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A general copper-catalyzed radical C(sp^3)–C(sp^2) cross-coupling to access 1,1-diarylalkanes under ambient conditions

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ABSTRACT

A general copper-catalyzed C(sp^3)–C(sp^2) cross-coupling of (hetero)benzyl bromides with the air- and moisture-stable aryl nucleophiles has been developed, providing a facile access to pharmaceutically useful 1,1-di(hetero)arylalkane and 1-aryl-1-heteroarylalkane scaffolds. Critical to the success is the utilization of a proline-based N,N,P-ligand to enhance the reducing capability of copper, thus easily converting benzyl bromides to the corresponding radical species via a single-electron transfer process under ambient conditions. The reaction features a broad substrate scope, covering (hetero)arylboronate esters, oxadiazoles, and benzo[*d*]oxazoles, as well as primary and secondary (hetero)benzyl bromides with excellent functional group tolerance.

1. Introduction

Transition metal-catalyzed C–C cross-coupling has emerged as a powerful tool for the construction of complex molecular frameworks from simple feedstocks in organic synthesis [1]. Despite the noble progress in palladium-catalyzed C(sp^2)–C(sp^2) cross-coupling of aryl/vinyl (pseudo)halides [2], the coupling of alkyl (pseudo)halides to forge the C(sp^3)–C(sp^2) bonds has been less developed due to the difficult oxidative addition process and the facile β-H elimination of the alkyl palladium complex [3]. In this context, the first-row transition metals (Fe, Co, Ni, and Cu) engage more easily in a single-electron transfer (SET) process owing to their high-spin electronic configurations and thus provide a pathway in the oxidative addition step of alkyl halides via a radical process [4]. In the past two decades, great efforts have been made to the first-row transition metal-catalyzed cross-coupling of alkyl halides with many organometallic reagents, such as organolithium reagent, Grignard reagent, and organozinc reagent, etc (Scheme 1A) [1c,4]. It should be noted that most of these organometallic reagents are sensitive to air or water, and are incompatible with many polar functional groups, thus thwarting the general application of the cross-coupling reactions [1c,4]. Therefore, the development of a general C(sp^3)–C(sp^2) cross-coupling of alkyl halides with air- and moisture-stable nucleophiles is highly urgent.

Aryl boronate esters and heterocycles are reported to be a class of air- and moisture-stable nucleophiles in the cross-coupling reactions [5,6]. Owing to the low cost and toxicity of copper [7], Hu, Fu and others have disclosed the copper-catalyzed cross-coupling of alkyl (pseudo)halides with heterocycles or arylboronates [8]. However, the reactions proceed at high temperature and it is necessary to develop a general copper-catalyzed C(sp^3)–C(sp^2) cross-coupling under ambient conditions. As part of our continuous interest in developing novel ligands to promote copper-catalyzed radical reactions [9], we found that a cinchona alkaloid-based multidentate N,N,P-ligand could greatly enhance the reducing

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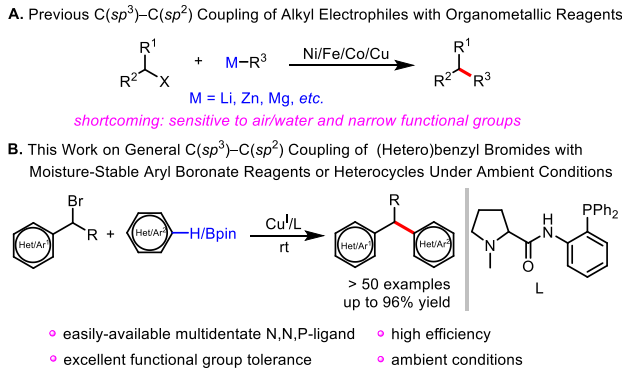


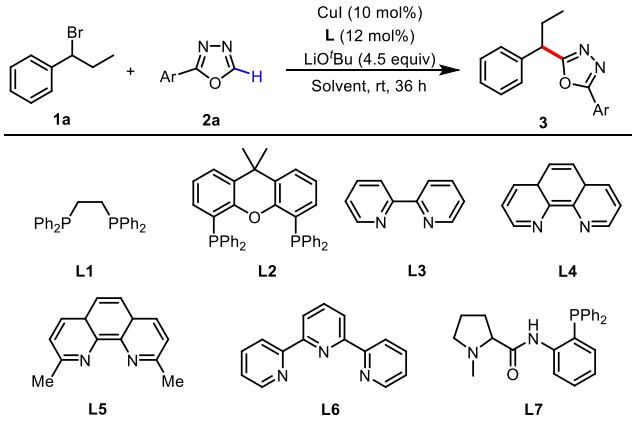
Scheme 1. The design of a general C(sp^3)–C(sp^2) cross-coupling.

capability of copper, thus easily undergoing a SET process with diverse alkyl halides under ambient conditions [9b]. Utilizing this strategy, we further realized the enantioconvergent cross-coupling of secondary alkyl halides with arylboronate esters or heterocycles [10] to construct the synthetically important 1,1-di(hetero)arylalkane scaffolds [11,12], which are important structural motifs in natural products and pharmaceuticals [13]. It should be noted that several drawbacks still existed in our developed approaches: (1) the structurally congested cinchona alkaloid-based multidentate N,N,P-ligands needed tedious synthesis; (2) due to the bulkiness of the utilized ligands, the reaction efficiency was low and the substrate scope was quite limited [10]. We surmise that the use of a less bulky N,N,P-ligand might be crucial to address this issue. Herein, we describe a general and efficient copper-catalyzed C(sp^3)–C(sp^2) cross-coupling of alkyl bromides with the air- and moisture-stable arylboronate esters or heterocycles to provide an expeditious synthesis of a library of 1,1-diarylalkanes under ambient conditions (Scheme 1B). Notably, the reaction efficiency is high and the scope is very broad, covering a number of (hetero)arylboronate esters and heterocycles, as well as primary and secondary benzyl-, and heterobenzyl bromides with excellent functional group tolerance.

2. Results and discussion

The oxadiazoles are a class of pharmaceutically important heterocycles which have been used as nucleophiles in cross-coupling reactions [5]. Based on the above assumption, we firstly investigated the cross-coupling of (1-bromopropyl)benzene **1a** with the bench-stable 1,3,4-oxadiazole **2a** under the catalysis of CuI in presence of LiO^{t}Bu in *N*,*N*-dimethylacetamide (DMA) at room temperature (Table 1). The initial trials with various types of bidentate ligands, such as 1,2-bis(diphenylphosphino)ethane **L1**, Xantphos **L2**, 2,2′-bypyridine **L3**, and 1,10-phenanthroline ligands (**L4** and **L5**) failed to afford the desired C(sp^3)–C(sp^2) coupling product **3** and most of the azole substrate **2a** was decomposed (Table 1, entries 1–5). Further screening of a tridentate ligand **L6** showed that it was not effective for the reaction (Table 1, entry 6). When we used the proline-derived N,N,P-ligand **L7** [9c], which was utilized in our previous C(sp^3)–C(sp) coupling reaction, the desired coupling product **3** was formed in 39% yield (Table 1, entry 7). Inspired by this result, we next screened different solvents and found that the reaction could afford **3** in 67% yield in dichloromethane (DCM), though the conversion was incomplete (Table 1, entries 8 and 9). We then used a cosolvent of DMA/DCM to improve both the reaction conversion and the yield of **3** (Table 1, entry 10). The conversion can reach to 90% and the desired product can be generated in 81% yield. Since the addition of water could not only increase the solubility of LiO^{t}Bu but also enhance the

Table 1
Screening of reaction conditions[a].



Entry	L	Solvent	Conversion (%)[c]	Yield(%)[c]
1	**L1**	DMA	88	0
2	**L2**	DMA	57	0
3	**L3**	DMA	75	0
4	**L4**	DMA	76	0
5	**L5**	DMA	46	0
6	**L6**	DMA	30	0
7	**L7**	DMA	100	39
8	**L7**	$PhCF_3$	48	23
9	**L7**	DCM	76	67
10	**L7**	DMA/DCM (1/2)	90	81
11[b]	**L7**	DMA/DCM (1/2)	100	91

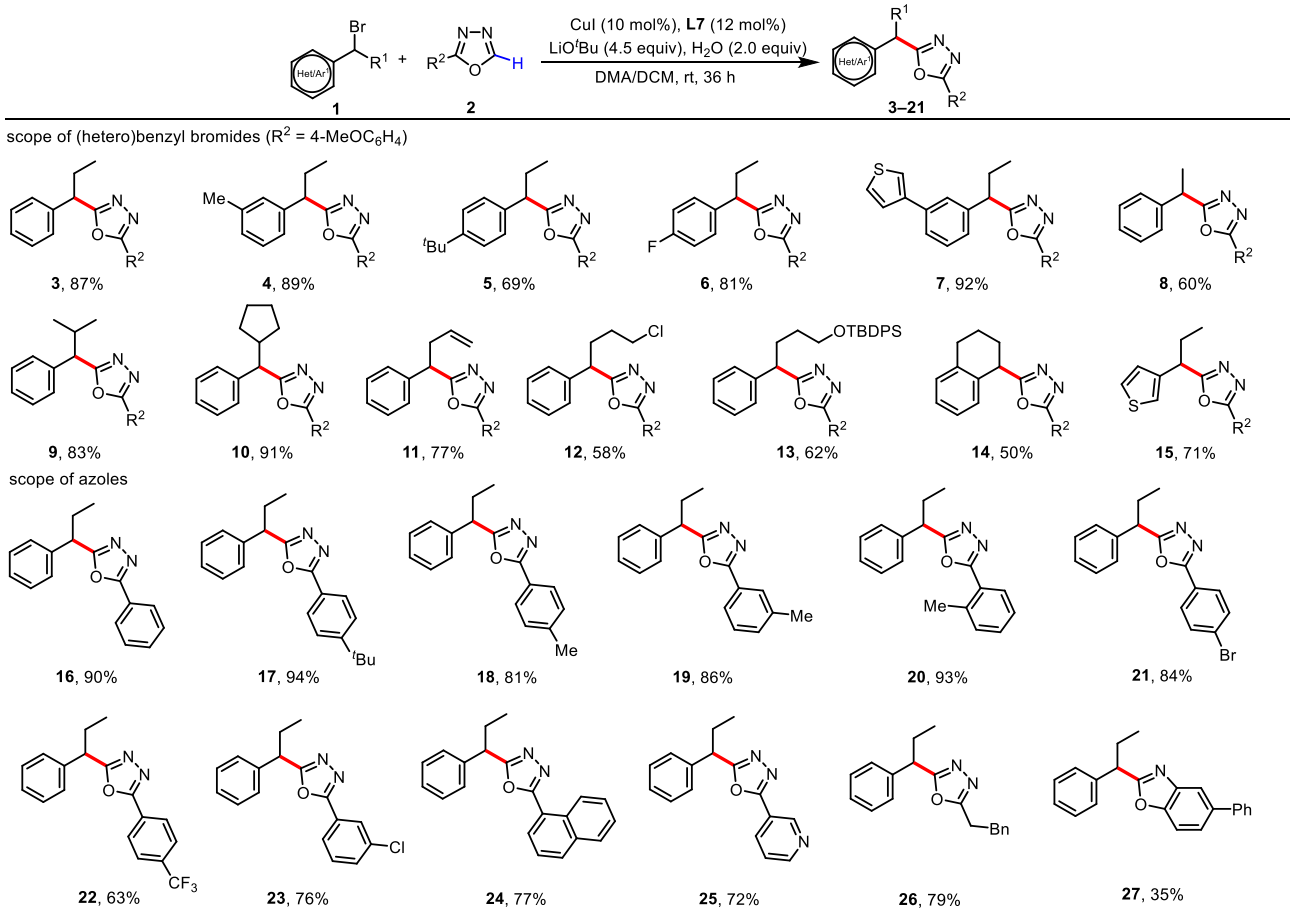
[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.05 mmol), CuI (10 mol%), **L** (12 mol %), LiO^{t}Bu (4.5 equiv) in solvent (0.60 mL) at room temperature for 36 h under argon.
[b] H_2O (2.0 equiv).
[c] Conversion of **2a** and yield of **3** were based on ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard.

transmetalation step with azoles to form the Cu–C bond [14], we added two equivalents of water to the reaction and both the conversion and the yield were further improved (Table 1, entry 11). At last, we identified the optimal conditions as follows: the reaction of **1a** with **2a** in the presence of 10 mol% of CuI, 12 mol% of **L7**, 4.5 equivalents of LiO^{t}Bu and 2.0 equivalents of H_2O in DMA/DCM (v/v = 1:2) afforded **3** in 91% yield.

With the optimal reaction conditions in hand, we next investigated the scope of the cross-coupling reaction (Table 2). The benzyl bromides with electron-donating or -withdrawing groups at *meta*, or *para* positions of phenyl rings were suitable for the reaction to provide **4**–**7** in 69–92% yields. The linear benzyl bromides possessing different functional groups, such as terminal alkene, chloride, and silyl ether, at the alkyl branch proceeded smoothly to deliver **8**–**13** in 58–91% yields under the standard conditions. More importantly, the 1-bromo-1,2,3,4-tetrahydronaphthalene was also a viable substrate to afford **14** in 50% yield. Furthermore, 3-(1-bromopropyl)thiophene was applicable to the cross-coupling reaction to furnish the 1,1-diheteroarylalkane product **15** in 71% yield. The aryl-substituted azoles with the electron-neutral **(16)**, -rich **(17**–**20)** or -withdrawing **(21**–**23)** group, a naphthalene group **(24)** and a pyridine group **(25)** were all compatible with the reaction conditions. Moreover, the alkylated azole underwent the cross-coupling reaction in high efficiency to generate **26** in 79% yield. In addition to the 1,3,4-oxadiazole derivatives, the medicinally relevant benzo[*d*]oxazole was also amenable to the cross-coupling, affording **27**, albeit with a moderate yield.

Aryl boronate esters have the unique feature of high stability, ready availability, and low toxicity, and thus they have found wide

Table 2
Substrate scope for the coupling with azoles [a].



[a]Reaction conditions: **1** (0.20 mmol), **2** (0.10 mmol), CuI (10 mol%), **L7** (12 mol%), LiO^{t}Bu (4.5 equiv), and H_2O (2.0 equiv) in DMA/DCM (1/2, 1.0 mL) at room temperature for 36 h under argon.

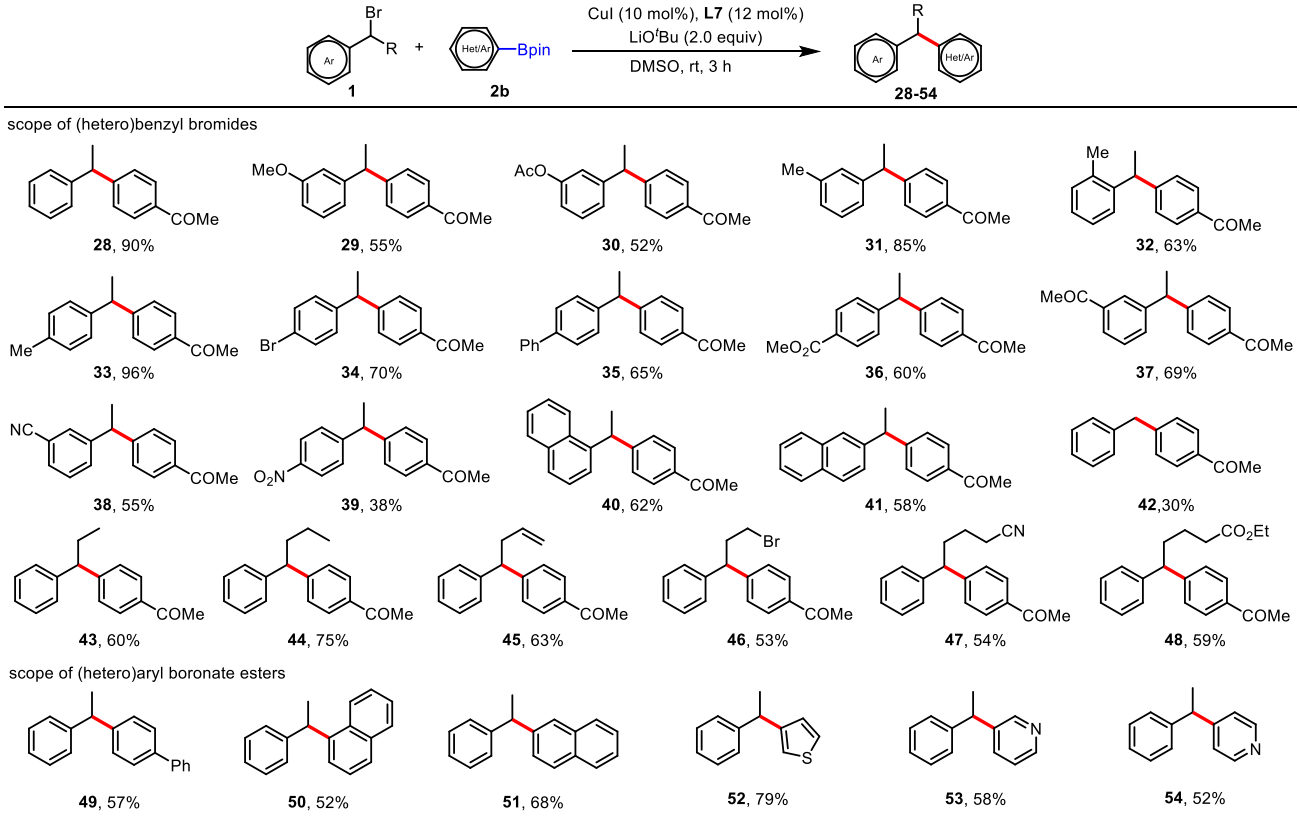
applications in the transition-metal catalyzed cross-coupling reactions [6]. As such, we switched our attention to the cross-coupling of benzyl bromides with pinacol-derived aryl boronate esters to provide straightforward access to a myriad of 1,1-diarylalkanes. The optimal conditions for cross-coupling of benzyl bromides with azoles were not suitable for the reaction of arylboronate esters and the reaction conditions were screened (Table S1 in the Supporting Information). Finally, we found that the reaction of (1-bromoethyl)benzene **1b** with 4-acetylphenylboronate ester **2b**, in the presence of CuI (10 mol%), the same ligand **L7** (12 mol%), and LiO^{t}Bu (2.0 equiv) in DMSO (2.4 mL) gave rise to **28** in 90% yield at room temperature under argon (Table S1, entry 4). Under the optimal conditions, a wide range of benzyl bromides with diverse substituents at the *meta*, *ortho*, and *para* positions of the aryl rings reacted well to give the desired 1,1-diarylalkanes **29**–**39** in up to 96% yield (Table 3). Many functional groups were left untouched, such as methoxyl **(29)**, acetyl **(30)**, bromide **(34)**, methoxycarbonyl **(36)**, carbonyl **(37)**, cyano **(38)**, and nitro **(39)** group, *etc*. In addition, the naphthalene-substituted alkyl bromides were also suitable for the reaction to provide **40** and **41** in good yields. The reaction was not limited to secondary benzyl bromides, and the primary benzyl bromide was a viable substrate to afford **42**, albeit with a lower yield. Notably, the functional groups at the linear chain of the benzyl bromides were also tolerated, such as the terminal alkene, bromide, nitrile as well as the ester group, as can be seen in the formation of **43**–**48**. Next, the scope of the arylboronate esters was also examined. Not only the aryl- and naphthyl-substituted boronate esters, but also the medicinally relevant thiophenyl- and pyridyl-substituted boronate esters were easily coupled under the standard conditions to deliver **49**–**54** in moderate to good yields.

On the basis of our previous works [10], we proposed a plausible mechanism as shown in Scheme 2. Cu^I first reacted with **L7** to form the Cu^I complex **I** in the presence of LiO^{t}Bu. This complex underwent a transmetalation step with the nucleophile **2** to afford the complex **II**, which reacted with benzyl bromides **1** via a single-electron transfer process to generate the Cu^{II} complex **III** and the benzyl radical **IV**. These two species underwent a coupling to furnish the desired 1,1-diarylalkane scaffolds and regenerated the complex **I** for the next catalytic cycle.

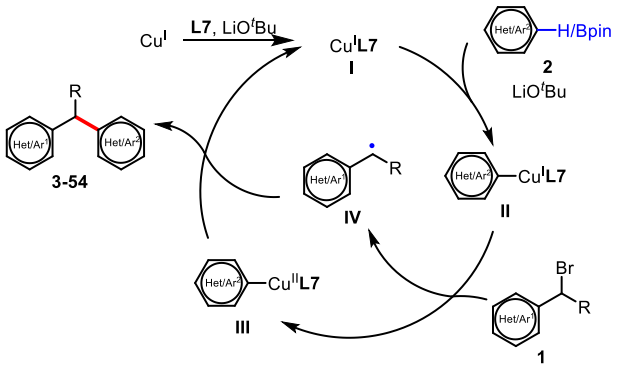
3. Conclusions

In sum, a general copper-catalyzed C(sp^3)–C(sp^2) cross-coupling of (hetero)benzyl bromides with the air- and moisture-stable nucleophiles has been developed, providing a versatile tool to a number of 1,1-diarylalkane scaffolds. It is crucial to use the proline-based N,N,P-ligand to enhance the reducing capability of copper catalyst, thus the reaction could proceed under ambient conditions. The substrate scope is quite broad, covering primary and secondary

Table 3
Substrate scope for the coupling with pinacol-derived (hetero)aryl boronate esters [a].



[a]Reaction conditions: **1** (0.30 mmol), **2** (0.20 mmol), CuI (10 mol%), **L7** (12 mol%), LiO^{t}Bu (2.0 equiv) in DMSO (2.4 mL) at room temperature for 3 h under argon



Scheme 2. A plausible reaction mechanism.

(hetero)benzyl bromides as well as aryl-, and heteroaryl boronate esters, oxadiazoles, and benzo[*d*]oxazoles with excellent functional group tolerance.

4. Experimental section

4.1. General experimental information

All reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. *N,N*-Dimethylacetamide (DMA) was purchased from Aladdin, which was redistilled with calcium hydride under argon atmosphere. Anhydrous dichloromethane (DCM) was purchased from JK and transferred under an argon atmosphere. LiO^{t}Bu (98%) was purchased from JK. CuI was purchased from TCL. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040−0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm) or iodine. NMR spectra were recorded on Bruker DPX-400 spectrometer at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Mass spectrometric data were obtained using Bruker Apex IV RTMS. The alkyl bromides [9c], azoles, arylboronic-pinacol esters [8a] were synthesized according to the reported procedures.

4.2. General procedures A for cross-coupling of racemic alkyl bromides with azole C(sp^2)–H bonds

To a flame-dried Schlenk tube equipped with a magnetic stir bar were added CuI (1.9 mg, 0.010 mmol, 10 mol%), **L7** (4.7 mg, 0.012 mmol, 12 mol%), LiO^{t}Bu (36 mg, 0.45 mmol, 4.5 equiv), and an appropriate azole (0.10 mmol, 1.0 equiv). The tube was evacuated and backfilled with argon for three times, and then, an appropriate alkyl bromide (0.20 mmol, 2.0 equiv), water (3.6 μL, 0.20 mmol, 2.0 equiv), and anhydrous *N,N*-dimethylacetamide (0.35 mL) and dichloromethane (0.70 mL) were sequentially added. The reaction mixture was stirred at room temperature for 36 h. The resulting

reaction mixture was diluted with 10 mL ethyl acetate and washed with brine (10 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 and filtered through a pad of celite. The organic solvent was removed under vacuum and the residue was purified by column chromatography on silica gel to afford the desired product.

4.2.1. 2-(4-Methoxyphenyl)-5-(1-phenylpropyl)-1,3,4-oxadiazole (3)

According to the general procedure A, the product **3** was obtained in (25.5 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.9 Hz, 2H), 7.40–7.34 (m, 4H), 7.31–7.27 (m, 1H), 6.98 (d, J = 8.9 Hz, 2H), 4.16 (t, J = 7.8 Hz, 1H), 3.86 (s, 3H), 2.42–2.31 (m, 1H), 2.20–2.09 (m, 1H), 1.00 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 164.8, 162.2, 139.1, 128.8, 128.6, 127.9, 127.5, 116.6, 114.4, 55.4, 45.1, 27.5, 12.2. **HRMS** (ESI) m/z calcd. for $C_{18}H_{19}N_2O_2$ $[M + H]^+$ 295.1441, found 295.1442.

4.2.2. 2-(4-Methoxyphenyl)-5-(1-(m-tolyl)propyl)-1,3,4-oxadiazole (4)

According to the general procedure A, the product **4** was obtained in (27.4 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95–7.91 (m, 2H), 7.26–7.20 (m, 1H), 7.16–7.14 (m, 2H), 7.08 (d, J = 7.8 Hz, 1H), 6.98–6.94 (m, 2H), 4.09 (t, J = 7.8 Hz, 1H), 3.85 (s, 3H), 2.38–2.28 (m, 1H), 2.34 (s, 3H), 2.17–2.06 (m, 1H), 0.98 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 164.8, 162.2, 139.0, 138.5, 128.7, 128.6(2), 128.6(0), 128.3, 124.9, 116.6, 114.4, 55.4, 45.1, 27.5, 21.5, 12.2. **HRMS** (ESI) m/z calcd. for $C_{19}H_{21}N_2O_2$ $[M + H]^+$ 309.1598, found 309.1597.

4.2.3. 2-(1-(4-(tert-Butyl)phenyl)propyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (5)

According to the general procedure A, the product **5** was obtained in (24.2 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96–7.92 (m, 2H), 7.37–7.34 (m, 2H), 7.30–7.27 (m, 2H), 6.98–6.95 (m, 2H), 4.12 (t, J = 7.8 Hz, 1H), 3.85 (s, 3H), 2.38–2.27 (m, 1H), 2.15–2.08 (m, 1H), 1.30 (s, 9H), 0.98 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 164.7, 162.1, 150.3, 136.0, 128.6, 127.5, 125.7, 116.6, 114.4, 55.4, 44.6, 34.5, 31.3, 27.6, 12.3. **HRMS** (ESI) m/z calcd. for $C_{22}H_{27}N_2O_2$ $[M + H]^+$ 351.2067, found 351.2067.

4.2.4. 2-(1-(4-Fluorophenyl)propyl)-5-(4-Methoxyphenyl)-1,3,4-oxadiazole (6)

According to the general procedure A, the product **6** was obtained in (25.3 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95–7.91 (m, 2H), 7.36–7.31 (m, 2H), 7.06–7.00 (m, 2H), 6.99–6.95 (m, 2H), 4.13 (t, J = 7.8 Hz, 1H), 3.86 (s, 3H), 2.38–2.27 (m, 1H), 2.15–2.04 (m, 1H), 0.98 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1 (d, J = 257.3 Hz), 163.3, 162.2, 160.9, 134.7 (d, J = 3.3 Hz), 129.5 (d, J = 8.1 Hz), 128.6, 116.4, 115.7 (d, J = 21.5 Hz), 114.4, 55.5, 44.3, 27.6, 12.1. **^{19}F NMR** (376 MHz, $CDCl_3$): δ −115.1. **HRMS** (ESI) m/z calcd. for $C_{18}H_{18}FN_2O_3$ $[M + H]^+$ 313.1347, found 313.1347.

4.2.5. 2-(4-Methoxyphenyl)-5-(1-(3-(thiophen-3-yl)phenyl) propyl)-1,3,4-oxadiazole (7)

According to the general procedure A, the product **7** was obtained in (34.6 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95–7.92 (m, 2H), 7.58 (t, J = 1.8 Hz, 1H), 7.51 (dt, J = 7.7, 1.4 Hz, 1H), 7.45 (t, J = 2.1 Hz, 1H), 7.39–7.35 (m, 3H), 7.29 (dt, J = 7.7, 1.5 Hz, 1H), 6.99–6.93 (m, 2H), 4.18 (t, J = 7.8 Hz, 1H), 3.84 (s, 3H), 2.44–2.33 (m, 1H), 2.22–2.10 (m, 1H), 1.01 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 164.9, 162.2, 141.9, 139.7, 136.4, 129.3, 128.6, 126.6, 126.4, 126.3, 126.1, 125.7, 120.7, 116.5, 114.4, 55.4, 45.2, 27.5, 12.3. **HRMS** (ESI) m/z calcd. for $C_{22}H_{21}N_2O_2S$ $[M + H]^+$ 377.1318, found 377.1319.

4.2.6. 2-(4-methoxyphenyl)-5-(1-phenylethyl)-1,3,4-oxadiazole (8)

According to the general procedure A, the product **8** was obtained in (17.1 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95–7.90 (m, 2H), 7.38–7.32 (m, 4H), 7.31–7.25 (m, 1H), 6.98–6.94 (m, 2H), 4.41 (q, J = 7.3 Hz, 1H), 3.85 (s, 3H), 1.81 (d, J = 7.3 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 164.9, 162.2, 140.5, 128.9, 128.6, 127.5, 127.3, 116.5, 114.4, 55.4, 37.5, 19.7. **HRMS** (ESI) m/z calcd. for $C_{17}H_{17}N_2O_2$ $[M + H]^+$ 281.1285, found 281.1282.

4.2.7. 2-(4-methoxyphenyl)-5-(2-methyl-1-phenylpropyl)-1,3,4-oxadiazole (9)

According to the general procedure A, the product **9** was obtained in (27.4 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.9 Hz, 2H), 7.42–7.40 (m, 2H), 7.35–7.32 (m, 2H), 7.28–7.24 (m, 1H), 7.02–6.94 (m, 2H), 3.91 (d, J = 10.1 Hz, 1H), 3.86 (s, 3H), 2.62–2.53 (m, 1H), 1.04 (d, J = 6.6 Hz, 3H), 0.88 (d, J = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 164.6, 162.2, 138.3, 128.7, 128.6, 128.5, 127.5, 116.6, 114.4, 55.5, 51.3, 32.6, 21.4, 20.8. **HRMS** (ESI) m/z calcd. for $C_{19}H_{21}N_2O_2$ $[M + H]^+$ 309.1598, found 309.1599.

4.2.8. 2-(cyclopentyl(phenyl)methyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (10)

According to the general procedure A, the product **10** was obtained in (30.4 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96–7.92 (m, 2H), 7.43–7.40 (m, 2H), 7.35–7.31 (m, 2H), 7.28–7.23 (m, 1H), 6.99–6.95 (m, 2H), 3.99 (d, J = 11.0 Hz, 1H), 3.85 (s, 3H), 2.85–2.74 (m, 1H), 1.92–1.83 (m, 1H), 1.72–1.51 (m, 5H), 1.37–1.27 (m, 1H), 1.22–1.16 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 164.6, 162.2, 139.1, 128.7, 128.6, 128.3, 127.4, 116.6, 114.4, 55.4, 49.2, 44.0, 31.6, 31.4, 25.1, 25.0. **HRMS** (ESI) m/z calcd. for $C_{21}H_{23}N_2O_2$ $[M + H]^+$ 335.1754, found 335.1755.

4.2.9. 2-(4-Methoxyphenyl)-5-(1-phenylbut-3-en-1-yl)-1,3,4-oxadiazole (11)

According to the general procedure A, the product **11** was obtained in (23.6 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95–7.91 (m, 2H), 7.39–7.32 (m, 4H), 7.30–7.26 (m, 1H), 6.98–6.95 (m, 2H), 5.83–5.73 (m, 1H), 5.11 (dq, J = 17.1, 1.5 Hz, 1H), 5.04–5.00 (m, 1H), 4.33 (t, J = 7.8 Hz, 1H), 3.85 (s, 3H), 3.10–7.91 (m, 1H), 2.89–2.81 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.1, 164.9, 162.2, 138.6, 134.6, 128.9, 128.6, 127.9, 127.6, 117.9, 116.5, 114.4, 55.5, 43.4, 38.4. **HRMS** (ESI) m/z calcd. for $C_{19}H_{19}N_2O_2$ $[M + H]^+$ 307.1441, found 307.1442.

4.2.10. 2-(4-Chloro-1-phenylbutyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (12)

According to the general procedure A, the product **12** was obtained in (19.8 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95–7.90 (m, 2H), 7.36 (d, J = 4.4 Hz, 4H), 7.32–7.28 (m, 1H), 6.98–6.95 (m, 2H), 4.25 (t, J = 7.8 Hz, 1H), 3.85 (s, 3H), 3.56 (td, J = 6.4, 2.1 Hz, 2H), 2.50–2.42 (m, 1H), 2.33–2.22 (m, 1H), 1.93–1.78 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.1, 165.0, 162.3, 138.6, 129.0, 128.6, 127.8(2), 127.7(8), 116.4, 114.4, 55.5, 44.4, 42.8, 31.5, 30.3. **HRMS** (ESI) m/z calcd. for $C_{19}H_{20}^{35}ClN_2O_2$ $[M + H]^+$ 343.1208, found 343.1210; for $C_{19}H_{20}^{37}ClN_2O_2$ $[M + H]^+$ 345.1178, found 345.1181.

4.2.11. 2-(4-((tert-Butyldiphenylsilyl)oxy)-1-phenylbutyl)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (13)

According to the general procedure A, the product **13** was obtained in 34.8 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96–7.89 (m, 2H), 7.65–7.61 (m, 4H), 7.42–7.30 (m, 10H), 7.29–7.25 (m, 1H), 6.98–6.94 (m, 2H), 4.24 (t, J = 7.9 Hz, 1H), 3.85 (s, 3H), 3.69 (t, J = 6.2 Hz, 2H), 2.45–2.35 (m, 1H), 2.26–2.16 (m, 1H), 1.62–1.56 (m, 2H), 1.03 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 164.8, 162.2, 139.1, 135.6, 133.8, 129.6, 128.9, 128.6, 127.9, 127.7, 127.5, 116.6, 114.4,

63.3, 55.5, 43.0, 30.6, 30.2, 26.9, 19.2. **HRMS** (ESI) *m/z* calcd. for $C_{35}H_{39}N_2O_3Si$ $[M + H]^+$ 563.2724, found 563.2730.

*4.2.12. 2-(4-methoxyphenyl)-5-(1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,4-oxadiazole **(14)***

According to the general procedure A, the product **14** was obtained in (15.3 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97–7.93 (m, 2H), 7.23–7.17 (m, 2H), 7.16–7.14 (m, 2H), 7.02–6.97 (m, 2H), 4.61 (t, *J* = 6.6 Hz, 1H), 3.88 (s, 3H), 3.02–2.86 (m, 2H), 2.35–2.22 (m, 2H), 2.19–2.10 (m, 1H), 1.97–1.88 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.6, 164.9, 162.2, 137.1, 133.0, 129.7, 129.1, 128.6, 127.2, 126.2, 116.6, 114.4, 55.5, 36.6, 29.2, 27.9, 21.0. **HRMS** (ESI) *m/z* calcd. for $C_{19}H_{19}N_2O_2$ $[M + H]^+$ 307.1441, found 307.1443.

*4.2.13. 2-(4-Methoxyphenyl)-5-(1-(thiophen-3-yl)propyl)-1,3,4-oxadiazole **(15)***

According to the general procedure A, the product **15** was obtained in (21.3 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99–7.95 (m, 2H), 7.32 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.23 (dd, *J* = 3.1, 1.3 Hz, 1H), 7.12 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.03–6.97 (m, 2H), 4.34 (t, *J* = 7.7 Hz, 1H), 3.88 (s, 3H), 2.35–2.24 (m, 1H), 2.22–2.10 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 164.8, 162.2, 139.3, 128.6, 127.0, 126.2, 122.2, 116.5, 114.4, 55.5, 40.3, 27.5, 12.1. **HRMS** (ESI) *m/z* calcd. for $C_{16}H_{17}N_2O_2S$ $[M + H]^+$ 301.1005, found 301.1006.

*4.2.14. 2-Phenyl-5-(1-phenylpropyl)-1,3,4-oxadiazole **(16)***

According to the general procedure A, the product **16** was obtained in (23.8 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01–7.99 (m, 2H), 7.52–7.44 (m, 3H), 7.38–7.32 (m, 4H), 7.30–7.25 (m, 1H), 4.16 (t, *J* = 7.8 Hz, 1H), 2.41–2.30 (m, 1H), 2.20–2.09 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 164.9, 138.9, 131.6, 129.0, 128.9, 127.9, 127.6, 126.9, 124.0, 45.1, 27.5, 12.2. **HRMS** (ESI) *m/z* calcd. for $C_{17}H_{17}N_2O$ $[M + H]^+$ 265.1335, found 265.1336.

*4.2.15. 2-(4-(tert-Butyl) phenyl)-5-(1-phenylpropyl)-1,3,4-oxadiazole **(17)***

According to the general procedure A, the product **17** was obtained in (30.1 mg, 94% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.38–7.32 (m, 4H), 7.29–7.25 (m, 1H), 4.16 (t, *J* = 7.8 Hz, 1H), 2.40–2.29 (m, 1H), 2.19–2.08 (m, 1H), 1.33 (s, 9H), 0.98 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 165.0, 155.2, 139.0, 128.8, 127.9, 127.5, 126.7, 125.9, 121.2, 45.1, 35.0, 31.1, 27.6, 12.2. **HRMS** (ESI) *m/z* calcd. for $C_{21}H_{25}N_2O$ $[M + H]^+$ 321.1961, found 321.1962.

*4.2.16. 2-(1-Phenylpropyl)-5-(p-tolyl)-1,3,4-oxadiazole **(18)***

According to the general procedure A, the product **18** was obtained in (22.5 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.38–7.32 (m, 4H), 7.29–7.25 (m, 3H), 4.15 (t, *J* = 7.8 Hz, 1H), 2.40 (s, 3H), 2.37–2.29 (m, 1H), 2.17–7.25 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 165.0, 142.1, 139.0, 129.7, 128.8, 127.9, 126.8, 121.2, 45.1, 27.6, 21.6, 12.2. **HRMS** (ESI) *m/z* calcd. for $C_{18}H_{19}N_2O$ $[M + H]^+$ 279.1492, found 279.1494.

*4.2.17. 2-(1-Phenylpropyl)-5-(m-tolyl)-1,3,4-oxadiazole **(19)***

According to the general procedure A, the product **19** was obtained (23.9 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (br s, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.38–7.34 (m, 4H), 7.33–7.24 (m, 3H), 4.16 (t, *J* = 7.8 Hz, 1H), 2.40 (s, 3H), 2.37–2.30 (m, 1H), 2.19–2.08 (m, 1H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 165.0, 139.0, 138.8, 132.4, 128.9, 127.9, 127.5, 127.4, 124.0, 123.9, 45.1, 27.5, 21.3, 12.2. **HRMS** (ESI) *m/z* calcd. for $C_{18}H_{19}N_2O$ $[M + H]^+$ 279.1492, found 279.1494.

*4.2.18. 2-(1-Phenylpropyl)-5-(o-tolyl)-1,3,4-oxadiazole **(20)***

According to the general procedure A, the product **20** (25.9 mg, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.39–7.34 (m, 4H), 7.30–7.25 (m, 4H), 4.18 (t, *J* = 7.8 Hz, 1H), 2.65 (s, 3H), 2.41–2.30 (m, 1H), 2.22–2.10 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 165.1, 139.0, 138.3, 131.7, 131.1, 128.9(3), 128.9(5), 127.9, 127.6, 126.1, 123.1, 45.1, 27.5, 22.0, 12.2. **HRMS** (ESI) *m/z* calcd. for $C_{18}H_{19}N_2O$ $[M + H]^+$ 279.1492, found 279.1494.

*4.2.19. 2-(4-Bromophenyl)-5-(1-phenylpropyl)-1,3,4-oxadiazole **(21)***

According to the general procedure A, the product **21** (28.9 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88–7.85 (m, 2H), 7.62–7.59 (m, 2H), 7.35 (d, *J* = 4.3 Hz, 4H), 7.31–7.27 (m, 1H), 4.15 (t, *J* = 7.8 Hz, 1H), 2.41–2.30 (m, 1H), 2.19–2.08 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 164.2, 138.8, 132.3, 128.9, 128.3, 127.9, 127.6, 126.2, 122.9, 45.1, 27.5, 12.2. **HRMS** (ESI) *m/z* calcd. for $C_{17}H_{16}^{79}BrN_2O$ $[M + H]^+$ 343.0441, found 343.0443, $C_{17}H_{16}^{81}BrN_2O$ $[M + H]^+$ 345.0420 found 345.0422.

*4.2.20. 2-(1-Phenylpropyl)-5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole **(22)***

According to the general procedure A, the product **22** was obtained in (15.7 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.9 Hz, 2H), 7.74 (d, *J* = 8.9 Hz, 2H), 7.38–7.33 (m, 4H), 7.31–7.27 (m, 1H), 4.18 (t, *J* = 7.8 Hz, 1H), 2.43–2.32 (m, 1H), 2.24–2.10 (m, 1H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 163.7, 138.6, 133.2 (q, *J* = 32.9 Hz), 128.9, 127.9, 127.7, 127.2, 126.0 (q, *J* = 3.9 Hz), 123.6 (q, *J* = 272.5 Hz), 45.2, 27.5, 12.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ −63.11. **HRMS** (ESI) *m/z* calcd. for $C_{18}H_{16}F_3N_2O$ $[M + H]^+$ 333.1209, found 333.1210.

*4.2.21. 2-(3-Chlorophenyl)-5-(1-phenylpropyl)-1,3,4-oxadiazole **(23)***

According to the general procedure A, the product **23** was obtained in (22.7 mg,76% yield) isolated. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (t, *J* = 1.8 Hz, 1H), 7.90 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.49–7.46 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.37–7.31 (m, 4H), 7.30–7.27 (m, 1H), 4.16 (t, *J* = 7.8 Hz, 1H), 2.41–2.30 (m, 1H), 2.20–2.09 (m, 1H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 163.8, 138.7, 135.1, 131.6, 130.4, 128.9, 127.9, 127.7, 126.8, 125.6, 125.0, 45.1, 27.5, 12.2. **HRMS** (ESI) *m/z* calcd. for $C_{17}H_{16}^{35}ClN_2O$ $[M + H]^+$ 299.0946, found 299.0947; for $C_{17}H_{15}^{37}ClN_2O$ $[M + H]^+$ 301.0916 found 301.0917.

*4.2.22. 2-(Naphthalen-1-yl)-5-(1-phenylpropyl)-1,3,4-oxadiazole **(24)***

According to the general procedure A, the product **24** was obtained in (22.3 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 7.3 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.91–7.88 (m, 1H), 7.66–7.62 (m, 1H), 7.58–7.51 (m, 2H), 7.43–7.35 (m, 4H), 7.31–7.27 (m, 1H), 4.23 (t, *J* = 7.8 Hz, 1H), 2.46–2.35 (m, 1H), 2.45–2.15 (m, 1H), 1.03 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 164.9, 139.0, 133.8, 132.4, 130.1, 128.9, 128.6, 128.3, 128.1, 128.0, 127.6, 126.7, 126.2, 124.8, 120.6, 45.1, 27.6, 12.2. **HRMS** (ESI) *m/z* calcd. for $C_{21}H_{19}N_2O$ $[M + H]^+$ 315.1492, found 315.1493.

*4.2.23. 2-(1-Phenylpropyl)-5-(pyridin-3-yl)-1,3,4-oxadiazole **(25)***

According to the general procedure A, the product **25** was obtained in (19.1 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.75 (br s, 1H), 8.31 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.43 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.38–7.34 (m, 4H), 7.31–7.27 (m, 1H), 4.18 (t, *J* = 7.8 Hz,

1H), 2.43–2.28 (m, 1H), 2.24–2.08 (m, 1H), 1.00 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 162.8, 152.3, 147.8, 138.6, 134.2, 129.0, 127.9, 127.7, 123.8, 120.6, 45.1, 27.5, 12.2. **HRMS** (ESI) *m/z* calcd. for $C_{16}H_{16}N_3O$ $[M + H]^+$ 266.1288, found 266.1288.

4.2.24. 2-Phenethyl-5-(1-phenylpropyl)-1,3,4-oxadiazole ***(26)***

According to the general procedure A, the product **26** was obtained in (23.1 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.31 (m, 2H), 7.30–7.17 (m, 6H), 7.14–7.11 (m, 2H), 4.03 (t, J = 7.8 Hz, 1H), 3.12–3.02 (m, 4H), 2.30–2.19 (m, 1H), 2.10–2.00 (m, 1H), 0.92 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 166.4, 139.5, 139.0, 128.8, 128.6, 128.3, 127.9, 127.5, 126.6, 45.0, 32.6, 27.2 (9), 27.2 (7), 12.13. **HRMS** (ESI) *m/z* calcd. for $C_{19}H_{21}N_2O$ $[M + H]^+$ 293.1648, found 293.1648.

4.2.25. 5-Phenyl-2-(1-phenylpropyl)benzo[d]oxazole ***(27)***

According to the general procedure A, the product **27** was obtained in (11.0 mg, 35% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (t, J = 1.2 Hz, 1H), 7.63–7.58 (m, 2H), 7.53–7.49 (m, 2H), 7.47–7.28 (m, 8H), 4.15 (t, J = 7.8 Hz, 1H), 2.49–2.38 (m, 1H), 2.24–2.11 (m, 1H), 1.00 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.8, 150.4, 141.9, 141.2, 139.8, 138.1, 128.9, 128.8, 128.0, 127.5, 127.4, 127.2, 124.2, 118.4, 110.5, 48.0, 27.6, 12.3. **HRMS** (ESI) *m/z* calcd. for $C_{22}H_{20}NO$ $[M + H]^+$ 313.1539, found 313.1539.

4.3. General procedures B for cross-coupling of racemic alkyl bromides with organoboronate esters

To a flame-dried Schlenk tube equipped with a magnetic stir bar were added CuI (3.8 mg, 0.020 mmol, 10 mol%), **L7** (9.4 mg, 0.024 mmol, 12 mol%), LiO^tBu (32 mg, 0.40 mmol, 2.0 equiv), and an appropriate organoboronate esters (0.20 mmol, 1.0 equiv). The tube was evacuated and backfilled with argon for three times, and then, an appropriate alkyl bromide (0.30 mmol, 1.5 equiv), and anhydrous DMSO (2.4 mL) were sequentially added. The reaction mixture was stirred at room temperature for 3 h. The resulting reaction mixture was diluted with 10 mL ethyl acetate and washed with brine (10 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 and filtered through a pad of celite. The organic solvent was removed under vacuum and the residue was purified by column chromatography on silica gel to afford the desired product.

4.3.1. 1-(4-(1-phenylethyl)phenyl)ethan-1-one ***(28)***

According to the general procedure B, the product **28** was obtained in (40.4 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.36–7.25 (m, 4H), 7.23–7.16 (m, 3H), 4.20 (q, J = 7.2 Hz, 1H), 2.56 (s, 3H), 1.65 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 152.0, 145.3, 135.1, 128.5(4), 128.4(9), 127.8, 127.5, 126.3, 44.8, 26.5, 21.5.

4.3.2. 1-(4-(1-(3-methoxyphenyl)ethyl)phenyl)ethan-1-one ***(29)***

According to the general procedure B, the product **29** was obtained in (28.0 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.27–7.16 (m, 1H), 6.87–6.69 (m, 3H), 4.17 (q, J = 7.2 Hz, 1H), 3.76 (s, 3H), 2.56 (s, 3H), 1.64 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 159.7, 151.8, 146.9, 135.1, 129.4, 128.5, 127.7, 120.0, 113.8, 111.1, 55.1, 44.7, 26.5, 21.4. **HRMS** (ESI) *m/z* calcd. for $C_{17}H_{19}O_2$ $[M + H]^+$ 255.1380, found 255.1379.

4.3.3. 3-(1-(4-acetylphenyl)ethyl)phenyl acetate ***(30)***

According to the general procedure B, the product **30** was obtained in (29.2 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 6.4 Hz, 2H), 7.38–7.27 (m, 3H), 7.07 (d, J = 7.6 Hz, 1H), 6.99–6.86 (m, 2H), 4.21 (q, J = 7.2 Hz, 1H), 2.57 (s, 3H), 2.27 (s, 3H), 1.65 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 169.4, 151.3, 150.8, 147.0, 135.3, 129.4, 128.6, 127.8, 125.1, 120.7, 119.6, 44.5, 26.6, 21.4, 21.1. **HRMS** (ESI) *m/z* calcd. for $C_{18}H_{19}O_3$ $[M + H]^+$ 283.1329, found 283.1329.

4.3.4. 1-(4-(1-(m-tolyl)ethyl)phenyl)ethan-1-one ***(31)***

According to the general procedure B, the product **31** was obtained in (40.5 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.33–7.07 (m, 6H), 4.36 (q, J = 7.2 Hz, 1H), 2.55 (s, 3H), 2.20 (s, 3H), 1.62 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 152.2, 142.3, 135.9, 135.1, 129.2, 128.5, 127.7, 127.4, 44.4, 26.5, 21.5, 20.9.

4.3.5. 1-(4-(1-(o-tolyl)ethyl)phenyl)ethan-1-one ***(32)***

According to the general procedure B, the product **32** was obtained in (30.0 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.33–7.07 (m, 6H), 4.36 (q, J = 7.2 Hz, 1H), 2.55 (s, 3H), 2.20 (s, 3H), 1.62 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 152.0, 142.9, 136.0, 135.0, 130.5, 128.5, 127.8, 126.6, 126.4, 126.1, 41.1, 26.5, 21.8, 19.7. **HRMS** (ESI) *m/z* calcd. for $C_{17}H_{19}O$ $[M + H]^+$ 239.1430, found 239.1431.

4.3.6. 1-(4-(1-(p-tolyl)ethyl)phenyl)ethan-1-one ***(33)***

According to the general procedure B, the product **33** was obtained in (45.8 mg, 96% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.33–7.07 (m, 6H), 4.36 (q, J = 7.2 Hz, 1H), 2.55 (s, 3H), 2.20 (s, 3H), 1.62 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 152.1, 145.2, 138.0, 135.1, 128.5, 128.4, 128.3, 127.8, 127.1, 124.5, 44.7, 26.5, 21.5, 21.4.

4.3.7. 1-(4-(1-(4-bromophenyl)ethyl)phenyl)ethan-1-one ***(34)***

According to the general procedure B, the product **34** was obtained in (42.4 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 4.16 (q, J = 7.2 Hz, 1H), 2.56 (s, 3H), 1.63 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 151.2, 144.3, 135.3, 131.5, 129.3, 128.6, 127.7, 120.1, 44.2, 26.5, 21.4. **HRMS** (ESI) *m/z* calcd. for $C_{16}H_{16}BrO$ $[M + H]^+$ 303.0379, found 303.0381.

4.3.8. 1-(4-(1-([1,1′-biphenyl]-4-yl)ethyl)phenyl)ethan-1-one ***(35)***

According to the general procedure B, the product **35** was obtained in (39.2 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92–7.85 (m, 2H), 7.59–7.53 (m, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.44–7.38 (m, 2H), 7.36–7.23 (m, 5H), 4.23 (q, J = 7.2 Hz, 1H), 2.55 (s, 3H), 1.68 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 151.8, 144.4, 140.7, 139.2, 135.2, 128.7, 128.6, 127.9, 127.8, 127.2, 127.1, 126.9, 44.5, 26.5, 21.5. **HRMS** (ESI) *m/z* calcd. for $C_{22}H_{21}O$ $[M + H]^+$ 301.1587, found 301.1589.

4.3.9. methyl 4-(1-(4-acetylphenyl)ethyl)benzoate ***(36)***

According to the general procedure B, the product **36** was obtained in (33.9 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.33–7.23 (m, 4H), 4.25 (q, J = 7.2 Hz, 1H), 3.89 (s, 3H), 2.57 (s, 3H), 1.67 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 166.8, 150.9, 150.5, 135.4, 129.8, 128.6, 128.3, 127.8, 127.6, 52.0, 44.7, 26.5, 21.2. **HRMS** (ESI) *m/z* calcd. for $C_{18}H_{19}O_3$ $[M + H]^+$ 283.1329, found 283.1330.

4.3.10. 1-(3-(1-(4-acetylphenyl)ethyl)phenyl)ethan-1-one ***(37)***

According to the general procedure B, the product **37** was obtained in (36.7 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 2H), 7.85 (s, 1H), 7.82–7.77 (m, 1H), 7.42–7.37 (m, 2H), 7.31 (d, J = 8.4 Hz, 2H), 4.27 (q, J = 7.2 Hz, 1H), 2.58 (s, 3H), 2.57 (s, 3H), 1.69 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.1, 197.6, 151.1, 145.9, 137.3, 135.3, 132.3, 128.7, 128.6, 127.7, 127.0, 126.6, 44.6,

26.6, 26.5, 21.4. **HRMS** (ESI) *m/z* calcd. for $C_{18}H_{19}O_2$ $[M + H]^+$ 267.1380, found 267.1380.

*4.3.11. 3-(1-(4-acetylphenyl)ethyl)benzonitrile **(38)***

According to the general procedure B, the product **38** was obtained in (30.7 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.4 Hz, 2H), 7.53–7.48 (m, 2H), 7.47–7.37 (m, 2H), 7.28 (d, J = 8.4 Hz, 2H), 4.24 (q, J = 7.2 Hz, 1H), 2.59 (s, 3H), 1.67 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 150.1, 146.8, 135.6, 132.2, 131.1, 130.1, 129.3, 128.8, 127.7, 118.8, 112.6, 44.4, 26.6, 21.2. **HRMS** (ESI) *m/z* calcd. for $C_{17}H_{16}NO$ $[M + H]^+$ 250.1226, found 250.1227.

*4.3.12. 1-(4-(1-(4-nitrophenyl)ethyl)phenyl)ethan-1-one **(39)***

According to the general procedure B, the product **39** was obtained in (20.5 mg, 38% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.32 (q, J = 7.2 Hz, 1H), 2.58 (s, 3H), 1.70 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 152.8, 149.9, 146.5, 135.7, 128.8, 128.4, 127.8, 123.8, 44.7, 26.5, 21.2. **HRMS** (ESI) *m/z* calcd. for $C_{16}H_{16}NO_3$ $[M + H]^+$ 270.1125, found 270.1125.

*4.3.13. 1-(4-(1-(naphthalen-1-yl)ethyl)phenyl)ethan-1-one **(40)***

According to the general procedure B, the product **40** was obtained in (34 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 8.0 Hz, 3H), 7.76 (d, J = 8.0 Hz, 1H), 7.51–7.36 (m, 4H), 7.29 (d, J = 8.0 Hz, 2H), 4.94 (q, J = 7.2 Hz, 1H), 2.51 (s, 3H), 1.76 (d, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 152.4, 140.4, 135.1, 134.0, 131.5, 128.8, 128.6, 127.7, 127.3, 126.0, 125.4, 124.3, 123.7, 40.6, 26.5, 22.2.

*4.3.14. 1-(4-(1-(naphthalen-2-yl)ethyl)phenyl)ethan-1-one **(41)***

According to the general procedure B, the product **41** was obtained in (31.8 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, J = 6.4 Hz, 2H), 7.82–7.76 (m, 2H), 7.74 (d, J = 8.4 Hz, 1H), 7.68 (s, 1H), 7.49–7.39 (m, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.26 (dd, J_1 = 8.8 Hz, J_1 = 2.0 Hz, 1H), 4.35 (q, J = 7.2 Hz, 1H), 2.55 (s, 3H), 1.74 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 151.8, 142.7, 135.2, 133.4, 132.1, 128.6, 128.1, 127.9, 127.7, 127.6, 126.5, 126.1, 125.6, 125.4, 44.8, 26.5, 21.4. **HRMS** (ESI) *m/z* calcd. for $C_{20}H_{19}O$ $[M + H]^+$ 275.1430, found 275.1430.

*4.3.15. 1-(4-benzylphenyl)ethan-1-one **(42)***

According to the general procedure B, the product **42** was obtained in (10.1 mg, 30% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.3 Hz, 2H), 7.32–7.27 (m, 4H), 7.24–7.16 (m, 3H), 4.04 (s, 2H), 2.58 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 146.8, 140.1 135.3, 129.1, 129.0, 128.7, 126.4, 41.9, 26.6.

*4.3.16. 1-(4-(1-phenylpropyl)phenyl)ethan-1-one **(43)***

According to the general procedure B, the product **43** was obtained in (28.6 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.39–7.13 (m, 7H), 3.85 (t, J = 8.0 Hz, 1H), 2.55 (s, 3H), 2.09 (dt, J = 14.8 Hz, J = 7.6 Hz, 2H), 0.90 (d, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 150.8, 144.1, 135.2, 128.6, 128.5, 128.1, 127.8, 126.3, 53.2, 28.3, 26.5, 12.6. **HRMS** (ESI) *m/z* calcd. for $C_{17}H_{19}O$ $[M + H]^+$ 239.1430, found 239.1432.

*4.3.17. 1-(4-(1-phenylbutyl)phenyl)ethan-1-one **(44)***

According to the general procedure B, the product **44** was obtained in (37.8 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 2H), 7.39–7.11 (m, 7H), 3.96 (t, J = 8.0 Hz, 1H), 2.54 (s, 3H), 2.09–1.96 (m, 2H), 1.35–1.21 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 151.0, 144.2, 135.1, 128.5(3), 128.4(7), 128.0, 127.8, 126.3, 51.0, 37.5, 26.5, 21.0, 14.0. **HRMS** (ESI) *m/z* calcd. for $C_{18}H_{21}O$ $[M + H]^+$ 253.1587, found 253.1587.

*4.3.18. 1-(4-(1-phenylbut-3-en-1-yl)phenyl)ethan-1-one **(45)***

According to the general procedure B, the product **45** was obtained in (31.5 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, J = 6.4 Hz, 2H), 7.36–7.25 (m, 4H), 7.24–7.16 (m, 3H), 5.79–5.61 (m, 1H), 5.08–4.91 (m, 2H), 4.07 (t, J = 8.0 Hz, 1H), 2.89–2.77 (m, 2H), 2.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 150.0, 143.5, 136.1, 135.2, 128.6, 128.5, 128.1, 127.8, 126.5, 116.7, 51.1, 39.5, 26.5. **HRMS** (ESI) *m/z* calcd. for $C_{18}H_{19}O$ $[M + H]^+$ 251.1430, found 251.1431.

*4.3.19. 1-(4-(3-bromo-1-phenylpropyl)phenyl)ethan-1-one **(46)***

According to the general procedure B, the product **46** was obtained in (33.6 mg, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.38–7.27 (m, 4H), 7.27–7.18 (m, 3H), 4.28 (t, J = 8.0 Hz, 1H), 3.31 (t, J = 6.8 Hz, 2H), 2.63–2.53 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 149.0, 142.3, 135.6, 128.8, 128.7, 128.1, 127.8, 126.9, 49.0, 37.8, 31.6, 26.5. **HRMS** (ESI) *m/z* calcd. for $C_{17}H_{18}BrO$ $[M + H]^+$ 317.0536, found 317.0538.

*4.3.20. 5-(4-acetylphenyl)-5-phenylpentanenitrile **(47)***

According to the general procedure B, the product **47** was obtained in (30 mg, 54% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.39–7.27 (m, 4H), 7.25–7.18 (m, 3H), 3.98 (t, J = 8.0 Hz, 1H), 2.56 (s, 3H), 2.35 (t, J = 7.2 Hz, 2H), 2.28–2.15 (m, 2H), 1.67–1.54 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 149.5, 142.9, 135.5, 128.8, 128.7, 128.6, 127.9, 127.8, 127.6, 126.8, 119.3, 50.6, 34.1, 26.5, 23.8, 17.1. **HRMS** (ESI) *m/z* calcd. for $C_{19}H_{20}NO$ $[M + H]^+$ 278.1539, found 278.1541.

*4.3.21. methyl 5-(4-acetylphenyl)-5-phenylpentanoate **(48)***

According to the general procedure B, the product **48** was obtained in (38.3 mg, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.31–7.25 (m, 2H), 7.25–7.15 (m, 3H), 4.10 (q, J = 7.2 Hz, 2H), 3.97 (t, J = 7.6 Hz, 1H), 2.55 (s, 3H), 2.32 (t, J = 7.2 Hz, 2H), 2.17–2.05 (m, 2H), 1.70–1.52 (m, 2H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 173.3, 150.3, 143.7, 135.2, 128.6(1), 128.5(8), 128.0, 127.7, 126.5, 60.2, 51.1, 34.7, 34.0, 26.5, 23.3, 14.2. **HRMS** (ESI) *m/z* calcd. for $C_{21}H_{25}O_3$ $[M + H]^+$ 325.1798, found 325.1800.

*4.3.22. 4-(1-phenylethyl)-1,1′-biphenyl **(49)***

According to the general procedure B, the product **49** was obtained in (29.5 mg, 57% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59–7.54 (m, 2H), 7.53–7.48 (m, 2H), 7.44–7.37 (m, 2H), 7.34–7.23 (m, 7H), 7.22–7.16 (m, 1H), 4.19 (t, J = 7.2 Hz, 1H), 1.67 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.2, 145.5, 141.0, 138.9, 128.7, 128.4, 128.0, 127.6, 127.1, 127.0(2), 126.9(9), 126.1, 44.4, 21.8.

*4.3.23. 1-(1-phenylethyl)naphthalene **(50)***

According to the general procedure B, the product **50** was obtained in (24.2 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09–7.98 (m, 1H), 7.89–7.80 (m, 1H), 7.73 (d, J = 6.8 Hz, 1H), 7.49–7.36 (m, 4H), 7.30–7.20 (m, 4H), 7.20–7.11 (m, 1H), 4.91 (t, J = 7.2 Hz, 1H), 1.75 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 141.5, 134.0, 131.7, 128.7, 128.4, 127.6, 127.0, 125.9, 125.8, 125.4, 125.3, 124.3, 123.9, 40.5, 22.5.

*4.3.24. 2-(1-phenylethyl)naphthalene **(51)***

According to the general procedure B, the product **51** was obtained in (31.6 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82–7.75 (m, 2H), 7.72 (d, J = 8.8 Hz, 1H), 7.69 (s, 1H), 7.47–7.37 (m, 2H), 7.34–7.22 (m, 5H), 7.21–7.15 (m, 1H), 4.30 (t, J = 7.2 Hz, 1H), 1.72 (d, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.2, 143.7, 133.5, 132.1, 128.4, 127.9, 127.7(3), 127.7(0), 127.5, 126.8, 126.1, 125.9, 125.3(4), 125.3(2), 44.8, 21.7.

*4.3.25. 3-(1-phenylethyl)thiophene **(52)***

According to the general procedure B, the product **52** was obtained in (29.7 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 7.24–7.17 (m, 4H), 6.98–6.94 (m, 1H), 6.87 (dd, $J_1 = 5.2$ Hz, $J_1 = 1.2$ Hz, 1H), 4.15 (q, $J = 7.2$ Hz, 1H), 1.62 (d, $J = 7.2$ Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.2, 146.2, 128.4, 127.8, 127.4, 126.1, 125.3, 119.8, 40.8, 22.2.

*4.3.26. 3-(1-phenylethyl)pyridine **(53)***

According to the general procedure B, the product **53** was obtained in (21.3 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (d, $J = 7.6$ Hz, 2H), 7.48 (d, $J = 7.6$ Hz, 1H), 7.35–7.26 (m, 2H), 7.25–7.14 (m, 4H), 4.17 (q, $J = 7.2$ Hz, 1H), 1.66 (d, $J = 7.2$ Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.3, 147.5, 144.9, 141.5, 134.9, 128.5, 127.5, 126.4, 123.3, 42.4, 21.5.

*4.3.27. 4-(1-phenylethyl)pyridine **(54)***

According to the general procedure B, the product **54** was obtained in (19.1 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (s, 2H), 7.34–7.27 (m, 2H), 7.25–7.16 (m, 3H), 7.13 (d, $J = 5.2$ Hz, 2H), 4.11 (q, $J = 7.2$ Hz, 1H), 1.63 (d, $J = 7.2$ Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.0, 149.8, 144.4, 128.6, 127.6, 126.6, 122.9, 44.2, 21.0.

Declaration of competing interest

The authors declare that they have no known competing finical interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132152.

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