Supporting Information

Pd-Catalyzed One-Pot Sequential Cross-Coupling Reactions of Tetrabromothiophene

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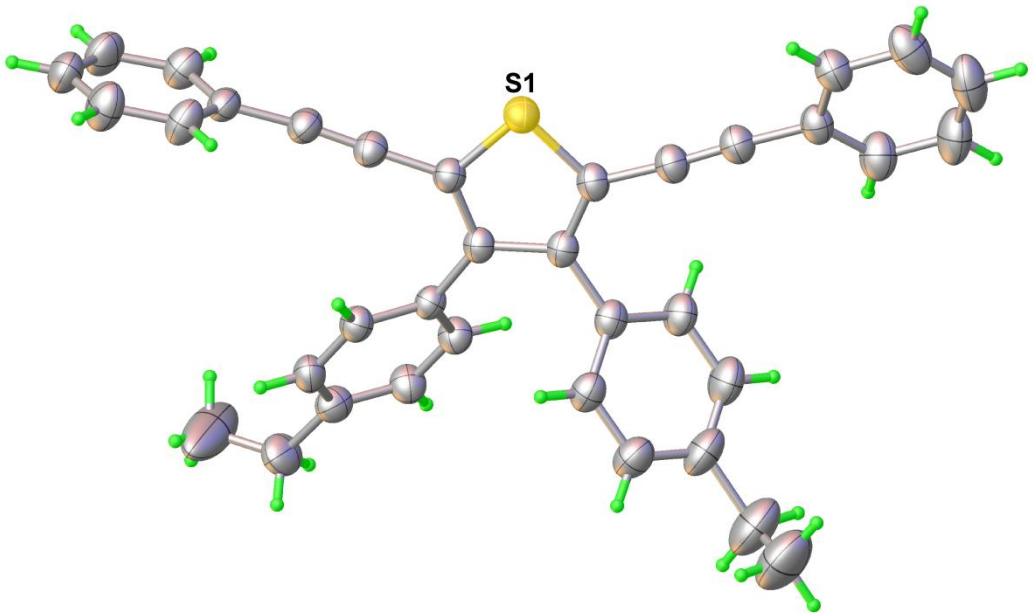
X-Ray crystallography study



The crystals of **6a** of suitable quality were obtained from hexane/CH_2Cl_2. The compound **6a** crystallized in monoclinic crystal system with space group P -1. The single-crystal X-ray data were collected on an Oxford XCalibur CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structures was solved using SIR-92 and refined by full matrix least square technique on F^2 using the SHELXL-97[5-6] program within the WinGX v 1.80.05 software package. In **6a** All hydrogen atoms were fixed at the calculated positions with isotropic thermal parameters and all non-hydrogen atoms were refined anisotropically. Atomic coordinates, bond lengths, bond angles, and thermal parameters for compounds **6a** has been deposited at the Cambridge Crystallographic Data Centre. CCDC deposit number for **6a** is **1576779**

Table 1. Crystallographic data and structural refinement parameters for compound.

Identification code	6a
Empirical formula	$C_{36}H_{28}S$
Formula weight	492.64
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P* -1

a	9.4120(7) Å
b	12.0734(14) Å
c	13.3979(14) Å
α	111.486(10)°
β	93.777(7)°
γ	100.958(8)°
Volume	1375.5(3) $Å^3$
Z	2
Density (calculated)	1.190 Mg/m^3
Absorption coefficient	0.140 mm^{-1}
F(000)	520
Crystal size	0.270 x 0.240 x 0.220 mm^3
Theta range for data collection	3.103 to 25.000°
Index ranges	$-10 \leq h \leq 11$, $-13 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected	9019
Independent reflections	4817 [*R*(int) = 0.0782]
Data completeness	99.6 %
Absorption correction	Multi-scan
Max. and min. transmission	0.970 and 0.963
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4817 / 0 / 335
Goodness-of-fit on F^2	1.077
Final *R* indices [I>2sigma(I)]	$R_1 = 0.0916$, $wR_2 = 0.2601$
R indices (all data)	$R_1 = 0.1165$, $wR_2 = 0.2968$
Largest diff. peak and hole	0.497 and -0.380 $e.Å^{-3}$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = \{[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]\}^{1/2}$

References

1. CrysAlisPro, Agilent Technologies, Version 1.171.34.49, **2011**.
2. Sheldrick, G. M., *ActaCryst*. **2008**, *A64*, 112.

3. Farrugia, L. J. WinGX Version 1.80.05, An integrated system of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data*;* Department of Chemistry, University of Glasgow,**1997-2009**.
4. Foresman, J. B.; Frisch, A. E. *Exploring Chemistry with Electronic Structure Methods*; Gaussian, Inc.: Pittsburgh, PA. **1995**. (b) Hehre, W. J., Radom, L., Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, **1985**.

Copies of ^{1}H and ^{13}C NMR

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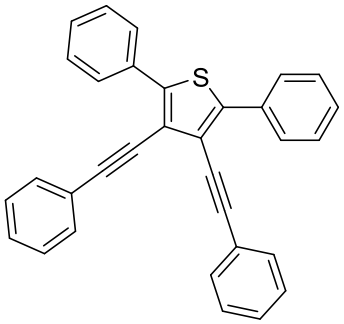
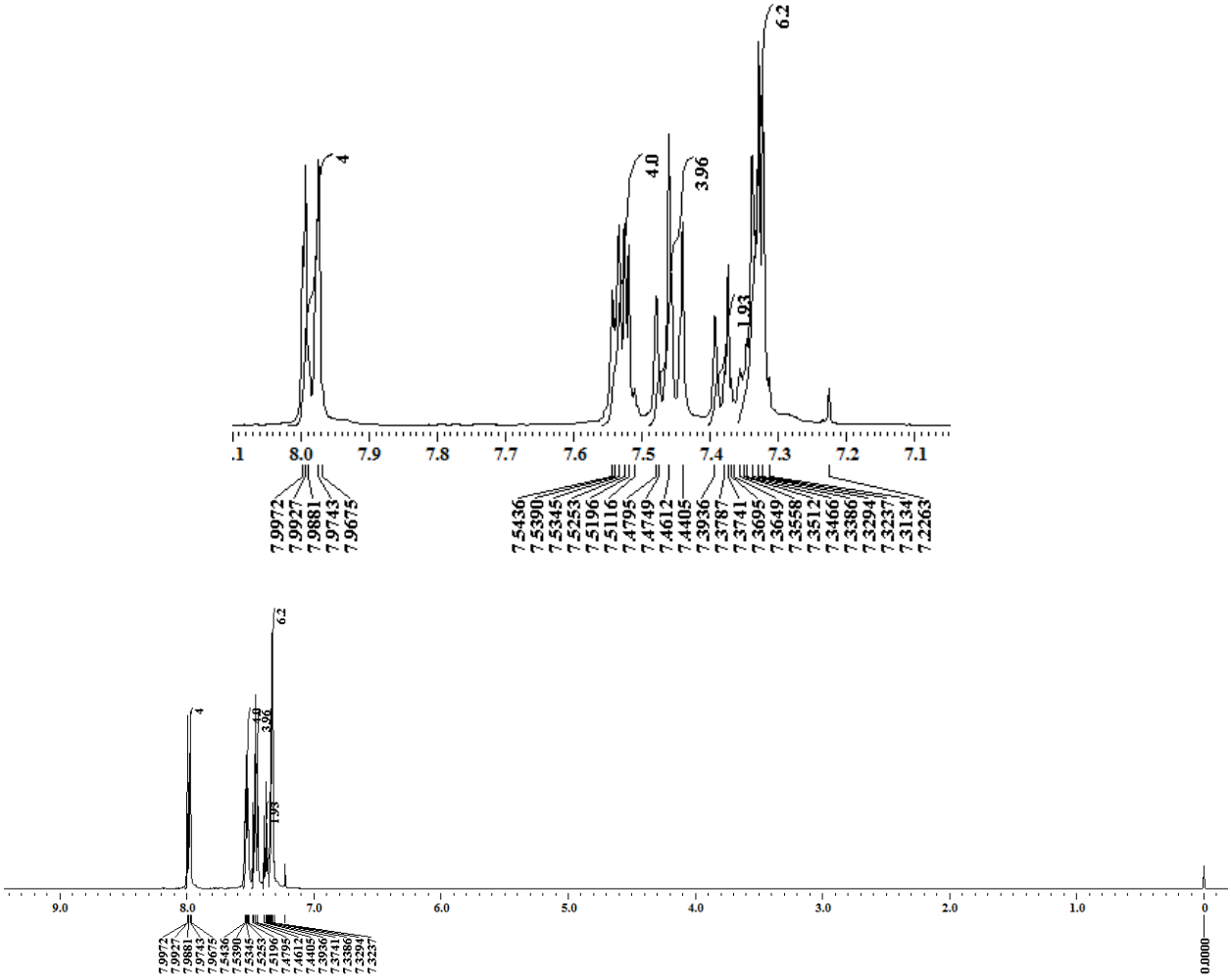


2,5-Diphenyl-3,4-bis(phenylethynyl)thiophene (4a)



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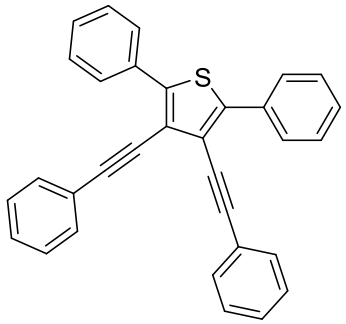

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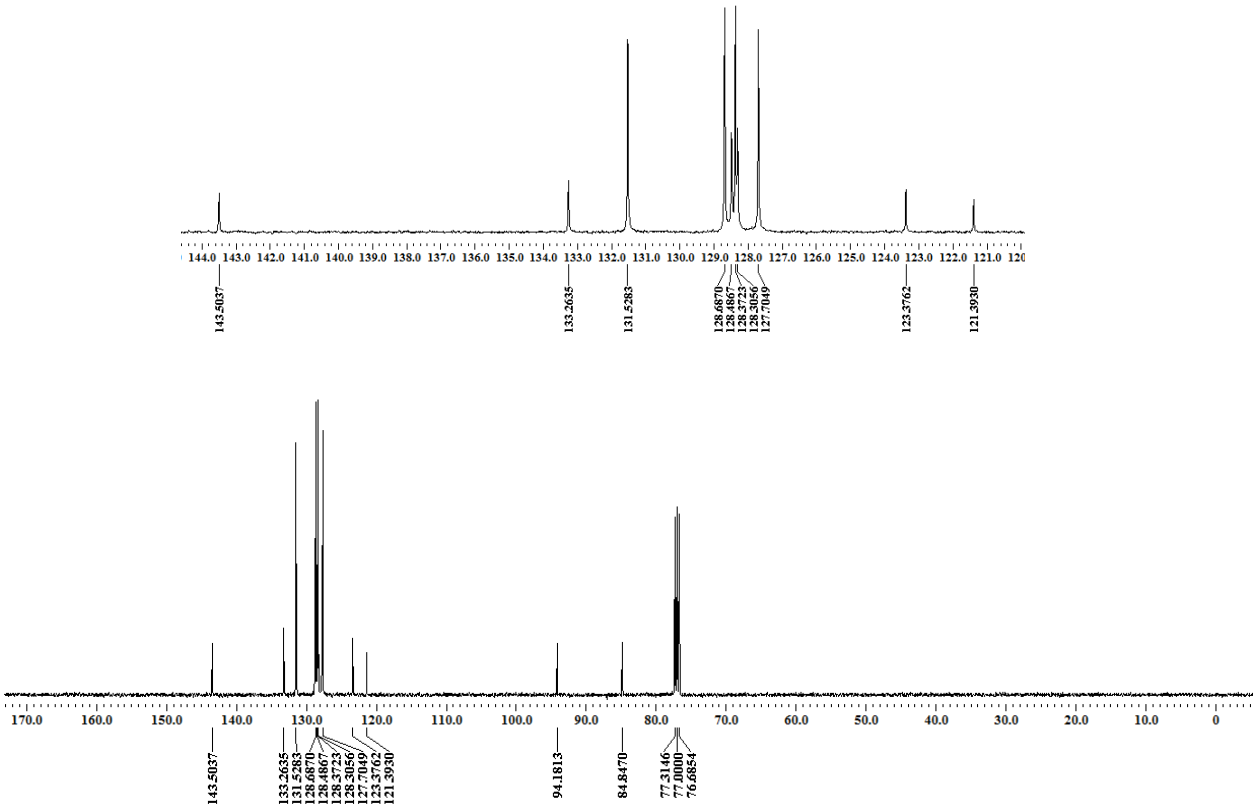

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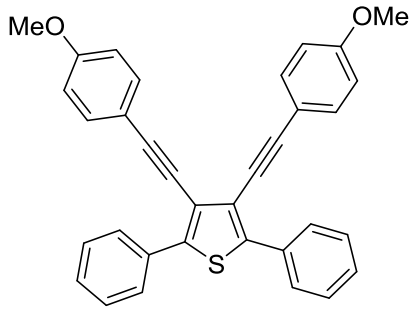

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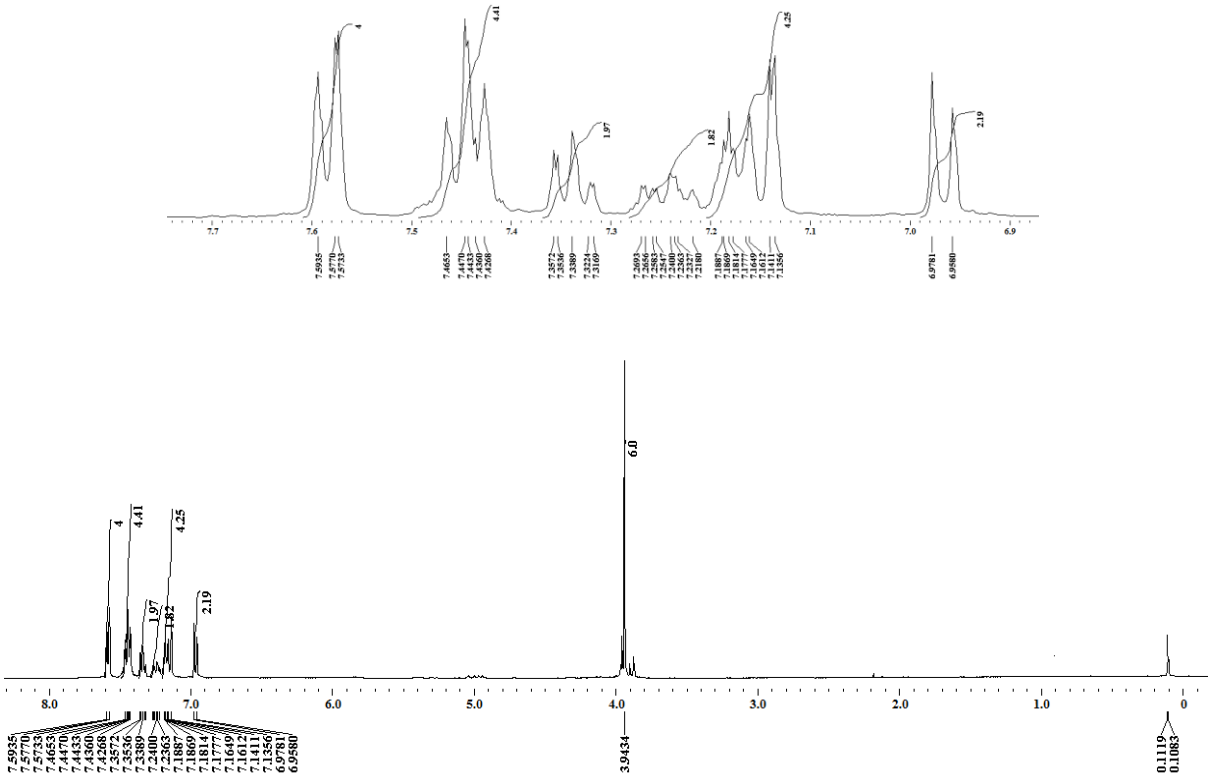

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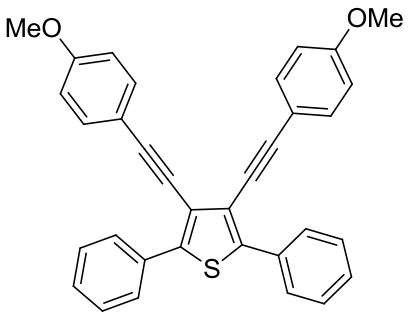

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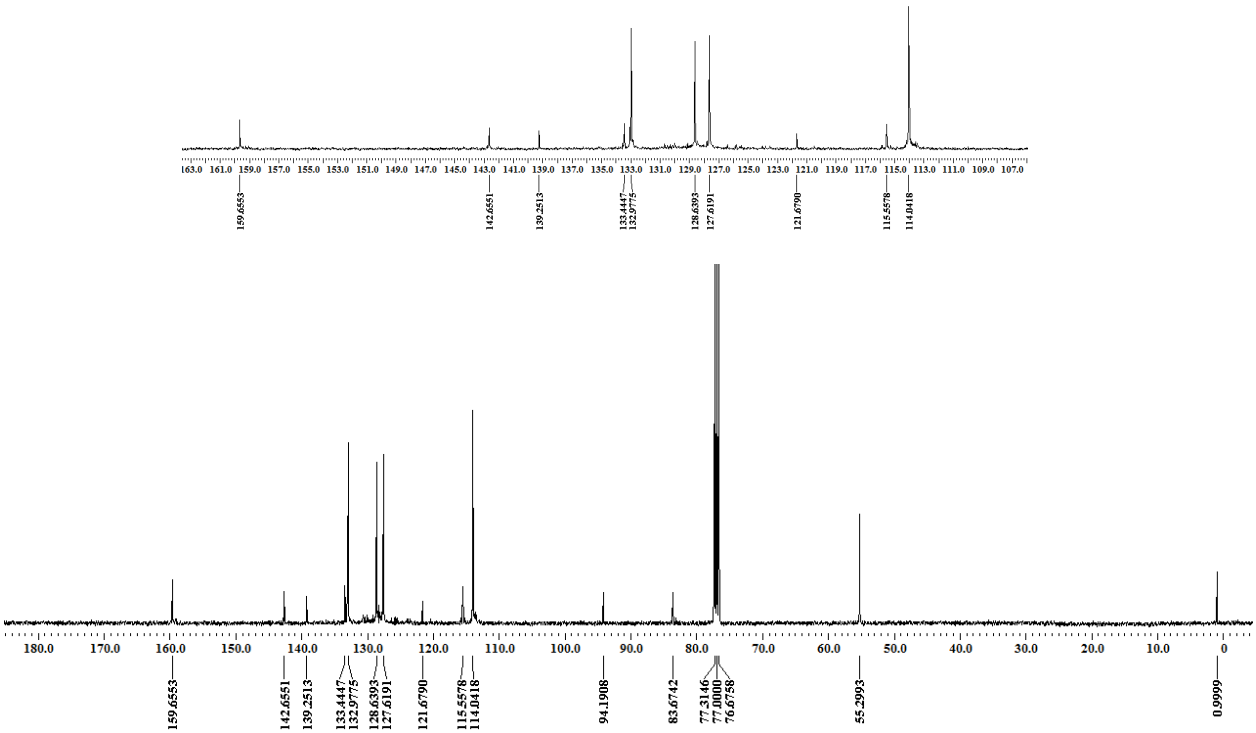

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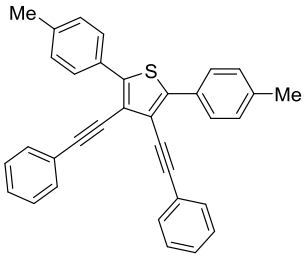

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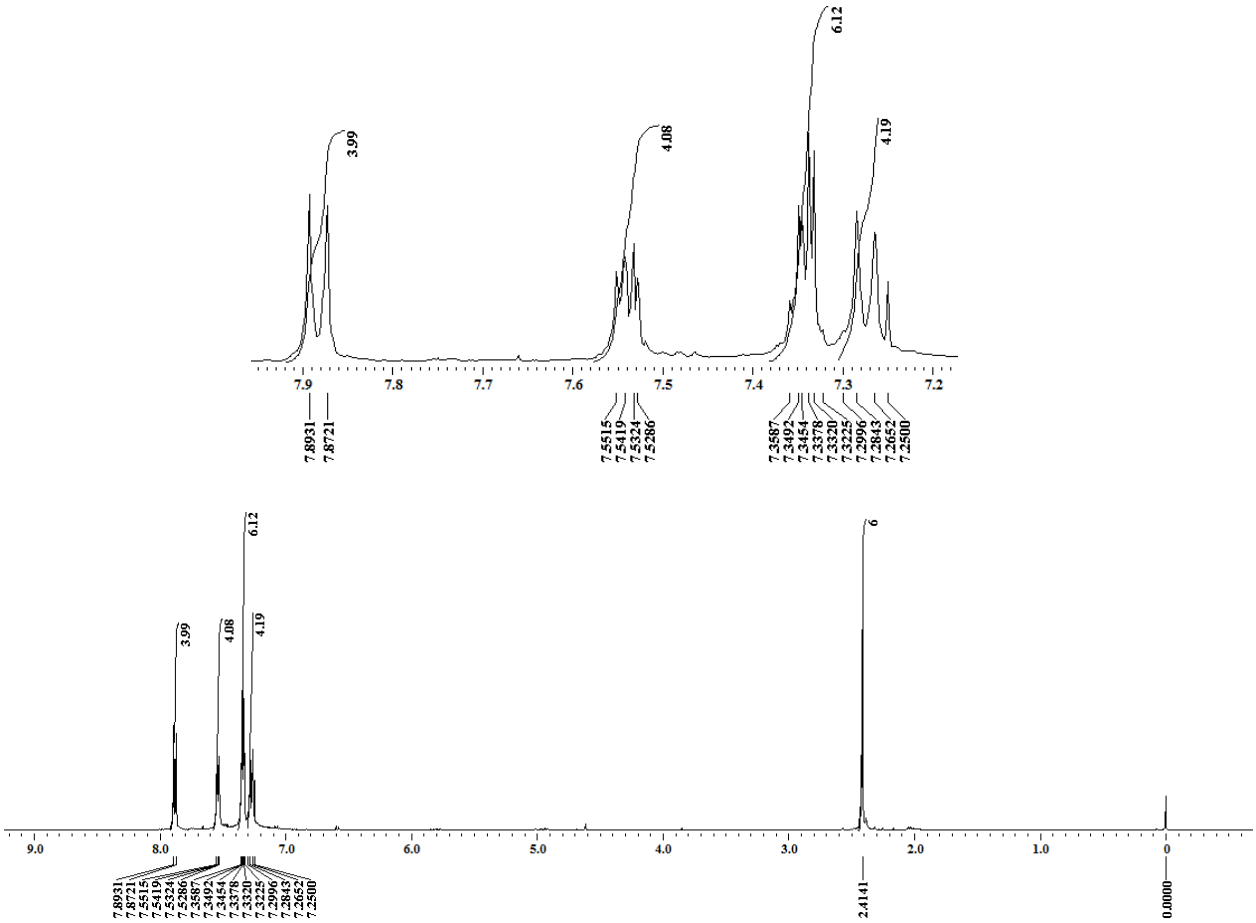

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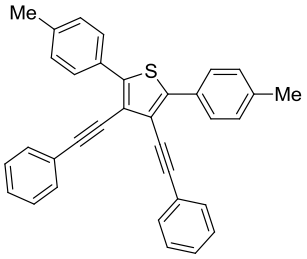

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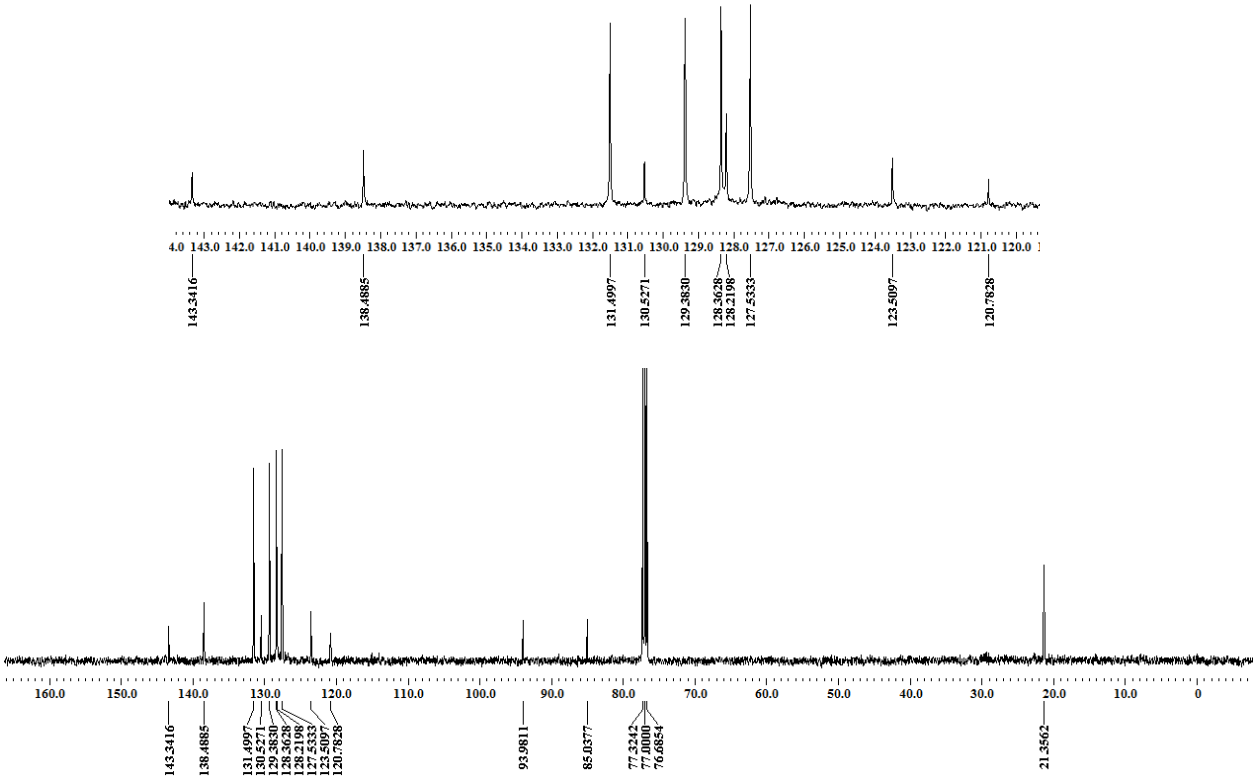

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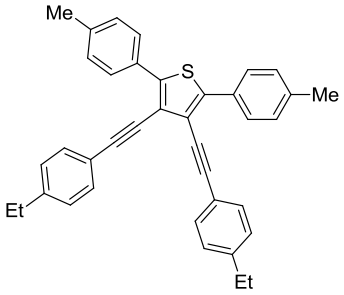

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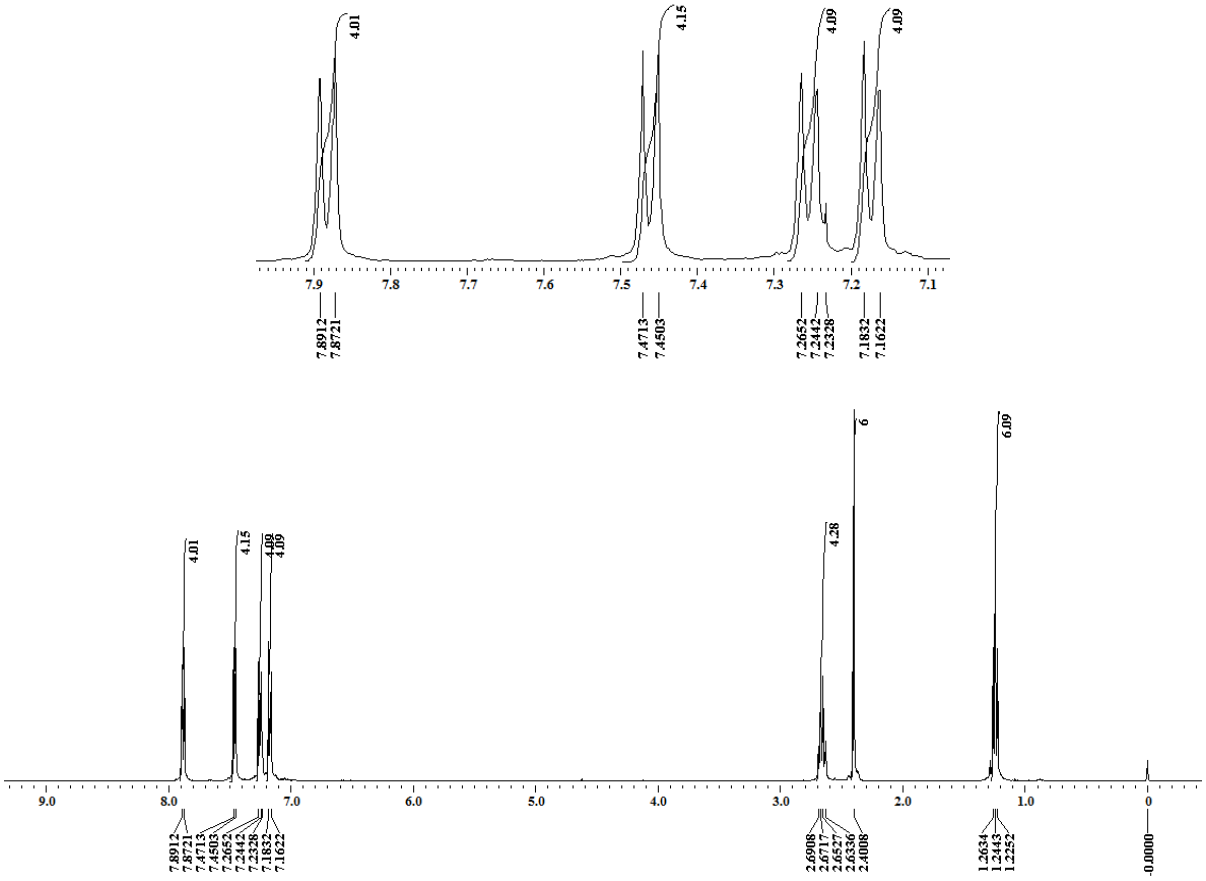

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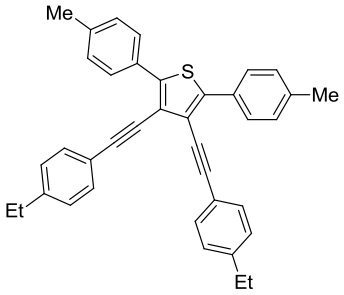

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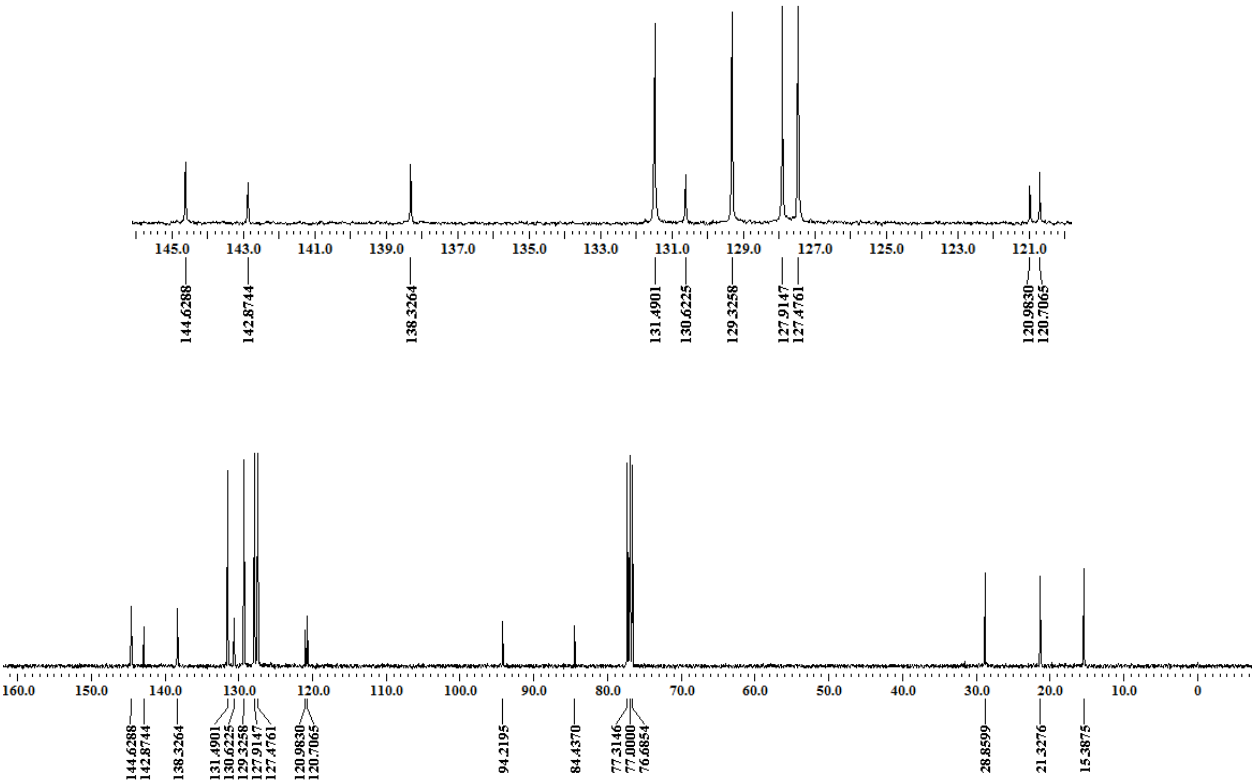

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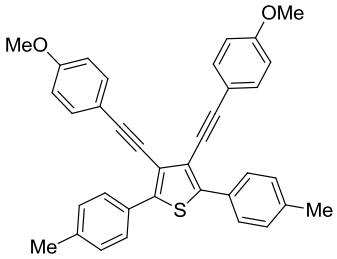

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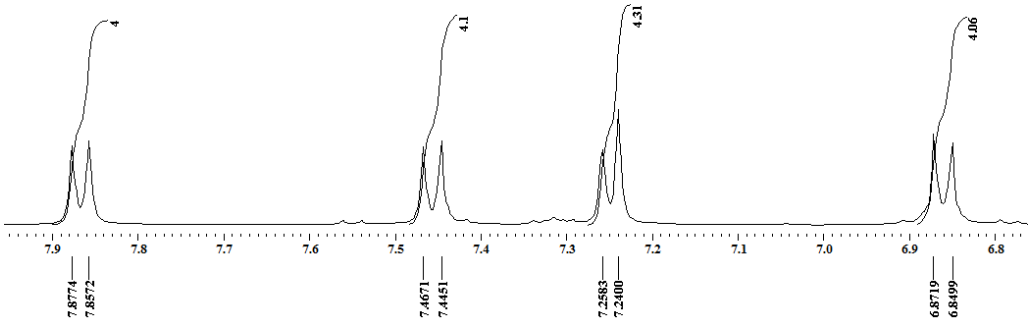

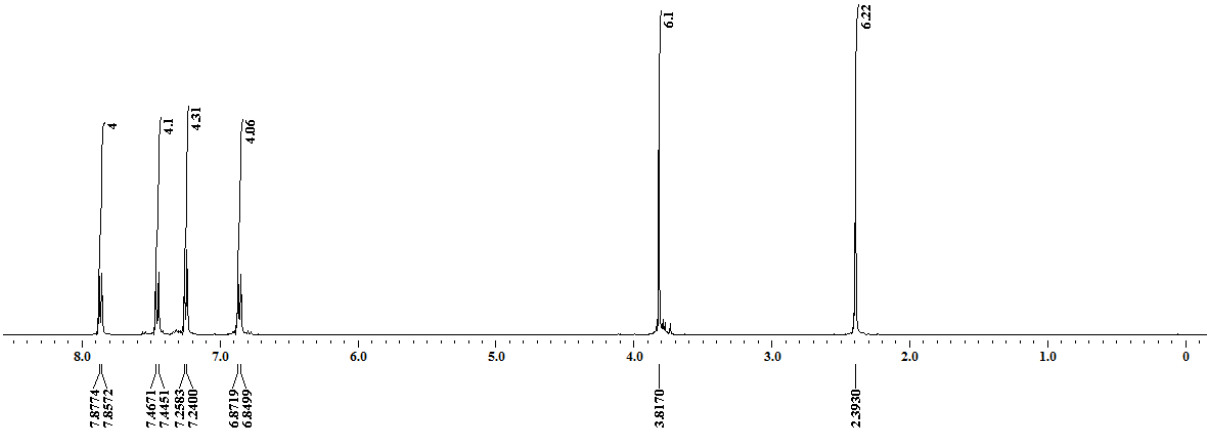

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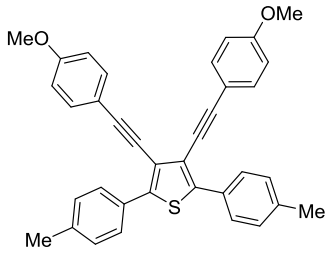

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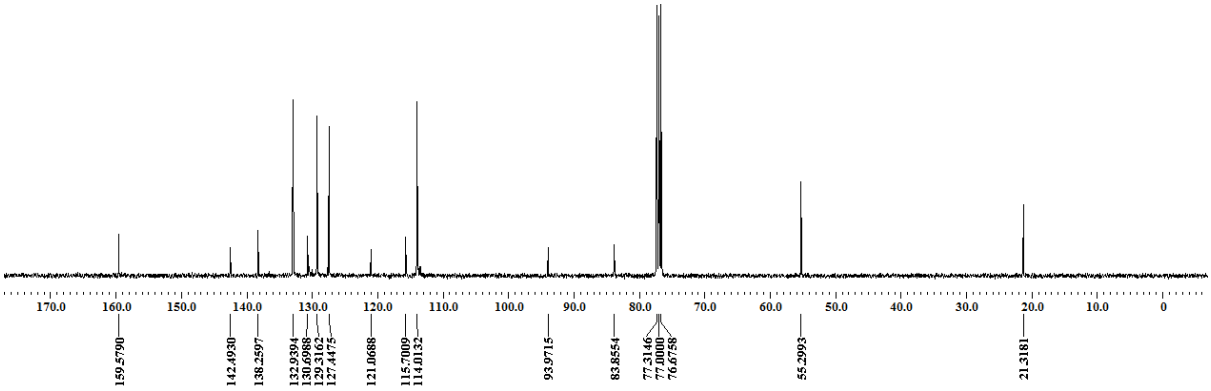

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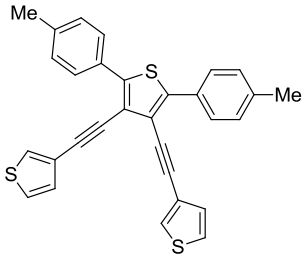
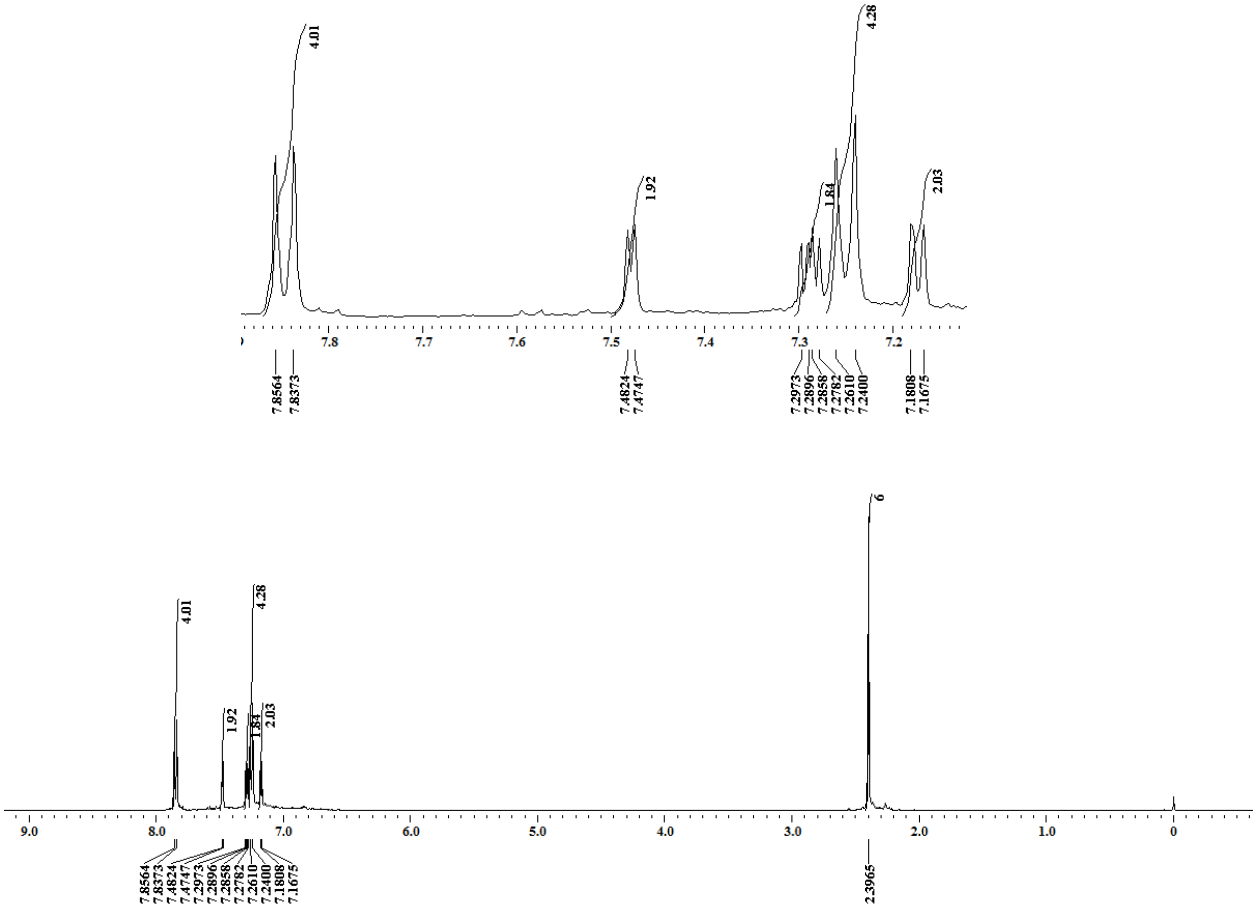


3,3'-((2,5-Di-*p*-tolylthiophene-3,4-diyl)bis(ethyne-2,1-diyl))dithiophene (4f)



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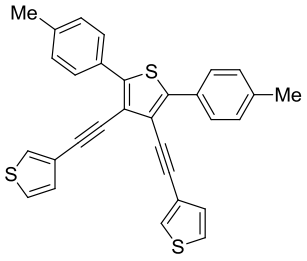
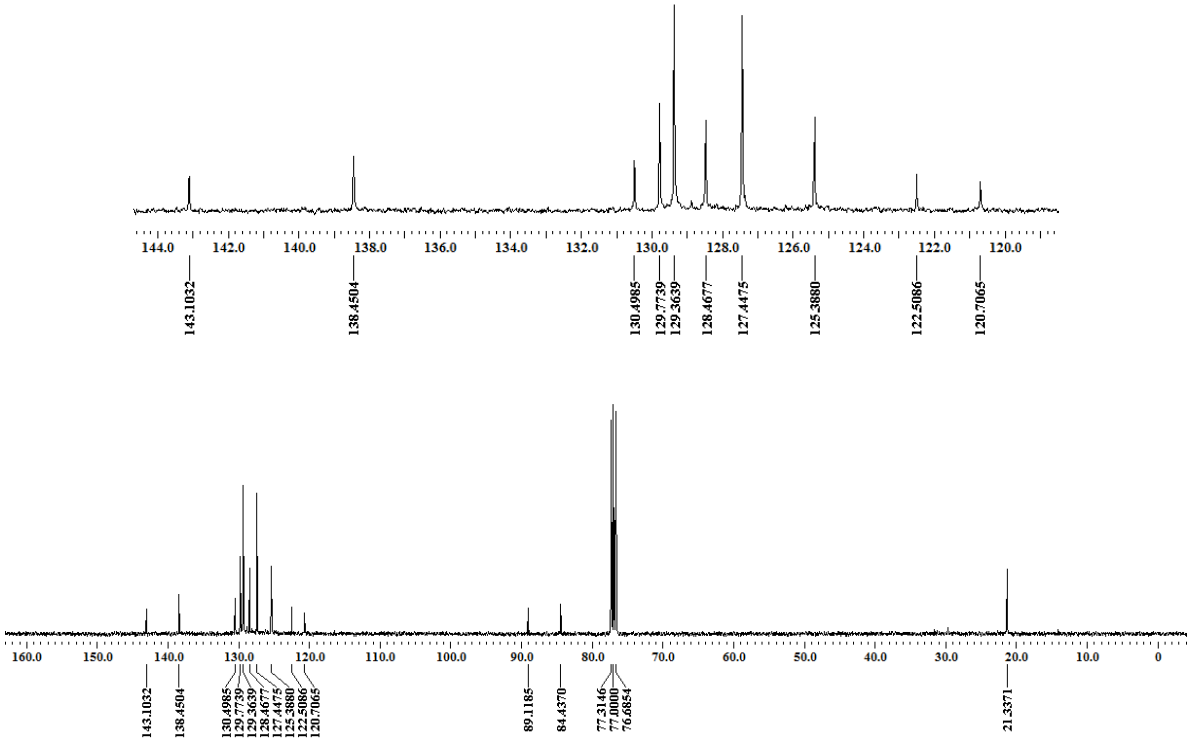


3,3'-((2,5-Di-*p*-tolylthiophene-3,4-diyl)bis(ethyne-2,1-diyl))dithiophene (4f)



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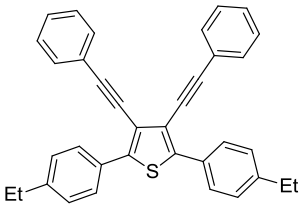

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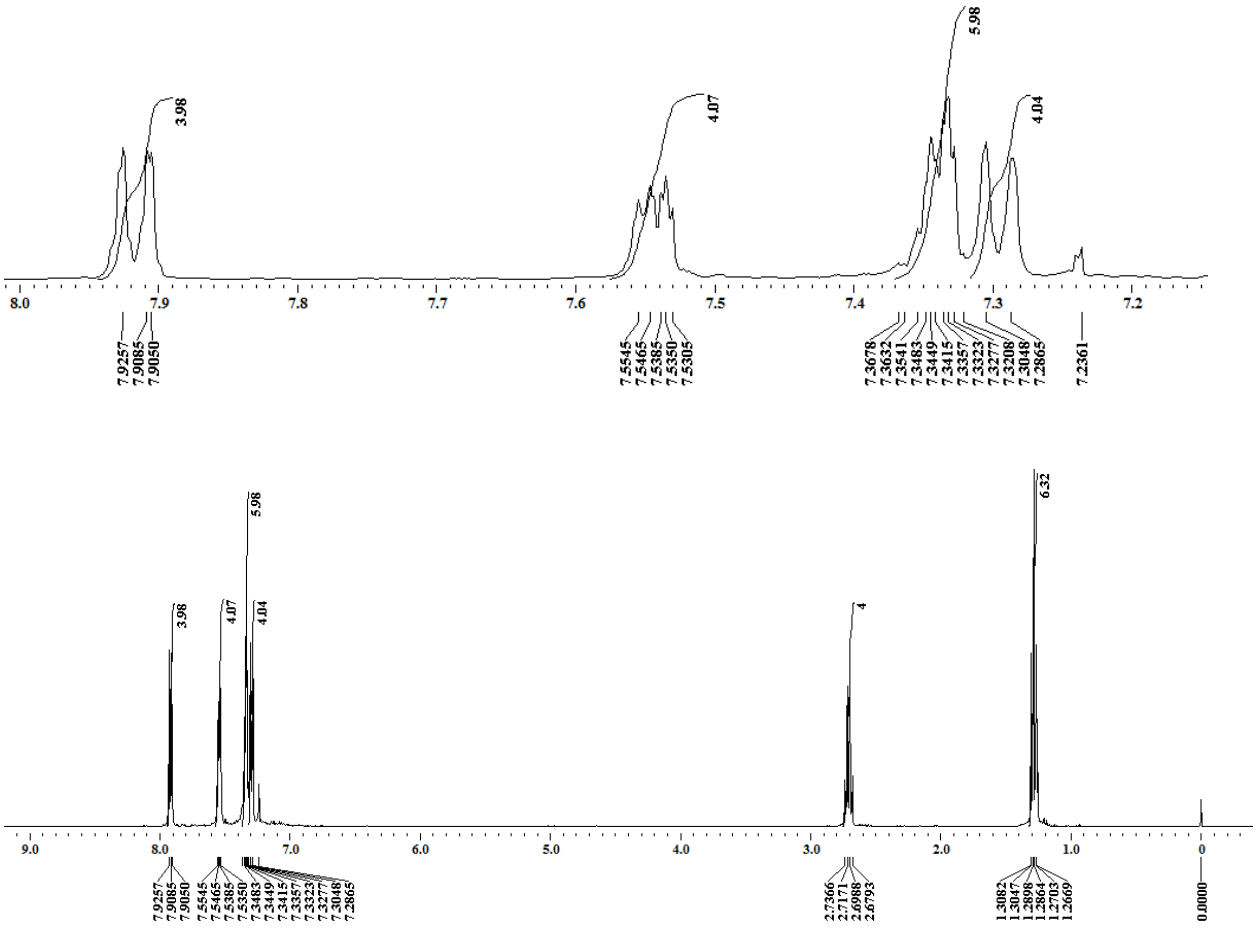

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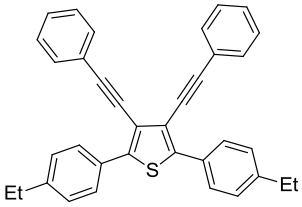

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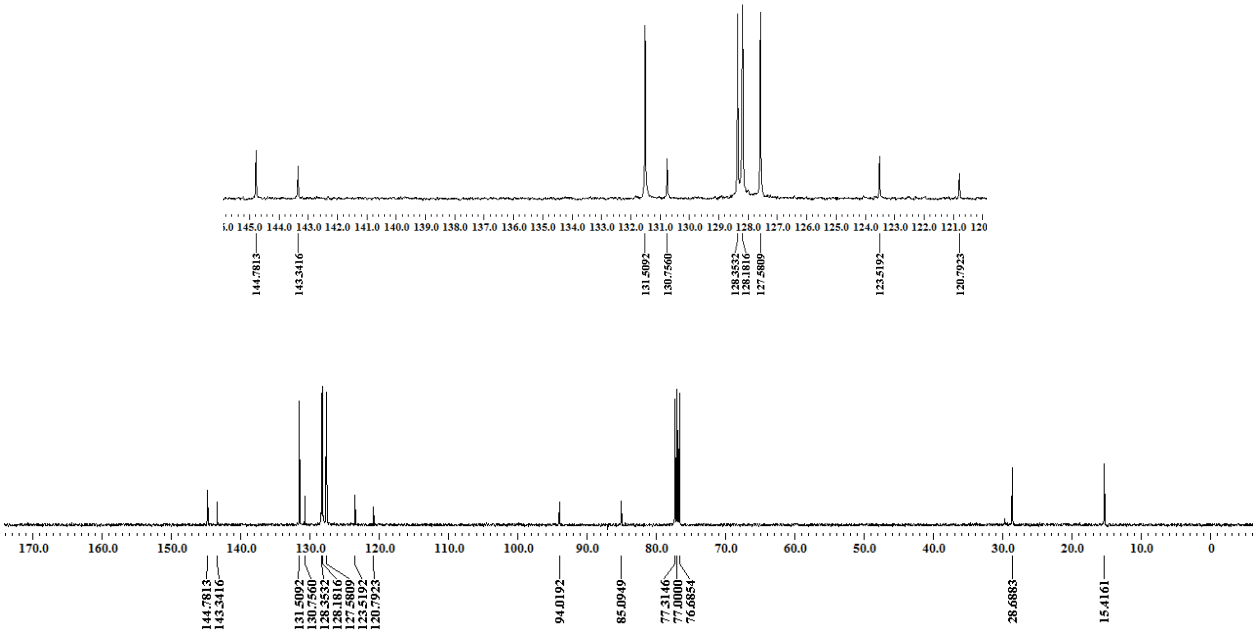

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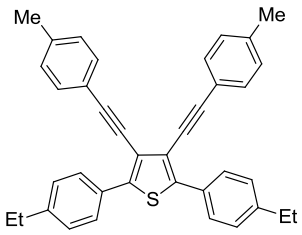

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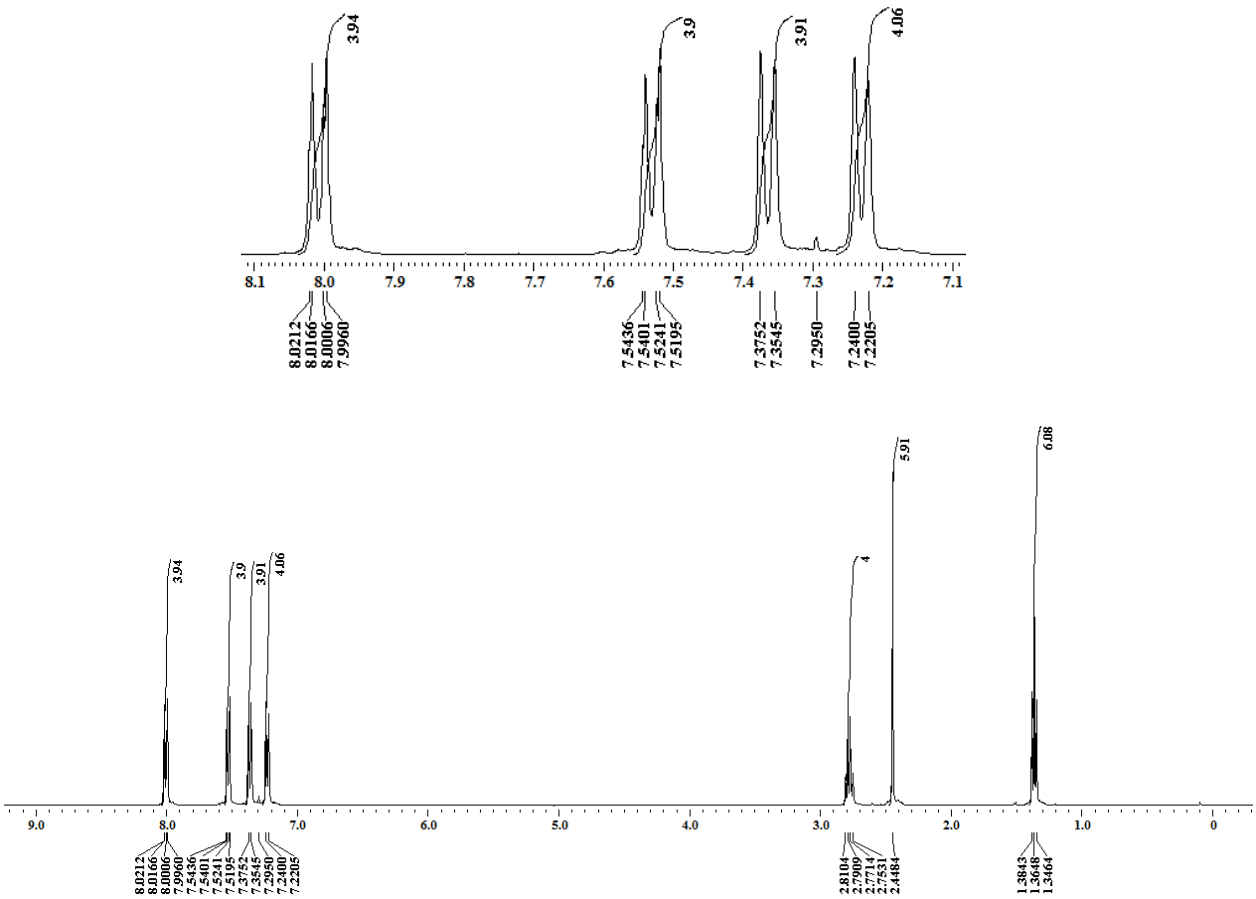

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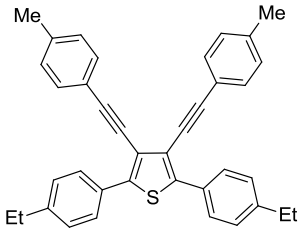

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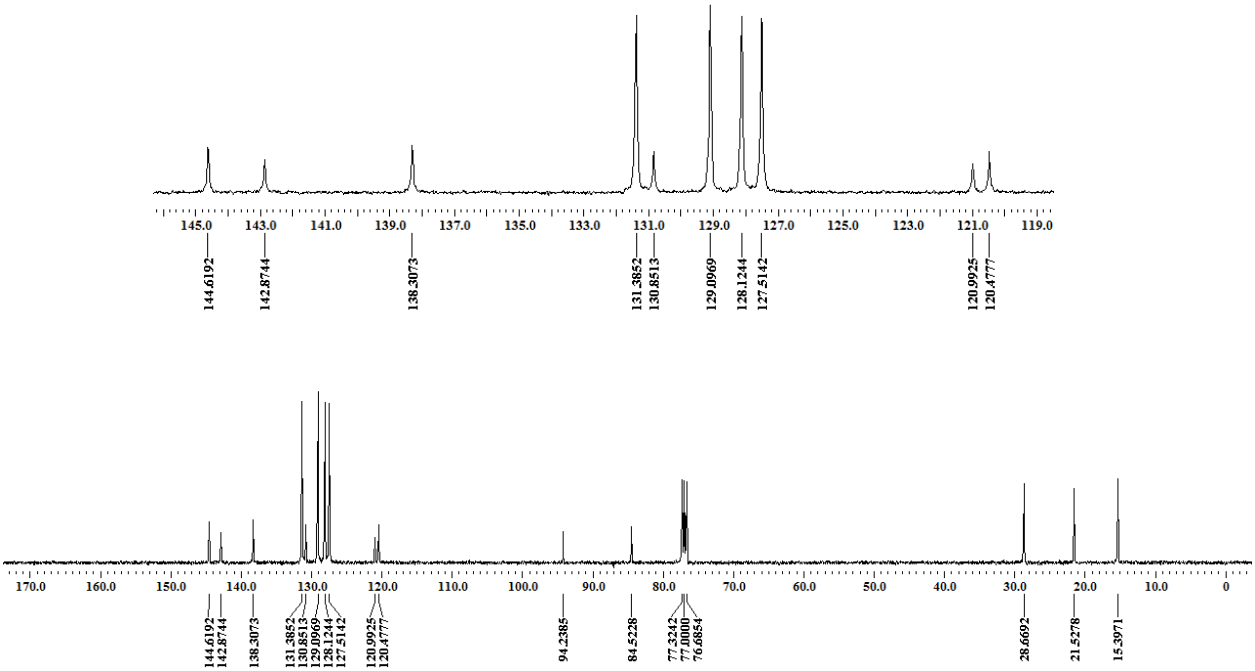

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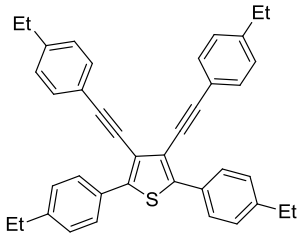

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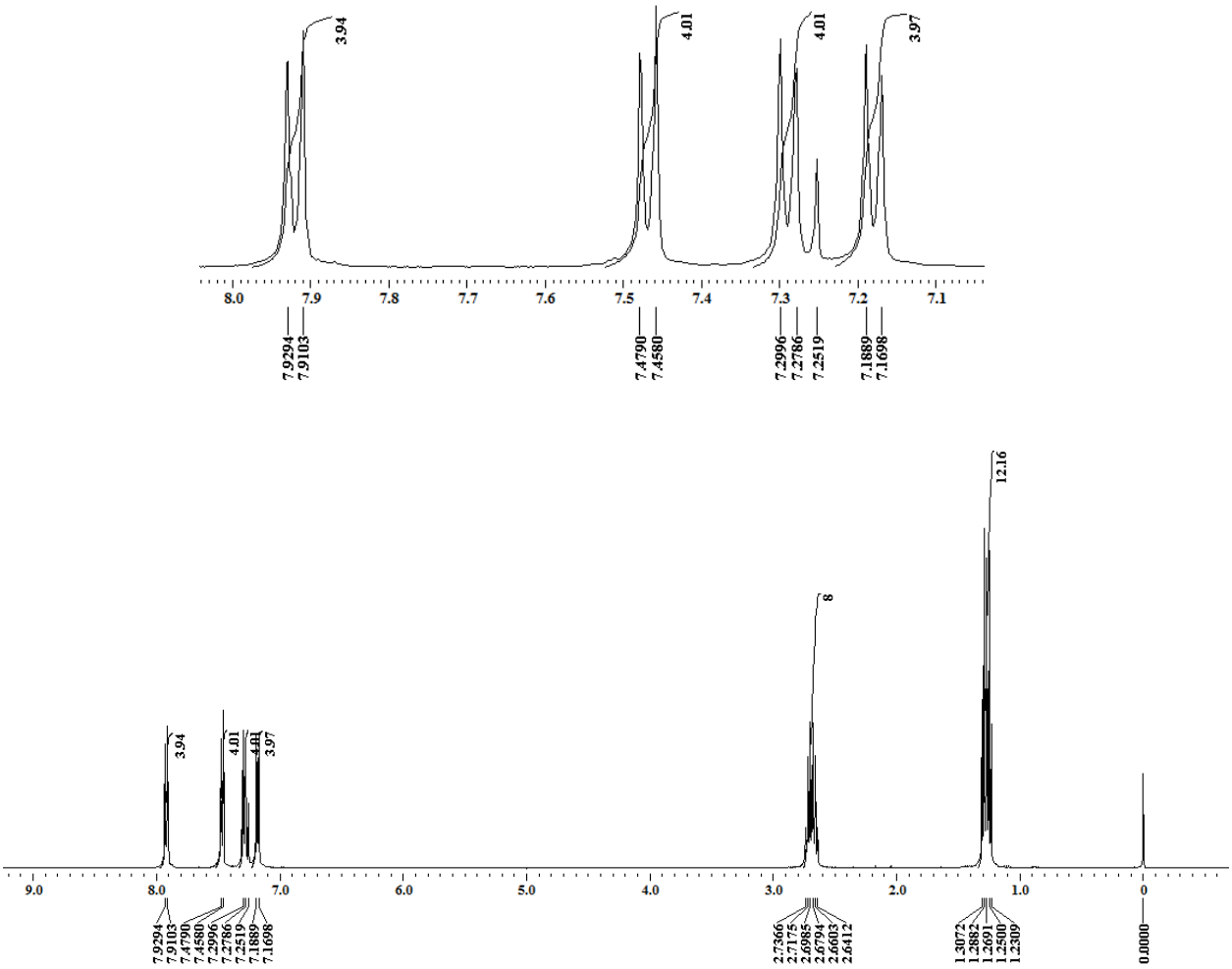

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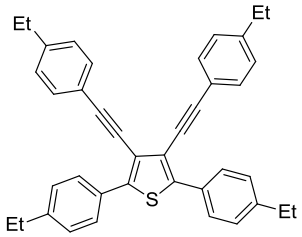

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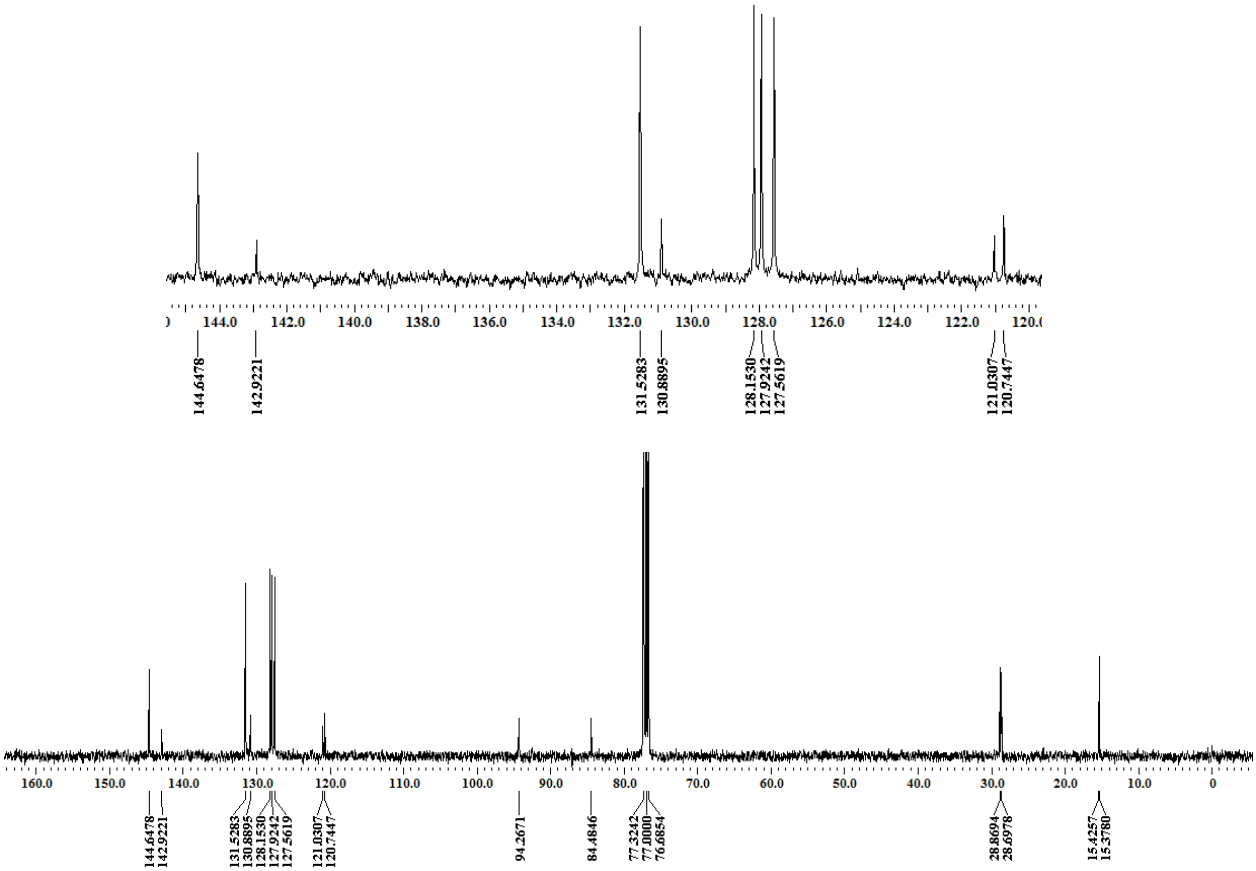

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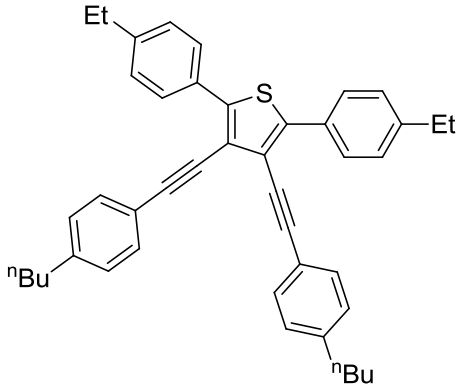

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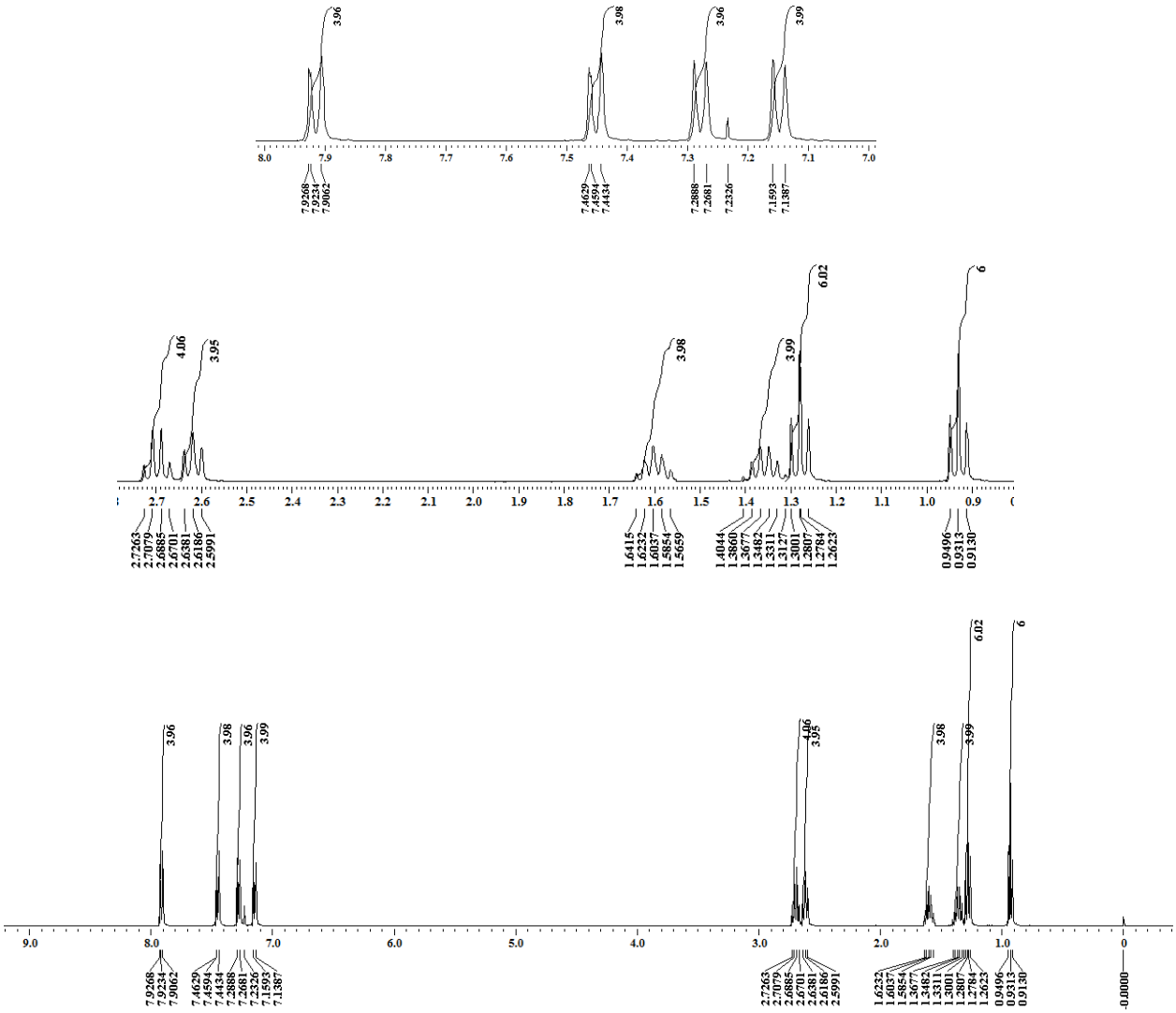

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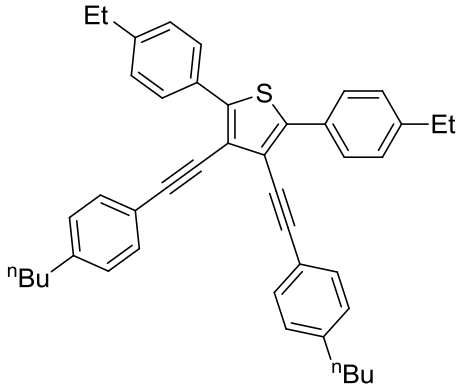

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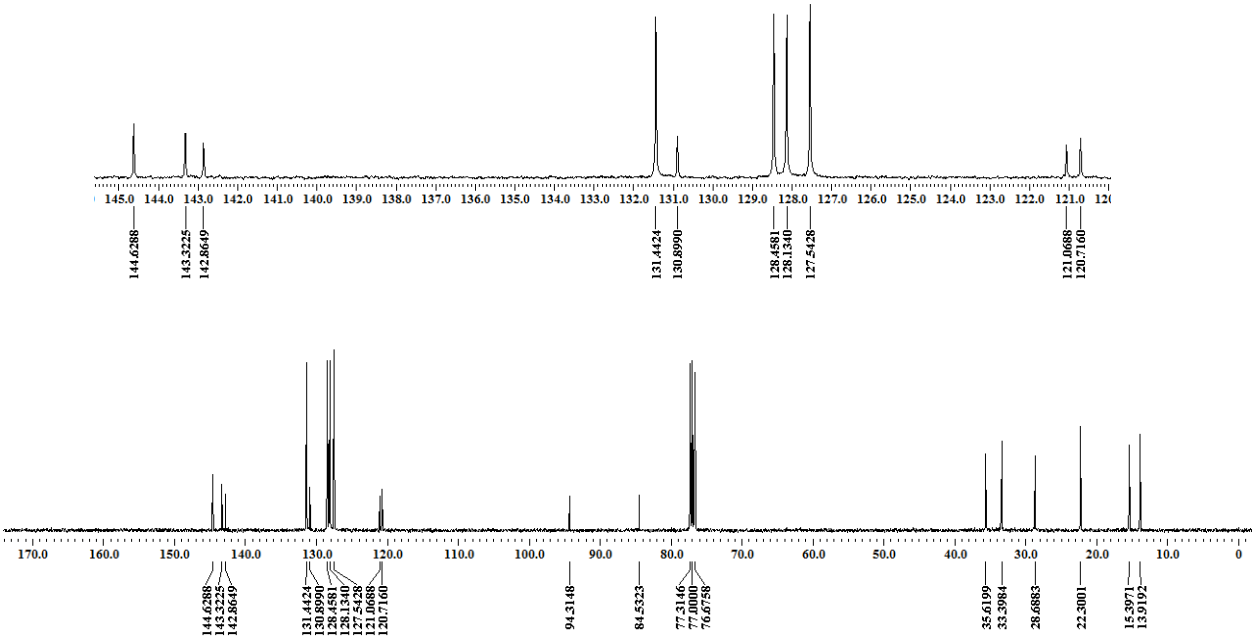

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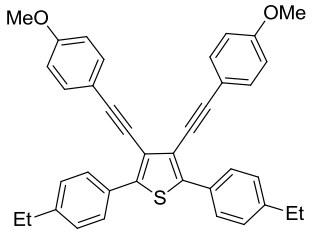

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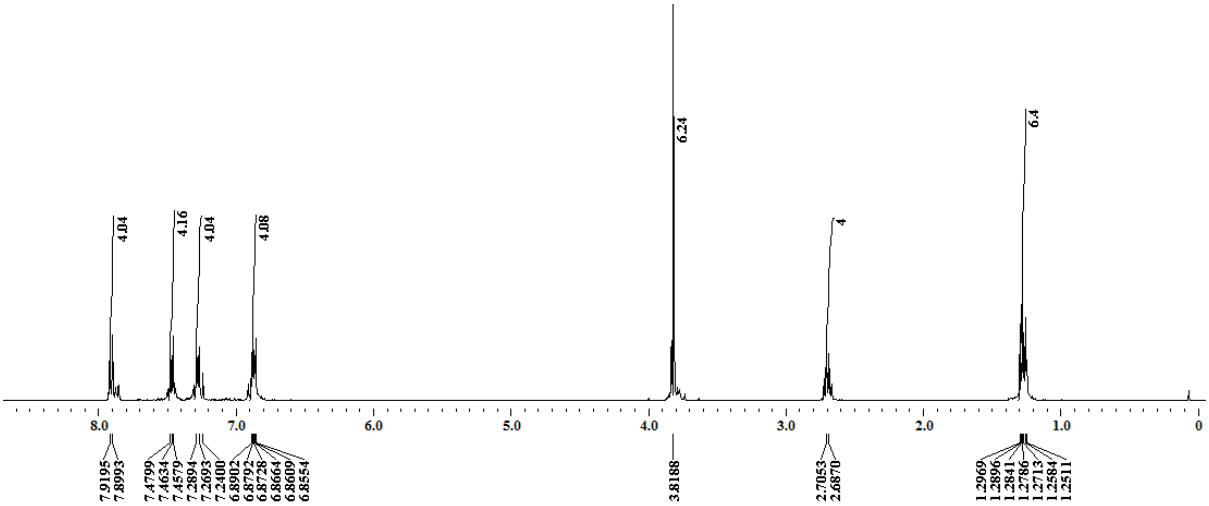

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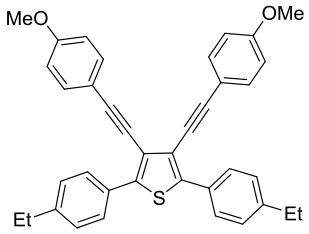

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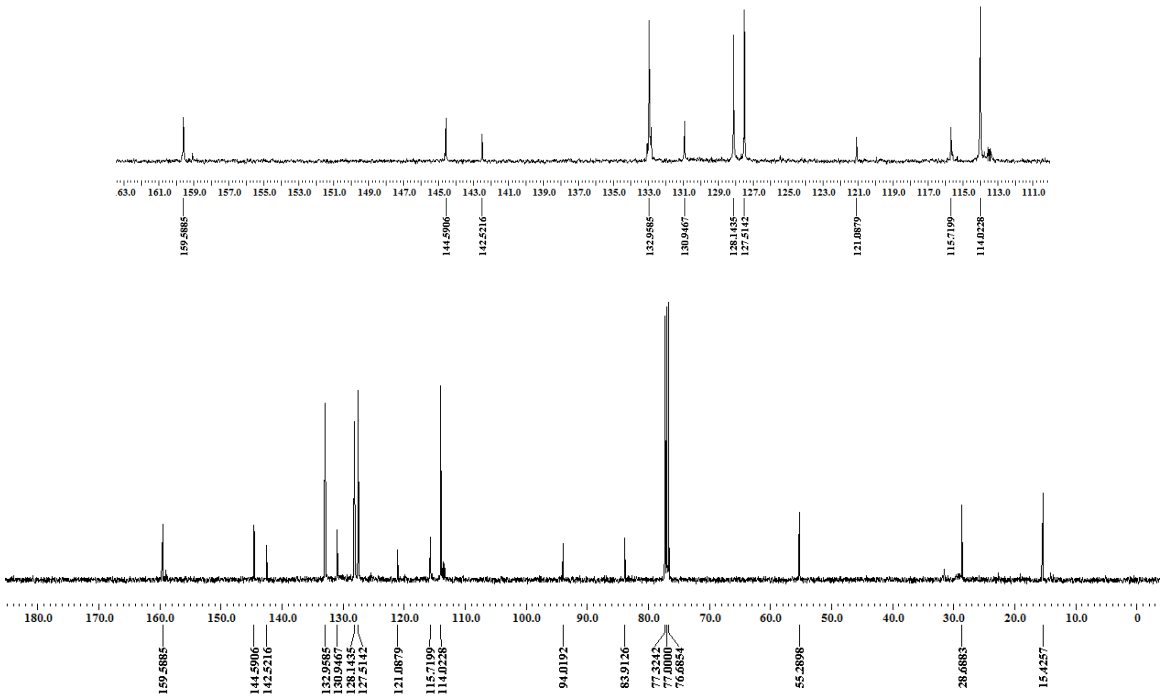
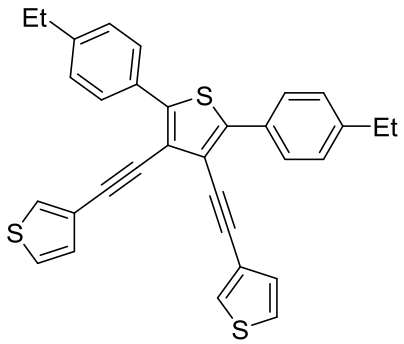
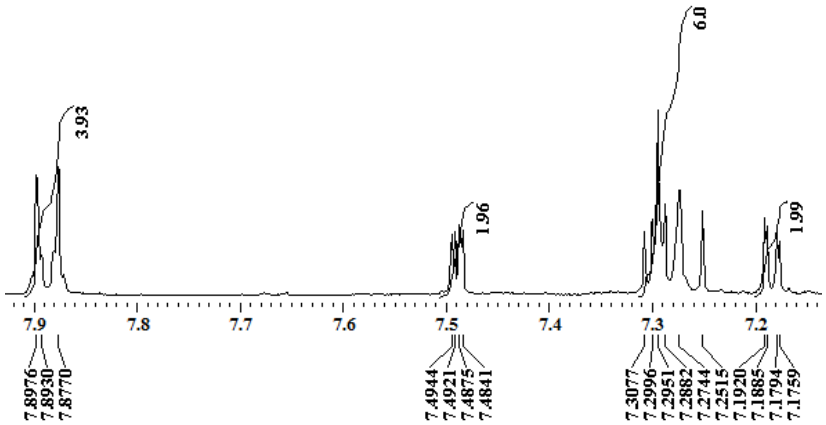
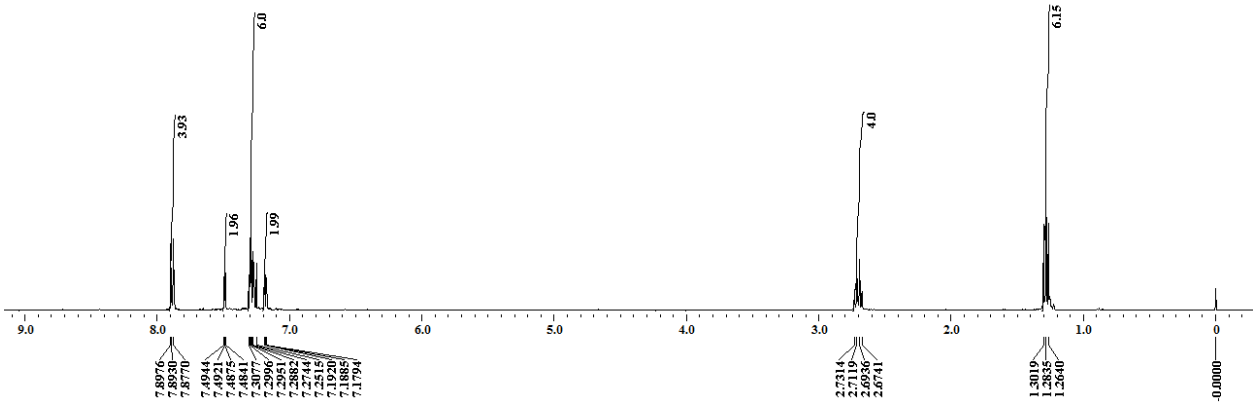


^{1}H NMR

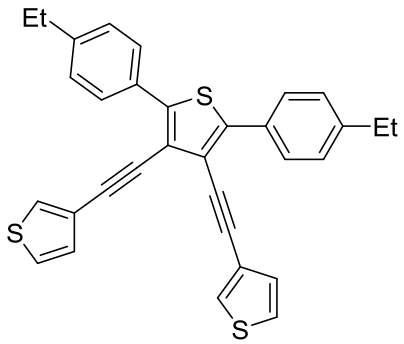


3,3'-((2,5-Bis(4-ethylphenyl)thiophene-3,4-diyl)bis(ethyne-2,1-diyl))dithiophene (4l)

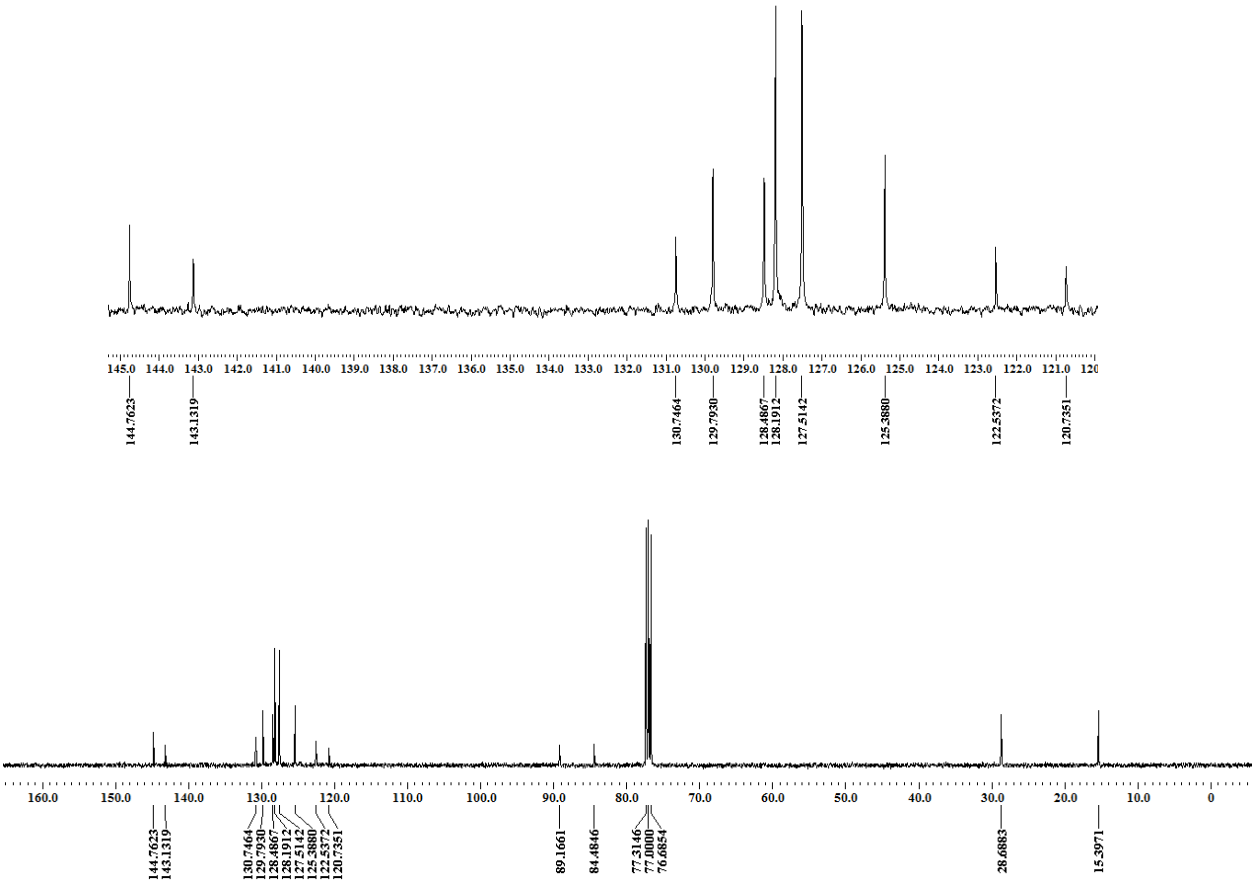




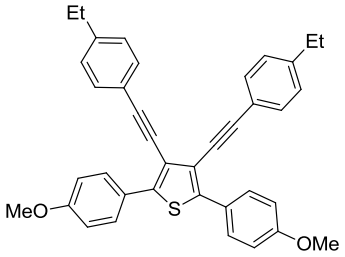
^{13}C NMR



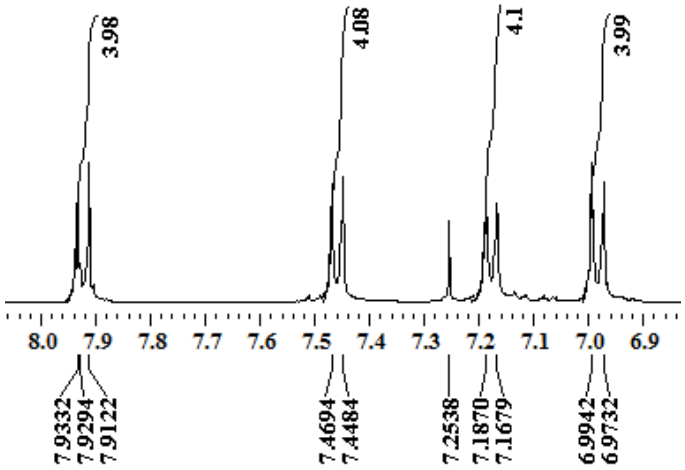
3,3'-((2,5-Bis(4-ethylphenyl)thiophene-3,4-diyl)bis(ethyne-2,1-diyl))dithiophene (4l)

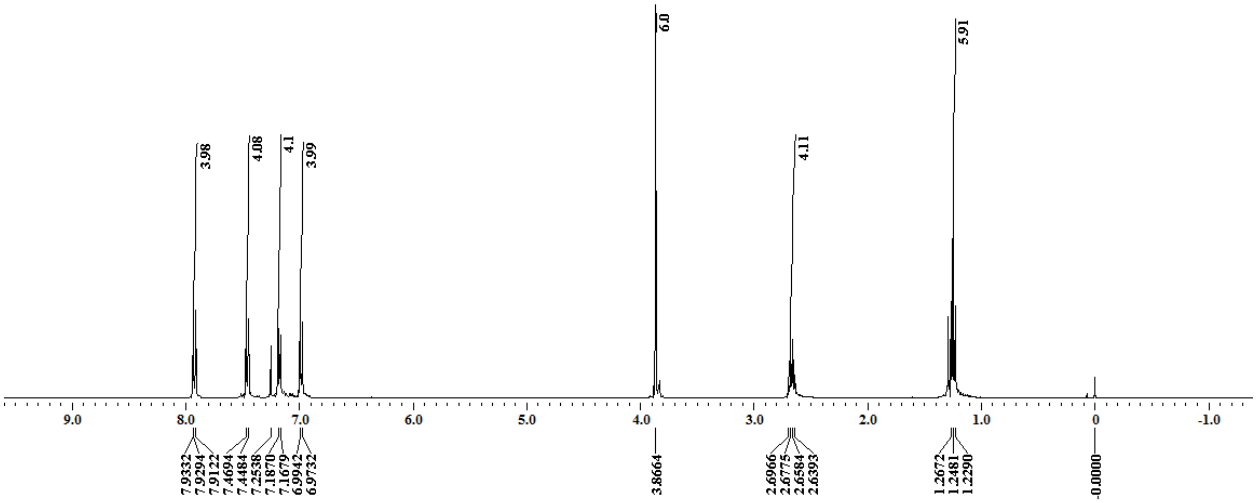


^{1}H NMR

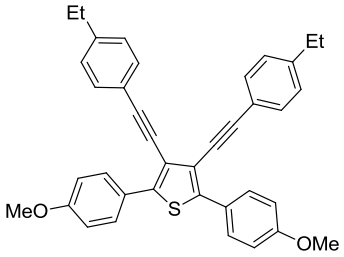


3,4-Bis((4-ethylphenyl)ethynyl)-2,5-bis(4-methoxyphenyl)thiophene (4m)

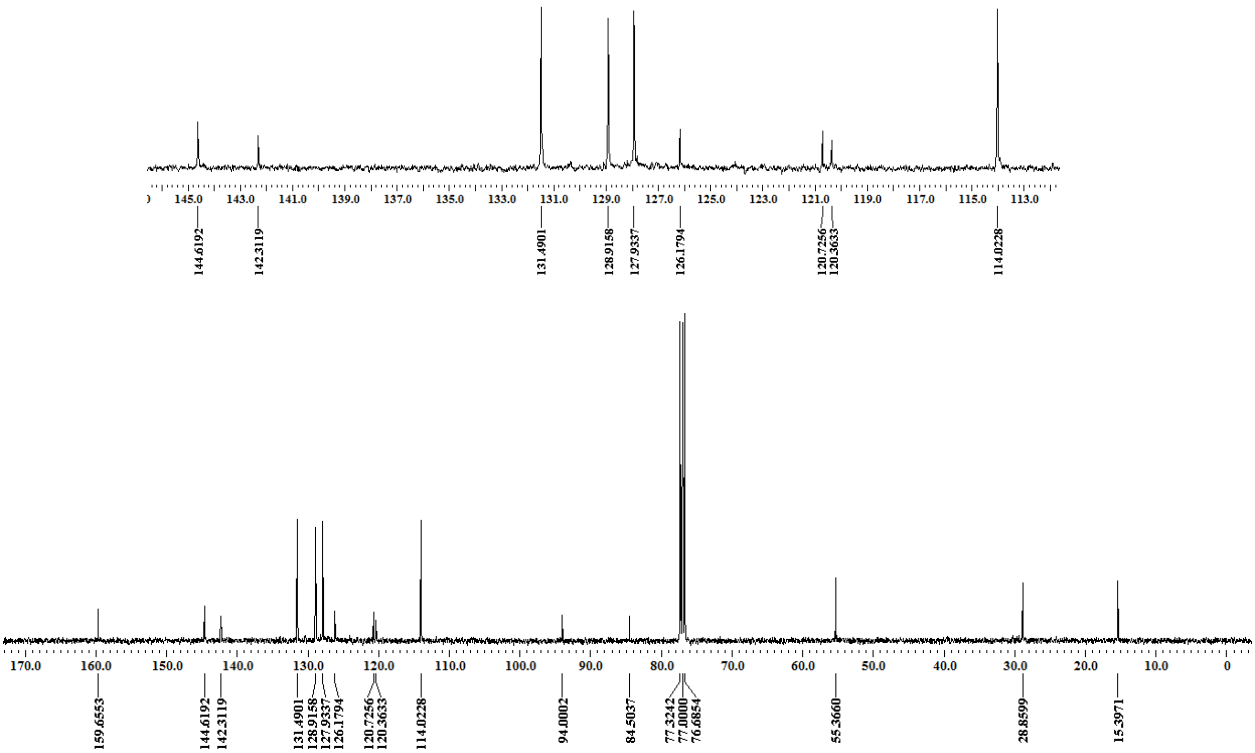




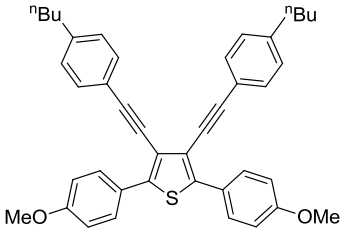
^{13}C NMR



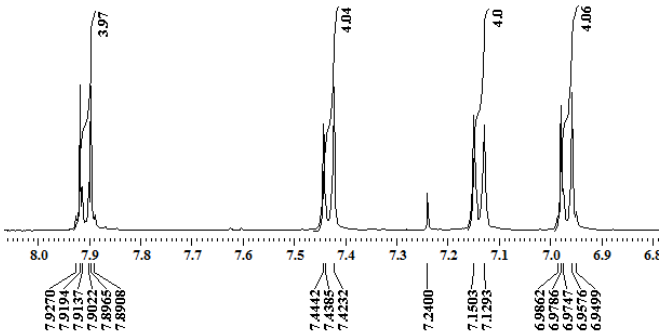
3,4-Bis((4-ethylphenyl)ethynyl)-2,5-bis(4-methoxyphenyl)thiophene (4m)

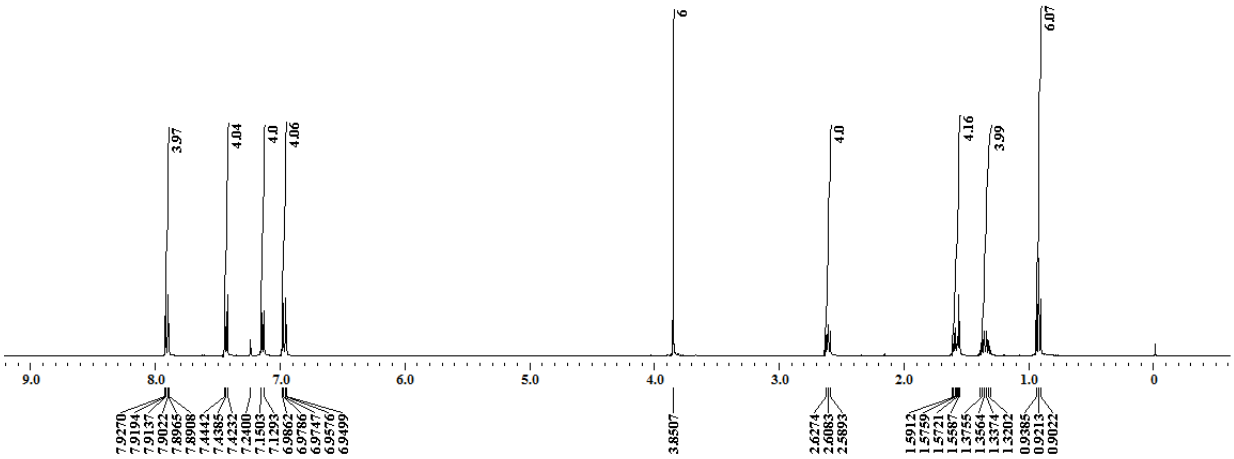


^{1}H NMR

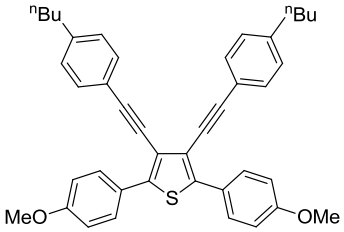


3,4-Bis((4-butylphenyl)ethynyl)-2,5-bis(4-methoxyphenyl)thiophene (4n)

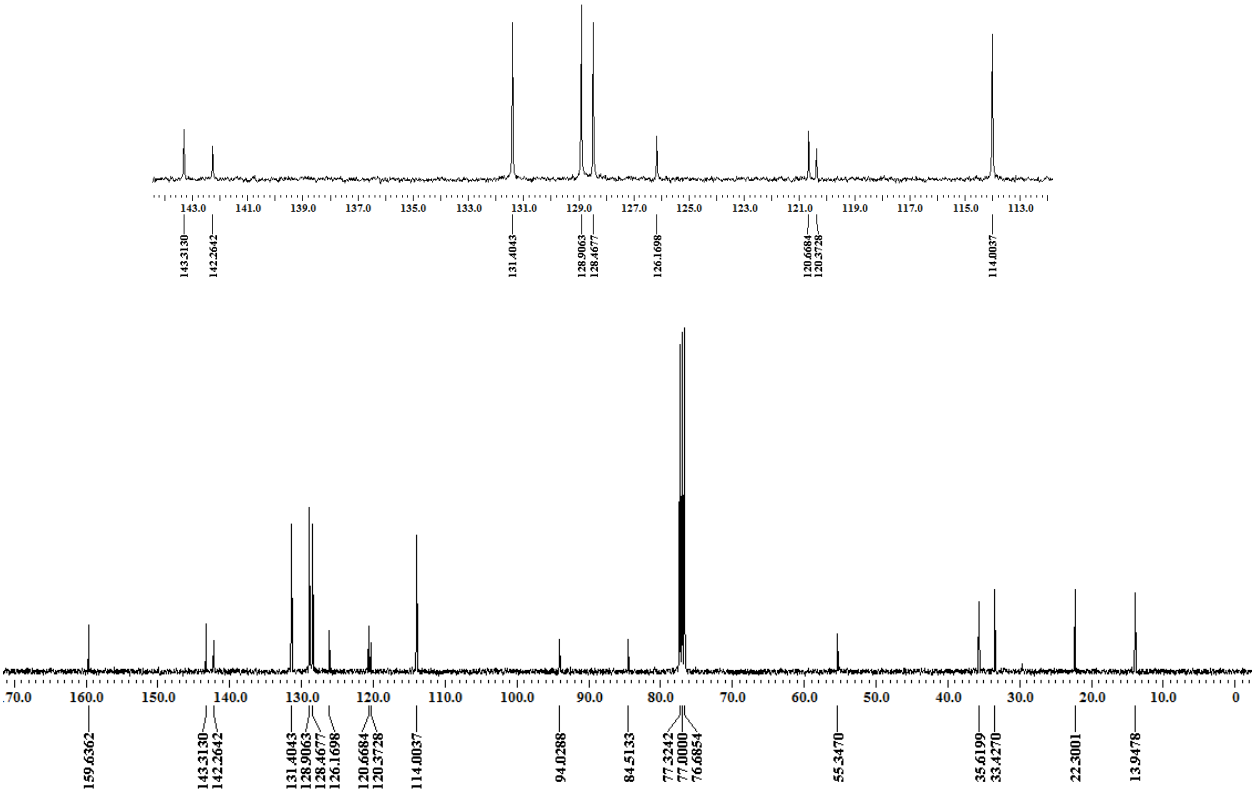




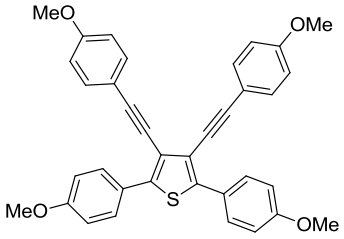
^{13}C NMR



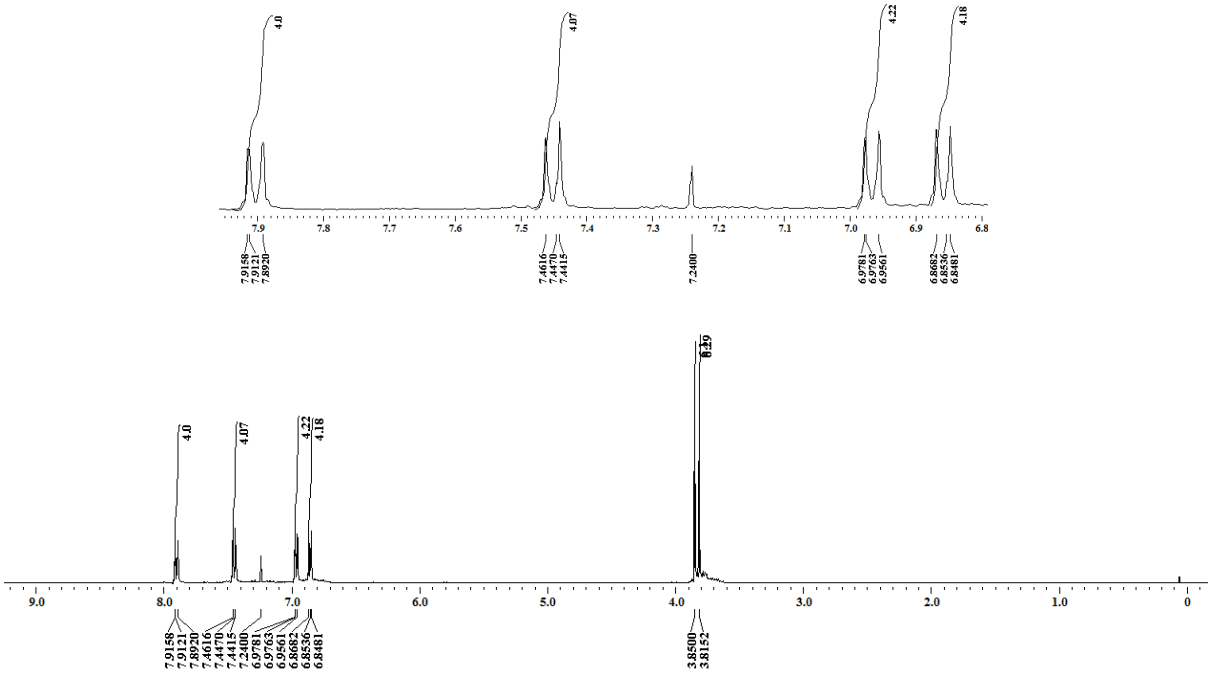
3,4-Bis((4-butylphenyl)ethynyl)-2,5-bis(4-methoxyphenyl)thiophene (4n)



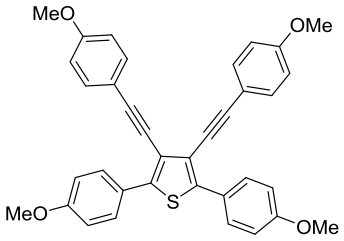
^{1}H NMR



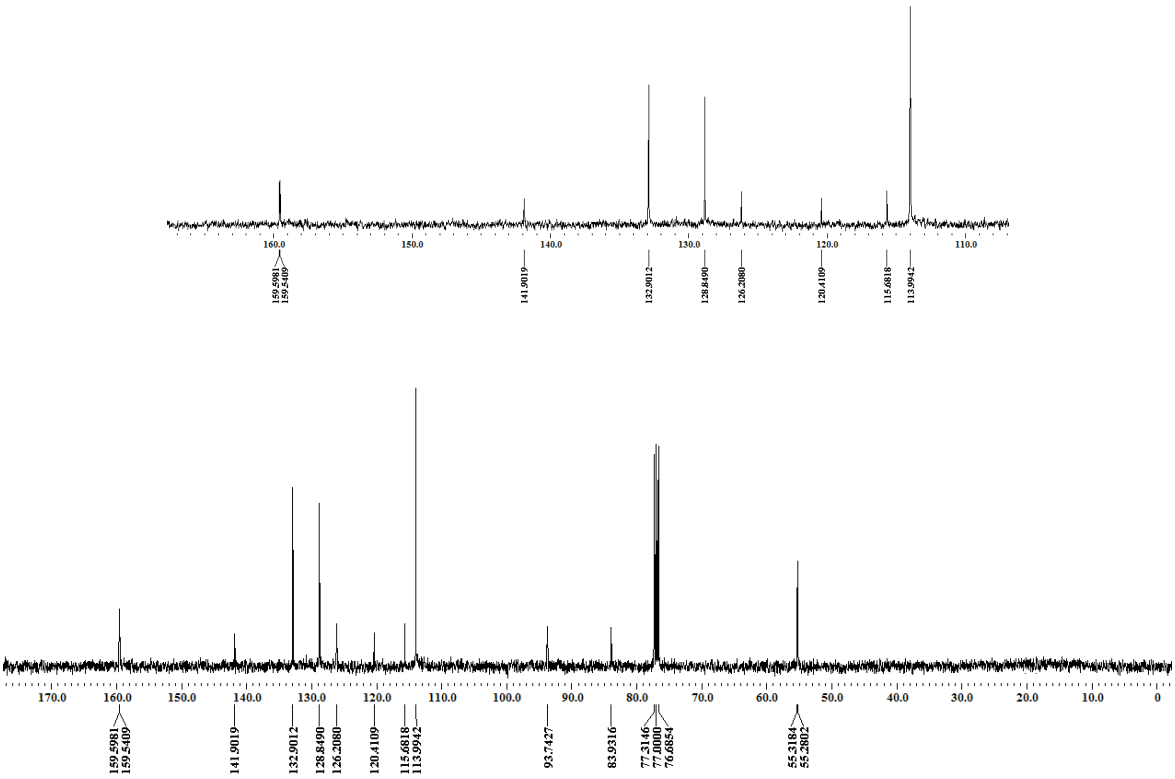
2,5-Bis(4-methoxyphenyl)-3,4-bis((4-methoxyphenyl)ethynyl)thiophene (4o)



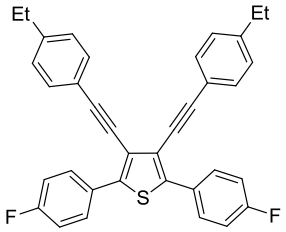
^{13}C NMR



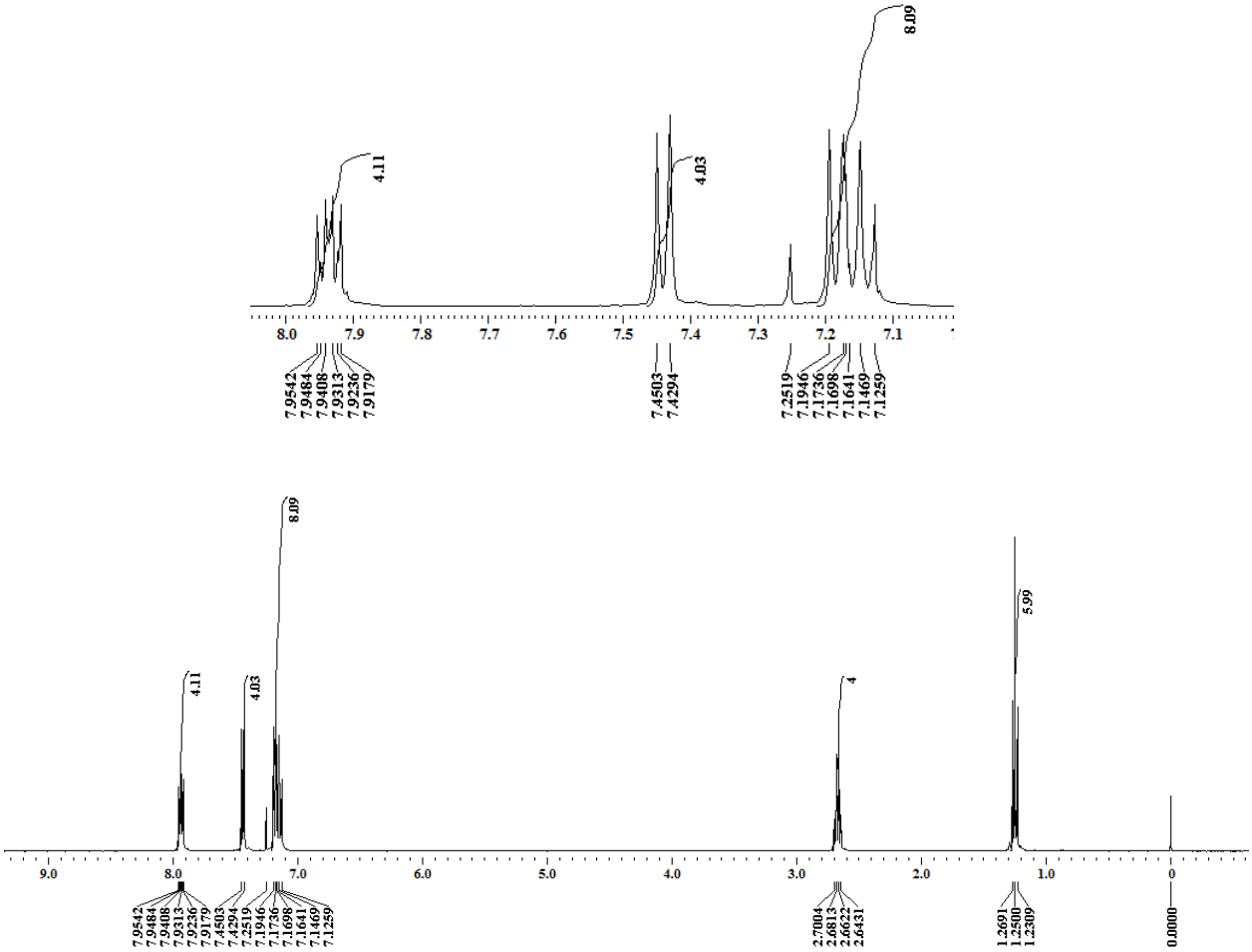
2,5-Bis(4-methoxyphenyl)-3,4-bis((4-methoxyphenyl)ethynyl)thiophene (4o)



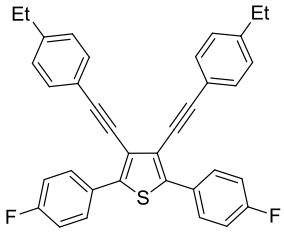
^{1}H NMR



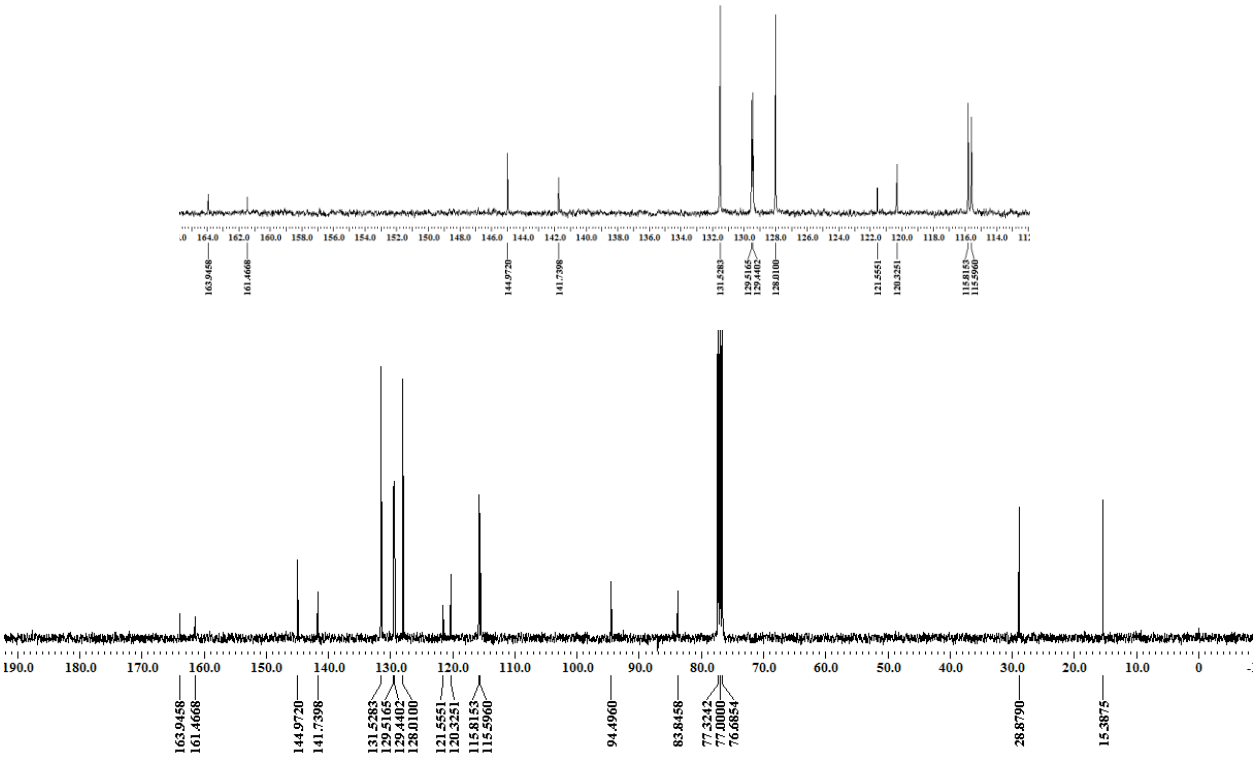
3,4-Bis((4-ethylphenyl)ethynyl)-2,5-bis(4-fluorophenyl)thiophene (4p)



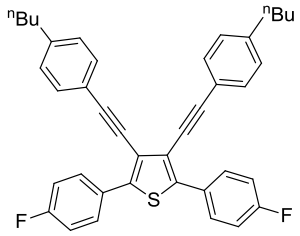
^{13}C NMR



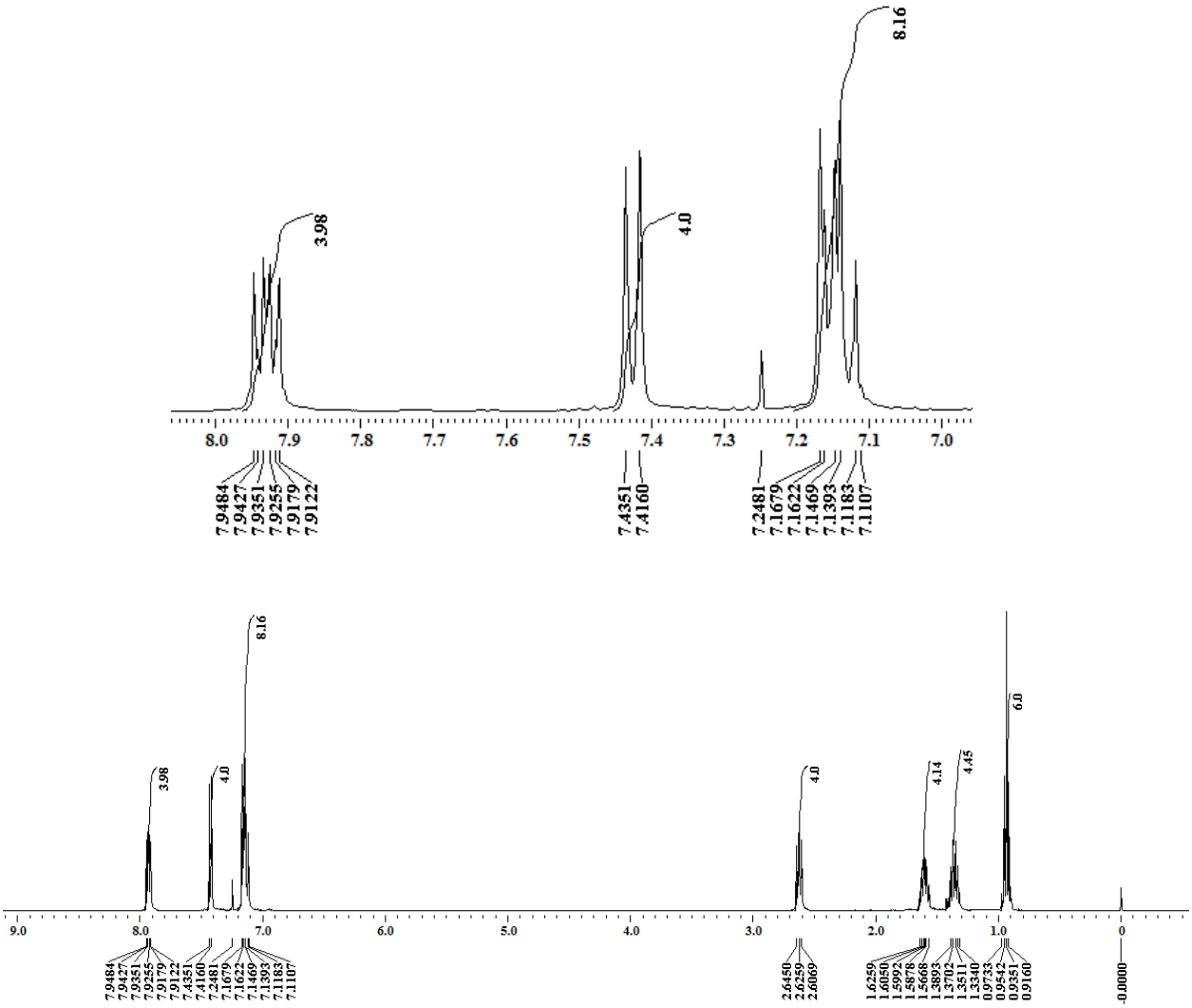
3,4-Bis((4-ethylphenyl)ethynyl)-2,5-bis(4-fluorophenyl)thiophene (4p)



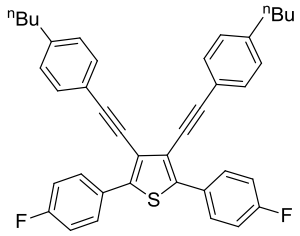
^{1}H NMR



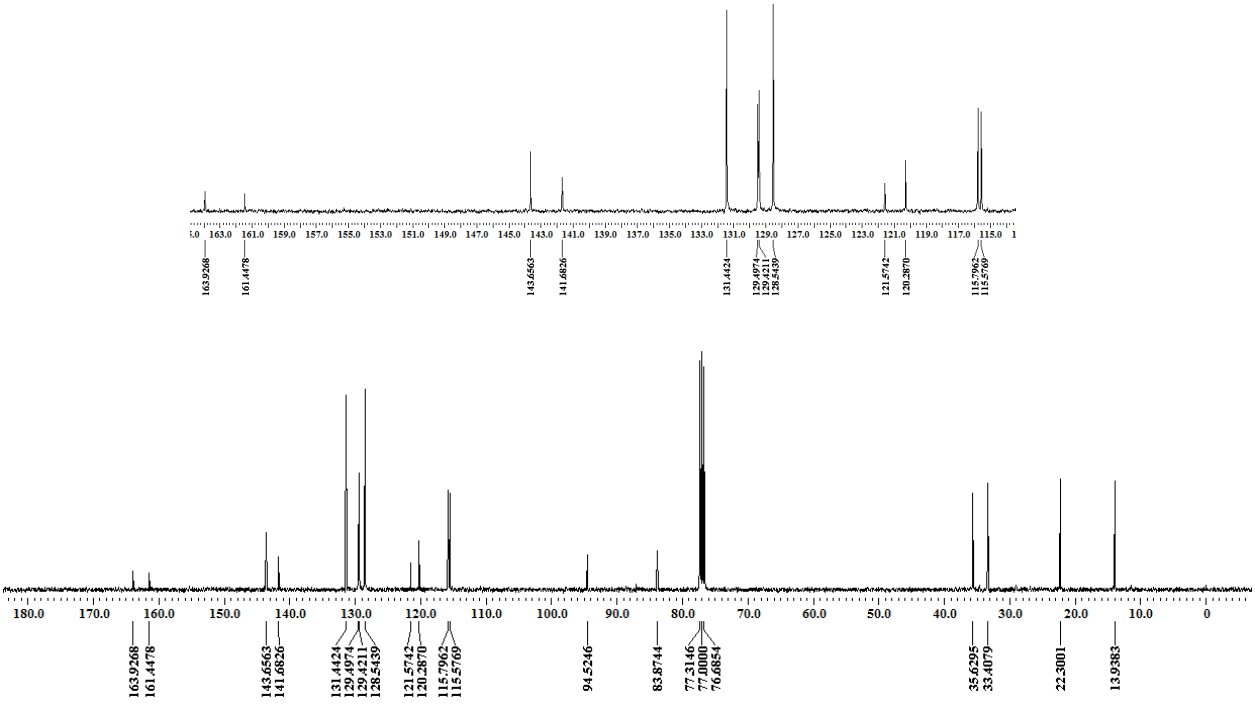
3,4-Bis((4-butylphenyl)ethynyl)-2,5-bis(4-fluorophenyl)thiophene (4q)



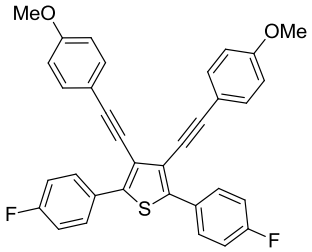
^{13}C NMR



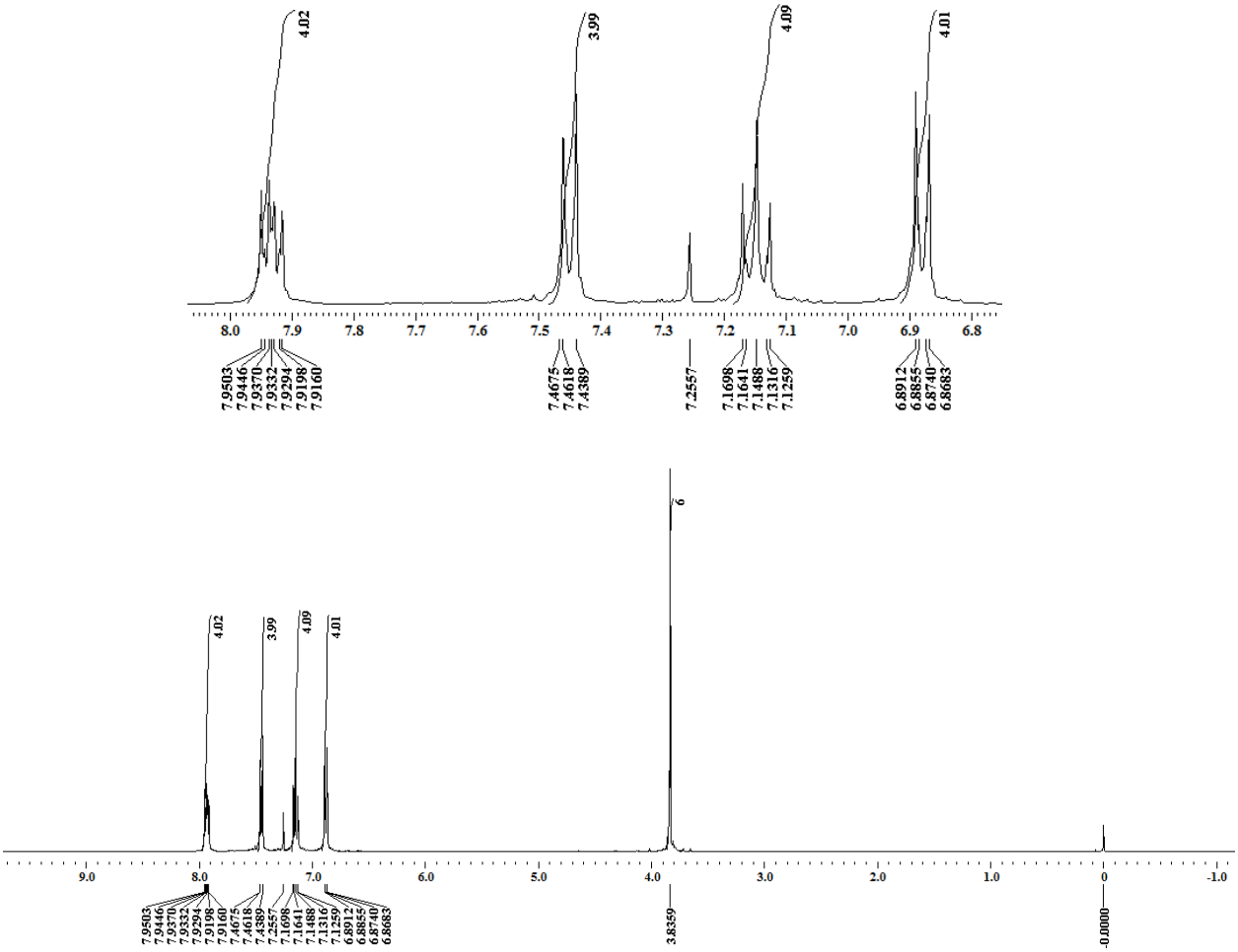
3,4-Bis((4-butylphenyl)ethynyl)-2,5-bis(4-fluorophenyl)thiophene (4q)



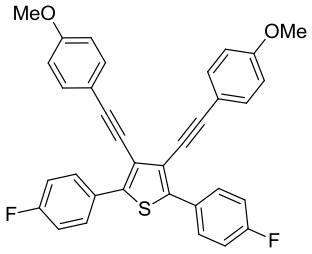
^{1}H NMR



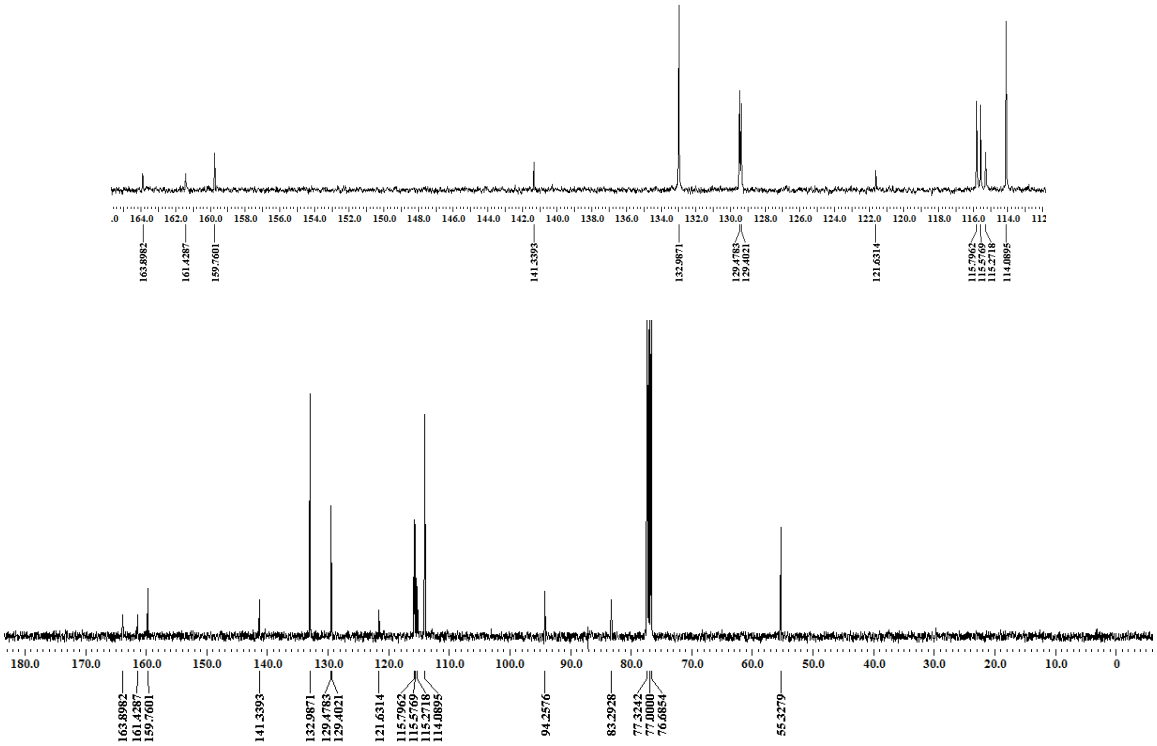
2,5-Bis(4-fluorophenyl)-3,4-bis((4-methoxyphenyl)ethynyl)thiophene (4r)



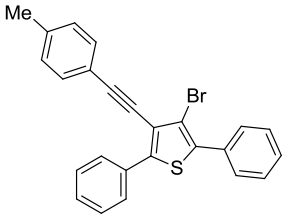
^{13}C NMR



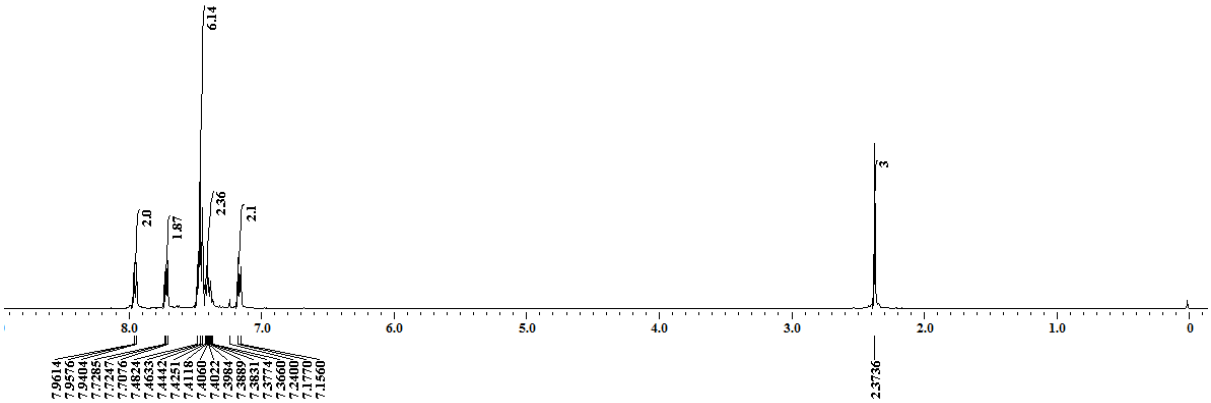
2,5-Bis(4-fluorophenyl)-3,4-bis((4-methoxyphenyl)ethynyl)thiophene (4r)



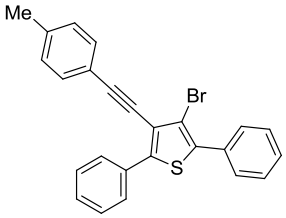
^{1}H NMR



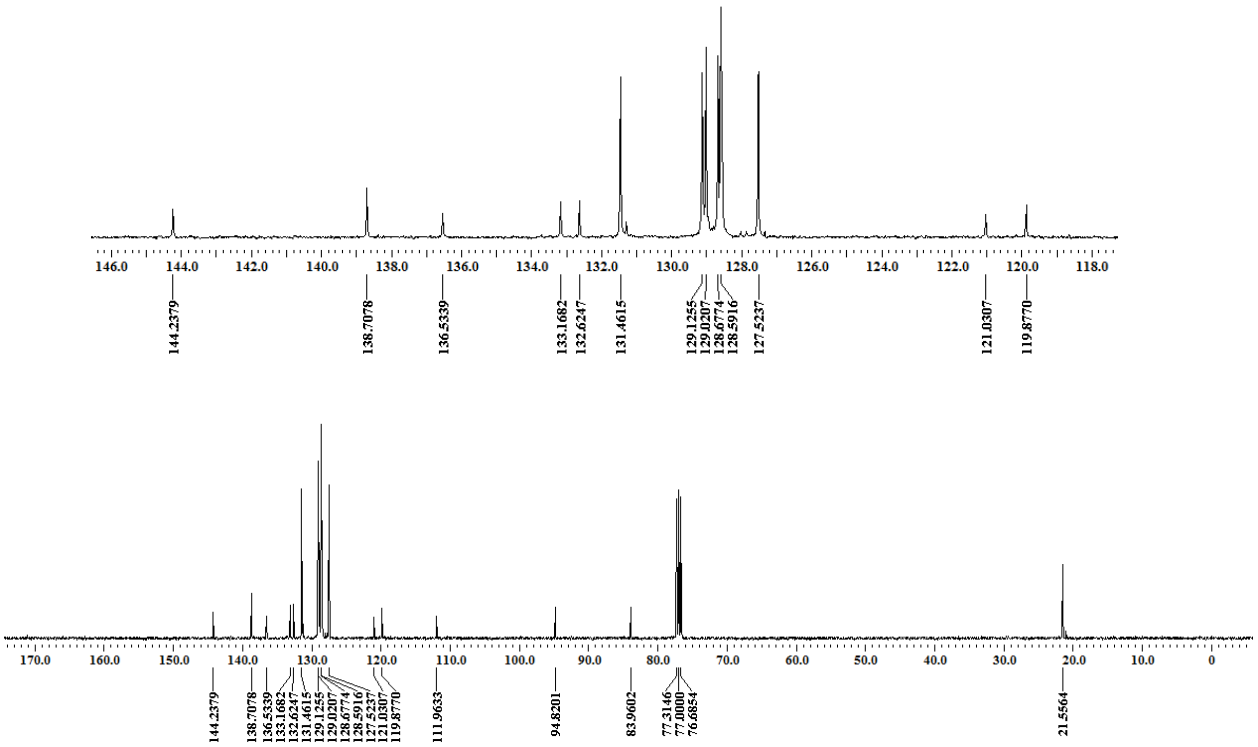
3-Bromo-2,5-diphenyl-4-(*p*-tolylethynyl)thiophene (5a)



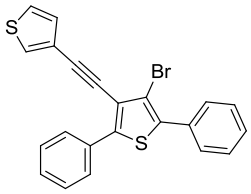
^{13}C NMR



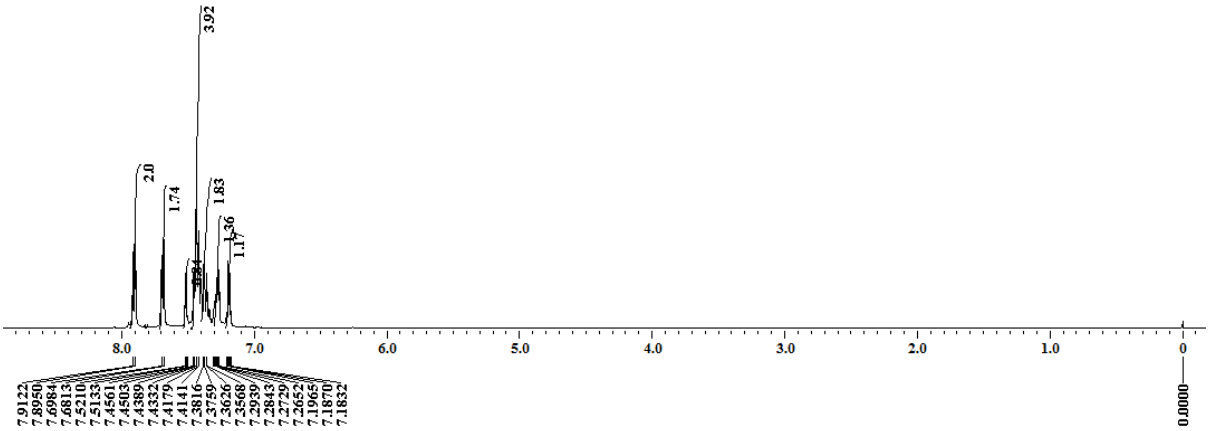
3-Bromo-2,5-diphenyl-4-(*p*-tolylethynyl)thiophene (5a)



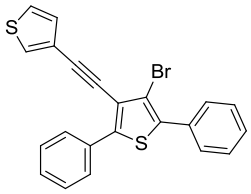
^{1}H NMR



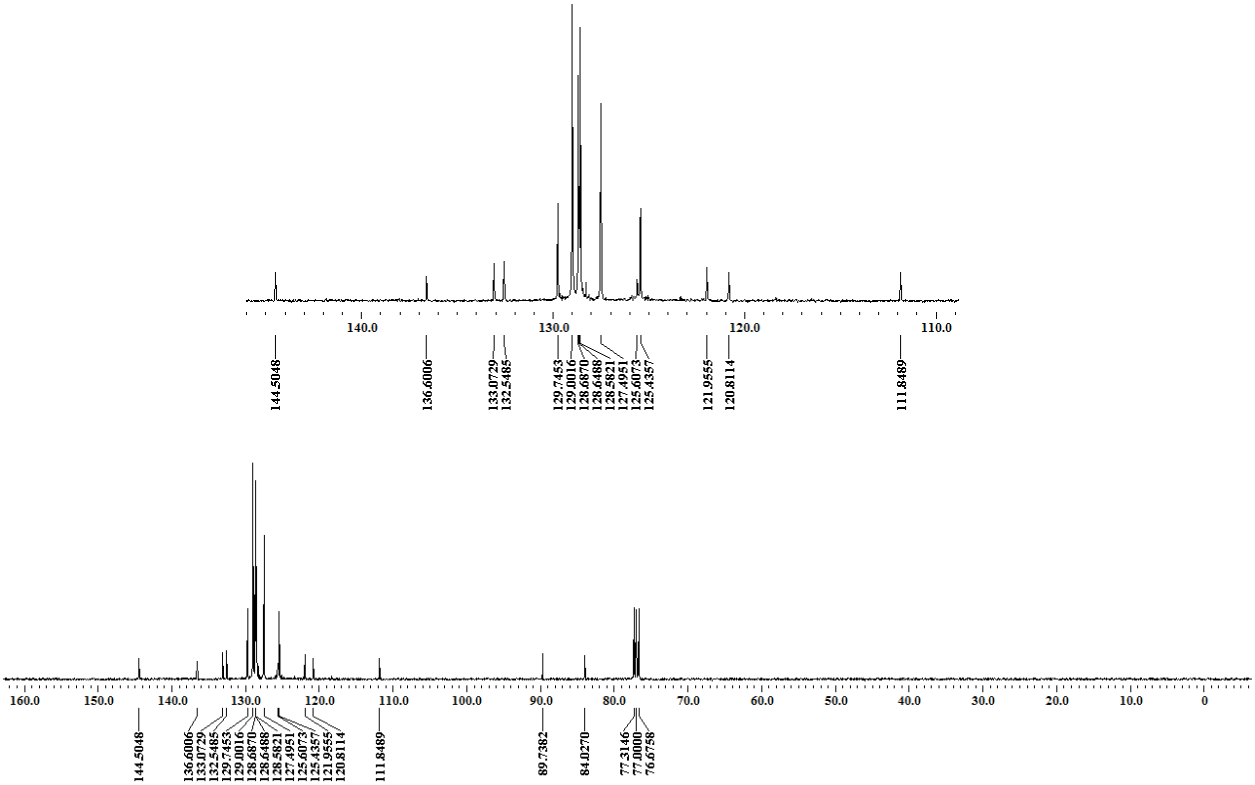
3-Bromo-2,5-diphenyl-4-(thiophen-3-ylethynyl)thiophene (5b)



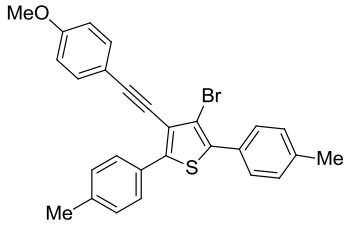
^{13}C NMR



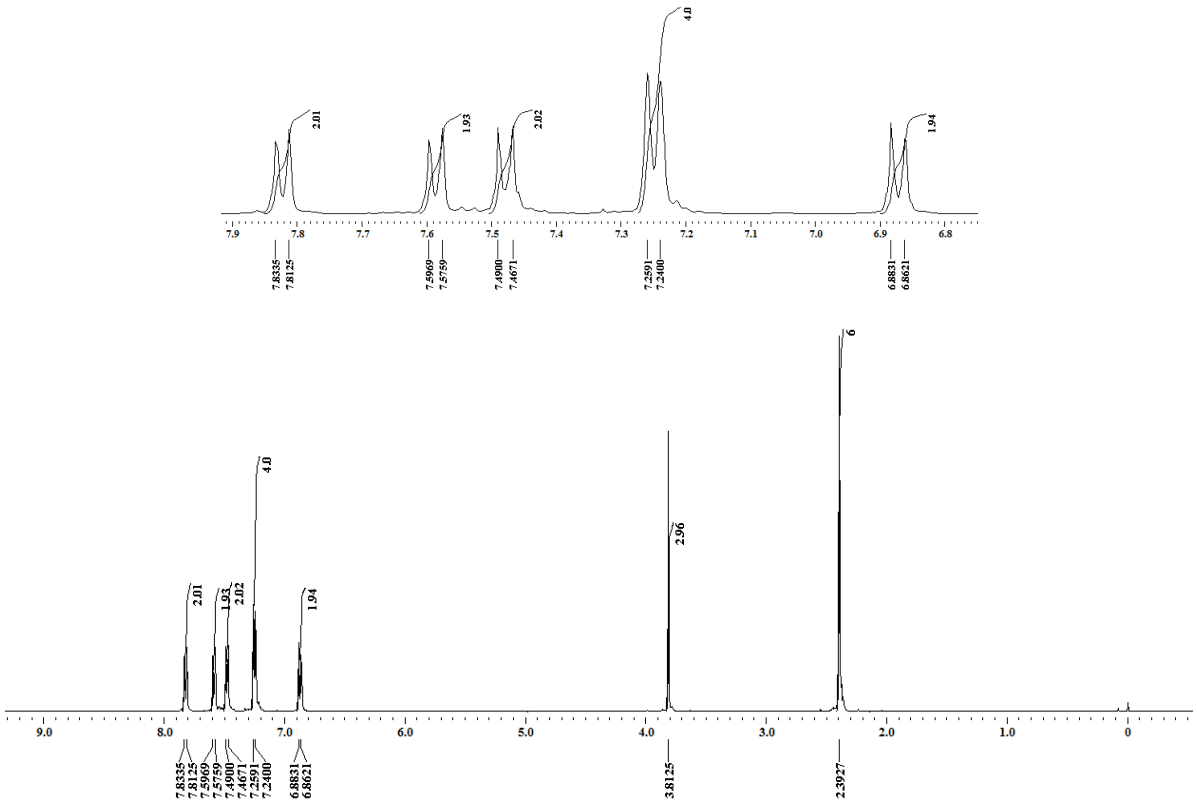
3-Bromo-2,5-diphenyl-4-(thiophen-3-ylethynyl)thiophene (5b)



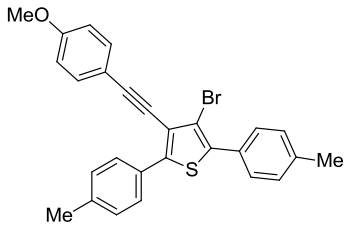
^{1}H NMR



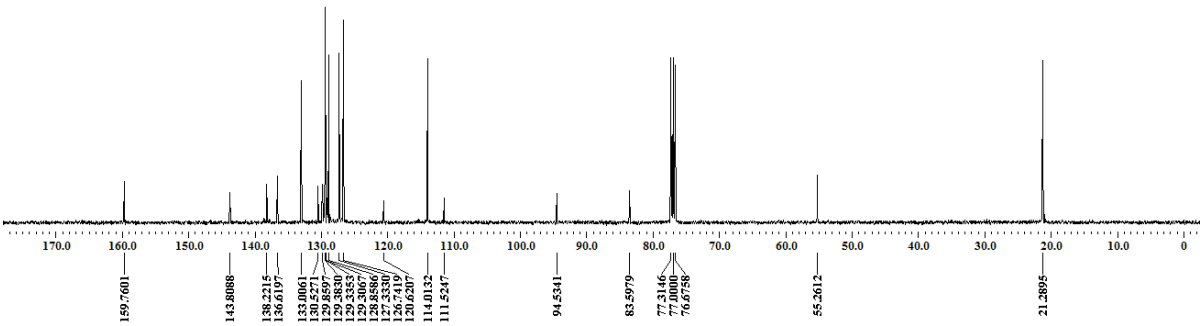
3-Bromo-4-((4-methoxyphenyl)ethynyl)-2,5-di-*p*-tolylthiophene (5c)



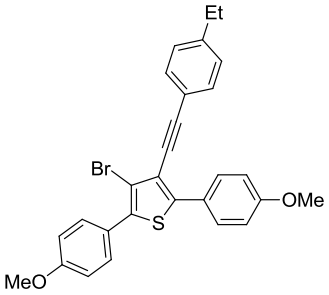
^{13}C NMR



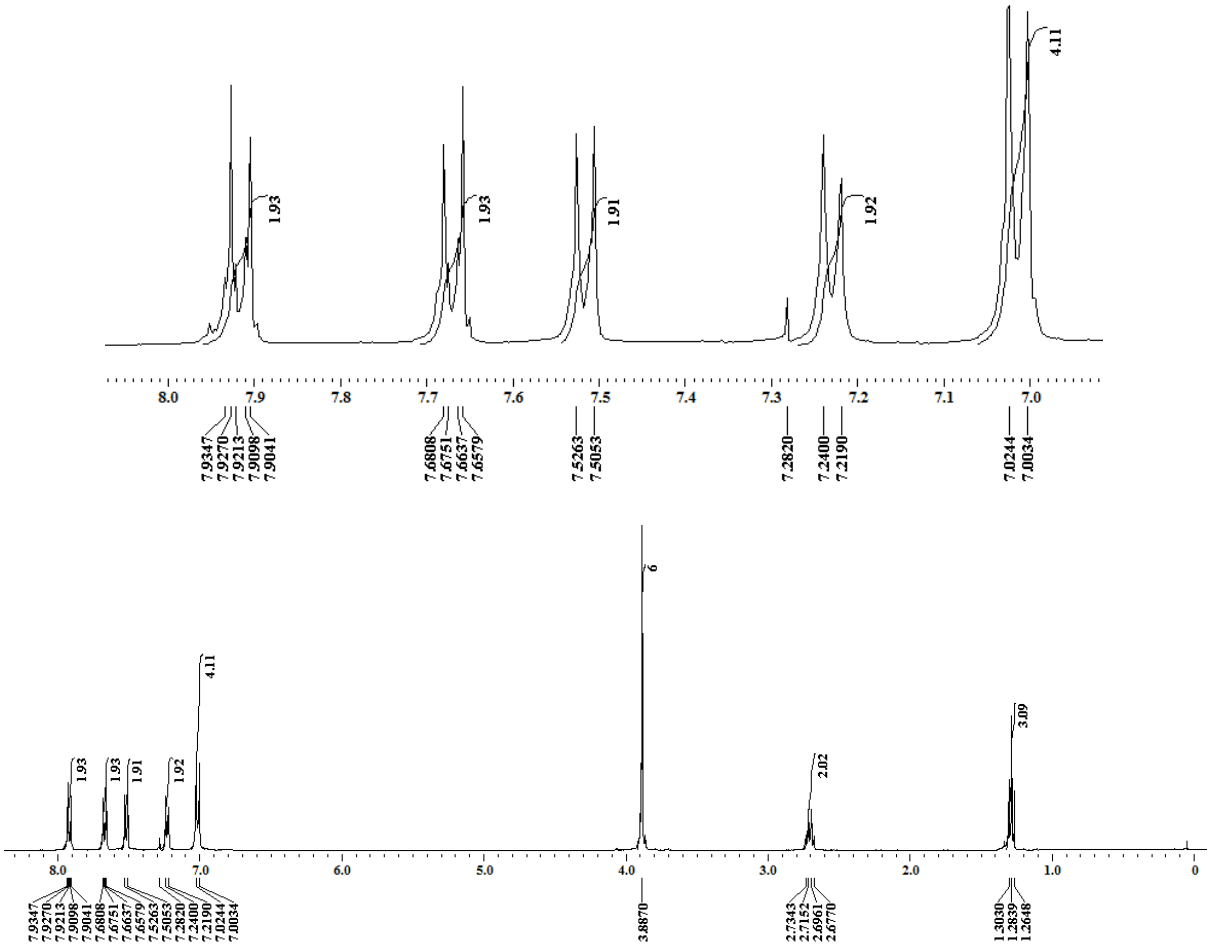
3-Bromo-4-((4-methoxyphenyl)ethynyl)-2,5-di-*p*-tolylthiophene (5c)



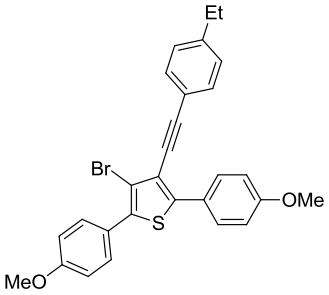
^{1}H NMR



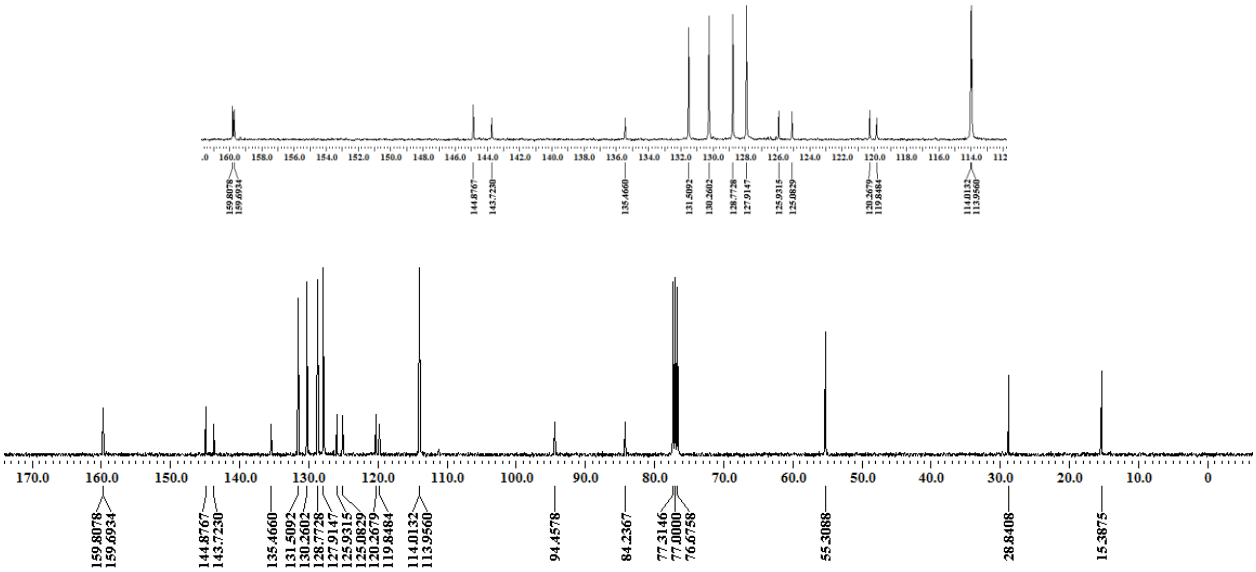
3-Bromo-4-((4-ethylphenyl)ethynyl)-2,5-bis(4-methoxyphenyl)thiophene (5d)



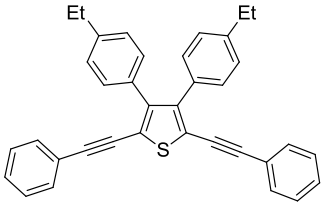
^{13}C NMR



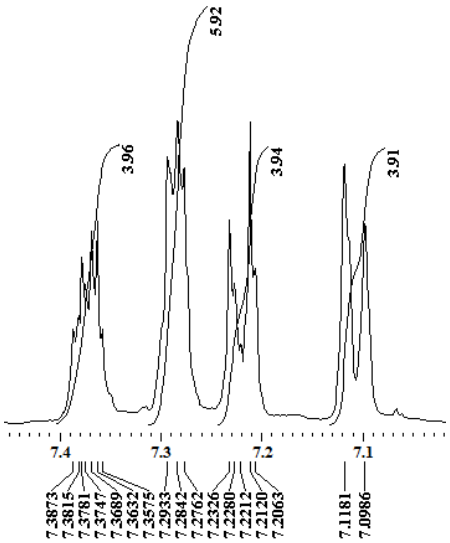
3-Bromo-4-((4-ethylphenyl)ethynyl)-2,5-bis(4-methoxyphenyl)thiophene (5d)

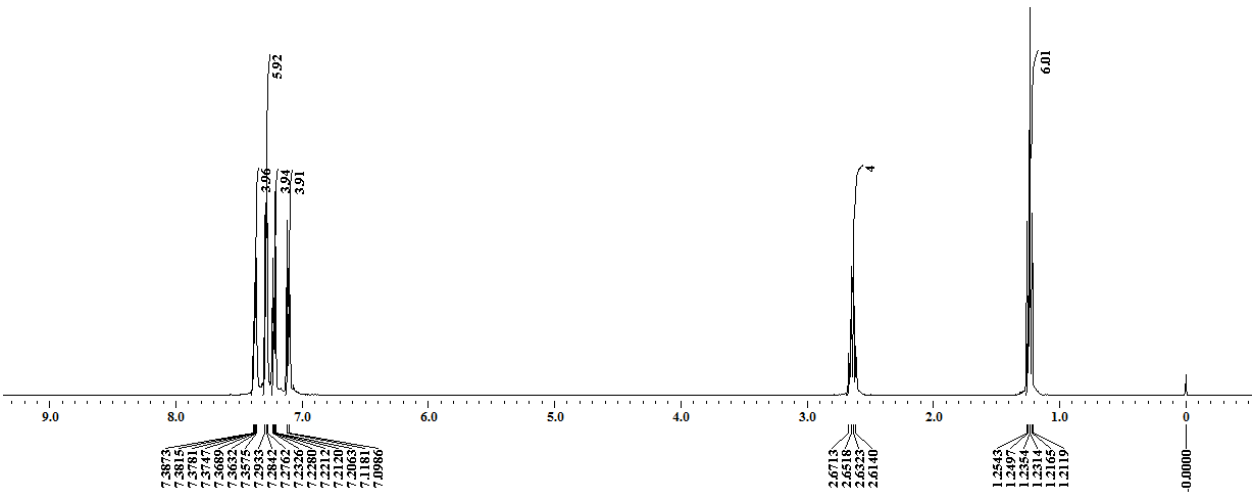


^{1}H NMR

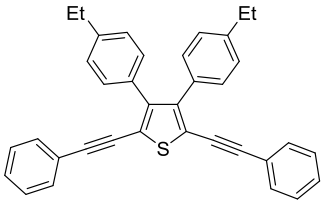


3,4-Bis(4-ethylphenyl)-2,5-bis(phenylethynyl)thiophene (6a)

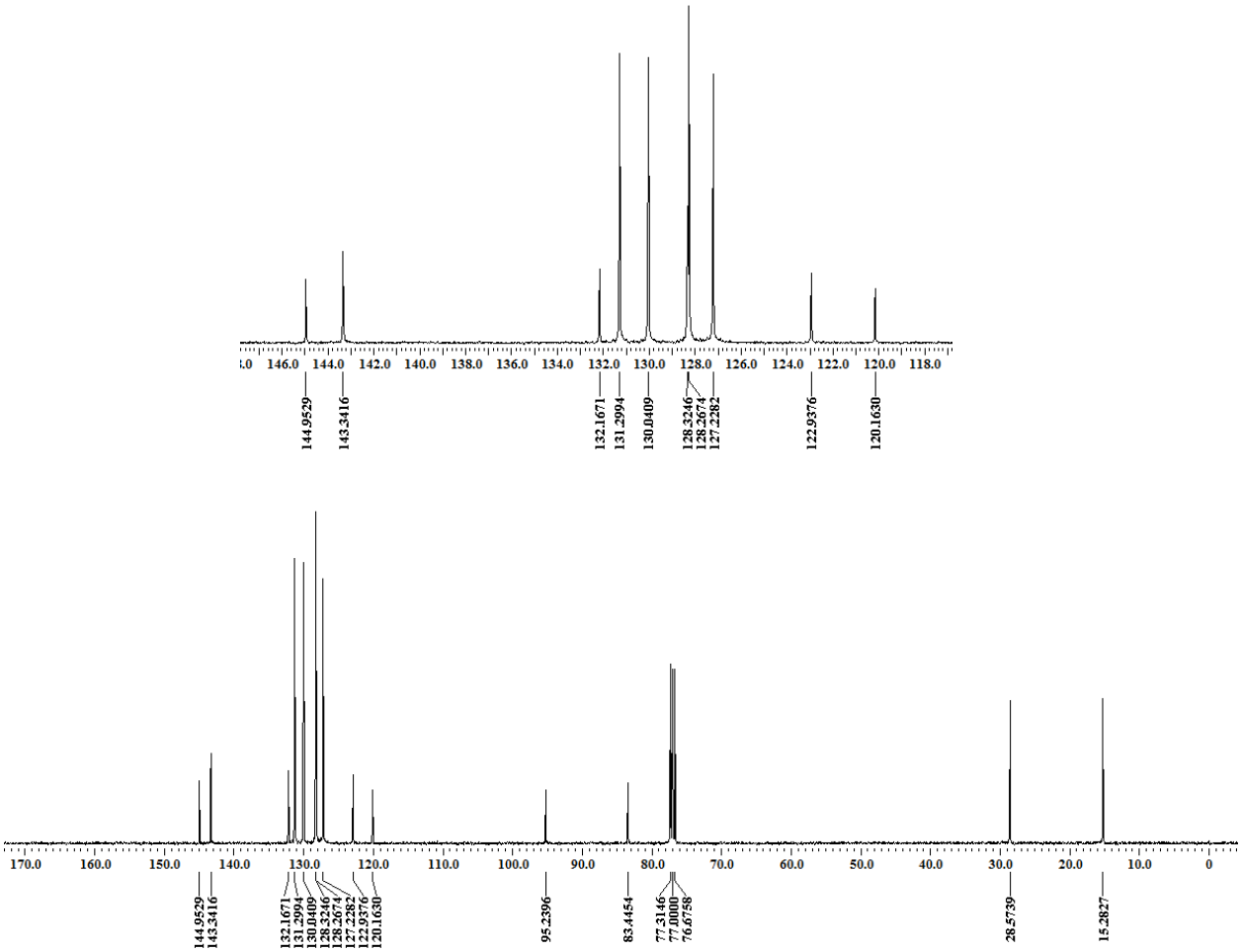




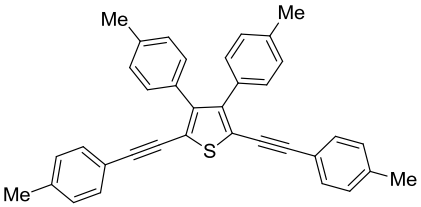
^{13}C NMR



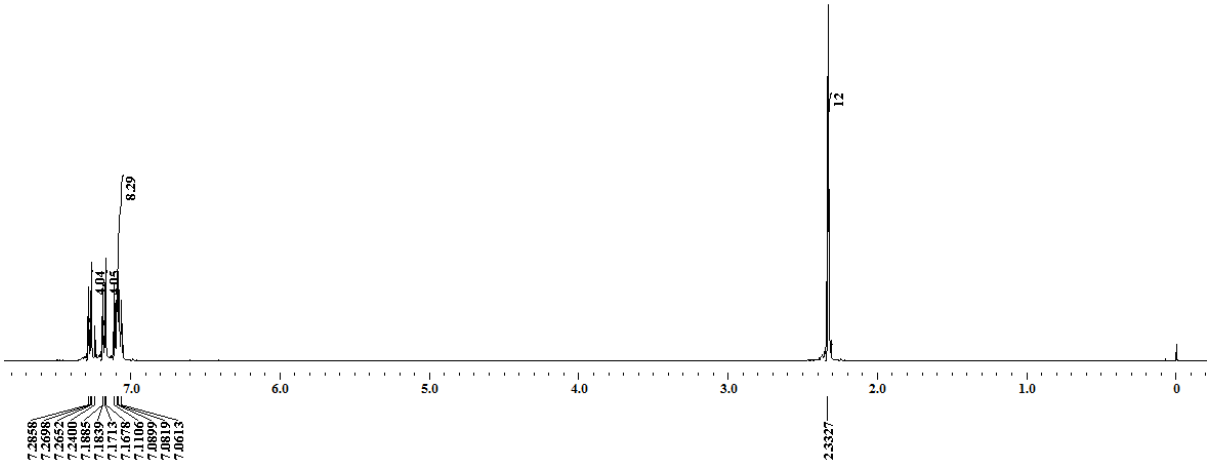
3,4-Bis(4-ethylphenyl)-2,5-bis(phenylethynyl)thiophene (6a)



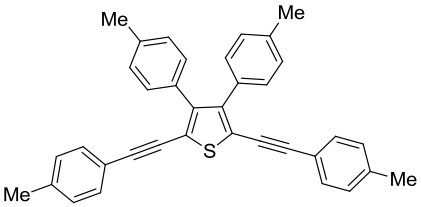
^{1}H NMR



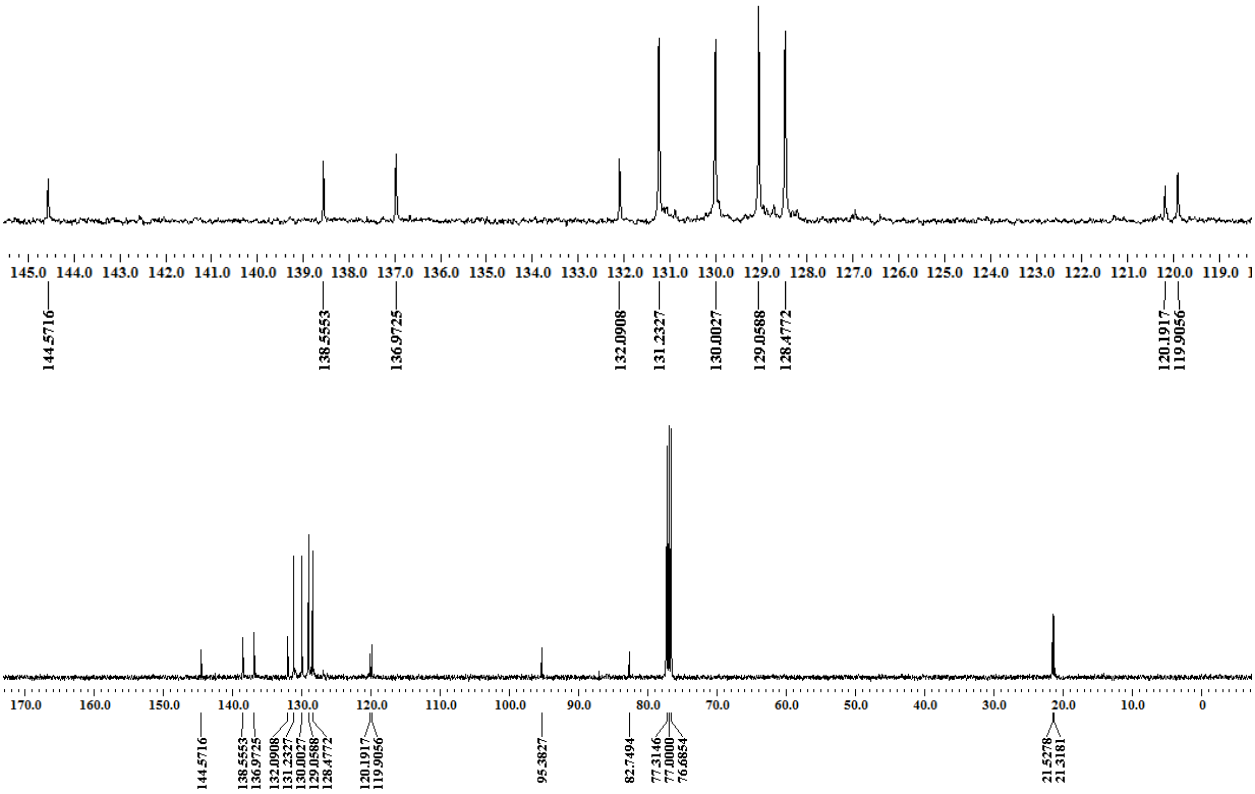
3,4-Di-*p*-tolyl-2,5-bis(*p*-tolylethynyl)thiophene (6b)



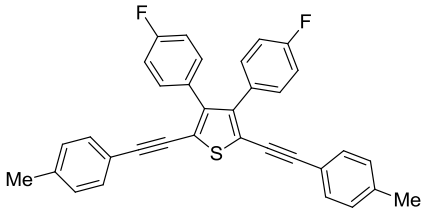
^{13}C NMR



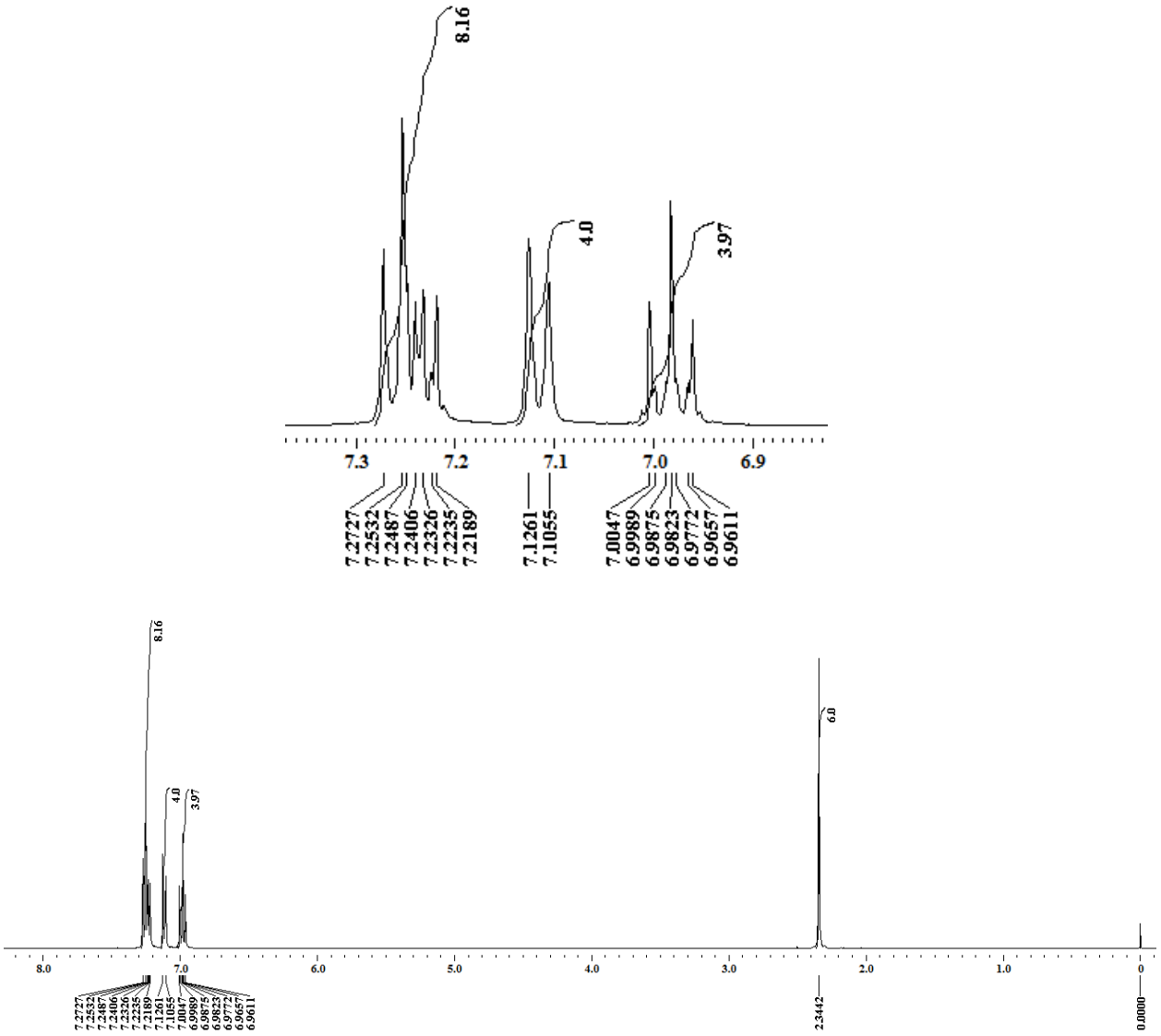
3,4-Di-*p*-tolyl-2,5-bis(*p*-tolylethynyl)thiophene (6b)



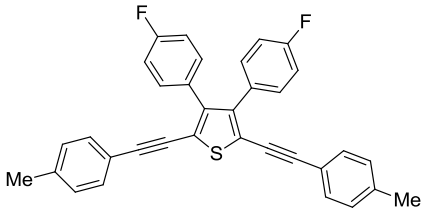
^{1}H NMR



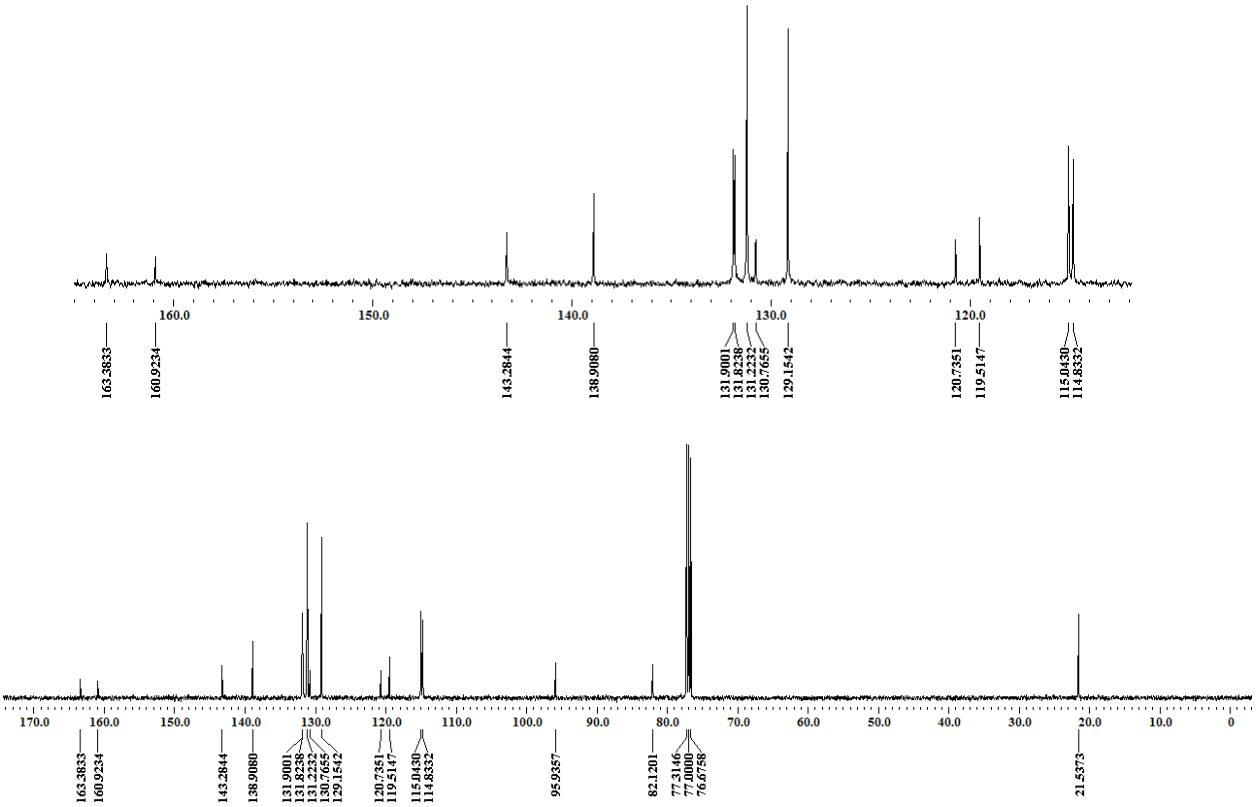
3,4-Bis(4-fluorophenyl)-2,5-bis(*p*-tolylethynyl)thiophene (6c)



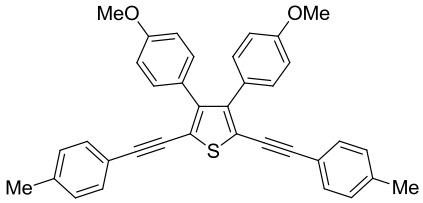
^{13}C NMR



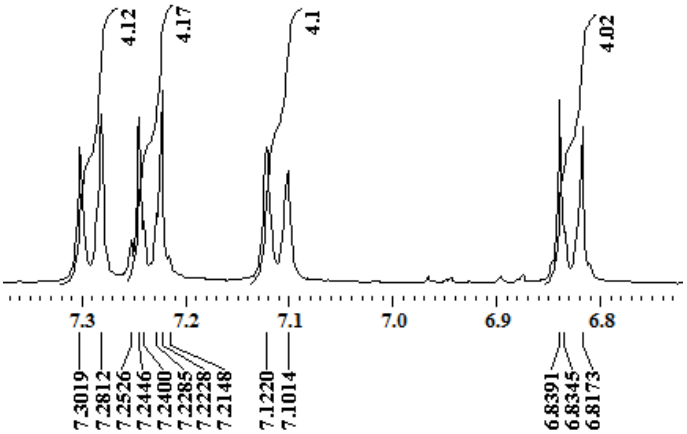
3,4-Bis(4-fluorophenyl)-2,5-bis(*p*-tolylethynyl)thiophene (6c)

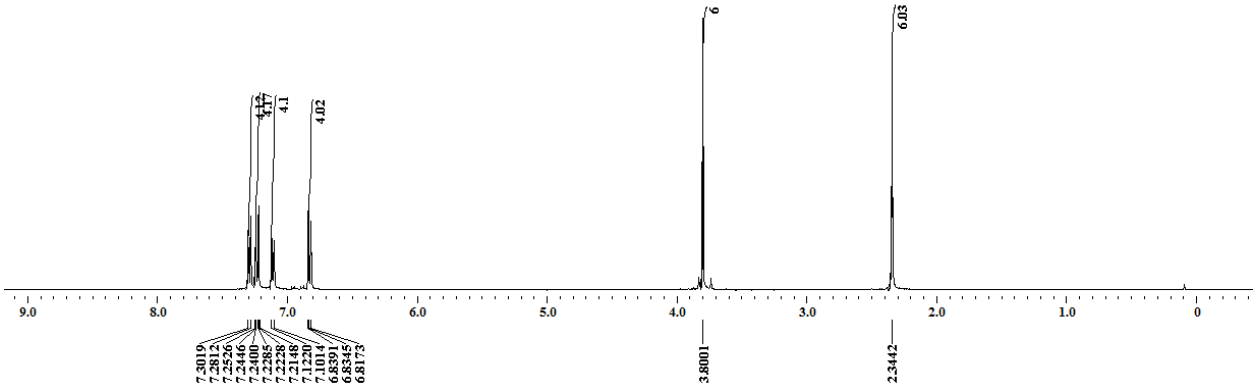


^{1}H NMR

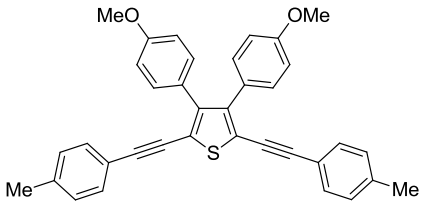


3,4-Bis(4-methoxyphenyl)-2,5-bis(*p*-tolylethynyl)thiophene (6d)

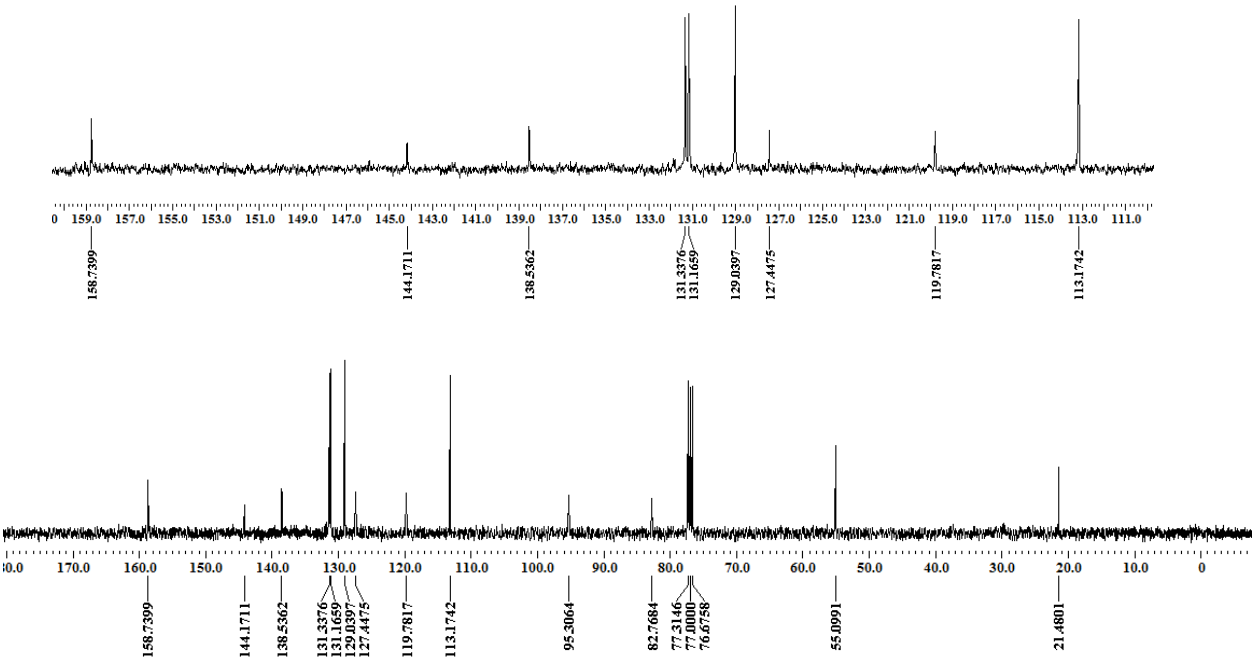




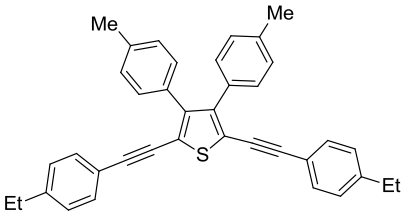
^{13}C NMR



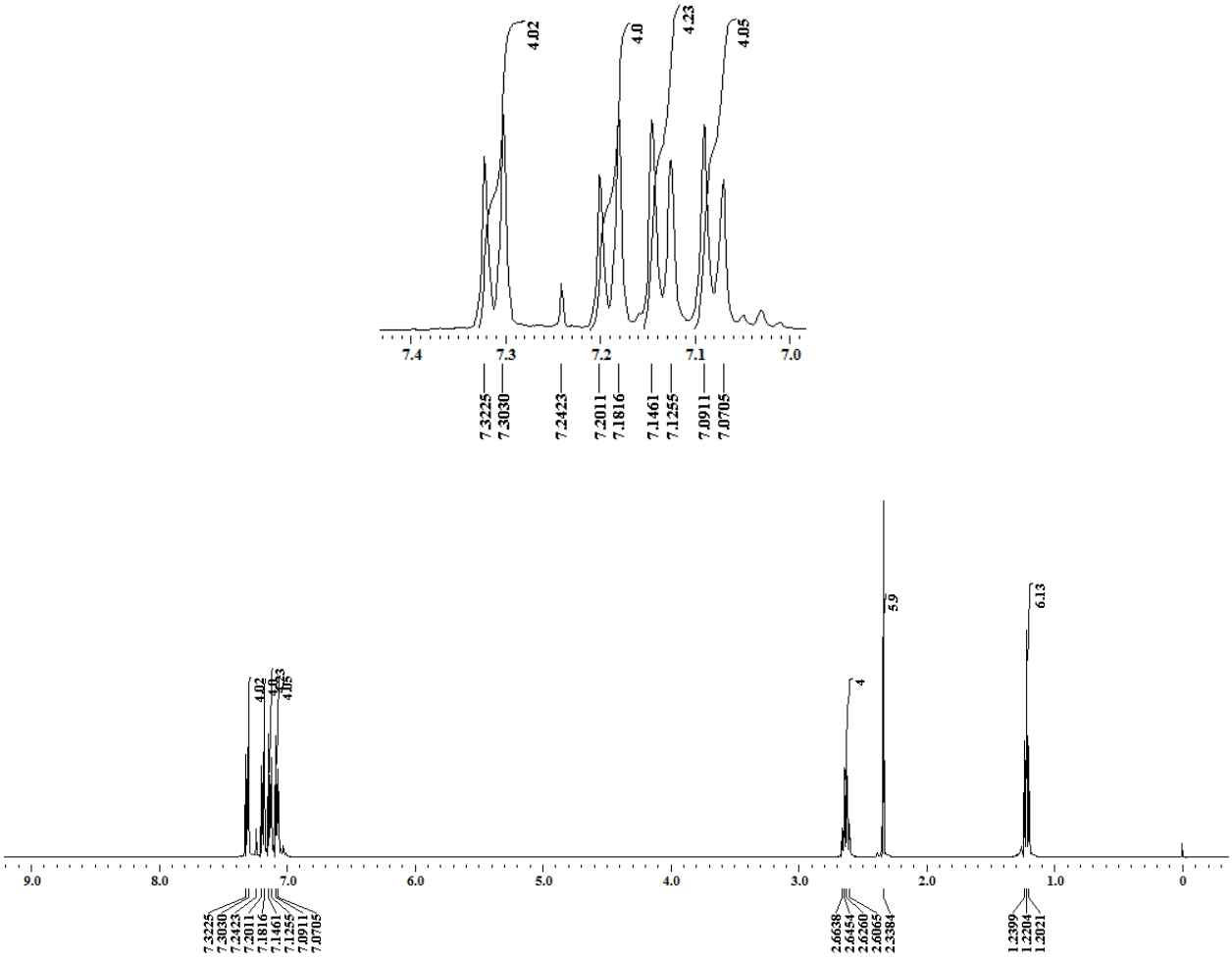
3,4-Bis(4-methoxyphenyl)-2,5-bis(*p*-tolylethynyl)thiophene (6d)



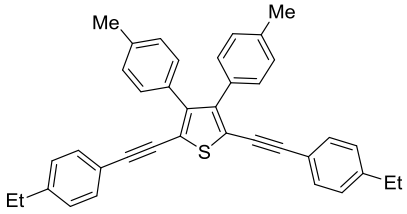
^{1}H NMR



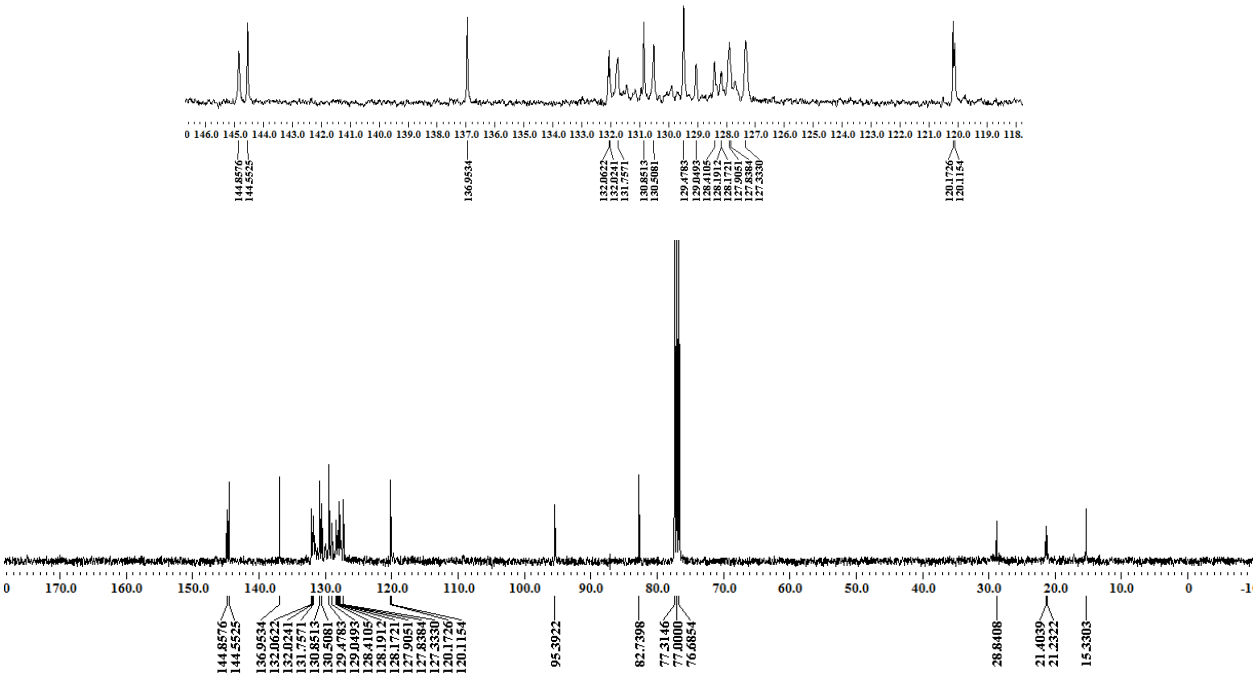
2,5-Bis((4-ethylphenyl)ethynyl)-3,4-di-*p*-tolylthiophene (6e)



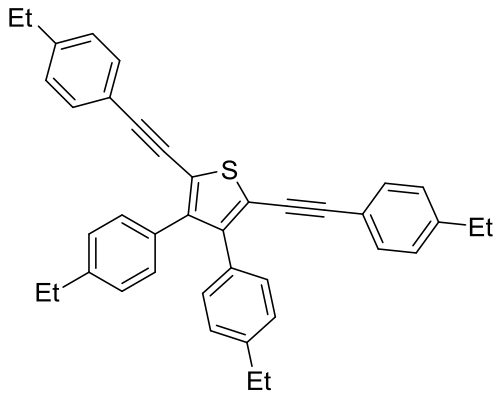
^{13}C NMR



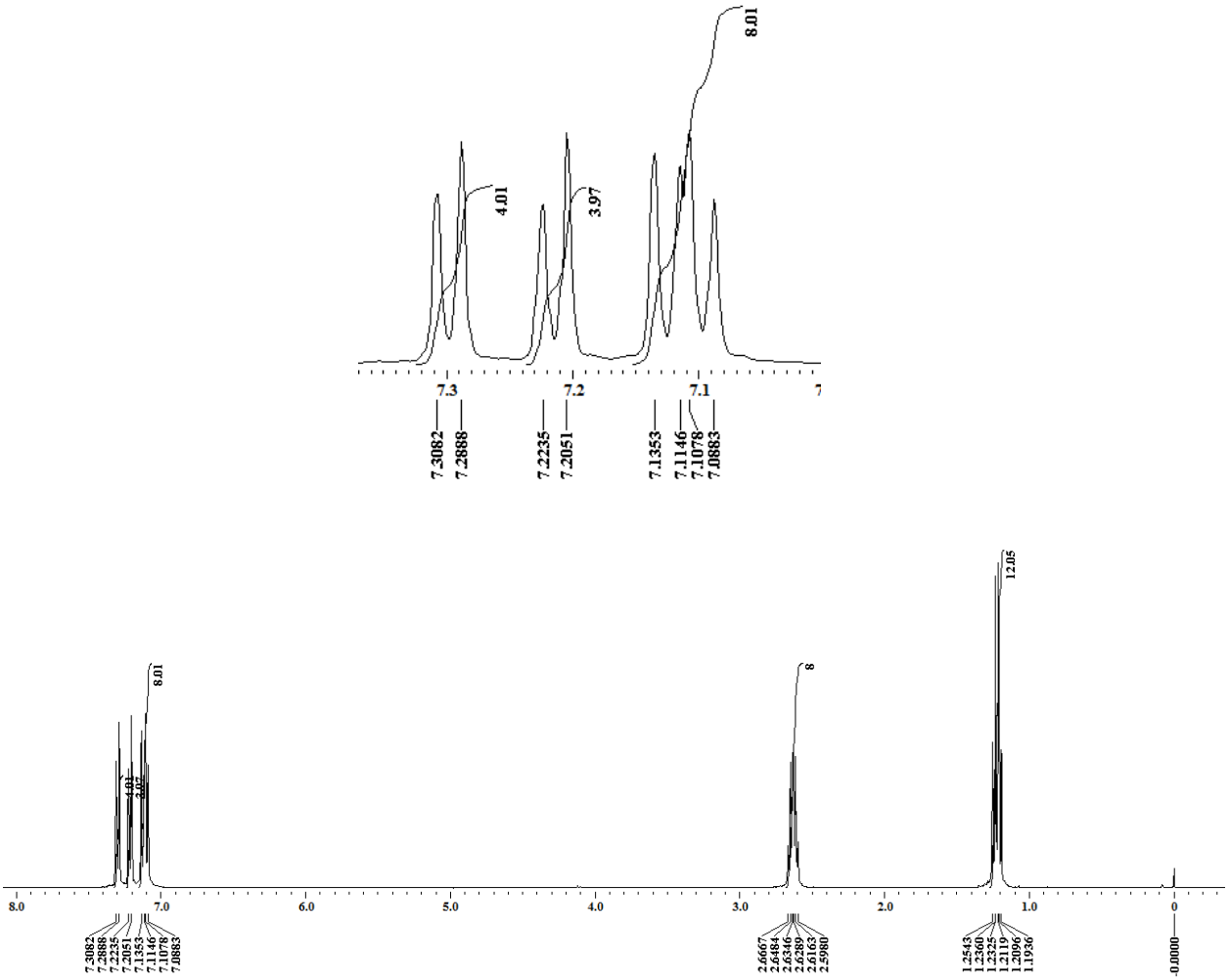
2,5-Bis((4-ethylphenyl)ethynyl)-3,4-di-*p*-tolylthiophene (6e)



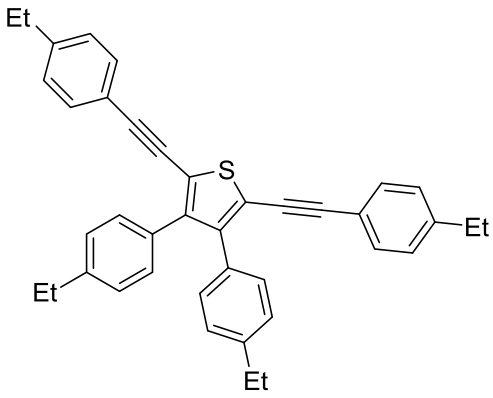
^{1}H NMR



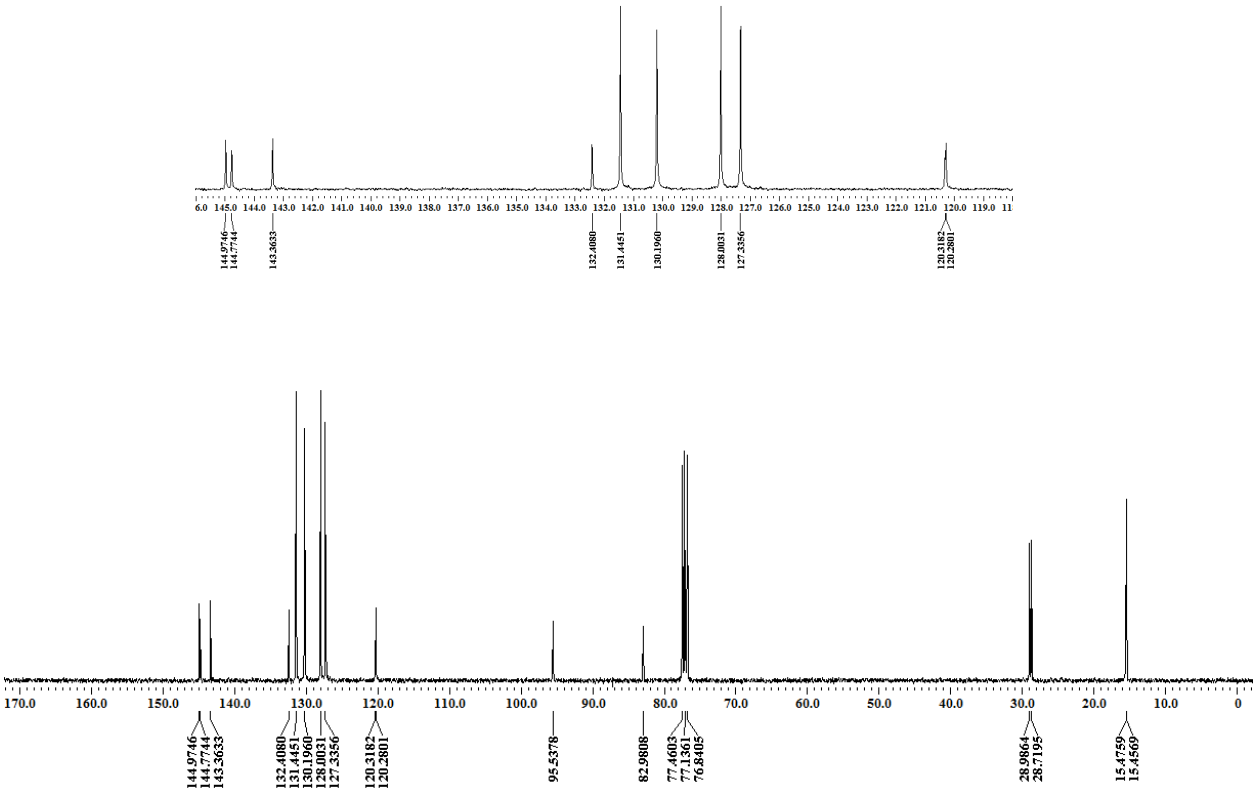
3,4-Bis(4-ethylphenyl)-2,5-bis((4-ethylphenyl)ethynyl)thiophene (6f)



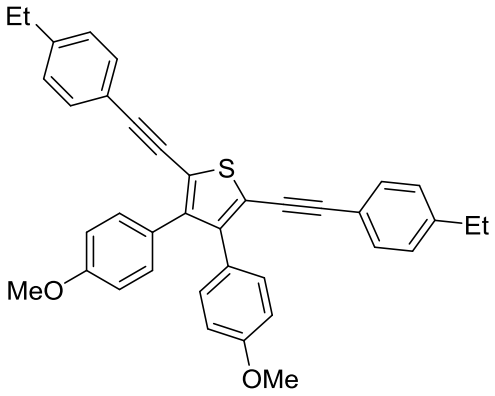
^{13}C NMR



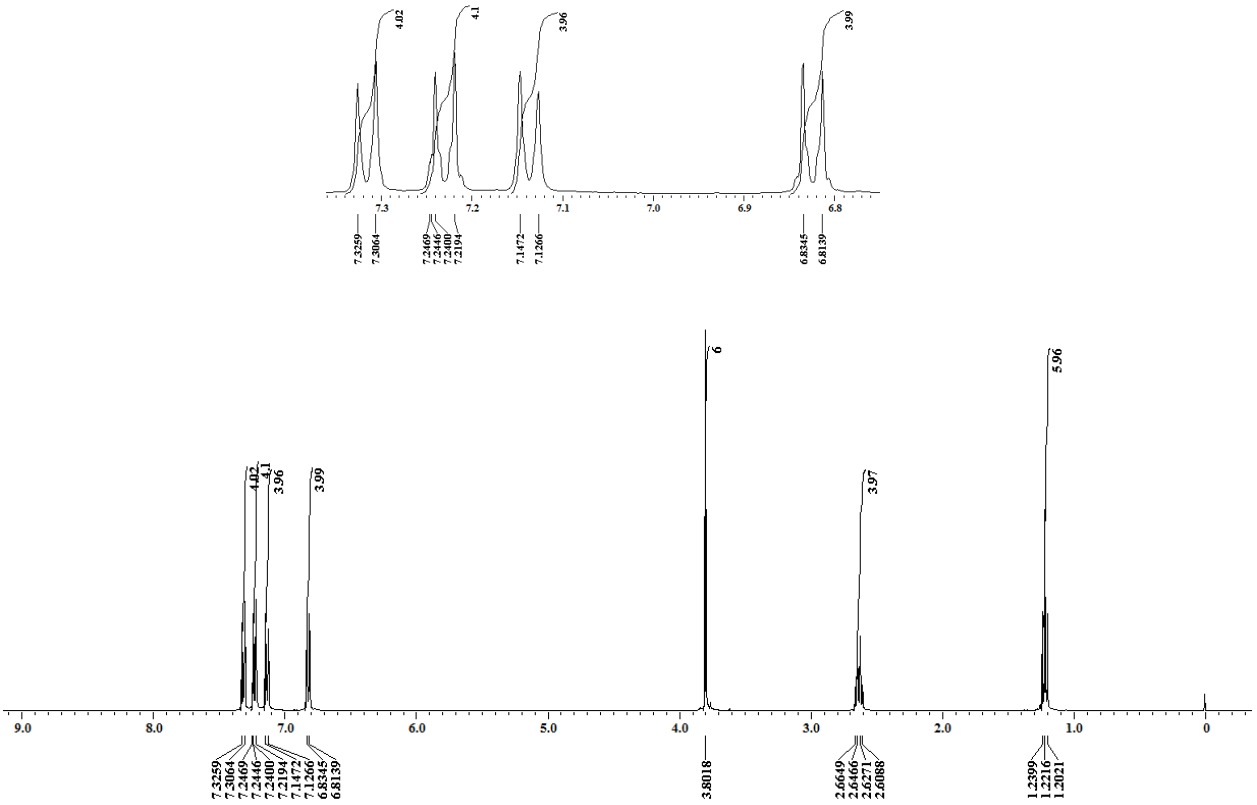
3,4-Bis(4-ethylphenyl)-2,5-bis((4-ethylphenyl)ethynyl)thiophene (6f)



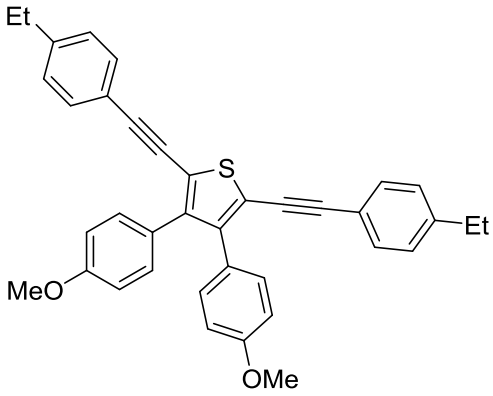
^{1}H NMR



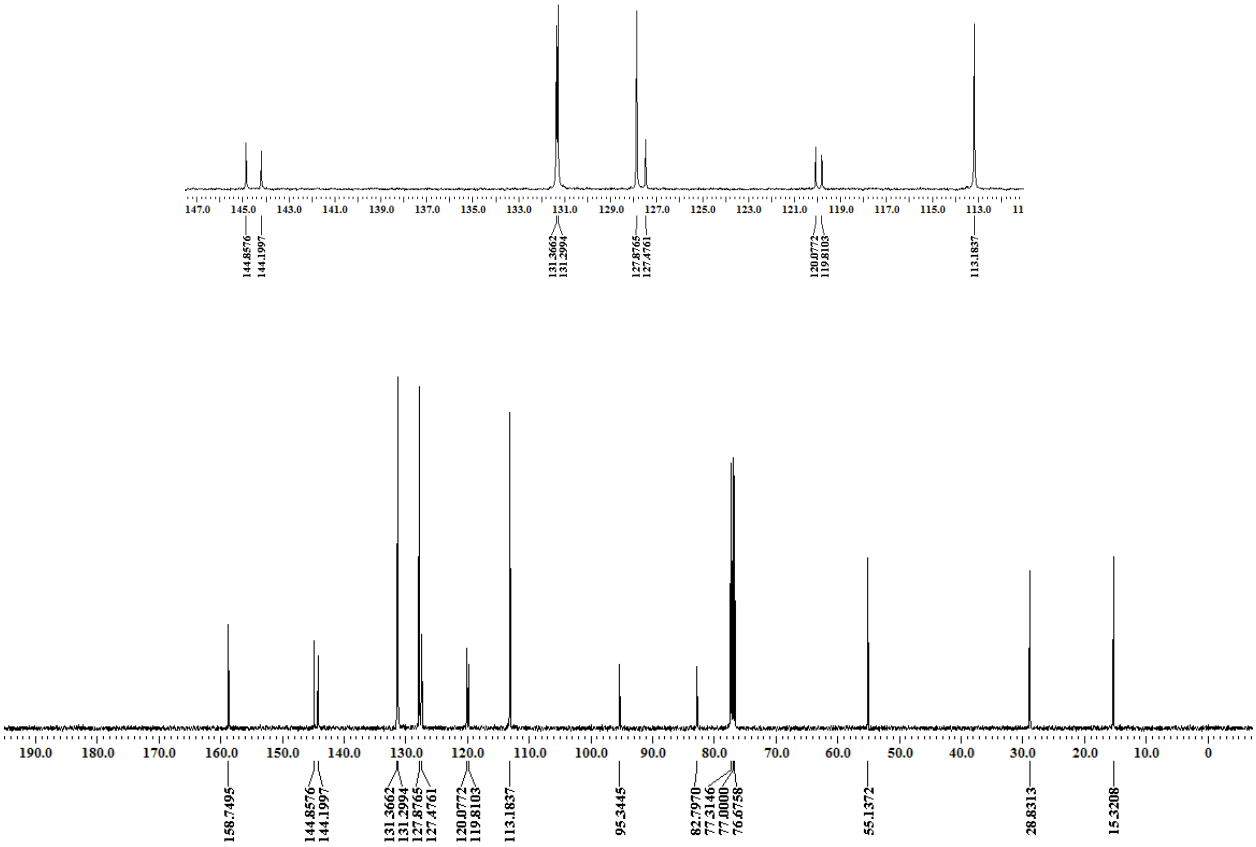
2,5-Bis((4-ethylphenyl)ethynyl)-3,4-bis(4-methoxyphenyl)thiophene (6g)



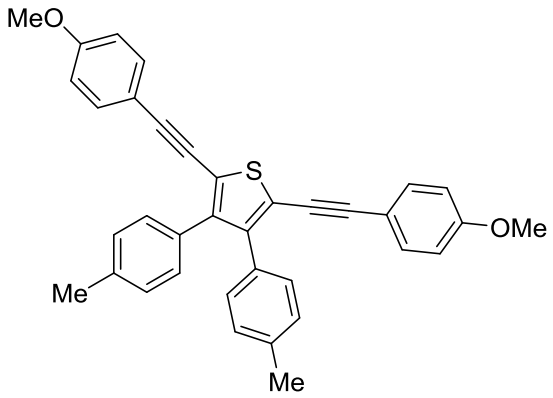
^{13}C NMR



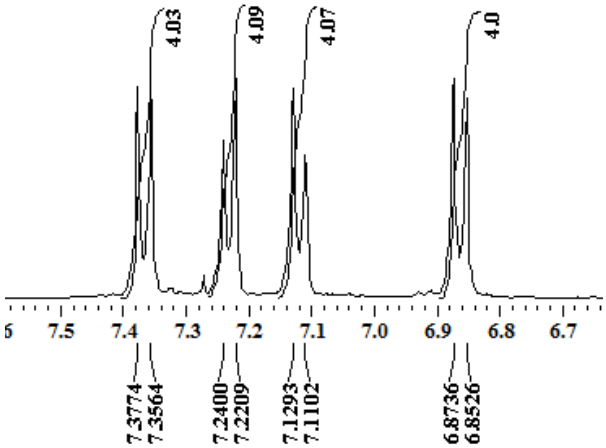
2,5-Bis((4-ethylphenyl)ethynyl)-3,4-bis(4-methoxyphenyl)thiophene (6g)

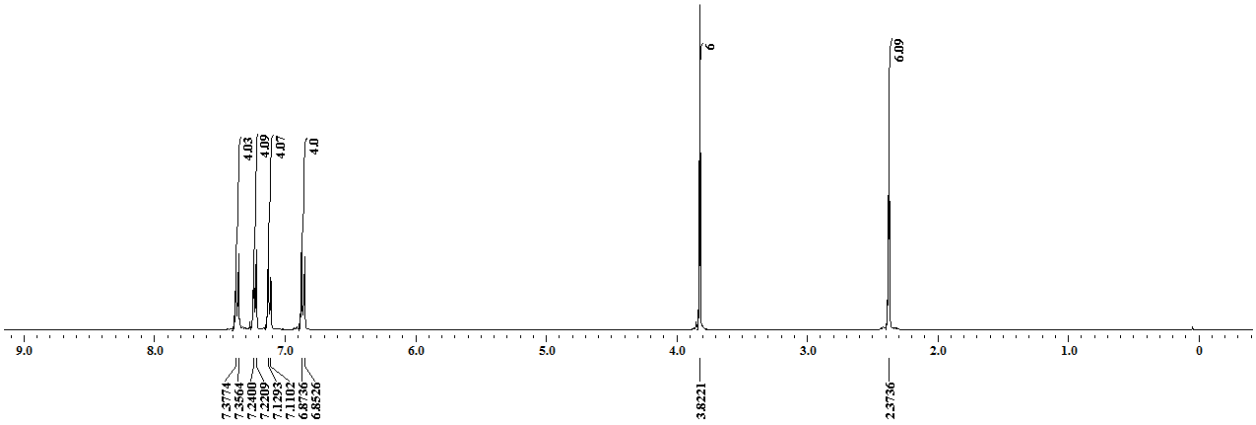


^{1}H NMR

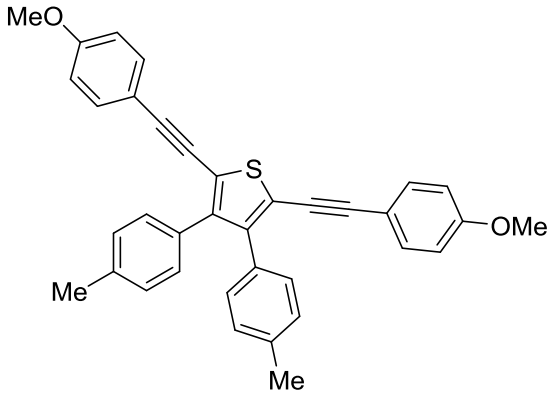


2,5-Bis((4-methoxyphenyl)ethynyl)-3,4-di-*p*-tolylthiophene (6h)

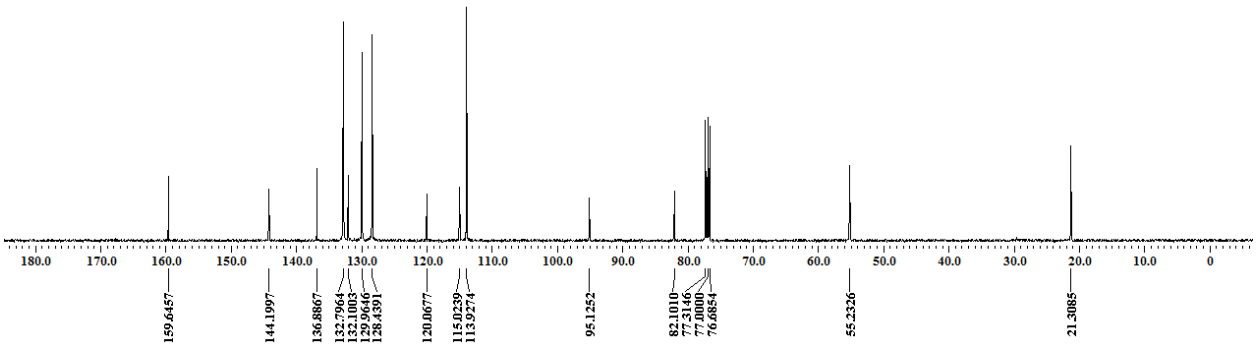




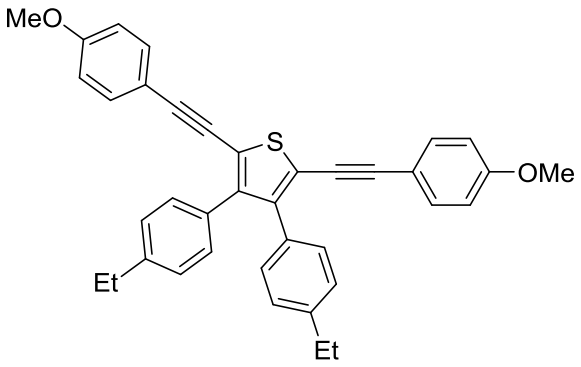
^{13}C NMR



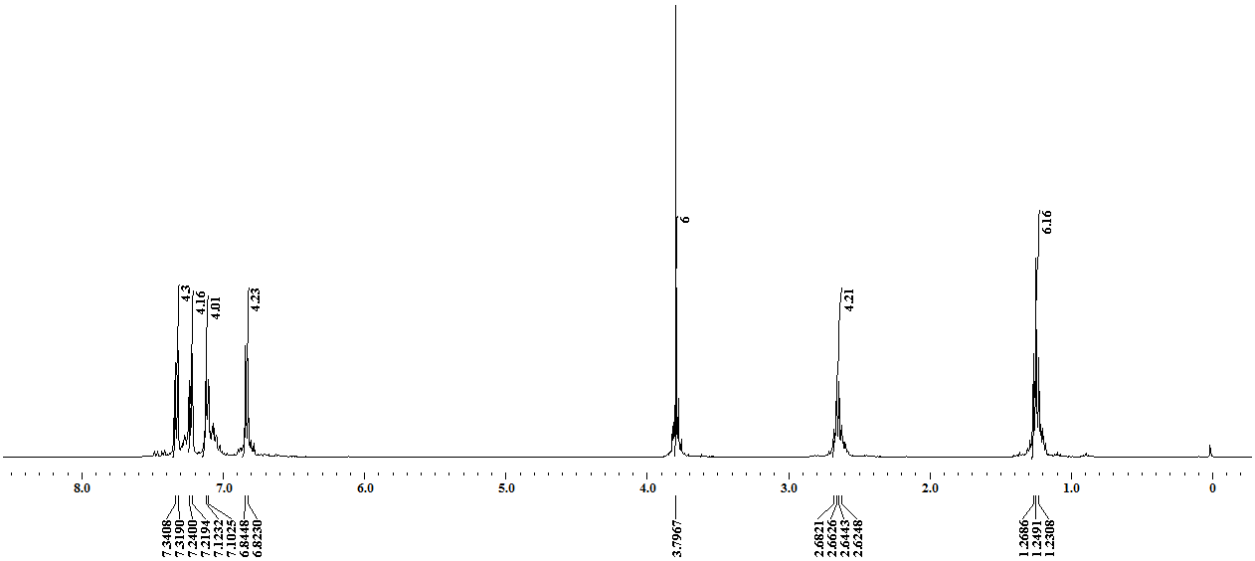
2,5-Bis((4-methoxyphenyl)ethynyl)-3,4-di-*p*-tolylthiophene (6h)



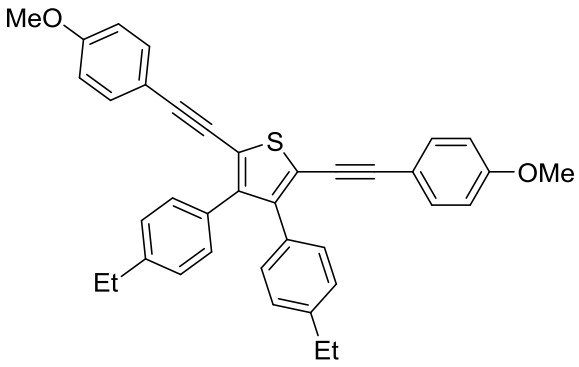
^{1}H NMR



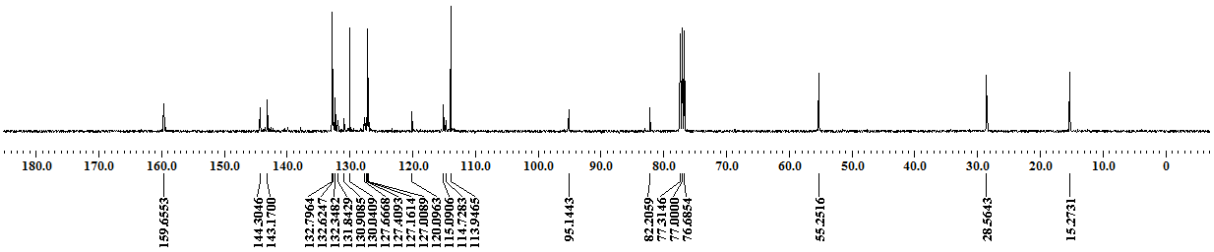
3,4-Bis(4-ethylphenyl)-2,5-bis((4-methoxyphenyl)ethynyl)thiophene (6i)



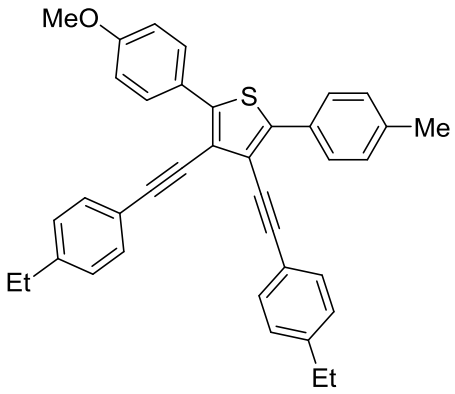
^{13}C NMR



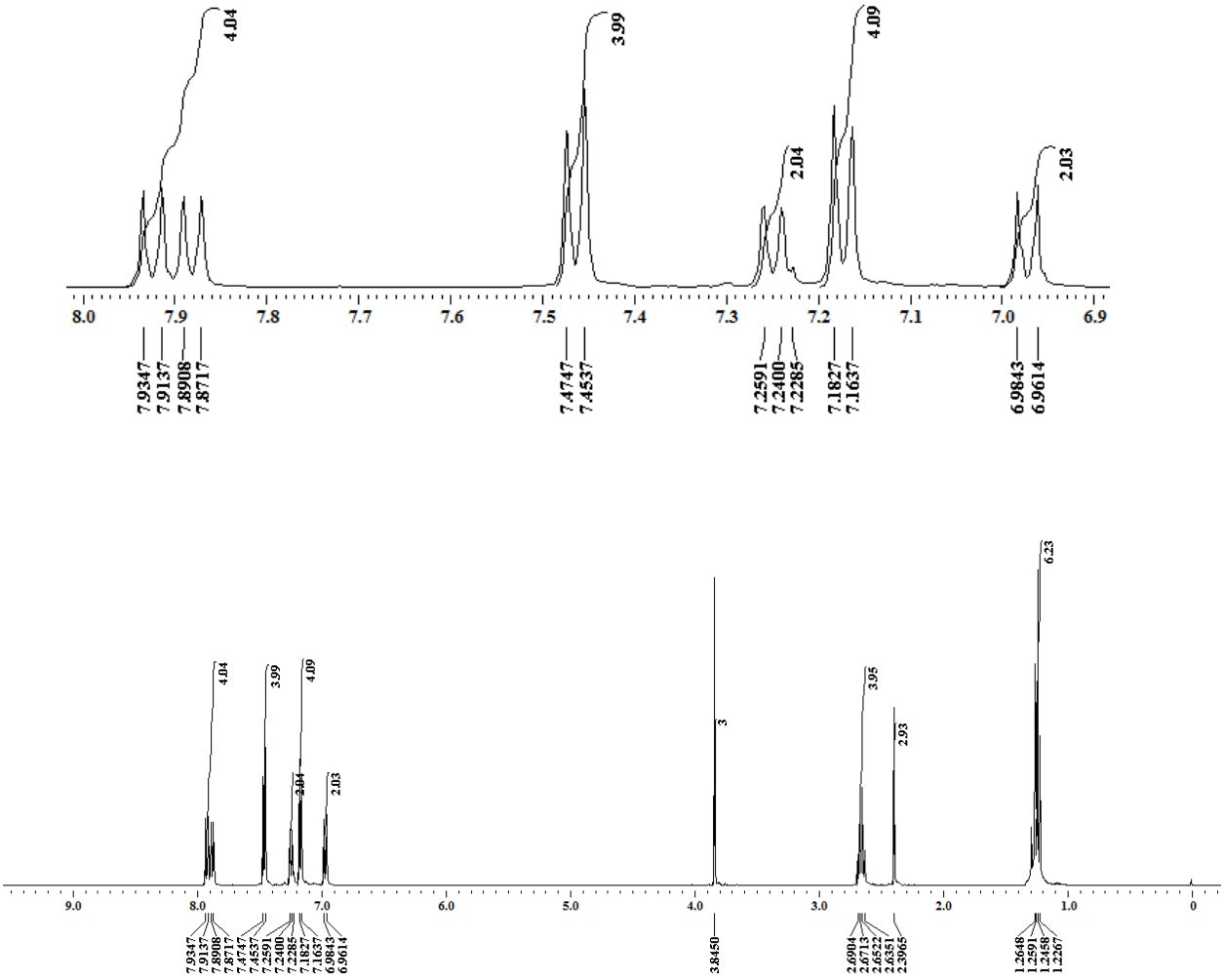
3,4-Bis(4-ethylphenyl)-2,5-bis((4-methoxyphenyl)ethynyl)thiophene (6i)



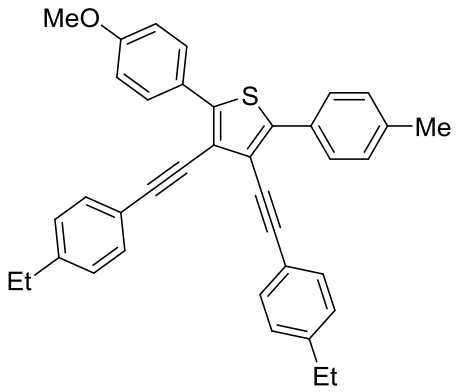
^{1}H NMR



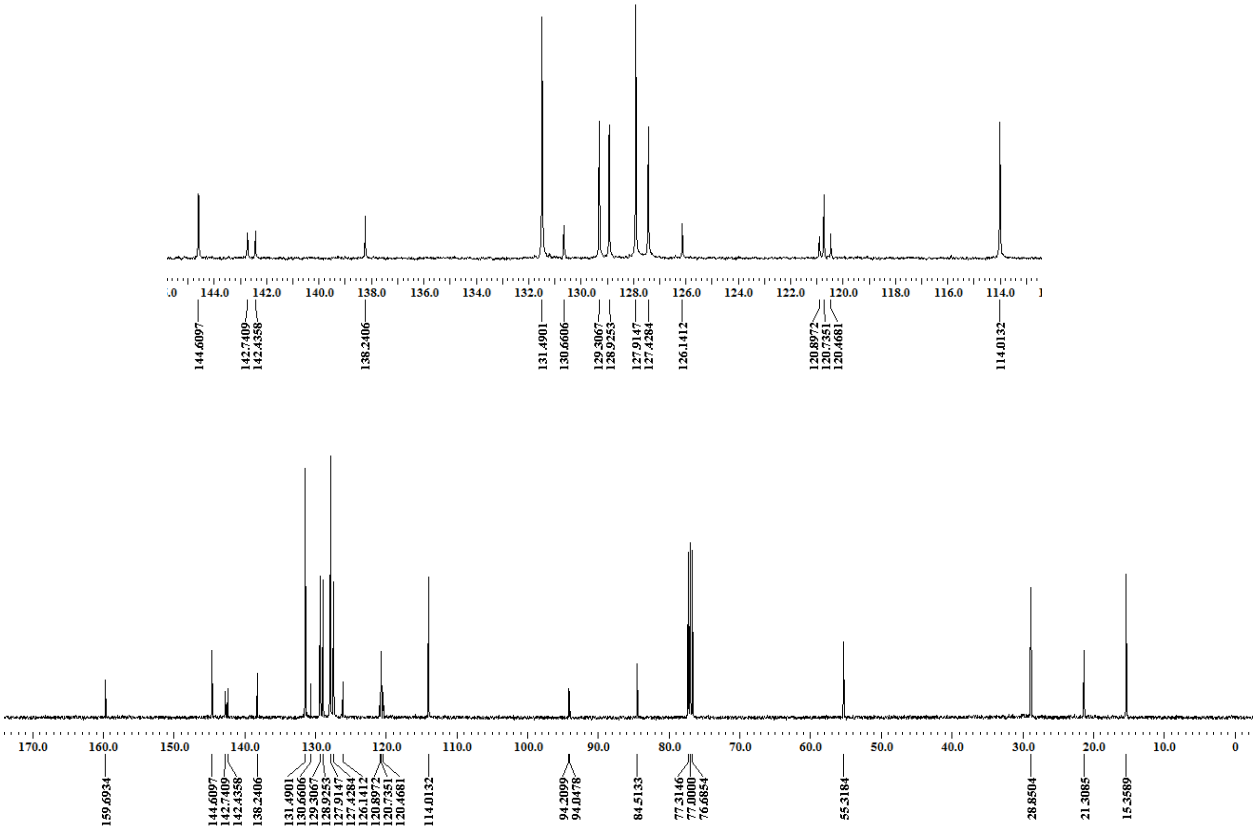
3,4-Bis((4-ethylphenyl)ethynyl)-2-(4-methoxyphenyl)-5-(*p*-tolyl)thiophene (7a)



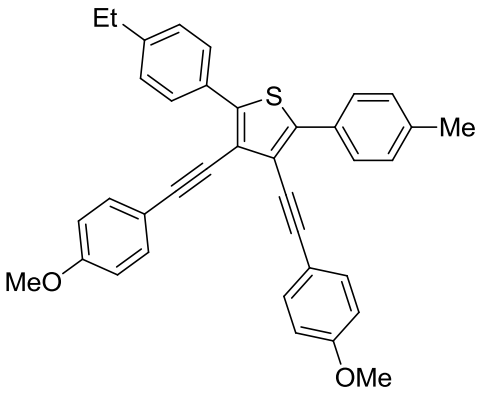
^{13}C NMR



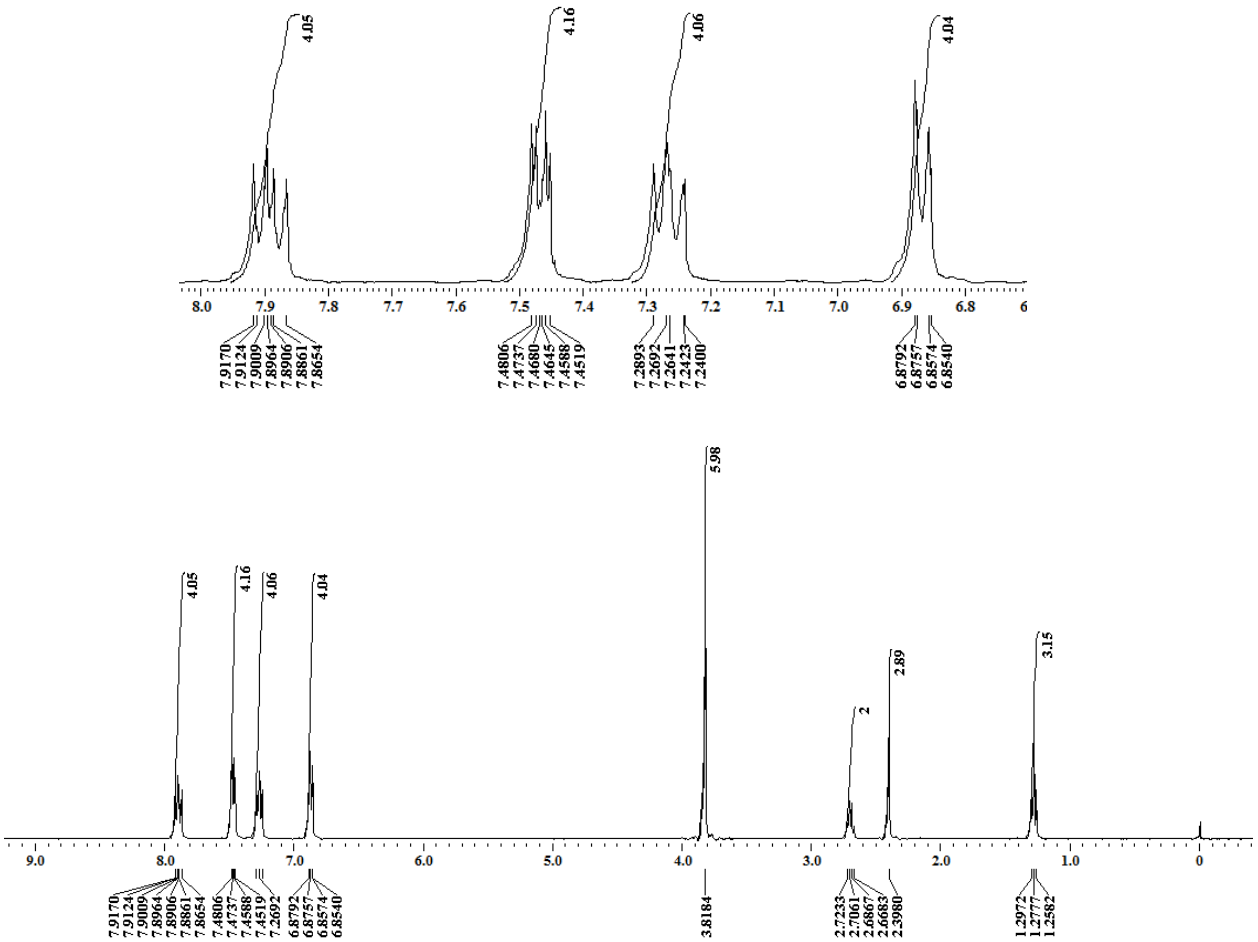
3,4-Bis((4-ethylphenyl)ethynyl)-2-(4-methoxyphenyl)-5-(*p*-tolyl)thiophene (7a)



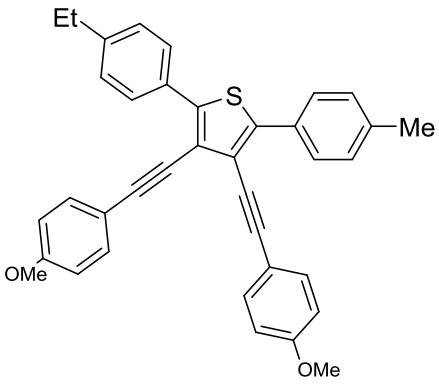
^{1}H NMR



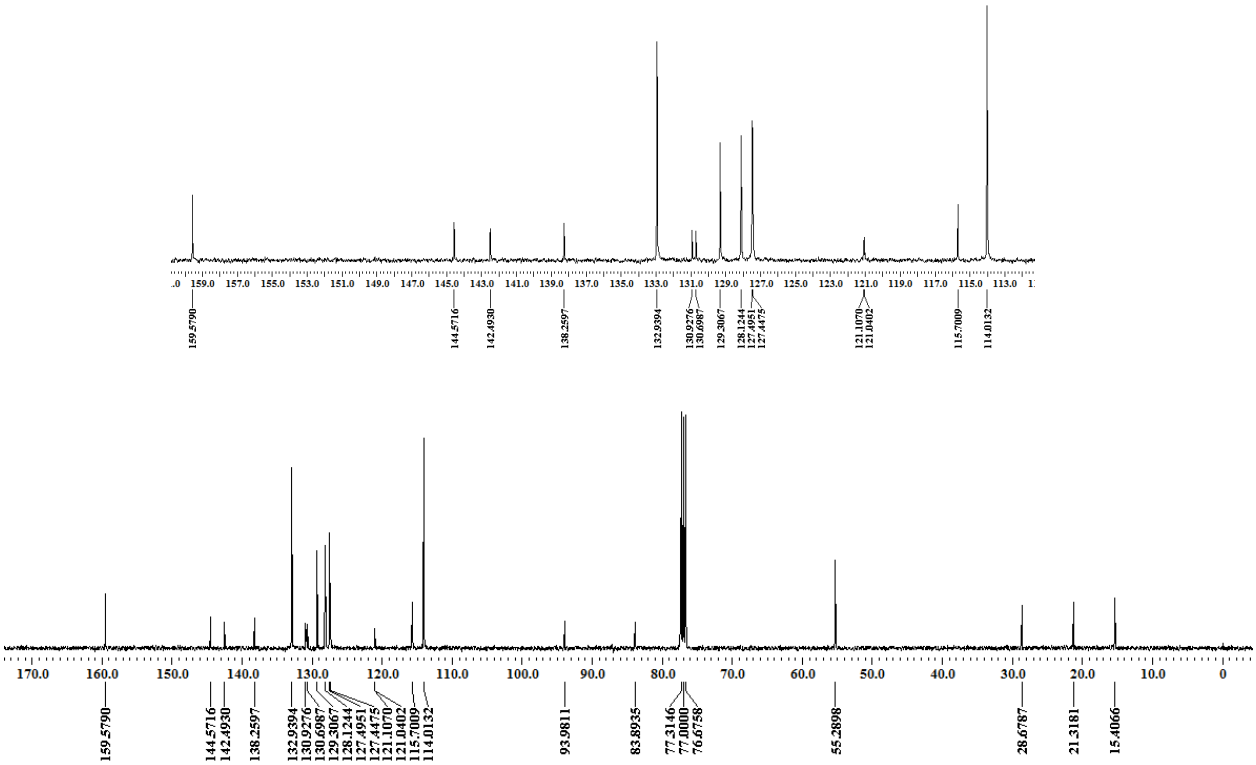
2-(4-Ethylphenyl)-3,4-bis((4-methoxyphenyl)ethynyl)-5-(*p*-tolyl)thiophene (7b)



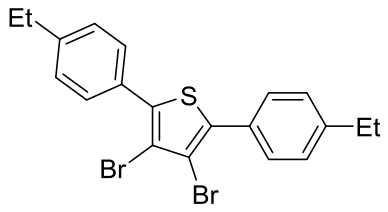
^{13}C NMR



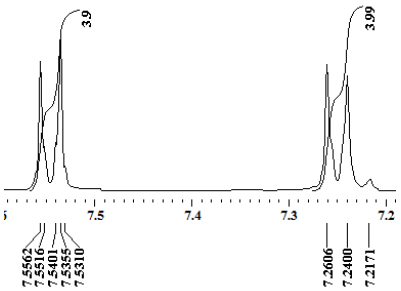
2-(4-Ethylphenyl)-3,4-bis((4-methoxyphenyl)ethynyl)-5-(*p*-tolyl)thiophene (7b)

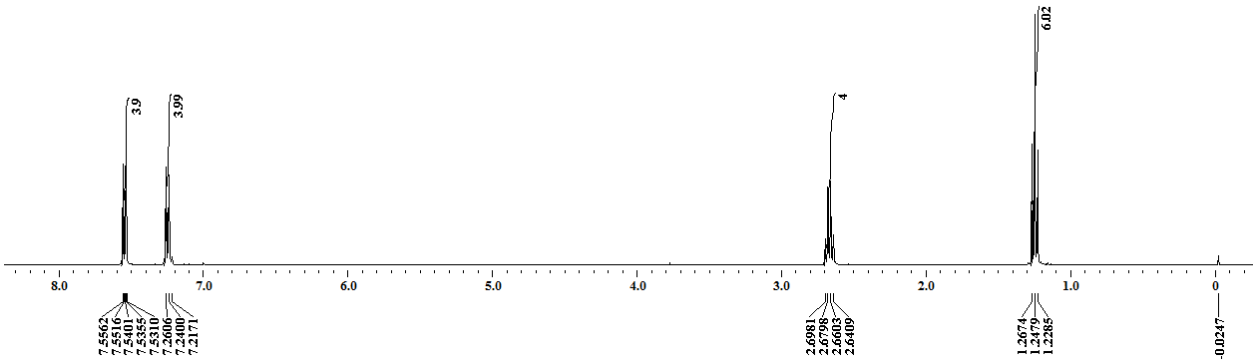


^{1}H NMR

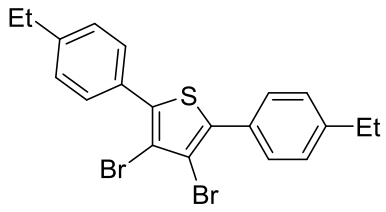


3,4-Dibromo-2,5-bis(4-ethylphenyl)thiophene (X)

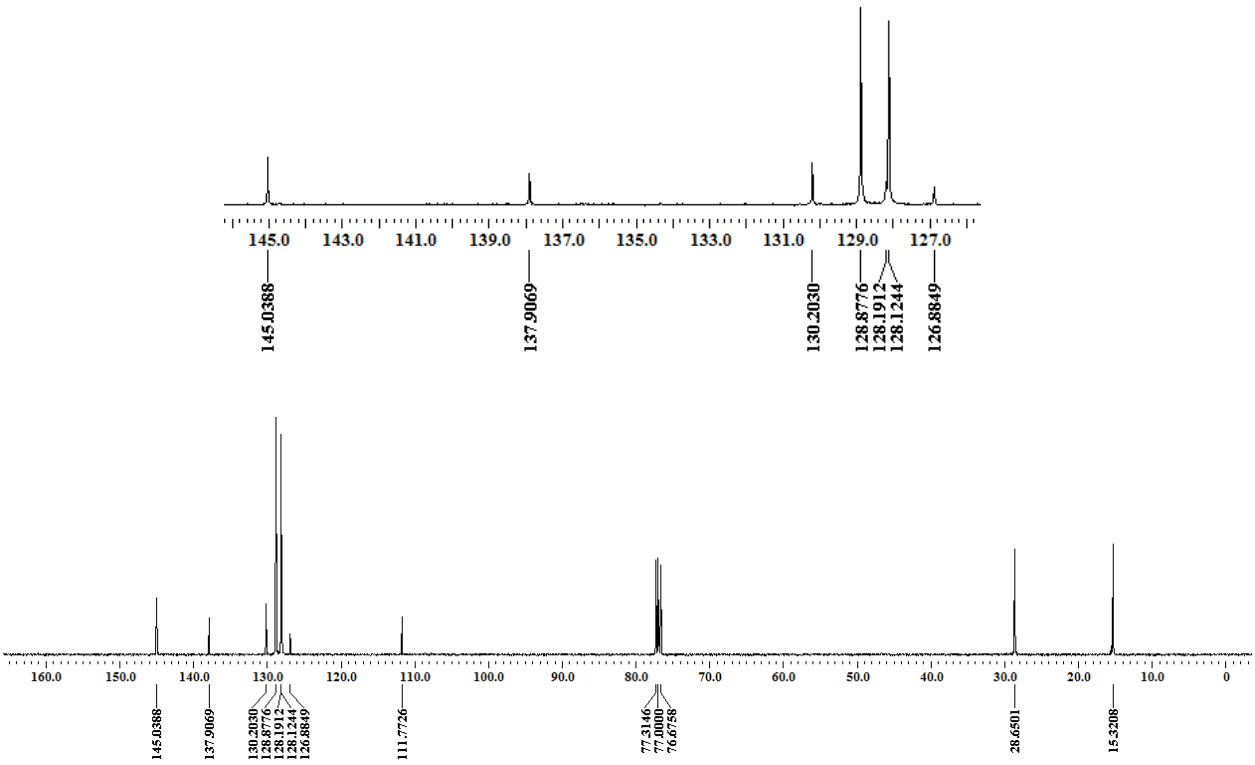




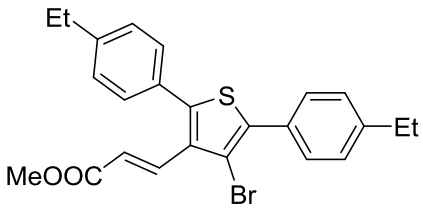
^{13}C NMR



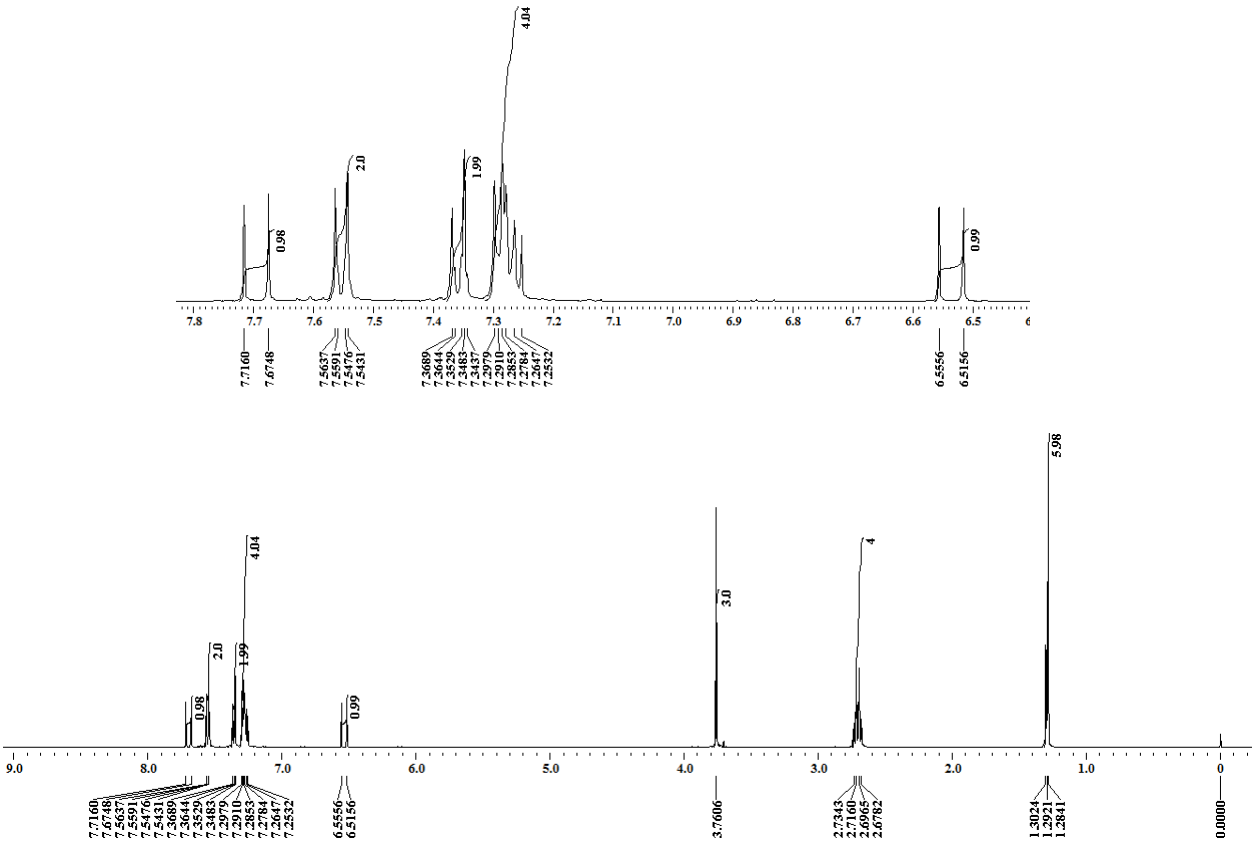
3,4-Dibromo-2,5-bis(4-ethylphenyl)thiophene (X)



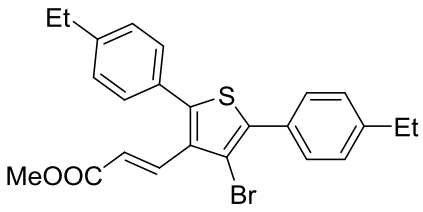
^{1}H NMR



Methyl (E)-3-(4-bromo-2,5-bis(4-ethylphenyl)thiophen-3-yl)acrylate (9)



^{13}C NMR



Methyl (E)-3-(4-bromo-2,5-bis(4-ethylphenyl)thiophen-3-yl)acrylate (9)