Supporting Information

Tunable C-H Arylation and Acylation of Azoles with Carboxylic

Acids by Pd/Cu Cooperative Catalysis

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1. General Information

All products reported in the manuscript have been previously described in literature unless noted otherwise. The reactions were carried out in Schlenk tube of 25 mL under N_2 atmosphere. Reagents were used as received unless otherwise noted, and solvents were purified according to the standard operation procedures.

UV-Vis absorption was recorded at room temperature on a Jiapeng-Shanghai ZF-7 UV analyzer. Column chromatography was performed using Silica Gel 60 (300-400 mesh). The reactions were monitored by GC and GC-MS, GC analysis was performed on GC 2014, and GC-MS results were recorded on GC-MS QP2010. The ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Brucker ADVANCE III spectrometer at 400 MHz, 100 MHz and 376 MHz respectively, and chemical shifts were reported in parts per million (ppm). All solvents and reagents were purchased from Tansoole, Meryer, Heowns, Energy Chemical, Alfa Aesar and Aladdin.

2. Optimization of Reaction Conditions^a

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		+ N	Solver	nt heat N	<u> </u>	=\ ⁺ N -	$\overline{\ }$	
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		2a			<u>(</u>	3a	\checkmark	
-	Entry	[Pd]	[Cu]	Ligand	Anhydride	Base	Solvent -	Total Yield (3a/4a) ^b
-	1	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	Су	>99% (25/1)
	2	-	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	Су	trace (-/-)
	3	Pd(TFA) ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	Су	94% (23/1)
	4	PdCl ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	Су	>99% (16/1)
	5	Pd(AcAc) ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	Су	>99% (12/1)
	6	Pd ₂ (dba) ₃	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	Су	>99% (2.5/1)
	7	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	-	Су	trace (-/-)
	8	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	Et ₃ N	Су	90% (29/1)
	9	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	Na ₂ CO ₃	Су	80% (12/1)
	10	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	KHCO ₃	Су	74% (7/1)
	11	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	K ₂ CO ₃	Су	47% (7:1)
	12	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	Cs ₂ CO ₃	Су	11% (5/1)
	13	Pd(OAc) ₂	-	dppp	Boc ₂ O	NaHCO ₃	Су	trace (-/-)
	14	Pd(OAc) ₂	Cu(OAc) ₂	dppp	Boc ₂ O	NaHCO ₃	Су	83% (3/1)
	15	Pd(OAc) ₂	CuBr ₂	dppp	Boc ₂ O	NaHCO ₃	Су	58% (28/1)
	16	Pd(OAc) ₂	CuCl	dppp	Boc ₂ O	NaHCO ₃	Су	88% (17/1)
	17	Pd(OAc) ₂	CuBr	dppp	Boc ₂ O	NaHCO ₃	Су	53% (17/1)
	18	Pd(OAc) ₂	Cu	dppp	Boc ₂ O	NaHCO ₃	Су	trace (-/-)
	19	Pd(OAc) ₂	CuCl ₂	-	Boc ₂ O	NaHCO ₃	Су	trace (-/-)
	20 ^c	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	Су	57% (2/1)
	21 ^d	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	Су	68% (3/1)
	22 ^e	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	Су	91% (6/1)
	23 ^f	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	Су	93% (12/1)
	24	Pd(OAc) ₂	CuCl ₂	PPh_3	Boc ₂ O	NaHCO ₃	Су	87% (1/9)
	25	Pd(OAc) ₂	CuCl ₂	CyPh ₂ P	Boc ₂ O	NaHCO ₃	Су	92% (1/5.5)
	26	Pd(OAc) ₂	CuCl ₂	Xantphos	Boc ₂ O	NaHCO ₃	Су	21% (1/2.5)
	27	Pd(OAc) ₂	CuCl ₂	dppm	Boc ₂ O	NaHCO ₃	Су	trace (-/-)
	28	Pd(OAc) ₂	CuCl ₂	dppe	Boc ₂ O	NaHCO ₃	Су	39% (1/7)
	29	Pd(OAc) ₂	CuCl ₂	dppb	Boc ₂ O	NaHCO ₃	Су	89% (1.3/1)
	30	Pd(OAc) ₂	CuCl ₂	dpppe	Boc ₂ O	NaHCO ₃	Су	>99% (1/2)
	31	Pd(OAc) ₂	CuCl ₂	dpph	Boc ₂ O	NaHCO ₃	Су	>99% (1/10)
	32	Pd(OAc) ₂	CuCl ₂	dppf	Boc ₂ O	NaHCO ₃	Су	12% (4/1)
	33	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	Toluene	74% (11/1)
	34	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	THF	81% (4/1)
	35	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	Dioxane	33% (10/1)
	36	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	PhOMe	16% (16/1)
	37	Pd(OAc) ₂	CuCl ₂	dppp	Boc ₂ O	NaHCO ₃	DMF	trace (-/-)
	38	Pd(OAc) ₂	CuCl ₂	dppp	-	NaHCO ₃	Су	N.D. (-/-)
	39	Pd(UAc) ₂	CuCl ₂	dppp	PIV ₂ O	NaHCO ₃	Су	16% (20/1)
	40	Pd(UAc) ₂	CuCl ₂	dppp	AC ₂ U	NaHCO ₃	Су	N.D. (-/-)
	41	Pd(UAc) ₂	CuCl ₂	dppp		NaHCO ₃	Су	trace (-/-)
	42 ⁹	Pa(UAC) ₂	CuCl ₂	appp	BOC ⁵ O	NAHCO ₃	Cy	96% (9/1)

^aReaction conditions: **1a** (0.75 mmol), **2a** (0.5 mmol), Pd catalyst (1 mol%, Pd/P =1:20), Cu salt (10 mol%), Phosphine ligand, Boc₂O (1.5 equiv), base (1.5 equiv), cyclohexane (Cy, 6 mL), 120 °C, 12 h, N₂ atmosphere. ^bGC yield using tridecane as an internal standard. ^c1 mol% dppp. ^d2 mol% dppp. ^e5 mol% dppp. ^f8 mol% dppp. ^g110 °C.

3. General Experimental Procedures



General procedure I for the Pd/Cu cooperatively catalyzed C-H arylation of azoles with carboxylic acids: An oven dried 25 mL Schlenk tube was charged with carboxylic acid 1 (0.75 mmol), $Pd(OAc)_2$ (0.005 mmol, 1 mol %), $CuCl_2$ (0.05 mmol, 10 mol %), dppp (0.05 mmol, 10 mol %) and NaHCO₃ (0.75 mmol, 1.5 equiv), then azoles 2 (0.5 mmol), Boc_2O (0.75 mmol, 1.5 equiv) and cyclohexane (6.0 mL) were added under a N₂ atmosphere. The reaction mixture was reacted at 120 °C for 12 h. After completion of the reaction, the reaction mixture was concentrated under vacuo. The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether-ethyl acetate-dichloromethane as eluent.



General procedure II for the Pd/Cu cooperative catalyzed the C-H arylation of azoles with carboxylic acids: An oven dried 25 mL Schlenk tube was charged with 2-naphthoic acid 1u (0.5 mmol), $Pd(OAc)_2$ (0.005 mmol, 1 mol %), $CuCl_2$ (0.05 mmol, 10 mol %), dppp (0.05 mmol, 10 mol %) and NaHCO₃ (0.75 mmol, 1.5 equiv), then azoles 2 (0.75 mmol), Boc_2O (0.5 mmol, 1.0 equiv) and cyclohexane (6.0 mL) were added under a N₂ atmosphere. The reaction mixture was reacted at 120 °C for 12 h. After completion of the reaction, the reaction mixture was concentrated under vacuo. The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether-ethyl acetate-dichloromethane as eluent.



General procedure III for the Pd/Cu cooperative catalyzed the C-H acylation of azoles with carboxylic acids: An oven dried 25 mL Schlenk tube was charged with 2-naphthoic acid 1 (0.75 mmol), $Pd(OAc)_2$ (0.005 mmol, 1 mol %), $CuCl_2$ (0.05 mmol, 10 mol %), Ph_2PCy (0.1 mmol, 20 mol %) and $NaHCO_3$ (0.75 mmol, 1.5 equiv), then azoles 2 (0.5 mmol), Boc_2O (0.5 mmol, 1.0 equiv) and cyclohexane (6.0 mL) were added under a N_2 atmosphere. The reaction mixture was

reacted at 120 °C for 12 h. After completion of the reaction, the reaction mixture was concentrated under vacuo. The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether-ethyl acetate-dichloromethane as eluent.



2-phenylbenzo[*d*]**oxazole (3a):**¹ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 100:1 (v:v) to afford a white solid in 95% yield (92.7 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.20-8.18 (m, 2H), 7.73-7.69 (m, 1H), 7.53-7.49 (m, 1H); 7.47-7.44 (m, 3H), 7.31-7.26 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 163.0, 150.8, 142.1, 131.5, 128.9, 127.6, 127.2, 125.1, 124.6, 120.0, 110.6. Characterization data matched those previously reported.



2-(*o***-tolyl)benzo[***d***]oxazole (3b):² The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 50:1 (v:v) to afford a white solid in 76% yield (79.5 mg). ¹H NMR (CDCl₃, 400 MHz) \delta 8.11-8.09 (m, 1H), 7.75-7.71 (m, 1H), 7.54-7.49 (m, 1H), 7.36-7.32 (m, 1H), 7.31-7.25 (m, 4H), 2.74 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) \delta 163.4, 150.3, 142.1, 138.3, 131.8, 130.9, 129.9, 126.2, 126.0, 125.0, 124.3, 120.1, 110.5, 22.2. Characterization data matched those previously reported.**

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2-(*m***-tolyl)benzo[***d***]oxazole (3c):¹ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 100:1 (v:v) to afford a white solid in 70% yield (73.2 mg). ¹H NMR (CDCl₃, 400 MHz) \delta 8.03 (s, 1H), 7.98 (d,** *J* **= 7.6 Hz, 1H), 7.72-7.68 (m, 1H), 7.54-7.49 (m, 1H), 7.34 (t,** *J* **= 7.6 Hz, 1H), 7.30-7.26 (m, 3H), 2.39 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) \delta 163.3, 150.7, 142.1, 138.7, 132.4, 128.8, 128.2, 127.0, 125.0, 124.8, 124.5, 120.0, 110.6, 21.3. Characterization data matched those previously reported.**



2-(*p***-tolyl)benzo[***d***]oxazole (3d):³ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 100:1 (v:v) to afford a white solid in 82% yield (85.8 mg). ¹H NMR (CDCl₃, 400**

MHz) δ 8.08 (d, J = 8.4 Hz, 2H), 7.72-7.68 (m, 1H), 7.53-7.49 (m, 1H), 7.29-7.26 (m, 4H), 2.38 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 163.3, 150.7, 142.1, 129.7, 127.6, 124.9, 124.5, 124.4, 119.8, 110.5, 21.7. Characterization data matched those previously reported.



2-(4-*tert***-butylphenyl)benzo[***d***]oxazole (3e):⁵ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 50:1 (v:v) to afford a white solid in 82% yield (103.0 mg). ¹H NMR (CDCl₃, 400 MHz) \delta 8.10 (d,** *J* **= 8.4 Hz, 2H), 7.69-7.67 (m, 1H), 7.49-7.44 (m, 3H), 7.27-7.21 (m, 2H), 1.28 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz) \delta 163.2, 155.1, 150.7, 142.2, 127.4, 125.9, 124.8, 124.4, 124.3, 119.8, 110.5, 35.0, 31.1. Characterization data matched those previously reported.**



2-(4-cyclohexylphenyl)benzo[*d*]**oxazole (3f):** The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 70% yield (97.1 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.18-8.15 (m, 2H), 7.78-7.74 (m, 1H), 7.57-7.53 (m, 1H), 7.35-7.30 (m, 4H), 2.59-2.53 (m, 1H), 1.92-1.84 (m, 4H), 1.78-1.74 (m, 1H), 1.50-1.35 (m, 4H), 1.31-1.20 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 163.2, 152.0, 150.6, 142.1, 127.6, 127.4, 124.8, 124.6, 124.4, 119.8, 110.4, 44.6, 34.1, 26.7, 26.0. CAS: 305360-81-0.



2-(2-methoxyphenyl)benzo[*d*]**oxazole (3g):**⁶ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 5:1 (v:v) to afford a white solid in 72% yield (91.2 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.13 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.85-7.80 (m, 1H), 7.60-7.56 (m, 1H), 7.50-7.46 (m, 1H), 7.35-7.31 (m, 2H), 7.10-7.05 (m, 2H), 4.00 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 161.5, 158.4, 150.2, 142.1, 132.7, 131.2, 124.9, 124.2, 120.6, 120.1, 116.1, 112.0, 110.4, 56.1. Characterization data matched those previously reported.



2-(4-methoxyphenyl)benzo[*d*]**oxazole (3h):**¹ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 60% yield (75.9 mg). ¹H

NMR (CDCl₃, 400 MHz) δ 8.15-8.11 (m, 2H), 7.69-7.65 (m, 1H), 7.49-7.46 (m, 1H), 7.29-7.22 (m, 2H), 6.98-6.94 (m, 2H), 3.82 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 163.2, 162.3, 150.6, 142.2, 129.4, 124.6, 124.4, 119.7, 119.6, 114.3, 110.4, 55.4. Characterization data matched those previously reported.



2-(4-phenoxyphenyl)benzo[*d*]**oxazole (3i):** The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 78% yield (112.1 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.13-8.09 (m, 2H), 7.67-7.63 (m, 1H), 7.47-7.43 (m, 1H), 7.32-7.27 (m, 2H), 7.26-7.19 (m, 2H), 7.11-7.07 (m, 1H), 7.01-6.98 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.7, 160.6, 155.7, 150.6, 142.1, 130.0, 129.4, 124.8, 124.5, 124.3, 121.6, 119.9, 119.7, 118.1, 110.4. CAS: 142629-40-1.



2-(4-acetoxyphenyl)benzo[*d*]**oxazole (3j):**¹⁰ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 5:1 (v:v) to afford a white solid in 80% yield (101.3 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.27 (d, *J* = 8.4 Hz, 2H), 7.78-7.74 (m, 1H), 7.58-7.54 (m, 1H), 7.36-7.32 (m, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 2.33 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 168.9, 162.2, 153.1, 150.7, 142.0, 128.9, 125.1, 124.7, 124.6, 122.2, 119.9, 110.5, 21.1. Characterization data matched those previously reported.



2-(4-trifluoromethoxyphenyl)benzo[*d*]**oxazole (3k):** The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 50:1 (v:v) to afford a white solid in 90% yield (125.6 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.21-8.17 (m, 2H), 7.70-7.66 (m, 1H), 7.51-7.46 (m, 1H), 7.29-7.25 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 161.6, 151.4(d, *J*_{C-F} = 1.8 Hz), 150.7, 141.9, 129.2, 125.6, 125.3, 124.7, 121.0, 120.3 (q, *J*_{C-F} = 256.8 Hz), 120.1, 110.6. ¹⁹F NMR (CDCl₃, 376 MHz) δ 57.7. HRMS(APCI): calcd for C₁₄H₈NO₂F₃ [M+H]⁺ m/z 280.0580; found 280.2579. m.p. 121.5-122.1 °C.



2-([1,1'-biphenyl]-2-yl)benzo[d]oxazole (31):8 The title compound was prepared according to the

general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a colorless liquid in 84% yield (114.0 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.10 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.57-7.53 (m, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.31-7.23 (m, 8H); ¹³C NMR (CDCl₃, 100 MHz) δ 163.7, 150.6, 142.3, 141.6, 140.9, 131.0, 130.9, 128.7, 128.0, 127.4, 127.2, 126.2, 124.8, 124.2, 120.0, 110.4. Characterization data matched those previously reported.



2-([1,1'-biphenyl]-3-yl)benzo[*d*]**oxazole (3m):**⁹ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 81% yield (109.9 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.41 (s, 1H), 8.13 (dt, *J*₁ = 8.0 Hz, *J*₂ = 1.6 Hz, 1H), 7.72-7.69 (m, 1H), 7.67-7.64 (m, 1H), 7.60-7.58 (m, 2H), 7.50-7.46 (m, 2H), 7.40-7.36 (m, 2H), 7.32-7.25 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.9, 150.7, 142.1, 141.9, 140.0, 130.2, 129.4, 128.9, 127.8, 127.6, 127.2, 126.3, 126.2, 125.2, 124.6, 120.0, 110.6. Characterization data matched those previously reported.



2-([1,1'-biphenyl]-4-yl)benzo[*d*]**oxazole (3n):**⁷ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 90% yield (122.1 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.29 (d, *J* = 8.4 Hz, 2H), 7.78-7.76 (m, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.56-7.54 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.38-7.30 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.8, 150.7, 144.1, 142.1, 139.9, 128.9, 128.0, 127.5, 127.1, 125.9, 125.0, 124.5, 119.9, 110.5. Characterization data matched those previously reported.



2-(4-methoxy-2-methylphenyl)benzo[*d*]oxazole (3o): ¹⁹ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 52% yield (62.2 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.13-8.11 (m, 1H), 7.77-7.73 (m, 1H), 7.55-7.50 (m, 1H), 7.33-7.27 (m, 2H), 6.85-6.82 (m, 2H), 3.82 (s, 3H), 2.79 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 163.4, 161.4, 150.1, 142.2, 140.9, 131.6, 124.4, 124.1, 119.7, 118.8, 116.9, 111.4, 110.2, 55.2, 22.5. Characterization data matched those previously reported.



2-(2,4-dimethylphenyl)benzo[*d*]**oxazole (3p):**²⁰ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 56% yield (62.5 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.80-7.75 (m, 1H), 7.58-7.53 (m, 1H), 7.35-7.30 (m, 2H), 7.14-7.12 (m, 2H), 2.77 (s, 3H), 2.37 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 163.6, 150.2, 142.2, 141.2, 138.7, 132.5, 129.9, 126.8, 124.7, 124.2, 123.4, 119.9, 110.3, 22.1, 21.3. Characterization data matched those previously reported.



2-(4-fluoro-2-methylphenyl)benzo[*d*]**oxazole (3q):** The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 75% yield (85.2 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.05-8.01 (m, 1H), 7.69-7.64 (m, 1H), 7.25-7.20 (m, 2H), 6.92-6.87 (m, 2H), 2.68 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 165.1, 162.5 (d, *J*_{C-F} = 18.8 Hz), 150.10, 142.0 (d, *J*_{C-F} = 5.7 Hz), 141.8, 132.0 (d, *J*_{C-F} = 9.1 Hz), 125.0, 124.4, 122.4 (d, *J*_{C-F} = 2.9 Hz), 120.0, 118.4 (d, *J*_{C-F} = 21.3 Hz), 113.2 (d, *J*_{C-F} = 21.4 Hz), 110.3, 22.2 (d, *J*_{C-F} = 1.1 Hz); ¹⁹F NMR (CDCl₃, 376 MHz) δ 109.2. CAS: 2417741-78-5.



2-(2-fluoro-4-methylphenyl)benzo[*d*]**oxazole (3r):** The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 58% yield (65.9 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.05-8.01 (m, 1H), 7.69-7.64 (m, 1H), 7.25-7.20 (m, 2H), 6.92-6.87 (m, 2H), 2.68 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 160.6 (d, *J*_{C-F} = 256.9 Hz), 159.6 (d, *J*_{C-F} = 5.6 Hz), 150.2, 144.4 (d, *J*_{C-F} = 8.4 Hz), 141.7, 130.0 (d, *J*_{C-F} = 2.0 Hz), 125.2 (d, *J*_{C-F} = 3.1 Hz), 125.1, 124.5, 120.1, 117.4 (d, *J*_{C-F} = 21.2 Hz), 112.5 (d, *J*_{C-F} = 10.5 Hz), 110.5, 21.4 (d, *J*_{C-F} = 1.0 Hz); ¹⁹F NMR (CDCl₃, 376 MHz) δ 111.0. CAS: 37135-23-2.



2-(4-chloro-2-methylphenyl)benzo[*d*]**oxazole (3s):** The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with

petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 76% yield (92.6 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.79-7.75 (m, 1H), 7.56-7.52 (m, 1H), 7.35-7.31 (m, 2H), 7.30-7.26 (m, 2H), 2.76 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.3, 150.1, 142.0, 140.6, 136.7, 131.6, 131.0, 126.2, 125.2, 124.6, 124.4, 120.1, 110.4, 22.10. HRMS(ESI): calcd for C₁₄H₁₀NOCl [M+H]⁺ m/z 244.0524; found 244.0523. m.p. 113.9-115.2 °C.



2-(4-fluorophenyl)benzo[*d*]**oxazole (3t):**² The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 88% yield (93.8 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.22-8.17 (m, 2H), 7.72-7.68 (m, 1H), 7.53-7.49 (m, 1H), 7.31-7.27 (m, 2H), 7.17-7.13 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 166.0, 163.5, 162.1, 150.7, 141.9, 129.8 (d, $J_{C-F} = 8.8$ Hz), 124.9 (d, $J_{C-F} = 48.1$ Hz), 123.4 (d, $J_{C-F} = 3.2$ Hz), 119.9, 116.2 (d, $J_{C-F} = 22.1$ Hz), 110.6. ¹⁹F NMR (CDCl₃, 376 MHz) δ 107.5. Characterization data matched those previously reported.



2-(4-chlorophenyl)benzo[*d*]**oxazole (3u):**³ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 82% yield (94.2 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.13-8.09 (m, 2H), 7.71-7.67 (m, 1H), 7.52-7.48 (m, 1H), 7.44-7.41 (m, 2H), 7.31-7.26 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.0, 150.7, 144.0, 137.8, 129.3, 128.8, 125.6, 125.3, 124.7, 120.0, 110.6. Characterization data matched those previously reported.



2-[4-(trifluoromethyl)phenyl]benzo[*d*]oxazole (3v):¹ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 81% yield (106.6 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.28 (d, *J* = 8.0 Hz, 2H), 7.74-7.69 (m, 3H), 7.55-7.51 (m, 1H), 7.34-7.29 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 161.4, 150.8, 141.8, 132.9 (q, *J*_{C-F} = 32.5 Hz), 130.3, 127.8, 125.9 (q, *J*_{C-F} = 3.7 Hz), 125.8, 124.9, 122.3 (q, *J*_{C-F} = 270.8 Hz), 120.3, 110.8. ¹⁹F NMR (CDCl₃, 376 MHz) δ 63.0. Characterization data matched those previously reported.



2-[4-benzoylphenyl]benzo[d]oxazole (3w):¹¹ The title compound was prepared according to the

general procedure I (130 °C) and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 60% yield (89.8 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.73-7.67 (m, 3H), 7.52-7.46 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.29-7.24 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 195.8, 161.9, 150.8, 142.0, 139.7, 137.1, 132.8, 130.4, 130.4, 130.0, 128.4, 127.4, 125.7, 124.8, 120.3, 110.7. Characterization data matched those previously reported.



2-(4-vinylphenyl)benzo[*d*]**oxazole (3x):**¹² The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 72% yield (79.7 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.14-8.11 (m, 2H), 7.70-7.66 (m, 1H), 7.50-7.44 (m, 3H), 7.28-7.23 (m, 2H), 6.68 (dd, J_1 = 17.6 Hz, J_2 = 11.2 Hz, 1H), 5.79 (dd, J_1 = 17.6 Hz, J_2 = 0.8 Hz, 1H) 5.29 (dd, J_1 = 11.2 Hz, J_2 = 0.8 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.8, 150.7, 142.1, 140.6, 136.0, 127.8, 126.6, 126.2, 125.1, 124.6, 119.9, 116.0, 110.5. Characterization data matched those previously reported.



2-(naphthalen-1-yl)benzo[*d*]**oxazole (3y):**¹ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 89% yield (112.5 mg). ¹H NMR (CDCl₃, 400 MHz) δ 9.46 (d, *J* = 8.8 Hz, 1H), 8.42 (dd, *J*₁ = 7.2 Hz, *J*₂ = 0.8 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.89-7.86 (m, 1H,)7.72-7.68 (m, 1H), 7.64-7.57 (m, 3H), 7.41-7.37 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.8, 150.1, 142.3, 133.9, 132.3, 130.7, 129.3, 128.6, 127.9, 126.4, 126.3, 125.2, 124.9, 124.5, 123.6, 120.2, 110.5. Characterization data matched those previously reported.



2-(naphthalen-2-yl)benzo[*d*]**oxazole (3z):**¹ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 90% yield (113.8 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.70 (s, 1H), 8.24 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.92-7.88 (m, 2H), 7.83-7.80 (m, 1H), 7.76-7.71 (m, 1H), 7.56-7.53 (m, 1H), 7.50-7.46 (m, 2H), 7.32-7.27 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 163.2, 150.8, 142.2, 134.7, 133.0, 128.9, 128.8, 128.1, 127.9, 127.8, 126.9, 125.2, 124.6, 124.4, 123.9, 120.0, 110.6. Characterization data matched those previously reported.



2-(benzo[*b***]thiophen-2-yl)benzo[***d***]oxazole (3aa):¹³ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 66% yield (82.9 mg). ¹H NMR (CDCl₃, 400 MHz) \delta 8.08 (s, 1H), 7.85-7.82 (m, 2H), 7.73-7.69 (m, 1H), 7.54-7.50 (m, 1H), 7.38-7.35 (m, 2H), 7.32-7.29 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) \delta 159.0, 150.7, 142.0, 141.2, 139.4, 129.3, 126.8, 126.4, 125.5, 125.1, 124.9, 124.9, 122.6, 120.1, 110.5. Characterization data matched those previously reported.**



2-(furan-3-yl)benzo[*d*]**oxazole (3ab):**⁴ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 60% yield (55.6 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.22 (s, 1H), 7.75-7.70 (m, 1H), 7.55-7.52 (m, 2H), 7.36-7.32 (m, 2H), 7.03 (d, *J* = 1.6 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 158.3, 150.18, 144.3, 144.3, 141.7, 124.9, 124.5, 119.6, 115.4, 110.3, 108.9. Characterization data matched those previously reported.



2-(thiophen-3-yl)benzo[*d*]**oxazole (3ac):**⁴ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a light yellow solid in 75% yield (75.5 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.10 (dd, J_1 = 2.8 Hz, J_2 = 1.2 Hz, 1H), 7.70 (dd, J_1 = 5.2 Hz, J_2 = 1.2 Hz, 1H), 7.67-7.65 (m, 1H), 7.47-7.44 (m, 1H), 7.35 (dd, J_1 = 5.2 Hz, J_2 = 3.2 Hz, 1H), 7.26-7.23 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 159.6, 150.3, 141.8, 129.2, 128.0, 126.9, 126.6, 125.0, 124.5, 119.8, 110.4. Characterization data matched those previously reported.



(E)-2-styrylbenzo[*d*]oxazole (3ad):¹⁴ The title compound was prepared according to the general procedure I (4 mol % Pd(OAc)₂, 130 °C) and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 58% yield (64.2 mg). ¹H NMR (CDCl₃, 400 MHz) δ 7.69 (d, *J* = 16.4 Hz, 1H), 7.64-7.61 (m, 1H), 7.51-7.48 (m, 2H), 7.45-7.40 (m, 1H), 7.34-7.22 (m, 5H), 6.98 (d, *J* = 16.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.7, 150.3, 142.1, 139.4, 135.1, 129.7, 128.9, 127.5, 125.2, 124.5, 119.8, 113.8, 110.3. Characterization data matched those previously reported.



(E)-2-(1,2-diphenylvinyl)benzo[*d*]oxazole (3ae):¹⁵ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 84% yield (124.9 mg). ¹H NMR (CDCl₃, 400 MHz) δ 7.95 (s, 1H), 7.72-7.69 (m, 1H), 7.51-7.48 (m, 1H), 7.46-7.42 (m, 3H), 7.39-7.37 (m, 2H), 7.31-7.25 (m, 2H), 7.18-7.13 (m, 3H), 7.10-7.08 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 164.6, 150.5, 142.2, 136.2, 135.6, 135.0, 130.3, 129.9, 129.1, 129.0, 128.6, 128.4, 128.2, 125.1, 124.3, 120.2, 110.3. Characterization data matched those previously reported.



2-(naphthalen-2-ylmethyl)benzo[*d*]**oxazole (3af):**²⁴ The title compound was prepared according to the general procedure I (dpph, 130 °C) and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a light yellow solid in 35% yield (45.4 mg). ¹H NMR (CDCl₃, 400 MHz) δ 7.82–7.79 (m, 4H), 7.72–7.68 (m, 1H), 7.50–7.43 (m, 4H), 7.31–7.25 (m, 2H), 4.42 (s, 2H); ¹³C NMR (101 MHz, CDCl₃): δ 165.1, 151.1, 141.3, 133.5, 132.5, 132.2, 128.5, 127.7, 127.7, 127.6, 126.9, 126.2, 125.9, 124.7, 124.2, 119.8, 110.4, 35.4. Characterization data matched those previously reported.



5-methyl-2-(naphthalen-2-yl)benzo[*d*]**oxazole** (**3ag**):¹¹ The title compound was prepared according to the general procedure II and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 69% yield (89.5 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.67 (s, 1H), 8.22 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.91-7.87 (m, 2H), 7.83-7.78 (m, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.51-7.45 (m, 2H), 7.33 (s, 1H), 7.10 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 2.44 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.7, 151.1, 140.0, 135.7, 134.6, 132.98, 128.9, 128.7, 127.9, 127.8, 127.7, 126.8, 125.9, 124.6, 123.9, 119.3, 110.7, 21.8. Characterization data matched those previously reported.



5-chloro-2-(naphthalen-2-yl)benzo[*d*]**oxazole (3ah):** The title compound was prepared according to the general procedure II and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 85% yield (118.9)

mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.60 (s, 1H), 8.13 (dd, $J_1 = 8.8$ Hz, $J_2 = 1.6$ Hz, 1H), 7.86-7.82 (m, 2H), 7.79-7.72 (m, 1H), 7.64 (s, 1H), 7.49-7.42 (m, 2H), 7.38 (d, J = 8.4 Hz, 1H), 7.20 (dd, $J_1 = 8.4$ Hz, $J_2 = 4.0$ Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 164.4, 149.3, 143.3, 134.8, 132.8, 130.0, 128.9, 128.8, 128.4, 128.0, 127.9, 126.9, 125.3, 123.8, 119.9, 111.2. Characterization data matched those previously reported. CAS: 95888-09-8.



2-(naphthalen-2-yl)benzo[*d*]**thiazole (3ai):**¹ The title compound was prepared according to the general procedure II and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 70% yield (91.5 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.53 (s, 1H), 8.18 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.94-7.88 (m, 3H), 7.84 (t, J = 3.4 Hz, 1H), 7.53-7.47 (m, 3H), 7.37 (t, J = 7.6 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 168.0, 154.2, 135.1, 134.5, 133.1, 130.9, 128.8, 127.8, 127.5, 127.4, 126.8, 126.3, 125.2, 124.4, 123.2, 121.6. Characterization data matched those previously reported.



2-(naphthalen-2-yl)oxazole (3aj):¹¹ The title compound was prepared according to the general procedure II and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 63% yield (61.5 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.52 (s, 1H), 8.12 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.91-7.87 (m, 2H), 7.83-7.81 (m, 1H), 7.71 (d, J = 0.8 Hz, 1H), 7.51-7.47 (m, 2H), 7.26 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.0, 138.6, 134.0, 132.9, 128.6, 128.54, 128.5, 127.8, 127.1, 126.6, 126.2, 124.7, 123.2. Characterization data matched those previously reported.



2-(naphthalen-2-yl)-5-phenyloxazole (3ak):¹ The title compound was prepared according to the general procedure II and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 92% yield (124.8 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.52 (s, 1H), 8.14 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.90-7.85 (m, 2H), 7.81-7.79 (m, 1H), 7.70 (d, J = 7.2 Hz, 2H), 7.50-7.45 (m, 2H), 7.44 (s, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 161.1, 151.3, 134.0, 132.9, 128.8, 128.6, 128.5, 128.3, 127.9, 127.8, 127.1, 126.6, 126.0, 124.6, 124.1, 123.5, 123.1. Characterization data matched those previously reported.



2-(naphthalen-2-yl)thiazole (3al):¹⁶ The title compound was prepared according to the general procedure II and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a yellow solid in 78% yield (82.4 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.42 (s, 1H), 8.06 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.91-7.86 (m, 3H), 7.83-7.80 (m, 1H), 7.51-7.46 (m, 2H), 7.31 (d, J = 3.2 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 168.4, 143.7, 134.0, 133.2, 130.9, 128.7, 128.5, 127.7, 126.9, 126.7, 125.9, 124.0, 118.9. Characterization data matched those previously reported.



2-(benzo[*d*][1,3]dioxol-5-yl)benzo[*d*]oxazole (3am):⁹ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 76% yield (90.9 mg). ¹H NMR (CDCl₃, 400 MHz) δ 7.67 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.63-7.59 (m, 1H), 7.54 (d, J = 1.6 Hz, 1H), 7.42-7.38 (m, 1H), 7.22-7.16 (m, 2H), 6.78 (d, J = 8.4 Hz, 1H), 5.90 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.7, 150.5, 150.4, 148.1, 142.0, 124.6, 124.4, 122.6, 121.0, 119.6, 110.3, 108.6, 107.5, 101.6. Characterization data matched those previously reported.



2-(3,4,5-trimethoxyphenyl)benzo[*d*]**oxazole (3an):**¹⁸ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 5:1 (v:v) to afford a light yellow solid in 83% yield (118.3 mg). ¹H NMR (CDCl₃, 400 MHz) δ 7.78-7.75 (m, 1H), 7.59-7.56 (m, 1H), 7.50 (s, 2H), 7.36-7.34 (m, 2H), 3.99 (s, 6H), 3.94 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.8, 153.5, 150.7, 142.0, 141.0, 125.0, 124.6, 122.2, 119.8, 110.4, 104.7, 60.9, 56.3. Characterization data matched those previously reported.



2-(6-(3-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)benzo[*d*]**oxazole (3ao):** The title compound was prepared according to the general procedure I (0.3 mmol 1, 0.2 mmol 2, 2.5 mL cyclohexane) and purified by column chromatography on silica gel and eluted with petroleum ether: dichloromethane = 2:1 (v:v) to afford a yellow solid in 88% yield (85.5 mg). ¹H NMR

(CDCl₃, 400 MHz) δ 8.78 (s, 1H), 8.32 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 8.05-8.00 (m, 3H), 7.64-7.60 (m, 2H), 7.55 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.40-7.35 (m, 2H), 7.00 (d, J = 8.4 Hz, 1H), 3.91 (s, 3H), 2.19 (d, J = 2.4 Hz, 6H), 2.11 (br, 3H), 1.81 (br, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 163.3, 158.9, 150.9, 142.3, 141.0, 139.0, 135.2, 132.6, 131.7, 129.3, 128.9, 127.9, 126.7, 125.9, 125.7, 125.1, 124.9, 124.6, 124.3, 123.9, 120.0, 112.1, 110.6, 55.2, 40.6, 37.2, 37.1, 29.1 HRMS (APCI): calcd for C₃₄H₃₁NO₂ [M+H]⁺ m/z 486.2428; found 486.2433. m.p. 265.6-266.8 °C.



4-(benzo[*d*]**oxazol-2-yl**)-*N*,*N*-**dipropylbenzenesulfonamide (3ap):** The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: dichloromethane = 1:2 (v:v) to afford a white solid in 72% yield (129.1 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.32-8.30 (m, 2H), 7.90-7.88 (m, 2H), 7.76-7.71 (m, 1H), 7.57-7.53 (m, 1H), 7.36-7.30 (m, 2H), 3.09-3.05 (m, 4H), 1.55-1.45 (m, 4H), 0.81 (t, *J* = 7.6 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 161.4, 150.9, 142.8, 141.9, 130.6, 128.1, 127.6, 125.9, 125.0, 120.5, 110.8, 49.9, 22.0, 11.2. HRMS(APCI): calcd for C₁₉H₂₂N₂O₃S [M+H]⁺ m/z 359.1424; found 359.1428. m.p. 191.1-129.7 °C.



4-(5-methylbenzo[*d*]**oxazol-2-yl**)-*N*,*N*-**dipropylbenzenesulfonamide (3aq):** The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: dichloromethane = 1:5 (v:v) to afford a white solid in 70% yield (130.4 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.34 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.40 (s, 1H), 7.20 (dd, *J*₁ = 8.4 Hz, *J*₂ = 0.8 Hz, 1H), 3.16-3.12 (m, 4H), 2.52 (s, 3H), 1.61-1.52 (m, 4H), 0.89 (t, *J* = 7.6 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 160.8, 151.1, 142.4, 139.7, 136.5, 130.7, 127.8, 127.5, 126.2, 119.7, 110.9, 49.9, 21.9, 21.8, 11.1. HRMS(APCI): calcd for C₂₀H₂₄N₂O₃S [M+H]⁺ m/z 373.1580; found 373.1580. m.p. 183.1-183.9 °C.



4-(5-chlorobenzo[*d*]**oxazol-2-yl**)-*N*,*N*-dipropylbenzenesulfonamide (3ar): The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: dichloromethane = 1:5 (v:v) to afford a white solid in 71% yield (139.5 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.36 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.37 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.0 Hz, 1H), 3.16-3.12 (m, 4H), 1.62-1.53 (m, 4H), 0.89 (t, *J* = 7.6 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.6, 149.4, 143.1, 143.0, 130.5, 130.0, 128.2, 127.6, 126.2, 120.3, 111.5, 49.9, 21.9, 11.1. HRMS(APCI): calcd for C₁₉H₂₁N₂O₃SCl [M+H]⁺ m/z 393.1034; found 393.1034. m.p. 208.9-209.5 °C.



4-(benzo[*d*]**thiazol-2-yl**)-*N*,*N*-**dipropylbenzenesulfonamide (3as):** The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: dichloromethane = 1:5 (v:v) to afford a white solid in 58% yield (108.6 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.20 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.94-7.91 (m, 3H), 7.55-7.50 (m, 1H), 7.45-7.41 (m, 1H), 3.15-3.11 (m, 4H), 1.62-1.52 (m, 4H), 0.89 (t, *J* = 7.6 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 165.7, 153.9, 142.0, 136.9, 135.2, 127.9, 127.6, 126.6, 125.8, 123.6, 121.7, 49.9, 21.9, 11.1. CAS: 301235-28-9.



4-(5-phenyloxazol-2-yl)-*N*,*N*-dipropylbenzenesulfonamide (3at):¹⁷ The title compound was prepared according to the general procedure I and purified by column chromatography on silica gel and eluted with petroleum ether: dichloromethane = 1:5 (v:v) to afford a white solid in 64% yield (123.0 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.49 (s, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.39-7.35 (m, 1H), 3.15-3.11 (m, 4H), 1.62-1.52 (m, 4H), 0.89 (t, *J* = 7.6 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 159.4, 152.2, 141.4, 130.6, 129.0, 128.8, 127.5, 127.4, 126.5, 124.3, 123.8, 49.8, 21.8, 11.1. Characterization data matched those previously reported.



benzo[*d*]**oxazol-2-yl(phenyl)methanone (4a):**²¹ The title compound was prepared according to the general procedure III (dpph 10 mol%) and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 20:1 (v:v) to afford a white solid in 90% yield (100.5 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.42 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.58-7.53 (m, 2H), 7.45-7.39 (m, 3H), 7.35-7.31 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 180.3, 156.9, 150.2, 140.6, 134.8, 134.1, 130.8, 128.4, 128.3, 125.6, 122.2, 111.7. Characterization data matched those previously reported.



benzo[*d*]**oxazol-2-yl(p-tolyl)methanone (4b):**²¹ The title compound was prepared according to the general procedure III and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 80% yield (94.9 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.46 (d, *J* = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.84 (d, J

1H), 7.55-7.50 (m, 1H), 7.47-7.43 (m, 1H), 7.35 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 180.0, 157.2, 150.3, 145.4, 140.7, 132.4, 131.1, 129.3, 128.2, 125.5, 122.2, 111.7, 21.8. Characterization data matched those previously reported.



benzo[*d*]**oxazol-2-yl(4-methoxyphenyl)methanone** (4c):²¹ The title compound was prepared according to the general procedure III and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 82% yield (103.8 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.62-8.58 (m, 2H), 7.94-7.91 (m, 1H), 7.70-7.68 (m, 1H), 7.54-7.50 (m, 1H), 7.47-7.43 (m, 1H), 7.04-7.01 (m, 2H), 3.90 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 178.7, 164.6, 157.4, 150.3, 140.7, 133.6, 128.1, 128.0, 125.5, 122.2, 113.9, 111.8, 55.6. Characterization data matched those previously reported.



benzo[*d*][1,3]dioxol-5-yl(benzo[*d*]oxazol-2-yl)methanone (4d):²¹ The title compound was prepared according to the general procedure III and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 5:1 (v:v) to afford a yellow solid in 75% yield (100.2 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.38 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 8.00 (d, J = 2.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.56-7.51 (m, 1H), 7.48-7.44 (m, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.10 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 178.2, 157.2, 153.1, 150.3, 148.1, 140.6, 129.5, 128.6, 128.2, 125.6, 122.2, 111.7, 110.2, 108.2, 102.1. Characterization data matched those previously reported.



benzo[*d*]**oxazol-2-yl(3,4,5-trimethoxyphenyl)methanone** (4e):²² The title compound was prepared according to the general procedure III and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 5:1 (v:v) to afford a yellow solid in 85% yield (133.2 mg). ¹H NMR (CDCl₃, 400 MHz) δ 7.96-7.94 (m, 3H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.58-7.54 (m, 1H), 7.51-7.46 (m, 1H), 3.99 (s, 3H), 3.99 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 178.9, 157.2, 152.9, 150.3, 144.0, 140.7, 129.8, 128.3, 125.6, 122.3, 111.8, 108.7, 61.0, 56.4. Characterization data matched those previously reported.



benzo[*d*]**oxazol-2-yl(4-phenoxyphenyl)methanone (4f):** The title compound was prepared according to the general procedure III and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a light yellow solid in 92% yield (145.0 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.61-8.57 (m, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.53-7.49 (m, 1H), 7.46-7.38 (m, 3H), 7.23-7.19 (m, 1H), 7.12-7.05 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 178.6, 163.2, 157.1, 154.9, 150.2, 140.6, 133.4, 130.0, 129.3, 128.1, 125.5, 124.8, 122.1, 120.4, 117.0, 111.7. HRMS(ESI): calcd for C₂₀H₁₃NO₃ [M+H]⁺ m/z 316.0968; found 316.0968. m.p. 66.2.-67.1 °C.



benzo[*d*]**oxazol-2-yl(4-dimethylaminophenyl)methanone (4g):** The title compound was prepared according to the general procedure III and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a yellow solid in 82% yield (109.2 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.56-8.52 (m, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.51-7.48 (m, 1H), 7.46-7.41 (m, 1H), 6.75-6.71 (m, 2H), 3.11 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 177.6, 158.2, 154.2, 150.2, 140.8, 133.5, 127.5, 125.2, 122.78, 121.8, 111.6, 110.7, 40.0. HRMS(ESI): calcd for C₁₆H₁₄N₂O₂ [M+H]⁺ m/z 267.1128; found 267.1128. m.p. 151.1-152.2 °C.



benzo[*d*]**oxazol-2-yl(naphthalen-2-yl)methanone (4h):**²¹ The title compound was prepared according to the general procedure III and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a light yellow solid in 78% yield (106.6 mg). ¹H NMR (CDCl₃, 400 MHz) δ 9.30 (s, 1H), 8.41 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.98-7.93 (m, 2H), 7.87 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.64-7.60 (m, 1H), 7.58-7.52 (m, 2H), 7.49-7.45 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 180.0, 157.1, 150.3, 140.7, 135.9, 134.2, 132.2, 132.1, 130.2, 129.2, 128.3, 128.2, 127.7, 126.8, 125.6, 125.2, 122.3, 111.7. Characterization data matched those previously reported.



benzo[*d*]**oxazol-2-yl(4-fluorophenyl)methanone** (**4i**):²¹ The title compound was prepared according to the general procedure III and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 81% yield (97.7 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.69-8.64 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.58-7.54 (m, 1H), 7.50-7.46 (m, 1H), 7.27-7.21 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 178.7, 166.6 (d, *J*_{C-F} = 255.8 Hz), 156.9, 150.3, 140.6, 133.9 (d, *J*_{C-F} = 9.4 Hz), 131.3 (d, *J*_{C-F} = 2.8 Hz), 128.5, 125.8, 122.3, 115.8 (d, *J*_{C-F} = 21.8 Hz), 111.8. ¹⁹F NMR (CDCl₃, 376 MHz) δ 102.5. Characterization data matched those previously reported.



benzo[*d*]**oxazol-2-yl(4-chlorophenyl)methanone (4j):**²¹ The title compound was prepared according to the general procedure III and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 75% yield (96.6 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.57-8.54 (m, 2H), 7.96-7.93 (m, 1H), 7.72-7.70 (m, 1H), 7.58-7.52 (m, 3H), 7.50-7.46 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 179.1, 156.8, 150.4, 141.0, 140.6, 133.2, 132.4, 129.0, 128.6, 125.8, 122.4, 111.8. Characterization data matched those previously reported.



benzo[*d*]**oxazol-2-yl(4-trifluoromethylphenyl)methanone** (**4k**):²¹ The title compound was prepared according to the general procedure III (dpph 10 mol%, 100°C) and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 66% yield (96.1 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.68 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.60-7.56 (m, 1H), 7.52-7.48 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 179.4, 156.6, 150.5, 140.6, 137.6 (d, *J*_{C-F} = 1.0 Hz), 135.2 (q, *J*_{C-F} = 32.6 Hz), 131.3, 128.9, 126.0, 125.5 (q, *J*_{C-F} = 3.7 Hz), 123.5(q, *J*_{C-F} = 271.4 Hz), 122.5, 111.9. ¹⁹F NMR (CDCl₃, 376 MHz) δ 63.3. Characterization data matched those previously reported.



(5-methylbenzo[*d*]oxazol-2-yl) (phenyl)methanone (41):²¹ The title compound was prepared according to the general procedure III and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 65% yield (77.1 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.55-8.52 (m, 2H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.69-7.65 (m, 1H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.49-7.48 (m, 1H), 7.28 (dd, *J*₁ = 8.0 Hz, *J*₂ = 0.8 Hz, 1H), 2.54 (s,

3H); ¹³C NMR (CDCl₃, 100 MHz) δ 180.4, 156.8, 150.7, 139.5, 138.6, 135.1, 134.1, 130.9, 128.5, 127.3, 121.6, 111.6, 22.05. Characterization data matched those previously reported.



(5-chlorobenzo[*d*]oxazol-2-yl) (phenyl)methanone (4m):²¹ The title compound was prepared according to the general procedure III and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 56% yield (72.1 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.53 (d, *J* = 8.0 Hz, 2H), 7.92-7.91 (m, 1H), 7.71-7.68 (m, 1H), 7.65-7.62 (m, 1H), 7.59-7.55 (m, 2H), 7.52-7.50 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 180.0, 158.0, 148.9, 141.6, 134.7, 134.5, 131.2, 131.0, 128.8, 128.6, 122.0, 112.6. Characterization data matched those previously reported.



benzo[*d*]**thiazol-2-yl(phenyl)methanone (4n):**²¹ The title compound was prepared according to the general procedure III (dpph 10 mol%) and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a light yellow solid in 66% yield (79.0 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.56 (d, *J* = 6.8 Hz, 2H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.69-7.65 (m, 1H), 7.62-7.53 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 185.4, 167.1, 153.9, 137.0, 135.0, 133.9, 131.3, 128.5, 127.6, 126.9, 125.7, 122.2. Characterization data matched those previously reported.



(thiazol-2-yl) (phenyl)methanone (4o):²³ The title compound was prepared according to the general procedure III (dpph 10 mol%) and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 10:1 (v:v) to afford a white solid in 56% yield (53.0 mg). ¹H NMR (CDCl₃, 400 MHz) δ 8.48-8.46 (m, 2H), 8.10 (d, *J* = 2.8 Hz, 1H), 7.73 (d, *J* = 2.8 Hz, 1H), 7.66-7.62 (m, 1H), 7.55-7.51 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 184.2, 167.8, 144.8, 135.1, 133.6, 131.0, 128.4, 126.2. Characterization data matched those previously reported.

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5. ¹H, ¹³C and ¹⁹F NMR Spectra of Products

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)





















¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)







¹³C NMR (100 MHz, CDCl₃)

















¹³C NMR (100 MHz, CDCl₃)





¹³C NMR (100 MHz, CDCl₃)





¹³C NMR (100 MHz, CDCl₃)







¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)
















¹H NMR (400 MHz, CDCl₃)











¹⁹F NMR (376 MHz, CDCl₃)











¹H NMR (400 MHz, CDCl₃)

















¹³C NMR (100 MHz, CDCl₃)







¹³C NMR (100 MHz, CDCl₃)













































































































¹H NMR (400 MHz, CDCl₃)











¹H NMR (400 MHz, CDCl₃)


















¹H NMR (400 MHz, CDCl₃)















¹H NMR (400 MHz, CDCl₃)















¹⁹F NMR (376 MHz, CDCl₃)





¹³C NMR (100 MHz, CDCl₃)

























