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Nickel-Mediated Decarbonylative Cross-Coupling of Phthalimides with in Situ Generated Diorganozinc Reagents

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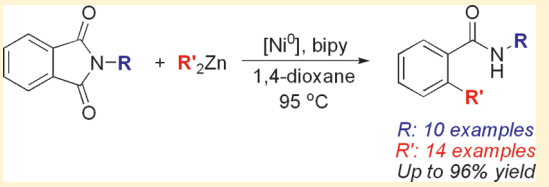
Supporting Information

ABSTRACT: The nickel-mediated cross-coupling of phthalimides with diorganozinc reagents proceeds via a decarbonylative process to produce ortho-substituted benzamides in high yields. In addition to tolerating diverse phthalimide functionality, including alkyl, aryl, and heteroatom containing substituents, this methodology proceeds smoothly with diorganozinc reagents prepared from aryl bromides and utilized without purification.



New cross-coupling methodologies for the construction of carbon−carbon bonds continually transform organic synthesis.[1] Through the gradual expansion of available nucleophilic and electrophilic coupling partners, innumerable previously unknown synthetic disconnects are now possible. The currently available battery of cross-coupling reactions includes diverse methods for the coupling of wide varieties of functional groups, often enhanced by the control of regiochemistry or stereochemistry and significant increases in molecular complexity. The utility of a given functional group, and cross-coupling methodologies as a whole, can be further increased by its controlled modification during the coupling process. For example, well-known decarboxylative coupling procedures utilize carboxylic acids[2−6] and esters[7,8] as the source of alkyl nucleophiles. Likewise, decarbonylation provides a means of controlled functional group modification. Since being first reported in 1965,[9] decarbonylative coupling has been achieved with functional groups including aldehydes,[10−14] carboxylic acids,[15] isopropenyl esters,[16] carboxylic anhydrides,[17−19] and only recently imides.[20,21]

The addition of carbon-based nucleophiles such as Grignard or alkyl lithium reagents to imines has long been known. The use of imides in transition metal-controlled cross-coupling methodologies has only recently been demonstrated in a decarbonylative fashion for reaction with alkynes and dienes.[19,20] Our efforts focused on the use of imides as electrophilic coupling partners in cross-coupling methodology with carbon nucleophiles. Herein we present the nickel-mediated decarbonylative coupling of diorganozinc reagents to phthalimides, a process that results in the creation of an unfunctionalized carbon−carbon bond. This decarbonylative methodology demonstrates significant functional group compatibility and is applicable to a broad range of diorganozinc reagents prepared from aryl bromides and utilized without purification. This cross-coupling of phthalimides with organozinc nucleophiles provides a highly efficient construction of ortho-substituted benzamides, which have been the focus of a number of studies of biologically active agents and pharmaceuticals.[22]

We were led to the decarbonylative coupling of imides with carbon nucleophiles through efforts to directly couple imides with diorganozinc reagents, where initial efforts began with conditions that were successful in related reactions of cyclic anhydrides.[23,24] In the presence of substoichiometric $Ni(acac)_2$ (acac = acetylacetonate) and bipyridine, *N*-phenylphthalimide was combined with an excess of diethylzinc in THF (Table 1, entry 2). Spectroscopic characterization of the isolated product indicated that instead of the ketamide product (**3**) anticipated from direct coupling of the imide and diethylzinc, decarbonylated product **2** was the sole product recovered, with unreacted imide making up the remainder of the mass balance.[25] More significantly, yields of the putative catalytic reaction closely matched the catalyst loading, suggesting a failure of nickel turnover. As efforts to induce catalysis were unsuccessful, we opted for the development of the metal-mediated process and turned our attention to the optimization of the nickel-mediated decarbonylative process. These efforts are summarized in Table 1.[26] Several solvents were screened, as well as a number of ligands. Bipyridine provides a significant increase in yield compared to PPh_3, pyridine, and pyphos [2-(2-(diphenylphosphino)ethyl)pyridine] (entries 4−8). No product was observed when the reaction is performed in the absence of nickel (entry 9), demonstrating that the reaction is nickel mediated. Ultimately, the coupling of phthalimide with Et_2Zn was achieved in 96% yield with the use of stoichiometric $Ni(acac)_2$ and bipy in dioxane at 95 °C (Table 1, entry 1). $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) also proved to be a viable metal source, and with the use of only 1.1 equiv of Et_2Zn provided the desired product in 92% yield (entry 10). The use of other organometallic reagents, including EtZnBr, was unsuccessful.

These optimized conditions were in turn utilized to examine the substrate scope of the decarbonylative coupling of diethylzinc to a range of phthalimides (Table 2). A variety of imide-nitrogen

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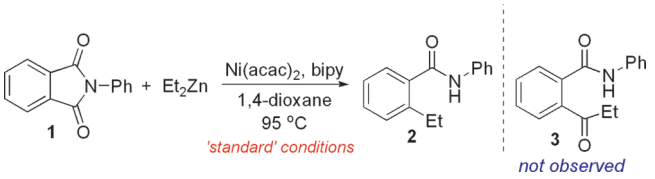
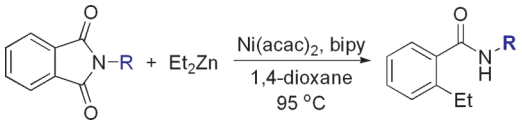
Table 1. Optimization of Reaction Conditions for Decarbonylative Coupling of Phthalimides with Diethylzinc



entry	change from "standard" conditions[a]	yield (%)
1	none	96
2	20 mol % $Ni(acac)_2$/bipy in THF at 50 °C	19
3	20 mol % $Ni(acac)_2$/bipy	18
4	10 mol % $Ni(COD)_2$/40 mol % PMe_3, 1.1 equiv of Et_2Zn[b]	<5
5	THF, 50 °C	60
6	pyphos instead of bipy	76
7	2 equiv of PPh_3 instead of bipy	6
8	2 equiv of pyridine instead of bipy	13
9	no bipyridine	0
10	no Ni source	0
11	$Ni(COD)_2$ instead of $Ni(acac)_2$	93
12	$Ni(COD)_2$, 1.1 equiv of Et_2Zn	92
13	EtZnBr instead of Et_2Zn[c]	<5

[a] "Standard" conditions: *N*-phenylphthalimide (0.9 mmol, 1.0 equiv), $Ni(acac)_2$ (1.0 equiv), bipyridine (1.1 equiv), Et_2Zn (3.0 equiv), in dioxane (2.5 mL) at 95 °C under an Ar atmosphere. [b] See ref 21. [c] Prepared from EtMgBr (1.0 equiv) and $ZnBr_2$ (1.0 equiv) in THF and used without purification.

Table 2. Scope of Phthalimides Amenable to Decarbonylative Cross-Coupling with Et_2Zn



entry[a]	R	product	yield (%)
1	Ph	**2**	96
2	4-Et-C_6H_4	**4**	89
3	4-*i*Pr-C_6H_4	**5**	92
4	3,5-$(CF_3)_2$-C_6H_3	**6**	97
5	2,5-$(OMe)_2$-C_6H_3	**7**	91
6	4-CO_2Et-C_6H_4	**8**	93
7	Bn	**9**	84
8	Me	**10**	65
9	CH_2CH_2Ph	**11**	85
10	$(CH_2)_3NMe_2$	**12**	81

[a] Conditions: phthalimide (0.9 mmol, 1.0 equiv), $Ni(acac)_2$ (1.0 equiv), bipyridine (1.1 equiv), Et_2Zn (3.0 equiv), in dioxane (2.5 mL) at 95 °C under an Ar atmosphere.

substitution was utilized in these reactions, including aromatic substituents with both electron-rich and electron-deficient substituents (entries 2−6), alkyl groups (entries 7−9), and aliphatic amines (entry 10). The reaction demonstrates significant functional group tolerance on the imide, including esters, ethers, halides, and amines, and proceeds with yields generally exceeding 75%. The decarbonylative coupling also proceeds with substituted phthalimides, as illustrated by the reaction of *N*-phenyl-4-methylphthalimide with Et_2Zn, but generates an inseparable mixture of two isomeric products.[27] The imide substrates are limited to phthalimide derivatives, as efforts using cyclic imides with saturated backbones, including cyclohexane-containing succinimide **13** and 3,4-dimethylsuccinimide **14**, have resulted in less than 10% of the desired product, with mass balance consisting of unreacted or hydrolyzed starting material (Scheme 1).

Scheme 1. Unsuccessful Substrates

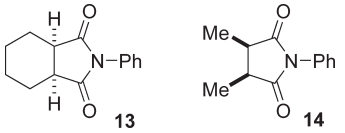
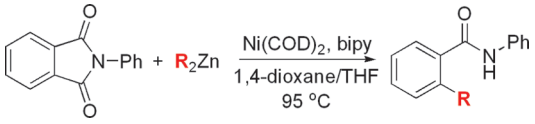


Table 3. Scope of Organozinc Nucleophiles Compatible with Phthalimide Cross-Coupling



entry[a]	R	product	yield (%)
1	Ph[b]	**15**	81
2	Ph[c]	**15**	77
3	4-MeO-C_6H_4	**16**	78
4	3-MeO-C_6H_4	**17**	69
5	2-MeO-C_6H_4	**18**	72
6	4-MeS-C_6H_4	**19**	93
7	4-F_3C-C_6H_4	**20**	71
8	4-F-C_6H_4	**21**	87
9	4-Me-C_6H_4	**22**	96
10	4-Me_2N-C_6H_4	**23**	96
11	3-Me-C_6H_4	**24**	75
12	3,5-$(F_3C)_2$-C_6H_3	**25**	77
13	3,4,5-$(MeO)_3$-C_6H_2	**26**	57[d]
14[e]	$CH_2CH_2CO_2Et$	**27**	83
15	Bu	**28**	69

[a] Conditions: phthalimide (0.9 mmol, 1.0 equiv), $Ni(COD)_2$ (1.0 equiv), bipyridine (1.1 equiv), R_2Zn (1.3 equiv, used without purification from RBr, *n*BuLi, and $ZnCl_2$ in 2 mL of THF), 1,4-dioxane (2.5 mL) at 95 °C under an Ar atmosphere. [b] Ph_2Zn from commercial source. [c] Ph_2Zn prepared from PhBr. [d] Obtained as an inseparable mixture with the biaryl homocoupling product. [e] Prepared from $ZnCl_2$ and (1-ethoxycyclopropoxy)trimethylsilane.

Of greater synthetic interest is the range of diorganozinc nucleophiles compatible with this reactivity. Commercially available diphenylzinc works smoothly in this reaction, providing benzanilide **15** in 81% yield (Table 3, entry 1). Unfortunately, the commercial availability of similar diorganozinc reagents is quite limited, and thus there is great importance in the ability to use nucleophiles prepared from corresponding aryl halides, preferably with minimum required purification. To this end, diphenylzinc was prepared via lithium−halogen exchange with bromobenzene by using *n*BuLi followed by reaction of the

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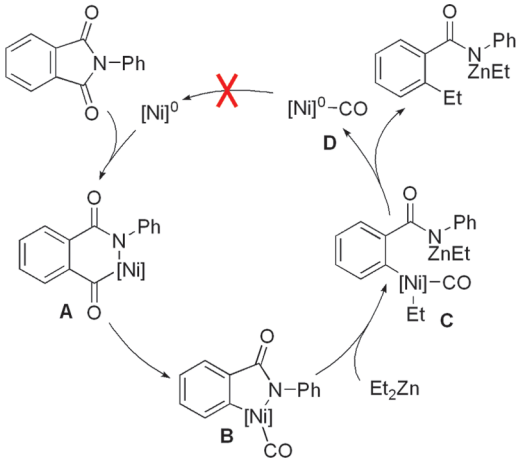
Scheme 2. Proposed Mechanism



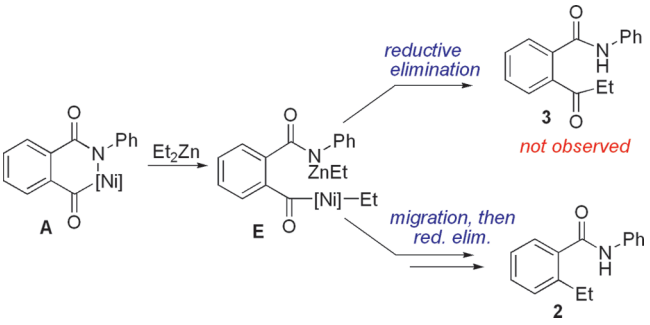
aryllithium reagent with zinc chloride. This THF solution of diphenylzinc was then utilized directly in the decarbonylation methodology, using $Ni(COD)_2$ rather than the bench stable $Ni(acac)_2$ in order to minimize the amount of nucleophile required to produce the active Ni^0 species. Much to our delight, the use of the unpurified diorganozinc reagent provided decarbonylated product **15** in a very similar yield (77%) to that obtained with use of the commercial diorganozinc reagent (81%).

Using this same nucleophile preparation, a series of diorganozinc reagents were tested under similar conditions. The reaction has proven to be remarkably resilient to changes in nucleophile substitution and electronics. Ortho, meta, and para substitution is tolerated, with relatively little influence upon the reaction yield (Table 3, entries 3−8). A number of heteroatom containing functionalities are tolerated, including ethers, thioethers, halides and amines. When prepared directly from the reaction of $ZnCl_2$ with (1-ethoxycyclopropoxy)trimethylsilane, esters are also competent nucleophiles (entry 13). To date, the reaction proceeds with all arylbromides for which the diorganozinc reagent can be successful generated. It is of note that common byproducts of low yielding reactions include biaryl species from Negishi-type coupling of the aryl nucleophile, presumably with unreacted aryl halide, and hydrolyzed starting material. In addition, efforts to utilize organozinc halide nucleophiles prepared in an analogous fashion have been unsuccessful.

In contemplating the reaction pathway, it is presumed that the reaction proceeds via oxidative addition of a Ni^0 species into the nitrogen−carbonyl bond of the cyclic imide to produce intermediate **A**[28] in analogy to more well studied anhydride reactions (Scheme 2).[29,30] Decarbonylation is anticipated to occur from this intermediate, producing metalacycle **B**,[31−33] which then undergoes subsequent transmetalation with the diorganozinc reagent. Reductive elimination from intermediate **C** releases the product as well as regenerating a Ni^0 species, now complexed to CO. Unfortunately, no turnover is observed, suggesting that the strong Ni−CO bond of the proposed intermediate precludes dissociation to regenerate the initial active species.[34,35] These observations also suggest that Ni−CO complex **D** is of insufficient nucleophilicity to undergo oxidative addition to another equivalent of the starting material.

A similar mechanism can be drawn with transmetalation preceding decarbonylation (Scheme 3). This mechanism has

Scheme 3. Alternative Transmetalation/Migration Mechanism



been deemed unlikely, however, as reductive elimination from intermediate **E** to generate the ketoamide product would presumably be competitive with decarbonylation, providing at least small amounts of the direct coupling product. No evidence for this direct product has been observed under any tested conditions.

In summary, the cross-coupling of diorganozinc nucleophiles with electrophilic phthalimides proceeds via a decarbonylative process to generate ortho-substituted benzamides and biaryls in excellent yields. This method, with its compatibility with in situ generated nucleophiles, provides a means of ready access to a wide variety of synthetically useful species.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring. Solvents, including toluene, tetrahydrofuran, and diethyl ether, were purged with argon and passed through two columns of neutral alumina or molecular sieves. All starting materials are commercially available and used without purification or prepared according to procedures provided.

Unless otherwise noted, all reactions were performed in oven-dried glassware under an inert atmosphere of N_2 or Ar. ^1H and ^{13}C NMR spectra were obtained using standard acquisition parameters and are referenced to TMS.

All phthalimides were obtained commercially or prepared via the condensation of phthalic acid with the appropriate amine in either refluxing toluene (Dean−Stark conditions) or refluxing acetic acid.[36] Products **4** and **15** match literature precedent (melting point only).[37,38] Full characterization data are provided for these compounds.

General Method for Decarbonylative Coupling with Et_2Zn. The general method will be illustrated with a specific example. $Ni(acac)_2$ (116 mg, 0.45 mmol), bipyridine (84 mg, 0.54 mmol), and *N*-*p*-isopropylphenylphthalimide (119 mg, 0.45 mmol) were combined in an oven-dried 25-mL round-bottomed flask and sealed with a septum. The flask was evacuated and refilled (3×) and placed under N_2. 1,4-Dioxane (2.5 mL) was added via syringe, followed by Et_2Zn (140 μL, 1.35 mmol) also via syringe. The dark solution was then suspended in a 95 °C oil bath and allowed to stir for 16 h. Following reaction, the reaction mixture was cooled to room temperature, the septum was removed, and the reaction mixture was diluted with Et_2O (15 mL). The addition of 2 M aq HCl (15 mL) quenched the reaction, which was then extracted with Et_2O (3 × 15 mL). The combined organic layers were washed with brine (15 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The resulting yellow oil was purified by column chromatography (10:1 hexane:ethyl acetate) to provide **5** in 92% yield.

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General Method for Decarbonylative Coupling with in Situ Generated Diorganozinc Reagents. The general method will be illustrated with a specific example. *p*-Bromothioanisole (272 mg, 1.34 mmol) was added to an oven-dried 10-mL round-bottomed flask, sealed with a septum, evacuated and refilled with Ar (3×) and dissolved in THF (2 mL). The reaction mixture was cooled to −78 °C and *n*BuLi (2.5 M, 536 μL, 1.34 mmol) was added dropwise with stirring at −78 °C for 30 min. In a separate flask, $ZnCl_2$ (91.3 mg, 0.67 mmol) was flame-dried under vacuum, then dissolved in THF (1 mL). This solution was then added to the solution of ArLi, still at −78 °C. The reaction was removed from the cold bath and allowed to warm to room temperature while stirring for 30 min.

In a separate 50-mL round-bottomed flask, *N*-phenylphthalimide (115 mg, 0.51 mmol) and bipyridine (84 mg, 0.54 mmol) were combined and transferred into an inert atmosphere glovebox, where $Ni(COD)_2$ (140 mg, 0.51 mmol) was added. This flask was sealed with a septum and removed from the glovebox, whereupon 1,4-dioxane (2.5 mL) was added, followed by the Ar_2Zn solution. The flask was then suspended in a 95 °C oil bath and allowed to stir for 16 h. Following reaction, the mixture was cooled to room temperature, the septum was removed, and the reaction mixture was diluted with Et_2O (15 mL). The addition of 2 M aq HCl (15 mL) quenched the reaction, which was then extracted with Et_2O (3 × 15 mL). The combined organic layers were washed with brine (15 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The resulting residue was purified by column chromatography (9:1 hexane:ethyl acetate) to provide **19** as a white solid in 93% yield.

2-Ethyl-*N*-phenylbenzamide (2): The title compound was prepared according to the general procedure for decarbonylation with diethylzinc. Column chromatography with 4:1 hex:EtOAc yielded **2** (97 mg, 0.43 mmol, 96% yield) as a yellowish oil. R_f 0.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.52−7.22 (mult, 6H), 7.15 (t, *J* = 7.3 Hz, 2H), 2.86 (qrt, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 142.6, 138.0, 136.2, 130.3, 129.6, 129.1, 126.6, 125.9, 124.5, 119.8, 26.3, 15.9. IR (NaCl) 3259, 3234, 1640, 1595, 1539, 1324 cm^{-1}. HRMS (ESI+) calcd for $[C_{15}H_{16}NO]^+$ 226.1226, found 226.1232.

2-Ethyl-*N*-(4-ethylphenyl)benzamide (4): The title compound was prepared according to general procedure for decarbonylation with diethylzinc. Column chromatography with 9:1 hex:EtOAc yielded **4** (101 mg, 0.40 mmol, 89%) as a white solid. R_f 0.52 (in 2:1 hex:EtOAc). Mp 110−111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (br s, 1H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.33−7.04 (mult, 6H), 2.73 (qrt, *J* = 7.8 Hz, 2H), 2.54 (qrt, *J* = 7.8 Hz, 2H), 1.14 (t, *J* = 7.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 142.4, 140.5, 136.3, 135.6, 130.1, 129.5, 128.3, 126.5, 125.7, 120.0, 28.3, 26.3, 15.8, 15.6. IR (NaCl) 3279, 2922, 2866, 1650, 1599, 1536, 1503, 1409, 1323, 1274 cm^{-1}. HRMS (ESI+) calcd for $[C_{17}H_{20}NO]^+$ 254.1539, found 254.1533.

2-Ethyl-*N*-(4-isopropylphenyl)benzamide (5): The title compound was prepared according to the general procedure for decarbonylation with diethylzinc. Column chromatography with 10:1 hex:EtOAc yielded **5** (111 mg, 0.41 mmol, 92% yield) as a viscous yellow oil. R_f 0.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.19 (mult, 9H), 2.90 (pent, *J* = 7.1 Hz, 1H), 2.84 (qrt, 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H), 1.25 (d, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 145.3, 142.5, 136.3, 135.6, 130.2, 129.6, 126.9, 126.6, 125.8, 120.0, 33.6, 26.3, 24.0, 15.9. IR (NaCl) 3286, 2960, 1651, 1597, 1517, 1411, 1320 cm^{-1}. HRMS (ESI+) calcd for $[C_{18}H_{22}NO]^+$ 268.1696, found 268.1699.

***N*-(3,5-Bis(trifluoromethyl)phenyl)-2-ethylbenzamide (6):** The title compound was prepared according to the general procedure for decarbonylation with diethylzinc. Column chromatography with 10:1 hex:EtOAc yielded **6** (158 mg, 0.43 mmol, 97% yield) as a white solid. R_f 0.19. Mp 123−124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.97 (br s, 1H), 7.64 (s, 1H), 7.44−7.20 (mult, 4H), 2.83 (qrt, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 142.9, 139.4, 134.8, 132.4 (qrt, J_{C-F} = 33 Hz), 131.0, 129.9, 126.5, 126.0, 123.1 (qrt, *J* = 273 Hz), 119.5 (qrt, J_{C-F} = 3.1 Hz), 117.7 (pent, J_{C-F} = 3.6 Hz), 26.3, 15.8. IR (NaCl) 3429, 2975, 1659, 1557, 1470, 1438, 1380, 1278 cm^{-1}. HRMS (ESI+) calcd for $[C_{17}H_{14}F_6NO]^+$ 362.0974, found 362.0970.

***N*-(2,5-Dimethoxyphenyl)-2-ethylbenzamide (7):** The title compound was prepared according to the general procedure for decarbonylation with diethylzinc. Column chromatography with 4:1 hexane:EtOAc yielded **7** as a white solid (117 mg, 0.41 mmol, 91% yield). R_f 0.23. Mp 119−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 2.9 Hz, 1H), 8.11 (br s, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.41 (dt, *J* = 7.3, 1.6 Hz), 7.35−7.24 (mult, 2H), 6.82 (d, *J* = 8.9 Hz, 1H), 6.62 (dd, *J* = 8.9, 3.0 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 2.88 (qrt, *J* = 7.5 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 153.8, 142.5, 142.2, 136.5, 130.3, 129.6, 128.2, 126.9, 125.9, 110.7, 108.8, 106.0, 56.1, 55.9, 26.3, 15.9. IR (NaCl) 3419, 2963, 2942, 1676, 1526, 1468 cm^{-1}. HRMS (ESI+) calcd for $[C_{17}H_{20}NO_3]^+$ 286.1438, found 286.1434.

Ethyl 4-(2-ethylbenzamido)benzoate (8): The title compound was prepared according to the general procedure for decarbonylation with diethylzinc. Column chromatography with 10:1 hexane:EtOAc yielded **8** as a yellowish solid (124 mg, 0.42 mmol, 93% yield). R_f 0.41 (in 2:1 hex:EtOAc). Mp 109−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (br s, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.34−7.09 (mult, 4H), 4.23 (qrt, *J* = 7.2 Hz, 2H), 2.73 (qrt, *J* = 7.4 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 166.1, 142.6, 142.2, 135.7, 130.7, 130.5, 129.6, 126.6, 126.0, 125.8, 118.9, 60.8, 26.3, 15.7, 14.3. IR (NaCl) 3303, 2972, 1713, 1682, 1651, 1595, 1536, 1309, 1272 1175, 1108 cm^{-1} . HRMS (ESI+) calcd for $[C_{18}H_{20}NO_3]^+$ 298.1438, found 298.1443.

***N*-Benzyl-2-ethylbenzamide (9):** The title compound was prepared according to the general procedure for decarbonylation with diethylzinc. Column chromatography with 10:1 hex:EtOAc yielded **9** (91 mg, 0.38 mmol, 84% yield) as a yellowish oil. R_f 0.13. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.24 (mult, 8H), 7.18 (dt, *J* = 7.5, 1.2 Hz, 1H), 4.62 (d, *J* = 5.7 Hz, 1H), 2.82 (qrt, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 142.4, 138.1, 136.0, 130.0, 129.5, 128.8, 127.8, 127.6, 126.6, 125.7, 43.9, 26.3, 15.9. IR (NaCl) 3328, 3281, 2962, 2931, 1633, 1531, 1310 cm^{-1}. HRMS (ESI+) calcd for $[C_{16}H_{18}NO]^+$ 240.1383, found 240.1385.

***N*-Methyl-2-ethylbenzamide (10):** The title compound was prepared according to the general procedure for decarbonylation with diethylzinc. Column chromatography with 10:1 hexane:EtOAc yielded **10** as a yellow oil (117 mg, 0.41 mmol, 65% yield). R_f 0.09 (in 2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.28 (mult, 2H), 7.27−7.24 (mult, 1H), 7.18 (dt, *J* = 7.4, 1.5 Hz, 1H), 2.99 (d, *J* = 5.1 Hz, 3H), 2.79 (qrt, *J* = 7.3, 2H), 1.23 (t, *J* = 7.3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 142.3, 136.3, 129.9, 129.4, 126.7, 125.7, 26.7, 26.4, 15.8. IR (NaCl) 3378, 2963, 1717, 1652, 1599, 1557, 1260, 1013 cm^{-1}. HRMS (ESI+) calcd for $[C_{10}H_{14}NO]^+$ 164.1070, found 164.1037.

2-Ethyl-*N*-phenethylbenzamide (11): The title compound was prepared according to the general procedure for decarbonylation with diethylzinc. Column chromatography with 10:1 hex:EtOAc yielded **11** (97 mg, 0.38 mmol, 85% yield) as a colorless oil. R_f 0.13. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.12 (mult, 9H), 5.79 (br s, 1H), 3.71 (qrt, *J* = 7.6 Hz, 2H), 2.93, (t, *J* = 7.6 Hz, 2H), 2.73 (qrt, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 142.2, 138.7, 136.2, 129.8, 129.3, 128.7, 128.6, 126.6, 126.5, 125.6, 40.7, 35.6, 26.2, 15.8. IR (NaCl) 3328, 3281, 2962, 2931, 1633, 1531, 1310 cm^{-1}. HRMS (ESI+) calcd for $[C_{17}H_{20}NO]^+$ 254.1539, found 254.1531.

***N*-(3-(Dimethylamino)propyl)-2-ethylbenzamide (12):** The title compound was prepared according to the general procedure for decarbonylation with diethylzinc. Column chromatography with 10:1

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hex:EtOAc yielded **12** (85 mg, 0.36 mmol, 81% yield) as a yellow solid. R_f 0.04. Mp 136−138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.10 (mult, 5H), 3.50 (qrt, J = 6.3 Hz, 2H), 2.81 (qrt, J = 7.4 Hz, 2H), 2.44 (t, J = 6.3 Hz, 2H), 2.22 (s, 6H), 1.76 (pent, J = 6.5 Hz, 2H), 1.20 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 142.2, 136.5, 129.6, 129.3, 126.6, 125.5, 58.3, 45.2, 39.3, 26.3, 26.2, 15.8. IR (NaCl) 3428, 2965, 2869, 1638, 1535, 1543, 1459, 1311 cm^{-1}. HRMS (ESI+) calcd for $[C_{14}H_{23}N_2O]^+$ 235.1805, found 235.1801.

***N*-Phenylbiphenyl-2-carboxamide (15):** The title compound was prepared according to the general procedure for decarbonylation with the in situ generated diarylzinc reagent. Column chromatography with 9:1 hex:EtOAc yielded **15** (110 mg, 0.40 mmol, 81% yield) as a white solid. R_f 0.40 (in 2:1 hex:EtOAc). Mp 119−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7 Hz, 1H), 7.58−7.31 (mult, 8H), 7.26−7.16 (mult, 2H), 7.10 (d, J = 7.7 Hz, 2H), 7.04 (t, J = 7.0 Hz, 1H), 6.97 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 139.9, 139.5, 137.5, 135.2, 130.6, 130.3, 129.4, 128.9, 128.8, 128.7, 128.0, 127.8, 124.3, 119.9. IR (NaCl) 3329, 3059, 1660, 1651, 1600, 1537, 1441, 1323 cm^{-1}. HRMS (ESI+) calcd for $[C_{19}H_{16}NO]^+$ 274.1226, found 274.1220.

4′-Methoxy-*N*-phenylbiphenyl-2-carboxamide (16): The title compound was prepared according to the general procedure for decarbonylation with in situ generated diarylzinc reagent. Column chromatography with 10:1 hex:EtOAc yielded **16** (121 mg, 0.40 mmol, 78% yield) as a white solid. R_f 0.22 (in 2:1 hex:EtOAc). Mp 143−144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.4 Hz, 1H), 7.51 (dt, J = 7.5, 1.8 Hz, 1H), 7.48−7.36 (mult, 4H), 7.23 (d, J = 7.9 Hz, 1H), 7.17 (d, J = 8.3 Hz, 2H), 7.05 (t, 7.0 Hz, 1H), 7.00−6.85 (mult, 4H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 159.6, 139.2, 137.7, 135.2, 132.2, 130.6, 130.4, 130.1, 129.6, 128.8, 127.5, 124.4, 119.9, 114.5, 55.4. IR (NaCl) 3380, 2962, 2836, 1653, 1600, 1539, 1437, 1320, 1249 cm^{-1}. HRMS (ESI+) calcd for $[C_{20}H_{18}NO_2]^+$ 304.1332, found 304.1336.

3′-Methoxy-*N*-phenylbiphenyl-2-carboxamide (17): The title compound was prepared according to the general procedure for decarbonylation with in situ generated diarylzinc reagent. Column chromatography with 10:1 hex:EtOAc yielded **17** (60 mg, 0.20 mmol, 39% yield) as an off white solid. R_f 0.15 (in 2:1 hex:EtOAc). Mp 104−105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.7 Hz, 1H), 7.46 (dt, J = 7.3, 1.8 Hz, 1H), 7.40 (dt, J = 7.5, 1.8 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.28 (t, J = 8.2 Hz, 1H), 7.15 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H), 7.01−6.83 (mult, 5H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 160.0, 141.4, 139.4, 137.6, 135.2, 130.6, 130.2, 130.0, 129.6, 128.8, 128.0, 124.4, 121.2, 120.0, 114.2, 114.1, 55.4. IR (NaCl) 3380, 3065, 2957, 2848, 1659, 1650, 1537, 1440, 1322 cm^{-1}. HRMS (ESI+) calcd for $[C_{20}H_{18}NO_2]^+$ 304.1332, found 304.1330.

2′-Methoxy-*N*-phenylbiphenyl-2-carboxamide (18): The title compound was prepared according to the general procedure for decarbonylation with in situ generated diarylzinc reagent. Column chromatography with 9:1 hex:EtOAc yielded **18** (111 mg, 0.37 mmol, 72% yield) as a white solid. R_f 0.18 (in 2:1 hex:EtOAc). Mp 128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.5 Hz, 1H), 7.47 (dt, J = 7.5, 1.7 Hz, 1H), 7.40 (dt, J = 7.4, 1.5 Hz, 1H), 7.34−7.22 (mult, 4H), 7.18−7.06 (mult, 4H), 7.02 (t, J = 7.4, 1H), 6.95 (tt, J = 7.1, 1.2 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 3.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 156.4, 137.9, 136.0, 135.8, 131.0, 130.7, 130.1, 129.9, 129.0, 127.9, 127.0, 124.0, 121.3, 119.5, 111.1, 55.6. IR (NaCl) 3391, 2959, 2871, 1777, 1686, 1599, 1531, 1365, 1248 cm^{-1}. HRMS (ESI+) calcd for $[C_{20}H_{18}NO_2]^+$ 304.1332, found 304.1334.

4′-(Methylthio)-*N*-phenylbiphenyl-2-carboxamide (19): The title compound was prepared according to the general procedure for decarbonylation with in situ generated diarylzinc reagent. Column chromatography with 9:1 hex:EtOAc yielded **19** (163 mg, 0.47 mmol, 93% yield) as a white solid. R_f 0.28 (in 2:1 hex:EtOAc). Mp 155−156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.3 Hz, 1H), 7.36−7.29 (mult, 3H), 7.27−7.05 (mult, 7H), 7.00 (t, J = 7.3 Hz, 1H), 6.88 (br s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 138.9, 137.5, 136.4, 135.3, 130.7, 130.3, 129.4, 129.2, 128.9, 127.8, 126.8, 124.5, 119.9, 15.7. IR (NaCl) 3383, 2965, 2846, 1658, 1608, 1539, 1432, 1324, 1242 cm^{-1}. HRMS (ESI+) calcd for $[C_{20}H_{18}NOS]^+$ 320.1104, found 320.1093.

***N*-Phenyl-4′-(trifluoromethyl)biphenyl-2-carboxamide (20):** The title compound was prepared according to the general procedure for decarbonylation with in situ generated diarylzinc reagent. Column chromatography with 10:1 hex:EtOAc yielded **20** (124 mg, 0.36 mmol, 71% yield) as a white solid. R_f 0.38 (in 2:1 hex:EtOAc). Mp 148 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.1 Hz, 1H), 7.63−7.43 (mult, 6H), 7.37 (d, J = 7.5 Hz, 1H), 7.21−7.08 (mult, 4H), 7.02 (t, J = 7.3 Hz, 1H), 6.86 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 143.6, 138.3, 137.3, 135.9, 130.8, 130.0, 129.1, 129.05, 129.0, 128.6, 125.7 (qrt, J_{C-F} = 3.7 Hz), 124.8, 124.1 (qrt, J_{C-F} = 271 Hz), 122.7, 119.9. IR (NaCl) 2920, 2849, 1650, 1443, 1324, 1119 cm^{-1}. HRMS (ESI+) calcd for $[C_{20}H_{15}F_3NO]^+$ 342.1100, found 342.1092.

4′-Fluoro-*N*-phenylbiphenyl-2-carboxamide (21): The title compound was prepared according to the general procedure for decarbonylation with in situ generated diarylzinc reagent. Column chromatography with 10:1 hex:EtOAc yielded **21** (129 mg, 0.44 mmol, 87% yield) as a white solid. R_f 0.34 (in 2:1 hex:EtOAc). Mp 137−139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.4 Hz, 1H), 7.58−7.37 (mult, 5 H), 7.31−7.05 (mult, 7H), 6.92 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 162.6 (d, J_{C-F} = 248 Hz), 138.45, 137.5, 135.9 (d, J_{C-F} = 3.1 Hz), 130.6 (d, J_{C-F} = 27 Hz), 130.5, 130.4, 129.3, 129.1, 129.0, 128.0, 124.6, 119.9, 115.9 (d, J_{C-F} = 21 Hz). IR (NaCl) 3282, 3131, 3063, 1658, 1650, 1537, 1514, 1440, 1323, 1224 cm^{-1}. HRMS (ESI+) calcd for $[C_{19}H_{15}FNO]^+$ 292.1132, found 292.1136.

4′-Methyl-*N*-phenylbiphenyl-2-carboxamide (22): The title compound was prepared according to the general procedure for decarbonylation with in situ generated diarylzinc reagent. Column chromatography with 9:1 hex:EtOAc yielded **22** (141 mg, 0.49 mmol, 96% yield) as a white solid. R_f 0.39 (in 2:1 hex:EtOAc). Mp 148−149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.0 Hz, 1H), 7.52, (dt, J = 7.5, 1.3 Hz, 1H), 7.45 (dt, J = 7.6, 1.3 Hz, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.27−7.20 (mult, 4H), 7.13 (d, J = 7.7 Hz, 2H), 7.05 (t, J = 7.3 Hz, 1H), 6.95 (br s, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 167.2, 139.6, 137.9, 137.6, 137.0, 135.2, 130.6, 130.4, 129.7, 129.5, 128.8, 128.7, 127.7, 124.3, 119.9, 21.2. IR (NaCl) 3282, 3053, 3020, 2921, 1656, 1599, 1536, 1438, 1322 cm^{-1}. HRMS (ESI+) calcd for $[C_{20}H_{18}NO]^+$ 288.1383, found 288.1382.

4′-(Dimethylamino)-*N*-phenylbiphenyl-2-carboxamide (23): The title compound was prepared according to the general procedure for decarbonylation with in situ generated diarylzinc reagent. Column chromatography with 10:1 hex:EtOAc yielded **23** (155 mg, 0.49 mmol, 96% yield) as a yellow solid. R_f 0.55 (in 2:1 hex:EtOAc). Mp 158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.2 Hz, 1H), 7.42, (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.2 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 7.20−7.04 (mult, 2H), 7.02 (br s, 1H), 6.97 (t, J = 7.2 Hz, 1H), 6.69 (d, J = 8.6 Hz, 2H), 2.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 150.3, 139.8, 137.8, 134.7, 130.6, 130.3, 129.76, 129.74, 128.7, 127.2, 126.9, 124.1, 120.1, 112.7, 40.4. IR (NaCl) 3299, 3059, 2889, 1659, 1611, 1529, 1440, 1320 cm^{-1}. HRMS (ESI+) calcd for $[C_{21}H_{21}N_2O]^+$ 317.1648, found 317.1652.

3′-Methyl-*N*-phenylbiphenyl-2-carboxamide (24): The title compound was prepared according to the general procedure for decarbonylation with in situ generated diarylzinc reagent. Column chromatography with 10:1 hex:EtOAc yielded **24** (110 mg, 0.38 mmol, 75% yield) as a yellow oil. R_f 0.45 (in 2:1 hex:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.3 Hz, 1H), 7.49−7.09 (mult, 10H), 7.05−6.93 (mult, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 139.9, 139.7, 138.7, 137.5, 135.1, 130.6, 130.3, 129.6, 129.5,

128.84, 128.81, 128.76, 127.8, 125.9, 124.3, 120.0, 21.3. IR (NaCl) 3323, 3029, 1651, 1600, 1537, 1440, 1323 cm^{-1}. HRMS (ESI+) calcd for $[C_{20}H_{18}NO]^+$ 288.1383, found 288.1385.

***N*-Phenyl-3′,5′-bis(trifluoromethyl)biphenyl-2-carboxamide (25):** The title compound was prepared according to the general procedure for decarbonylation with in situ generated diarylzinc reagent. Column chromatography with 10:1 hex:EtOAc yielded **25** (158 mg, 0.39 mmol, 77% yield) as an off-white solid. R_f 0.38 (in 2:1 hex:EtOAc). Mp 128−129 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.77 (s, 1H), 7.64 (d, J = 7.1 Hz, 1H), 7.57−7.36 (mult, 4H), 7.28−7.15 (mult, 4H), 7.04 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 142.0, 137.0, 136.2, 131.9 (qrt, J_{C-F} = 36 Hz), 130.9, 130.4, 129.0, 128.8, 128.3, 125.0, 123.3 (qrt, J_{C-F} = 273 Hz), 121.5 (mult), 120.1, 119.7. IR (NaCl) 3473, 2924, 1651, 1602, 1541, 1379, 1278 cm^{-1}. HRMS (ESI+) calcd for $[C_{21}H_{14}F_6NO]^+$ 410.0974, found 410.0978.

Ethyl 3-(2-(Phenylcarbamoyl)phenyl)propanoate (27): The diorganozinc reagent, bis(3-ethoxy-3-oxopropyl)zinc, was prepared according to literature precedent and used without further purification[39] in the general procedure for decarbonylation with in situ generated diarylzinc reagent. Column chromatography with 50:1 CH_2Cl_2:Et_2O yielded **27** (126 mg, 0.42 mmol, 83% yield) as a yellow oil. R_f 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (br s, 1H), 7.63 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 7.6, 1H), 7.36−7.15 (mult, 5H), 7.07 (t, J = 7.3 Hz, 1 H), 4.03 (qrt, J = 7.3 Hz, 2H), 3.05 (t, J = 6.9 Hz, 2H), 2.76 (t, J = 6.9 Hz, 2H), 1.14 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 168.0, 138.4, 137.7, 137.2, 130.3, 129.2, 129.0, 127.9, 126.6, 126.5, 124.3, 119.9, 60.8, 35.0, 27.2, 14.1. IR (NaCl) 3327, 3061, 2976, 2932, 1729, 1712, 1649, 1599, 1535, 1430 cm^{-1}. HRMS (ESI+) calcd for $[C_{18}H_{20}NO_3]^+$ 298.1438, found 298.1432.

2-Butyl-*N*-phenylbenzamide (28): The diorganozinc reagent was prepared by addition of *n*BuLi (2 equiv) with $ZnCl_2$ in THF at 0 °C and was used in the general procedure for decarbonylation with in situ generated diarylzinc reagent. Column chromatography with 9:1 hexane:EtOAc yielded **28** (88 mg, 0.35 mmol, 69% yield) as a white solid. R_f 0.34 in 4:1 hexane:EtOAc. Mp 107−108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.9 Hz, 2H), 7.48−7.19 (mult, 6H), 7.14 (t, J = 7.2 Hz, 1H), 2.81 (t, J = 7.9 Hz, 2H), 1.64 (br s, 1H), 1.61 (mult, 2H), 1.35 (hex, J = 7.5 Hz, 2H), 0.88 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 168.2, 141.3, 138.0, 136.5, 130.4, 130.2, 129.2, 126.7, 125.9, 124.6, 119.9, 33.9, 32.9, 22.6, 13.9. IR (NaCl) 3273, 2956, 2922, 2853, 1653, 1598, 1534, 1438, 1323. HRMS (ESI+) calcd for $[C_{17}H_{20}NO]^+$ 254.1539, found 254.1534.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and characterization material for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) A similar transformation with carboxylic anhydrides, but with limited diorganozinc scope, has been described. See ref 18.
(26) A more comprehensive list of optimization efforts is included in the Supporting Information.
(27) The two isomeric products were obtained in a 1:1.2 ratio and identified as decarbonylative alkylation products by mass spectrometry. Conclusive identification of the structure of the isomers in the mixture was unsuccessful.
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