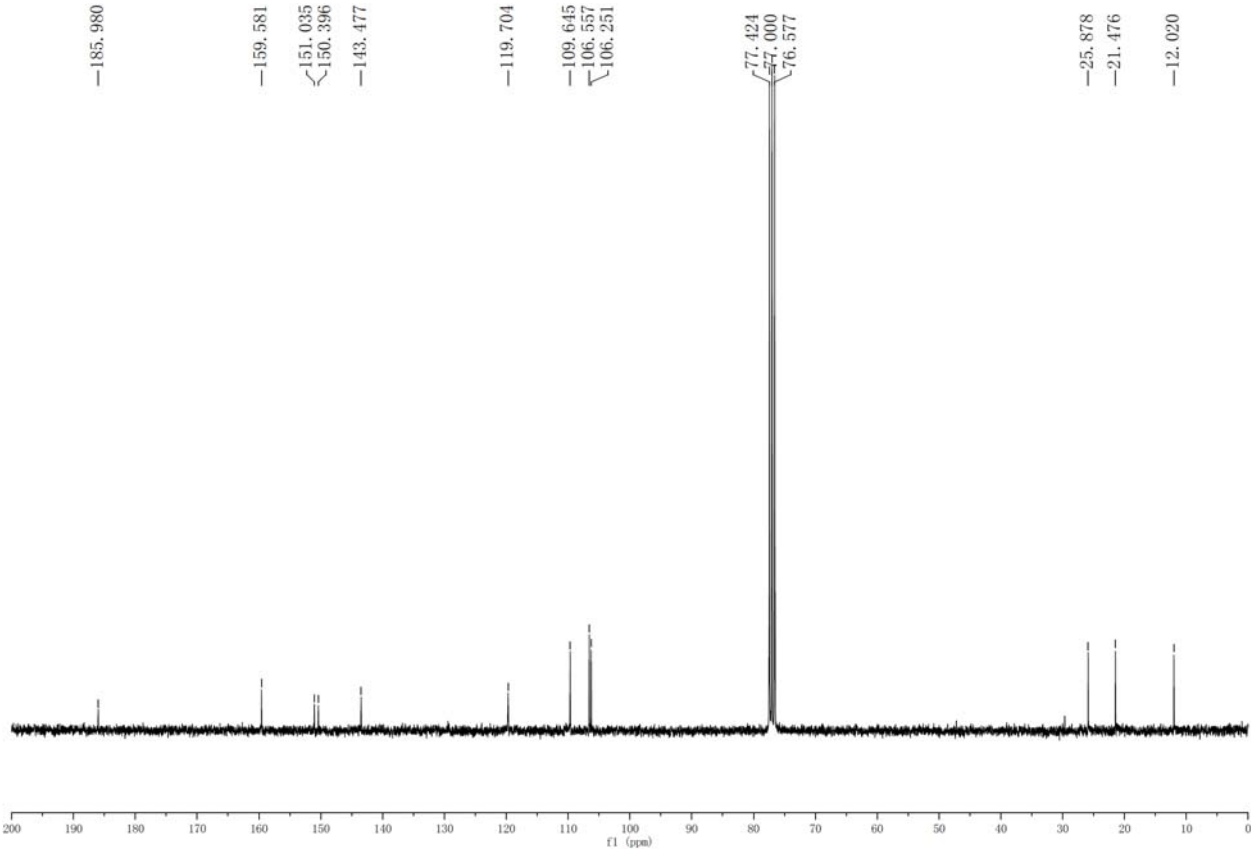
1-(5-(5-Ethylfuran-2-yl)thiophen-2-yl)ethanone (3w).



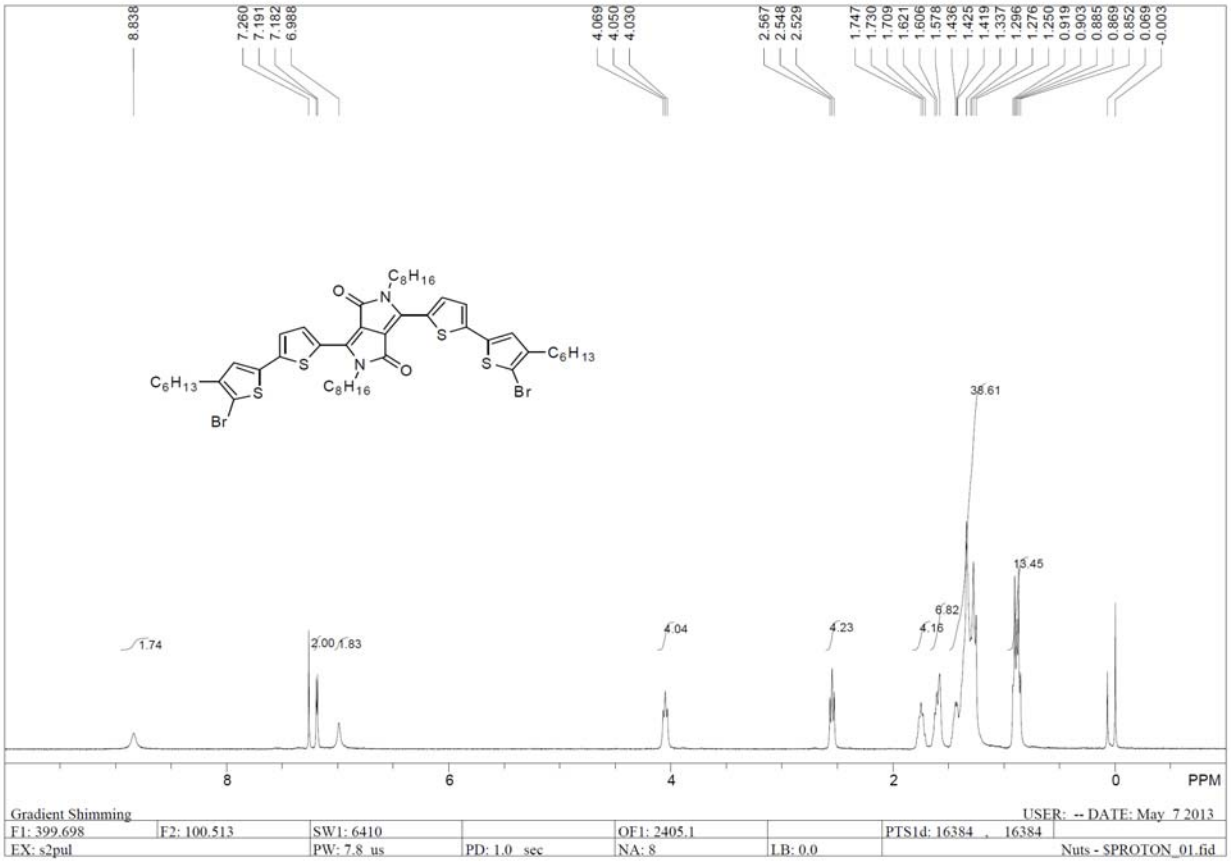


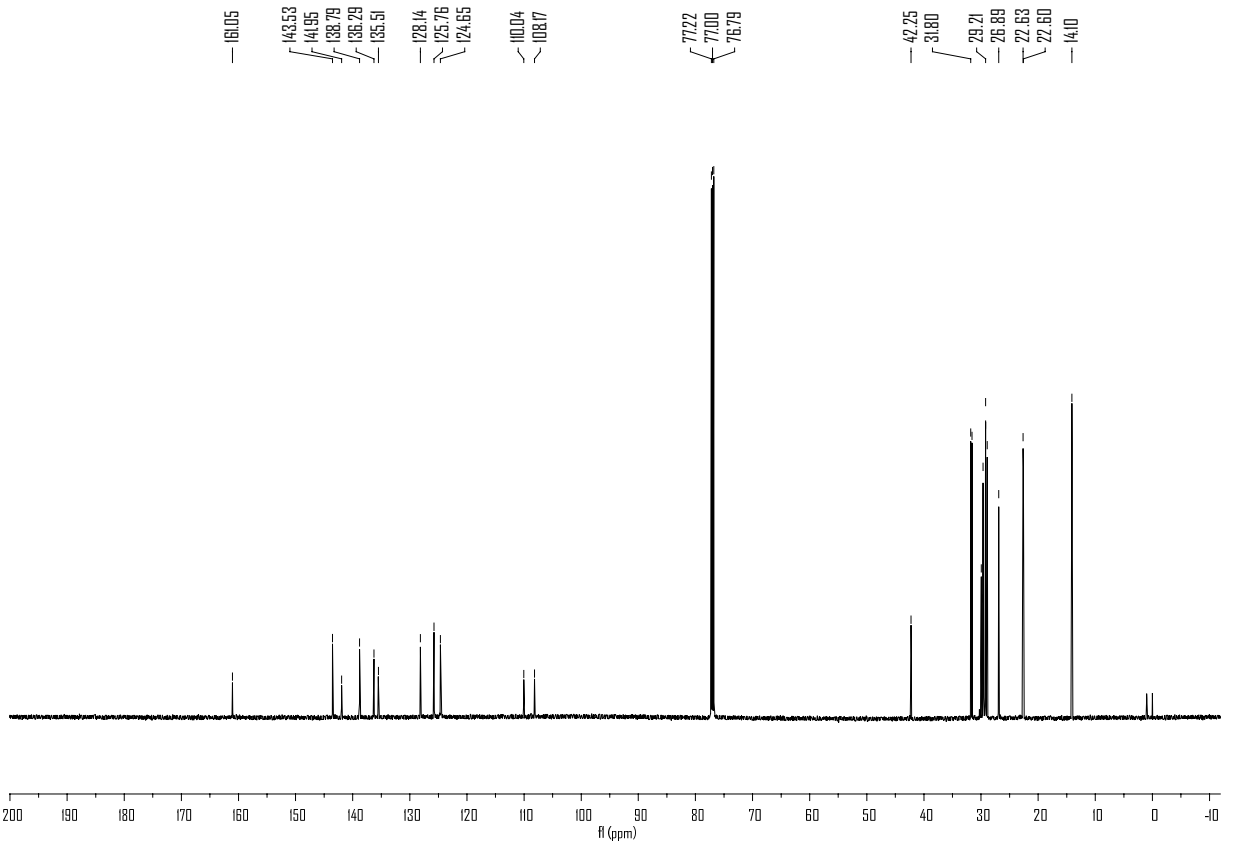
1-(5'-Ethyl-[2,2'-bifuran]-5-yl)ethanone (3x).



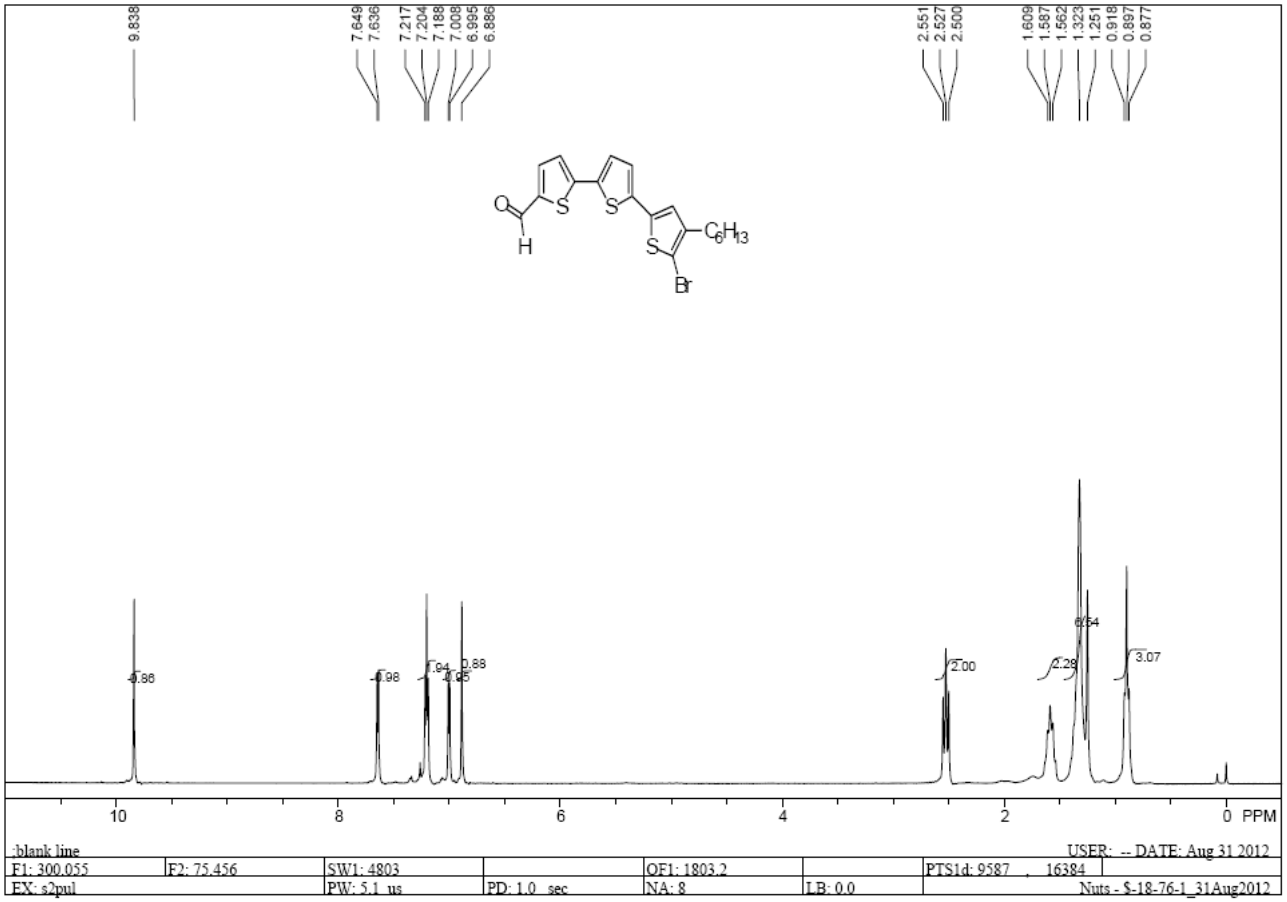


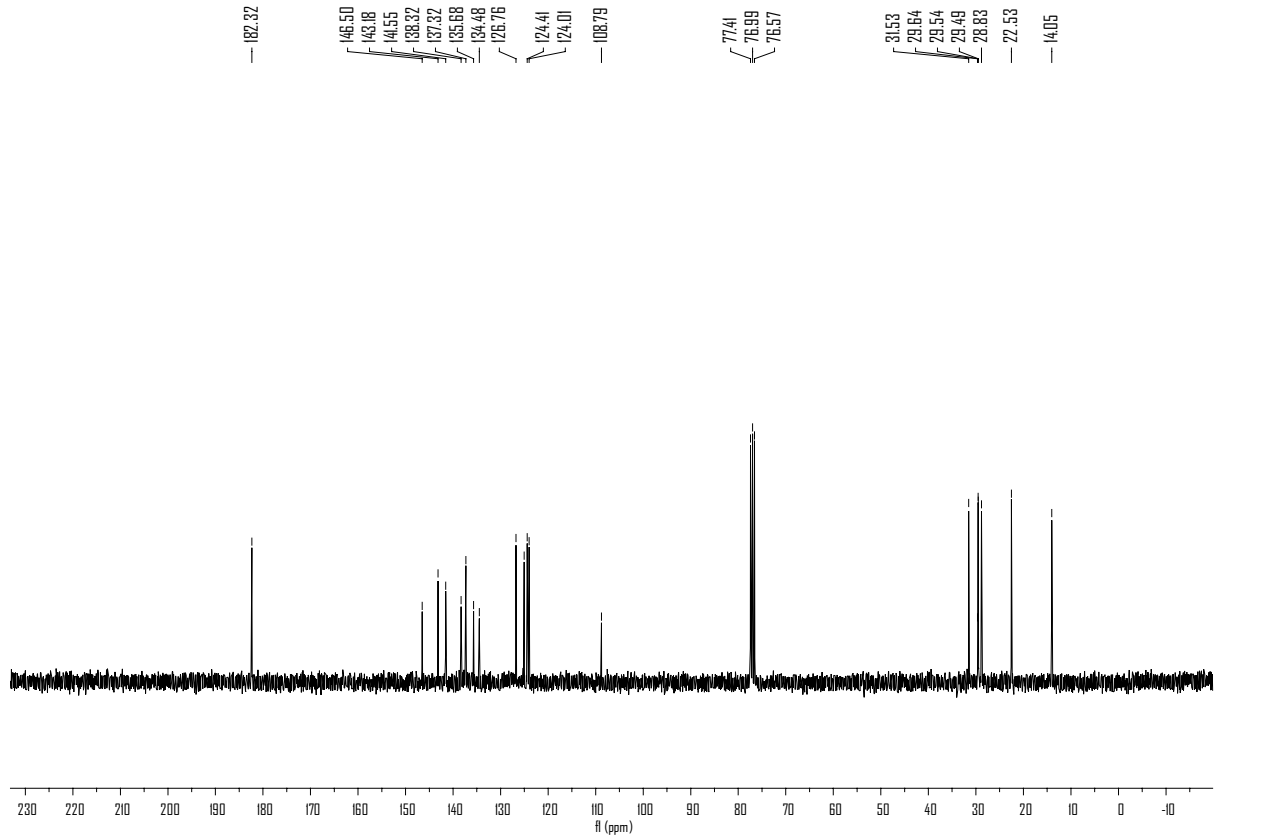
3,6-bis(5'-bromo-4'-hexyl-[2,2'-bithiophen]-5-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3y)



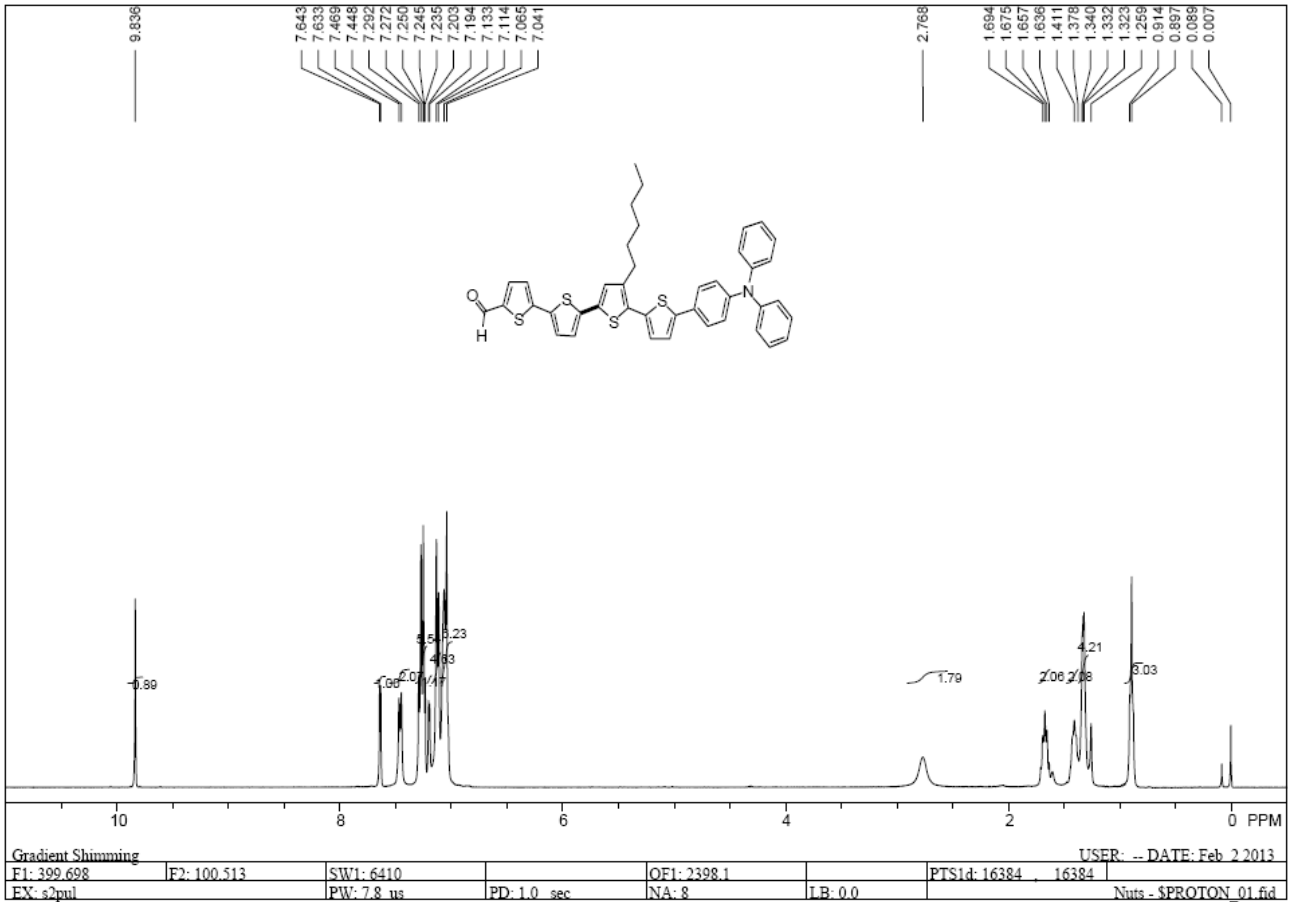


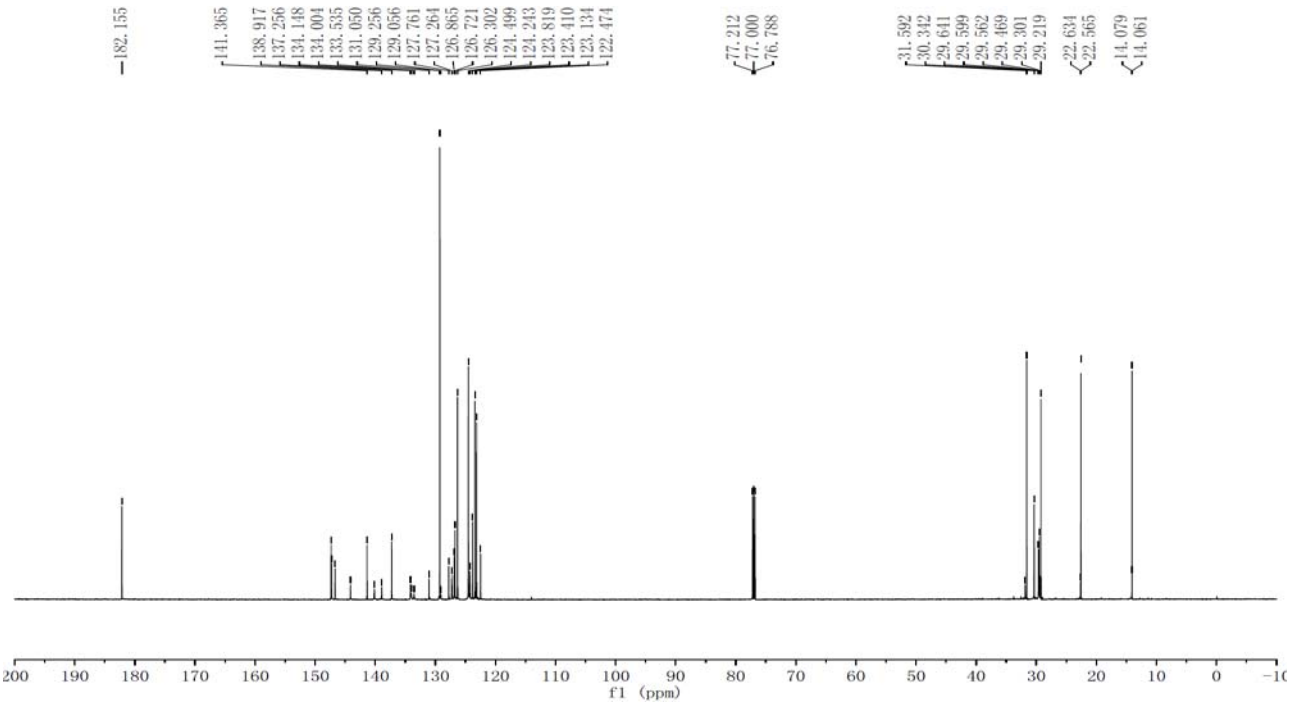
5''-Bromo-4''-hexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (5).



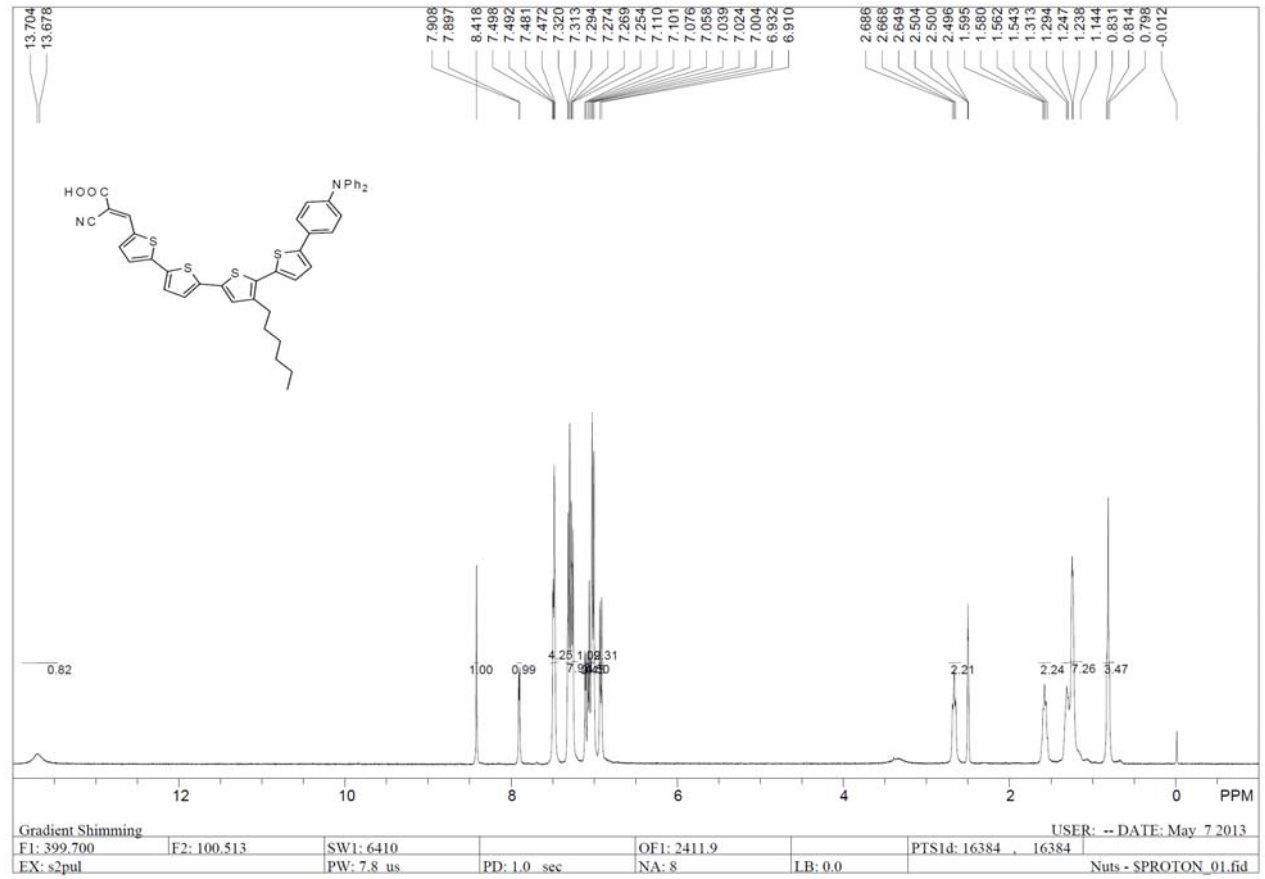


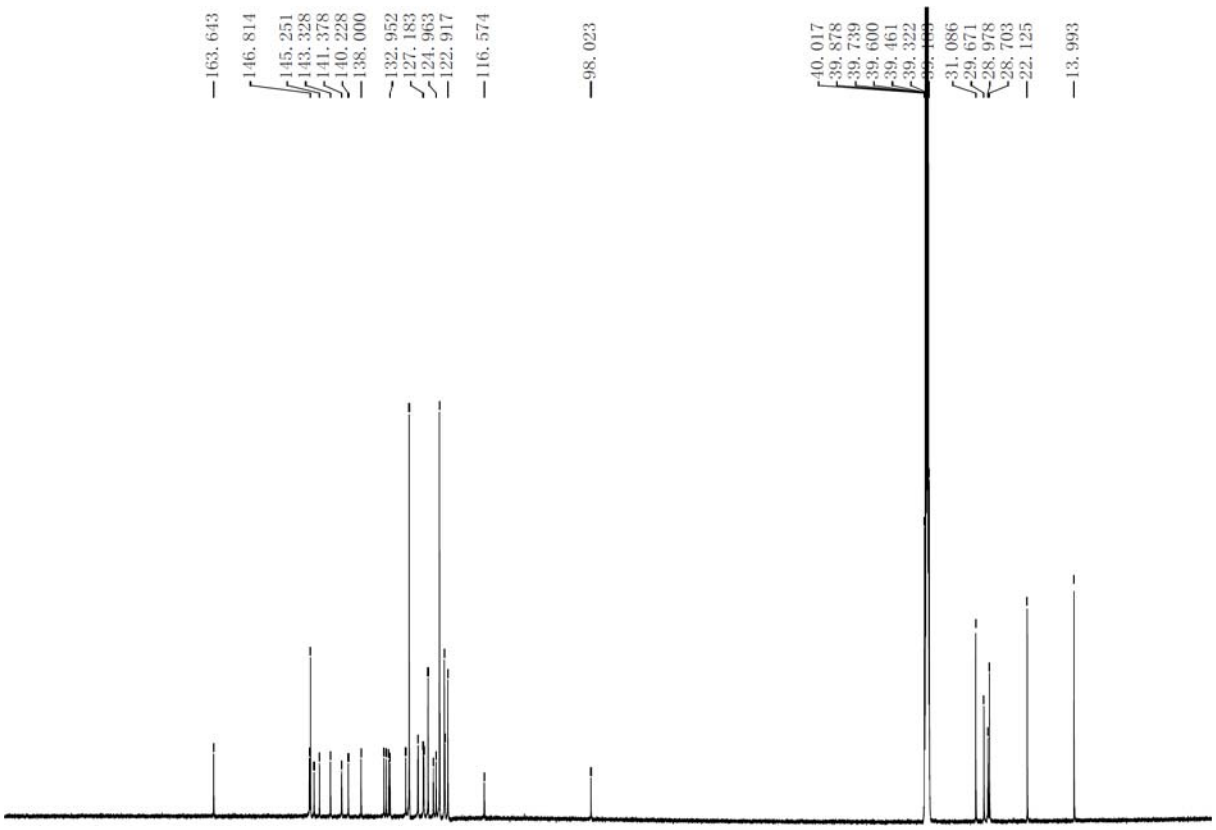
5'''-(4-(diphenylamino)phenyl)-4''-hexyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5-carbaldehyde (6).



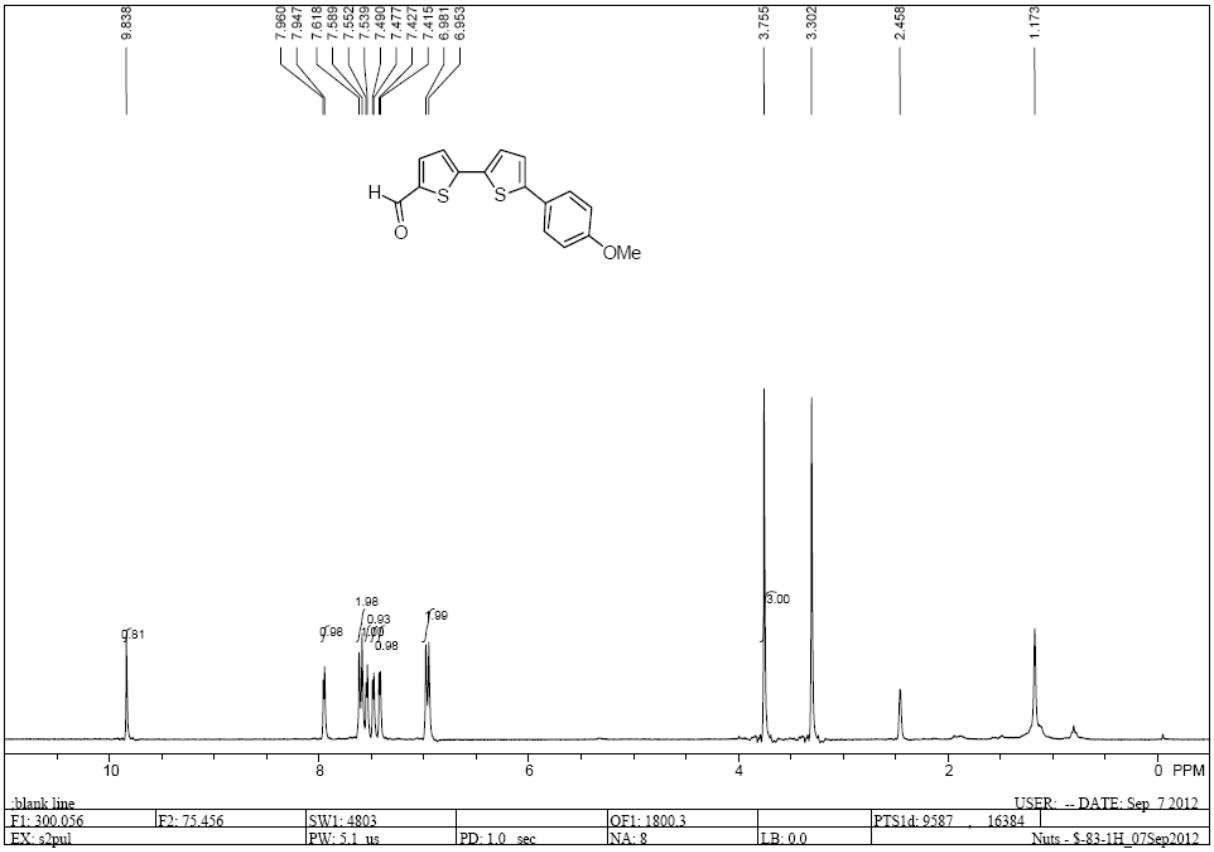


2-Cyano-3-(5'''-(4-(diphenylamino)phenyl)-4''-hexyl-[2,2':5',2'':5'',2'''-quaterthiophen]-5-yl)acrylic (7).

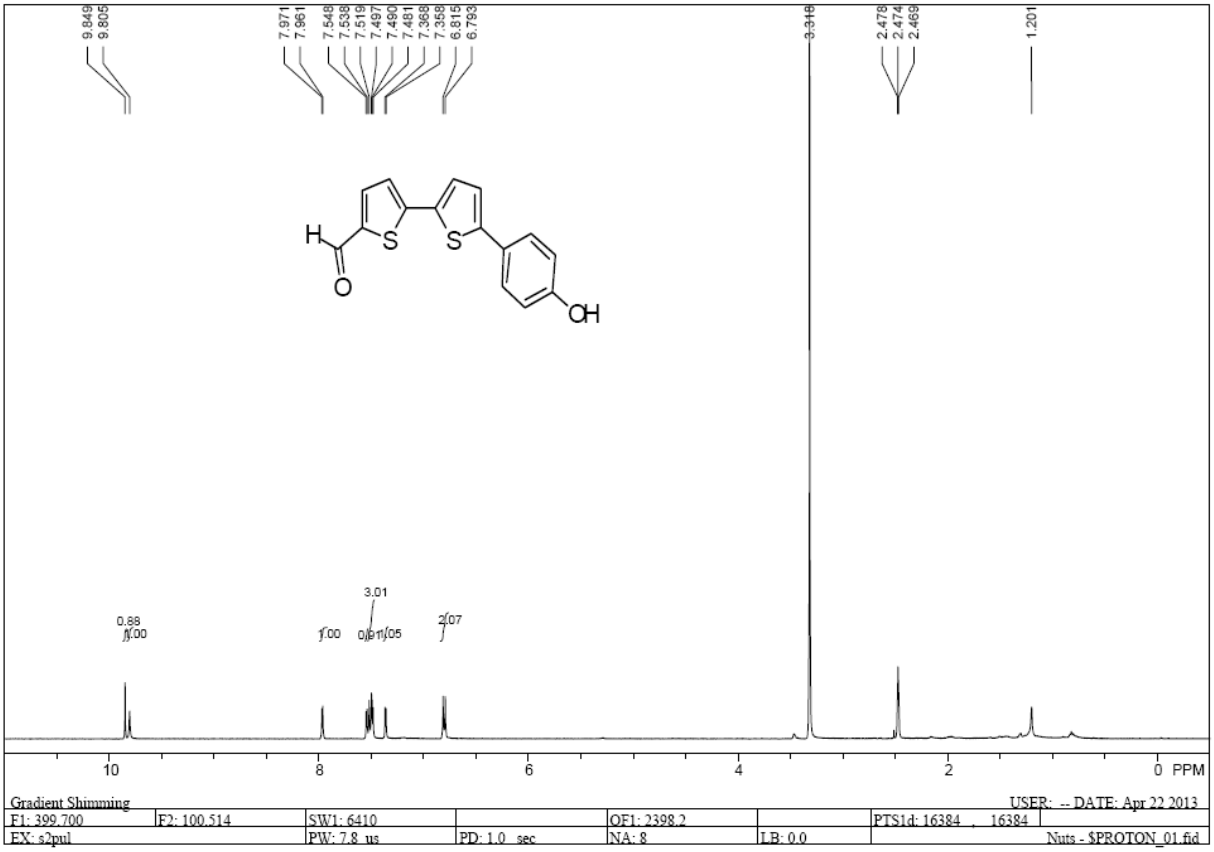


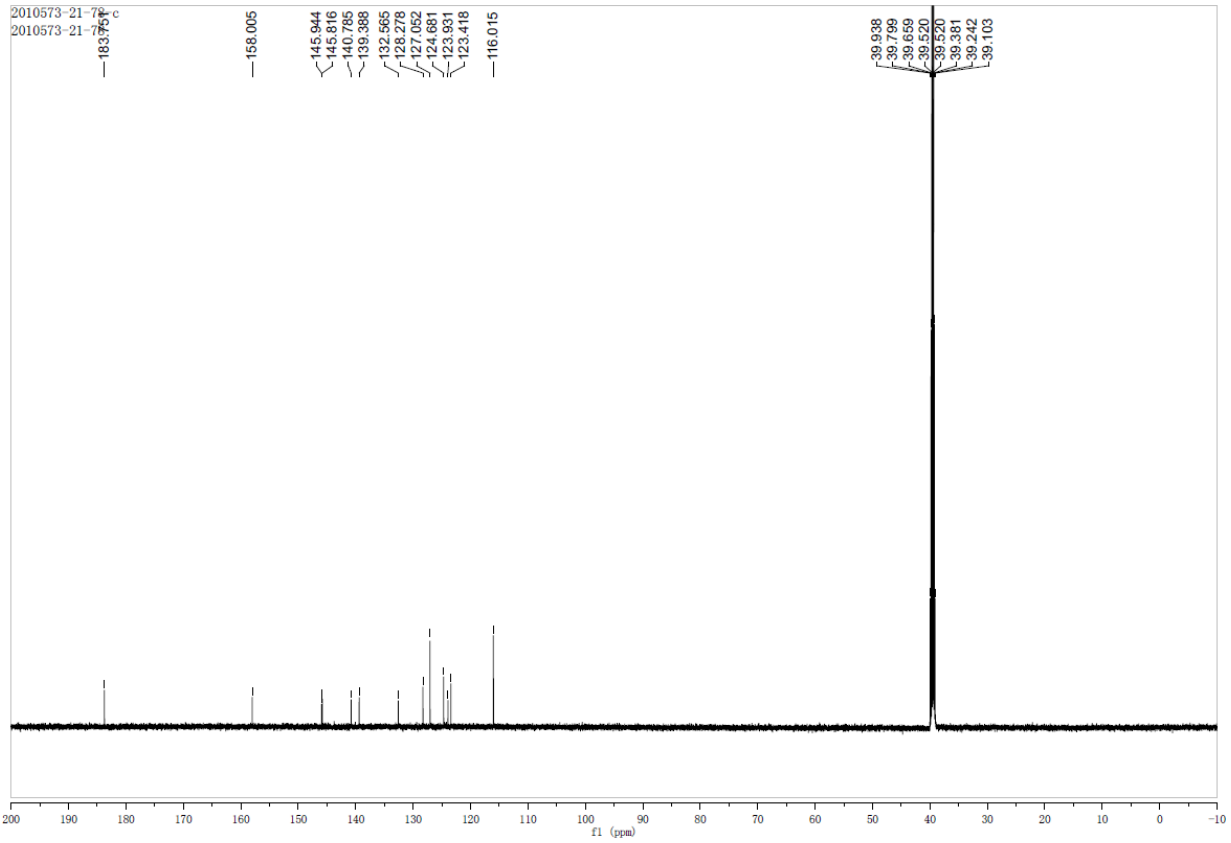


5'-(4-Methoxyphenyl)-[2,2'-bithiophene]-5-carbaldehyde (9)



5'-(4-hydroxyphenyl)-[2,2'-bithiophene]-5-carbaldehyde (10).

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2010573-21-7c
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124.681
123.931
123.418
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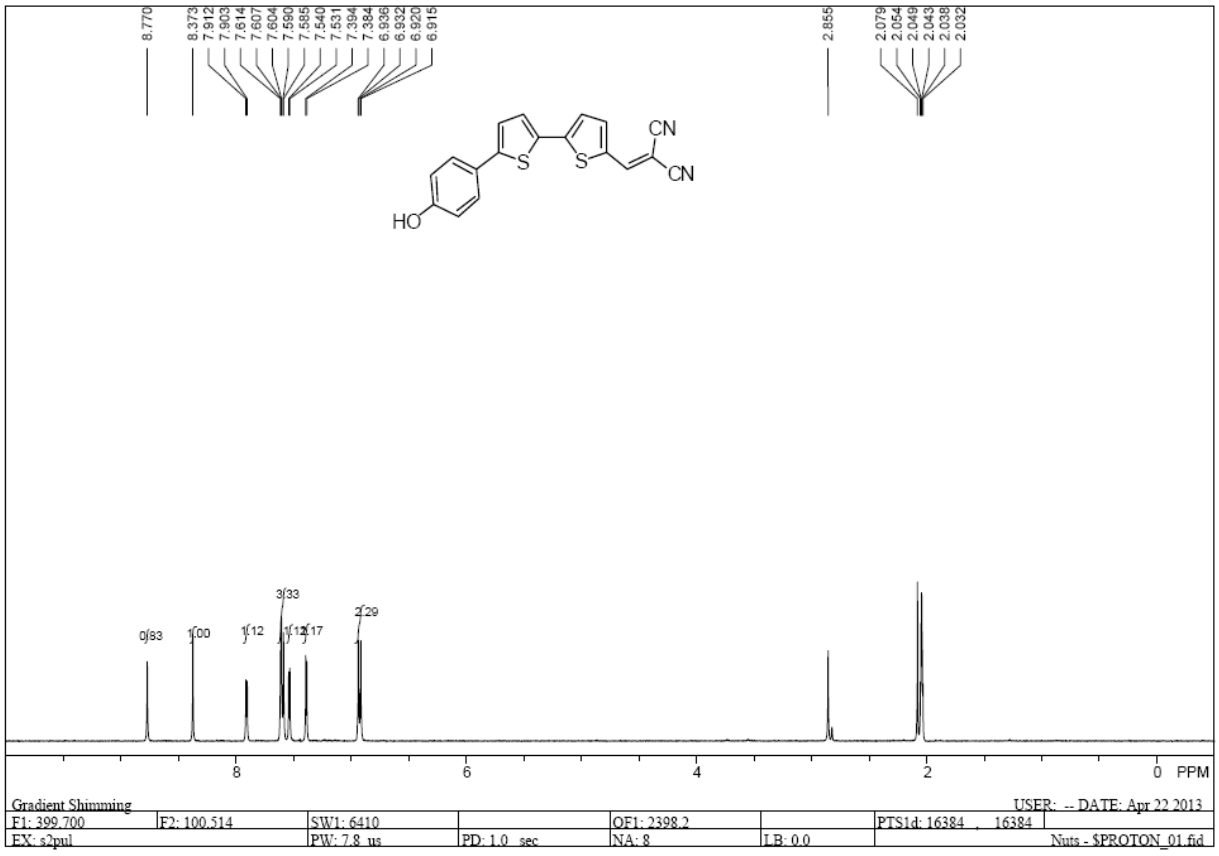
39.659
39.520
39.520
39.381
39.242
39.103
f1 (ppm)

Compound **11**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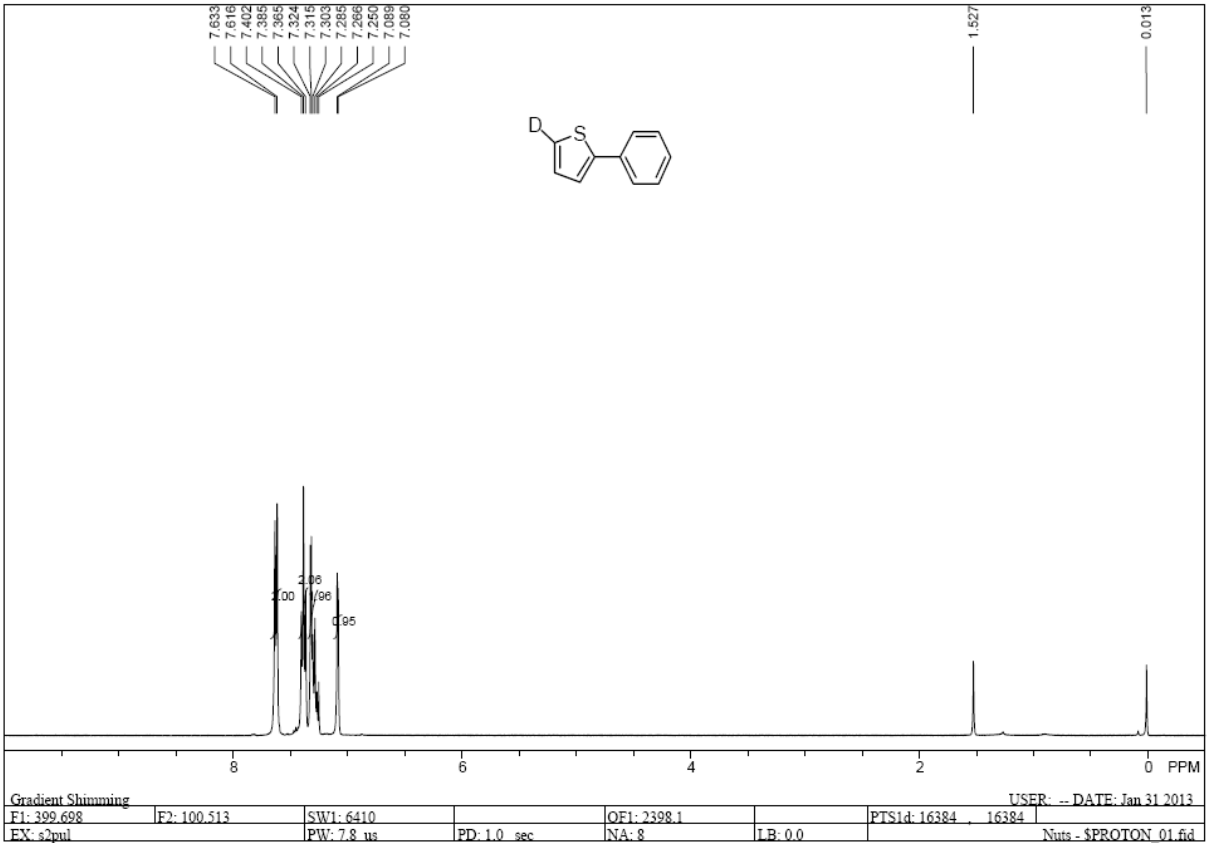
6.936
6.932
6.920
6.915
2.855
2.079
2.054
2.049
2.043
2.038
2.032
CN
CN
S
S
HO
0.83
1.00
1.12
3.33
1.12
1.17
2.29
PPM
Gradient Shimming
USER: -- DATE: Apr 22 2013
F1: 399.700
F2: 100.514
SW1: 6410
OF1: 2398.2
PTS1d: 16384 16384
EX: s2pul
PW: 7.8 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $PROTON_01.fid

d-**2h**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7.080
1.527
0.013
D
S
2.00
2.06
0.96
0.95
8
6
4
2
0 PPM
Gradient Shimming
USER: -- DATE: Jan 31 2013
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F2: 100.513
SW1: 6410
OF1: 2398.1
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PD: 1.0 sec
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LB: 0.0
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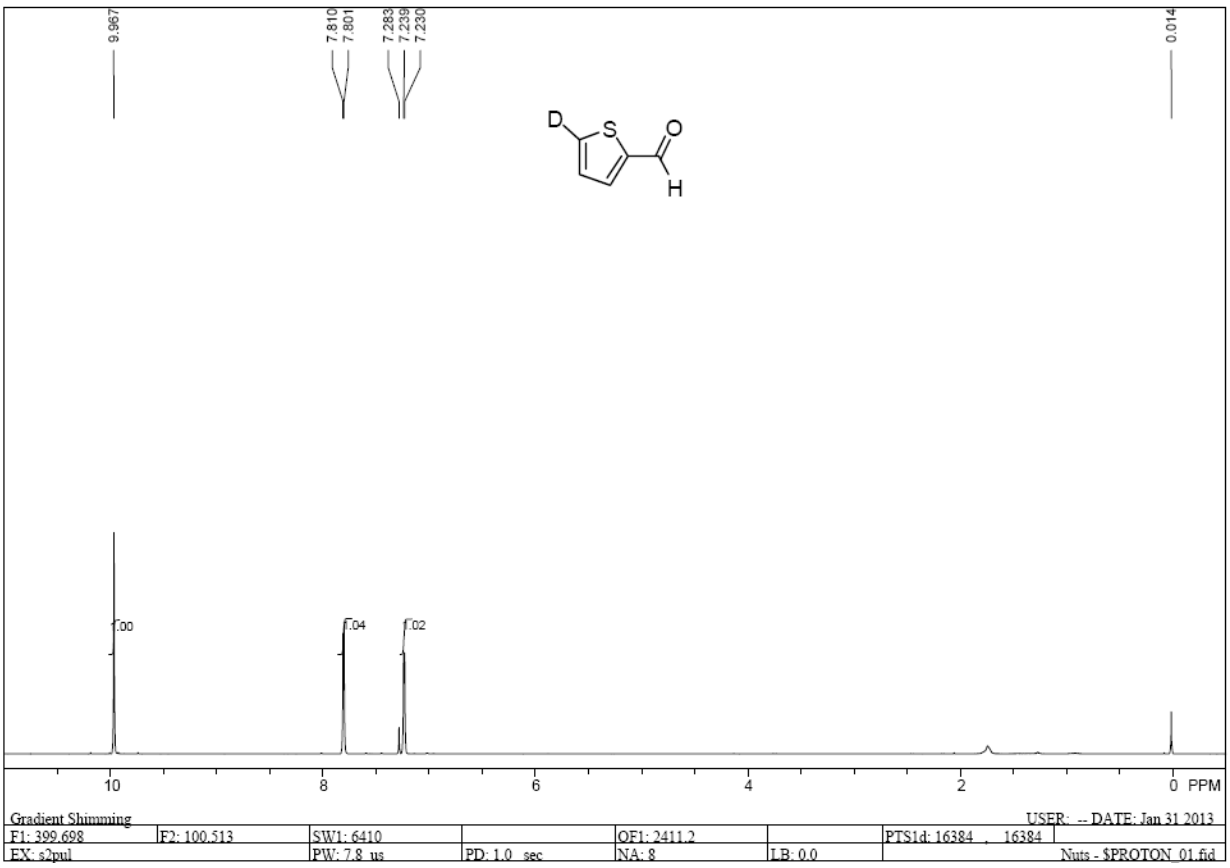
d-**1e**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7.239
7.230
0.014
D
S
O
H
1.00
1.04
1.02
10
8
6
4
2
0 PPM
Gradient Shimming
USER: -- DATE: Jan 31 2013
F1: 399.698
F2: 100.513
SW1: 6410
OF1: 2411.2
PTS1d: 16384 , 16384
EX: s2pul
PW: 7.8 us
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $PROTON_01.fid