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Preparation of 3,4,5-Trisubstituted Oxazolones by Pd-Catalyzed Coupling of *N*-Alkynyl *tert*-Butyloxycarbamates with Aryl Halides and Related Electrophiles

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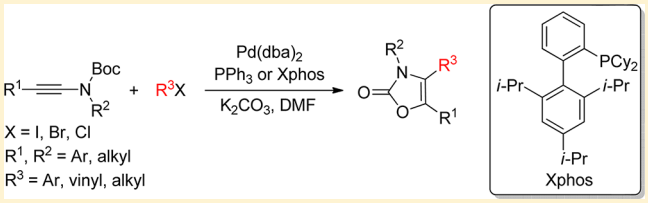
Supporting Information

ABSTRACT: A novel palladium-catalyzed approach for the assembly of 3,4,5-trisubstituted oxazolones has been achieved by the coupling of *N*-alkynyl *tert*-butyloxycarbamates with aryl halides and related electrophiles, which involves an oxidative addition followed by oxypalladation/reductive elimination. The reaction provides a convenient access to diversely substituted oxazolones in satisfactory yields and shows good functional group compatibility.



Oxazolones occur in a number of natural products and pharmacological active compounds and have attracted extensive interest in organic chemistry. For example, oxazolones are known to be versatile starting materials for the cycloaddition reaction,[1−3] radical reaction,[4,5] and assembly of synthetic useful functionalized heterocycles.[6,7] However, there are only limited methods for the effective synthesis of multisubstituted oxazolones.[8−13] A powerful method for the production of 3,5-disubstituted oxazolones featuring a Au-catalyzed cyclization of *N*-alkynyl *tert*-butyloxycarbamates has been developed by Hashmi[14] and Gagosz,[15] independently. In 2008, Jiang and co-workers reported an efficient approach to oxazolones from propargylic alcohols and carbon dioxide under supercritical conditions.[16] More recently, the Lautens group described an elegant synthesis of 3,5-disubstituted oxazolones using a Pd-catalyzed transformation of *β*,*β*-dibromoenamides.[17] Despite the success of these methods, an effective and general synthesis of 3,4,5-trisubstituted oxazolones from readily available starting materials constitutes a demanding goal. Given our continuing interest in the Pd-catalyzed functionalization of heteroatom-substituted acetylenes,[18−25] we describe herein a facile access to 3,4,5-trisubstituted oxazolones by the Pd(0)-catalyzed coupling of *N*-alkynyl *tert*-butyloxycarbamates with aromatic halides and related electrophiles.

Conditions for the new Pd-catalyzed approach to 3,4,5-trisubstituted oxazolones were explored by the reaction of *N*-alkynyl *tert*-butyloxycarbamate **1a** with iodobenzene (**2a**). As a result, treating **1a** with 5 mol % of $Pd(dba)_2$, 10 mol % of PPh_3 and 1.5 equiv of Cs_2CO_3 in DMF at 70 °C for 8 h produced the desired product **4** in 18% yield (Table 1, entry 1). This result prompted us to investigate the suitable reaction parameters. To our delight, the readily available K_2CO_3 or Na_2CO_3 performed best, and the yield was improved to 92% (Table 1, entries 4 and 5). Polar solvents, such as DMF, DMSO, MeCN, and NMP, worked well for this reaction, whereas nonpolar solvents including dioxane and toluene just led to the recovery of starting material **1a**, probably due to the low solubility of K_2CO_3 in these solvents (Table 1, entries 5−10). The omission of PPh_3 ligand resulted in low conversion (Table 1, entry 11). Interestingly, the ligand evaluation (Table 1, entries 12−18) revealed that the readily accessible PPh_3 was the most effective ligand for this transformation, thus making this reaction rather practical and attractive for the synthetic community. Other palladium sources such as $Pd(OAc)_2$ and $Pd(PPh_3)_4$ could also promote the reaction, albeit in relative lower yields (Table 1, entries 19 and 20, respectively). Therefore, 5 mol % of $Pd(dba)_2$, 10 mol % of PPh_3, and 1.5 equiv of K_2CO_3 in DMF at 70 °C were chosen as the best conditions for the Pd-catalyzed coupling of *N*-alkynyl *tert*-butyloxycarbamates with aromatic iodides.

The optimized reaction conditions appeared to be remarkably general. As shown in Table 2, a wide range of aryl iodides coupled smoothly with **1a** to provide 3,4,5-trisubstituted oxazolones in moderate to excellent yields (Table 2, entries 1−9). For instance, 1-bromo-4-iodobenzene (**2e**) and 4-iodobenzaldehyde (**2f**) formed the desired products **8** and **9** in 90 and 81% yield, respectively (Table 2, entries 5 and 6). The X-ray analysis of **10** clearly demonstrated the structure of 3,4,5-trisubstituted oxazolone products.

In addition, the more accessible aryl bromides proved to be competent substrates for this reaction, giving rise to 3,4,5-trisubstituted oxazolones in good yields, albeit at an elevated reaction temperature (Table 2, entries 10−25). Various functional groups, such as F, Cl, Br, OMe, CO_2Et, CHO, $COCH_3$, and CN, turned out to be well tolerated under the optimized conditions. For example, 4-chloroiodobenzene (**3d**) generated **7** in 80% yield, while 2-chloroiodobenzene (**3e**) gave rise to **13** in 82% yield (Table 2, entries 13 and 14), indicating that yield remained high independent of where the chlorine

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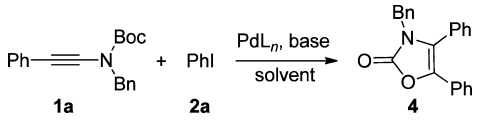
Table 1. Optimization of Reaction Parameters[a]



entry	Pd catalyst	base	ligand	solvent	yield (%)[b]
1	$Pd(dba)_2$	Cs_2CO_3	PPh_3	DMF	18
2	$Pd(dba)_2$	Et_3N	PPh_3	DMF	52
3	$Pd(dba)_2$	*t*-BuOK	PPh_3	DMF	18
4	$Pd(dba)_2$	Na_2CO_3	PPh_3	DMF	92
5	$Pd(dba)_2$	K_2CO_3	PPh_3	DMF	92 (94)[c]
6	$Pd(dba)_2$	K_2CO_3	PPh_3	DMSO	72
7	$Pd(dba)_2$	K_2CO_3	PPh_3	CH_3CN	90
8	$Pd(dba)_2$	K_2CO_3	PPh_3	NMP	75
9	$Pd(dba)_2$	K_2CO_3	PPh_3	dioxane	trace
10	$Pd(dba)_2$	K_2CO_3	PPh_3	toluene	NR
11	$Pd(dba)_2$	K_2CO_3	/	DMF	43
12	$Pd(dba)_2$	K_2CO_3	P(*o*-tol)$_3$	DMF	44
13	$Pd(dba)_2$	K_2CO_3	P(*p*-tol)$_3$	DMF	46
14	$Pd(dba)_2$	K_2CO_3	P(2-furyl)$_3$	DMF	85
15	$Pd(dba)_2$	K_2CO_3	$PCy_3{\cdot}HBF_4$	DMF	36
16	$Pd(dba)_2$	K_2CO_3	Xphos	DMF	87
17	$Pd(dba)_2$	K_2CO_3	dppe	DMF	51
18	$Pd(dba)_2$	K_2CO_3	dppb	DMF	80
19	$Pd(OAc)_2$	K_2CO_3	PPh_3	DMF	55
20	$Pd(PPh_3)_4$	K_2CO_3	/	DMF	85

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.30 mmol), Pd catalyst (0.013 mmol), ligand (0−0.025 mmol), and base (0.38 mmol) in 1 mL of solvent at 70 °C for 8 h. [b]Isolated yield. [c]Yield on a 10 mmol scale.

atom was positioned. Notably, the reaction of 4-iodoanisole (**2h**) and 4-bromoanisole (**3i**) afforded oxazolone **11** in only moderate yields, thus implying that the oxidative addition of electron-rich carbon−halide bonds might be difficult under the standard conditions. It was reported that electron-rich phosphine ligands such as Xphos[26] can accelerate the oxidative addition. On the other hand, Xphos turned out to be one of the most effective ligands in the initial optimization of the reaction conditions (Table 1, entry 16). As such, we used Xphos as the ligand for these two substrates, and as expected, the reaction provided **11** in good yields within 4 h (Table 2, entries 8 and 18).

We found that the steric hindrance has some effect on this reaction. For instance, 4-bromoacetophenone (**3k**) reacted well with **1a** to generate 3,4,5-trisubstituted oxazolone **12** in 74% yield, while the reaction of 2-bromoacetophenone (**3l**, Table 2, entry 21) failed to proceed. 2-Bromomesitylene (**3m**, Table 2, entry 22) did not provide the expected product, either. As for heteroaryl bromides, 2-bromopyridine (**3n**), 2-bromothiophene (**3o**), and 3-bromothiophene (**3p**), for example, participated well in this reaction and produced the desired oxazolones in good yields (Table 2, entries 23−25, respectively). In the case of alkenyl halides, the reaction of *β*-bromostyrene (**3q**) only led to trace of the desired product, while *α*-bromostyrene (**3r**) furnished **19** in 71% yield under the same conditions (Table 2, entries 26 and 27, respectively). We also extended this reaction to benzyl bromide (**3s**), and the reaction occurred successfully to provide **20** in 81% yield (Table 2, entry 28). In contrast, chlorobenzene (**3t**) proved to be a hindered substrate, only leading to oxazolone **4** in 37% yield. Fortunately, applying Xphos[26] instead of PPh_3 as the ligand resulted in full conversion of chlorobenzene and an isolated yield of 84% of product **4** (Table 2, entry 29).

The scope of the reaction with *N*-alkynyl *tert*-butyloxycarbamates was also briefly investigated. For example, *N*-alkynyl *tert*-butyloxycarbamates **1b** and **1c** gave rise to 3,4,5-trisubstituted oxazolones **21** and **22** in respective yields of 84 and 93% (Table 2, entries 34 and 35). Besides the *N*-Bn substrate **1a**, *N*-alkynyl *tert*-butyloxycarbamates, including **1j**, **1k**, and **1l**, coupled with **2a** smoothly to give the corresponding products in good yields (Table 2, entries 42−44). Furthermore, the reaction of aliphatic *N*-alkynyl *tert*-butyloxycarbamates took place well to form the desired products in reasonable yields (Table 2, entries 45 and 46).

Having established an expeditious route to 3,4,5-trisubstituted oxazolones, the applicability of this protocol was briefly studied (Scheme 1). Hakimelahi et al. reported that phenanthro[9,10-*d*]oxazol-2-ones could be synthesized by a photolytic closure of 4,5-diphenyl-oxazol-2-ones.[27] Using this photochemical procedure, we found that the resultant 3,4,5-trisubstituted oxazolone **7** could be smoothly converted into 3-benzyl-6-chlorophenanthro[9,10-*d*]oxazol-2-one (**34**) in 61% yield. In addition, a substituted naphtho[1,2-*d*]oxazol-2-one **35** was synthesized from **19** in good yield (Scheme 1). The structure of **35** was identified by the X-ray diffraction analysis.

We propose that the Pd-catalyzed coupling of *N*-alkynyl *tert*-butyloxycarbamates with aromatic halides and related electrophiles proceeds according to the mechanism illustrated in Scheme 2. The oxidative addition of carbon−halide bond of R^3X to Pd^0 catalyst forms the palladium intermediate **I**, followed by the oxypalladation of C−C triple bond[28−43] via the intermediate **II** to provide a palladium species **III**. A similar cationic intermediate has also been suggested in previous studies on the cycloisomerization of *N*-alkynyl *tert*-butyloxycarbamates.[14,15,24] Finally, the cleavage of C−O bond of the *tert*-butyloxy group in the intermediate **III** as well as reductive elimination results in the formation of 3,4,5-trisubstituted oxazolones with regeneration of the palladium catalyst (Scheme 2).

In conclusion, we have developed here a new method for the preparation of highly substituted oxazolones by a Pd-catalyzed coupling of *N*-alkynyl *tert*-butyloxycarbamates with aryl halides and related electrophiles that involves an oxidative addition followed by oxypalladation/reductive elimination sequence. The reaction proceeds smoothly to afford 3,4,5-trisubstituted oxazolones in satisfactory yields with good functional group tolerance. Moreover, the resulting products are applicable to the construction of phenanthrene and naphthalene derivatives, and we believe that it will be useful for the synthetic community.

EXPERIMENTAL SECTION

General Methods. Column chromatography was performed using silica gel (300−400 mesh). The ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a 400 MHz NMR spectrometer. High-resolution mass spectra (HRMS) analyses were carried out using electron ionization−quadrupole or electrospray ionization−time-of-flight (ESI-TOF) mass spectrometry. $Pd(PPh_3)_4$, $Pd(OAc)_2$, $Pd(dba)_2$, and other reagents were obtained commercially and used without further purification. The *N*-alkynyl *tert*-butyloxycarbamate substrates were prepared from bromoalkynes with secondary *tert*-butyloxycarbamates according to Gagosz's method.[15] To a solution of a phenylethynyl bromide (90 mg, 0.5 mmol) in 2 mL of toluene was added *tert*-butyl benzylcarbamate (124 mg, 0.6 mmol), K_3PO_4 (254 mg, 1.2 mmol), $CuSO_4{\cdot}5H_2O$ (25 mg, 0.1 mmol), and 1.10-

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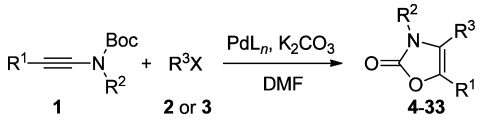
Table 2. Scope and Limitations of the Reaction[a]



1 2 or 3 4-33

entry	R^1/R^2	R^3X	temp (°C)	time (h)	yield (%)[b]
1	Ph/Bn (**1a**)	PhI (**2a**)	70	8	92 (**4**)
2	Ph/Bn (**1a**)	2-CH_3-C_6H_4I (**2b**)	70	8	82 (**5**)
3	Ph/Bn (**1a**)	4-F-C_6H_4I (**2c**)	70	8	84 (**6**)
4	Ph/Bn (**1a**)	4-Cl-C_6H_4I (**2d**)	70	8	91 (**7**)
5	Ph/Bn (**1a**)	4-Br-C_6H_4I (**2e**)	70	8	90 (**8**)
6	Ph/Bn (**1a**)	4-CHO-C_6H_4I (**2f**)	70	8	81 (**9**)
7	Ph/Bn (**1a**)	4-CO_2Et-C_6H_4I (**2g**)	70	8	84 (**10**)
8	Ph/Bn (**1a**)	4-OMe-C_6H_4I (**2h**)	70	8/4[c]	38/65[c] (**11**)
9	Ph/Bn (**1a**)	4-CH_3CO-C_6H_4I (**2i**)	70	8	81 (**12**)
10	Ph/Bn (**1a**)	PhBr (**3a**)	110	8	84 (**4**)
11	Ph/Bn (**1a**)	2-CH_3-C_6H_4Br (**3b**)	110	8	78 (**5**)
12	Ph/Bn (**1a**)	4-F-C_6H_4Br (**3c**)	110	8	77 (**6**)
13	Ph/Bn (**1a**)	4-Cl-C_6H_4Br (**3d**)	110	8	80 (**7**)
14	Ph/Bn (**1a**)	2-Cl-C_6H_4Br (**3e**)	110	8	82 (**13**)
15	Ph/Bn (**1a**)	4-CHO-C_6H_4Br (**3f**)	110	8	81 (**9**)
16	Ph/Bn (**1a**)	3-CHO-C_6H_4Br (**3g**)	110	8	91 (**14**)
17	Ph/Bn (**1a**)	4-CO_2Et-C_6H_4Br (**3h**)	110	8	85 (**10**)
18	Ph/Bn (**1a**)	4-OMe-C_6H_4Br (**3i**)	110	8/4[c]	47/72[c] (**11**)
19	Ph/Bn (**1a**)	3-CN-C_6H_4Br (**3j**)	110	8	93 (**15**)
20	Ph/Bn (**1a**)	4-CH_3CO-C_6H_4Br (**3k**)	110	8	74 (**12**)
21	Ph/Bn (**1a**)	2-CH_3CO-C_6H_4Br (**3l**)	110	8	complex
22	Ph/Bn (**1a**)	2,4,6-$(Me)_3$-C_6H_2Br (**3m**)	110	8	complex
23	Ph/Bn (**1a**)	2-bromopyridine (**3n**)	110	8	70 (**16**)
24	Ph/Bn (**1a**)	2-bromothiophene (**3o**)	110	8	85 (**17**)
25	Ph/Bn (**1a**)	3-bromothiophene (**3p**)	110	8	77 (**18**)
26	Ph/Bn (**1a**)	*β*-bromostyrene (**3q**)	110	8	complex
27	Ph/Bn (**1a**)	*α*-bromostyrene (**3r**)	110	8	71 (**19**)
28	Ph/Bn (**1a**)	BnBr (**3s**)	80	8	81 (**20**)
29	Ph/Bn (**1a**)	PhCl (**3t**)	110	8/4[c]	37/84[c] (**4**)
30	Ph/Bn (**1a**)	2-CH_3-C_6H_4Cl (**3u**)	110	4[c]	77[c] (**5**)
31	Ph/Bn (**1a**)	4-F-C_6H_4Cl (**3v**)	110	4[c]	82[c] (**6**)
32	Ph/Bn (**1a**)	4-CHO-C_6H_4Cl (**3w**)	110	3[c]	73[c] (**9**)
33	Ph/Bn (**1a**)	4-CH_3CO-C_6H_4Cl (**3x**)	110	3[c]	72[c] (**12**)
34	4-CH_3-C_6H_4/Bn (**1b**)	PhI (**2a**)	70	8	84 (**21**)
35	4-F-C_6H_4/Bn (**1c**)	PhI (**2a**)	70	8	93 (**22**)
36	4-Cl-C_6H_4/Bn (**1d**)	PhI (**2a**)	70	8	83 (**23**)
37	4-Br-C_6H_4/Bn (**1e**)	PhI (**2a**)	70	8	71 (**24**)
38	3-Br-C_6H_4/Bn (**1f**)	PhI (**2a**)	70	8	68 (**25**)
39	4-OMe-C_6H_4/Bn (**1g**)	PhI (**2a**)	70	8	95 (**26**)
40	3,4-$(OMe)_2$-C_6H_3/Bn (**1h**)	PhI (**2a**)	70	8	90 (**27**)
41	2-naphthyl/Bn (**1i**)	PhI (**2a**)	70	8	85 (**28**)
42	Ph/Ph (**1j**)	PhI (**2a**)	70	8	92 (**29**)
43	Ph/4-Cl-C_6H_4 (**1k**)	PhI (**2a**)	70	8	85 (**30**)
44	Ph/Cy (**1l**)	PhI (**2a**)	70	8	61 (**31**)
45	TBDPSO$(CH_2)_2$/Ph (**1m**)	PhI (**2a**)	70	8	72 (**32**)
46	*n*-C_8H_{17}/Ph (**1n**)	PhI (**2a**)	70	8	71 (**33**)

[a]Reaction conditions: **1** (0.25 mmol), R^3X (0.30 mmol), $Pd(dba)_2$ (0.013 mmol), PPh_3 (0.025 mmol), and K_2CO_3 (0.38 mmol) in 1 mL of DMF. [b]Isolated yield. [c]Xphos was used.

phenanthroline (31 mg, 0.2 mmol). After stirring at 80 °C for 48 h, the reaction mixture was cooled and filtered through Celite. The filtrate was concentrated and purified by column chromatography on silica gel (petroleum ether/EtOAc = 8/1) to afford 92 mg (yield 60%) of *N*-alkynyl *tert*-butyloxycarbamate **1a**[15] as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.56 (s, 9H), 4.69 (s, 2H), 7.27−7.50 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.0, 53.5, 70.9, 82.4, 84.3, 123.8, 126.9, 127.7, 128.0, 128.1, 128.4, 130.5, 136.5, 153.7; MS (EI, *m*/*z*) 307 (M^+, 16), 250 (26), 206 (13), 173 (11).

General Procedure for Pd-Catalyzed Synthesis of 3,4,5-Trisubstituted Oxazolones. To a mixture of **1a** (77 mg, 0.25 mmol), $Pd(dba)_2$ (7.5 mg, 0.013 mmol), K_2CO_3 (52 mg, 0.38 mmol) and PPh_3 (6.5 mg, 0.025 mmol) in 1 mL of DMF was added **2a** (61 mg, 0.3 mmol) under nitrogen atmosphere. After stirring at 70 °C for 8 h, the reaction mixture was quenched with water, extracted with

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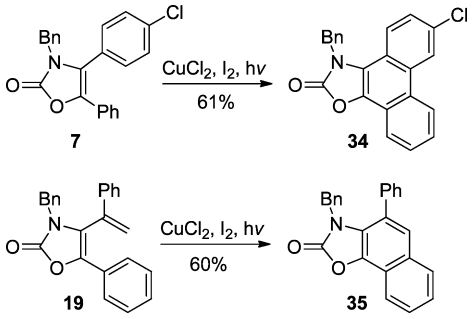
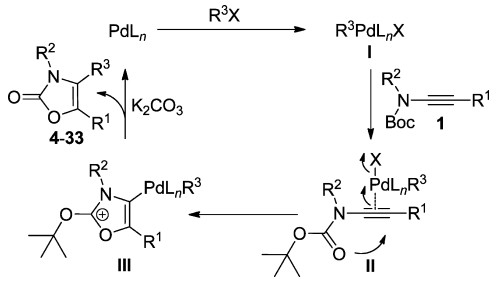
Scheme 1. Transformations of 3,4,5-Trisubstituted 2-Oxazolones



Scheme 2. Proposed Mechanism



ethyl acetate, washed with brine, dried over Na_2SO_4 and concentrated. Column chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave 92% (75 mg) of compound **4**[44] as a yellow solid: mp 96−98 °C. Compound **4** was also prepared from **3a** in 84% yield (68 mg) using the general procedure except the reaction temperature was 110 °C: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.68 (s, 2H), 6.95−7.10 (m, 2H), 7.16−7.32 (m, 10H), 7.40−7.50 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.6, 123.3, 124.2, 126.9, 127.5, 127.6, 127.6, 127.7, 128.4, 128.5, 129.2, 130.0, 130.5, 134.5, 136.0, 154.8 (C═O); IR (KBr) 3034, 1754, 1496, 1445, 1054 cm^{-1}; MS (EI, *m*/*z*) 327 (M^+, 11), 283 (1), 194 (100), 165 (20).

Compound ***5***. It was prepared from **2b**, **3b**, and **3u** in respective yields of 82% (70 mg), 78% (67 mg), and 77% (66 mg); yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.84 (s, 3H), 4.52 (d, *J* = 15.2 Hz, 1H), 4.65 (d, *J* = 15.2 Hz, 1H), 6.87−6.98 (m, 2H), 7.10−7.25 (m, 9H), 7.27−7.39 (m, 2H), 7.41−7.50 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.0, 45.7, 122.0, 123.5, 126.4, 126.6, 127.4, 127.8, 127.9, 128.0, 128.4, 128.5, 130.4, 130.7, 131.1, 134.3, 135.9, 139.1, 154.9 (C═O); IR (KBr) 3063, 3033, 1755, 1602, 1379, 1055 cm^{-1}; MS (EI, *m*/*z*) 341 (M^+, 8), 327 (1), 250 (15), 222 (25), 179 (21); HRMS (EI) calcd for $C_{23}H_{19}NO_2$ (M^+) 341.1416, found 341.1411.

Compound ***6***. It was prepared from **2c**, **3c**, and **3v** in respective yields of 84% (72 mg), 77% (66 mg), and 82% (71 mg); white solid: mp 104−106 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.67 (s, 2H), 6.95−7.05 (m, 2H), 7.12 (t, *J* = 8.4 Hz, 2H), 7.20−7.42 (m, 10H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −110.0; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.6, 116.5 (d, *J* = 22.6 Hz), 122.1, 123.0 (d, *J* = 3.0 Hz), 124.2, 127.4, 127.5, 127.8 (d, *J* = 4.6 Hz), 128.5, 128.6, 132.6, 132.7, 134.8, 135.9, 154.7 (C═O), 163.5 (d, *J* = 250.0 Hz); IR (KBr) 3054, 1754, 1606, 1514 cm^{-1}; MS (EI, *m*/*z*) 345 (M^+, 6), 254 (7), 226 (7), 183 (6); HRMS (EI) calcd for $C_{22}H_{16}FNO_2$ (M^+) 345.1165, found 345.1169.

Compound ***7***. It was prepared from **2d** and **3d** in respective yields of 91% (82 mg) and 80% (72 mg); white solid: mp 159−161 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.68 (s, 2H), 6.90−7.01 (m, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.21−7.32 (m, 8H), 7.40 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.7, 122.0, 124.3, 125.4, 127.3, 127.5, 127.8, 127.9, 128.5, 128.6, 129.6, 131.9, 134.8, 135.8, 136.2, 154.7 (C═O); IR (KBr) 3093, 3032, 1754, 1598, 1444 cm^{-1}; MS (EI, *m*/*z*) 363 (1), 361 (M^+, 3), 270 (5), 272 (1), 235 (3); HRMS (EI) calcd for $C_{22}H_{16}ClNO_2$ (M^+) 361.0870, found 361.0867.

Compound ***8***. 90% yield (91 mg); white solid: mp 166−168 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.67 (s, 2H), 6.99−7.10 (m, 4H), 7.15−7.30 (m, 8H), 7.56 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.7, 122.0, 124.3, 124.5, 125.9, 127.3, 127.8, 127.9, 128.5, 128.6, 132.1, 132.5, 134.8, 135.9, 154.7 (C═O); IR (KBr) 3089, 1754, 1597, 1343, 1057 cm^{-1}; MS (EI, *m*/*z*) 407 (8), 405 (M^+, 10), 316 (6), 314 (8), 235 (12); HRMS (EI) calcd for $C_{22}H_{16}BrNO_2$ (M^+) 405.0364, found 405.0363.

Compound ***9***. It was prepared from **2f**, **3f**, and **3w** in respective yields of 81% (72 mg), 81% (72 mg), and 73% (65 mg); white solid: mp 165−167 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.71 (s, 2H), 6.91−7.02 (m, 2H), 7.09−7.25 (m, 8H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 10.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.9, 122.0, 124.6, 127.1, 127.3, 127.9, 128.2, 128.5, 128.6, 130.2, 131.2, 133.1, 135.2, 135.7, 136.9, 154.8 (C═O), 191.2; IR (KBr) 3047, 2815, 2730, 1757, 1701, 1604, 1374 cm^{-1}; MS (EI, *m*/*z*) 355 (M^+, 5), 326 (1), 264 (2), 208 (5), 165 (6); HRMS (EI) calcd for $C_{23}H_{17}NO_3$ (M^+) 355.1208, found 355.1208.

Compound ***10***. It was prepared from **2g** and **3h** in respective yields of 84% (84 mg) and 85% (85 mg); white solid: mp 117−119 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.43 (t, *J* = 7.2 Hz, 3H), 4.42 (q, *J* = 7.2 Hz, 2H), 4.69 (s, 2H), 6.95−7.02 (m, 2H), 7.10−7.25 (m, 8H), 7.30 (d, *J* = 8.0 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 45.8, 61.4, 122.3, 124.5, 127.3, 127.4, 127.9, 128.0, 128.5, 128.6, 130.2, 130.6, 131.5, 131.8, 134.9, 135.8, 154.8 (C═O), 165.7; IR (KBr) 3029, 1754, 1714, 1607, 1445 cm^{-1}; MS (EI, *m*/*z*) 399 (M^+, 2), 326 (1), 308 (1), 235 (12), 105 (100); HRMS (EI) calcd for $C_{25}H_{21}NO_4$ (M^+) 399.1471, found 399.1477. Crystal data for **10** ($C_{25}H_{21}NO_4$, 399.43): monoclinic, space group C2/c, *a* = 22.874(3) Å, *b* =14.556(2) Å, *c* = 12.4930(12) Å, volume = 4145.3(9) Å^3, *Z* = 8, specimen 0.341 × 0.237 × 0.187 mm^3, *T* = 296(2) K, SIEMENS P4 diffractometer, absorption coefficient 0.087 mm^{-1}, reflections collected 16761, independent reflections 4747 [*R*(int) = 0.0542], refinement by full-matrix least-squares on F^2, data/restraints/parameters 4747/0/272, goodness-of-fit on F^2 = 0.983, final *R* indices [$I>2\sigma(I)$] *R*1 = 0.0537, *wR*2 = 0.1286, *R* indices (all data) *R*1 = 0.1282, *wR*2 = 0.1629, largest diff peak and hole 0.159 and −0.180 eÅ^{-3}. Crystallographic data for compound **10** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 896886.

Compound ***11***. It was prepared from **2h** and **3i** in respective yields of 65% (58 mg) and 72% (64 mg) using Xphos instead of PPh_3; white solid: mp 122−124 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.87 (s, 3H), 4.66 (s, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.98−7.10 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.25−7.40 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.5, 55.3, 114.7, 118.8, 123.2, 124.1, 127.5, 127.7, 127.9, 128.4, 128.5, 132.0, 134.5, 136.2, 154.9 (C═O), 160.7; IR (KBr) 3054, 1754, 1606, 1514 cm^{-1}; MS (EI, *m*/*z*) 357 (M^+, 6), 326 (1), 266 (20), 238 (8), 133 (8); HRMS (EI) calcd for $C_{23}H_{19}NO_3$ (M^+) 357.1365, found 357.1362.

Compound ***12***. It was prepared from **2i**, **3k**, and **3x** in respective yields of 81% (75 mg), 74% (68 mg), and 72% (66 mg); white solid: mp 148−150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.66 (s, 3H), 4.69 (s, 2H), 6.92−7.08 (m, 2H), 7.12−7.25 (m, 8H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.7, 45.8, 122.1, 124.5, 127.2, 127.3, 127.9, 128.1, 128.5, 128.6, 129.0, 130.8, 131.7, 135.0, 135.7, 137.9, 154.8 (C═O), 197.2; IR (KBr) 3054, 1755, 1682, 1604, 1380 cm^{-1}; MS (EI, *m*/*z*) 369 (M^+, 4), 278 (5), 250 (1), 207 (4); HRMS (EI) calcd for $C_{24}H_{19}NO_3$ (M^+) 369.1365, found 369.1364.

Compound ***13***. 82% yield (74 mg); yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.45 (d, *J* = 15.2 Hz, 1H), 4.88 (d, *J* = 15.2 Hz, 1H), 6.88−6.98 (m, 2H), 7.05−7.12 (m, 1H), 7.18−7.30 (m, 9H), 7.39−7.50 (m, 1H), 7.54−7.61 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 46.0, 120.1, 123.9, 126.3, 127.4, 127.4, 127.7, 127.8, 128.4, 128.5, 130.1, 131.7, 133.1, 135.3, 135.6, 135.7, 154.7 (C═O); IR (KBr) 3063, 1758, 1600, 1383, 1237 cm^{-1}; MS (EI, *m*/*z*) 363 (3), 361 (M^+, 9), 272 (1), 270 (4), 235 (15); HRMS (EI) calcd for $C_{22}H_{16}ClNO_2$ (M^+) 361.0870, found 361.0863.

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Compound ***14***. 91% yield (81 mg); yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.68 (s, 2H), 6.86−7.01 (m, 2H), 7.12−7.30 (m, 8H), 7.38−7.50 (m, 1H), 7.52−7.70 (m, 2H), 7.99 (d, J = 7.6 Hz, 1H), 9.90 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.9, 121.7, 124.4, 127.2, 127.3, 127.9, 128.0, 128.2, 128.5, 128.6, 130.0, 130.5, 132.1, 135.1, 135.8, 136.3, 137.0, 154.7 (C═O), 190.9; IR (KBr) 3062, 2834, 2728, 1751, 1600, 1447 cm^{-1}; MS (EI, m/z) 355 (M^+, 6), 326 (2), 264 (3), 242 (7); HRMS (EI) calcd for $C_{23}H_{17}NO_3$ (M^+) 355.1208, found 355.1215.

Compound ***15***. 93% yield (82 mg); yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.68 (s, 2H), 6.90−7.02 (m, 2H), 7.15−7.30 (m, 8H), 7.39 (s, 1H), 7.41−7.50 (m, 1H), 7.55−7.61 (m, 1H), 7.75 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.9, 113.5, 117.4, 120.7, 124.4, 126.8, 127.2, 128.0, 128.3, 128.6, 128.7, 130.1, 133.3, 134.1, 134.9, 135.3, 135.5, 154.5 (C═O); IR (KBr) 3064, 2231, 1755, 1602, 1351 cm^{-1}; MS (EI, m/z) 352 (M^+, 12), 326 (1), 261 (5), 190 (7); HRMS (EI) calcd for $C_{23}H_{16}N_2O_2$ (M^+) 352.1212, found 352.1213.

Compound ***16***. 70% yield (57 mg); yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.03 (s, 2H), 6.90−7.03 (m, 2H), 7.12−7.41 (m, 10H), 7.50−7.64 (m, 1H), 8.78−8.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.7, 122.1, 123.8, 125.4, 125.9, 127.3, 127.6, 128.4, 128.5, 128.5, 136.2, 136.3, 136.8, 147.4, 150.2, 154.8 (C═O); IR (KBr) 3062, 1755, 1585, 1349, 1054 cm^{-1}; MS (EI, m/z) 328 (M^+, 20), 237 (59), 223 (3), 209 (15), 167 (40); HRMS (EI) calcd for $C_{21}H_{16}N_2O_2$ (M^+) 328.1212, found 328.1210.

Compound ***17***. 85% yield (71 mg); white solid: mp 122−124 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.73 (s, 2H), 6.99 (d, J = 3.6 Hz, 1H), 7.02−7.15 (m, 3H), 7.17−7.30 (m, 6H), 7.35−7.42 (m, 2H), 7.55 (d, J = 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.6, 115.9, 124.6, 126.3, 127.3, 127.4, 127.8, 127.9, 128.1, 128.4, 128.5, 129.8, 131.5, 136.0, 136.9, 154.4 (C═O); IR (KBr) 3070, 1745, 1597, 1382, 1245, 1053 cm^{-1}; MS (EI, m/z) 333 (M^+, 10), 275 (1), 242 (29), 214 (2), 176 (2); HRMS (EI) calcd for $C_{20}H_{15}NO_2S$ (M^+) 333.0823, found 333.0822.

Compound ***18***. 77% yield (64 mg); yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.70 (s, 2H), 6.85−6.95 (m, 1H), 7.02−7.11 (m, 2H), 7.20−7.37 (m, 9H), 7.39−7.51 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.7, 118.4, 124.3 126.7, 127.3, 127.3, 127.7, 127.8, 128.0, 128.5, 128.5, 128.6, 135.3, 136.2, 154.8 (C═O); IR (KBr) 3065, 1744, 1600, 1382, 1242, 1053 cm^{-1}; MS (EI, m/z) 333 (M^+, 6), 242 (12), 214 (2), 171 (3); HRMS (EI) calcd for $C_{20}H_{15}NO_2S$ (M^+) 333.0823, found 333.0820.

Compound ***19***. 71% yield (63 mg); yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.53 (s, 2H), 5.47 (s, 1H), 6.02 (s, 1H), 7.07−7.20 (m, 2H), 7.21−7.42 (m, 11H), 7.55−7.65 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.8, 122.4, 122.5, 124.4, 126.1, 127.5, 127.6, 127.7, 127.8, 128.4, 128.5, 129.0, 129.1, 135.4, 135.5, 136.0, 136.3, 154.9 (C═O); IR (KBr) 3060, 3031, 1747, 1600, 1348 cm^{-1}; MS (EI, m/z) 353 (M^+, 38), 262 (30), 219 (24), 191 (59), 156 (14); HRMS (EI) calcd for $C_{24}H_{19}NO_2$ (M^+) 353.1416, found 353.1421.

Compound ***20***. 81% yield (69 mg); white solid: mp 147−149 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.91 (s, 2H), 4.61 (s, 2H), 7.18 (d, J = 6.8 Hz, 4H), 7.27−7.42 (m, 9H), 7.48−7.60 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.3, 45.4, 120.7, 125.0, 126.9, 127.3, 127.6, 127.8, 127.9, 128.1, 128.8, 129.2, 135.4, 136.0, 136.2, 155.4 (C═O); IR (KBr) 3061, 2925, 1758, 1494, 1396 cm^{-1}; MS (EI, m/z) 341 (M^+, 4), 250 (1), 207 (2), 178 (2), 144 (3); HRMS (EI) calcd for $C_{23}H_{19}NO_2$ (M^+) 341.1416, found 341.1414.

Compound ***21***. 84% yield (72 mg); white solid: mp 112−114 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3H), 4.67 (s, 2H), 7.01 (d, J = 8.4 Hz, 4H), 7.15−7.30 (m, 7H), 7.39−7.51 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1, 45.6, 122.5, 124.3, 124.9, 127.1, 127.5, 127.7, 128.5, 129.0, 129.1, 129.8, 130.6, 134.7, 136.1, 137.6, 154.9 (C═O); IR (KBr) 3061, 1751, 1517, 1346, 1056 cm^{-1}; MS (EI, m/z) 341 (M^+, 6), 250 (19), 234 (7), 173 (13); HRMS (EI) calcd for $C_{23}H_{19}NO_2$ (M^+) 341.1416, found 341.1416.

Compound ***22***. 93% yield (80 mg); white solid: mp 80−82 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.67 (s, 2H), 6.89 (t, J = 8.8 Hz, 2H), 6.95−7.10 (m, 2H), 7.17−7.25 (m, 7H), 7.38−7.47 (m, 2H), 7.49−7.60 (m, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −112.8; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.7, 115.5 (d, J = 21.2 Hz), 122.9, 124.0 (d, J = 2.9 Hz), 126.2 (d, J = 7.6 Hz), 126.8, 127.5, 127.8, 128.5, 129.3, 130.1, 130.6, 133.8, 136.0, 154.7 (C═O), 163.2 (d, J = 247.0 Hz); IR (KBr) 3050, 1754, 1606, 1514 cm^{-1}; MS (EI, m/z) 345 (M^+, 2), 297 (1), 254 (2), 226 (4), 183 (4); HRMS (EI) calcd for $C_{22}H_{16}FNO_2$ (M^+) 345.1165, found 345.1166.

Compound ***23***. 83% yield (75 mg); yellow solid: mp 156−158 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.67 (s, 2H), 6.90−7.02 (m, 2H), 7.17 (s, 4H), 7.19−7.25 (m, 5H), 7.44 (t, J = 7.6 Hz, 2H), 7.60−7.70 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.7, 123.8, 125.4, 126.2, 126.7, 127.5, 127.8, 128.5, 128.7, 129.4, 130.2, 130.5, 133.3, 133.6, 135.9, 154.6 (C═O); IR (KBr) 3087, 3062, 1757, 1666, 1499, 1350 cm^{-1}; MS (EI, m/z) 363 (3), 361 (M^+, 10), 272 (3), 270 (9), 165 (2); HRMS (EI) calcd for $C_{22}H_{16}ClNO_2$ (M^+) 361.0870, found 361.0864.

Compound ***24***. 71% yield (72 mg); yellow solid: mp 130−132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.67 (s, 2H), 6.81−6.97 (m, 2H), 6.99−7.10 (m, 2H), 7.12−7.25 (m, 5H), 7.27−7.38 (m, 2H), 7.41−7.50 (m, 2H), 7.51−7.61 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.7, 121.5, 123.9, 125.7, 126.6, 126.7, 127.5, 127.8, 128.5, 129.4, 130.2, 130.4, 131.6, 133.6, 135.9, 154.6 (C═O); IR (KBr) 3086, 3062, 1758, 1496, 1350, 1070 cm^{-1}; MS (EI, m/z) 407 (11), 405 (M^+, 14), 316 (9), 314 (11), 235 (12); HRMS (EI) calcd for $C_{22}H_{16}BrNO_2$ (M^+) 405.0364, found 405.0361.

Compound ***25***. 68% yield (69 mg); yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.67 (s, 2H), 6.91−7.05 (m, 3H), 7.09−7.15 (m, 1H), 7.19−7.35 (m, 6H), 7.40−7.50 (m, 3H), 7.51−7.59 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.7, 122.6, 124.5, 126.5, 127.1, 127.5, 127.8, 128.5, 129.4, 129.6, 129.9, 130.3, 130.4, 133.0, 135.8, 154.5 (C═O); IR (KBr) 3086, 3055, 1758, 1496, 1347 cm^{-1}; MS (EI, m/z) 407 (17), 405 (M^+, 21), 316 (19), 314 (24), 235 (35); HRMS (EI) calcd for $C_{22}H_{16}BrNO_2$ (M^+) 405.0364, found 405.0368.

Compound ***26***. 95% yield (85 mg); yellow solid: mp 156−158 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.74 (s, 3H), 4.67 (s, 2H), 6.69−6.80 (m, 2H), 6.97−7.09 (m, 2H), 7.15−7.25 (m, 7H), 7.41 (t, J = 7.6 Hz, 2H), 7.48−7.51 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.5, 55.1, 113.8, 120.3, 121.5, 125.8, 127.1, 127.4, 127.6, 128.4, 129.1, 129.8, 130.6, 134.6, 136.1, 154.9 (C═O), 159.0; IR (KBr) 3054, 1754, 1606, 1514 cm^{-1}; MS (EI, m/z) 357 (M^+, 3), 327 (10), 266 (2), 135 (100); HRMS (EI) calcd for $C_{23}H_{19}NO_3$ (M^+) 357.1365, found 357.1360.

Compound ***27***. 90% yield (87 mg); yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.57 (s, 3H), 3.80 (s, 3H), 4.66 (s, 2H), 6.69 (d, J = 8.4 Hz, 1H), 6.73−6.80 (m, 1H), 6.86−6.90 (m, 1H), 6.98−7.10 (m, 2H), 7.14−7.25 (m, 5H), 7.37−7.50 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.6, 55.3, 55.7, 107.4, 110.9, 117.0, 120.5, 121.7, 127.2, 127.4, 127.6, 128.4, 129.1, 129.8, 130.7, 134.5, 136.0, 148.5, 148.6, 154.8 (C═O); IR (KBr) 3072, 3015, 1757, 1589, 1612, 1447 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{21}NO_4$ (M^+) 387.1471, found 387.1465.

Compound ***28***. 85% yield (80 mg); white solid: mp 129−131 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.72 (s, 2H), 6.96−7.07 (m, 2H), 7.12−7.20 (m, 1H), 7.22−7.34 (m, 5H), 7.38−7.62 (m, 6H), 7.66−7.75 (m, 2H), 7.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 45.7, 121.9, 123.4, 123.7, 125.0, 126.2, 126.4, 127.0, 127.5, 127.7, 128.0, 128.1, 128.5, 129.2, 130.1, 130.7, 132.4, 133.0, 134.6, 136.0, 154.8 (C═O); IR (KBr) 3061, 1751, 1624, 1384, 1048 cm^{-1}; MS (EI, m/z) 377 (M^+, 2), 286 (1), 215 (4), 155 (100), 127 (43); HRMS (EI) calcd for $C_{26}H_{19}NO_2$ (M^+) 377.1416, found 377.1412.

Compound ***29***. 92% yield (72 mg); white solid: mp 191−193 °C;[45] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09−7.20 (m, 2H), 7.24−7.41 (m, 13H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.5, 125.0, 126.8, 127.0, 127.5, 127.8, 128.0, 128.4, 128.9, 129.5, 130.2, 133.5, 135.0, 153.5 (C═O); IR (KBr) 1750, 1594, 1374, 1267 cm^{-1}; MS (EI, m/z) 313 (M^+, 13), 254 (1), 236 (2), 180 (100), 165 (28).

Compound ***30***. 85% yield (74 mg); white solid: mp 218−220 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.08 (d, J = 8.4 Hz, 2H), 7.20−7.32 (m, 7H), 7.34−7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.1, 125.0, 126.7, 127.3, 128.0, 128.2, 128.5, 129.2, 129.7, 130.2, 132.1, 133.6, 135.3, 153.3 (C═O); IR (KBr) 3476, 1746, 1594, 1493, 1374 cm^{-1}; MS (EI, m/z) 349 (5), 347 (M^+, 15), 270 (1), 216 (32), 214

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(100); HRMS (EI) calcd for $C_{21}H_{14}ClNO_2$ (M^+) 347.0713, found 347.0710.

Compound **31**. 61% yield (49 mg); yellow solid: mp 151−153 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.05−1.19 (m, 3H), 1.50−1.60 (m, 1H), 1.69−1.81 (m, 4H), 2.10−2.22 (m, 2H), 3.25−3.38 (m, 1H), 7.11−7.22 (m, 5H), 7.28−7.47 (m, 2H), 7.51−7.61 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.7, 25.6, 29.7, 54.4, 123.6, 124.1, 127.3, 127.7, 128.0, 128.3, 129.5, 130.1, 130.7, 134.0, 153.6 (C═O); IR (KBr) 3050, 2926, 2855, 1760, 1588, 1158 cm^{-1}; MS (EI, *m*/*z*) 319 (M^+, 4), 237 (83), 180 (12); HRMS (EI) calcd for $C_{21}H_{21}NO_2$ (M^+) 319.1572, found 319.1570.

Compound **32**. 72% yield (93 mg); yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.09 (s, 9H), 2.83 (t, *J* = 6.0 Hz, 2H), 4.01 (t, *J* = 6.0 Hz, 2H), 7.05−7.20 (m, 4H), 7.22−7.35 (m, 6H) 7.36−7.50 (m, 6H), 7.60−7.72 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.3, 26.9, 28.6, 61.2, 125.0, 126.4, 126.6, 127.4, 127.8, 128.5, 128.6, 129.0, 129.1, 129.8, 133.4, 134.3, 135.3, 135.5, 154.3 (C═O); IR (KBr) 3070, 2930, 2857, 1762, 1598, 1381 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{33}NO_3Si$ (M^+) 519.2230, found 519.2227.

Compound **33**. 71% yield (62 mg); yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.20−1.40 (m, 10H), 1.61−1.72 (m, 2H), 2.44 (t, *J* = 7.6 Hz, 2H), 6.97−7.08 (m, 2H), 7.12−7.20 (m, 2H) 7.22−7.25 (m, 1H), 7.28−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 22.6, 24.8, 27.5, 28.9, 29.0, 29.1, 31.7, 123.0, 126.2, 126.9, 127.2, 128.4, 128.5, 128.8, 129.0, 134.2, 138.3, 154.3 (C═O); IR (KBr) 3061, 2926, 2855, 1766, 1598, 1158 cm^{-1}; MS (EI, *m*/*z*) 349 (M^+, 20), 276 (1), 250 (100), 204 (5), 180 (21); HRMS (EI) calcd for $C_{23}H_{27}NO_2$ (M^+) 349.2042, found 349.2040.

Compound **34**. It was prepared from **7** according to the method described in the literature[27] in 61% yield (55 mg); white solid: mp 255−257 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.55 (s, 2H), 7.28−7.54 (m, 6H), 7.61−7.74 (m, 1H), 7.75−7.83 (m, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.68 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 47.9, 119.0, 120.3, 120.5, 121.5, 122.4, 123.3, 123.9, 126.2, 126.3, 126.6, 127.7, 128.1, 128.4, 129.2, 129.8, 131.9, 135.5, 135.6, 156.0 (C═O); IR (KBr) 3085, 1754, 1522, 1355, 1052 cm^{-1}; MS (EI, *m*/*z*) 361 (1), 359 (M^+, 3), 268 (25), 177 (100); HRMS (EI) calcd for $C_{22}H_{14}ClNO_2$ (M^+), 359.0713, found 359.0720.

Compound **35**. 60% yield (53 mg); white solid: mp 148−150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.89 (s, 2H), 6.60 (d, *J* = 7.2 Hz, 2H), 7.01−7.15 (m, 3H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.41−7.57 (m, 3H), 7.60−7.71 (m, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 46.9, 118.6, 119.4, 124.2, 125.3, 125.7, 126.3, 126.3, 127.2, 127.3, 128.0, 128.1, 128.2, 128.3, 129.3, 129.7, 135.3, 136.8, 137.3, 156.1 (C═O); IR (KBr) 3077, 1753, 1518, 1355, 1052 cm^{-1}; MS (EI, *m*/*z*) 352 (5), 351 (M^+, 18), 260 (56), 232 (64), 203 (100); HRMS (EI) calcd for $C_{24}H_{17}NO_2$ (M^+) 351.1259, found 351.1267. Crystal data for **35** ($C_{24}H_{17}NO_2$, 351.39): monoclinic, space group P2(1)/c, *a* = 6.9736(2) Å, *b* =17.1873(6) Å, *c* = 15.2945(5) Å, volume =1819.13(10) Å^3, *Z* = 4, specimen 0.52 × 0.32 × 0.12 mm^3, *T* = 296(2) K, SIEMENS P4 diffractometer, absorption coefficient 0.082 mm^{-1}, reflections collected 28522, independent reflections 4165 [*R*(int) = 0.0328], refinement by full-matrix least-squares on F^2, data/restraints/parameters 4165/0/245, goodness-of-fit on F^2 = 1.026, final *R* indices [$I>2\sigma(I)$] *R*1 = 0.0396, *wR*2 = 0.0987, *R* indices (all data) *R*1 = 0.0639, *wR*2 = 0.1127, largest diff peak and hole 0.149 and −0.133 eÅ^{-3}. Crystallographic data for compound **35** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 896692.

■ ASSOCIATED CONTENT

Supporting Information

Spectroscopic data of products **4**−**35** and crystal data (CIF) for **10** and **35**. 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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