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Tetrahedron
Tetrahedron 60 (2004) 3927–3934

Substituent effects on the cyclization mode of 7-sulfonyl-3-hepten-1,5-diynes and 11-sulfonylundeca-3,7-dien-1,5,9-triynes

Huey-Juan Wu, Chi-Fong Lin, Jeng-Lin Lee, Wen-Der Lu, Chia-Ying Lee, Chin-Chau Chen and Ming-Jung Wu*

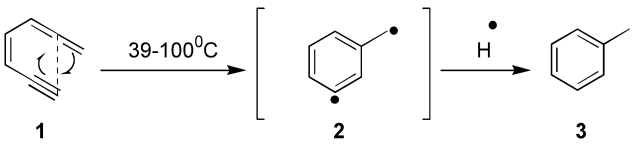
School of Chemistry, Kaohsiung Medical University, Kaohsiung, Taiwan

Received 16 July 2003; revised 16 February 2004; accepted 18 February 2004

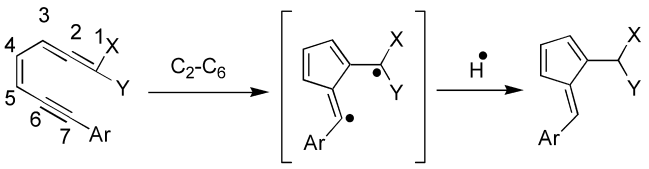
Abstract—In probing of cycloaromatization of 7-phenylsulfonyl-3-hepten-1,5-diyne systems to generate biradical intermediates under an alkaline condition suggested that the aryl moiety on C3–C4 also plays an important role to switch the Myers cyclization to Schmittel cyclization in the allen–enyne system, although the aryl group on the alkyne terminus does not work in the proceeding of the cycloaromatization. For example, treatment of 1-phenyl-7-phenylsulfonyl-3-hepten-1,5-diyne (**8**) with triethylamine in the presence of 1,4-cyclohexadiene in benzene offered biphenyl **13** in 51% yield. Under the same reaction conditions, cyclization of 1-(2-phenylethynyl)-2-(3-phenylsulfonyl-1-propynyl) benzene (**28**) gave naphthalene **34** in 42% yield along with indene **35** in 32% yield. Moreover, the substituent effect also occurred in the cyclization of 11-phenylsulfonylundeca-3,7-diene-1,5,9-triyne (**38**), which provided indene **39** in 50% yield as the major product.

1. Introduction

The modes of cyclization of enediynes and related conjugated systems to form a diradical intermediates have attracted considerable attention due to numerous biological active antitumor antibiotics proceeded via the unique diradical intermediates to cleave DNA strands.[1] In the studies of the mechanism for DNA cleavage activity of neocarzinostatin cheomophore, Myers reported that a molecule containing (*Z*)-1,2,4-heptatrien-6-yne (**1**) undergo spontaneous cyclization to give α,3-didehydrotoluene (**2**) intermediate and provided toluene (**3**) after hydrogen abstraction.[2] (Eq. 1) On the other hand, Schmittel found that a novel thermal Schmittel (C_2–C_6) cyclization was observed, while the hydrogen at the alkyne terminus was replaced with an aryl group.[3] (Eq. 2) Although the role of the aryl group is not clear, stabilization of vinyl radical was considered.



(1)



(2)

In our studies[4] on the base-catalyzed cyclization of 7-sulfonyl-3-hepten-1,5-diynes, it was found that treatment of compound **4** with triethylamine in the presence of 1,4-cyclohexadiene in benzene at room temperature for 24 h provided the Myers cyclization product **5** in 45% yield.[4] (Eq. 3) Cyclization of compound **6** as well as the same reaction conditions except at refluxing temperature gave naphthalene **7** in 30% yield.[5] (Eq. 4)

Keywords: Enynes; Radicals; Cyclization.
* Corresponding author. Tel.: +886-7-3121101x2220; fax: +886-7-3125339; e-mail address: mijuwu@cc.kmu.edu.tw

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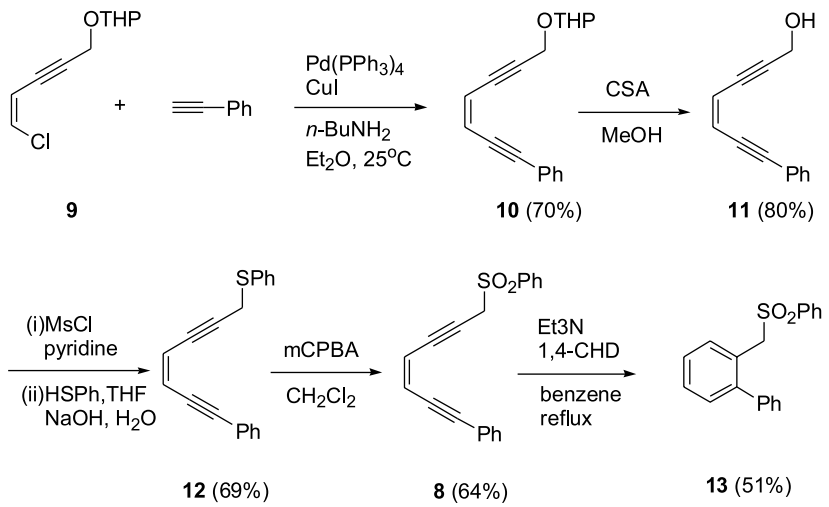
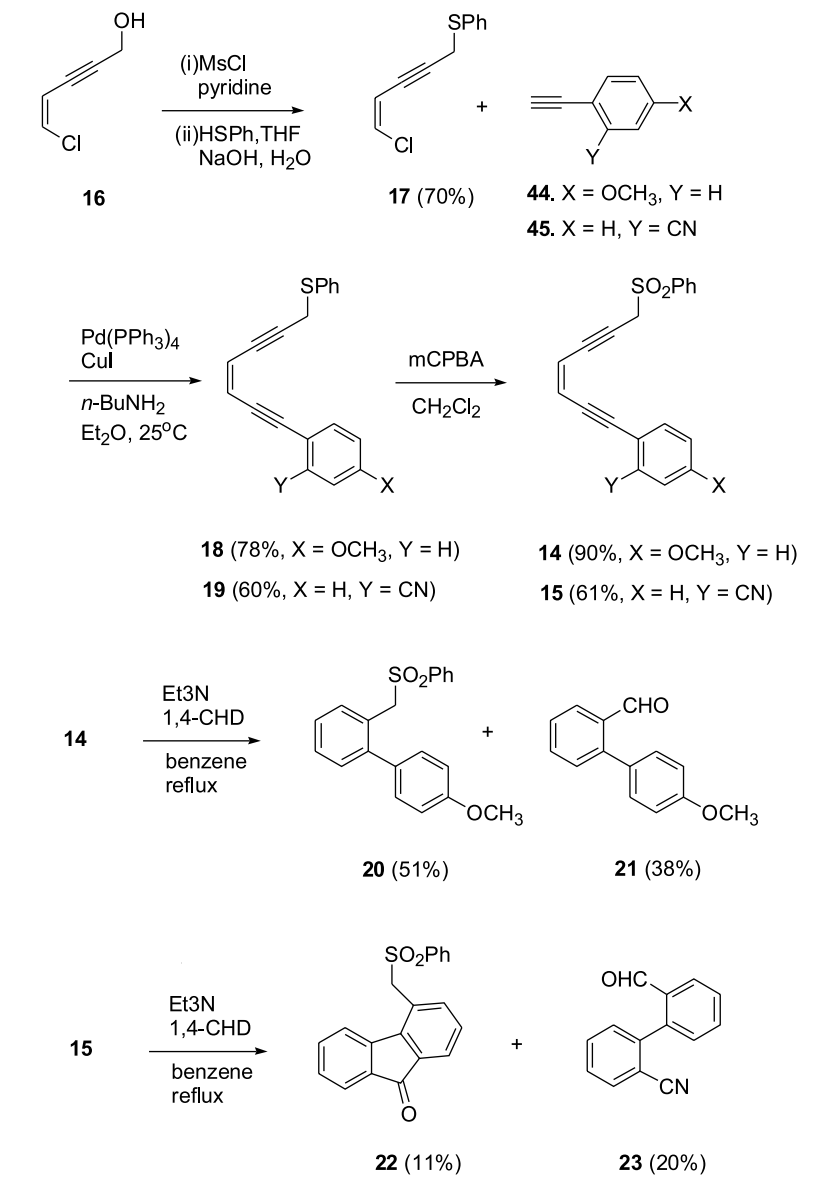
doi:10.1016/j.tet.2004.02.067



Scheme 1.



Scheme 2.

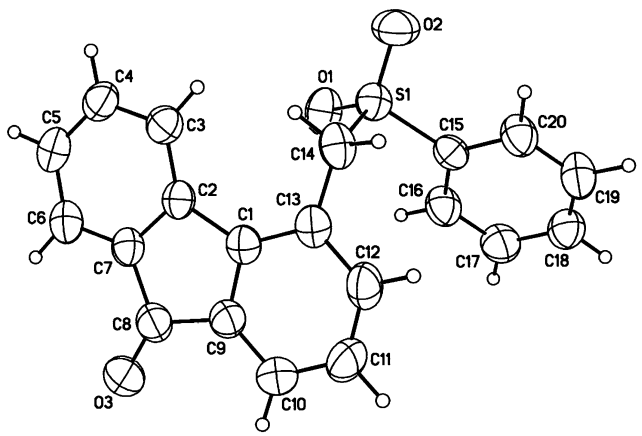
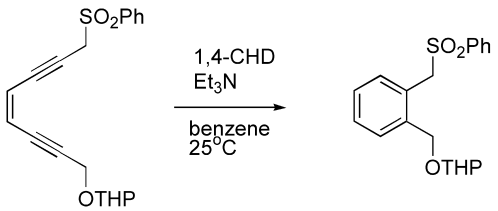
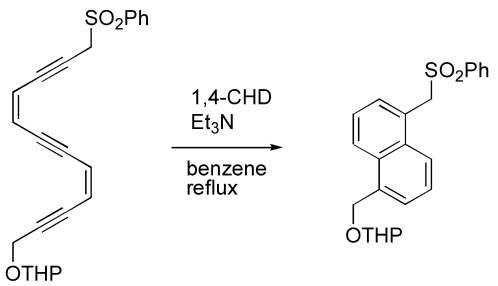


Figure 1. The X-ray crystallography of compound **22**.



(3)

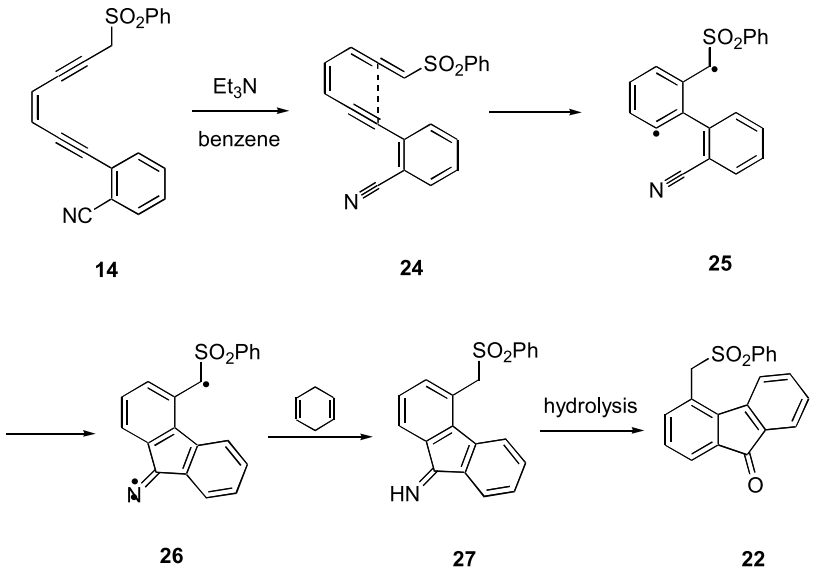


(4)

2. Result and discussion

We were then interested in the substituent effects on the alkyne terminus in this system. Thus, compound **8** was prepared as shown in Scheme 1. Palladium-catalyzed coupling reaction of vinyl chloride **9** with phenyl acetylene gave enediyne **10** in 70% yield. Treatment of **10** with catalytic amount of camphor sulfonic acid in methanol offered **11** in 80% yield. Alcohol **11** was then converted to sulfide **12** in 69% yield by a reported procedure (MsCl, pyridine; PhSH, NaOH).[4] Finally, oxidation of **12** using *m*CPBA as oxidizing agent provided compound **8** in 64% yield. Treatment of compound **8** with triethylamine in the presence of 1,4-cyclohexadiene in benzene at room temperature for 24 h yielded **13** in 51%. No Schmittel cyclization product was observed.

In order to have more insight of the substituent effects on the mode of cyclization, analogs **14** and **15** were generated, in which compound **14** bearing an electron-donating group (methoxy group) and compound **15** bearing electron-withdrawing group (cyano group) on the phenyl ring. The synthesis of **14** and **15** were outlined in Scheme 2. First of all, vinyl chloride **16** was converted to the corresponding sulfide **17** by the standard procedure as described above. Sulfide **17** was then coupled with 4-methoxyphenyl acetylene and 2-cyanophenyl acetylene using tetrakis(triphenylphosphine)palladium(0) as the cataylyst to give enediynes **18** and **19** in 78 and 60% yields, respectively. Oxidation of **18** and **19** with *m*CPBA gave sulfones **14** and **15** in 90 and 61% yields. Base-catalyzed cycloaromatization of **14** gave biphenyl **20** in 51% yield and aldehyde **21** in 38% yield. Treatment of **15** with triethylamine in the presence of 1,4-cyclohexadiene in benzene at 80 °C for 21 h gave **22** in 11% yield and **23** in 20% yield. The structure of **22** was unambigueous determined by X-ray crystallography (Fig. 1). A mechanism for the formation of **22** is proposed as outlined in Scheme 3. Base-catalyzed isomerization of propargyl sulfone **14** gave allenyl sulfone **24**. The allen–enyne system then undergoes spontaneous cyclization to give diradical intermediate **25**. The σ-radical

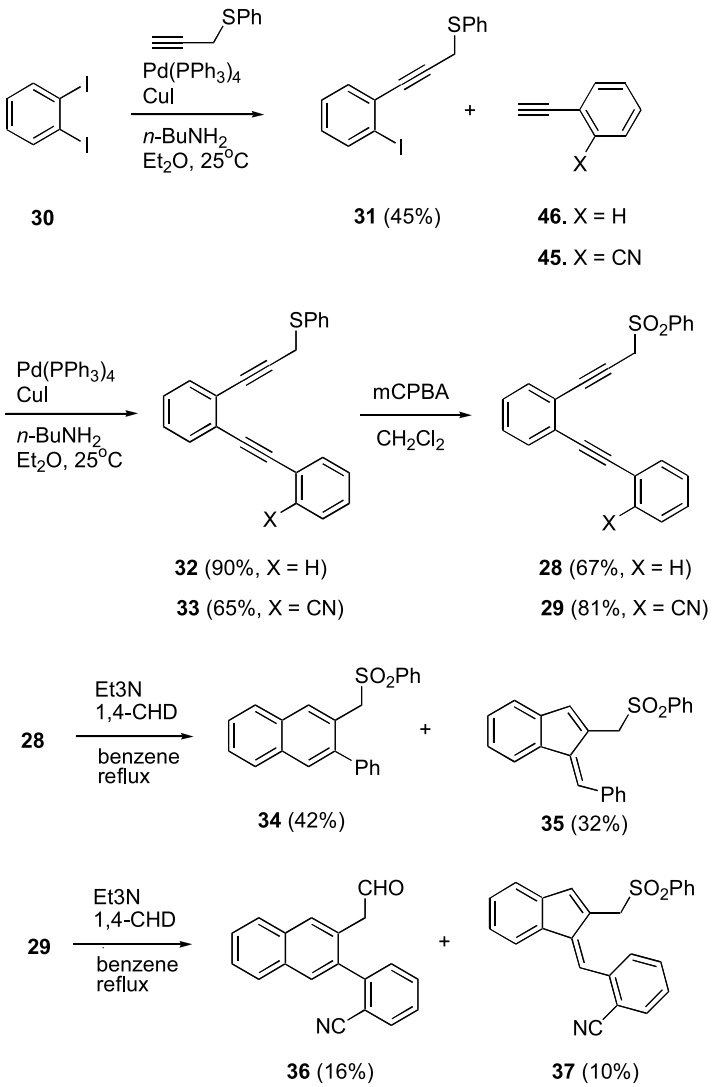


Scheme 3.

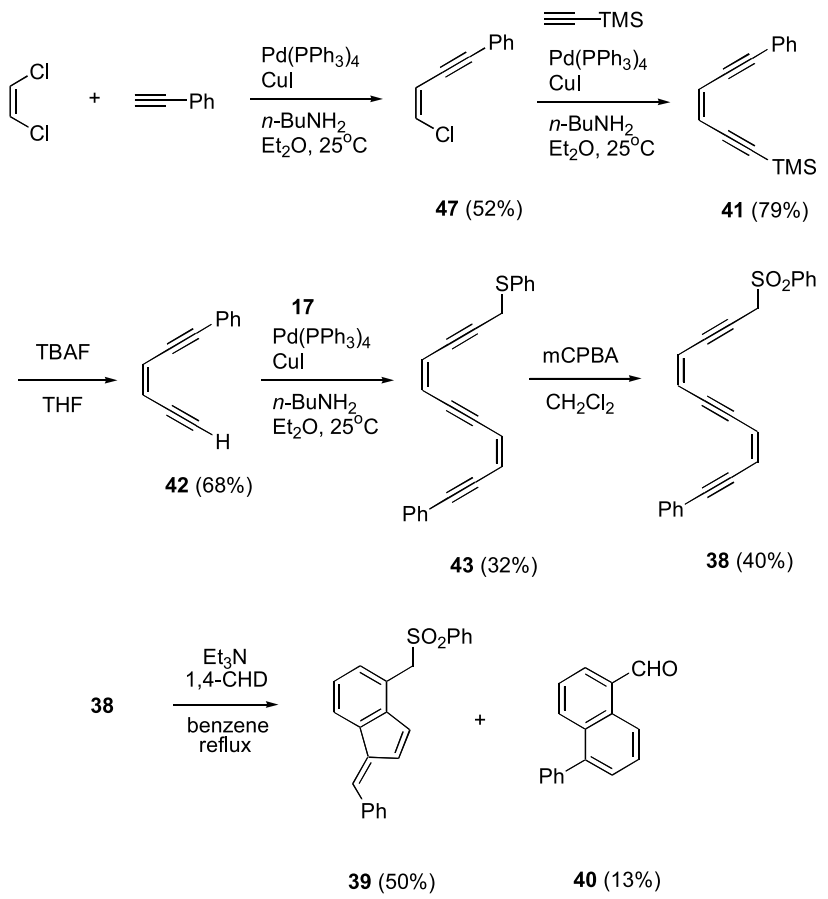
then added to the cyano group to give **26**. After hydrogen abstraction, imine **27** was formed. Hydrolysis of imine **27** during the workup gave compound **22**. All of the characterized products were formed through the pathway of Myers cyclization. The aryl substituents on the alkyne terminus seem to have no effect to switch Myers cyclization to Schmittel cyclization in this system.

On the other hand, the cyclized pathway of compounds **28** and **29** were explored. The preparation of **28** and **29** were summarized in Scheme 4. Palladium-catalyzed coupling reaction of 1,2-diiodobenzene (**30**) with propargyl sulfide offered **31** in 45% yield. Compound **31** was then coupled with phenylacetylene and 2-cyanophenylacetylene[6] gave **32** and **33** in 90 and 65% yields, respectively. Oxidation of sulfides **32** and **33** with *m*CPBA formed sulfones **28** and **29** in 67 and 81% yields, respectively. Base-catalyzed cycloaromatization of **28** gave naphthalene **34** in 42% yield and benzylidenylindene **35** in 32% yield. The formation of compound **35** was proposed to go through the pathway of Schmittel cyclization. Similar results were observed from the cyclization of **29**. Naphthalene carbaldehyde **36** was isolated in 16% yield along with indene **37** in 10% yield. The structure determination of **37** was based on the ^{1}H and ^{13}C NMR and Mass spectrometry. Using HMBC, it was observed the correlation between the quaternary carbon attached to the cyano group and the vinyl proton to confirm the structure assignment. According to the results of Schemes 2 and 4, it was suggested that the aryl group on the alkyne terminus was not the only factor to switch the cyclization mode in allen–enynes from Myers cyclization to Schmittel cyclization. The aryl moiety at C3 and C4 plays an important role to affect the mode of allen–enyne cyclization.

Further exploration of the substituent effect on the cyclization of allen–enyne conjugated systems, (*Z*,*Z*)-1-phenyl-11-phenylsulfonylundeca-3,7-diene-1,5,9-triyne (**38**) was synthesized (Scheme 5). Vinyl chloride **47** was first prepared by palladium-catalyzed coupling of *cis*-1,2-dichloroethylene with phenylacetylene in 52% yield. Treatment of **47** with trimethylsilylacetylene using tetrakis(triphenylphosphine)palladium(0) as the catalyst offered enediyne **41** in 79% yield. The TMS group was removed by treatment of **41** with TBAF in dry THF solution to give **42** in 68% yield. Compound **42** was then coupled with **17** to form



Scheme 4.



Scheme 5.

dienetriyne **43** in 32% yield. Finally, sulfone **38** was isolated in 40% yield by oxidation of **43** with *m*CPBA. Treatment of compound **38** with triethylamine and 1,4-cyclohexadiene in refluxing benzene for 22 h gave indene **39** in 50% yield and aldehyde **40** in 13% yield. By comparison of these results to that of cyclization of **6**, we predict that the phenyl group on the alkyne terminus will affect the second cyclization pathway that switch the 6-*endo* pathway to 5-*exo* manner.

3. Conclusion

In conclusion, we have found that the substituents on allen–enyne system affect the modes of cycloaromatization reaction. It is demonstrated that the phenyl group on the alkyne terminus is required to switch the Myers cyclization to Schmittel cyclization in allen–enyne conjugated systems, although that is not the only factor. The aryl moiety on C3–C4 also acts as an important role for this change. We also found that the phenyl group on the alkyne terminus on the 11-phenylsulfonylundeca-3,7-diene-1,5,9-triynes will switch the second cyclization pathway from 6-*endo* to 5-*exo* manner.

4. Experimental

4.1. General procedure for the coupling reaction of aryl or vinyl halides with terminal acetylenes (method A)

A degassed solution of aryl or vinyl halide (12 mmol) in dry ether (30 mL) containing $Pd(PPh_3)_4$ (0.8 mmol) and CuI (3.2 mmol) was added to a solution of 2-substituted-1-ethene (24 mmol) containing *n*-butylamine (34 mmol). The resulting solution was stirred for 6 h at 25 °C, quenched with saturated aqueous NH_4Cl and Na_2CO_3 solutions and extracted with EtOAc. The organic layer was separated and dried over $MgSO_4$. After filtration, the solvent was evaporated in vacuo. The residue was purified by flash chromatography to give the products.

4.2. General procedure for oxidation of the propargyl sulfides (method B)

To a solution of propargyl sulfide (1 mmol) in dry CH_2Cl_2 (15 mL), *m*CPBA (2.5 mmol) was added to the solution and stirred for 3 h at 25 °C, then quenched with saturated aqueous $NaHCO_3$ solutions and extracted with EtOAc. The organic layer was separated and dried over $MgSO_4$. After filtration, the solvent was evaporated in vacuo. The residue was purified by flash chromatography to give the products.

4.3. General method for thermolysis of enediynes (method C)

The degassed solution of enediyne (1 mmol) in benzene (0.01 M) in the presence of 1,4-cyclohexadiene (1.5 M) was treated with Et_3N (5 equiv.) at 80 °C for 24 h. The result solution was quenched with saturated aqueous NaCl solutions and extracted with EtOAc. The organic layer was separated and dried over $MgSO_4$. After filtration, the

solvent was evaporated in vacuo. The residue was purified by flash chromatography to give the products.

4.3.1. (*Z*)-1-Phenyl-7-phenylsulfonyl-3-hepten-1,5-diyne (8). Obtained in 64% yield as an oil according to method B. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.05–8.00 (m, 2H), 7.56–7.39 (m, 7H), 6.07 (d, 1H, J=11.2 Hz), 5.81 (dt, 1H, J=11.0, 2.2 Hz), 4.20 (d, 2H, J=2.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 137.7, 134.1, 131.9, 129.0, 128.9, 128.8, 128.3, 122.6, 121.6, 117.4, 97.8, 86.4, 85.0, 84.3, 49.7. MS (EI): 306 (M^+, 7), 165 (100), 139 (35), 77 (42). HRMS (EI) calcd for $C_{19}H_{14}O_2S$ 306.0717, found 306.0719.

4.3.2. (*Z*)-1-Phenyl-7-(2-tetrahydropyranyl)oxy-3-hepten-1,5-diyne (10). Obtained in 70% yield as an oil according to method A. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.51–7.30 (m, 5H), 6.02 (d, 1H, J=7.4 Hz), 5.92 (dt, 1H, J=1.8, 7.4 Hz), 4.93–4.89 (m, 1H), 4.5 (s, 2H), 3.81–3.79 (m, 1H), 3.54–3.47 (m, 1H), 1.88–1.40 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 131.7, 128.5, 128.2, 122.9, 119.8, 118.9, 96.6, 94.6, 93.3, 86.8, 83.3, 54.7, 30.6, 30.2, 25.4, 25.3. MS (EI): 266 (M^+, 7), 152 (25), 166 (54), 165 (100). HRMS (EI) calcd for $C_{18}H_{18}O_2$ 266.1313, found 266.1310.

4.3.3. (*Z*)-1-Phenyl-7-hydroxy-3-hepten-1,5-diyne (11). Obtained in 80% yield as an oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.51–7.30 (m, 5H), 6.40 (d, 1H, J=10.8 Hz), 5.92 (dt, 1H, J=1.8, 11 Hz), 4.51 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 131.7, 128.7, 128.3, 122.8, 120.1, 118.6, 112.3, 95.3, 86.7, 83.1, 51.7. MS (EI): 182 (M^+, 100), 152 (87), 153 (88). HRMS (EI) calcd for $C_{13}H_{10}O$ 182.0732, found 182.0732.

4.3.4. (*Z*)-1-Phenyl-7-(phenylthionyl)-3-hepten-1,5-diyne (12). Obtained in 90% yield as an oil according to method A. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.80–7.75 (m, 2H), 7.49–7.41 (m, 5H), 7.36–7.31 (m, 3H), 6.00 (d, 1H, J=11.0 Hz), 5.92 (dt, 1H, J=9.8, 1.8 Hz), 3.87 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) (135.2, 132.0, 130.1, 129.0, 128.7, 128.4, 126.9, 122.1, 119.9, 119.1, 96.8, 94.6, 93.6, 86.9, 81.0. MS (EI): 274 (M^+, 9), 84 (100), 49 (63), 35 (50). HRMS (EI) calcd for $C_{19}H_{14}S$ 274.0813, found 274.0805.

4.3.5. 2-(Phenylsulfonyl)methylphenylbenzene (13). Obtained in 51% yield as an solid according to general method C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.66–7.60 (m, 2H), 7.58–7.31 (m, 9H), 6.84–6.81 (m, 2H), 4.41 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 143.6, 139.6, 138.5, 133.4, 131.4, 130.2, 129.0, 128.8, 128.6, 128.4, 128.1, 127.5, 127.1, 125.4, 58.8. MS (EI): 308 (M^+, 10), 166 (45), 165 (100), 77 (48). HRMS (EI) calcd for $C_{19}H_{16}O_2S$ 308.0873, found 308.0875.

4.3.6. 2-((7-Phenylsulfonyl)-3(*Z*)-hepten-1,5-diynyl)-benzonitrile (15). Obtained in 61% yield as an oil according to method B. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.10–8.03 (m, 2H), 7.65–7.38 (m, 7H), 6.12 (d, 1H, J=10.6 Hz), 5.90 (dt, 1H, J=10.2, 2.2 Hz), 4.29 (d, 2H, J=2.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 137.8, 133.9, 132.8, 132.6, 132.4, 128.8, 128.8, 128.7, 126.4, 120.4, 120.4, 117.1, 115.0, 92.9, 92.2, 86.2, 84.3, 49.7. MS (EI): 331 (M^+, 9), 190 (100), 77 (43), 51 (22). HRMS (EI) calcd for $C_{20}H_{13}O_2SN$ 331.0667, found 331.0670.

4.3.7. (*Z*)-1-Chloro-5-phenylthionyl-1-penten-3-yne (17). Obtained in 70% yield as an oil according to method A. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.52–7.48 (m, 2H), 7.38–7.27 (m, 3H), 6.35 (d, 1H, J=8.0 Hz), 5.83 (dt, 1H, J=4.0, 8.0 Hz), 3.82 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 134.9, 130.3, 128.9, 128.8, 128.6, 126.9, 111.7, 93.7, 51.0.

4.3.8. (*Z*)-1-(4-Methoxyphenyl))-7-(phenylthionyl)-3-hepten-1,5-diyne (18). Obtained in 78% yield as an oil according to method A. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.37–7.52 (m, 9H), 6.85 (d, 2H, J=9.0 Hz), 5.98 (d, 1H, J=10.8 Hz), 5.82 (d, 1H, J=10.8 Hz), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 159.8, 135.3,133.4, 130.0, 128.9, 126.8, 120.0, 118.0, 115.1, 114.1, 113.9, 93.2, 85.9, 81.3, 77.3, 55.2. MS (EI): 304 (M^+, 33), 196 (16), 152 (53), 195 (100). HRMS (EI) calcd for $C_{20}H_{16}SO$ 304.0919, found 304.0920.

4.3.9. 2-(7-Phenylthionyl)-3(*Z*)-hepten-1,5-diynylbenzonitrile (19). Obtained in 60% yield as an oil according to method A. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.63–7.33 (m, 9H), 6.09–5.92 (m, 2H), 3.91 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 135.1, 132.6, 132.5, 132.1, 129.5, 128.6, 128.4, 127.3, 126.4, 121.4, 118.4, 117.1, 114.7, 95.3, 92.7, 92.1, 80.4, 58.9. MS (EI): 299 (M^+, 54), 298 (55), 190 (100). HRMS (EI) calcd for $C_{20}H_{13}SN$ 299.0769, found 299.0767.

4.3.10. 2-(Phenylsulfonylmethyl)phenyl-4-methoxybenzene (20). Obtained in 51% yield as an oil according to method C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.62–7.33 (m, 2H), 7.58–7.32 (m, 7H), 6.78 (m, 4H), 4.41 (s, 2H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 158.7, 143.4, 138.6, 133.4, 132.1, 131.4, 130.4, 130.2, 128.8, 128.6, 128.5, 128.5, 127.3, 125.6, 113.5, 112.0, 58.9, 55.2. MS (EI): 338 (M^+, 18), 198 (42), 165 (60), 197 (100). HRMS (EI) calcd for $C_{20}H_{18}SO_3$ 338.0979, found 338.0977.

4.3.11. 2-(4-Methoxyphenyl)benzaldehyde (21). Obtained in 38% yield as an oil according to method C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 9.99 (s, 1H), 7.99 (s, 1H), 7.64–7.60 (m, 1H), 7.48–7.42 (m, 2H), 7.32–7.30 (m, 2H), 7.01–6.99 (m, 2H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 192.6, 133.5, 133.4, 132.4, 131.3, 131.2, 130.7, 127.6, 127.3, 113.9, 112.0, 55.4. MS (EI): 212 (M^+, 100), 115 (32), 141 (45). HRMS (EI) calcd for $C_{14}H_{12}O_2$ 212.0835, found 212.0837.

4.3.12. 1-Phenylsulfonylmethylfluorenone (22) and 2-(2-formylphenyl)benzonitrile (23). Compound **22** was obtained in 11% yield as an oil and compound **23** was obtained in 20% yield as an solid according to general method C. Compound **22**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.72–7.62 (m, 2H), 7.57–7.39 (m, 10H), 4.69 (s, 2H); MS (EI): 334 (M^+, 12), 305 (35), 213 (100), 77 (61). HRMS (EI) calcd for $C_{20}H_{14}O_3S$ 334.0664, found 334.0660. Compound **23**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.47 (s, 1H), 8.00–7.90 (m, 2H), 7.78 (d, 1H, J=8.0 Hz), 7.70–7.50 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 190.8, 143.0, 137.7, 137.6, 135.4, 131.0, 130.4, 130.0, 129.1, 128.8, 128.3, 126.7, 124.5, 120.5. MS (EI): 207 (M^+, 25), 206 (100), 152 (49), 57 (67). HRMS (EI) calcd for $C_{14}H_9ON$ 207.0684, found 207.0683.

4.3.13. 1-(2-Phenylethynyl)-2-(3-phenylsulfonylpropynyl)benzene (28). Obtained in 67% yield as an oil according to method B. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.03 (td, 2H, J=8.0, 1.4 Hz), 7.56–7.45 (m, 6H), 7.36–7.25 (m, 6H), 4.26 (s, 2H); MS (EI): 356 (M^+, 13), 216 (18), 215 (100), 213 (25), 149(13). HRMS (EI) calcd for $C_{23}H_{16}O_2S$ 356.0872, found 356.0877.

4.3.14. 2-(2-(2-(3-Phenylsulfonylpropynyl)phenyl)-ethynyl)benzonitrile (29). Obtained in 81% yield as a solid according to method B. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.04–8.01 (m, 2H), 7.69–7.60 (m, 4H), 7.59–7.31 (m, 7H), 4.37 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 137.9, 133.9, 133.8, 132.7, 132.5, 132.4, 129.0, 128.9, 128.8, 128.7, 128.4, 126.8, 124.9, 124.4, 117.3, 115.0, 92.8, 89.3, 85.5, 81.7, 49.7. Anal. Calcd for $C_{24}H_{15}O_2SN$: C, 75.57; H, 3.97; N, 3.68. Found: C, 75.57; H, 3.97; N, 3.65.

4.3.15. 2-(3-Phenylthionylpropynyl)iodobenzene (31). Obtained in 45% yield as an oil according to method A. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.75 (d, 1H, J=8.2 Hz), 7.58–7.53 (m, 2H), 7.37–7.27 (m, 5H), 7.14 (dt, 1H, J=2.0, 8.4 Hz), 3.92 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 138.6, 135.1, 132.8, 130.2, 129.4, 129.3, 128.9, 127.6, 126.8, 100.6, 89.2, 85.3, 50.1. MS (EI): 349 (M^+, 83), 123 (52), 114 (66), 241 (100). HRMS (EI) calcd for $C_{18}H_{18}O_2$ 349.9625, found 349.9627.

4.3.16. 2-(2-Phenylethynyl)-1-(3-phenylthiopropynyl)-benzene (32). Obtained in 90% yield as an oil according to method A. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.95 (td, 2H, J=8.0, 1.4 Hz), 7.59–7.40 (m, 6H), 7.30–7.21 (m, 6H), 3.84 (s, 2H); MS (EI): 324 (M^+, 10), 215 (70), 213 (100), 149 (13). HRMS (EI) calcd for $C_{23}H_{16}S$ 324.0974, found 324.0970.

4.3.17. 2-(2-(2-(3-Phenylthiopropynyl)phenyl)ethynyl)-benzonitrile (33). Obtained in 65% yield as an oil according to method A. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.67–7.16 (m, 13H), 3.98 (d, 2H, J=4.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 135.4, 132.7, 132.6, 132.5, 132.3, 132.2, 130.1, 128.8, 128.8, 128.2, 127.9, 127.0, 126.7, 125.7, 124.5, 117.5, 115.0, 94.4, 90.3, 88.9, 81.7, 46.2. MS (EI): 349 (M^+, 35), 240 (100), 238 (53), 109 (81). HRMS (EI) calcd for $C_{24}H_{15}SN$ 349.0921, found 349.0921.

4.3.18. 3-Phenyl-2-phenylsulfonylmethylnaphthalene (34) and 2-phenylsulfonyl methylene-1-benzylidene-indene (35). Compound **34** was obtained in 42% yield and compound **35** was obtained in 32% yield as an solid according to general method C. Compound **34**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.53 (s, 1H), 7.89 (dd, 2H, J=7.2, 1.6 Hz), 7.68–7.31 (m, 13H), 4.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 146.4, 139.4, 134.2, 133.9, 133.5, 133.2, 132.6, 131.7, 129.9, 129.3, 129.3, 129.0, 128.9, 128.8, 128.5, 128.2, 127.8, 54.5. MS(EI): 358 (M^+, 10), 215 (100), 149 (32). HRMS (EI) calcd for $C_{23}H_{18}O_2S$ 358.1028, found 358.1023. Compound **35**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.83 (dd, 2H, J=7.0, 1.6 Hz), 7.81–7.16 (m, 11H), 6.98–6.90 (m, 2H), 6.81 (s, 1H), 4.41(s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 142.2, 139.0, 138.4, 135.8, 135.4, 134.5, 133.7, 132.6, 129.2, 128.9, 128.9, 128.8, 128.4, 128.3, 128.1, 125.7, 121.2, 55.4. HRMS (EI) calcd for $C_{23}H_{18}O_2S$ 358.1028, found 358.1027.

4.3.19. 2-(2-(3-Formylnaphthonyl))benzonitrile (36) and 2-phenylsulfonylmethylene-1-(2-cycnobenzylidene)-indene (37). Compound **36** was obtained in 16% yield as an oil and compound **37** was obtained in 10% yield as an solid according to general method. Compound **36**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.49 (s, 1H), 9.13 (dd, 1H, J=7.6, 1.2 Hz), 8.50 (s, 1H), 8.33 (dd, 1H, J=7.6, 1.2 Hz), 7.93 (d, 1H, J=7.6 Hz), 7.75–7.66 (m, 2H), 7.68–7.32 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 191.0, 142.6, 142.0, 136.5, 135.0, 132.2, 132.2, 132.1, 130.6, 129.8, 129.6, 129.4, 128.6, 127.6, 127.5, 126.3, 124.6, 123.8. MS (EI): 257 (M^+, 13), 242 (100), 77 (25). HRMS (EI) calcd for $C_{18}H_{11}ON$ 257.0841, found 257.0840. Compound **37**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.90–7.87 (m, 2H), 7.74 (d, 1H, J=7.6 Hz), 7.62–7.47 (m, 8H), 7.19 (d, 2H, J=1.2 Hz), 7.07 (s, 1H), 6.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 142.3, 139.7, 138.3, 137.1, 134.0, 133.7, 133.0, 132.4, 130.4, 129.1, 128.9, 128.7, 128.6, 128.5, 128.4, 127.2, 127.1, 126.0, 123.0, 121.6, 117.2, 112.4. MS (EI): 383 (M^+, 10), 242 (100), 240 (50), 77 (25). HRMS (EI) calcd for $C_{24}H_{17}O_2SN$ 383.0981, found 383.0970.

4.3.20. (*Z*,*Z*)-1-(2-Phenyl)-11-phenylsulfonylundeca-3,7-diene-1,5,9-triyne (38). Obtained in 40% yield as an oil according to method B. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.95–7.30 (m, 10H), 6.14–5.79 (m, 4H), 3.88 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.0, 134.6, 134.1, 133.8, 131.9, 130.9, 130.2, 129.8, 129.0, 128.8, 128.3, 128.2, 121.2, 120.4, 119.0, 118.3, 112.3, 112.1, 49.3. MS (EI): 356 (M^+, 1), 156 (48), 139 (46), 91 (100). HRMS (EI) calcd for $C_{23}H_{16}O_2S$ 356.0875, found 356.0877.

4.3.21. 2-Phenylsulfonylmethyl-1-(2-benzylidene)indene (39). Obtained in 50% yield as an solid according to method C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.66–7.37 (m, 13H), 7.25 (s, 1H), 6.61 (d, 4H, J=5.6 Hz), 6.52 (d, 1H, J=5.6 Hz), 4.45 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 145.6, 141.0, 136.3, 135.1, 133.3, 130.7, 129.7, 129.3, 128.9, 128.7, 128.6, 128.4, 127.8, 126.8, 125.2, 124.9, 123.6, 120.0, 119.5. MS (EI): 358 (M^+, 18), 217 (100), 215 (74), 202 (53). HRMS (EI) calcd for $C_{23}H_{18}O_2S$ 358.1028, found 358.1026.

4.3.22. 5-Phenyl-naphthaldehyde (40). Obtained in 13% yield as an solid according to method C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.25 (s, 1H), 7.92 (d, 1H, J=7.2 Hz), 7.86 (dd, 1H, J=7.2, 1.2 Hz), 7.72 (d, 1H, J=7.2 Hz), 7.76–7.20 (m, 3H), 7.49–7.40 (m, 4H), 7.31 (d, 1H, J=7.4 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 192.4, 136.4, 132.4, 131.4, 130.8, 130.4, 129.8, 129.7, 129.2, 129.1, 128.9, 128.8, 128.4, 125.2, 124.1. MS (EI): 232 (M^+, 39), 203 (72), 202 (63), 149(100). HRMS (EI) calcd for $C_{17}H_{12}O$ 232.0887, found 232.0884.

4.3.23. (*Z*)-1-Phenyl-3-hexen-1,5-diyne (42). Obtained in 68% yield as an oil according to method A. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.53–7.30 (m, 5H), 5.89 (d, 2H, J=7.0 Hz), 3.42 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 129.6, 126.5, 126.2, 121.1, 118.6, 117.3, 101.2, 100.2, 95.5, 85.0; MS (EI): 152 (M^+, 100). HRMS (EI) calcd for $C_{12}H_{18}$ 152.0626, found 152.0625.

4.3.24. (*Z*,*Z*)-1-Phenyl-11-phenylthioundeca-3,7-diene-1,5,9-triyne (43). Obtained in 32% yield as an oil according

to method A. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.51–7.30 (m, 9H), 6.13–5.82 (m, 4H), 3.58 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 135.2, 131.9, 129.8, 128.8, 128.6, 128.3, 126.6, 123.0, 119.9, 119.7, 119.3, 119.1, 97.8, 94.6, 94.3, 87.3, 81.0, 23.6. MS (EI): 324 (M^+, 11), 189 (55), 215 (70), 213 (100), 189 (55). HRMS (EI) calcd for $C_{23}H_{16}S$ 324.0950, found 324.0951.

4.3.25. (*Z*)-1-Chloro-4-phenyl-1-buten-3-yne (47). Obtained in 52% yield as an oil according to method A.^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.56–7.34 (m, 5H), 6.44 (d, 2H, J=7.4 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 131.6, 128.7, 128.3, 122.6, 112.2, 112.0, 97.4, 83.2. MS (EI): 162 (M^+, 82), 202 (77), 127 (100); HRMS (EI) calcd for $C_{10}H_7Cl$ 162.0234, found 162.0235.

Acknowledgements

We thank the National Science Council of the Republic of China for financial support of this program.

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