Stereoselective Aminoiiodination of Activated Alkynes with Organoiodine(III) Reagents and Amines via Multiple-Site Functionalization: Access to Iodinated Enamines and N-Aryl Indoles

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Abstract: A stereoselective aminoiiodination of activated alkynes with PhI(OAc)$_2$ and amines via multiple-site functionalization to afford (Z)diethyl 2-(diphenylamino)-3-iodomaleate derivatives with superior yields has been described. The key feature of this reaction is the incorporation of iodide and aryl group concurrently in the same molecule in a stereoselective manner by employing PhI(OAc)$_2$ as electrophilic reagent as well as iodide and aryl group source. The high stereoselectivity of the reaction can be explained based on the structure of the possible intermediates, the conformations of which controlled by the hydrogen bonding, steric hindrance and electrostatic attractions. This reaction proceeds under mild conditions, providing various dialkyl 2-(diphenylamino)-3-iodomaleates by a single operation starting from activated alkynes. The robustness of our strategy is revealed by making of bis (dialkyl 2-(diphenylamino)-3-iodomaleate) derivatives involving formation of four new C-N bonds and two C-I bonds with a single step. The synthesized inactive 3° enamines (dialkyl 2-(diphenylamino)-3-iodomaleates) could be further transformed into highly substituted indoles via Pd catalyzed C-H and C-I activation under non-acidic conditions.
Introduction

Alkyne difunctionalizations have attracted intensive attention in recent years particularly in developing regio and stereoselective reactions to access multifunctional alkene products with broad synthetic and biological applications. For example the azidativehalo, sulfonative, aminohalogenative, silylzincative iodoacyloxylation and perfluoroalkylative difunctionalizations of alkynes have been successfully realized for the synthesis of various difunctionalization products. In this context, methods to produce halogenated enamines via aminohalogenation of alkynes are very attractive owing to the utility of these compounds in medicinal chemistry and organic synthesis. Accordingly, considerable efforts have been made to their syntheses resulting in various synthetic strategies. For example cyclic enaminones, 2-alkynyloxycarbonyl azides/amines/O-propargyl carbamates have been typically employed as precursors for halogenated enamines and catalyzed by metal or non-metals with various halogen sources.

Scheme 1. Aminohalogenation of Alkynes and Our Strategy

Furthermore, dehydrogenative aminohalogenation of alkenes via Pd catalysis was developed by Jiang and co-workers for the synthesis of brominated enamines. Later Li et al. developed Nickel or Diacetoxyiodobenzene promoted halogenation of enamines and enamides. However, examples of alkyne aminohalogenation towards halogenated enamines are scarce (Scheme 1a &b). For instance, Headley & Li and co-workers demonstrated the aminochlorination of arylalkynes with N,N dichlorobenzenesulfonamide (Scheme 1a). In 2014, Liang and Zhang et al. described the
aminohalogenation of alkynes with N-haloimides activated by DBU (Scheme 1b). Despite this progress, developing the multiple-site functionalization of C-C multiple bonds with reagents as both halogen source as well as promoter in a stereoselective manner remains an intriguing challenge. As part of our ongoing study on multiple functionalization reactions of alkynes and amines using azides as nitrogen source and organoiodine compounds as promoter, we fancied to synthesize iodinated enamines directly from alkynes and amines by using organoiodine reagents as both iodine and aryl group source.

Scheme 2. Plausible Conformations of Intermediates for Stereoselectivity of the Reaction

Organoiiodine(III) compounds are usually used as oxidants and electrophilic reagents where only one ligand of iodine(III) is removed by the substrate or replacement of both ligands with external nucleophile followed by its decomposition into radicals. However, sequential removal of two ligands from the iodine(III) reagent by active C-H bond of substrate and incorporation of iodobenzene into the same substrate would indubitably make the reactions atom economic, but such organic transformations are not much explored. On the other hand, compared with known aminohalogenation of alkynes, this multiple-site functionalization would be of great importance to produce synthetically potential halogenated enamines in a stereoselective manner. The high stereoselectivity of the reaction can be explained based on the structure
of the possible intermediates. The conformations of intermediates are controlled by the hydrogen bonding, steric hindrance and electrostatic attractions as shown in scheme 2. These type of interactions have never been explored for stereoselective alkyne aminohalogenation. Herein we report the first example of a highly stereoselective multiple-site functionalization of activated alkenes with amines and organoiodine(III) (Scheme 1c) as the halo and aryl group source for haloenamines. We have also successfully employed these relatively inactive 3\(^\circ\) enamines in intramolecular cyclizations via Pd catalyzed C-H and C-I activation resulting in highly functionalized indoles.

Table 1. Optimization reaction of Aminohalogenation of Alkynes\(^a\)

<table>
<thead>
<tr>
<th>entry</th>
<th>iodine(III) (equiv)</th>
<th>base (equiv)</th>
<th>solvent</th>
<th>yield (%)(^b)</th>
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<tbody>
<tr>
<td>1</td>
<td>PIDA (1.5)</td>
<td>-----</td>
<td>DCE</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>PIDA (1.5)</td>
<td>-----</td>
<td>DCE</td>
<td>31(^c)</td>
</tr>
<tr>
<td>3</td>
<td>PIDA (1.5)</td>
<td>-----</td>
<td>DCE</td>
<td>0(^d)</td>
</tr>
<tr>
<td>4</td>
<td>PIDA (1.5)</td>
<td>-----</td>
<td>DCE</td>
<td>0(^e)</td>
</tr>
<tr>
<td>5</td>
<td>PIDA (1.5)</td>
<td>Cs(_2)CO(_3) (1.0)</td>
<td>DCE</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>PIDA (1.5)</td>
<td>Cs(_2)CO(_3) (1.5)</td>
<td>DCE</td>
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</tr>
<tr>
<td>7</td>
<td>PIDA (1.5)</td>
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<td>50</td>
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<td>DABCO (1.5)</td>
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<td>73</td>
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<tr>
<td>14</td>
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<td>Cs(_2)CO(_3) (1.5)</td>
<td>DCE</td>
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<tr>
<td>16</td>
<td>PIDA (2.5)</td>
<td>Cs(_2)CO(_3) (2.0)</td>
<td>DCE</td>
<td>84</td>
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<tr>
<td>Entry</td>
<td>PIDA (mmol)</td>
<td>Cs$_2$CO$_3$ (mmol)</td>
<td>Base</td>
<td>Yield (%)</td>
</tr>
<tr>
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<td>-------------</td>
<td>---------------------</td>
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<td>1.5</td>
<td>THF</td>
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<td>26</td>
<td>PhI(OH)(OTs) (2.5)</td>
<td>1.5</td>
<td>DCE</td>
<td>ND</td>
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</table>

*Reaction conditions: Alkyne 1a (1 mmol), Amine 2a (1 mmol), PIDA 3a (2.5 mmol), Base, dry solvent 3 mL, rt (27 °C) for 8-18 h; *$^a*$Isolated yield after silica column chromatography; *$^b*$Na$_2$SO$_4$ (4 equiv); *$^c*$TBAI (2 equiv); *$^d*$NBS (2 equiv); ND = Not detected.

**Results and discussion**

We choose diethyl acetylenedicarboxylate 1a, aniline 2a and phenylisodine(III) diacetate (PIDA) 3a as the model substrates to initiates our studies. At the beginning, the reaction was performed at room temperature in dichloromethane (DCE). To our delight, we observed the formation of desired product 4aaa in 31% yield with (Z)-configuration (Table 1, entry 1). The structure and stereochemistry of 4aaa was determined by the X-ray crystallography analysis (Supporting information, SI). With this promising result in hand, we further optimized the reaction conditions. When reaction was carried out in the presence of 4 equiv of Na$_2$SO$_4$ as additive, the product 4aaa was yielded in 31 % after 18 h reaction time (Table 1, entry 2). No product was obtained when the reaction was performed with TBAI and NBS as additives (entries 3&4). We then turned our attention to the screening of bases to improve the reaction performance. When reaction performed with Cs$_2$CO$_3$ pleasingly, the product 4aaa was obtained in 67% yield in 12 h (entries 5&6). Other bases such as K$_2$CO$_3$, K$_3$PO$_4$, NaHCO$_3$, Na$_2$CO$_3$, and DABCO did not improve the yield of the product (entries 7-11). We then screened the equivalents of PIDA and Cs$_2$CO$_3$ (entries 12-17), 1.5 equiv of Cs$_2$CO$_3$ and 2.5 equiv
of PIDA were found to be the best conditions to afford the product 4aaa in 84 % yield after 8 h (entry 14). Among the solvents tested, DCE was found to be the best solvent choice (entries 18-23). In our attempts to further improve the yield, we have screened other organoiodine sources, unfortunately our attempts went in vain (entries 24-26).

In order to realize the versatility of this newly developed method, we anticipated to apply it to a series of amines having neutral, electron donating and withdrawing substituents on phenyl ring. This results demonstrated that the substrates containing neutral and electron donating groups on phenyl ring afforded the products (Table 2(A)) in good to very good yield. The weak electron withdrawing substituents on phenyl ring resulted in relatively low yields (Table 2(B)). Presence of both weak electron withdrawing and donating groups on the same phenyl ring gave the products fairly in good yields (Table 2, 4fab & 4maa). Organoiiodine with strong electron withdrawing groups (-CO₂Me, NO₂) gave the products in excellent yields (Table 2(C)), this may be due to stabilization of intermediate V (Scheme 5). It is worth to mention here that, the robustness of our strategy is demonstrated by the synthesis of derivatives (Table 2 (D), 4a"aa & 4a"ab) involving formation of four new C-N bonds and two C-I bonds in single step. After developing successful syntheses of halogenated enamines, we envisaged that it would be appropriate to check the scalability of our protocol for the synthesis halogenated enamines owing to their synthetic utility. Accordingly, we performed the reaction on gram scale for the synthesis of halogenated enamine resulted in 72% yield (Table 2, 4aaa).

**Table 2. Substrate Scope of Aminoidination Reaction**

\[
\text{R}^1\text{-NH}_2 + \text{EWG} + \text{EWG} + \text{I}^- + \text{OAc} \rightarrow \text{Cs}_2\text{CO}_3 (1.5 \text{equiv}) \rightarrow \text{R}^1\text{-N} = \text{I} + \text{DCE, rt}
\]
A Reaction conditions: Alkyne 1a (1 mmol), Amine 2a (1 mmol), PIDA 3a (2.5 mmol), Cs₂CO₃ (1.5 mmol), dry DCE 3 mL, rt (27 °C) for 8-14 h; b Isolated yield after silica column chromatography.

Owing to the importance of halogenated enamines as flexible building blocks in organic synthesis, we envisioned to employ them in organic transformations. In this direction, we thought to perform transition-metal catalyzed intramolecular cyclizations by C-I and (sp²)C-H activation. However, less reactive 3° enamines than 2° enamine homologues in transition-metal catalyzed C-H activation reactions are scarce¹⁷ and poses a daunting challenge. The conversion of such enamines to indoles was accomplished by improving the electrophilicity of Pd catalysts under acidic conditions.¹⁸

![Chemical Structures](image1.png)

(A) Scope of Arylamines with neutral and electron donating substituents and Alkynes

<table>
<thead>
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<th>R¹</th>
<th>R²</th>
<th>EWG</th>
<th>yield (%)²</th>
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<tr>
<td>C₆H₅⁻</td>
<td>H</td>
<td>CO₂Et</td>
<td>4aaa, 84</td>
</tr>
<tr>
<td>C₆H₄⁻</td>
<td>H</td>
<td>CO₂Me</td>
<td>4aab, 82</td>
</tr>
<tr>
<td>3-Me-C₆H₄⁻</td>
<td>H</td>
<td>CO₂Et</td>
<td>4caa, 85</td>
</tr>
<tr>
<td>3,5-di Me-C₆H₄⁻</td>
<td>H</td>
<td>CO₂Et</td>
<td>4daa, 82</td>
</tr>
<tr>
<td>2-isopropyl-C₆H₄⁻</td>
<td>H</td>
<td>CO₂Me</td>
<td>4eab, 78</td>
</tr>
<tr>
<td>2-Br-3-Me-C₆H₄⁻</td>
<td>H</td>
<td>CO₂Me</td>
<td>4fba, 77</td>
</tr>
<tr>
<td>4-Oe-C₆H₄⁻</td>
<td>H</td>
<td>CO₂Et</td>
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<tr>
<td>4-Oe-C₆H₄⁻</td>
<td>H</td>
<td>CO₂Me</td>
<td>4gab, 80</td>
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<tr>
<td>3,4,5-Oe-C₆H₄⁻</td>
<td>H</td>
<td>CO₂Et</td>
<td>4haa, 75</td>
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</table>

(B) Scope of Arylamines with weak electron withdrawing groups and Alkynes

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<th>R²</th>
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<tr>
<td>2-F-C₆H₄⁻</td>
<td>H</td>
<td>CO₂Me</td>
<td>4iab, 88</td>
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<td>4-Cl-C₆H₄⁻</td>
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<td>H</td>
<td>CO₂Me</td>
<td>4kab, 83</td>
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<tr>
<td>2-Br-C₆H₄⁻</td>
<td>H</td>
<td>CO₂Et</td>
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<td>2-Me₂-N=N-C₆H₄⁻</td>
<td>H</td>
<td>CO₂Et</td>
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(C) Scope of Organoiiodine(III) reagents and Alkynes

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<th>R²</th>
<th>EWG</th>
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<td>C₆H₄⁻</td>
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<td>4abb, 87</td>
</tr>
<tr>
<td>4-Oe-C₆H₄⁻</td>
<td>CO₂Me</td>
<td>CO₂Me</td>
<td>4gbb, 77</td>
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<td>2-Br-4-Me-C₆H₄⁻</td>
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<td>3-NO₂</td>
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<tr>
<td>2,4-di Me-C₆H₄⁻</td>
<td>4-F</td>
<td>CO₂Et</td>
<td>4oda, 87</td>
</tr>
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</table>

(D) Scope of aliphatic amines and Alkynes

| ![Chemical Structures](image2.png) |

⁴Reactivity conditions: Alkyne 1a (1 mmol), Amine 2a (1 mmol), PIDA 3a (2.5 mmol), Cs₂CO₃ (1.5 mmol), dry DCE 3 mL, rt (27 °C) for 8-14 h; Isolated yield after silica column chromatography.
Herein we delighted to employ these iodinated enamines for smooth transformation to \(N\)-aryl indoles via palladium-catalyzed intramolecular cyclization under non-acidic conditions. It was noted that iodinated enamines containing weak electron withdrawing and electron donating groups on phenyl rings provided the indoles with good yields than those having electron-withdrawing groups (Scheme 3).

**Scheme 3. \(N\)-aryl Indole Synthesis from Iodinated Enamines via Pd-Catalyzed Intramolecular Cyclization**

\[ \text{Reaction conditions: Iodoenamine } 4 \text{ (1 mmol), Pd(OAc)\textsubscript{2} (10\% mol), Cu(OAc)\textsubscript{2} (1.2 eqquiv), Cs\textsubscript{2}CO\textsubscript{3} (1.5 mmol), dry DMF 1.5 mL, at 120 °C for 20 h.} \]

To investigate the reaction mechanism, we performed couple of control experiments (Scheme 4).

The addition of TEMPO uninhibited the formation of \(4\text{aaa}\) (Scheme 4(i)), suggesting that reaction might proceed through ionic pathway. To further rule out the radical pathway, we performed a radical clock experiment under standard conditions, which afforded only the halogenated enamine product \(4\text{rab}\) and no other ring-opened coupling products (Scheme 4(ii)).
Scheme 4. Control Experiments

(i) Ph-NH₂ + EtO₂C-C≡CO₂Et + 1a 2a

(ii) Radical clock experiment:

Based on the above experiments and literature reports we have formulated the following plausible mechanism (scheme 5). The intermolecular reaction of 1a and 2a generates hydroamination product I which undergo ligand exchange with PIDA by the loss of acetic acid to give intermediate II, which would further transformed to intermediate (IV) by the loss of one more acetic acid, which followed by subsequent rearrangement leads to the formation of a zwitterion (V) which then afford the final product 4aaa.

Scheme 5. Plausible Mechanism for Aminohalogenation of Alkynes

In summary, we have developed a novel and facile approach for the stereoselective alkyne aminoisodination using amines, phenylidione(III) diacetate (PIDA) as iodide and aryl moiety source as well as promoter. The key feature of this reaction is the incorporation of iodide and aryl group concurrently in the same molecule in a stereoselective manner. The advantages of this method are metal-free, mild reaction conditions and scalability. We have also successfully employed these inactive iodinated 3° enamines in intramolecular cyclizations via Pd catalyzed C-H and C-I activation resulting in highly functionalized indoles. Further exploration of iodinated 3° enamines are currently under way in our laboratory.
Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, characterization data, and copies of NMR (PDF).

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Experimental Section

General Considerations: IR spectra were recorded on a FTIR spectrophotometer. $^1$H NMR spectra were recorded on 400 MHz spectrometer at 295 K in CDCl$_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ$_H$ = 0.00 ppm) or CHCl$_3$ (δ$_H$ = 7.25 ppm). $^{13}$C NMR spectra were recorded on 100 MHz spectrometer at 25 °C in CDCl$_3$; chemical shifts (δ ppm) are reported relative to CHCl$_3$ [δ$_C$ = 77.00 ppm (central line of triplet)]. In the $^1$HNMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, dd = doublet of doublets, m = multiplet and br s. = broad singlet. The assignment of signals was confirmed by $^1$H, $^{13}$C CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded using Q-TOF multimode source. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Hypervalent iodine reagents phenyliodine bis(trifluoroacetate) (PIFA) and phenyliodine diacetate (PIDA) were purchased from Sigma Aldrich. Other reagents were purchased as reagent grade and used without further purification. All dry solvents were used. CH$_3$CN and DCE were dried over CaH$_2$, DCM & DMF were dried over anhydrous P$_2$O$_5$, and ethyl acetate (EtOAc) was dried over Na$_2$CO$_3$ and distilled before use.
All small scale dry reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of petroleum ether and ethyl acetate as eluents. All reactions were performed under air atmosphere in standard glassware, heated at 80 °C for 3 h before use. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 °C was used. Organic solutions were concentrated by rotary evaporation under vacuum. Acme’s silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).


Aniline 1a (50 mg, 1 mmol) was taken in a dried round bottom flask, and dialkyl acetylenedicarboxylate 2a (91.3 mg, 1 mmol) was then added slowly with thorough mixing to form a homogeneous paste, then add 0.5 mL DCE solvent (if required). After confirming the formation of enamine (monitored by TLC), then added 4 mL DCE solvent, followed by addition of Cs₂CO₃ (261.959 mg, 1.5 mmol), phenyliodine(III) diacetate (PIDA) 3a (431.614 mg, 2.5 mmol) in portion wise for 20 min. The progress of the reaction was monitored by TLC. The reaction mixture was quenched by addition of saturated solution of NaHCO₃ and extracted with ethyl acetate (EtOAc), dried over MgSO₄, and concentrated in vacuo. The residue was purified through a silica gel column chromatography using petroleum ether/ethyl acetate (0.2/9.8) as eluent to yield (209 mg, 84%). All compounds (4aaa-4rab) were unknown and confirmed by FTIR, ¹H NMR, ¹³C NMR and HR-MS spectral analyses.

2. General Procedure-II for Aminoidination of Alkyne Using Synthesis of 4a”aa as an Example.

p-Phenylenediamine 1a” (50 mg, 1 mmol) was taken in a dried round bottom flask, and dialkyl acetylenedicarboxylate 2a (157.35 mg, 2 mmol) was then added slowly with thorough mixing to form a homogeneous paste, then add 2 mL DCE solvent (if required). After confirming the formation of enamine (monitored by TLC), then added 8 mL DCE solvent, followed by addition of Cs₂CO₃ (451.58 mg, 3.0 mmol), phenyliodine(III) diacetate (PIDA) 3a (744.05 mg, 5.0 mmol) in portion wise for 20 min. The progress of the reaction was monitored by TLC. The reaction mixture was quenched by addition of saturated solution of NaHCO₃ and extracted with ethyl acetate (EtOAc), dried over MgSO₄, and concentrated in
vacuo. The residue was purified through a silica gel column chromatography using petroleum ether/ethyl acetate (0.2/9.8) as eluent to yield (212.55 mg, 54%). Compounds 4a"aa and 4a"ab were unknown and confirmed by FTIR, $^1$H NMR, $^{13}$C NMR and HR-MS spectral analyses.


To a mixture of N-diaryl β-iodinated enamine 4a (50 mg, 1.0 mmol), Pd(OAc)$_2$ (2.4 mg, 0.1 mmol) and Cu(OAc)$_2$ (23.32 mg, 1.2 mmol) was added 1.5 mL of dry DMF in an oven dried 15 mL schlenk tube. The reaction mixture was stirred at 120 °C for 20 h. After cooling the reaction mixture to room temperature, then the reaction mixture was quenched by addition of water and extracted with ethyl acetate followed by water wash for two times, dried over MgSO$_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (0.2/9.8) as eluent to yield N-Aryl indole product 5a (26.82 mg, 74%). Compounds 5a-5h were unknown and confirmed by FTIR, $^1$H NMR, $^{13}$C NMR and HR-MS spectral analyses.

General procedure (GP-IV) for the synthesis organoiodine(III) reagents (3b, 3c & 3d)$^{19}$:

Compounds 3b, 3c and 3d were prepared according to the literature method.$^{18}$ To a solution of substituted iodobenzene (1.0 mmol) in AcOH was added mCPBA (ca. 65%, 1.15 mmol). The mixture was stirred at room temperature for 2 h. Then, H$_2$O was added to the reaction mixture and then it was extracted with CHCl$_3$. After being dried over Na$_2$SO$_4$, filtration, and removal of the solvent Et$_2$O and hexane were added to the residue, and the mixture was cooled to 0°C to induce precipitation. After filtration, the solids were washed with a mixture of Et$_2$O and hexane to provide products (Diacetoxyiodo)benzene derivatives (3b, 3c and 3d).

(Z)Diethyl 2-(diphenylamino)-3-iodomaleate (4aaa)

Deep yellow solid (209 mg, 84%). m.p. = 54-56 °C (recrystallized by placing inside the refrigerator); FR-IR (MIR-ATR, 4000-600 cm$^{-1}$): $\nu_{max}$ = 3034.9, 2980.5, 2936.4, 1729.9, 1491.7, 1288.1, 1219.4, 1041.4, 1027.6, 838.2, 756.9, 695.1; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H$ = 7.30 (m, 4H); 7.11 (m, 6H); 4.26 (q, J = 7.2
(Z)Dimethyl 2-(diphenylamino)-3-iodomaleate (4aab)

Yellow oil (197 mg, 82%); FT-IR: (MIR-ATR, 4000-600 cm⁻¹): ν_max = 3033.1, 3006.6, 2949.9, 2849.1, 1732.8, 1550.3, 1489.7, 1434.1, 1288.7, 1223.3, 1147.4, 1042.8, 988.8, 757.4, 695.2; ¹H NMR (CDCl₃, 400 MHz): δ_H = 7.30 (m, 4H); 7.1 (m, 6H); 3.80 (s, 3H); 3.57 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 166.2, 164.5, 149.5, 144.1, 129.3, 124.7, 124.0, 86.9, 53.5, 52.9; HR-MS (ESI+) m/z value calculated for [C₁₂H₁₈KNO₄]⁺ = [M+K]⁺: 475.9756; found: 475.9749.

(Z)Diethyl 2-iodo-3-(phenyl(m-tolyl)amino)maleate (4caa)

Yellow oil (190 mg, 85%); FT-IR: (MIR-ATR, 4000-600 cm⁻¹): ν_max = 2936.66, 1731.04, 1701.04, 1592.15, 1503.53, 1459.87, 1421.39, 1234.69, 1206.48, 1128.33, 1008.78, 759.89, 699.87; ¹H NMR (CDCl₃, 400 MHz): δ_H = 2.76 - 7.32 (m, 2H); 7.14 - 7.19 (m, 1H); 7.10 (d, J = 6.85 Hz, 3H); 6.87 - 6.93 (m, 3H); 4.24 (q, J = 7.17 Hz, 2H); 4.02 (q, J = 7.34 Hz, 2H); 2.29 (s, 3H); 1.31 (t, J = 7.09 Hz, 3H); 0.97 (t, J = 7.09 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): 165.9, 163.9, 149.5, 144.3, 144.2, 139.1, 129.2, 129.0, 125.4, 124.6, 124.4, 124.2, 121.2, 87.4, 62.6, 62.0, 21.4, 14.0, 13.6; HR-MS (ESI+) m/z value calculated for [C₂₁H₂₁NO₄]⁺ = [M+H]⁺: 480.0670; found: 480.0672.

(Z)Diethyl 2-((3,5-dimethylphenyl)(phenyl)amino)-3-iodomaleate (4daa)

Yellow oil (166 mg, 82%); FT-IR: (MIR-ATR, 4000-600 cm⁻¹): ν_max = 2998.4, 2945.1, 2818.4, 1718.9, 1600.3, 1500.6, 1498.4, 1419.3, 1216.5, 1200.8, 1143.4, 1100.8, 1032, 769.7, 693.2; ¹H NMR (CDCl₃, 400 MHz): δ_H = 7.23 (d, J = 6.4 Hz, 2H); 7.07, (m, 2H); 6.97 (m, 3H); 6.83 (br, s, 1H); 4.21 (d, J = 7.3 Hz, 2H); 3.98 (d, J = 7.3 Hz, 2H); 2.28 (s, 3H); 2.04 (s, 3H); 1.31 (t, J = 7.04 Hz, 3H); 0.96 (t, J = 7.04 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 165.8, 163.9, 151.7, 144.8, 141.2, 136.2, 133.7, 131.4, 129.0, 128.8, 127.7, 123.9, 123.2, 80.2, 62.5, 61.9, 21.7, 20.9, 18.8, 14.0, 13.6; HR-MS (ESI+) m/z value calculated for [C₂₂H₂₃NO₄]⁺ = [M+H]⁺: 494.0828; found: 494.0824.

(Z)Dimethyl 2-iodo-3-((2-isopropylphenyl)(phenyl)amino)maleate (4eab)

Yellow oil (138 mg, 78%); FT-IR: (MIR-ATR, 4000-600 cm⁻¹): ν_max = 2977.4, 2918.4, 1712.9, 1683.3, 1501.6, 1496.4, 1427.3, 1215.4, 1202.6, 1133.4, 1022.4, 767.7, 694.2; ¹H NMR (CDCl₃, 400 MHz): δ_H = 7.31 - 7.35 (m, 1H); 7.23 - 7.30 (m, 3H); 7.11 - 7.18 (m, 2H); 7.06 (t, J = 7.34 Hz, 1H); 6.94 - 7.04 (m, 1H), 6.86 (br. s., 1H), 3.76 (s, 3H), 3.50 (s, 3H), 3.17 (sept, J = 6.85 Hz, 1H), 1.04 - 1.24 (d, 6H); ¹³C NMR
(CDCl₃, 100 MHz): δ = 166.0, 164.8, 152.9, 147.2, 145.5, 140.6, 129.3, 129.0, 128.0, 127.4, 126.6, 124.4, 124.2, 53.5, 52.7, 28.0; HR-MS (ESI+) m/z value calculated for [C₂₂H₂₄INO₄]⁺ = [M+H]⁺: 480.0672; found: 480.0668.

(Z)Dimethyl 2-((2-bromo-5-methylphenyl)(phenyl)amino)-3-iodomaleate (4fab)

Yellow oil (110 mg, 77%); FT-IT: (MIR-ATR, 4000-600 cm⁻¹): νₘₐₓ = 3002.8, 2928.4, 2890.4, 1720.6, 1555.7, 1429.7, 1420, 1230.6, 1078.9, 985.7, 760.5, 695.3; ¹H NMR (CDCl₃, 400 MHz): δ_H = 7.42 (s, 1H); 7.22 (d, J = 7.8 Hz, 2H); 7.12 (d, J = 8.3 Hz, 3H); 7.08 (s, 1H); 7.06 (s, 1H); 3.78 (s, 3H); 3.55 (s, 3H); 2.34 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 166.1, 164.5, 151.2, 144.3, 139.3, 138.3, 134.7, 129.7, 129.4, 129.1, 124.0, 123.1, 82.2, 53.5, 52.8, 20.8; HR-MS (ESI+) m/z value calculated for [C₁₉H₁₇BrINaNO₄]⁺ = [M+Na]⁺: 553.9260; found: 553.9251.

(Z)Diethyl 2-ido-3-((4-methoxyphenyl)(phenyl)amino)maleate (4gaa)

Yellow oil (157 mg, 78%); FT-IR: (MIR-ATR, 4000-600 cm⁻¹): νₘₐₓ = 2981.42, 1729.22, 1555.32, 1490.18, 1290.53, 1227.06, 1193.16, 1043.82, 758.67, 694.93; ¹H NMR (CDCl₃, 400 MHz): δ_H = 7.24 - 7.30 (m, 2H), 6.99 - 7.10 (m, 5H), 6.81 - 6.87 (m, 2H), 4.23 (q, J = 7.01 Hz, 2H), 4.02 (q, J = 7.34 Hz, 2H), 3.80 (s, 3H), 1.31 (t, J = 7.09 Hz, 3H), 0.99 (t, J = 7.09 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): 165.8, 164.1, 157.1, 150.2, 144.8, 137.1, 129.2, 126.7, 124.0, 123.3, 114.4, 85.0, 62.6, 62.0, 55.5, 14.0, 13.6; HR-MS (ESI+) m/z value calculated for [C₂₁H₂₂IKΝO₃]⁺ = [M+K]⁺: 534.0174; found: 534.0192.

(Z)Dimethyl 2-ido-3-((4-methoxyphenyl)(phenyl)amino)maleate (4gab)

Yellow oil (152 mg, 80%); FT-IR: (MIR-ATR, 4000-600 cm⁻¹): νₘₐₓ = 2950.15, 2837.74, 1731.23, 1546.86, 1505.44, 1433.68, 1242.06, 1220.03, 1145.92, 1031.65, 835.86, 758.74, 693.82; ¹H NMR (CDCl₃, 400 MHz): δ_H = 7.25 - 7.28 (m, 3H), 7.07 (d, J = 8.80 Hz, 2H), 7.01 (d, J = 7.82 Hz, 2H), 6.84 (d, J = 8.80 Hz, 2H), 3.79 (s, 3H), 3.80 (s, 3H), 3.57 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 163.9, 157.2, 144.7, 137.0, 136.9, 129.2, 126.7, 124.2, 123.4, 114.5, 55.5, 53.5, 52.8; HR-MS (ESI+) m/z value calculated for [C₁₉H₁₈IKΝO₃]⁺ = [M+K]⁺: 505.9860; found: 505.9868.

(Z)Diethyl 2-ido-3-(phenyl(3,4,5-trimethoxyphenyl)amino)maleate (4haa)

Yellow oil (114 mg, 75%); FT-IR: (MIR-ATR, 4000-600 cm⁻¹): νₘₐₓ = 2980.42, 1730.22, 1550.30, 1480.19, 1295.50, 1220.16, 1193.28, 1040.76, 750.69, 681.90; ¹H NMR (CDCl₃, 400 MHz): δ_H = 7.70 (d, J = 7.34 Hz, 1H), 7.31 (t, J = 7.83 Hz, 2H), 7.11 (s, 2H), 6.32 (s, 2H), 4.25 (q, J = 7.34 Hz, 2H), 4.05 (q, J = 7.34 Hz, 2H), 3.83 (s, 3H), 3.75 (s, 6H), 1.32 (t, J = 7.09 Hz, 3H), 1.01 (t, J = 7.34 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): 165.8, 164.0, 153.6, 149.5, 144.1, 140.1, 137.5, 135.3, 130.3, 129.2, 127.5, 124.5, 124.1, 101.8,
87.2, 62.7, 62.1, 61.0, 56.2, 13.9, 13.6; HR-MS (ESI+) m/z value calculated for [C_{23}H_{26}INaNO_4]^+ = [M+Na]^+: 578.0650; found: 578.0652.

(Z)Dimethyl 2-((2-fluorophenyl)(phenyl)amino)-3-iodomaleate (4iab)

Yellow oil; (180 mg, 88%); FT-IR: (MIR-ATR,4000-600 cm⁻¹): ν_max = 2951.5, 1990.1, 1731.9, 1590.7, 1497.3, 1434.2, 1299.9, 1230.6, 1043.2, 988.9, 757.4, 695.0; ¹H NMR (CDCl₃, 400 MHz): δ_H = 7.27 (m, 4H); 7.12 (m, 3H); 6.97 (d, J = 7.8 Hz, 2H); 3.80 (s, 3H); 3.58 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 166.1, 164.1, 158.9, 156.4, 149.5, 136.4, 129.2, 124.9, 124.4, 121.7, 117.0, 116.8, 86.0, 53.5, 52.9; HR-MS(ESI+) m/z value calculated for [C_{18}H_{16}INO₄]^+ = [M+H]^+ : 456.0103; found: 456.0096.

(Z)Diethyl 2-((4-chlorophenyl)(phenyl)amino)-3-iodomaleate (4jaa)

Yellow oil (167 mg, 85%); FT-IR: (MIR-ATR, 4000-600 cm⁻¹): ν_max = 2980.5, 2926.9, 2850.7, 1725.5, 1586.9, 1554.1, 1486.6, 1366.3, 1283.9, 1213.8, 1147.2, 1091.3, 1040.8, 823.6, 758.3, 695.5; ¹H NMR (CDCl₃, 400 MHz): δ_H = 7.23 - 7.32 (m, 4H), 7.01 - 7.14 (m, 5H), 4.22 - 4.29 (q, J = 7.34 Hz, 2H), 4.03 (q, J = 7.34 Hz, 2H), 1.29 - 1.34 (t, J = 7.09 Hz, 3H), 1.00 (t, J = 7.09 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 165.7, 163.6, 148.6, 143.9, 142.9, 129.4, 124.8, 123.8, 89.7, 62.8, 62.2, 13.9, 13.6; HR-MS (ESI+) m/z calculated for [C_{20}H_{20}ClINO₄]^+ = [M+H]^+: 500.0126; found: 500.0139.

(Z)Diethyl 2-((4-bromophenyl)(phenyl)amino)-3-iodomaleate (4kaa)

Yellow oil (140 mg, 88%); FT-IR: (MIR-ATR, 4000-600 cm⁻¹): ν_max = 2890.20, 1730.71, 1520.35, 1461.81, 1368.26, 1294.03, 1229.20, 1175.10, 1020.22, 754.92, 605.23; ¹H NMR (CDCl₃, 400 MHz): δ_H = 7.36 - 7.42 (m, 2H), 7.27 - 7.32 (m, 2H), 7.07 - 7.14 (m, 3H), 6.94 - 7.00 (m, 2H), 4.26 (q, J = 7.17 Hz, 2H), 4.04 (q, J = 6.85 Hz, 2H), 1.32 (t, J = 7.09 Hz, 3H), 1.00 (t, J = 7.09 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 165.7, 163.5, 148.4, 143.8, 143.4, 132.3, 129.4, 125.1, 124.8, 123.8, 117.1, 90.2, 62.8, 62.2, 13.9, 13.6; HR-MS (ESI+) m/z value calculated for [C_{20}H_{20}BrINO₄]^+ = [M+H]^+: 547.9650; found: 547.9652.

(Z)Dimethyl 2-((4-bromophenyl)(phenyl)amino)-3-iodomaleate (4kab)

Yellow oil (125 mg, 83%); FT-IR(MIR-ATR, 4000-600 cm⁻¹): ν_max = 2951.6, 2923.2, 2851.3, 1729.9, 1552.4, 1485.4, 1433.2, 1219.9, 1146.6, 1043, 986.7, 816, 733, 695; ¹H NMR (CDCl₃, 400 MHz): δ_H = 7.40 (d, J = 8.8 Hz, 2H); 7.31 (m, 2H); 7.13 (s, 1H); 7.08 (d, J = 7.8 Hz, 2H); 6.96 (d, J = 8.8 Hz, 2H); 3.81 (s, 3H); 3.59 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 166.1, 164.1, 148.6, 143.7, 143.3, 132.4, 129.4, 125.1, 124.9, 123.9, 117.3, 88.9, 53.6, 53.0; HR-MS (ESI+) m/z value calculated for [C_{18}H_{15}BrINO₄]^+ = [M+K]^+: 514.9229; found: 514.9225.

(Z)Diethyl 2-((2-bromophenyl)(phenyl)amino)-3-iodomaleate (4laa)
Yellow oil (126 mg, 79%); FT-IR: (MIR-ATR, 4000-600 cm$^{-1}$): $\nu_{\text{max}} = 2892.21, 1720.74, 1527.45, 1471.88, 1368.26, 1294.03, 1219.26, 1176.16, 1026.28, 754.92, 604.33; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H = 7.57 - 7.61$ (m, 1H), 7.31 - 7.37 (m, 2H), 7.21 - 7.30 (m, 2H), 6.98 - 7.15 (m, 3H), 6.75 (br. s., 1H), 4.23 (q, $J = 6.85$ Hz, 2H), 4.00 (q, $J = 6.85$ Hz, 2H), 1.30 (t, $J = 7.09$ Hz, 3H), 0.97 (t, $J = 7.09$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): 165.7, 163.8, 150.6, 144.3, 142.1, 134.4, 129.8, 129.1, 128.6, 127.7, 124.3, 123.3, 85.0, 62.6, 62.0, 13.9, 13.5; HR-MS (ESI+) m/z value calculated for [C$_{20}$H$_{20}$BrNO$_3$]$^+$ = [M+H]$^+$: 547.9655; found: 547.9656

(Z)Diethyl 2-iodo-3-((2-methyl-3-nitrophenyl)(phenyl)amino)maleate (4maa)

Yellow oil (129 mg, 75%); FT-IR: (MIR-ATR, 4000-600 cm$^{-1}$): $\nu_{\text{max}} = 3018, 2949.9, 1707, 1550.3, 1350, 1288.7, 1199, 1074, 731, 695.2; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H = 7.72$ (d, $J = 7.83$ Hz, 1H), 7.51 (d, $J = 7.82$ Hz, 1H), 7.36 (t, $J = 8.07$ Hz, 1H), 7.27 (s, 2H), 7.08 - 7.14 (m, 1H), 7.01 (br. s., 1H), 6.76 (br. s., 1H), 4.24 (q, $J = 7.34$ Hz, 2H), 4.02 (q, $J = 7.01$ Hz, 2H), 2.21 (s, 3H), 1.32 (t, $J = 7.09$ Hz, 3H), 0.99 (t, $J = 7.09$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): 165.4, 163.6, 152.0, 150.5, 144.4, 137.5, 131.9, 130.9, 129.5, 127.3, 126.8, 124.8, 122.0, 85.6, 77.4, 77.1, 76.7, 62.8, 62.3, 15.9, 13.9, 13.5; HR-MS (ESI+) m/z value calculated for [C$_{21}$H$_{15}$IN$_2$NaO$_6$]$^+$ = [M+Na]$^+$: 547.0342; found: 547.0322

(Z)Diethyl 2-iodo-3-((4-(methoxycarbonyl)phenyl)(phenyl)amino)maleate (4aba)

Yellow oil (252 mg, 90%); FT-IR: (MIR-ATR, 4000-600 cm$^{-1}$): $\nu_{\text{max}} = 2982.2, 2952.2, 1714.8, 1590.5, 1506.7, 1489.8, 1434.6, 1366.6, 1271.9, 1216.4, 1175.6, 1106.7, 1039.5, 767.5, 695.5; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H = 7.96$ (d, $J = 8.8$ Hz, 2H), 7.34 (m, 2H), 7.17 (m, 3H), 7.07 (d, $J = 8.3$ Hz, 2H), 4.29 (q, $J = 7.2$ Hz, 2H), 4.05 (q, $J = 6.8$ Hz, 2H), 3.89 (s, 3H), 1.35 (t, $J = 7.3$ Hz, 3H), 1.01 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): 166.6, 165.7, 163.1, 148.5, 147.2, 143.1, 131.0, 129.5, 125.5, 124.8, 124.7, 121.2, 93.7, 62.8, 62.3, 52.0, 13.9, 13.6; HR-MS (ESI+) m/z value calculated for [C$_{22}$H$_{21}$INaO$_6$]$^+$ = [M+Na]$^+$: 523.0492; found: 523.0488

(Z)Diethyl 2-iodo-3-((4-(methoxycarbonyl)phenyl)(4-methoxyphenyl)amino)maleate (4abb)

Yellow oil (231 mg, 87%); FR-IR: (MIR-ATR, 4000-600 cm$^{-1}$): $\nu_{\text{max}} = 3001.0, 2951.4, 2842.4, 1713.4, 1589.6, 1489.4, 1432.9, 1271.4, 1217.8, 1104.8, 1039.7, 800.8, 760.9, 695.6; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H = 7.96$ (d, $J = 8.8$ Hz, 2H), 7.34 (m, 2H), 7.18 (d, $J = 8.3$ Hz, 3H), 7.05 (d, $J = 8.8$ Hz, 2H), 3.89 (s, 3H), 3.84 (s, 3H), 3.6 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): 166.6, 166.1, 163.8, 148.3, 147.5, 142.9, 131.1, 129.6, 125.6, 124.9, 124.7, 121.2, 92.7, 53.6, 53.0, 52.0; HR-MS (ESI+) m/z value calculated for [C$_{20}$H$_{13}$IKNO$_6$]$^+$ = [M+K]$^+$$[H_2O]$: 515.9705; found: 515.9703

(Z)Dimethyl 2-ido-3-((4-(methoxycarbonyl)phenyl)(4-methoxyphenyl)amino)maleate (4gbb)
Yellow oil (164 mg, 77%); FT-IR (MIR-ATR, 4000-600 cm\(^{-1}\)) \(\nu_{\text{max}} = 2952.1, 2924.2, 2851.7, 1719.9, 1605.7, 1506.6, 1434.1, 1277.0, 1245.4, 1176.7, 1109.6, 1035.7, 838.2, 769.1, 696.9; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta_{\text{H}} = 7.93\) (d, \(J = 8.8\) Hz, 2H); 7.14 (d, \(J = 8.8\) Hz, 2H); 6.96 (d, \(J = 8.8\) Hz, 2H); 6.88 (d, \(J = 8.8\) Hz, 2H); 3.89 (s, 3H); 3.82 (s, 3H); 3.61 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): 166.6, 166.0, 164.0, 157.8, 148.8, 148.1, 135.5, 131.0, 127.3, 124.4, 120.0, 114.7, 90.3, 55.5, 53.6, 53.0, 52.0; HR-MS (ESI+) m/z value calculated for \([\text{C}_{21}\text{H}_{22}\text{I\text{NO}}_7]^+ = [\text{M+H}]^+\): 525.0284; found: 525.0280.

(Z)Dimethyl 2-((4-bromophenyl)(4-(methoxycarbonyl)phenyl)amino)-3-iodomaleate (4kbb)

Yellow oil (152 mg, 91%); FT-IR (MIR-ATR, 4000-600 cm\(^{-1}\)) \(\nu_{\text{max}} = 3000.51, 2950.90, 2838.30, 1715.90, 1595.42, 1498.90, 1423.12, 1270.81, 1222.7, 1094.96, 1049.98, 976.85, 819.89, 769.51, 685.30; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta_{\text{H}} = 7.96\) (d, \(J = 8.80\) Hz, 2H); 7.46 (d, \(J = 8.80\) Hz, 2H); 7.04 (d, \(J = 8.31\) Hz, 4H); 3.90 (s, 3H); 3.84 (s, 3H); 3.62 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): 166.5, 165.9, 163.5, 147.9, 146.7, 142.1, 132.7, 131.8, 131.2, 126.0, 125.3, 121.2, 118.5, 116.2, 94.1, 53.7, 53.2, 52.1, 29.7; HR-MS (ESI+) m/z value calculated for \([\text{C}_{20}\text{H}_{17}\text{BrIKNO}_3]^+ = [\text{M+K}]^+\): 611.8920; found: 611.8921.

(Z)Diethyl 2-((2-bromo-5-methylphenyl)(4-(methoxycarbonyl)phenyl)amino)-3-iodomaleate (4nba)

Yellow oil (136 mg, 86%); FT-IR: (MIR-ATR, 4000-600 cm\(^{-1}\)) \(\nu_{\text{max}} = 2981.3, 2951.9, 1714.3, 1606.8, 1565, 1486.9, 1434.4, 1275, 1215.6, 1104.8, 1014.3, 850.3, 768.5, 735.2, 696.5; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta_{\text{H}} = 7.93\) (m, 2H); 7.45 (s, 1H); 7.24 (s, 1H); 7.18 (s, 1H); 6.95 (br, s, 1H); 6.74 (br, s, 1H); 4.25 (q, \(J = 7.1\) Hz, 2H); 4.03 (q, \(J = 6.8\) Hz, 2H); 3.88 (s, 3H); 2.36 (s, 3H); 1.32 (t, \(J = 7.1\) Hz, 3H); 1.02 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 166.6, 165.6, 163.5, 149.0, 148.4, 138.7, 138.3, 134.8, 130.8, 129.7, 129.3, 124.8, 123.0, 89.3, 67.1, 62.8, 62.3, 52.0, 20.8, 13.9, 13.6; HR-MS (ESI+) m/z value calculated for \([\text{C}_{23}\text{H}_{25}\text{BrIKNO}_3]^+ = [\text{M+K}]^+\): 614.9753; found: 614.9749.

(Z)Diethyl 2-iodo-3-((3-nitrophenyl)(phenyl)amino)maleate (4aca)

Yellow oil (218 mg, 84%); FT-IR: (MIR-ATR, 4000-600 cm\(^{-1}\)) \(\nu_{\text{max}} = 3006.1, 2944.9, 1732.9, 1558.3, 1499.7, 1444.1, 1288.7, 1144.4, 1032.8, 968.8, 747.4, 665.4; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta_{\text{H}} = 7.88 - 7.93\) (m, 2 H), 7.43 - 7.48 (m, 1 H), 7.33 - 7.39 (m, 3 H), 7.14 - 7.22 (m, 3 H), 4.29 (q, \(J=7.35\) Hz, 2 H), 4.06 (q, \(J=7.35\) Hz, 2 H), 1.34 (t, \(J=7.09\) Hz, 3 H), 1.01 (t, \(J=7.09\) Hz, 3 H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): 165.5, 163.0, 149.2, 147.2, 145.7, 142.9, 130.1, 129.7, 127.9, 125.7, 124.2, 118.2, 117.0, 93.8, 63.0, 62.4, 13.9, 13.6; HR-MS (ESI+) m/z value calculated for \([\text{C}_{20}\text{H}_{13}\text{IN}_2\text{NaO}_5]^+ = [\text{M+Na}]^+\): 533.0185; found: 533.0188.

(Z)Dimethyl 2-((4-fluorophenyl)(phenyl)maleate)-3-iodomaleate (4adb)

Yellow oil (220 mg, 90%); FT-IR: (MIR-ATR, 400-600 cm\(^{-1}\)) \(\nu_{\text{max}} = 2952.9, 2916.2, 2849.7, 1730.8, 1678.8, 1551.7, 1502.6, 1216.4, 1148.9, 616.8; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta_{\text{H}} = 7.29\) (m, 2H); 7.09 (m,
$3$H); $7.02$ (m, 4H); $3.80$ (s, 3H); $3.58$ (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 166.1, 164.4, 161.1, 158.7, 149.6, 144.3$ 129.4 126.2, 124.6, 123.5, 116.3, 116.1, 86.5, 53.6, 53.9; HR-MS (ESI+) m/z value calculated for [C$_{13}$H$_{15}$FNO$_3$]$^+$ = (M+NH$_4$)$^+\cdot$[H$_2$O]: 455.0262; found: 455.0255.

**(Z)Dimethyl 2-((2,4-dimethylphenyl)(4-fluorophenyl)amino)-3-iodomaleate (4oda)**

Yellow oil (173 mg, 87%); FT-IR: (MIR-ATR, 4000-600 cm$^{-1}$): $\nu_{\text{max}} = 2918.74, 2850.71, 1733.96, 1543.47, 1502.20, 1212.56, 1045.19, 966.76, 828.20, 734.06$; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H = 6.79 - 7.06$ (m, 7 H), $4.20$ (q, $J = 6.85$ Hz, 2H), $3.99$ (q, $J = 7.34$ Hz, 2H), $2.31$ (s, 3H), $2.06$ (s, 3H), $1.29$ (t, $J = 7.09$ Hz, 3H), $1.00$ (t, $J = 7.09$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): 165.6, 164.2, 160.5, 158.1, 151.9, 141.1, 141.0, 139.4, 136.8, 135.9, 132.3, 128.1, 127.8, 124.9, 124.8, 115.9, 115.7, 79.4, 62.6, 62.0, 21.0, 19.0, 14.0, 13.6; HR-MS (ESI+) m/z value calculated for [C$_{22}$H$_{23}$FNO$_4$]$^+$ = [M+H]$^+$: 514.0789; found: 514.0784.

**(Z)Diethyl 2-(butyl(phenyl)amino)-3-iodomaleate (4paa)**

Yellow oil (216 mg, 71%); FT-IR (MIR-ATR, 4000-600 cm$^{-1}$) $\nu_{\text{max}} = 3002.1, 2951.7, 1724.9, 1610.7, 1516.6, 1424.1, 1247.0, 1228.4, 1173.7, 1033.7, 832.2, 767.1, 691.9$; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H = 7.24 - 7.31$ (m, 2H), $6.92 - 7.00$ (m, 3H), $4.21$ (dq, $J = 17.61, 7.17$ Hz, 4H), $3.51 - 3.62$ (m, 2H), $1.66 - 1.76$ (m, 2H), $1.35 - 1.41$ (m, 2H), $1.31$ (t, $J = 7.09$ Hz, 3H), $1.20$ (t, $J = 7.09$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): 165.7, 164.2, 151.1, 145.1, 137.5, 129.2, 122.7, 122.3, 119.9, 85.0, 77.4, 77.1, 76.8, 62.5, 62.1, 52.3, 31.1, 20.2, 14.0, 13.9, 13.8; HR-MS (ESI+) m/z value calculated for [C$_{16}$H$_{12}$INaO$_4$]$^+$ = [M+Na]$^+$: 468.0648; found: 468.0644.

**(Z)Diethyl 2-(benzyl(phenyl)amino)-3-iodomaleate (4qaa)**

Yellow oil (168 mg, 75%); FT-IR (MIR-ATR, 4000-600 cm$^{-1}$) $\nu_{\text{max}} = 3062.2, 3030, 2949.92, 1730.9, 1699.3, 1621.9, 1540.1, 1241.4, 1030.4, 998.0, 808.4, 730.44, 696.07$; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H = 7.42$ (d, $J = 7.34$ Hz, 2H), $7.33$ (t, $J = 7.58$ Hz, 2H), $7.20 - 7.26$ (m, 3H), $6.93 - 6.99$ (m, 3H), $4.82$ (s, 2H), $4.23$ (q, $J = 6.85$ Hz, 2H), $4.14$ (q, $J = 7.34$ Hz, 2H), $1.31$ (t, $J = 7.09$ Hz, 3H), $1.13$ (t, $J = 7.09$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): 165.7, 164.1, 151.1, 145.5, 137.8, 129.1, 128.5, 127.3, 122.6, 120.3, 62.6, 62.2, 56.6, 13.9, 13.7; HR-MS (ESI+) m/z value calculated for [C$_{23}$H$_{22}$NO$_4$]$^+$ = [M+H]$^+$: 480.0670; found: 480.0672.

**(Z)Dimethyl 2-(cyclopropyl(phenyl)amino)-3-iodomaleate (4rab)**

Yellow oil (239 mg, 68%); FT-IR (MIR-ATR, 4000-600 cm$^{-1}$) $\nu_{\text{max}} = 2988.1, 2924.0, 1726.4, 1645.6, 1501.6, 1444.1, 1287.4, 1245.4, 1103.6, 1035.7, 818.2, 734.2, 636.3; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H = 7.25 - 7.31$ (m, 2H), $7.05$ (d, $J = 7.83$ Hz, 2H), $6.95$ (t, $J = 7.34$ Hz, 1H), $3.85$ (s, 3H), $3.71$ (s, 3H), $2.86 - 2.92$ (m, 1H), $0.85 - 0.91$ (m, 4H); $^{13}$C NMR (CDCl$_3$, 100 MHz): 164.6, 163.7, 145.0, 129.2, 121.0, 116.2,
96.7, 53.5, 53.0, 32.2, 8.6; HR-MS (ESI+) m/z value calculated for [C_{15}H_{16}IKNO_{4}]^+ = [M+K]^+: 439.9760; found: 439.9761.

(Z)Tetraethyl 3,3’-(1,4-phenylenebis(phenylmethylene))bis(2-iodomaleate) (4a”aa)

Yellow oil (212 mg, 54%); FT-IR (MIR-ATR, 4000-600 cm\(^{-1}\)) \(v_{\text{max}} = 2952, 2853.9, 1737.7, 1695.7, 1536.6, 1438.1, 1345.4, 1186.7, 1015.7, 828.4, 769.3, 676.2; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta_{\text{H}} = 7.25 - 7.33 \text{ (m, 6H), 7.05 - 7.10 \text{ (m, 8H), 4.25 (q, J = 7.01 Hz, 4H), 4.04 (q, J = 6.85 Hz, 4H), 1.32 (t, J = 7.34 Hz, 6H), 1.02 (t, J = 7.09 Hz, 6H); }\(^{13}\)C NMR (CDCl\(_3\), 100 MHz). 165.8, 163.8, 149.2, 144.2, 140.7, 129.3, 125.2, 124.5, 123.5, 88.2, 62.7, 62.1, 13.9, 13.7; HR-MS (ESI+) m/z value calculated for [C_{34}H_{35}I_{2}N_{5}O_{8}]^+ = [M+H]^+: 853.0480; found: 853.0483.

(Z)Tetramethyl 3,3’-(1,4-phenylenebis(phenylmethylene))bis(2-iodomaleate) (4a”ab)

Yellow oil (225 mg, 61%); FT-IR (MIR-ATR, 4000-600 cm\(^{-1}\)) \(v_{\text{max}} = 2953.2, 2948, 1709, 1688, 1508.4, 1495.3, 1434.2, 1214.3, 1183, 1119.4, 1032.7, 752.4, 691.5; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta_{\text{H}} = 7.27 - 7.33 \text{ (m, 4H), 7.06 - 7.14 \text{ (m, 6H), 7.04 (s, 4H), 3.80 (s, 6H), 3.59 (s, 6H); }\(^{13}\)C NMR (CDCl\(_3\), 100 MHz). 166.1, 164.4, 149.5, 143.9, 140.7, 129.4, 125.2, 124.8, 123.6, 86.9, 53.6, 53.0; HR-MS (ESI+) m/z value calculated for [C_{30}H_{27}I_{2}N_{5}O_{8}]^+ = [M+H]^+: 796.9855; found: 796.9857.

Diethyl 1-phenyl-1H-indole-2,3-dicarboxylate (5a)

Yellow liquid (29 mg, 81%); FT-IR (MIR-ATR, 4000–600 cm\(^{-1}\)) \(v_{\text{max}} = 2950, 1737, 1707, 1539, 1501, 1451, 1437, 1257, 1208, 1178, 1063, 788, 755, 718; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta_{\text{H}} = 8.15 \text{ (d, J = 6.85 Hz, 1H), 7.41 - 7.48 \text{ (m, 3H), 7.33 - 7.37 (m, 2H), 7.18 - 7.26 (m, 2H), 7.10 - 7.14 \text{ (m, 1H), 4.35 (q, J = 7.34 Hz, 2H), 4.16 (q, J = 7.01 Hz, 2H), 1.35 (t, J = 7.09 Hz, 3H), 1.05 (t, J = 7.09 Hz, 3H); }\(^{13}\)C NMR (CDCl\(_3\), 100 MHz): 164.0, 162.4, 137.3, 136.5, 136.3, 129.6, 129.0, 127.3, 125.3, 124.6, 123.0, 122.3, 111.2, 108.3, 62.1, 60.4, 14.4, 13.8; HR-MS (ESI+) m/z calculated for [C_{20}H_{19}NNaO_{4}]^+ = [M+Na]^+: 360.1206; found: 360.12061.

Diethyl 1-(o-tolyl)-1H-indole-2,3-dicarboxylate (5b)

Yellow liquid (28.20 mg, 75%); FT-IR (MIR-ATR, 4000–600 cm\(^{-1}\)) \(v_{\text{max}} = 2981, 1735, 1700, 1411, 1253, 1181, 1111, 1054, 1010, 737, 610; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta_{\text{H}}=8.15 \text{ (d, J = 7.82 Hz, 1H), 7.16 - 7.36 (m, 7H), 6.82 (d, J = 8.31 Hz, 1H), 4.34 (q, J = 7.17 Hz, 2H), 4.10 (q, J = 7.34 Hz, 2H), 1.92 (s, 3H), 1.34 (t, J = 7.09 Hz, 3H), 0.98 (t, J = 7.09 Hz, 3H); }\(^{13}\)C NMR (CDCl\(_3\), 100 MHz): 164.1, 162.1, 137.2, 137.2, 136.2, 135.2, 131.0, 129.7, 128.8, 126.9, 125.1, 124.7, 122.9, 122.3, 111.2, 108.1, 61.9, 60.4, 17.3, 14.4, 13.7; HR-MS (ESI+) m/z calculated for [C_{21}H_{21}NNaO_{4}]^+ = [M+Na]^+: 374.1362; found: 374.1360.
**Diethyl 1-(4-bromophenyl)-IH-indole-2,3-dicarboxylate (5c)**

Brown liquid (15 mg, 40%); FT-IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2981.52, 1735.50, 1705.87, 1540.89, 1495.40, 1451.37, 1416.97, 1381.75, 1255.68, 1200.29, 1091.59, 1041.43, 748.16, 603.76; ¹H NMR (CDCl₃, 400 MHz): δ_H = 8.22 (d, J = 7.34 Hz, 1H), 7.67 (d, J = 7.82 Hz, 2H), 7.29 - 7.36 (m, 4H), 7.17 (d, J = 7.34 Hz, 1H), 4.42 (q, J = 6.85 Hz, 2H), 4.27 (q, J = 6.85 Hz, 2H), 1.42 (t, J = 7.09 Hz, 3H), 1.20 (t, J = 7.09 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): 163.9, 162.2, 138.8, 137.2, 135.8, 135.5, 132.8, 129.7, 129.2, 129.1, 128.9, 127.1, 125.3, 124.9, 123.2, 122.9, 122.5, 110.9, 109.0, 62.3, 60.6, 60.5, 14.4, 13.9; HR-MS (ESI+) m/z calculated for [C₂₀H₁₈BrNNaO₄]⁺ = [M+Na]⁺: 439.0344; found: 439.0344.

**Diethyl 1-(4-bromophenyl)-IH-indole-2,3-dicarboxylate (5c')**

Yellow liquid (12 mg, 32%); FT-IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2981, 1702, 1443, 1409, 1251, 1179, 1061, 694; ¹H NMR (CDCl₃, 400 MHz): δ_H = 8.29 (d, J = 1.47 Hz, 1H), 7.42 - 7.47 (m, 3H), 7.27 - 7.34 (m, 3H), 6.98 (d, J = 8.80 Hz, 1H), 4.34 (q, J = 6.85 Hz, 2H), 4.13 - 4.18 (m, 2H), 1.34 (t, J = 7.09 Hz, 3H), 1.05 (t, J = 7.09 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): 163.5, 161.9, 137.2, 136.0, 135.9, 129.7, 129.3, 127.7, 127.1, 126.8, 124.9, 116.6, 112.7, 107.6, 77.4, 77.1, 76.8, 62.3, 60.6, 14.4, 13.8; HR-MS (ESI+) m/z calculated for [C₂₀H₁₈BrNNaO₄]⁺ = [M+Na]⁺:440.0291; found:440.0290.

**Diethyl 5-bromo-1-phenyl-IH-indole-2,3-dicarboxylate (5d)**

Brown liquid (26 mg, 66%); FT-IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2924.22, 2852.73, 1735.49, 1703.19, 1538.89, 1505.74, 1451.12, 1411.88, 1379.90, 1255.30, 1182.41, 1150.48, 1110.04, 1054.63, 1012.64, 790.45, 736.98, 611.61; ¹H NMR (CDCl₃, 400 MHz): δ_H = 8.19 - 8.26 (m, 1H), 7.47 - 7.55 (m, 2H), 7.27 - 7.41 (m, 4H), 7.16 (d, J = 7.34 Hz, 1H), 4.42 (q, J = 7.17 Hz, 2H), 4.27 (q, J = 7.17 Hz, 2H), 1.42 (t, J = 7.09 Hz, 3H), 1.19 (t, J = 7.09 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): 163.9, 162.2, 137.2, 135.9, 135.0, 135.0, 129.8, 128.6, 125.3, 124.9, 123.2, 122.4, 110.9, 109.0, 62.3, 60.6, 14.4, 13.8; HR-MS (ESI+) m/z calculated for [C₂₂H₂₁NNaO₄]⁺ = [M+Na]⁺: 388.1519; found: 388.1516.

**Diethyl 1-(4-chlorophenyl)-IH-indole-2,3-dicarboxylate (5e)**

Yellow liquid (27 mg, 64%); FT-IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2949, 1704, 1538, 1477, 1436, 1250, 1206, 1174, 1074, 1073, 748; ¹H NMR (CDCl₃, 400 MHz): δ_H = 8.15 - 8.20 (m, 1H), 7.75 - 7.79 (m, 1H), 7.39 - 7.51 (m, 3H), 7.29 - 7.36 (m, 2H), 6.93 (d, J = 7.34 Hz, 1H), 3.97 (s, 3H), 3.77 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 164.5, 162.0, 137.3, 136.0, 134.2, 133.7, 131.0, 130.5, 128.4, 125.3, 125.1, 123.3,
Diethyl 1-(4-methoxyphenyl)-1H-indole-2,3-dicarboxylate (5f & 5f’)

Yellow liquid (28 mg, 72%); FT-IR (MIR-ATR, 4000–600 cm⁻¹) νmax = 2980, 1868, 1827, 1482, 1454, 1411, 1252, 1209, 1159, 1117, 1058, 102, 758, 697; ¹H NMR (CDCl₃, 400 MHz): δH = 8.19 - 8.24 (m, 1H), 7.69 (d, J = 1.96 Hz, 1H), 7.47 - 7.55 (m, 3H), 7.39 - 7.43 (m, 2H), 7.25 - 7.36 (m, 4H), 7.15 (d, J = 7.83 Hz, 1H), 7.09 (d, J = 8.80 Hz, 1H), 7.00 - 7.04 (m, 2H), 6.93 (dd, J = 9.05, 2.69 Hz, 1H), 4.41 (qd, J = 7.17, 2.93 Hz, 4H), 4.24 (dq, J = 11.31, 7.15 Hz, 4H), 3.91 (s, 3H), 3.88 (s, 2H), 1.41 (td, J = 7.09, 3.42 Hz, 6H), 1.17 (t, J = 7.09 Hz, 3H), 1.13 (t, J = 7.09 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): 164.2, 164.1, 162.3, 159.9, 156.5, 137.7, 136.6, 136.2, 132.4, 129.5, 128.9, 128.6, 127.1, 126.2, 125.4, 125.2, 124.5, 122.9, 122.2, 115.5, 114.6, 112.1, 111.2, 107.8, 103.0, 62.1, 62.1, 60.3, 60.3, 55.7, 55.6, 14.4, 14.4, 13.9, 13.8; HR-MS (ESI+) m/z calculated for [C₂₁H₂₁NNaO₅]⁺ = [M+Na]⁺: 390.1312; found: 390.1314.

Diethyl 1-(2,4-dimethylphenyl)-1H-indole-2,3-dicarboxylate (5g)

Yellow semisolid (30.46 mg, 78%); IR (MIR-ATR, 4000–600 cm⁻¹) νmax = 2981, 1735, 1700, 1411, 1253, 1245, 122.9, 122.2, 115.5, 114.6, 112.1, 111.2, 107.8, 61.9, 60.3, 21.3, 17.2, 14.4, 13.7; HR-MS (ESI+) m/z calculated for [C₂₂H₂₃NNaO₄]⁺ = [M+Na]⁺: 388.1535; found: 388.1535.

Diethyl 1-(3-methyl-2-nitrophenyl)-1H-indole-2,3-dicarboxylate (5h)

Yellow liquid (28.8 mg, 68%); IR (MIR-ATR, 4000–600 cm⁻¹) νmax = 2985, 1740, 1704, 1531, 1350, 1261, 1199, 1199, 1174, 1074, 731; ¹H NMR (CDCl₃, 400 MHz): δH = 8.14 (d, J = 6.85 Hz, 1H), 7.98 (dd, J = 7.83, 0.98 Hz, 1H), 7.40 - 7.51 (m, 2H), 7.20 - 7.32 (m, 2H), 6.80 (d, J = 7.82 Hz, 1H), 4.37 (q, J = 7.34 Hz, 2H), 4.14 (q, J = 7.09, 1.22 Hz, 2H), 2.06 (s, 3H), 1.36 (t, J = 7.09 Hz, 3H), 1.05 (t, J = 7.09 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): 163.8, 161.4, 151.0, 137.7, 137.2, 134.8, 133.5, 133.0, 127.2, 125.6, 125.2, 123.4, 122.7, 110.8, 110.2, 77.4, 77.1, 76.8, 62.1, 60.7, 14.4, 14.1, 13.8; HR-MS (ESI+) m/z calculated for [C₂₂H₂₉N₂NaO₆]⁺ = [M+Na]⁺: 419.1219; found: 419.1219.
References:


