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Article

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Modular Approaches to Diversified Soft Lewis Basic Complexants through Suzuki-Miyaura Cross-Coupling of Bromoheteroarenes with Organotrifluoroborates

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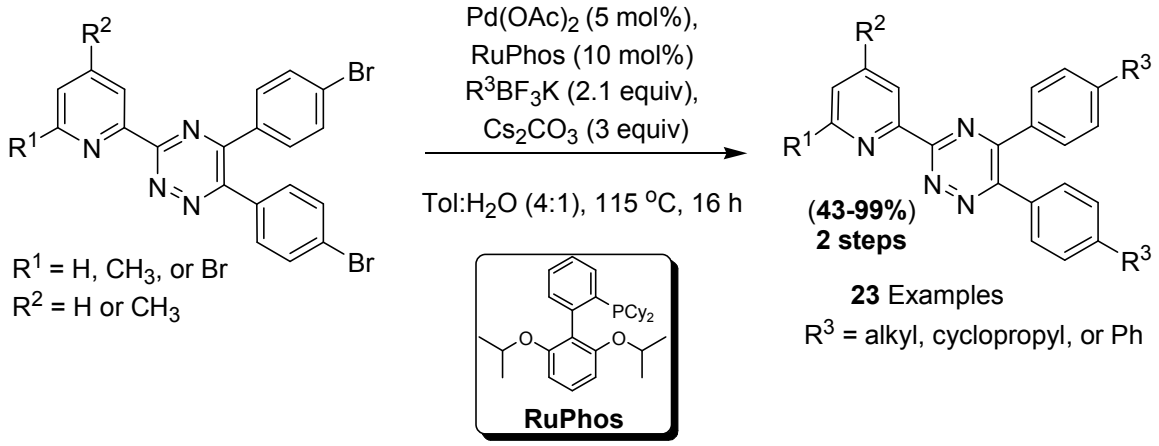


Abstract

Remediation or transmutation of spent nuclear fuel obtained as a function of energy production and legacy waste remains a significant environmental concern. Substantive efforts over the last three decades have focused on the potential of soft-Lewis basic complexants for the chemoselective separation of trivalent actinides from lanthanides in biphasic solvent systems. Recent efforts in this laboratory have focused on the concept of modularity to rapidly prepare complexants and complexant scaffolds not easily accessible via traditional linear methods in a convergent manner to better understand solubility and complexation structure/activity function in process-relevant solvents. The current work describes an efficient method for the construction of diversified complexants through multi-Suzuki-Miyaura cross-coupling of bromoheteroarenes with organotrifluoroborates affording efficient access to 22 novel materials in 43–99% yield over

two, three, or four cross-couplings on the same scaffold. Optimization of the catalyst/ligand system, application, and limitations are reported herein.

Introduction

The preparation of functionalized 1,2,4-triazinyl complexants for use in separation science,[1] materials,[2] and pharmaceuticals[3] is wide and varied. This laboratory has been working on the design, synthesis, and evaluation of soft-Lewis basic nitrogen donor complexants for chemoselective minor-actinide separation of Am^{3+} over lanthanides in spent nuclear fuel.[4] Effective sequestration of the minor actinides is required due to their strong neutron adsorbing properties which preclude their inclusion in more advanced fuels. Kolarik demonstrated the utility of 1,2,4-triazinyl moiety for chemoselective separations with the synthesis of 2,6-*bis*-(5,6-dialkyl-1,2,4-triazin-3-yl) pyridines (BTPs) as selective heterocyclic complexants for trivalent actinides [An(III)] over trivalent lanthanides [Ln(III)].[5] The formation of 1,2,4-triazines in the literature was first reported by Case.[6] Previous results from this laboratory highlighted the ability to access complexants derived from a variety of complexant scaffolds including mono-1,2,4-triazinylpyridines (MTP), bis-1,2,4-triazinylpyridines (BTP),[7] and bis-triazinylphenanthrolines (BTPhen)[8] via telescoped-condensation through the requisite hydrazonamide precursor and a 1,2-dicarbonyl without additives, prolonged reaction times, or complicated isolation procedures (Figure 1). The preparation of functionalized bis-1,2,4-triazinylbipyridines has also been reported.

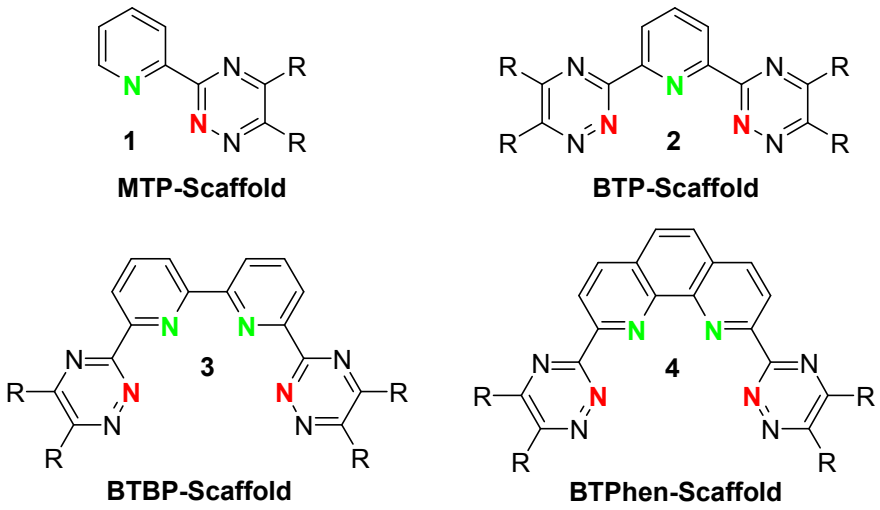


Figure 1. Common Soft-N-donor 1,2,4-triazinyl scaffolds.

One of the key challenges in this area is the development of a complexant which displays high distribution values for An(III) in biphasic media, while possessing robust stability to hydro- and radiolytic degradation. Ideally a suitable complexant should also maintain solubility in inexpensive, process-relevant solvents including C7SB-Isopar, decane, or octanol. Triazinyl complexants possessing two or more α-hydrogens relative to the 1,2,4-triazine are susceptible to oxidative degradation in higher concentrations of nitric acid which adds an additional avenue of complexity. Solubility of polar nitrogen-based complexants in nonpolar solvents presents obvious challenges, but also substantive opportunities for novel material and method development. Juxtaposition of favorable complexation and solubility properties serves as a strategic goal of work in this laboratory. The incorporation of an aromatic substituent directly on the 1,2,4-triazine offers the potential for improved stability, but at a cost of decreased solubility. The balancing of material robustness and solubility is a key focus of the current study. A merged strategy towards favorable solubility and complexation performance could be realized by employing metal-mediated cross-coupling strategies to diversify functionality necessary for solubility by increasing the aliphatic nature of the substituents. Linear routes to

functionalized complexants through condensation methods are inefficient for the rapid production of diversified substrates, often requiring the preparation of the 1,2-dicarbonyl moiety prior to the condensation event due to limited commercial availability. Modular approaches through a common haloheteroarene scaffold which provide rapid access to functionally diverse materials offer the potential for improved outcomes. It is postulated that triazinyl functionality plays a limited role in chelation efficacy, but solubility performance of complexants could potentially be improved by incorporation of aliphatic moieties via the Suzuki-Miyaura cross-coupling. The ubiquity of the Suzuki-Miyaura cross-coupling in the preparation of diversified arenes,[9] functionalized heterocycles,[10] complex natural products,[11] and commodity chemicals in organic and aqueous environments[12] is understood.

Examples of multiple Suzuki-Miyaura couplings[13] executed on similar electronic environments present on a discrete scaffold with any degree of functionality are not extensive in the primary literature.[14] Although efficient methods for the functionalization of unhindered aryl halides via the Suzuki-Miyaura coupling are extensive with low catalyst/ligand loadings, applications to nitrogen containing heterocyclic moieties frequently results in lower turnover numbers and isolated yield. Inspired by the elegant work of Buchwald[15] and Molander[16] in this area we set out to define the reaction parameters for an efficient multi cross-coupling protocol for haloheteroarene complexant scaffolds. Frequently, synthetic preparation of functionalized 1,2-dicarbonyls can involve several nonconvergent reaction steps. Previous work in the group with standard condensation methods of hydrazonamides towards the 1,2,4-triazine have demonstrated that the electronic donating ability of the *p*-substituent of a 4,4'-benzil derivative can play an important role in the outcome of the condensation event. As an example, deactivating or electron withdrawing functionality typically results in high conversion and good

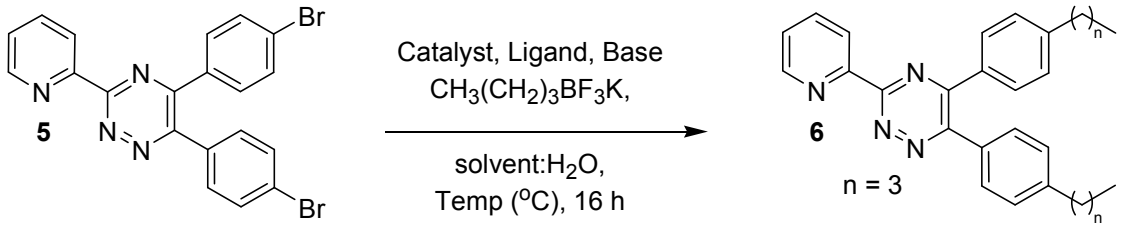
isolated yield. The converse is also true when working with 4,4'-benzils with resident electron donating substituents. A convergent approach leveraging modularity of a discrete complexant scaffold and subsequent diversification through metal-mediated cross-coupling would appear relevant and timely towards mitigating inconsistent condensation performance. Several issues of concern prior to project initiation included the potential for dative chelation of the substrate to the metal, the necessity of multiple cross-couplings thereby increasing the probability of unwanted side reactions, and the challenge of executing cross-coupling of functionalized heteroarenes with sp^3-hybridized organotrifluoroborates. Herein we report a general method for the Suzuki-Miyaura cross-coupling of haloheteroarenes containing one, two, or three reaction sites with various sp^3 and sp^2-hybridized organotrifluoroborates in modest to excellent isolated yield over one, two, three, or four steps, respectively.

Results and Discussion

A summary of method development conditions explored is described in Table 1. As part of due diligence all conditions listed were discretely evaluated with five organoboron reagents including: potassium butyltrifluoroborate, 2-methylpropylboronic acid, (2-methylpropyl)boronic acid N-methyliminodiacetic acid (MIDA) ester,[17] potassium phenyltrifluoroborate, and phenylboronic acid. These organoboron reagents were studied to ascertain any relationship between successful metal-mediated coupling with a given catalyst/ligand combination in concert with a particular organoboron reagent. Molander has reported the frequent necessity of optimizing coupling conditions to a specific organoboron reagent. With respect to sp^3 reagents, 2-methylpropylboronic acid and (2-methylpropyl)boronic acid MIDA ester were unsuccessful in all conditions screened. Cross-coupling with phenylboronic acid afforded modest levels of conversion with entries (2, 11, and 13) and potassium phenyltrifluoroborate was successful with

entries (2, 6, and 7). Due to incomplete conversion and a sizeable impurity profile, each of the aforementioned reactions was not further pursued and specific reasons for the lack of conversion to the desired products remains unclear. The aforementioned observations are commensurate with previous observations on the challenge of developing a cross-coupling protocol for a given substrate that is suitable for all organoboron reagents.

Table 1. Double Suzuki-Miyaura Cross-Coupling of Complexant Scaffolds Method Development



Entry	Catalyst	Ligand	Base	Solvent	Temp (°C)	Yield (%)
1	PEPPSI (5 mol %)	-----	KO*t*Bu (1.3 equiv)	IPA (0.5 M)	23	0
2	$PdCl_2$(dppf) CH_2Cl_2 (4 mol %)	----	Cs_2CO_3 (3 equiv)	CPME:H_2O (10:1)-0.1 M	90	0
3	$PdCl_2$ (4 mol %)	PPh_3 (12 mol %)	Cs_2CO_3 (3 equiv)	THF:H_2O (9:1)-0.5 M	66	0
4	$Pd(OAc)_2$ (4 mol %)	[*n*BuPAd_2] HI (6 mol %)	Cs_2CO_3 (3 equiv)	Tol:H_2O (10:1)-0.25 M	100	< 20
5	$Pd(MeCN)_2Cl_2$ (5 mol %)	CyPF-*t*Bu (10 mol %)	K_3PO_4 (3 equiv)	Tol:H_2O (9:1)-0.5 M	100	11
6	$Pd_2(dba)_3$ (5 mol %)	CyPF-*t*Bu (10 mol %)	K_3PO_4 (3 equiv)	Tol:H_2O (9:1)-0.3 M	100	0
7	SPhos Pd G2 precatalyst (5 mol %)	SPhos (10 mol %)	Cs_2CO_3 (3 equiv)	Tol:H_2O (9:1)-0.25 M	100	0
8	*t*BuBrettPhos precatalyst (5 mol %)	*t*BuBrettPhos (10 mol %)	K_3PO_4 (3 equiv)	Tol:H_2O (9:1)-0.5 M	100	8
9	RockPhos precatalyst (5 mol %)	RockPhos (10 mol %)	K_3PO_4 (3 equiv)	Tol:H_2O (9:1)-0.5 M	100	0
10	RuPhos precatalyst (5 mol %)	RuPhos (10 mol %)	K_3PO_4 (3 equiv)	Tol:H_2O (9:1)-0.5 M	100	67
11	$PdCl_2$(COD) (5 mol %)	RuPhos (10 mol %)	K_3PO_4 (3.5 equiv)	*t*BuOH:H_2O (1:1)-0.1 M	110	0
12	$Pd_2(dba)_3$ (5 mol %)	RuPhos (10 mol %)	K_2CO_3 (2 equiv)	Tol:H_2O (19:1)-0.1 M	120	91
13	$Pd(OAc)_2$ (5 mol %)	SPhos (10 mol %)	$K_3PO_4 \cdot H_2O$ (3 equiv)	CpMe:H_2O (9:1)-0.5 M	23	0
14	$Pd(OAc)_2$	RuPhos	Cs_2CO_3	CpMe:H_2O	100	50

	(5 mol %)	(10 mol %)	(3 equiv)	(4:1)-0.2 M		
15	$Pd(OAc)_2$ (5 mol %)	RuPhos (10 mol %)	Cs_2CO_3 (3 equiv)	Tol:H_2O (4:1)-0.2 M	100	97

Key: PyCF-*t*Bu = 1-dicyclohexylphosphino-2-di-*t*-butylphosphinoethylferrocene

Utilization of the Pd-N-heterocyclic carbene based PEPPSI catalyst (entry 1) developed by Organ was unsuccessful with **5**.[18] Tetrakis(triphenylphosphine)palladium(0),[19] $PdCl_2(dppf)\cdot CH_2Cl_2$,[20] $PdCl_2$, as well as adaptation of the Molander procedures[21] using $Pd(OAc)_2$ and the air stable iodide salt of diadamantylbutylphosphine (entries 2–4) afforded little to no conversion of the starting material to the requisite dialkyl moiety. Adaptation of established Hartwig amination conditions[22] to the transformation of interest (entry 56) was also unsuccessful. Screening of our recently disseminated procedure for Pd-catalyzed diamination[23] in the context of the current Suzuki-Miyaura cross-couplings (entry 6) also proved unfruitful. Entries 7–9 evaluated functionalized alkylbiarylphosphine ligands[24] with the methanesulfonic acid matched Pd(II) precatalysts developed in the Buchwald laboratories[25] to promote oxidative addition and subsequent reductive elimination, without substantive success. However, minimal conversion of 8 mol % was observed in the case of entry 8 using *t*BuBrettPhos. A significant productive result was observed in the case of entry 10 using the Buchwald RuPhos ligand and matched precatalysts. Further exploration of alkoxy-substituted dialkylbiaryl phosphines with various palladium catalysts seemed prudent. Variability of Pd-sources provided substantive improvement in the case of entry 12.[26] Near quantitative conversion of starting material was observed in entry 15 changing from a Pd^0 source to Pd(II).[27] Use of toluene resulted in a cleaner impurity profile upon evaluation of the crude reaction mixture by NMR (entry 15), therefore affording a potentially useful candidate system.[28]

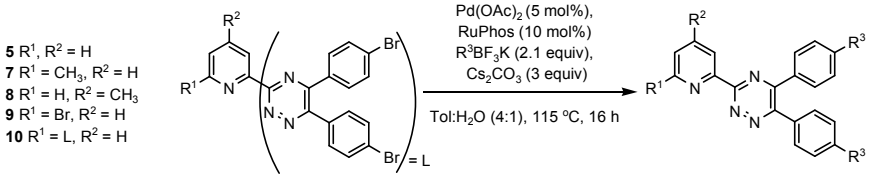
After proceeding with the conditions in entry 15 as the candidate system additional optimization was undertaken to improve overall reaction time. A base-screening revealed no

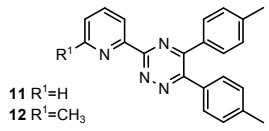
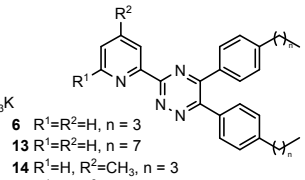
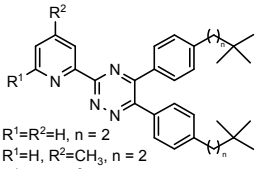
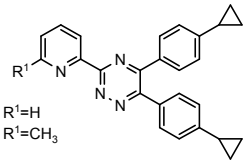
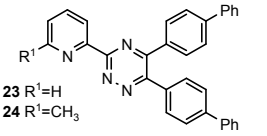
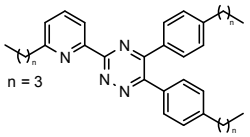
substantive improvement over the candidate system as stronger bases such as LiHMDS or NaO*t*Bu afforded no conversion and weaker bases such as K_2CO_3 or K_3PO_4 provided lower conversion relative to Cs_2CO_3. The use of higher boiling solvents including *n*BuOH, DMF, and *p*-xylene were studied to evaluate any correlation between solvent dielectric constant and/or higher temperature without substantive improvement. Evaluation of higher reaction concentration at 0.5, 1.0, and 2.0 M in toluene did not provide any advantage over the initial concentration of 0.25 M with respect to improving reaction time. Increasing the equivalents of the organotrifluoroborate also did not lead to higher conversion. During the course of scaffold evaluation it was observed that the impurity profile of certain reactions could be improved with increased catalyst/ligand loading. With a viable proof of concept established, we embarked on applying the method to scaffolds with one, two, three, or four reaction sites (Table 2).

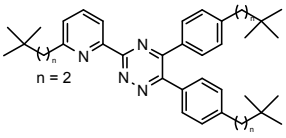
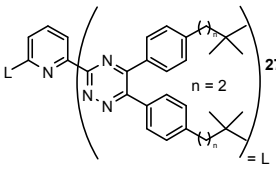
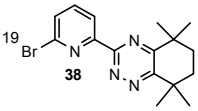
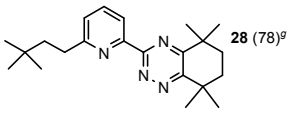
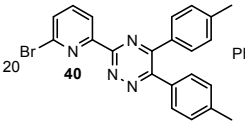
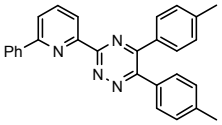
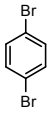
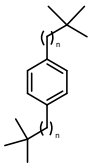
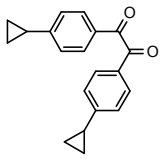
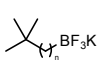
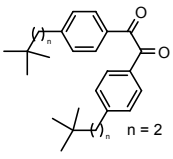
Table 2 highlights the diversity of scaffold derivatives suitable for multi Suzuki-Miyaura cross-coupling using the optimized reaction conditions. Treatment of scaffolds **5** and **7** with potassium methyltrifluoroborate afforded the dialkylated *p*-tolyl derivatives (**11**–**12**). Evaluation of **5** and related scaffold congeners (**7** and **8**) with butyl and octyltrifluoroborate reagents was successful in entries 3–8, although entry 4 with scaffold **5** did demonstrate inconsistent conversion. Utilization of branched alkyltrifluoroborates was also amenable to the reaction conditions. Scaffolds (**5**, **7**–**8**) in entries (9–11) provided the desired dialkylated products in good isolated yield over two steps. A secondary goal from the beginning of this project was to establish reaction conditions that would be tolerant of a wide variety of organotrifluoroborates with various atomic hybridizations, steric, and electronic properties. Incorporation of the challenging cyclopropyl moiety via double Suzuki-Miyaura cross-coupling with the described method was successful for the preparation of **21** and **22**. Evaluation of sp^2-hybridized

trifluoroborates for the production of the phenyl derivatives (entries 14–15) also was successful.[29] The next series of experiments sought to expand the diversity of scaffold application by studying the efficacy of the method towards scaffolds with three or four reaction sites, respectively, as well as 6-bromopyridinyl complexant scaffolds.

Table 2. Suzuki-Miyaura Cross-Coupling with Diversified Organotrifluoroborates



Entry	Substrate	RBF_3K	Product	Yield[a]
1	**5**	CH_3BF_3K	 **11** R^1=H, **12** R^1=CH_3	**11** (56)[b]
2	**7**			**12** (99)
3	**5**	$CH_3(CH_2)_nBF_3K$ n = 3, or 7	 **6** R^1=R^2=H, n = 3; **13** R^1=R^2=H, n = 7; **14** R^1=H, R^2=CH_3, n = 3; **15** R^1=H, R^2=CH_3, n = 7; **16** R^1=CH_3, R^2=H, n = 3; **17** R^1=CH_3, R^2=H, n = 7	**6** (97)
4	**5**			**13** (48)[b, c]
5	**7**			**14** (45)
6	**7**			**15** (61)
7	**8**			**16** (92)
8	**8**			**17** (80)
9	**5**		 **18** R^1=R^2=H, n = 2; **19** R^1=H, R^2=CH_3, n = 2; **20** R^1=CH_3, R^2=H, n = 2	**18** (91)[d]
10	**7**			**19** (74)
11	**8**			**20** (89)
12	**5**		 **21** R^1=H, **22** R^1=CH_3	**21** (62)
13	**7**			**22** (87)
14	**5**	$PhBF_3K$	 **23** R^1=H, **24** R^1=CH_3	**23** (60)
15	**7**			**24** (52)[b,d]
16	**9**	$CH_3(CH_2)_3BF_3K$	 n = 3	**25** (47)[e]

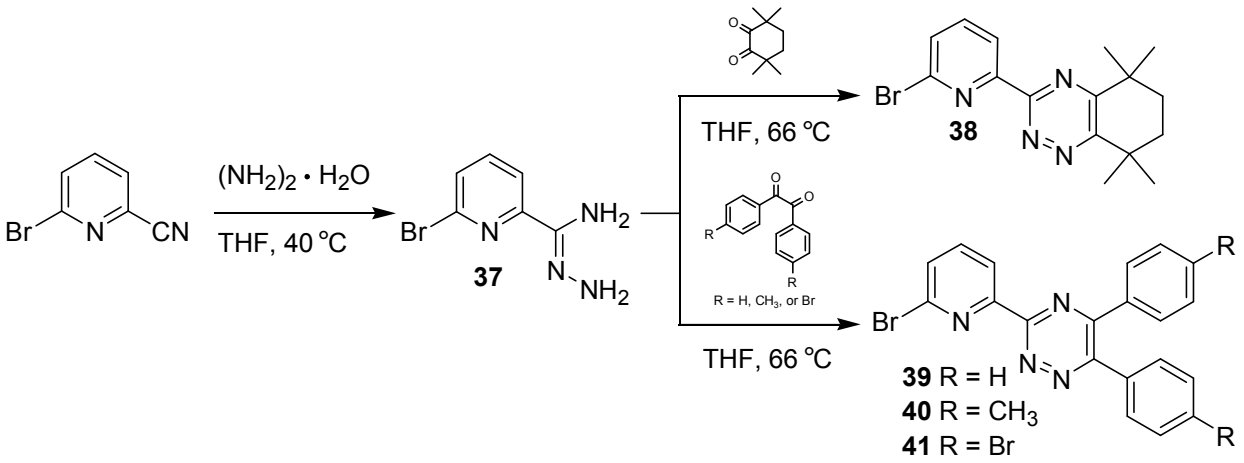
Entry	Substrate	RBF_3K	Product	Yield[a]
17	**9**		 n = 2	**26** (52)[e]
18	**10**		 n = 2, = L	**27** (71)[f]
19	 **38**			**28** (78)[g]
20	 **40**	$PhBF_3K$		**29** (64)[h]
21			 n = 2	**30** (99)[i]
22	4,4'-dibromobenzil			**31** (43)
23	4,4'-dibromobenzil		 n = 2	**32** (78)

[a]Isolated, purified yield over one, two, or three synthetic steps depending on scaffold: **5**, **7**-**8**, **9**, or **10**, [b]10.0 mol % catalyst, 20 mol % ligand, utilized, [c]Average yield from 3 experiments, [d]Average yield from 2 experiments [e] 15 mol % catalyst, 30 mol % ligand, 3.15 equiv of RBF_3K utilized, [f]40 mol % catalyst, 80 mol % ligand, 4.20 equiv of RBF_3K utilized, [g]10 mol % catalyst, 20 mol % ligand, 1.05 equiv of RBF_3K utilized, [h]5 mol % catalyst, 10 mol % ligand, 1.05 equiv of RBF_3K utilized, [i]Yield calculated from ^1H NMR of crude reaction mixture,

At this point in the study we wished to ascertain the applicability of the optimized conditions towards substrates with more than two reactive sites. Treatment of 5,6-bis-(4-bromo-phenyl)-3-(6-bromo-pyridin-2-yl)-[1,2,4]triazine with 15 mol % of $Pd(OAc)_2$ and 30 mol % of RuPhos provided the desired trialkylated compounds **25** and **26** in acceptable isolated yield over three steps even though each of the reactions performed involved metal-mediated cross-coupling at two very electronically diverse sites. With the momentum of the previous results serving as impetus, we next evaluated a tetrabromo-BTP previously prepared in this laboratory under the described conditions. Much to our delight complete conversion of scaffold **10** was obtained at 10/20 mol % catalyst/ligand loading per reaction site for a substrate which has the potential to serve as a dative ligand for palladium and contains four reaction sites. Purification of this material was challenging, but the desired product could be accessed in 71% yield under the reported conditions.

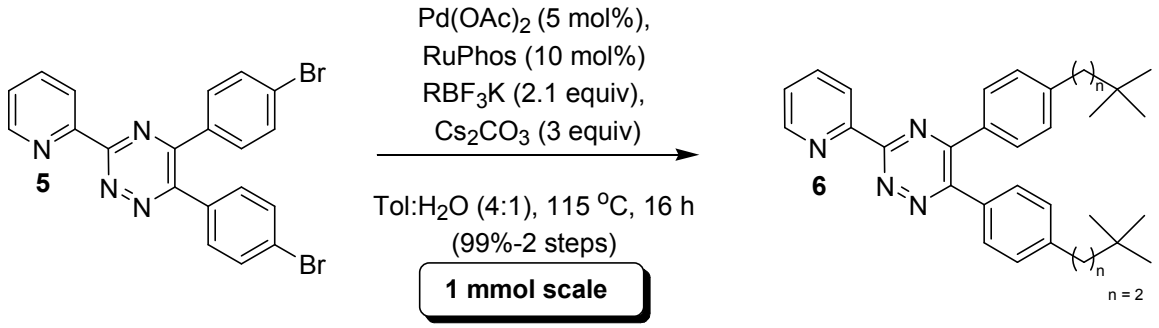
Evaluation of cross-coupling with 6-bromotriazinyl pyridine scaffolds was investigated next. Preparation of these novel scaffolds was executed via treatment of the requisite pyridinecarbonitrile with hydrazine hydrate at elevated temperature, followed by direct isolation and telescoping of the intermediary hydrazonamide to the corresponding 1,2,4-triazinyl derivative via condensation with an appropriate 1,2-dicarbonyl pursuant to methods developed in this laboratory (Scheme 1).[30]

Scheme 1. Preparation of Novel 6-bromotriazinyl Pyridine Scaffolds Utilized



Treatment with potassium organotrifluoroborates (entries 19–20) proved amenable to the described conditions, although an increase in catalyst and ligand loading was required to maintain high levels of conversion.[31] The broad applicability of the described work is not just limited to multiple Suzuki-Miyaura couplings of complexant scaffolds. Alternatively explored substrates including 1,4-dibromobenzene (entry 21), as well as 4,4'-dibromobenzil all successfully underwent the reported transformation (entries 22–23). The case of 4,4'-dibromobenzil is very instructive given the ability to utilize the derived compounds in subsequent condensation chemistry to afford more diverse complexants which may not be suitable for metal-mediated cross-coupling. In order to validate the applicability of the described method towards the preparation of larger quantities of material, a ten-fold scale-up experiment with 1 mmol of **5** was executed with potassium 3,3-dimethylbutyltrifluoroborate (Scheme 2). Thus, treatment of **5** using the standard conditions afforded quantitative conversion of the starting material by NMR and resulted in a 99% isolated yield upon purification by automated flash-column chromatography.

Scheme 2. Double Suzuki-Miyaura Cross-Coupling Scale-Up Reaction



A proposed catalytic cycle for the conversion of **5** is described in Figure 2. Treatment of palladium acetate with the RuPhos ligand affords Pd^0 which complexes an additional RuPhos to provide the postulated catalytically active species. Oxidative addition of the catalyst into the C-Br bond of the heteroarene scaffold **5** affords a palladium (II) intermediate (**33**) for ligand exchange. Sigma-bond metathesis of an *in situ* generated alkoxide provides intermediate **34**. Transmetallation of the organohydroxyborate species (**35**) followed by reductive elimination affords the new C-C bond (**36**) and regenerates the putative catalytically-active species for additional turnovers. Whether the substrate scope evaluated undergoes iterative coupling via **36**, or a related intermediate, progressing through the described catalytic cycle for each discrete coupling or if simultaneous di-, tri-, or tetracoupling occurs is subject to interpretation as a concrete mechanistic hypothesis was not evaluated in the context of the described work.

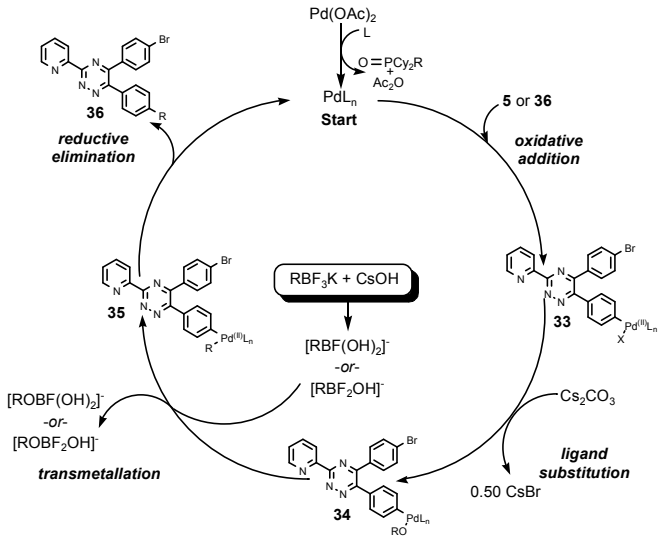


Figure 2. Proposed Catalytic Cycle for Suzuki-Miyaura Coupling of Complexant Scaffolds.

Conclusion

In summary, we have developed an efficient set of reaction parameters for the efficient preparation of multi cross-coupled complexant scaffolds. The described method accomplishes the desired mono-, di-, and tri- Suzuki-Miyaura cross-couplings on bromoheteroarene complexant scaffolds with modest loadings as low as 2.5 mol % of catalyst and 5.0 mol % of ligand per reaction site for several MTP-derivatives enabling for the first time modulation of electronic and solubility properties of a given complexant scaffold directly from a common precursor without the inefficiency of linear synthetic routes anchored in condensation strategies. The twenty-three examples described highlight the versatility of the transformation with structurally diverse scaffolds as well as electronically and sterically varied sp^2 and sp^3 hybridized organotrifluoroborates. The novel complexants prepared will be evaluated in the context of biphasic separation assays with Am^{3+}. Future work will focus on delineation of the listed method to additional BTP and BTPhen scaffold for thorough analysis of complexant core rigidity on performance with the same substituents, as well achieving success on currently recalcitrant examples.

Experimental Section

Preparation of scaffolds **5**, **7–8**, and **10** has been previously reported.[32]

General. All reagents were purchased from U.S. chemical suppliers, stored according to published protocols, and used as received unless indicated otherwise. All experiments were performed in oven- or flame-dried glassware under an inert atmosphere of Ar except where indicated. Reaction progress was monitored using thin-layer chromatography on glass-backed silica gel plates and/or ^{1}H-NMR analysis of crude reaction mixtures. R_F values for compounds that resulted in a concentrically observed spot on normal phase silica gel are reported using the conditions listed. All reported yields listed are for pure compounds and corrected for residual solvent, if applicable, from ^{1}H NMR spectroscopy unless otherwise indicated. Infrared spectral data was acquired from the (form) listed. All ^{1}H and ^{13}C NMR chemical shifts are reported using the δ scale and are referenced to the residual solvent signal: $CDCl_3$ (δ 7.26) or DMSO-d_6 (δ 2.50) for ^{1}H-NMR and chloroform (δ 77.0), DMSO-d_6 (δ 39.52) for ^{13}C-NMR. Splittings are reported as follows: (s) = singlet, (d) = doublet, (t) = triplet, (dd) = doublet of doublets, (dt) = doublet of triplets, (br) = broad, and (m) = multiplet. High resolution mass spectrometry (HRMS) data was obtained utilizing electron impact ionization (EI) with a magnetic sector (EBE trisector), double focusing-geometry mass analyzer unless indicated otherwise.

General Procedure for Suzuki-Miyaura Coupling of Complexant Scaffolds. To an 8 mL reaction vial equipped with a magnetic stir bar at ambient temperature were charged $Pd(OAc)_2$, RuPhos, Cs_2CO_3 (3 equiv), the requisite substrate (0.107 mmol), and the desired organotrifluoroborate (equivalents listed for each reaction). The mixture was slurried in Tol:H_2O (4:1) (0.2 M) and heated to 115 °C for 16 hours upon which time the crude mixture was analyzed by ^{1}H NMR. Absorption of the crude mixture onto normal phase silica gel followed by

purification on a 4 g normal phase silica gel column by automated flash-column chromatography using an EtOAc:hexanes or MTBE:hexanes gradient mobile phases afforded the desired product in the reported yield.

3-Pyridin-2-yl-5,6-di-*p*-tolyl-[1,2,4]triazine (11). Prepared according to the general procedure discussed above with substrate **5**: (10.0 mol % catalyst, 20.0 mol % ligand, 2.10 equiv CH_3BF_3K), R_F = 0.24, 100% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0204 g, 56%; orange oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.93 (d, *J* = 4.5 Hz, 1H), 8.70 (d, *J* = 8.0 Hz, 1H), 7.94 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.50–7.47 (m, 1H), 7.21 (7.8 Hz, 2H), 7.19 (7.8 Hz, 2H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.3, 156.4, 156.1, 152.9, 150.3, 141.2, 139.9, 137.2, 132.9, 132.6, 129.9, 129.4, 129.34, 129.27, 125.3, 124.1, 21.5, 21.4; IR ($CDCl_3$): $\bar{\upsilon}_{max}$ = 3032, 2972, 2921, 1608, 1585, 1491, 1389, 1369, 821 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{22}H_{18}N_4$: 338.1531; found: 338.1536.

3-(6-Methyl-pyridin-2-yl)-5,6-di-*p*-tolyl-[1,2,4]triazine (12). Prepared according to the general procedure discussed above with substrate **7**: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of CH_3BF_3K), R_F = 0.29, 50% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0376 g, 99%; yellow solid; mp 146.8–149.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 7.5 Hz, 1H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.58–7.55 (m, 2H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.78 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.6, 159.4, 156.1, 155.8, 152.6, 141.2, 139.8, 137.1, 133.0, 132.7, 129.9, 129.4, 129.3, 129.2, 125.1, 121.3, 24.9, 21.5, 21.4; IR ($CDCl_3$): $\bar{\upsilon}_{max}$ = 3031, 2921, 2859, 1609, 1590, 1492, 1382, 1360, 819, 724 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{23}H_{20}N_4$: 352.1688; found: 352.1689.

5,6-Bis-(4-butyl-phenyl)-3-pyridin-2-yl-[1,2,4]triazine (6). Prepared according to the general procedure discussed above with substrate **5**: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $CH_3(CH_2)_3BF_3K$), R_F = 0.36, 100% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0439 g, 97%; orange gum; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.03 (d, *J* = 4.4 Hz, 1H), 8.80 (d, *J* = 8.0 Hz, 1H), 8.07 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.61–7.60 (m, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.66–1.56 (m, 4H), 1.41–1.30 (m, 4H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.7, 156.7, 156.3, 151.4, 148.8, 146.6, 145.2, 139.2, 132.53, 132.50, 130.2, 129.4, 128.7, 128.6, 125.9, 124.4, 35.51, 35.46, 33.2, 33.1, 22.3, 22.2, 13.90, 13.87 ; IR ($CDCl_3$): $\bar{\upsilon}_{max}$ = 3032, 2956, 2929, 2858, 1609, 1584, 1467, 1452, 1389, 1369, 836 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{28}H_{30}N_4$: 422.2470; found: 422.2475.

5,6-Bis-(4-octyl-phenyl)-3-pyridin-2-yl-[1,2,4]triazine (13). Prepared according to the general procedure discussed above with substrate **5**: (10.0 mol % catalyst, 20.0 mol % ligand, 2.10 equiv of $CH_3(CH_2)_7BF_3K$), R_F = 0.55, 100% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0248 g, 48% (average yield from three experiments: 58%, 53%, 34%); brown gum; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.16 (d, *J* = 4.5 Hz, 1H), 8.92 (d, *J* = 8.2 Hz, 1H), 8.24 (t, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.75 (br-t, *J* = 6.5 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.68–1.57 (m, 4H), 1.36–1.20 (br-m, 20H), 0.92–0.85 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.6, 157.0, 156.4, 150.2, 147.8, 147.0, 145.5, 140.8, 132.4, 132.1, 130.5, 129.4, 128.8, 128.7, 126.3, 124.7, 35.9, 35.8, 31.8, 31.4, 31.0, 31.X (overlaps with 31.0), 29.41 (29.3X; three resonances overlap with 29.41), 29.25, 29.22, 22.6, 22.5X (overlaps with 22.6), 14.1,

14.0X (overlaps with 14.1); IR ($CDCl_3$): $\bar{\upsilon}_{max}$ = 3032, 2925, 2854, 1609, 1493, 1467, 1390, 1369, 835 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{36}H_{46}N_4$: 534.3722; found: 534.3734.

5,6-Bis-(4-butyl-phenyl)-3-(4-methyl-pyridin-2-yl)-[1,2,4]triazine (14). Prepared according to the general procedure discussed above with substrate **7**: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $CH_3(CH_2)_3BF_3K$), R_F = 0.34, 50% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0184 g, 45%; yellow-orange gum; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 8.2 Hz, 1H), 8.30 (t, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 3.26 (s, 3H), 2.66 (t, *J* = 8.0 Hz, 2H), 2.63 (t, *J* = 8.0 Hz, 2H), 1.67–1.55 (m, 4H), 1.42–1.29 (m, 4H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.6, 157.5, 156.6, 155.2, 147.9, 147.1, 145.8, 144.0, 132.0, 131.9, 130.9, 129.5, 128.85, 128.82, 128.7, 123.6, 35.59, 35.52, 33.2, 33.1, 22.3, 22.2, 21.3, 13.92, 13.88; IR (neat): $\bar{\upsilon}_{max}$ = 3030, 2955, 2927, 2857, 1609, 1590, 1490, 1454, 1381, 1359, 833, 796 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{29}H_{32}N_4$: 436.2627; found: 436.2619.

3-(4-Methyl-pyridin-2-yl)-5,6-bis-(4-octyl-phenyl)-[1,2,4]triazine (15). Prepared according to the general procedure discussed above with substrate **7**: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $CH_3(CH_2)_7BF_3K$), R_F = 0.47, 50% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0314 g, 61%; brown-orange gum; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 8.2 Hz, 1H), 8.09 (t, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 3.04 (s, 3H), 2.67–2.59 (m, 4H), 1.67–1.56 (m, 4H), 1.38–1.20 (br-m, 20H), 0.91–0.83 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.4, 157.7, 156.9, 156.3, 150.1, 146.6, 145.3, 140.7, 132.4, 132.36, 130.4, 129.4, 128.7, 128.66, 127.0, 122.5, 35.8, 35.78, 31.82, 31.8X (overlaps with 31.82), 31.1,

31.0, 29.38, 29.3X (overlaps with 29.38), 29.22, 29.2X (overlaps with 29.22), 29.17, 29.1X (overlaps with 29.17), 22.62, 22.6X (overlaps with 22.62), 14.16, 14.1X (overlaps with 14.16); IR (neat): $\bar{\upsilon}_{max}$ = 3031, 2923, 2853, 1609, 1590, 1492, 1464, 1381, 1360, 830 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{37}H_{48}N_4$: 548.3879; found: 548.3887.

5,6-Bis-(4-butyl-phenyl)-3-(6-methyl-pyridin-2-yl)-[1,2,4]triazine (16). Prepared according to the general procedure discussed above with substrate **8**: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $CH_3(CH_2)_3BF_3K$), R_F = 0.40, 50% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0429 g, 92%; orange solid; mp 79.9–84.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 7.0 Hz, 1H), 7.97 (t, *J* = 7.0 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.92 (s, 3H), 2.68–2.60 (m, 4H), 1.65–1.56 (m, 4H), 1.40–1.30 (m, 4H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.9, 158.8, 156.6, 156.1, 151.1, 146.4, 145.1, 139.3, 132.7, 132.6, 130.2, 129.4, 128.7, 128.6, 126.2, 122.0, 35.51, 35.46, 33.3, 33.1, 23.7, 22.3, 22.2, 13.91, 13.87; IR (neat): $\bar{\upsilon}_{max}$ = 3030, 2928, 2858, 1609, 1590, 1491, 1464, 1381, 1360, 833, 796, 729 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{29}H_{32}N_4$: 436.2627; found: 436.2617.

3-(6-Methyl-pyridin-2-yl)-5,6-bis-(4-octyl-phenyl)-[1,2,4]triazine (17). Prepared according to the general procedure discussed above with substrate **8**: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $CH_3(CH_2)_7BF_3K$), R_F = 0.51, 50% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0473 g, 80%; orange gum; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 8.0 Hz, 1H), 8.04 t, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 3.00 (s, 3H), 2.65–2.59 (m, 4H), 1.67–1.55 (m, 4H), 1.38–1.21 (br-m, 20H), 0.90–0.84 (m, 6H); ^{13}C NMR (125 MHz,

$CDCl_3$): δ = 158.5, 158.1, 156.8, 156.2, 150.4, 146.6, 145.3, 140.2, 132.5, 132.4, 130.4, 129.4, 128.73, 128.66, 126.8, 122.3, 35.9, 35.8, 31.8, 31.7X (overlaps with 31.8), 31.1, 31.0, 29.4, 29.3X (overlaps with 29.4), 29.24, 29.2X (overlaps with 29.24), 29.19, 29.1X (overlaps with 29.19), 32.2, 22.6, 22.5X (overlaps with 22.6), 14.1, 14.0X (overlaps with 14.1); IR ($CDCl_3$): $\bar{\upsilon}_{max}$ = 3030, 2925, 2854, 1609, 1590, 1493, 1465, 1381, 1360 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{37}H_{48}N_4$: 548.3879; found: 548.3871.

5,6-Bis-[4-(3,3-dimethyl-butyl)-phenyl]-3-pyridin-2-yl-[1,2,4]triazine (18). Prepared according to the general procedure discussed above with substrate **5**: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $(CH_3)_3C(CH_2)_2BF_3K$), R_F = 0.51, 100% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0467 g, 91% (average yield from two experiments: 94%, 89%); yellow-orange solid; mp 151.3–157.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.06 (d, *J* = 5.0 Hz, 1H), 8.83 (d, *J* = 8.0 Hz, 1H), 8.12 (t, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.67–7.63 (br-m, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.65–2.57 (m, 4H), 1.56–1.47 (m, 4H), 0.97 (s, 9H), 0.95 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.1, 156.8, 156.3, 150.8, 148.3, 147.5, 146.0, 140.0, 132.4, 132.3, 130.4, 129.5, 128.72, 128.65, 126.1, 124.5, 45.9, 45.8, 31.3, 31.2, 30.6, 30.5X (overlaps with 30.6), 29.3, 29.2X (overlaps with 29.3); IR (neat): $\bar{\upsilon}_{max}$ = 3055, 2928, 1587, 1488, 1443, 1432, 1372, 1350, 825, 773 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{32}H_{38}N_4$: 478.3096; found: 478.3105.

5,6-Bis-[4-(3,3-dimethyl-butyl)-phenyl]-3-(4-methyl-pyridin-2-yl)-[1,2,4]triazine (19). Prepared according to the general procedure discussed above with substrate **7**: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $(CH_3)_3C(CH_2)_2BF_3K$), R_F = 0.53, 50% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0390 g, 74%; orange solid; mp 137.9–144.4°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 8.0 Hz, 1H), 8.03 (t, *J* = 8.0

Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.98 (s, 3H), 2.65–2.56 (m, 4H), 1.56–1.46 (m, 4H), 0.97 (s, 9H), 0.95 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.6, 158.3, 156.7, 156.1, 150.6, 147.2, 145.9, 140.0, 132.5, 132.4, 130.4, 129.5, 128.7, 128.6, 126.6, 122.2, 45.84, 45.77, 31.2, 31.1, 30.58, 30.5X (overlaps with 30.58), 29.31, 29.2X (overlaps with 29.31), 23.4; IR (neat): $\bar{\upsilon}_{max}$ = 3031, 2953, 2865, 1609, 1492, 1383, 1364, 727, cm^{-1}; HRMS (EI): *m/z* calculated for $C_{33}H_{40}N_4$: 492.3253; found: 492.3236.

5,6-Bis-[4-(3,3-dimethyl-butyl)-phenyl]-3-(6-methyl-pyridin-2-yl)-[1,2,4]triazine (20). Prepared according to the general procedure discussed above with substrate **8**: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $(CH_3)_3C(CH_2)_2BF_3K$), R_F = 0.59, 50% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0473 g, 89%; orange solid; mp 145.1–149.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.60 (d, *J* = 7.5 Hz, 1H), 8.01 (t, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 2.96 (s, 3H), 2.64–2.55 (m, 4H), 1.54–1.45 (m, 4H), 0.96 (s, 9H), 0.94 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.6, 158.4, 156.6, 156.1, 150.7, 147.2, 145.9, 139.8, 132.6, 132.5, 130.4, 129.5, 128.7, 128.6, 126.5, 122.2, 45.85, 45.77, 31.25, 31.15, 30.6, 30.5X (overlaps with 30.6), 29.3, 29.2X (overlaps with 29.3), 23.4, ;IR ($CDCl_3$): $\bar{\upsilon}_{max}$ = 3004, 2926, 2854, 1609, 1591, 1491, 1383, 1361, 827, 731 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{33}H_{40}N_4$: 492.3253; found: 492.3258.

5,6-Bis-(4-cyclopropyl-phenyl)-3-pyridin-2-yl-[1,2,4]triazine (21). Prepared according to the general procedure discussed above with substrate **5**: (10.0 mol % catalyst, 20.0 mol % ligand, 2.10 equiv of $C_3H_5BF_3K$), EtOAc/hexanes (gradient); isolated yield 0.0260 g, 62% (average of two experiments: 46%, 78%); orange film; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.11 (d, *J* = 5.0 Hz,

1H), 8.86 (d, *J* = 8.2 Hz, 1H), 8.17 (t, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.69 (br-t, *J* = 6.50 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 1.96–1.86 (m, 2H), 1.07–1.00 (m, 4H), 0.79–0.73 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.7, 156.6, 156.0, 150.4, 148.4, 148.0, 146.8, 140.3, 132.1, 131.8, 130.4, 129.4, 126.2, 125.8, 125.7, 124.5, 20.5, 20.4X (overlaps with 20.5), 15.6, 15.5, 10.2, 10.0; IR ($CDCl_3$): $\bar{\upsilon}_{max}$ = 3005, 1608, 1492, 1391, 1371, 903, 728 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{26}H_{22}N_4$: 390.1844; found: 390.1847.

5,6-Bis-(4-cyclopropyl-phenyl)-3-(6-methyl-pyridin-2-yl)-[1,2,4]triazine (22). Prepared according to the general procedure discussed above with substrate **7**: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $C_3H_5BF_3K$), R_F = 0.27, 50% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0379 g, 87%; orange-yellow solid; mp 128.7–130.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.58 (d, 8.2 Hz, 1H), 7.99 (t, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 2.94 (s, 3H), 1.95–1.86 (m, 2H), 1.05–1.00 (m, 4H), 0.78–0.72 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.7, 158.5, 156.4, 155.8, 150.8, 148.0, 146.5, 139.5, 132.3, 132.2, 130.3, 129.4, 126.4, 125.7, 125.6, 122.0, 23.55, 23.5X (2 resonances overlap with 23.55), 15.6, 15.4, 10.2, 9.9; IR ($CDCl_3$): $\bar{\upsilon}_{max}$ = 3004, 2926, 2854, 1609, 1591, 1491, 1383, 1361, 827, 731 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{27}H_{24}N_4$: 404.2001; found: 404.1991.

5,6-Bis-biphenyl-4-yl-3-pyridin-2-yl-[1,2,4]triazine (23). Prepared according to the general procedure discussed above with substrate **5**: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $C_6H_6BF_3K$), R_F = 0.34, 100% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0298 g, 60%; orange solid; mp 126.9–131.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.95 (d, *J* = 5.0 Hz, 1H), 8.74 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.96 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.86–7.84 (m,

2H), 7.81–7.78 (m 2H), 7.68–7.61 (m, 8H), 7.51–7.49 (m, 1H), 7.48–7.44 (m, 4H), 7.40–7.36 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.6, 156.1, 155.9, 152.9, 150.5, 143.6, 142.6, 140.1, 139.9, 137.1, 134.5, 134.2, 130.5, 130.0, 128.9, 128.8X (overlaps with 128.9), 128.0, 127.9, 127.34, 127.27, 127.13, 127.11, 125.4, 124.2; IR ($CDCl_3$): $\bar{\upsilon}_{max}$ = 3029, 3001, 1606, 1583, 1483, 1388, 1370, 860, 768, 698 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{32}H_{22}N_4$: 462.1844; found: 462.1853.

5,6-Bis-biphenyl-4-yl-3-(6-methyl-pyridin-2-yl)-[1,2,4]triazine (24). Prepared according to the general procedure discussed above with substrate **7**: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $C_6H_6BF_3K$), R_F = 0.45, 100% EtOAc; eluent, EtOAc/hexanes (gradient); isolated yield 0.0211 g, 52%; orange solid; mp 131.7–138.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 7.5 Hz, 1H), 7.86 (br-d, *J* = 8.0 Hz, 2H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.68–7.61 (m, 8H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.40–7.35 (m, 3H), 2.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.8, 159.5, 155.8, 155.5, 152.4, 143.6, 142.5, 140.1, 140.0, 137.2, 134.5, 134.3, 130.5, 130.0, 128.9, 128.8X (overlaps with 128.9), 128.0, 127.8, 127.3, 127.2, 127.12, 127.10, 125.2, 121.4, 24.9; IR (neat): $\bar{\upsilon}_{max}$ = 3031, 2963, 1606, 1485, 1383, 1360, 728, 696 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{33}H_{24}N_4$: 476.2001; found: 476.2014.

5,6-Bis-(4-butyl-phenyl)-3-(6-butyl-pyridin-2-yl)-[1,2,4]triazine (25). Prepared according to the general procedure discussed above with substrate **9**: (15.0 mol % catalyst, 30.0 mol % ligand, 3.15 equiv of $CH_3(CH_2)_3BF_3K$), R_F = 0.86, 40 % EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0207 g, 47%; brown-orange gum; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 7.8 Hz, 1H), 781 (t, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.02–2.98 (m, 2H), 2.68–2.61 (m, 4H), 1.86–1.80 (m, 2H), 1.66–1.57 (m, 4H), 1.51–1.43 (m, 2H), 1.41–1.31

(m, 4H), 0.98 (t, J = 7.5 Hz, 3H), 0.96–0.91 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.5, 160.8, 156.0, 155.7, 152.6, 146.1, 144.7, 137.0, 133.2, 132.9, 129.9, 129.4, 128.6, 128.5, 124.2, 121.4, 38.3, 35.52, 35.48, 33.29, 33.21, 32.0, 22.6, 22.32, 22.26, 14.0, 13.92, 13.89; IR (neat): $\tilde{\upsilon}_{max}$ = 3031, 2956, 2928, 2858, 1589, 1572, 1491, 1457, 1382, 1362, 832, 728 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{32}H_{38}N_4$: 478.3096; found: 478.3087.

5,6-Bis-[4-(3,3-dimethyl-butyl)-phenyl]-3-[6-(3,3-dimethyl-butyl)-pyridin-2-yl]-[1,2,4]triazine (26). Prepared according to the general procedure discussed above with substrate **9**: (20.0 mol % catalyst, 40.0 mol % ligand, 3.15 equiv of $(CH_3)_3C(CH_2)_2BF_3K$), R_F = 0.71, 30% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0220 g, 52%; orange-yellow solid; mp 160.9–163.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (d, J = 8.2 Hz, 1H), 8.08 (br-t, J = 8.2 Hz, 1H), 7.86 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.2 Hz, 1H), 7.21 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 3.38–3.29 (br-s, 2H), 2.64–2.56 (m, 4H), 1.79–1.74 (m, 2H), 1.55–1.46 (m, 4H), 1.04 (s, 9H), 0.97 (s, 9H), 0.95 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.5, 158.2, 156.6, 156.0, 150.4, 147.2, 145.9, 140.2, 132.6, 132.4, 130.59, 129.5, 128.65, 128.58, 125.7, 124.4, 45.84, 45.78, 44.0, 31.3, 31.2, 30.8, 30.7X (overlaps with 30.8), 30.6, 29.4, 29.32, 29.31; IR ($CDCl_3$): $\tilde{\upsilon}_{max}$ = 3036, 2951, 2864, 1610, 1587, 1490, 1466, 1391, 1362, 834 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{38}H_{50}N_4$: 562.4035; found: 562.4044.

1,4-Bis-(3,3-dimethylbutyl)-Bis-[1,2,4]-triazinylpyridine (27). Prepared according to the general procedure discussed above with substrate **10**: (40.0 mol % catalyst, 80.0 mol % ligand, 4.20 equiv of $(CH_3)_3C(CH_2)_2BF_3K$), R_F = 0.57, 50 % EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0669 g, 71%; orange solid; mp 214.1-217.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.87 (d, J = 7.8 Hz, 2H), 8.18 (t, J = 7.8 Hz, 1H), 7.76 (d, J = 8.0 Hz, 4H), 7.61 (d, J = 8.0 Hz, 4H), 7.23 (d, J = 8.0 Hz, 4H), 7.21 (d, J = 8.0 Hz, 4H), 2.66–2.60 (m, 8H), 1.56–1.50

(m, 8H), 0.98 (s, 18H), 0.97 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.2, 156.3, 156.0, 153.7, 149.9, 145.6, 138.2, 133.0, 132.8, 130.1, 129.4, 128.6, 128.5, 125.3, 45.89, 45.85, 31.3, 31.2, 30.6, 30.5X (overlaps with 30.6), 29.3, 29.3X (overlaps with 29.3); IR ($CDCl_3$): $\bar{\upsilon}_{max}$ = 3032, 2953, 2865, 1609, 1493, 1365 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{59}H_{71}N_7$: 877.5771; found: 877.5806.

3-[6-(3,3-Dimethyl-butyl)-pyridin-2-yl]-5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazine (28). Prepared according to the general procedure discussed above: (10.0 mol % catalyst, 20.0 mol % ligand, 1.05 equiv of $(CH_3)_3C(CH_2)_2BF_3K$), R_F = 0.78, 50% EtOAc:hexanes; eluent, MTBE/hexanes (gradient); isolated yield 0.0293 g, 78%; yellow gum; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 7.8 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 2.97–2.92 (m, 2H), 1.86 (s, 4H), 1.75–1.70 (m, 2H), 1.49 (s, 6H), 1.41 (s, 6H), 0.99 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.0, 163.9, 162.7, 161.2, 153.2, 136.9, 123.8, 120.9, 43.9, 37.1, 36.4, 34.1, 33.8, 33.3, 30.6, 29.7, 29.4, 29.2; IR ($CDCl_3$): $\bar{\upsilon}_{max}$ = 3064, 2938, 2860, 1588, 1571, 1508, 1455, 1388, 1372. 1361, 819, 719 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{22}H_{32}N_4$: 352.2627; found: 352.2629.

3-(6-Phenyl-pyridin-2-yl)-5,6-di-*p*-tolyl-[1,2,4]triazine (29). Prepared according to the general procedure discussed above: (5.0 mol % catalyst, 10.0 mol % ligand, 1.05 equiv of $C_6H_6BF_3K$), R_F = 0.78, 50% EtOAc:hexanes; eluent, EtOAc/hexanes (gradient); isolated yield 0.0240 g, 64%; brown-yellow solid; mp 210.3–213.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 7.5 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 2H), 8.14–8.07 (br-m, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.0 Hz, 2H), 7.51–7.46 (m, 1H), 7.21 (d, *J* = 4.5 Hz, 2H), 7.20 (d, *J* = 4.5 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.5, 157.8, 156.1, 155.8, 152.9, 141.3, 140.0, 138.9, 137.8, 133.0, 132.87, 129.9, 129.8X

(overlaps with 129.9), 129.4, 129.3, 129.2X (overlaps with 129.3), 128.7, 127.2, 122.4, 121.9, 21.5, 21.5; IR (neat): $\bar{\upsilon}_{max}$ = 3033, 2922, 2854, 1608, 1579, 1488, 1461, 1378, 822, 765, 698 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{28}H_{22}N_4$: 414.1844; found: 414.1859.

1,4-Bis-(3,3-dimethyl-butyl)-benzene (30). Prepared according to the general procedure discussed above with 1,4-dibromobenzene: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $(CH_3)_3C(CH_2)_2BF_3K$), R_F = 0.80, 10% EtOAc:hexanes; eluent, MTBE/hexanes (gradient); isolated yield 0.0258 g, 99%; white solid; mp 79.1–81.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (s, 4H), 2.56–2.51 (m, 4H), 1.51–1.46 (m, 4H), 0.96 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.6, 128.2, 45.5, 30.7, 30.5, 29.3; IR (neat): $\bar{\upsilon}_{max}$ = 2954, 2866, 1514, 1467, 1365, 906, 730 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{18}H_{30}$: 246.2348; found: 246.2340.

1,2-Bis-(4-cyclopropyl-phenyl)-ethane-1,2-dione (31). Prepared according to the general procedure discussed above with 4,4'-dibromobenzil: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $C_3H_5BF_3K$), R_F = 0.79, 30 % EtOAc:hexanes; eluent, MTBE/hexanes (gradient); isolated yield 0.0169 g, 43%; light yellow solid; mp 85.0–91.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.4 Hz, 4H), 7.13 (d, *J* = 8.4 Hz, 4H), 1.98–1.91 (m, 2H), 1.12–1.06 (m, 4H), 0.82–0.77 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_{36}$): δ = 194.4, 152.7, 130.5, 130.1, 125.8, 16.0, 10.8; IR ($CDCl_3$): $\bar{\upsilon}_{max}$ = 3086, 3004, 2972, 1667, 1601, 1220, 1170 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{20}H_{18}O_2$: 290.1307; found: 290.1309.

1,2-Bis-[4-(3,3-dimethyl-butyl)-phenyl]-ethane-1,2-dione (32). Prepared according to the general procedure discussed above with 4,4'-dibromobenzil: (5.0 mol % catalyst, 10.0 mol % ligand, 2.10 equiv of $(CH_3)_3C(CH_2)_2BF_3K$), R_F = 0.90, 30% EtOAc:hexanes; eluent, MTBE/hexanes (gradient); isolated yield 0.0401 g, 78%; off-white solid; mp 73.9–78.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.2 Hz, 4H), 7.30 (d, *J* = 8.2 Hz, 4H), 2.66–2.61 (m,

4H), 1.52–1.47 (m, 4H), 0.96 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.5, 151.7, 130.8, 130.1, 129.0, 45.8, 31.7, 30.6, 29.2; IR (neat): $\bar{\upsilon}_{max}$ = 3031, 2954, 2866, 1671, 1604, 1217, 1172, 732 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{26}H_{34}O_2$: 378.2559; found: 378.2556.

6-Bromo-2-hydrazonamide (37). To an 8 mL reaction vial equipped with a magnetic stirring bar at ambient temperature was charged 6-pyridine-2-carbonitrile (0.500 g, 2.73 mmol, 1.00 equiv). After dissolution in anhydrous THF (4.00 mL, 8.00 vol) the clear solution was cooled to 0 °C treated drop wise with hydrazine monohydrate (60-65% hydrazine) (1.28 mL, 16.39 mmol, 6.00 equiv) and continued for one hour. Afterwards, the homogeneous mixture was allowed to gradually warm to ambient temperature and heated to 40 °C for 12 hours. Afterwards, the heterogeneous mixture was filtered under vacuum at ambient temperature to afford a white filter cake that was conditioned with 5 mL of 0 °C hexanes. The resulting solids were analyzed by ^{1}H NMR confirming consumption of all starting material and were telescoped directly to the condensation step with the appropriate 1,2-dicarbonyl without further purification. R_F = 0.48, 25% EtOAc:hexanes; white solid; mp 214.1–221.5 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.89 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 5.61 (br-s, 2H), 5.50 (br-s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 153.3, 141.4, 139.6, 139.3, 126.7, 118.3; IR (neat): $\bar{\upsilon}_{max}$ = 3444, 3253, 3169, 1642, 1579, 1546, 1450, 1397, 1374, 799 cm^{-1}; HRMS (EI): *m/z* calculated for $C_6H_7BrN_4$: 213.9854; found: 213.9853.

3-(6-Bromo-pyridin-2-yl)-5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazine (38). To an 8 mL reaction vial equipped with a magnetic stir bar at ambient temperature was added **37** (0.120 g, 0.56 mmol, 1.00 equiv) and 3,3,6,6-tetramethyl-cyclohexane-1,2-dione (0.094 g, 0.56 mmol, 1.00 equiv) in anhydrous THF (1.10 mL, 0.5 M). The resulting yellow-colored mixture was heated to 66 °C for 12 hours. Afterwards the mixture was cooled to ambient temperature

and adsorbed onto 5 g of normal phase SiO_2. The adsorbed solids were purified using automated flash-column chromatography with standard UV detection at 254 nm on a 5 g normal phase silica gel column and elution with an EtOAc:hexanes gradient mobile phase. The requisite fractions were concentrated under reduced pressure at ambient temperature to afford the title compound. R_F = 0.74, 40% EtOAc:hexanes; EtOAc/hexanes (gradient); isolated yield 0.165 g, 85% (over two steps from **37**); yellow solid; mp 119.5–123.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 1.86 (br-s, 4H), 1.49 (s, 6H), 1.41 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.5, 163.4; 159.8; 154.7; 142.7; 139.0; 129.6; 122.4; 37.3; 36.5; 33.7; 33.3; 29.7; 29.2; IR (neat): $\tilde{\upsilon}_{max}$ = 3063, 2964, 2932, 1578, 1557, 1517, 1503, 1456, 1386, 809, 742 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{16}H_{19}BrN_4$: 346.0793; found: 346.0792.

3-(6-Bromo-pyridin-2-yl)-5,6-diphenyl-[1,2,4]triazine (39). To an 8 mL reaction vial equipped with a magnetic stir bar at ambient temperature was added **37** (0.120 g, 0.56 mmol, 1.00 equiv) and benzil (0.117 g, 0.56 mmol, 1.00 equiv) in anhydrous THF (1.10 mL, 0.5 M). The resulting yellow-colored mixture was heated to 66 °C for 12 hours. Afterwards the mixture was cooled to ambient temperature and adsorbed onto 5 g of normal phase SiO_2. The adsorbed solids were purified using automated flash-column chromatography with standard UV detection at 254 nm on a 5 g normal phase silica gel column and elution with an EtOAc:hexanes gradient mobile phase. The requisite fractions were concentrated under reduced pressure at ambient temperature to afford the title compound. R_F = 0.71, 40% EtOAc:hexanes; EtOAc/hexanes (gradient); isolated yield 0.208 g, 96% (over two steps from **37**); yellow solid; mp 161.3–166.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 7.8 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.73–7.67 (m, 3H), 7.66–7.63 (m, 2H), 7.48–7.43 (m, 2H), 7.42–7.35 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ

= 159.6, 156.6, 156.2, 153.9, 142.9, 139.2, 135.4, 130.9, 130.1, 130.0, 129.9, 129.5, 128.7, 128.6, 122.9; IR (neat): $\tilde{\upsilon}_{max}$ = 3058, 1575, 1557, 1492, 1443, 1377, 1359, 768, 696 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{20}H_{13}BrN_4$: 388.0324; found: 388.0324.

3-(6-Bromo-pyridin-2-yl)-5,6-di-*p*-tolyl-[1,2,4]triazine (40). To an 8 mL reaction vial equipped with a magnetic stir bar at ambient temperature was added **37** (0.040 g, 0.18 mmol, 1.00 equiv) and 4,4'-dimethylbenzil (0.045 g, 0.18 mmol, 1.00 equiv) in anhydrous THF (0.37 mL, 0.5 M). The resulting yellow-colored mixture was heated to 66 °C for 12 hours. Afterwards the mixture was cooled to ambient temperature and adsorbed onto 5 g of normal phase SiO_2. The adsorbed solids were purified using automated flash-column chromatography with standard UV detection at 254 nm on a 5 g normal phase silica gel column and elution with an EtOAc:hexanes gradient mobile phase. The requisite fractions were concentrated under reduced pressure at ambient temperature to afford the title compound. R_F = 0.35, 25% EtOAc:hexanes; EtOAc/hexanes (gradient); isolated yield 0.041 g, 52% (over two steps from **37**); yellow solid; mp 133.2–136.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 7.8 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.3, 156.4, 155.9, 154.1, 142.8, 141.4, 140.1, 139.1, 132.6, 132.4, 129.9, 129.37, 129.3X (two resonances overlap with 129.37), 129.30, 122.8, 21.49, 21.40; IR ($CDCl_3$): $\tilde{\upsilon}_{max}$ = 3037, 2921, 2863, 1608, 1573, 1556, 1487, 1373 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{22}H_{17}BrN_4$: 416.0637; found: 416.0637.

5,6-Bis-(4-bromo-phenyl)-3-(6-bromo-pyridin-2-yl)-[1,2,4]triazine (41). To an 8 mL reaction vial equipped with a magnetic stir bar at ambient temperature was added **37** (0.050 g, 0.23 mmol, 1.00 equiv) and 4,4'-dibromobenzil (0.086 g, 0.23 mmol, 1.00 equiv) in anhydrous THF (0.47

mL, 0.5 M). The resulting yellow-colored mixture was heated to 66 °C for 12 hours. Afterwards the mixture was cooled to ambient temperature and adsorbed onto 5 g of normal phase SiO_2. The adsorbed solids were purified using automated flash-column chromatography with standard UV detection at 254 nm on a 5 g normal phase silica gel column and elution with an EtOAc:hexanes gradient mobile phase. The requisite fractions were concentrated under reduced pressure at ambient temperature to afford the title compound. R_F = 0.58, 25% EtOAc:hexanes; EtOAc/hexanes (gradient); isolated yield 0.126 g, 99% (over two steps from **37**); yellow solid; mp 192.7–196.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.62 (d, *J* = 7.8 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.60–7.50 (m, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.7, 155.4, 154.9, 153.5, 143.0, 139.2, 133.9, 133.7, 132.19. 132.13, 131.5, 131.0, 130.4, 126.2, 125.0, 123.0; IR (neat): $\tilde{\upsilon}_{max}$ = 3054, 2926, 2854, 1617, 1486, 1374, 1358, 828, 795 cm^{-1}; HRMS (EI): *m/z* calculated for $C_{20}H_{11}Br_3N_4$: 543.8539; found: 543.8534.

Associated Content

Supporting Information. Copies of ^{1}H and ^{13}C NMR spectra as well as purification chromatograms for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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[29] Preparation of the vinyl derivative was unsuccessful with potassium vinyltrifluoroborate.
[30] For procedures on the preparation of 6-bromopyridinyl scaffolds (**38**–**41**) please see Scheme 2 in the included experimental section.
[31] Cross-coupling of the 6-bromo- MTP-phenyl was successful with potassium butyl-, 3,3-dimethylbutyl-, and cyclopropyl trifluoroborates in high conversion with 10 mol % catalyst and 20 mol % ligand by ^{1}H NMR, but purification to publication standards proved elusive.
[32] Please see reference 6 for the preparation of **5** and **10** and reference 21 for the preparation of **7**–**8**.