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Aminocarbonylations Employing $Mo(CO)_6$ and a Bridged Two-Vial System: Allowing the Use of Nitro Group Substituted Aryl Iodides and Aryl Bromides

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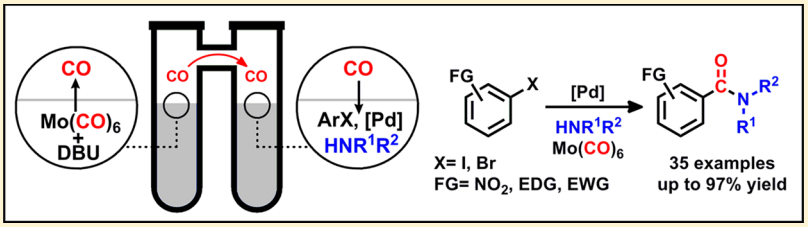
Supporting Information



ABSTRACT: A bridged two-vial system aminocarbonylation protocol where $Mo(CO)_6$ functions as an external *in situ* solid source of CO has been developed. For the first time both nitro group containing aryl/heteroaryl iodides and bromides gave good to excellent yields in the $Mo(CO)_6$-mediated and palladium(0)-catalyzed conversion to benzamides, while the identical one-vessel protocol afforded extensive reduction of the nitro functionality. The above-mentioned bridged two-compartment protocol furnished good results with both primary amines and secondary amines and sluggish aniline nucleophiles at 65−85 °C reaction temperatures.

Incorporation of the carbonyl moiety into organic molecules using a three-component matrix with carbon monoxide (CO), an organic halide, and a nucleophilic component is a simple and diverse approach to the formation of benzoic and cinnamyl acid derivatives, e.g., amides, esters, ketones, and anhydrides.[1−3] The most versatile method for this class of reactions is the palladium(0)-catalyzed carbonylation reaction employing aryl or vinyl halides (or halide surrogate), initially disclosed by Heck in the 1970s.[4] The catalytic process follows a pathway starting with oxidative addition of palladium(0) to the organohalide and coordination of CO to the metal center in the organopalladium complex followed by migratory 1,1-insertion to form an acylpalladium species, and subsequent nucleophilic attack liberates the carbonyl-containing product and the regenerated Pd(0) catalyst.[2,5]

As a result of its ability to bind to hemoglobin and inhibit oxygen transport from the lungs, CO is highly poisonous. In addition, the gas is odorless, invisible, and flammable. Furthermore, the use of highly specialized equipment capable of withstanding elevated pressure has often been necessary to enable safe handling of CO in a standard laboratory environment. Accordingly the development of alternative and safer sources of CO for small scale synthesis, for example, solid reagents that can release CO in a controlled manner, has gained considerable interest over the past decade. In our group, we have extensively investigated molybdenum hexacarbonyl as a solid substitute for gaseous CO.[6] The *in situ* CO-releasing ability of $MoCO_6$ has been previously demonstrated in a range of palladium(0)-catalyzed one-pot carbonylative reactions using DBU to chemically liberate free CO by a ligand exchange process[7−10] or by elevating the reaction temperature without the presence of activating additives.[11] By including $Mo(CO)_6$ in the reaction system we have been able to carbonylate a wide range of aryl and vinyl electrophiles, although the use of a nitro-containing aromatic substrate has not been realized due to concomitant Mo-mediated reduction to the corresponding aniline group.[12,13] The Ar-NO_2 group is an import functionality and a versatile synthetic handle, and we were therefore interested in developing a nitro group compatible $Mo(CO)_6$ carbonylation method.

Skrydstrup and co-workers have recently utilized a two-chamber system for the Pd-activated release of CO from 9-methyl-fluorene-9-carbonyl chloride and F^--mediated CO liberation from methyldiphenylsilacarboxylic acid with excellent results.[14−16] In these protocols CO is released in one compartment while the carbonylative reaction occurs in the other vial after free diffusion of the gas. Using a two-compartment reaction setup, the synthesis of nitro-containing products would be possible with $Mo(CO)_6$ as solid source of CO. Furthermore, the workup would also be facilitated due to the absence of complex molybdenum-containing species formed during the reaction.

Herein, we report a series of efficient palladium(0)-catalyzed aminocarbonylations using $Mo(CO)_6$ and a bridged two-vessel

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system, including examples of aryl iodides and bromides carrying nitro group functionalities.

To evaluate the release of carbon monoxide from solid $Mo(CO)_6$, a model reaction was set up using the bridged two-vial system depicted in Figure 1. Etherous solvents have been

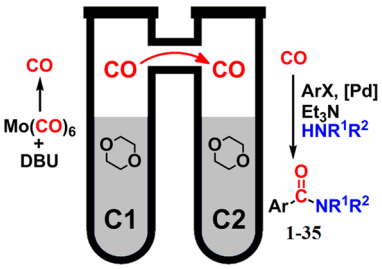
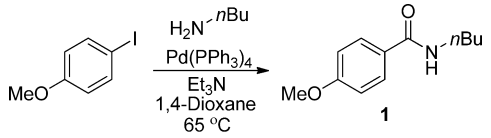


Figure 1. Schematic representation of the two-compartment vessel used; C1 is the CO-producing chamber and C2 is the CO-accepting chamber. X = I or Br.

proven to be appropriate solvents for carbonylation reactions, and 1,4-dioxane (bp 101 °C) was chosen as solvent in both chambers, due to its relatively high boiling point.[17] This may be important since the two compartments are interconnected and transport of solvents may cause uneven distribution of solvent and ultimately alter the reaction properties. CO-releasing vessel C1 was charged with $Mo(CO)_6$, and the reaction vial C2 was charged with 1 equiv of 4-iodoanisole using 2 equiv of *n*-butylamine as the nucleophile and 2 equiv of Et_3N as the base (Figure 1). The Pd/triphenylphosphine catalytic system has previously served as a general catalyst for aminocarbonylations of aryl iodides, and tetrakis(triphenylphosphine)palladium(0) was selected for this reason.[18,19] Next, both vials were sealed, DBU was added through the septa to C1, and both vials were placed into a heating block. Gratifyingly full conversion of the aryl iodide was observed after 15 h of heating at 65 °C using 0.5 equiv of $Mo(CO)_6$ and 5% $Pd(PPh_3)_4$, furnishing an excellent 95% isolated yield of aryl amide **1** (Table 1, entry 2). The addition of 1 equiv of $Mo(CO)_6$ gave similar results (94%), but when 0.3 equiv of $Mo(CO)_6$ was used, the yield decreased slightly to 88%. A reduction in reaction time from 15 to 5 h gave only 52% of **1**. Because a shorter reaction time or decreased catalyst loading led to incomplete conversion, the conditions for entry 2 were chosen for further evaluation. A reaction on a 2 mmol scale was also performed, giving 92% yield (Table 1, entry 10).[20]

Next we sought to examine the scope and limitations of the new two-chamber method using various aryl iodides and amine nucleophiles. As can be seen from Table 2, primary amines performed well, and the secondary benzamide products were isolated in good to excellent yields (81−97%, **1**−**11**); however, when secondary amines and aniline were used, low conversions were observed. Inspired by the work by Odell et al. the nucleophilic catalyst 4-dimethylaminopyridine (DMAP) was added to the reaction mixture.[21] This resulted in full consumption of the starting material, and good isolated yields of the desired products were observed (69−89%, **12**−**20**), although in the case of aniline the temperature had to be increased to 85 °C. Notably, aryl iodides containing electron-donating or electron-withdrawing substituents were found to be suitable substrates. In addition, full chemoselectivity was observed in the reaction of 1-bromo-4-iodobenzene, and no traces of product arising from oxidative addition to the Ar−Br

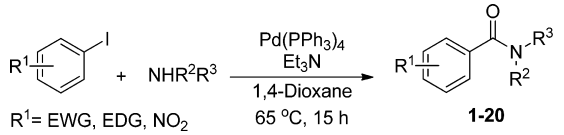
Table 1. Optimization of Reaction Conditions for the Aminocarbonylation of 4-iodoanisole with $Mo(CO)_6$ and DBU in the CO-Producing Vial (C1)

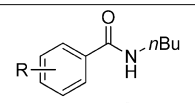


n	time (h)	$Pd(PPh_3)_4$ (mol %)	$Mo(CO)_6$ (equiv)	yield (%)[a]
1	15	5	1	94
2	15	5	0.5	95
3	5	3	0.5	61
4	15	5	0.3	88
5	5	5	0.3	52
6	5	5	0.5	69
7	15	3	1	75
9	15	1	0.5	14
10	15	5	0.5	92[b]

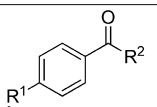
[a]Isolated yield, >95% purity (GC−MS and ^1H NMR). Reaction conditions: One of the H-shaped vial chambers (C1) was loaded with $Mo(CO)_6$. The other chamber (C2) was loaded with 4-iodoanisole (0.5 mmol) and $Pd(PPh_3)_4$. 1,4-Dioxane (6 mL, 3 mL in each chamber) was added to the two chambers, and to C2 were added Et_3N (1 mmol) and *n*-butylamine (1 mmol). After capping, DBU (0.75 mmol) was added to C1, and the two chambers were heated at 65 °C for 5−15 h. [b]The reaction was performed on a 2.0 mmol scale.

Table 2. Bridged Two-Vial Aminocarbonylation of Aryl Iodides and Nitro-Substituted Aryl Iodides; All Yields Are Isolated Yields

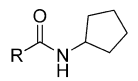




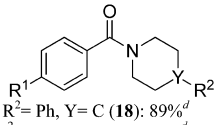
R= 4-OMe (**1**): 20%[a], 95%, 92%[b]
R= 3-OMe (**2**): 91%
R= 2-OMe (**3**): 92%
R= 4-Ph (**4**): 97%
R= 2-Me (**5**): 83%
R= 4-CN (**6**): 81%
R= 4-NO_2 (**7**): 12%[a], 92%
R= 3-NO_2 (**8**): 83%
R= 2-NO_2 (**9**): 78%



R[1]= 4-OMe, R[2]= NHC_6H_5 (**12**): 46%, 87%[c,d]
R[1]= 4-OMe, R[2]= 1-pyrrolidinyl (**13**): 77%[d]
R[1]= 4-NO_2, R[2]= 1-pyrrolidinyl (**14**): 86%[d]
R[1]= 3-NO_2, R[2]= NHC_6H_5 (**15**): 75%[c,d]
R[1]= 3-NO_2, R[2]= NHC_6H_4-4-NO_2 (**16**): 71%[c,d]
R[1]= 4-NO_2, R[2]= NHC_6H_4-4-NO_2 (**17**): 77%[c,d]



R= C_6H_4-4-OMe (**10**): 92%
R= 3-thiophenyl (**11**): 87%



R[1]= CN, R[2]= Ph, Y= C (**18**): 89%[d]
R[1]= Br, R[2]= Me, Y= C (**19**): 69%[d]
R[1]= 4-NO_2, R[2]= C_6H_4-4-NO_2, Y= N (**20**): 74%[d]

[a]All reagents were placed in a single vial. [b]The reaction was performed on a 2 mmol scale. [c]85 °C. [d]1 mmol of DMAP was added to C2.

bond were detected. Finally, a one-pot, one-vessel reaction was performed that resulted in only modest conversion and low isolated yield (20% of **1**). This result implies that the two-compartment reaction is a much more efficient process, and the presence of $Mo(CO)_6$ may in fact impede the catalytic carbonylation reaction at these moderate temperatures.[22]

As mentioned above, the reductive properties of $Mo(CO)_6$ has precluded the use of nitro group containing substrates in $Mo(CO)_6$-mediated aminocarbonylations.[12,13] For example, a

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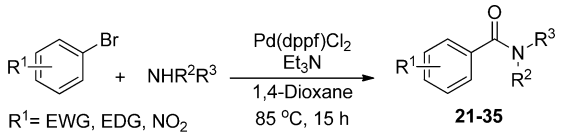
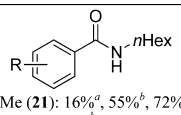
one-pot reaction using $Mo(CO)_6$, 1-iodo-4-nitrobenzene, and *n*-butylamine at 65 °C resulted in the formation of a complex mixture of aniline derived side products, yielding only 12% of the desired nitro containing benzamide **7**. Using the two-chamber methodology, the reactions of mononitroaryl iodides instead proceeded smoothly for all isomers with isolated yields ranging from 71% to 92% (**7**–**9**). The use of the less reactive aniline nucleophiles, furnished good yields of the amino-carbonylations products when DMAP was used (**15**–**17**). Importantly, no reduced products were detected in the crude reaction mixture from any example in Table 2 as observed by GC–MS, LC–MS and ^{1}H NMR.

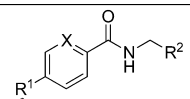
The preparative scope of the two-vial carbonylation method was further expanded to include aryl bromides (Table 3), an

Table 3. Bridged Two-Vial Aminocarbonylation of Aryl Bromides and Nitro-Substituted Aryl Bromides; All Yields Are Isolated Yields

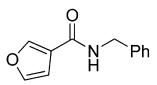




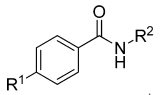
R= 4-OMe (**21**): 16%[a], 55%[b], 72%[c], 88%
R= 3-NO_2 (**22**): 61%[b], 78%
R= 2-NO_2 (**23**): 55%
R= 4-NO_2 (**24**): 0%[a], 81%
R= 2-naphthyl (**25**): 93%
R= 4-CN (**26**): 89%
R= 2-Me (**27**): 52%
R= 2-Ph (**28**): 32%



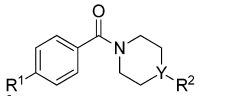
R^1= NO_2, R^2=C_6H_4-4-Cl, X= C (**31**): 81%
R^1= H, R^2= 2-tetrahydrofuryl, X= N (**32**): 41%



(**33**): 79%



R^1=H, R^2= Ph (**29**): 27%, 83%[d]
R^1= CHO R^2= cyclopentyl (**30**): 69%



R^1= Cl, R^2= C_6H_3-2,3-di-Cl, Y= N (**34**): 74%
R^1= CH_2CH, R^2= Me, Y= C (**35**): 78%

[a]All reagents were placed in the same chamber. [b]5 mol % of $Pd(PPh_3)_4$ was used. [c]Without nitrogen flush prior to heating. [d]1 mmol of DMAP was added to C2.

improvement in terms of both costs and commercial availability. Aryl bromides are less prone to undergo oxidative addition than iodides, thus demanding higher temperatures and a more active catalytic system. When 4-bromoanisole and *n*-hexylamine were reacted with $Pd(PPh_3)_4$ at a slightly elevated temperature (85 °C), the corresponding carbonylated product was isolated in 55% yield (**21**). However, upon changing the precatalyst to [1,1′-bis(diphenylphosphino)ferrocene]-dichloropalladium ($Pd(dppf)Cl_2$), full conversion was observed and the corresponding product was isolated in 72% yield. Small amounts of *N*,*N*′-dihexylurea originating from the nucleophile were detected in the reaction mixture, suggesting that competition from a Pd(II)-catalyzed carbonylation had occurred.[23] Flushing the vial with nitrogen prior to heating solved this problem and yielded product **21** in an improved 88% yield. The reaction was again found to be robust and highly chemoselective as aryl bromides equipped with a set of different functional groups as well as primary, secondary, and aniline nucleophiles all performed well. Notably, formyl-substituted compound **30** underwent a clean reaction without reduction to the benzyl alcohol. Rewardingly and despite the 85 °C reaction temperature, only trace amounts of aniline derived byproducts from concomitant reduction of aromatic nitro moieties were detected. Unfortunately, low yields were obtained with 2-bromobiphenyl and sluggish 2-bromopyridine due to low conversion and competitive dehalogenation (according to GC–MS), respectively.

Conclusions. A number of CO gas-free two-chamber methods have been developed to synthesize benzamides containing EWG/EDG or heterocycles via palladium(0)-catalyzed aminocarbonylation reactions of aryl/heteroaryl iodides and bromides using $Mo(CO)_6$ as a solid CO releasing solid reagent. CO gas was released in one of the bridged reaction vials by chemical liberation with DBU. After release the gas was able to diffuse to a second accepting vial where it could participate in the aminocarbonylation reaction. Importantly, nitro group containing benzamide products were synthesized in good to excellent yields with only negligible formation of aniline byproducts arising from nitro group reduction.

EXPERIMENTAL SECTION

General Information. Palladium catalysts were purchased from Sigma-Aldrich. Analytical thin-layer chromatography was performed on silica gel 60 F-254 plates and visualized with UV light. Flash column chromatography was performed on silica gel 60 (40–63 μm). ^{1}H and ^{13}C NMR spectra were recorded at 400 and 101 MHz, respectively, using MeOD, DMSO-d_6 or $CDCl_3$ as a solvent. Chemical shifts for ^{1}H and ^{13}C are referenced via the residual solvent signal. *Caution! The closed-vessel carbonylation reactions described in this paper should not be repeated on a larger scale or at higher temperatures than reported as this could result in an explosion unless an appropriate pressure relief device is used.*

General Procedure for the Aminocarbonylation Using Aryl Iodies Yielding 1–20. Chamber two (C2) was loaded with aryl iodide (0.5 mmol), $Pd(PPh_3)_4$ (29 mg, 5 mol %), Et_3N (139 μL, 1 mmol), and the corresponding nucleophilic amine (1 mmol). For carbonylations using aryl iodides with secondary amines or aniline, DMAP (61 mg, 0.5 mmol) was added to C2. To chamber one (C1) was added $Mo(CO)_6$ (66 mg, 0.25 mmol), and thereafter 1,4-dioxane (3 + 3 mL) was added to C1 and C2. The two chambers were capped with a gastight cap, and DBU (112 μL, 0.75 mmol) was added to C1. The sealed double vial was heated in a heat block at 65 °C (85 °C for nucleophilic anilines) for 15 h with vigorous stirring.

General Procedure for the Aminocarbonylation Using Aryl Bromides Yielding 21–35. Chamber two (C2) was loaded with aryl bromide (0.5 mmol), $Pd(dppf)Cl_2$ (18 mg, 5 mol %), Et_3N (139 μL, 1 mmol), and the corresponding nucleophilic amine (1 mmol). For carbonylations using aryl bromides with aniline, DMAP (61 mg, 0.5 mmol) was added to C2. To chamber one (C1) was added $Mo(CO)_6$ (66 mg, 0.25 mmol), and thereafter 1,4-dioxane (3 + 3 mL) was added to C1 and C2. The two chambers were capped with a gastight cap and flushed with nitrogen for 2 min after which DBU (112 μL, 0.75 mmol) was added to C1. The sealed double vial was heated in a heat block at 85 °C for 15 h with vigorous stirring.

Workup Procedure for 1–35. After careful evacuation of excess CO, the crude mixture from C2 was evaporated to dryness. The residue was dissolved in small amount of DCM and purified by column chromatography, eluted with *n*-pentane/EtOAc (7:1–2:1) or $CHCl_3$/MeOH (20:1) to yield products **1**–**35**. (In the case of aniline and 4-nitroaniline, the crude mixture was evaporated, taken up in 20 mL of DCM, washed with 3 × 10 mL 3 M HCl, and evaporated prior to purification).

***N*-Butyl-4-methoxybenzamide (1).**[24] Brown solid (98 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.17 (brs, 1H), 3.83 (s, 3H), 3.52–3.33 (m, 2H), 1.64–1.48 (m, 2H), 1.45–1.32 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 162.0, 128.6, 127.1, 113.7, 55.4,

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39.8, 31.8, 20.1, 13.8; MS (ESI) calcd for $C_{12}H_{17}NO_2$ $[M + H]^+$ m/z 208, found m/z 208.

***N*-Butyl-3-methoxybenzamide (2).** Brown oil (94 mg, 91%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.40−7.30 (m, 3H), 7.09−7.03 (m, 1H), 3.82 (s, 3H), 3.36 (t, J = 7.2 Hz, 2H), 1.63−1.54 (m, 2H), 1.47−1.33 (m, 2H), 0.96 (t, J = 7.4 Hz, 1H); ^{13}C NMR (101 MHz, CD_3OD) δ 167.1, 162.0, 128.6, 127.1, 113.7, 55.4, 39.8, 31.8, 20.1, 13.8; HRMS (ESI) calcd for $C_{12}H_{17}NO_2$ $[M + H]^+$ m/z 208.1338, found m/z 208.1340.

***N*-Butyl-2-methoxybenzamide (3).** Brown oil (95 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, J = 7.8, 1.8 Hz, 1H), 7.83 (brs, 1H), 7.42 − 7.34 (m, 1H), 7.03 (td, J = 7.6, 1.0 Hz, 1H), 6.93 (d, J = 9.1 Hz, 1H), 3.91 (s, 3H), 3.51−3.38 (m, 2H), 1.65−1.50 (m, 2H), 1.47−1.27 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 157.4, 132.5, 132.2, 121.8, 121.3, 111.3, 56.0, 39.5, 31.7, 20.3, 13.8; HRMS calcd for $C_{12}H_{17}NO_2$ $[M + H]^+$ m/z 208.1338, found m/z 208.1336.

***N*-Butyl-[1,1′-biphenyl]-4-carboxamide (4).** Light brown solid (123 mg, 97%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 7.61−7.57 (m, 2H), 7.49−7.42 (m, 2H), 7.41−7.34 (m, 1H), 6.33 (brs, 1H), 3.56−3.38 (m, 2H), 1.69−1.53 (m, 2H), 1.52−1.35 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 144.2, 140.2, 133.6, 129.0, 128.0, 127.5, 127.3, 40.0, 31.9, 20.3, 13.9; HRMS calcd for $C_{17}H_{19}NO$ $[M + H]^+$ m/z 254.1545, found m/z 254.1552.

***N*-Butyl-2-methylbenzamide (5).**[25] Brown oil (79 mg, 83%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 (brs, 1H), 7.33−7.26 (m, 2H), 7.24−7.17 (m, 2H), 3.27−3.17 (m, 2H), 2.32 (s, 3H), 1.55−1.43 (m, 2H), 1.40−1.28 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.0, 137.6, 134.9, 130.3, 129.0, 126.9, 125.4, 38.5, 31.2, 19.7, 19.3, 13.7; MS (ESI) calcd for $C_{12}H_{17}NO$ $[M + H]^+$ m/z 192, found m/z 192.

***N*-Butyl-4-cyanobenzamide (6).**[24] Off-white solid (82 mg, 81%); ^{1}H NMR (400 MHz, CD_3OD) δ 7.94 (d, J = 8.7 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H), 3.39 (t, J = 7.2 Hz, 2H), 1.66−1.53 (m, 2H), 1.50−1.33 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, CD_3OD) δ 168.3, 140.1, 133.5, 129.1, 119.1, 115.9, 40.9, 32.5, 21.2, 14.1; MS (ESI) calcd for $C_{12}H_{14}N_2O$ $[M + H]^+$ m/z 203, found m/z 203.

***N*-Butyl-4-nitrobenzamide (7).**[26] Brown crystals (102 mg, 92%); mp 99−101 °C, lit.[27] 100−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 9.0 Hz, 2H), 7.91 (d, J = 9.0 Hz, 2H), 6.38 (brs, 1H), 3.46 (td, J = 7.2, 5.7 Hz, 2H), 1.66−1.54 (m, 2H), 1.48−1.28 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 149.6, 140.6, 128.2, 123.9, 40.3, 31.7, 20.3, 13.9; MS (ESI) calcd for $C_{11}H_{14}N_2O_3$ $[M + H]^+$ m/z 223, found m/z 223.

***N*-Butyl-3-nitrobenzamide (8).** Brown solid (92 mg, 83%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 (brs, 1H), 8.68−8.65 (m, 1H), 8.38−8.33 (m, 1H), 8.29−8.25 (m, 1H), 7.76 (t, J = 8.0 Hz, 1H), 3.34−3.25 (m, 2H), 1.58−1.47 (m, 2H), 1.40−1.25 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.9, 147.8, 136.0, 133.6, 130.1, 125.7, 121.9, 39.1, 31.1, 19.7, 13.7; HRMS (ESI) calcd for $C_{11}H_{14}N_2O_3$ $[M + H]^+$ m/z 223.1083, found m/z 223.1082.

***N*-Butyl-2-nitrobenzamide (9).** Light brown solid (87 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.1 Hz, 1H), 7.66−7.60 (m, 1H), 7.57−7.51 (m, 1H), 7.47 (dd, J = 7.4, 1.5 Hz, 1H), 6.00 (brs, 1H), 3.45−3.37 (m, 2H), 1.64−1.54 (m, 2H), 1.46−1.43 (m, 2H), 0.95 (d, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 146.5, 133.8, 133.3, 130.4, 128.8, 124.6, 40.1, 31.4, 20.2, 13.9; HRMS (ESI) calcd for $C_{11}H_{14}N_2O_3$ $[M + H]^+$ m/z 223.1083, found m/z 223.1081.

***N*-Cyclopentyl-4-methoxybenzamide (10).** Brown solid (101 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.9 Hz, 1H), 6.88 (d, J = 8.9 Hz, 1H), 6.07 (brs, 1H), 4.46−4.26 (m, 1H), 3.82 (s, 3H), 2.15−1.98 (m, 2H), 1.77−1.57 (m, 4H), 1.52−1.40 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 162.1, 128.7, 127.3, 113.7, 55.5, 51.7, 33.4, 23.9; HRMS calcd for $C_{13}H_{17}NO_2$ $[M + H]^+$ m/z 220.1338, found m/z 220.1332.

***N*-Cyclopentylthiophene-3-carboxamide (11).** Off-white crystals (85 mg, 87%); mp 141−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 3.0, 1.3 Hz, 1H), 7.37 (dd, J = 5.1, 1.3 Hz, 1H), 7.30 (dd, J = 5.1, 3.0 Hz, 1H), 6.08 (brs, 1H), 4.45−4.22 (m, 1H), 2.15−1.97 (m, 2H), 1.78−1.52 (m, 4H), 1.52−1.36 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 138.0, 127.9, 126.4, 126.2, 51.6, 33.3, 23.9; HRMS calcd for $C_{10}H_{13}NOS$ $[M + H]^+$ m/z 196.0796, found m/z 196.0798.

4-Methoxy-*N*-phenylbenzamide (12).[27] White crystals (99 mg, 87%); mp 169−171 °C, lit.[25] Mp 171 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.9 Hz, 2H), 7.78 (brs, 1H), 7.63 (d, J = 8.7 Hz, 2H), 7.40−7.33 (m, 2H), 7.31−7.25 (m, 1H), 7.14 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 162.7, 138.2, 129.2, 129.0, 127.3, 124.6, 120.4, 114.2, 55.6 ; MS (ESI) calcd for $C_{14}H_{13}NO_2$ $[M + H]^+$ m/z 228, found m/z 228.

***N*-(*p*-Methoxybenzoyl)pyrrolidine (13).**[28] Brown solid (79 mg, 77%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H), 3.49−3.39 (m, 4H), 1.94−1.66 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 160.3, 129.2, 129.1, 113.3, 55.2, 49.1, 46.0, 26.1, 23.9; MS (ESI) calcd for $C_{12}H_{15}NO_2$ $[M + H]^+$ m/z 206, found m/z 206.

(4-Nitrophenyl)(pyrrolidin-1-yl)methanone (14).[28] Beige solid (95 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 3.66 (t, J = 6.9 Hz, 2H), 3.37 (t, J = 6.6 Hz, 2H), 2.05−1.86 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 148.5, 143.3, 128.3, 123.8, 49.6, 46.5, 26.5, 24.5; MS (ESI) calcd for $C_{11}H_{12}N_2O_3$ $[M + H]^+$ m/z 221, found m/z 221.

3-Nitro-*N*-phenylbenzamide (15).[27] Yellow solid (91 mg, 75%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.58 (brs, 1H), 8.79 (s, 1H), 8.51−8.36 (m, 2H), 7.84 (t, J = 8.0 Hz, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.38 (t, J = 7.9 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.3, 147.7, 138.7, 136.3, 134.2, 130.2, 128.7, 126.1, 124.1, 122.4, 120.6; MS (ESI) calcd for $C_{13}H_{10}N_2O_3$ $[M + H]^+$ m/z 243, found m/z 243.

3-Nitro-*N*-(4-nitrophenyl)benzamide (16). Yellow solid (102 mg, 71%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.15 (brs, 1H), 8.79 (t, J = 2.0 Hz, 1H), 8.47−8.38 (m, 2H), 8.26 (d, J = 9.2 Hz, 2H), 8.05 (d, J = 9.2 Hz, 2H), 7.84 (t, J = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.2, 147.8, 145.0, 142.9, 135.6, 134.5, 130.4, 126.7, 124.9, 122.7, 120.3; HRMS (ESI) calcd for $C_{13}H_9N_3O_5$ $[M + H]^+$ m/z 288.0620, found m/z 288.0627.

4-Nitro-*N*-(4-nitrophenyl)benzamide (17).[29] Yellow solid (111 mg, 77%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.10 (brs, 1H), 8.40 (d, J = 9.0 Hz, 2H), 8.30 (d, J = 9.4 Hz, 2H), 8.21 (d, J = 9.0 Hz, 2H), 8.07 (d, J = 9.4 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.7, 149.5, 144.9, 142.9, 139.8, 129.5, 124.9, 123.6, 120.1; LC−MS (ESI) calcd for $C_{13}H_9N_3O_5$ $[M + H]^+$ m/z 288, found m/z 288.

(4-(4-Phenylpiperidine-1-carbonyl)benzonitrile (18). White solid (129 mg, 89%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 7.33−7.25 (m, 4H), 7.22−7.16 (m, 1H), 4.70−4.58 (m, 1H), 3.57−3.46 (m, 1H), 3.25−3.10 (m, 1H), 2.94−2.75 (m, 2H), 1.90−1.78 (m, 1H), 1.75−1.55 (m, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.3, 145.5, 141.0, 132.6, 128.4, 127.6, 126.8, 126.2, 118.4, 111.9, 47.5, 42.0, 41.7, 33.0, 32.6; HRMS (ESI) calcd for $C_{19}H_{18}N_2O$ $[M + H]^+$ m/z 291.1497, found m/z 291.1498.

(4-Bromophenyl)(4-methylpiperidin-1-yl)methanone (19). Brown solid (97 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 4.64 (brs, 1H), 3.66 (brs, 1H), 2.97 (brs, 1H), 2.76 (brs, 1H), 1.85−1.54 (m, 3H), 1.30−1.01 (m, 2H), 0.97 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 135.5, 131.8, 128.7, 123.8, 48.2, 42.7, 34.8, 33.9, 31.3, 21.8; HRMS (ESI) calcd for $C_{13}H_{16}BrNO$ $[M + H]^+$ m/z 282.0494, found m/z 282.0493.

(4-Nitrophenyl)(4-(4-nitrophenyl)piperazin-1-yl)methanone (20). Yellow solid (132 mg, 74%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (d, J = 8.9 Hz, 2H), 8.07 (d, J = 9.5 Hz, 2H), 7.74 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 9.5 Hz, 2H), 3.79 (s, 2H), 3.63 (s, 2H), 3.47 (s, 4H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.3, 154.3, 147.9, 141.9, 137.2, 128.4, 125.7, 123.8, 112.8, 46.3, 46.1, 45.7, 41.2; HRMS (ESI) calcd for $C_{17}H_{16}N_4O_5$ $[M + H]^+$ m/z 357.1199, found m/z 357.1196.

***N*-Hexyl-4-methoxybenzamide (21).**[14] Light brown solid (104 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.27 (brs, 1H), 3.82 (s, 3H), 3.40 (td, J = 7.3,

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5.7 Hz, 2H), 1.64−1.47 (m, 2H), 1.40−1.24 (m, 6H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 162.1, 128.7, 127.3, 113.7, 55.5, 40.2, 31.6, 29.8, 26.8, 22.7, 14.1.; MS (ESI) calcd for $C_{14}H_{21}NO_2$ $[M + H]^+$ m/z 236, found m/z 236.

***N*-Hexyl-3-nitrobenzamide (22).** White solid (98 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (td, J = 1.9, 0.8 Hz, 1H), 8.31 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 8.15 (ddd, J = 7.7, 1.7, 1.1 Hz, 1H), 7.65−7.57 (m, 1H), 6.66 (brs, 1H), 3.52−3.40 (m, 2H), 1.69−1.55 (m, 2H), 1.43−1.22 (m, 6H), 0.87 (d, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 148.2, 136.6, 133.4, 129.9, 126.0, 121.8, 40.6, 31.6, 29.6, 26.8, 22.6, 14.1; HRMS (ESI) calcd for $C_{13}H_{18}N_2O_3$ $[M + H]^+$ m/z 251.1396, found m/z 251.1397.

***N*-Hexyl-2-nitrobenzamide (23).** Brown oil (69 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.2, 1.3 Hz, 1H), 7.60 (td, J = 7.5, 1.3 Hz, 1H), 7.53−7.47 (m, 1H), 7.42 (dd, J = 7.5, 1.5 Hz, 1H), 6.25 (brs, 1H), 3.39−3.28 (m, 2H), 1.60−1.50 (m, 2H), 1.38−1.20 (m, 6H), 0.91−0.83 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 146.5, 133.7, 133.2, 130.3, 128.8, 124.5, 40.3, 31.5, 29.2, 26.6, 22.6, 14.1; HRMS (ESI) calcd for $C_{13}H_{18}N_2O_3$ $[M + H]^+$ m/z 251.1396, found m/z 251.1398.

***N*-Hexyl-4-nitrobenzamide (24).** Off-white crystals (101 mg, 81%); mp 62−64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.9 Hz, 2H), 7.92 (d, J = 8.9 Hz, 2H), 6.39 (brs, 1H), 3.45 (td, J = 7.3, 5.7 Hz, 2H), 1.68−1.54 (m, 2H), 1.41−1.27 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 149.6, 140.6, 128.2, 123.9, 40.6, 31.6, 29.6, 26.8, 22.7, 14.1; HRMS (ESI) calcd for $C_{13}H_{18}N_2O_3$ $[M + H]^+$ m/z 251.1396, found m/z 251.1395.

***N*-Hexyl-2-naphthamide (25).** Yellow crystals (119 mg, 93%); mp 96−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.87−7.79 (m, 4H), 7.55−7.44 (m, 2H), 6.75 (brs, 1H), 3.46 (q, J = 7.2, 6.6 Hz, 2H), 1.67−1.56 (m, 2H), 1.40−1.25 (m, 6H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 134.7, 132.7, 132.2, 128.9, 128.3, 127.7, 127.5, 127.4, 126.6, 123.8, 40.4, 31.6, 29.7, 26.8, 22.6, 14.1; HRMS (ESI) calcd for $C_{17}H_{21}NO$ $[M + H]^+$ m/z 256.1701, found m/z 256.1706.

4-Cyano-*N*-hexylbenzamide (26). White solid (102 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 8.7 Hz, 2H), 6.62 (brs, 1H), 3.46−3.35 (m, 2H), 1.57 (q, J = 7.8 Hz, 2H), 1.38−1.22 (m, 6H), 0.89−0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 138.9, 132.4, 127.8, 118.1, 114.8, 40.5, 31.5, 29.5, 26.7, 22.6, 14.1; HRMS (ESI) calcd for $C_{14}H_{18}N_2O$ $[M + H]^+$ m/z 231.1497, found m/z 231.1493.

***N*-Hexyl-2-methylbenzamide (27).** Off-white solid (57 mg, 52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.26 (m, 2H), 7.21−7.14 (m, 2H), 5.82 (brs, 1H), 3.52−3.31 (m, 2H), 2.42 (s, 3H), 1.63−1.50 (m, 2H), 1.43−1.26 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 137.0, 136.0, 131.0, 129.8, 126.7, 125.8, 39.9, 31.6, 29.8, 26.7, 22.7, 19.8, 14.1; HRMS (ESI) calcd for $C_{14}H_{21}NO$ $[M + H]^+$ m/z 220.1701, found m/z 220.1699.

***N*-Hexyl-[1,1′-biphenyl]-2-carboxamide (28).** White solid (44 mg, 32%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.5, 1.6 Hz, 1H), 7.47 (td, J = 7.5, 1.6 Hz, 1H), 7.43−7.33 (m, 7H), 5.16 (brs, 1H), 3.20−3.06 (m, 2H), 1.28−1.08 (m, 6H), 1.04−0.94 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 140.5, 139.5, 136.1, 130.3, 130.1, 129.0, 128.9, 128.8, 127.9, 127.7, 40.0, 31.6, 29.0, 26.5, 22.6, 14.2; HRMS (ESI) calcd for $C_{19}H_{23}NO$ $[M + H]^+$ m/z 282.1858, found m/z 282.1859.

***N*-Phenylbenzamide (29).**[30] Yellow crystals (82 mg, 83%); mp 162−164 °C (lit.[29] 163−164 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.85 (m, 2H), 7.85 (brs, 1H), 7.67−7.63 (m, 2H), 7.58−7.52 (m, 1H), 7.52−7.45 (m, 2H), 7.41−7.34 (m, 2H), 7.19−7.12 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 138.1, 135.2, 132.0, 129.2, 128.9, 127.1, 124.7, 120.3; MS (ESI) calcd for $C_{13}H_{11}NO$ $[M + H]^+$ m/z 198, found m/z 198.

***N*-Cyclopentyl-4-formylbenzamide (30).** Yellow crystals (75 mg, 69%); mp 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.87 (s, 4H), 6.46 (brs, 1H), 4.45−4.29 (m, 1H), 2.14−1.99 (m, 2H), 1.78−1.57 (m, 4H), 1.55−1.43 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 166.2, 140.2, 138.0, 129.8, 127.7, 52.0, 33.2, 23.9; HRMS (ESI) calcd for $C_{13}H_{15}NO_2$ $[M + H]^+$ m/z 218.1181, found m/z 218.1179.

***N*-(4-Chlorobenzyl)-4-nitrobenzamide (31).** Off-white crystals (118 mg, 81%); mp 169−171 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.39 (brs, 1H), 8.32 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 8.8 Hz, 2H), 7.45−7.29 (m, 4H), 4.49 (d, J = 5.9 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.7, 149.1, 139.8, 138.2, 131.5, 129.2, 128.8, 128.3, 123.6, 42.2; HRMS (ESI) calcd for $C_{14}H_{11}ClN_2O_3$ $[M + H]^+$ m/z 291.0536, found m/z 291.0534.

***N*-((Tetrahydrofuran-2-yl)methyl)picolinamide (32).** White solid (42 mg, 41%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (ddd, J = 4.8, 1.7, 0.9 Hz, 1H), 8.33 (brs, 1H), 8.18 (dt, J = 7.8, 1.2 Hz, 1H), 7.83 (td, J = 7.8, 1.7 Hz, 1H), 7.40 (ddd, J = 7.8, 4.8, 1.2 Hz, 1H), 4.09 (qd, J = 7.0, 3.7 Hz, 1H), 3.96−3.87 (m, 1H), 3.83−3.68 (m, 2H), 3.50−3.39 (m, 1H), 2.13−1.96 (m, 1H), 1.95−1.86 (m, 2H), 1.68−1.58 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 150.0, 148.3, 137.4, 126.2, 122.3, 77.9, 68.4, 43.3, 28.9, 26.0; HRMS (ESI) calcd for $C_{11}H_{14}N_2O_2$ $[M + H]^+$ m/z 207.1134, found m/z 207.1130.

***N*-Benzylfuran-3-carboxamide (33).** Brown crystals (79 mg, 79%); mp 117−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.41−7.36 (m, 1H), 7.35−7.23 (m, 5H), 6.64 (s, 1H), 6.59 (brs, 1H), 4.55−4.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 145.0, 143.8, 138.3, 128.8, 127.9, 127.6, 122.5, 108.5, 43.6; HRMS (ESI) calcd for $C_{12}H_{11}NO_2$ $[M + H]^+$ m/z 202.0868, found m/z 202.0872.

(4-Chlorophenyl)(4-(2,3-dichlorophenyl)piperazin-1-yl)-methanone (34). White solid (136 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.36 (m, 4H), 7.22−7.13 (m, 2H), 6.93 (dd, J = 7.7, 1.8 Hz, 1H), 3.94 (s, 2H), 3.60 (s, 2H), 3.17−2.92 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 150.6, 136.1, 134.4, 134.1, 129.0, 128.8, 127.9, 127.7, 125.5, 118.9, 51.8, 51.4, 48.2, 42.6; HRMS (ESI) calcd for $C_{17}H_{15}Cl_3N_2O$ $[M + H]^+$ m/z 369.0328, found m/z 369.0329.

(4-Methylpiperidin-1-yl)(4-vinylphenyl)methanone (35). Yellow oil (89 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 6.75−6.65 (m, 1H), 5.77 (dd, J = 17.6, 0.7 Hz, 1H), 5.29 (dd, J = 10.9, 0.7 Hz, 1H), 4.65 (s, 1H), 3.73 (s, 1H), 3.05−2.68 (m, 2H), 1.78−1.54 (m, 3H), 1.27−1.06 (m, 2H), 0.96 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 138.7, 136.2, 135.8, 127.3, 126.2, 115.1, 48.1, 42.6, 34.8, 33.9, 31.3, 21.8; HRMS (ESI) calcd for $C_{15}H_{19}NO$ $[M + H]^+$ m/z 230.1545, found m/z 230.1541.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra and chromatograms. 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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