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Submitted date: 14/02/2019 • Posted date: 14/02/2019

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Citation information: van Leest, Nicolaas P.; grooten, Lars; Ivar van der Vlugt, Jarl; de Bruin, Bas (2019):  
Uncatalysed Oxidative C–H Amination of 9,10-Dihydro-9-Heteroanthracenes: A Mechanistic Study.  
ChemRxiv. Preprint.

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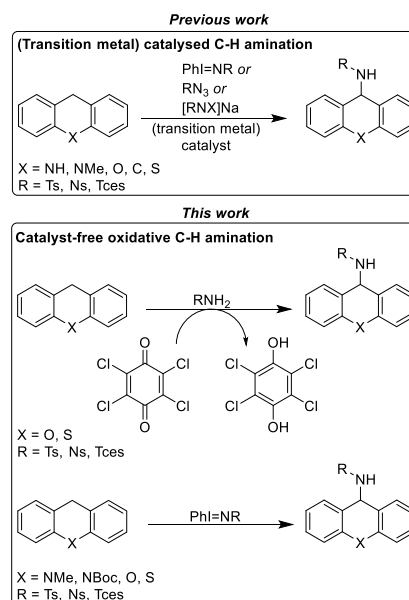
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# Uncatalysed Oxidative C–H Amination of 9,10-Dihydro-9-Heteroanthracenes: A Mechanistic Study

Nicolaas P. van Leest, Lars Grooten, Jarl Ivar van der Vlugt and Bas de Bruin\*<sup>[a]</sup>

**Abstract:** A new method for the one-step C–H amination of xanthene and thioxanthene with sulfonamides is reported, without the need for any metal catalyst. A benzoquinone is employed as a hydride (or two-electron and one-proton) acceptor. Moreover, a previously unknown and uncatalysed reaction between iminoiodanes and xanthene, thioxanthene and dihydroacridines (9,10-dihydro-9-heteroanthracenes or dihydroheteroanthracenes) is disclosed. The reactions proceed via hydride transfer from the heteroarene substrate to the iminoiodane or benzoquinone, followed by conjugate addition of the sulfonamide to the oxidized heteroaromatic compounds. These findings may have important mechanistic implications for metal-catalysed C–H amination processes involving nitrene transfer from iminoiodanes to dihydroheteroanthracenes. Due to the weak C–H bond, xanthene is an often-employed substrate in mechanistic studies of C–H amination reactions, which are generally proposed to proceed via metal-catalysed nitrene insertion, especially for reactions involving nitrene or imido complexes that are less reactive (i.e. less strongly oxidizing). However, these substrates clearly undergo non-catalysed (proton-coupled) redox coupling with amines, thus providing alternative pathways to the widely assumed metal-catalysed pathways.



**Figure 1.** Comparison between previously reported (transition metal) catalysed amination of C–H bonds and the catalyst-free protocols presented in this work.

## Introduction

The development of new synthetic methods for the synthesis of (secondary) amines is a constantly evolving field, due to the ever increasing demand for nitrogen containing compounds in e.g. pharmaceuticals and agrochemicals.<sup>[1]</sup> Direct (*sp*<sup>3</sup>) C–H amination via metal-nitrene intermediates has received increasing attention in the last two decades, as no pre-functionalisation of the hydrocarbon substrates is required.<sup>[2–5]</sup> Key developments are the use of activated<sup>[6–8]</sup> and non-activated organic azides,<sup>[9–14]</sup> Haloamine-T<sup>[15,16]</sup> and (in situ generated) iminoiodanes (PhI=NR) as nitrene precursors (Figure 1).<sup>[17–22]</sup> Transition metal complexes have proven to be excellent catalysts for these amination reactions, and the commonly accepted mechanism comprises the formation of a reactive metal-nitrene intermediate, followed by stepwise hydrogen atom abstraction and radical recombination or concerted insertion of the nitrene into the C–H bond.<sup>[3,5,23]</sup> In addition, organocatalysts are reported that are also capable of nitrene transfer.<sup>[24,25]</sup>

Our group is interested in the formation and characterisation of new metal-nitrene complexes from known nitrene precursors and ideally directly from primary amines. As others, we adopted the reasoning that successful nitrene transfer could be dictated by the relative bond dissociation free energy (BDFE) of the C–H bond, with a lower BDFE expectedly resulting in faster nitrene insertion.<sup>[24,26–32]</sup> Dihydroheteroanthracenes (xanthene, thioxanthene and dihydroacridine derivatives) have low C–H bond dissociation energies (BDE) in the range of 74–81 kcal mol<sup>–1</sup>.<sup>[33]</sup> Therefore, dihydroheteroanthracenes are often assumed to be suitable model substrates to test for basic C–H amination activity, even for relatively non-reactive nitrene intermediates.<sup>[34]</sup> Especially xanthene is a commonly used substrate to investigate reaction kinetics of such reactions.<sup>[27–30,32]</sup>

In the course of our investigations, we initially reasoned in a similar manner. However, much to our surprise, we observed that sulfonamides are able to react with xanthene and thioxanthene in the presence of a benzoquinone derivative as a sacrificial oxidant and base, without the need for a (transition metal) catalyst. Even more interestingly, we also observed that dihydroheteroanthracenes react with commonly used iminoiodanes to afford the corresponding amination product in the absence of any catalyst (Figure 1). To the best of our knowledge, this background reaction has not been reported in literature. In this contribution, we disclose the details of catalyst-free amination reactions of dihydroheteroanthracenes. The obtained insights are of considerable interest for researchers interested in (transition metal) catalysed nitrene transfer, as we describe hitherto

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unknown, uncatalysed background reactions and report a new mechanism for amination of dihydroheteroanthracenes that is very different from the generally accepted (metal) catalysed nitrene transfer processes.

## Results and Discussion

During our efforts to develop new (transition) metal catalysed  $sp^3$  C–H amination strategies directly from amines, we stumbled across the uncatalysed amination of xanthene with *p*-toluenesulfonamide (TsNH<sub>2</sub>) in the presence of tetrachloro-*p*-benzoquinone (chloranil) as an oxidant. We decided to optimize the reaction conditions of this reaction (Table 1) in order to shine more light on this unexpected reaction. The C–H aminated product **1** was obtained in 22–48% yield after 20 hours at 30 °C in solvents most commonly used in nitrene transfer reactions (entries 1–4). Decreasing the reaction time to 5 hours resulted in a lower yield, whereas increasing the reaction temperature to 60 °C afforded **1** in 43% yield in benzene (entries 5 and 6). Performing the reaction at 60 °C for a longer time (20 hours) in benzene led to the formation of **1** in 72% or 83% in the presence and absence of light, respectively (entries 7 and 8). The conditions in entry 8 proved to be the optimal reaction conditions. For practical purposes we employed the conditions in entry 7 for further screening (*vide infra*). Dilution of the total concentration from 50 mM to 25 mM, increasing the amount of chloranil or performing the reaction under an argon atmosphere did not improve the yield (see Table S1 in the Supporting Information). It is worth mentioning that the reaction can be performed without drying the solvent and that the only by-product is xanthone (3–7%).<sup>[36]</sup>

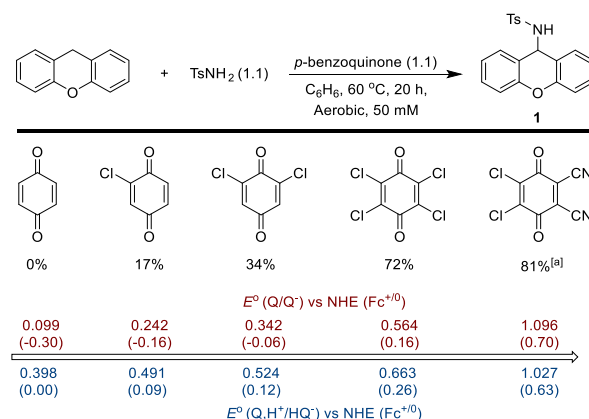
With the optimized conditions in hand, we screened various *p*-benzoquinone derivatives for their reactivity in the amination of xanthene by TsNH<sub>2</sub> (Scheme 1). The mildly oxidizing parent *p*-benzoquinone did not lead to conversion of xanthene. However, the use of 2-chloro-*p*-benzoquinone, 2,6-dichloro-*p*-benzoquinone, chloranil or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) afforded **1** in 17, 34, 72 and 81%, respectively. The trends in the yield of **1** nicely correlate with the reported 1e<sup>−</sup> and 2e<sup>−</sup>/1H<sup>+</sup> reduction potentials of the corresponding benzoquinones.<sup>[35]</sup> The more oxidizing quinones lead to higher yields, therefore indicating that oxidation of one of the substrates is involved in the reaction mechanism. DDQ, the strongest oxidant employed, is capable of oxidizing **1** to the corresponding imine, which was detected as a side product (10% yield). Moreover, when using this oxidant 9% of xanthone was formed. Other quinones showed the same correlation between yield and redox potential, but afforded larger amounts of (unidentified) side products (Table S2 in the SI).

A small, but representative substrate scope of different sulfonamides and dihydroheteroanthracenes was explored, as shown in Scheme 2. TsNH<sub>2</sub> and 2,2,2-trichloroethoxysulfonamide (TcesNH<sub>2</sub>) form **1** (72%) and **2** (67%) in comparable yields. However, the use of *p*-nitrobenzenesulfonamide (NsNH<sub>2</sub>) yields only 15% of **3** with a considerable amount of xanthone. This is

**Table 1.** Optimization of the reaction conditions for the amination of xanthene with TsNH<sub>2</sub> and chloranil.

Entry	Solvent	Temp (°C)	Time (h)	Yield <sup>[a]</sup>
1	C <sub>6</sub> H <sub>6</sub>	30	20	26%
2	PhCH <sub>3</sub>	30	20	22%
3	MeCN	30	20	23%
4	CH <sub>2</sub> Cl <sub>2</sub>	30	20	48%
5	C <sub>6</sub> H <sub>6</sub>	30	5	18%
6	C <sub>6</sub> H <sub>6</sub>	60	5	43%
7	C <sub>6</sub> H <sub>6</sub>	60	20	72%
<b>8<sup>[b]</sup></b>	<b>C<sub>6</sub>H<sub>6</sub></b>	<b>60</b>	<b>20</b>	<b>83%</b>

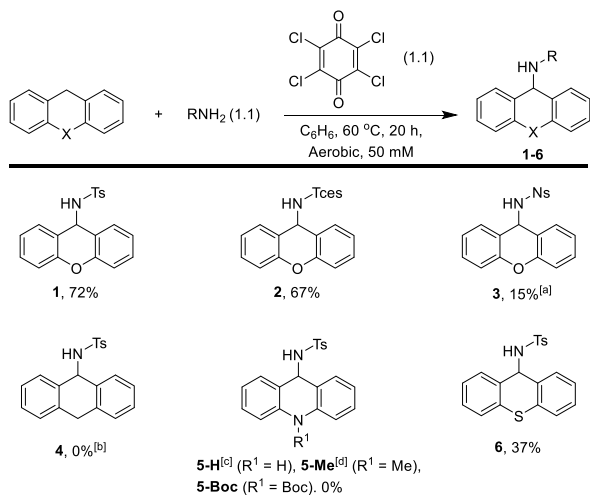
[a] Based on <sup>1</sup>H-NMR integration using 1,3,5-tris-(*tert*-butyl)benzene as an internal standard. [b] Performed in absence of light.



**Scheme 1.** Screening of various *p*-benzoquinones for the synthesis of **1** from xanthene and TsNH<sub>2</sub>. Yields based on <sup>1</sup>H NMR integration using 1,3,5-tris-(*tert*-butyl)benzene as internal standard. [a] 10% oxidation of **1** to the imine and 9% xanthone observed. Potentials for the 1e<sup>−</sup> (Q/Q<sup>•−</sup>) and 2e<sup>−</sup>/1H<sup>+</sup> (Q,H<sup>•+</sup>/HQ<sup>•−</sup>) couples versus NHE in water.<sup>[35]</sup> Potentials versus Fc<sup>+/0</sup> are estimated by a correction of −0.40 V versus NHE.<sup>[37]</sup>

most likely caused by the reduced nucleophilicity of NsNH<sub>2</sub> compared to TsNH<sub>2</sub> and TcesNH<sub>2</sub>, thus leading to higher yields of reaction products stemming from reaction with H<sub>2</sub>O (which is present in the solvent, *vide infra*). 9,10-Dihydroanthracene did not afford the desired product **4**, but generated anthracene in 22% yield. Similarly, various 9,10-dihydroacridine derivatives did not afford the desired products **5–H**, **5–Me** or **5–Boc**; 9,10-dihydroacridine was quantitatively converted to acridine, *N*-methylidihydroacridine was oxidised to unidentified products and *N*-Boc-9,10-dihydroacridine was not converted. However,

thioxanthene reacted in a similar manner as xanthene producing product **6** in 37% yield. Other hydrocarbon substrates with weak C–H bonds, e.g. ethylbenzene and cyclohexadiene, did not afford the desired aminated products (Table S3 in the SI).

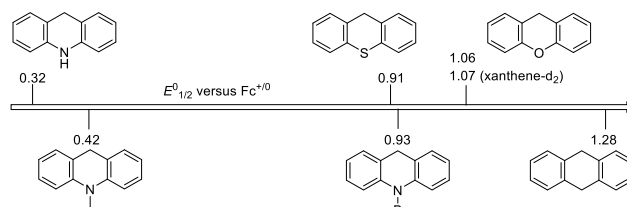


**Scheme 2.** Substrate scope with different amines and dihydroheteroanthracenes. R = Ts, Tces or Ns. Yields based on <sup>1</sup>H NMR integration using 1,3,5-tris-(*tert*-butyl)benzene or 1,3,5-trimethoxybenzene as an internal standard. [a] 28% xanthone formation. [b] 22% anthracene formation. [c] Quantitative conversion to acridine. [d] Quantitative conversion of substrate, no conversion of TsNH<sub>2</sub>.

Tetrachloro-*p*-hydroquinone formation was observed by <sup>1</sup>H NMR spectroscopy for all reactions where the dihydroheteroanthracene was converted. We also obtained crystals of tetrachloro-*p*-hydroquinone from the reaction mixture, and single crystal X-ray diffraction analysis of these crystals confirmed the formation of the aromatic hydroquinone (Figure S23 in the SI). This, in combination with the observed oxidation of the dihydroheteroanthracenes and absence of reaction between chloranil and TsNH<sub>2</sub>, proves that chloranil is acting as a proton and electron acceptor in the oxidative amination process. Moreover, in absence of a sulfonamide, the only formed product is xanthone.<sup>[36]</sup> To rule out the possible involvement of xanthone in the formation of **1** through nucleophilic reaction of the sulfonamide with the carbonyl moiety, we also tested xanthone as the substrate under the same reaction conditions. However, neither in presence or absence of chloranil we observed formation of any product. We therefore rule out that xanthone is involved in the formation of the C–H aminated product **1**. Moreover, we exclude the involvement of oxygen-sensitive free-radical species that result from single-electron transfer, as the conversion and yield do not change in presence or absence of oxygen (*vide supra*).

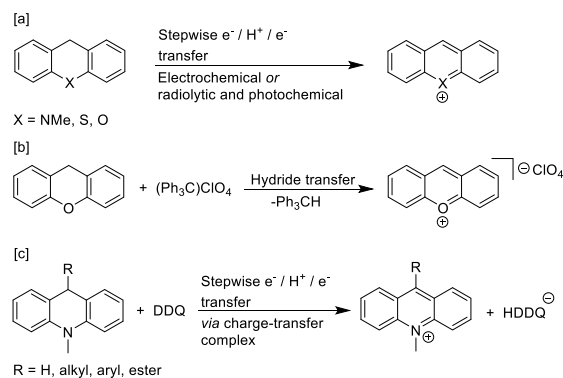
Surprised by these results, we wondered if these reactions could perhaps proceed via two-electron oxidation and deprotonation of the dihydroheteroanthracenes followed by nucleophilic attack of the amine. We therefore investigated the redox potentials of the dihydroheteroanthracenes with cyclic

voltammetry and differential pulse voltammetry (Figure S24 and S25). All observed electrochemical oxidations were found to be irreversible, with the potentials varying from +0.32 V (dihydroacridine) to +1.28 V (dihydroanthracene) versus Fc<sup>+/0</sup>, see Figure 2. These potentials seem to be too high for outer-sphere single-electron transfer from the dihydroheteroanthracene to chloranil in absence of a proton donor ( $E^0_{1/2} = -0.43$  V versus Fc<sup>+/0</sup> in DCM, see Figure S27 in the SI).



**Figure 2.**  $E^0_{1/2}$  versus Fc<sup>+/0</sup> in DCM for various dihydroheteroanthracenes, obtained from DPV measurements in a three-electrode cell with a glassy carbon working electrode, Pt auxiliary electrode and leak-free Ag/AgCl 3.0 M KCl reference electrode.

However, as alternative, the reaction could perhaps proceed via a hydride transfer step from the dihydroheteroanthracenes to chloranil, followed by conjugate addition of the sulfonamide to the cationic heteroanthracenium derivative. The two-electron oxidation and deprotonation of xanthene, thioxanthene and *N*-methyl-dihydroacridine has previously been studied by electrochemical or combined radiolytic and photochemical oxidation and hydride transfer to triphenylmethyl perchlorate (Scheme 3a and 3b).<sup>[37–39]</sup>



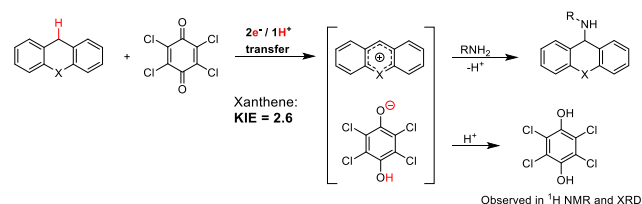
**Scheme 3.** [a] Electrochemical or combined radiolytic and photochemical stepwise two-electron and one-proton transfer from dihydroheteroanthracenes.<sup>[37,38]</sup> [b] Chemical hydride transfer of xanthene to (Ph<sub>3</sub>C)ClO<sub>4</sub>.<sup>[40]</sup> [c] Stepwise two-electron and one-proton transfer from 9-substituted 10-methyl-9,10-dihydroacridines to DDQ.<sup>[41]</sup>

The hydride transfer reactions were shown to proceed through sequential electron-proton-electron transfer to form the heteroanthracenium ions. Moreover, hydride transfer from different 9-substituted 10-methyl-9,10-dihydroacridines (0.41 <

$E_{ox}^0 < 0.52$  V versus  $Fc^{+/0}$ ) to DDQ ( $E_{1/2}^0 = +0.70$  V versus  $Fc^{+/0}$ ) has been studied in detail and was shown to proceed through formation of a charge-transfer complex, followed by stepwise electron-proton-electron transfer within the charge-transfer complex (Scheme 3c).<sup>[41]</sup> Interestingly, it was shown that the initial electron transfer step is in equilibrium and the proton transfer is rate determining. Moreover, the separately prepared xanthylium ion (obtained by hydride transfer of xanthene to triphenylmethyl perchlorate) was recently indeed shown to react with 4-cyclohepta-2,4,5-trien-1-yl)aniline and pyrimidin-2-amine to produce aminated products.<sup>[38,41]</sup> These data and observations suggest that the reactions in Scheme 2 might indeed proceed via initial hydride transfer as well.

To test our hypothesis that chloranil might act as a hydride acceptor, we performed an intermolecular kinetic isotope competition study with xanthene, xanthene- $d_2$ ,  $TsNH_2$  and chloranil. This led to a kinetic isotope effect (KIE) of 2.6, clearly indicating that a proton or hydride transfer step is involved in the rate determining step or in a pre-equilibrium leading to the rate determining step. To obtain more insight in this step, we monitored the reaction under standard conditions in absence of sulfonamide. We were unable to detect the formation of the xanthylium cation by  $^1H$  NMR spectroscopy. However, under aerobic conditions larger amounts of oxidised products (xanthone and xanthidrol) were observed than when the reaction was performed under argon. This indicates that hydride transfer from xanthene to chloranil is in a thermodynamically unfavourable equilibrium with the xanthylium ion and the 2,3,5,6-tetrachloro-4-hydroxyphenoxyl anion. However, in presence of a nucleophile ( $H_2O$  or sulfonamide) the xanthylium cation can react to form the aminated or hydrated products (*vide supra*).

We therefore propose that chloranil acts as a hydride (or one-proton and two-electron) acceptor for dihydroheteroanthracene oxidation to form the heteroanthracenium ion and the 2,3,5,6-tetrachloro-4-hydroxy-phenoxyl anion (Figure 3). Subsequent conjugate addition of the sulfonamide to the heteroanthracenium ion leads to product formation. The products **4** and **5** are not formed, probably because the oxidised substrates from anthracene and acridine are not electrophilic enough to react with the weakly nucleophilic  $TsNH_2$ . A control reaction with acridine as the substrate indeed confirmed this (Scheme S4 in the SI).

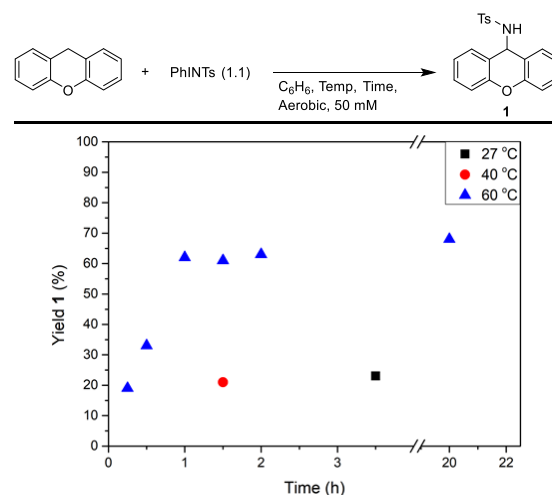


**Figure 3.** Proposed reaction mechanism for the amination reaction with chloranil and sulfonamides. X = O or S, R = Ts, Tces or Ns. Intermolecular KIE (2.6) for the formation of **1**.

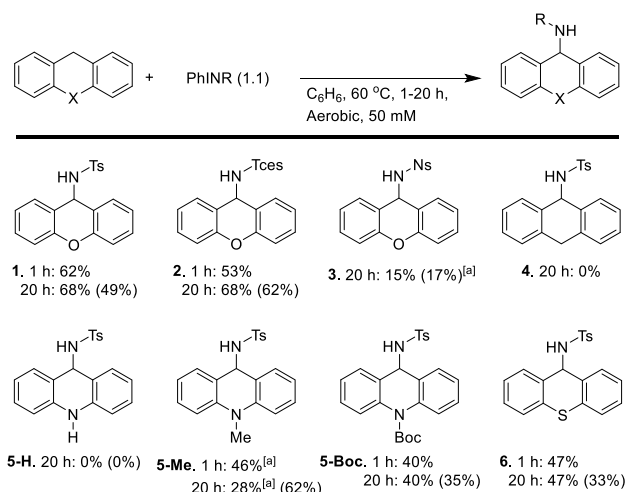
Intrigued by the results obtained using the combination of chloranil as the hydride (or two-electron and one-proton) acceptor and sulfonamides as the nitrogen source in the amination of

xanthene and thioxanthene, we wondered whether the oxidant and nitrogen group donor could also be combined in a single reagent. We therefore decided to investigate the use of hypervalent iodine reagents such as PhINTs could be used as amide delivering oxidant in absence of a transition metal catalyst. PhINTs is a common nitrene precursor for C–H amination and alkene aziridination reactions in combination with various transition metal catalysts, but the free iminoiodane is considered to be non-reactive towards hydrocarbons.<sup>[43]</sup> The hypervalent iodine oxidant can be synthesised separately or formed *in situ* from  $TsNH_2$  and di-(pivaloyloxy)iodobenzene ( $PhI(OPiv)_2$ ). To the best of our knowledge, there is no report on the direct (non-catalysed) use of PhINTs for net C–H amination. Recently though, the use of an *in situ* generated hypervalent iodine reagent from PhI and *m*CPBA was reported for a dehydrogenative C–H imination reaction with benzylic anilines.<sup>[44]</sup>

However, much to our surprise the reaction between xanthene and PhINTs cleanly afforded **1** in 62% yield after 60 minutes and 68% yield (49% yield with *in situ* generated PhINTs) after 20 hours, see Figure 4 and Scheme 4. Performing the reaction at lower temperatures afforded **1** in 23% yield after 3.5 hours at 27 °C, or 21% after 1.5 hours at 40 °C. However, at 60 °C, the reaction almost reached full conversion after 1 hour. Using PhINTces and PhINNcs afforded **2** and **3** after 20 hours in comparable yields as observed for the amination reaction described in Scheme 2. Dihydroanthracene did not afford **4** and reactions with ethylbenzene and 1,4-cyclohexadiene also did not lead to the desired products. However, **5-Me** (46%), **5-Boc** (40%) and **6** (47%) were obtained from the corresponding dihydroacridines and thioxanthene after 1 hour. Interestingly, the yield of **5-Me** is higher after 1 hour than after 20 hours, suggesting that the product is further converted under these reaction conditions. This was also supported by the observation of several unidentified by-products. In general (except for **5-Me**) the highest yields were obtained with pre-formed iminoiodane.



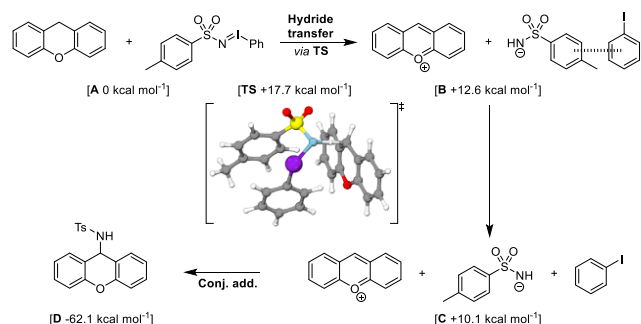
**Figure 4.** Formation of **1** from xanthene and PhINTs at different temperatures and reaction times. Yields based on  $^1H$  NMR integration using 1,3,5-tris-(*tert*-butyl)benzene as an internal standard.



**Scheme 4.** C–H Amination of dihydroheteroanthracenes by PhINR (R = Ts, Tces, Ns). Yields in parentheses concern reactions using *in situ* generated PhINR, generated from  $\text{RNH}_2$  and  $\text{Ph}(\text{OPiv})_2$  in the presence of MgO. Yields based on  $^1\text{H}$  NMR integration using 1,3,5-tris-(*tert*-butyl)benzene or 1,3,5-trimethoxybenzene as an internal standard. [a] Unidentified by-products formed.

Mechanistic insight was obtained from an intermolecular competition experiment between xanthene and xanthene- $d_2$  in the reaction with PhINTs, which gave a KIE of 2.1. Analogous to the  $2e^- / 1\text{H}^+$  transfer described above, this suggests that proton or hydride transfer is involved in, or before, the rate determining step. Moreover, the reaction of dihydroacridine with PhINTs, which did not afford the desired product **5-H**, gave quantitative conversion to acridine, iodobenzene and  $\text{TsNH}_2$ . Hydride (or two-electron and one-proton) transfer from the substrate to the iminoiodane is thus a feasible process. For acridine the reaction stops at this point, whereas for the substrates that afford the respective desired product this step is followed by conjugate addition of the sulfonamide to the oxidised substrate.

Based on the above combined data, we propose the reaction mechanism shown in Scheme 5. The mechanism is supported by DFT calculations at the B3LYP/def2-TZVP/disp3 level of theory with implicit solvation in benzene (COSMO), a method that typically affords reliable energies for charged intermediates.<sup>[35]</sup> Endergonic hydride transfer from xanthene to the nitrogen atom in PhINTs ( $\Delta G^\circ = +12.6 \text{ kcal mol}^{-1}$  at 298 K) affords intermediate **B** through transition state **TS** ( $\Delta G^\ddagger = +17.7 \text{ kcal mol}^{-1}$ ). Simultaneously with the hydride transfer, heterolytic cleavage of the I–N bond is observed, as the bond elongates from 1.999 Å (**A**) to 2.447 Å (**TS**). The I–N bond is completely cleaved in **B**, wherein iodobenzene and the anionic tosylamide remain as a close-contact pair. Slightly exergonic breaking of this close contact pair affords the negatively charged tosylamido and positively charged xanthylum ion (**C**,  $\Delta G^\circ = +10.1 \text{ kcal mol}^{-1}$ ). Product **D** is formed by a virtually barrierless conjugate addition in an overall highly exergonic reaction ( $\Delta G^\circ = -62.1 \text{ kcal mol}^{-1}$ ). The use of dihydroacridine as the substrate is believed to follow the same mechanism until intermediate **C**, after which the tosylamide deprotonates the cationic *N*-protonated-acridinium cation to afford acridine and  $\text{TsNH}_2$ , as was experimentally observed.



**Scheme 5.** Proposed mechanism for the C–H amination of xanthene with PhINTs. Energies in  $\Delta G^\circ$  at 298 K calculated with DFT at the B3LYP/def2-TZVP/disp3/m4-grid/COSMO(benzene) level of theory. Graphical representation of **TS** generated with IboView. Grey = C, white = H, purple = I, yellow = S, red = O, blue = N.

## Conclusions

To conclude, we have shown that xanthene and thioxanthene can be aminated at the bridgehead  $sp^3$  C–H position using chloranil (or a related benzoquinone) as the oxidant and with sulfonamides as the nitrogen donor. The latter acts as a hydride (or two-electron and one-proton) acceptor and the amination step proceeds through conjugate addition of an anionic sulfonamido intermediate to the formed heteroanthracenium ion. We have also demonstrated that often-employed iminoiodanes can react in an uncatalysed manner with xanthene, thioxanthene and dihydroacridines to afford the  $sp^3$  C–H aminated products. The key mechanistic step is a hydride transfer from the dihydroheteroanthracene to the iminoiodane. This finding is relevant for the chemical community interested in (the mechanisms of) nitrene transfer catalysis, as it describes a previously unknown background reaction that may compete with the postulated catalytic cycles. We would therefore like to emphasise that this uncatalysed process should be carefully considered when using xanthene-like substrates in mechanistic studies of catalytic nitrene transfer reactions.

## Experimental Section

**General procedure for the oxidative amination with chloranil:** A 4.0 mL vial was charged with  $\text{TsNH}_2$ ,  $\text{NsNH}_2$  or  $\text{TcesNH}_2$  (0.11 mmol, 1.1 eq), the dihydroheteroanthracene (0.10 mmol, 1.0 eq), chloranil (0.11 mmol, 1.1 eq) and benzene (2.0 mL). The resulting suspension was stirred, with a closed cap, under aerobic conditions at 60 °C for 20 h. After cooling to room temperature and concentration under reduced pressure, the yield was determined by  $^1\text{H}$  NMR, using 1,3,5-tris-(*tert*-butyl)benzene or 1,3,5-trimethoxybenzene as an internal standard.

**General procedure for the oxidative amination with PhINR:** A 4.0 mL vial was charged with the PhINTs, PhINNs or PhINTces (0.11 mmol, 1.1 eq), the dihydroheteroanthracene (0.10 mmol, 1.0 eq) and benzene (2.0 mL). The resulting suspension was stirred, with a closed cap, under aerobic conditions at 60 °C for 20 h (or 1 hour if specified). After cooling to room temperature and concentration under reduced pressure, the yield

was determined by  $^1\text{H}$  NMR, using 1,3,5-tris-(*tert*butyl)benzene or 1,3,5-trimethoxybenzene as an internal standard.

## Acknowledgements

Financial support from The Netherlands Organisation for Scientific Research (NWO TOP-Grant 716.015.001) is gratefully acknowledged. Ed Zuidinga is thanked for MS measurements.

## Conflict of interest

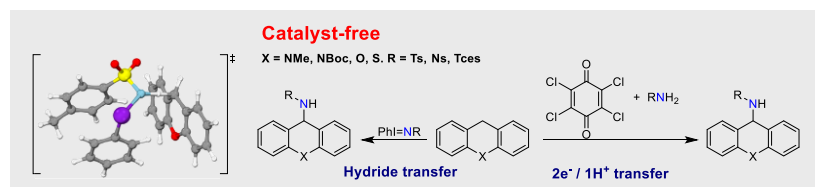
The authors declare no conflicts of interest.

**Keywords:** C–H amination • Iminoiodane • Benzoquinone • Dihydroheteroanthracene • Hydride Transfer

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## Entry for the Table of Contents



The previously unknown direct and uncatalysed C–H amination of dihydroheteroanthracenes is demonstrated by usage of iminoiodanes or sulfonamides and chloranil. The reactions proceed through hydride (or two-electron, one-proton) transfer from the dihydroanthracene to the iminoiodane or benzoquinone followed by conjugate addition of the amide or amine.

Nicolaas P. van Leest, Lars Grooten, Jarl Ivar van der Vlugt and Bas de Bruin\*

### Uncatalysed Oxidative C–H Amination of 9,10-Dihydro-9-Heteroanthracenes: A Mechanistic Study



## Supporting information for:

# Uncatalysed Oxidative C–H Amination of 9,10-dihydro-9-heteroanthracenes: A Mechanistic Study

Nicolaas P. van Leest, Lars Grooten, Jarl Ivar van der Vlugt and Bas de Bruin\*

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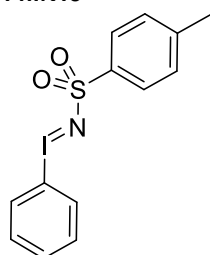
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## General considerations

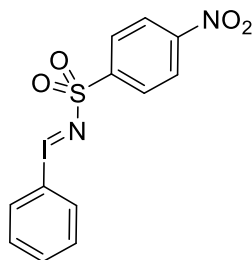
All reagents were of commercial grade and used without further purification. CH<sub>2</sub>Cl<sub>2</sub> was distilled from CaH<sub>2</sub>, toluene was distilled from sodium and CH<sub>3</sub>CN was dried over molecular sieves prior to use. To ensure that no traces of metals were present during the reaction, all reactions were carried out in new single-use vials and stirring bars were cleaned with aqua regia (conc. aqueous HCl and HNO<sub>3</sub> in a 3 to 1 ratio) prior to use. NMR spectra (<sup>1</sup>H and <sup>13</sup>C) were measured on a Bruker DRX 500, Bruker AMX 400, Bruker DRX 300 or Varian Mercury 300 spectrometer at r.t. and referenced to external SiMe<sub>4</sub> or solvent, respectively. High resolution mass spectra were recorded on an AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer (JEOL, Japan). GCMS (EI) Filament Ionizing voltage 70V, DIP (Direct insertion probe) (EI) Filament Ionizing voltage 70V. FD/FI probe (FD/FI) equipped with FD Emitter, Carbotec or Linden (Germany), FD 13 μm. Current rate 51.2 mA/min over 1.2 min. FI Emitter, Carbotec or Linden (Germany), FI 10 μm. Flashing current 40 mA on every spectra of 30 ms. Typical measurement conditions are: Counter electrode -10kV, Ion source 37V. Electrochemical measurements were conducted using a 663 VA stand with a PGSTAT302N potentiostat (Metrohm/Autolab).

## Synthesis of known compounds

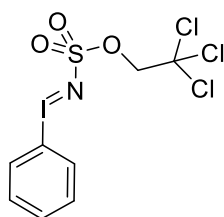
### PhINTs



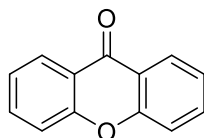
PhINTs was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.<sup>[51]</sup> PhI(OAc)<sub>2</sub> (3.22 g; 10.0 mmol; 1.0 eq) was added to a stirred solution of KOH (1.40 g; 25.0 mmol; 2.5 eq) and TsNH<sub>2</sub> (1.88 g; 11 mmol; 1.1 eq) in MeOH (40 mL) at 0 °C in absence of light. The solution was stirred for 2 h at 0-10 °C, 1 h at r.t. and poured into H<sub>2</sub>O (230 mL). The solution was left to stand overnight, filtered and the precipitate was washed with ice-cold MeOH (12 mL), DCM (500 mL) and hexanes (200 mL). The product was obtained as a white solid in 1.17 g; 3.13 mmol; 31.3% isolated yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.69 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 3H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 2.27 (s, 3H).

**PhINNs**

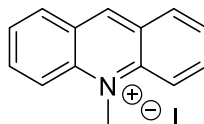
PhINNs was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.<sup>[52]</sup> PhI(OAc)<sub>2</sub> (3.00 g; 9.3 mmol; 1.2 eq) was added portionwise to a stirred solution of KOH (1.09 g; 19.38 mmol; 2.5 eq) and NsNH<sub>2</sub> (1.57 g; 7.75 mmol; 1.0 eq) in MeOH (35 mL) at 0 °C under an N<sub>2</sub> atmosphere. The yellow suspension was stirred for 30 min at 0 °C and for 3 h at r.t., after which stirring was stopped and the reaction mixture was left to stand overnight in absence of light. The yellow precipitate was collected by filtration was washed with ice-cold MeOH (3 times 15 mL) and dried *in vacuo* at 60 °C. The product was obtained as a yellow solid in 2.84 g; 7.03 mmol; 90.6% isolated yield. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 8.03 (d, *J* = 8.8 Hz, 2H), 7.85 – 7.63 (m, 4H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 2H).

**PhINTces**

PhINTces was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.<sup>[53]</sup> TcesNH<sub>2</sub> (685.4 mg; 3.0 mmol; 1.0 eq) and KOH (420.8 mg; 7.5 mmol; 2.5 eq) were dissolved in MeOH (11 mL) and cooled to -5 °C. PhI(OAc)<sub>2</sub> (966.3 mg; 3.0 mmol; 1.0 eq) was added portionwise and the yellow suspension was stirred under exclusion of light for 30 min at -5 °C and then 2.5 h at r.t., after which ice-cold H<sub>2</sub>O (20 mL) was added. The suspension was stirred at 0 °C until a fine white solid had formed, which was collected by filtration, washed with H<sub>2</sub>O (25 mL), ice-cold MeOH (4 mL) and EtOAc (20 mL) and then dried *in vacuo*. PhINTces was obtained as a white powder in 244.4 mg; 0.57 mmol; 18.9% isolated yield. The <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 4.21 (s, 2H).

**Xanthone**

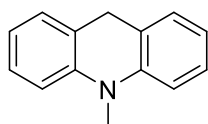
Xanthone was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.<sup>[54]</sup> Xanthene (273.33 mg; 1.5 mmol, 1.0 eq) was dissolved in DMSO (7.0 mL) and stirred at 30 °C for 18 h under aerobic conditions. H<sub>2</sub>O (25 mL) was added and the white suspension was filtered. The residue was washed with H<sub>2</sub>O (3 times 7 mL), dissolved in DCM, washed again with H<sub>2</sub>O and dried over Na<sub>2</sub>SO<sub>4</sub>. Purification by column chromatography (silica, 100% pentane to 100% DCM) afforded xanthone as a white solid in 30.1 mg; 0.15 mmol; 10% isolated yield. <sup>1</sup>H NMR (400 MHz, chloroform-*d*) δ 8.35 (d, *J* = 7.9 Hz, 2H), 7.73 (apparent t, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.39 (app. t, *J* = 7.6 Hz, 2H).

**N-methylacridinium**

*N*-methylacridinium iodide was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.<sup>[55]</sup> Acridine (1.40 g; 7.81 mmol; 1.0 eq) and MeI (6.0 mL; 96.4 mmol; 12.3 eq) were placed in a flame dried pressure tube and brought under argon. The resulting orange solution was heated to 60 °C for 4.5 h in the closed tube. The resulting dark red suspension was cooled to r.t. and diluted with EtOAc. The solution was concentrated under reduced pressure to dryness and the solid was washed with hexanes (300 mL) and dried *in vacuo*. *N*-methylacridinium iodide was obtained as a red solid in 1.67 g; 5.20 mmol; 66.6% isolated yield. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.20 (s, 1H), 8.80 (d, *J* = 9.3 Hz, 2H), 8.74 – 8.55 (m, 2H), 8.47 (ddd, *J* = 9.0, 6.8, 1.6 Hz, 2H), 8.05 (dd, *J* = 8.3, 6.8 Hz, 2H), 4.86 (s, 3H).

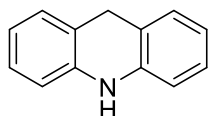
**N-methyl-dihydroacridine**

*N*-methyl-dihydroacridine was prepared according to a literature procedure<sup>[55]</sup> and the spectroscopic data of the product matched those previously reported.<sup>[56]</sup> Under aerobic conditions, *N*-methylacridinium iodide (700 mg; 2.18 mmol, 1.0 eq) was dissolved in dry MeOH (10 mL). To this stirring solution at r.t., NaBH<sub>4</sub> (250 mg; 6.61 mmol, 3.0 eq) was added in one portion and stirred for 5 min. The reaction mixture was quenched at 0 °C by slow addition of H<sub>2</sub>O (10 mL). The suspension was filtered and the residue



washed with H<sub>2</sub>O (200 mL) and dried *in vacuo* at 60 °C. *N*-methyldihydroacridine was obtained as a green-grey solid in 408 mg; 2.09 mmol; 95.8% isolated yield. <sup>1</sup>H NMR (300 MHz, chloroform-*d*) δ 7.24 – 7.07 (m, 4H), 7.03 – 6.75 (m, 4H), 3.89 (s, 2H), 3.38 (s, 3H). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.19 (m, 4H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.90 (apparent t, *J* = 7.4 Hz, 2H), 3.82 (s, 2H), 3.33 (s, 3H).

### 9,10-dihydroacridine

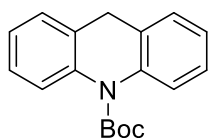


9,10-dihydroacridine was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.<sup>[57]</sup> Under an argon atmosphere, Na (69 mg; 3.0 mmol; 6.0 eq, dispersion in oil) was suspended in dry THF (1.5 mL). The suspension was cooled to 0 °C and 15-crown-5 (595.3 μL; 3.0 mmol; 6.0 eq) was added under vigorous stirring. After 5 min. a solution of acridine (89.6 mg; 0.5 mmol; 1.0 eq) and *i*PrOH (229.6 μL; 3.0 mmol; 6.0 eq) in dry THF (2.0 mL) was added. The suspension was stirred at 0 °C for 10 min. and aqueous saturated NH<sub>4</sub>Cl (2.0 mL) was added. The mixture was further diluted with H<sub>2</sub>O (20 mL) and brine (50 mL) and extracted with Et<sub>2</sub>O (2 times 50 mL). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Purification by column chromatography (silica, EtOAc:hexanes 10-100%) afforded 9,10-dihydroacridine as a white solid in 49.2 mg; 0.271 mmol; 54.3% isolated yield. <sup>1</sup>H NMR (400 MHz, chloroform-*d*) δ 7.22 – 7.00 (m, 4H), 6.87 (t, *J* = 7.4 Hz, 2H), 6.68 (d, *J* = 7.9 Hz, 2H), 5.95 (s, 1H), 4.07 (s, 2H).

Alternatively, 9,10-dihydroacridine was prepared in higher yield according to a literature procedure and the spectroscopic data of the product matched those previously reported.<sup>[58]</sup> A flame-dried Schlenk was charged with acridine (179.1 mg; 1.0 mmol; 1.0 eq), diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Hantsch ester, 633.2 mg; 2.5 mmol; 1.0 eq) and Fe(OTf)<sub>2</sub> (7.1 mg; 0.02 mmol; 2 mol%) and brought under argon. Degassed CDCl<sub>3</sub> (2.0 mL) was added and the yellow suspension was stirred at 40 °C for 21 h. The resulting green suspension was concentrated and purified by column chromatography (silica, hexanes:EtOAc = 9:1) to afford the product as an off-white solid in 167.7 mg; 9.25 mmol; 92.5% isolated yield.

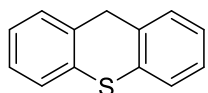
<sup>1</sup>H NMR (400 MHz, chloroform-*d*) δ 7.27 – 6.97 (m, 4H), 6.87 (t, *J* = 7.4 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 2H), 5.95 (s, 1H), 4.07 (s, 2H).

### *N*-Boc-9,10-dihydroacridine



*N*-Boc-9,10-dihydroacridine was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.<sup>[59]</sup> 9,10-dihydroacridine (28.7 mg; 0.158 mmol; 1.0 eq), Boc<sub>2</sub>O (120.9 mg; 0.554 mmol; 3.5 eq) and DMAP (32.5 mg; 0.263 mmol; 1.7 eq) were dissolved in MeCN (6.0 mL) at 0 °C and the solution was argon sparged for 3 min. The reaction mixture was stirred at 30 °C for 24 h and then diluted with Et<sub>2</sub>O (7.0 mL). The organic solution was washed with aqueous saturated NH<sub>4</sub>Cl (3 times 20 mL), brine (2 times 20 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. Purification by column chromatography (silica, hexanes:EtOAc = 9:1) afforded *N*-Boc-9,10-dihydroacridine as a slightly yellow solid in 36.9 mg; 0.131 mmol; 83.0% isolated yield. <sup>1</sup>H NMR (300 MHz, chloroform-*d*) δ 7.69 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 4H), 7.22 – 7.11 (m, 2H), 3.85 (s, 2H), 1.60 (s, 9H).

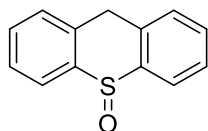
### Thioxanthene



Thioxanthene was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.<sup>[510]</sup> LiAlH<sub>4</sub> (0.406 g; 10.69 mmol; 2.3 eq) was suspended in dry THF (25.0 mL) and cooled to 0 °C. AlCl<sub>3</sub> (1.12 g; 8.40 mmol; 1.8 eq) in THF (25 mL) and thioxanthone (1.0 g; 4.71 mmol; 1.0 eq) were added and the resulting suspension was heated to reflux for 1 h. The reaction mixture was cooled to 0 °C and EtOAc and H<sub>2</sub>O were added slowly to quench the remaining LiAlH<sub>4</sub>. The product was extracted in EtOAc (3 times 75 mL) and the combined organic fractions were washed with aqueous HCl (5%, 3 times 100 mL), aqueous saturated NH<sub>4</sub>Cl (3 times 100 mL), brine (3 times 100 mL) and dried over MgSO<sub>4</sub>. Concentration and drying under reduced pressure afforded thioxanthene as a white

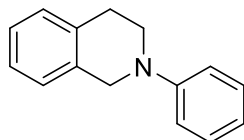
crystalline solid in 905.6 mg; 4.567 mmol; 97.0% isolated yield.  $^1\text{H}$  NMR (400 MHz, chloroform- $d$ )  $\delta$  7.45 (dd,  $J$  = 7.2, 2.0 Hz, 2H), 7.32 (d,  $J$  = 6.6 Hz, 2H), 7.26 – 7.04 (m, 4H), 3.86 (s, 2H).

**9H-thioxanthene-10-monooxide**



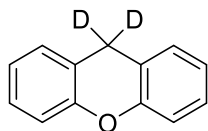
9H-Tthioxanthene-10-monooxide was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.<sup>[S10]</sup> Thioxanthene (200 mg; 1.0 mmol; 1.0 eq) was dissolved in DCM (20 mL), *m*-CPBA (224 mg; 1.3 mmol; 1.3 eq) was added and the solution was stirred at r.t. for 26 h. The reaction mixture was washed with aqueous saturated  $\text{NaHCO}_3$  (3 times 20 mL), brine (3 times 20 mL) and dried over  $\text{Na}_2\text{SO}_4$ . Purification by column chromatography (silica, hexanes:EtOAc = 3:1,  $R_f$  = 0.3) afforded 9H-thioxanthene-10-monooxide as a white solid in 129.7 mg; 0.605 mmol; 60.5% isolated yield.  $^1\text{H}$  NMR (400 MHz, chloroform- $d$ )  $\delta$  7.92 (d,  $J$  = 7.4 Hz, 2H), 7.52 – 7.26 (m, 6H), 4.16 (d,  $J$  = 16.5 Hz, 1H), 3.77 (d,  $J$  = 16.7 Hz, 1H).

**2-phenyl-1,2,3,4-tetrahydroisoquinoline**



2-Phenyl-1,2,3,4-tetrahydroisoquinoline was prepared according to a literature procedure<sup>[S11]</sup> and the spectroscopic data of the product matched those previously reported.<sup>[S12]</sup>  $\text{Pd}(\text{dba})_2$  (139.2 mg; 0.242 mmol; 5.5 mol%) and *rac*-BINAP (224.1 mg; 0.36 mmol; 8.2 mol%) were charged into a flame-dried Schlenk under argon, then dissolved in toluene (12 mL) and heated to reflux for 15 min.  $\text{KO}^t\text{Bu}$  (920 mg; 8.2 mmol; 1.86 eq), PhBr (460.6  $\mu\text{L}$ ; 4.4 mmol; 1.0 eq) and 1,2,3,4-tetrahydroisoquinoline (1101.6  $\mu\text{L}$ ; 8.8 mmol; 2.0 eq) were added and the solution was kept at reflux for 16 h. The reaction mixture was cooled to r.t., filtered over Celite and concentrated under reduced pressure. 2-phenyl-1,2,3,4-tetrahydroisoquinoline was obtained after column chromatography (silica, 40-60 petroleum ether:EtOAc = 99:1) as a yellow solid in 266.3 mg; 1.27 mmol; 28.9% isolated yield.  $^1\text{H}$  NMR (400 MHz, chloroform- $d$ )  $\delta$  7.30 (t,  $J$  = 7.7 Hz, 2H), 7.18 (d,  $J$  = 3.6 Hz, 4H), 6.99 (d,  $J$  = 8.1 Hz, 2H), 6.84 (t,  $J$  = 7.3 Hz, 1H), 4.42 (s, 2H), 3.57 (t,  $J$  = 5.9 Hz, 2H), 3.00 (t,  $J$  = 5.9 Hz, 2H).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.30 – 7.18 (m, 3H), 7.18 – 7.10 (m, 3H), 7.00 (d,  $J$  = 8.1 Hz, 2H), 6.74 (t,  $J$  = 7.3 Hz, 1H), 4.37 (s, 2H), 3.53 (t,  $J$  = 6.0 Hz, 2H), 2.90 (t,  $J$  = 6.0 Hz, 2H).

**Xanthene- $d_2$**



Xanthene- $d_2$  was prepared according to an adapted literature procedure<sup>[S13]</sup> and the spectroscopic data of the product matched those previously reported.<sup>[S14]</sup> Xanthene (455.6 mg; 2.5 mmol; 1.0 eq) and NaH (210 mg of a 60 wt% dispersion in paraffin oil, 5.25 mmol; 2.1 eq) were placed in a flame-dried Schlenk and brought under argon. Degassed DMSO- $d_6$  (5.0 mL) and benzene (3.0 mL) were added and the resulting red suspension was stirred over night at 35 °C. Degassed  $\text{D}_2\text{O}$  (5.0 mL) was added slowly and the benzene was removed from the resulting suspension under reduced pressure. The suspension was filtered and the residue washed with  $\text{H}_2\text{O}$  (300 mL) to afford a light yellow solid. This solid was washed with hexanes (10 mL) on the filter (the yellow filtrate still contains a substantial amount of xanthene- $d_2$ ) to afford xanthene- $d_2$  as a white solid in 124 mg; 0.67 mmol; 26.9% isolated yield.  $^1\text{H}$  NMR (400 MHz, chloroform- $d$ )  $\delta$  7.24 – 7.12 (m, 1H), 7.11 – 6.95 (m, 1H).

**General method for amination with chloranil**

A 4.0 mL vial was charged with  $\text{TsNH}_2$ ,  $\text{NsNH}_2$  or  $\text{TcesNH}_2$  (0.11 mmol, 1.1 eq), the dihydroheteroanthracene (0.10 mmol, 1.0 eq), chloranil (0.11 mmol, 1.1 eq) and benzene (2.0 mL). The resulting suspension was stirred, with a closed cap, under aerobic conditions at 60 °C for 20 h. The reaction mixture was then diluted with  $\text{CHCl}_3$  (3.0 mL), transferred to a round bottom flask, and concentrated under reduced pressure. To the obtained solid was added 1,3,5-tris-(tert-butyl)benzene (0.02 mmol) and  $\text{CDCl}_3$  (1.0 mL) for compounds **1**, **2**, **3** and **4**, or 1,3,5-trimethoxybenzene (0.02 mmol) in DMSO- $d_6$  (1.0 mL) for compounds **5** and **6**, as an internal NMR standard. The suspension was sonicated briefly to ensure complete solvation of the dihydroheteroanthracene and the desired

product. Partially undissolved benzoquinone and hydroquinone was removed by filtration over a Teflon syringe filter and the conversion and yield were determined by  $^1\text{H}$  NMR.

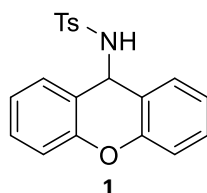
### General method for amination with PhINTs, PhINNs and PhINTces

A 4.0 mL vial was charged with PhINTs, PhINNs or PhINTces (0.11 mmol, 1.1 eq), the dihydroheteroanthracene (0.10 mmol, 1.0 eq) and benzene (2.0 mL). The resulting suspension was stirred, with a closed cap, under aerobic conditions at 60 °C for 20 h (or 1 h if specified). The reaction mixture was then diluted with  $\text{CHCl}_3$  (3.0 mL), transferred to a round bottom flask, and concentrated under reduced pressure. To the obtained solid was added 1,3,5-tris-(tert-butyl)benzene (0.02 mmol) and  $\text{CDCl}_3$  (1.0 mL) for compounds **1**, **2**, **3** and **4**, or 1,3,5-trimethoxybenzene (0.02 mmol) in  $\text{DMSO}-d_6$  (1.0 mL) for compounds **5** and **6**, as an internal NMR standard. The suspension was sonicated briefly to ensure complete solvation of the dihydroheteroanthracene and the desired product. Partially undissolved benzoquinone and hydroquinone was removed by filtration over a Teflon syringe filter and the conversion and yield were determined by  $^1\text{H}$  NMR.

### General method for amination with *in situ* generated PhINTs, PhINNs and PhINTces

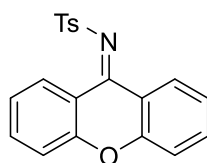
A 4.0 mL vial was charged with  $\text{TsNH}_2$ ,  $\text{NsNH}_2$  or  $\text{TcesNH}_2$  (0.11 mmol, 1.1 eq),  $\text{PhI}(\text{OPiv})_2$  (0.11 mmol, 1.1 eq),  $\text{MgO}$  (0.22 mmol, 2.2 eq), the dihydroheteroanthracene (0.10 mmol, 1.0 eq) and benzene (2.0 mL). The resulting suspension was stirred, with a closed cap, under aerobic conditions at 60 °C for 20 h. The reaction mixture was then diluted with  $\text{CHCl}_3$  (3.0 mL), transferred to a round bottom flask, and concentrated under reduced pressure. To the obtained solid was added 1,3,5-tris-(tert-butyl)benzene (0.02 mmol) and  $\text{CDCl}_3$  (1.0 mL) for compounds **1**, **2**, **3** and **4**, or 1,3,5-trimethoxybenzene (0.02 mmol) in  $\text{DMSO}-d_6$  (1.0 mL) for compounds **5** and **6**, as an internal NMR standard. The suspension was sonicated briefly to ensure complete solvation of the dihydroheteroanthracene and the desired product. Partially undissolved benzoquinone and hydroquinone was removed by filtration over a Teflon syringe filter and the conversion and yield were determined by  $^1\text{H}$  NMR.

### Characterisation of known products

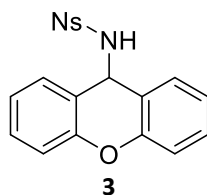


This compound is known in literature.<sup>[S15]</sup> **1** can be obtained in pure form by column chromatography (silica hexanes:EtOAc = 1:0.5) of the crude reaction mixture.

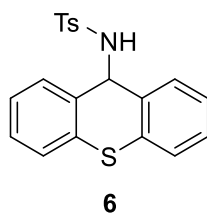
$^1\text{H}$  NMR (300 MHz, chloroform-*d*)  $\delta$  7.81 (d,  $J$  = 8.3 Hz, 2H), 7.34 (d,  $J$  = 8.0 Hz, 2H), 7.34 – 7.22 (m, 2H), 7.17 (dd,  $J$  = 7.8, 1.6 Hz, 2H), 7.09 (dd,  $J$  = 8.3, 1.2 Hz, 2H), 7.00 (td,  $J$  = 7.5, 1.2 Hz, 2H), 5.79 (d,  $J$  = 8.6 Hz, 1H), 4.86 (d,  $J$  = 8.6 Hz, 1H), 2.48 (s, 3H). The resonance at  $\delta$  2.48 ppm was used to calculate the yield.



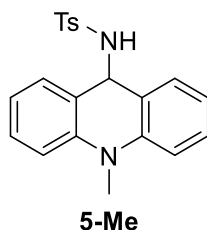
This compound is known in literature and the following spectral data is as therein reported.<sup>[S3]</sup>  $^1\text{H}$  NMR (600 MHz, chloroform-*d*)  $\delta$  8.73 (dd,  $J$  = 8.3, 1.6 Hz, 2H), 8.02 – 7.98 (m, 2H), 7.74 (ddd,  $J$  = 8.5, 7.1, 1.6 Hz, 2H), 7.50 (ddd,  $J$  = 8.4, 1.2, 0.4 Hz, 2H), 7.40 (ddd,  $J$  = 8.3, 7.1, 1.2 Hz, 2H), 7.37 – 7.34 (m, 2H), 2.46 (s, 3H). The resonance at  $\delta$  8.73 ppm was used to calculate the yield.



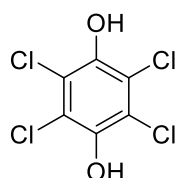
This compound is known in literature.<sup>[S15]</sup> **3** can be obtained in pure form by preparative TLC (silica DCM,  $R_f$  = 0.4) of the crude reaction mixture.  $^1\text{H}$  NMR (400 MHz, chloroform-*d*)  $\delta$  8.32 (d,  $J$  = 8.5 Hz, 2H), 7.99 (d,  $J$  = 8.5 Hz, 2H), 7.31 (t,  $J$  = 8.1 Hz, 2H), 7.20 (d,  $J$  = 7.8 Hz, 2H), 7.13 (d,  $J$  = 8.2 Hz, 2H), 7.02 (t,  $J$  = 7.6 Hz, 2H), 5.88 (d,  $J$  = 7.9 Hz, 1H), 5.03 (d,  $J$  = 7.9 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  151.53, 147.28, 129.84, 129.13, 128.03, 124.17, 123.66, 119.56, 118.72, 116.96, 50.22. HRMS-FD<sup>+</sup> ( $m/z$ ) calculated for  $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_5\text{S}$  382.0623, found 382.0609 [ $\text{M}$ ]<sup>+</sup>). The resonances at  $\delta$  5.88 and 5.03 ppm were used to calculate the yield.



This compound is known in literature and the following spectral data is as therein reported.<sup>[S16]</sup> <sup>1</sup>H NMR (400MHz, DMSO-*d*<sub>6</sub>) δ 8.76 (d, *J* = 8.4Hz, 1H), 7.65 (d, *J* = 8.3Hz, 2H), 7.50–7.46 (m, 2H), 7.37–7.28 (m, 4H), 7.28–7.19 (m, 4H), 5.23 (d, *J* = 8.4 Hz, 1H), 2.35 (s, 3H). The resonance at δ 2.35 ppm was used to calculate the yield.

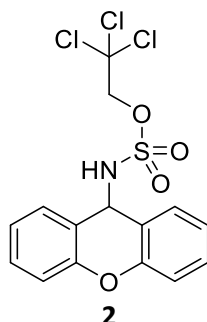


This compound is known in literature and the following spectral data is as therein reported.<sup>[S17]</sup> <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.16 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.26–7.22 (m, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 7.02 (dd, *J* = 7.4, 1.1 Hz, 2H), 6.84–6.80 (m, 2H), 5.43 (d, *J* = 7.7 Hz, 1H), 3.39 (s, 3H), 2.38 (s, 3H). The resonance at δ 2.38 ppm was used to calculate the yield.



This compound is known in literature and the following spectral data is as therein reported.<sup>[S18,S19]</sup> <sup>1</sup>H NMR (400 MHz, chloroform-*d*) δ 5.66 (2H). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.35 (s, 2H).

## Characterisation of new compounds



### 2,2,2-trichloroethyl (9H-xanthen-9-yl)sulfamate (2)

This compound was synthesised according to the general method for amination of xanthene with chloranil and TcesNH<sub>2</sub>, and can be purified by preparative TLC using DCM as the eluent (*R*<sub>f</sub> = 0.8) to afford the product as a yellow solid. The NMR and mass spectra can be found in Figure S1, Figure S2, Figure S3, Figure S4, Figure S5 and Figure S6.

HRMS-FD<sup>+</sup> (*m/z*) calculated for C<sub>15</sub>H<sub>12</sub>Cl<sub>3</sub>NO<sub>4</sub>S: 406.9553, found: 406.9568 [M]<sup>+</sup>.

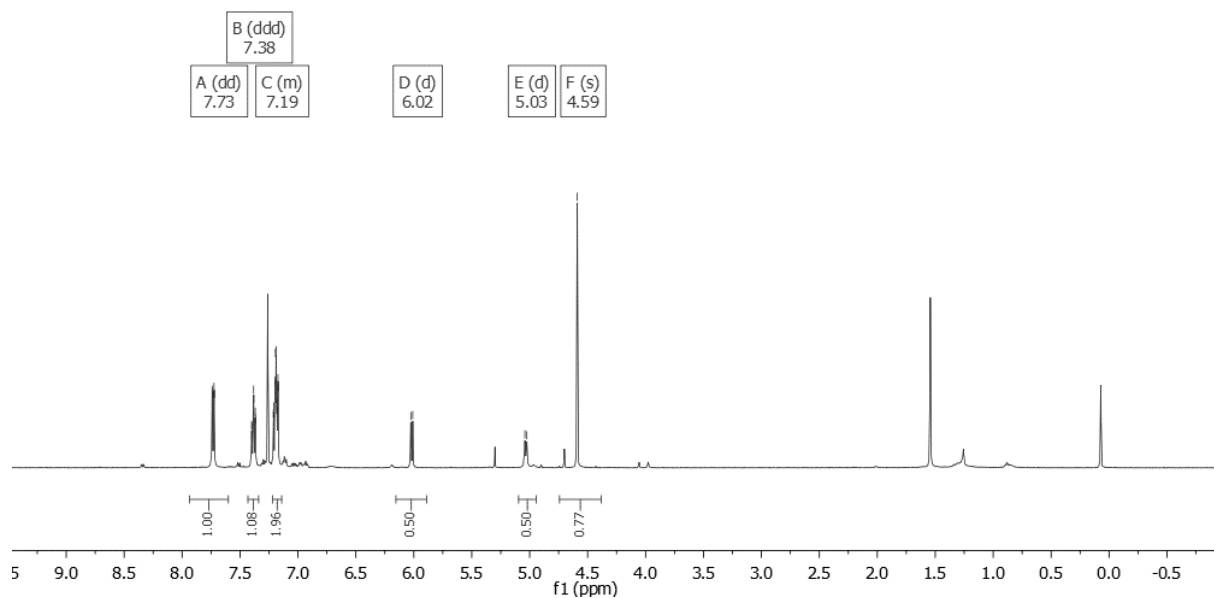
<sup>1</sup>H NMR (500 MHz, chloroform-*d*) δ 7.73 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.38 (ddd, *J* = 8.6, 7.3, 1.7 Hz, 2H), 7.23 – 7.11 (m, 4H), 6.02 (d, *J* = 8.2 Hz, 1H), 5.04 (d, *J* = 8.2 Hz, 1H), 4.59 (s, 2H).

<sup>13</sup>C NMR (126 MHz, chloroform-*d*) δ 151.43, 130.17, 129.94, 124.02, 119.29, 117.03, 93.39, 78.21, 51.02.

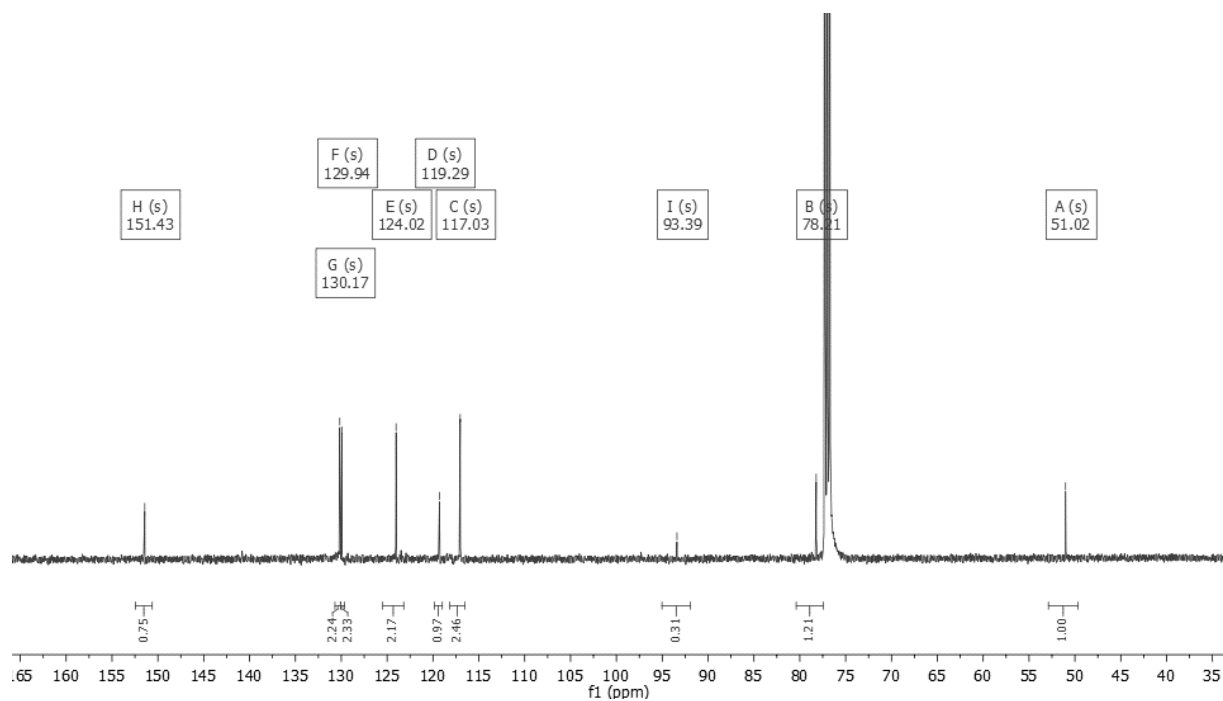
<sup>1</sup>H-<sup>1</sup>H COSY NMR (300 MHz, chloroform-*d*) δ 5.04 - 6.02, 7.23-7.11 – 7.38, 7.23-7.11 – 7.73.

<sup>1</sup>H-<sup>13</sup>C HSQC NMR (500 MHz, chloroform-*d*) δ 4.59 - 78.21, 6.02 – 51.02, 7.20 – 117.03, 7.21 – 124.02, 7.38 – 130.17, 7.73 – 129.94.

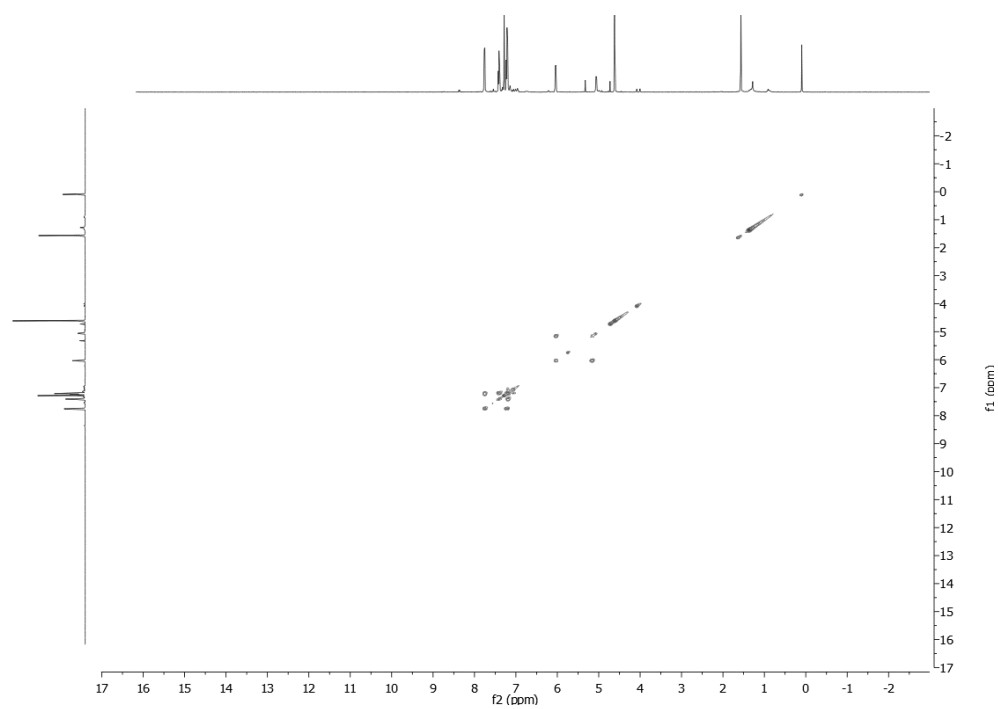
<sup>1</sup>H-<sup>13</sup>C HMBC NMR (500 MHz, chloroform-*d*) δ 4.59 – 93.39, 6.02 – 119.29, 6.02 – 129.94, 6.02 – 151.43, 7.19 – 117.03, 7.20 – 119.29, 7.18 – 124.02, 7.18 – 151.43, 7.73 – 51.02, 7.73 – 130.17, 7.73 – 151.43.



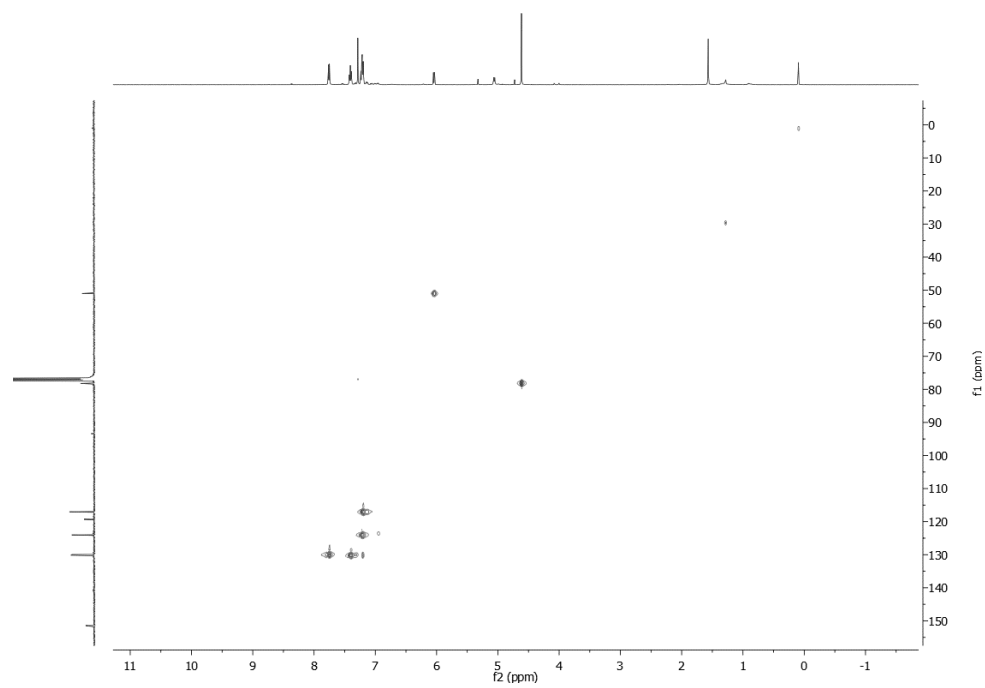
**Figure S1** <sup>1</sup>H NMR spectrum of **2** in CDCl<sub>3</sub>.



**Figure S2** <sup>13</sup>C NMR spectrum of **2** in CDCl<sub>3</sub>.

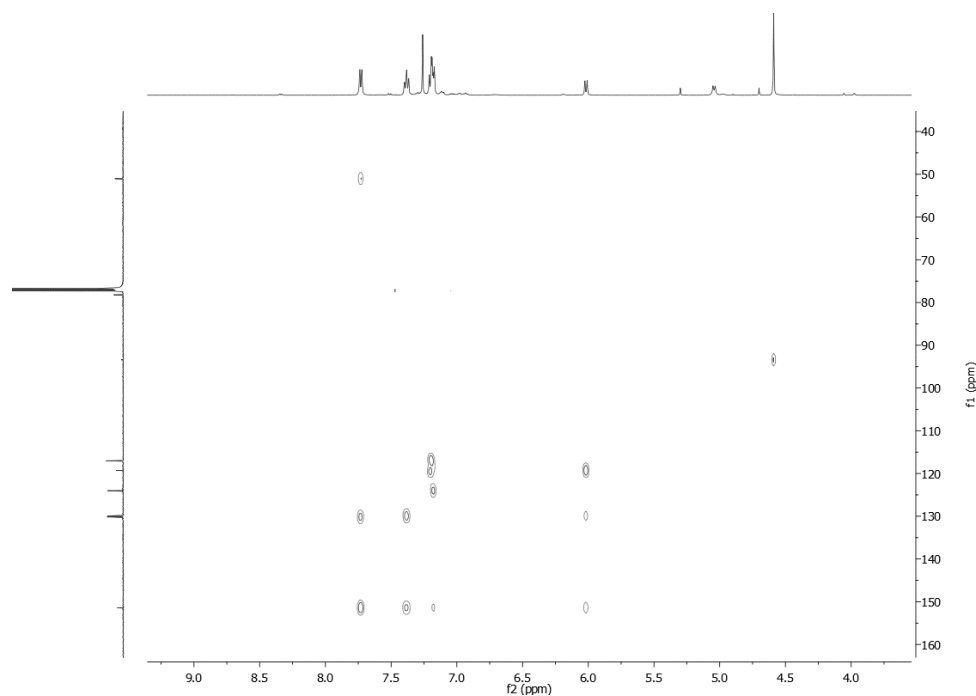


**Figure S3**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **2** in  $\text{CDCl}_3$ .

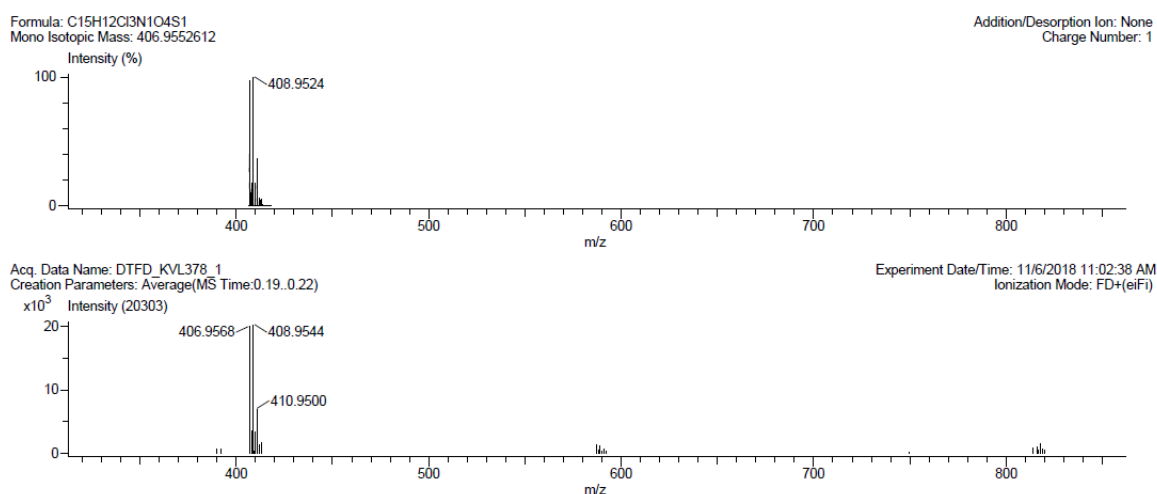


**Figure S4**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of **2** in  $\text{CDCl}_3$ .

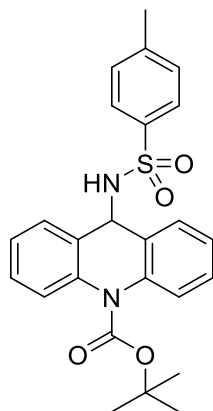




**Figure S5**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of **2** in  $\text{CDCl}_3$ .



**Figure S6** Simulated (top) and experimental (bottom) HRMS-FD<sup>+</sup> spectrum of **2**.



***tert*-butyl 9-((4-methylphenyl)sulfonamido)acridine-10(9H)-carboxylate (5-Boc)**

This compound was synthesised according to the general method for amination of *N*-Boc-9,10-dihydroacridine with PhINTs and can be purified by preparative TLC using hexanes : ethyl acetate (3 : 1) as the eluent ( $R_f$  = 0.6), to afford the product as a yellow solid in 31.1% isolated yield. The NMR and mass spectra can be found in Figure S7, Figure S8, Figure S9, Figure S10, Figure S11 and Figure S12.

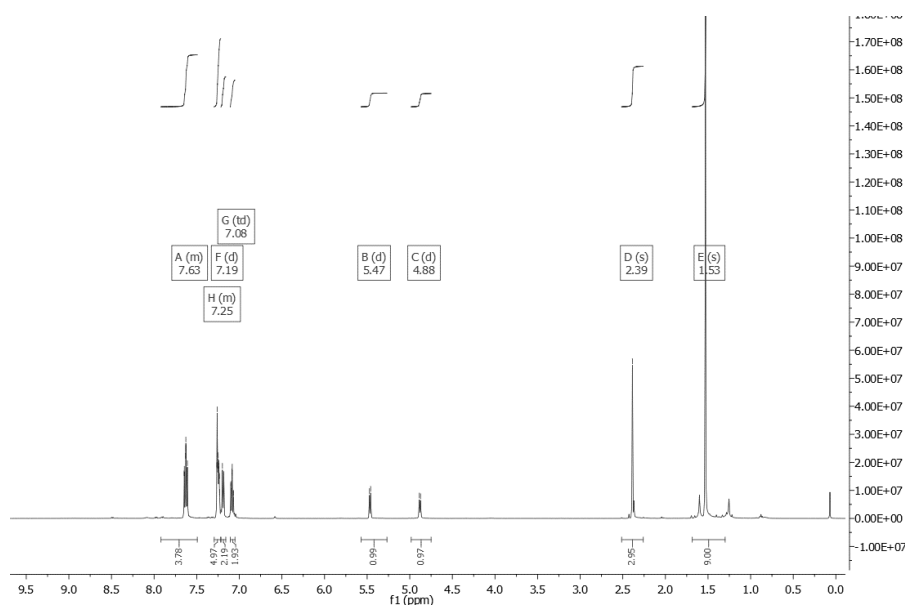
HRMS-FD<sup>+</sup> ( $m/z$ ) calculated for  $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_4\text{S}$ : 450.1613, found: 450.1597 [ $\text{M}$ ]<sup>+</sup>.

$^1\text{H}$  NMR (500 MHz, chloroform- $d$ )  $\delta$  7.92 – 7.49 (m, 4H), 7.29 – 7.22 (m, 4H), 7.19 (d,  $J$  = 7.7 Hz, 2H), 7.08 (td,  $J$  = 7.5, 1.1 Hz, 2H), 5.47 (d,  $J$  = 7.0 Hz, 1H), 4.88 (d,  $J$  = 7.1 Hz, 1H), 2.39 (s, 3H), 1.53 (s, 9H).

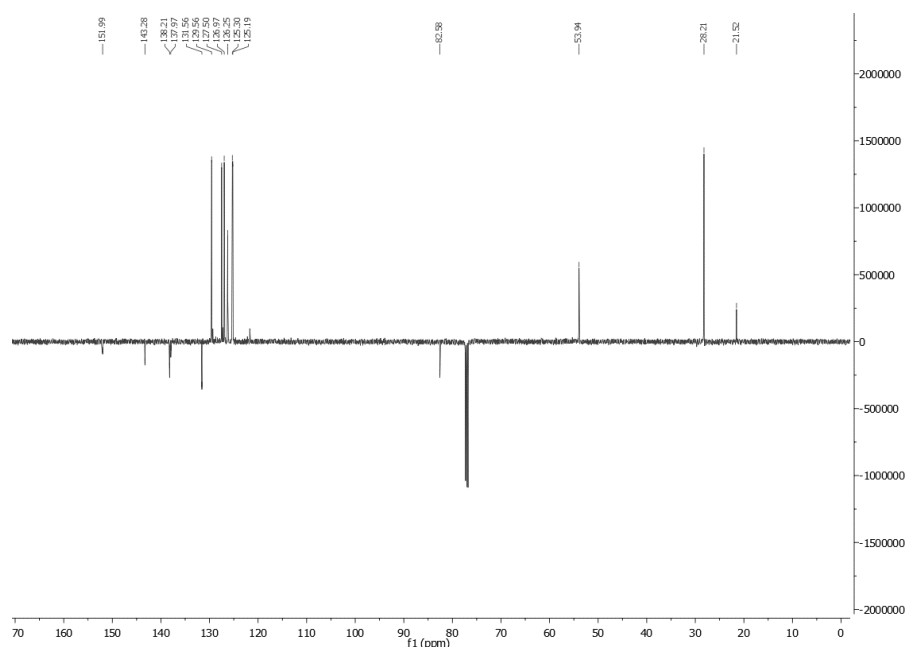
$^{13}\text{C}$ -APT NMR (126 MHz, chloroform- $d$ )  $\delta$  151.99 (C), 143.28 (C), 138.21 (C), 137.97 (C), 131.56 (C), 129.56 (CH), 127.50 (CH), 126.97 (CH), 126.25 (CH), 125.30 (CH), 125.19 (CH), 82.58 (C), 53.94 (CH), 28.21 ( $\text{CH}_3$ ), 21.52 ( $\text{CH}_3$ ).

**5-Boc**

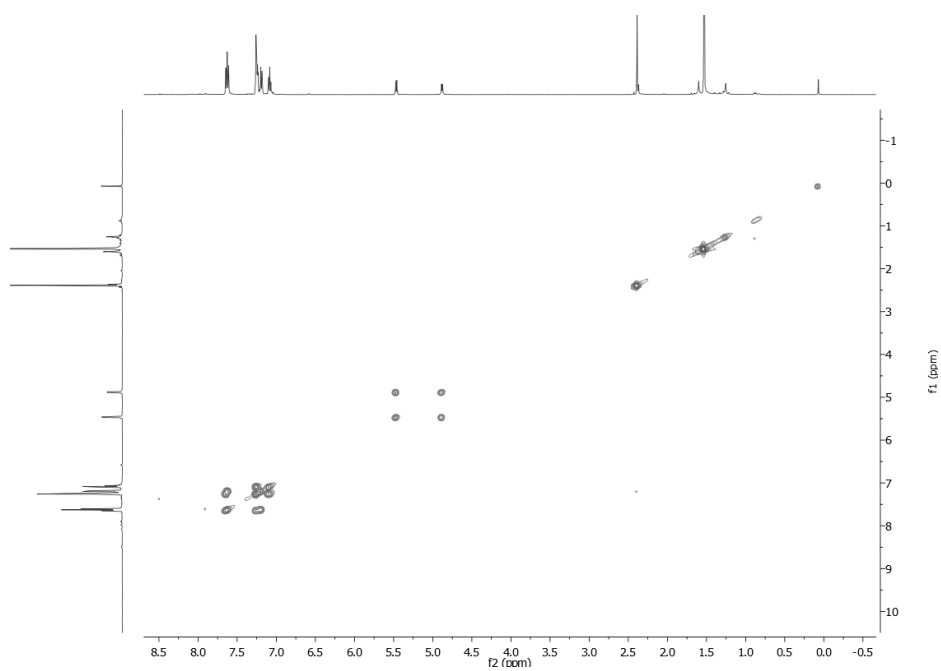
$^1\text{H}$ - $^1\text{H}$  COSY NMR (500 MHz, chloroform-*d*)  $\delta$  4.88-5.47, 7.08-7.25, 7.20-7.62, 7.24-7.64.  
 $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR (500 MHz, chloroform-*d*)  $\delta$  1.53-28.21, 2.39-21.52, 5.47-53.94, 7.08-125.30, 7.21-129.56, 7.26-126.25, 7.27-127.50, 7.63-126.97, 7.66-125.19.  
 $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR (500 MHz, chloroform-*d*)  $\delta$  1.53-28.21, 1.53-82.58, 2.39-129.56, 2.39-143.28, 5.47-126.25, 5.47-131.56, 5.47-138.21, 7.08-131.56, 7.19-51.52, 7.19-129.56, 7.25-138.21, 7.25-53.94, 7.25-127.50, 7.26-126.25, 7.62-126.97, 7.62-143.28, 7.63-125.28, 7.64-131.56, 7.64-138.21.



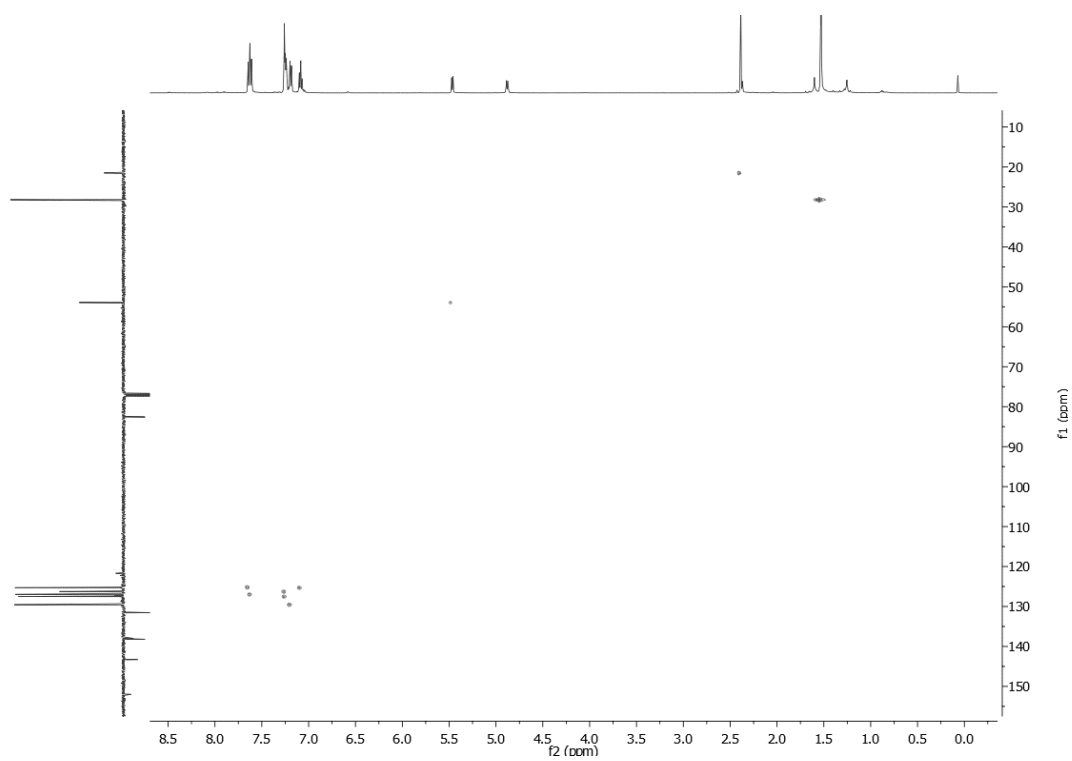
**Figure S7**  $^1\text{H}$  NMR spectrum of **5-Boc** in  $\text{CDCl}_3$ .



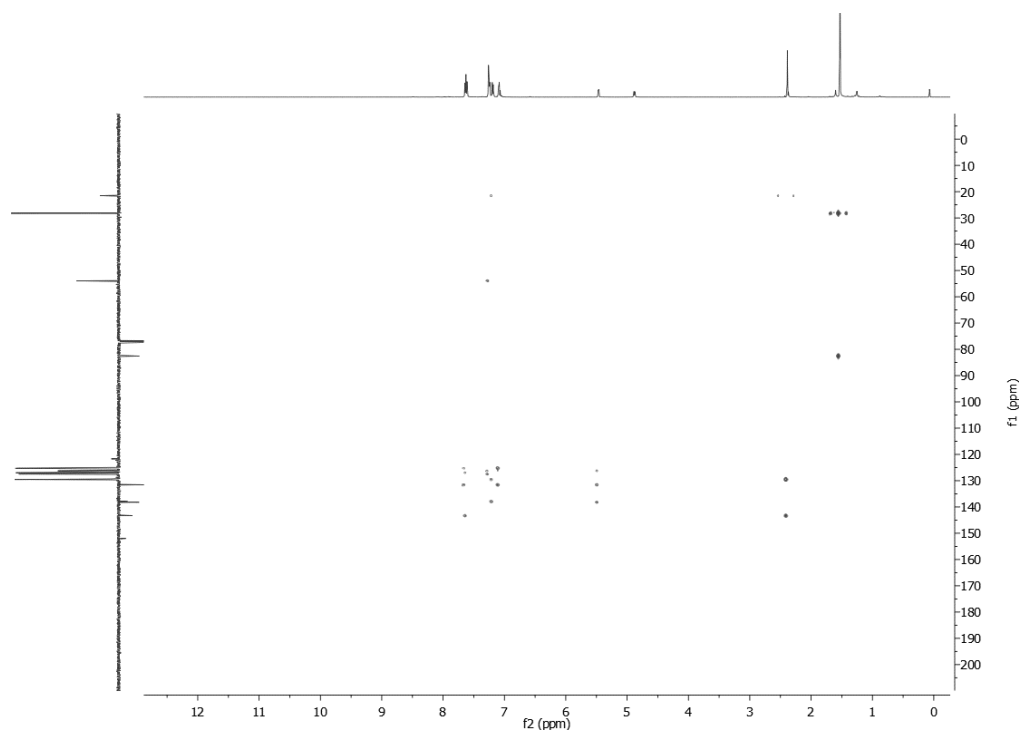
**Figure S8**  $^{13}\text{C}$ -APT NMR spectrum of **5-Boc** in  $\text{CDCl}_3$ .



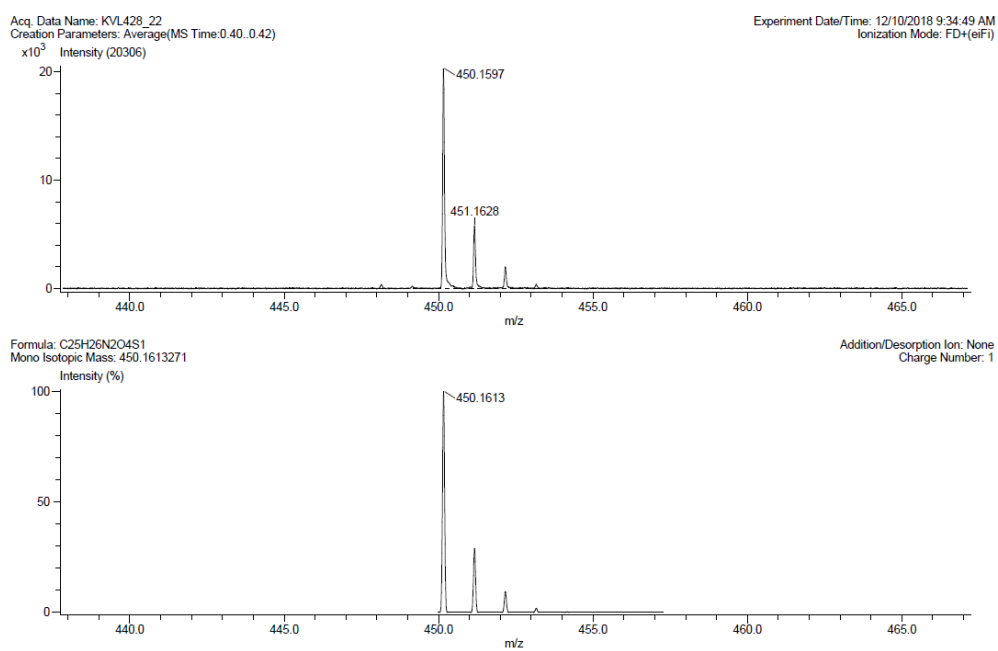
**Figure S9**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **5-Boc** in  $\text{CDCl}_3$ .



**Figure S10**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of **5-Boc** in  $\text{CDCl}_3$ .



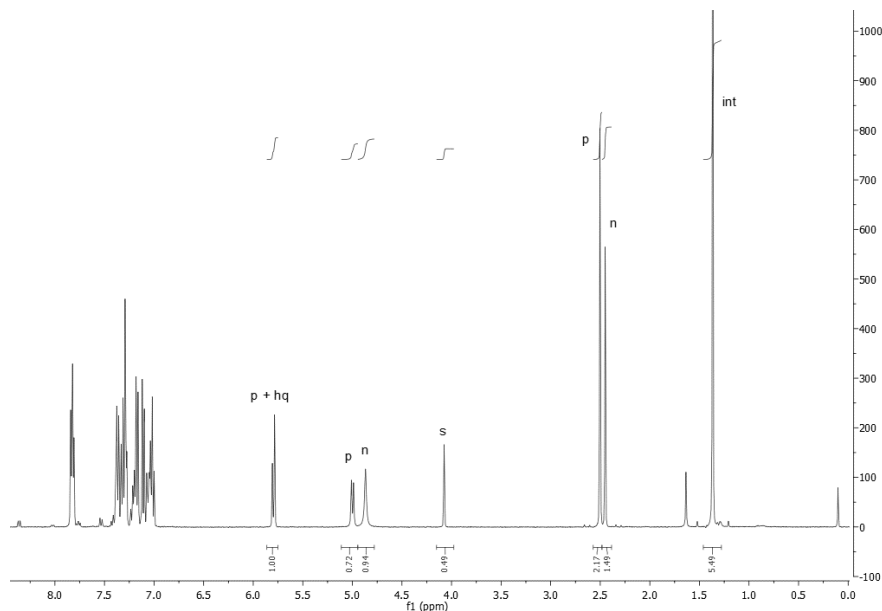
**Figure S11**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of **5-Boc** in  $\text{CDCl}_3$ .



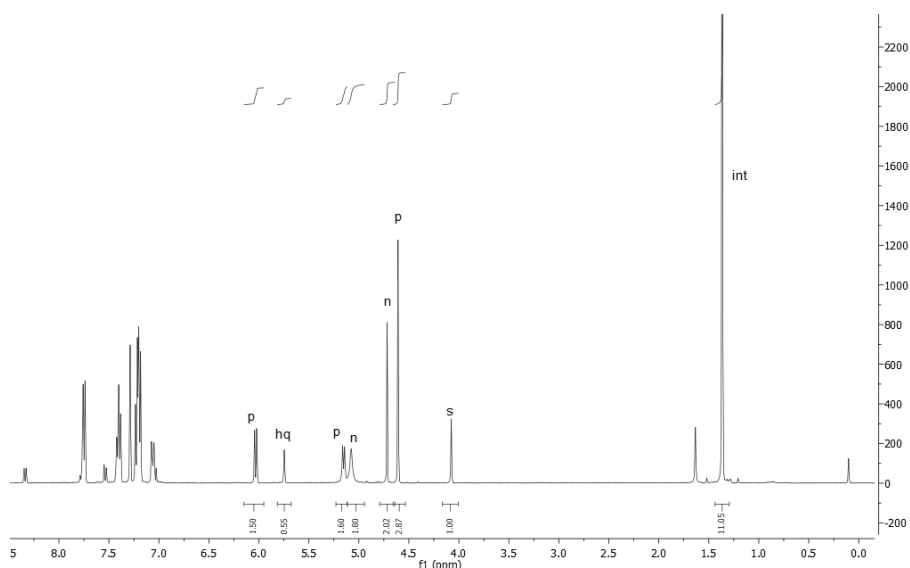
**Figure S12** Experimental (top) and simulated (bottom) HRMS-FD<sup>+</sup> spectrum of **5-Boc**.

## <sup>1</sup>H NMR spectra of crude reaction mixtures

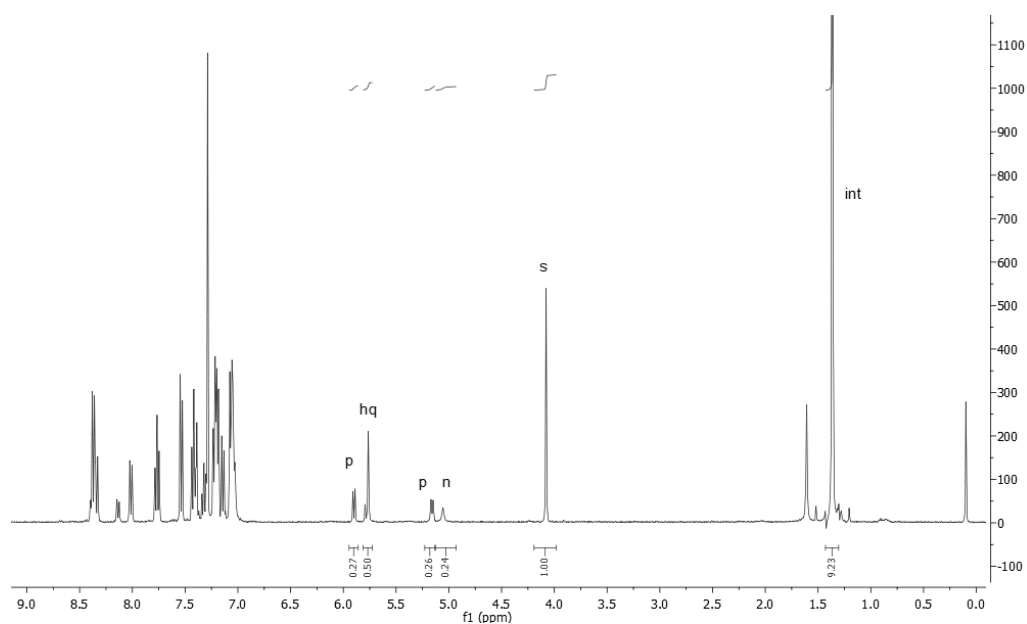
The crude <sup>1</sup>H NMR spectra of the obtained products can be found in Figure S13, Figure S14, Figure S15, Figure S16, Figure S17, Figure S8, Figure S9, Figure S20, Figure S22 and Figure S23. The following labeling code is used: **int** (internal standard), **s** (dihydroheteroanthracene), **n** (TsNH<sub>2</sub> or PhINTs), **p** (product), **hq** (1,2,4,5-tetrachloro-*para*-hydroquinone).



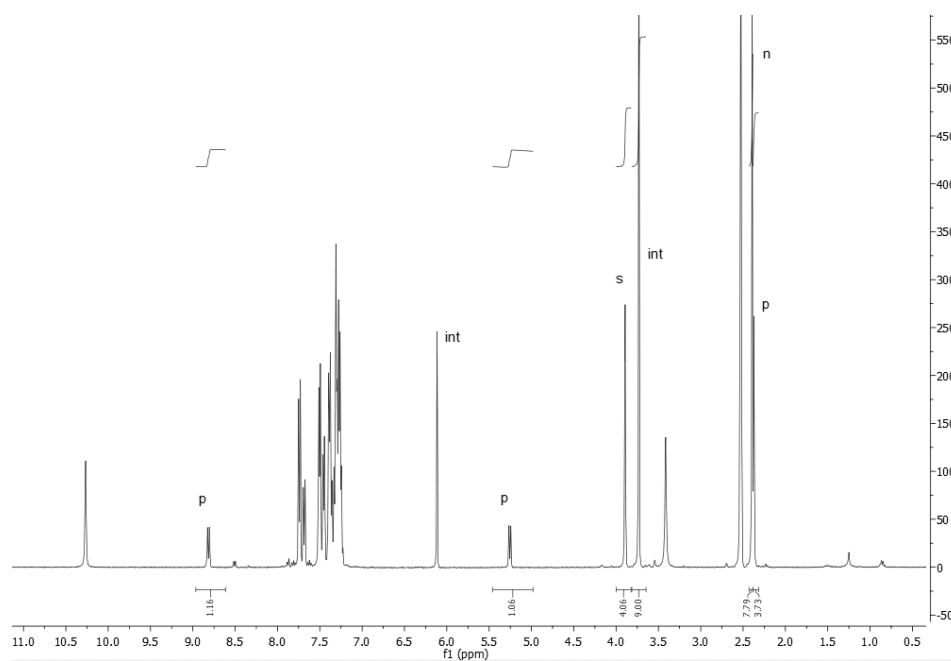
**Figure S13** Crude reaction mixture in CDCl<sub>3</sub> for the reaction between xanthene, TsNH<sub>2</sub> and chloranil to afford **1** under the optimised reaction conditions. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.



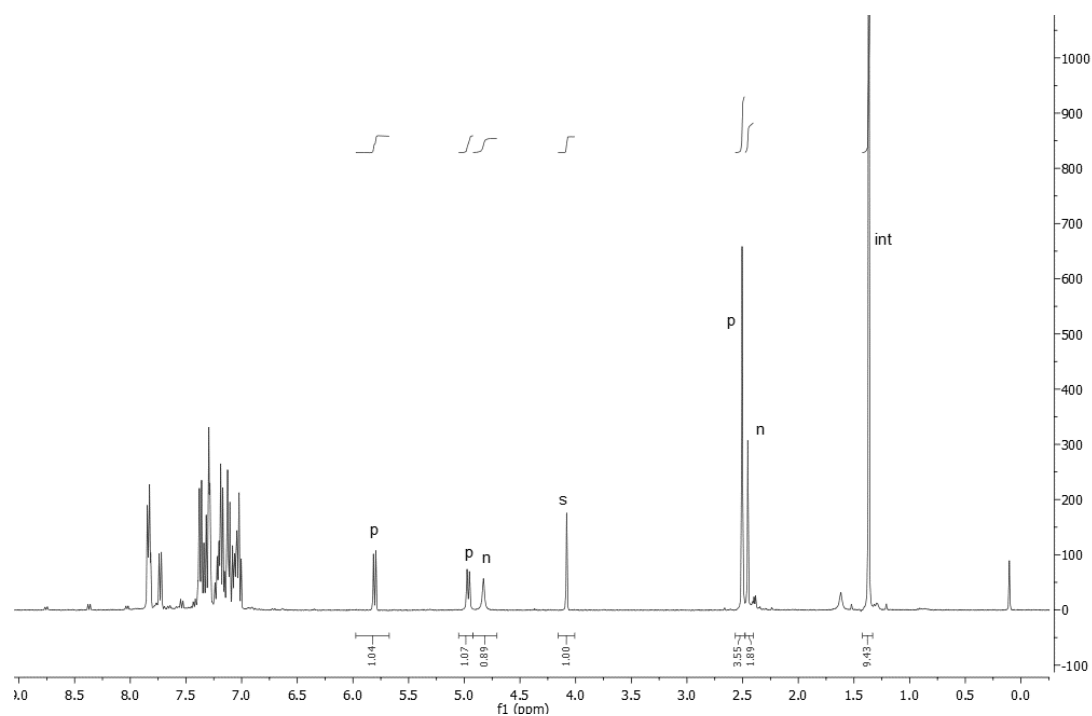
**Figure S14** Crude reaction mixture in CDCl<sub>3</sub> for the reaction between xanthene, TcesNH<sub>2</sub> and chloranil to afford **2** under the optimised reaction conditions. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.



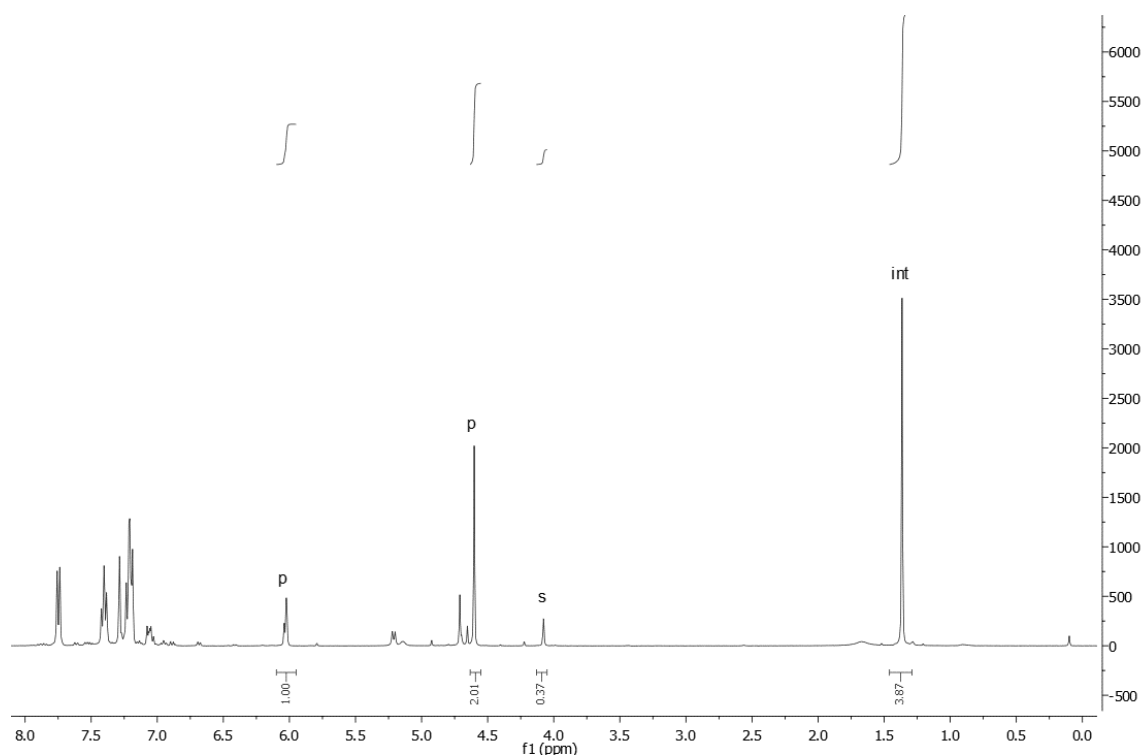
**Figure S15** Crude reaction mixture in  $\text{CDCl}_3$  for the reaction between xanthene,  $\text{NsNH}_2$  and chloranil to afford **3** under the optimised reaction conditions. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.



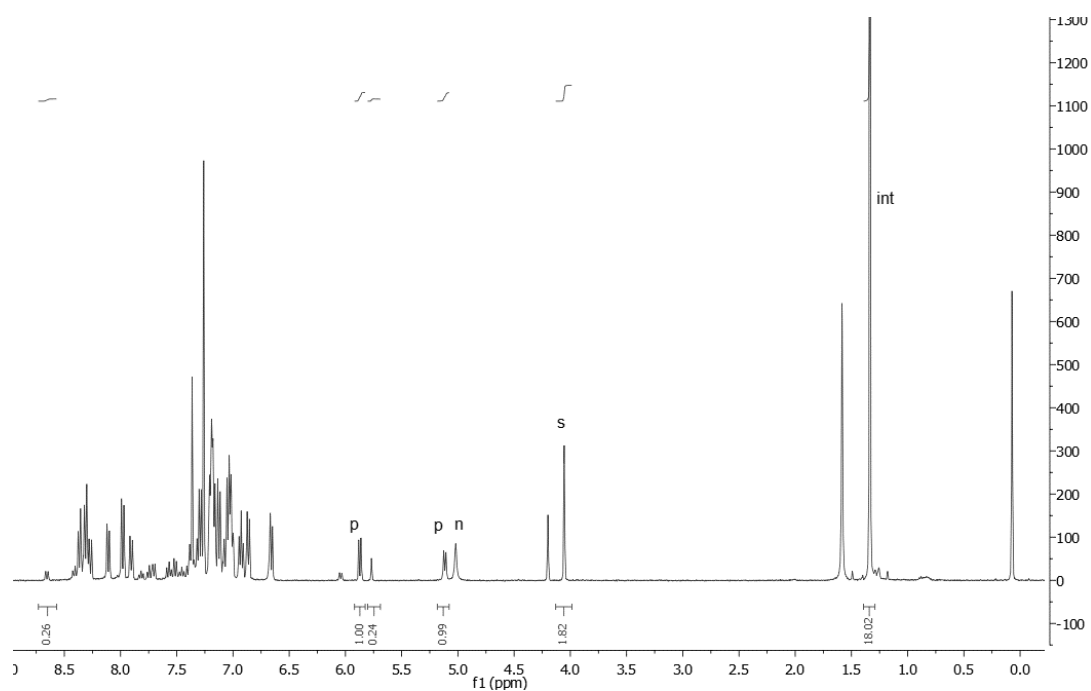
**Figure S16** Crude reaction mixture in  $\text{DMSO}-d_6$  for the reaction between thioxanthene,  $\text{TsNH}_2$  and chloranil to afford **6** under the optimised reaction conditions. 0.03 mmol 1,3,5-trimethoxybenzene as internal standard.



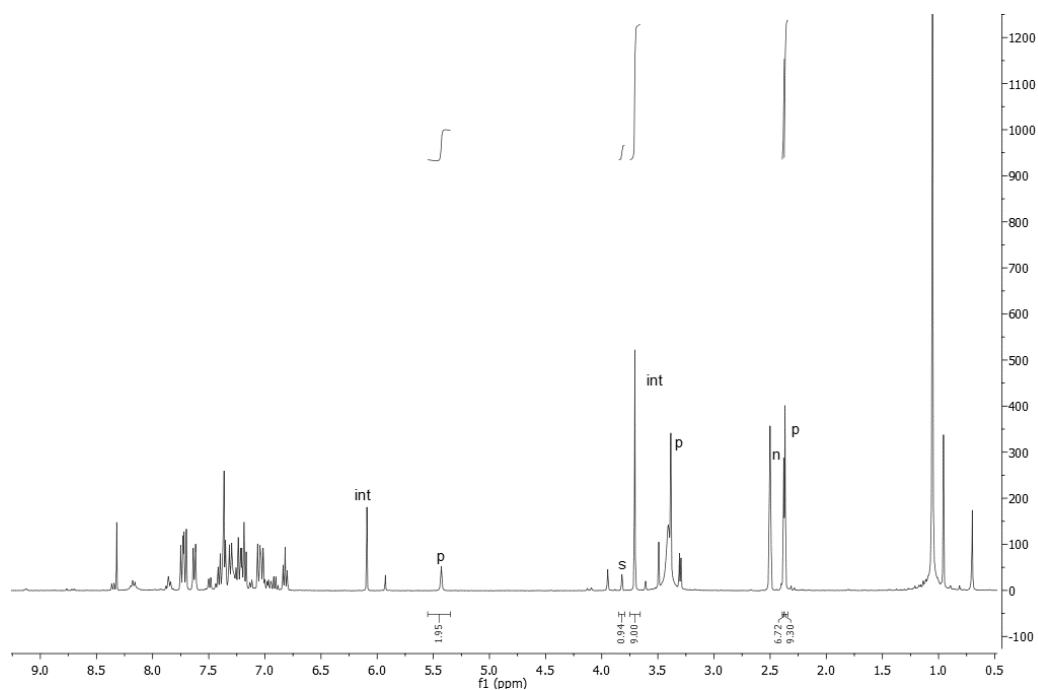
**Figure S17** Crude reaction mixture in  $\text{CDCl}_3$  for the reaction between xanthene and PhINTs to afford **1**. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.



**Figure S18** Crude reaction mixture in  $\text{CDCl}_3$  for the reaction between xanthene and PhINTces to afford **2**. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

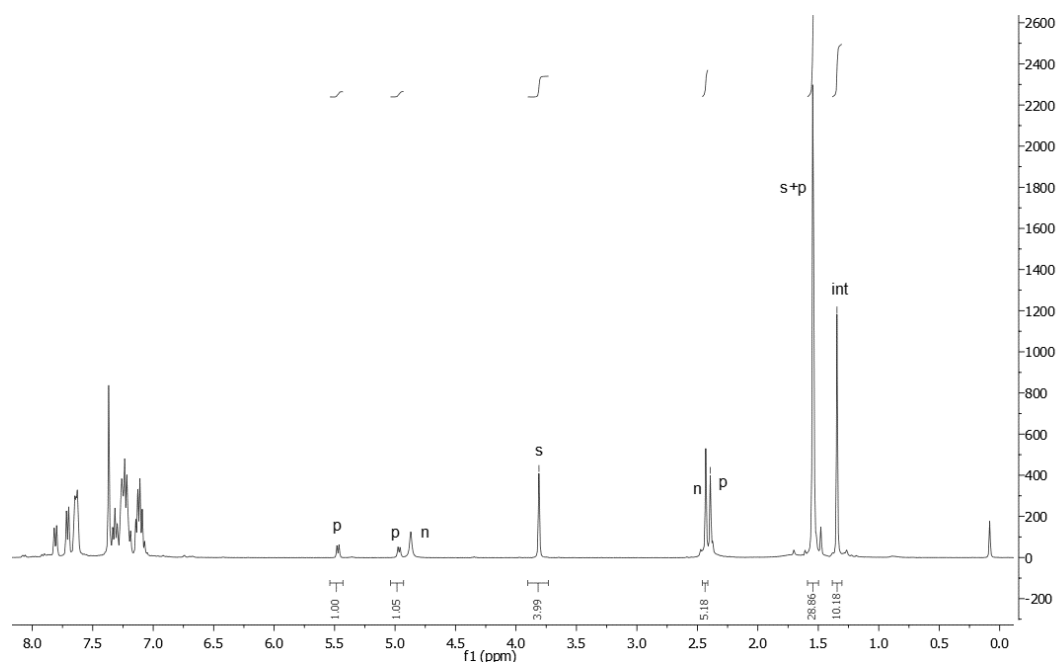


**Figure S19** Crude reaction mixture in CDCl<sub>3</sub> for the reaction between xanthene and PhINNs to afford **3**. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

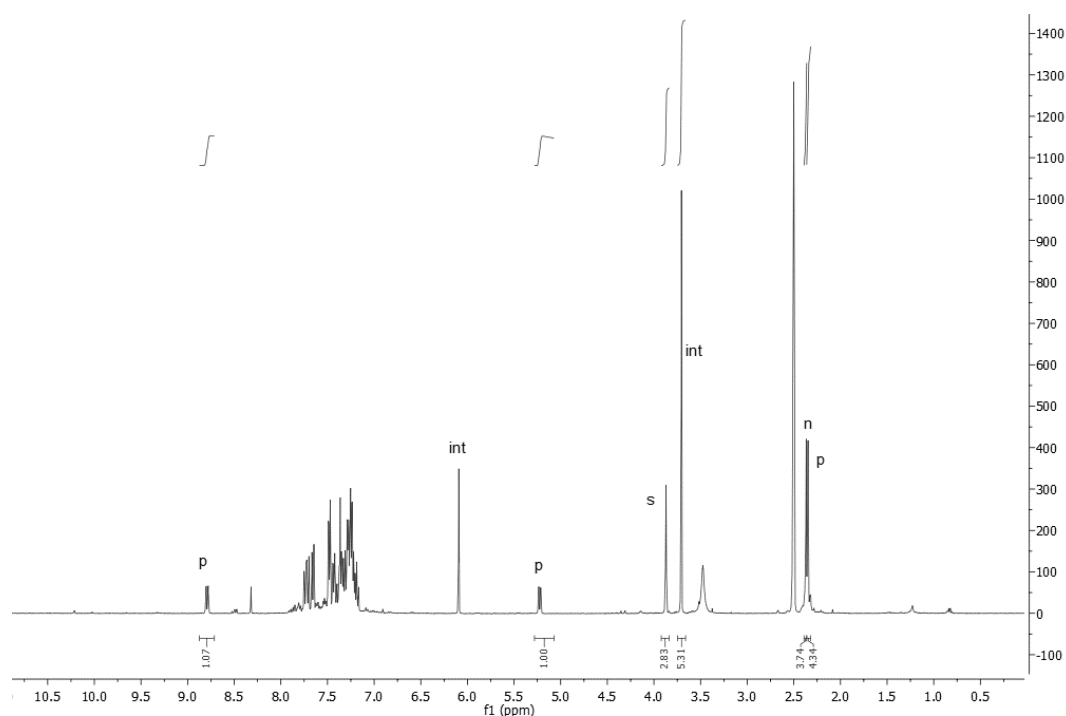


**Figure S20** Crude reaction mixture in DMSO-d<sub>6</sub> for the reaction between *N*-methyldihydroacridine, PhI(OPiv)<sub>2</sub> and TsNH<sub>2</sub> to afford **5-Me**. 0.01 mmol 1,3,5-trimethoxybenzene as internal standard.





**Figure S21** Crude reaction mixture in  $\text{CDCl}_3$  for the reaction between *N*-Boc-9,10-dihydroacridine and PhINTs to afford **5-Boc**. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.



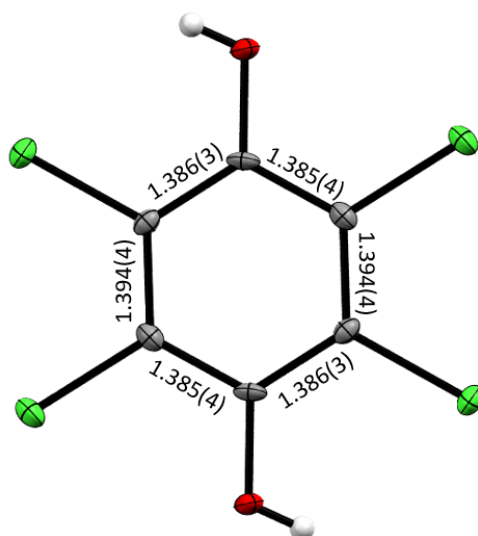
**Figure S22** Crude reaction mixture in  $\text{DMSO-d}_6$  for the reaction between thioxanthene and PhINTs to afford **6**. 0.01 mmol 1,3,5-trimethoxybenzene as internal standard.

### XRD structure of 1,2,4,5-tetrachloro-*para*-hydroquinone

Single crystals suitable for CRD analysis were grown from the reaction mixture by slow evaporation of  $\text{CDCl}_3$  from an NMR tube sample. The crystal structure for 1,2,4,5-tetrachloro-*para*-hydroquinone is displayed in Figure S23 and has been reported before in literature.<sup>[S20,S21]</sup> As can be seen in Figure S23, the C-C bond lengths are typical for an aromatic ring and therefore confirm that the molecule is reduced from chloranil to 1,2,4,5-tetrachloro-*para*-hydroquinone.

X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator ( $\lambda = 0.71073 \text{ \AA}$ ) and a CMOS Photon 50 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX2 software.<sup>[S22]</sup> Absorption correction and scaling was performed with SADABS.<sup>[S23]</sup> The structures were solved using intrinsic phasing with the program SHELXT.<sup>[S23]</sup> Least-squares refinement was performed with SHELXL-2013<sup>[S24]</sup> against  $F^2$  of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times  $U_{eq}$  of the attached C atoms.

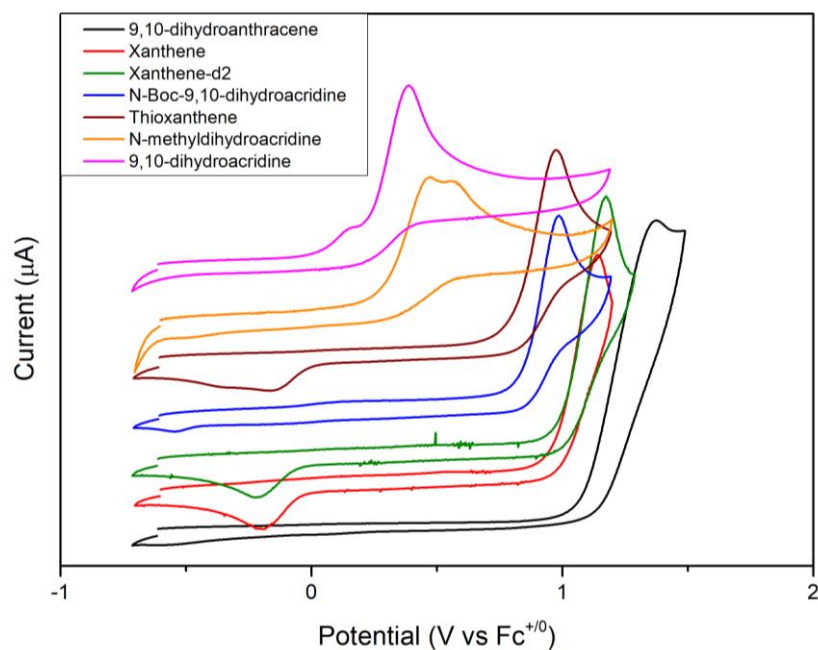
**1,2,4,5-tetrachloro-*para*-hydroquinone**  $\text{C}_6\text{Cl}_4\text{O}_2\text{H}_2$ ,  $F_w = 247.88$ , monoclinic,  $P 2_1/n$ ,  $a = 8.2295(6)$ ,  $b = 4.7783(4)$ ,  $c = 10.3635(8) \text{ \AA}$ ,  $\beta = 97.582(2)^\circ$ ,  $V = 403.96(5) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 2.038 \text{ g/cm}^3$ ,  $\mu = 1.410 \text{ mm}^{-1}$ . 5205 Reflections were measured. 715 Reflections were unique ( $R_{\text{int}} = 0.0364$ ), of which 638 were observed [ $I > 2\sigma(I)$ ]. 58 Parameters were refined with 0 restraints. Residual electron density between  $-0.306$  and  $0.361 \text{ e/\AA}^3$ .



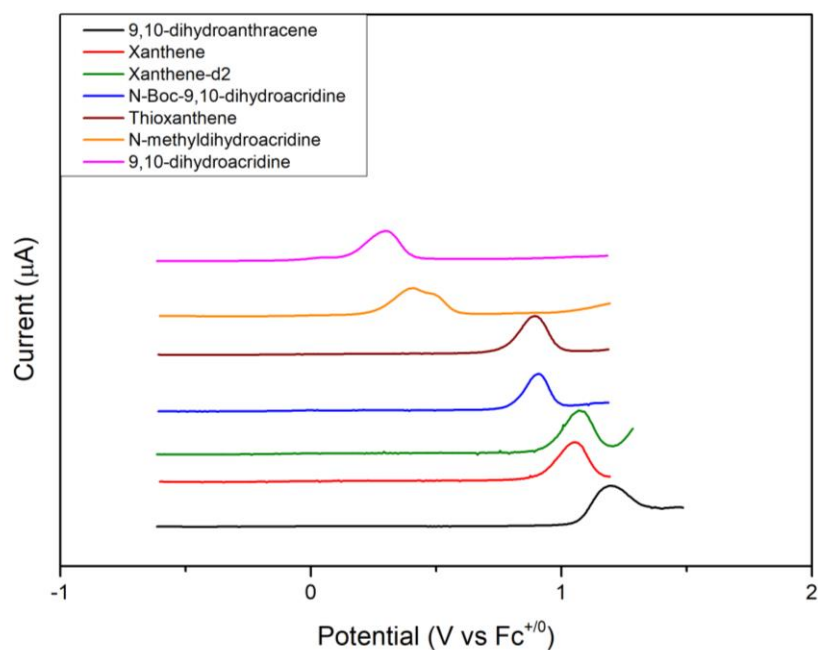
**Figure S23** ORTEP plot (set at 50% probability level) of 1,2,4,5-tetrachloro-*para*-hydroquinone with relevant bond lengths. Green = Cl, grey = C, red = O, white = H.

### Determination of the oxidation potentials for different dihydroheteroanthracenes

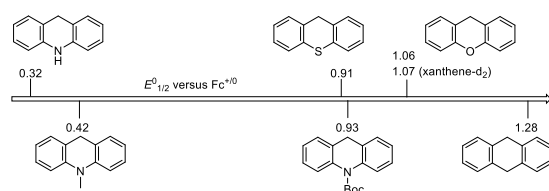
The oxidation potentials ( $E^{0/1}$ ) versus  $\text{Fc}^{0/+}$  in DCM for various dihydroheteroanthracenes were obtained from differential pulse voltammetry (DPV, Figure S25) and cyclic voltammetry (CV, Figure S24). A schematic overview is shown in Figure S26. The reduction potentials ( $E^{0/1}$ ) versus  $\text{Fc}^{0/+}$  in DCM of chloranil were also measured with CV and found to be  $-0.43$  and  $-1.15 \text{ V}$  vs  $\text{Fc}^{0/+}$  (Figure S27). All measurements were conducted in a single-compartment three electrode cell with glassy carbon (working electrode), Leak-free Ag/AgCl 3.0M KCl (reference electrode) and Pt wire (auxiliary electrode) with an 1 mM analyte and 0.1M  $[\text{NBu}_4]\text{PF}_6$  supporting electrolyte concentration.



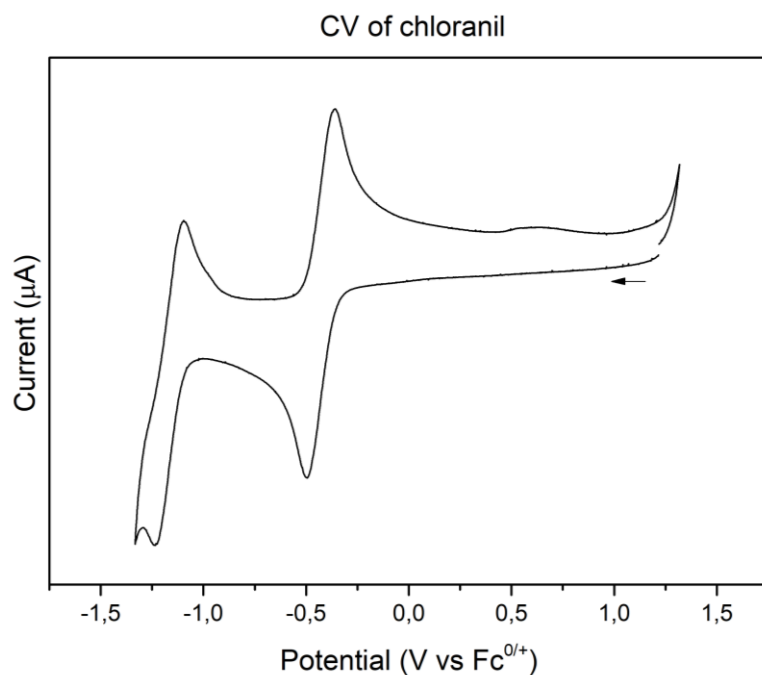
**Figure S24** Measured cyclic voltammograms of various dihydroheteroanthracenes measured in DCM.



**Figure S25** Measured differential pulse voltammograms of various dihydroheteroanthracenes measured in DCM.



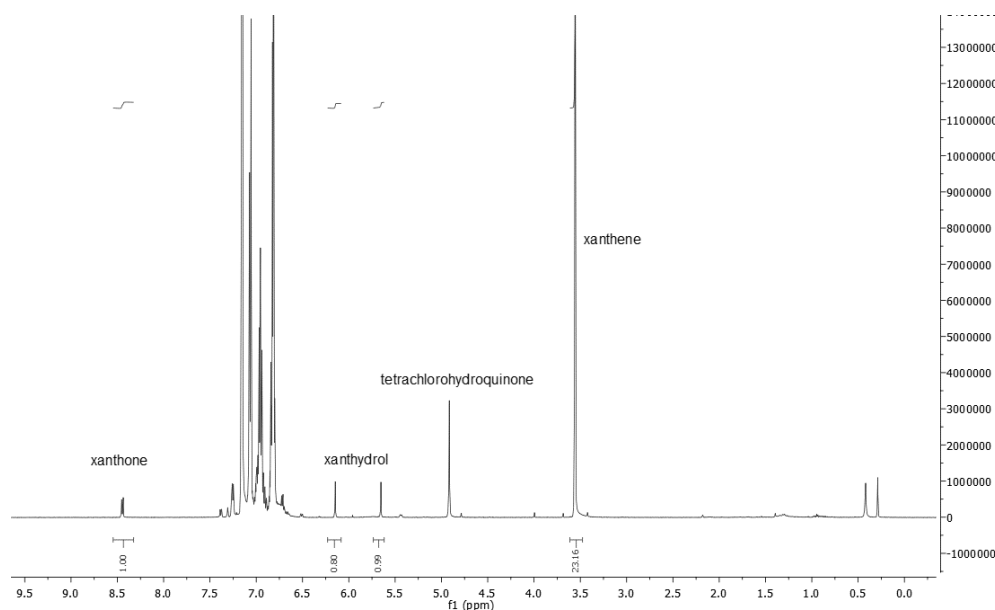
**Figure S26**  $E^{\circ}_{1/2}$  versus  $Fc^{+/0}$  for various dihydroheteroanthracenes in DCM, obtained from DPV measurements.



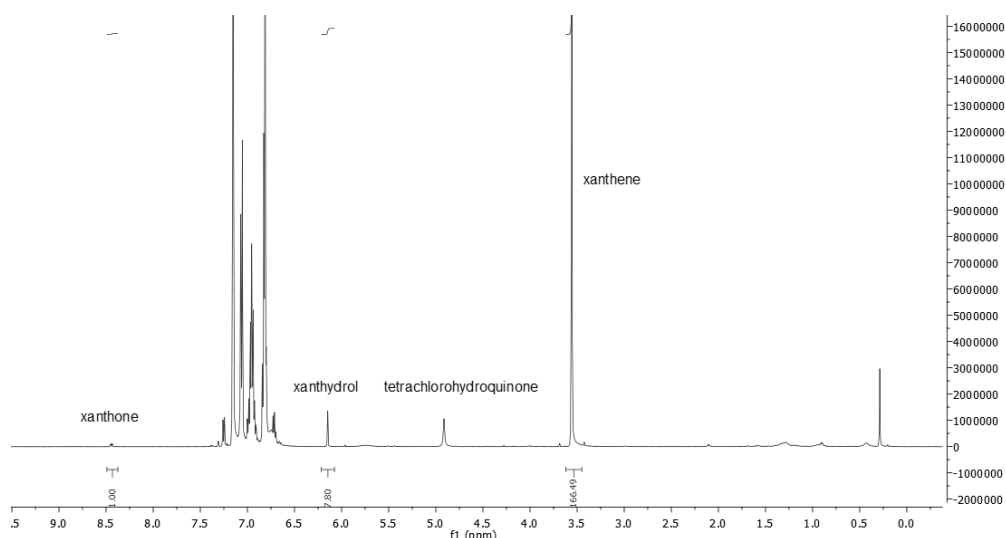
**Figure S27** Measured cyclic voltammogram of chloranil measured in DCM.

### Reaction between xanthene and chloranil

In order to gain insight in the possible formation of the xanthylum cation upon reaction between xanthene and chloranil, the conversion of xanthene was monitored after 2 hours under the standard reaction conditions in absence of amine under aerobic conditions (Figure S28) and under argon (Figure S29). As can be seen, no formation of the xanthylum ion can be observed. However, xanthone<sup>[S25]</sup> (4% versus 0.6%), xanthidrol<sup>[S19]</sup> (3.5% versus 2.3%) and tetrachlorohydroquinone are formed in larger amounts under aerobic conditions than in a reaction under argon. This indicates that the xanthylum cation and the 2,3,5,6-tetrachloro-4-hydroxy-phenoxy anion (which are in equilibrium with xanthene and chloranil) are formed as transient species that subsequently react with water as the nucleophile.



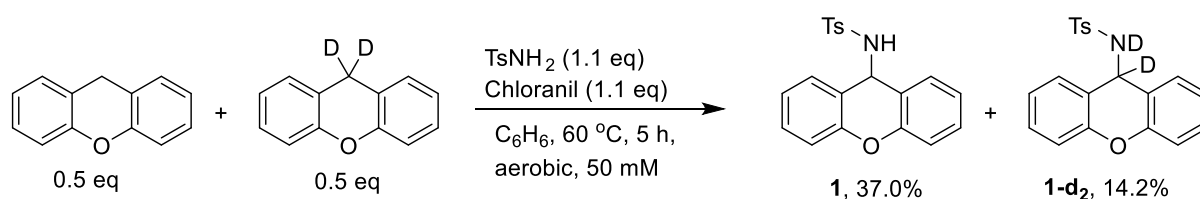
**Figure S28** Crude reaction mixture of the reaction between xanthene and chloranil after 2 hours at 60 °C under aerobic conditions.



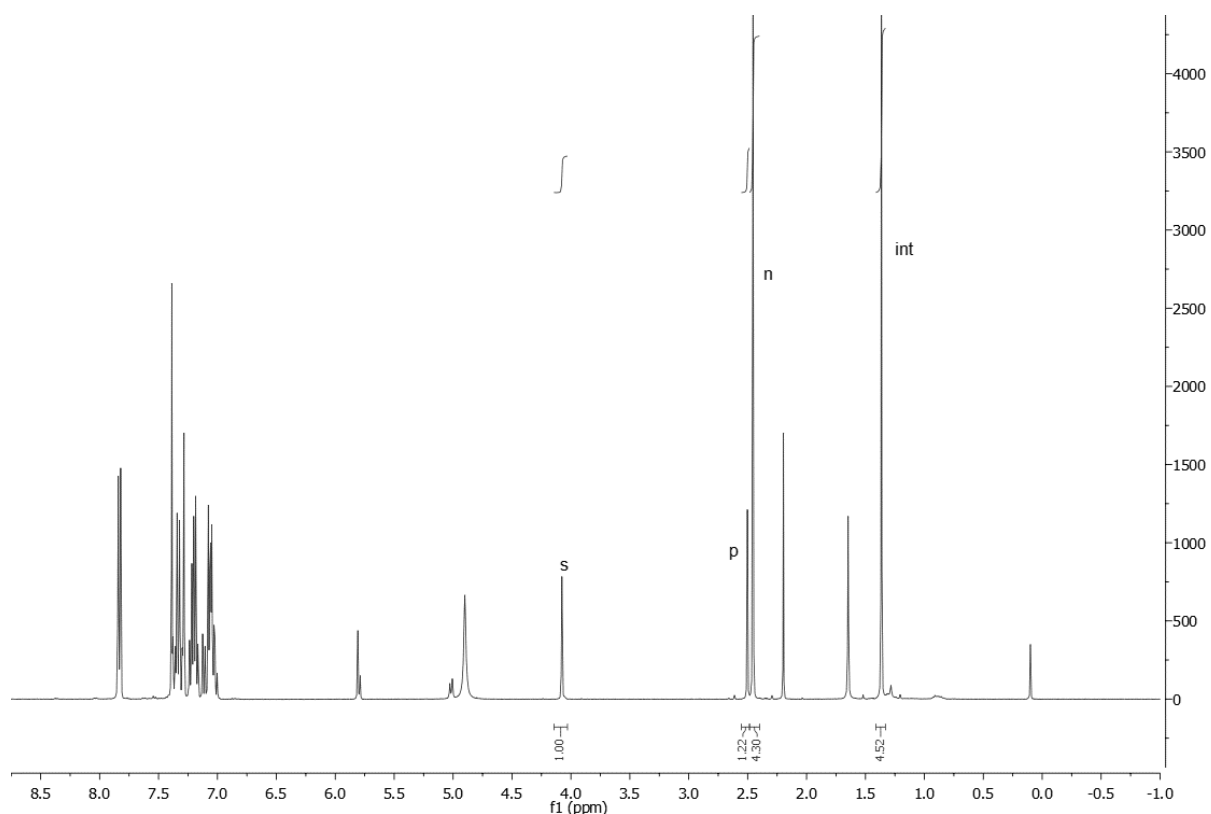
**Figure S29** Crude reaction mixture of the reaction between xanthene and chloranil after 2 hours at 60 °C under argon.

### Measurement of the kinetic isotope effect

The kinetic isotope effect (KIE) for the reaction between xanthene, chloranil and TsNH<sub>2</sub> was determined from an intermolecular competition experiment between xanthene (0.5 eq) and xanthene-*d*<sub>2</sub> (0.5 eq) under the standard reaction conditions (Scheme S1 and Figure S30). The KIE value was found to be 2.6. After 5 hours, 37.0% of xanthene was converted to the desired product **1** and 14.2% of xanthene-*d*<sub>2</sub> was converted to **1-d**<sub>2</sub>.

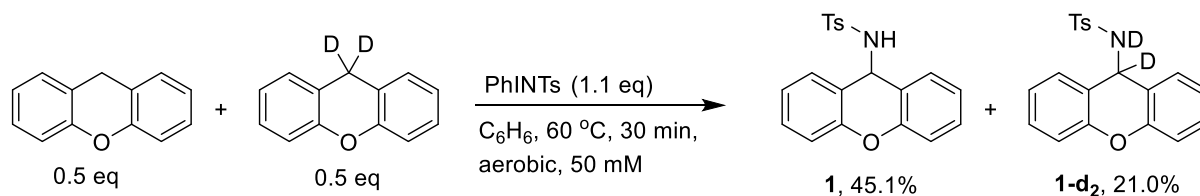


**Scheme S1** Reaction for the determination of the intermolecular KIE between TsNH<sub>2</sub>, chloranil, xanthene and xanthene-*d*<sub>2</sub>.

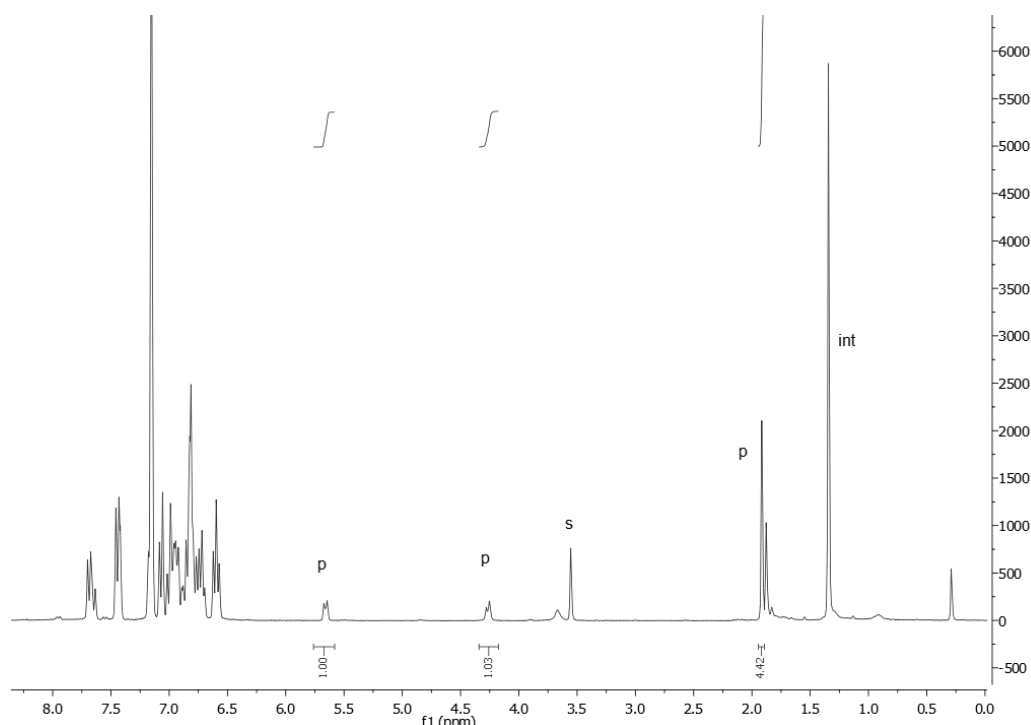


**Figure S30** Crude reaction mixture in  $\text{CDCl}_3$  for the reaction between  $\text{TsNH}_2$ , chloranil, xanthene and xanthene- $d_2$  to afford **1** and **1- $d_2$** . 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

The kinetic isotope effect (KIE) for the reaction between xanthene and PhINTs was determined from an intermolecular competition experiment between xanthene (0.5 eq) and xanthene- $d_2$  (0.5 eq) at 60 °C for 30 min at a 50 mM concentration (Scheme S2 and Figure S31) and found to be 2.1. After 30 min, 45.1% of xanthene was converted to the desired product **1** and 21.0% of xanthene- $d_2$  was converted to **1- $d_2$** .



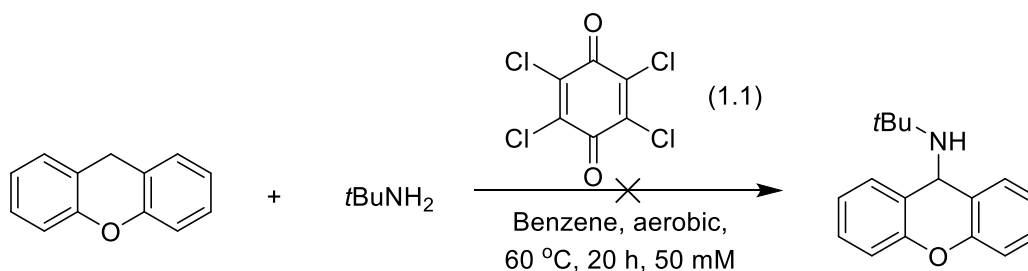
**Scheme S2** Reaction for the determination of the intermolecular KIE between PhINTs, xanthene and xanthene- $d_2$ .



**Figure S31** Crude reaction mixture in  $C_6D_6$  for the reaction between PhINTs, xanthene and xanthene- $d_2$  to afford **1** and **1- $d_2$** . 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

### Additional experiments on the amination of hydrocarbons

Amination of xanthene with chloranil and  $tBuNH_2$  as the electrophile (Scheme S3) did not afford the desired product because  $tBuNH_2$  was immediately oxidised by chloranil. Additional optimisation parameters for the amination of xanthene with  $TsNH_2$  and chloranil can be found in Table S1. Benzoquinones which were employed in the amination of xanthene with  $TsNH_2$  and were not reported in the main text can be found in Table S2. Additional hydrocarbon substrates in the amination with  $TsNH_2$  and chloranil (Table S3) or PhINTs (Table S4) are also included. Control reactions were performed to rule out xanthone as an intermediate in the amination reaction and to investigate if acridine or *N*-methylacridinium iodide are nucleophilic enough to allow reaction with the amine (Table S5). Moreover, a control reaction between acridine and PhINTs also did not afford the desired product as expected (Scheme S4).



**Scheme S3** Attempted amination of xanthene with chloranil and  $tBuNH_2$ .

**Table S1** Additional optimisation parameters for the amination of xanthene with TsNH<sub>2</sub> and chloranil. [a] Reaction under argon atmosphere. Yields calculated using <sup>1</sup>H NMR with 1,3,5-tris-(tert-butyl)benzene as an internal standard.

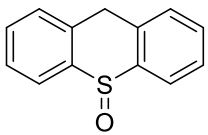
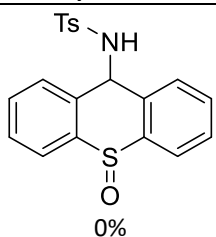
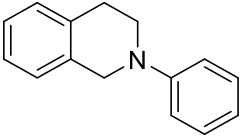
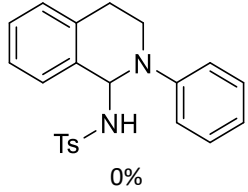
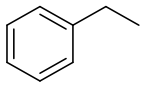
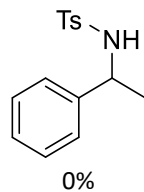

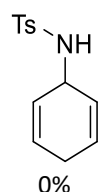
Entry	Equiv. chloranil	Concentration (mM)	Time (h)	Yield
1 <sup>[a]</sup>	3	25	20	31%
2	3	25	20	32%
3	3	50	20	30%
4	3	25	65	72%
5	1	25	65	52%

**Table S2** Screening of additional benzoquinones in the amination of xanthene with TsNH<sub>2</sub>. Yields calculated using <sup>1</sup>H NMR with 1,3,5-tris-(tert-butyl)benzene as an internal standard.

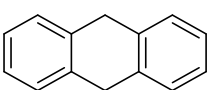
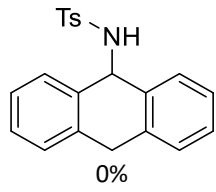
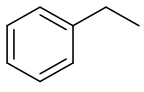
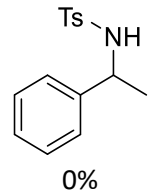
Entry	Benzoquinone	By-products	Yield
1		Imine of <b>1</b> (16%) and xanthone (20%)	41%
2		-	0%
3		Unknown	27%
4		Xanthone (10%)	37%



**Table S3** Screening of additional hydrocarbons in the amination reaction with TsNH<sub>2</sub> and chloranil.

$\text{Substrate} + p\text{TsNH}_2 (1.1) \xrightarrow[\text{C}_6\text{H}_6, 60^\circ\text{C}, 20\text{ h, aerobic, 50 mM}]{\text{Chloranil (1.1)}} \text{Product}$			
Entry	Substrate	Envisioned product and yield	By-product
1		 0%	-
2		 0%	86% conversion to unknown products
3		 0%	-
4		 0%	-

**Table S4** Screening of additional hydrocarbons in the amination reaction with PhINTs.

$\text{Substrate} + \text{PhINTs} (1.1) \xrightarrow[\text{C}_6\text{H}_6, 60^\circ\text{C}, 20\text{ h, aerobic, 50 mM}]{\text{PhINTs (1.1)}} \text{Product}$			
Entry	Substrate	Envisioned product and yield	
1		 0%	
2		 0%	

**Table S5** [a] No conversion was observed with or without chloranil. [b] To completely dissolve the substrate a 1:1 mixture of MeCN and C<sub>6</sub>H<sub>6</sub> was used. [c] In absence of chloranil no conversion was observed.

<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;"> <chem>O=C1C(Cl)=C(Cl)C(Cl)=C1Cl</chem>              (1.1)         </div> <div style="margin: 0 10px;"> <math>\xrightarrow{\text{X}}</math> </div> <div style="text-align: center;"> <math>\longrightarrow</math> </div> </div>		
Substrate	+ <i>p</i> TsNH <sub>2</sub> (1.1)	Conversion
C <sub>6</sub> H <sub>6</sub> , 60 °C, 20 h, aerobic, 50 mM		
Entry	Substrate	Conversion
1 <sup>[a]</sup>	<chem>O=C1c2ccccc2Oc3ccccc13</chem>	0%
2 <sup>[b,c]</sup>	<chem>[I-].[n+]1c2ccccc2c3ccccc13</chem>	39% to unknown products
3	<chem>c1ccc2c(c1)c3ccccc3n2</chem>	0%

<chem>c1ccc2c(c1)c3ccccc3n2</chem>	+	PhINTs (1.1)	$\xrightarrow{\text{X}}$	$\longrightarrow$	No conversion
C <sub>6</sub> H <sub>6</sub> , 60 °C, 20 h, aerobic, 50 mM					

**Scheme S4** Control reaction between acridine and PhINTs.

## Computational studies

DFT geometry optimizations were performed using TURBOMOLE<sup>[526]</sup> coupled to the PQS Baker optimizer<sup>[527,528]</sup> via the BOpt package<sup>[529]</sup> at the B3LYP<sup>[530,531]</sup>/def2-TZVP<sup>[532,533]</sup> level of theory (m4 grid), on full models with implicit solvation by benzene (COSMO<sup>[534]</sup>,  $\epsilon = 2.27$ ), using Grimme's version 3 (disp3, "zero damping") dispersion corrections.<sup>[535]</sup> All minima (no imaginary frequencies) were characterized by numerically calculating the Hessian matrix for **A**, **B**, **C** and **TS** or an analytical approximation for **D**. For **D** the numerical calculation of the Hessian matrix did not work for unknown reasons. The transition state (**TS**) was characterised by one imaginary frequency along the reaction coordinate in the numerically calculated Hessian. The graphical representation of **TS** was generated using IboView. The xyz coordinates and Gibbs free energies at 298K (kcal mol<sup>-1</sup>) of all intermediates can be found below.

### Xanthene

-361666.3992 kcal mol<sup>-1</sup>

H	0.5643286	0.1007100	0.1264099
C	0.3179215	0.0476845	1.1811793
C	-0.3133584	-0.0946915	3.8777822
C	-0.2932686	-1.1074163	1.6685475
C	0.6056132	1.1218879	2.0134964
C	0.2825820	1.0492018	3.3671391
C	-0.5939672	-1.1609369	3.0279647
H	1.0774550	2.0091917	1.6111576
H	0.5011988	1.8796249	4.0266712
H	-0.5644976	-0.1826277	4.9269400
C	-0.6601887	-2.2563756	0.7649442
H	0.1431800	-2.4414006	0.0467488
H	-1.5393633	-1.9816722	0.1685487
C	-0.9594056	-3.5119417	1.5428535
C	-1.2263751	-3.4435838	2.9086293
O	-1.1850088	-2.2596039	3.6089486
C	-1.0150487	-4.7634336	0.9296783
H	-0.8027522	-4.8329540	-0.1315492
C	-1.3420041	-5.9077336	1.6459950
H	-1.3820241	-6.8675794	1.1470981
C	-1.5557091	-4.5791454	3.6433372
H	-1.7540897	-4.4769405	4.7024602
C	-1.6179471	-5.8110324	3.0085214
H	-1.8742709	-6.6952315	3.5784978

### PhINTs

-880561.456 kcal mol<sup>-1</sup>

S	2.4845869	0.1768028	1.9803111
O	3.6024573	-0.5218027	1.3847523
O	2.5306365	1.6224819	2.0936559
C	1.0278911	-0.2207515	1.0292827
C	-1.3425396	-0.9493265	-0.2588498
C	-0.0321096	0.6762408	0.9736024
C	0.9247061	-1.4725565	0.4278897
C	-0.2530469	-1.8251372	-0.2125350
C	-1.2094044	0.3051800	0.3353657
H	0.0647219	1.6514162	1.4312991
H	1.7601438	-2.1587199	0.4703241
H	-0.3336775	-2.8017569	-0.6763606
H	-2.0397600	1.0009512	0.3081968
C	-2.6182155	-1.3492892	-0.9494132
H	-2.5351835	-1.2075871	-2.0310326

H	-3.4628017	-0.7529586	-0.6017180
H	-2.8472268	-2.4027756	-0.7770967
N	2.3020112	-0.5943590	3.4228854
I	1.0359737	0.3150361	4.6736671
C	-0.8400442	-0.5249957	4.0643629
C	-3.2130312	-1.5962450	3.1949073
C	-0.8192996	-1.7701283	3.4606810
C	-2.0026834	0.2068132	4.2487035
C	-3.2026701	-0.3501469	3.8127442
C	-2.0260546	-2.3002384	3.0160985
H	0.1131503	-2.2969536	3.3073238
H	-1.9879781	1.1900270	4.7010467
H	-4.1241127	0.2030686	3.9442478
H	-2.0312669	-3.2639127	2.5232605
H	-4.1471728	-2.0163766	2.8443972

#### Transition state (TS)

-1242210.122 kcal mol<sup>-1</sup>

S	2.2959786	-2.5593361	0.9744330
O	2.6498853	-3.7391783	1.7482777
O	2.0539319	-2.7274871	-0.4441629
C	0.7843275	-1.8977329	1.6698115
C	-1.5239589	-0.7620015	2.7688284
C	-0.3075388	-1.6268688	0.8555492
C	0.7323784	-1.6075580	3.0311738
C	-0.4143167	-1.0489706	3.5696271
C	-1.4525302	-1.0620310	1.4093036
H	-0.2540967	-1.8491745	-0.2012511
H	1.5861806	-1.8034485	3.6630642
H	-0.4399770	-0.8104459	4.6263182
H	-2.2986386	-0.8433328	0.7677028
C	-2.7624596	-0.1504560	3.3665303
H	-3.3272356	0.4143775	2.6231294
H	-2.5136941	0.5193831	4.1919271
H	-3.4253695	-0.9248047	3.7640908
N	3.4719344	-1.4542133	1.2819152
I	2.9314349	0.5600949	0.0018301
C	2.0845572	1.3879198	1.7481089
C	0.9546201	2.3276525	4.0814404
C	2.8363091	1.3701956	2.9153664
C	0.7828159	1.8693360	1.7170011
C	0.2236142	2.3466186	2.8984593
C	2.2575390	1.8384125	4.0892409
H	3.8438725	0.9830793	2.9159946
H	0.2038765	1.8531800	0.8043068
H	-0.7952695	2.7127963	2.8915983
H	2.8310821	1.8083266	5.0065467
H	0.5058845	2.6859331	4.9994826
H	7.0687148	-1.8226396	1.6892461
C	6.9396634	-1.0445650	2.4318754
C	6.5632677	0.9640634	4.3243499
C	5.8965448	-1.1702076	3.3567145
C	7.7796504	0.0559479	2.4470296
C	7.5868802	1.0643642	3.3945971
C	5.7279573	-0.1475254	4.2977518
H	8.5792923	0.1378928	1.7223220
H	8.2386163	1.9287111	3.4086272

H	6.3963035	1.7301023	5.0702873
C	4.9227990	-2.2691874	3.3051567
H	5.2929286	-3.2052694	2.8938430
H	4.1781199	-1.9000300	2.3813724
C	4.0859841	-2.4033240	4.5038079
C	3.9755774	-1.3206974	5.3855124
O	4.7210748	-0.1783990	5.2286901
C	3.3254653	-3.5481565	4.7731537
H	3.3902302	-4.3814953	4.0877780
C	2.4665063	-3.5936520	5.8578096
H	1.8766304	-4.4819162	6.0425463
C	3.1082582	-1.3491233	6.4715096
H	3.0497733	-0.4861984	7.1217594
C	2.3482855	-2.4861689	6.7007632
H	1.6683396	-2.5137923	7.5428522

#### Xanthenium cation

-361163.7755 kcal mol<sup>-1</sup>

H	0.0263904	0.5598703	0.4058568
C	-0.0150758	0.3626682	1.4693415
C	-0.1203425	-0.1940097	4.2381428
C	0.0569834	-0.9826308	1.9189766
C	-0.1347481	1.3806679	2.3759790
C	-0.1870546	1.0981730	3.7596137
C	0.0012035	-1.2302017	3.3178524
H	-0.1904080	2.4072385	2.0404761
H	-0.2820650	1.9159603	4.4623060
H	-0.1598733	-0.4182721	5.2950769
O	0.0652427	-2.4870531	3.7946155
C	0.1831614	-3.5500439	2.9777588
C	0.2446988	-3.3767927	1.5680367
C	0.1793226	-2.0777409	1.0631242
H	0.2242082	-1.9171451	-0.0084090
C	0.3699252	-4.5324231	0.7519410
H	0.4179401	-4.4092931	-0.3223995
C	0.2421197	-4.8115505	3.5612748
H	0.1925951	-4.9068894	4.6371244
C	0.4278919	-5.7725267	1.3276208
H	0.5234166	-6.6565689	0.7121171
C	0.3634222	-5.9078939	2.7327626
H	0.4110458	-6.8965426	3.1708106

#### [Phi-NHTs] Close contact pair

-881051.4543 kcal mol<sup>-1</sup>

S	2.4806523	-1.0543867	1.9044638
O	3.5254141	-0.6740501	0.9420607
O	2.3428924	-0.1540697	3.0548410
C	0.9402844	-0.7566387	0.9880062
C	-1.5303020	-0.1925540	-0.2276984
C	0.6672613	0.5239955	0.5089057
C	-0.0088139	-1.7556131	0.8326385
C	-1.2321602	-1.4737479	0.2291872
C	-0.5530460	0.7990510	-0.0894064
H	1.4068618	1.3056769	0.6290337
H	0.2031194	-2.7405825	1.2271921
H	-1.9752957	-2.2589913	0.1394585
H	-0.7636389	1.8046630	-0.4375512

C	-2.8820692	0.1408463	-0.8013189
H	-2.7968945	0.7792131	-1.6842941
H	-3.4848614	0.6834586	-0.0658062
H	-3.4310061	-0.7596186	-1.0827759
I	-2.7086620	2.1715662	2.8971103
C	-2.1662246	0.2081472	3.5043311
C	-1.4704861	-2.3543087	4.2734980
C	-0.8294663	-0.0942272	3.7200661
C	-3.1659039	-0.7467648	3.6616642
C	-2.8069284	-2.0338344	4.0513423
C	-0.4862287	-1.3882593	4.1046798
H	-0.0418458	0.6266368	3.5560857
H	-4.2031941	-0.4987253	3.4814673
H	-3.5781504	-2.7856484	4.1719103
H	0.5623841	-1.6311962	4.2154326
H	-1.1931741	-3.3617539	4.5587537
N	2.5121577	-2.5281119	2.3861240
H	2.8573249	-3.1001719	1.6185983

#### PhI

-332099.7693 kcal mol<sup>-1</sup>

I	-0.5163384	0.0797538	3.1772440
C	-1.5662271	-0.9757551	4.6857654
C	-2.9405156	-2.3574689	6.6598907
C	-1.0246338	-2.1478243	5.2031428
C	-2.7852192	-0.4847358	5.1415167
C	-3.4691322	-1.1837892	6.1325074
C	-1.7202738	-2.8357950	6.1937238
H	-0.0763286	-2.5237170	4.8439967
H	-3.2003308	0.4272368	4.7346291
H	-4.4186145	-0.8042855	6.4895852
H	-1.3014380	-3.7488237	6.5986903
H	-3.4769480	-2.8967958	7.4303081

#### TsNH anion

-548954.2452 kcal mol<sup>-1</sup>

H	0.7581744	0.1896628	0.0568123
C	0.4415482	0.1291380	1.0902007
C	-0.3532491	-0.0464580	3.7392996
C	0.1171214	-1.1153846	1.6260545
C	0.3656429	1.2722831	1.8762874
C	-0.0330631	1.2063308	3.2142314
C	-0.2765687	-1.1959311	2.9585470
H	0.6229925	2.2343132	1.4442660
H	-0.5121119	-2.1653240	3.3788154
H	-0.6626688	-0.1264450	4.7767615
S	0.1346479	-2.5935551	0.5704726
O	1.2403547	-2.3488462	-0.3544705
O	0.3362713	-3.6912655	1.5281236
N	-1.2101137	-2.6291825	-0.2058806
H	-1.9182267	-3.0038452	0.4228752
C	-0.0762552	2.4447398	4.0733940
H	0.8888414	2.6214195	4.5600292
H	-0.8267465	2.3567577	4.8619977
H	-0.3085908	3.3325922	3.4811830

#### Product 1

-910190.215 kcal mol<sup>-1</sup>

H	0.1243435	0.7534127	1.9364954
C	0.3072727	0.1186842	2.7932268
C	0.7711427	-1.5075887	4.9942322
C	-0.0236161	-1.2374706	2.7135882
C	0.8518743	0.6604153	3.9461832
C	1.0764916	-0.1586699	5.0539104
C	0.2306690	-2.0409321	3.8241474
H	1.0998830	1.7132095	3.9853821
H	1.4984787	0.2547792	5.9613356
H	0.9483391	-2.1676236	5.8333871
C	-0.6803645	-1.8166271	1.4841877
H	-0.1629562	-1.4588026	0.5922957
C	-0.6420319	-3.3258388	1.4967982
C	-0.3487231	-4.0204027	2.6653880
O	-0.0181433	-3.3868419	3.8389502
C	-0.9523304	-4.0591052	0.3494603
H	-1.2014240	-3.5194795	-0.5562904
C	-0.9732905	-5.4446008	0.3718876
H	-1.2182498	-5.9975992	-0.5257053
C	-0.3726043	-5.4132395	2.7067727
H	-0.1406766	-5.9134373	3.6380883
C	-0.6861221	-6.1216073	1.5586026
H	-0.7044775	-7.2039140	1.5865430
N	-2.0837467	-1.3460123	1.3643095
H	-2.5666278	-1.1252271	2.2249912
S	-2.6285250	-0.5090078	0.0672796
O	-2.1424053	-1.1903213	-1.1062179
O	-4.0368340	-0.3143365	0.2982856
C	-1.8349608	1.0805403	0.1142241
C	-0.4758848	3.5093012	0.3560199
C	-2.3085920	2.0523805	0.9929112
C	-0.6987336	1.3134788	-0.6528543
C	-0.0274973	2.5238710	-0.5250545
C	-1.6283950	3.2545411	1.1075178
H	-3.1989640	1.8659316	1.5787832
H	-0.3468272	0.5556611	-1.3390982
H	0.8602488	2.7020728	-1.1202361
H	-1.9960258	4.0088715	1.7932199
C	0.2394617	4.8276895	0.4734456
H	0.2039147	5.2089932	1.4952804
H	-0.2311568	5.5764815	-0.1704945
H	1.2840666	4.7433710	0.1718205

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