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Synthesis of Benzyl Hydrazine Derivatives *via* Amination of Benzylic C (sp^3)–H Bonds with Dialkyl Azodicarboxylates

A. Samzadeh-Kermani

A novel synthesis of benzyl hydrazines through oxidative amination of benzylic C–H bonds has been developed. The resulting aminated products are accessed directly from the reaction of alkylarenes with dialkyl/diphenyl azodicarboxylates using Cu_2O/Phen as catalytic system. The protocol proceeded smoothly and a decent range of *N*-sustituted hydrazides were synthesized in acceptable to good yields. Both primary and secondary sp^3 C–H sources afford only monoamination products.

Introduction

C–H functionalization is noted as an efficient and highly atome conomic method for the formation of various chemical compounds.[1-3] In recent years, transition-metal and organo-catalyst catalyzed C–H amination has made considerable achievements. Particularly, selective amination of sp^3 C–H bonds of alkyl benzenes has attracted much attention due to the high prevalence of C–N bonds in pharmaceuticals, agrochemicals, polymers, etc.[4]

Benzylic amines are important substructures in biologically active compounds[5] and the synthesis of such structures is typically achieved through functional group interconversion processes. As such, catalytic methods for selective amination of benzylic C–H bonds would provide a strategic means to utilize this resource. In this context, transition-metal-catalyzed nitrene insertions into C-H bonds serve as direct and impactful procedure for the synthesis of benzylic amine skeletons.[6-8] Powell reported on the copper-catalyzed amination of benzylic C-H Bonds with sulfonamides resulting in the *N*-benzylated sulfonamide products.[9] Emmert has also utilized *N*-acetoxybenzenesulfonamides as amination reagents for direct amination of benzylic C-H bond.[10] Copper-catalyzed amidation of benzylic hydrocarbons provides an efficient route to produce *N*-benzyl amide derivatives.[11] Amination of benzylic C-H bond with imidazole has been reported *via* iron-catalyzed oxidative activation of benzylic C-H Bonds.[12] Zhu and co-workers have developed an organo-catalytic route for amination of benzylic C–H bonds.[13] Bolm developed a versatile route to *N*-benzylated sulfoximines through the iron-catalyzed cross-dehydrogenative coupling of sulfoximines with diarylmethanes.[14] Muller has developed an outstanding stereoselective amination of benzylic C-H with sulfonimidamides catalytic in chiral rhodium (II) complex.[15] Intramolecular allylic and benzylic C-H amination has also been developed.[16-18] Pandey reported a benzylic C(sp^3)–H amination *via* visible-light-photoredox catalysis.[19] DeBoef and co-workers have disclosed an interesting chemo-selective amination of aromatic C-H bond over benzylic C-H ones.[20] Catalytic sp^3 C–H amination are also very well recapitulated in recent reviews.[21-22]

The alkyl hydrazine scaffold is a common motif in medicinal chemistry and pharmaceuticals.[23-24] Despite alkyl hydrazines structural simplicity they are generally difficult to access. Direct synthesis from unprotected hydrazine is known to be difficult and low yielding, generally giving rise to complex mixtures of products.[25-26] Dialkyl azodicarboxylates (DAAD) have been broadly employed as the amination partner for the synthesis of *N*-aryl hydrazides.[27-30] Inspired by previous reports, we herein report a general and direct method for the synthesis of benzyl/phenyl hydrazine derivatives through benzylic C-H amination with azodicarboxylates using Cu_2O/Phen as catalytic system.

Results and Discussion

To begin our study, we chose toluene **(1a)** and diisopropyl azodicarboxylate (**2a**) as model substrates (Table 1). We initially examined di-*tert*-butyl peroxide (DTBP) as an oxidant without any catalyst. While in the absence of a catalyst none of the targeted diisopropyl 1-benzylhydrazine-1,2-dicarboxylate (**3a**) was detected (entry 1), the use of $FeCl_2$ led to a promising 23% yield (entry 2). When the reaction was performed with $FeCl_2.4H_2O$ instead of $FeCl_2$, the yield dropped to 11% (entry 3). Subsequent screening of catalyst source revealed that Cu_2O represented the optimum source of catalyst for the reaction (entries 4–11). Although, CuCl and $[MeCN]_4Cu(I)PF_6$ showed also a decent catalytic efficiency (entries 12 and 13). Commencing from previous works, the effect of ligand on reaction outcome was also examined (entries 14-18). Among the ligands examined, only 1,10-Phenantroline (phen) improved the yield of the desired product (entry 14). While the exact function of

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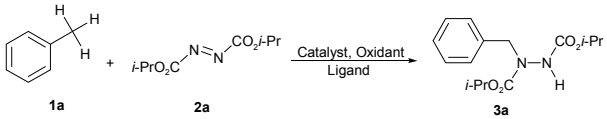
ligand is unclear, we found that the presence of ligand suppresses the formation of compound **4** (see scheme 1a). Moreover, phen is known ligand for copper-catalyzed C-N bond formation[27] and it capable of bidentate coordination to copper salts, as such a working hypothesis is that it increases the solubility of copper salts in such non-polar media. Attempts to use alternative oxidants such as *tert*-butyl hydroperoxide (TBHP), dioxygen, $PhI(OAc)_2$, and $(NH_4)_2S_2O_8$ were unsatisfactory (Table 1, entries 19–22). However, reaction conducted with benzoyl peroxide (BPO) as the oxidant source formed the desired product in moderated yield (entry 23). Note that the reaction conducted with 1.5 equiv of DTBP, formed the desired product in 84% yield (entry 24). The study also indicates that the presence of H_2O inhibits the reaction (entry 25) which also is in favor of proposed reaction pathway (Scheme 2). The yield remained almost unchanged by reducing the amount of catalyst to 0.10 mmol (entry 26) however, the reaction proceeded poorly as the amount of catalyst reduced further (not shown in Table 1). Unfortunately, reducing the amount of the toluene resulted in diminished yields (entry 27).

Table 1. Optimization of the reaction conditions[a]



1a 2a 3a

Entry	Catalyst	Oxidant	Ligand	Yield (%)
1	-	DTBP	-	-
2	$FeCl_2$	DTBP	-	23
3	$FeCl_2.4H_2O$	DTBP	-	traces
4	$FeCl_3$	DTBP	-	19
5	$Fe(acac)_3$	DTBP	-	traces
6	CuBr	DTBP	-	37
7	CuI	DTBP	-	31
8	$Cu(OAc)_2$	DTBP	-	37
9	CuO	DTBP	-	23
10	Cu_2O	DTBP	-	63
11	Cu	DTBP	-	22
12	CuCl	DTBP	-	46
13	$[MeCN]_4CuPF_6$	DTBP	-	53
14	Cu_2O	DTBP	Phen	89
15	Cu_2O	DTBP	Bipyr	59
16	Cu_2O	DTBP	L1	46
17	Cu_2O	DTBP	L2	39
18	Cu_2O	DTBP	DMAP	50
19	Cu_2O	TBHP	Phen	26
20	Cu_2O	O_2	Phen	-
21	Cu_2O	$PhI(OAc)_2$	Phen	traces
22	Cu_2O	$(NH_4)_2S_2O_8$	Phen	traces
23	Cu_2O	BPO	Phen	59
24	Cu_2O	DTBP	Phen	84[b]
25	Cu_2O	DTBP	Phen	traces[b,c]
26	Cu_2O	DTBP	Phen	81[b,d]
27	Cu_2O	DTBP	Phen	61[e]

[a] Reaction conditions: **1a** (2.0 mL), **2a** (1.0 mmol), catalyst (0.15 mmol), ligand (0.10 mmol), oxidant (2.0 mmol), 4 Å MS (300 mg), 110 °C for 28 h, in a sealed tube under an argon atmosphere. [b] 1.5 mmol of DTBP was used. [c] 1 mL of H_2O was used. [d] 0.10 mmol of Cu_2O and 0.06 mmol of Phen were used. [e] 1.0 mL of **1a** was used. Phen = 1,10-Phenantroline, Bipyr = bipyridine, L1 = 1,3-diphenylpropanedione, L2 = 1,3-indanedione, DMAP = 4-dimethylamino pyridine.

Under the optimized conditions, the oxidative amination of a variety of benzylic hydrocarbons was investigated (Table 2). *p*-, *m*-, And *o*-xylenes were tolerated (**1b**–**1d**). *p*- And *m*- xylenes afforded the corresponding aminated products in good yields however, *o*-xylene gave a lower yield probably due to the steric hindrance of the product (entries 2-4). The amination reactions of xylene derivatives with **2a** only yielded monoaminated products. Further study on the reaction of xylene derivatives indicated that the presence of ligand inhibited the formation of the double amination byproduct and simultaneously increasing the product yield (please see SI section). To our delight, mesitylene could couple with **2a** to give an excellent yield of the desired product **3e** (entry 5). Halogen-containing alkyl benzenes were also examined. The results showed that halogens could be well tolerated in this amination reaction (**3f**–**3h**), providing a great opportunity for subsequent cross-coupling reactions (entries 6-8)**.** Toluene with methylthio motif afforded the product **3i** in moderate yield (entry 9). Toluene containing phenyl or methoxycarbonyl moieties **3j** and **3k** could react, and the corresponding products were obtained in moderate yields (entries 10-11). It could be deduced that the reaction does not proceed *via* methylenyl cation intermediate. 1-Methoxy-4-methylbenzene (**1l**) also afforded a good yield (entry 12). Direct *N*-alkylation of **2a** with secondary benzylic hydrocarbons like ethylbenzene (**1m**) and propylbenzene (**1n**) were also successful, but the yields were comparatively lower (entries 13 and 14). The yield of a tertiary benzylic hydrocarbon was at a trace level (detected by GC analysis, not shown in Table 2). Ungratefully, cyclohexane did not work as a reaction partner with **2a** and no product arising from the amination of sp^3 C–H bond of cyclohexane is detected by GC analysis of the crude reaction mixture (not shown in Table 2). We were pleased to note that diphenylmethane (**1o**) oxidatively aminated to afford product **3o** in moderate yield (entry 15). The selectivity of primary and secondary benzylic substrate was also examined using 4-ethyltoluene (**1p**) (entry 16).[31] Other dialkyl azodicarboxylates **2b**-**2d** were also examined as the amination source and the corresponding *N*-benzylated products were achieved in good yields (entries 17-22). Diphenyl azodicarboxylates (**2e**) was also tolerated (entry 23). The reaction conducted with dibenzyl azodicarboxylate (**2f**) formed a complex reaction mixture (entry 24). Additionally, our optimized reaction conditions were not suitable for amination of sp^3 C–H of heteroaromatic substrates and the presence of –OH, CH_3COO-, CH_3CO-, HCO-, $-NH_2$, $-NO_2$, or -CN moiety on aromatic ring was not compatible with this amination reaction.

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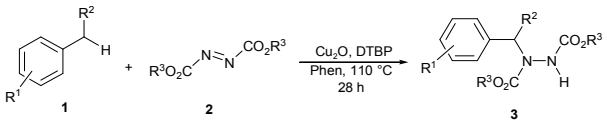
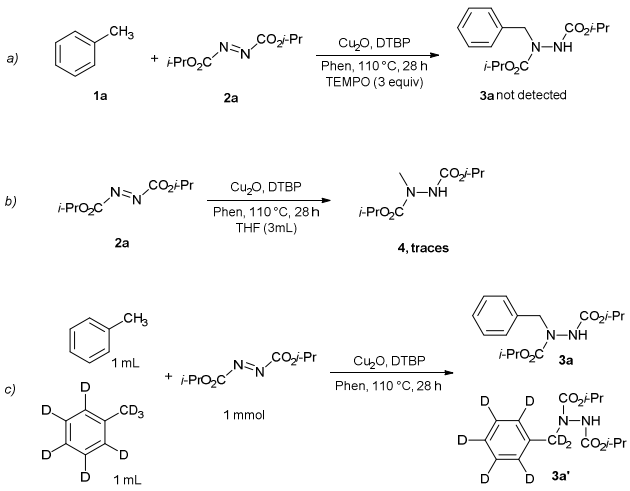
Table 2. Amination of sp3 C-H with **2**



Entry	1	R^1	R^2	2	R^3	Yield (%)
1	**a**	H	H	**a**	*i*-Pr	**3a**, 81
2	**b**	4-Me	H	**a**	*i*-Pr	**3b**, 85
3	**c**	3-Me	H	**a**	*i*-Pr	**3c**, 83
4	**d**	2-Me	H	**a**	*i*-Pr	**3d**, 53
5	**e**	3,5-dimethyl	H	**a**	*i*-Pr	**3e**, 89
6	**f**	4-Br	H	**a**	*i*-Pr	**3f**, 75
7	**g**	3-Cl	H	**a**	*i*-Pr	**3g**, 70
8	**h**	4-I	H	**a**	*i*-Pr	**3h**, 74
9	**i**	4-MeS	H	**a**	*i*-Pr	**3i**, 48
10	**j**	2-Ph	H	**a**	*i*-Pr	**3j**, 65
11	**k**	4-MeOCO	H	**a**	*i*-Pr	**3k**, 52
12	**l**	4-MeO	H	**a**	*i*-Pr	**3l**, 92
13	**m**	H	Me	**a**	*i*-Pr	**3m**, 64
14	**n**	H	Et	**a**	*i*-Pr	**3n**, 62
15	**o**	H	Ph	**a**	*i*-Pr	**3o**, 55
16	**p**	4-Et	H	**a**	*i*-Pr	**3p**, 51
						3p′ , 27
17	**a**	H	H	**b**	Et	**3q**, 82
18	**b**	4-Me	H	**b**	Et	**3r**, 83
19	**e**	3,5-dimethyl	H	**b**	Et	**3s**, 91
20	**l**	4-MeO	H	**b**	Et	**3t**, 89
21	**a**	H	H	**c**	Cy	**3u**, 84
22	**a**	H	H	**d**	*t*-Bu	**3v**, 76
23	**a**	H	H	**e**	Ph	**3w**, 90
24	**a**	H	H	**f**	Bn	complicated

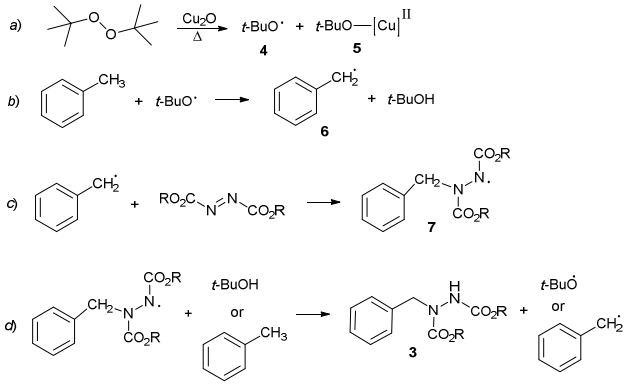
[a] Reaction conditions: **1** (2.0 mL), **2** (1.0 mmol), Cu_2O (0.10 mmol), Phen (0.06 mmol), DTBP (1.5 mmol), 4 Å MS (300 mg), 110 °C for 28 h, in a sealed tube under an argon atmosphere.

To investigate the details of the mechanism for this reaction, we performed some additional experiments. Adding the radical scavenger such as 2,2,6,6-tetramethylpiperidinoxyl (TEMPO) into the reaction mixture completely suppressed the formation of the desired product which implied a radical process was involved in this benzylic C-H amination (Scheme *1a*). In the absence of toluene, a traces amount of **4** was obtained which can indicate that hydrazide radical is formed during the reaction progress (*Scheme 1b*). In addition, an intermolecular competing kinetic isotope effect (KIE) experiment was performed and it was observed with the k_H/k_D = 4.6 (*Scheme 1c*). This experiment indicates that the hydrogen abstraction of the sp^3 C–H bond should be involved in reaction pathway.



Scheme 1. Investigation into the reaction pathway

Based on our experimental results and previous reports,[32-34] possible mechanism is depicted in Scheme 2. Firstly, DTBP decomposes to the *tert*-butoxyl radical and species **5** in the presence of Cu_2O. Next, hydrogen is abstracted from the C-H bond of methyl in toluene, giving the benzyl radical **6**.[33] Then addition of radical species of **6** to the nitrogen–nitrogen double bond of azodicarboxylate generates the radical intermediate **7**.[30] Finally, the intermediate **7** is converted to the desired product **3** by the action of *t*-BuOH or toluene. The latter is supported by the fact that the reaction conducted with 1.5 equiv of DTBP also formed the desired product in good yield (Table 1, entry 24). Unfortunately, the exact role of copper salts and how do it catalyze this transformation is still unclear, but it should be noted that the reaction did not work well in absence of a catalyst source.



Scheme 2. Plausible mechanism for the formation of *N*-benzyl hydrazide derivatives

Experimental

All reagents, catalysts, and solvents were obtained from commercial sources (Aldrich, Acros, Merck, Fluka). Solvents were dried over molecular sieves 3Å or 4Å before the use. Molecular sieves were activated in vacuum oven at 180 ˚C for 12 h and stored

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under vacuum at 100 °C in the presence of P_4O_{10}. The copper catalysts were typically weighted into smaller vials containing about 500 mg of reagent in a glovebox and sealed. The smaller containers were transferred outside the glovebox, stored in a desiccator while being utilized and kept for no more than 2 weeks outside the glovebox. *tert*-Butyl hydroperoxide (TBHP), di-*tert*-butyl peroxide (DTBP), and benzoyl peroxide (BPO) were stored refrigerated. All reactions were carried out in Schlenk tube (25 mL) using oven-dried and/or flame dried glassware under a pure and dry argon atmosphere. Mp: Electrothermal-9100 apparatus. IR Spectra: Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra: Bruker DRX-500 AVANCE instrument; in $CDCl_3$ at 500.1 and 125.7MHz, resp; δ in ppm, J in Hz. EI-MS (70 eV): Finnigan-MAT-8430 mass spectrometer, in m/z. Elemental analyses (C, H, N) were performed with a Heraeus CHN-O-Rapid analyzer. The results agreed favourably with the calculated values Column chromatography was performed using Silica gel 60 (particle size 63-200 µm) (Merck, item number 7734-3). The reactions were monitored by thin layer chromatography (Silica gel 60, Merck, item number 116835) using UV light (254 nm) to visualize the course of the reactions.

General procedure for synthesis of compound 3. An oven-dried Schlenk tube (25 mL) equipped with a magnetic stir bar was charged with dialkyl azodicarboxylate (1.0 mmol), Cu_2O powder (0.10 mmol, 14 mg), phen (0.06 mmol, 11 mg), and 4 Å MS (300 mg). The tube was evacuated and backfilled with argon (three times). DTBP (1.5 mmol) and the benzylic hydrocarbon (2.0 mL) were added by syringe. The mixture was stirred for appropriate times (see Table 2) at 110 ˚C. After cooling to room temperature, the mixture was diluted with EtOAc, filtered, and concentrated under reduced pressure. The residue was purified with column chromatography on silica gel (eluent gradient of EtOAc/hexane, 1:8 to 1:4) to give the corresponding products **3** in the yields listed in Tables **2**, **3**.

Conclusion

In summary, we have developed a novel Cu_2O promoted approach for the synthesis of *N*-Alkyl hydrazides using readily available starting materials through the benzylic C-H functionalization with dialkyl azodicarboxylates. The effects of electronic and steric variations of substrates on reaction outcome have been examined. The inexpensive and readily available catalyst-ligand-oxidant system is of practical interest for *N*-alkylation of azodicarboxylates. The reaction is completely selective for monoamination and no compounds arising from diamination of xylene derivatives are detected by crude GC-MS analysis.

Acknowledgements

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Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

Diisopropyl 1-benzylhydrazine-1,2-dicarboxylate (3a)
Colorless solid, mp: 95-96.5 ˚C; yield: 0.24 g (81%). IR (KBr) (ν_{max}, cm^{-1}): 3292, 3035, 2927, 1618, 1555, 1322, 1140. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.20 (6 H, d, ^3J = 5.8 Hz, 2 Me), 1.26 (6 H, d, ^3J = 6.1 Hz, 2 Me), 4.44 (2 H, br s, CH_2), 5.02-5.06 (2 H, m, 2 CHO), 6.71 (1 H, br s, NH), 7.15 (1 H, t, ^3J = 6.8 Hz, CH), 7.23 (2 H, d, ^3J = 6.4 Hz, 2 CH), 7.29 (2 H, d, ^3J = 6.4 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 21.4 (2 Me), 21.5 (2 Me), 58.2 (CH_2), 70.1 (CHO), 71.1 (CHO), 127.0 (2 CH), 127.8 (CH), 129.4 (2 CH), 136.4 (C), 154.6 (C=O), 156.3 (C=O). MS: *m/z* (%) = 294 (M^+, 1), 235 (51), 207 (35), 120 (24), 103 (89), 91 (100), 87 (76). Anal. Calcd for $C_{15}H_{22}N_2O_4$ (294.35): C, 61.21; H, 7.53; N, 9.52%. Found: C, 61.41; H, 7.68; N, 9.63%.

Diisopropyl 1-(4-methylbenzyl)hydrazine-1,2-dicarboxylate (3b)
Colorless solid, mp: 110-112 ˚C; yield: 0.26 g (85%). IR (KBr) (ν_{max}, cm^{-1}): 3308, 3066, 2923, 1633, 15391, 1311, 1291, 1083. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.21 (6 H, d, ^3J = 6.0 Hz, 2 Me), 1.23 (6 H, d, ^3J = 6.4 Hz, 2 Me), 2.27 (3 H, s, Me), 4.47 (2 H, br s, CH_2), 4.98-5.06 (2 H, m, 2 CHO), 6.82 (1 H, br s, NH), 7.16 (2 H, d, ^3J = 6.8 Hz, 2 CH), 7.21 (2 H, d, ^3J = 6.8 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 21.9 (2 Me), 22.1 (2 Me), 24.2 (Me), 57.6 (CH_2), 69.7 (CHO), 70.5 (CHO), 127.2 (2 CH), 129.1 (2 CH), 135.2 (C), 138.2 (C), 154.5 (C=O), 156.1 (C=O). MS: *m/z* (%) = 308 (M+, 7), 249 (52), 221 (24), 134 (28), 133 (78), 105 (100), 103 (88), 87 (53). Anal. Calcd for $C_{16}H_{24}N_2O_4$ (308.38): C, 62.32; H, 7.84; N, 9.08%. Found: C, 62.49; H, 7.95; N, 9.27%.

Diisopropyl 1-(3-methylbenzyl)hydrazine-1,2-dicarboxylate (3c): Colorless solid, mp: 101-103 °C; yield: 0.26 g (83%). IR (KBr) (ν_{max}, cm^{-1}): 3271, 3074, 2934, 1635, 1550, 1318, 1110. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.20 (6 H, d, ^3J = 6.7 Hz, 2 Me), 1.23 (6 H, d, ^3J = 6.2 Hz, 2 Me), 2.34 (3 H, s, Me), 4.59 (2 H, br s, CH_2), 4.91-4.98 (2 H, m, 2 CHO), 6.85 (1 H, br s, NH), 7.06 (1 H, d, ^3J = 6.6 Hz, CH), 7.25-7.33 (3 H, m, 3 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 21.5 (2 Me), 21.7 (2 Me), 24.7 (Me), 58.1 (CH_2), 70.1 (CHO), 70.7 (CHO), 124.6 (CH), 126.2 (CH), 130.3 (CH), 130.5 (CH), 137.8 (C), 139.6 (C), 156.0 (C=O), 156.2 (C=O). MS: *m/z* (%) = 308 (M^+, 2), 249 (34), 221 (28), 163 (45), 149 (48), 135 (79), 105 (100), 103 (89), 87 (66). Anal. Calcd for $C_{16}H_{24}N_2O_4$ (308.38): C, 62.32; H, 7.84; N, 9.08%. Found: C, 62.43; H, 7.98; N, 9.20%.

Diisopropyl 1-(2-methylbenzyl)hydrazine-1,2-dicarboxylate (3d): Colorless solid, mp: 90-92 °C; yield: 0.16 g (53%). IR (KBr) (ν_{max}, cm^{-1}): 3256, 3036, 2983, 1691, 1527, 1382, 1257, 1109. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.19 (6 H, d, ^3J = 6.2 Hz, 2 Me), 1.25 (6 H, d, ^3J = 6.0 Hz, 2 Me), 2.36 (3 H, s, Me), 4.60 (2 H, br s, CH_2), 4.96-5.02 (2 H, m, 2 CHO), 6.71 (1 H, br s, NH), 7.19 (1 H, t, ^3J = 6.6 Hz, CH), 7.29-7.32 (2 H, m, 2 CH), 7.34 (1 H, d, ^3J = 6.1 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 21.0 (2 Me), 21.1 (2 Me), 31.4 (Me), 55.3 (CH_2), 69.1 (CHO), 69.5 (CHO), 126.5 (CH), 127.1 (CH), 127.4 (CH), 129.7 (CH), 136.4 (C), 142.0 (C), 154.7 (C=O), 156.3 (C=O). MS: *m/z* (%) = 308 (M^+, 3), 249 (23), 221 (36), 148 (52), 135 (68), 105 (100), 103 (90), 87 (79). Anal. Calcd for $C_{16}H_{24}N_2O_4$ (308.38): C, 62.32; H, 7.84; N, 9.08%. Found: C, 62.50; H, 7.94; N, 9.16%.

Diisopropyl 1-(3,5-dimethylbenzyl)hydrazine-1,2-dicarboxylate (3e): Colorless solid, mp: 133-135 °C; yield: 0.29 g (89%). IR (KBr) (ν_{max}, cm^{-1}): 3286, 3008, 2983, 1669, 1519, 1316, 1249, 1107. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.20 (6 H, d, ^3J = 6.1 Hz, 2 Me), 1.23 (6 H, d, ^3J = 5.8 Hz, 2 Me), 2.33 (6 H, s, 2 Me), 4.49 (2 H, br s, CH_2), 4.94-4.99 (2 H, m, 2 CHO), 6.62 (1 H, br s, NH), 7.13 (2 H, s, 2 CH), 7.28 (1 H, s, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 21.9 (2 Me), 22.0 (2 Me), 24.7 (2 Me), 56.4 (CH_2), 69.1 (CHO), 69.7 (CHO), 125.6 (2 CH), 130.0 (CH), 139.2 (2 C), 139.8 (C), 154.3 (C=O), 155.2 (C=O). MS: *m/z* (%) = 322 (M^+, 11), 263 (23), 235 (31), 183 (16), 149 (51), 147 (27), 162 (68), 119 (100), 103 (81), 87 (73). Anal.Calcd for $C_{17}H_{26}N_2O_4$ (322.41): C, 63.33; H, 8.13; N, 8.69%. Found: C, 63.50; H, 8.29; N, 8.88%.

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Diisopropyl 1-(4-bromobenzyl)hydrazine-1,2-dicarboxylate (3f): Colorless solid, mp: 137-139 °C; yield: 0.28 g (75%). IR (KBr) (ν_{max}, cm^{-1}): 3284, 3034, 2925, 1639, 1524, 1383, 1261, 1108, 596. ^1H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.22 (6 H, d, ^3J = 6.1 Hz, 2 Me), 1.24 (6 H, d, ^3J = 6.0 Hz, 2 Me), 4.68 (2 H, br s, CH_2), 4.96-5.05 (2 H, m, 2 CHO), 6.81 (1 H, br s, NH), 7.28 (2 H, d, ^3J = 6.7 Hz, 2 CH), 7.62 (2 H, d, ^3J = 6.7 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 20.7 (2 Me), 21.8 (2 Me), 56.3 (CH_2), 69.1 (CHO), 70.0 (CHO), 119.1 (C), 128.9 (2 CH), 131.2 (2 CH), 137.8 (C), 155.3 (C=O), 156.0 (C=O). MS: *m/z* (%) = 372 (M^+, 3), 374 (M^++2, 3), 313 (29), 285 (19), 212 (43), 199 (67), 169 (100), 103 (82), 87 (76). Anal.Calcd for $C_{15}H_{21}BrN_2O_4$ (373.25): C, 48.27; H, 5.67; N, 7.51; Br, 21.41%. Found: C, 48.44; H, 5.85; N, 7.78; Br, 21.45%.

Diisopropyl 1-(3-chlorobenzyl)hydrazine-1,2-dicarboxylate (3g): Colorless solid, mp: 106-108 °C; yield: 0.23 g (70%). IR (KBr) (ν_{max}, cm^{-1}): 3291, 3063, 2983, 1634, 1514, 1380, 1249, 1106, 727. ^1H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.23 (6 H, d, ^3J = 6.1 Hz, 2 Me), 1.25 (6 H, d, ^3J = 5.7 Hz, 2 Me), 4.74 (2 H, br s, CH_2), 4.95-5.06 (2 H, m, 2 CHO), 6.76 (1 H, br s, NH), 7.12-7.21 (2 H, m, 2 CH), 7.24-7.34 (2 H, m, 2 CH), 7.54 (1 H, s, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 22.1 (2 Me), 22.3 (2 Me), 59.2 (CH_2), 69.1 (CHO), 70.5 (CHO), 123.1 (CH), 125.5 (CH), 127.3 (CH), 132.1 (CH), 135.7 (C), 142.1 (C), 154.2 (C=O), 156.0 (C=O). MS: *m/z* (%) = 328 (M^+, 8), 269 (23), 241 (37), 183 (16), 167 (68), 155 (45), 125 (100), 103 (91), 87 (84). Anal.Calcd for $C_{15}H_{21}ClN_2O_4$ (328.79): C, 54.80; H, 6.44; N, 8.52; Cl, 10.78%. Found: C, 54.97; H, 6.65; N, 8.58; Cl, 10.86%.

Diisopropyl 1-(4-iodobenzyl)hydrazine-1,2-dicarboxylate (3h): Colorless solid, mp: 144-146 °C; yield: 0.31 g (74%). IR (KBr) (ν_{max}, cm^{-1}): 3286, 3041, 2926, 1639, 1564, 1414, 1285, 1079, 539. ^1H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.19 (6 H, d, ^3J = 5.7 Hz, 2 Me), 1.23 (6 H, d, ^3J = 6.2 Hz, 2 Me), 4.53 (2 H, br s, CH_2), 5.04-5.10 (2 H, m, 2 CHO), 6.91 (1 H, br s, NH), 7.49 (1 H, d, ^3J = 6.8 Hz, CH), 7.72 (1 H, d, ^3J = 6.8 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 21.1 (2 Me), 21.3 (2 Me), 59.1 (CH_2), 70.2 (CHO), 71.1 (CHO), 98.0 (C), 130.1 (2 CH), 136.2 (C), 138.3 (2 CH), 154.2 (C=O), 156.1 (C=O). MS: *m/z* (%) = 420 (M^+, 1), 361 (21), 333 (17), 318 (35), 259 (78), 217 (100), 103 (85), 87 (74). Anal.Calcd for $C_{15}H_{21}IN_2O_4$ (420.25): C, 42.87; H, 5.04; N, 6.67; I, 30.20%. Found: C, 43.03; H, 5.21; N, 6.82; I, 30.27%.

Diisopropyl 1-(4-(methylthio)benzyl)hydrazine-1,2-dicarboxylate (3i): Colorless solid, mp: 111-113 °C; yield: 0.16 g (48%). IR (KBr) (ν_{max}, cm^{-1}): 3282, 3065, 2926, 1632, 1511, 1380, 1258, 1107, 973. ^1H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.21 (6 H, d, ^3J = 5.7 Hz, 2 Me), 1.23 (6 H, d, ^3J = 5.8 Hz, 2 Me), 2.71 (3 H, s, Me), 4.59 (2 H, br s, CH_2), 4.93-4.99 (2 H, m, 2 CHO), 6.68 (1 H, br s, NH), 7.23 (2 H, d, ^3J = 6.9 Hz, 2 CH), 7.34 (2 H, d, ^3J = 6.9 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 15.2 (Me), 21.0 (2 Me), 22.4 (2 Me), 56.2 (CH_2), 70.1 (CHO), 70.9 (CHO), 126.2 (2 CH), 129.0 (2 CH), 134.3 (C), 142.6 (C), 154.8 (C=O), 156.1 (C=O). MS: *m/z* (%) = 340 (M^+, 1), 297 (12), 280 (17), 239 (31), 180 (56), 152 (22), 138 (100), 123 (61), 91 (45). Anal.Calcd for $C_{16}H_{24}N_2O_4S$ (340.44): C, 56.45; H, 7.11; N, 8.23; S, 9.42%. Found: C, 56.63; H, 7.24; N, 8.42; Br, 9.52%.

Diisopropyl 1-([1,1'-biphenyl]-3-ylmethyl)hydrazine-1,2-dicarboxylate (3j): Colorless solid, mp: 135-137 °C; yield: 0.27 g (65%). IR (KBr) (ν_{max}, cm^{-1}): 3297, 3062, 2927, 1628, 1536, 1447, 1328, 1256, 1083, 846. ^1H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.21 (6 H, d, ^3J = 6.1 Hz, 2 Me), 1.25 (6 H, d, ^3J = 6.3 Hz, 2 Me), 4.69 (2 H, br s, CH_2), 5.01-5.09 (2 H, m, 2 CHO), 6.92 (1 H, br s, NH), 7.35-7.80 (8 H, m, 8 CH), 7.94 (1 H, s, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 22.1 (2 Me), 22.4 (2 Me), 60.1 (CH_2), 70.1 (CHO), 70.5 (CHO), 124.2 (CH), 126.6 (CH), 127.3 (CH), 128.1 (2 CH), 129.3 (2 CH), 130.1 (CH), 132.4 (CH), 141.2 (C), 142.8 (C), 143.5 (C), 155.7 (C=O), 156.4 (C=O). MS: *m/z* (%) = 370 (M^+, 3), 310 (18), 268 (21), 209 (47), 167 (64), 91 (38), 77 (100). Anal.Calcd for $C_{21}H_{26}N_2O_4$ (370.45): C, 68.09; H, 7.07; N, 7.56%. Found: C, 68.29; H, 7.25; N, 7.64%.

Diisopropyl 1-(4-(methoxycarbonyl)benzyl)hydrazine-1,2-dicarboxylate (3k): Colorless oil, yield: 0.18 g (52%). IR (KBr) (ν_{max}, cm^{-1}): 3279, 3040, 2982, 1731, 1690, 1519, 1462, 1384, 1245, 1111. ^1H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.21 (6 H, d, ^3J = 6.1 Hz, 2 Me), 1.23 (6 H, d, ^3J = 6.0 Hz, 2 Me), 3.79 (3 H, s, OMe), 4.81 (2 H, br s, CH_2), 4.97-5.04 (2 H, m, 2 CHO), 6.65 (1 H, br s, NH), 7.29 (2 H, d, ^3J = 6.6 Hz, 2 CH), 8.01 (2 H, d, ^3J = 6.6 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 21.9 (2 Me), 23.1 (2 Me), 53.6 (OMe), 59.1 (CH_2), 70.3 (CHO), 71.2 (CHO), 127.5 (2 CH), 129.7 (C), 131.2 (2 CH), 143.1 (C), 155.7 (C=O), 156.8 (C=O), 168.1 (C=O). MS: *m/z* (%) = 352 (M^+, 1), 293 (14), 265 (23), 251 (44), 191 (51), 135 (73), 103 (100), 87 (75). Anal.Calcd for $C_{17}H_{24}N_2O_6$ (352.39): C, 57.94; H, 6.87; N, 7.95%. Found: C, 58.11; H, 7.02; N, 8.06%.

Diisopropyl 1-(4-methoxybenzyl)hydrazine-1,2-dicarboxylate (3l): Colorless solid, mp: 120-122 °C; yield: 0.30 g (92%). IR (KBr) (ν_{max}, cm^{-1}): 3279, 3062, 2927, 1628, 1536, 1447, 1328, 1256, 1083. ^1H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.19 (6 H, d, ^3J = 5.9 Hz, 2 Me), 1.22 (6 H, d, ^3J = 6.1 Hz, 2 Me), 3.90 (3 H, s, OMe), 4.62 (2 H, br s, CH_2), 4.93-4.99 (2 H, m, 2 CHO), 6.65-6.90 (3 H, m, NH and 2 CH), 7.15 (2 H, d, ^3J = 6.8 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 22.1 (2 Me), 22.9 (2 Me), 56.1 (OMe), 57.6 (CH_2), 70.2 (CHO), 71.3 (CHO), 114.7 (2 CH), 127.9 (2 CH), 129.3 (C), 159.4 (C), 155.3 (C=O), 156.1 (C=O). MS: *m/z* (%) = 324 (M^+, 15), 265 (16), 237 (28), 163 (72), 121 (100), 103 (89), 87 (84). Anal.Calcd for $C_{16}H_{24}N_2O_5$ (324.38): C, 59.24; H, 7.46; N, 8.64%. Found: C, 59.41; H, 7.63; N, 8.79%.

Diisopropyl 1-(1-phenylethyl)hydrazine-1,2-dicarboxylate (3m): Colorless solid, mp: 81-83 °C; yield: 0.20 g (64%). IR (KBr) (ν_{max}, cm^{-1}): 3273, 3051, 2984, 1639, 1511, 1382, 1250, 1104. ^1H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.20 (6 H, d, ^3J = 6.2 Hz, 2 Me), 1.25 (6 H, d, ^3J = 6.4 Hz, 2 Me), 1.62 (3 H, d, ^3J = 5.8 Hz, Me), 4.90-4.98 (2 H, m, 2 CHO), 5.11 (1 H, q, ^3J = 5.8 Hz, 2 Me), 6.73 (1 H, br s, NH), 7.26-7.35 (5 H, m, 5 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 17.2 (Me), 22.1 (2 Me), 22.5 (2 Me), 64.2 (CH), 70.3 (CHO), 71.1 (CHO), 126.1 (CH), 126.3 (2 CH), 128.6 (2 CH), 142.4 (C), 154.6 (C=O), 156.1 (C=O). MS: *m/z* (%) = 308 (M^+, 6), 249 (18), 221 (25), 147 (56), 105 (91), 103 (82), 87 (67), 77 (100). Anal. Calcd for $C_{16}H_{24}N_2O_4$ (308.38): C, 62.32; H, 7.84; N, 9.08%. Found: C, 62.48; H, 7.97; N, 9.220%.

Diisopropyl 1-(1-phenylpropyl)hydrazine-1,2-dicarboxylate (3n): Colorless solid, mp: 83-85 °C; yield: 0.20 g (62%). IR (KBr) (ν_{max}, cm^{-1}): 3284, 3041, 2985, 1639, 1514, 1458, 1380, 1254, 1107. ^1H NMR (500.1 MHz, $CDCl_3$): δ_H = 0.89 (3 H, t, ^3J = 5.7 Hz, Me), 1.20 (6 H, d, ^3J = 6.1 Hz, 2 Me), 1.26 (6 H, d, ^3J = 6.3 Hz, 2 Me), 1.97-2.08 (2 H, m, CH_2), 4.76-4.84 (1 H, m, CH), 5.01-5.09 (2 H, m, 2 CHO), 6.60 (1 H, br s, NH), 7.20-7.35 (5 H, m, 5 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 11.1 (Me), 21.6 (2 Me), 21.8 (2 Me), 31.8 (CH_2), 70.1 (CHO), 70.6 (CHO), 79.2 (CH), 126.7 (CH), 127.3 (2 CH), 129.8 (2 CH), 141.9 (C), 154.2 (C=O), 156.1 (C=O). MS: *m/z* (%) = 322 (M^+, 5), 293 (11), 262 (20), 221 (38), 161 (48), 119 (78), 103 (78), 87 (76), 77(100). Anal. Calcd for $C_{17}H_{26}N_2O_4$ (322.41): C, 63.33; H, 8.13; N, 8.69%. Found: C, 63.56; H, 8.31; N, 8.82%.

Diisopropyl 1-benzhydrylhydrazine-1,2-dicarboxylate (3o): Colorless solid, mp: 161-163 °C; yield: 0.20 g (55%). IR (KBr) (ν_{max}, cm^{-1}): 3279, 3055, 2984, 1637, 1508, 1462, 1382, 1249, 1181, 1103. ^1H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.23 (6 H, d, ^3J = 6.1 Hz, 2 Me), 1.25 (6 H, d, ^3J = 6.0 Hz, 2 Me), 4.95-5.02 (2 H, m, 2 CHO), 6.32 (1 H, s, CH), 6.87 (1 H, br s, NH), 7.20-7.61 (10 H, m, 10 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 21.8 (2 Me), 22.0 (2 Me), 69.7 (CHO), 70.5 (CHO), 72.1 (CH), 125.5 (CH), 125.7 (CH), 126.0 (2 CH), 126.3 (2 CH), 128.7 (2 CH), 128.8 (2 CH), 143.1 (C), 143.2 (C), 154.9 (C=O), 156.1 (C=O). MS: *m/z* (%) = 370 (M^+, 1), 311 (15), 283 (30), 269 (45), 209 (608), 167 (100), 103 (87), 91 (67), 77 (86). Anal. Calcd for $C_{21}H_{26}N_2O_4$ (370.45): C, 68.09; H, 7.07; N, 7.56%. Found: C, 68.28; H, 7.25; N, 7.69%.

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Diisopropyl 1-(4-ethylbenzyl)hydrazine-1,2-dicarboxylate (3p): Colorless solid, mp: 113-115 °C; yield: 0.16 g (51%). IR (KBr) (ν_{max}, cm^{-1}): 3384, 3065, 2933, 1666, 1549, 1451, 1376, 1253, 1166, 1089, 1027. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 0.98 (3 H, t, ^3J = 5.6 Hz, Me), 1.21 (6 H, d, ^3J = 6.1 Hz, 2 Me), 1.23 (6 H, d, ^3J = 6.0 Hz, 2 Me), 2.95 (2 H, q, ^3J = 5.8 Hz, CH_2), 4.67 (2 H, br s, CH_2), 4.96-5.04 (2 H, m, 2 CHO), 6.74 (1 H, br s, NH), 7.15 (2 H, d, ^3J = 6.9 Hz, 2 CH), 7.27 (2 H, d, ^3J = 6.9 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 17.2 (Me), 21.1 (2 Me), 21.5 (2 Me), 37.3 (CH_2), 57.1 (CH_2), 69.1 (CHO), 70.8 (CHO), 128.1 (2 CH), 129.7 (2 CH), 135.0 (C), 140.3 (C), 154.8 (C=O), 156.3 (C=O). MS: *m/z* (%) = 322 (M^+, 11), 263 (21), 235 (23), 221 (46), 161 (67), 119 (100), 103 (87), 87 (66). Anal. Calcd for $C_{17}H_{26}N_2O_4$ (322.41): C, 63.33; H, 8.13; N, 8.69%. Found: C, 63.57; H, 8.29; N, 8.84%.

Diisopropyl 1-(1-(*p*-tolyl)ethyl)hydrazine-1,2-dicarboxylate (3p′): Colorless solid, mp: 103-105 °C; yield: 0.09 g (27%). IR (KBr) (ν_{max}, cm^{-1}): 3299, 3040, 2926, 1624, 1538, 1449, 1332, 1249, 1173, 1024. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.19 (6 H, d, ^3J = 5.9 Hz, 2 Me), 1.21 (6 H, d, ^3J = 6.2 Hz, 2 Me), 1.72 (3 H, d, ^3J = 6.6 Hz, Me), 2.27 (3 H, s, Me), 4.90-4.98 (2 H, m, 2 CHO), 5.15 (1 H, q, ^3J = 6.6 Hz, CH), 6.78 (1 H, br s, NH), 7.11 (2 H, d, ^3J = 6.2 Hz, 2 CH), 7.30 (2 H, d, ^3J = 6.2 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 17.8 (Me), 22.1 (2 Me), 22.5 (2 Me), 24.7 (Me), 70.1 (CHO), 70.3 (CHO), 74.8 (CH), 127.1 (2 CH), 129.5 (2 CH), 137.1 (C), 140.5 (C), 154.7 (C=O), 155.8 (C=O). MS: *m/z* (%) = 322 (M^+, 7), 263 (22), 235 (28), 221 (16), 161 (53), 119 (100), 103 (89), 87 (72). Anal. Calcd for $C_{17}H_{26}N_2O_4$ (322.41): C, 63.33; H, 8.13; N, 8.69%. Found: C, 63.54; H, 8.28; N, 8.77%.

Diethyl 1-benzylhydrazine-1,2-dicarboxylate (3q): Colorless solid, mp: 87-89 °C; yield: 0.22 g (82%). IR (KBr) (ν_{max}, cm^{-1}): 3297, 3064, 2944, 1659, 1552, 1451, 1368, 1284, 1167, 1088. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.22-1.34 (6 H, m, 2 Me), 4.22-4.31 (4 H, m, 2 CH_2), 4.67 (2 H, br s, CH_2), 6.65 (1 H, br s, NH), 7.25-7.36 (5 H, m, 5 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 18.1 (Me), 18.3 (Me), 58.9 (CH_2), 64.1 (CH_2O), 64.9 (CH_2O), 125.3 (CH), 126.1 (2 CH), 129.1 (2 CH), 137.3 (C), 156.1 (C=O), 156.6 (C=O). MS: *m/z* (%) = 266 (M^+, 14), 221 (19), 193 (24), 179 (48), 133 (67), 91 (100), 89 (89), 74 (58). Anal. Calcd for $C_{13}H_{18}N_2O_4$ (266.30): C, 58.63; H, 6.81; N, 10.52%. Found: C, 58.85; H, 6.99; N, 10.66%.

Diethyl 1-(4-methylbenzyl)hydrazine-1,2-dicarboxylate (3r): Colorless solid, mp: 100-102 °C; yield: 0.23 g (83%). IR (KBr) (ν_{max}, cm^{-1}): 3268, 3072, 2927, 1650, 1551, 1427, 1365, 1228, 1118, 1051. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.25-1.33 (6 H, m, 2 Me), 2.28 (3 H, s, Me), 4.20-4.27 (4 H, m, 2 CH_2), 4.61 (2 H, br s, CH_2), 6.58 (1 H, br s, NH), 7.14 (2 H, d, ^3J = 6.7 Hz, 2 CH), 7.28 (2 H, d, ^3J = 6.7 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 14.4 (Me), 14.5 (Me), 23.7 (Me), 58.1 (CH_2), 62.3 (CH_2O), 62.8 (CH_2O), 127.2 (2 CH), 128.7 (2 CH), 135.1 (C), 137.9 (C), 155.2 (C=O), 156.5 (C=O). MS: *m/z* (%) = 280 (M^+, 7), 235 (18), 207 (34), 193 (41), 147 (57), 105 (100), 89 (81), 74 (57). Anal. Calcd for $C_{14}H_{20}N_2O_4$ (280.32): C, 59.99; H, 7.19; N, 9.99%. Found: C, 60.18; H, 7.36; N, 10.16%.

Diethyl 1-(3,5-dimethylbenzyl)hydrazine-1,2-dicarboxylate (3s) Colorless solid, mp: 121-123 °C; yield: 0.27 g (91%). IR (KBr) (ν_{max}, cm^{-1}): 3312, 3041, 2933, 1628, 1546, 1460, 1320, 1267, 1056. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.23-1.37 (6 H, m, 2 Me), 2.25 (6 H, s, 2 Me), 4.21-4.30 (4 H, m, 2 CH_2), 4.54 (2 H, br s, CH_2), 6.84 (1 H, br s, NH), 7.13 (2 H, s, 2 CH), 7.19 (1 H, s, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 14.1 (Me), 14.2 (Me), 25.1 (2 Me), 56.3 (CH_2), 62.1 (CH_2O), 62.4 (CH_2O), 126.0 (2 CH), 130.4 (CH), 139.7 (2 C), 142.1 (C), 155.6 (C=O), 156.3 (C=O). MS: *m/z* (%) = 294 (M^+, 11), 249 (16), 221 (27), 207 (46), 161 (57), 119 (100), 89 (71), 74 (52). Anal. Calcd for $C_{15}H_{22}N_2O_4$ (294.35): C, 61.21; H, 7.53; N, 9.52%. Found: C, 61.38; H, 7.70; N, 9.69%.

Diethyl 1-(4-methoxybenzyl)hydrazine-1,2-dicarboxylate (3t) Colorless solid, mp: 108-110 °C; yield: 0.26 g (89%). IR (KBr) (ν_{max}, cm^{-1}): 3283, 3072, 2963, 1658, 1541, 1488, 1368, 1221, 1088. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.21-1.36 (6 H, m, 2 Me), 3.79 (3 H, s, MeO), 4.18-4.35 (4 H, m, 2 CH_2), 4.57 (2 H, br s, CH_2), 6.67-7.10 (3 H, m, NH and 2 CH), 7.19 (2 H, d, ^3J = 6.4 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 15.0 (Me), 15.3 (Me), 57.4 (MeO), 58.1 (CH_2), 63.1 (CH_2O), 63.5 (CH_2O), 114.1 (2 CH), 129.3 (2 CH), 130.9 (C), 154.6 (C=O), 155.7 (C=O), 160.5 (C). MS: *m/z* (%) = 296 (M^+, 15), 251 (22), 223 (28), 209 (44), 209 (44), 163 (51), 121 (100), 89 (85), 74 (61). Anal. Calcd for $C_{14}H_{20}N_2O_5$ (296.32): C, 56.75; H, 6.80; N, 9.45%. Found: C, 56.93; H, 6.98; N, 9.61%.

Dicyclohexyl 1-benzylhydrazine-1,2-dicarboxylate (3u): Colorless solid, mp: 167-169 °C; yield: 0.31 g (84%). IR (KBr) (ν_{max}, cm^{-1}): 3276, 3043, 2978, 1652, 1563, 1471, 1352, 1234, 1067. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.13-1.83 (20 H, m, 10 CH_2), 4.50 (2 H, br s, CH_2),4.85-4.96 (2 H, m, 2 CH), 6.21 (1 H, br s, NH), 7.29 (2 H, d, ^3J = 6.7 Hz, 2 CH), 7.35 (1 H, d, ^3J = 6.7 Hz, CH), 7.42 (2 H, d, ^3J = 6.6 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 24.8 (2 CH_2), 25.3 (2 CH_2), 29.1 (CH_2), 29.2 (CH_2), 33.8 (2 CH_2), 34.2 (2 CH_2), 58.1 (CH_2), 74.3 (CH), 74.8 (CH), 126.5 (CH), 127.5 (2 CH), 129.2 (2 CH), 136.1 (C), 158.1 (C=O), 159.2 (C=O). MS: *m/z* (%) = 374 (M^+, 4), 283 (26), 282 (47), 274 (28), 232 (39), 133 (57), 91 (100), 77 (43), 83 (67). Anal. Calcd for $C_{21}H_{30}N_2O_4$ (374.48): C, 67.35; H, 8.08; N, 7.48%. Found: C, 67.56; H, 8.27; N, 7.60%.

Di-*tert*-butyl 1-benzylhydrazine-1,2-dicarboxylate (3v): Colorless solid, mp: 104-106 °C; yield: 0.25 g (76%). IR (KBr) (ν_{max}, cm^{-1}): 3295, 3051, 2978, 1648, 1563, 1462, 1331, 1213, 1052. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 1.49 (9 H, s, 3 Me), 1.52 (9 H, s, 3 Me), 4.45 (2 H, br s, CH_2), 6.49 (1 H, br s, NH), 7.24-7.33 (3 H, m, 3 CH), 7.37 (2 H, d, ^3J = 6.7 Hz, 2 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 30.8 (3 Me), 31.1 (3 Me), 59.4 (CH_2), 83.7 (C), 83.9 (CH), 126.7 (CH), 129.7 (2 CH), 130.9 (2 CH),137.5 (C), 157.8 (C=O), 160.4 (C=O). MS: *m/z* (%) = 322 (M^+, 1), 265 (18), 248 (23), 221 (36), 206 (40), 133 (57), 91 (100), 77 (38), 57 (83). Anal. Calcd for $C_{17}H_{26}N_2O_4$ (322.41): C, 63.33; H, 8.13; N, 8.69%. Found: C, 63.54; H, 8.28; N, 8.78%.

Diphenyl 1-benzylhydrazine-1,2-dicarboxylate (3w): Colorless solid, mp: 153-155.5 °C; yield: 0.33 g (90%). IR (KBr) (ν_{max}, cm^{-1}): 3266, 3063, 3030, 2954, 1672, 1555, 1442, 1308, 1246, 1024. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H = 4.34 (2 H, br s, CH_2), 6.61 (1 H, br s, NH), 7.16-7.51 (15 H, m, 15 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 62.7 (CH_2), 118.5 (2 CH), 118.9 (2 CH), 124.7 (CH), 124.9 (CH), 125.1 (CH), 128.3 (2 CH), 128.5 (2 CH), 129.3 (2 CH), 129.4 (2 CH), 137.8 (C), 154.2 (C), 154.4 (C), 156.7 (C=O), 158.2 (C=O). MS: *m/z* (%) = 362 (M^+, 7), 285 (14), 269 (31), 226 (21), 136 (47), 133 (68), 91 (100), 77 (79), 54 (43). Anal. Calcd for $C_{21}H_{18}N_2O_4$ (362.39): C, 69.60; H, 5.01; N, 7.73%. Found: C, 69.85; H, 5.25; N, 7.95%.

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Copper(I)/Phen catalysed functionalization of benzylic C–H bonds with Dialkyl Azodicarboxylates