Supporting Information for

Synthesis of Substituted Thiophenes by Palladium-Catalyzed Heterocyclodehydration of 1-Mercapto-3-yn-2-ols in Conventional and Non-conventional Solvents

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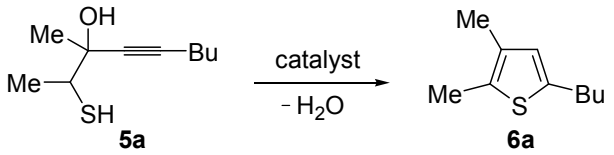
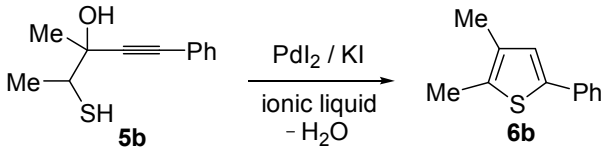
Table S1. Heterocyclodehydration of 2-Mercapto-3-methylnon-4-yn-3-ol (5a) to 5-Butyl-2,3-dimethylthiophene (6a) Under Various Reaction Conditions[a]



entry	catalyst	solvent	T (°C)	concentration of **5a**[b]	conversion of **5a**[c] (%)	Yield of **6a**[d] (%)
1	PdI_2+10KI	MeOH	80	0.2	100	77
2	PdI_2+10KI	MeOH	50	0.2	44	38
3	PdI_2+10KI	MeOH	50	0.5	87	78
4	PdI_2+10KI	MeOH	50	1	81	70
5	PdI_2+10KI	MeOH	50	0.05	27	25
6	PdI_2+10KI	DMA	50	0.2	56	35
7	PdI_2+5KI	MeOH	50	0.2	35	30
8	PdI_2+100KI	MeOH	50	0.2	65	35
9	$PdCl_2$+10KCl	MeOH	50	0.2	27	13
10	$PdCl_2(PPh_3)_2$	MeOH	50	0.2	38	20
11	$Pd(PPh_3)_4$	MeOH	50	0.2	11	8
12	$Pd(dba)_2$	MeOH	50	0.2	7	1
13	$CuCl_2$	MeOH	50	0.2	20	2
14	CuCl	MeOH	50	0.2	24	2
15	CuI	MeOH	50	0.2	18	3
16	$ZnCl_2$	MeOH	50	0.2	9	2

[a] All heterocyclodehydration reactions were carried out for 2 h in the presence of 1 mol % of catalyst [b] Mmol of starting **5a** per mL of solvent [c] Determined by GLC [d] GLC yield based on starting thiol **5a**.

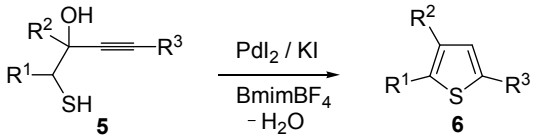
Table S2. Heterocyclodehydration of 2-Mercapto-3-methylnon-4-yn-3-ol (5a) to 5-Butyl-2,3-dimethylthiophene (6a) in Different Ionic Liquids[a]



entry	ionic liquid	conversion of **5b**[b] (%)	yield of **6b**[c] (%)
1	$BmimBF_4$	100	82
2	BmimOTf	96	50
3	$BmimPF_6$	100	54
4	BmimCl	79	28
5	$BmimNTf_2$	100	55

[a] All heterocyclodehydration reactions were carried out at 80 °C for 24 h with a substrate concentration of 0.2 mmol of **5b** per mL of solvent in the presence of PdI_2 (1 mol %) and KI (KI:PdI_2 molar ratio = 10). [b] Determined by GLC. [c] Isolated yield, based on starting **5b**.

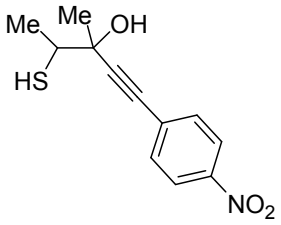
Table S3. Recyclable Catalytic Synthesis of Substituted Thiophenes 6 by PdI_2/KI-Catalyzed Heterocyclodehydration of 1-Mercapto-3-yn-2-ols 5 in $BmimBF_4$[a]



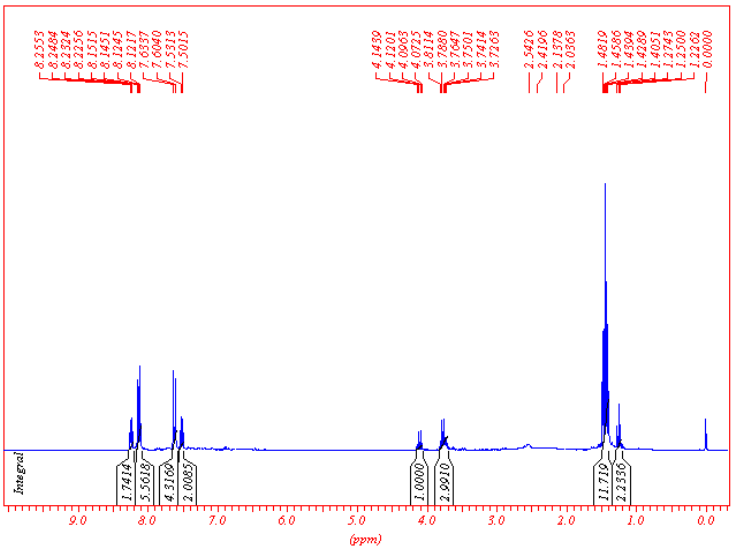
Entry	5	6	Yield of 6 (%)[c]						
			Run 1[b]	Run 2[b]	Run 3[b]	Run 4[b]	Run 5[b]	Run 6[b]	Run 7[b]
1	5b	6b	81	83	80	79	79	78	79
2	5e	6e	71	72	71	70	70	71	69
3	5g	6g	78	77	77	76	76	77	76
4	5h	6h	67	66	67	66	66	65	65

[a] All reactions were carried out at 80 °C for 24 h in $BmimBF_4$ as the solvent (0.2 mmol of starting 5 per mL of solvent). Conversion of 5 was quantitative in all cases. [b] Run 1 corresponds to the 1st experiment, the next runs to recycles. See text for details. [c] Isolated yield based on starting 5.

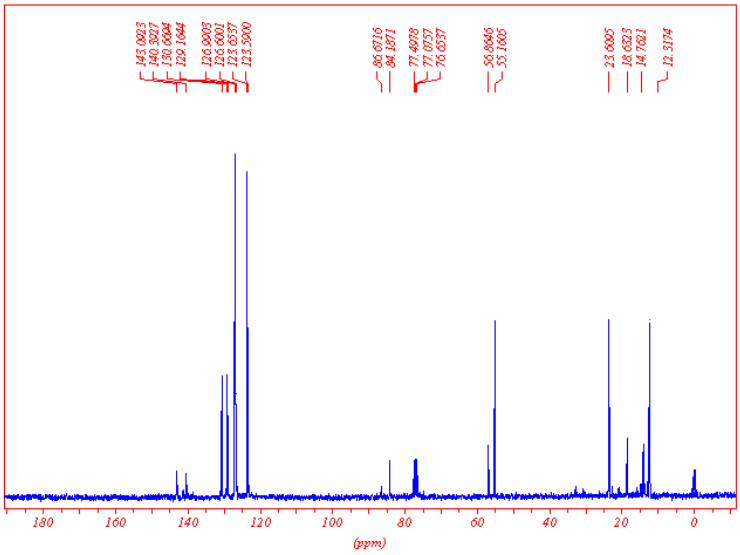
4-Mercapto-3-methyl-1-(4-nitrophenyl)pent-1-yn-3-ol (**5d**)



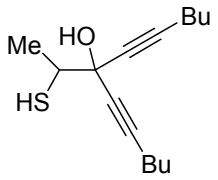
^{1}H NMR (300 MHz, $CDCl_3$)



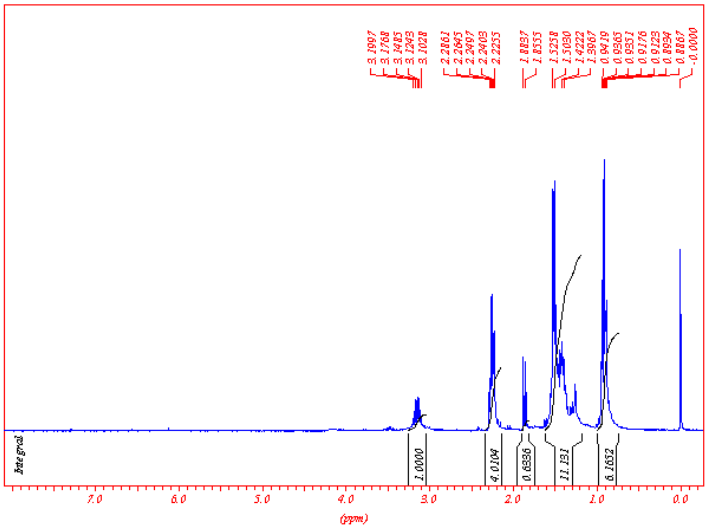
^{13}C NMR (75 MHz, $CDCl_3$)



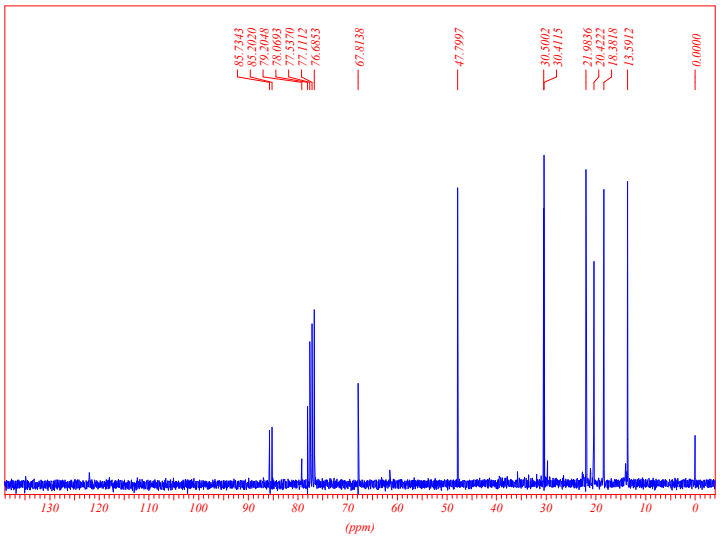
7-(1-Mercaptoethyl)trideca-5,8-diyn-7-ol (**5g**)



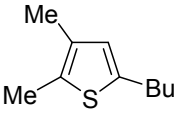
^{1}H NMR (300 MHz, $CDCl_3$)



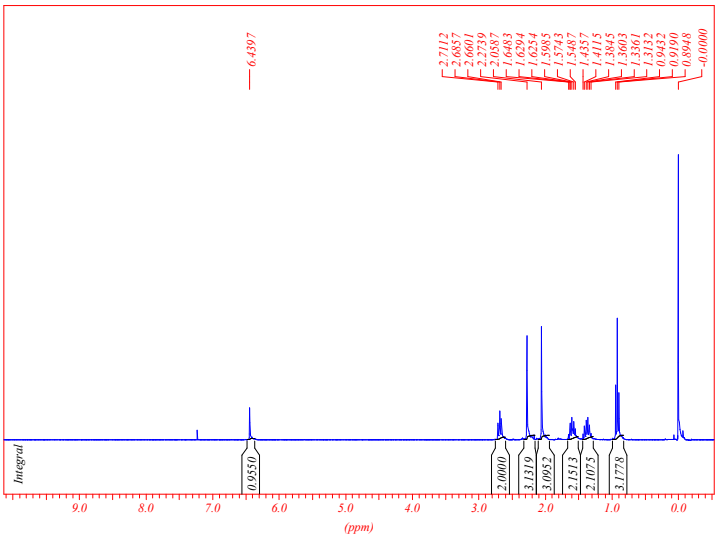
^{13}C NMR (75 MHz, $CDCl_3$)



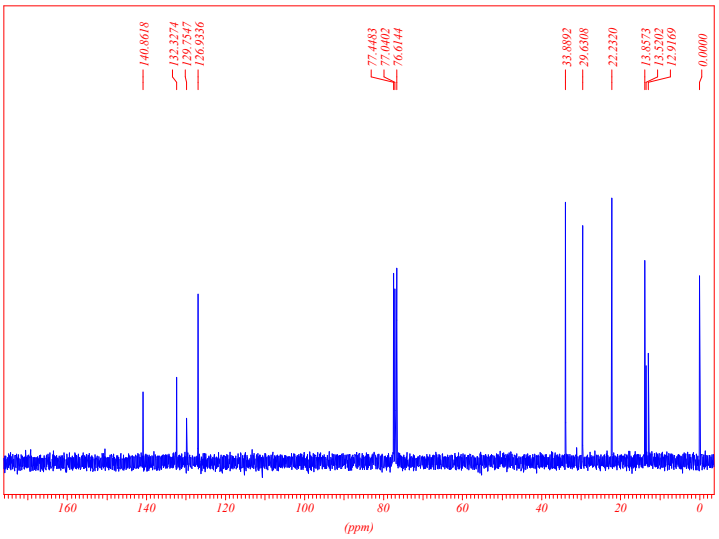
5-Butyl-2,3-dimethylthiophene (**6a**)



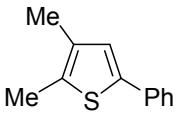
^{1}H NMR (300 MHz, $CDCl_3$)



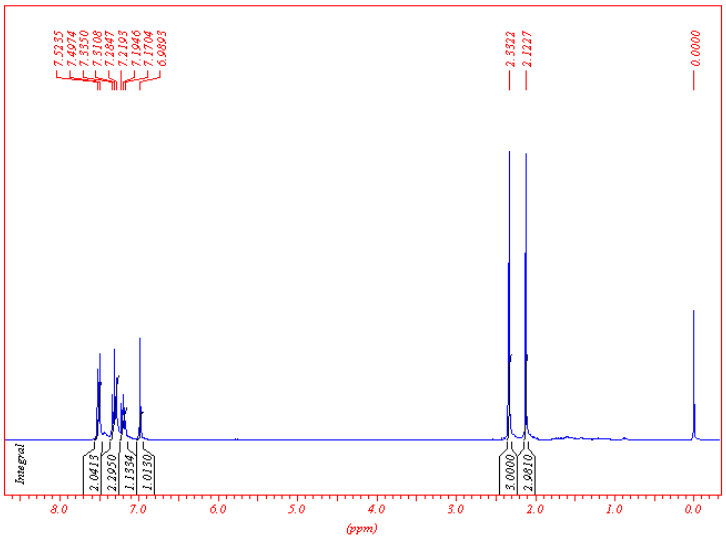
^{13}C NMR (75 MHz, $CDCl_3$)



2,3-Dimethyl-5-phenylthiophene (**6b**)



^{1}H NMR (300 MHz, $CDCl_3$)



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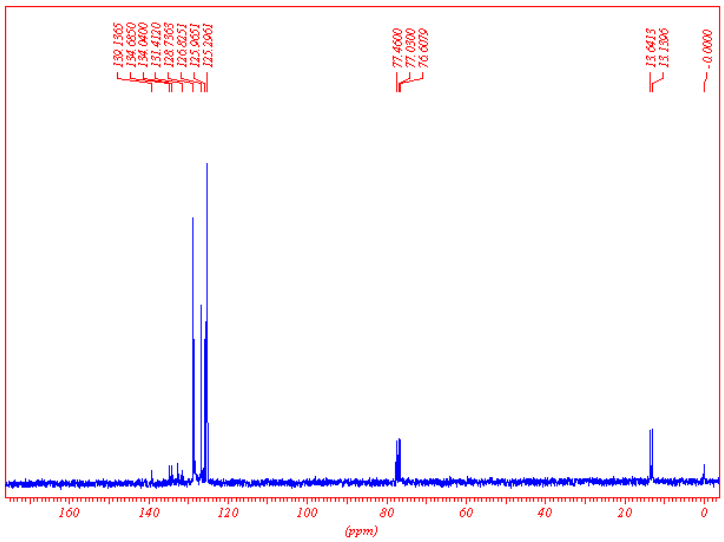
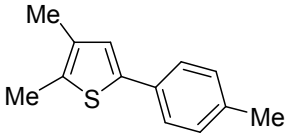


2,3-Dimethyl-5-p-tolylthiophene (**6c**)



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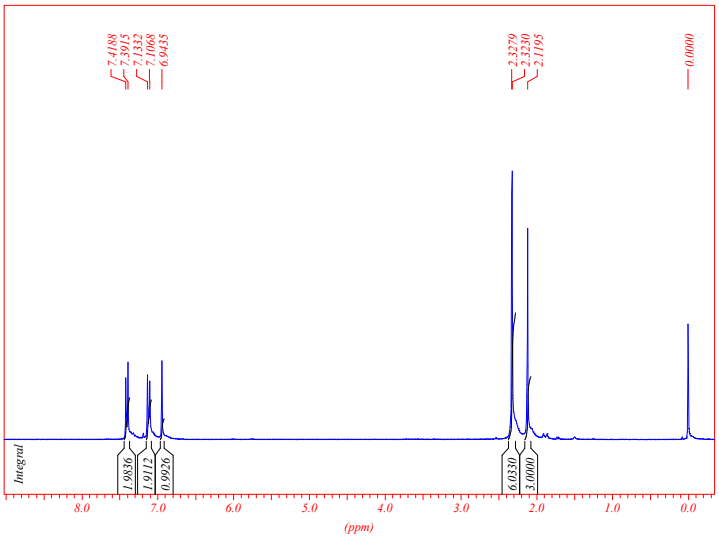
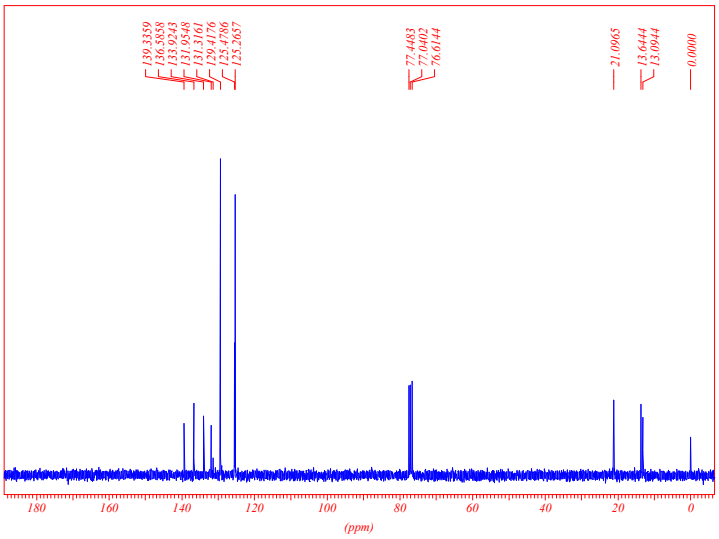
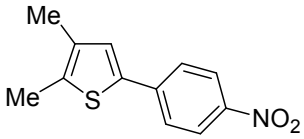


^{13}C NMR (75 MHz, $CDCl_3$)



2,3-Dimethyl-5-(4-nitrophenyl)thiophene (**6d**)



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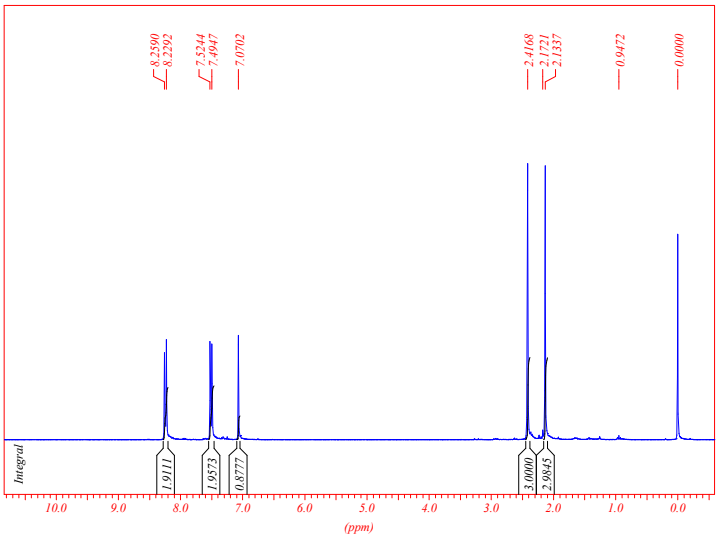
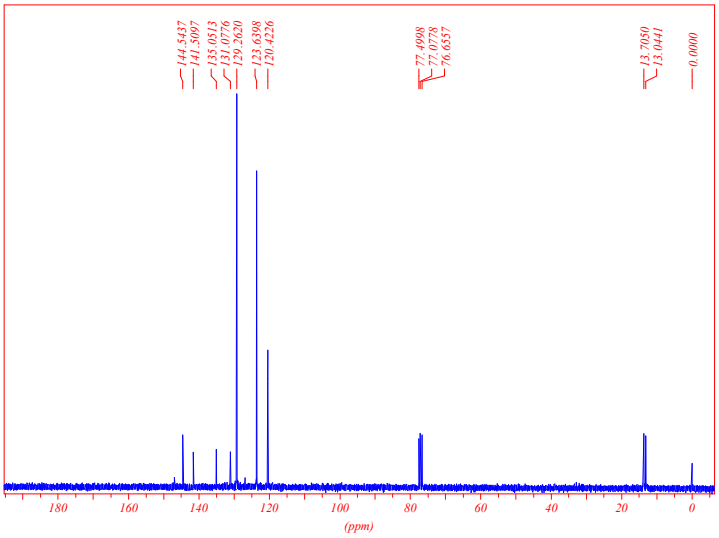
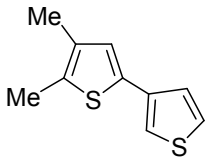


^{13}C NMR (75 MHz, $CDCl_3$)



2,3-Dimethyl-5-(thiophen-3-yl)thiophene (**6e**)



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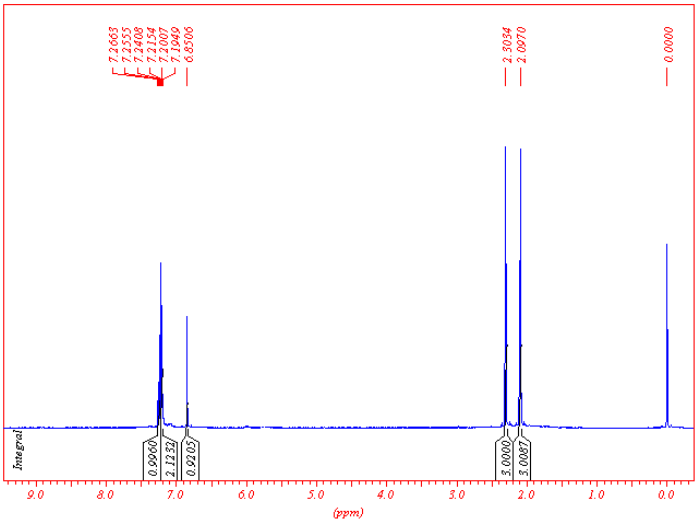

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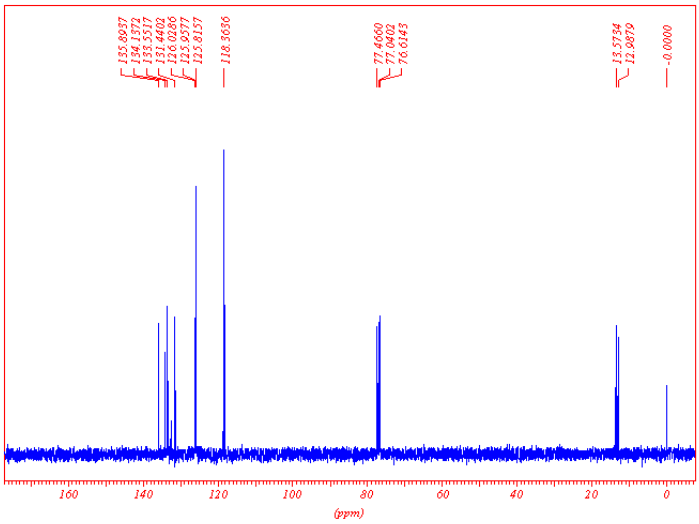
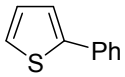


2-Phenylthiophene (**6f**)



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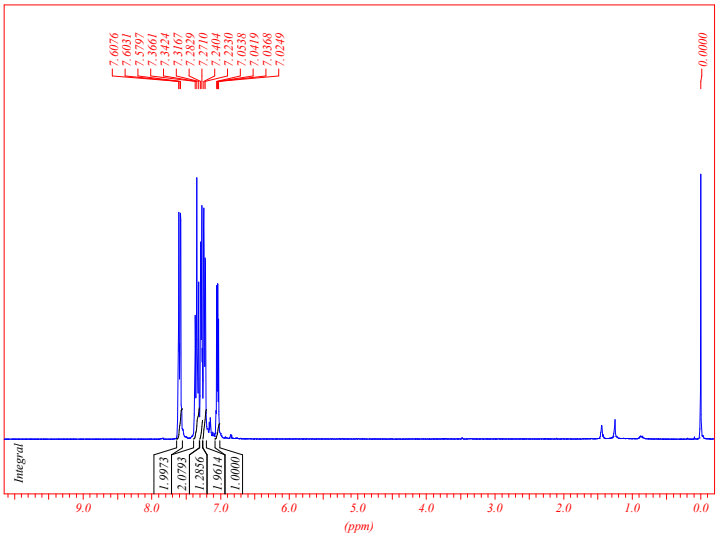

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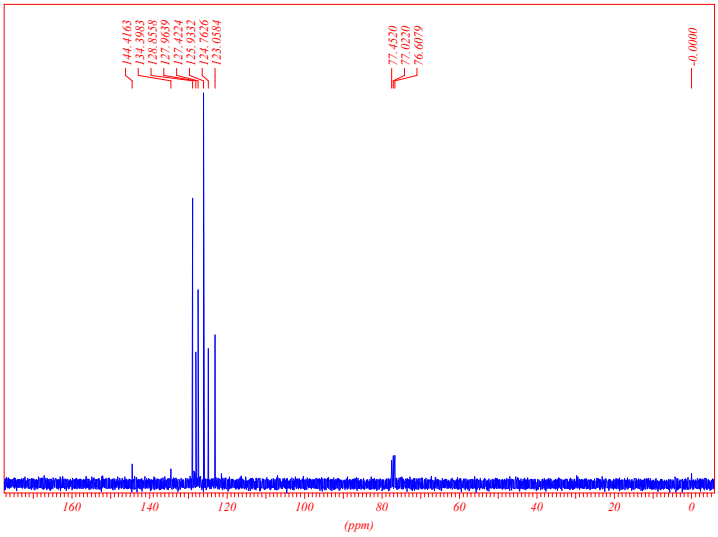
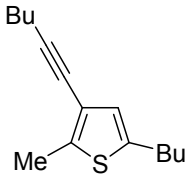
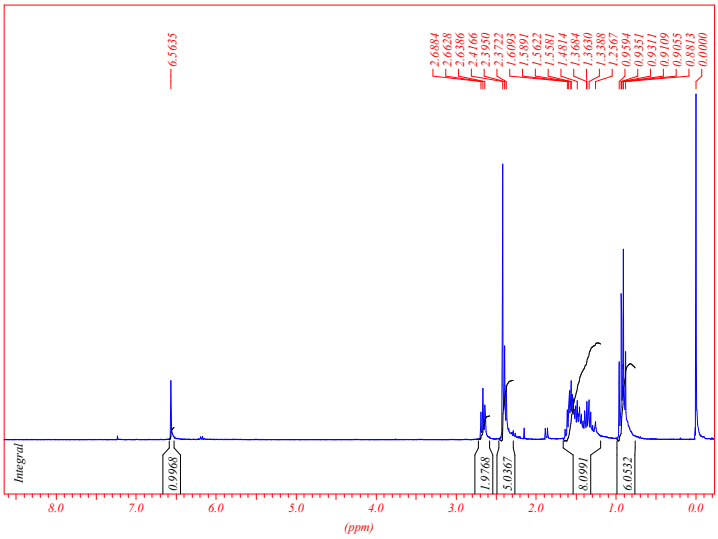


5-Butyl-3-hex-1-ynyl-2-methylthiophene (**6g**)



^{1}H NMR (300 MHz, $CDCl_3$)



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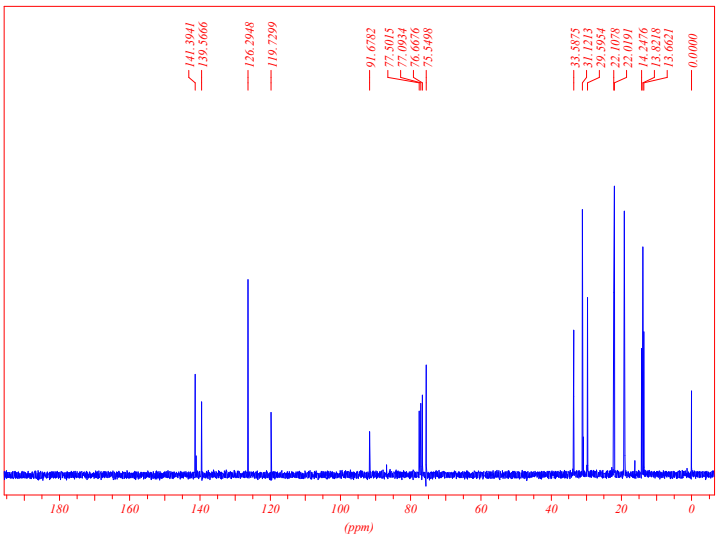
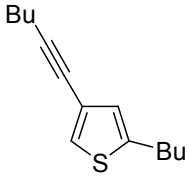
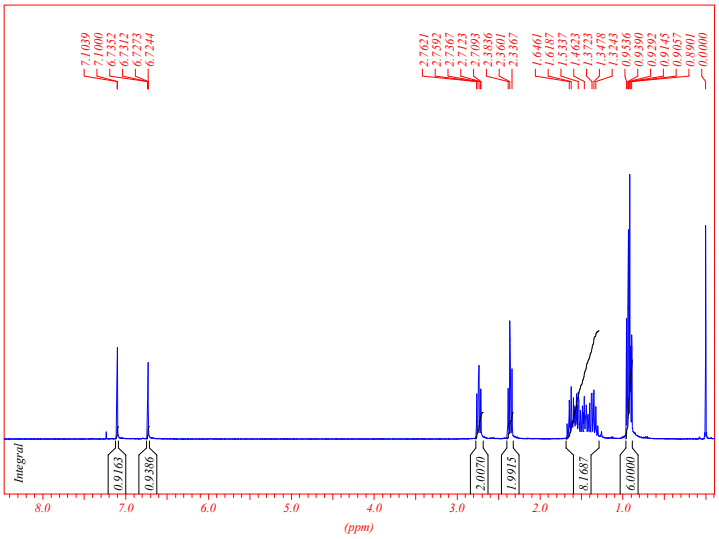


2-Butyl-4-hex-1-ynylthiophene (**6h**)



^{1}H NMR (300 MHz, $CDCl_3$)



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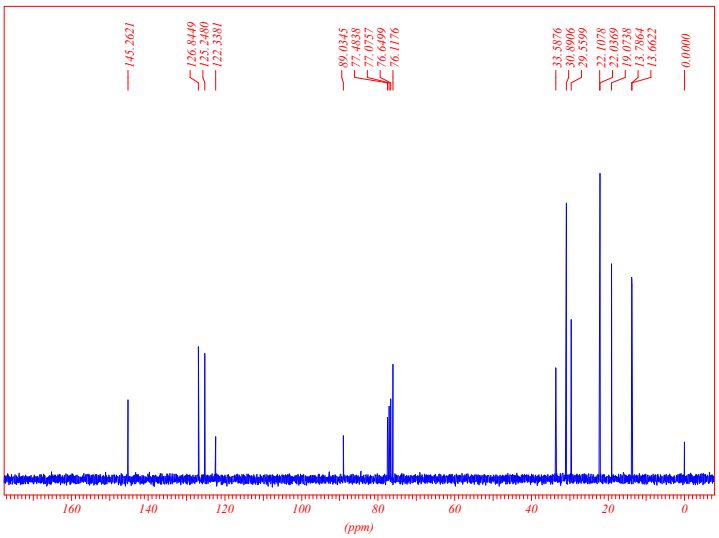
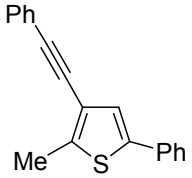
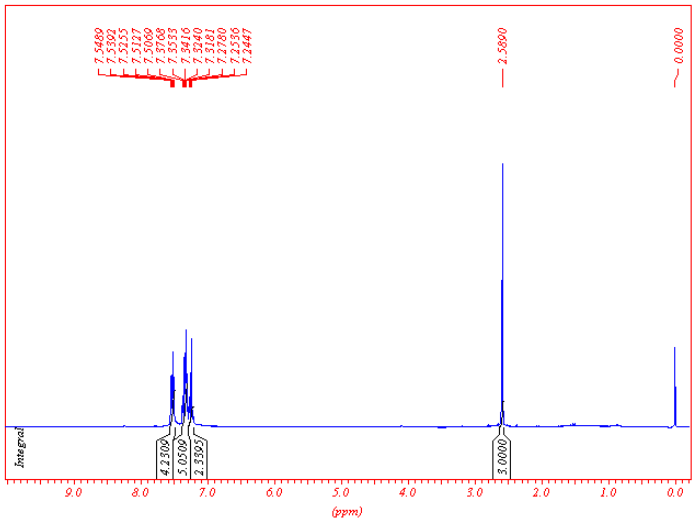
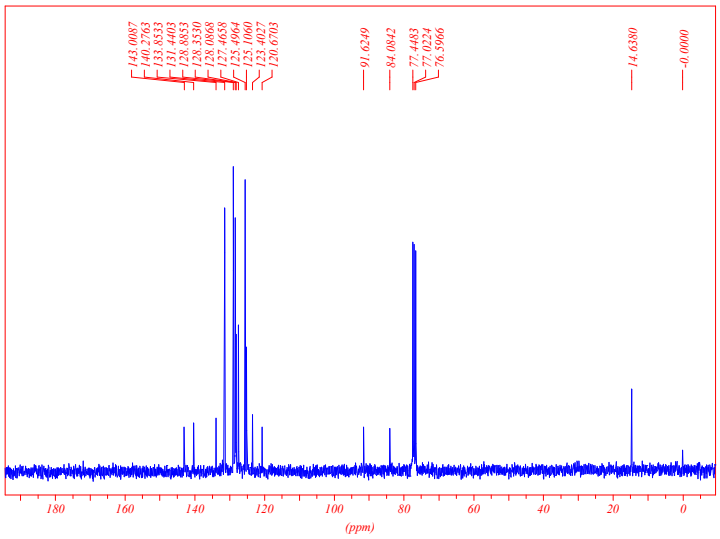


2-Methyl-5-phenyl-3-phenylethynylthiophene (**6i**)



^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)