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Stereoselective Heck-type Cross-Coupling Reactions of Iodine Heterocyclic Compounds with Olefins

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Abstract—Polyfunctional molecules are prepared by a modified stereoselective Heck-type cross-coupling reaction between iodine heterocyclic compounds and olefins in DMF using $Pd(OAc)_2$ as a catalyst in the presence of bases (Na_2CO_3 or K_2CO_3). This coupling reaction proceeds smoothly at room temperature and gave coupling products in high yields. © 2000 Elsevier Science Ltd. All rights reserved.

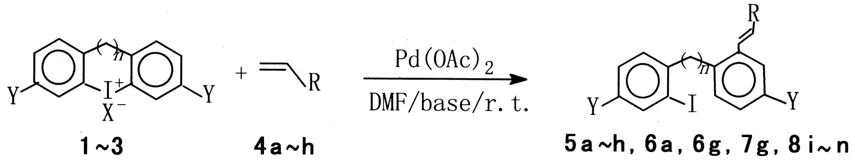
Introduction

The palladium-catalyzed cross-coupling of olefins with organic electrophiles (i.e. halides and triflates) in the presence of bases is known as the Heck reaction[1] and it has become an extremely powerful tool in organic synthesis. However, coupling with aryl or vinyl halides and triflates usually requires a longer reaction time and a higher temperature.[2,3] In connection with our programs to utilize hypervalent iodine salts[4,5] and iodanes[6,7] as electrophiles for palladium-catalyzed C–C bond formation,[8,9] we report here the palladium-catalyzed cross-coupling of olefins with iodine heterocyclic compounds using $Pd(OAc)_2$ as a catalyst at an ambient temperature in detail (Scheme 1).

Results and Discussion

Palladium-catalyzed arylation of olefins by iodine heterocyclic compounds

At first, we studied the effect of catalysts and bases on the yield of 3,7-bis(*N*,*N*-dimethylamino)-10*H*-dibenz[b,e]iodinium iodide in the reaction of acrolein with 3,7-bis(*N*,*N*-dimethylamino)-10*H*-dibenz[b,e] iodinium iodide in various solvents. The results are shown in Table 1. The reaction proceeded smoothly at room temperature in the presence of $PdCl_2$, Pd, $PdCl_2(PPh_3)_2$, $Pd(OAc)_2$ and $Pd(dba)_2$. The $Pd(OAc)_2$ was found to be the most effective catalyst for this cross-coupling and only a



$X^- = HSO_4^-$, HCO_2^-, Cl^-, I^-

$X^- = I^-$: n=1; Y = NMe_2 (**1**); R = CHO (**5a**), COMe (**5b**), COEt (**5c**), COOMe (**5d**), CN (**5e**), COOH (**5f**), $CONH_2$ (**5g**), $PO(OEt)_2$ (**5h**), *p*-$PhNO_2$ (**8i**), *m*-$PhNO_2$ (**8j**), PhH (**8k**), *p*-PhBr (**8l**), *m*-PhBr (**8m**), *p*-PhCl (**8n**).

$X^- = I^-$: n=1; Y = NO_2 (**2**); R = CHO (**6a**), $CONH_2$ (**6g**)

$X^- = I^-$: n=0; Y = H (**3**); R = $CONH_2$ (**7g**)

Scheme 1.

Keywords: iodine heterocycles; Pd-catalyzed; coupling reaction.

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Table 1. Optimization of catalytic system in cross-coupling of 3,7-bis(*N*,*N*-dimethylamino)-10*H*-dibenz [b,e]iodinium iodide (**1**) with acrolien (**4a**) (reactions were carried out at room temperature in solvent (10 ml) by using 1 mmol of 3,7-bis(*N*,*N*-dimethylamino)-10*H*-dibenz[b,e]iodinium iodide (**1**), 2–5 mmol acrolein (**4a**), base and 2.5 mol% of catalyst under argon)

Entry	Catalyst	Base (mol. equiv.)	Solvent	Time (h)	Yield (%)[a]
1	$Pd(OAc)_2$	Na_2CO_3 (2)	DMF	2	90
2	$Pd(OAc)_2$	Na_2CO_3 (2)	DMF/H_2O	2	53
3	$Pd(OAc)_2$	Bu_3N (2.5)	DMF	2	87
4	$Pd(OAc)_2$	NaOAc (2)	DMF	2	72
5	$Pd(OAc)_2$	NaOH (3)	DMF	3	68
6	$Pd(OAc)_2$	Na_2CO_3 (2.5)	MeCN	2	40
7	$Pd(OAc)_2$	K_2CO_3 (2)	DMF	2	86
8	$Pd(OAc)_2$	NaOEt (2)	DMF	1.5	54
9	$Pd(OAc)_2$	KOH (3)	DMF	3	62
10	$PdCl_2$	Na_2CO_3 (2)	DMF	2	78
11	Pd	Na_2CO_3 (2)	DMF	6	52
12	$Pd(PPh_3)Cl_2$	Na_2CO_3 (2)	DMF	3	71
13	$Pd(PPh_3)_4$	Na_2CO_3 (2)	DMF	1	Complex[b]
14	$Pd(dba)_2$	Na_2CO_3 (2)	DMF	2	88

[a] Isolated yield of cross-coupling product based on iodine heterocyclic compounds employed.

[b] Expected cross-coupling product is very little.

Table 2. Cross-coupling reaction of iodine heterocyclic compounds **1–3** having various anions with acrylamide (**4g**) in DMF (reactions were carried out at room temperature in solvent (10 ml) by using 1 mmol of iodine heterocyclic compound (**1–3**), 2 mmol acrylamide (**4g**) and 2.5 mol% of catalyst under argon)

Entry	Iodine heterocycle	Anion	Temperature (°C)	Time (h)	Products	Yield (%)[a]
1	**1**	HSO_4^-	25	16	**5g**	51
2	**2**	HSO_4^-	50	20	**6g**	27
3	**3**	HSO_4^-	50	24	**7g**	[b]
4	**1**	HCO_2^-	25	16	**5g**	56
5	**2**	HCO_2^-	50	24	**6g**	30
6	**3**	HCO_2^-	50	24	**7g**	[b]
7	**1**	NO_3^-	25	16	**5g**	45
8	**2**	NO_3^-	50	24	**6g**	[b]
9	**3**	NO_3^-	50	24	**7g**	[b]
10	**1**	Cl^-	25	16	**5g**	58
11	**2**	Cl^-	50	24	**6g**	[b]
12	**3**	Cl^-	50	24	**7g**	[b]
13	**1**	I^-	25	2	**5g**	91
14	**2**	I^-	25	18	**6g**	53
15	**3**	I^-	25	16	**7g**	34

[a] Isolated yield of cross-coupling product based on iodine heterocyclic compounds employed.

[b] Expected cross-coupling product is very little.

Table 3. Cross-coupling reaction of iodine heterocyclic iodides with α,β-unsaturated carbonyl compounds in DMF (reactions were carried out in DMF (10 ml) at room temperature using 1 mmol iodine heterocyclic iodides, 2–5 mmol α,β-unsaturated carbonyl compounds, base and 2.5 mol% $Pd(OAc)_2$ under argon)

Entry	Iodine heterocycle	R	Base (mmol)	Time (h)	Product	Yield (%)[a]
1	**1**	CHO	Na_2CO_3 (2)	2	**5a**	90
2	**1**	$COCH_3$	Na_2CO_3 (2)	2	**5b**	80
3	**1**	COC_2H_5	Na_2CO_3 (2)	2.5	**5c**	82
4	**1**	CO_2CH_3	Na_2CO_3 (2.5)	3	**5d**	85
5	**1**	CN	Na_2CO_3 (2)	4	**5e**	70
6	**1**	COOH	K_2CO_3 (3)	4	**5f**	68
7	**1**	$CONH_2$	Na_2CO_3 (2.5)	6	**5g**	91
8	**1**	$PO(OC_2H_5)_2$	Na_2CO_3 (3)	5	**5h**	65
9	**2**	$CONH_2$	K_2CO_3 (2.5)	18	**6g**	43
10	**2**	CHO	K_2CO_3 (3)	20	**6a**	12
11	**2**	$COCH_3$	K_2CO_3 (3)	48	**6d**	[b]
12	**3**	$CONH_2$	K_2CO_3 (3)	16	**7g**	34
13	**3**	CHO	K_2CO_3 (3)	48	**7a**	[b]

[a] Isolated yield.

[b] Can not be isolated.

Table 4. Cross-coupling reaction of iodine heterocyclic iodides with substituted styrenes in DMF (reactions were conducted in DMF (10 ml) at room temperature using 1 mmol iodine heterocyclic compounds, 2–5 mmol substituted styrenes containing a little hydroquinone and 2.5 mol% $Pd(OAc)_2$ under argon)

Entry	Iodine heterocycle	R	Base (mmol)	Time (h)	Product	Yield (%)[a]
1	**1**	*p*-NO_2	Na_2CO_3 (3)	16	**8i**	88
2	**1**	*m*-NO_2	Na_2CO_3 (3)	24	**8j**	78
3	**1**	H	Na_2CO_3 (3)	24	**8k**	51
4	**1**	*p*-Br	K_2CO_3 (3)	24	**8l**	72
5	**1**	*m*-Br	K_2CO_3 (3)	24	**8m**	74
6	**1**	*p*-Cl	K_2CO_3 (3)	24	**8n**	76
7	**1**	*p*-Ome	K_2CO_3 (3)	48	–	[b]
8	**1**	3,4-*di*-Ome	K_2CO_3 (3)	48	–	No reaction
9	**2**	*p*-NO_2	K_2CO_3 (3)	48	–	No reaction
10	**2**	H	K_2CO_3 (3)	48	–	No reaction
11	**3**	*p*-NO_2	K_2CO_3 (3)	48	–	No reaction
12	**3**	H	K_2CO_3 (3)	48	–	No reaction

[a] Isolated yield.

[b] Expected product can not be isolated.

trans-stereoselective product was obtained. The reaction occurred more quickly in the presence of $Pd(PPh_3)_4$ catalyst, but the product is a more complex mixture (Table 1, entry 13).

Next, we examined the cross-coupling reaction of iodine heterocyclic having various anions with the α,β-unsaturated carbonyl compound acrylamide under established conditions (Table 2). The results show that the same iodine heterocyclic compounds having different anions exhibit different reaction activity. Their reactivity order is $I^- < Cl^- < HCO_2^- < HSO_4^- \approx NO_3^-$.

Representative results of iodine heterocyclic iodide **1**, **2**, **3** with a number of α,β-unsaturated carbonyl compounds and substituted styrenes are summarized in Tables 3 and 4, respectively. When α,β-unsaturated carbonyl compounds were used, the coupling reaction of iodine heterocyclic iodide **1** was completed within 2–6 h at room temperature in a DMF solution of Na_2CO_3 or K_2CO_3 in the presence of 2.5 mol% $Pd(OAc)_2$. However, the reaction of iodine heterocyclic iodide **2** and **3** occurred very slowly under such conditions and the yield of cross-coupling products did not exceed 50% (Table 3, entry 9–13). Therefore, it may be concluded that the electron donating group in the iodine heterocycle iodide accelerates the reaction. Comparing the reaction of **3** with **1**, it is apparent that the reactivity of iodine heterocyclic iodide with the six member ring was higher than that with the five-membered ring.

The cross-coupling reaction of iodine heterocyclic compound **1** with substituted styrenes occurred very slowly under such conditions. It is important to note that substituted styrenes bearing electron withdrawing groups can react readily with iodine heterocyclic iodide in the presence of a base to give *trans*-stereoselective cross-coupling products in higher yield. While substituted styrenes bearing more than one electron donating group are difficult to react with iodine heterocyclic iodide, iodine heterocyclic iodides **2** and **3** do not undergo any reaction with styrenes.

In summary, we have explored the Pd-catalyzed cross-coupling reaction of the iodine heterocyclic compounds **1**–**3** with olefins and established a stereoselective synthesis of (*E*)-substituted olefins in moderate to good yield. The cross-coupling reactivity of iodine heterocyclic iodide bearing electron donating groups are higher than that bearing electron withdrawing groups. The reactivity of iodine heterocyclic iodide with a six-number ring is better than that with a five-number ring. When iodine heterocyclic compounds contain different anions, they showed distinct reactivity.

Experimental

General information

IR spectra were taken on a Nicolet 179SX FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Bruker AM-400 or FC-80A instrument. Mass spectra (MS) were measured on an HP-5988AG CMS spectrometer. CHN contents were determined with Carlo-Erba 1106 elemental analyzer. All reactions were carried out under argon atmosphere and monitored by thin-layer chromatography. Melting points are uncorrected. Iodine heterocyclic compounds, 3,7-bis(*N*,*N*-dimethylamino)-10*H*-dibenz[b,e]iodinium (**1**), 3,7-bisnitro-10*H*-dibenz[b,e]iodinium (**2**) and diphenyleneiodonium(**3**) were synthesized according to the literature.[10–12] α,β-Unsaturated compounds were obtained commercially and used as received. Substituted styrene were prepared according to the known procedures.[13]

Palladium-catalyzed cross-coupling reaction of olefins with iodine heterocyclic compounds (general method)

The olefin (2–5 mmol) was added to the mixture of $Pd(OAc)_2$ (0.025 mmol) and iodine heterocyclic compound (1 mmol) in DMF(10 ml) under stirring at room temperature, then K_2CO_3 or Na_2CO_3 (2–3 mmol) was added. Reaction course was monitored by TLC analyses. After completion of the reaction, the mixture was quenched with 20 ml of saturated NH_4Cl aqueous solution and then extracted with diethyl ether (3×10 ml). The ether layer was dried over anhydrous $MgSO_4$ and evaporated. The crude product was separated by flash chromatography on silica gel (eluents, ethyl acetate/petroleum ether=1:1) to give the products:

5a. Yellow crystal, mp 136–137°C; ^{1}H NMR (80 MHz, CDCl$_3$), δ (ppm): 2.91 (s, 6H), 2.99 (s, 6H), 4.03 (s, 2H), 6.59 (d, 1H, J=15.4 Hz), 6.64–7.23 (m, 6H), 7.71 (d, 1H, J=15.4 Hz), 9.66 (d, 1H, J=7.9 Hz). IR (cm^{-1}): 3020, 1674, 1596, 952 and 976. MS: m/z (%) 434 (M$^+$, 40), 307 (20), 246 (40), 260 (30) and 174 (100). Anal. Calcd For C$_{20}$H$_{23}$IN$_2$O: C, 55.31; H, 5.34; N, 6.45. Found: C, 55.28; H, 5.64; N, 6.48%.

5b. Yellow crystal, mp 164–165°C; ^{1}H NMR (80 MHz, CDCl$_3$), δ (ppm): 2.33(s, 3H), 2.91 (s, 6H), 2.99 (s, 6H), 4.04 (s, 2H), 6.55 (d, 1H, J=16 Hz), 6.61–7.23 (m, 6H), 7.67 (d, 1H, J=16 Hz). IR (cm^{-1}): 3020, 1660, 953 and 975. MS: m/z (%) 448 (M$^+$, 100), 405 (37), 277 (28) and 188 (75). Anal. Calcd For C$_{21}$H$_{25}$IN$_2$O: C, 56.26; H, 5.62; N, 6.24. Found: C, 56.41; H, 5.43; N, 5.98%.

5c. Yellow crystal, mp 124–125°C; ^{1}H NMR (80 MHz, CDCl$_3$), δ (ppm): 1.13 (t, 3H, J=7.3 Hz), 2.68 (q, 2H, J=7.3 Hz), 2.91 (s, 6H), 2.99 (s, 6H), 4.04 (s, 2H), 6.48 (d, 1H, J=16 Hz), 6.62–7.24 (m, 6H), 7.63 (d, 1H, J=16.0 Hz). IR (cm^{-1}): 3020, 1660, 1599, 950 and 980. MS: m/z (%) 462 (M$^+$, 65), 405 (30), 390 (17) and 277 (22). Anal. Calcd For C$_{22}$H$_{27}$IN$_2$O: C, 57.15; H, 5.89; N, 6.06. Found: C, 57.21; H, 6.07; N, 6.11%.

5d. Green needle crystal, mp 131–132°; ^{1}H NMR (80 MHz, CDCl$_3$), δ (ppm): 2.91 (s, 6H), 2.99 (s, 6H), 3.61 (s, 3H), 4.02 (s, 2H), 6.35 (d, 1H, J=15.6 Hz), 6.63–7.24 (m, 6H), 7.97 (d, 1H, J=15.6 Hz). IR (cm^{-1}): 3020, 1706, 1595, 946 and 975. MS: m/z (%) 464 (M$^+$, 100), 277 (22) and 264 (29). Anal. Calcd For C$_{21}$H$_{25}$IN$_2$O$_2$: C, 54.32; H, 5.43; N, 6.03. Found: C, 54.37; H, 5.46; N, 6.22%.

5e. Yellow–brown crystal, mp 148–149°C; ^{1}H NMR (80 MHz, CDCl$_3$), δ (ppm): 2.93 (s, 6H), 2.99 (s, 6H), 3.95 (s, 2H), 5.77 (d, 1H, J=16.5 Hz), 6.62–7.25 (m, 6H), 7.62 (d, 1H, J=16.5 Hz). IR (cm^{-1}): 3020, 2208, 1598, and 957. MS: m/z (%) 431 (M$^+$, 100), 304 (12), and 289 (10). Anal. Calcd For C$_{20}$H$_{22}$IN$_3$: C, 55.70; H, 5.14; N, 9.74. Found: C, 55.83; H, 5.32; N, 9.80%.

5f. Green crystal, mp 157–158°C; ^{1}H NMR (80 MHz, CDCl$_3$), δ (ppm): 2.91 (s, 6H), 2.99 (s, 6H), 4.03 (s, 2H), 6.42 (d, 1H, J=15.9 Hz), 6.62–7.21 (m, 6H), 7.83 (d, 1H, J=15.9 Hz), 11.8 (br., 1H). IR (cm^{-1}): 3020, 1678, 1599, 951 and 979. MS: m/z (%) 450 (M$^+$, 100), 277 (30) and 264 (55). Anal. Calcd For C$_{20}$H$_{23}$IN$_2$O$_2$: C, 53.34; H, 5.15; N, 6.22. Found: C, 53.33; H, 5.45; N, 6.35%.

5g. Yellow–green crystal, mp 166–167°C; ^{1}H NMR (80 MHz, CDCl$_3$), δ (ppm): 2.91 (s, 6H), 2.98 (s, 6H), 4.02 (s, 2H), 5.67 (br., s, 2H), 6.33 (d, 1H, J=15.6 Hz), 6.63–7.23 (m, 6H), 7.77 (d, 1H, J=15.6 Hz). IR (cm^{-1}): 3300(d), 1685, 1596, 980 and 957. MS: m/z (%) 449 (M$^+$, 100), 390 (52), 322 (41), 277 (100), and 189 (62). Anal. Calcd. For C$_{21}$H$_{25}$IN$_2$O$_2$: C, 54.32; H, 5.43; N, 6.03. Found: C, 54.37; H, 5.46; N, 6.22%. Anal. Calcd For C$_{20}$H$_{24}$IN$_3$O: C, 53.46; H, 5.38; N, 9.35. Found: C, 53.50; H, 5.62; N, 9.66%.

5h. Yellow crystal, mp 67–68°C; ^{1}H NMR (80 MHz, CDCl$_3$), δ (ppm): 1.29 (t, 6H), 2.89 (s, 6H), 2.96 (s, 6H), 3.51 (q, 4H), 4.10 (s, 2H), 5.82 (dd, 1H, J_1=16.3 Hz, J_2=19.3 Hz), 6.62 (1H, J=16.3 Hz), 6.59–7.20 (m, 6H). IR (cm^{-1}): 2970, 1678, 1599, 1164, 1116 and 960. MS: m/z (%) 542(M$^+$, 22), 516(9), 389(75) 315(6), 277(100), 43(65). Anal. Calcd For C$_{23}$H$_{32}$IN$_2$O$_3$P: C, 50.93; H, 5.95; N, 5.17. Found: C, 51.02; H, 5.87; N, 5.30%.

6a. Yellow crystal, mp 162–163°C; ^{1}H NMR (80 MHz, CDCl$_3$), δ (ppm): 3.03 (s, 2H), 6.94 (d, 1H, J=15.6 Hz), 7.05 (d, 1H, J=15.6 Hz), 7.76–8.28 (m, 6H), 9.94 (d, 1H, J=8.1 Hz). IR (cm^{-1}): 3021, 1697, 1608, 972 and 958. MS: m/z (%) 438 (M$^+$, 12), 311 (25), 262 (41) and 206 (10). Anal. Calcd For C$_{16}$H$_{11}$IN$_2$O$_5$: C, 43.85; H, 2.53 N, 6.40. Found: C, 43.69; H, 2.66; N, 6.64%.

6g. Yellow crystal, mp 196–197°C; ^{1}H NMR (80 MHz, CDCl$_3$), δ (ppm): 3.02 (s, 2H), 6.81 (d, 1H, J=15.2 Hz), 8.92 (d, 1H, J=15.2 Hz), 7.76–8.28 (m, 6H), 8.78 (br., 2H). IR (cm^{-1}): 3400 (d), 1690, 1610, 968 and 957. MS: m/z (%) 453 (M$^+$, 6), 326 (10), 201 (14) 287 (100) and 75 (38). Anal. Calcd For C$_{16}$H$_{12}$IN$_3$O$_5$: C, 42.39; H, 2.70; N, 9.27. Found: C, 41.99; H, 2.71; N, 9.42%.

7g. Pale yellow crystal, mp 60–61°C; ^{1}H NMR (80 MHz, CDCl$_3$), δ (ppm): 6.42 (d, 1H, J=15.7 Hz), 7.67 (d, 1H, J=15.7 Hz), 7.04–7.60 (m, 6H), 8.02 (br., 2H). IR (cm^{-1}): 3310 (d), 1670, 1614, 962 and 951. MS: m/z (%) 349 (M$^+$, 9), 279 (11) and 221 (100). Anal. Calcd For C$_{15}$H$_{12}$INO: C, 51.62; H, 3.47; N, 4.03. Found: C, 51.68; H, 3.42; N, 4.06%.

8i. Orange–reddish crystal, mp 166–167°C; ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 8.18 (d, 2H, J=8.7 Hz), 7.57 (d, 2H, J=8.7 Hz), 7.38 (d, 1H, J=16 Hz), 7.22 (s, 1H), 7.00 (d, 1H, J=8.6 Hz), 6.98 (d, 1H, J=16 Hz), 6.75 (s, 1H), 6.71 (d, 1H, J=8.6 Hz), 6.59 (d, 1H, J=8.6 Hz), 6.58 (d, 1H, J=8.5 Hz), 4.02 (s, 2H), 3.00 (s, 6H), 2.88 (s, 6H). IR (cm^{-1}): 1598, 1508, 1338, 1224, 953, 801, 731. MS: m/z (%) 527 (M$^+$, 100), 400 (9), 391 (18) and 264 (15). Anal. Calcd For C$_{25}$H$_{26}$IN$_3$O$_2$: C, 56.93; H, 4.97; N, 7.96. Found: C, 57.04; H, 5.12; N, 8.03%.

8j. Yellow crystal, mp 124–125°C; ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 8.22 (s, 1H), 8.02 (d, 1H, J=8.2 Hz), 7.68 (d, 1H, J=8.0 Hz), 7.37 (d, 1H, J=16 Hz), 7.36 (d, 1H, J=7.8 Hz), 7.21 (t, 1H, J=7.6 Hz), 7.08 (d, 1H, J=16 Hz), 6.95 (s, 1H), 6.92 (d, 1H, J=8.0 Hz), 6.74 (d, 1H, J=8.2 Hz), 6.66 (d, 1H, J=7.6 Hz), 6.57 (s, 1H), 3.97 (s, 2H), 3.01 (s, 6H), 2.87 (s, 6H). IR (cm^{-1}): 1608, 1527, 1348, 1224, 940, 805 and 731. MS: m/z (%) 527(M$^+$, 4), 399 (100), 355 (12) and 277 (32). Anal. Calcd For C$_{25}$H$_{26}$IN$_3$O$_2$: C, 56.93; H, 4.97; N, 7.96. Found: C, 56.84; H, 4.92; N, 8.01%.

8k. Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.50 (d, 1H, J=7.6 Hz); 7.36 (t, 1H, J=7.6 Hz), 7.29 (d, 1H, J=16.2 Hz), 7.26 (s, 1H), 7.24 (d, 1H, J=6.4 Hz), 7.09 (s, 1H), 7.00 (d, 1H, J=16.2 Hz), 6.97 (d, 1H, J=8.4 Hz), 6.82 (d, 1H, J=8.5 Hz), 6.77 (d, 1H, J=8.5 Hz), 6.75 (d, 1H, J=8.4 Hz), 6.63 (d, 1H, J=8.6 Hz), 6.62 (d, 1H, J=8.6 Hz), 4.04 (s, 2H), 3.02 (s, 6H), 2.92 (s, 6H). IR (cm^{-1}): 1600, 1500, 1352, 1226, 956, 800 and 732. MS: m/z (%) 482 (M$^+$, 53), 355 (21), 391 (30) 264 (100) and

91 (9). Anal. Calcd For $C_{25}H_{27}IN_2$: C, 62.24; H, 5.64; N, 5.80. Found: C, 62.22; H, 5.21; N, 5.93%.

8l. Light yellow crystal; mp: 106–107°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.37 (d, 2H, J=8.2 Hz), 7.25 (d, 2H, J=8.2 Hz), 7.21 (d, 1H, J=17 Hz), 7.17 (s, 1H), 7.16 (s, 1H), 7.15 (d, 1H, J=8.2 Hz), 6.90 (d, 1H, J=17 Hz), 6.74 (d, 2H, J=8.0 Hz), 6.56 (d, 1H, J=8.0 Hz), 3.83 (s, 2H), 2.99 (s, 6H), 2.69 (s, 6H). IR (cm^{-1}): 1590, 1509, 1348, 1228, 935, 821, 747; MS: *m/z* (%) 562 (M^+, 2), 560 (M, 2), 432 (100), 434 (93) 388 (11), 308 (7). Anal. Calcd For $C_{25}H_{26}BrIN_2$: C, 53.47; H, 4.67; N, 4.99. Found: C, 53.80; H, 5.00; N, 5.21%.

8m. Light yellow crystal; mp: 93–94°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.65 (s, 1H), 7.41 (d, 1H, J=8.1 Hz), 7.28 (d, 1H, J=8.1 Hz), 7.23 (d, 1H, J=16 Hz), 7.22 (d, 1H, J=7.6 Hz), 7.19 (t, 1H, J=8.2 Hz), 6.90 (d, 1H, J=16 Hz), 6.80 (s, 1H), 6.79 (d, 1H, J=8.2 Hz), 6.77 (d, 1H, J=8.2 Hz), 6.74 (d, 1H, J=8.1 Hz), 6.63 (s, 1H), 4.05 (s, 2H), 3.06 (s, 6H), 3.00 (s, 6H). IR (cm^{-1}): 1601, 1503, 1351, 1226, 908 and 731. MS: *m/z* (%) 562 (M^+, 8), 560 (M, 8), 433 (10), 435 (10) 391 (28) and 264 (100). Anal. Calcd For $C_{25}H_{26}BrIN_2$: C, 53.47; H, 4.67; N, 4.99. Found: C, 53.78; H, 4.98; N, 4.76%.

8n. Yellow crystal; mp: 87–88°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.39 (d, 2H, J=8.4 Hz), 7.28 (d, 2H, J=8.4 Hz), 7.24 (d, 1H, J=16 Hz), 7.17 (s, 1H), 7.12 (s, 1H), 6.95 (d, 1H, J=8.4 Hz), 6.90 (d, 1H, J=16 Hz), 6.72 (d, 1H, J=8.4 Hz), 6.59 (d, 1H, J=8.6 Hz), 6.58 (d, 1H, J=8.6 Hz), 3.99 (s, 2H), 2.99 (s, 6H), 2.88 (s, 6H). IR (cm^{-1}): 1601, 1500, 1351, 1226, 956, 806 and 731. MS: *m/z* (%) 516 (M^+, 31), 389 (33), 388 (42), 344 (11), 299 (6) and 264 (100). Anal. Calcd For $C_{25}H_{26}ClIN_2$: C, 58.08; H, 5.07; N, 5.42. Found: C, 57.94; H, 5.16; N, 5.54%.

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