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Article

Synthesis of 1,3-Diynes via Detelluration of Bis(ethynyl)tellurides

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Neste artigo é descrita a síntese de sistemas diínicos conjugados contendo substituintes elétron-atratores e elétron-doadores via a deteluração catalizada por paládio de bis-(ariletinil)teluretos e bis-(alquiletinil)teluretos. Este procedimento foi realizado sob condições atmosféricas em DMF usando $Pd(Oac)_2$ como catalisador e AgOAc como um aditivo na presença de trietilamina. Esta rota oferece acesso eficiente a sistemas diínicos conjugados em um curto período de tempo. A estrutura cristalográfica por difração de raios X do telureto de bis(p-toluiletinila) e a conformação no estado sólido mostram uma cadeia supramolecular alinhada ao longo do eixo b, sustentada por interações CH…π.

The synthesis of symmetric conjugated diyne systems with electron-withdrawing or electron-donating substituents via a palladium-catalyzed detelluration of bis(arylethynyl)tellurides and bis(alkylethynyl)tellurides is described. This procedure is effected under atmospheric conditions in DMF using $Pd(OAc)_2$ as a catalyst and AgOAc as an additive in the presence of triethylamine. This route offers efficient access to conjugated diyne systems in short reaction time. X-ray crystallographic structure and solid-state conformation of bis(p-tolylethynyl)telluride show a supramolecular chain aligned along the b axis, sustained by C-H…π interactions.

Keywords: tellurium, bis(phenylethynyl)tellurides, bis(alkynylethynyl)tellurides, detelluration, diynes, palladium

Introduction

Organotellurium compounds play an important role in organic synthesis, and they have received considerable attention because of their potential availability and useful biological activity.[1] As reported by Bergman and co-workers[2] more than three decades ago, aryltelluriums undergo detelluration upon treatment with degassed Raney nickel to afford biaryl compounds. Although the reaction is interesting and synthetically useful, the necessity of more than a stoichiometric amount of the required metal is still a serious drawback. However, attempted transition metal-catalyzed detellurations have been unsuccessful to date.[2,3]

Compounds containing chains of conjugated triple bonds[4,5] are of paramount importance as versatile and useful building blocks in organic synthesis. Among these compounds, 1,3-butadiynes[6] have been prominently utilized as substructures in the formation of valuable intermediates for natural products[7] and pharmaceuticals such as antitumor,[8] antibacterial,[9] anti-inflammatory,[10] and antifungal agents.[11]

These conjugated diynes also serve as the core functional group in organic molecular materials such as linearly σ-conjugated acetylenic oligomers and polymers,[12] macrocycles[13] (Figure 1), and supramolecular scaffolds.[14] Oxidative dimerization of *sp*-hybridized terminal alkynes mediated by Cu(I) or Cu(II) salts under either catalytic or stoichiometric conditions is the most commonly used synthetic methodology for obtaining symmetrically substituted 1,3-butadiyne.

These approaches include Glaser's coupling,[15] Eglinton's coupling,[16] and Hay's coupling.[17] In these reactions, the transmetalation of an alkynyl group to copper is proposed to generate an alkynylcopper species that undergoes subsequent oxidative dimerization to give the corresponding 1,3-butadiynes.[18]

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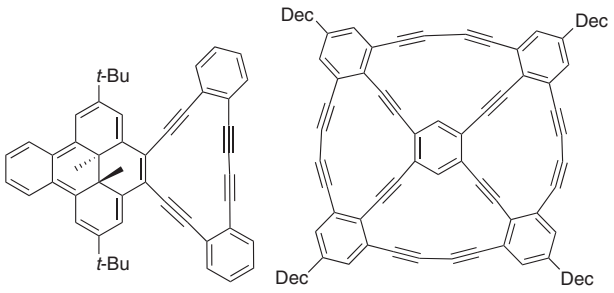
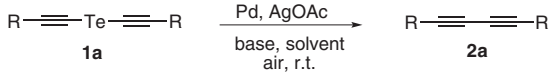


Figure 1. Structure of diyne macrocycles.

Results and Discussion

Herein, we describe a convenient protocol for the synthesis of symmetrical conjugated diynes through the palladium-catalyzed detelluration of functionalized bis(arylethynyl)tellurides and bis(alkylethynyl) tellurides at room temperature in presence of air (Scheme 1).



Scheme 1. Synthesis of conjugated diynes.

The approach to preparing symmetrical conjugated diynes **2a**-**j** was based on a palladium-catalyzed detelluration reaction of functionalized bis(phenylethynyl)tellurides and bis(alkylethynyl) tellurides **1a**-**j**. The parent precursors bis(arylethynyl)telluride **1a**-**j** were conveniently prepared in good to moderate yields according to the procedure described by Engman and Stern .[19]

We initially optimized the conditions for the detelluration of functionalized bis(phenylethynyl)telluride **1**. To find optimal conditions for the detelluration reaction, bis(phenylethynyl) telluride **1a** was selected as a model substrate, and a variety of catalysts were screened as described in Table 1. All reactions were monitored by TLC and GC/MS.

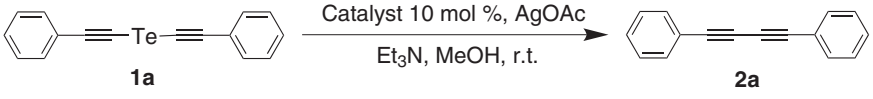
We initially surveyed palladium catalysts for use in this detelluration reaction. A comparison of different palladium catalysts such as $PdCl_2(dppf)\cdot CH_2Cl_2$, $Pd(OAc)_2$, $PdCl_2PEPPSI$-^{i}Pr, $PdCl_2$, and $PdCl_2(PhCN)_2$ (72%, 52%, 50%, 31% and 46% yields, respectively). Although the best yield (72% yield) was obtained using $PdCl_2(dppf)\cdot CH_2Cl_2$, we choose $Pd(OAc)_2$ as catalyst due its availability in our laboratory. No product formation was observed using catalysts such as $Fe(acac)_2$, CuCl and $NiCl_2(dppe)$ (entries 8-10). The reaction also did not proceed in the absence of a Pd catalyst (Table 1, entry 1).

One equiv. of AgOAc was used as an additive, along with 4 equiv. of triethylamine, and MeOH as solvent.

After the determination of the optimal catalyst for this transformation, we then studied the influence of the base. In our initial attempts, we used triethylamine, and the desired compound was obtained in 72% yield. We also attempted the same reaction with some other organic and inorganic bases such as NaOAc, Cs_2CO_3, K_2CO_3, DIPEA, pyridine and cyclohexylamine, obtaining the detelluration product in yields ranging from 27% to 67%.

To further determine the optimal conditions for the detelluration reaction, we performed the model reaction in various solvents. When MeOH, 1,4-dioxane, toluene and CH_3CN were employed, the reaction yields were poor or moderate (52%, 44%, 38% and 58%, respectively). While

Table 1. Effect of a catalyst on the detelluration reaction of bis(phenylethynyl)telluride **1a**



entry	Catalyst[a]	Yield / (%)[b]
1	-	nr
2	$PdCl_2(dppf)\cdot CH_2Cl_2$	72
3	$PdCl_2PEPPSI$-^{i}Pr	50
4	$Pd(OAc)_2$	52
5	$PdCl_2$	31
6	$PdCl_2(PhCN)_2$	46
7	$Fe(acac)_2$	nr
8	CuCl	nr
9	$NiCl_2(dppf)$	nr

Reaction conditions: bis(phenylethynyl)telluride **1a** (1 equiv.), catalyst (10 mol %), Et_3N (4 equiv.), AgOAc (1.0 equiv.), MeOH (5 mL), r.t. [a]10 mol % of catalyst under air atmosphere. [b]Yields of isolated products. nr: no reaction.

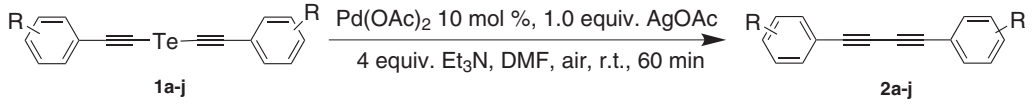
using DMSO as solvent provided a good yield (72%), DMF provided the best yield of the desired product (86%).

From these studies, it was determined that a reaction mixture containing 1.0 equiv. of bis(phenylethynyl)telluride **1a**, 4 equiv. of Et_3N, 1 equiv. of AgOAc, and 10 mol % of $Pd(OAc)_2$ in 5 mL of DMF at room temperature stirred under atmospheric conditions for 60 min provided the best conditions for the synthesis of conjugated diyne **2a**. To demonstrate the efficiency of this detelluration reaction, we then explored its generality with a variety of bis(arylethynyl)tellurides and bis(alkylethynyl)tellurides. The results are summarized in Table 2.

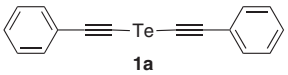
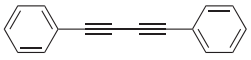
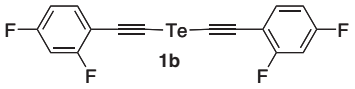
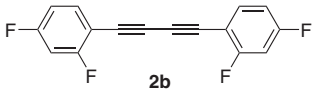
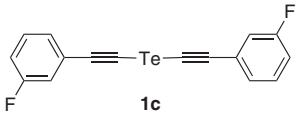
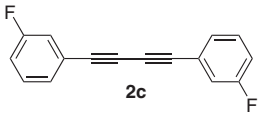
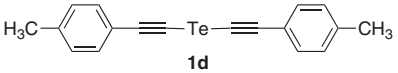
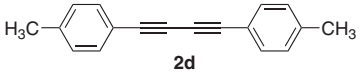
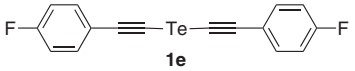
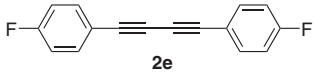
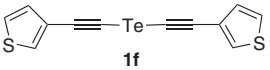
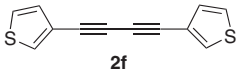
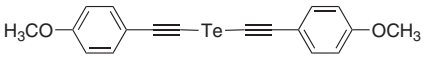
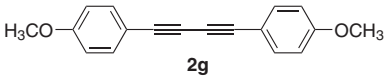
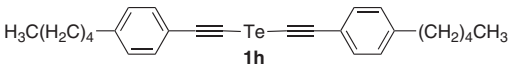
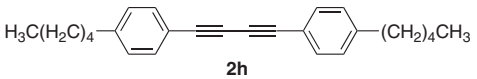
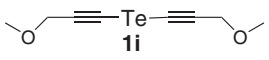
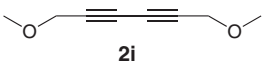
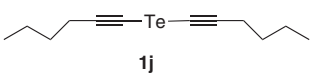
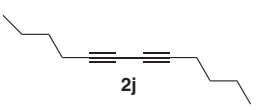
After optimizing the conditions for the synthesis of symmetrical conjugated diyne **2a**, it was synthesized a series of conjugated diynes (**2a**-**j**) in 21-86% yields (see Table 2 and Experimental). The reaction was carried out at room temperature. The reaction proceeded with electron-withdrawing substituents attached to the alkynyltelluride and with electron-donation substituents. All of the obtained products provided ^1H and ^{13}C NMR spectra that were in full agreement with their assigned structures.

On the basis of available literature[20] we propose a possible catalytic cycle for the detelluration reaction of

Table 2. Detelluration reaction of bis(arylethynyl)tellurides and bis(alkylethynyl)tellurides



1a-j 2a-j

Bis(alkynyl)tellurides	Diynes	Yield[a] / (%)
 **1a**	 **2a**	86
 **1b**	 **2b**	60
 **1c**	 **2c**	65
 **1d**	 **2d**	38
 **1e**	 **2e**	52
 **1f**	 **2f**	44
 **1g**	 **2g**	39
 **1h**	 **2h**	47
 **1i**	 **2i**	65
 **1j**	 **2j**	89[b]

[a]Isolated yields. [b]Yield by CG-MS, the product was not isolated by column.

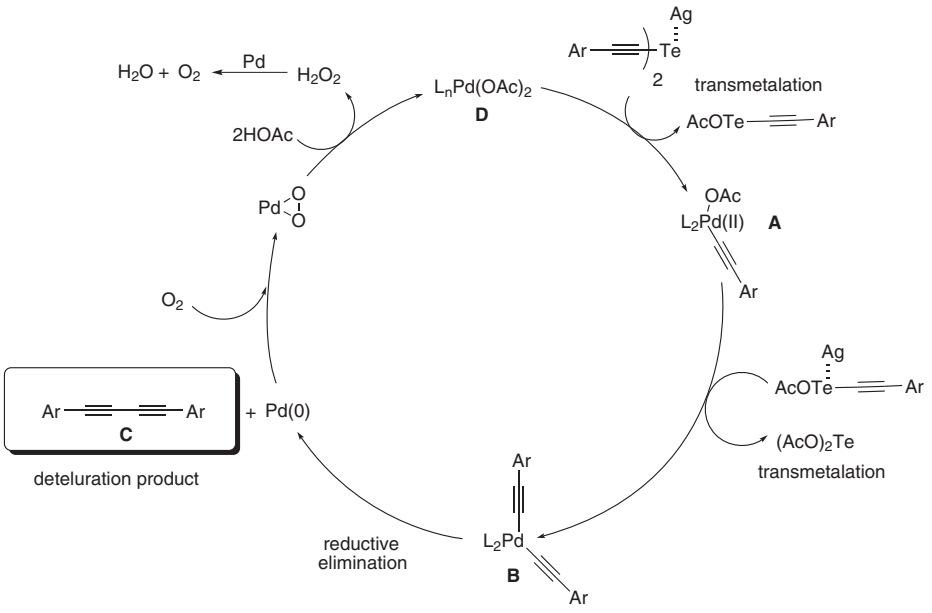


Figure 2. Possible catalytic cycle of the homocoupling reaction of alkynylditellurides.

bis(arylethynyl)tellurides and bis(alkylethynyl)tellurides as described in Figure 2.

According to this cycle the reaction proceeds by the formation of Pd(II) complex with acetylene followed by the conversion of this intermediate into another palladium species **B**, which leads the formation of conjugated diyne **C** along the reduction of the Pd(II) complex to Pd(0). The palladium species is later oxidized in the presence of O_2 to give the initial Pd(II) species completing the cycle.

Due to our ongoing interest in tellurium structures, especially those involving π-interactions, the crystal and molecular structure of the bis-(*p*-tolylethynyl)telluride starting material was determined.[21] The tellurium atom is located on a crystallographic twofold axis with the C-Te-C angle being 92.23 (15)°. The dihedral angle formed between the phenyl rings is 87.27 (7)° (Figure 3).

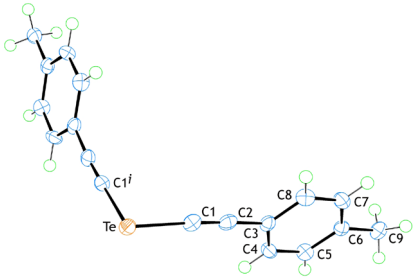


Figure 3. Molecular structure of bis(*p*-tolylethynyl)telluride showing numbering scheme and displacement ellipsoids at the 70% probability level. Symmetry operation i: -x, y, 3/2-z.

In the crystal structure, the telluride molecules are connected into supramolecular chains along the b axis via C-H...π interactions, as shown in Figure 4.

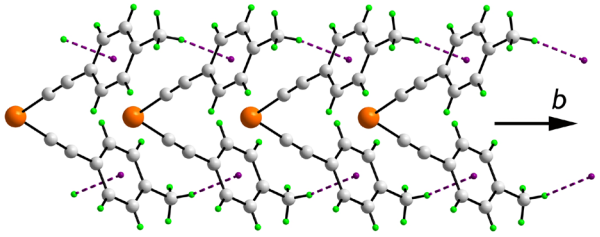


Figure 4. Supramolecular chain aligned along the b axis, sustained by C-H…π interactions.

Conclusions

In summary, we demonstrated the synthesis of functionalized symmetrical 1,3-diyne systems through the palladium-catalyzed detelluration reaction of bis(arylethynyl) tellurides and bis(alkylethynyl)tellurides. The use of this methodology for the synthesis of more complex polyacetylenic compounds is currently under study in our laboratory.

Experimental

Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 300 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant *(J)* in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 75 MHz. Spectra were

recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet) and m (multiplet). Column chromatography was performed using silica gel (230-400 mesh) following the methods described by Still *et al.*[22] Thin layer chromatography (TLC) was performed using silica gel F_{254}, 0.25 mm thickness from Merck. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other solvents were ACS or HPLC grade unless otherwise noted. Air and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques. Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to a controller.

*General experimental procedure for preparing conjugated diyne compounds **2a-j***

A suspension of bis(phenylethynyl)telluride (**1a**) (0.0824 g, 0.25 mmol), $PdOAc_2$ (5.6 mg, 10% mol), triethylamine (0.101 g, 1 mmol) and silver(I) acetate (0.041 g, 0.25 mmol) in 5 mL of DMF was stirred at room temperature under air for 60 min. The reaction mixture was then diluted with ethyl acetate (25 mL), and the organic layer was washed with a saturated solution of NH_4Cl (2 × 10 mL) and water (2 × 10 mL), dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash silica column chromatography using hexane as the eluent and subsequently characterized.

*Bis(phenylethynyl)telluride (**1a**)[19]*

Yield 86%; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.30-7.38 (m, 6H), 7.47-7.56 (m, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz,) δ (ppm) 73.7; 81.3; 121.6; 128.4; 129.5; 132.3; EM *m/z* (%) 202 (100), 200 (24), 150 (8), 101 (13), 88 (10).

*1,4-Bis(2,5-fluorophenylethynyl)telluride (**1b**)*

Red solid; mp 187-188 °C. Yield 60%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 6.84 (dd, 1H, *J* 5.2 Hz, *J* 13.0 Hz) 7.45 (dd, 1H, *J* 8.0 Hz, *J* 15.3 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 165.4 (d, *J* 11.9 Hz, C-F), 161.8 (d, *J* 46.4 Hz, C-F), 135.1 (d, *J* 2.3 Hz, C-F), 1 1.76 (d, *J* 3.7 Hz, C-F), 108.0 (d, *J* 4.2 Hz, C-F),104.8 (d, *J* 19 Hz, C-F), 48.6 (2C), 29.4 (2C). ^{125}Te NMR ($CDCl_3$, 95 MHz) δ (ppm) 374.1. EM *m/z* (%) 274.2 (100), 275.2 (16), 138.2 (15), 223.2 (6). IR (KBr) ν_{max}/cm^{-1}: 3440, 3099, 2139, 1613, 1586, 1142, 1096, 967, 855, 779, 729, 512, 498, 485. HRMS (ESI) calc. for $C_{16}H_6F_4TeNa^+$ 426.9365; found 426.9368.

*1,3-Bis(m-fluorophenylethynyl)telluride (**1c**)*

White solid; mp 129-130 °C. Yield 58%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 6.96-7.14 (m, 8H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 44.5 (2C); 111.5 (2C); 116.4 (d, J^1 21.1 Hz, C-F); 118.8 (d, J^2 22.8 Hz, C-F); 124.4 (d, J^3 9.36 Hz, C-F); 129.9 (d, J^4 3.03 Hz, C-F); 129.8 (d, J^5 8.64 Hz, C-F); 162.2 (d, J^6 245.5 Hz, C-F). ^{125}Te NMR($CDCl_3$, 95 MHz) δ (ppm) 374.1. EM *m/z* (%) 238.1 (100), 236.1 (13), 218.1 (6), 217.2 (5), 168.2 (4), 119.2 (16). IR (KBr) ν_{max}/cm^{-1}: 3440, 3067, 2143, 1604, 1581, 1484, 1423, 1266, 1136, 941, 872, 784, 678, 571, 517, 457. HRMS (ESI) calc. for $C_{16}H_8F_2TeNa^+$ 390.9553; found 390.9538.

*1,4-Bis(p-tolylphenylethynyl)telluride (**1d**)[23]*

Yield 52%; ^{1}H NMR (CDCl3, 300 MHz) δ (ppm) 2.35 (s, 6H); 7.40 (d, *J* 7.8 Hz, 4H); 7.12 (d, *J* 7.8 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75.5 MHz,) δ (ppm) 21.6 (2C); 73.5 (2C); 81.6 (2C); 118.8 (2C); 129.2 (4C); 132.4 (4C); 139.5 (2C); EM *m/z* (%) 230 (100); 215 (17); 115 (17); 101 (15).

*1,4-Bis(p-fluorophenylethynyl)telluride (**1e**)*

White solid, mp 129-130 °C. Yield 51%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 6.91 (t, J^1 and J^2 8.52 Hz, 4H); 7.45 (dd, J^1 and J^2 5.37 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 42.7 (2C); 111.6 (2C); 115.6 (d, J^1 22.0 Hz, C-F); 118.9 (d, J^2 3.5 Hz, C-F); 134.2 (d, J^3 8.5 Hz, C-F); 162.9 (d, J^4 249.3 Hz, C-F). ^{125}Te NMR($CDCl_3$, 95 MHz) δ (ppm) 364.5. EM *m/z* (%) 264.2 (100), 265.1 (33), 249.2 (32), 233.6 (6), 231.4 (6), 221.1 (41), 220,2 (95), 201.5 (5.75), 200,4 (6) 132.3 (13), 117.1(5), 116.1 (8). IR (KBr) ν_{max}/cm^{-1}: 3443, 3099, 3080, 2143, 1595, 1503, 1480, 1224, 1209, 1150, 1096, 838, 749, 533. HRMS (ESI) calc. for $C_{16}H_8F_2TeNa^+$ 390.9553, found 390.9538.

*1,4-Bis(3-thyenyletynyl)telluride (**1f**)*

White solid, mp 100-101°C. Yield 67%, ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.14 (dd, J^1 and J^2 1.14 Hz, 2H); 7.25 (t, *J* 3.0 Hz, 2H); 7.57 (dd, J^1 1.2 Hz and J^2 1.14 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 42.7 (2C); 107.6 (2C); 122.1 (2C); 125.2 (2C); 130.1 (2C); 130.8 (2C). ^{125}Te NMR ($CDCl_3$, 95 MHz) δ (ppm) 364.4. EM *m/z* (%) 214.1 (100), 169,2 (19), 156.2 (4), 144.2 (6), 126.2 (4), 107.2 (11), 69.1 (6), 45.0. IR (KBr) ν_{max}/cm^{-1}: 3431, 3099, 2129, 1352, 1075, 940, 933, 865, 825, 783, 692, 670, 621, 582. HRMS (ESI) calc. for $C_{12}H_6S_2TeNa^+$ 366.887; found 366.8855.

*1,4-Bis(4-methoxyphenylethynyl)telluride (**1g**)*[23]

Yield: 58% ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.37 (d, *J* 8.5 Hz, 4H); 6.67 (dd, J^1 2.6 Hz and J^2 8.5 Hz, 4H); 3.79 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz,) δ (ppm) 20.9 (2C), 55.2 (2C), 111.2 (2C), 115.0 (4C), 129,8 (2C), 134.0 (4C), 143.1 (2C), 160.1 (2C), EM *m/z* (%) 264.2 (100), 220.2 (95), 221.1 (41), 249.2 (32), 110.2 (21), 218.2 (10). IR (KBr) ν_{max}/cm^{-1}: 3437, 3005, 2984, 2958, 2936, 2903, 2891, 2838, 2824, 2154, 1463, 1440, 1432, 1427, 1348, 1273, 1187, 1082, 1069, 995, 976, 899, 880, 606, 590. HRMS (ESI) calc. for $C_{18}H_{14}O_2TeNa^+$, found 414.9851.

*1,4-Bis(p-pentylphenylethynyl)telluride (**1h**)*

Yellow solid; mp 57-58 °C. Yield: 50%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 0.89 (t, *J* 6.6 Hz, 6H); 1.33 (m, 8H); 1.60 (m, 4H); 2.61 (m, 4H); 7.14 (d, *J* 8.0 Hz, 4H), 7.39 (d, *J* 7.8 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 14.0 (2C); 22.5 (2C); 30.96 (2C); 35.9 (2C); 42.1(2C); 112.8 (2C); 120.1 (2C); 128.4 (2C); 132.1 (2C); 144.3 (2C). ^{125}Te NMR($CDCl_3$, 95 MHz) δ (ppm) 357.6. EM *m/z* (%) 285.3 (100), 342.3 (92), 228.1 (61), 343.3 (25), 226.1 (12), 41.1 (9). IR (KBr) ν_{max}/cm^{-1}: 3435, 3024, 2955, 2929, 2855, 2141, 1503, 1466, 842, 825, 815, 723, 572, 530. HRMS (ESI) calc. for $C_{26}H_{30}TeNa^+$ 495.1307; found 495.1286.

*1,4-Bis(methoxyethynyl)telluride (**1i**)*

Yellow solid, mp 44-45 °C. Yield 78%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 4.32 (s, 4H); 3.39 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz,) δ (ppm) 40.2 (2C); 57.4 (2C); 60.6 (2C); 109.9 (2C). EM *m/z* (%) 69.0 (100), 77.1 (14), 78.1(14), 63.1 (13), 51.1 (11), 53.0 (8).

*1,4-Bis(butylethynyl)telluride (**1j**)*[24]

Yellow oil; ^{1}H NMR ($CDCl_3$,300 MHz) δ (ppm) 0.90 (t, *J* 7.2 Hz, 6H); 1.36-1.57 (m, 8H); 2.50 (t, *J* 6.9 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 13.6 (2C); 20.7 (2C); 21.9 (2C); 30.8 (4C); 114.3 (2C).

General procedure to homocoupling reaction

A suspension of bis(phenylethynyl)telluride (**1a**) (0.0824 g; 0.25 mmol), $Pd(OAc)_2$ (0.0056 g, 10% mol), triethylamine (0.101 g; 1 mmol) and silver acetate (0.041 g, 0.5 mmol) in 5 mL of DMF was stirred at room temperature, under air atmospheric by 60 min. The reaction mixture was diluted with ethyl acetate (25 mL), and the organic layer washed with NH_4Cl (2 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash silica column chromatography using hexane as eluent and subsequently characterized.

*1,4-Bis(phenylbuta-1,3-diyne (**2a**)*[25]

Yield 86%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.30-7.38 (m, 6H), 7.47-7.56 (m, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz,) δ (ppm) 73.7; 81.3; 121.6; 128.4; 129.5; 132.3.

*1,4-Bis(2,4-difluorophenyl)buta-1,3-diyne (**2b**)*

White solid; mp 187-188 °C. Yield 60%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 6.83-6.90 (m, 4H); 7.54-7.46 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 29.7 (2C); 74.8 (2C); 104.6 (d, *J* 1.3 Hz, C-F); 111.9 (d, *J* 25.7, C-F); 135.3 (d, *J* 9.9 Hz, C-F); 160.1 (d, *J* 196.0 Hz, C-F); 165.6 (d, *J* 53.8 Hz, C-F). IR (KBr) ν_{max}/cm^{-1}: 3439, 3101, 2955, 2924, 2854, 1730, 1609, 1582, 1496, 1468, 1435, 1299, 1268, 1143, 1098, 965, 857, 852, 812, 741, 710, 612, 601, 508, 475, 429. Microanalysis Calc. 70.25% C, 2.46% H; found 70.44% C; 2.54% H.

*1,3-Bis(m-fluorophenyl)buta-1,3-diyne (**2c**)*[26]

Yield 65%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.22-7.29 (m, 8H). ^{13}C NMR ($CDCl_3$, 75.5 MHz,) δ (ppm) 74.4 (2C); 80.6 (2C); 116.9 (d, J^1 21.0 Hz, C-F); 119.2 (d, J^2 22.9 Hz, C-F); 123.4 (d, J^3 9.5 Hz, C-F); 128.4 (d, J^4 3.1 Hz, C-F); 130.1 (d, J^5 8.6 Hz, C-F); 162.2 (d, J^6 245.8 Hz, C-F).

*1,4-Bis(p-tolyl)buta-1,3-diyne (**2d**)*[27]

Yield 52%. ^{1}H NMR ($CDCl_3$, 300 MHz,) δ (ppm) 2.35 (s, 6H); 7.40 (d, *J* 7.8 Hz, 4H); 7.12 (d, *J* 7.8 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75.5 MHz,) δ (ppm) 21.6 (2C); 73.5 (2C); 81.6 (2C); 118.8 (2C); 129.2 (4C); 132.4 (4C); 139.5 (2C).

*1,4-Bis(p-fluorophenyl)buta-1,3-diyne (**2e**)*[28]

Yield 47%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ(ppm) 7.03 (dd, 1H, *J* 7.8 Hz, *J* 9.7 Hz); 7.51 (ddd, *J* 2.2 Hz, *J* 5.3 Hz, *J* 6.9 Hz). ^{13}C NMR ($CDCl_3$,75.5 MHz) δ (ppm) 73.5 (2C); 80.4 (2C); 115.9 (d, J^1 22.1 Hz, C-F); 117.8 (d, J^2 3.56 Hz, C-F); 134.5 (d, J^3 8.50 Hz, C-F); 163.0 (d, J^4 250.1 Hz, C-F).

*1,3-Bis(3-thyenyl)buta-1,3-diyne (**2f**)*[28]

Yield 44%; ^{1}H NMR ($CDCl_3$, 300 MHz,) δ (ppm) 7.12 (d, *J* 5.0 Hz, 2H); 7.25-7.28 (m, 2H); 7.58 (d, *J* 2.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 73.6 (2C); 121.0 (2C); 125.6 (4C); 131.2 (4C).

*1,4-Bis(p-methoxyphenyl)buta-1,3-diyne (**2g**)*[28]

Yield 39%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.42 (d, *J* 8.5 Hz, 4H); 6.69 (dd, J^1 2.5 Hz and J^2 8.5 Hz, 4H); 3.80 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 55.2 (2C); 55.2 (2C); 67.9 (2C); 80.8 (2C); 111.4 (2C); 115.2 (4C); 134.3 (4C); 160,0 (2C).

*1,4-Bis(p-penthylphenyl)buta-1,3-diyne (**2h**)*[29]

Yield 38%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 0.87 (m, 6H); 1.30 (m, 8H); 1.59 (t, *J* 7.0 Hz, 4H); 2.59 (m, 4H); 7.12 (dd, J^1 3.8 Hz and J^2 7.9 Hz, 4H); 7.40 (t, *J* 8.6 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 13.9 (2C); 22.5 (2C); 31.4 (4C); 35.9 (2C); 73.5 (2C); 83.9 (2C); 119.0 (2C); 128.5 (4C); 132.4 (4C); 144.4 (2C).

*1,6-Dimethoxy-2,4-hexadiyne (**2i**)*[29]

Yield 21%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 3.39 (s, 6H); 4.18 (s, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ (ppm) 57.4 (2C); 59.8 (2C); 70.1 (2C); 75.1 (2C).

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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References

1. Patai, S.; Rappoport, Z.; *The Chemistry of Organic Selenium and Tellurium Compounds*, Wiley: Chichester, 1986, vol. 1; Irgolic, K. Y. In *Houben-Weyl Methoden der Organischen Chemie*; Müller, E., ed., 4th ed., vol. E12b, G. Thieme: Stuttgart, 1990; Petragnani, N.; Stefani, H. A. *Tetrahedron* **2005**, *61*, 1613; Petragnani, N.; Stefani, H. A. In *Tellurium in Organic Chemistry*; Second, Updated and Enlarged Edition, Academic Press, Elsevier: Amsterdam, 2007.
2. Bergman, J.; Carlsson, R.; Sjöberg, B.; *Org. Synth.* **1977**, *57*, 18; Bergman, J.; *Tetrahedron* **1972**, *28*, 3323; Bergman, J.; Engman, L.; *Tetrahedron* **1980**, *36*, 1275.
3. Barton, D. H. R.; Ozbalik, N.; Ramesh, M.; *Tetrahedron Lett.* **1988**, *29*, 3533.
4. Stang, P. J.; Diederich, F.; *Modern Acetylene Chemistry*, VCH: Weinheim, Germany, 1995, p. 506; Patai, S.; *The Chemistry of the Carbon-Carbon Triple Bond*, Wiley-Interscience: London, 1978.
5. Damle, S. V.; Seomoon, D.; Lee, P. H.; *J. Org. Chem*. **2003**, *68*, 7085.
6. For general reviews on coupling reactions between *sp*-carbon centers, see: Sonogashira, K. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., eds.; Pergamon: Oxford, 1991, Vol. 3, pp. 551-561; Siemsen, P.; Livingston, R. C.; Diederich, F.; *Angew. Chem., Int. Ed*. **2000**, *39*, 2632.
7. Bohlmann, F.; Burkhardt, T.; Zdero, C.; *Naturally Occurring Acetylenes*, Academic Press: London, 1973, p. 548.
8. Mayer, S. F.; Steinreiber, A.; Orru, R. V. A.; Faber, K.; *J. Org. Chem*. **2002**, *67*, 9115.
9. Stefani, H. A.; Costa, I. M.; Zeni, G.; *Tetrahedron Lett*. **1999**, *40*, 9215.
10. Zeni, G.; Panatieri, R. B.; Lissner, E.; Menezes, P. H.; Braga, A. L.; Stefani, H. A.; *Org. Lett*. **2001**, *3*, 819.
11. Stüts, A.; *Angew. Chem., Int. Ed.* **1987**, *26*, 320.
12. Diederich, F.; Rubin, Y.; *Angew. Chem., Int. Ed.* **1992**, *31*, 1101; Tour, J. M.; *Chem. Rev*. **1996**, *96*, 537; Martin, R. E.; Diederich, F.; *Angew. Chem., Int. Ed*. **1999**, *38*, 1350.
13. Kimball, D. B.; Haley, M. M.; Mitchell, R. H.; Ward, T. J.; Bandyopadhyay, S.; Williams, R. V; Armantrout, J. A.; *J. Org. Chem.* **2002**, *67*, 8798.
14. O'Connor, M. J.; Haley, M. M.; *Org. Lett.* **2004**, *6*, 2385.
15. Stefani, H. A.; Guarezemini, A. S.; Cella, R.; *Tetrahedron* **2010**, *66*, 7871.
16. Eglinton, G.; Galbraith, A. R.; *J. Chem. Soc*. **1959**, 889.
17. Hay, A. S.; *J. Org. Chem*. **1962**, *27*, 3320.
18. Taylor, R. J. K.; *Organocopper Reagents*, Oxford University Press: New York, 1994, p. 352.
19. Engman, L.; Stern, D.; *Organometallics* **1993**, *12*, 1445.
20. Punniyamurthy, T.; Velusamy, S.; Iqbal, J.; *Chem. Rev.* **2005**, *105*, 2329.
21. Caracelli, I.; Zukerman-Schpector, J.; Pena, J. M.; Stefani, H. A.; Tiekink, E. R. T.; *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2010**, *66*, o685.
22. Still, W.C.; Kahn, M.; Mitra, A.; *J. Org. Chem*. **1978**, *43*, 2923.
23. Murai, T.; Imaeda, K.; Kajita, S.; Kimura, K.; Ishihara, K.; Kato, S.; *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *67*, 239.
24. Citeau,G. A.; Giolando, D. M.; *J. Organomet. Chem*. **2001**, *625*, 23.
25. Coste, A.; Couty, F.; Evano, G.; *Synthesis* **2010**, *9*, 1500.
26. Jiang, H-F.; Liu, H-L.; Zhan, H-Y.; Zhou, L.; *Chin. J. Chem*. **2007**, *25*, 1413.
27. Chen, S-N.; Wu, W-Y.; Tsai, F-Y.; *Green Chem.* **2009**, *11*, 269.
28. Wang, D.; Li, J.; Li, N.; Gao, T.; Hou, S.; Chen, B.; *Green Chem.* **2010**, *12*, 45.
29. Stefani, H. A.; Singh, F. V.; Amaral, M. F. Z. J.; *Tetrahedron Lett*. **2009**, *50*, 2636.

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Supplementary Information

Synthesis of 1,3-Diynes via Detelluration of Bis(ethynyl)tellurides

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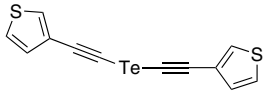
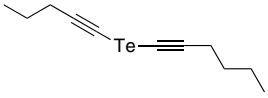
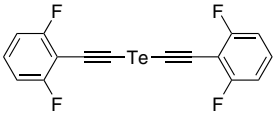
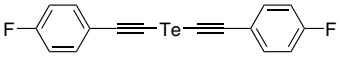
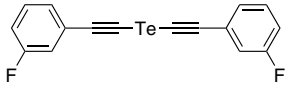
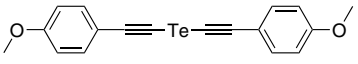
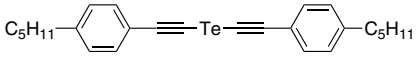
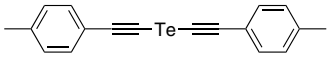
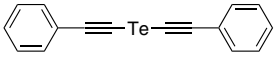
Table S1. Chemical shifts for ^{127}Te

Tellurides	^{125}Te NMR (δ ppm, $CDCl_3$)
	364.48
	332.57
	387.55
	364.52
	374.18
	348.06
	357.60
	357.83
	362.78

All spectra were obtained using diphenyl ditelluride as internal standard. Te_2Ph_2 ($CDCl_3$, δ (^{125}Te) = 421.8 ppm).

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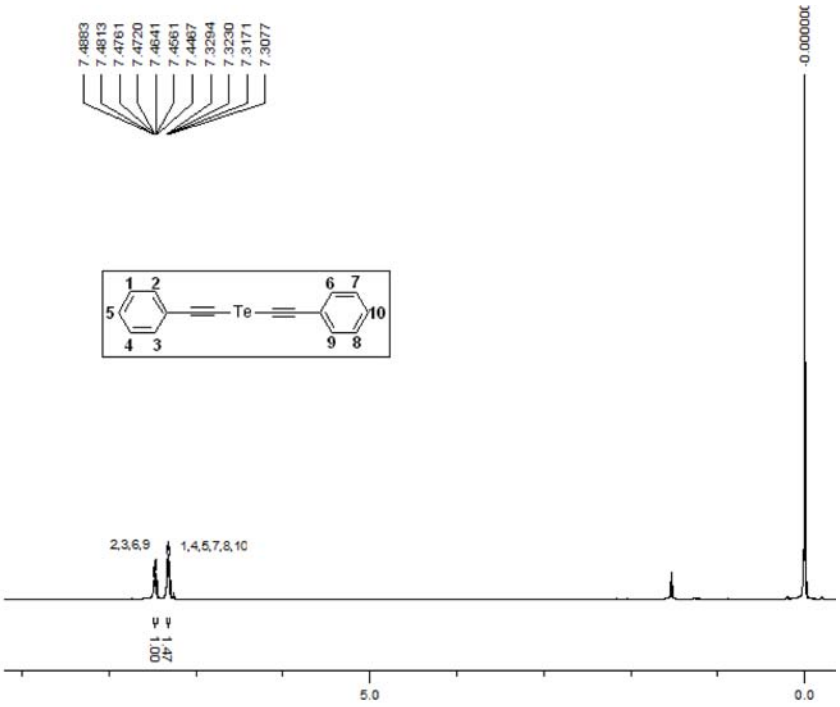

Figure S1. ^{1}H NMR ($CDCl_3$, 300 MHz) of **1a**.

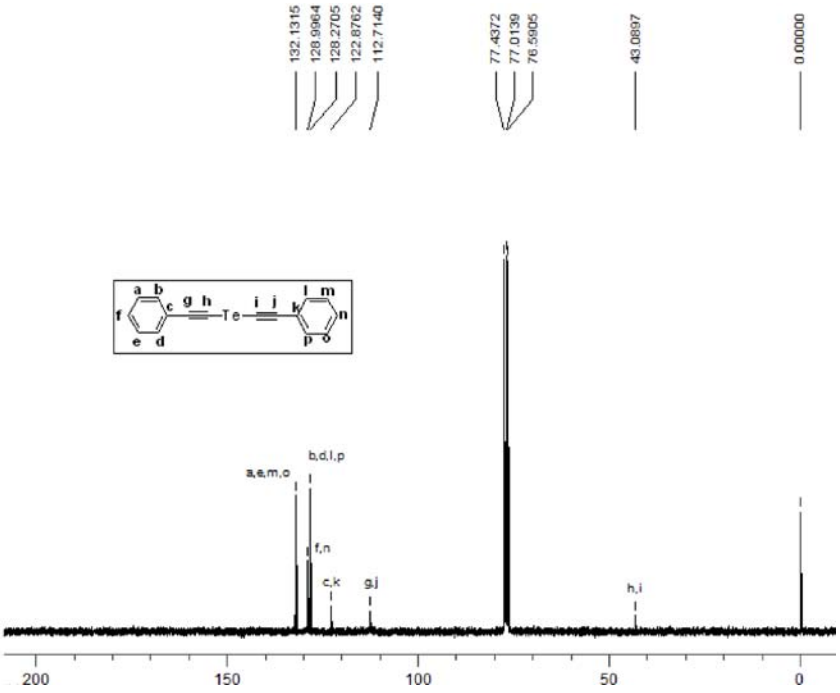

Figure S2. ^{13}C NMR ($CDCl_3$, 300 MHz) of **1a**.

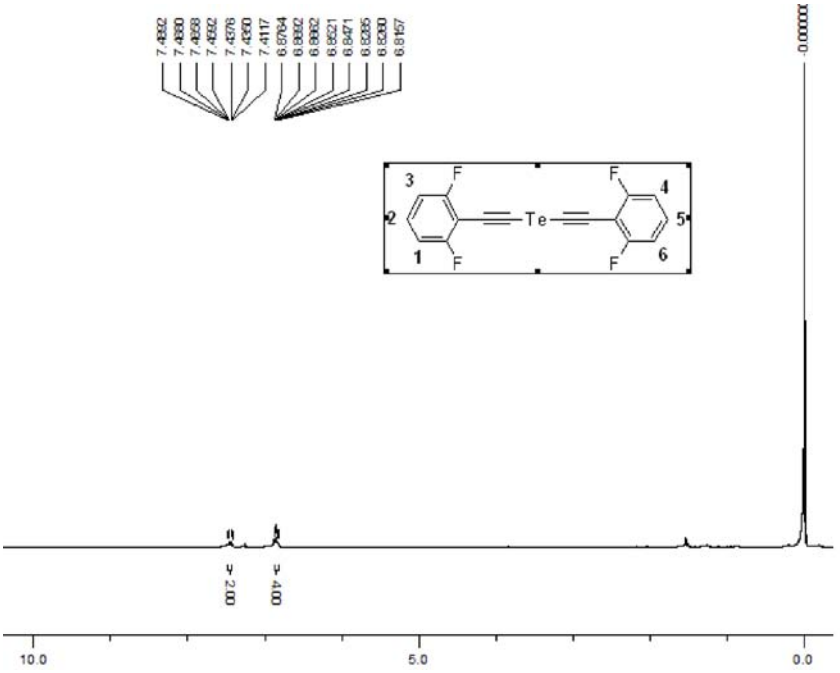

Figure S3. ^{1}H NMR ($CDCl_3$, 300 MHz) of **1b**.

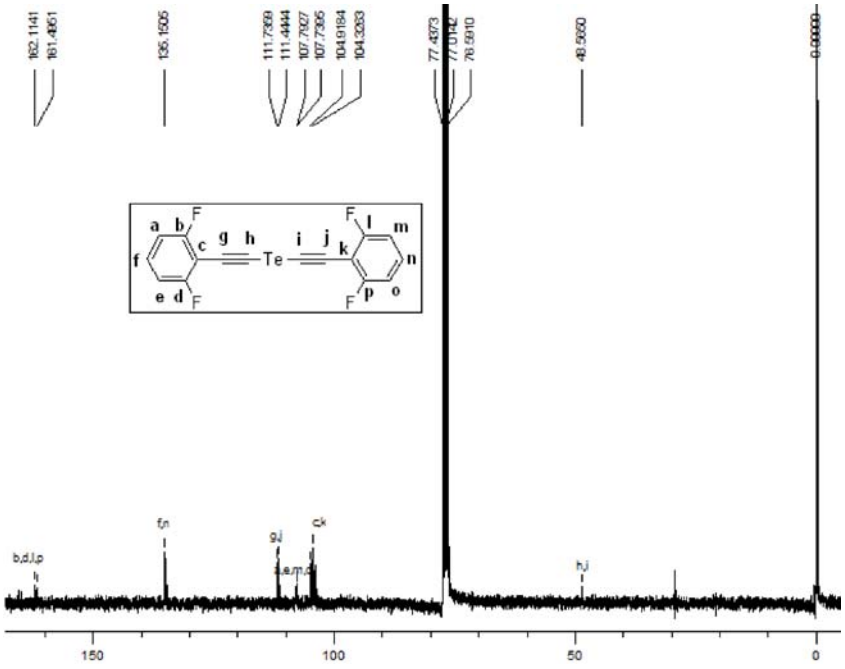

Figure S4. ^{13}C NMR ($CDCl_3$, 300 MHz) of **1b**.

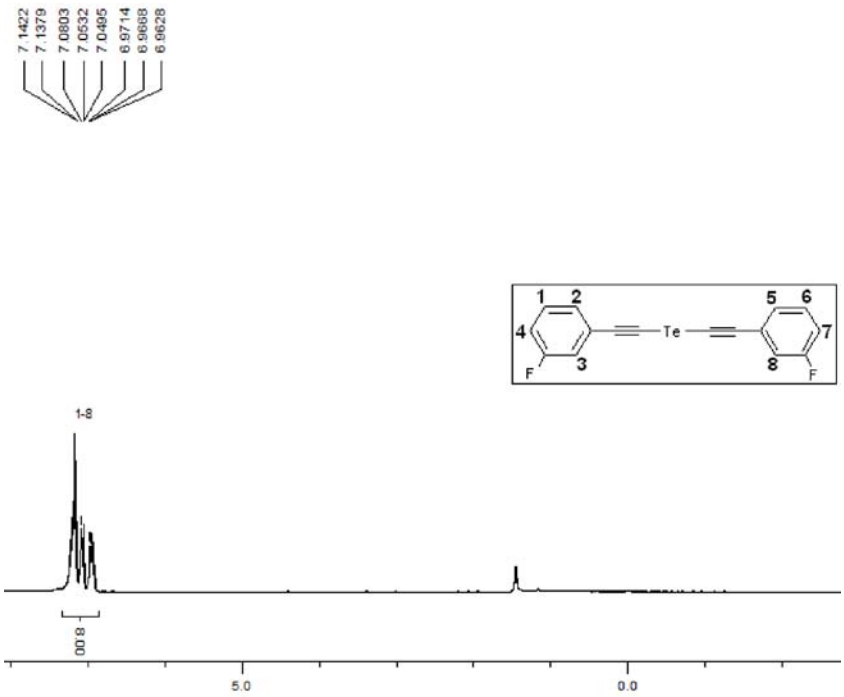

Figure S5. ^{1}H NMR ($CDCl_3$, 300 MHz) of **1c**.

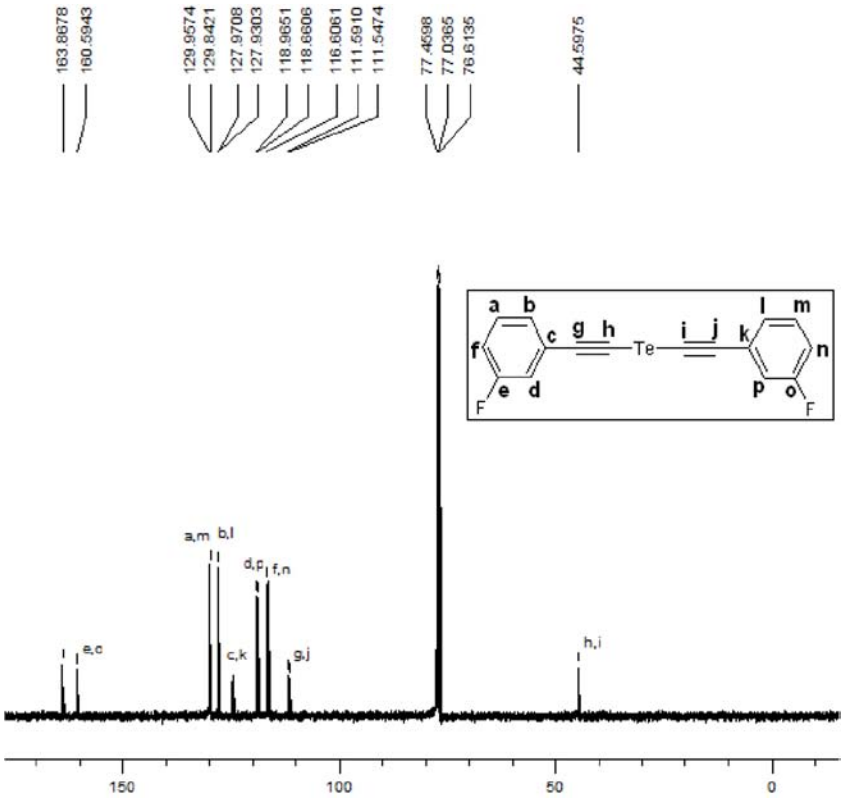

Figure S6. ^{13}C NMR ($CDCl_3$, 300 MHz) of **1c**.

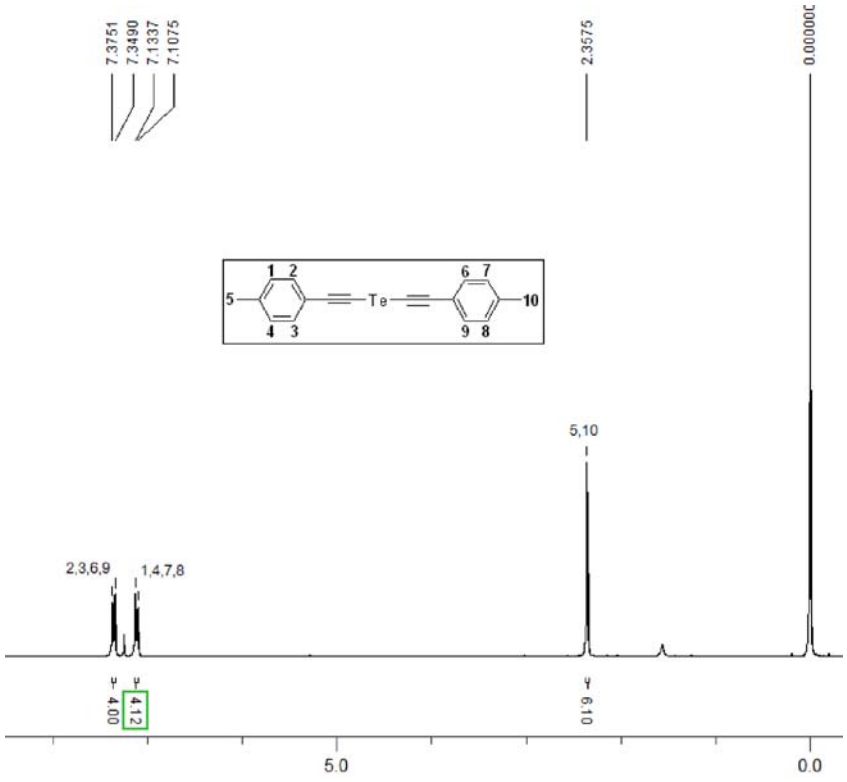

Figure S7. ^{1}H NMR ($CDCl_3$, 300 MHz) of **1d**.

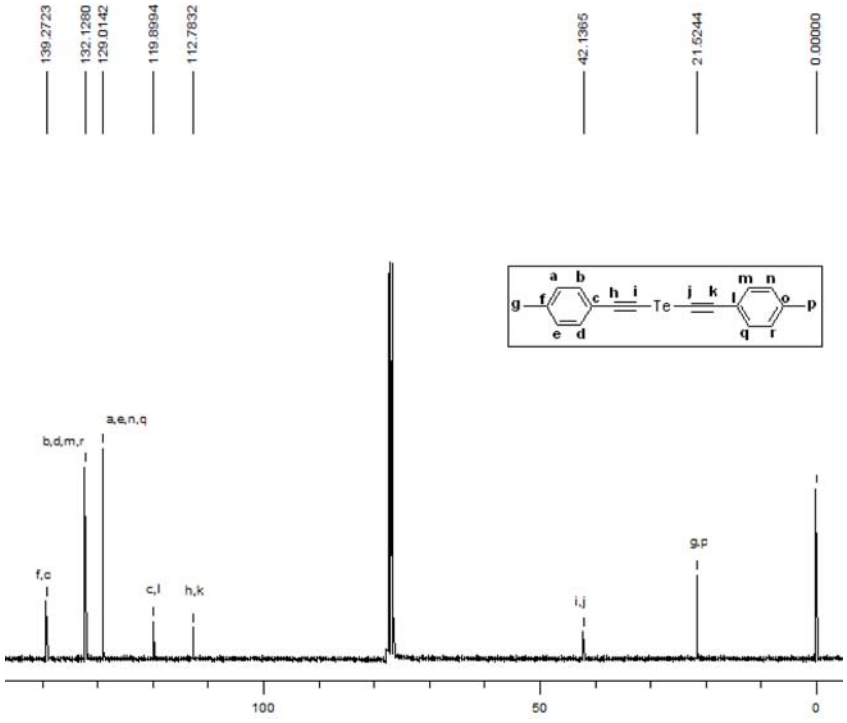

Figure S8. ^{13}C NMR ($CDCl_3$, 300 MHz) of **1d**.

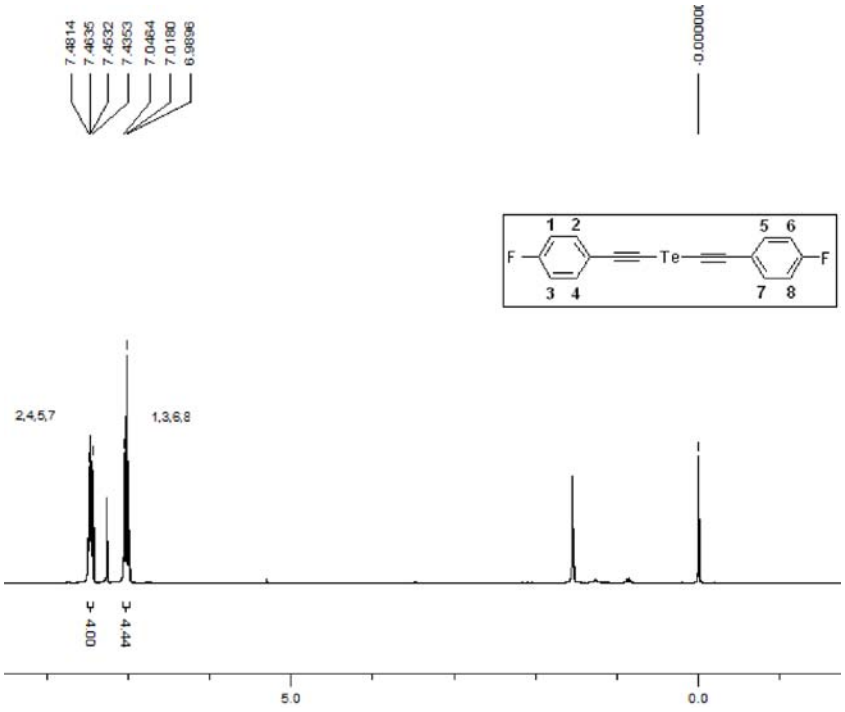

Figure S9. ^{1}H NMR ($CDCl_3$, 300 MHz) of **1e**.

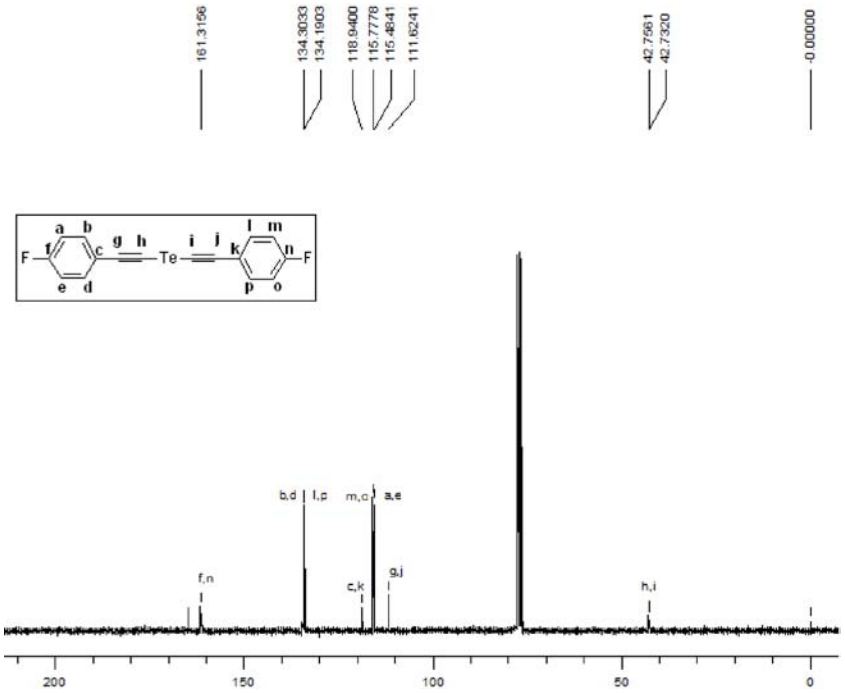

Figure S10. ^{13}C NMR ($CDCl_3$, 300 MHz) of **1e**.

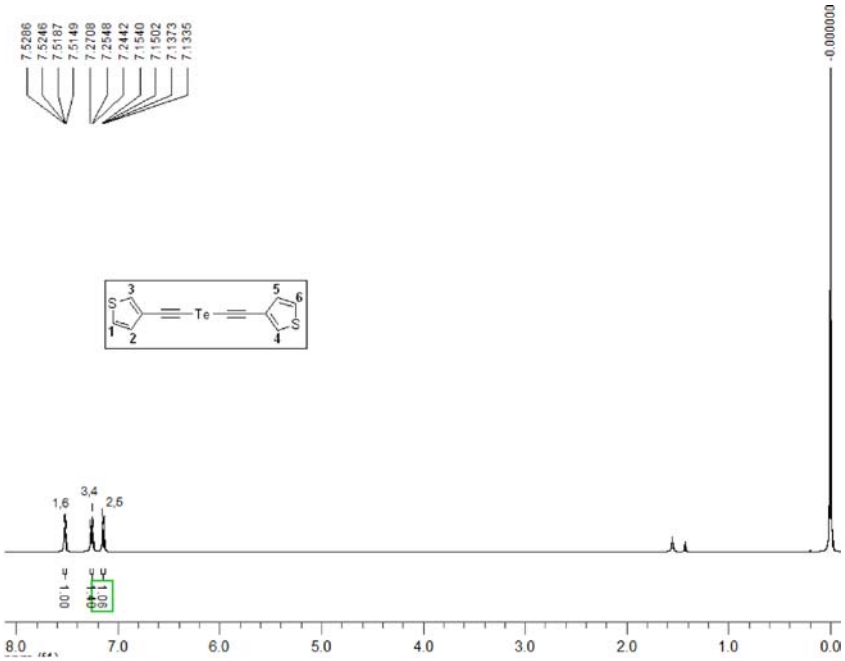

Figure S11. ^{1}H NMR ($CDCl_3$, 300 MHz) of **1f**.

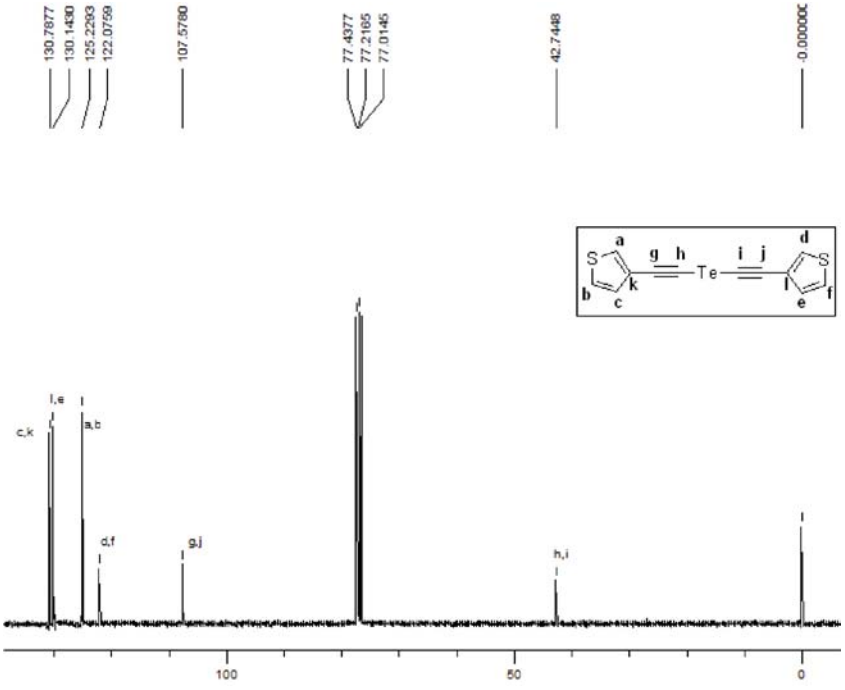

Figure S12. ^{13}C NMR ($CDCl_3$, 300 MHz) of **1f**.

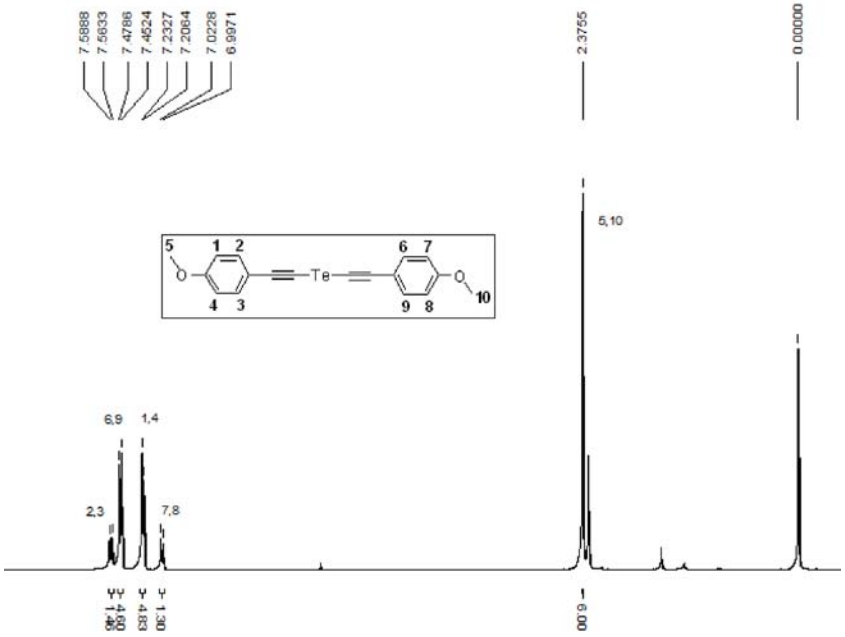

Figure S13. ^{1}H NMR ($CDCl_3$, 300 MHz) of **1g**.

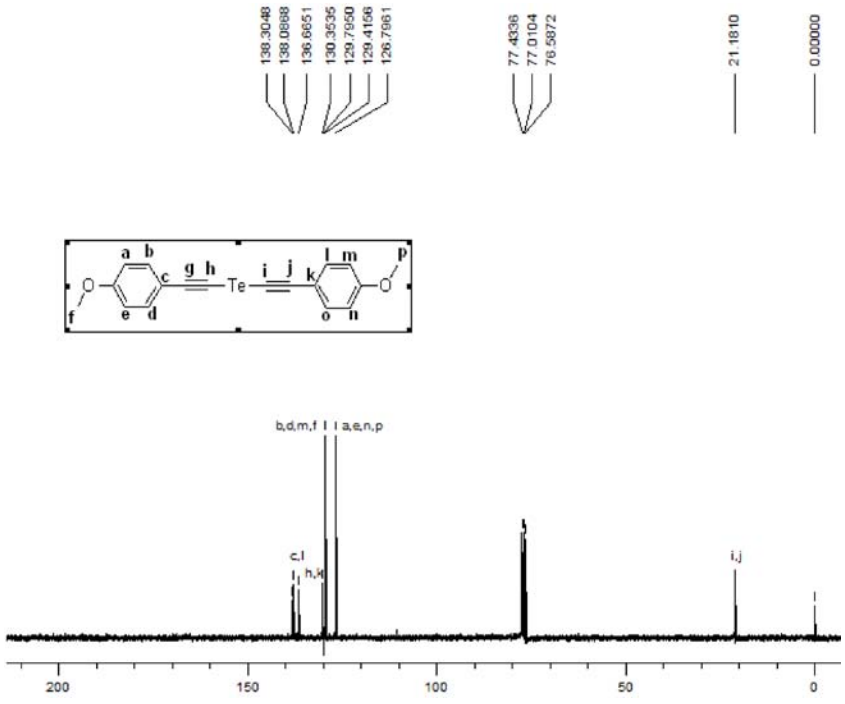

Figure S14. ^{13}C NMR ($CDCl_3$, 300 MHz) of **1g**.

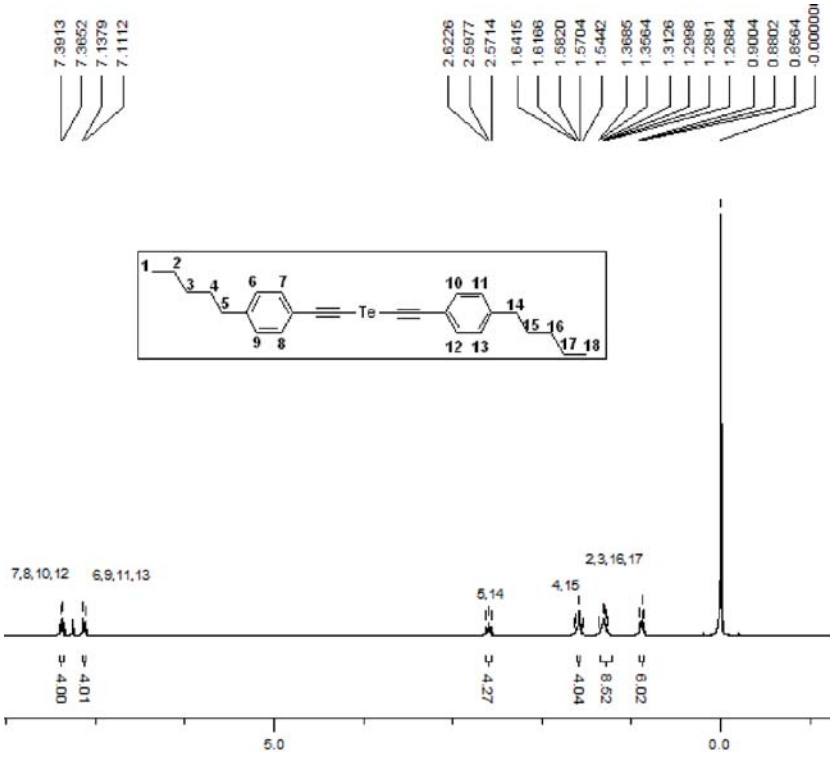

Figure S15. ^{1}H NMR ($CDCl_3$, 300 MHz) of **1h**.

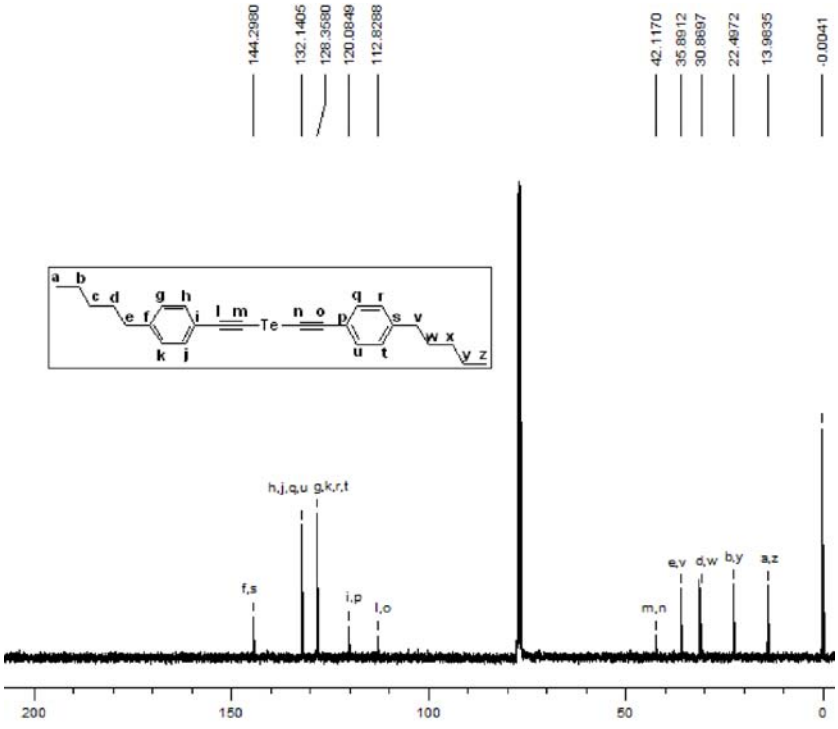

Figure S16. ^{13}C NMR ($CDCl_3$, 300 MHz) of **1h**.

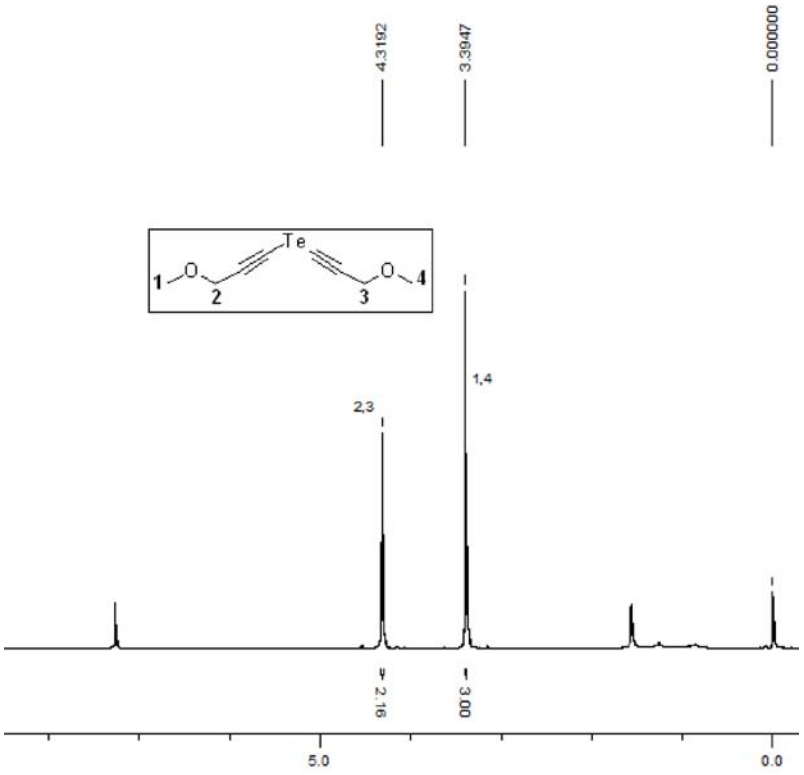

Figure S17. ^{1}H NMR ($CDCl_3$, 300 MHz) of **1i**.

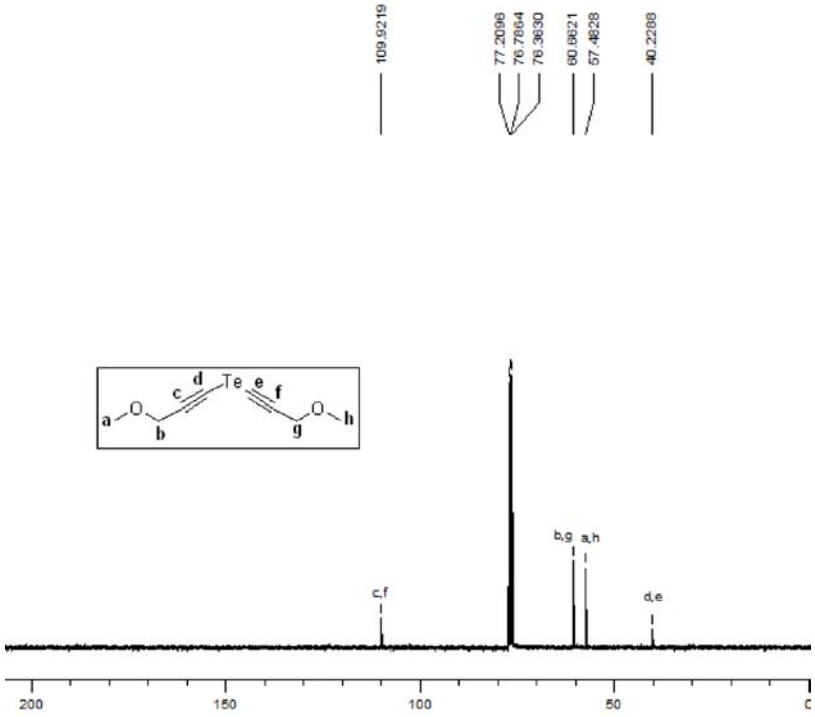

Figure S18. ^{13}C NMR ($CDCl_3$, 300 MHz) of **1i**.

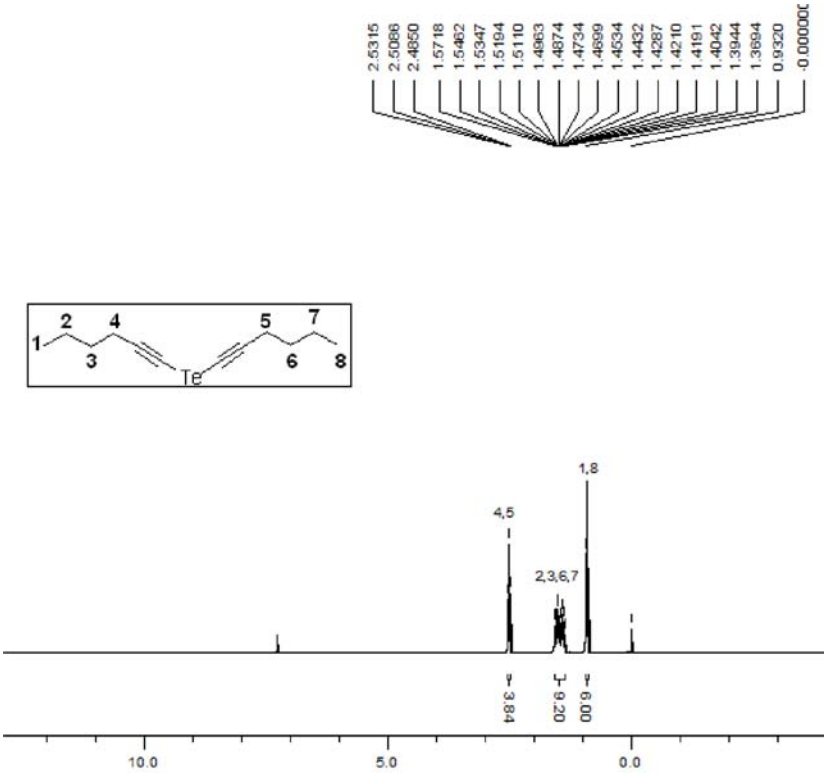

Figure S19. ^{1}H NMR ($CDCl_3$, 300 MHz) of **1j**.

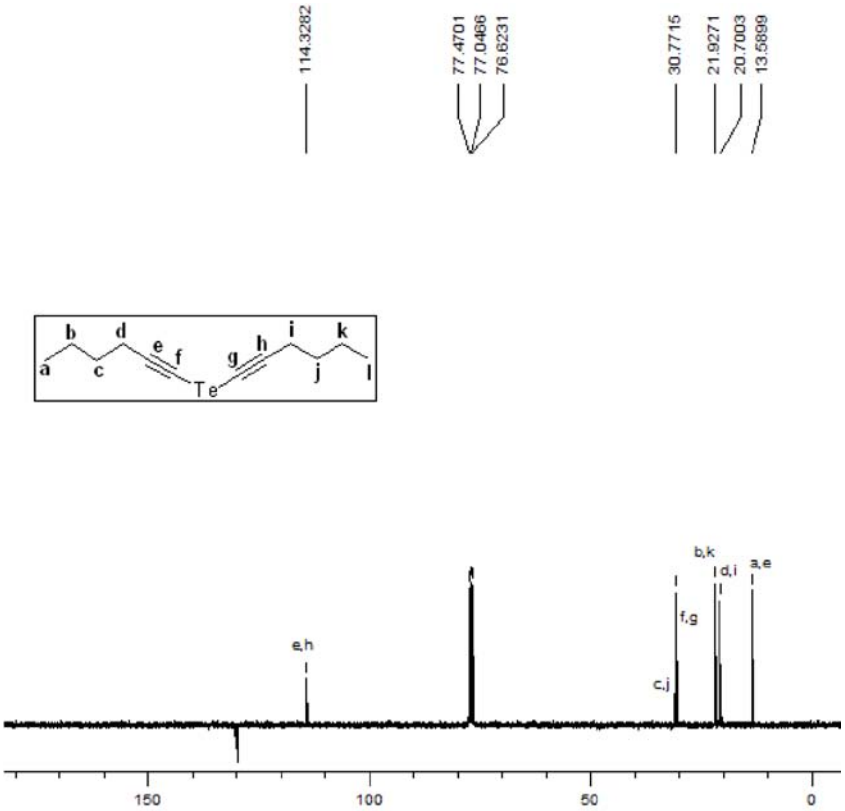

Figure S20. ^{13}C NMR ($CDCl_3$, 300 MHz) of **1j**.

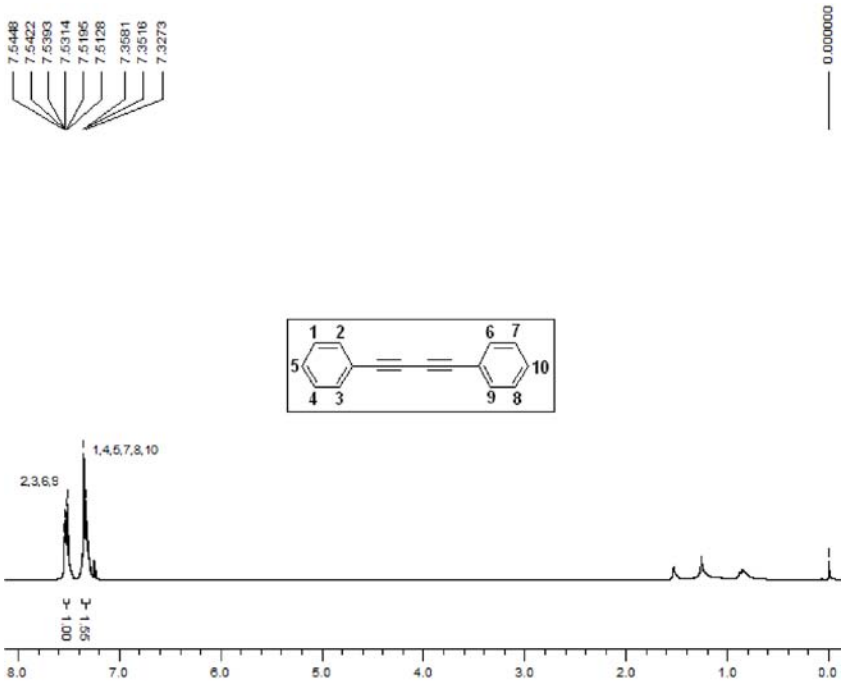

Figure S21. ^{1}H NMR ($CDCl_3$, 300 MHz) of **2a**.

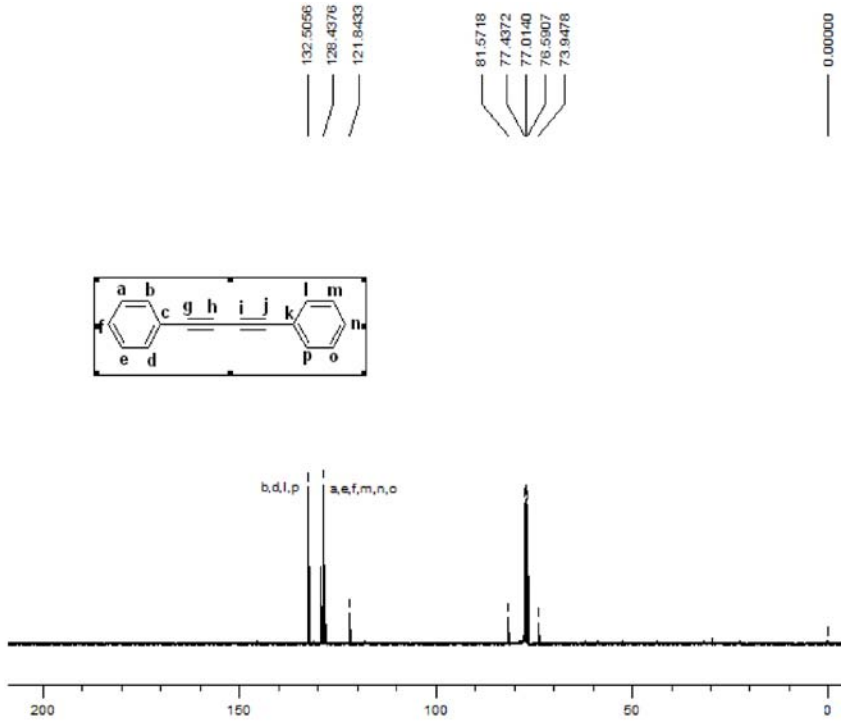

Figure S22. ^{13}C NMR ($CDCl_3$, 300 MHz) of **2a**.

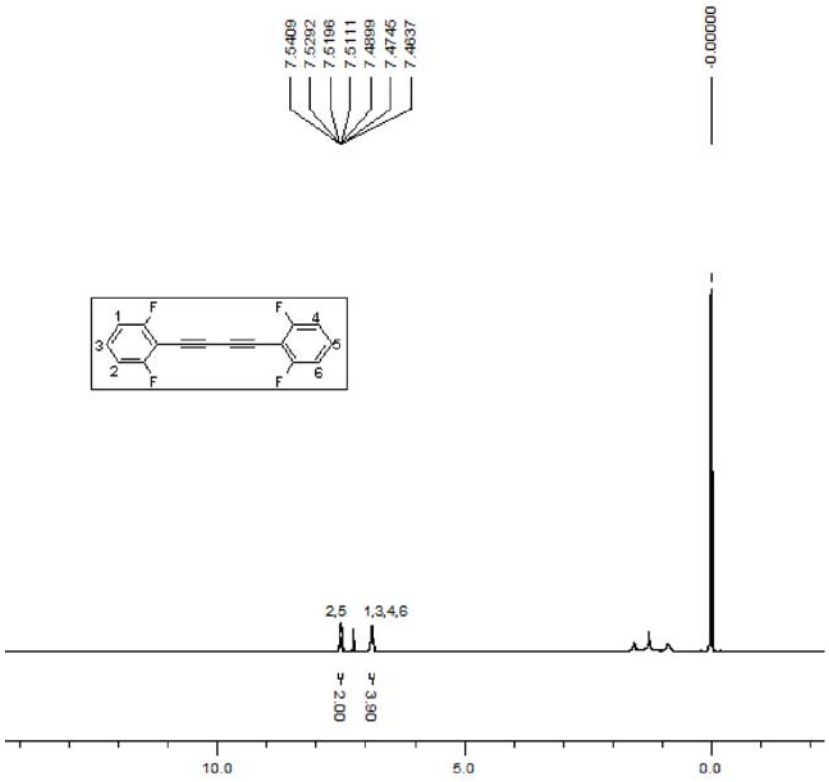

Figure S23. ^{1}H NMR ($CDCl_3$, 300 MHz) of **2b**.

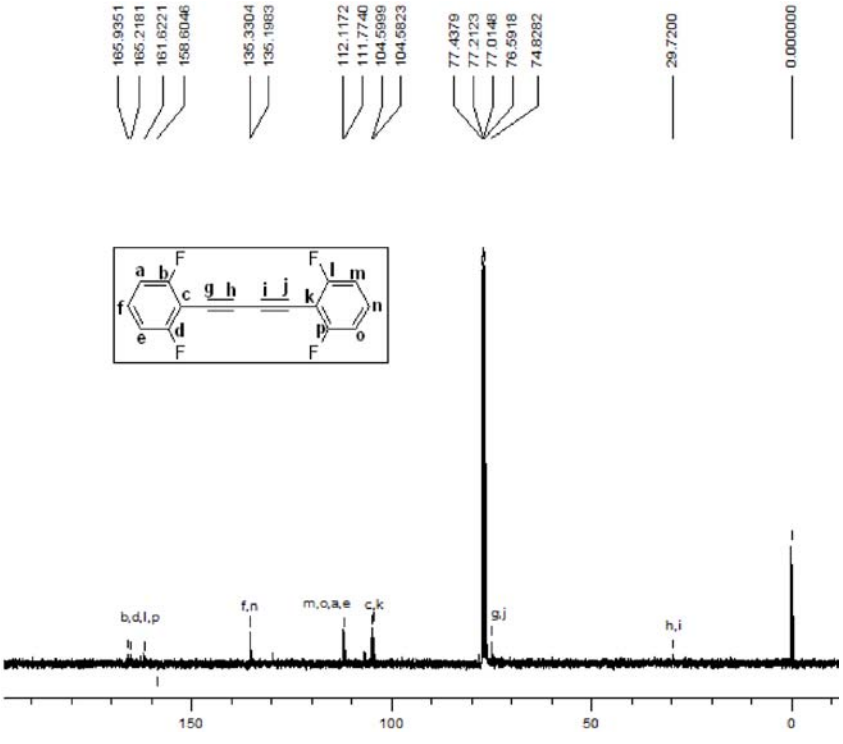

Figure S24. ^{13}C NMR ($CDCl_3$, 300 MHz) of **2b**.

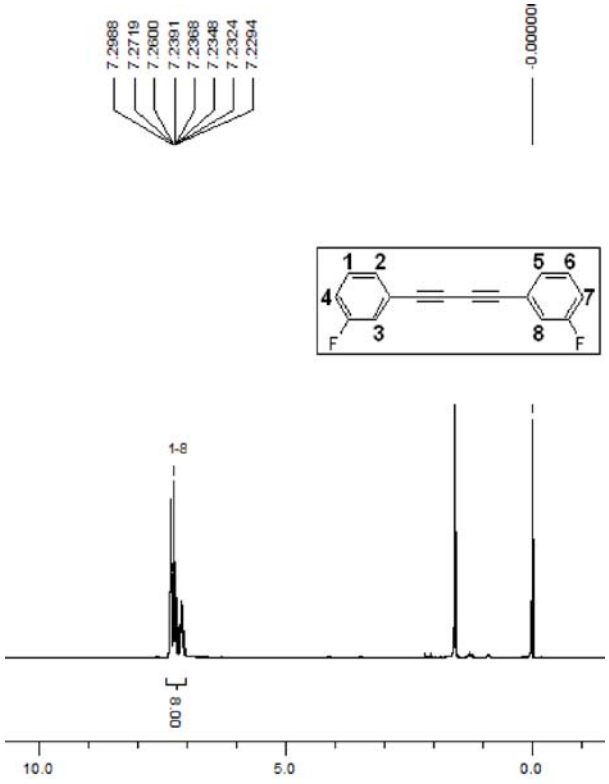

Figure S25. ^{1}H NMR ($CDCl_3$, 300 MHz) of **2c**.

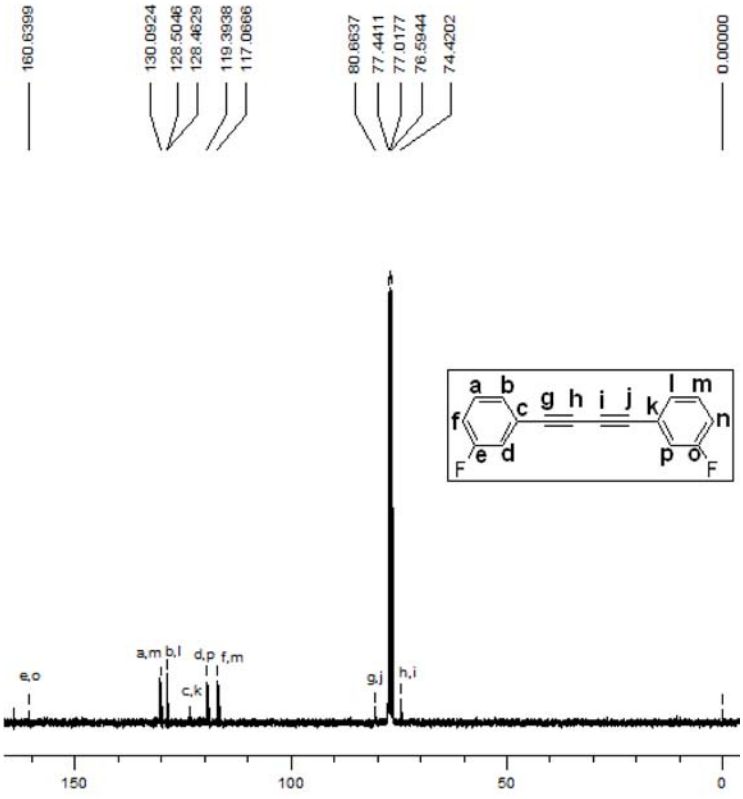

Figure S26. ^{13}C NMR ($CDCl_3$, 300 MHz) of **2c**.

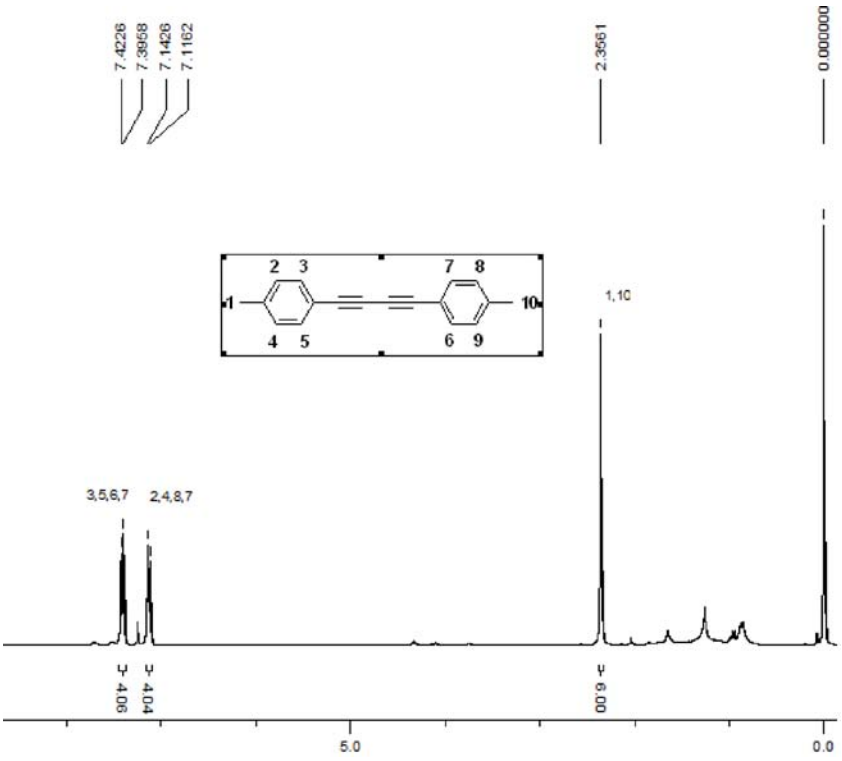

Figure S27. ^{1}H NMR ($CDCl_3$, 300 MHz) of **2d**.

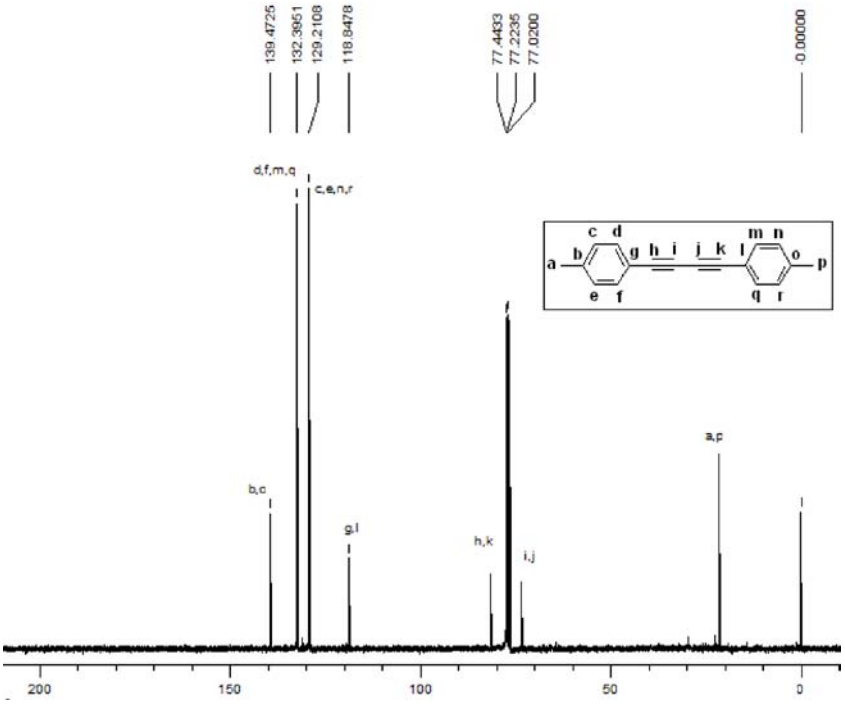

Figure S28. ^{13}C NMR ($CDCl_3$, 300 MHz) of **2d**.

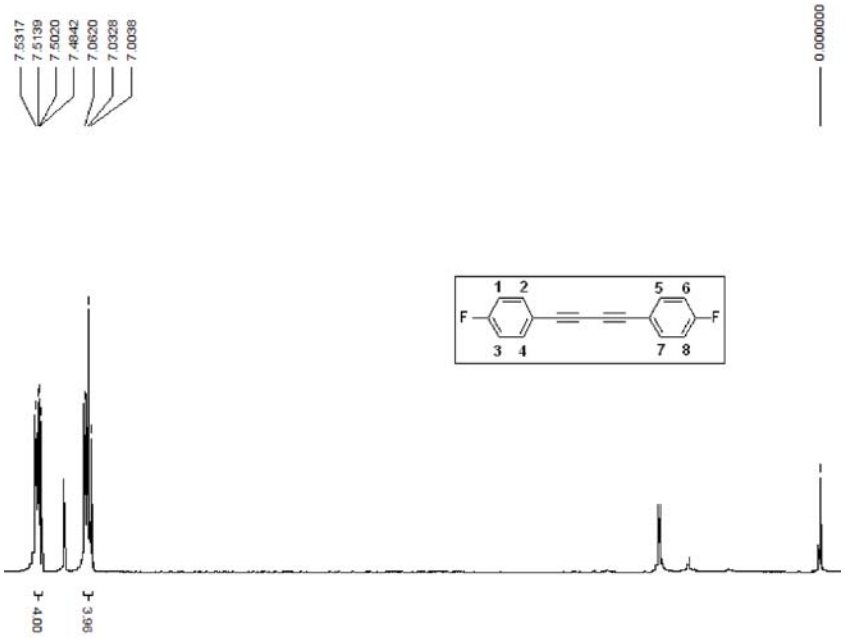

Figure S29. ^{1}H NMR ($CDCl_3$, 300 MHz) of **2e**.

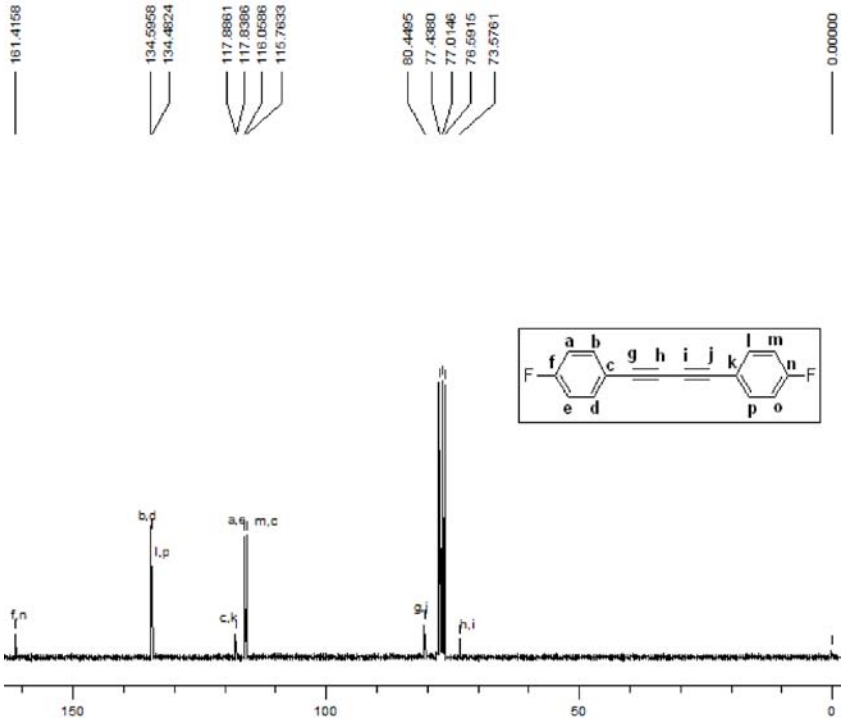

Figure S30. ^{13}C NMR ($CDCl_3$, 300 MHz) of **2e**.

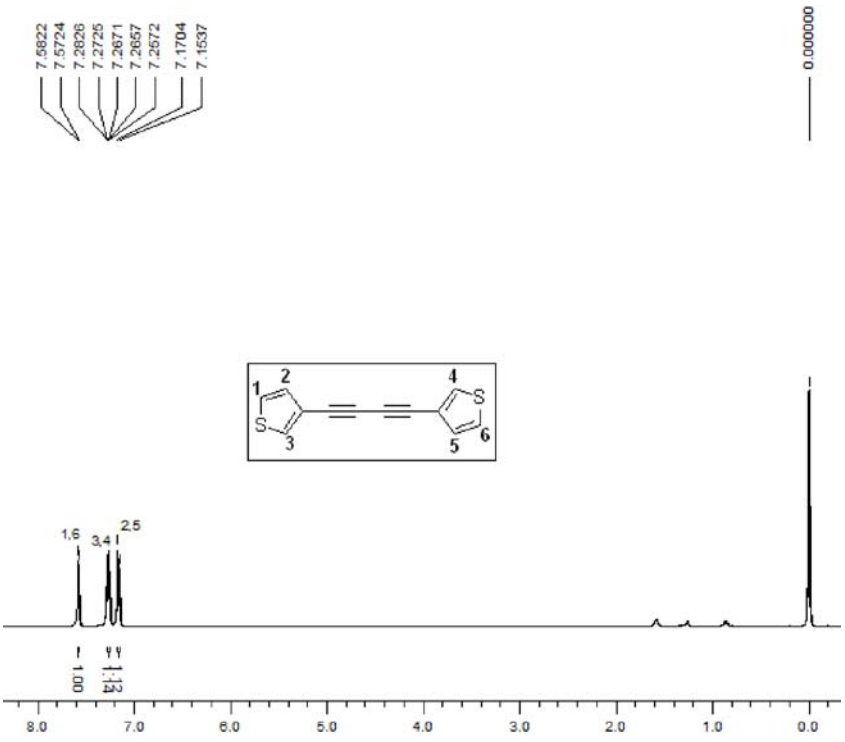

Figure S31. ^{1}H NMR ($CDCl_3$, 300 MHz) of **2f**.

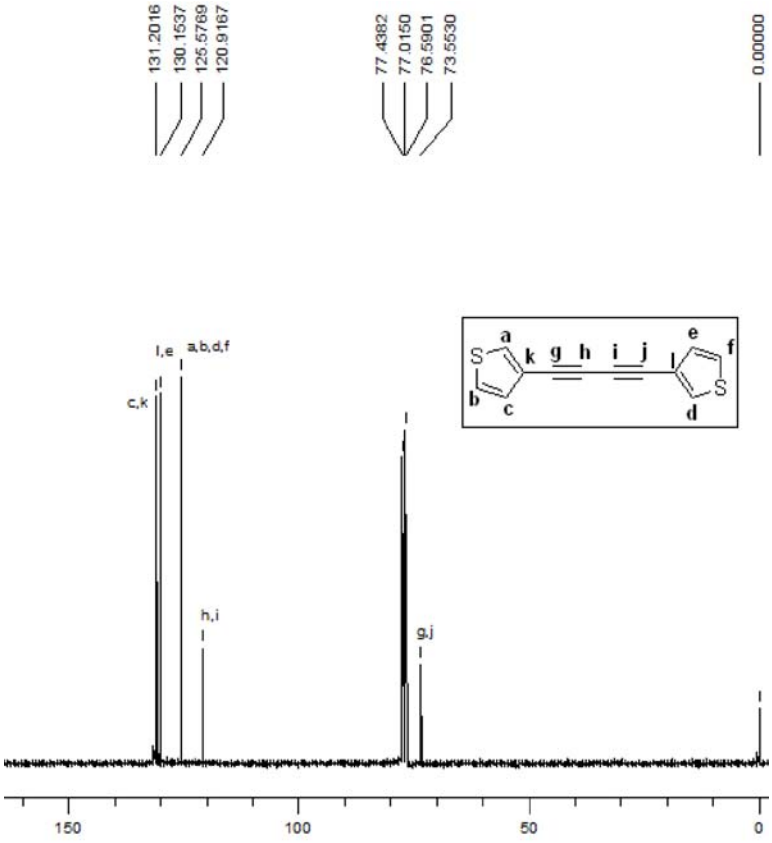

Figure S32. ^{13}C NMR ($CDCl_3$, 300 MHz) of **2f**.

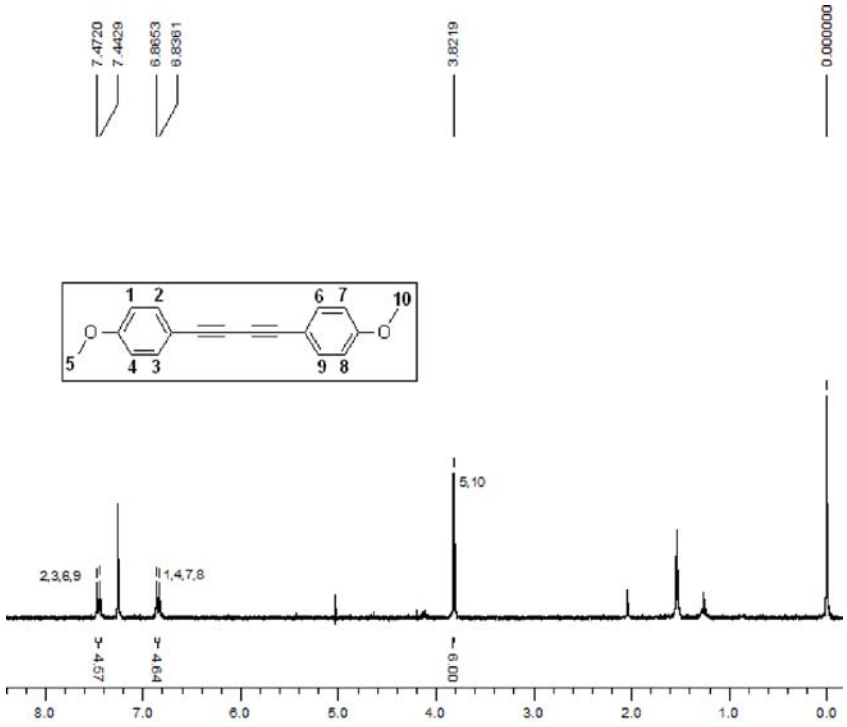

Figure S33. ^{1}H NMR ($CDCl_3$, 300 MHz) of **2g**.

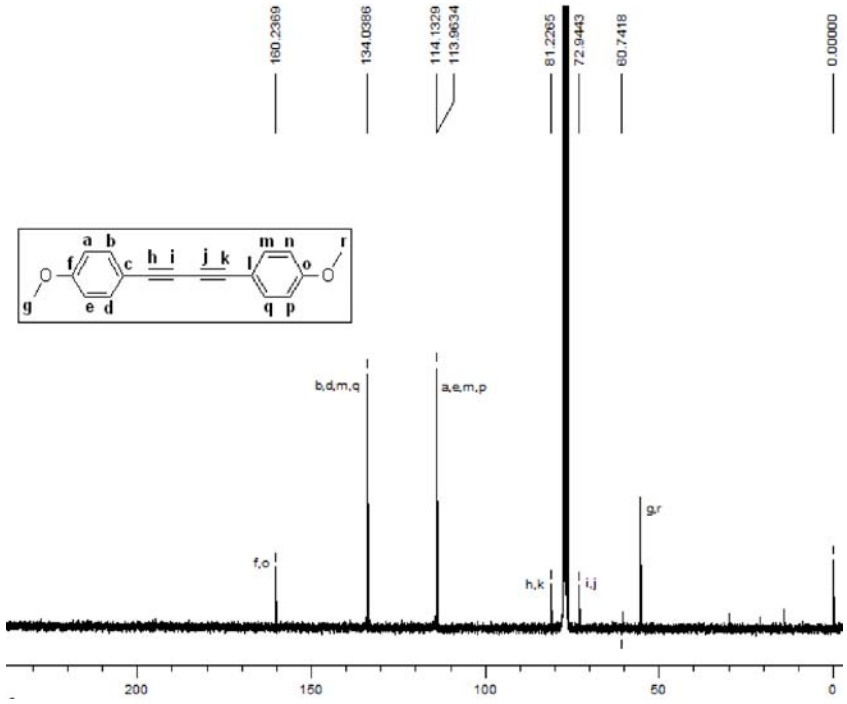

Figure S34. ^{13}C NMR ($CDCl_3$, 300 MHz) of **2g**.

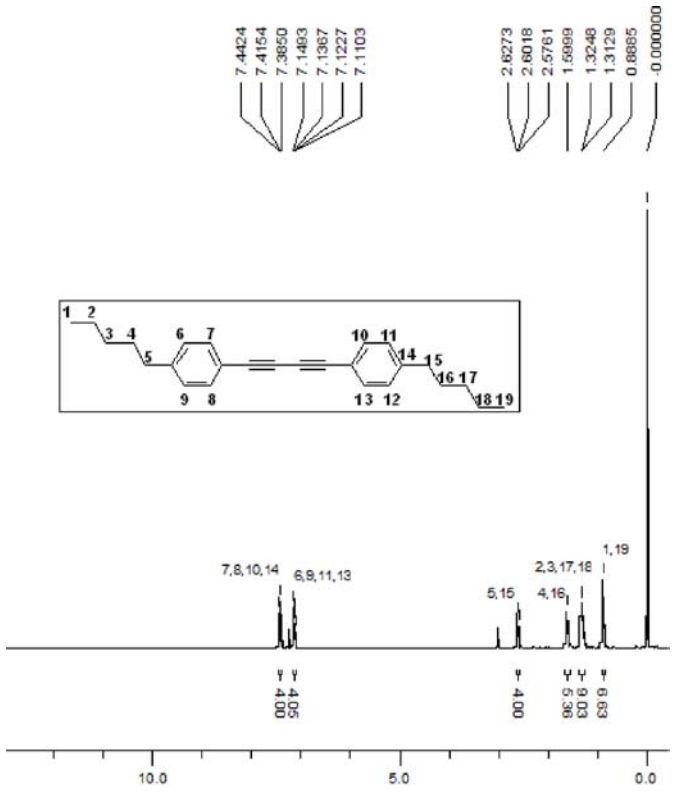

Figure S35. ^{1}H NMR ($CDCl_3$, 300 MHz) of **2h**.

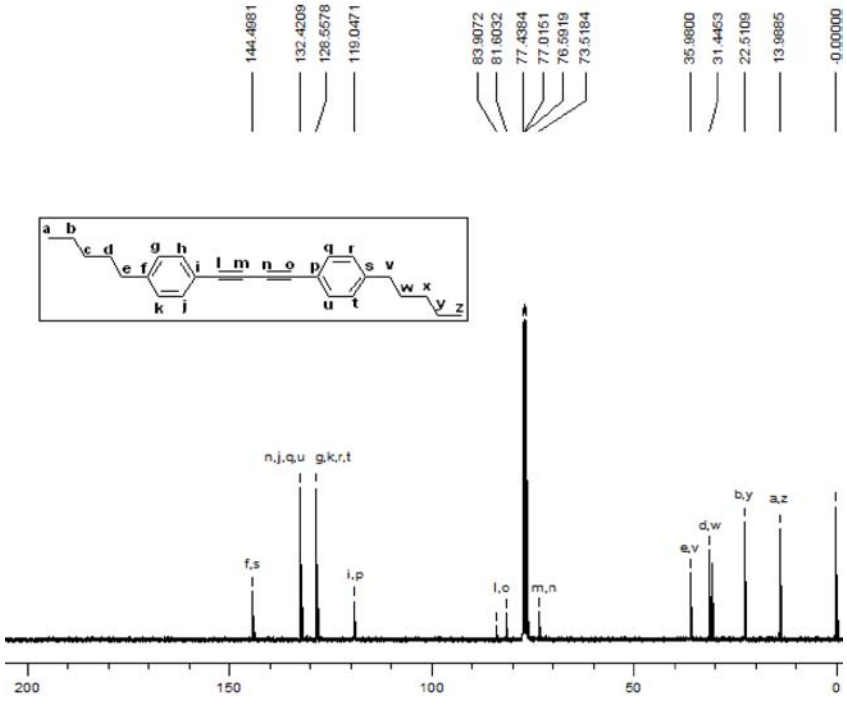

Figure S36. ^{13}C NMR ($CDCl_3$, 300 MHz) of **2h**.

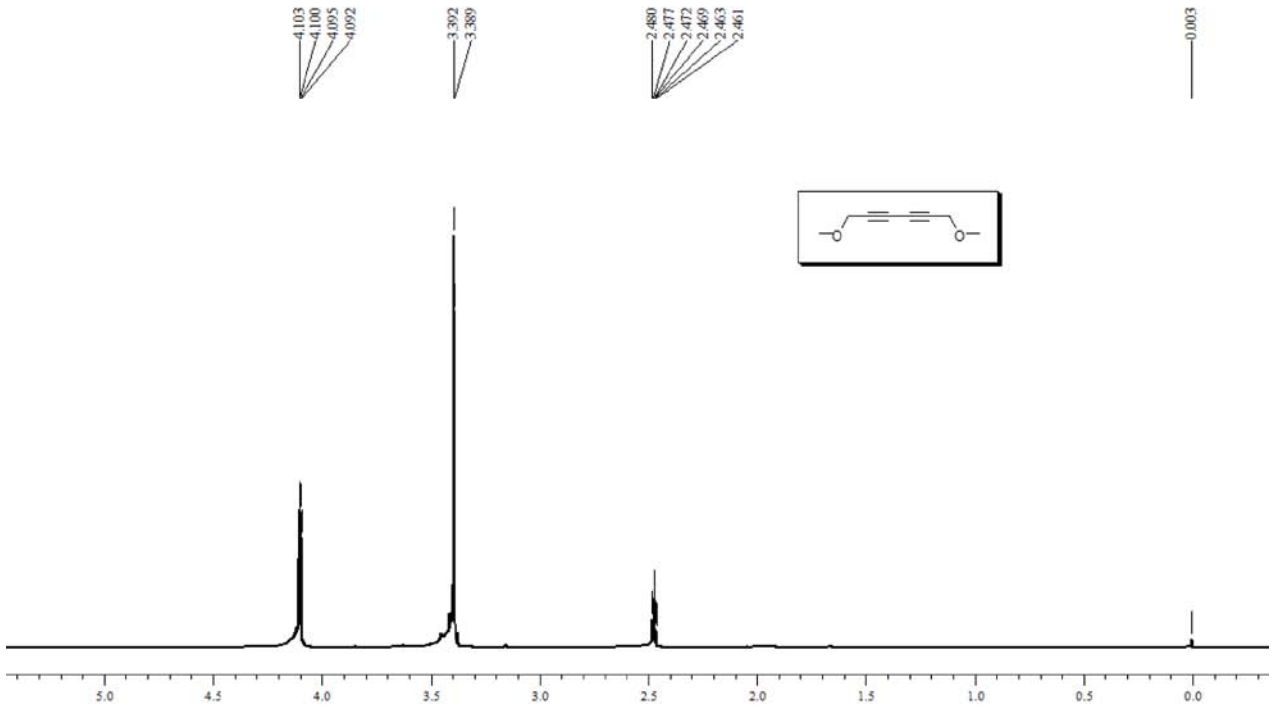

Figure S37. ^{1}H NMR ($CDCl_3$, 300 MHz) of **2i**.

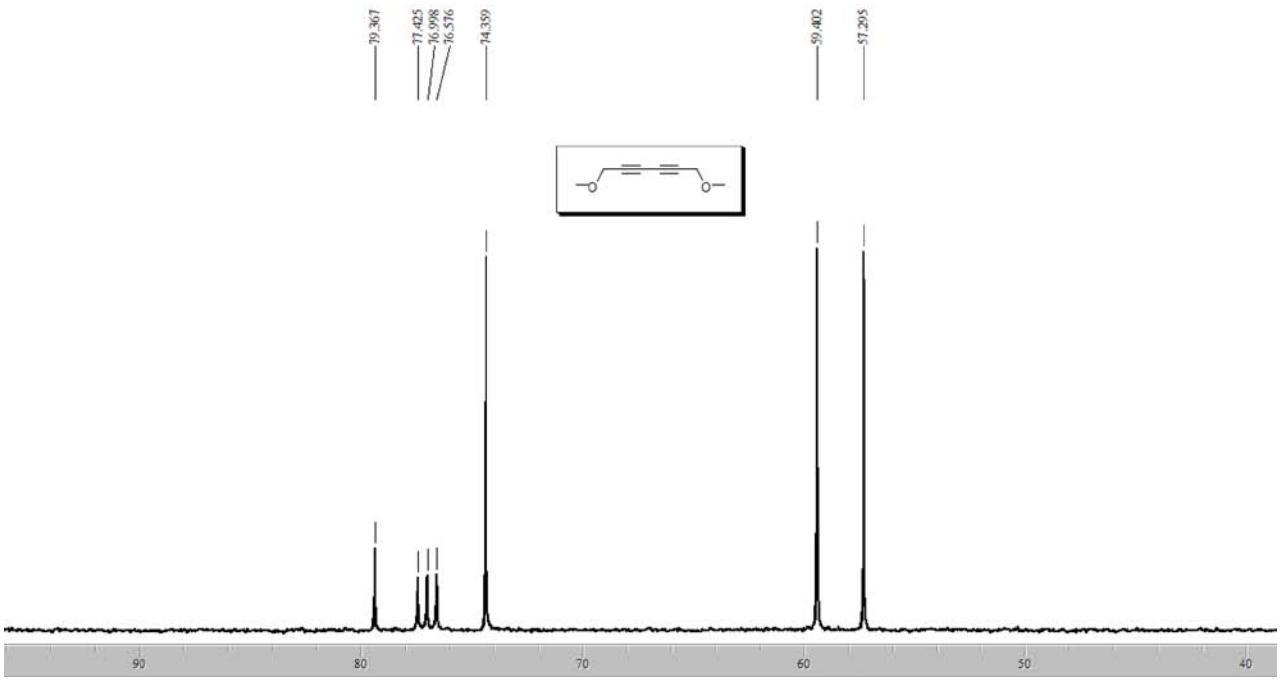

Figure S38. ^{13}C NMR ($CDCl_3$, 300 MHz) of **2i**.