Supporting Information

for

Palladium-Catalyzed C-H Bond Activation for the Assembly

of N-Aryl Carbazoles with Aromatic Amines as Nitrogen

Sources

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1. General information

All chemicals were purchased from Adamas Reagent, Ltd, Energy chemical company, J&K Scientific Ltd, Alfa Aesa chemical company and so forth. Unless otherwise stated, all experiments were conducted in a seal tube under air atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

¹H-NMR and ¹³C-NMR spectra were recorded in CDCl₃ on a Bruker Avance 500 spectrometer (500 MHz ¹H, 125 MHz ¹³C) at room temperature. Chemical shifts were reported in ppm on the scale relative to CDC₁₃ (δ = 7.26 for ¹H-NMR , δ = 77.00 for ¹³C-NMR) or DMSO-d6 (δ = 2.50 for ¹H-NMR, δ = 39.60 for ¹³C-NMR) as an internal reference. High resolution mass spectra were recorded using Q-TOF time-of-flight mass spectrometer. Coupling constants (J) were reported in Hertz (Hz).

The starting materials 2-iodobiphenyl and arylamine were purchased from commercial suppliers. Other 2-iodobiaryl were synthetized according to methods reported by previous literatures.¹

^{1.} C. Shao, B. Zhou, Z. Wu, X. Ji and Y. Zhang, Adv. Synth. Catal. 2018, 5, 887.

2. General procedure for the synthesis of 3 and 4



A dry sealed tube equipped with a magnetic stir bar was charged with 1 (0.2 mmol), aniline 2 (0.24 mmol, 1.2 equiv), $Pd(OAc)_2$ (2.2 mg, 5 mol%), PPh_3 (5.2 mg, 10 mol%), $Cu(OAc)_2$ (0.2 mol, 1.0 equiv), Cs_2CO_3 (0.2 mmol, 1.0 equiv) and DMF (2 mL). Upon completion of the reaction, Upon completion of the reaction, ethyl acetate was added to the mixture, and then washed with saturated brine. The combined water layers were extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether/Ethyl acetate = 100:1) to give the desired product **3** or **4**.

3. Crystal data of 3a and 5

Crystallographic data for compound **3a** (CCDC-1916897) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



ORTEP view with ellipsoids (at the 30% probability level)

Bond precision:	C-C = 0.00)54 A	Wavelength=0.71073		
Cell:	a=38.272(3)	b=12.8	163(8)	c=10.858(1)
	alpha=90		beta=9	0	gamma=90
Temperature:	293 K				
	Calculated			Reported	
Volume	5325.9(7)			5325.9(7)	
Space group	Fdd2			Fdd2	
Hall group	F 2 -2d			F 2 -2d	
Moiety formula	C18 H13 N			C18 H13 N	
Sum formula	C18 H13 N			C18 H13 N	
Mr	243.29			243.29	
Dx,g cm-3	1.214			1.214	
Z	16			16	
Mu (mm-1)	0.071			0.071	
F000	2048.0			2048.0	
F000'	2048.72				
h,k,lmax	52,17,14			51,17,14	
Nref	3622[1901]			2768	
Tmin, Tmax	0.992,0.993			0.749,1.00	0.0
Tmin'	0.992				
Correction meth AbsCorr = MULTI	od= # Report -SCAN	ed T L	imits: 1	Tmin=0.749 1	[max=1.000
Data completene	ss= 1.46/0.7	6	Theta (max) = 29.19	5
R(reflections)=	0.0508(175	51)	wR2(re	flections)=	0.1077(2768)
S = 1.036	i	Npar= 1	172		

Crystallographic data for compound **5** (CCDC-1969291) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



Bond precision:	C-C = 0.0038 A	Wavelength=0.71073		
Cell:	a=9.0542(4)	b=12.4973(6)	c=18.9834(7)	
	alpha=90	beta=90	gamma=90	
Temperature:	298 K			
	Calculated	Reported		
Volume	2148.03(16)	2148.03(16)	
Space group	P 21 21 21	P 21 21	21	
Hall group	P 2ac 2ab	P 2ac 2a	b	
Moiety formula	C30 H20 N2	C30 H20 1	N2	
Sum formula	C30 H20 N2	С30 Н20 1	N2	
Mr	408.48	408.48		
Dx,g cm-3	1.263	1.263		
Z	4	4		
Mu (mm-1)	0.074	0.074		
F000	856.0	856.0		
F000'	856.30			
h,k,lmax	12,17,26	12,17,25		
Nref	6004[3384]	5185		
Tmin, Tmax	0.991,0.993	0.843,1.	000	
Tmin'	0.991			
Correction metho AbsCorr = MULTI-	od= # Reported T L. -SCAN	imits: Tmin=0.843	Tmax=1.000	
Data completeness= 1.53/0.86 Theta(max)= 29.530				
R(reflections)=	0.0482(3651)	wR2(reflections)	= 0.0913(5185)	
S = 1.041	Npar= 2	.89		

ORTEP view with ellipsoids (at the 30% probability level)

4. Characterization data for products

9-phenyl-9H-carbazole (3a) (CAS Number: 1150-62-5)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (43.8 mg, 90%). ¹H NMR (500 MHz, CDCl₃) δ 8.24 (d, *J* = 7.8 Hz, 2H), 7.71 – 7.60 (m, 4H), 7.58 – 7.45 (m, 5H), 7.38 (ddd, *J* = 7.9, 5.6, 2.4 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 140.9, 137.7, 129.8, 127.4, 127.1, 125.9, 123.3, 120.3, 119.9, 109.7.

9-(p-tolyl)-9H-carbazole (3b) (CAS Number: 19264-73-4)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (36.1 mg, 70%).¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.37 (m, 8H), 7.30 (ddd, *J* = 8.0, 6.2, 1.9 Hz, 2H), 2.51 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 141.1, 137.3, 135.0, 130.4, 127.0, 125.8, 123.2, 120.2, 119.7, 109.8, 21.2. HRMS (ESI, m/z) calcd for C₁₉H₁₆N [M+H]⁺: 258.1277; found:

258.1272.

9-(4-isopropylphenyl)-9H-carbazole (3c)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (46.7 mg, 82%). m.p. 135-137 °C ¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 7.8 Hz, 2H), 7.56 – 7.34 (m, 8H), 7.29 (td, *J* = 6.9, 6.1, 2.5 Hz, 2H), 3.06 (p, *J* = 6.9 Hz, 1H), 1.37 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 148.2, 141.1, 135.2, 127.8, 127.0, 125.8, 123.2, 120.2, 119.7, 109.9, 33.9, 24.0. HRMS (ESI,

m/z) calcd for $C_{21}H_{20}N$ [M+H]⁺: 286.1590; found: 286.1592.

9-(4-(methylthio)phenyl)-9H-carbazole (3d) (CAS Number: 57103-12-5)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (22.0 mg, 38%).¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.53 – 7.45 (m, 4H), 7.45 – 7.36 (m, 4H), 7.29 (ddd, *J* = 7.9, 6.6, 1.5 Hz, 2H), 2.59 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 140.9, 137.9, 134.6, 127.7, 127.56, 125.9, 123.3, 120.3, 119.9, 109.7, 15.9.

4-(9H-carbazol-9-yl)benzonitrile (3e) (CAS Number: 57103-17-0)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 50:1, v/v) to give the product as a white solid (35.9 mg, 67%).¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 7.8 Hz, 2H), 7.94 – 7.87 (m, 2H), 7.76 – 7.70 (m, 2H), 7.45 (dd, *J* = 6.1, 1.4 Hz, 4H), 7.35 (ddd, *J* = 8.0, 6.2, 2.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 142.0, 139.9, 133.9, 127.1, 126.3, 124.0, 121.0, 120.6, 118.3, 110.4, 109.5.

1-(4-(9H-carbazol-9-yl)phenyl)ethan-1-one (3f) (CAS Number: 142116-85-6)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 60:1, v/v) to give the product as a white solid (20.5 mg, 36%). ¹H NMR (500 MHz, CDCl₃) δ 8.25 – 8.19 (m, 2H), 8.17 – 8.13 (m, 2H), 7.74 – 7.69 (m, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.43 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.35 – 7.30 (m, 2H), 2.71 (s, 3H).¹³C NMR (125 MHz, CDCl₃) δ 197.0, 142.2, 140.2, 135.5, 130.1, 126.5, 126.2, 123.8, 120.6, 120.4, 109.7,



ethyl 4-(9H-carbazol-9-yl)benzoate (3g) (CAS Number: 717881-64-6)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 30:1, v/v) to give the product as a white solid (39.7 mg, 63%).¹H NMR (500 MHz, CDCl₃) δ 8.38 – 8.25 (m, 2H), 8.16 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.75 – 7.66 (m, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.44 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 2H), 7.33 (td, *J* = 7.4, 6.9, 1.2 Hz, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 165.9, 141.9, 140.2,

131.3, 129.0, 126.3, 126.1, 123.7, 120.5, 120.4, 109.7, 61.2, 14.4. 9-(4-fluorophenyl)-9H-carbazole (3h) (CAS Number: 57103-14-7)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (48.0 mg, 92%).¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.57 – 7.51 (m, 2H), 7.43 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 2H), 7.37 – 7.28 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 161.6 (d, *J* = 246.3 Hz), 141.0, 133.6 (d, *J* = 3.8 Hz), 129.0 (d, *J* = 8.8 Hz), 126.0, 123.3, 120.3, 120.0, 116.8 (d, *J* = 23.8 Hz), 109.5.

¹⁹F NMR (471 MHz, CDCl₃) δ -113.7.

9-(4-chlorophenyl)-9H-carbazole (3i) (CAS Number: 19264-71-2)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (45.4 mg, 82%). ¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 7.7 Hz, 2H), 7.59 (dt, *J* = 7.5, 2.5 Hz, 2H), 7.55 – 7.48 (m, 2H), 7.46 – 7.36 (m, 4H), 7.35 – 7.28 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 140.7, 136.2, 133.0, 130.1, 128.4, 126.1, 123.4, 120.4, 120.2, 109.5.

9-(4-bromophenyl)-9H-carbazole (3j) (CAS Number: 57102-42-8)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (30.8 mg, 48%).¹H NMR (500 MHz, CDCl₃) δ 8.15 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.77 - 7.67 (m, 1H), 7.49 - 7.44 (m, 1H), 7.42 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.38 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.31 (ddd, *J* = 7.9, 6.9, 1.2 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 140.6, 136.8, 133.1, 128.7, 126.1, 123.5, 120.9, 120.4,

120.2, 109.5.

9-(3-fluorophenyl)-9H-carbazole (3k) (CAS Number: 81329-47-7)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (45.9 mg, 88%). ¹H NMR (500 MHz, CDCl₃) δ 8.16 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.58 (td, *J* = 8.1, 6.3 Hz, 1H), 7.50 – 7.38 (m, 5H), 7.36 – 7.30 (m, 3H), 7.19 (tdd, *J* = 8.3, 2.5, 0.9 Hz, 1H).¹³C NMR (125 MHz, CDCl₃) δ 163.4 (d, *J* = 246.3 Hz), 140.5, 139.3 (d, *J* = 10.0 Hz), 131.0 (d, *J* = 8.8 Hz), 126.1, 123.5, 122.7

(d, J = 2.5 Hz), 120.4, 120.3, 114.4 (d, J = 21.3 Hz), 114.3 (d, J = 23.8 Hz), 109.7. ¹⁹F NMR (471 MHz, CDCl₃) δ -110.5.

9-(3-(trifluoromethyl)phenyl)-9H-carbazole (3l) (CAS Number: 1241949-50-7)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (56.0 mg, 90%).¹H NMR (500 MHz, CDCl₃) δ 8.16 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.82 – 7.72 (m, 3H), 7.48 – 7.38 (m, 4H), 7.33 (ddd, *J* = 7.9, 6.9, 1.2 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 140.5, 138.5, 132.6 (q, *J* = 32.5 Hz), 130.6, 130.4, 126.2, 124.1 (q, *J* = 3.8 Hz), 123.9 (q, J = 3.8 Hz), 123.7

(q, J = 271.3 Hz), 123.6, 120.5, 120.4, 109.4. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.7.

9-(o-tolyl)-9H-carbazole (3m) (CAS Number: 19155-50-1)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (45.2 mg, 88%).¹H NMR (500 MHz, CDCl₃) δ 8.18 (dt, *J* = 7.8, 0.9 Hz, 2H), 7.48 (ddd, *J* = 8.4, 7.3, 2.0 Hz, 2H), 7.44 – 7.36 (m, 4H), 7.29 (td, *J* = 7.4, 7.0, 1.0 Hz, 2H), 7.06 (dt, *J* = 8.2, 0.9 Hz, 2H), 1.99 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 141.2, 137.4, 136.0, 131.5, 129.3, 128.7, 127.3, 125.9, 123.0, 120.3, 119.5,

109.8, 17.6.

9-(2-chlorophenyl)-9H-carbazole (3n) (CAS Number: 19155-51-2)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (30.5 mg, 55%).¹H NMR (500 MHz, CDCl₃) δ 8.16 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.72 – 7.67 (m, 1H), 7.54 – 7.47 (m, 3H), 7.41 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 2H), 7.30 (td, *J* = 7.5, 1.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 140.9, 135.1, 133.8, 131.01, 130.9, 129.8, 128.1, 125.9, 123.3, 120.3, 120.0, 110.0.

9-(2-isopropylphenyl)-9H-carbazole (30)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (42.8 mg, 75%). m.p. 111-113 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, J = 7.7 Hz, 2H), 7.61 (dd, J = 7.9, 1.7 Hz, 1H), 7.56 (td, J = 7.6, 1.4 Hz, 1H), 7.41 (ddt, J = 9.1, 7.5, 1.6 Hz, 3H), 7.34 – 7.27 (m, 3H), 7.06 (d, J = 8.2 Hz, 2H), 2.62 (p, J = 6.9 Hz, 1H), 1.08 (d, J = 6.9 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ

148.5, 142.0, 134.6, 129.6, 129.4, 127.2, 127.1, 125.9, 122.9, 120.2, 119.4, 109.7, 28.0, 23.9. HRMS (ESI, m/z) calcd for C₂₁H₂₀N [M+H]⁺: 286.1590; found: 286.1584. **9-(3,4-dimethylphenyl)-9H-carbazole (3p) (CAS Number: 204066-04-6)**



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (47.7 mg, 88%). ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 7.7 Hz, 2H), 7.42 (q, *J* = 5.6, 4.2 Hz, 4H), 7.39 – 7.33 (m, 2H), 7.30 (dtd, *J* = 7.9, 5.6, 3.4 Hz, 3H), 2.41 (s, 3H), 2.39 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 141.1 138.3, 136.0, 135.2, 130.8, 128.1, 125.8, 124.4, 123.2, 120.2, 119.6, 109.8, 19.9, 19.5.

9-(naphthalen-2-yl)-9H-carbazole (3q) (CAS Number: 34292-03-0)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (25.8 mg, 44%).¹H NMR (500 MHz, CDCl₃) δ 8.20 (d, *J* = 7.8 Hz, 2H), 8.12 - 8.03 (m, 2H), 7.99 (dd, *J* = 6.2, 3.4 Hz, 1H), 7.93 (dd, *J* = 6.2, 3.3 Hz, 1H), 7.69 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.61 (dt, *J* = 6.3, 3.5 Hz, 2H), 7.52 - 7.41 (m, 4H), 7.34 (t, *J* = 7.4 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 141.0, 135.1,

134.0, 132.4, 129.8, 127.92, 127.9, 126.8, 126.5, 126.0, 125.4, 125.3, 123.4, 120.3, 120.0, 109.8.

9-(pyridin-2-yl)-9H-carbazole (3r) (CAS Number: 23866-67-3)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a white solid (20.1 mg, 41%).¹H NMR (500 MHz, CDCl₃) δ 8.74 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 8.14 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.93 (ddd, *J* = 8.2, 7.4, 2.0 Hz, 1H), 7.85 (dt, *J* = 8.3, 0.9 Hz, 2H),

7.65 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.46 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 2H), 7.37 – 7.28 (m, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 151.8, 149.6, 139.5, 138.4, 126.2, 124.3, 121.2, 120.9, 120.2, 119.0, 111.1.

2-methyl-9-phenyl-9H-carbazole (4a) (CAS Number: 2080745-13-5)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum) to give the product as a white solid (42.1 mg, 82%). ¹H NMR (500 MHz, CDCl₃) δ 8.15 (dt, *J* = 7.6, 1.0 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.71 – 7.56 (m, 4H), 7.53 – 7.48 (m, 1H), 7.45 – 7.39 (m, 2H), 7.31 (ddd, *J* =

8.0, 5.4, 2.7 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.16 (dd, *J* = 8.0, 1.4 Hz, 1H), 2.54 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 141.4, 141.0, 137.8, 136.1, 129.8, 127.4, 127.2, 125.3, 123.5, 121.4, 121.1, 120.0, 119.9, 119.8, 109.8, 109.6, 22.1.

2-(tert-butyl)-9-phenyl-9H-carbazole (4b) (CAS Number: 2080745-14-6)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (37.7 mg, 63%).¹H NMR (500 MHz, CDCl₃) δ 8.13 (dt, *J* = 7.7, 1.0 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.57 (m, 4H), 7.52 – 7.46 (m, 1H), 7.46 – 7.35 (m, 4H),

7.28 (ddd, J = 8.0, 6.2, 1.9 Hz, 1H), 1.41 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 149.7, 141.1, 141.0, 137.8, 129.8, 127.3, 127.1, 125.3, 123.3, 120.9, 120.0, 119.7, 118.0, 109.6, 106.1, 35.2, 31.7.

2-methoxy-9-phenyl-9H-carbazole (4c) (CAS Number: 1357929-88-4)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 50:1, v/v) to give the product as a white solid (43.7 mg, 80%).¹H NMR (500 MHz, CDCl₃) δ 8.07 (dt, *J* = 7.8, 1.0 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.61 – 7.57 (m, 2H), 7.52 – 7.47 (m, 1H), 7.40 – 7.34 (m, 2H), 7.29 (ddd, *J* = 8.1, 6.3,

1.9 Hz, 1H), 6.94 (dd, J = 8.5, 2.3 Hz, 1H), 6.91 (d, J = 2.2 Hz, 1H), 3.86 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 159.2, 142.2, 141.1, 137.7, 129.9, 127.5, 127.1, 124.6, 123.5, 121.0, 120.0, 119.4, 117.2, 109.5, 108.5, 94.0, 55.6.

2,9-diphenyl-9H-carbazole (4d) (CAS Number: 1187235-30-8)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, pure petroleum ether) to give the product as a white solid (53.0 mg, 83%).¹H NMR (500 MHz, CDCl₃) δ 8.21 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.18 (dq, *J* = 7.8, 1.0 Hz, 1H), 7.69 – 7.63 (m, 3H), 7.63 – 7.59 (m, 4H), 7.56 (dt, *J* = 8.1, 1.5 Hz, 1H), 7.50 (ddt, *J* = 7.6, 6.1, 2.0 Hz,

1H), 7.48 – 7.40 (m, 4H), 7.38 – 7.29 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 142.0, 141.4, 141.4, 139.5, 137.6, 129.9, 128.7, 127.5, 127.2, 127.1, 125.9, 123.1, 122.6, 120.5, 120.3, 120.0, 119.6, 109.8, 108.3.

2-fluoro-9-phenyl-9H-carbazole (4e)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (47.0 mg, 90%). m.p. 73-75 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.12 (d, J = 1.1 Hz, 1H), 8.10 (d, J = 1.1 Hz, 1H), 8.07 (dd, J = 8.5, 5.4 Hz, 2H), 7.67 – 7.60 (m, 4H), 7.60 – 7.53 (m, 4H), 7.53 – 7.47 (m, 2H), 7.45 – 7.38 (m,

4H), 7.32 (ddd, J = 8.0, 4.9, 3.3 Hz, 2H), 7.10 (dd, J = 9.9, 2.3 Hz, 2H), 7.04 (ddd, J = 9.3, 8.5, 2.3 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 162.1 (d, J = 241.3 Hz), 141.6 (d, J = 12.5 Hz), 141.4 (d, J = 1.3 Hz), 137.2, 130.0, 127.8, 126.9, 125.5, 123.0, 121.2 (d, J = 10.0 Hz), 120.3, 119.9, 119.7, 109.8, 108.0 (d, J = 25.0 Hz), 96.7 (d, J = 27.5 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -114.9. HRMS (ESI, m/z) calcd for C₁₈H₁₂FNNa [M+H]⁺: 284.0846; found: 284.0838.

9-(4-nitrophenyl)-9H-carbazole (4f) (CAS Number: 1257982-94-7)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 5:1, v/v) to give the product as a yellow solid (47.2 mg, 82%).¹H NMR (500 MHz, CDCl₃) δ 8.27 (d, *J* = 1.9 Hz, 1H), 8.24 – 8.15 (m, 3H), 7.67 (dd, *J* = 8.8, 6.7 Hz, 2H), 7.54 (dtd, *J* = 13.1, 7.6,

7.0, 1.3 Hz, 4H), 7.43 (d, J = 8.3 Hz, 1H), 7.40 – 7.33 (m, 1H).¹³C NMR (125 MHz, CDCl₃) δ 146.0, 143.2, 139.9, 136.4, 130.3, 128.5, 128.3, 128.2, 127.1, 121.8, 121.4, 121.1, 120.3, 115.2, 110.5, 106.1.

9-phenyl-9H-carbazole-2-carbaldehyde (4g) (CAS Number: 1353684-87-3)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a yellow solid (47.7 mg, 88%).¹H NMR (500 MHz, CDCl₃) δ 10.09 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.21 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.92 (d, *J* = 1.2 Hz, 1H), 7.82 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.68 - 7.61 (m, 2H), 7.58 - 7.48 (m,

4H), 7.43 (dd, J = 8.3, 0.9 Hz, 1H), 7.35 (ddd, J = 8.0, 6.9, 1.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 192.5, 142.7, 140.6, 136.9, 134.2, 130.1, 128.4, 128.1, 127.8, 127.2, 122.3, 121.7, 121.3, 120.6, 120.6, 111.4, 110.2.

3-methyl-9-phenyl-9H-carbazole (4h) (CAS Number: 1202362-88-6)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (38.6 mg, 75%).¹H NMR (500 MHz, CDCl₃) δ 8.15 (dt, J = 7.8, 1.0 Hz, 1H), 8.00 – 7.96 (m, 1H), 7.67 – 7.56 (m, 4H), 7.50 – 7.39 (m, 3H), 7.35 (d, J = 8.3 Hz, 1H), 7.30 (ddd, J = 7.9, 6.4, 1.7 Hz, 1H), 7.26 (dd, J = 8.4, 1.7 Hz, 1H), 2.59 (s,

3H). ¹³C NMR (125 MHz, CDCl₃) δ 141.0, 139.1, 137.9, 129.8, 129.2, 127.2, 127.0, 125.7, 123.5, 123.2, 120.2, 119.7, 109.7, 109.4, 21.4.

3-chloro-9-phenyl-9H-carbazole (4i) (CAS Number: 193686-61-2)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (51.5 mg, 93%).¹H NMR (500 MHz, CDCl₃) δ 8.11 (dd, J = 7.2, 1.4 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.56 – 7.52 (m, 2H), 7.52 – 7.47 (m, 1H), 7.45 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.41 (dt, J = 8.3, 1.0 Hz, 1H), 7.37 (dd, J = 8.7, 2.0 Hz, 1H), 7.35 – 7.28 (m, 2H).¹³C NMR (125 MHz, CDCl₃) δ 141.3, 139.2,

137.3, 129.9, 127.7, 127.0, 126.6, 125.9, 125.3, 124.5, 122.4, 120.4, 120.2, 120.0, 110.8, 110.0.

9-phenyl-3-(trifluoromethyl)-9H-carbazole (4j) (CAS Number: 1417618-06-4)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a white solid (52.9 mg, 85%).¹H NMR (500 MHz, CDCl₃) δ 8.44 (dt, J = 1.7, 0.8 Hz, 1H), 8.20 (dt, J = 7.8, 1.0 Hz, 1H), 7.70 – 7.61 (m, 3H), 7.58 – 7.51 (m, 3H), 7.51 – 7.41 (m, 3H), 7.37 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H).¹³C NMR (125 MHz, CDCl₃)

δ 142.3, 141.6, 137.0, 130.1, 128.1, 127.1, 126.9, 125.2 (q, J = 270.0 Hz), 123.0, 122.8, 122.7 (q, J = 3.8 Hz), 122.1 (q, J = 32.5 Hz), 120.7, 120.5, 117.9 (q, J = 3.8 Hz), 110.2, 109.9. ¹⁹F NMR (471 MHz, CDCl₃) δ -60.1.

9-phenyl-3-(trifluoromethoxy)-9H-carbazole (4k)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a pale oil (49.7 mg, 76%).¹H NMR (500 MHz, CDCl₃) δ 8.13 (dt, *J* = 7.7, 1.0 Hz, 1H), 8.00 (dd, *J* = 2.4, 1.2 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.57 – 7.53 (m, 2H), 7.52 – 7.48 (m, 1H), 7.46 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.41 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.32 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H),

7.28 (ddd, J = 8.9, 2.4, 0.9 Hz, 1H).¹³C NMR (125 MHz, CDCl₃) δ 142.8 (q, J = 2.5 Hz), 141.7, 139.1, 137.2, 130.0, 127.8, 127.1, 126.8, 123.7, 122.7, 120.8 (q, J = 253.8 Hz), 120.5, 120.3, 119.6, 113.2, 110.3, 110.1. ¹⁹F NMR (471 MHz, CDCl₃) δ -58.1. HRMS (ESI, m/z) calcd for C₁₉H₁₃F₃NO [M+H]⁺: 328.0944; found: 328.0945.

methyl 9-phenyl-9H-carbazole-3-carboxylate (4l)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 30:1, v/v) to give the product as a white solid (45.8 mg, 76%). m.p. 75-77 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.92 – 8.85 (m, 1H), 8.20 (dt, *J* = 7.7, 1.0 Hz, 1H), 8.11 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.58 – 7.54 (m, 2H), 7.54 – 7.49 (m, 1H), 7.45 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.42 – 7.37 (m,

2H), 7.35 (ddd, J = 8.0, 7.0, 1.2 Hz, 1H), 3.99 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 167.8, 143.5, 141.6, 137.0, 130.0, 128.0, 127.5, 127.1, 126.6, 123.3, 123.1, 122.9, 121.8, 120.8, 120.6, 110.2, 109.3, 52.0. HRMS (ESI, m/z) calcd for C₂₀H₁₆NO₂ [M+H]⁺: 302.1176; found: 302.1181.

4-methyl-9-phenyl-9H-carbazole (4m)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 100:1, v/v) to give the product as a colourless oil (17.0 mg, 33%).¹H NMR (500 MHz, CDCl₃) δ 8.26 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.58 – 7.53 (m, 2H), 7.48 (ddt, *J* = 7.8, 6.8, 1.4 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.35 – 7.28 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.08 (dt, *J* = 7.1, 0.9 Hz, 1H), 2.95

(s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 141.1, 140.9, 137.7, 133.4, 129.8, 127.5, 127.5, 125.6, 125.2, 123.9, 122.6, 121.7, 121.4, 119.8, 109.5, 107.3, 20.9. HRMS (ESI, m/z) calcd for C₁₉H₁₆N [M+H]⁺: 258.1277; found: 258.1274.

7-phenyl-7H-benzofuro[2,3-b]carbazole (4n) (CAS Number: 1849662-52-7)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, PE:EA = 50:1, v/v) to give the product as a white solid 45.3 mg, 68%).¹H NMR (500 MHz, CDCl₃) δ 8.62 (dt, *J* = 7.5, 1.2 Hz, 1H), 8.04 – 7.97 (m, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.78 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.69 – 7.61 (m, 4H), 7.56 – 7.51 (m, 1H), 7.51 – 7.37 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 156.2, 151.2,

141.4, 140.6, 137.6, 129.9, 127.8, 127.3, 125.7, 125.2, 125.1, 122.8, 122.7, 121.0, 120.6, 119.7, 117.9, 116.4, 111.6, 109.8, 108.6, 105.5.

9-phenyl-9H-pyrido[3,4-b]indole (40) (CAS Number: 1899836-00-0)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a white solid (22.4 mg, 46%).¹H NMR (500 MHz, CDCl₃) δ 8.86 (s, 1H), 8.63 – 8.39 (m, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 3.9 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.56 – 7.46 (m, 3H), 7.39 – 7.33 (m, 1H). ¹³C NMR (125 MHz,

CDCl₃) δ 141.6, 137.0, 136.8, 130.2, 129.1, 129.0, 128.7, 128.1,127.0, 126.9, 121.8, 121.5, 120.7, 111.6, 110.6.

1,3-di(9H-carbazol-9-yl)benzene (5) (CAS Number: 550378-78-4)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 100:1, v/v) to give the product as a white solid (28.6 mg, 70%). ¹H NMR (500 MHz, CDCl₃) δ 8.17 (dt, *J* = 7.7, 1.0 Hz, 4H), 7.91 – 7.80 (m, 2H), 7.72 (dd, *J* =

7.9, 2.1 Hz, 2H), 7.56 (dt, J = 8.2, 0.9 Hz, 4H), 7.46 (ddd, J = 8.3, 7.1, 1.2 Hz, 4H), 7.33 (td, J = 7.5, 7.0, 1.0 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 140.6, 139.4, 131.2, 126.2, 125.9, 125.4, 123.6, 120.4, 120.3, 109.7.

5. NMR spectroscopic data

9-phenyl-9H-carbazole (3a)

8,222 2,22 2,222 2





9-(p-tolyl)-9H-carbazole (3b)





-2.51

9-(4-isopropylphenyl)-9H-carbazole (3c)



9-(4-(methylthio)phenyl)-9H-carbazole (3d)



4-(9H-carbazol-9-yl)benzonitrile (3e)



1-(4-(9H-carbazol-9-yl)phenyl)ethan-1-one (3f)



ethyl 4-(9H-carbazol-9-yl)benzoate (3g)





9-(4-fluorophenyl)-9H-carbazole (3h)

8, 17 2, 16 2, 16 2, 16 2, 15 2,



CDCI₃ (500 MHz)





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)

9-(4-chlorophenyl)-9H-carbazole (3i)

28.15 28.16 28.16 20.00 20



CDCI₃ (500 MHz)



9-(4-bromophenyl)-9H-carbazole (3j)





9-(3-fluorophenyl)-9H-carbazole (3k)







20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)

9-(3-(trifluoromethyl)phenyl)-9H-carbazole (3l)





100 90 f1 (ppm)



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)

9-(o-tolyl)-9H-carbazole (3m)





-1.99

9-(2-chlorophenyl)-9H-carbazole (3n)





9-(2-isopropylphenyl)-9H-carbazole (30)





CDCI₃ (500 MHz)





CDCI₃ (126 MHz)



100 90 f1 (ppm)

9-(3,4-dimethylphenyl)-9H-carbazole (3p)



9-(naphthalen-2-yl)-9H-carbazole (3q)





9-(pyridin-2-yl)-9H-carbazole (3r)





2-methyl-9-phenyl-9H-carbazole (4a)



CDCI₃ (500 MHz)



2-(tert-butyl)-9-phenyl-9H-carbazole (4b)



-1.41

2-methoxy-9-phenyl-9H-carbazole (4c)



2,9-diphenyl-9H-carbazole (4d)



2-fluoro-9-phenyl-9H-carbazole (4e)



CDCI₃ (500 MHz)







20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)

2-nitro-9-phenyl-9H-carbazole (4f)



CDCI₃ (500 MHz)



9-phenyl-9H-carbazole-2-carbaldehyde (4g)





CDCI₃ (500 MHz)



3-methyl-9-phenyl-9H-carbazole (4h)



100 90 f1 (ppm)

3-chloro-9-phenyl-9H-carbazole (4i)



100 90 f1 (ppm)

9-phenyl-3-(trifluoromethyl)-9H-carbazole (4j)







20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)

9-phenyl-3-(trifluoromethoxy)-9H-carbazole (4k)







20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -21 f1 (ppm)



4-methyl-9-phenyl-9H-carbazole (4m)





7-phenyl-7H-benzofuro[2,3-b]carbazole (4n)





9-phenyl-9H-pyrido[3,4-b]indole (40)



CDCI₃ (500 MHz)



1,3-di(9H-carbazol-9-yl)benzene (5)



CDCI₃ (500 MHz)

