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Synthesis of Unsymmetrical Diaryl Acetamides, Benzofurans, Benzophenones, and Xanthenes by Transition-Metal-Free Oxidative Cross-Coupling of sp^3 and sp^2 C−H Bonds

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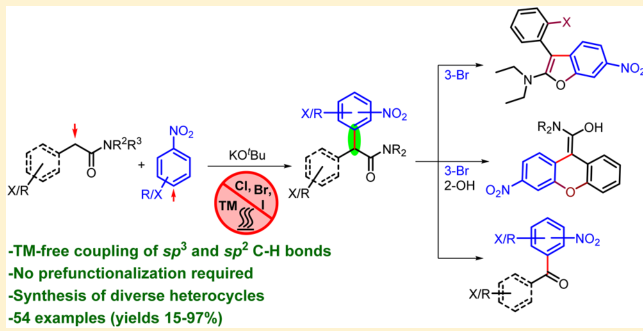
Supporting Information

ABSTRACT: A chemo- and regioselective intermolecular sp^3 C−H and sp^2 C−H coupling reaction for C−C bond formation is described to access unsymmetrical diaryl acetamides under TM-free conditions from *sec*- and *tert*-arylacetamides and nitroarenes using *tert*-butoxide base in DMSO at room temperature. The coupling partners with sensitive functionalities such as chloro, bromo, hydroxy, and cyano were also amenable to the developed reaction. Synthesized α-(2/4-nitroaryl) phenylacetamides have been transformed into biologically important benzofurans, xanthenes, diaryl indoles, and unsymmetrical benzophenones by novel routes without applying a transition metal. Overall, an economical, yet efficient, strategy has been devised to access unsymmetrical diarylacetamides with the possibility of their further elaboration into a variety of biologically important heterocycles. Mechanistic understanding suggests that the reaction proceeds by a nucleophilic addition of a phenylacetamide carbanion, which is generated in the presence of *tert*-butoxide base, to the *para* or *ortho* (if *para* is substituted) position of nitrobenzene. The formed α-(4-nitrocyclohexa-2,4-dien-1-yl) phenylacetamide anion intermediate oxidized by a basic solution of DMSO or atmospheric oxygen led to the desired sp^3 C−H and sp^2 C−H coupled α-(2/4-nitroaryl) phenylacetamides.



■ INTRODUCTION

The direct transition-metal-free cross-coupling of two C−H bonds to form a new C−C bond is a sustainable approach to the synthesis of organic molecules as this strategy is highly atom economical, avoids costly transition metals and ligands, and generates water as side product.[1] Moreover, mild reaction conditions make this approach regio- and chemoselective and tolerate various groups such as halides, NO_2, and OH which provide an easy synthetic handle for later stage transformations.

Amides are common building blocks for the construction of fine chemicals, alkaloids, herbicidal, pharmaceuticals (analgesic; BRL 37959 with low gastric irritancy and potential anticancer agents), chromophores, and materials relevant molecules.[2,3] C−H functionalization in amides, particularly for C−C bond formation, is accomplished by metalation using organolithium reagents, followed by coupling with alkyl halides (Scheme 1).[4a] Light-induced base-mediated intramolecular C−C coupling reactions in α,β-unsaturated amides or *ortho*-halobenzamides are well-documented by Rossi et al. involving electron transfer processes.[4b] Arylation of a benzylic C−H bond in amide has also been realized with aryl halides coupling partners using a Pd catalyst in the presence of strong base such as *tert*-butoxide or potassium bis(trimethyl silyl) amide under heating conditions.[5,6] In an alternative method, zinc-enolate was prepared from amide by the reaction of *sec*-BuLi, followed by the addition of $ZnCl_2$. The zinc-enolate, which was generated *in situ*, smoothly reacted with aryl bromides under Pd-catalyzed conditions at 25−70 °C.[6c]

Ni-catalyzed reaction of α-haloamides with arylboronic acid substrates has also been described for the α-arylation of amides.[7] Nonetheless, the developed methodologies require prefunctionalized coupling partners α-halo-acetamides, haloarenes, or phenylboronic acids and harsh reaction conditions. Prefunctionalized substrates not only lower the economy and generate byproducts but also restrict the substrate scope due to incompatibility of other functional groups in the prefunctionalized substrates. The TM-free direct functionalization of the sp^3 C−H bond in acetamides under mild reaction conditions has not been presented. A mild method may also enable chemoselective C−H arylation in *sec*-amides over the N−H bond, which has not been addressed to date due to nearly the similar reactivity of the N−H bond ($pK_a \leq 20$ for N−H and $pK_a \geq 26$ for the C−H bond). On the other hand, *sec*-amides are better substrates for further functionalizations due to their facile conversion into acid and are also viable coupling partners for inter- and intramolecular C−N or X−N (X = S, Se, P) bond forming reactions.

TM-free approaches for the construction of C−C and C−N bonds are being explored by many researchers in recent

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Scheme 1. Synthetic Routes to Aryl Acetamides

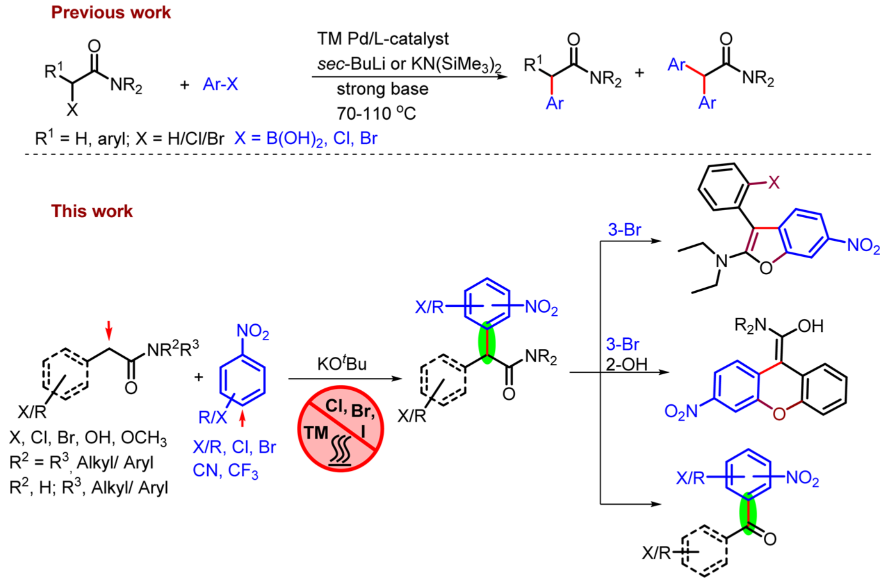
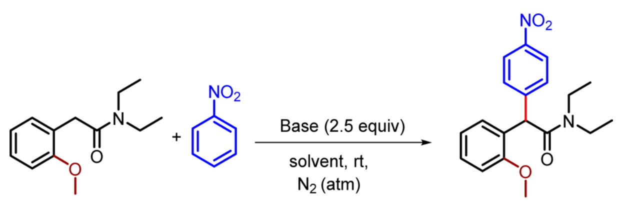


Table 1. Optimization of Reaction Conditions[a]



1

Entry	Base	Solvent	Time (h)	Yield 1 (%)
1	Na_2CO_3	DMSO	12	NR
2	K_2CO_3	DMSO	12	NR
3	Cs_2CO_3	DMSO	12	NR
4	LiO^{t}Bu	DMSO	12	NR
5	KOH	DMSO	4	25
6	NaOH	DMSO	4	18
7	KH	DMSO	4	60
8	NaH	DMSO	4	55
9	**KO^{t}Bu**	**DMSO**	**4**	**(54)[b] (65)[c]**
10	NaO^{t}Bu	DMSO	4	59
11	KO^{t}Bu	DMF	4	42
12	KO^{t}Bu	CH_3CN	4	NR
13	KO^{t}Bu	Benzene	4	NR
14	KO^{t}Bu	DME	4	trace
15	KO^{t}Bu	EtOH	12	NR
16[d]	KO^{t}Bu	DMSO	4	32
17[e]	KO^{t}Bu	DMSO	4	20

[a]Reactions were carried out using amide (0.22 mmol), nitrobenzene (0.27 mmol), and KO^{t}Bu (0.56 mmol) in an inert atmosphere for the indicated time. [b]Yield of **1** was obtained and was carried out in an open flask in the presence of air. [c]Yield of **1** was obtained and was carried out under a nitrogen atmosphere. [d]Reaction was carried out in the presence of $(NH_4)_2S_2O_8$ (0.4 mmol). [e]Reaction was carried out in the presence of $K_2S_2O_8$ (0.4 mmol) used.

times.[1,8−10] Particular interest is the coupling of the C−H bond with arenes for the synthesis of various organic molecules containing an alkyl−aryl bond. Nitroarenes are easily available aromatic substrates; moreover, many of the nitroarenes are economical than other substituted benzenes. Also, the nitro group has wide scope in organic synthesis and the chemical industry as this can be easily manipulated by various methods into indole and carbazole heterocyclic rings and used as a leaving group in biaryl cross-coupling.[10] Our group has also studied C−C and C−N coupling reactions for the synthesis and

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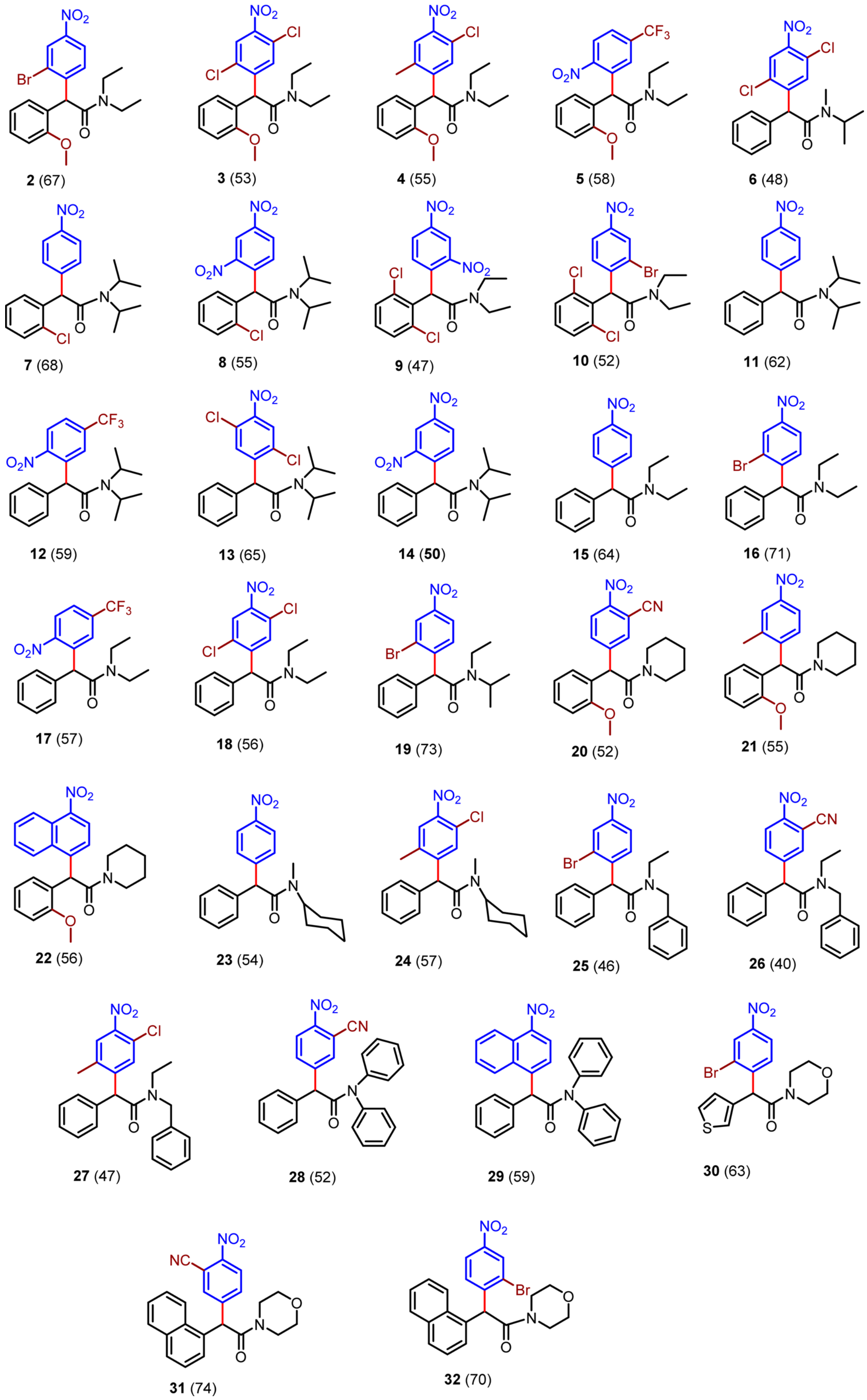
Table 2. Substrate Scope with Regard to *tert*-Amide and Nitroarenes



applications of heterocycles, namely, phenanthridiones, isoindolinones, biaryls, aryl indoles, dihydropyridin-2(1*H*)-ones, and pyridin-2(1*H*)-ones.[11] Nonetheless, intermolecular cross-coupling of sp^3 C−H and sp^2 C−H bonds has not been studied by us. Here, we present *tert*-butoxide base-mediated oxidative coupling of amides with nitroarenes for the synthesis of α-arylated amides at room temperature. Synthesized α-arylated amides were further transformed into unsymmetrical diaryl ketones, 3-aryl-benzofurans, 9*H*-xanthen-9-ylidene, and α-indole aryl amides.

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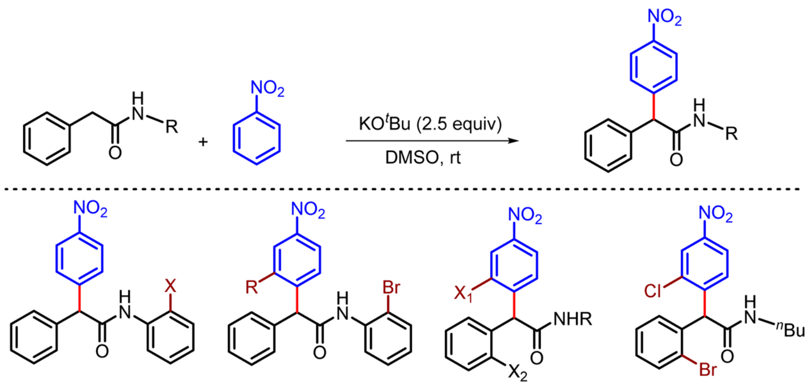
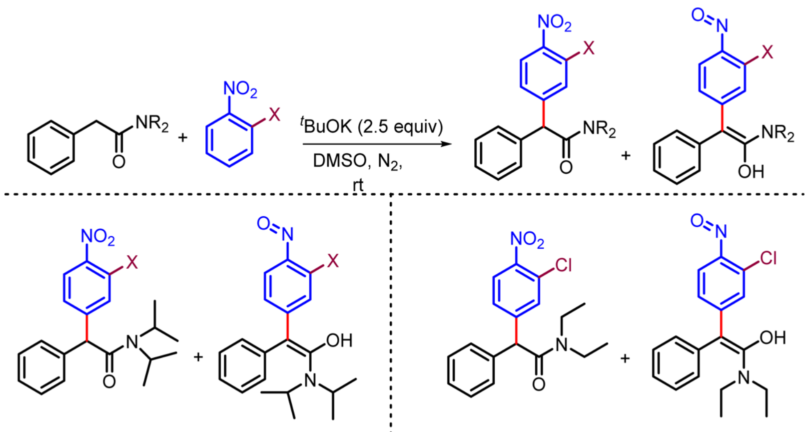
Scheme 2. Synthesis of α-(4-Nitrophenyl)phenyl-*sec*-acetamides



33 X, H (56)
34 X, F (60)
35 R, H (56)
36 R, CH_3 (53)
37 X_1, Cl, X_2, Br, R, Benz (58)
38 X_1, F, X_2, H, R, ^{i}Pr (66)
39 (64)

Scheme 3. Synthesis of α-(4-Nitroso- and nitrophenyl)-phenylacetamides[a]



40 X, **Cl** (40%)
42 X, **F** (60%)
41 X, **Cl** (55%)[a]
43 X, **F** (35%)[a]
44 (30%)
45 (35%)[a]

[a]Nitroso compounds **41**, **43**, and **45** were obtained as a mixture of diastereomers

■ RESULTS AND DISCUSSION

Optimization of reaction conditions was performed on phenyl ring substituted *N*,*N*-diethyl-acetamide and nitrobenzene substrates and is listed in Table 1. Weak bases sodium and potassium carbonates were found ineffective for the promotion of sp^3 and sp^2 C−C coupling reaction (Table 1, entries 1 and 2).

Cesium carbonate and lithium *tert*-butoxide also failed to yield coupled product **1** (Table 1, entries 3 and 4). Strong protic bases KOH and NaOH were poorly effective as they provided 25% and 18% yields, respectively, in DMSO (Table 1, entries 5 and 6). Sodium and potassium hydrides lead further improvement in the yields by 25% (Table 1, entries 7 and 8). Economical sodium and potassium *tert*-butoxides were noticed to be a better base for the coupling of sp^3 and sp^2 C−H bonds (Table 1, entries 9 and 10). Although various other solvents, DMF, acetonitrile, and DME, were screened, DMSO was found to be superior (Table 1, entries 11−15). Worth noticing, the reaction provided a slightly better yield of **1** under a strict nitrogen atmosphere than under air in DMSO. We also screened external oxidants ammonium persulfate and potassium persulfate; disappointingly, low yields of **1** were realized.

After screening of various conditions, the scope with regard to phenylacetamide and nitroarene substrates was explored, and results are summarized in Table 2 and Scheme 2. Methoxy, chloro, dichloro, and bromo substituents in the phenyl ring of acetamides were well-tolerated under the optimized mild reaction conditions and we obtained methoxy and halo substituted phenyl-(α-nitrophenyl)-acetamides **2−10** in nearly the same yields. It seems that the addition of a nucleophile in nitrobenzenes is favorable at the *para*- or *ortho*-C−H bond over the C−halogen bond at room temperature, and therefore, substitution of halogen in nitrobenzene was not observed.[10f,i]

Functional group tolerance in nitrobenzene was studied under the optimized reaction conditions for the TM-free coupling of sp^3 and sp^2 C−H bonds. Functional groups such as cyano, nitro, methyl, trifluoromethyl, and halogens (fluoro, chloro, dichloro, bromo) in nitrobenzene tolerated well under the optimized reaction conditions and yielded variously substituted α-nitrophenyl acetamides **2−4**, **6**, **8−10**, **13−16**, **18−21**, **24−28**, and **30−32**. Interestingly, the expected *SNAr*-coupling of halo-nitrobenzene with acetamide was not observed. The presence of a halo substituent in the product is important for late-stage transformation of molecules (*vide infra*). Here, halogen substituents are well-tolerated in nitrobenzenes as well as in benzene and aniline rings of phenylacetamides because of mild reaction conditions. When *para*-trifluoromethyl nitrobenzene was employed under TM-free coupling of sp^3 and sp^2 C−H bonds, the acetamide coupled

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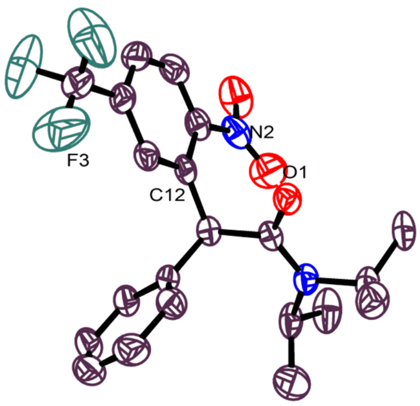
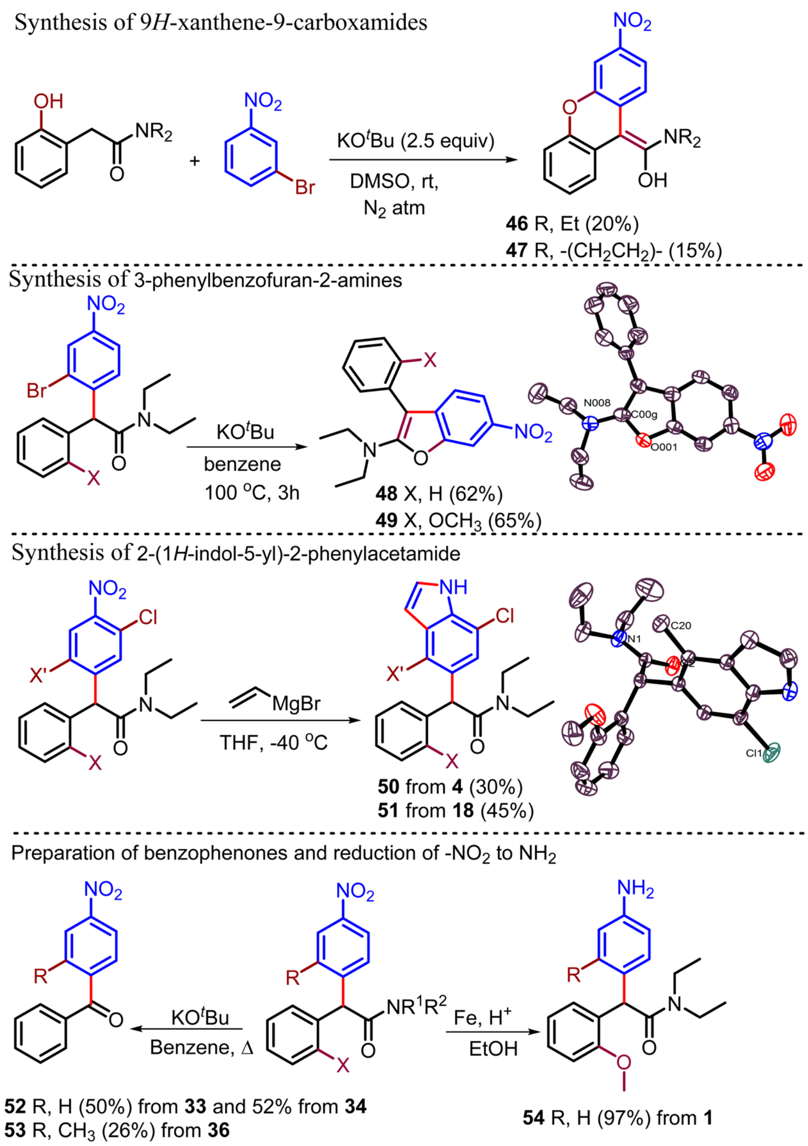


Figure 1. ORTEP diagrams of **12** and **14**. **14** shows strong N···O [2.886(2) Å] van der Waals radii of N + O = 3.07 Å. ORTEP views of **41**, **43**, **48**, and **50** are presented in the SI.

Scheme 4. Synthesis of Advanced Heterocyclic Molecules



at the *ortho* position to the nitro group, leading to *ortho*-nitro substituted phenyl phenylacetamides **5**, **12**, and **17** in moderate (58, 59, and 57%) yields, respectively. Furthermore, different aryls substrates such as 1-nitronaphthalene, heteroaryl thiophenyl, and naphthyl acetamides were amenable to the reaction conditions and provided nitronaphthyl acetamides **22** and **29**, α-(4-nitrophenyl) thiophenyl, naphthyls acetamide (**30**−**32**) in good yields.

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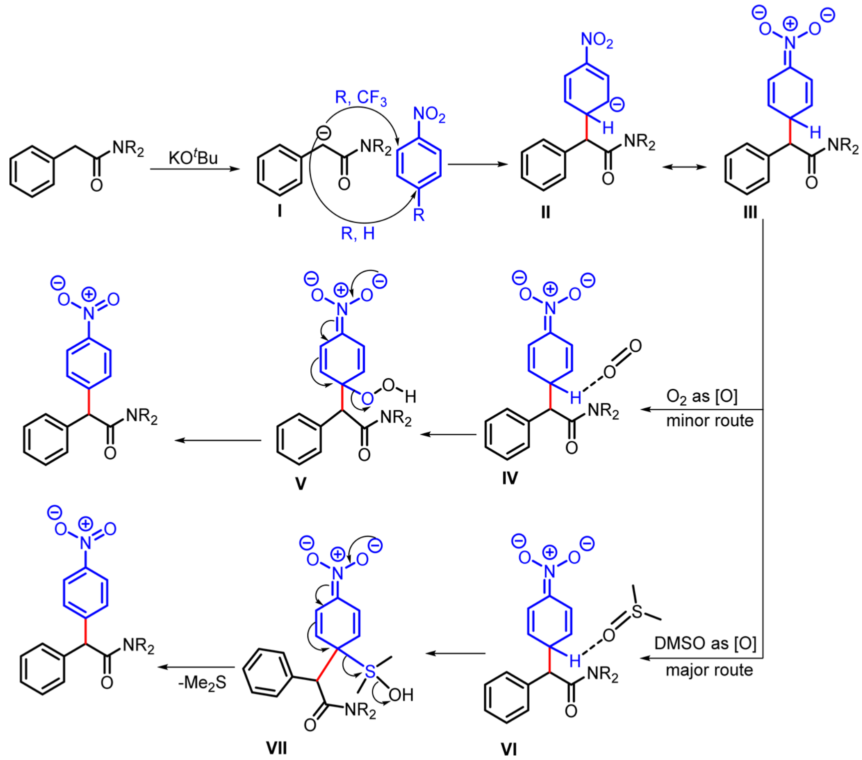
Scheme 5. Plausible Mechanism for the Coupling of Phenylacetamide with Nitroarene



It is apparent from Table 2 that various *N,N*-dialkyl, *N,N*-unsymmetrical dialkyl, *N*-alkyl-*N*-aryl, and *N,N*-diaryl substituted phenyl acetamide substrates can be smoothly reacted with nitroarenes under TM-free coupling reactions.

Next, *sec*-acetamide substrates having an acidic N−H bond were explored under the TM-free reaction conditions (Scheme 2). *N*-^{n}Alkyl, *N*-^{sec}alkyl, *N*-aryl, *N*-(halo)aryl, and *N*-benzyl substituted *sec*-acetamide substrates coupled with nitrobenzenes and 4-nitrophenyl acetamides **33−39** were obtained chemoselectively despite the presence of a reactive NH functionality. This could be due to stabilization of the amidate anion by hydrogen bonding over the carbanion nucleophile, or alternatively, poor reactivity of the amidate nucleophile could be due to its hard nature.[11c,13]

When *ortho*-chloro and fluoro substituted nitrobenzenes, lacking other substitution in the ring, were treated with phenylacetamides under optimized reaction conditions, the formation of nitroso products **41**, **43**, and **45** was also realized along with the desired unsymmetrical diaryl acetamides **40**, **42**, and **44**, respectively (Scheme 3). It occurs that the *ortho*-halonitrobenzene substrates act as an oxidant for the formation of nitroso products (for mechanistic understanding, see the SI, page S2 and Scheme S1).

The structures of nitro- and nitrosophenyl acetamides **12**, **14**, **41**, and **43** and further functionalized nitrophenyl acetamides **48** and **50** (*vide infra*) are established by single-crystal X-ray structure study (Figure 1; see the SI, pages S155−S211 for details).

Next, synthesized α-(2/4-nitrophenyl) phenylacetamides were further investigated for the synthesis of advanced heterocycles (Scheme 4).

Reaction of 3-bromo-nitrobenzene with 2-hydroxyphenyl acetamide yielded xanthenes **46** and **47**. Earlier methylene-9-xanthenes having chromophoric and plasticizing properties[2a] were accessed by multisteps, including a ring-closure step by the TM catalyst, particularly, Pd.[12] Here, cleavage of four bonds occurred by the KO^{t}Bu, which lead to the formation of xanthenes **46** and **47** in 20% and 15% yields, respectively, in a single pot.

3-Phenyl benzofurans possess antimicrobial and antifungal activities and also act as pharmacological molecular switches for K^+ and Cl^- channels.[14] Synthesis of 3-phenylbenzofurans involved multisteps from *ortho*-hydroxy acetophenone involving the use of PhMgBr, followed by cyclization in the presence of CuI and Pd catalysts.[14,15] Here, 3-phenyl benzofurans **48** and **49** were obtained from 2-(2-bromo-4-nitrophenyl)-acetamides **2** and **16** in 62% and 65% yields under TM-free conditions.

Reaction of vinylmagnesium bromide with nitrophenylacetamides **4** and **18** formed novel heterocyclic indoles **50** and **51** in 30% and 45% yields, respectively. Prolonged heating of synthesized α-nitrophenyl acetamides **33**, **34**, and **36** with KO^{t}Bu resulted into the formation of unsymmetrical benzofurans **52** and **53** via the cleavage of the unstrained C−C bond.

■ MECHANISM

The tentative mechanism of the reaction is depicted in Scheme 5. We believe that reaction promoted by abstraction of a proton from the 2-phenyl acetamide substrate by KO^{t}Bu leads to carbanion **I**, which may add to the *para* position of nitrobenzene chemoselectively.

The resulting coupled carbanion **II** would be stabilized by the nitro group, forming 2-(4-nitrocyclohexa-2,4-dien-1-yl)-2-phenylacetamide anion **III**. This intermediate **III** could undergo oxidation by aerial oxygen via intermediates **IV** and **V** and furnish 4-nitrophenyl phenyl acetamide **1** along with the concomitant generation of peroxide as a byproduct.[10f] DMSO could also oxidize anion **III** into 4-nitrophenyl phenyl

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acetamide **1** via intermediates **VI** and **VII** and reduced itself to dimethyl sulfide. The formation of dimethyl sulfide is established by GC-mass and ^{1}H NMR analysis of the crude reaction mixture (for details, see the SI, pages S153 and S154). In few cases, as shown in Scheme 3 (*vide supra*), coupling partner nitrobenzene having an electron-withdrawing halogen substituent also serves as an oxidant and thus produced (4-nitrosophenyl) acetamides **41**, **43**, and **45** (for details, see the SI, page S2).

■ CONCLUSION

We have presented an elegant method to prepare unsymmetrically substituted diaryl acetamides from readily accessible acetamides and nitroarenes under TM-free mild conditions. The developed protocols tolerate sensitive functional groups, namely, hydroxyl, chloride, cyanide, and bromide, in the arene rings, which enable constructing several elaborated molecules such as benzofurans, xanthenes, indoles, and unsymmetrical benzophenones. Interestingly, the sp^3 C−H bond in *sec-N*-alkyl and aryl arylacetamides has also been chemoselectively coupled with nitroarenes over the N−H bond. This method is simple, general, and practical and thus holds promise for the preparation of structurally diverse arylated carbonyl compounds. The synthesis of versatile nitrosoaryl acetamides and its reaction mechanism will be investigated in the future.

■ EXPERIMENTAL SECTION

General Experimental Details. All reactions were carried out in oven-dried glassware with magnetic stirring. Nitroarenes and phenyl acetic acid used in this study were obtained from commercial sources and used without further purification. Solvents DMSO, DMF, acetonitrile, benzene, EtOH, and DME were also obtained from commercial sources. Dichloromethane was dried over calcium hydride, distilled, and stored over molecular sieves. Silica gel (230−400 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates. All NMR experiments were carried out on 400/500 MHz spectrometers in $CDCl_3$ or DMSO-d_6, and NMR chemical shifts are reported in ppm referenced to the solvent peaks of $CDCl_3$ (7.26 ppm for ^{1}H and 77.16 (±0.06) ppm for ^{13}C, respectively) or DMSO-d_6 (3.31 ppm for H_2O, 2.47 ppm for ^{1}H, and 39.50 ppm for ^{13}C, respectively). The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), td (triplet of doublet), and m (multiplet). High-resolution mass analysis is performed on quadruple time-of-flight (TOF-Q) equipped with an ESI and APCI source. Single-crystal X-ray data for compounds **12**, **50**, **14**, **41**, **43**, and **48** (CCDC Nos. 1455187, 1455188, 1455189, 1455190, 1455191, and 1473220 respectively) were collected using a single-crystal diffractometer equipped with a CMOS Photon 100 detector, and Mo−Kα radiation (λ = 0.71073 Å) was used.

Preparation of *N,N*-Diethyl-2-(2-methoxyphenyl)acetamide (Substrate for 1, 2, 3, 4, and 5). General Procedure for Phenyl Acetamides. Substrates were prepared by following a literature procedure with minor modifications.[11d] To a solution of 2-(2-methoxyphenyl)acetic acid (1.0 g, 6 mmol) in dichloromethane (8 mL) was added thionyl chloride (0.7 mL, 9 mmol) and dimethylformamide (5 μL, 0.06 mmol) under a nitrogen atmosphere. The resulting mixture was stirred at room temperature for 1 h. The solvent was removed in vacuo to give 2-(2-methoxyphenyl) acetyl chloride (1.13 g, 100%) as a liquid. This liquid was used for amide preparation without further characterization. To a stirred solution of 2-(2-methoxyphenyl)acetyl chloride in CH_2Cl_2 (25 mL), diethyl amine (1.9 mL, 18.0 mmol) in CH_2Cl_2 (15 mL) was added dropwise using a dropping funnel at 0 °C. After complete addition, the reaction mixture was stirred for 4−5 h at 0 °C to room temperature. After completion of the reaction, a 10% HCl aqueous solution (30 mL) was added to the reaction mixture. The resulting solution was extracted with CH_2Cl_2 (30 mL × 3), and the organic layer was washed with brine (40 mL), dried over Na_2SO_4, and concentrated on a rotary evaporator under vacuum. A brown liquid was obtained; the compound was pure enough and proceeded for the next step. Brown liquid, Yield 1282 mg (95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 7.0 Hz, 2H), 6.93 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 3.83 (s, 3H), 3.68 (s, 2H), 3.41 (q, J = 7.1 Hz, 2H), 3.33 (q, J = 7.1 Hz, 2H), 1.14 (q, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 156.8, 130.0, 127.9, 124.4, 120.7, 110.3, 55.4, 42.3, 40.2, 34.5, 14.2, 13.0; HRMS (ESI) m/z calcd for $C_{13}H_{19}NO_2$ [M + H]$^+$ 222.1489, found 222.1517. By following this method, arylacetamide substrates for **6**−**47** were prepared. Arylacetamide substrates for **11**−**14**, **19**, **40**−**43**,[16] **23**, **24**,[17] **33**,[18] and **38**[19] are known.

*N-Isopropyl-N-methyl-2-phenylacetamide (Substrate for **6**).* Yellow liquid, Yield 1292 mg (92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 7.6 Hz, 4H), 7.22 (d, J = 7.8 Hz, 6H), 4.93−4.86 (m, 1H), 4.11−4.03 (m, 1H), 3.74 (s, 2H), 3.68 (s, 2H), 2.77 (s, 3H), 2.75 (s, 3H), 1.05 (d, J = 6.8 Hz, 6H), 1.01 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.3, 135.5, 135.2, 128.6, 128.5, 126.63, 126.59, 48.4, 44.0, 41.8, 41.4, 28.6, 25.9, 20.2, 19.4; HRMS (ESI) m/z calcd for $C_{12}H_{17}NO$ [M + H]$^+$ 192.1383, found 192.1407.

*2-(2-Chlorophenyl)-N,N-diisopropylacetamide (Substrate for **7** and **8**).* Cream crystalline solid, Yield 1307 mg (88%), mp 31−33 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 7.5, 1.6 Hz, 1H), 7.28 (dd, J = 7.4, 1.7 Hz, 1H), 7.22−7.14 (m, 2H), 3.95−3.88 (m, 1H), 3.74 (s, 2H), 3.47−3.35 (m, 1H), 1.40 (d, J = 6.8 Hz, 6H), 1.10 (d, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 134.2, 133.9, 130.6, 129.4, 128.1, 126.9, 49.2, 45.9, 40.3, 20.7, 20.5; HRMS (ESI) m/z calcd for $C_{14}H_{20}ClNO$ [M + H]$^+$ 254.1306, found 254.1315.

*2-(2,6-Dichlorophenyl)-N,N-diethylacetamide (Substrate for **9** and **10**).* Light brown solid, Yield 1153 mg (91%), mp 64−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 2H), 7.11 (t, J = 8.06 Hz, 1H), 3.99 (s, 2H), 3.48−3.38 (m, 4H), 1.29 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 136.2, 133.1, 128.4, 127.9, 42.3, 40.7, 35.9, 14.3, 13.1; HRMS (ESI) m/z calcd for $C_{12}H_{15}Cl_2NO$ [M + H]$^+$ 260.0603, found 260.0617.

*N,N-Diisopropyl-2-phenylacetamide (Substrate for **11**, **12**, **13**, **14**, **40**, **41**, **42**, and **43**).* Cream crystalline solid, Yield 1496 mg (93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.25 (m, 2H), 7.24−7.17 (m, 3H), 3.99−3.87 (m, 1H), 3.66 (s, 2H), 3.34 (s, 1H), 1.39 (d, J = 6.8 Hz, 6H), 0.98 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 135.9, 128.6, 128.4, 126.5, 49.4, 45.8, 43.5, 20.6, 20.5; GC-LRMS m/z calcd for $C_{14}H_{21}NO$ [M]$^+$ 219.2, found 219.1.

*N,N-Diethyl-2-phenylacetamide (Substrate for **15**, **16**, **17**, **18**, **44**, and **45**).* Mustard liquid, Yield 1347 mg (96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.17(m, 5H), 3.67 (s, 2H), 3.37 (q, J = 7.1 Hz, 2H), 3.27 (q, J = 7.1 Hz, 2H), 1.08 (dt, J = 16.3, 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 135.5, 128.61, 128.55, 126.6, 42.3, 40.9, 40.1, 14.1, 12.9; HRMS (ESI) m/z calcd for $C_{12}H_{17}NO$ [M + H]$^+$ 192.1383, found 192.1363.

*N-Ethyl-N-isopropyl-2-phenylacetamide (Substrate for **19**).* Pale yellow liquid, Yield 1356 mg (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.19 (m, 10H), 4.72−4.62 (m, 1H), 4.07−3.97 (m, 1H), 3.72 (s, 2H), 3.67 (s, 2H), 3.26−3.18 (m, 4H), 1.19−1.11 (m, 12H), 1.01 (d, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.0, 135.7, 135.6, 28.7, 128.62, 128.57, 128.5, 126.6, 100.0, 48.9, 45.7, 41.8, 41.3, 37.8, 35.5, 21.0, 20.5, 16.7, 14.7; GC-LRMS m/z calcd for $C_{13}H_{19}NO$ [M]$^+$ 205.1, found 205.1.

*2-(2-Methoxyphenyl)-1-(piperidin-1-yl)ethan-1-one (Substrate for **20**, **21**, and **22**).* Pale yellow liquid, Yield 1147 mg (82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.17 (m, 2H), 6.92−6.82 (m, 2H), 3.81 (s, 3H), 3.67 (s, 2H), 3.58−3.54 (m, 2H), 3.37−3.33 (m, 2H), 1.59−1.47 (m, 4H), 1.39−1.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 156.6, 129.8, 127.9, 124.1, 120.7, 110.3, 55.4, 47.1, 42.9, 34.5, 26.3, 25.6, 24.6; HRMS (ESI) m/z calcd for $C_{14}H_{19}NO_2$ [M + H]$^+$ 234.1489, found 234.1511.

*N-Cyclohexyl-N-methyl-2-phenylacetamide (Substrate for **23** and **24**).* Cream solid, Yield 1459 mg (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.16 (m, 10H), 4.50−4.39 (m, 1H), 3.71 (d, J = 17.0 Hz, 4H), 3.62−3.52 (m, 1H), 2.78 (d, J = 4.9 Hz, 6H), 1.78−1.69 (m,

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4H), 1.65−1.56 (m, 4H), 1.45−1.02 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.5, 135.7, 135.3, 128.63, 128.60, 126.7, 126.6, 57.2, 52.5, 41.9, 41.8, 30.7, 29.9, 29.8, 27.3; 25.8, 25.63, 25.60, 25.2; GC-LRMS m/z calcd for $C_{15}H_{21}NO$ $[M]^+$ 231.2, found 231.1.

*N-Benzyl-N-ethyl-2-phenylacetamide (Substrate for **25**, **26**, and **27**).* Mustard liquid, Yield 1561 mg (84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.20 (m, 18H), 7.11 (d, J = 7.3 Hz, 2H), 4.60 (s, 2H), 4.48 (s, 2H), 3.78 (s, 2H), 3.68 (s, 2H), 3.43 (q, J = 7.1 Hz, 2H), 3.27 (q, J = 7.1 Hz, 2H), 1.07 (dt, J = 18.7, 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 170.9, 137.8, 137.0, 135.3, 135.2, 128.9, 128.8, 128.75, 128.68, 128.5, 128.1, 128.0, 127.6, 127.3, 126.80, 126.77, 126.4, 50.9, 47.7, 41.9, 41.11, 41.07, 40.8, 13.6, 12.5; HRMS (ESI) m/z calcd for $C_{17}H_{19}NO$ $[M + H]^+$ 254.1539, found 254.1539.

*N,N,2-Triphenylacetamide (Substrate for **28** and **29**).* Green solid, Yield 1698 mg (80%), mp 50−53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.14 (m, 13H), 7.13−7.08 (m, 2H), 3.65 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 142.8, 135.1, 129.3, 129.1, 128.4, 126.7, 121.0, 117.8, 42.2; HRMS (ESI) m/z calcd for $C_{20}H_{17}NO$ $[M + H]^+$ 288.1383, found 288.1397.

*1-Morpholino-2-(thiophen-3-yl)ethan-1-one (Substrate for **30**).* Cream solid, Yield 1112 mg (75%), mp 71−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 4.9, 3.0 Hz, 1H), 7.04 (d, J = 1.7 Hz, 1H), 6.99−6.96 (m, 1H), 3.70 (s, 2H), 3.62 (s, 4H), 3.50−3.47 (m, 2H), 3.44−3.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 134.6, 128.0, 126.2, 122.0, 66.8, 66.5, 46.6, 42.2, 35.7; HRMS (ESI) m/z calcd for $C_{10}H_{13}NO_2S$ $[M + Na]^+$ 234.0559, found 234.0570.

*1-Morpholino-2-(naphthalen-1-yl)ethan-1-one (Substrate for **31** and **32**).* White solid, Yield 1266 mg (92%), mp 87−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.2 Hz, 1H), 7.89−7.83 (m, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.56−7.47 (m, 2H), 7.44−7.39 (m, 1H), 7.32 (d, J = 7.0 Hz, 1H), 4.14 (s, 2H), 3.68 (s, 4H), 3.51−3.39 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 133.9, 131.8, 131.0, 128.9, 127.9, 126.5, 126.2, 125.9, 125.5, 123.3, 66.9, 66.5, 46.5, 42.2, 38.2; HRMS (ESI) m/z calcd for $C_{16}H_{17}NO_2$ $[M + Na]^+$ 278.1151, found 278.1168.

*N,2-Diphenylacetamide (Substrate for **33**).* Cream solid, Yield 1241 mg (80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 16.7, 7.5 Hz, 4H), 7.33−7.24 (m, 6H), 7.07 (t, J = 7.4 Hz, 1H), 3.71 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 137.7, 134.5, 129.5, 129.2, 129.0, 127.7, 124.5, 119.9, 44.8; GC-LRMS m/z calcd for $C_{14}H_{13}NO$ $[M]^+$ 211.0997, found 211.1.

*N-(2-Fluorophenyl)-2-phenylacetamide (Substrate for **34**).* Cream solid, Yield 1400 mg (83%), mp 85−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (t, J = 8.0 Hz, 1H), 7.42−7.30 (m, 6H), 7.11−7.05 (m, 1H), 7.03−6.97 (m, 2H), 3.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 152.4 (d, J = 243.2 Hz), 134.1, 129.5, 129.3, 127.8, 126.2 (d, J = 10 Hz), 124.54 (d, J = 3.7 Hz), 124.46 (d, J = 7.9 Hz), 121.7, 114.7 (d, J = 19.1 Hz), 44.9; HRMS (ESI) m/z calcd for $C_{14}H_{12}FNO$ $[M + H]^+$ 230.0976, found 230.0988.

*N-(2-Bromophenyl)-2-phenylacetamide (Substrate for **35** and **36**).* Cream solid, Yield 1683 mg (79%), mp 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.1 Hz, 1H), 7.63 (s, 1H), 7.41 (t, J = 7.2 Hz, 3H), 7.37−7.32 (m, 3H), 7.29−7.25 (m, 1H), 6.92 (td, J = 8.0, 1.3 Hz, 1H), 3.78 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 135.5, 133.9, 132.2, 129.9, 129.4, 128.3, 127.9, 125.2, 121.4, 113.2, 45.2; HRMS (ESI) m/z calcd for $C_{14}H_{12}BrNO$ $[M + H]^+$ 290.0175, found 290.0174.

*N-Benzyl-2-(2-bromophenyl)acetamide (Substrate for **37**).* White solid, Yield 781 mg (79%), mp 120−122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, J = 8.0, 1.1 Hz, 1H), 7.39 (dd, J = 7.6, 1.7 Hz, 1H), 7.33 (dd, J = 7.9, 6.6 Hz, 3H), 7.29−7.24 (m, 3H), 7.18 (td, J = 7.7, 1.7 Hz, 1H), 5.84 (s, 1H), 4.46 (d, J = 5.8 Hz, 2H), 3.79 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 138.1, 134.8, 133.2, 131.8, 129.2, 128.7, 128.1, 127.6, 127.4, 125.0, 44.0, 43.7; HRMS (ESI) m/z calcd for $C_{15}H_{14}BrNO$ $[M + H]^+$ 304.0332, found 304.0334.

*N-Isopropyl-2-phenylacetamide (Substrate for **38**).* White solid, Yield 1180 mg (91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 7.2 Hz, 2H), 7.27−7.21 (m, 3H), 5.27 (s, 1H), 4.07−3.99 (m, 1H), 3.50 (s, 2H), 1.04 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 135.2, 129.3, 128.9, 127.2, 44.0, 41.5, 22.6; GC-LRMS m/z calcd for $C_{11}H_{15}NO$ $[M]^+$ 177.1, found 177.1.

*2-(2-Bromophenyl)-N-butylacetamide (Substrate for **39**).* White solid, Yield 1012 mg (81%), mp 132−133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.53 (m, 1H), 7.35−7.25 (m, 2H), 7.16−7.09 (m, 1H), 5.40 (s, 1H), 3.66 (s, 2H), 3.19 (dd, J = 13.1, 7.0 Hz, 2H), 1.44−1.36 (m, 2H), 1.29−1.20 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 135.1, 133.1, 131.7, 129.1, 128.0, 125.0, 44.1, 39.5, 31.5, 20.0, 13.7; HRMS (ESI) m/z calcd for $C_{12}H_{16}BrNO$ $[M + H]^+$ 270.0488, found 270.0492.

*N,N-Diethyl-2-(2-hydroxyphenyl)acetamide (Substrate for **46**).* Brown liquid, Yield 772 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.18−7.13 (m, 1H), 7.02−6.99 (m, 1H), 6.96 (d, J = 7.5 Hz, 1H), 6.79 (td, J = 7.4, 0.9 Hz, 1H), 3.69 (s, 2H), 3.48 (q, J = 7.2 Hz, 2H), 3.37 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 157.3, 130.4, 129.0, 121.2, 119.8, 118.2, 43.5, 41.3, 36.9, 14.8, 12.9; HRMS (ESI) m/z calcd for $C_{12}H_{17}NO_2$ $[M + H]^+$ 208.1332, found 208.1352.

*2-(2-Hydroxyphenyl)-1-(piperidin-1-yl)ethan-1-one (Substrate for **47**).* Cream solid, Yield 1233 mg (85%), mp 79−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.15 (td, J = 8.1, 1.5 Hz, 1H), 7.02−6.98 (m, 1H), 6.95 (dd, J = 8.0, 0.6 Hz, 1H), 6.80 (td, J = 7.4, 1.0 Hz, 1H), 3.72 (s, 2H), 3.63−3.59 (m, 2H), 3.57−3.53 (m, 2H), 1.64−1.51 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 157.2, 130.1, 128.9, 121.0, 120.0, 118.1, 48.1, 43.4, 36.5, 26.5, 25.3, 24.2; HRMS (ESI) m/z calcd for $C_{13}H_{17}NO_2$ $[M + Na]^+$ 242.1151, found 242.1160.

General Procedure for α-Arylation of Amide. *N,N*-Diethyl-2-(2-methoxyphenyl)-2-(4-nitrophenyl)acetamide (1). To a single neck flask, KO^{t}Bu (280.5 mg, 2.5 mmol) was added in one portion to the solution of the *N,N*-diethyl-2-(2-methoxyphenyl)acetamide (221.3 mg, 1 mmol) and nitroarene (148 mg, 1.2 mmol) in DMSO (4 mL) at room temperature. The resulting reaction mixture was stirred at room temperature for 4 h under N_2. Next, a saturated aqueous NaCl solution (15 mL) was added and the resulting mixture was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography by using ethyl acetate/hexane (10/90). The desired compound **1** was obtained as a yellow solid. Yield 222 mg (65%), mp 102−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.28−7.24 (m, 1H), 7.17 (d, J = 7.3 Hz, 1H), 6.92 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 5.62 (s, 1H), 3.77 (s, 3H), 3.50−3.41 (m, 1H), 3.38−3.17 (m, 3H), 1.12 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 156.3, 147.3, 146.8, 130.3, 129.1, 128.9, 127.0, 123.3, 121.0, 110.6, 55.5, 47.3, 42.2, 40.7, 14.3, 12.8; HRMS (ESI) m/z calcd for $C_{19}H_{22}N_2O_4$ $[M + Na]^+$ 365.1472, found 365.1500.

*2-(2-Bromo-4-nitrophenyl)-N,N-diethyl-2-(2-methoxyphenyl)-acetamide (**2**).* White solid, Yield 153 mg (67%), mp 86−88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 2.3 Hz, 1H), 8.00 (dd, J = 8.6, 2.3 Hz, 1H), 7.34−7.29 (m, 1H), 7.22−7.15 (m, 2H), 6.97 (t, J = 7.3 Hz, 1H), 6.89 (d, J = 8.2 Hz, 1H), 5.91 (s, 1H), 3.74 (s, 3H), 3.49−3.32 (m, 2H), 3.30−3.14 (m, 2H), 1.13 (td, J = 7.1, 3.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 156.5, 147.2, 146.9, 131.8, 129.3, 129.2, 127.4, 125.7, 125.1, 121.9, 121.0, 110.8, 55.5, 48.2, 42.3, 40.7, 13.9, 12.7; HRMS (ESI) m/z calcd for $C_{19}H_{21}BrN_2O_4$ $[M + H]^+$ 421.0757, found 421.0760.

*2-(2,5-Dichloro-4-nitrophenyl)-N,N-diethyl-2-(2-methoxyphenyl)-acetamide (**3**).* Yellow solid, Yield 118 mg (53%), mp 126−128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.37−7.32 (m, 1H), 7.23 (dd, J = 8.0, 1.8 Hz, 1H), 7.12 (s, 1H), 7.03−6.98 (m, 1H), 6.91 (d, J = 8.1 Hz, 1H), 5.86 (s, 1H), 3.75 (s, 3H), 3.53−3.44 (m, 1H), 3.36−3.28 (m, 1H), 3.27−3.19 (m, 1H), 3.18−3.09 (m, 1H), 1.12 (q, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 156.4, 146.1, 144.7, 134.1, 133.0, 129.7, 129.1, 126.0, 125.4, 124.6, 121.2, 110.9, 55.6, 45.4, 42.3, 40.8, 13.8, 12.6; HRMS (ESI) m/z calcd for $C_{19}H_{20}Cl_2N_2O_4$ $[M + H]^+$ 411.0873, found 411.0897.

*2-(5-Chloro-2-methyl-4-nitrophenyl)-N,N-diethyl-2-(methoxy-phenyl)acetamide (**4**).* Orange solid, Yield mg (55%), mp 98−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.27 (d, J = 9.2 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 6.99 (t, J = 7.5

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Hz, 1H), 6.92 (d, J = 8.2 Hz, 1H), 5.64 (s, 1H), 3.81 (s, 3H), 3.44 (q, J = 7.1 Hz, 2H), 3.28–3.12 (m, 2H), 2.34 (s, 3H), 1.16 (dd, J = 12.4, 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 156.3, 145.9, 145.0, 136.5, 132.5, 129.4, 129.1, 126.8, 125.6, 124.5, 121.1, 110.6, 55.5, 44.5, 42.2, 40.8, 19.2, 14.0, 12.7; HRMS (ESI) m/z calcd for $C_{20}H_{23}ClN_2O_4$ $[M + H]^+$ 391.1419, found 391.1431.

*N,N-Diethyl-2-(2-methoxyphenyl)-2-(2-nitro-5-(trifluoromethyl)-phenyl)acetamide (**5**).* Light yellow solid, Yield 161 mg (58%), mp 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 1H), 7.57 (dd, J = 8.5, 1.4 Hz, 1H), 7.38 (d, J = 10.1 Hz, 1H), 7.35–7.27 (m, 2H), 7.00 (td, J = 7.5, 0.7 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 6.06 (s, 1H), 3.69 (s, 3H), 3.52–3.43 (m, 1H), 3.39–3.30 (m, 1H), 3.25–3.10 (m, 2H), 1.14 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 156.3, 151.4, 136.3, 133.7 (q, J = 33.0 Hz), 129.74 (q, J = 4.0 Hz), 129.68, 128.9, 125.2, 124.4 (q, J = 3.6 Hz), 124.3, 123.5 (q, J = 272.9 Hz), 121.3, 110.9, 55.4, 43.8, 42.1, 40.6, 13.5, 12.6; HRMS (ESI) m/z calcd for $C_{20}H_{21}F_3N_2O_4$ $[M + H]^+$ 411.1526, found 411.1534.

*2-(2,5-Dichloro-4-nitrophenyl)-N-isopropyl-N-methyl-2-phenyl-acetamide (**6**).* Yellow solid, Yield 183 mg (48%), mp 120–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.43–7.35 (m, 6H), 7.28–7.24 (m, 4H), 7.07 (d, J = 6.6 Hz, 2H), 5.64 (s, 1H), 5.52 (s, 1H), 4.93–4.86 (m, 1H), 4.14–4.06 (m, 1H), 2.83 (s, 3H), 2.80 (s, 3H), 1.24 (d, J = 6.6 Hz, 3H), 1.12 (d, J = 6.8 Hz, 3H), 1.05 (d, J = 6.8 Hz, 3H), 0.79 (d, J = 6.5 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.6, 168.3, 146.3, 145.2, 145.1, 135.9, 135.3, 134.7, 134.5, 132.5, 132.4, 129.57, 129.55, 129.0, 128.9, 128.39, 128.38, 126.0, 125.73, 125.68, 52.7, 52.3, 48.6, 44.9, 28.5, 26.4, 20.4, 19.8, 19.4, 19.3; HRMS (ESI) m/z calcd for $C_{18}H_{18}Cl_2N_2O_3$ $[M + H]^+$ 381.0767, found 381.0780.

*2-(2-Chlorophenyl)-N,N-diisopropyl-2-(4-nitrophenyl)acetamide (**7**).* White solid, Yield 200 mg (68%), mp 131–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.8 Hz, 2H), 7.41–7.37 (m, 3H), 7.26–7.23 (m, 2H), 7.22–7.19 (m, 1H), 5.63 (s, 1H), 3.94–3.87 (m, 1H), 3.43–3.36 (m, 1H), 1.42 (dd, J = 6.7, 4.4 Hz, 6H), 1.06 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 147.0, 145.8, 136.5, 133.8, 130.5, 130.1, 129.8, 129.0, 127.3, 123.6, 52.8, 49.3, 46.4, 20.8, 20.5, 20.1, 20.0; HRMS (ESI) m/z calcd for $C_{20}H_{23}ClN_2O_3$ $[M + H]^+$ 375.1470, found 375.1497.

*2-(2-Chlorophenyl)-2-(2,4-dinitrophenyl)-N,N-diisopropylacet-amide (**8**).* Pale yellow solid, Yield 100 mg (55%), mp 94–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 2.3 Hz, 1H), 8.22 (dd, J = 8.7, 2.3 Hz, 1H), 7.50–7.45 (m, 2H), 7.41–7.36 (m, 2H), 7.00 (d, J = 8.7 Hz, 1H), 6.25 (s, 1H), 3.81–3.74 (m, 1H), 3.40–3.33 (m, 1H), 1.40 (dd, J = 6.7, 2.1 Hz, 6H), 1.33 (d, J = 6.6 Hz, 3H), 0.68 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 149.1, 146.7, 141.7, 134.4, 134.0, 133.0, 130.5, 130.4, 130.2, 127.8, 126.7, 120.2, 50.4, 49.8, 46.6, 20.4, 20.3, 19.9, 19.6; HRMS (ESI) m/z calcd for $C_{20}H_{22}ClN_3O_5$ $[M + H]^+$ 420.1321, found 420.1320.

*2-(2,6-Dichlorophenyl)-2-(2,4-dinitrophenyl)-N,N-diethylacet-amide (**9**).* Pale yellow semisolid, Yield 100 mg (47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J = 2.4 Hz, 1H), 8.27 (dd, J = 8.7, 2.4 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.37–7.30 (m, 1H), 7.07 (d, J = 8.67 Hz, 1H), 6.72 (s, 1H), 3.47–3.38 (m, 1H), 3.34–3.25 (m, 1H), 3.17–3.03 (m, 2H), 1.12 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 149.9, 146.9, 139.1, 136.9, 132.6, 131.5, 130.5, 129.9, 126.7, 120.4, 50.0, 42.1, 41.3, 13.0, 12.5; HRMS (ESI) m/z calcd for $C_{18}H_{17}Cl_2N_3O_5$ $[M + H]^+$ 426.0618, found 426.0635.

*2-(2-Bromo-4-nitrophenyl)-2-(2,6-dichlorophenyl)-N,N-diethyl-acetamide (**10**).* Buff solid, Yield 162 mg (52%), mp 97–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 2.3 Hz, 1H), 8.05 (dd, J = 8.6, 2.3 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.28–7.24 (m, 1H), 7.19 (d, J = 8.6 Hz, 1H), 6.06 (s, 1H), 3.53–3.44 (m, 1H), 3.41–3.31 (m, 1H), 3.18–3.01 (m, 2H), 1.17 (t, J = 7.1 Hz, 3H), 1.02 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 147.2, 144.5, 136.5, 133.8, 131.0, 129.84, 129.77, 127.7, 126.1, 122.2, 53.3, 42.1, 40.9, 13.4, 12.6; HRMS (ESI) m/z calcd for $C_{18}H_{17}BrCl_2N_2O_3$ $[M + H]^+$ 458.9872, found 458.9900.

*N,N-Diisopropyl-2-(4-nitrophenyl)-2-phenylacetamide (**11**).* Pale yellow solid, Yield 145 mg (62%), mp 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.9 Hz, 2H), 7.61 (d, J = 8.9 Hz, 2H), 7.43–7.34 (m, 5H), 6.50 (s, 1H), 3.68–3.61 (m, 1H), 3.41–3.34 (m, 1H), 1.47 (dd, J = 10.0, 6.8 Hz, 6H), 0.60 (d, J = 6.4 Hz, 3H), 0.52 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 149.3, 147.2, 140.7, 129.6, 128.6, 128.3, 128.1, 123.4, 80.3, 49.7, 47.5, 19.9, 19.8, 19.1, 19.0; HRMS (ESI) m/z calcd for $C_{20}H_{24}N_2O_3$ $[M + H]^+$ 341.1860, found 341.1889.

*N,N-Diisopropyl-2-(2-nitro-5-(trifluoromethyl)phenyl)-2-phenyl-acetamide (**12**).* Pale yellow solid, Yield 134 mg (48%), mp 114–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 7.63–7.57 (m, 1H), 7.46–7.36 (m, 3H), 7.31–7.26 (m, 2H), 7.05 (s, 1H), 5.85 (s, 1H), 4.08–4.01 (m, 1H), 3.35–3.29 (m, 1H), 1.38 (dd, J = 11.5, 6.8 Hz, 6H), 1.29 (d, J = 6.7 Hz, 3H), 0.62 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 150.8, 137.9, 136.0, 134.1 (q, J = 33.1 Hz), 129.53, 129.47, 129.1 (q, J = 3.9 Hz), 128.3, 125.0, 124.6 (q, J = 3.6 Hz), 122.9 (q, J = 273.2 Hz), 53.3, 49.6, 46.5, 20.4, 20.3, 19.9, 19.5; HRMS (ESI) m/z calcd for $C_{21}H_{23}F_3N_2O_3$ $[M + H]^+$ 409.1734, found 409.1732.

*2-(2,5-Dichloro-4-nitrophenyl)-N,N-diisopropyl-2-phenylacet-amide (**13**).* Pale yellow solid, Yield 182 mg (65%), mp 132–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.45–7.35 (m, 3H), 7.30–7.25 (m, 2H), 6.94 (s, 1H), 5.52 (s, 1H), 4.08–3.98 (m, 1H), 3.41–3.31 (m, 1H), 1.42 (d, J = 6.8 Hz, 6H), 1.24 (d, J = 6.7 Hz, 3H), 0.73 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 146.1, 145.7, 135.9, 134.5, 132.6, 129.6, 129.0, 128.4, 126.0, 125.6, 53.9, 49.7, 46.5, 20.7, 20.4, 20.1, 19.8; HRMS (ESI) m/z calcd for $C_{20}H_{22}Cl_2N_2O_3$ $[M + H]^+$ 409.1080, found 409.1085.

*2-(2,4-Dinitrophenyl)-N,N-diisopropyl-2-phenylacetamide (**14**).* Buff solid, Yield 158 mg (41%), mp 123–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 2.4 Hz, 1H), 8.20 (dd, J = 8.7, 2.4 Hz, 1H), 7.47–7.38 (m, 3H), 7.i31–7.27 (m, 2H), 7.04 (d, J = 8.7 Hz, 1H), 5.92 (s, 1H), 4.06–3.99 (m, 1H), 3.37–3.30 (m, 1H), 1.38 (t, J = 6.7 Hz, 6H), 1.31 (d, J = 6.7 Hz, 3H), 0.63 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 148.8, 146.5, 143.6, 135.9, 133.7, 129.7, 129.4, 128.5, 126.5, 120.0, 53.7, 49.8, 46.6, 20.4, 20.3, 19.9, 19.5; HRMS (ESI) m/z calcd for $C_{20}H_{23}N_3O_5$ $[M + H]^+$ 386.1710, found 386.1739.

*N,N-Diethyl-2-(4-nitrophenyl)-2-phenylacetamide (**15**).* Cream solid, Yield 156 mg (64%), mp 69–70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.7 Hz, 2H), 7.40–7.25 (m, 7H), 5.23 (s, 1H), 3.54–3.46 (m, 1H), 3.40–3.29 (m, 2H), 3.28–3.19 (m, 1H), 1.14 (td, J = 7.1, 1.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 147.7, 146.9, 138.2, 130.2, 129.1, 128.6, 127.7, 123.5, 54.4, 42.3, 40.9, 14.7, 12.8; HRMS (ESI) m/z calcd for $C_{18}H_{20}N_2O_3$ $[M + Na]^+$ 335.1366, found 335.1346.

*2-(2-Bromo-4-nitrophenyl)-N,N-diethyl-2-phenylacetamide (**16**).* Cream solid, Yield 175 mg (71%), mp 85–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 2.2 Hz, 1H), 8.06 (dd, J = 8.7, 2.2 Hz, 1H), 7.43–7.34 (m, 3H), 7.31–7.25 (m, 3H), 5.68 (s, 1H), 3.54–3.46 (m, 1H), 3.44–3.34 (m, 2H), 3.32–3.23 (m, 1H), 1.17 (q, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 147.4, 147.0, 137.1, 132.5, 129.3, 128.9, 128.0, 127.4, 124.6, 122.0, 54.4, 42.4, 40.8, 14.0, 12.6; HRMS (ESI) m/z calcd for $C_{18}H_{19}BrN_2O_3$ $[M + H]^+$ 391.0652, found 391.0651.

*N,N-Diethyl-2-(2-nitro-5-(trifluoromethyl)phenyl)-2-phenylacet-amide (**17**).* Yellow liquid, Yield 160 mg (42%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.61 (dd, J = 8.4, 1.2 Hz, 1H), 7.43–7.34 (m, 3H), 7.29–7.25 (m, 2H), 7.21 (s, 1H), 5.81 (s, 1H), 3.46–3.28 (m, 3H), 3.24–3.15 (m, 1H), 1.12 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 150.8, 137.1, 136.3, 134.1 (q, J = 33.5 Hz), 129.7 (q, J = 4.0 Hz), 129.5, 129.2, 128.3, 124.8 (q, J = 3.3 Hz), 122.9 (q, J = 273.1 Hz), 120.7, 51.2, 42.3, 40.7, 13.5, 12.5; HRMS (ESI) m/z calcd for $C_{19}H_{19}F_3N_2O_3$ $[M + Na]^+$ 403.1240, found 403.1267.

*2-(2,5-Dichloro-4-nitrophenyl)-N,N-diethyl-2-phenylacetamide (**18**).* Yellow solid, Yield 167 mg (56%), mp 91–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.43–7.35 (m, 3H), 7.26 (d, J = 6.9 Hz, 2H), 7.16 (s, 1H), 5.56 (s, 1H), 3.53–3.45 (m, 1H), 3.38–3.29 (m,

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2H), 3.24–3.14 (m, 1H), 1.13 (q, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 146.3, 144.9, 136.2, 134.8, 132.4, 129.5, 128.8, 128.3, 126.0, 125.6, 51.8, 42.4, 40.9, 14.0, 12.6; HRMS (APCI) m/z calcd for $C_{18}H_{18}Cl_2N_2O_3$ $[M + H]^+$ 381.0767, found 381.0782.

*2-(2-Bromo-4-nitrophenyl)-N-ethyl-N-isopropyl-2-phenylacetamide (**19**).* Buff solid, Yield 216 mg (73%), mp 68–70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 1.9 Hz, 2H), 8.04–7.98 (m, 2H), 7.41–7.31 (m, 6H), 7.28–7.23 (m, 5H), 7.09 (d, J = 8.7 Hz, 1H), 5.69 (s, 1H), 5.59 (s, 1H), 4.59–4.48 (m, 1H), 4.14–4.07 (m, 1H), 3.29 (q, J = 6.9 Hz, 2H), 3.25–3.15 (m, 2H), 1.27–1.15 (m, 15H), 0.81 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 168.2, 147.8, 147.5, 146.95, 146.92, 137.3, 136.9, 132.6, 132.4, 129.3, 129.2, 129.0, 128.9, 128.1, 127.9, 127.5, 127.4, 124.8, 124.6, 122.04, 122.02, 55.2, 55.1, 49.0, 47.3, 38.7, 36.1, 21.3, 20.5, 20.3, 20.2, 16.2, 14.3; HRMS (ESI) m/z calcd for $C_{19}H_{21}BrN_2O_3$ $[M + Na]^+$ 427.0628, found 427.0613.

*5-(1-(2-Methoxyphenyl)-2-oxo-2-(piperidin-1-yl)ethyl)-2-nitrobenzonitrile (**20**).* Yellow liquid, Yield 127 mg (52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.6 Hz, 1H), 7.70 (d, J = 1.8 Hz, 1H), 7.62 (dd, J = 8.6, 1.8 Hz, 1H), 7.35–7.27 (m, 2H), 7.01 (t, J = 7.3 Hz, 1H), 6.89 (d, J = 8.2 Hz, 1H), 5.62 (s, 1H), 3.76 (s, 3H), 3.41–3.35 (m, 1H), 3.26–3.22 (m, 2H), 1.61–1.46 (m, 5H), 1.41–1.35 (m, 1H), 1.10–1.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 155.9, 147.9, 146.8, 136.8,134.9, 129.8, 128.5, 125.0, 124.9, 121.4, 115.4, 111.0, 107.3, 55.6, 47.4, 46.9, 43.5, 25.9, 25.5, 24.3; HRMS (ESI) m/z calcd for $C_{21}H_{21}N_3O_4$ $[M + H]^+$ 380.1605, found 380.1629.

*2-(2-Methoxyphenyl)-2-(2-methyl-4-nitrophenyl)-1-(piperidin-1-yl)ethan-1-one (**21**).* Mustard solid, Yield 149 mg (55%), mp 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 2.1 Hz, 1H), 7.93 (dd, J = 8.6, 2.2 Hz, 1H), 7.31–7.26 (m, 1H), 7.17 (d, J = 8.6 Hz, 1H), 7.09 (dd, J = 7.6, 1.3 Hz, 1H), 6.94 (t, J = 7.3 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 5.72 (s, 1H), 3.75 (s, 3H), 3.69–3.63 (m, 1H), 3.59–3.52 (m, 1H), 3.27 (t, J = 5.1 Hz, 2H), 2.37 (s, 3H), 1.59–1.52 (m, 4H), 1.41–1.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 156.3, 146.6, 145.9, 137.8, 130.1, 129.7, 128.9, 125.9, 124.8, 120.92, 120.90, 110.7, 55.6, 46.9, 44.6, 43.4, 26.1, 25.7, 24.5, 19.7; HRMS (ESI) m/z calcd for $C_{21}H_{24}N_2O_4$ $[M + H]^+$ 369.1809, found 369.1831.

*2-(2-Methoxyphenyl)-2-(4-nitronaphthalen-1-yl)-1-(piperidin-1-yl)ethan-1-one (**22**).* Brown liquid, Yield 145 mg (56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 8.6 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.5 Hz, 1H), 7.66 (dd, J = 11.5, 4.0 Hz, 1H), 7.62–7.57 (m, 1H), 7.33–7.26 (m, 2H), 7.04 (dd, J = 7.5, 1.4 Hz, 1H), 6.92 (dd, J = 7.9, 4.5 Hz, 2H), 6.33 (s, 1H), 3.81 (s, 3H), 3.55–3.23 (m, 4H), 1.63–1.46 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 156.1, 146.2, 142.9, 132.5,130.4, 128.9, 128.7, 127.7, 126.2, 125.5, 125.2, 123.9, 123.8, 123.3, 120.9, 110.6, 55.7, 47.1, 44.4, 43.5, 26.2, 25.7, 24.5; HRMS (ESI) m/z calcd for $C_{24}H_{24}N_2O_4$ $[M + H]^+$ 405.1809, found 405.1831.

*N-Cyclohexyl-N-methyl-2-(4-nitrophenyl)-2-phenylacetamide (**23**).* Yellow semisolid, Yield 124 mg (54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J = 8.8, 1.9 Hz, 4H), 7.38–7.35 (m, 4H), 7.34–7.23 (m, 10H), 5.26 (d, J = 15.0 Hz, 2H), 4.50–4.44 (m, 1H), 3.66–3.56 (m, 1H), 2.85 (s, 3H), 2.81 (s, 3H), 1.83–1.75 (m, 3H), 1.64 (d, J = 15.7 Hz, 6H), 1.39–1.14 (m, 11H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 170.0, 169.9, 147.71, 147.65, 146.83, 146.82, 138.2, 137.9, 130.3, 130.2, 129.13, 129.11, 128.7, 128.6, 127.74, 127.66, 123.4, 57.2, 55.3, 55.1, 53.3, 31.1, 30.6, 29.92, 29.90, 29.73, 29.71, 25.9, 25.8, 25.7, 25.6, 25.5, 25.1; HRMS (ESI) m/z calcd for $C_{21}H_{24}N_2O_3$ $[M + H]^+$ 353.1860, found 353.1865.

*2-(5-Chloro-2-methyl-4-nitrophenyl)-N-cyclohexyl-N-methyl-2-phenylacetamide (**24**).* Pale yellow solid, Yield 148 mg (57%), mp 170–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 6.3 Hz, 2H), 7.40–7.30 (m, 6H), 7.23–7.16 (m, 4H), 7.07 (d, J = 6.3 Hz, 2H), 5.26 (d, J = 14.6 Hz, 2H), 4.51–4.44 (m, 1H), 3.60–3.44 (m, 1H), 2.85 (s, 3H), 2.78 (s, 3H), 2.32 (d, J = 2.9 Hz, 6H), 1.85–1.61 (m, 8H), 1.50–1.27 (m, 7H), 1.21–0.89 (m, 5H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.5, 169.4, 145.93, 145.90, 145.55, 145.51, 136.6, 136.2, 136.1, 136.0, 132.7, 129.24, 129.23, 129.17, 129.16, 128.0, 127.9, 127.02, 126.96, 124.69, 124.68, 114.1, 57.3, 53.4, 52.4, 52.3, 30.9, 30.5, 30.0, 29.8, 29.7, 27.9, 26.0, 25.8, 25.64, 25.58, 25.5, 25.1, 19.3, 19.2; HRMS (ESI) m/z calcd for $C_{22}H_{25}ClN_2O_3$ $[M + Na]^+$ 423.1446, found 423.1472.

*N-Benzyl-2-(2-bromo-4-nitrophenyl)-N-ethyl-2-phenylacetamide (**25**).* Cream solid, Yield 105 mg (46%), mp 142–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 2.3 Hz, 1H), 8.38 (d, J = 2.3 Hz, 1H), 8.05 (t, J = 2.1 Hz, 1H), 8.03 (t, J = 2.1 Hz, 1H), 7.40–7.24 (m, 19H), 7.22 (d, J = 6.7 Hz, 1H), 7.13 (d, J = 6.7 Hz, 2H), 5.72 (s, 1H), 5.64 (s, 1H), 4.67 (d, J = 14.8 Hz, 1H), 4.62 (d, J = 14.8 Hz, 1H), 4.50 (d, J = 16.8 Hz, 1H), 4.39 (d, J = 16.8 Hz, 1H), 3.64–3.55 (m, 1H), 3.42–3.21 (m, 3H), 1.12 (dt, J = 14.2, 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.4, 147.2, 147.05, 146.99, 146.90, 137.4, 136.9, 136.8, 136.4, 132.5, 132.4, 129.3, 129.0, 128.9, 128.8, 128.6, 128.2, 128.1, 128.0, 127.8, 127.55, 127.54, 127.46, 126.9, 124.63, 124.62, 122.14, 122.06, 54.5, 54.4, 51.0, 48.3, 42.0, 41.9, 13.5, 12.1; HRMS (ESI) m/z calcd for $C_{23}H_{21}BrN_2O_3$ $[M + Na]^+$ 475.0628, found 475.0627.

*N-Benzyl-2-(3-cyano-4-nitrophenyl)-N-ethyl-2-phenylacetamide (**26**).* Olive liquid, Yield 100 mg (40%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 1.5 Hz, 1H), 7.65 (dd, J = 8.6, 1.6 Hz, 1H), 7.48–7.34 (m, 12H), 7.32–7.26 (m, 4H), 7.24–7.15 (m, 6H), 5.32 (s, 1H), 5.12 (s, 1H), 4.73 (d, J = 14.8 Hz, 1H), 4.57 (d, J = 17.4 Hz, 1H), 4.49 (d, J = 14.8 Hz, 1H), 4.35 (d, J = 17.4 Hz, 1H), 3.91–3.83 (m, 1H), 3.43–3.30 (m, 1H), 3.26–3.16 (m, 2H), 1.19–1.09 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.4, 148.0, 147.8, 147.11, 147.06, 137.1, 136.9, 136.5, 136.43, 136.37, 136.35, 134.55, 134.50, 129.7, 129.6, 129.3, 128.7, 128.5, 128.4, 128.24, 128.16, 128.06, 127.7, 125.9, 125.3, 125.2, 115.09, 115.05, 107.9, 107.8, 107.7, 54.2, 54.1, 51.0, 48.5, 42.7, 42.0, 14.1, 12.6; HRMS (ESI) m/z calcd for $C_{24}H_{21}N_3O_3$ $[M + H]^+$ 400.1656, found 400.1675.

*N-Benzyl-2-(5-chloro-2-methyl-4-nitrophenyl)-N-ethyl-2-phenylacetamide (**27**).* Dark orange solid, Yield 118 mg (47%), mp 85–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.61 (s, 1H), 7.39–7.25 (m, 14H), 7.24–7.10 (m, 8H), 5.29 (s, 1H), 5.11 (s, 1H), 4.72 (d, J = 14.7 Hz, 1H), 4.54 (d, J = 14.7 Hz, 1H), 4.40 (d, J = 17.2 Hz, 1H), 4.30 (d, J = 17.2 Hz, 1H), 3.70–3.62 (m, 1H), 3.51–3.43 (m, 1H), 3.31–3.21 (m, 1H), 3.20–3.10 (m, 1H), 2.31 (s, 3H), 1.98 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.9, 146.1, 146.0, 144.9, 144.7, 137.4, 136.9, 136.6, 136.5, 136.3, 136.1, 132.7, 132.6, 129.24, 129.21, 129.17, 129.14, 128.9, 128.7, 128.2, 128.02, 127.99, 127.95, 127.6, 127.1, 127.0, 126.2, 124.8, 124.6, 51.7, 50.9, 48.3, 42.8, 41.8, 19.4, 19.1, 13.7, 12.4; HRMS (ESI) m/z calcd for $C_{24}H_{23}ClN_2O_3$ $[M + H]^+$ 423.1470, found 423.1464.

*2-(3-Cyano-4-nitrophenyl)-N,N,2-triphenylacetamide (**28**).* White solid, Yield 158 mg (52%), mp 170–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.6 Hz, 1H), 7.77–7.70 (m, 2H), 7.41–7.29 (m, 8H), 7.23–7.08 (m, 7H), 5.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 147.5, 147.2, 142.0, 141.9, 136.8, 136.1, 134.3, 130.1, 129.4, 129.1, 128.8, 128.5, 128.3, 126.8, 126.2, 125.4, 115.0, 107.9, 54.8; HRMS (ESI) m/z calcd for $C_{27}H_{19}N_3O_3$ $[M + H]^+$ 434.1499, found 434.1477.

*2-(4-Nitronaphthalen-1-yl)-N,N,2-triphenylacetamide (**29**).* Dark brown solid, Yield 141 mg (59%), mp 128–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 8.7 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.6 Hz, 1H), 7.69–7.59 (m, 2H), 7.55–7.51 (m, 1H), 7.34–7.16 (m, 13H), 7.08 (d, J = 6.3 Hz, 2H), 5.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 146.4, 142.7, 142.3, 142.1, 137.8, 132.2, 129.9, 129.2, 129.1, 129.0, 128.7, 128.41, 128.39, 127.8, 127.6, 126.5, 126.2, 126.0, 125.4, 123.9, 123.3, 123.2, 52.2; HRMS (ESI) m/z calcd for $C_{30}H_{22}N_2O_3$ $[M + H]^+$ 459.1703, found 459.1695.

*2-(2-Bromo-4-nitrophenyl)-1-morpholino-2-(thiophen-3-yl)ethan-1-one (**30**).* Olive liquid, Yield 152 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 2.3 Hz, 1H), 8.06 (dd, J = 8.6, 2.3 Hz, 1H), 7.40 (dd, J = 4.9, 3.0 Hz, 1H), 7.20 (d, J = 8.7 Hz, 2H), 6.96 (dd, J = 5.0, 1.1 Hz, 1H), 5.70 (s, 1H), 3.78–3.66 (m, 2H), 3.67–3.58 (m, 3H), 3.57–3.51 (m, 1H), 3.46–3.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 147.2, 146.4, 136.1, 132.0, 127.7, 127.49, 127.46, 124.3, 124.1, 122.4, 66.8, 66.4, 49.6, 46.5, 42.7; HRMS (ESI) m/z calcd for $C_{16}H_{15}BrN_2O_4S$ $[M + H]^+$ 411.0009, found 410.9991.

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*5-(2-Morpholino-1-(naphthalen-1-yl)-2-oxoethyl)-2-nitrobenzonitrile (**31**)*. Mustard liquid, Yield 178 mg (74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.6 Hz, 1H), 7.95−7.90 (m, 2H), 7.74−7.70 (m, 2H), 7.61−7.47 (m, 5H), 5.91 (s, 1H), 3.92−3.86 (m, 1H), 3.77−3.71 (m, 1H), 3.67−3.61 (m, 1H), 3.58−3.52 (m, 1H), 3.47−3.42 (m, 1H), 3.35−3.29 (m, 1H), 3.14−3.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 147.2, 147.0, 136.5, 134.7,134.5, 131.3, 130.2, 129.8, 129.7, 127.6, 126.6, 126.2, 125.7, 125.3, 121.9, 115.1, 107.9, 66.6, 66.1, 51.0, 46.3, 42.8; HRMS (ESI) m/z calcd for $C_{23}H_{19}N_3O_4$ $[M + H]^+$ 402.1448, found 402.1455.

*2-(2-Bromo-4-nitrophenyl)-1-morpholino-2-(naphthalen-1-yl)-ethan-1-one (**32**)*. Pale pink solid, Yield 191 mg (70%), mp 107−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 2.3 Hz, 1H), 7.93−7.88 (m, 3H), 7.57−7.53 (m, 3H), 7.51−7.42 (m, 2H), 6.94 (d, J = 8.6 Hz, 1H), 6.26 (s, 1H), 3.83−3.67 (m, 4H), 3.57−3.51 (m, 1H), 3.47−3.40 (m, 1H), 3.30−3.24 (m, 1H), 3.18−3.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 147.3, 146.5, 134.4, 132.2, 131.8, 130.7, 129.5, 129.4, 127.5, 127.4, 126.9, 126.4, 125.5, 124.6, 122.5, 122.3, 66.8, 66.3, 51.4, 46.4, 42.7; HRMS (ESI) m/z calcd for $C_{22}H_{19}BrN_2O_4$ $[M + Na]^+$ 477.0420, found 477.0427.

*2-(4-Nitrophenyl)-N,2-diphenylacetamide (**33**)*. Cream solid, Yield 132 mg (56%), mp 128−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.7 Hz, 2H), 7.61 (s, 1H), 7.47−7.41 (m, 4H), 7.39−7.33 (m, 3H), 7.31−7.25 (m, 4H), 7.10 (t, J = 7.4 Hz, 1H), 5.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 147.1, 146.4, 137.7, 137.3, 130.0, 129.4, 129.1, 128.8, 128.3, 125.0, 123.8, 120.0, 59.3; HRMS (ESI) m/z calcd for $C_{20}H_{16}N_2O_3$ $[M + H]^+$ 333.1234, found 333.1233.

*N-(2-Fluorophenyl)-2-(4-nitrophenyl)-2-phenylacetamide (**34**)*. Cream solid, Yield 183 mg (60%), mp 138−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (t, J = 7.4 Hz, 1H), 8.17 (d, J = 8.6 Hz, 2H), 7.66 (bs, 1H), 7.50 (d, J = 8.5 Hz, 2H), 7.42−7.31 (m, 5H), 7.14−7.01 (m, 3H), 5.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 152.6 (d, J = 243.6 Hz), 147.2, 146.2, 137.4, 129.9, 129.5, 128.8, 128.4, 125.8 (d, J = 10.1 Hz), 125.1 (d, J = 7.8 Hz), 124.7 (d, J = 3.7 Hz), 123.9, 121.9, 114.9 (d, J = 19.1 Hz), 59.5; HRMS (ESI) m/z calcd for $C_{20}H_{15}FN_2O_3$ $[M + H]^+$ 351.1139, found 351.1134.

*N-(2-Bromophenyl)-2-(4-nitrophenyl)-2-phenylacetamide (**35**)*. Cream solid, Yield 134 mg (56%), mp 150−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 8.7 Hz, 2H), 7.82 (bs, 1H), 7.53 (d, J = 8.7 Hz, 2H), 7.47 (dd, J = 8.0, 0.9 Hz, 1H), 7.44−7.39 (m, 2H), 7.38−7.28 (m, 4H), 7.00−6.95 (m, 1H), 5.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 147.2, 146.1, 137.3, 135.2, 132.3, 130.1, 129.6, 129.1, 128.49, 128.48, 125.8, 124.0, 121.7, 113.5, 60.0; HRMS (ESI) m/z calcd for $C_{20}H_{15}BrN_2O_3$ $[M + H]^+$ 411.0339, found 411.0347.

*N-(2-Bromophenyl)-2-(2-methyl-4-nitrophenyl)-2-phenylacetamide (**36**)*. Brown solid, Yield 155 mg (53%), mp 130−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, J = 8.2, 0.9 Hz, 1H), 8.10−8.04 (m, 2H), 7.83 (s, 1H), 7.47−7.25 (m, 8H), 6.98 (td, J = 8.0, 1.3 Hz, 1H), 5.32 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 147.1, 144.8, 139.0, 136.4, 135.1, 132.3, 129.7, 129.5, 129.3, 128.6, 128.5, 125.6, 121.6, 121.5, 113.5, 57.5; 20.0; HRMS (ESI) m/z calcd for $C_{21}H_{17}BrN_2O_3$ $[M + H]^+$ 425.0495, found 425.0497.

*N-Benzyl-2-(2-bromophenyl)-2-(2-chloro-4-nitrophenyl)acetamide (**37**)*. Buff solid, Yield 176 mg (58%), mp 129−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 2.3 Hz, 1H), 8.03 (dd, J = 8.6, 2.3 Hz, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.34−7.26 (m, 6H), 7.24−7.18 (m, 3H), 6.08 (s, 1H), 5.67 (s, 1H), 4.55−4.43 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 147.5, 143.4, 137.5, 136.2, 135.6, 133.6, 131.0, 130.1, 129.8, 128.8, 128.1, 127.80, 127.78, 125.4, 124.7, 121.8, 55.5, 44.2; HRMS (ESI) m/z calcd for $C_{21}H_{16}BrClN_2O_3$ $[M + H]^+$ 459.0106, found 459.0081.

*2-(2-Fluoro-4-nitrophenyl)-N-isopropyl-2-phenylacetamide (**38**)*. Yellowish orange solid, Yield 208 mg (66%), mp 118−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.6, 1.8 Hz, 1H), 7.89 (dd, J = 9.6, 2.2 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.38−7.31 (m, 3H), 7.29−7.26 (m, 2H), 5.52 (s, 1H), 5.10 (s, 1H), 4.15−4.05 (m, 1H), 1.11 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.69, 159.96 (d, J = 250.7 Hz), 147.71 (d, J = 9.0 Hz), 136.81, 134.72 (d, J = 14.6 Hz), 131.34 (d, J = 4.0 Hz), 129.27, 128.71, 128.14, 119.27 (d, J = 3.6 Hz), 111.12 (d, J = 27.8 Hz), 51.64 (d, J = 1.9 Hz), 42.13, 22.47; HRMS (ESI) m/z calcd for $C_{17}H_{17}FN_2O_3$ $[M + H]^+$ 317.1296, found 317.1298.

*2-(2-Bromophenyl)-N-butyl-2-(2-chloro-4-nitrophenyl)acetamide (**39**)*. White solid, Yield 153 mg (64%), mp 142−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 2.3 Hz, 1H), 8.03 (dd, J = 8.6, 2.3 Hz, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.34−7.26 (m, 3H), 7.23−7.18 (m, 1H), 5.78 (s, 1H), 5.60 (s, 1H), 3.35−3.22 (m, 2H), 1.50−1.43 (m, 2H), 1.33−124 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 147.4, 143.6, 136.5, 135.7, 133.6, 131.0, 130.0, 129.7, 128.1, 125.5, 124.7, 121.8, 55.6, 39.9, 31.4, 20.2, 13.6; HRMS (ESI) m/z calcd for $C_{18}H_{18}BrClN_2O_3$ $[M + Na]^+$ 447.0082, found 447.0086.

*2-(3-Chloro-4-nitrophenyl)-N,N-diisopropyl-2-phenylacetamide (**40**)*. Yellow solid, Yield 102 mg (40%), mp 85−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 1H), 7.38−7.28 (m, 4H), 7.26−7.23 (m, 2H), 7.20 (dd, J = 8.4, 1.7 Hz, 1H), 5.14 (s, 1H), 4.03−3.95 (m, 1H), 3.45−3.36 (m, 1H), 1.41 (t, J = 6.8 Hz, 6H), 1.18 (d, J = 6.7 Hz, 3H), 0.80 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 147.0, 146.2, 137.8, 132.7, 129.3, 128.8, 128.5, 127.9, 126.9, 125.4, 55.9, 49.3, 46.4, 21.1, 20.7, 20.1, 20.0; HRMS (ESI) m/z calcd for $C_{20}H_{23}ClN_2O_3$ $[M + H]^+$ 375.1470, found 375.1485.

*(E)-2-(3-Chloro-4-nitrosophenyl)-1-(diisopropylamino)-2-phenylethen-1-ol (**41**)*. Yellow solid, Yield 135 mg (55%), mp 189−190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 2H), 7.47−7.36 (m, 10H), 7.22−7.13 (m, 3H), 7.04−6.97 (m, 2H), 6.88 (dd, J = 10.0, 1.7 Hz, 1H), 3.92−3.83 (m, 2H), 3.41−3.31 (m, 2H), 1.65−1.54 (m, 6H), 1.42 (d, J = 6.0 Hz, 6H), 1.19−1.06 (m, 6H), 0.57 (d, J = 6.4 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 167.84, 167.83, 147.764, 147.756, 143.12, 134.40, 134.38, 130.45, 130.41, 129.82, 129.71, 129.41, 129.28, 129.14, 129.09, 128.91, 128.81, 128.69, 128.67, 128.40, 127.49, 117.56, 117.17, 51.01, 50.97, 46.08, 46.04, 20.84, 20.65, 19.75, 19.70; HRMS (ESI) m/z calcd for $C_{20}H_{23}ClN_2O_2$ $[M + H]^+$ 359.1521, found 359.1547.

*2-(3-Fluoro-4-nitrophenyl)-N,N-diisopropyl-2-phenylacetamide (**42**)*. Pale yellow solid, Yield 118 mg (60%), mp 79−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (t, J = 8.1 Hz, 1H), 7.42−7.31 (m, 3H), 7.25 (d, J = 6.0 Hz, 2H), 7.11−7.04 (m, 2H), 5.17 (s, 1H), 4.05−3.94 (m, 1H), 3.47−3.34 (m, 1H), 1.41 (t, J = 6.1 Hz, 6H), 1.18 (d, J = 6.7 Hz, 3H), 0.79 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 155.4 (d, J = 264.8 Hz), 149.9 (d, J = 8.0 Hz), 137.6, 135.8, 129.3, 128.5, 127.9, 125.69 (d, J = 2.6 Hz), 125.47 (d, J = 3.74 Hz), 119.52 (d, J = 21.5 Hz), 56.07, 56.06, 46.4, 21.1, 20.7, 20.1, 19.9; HRMS (ESI) m/z calcd for $C_{20}H_{23}FN_2O_3$ $[M + H]^+$ 359.1765, found 359.1790.

*(E)-1-(Diisopropylamino)-2-(3-fluoro-4-nitrosophenyl)-2-phenylethen-1-ol (**43**)*. Yellow solid, Yield 66 mg (35%), mp 186−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 2H), 7.44−7.33 (m, 10H), 7.17−7.08 (m, 2H), 6.96 (dd, J = 10.1, 1.5 Hz, 1H), 6.84 (dd, J = 10.0, 1.5 Hz, 1H), 6.66 (dd, J = 14.5, 1.5 Hz, 1H), 6.49 (dd, J = 14.0, 1.4 Hz, 1H), 3.93−3.84 (m, 2H), 3.39−3.31 (m, 2H), 1.57 (d, J = 5.8 Hz, 6H), 1.42 (d, J = 5.9 Hz, 6H), 1.11 (d, J = 6.5 Hz, 6H), 0.56 (d, J = 5.7 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.09, 168.06, 155.56 (d, J = 259.0 Hz), 154.89 (d, J = 259.0 Hz), 144.74 (d, J = 5.9 Hz), 144.66 (d, J = 5.9 Hz), 142.99 (d, J = 9.8 Hz), 142.91 (d, J = 9.8 Hz), 134.63, 134.60, 130.02, 129.41, 129.33, 129.13, 128.95, 128.87, 128.84, 128.75, 128.57 (d, J = 7.5 Hz), 128.48 (d, J = 7.2 Hz), 117.07, 116.69, 109.52 (d, J = 19.3 Hz), 108.74, 51.02, 50.95, 46.043, 46.041, 20.82, 20.65, 19.68, 19.66; HRMS (ESI) m/z calcd for $C_{20}H_{23}FN_2O_2$ $[M + H]^+$ 343.1816, found 343.1841.

*2-(3-Chloro-4-nitrophenyl)-N,N-diethyl-2-phenylacetamide (**44**)*. Mustard liquid, Yield 104 mg (30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 1H), 7.39−7.24 (m, 7H), 5.15 (s, 1H), 3.55−3.46 (m, 1H), 3.39−3.27 (m, 2H), 3.26−3.16 (m, 1H), 1.13 (td, J = 7.1, 1.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 146.6, 146.4, 137.6, 132.6, 129.2, 128.54, 128.51, 127.9, 127.0, 125.5, 54.0, 42.3, 40.9, 14.6, 12.8; HRMS (ESI) m/z calcd for $C_{18}H_{19}ClN_2O_3$ $[M + H]^+$ 347.1157, found 347.1165.

*(E)-2-(3-Chloro-4-nitrosophenyl)-1-(diethylamino)-2-phenylethen-1-ol (**45**)*. Yellow solid, Yield 116 mg (35%), mp 140−141 °C;

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^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 2H), 7.44−7.36 (m, 10H), 7.22−7.14 (m, 3H), 7.02 (dd, *J* = 10.1, 1.7 Hz, 1H), 6.94 (d, *J* = 1.7 Hz, 1H), 6.83 (dd, *J* = 10.0, 1.7 Hz, 1H), 3.53−3.46 (m, 4H), 3.24−3.17 (m, 4H), 1.22−1.17 (m, 6H), 0.82−0.76 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.19, 147.73, 147.71, 141.97, 141.89, 134.45, 134.41, 130.76, 130.36, 130.17, 129.48, 129.45, 129.38, 129.36, 129.31, 129.26, 126.21, 128.99, 128.88, 128.28, 127.26, 117.70, 117.32, 42.75, 42.73, 39.01, 13.50, 13.46, 12.65; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{19}ClN_2O_2$ [M + H]$^+$ 331.1208, found 331.1211.

(E)-(Diethylamino)(3-nitro-9H-xanthen-9-ylidene)methanol (**46**). Light brown solid, Yield 63 mg (20%), mp 116−117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.2 Hz, 1H), 7.95 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 7.41−7.36 (m, 1H), 7.29 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.22−7.16 (m, 2H), 6.92 (bs, 1H), 3.44−3.28 (m, 2H), 2.71−2.62 (m, 2H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 149.7, 149.0, 148.6, 130.4, 129.3, 129.2, 127.9, 124.8, 121.8, 118.1, 116.8, 112.6, 67.8, 42.1, 41.8, 12.0, 11.5. HRMS (APCI) *m*/*z* calcd for $C_{18}H_{18}N_2O_4$ [M − H]$^+$ 325.1183, found 325.1182.

(E)-(3-Nitro-9H-xanthen-9-ylidene)(piperidin-1-yl)methanol (**47**). Light brown solid, Yield 46 mg (15%), mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.2 Hz, 1H), 7.95 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 7.40−7.36 (m, 1H), 7.30 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.21−7.16 (m, 2H), 6.87 (s, 1H), 3.73−3.52 (m, 2H), 2.71 (s, 2H), 1.62−1.35 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 149.7, 148.9, 148.5, 130.4, 129.24, 129.15, 127.7, 124.8, 121.8, 118.2, 116.9, 112.6, 68.0, 46.9, 45.7, 25.5, 24.4, 23.9; HRMS (APCI) *m*/*z* calcd for $C_{19}H_{18}N_2O_4$ [M − H]$^+$ 337.1183, found 337.1194.

General Procedure for the Synthesis of Benzofurans. *N,N*-Diethyl-6-nitro-3-phenylbenzofuran-2-amine (48). In a 15 mL capacity sealed tube containing 1 mL of benzene, 2-(2-bromo-4-nitrophenyl)-*N,N*-diethyl-2-phenylacetamide **16** (50 mg, 0.13 mmol) and potassium *tert*-butoxide (44 mg, 0.38 mmol, 3 equiv) were heated at 100 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 3 h at 100 °C and then cooled to room temperature. The reaction mixture was poured into water (15 mL) and extracted with ethyl acetate (3 × 10 mL) and dried over Na_2SO_4, and the solvent was removed in vacuo. The resulting compound was purified by column chromatography (silica gel, hexane/ethyl acetate, 8/2). Brick red solid, Yield 25 mg (62%), mp 64−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.9 Hz, 1H), 8.02 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.45−7.37 (m, 4H), 7.35−7.31 (m, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 3.35 (q, *J* = 7.1 Hz, 4H), 1.11 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 147.6, 140.6, 139.6, 132.6, 130.0, 128.6, 127.2, 120.0, 114.5, 105.4, 94.7, 43.8, 13.5; HRMS (APCI) *m*/*z* calcd for $C_{18}H_{18}N_2O_3$ [M + H]$^+$ 311.1390, found 311.1410. Compound **49** was obtained by following the same method.

N,N-Diethyl-3-(2-methoxyphenyl)-6-nitrobenzofuran-2-amine (**49**). Brick red liquid, Yield 26 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 1.9 Hz, 1H), 7.99 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.37−7.32 (m, 1H), 7.29 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.03−6.95 (m, 2H), 6.87 (d, *J* = 8.7 Hz, 1H), 3.77 (s, 3H), 3.33 (q, *J* = 7.1 Hz, 4H), 1.09 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 157.7, 147.6, 140.3, 140.1, 132.3, 129.1, 121.1, 120.6, 119.9, 114.6, 110.9, 105.2, 89.8, 55.3, 43.4, 13.6; HRMS (APCI) *m*/*z* calcd for $C_{19}H_{20}N_2O_4$ [M + H]$^+$ 341.1496, found 341.1506.

General Procedure for Synthesis of Indoles. 2-(7-Chloro-4-methyl-1*H*-indol-5-yl)-*N,N*-diethyl-2-(2-methoxyphenyl)acetamide (50). 2-(5-Chloro-2-methyl-4-nitrophenyl)-*N,N*-diethyl-2-(2-methoxyphenyl)acetamide **4** (40 mg, 0.1 mmol) was dissolved in THF (1 mL), and the solution was cooled to −40 °C. Then, vinylmagnesium bromide (0.4 mL, 1.0 M in THF, 3.0 equiv) was added dropwise over 15 min. After completion of the addition, the reaction mixture was stirred at −40 °C. The progress of the reaction was monitored by TLC. When all the starting material was consumed, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (5 mL) and extracted with ethyl acetate (3 × 10 mL), and the combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. The crude product was purified by column chromatography (hexane/ethyl acetate. (80/20). Yellow solid, Yield 10 mg (30%), mp 220−222 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.24 (s, 1H), 7.21−7.14 (m, 2H), 6.85−6.77 (m, 3H), 6.55 (s, 1H), 5.70 (s, 1H), 3.83 (s, 3H), 3.63−3.54 (m, 1H), 3.31−3.19 (m, 2H), 3.09−3.00 (m, 1H), 2.33 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 156.5, 132.0, 130.3, 129.9, 128.9, 128.8, 127.7, 126.8, 124.4, 122.5, 120.6, 114.2, 109.9, 102.5, 55.4, 44.5, 42.1, 40.7, 15.0, 13.9, 12.8; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{25}ClN_2O_2$ [M + H]$^+$ 385.1677, found 385.1681. Compound **51** was obtained by following the same method.

2-(4,7-Dichloro-1H-indol-5-yl)-N,N-diethyl-2-phenylacetamide (**51**). Pale yellow liquid, Yield 18 mg (45%); ^{1}H NMR (400 MHz, DMSO) δ 11.79 (s, 1H), 7.49 (t, *J* = 2.7 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.23 (dd, *J* = 19.5, 7.2 Hz, 3H), 6.81 (s, 1H), 6.55−6.51 (m, 1H), 5.67 (s, 1H), 3.24 (dd, *J* = 12.1, 7.1 Hz, 4H), 1.01 (dt, *J* = 10.4, 7.0 Hz, 6H); ^{13}C NMR (100 MHz, DMSO) δ 174.6, 144.0, 137.3, 134.3, 134.1, 133.8, 133.4, 133.2, 132.3, 127.8, 127.4, 119.8, 106.4, 55.1, 46.9, 45.2, 19.3, 17.8; HRMS (ESI) *m*/*z* calcd for $C_{20}H_{20}Cl_2N_2O$ [M + H]$^+$ 375.1025, found 375.1053.

General Procedure for Synthesis of Benzophenones. (4-Nitrophenyl)(phenyl)methanone (52). In a 15 mL capacity sealed tube containing 1 mL of benzene, 2-(4-nitrophenyl)-*N*,2-diphenylacetamide **33** (50 mg, 0.15 mmol) and potassium *tert*-butoxide (52 mg, 0.45 mmol, 3 equiv) were heated at 100 °C. The progress of the reaction was monitored by TLC. The reaction mixture was refluxed for 12 h at 100 °C and then cooled to room temperature. The reaction mixture was poured into water (15 mL) and extracted with ethyl acetate (3 × 10 mL) and dried over Na_2SO_4, and the solvent was removed in vacuo. The resulting compound was purified by column chromatography (silica gel, hexane/ethyl acetate, 7/3). Buff solid, Yield 18 mg (52%), mp 119−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.81−7.77 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 149.9, 142.9, 136.3, 133.5, 130.7, 130.1, 128.7, 123.6; HRMS (APCI) *m*/*z* calcd for $C_{13}H_9NO_3$ [M + H]$^+$ 228.0655, found 228.0663. Compound **53** was obtained by following the same method.

(2-Methyl-4-nitrophenyl)(phenyl)methanone (**53**). Yellow liquid, Yield 8 mg (26%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17−8.09 (m, 2H), 7.76 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51−7.43 (m, 3H), 2.38 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 148.5, 144.8, 138.3, 136.3, 134.2, 130.0, 128.9, 128.7, 125.7, 120.6, 19.8; HRMS (APCI) *m*/*z* calcd for $C_{14}H_{11}NO_3$ [M + H]$^+$ 242.0812, found 242.0830.

General Procedure for Reduction of $-NO_2$ to NH_2. 2-(4-Aminophenyl)-*N,N*-diethyl-2-(2-methoxyphenyl)acetamide (54). In a 10 mL round-bottom flask equipped with a stir bar, *N,N*-Diethyl-2-(2-methoxyphenyl)-2-(4-nitrophenyl)acetamide **1** (40 mg, 0.12 mmol, 1 equiv) was added in 4 mL of ethanol/water (4:1). After that, iron powder (67 mg, 1.2 mmol, 10 equiv) and HCl (0.1 mL) were added. The reaction mixture was heated under reflux for 4 h and then cooled to room temperature. The reaction mixture was poured into aqueous saturated sodium bicarbonate (5 mL) and extracted with ethyl acetate (3 × 10 mL). The extractions were then washed with brine and dried over Na_2SO_4, and the solvent was removed in vacuo. The resulting compound was purified by column chromatography (silica gel, hexane/ethyl acetate, 65/35), which resulted in a light brown liquid. Yield 36 mg, (97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (td, *J* = 7.9, 1.6 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.95 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.83 (t, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 5.39 (s, 1H), 3.79 (s, 3H), 3.50−3.25 (m, 4H), 3.23−3.13 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 156.4, 144.3, 130.2, 130.0, 129.7, 129.2, 127.8, 120.5, 115.9, 110.1, 55.4, 47.1, 42.2, 40.6, 14.0, 12.8; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{24}N_2O_2$ [M + H]$^+$ 313.1911, found 313.1917.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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[1]H, [13]C NMR and mass spectra of synthesized acetamides (substrates for **1–47**), α-arylated amides (**1–45**), and functionalized products (**46–54**) and X-ray crystallographic data (PDF)

Crystallographic data for **12** (CCDC No. 1455187) (CIF)

Crystallographic data for **50** (CCDC No. 1455188) (CIF)

Crystallographic data for **14** (CCDC No. 1455189) (CIF)

Crystallographic data for **41** (CCDC No. 1455190) (CIF)

Crystallographic data for **43** (CCDC No. 1455191) (CIF)

Crystallographic data for **48** (CCDC No. 1473220) (CIF)

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Notes

The authors declare no competing financial interest.

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