Communication

Phosphine-Mediated Iterative Arene Homologation Using Allenes

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Phosphine-Mediated Iterative Arene Homologation Using Allenes

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Supporting Information Placeholder

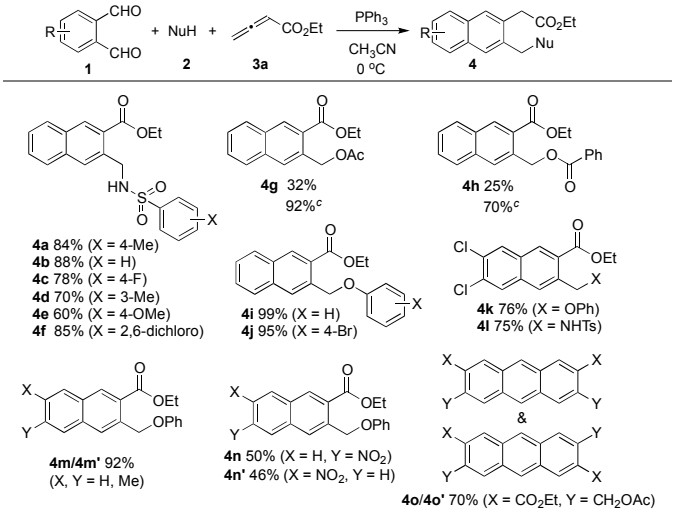
ABSTRACT: A PPh_3-mediated multicomponent reaction between *o*-phthalaldehydes, nucleophiles, and monosubstituted allenes furnishes functionalized non–C_2-symmetric naphthalenes in synthetically useful yields. When the *o*-phthalaldehydes were reacted with 1,3-disubstituted allenes in the presence of PPh_2Et, naphthalene derivatives were also obtained, in up to quantitative yields. The mechanism of the latter transformation is straightforward: aldol addition followed by Wittig olefination and dehydration. The mechanism of the former is a tandem γ-umpolung/aldol/Wittig/dehydration process, established through the preparation of putative reaction intermediates and mass spectrometric analysis. This transformation can be applied iteratively to prepare anthracenes and tetracenes when employing carboxylic acids as pronucleophiles.

The reactivity of electron-deficient allenes under the conditions of phosphine catalysis has been investigated extensively.[1] Many reports have appeared of the reactions of monosubstituted allenes with activated olefin[2] and imine[3] electrophiles to construct carbocyclic and azacyclic compounds. In contrast, few examples are known of the reactions between monosubstituted allenes and aldehyde electrophiles under the influence of phosphine catalysts.[4] In general, the union of an allenoate and an aldehyde in the presence of a phosphine results in the formation of an olefin through a Wittig-like process.[5] Interestingly, all such reports have described reactions between α- or γ-substituted allenoates and aldehydes. In contrast, Wittig reactions involving simple allenoates are rare. We are aware of only one example of the formation of a pyrrolizine, as a minor product (6%), through intramolecular Wittig olefination between ethyl allenoate (**3a**) and pyrrole-2-carboxaldehyde.[6] Herein, we report Wittig olefination between monosubstituted allenes and *o*-phthalaldehydes to give highly functionalized naphthalenes and higher-order acenes.

Functionalized naphthalenes are valuable building blocks for the synthesis of many important small molecules (e.g., pharmaceuticals, chiral reagents, liquid crystals, organic dyes).[7] Many recent syntheses of functionalized naphthalenes have employed costly transition metals or have required several steps to prepare the starting materials.[8] Our phosphine-mediated multicomponent cascade reaction described herein—between *o*-phthalaldehydes, nucleophiles, and monosubstituted allenes—is an efficient and mild method for synthesizing functionalized naphthalenes from readily available starting materials.

We surveyed the reaction between ethyl allenoate (**3a**), *o*-phthalaldehyde (**1a**), and *p*-toluenesulfonamide by varying the phosphine (stoichiometric), the solvent, the ratio between the reactants, the reaction temperature, and the concentration.[9] The optimized reaction conditions featured PPh_3 (1 equiv) as the mediator, an *o*-phthalaldehyde (1 equiv), a nucleophile (2 equiv), and ethyl allenoate (3 equiv) in CH_3CN at 0 °C.

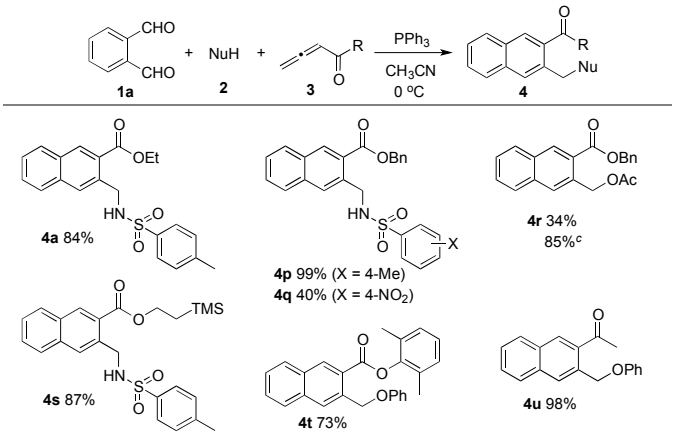
Table 1. Arene homologation using ethyl allenoate 3a[a, b]



[a]Reaction performed by adding **3a** (1.5 mmol) in CH_3CN (8 mL) via syringe pump (rate: 2 mL/h) at 0 °C to a solution of an *o*-phthalaldehyde (0.5 mmol), a nucleophile (1 mmol), and PPh_3 (0.5 mmol) in CH_3CN (4 mL). [b]Isolated yields. [c]A sodium carboxylate (1 mmol) was added.

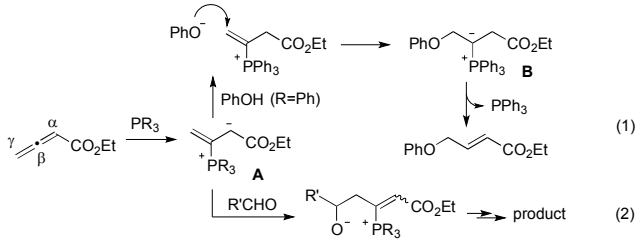
Tables 1 and 2 reveal the scope of this three-component cascade reaction. As the nucleophilic component, benzenesulfonamides bearing electron-withdrawing or -donating substituents generated the naphthalene derivatives **4a–f** in high yields. With acetic acid and benzoic acid as nucleophiles, the efficiencies of the reactions were poor, giving low yields of the naphthalene derivatives **4g** and **4h**, respectively. Adding an equimolar amount of sodium acetate or sodium benzoate as a buffer improved the yields of **4g** and **4h** dramatically.[10] When using phenol and *p*-bromophenol as the nucleophiles, the naphthalene derivatives **4i** and **4j**, respectively, were formed quantitatively. Examining substituted phthalaldehydes, we found that 4,5-dichlorophthalaldehyde also participated in the reaction, furnishing the naphthalene derivatives **4k** and **4l** in good yields. Asymmetric 4-methylphthalaldehyde furnished the inseparable isomers **4m** and **4m´** in 92% yield. When using 4-nitrophthalaldehyde, we separated the two isomers **4n** and **4n´** in 50 and 46% yields, respectively.[11] Lastly, the combination of benzene-1,2,4,5-tetracarbaldehyde and acetic acid resulted in the expected anthracenes **4o** and **4o´** in a combined yield of 70%.[12]

Table 2. Arene homologation using phthalaldehyde 1a[a, b]



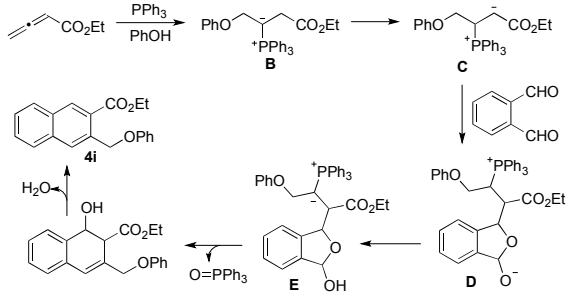
[a]Reaction performed by adding **3** (1.5 mmol) in CH_3CN (8 mL) via syringe pump (rate: 2 mL/h) at 0 °C to a solution of **1a** (0.5 mmol), a nucleophile (1 mmol), and PPh_3 (1 mmol) in CH_3CN (4 mL). [b]Isolated yields. [c]NaOAc (1 mmol) was added.

We further investigated the reaction scope by treating **1a** with a suite of allenes and nucleophiles (Table 2). The reaction of *p*-toluenesulfonamide and benzyl allenoate provided the naphthalene **4p** quantitatively, while that of *p*-nitrobenzenesulfonamide produced **4q** in only 40% yield, presumably because of attenuated nucleophilicity. By adding NaOAc as a buffer, the yield of the naphthalene **4r** improved from 34 to 85%.[10] The combinations of 2-(trimethylsilyl)ethyl buta-2,3-dienoate/*p*-toluenesulfonamide and 2,6-dimethylphenyl buta-2,3-dienoate/phenol produced the desired products **4s** (87%) and **4t** (73%), respectively. The reaction of penta-3,4-dien-2-one and phenol gave the naphthalene **4u** in 98% yield.



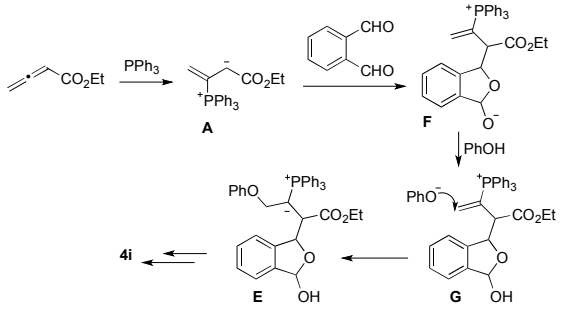
While phosphine-catalyzed γ-umpolung additions of nucleophiles to allenoates have been documented amply (eq 1),[10,13] reactions between monosubstituted allenes and aldehydes other than salicylaldehyde (derivatives) have been scarce.[4a–e] In those limited examples, the phosphonium dienolate **A** has added to the aldehyde at its γ-carbon (eq 2). Based on this prior knowledge, we postulated a credible process involving a sequence of γ-umpolung addition, aldol reaction, Wittig olefination, and dehydration (Scheme 1). Here, the ylide intermediate **B** from the initial γ-umpolung addition undergoes proton transfer to form the phosphonium enolate **C**, which adds to **1a** to form the lactolate **D**. Upon proton transfer, the ylide **E** is formed and undergoes Wittig olefination. Subsequent dehydration provides the naphthalene **4i**. Notably, only the γ-umpolung addition product was obtained when **1a** was replaced with benzaldehyde, suggesting that the phthalaldehyde plays a crucial role in the progression of the cascade sequence by forming the lactol substructure. Indeed, when we attempted to prepare the adduct between **1a** and allenoate, we isolated the corresponding lactol product (see compound **6** in eq 5).

Scheme 1. γ-Umpolung/aldol/Wittig/dehydration sequence

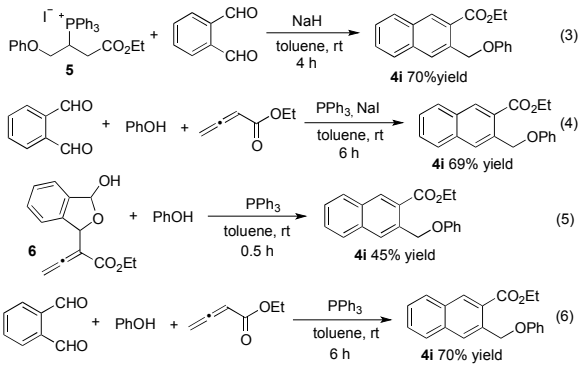


Although γ-umpolung addition/aldol reaction/Wittig olefination/dehydration is the likely course of events for the phthalaldehyde-to-naphthalene conversion, we could not exclude the alternative sequence of aldol/γ-umpolung/Wittig/dehydration (Scheme 2). In this scenario, the phosphonium dienolate **A** adds to **1a** to form the phosphonium lactolate **F**. Deprotonation of phenol by lactolate provides the phenoxide nucleophile, γ-umpolung addition of which yields the lactol ylide **E**, ready for intramolecular Wittig olefination and eventual formation of the naphthalene **4i**.

Scheme 2. Aldol/γ-umpolung/Wittig/dehydration sequence

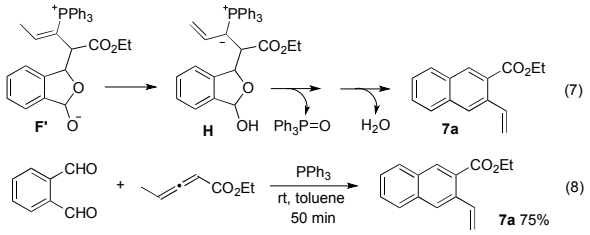


To establish the greater likelihood between the two possible mechanisms, we prepared the phosphonium salt **5** (precursor to **B**) and the lactol **6** (precursor to **F**).[9] Mixing **5** with NaH (1 equiv) and **1a** (1 equiv) in toluene at room temperature for 4 h yielded the naphthalene **4i** in 70% isolated yield (eq 3). Because the optimized conditions for the three-component reaction differed from those of the reaction described above, we also ran the coupling reaction between **1a**, 1 equiv of phenol, 1 equiv of the allenoate, 1 equiv of PPh_3, and 1 equiv of NaI as an additive (eq 4). This reaction, in toluene at room temperature, went to completion within 6 h and produced the naphthalene **4i** in 69% isolated yield. Alternatively, when we mixed the lactol allenoate **6** with PPh_3 (1 equiv) and phenol (1 equiv) in toluene at room temperature, we obtained the expected product **4i** in 45% yield within only 30 min (eq 5). A control reaction between **1a**, phenol (1 equiv), **3a** (1 equiv), and PPh_3 (1 equiv) in toluene at room temperature resulted in **4i** in 70% isolated yield after 6 h (eq 6). Thus, the NaI additive in eq 4 had no effect on the coupling reaction.



Although inconclusive, the experiments in eqs 3–6 hinted at the following possibility. If the aldol reaction occurred before the umpolung reaction, the rate-limiting step for the scenario in Scheme 2 would be the addition of the phosphonium dienolate **A** to **1a** because the conversion of the lactol **6** to the product took only 30 min. If the umpolung addition were the first event of the cascade reaction (i.e., Scheme 1), the conversion of the ylide **B** to the phosphonium enolate **C** or the addition of the enolate **C** to **1a** would likely be the slowest step. Indeed, the pK_a of the ylide **B** (21 in DMSO) is lower than that of the enolate **C** (30 in DMSO).[14] Thus, despite unfavorable thermodynamics, the phosphonium dienolate **A** is likely to be funneled into the ylide **B** as a result of rapid protonation by acidic phenol and the subsequent γ-addition.

Consequently, we envisioned a reaction between an allenoate and **1a** in the absence of a pronucleophile. The presumed intermediate **F′**, we deduced, might form the ylide **H**, which should undergo facile intramolecular Wittig olefination and dehydration to form the naphthalene **7a** (eq 7). Delightedly, the reaction between **1a**, ethyl 2,3-pentadienoate (1 equiv), and PPh_3 (1 equiv) in toluene at room temperature for 50 min gave **7a** in 75% isolated yield (eq 8). This outcome not only provides an alternative pathway for arene homologation but also discounts the aldol–before–γ-umpolung addition scenario. Considering that the γ-umpolung/Wittig/dehydration sequence of the lactol **6** took 30 min and the aldol/Wittig/dehydration sequence of **1a** and ethyl 2,3-pentadienoate (through intermediate **F′**) took 50 min, the three-component arene homologation would have been complete within 1 h if the reaction had occurred through the aldol-first route. Therefore, the reaction likely proceeds through initial γ-umpolung addition, with the rate-limiting step being not the aldol addition of **C** to **1a** but the conversion of the ylide **B** to the enolate **C**.



Monitoring the reaction with high-resolution mass spectrometry (HRMS) confirmed our suspicions. After a reaction time of 3 min (8.3% **4i** formation), the HRMS trace displayed **A** ($[M + H]^+$, *m/z* 375.1514) and **B** ($[M + Na]^+$, *m/z* 491.1752), but no **F** ($[M + H]^+$, *m/z* 509.1882).[9] Although the reaction progressed steadily with the peak for **B** clearly present throughout, the peak corresponding to the phosphonium lactolate **F** was barely evident after 40 min (37.5% **4i** formation) and was clearly visible only after 4 h (63.2% **4i** formation), suggesting that γ-addition–first is the dominant reaction pathway.

Examination of a range of phosphines, solvents, and reaction temperatures revealed that addition of γ-substituted allenoates (2 equiv) to a mixture of a phthalaldehyde and PPh_2Et (1 equiv) in toluene at room temperature was optimal for arene homologation (Table 3). After stirring for 30 to 45 min, we obtained the desired arenes **7a**–**g** in excellent yields. 4,5-Dichlorophthalaldehyde was converted quantitatively to the naphthalene **7b**. When using naphthalene-2,3-dicarbaldehyde in this reaction, the anthracene **7c** was obtained in 100% isolated yield. Ethyl hexa-2,3-dienoate and ethyl 4-cyclopentylbuta-2,3-dienoate were produced the naphthalenes **7d** and **7e**, respectively, as *E*-stereoisomers. *tert*-Butyl penta-2,3-dienoate and benzyl penta-2,3-dienoate gave their expected products **7f** (93%) and **7g** (97%), respectively.

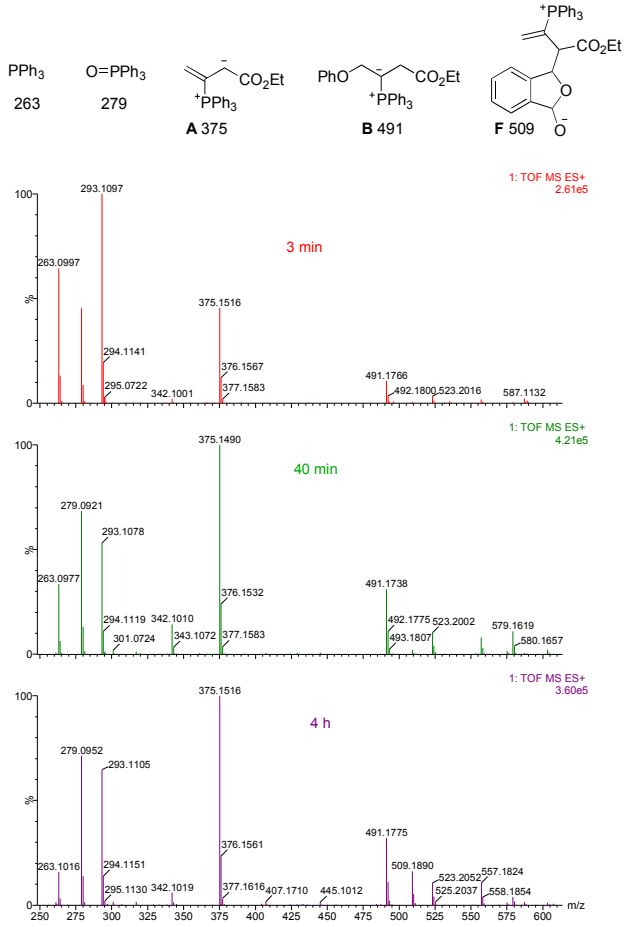
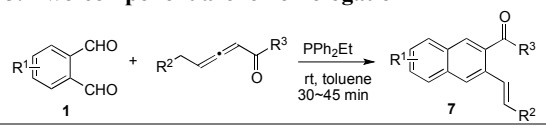
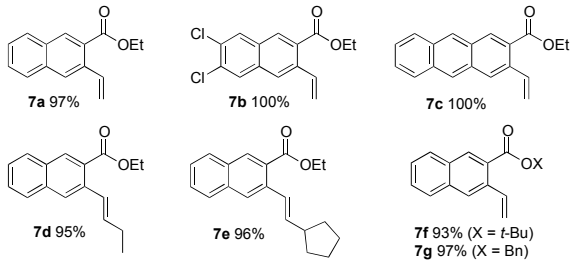


Figure 1. High-resolution mass spectra recorded during the reaction of eq 6 (*m/z* values for $[M + H]^+$ or $[M + Na]^+$ ions)

Table 3. Two-component arene homologation[a, b]





[a]Reaction performed with a dialdehyde (0.4 mmol), an allenoate (0.8 mmol), and PPh_2Et (0.4 mmol) in toluene (4 mL) at room temperature. [b]Isolated yields.

The utility of the multicomponent reaction is further illustrated in the synthesis of the 2,3-disubstituted tetracene **11** (Scheme 3). Reduction of the ester groups of the naphthalene **4g** yielded a diol, which was oxidized to naphthalene-2,3-dicarbaldehyde (**8**) with high efficiency. Repetition of the annulation, reduction, and oxidation sequence provided anthracene-2,3-dicarbaldehyde (**10**), which underwent another annulation to provide the tetracene **11**. A variety of 2,3-substituted tetracenes should be readily obtainable from **11** through functional group manipulation, with potential applications in solar cells and light-emitting materials.[15]

Scheme 3. Iterative synthesis of anthracene and tetracene

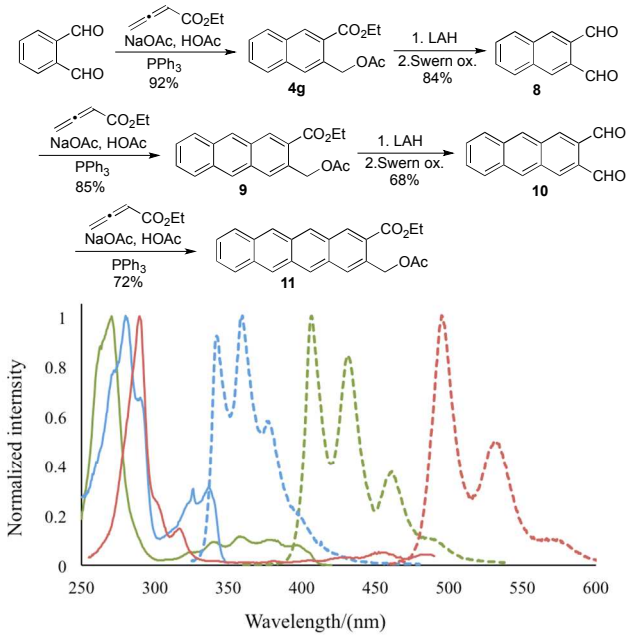


Figure 2. Excitation (solid lines) and emission (dashed lines) spectra of **4g** (blue lines), **9** (green lines), and **11** (red lines).

We obtained fluorescence excitation and emission spectra for compounds **4g**, **9**, and **11** (Figure 2). Stronger transitions appeared in the range 250–300 nm, with weaker transitions in the range 300–500 nm. A bathochromic shift occurred upon proceeding from **4g** (326 nm) to **9** (358 nm) to **11** (450 nm). A bathochromic shift also occurred in the fluorescence emissions from **4g** to **9** to **11**, with 0–0 transitions at 342, 406, and 495 nm, respectively. The quantum yields for the substituted polyacenes **4g**, **9**, and **11** were 0.18, 0.65, and 0.15, respectively. These observations match well with reported photophysical data of 2-carbonylpolyacenes.[16]

In conclusion, we have developed a phosphine-mediated multicomponent reaction between allenes, *o*-phthalaldehydes, and nucleophiles that provides non–C_2-symmetric naphthalene, anthracene, and tetracene derivatives. A mechanistic investigation involving the synthesis of putative intermediates and reaction monitoring through HRMS revealed that this conversion occurs through a γ-umpolung/aldol/Wittig/dehydration cascade. A combination of phthalaldehydes and 1,3-disubstituted allenes also produces naphthalenes through an aldol/Wittig/dehydration sequence. This arene homologation can also be applied iteratively to prepare higher-order acenes.

ASSOCIATED CONTENT

Supporting Information.
Experimental procedures and analytical data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The structures of **4o** and **4o´** were identified using ^{1}H NMR spectroscopy. See the detailed information in the Supporting Information.

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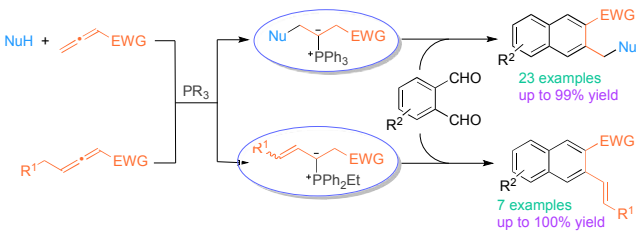
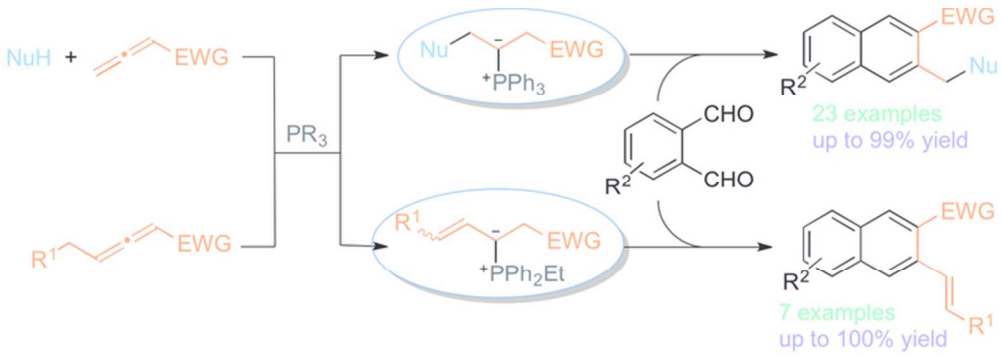
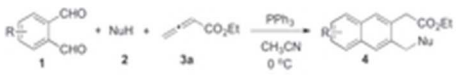
TOC Graphic


NuH +
EWG
R1
EWG
PR3
Nu
EWG
+PPh3
R1
EWG
+PPh2Et
CHO
CHO
R2
R2
EWG
Nu
23 examples
up to 99% yield
R2
EWG
R1
7 examples
up to 100% yield

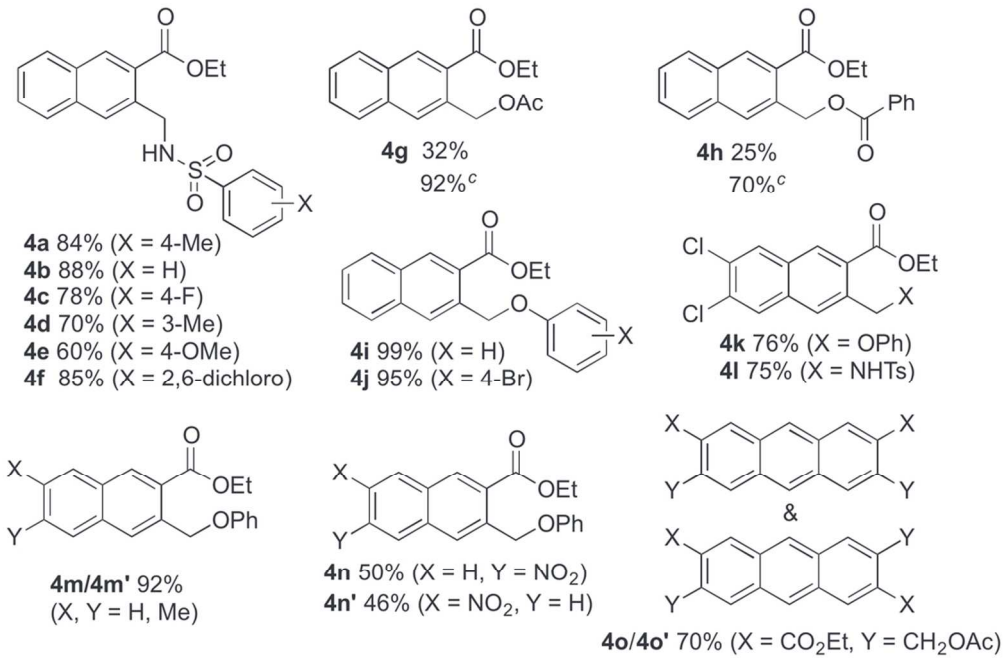
TOC Graphic



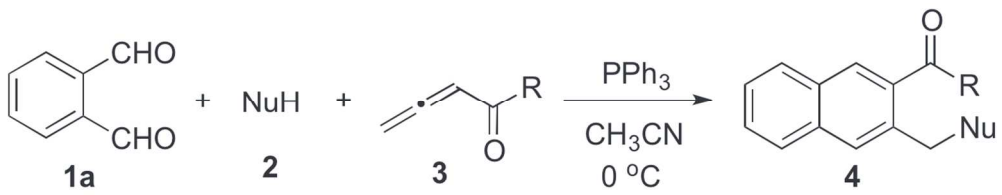
67x29mm (300 x 300 DPI)



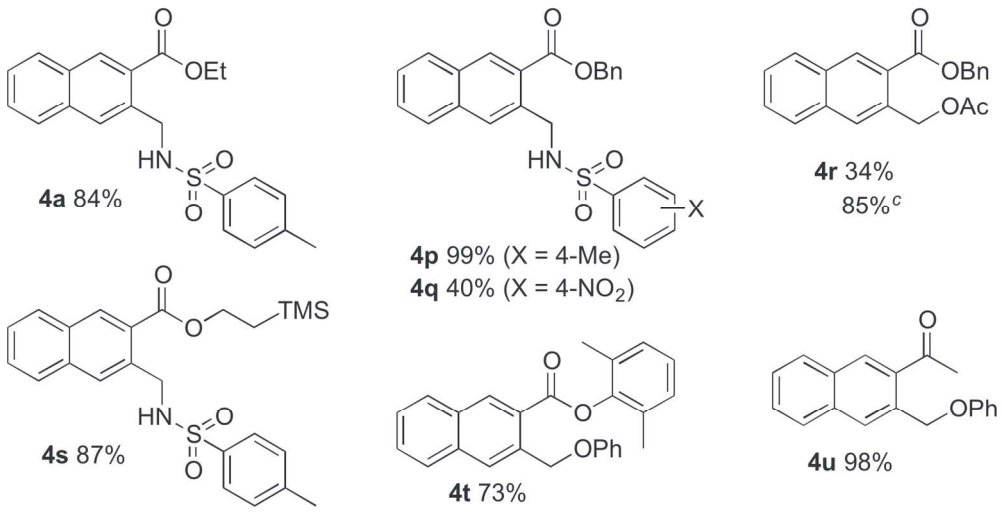
19x2mm (300 x 300 DPI)



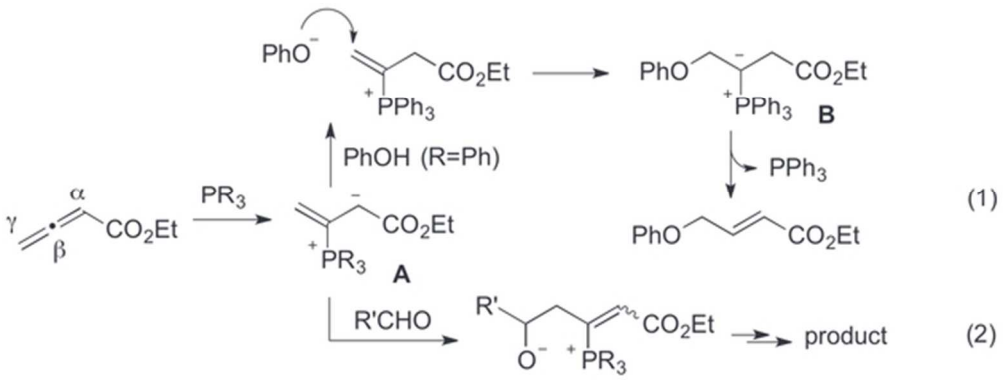
99x65mm (300 x 300 DPI)



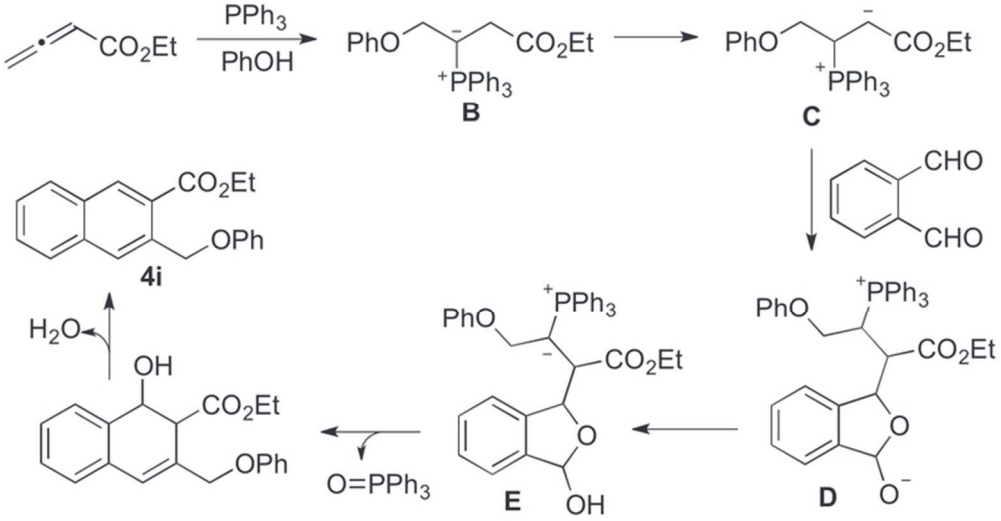
118x23mm (300 x 300 DPI)



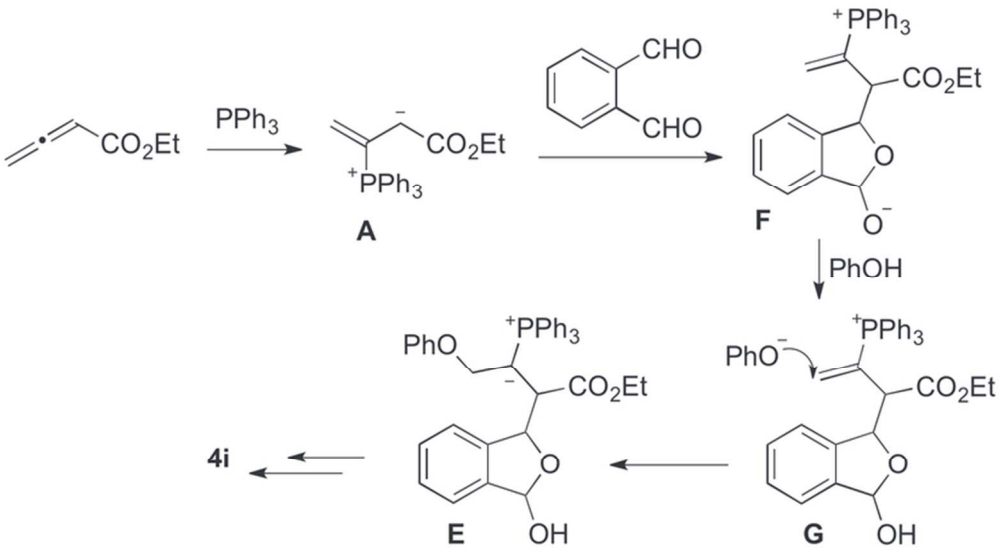
142x72mm (300 x 300 DPI)



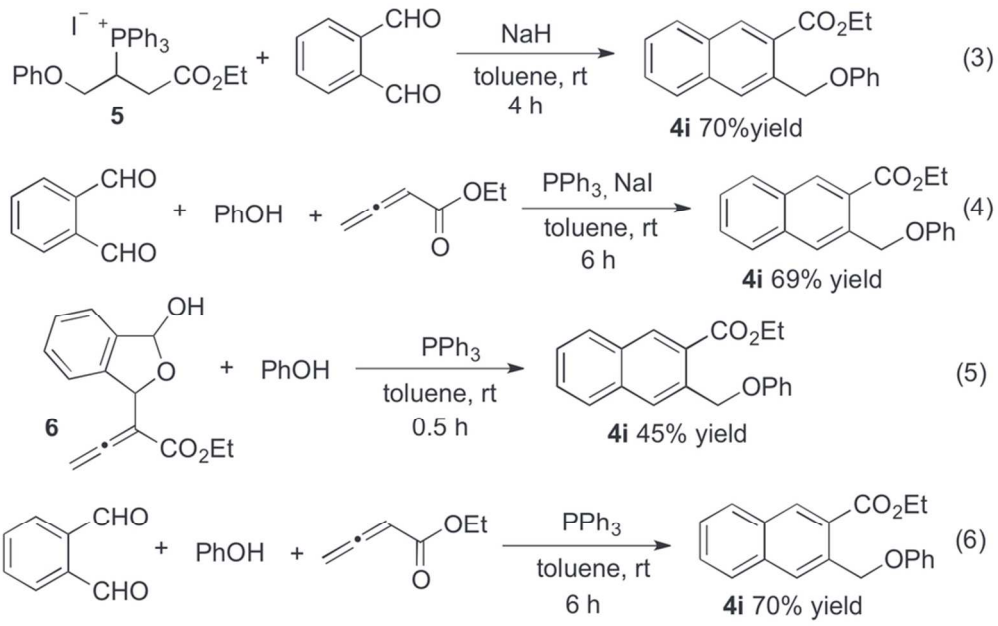
53x20mm (300 x 300 DPI)



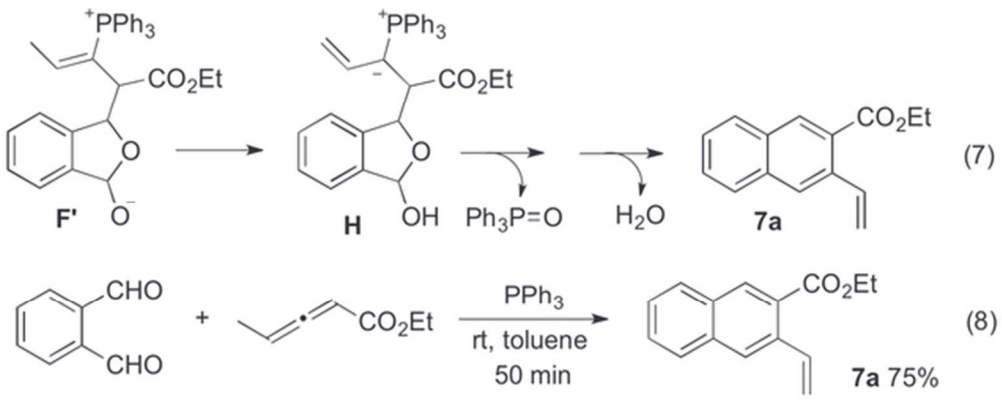
67x35mm (300 x 300 DPI)



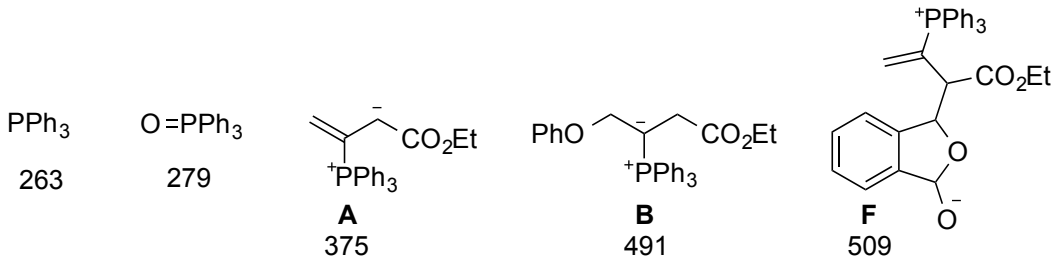
69x38mm (300 x 300 DPI)

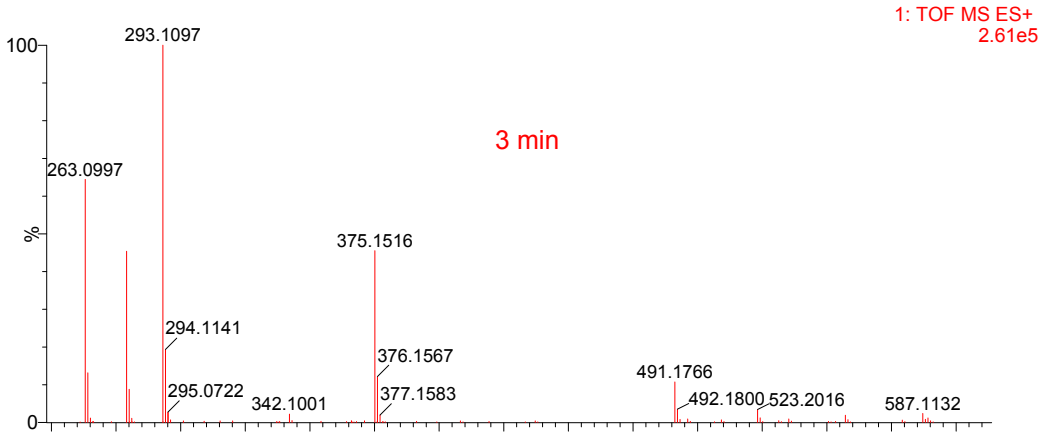


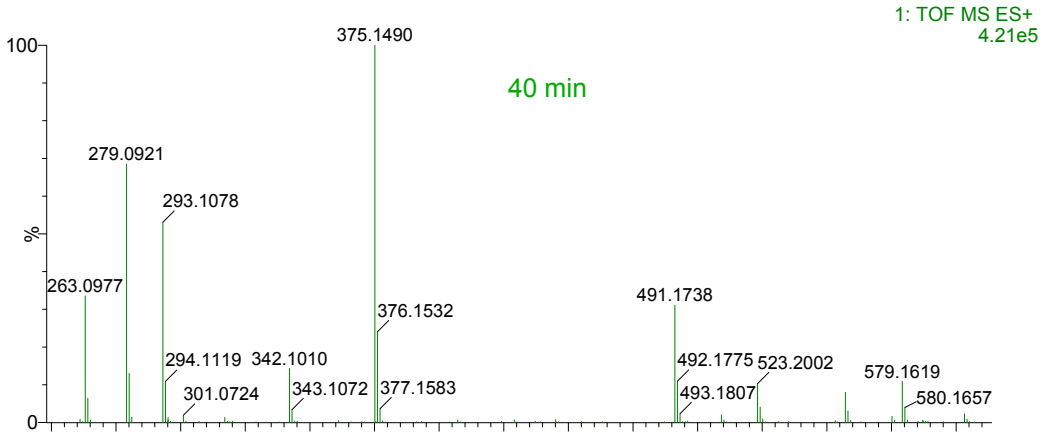
85x53mm (300 x 300 DPI)

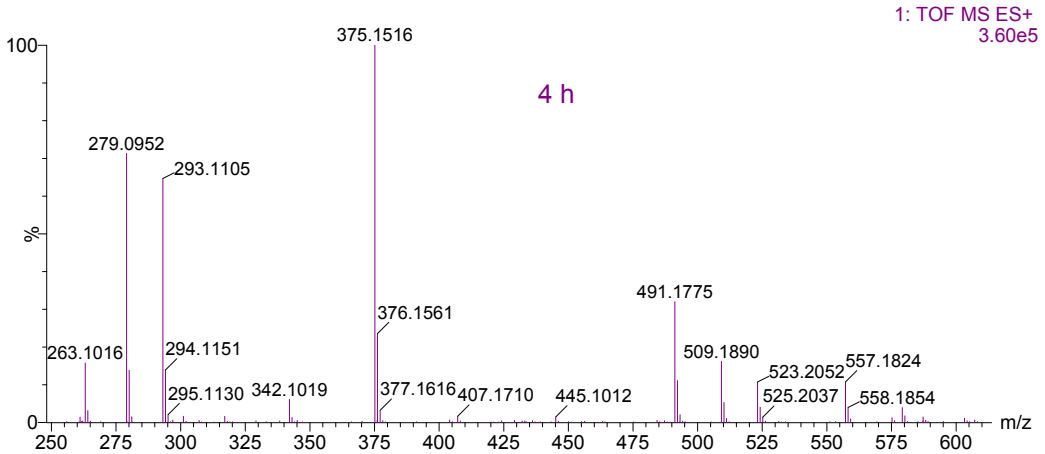


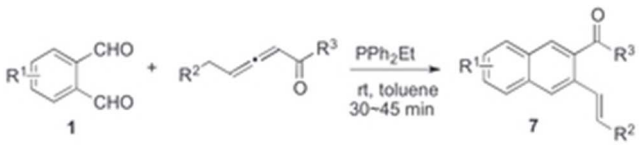
53x21mm (300 x 300 DPI)


PPh3
263
O=PPh3
279
CO2Et
+PPh3
A
375
PhO
CO2Et
+PPh3
B
491
+PPh3
CO2Et
O
O
F
509

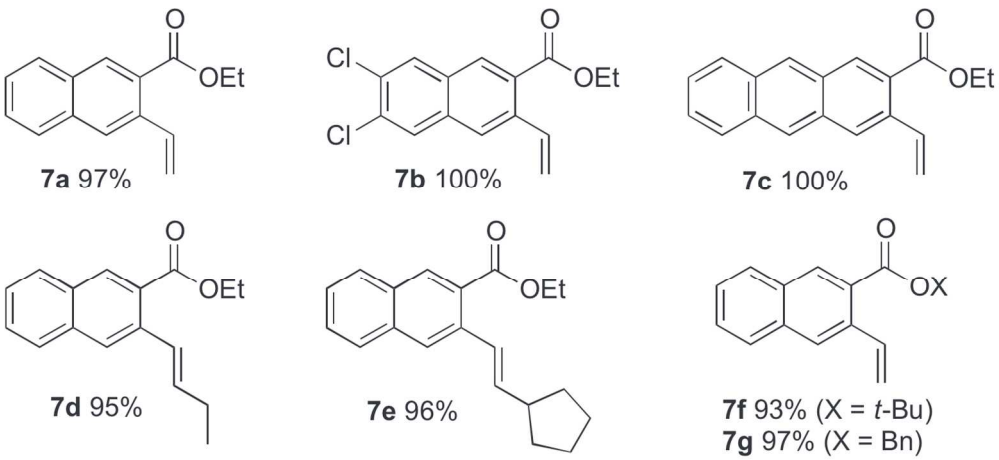

1: TOF MS ES+
2.61e5
3 min
100
%
0
293.1097
263.0997
375.1516
294.1141
376.1567
295.0722
342.1001
377.1583
491.1766
492.1800
523.2016
587.1132


1: TOF MS ES+
4.21e5
40 min
100
%
0
375.1490
279.0921
293.1078
263.0977
376.1532
491.1738
294.1119
342.1010
492.1775
523.2002
579.1619
301.0724
343.1072
377.1583
493.1807
580.1657

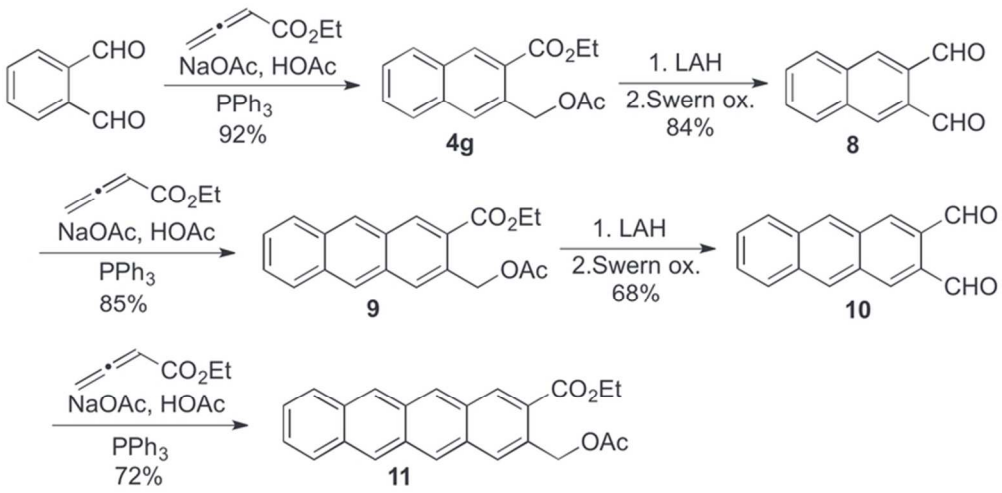

1: TOF MS ES+
3.60e5
4 h
100
%
0
375.1516
279.0952
293.1105
491.1775
376.1561
263.1016
294.1151
509.1890
523.2052
557.1824
295.1130
342.1019
377.1616
407.1710
445.1012
525.2037
558.1854
250
275
300
325
350
375
400
425
450
475
500
525
550
575
600
m/z



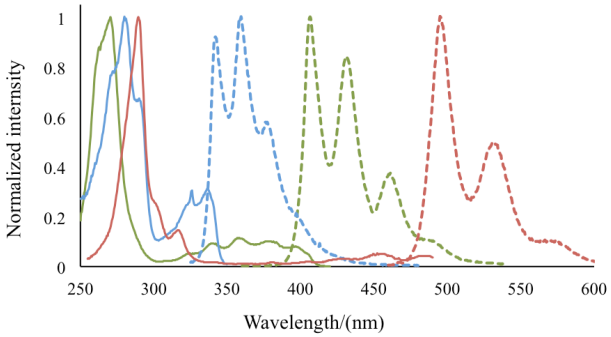
26x5mm (300 x 300 DPI)



130x60mm (300 x 300 DPI)



70x34mm (300 x 300 DPI)


Normalized intensity
1
0.8
0.6
0.4
0.2
0
250
300
350
400
450
500
550
600
Wavelength/(nm)