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Mechanochemistry-driven solvent-free synthesis of biologically relevant diversely substituted 2-amino-1,4-naphthoquinones

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We, herein, present a practical and straightforward alternative mechanochemistry-driven strategy for the regioselective amination of biologically promising 1,4-naphthoquinone scaffolds to access functionalised 2-amino-1,4-naphthoquinones under additive- and solvent-free conditions. The notable features of the present method are solvent-free synthesis, avoidance of any additive and heating, broad substrate scope, good yields, shorter reaction times (in minutes), reusability of the solid surface, gram-scale synthesis, a clean reaction profile, and operational simplicity. In addition, a series of new selenylated derivatives of some selected 2-amino-1,4-naphthoquinones were prepared as part of an extended synthetic application.

1 Introduction

1,4-Naphthoquinones represent an important sub-class of the quinonoid family and are widely available in naturally occurring compounds exhibiting various biological activities.[1] Hence, chemists have devoted significant efforts to the synthesis of a large variety of 1,4-naphthoquinone derivatives, possessing a wide range of biological, pharmacological, and agrochemical properties, along with a broad spectrum of their applications.[2–4] A literature survey also revealed such potential applications shown by a handful of 2-amino-1,4-naphthoquinone derivatives.[5] Fig. 1 offers some representative examples of such compounds.[6]

In recent times, synthetic organic chemists have been motivated to functionalise the 2-amino-1,4-naphthoquinone moiety to access certain targeted molecular scaffolds of interest,[5] and so, operationally simple and practical methods to have diverse 2-amino-1,4-naphthoquinones as the starting templates are warranted. During our literature survey, we encountered a handful of major synthetic reports for synthesising 2-amino-1,4-naphthoquinones. In 2008, Liu and co-workers[7a] synthesised 2-amino-1,4-naphthoquinone derivatives by irradiating a mixture of 1,4-naphthoquinones and amines with ultrasound using molecular iodine as a catalyst in ethanol. In 2011, Lisboa and co-workers[7b] reported Cu(I)-catalysed C–H functionalisation of 1,4-naphthoquinones by oxidative coupling with anilines to synthesise these compounds under heating in acetic acid. Later, in 2021, Dong et al.[7c] developed a room temperature-based protocol using potassium tert-butoxide as a basic catalyst, and Bhuyan and Baishya[7d] reported a bismuth

trichloride-catalysed protocol for a similar transformation in the next year. Very recently, advanced synthetic protocols by fruitful applications of electrochemical cells[7e] and visible light[7f] have been demonstrated for the green synthesis of 2-amino-1,4-naphthoquinones. Although these methods possess certain merits of their own, they are still associated with some other shortcomings such as using metal catalysts, heating, and long reaction times in hours (0.5–4 h).

As part of our green chemistry-driven organic synthesis,[8] we were thus thrilled to develop a straightforward and practical strategy as an alternative synthetic method for the regioselective amination of naphthalene-1,4-dione scaffolds with a wide array of aromatic and aliphatic amines to synthesise functionalised 2-amino-1,4-naphthoquinones. Accordingly, we have been successful in unearthing a mechanochemical strategy for the synthesis of a diverse series of 2-(alkyl/aryl-amino)naphthalene-1,4-diones (**3**) upon high-speed ball-milling of 1,4-naphthoquinones (**1**) with a variety of amine derivatives (**2**) using basic alumina as a surface without any additives under neat conditions (Scheme 1). The significant advances of this alternative protocol are solvent-free synthesis, avoidance of any additive and heating, broad substrate scope, good yields, shorter reaction times (in minutes), reusability of the solid surface, gram-scale synthesis, a clean reaction profile, and operational simplicity. Mechanochemical synthesis and the application of a high-speed ball-mill as a green energy tool are now well-regarded in organic synthesis.[9]

2 Results and discussion

We initiated our study with our model reaction between 1,4-naphthoquinone (**1**; 0.5 mmol) and aniline (**2a**; 0.5 mmol) upon simply grinding the mixture of the reactants under neat conditions in a ball-mill using 7 stainless steel balls and neutral

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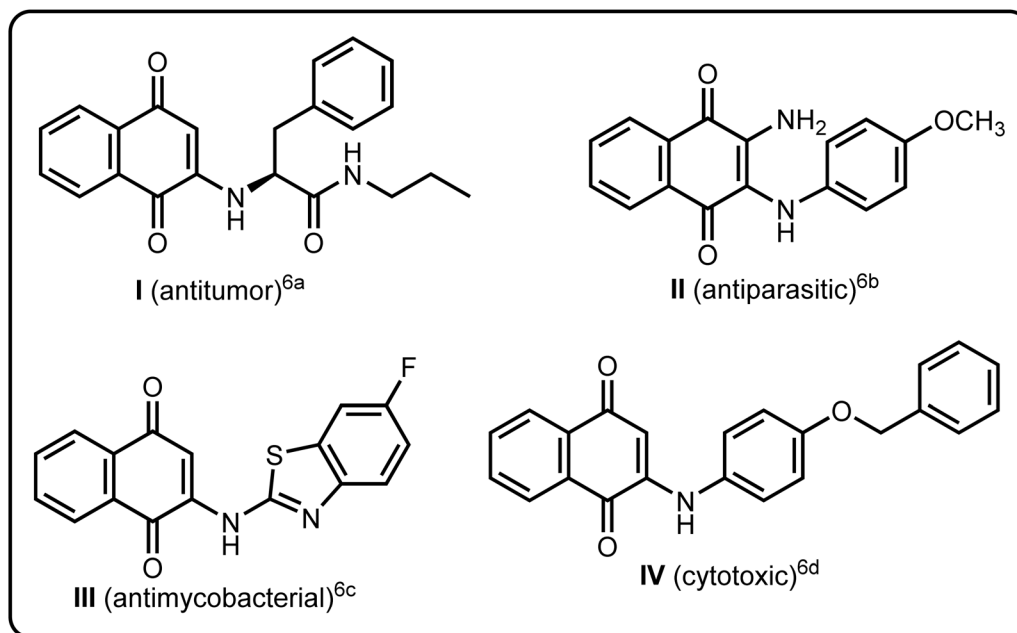
Fig. 1 Representative examples of a few naturally occurring bioactive 1,4-naphthoquinones.[6]

alumina (1.5 g) as a surface at 550 rpm for 60 min when we could not isolate the desired product (Table 1, entry 1). Then, we performed three trial reactions with the model entry using basic alumina (1.5 g) as a surface under the same ball-milling conditions for 5, 10 and 15 min, and delightfully isolated our desired product, 2-(phenylamino)naphthalene-1,4-dione (**3a**), respectively, in 80%, 92%, and 88% yields (Table 1, entries 2–4). Compound **3a** was fully characterised by its detailed spectral (¹H NMR, ¹³C NMR and HRMS) studies. However, the model reaction, when performed using acidic alumina (1.5 g) as a surface under the same ball-milling conditions, furnished a much lower yield of 28% within 10 min (Table 1, entry 5). Silica and sodium chloride (NaCl) were also found to be ineffi-cient surfaces for the transformation (Table 1, entries 6 and 7). Next, we checked the effect of the number of balls and frequency of rotation (rpm) of the balls within the ball-mill machine with the model reaction using basic alumina surface (Table 1, entries 8–11). We also performed the model reaction

by stirring the reactants dissolved in various solvents (namely, acetonitrile, dimethylsulfoxide, water, methanol, and ethanol; 1.5 mL) without any additives under ambient conditions for 240 min to validate the impact of mechanochemical grinding (Table 1, entries 12–16). We isolated compound **3a** only when performing the model reaction in water, methanol, and ethanol with respective yields of 18%, 26% and 24% (Table 1, entries 14–16). We also carried out the model reaction using basic alumina in catalytic amounts (Table 1, entries 17–20) in the presence of methanol and ethanol as the solvents under stirring at ambient temperature for 720 min, where no remarkable improvement was noticed. Besides, we checked the model reaction in a methanol medium in the absence (Table 1, entry 21) or presence of basic alumina (Table 1, entry 22) upon stirring at ambient temperature for 720 min in an oxygen atmosphere, and we did not observe any noticeable improvement in the product yield, thereby justifying the use of high-speed ball-mill for this transformation (Table 1, entry 3).
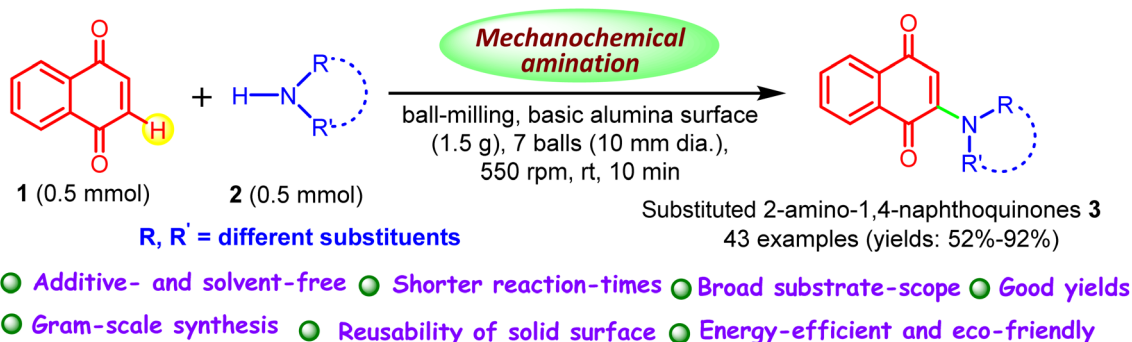
Scheme 1 Mechanochemical synthesis of functionalised 2-amino-1,4-naphthoquinones.

Table 1 Optimisation of reaction conditions[a,b]

1 (0.5 mmol)   +   2a (0.5 mmol)   → (experimental conditions) →   3a
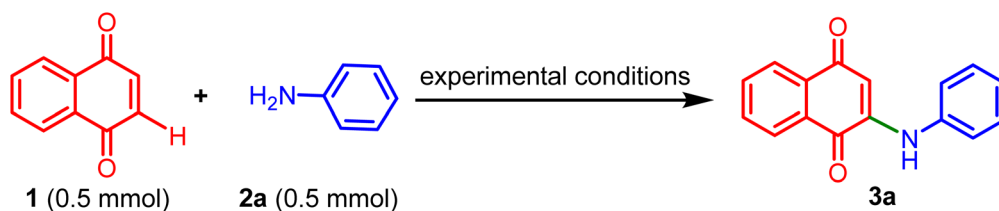
Entry	Solvent (1.5 mL)	Surface (1.5 g)	Condition	No. of balls/rpm	Time (min)	Yield[a,b] (%)
1	—	Neutral alumina	Ball-milling	7/550	60	—
2	—	Basic alumina	Ball-milling	7/550	5	80
3	**—**	**Basic alumina**	**Ball-milling**	**7/550**	**10**	**92**
4	—	Basic alumina	Ball-milling	7/550	15	88
5	—	Acidic alumina	Ball-milling	7/550	10	28
6	—	Silica	Ball-milling	7/550	10	Trace
7	—	NaCl	Ball-milling	7/550	10	Trace
8	—	Basic alumina	Ball-milling	7/600	10	88
9	—	Basic alumina	Ball-milling	7/450	10	60
10	—	Basic alumina	Ball-milling	8/550	10	84
11	—	Basic alumina	Ball-milling	6/550	10	68
12	CH_3CN	—	Stirring at rt	—	240	Trace
13	DMSO	—	Stirring at rt	—	240	Trace
14	H_2O	—	Stirring at rt	—	240	18
15	MeOH	—	Stirring at rt	—	240	26
16	EtOH	—	Stirring at rt	—	240	24
17	MeOH	Basic alumina (20 mol%)	Stirring at rt	—	720	30
18	EtOH	Basic alumina (20 mol%)	Stirring at rt	—	720	26
19	MeOH	Basic alumina (50 mol%)	Stirring at rt	—	720	38
20	MeOH	Basic alumina (1 equiv.)	Stirring at rt	—	720	32
21[c]	MeOH	—	Stirring at rt	—	720	32
22[c]	MeOH	Basic alumina (50 mol%)	Stirring at rt	—	720	38
23[d]	—	Basic alumina	Ball milling	7/550	10	92

[a] Reaction conditions: a mixture of 1,4-naphthoquinone (**1**; 0.5 mmol) and aniline (**2a**; 0.5 mmol) was reacted either under ball milling (using a 25 mL of stainless-steel jar and balls of 10 mm in diameter, and rotation in an inverted direction with a break of 5 s at 2.5 min interval) in the absence or presence of 1.5 g of varying surfaces (namely, neutral alumina, acidic alumina, basic alumina and silica), or under stirring in 1.5 mL of varying solvents (namely, acetonitrile, dimethylsulfoxide, methanol, ethanol and water) at room temperature (25–28 °C). [b] Isolated yields. [c] Under an O_2 atmosphere. [d] Using a tungsten carbide jar and balls. The pH was measured (1.5 g of acidic/neutral/basic alumina suspended in 5 mL of distilled water, followed by stirring for 10 min and then leaving undisturbed for 1 h) for acidic alumina as 6.13, neutral alumina as 7.07, and basic alumina as 8.01.
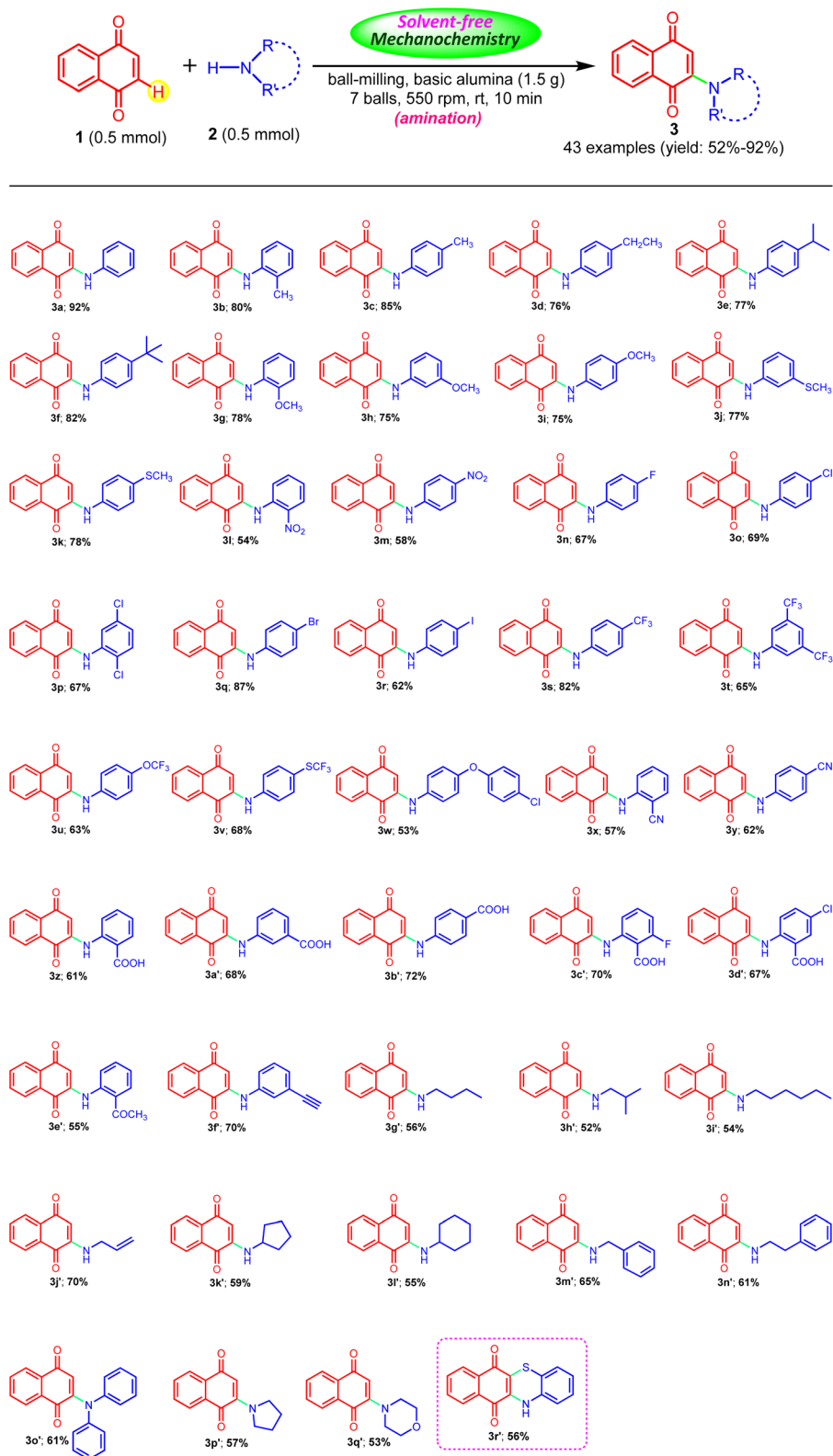
Eventually, we arrived at the most suited mechanochemical reaction conditions for this transformation as to grind the mixture of **1** (0.5 mmol; 1.0 equiv.) and aniline (**2a**; 0.5 mmol; 1.0 equiv.) in a ball-mill using basic alumina (1.5 g) as the solid surface, 7 stainless steel balls (10 mm in diameter) milled for just 10 min (rotation in an inverted direction with a 5 s break at 2.5 min interval) at 550 rpm to isolate **3a** with 92% yield (Table 1, entry 3). We also conducted a control experiment using a tungsten carbide jar and balls to rule out any catalytic intervention by stainless steel (Table 1, entry 17). All these experimental results are compiled in Table 1. The compound **3a** is known, and its physical and spectral properties are consistent with previously reported data, confirming its identity as described in the literature.[7a–c]

Upon having the optimised reaction conditions at hand, we then performed reactions between 1,4-naphthoquinone (**1**) and five different aniline derivatives, namely, *o*-toluidine (**2b**), *p*-toluidine (**2c**), 4-ethylaniline (**2d**), 4-isopropylaniline (**2e**), and 4-

tert-butylaniline (**2f**), under the standard ball-milling conditions. All the reactions occurred efficiently and afforded the desired aminated products, 2-(arylamino)naphthalene-1,4-diones **3b–3f**, with respective yields of 80%, 85%, 76%, 77% and 82% within 10 min (Table 2, compounds **3b–3f**). Encouraged by these results, we then carried out the amination reaction of 1,4-naphthoquinone **1** with a sincerely screened diverse set of twenty-six different anilines **2** containing varying functionalities such as OCH_3, SCH_3, NO_2, F, Cl, di-Cl, Br, I, CF_3, di-CF_3, OCF_3, SCF_3, –O(4-ClC_6H_4), CN, $COCH_3$, COOH, and ethynyl under the optimised reaction conditions. Delightfully, all the transformations proceeded smoothly, and we isolated the desired products **3g–3z** and **3a′–3f′** with moderate to excellent yields ranging from 53% to 87% within the short reaction time of 10 min (Table 2, compounds **3g–3z** and **3a′–3f′**).

We then planned to check the amination reaction of a 1,4-naphthoquinone substrate with primary aliphatic amines and performed the reaction with eight varying such amines, namely,

Table 2 Mechanochemical synthesis of diversely substituted 2-amino-1,4-naphthoquinones (**3**)[a,b]

Reaction scheme: **1** (0.5 mmol) + **2** (0.5 mmol) → Solvent-free Mechanochemistry, ball-milling, basic alumina (1.5 g), 7 balls, 550 rpm, rt, 10 min (amination) → **3**, 43 examples (yield: 52%–92%)

3a; 92% | 3b; 80% | 3c; 85% | 3d; 76% | 3e; 77%

3f; 82% | 3g; 78% | 3h; 75% | 3i; 75% | 3j; 77%

3k; 78% | 3l; 54% | 3m; 58% | 3n; 67% | 3o; 69%

3p; 67% | 3q; 87% | 3r; 62% | 3s; 82% | 3t; 65%

3u; 63% | 3v; 68% | 3w; 53% | 3x; 57% | 3y; 62%

3z; 61% | 3a'; 68% | 3b'; 72% | 3c'; 70% | 3d'; 67%

3e'; 55% | 3f'; 70% | 3g'; 56% | 3h'; 52% | 3i'; 54%

3j'; 70% | 3k'; 59% | 3l'; 55% | 3m'; 65% | 3n'; 61%

3o'; 61% | 3p'; 57% | 3q'; 53% | 3r'; 56%

[a] Reaction conditions: a mixture of 1,4-naphthoquinone (**1**; 0.5 mmol) and amines (**2**; 0.5 mmol) was ball-milled under neat conditions using 7 stainless-steel balls (10 mm in diameter) in a 25 mL stainless-steel jar at 550 rpm for 10 min (and rotation in an inverted direction with a break of 5 s at each 2.5 min interval) using basic alumina (1.5 g) as the surface. [b] Isolated yields.
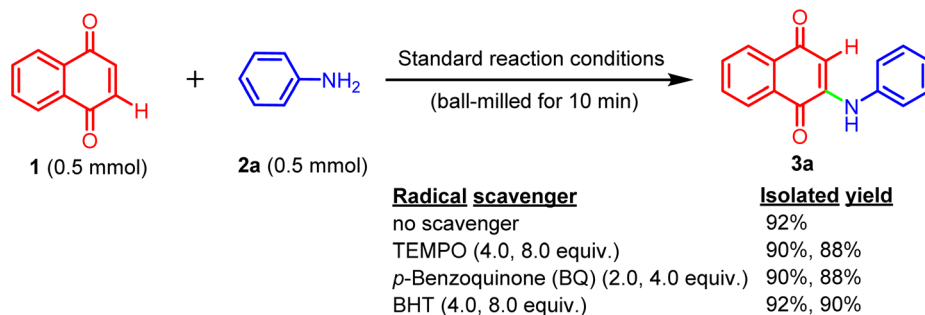
**Scheme 2** Control experiments (experiments with radical scavengers).

n-butylamine (**2g′**), isobutylamine (**2h′**), *n*-hexylamine (**2i′**), allylamine (**2j′**), cyclopentanamine (**2g′**), cyclohexamine (**2g′**), phenylmethanamine (**2g′**), and 2-phenylethan-1-amine (**2g′**); all the reactions occurred smoothly, furnishing the desired aminated products **3g′–3n′** with moderate to good yields ranging from 52% to 70%, within 10 min (Table 2, compounds **3g′–3n′**). We further extended the scope of the reaction with another set of three secondary amines, namely, *N,N*-diphenylamine (**2o′**), pyrrolidine (**2p′**), and morpholine (**2q′**) and prepared the corresponding 2-amino-naphthalene-1,4-diones **3o′–3q′** utilising the identical reaction conditions in 61%, 57% and 53%, respectively, within 10 min (Table 2, compounds **3o′–3q′**). Interestingly, when we carried out the reaction between 1,4-naphthoquinone and 2-aminobenzenethiol (**2r′**) under similar ball-milling conditions, we isolated the cyclised product 11*H*-benzo[*b*]phenothiazine-6,11(12*H*)-dione (**3r′**) in 56% yield within the same time-frame of 10 min (Table 2, compound **3r′**). Table 2 summarises all these results. The reactivity of the different types of amines used in this transformation can now be analyzed from the product yields. In the case of aromatic amines containing electron-donating groups (namely, alkyls, methoxy, thimethyl, and bromo), they furnished good yields (76–87%), and those containing electron-withdrawing groups (namely, nitro, fluoro, chloro, trifluoromethyl, trifluoromethoxy, cyano, and carboxylic acid) gave relatively low yields (54–72%), as expected. Aliphatic amines afforded moderate yields (52–70%).

All the isolated products **3** were purified by the column chromatographic technique (see Experimental) and characterised based on their detailed spectral studies. Compounds except **3e**, **3w**, **3c′–3f′**, **3k′**, and **3l′** are known, and their physical and spectral properties are found to be similar to those reported in the literature.[7]

At this stage, we focused on shedding possible light on this mechanochemical amination at the C-2 position of the 1,4-naphthoquinone moiety upon ball-milling the substrate molecules with amines on a basic alumina surface. For this purpose, we first conducted a set of control experiments (Scheme 2) with the model reaction in the presence of three different radical scavengers, namely, TEMPO, *p*-benzoquinone (BQ), and butylated hydroxytoluene (BHT). None of the radical scavengers could inhibit the reaction even at their much higher equivalencies (Scheme 2), suggesting that the reaction proceeds through an ionic pathway.

From the experimental results (Table 1), we observed that among the three types of alumina (acidic, basic and neutral) used as the surface, only the basic alumina came out as the most superior surface-cum-catalyst for this chemical conversion. This is because basic alumina (α-alumina), an activated form of aluminium oxide (Al_2O_3), comprising a hexagonal close-packed structure, with aluminium ions surrounded by oxygen anions in a layered arrangement, can act as both an acid and a base, depending upon the conditions.[10] On the contrary, acidic alumina, primarily γ-Al_2O_3, shows only acidic property,
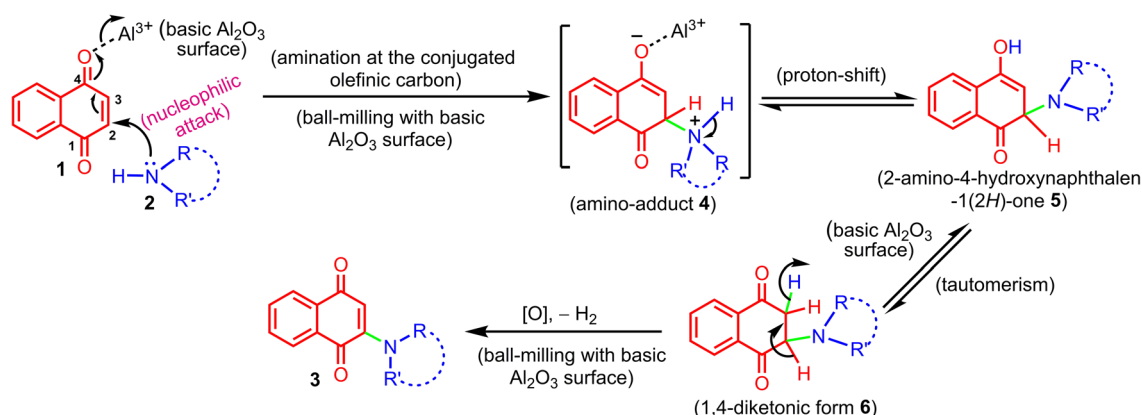
Scheme 3 Proposed mechanism for the ball mill-assisted C-2 amination of 1,4-naphthoquinones **1**.
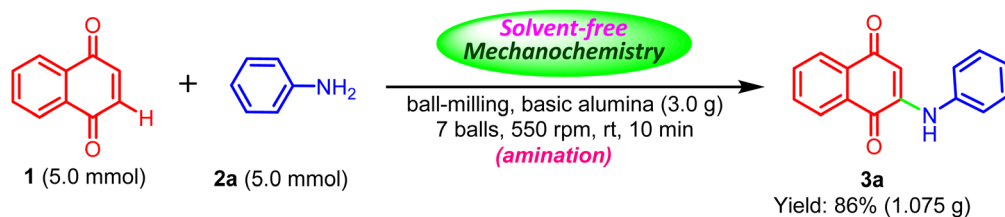
Scheme 4 Gram-scale synthetic application of a representative entry (model reaction).

which is anticipated to reduce the nucleophilic activity of amine substrates due to a strong interaction with the amino-nitrogen atom,[11] as we observed in our experiment as well. Based on our observations, we thus propose a possible mechanism for this transformation, as outlined in Scheme 3. Initially, the C-2 centre of naphthoquinone **1** is activated by the electrostatic attraction of Al^{3+} ion (from basic Al_2O_3 surface) through its coordinating effect with the unshared electron pair(s) of carbonyl oxygen at C-4, which triggers the nucleophilic attack by amine **2** at this 1,3-conjugated sp^2-cabon centre (C-2), resulting in the formation of amino-adduct **4**.[12] Upon a proton shift, intermediate **4** gives 2-amino-4-hydroxynaphthalen-1(2H)-one **5**, which rapidly tautomerizes to 2-amino-2,3-dihydronaphthalene-1,4-dione **6**. Finally, intermediate **6** undergoes oxidation in the presence of basic alumina[7b,c,13] under the reaction conditions to afford the desired product **3**.

To validate the synthetic applicability of the present mechanochemical method to some extent on a larger scale, we carried out gram-scale synthesis (5.0 mmol scale; 10-fold enhancement; Scheme 4) for one representative entry with 1,4-naphthoquinone (**1**) and aniline (**2a**), and isolated the desired product, 2-amino-1,4-naphthaquinone (**3a**) with 86% yield, an almost similar yield obtained for sub-millimolar scale reactions

(Table 2, compounds **3a**), within the same reaction time (Scheme 4).

We then attempted to examine the reusability of the solid surface (basic alumina) with the model reaction, and to our delight, the solid surface was successfully reused for up to the fourth cycle without appreciable loss in its activity (we isolated the product **3a** in 92%, 86%, 80%, and 74% yields within the same time-frame of 10 min for each response). However, the activity of the surface was found to be reduced in the fifth run (isolated yield of **3a** was 56%). All these experimental outcomes are shown in Fig. 2. It is worth noting that after collecting the solid surface during the work-up of a reaction, it was pre-heated at 70 °C in an oven for further use.

Finally, we carried out an extended synthetic application with three representative entries (namely, **3e**, **3o**, and **3w**) of the synthesised 2-amino-1,4-naphthoquinones by preparing their respective selenylated products, namely, 2-((4-isopropylphenyl)amino)-3-(phenylselanyl)naphthalene-1,4-dione (**10e**), 2-((4-chlorophenyl)amino)-3-(phenylselenyl)naphthalene-1,4-dione (**10o**) and 2-((4-(4-chlorophenoxy)phenyl)amino)-3-(phenylselanyl)naphthalene-1,4-dione (**10w**), following the reported electrochemical[5a] and photochemical[8h] methods. The reaction schemes are outlined in Scheme 5. The three selenylated compounds are new and are fully characterised by their detailed spectral studies (Experimental).
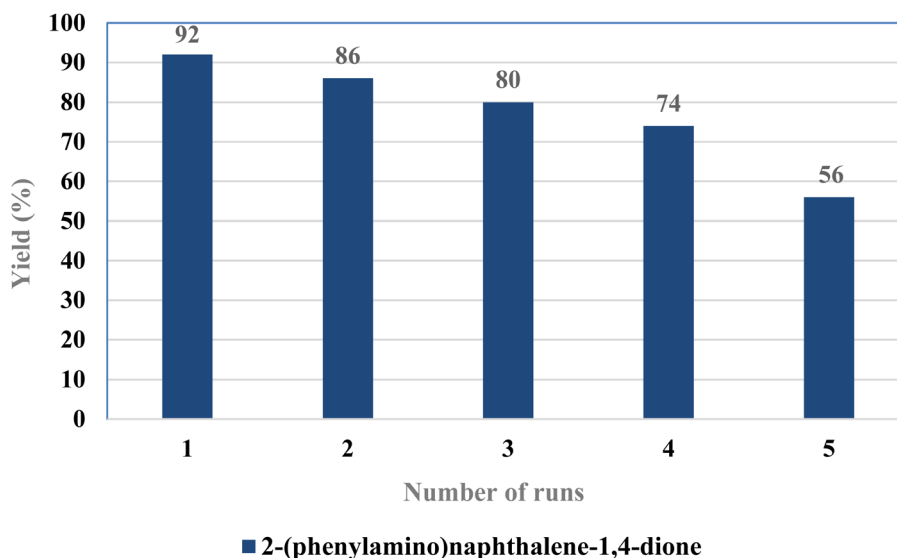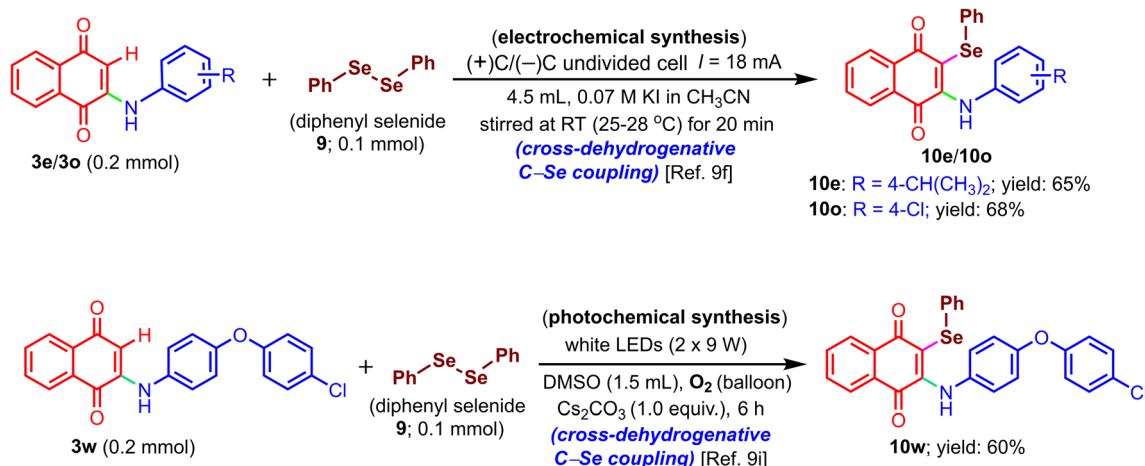

Fig. 2 Reusability of the solid surface.

Scheme 5 Synthetic application: selenylation of three selected 2-amino-1,4-naphthoquinones (**3e**, **3o**, and **3w**).

3 Conclusions

In summary, we have developed a mechanochemistry-driven regioselective amination strategy as an efficient and practical alternative synthetic protocol for accessing functionalised 2-amino-1,4-naphthoquinones upon high-speed ball-milling of 1,4-naphthoquinones with diverse amines using basic alumina as a surface without any additives under neat conditions. The salient features of this alternative protocol are solvent- and additive-free synthesis, no external heating, tolerance of various functional groups in amines, good yields, shorter reaction times (in minutes), reusability of the solid surface, gram-scale synthesis, a clean reaction profile, and operational simplicity. In addition, some of the synthesised 2-amino-1,4-naphthoquinones were used as synthons to prepare their corresponding selenylated products.

4 Experimental section

Chemicals and solvents used in this work were obtained from reputed companies. ^{1}H-, ^{13}C-, and ^{19}F-NMR spectra were recorded at 400, 100, and 376 MHz, respectively, using a Bruker DRX spectrometer. A Waters (G2-XS Q-TOF) high-resolution mass spectrometer was used to collect HRMS spectra. A PM 100, Retsch GmbH, Germany, ball-milling apparatus was used for the mechanochemical reactions. The melting points were recorded using a Chemiline CL-725 melting point apparatus and are uncorrected. Thin Layer Chromatography (TLC) was performed using silica gel 60 F254 (Merck) plates.

4.1 General procedure for the synthesis of functionalised 2-amino-1,4-naphthoquinones (3)

A mixture of 1,4-naphthoquinone (**1**; 0.5 mmol) and amines (**2**; 0.5 mmol) was ball-milled in a 25 mL stainless steel jar with seven balls (10 mm in diameter) made of the same material and basic alumina (1.5 g) as the surface at 550 rpm for 10 minutes. The ball-milling operation was done following an inverted directional mode, with intervals of 2.5 minutes and breaks of 5

seconds. Upon completion of the reaction (monitored by TLC), the resulting mixture was transferred into a 250 mL separating funnel, followed by adding 30 mL of ethyl acetate-water mixture (3 : 1 v/v) with constant shaking for 5 minutes. The organic layer was separated upon settling and dried over anhydrous sodium sulfate. The solvent was then removed using a rotary evaporator to obtain a crude mass, which was subjected to column chromatographic purification using EtOAc–hexane mixtures as eluents to yield pure products of substituted 2-amino-1,4-naphthoquinones **3** (**3a–3z**, and **3a′–3r′**).

4.2 Gram-scale synthesis of one representative compound 3a

A mixture of 1,4-naphthoquinone (**1**; 5.0 mmol) and aniline (**2a**; 5.0 mmol) was ball-milled in a similar fashion in a 25 mL stainless steel jar with seven balls (10 mm in diameter) made of the same material and basic alumina (3.0 g) as the surface at 550 rpm for 10 minutes (monitored by TLC). After each reaction, the resulting reaction mixture was worked up and purified following the same procedure, as mentioned in the general method, to obtain pure product **3a** in 86% (1.075 g) yield.

4.3. Physical and spectral data of the synthesised 2-amino-1,4-naphthoquinones 3, 10a, 10o, and 10w are given below

4.3.1 2-(Phenylamino)naphthalene-1,4-dione (3a).[7a]
Brownish red solid; yield: 92% (115 mg, 0.5 mmol scale; hexane/EtOAc 95 : 5 as eluent), mp = 191–192 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.11–8.07 (m, 2H, Ar–H), 7.73 (td, 1H, J = 7.6 and 1.2 Hz, Ar–H), 7.64 (td, 1H, J = 7.6 and 0.8 Hz, Ar–H), 7.55 (br s, 1H, –NH), 7.42–7.38 (m, 2H, Ar–H), 7.24–7.23 (m, 2H, Ar–H), 7.19 (t, 1H, J = 7.6 Hz, Ar–H), 6.39 (s, 1H, Ar–H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 184.11 (*C*O), 182.24 (*C*O), 144.89 (*C*), 137.57 (*C*), 135.08 (*C*H), 133.44 (*C*), 132.51 (2 × *C*H), 130.56 (*C*), 129.85 (2 × *C*H), 126.69 (*C*H), 126.32 (*C*H), 125.78 (*C*H), 122.77 (*C*H), 103.5 (*C*H) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{16}$H$_{11}$NO$_2$H; 250.0863; found: 250.0881.

4.3.2 2-(*o*-Tolylamino)naphthalene-1,4-dione (3b).[7a]
Red solid; yield: 80% (105 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 140–141 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ =

8.14–8.09 (m, 2H, Ar–H), 7.78–7.74 (m, 1H, Ar–H), 7.69–7.65 (m, 1H, Ar–H), 7.33–7.27 (m, 3H, Ar–H and –N*H*), 7.22–7.18 (m, 1H, Ar–H), 5.97 (s, 1H, Ar–H), 2.29 (s, 3H, –C*H*$_3$) ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{17}$H$_{13}$NO$_2$H; 264.1019; found: 264.1030.

4.3.3   2-(*p*-Tolylamino)naphthalene-1,4-dione   (3c).[7a] Brownish red solid; yield: 85% (112 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent) mp = 194–196 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.12–8.09 (m, 2H, Ar–H), 7.77–7.73 (m, 1H, Ar–H), 7.66 (t, 1H, *J* = 7.6 Hz, Ar–H), 7.51 (br s, 1H, –N*H*), 7.22 (d, 2H, *J* = 8.4 Hz, Ar–H), 7.16 (d, 2H, *J* = 8.4 Hz, Ar–H), 6.35 (s, 1H, Ar–H), 2.36 (s, 3H, Ar–C*H*$_3$) ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{17}$H$_{13}$NO$_2$H; 264.1019; found: 264.1037.

4.3.4   2-((4-Ethylphenyl)amino)naphthalene-1,4-dione (3d).[14] Red solid; yield: 76% (105 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 149–152 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.22 (s, 1H, –N*H*), 8.06 (dd, 1H, *J* = 8.0 Hz and 1.2 Hz, Ar–H), 7.95–7.93 (m, 1H, Ar–H), 7.88–7.84 (m, 1H, Ar–H), 7.79–7.76 (m, 1H, Ar–H), 7.28 (s, 4H, Ar–H), 6.04 (s, 1H, Ar–H), 2.64–2.59 (m, 2H, –C*H*$_2$CH$_3$), 1.19 (t, 3H, *J* = 7.6 Hz, –CH$_2$-C*H*$_3$) ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{18}$H$_{17}$NO$_2$H; 278.1181; found: 278.1167.

4.3.5   2-((4-Isopropylphenyl)amino)naphthalene-1,4-dione (3e). Brownish red solid; yield: 77% (115 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 140–141 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.21 (s, 1H, –N*H*), 8.06 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.94 (d, 1H, *J* = 7.6 Hz, Ar–H), 7.86 (t, 1H, *J* = 7.2 Hz, Ar–H), 7.78 (t, 1H, *J* = 7.6 Hz, Ar–H), 7.31 (s, 4H, Ar–H), 6.05 (s, 1H, Ar–H), 2.94–2.87 (m, 1H, –C*H*), 1.21 (d, 6H, *J* = 7.2 Hz, 2 × –C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ = 182.45 (*C*O), 181.66 (*C*O), 146.39 (*C*), 145.64 (*C*), 135.67 (*C*), 134.91 (*C*H), 132.65 (*C*), 132.58 (*C*H), 130.43 (*C*), 127.11 (2 × CH), 126.12 (*C*H), 125.27 (*C*H), 123.80 (2 × *C*H), 101.56 (*C*H), 33.00 (–*C*H(CH$_3$)$_2$), 23.87 (–CH(*C*H$_3$)$_2$) ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{19}$H$_{18}$NO$_2$H; 292.1332; found: 292.1352.

4.3.6   2-((4-(*tert*-Butyl)phenyl)amino)naphthalene-1,4-dione (3f).[15] Brownish red solid; yield: 82% (125 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 134–135 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.21 (s, 1H, –N*H*), 8.05 (d, 1H, *J* = 7.6 Hz, Ar–H), 7.94 (d, 1H, *J* = 7.6 Hz, Ar–H), 7.85 (t, 1H, *J* = 7.2 Hz, Ar–H), 7.79–7.75 (m, 1H, Ar–H), 7.45 (d, 2H, *J* = 8.4 Hz, Ar–H), 7.30 (d, 2H, *J* = 8.8 Hz, Ar–H), 6.06 (s, 1H, Ar–H), 1.29 (s, 9H, –C(C*H*$_3$)$_3$) ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{20}$H$_{19}$NO$_2$H, 306.1489; found: 306.1471.

4.3.7   2-((2-Methoxyphenyl)amino)naphthalene-1,4-dione (3g).[5a] Brownish red solid; yield: 78% (109 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 154–155 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.14–8.10 (m, 2H, Ar–H), 7.99 (br s, 1H, –N*H*), 7.76 (td, 1H, *J* = 7.6 and 1.2 Hz, Ar–H), 7.69–7.65 (m, 1H, Ar–H), 7.44–7.42 (m, 1H, Ar–H), 7.15 (td, 1H, *J* = 8.0 and 1.6 Hz, Ar–H), 7.03–6.99 (m, 1H, Ar–H), 6.98–6.96 (m, 1H, Ar–H), 6.49 (s, 1H, Ar–H), 3.92 (s, 3H, Ar–OC*H*$_3$) ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{17}$H$_{13}$NO$_3$H; 280.0974; found: 280.0980.

4.3.8   2-((3-Methoxyphenyl)amino)naphthalene-1,4-dione (3h).[5a] Brownish red solid; yield: 75% (105 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 162–163 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.13–8.09 (m, 2H, Ar–H), 7.78–7.74 (m, 1H, Ar–

H), 7.69–7.65 (m, 1H, Ar–H), 7.55 (br s, 1H, –N*H*), 7.34–7.29 (m, 1H, Ar–H), 6.87 (dd, 1H, *J* = 8.0 and 1.6 Hz, Ar–H), 6.81–6.79 (m, 1H, Ar–H), 6.75 (dd, 1H, *J* = 8.0 and 2.4 Hz, Ar–H), 6.45 (s, 1H, Ar–H), 3.83 (s, 3H, Ar–OC*H*$_3$) ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{17}$H$_{13}$NO$_3$H; 280.0974; found: 280.0961.

4.3.9   2-((4-Methoxyphenyl)amino)naphthalene-1,4-dione (3i).[7a] Brownish red solid; yield: 75% (105 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 152–153 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.12–8.09 (m, 2H, Ar–H), 7.77–7.73 (m, 1H, Ar–H), 7.68–7.64 (m, 1H, Ar–H), 7.44 (br s, 1H, –N*H*), 7.20 (d, 2H, *J* = 8.8 Hz, Ar–H), 6.95 (d, 2H, *J* = 8.8 Hz, Ar–H), 6.22 (s, 1H, Ar–H), 3.83 (s, 3H, Ar–OC*H*$_3$) ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{17}$H$_{13}$NO$_3$H; 280.0974; found: 280.0990.

4.3.10   2-((3-(Methylthio)phenyl)amino)naphthalene-1,4-dione (3j).[5a] Red solid; yield: 77% (115 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 174–175 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.13–8.09 (m, 2H, Ar–H), 7.79–7.75 (m, 1H, Ar–H), 7.69–7.65 (m, 1H, Ar–H), 7.54 (br s, 1H, –N*H*), 7.35–7.31 (m, 1H, Ar–H), 7.13–7.12 (m, 1H, Ar–H), 7.09–7.04 (m, 2H, Ar–H), 6.42 (s, 1H, Ar–H), 2.51 (s, 3H, Ar–SC*H*$_3$) ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{17}$H$_{13}$NO$_2$SH; 296.0745; found: 296.0770.

4.3.11   2-((4-(Methylthio)phenyl)amino)naphthalene-1,4-dione (3k).[5a] Brownish red solid; yield: 78% (115 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 178–179 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.09 (d, 2H, *J* = 6.8 Hz, Ar–H), 7.74 (t, 1H, *J* = 7.6 Hz, Ar–H), 7.65 (t, 1H, *J* = 7.6 Hz, Ar–H), 7.54 (br s, 1H, –N*H*), 7.29 (d, 2H, *J* = 8.4 Hz, Ar–H), 7.19 (d, 2H, *J* = 8.4 Hz, Ar–H), 6.34 (s, 1H, Ar–H), 2.49 (s, 3H, Ar–SC*H*$_3$) ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{17}$H$_{13}$NO$_2$SH; 296.0745; found: 296.0759.

4.3.12   2-((2-Nitrophenyl)amino)naphthalene-1,4-dione (3l).[16] Brownish orange solid; yield: 54% (79 mg, 0.5 mmol scale, hexane/EtOAc 93 : 7 as eluent), mp = 225–226 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.74 (s, 1H, –N*H*), 8.19 (d, 1H, *J* = 8.0 Hz, Ar–H), 8.10 (d, 1H, *J* = 7.6 Hz, Ar–H), 7.98 (d, 1H, *J* = 7.6 Hz, Ar–H), 7.92–7.88 (m, 1H, Ar–H), 7.85–7.78 (m, 3H, Ar–H), 7.44 (t, 1H, *J* = 7.6 Hz, Ar–H), 6.25 (s, 1H, Ar–H) ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{16}$H$_{11}$N$_2$O$_4$H; 295.0713; found: 295.0694.

4.3.13   2-((4-Nitrophenyl)amino)naphthalene-1,4-dione (3m).[5a] Brownish red solid; yield: 58% (85 mg, 0.5 mmol scale, hexane/EtOAc 94 : 6 as eluent), mp = 158–160 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.65 (s, 1H, –N*H*), 8.28 (d, 2H, *J* = 8.8 Hz, Ar–H), 8.09 (d, 1H, *J* = 8.0 Hz, Ar–H), 7.99 (d, 1H, *J* = 8.0 Hz, Ar–H), 7.91–7.87 (m, 1H, Ar–H), 7.85–7.81 (m, 1H, Ar–H), 7.67 (d, 2H, *J* = 8.4 Hz, Ar–H), 6.52 (s, 1H, Ar–H) ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{16}$H$_{11}$N$_2$O$_4$H, 295.0713; found: 295.0725.

4.3.14   2-((4-Fluorophenyl)amino)naphthalene-1,4-dione (3n).[7b] Red solid; yield: 67% (90 mg, 0.5 mmol scale, hexane/EtOAc 96 : 4 as eluent), mp = 245–248 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.25 (s, 1H, –N*H*), 8.05 (d, 1H, *J* = 6.8 Hz, Ar–H), 7.94 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.87–7.84 (m, 1H, Ar–H), 7.80–7.76 (m, 1H, Ar–H), 7.42–7.39 (m, 2H, Ar–H), 7.28 (t, 2H, *J* = 8.8 Hz, Ar–H), 5.98 (s, 1H, Ar–H) ppm. ^{19}F NMR (376 MHz, DMSO-d$_6$): δ = –116.54 ppm. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for C$_{16}$H$_{10}$FNO$_2$H, 268.0774; found: 268.0757.

4.3.15   2-((4-Chlorophenyl)amino)naphthalene-1,4-dione (3o).[7b] Red solid; yield: 69% (98 mg, 0.5 mmol scale, hexane/EtOAc 97 : 3 as eluent), mp = 248–249 °C. ^{1}H NMR (400 MHz,

CDCl$_3$): δ = 8.13–8.09 (m, 2H, Ar–H), 7.79–7.75 (m, 1H, Ar–H),7.68 (t, 1H, J = 7.6 Hz, Ar–H), 7.52 (br s, 1H, –NH), 7.39 (d, 2H, J = 8.4 Hz, Ar–H), 7.22 (d, 2H, J = 8.8 Hz, Ar–H), 6.36 (s, 1H, Ar–H) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{16}$H$_{10}$ClNO$_2$H, 284.0478; found: 284.0469.

4.3.16   2-((2,5-Dichlorophenyl)amino)naphthalene-1,4-dione (3p).[5a] Yellowish red solid; yield: 67% (106 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 192–193 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.16–8.11 (m, 2H, Ar–H), 7.84 (br s, 1H, –NH), 7.81–7.77 (m, 1H, Ar–H), 7.73–7.68 (m, 1H, Ar–H), 7.48 (d, 1H, J = 2.4 Hz, Ar–H), 7.41 (d, 1H, J = 8.8 Hz, Ar–H), 7.12 (dd, 1H, J = 8.8 and 2.4 Hz, Ar–H), 6.43 (s, 1H, Ar–H) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{16}$H$_9$Cl$_2$NO$_2$H, 318.0089; found: 318.0110.

4.3.17   2-((4-Bromophenyl)amino)naphthalene-1,4-dione (3q).[7b] Red solid; yield: 87% (142 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 260–263 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.29 (s, 1H, –NH), 8.07 (d, 1H, J = 7.2 Hz, Ar–H), 7.96 (d, 1H, J = 7.2 Hz, Ar–H), 7.89–7.86 (m, 1H, Ar–H), 7.82–7.78 (m, 1H, Ar–H), 7.62 (d, 2H, J = 8.8 Hz, Ar–H), 7.37 (d, 2H, J = 8.4 Hz, Ar–H), 6.15 (s, 1H, Ar–H) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{16}$H$_{10}$BrNO$_2$H, 327.9973; found: 327.9988.

4.3.18   2-((4-Iodophenyl)amino)naphthalene-1,4-dione (3r).[17] Purple solid; yield: 62% (116 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 234–237 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.13 (t, 2H, J = 7.6 Hz, Ar–H), 7.80–7.76 (m, 1H, Ar–H), 7.71–7.68 (m, 3H, Ar–H and –NH), 7.33 (d, 2H, J = 8.8 Hz, Ar–H), 6.53 (s, 1H, Ar–H) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{16}$H$_{10}$INO$_2$H, 375.9834; found: 375.9840.

4.3.19   2-((4-(Trifluoromethyl)phenyl)amino)naphthalene-1,4-dione (3s).[5a] Orange red solid; yield: 82% (130 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 192–193 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.15–8.11 (m, 2H, Ar–H), 7.81–7.67 (m, 4H, Ar–H and –NH), 7.39 (d, 2H, J = 7.6 Hz, Ar–H), 6.53 (s, 1H, Ar–H) ppm. ^{19}F NMR (376 MHz, CDCl$_3$): δ = −62.26 ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{16}$H$_{11}$F$_3$NO$_2$H, 318.0742; found: 318.0729.

4.3.20   2-((3,5-Bis(trifluoromethyl)phenyl)amino)naphthalene-1,4-dione (3t).[5a] Brownish red solid; yield: 65% (125 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 199–200 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.15–8.12 (m, 2H, Ar–H), 7.82–7.78 (m, 2H, Ar–H), 7.74–7.69 (m, 3H, Ar–H and –NH), 6.45 (s, 1H, Ar–H) ppm. ^{19}F NMR (376 MHz, CDCl$_3$): δ = −63.01 ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{18}$H$_9$F$_6$NO$_2$H, 386.0616; found: 386.0632.

4.3.21   2-((4-(Trifluoromethoxy)phenyl)amino)naphthalene-1,4-dione (3u).[5a] Red solid; yield: 63% (105 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 228–230 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.35 (s, 1H, –NH), 8.07–8.05 (m, 1H, Ar–H), 7.96–7.94 (m, 1H, Ar–H), 7.86 (td, 1H, J = 7.6 and 1.2 Hz, Ar–H), 7.79 (td, 1H, J = 7.2 and 1.2 Hz, Ar–H), 7.51 (d, 2H, J = 8.8 Hz, Ar–H), 7.43 (d, 2H, J = 8.8 Hz, Ar–H), 6.13 (s, 1H, Ar–H) ppm. ^{19}F NMR (376 MHz, DMSO-d$_6$): δ = −56.98 ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{17}$H$_{10}$F$_3$NO$_3$H, 334.0691; found: 334.0696.

4.3.22   2-((4-((Trifluoromethyl)thio)phenyl)amino)naphthalene-1,4-dione (3v).[5a] Brownish red solid; yield: 68% (119 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 223–224 °C. ^{1}H NMR (400 MHZ, CDCl$_3$): δ = 8.14–8.09 (m, 2H, Ar–H), 7.79–7.76 (m, 1H, Ar–H), 7.71–7.67 (m, 3H, Ar–H and –NH), 7.35–7.32 (m, 2H, Ar–H), 6.53 (s, 1H, Ar–H) ppm. ^{19}F NMR (376 MHz, CDCl$_3$): δ = −43.02 ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{17}$H$_{10}$F$_3$NO$_2$SH, 350.0463; found: 350.0481.

4.3.23   2-((4-(4-Chlorophenoxy)phenyl)amino)naphthalene-1,4-dione (3w). Red solid; yield: 53% (99 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 195–196 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.26 (s, 1H, –NH), 8.05 (d, 1H, J = 7.2 Hz, Ar–H), 7.94 (d, 1H, J = 7.2 Hz, Ar–H), 7.87–7.83 (m, 1H, Ar–H), 7.79–7.77 (m, 1H, –NH), 7.45–7.39 (m, 4H, Ar–H), 7.11 (d, 2H, J = 8.4 Hz, Ar–H), 7.06 (d, 2H, J = 8.8 Hz, Ar–H), 6.05 (s, 1H, Ar–H) ppm. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ = 182.56 (CO), 181.59 (CO), 155.78 (C), 153.40 (C), 146.51 (2C), 134.94 (CH), 133.87 (C), 132.64 (CH), 130.45 (C), 129.96 (2 × CH), 127.25 (C), 126.14 (CH), 125.79 (2 × CH), 125.32 (CH), 120.15 (2 × CH), 119.76 (2 × CH), 101.72 (CH) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{22}$H$_{14}$ClNO$_3$H, 376.0735; found: 376.0740.

4.3.24   2-((1,4-Dioxo-1,4-dihydronaphthalen-2-yl)amino)benzonitrile (3x).[7b] Red solid; yield: 57% (78 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 289–291 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.45 (s, 1H, –NH), 8.09 (d, 1H, J = 7.6 Hz, Ar–H), 7.95 (d, 2H, J = 7.6 Hz, Ar–H), 7.89–7.86 (m, 1H, Ar–H), 7.84–7.79 (m, 2H, Ar–H), 7.59 (d, 1H, J = 8.0 Hz, Ar–H), 7.51–7.48 (m, 1H, Ar–H), 5.69 (s, 1H, Ar–H) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{17}$H$_{10}$N$_2$O$_2$H, 275.0821; found: 275.0811.

4.3.25   4-((1,4-Dioxo-1,4-dihydronaphthalen-2-yl)amino)benzonitrile (3y).[7b] Red solid; yield: 62% (85 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = >300 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.50 (s, 1H, –NH), 8.08 (d, 1H, J = 8.0 Hz, Ar–H), 7.97 (d, 1H, J = 8.0 Hz, Ar–H), 7.89–7.79 (m, 4H, Ar–H), 7.60 (d, 2H, J = 8.4 Hz, Ar–H), 6.40 (s, 1H, Ar–H) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{17}$H$_{10}$N$_2$O$_2$H, 275.0821; found: 275.0810.

4.3.26   2-((1,4-Dioxo-1,4-dihydronaphthalen-2-yl)amino)benzoic acid (3z).[7b] Red solid; yield: 61% (90 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 138–141 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 10.79 (s, 1H, –NH), 8.09–8.03 (m, 2H, Ar–H), 7.98 (d, 1H, J = 7.2 Hz, Ar–H), 7.90–7.87 (m, 1H, Ar–H), 7.82 (t, 1H, J = 7.2 Hz, Ar–H), 7.69 (d, 2H, J = 3.6 Hz, Ar–H), 7.25–7.21 (m, 1H, Ar–H), 6.56 (s, 1H, Ar–H) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{11}$H$_{11}$NO$_4$H, 294.0766; found: 294.0777.

4.3.27   3-((1,4-Dioxo-1,4-dihydronaphthalen-2-yl)amino)benzoic acid (3a′).[7b] Orange solid; yield: 68% (100 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 263–266 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.35 (s, 1H, –NH), 8.05 (d, 1H, J = 7.6 Hz, Ar–H), 7.94 (d, 2H, J = 6.8 Hz, Ar–H), 7.84 (t, 1H, J = 7.2 Hz, Ar–H), 7.79–7.76 (m, 2H, Ar–H), 7.64 (d, 1H, J = 8.4 Hz, Ar–H), 7.58–7.54 (m, 1H, Ar–H), 6.11 (s, 1H, Ar–H) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{11}$H$_{11}$NO$_4$H, 294.0766; found: 294.0780.

4.3.28   4-((1,4-Dioxo-1,4-dihydronaphthalen-2-yl)amino)benzoic acid (3b′).[7b] Red solid; yield: 72% (105 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = >300 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 12.89 (br s, 1H, –COOH), 9.42 (s, 1H, –

N*H*), 8.07 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.99–7.96 (m, 3H, Ar–H), 7.87 (t, 1H, *J* = 7.2 Hz, Ar–H), 7.82–7.79 (m, 1H, Ar–H), 7.53 (d, 2H, *J* = 8.4 Hz, Ar–H), 6.36 (s, 1H, Ar–H) ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for $C_{11}H_{11}NO_4H$, 294.0766; found: 294.0751.

4.3.29 2-((1,4-Dioxo-1,4-dihydronaphthalen-2-yl)amino)-6-fluorobenzoic acid (3c′). Brownish red solid; yield: 70% (109 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = >300 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 9.82 (s, 1H, –N*H*), 8.06–7.96 (m, 2H, Ar–H), 7.86–7.79 (m, 2H, Ar–H), 7.63–7.59 (m, 1H, Ar–H), 7.42 (d, 1H, *J* = 4.8 Hz, Ar–H), 7.09 (br s, 1H, Ar–H), 6.32 (d, 1H, *J* = 6.0 Hz, Ar–H) ppm. ¹³C{¹H} NMR (100 MHz, DMSO-d₆): δ = 183.70 (*C*O), 181.79 (*C*O), 166.17 (*C*OOH), 161.43 (d, $J_{C–F}^1$ = 250 Hz, *C*), 145.37 (*C*), 135.68 (2 × *C*H), 134.06 (d, $J_{C–F}^3$ = 11 Hz, *C*), 133.63 (2 × *C*H), 132.90 (*C*), 130.80 (*C*), 126.92 (*C*H), 126.03 (*C*H), 119.28 (*C*H), 112.93 (d, $J_{C–F}^2$ = 23 Hz, *C*), 105.25 (*C*H) ppm. ¹⁹F NMR (376 MHz, DMSO-d₆): δ = –108.85 ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for $C_{17}H_{11}FNO_4H$, 312.0667; found: 312.0650.

4.3.30 5-Chloro-2-((1,4-dioxo-1,4-dihydronaphthalen-2-yl)amino)benzoic acid (3d′). Brownish red solid; yield: 67% (110 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = >300 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 10.73 (s, 1H, –N*H*), 8.06 (d, 1H, *J* = 7.6 Hz, Ar–H), 7.96 (d, 2H, *J* = 7.2 Hz, Ar–H), 7.89–7.86 (m, 1H, Ar–H), 7.83–7.79 (m, 1H, Ar–H), 7.71 (s, 2H, Ar–H), 6.53 (s, 1H, Ar–H) ppm. ¹³C{¹H} NMR (100 MHz, DMSO-d₆): δ = 183.39 (*C*O), 181.28 (*C*O), 167.64 (*C*OOH), 143.47 (*C*), 139.13 (*C*H), 135.12 (*C*H), 133.82 (*C*H), 133.17 (*C*H), 132.23 (*C*), 131.20 (*C*H), 130.24 (*C*), 126.72 (*C*), 126.46 (*C*H), 125.49 (*C*H), 122.37 (*C*), 121.27 (*C*), 105.62 (*C*H) ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for $C_{17}H_{10}ClNO_4H$, 328.0371; found: 328.0377.

4.3.31 2-((2-Acetylphenyl)amino)naphthalene-1,4-dione (3e′). Brownish yellow solid; yield: 55% (80 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 192–193 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 11.01 (s, 1H, –N*H*), 8.12–8.07 (m, 2H, Ar–H), 7.96 (d, 1H, *J* = 7.2 Hz, Ar–H), 7.89–7.86 (m, 1H, Ar–H), 7.83–7.79 (m, 1H, Ar–H), 7.69–7.68 (m, 2H, Ar–H), 7.29–7.26 (m, 1H, –N*H*), 6.53 (s, 1H, Ar–H), 2.66 (s, 3H, –COC*H₃*) ppm. ¹³C{¹H} NMR (100 MHz, DMSO-d₆): δ = 201.99 (Ar–*C*OCH₃), 183.26 (*C*O), 181.37 (*C*O), 143.94 (*C*), 138.99 (*C*), 135.04 (*C*H), 134.40 (*C*H), 133.07 (*C*H), 132.68 (*C*H), 132.25 (*C*), 130.23 (*C*), 126.39 (*C*H), 126.17 (*C*), 125.41 (*C*H), 123.40 (*C*H), 120.98 (*C*H), 105.54 (*C*H), 28.83 (Ar–COC*H₃*) ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for $C_{18}H_{14}NO_3H$, 292.0968; found: 292.0979.

4.3.32 2-((3-Ethynylphenyl)amino)naphthalene-1,4-dione (3f′). Red solid; yield: 70% (96 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 214 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 9.25 (s, 1H, –N*H*), 8.05 (d, 1H, *J* = 8.0 Hz, Ar–H), 7.87–7.83 (m, 1H, Ar–H), 7.8–7.76 (m, 1H, Ar–H), 7.45 (d, 1H, *J* = 6.0 Hz, Ar–H), 7.32–7.29 (m, 1H, Ar–H), 6.09 (s, 1H, Ar–H), 4.25 (s, 1H, –C≡C*H*) ppm. ¹³C{¹H} NMR (100 MHz, DMSO-d₆): δ = 182.82 (*C*O), 181.47 (*C*O), 146.05 (*C*), 138.58 (*C*), 134.99 (*C*H), 132.82 (*C*H), 132.51 (*C*), 130.45 (*C*), 129.86 (*C*H), 128.43 (*C*H), 126.53 (*C*H), 126.22 (*C*H), 125.36 (*C*H), 124.29 (*C*H), 122.71 (*C*), 102.65 (*C*H), 82.92 (–*C*≡CH), 81.46 (–C≡*C*H) ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for $C_{18}H_{11}NO_2H$, 274.0863; found: 274.0840.

4.3.33 2-(Butylamino)naphthalene-1,4-dione (3g′).[7a] Red solid; yield: 56% (64 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 125–127 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.10–8.08 (m, 1H, Ar–H), 8.04–8.02 (m, 1H, Ar–H), 7.71 (td, 1H, *J* = 7.6 Hz and 1.2 Hz, Ar–H), 7.74 (td, 1H, *J* = 7.6 Hz and 1.2 Hz, Ar–H), 5.89 (br s, 1H, –N*H*), 5.72 (s, 1H, Ar–H), 3.20–3.15 (m, 2H, –NHC*H₂*CH₂CH₂CH₃), 1.69–1.64 (m, 2H, –NHCH₂C*H₂*CH₂CH₃), 1.48–1.40 (m, 2H, –NHCH₂CH₂C*H₂*CH₃), 0.98–0.95 (m, 3H, –NHCH₂CH₂CH₂C*H₃*) ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for $C_{14}H_{15}NO_2H$, 230.1181; found: 230.1177.

4.3.34 2-(Isobutylamino)naphthalene-1,4-dione (3h′).[5a] Brownish red solid; yield: 52% (60 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 165–167 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.09–8.08 (m, 1H, Ar–H), 8.04–8.02 (m, 1H, Ar–H), 7.73–7.69 (m, 1H, Ar–H), 7.59 (td, 1H, *J* = 7.6 and 1.2 Hz, Ar–H), 5.99 (br s, 1H, –N*H*), 5.72 (s, 1H, Ar–H), 2.99 (t, 2H, *J* = 6.4 Hz, –NHC*H₂*CH(CH₃)₂), 2.04–1.94 (m, 1H, –NHCH₂C*H*(CH₃)₂), 1.00 (d, 6H, *J* = 6.8 Hz, –NHCH₂CH(C*H₃*)₂) ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for $C_{14}H_{15}NO_2H$, 230.1181; found: 230.1193.

4.3.35 2-(Hexylamino)naphthalene-1,4-dione (3i′).[5a] Brownish red solid; yield: 54% (69 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 180–182 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 7.97–7.92 (m, 2H, Ar–H), 7.83–7.79 (m, 1H, Ar–H), 7.73–7.70 (m, 1H, Ar–H), 7.56 (br s, 1H, –N*H*), 5.65 (s, 1H, Ar–H), 3.15 (q, 2H, *J* = 6.8 Hz, –NHC*H₂*CH₂CH₂CH₂CH₂CH₃), 1.57–1.54 (m, 2H, –NHCH₂C*H₂*CH₂CH₂CH₂CH₃), 1.27 (s, 6H, –NHCH₂CH₂C*H₂*C*H₂*C*H₂*CH₃), 0.87–0.83 (m, 3H, –NHCH₂CH₂CH₂CH₂CH₂C*H₃*) ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for $C_{16}H_{19}NO_2H$, 258.1494; found: 258.1498.

4.3.36 2-(Allylamino)naphthalene-1,4-dione (3j′).[5a] Red solid; yield: 70% (75 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 162–163 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.08 (d, 1H, *J* = 8 Hz, Ar–H), 8.04 (d, 1H, *J* = 7.6 Hz, Ar–H), 7.72 (t, 1H, *J* = 7.6 Hz, Ar–H), 7.60 (t, 1H, *J* = 7.6 Hz, Ar–H), 6.03 (br s, 1H, –N*H*), 5.92–5.83 (m, 1H, Ar–H), 5.74 (s, 1H, –CH₂-C*H*=CH₂), 5.32–5.26 (m, 2H, –CH₂–CH=C*H₂*), 3.85–3.82 (m, 2H, –C*H₂*–CH=CH₂) ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for $C_{13}H_{11}NO_2H$, 214.0864; found: 214.0855.

4.3.37 2-(Cyclopentylamino)naphthalene-1,4-dione (3k′). Red solid; yield: 59% (71 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 106–108 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.07 (d, 1H, *J* = 7.6 Hz, Ar–H), 7.99 (d, 1H, *J* = 7.6 Hz, Ar–H), 7.71–7.67 (m, 1H, Ar–H), 7.57 (dd, 1H, *J* = 7.6 and 1.2 Hz, Ar–H), 5.86 (br s, 1H, –N*H*), 5.73 (s, 1H, Ar–H), 3.79–3.72 (m, 1H, –C*H*), 2.06–2.02 (m, 2H, –C*H₂*), 1.75–1.69 (m, 2H, –C*H₂*), 1.67–1.57 (m, 4H, 2 × –C*H₂*) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 182.89 (*C*O), 182.12 (*C*O), 147.49 (*C*), 134.80 (*C*H), 133.78 (*C*), 131.94 (*C*H), 130.58 (*C*), 126.30 (*C*H), 126.21 (*C*H), 101.40 (*C*H), 53.86 (*C*H), 32.78 (2 × *C*H), 24.14 (2 × *C*H) ppm. HRMS (ESI-TOF): *m/z* [M + H]⁺ calcd for $C_{15}H_{16}NO_2H$, 242.1176; found: 242.1170.

4.3.38 2-(Cyclohexylamino)naphthalene-1,4-dione (3l′). Red solid; yield: 55% (70 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 131–132 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.08 (d, 1H, *J* = 7.6 Hz, Ar–H), 8.03 (d, 1H, *J* = 7.6 Hz, Ar–H), 7.73–7.69 (m, 1H, Ar–H), 7.59 (t, 1H, *J* = 7.6 Hz, Ar–H), 5.85 (d, 1H, *J* = 6.4 Hz, –N*H*), 5.74 (s, 1H, Ar–H), 3.29–3.27 (m, 1H, –C*H*),

2.03 (d, 2H, $J = 12$ Hz, –CH_2), 1.77 (s, 4H, –CH_2), 1.39–1.28 (m, 4H, –CH_2) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): $\delta = 183.09$ (CO), 182.29 (CO), 146.88 (C), 134.86 (CH), 133.80 (C), 131.98 (CH), 130.68 (C), 126.38 (CH), 126.23 (CH), 100.84 (CH), 51.25 (CH), 32.01 ($2 \times$ –CH_2), 25.58 (–CH_2), 24.69 ($2 \times$ –CH_2) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{16}$H$_{18}$NO$_2$H, 256.1332; found: 256.1314.

4.3.39 2-(Benzylamino)naphthalene-1,4-dione (3m′).^{7a} Yellowish solid; yield: 65% (85 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 155–157 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): $\delta = 8.22$–8.19 (m, 1H, Ar–H), 7.99 (d, 1H, $J = 7.6$ Hz, Ar–H), 7.89 (d, 1H, $J = 6.8$ Hz, Ar–H), 7.83–7.79 (m, 1H, Ar–H), 7.75–7.71 (m, 1H, Ar–H), 7.34 (d, 4H, $J = 4.4$ Hz, Ar–H), 7.27–7.24 (m, 1H, –NH), 5.55 (s, 1H, Ar–H), 4.44 (d, 2H, $J = 6.8$ Hz, –NHCH_2Ph) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{17}$H$_{13}$NO$_2$H, 264.1025; found: 264.1018.

4.3.40 2-(Phenethylamino)naphthalene-1,4-dione (3n′).^{5a} Orange solid; yield: 61% (84 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 124–125 °C. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.08$ (d, 1H, $J = 7.2$ Hz, Ar–H), 7.99 (d, 1H, $J = 7.6$ Hz, Ar–H), 7.70 (t, 1H, $J = 7.6$ Hz, Ar–H), 7.58 (td, 1H, $J = 7.6$ Hz, $J = 0.8$ Hz, Ar–H), 7.34–7.30 (m, 2H, Ar–H), 7.25–7.19 (m, 3H, Ar–H), 5.95 (br s, 1H, –NH), 5.76 (s, 1H, Ar–H), 3.46–3.41 (m, 2H, –NHCH_2CH$_2$Ph), 2.96 (t, 2H, $J = 7.2$ Hz, –NHCH$_2$CH_2Ph) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{18}$H$_{15}$NO$_2$H, 278.1181; found: 278.1165.

4.3.41 2-(Diphenyl-l4-azanyl)naphthalene-1,4-dione (3o′).^{7a} Blue solid; yield: 61% (99 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 158–161 °C. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.19$–8.13 (m, 2H, Ar–H), 8.12–8.09 (m, 1H, Ar–H), 7.77–7.75 (m, 2H, Ar–H), 7.56 (d, 2H, $J = 8.8$ Hz, Ar–H), 7.36–7.32 (m, 2H, Ar–H), 7.18 (d, 2H, $J = 7.6$ Hz, Ar–H), 7.11 (s, 1H, Ar–H), 7.09 (d, 1H, $J = 3.6$ Hz, Ar–H), 7.05 (s, 1H, Ar–H), 5.99 (s, 1H, Ar–H) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{22}$H$_{15}$NO$_2$H, 326.1181; found: 326.1199.

4.3.42 2-(Pyrrolidin-1-yl)naphthalene-1,4-dione (3p′).^{7a} Red solid; yield: 57% (65 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 140–142 °C. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.04$ (d, 1H, $J = 7.6$ Hz, Ar–H), 7.98 (d, 1H, $J = 7.6$ Hz, Ar–H), 7.69–7.65 (m, 1H, Ar–H), 7.59–7.55 (m, 1H, Ar–H), 5.72 (s, 1H, Ar–H), 3.94 (br s, 2H, –CH_2), 3.39 (br s, 2H, –CH_2), 1.98 (t, 4H, $J = 6.8$ Hz, $2 \times$ –CH_2) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{14}$H$_{13}$NO$_2$H, 228.1025; found: 228.1017.

4.3.43 2-Morpholinonaphthalene-1,4-dione (3q′).^{7a} Yellow solid; yield: 53% (64 mg, 0.5 mmol scale, hexane/EtOAc 95 : 5 as eluent), mp = 148–150 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$): $\delta = 7.89$ (t, 2H, $J = 7.6$ Hz, Ar–H), 7.81–7.77 (m, 1H, Ar–H), 7.76–7.72 (m, 1H, Ar–H), 6.01 (s, 1H, Ar–H), 3.73–3.70 (m, 4H, $2 \times$ –CH_2), 3.49–3.46 (m, 4H, $2 \times$ –CH_2) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{14}$H$_{13}$NO$_3$H, 244.0974; found: 244.0960.

4.3.44 11H-Benzo[b]phenothiazine-6,11(12H)-dione (3r′).^{18} Red solid; yield: 56% (78 mg, 0.5 mmol scale, hexane/EtOAc 91 : 9 as eluent), mp = 108–111 °C. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.88$–8.85 (m, 1H, Ar–H), 8.30–8.28 (m, 1H, Ar–H), 7.94 (d, 1H, $J = 7.6$ Hz, Ar–H), 7.79–7.72 (m, 2H, Ar–H), 7.49–7.45 (m, 1H, Ar–H), 7.42 (d, 2H, $J = 3.6$ Hz, Ar–H), 6.84 (s, 1H, Ar–H) ppm. HRMS

(ESI-TOF): m/z [M + H]$^+$ calcd for C$_{16}$H$_{19}$NO$_2$SH, 280.0432; found: 280.0451.

4.3.45 2-((4-Isopropylphenyl)amino)-3-(phenylselanyl) naphthalene-1,4-dione (10e). Red solid; yield: 67% (60 mg, 0.2 mmol scale), hexane/EtOAc 97 : 3 as eluent, mp = 184–186 °C. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.16$–8.09 (m, 2H, Ar–H), 7.85 (br s, 1H, –NH), 7.75–7.65 (m, 2H, Ar–H), 7.10–7.07 (m, 1H, Ar–H), 7.01–6.97 (m, 4H, Ar–H), 6.86 (d, 2H, $J = 7.2$ Hz, Ar–H), 6.59 (d, 2H, $J = 8$ Hz, Ar–H), 2.90–2.84 (m, 1H, –CH), 1.25 (d, 6H, $J = 6.4$ Hz, $2 \times$ –CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): $\delta = 181.76$ (CO), 180.56 (CO), 145.36 (C), 143.54 (C), 134.80 (CH), 134.29 (C), 133.50 (C), 132.85 (CH), 131.23 ($2 \times$ CH), 130.61 (C), 129.85 (C), 128.97 (C), 128.62 ($2 \times$ CH), 127.19 (CH), 126.96 (CH), 126.62 (CH), 125.95 ($2 \times$ CH), 122.59 ($2 \times$ CH), 33.82 (–CH(CH$_3$)$_2$), 24.22 (–CH(CH$_3$)$_2$) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{25}$H$_{21}$NO$_2$SeH, 448.0810; found: 448.0818.

4.3.46 2-((4-Chlorophenyl)amino)-3-(phenylselenyl) naphthalene-1,4-dione (10o). Reddish black solid; yield: 79% (69 mg, 0.2 mmol scale), hexane/EtOAc 96 : 4 as eluent, mp = 170–172 °C. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.13$ (qd, 2H, $J = 7.6$ and 1.2 Hz, Ar–H), 7.77–7.72 (m, 2H, Ar–H), 7.71–7.66 (m, 1H, Ar–H), 7.13–7.08 (m, 2H, –NH and Ar–H), 7.02 (t, 2H, $J = 7.6$ Hz, Ar–H), 6.87–6.84 (m, 2H, Ar–H), 6.54 (d, 2H, $J = 8.4$ Hz, Ar–H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): $\delta = 181.99$ (CO), 180.31 (CO), 142.54 (C), 134.90 (CH), 134.75 (C), 133.23 (C), 133.13 (CH), 131.43 ($2 \times$ CH), 130.48 (C), 129.41 (C), 129.12 (C), 128.71 ($2 \times$ CH), 127.88 ($2 \times$ CH), 127.24 (CH), 127.04 (CH), 126.96 (CH), 123.31 ($2 \times$ CH), 114.92 (C) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{22}$H$_{14}$NO$_2$SeH; 439.9951; found: 439.9938.

4.3.47 2-((4-(4-Chlorophenoxy)phenyl)amino)-3- (phenylselanyl)naphthalene-1,4-dione (10w). Reddish black solid; yield: 57% (63 mg, 0.2 mmol scale), hexane/EtOAc 98 : 2 as eluent, mp = 225–227 °C. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 8.16$–8.11 (m, 2H, Ar–H), 7.83 (br s, 1H, –NH), 7.76–7.72 (m, 1H, Ar–H), 7.70–7.66 (m, 1H, Ar–H), 7.30 (d, 2H, $J = 8.8$ Hz, Ar–H), 7.12 (t, 1H, $J = 7.2$ Hz, Ar–H), 7.07–7.03 (m, 2H, Ar–H), 6.95–6.93 (m, 4H, Ar–H), 6.79 (d, 2H, $J = 8.8$ Hz, Ar–H), 6.65 (d, 2H, $J = 8.8$ Hz, Ar–H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): $\delta = 181.74$ (CO), 180.45 (CO), 156.20 (C), 153.56 (C), 143.53 (C), 134.92 (CH), 133.40 (C), 132.99 (CH), 132.43 (2C), 131.11 ($2 \times$ CH), 130.52 (C), 129.88 ($2 \times$ CH), 128.76 ($2 \times$ CH), 128.35 (C), 127.27 (CH), 127.01 (CH), 126.83 (CH), 124.22 ($2 \times$ CH), 119.81 ($2 \times$ CH), 118.66 ($2 \times$ CH), 113.30 (C) ppm. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for C$_{28}$H$_{18}$ClNO$_3$SeH, 532.0213; found: 532.0221.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this study are available in the published article and its SI.

Scanned copies of ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR (for **3n**, **3s**, **3t**, **3u**, and **3v**, and **3c′**) of the synthesised compounds are supplemented. See DOI: https://doi.org/10.1039/d5mr00068h.

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