Supporting Information

Ortho-Selective C-H Arylation of Phenols with *N*-Carboxyindoles under Brønsted Acid- or Cu(I)-Catalysis

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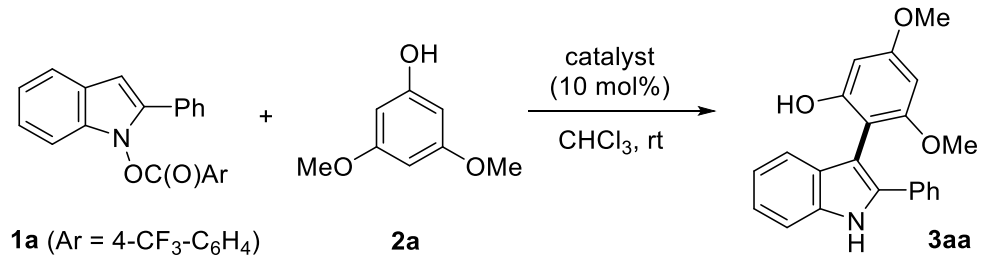
1. General Information

All solvents were dried and distilled according to standard methods before use.[1] 2-Iodo or 2-bromonitrobenzene derivatives and terminal alkynes were purchased from TCI or Alfa Aesar and were used as received. Ni powder (99.99%) was purchased from Sakamoto Yakuhin Kogyo Co., Ltd. $Cu(OTf)_2$, $[Cu(OTf)]_2 \cdot C_6H_6$, $Cu(MeCN)_4 \cdot BF_4$, $HNTf_2$ was purchased from Sigma Aldrich. TLC (thin-layer chromatography) analysis was carried out on Merck silica gel 60 F254 TLC plates and was visualized with UV lamp and $KMnO_4$ solution. Flash chromatography was performed on Kieselgel 60 (230-400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker (400 MHz) spectrometer with TMS as an internal standard. High resolution mass spectra (HRMS) were obtained from Organic Chemistry Research Center in Sogang University.

2. Optimization Study

Details of the reaction optimization for the catalyst (Table S1), solvents screening (Table S2) and the effect of O-acyl group (leaving group) in the indole (Tables S3), the effect of the concentration (Table S4) and the effect of O-acyl group on the enantioselectivity (Tables S5 and 6) were summarized as follows.

Table S1. Coupling of **1a** and **2a**: Brønsted and Lewis acid catalysis[a]

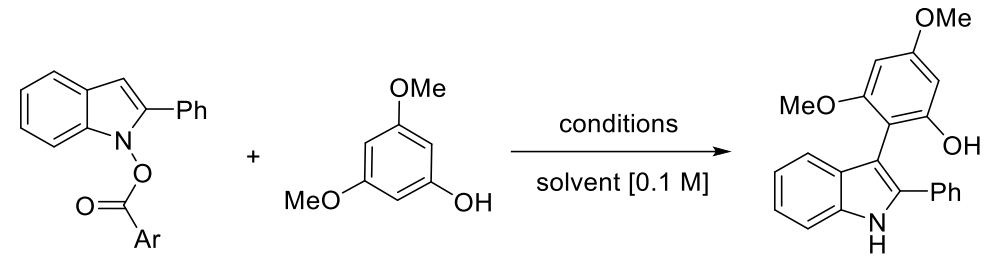


1a (Ar = 4-CF_3-C_6H_4) **2a** **3aa**

Entry	Catalyst	Time	Conv (%)	**3aa**[b]
1	$(PhO)_2P(O)OH$	4 d	40	26
2	CF_3CO_2H	3.5 d	79	43
3	CH_3SO_3H	3 d	89	54
4	TfOH	12 h	>95	84
5	$HBF_4{\cdot}OEt_2$	8 h	>95	86
6	$HNTf_2$	16 h	>95	83
7[c]	$HNTf_2$	8 h	>95	85
8	$HNTf_2$ (1 mol%)[d]	24 h	>95	85
9	$AuCl(PPh_3)$, AgOTf	45 h	20	10
10	AgOTf	45 h	70	40
11	$In(OTf)_3$	3 d	69	55
12	$Fe(OTf)_3$	1 d	>95	96
13	$Zn(OTf)_2$	2.5 d	>95	96
14	$Cu(OTf)_2$	0.5 h	>95	53[e]
15	CuBr	5 h	>95	96
16	$Cu(MeCN)_4{\cdot}BF_4$	10 min	>95	74
17	$[Cu(OTf)]_2{\cdot}C_6H_6$[d]	5 min	>95	76[e]
18	$[Cu(OTf)]_2{\cdot}C_6H_6$ (1 mol%)[d]	40 min	>95	88
19[f]	$[Cu(OTf)]_2{\cdot}C_6H_6$ (0.1 mol%)[d]	1.5 h	>95	93
20[f]	$[Cu(OTf)]_2{\cdot}C_6H_6$ (0.01 mol%)[d]	28 h	>95	94
21[f]	$[Cu(OTf)]_2{\cdot}C_6H_6$ (0.01 mol%)[d]	4 h	>95	98
22[f],[g]	$[Cu(OTf)]_2{\cdot}C_6H_6$ (0.1 mol%)[d]	8 h	>95	89

[a] **1a** (0.1 mmol), **2a** (0.2 mmol) and catalyst (10 mol%) in $CHCl_3$ (0.1 M). [b] Determined by ^1H NMR with CH_2Br_2 as an internal standard. [c] $CHCl_3$ (0.2 M). [d] Catalyst was added as a stock solution in $CHCl_3$ (entries 1 and 7) and in EtOAc (entries 16-21). [e] Messy mixture due to partial decomposition. [f] $CHCl_3$ (0.05 M). [g] 1.2 Equiv. of **2a** was used.

Table S2. Solvent screening

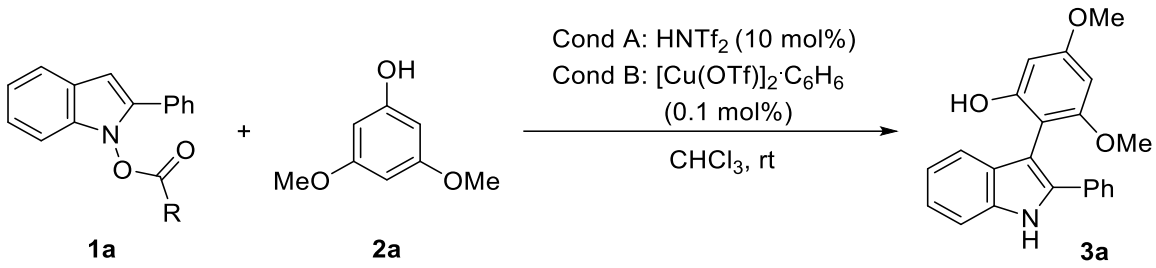


1a (0.1 mmol) (Ar = 4-$CF_3C_6H_4$) **2a** (2.0 eq) **3aa**

Entry	Catalyst	Solvent	Time (h)	Yield (%)[a]
1	$[Cu(OTf)]_2{\cdot}C_6H_6$ (0.1 mol%)	$CHCl_3$	1.5	94
2		CH_2Cl_2	24	69
3		DCE	29	43
4		THF	24	-[b,c]
5		toluene	15	87
6		C_6H_6	25	90
7		C_6H_5Cl	2	93
8		*n*-Hex	30	32[c]
9		EtOAc	20	22[c]
10		Et_2O	30	15[c]
11		EtOH	30	-[b,c]
12		CH_3CN	30	-[b,c]
13	$HNTf_2$ (10 mol%)	$CHCl_3$	8	80
14		CH_2Cl_2	9	69
15		DCE	3.5	65
16		toluene	9	77
17		C_6H_6	11	75
18		C_6H_5Cl	24	74
19		$C_6H_5CF_3$	11	80
20		*n*-Hex	44	60[c]
21		Et_2O	44	13[c]
22		CH_3CN	9	-[b,c]

[a]Determined by ^1H NMR using the CH_2Br_2. [b]Trace amount of product was observed. [c]Poor conversion and starting materials remained.

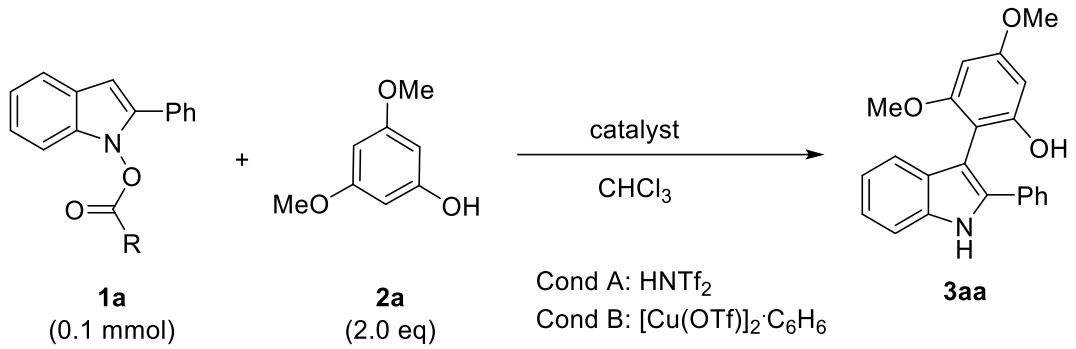
Table S3. The effect of *O*-acyl group



Entry	R	Cond[b]	Time (h)	**3aa** (%)[c]
1	CH_3 (**1a-1**)	A	8	72
2		B	1.2	85
3	^{t}Bu (**1a-2**)	A	24	70
4		B	1.2	90
5	Ph (**1a-3**)	A	8	64
6		B	1	84
7	4-MeO-C_6H_4 (**1a-4**)	A	8	63
8		B	5	76
9	2,4,6-Me_3-C_6H_2 (**1a-5**)	A	3	64
10		B	0.5	89
11	4-Cl-C_6H_4 (**1a-6**)	A	41	70
12		B	1.4	88
13	4-NO_2-C_6H_4 (**1a-7**)	A	42	73
14		B	4	71
15	4-CF_3-C_6H_4 (**1a**)	A	8	85
16		B	1.2	94
17	*N*-OH-2-Ph-indole	A	24	trace
18		B	24	trace

[a]**1a** (0.1 mmol) and **2a** (0.2 mmol). [b]Condition A: $HNTf_2$ (10 mol%) in $CHCl_3$ (0.1 M); Condition B: $[Cu(OTf)]_2{\cdot}C_6H_6$ (0.1 mol%) in $CHCl_3$ (0.05 M). [c]Determined by ^{1}H NMR using the CH_2Br_2 as an internal standard.

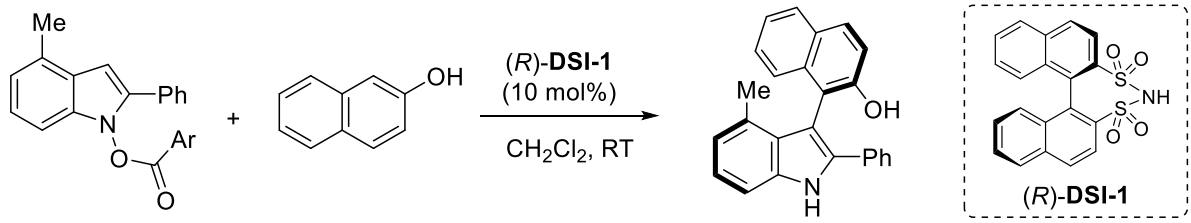
Table S4. The effect of concentration



Entry	Condition[b]	Conc	Time (h)	Yield (%)[c]
1	A	0.05 M	24	80
2		0.1 M	16	83
3		0.2 M	8	85
4	B	0.01 M	3	92
5		0.05 M	1.2	95
6		0.1 M	1.5	93
7		0.2 M	5	89

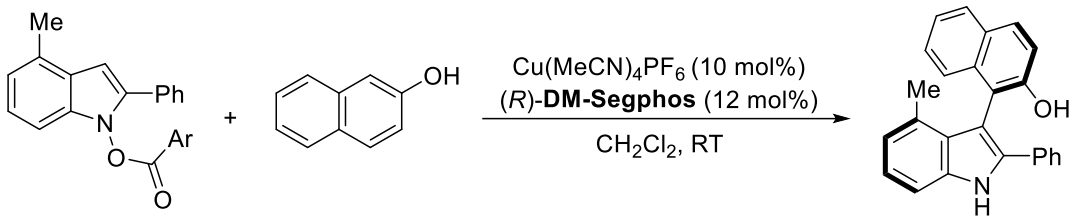
[a]**1a** (0.1 mmol) and **2a** (0.2 mmol) in $CHCl_3$. [b]Condition A: $HNTf_2$ (10 mol%); Condition B: $[Cu(OTf)]_2{\cdot}C_6H_6$ (0.1 mol%). [c]Determined by ^1H NMR using the CH_2Br_2 as an internal standard.

Table S5. The effect of leaving group on the enantioselectivity of the Brønsted acid-catalyzed heterobiaryl synthesis



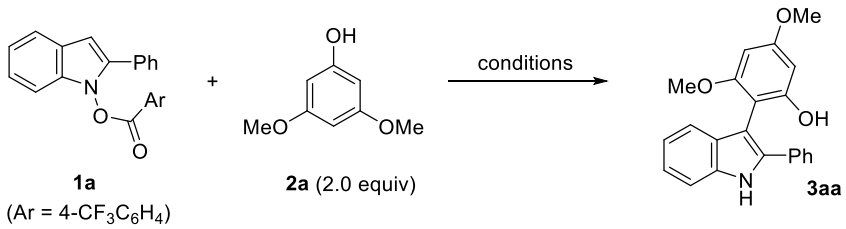
Entry	Ar	Time	Yield (%)	ee (%)
1	4-$CF_3C_6H_4$	3 d	91	19
2	4-$OMeC_6H_4$	6 d	54	15
3	2-Naph	6 d	85	13

Table S6. The effect of leaving group on the enantioselectivity of the Cu(I)-catalyzed heterobiaryl synthesis



Entry	Ar	Yield (%)	ee (%)
1	4-$CF_3C_6H_4$	20	67
2	4-$OMeC_6H_4$	22	68
3	2-Naph	24	69

3. General Condition for C-H Arylation of Phenols



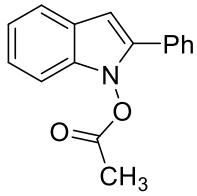
Condition A ($HNTf_2$)

In an oven-dried vial, 2-phenyl-1*H*-indol-1-yl 4-(trifluoromethyl)benzoate **1a** (38.1 mg, 0.1 mmol), corresponding phenol (30.8 mg, 0.2 mmol) were dissolved in 0.4 mL $CHCl_3$. To this was added $HNTf_2$ (2.8 mg, 0.1 mL of 0.1 M stock solution in $CHCl_3$) at room temperature. When the reaction was judged to be complete by TLC, reaction mixture was concentrated in *vacuo* and the residue was purified by flash column chromatography (SiO_2, EtOAc:Hex = 1:15) to afford 29.1 mg of **3aa** (85%) as a white solid.

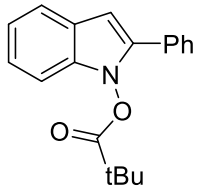
Condition B ($[Cu(OTf)]_2{\cdot}C_6H_6$)

In an oven-dried vial, 2-phenyl-1*H*-indol-1-yl 4-(trifluoromethyl)benzoate **1a** (38.1 mg, 0.1 mmol), corresponding phenol (30.8 mg, 0.2 mmol) were dissolved in $CHCl_3$ (2.0 mL). To this was added $[Cu(OTf)]_2{\cdot}C_6H_6$ (0.005 mg, 0.01 mL of 0.001 M stock solution in ethyl acetate) at room temperature. When the reaction was judged to be complete by TLC, reaction mixture was filtered through a cotton plug. The filtrate was concentrated in *vacuo* and the residue was purified by flash column chromatography (SiO_2, EtOAc:Hex = 1:15) to afford 34.1 mg of **3aa** (99%) as a white solid.

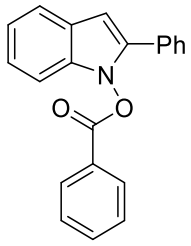
4. Characterization of Products



1a-1, white solid (EtOAc:Hex = 1:50); mp 67-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.59 (m, 3H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.25 – 7.24 (m, 2H), 7.19 – 7.18 (m, 1H), 6.64 (s, 1H), 2.24 (s, 3H) ;^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 140.3, 137.2, 130.5, 128.9, 128.3, 127.6, 125.3, 123.5, 122.0, 121.2, 109.4, 100.7, 18.3; IR (ATR): ṽ = 3087, 3064, 3037, 1803, 1452, 1367, 1302, 1169, 1041, 906, 835, 728, 695 cm^{-1}; LRMS (APCI) Calcd for $C_{16}H_{14}NO_2^+$ $[M+H]^+$ 252.1, found 252.2.

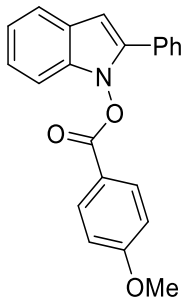


1a-2, red solid (EtOAc:Hex = 1:50); mp 46-48 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.3 Hz, 3H), 7.42 (t, *J* = 7.1 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.19 – 7.15 (m, 2H), 6.64 (s, 1H), 1.28 (t, 9H) ;^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 140.9, 137.4, 130.4, 128.6, 128.3, 128.2, 125.5, 123.4, 121.9, 121.3, 109.2, 100.5, 38.5, 27.6 ; IR (ATR): ṽ = 3059, 3028, 2974, 2937, 2906, 2874, 1790, 1477, 1445, 1369, 1332, 1302, 1230, 1063, 1018, 909, 735, 695 cm^{-1}; LRMS (APCI) Calcd for $C_{19}H_{20}NO_2^+$ $[M+H]^+$ 294.1, found 294.2.

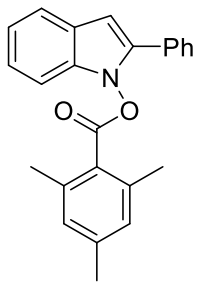


1a-3, orange sticky solid (EtOAc:Hex = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.62 (m, 4H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.17 (m,

4H), 6.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 140.8, 137.7, 134.6, 130.4, 130.3, 129.0, 128.8, 128.3, 127.7, 126.6, 125.5, 123.6, 122.1, 121.2, 109.7, 101.0; IR (ATR): ṽ = 3064, 1766, 1451, 1228, 1180, 1043, 998, 906, 836, 738, 703, 694, 647, 603, 589 cm^{-1}; LRMS (APCI) Calcd for $C_{21}H_{16}NO_2^+$ $[M+H]^+$ 314.1, found 314.2.

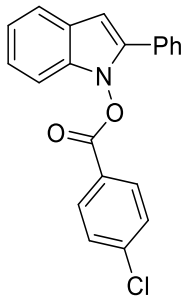


1a-4, white solid (EtOAc:Hex = 1:30); mp 125-127 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.24 – 7.17 (m, 2H), 6.97 (d, *J* = 9.0 Hz, 1H), 6.71 (s, 1H), 3.89 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 164.5, 140.6, 137.6, 132.5, 130.5, 128.8, 128.2, 127.7, 125.4, 123.5, 121.9, 121.2, 118.5, 114.3, 109.6, 100.7, 55.6; IR (ATR): ṽ =3059, 3032, 2937, 2838, 1760, 1603, 1510, 1452, 1318, 1247, 1169, 1044, 1025, 993, 844, 741, 693 cm^{-1}; LRMS (APCI) Calcd for $C_{22}H_{18}NO_3^+$ $[M+H]^+$ 344.1, found 344.2.

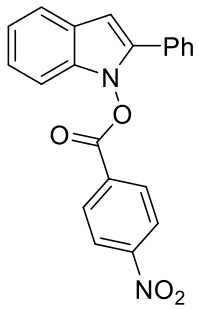


1a-5, white solid (EtOAc:Hex = 1:50); mp 120-122 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 – 7.64 (m, 3H), 7.47 – 7.36 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 6.85 (s, 1H), 6.69 (s, 1H), 2.29 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 141.2, 141.0, 137.5, 136.7, 130.6, 128.9, 128.7, 128.6, 128.4, 126.3, 125.5, 123.4, 121.8, 121.2, 110.0, 101.0, 21.2, 20.0; IR (ATR): ṽ = 3063, 3027, 2969, 2923, 1779, 1449, 1291, 1224, 1155, 1033,

983, 906, 836, 798, 732, 650, 603 cm^{-1}; LRMS (APCI) Calcd for $C_{24}H_{22}NO_2^+$ $[M+H]^+$ 356.2, found 356.2.

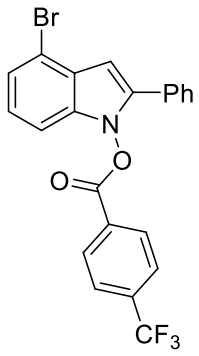


1a-6, orange solid (EtOAc:Hex = 1:50); mp 105-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.64 (t, *J* = 7.1 Hz, 3H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.19 (td, *J* = 1.9, 6.4 Hz, 1H), 6.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 141.3, 141.0, 137.9, 131.6, 130.4, 129.4, 128.9, 128.4, 127.7, 125.7, 125.0, 123.8, 122.3, 121.4, 109.8, 101.4; IR (ATR): ṽ = 3063, 3031, 1769, 1593, 1488, 1445, 1245, 1092, 1044, 999, 906, 728, 694 cm^{-1}; LRMS (APCI) Calcd for $C_{21}H_{15}ClNO_2^+$ $[M+H]^+$ 348.1, found 348.0.

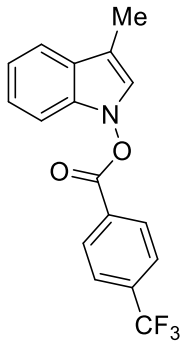


1a-7 Yellow solid (EtOAc:Hex = 1:30); mp 121-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.9 Hz, 2H), 8.26 (d, *J* = 9.0 Hz, 2H), 7.64 (t, *J* = 5.6 Hz, 3H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.20 (m, 3H), 6.73 (s, 1H) ;^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 151.3, 141.4, 138.1, 131.9, 131.3, 130.1, 128.8, 128.4, 127.6, 125.9, 124.0, 123.8, 122.6, 121.3, 109.8, 102.0; IR (ATR): ṽ = 3113, 3077, 3054, 1773, 1527, 1346, 1226, 1044, 1028, 1006, 907, 857, 730, 712 cm^{-1}; LRMS (APCI) Calcd for $C_{21}H_{15}N_2O_4^+$ $[M+H]^+$ 359.1, found

359.2.

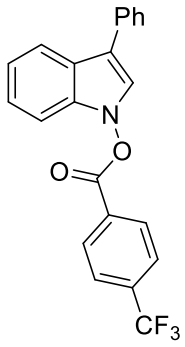


1r, orange solid (EtOAc:Hex:Et_3N = 1:19:2); mp 50-52 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 140.9, 137.2, 136.1 (q, J_{CF} = 32.8 Hz), 130.7, 129.6, 129.4, 128.9, 128.7, 127.8, 126.0 (q, J_{CF} = 3.7 Hz), 124.9, 124.4, 123.3 (q, J_{CF} = 271.6 Hz), 115.3, 108.4, 100.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4; IR (ATR): ṽ = 3072, 2998, 1777, 1413, 1323, 1247, 1178, 1133, 1067, 1003, 860, 758, 695 cm^{-1}; LRMS (APCI) Calcd for $C_{22}H_{14}BrF_3NO_2^+$ $[M+H]^+$ 460.0, found 460.0.

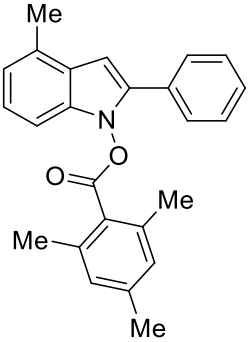


1x, orange solid (EtOAc:Hex:Et_3N = 1:19:2); mp 84-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.28 – 7.17 (m, 3H), 7.02 (d, *J* = 1.1 Hz, 1H), 2.34 (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 136.8, 135.8 (q, J_{CF} = 32.6 Hz), 130.6, 130.1, 126.5, 126.0 (q, J_{CF} = 3.6 Hz), 124.5, 123.5, 123.4 (q, J_{CF} = 273 Hz), 121.2, 119.5, 112.4, 109.3, 9.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3; IR (ATR):

$\tilde{\nu}$ = 3030, 2971, 1775, 1455, 1376, 1347, 1231, 1205, 1124, 1067, 1041, 1005, 861, 735, 695 cm^{-1}; LRMS (APCI) Calcd for $C_{17}H_{13}F_3NO_2^+$ $[M+H]^+$ 320.1, found 320.0.

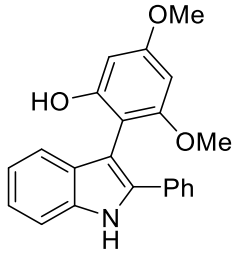


1y, yellow solid (EtOAc:Hex:Et_3N = 1:19:2); mp 94-98 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.41 (s, 1H), 7.36 – 7.22 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 136.1 (q, J_{CF} = 32.8 Hz), 135.7, 134.1, 130.8, 129.7, 128.9, 127.8, 126.8, 126.1 (q, J_{CF} = 3.7 Hz), 123.8, 123.5, 123.4 (q, J_{CF} = 272 Hz), 123.1, 121.8, 120.4, 117.1, 109.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3; IR (ATR): $\tilde{\nu}$ = 3027, 2971, 1779, 1455, 1376, 1347, 1322, 1231, 1205, 1129, 1065, 1005, 860, 738, 695 cm^{-1}; LRMS (APCI) Calcd for $C_{22}H_{15}F_3NO_2^+$ $[M+H]^+$ 382.1, found 382.0.

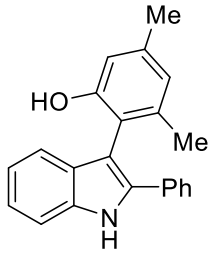


1z, orange solid (EtOAc:Hex:Et_3N = 1:19:2); mp 116-118 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 1.5, 8.3 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 8.1 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.82 (s, 2H), 6.69 (s, 1H), 2.58 (s, 3H), 2.60 (s, 3H), 2.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 141.0, 140.4, 137.0,

136.8, 130.7, 128.9, 128.9, 128.7, 128.6, 128.3, 125.1, 123.6, 123.1, 107.5, 99.6, 21.2, 20.0, 18.3; IR (ATR): ṽ = 3055, 3024, 2970, 2920, 2857, 1775, 1610, 1483, 1447, 1379, 1335, 1226, 1155, 1031, 982, 946, 911,853, 835, 758, 733, 695, 648 cm^{-1}; LRMS (APCI) Calcd for $C_{25}H_{24}NO_2^+$ $[M+H]^+$ 370.2, found 370.2.

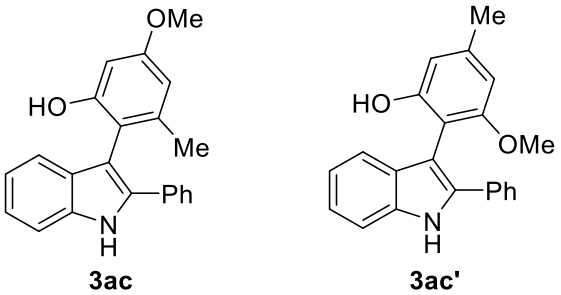


3aa (condition **A**: 28.1 mg, 85%; condition **B**: 33.9 mg, 99%); white solid (EtOAc:Hex = 1:15); mp 150-152 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.46 – 7.42 (m, 3H) , 7.34 – 7.22 (m, 5H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.26 (d, *J* = 2.3 Hz, 1H), 6.18 (d, *J* = 2.4 Hz, 1H), 5.22 (s, 1H), 3.84 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 159.5, 155.7, 136.3, 136.1, 132.3, 129.3, 128.2, 127.9, 126.5, 123.0, 120.5, 119.9, 111.2, 103.2, 102.2, 92.7, 92.0, 55.7, 55.4; IR (ATR): ṽ = 3498, 3394, 3059, 3001, 2924, 2847, 1626, 1582, 1509, 1456, 1327, 1305, 1208, 1147, 1100, 905, 815, 727 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{19}NO_3Na^+$ $[M+Na]^+$ 368.1257, found 368.1257.



3ab (condition **A**: 16.3 mg, 52%; condition **B**: 29.7 mg, 95%); white solid (EtOAc:Hex = 1:20); mp 202-204 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.34 – 7.25 (m, 5H), 7.12 (td, *J* = 0.8, 7.7 Hz, 1H), 6.72 (s, 1H), 6.70 (s, 1H), 5.02 (s, 1H), 2.36 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 139.0, 138.8, 136.3, 135.6, 132.0, 129.1, 129.0, 128.1, 126.2, 123.3, 123.0, 120.7, 119.9, 117.0, 113.0, 111.0,

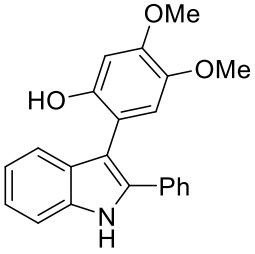
106.4, 21.1, 20.1; IR (ATR): ṽ = 3489, 3400, 3059, 2919, 2861, 1626, 1568, 1507, 1484, 1456, 1301, 1259, 1168, 1044, 908, 841, 740, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{19}NONa^+$ $[M+Na]^+$ 336.1359, found 336.1358.



3ac **3ac'**

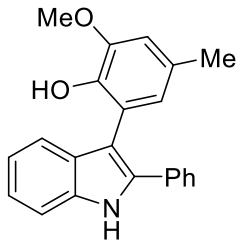
3ac:**3ac'** = 6:1 (separable)

3ac (condition **A**: 21.8 mg, 66%; condition **B**: 30.2 mg, 92%, 6:1 mixture of regioisomer); white solid (EtOAc:Hex = 1:15); mp 76-80 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.34 – 7.25 (m, 5H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.48 (d, *J* = 2.5, 1H), 6.46 (d, *J* = 2.4 Hz, 1H), 5.12 (s, 1H), 3.83 (s, 3H), 1.92 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 155.4, 140.3, 136.4, 135.9, 132.0, 129.3, 129.1, 128.1, 126.3, 123.3, 120.7, 119.8, 112.6, 111.2, 108.5, 106.1, 98.0, 55.3, 20.5; IR (ATR): ṽ = 3489, 3399, 3064, 2924, 2842, 1623, 1575, 1507, 1456, 1328, 1196, 1145, 1058, 1031, 908, 839, 734, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{19}NO_2Na^+$ $[M+Na]^+$ 352.1308, found 352.1311.

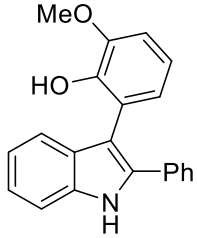


3ad (condition **A**: 26.2 mg, 76%; condition **B**: 31.1 mg, 90%); light purple solid (Et_2O:Hex = 1:5); mp 216-218 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 7.49 – 7.45 (m, 4H), 7.37 – 7.27 (m, 4H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.77 (s, 1H), 6.65 (s, 1H), 4.91 (s, 1H), 3.92 (s, 3H), 3.74 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 148.1, 143.0, 136.2, 135.2, 131.7, 129.2, 128.2, 123.3, 120.8, 119.7, 114.5, 111.2, 111.0, 108.0, 100.1, 56.5, 55.9; IR (ATR): ṽ = 3512, 3349, 3059, 3005, 2937, 2833, 1626, 1568, 1507, 1484, 1456, 1301, 1259, 1168, 1044, 908,

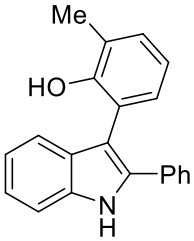
841, 740, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{19}NO_3Na^+$ $[M+Na]^+$ 368.1257, found 368.1257.



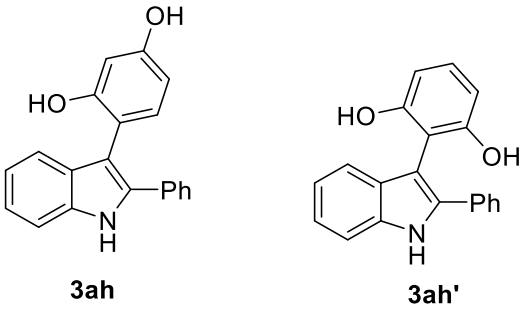
3ae (condition **A**: 11.0 mg, 33%; condition **B**: 21.3 mg, 65%); white solid (EtOAc:Hex = 1:15); mp 188-190 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.50 – 7.44 (m, 3H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.31 (t, *J* = 7.1 Hz, 2H), 7.28 – 7.20 (m, 2H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.72 (s, 1H), 6.71 (s, 1H), 5.39 (s, 1H), 3.92 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 141.4, 135.9, 134.7, 132.7, 129.2, 129.0, 128.7, 127.6, 127.1, 124.4, 122.7, 120.8, 120.3, 120.2, 111.0, 110.9, 109.7, 55.9, 21.1; IR (ATR): $\tilde{\nu}$ = 3512, 3394, 3055, 2937, 2856, 1599, 1483, 1457, 1328, 1286, 1209, 1157, 1132, 1070, 908, 837, 733, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{19}NO_2Na^+$ $[M+Na]^+$ 352.1308, found 352.1305.



3af (condition **A**: no desired product; condition **B**: 15.3 mg, 49%); white solid (EtOAc:Hex = 1:15); mp 166-168 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.49 – 7.40 (m, 4H), 7.33 – 7.20 (m, 4H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.90 – 6.86 (m, 3H), 5.59 (s, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 143.7, 136.0, 134.9, 132.7, 129.1, 128.7, 127.7, 127.3, 124.5, 122.8, 121.3, 120.33, 120.28, 119.7, 110.9, 109.9, 109.7, 56.0 ; IR (ATR): $\tilde{\nu}$ = 3507, 3390, 3059, 2923, 2842, 1604, 1457, 1329, 1279, 1224, 1067, 993, 907, 731, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{17}NO_2Na^+$ $[M+Na]^+$ 338.1151, found 338.1153.



3ag (condition **A**: 6.8 mg, 23%; condition **B**: 7.4 mg, 25%); colorless oil (Et_2O:Hex = 1:10); ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.48 –7.40 (m, 4H), 7.34 – 7.25 (m, 4H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.17-7.12 (m, 1H), 7.09 (dd, *J* = 1.2, 7.6 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 5.25 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 136.1, 135.2, 131.8, 130.4, 129.4, 129.0, 128.9, 128.1, 127.0, 125.5, 124.4, 123.3, 120.8, 120.1, 119.9, 111.0, 108.4, 16.3; IR (ATR): ṽ = 3514, 3397, 3204, 3060, 2974, 2920, 2857, 1706, 1647, 1598, 1448, 1328, 1229, 1197, 1107, 851, 744, 697 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{17}NONa^+$ $[M+Na]^+$ 322.1202, found 322.1203.

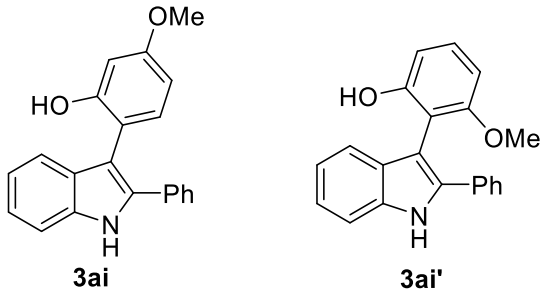


3ah:**3ah'** = 10:1 (separable)

3ah/3ah' (condition **A**: 5.8 mg, 19%; condition **B**: 23.9 mg, 78%)

3ah: white solid (Toluene:Et_2O = 19:1); mp 128-130 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.48 – 7.40 (m, 4H), 7.36 – 7.24 (m, 4H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 2.5 Hz, 1H), 6.46 (dd, *J* = 2.6 Hz, 8.2 Hz, 1H), 5.22 (s, 1H), 4.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 154.9, 136.1, 135.3, 132.6, 131.8, 129.3, 129.0, 128.2, 127.0, 123.3, 120.8, 119.8, 113.2, 111.0, 108.1, 107.7, 102.6; IR (ATR): ṽ = 3505, 3395, 3026, 2970, 2940, 1739, 15123, 1446, 1366, 1304, 1229, 1217, 1203, 1146, 1116, 976, 958, 848, 747, 693 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{15}NO_2Na^+$ $[M+Na]^+$ 324.0995, found 324.0994.

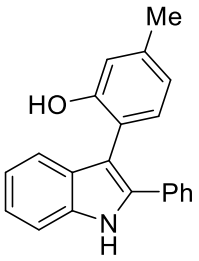
3ah': yellow sticky oil (Toluene:Et_2O = 19:1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.40-7.30 (m, 5H), 7.24 (t, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 2H), 4.98 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 137.2, 136.5, 130.9, 130.0, 129.3, 128.9, 128.6, 126.5, 124.0, 121.4, 119.7, 111.3, 107.2, 100.3; IR (ATR): ṽ = 3493, 3402, 3063, 3024, 2968, 2853, 1738, 1590, 1461, 1371, 1230, 1204, 1176, 1148, 1008, 971, 785, 759, 747, 691 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{15}NO_2Na^+$ $[M+Na]^+$ 324.0995, found 324.0994.



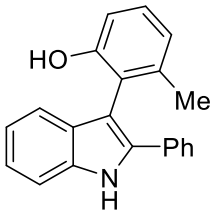
3ai **3ai'**

3ai:**3ai'** = 14:1 (inseparable)

3ai (condition **A**: 13.2 mg, 42%; condition **B**: 28.3 mg, 90%, 14:1 mixture of regioisomer); white solid (EtOAc:Hex = 1:15); mp 110-112 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 7.49 – 7.42 (m, 4H), 7.37 – 7.27 (m, 4H), 7.19 – 7.13 (m, 2H), 6.62 (d, *J* = 2.6 Hz, 1H), 6.56 (dd, *J* = 2.6 Hz, 8.4 Hz, 1H), 5.21 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 154.8, 136.1, 135.2, 132.4, 131.8, 129.3, 129.0, 128.2, 127.0, 123.3, 120.8, 119.8, 112.9, 111.1, 107.8, 107.1, 100.9, 55.4; IR (ATR): ṽ = 3503, 3399, 3059, 2924, 2861, 1625, 1510, 1446, 1317, 1247, 1219, 1199, 1147, 1030, 945, 907, 833, 729, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{17}NO_2Na^+$ $[M+Na]^+$ 338.1151, found 338.1150.



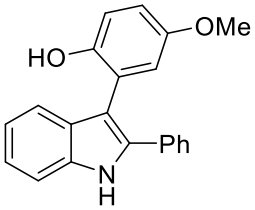
3aj



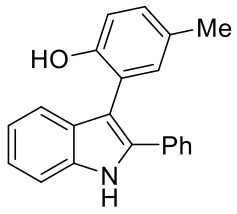
3aj'

3aj:**3aj'** = 1.7:1 (inseparable)

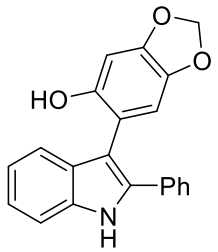
3aj/3aj' (condition **A**: 6.8 mg, 23%; condition **B**: 19.4 mg, 65%, 1.7:1 mixture of regioisomer); white solid (Et_2O:Hex = 1:10); mp 74-76 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 0.6H), 8.44 (s, 1H), 7.48 – 7.12 (m, 16H), 6.90 – 6.86 (m, 2.1H), 6.79 (d, *J* = 7.6 Hz, 1H), 5.12 (s, 1H), 5.10 (s, 0.6H), 2.38 (s, 3H), 1.95 (s, 1.8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 153.6, 139.4, 139.2, 136.3, 136.1, 135.6, 135.1, 131.9, 131.8, 131.5, 129.1, 129.0, 128.9, 128.8, 128.1, 127.0, 126.2, 123.3, 122.0, 121.6, 120.8, 120.1, 119.9, 117.5, 116.0, 112.3, 111.0, 108.2, 106.3, 21.4, 20.2; IR (ATR): ṽ = 3507, 3403, 3061, 3009, 2918, 2857, 1510, 1485, 1456, 1326, 1307, 1281, 1244, 1215, 1175, 1153, 1074, 1029, 1009, 972, 934, 742, 693 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{17}NONa^+$ $[M+Na]^+$ 322.1202, found 322.1203.



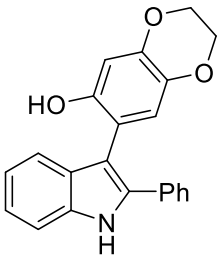
3ak (condition **A**: 15.8 mg, 50%; condition **B**: 21.4 mg, 68%); white solid (EtOAc:Hex = 1:15); mp 84-86 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.50 – 7.42 (m, 4H), 7.37 – 7.26 (m, 4H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.87 (dd, *J* =3.0, 8.8 Hz, 1H), 6.84 (d, *J* = 3.0 Hz, 1H), 4.86 (s, 1H), 3.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 147.9, 136.2, 135.2, 131.7, 129.0, 128.9, 128.3, 127.1, 123.3, 121.3, 120.9, 120.0, 116.5, 116.2, 115.0, 111.1, 108.3, 55.8; IR (ATR): ṽ = 3512, 3398, 3059, 2942, 2833, 1503, 1484, 1456, 1329, 1262, 1217, 1164, 1036, 908, 813, 764, 731, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{17}NO_2Na^+$ $[M+Na]^+$ 338.1151, found 338.1151.



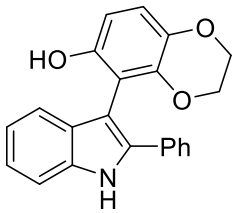
3al (condition **A**: 6.1 mg, 20%; condition **B**: 17.6 mg, 59%); white solid (Et_2O:Hex = 1:10); mp 68-70 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 7.45 – 7.38 (m, 4H), 7.32 – 7.21 (m, 4H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.03 (s, 1H), 2.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6, 136.2, 135.0, 132.1, 131.8, 129.8, 129.7, 129.2, 129.0, 128.2, 127.0, 123.3, 120.8, 120.3, 119.9, 115.2, 111.1, 108.3, 20.6; IR (ATR): ṽ = 3515, 3401, 3065, 3022, 2922, 2862, 1602, 1503, 1485, 1456, 1402, 1327, 1273, 1233, 1218, 1184, 1158, 1074, 1030, 817, 743, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{17}NONa^+$ $[M+Na]^+$ 322.1202, found 322.1202.



3am (condition **A**: 20.4 mg, 62%; condition **B**: 28.4 mg, 86%); white solid (EtOAc:Hex = 1:15); mp 92-94 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.49 – 7.42 (m, 4H), 7.39 – 7.27 (m, 4H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.70 (s, 1H), 6.60 (s, 1H), 5.96 (d, *J* = 1.6 Hz, 2H), 4.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 148.0, 141.4, 136.1, 135.4, 131.7, 129.1, 129.0, 128.3, 127.0, 123.3, 120.9, 119.7, 111.8, 111.1, 110.5, 107.9, 101.2, 97.8; IR (ATR): ṽ = 3498, 3400, 3059, 2888, 1647, 1502, 1477, 1376, 1328, 1289, 1220, 1174, 1037, 933, 908, 834, 744 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{15}NO_3Na^+$ $[M+Na]^+$ 352.0944, found 352.0941.



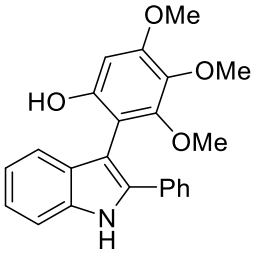
3an



3an'

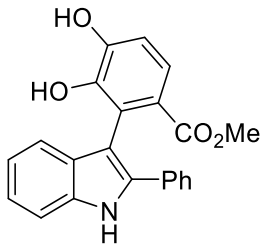
3an:**3an'** = 3.3:1 (inseparable)

3an (condition **A**: 16.5 mg, 48%; condition **B**: 31.4 mg, 92%, 3.3:1 mixture of regioisomer); white solid (Et_2O:Hex = 1:5); mp 134-136 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 0.3H), 8.44 (s, 1H), 7.46 –7.10 (m, 11.7H), 6.84 (d, *J* = 8.8 Hz, 0.3H), 6.77 (s, 1H), 6.56 (d, *J* = 8.8 Hz, 0.3H), 6.56 (s, 1H), 4.90 (s, 0.3H), 4.89 (s, 1H), 4.27 – 4.22 (m, 2H), 4.21 – 4.15 (m, 2H), 4.12 – 3.95 (m, 1.1H), 3.81 – 3.75 (m, 0.3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 148.3, 143.9, 141.8, 137.5, 136.3, 136.1, 135.2, 132.3, 131.7, 129.3, 129.0, 128.9, 128.6, 128.2, 128.1, 127.0, 126.5, 123.3, 123.2, 120.8, 119.9, 119.8, 119.3, 117.1, 113.5, 111.3, 111.1, 109.8, 107.7, 107.6, 104.0, 103.0, 64.7, 64.4, 64.2, 63.9; IR (ATR): ṽ = 3511, 3398, 3061, 3013, 2979, 2927, 2870, 1506, 1486, 1457, 1370, 1332, 1302, 1249, 1230, 1215, 1168, 1142, 1066, 927, 891, 742, 684 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{17}NO_3Na^+$ $[M+Na]^+$ 366.1101, found 366.1102.

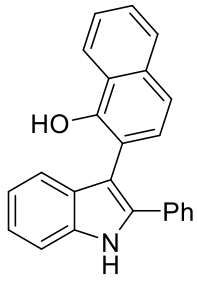


3ao (condition **A**: 11.4 mg, 30%; condition **B**: 33.9 mg, 90%); white solid (EtOAc:Hex = 1:15); mp 184-186 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 7.45 – 7.40 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.19 (m, 4H), 7.11 (dt, *J* = 0.9, 7.9 Hz, 1H), 6.43 (s, 1H), 5.04 (s, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 152.7, 150.8, 136.3, 136.2, 136.0, 132.1, 129.4, 128.9, 128.1, 126.6, 123.1, 120.7, 119.7, 111.2, 106.5, 103.2, 94.9, 61.2, 60.7, 55.9; IR (ATR): ṽ = 3502, 3346, 3065, 3013, 2935, 2836, 1615, 1504, 1482, 1458, 1447, 1407, 1327, 1298, 1225, 1195, 1145, 1105, 1080, 1043, 997,

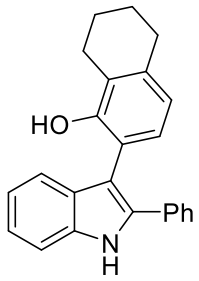
822, 745, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{21}NO_4Na^+$ $[M+Na]^+$ 398.1363, found 398.1363.



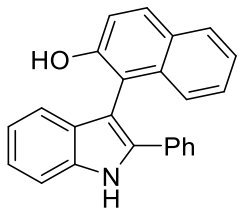
3ap (condition **A**: no desired product; condition **B**: 27.6 mg, 77%); white solid (MeOH :DCM: = 1:100); mp 218-220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.33 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 7.10 (t, *J* = 8.4 Hz, 1H), 7.01 (dd, *J* = 0.6, 8.5 Hz, 1H), 5.72 (s, 1H), 5.35 (s, 1H), 3.43 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 147.6, 141.2, 136.2, 135.1, 131.6, 129.0, 128.8, 128.2, 126.7, 124.5, 123.9, 123.3, 121.7, 120.9, 119.2, 114.1, 111.2, 105.9, 51.7; IR (ATR): ṽ = 3494, 3364, 3065, 3009, 2953, 1708, 1590, 1489, 1447, 1433, 1360, 1248, 1211, 1135, 1043, 1000, 912, 737, 687 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{17}NO_4Na^+$ $[M+Na]^+$ 382.1050, found 382.1050.



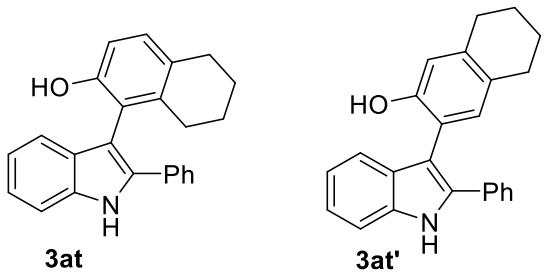
3aq (condition **A**: 17.8 mg, 53%; condition **B**: 32.4 mg, 96%); light pink solid (EtOAc:Hex = 1:20); mp 184-186 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 8.31 (d, *J* = 8.9 Hz), 7.86 (d, *J* = 8.0 Hz), 7.57 – 7.49 (m, 3H), 7.49 – 7.42 (m, 4H), 7.37 – 7.30 (m, 2H), 7.30 – 7.25 (m, 3H), 7.18 (t, *J* = 7.2 Hz, 1H), 5.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 136.2, 135.5, 134.3, 131.7, 129.3, 129.0, 128.9, 128.2, 127.6, 127.1, 126.3, 125.2, 124.4, 123.4, 122.6, 121.0, 120.1, 120.0, 113.9, 111.2, 108.3; IR (ATR): ṽ = 3507, 3411, 3059, 2924, 2851, 1571, 1456, 1381, 1326, 1267, 1237, 1200, 1145, 1075, 907, 807, 743, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{17}NONa^+$ $[M+Na]^+$ 358.1202, found 358.1202.



3ar (condition **A**: 17.4 mg, 51%; condition **B**: 32.1 mg, 94%); white solid (EtOAc:Hex = 1:25); mp 185-187 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.47 –7.41 (m, 4H), 7.35 – 7.23 (m, 4H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 5.22 (s, 1H), 2.90 – 2.65 (m, 4H), 1.90 – 1.79 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 138.2, 136.1, 135.1, 131.9, 129.2, 128.9, 128.2, 128.0, 127.1, 123.9, 123.2, 121.0, 120.7, 120.1, 116.6, 111.0, 108.7, 31.0, 29.7, 23.3, 22.9, 22.9; IR (ATR): ṽ = 3512, 3403, 3059, 2930, 1456, 1435, 1318, 1231, 1156, 1072, 969, 904, 822, 798, 749, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{21}NONa^{+}$ $[M+Na]^{+}$ 362.1515, found 362.1517.

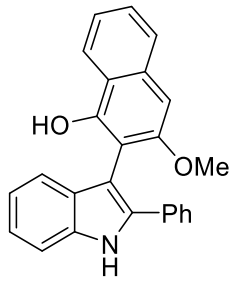


3as (condition **A**: 27.2 mg, 81%; condition **B**: 33.4 mg, 99%); white solid (EtOAc:Hex = 1:20); mp 64-66 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H), 7.85 (t, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.19 (m, 9H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.1 Hz, 1H), 5.38 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 136.5, 136.5, 134.3, 131.6, 129.9, 129.8, 129.3, 129.0, 128.3, 126.6, 126.5, 125.3, 123.5, 123.4, 120.9, 120.3, 117.4, 113.3, 111.2, 105.0; IR (ATR): ṽ = 3498, 3403, 3059, 1619, 1596, 1456, 1385, 1326, 1265, 1204, 1144, 971, 905, 815, 726, 693 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{17}NONa^{+}$ $[M+Na]^{+}$ 358.1202, found 358.1201.



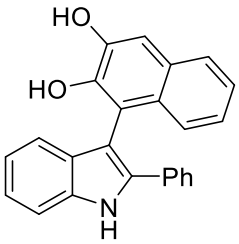
3at:**3at'** = 2:1 (inseparable)

3at/3at' (condition **A**: 16.4 mg, 48%; condition **B**: 30.8 mg, 90%, 2:1 mixture of regioisomer); white solid (EtOAc:Hex = 1:25); mp 96-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.45 (s, 0.5H), 7.47-7.33 (m, 5H), 7.32-7.20 (m, 7H), 7.15-7.07 (m, 1.5H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.96 (s, 0.5H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.72 (s, 0.5H), 4.97 (s, 0.5H), 4.96 (s, 1H), 2.82-2.70 (m, 3H), 2.70-2.60 (m, 1H), 2.39-2.25 (m, 1H), 2.21-2.10 (m, 1H), 1.85-0.95 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 151.3, 138.0, 137.9, 136.4, 136.2, 135.4, 134.9, 132.0, 131.9, 131.9, 130.0, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.3, 128.1, 128.0, 127.0, 126.1, 123.3, 123.2, 120.7, 120.0, 119.9, 119.4, 118.0, 115.2, 112.2, 111.1, 111.0, 108.4, 106.4, 29.5, 29.4, 28.6, 27.7, 23.5, 23.3, 23.2, 23.1; IR (ATR): ṽ = 3498, 3399, 3050, 2928, 2856, 2833, 1601, 1473, 1456, 1326, 1243, 1176, 907, 731, 693 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{21}NONa^{+}$ $[M+Na]^{+}$ 362.1515, found 362.1516.

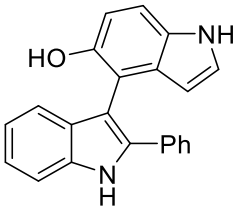


3au (condition **A**: 21.5 mg, 59%; condition **B**: 31.2 mg, 85%); white solid (EtOAc:Hex = 1:15); mp 216-218 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.43 (m, 4H), 7.37 – 7.24 (m, 6H), 7.13 (td, *J* = 0.9, 7.9 Hz, 1H), 6.85 (s, 1H), 5.73 (s, 1H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 150.7, 136.5, 136.3, 134.7, 132.3, 129.0, 128.8, 128.0, 126.9, 126.4, 126.3, 123.2, 122.8, 122.7, 120.8, 120.1, 120.0, 111.2, 107.0, 103.5, 98.3, 55.5; IR (ATR): ṽ = 3489, 3407, 3059, 2933, 2883, 1633, 1601, 1574,

1504, 1457, 1396, 1327, 1289, 1266, 1194, 1132,1097, 907, 816, 731 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{19}NO_2Na^+$ $[M+Na]^+$ 388.1308, found 388.1309.

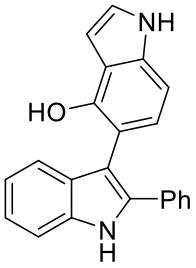


3av (condition **A**: 25.4 mg, 72%; condition **B**: 33.2 mg, 95%); white solid (EtOAc:Hex = 1:7); mp 108-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.36 – 7.26 (m, 4H), 7.25 – 7.20 (m, 3H), 7.16 – 7.11 (m, 2H), 7.08 (td, *J* = 0.9, 6.8 Hz, 1H), 5.71 (s, 1H), 5.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 141.8, 136.5, 136.3, 131.5, 130.0, 129.5, 129.1, 129.0, 128.4, 127.0, 126.5, 125.2, 124.2, 124.1, 123.5, 120.9, 120.2, 114.2, 111.2, 110.3, 104.9; IR (ATR): $\tilde{\nu}$ = 3494, 3411, 3059, 1514, 1456, 1291, 1238, 1171, 1130, 907, 733 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{17}NO_2Na^+$ $[M+Na]^+$ 374.1151, found 374.1154.

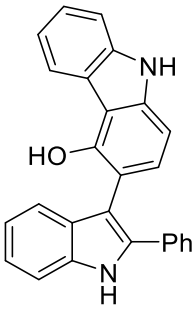


3aw (condition **A**: 15.0 mg, 46%; condition **B**: 29.3 mg, 90%); brown solid (EtOAc:Hex = 1:15); mp 172-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.05 (s, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.20 (m, 3H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.05 (s, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.04 (s, 1H), 4.97 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 136.4, 135.4, 132.1, 130.9, 129.2, 128.89, 128.86, 128.0, 126.6, 124.7, 123.1, 120.6, 120.5, 111.5, 111.4, 111.0, 110.3, 106.7, 102.5; IR (ATR): $\tilde{\nu}$ = 3507, 3408, 3055, 2928, 1506, 1483, 1438, 1407, 1326, 1240, 1220, 1165, 1075, 907, 864, 729, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{16}N_2ONa^+$

$[M+Na]^+$ 347.1155, found 347.1154.

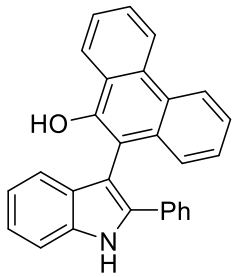


3ax (condition **A**: 10.4 mg, 32%; condition **B**: 24.2 mg, 74%); white solid (EtOAc:Hex = 1:15); mp 150-152 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.14 (s, 1H), 7.47 – 7.40 (m, 4H), 7.28 – 7.20 (m, 4H), 7.16 – 7.10 (m, 2H), 7.05 (d, *J* = 8.3 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.70 (s, 1H), 5.49 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 137.5, 136.1, 135.1, 132.1, 129.6, 128.8, 127.9, 127.0, 126.1, 123.1, 122.9, 120.6, 120.1, 117.4, 110.9, 109.2, 108.9, 104.1, 100.2; IR (ATR): ṽ = 3510, 3407, 3055, 3015, 1474, 1456,1445, 1412, 1340, 1256, 1215, 1075, 1043, 996, 856, 743, 694, 667, 588, 564 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{16}N_2ONa^+$ $[M+Na]^+$ 347.1155, found 347.1154.

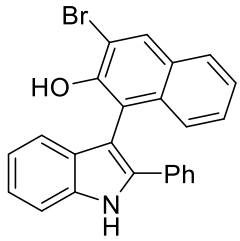


3ay (condition **A**: 10.2 mg, 27%; condition **B**: 36.0 mg, 96%); white solid (Et_2O:Hex = 1:5); mp 148-150 ºC; ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 10.70 (s, 1H), 10.31 (s, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 7.70 (s, 1H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.51 (d, 8.1 Hz, 1H), 7.50 (d, 8.1 Hz, 1H), 7.35 (t, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.23 – 7.11 (m, 4H), 7.04 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ 151.3, 141.6, 139.7, 136.7, 135.6, 133.1, 130.6, 129.7, 128.4, 127.3, 127.1, 124.5, 123.1, 122.9, 122.2, 119.6, 119.5, 118.7, 112.0, 111.1, 110.7, 110.2, 108.9, 102.8; IR (ATR): ṽ = 3502, 3407, 3057, 3009, 1639, 1611, 1502,

1485, 1446, 1325, 1248, 1214, 1176, 1075, 1039, 1008, 742, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{18}N_2ONa^+$ $[M+Na]^+$ 397.1311, found 397.1313.

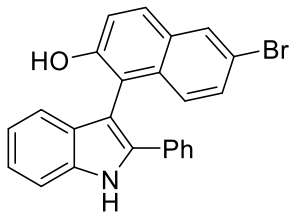


3az (condition **A**: 27.6 mg, 72%; condition **B**: 37.6 mg, 98%); brown solid (EtOAc:Hex = 1:20); mp 114-116 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 8.3 Hz, 1H), 8.70 (d, *J* = 7.8 Hz, 1H), 8.67 (s, 1H), 8.36 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.73 (t, *J* = 8.4 Hz, 1H), 7.65 (t, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.44 – 7.38 (m, 2H), 7.37 – 7.27 (m, 2H), 7.20 – 7.13 (m, 4H), 7.06 (t, *J* = 7.9 Hz, 1H), 5.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 136.6, 136.5, 132.8, 131.5, 131.4, 129.8, 129.0, 128.2, 127.2, 127.0, 126.7, 126.4, 126.3, 125.7, 125.0, 123.9, 123.5, 123.3, 122.6, 122.5, 120.8, 120.3, 111.1, 109.3, 105.2; IR (ATR): ṽ = 3498, 3419, 3065, 3013, 1598, 1492, 1449, 1424, 1402, 1325, 1305, 1286, 1260, 1214, 1156, 1109, 1086, 1024, 746, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{19}NONa^+$ $[M+Na]^+$ 408.1359, found 408.1358.

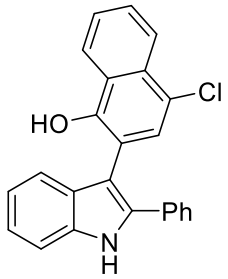


3aaa (condition **A**: 21.2 mg, 51%; condition **B**: 38.6 mg, 93%); white solid (EtOAc:Hex = 1:25); mp 206-208 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.16 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 8.4 Hz), 7.36 –7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 7.24 – 7.19 (m, 3H) , 7.13 – 7.05 (m, 2H), 5.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 136.5, 136.4, 133.4, 132.2, 131.5, 129.7, 129.4, 129.1, 128.3, 127.3, 126.9, 126.5, 125.5,

124.3, 123.5, 121.0, 120.0, 115.2, 111.4, 111.2, 105.0; IR (ATR): ṽ = 3466, 3413, 3058, 1579, 1492, 1448, 1378, 1325, 1263, 1205, 1145, 907, 744, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{16}BrNONa^+$ [M+Na]+ 436.0307, found 436.0307.

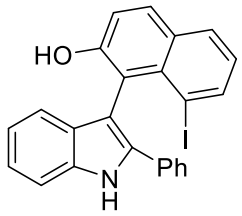


3aab (condition **A**: 22.6 mg, 55%; condition **B**: 40.6 mg, 98%); white solid (EtOAc:Hex = 1:25); mp 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 7.99 (s, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.54 (d, *J* = 8.2, 1H), 7.34 – 7.29 (m, 6H), 7.25 – 7.21 (m, 3H), 7.14 – 7.07 (m, 2H), 5.41 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 136.6, 136.5, 132.7, 131.4, 130.4, 130.1, 129.8, 129.5, 129.1, 128.9, 128.4, 127.1, 126.4, 123.6, 121.0, 120.0, 118.5, 117.1, 113.6, 111.2, 104.3; IR (ATR): ṽ = 3489, 3420, 3059, 1587, 1492, 1456, 1403, 1380, 1336, 1205, 1161, 1144, 1069, 930, 907, 879, 813, 734 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{16}BrNONa^+$ [M+Na]+ 436.0307, found 436.0307.

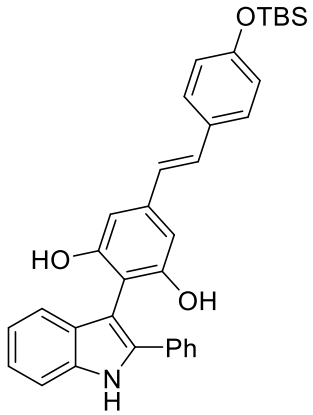


3aac (condition **A**: 15.3 mg, 41%; condition **B**: 25.5 mg, 69%); white solid (EtOAc:Hex = 1:25); mp 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 8.4 Hz, 1H), 7.56 (t, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.47 (s, 1H), 7.46 – 7.40 (m, 3H), 7.34 – 7.27 (m, 4H), 7.17 (t, *J* = 8.0 Hz, 1H), 5.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 136.1, 135.7, 131.3, 131.1, 129.1, 128.7, 128.5, 127.3, 127.0, 125.9, 125.3, 124.3, 123.6, 123.0, 122.8, 121.1, 119.7, 114.2, 111.2, 107.1; IR (ATR):

$\tilde{\nu}$ = 3507, 3421, 3059, 2928, 1599, 1456, 1415, 1365, 1324, 1265, 1033, 1004, 905, 727, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{16}ClNONa^+$ $[M+Na]^+$ 392.0813, found 392.0811.

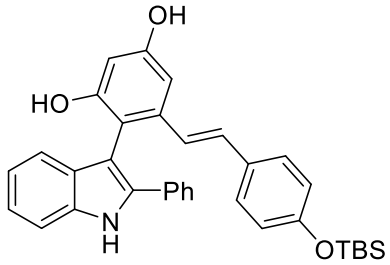


3aad (condition **A**: 25.4 mg, 55%; condition **B**: 45.3 mg, 98%); white solid (EtOAc:Hex = 1:15); mp 102-106 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.06 (d, *J* = 7.4 Hz, 1H), 7.86 – 7.77 (m, 3H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.10 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 5.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 142.8, 137.5, 136.1, 133.0, 132.1, 131.8, 131.1, 130.5, 130.1, 128.9, 128.1, 126.6, 124.2, 123.5, 121.0, 120.2, 117.5, 113.6, 111.1, 104.4, 89.7; IR (ATR): $\tilde{\nu}$ = 3518, 3377, 3030, 2995, 1759, 1607, 1454, 1376, 1247, 1241, 1058, 826, 743, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{16}INONa^+$ $[M+Na]^+$ 484.0169, found 484.0173.

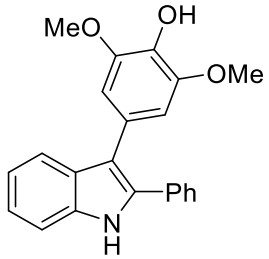


3aae (condition **A**: 14.8 mg, 28%); sticky yellow oil (EtOAc:Hex = 1:9); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 7.54 – 7.48 (m, 3H), 7.44–7.30 (m, 7H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.09 (d, *J* = 16.2 Hz, 1H), 6.93 (d, *J* = 16.2 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.79 (s, 2H), 4.99 (s, 2H), 1.00 (s, 9H), 0.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 154.8, 139.7, 137.1, 136.5, 130.9, 130.6, 129.3, 129.0, 128.9, 128.6, 127.8, 126.4, 124.0, 121.5, 120.3, 119.8, 111.3,

106.5, 105.3, 100.4, 25.7, 18.3, -4.4; IR (ATR): ṽ = 3502, 3402, 3061, 3026, 2953, 2928, 2857, 1601, 1557, 1509, 1446, 1327, 1263, 1168, 1039, 1009, 962, 911, 839, 746, 693 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{35}NO_3SiNa^+$ $[M+Na]^+$ 556.2278, found 556.2279.

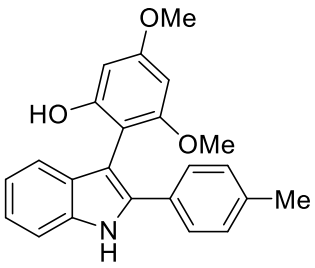


3aae' (condition **B**: 38 mg, 71%); pink solid (EtOAc:Hex = 1:9); mp 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.34 – 7.21 (m, 5H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 2.5 Hz, 1H), 6.83 (d, *J* = 16.4 Hz, 1H), 6.67 – 6.60 (m, 3H), 6.46 (d, *J* = 2.4 Hz, 1H), 5.17 (s, 1H), 4.77 (s, 1H), 0.93 (s, 9H), 0.13 (s, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 155.6, 155.4, 139.9, 136.7, 136.3, 131.8, 130.9, 129.7, 129.5, 129.1, 128.3, 127.8, 126.7, 125.1, 123.5, 121.1, 120.2, 112.5, 111.1, 105.2, 104.2, 101.5, 25.8, 18.3, -4.3; IR (ATR): ṽ = 3503, 3399, 3064, 3037, 2952, 2928, 2856, 1600, 1508, 1456, 1326, 1253, 1148, 1008, 906, 838, 781, 729, 693 cm^{-1}; HRMS (ESI) Calcd for C34H35NO3SiNa+ [M+Na]+ 556.2278, found 556.2279.

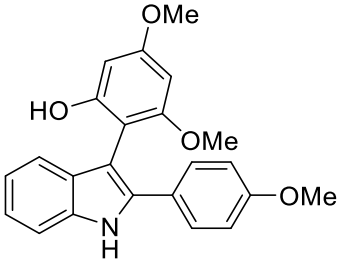


3aaf (condition **A**: 29.7 mg, 86%; condition **B**: 30.1 mg, 87%); white solid (EtOAc:Hex = 1:10); mp 204-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 1H) , 7.47 – 7.38 (m, 3H), 7.36 – 7.21 (m, 4H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.65 (s, 2H), 5.23 (s, br, 1H), 3.75 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 135.9, 133.9, 133.4, 132.7, 128.7, 128.6, 128.2, 127.7, 126.2, 122.7, 120.5, 119.6, 115.1, 111.0, 106.9, 56.3; IR (ATR): ṽ = 3465, 3369, 3031, 2971, 1603, 1517, 1456, 1376, 1345, 1297, 1231, 1206, 1112, 847, 774, 746, 698 cm^{-1};

HRMS (ESI) Calcd for $C_{22}H_{19}NO_3Na^+$ $[M+Na]^+$ 368.1257, found 368.1259.

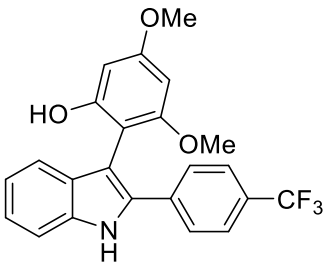


3ba (condition **A**: 31.6 mg, 88%; condition **B**: 33.6 mg, 93%); white solid (EtOAc:Hex = 1:15); mp 194-196 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 8.2 Hz, 1H), 7.14 –7.09 (m, 3H), 6.25 (d, *J* = 2.4 Hz, 1H), 6.19 (d, *J* = 2.4 Hz, 1H), 5.21 (s, 1H), 3.84 (s, 3H), 3.57 (s, 3H), 2.33 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 159.6, 155.6, 137.9, 136.2, 129.6, 129.4, 129.4, 126.3, 122.8, 120.5, 119.9, 111.0, 102.9, 102.1, 92.6, 91.9, 55.7, 55.4, 21.3; IR (ATR): ṽ = 3489, 3401, 3055, 3001, 2942, 2838, 1626, 1583, 1490, 1454, 1328, 1306, 1208, 1148, 1100, 1049, 909, 819, 733 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{21}NO_3Na^+$ $[M+Na]^+$ 382.1414, found 382.1415.

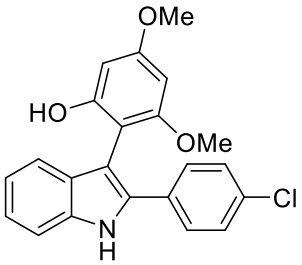


3ca (condition **A**: 14.6 mg, 39%; condition **B**: 30.4 mg, 81%); white solid (EtOAc:Hex = 1:15); mp 158-160 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.36 – 7.31 (m, 3H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 1H), 6.25 (d, *J* = 2.4 Hz, 1H), 6.19 (d, *J* = 2.4 Hz, 1H), 5.26 (s, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 159.6, 159.3, 155.7, 136.2, 136.1, 129.5, 127.7, 124.8, 122.6, 120.4, 119.7, 114.3, 111.1, 102.4, 102.1, 92.7, 92.0, 55.7, 55.4, 55.2; IR (ATR): ṽ = 3480, 3399, 3064, 3005, 2960, 2937, 2838, 1614, 1580, 1518, 1490, 1455, 1250, 1208, 1148, 1100, 1030, 909, 833, 731 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{21}NO_4Na^+$ $[M+Na]^+$ 398.1363,

found 398.1361.

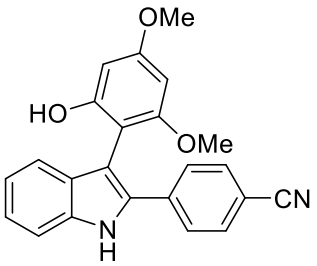


3da (condition **A**: 31.4 mg, 76%; condition **B**: 41.0 mg, 99%); white solid (EtOAc:Hex = 1:15); mp 164-166 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (s, 1H), 7.57 – 7.50 (m, 4H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.27 (d, *J* = 2.3 Hz, 1H), 6.18 (d, *J* = 2.3 Hz, 1H), 5.15 (s, 1H), 3.85 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 159.3, 155.6, 136.5, 135.7, 134.3, 129.4 (q, J_{CF} = 32.5 Hz), 129.1, 126.3, 125.7 (q, J_{CF} = 3.7 Hz), 124.1 (q, J_{CF} = 270 Hz), 123.7, 120.9, 120.1, 120.0, 104.9, 101.6, 92.9, 92.1, 55.6, 55.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.6; IR (ATR): $\tilde{\nu}$ = 3476, 3378, 3005, 2946, 2842, 1618, 1583, 1521, 1456, 1322, 1253, 1210, 1149, 1117, 1066, 910, 843, 818, 732 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{18}F_3NO_3Na^+$ $[M+Na]^+$ 436.1131, found 436.1131.

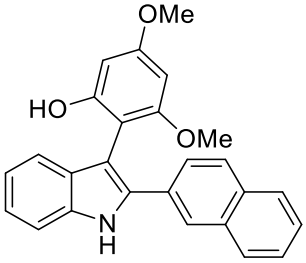


3ea (condition **A**: 28.8 mg, 76%; condition **B**: 37.2 mg, 98%); white solid (EtOAc:Hex = 1:15); mp 172-174 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.23 (m, 3H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 6.18 (d, *J* = 2.4 Hz, 1H), 5.16 (s, 1H), 3.85 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 159.4, 155.6, 136.3, 134.9, 133.8, 130.8, 129.2, 129.0, 127.6, 123.3, 120.8, 120.0, 111.2, 103.8, 101.6, 92.7, 92.0, 55.6, 55.4; IR (ATR): $\tilde{\nu}$ = 3494, 3391,

3059, 2937, 2838, 1626, 1583, 1509, 1454, 1329, 1208, 1149, 1099, 1049, 909, 831, 728 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{18}ClNO_3Na^+$ $[M+Na]^+$ 402.0867, found 402.0868.

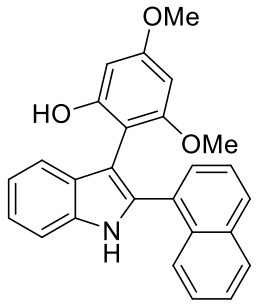


3fa (condition **A**: no desired product; condition **B**: 26.0 mg, 70%); white solid (EtOAc:Hex = 1:15); mp 141-143 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 7.60 (d, *J* = 8.5, Hz, 2H), 7.55 (d, *J* = 8.5, Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.28 (d, *J* = 2.3 Hz, 1H), 6.18 (d, *J* = 2.3 Hz, 1H), 5.10 (s, 1H), 3.86 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 159.1, 155.6, 136.9, 136.7, 133.7, 132.5, 129.0, 126.5, 124.1, 121.0, 120.3, 118.8, 111.5, 110.6, 106.0, 101.3, 93.0, 92.1, 55.6, 55.4; IR (ATR): $\tilde{\nu}$ = 3485, 3367, 2937, 2838, 2226, 1605, 1583, 1454, 1329, 1305, 1210, 1150, 1100, 910, 841, 732 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{18}N_2O_3Na^+$ $[M+Na]^+$ 393.1210, found 393.1210.

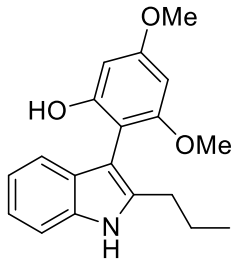


3ga (condition **A**: 32.3 mg, 82%; condition **B**: 37.8 mg, 95%); white solid (EtOAc:Hex = 1:15); mp 177-179 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H), 7.95 (s, 1H), 7.82 – 7.71 (m, 3H), 7.53 (dd, *J* = 1.8, 8.6 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 8.2 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.27 (d, *J* = 2.4 Hz, 1H), 6.20 (d, *J* = 2.3 Hz, 1H), 5.26 (s, 1H), 3.85 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 159.6, 155.8, 136.5,

136.0, 133.4, 132.8, 129.9, 129.4, 128.4, 128.2, 127.7, 126.4, 126.3, 125.1, 124.5, 123.1, 120.6, 120.0, 111.2, 103.8, 102.3, 92.8, 92.0, 55.7, 55.4; IR (ATR): $\tilde{\nu}$ = 3494, 3399, 3055, 2955, 2937, 2838, 1625, 1583, 1511, 1454, 1329, 1307, 1208, 1148, 1099, 909, 817, 733 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{21}NO_3Na^+$ $[M+Na]^+$ 418.1414, found 418.1413.

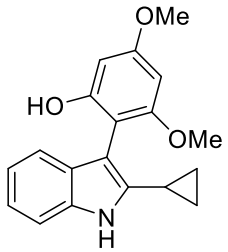


3ha (condition **A**: 6.0 mg, 15%; condition **B**: 33.2 mg, 84%); white solid (Et_2O:Hex = 1:7); mp 126-128 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.78 (dd, *J* = 1.1, 7.7 Hz, 1H) 7.45 – 7.31 (m, 6H), 7.25 (t, *J* = 8.1 Hz, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 6.09 (d, *J* = 2.3 Hz, 1H), 5.95 (d, *J* = 2.3 Hz, 1H), 5.33 (s, 1H), 3.67 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 159.3, 155.6, 136.3, 133.7, 131.8, 130.3, 128.9, 128.4, 128.2, 126.4, 126.0, 125.7, 125.3, 122.8, 120.5, 120.1, 111.2, 105.6, 101.9, 92.4, 91.5, 55.2; IR (ATR): $\tilde{\nu}$ = 3498, 3394, 3050, 2965, 2838, 1626, 1583, 1453, 1303, 1208, 1147, 1098, 906, 804, 777, 727 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{21}NO_3Na^+$ $[M+Na]^+$ 418.1414, found 418.1412.

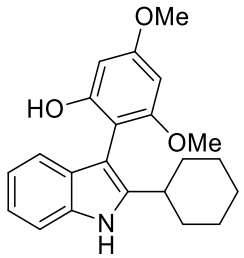


3ia (condition **A**: 23.3 mg, 75%; condition **B**: 22.6 mg, 72%); sticky yellow oil (Et_2O:Hex = 1:7); ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 8.2 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.29 (d, *J* = 2.4 Hz, 1H), 6.19 (d, *J* = 2.4

Hz, 1H), 5.23 (s, 1H), 3.85 (s, 3H), 3.68 (s, 3H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.64 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 159.4, 155.9, 139.3, 135.8, 128.2, 121.7, 120.1, 119.1, 110.6, 102.3, 101.7, 92.2, 91.5, 55.6, 55.4, 28.8, 22.4, 13.9; IR (ATR): ṽ = 3476, 3397, 2959, 2928, 2874, 2838, 1627, 1615, 11584, 1501, 1457, 1305, 1206, 1146, 1099, 10555, 909, 815, 735 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{21}NO_3Na^+$ $[M+Na]^+$ 334.1414, found 334.1415.

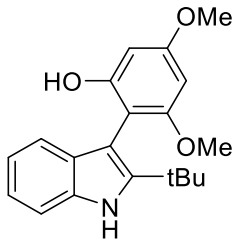


3ja (condition **A**: 11.3 mg, 37%; condition **B**: 11.2 mg, 36%); white solid (Et_2O:Hex = 1:7); mp 58-60 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.28 – 7.19 (m, 2H), 7.13 (t, *J* = 8.2 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.29 (d, *J* = 2.3 Hz, 1H), 6.20 (d, *J* = 2.3 Hz, 1H), 5.34 (s, 1H), 3.84 (s, 3H), 3.68 (s, 3H), 1.94 – 1.85 (m, 1H), 0.94 – 0.84 (m, 2H), 0.79 – 0.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 159.5, 155.8, 139.4, 135.3, 128.6, 121.8, 120.1, 119.0, 110.6, 103.0, 101.7, 92.3, 91.5, 55.7, 55.4, 8.4, 7.3, 6.9; IR (ATR): ṽ = 3480, 3398, 3055, 3005, 2838, 2838, 1627, 1583, 1504, 1457, 1339, 1306, 1207, 1146, 1098, 909, 815, 733 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{19}NO_3Na^+$ $[M+Na]^+$ 332.1257, found 332.1257.

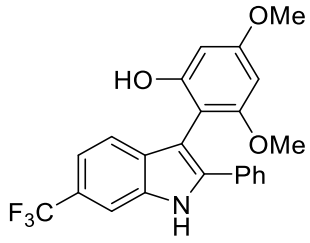


3ka (condition **A**: 14.4 mg, 41%; condition **B**: 20.5 mg, 84%); white solid (EtOAc:Hex = 1:100); mp 183-185 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 6.4 Hz, 1H), 7.16 (t, *J* = 7.1 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.30 (d, *J* = 2.3 Hz,

1H), 6.20 (d, *J* = 2.2 Hz, 1H), 5.24 (s, 1H), 3.85 (s, 3H), 3.67 (s, 3H), 2.63 (tt, *J* = 3.2, 12.0 Hz, 1H), 1.98 (d, *J* = 12.6 Hz, 1H), 1.87 – 1.67 (m, 4H), 1.50 – 1.36 (m, 2H), 1.36 – 1.18 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 159.5, 156.0, 144.1, 135.7, 128.2, 121.7, 120.1, 119.1, 110.8, 101.9, 100.6, 92.3, 91.6, 55.6, 55.4, 36.5, 33.1, 32.8, 26.5, 26.1; IR (ATR): ṽ = 3476, 3408, 2850, 2927, 1615, 1584, 1502, 1457, 1307, 1207, 1146, 1099, 1056, 909, 815, 730 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{25}NO_3Na^+$ $[M+Na]^+$ 374.1727, found 374.1727.

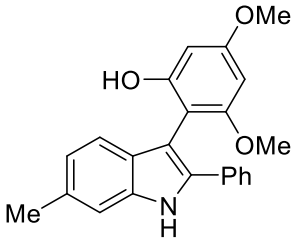


3la (condition **A**: 10.8 mg, 33%; condition **B**: 27.8 mg, 85%); white solid (EtOAc:Hex = 1:20); mp 78-80 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.16 (t, *J* = 7.0 Hz, 1H), 7.13 (d, *J* = 9.0 Hz, 1H), 7.03 (t, *J* = 7.0 Hz, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 6.17 (d, *J* = 2.4 Hz, 1H), 5.04 (s, 1H), 3.85 (s, 3H), 3.65 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 159.7, 155.9, 146.3, 134.7, 129.8, 121.9, 120.0, 118.7, 110.5, 103.4, 100.1, 92.0, 91.4, 55.5, 55,4, 33.2, 29.9; IR (ATR): ṽ = 3485, 3412, 2960, 2910, 2874, 2838, 1613, 1584, 1456, 1315, 1198, 1098, 907, 813, 727 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{23}NO_3Na^+$ $[M+Na]^+$ 348.1570, found 348.1573.

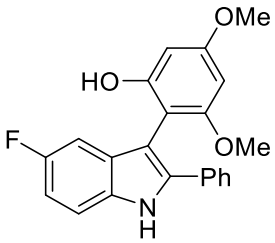


3ma (condition **A**: 32.2 mg, 78%; condition **B**: 37.6 mg, 91%); white solid (EtOAc:Hex = 1:15); mp 132-134 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 7.72 (s, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.38 – 7.29 (m, 4H), 6.26 (d, *J* = 2.3 Hz, 1H), 6.19 (d, *J*

= 2.3 Hz, 1H), 5.06 (s, 3H), 3.85 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 159.4, 155.6, 138.8, 135.1, 131.7, 131.5, 128.9, 128.6, 126.5, 125.1 (q, J_{CF} = 270 Hz), 124.8 (q, J_{CF} = 31.8 Hz), 120.3, 117.2 (q, J_{CF} = 3.3 Hz), 108.7 (q, J_{CF} = 4.3 Hz), 103.6, 101.3, 92.9, 92.1, 55.7, 55.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -60.7; IR (ATR): ṽ = 3511, 3358, 3010, 2942, 2842, 1622, 1584, 1513, 1459, 1337, 1210, 1150, 1104, 1052, 910, 818, 733, 693 cm^{-1}; HRMS (ESI) Calcd for C_{23}H18F3NO3Na+ [M+Na]+ 436.1131, found 436.1132.

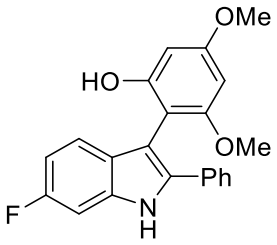


3na (condition **A**: 26.6 mg, 74%; condition **B**: 34.6 mg, 96%); white solid (EtOAc:Hex = 1:15); mp 208-210 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 6.9 Hz, 2H), 7.24 – 7.16 (m, 3H), 6.94 (dd, *J* = 0.9 ,8.1 Hz, 1H), 6.25 (d, *J* = 2.3 Hz, 1H), 6.17 (d, *J* = 2.3 Hz, 1H), 5.24 (s, 1H), 3.83 (s, 3H), 3.53 (s, 3H), 2.46 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 159.5, 155.6, 136.7, 135.3, 133.0, 132.5, 128.8, 127.7, 127.2, 126.3, 122.3, 119.6, 110.0, 103.2, 102.2, 92.6, 91.9, 55.6, 55.4, 21.8; IR (ATR): ṽ = 3485, 3394, 3001, 2937, 2838, 1624, 1583, 1509, 1455, 1341, 1308, 1209, 1148, 1100, 909, 810, 732 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{21}NO_3Na^+$ [M+Na]$^+$ 382.1414, found 382.1415.

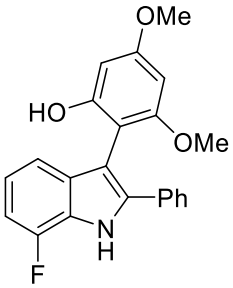


3oa (condition **A**: 32.0 mg, 88%; condition **B**: 34.2 mg, 94%); white solid (EtOAc:Hex = 1:15); mp 123-125 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.43 (dd, *J* = 1.6, 8.3 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.01 – 6.94 (m, 2H), 6.24 (d, *J* = 2.3 Hz, 1H), 6.18 (d, *J* = 2.3 Hz, 1H), 5.13 (s, 1H), 3.84 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 159.4, 158.4 (d, J_{CF} = 234 Hz), 155.5, 137.8, 132.7, 131.9, 130.0 (d, J_{CF} = 9.7 Hz), 128.9, 128.2, 126.4, 111.9

(d, J_{CF} = 9.4 Hz), 111.4 (d, J_{CF} = 26.3 Hz), 104.8 (d, J_{CF} = 23.7 Hz), 103.5 (d, J_{CF} = 4.8 Hz), 101.6, 92,8, 92.0, 55.7, 55.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -123.2; IR (ATR): ṽ = 3503, 3421, 3059, 3005, 2942, 2842, 1621, 1580, 1510, 1481, 1312, 1207, 1147, 1097, 1048, 908, 797, 731, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{18}FNO_3Na$+ [M+Na]+ 386.1163, found 386.1162.

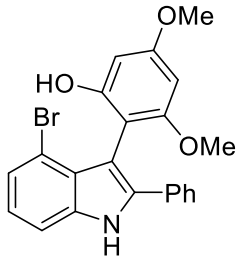


3pa (condition **A**: 28.8 mg, 79%; condition **B**: 34.8 mg, 96%); white solid (EtOAc:Hex = 1:15); mp 144-146 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 7.41 (dd, *J* = 1.6, 8.4 Hz, 2H), 7.36 – 7.25 (m, 3H), 7.22 (dd, *J* = 5.3, 8.7 Hz, 1H), 7.09 (dd, *J* = 2.2, 9.4 Hz, 1H), 6.87 (td, *J* = 2.3, 9.6 Hz, 1H), 6.25 (d, *J* = 2.3 Hz, 1H), 6.19 (d, *J* = 2.4 Hz, 1H), 5.16 (s, 1H), 3.84 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 160.6 (d, J_{CF} = 218 Hz), 159.3, 155.6, 136.3 (d, J_{CF} = 3.5 Hz), 136.2 (d, J_{CF} = 12.5 Hz), 132.0, 128.9, 128.0, 126.2, 125.8, 120.8 (d, J_{CF} = 10.1 Hz), 109.3 (d, J_{CF} = 24.3 Hz), 103.3, 101.7, 97.5 (d, J_{CF} = 26.1 Hz), 92.8, 92.0, 55.7, 55.4 ; ^{19}F NMR (376 MHz, $CDCl_3$): δ -119.5; IR (ATR): ṽ = 3498, 3385, 3069, 2960, 2937, 2842, 1625, 1580, 1509, 1446, 1312, 1250, 1209, 1146, 1098, 1050, 969, 908, 816, 731 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{18}FNO_3Na^+$ [M+Na]$^+$ 386.1163, found 386.1165.

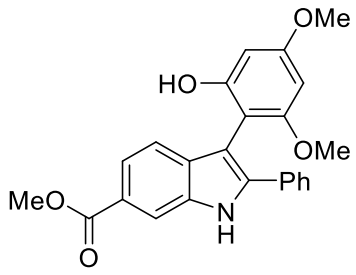


3qa (condition **A**: 7.0 mg, 19%; condition **B**: 26.2 mg, 72%); white solid (EtOAc:Hex = 1:15); mp 162-164 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 7.47 (dd, *J* = 1.2, 8.0 Hz, 2H), 7.38 – 7.27 (m, 3H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.02 (td, *J* = 4.7, 7.8 Hz, 1H), 6.98 – 6.92 (m,

1H), 6.25 (d, J = 2.3 Hz, 1H), 6.18 (d, J = 2.3 Hz, 1H), 5.14 (s, 1H), 3.84 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 159.5, 155.6, 149.5 (d, J_{CF} = 243 Hz), 137.0, 132.9 (d, J_{CF} = 4.9 Hz), 131.8, 128.9, 128.3, 126.5, 124.6 (d, J_{CF} = 13.2 Hz), 120.8 (d, J_{CF} = 6.0 Hz), 115.7 (d, J_{CF} = 3.4 Hz), 107.8 (d, J_{CF} = 16.1 Hz), 105.6 (d, J_{CF} = 2.7 Hz), 101.6, 92.7, 92.0, 55.6, 55.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -135.7; IR (ATR): ṽ = 3503, 3349, 3059, 2960, 2937, 2842, 1624, 1581, 1502, 1449, 1319, 1232, 1205, 1146, 1094, 1059, 953, 907, 768, 727, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{18}FNO_3Na^+$ $[M+Na]^+$ 386.1163, found 386.1162.

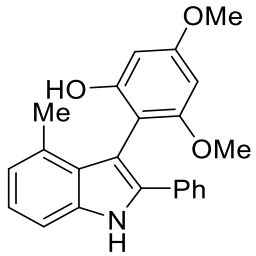


3ra (condition **A**: 30.9 mg, 69%; condition **B**: 22.0 mg, 49%); white solid (EtOAc:Hex = 1:10); mp 166-168 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 7.42 – 7.36 (m, 2H), 7.32 (d, J = 8.1 Hz, 1H), 7.29 – 7.21 (m, 4H), 7.02 (t, J = 7.8 Hz, 1H), 6.20 (d, J = 2.3 Hz, 1H), 6.16 (d, J = 2.3 Hz, 1H), 5.01 (s, 1H), 3.81 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 160.6, 137.7, 137.3, 131.5, 128.9, 128.3, 127.2, 126.9, 125.1, 123.6, 114.5, 110.5, 103.4, 102.4, 92.1, 91.6, 55.8, 55.3; IR (ATR): ṽ = 3522, 3362, 2996, 1759, 1584, 1454, 1376, 1247, 1149, 1103, 1056, 925, 778, 748, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{18}BrNO_3Na^+$ $[M+Na]^+$ 446.0362, found 446.0361.

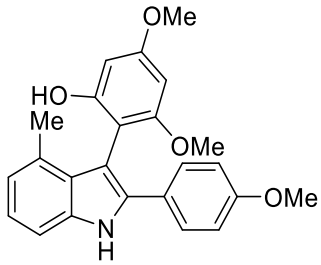


3sa (condition **A**: 21.4 mg, 53%; condition **B**: 37.4 mg, 93%); white solid (EtOAc:Hex = 1:7); mp 143-145 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 8.22 (s, 1H), 7.79 (dd, J = 1.3,

8.4 Hz, 1H), 7.49 (dd, *J* = 1.8, 8.1 Hz, 2H), 7.37 – 7.28 (m, 4H), 6.26 (d, *J* = 2.3 Hz, 1H), 6.18 (d, *J* = 2.3 Hz, 1H), 5.15 (s, 1H), 3.93 (s, 3H), 3.84 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 161.4, 159.4, 155.6, 139.6, 135.6, 133.1, 131.8, 128.8, 128.5, 126.7, 124.2, 121.4, 119.5, 113.7, 103.8, 101.5, 92.8, 92.0, 55.6, 55.4, 52.1; IR (ATR): ṽ = 3498, 3352, 3055, 3005, 2946, 2838, 1693, 1617, 1582, 1513, 1457, 1435, 1324, 1291, 1211, 1149, 1097, 986, 910, 768, 731, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{21}NO_5Na^+$ $[M+Na]^+$ 426.1312, found 426.1312.

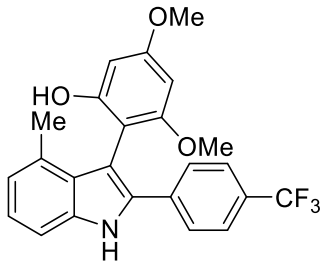


3ta (condition **A**: 24.8 mg, 69%; condition **B**: 32.0 mg, 89%); white solid (EtOAc:Hex = 1:15); mp 162-164 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.48 (s, 1H), 7.41 (d, *J* = 7.1 Hz, 2H), 7.33 – 7.22 (m, 4H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 7.1 Hz, 1H), 6.21 (d, *J* = 2.3 Hz, 1H), 6.16 (d, *J* = 2.3 Hz, 1H), 5.16 (s, 1H), 3.83 (s, 3H), 3.63 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 160.0, 156.0, 136.5, 136.1, 132.2, 131.8, 128.8, 127.9, 127.8, 122.8, 121.9, 109.1, 104.2, 102.8, 92.1, 91.5, 55.7, 55.3, 18.4; IR (ATR): ṽ = 3471, 3394, 3010, 2942, 2842, 1625, 1581, 1503, 1447, 1325, 1209, 1146, 1096, 907, 816, 753, 693 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{21}NO_3Na^+$ $[M+Na]^+$ 382.1414, found 382.1411.

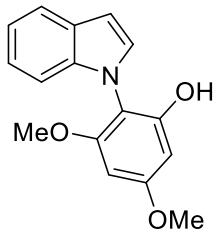


3ua (condition **A**: 20.0 mg, 51%; condition **B**: 29.0 mg, 74%); white solid (EtOAc:Hex = 1:10); mp 100-102 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.24 –

7.19 (m, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.81 (m, 3H), 6.20 (d, *J* = 2.2 Hz, 1H), 6.16 (d, *J* = 2.2 Hz, 1H), 5.18 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 160.1, 159.2, 156.0, 136.3, 136.1, 131.6, 128.0, 127.9, 124.7, 122.5, 121.8, 114.2, 108.8, 104.2, 101.8, 92.0, 91.4, 55.6, 55.3, 55.2, 18.3; IR (ATR): ṽ = 3476, 3399, 2960, 2937, 2838, 1625, 1580, 1517, 1489, 1455, 1323, 1250, 1209, 1148, 1099, 1030, 909, 833, 731 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{23}NO_4Na^+$ $[M+Na]^+$ 412.1519, found 412.1520.

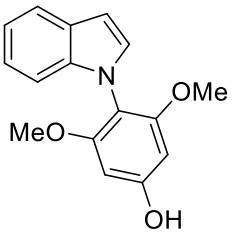


3va (condition **A**: 37.4 mg, 87%; condition **B**: 42.4 mg, 99%); white solid (Et_2O:Hex = 1:7); mp 200-202 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 7.1 Hz, 1H), 6.22 (d, *J* = 2.3 Hz, 1H), 6.17 (d, *J* = 2.3 Hz, 1H), 5.07 (s, 1H), 3.83 (s, 3H), 3.61 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 159.8, 155.9, 136.8, 135.6, 134.3, 132.2, 129.4(q, J_{CF} = 32.4 Hz), 127.8, 126.6, 125.7(q, J_{CF} = 3.8 Hz),124.1(q, J_{CF} = 270 Hz), 123.6, 122.3, 109.1, 104.6, 103.5, 92.3, 91.6, 55.6, 55.3, 18.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7; IR (ATR): ṽ = 3476, 3385, 3055, 3005, 2946, 2842, 1618, 1582, 1521, 1456, 1322, 1210, 1166, 1149, 1117, 1102, 1066, 909, 843, 818, 759, 731 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{20}F_3NO_3Na^+$ $[M+Na]^+$ 450.1287, found 450.1286.

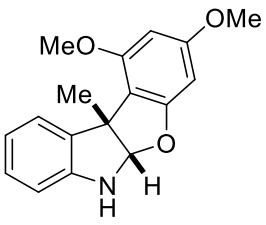


5wa (condition **A**: 9.5 mg, 35%); colorless sticky oil (EtOAc:Hex = 1:10 to 1:5); ^{1}H NMR (400

MHz, $CDCl_3$): δ 7.71 – 7.67 (m, 1H), 7.21 – 7.13 (m, 2H), 7.09 (d, *J* = 3.2 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.71 (d, *J* = 3.2 Hz, 1H), 6.29 (d, *J* = 2.6 Hz, 1H), 6.19 (d, *J* = 2.6 Hz, 1H), 4.96 (s, 1H), 3.85 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 157.5, 154.2, 137.1, 129.7, 128.6, 122.5, 121.0, 120.5, 110.3, 107.7, 103.8, 92.8, 92.1, 55.9, 55.6; IR (ATR): ṽ = 3461, 3017, 2946, 2971, 1592, 1520, 1456, 1372, 1366, 1352, 1230, 1217, 1206, 1151, 1133, 1108, 1047, 817, 766, 744 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{15}NO_3Na^+$ $[M+Na]^+$ 292.0944, found 292.0940.

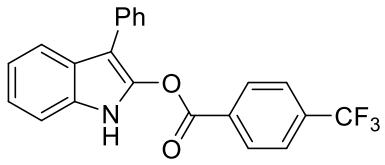


5wa' (condition **A**: 2.5 mg, 9%); yellow sticky oil (EtOAc:Hex = 1:10 to 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 – 7.63 (m, 1H), 7.13 – 7.07 (m, 3H), 6.98 – 6.94 (m, 1H), 6.64 (d, *J* = 2.9 Hz, 1H), 6.19 (s, 2H), 5.02 (s, br, 1H), 3.64 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 156.7, 137.3, 130.0, 128.0, 121.5, 120.6, 119.4, 110.6, 101.8, 92.4, 56.0; IR (ATR): ṽ = 3456, 3016, 2970, 2946, 1698, 1598, 1521, 1455, 1373, 1366, 1352, 1230, 1217, 1206, 1129, 997, 895, 817, 745 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{15}NO_3Na^+$ $[M+Na]^+$ 292.0944, found 292.0940.

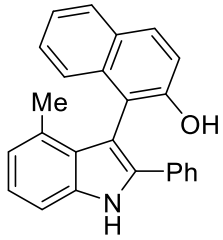


6xa (condition **A**: 6.2 mg, 22%; condition **B**: 2.3 mg, 8%); yellow sticky oil (EtOAc:Hex = 1:10 to 1:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.4, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.05 – 5.98 (m, 3H), 4,93 (s, 1H), 3.87 (s, 3H), 3.72 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 160.5, 157.2, 146.9, 134.0, 127.8, 124.3, 119.6, 111.5, 109.0, 105.3, 91.8, 88.6, 56.3, 55.6, 55.3, 23.5; IR (ATR): ṽ = 3461,

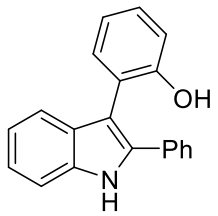
3017, 2971, 2943, 1612, 1500, 1455, 1373, 1366, 1352, 1230, 1217, 1205, 1149, 1075, 946, 811, 748 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}NO_3Na^+$ $[M+Na]^+$ 306.1101, found 306.1105.



7y white foam (EtOAc:Hex = 1:10); ^1H NMR (400 MHz, $CDCl_3$): δ 9.32 (s, 1H), 8.29 (d, *J* = 8.1 Hz, 2H) ,7.43 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 139.3, 135.7 (q, J_{CF} = 32.7 Hz), 132.8, 131.5, 131.3, 130.8, 128.7, 128.6, 126.3, 125.9 (q, J_{CF} = 3.7 Hz), 124.9, 123.4 (q, J_{CF} = 271.4 Hz), 122.5, 121.0, 119.4, 111.3, 102.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3; IR (ATR): ṽ = 3456, 3017, 2971, 1738, 1456, 1436, 1412, 1371, 1366, 1353, 1325, 1259, 1230, 1217, 1131, 1114, 1067, 1015, 769, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{14}F_3NO_2Na^+$ $[M+Na]^+$ 404.0869, found 404.0870.



3zr white solid (EtOAc:Hex = 1:20); mp 98-100 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.21 (m, 5H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.15 – 7.10 (m, 3H), 6.81 (d, *J* = 7.1 Hz, 1H), 5.42 (s, 1H), 1.78 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 136.7, 136.4, 135.4, 132.1, 131.7, 129.8, 128.9, 128.1, 128.0, 126.7, 126.6, 125.2, 123.3, 122.2, 116.9, 115.3, 109.0, 104.6, 18.3; IR (ATR): ṽ = 3478, 3393, 3055, 3019, 2956, 2920, 2857, 2250, 1616, 1597, 1492, 1464, 1447, 1428, 1383, 1326, 1262, 1201, 1142, 906, 816, 750, 727, 694, 644 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{19}NONa^+$ $[M+Na]^+$ 372.1359, found 372.1360.



10 (13.6mg, 48%); yellow sticky oil (EA:Hex = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.42 – 7.32 (m, 4H), 7.28 – 7.17 (m, 6H), 7.08 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 5.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 136.1, 135.2, 131.9, 131.7, 129.1, 129.0, 128.3, 127.1, 123.4, 120.9, 120.7, 120.6, 119.8, 115.4, 111.1, 108.1; IR (ATR): $\tilde{\nu}$ = 3510, 3413, 3062, 2932, 2854, 1607, 1581, 1503, 1481, 1459, 1444, 1333, 1281, 1255, 1233, 1211, 1170, 1155, 1033, 974, 744, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{15}NONa^{+}$ $[M+Na]^{+}$ 308.1046, found 308.1045.

5. Unsuccessful Substrates

Nucleophilic arenes in Chart S1 resulted in little conversion of **1a** and in some cases, unidentified byproducts formed in small amount.

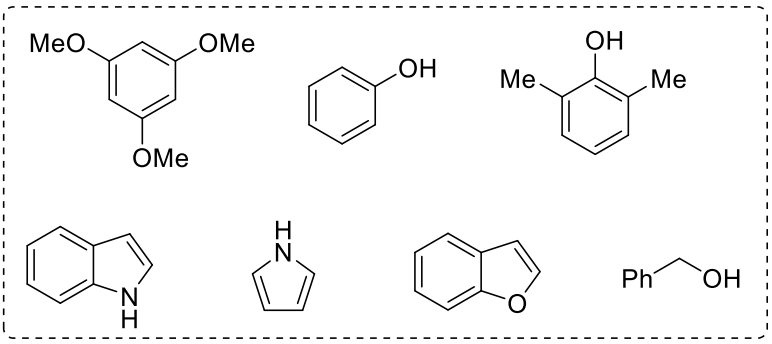
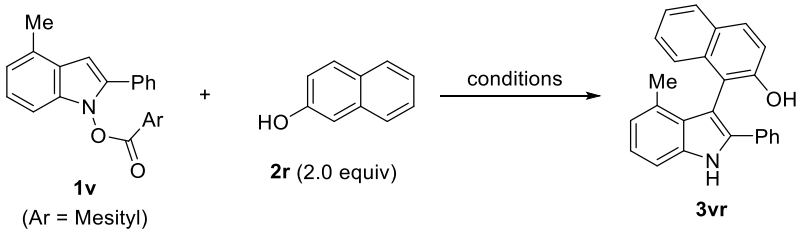


Chart S1. Unreactive substrates under both conditions A and B (rt~60 ºC).

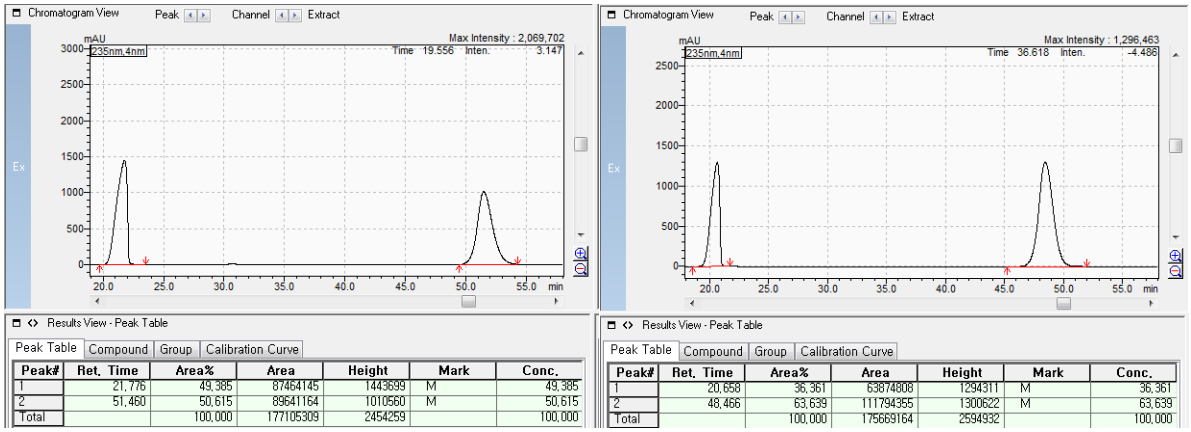
6. Enantioselective Indolylation of Phenols



Condition 1 (Chiral disulfonimide)

In an oven-dried vial, 4-methyl-2-phenyl-1*H*-indol-1-yl 2,4,6-trimethylbenzoate **1v** (36.9 mg, 0.1 mmol), 2-naphthol **2r** (28.8 mg, 0.2 mmol) were dissolved in 1.0 mL CH_2Cl_2. To this was added **DSI-1** (2.0 mg, 10 mol%) at room temperature. When the reaction was judged to be complete by TLC, reaction mixture was concentrated in *vacuo* and the residue was purified by flash column chromatography (SiO_2, EtOAc:Hex = 1:20) to afford 34.5 mg of **3vr** (99%, 27% ee) as a white solid.

Chiral assay was conducted on Chiralpak® IA column using IPA:*n*Hex (20:80) as an eluent (1 mL/min).

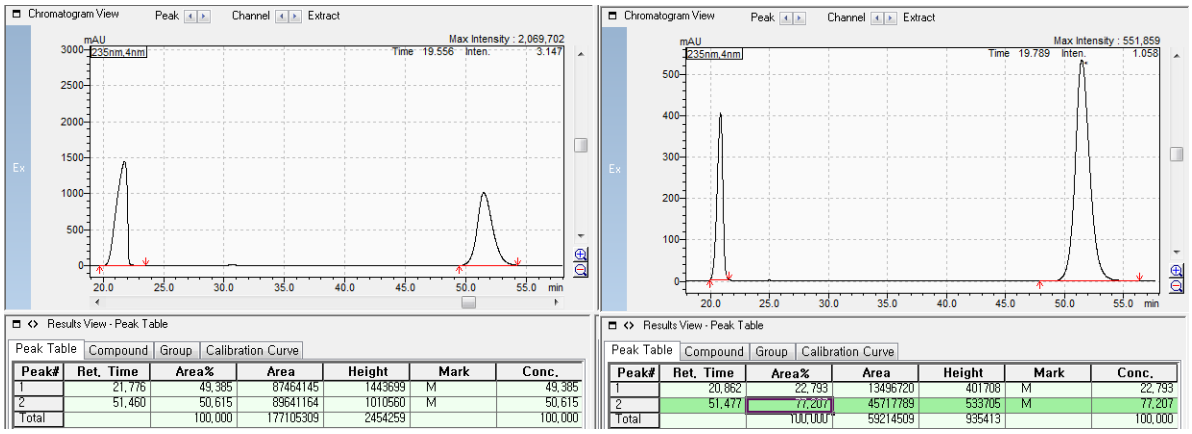


[(±)-**3vr**] [(27% ee)-**3vr**]

Condition 2 (Chiral Cu(I)/DM-Segphos)

In glove box, $Cu(MeCN)_4PF_6$ (3.8 mg, 0.01 mmol) and (*R*)-DM-Segphos (8.6 mg, 0.12 mmol) were dissolved in 1.0 mL CH_2Cl_2 and stirred at room temperature for 1 hour. In another vial, 4-methyl-2-phenyl-1*H*-indol-1-yl 2,4,6-trimethylbenzoate **1v** (36.9 mg, 0.1 mmol), 2-naphthol **2r** (28.8 mg, 0.2 mmol) were dissolved in 1.0 mL CH_2Cl_2. To this was added 1.0 mL of premade Cu(I)/DM-Segphos catalyst at room temperature. The reaction mixture was taken out of glove box and stirred at room temperature. When the reaction was judged to be complete by TLC, reaction mixture was concentrated in *vacuo* and the residue was purified by flash column chromatography (SiO_2, EtOAc:Hex = 1:20) to afford 7.6 mg of **3vr** (22%, 54% ee) as a white solid.

Chiral assay was conducted on Chiralpak® IA column using IPA:*n*Hex (20:80) as an eluent (1 mL/min).

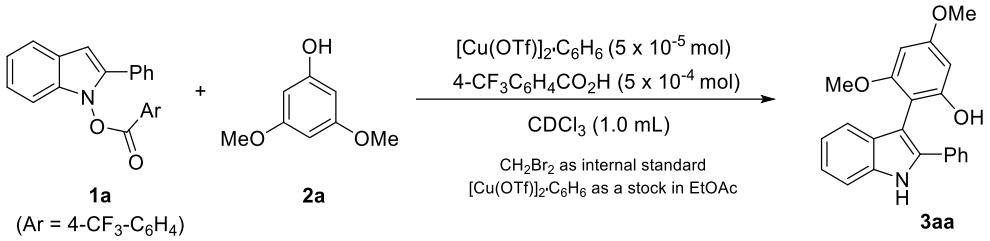


[(±)-**3vr**] [**3vr** (54%ee)]

7. Mechanistic Study

7.1. The Reaction Orders

The reaction orders were determined by variable time normalization analysis (VTNA) as reported by Burés.[3]



In an oven-dried NMR tube, below-prescribed amount of 2-phenyl-1H-indol-1-yl 4-(trifluoromethyl)benzoate (**1a**), 3,5-dimethoxyphenol (**2a**), and 4-$CF_3C_6H_4CO_2H$ (9.5 mg, 0.050 mmol) was dissolved in $CDCl_3$ (1.0 mL) with dibromomethane (17.4 mg, 0.100 mmol) as an internal standard. Then, $[Cu(OTf)]_2{\cdot}C_6H_6$ (0.00250 mg, 0.000050 mmol, 20.0 μL of 0.00250 M stock solution in ethyl acetate) was added and the stopwatch was started. The progress of the reaction was monitored by ^1H NMR spectrometer (probe temperature at 298 K). For volumetric measurements, Finnpipette F1 from Thermo Scientific was used.

The order in [**1a**] and [**2a**] was determined by Burés' method based on normalized time scale, time*[**1a**]^n, time*[**2a**]^n, and time*[cat]^n.[3,4] From the normalized time scale method, the best overlay was obtained when the time is normalized by time*[**1a**]^1, time*[**2a**]^1 and time*[**Cu**$_2$]$^{1/2}$ (where Cu_2 = $[Cu(OTf)]_2{\cdot}C_6H_6$). (Later in the reaction, some deviation from the overlay was observed, presumably due to partial decomposition of the catalyst)

From these analyses, the reaction order was determined as the first order in [**1a**], the first order in [**2a**], and a half order in the pre-catalyst, $[Cu(OTf)]_2{\cdot}C_6H_6$. The latter indicated that the active catalyst has monomeric form, such as Cu(OTf) and that the order in the monomeric catalyst [Cu(OTf)] is one.

7.1.1. The Order in [1a]

1a	**2a**	$[Cu(OTf)]_2{\cdot}C_6H_6$	$ArCO_2H$	CH_2Br_2	$CDCl_3$
0.0400 mmol	0.100 mmol	5.0 x 10^{-5} mmol	5.0 x 10^{-4} mmol	0.105 mmol	1.00 mL
0.0500 mmol	0.100 mmol	5.0 x 10^{-5} mmol	5.0 x 10^{-4} mmol	0.088 mmol	1.00 mL
0.0600 mmol	0.100 mmol	5.0 x 10^{-5} mmol	5.0 x 10^{-4} mmol	0.086 mmol	1.00 mL

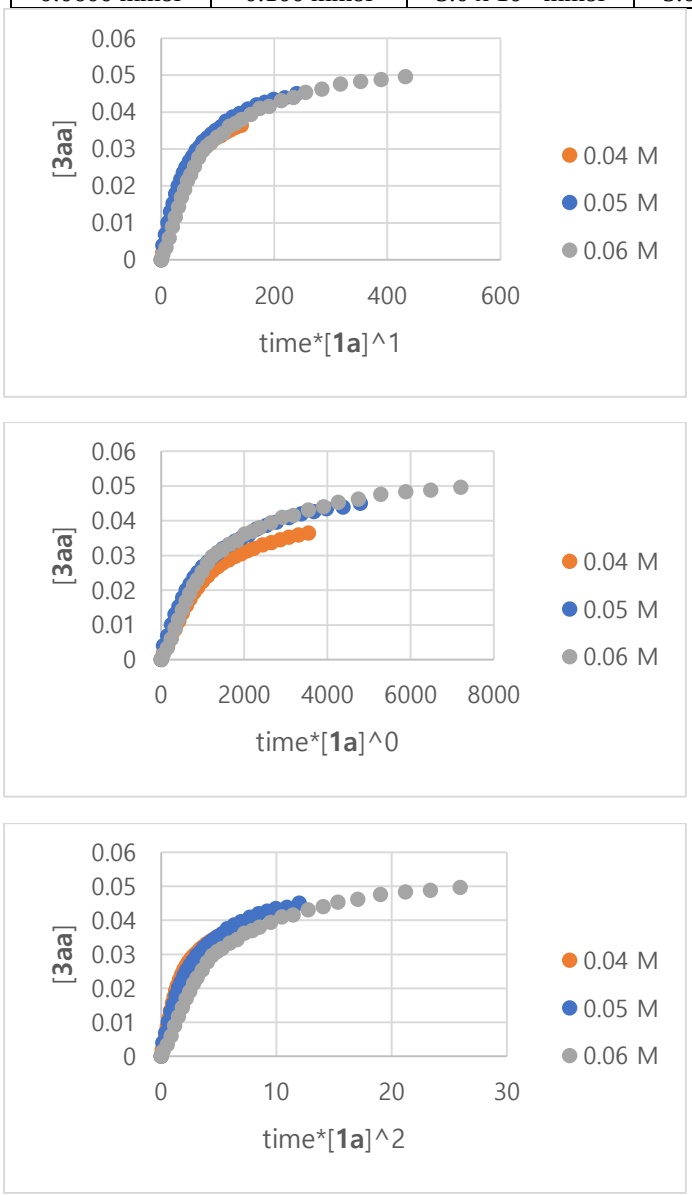


Figure S3. Comparison of different VTNA with change in [**1a**] power.

7.1.2. Order in [2a]

1a	**2a**	$[Cu(OTf)]_2 \cdot C_6H_6$	$ArCO_2H$	CH_2Br_2	$CDCl_3$
0.0500 mmol	0.100 mmol	5.0 x 10^{-5} mmol	5.0 x 10^{-4} mmol	0.105 mmol	1.00 mL
0.0500 mmol	0.150 mmol	5.0 x 10^{-5} mmol	5.0 x 10^{-4} mmol	0.089 mmol	1.00 mL
0.0500 mmol	0.200 mmol	5.0 x 10^{-5} mmol	5.0 x 10^{-4} mmol	0.088 mmol	1.00 mL

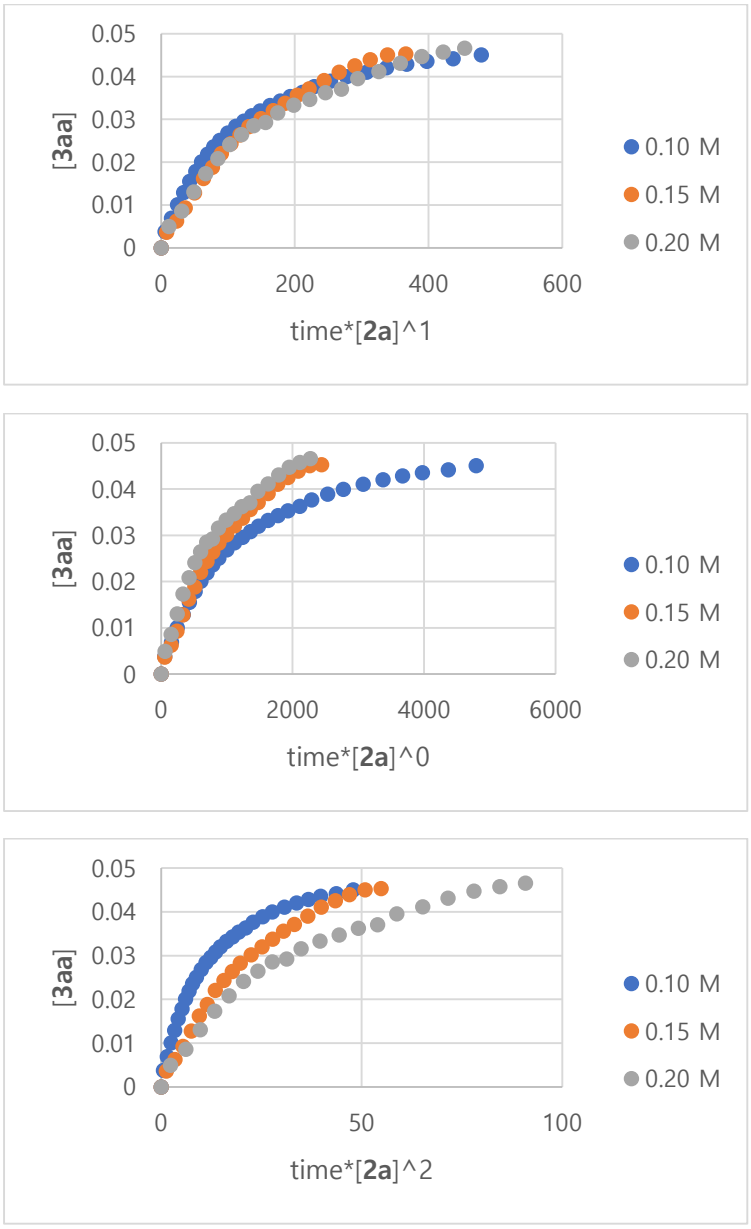


Figure S4. Comparison of different VTNA with change in [**2a**] power.

7.1.3. Order in [catalyst]

1a	2a	$[Cu(OTf)]_2{\cdot}C_6H_6$	$ArCO_2H$	$CDCl_3$
0.0500 mmol	0.100	5.0 x 10^{-5} mmol	5.0 x 10^{-4} mmol	1.00 mL
0.0500 mmol	0.100	2.5 x 10^{-5} mmol	5.0 x 10^{-4} mmol	1.00 mL
0.0500 mmol	0.100	1.2 x 10^{-5} mmol	5.0 x 10^{-4} mmol	1.00 mL

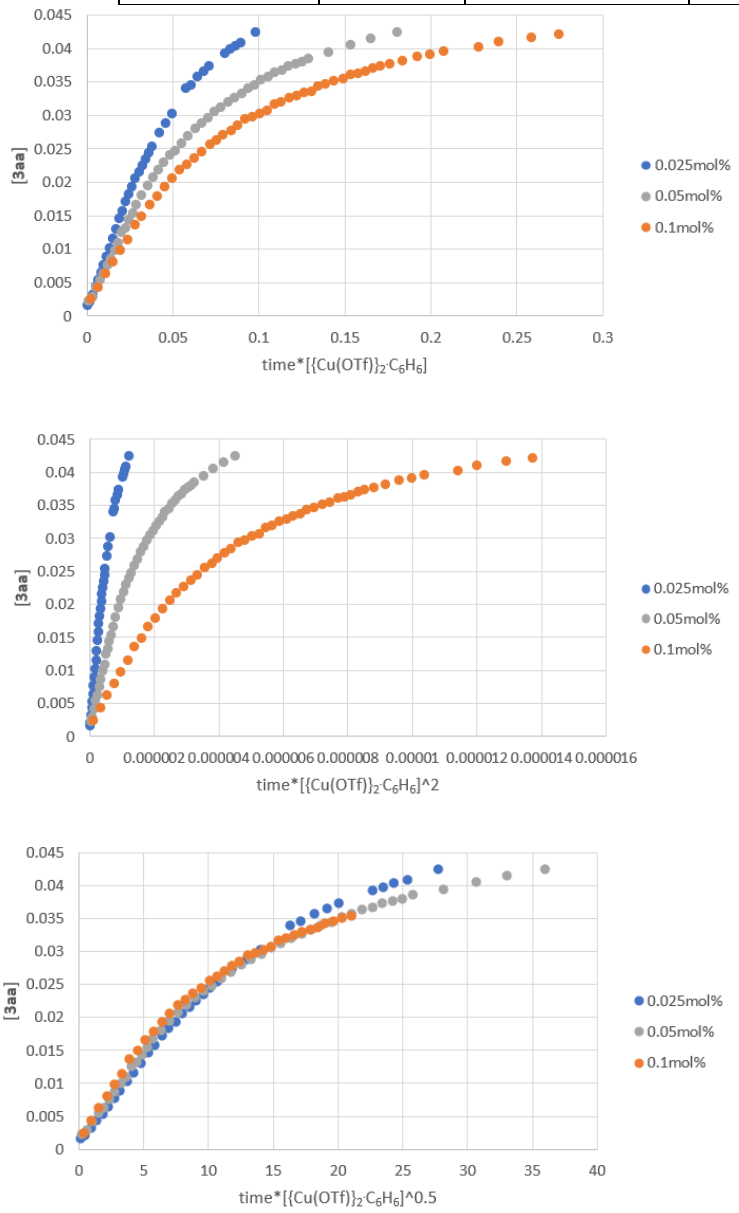
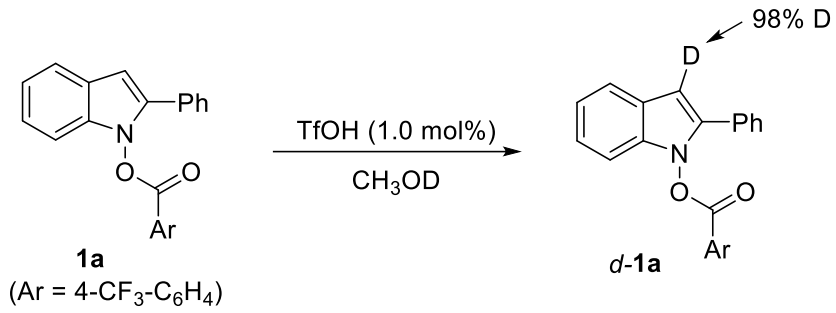


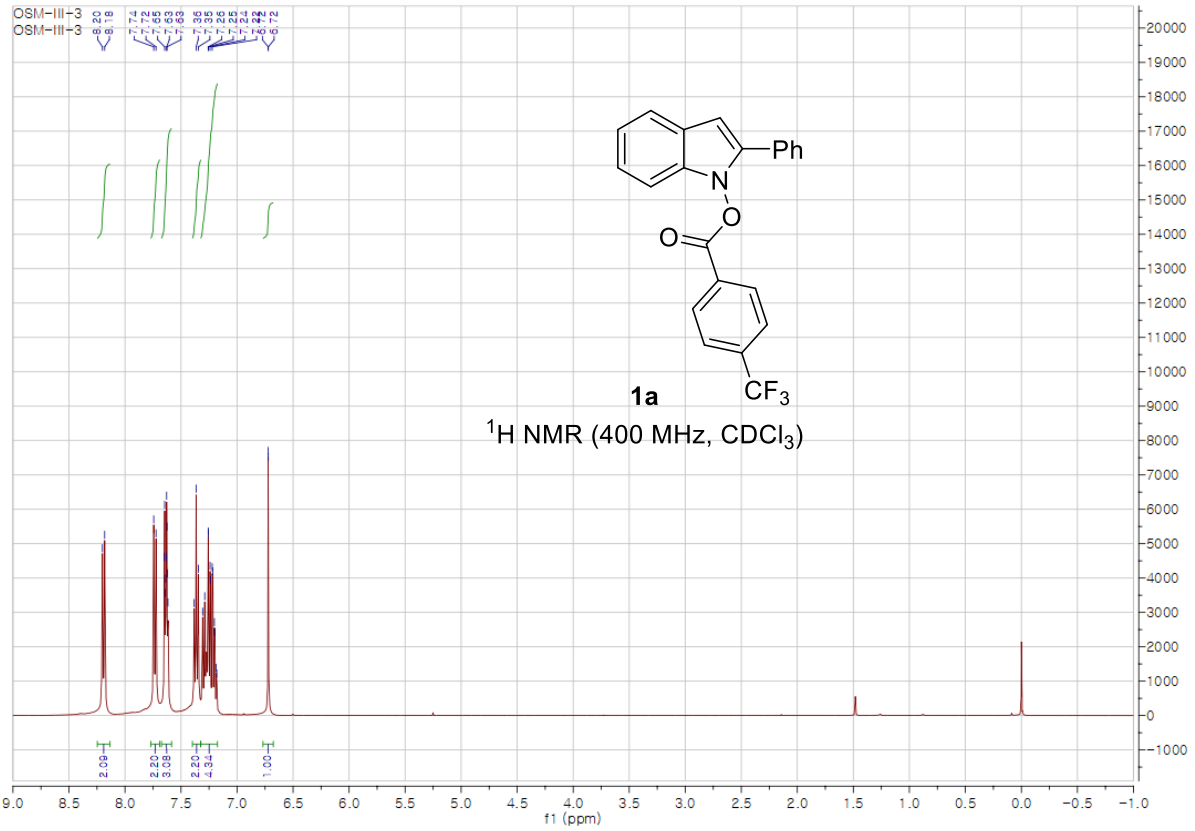
Figure S5. Comparison of different VTNA with change in [**Cu**$_2$] power.

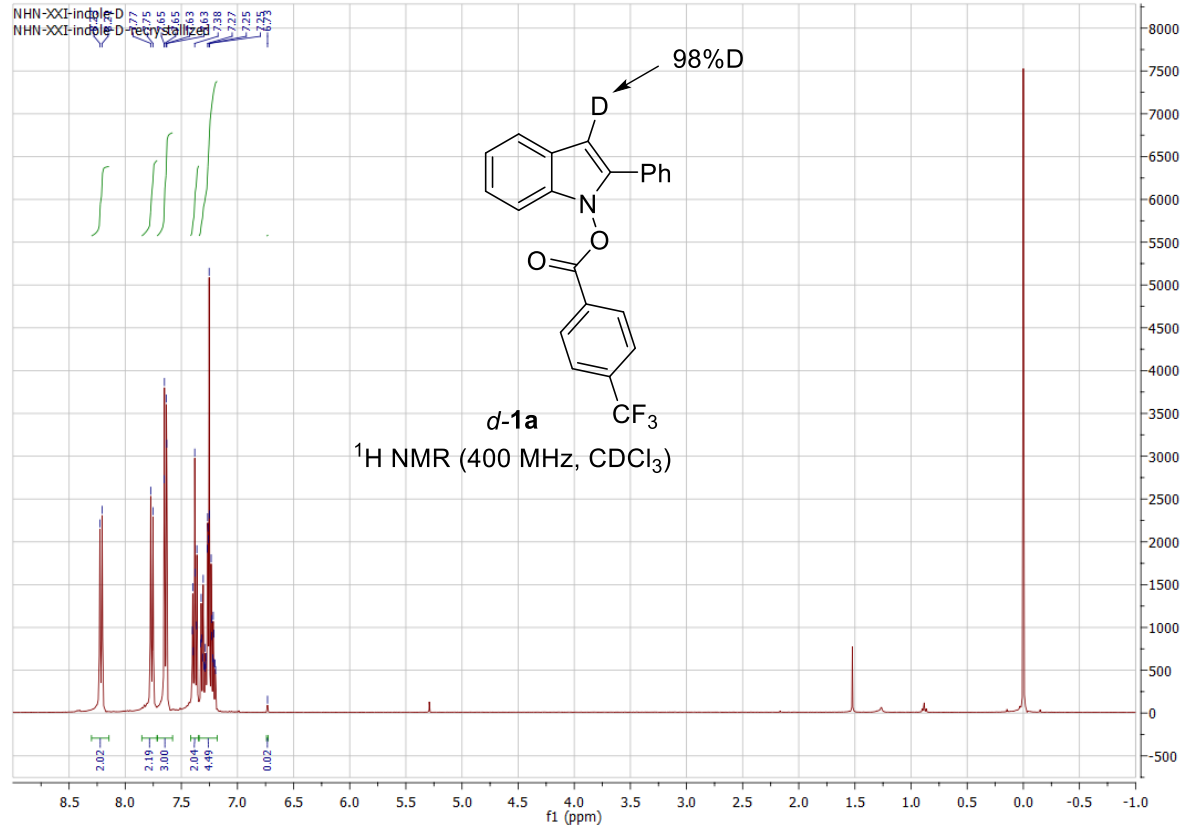
7.2. Kinetic Isotope Effect

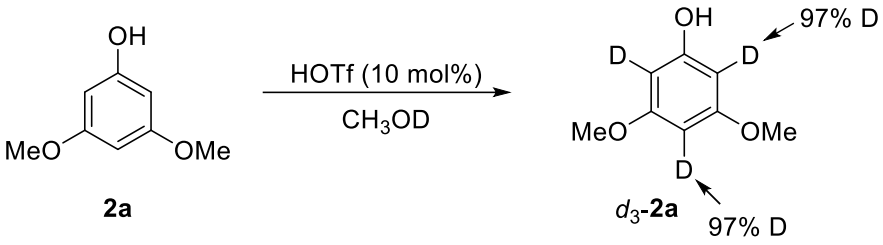
7.2.1. Synthesis of *d*-Labelled Compounds[5]



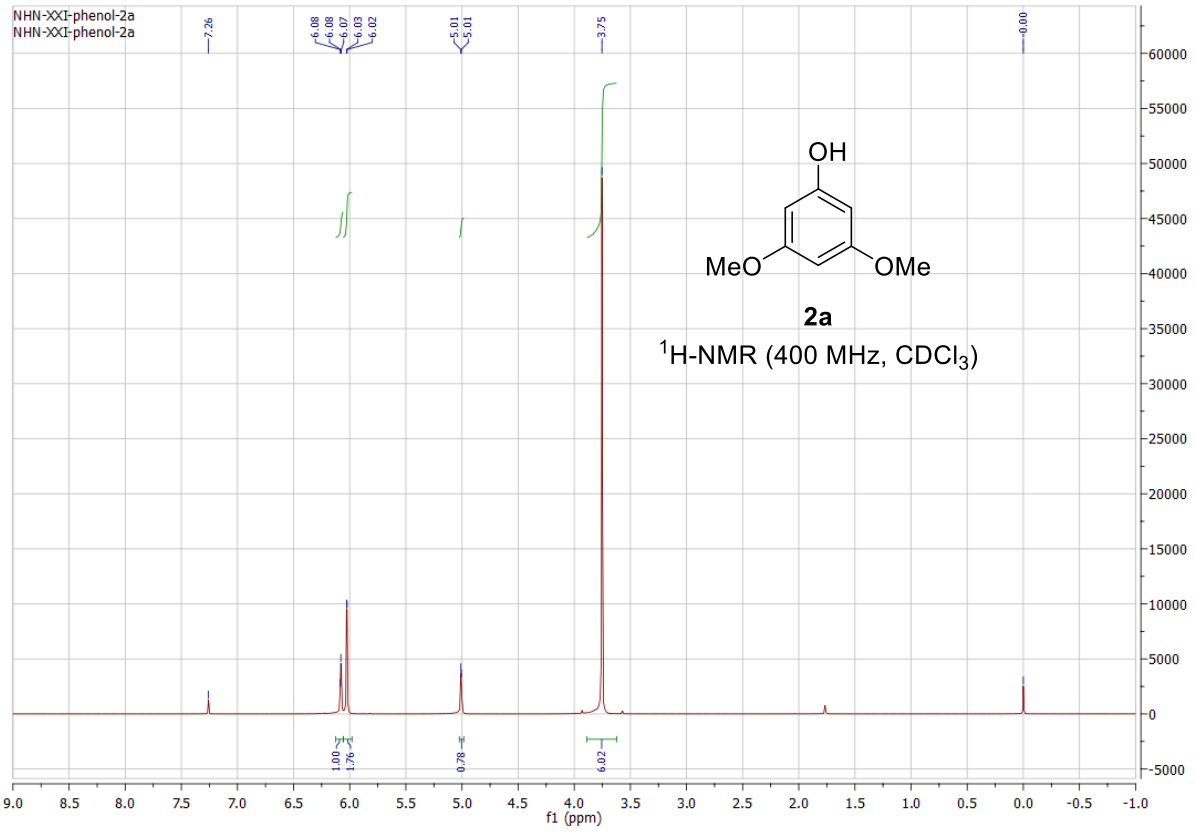
To a solution of **1a** (200.0 mg, 0.52 mmol) in CH_3OD (2.60 mL) was added TfOH (0.8 mg, 0.005 mmol) at room temperature. The reaction mixture was stirred at 35 ^oC for 24 h. When the reaction was judged to be complete by crude ^1H-NMR of an aliquot, the reaction mixture was cooled to room temperature, quenched by adding 1 drop of Et_3N. Solvent was evaporated and the residue was purified by flash column chromatography (SiO_2, EtOAc:Hex = 1:19 to 1:9) to afford 193.5 mg deuterated **1a** (96% yield, 98% deuterium incorporation) as a white solid.

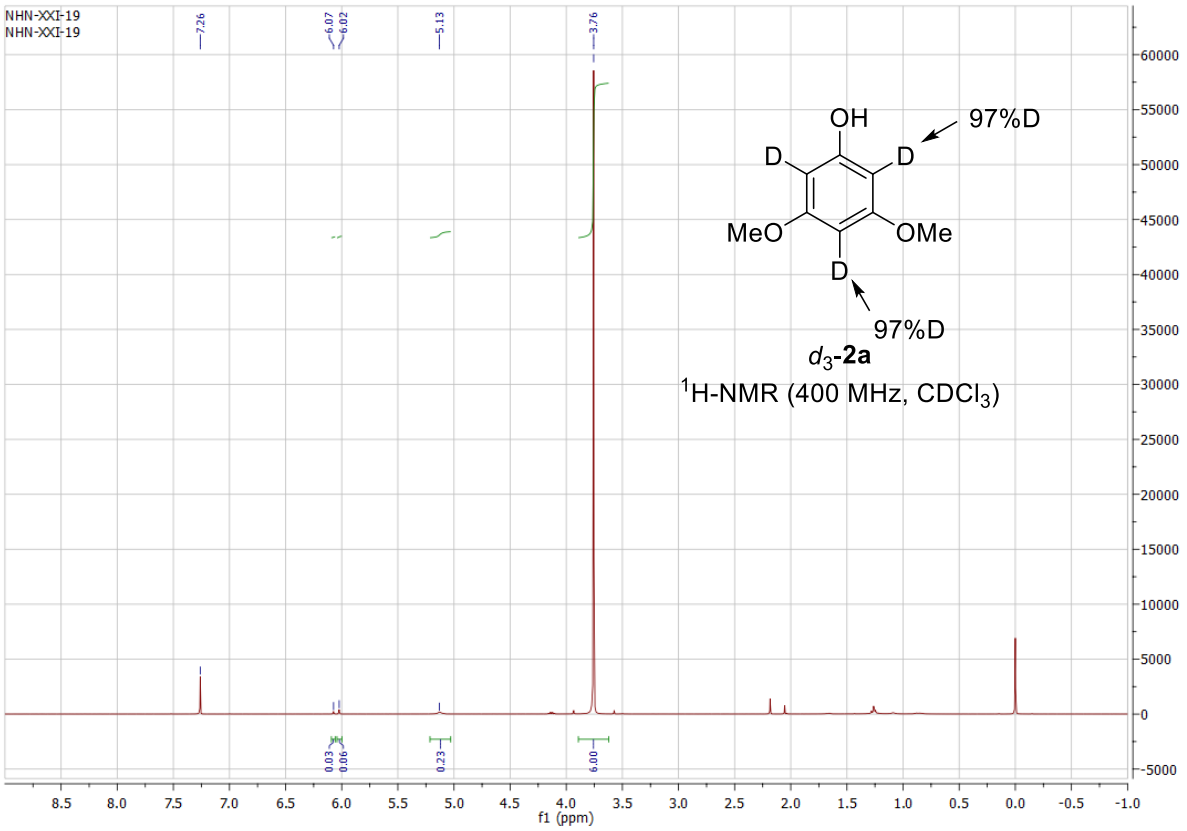

OSM-III-3
OSM-III-3
Ph
N
O
O
CF3
1a
1H NMR (400 MHz, CDCl3)
f1 (ppm)


NHN-XXI-indole-D
NHN-XXI-indole-D-recrystallized
98%D
D
Ph
N
O
O
CF3
d-1a
1H NMR (400 MHz, CDCl3)
f1 (ppm)

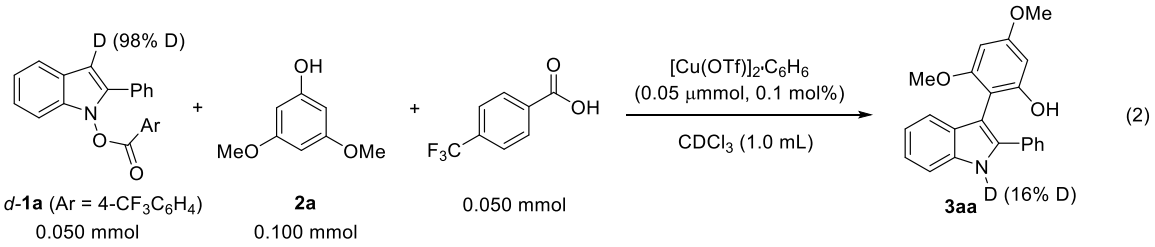


To a solution of 3,5-dimethoxyphenol (770.8 mg, 5.0 mmol) in CH_3OD (5.0 mL) was added TfOH (75.0 mg, 0.5 mmol) at room temperature. The reaction mixture was stirred at room temperature for 7 h. After 7 h, all CH_3OD was evaporated and another 5.0 mL of fresh CH_3OD was added. The reaction mixture was stirred at room temperature until the crude ^{1}H-NMR of an aliquot indicated 97% deuterium incorporation. The reaction was then neutralized by adding solid $NaHCO_3$ (168.0 mg, 2.0 mmol). The solid was filtered off through a cotton plug and the residue was concentrated and purified by flash column chromatography (flame dried SiO_2 under vacuum, Et_2O as an eluent) to afford 683.9 mg 2,4,6-[D3]-3,5-dimethoxyphenol (87%, 97% deuterium incorporation) as a sticky colorless oil.





As a control, possible isotope exchange of starting materials (*d*-**1a** and d_3-**2a**) during the reaction were recorded. Deuterium content in the remaining *d*-**1a** did not change throughout the reaction. In d_3-**2a**, there was slow exchange of its *ortho*- and *para*-protons (less than 25% exchange of the *ortho*-proton at 84% conversion).

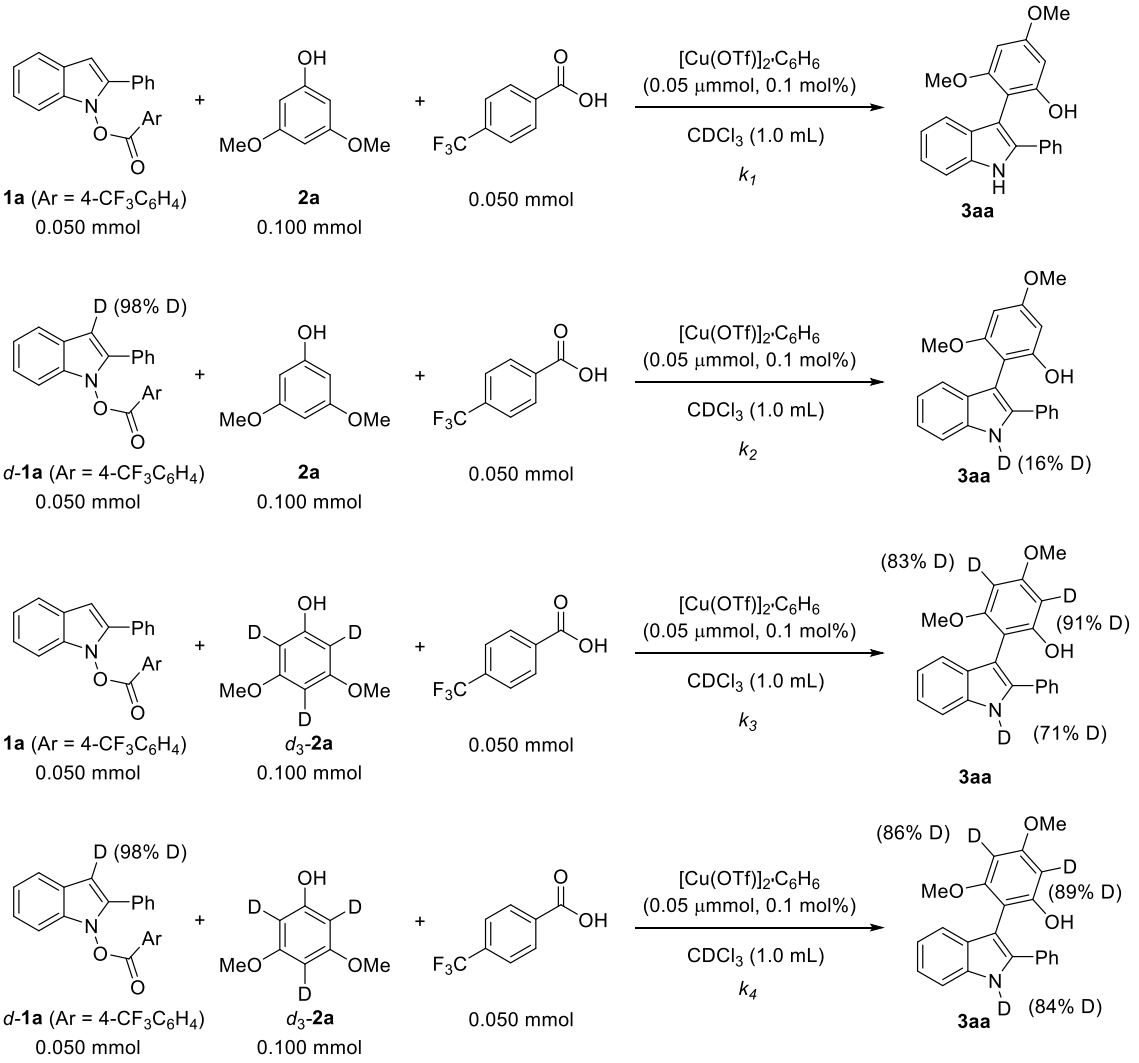


Time (s)	Conv. (%)	% D (*d*-**1a**)
0	0	98%
1206	12	98%
7835	84.5	97%

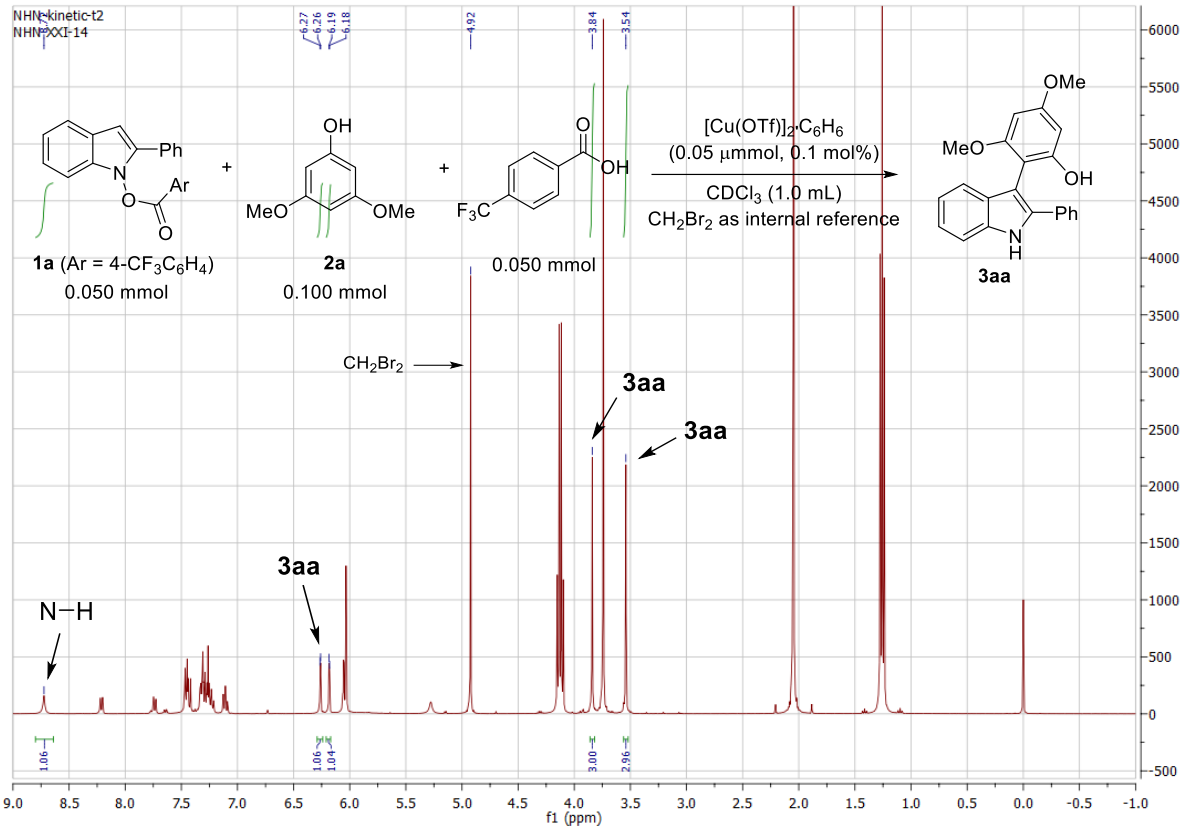
Time (s)	Conv. (%)	% D para (d_3-**2a**)	% D ortho (d_3-**2a**)
0s	0	95%	93%
3025s	53.4	89%	81%
8089s	83.6	87%	75%

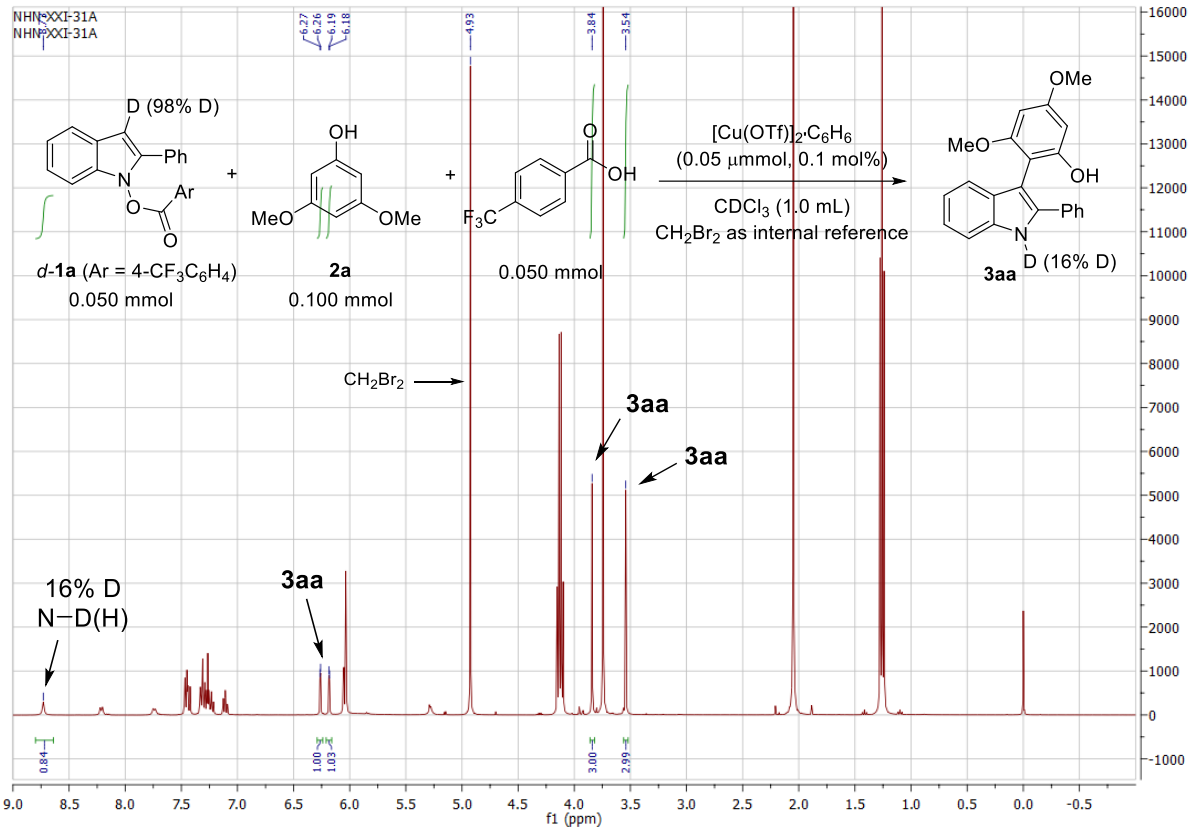
7.2.2. Measurement of the Kinetic Isotope Effect

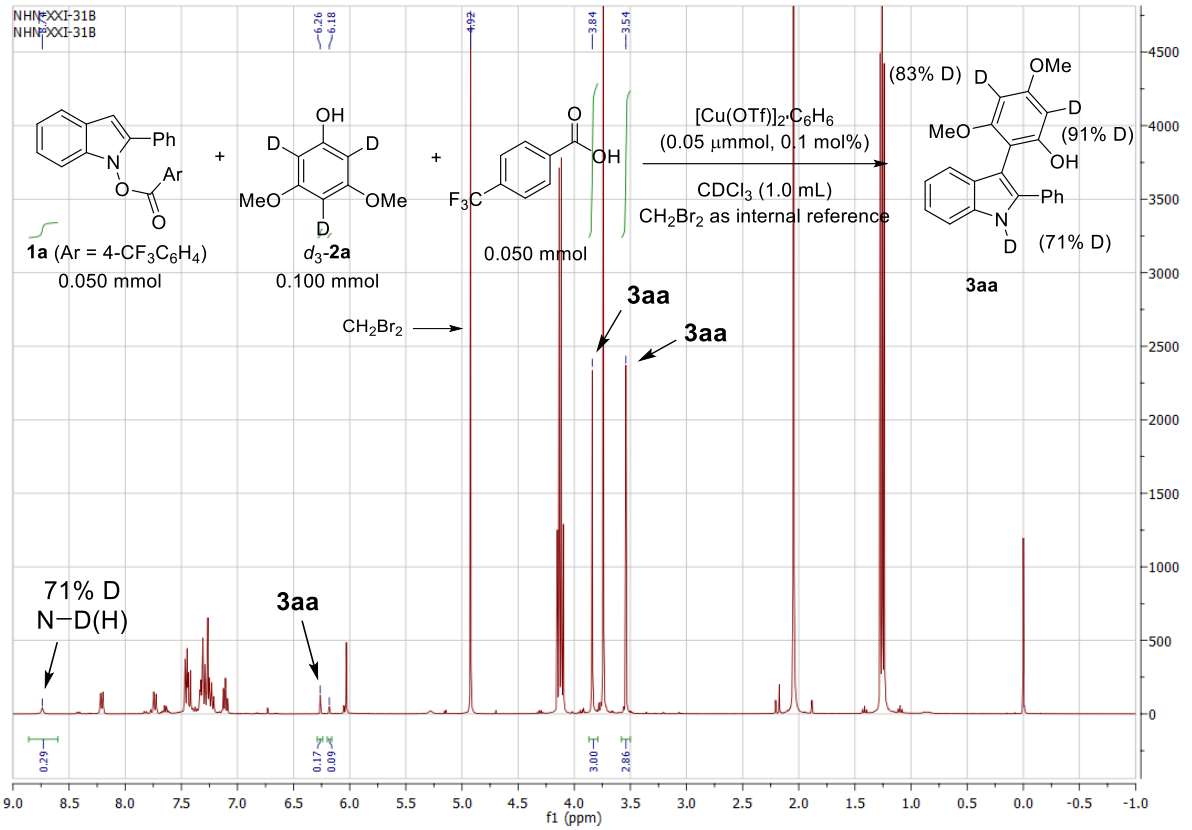
According to the Eqs (1)-(4), the k_{obs} (sec^{-1}) was measured in duplicate.

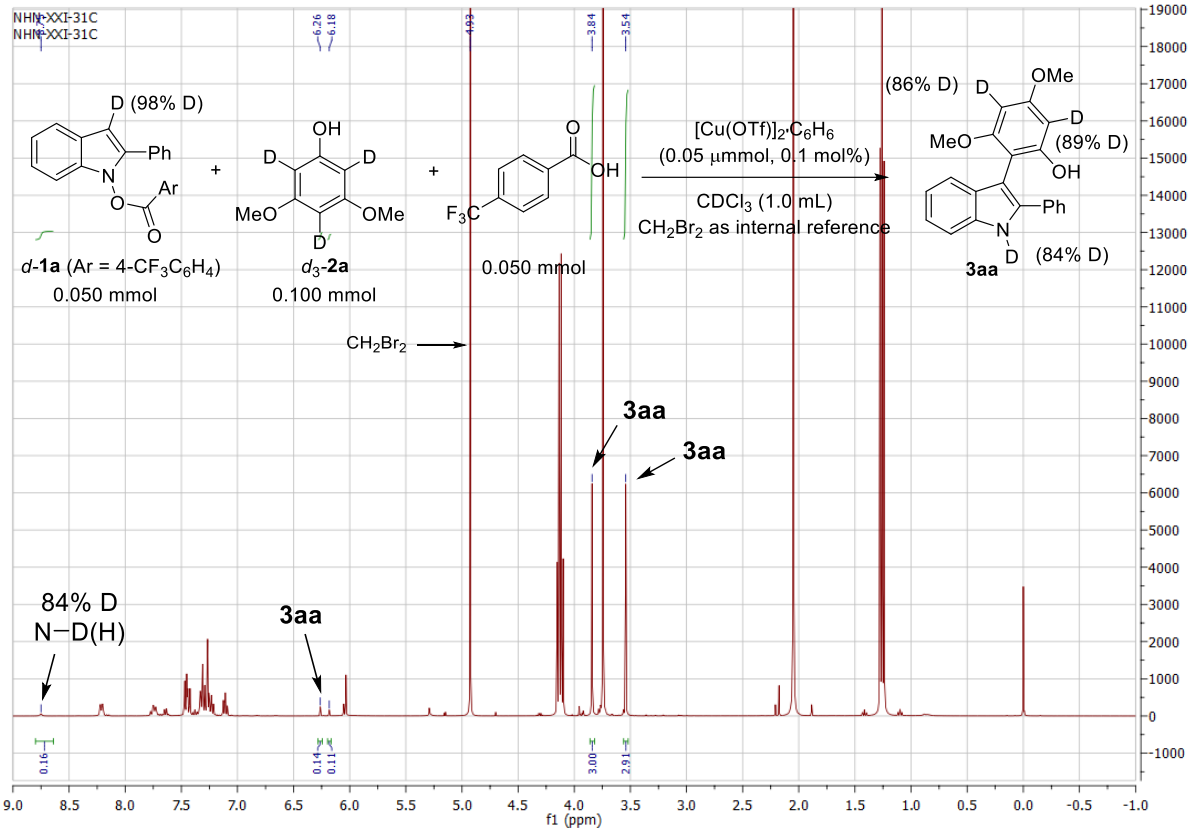


	1st exp	2nd exp	average
k_1 (sec^{-1})	4.20 x 10^{-4}	4.26 x 10^{-4}	4.23 x 10^{-4}
k_2 (sec^{-1})	2.49 x 10^{-4}	2.43 x 10^{-4}	2.46 x 10^{-4}
k_3 (sec^{-1})	1.95 x 10^{-4}	2.11 x 10^{-4}	2.03 x 10^{-4}
k_4 (sec^{-1})	1.40 x 10^{-4}	1.35 x 10^{-4}	1.38 x 10^{-4}
k_H/k_D (k_1/k_2)	1.72		
k_H/k_D (k_1/k_3)	2.08		
k_H/k_D (k_1/k_4)	3.06		

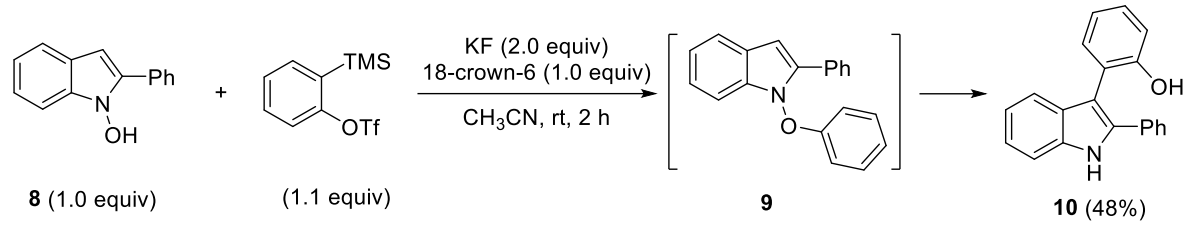

NHN-kinetic-t2
NHN-XXI-14
Ph
N
O
Ar
O
1a (Ar = 4-CF3C6H4)
0.050 mmol
+
OH
MeO
OMe
2a
0.100 mmol
+
O
OH
F3C
0.050 mmol
[Cu(OTf)]2·C6H6
(0.05 μmmol, 0.1 mol%)
CDCl3 (1.0 mL)
CH2Br2 as internal reference
OMe
MeO
OH
Ph
N
H
3aa
CH2Br2
3aa
3aa
3aa
N−H
1.06
1.06
1.04
3.00
2.96
f1 (ppm)


NHN-XXI-31A
NHN-XXI-31A
D (98% D)
Ph
N
O
Ar
O
d-1a (Ar = 4-CF3C6H4)
0.050 mmol
+
OH
MeO
OMe
2a
0.100 mmol
+
O
OH
F3C
0.050 mmol
[Cu(OTf)]2·C6H6
(0.05 μmmol, 0.1 mol%)
CDCl3 (1.0 mL)
CH2Br2 as internal reference
OMe
MeO
OH
Ph
N
D (16% D)
3aa
CH2Br2
3aa
3aa
3aa
16% D
N−D(H)
0.84
1.00
1.03
3.00
2.99
f1 (ppm)


NHN-XXI-31B
NHN-XXI-31B
Ph
Ar
O
O
N
1a (Ar = 4-CF3C6H4)
0.050 mmol
OH
D
D
MeO
OMe
D
d3-2a
0.100 mmol
O
OH
F3C
0.050 mmol
[Cu(OTf)]2·C6H6
(0.05 μmmol, 0.1 mol%)
CDCl3 (1.0 mL)
CH2Br2 as internal reference
(83% D)
OMe
D
D
MeO
(91% D)
OH
Ph
N
D
(71% D)
3aa
CH2Br2
3aa
3aa
71% D
N–D(H)
3aa
f1 (ppm)

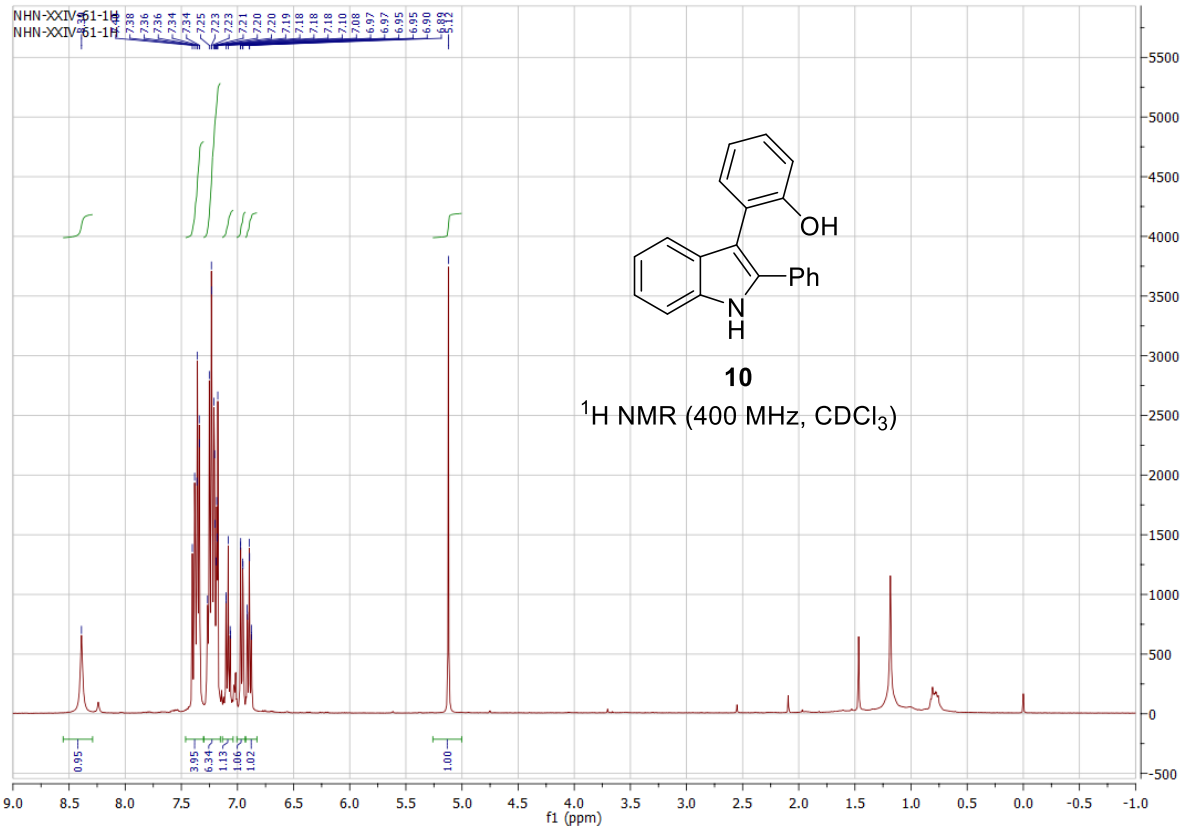

NHN-XXI-31C
NHN-XXI-31C
D (98% D)
Ph
Ar
O
O
N
d-1a (Ar = 4-CF3C6H4)
0.050 mmol
OH
D
D
MeO
OMe
D
d3-2a
0.100 mmol
O
OH
F3C
0.050 mmol
[Cu(OTf)]2·C6H6
(0.05 μmmol, 0.1 mol%)
CDCl3 (1.0 mL)
CH2Br2 as internal reference
(86% D)
OMe
D
D
MeO
(89% D)
OH
Ph
N
D
(84% D)
3aa
CH2Br2
3aa
3aa
84% D
N–D(H)
3aa
f1 (ppm)

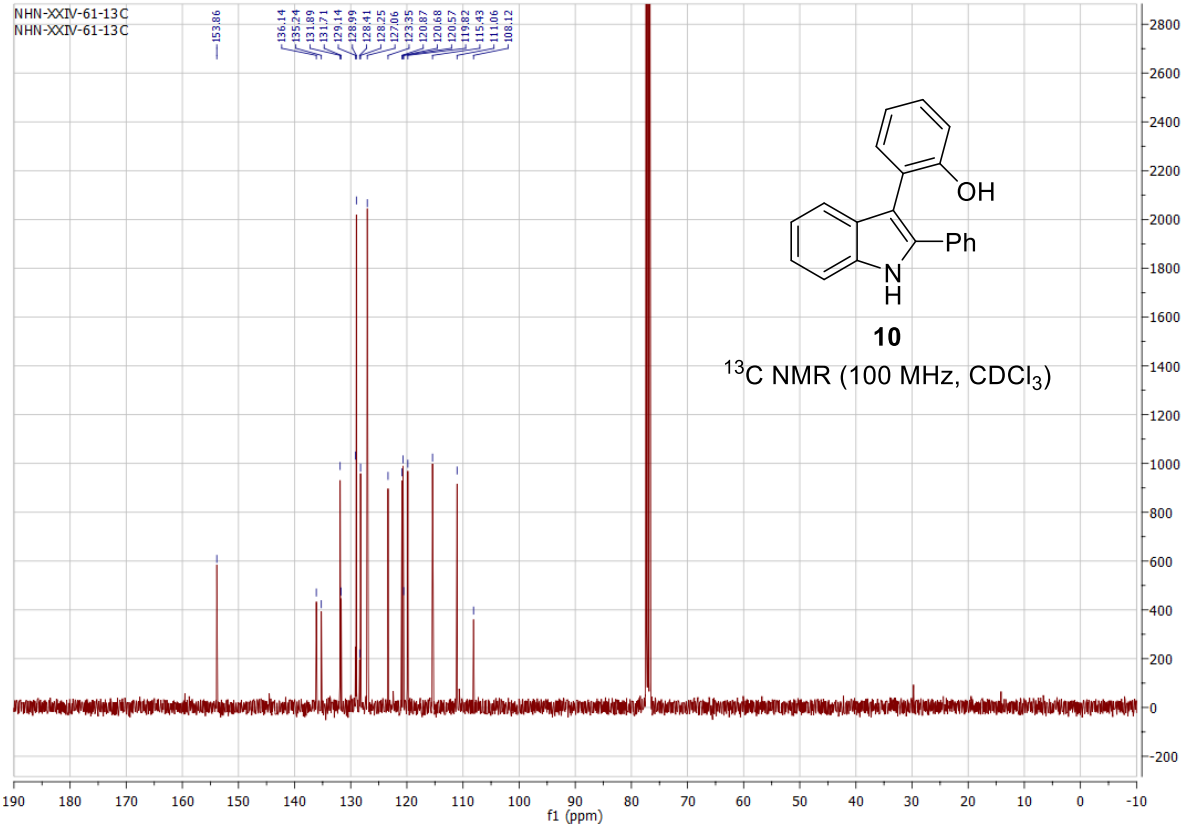
7.3. Attempted Synthesis of *N*-Phenoxy-2-phenyl-indole, 9



8 (1.0 equiv) (1.1 equiv) **9** **10** (48%)

In an oven-dried vial, 2-phenyl-1*H*-indol-1-ol **8** (20.9 mg, 0.1 mmol), potassium fluoride (11.6 mg, 0.2 mmol), and 18-crown-6 (26.4 mg, 0.1 mmol) were dissolved in CH_3CN (1.0 mL). To this was added dropwise 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (32.8 mg, 0.11 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 hours. When the reaction was judged to be complete by TLC, reaction mixture was filtered through a cotton plug. The filtrate was concentrated in *vacuo* and the residue was purified by flash column chromatography (SiO_2, EtOAc:Hex = 1:10) to afford 13.6 mg of **10** (48%) as a yellow sticky oil.


NHN-XXIV-61-1H
OH
Ph
N
H
10
1H NMR (400 MHz, CDCl3)
f1 (ppm)


NHN-XXIV-61-13C
OH
Ph
N
H
10
13C NMR (100 MHz, CDCl3)
f1 (ppm)

9. References

1. Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*; Elsevier: Oxford, **2009**.

2. Synthetic procedure of the N-acyloxyindoles and characterization data of all other derivatives were reported. S. M. Oh; S. Shin, *Bul. Kor. Chem. Soc.* **2021**, *42*, 925.

3. Burés, J. *Angew. Chem. Int. Ed.* **2016**, *55*, 16084.

4. Burés, J. *Angew. Chem. Int. Ed.* **2016**, *55*, 2028.

5. Fischer, O. ; Hubert, A.; Heinrich, M. R. *J. Org. Chem.* **2020**, *85*, 11856.