Utilization of copper on iron catalyst for the synthesis of biaryl systems and benzoxazines via oxidative arylation of anilide derivatives

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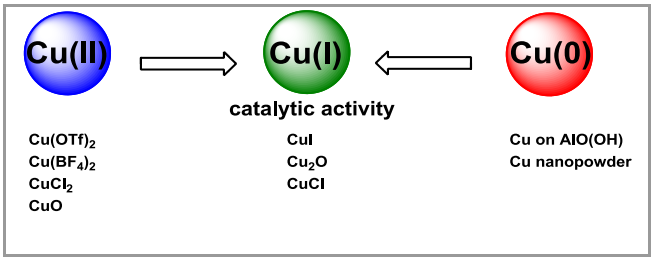
Abstract: Heterogeneous copper on iron catalyst serves as an efficient alternative copper source for arylation reactions using hypervalent iodonium salts. The copper (0) catalyst affords meta-arylation of pivalanilides, while 2-ethynylanilides undergo oxidative carboarylation-ring closure with diaryliodonium salts.

Key words: biaryls, copper, coupling, heterocycles, iron

The synthesis of biaryl systems and heterocyclic compounds via aromatic C-H bond functionalization and oxidative ring closure play important roles in organic chemistry. The biaryl motif and heterocyclic rings are often found in natural products and biologically active compounds.[1] In traditional cross-coupling reactions, prefunctionalization of the aromatic coupling partner and the utilization of metallo-organic reagents are required for efficient coupling. This chemical requirement for a coupling reaction leads to the formation of significant amount of byproducts originated from reagents, solvent or additives during the synthetic steps. To overcome these drawbacks, the use of C-H activation reactions serves as a useful alternative in which preactivation of the aromatic compounds is not necessary.[2] A variety of substituted aryl groups can be regioselectively transferred through C-H functionalization in transition-metal catalyzed oxidative couplings with the aid of hypervalent iodonium salts.[3] During the last decade several methods were developed, where diaryliodonium salts were applied for regioselective substitution of aromatic (*ortho*[4]- and *meta*-[5] positions) and heteroaromatic compounds (C2 and C3 substitution of indoles via palladium- and copper-catalysis were reported).[6] The choice of the catalyst often determines the site selectivity of the reactions.[7]

In addition to the direct functionalization of C-H bond with iodonium salts, several methods were developed recently for the construction of heterocycles in copper-catalyzed oxidative ring closures using iodonium salts. Based on this strategy, pyrroloindolines were synthetized via an arylation-cyclization cascade by MacMillan,[8] the preparation of substituted oxazines was reported by Gaunt[9] and an unusual 6-*exo*-dig cyclization of 2-ethynyl-anilides was developed in our laboratory yielding diversely substituted benzoxazines.[10]

The use of Cu(II)-species as precatalyst for C-H activation reactions performed under homogeneous catalytic conditions is prevalent.[6,7,11] In these transformations, the most frequently used copper sources are $Cu(OTf)_2$, $CuCl_2$ and CuO. Although, the catalyst is added to the reactions as a Cu^{2+} salt, it is believed that Cu(I)-species are responsible for the catalytic activity.[7,12] In general handling of copper(I) salts are difficult, while some of the copper(II) salts are toxic, air- and moisture sensitive, or expensive; therefore their use is not always practical.

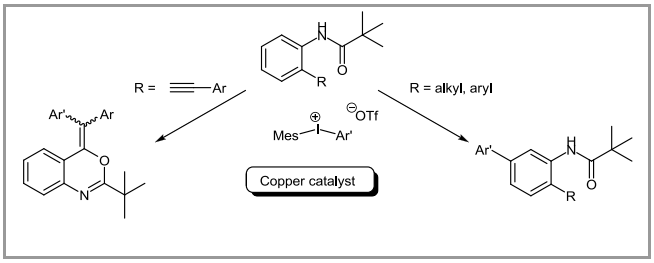


Scheme 1 Two possible approaches to the formation of Cu(I) species for C-H activation reactions.

The catalytically active Cu(I) species can also be generated from Cu(0) (Scheme 1). Copper metal is cheap, easily accessible, and stable in air. Moreover, in some cases, its separation from the reaction mixture is quite simple. Interestingly, the use of elemental copper for the generation of Cu(I) species is rare in oxidative chemistry. As an example, application of Cu on AlO(OH) for *meta*-selective C-H bond arylation was reported by Park et al.[13]

Previously our research group has developed a heterogeneous copper on iron catalyst, which is composed of copper nanoparticles on the surface of micron sized iron particles. The catalyst composition can be easily prepared from readily available reagents such as iron powder and $CuSO_4$ under aqueous conditions. Our copper on iron catalyst system contains 5 w/w% Cu, where the copper is electrochemically deposited on the surface of the iron. The heterogeneous catalyst can stir the reaction and also can be easily separated from the reaction mixture using an external magnetic field. Additionally, the use of Cu/Fe catalyst significantly reduced the copper contamination of the organic products.[14] The Cu/Fe catalyst has already been successfully applied in C-S and C-N bond forming reactions by our research group.[15]

We aimed to study the applicability of the copper on iron heterogeneous catalyst in two different novel oxidative coupling reactions utilizing hypervalent iodonium salts: 1. *meta*-selective arylation of pivalanilides,[7] and 2. Synthesis of benzoxazine derivatives via carboarylation-ring closure reaction of ortho ethynyl anilides (Scheme 2.).[10]



Scheme 2 Meta-selective arylation of substituted pivalanilides and oxidative ring closure of 2-arylethynyl anilides

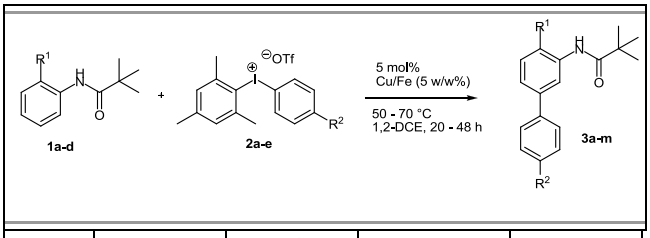
The applicability of copper on iron catalyst for the *meta*-selective arylation the reaction between 2-methyl-pivalanilide and phenyl(mesityl)iodonium triflates was evaluated using the reaction conditions of the homogeneous version.[7] To our delight, addition of 1.5 equiv. mesityl(phenyl)iodonium triflate to the pivalanilide in the presence of 5 mol% 5 w/w% Cu/Fe provides 94% conversion (79% isolated yield, Table 1, entry 1) in DCE in 20 hours at 50°C. These conditions proved to be the most ideal set of parameters for the efficient coupling.

The substrate scope of the reaction was evaluated using substituted pivalanilides **(1a-d)** bearing different functional groups (Me, t-Bu, OMe, Ph) in *ortho* position, which were prepared from commercially available anilines and pivaloyl chloride.[16] The syntheses of aryl(mesityl)iodonium salts bearing COOEt, F, Cl and Br groups on the aryl part **(2b-e)** were carried out according to the modified[10] procedure of Olofsson.[17]

Arylations of the four pivalanilide substrates **(1a-d)** were performed with substituted aryl mesityl iodonium salts (**2b-e**) (Table 1, Entries 2-13). Aromatic groups bearing esters function were straightforwardly introduced into the meta position of the anilides with **2b** and the biaryl products **(3b-d)** were isolated in 54-83%, depending on the substituent of the anilide. Comparing the results among the halogen-substituted aryl iodonium salts, the highest yield were obtained in case of the bromo substituted derivatives **(3k-m)** (70-79%) while aromatic groups containing chloro **(3h-j)** and fluoro **(3e-g)** function gave lower yield on the average (47-74% and 53-72%).

After demonstrating the applicability of Cu/Fe catalyst in meta- selective arylation, we aimed to study its catalytic activity in other oxidative coupling reaction.

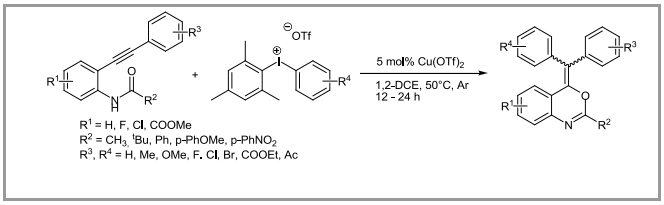
Table 1 Substrate scope using different functional groups[a]



Entry	R^1	R^2	Product	Yield (%)
1	Me	H	**3a**	79
2	Me	COOEt	**3b**	83
3	OMe	COOEt	**3c**	61
4	Ph	COOEt	**3d**	54
5	Me	F	**3e**	57
6	*t*-Bu	F	**3f**	68
7	Ph	F	**3g**	53
8	Me	Cl	**3h**	65
9	*t*-Bu	Cl	**3i**	47
10	Ph	Cl	**3j**	74[c]
11	Me	Br	**3k**	75
12	*t*-Bu	Br	**3l**	79
13	Ph	Br	**3m**	70[c]

[a] Reaction conditions: The reactions were performed with 0.5 mmol pivalanilide, 0.75 mmol aryl(mesityl)iodonium triflate and 32.2 mg Cu/Fe catalyst in 2.5 ml 1,2-DCE at 50/ 70°C for 20-48 hours.
[b] yield of isolated product
[c] arylation reaction was conducted at 70 °C.

A novel procedure was developed in our laboratory for the synthesis of 4-diarylmethylene-benzoxazines through oxidative ring closure of ethynylanilides with diaryliodonium salt, where $Cu(OTf)_2$ was used as catalyst (Scheme 3). In continuation of our work, we aimed to examine the applicability of Cu/Fe catalyst in the oxidative carboarylation and ring closure reaction for the synthesis of benzoxazine derivatives.

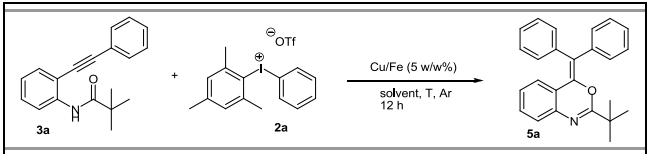


Scheme 3. Oxidative ring closure of 2-arylethynyl anilides under homogeneous catalytic conditions

The optimization reactions were carried out with N-(2-(phenylethynyl)phenyl)pivalamide and 1.2 equiv. mesityl(phenyl)iodonium triflate varying the solvent (Table 2, entries 1-4), the catalyst loading (Table 2, entries 5-7) and the temperature (Table 2, entries 8-10). The highest conversion was reached when the reaction was performed in 1,2-dichloroethane at 50°C in the presence of 5 mol% Cu/Fe catalyst. This finding

is identical with the best condition applied in the homogeneous version of this transformation.[10]

Table 2 Optimization of reaction conditions [a]



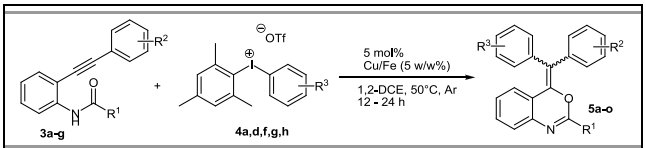
Entry	Solvent	Cu/Fe (mol%)	*T* / °C	Conversion (%)
1	**THF**	5	50	6
2	**DMF**	5	50	0
3	**toluene**	5	50	45
4	**1,2-DCE**	5	50	89
5	1,2-DCE	**2.5**	50	81
6	1,2-DCE	**5**	50	89
7	1,2-DCE	**10**	50	87
8	1,2-DCE	5	**25**	14
9	1,2-DCE	5	**50**	89
10	1,2-DCE	5	**80**	76

[a] reactions were performed in 0.1 mmol scale and GC-MS conversions were measured after 12 hours stirring under inert atmosphere.

After the optimization process, we studied the substrate scope of the procedure. Several substituted arylethynyl-anilides were treated with mesityl(phenyl)iodonium triflate in the presence of Cu/Fe catalyst under the optimized reaction conditions. The 4-diphenylmethylenebenzoxazine **(5a)** was isolated with 58% yield (Table 3, entry 1). The presence of electron donating methyl group in all positions on the phenyl ring in 2-arylethynyl pivalanilides resulted in increased yields compared to the unsubstituted derivative, affording the desired products **5b-d** in 67%, 66% and 71% yield respectively (Table 3, entries 2-4). The strongly electron donating methoxy group decreased the efficiency of the reaction and compound **5e** was isolated in 37% (Table 3, entry 5). Arylethynyl anilide containing the chlorophenyl group (Table 3, entry 6) gave product **5f** (68%), while the reaction using the substrate containing the strongly electron withdrawing nitro group provided the desired product **(5g)** in 50% yield (Table 3, entry 7). In cases where nonsymmetrically substituted alkene derivatives are formed, the ^{1}H NMR measurements showed the presence of mixture of geometric isomers (The isomeric ratios are indicated in Table 3).

After functionalization of different arylethynyl anilides with phenylmesityliodonium triflate, the diversity of the product structure was expanded with the use of substituted aryl(mesityl)iodonium triflates. Using *para*- and *meta* methyl substituted iodonium salts, the appropriate products **(5b and 5c)** were obtained in 44% and 61% yields respectively (Table 3, entry 8,9).

Table 3 Substrate scope using different functional groups.[a]



Entry	R^1	R^2	R^3	Product	E/Z ratio	Yield (%)
1	^{t}Bu	H	H	**5a**	-	58
2	^{t}Bu	*p*-Me	H	**5b**	2/3	67
3	^{t}Bu	*m*-Me	H	**5c**	2/3	66
4	^{t}Bu	*o*-Me	H	**5d**	1/1.2	71
5	^{t}Bu	*p*-OMe	H	**5e**	1/2	37
6	^{t}Bu	*p*-Cl	H	**5f**	1/2.3	68
7	^{t}Bu	*p*-NO_2	H	**5g**	2/7	50
8	^{t}Bu	H	*p*-Me	**5b**	3/2	44
9	^{t}Bu	H	*m*-Me	**5c**	1.8/1	61
10	^{t}Bu	H	*p*-Cl	**5f**	9/5	54
11	^{t}Bu	H	*p*-NO_2	**5h**	.	0
12	^{t}Bu	*p*-Me	*p*-Me	**5i**	-	31
13	^{t}Bu	*m*-Me	*m*-Me	**5j**	-	61
14	^{t}Bu	*p*-Cl	*p*-Cl	**5k**	-	59
15	Ph	H	H	**5l**	-	70

[a] Reaction conditions: The reactions were performed with 0.35 mmol 2-arylethynyl-anilide, 0.42 mmol aryl(mesityl)iodonium triflate and 22.2 mg Cu/Fe catalyst in 3 ml 1,2-DCE at 50°C for 12-24 hours.

The *para*-chloro substituted derivative **(5f)** was also successfully prepared in 54% isolated yield (Table 3, entry 10). When the reaction was carried out with (4-nitrophenyl)(mesityl)iodonium triflate, the reaction did not afford the desired product **(5h)** (Table 3, entry 11). Compounds containing substituents on the phenyl ring of both the iodonium salt and the arylethynylanilide were also successfully reacted in the Cu/Fe catalyzed reaction, and the expected products **(5i-k)** were isolated in 31-61% yield (Table 3, entries 12-14).

When the *tert*-butyl group of the amide moiety was replaced with phenyl group the reaction provided the appropriate benzoxazine product **(5l)** in 70% yield (Table 3, entry 15).

In conclusion, we successfully extended the application of copper on iron catalyst in the field of coupling chemistry. We have shown that Cu/Fe can be efficiently utilized in *meta*-selective arylation reactions of *ortho*-substituted pivalanilides with diaryliodonium triflates. We also demonstrated that our copper on iron catalyst also serves as an efficient catalyst in ring closing reaction of 2-arylethynyl anilides and hypervalent iodonium salts for the preparation of diaryl substituted methylene-benzoxazines in good yields. Furthermore the catalyst can be easily prepared, is stable in air, and is not

sensitive to heat. Its separation from reaction mixture can be simply achieved using an external magnetic field. These properties of the catalyst would make its use advantageous in the oxidative transformations examined compared to the previously used homogenous copper sources.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance-250 spectrometer operating at 250 MHz and 62.5 MHz using DMSO-d_6 or $CDCl_3$ as solvent. Chemical shifts are given in ppm relative to TMS, or to the residual solvent peak of DMSO and $CDCl_3$ as internal standards. Coupling constants (J) are reported in Hertz (Hz). Infrared spectra were recorded on Bruker Alpha single-reflection diamond ATR spectrometer as solids or thin films. In the IR spectra, only the strongest/structurally most important peaks (n, cm^{-1}) are listed. HRMS were measured on an Agilent Technologies 6210 Time of Flight mass spectrometer. Melting points were recorded on Büchi 501 apparatus and are reported uncorrected. All solvents used were distilled using standard methods. 1,2-dichloroethane were distilled from calcium hydride. All mixed solvent systems are reported as v/v solutions. All reactions were monitored by TLC using Merck DC pre coated TLC plates with 0.25 mm Kieselgel 60 F_{254}. Visualization was performed with a 254 nm UV lamp. *M*-CPBA was dried under high vacuum at room temperature and was stored under argon. All other chemicals were used as received without further purification.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

General procedure for the preparation of copper on iron catalyst

A round-bottom flask was charged with iron powder (5.00 g, 89.5 mmol) and H_2O (deoxygenated with argon) (50 mL). The mixture was stirred vigorously with a mechanical stirrer and a solution of $CuSO_4$ (126 mg, 0.79 mmol) in H_2O (50 mL) was added dropwise under argon atmosphere over 1 h, and the stirring was continued for 3 h. The catalyst was separated with a magnet and washed with deoxygenated H_2O (5×20 mL) then acetone (3×20 mL) and dried under reduced pressure.

General procedure for the *meta*-selective arylation of pivalanilides:

0.5 mmol pivalanilide, 0.75 mmol iodonium salt and 32.2 mg Cu/Fe (5 mol%) was measured into a 4 ml vial. 2.5 ml abs. DCE was added and the reaction mixture was stirred at 50/70 °C for 20/48hours. Reaction mixture was separated from the catalyst with a magnetic bar, then evaporated. Purification of the crude product was achieved with column chromatography using gradient elution. If needed, further purification was done by preparative thin layer chromatography. The products were dried in vacuum oven (at 30 °C).

N-(4-methylbiphenyl-3-yl)pivalamide (3a)[7]

Followed the general procedure the reaction was performed with 57.3 mg (0.3 mmol) N-*o*-tolyl pivalanilide, 212 mg (0.45 mmol) mesityl(phenyl) iodonium triflate and 19.2 mg (5 mol%) Cu/Fe for 20 h at 50°C. After evaporation of the solvent the crude product was purified with column chromatography on silica gel with gradient elution (Hexanes-Ethyl acetate eluent: 75:1 → 50:1 →25:1 →20:1 →10:1 →5:1) affording the product as white solid (63 mg, 0.24 mmol, 79%).

Mp 109-110 °C (lit. 110-112 °C). R_f = 0.31 (Hexane-EtOAc, 8:1).)

IR (solid): 3311; 3031; 2963; 2923; 2868; 1649; 1507; 1486; 1455; 1395; 1275; 1204; 1165; 882 cm^{-1}.

^{1}H NMR (250MHz, $CDCl_3$): δ = 1.28 (s, 9 H), 2.21 (s, 3 H), 7.52 (dt, 6 H, J = 9.4 Hz), 7.54 (d, 2H, J = 7.5 Hz), 8.12 (s, 1H).

^{13}C NMR (250 MHz, $CDCl_3$): δ = 17.7; 28.1; 40.2; 121.8; 123.8; 127.5; 127.6; 127.9; 129.0; 131.1; 136.6; 140.4; 141.0. 177.0

MS (EI, 70 eV): *m/z* (%): 267 (30%); 210 (7%); 183 (32%); 165 (9%); 115 (5%); 85 (5%); 57 (100%).

Ethyl 4'-methyl-3'-pivalamidobiphenyl-4-carboxylate (3b)[7]

Followed the general procedure the reaction was performed with 95.6 mg (0.5 mmol) N-*o*-tolyl pivalanilide, 408 mg (0.75 mmol) mesityl(4-ethoxycarbonylphenyl)iodonium triflate and 32.2 mg (5 mol%) Cu/Fe for 20 h at 50°C. After evaporation of the solvent the remained residue was dissolved in 10 ml ethyl-acetate and extracted by 3x10 ml 1 M NaOH. The aqueous phase was washed by 10 ml ethyl-acetate and the organic phase was extracted again with 3x10 ml 1 M NaOH. The two organic phases were united and dried on $MgSO_4$. After evaporation of the solvent the crude product was purified with column chromatography on silica gel with gradient elution (Hexanes-Ethyl acetate eluent: 50:1 → 25:1 → 20:1 → 15:1 → 10:1 → 5:1) affording the product as white solid (141 mg, 0.42 mmol, 83%).

Mp 115 °C. R_f = 0.18 (Hexane-EtOAc, 8:1)

IR (solid): 3306; 2956; 2922; 2867; 1738; 1650; 1480; 1395; 1363; 1275; 1239; 1214; 1168; 1093; 1048; 1011; 941; 907; 883; 841 cm^{-1}.

^{1}H NMR (250MHz, $CDCl_3$): 1.36 (s, 9H), 1.41 (t, 3H, J^1=J^2 = 7.00 Hz), 2.30 (s, 3H), 4.39 (q, 2H, J^1=J^4 = 10.50 Hz, J^2=J^3 = 3.50 Hz), 7.27 (m, 3H), 7.67 (d, 2H, J = 4.00 Hz), 8.07 (d, 2H, J = 4.25 Hz), 8.24 (s, 1H).

^{13}C NMR (250 MHz, $CDCl_3$): δ =14.8; 17.8; 28.1; 40.6; 61.4; 121.8; 123.9; 127.2; 128.7; 129.4; 130.5; 131.4; 136.8; 139.1; 145.5; 167.0; 177.1.

MS (EI, 70 eV): *m/z* (%): 339.2 (100%); 294.1 (20%); 255.2 (51%); 226.1 (22%); 181.1 (22%); 152.1 (11%); 85.1 (11%).

Ethyl 4'-methoxy-3'-pivalamidobiphenyl-4-carboxylate (3c)

Followed the general procedure the reaction was performed with 104 mg (0.5 mmol) N-*o*-methoxyphenyl pivalanilide, 408 mg (0.75 mmol) mesityl(4-ethoxycarbonylphenyl) iodonium triflate and 32 mg (5 mol%) Cu/Fe for 20 h at 50°C. After evaporation of the solvent the remained residue was dissolved in 10 ml ethyl-acetate and extracted with 3x10 ml 1 M NaOH. The aqueous phase was washed with 10 ml ethyl-acetate and the organic phase was extracted again with 3x10 ml 1 M. The two organic phases were united and dried on $MgSO_4$. After evaporation of the solvent the crude product was purified with column chromatography on silica gel with gradient elution (Hexanes-Ethyl acetate eluent: 50:1 → 25:1 → 20:1 → 15:1 → 10:1 → 5:1) affording the product as white solid (109 mg, 0.31 mmol, 61%).

Mp 80 °C. R_f = 0.27 (Hexane-EtOAc, 8/1).

IR (solid): 3440; 2975; 2911; 2871; 2839; 1713; 1670; 1605; 1594; 1537; 1506; 1477; 1431; 1404; 1365; 1326; 1286; 1256; 1175; 1158; 1127; 1104; 1051; 1019; 922; 893; 859; 811 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.27 (s, 9H), 1.33 (t, 3H, J^1=J^2 = 7.00 Hz), 3.87 (s, 3H), 4.31 (q, 2H, J^1=J^4 = 10.75 Hz , J^2=J^3 = 3.5 Hz), 6.87 (d, 1H, J = 4.25 Hz), 7.23 (m, 1H), 7.60 (d, 2H, 4.25 Hz), 7.97 (d, 2H, J = 4.25 Hz), 8.11 (s, 1H), 8.75 (d, 1H, J = 1.0 Hz).

^{13}C NMR (250 MHz, $CDCl_3$): δ =14.8; 28.0; 40.5; 56.4; 61.3; 110.4; 118.8; 122.5; 127.1; 128.7; 129.0; 130.3; 133.3; 145.4; 148.5; 167.1; 177.2.

MS (EI, 70 eV): *m/z* (%): 355 (73%); 310 (11%); 271 (20%); 256 (27%); 228 (7%); 200 (11%); 183 (7%); 167 (16%); 139 (21%); 85 (5%); 57 (100%).

HRMS: *m/z* $[M + H]^+$ calcd for $C_{21}H_{25}NO_4$: 356.1856; found: 356.1852.

Ethyl 4'-phenyl-3'-pivalamidobiphenyl-4-carboxylate (3d)

Followed the general procedure the reaction was performed with 127 mg (0.5 mmol) biphenyl-2-pivalanilide, 408 mg (0.75 mmol) mesityl(4-ethoxycarbonylphenyl)iodonium triflate and 32 mg (5 mol%) Cu/Fe for 20 h at 70°C. After evaporation of the solvent the remained residue was dissolved in 10 ml ethyl-acetate and extracted with 3x10 ml 1 M NaOH. The aqueous phase was washed with 10 ml ethyl-acetate and the organic phase was extracted again with 3x10 ml 1 M. The two organic phases were united and dried on $MgSO_4$. After evaporation of the solvent the crude product was purified with column chromatography on silica gel with gradient elution (Hexanes-Ethyl acetate eluent: 50:1 → 25:1 → 20:1 → 15:1 → 10:1 → 5:1) affording the product as white solid (108 mg, 0.27 mmol, 54%).

Mp 109-112 °C. R_f = 0.15 (Hexane-EtOAc, 8:1).

IR (solid): 3377; 3084; 3054; 3033; 2966; 2928; 2871; 1717; 1666; 1608; 1581; 1553; 1527; 1497; 1462; 1443; 1421; 1394; 1367; 1310; 1270; 1211; 1177; 1158; 1124; 1100; 1018; 1008; 930; 885; 856; 825 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.04 (s, 9H), 1.34 (t, 3H, J^1 = J^2 = 5.0 Hz), 4.32 (q, 2H, J = 7.5 Hz), 7.24-7.49 (m, 8H), 7.67 (d, 2H, J = 7.5 Hz), 8.02 (d, 2H, J = 7.5 Hz), 8.68 (s, 1H).

^{13}C NMR (250 MHz, $CDCl_3$) δ = 14.7; 27.7; 40.3; 61.3; 120.1; 123.0; 127.5; 128.7; 129.6; 130.4; 130.8; 132.2; 136.1; 138.0; 140.6; 145.3; 167.0; 177.0.

MS (EI, 70 eV): *m/z* (%): 401 (50%); 344 (10%); 317 (28%); 288 (13%); 241 (14%); 207 (4%); 167 (5%); 85 (4%); 57 (100%).

HRMS: *m/z* $[M + H]^+$ calcd for $C_{26}H_{27}NO_3$: 402.2064; found: 402.2060.

N-(4'-fluoro-4-methylbiphenyl-3-yl)pivalamide (3e)[19]

Followed the general procedure the reaction was performed with 95.6 mg (0.5 mmol) N-*o*-tolyl pivalanilide, 368 mg (0.75 mmol) mesityl(4-fluorophenyl) iodonium triflate and 32.2 mg (5 mol%) at 50 ˚C for 20 h. After evaporation of the solvent the crude product was purified with column chromatography on silica gel with gradient elution (Toluene-Hexanes-Ethyl acetate eluent : 25:25:1 → 12.5:12.5:1 → 5:5:1) affording the product as yellow oil (purity 78%). For further purification the oil was dissolved in ethyl acetate and it was purified by preparative thin layer chromatography using Toluene: MeOH = 10/1 as eluent. The product was obtained as white solid (81 mg, 0.28 mmol, 57%).

Mp 107-109 °C. R_f = 0.61 (Toluene-MeOH, 10:1).

IR (solid): 3299; 3034; 2962; 2928; 2870; 1649; 1598; 1571; 1510; 1492; 1455; 1389; 1367; 1289; 1262; 1222; 1202; 1158; 1096; 1014; 932; 876; 839 cm^{-1}.

^{1}H NMR (250MHz, $CDCl_3$): δ = 1.27 (s, 9H), 2.19 (s, 3H), 6.99 (t, 2H, J^1 = J^2 = 8.5 Hz), 7.14 (s, 2H), 7.26 (s, 1H), 7.47 (m, 2H), 8.07 (s, 1H).

^{13}C NMR (250 MHz, $CDCl_3$): δ = 17.7; 28.1; 40.2; 121.8; 123.8; 127.5; 127.9; 129.0; 131.1; 136.6; 140.4; 141.0; 177.1.

MS (EI, 70 eV): *m/z* (%): 285.1 (54.2%); 228.1 (4.2%); 201.1 (45.8%); 170.1 (7.5%); 133.1 (4.2%); 85.1 (6.7%); 57.1 (100%).

N-(4-tert-butyl-4'-fluorobiphenyl-3-yl)pivalamide (3f)

Followed the general procedure the reaction was performed with 116.6 mg (0.5 mmol) N-*o*-*t*-butylphenyl pivalanilide, 368 mg (0.75 mmol) mesityl(4-fluorophenyl) iodonium triflate and 32.2 mg

(5 mol%) Cu/Fe at 50˚C for 20 h. After evaporation of the solvent the crude product was purified with column chromatography on silica gel (Toluene: Hexanes-Ethyl-acetate eluent in 2.5:12.5:1 ratio) affording the product as yellow oil (purity: 82%). For further purification the oil was dissolved in ethyl acetate and it was purified by preparative thin layer chromatography using Toluene-MeOH, 10:1 as eluent. The product was obtained as white solid (111 mg, 0.34 mmol, 68%).

Mp 142°C. R_f = 0.65 (Toluene:MeOH, 10:1).

IR (solid): 3265; 3004; 2960; 2932; 2870; 1645; 1507; 1492; 1476; 1418; 1398; 1367; 1280; 1218; 1173; 1158; 1095; 1046; 1027; 1014; 943; 909; 882; 842; 820 cm^{-1};.

^{1}H NMR (250MHz, $CDCl_3$): δ = 1.29 (s, 9H), 1.37 (s, 9H), 7.00 (t, 2H, J^1 = J^2 = 8.75 Hz), 7.20 (m, 1H), 7.36 (d, 1H, J = 4.25 Hz), 7.47 (m, 3H), 7.88 (d, 1H, J = 2.0 Hz).

^{13}C NMR (250 MHz, $CDCl_3$): δ = 28.1; 31.0; 34.7; 40.0; 115.7; 116.1; 124.2; 125.9; 127.4; 129.0; 129.1; 136.4; 139.1; 140.8; 176.7.

MS (EI, 70 eV): *m/z* (%):327 (21%); 270 (100%); 228 (23%); 185 (9%); 57 (82%).

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{21}H_{26}NOF$: 350.1891; found: 350.1884.

N-(4'-fluoro-4-phenylbiphenyl-3-yl)pivalamide(3g)

Followed the general procedure the reaction was performed with 127 mg (0.5 mmol) biphenyl-2-pivalanilide, 368 mg (0.75 mmol) mesityl(4-fluorophenyl) iodonium triflate and 32.2 mg (5 mol%) Cu/Fe at 50˚C for 20 h. After evaporation of the solvent the remaining residue was purified by flash chromatography on silica gel (Eluent: Hexanes-Ethyl acetate, 5:1) and the product was isolated with 71% purity as yellow oil. For further purification the oil was dissolved in ethyl acetate and it was purified by preparative thin layer chromatography using Toluene: Methanol = 10:1 as eluent. The pure product was obtained as white solid (92 mg, 0.26 mmol, 53%).

Mp 115°C. R_f = 0.65 (Hexane-EtOAc, 5:1); Rf = 0.86 (Toluene-MeOH, 10:1).

IR (solid): 3428; 3064; 2970; 2955; 2928; 2864; 1684; 1597; 1560; 1533; 1502; 1460; 1443; 1422; 1394; 1361; 1306; 1211; 1155; 1122; 1096; 1076; 1028; 1008; 919; 898; 846; 821 cm^{-1}.

^{1}H NMR (250MHz, $CDCl_3$): δ = 1.13 (s, 9H), 7.12 (t, 2H, J^1 = J^2 = 7.5 Hz), 7.50 (m, 8H), 7.66 (t, 2H, J = 7.5 Hz), 8.70 (s, 1H).

^{13}C NMR (250 MHz, $CDCl_3$): δ = 28.0; 40.4; 115.8; 116.2; 119.6; 119.7; 122.7; 128.6; 129.1; 129.3; 129.6; 129.7; 131.4; 136.1; 138.2; 141.0; 177.0.

MS (EI, 70 eV): *m/z* (%): 347 (92%); 290 (18%); 263 (69%); 241 (8%); 167 (8%); 57 (100%).

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{23}H_{22}NOF$: 370.1578; found: 370.1583.

N-(4'-chloro-4-methylbiphenyl-3-yl)pivalamide (3h)

Followed the general procedure the reaction was performed with 95.6 mg (0.5 mmol) N-*o*-tolyl pivalanilide, 380 mg (0.75 mmol) mesityl(4-chlorophenyl) iodonium triflate and 32.2 (5 mol%) mg Cu/Fe at 50˚C for 20 h. After evaporation of the solvent the crude product was purified with column chromatography on silica gel (Toluene: Hexanes: Ethyl acetate eluent in the ratio of 12.5:12.5:1) affording the product as yellow oil (purity:78%). For further purification the yellow oil was dissolved in ethyl acetate and it was purified by preparative thin layer chromatography using Toluene: Methanol = 10:1 as eluent. The product was obtained as white solid (85 mg, 0.28 mmol, 65%).

Mp 148°C. R_f = 0.63 (Toluene-MeOH, 10:1).

IR (solid): 3312; 3031; 2965; 2924; 2901; 2860; 1649; 1612; 1517; 1499; 1479; 1455; 1397; 1382; 1364; 1309; 1285; 1222; 1202; 1165; 1130; 1093; 1083; 1038; 1011; 990; 957; 930; 906; 882; 834; 809; 768 cm^{-1}.

^{1}H NMR (250MHz, $CDCl_3$): δ = 1.27 (s, 9H), 2.19 (s, 3H), 7.15 (brs, 2H), 7.27 (d, 3H, J = 4.25 Hz), 7.44 (d, 2H, J = 4.25 Hz), 8.09 (s, 1H).

^{13}C NMR (250 MHz, $CDCl_3$): δ = 17.7; 28.1; 40.3; 121.5; 123.5; 128.1; 128.7; 129.2; 131.3; 133.6; 136.8; 139.0; 139.5; 177.1.

MS (EI, 70 eV): *m/z* (%): 301 (27%); 244 (4%); 217 (19%); 180 (7%); 152 (8%); 85 (7%); 57 (100%).

HRMS: *m/z* [M + H]$^+$ calcd for $C_{18}H_{20}NOCl$: 302.1306; found: 302.1299.

N-(4-tert-butyl-4'-chlorobiphenyl-3-yl)pivalamide (3i)

Followed the general procedure the reaction was performed with 116.6 mg (0.5 mmol) N-*o*-tolyl pivalanilide, 380 mg (0.75 mmol) mesityl(4-chlorophenyl) iodonium triflate and 32.2 mg (5 mol%) Cu/Fe at 50˚C for 20 h. After evaporation of the solvent purification of the crude product with flash chromatography on silica gel (Hexanes-Ethyl acetate, 5:1, as eluent) afforded the product as yellow oil (Purity: 79%). The yellow oil was dissolved in ethyl acetate and it was purified by preparative thin layer chromatography using Toluene-Methanol, 10:1 as eluent. The product is afforded as white solid (81 mg, 0.24 mmol, 47%).

Mp 122-144°C. R_f = 0.37 (Hexane-EtOAc, 5:1); R_f = 0.74 (Toluene-MeOH, 10:1).

IR (solid): 3306; 2956; 2922; 2867; 1738; 1650; 1480; 1395; 1363; 1275; 1239; 1214; 1168; 1093; 1048; 1011; 941; 907; 883; 841 cm^{-1}.

^{1}H NMR (250MHz, $CDCl_3$): δ = 1.29 (s, 9H), 1.37 (s, 9H), 7.25 (m, 3H), 7.37 (d, 1H, J = 4.13 Hz), 7.45 (d, 3H, J = 4.25 Hz), 7.90 (d, 1H, J = 1.0 Hz).

^{13}C NMR (250 MHz, $CDCl_3$): δ = 28.1; 31.0; 34.8; 40.0; 124.2; 125.8; 127.5; 128.7; 129.2; 133.7; 136.5; 138.8; 139.1; 141.2; 176.7.

MS (EI, 70 eV): *m/z* (%): 343 (15%); 286 (100%); 244 (18%); 193 (8%); 165 (11%); 57 (100%).

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{21}H_{26}NOCl$: 366.1595; found: 366.1593.

N-(4'-chloro-4-phenylbiphenyl-3-yl)pivalamide (3j)

Followed the general procedure the reaction was performed with 127 mg (0.5 mmol) biphenyl-2-pivalanilide, 380 mg (0.75 mmol) mesityl(4-chlorophenyl) iodonium triflate and 32 mg (5 mol%) Cu/Fe at 70˚C for 20 h. After evaporation of the solvent purification of the crude product with flash chromatography on silica gel (Hexanes-Ethyl acetate, 5:1 as eluent) the product as yellow oil (purity: 86%). For further purification the yellow oil was dissolved in ethyl acetate and it was purified by preparative thin layer chromatography using Toluene-Methanol, 10:1 as eluent. The product was obtained as white solid (135 mg, 0.37 mmol, 74%).

Mp 137°C. R_f = 0.48 (Hexane-EtOAc, 2:1). R_f = 0.75 (Toluene-MeOH, 20:1).

IR (solid): 3434; 3383; 3038; 2965; 2946; 2929; 2867; 1677; 1581; 1551; 1523; 1486; 1470; 1460; 1442; 1418; 1385; 1303; 1277; 1249; 1208; 1154; 1127; 1087; 1025; 1007; 929; 882 cm^{-1}.

^{1}H NMR (250MHz, $CDCl_3$): δ = 1.13 ppm (s, 9H), 7.30 – 7.65 ppm (m, 12H), 8.71 ppm (d, *J* = 1.5 Hz, 1H).

^{13}C NMR (250 MHz, $CDCl_3$): δ = 27.5; 40.0; 119.4; 122.3; 128.4; 128.6; 129.0; 129.3; 129.4; 130.3; 131.4; 133.7; 135.8; 137.7; 139.1; 140.2; 176.5.

MS (EI, 70 eV): *m/z* (%): 363 (28%); 306 (6%); 279 (28%); 243 (13%); 85 (6%); 57 (100%).

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{23}H_{22}NOCl$: 386.1282; found: 386.1283.

N-(4'-bromo-4-methylbiphenyl-3-yl)pivalamide (3k)[13]

Followed the general procedure the reaction was performed with 95.5 mg (0.5 mmol) biphenyl-2-pivalanilide, 413.4 mg (0.75 mmol) mesityl(4-bromophenyl) iodonium triflate and 32.5 mg (5 mol%) Cu/Fe at 50˚C for 20 h. After evaporation of the solvent purification of the crude product with flash chromatography on silica gel (Hexanes-Ethyl acetate, 2:1 as eluent) afforded the product as yellow oil (purity: 89%). The yellow oil was solved in ethyl acetate and it was purified by preparative thin layer chromatography using Toluene-Methanol, 20:1 as eluent. Rf = 0.62. The product is afforded as white solid (129 mg, 0.37 mmol, 75%).

Mp 141-142°C. R_f = 0.68 (Hexane-EtOAc, 2:1). (Toluene-MeOH, 20:1).

IR (solid): 3312; 3030; 2965; 2924; 2861; 1738; 1649; 1479; 1378; 1273; 1241; 1222; 1202; 1165; 1070; 1044; 1007; 930; 905; 882; 884 cm^{-1}.

^{1}H NMR (250MHz, $CDCl_3$): δ = 1.36 (s, 9H), 2.28 (s, 3H), 7.24 ppm (t, 2 H, J^1 = J^2 = 10.0 Hz), 7.50 (m, 4H), 7.65 ppm (q, 2H, *J* = 7.5 Hz), 8.15 ppm (s, 1H).

^{13}C NMR (250 MHz, $CDCl_3$): δ = 17.7; 28.2; 40.4; 121.5; 121.8; 123.6; 128.4; 129.0; 131.3; 132.1; 136.7; 139.0; 140.0; 177.2.

MS (EI, 70 eV): *m/z* (%): 345 (15%); 261 (14%); 180 (9%); 153 (11%); 85 (6%); 57 (100%).

N-(4'-bromo-4-tert-butylbiphenyl-3-yl)pivalamide (3l)

Followed the general procedure the reaction was performed with 116.6 mg (0.5 mmol) N-*o*-*t*-butyl-phenyl pivalanilide, 413.4 mg (0.75 mmol) mesityl(4-bromophenyl) iodonium triflate and 32.5 mg (5 mol%) Cu/Fe at 50˚C for 20 h. After evaporation of the solvent purification of the crude product with flash chromatography on silica gel (Hexanes-Ethyl acetate, 5:1 as eluent) afforded the product as yellow oil (purity 78%). For further purification the yellow oil was dissolved in ethyl acetate and it was purified by preparative thin layer chromatography using Toluene-Methanol, 10:1 as eluent. The product was obtained as white solid (153 mg, 0.39 mmol, 79%).

Mp 126°C. R_f = 0.40 (Hexane-EtOAc, 5:1). R_f = 0.74 (Toluene-MeOH, 20:1)

IR (solid): 3305; 2956; 2921; 2902; 2867; 1737; 1650; 1477; 1394; 1361; 1273; 1238; 1214; 1167; 1095; 1070; 1048; 1007; 941; 906; 883 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.30 (s, 9H), 1.37 (s, 9H), 7.21 – 7.32 (m, 1H), 7.46 – 7.54 (m, 6H), 7.91 (d, *J* = 2.0 Hz, 1H).

^{13}C NMR (250 MHz, $CDCl_3$) δ = 27.8; 30.7; 34.5; 39.7; 121.6; 123.9; 125.5; 127.3; 128.8; 131.9; 136.2; 138.5; 139.3; 141.0; 176.5.

MS (EI, 70 eV): *m/z* (%): 387 (22%); 330 (100%); 288 (24%); 251 (9%); 209 (7%); 193 (15%); 165 (17%); 139 (7%); 57 (85%).

HRMS: *m/z* $[M + H]^+$ calcd for $C_{21}H_{26}NOBr$: 388.1271; found: 388.1263.

N-(4'-bromo-4-phenylbiphenyl-3-yl)pivalamide (3m)

Followed the general procedure the reaction was performed with 127 mg (0.5 mmol) biphenyl-2-pivalanilide, 413.4 mg (0.75 mmol) mesityl(4-bromophenyl) iodonium triflate and 32.5 mg (5 mol%) Cu/Fe at 50˚C for 20 h. After evaporation of the solvent purification of the crude product with flash chromatography on silica gel (Hexanes-Ethyl acetate, 5:1 as eluent) afforded the product as yellow oil (purity: 77%). For further purification the yellow oil was dissolved in ethyl acetate and it was purified by preparative thin layer chromatography using Toluene-

Methanol, 10:1 as eluent. The product was obtained as white solid (143 mg, 0.35 mmol, 70%).

Mp 119°C. R_f = 0.60 (Hexane-EtOAc, 5:1). R_f = 0.86 (Toluene-MeOH, 20:1).

IR (solid): 3430; 3081; 3062; 3023; 2970; 2953; 2926; 2864; 1743; 1684; 1578; 1555; 1530; 1477; 1460; 1445; 1421; 1384; 1304; 1279; 1245; 1209; 1160; 1141; 1124; 1069; 1004; 919; 896 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$) δ = 1.13 (s, 9H), 7.12 – 7.74 (m, 12H), 8.71 (s, 1H).

^{13}C NMR (250 MHz, $CDCl_3$) δ = 27.5; 40.0; 119.3; 121.9; 122.3; 128.4; 128.9; 129.3; 129.4; 130.4; 131.5; 131.9; 135.8; 137.7; 139.6; 140.2; 176.7.

MS (EI, 70 eV): *m/z* (%): 409 (25%); 407 (25%); 323 (25%); 241 (19%); 57 (100%).

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{23}H_{22}NOBr$: 430.0777; found: 430.0780.

General procedure for the synthesis of 2-tert-butyl-4-(diarylmethylene)-4H-benzo[d][1,3]oxazines

N-(2-(arylylethynyl)phenyl)pivalamide (0.35 mmol, 1.0 equiv.), aryl(mesityl)iodonium trifluoromethanesulfonate (0.42 mmol, 1.2 equiv.) and Cu/Fe (22.2 mg, 0.0175 mmol, 5 mol%) were placed in a 4 ml vial, which was sealed with rubber septa, evacuated then charged with argon. 1,2-dichloroethane (3 ml) was added, and the reaction mixture was stirred at 50°C for the indicated time. The catalyst was separated from the reaction mixture with a magnet. The reaction mixture was diluted with CH_2Cl_2 (15 ml), washed twice with saturated sodium bicarbonate solution (15 ml), the aqueous phase was extracted with CH_2Cl_2 (15 ml), and the combined organic phases were dried over magnesium sulphate and evaporated *in vacuo*. The crude product was purified by column chromatography.

2-tert-butyl-4-(diphenylmethylene)-4H-benzo[d][1,3]oxazine[10] (5a)

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)pivalamide (97.1 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg, 0.42 mmol). Reaction time: 12 h. The crude product was purified by column chromatography on Brockmann II type neutral alumina with hexanes/ dichloromethane 100/ 1 to give a yellow solid (72 mg, 0.203 mmol, 58%).

Mp 167 – 169 °C. R_f: 0.72 (hexanes-ethyl acetate, 7:1);

IR (solid): 2975; 1640; 1615; 1597; 1456; 1219; 1136; 1061 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.02 ppm (s, 9H, CH_3); 6.54 ppm (d, *J* = 7.7 Hz, 1H, Ar-H); 6.68 ppm (ddd, *J* = 8.6 Hz and 5.9 Hz and 2.7 Hz, 1H, Ar-H); 7.07 ppm (dd, *J* = 5.1 Hz and 2.0 Hz, 1H, Ar-H); 7.10 – 7.16 ppm (m, 2H, Ar-H); 7.17 – 7.22 ppm (m, 8H, Ar-H).

^{13}C NMR (62.5 Hz, $CDCl_3$): δ = 27.5; 37.3; 120.7; 121.6; 125.6; 126.0; 126.8; 127.0; 127.5; 127.8; 129.1; 129.9; 130.0; 130.9; 140.1; 140.6; 141.3; 141.6; 167.1.

MS (EI, 70 eV): *m/z* (%): 353 (100%); 296 (45%); 280 (10%); 268 (27%); 165 (36%); 57 (9%).

(E/Z)-4-((4-methylphenyl)(phenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine[10](5b)

Prepared according to the general procedure from N-(2-((4-methylphenyl)ethynyl)phenyl)pivalamide (102.0 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol). Reaction time: 12 h. The crude product was purified by column chromatography on Brockmann II type neutral alumina with hexanes-dichloromethane, 100:1 to give a pale yellow solid (87 mg, 0.24 mmol, 67%). Isomer ratio E/ Z = 2/ 3 (from ^1H NMR).

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)pivalamide (97.1 mg, 0.35 mmol) with 4-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (204.2 mg 0.42 mmol), Reaction time: 18 h. The crude product was purified by column chromatography on Brockmann II type neutral alumina with hexanes/ dichloromethane 100/ 1 to give a pale yellow solid (57 mg, 0.16 mmol, 44%). Isomer ratio E/ Z = 3/ 2 (from ^1H NMR).

Mp 108 – 110 °C; R_f: 0.73 (hexanes-ethyl acetate, 7:1);

IR (solid): 2959, 2925, 1636, 1594, 1455, 1275, 1219, 1140, 1059, 828, 761, 695 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.02 ppm (s, 6H, CH_3); 1.05 ppm (s, 9H, CH_3); 2.26 ppm (s, 3H, CH_3); 2.27 (s, 2H, CH_3); 6.51 ppm (d, *J* = 8.0 Hz, 1H, Ar-H); 6.61 ppm (d, *J* = 8.0 Hz, 1H, Ar-H); 6.77 – 6.64 ppm (m, 2H, Ar-H); 7.02 ppm (d, *J* = 8.7 Hz, 4H, Ar-H); 7.12 – 7.05 ppm (m, 5H, Ar-H); 7.15 ppm (m, 3H, Ar-H); 7.21 ppm (m, 5H, Ar-H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 21.41; 27.5; 27.6; 37.27; 37.30; 120.72; 120.75; 121.80; 121.84; 125.6; 126.0; 126.7; 127.0; 127.4; 127.7; 128.4; 129.0; 129.7; 129.8; 129.9; 130.0; 130.7; 130.9; 136.4; 137.1; 137.2; 137.6; 140.3; 140.9; 141.4; 167.22; 167.24.

MS (EI, 70 eV): *m/z* (%): 367 (100%); 310 (63%); 296 (28%); 282 (24%); 267 (25%); 178 (23%); 165 (50%); 57 (30%).

(E/Z)-4-((3-methylphenyl)(phenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine[10] (5c)

Prepared according to the general procedure from N-(2-((3-methylphenyl)ethynyl)phenyl)pivalamide (102.0 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol). Reaction time: 12 h. The crude product was purified by column chromatography on Brockmann II type neutral alumina with hexanes-dichloromethane 100:1 to give a yellow solid (85 mg, 0.23 mmol, 66%). Isomer ratio E/ Z = 2/ 3 (from 1H NMR).

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)pivalamide (97.1 mg, 0.35 mmol) with (3-methylphenyl)(mesityl)iodonium trifluoromethanesulfonate (204.2 mg 0.42 mmol) Reaction time: 12 h. The crude product was purified by column chromatography on Brockmann II type neutral alumina with hexanes-dichloromethane 100:1 to give a yellow solid (79 mg, 0.21 mmol, 61%). Isomer ratio E/ Z = 1.8/ 1 (from ^{1}H NMR).

Mp 128 – 130 °C. R_f: 0.67 (hexanes-ethyl acetate, 7:1);

IR (solid): 3055; 3017; 2972; 2928; 2865; 1639; 1597; 1455; 1219; 1139; 1062 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 ppm (s, 4.5H, CH_3); 1.03 ppm (s, 9H, CH_3); 2.18 ppm (s, 1.5H, CH_3); 2.22 ppm (s, 3H, CH_3); 6.53 ppm (t, *J* = 9.1 Hz, 1.5H, Ar-H); 6.65 – 6.71 ppm (m, 1.5H, Ar-H); 6.92 – 7.03 ppm (m, 4H, Ar-H), 7.06 – 7.09 ppm (m,5.5H, Ar-H); 7.13 – 7.24 ppm (m, 8H, Ar-H).

^{13}C NMR (62.5 Hz, $CDCl_3$): δ = 21.5; 21.6; 27.5; 37.3; 120.9; 121.7; 125.56; 125.59; 126.0; 126.7; 127.0; 127.1; 127.5; 127.6; 127.7; 127.75; 127.82; 128.3; 128.9; 129.1; 129.8; 130.0; 130.8; 130.9; 131.4; 137.0; 138.7; 139.9; 140.7; 141.3; 141.5; 167.2; 167.3.

MS (EI, 70 eV): *m/z* (%): 367 (100%); 310 (60%); 296 (30%); 282 (24%); 267 (28%); 178 (25%); 165 (53%); 57 (31%).

(E,Z)-2-tert-butyl-4-((2-methylphenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine[10] (5d)

Prepared according to the general procedure from N-(2-((2-methylphenyl)ethynyl)phenyl)pivalamide (102.0 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg, 0.42 mmol) Reaction time: 12 h. The crude product was purified by column chromatography on silica gel hexanes-ethyl acetate, 50:1 to give a yellow oil (91 mg, 0.25 mmol, 71%). Isomer ratio E/ Z = 1/1.2 (from ^{1}H NMR).

R_f: 0.73 (hexanes-ethyl acetate, 7:1).

IR (thin film): 3058; 3018; 2970; 2928; 2867; 1642; 1598; 1456; 1273; 1218; 1139; 1061; 1029 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 ppm (s, 7.5H, CH_3); 1.06 ppm (s, 9H, CH_3); 2.01 ppm (s, 3H, CH_3); 2.23 ppm (s, 2.5H, CH_3); 6.32 ppm (d, *J* = 7.7 Hz, 1H, Ar-H); 6.66 ppm (ddd, *J* = 8.6 Hz and 6.4 Hz and 2.3 Hz, 1H, Ar-H); 6.75 ppm (m, 2H, Ar-H); 7.03 – 7.12 ppm (m, 12H, Ar-H); 7.15 – 7.27 ppm (m, 9H, Ar-H).

^{13}C NMR (62.5 Hz, $CDCl_3$): δ = 19.9; 20.1; 27.2; 27.5; 37.2; 37.4; 119.4; 119.9; 121.1; 122.0; 125.7; 125.8; 126.0; 126.1; 126.4; 126.6; 126.8; 127.1; 127.3; 127.7; 128.0; 128.9; 129.7; 129.8; 130.0; 130.1; 131.0; 131.2; 136.6; 137.8; 139.0; 139.7; 139.9; 141.0; 141.4; 141.48; 141.8; 167.1; 167.4.

MS (EI, 70 eV): *m/z* (%): 367 (100%); 310 (55%); 296 (23%); 282 (23%); 178 (47%); 165 (23%); 57 (55%).

(E/Z)-2-tert-butyl-4-((4-methoxyphenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine[10] (5e)

Prepared according to the general procedure from N-(2-((4-methoxyphenyl)ethynyl)phenyl)pivalamide (107.6 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol) Reaction time: 24 h. The crude product was purified by column chromatography on silica gel with hexane-ethyl acetate 50:1 to give a bright yellow oil (50 mg, 0.13 mmol, 37%). Isomer ratio E/ Z = 1/ 2 (from 1H NMR)

R_f: 0.61 (hexanes-ethyl acetate, 7:1).

IR (thin film): 3058; 3031; 2958; 2925; 2853; 1639; 1601; 1509; 1456; 1245; 1218; 1171; 1137; 1032; 834 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 ppm (s, 4.5H, CH_3); 1.07 ppm (s, 9H, CH_3); 3.73 ppm (s, 3H, CH_3); 3.74 ppm (s, 1.5H, CH_3); 6.50 ppm (d, J= 8.0 Hz, 1H, Ar-H); 6.72 – 6.59 (m, 1.5H, Ar-H); 6.77 ppm (d, *J* = 8.8 Hz, 3H, Ar-H); 7.11 – 7.05 ppm (m,4H, Ar-H); 7.19 – 7.12 ppm (m, 5H, Ar-H); 7.24 – 7.19 ppm (m, 5H).

^{13}C NMR (62.5 Hz, $CDCl_3$): δ = 27.5; 27.6; 37.27; 37.33; 55.4; 113.1; 114.5; 120.5; 121.9; 122.0; 125.55; 125.61; 125.95; 126.03; 127.0; 127.5; 127.7; 129.0; 129.7; 129.8; 130.0; 131.0; 131.3; 132.0; 132.6; 140.9; 141.1; 141.3; 158.4; 167.3.

(E,Z)-2-tert-butyl-4-((4-chlorophenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine[10] (5f)

Prepared according to the general procedure from N-(2-((4-chlorophenyl)ethynyl)phenyl)pivalamide (109.1 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol) Reaction time: 16 h. The crude product was purified by column chromatography on Brockmann II type neutral alumina with hexane-dichloromethane 100:1 to give a pale yellow solid (92 mg, 0.24 mmol, 68%). Isomer ratio E/ Z = 1/ 2.3 (from ^{1}H NMR).

Prepared according to the general procedure from N-(2-(phenylethynyl)phenyl)pivalamide (97.1 mg, 0.35 mmol) with (4-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (212.8 mg 0.42 mmol) Reaction time: 16 h. The crude product was purified by column chromatography on Brockmann II type neutral alumina with hexane/ dichloromethane 100/ 1 to give a pale yellow solid (73 mg, 0.19 mmol, 54%). Isomer ratio E/ Z = 9/ 5 (from 1H NMR)

Mp 121 – 123 °C. *Rf*: 0.70 (hexanes-ethyl acetate, 7:1);

IR (solid): 2695; 1638; 1594; 1487; 1455; 1219; 1140; 1087; 1059; 1015; 832; 757 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.01 ppm (s, 3.5H, CH_3); 1.05 ppm (s, 9H, CH_3); 6.51 ppm (d, *J* = 7.8 Hz, 1H, Ar-H); 6.60 ppm (d, *J* = 7.9 Hz, 1H, Ar-H); 6.69 ppm (m, 1H, Ar-H); 6.76 ppm (m, 0.4H, Ar-H); 7.04 – 7.14 ppm (m, 6.5H, Ar-H); 7.16 – 7.24 ppm (m, 10H, Ar-H).

^{13}C NMR (62.5 Hz, $CDCl_3$): δ = 27.5; 27.6; 37.3; 119.3; 119.5; 121.2; 121.3; 125.76; 125.82; 126.1; 126.2; 126.9; 127.0; 127.7; 127.9; 128.0; 129.2; 129.3; 130.0; 130.1; 130.2; 130.9; 131.4; 132.3; 133.4; 138.6; 139.2; 139.7; 140.3; 141.3; 141.4; 142.1; 142.2; 166.8; 167.1.

MS (EI, 70 eV): *m/z* (%): 387 (100%); 330 (50%); 295 (20%); 267 (34%); 239 (20%); 165 (65%); 57 (35%).

2-tert-butyl-4-((4-nitrophenyl)(phenyl)methylene)-4H-benzo[d][1,3]oxazine[10] (5g)

Prepared according to the general procedure from N-(2-((4-nitrophenyl)ethynyl)phenyl)pivalamide (112.8 mg, 0.35 mmol) with mesityl(phenyl)iodonium trifluoromethanesulfonate (198.4 mg 0.42 mmol) Reaction time: 17 h. The crude product was purified by column chromatography on Brockmann II type neutral alumina with hexanes-dichloromethane 100:1 to give a bright yellow solid (70 mg, 0.18 mmol, 50%). Isomer ratio E/ Z = 2/ 7 (from 1H NMR).

Mp 130-132 °C. R_f: 0.53 (hexanes-ethyl acetate 7:1);

IR (solid): 3061; 2958; 2922; 2851; 1639; 1578; 1511; 1455; 1337; 1272; 1218; 1139; 1061 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.05 ppm (s, 2H, CH_3); 1.09 ppm (s, 7H, CH_3); 6.57 (d, *J* = 8.0 Hz, 1H, Ar-H); 6.77 ppm (t, *J* = 6.2 Hz, 1H, Ar-H); 7.23 – 7.11 ppm (m, 4H, Ar-H); 7.34 – 7.26 ppm (m, 3H, Ar-H); 7.42 ppm (d, *J* = 8.6 Hz, 2H Ar-H); 8.11 ppm (d, *J* = 8.4 Hz, 2H, Ar-H).

^{13}C NMR (62.5 Hz, $CDCl_3$): δ = 27.5; 27.6; 37.4; 118.2; 120.6; 123.2; 124.2; 126.1; 126.2; 126.4; 126.9; 127.3; 127.5; 128.20; 128.22; 129.0; 129.6; 130.2; 130.8; 130.9; 131.1; 131.9; 139.7; 141.4; 144.1; 146.2; 147.2; 166.2.

MS (EI, 70 eV): *m/z* (%): 398 (100%); 341 (38%); 295 (70%); 267 (50%); 239 (33%); 165 (40%); 57 (65%).

4-(bis(4-methylphenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine[10] (5i)

Prepared according to the general procedure from N-(2-((4-methylphenyl)ethynyl)phenyl)pivalamide (102.0 mg, 0.35 mmol) with 4-methylphenyl(mesityl)iodonium trifluoromethane-sulfonate (204.2 mg 0.42 mmol) Reaction time: 12 h. The crude product was purified by column chromatography on Brockmann II type neutral alumina with hexanes-dichloromethane 50:1 to give a pale yellow solid (42 mg, 0.11 mmol, 31%).

Mp 138-140 °C. R_f: 0.72 (hexanes-ethyl acetate, 7:1);

IR (solid): 2958; 2921; 1638; 1602; 1509; 1455; 1273; 1219; 1137; 1059; 1021; 818 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.04 ppm (s, 9H, CH_3); 2.26 ppm (s, 3H, CH_3); 2.27 ppm (s, 3H, CH_3); 6.57 ppm (d, *J* = 7.9 Hz; 1H, Ar-H); 6.71 ppm (dt, *J* = 8.6 Hz and 4.4 Hz, 1H, Ar-H); 7.00 ppm (s, 1H, Ar-H); 7.03 – 7.15 ppm (m, 10H, Ar-H).

^{13}C NMR (62.5 Hz, $CDCl_3$): δ = 21.43; 21.45; 27.5; 37.28; 120.7; 122.0; 125.5; 125.9; 127.0; 128.4; 129.6; 129.8; 129.9; 130.8; 136.4; 137.2; 137.3; 137.8; 141.1; 141.3; 167.3.

MS (EI, 70 eV): *m/z* (%): 381 (100%); 324 (50%); 310 (32%); 296 (15%); 281 (18%); 179 (33%); 57 (35%).

4-(bis(3-methylphenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine[10] (5j)

Prepared according to the general procedure from N-(2-((3-methylphenyl)ethynyl)phenyl)pivalamide (102.0 mg, 0.35 mmol) with (3-methylphenyl)(mesityl)iodonium trifluoromethanesulfonate (204.2 mg 0.42 mmol) Reaction time: 12 h. The crude product was purified by column chromatography on Brockmann II type neutral alumina with hexanes-dichloromethane 100:1 to give a yellow solid (81 mg, 0.21 mmol, 61%).

Mp 103-105 °C. R_f: 0.79 (hexanes-ethyl acetate, 7:1);

IR (solid): 3033, 2958, 2924, 1642, 1598, 1456, 1218, 1137, 1063 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.03 ppm (s, 9H, CH_3); 2.18 ppm (s,3H, CH_3); 2.23 ppm (s, 3H, CH_3); 6.53 ppm (d, *J* = 8.1 Hz, 1H, Ar-H); 6.69 ppm (ddd, *J* = 8.4 Hz and 5.3 Hz and 3.4 Hz, 1H, Ar-H); 6.92 – 7.01 ppm (m, 5H, Ar-H); 7.05 – 7.13 ppm (m, 5H, Ar-H).

^{13}C NMR (62.5 Hz, $CDCl_3$): δ = 21.5; 21.6; 27.5; 37.3; 120.9; 121.8; 125.6; 126.0; 127.00; 127.03; 127.5; 127.6; 127.8; 128.3; 128.9; 129.8; 130.7; 131.4; 137.0; 138.7; 140.0; 140.5; 141.3; 141.4; 167.2.

MS (EI, 70 eV): *m/z* (%): 381 (100%); 324 (48%); 310 (37%); 281 (15%); 178 (24%); 57 (28%).

4-(bis(4-chlorophenyl)methylene)-2-tert-butyl-4H-benzo[d][1,3]oxazine[10] (5k)

Prepared according to the general procedure from N-(2-((4-chlorophenyl)ethynyl)phenyl)pivalamide (109.1 mg, 0.35 mmol) with (4-chlorophenyl)(mesityl)iodonium trifluoromethane sulfonate (212.8 mg 0.42 mmol) Reaction time: 24 h. The crude product was purified by column chromatography on Brockmann II type neutral alumina with hexanes-dichloromethane 100:1 to give a pale yellow solid (87 mg, 0.21 mmol, 59%).

Mp 120-122 °C. R_f: = 0.79 (hexanes-ethyl acetate, 7:1);

IR (solid): 2963; 1636; 1608; 1585; 1489; 1455; 1217; 1140; 1088; 1012; 827 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.13 ppm (s, 9H, CH_3); 6.67 ppm (d, *J* = 7.9 Hz, 1H, Ar-H); 6.87 ppm (t, *J* = 7.0 Hz, 1H, Ar-H); 7.16 ppm (d, *J* = 8.5 Hz, 2H, Ar-H); 7.22 ppm (d, *J* = 6.4 Hz, 4H, Ar-H); 7.35 – 7.26 ppm (m, 4H, Ar-H).

^{13}C NMR (62.5 Hz, $CDCl_3$): δ = 27.6; 37.3; 118.1; 121.0; 126.0; 126.3; 126.9; 128.1; 129.5; 130.4; 131.4; 132.4; 132.7; 133.7; 138.2; 138.9; 141.4; 142.6; 166.8.

MS (EI, 70 eV): *m/z* (%): 421 (91%); 364 (42%); 329 (52%); 301 (35%); 267 (45%); 239 (45%); 199 (90%); 190 (22%); 163 (57%); 57 (100%).

4-(diphenylmethylene)-2-phenyl-4H-benzo[d][1,3]oxazine [10](5l)

N-(2-(phenylethynyl)phenyl)benzamide (104.1 mg, 0.35 mmol, 1.0 equiv.), aryl(mesityl)iodonium trifluoromethane sulfonate (198.3 mg, 0.42 mmol, 1.2 equiv.) and Cu/Fe (22.2 mg, 0.0175 mmol, 5 mol%) were placed in a 4 ml vial, which was sealed with rubber septa, evacuated then charged with argon. 1,2-dichloroethane (3 ml) was added, and the reaction mixture was stirred at 50°C for 17 hours. The catalyst was separated from the reaction mixture with a magnet. The reaction mixture was diluted with CH_2Cl_2 (15 ml), washed twice with saturated sodium bicarbonate solution (15 ml), the aqueous phase was extracted with CH_2Cl_2 (15 ml), and the combined organic phases were dried over magnesium sulfate and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel with hexane-ethyl acetate 50:1 to give a bright yellow solid (91 mg, 0.24 mmol, 70%).

Mp 187 – 189 °C. R_f = 0.64 (hexanes-ethyl acetate, 7:1);

IR (solid): 3055; 1738; 1633; 1612; 1591; 1574; 1449; 1243; 1069; 1024 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.58 ppm (d, J= 7.8 Hz, 1H, Ar-H); 6.72 ppm (t, J= 7.6 Hz, 1H, Ar-H); 7.11 ppm (t, J= 7.5 Hz, 1H, Ar-H); 7.35 – 7.19 ppm (m, 14H, Ar-H); 7.79 ppm (d, J= 7.4 Hz, 2H, Ar-H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 121.5; 122.0; 126.0; 126.4; 127.1; 127.2; 127.7; 128.0; 128.1; 128.4; 129.2; 130.1; 130.9; 131.2; 131.7; 140.1; 140.6; 141.5; 141.6; 156.2.

MS (EI, 70 eV): *m/z* (%): 373 (97%); 356 (10%); 344 (66%); 267 (20%); 239 (42%); 179 (30%); 165 (100%); 77 (20%).

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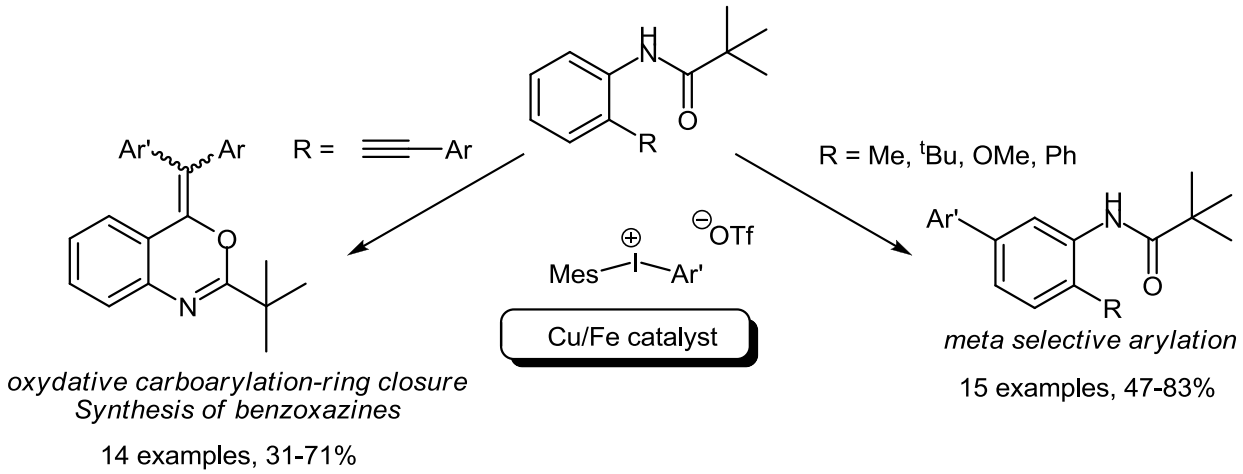

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