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Supporting Information

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

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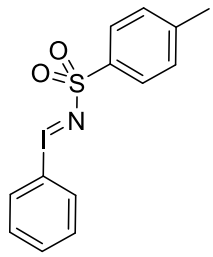
General considerations

All reagents were of commercial grade and used without further purification. CH_2Cl_2 was distilled from CaH_2, toluene was distilled from sodium and CH_3CN 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_3 in a 3 to 1 ratio) prior to use. NMR spectra (^{1}H and ^{13}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 $SiMe_4$ 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

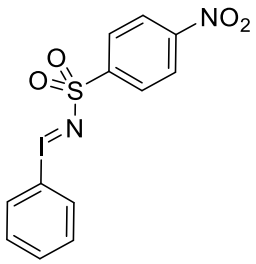
PhINTs



PhINTs was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.[S1] $PhI(OAc)_2$ (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 $TsNH_2$ (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_2O (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. ^{1}H NMR (400 MHz, DMSO-d_6) 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).

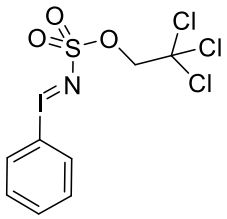
PhINNs

PhINNs was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.[S2] $PhI(OAc)_2$ (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 $NsNH_2$ (1.57 g; 7.75 mmol; 1.0 eq) in MeOH (35 mL) at 0 °C under an N_2 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



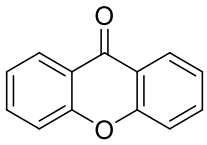
overnight in absence of light. The yellow precipitate was collected by filtration was washed with ice-cold MeOH (3 times 15 mL) and dried *in vacuo* at 60 °C. The product was obtained as a yellow solid in 2.84 g; 7.03 mmol; 90.6% isolated yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.03 (d, *J* = 8.8 Hz, 2H), 7.85 – 7.63 (m, 4H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 2H).

PhINTces



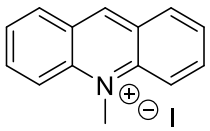
PhINTces was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.[S3] $TcesNH_2$ (685.4 mg; 3.0 mmol; 1.0 eq) and KOH (420.8 mg; 7.5 mmol; 2.5 eq) were dissolved in MeOH (11 mL) and cooled to -5 °C. $PhI(OAc)_2$ (966.3 mg; 3.0 mmol; 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_2O (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_2O (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 ^{1}H NMR (400 MHz, DMSO-d_6) 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



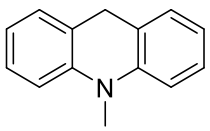
Xanthone was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.[S4] Xanthene (273.33 mg; 1.5 mmol, 1.0 eq) was dissolved in DMSO (7.0 mL) and stirred at 30 °C for 18 h under aerobic conditions. H_2O (25 mL) was added and the white suspepsion was filtered. The residue was washed with H_2O (3 times 7 mL), dissolved in DCM, washed again with H_2O and dried over Na_2SO_4. 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. ^{1}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**



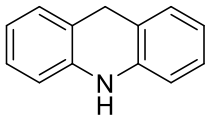
N-methylacridinium iodide was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.[S5] Acridine (1.40 g; 7.81 mmol; 1.0 eq) and MeI (6.0 mL; 96.4 mmol; 12.3 eq) were placed in a flame dried pressure tube and brought under argon. The 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. ^{1}H NMR (300 MHz, DMSO-d_6) 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-methyldihydroacridine was prepared according to a literature procedure[S5] and the spectroscopic data of the product matched those previously reported.[S6] 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., $NaBH_4$ (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_2O (10 mL). The suspension was filtered and the residue washed with H_2O (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. ^{1}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). ^{1}H NMR (400 MHz, DMSO-d_6) 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).

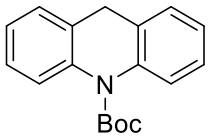
9,10-dihydroacridine



9,10-dihydroacridine was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.[S7] 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_4Cl (2.0 mL) was added. The mixture was further diluted with H_2O (20 mL) and brine (50 mL) and extracted with Et_2O (2 times 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ 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. ^{1}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).

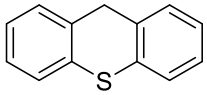
Alternatively, 9,10-dihydroacridine was prepared in higher yield according to a literature procedure and the spectroscopic data of the product matched those previously reported.[S8] A flame-dried Schlenk was charged with acridine (179.1 mg; 1.0 mmol; 1.0 eq), diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Hantsch ester, 633.2 mg; 2.5 mmol; 1.0 eq) and $Fe(OTf)_2$ (7.1 mg; 0.02 mmol; 2 mol%) and brought under argon. Degassed $CDCl_3$ (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 (solica, hexanes:EtOAc = 9:1) to afford the product as on off-white solid in 167.7 mg; 9.25 mmol; 92.5% isolated yield.
^{1}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**



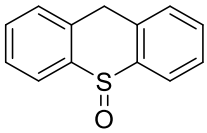
N-Boc-9,10-dihydroacridine was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.[S9] 9,10-dihydroacridine (28.7 mg; 0.158 mmol; 1.0 eq), Boc_2O (120.9 mg; 0.554 mmol; 3.5 eq) and DMAP (32.5 mg; 0.263 mmol; 1.7 eq) were dissolved 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_2O (7.0 mL). The organic solution was washed with aqueous saturated NH_4Cl (3 times 20 mL), brine (2 times 20 mL) and dried over Na_2SO_4. 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. ^{1}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



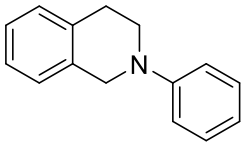
Thioxanthene was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.[S10] $LiAlH_4$ (0.406 g; 10.69 mmol; 2.3 eq) was suspended in dry THF (25.0 mL) and cooled to 0 °C. $AlCl_3$ (1.12 g; 8.40 mmol; 1.8 eq) in THF (25 mL) and thioxanthone (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_2O were added slowly to quench the remaining $LiAlH_4$. 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_4Cl (3 times 100 mL), brine (3 times 100 mL) and dried over over $MgSO_4$. 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}H NMR (400 MHz, chloroform-*d*) δ 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).

9*H*-thioxanthene-10-monooxide



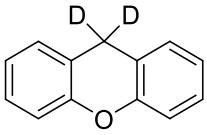
9*H*-Tthioxanthene-10-monooxide was prepared according to a literature procedure and the spectroscopic data of the product matched those previously reported.[S10] Thioxanthene (200 mg; 1.0 mmol; 1.0 eq) was dissolved in DCM (20 mL), *m*-CPBA (224 mg; 1.3 mmol; 1.3 eq) was added and the solution was stirred at r.t. for 26 h. The reaction mixture was washed with aqueous saturated $NaHCO_3$ (3 times 20 mL), brine (3 times 20 mL) and dried over Na_2SO_4. Purification by column chromatography (silica, hexanes:EtOAc = 3:1, R_f = 0.3) afforded 9*H*-thioxanthene-10-monooxide as a white solid in 129.7 mg; 0.605 mmol; 60.5% isolated yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 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[S11] and the spectroscopic data of the product matched those previously reported.[S12] $Pd(dba)_2$ (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. KO*t*Bu (920 mg; 8.2 mmol; 1.86 eq), PhBr (460.6 µ;, 4.4 mmol; 1.0 eq) and 1,2,3,4-tetrahydroisoquinoline (1101.6 µL; 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}H NMR (400 MHz, chloroform-*d*) δ 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}H NMR (400 MHz, DMSO-d_6) δ 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[S13] and the spectroscopic data of the product matched those previously reported.[S14] 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 D_2O (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 H_2O (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}H NMR (400 MHz, chloroform-*d*) δ 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 $TsNH_2$, $NsNH_2$ or $TcesNH_2$ (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 $CHCl_3$ (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 $CDCl_3$ (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}H NMR.

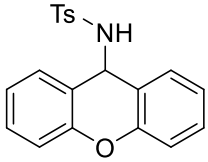
General method for amination with PhINTs, PhINNs and PhINTces

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 $CHCl_3$ (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 $CDCl_3$ (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}H NMR.

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

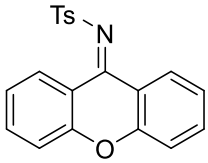
A 4.0 mL vial was charged with $TsNH_2$, $NsNH_2$ or $TcesNH_2$ (0.11 mmol, 1.1 eq), $PhI(OPiv)_2$ (0.11 mmol, 1.1 eq), MgO (0.22 mmol, 2.2 eq), the dihydroheteroanthracene (0.10 mmol, 1.0 eq) and benzene (2.0 mL). The resulting suspension was stirred, with a closed cap, under aerobic conditions at 60 °C for 20 h. The reaction mixture was then diluted with $CHCl_3$ (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 $CDCl_3$ (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}H NMR.

Characterization of known products

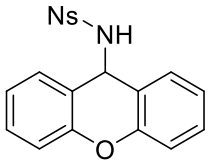


1

This compound is known in literature.[S15] **1** can be obtained in pure form by column chromatography (silica hexanes:EtOAc = 1:0.5) of the crude reaction mixture.
^{1}H NMR (300 MHz, chloroform-*d*) δ 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 δ 2.48 ppm was used to calculate the yield.

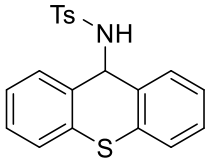


This compound is known in literature and the following spectral data is as therein reported.[S3] ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.73 (dd, *J* = 8.3, 1.6 Hz, 2H), 8.02 – 7.98 (m, 2H), 7.74 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 2H), 7.50 (ddd, *J* = 8.4, 1.2, 0.4 Hz, 2H), 7.40 (ddd, *J* = 8.3, 7.1, 1.2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



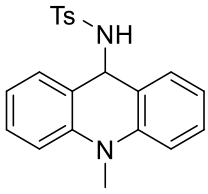
3

This compound is known in literature.[S15] **3** can be obtained in pure form by preparative TLC (silica DCM, R_f = 0.4) of the crude reaction mixture. ^{1}H NMR (400 MHz, chloroform-*d*) δ 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}C NMR (101 MHz, Chloroform-*d*) δ 151.53, 147.28, 129.84, 129.13, 128.03, 124.17, 123.66, 119.56, 118.72, 116.96, 50.22. HRMS-FD$^+$ (*m*/*z*) calculated for $C_{19}H_{14}N_2O_5S$ 382.0623, found 382.0609 [M]$^+$). The resonances at δ 5.88 and 5.03 ppm were used to calculate the yield.



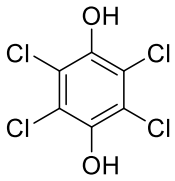
6

This compound is known in literature and the following spectral data is as therein reported.[S16] ^{1}H NMR (400MHz, DMSO-*d*$_6$) 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.



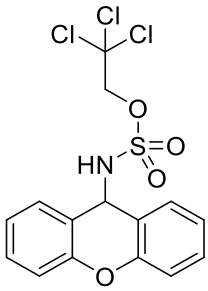
5-Me

This compound is known in literature and the following spectral data is as therein reported.[S17] ^{1}H NMR (400 MHz, DMSO-*d*6): 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.[S18,S19] ^{1}H NMR (400 MHz, chloroform-*d*) δ 5.66 (2H). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 9.35 (s, 2H).

Characterization of new compounds



2

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$_2$, and can be purified by preparative TLC using DCM as the eluent (R$_f$ = 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$^+$ (*m*/*z*) calculated for $C_{15}H_{12}Cl_3NO_4S$: 406.9553, found: 406.9568 $[M]^+$.

^{1}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).

^{13}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.

^{1}H-^{1}H COSY NMR (300 MHz, chloroform-*d*) δ 5.04 - 6.02, 7.23-7.11 – 7.38, 7.23-7.11 – 7.73.

^{1}H-^{13}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.

^{1}H-^{13}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.

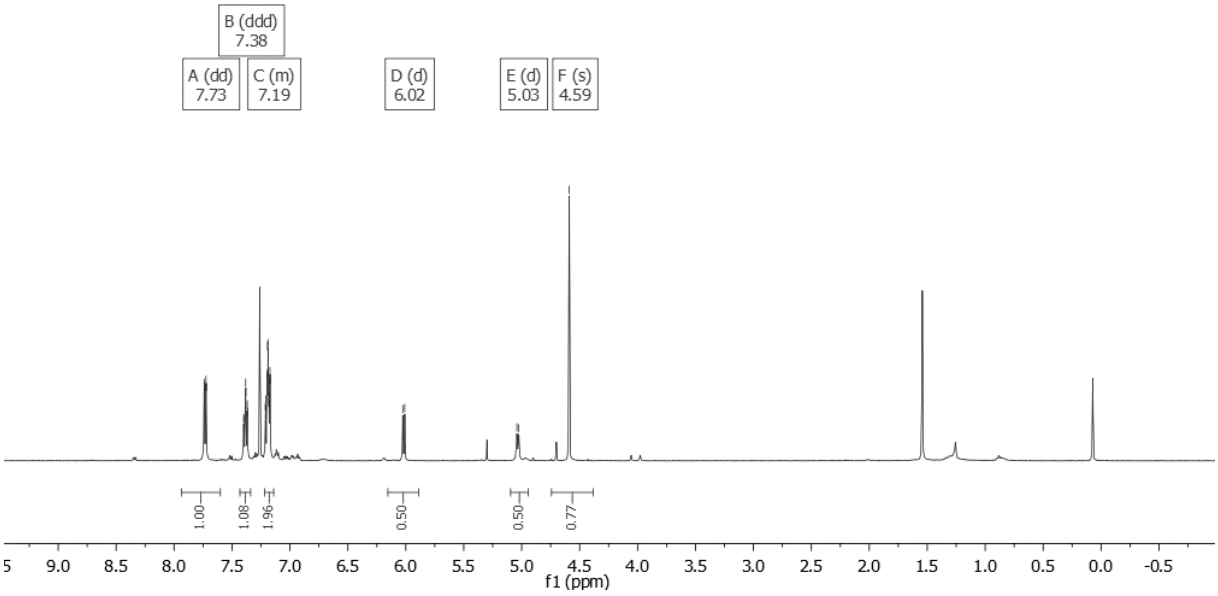


Figure S1 ^{1}H NMR spectrum of **2** in $CDCl_3$.

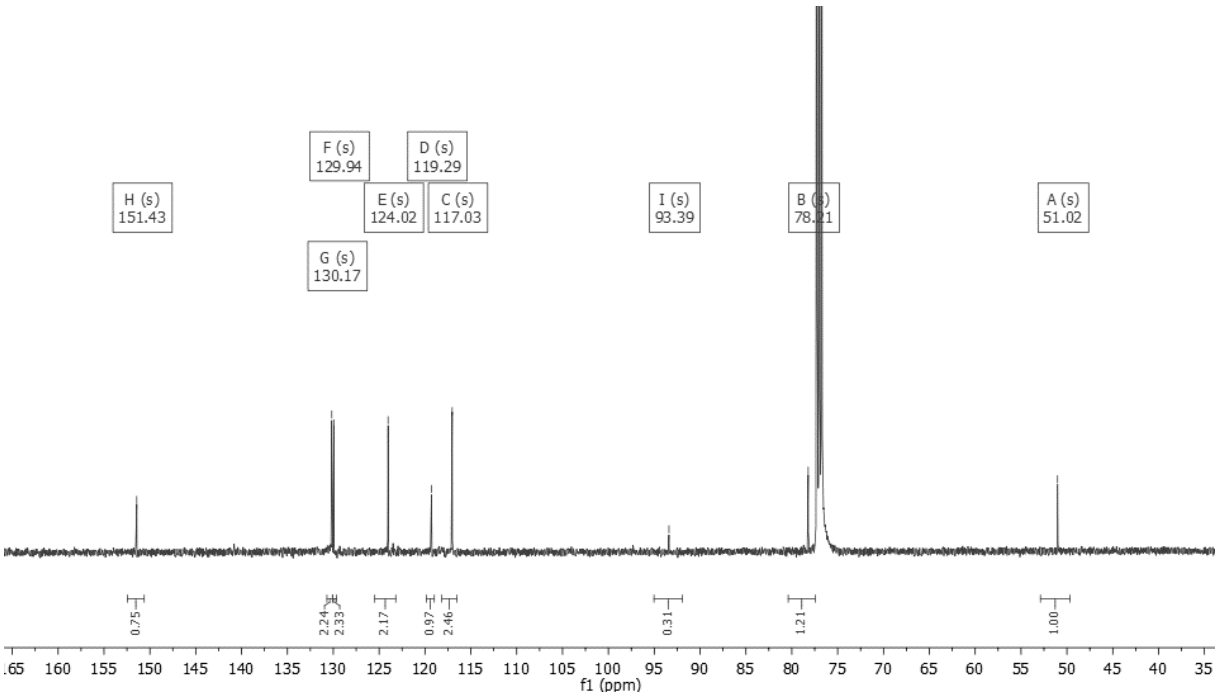


Figure S2 ^{13}C NMR spectrum of **2** in $CDCl_3$.

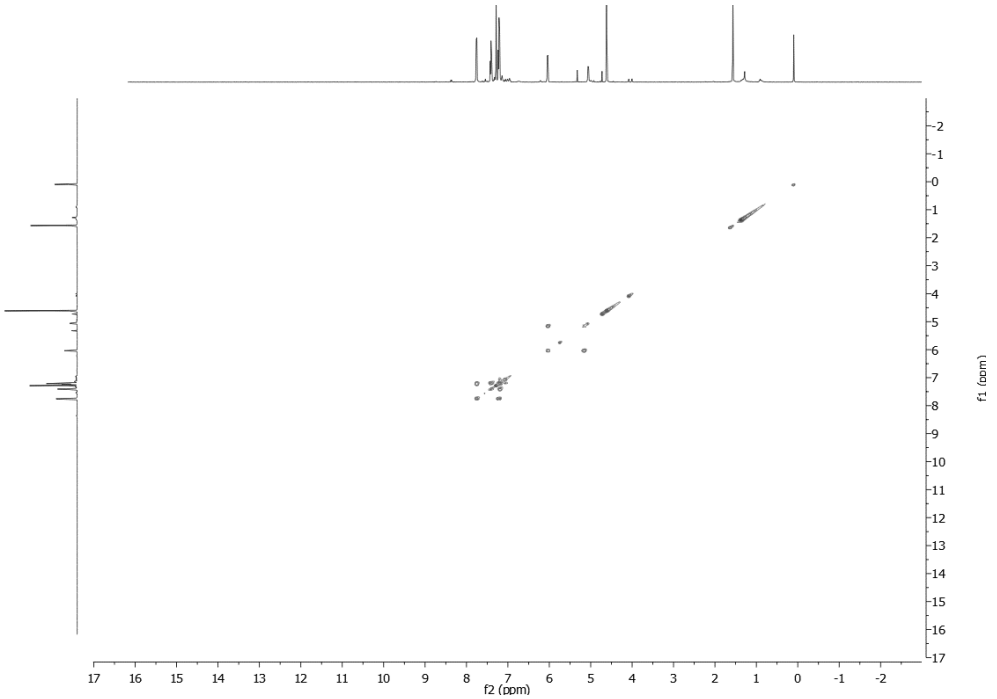


Figure S3 ^{1}H-^{1}H COSY NMR spectrum of **2** in $CDCl_3$.

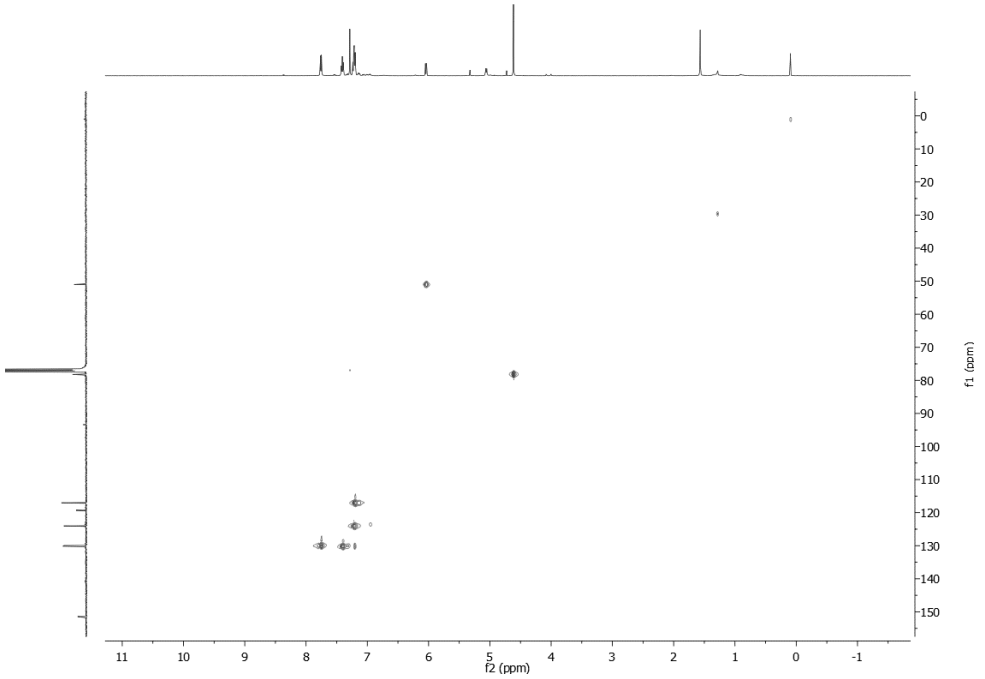


Figure S4 ^{1}H-^{13}C HSQC NMR spectrum of **2** in $CDCl_3$.

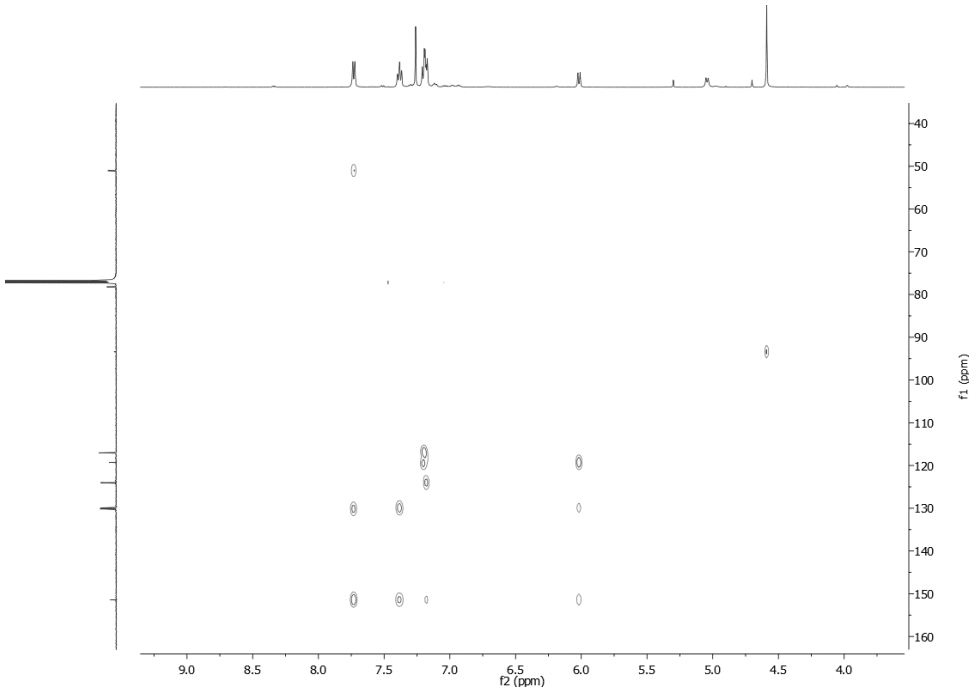


Figure S5 ^{1}H-^{13}C HMBC NMR spectrum of **2** in $CDCl_3$.

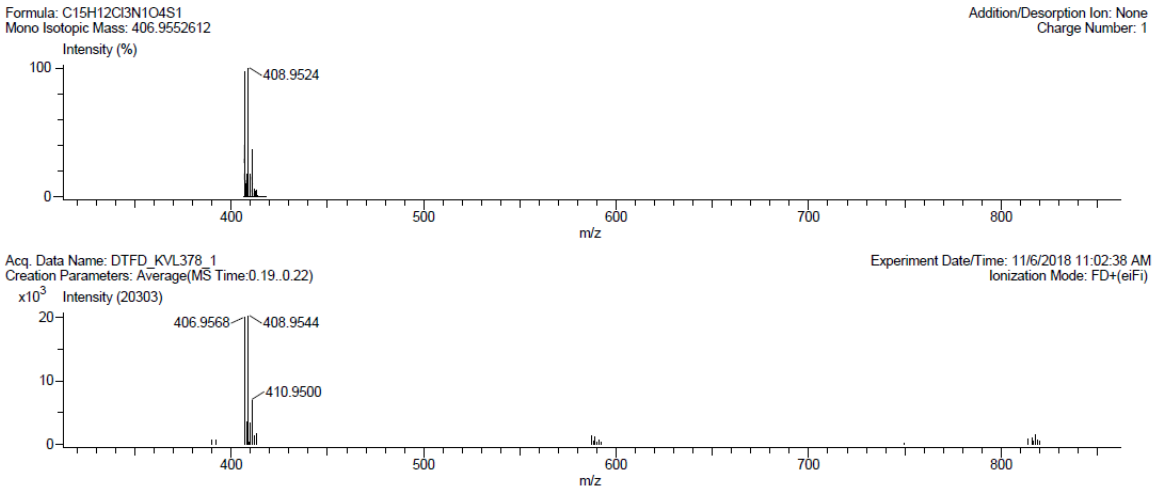
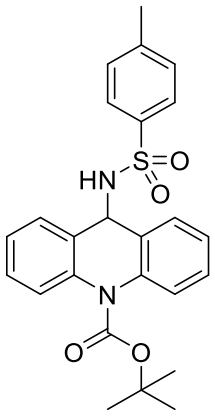


Figure S6 Simulated (top) and experimental (bottom) HRMS-FD^{+} spectrum of **2**.



5-Boc

***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$^+$ (*m*/*z*) calculated for $C_{25}H_{26}N_2O_4S$: 450.1613, found: 450.1597 $[M]^+$.

^{1}H NMR (500 MHz, chloroform-*d*) δ 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}C-APT NMR (126 MHz, chloroform-*d*) δ 151.99 (*C*), 143.28 (*C*), 138.21 (*C*), 137.97 (*C*), 131.56 (*C*), 129.56 (*C*H), 127.50 (*C*H), 126.97 (*C*H), 126.25 (*C*H), 125.30 (*C*H), 125.19 (*C*H), 82.58 (*C*), 53.94 (*C*H), 28.21 (*C*H$_3$), 21.52 (*C*H$_3$).

^{1}H-^{1}H COSY NMR (500 MHz, chloroform-*d*) δ 4.88-5.47, 7.08-7.25, 7.20-7.62, 7.24-7.64.

^{1}H-^{13}C HSQC NMR (500 MHz, chloroform-*d*) δ 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}H-^{13}C HMBC NMR (500 MHz, chloroform-*d*) δ 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.

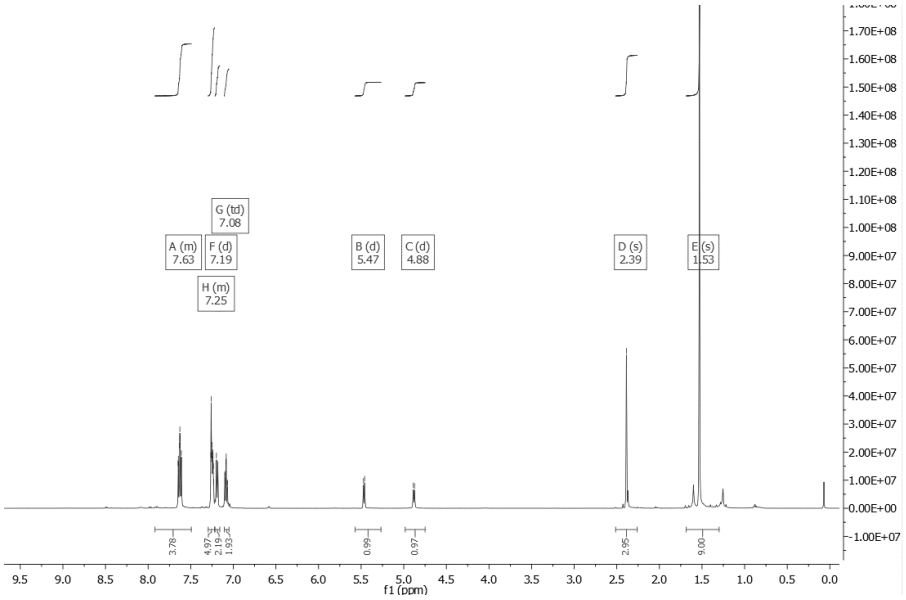


Figure S7 ^{1}H NMR spectrum of **5-Boc** in $CDCl_3$.

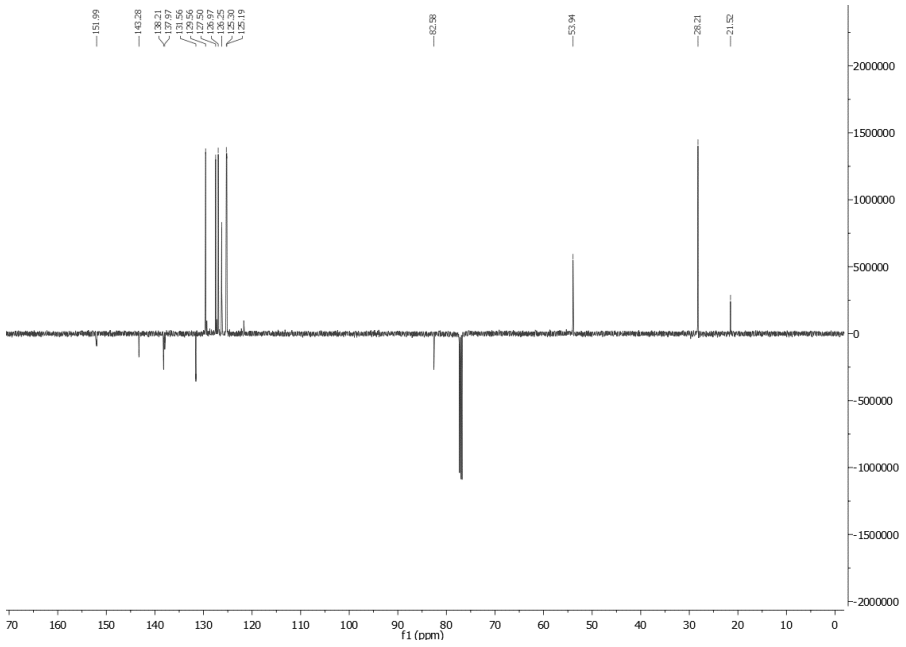


Figure S8 ^{13}C-APT NMR spectrum of **5-Boc** in $CDCl_3$.

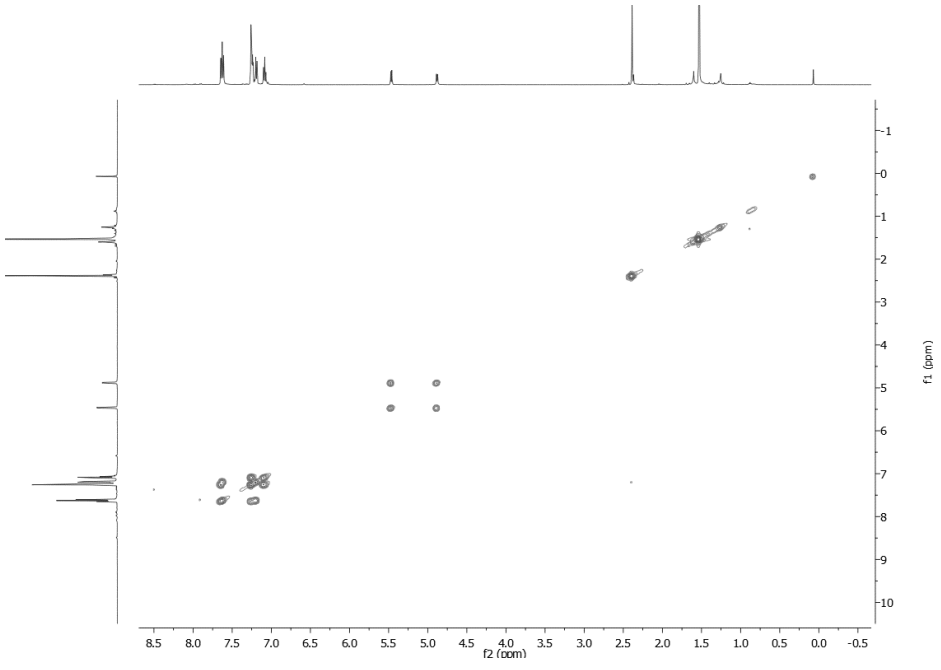


Figure S9 ^{1}H-^{1}H COSY NMR spectrum of **5-Boc** in $CDCl_3$.

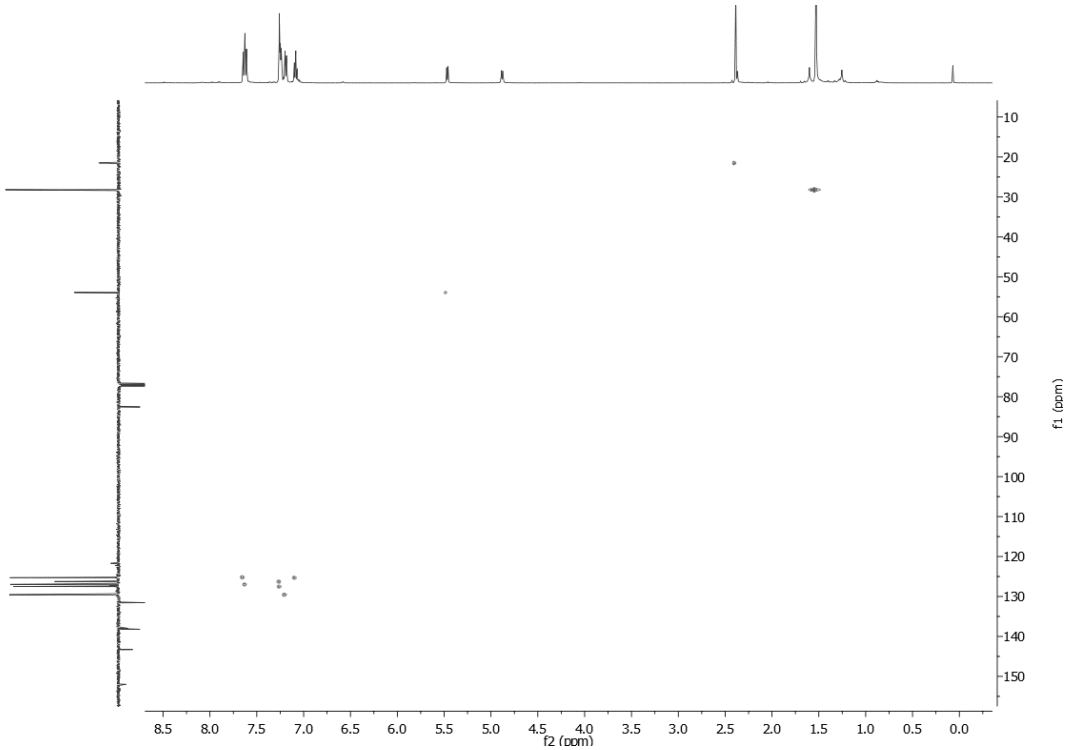


Figure S10 ^{1}H-^{13}C HSQC NMR spectrum of **5-Boc** in $CDCl_3$.

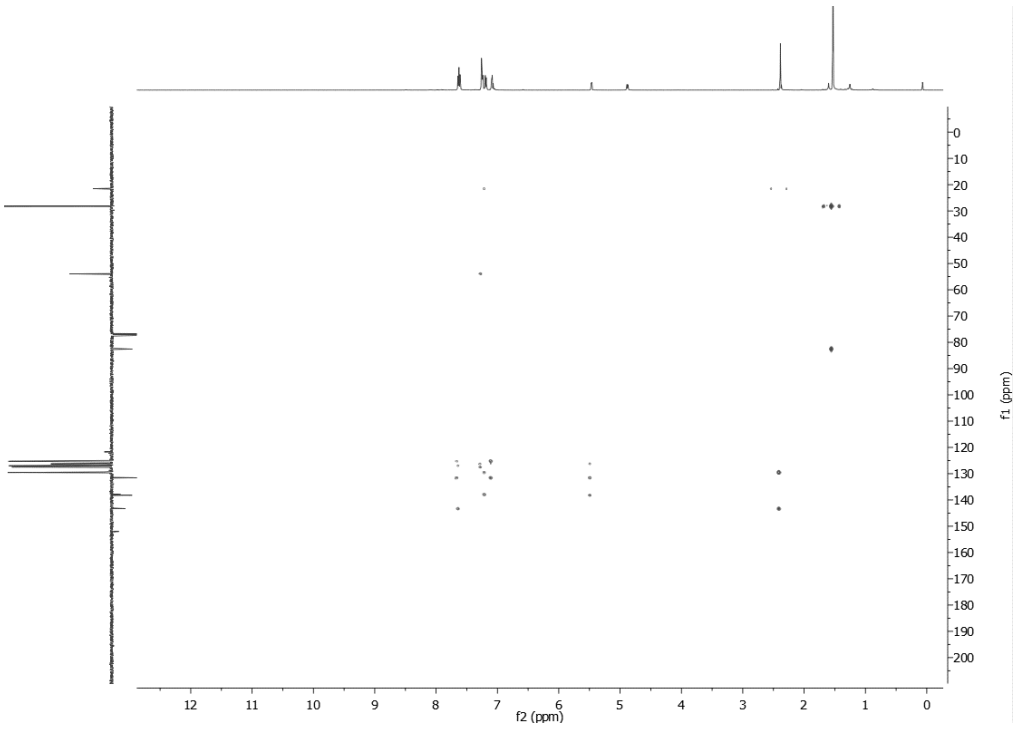


Figure S11 ^{1}H-^{13}C HMBC NMR spectrum of **5-Boc** in $CDCl_3$.

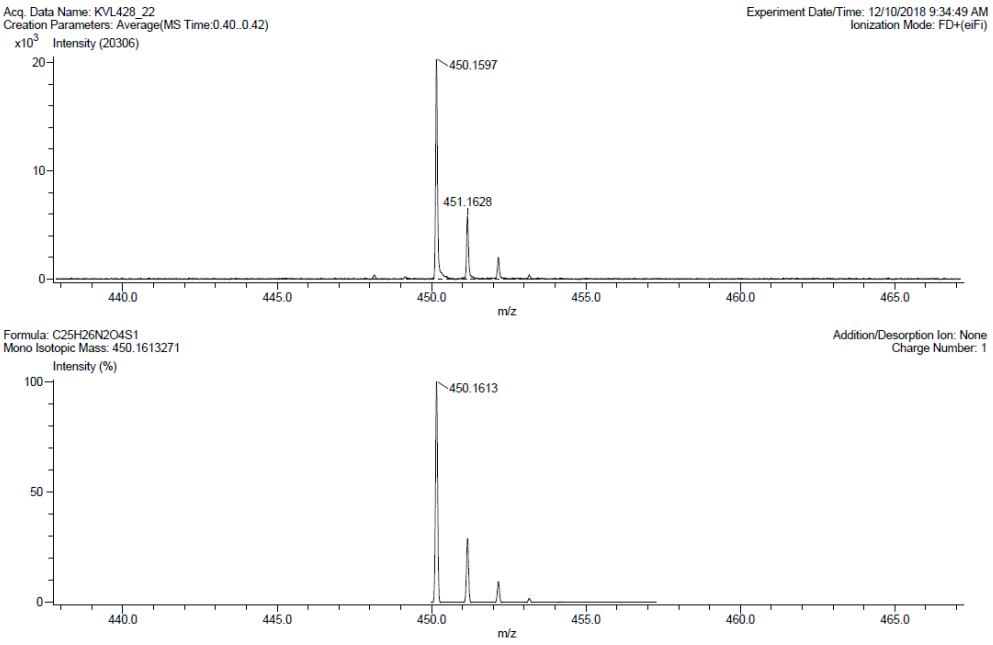


Figure S12 Experimental (top) and simulated (bottom) HRMS-FD$^+$ spectrum of **5-Boc**.

^{1}H NMR spectra of crude reaction mixtures

The crude ^{1}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 S21, Figure S22, Figure S23, Figure S24 and Figure S25. The following labeling code is used: **int** (internal standard), **s** (dihydroheteroanthracene), **n** ($TsNH_2$ or PhINTs), **p** (product), **hq** (1,2,4,5-tetrachloro-*para*-hydroquinone).

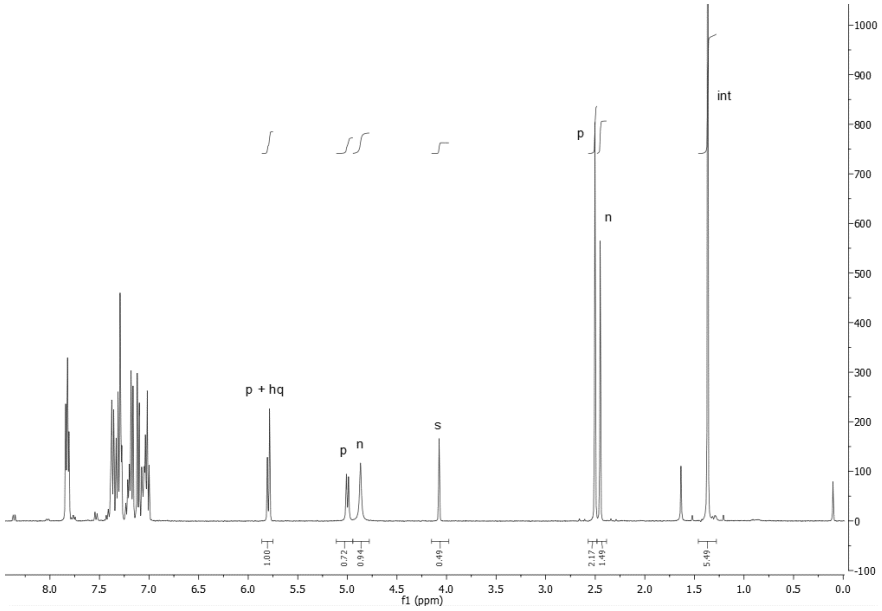


Figure S13 Crude reaction mixture in $CDCl_3$ for the reaction between xanthene, $TsNH_2$ and chloranil to afford **1** under the optimized reaction conditions. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

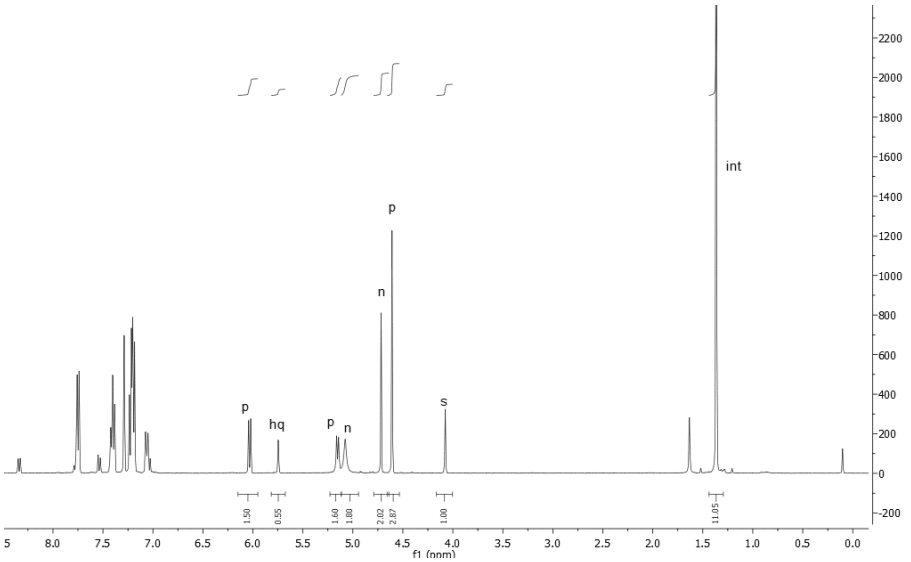


Figure S14 Crude reaction mixture in $CDCl_3$ for the reaction between xanthene, $TcesNH_2$ and chloranil to afford **2** under the optimized reaction conditions. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

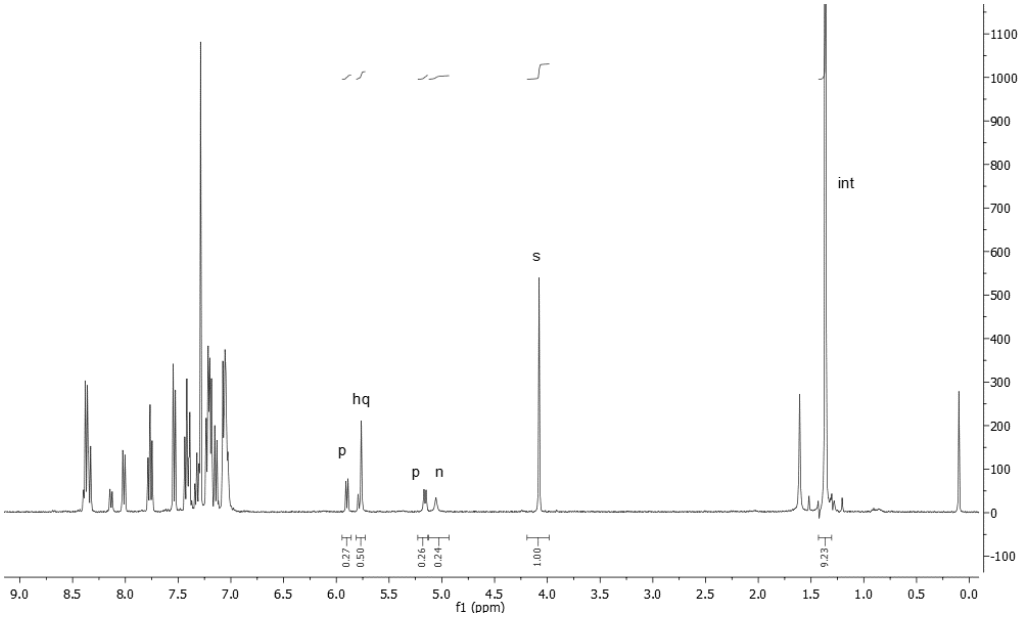


Figure S15 Crude reaction mixture in $CDCl_3$ for the reaction between xanthene, $NsNH_2$ and chloranil to afford **3** under the optimized reaction conditions. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

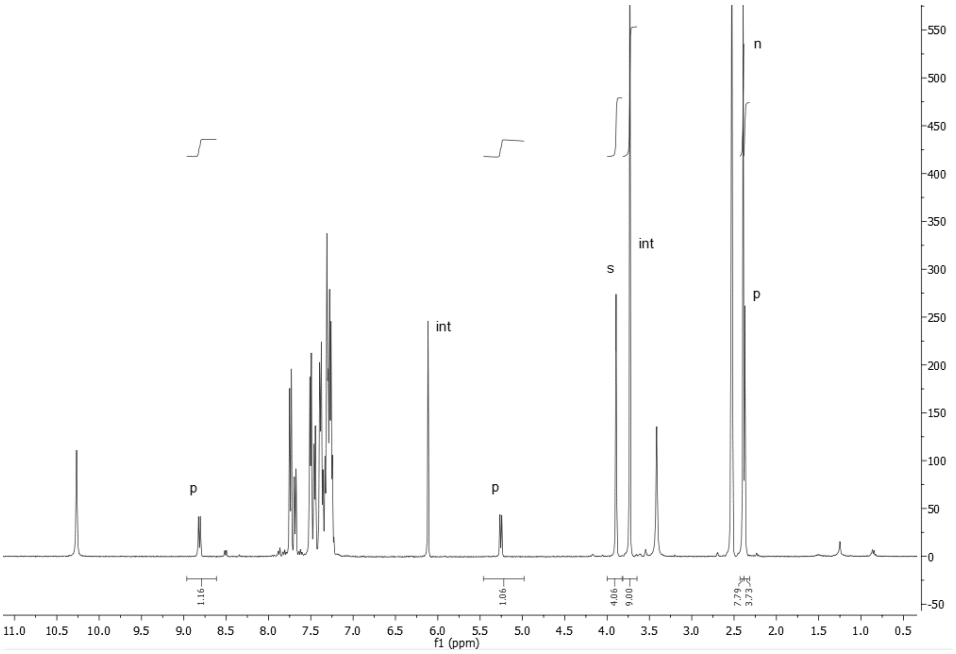


Figure S16 Crude reaction mixture in DMSO-d_6 for the reaction between thioxanthene, $TsNH_2$ and chloranil to afford **6** under the optimized reaction conditions. 0.03 mmol 1,3,5-trimethoxybenzene as internal standard.

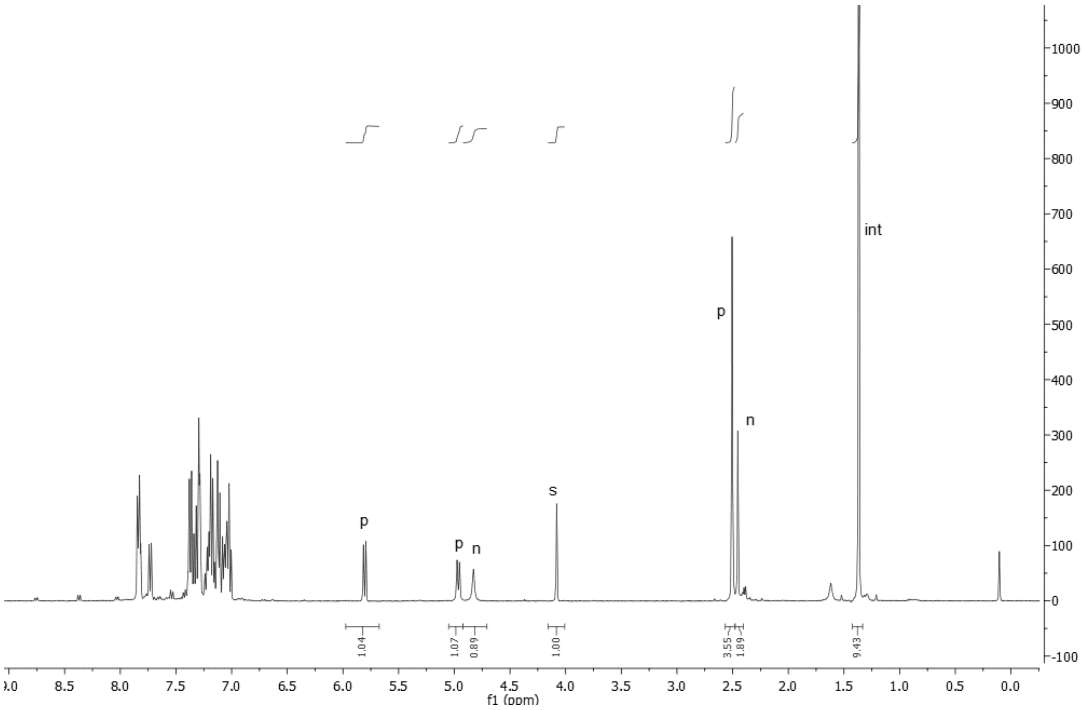


Figure S17 Crude reaction mixture in $CDCl_3$ for the reaction between xanthene and PhINTs to afford **1**. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

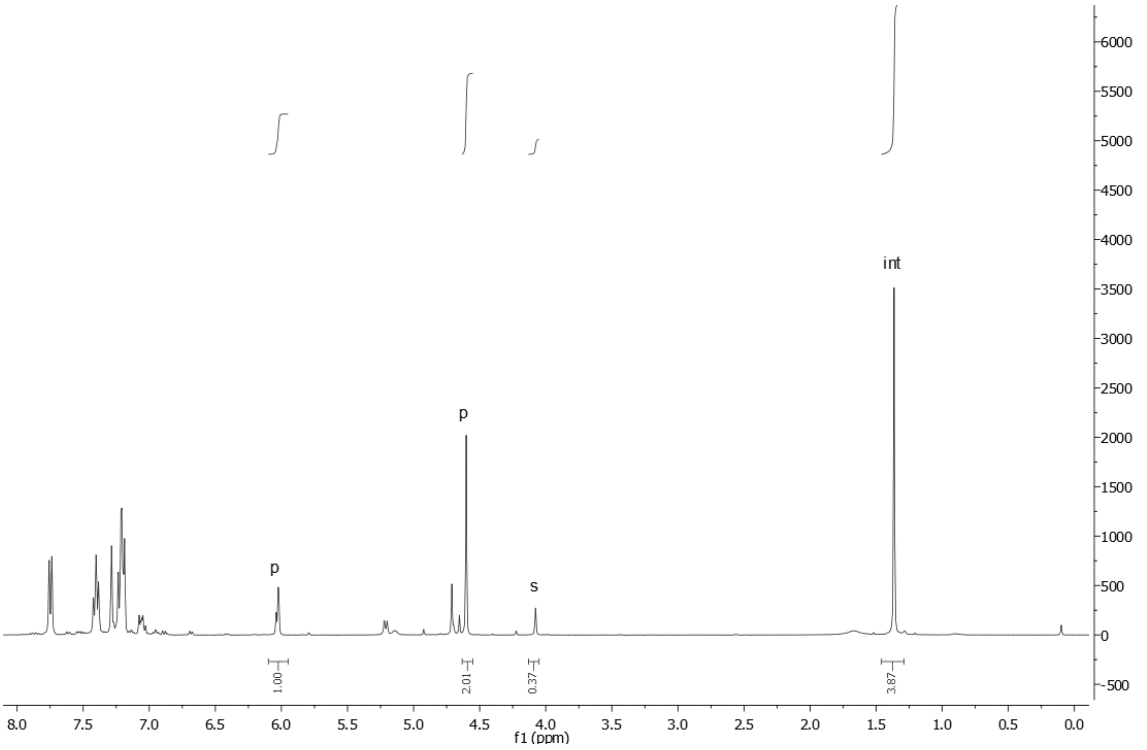


Figure S18 Crude reaction mixture in $CDCl_3$ for the reaction between xanthene and PhINTces to afford **2**. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

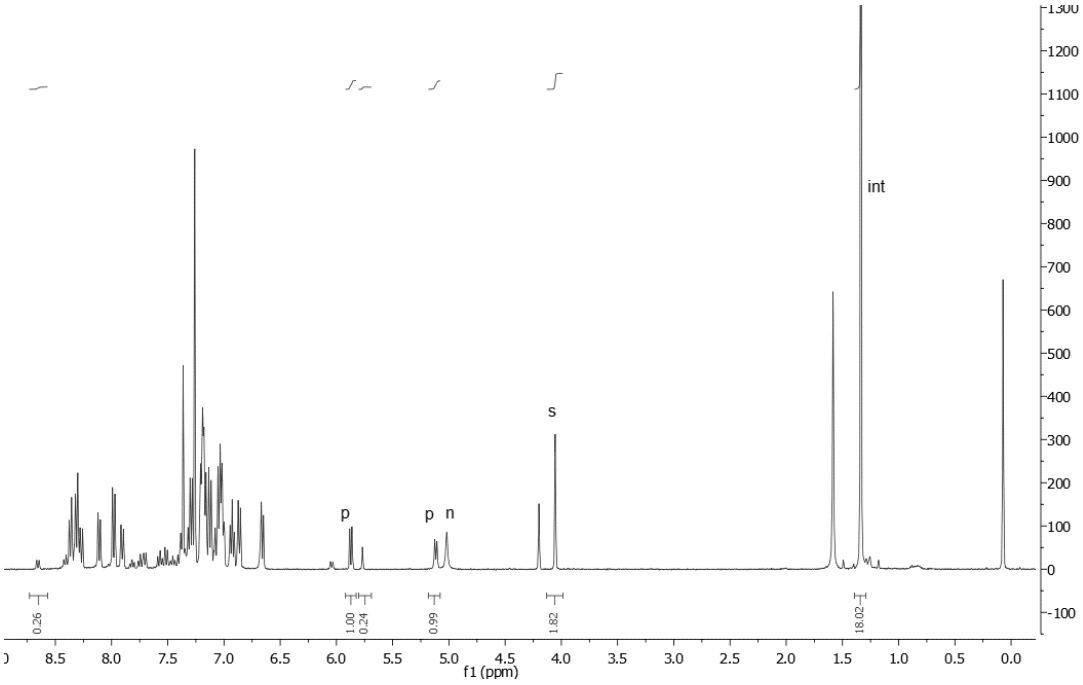


Figure S19 Crude reaction mixture in $CDCl_3$ for the reaction between xanthene and PhINNs to afford **3**. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

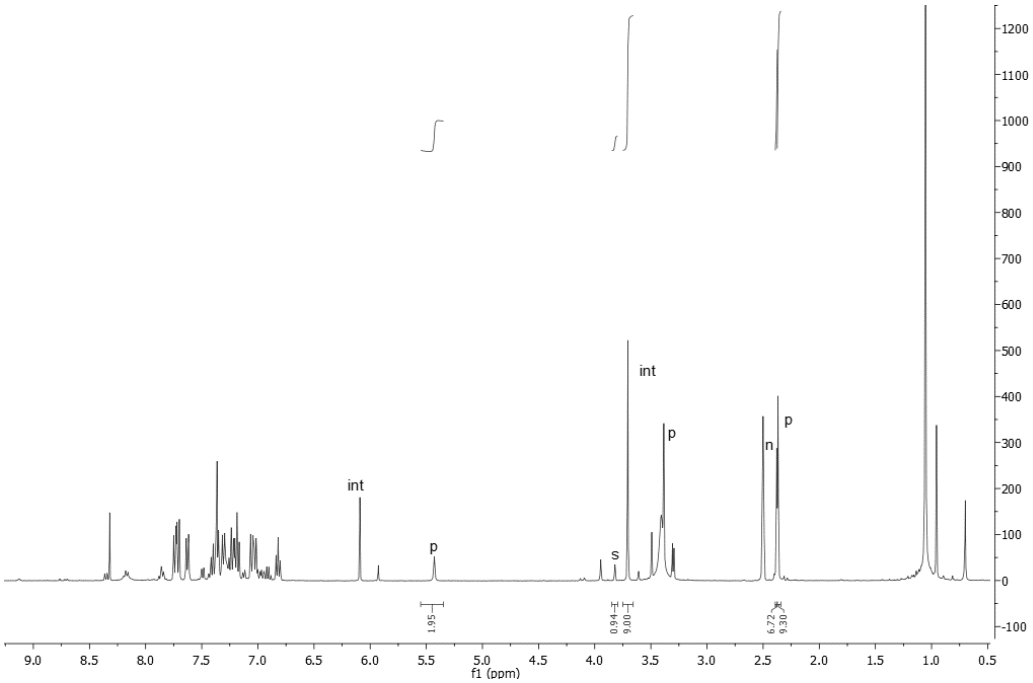


Figure S20 Crude reaction mixture in DMSO-d_6 for the reaction between *N*-methyldihydroacridine, $PhI(OPiv)_2$ and $TsNH_2$ to afford **5-Me**. 0.01 mmol 1,3,5-trimethoxybenzene as internal standard.

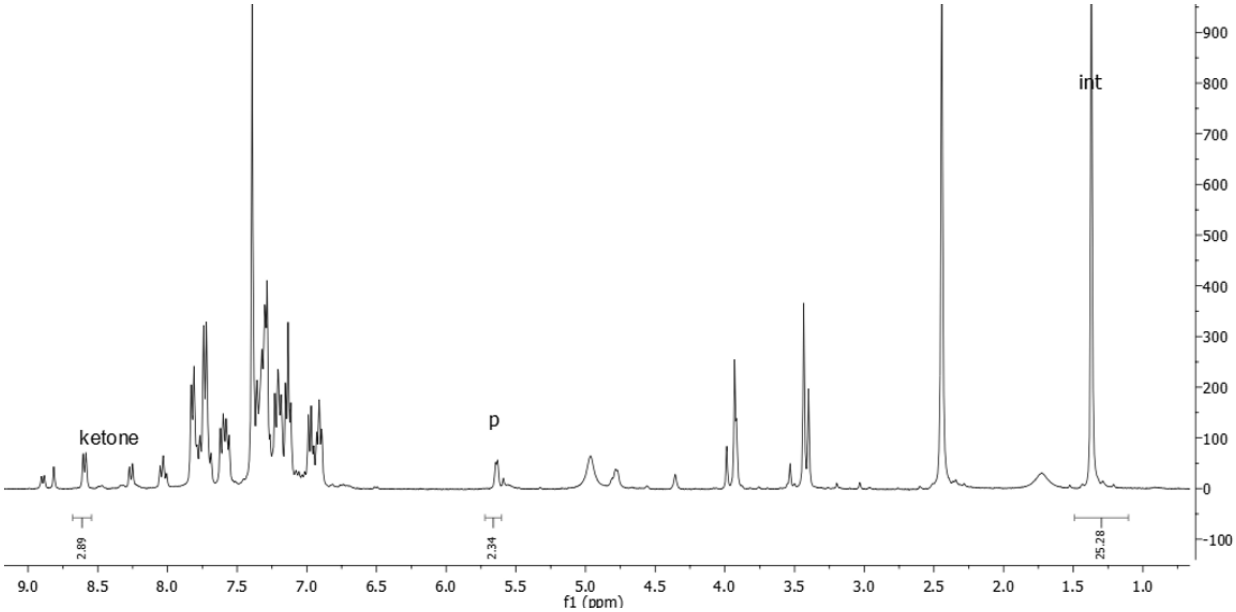


Figure S21 Crude reaction mixture in $CDCl_3$ for the reaction between *N*-methyldihydroacridine and PhINTs after 20 hours to afford **5-Me**. 0.01 mmol 1,3,5-trimethoxybenzene as internal standard. See reference [S20] for the identification of the ketone.

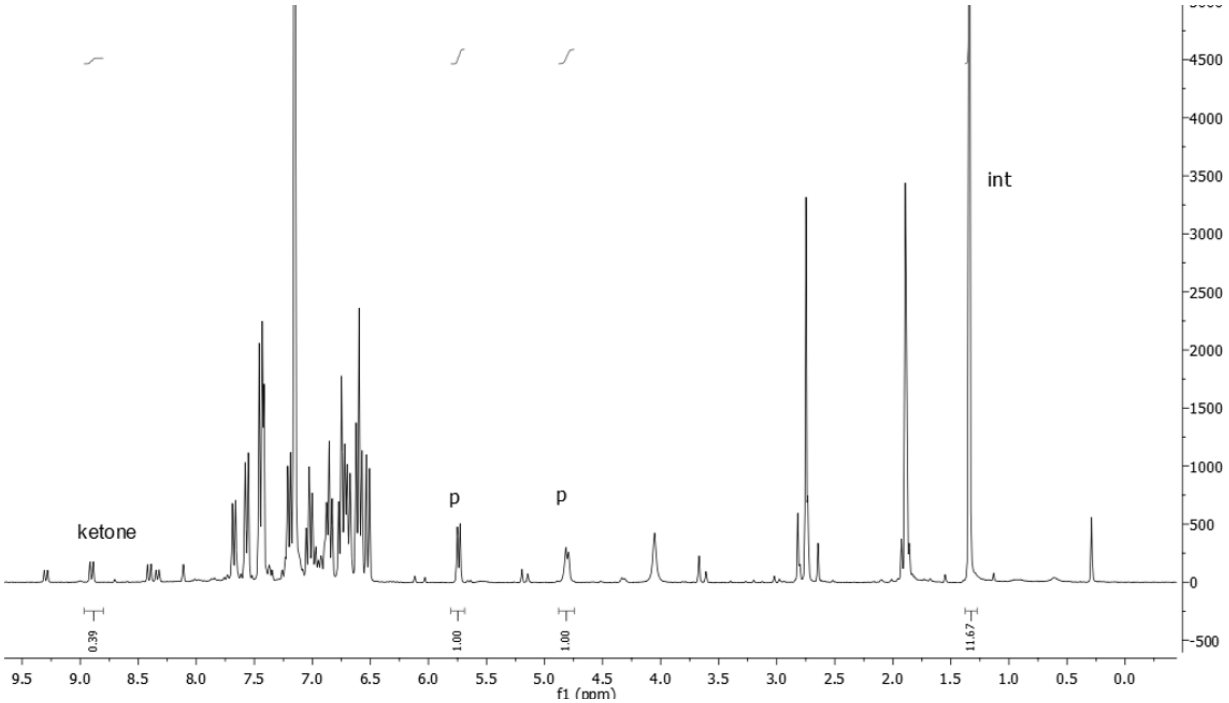


Figure S22 Crude reaction mixture in $CDCl_3$ for the reaction between *N*-methyldihydroacridine and PhINTs after 1 hour to afford **5-Me**. 0.01 mmol 1,3,5-trimethoxybenzene as internal standard. See reference [S20] for the identification of the ketone.

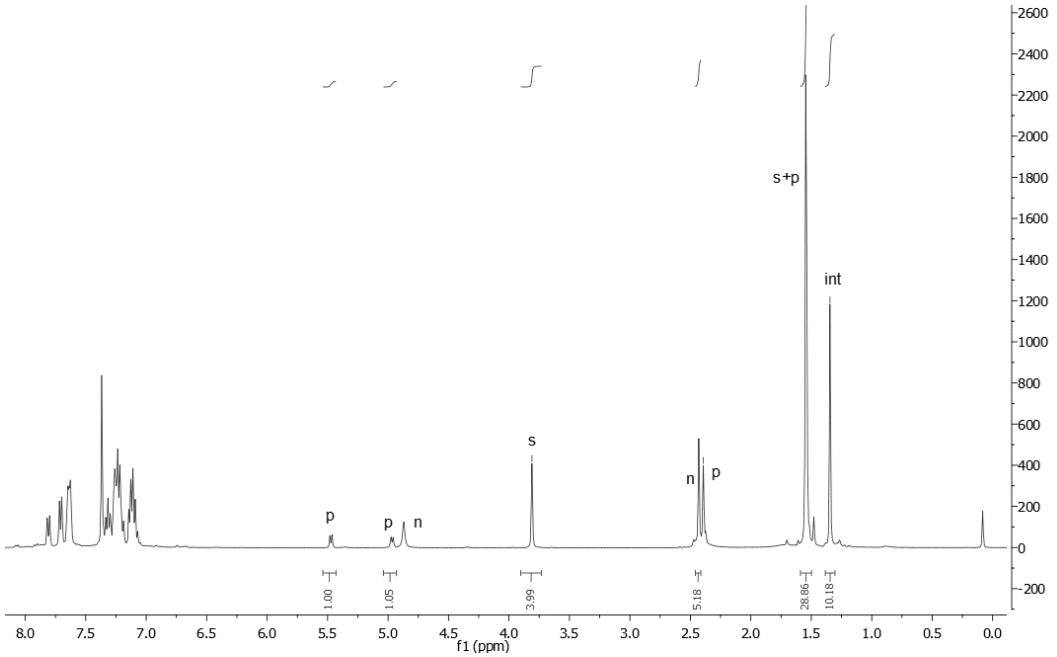


Figure S23 Crude reaction mixture in $CDCl_3$ for the reaction between *N*-Boc-9,10-dihydroacridine and PhINTs to afford **5-Boc**. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

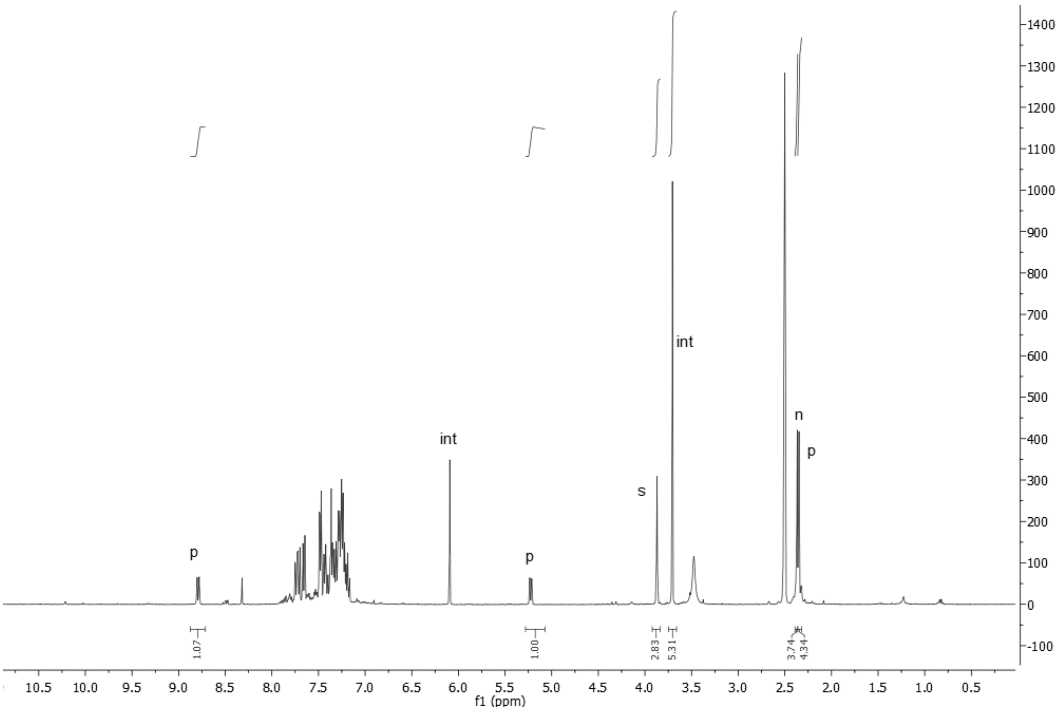


Figure S24 Crude reaction mixture in DMSO-d_6 for the reaction between thioxanthene and PhINTs to afford **6.** 0.01 mmol 1,3,5-trimethoxybenzene as internal standard.

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 $CDCl_3$ from an NMR tube sample. The crystal structure for 1,2,4,5-tetrachloro-*para*-hydroquinone is displayed in Figure S25 and has been reported before in literature.[S21,S22] As can be seen in Figure S25, 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 (λ = 0.71073 Å) and a CMOS Photon 50 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX2 software.[S23] Absorption correction and scaling was performed with SADABS.[S24] The structures were solved using intrinsic phasing with the program SHELXT.[S24] Least-squares refinement was performed with SHELXL-2013[S25] 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 $C_6Cl_4O_2H_2$, Fw = 247.88, monoclinic, *P* $2_1/n$, a = 8.2295(6), b = 4.7783(4), c = 10.3635(8) Å, β = 97.582(2)°, V = 403.96(5) Å^3, *Z* = 2, D_x = 2.038 g/cm^3, μ = 1.410 mm^{-1}. 5205 Reflections were measured. 715 Reflections were unique (R_{int} = 0.0364), of which 638 were observed [I>2σ(I)]. 58 Parameters were refined with 0 restraints. Residual electron density between -0.306 and 0.361 e/Å^3.

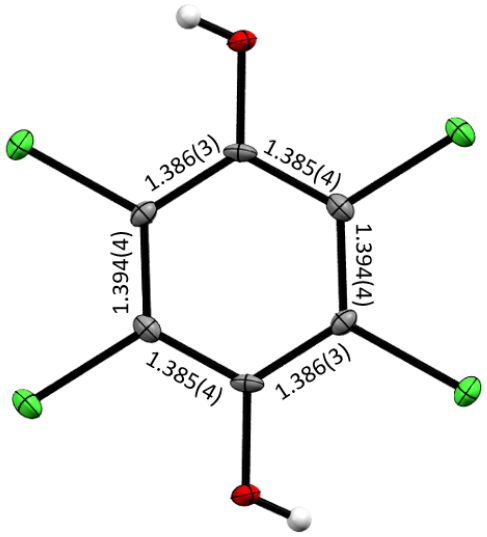


Figure S25 ORTEP plot (set at 50% probability level) of 1,2,4,5-tetrachloro-para-hydroquinone with relevant bond lengths. Green = Cl, grey = C, red = O, white = H.

Determination of the oxidation potentials for different dihydroheteroanthracenes

The oxidation potentials ($E^{o}_{½}$) versus $Fc^{0/+}$ in DCM for various dihydroheteroanthracenes were obtained from differential pulse voltammetry (DPV, Figure S27) and cyclic voltammetry (CV, Figure S26), A schematic overview is shown in Figure S28. The reduction potentials ($E^{o}_{½}$) versus $Fc^{0/+}$ in DCM of chloranil were also measured with CV and found to be −0.43 and −1.15 V vs $Fc^{0/+}$ (Figure S29). 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 $[NBu_4]PF_6$ supporting electrolyte concentration.

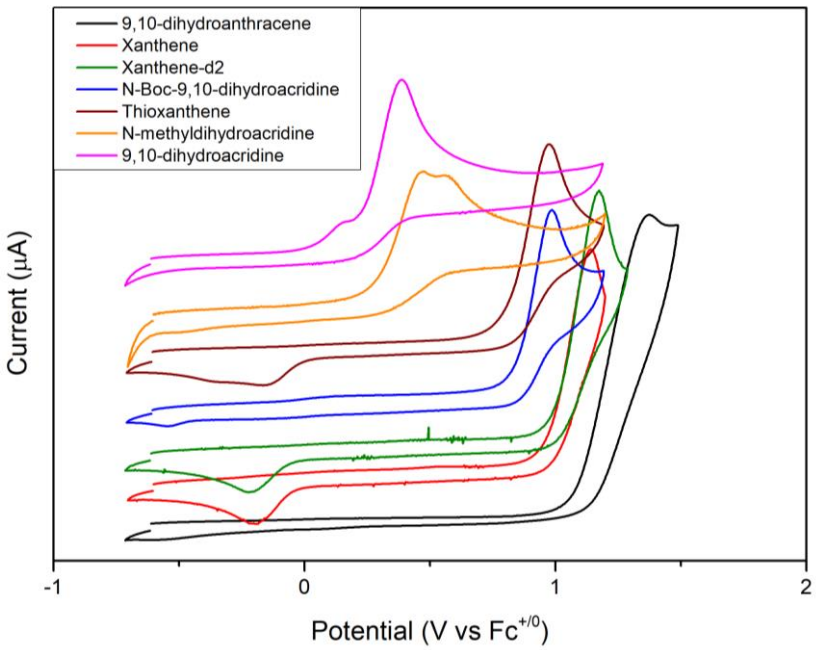


Figure S26 Measured cyclic voltammograms of various dihydroheteroanthracenes measured in DCM.

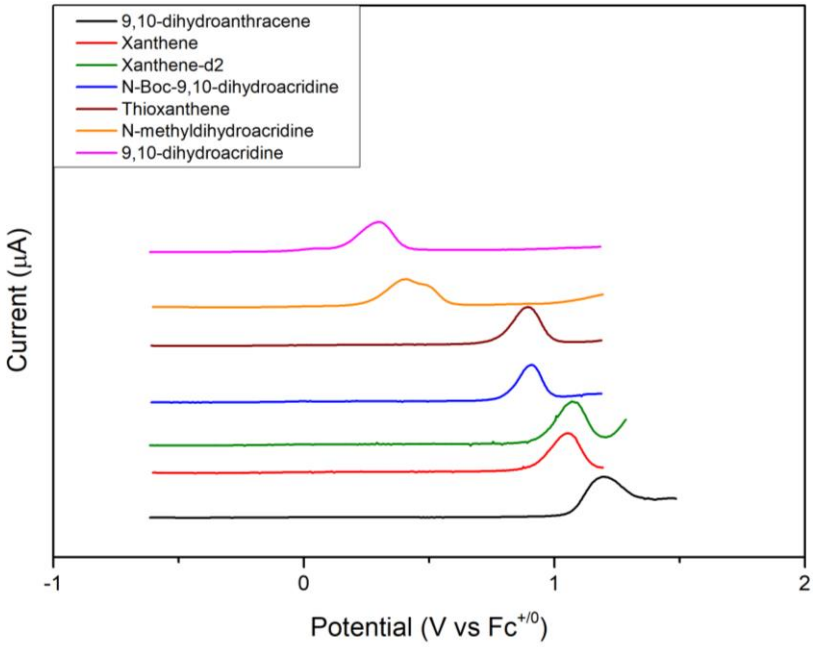


Figure S27 Measured differential pulse voltammograms of various dihydroheteroanthracenes measured in DCM.

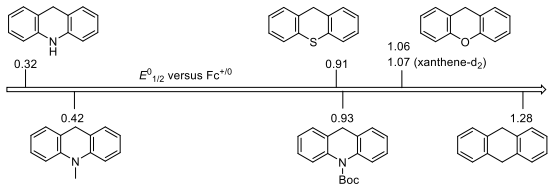


Figure S28 $E^{o}_{½}$ versus $Fc^{+/0}$ for various dihydroheteroanthracenes in DCM, obtained from DPV measurements.

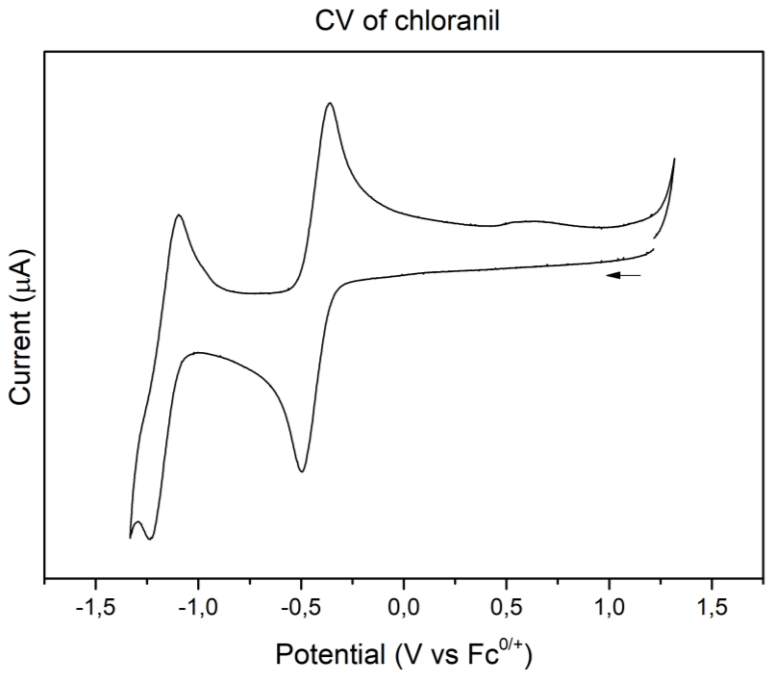


Figure S29 Measured cyclic voltammogram of chloranil measured in DCM.

Reaction between xanthene and chloranil

In order to gain insight in the possible formation of the xanthylium 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 S30) and under argon (Figure S31). As can be seen, no formation of the xanthylium ion can be observed. However, xanthone[S26] (4% versus 0.6%), xanthydrol[S19] (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 xanthylium cation and the 2,3,5,6-tetrachloro-4-hydroxy-phenoxyl anion (which are in equilibrium with xanthene and chloranil) are formed as transient species that subsequently react with water as the nucleophile.

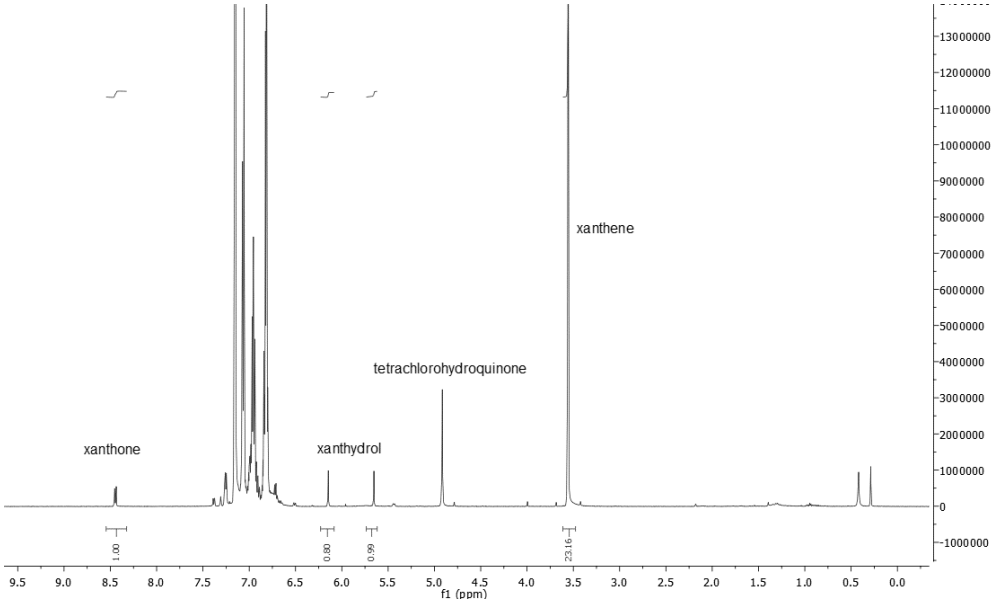


Figure S30 Crude reaction mixture of the reaction between xanthene and chloranil after 2 hours at 60 °C under aerobic conditions.

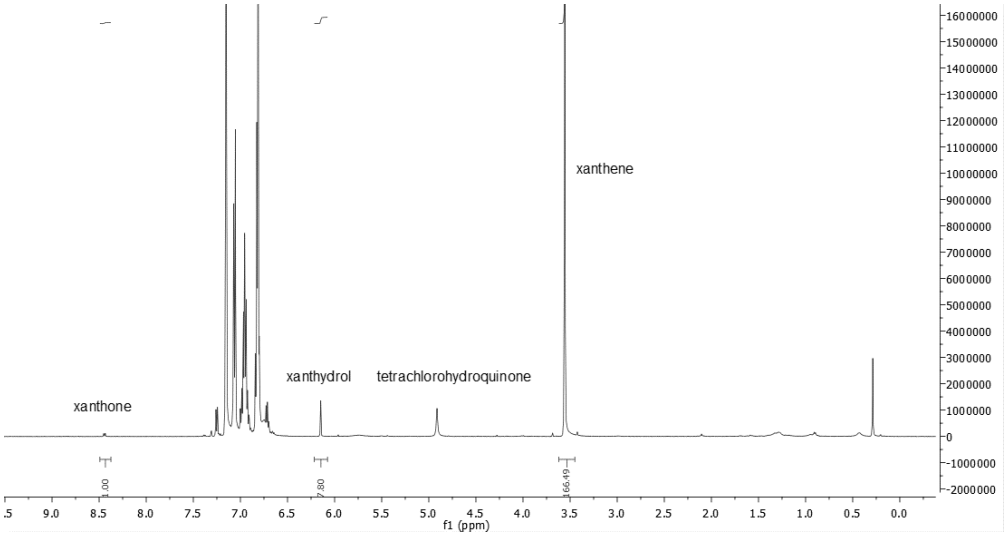
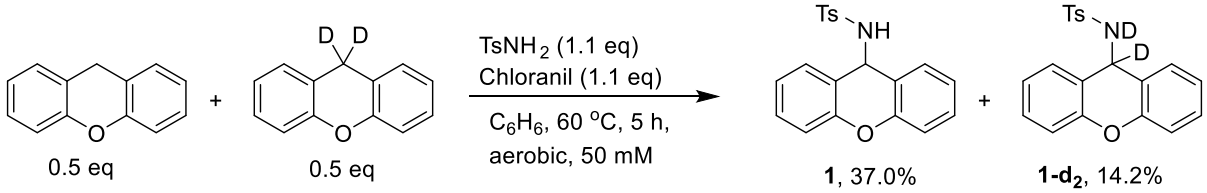


Figure S31 Crude reaction mixture of the reaction between xanthene and chloranil after 2 hours at 60 °C under argon.

Measurement of the kinetic isotope effect

The kinetic isotope effect (KIE) for the reaction between xanthene, chloranil and $TsNH_2$ was determined from an intermolecular competition experiment between xanthene (0.5 eq) and xanthene-d_2 (0.5 eq) under the standard reaction conditions (Scheme S1 and Figure S32) 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_2 was converted to **1-d$_2$**.



Scheme S1 Reaction for the determination of the intermolecular KIE between $TsNH_2$, chloranil, xanthene and xanthene-d_2.

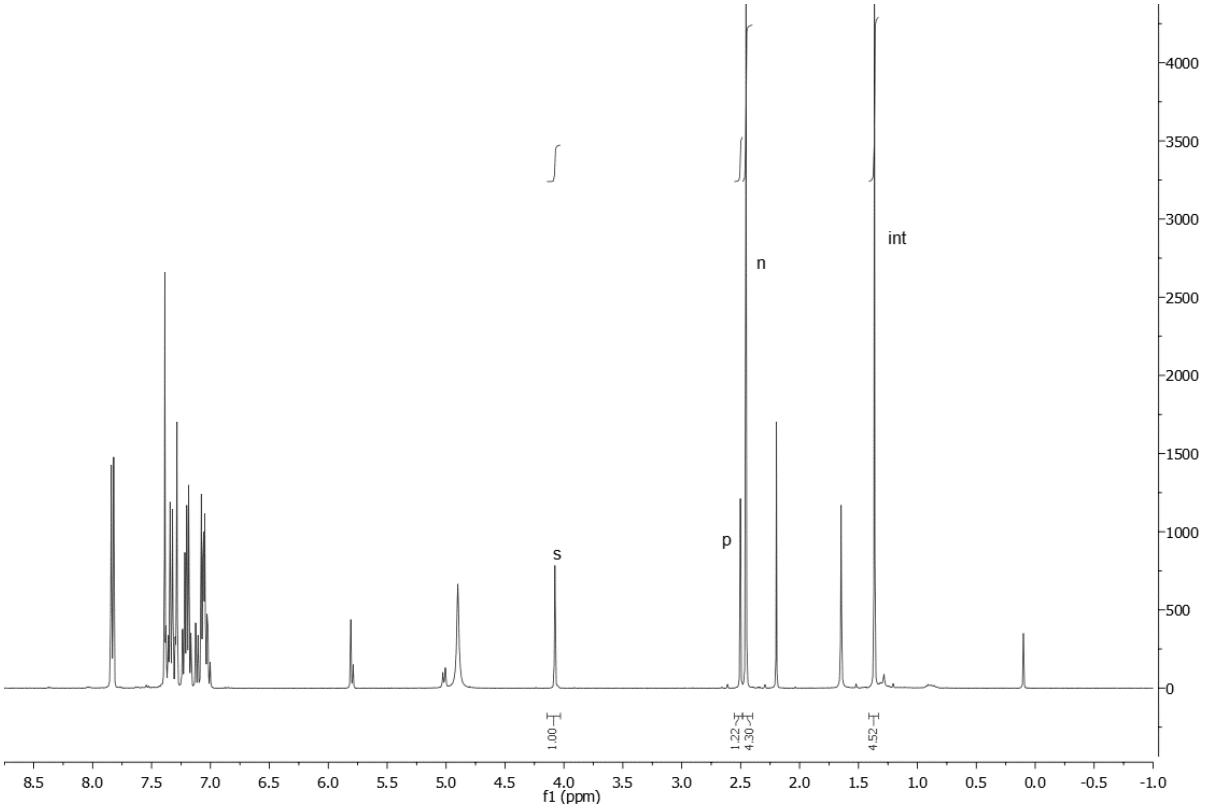
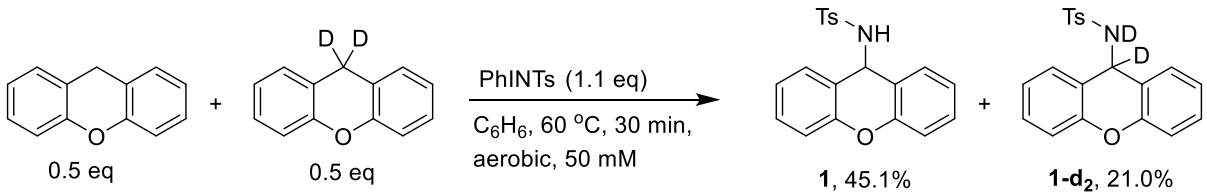


Figure S32 Crude reaction mixture in $CDCl_3$ for the reaction between $TsNH_2$, chloranil, xanthene and xanthene-d_2 to afford **1** and **1-d_2**. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

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 S33) 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.

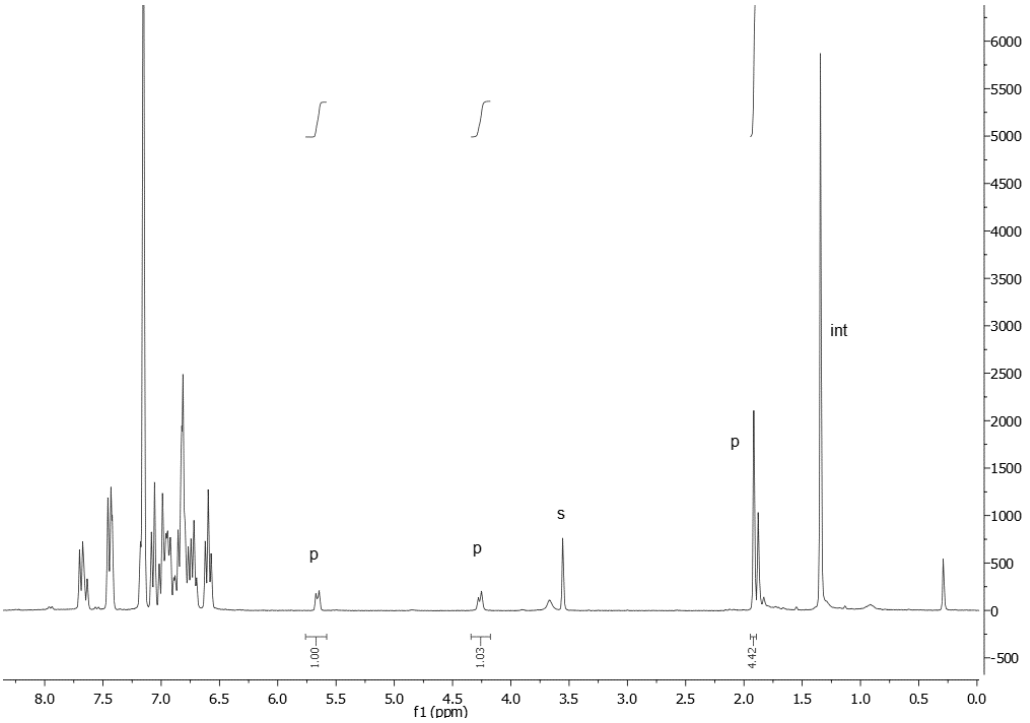


Figure S33 Crude reaction mixture in C_6D_6 for the reaction between PhINTs, xanthene and xanthene-d_2 to afford **1** and **1-d_2**. 0.01 mmol 1,3,5-tris-(tert-butyl)benzene as internal standard.

Time profile for the reaction between xanthene, $TsNH_2$ and chloranil

The reaction between xanthene, $TsNH_2$ and chloranil was monitored over time in an NMR tube in presence of 1,3,5-tris-(tert-butyl)benzene as an internal standard to obtain more insight in the formation of xanthone and the imine of **1**. As can be seen in Figure S34 and Figure S35, xanthene conversion goes paired with formation of equimolar amounts of **1** and tetrachlorohydroquinone. Over the whole course of the reaction, linearly increasing formation of xanthone is observed (up to 2% after 20 hours). Formation of the imine of **1** starts after 9 hours and slowly increases to 0.3%. The formation of xanthone is not changed by the presence of the imine of **1**, thereby confirming that xanthone formation is caused by the reaction of water with the *in situ* formed xanthylium cation, and not (or for a minor part) by hydrolysis of the imine of **1**.

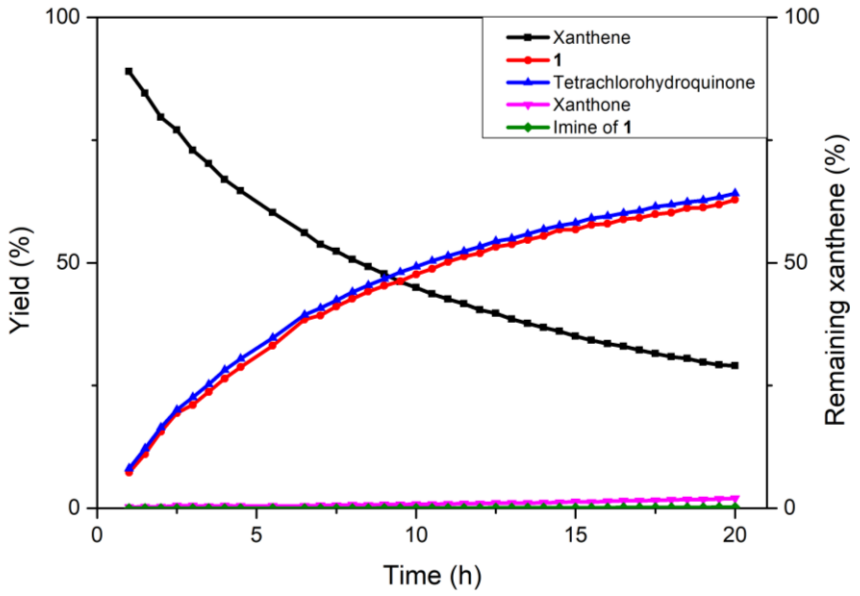


Figure S34 Formation of **1**, tetrachlorohydroquinone, xanthone imine of **1** and remaining xanthene over time in the reaction of xanthene with $TsNH_2$ and chloranil under standard conditions. The reaction was performed in an NMR tube.

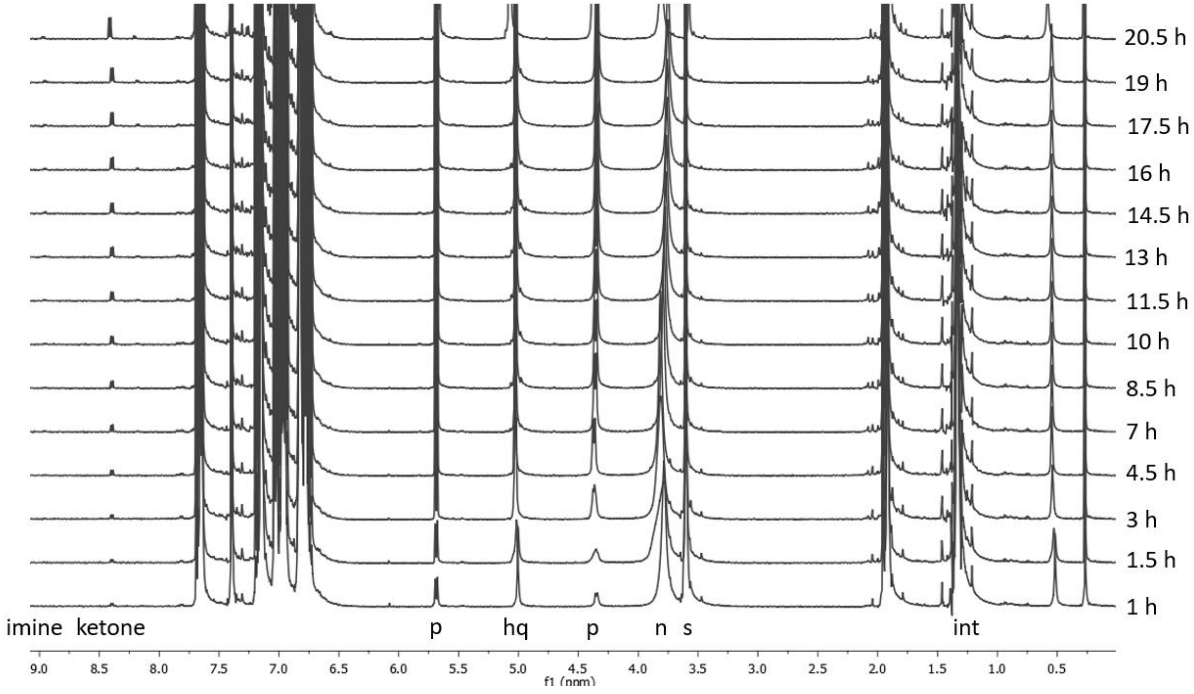
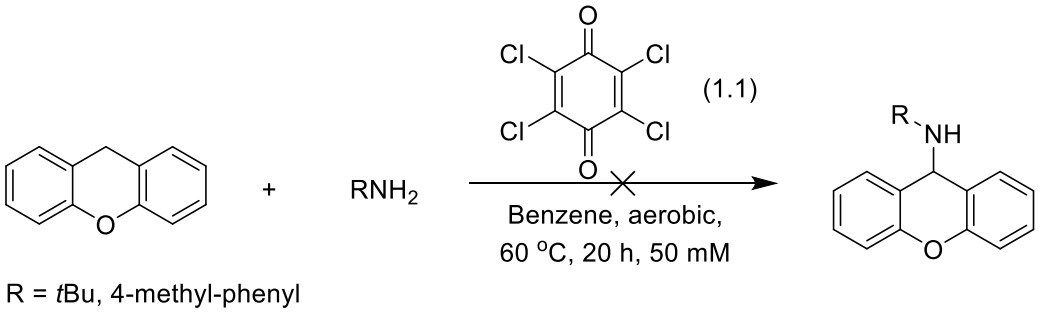


Figure S35 Selected spectra showing the formation **1**, tetrachlorohydroquinone, xanthone imine of **1** and remaining xanthene over time in the reaction of xanthene with $TsNH_2$ and chloranil under standard conditions. The reaction was performed in an NMR tube.

Additional experiments on the amination of hydrocarbons

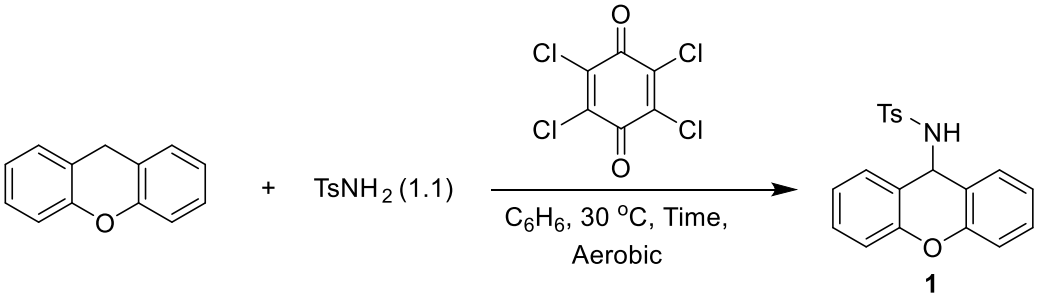
Amination of xanthene with chloranil and *t*$BuNH_2$ or 4-methyl-aniline as the electrophile (Scheme S3) did not afford the desired products because *t*$BuNH_2$ and 4-methyl-aniline were immediately oxidized by chloranil.

Additional optimization 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).



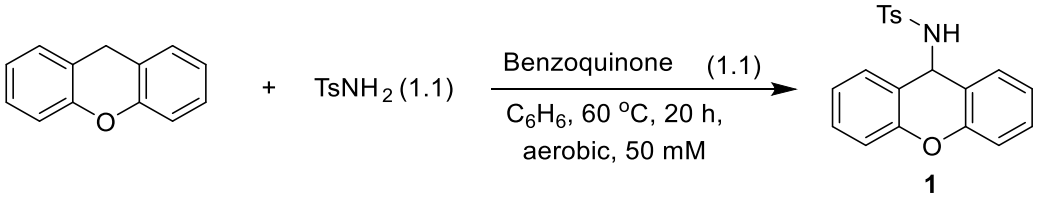
Scheme S3 Attempted amination of xanthene with chloranil and *t*$BuNH_2$ or 4-methyl-aniline.

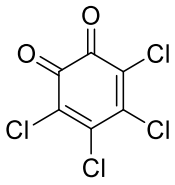
Table S1 Additional optimization parameters for the amination of xanthene with $TsNH_2$ and chloranil. [a] Reaction under argon atmosphere. Yields calculated using ^1H NMR with 1,3,5-tris-(tert-butyl)benzene as an internal standard.



Entry	Equiv. chloranil	Concentration (mM)	Time (h)	Yield
1[a]	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 $TsNH_2$. Yields calculated using ^1H NMR with 1,3,5-tris-(tert-butyl)benzene as an internal standard.



Entry	Benzoquinone	By-products	Yield
1		Imine of **1** (16%) and xanthone (20%)	41%

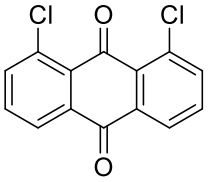
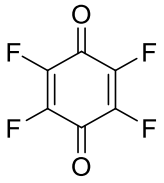
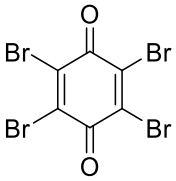
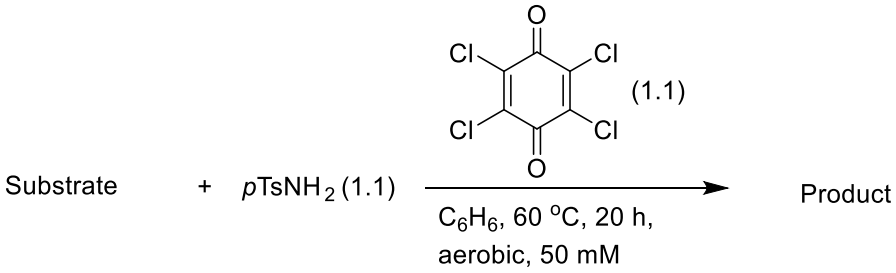
2		-	0%
3		Unknown	27%
4		Xanthone (10%)	37%

Table S3 Screening of additional hydrocarbons in the amination reaction with $TsNH_2$ and chloranil.



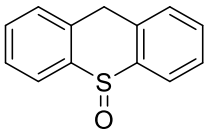
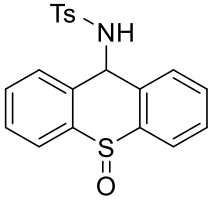
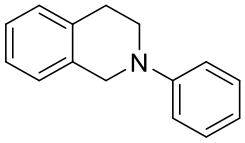
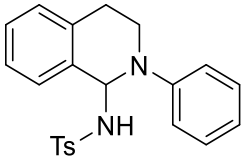
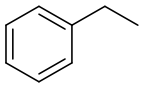
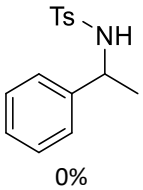
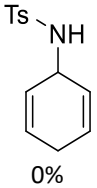
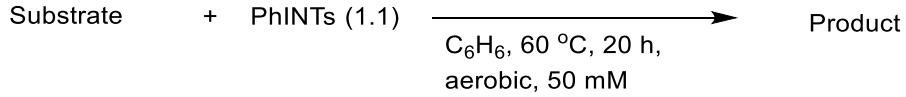
Entry	Substrate	Envisioned product and yield	By-product
1		 0%	-
2		 0%	86% conversion to unknown products
3		 0%	-
4		 0%	-

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



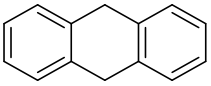
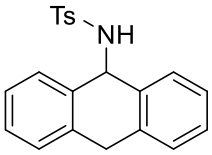
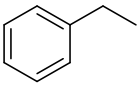
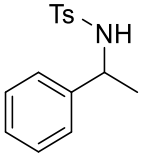
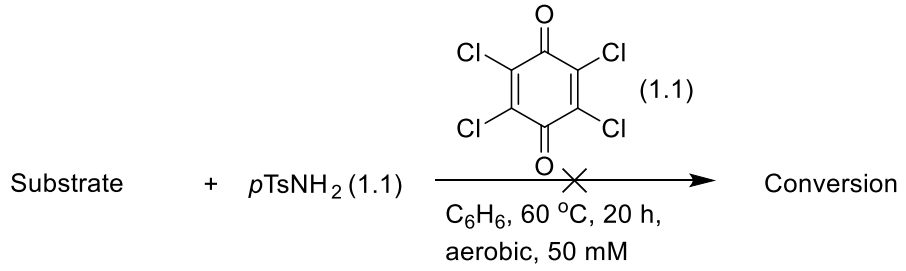
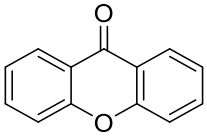
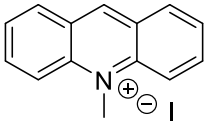
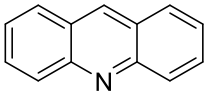
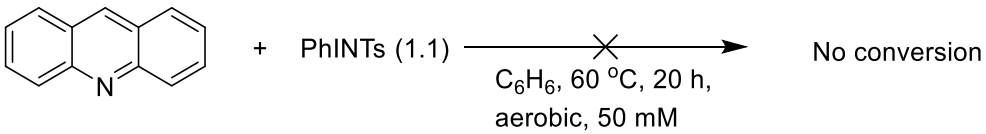
Entry	Substrate	Envisioned product and yield
1		 0%
2		 0%

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_6H_6 was used. [c] In absence of chloranil no conversion was observed.



Entry	Substrate	Conversion
1[a]		0%
2[b,c]		39% to unknown products
3		0%



Scheme S4 Control reaction between acridine and PhINTs.

Computational studies

DFT geometry optimizations were performed using TURBOMOLE[S27] coupled to the PQS Baker optimizer[S28,S29] via the BOpt package[S30] at the B3LYP[S31,S32]/def2-TZVP[S33,S34] level of theory (m4 grid), on full models with implicit solvation by benzene (COSMO[S35], ε = 2.27), using Grimme's version 3 (disp3, "zero damping") dispersion corrections.[S36] 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 characterized 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^{-1}) of all intermediates can be found below.

Xanthene

-361666.3992 kcal mol^{-1}

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^{-1}

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^{-1}

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^{-1}

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^{-1}

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^{-1}

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^{-1}

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^{-1}

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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