Electronic Supplementary Information for Dalton Transactions

Supplementary Material (ESI) for

A Robust Hydrophilic Pyridine-Bridged Bis-benzimidazolylidene Palladium Pincer Complex: Synthesis and Its Catalytic Application towards Suzuki-Miyaura Couplings in Aqueous Solvents

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Contents :

1 . General

All commercial reagents and solvents were used directly as purchased without further purification. All reactions were carried out under air unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on JeOL-ECA 400 and Bruker 500 DRX spectrometers. ESI-MS spectra were recorded on a micrOTOF II instrument. GC-MS spectra were recorded on Agilent Technologies 1890A GC system and 5975C inert MSD with Triple-Axis Detector. CEM Discover microwave instrument was applied for the palladation. Compound **4** was synthesized as literature procedure.[1]

2 . Synthesis of pyridine-bridged benzimidazolylidene palladium complexes

Synthesis of 2,6-bis-benzimidazolyl isonicotinic acid 5:[2,3] A mixture of CuI (516 mg, 2.71mmol), Cs_2CO_3 (8830 mg, 27.1 mmol), benzimadazole (2242mg, 18.98 mmol), and methyl 2,6-dibromoisonicotinate **4** (2000 mg, 6.7 mmol) in 15 mL dry DMF was stirred at room temperature for 30 min under argon, and then allowed to be heated at 140^{o}C for 48 hours. After cooled to ambient temperature, DMF was removed under vacuum with heating. Then 10 mL EtOAc was added and resulting suspension was heated to reflux. After hot filtration, the insoluble solid was dissolved in MeOH and precipitated with ether leading to form a blue-white solid. Further purification by flash column chromatograph with MeOH afforded a white solid (83 %). ^{1}H NMR (500MHz, DMSO-d_6, 298K): δ = 9.1 (s, 2H), 8.21 (dt, *J* = 7.2 Hz, 2H), 8.15 (bs, 2H), 7.81-7.83 (dt, *J* = 6.8 Hz, 2H), 7.35-7.41 (m, 4H), 5.75 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, 298K): δ= 165.41, 158.05, 149.41, 145.16,143.46, 132.78, 124.93, 124.03, 120.95, 114.27, 112.67. HR-MS (ESI) for $C_{20}H_{13}N_5O_2$: m/z = 354.1069 ([M-1]$^{+}$, Calcd.); 354.0989 (Found).

Synthesis of pyridine-bridged bis-benzimdazolium dibromide 6: the mixture of 2,6-bis-benzimidazolyl isonicotinic acid **5** (1g, 2.81mmol) and 10 mL butyl bromide and heated to 90 ^{o}C for 72 h. Excess butyl bromide was distilled off under vacume distillation, reaction mixture was dissolved in minimum amount of MeOH and recrystallized with ether

leading to form a yellowish solid (73 %).^{1}H NMR (500MHz, DMSO-d_6, 298K): δ = 10.87 (s, 1H), 8.74 (s, 2H), 8.44 (d, *J* = 8.5 Hz, 2H), 8.30 (d, *J* = 8.3 Hz, 2H), 8.30 (bd, *J* = 8.3 Hz, 2H), 7.81 (t, *J* = 7.5 Hz, 2H), 7.72 (t, *J* = 7.5 Hz, 2H), 4.69 (t, *J* = 7.3 Hz, 4H), 2.06 (quintet, *J* = 7.3 Hz, 4H), 1.49 (sextex, *J* = 7.5Hz, 4H), 1.00 (t, *J* = 7.3 Hz, 6H).^{13}C NMR (100 MHz, DMSO-d_6, 298K): δ = 170.09, 164.14, 147.40, 143.42, 131.86, 129.65, 127.96, 127.45, 117.25, 115.89, 114.39, 47.30, 30.5, 19.20, 13.54. HR-MS (ESI) for $C_{28}H_{31}Br_2N_5O_2$: m/z = 628.0845 ([M+1]$^+$, Calcd.); 628.0747 (Found).

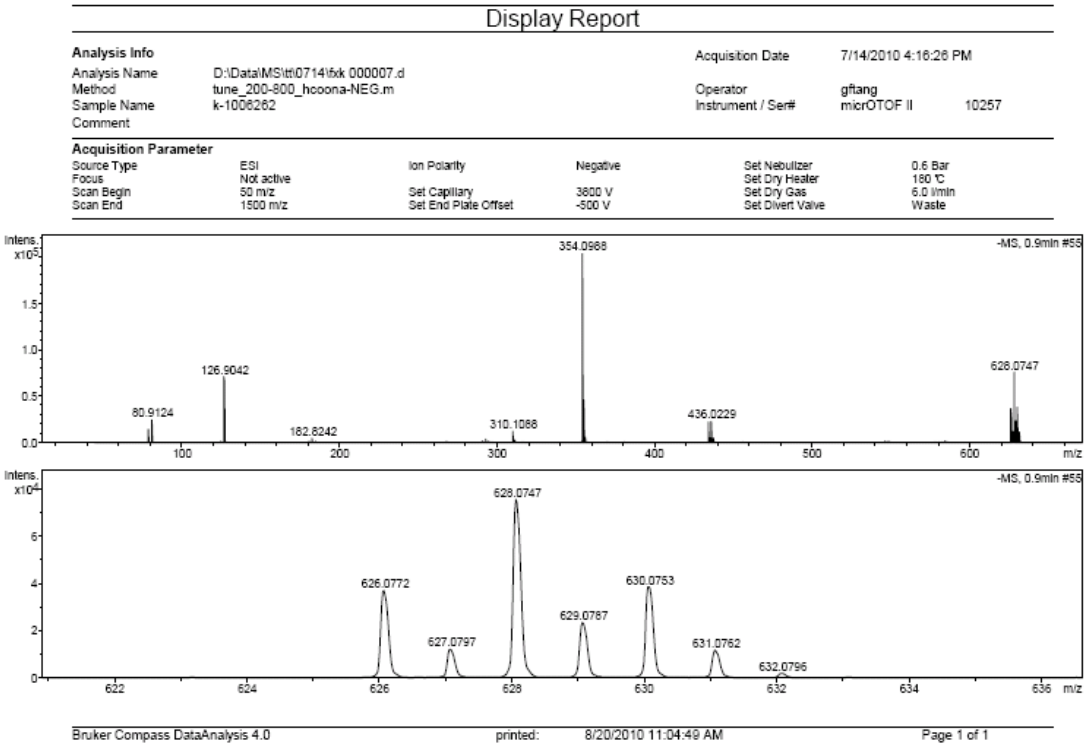


Fig. S1. The HR-MS spectrum of salt **6**.

Synthesis of pyridine-bridged bis(benzimidazol-2-ylidene palladium complex 3. A suspension of pyridine-bridged bis-benzimidazolium dibromide **6** (628 mg, 1 mmol) and $Pd(OAc)_2$ (224 mg,1 mmol) was stirred in DMSO (8 mL) for 1 h at room temperature under vacuum. After refilling the argon, the mixture was heated under stirring in the open vessel model at165 ^{o}C for 25 min (at 40 W with a CEM Discover microwave instrument). DMSO was removed under vacuum with heating. After cooling to room temperature, the resulting residue was washed with MeOH (5× 10 mL) to afford crude compounds. Further

purification by crystallization from hot MeOH and cold Et_2O afforded a grayish orange solid; yield: 495 mg (68 %).^{1}H NMR (DMSO-d_6, 400 MHz, 398 K): δ = 9.35 (s, 2H), 7.72 (d, *J* = 7.8 Hz, 4 H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 2 H), 4.88 (t, *J* = 7.5 Hz, 4 H), 2.23 (quintet, *J* = 7.3 Hz, 4 H), 1.57 (quintet, *J* = 7.5 Hz, 4H), 1.07 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (DMSO-d_6,100 MHz, 378 K): δ=180.86, 168.52, 167.35, 141.84, 134.39, 134.35,124.30, 123.94, 112.93, 112.90, 111.29, 48.19, 30.86, 20.05,13.97; HR-MS (ESI) for $C_{28}H_{29}BrN_5O_2Pd$: m/z = 654.0519 ($[M-Br]^+$, Calcd.); 654.0470 (Found).

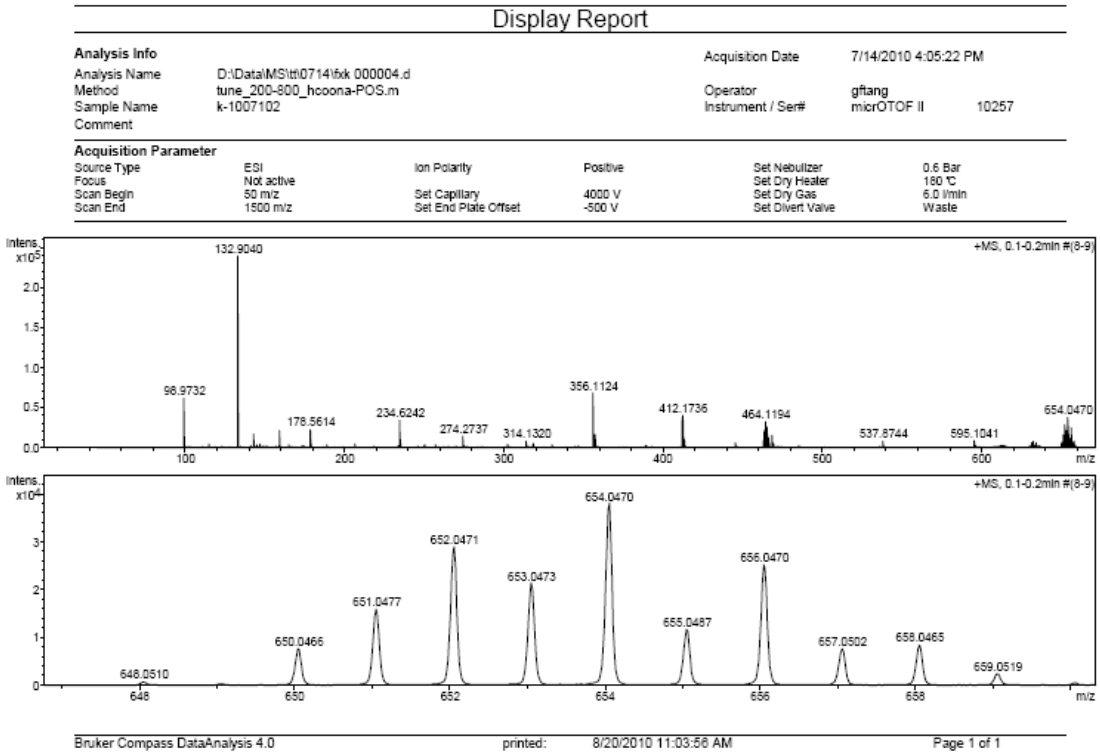


Fig. S1. The HR-MS spectrum of palladium pincer complex **3**.

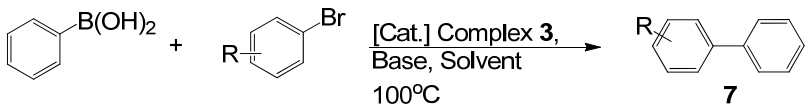
3 . Suzuki-coupling of bromoarene with aryl boronic acid catalyzed by pyridine-bridged palladium pincer complex 3 in aqueous solvents

General procedure for the Suzuki–Miyaura coupling reactions and catalyst recycling: 1 mL of 50 ppm palladium pincer complex **3** aqueous solution (or in mixture solvents) was added to the 5-mL flask containing bromoarene (1 mmol), aryl boronic acid (1.5 mmol) and K_2CO_3 (2 mmol) under air. After heating at 100 ^{o}C for 3 h or certain time

(monitored by TLC), the reaction mixture was allowed to cool to room temperature and the aqueous layer was extracted with ether (3×5 mL). The combined organic extracts were dried over anhydrous sodium sulfate. After evaporation under vacuum, the crude product was purified by flash column chromatography (hexane/EtOAc = 100/1).

As for solid biaryl products, a more convenient isolation process is requested: after the reaction mixture cool to the room temperature, the product was obtained by simply filtration and then washing with few drops of water in order to get rid of adsorptive impurities such catalyst, base and boronic acid, which is pure enough for the NMR analysis. The filtrate containing the catalyst could be applied for the next catalytic cycle by adding bromoarene (1 mmol), aryl boronic acid (1.5 mmol) and base. Due to a very low catalyst loading, carefully filtration is required to transfer most of catalyst into the filtrate; up to three cycles an almost quantitative isolated yield could be realized. Further recycling of catalyst and base in the filtrate resulted in a stochastic yield, which may be aroused by ineluctable product adsorption and hardly transferring all the catalyst and base with such low catalyst loading for several times.

Table S1. Suzuki-coupling of bromoarenes with phenyl boronic acid catalyzed by pyridine-bridged palladium pincer complex **3** in water.[a]

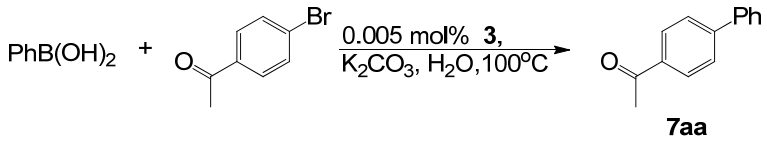


Entry	[Cat.] (mol%)	R	Solvent	Base	Time (h.)	Product	Yield (%)[b]
1	0.005	H	H_2O	K_2CO_3	**8**	**7b**	58
2	0.005	4-Me	H_2O	K_2CO_3	**8**	**7e**	22
3	0.005	4-Me	MeOH	K_2CO_3	**24**	**7e**	trace
4	0.005	4-Me	H_2O/MeOH = 1:1	Na_2CO_3	**8**	**7e**	86
5	0.005	4-Me	H_2O/MeOH = 1:1	Cs_2CO_3	**3**	**7e**	98
6	0.005	4-Me	H_2O/MeOH = 1:1	K_3PO_4	**8**	**7e**	76
7	0.005	4-Me	H_2O/MeOH = 1:1	KOH	**8**	**7e**	84
8	0.005	4-NO_2	H_2O	K_2CO_3	**8**	**7k**	78
9	0.005	3,5-$(CF_3)_2$	H_2O	K_2CO_3	**8**	**7l**	11

10	0.005	1-Naph.	H_2O	K_2CO_3	**8**	**7m**	4
11	0.0008	4-CN	H_2O	K_2CO_3	**36**	**7h**	95
12	0.0008	4-F	H_2O	K_2CO_3	**24**	**7j**	trace

[a] Reaction conditions: 0.5 mmol bromoarenes, 0.75 mmol phenyl boronic acid, 1 mmol base in 1 mL solvent at 100°C with palladium pincer complex **3** under air. [b] Isolated yield.

Table S2. Recycling experiments of palladium pincer complex **3** in the Suzuki-Miyaura coupling of 4-bromoactophenone with phenyl boronic acid. [a]

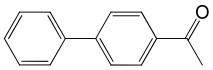


7aa

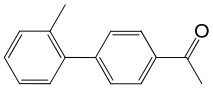
Run	1	2	3	4	5
Yield(%)[b]	>99	99	98	65	trace

[a] Reaction conditions: 0.5 mmol 4-bromoactophenone, 0.75 mmol phenyl boronic acid, 1 mmol K_2CO_3 in 1 mL H_2O at 100°C with palladium pincer complex **3** under air. [b] Isolated yield.

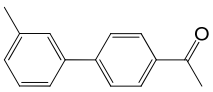
4. Analytical data of the coupling products



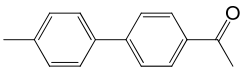
7aa: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.04 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 7.0 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 2.65 (s, 3H). GC-MS: *m/z* = 196.1 [M^+], 181.1, 152.1.



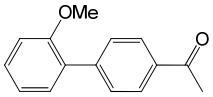
7ab: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) : δ = 8.02 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.20-7.32 (m, 4H), 2.65 (s, 3H), 2.28 (s, 3H). GC-MS: m/z = 210 [M^+].



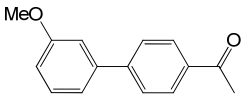
7ac: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.02 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.44 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 2.64 (s, 3H), 2.44 (s, 3H). GC-MS: m/z = 210 [M^+], 195 [M-Me^+], 165, 152.



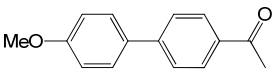
7ad: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 7.82 (d, *J* = 8.6 Hz, 4H), 7.61 (d, *J* = 8.6 Hz, 4H), 2.59 (s, 6H). GC-MS: m/z = 210 [M^+], 195[M-Me^+], 165, 152.



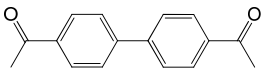
7ae: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.01 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.36 (q, *J* = 8.5 Hz, 2H), 7.06 (t, *J* = 7.0 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 3.83 (s, 3H), 2.64 (s, 3H). GC-MS: m/z = 226 [M^+].



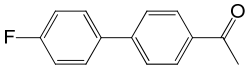
7af: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.02 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.15 (s, 1H), 6.95 (d, *J* = 6.8Hz, 1H), 3.88 (s, 3H), 2.64 (s, 3H). GC-MS: m/z = 226 [M^+].



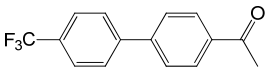
7ag: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.01 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 6.8 Hz, 2H), 3.87 (s, 3H), 2.63 (s, 3H). GC-MS: m/z = 226 [M^+], 211[M-Me^+].



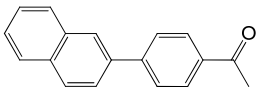
7ah: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.22 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 6.2 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 1H), 2.66 (d, *J* = 7.8 Hz, 6H). GC-MS: m/z = 238 [M^+], 223 [M-Me^+], 152.



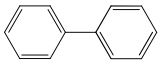
7ai: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.03 (d, *J* = 10.1 Hz, 2H), 7.55-7.68 (m, 4H), 7.16 (t, *J* = 8.6 Hz, 2H), 2.64 (s, 3H). GC-MS: m/z = 214 [M^+], 199, 170.



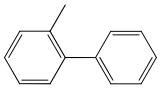
7aj: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.06 (d, *J* = 8.4 Hz, 2H), 7.73 (s, 4H), 7.70 (d, *J* = 8.4 Hz, 2H), 2.66(s, 3H). GC-MS: m/z = 264 [M^+], 249 [M-Me^+], 201, 152.



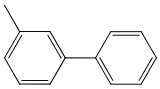
7al: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.08 (d, *J* = 9.4 Hz, 3H), 7.72-8.01 (m, 6H), 7.53 (t, *J* = 3.8 Hz, 2H), 2.67 (s, 3H). GC-MS: m/z = 246 [M^+], 231 [M-Me^+], 202.



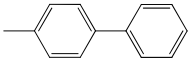
7b: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.60 (d, *J* = 7.2 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.35 (t, *J* = 7.3 Hz, 2H). GC-MS: *m/z* = 154 [M]$^+$, 76.



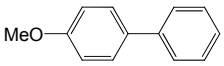
7c: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.45-7.23 (m, 9H), 2.28 (s, 3H). GC-MS: *m/z* = 168.1 [M]$^+$, 153.1, 115.1. GC-MS: *m/z* = 168 [M]$^+$.



7d: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.59 (d, *J* = 7.0 Hz, 2H), 7.47-7.38 (m, 4H), 7.37-7.31 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 2.43 (s, 3H). GC-MS: *m/z* = 168.2 [M]$^+$, 152.1, 115.1.

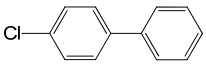


7e: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 7.58 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 2.40 (s, 3H). GC-MS: *m/z* = 168.1 [M]$^+$, 152.1, 115.1.

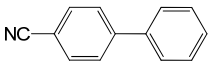


7f: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 7.54 (t, *J* =8.8 Hz, 4H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H). GC-MS: *m/z* = 184 [M] $^+$,169

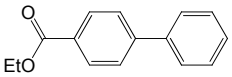
[M-Me] $^{+}$.



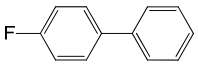
7g: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 7.50-7.63 (m, 4H), 7.31-7.50 (m, 5H). GC-MS: *m/z* = 188 [M] $^{+}$, 152, 76.



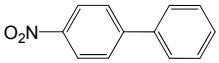
7h: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 7.73 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H). GC-MS: *m/z* = 179.1 $[M]^{+}$, 151.1.



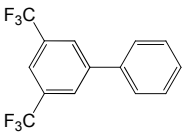
7i: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.12 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). GC-MS: *m/z* = 228 [M+2] $^{+}$, 200, 183, 155.



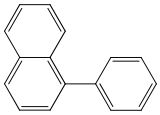
7j: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 7.51-7.63 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 8.6 Hz, 2H). GC-MS: *m/z* = 172 [M] $^{+}$



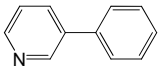
7k: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.46(t, *J* = 2.0 Hz, 1H), 8.21 (dq, *J* = 8.2 Hz, 1H), 7.92(dq, *J* = 7.8 Hz, 1H), 7.59-7.70 (m, 3H), 7.41-7.56 (m, 3H). GC-MS: *m/z* = 199 [M] $^{+}$, 152.



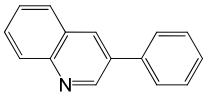
7l: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.02 (s, 2H), 7.86 (s, 1H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.42-7.58 (m, 3H). GC-MS: m/z = 290 $[M^{+}]$, 271, 201, 152.



7m: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 7.70-8.20 (m, 3H), 7.29-7.65 (m, 9H). GC-MS: m/z = 204 [M^+].



7n: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 8.86 (s, 1H), 8.60 (d, *J* = 4.8 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.43-7.35 (m, 2H). GC-MS: *m/z* = 155 $[M]^+$, 127, 102.



7o: ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ = 9.17 (d, *J* = 2.1 Hz, 1H), 8.24 (s, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.64-7.72 (m, 3H), 7.48-7.56 (m, 3H), 7.40 (t, *J* = 7.3 Hz, 1H). GC-MS: *m/z* = 205 $[M]^+$.

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3. Z Xi, F. Liu, Y. Zhou, W. Chen, *Tetrahedron,* 2008, **64**, 4254.