

Final Report

**Synthesis of Chromophores for
Nonlinear Optics Applications**

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14. ABSTRACT Two series of benzoate-ethynylene oligomers bearing cholesteryl- and cholesteryl-6-oxo-hexyl- as mesogen groups were selectively synthesized by a monodirectional iterative divergent-convergent approach by the Sonogashira-Heck cross-coupling reaction. These oligomers that are terminated by an acetylene group are of special interest to Dr. Thomas Cooper AFOSR in order to consequently be cross-coupled to platinum complexes to get symmetrical platinum(II)-2, 4 and 6 benzoate-ethynylene oligomers with potential applications in non linear optics. Their chemical structures were analyzed by ¹ H, ¹³ C APT, DEPT-135, UV-Vis and fluorescence spectroscopy.					
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SYNTHESIS OF CHROMOPHORES FOR NONLINEAR OPTICS APPLICATIONS

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Grant Objectives: no changes.

Status of Effort: all research objectives have been met.

Summary: Two series of benzoate-ethynylene oligomers bearing cholesteryl- and cholesteryl-6-oxo-hexyl- as mesogen groups were selectively synthesized by a monodirectional interactive, divergent-convergent approach by the Sonogashira-Heck cross-coupling reaction [1a-c]. Their chemical structures were analyzed by ^1H , ^{13}C APT, DEPT-135, UV-Vis and fluorescence spectroscopy.

Accomplishments:

Molecules that were synthesized per the grant. The strategy for the synthesis of the two series of oligomers consisted in obtaining three bi-functional monomers for each oligomer series: **7**, **9**, **11** (Scheme 1) and **24**, **26**, **28** (Scheme 3) in amounts greater than the usual few milligrams. Then, by selective reaction by the step-by-step approach, the oligomers were constructed using the two sets of reactions depicted in Schemes 2 and 4. Up to now we have previously afforded approximately one gram of the ligands **7**, **15**, **24**, **32**. Ligands **19** and **36** have also been prepared and ready for delivery to Dr. Thomas Cooper, including those of Scheme 6: **41** and **42**. We believe that once **43** bears the platinum atom, its photovoltaic properties could be quite interesting. However, we await Dr. Cooper's opinion to decide if we synthesize **43** instead of **42**.

AFOSR Follow-up. Dr. Thomas Cooper is going to cross-couple platinum to the afforded ligands that were prepared and supplied to him in order to generate oligomer models depicted in Scheme 5. In this respect, we received the platinized oligomer **40**. Once we will have all of the

oligomers, **37-42**, we will survey:

- Cyclic voltammetry: E_{ox} , E_{red} , HOMO, LUMO, E_g .
- Mesomorphic properties: DSC, TGA, SAXs
- Thin films properties (electrical, optical and morphological)
- Photovoltaic properties (J-V curves in dark and under solar simulator illumination)

References: 1(a) Dieck, H.A.; Heck, R.F. *J. Organomet. Chem.*; **1975**, 93, 259; (b) Heck, R.F. *Palladium Reagent in Organic Syntheses*; Academic Press: New York, **1990**; (c) Amatore, C.; Lutand, A.; Suarez, A. *J. Am. Chem. Soc.*; **1993**, 115, 9531.

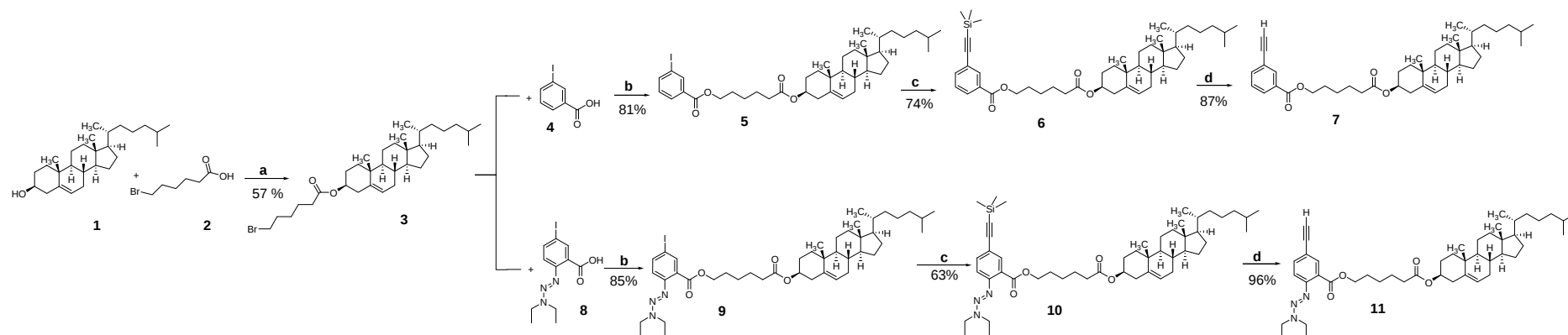
Schemes 1 through 6 follow and include experimental conditions and reagents used.

Personnel Supported: Dr. Eduardo Arias, Dr. Ivana Moggio, Dr. Ronald Ziolo, Ms. Diana Iris Medellin, Mr. Miguel Angel Contreras and Ms. Karla Guadalupe Gutierrez Cuevas.

New Discoveries: there are no inventions to be patented as a result of this research grant. The results claimed that report new molecules are important for basic research.

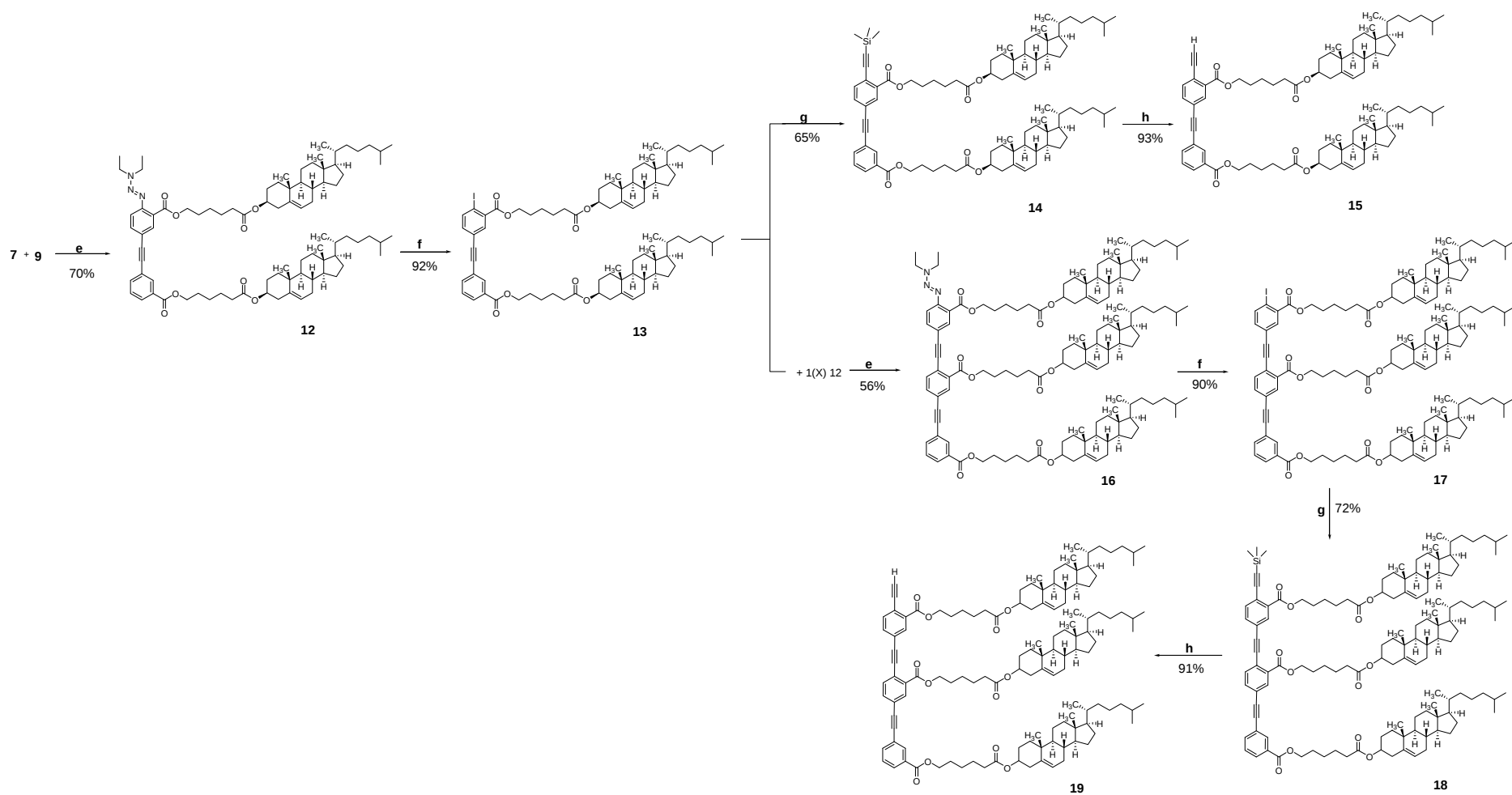
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Scheme 1



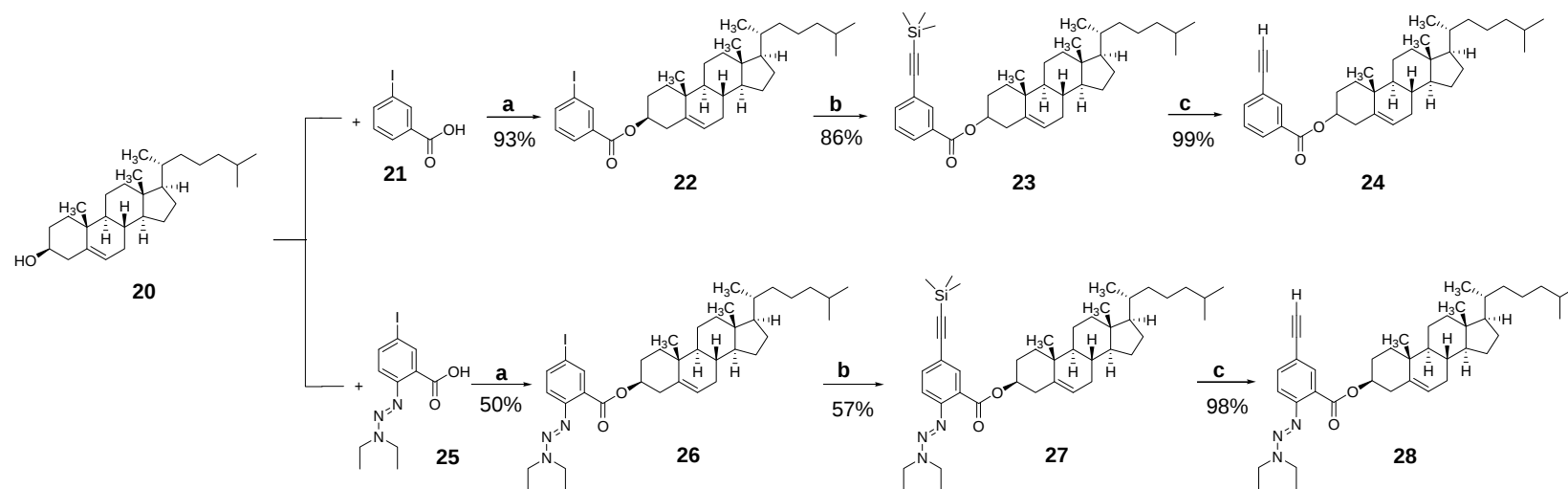
Reagents and conditions: **(a)** DCC/DMAP, CH_2Cl_2 , rt, 24 h; **(b)** DBU, Toluene, reflux, 16 h; **(c)** $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2$ (2.5 % mol), CuI (1.5 % mol), TMSA, Et_3N , 80 °C, 16 h; **(d)** TBAF, THF, r.t., 30 seg.; **(e)** CH_3I , 16 h.

Scheme 2

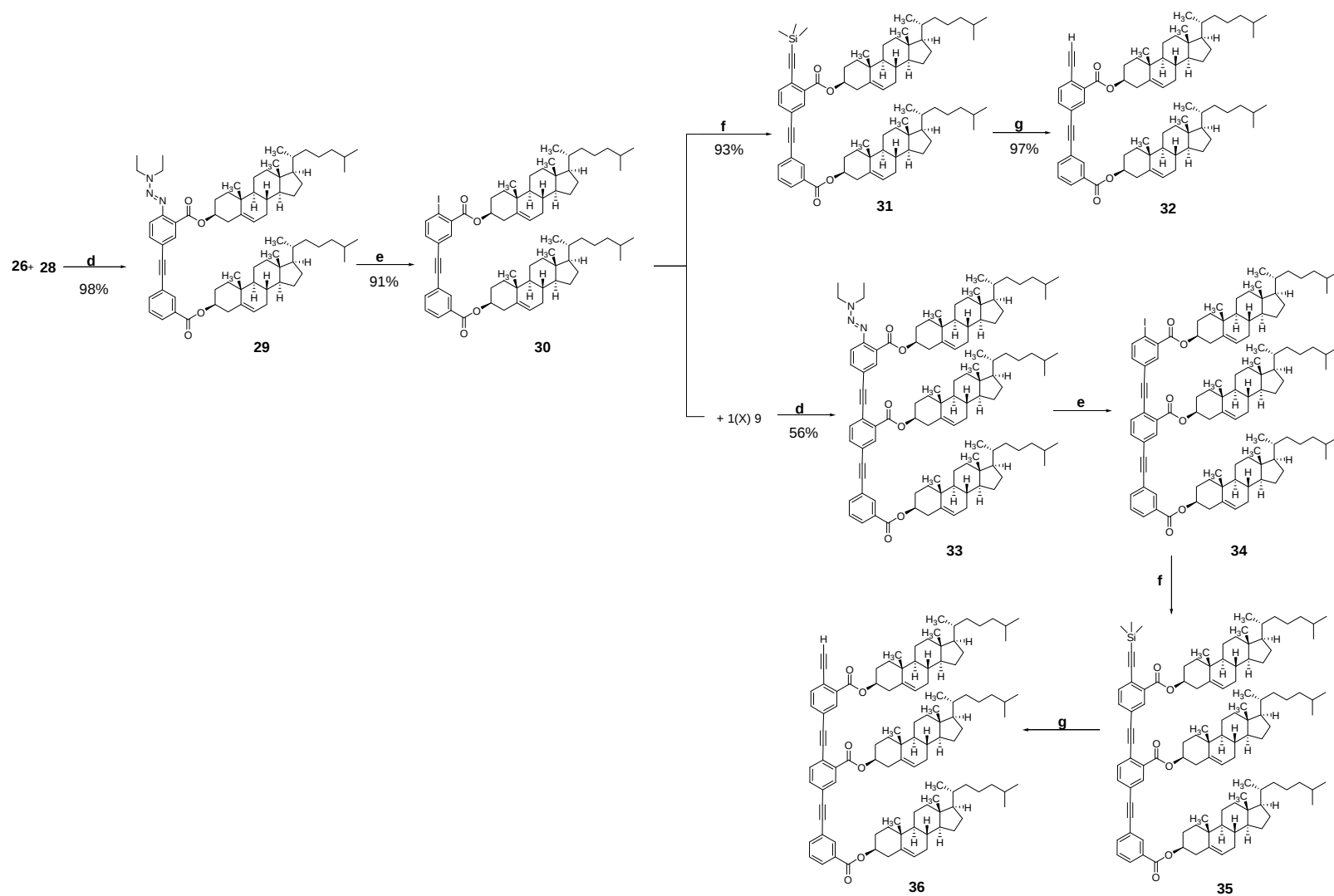


Reagents and conditions: **(e)** $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2$ (2.5 % mol), CuI (1.5 % mol), Et_3N , 80 °C, 16 h; **(f)** CH_3I , 16 h.; **(g)** $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2$ (2.5 % mol), CuI (1.5 % mol), TMSA, Et_3N , 80 °C, 16 h; **(h)** TBAF, THF, r.t., 30 seg.

Scheme 3

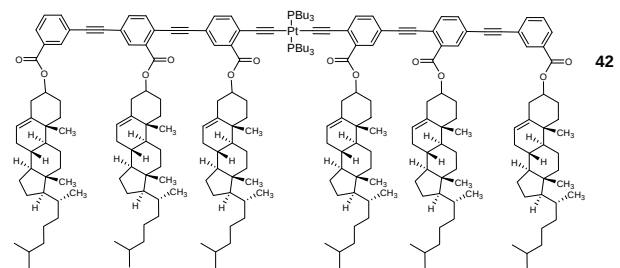
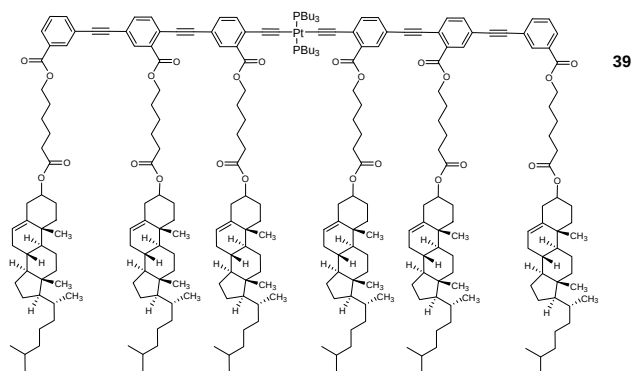
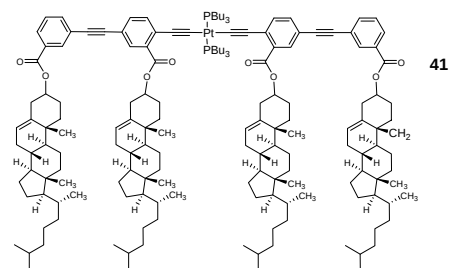
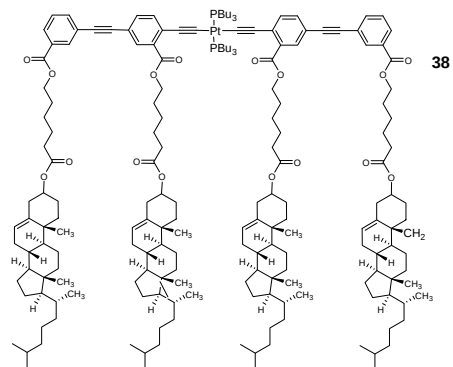
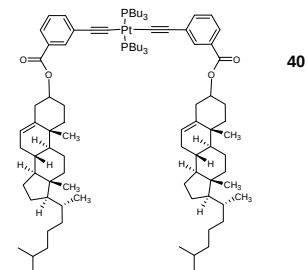
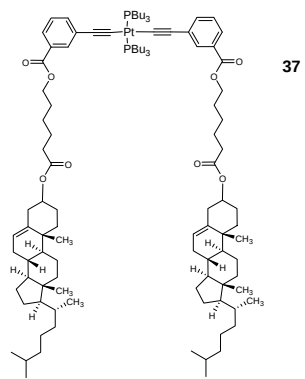


Scheme 4



Reagents and conditions: **(d)** $[(C_6H_5)_3P]_2PdCl_2$ (2.5 % mol), CuI (1.5 % mol), Et_3N , 80 °C, 16 h; **(e)** CH_3I , 16 h.; **(f)** $[(C_6H_5)_3P]_2PdCl_2$ (2.5 % mol), CuI (1.5 % mol), TMSA, Et_3N , 80 °C, 16 h; **(g)** TBAF, THF, r.t., 3min.

Scheme 5



Scheme 6

