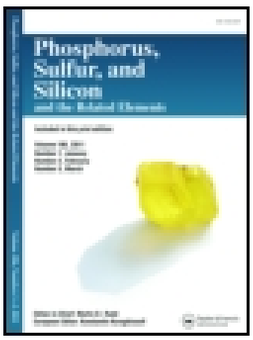

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ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: http://www.tandfonline.com/loi/gpss20

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To cite this article: Ali Varasteh Moradi (2017): ZnO-nanoparticles as an efficient catalyst for the synthesis of tetrasubstituted cyclopentadienones using sulfonoketenimides and enaminoesters, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2017.1370593

To link to this article: http://dx.doi.org/10.1080/10426507.2017.1370593

ZnO-nanoparticles as an efficient catalyst for the synthesis of tetrasubstituted cyclopentadienones using sulfonoketenimides and enaminoesters

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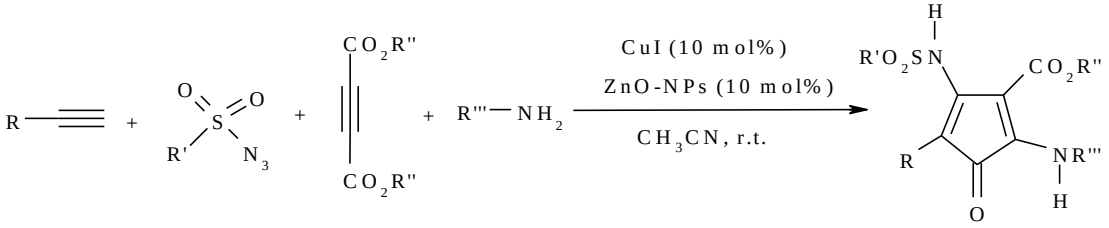
Abstract

A convenient and efficient approach to the synthesis of substituted cyclopentadienes is reported based on the reaction of sulfonoketenimides and enaminoesters in good yield. In these reactions, sulfonoketenimides is produced from the reaction of terminal alkynes and sulfonyl azides in the presence of copper iodide and enaminoesters is prepared *via* the reaction of dialkyl acetylenedicarboxylates and primary amines in the presence of ZnO-nanoparticles.



Keywords

ZnO-nanoparticles; Dialkyl acetylenedicarboxylates; Primary amines; sulfonoketenimides.

Introduction

Multicomponent reactions (MCR) are interesting due to their potential for high synthetic efficiency and production of complex organic compounds [1-7]. The cyclopentadiene ring system has enjoyed significant research attention for more than half a century in organic chemistry and the other research fields [8-15]. Cyclopentadiene is a important diene that is employed in Diels–Alder reactions. Therefore, the expansion of efficient synthetic methods to producing of cyclopentadienes has been of interest [16-18]. As well, cyclopentadienes are as forerunners for the creation of transition-metal complexes in coordination chemistry [19]. Also, among the various procedures that produce ketenimines, the copper-catalyzed azide-alkyne cycloaddition reaction has been previously documented [20-22]. Ketenimine intermediates generated through these could be trapped by diverse nucleophiles [23-28]. In this paper, we show an efficient synthesis of cyclopentadiene derivatives in good yield *via* the reaction of sulfonoketenimides **6** that is produced from the reaction of terminal alkynes **1** and sulfonyl azides **2** in the presence of catalytic amount of copper iodide with intermediate **7** that is generated from the reaction of dialkyl acetylenedicarboxylate **3** and primary amines **4** in the presence of ZnO-NPs [29] (Scheme 1).

Result and discussion

In these reactions, the first step is optimization of reaction conditions for achieving to best conditions for producing of cyclopentadine derivatives **8** (Scheme 1). The conditions of the reaction involving solvent and catalyst were optimized. For the generation of intermediate **6**, several catalysts such as CuI, CuBr, CuCl and copper powder were tested. Among them CuI give the best results. Also, several solvents such as CH_3CN, DMF, H_2O, toluene, diethyl ether and

solvent-free conditions were employed with CH_3CN as the best solvent. For preparation of compound **8**, ZnO-nanoparticles, CM-ZnO, pyridine, piperidine, CuO-NPs and TiO_2-NPs were tested as catalysts. Among them, ZnO-NPs are the best catalyst (Table 1).

Under the optimized conditions described above, cyclopentadiene derivatives **8** are generated in good yields with the amount of ZnO-NPs given as 10 mol%. Using an amount greater than 10mol% does not improve the yield of reactions. The ZnO-NPs that is used in these reactions can be reused five times without considerable loss of activity. The catalyst was filtered after each reaction and washed completely with ethyl acetate. Then, it was dried at room temperature for 24 h and used for the next catalytic cycle. ZnO-nanoparticles were prepared according to literature and SEM and XRD image are confirmed the structure of nanoparticles [28]. The structures of compounds **8a-h** were assigned by IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. For example, in the ^{1}H NMR spectrum of **8a** showed one singlet for methyl protons at (δ 2.36 ppm), one singlet at (*δ*3.45 ppm) for NMe protons and one singlet for methoxy proton at (δ3.75 ppm). Also, two singlets were seen at 7.45 and 8.58 ppm for NH protons along with signals for aromatic moiety. The ^{13}C NMR spectrum of **8a** showed two signals for carbonyl group at 161.5 and 189.7 ppm in agreement with the proposed structure. In addition the mass spectrum of **8a** displays the molecular ion peak for the appropriate m/z values. A proposed mechanism for the producing of compound **8** is shown in Scheme 2 [23-28]. Enaminone **7** as a nucleophile, is generated from the initial addition of dialkyl acetylenedicarboxylate **3** to primary amines **4** [28]. Also, the copper acetylide **9** that is formed from terminal alkyne **1** and CuI is converted to ketenimine **6** after the reaction with sulfonyl azides **2** by confirmed transformations [23-28]. Ketenimine **6** were reacted with intermediate **7** in the presence of ZnO-NPs to generate intermediate **12** that is finally

converted to product **8** by intramolecular cyclization and imine-enamine tautomerization (Scheme 2) [23-28].

Conclusion

Sulfonoketenimides generated from the reaction of terminal alkynes and sulfonyl azides react with an intermediate that is generated from the reaction of dialkyl acetylenedicarboxylate and primary amines in the presence of ZnO-NPs (10 mol%) to produce cyclopentadiene derivatives in good yields.

Experimental

All chemicals employed in this work were prepared from Fluka (Buchs, Switzerland) and were performed without additional purification. Nanoparticles of ZnO were synthesized according to the literature report [29]. The morphology of nanostructure of ZnO was determined by scanning electron microscopy (SEM). X-ray diffraction (XRD) analysis was performed at room temperature using a Holland Philips Xpert X-ray powder diffractometer with Cu Ka radiation (λ=0.15406 nm), over the 2θ collection range of 20–80° [29]. Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN–O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MAT 8430 spectrometer operating at an ionization potential of 70 eV. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H, and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500.1 and 125.8 MHz, respectively. ^{1}H, and ^{13}C, spectra were obtained for solutions in $CDCl_3$ using TMS as internal standard or 85% H_3PO_4 as external standard**.** The Supplemental Materials contains sample characterization data for the products 8, and the known catalyst (Figures S 1 – S 8).

General procedure for preparation of compounds 8

In one pot, to a mixture of sulfonyl azide **2** (1.2 mmol), alkyne **1** (1 mmol) and CuI (0.1 mmol) was added Et_3N (2 mmol) in CH_3CN (5 mL). In another pot, to a mixture of dialkyl acetylenedicarboxylate **3** (1 mmol) and primary amines **4** (1 mmol) in CH_3CN (5 mL) was added ZnO-NPs (10 mol%) at room temperature after 20 min. After 10 min, the sulfonoketenimides that was synthesized in the first pot was added to the second pot. After completion of reaction (1 h, monitored by TLC), the catalyst was removed by filtration. The solvent was evaporated from the mixture and residue was purified by column chromatography (4:1 hexane/EtOAc) to afford products , **8.**

Methyl 2-(methylamino)-5-{[(4-methylphenyl) sulfonyl]amino}-3-oxo-4-phenyl-1,4-cyclopentadiene-1-carboxylate (8a)

Pale yellow powders, m.p. 127-129 ^oC; yield: 0.77 g (94%). IR (KBr) (γ_{max}/cm^{-1}): 1735, 1692, 1595, 1487, 1378, 1285, 1129 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.36 (3 H, s, Me), 3.45 (3 H, s, NMe), 3.75 (3 H, s, MeO), 7.36 (1 H, t, ^3J = 7.5 Hz, CH), 7.42 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.45 (1 H, s, NH), 7.62 (2 H, t, ^3J = 7.5 Hz, 2 CH), 7.72 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.83 (2 H, d, ^3J = 7.6 Hz, 2 CH), 8.58 (1 H, s, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5 (CH_3), 38.4 (NCH_3), 51.6 (MeO), 120.6 (C), 120.8 (C), 125.8 (2CH), 126.4 (2 CH), 127.2 (2 CH), 128.4 (CH), 130.7 (2 CH), 134.2 (C), 137.6 (C), 141.3 (C), 142.5 (C), 143.4 (C), 161.5 (C=O), 189.7 (C=O) ppm. MS (EI, 70 eV): m/z (%) = 412 (M^+, 15), 381 (86), 77 (46), 31 (100). Anal.Calcd for $C_{21}H_{20}N_2O_5S$ (412.46): C, 61.15; H, 4.89; N, 6.79. Found: C, 61.26; H, 4.98; N, 6.92.

Methyl 2-(ethylamino)- 3-oxo-5-[(phenylsulfonyl)amino]-4-propyl-1,4-cyclopentadiene-1-carboxylate (8b)

Yellow powders, m.p. 138-140 ^{o}C; yield: 0.69g (92%). IR (KBr) (γ_{max}/cm^{-1}): 1737, 1694, 1587, 1488, 1382, 1292, 1134 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 (3 H, t, ^{3}J = 7.3 Hz, Me), 1.28 (3 H, t, ^{3}J = 7.3 Hz, Me), 1.54-1.59 (2 H, m, CH_2), 1.98 (2 H, t, ^{3}J = 7.3 Hz, CH_2), 3.27 (2 H, t, ^{3}J = 7.3 Hz, Me), 3.78 (3 H, s, MeO), 7.46 (2 H, t, ^{3}J = 7.6 Hz, 2 CH), 7.48 (1 H, s, NH), 7.56 (1 H, t, ^{3}J = 7.5 Hz, CH), 7.78 (2 H, d, ^{3}J = 7.6 Hz, 2 CH), 8.28 (1 H, s, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.6 (CH_3), 15.7 (Me), 22.8 (CH_2), 31.6 (CH_2), 38.2 (CH_2), 52.3 (MeO), 119.3 (C), 123.4 (C), 125.2 (2 CH), 128.6 (2 CH), 134.5 (CH), 143.2 (C), 144.6 (C), 145.4 (C), 162.6 (C=O), 190.4 (C=O) ppm. MS (EI, 70 eV): m/z (%) = 378 (M^+, 20), 347 (82), 77 (58), 31 (100). Anal.Calcd for $C_{18}H_{22}N_2O_5S$ (378.44): C, 57.13; H, 5.86; N, 7.40. Found: C, 57.26; H, 5.96; N, 7.54.

Methyl 2-(butylamino)- 3-oxo-5-[(methylsulfonyl) amino]-4-butyl-1,4-cyclopentadiene-1-carboxylate (8c)

Pale yellow powders, m.p. 127-129 ^{o}C; yield: 0.64g (89%). IR (KBr) (γ_{max}/cm^{-1}): 1739, 1692, 1584, 1476, 1385, 1293, 1142 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (3 H, t, ^{3}J = 7.3 Hz, Me), 1.14 (3 H, t, ^{3}J = 7.3 Hz, Me), 1.36-1.42 (4 H, m, 2 CH_2), 1.48-1.56 (4 H, m, 2 CH_2), 2.75 (2 H, t, ^{3}J = 7.3 Hz, CH_2), 3.25 (2 H, t, ^{3}J = 7.3 Hz, Me), 3.32 (3 H, s, Me), 3.78 (3 H, s, MeO), 7.52 (1 H, s, NH), 8.14 (1 H, s, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.2 (CH_3), 14.4 (Me), 21.3 (CH_2), 22.8 (CH_2), 29.5 (2 CH_2), 30.2 (CH_2), 41.2 (CH_3), 43.6 (CH_2), 51.8 (MeO), 118.6 (C), 119.7 (C), 140.2 (C), 144.2 (C), 162.4 (C=O), 191.2 (C=O) ppm. MS (EI, 70 eV): m/z

(%) = 358 (M^+, 15), 327 (76), 31 (100). Anal.Calcd for $C_{16}H_{26}N_2O_5S$ (358.45): C, 53.61; H, 7.31; N, 7.82. Found: C, 53.76; H, 7.45; N, 7.96.

Ethyl 2-(propylamino)- 3-oxo-5-[(methylsulfonyl)amino]-4-propyl-1,4-cyclopentadiene-1-carboxylate (8d)

Pale yellow powders, m.p. 126-128 ^oC; yield: 0.62g (90%). IR (KBr) (γ_{max}/cm^{-1}): 1736, 1687, 1587, 1477, 1387, 1295, 1146 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.95 (3 H, t, ^3J = 7.3 Hz, Me), 1.06 (3 H, t, ^3J = 7.3 Hz, Me), 1.28 (3 H, t, ^3J = 7.4 Hz, Me), 1.46-1.53 (2 H, m, CH_2), 1.59-1.68 (2 H, m, CH_2), 2.63 (2 H, t, ^3J = 7.4 Hz, CH_2), 3.18 (2 H, t, ^3J = 7.4 Hz, Me), 3.34 (3 H, s, Me), 4.24 (2 H, q, ^3J = 7.4 Hz, CH_2O), 7.48 (1 H, s, NH), 8.16 (1 H, s, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.2 (CH_3), 14.0 (Me), 14.6 (Me), 23.2 (CH_2), 24.3 (CH_2), 31.5 (CH_2), 41.6 (CH_3), 45.8 (CH_2), 62.4 (CH_2O), 118.8 (C), 122.3 (C), 143.6 (C), 144.8 (C), 162.5 (C=O), 192.4 (C=O) ppm. MS (EI, 70 eV): m/z (%) = 344 (M^+, 15), 299 (68), 45 (100). Anal.Calcd for $C_{15}H_{24}N_2O_5S$ (344.43): C, 52.31; H, 7.02; N, 8.13. Found: C, 52.44; H, 7.18; N, 8.28.

Methyl 2-(benzylamino)-3-oxo-5-{[(4-methylphenyl)sulfonyl]amino}-4-butyl-1,4-cyclopentadiene-1-carboxylate (8e)

Yellow powders, m.p. 148-150 ^oC; yield: 0.87 g (93%). IR (KBr) (γ_{max}/cm^{-1}): 1742, 1698, 1596, 1492, 1383, 1287, 1135 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.12 (3 H, t, ^3J = 7.4 Hz, Me), 1.37-1.46 (2 H, m, CH_2), 1.52-1.63 (2 H, m, CH_2), 2.34 (3 H, s, Me), 2.73 (2 H, t, ^3J = 7.4 Hz, CH_2), 3.78 (3 H, s, MeO), 4.52 (2 H, s, NCH_2), 7.32 (1 H, t, ^3J = 7.4 Hz, CH), 7.38 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.47 (1 H, s, NH), 7.52 (2 H, d, ^3J = 7.5 Hz, 2 CH), 7.58 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.72 (2 H, d, ^3J = 7.6 Hz, 2 CH), 8.48 (1 H, s, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.6 (CH_3), 21.5 (Me), 22.6 (CH_2), 28.4 (CH_2), 30.2 (CH_2), 46.2 (NCH_2), 52.3 (MeO), 118.6 (C),

121.2 (C), 125.7 (2 CH), 126.3 (CH), 127.3 (2 CH), 128.2 (2 CH), 129.4 (2 CH), 137.3 (C), 137.9 (C), 138.6 (C), 142.3 (C), 142.8 (C), 162.3 (C=O), 192.7 (C=O) ppm. MS (EI, 70 eV): m/z (%) = 468 (M^+, 20), 437 (68), 77 (56), 31 (100). Anal.Calcd for $C_{25}H_{28}N_2O_5S$ (468.57): C, 64.08; H, 6.02; N, 5.98. Found: C, 64.23; H, 6.18; N, 6.16.

Methyl 2-(4-methoxybenzylamino)-3-oxo-5-[(methylsulfonyl)amino]-4-phenyl-1,4-cyclopentadiene-1-carboxylate (8f)

Pale yellow powders, m.p. 153-155 ^oC; yield: 0.87 g (85%). IR (KBr) (γ_{max}/cm^{-1}): 1739, 1698, 1586,1467, 1374, 1293, 1127 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.36 (3 H, s, Me), 3.78 (3 H, s, MeO), 3.85 (3 H, s, MeO), 4.53 (2 H, s, NCH_2), 7.12 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.28 (2 H, d, ^3J = 7.6 Hz, 2 CH), 7.35 (1 H, t, ^3J = 7.5 Hz, CH), 7.45 (1 H, s, NH), 7.56 (2 H, t, ^3J = 7.5 Hz, 2 CH), 7.83 (2 H, d, ^3J = 7.6 Hz, 2 CH), 8.53 (1 H, s, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 41.2 (CH_3), 46.3 (CH_2), 51.6 (MeO), 55.6 (MeO), 114.6 (2 CH), 121.3 (C), 121.8 (C), 126.6 (2 CH), 128.4 (CH), 129.5 (2 CH), 130.6 (2 CH), 132.2 (C), 133.8 (C), 141.3 (C), 144.7 (C), 158.6 (C), 162.6 (C=O), 191.8 (C=O) ppm. MS (EI, 70 eV): m/z (%) = 442 (M^+, 15), 411 (72), 121 (100), 77 (62), 31 (100). Anal.Calcd for $C_{22}H_{22}N_2O_6S$ (442.49): C, 59.72; H, 5.01; N, 6.33. Found: C, 59.87; H, 5.18; N, 6.46.

Methyl 2-(4-methoxybenzylamino)-3-oxo-5-[(methylsulfonyl)amino]-4-butyl-1,4-cyclopentadiene-1-carboxylate (8g)

Yellow powders, m.p. 162-164 ^oC; yield: 0.73 g (87%). IR (KBr) (γ_{max}/cm^{-1}): 1740, 1689, 1594,1478, 1375, 1286, 1129 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.96 (3 H, t, ^3J = 7.4 Hz, Me), 1.37-1.45 (2 H, m, CH_2), 1.48-1.59 (2 H, m, CH_2), 2.78 (2 H, t, ^3J = 7.3 Hz, CH_2), 3.34 (3 H, s, Me), 3.78 (3 H, s, MeO), 3.85 (3 H, s, MeO), 4.52 (2 H, s, NCH_2), 7.17 (2 H, d, ^3J = 7.8 Hz,

2 CH), 7.33 (2 H, d, ^{3}J = 7.8 Hz, 2 CH), 7.48 (1 H, s, NH), 8.24 (1 H, s, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.6 (CH_2), 28.7 (CH_2), 30.4 (CH_2), 41.3 (CH_3), 46.5 (CH_2), 52.3 (MeO), 55.7 (MeO), 114.5 (2 CH), 118.6 (C), 121.7 (C), 129.6 (2 CH), 132.4 (C), 140.6 (C), 142.3 (C), 159.2 (C), 161.8 (C=O), 192.3 (C=O) ppm. MS (EI, 70 eV): m/z (%) = 422 (M^+, 15), 391 (86), 121 (100), 77 (68), 31 (100). Anal.Calcd for $C_{20}H_{26}N_2O_6S$ (422.49): C, 56.86; H, 6.20; N, 6.63. Found: C, 56.98; H, 6.37; N, 6.78.

Ethyl 2-(4-methylbenzylamino)-3-oxo-5-[(methylsulfonyl)amino]-4-propyl-1,4-cyclopentadiene-1-carboxylate (8h)

Pale yellow powders, m.p. 149-151 ^{o}C; yield: 0.71 g (87%). IR (KBr) (γ_{max}/cm^{-1}): 1738, 1682, 1587,1486, 1378, 1295, 1137 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 (3 H, t,^{3}J = 7.4 Hz, Me), 1.24 (3 H, t, ^{3}J = 7.4 Hz, Me), 1.59-1.62 (2 H, m, CH_2), 2.34 (3 H, s, CH_3), 2.62 (2 H, t, ^{3}J = 7.4 Hz, CH_2), 3.34 (3 H, s, Me), 4.22 (2 H, q, ^{3}J = 7.4 Hz, CH_2O), 4.53 (2 H, s, NCH_2), 7.23 (2 H, d, ^{3}J = 7.8 Hz, 2 CH), 7.33 (2 H, d, ^{3}J = 7.8 Hz, 2 CH), 7.47 (1 H, s, NH), 8.26 (1 H, s, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.2 (Me), 14.3 (Me), 21.2 (Me), 23.4 (CH_2), 31.7 (CH_2), 41.4 (Me), 46.5 (CH_2), 63.4 (CH_2O), 120.7 (C), 122.3 (C), 127.4 (2 CH), 128.6 (2 CH), 131.2 (C), 135.8 (C), 142.7 (C), 146.6 (C), 162.5 (C=O), 192.7 (C=O) ppm. MS (EI, 70 eV): m/z (%) = 406 (M^+, 15), 361 (64), 105 (100), 77 (58), 45 (100). Anal.Calcd for $C_{20}H_{26}N_2O_5S$ (406.49): C, 59.09; H, 6.45; N, 6.89. Found: C, 59.22; H, 6.63; N, 6.98.

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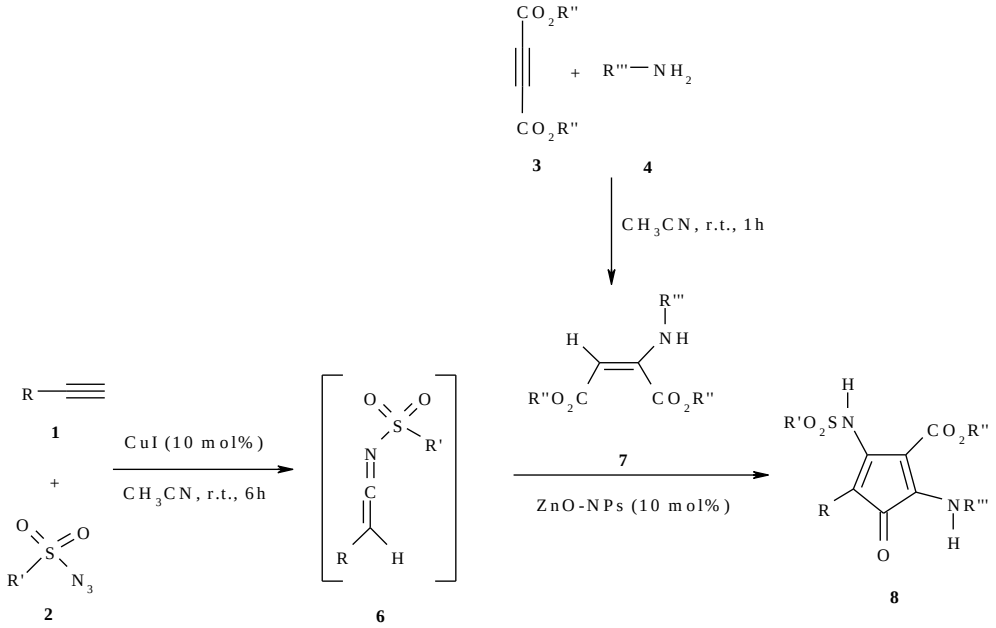
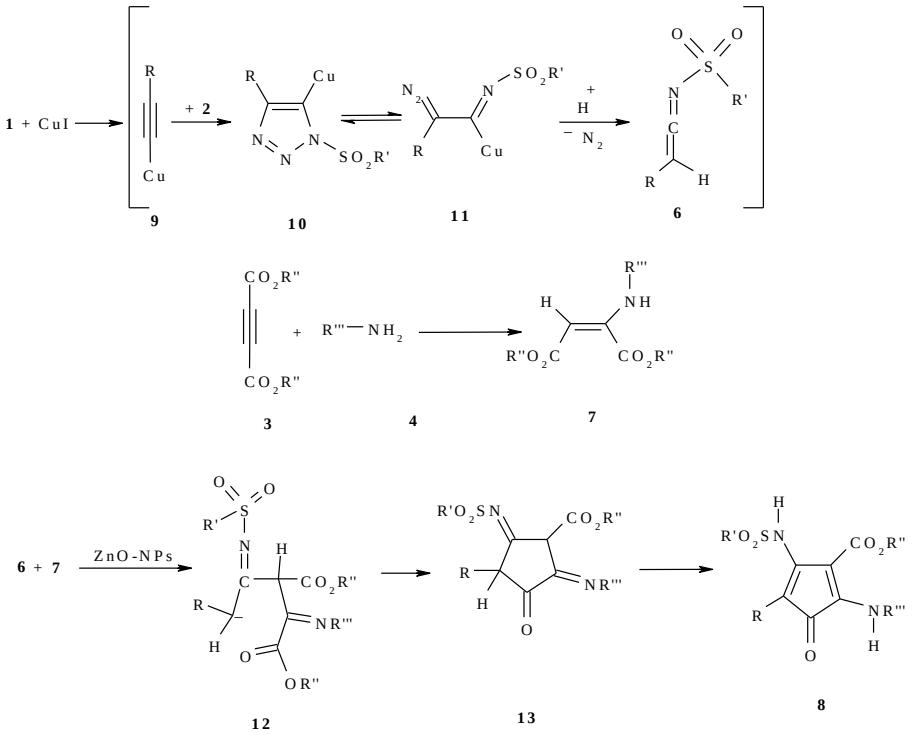
Table 1. Optimization the reaction condition for formation of **8a**.

Entry	Catalyst	Mol % of Catalyst	Yeild (%)
1	none	none	-----
2	CM-ZnO	10 mol%	28
3	CM-ZnO	15 mol%	30
4	NP-ZnO	5 mol%	85
5	**NP-ZnO**	**10 mol%**	**94**
6	NP-ZnO	15 mol%	95
7	NP-ZnO	20 mol%	87
8	KF/CP NPs	10 mol%	75
9	CuO NPs	10 mol%	58
10	TiO_2NPs	10 mol%	45



8	R	R'	R"	R"'	Yield % of **8**
a	Ph	*p*-tol	Me	Me	94
b	*n*-Pr	Ph	Me	Et	92
c	*n*-Bu	Me	Me	n-Bu	89
d	*n*-Pr	Me	Et	n-Pr	90
e	*n*-Bu	*p*-tol	Me	Bn	93
f	Ph	Me	Me	4-MeO-Bn	85
g	*n*-Bu	Me	Me	4-MeO-Bn	87
h	*n*-Pr	Me	Et	4-Me-Bn	87

Scheme 1 Synthesis of cyclopentadiene derivatives **8**



Scheme 2. Proposed mechanism for the synthesis of cyclopentadiene **8**.