Diversity oriented approach to polycyclics via cross-ene metathesis and Diels–Alder reaction as key steps

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Abstract. Polycyclics containing biaryls have been prepared via application of cross-ene metathesis and the Diels–Alder reaction. Here, ethylene and 1,5-hexadiene were used as a cross-metathesis partners to generate key diene intermediates.

Keywords. Diversity-oriented synthesis; aryl acetylenes; metathesis; Diels–Alder reaction; α -amino acids.

1. Introduction

Polycyclics are useful entities in several areas of chemical sciences.¹ Since a major portion of the present work described here deals with biaryl derivatives, we include a brief introduction to this interesting class of molecules.² Biaryl-containing compounds (figure 1) are useful in material science, pharmaceuticals, polymers³ and ligands for catalysis. Classical methods for the synthesis of biaryls are based on cross-coupling (e.g., Suzuki,⁴ Stille,⁵ Negishi⁶ and Kharasch coupling⁷ of two aromatic moieties in the presence of a transition-metal catalyst. However, in some instances, these methods suffer from at least one of the following drawbacks: low yields, scrambling products and hydrolysis product, etc. Therefore, development of an alternative strategy to highly functionalized biaryls is warranted. For example, non-transition metal based methods⁸ such as Diels–Alder (DA) cycloaddition is an alternative for the construction of a variety of biaryls because a wide range of structurally diverse biaryls can be assembled via this approach by varying the diene and dienophile components.

2. Experimental

2.1 Materials and characterization

Melting points were recorded on Lab hosp or Veego melting point apparatus. Infrared (IR) spectra were recorded on Nicolet Impact-400 FTIR spectrometer in

KBr/CHCl₃. ¹H NMR (300 and 400 MHz), ¹³C NMR (75 and 100.6 MHz) spectral data were determined at RT on a Varian VXR 400 in CDCl₃ solution. Coupling constants (*J* values) are given in Hertz (Hz). The high-resolution mass measurements were carried out using Micromass Q-ToF spectrometer. Analytical thin layer chromatography (TLC) was performed on (10 × 5 cm) glass plates coated with Acme's silica gel G or GF 254 (containing 13% calcium sulphate as a binder). Silica gel was coated on glass plates using 'Sandwich Technique'. Column chromatography was performed using Acme's silica gel (100–200 mesh) using double spray bellows for application of pressure and the column was eluted with ethyl acetate-petroleum ether mixture.

2.1a General procedure for the preparation homo allyl dienes: To a degassed solution of 4-ethynyl-1,2-dimethoxybenzene **10** (100 mg, 0.61 mmol) and 1,5-hexadiene (100 mg, 1.22 mmol) in toluene (10 mL) was added Grubbs second generation catalyst (20 mg, 4 mol%) and the reaction mixture heated at 90°C for 12 h. At the conclusion of the reaction (TLC monitoring), the reaction mixture was concentrated and the crude product was purified by a flash column chromatography using petroleum ether (PE) as an eluent to afford **11** (110 mg, 73%) as a colourless liquid.

2.1b General procedure for the Diels–Alder reaction of homo allyl butadiene derivatives with naphthoquinone: To a solution of **24** (50 mg, 0.162 mmol) in toluene (10 mL), 1,4-naphthoquinone (25.5 mg, 0.162 mmol) was added and heated at 100°C. At the conclusion of

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Figure 1. Various biaryl containing molecules.

the reaction (14 h, TLC monitoring), solvent was evaporated and the residue was charged on a silica gel column. Elution of the column with 5% ethyl acetate/petroleum ether gave the desired product **31** as a yellowish thick liquid (40 mg, 52%).

2.1c General procedure for the Diels–Alder reaction of homo allyl butadiene derivatives followed by aromatization: To a solution of the diene **21** (115 mg, 0.43 mmol) in toluene (5 mL) was added dimethyl acetylenedicarboxylate (124 mg, 0.87 mmol) and the reaction mixture was heated at 90°C for 24 h. At the conclusion of the reaction (TLC monitoring), the solvent was concentrated at reduced pressure and the crude product obtained was purified by a silica-gel column chromatography, using EtOAc/PE to afford the DA adduct as a semi solid. Later, aromatization of the DA adduct was carried out with DDQ (153 mg, 0.67 mmol) in refluxing toluene (10 mL) for 30 h. Then, the solvent was removed at reduced pressure and the crude product was purified by flash silica gel column chromatography by using (EtOAc/PE) mixture to afford the aromatized product **28** (128 mg, 72%) as a semi-solid.

2.1d General procedure for the preparation of 1,3-dienes and Diels–Alder reaction followed by aromatization: A solution of **10** (100 mg, 0.61 mmol) in toluene (10 mL) was degassed with N₂ for 10 min and

then the Grubbs second generation catalyst (26 mg, 5 mol %) was added. The reaction mixture was stirred under ethylene atmosphere (1 atm, balloon pressure) and stirred at RT for 24 h. At the conclusion of the reaction (TLC monitoring), the solvent was concentrated and the crude product was purified by a flash silica-gel column chromatography using EtOAc/PE to afford **32** (85 mg, 73%) as a brownish liquid. Later, the diene **32** (95 mg, 0.5 mmol) in toluene (10 mL) was added dimethyl acetylenedicarboxylate (142 mg, 1.0 mmol) and the mixture was heated at 90°C for 24 h. At the conclusion of the reaction (TLC monitoring) the DA adduct was oxidized with DDQ (181 mg, 0.79 mmol) in refluxing toluene (10 mL) for 36 h. Then, the solvent was removed at reduced pressure and the crude product obtained was purified by flash silica-gel column chromatography with 5% EtOAc/PE mixture to afford the aromatized product **36** (110 mg, 66%) as a semi-solid.

2.2 Physical measurements

2.2a 1,2-Dimethoxy-4-(octa-1,3,7-trien-2-yl)benzene (11): $R_f = 0.74$ (silica gel, petroleum ether) IR (Neat) $\nu_{\max}$: 740, 810, 1265, 1516, 1601, 2928 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 2.15–2.23 (m, 4H), 3.87 (s, 3H), 3.89 (s, 3H), 4.95–4.99 (m, 2H), 5.05 (d, $J = 2.0$ Hz, 1H), 5.14 (d, $J = 1.2$ Hz, 1H), 5.67–5.79 (m, 2H), 6.30 (d, $J = 15.2$ Hz, 1H), 6.83–6.88 (m, 3H)

ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 32.3, 33.5, 55.9, 56.0, 110.8, 111.6, 114.2, 114.9, 120.6, 131.9, 133.4, 133.6, 138.2, 147.7, 148.5 ppm.

2.2b 1-Chloro-4-(octa-1,3,7-trien-2-yl)benzene (20): $R_f = 0.71$ (silica gel, petroleum ether) IR (Neat) ν_{max} : 1011, 1604, 2854, 2925, 3054 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.13–2.31 (m, 4H), 4.95–4.99 (m, 2H), 5.04 (d, $J = 1.2$ Hz, 1H), 5.58–5.62 (m, 1H), 5.76–5.78 (m, 1H), 6.00–6.03 (m, 2H), 7.22–7.27 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 22.0, 23.0, 32.4, 33.5, 115.1, 115.4, 123.5, 125.4, 126.8, 128.4, 128.6, 129.8, 131.6, 134.0, 138.2, 139.2, 147.1 ppm.

2.2c 1-Bromo-4-(octa-1,3,7-trien-2-yl)benzene (21): $R_f = 0.89$ (silica gel, petroleum ether). IR (Neat) ν_{max} : 741, 835, 1011, 1604, 2854, 2925, 3054 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.15–2.22 (m, 4H), 4.97–5.01 (m, 2H), 5.06 (d, $J = 2.4$ Hz, 1H), 5.58–5.64 (m, 1H), 5.66–5.78 (m, 1H), 6.00–6.08 (m, 1H), 6.25–7.36 (m, 1H), 7.24 (dd, $J_1 = 8.4$, $J_2 = 1.6$ Hz, 2H), 7.46 (dd, $J_1 = 8.8$, $J_2 = 2.0$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 22.0, 23.0, 32.3, 33.5, 115.1, 115.4, 121.4, 123.6, 125.3, 127.2, 128.3, 130.1, 131.3, 131.5, 134.0, 138.1, 139.6, 147.1 ppm.

2.2d 1-Iodo-4-(octa-1,3,7-trien-2-yl)benzene (22): $R_f = 0.75$ (silica gel, petroleum ether). IR (Neat) ν_{max} : 740, 821, 1265, 1485, 1582, 2925, 3054 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.16–2.23 (m, 4H), 4.97–5.00 (m, 3H), 5.12 (d, $J = 0.9$ Hz, 1H), 5.58–5.78 (m, 1H), 5.79–5.86 (m, 1H), 6.29 (d, $J = 15.5$ Hz, 1H), 7.06 (d, $J = 8.2$ Hz, 2H), 7.67 (d, $J = 8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 32.4, 33.5, 78.8, 93.0, 115.1, 115.4, 130.4, 131.5, 133.7, 134.0, 137.2, 137.3, 138.0, 138.2, 140.3, 147.1 ppm.

2.2e Ethyl 4-methylene-2-(4-methoxyphenylsulfonamido)deca-5,9-dienoate (23): ^1H NMR (400 MHz, CDCl_3): δ 1.18 (2t, 3H for E&Z), 2.03–2.06 (m, 2H), 2.12–2.16 (m, 2H), 2.41 (s, 3H), 2.54–2.59 (m, 2H), 3.91–3.95 (m, 2H), 4.02–4.07 (m, 1H), 4.86–5.06 (m, 5H), 5.63–5.68 (m, 1H), 5.77–5.79 (m, 1H), 5.92–5.93 (m, 1H), 7.26–7.27 (m, 2H), 7.68–7.70 (m, 2H) ppm.

2.2f (R)-Tert-butyl-2,2-dimethyl-4-(octa-1,3,7-trien-2-yl)oxazolidine-3-carboxylate (24): ^1H NMR (400 MHz, CDCl_3): δ 1.35 (s, 9H), 1.6–1.8 (m, 6H), 2.1–2.3 (m, 4H), 3.75 (t, 1H, $J_1 = 6.4$ Hz, $J_2 = 7.6$ Hz) 4.13 (t, 1H, $J_1 = 8.0$ Hz, $J_2 = 7.2$ Hz) 4.6–4.8 (m, 1H), 4.9–5.1 (m, 4H), 5.4–5.6 (m, 1H), 5.8–6.2 (m, 2H) ppm.

2.2g Dimethyl 5-(but-3-enyl)-4'-methoxybiphenyl-3,4-dicarboxylate (26): IR (Neat) ν_{max} : 741, 1266, 1523, 1732, 2926 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.40 (dd, $J_1 = 8$, $J_2 = 1.2$ Hz, 2H), 2.75–2.79 (m, 2H) 3.86 (s, 3H), 3.91 (s, 3H), 3.95 (s, 3H), 4.99–5.01 (m, 2H), 5.80–5.88 (m, 1H), 6.99 (d, $J = 4.8$ Hz, 2H), 7.52–7.56 (m, 3H), 8.02 (d, $J = 1.6$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 35.3, 52.5, 52.6, 55.4, 114.4, 115.5, 126.1, 128.3, 128.7, 131.8, 133.0, 137.5, 140.0, 141.8, 159.8, 166.5, 169.8 ppm; HRMS(Q-ToF): m/z calcd for $\text{C}_{21}\text{H}_{23}\text{O}_5$ $[\text{M}+\text{H}]^+$: 355.1545 found 355.1537.

2.2h Dimethyl 3-(but-3-enyl)-5-(4-bromophenyl) cyclohexa-3,5-diene-1,2-dicarboxylate (28): $R_f = 0.36$ (silica gel, EtOAc/petroleum ether). IR (Neat) ν_{max} : 740, 1072, 1265, 1605, 1735, 2854 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.40 (dd, $J_1 = 14.8$, $J_2 = 6.8$ Hz, 2H), 2.77 (t, $J = 8.4$ Hz, 2H), 3.91 (s, 3H), 3.95 (s, 3H), 5.02–5.07 (m, 2H), 5.81–5.85 (m, 1H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 1.6$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 2H), 8.02 (d, $J = 1.2$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 33.1, 35.4, 52.8, 94.3, 115.8, 126.4, 128.97, 129.1, 132.1, 134.2, 137.4, 138.3, 139.0, 140.4, 141.2, 166.3, 169.7 ppm.

2.2i Dimethyl 3-(but-3-enyl)-5-(4-iodophenyl) cyclohexa-3,5-diene-1,2-dicarboxylate (29): $R_f = 0.61$ (silica gel, 5% EtOAc/petroleum ether). IR (Neat) ν_{max} : 743, 1262, 1582, 1738, 2929 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.40 (dd, $J_1 = 14.4$, $J_2 = 6.8$ Hz, 2H), 2.77 (t, $J = 8$ Hz, 2H) 3.91 (s, 3H), 3.95 (s, 3H), 4.99–5.07 (m, 2H), 5.83–5.85 (m, 1H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 1.6$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 2H), 8.02 (d, $J = 1.2$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 33.0, 35.4, 52.8, 94.3, 115.8, 126.4, 128.9, 129.1, 132.1, 134.2, 137.4, 138.3, 139.0, 140.4, 141.7, 169.7 ppm; Anal. Calcd for $\text{C}_{20}\text{H}_{19}\text{IO}_4$: C, 53.35; H, 4.25; found: C, 52.47; H, 3.19.

2.2j Dimethyl 3-(but-3-enyl)-5-ethoxy-2-(4-methoxyphenylsulfonamido)-3-oxopropyl phthalate (30): IR (Neat) ν_{max} : 3055, 2985, 1737, 1266 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.17 (t, $J = 7.2$ Hz, 3H), 2.29–2.40 (m, 5H), 2.58–2.66 (m, 1H), 2.99 (1/2 Abq, $J = 13.7$, 6.7 Hz, 1H), 3.10 (1/2 Abq, $J = 13.7$, 5.5 Hz, 1H), 3.85–3.93 (m, 5H), 4.11–4.16 (m, 1H), 5.00–5.04 (m, 2H), 5.20 (d, $J = 9$ Hz, 1H), 5.79–5.85 (m, 1H), 7.17–7.23 (m, 3H), 7.53–7.59 (m, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 14.1, 21.7, 32.8, 35.3, 39.0, 52.7, 56.6, 62.3, 115.7, 127.2, 128.2, 128.9, 134.1, 135.2, 136.5, 136.5, 136.7, 137.4, 139.9, 143.9, 166.0, 169.7, 170.7 ppm;

HRMS(Q-ToF): m/z calcd for $C_{26}H_{32}NO_8S$ $[M+H]^+$: 518.1863 found 518.1849.

2.2k (4*R*)-*Tert*-butyl-4-(4-(*but*-3-enyl)-9,10-dioxo-1,4,4a,9,9a,10-hexahydroanthracen-2-yl)-2,2-Dimethylloxazolidine-3-carboxylate (**31**): 1H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 9H), 1.4–1.6 (m, 6H), 1.6–2.2 (m, 9H), 3.7–3.9 (m, 1H), 4.1–4.2 (m, 1H), 4.35–4.45 (m, 1H), 4.9–5.1 (m, 2H), 5.76–5.80 (m, 2H), 7.7–7.9 (m, 2H), 8.1–8.3 (m, 2H) ppm.

2.2l Dimethyl 4'-chlorobiphenyl-3, 4-dicarboxylate (**37**): R_f = 0.85 (silica gel, 5% EtOAc/petroleum ether). IR (Neat) ν_{max} : 740, 1266, 1497, 1731, 2954 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 3H), 3.94 (s, 3H), 7.44 (dd, J_1 = 6.8, J_2 = 2.0 Hz, 3H), 7.54

dd, J_1 = 6.8, J_2 = 2.0 Hz, 2H), 7.70 (dd, J_1 = 8, J_2 = 2.0 Hz, 1H), 7.85 (dd, J_1 = 8.0, J_2 = 1.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.8, 52.9, 127.3, 127.4, 128.6, 129.4, 130.3, 133.3, 134.9, 137.5, 143.2, 167.6, 168.3 ppm.

2.2m Dimethyl 4'-bromobiphenyl-3,4-dicarboxylate (**38**): R_f = 0.38 (silica gel, EtOAc/petroleum ether). IR (Neat) ν_{max} : 743, 819, 1265, 1734, 2852 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 3H), 3.94 (s, 3H), 7.45 (d, J = 2.4 Hz, 2H), 7.60 (d, J = 1.6 Hz, 2H), 7.70 (dd, J_1 = 8, J_2 = 1.8 Hz, 1H), 7.85 (dd, J_1 = 9.2, J_2 = 2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.8, 52.9, 123.0, 127.3, 128.9, 129.2, 129.9, 130.4, 132.3, 133.3, 138.0, 143.2, 167.6, 168.2 ppm; HRMS (Q-ToF): m/z calcd for $C_{16}H_{13}BrO_4$ $[M+H]^+$: 349.0078 found 349.0075.

Scheme 1. Preparation of various phenyl acetylene derivatives.

Scheme 2. Preparation and DA reaction of homoallyl 1, 3-butadiene derivatives.

Scheme 3. General strategy for the synthesis of homoallyl 1, 3-butadiene derivatives and their DA reaction.

3. Results and Discussion

Recently, Kotha and Seema reported a preliminary communication involving the application of cross-ene

metathesis (CEM) and the DA reaction as key steps for assembling the biaryl derivatives.⁹ Herein, we report the full details about the preparation of biaryls and two amino acid derivatives as additional examples.¹⁰

Table 1. Preparation of homoallyl 1,3-dienes and aromatized/DA products.

Sr. No.	Substrate	Product	Product
1	10	11 (74%)	25 (75%)
2	13	19 (65%)	26 (66%)
3	14	20 (75%)	27 (60%)
4	15	21 (88%)	28 (72%)
5	16	22 (86%)	29 (82%)
6	17	23 (63%)	30 (73%)
7	18	24 (81%)	31 (52%)

Toward the synthesis of biaryl derivatives, commercially available acetophenones were chosen as starting materials. These acetophenones **7** were converted to aryl acetylenes by the Vilsmeier formylation followed by the base treatment (scheme 1).¹¹

Initially, CEM was performed starting with 3,4-dimethoxyphenyl acetylene and 4-methoxyphenyl acetylene (**10** and **13**) using 1,5-hexadiene as a cross-coupling partner in the presence of the Grubbs Second generation (G-II) catalyst under toluene reflux (scheme 2). Under these conditions cross-enyne product **11** has been generated and later it was converted to the corresponding 3,4-dimethoxy biaryl system **12** by intramolecular metathesis and aromatization sequence.

When the same reaction was carried out in toluene at 90°C, an inseparable mixture of *cis-trans* isomers of **11** was formed in 74% yield.¹² Similarly, halogen containing aryl acetylenes **14–16** were subjected to CEM with 1,5-hexadiene using the Grubbs first generation catalyst (G-I) in DCM at RT under nitrogen (scheme 3). Again, inseparable mixture of *cis-trans* isomers of diene was obtained in good yield. Since the dienes generated are converted to corresponding aromatic products by the DA reaction and aromatization sequence; the geometry of the double bond in the diene is of no consequence.

When these dienes were subjected to the DA reaction with dienophile such as dimethyl acetylenedicarboxylate (DMAD)¹³ in toluene at 90°C for 24 h, the formation of the cycloadduct was observed (TLC monitoring). The DA adduct formed was directly subjected to aromatization sequence with MnO₂ in 1,4-dioxane, and also using DDQ in toluene. It was observed that the reaction using DDQ in refluxing toluene gave better yield of the aromatized products (table 1). To expand the scope of the CEM methodology, we have prepared acetylene derivatives such as **17** and **18** containing

α -amino acid moiety. The preparation of **17**¹⁴ and **18**,¹⁵ started with readily available starting materials such as glycine and serine by using the known methodology. The acetylenes building blocks **17** and **18** were subjected to CEM with 1,5-hexadiene in the presence of G-I. The resulting dienes **23** and **24** were subjected to the DA reactions with DMAD and naphthoquinone respectively. We observed that naphthoquinone DA adduct was not converted to the corresponding aromatized product even after prolonged heating in toluene at 100°C.

In the second strategy, the compound **13** was subjected to cross-metathesis in the presence of ethylene (1 atm pressure) by using the Grubbs second generation catalyst in toluene at RT. However, it was found that at 90°C, the required building block was obtained in an acceptable yield.¹⁶ Halogenated phenylacetylene derivatives **14–16** delivered the required dienes in the presence of G-II in DCM at RT for 24 h (scheme 4). The disappearance of acetylene portion and the appearance of new peaks at δ 5.12–5.29 ppm and at δ 6.66 ppm in ¹H NMR spectroscopy indicate the formation of diene. These experiments indicated that toluene is a better solvent for cross-enyne metathesis under ethylene atmosphere as well as 1,5-hexadiene conditions with substrates such as 4-methoxy and 3,4-dimethoxy phenylacetylenes. DCM seems to be a better solvent for halogenated phenylacetylene substrates for cross-metathesis under ethylene or 1,5-hexadiene conditions. The dienes obtained during cross-metathesis sequence were subjected to the DA reaction with the dienophile such as DMAD under toluene reflux conditions, to deliver the corresponding DA adducts. Since we observed that these dienes are prone to polymerize under toluene reflux conditions, the DA reaction was performed in toluene at 90°C for 14–24 h that gave better yield of the DA adducts (TLC monitoring). The

Scheme 4. General strategy for the synthesis of 1,3-butadiene derivatives and their DA reaction.

Table 2. List of compounds prepared by CEM, DA reaction and aromatization sequence.

Sr. No.	Product	Product
1	32 (73%)	36 (66%)
2	33 (70%)	37 (65%)
3	34 (83%)	38 (82%)
4	35 (63%)	39 (86%)

DA products were further subjected to aromatization sequence using DDQ under refluxing toluene to deliver the aromatized products (table 2).

4. Conclusions

We have demonstrated that cross-ene metathesis of acetylene derivatives in the presence of 1,5-hexadiene or ethylene followed by a Diels–Alder reaction and aromatization sequence furnished polycyclics. The generality of this methodology has been established with a variety of acetylene derivatives. Moreover, this methodology offers several diversity points. The first option is to choose a variety of acetylene derivatives. The second option involves the selection of various partners during olefin cross-metathesis and the third option is to use dienophiles during the DA reaction. The olefin present at the end of the metathesis sequence offers an additional handle for further synthetic manipulation.

Supplementary Information

¹H and ¹³C NMR (Figures S1 to S10) are given in Supplementary Information available free of charge in www.ias.ac.in/chemsci.

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