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One-Pot Synthesis and Structure–Property Relationship of Aminomaleimides: Fluorescence Efficiencies in Monomers and Aggregates Easily Tuned by Switch of Aryl and Alkyl

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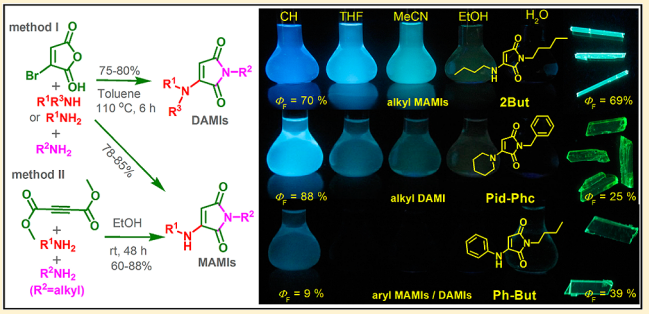
Supporting Information

ABSTRACT: Organic fluorophores have attracted great interest owing to their wide applications. They usually contain an electron-conjugated system with an aromatic moiety and show high emission in dilute solutions but weaker or even no emission upon aggregation. Here, a simple one-pot, three-component reaction (3CR) (method I) for the synthesis of various di- and monosubstituted aminomaleimides (DAMIs and MAMIs) has been developed, and the reported 3CR (method II) has been found to be efficient only for the synthesis of MAMIs with R^2 = alkyl. Twelve AMIs were designed and synthesized for investigation of the influence of structures on their optical properties in monomers and aggregates. It was found that alkyl MAMIs, alkyl DAMIs, and aryl AMIs/DAMIs show very different fluorescence efficiencies in different solvents, and only MAMIs with butyl and oleyl show high emissions in powders similar to those in nonpolar solutions. Single-crystal structures indicate that their fluorescence efficiencies in aggregates mainly correlate with molecular packing modes. The efficient synthesis method, the sensitive fluorescence on–off response to protic solvents or polar solvents, and the unusual high emissions of AMI without any aromatic moiety in both monomer and aggregates are expected to attract great interest in the fields of application and theory.



INTRODUCTION

Organic fluorophores have attracted great interest owing to their wide applications. They generally contain rigid aromatic groups and are highly emissive in dilute solutions but show less or even no emission upon aggregation,[1] which is frequently referred to as the aggregation-caused quenching (ACQ) effect. Because fluorophores are usually used in relatively concentrated solutions or solid states, the ACQ effect becomes a thorny problem in many practical applications. Therefore, different methods have been developed to overcome the effect, such as increasing distance by introduction of bulky substituents,[2−4] controlling *J*-aggregation,[5−7] and cross-dipole molecular packing modes.[8] In 2001, a propeller-like fluorophore, 1-methyl-1,2,3,4,5-pentaphenylsilole, was found to be not emissive in solutions but strongly emissive upon aggregation, which was termed as aggregation-induced emission (AIE).[9] The AIE characteristics overcome the ACQ effect fundamentally. For the past decade, AIE compounds have been shown to have great advantages in many areas such as organic light-emitting diodes (OLEDs),[10,11] chemo/biosensors,[12−16] and bioimaging.[17,18] Experimental results prove that AIE fluorophores generally possess twist molecular structures with aromatic rotors that efficiently prevent $\pi-\pi$ stacking.[19−22] In spite of their comprehensive applications, the AIE compounds are limited to the application in solutions because they are not emissive in monomers. Therefore, the fluorophores with high fluorescence efficiency in both dilute solutions and aggregates are expected to have wider scope of applications and still remain an interesting topic. For example, Yuan et al. have tried to obtain high fluorescence efficiencies in both solutions and aggregates via conjugation-induced rigidity in twisting molecules.[23]

Maleimides, a class of organic fluorophores with many interesting properties such as tunable emission wavelength,[24] sensitivity to solvent polarity,[24,25] and high selective reactivity to thiol,[26,27] have been used as OLED materials,[28,29] metal ion sensors,[30,31] pH sensors,[32] cell imaging dyes,[26,27,33] etc. Recently, 2-arylamino-*N*-arylmaleimides have been found to have AIE characteristics[32,34] and mechanochromic luminescence.[35] All reported maleimides contain aromatic moieties except two alkylaminomaleimides and four alkylaminobromomaleimides, as reported in 2015 by the O'Reilly group.[36]

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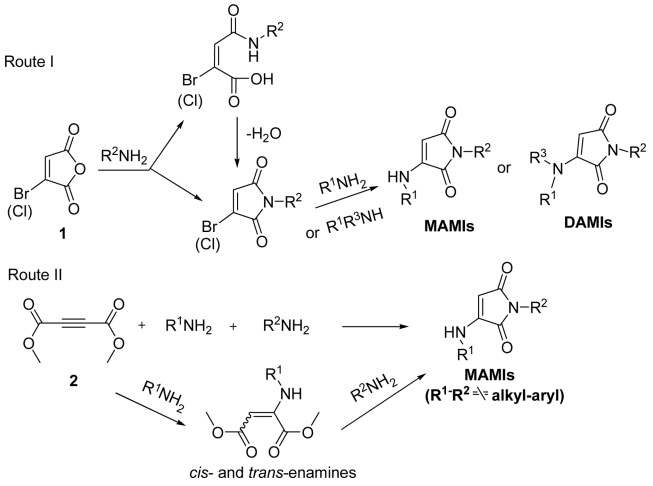
However, they only studied the optical properties of these aminomaleimids (AMIs) in different solutions.

In our previous research on the multicomponent reaction (MCR) of but-2-ynedioate, primary amine and aldehyde for the synthesis of hetereocycles,[37,38] we obtained a byproduct, 2-butylamino-*N*-butylmaleimide (**2But** in Scheme 3), whose bright cyan light on the thin-layer chromatography plate under daylight, like a fluorescent stick, impressed us deeply. However, we did not pay any attention to the optical properties but the synthetic methodology[37−39] until we developed a convenient five-component reaction for the synthesis of a series of novel C6-unsubstituted tetrahydropyrimidines (THPs) with useful AIE characteristics.[40] Interestingly, we found that THPs possess unconventional intramolecular through-space electronic conjugation[22] and can be used as fluorescent sensors for copper ions,[41] the critical micelle concentration (CMC) of ionic surfactants,[42,43] and temperature.[44] In the process of the investigation into the application of THPs as fluorescent sensors, we found that although AIE THPs possess the advantage of highly sensitive fluorescence on−off change, it is difficult to prepare samples for optical measurements because they are used as suspensions[41−43] or solid states[44] whose sizes influence sample stabilities[41−43] or optical properties[44] and hence are needed to be controlled with suitable methods, which increase experimental procedures and difficulties. At this point, an assumption came to mind that if a fluorophore can be used as a fluorescence on−off sensor in solution, it will be advantageous both in the high sensitivity of fluorescence on−off change and in the convenience and simplicity of sample preparation. The simple molecular structure and strong solid-state fluorescence of **2But** excited our interest so that we raised the following questions: Can **2But** be used as a fluorescence on−off sensor in solution? Does it show AIE, ACQ, or high emission in both monomers and aggregates? What is the influence of substituents on the optical properties of AMIs? To answer these questions, we synthesized AMIs with aryl and alkyl substituents and studied their optical properties in different solvents and powders via steady-state absorption, excitation and emission spectra, as well as fluorescence quantum yields (Φ_F). Here, the results are reported.

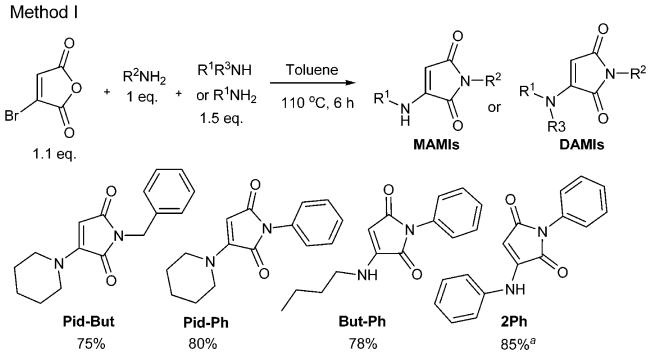
RESULTS AND DISCUSSION

Design and Synthesis. AMIs can generally be synthesized from 3-halofuran-2,5-dione (**1**) via route I[45,46] or from dimethyl but-2-ynedioate (**2**) via route II[34,47−50] (Scheme 1). Route I contains a two-step[46] and a three-step reaction[45] that can afford both various monosubstituted aminomaleimides (MAMIs) and disubstituted aminomaleimides (DAMIs). However, the two-step[46] and three-step reactions[45] in route I can afford only 8−35% total yields. Route II includes a two-step reaction. In our previous work,[38] we studied the influence of solvents on the reaction of **2** and primary amines (R^1NH_2) and found that protic and aprotic solvents, respectively, favor the formation of *cis*- and *trans*-enamines, but only a mixture of *cis*- and *trans*-enamines (*cis*/*trans* = 97:3) was obtained because they were interconvertible during processes of separation and purification. The reaction of **2** and R^1NH_2 (R^1 = alkyl or aryl without strong electron-withdrawing groups such as NO_2^-), acting as an exothermic reaction, can be conducted at room temperature in different solvents in yields greater than 98%. The two-step reactions in route II can proceed in one pot, with good to excellent yields.[34,47,48,50,51] The one-pot reaction can proceed successfully at room temperature when R^2 is alkyl[50,51] but only at a temperature higher than 180 °C when R^2 is aryl without electron-withdrawing groups and R^1 is aryl.[34,47,48] The synthesis of MAMIs with R^1−R^2 = alkyl−aryl and DAMIs via the one-pot reaction has not been reported. In this study, we tried the synthesis under different conditions but failed. Then, we optimized solvents and temperature and found that both MAMIs and DAMIs could be synthesized by the one-pot, three-component reaction (3CR) in good yields (method I depicted in Scheme 2). With the highly efficient 3CR in hand, we synthesized MAMIs with R^2 = aryl and DAMIs via the 3CR in Scheme 2 and MAMIs with R^1 = alkyl via the reported 3CR[51] in Scheme 3.

Scheme 1. Two Conventional Routes for the Synthesis of MAMIs and DAMIs



Scheme 2. Synthesis of DAMIs or MAMIs with R^2 = Aryl via the Developed 3CR in This Work[a]



[a]A certain amount (0.5 times the amount of toluene) of *N*,*N*-dimethylformamide was needed to dissolve the intermediate for the synthesis of **2Ph**.

Optical Properties of 2But in Different Solvents and Aggregate Sizes. The optical properties of **2But** in different solvents were investigated first. As depicted in Figure 1, **2But** shows an obvious red shift in absorption (λ_{ab}) (39 nm) (Figure 1b) and emission peaks (λ_{em}) (85 nm) (Figure 1a,c) from nonpolar cyclohexane (CH) to polar water. Meanwhile, the fluorescence was quenched in water. The detailed optical data of **2But** are listed in Table 1. Compared with the optical data of **2But** in CH, polar aprotic solvents THF and MeCN displayed a small influence on λ_{ab} (red shift of 12 and 20 nm, respectively) and Φ_F (1.1 and 1.6 times lower, respectively) and almost no

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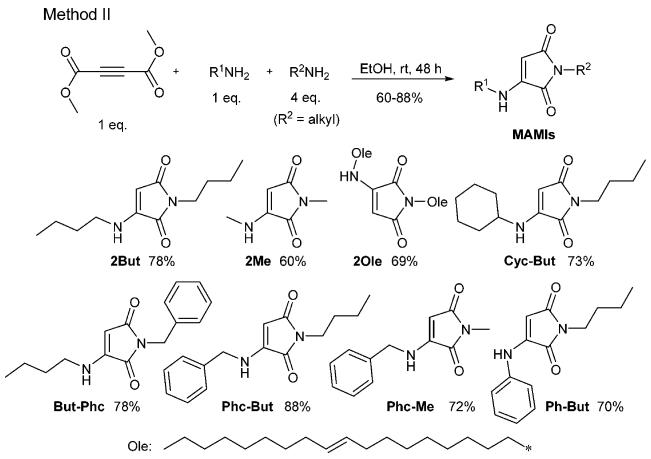
Scheme 3. Synthesis of MAMIs with R^2 = Alkyl via the Reported 3CR[51]



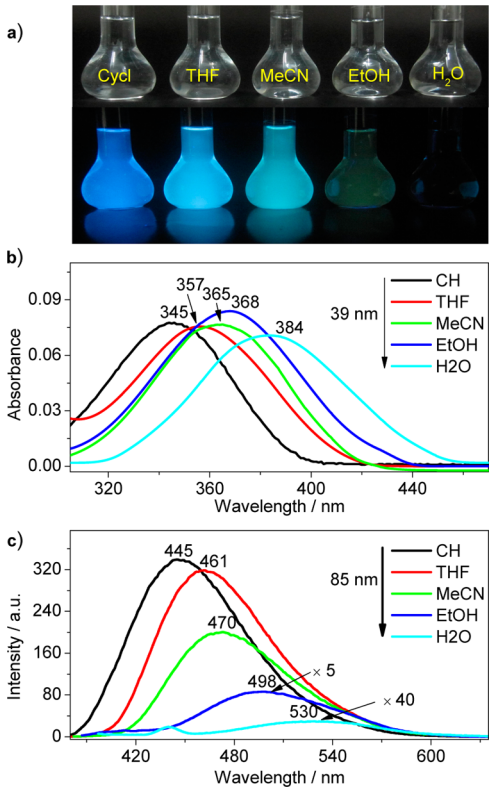


Figure 1. Optical properties of **2But** in cyclohexane (CH), tetrahydrofuran (THF), acetonitrile (MeCN), ethanol (EtOH), and water (H_2O) (2.00 × 10^{-5} M). (a) **2But** in different solvents under daylight (top) and UV light (365 nm) (bottom). (b) Absorption spectra and (c) emission spectra (excited at the peak marked in (b); excitation and emission slit widths: 3 and 3 nm).

influence on Stokes shift (Δs) (red shift of only 4 and 5 nm, respectively). However, protic solvents such as ethanol (EtOH) and water caused a sharp decrease of Φ_F (23 and 700 times lower, respectively), a distinct red shift of λ_{ab} (23 and 39 nm, respectively), and changes in Δs (30 and 46 nm, respectively). The fluorescence quenching and the large changes in λ_{ab} and Δs are expected to be caused by hydrogen bonding between protic solvent and **2But**, as reported with many fluorophores containing a carbonyl group.[52−55]

Table 1. Optical Properties of 2But in Solutions and Aggregates

solution or aggregate	ε^a/ cm^{-1} M^{-1}	λ_{ab}/ nm	λ_{em}/ nm	Δs/nm (cm^{-1})	$\Phi_F{}^b$/%
CH	4165	345	445	100 (6514)	70
THF	3915	357	461	104 (6319)	62/63[c]
MeCN	4040	365	470	105 (6121)	44
EtOH	5955	368	498	130 (7094)	3
H_2O	3220	384	530	146 (7174)	0.1
crystal-L		427[d]	480	53 (2641)	50[c]
crystal-S		395[d]	476	81 (4308)	56[c]
powder		380[d]	472	92 (5129)	69[c]

[a]Molar absorption coefficient of **2But** in solution (2.00 × 10^{-5} M). [b]Relative quantum yields with 9,10-diphenylanthracence in ethanol (5.00 × 10^{-6} M) as standard (Φ_F = 0.95)[56] (excited at 350 nm). [c]Absolute quantum yield determined via calibrated integrating sphere (excited at 350 nm). [d]Lower-energy excitation peak in Figure 2b.

The optical properties of **2But** in solids were investigated to understand the influence of aggregation on its optical properties. Since the fluorescence efficiencies of conventional organic fluorophores correlate with aggregate sizes,[57−61] the Φ_F values of **2But** in different aggregate sizes were measured. As shown in Figure 2, when aggregate size decreases from a large

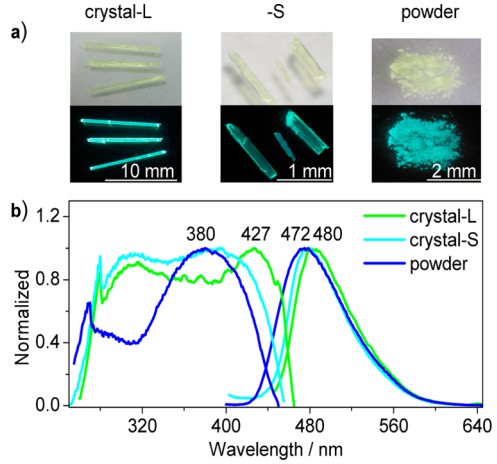


Figure 2. Optical properties of **2But** in different sizes of aggregates. (a) Photos taken under daylight (top) and UV light (365 nm) (bottom). (b) Excitation (left) and emission (right) spectra. L and S represent large and small, respectively.

crystal to powder (ground crystals) (Figure 2a), **2But** shows a blue shift of 47 nm in λ_{em} (left spectra in Figure 2b) but a blue shift of only 8 nm in λ_{em} (right spectra in Figure 2b). Meanwhile, the Φ_F increases from 50 to 69% (Table 1). The fluorescence quantum yield (69%) of **2But** in powder is almost the same as that (70%) in CH; that is, the fluorescence efficiencies of **2But** in aggregates and monomers are almost the same. The distinct blue shift in excitation spectra of **2But** with a decrease of aggregate sizes is because Coulombic interaction energies between molecules become smaller, resulting in the wider band gaps.[58,62,63] The slight changes in the λ_{em} and Φ_F with aggregate size could mainly arise from the reabsorption of higher-energy fluorescence[64] because the Stokes shift (53 nm) of **2But** in crystals is much smaller than that (92 nm) in powder.

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Table 2. Optical Properties of AMIs in Solvents and Powder

entry	AMIs	solution/powder[a]	ε[b]/cm^{-1} M^{-1}	λ_{ab}/nm	λ_{em}/nm	Φ_F[c]/%
1	**2But**	CH	4165	345	445	70
		THF	3915	357	461	62
		MeCN	4040	365	470	44
		EtOH	5955	368	498	3
		water	3220	384	530	0.1
		powder		380[d]	472	69[e]
2	**2Ol**	CH	5655	346	446	72
		THF	7100	357	464	53
		MeCN	7040	359	472	36
		EtOH	9675	365	499	2
		water[f]	1950	362	491	3
		powder		440[d]	485	62[e]
3	**2Me**	CH	5305	343	448	65
		THF	7850	356	462	45
		MeCN	7660	357	473	26
		EtOH	7805	361	496	2
		water	7490	374	529	0.1
		powder		437[d]	483	34[e]
4	**Cyc-But**	CH	3860	345	445	71
		THF	6100	358	463	48
		MeCN	5545	363	472	34
		EtOH	6105	367	500	2
		water	2575	379	535	0.03
		powder		440[d]	486	34[e]
5	**But-Phc**	CH	3150	344	448	71
		THF	3850	357	463	69
		MeCN	4775	358	470	40
		EtOH	4895	361	495	5.4
		water	2460	381	526	0.3
		powder		434[d]	486	31[e]
6	**Phc-But**	CH	3040	344	446	70
		THF	3640	357	460	63
		MeCN	3285	359	473	43
		EtOH	4435	364	496	5.0
		water	1680	380	527	0.3
		powder		433[d]	488	18[e]
7	**Phc-Me**	CH	3040	344	446	66
		THF	2910	357	461	45
		MeCN	3200	360	470	43
		EtOH	4525	367	497	0.1
		water	4785	377	527	0.0
		powder		438	486	21[e]
8	**Pid-Phc**	CH	2315	370	464	88
		THF	2465	380	476	7
		MeCN	6705	382	490	1
		EtOH	5620	388	516	1
		water	3680	405	547	0.3
		powder		464[d]	506	25[e]
9	**2Ph**	CH	3505	370	447	0.3
		THF	3065	379	435	0.9
		MeCN	4690	380	ne[g]	ne[g]
		EtOH	3085	382	ne[g]	ne[g]
		powder		449[d]	496	17[e]
10	**Ph-But**	CH	7235	366	450	8.6
		THF	6670	375	454	0.0
		MeCN	6535	378	ne[g]	ne[g]
		EtOH	8075	384	ne[g]	ne[g]
		powder		440[d]	492	39[e]
11	**But-Ph**	CH	2035	352	452	2
		THF	2505	363	473	0.5
		MeCN	3400	367	460	0.3
		EtOH	4575	372	ne[g]	ne[g]
		powder		414[d]	474	38[e]
12	**Pid-Ph**	CH	4335	371	486	0.7
		THF	4365	378	491	1
		MeCN	5055	382	495	0.9
		EtOH	4425	390	520	0.6
		powder			ne[g]	ne[g]

[a]Ground crystals or as-prepared solid. [b]Molar absorption coefficient of AMIs in solution (2.00×10^{-5} M). [c]Relative quantum yields with 9,10-diphenylanthracence in ethanol (5.00×10^{-5} M) as standard (Φ_F = 0.95)[56] (excited at 350 nm). [d]Lower-energy peak in the excitation spectrum. [e]Absolute quantum yield determined via calibrated integrating sphere (excited at 350 nm). [f]**2Ol** is not completely soluble in water. [g]No emission.

Optical Properties of Other AMIs in Different Solvents and Powder. **2But** possesses high emission in both monomers and aggregates, and its high emission is quenched in protic solvents. What about the optical properties of other AMIs with aliphatic or aromatic substituents? To answer this question, we designed and synthesized 11 other AMIs (molecular structures are shown in Schemes 2 and 3). The optical properties of all synthesized AMIs in different solvents and powder are listed in Table 2. It can be seen that substituents show great influences on the Φ_F values of AMIs in different solvents. According the substituent influence on Φ_F, AMIs can be classified into three types: dialkyl MAMIs (entries 1−7), trialkyl DAMIs (entry 8), and aryl AMIs (entries 9−12). The fluorescence efficiencies of dialkyl MAMIs are high in nonpolar solvent CH (Φ_F = 65−72%), moderate in polar solvents such as THF and MeCN (Φ_F = 34−69%), and very low in protic solvents such as EtOH and water (0.03−3%). They have almost the same λ_{ab} and λ_{em} values in CH, which proves that their emissions arise from the same aminomaleimide skeleton. However, only **2Ol** and **2But** are highly emissive in powder (Φ_F = 62 and 69%), and other dialkyl MAMIs display much lower fluorescence efficiencies (Φ_F = 18−34%). In other words, only MAMIs with long-chain alkyl demonstrate high emission in both monomers and aggregates, and other dialkyl MAMIs show the ACQ effect.

Alkyl DAMI **Pid-Phc** (entry 8) is highly emissive (Φ_F = 88%) in CH, but there is almost no emission in aprotic polar and protic solvents. Compared with dialkyl MAMI **But-Phc** in CH (entry 5), **Pid-Phc** shows a red shift of 26 nm in λ_{ab} and an 18% increase in Φ_F, which means that the substitution of hydrogen on N by alkyl increases the electron conjugation and hence leads to a red shift in λ_{ab} and enhancement in Φ_F. In addition, the emission of **Pid-Phc** is quenched not only by protic solvents but also by polar aprotic solvents. The moiety −N−C═C−C═O in AMIs, a typical electron donor and acceptor structure, usually causes twisted intramolecular charge transfer (TICT) and leads to fluorescence quenching in polar solvent.[65−68] Therefore, the fluorescence quenching of **Pid-Phc** in polar solvents is expected to be caused by TICT. The reason why the fluorescence of alkyl MAMIs is not quenched in polar solvent might be that the intramolecular hydrogen bond (HB)

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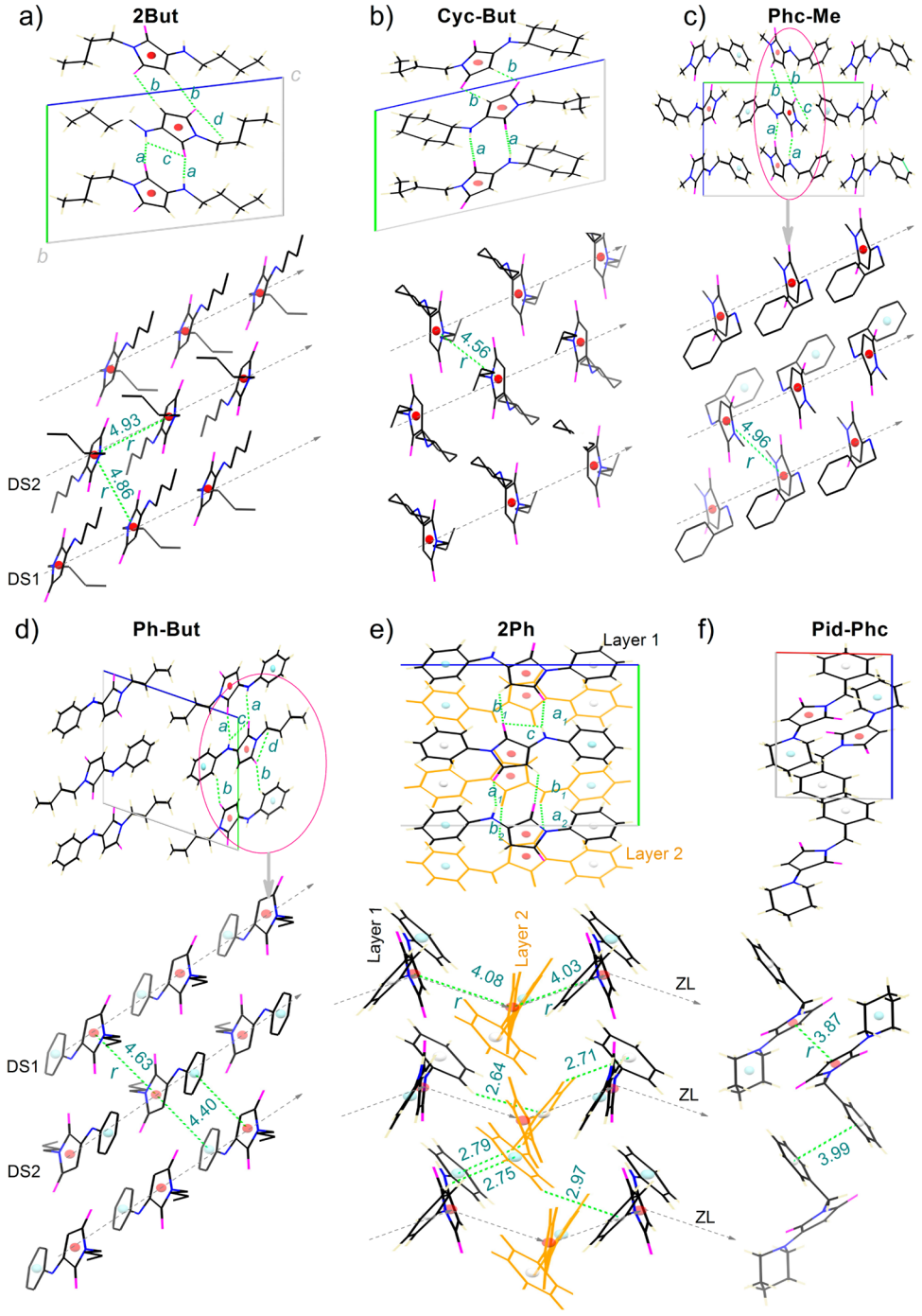

Figure 3. Molecular alignments of **2But** (CCDC 1430703), **Cyc-But** (CCDC 1513071), **Phc-Me** (CCDC 1513072), **Ph-But** (CCDC 1513073), **Ph** (CCDC 938824),[34] and **Pid-Phc** (CCDC 1430704) in single crystals. (a–e) Front view (top) and side view (bottom). Hydrogen atoms in the side view were omitted for clarity. The molecules in (e) marked in different colors indicate different molecular conformations.

between hydrogen on N and the adjacent carbonyl oxygen prevents the rotation of the C–N bond in the –N–C=C–C=O moiety; that is, it prevents the TICT effect. Although the Φ_F of **Pid-Phc** is 88% in CH, its Φ_F in powder is only 25%, which means that it displays a stronger ACQ effect.

Aryl AMIs (entries 9–12) display very weak or almost no emission in different solvents owing to nonradiative transition that is caused by phenyl rotation as common AIE compounds with aromatic rotors.[9,20,22] Compared with **2But** in CH (entry 1), **Ph-But** (entry 10) and **But-Ph** (entry 11) show red shifts of 21 and 7 nm in λ_{ab}, respectively, which indicates that phenyl at different positions could enhance the electron conjugation to various extents. The Φ_F values of aryl MAMIs **2Ph**, **Ph-But**, and **But-Ph** in powder are 17, 39, and 38%, respectively, and aryl DAMI is not emissive (entry 12). That is, aryl MAMIs show an AIE effect, and aryl DAMI is not emissive in both monomers and aggregates.

Single-Crystal Structures of Alkyl and Aryl AMIs. The excitation peaks of AMIs in powders are distinctly red-shifted (35–95 nm red shift) compared with their λ_{ab} values in CH (Table 2), which indicates that the red-shifted emissions in powder originate from aggregates rather than molecular

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planarization.[69] The formations of dimers,[70] excimers,[71−73] short-range ring interactions,[22] and *J*-aggregates (aggregates where molecules are arranged head-to-tail)[5,74,75] usually cause such red-shifted emissions in aggregates. To understand the red-shifted emission of AMIs in aggregates, the single-crystal structures of alkyl MAMIs (**2But**, **Cyc-But**, and **Phc-Me**) and DAMI (**Pid-Phc**), aryl MAMI **Ph**, as well as aryl/alkyl MAMI **Ph-But** were investigated. (All single-crystal structures are measured in this work except for that of **Ph**,[34] and the main crystallographic data of these AMIs are shown in Table S1 in the Supporting Information.)

From the molecular packing on the *bc* plane shown in Figure 3a−d, it can be seen that the molecules of dialkyl MAMIs (**2But**, **Cyc-But**, and **Phc-Me**) and aryl/alkyl MAMI **Ph-But** are connected as dimers via two N−H···O (2.08−2.28 Å, 160−169°) HBs (marked as green *a*), and the dimers are connected by two weaker C−H···O bonds (2.47−2.54 Å, 142−177°) (marked as green *b*). Weak intramolecular HBs could be observed (marked as green *c* and *d*). The dimers are packed as two parallel stairs with a central ring co-plane and the nitrogen atom of central ring on an opposite site (DS1 and DS2 represent two parallel stairs packed via dimers). Although all of these MAMIs show similar dimer-packed parallel stairs, the short-range ring interactions with the distance (*r*) between ring centers shorter than 5 Å are different. The short-range ring interactions between stairs exist in all MAMIs, but the interactions along the stair direction are observed only in **2But**. Compared with the λ_{ab} (345 and 344 nm, respectively) and Φ_F (71 and 66%, respectively) values of **Cyc-But** and **Phc-Me** in CH, **2But** in CH has almost the same λ_{ab} (345 nm) and Φ_F (70%) values. However, **2But** in powders is obviously different from **Cyc-But** and **Phc-Me** in powder in terms of the values of λ_{ex} (380 nm vs 440 and 438 nm, respectively) and Φ_F (69% vs 34 and 21%, respectively). Since they have almost the same optical properties in monomers and similar molecular packing modes (dimer-packed parallel stairs), the distinctly different optical properties between them are assumed to come from the different intermolecular interactions along the stair direction.

The molecular arrangement on the *bc* plane of diaryl MAMI **2Ph** (top of Figure 3e) is different from those of dialkyl or alky/aryl MAMIs. The molecules on the *bc* plane are connected as layers rather than dimers via intermolecular N−H···O and C−H···O. Since four different conformations exist in single crystals, the two kinds of intermolecular HBs are different in different layers (N−H···O in layer 1 and 2: 2.12 Å, 162° and 2.13 Å, 159°, marked as a_1 and a_2, respectively; C−H···O in layer 1 and 2: 2.42 Å, 130° and 2.43 Å, 132°, marked as b_1 and b_2). From the side view (bottom of Figure 3e), it can be seen that the molecules are placed as zigzag lines (ZLs) via short-range ring interactions between the central rings with r = 4.08 and 4.03 Å. The dihedral angle between the central rings along the zigzag lines is equal to 18°, with the nitrogen atom of the central ring on the opposite site. In addition, there are five weak C−H···π bonds (2.64−2.97 Å, 132−144°) between the adjacent molecules. All molecules of **2Ph** in aggregates are connected as a net by intermolecular HBs and short-range ring interactions. Since the distance *r* along zigzag lines is nearly 4 Å, which means the existence of strong $\pi-\pi$ interactions, the large red-shift emission of **2Ph** is expected to originate mainly from the zigzag line arrangement.

The molecular packing of DAMI **Pid-Phc** is shown in Figure 3f. Without hydrogen on the N atom, that is, without intermolecular N−H···O, the distance *r* between the central rings becomes shorter (3.87 Å) and forms slipped parallel dimers,[76,77] which will lead to excimer formation and hence fluorescence decrease or quenching.[1] This explains a distinct fluorescence decrease of **Pid-Phc** in powder (Φ_F = 25%) compared to that in CH (Φ_F = 88%) and the almost no emission of **Pid-Ph** in powder.

The single-crystal structures of these AMIs indicate that intermolecular N−H···O and $\pi-\pi$ stacking interactions are two important factors influencing molecular packing of AMIs. For dialkyl or aryl/alkyl MAMIs, the intermolecular hydrogen bond N−H···O is the main factor that leads to formation of hydrogen-bonded dimers that are packed as parallel stairs with r > 4.56 Å; for diaryl MAMIs, an intermolecular $\pi-\pi$ stacking interaction becomes the main factor, which leads to $\pi-\pi$-packed zigzag arrangement with r = 4.03 and 4.08 Å; for DAMIs without hydrogen on the nitrogen atom, that is, without intermolecular N−H···O, $\pi-\pi$ stacking interaction leads to the formation of $\pi-\pi$-packed slipped parallel dimers with r = 3.87 Å. These molecular packing modes and the r values show great influence on the fluorescence efficiencies of AMIs. Only the parallel stair-like arrangement packed via hydrogen-bonded dimers with r = 4.931 Å in **2But** gives high solid-state emission.

CONCLUSION

In this study, we have investigated the synthesis and structure−property relationship of AMIs. A 3CR based on 3-halofuran-2,5-dione (method I) has been developed for the synthesis of DAMIs and MAMIs with different substituents in overall yields (75−85%) much higher than those (8−35%) of the reported two-step or three-step reactions in route I. In addition, we found that the reported 3CR based on dimethyl but-2-ynedioate (method II) is suitable for the synthesis of *N*-alky MAMIs but limited to the synthesis of DAMIs and *N*-aryl MAMIs. Furthermore, 12 AMIs were designed and synthesized for investigation of the relationship between structures and optical properties. Our experimental results indicate that the fluorescence efficiencies of AMIs in monomers and aggregates can be easily tuned by switching alkyl and aryl: alkyl AMIs show high emission in both monomers and aggregates or the ACQ effect, whereas AMIs with aryl display almost no emission in both monomers and aggregates or the AIE effect. The high emissions (Φ_F up to 88%) of AMIs in monomers, proving to originate from the aminomaleimide skeleton, will be quenched in protic solvents by the hydrogen bonding effect for alkyl MAMIs, in polar solvents by TICT effect for alkyl DMIs, or in different solvents by the rotations of aryl for AMIs with aryl. The red-shifted emissions of AMIs in aggregates as compared to those in monomers mainly correlate with intermolecular N−H···O and $\pi-\pi$ stacking interactions that cause formation of dimer-packed parallel stair-like arrangements, zigzag lines, or $\pi-\pi$-stacked dimers. The simple synthesis method, high emission in both monomers and aggregates, and sensitive response to protic and polar solvents of AMIs are useful for practical applications. Further investigation into the applications of AMIs as bio- and chemical fluorescent sensors are underway in our laboratory.

EXPERIMENTAL SECTION

Materials and Instruments. All chemicals used in this study were obtained from commercial suppliers and used without further purification. For measurement of the optical spectra of samples,

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spectroscopically pure solvents and doubly distilled water were used. All melting points were taken on a micro-melting-point apparatus and are uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded on a 400 MHz NMR spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Low-resolution and high-resolution mass spectra were obtained using electrospray ionization (ESI) and quadrupole linear ion-trap techniques. IR spectra were obtained as liquid films on potassium bromide pellets with a Fourier transform infrared spectroscope. Photos were taken on a Canon PC1356. The absorption and fluorescence excitation and emission properties were analyzed by a UV−vis spectrophotometer (measurement wavelength range = 190−100 nm; wavelength accuracy = ±2 nm) and a spectrofluorophotometer (150 W xenon lamp; measurement wavelength range = 220−750 nm; wavelength accuracy = ±1.5 nm; S/N ratio = 150; slit width = 1.5/3/5/10/15/20). The absolute fluorescence quantum yields were measured using a calibrated integrating sphere.

General Procedure for the One-Pot Synthesis of *N*-Alky1 MAMIs (Entries 1−7 and 10 in Table 2). The intermediate enamines were prepared by the addition reaction of dimethyl but-2-ynedioate and primary amine as described in our previous work.[38] That is, the mixture of EtOH (6 mL), dimethyl but-2-ynedioate (284 mg, 2 mmol), and primary amine (2 mmol) was kept at room temperature for 5−10 min for the synthesis of intermediate enamines. Then, to the reaction mixture was added primary aliphatic amine (8 mmol). After the reaction was completed (stirred at room temperature for 48 h), the product mixtures were purified by column chromatography with petroleum ether/ethyl acetate (6:1) as eluent to afford the desired products (60−88% yields).

General Procedure for the One-Pot Synthesis of *N*-Aryl MAMIs (Entries 9 and 11 in Table 2) and DAMIs (Entries 8 and 12 in Table 2). Bromomaleic anhydride (389 mg, 2.2 mmol) and primary amine (2 mmol) were added into 4 mL of toluene in sequence, kept at rt for 10 min, and then at 110 °C for 6 h. Then, to the reaction mixture was added primary or secondary amine (3 mmol). The reaction mixture was stirred until the temperature was reduced to room temperature, and then the solution was removed by compressed air. Then crude product was separated by column chromatography with petroleum ether/ethyl acetate (6:1) as eluent to afford the desired products (75−85% yield).

Preparation of 2But in Different Aggregate Sizes. Different sizes of crystals of **2But** were prepared by recrystallization from dichloromethane/*n*-hexance solution at room temperature for different times.

Preparation of AMIs in Different Solvents (2.00×10^{-5} M). Tetrahydrofuran stock solutions of 12 AMIs with a concentration of 1 mM were prepared. One hundred microliters of the stock solution was then transferred to 5 mL volumetric flasks, with tetrahydrofuran removed by N_2, and then the flasks were filled to the mark with corresponding solvents for preparation of different solutions of 12 AMIs except for their tetrahydrofuran solutions. The tetrahydrofuran solutions of 12 AMIs were prepared by adding 100 μL of tetrahydrofuran stock solutions into a 5 mL volumetric flask and then filling the flasks to the mark with tetrahydrofuran.

Structure Characteristics of 12 AMIs in Table 2. *2-Butylamino-N-butylmaleimide (**2But**):* 78% (350 mg, 1.56 mmol) yield, light yellow solid, mp = 81.0−81.3 °C; IR (KBr) ν_{max} = 3321, 3097, 2955, 2933, 2866, 1689, 1636, 1448, 1035, 783 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.34 (s, 1H), 4.80 (s, 1H), 3.48 (t, J = 7.2 Hz, 2H), 3.21−3.16 (m, 2H), 1.71−1.52 (m, 4H), 1.49−1.28 (m, 4H), 0.98 (t, J = 7.2 Hz, 3H); 0.94 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.6, 167.6, 149.2, 83.7, 43.9, 37.3, 30.8, 30.5, 20.0, 13.6 ppm; MS (ESI) m/z 225 (M + H$^+$, 100), 449 (2M + H$^+$, 95) and HR-ESI-MS for $C_{12}H_{20}N_2O_2$ ([M + Na]$^+$) calcd 247.1417; found 247.1414. The compound has CAS Registry Number 457959-70-5, but no reference on it has been found by SciFinder.

*2-Oleylamino-N-oleylmaleimide (**2Ol**):* 69% (845 mg, 1.38 mmol) yield, yellow solid, mp = 62.5−62.6 °C; IR (KBr) ν_{max} = 3477, 3334, 2955, 2915, 2849, 1692, 1643, 1469, 1099, 1266, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.37−5.33 (m, 4H), 4.76 (s, 1H), 3.43 (t, J = 7.2 Hz, 2H), 3.14 (q, J = 6.8 Hz, 2H), 2.00 (s, 5H), 1.63−1.53 (m, 6H), 1.25 (s, 47H), 0.89−0.85 (t, J = 6.4 Hz, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.6, 167.6, 149.2, 123.0, 129.9, 83.7, 44.3, 37.6, 32.5, 31.9, 29.3, 27.2, 26.8, 22.6, 14.1 ppm; MS (ESI) m/z 635 (M + H$^+$, 10), 301 (100) and HR-ESI-MS for $C_{40}H_{72}N_2O_2$ ([M + H]$^+$) calcd 613.5667; found 613.5654.

*2-Methylamino-N-methylmaleimide (**2Me**):* 60% (168 mg, 1.2 mmol) yield, yellow solid, mp = 147.2−147.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.43 (s, 1H), 4.84 (s, 1H), 2.98 (s, 1H), 2.95 (d, J = 5.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.5, 167.4, 150.4, 84.1, 30.5, 23.4 ppm; ^{1}H and ^{13}C NMR spectra are consistent with the previous literature.[51]

*2-Cyclohexylamino-N-butylmaleimide (**Cyc-But**):* 73% (365 mg, 1.46 mmol) yield, light yellow solid, mp = 73.8−74.1 °C; IR (KBr) ν_{max} = 3327, 3021, 2930, 2858, 1698, 1633, 1452, 1439, 1379, 1335, 1169, 1108, 1049 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.34 (d, J = 6.8, 1H), 4.77 (s, 1H), 3.47 (t, J = 7.2, 2H), 3.18−3.15 (m, 1H), 2.02−1.99 (m, 2H), 1.82−1.53 (m, 5H), 1.42−1.24 (m, 7H), 0.93 (t, J = 7.2, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.7, 167.8, 147.9, 83.4, 53.1, 37.3, 31.9, 30.8, 25.3, 24.4, 19.9, 13.6 ppm; MS (ESI) m/z 635 (M − H$^+$, 30), 75 (100) and HR-ESI-MS for $C_{14}H_{22}N_2O_2$ ([M + H]$^+$) calcd 251.1754; found 251.1769.

*2-Butylamino-N-benzylmaleimide (**But-Phc**):* 78% (403 mg, 1.56 mmol) yield, light yellow solid, mp = 107.2−107.6 °C; IR (KBr) ν_{max} = 3323, 3117, 2923, 1739, 1701, 1617, 1402, 1053, 696, 654 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38−7.27 (m, 5H), 5.35 (s, 1H), 4.84 (s, 1H), 4.65 (s, 2H), 3.20−3.15 (m, 2H), 1.67−1.58 (m, 2H), 1.44−1.39 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.3, 167.2, 149.3, 136.8, 128.5, 83.9, 44.0, 41.0, 30.5, 19.9, 13.6 ppm; MS (ESI) m/z 259 (M + H$^+$, 90), 534 (2M + NH_4^+, 100) and HR-ESI-MS for $C_{15}H_{18}N_2O_2$ ([M + H]$^+$) calcd 259.1441; found 259.1439. The compound has CAS Registry Number 607692-63-7, but no reference on it has been found by SciFinder.

*2-Benzylamino-N-butylmaleimide (**Phc-But**):* 88% (454 mg, 1.76 mmol) yield, yellow solid, mp = 121.3−121.9 °C; IR (KBr) ν_{max} = 3332, 3125, 2953, 2862, 1749, 1698, 1620, 1444, 1026, 781, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42−7.18 (m, 5H), 5.67 (s, 1H), 4.86 (s, 1H), 4.35 (d, J = 5.6 Hz, 2H), 3.48 (t, J = 7.2 Hz, 2H), 1.61−1.54 (m, 2H), 1.38−1.28 (m, 2H), 0.94 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.5, 167.5, 148.8, 135.7, 128.9, 128.2, 127.7, 85.3, 48.4, 37.8, 30.7, 19.9, 13.6 ppm; HR-ESI-MS for $C_{15}H_{18}N_2O_2$ ([M + H]$^+$) calcd 259.1441; found 259.1445. The compound has CAS Registry Number 607692-56-8, but no reference on it has been found by SciFinder.

*2-Benzylamino-N-methylmaleimide (**Phc-Me**):* 72% (311 mg, 1.44 mmol) yield, yellow solid, mp = 151.2−151.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38−7.29 (m, 5H), 5.69 (s, 1H), 4.88 (s, 1H), 4.37 (d, J = 5.6 Hz, 2H), 2.99 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.4, 167.6, 149.0, 135.6, 129.0, 128.2, 127.6, 85.4, 48.4, 23.4 ppm; ^{1}H and ^{13}C NMR spectra correspond well with those in the literature.[50]

*2-(Piperidin-1-yl)-N-benzylmaleimide (**Pid-Phc**):* 75% (405 mg, 1.5 mmol) yield, light yellow solid, mp = 107.3−107.8 °C; IR (KBr) ν_{max} = 2919, 2851, 1701, 1652, 1618, 1540, 1455, 1399, 697, 654 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45−7.22 (m, 5H), 4.91 (s, 1H), 4.64 (s, 2H), 3.66 (b, 4H), 1.68 (b, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.6, 167.0, 150.4, 137.1, 128.5, 128.3, 127.4, 87.9, 48.4, 40.9, 25.5, 23.9 ppm; MS (ESI) m/z 271 (M + H$^+$, 50), 558 (2M + NH_4^+, 100) and HR-ESI-MS for $C_{16}H_{18}N_2O_2$ ([M + H]$^+$) calcd 271.1441; found 271.1435.

*2-Phenylamino-N-phenylmaleimide (**2Ph**):* 85% (449 mg, 1.7 mmol) yield, yellow solid, mp = 245.4−245.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52−7.20 (m, 11H), 5.70 (s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.2, 167.0, 142.4, 138.2, 131.6, 129.8, 129.0, 127.6, 125.8, 124.8, 118.9, 89.1 ppm. ^{1}H and ^{13}C NMR spectra correspond well with those in the literature.[78]

*2-Phenylamino-N-butylmaleimide (**Ph-But**):* 70% (342 mg, 1.4 mmol) yield, yellow solid, mp = 139.3−139.9 °C; IR (KBr) ν_{max} = 3313, 3121, 2956, 2863, 1756, 1686, 1638, 1446, 1421, 1183, 748, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44−7.16 (m, 6H), 5.52 (s,

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1H), 3.56 (t, J = 7.2 Hz, 3H) 1.66−1.59 (m, 2H), 1.39−1.34 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.8, 168.3, 142.3, 138.4, 129.7, 124.4, 118.7, 88.9, 37.7, 30.7, 20.0, 13.6 ppm; MS (ESI) m/z 245 (M + H^+, 5), 102 (100) and HR-ESI-MS for $C_{14}H_{16}N_2O_2$ ([M + H]$^+$) calcd 245.1285; found 245.1299.

*2-Butylamino-N-phenylmaleimide (**But-Ph**):* 78% (381 mg, 1.56 mmol) yield, yellow solid, mp = 138.5−138.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48−7.32 (m, 5H), 5.53 (s, 1H), 4.99 (s, 1H), 3.26 (q, J = 7.2 Hz, 2H), 1.73−1.66 (m, 2H), 1.51−1.42 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171. 0, 166.3, 149.0, 131.9, 128.9, 127.2, 125.8, 84.2, 44.1, 30.5, 20.0, 13.6 ppm; ^{1}H and ^{13}C NMR spectra correspond well with those in the literature.[79]

*2-(Piperidin-1-yl)-N-phenylmaleimide (**Pid-Ph**):* 80% (410 mg, 1.6 mmol) yield, light yellow solid, mp = 107.8−108.1 °C; IR (KBr) ν_{max} = 3101, 2923, 2851, 1749, 1697, 1648, 1612, 1448, 1383, 766, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47−7.32 (m, 5H), 5.07 (s, 1H), 3.74 (b, 4H), 1.74 (b, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.8, 166.1, 149.9, 131.9, 128.8, 127.2, 126.4, 88.32, 77.3, 77.2, 76.9, 76.6, 25.6, 23.9 ppm; MS (ESI) m/z 279 (M + Na^+, 40), 102 (100) and HR-ESI-MS for $C_{15}H_{16}N_2O_2$ ([M + H]$^+$) calcd 257.1285; found 257.1278. ^{1}H and ^{13}C NMR spectra correspond well with those in the literature.[80]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02706.

Table S1, ^{1}H and ^{13}C NMR spectrum copies of 12 AMIs in Table 2, and thermal ellipsoid plots (PDF)
X-ray data for **2But** (CIF)
X-ray data for **Cyc-But** (CIF)
X-ray data for **Ph-But** (CIF)
X-ray data for **Phc-Me** (CIF)
X-ray data for **Pid-Phc** (CIF)

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Notes

The authors declare no competing financial interest.

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