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Highly diastereoselective synthesis of new chromenylaminoanthraquinones through a one-pot, three-component hetero Diels–Alder reaction

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Abstract—A new, efficient, and diastereoselective one-pot synthesis of cis-fused pyrano and furano chromenylaminoanthraquinones through hetero Diels–Alder reaction of 1-aminoanthraquinone and salicylaldehydes with electron-rich alkenes such as 3,4-dihydro-2*H*-pyran, 2,3-dihydrofuran, and ethyl vinyl ether under mild conditions is reported.

Aminoanthraquinones have attracted considerable attention from both synthetic and medicinal chemists due to their biological activities covering a wide range of applications. In recent years, the problem of multidrug resistance (MDR) towards numerous antitumor compounds has also become important and much effort has been directed towards incorporation of a five- or six-membered heterocyclic ring in the anthracenedione moiety.[1] Several aminoanthraquinone derivatives were identified as DNA intercalating agents[2] and the antitumor antibiotics, daunomycin, and adriamycin[3] are examples of derivatives. Anthraquinone derivatives have been utilized for the activation of human telomerase reverse transcriptase expression.[4] Annulated arene heterocycles and carbocycles such as chromanones,[5] chromans,[6] quinolines,[7] and tetrahydroquinolines[8] are present as important core structures in many biologically active natural products and pharmaceuticals. 2*H*-1-Benzopyrans (chromenes) and 3,4-dihydro-2*H*-1-benzopyrans (chromans) are important classes of oxygenated heterocycles that have attracted much synthetic interest because of the biological activity of naturally occurring representatives.[9] Numerous 4-aminobenzopyrans and their derivatives have drawn considerable attention in the last decade as the modulators of potassium channels influencing cardiac activity of the heart and blood pressure.[10]

The hetero Diels–Alder reaction is an important carbon–carbon bond forming process in organic chemistry. It is also a versatile tool for the synthesis of six-membered heterocyclic compounds and biologically active natural products. The appropriate choice of aldehyde and amine in the hetero Diels–Alder reaction provides a facile entry to bis-heterocyclic systems, which is an essential moiety in many active pharmaceuticals.

A number of Lewis acids such as lanthanide triflates, $Yb(OTf)_3$, $Sc(OTf)_3$, $BF_3{\cdot}Et_2O$ and $GdCl_3$ were found to catalyze this reaction.[11] Despite improvements by performing these hetero Diels–Alder reactions in one-pot through coupling with aldehydes catalyzed by Lewis acids, efficient, and mild reaction conditions are still required for these transformations. In general, most imines are hygroscopic, are unstable at high temperatures and are difficult to purify through distillation or column chromatography. Therefore, developing simple and convenient procedures for preparing imines in one-pot is important. Triphenylphosphonium perchlorate (TPPP) is mild and does not require anhydrous conditions. Due to its catalytic efficiency and the ready availability of starting materials, this reaction constitutes the most attractive strategy for the synthesis of chromenylaminoanthraquinone derivatives. The use of a convergent three-component reaction between aldehydes, aminoanthraquinone, and alkenes in which

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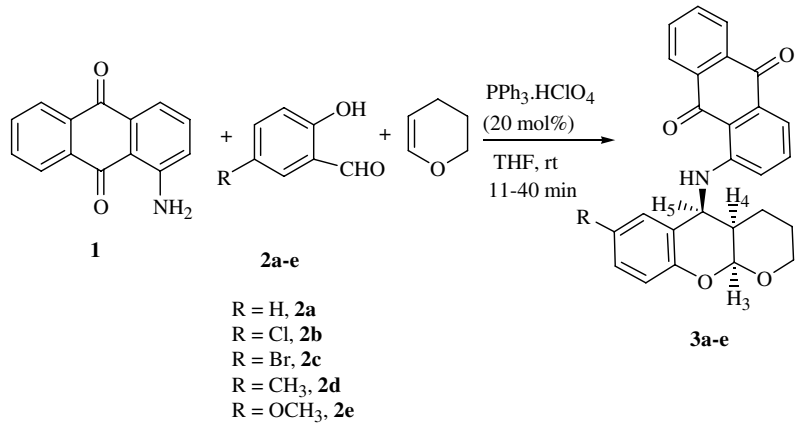


Scheme 1.

Table 1. TPPP catalyzed synthesis of pyranochromenylaminoanthraquinones

Entry	R	Product	Time (min)	Yield (%)
1	H	**3a**	20	71
2	Cl	**3b**	27	65
3	Br	**3c**	40	53
4	CH_3	**3d**	15	80
5	OCH_3	**3e**	11	90

the heterocycle is assembled in one-pot is of a particular note and especially valuable for its potential application in combinatorial synthesis.

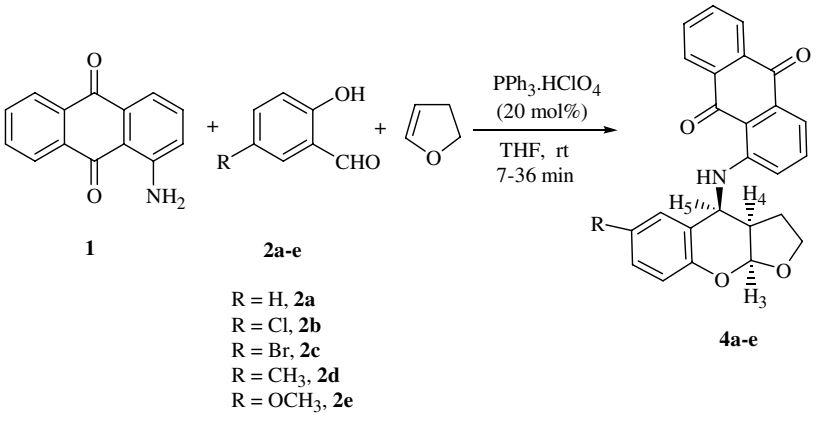
In this letter, we describe a new and highly efficient protocol for the stereoselective synthesis of cis-fused pyrano and furano chromenylaminoanthraquinones. The reaction of an imine, generated in situ from salicylaldehyde and 1-aminoanthraquinone cycloaddition with 3,4-dihydro-2*H*-pyran, 2,3-dihydrofuran, or ethyl vinyl ether catalyzed by TPPP gave exclusively *cis*-chromenylaminoanthraquinones in good yields.

To a stirred solution of 1-aminoanthraquinone **1**, salicylaldehyde **2**, and 3,4-dihydro-2*H*-pyran in THF, was added a catalytic amount of TPPP (20 mol %) at room temperature and the reaction stirred for about 20 min. The reaction proceeded smoothly and afforded the corresponding pyranochromenylaminoanthraquinone **3a** in a 71% yield (Scheme 1). Several examples illustrating this procedure for the synthesis of cis-fused pyranochromenylaminoanthraquinones are summarized in Table 1. In all cases, the three-component, one-pot reaction yielded the products as single diastereomers with cis-configuration. The stereochemistry of **3a** was assigned based on the coupling constant values and also by NOE studies. The six-membered tetrahydropyran rings are cis-fused, $J_{3-4} = 2.4$ Hz between H3 (δ 5.70) and H4 (δ 2.51). Also, $J_{4-5} = 5.9$ Hz (H5, δ 5.28) in **3a** and the presence of NOE's between H3–H4 and H4–H5 conforms that H5 is cis to H4.

Extending the methodology further, we examined the reactivity of dihydrofuran with salicylaldehydes and

Table 2. Synthesis of furanochromenylaminoanthraquinones catalyzed by TPPP

Entry	R	Product	Time (min)	Yield (%)
1	H	**4a**	12	82
2	Cl	**4b**	20	68
3	Br	**4c**	36	55
4	CH_3	**4d**	10	88
5	OCH_3	**4e**	7	92



Scheme 2.

1-aminoanthraquinone catalyzed by TPPP. The reaction was highly diastereoselective and afforded the corresponding cis-fused furanochromenylaminoanthraquinone **4a** in a good yield (Scheme 2 and Table 2). The stereochemistry of the products was confirmed by

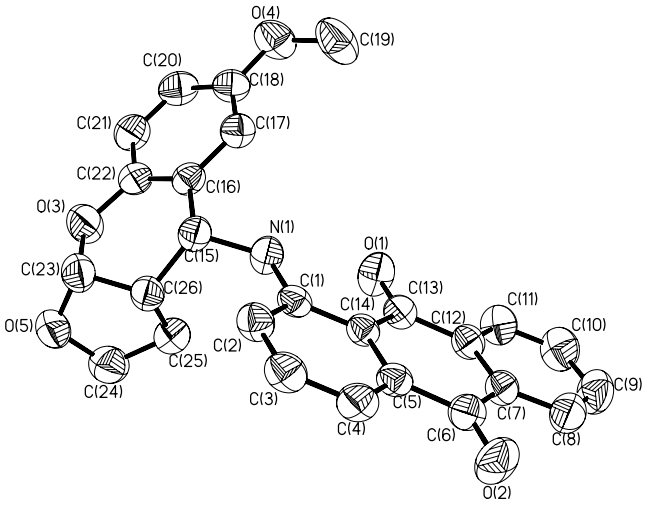


Figure 1. ORTEP diagram of **4e**.

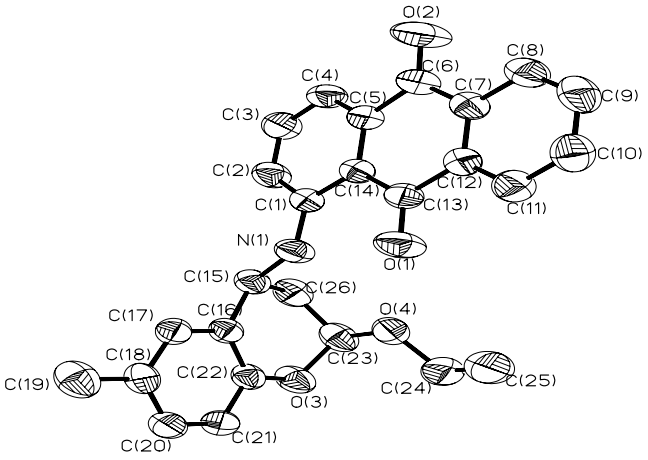


Figure 2. ORTEP diagram of **5d**.

Table 3. TPPP catalyzed formation of chromenylaminoanthraquinones

Entry	R	Product	Time (min)	Yield (%)
1	H	**5a**	30	60
2	Cl	**5b**	41	52
3	Br	**5c**	50	45
4	CH_3	**5d**	26	70
5	OCH_3	**5e**	21	72

^{1}H NMR and NOE studies. The six-membered tetrahydropyran and five-membered tetrahydrofuran rings were cis-fused, as indicated by the coupling constant $J_{3-4} = 5.9$ Hz between H3 (δ 5.93) and H4 (δ 3.12) for product **4a**. Also, $J_{4-5} = 3.3$ Hz (H5, 5.08) for **4a** and the presence of NOE's between H3–H4 and H4–H5, supports that H5 is cis to H4. The structures of **4a** and **4e** (Fig. 1) were also confirmed by single crystal X-ray analysis.[12]

Furthermore, the reaction between the imine generated from 1-aminoanthraquinone with salicylaldehydes and ethyl vinyl ether afforded **5a**–**e** (Scheme 3 and Table 3). Ethyl vinyl ether also exhibited analogous behavior to that of dihydropyran and dihydrofuran with respect to the stereochemistry of the products. The stereochemistry was assigned by ^{1}H NMR spectroscopy based on the chemical shift and coupling constant value $J_{H1-2a} = 3.2$ Hz between H1 (δ 5.44) and H2a (δ 3.97) for **5a**. The structure of products **5c**–**5e** were also confirmed by single crystal X-ray analysis[13] (Fig. 2).

In summary, we have described a novel and practical method for the synthesis of cis-fused pyrano and furanochromenylaminoanthraquinones.[14] In addition to its simplicity and mild reaction conditions, this procedure has advantages of high yields, easy availability and flexibility of starting materials, short reaction times, and useful diastereoselectivity.

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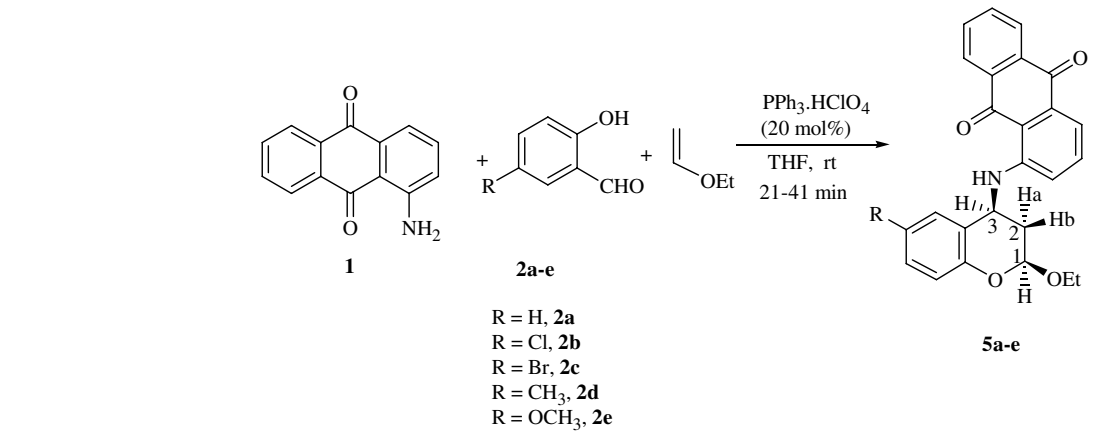

Scheme 3.

school. G.V. and D.K.S. thank the CSIR for junior research fellowships. We thank Mr. P. Raghavaiah for his help in solving the crystal structures of the compounds.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.10.104.

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12. The CCDC deposition number for **4a** is 615199; molecular formula: $C_{25}H_{19}NO_4$, chemical formula weight 397.41, monoclinic, unit cell parameters: *a* 13.164(4), *b* 11.071(3), *c* 14.675(4), β 114.476(5) and space group *P*2(1)/c. The CCDC deposition number for **4e** is 615200; molecular formula: $C_{26}H_{21}NO_5$, chemical formula weight 427.44, monoclinic, unit cell parameters: *a* 7.8621(9), *b* 27.052(3), *c* 9.8538(11), β 99.510(2) and space group *P*2(1)/c.
13. The CCDC deposition number for **5c** is 615198; molecular formula: $C_{100}H_{79}Br_4N_4O_{16}$ (tetramer), chemical formula weight 1912.31, monoclinic, unit cell parameters: *a* 15.0557(11), *b* 31.951(2), *c* 18.3675(13), β 106.9290(10), and space group *P*2(1)/n. The CCDC deposition number for **5d** is 615201; molecular formula: $C_{26}H_{23}NO_4$, chemical formula weight 413.45, monoclinic, unit cell parameters: *a* 15.508(4), *b* 11.162(3), *c* 12.383(3), β 105.454(4), and space group *P*2(1)/c. The CCDC deposition number for **5e** is 619659; molecular formula: $C_{78}H_{69}N_3O_{15}$ (trimer), chemical formula weight 1288.36, triclinic, unit cell parameters: *a* 11.662(6), *b* 12.589(6), *c* 22.418(11), α 86.591(8), β 78.809(8), γ 83.774(8), and space group *P*−1.
14. General experimental procedure: To a solution of salicylaldehyde (2.5 mmol), 1-aminoanthraquinone (2.5 mmol), 3,4-dihydro-2*H*-pyran, 2,3-dihydrofuran or ethyl vinyl ether (6.25 mmol) in THF, was added TPPP (20 mol %) and the reaction stirred at room temperature for the appropriate time. After completion of the reaction, as

indicated by the TLC, excess THF was distilled off and the residue was poured into water (50 mL) and extracted with DCM (3×20 mL). The organic layer was dried over Na_2SO_4 and distilled under reduced pressure. The residue was chromatographed over silica gel (100–200 mesh size) and eluted with hexane–ethyl acetate to afford pure cis-fused chromenylaminoanthraquinone as a red solid. Spectral data for 1-(3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromen-5-ylamino)-9,10-dihydro-9,10-anthracenedione **3a**: yield 71%; mp: 222 °C; IR (KBr): 3238, 3063, 2945, 2885, 1720, 1666, 1452, 1267, 1093, 979 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$) δ: 10.22 (1H, d, $J = 7.9$ Hz, N*H*), 8.26–8.30 (2H, m, ArC*H*-5/8), 7.74–7.78 (2H, m, ArC*H*-6/7), 7.62–7.71 (2H, m, ArC*H*-3/4), 7.34 (1H, d, $J = 7.2$ Hz, ArC*H*-2), 7.21–7.27 (2H, m, ArC*H*), 6.95–6.98 (2H, m, ArC*H*), 5.70 (1H, d, $J = 2.4$ Hz, OC*H*O), 5.28 (1H, t, $J = 5.9$ Hz, NH–C*H*), 3.79–4.06 (2H, m,OCH_2), 2.51 (1H, q, $J = 5.3$ Hz), 1.72–1.82 (3H, m), 1.51–1.56 (1H, m); ^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ: 185.5 (Ar*C*-9), 183.5 (Ar*C*-10), 152.9 (Ar*C*–O), 151.3 (Ar*C*-1), 135.7, 135.0, 134.8, 134.1, 33.2, 132.9, 132.2, 129.3, 126.9, 126.8, 126.6, 121.4, 120.6, 117.7, 116.4, 113.6 (aromatic *C*); 96.1, 60.9, 50.9, 35.8, 24.1, 17.6 (aliphatic *C*); LC-MS: $m/z = 412$ ($M+H^+$), positive mode; Anal. Calcd for $C_{26}H_{21}NO_4$: C, 75.90; H, 5.14; N, 3.40; found: C, 75.92; H, 5.16; N, 3.33. 1-(2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-ylamino)-9,10-dihydro-9,10-anthracenedione **4a**: yield 82%; mp: 111 °C; IR (KBr): 3250, 3069, 2959, 1668, 1265, 1039, 802, 707 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$) δ: 10.23 (1H, d, $J = 8.0$ Hz, N*H*), 8.19–8.24 (2H, m, ArC*H*-5/8), 7.61–7.73 (3H, m, ArC*H*-4/6/7), 7.50 (1H, t, $J = 8.0$ Hz, ArC*H*-3), 7.17–7.20 (2H, m, ArC*H*), 7.07 (1H, d, $J = 8.4$ Hz, ArC*H*-2), 6.90–6.93 (2H, m, ArC*H*), 5.93 (1H, d, $J = 5.9$ Hz, OC*H*O), 5.08 (1H, t, $J = 3.3$ Hz, NH–C*H*); 3.79–3.85 (2H, m, OCH_2), 3.12–3.20 (1H, m), 2.06–2.16 (1H, m), 1.70–1.81 (1H, m); ^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ: 185.7 (Ar*C*-9), 183.5 (Ar*C*-10), 152.9 (Ar*C*–O), 151.4 (Ar*C*-1), 135.8, 135.2, 134.9, 134.1, 133.3, 133.0, 129.2, 126.9, 126.8, 125.9, 124.2, 122.3, 118.3, 118.2, 117.6, 116.6 (aromatic *C*); 102.5, 68.2, 48.8, 44.1, 24.8 (aliphatic *C*); LC-MS: $m/z = 398$ ($M+H^+$), positive mode; Anal. Calcd for $C_{25}H_{19}NO_4$: C, 75.55; H, 4.82; N, 3.52; found: C, 75.54; H, 4.87; N, 3.64. 1-(2-Ethoxy-6-methyl-3,4-dihydro-2*H*-4-chromenylamino)-9,10-dihydro-9,10-anthracenedione **5a**: yield 60%; mp: 153 °C; IR (KBr): 3246, 3069, 2968, 2885, 1664, 1267, 1111, 1020, 952, 895 cm^{-1}; ^1H NMR (400 MHz, TMS, $CDCl_3$) δ: 10.42 (1H, d, $J = 9.0$ Hz, N*H*), 8.22–8.25 (2H, m, ArC*H*-5/8), 7.64–7.73 (2H, m, ArC*H*-6/7), 7.75–7.63 (2H, m, ArC*H*-3/4), 7.34–7.37 (2H, m, ArC*H*), 7.21 (1H, d, $J = 8.5$ Hz, ArC*H*-2), 6.95–6.97 (2H, m, ArC*H*), 5.44 (1H, t, $J = 3.2$ Hz, OC*H*OCH_2CH_3), 5.04 (1H, m, NH–C*H*), 3.97–4.03 (1H, m), 3.64–3.70 (1H, m), 2.36–2.42 (2H, m, OCH_2CH_3), 1.31 (3H, t, $J = 7.0$ Hz, OCH_2CH_3); ^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ: 184.4 (Ar*C*-9), 183.9 (Ar*C*-10), 151.4 (Ar*C*–O), 150.4 (Ar*C*-1), 135.2, 135.1, 133.9, 132.9, 132.8, 131.5, 129.4, 129.1, 126.7, 126.6, 123.4, 121.6, 117.7, 117.3, 115.6, 113.5 (aromatic *C*); 96.7, 64.4, 44.1, 33.1, 15.0 (aliphatic *C*); LC-MS: $m/z = 422$, showing +23 sodium adduct ion, positive mode; Anal. Calcd for $C_{25}H_{21}NO_4$: C, 75.17; H, 5.30; N, 3.51; found: C, 75.17; H, 5.31; N, 3.83.