Supporting Information

Novel Bisimidazolium Pincers as Low Loading Ligands for *in situ* Palladium-Catalyzed Suzuki-Miyaura Reaction in Ambient Atmosphere

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I. General Remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $Pd(OAc)_2$ was purchased from Shanxi Kai Da Chemical Engineering (China) CO., Ltd. Cyanuric chloride was purchased from AstaTech (Chengdu) Biopharm CO., Ltd, and recrystallized twice by petroleum ether before use. Acetonitrile was dried by refluxing for at least 6 hours with CaH_2, then distilled and stored under N_2. *N*-Substituted imidazoles **2a**-**2g**[1] and ligand **3b′**[2] were synthesized according to published procedures. The test tube for Suzuki reaction must be soaked by HNO_3 for at least 48 hours prior to use. $Pd(OAc)_2$ and bisimidazolium ligands were prepared to use as the 5×10^{-4} M stock solutions in acetonitrile and methanol, respectively.

NMR spectra were obtained on a Bruker AMX-400 or a Varian INOVA 400 MHz spectrometer. The ^1H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF Premier (ESI). Elemental analysis was measured using a Euro EA-3000 elemental analyzer. Melting points were determined with XRC-1 instrument and are uncorrected.

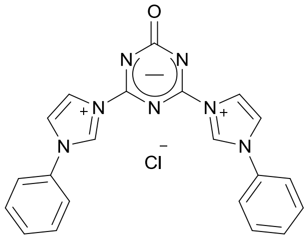
X-Ray single-crystal diffraction data were collected on an Oxford CrysAlis CCD diffractometer for **3a** (PF_6^-) and Xcalibur Eos diffractometer for **4**, respectively. The crystallographic data are summarized in Table S1.

II. General Procedure for the Synthesis of the Bisimidazolium Ligands

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with cyanuric chloride (0.184 g, 1.0 mmol) in dry acetonitrile under N_2 atmosphere. A solution of the *N*-substituted imidazole (2.2 mmol) in dry acetonitrile was added dropwise at room temperature within 30 minutes. After the suspension was heated at 110 °C for an indicated time, the reaction mixture was then cooled down to room temperature and filtered. The crude product was purified by column chromatography on silica gel to afford the pure product.

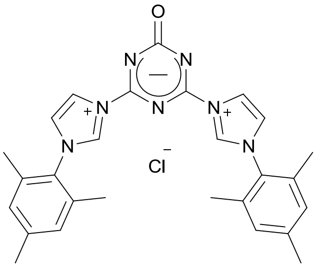
For **3g**, *n*-butyl imidazole (0.273 g, 2.2 mmol) in dry acetonitrile was added dropwise to a solution of cyanuric chloride (0.184 g, 1.0 mmol) in dry acetonitrile under N_2 atmosphere at 0 °C within 10 minutes. The suspension was reacted at 0 ℃ for further 20 minutes. Then the white precipitate was quickly filtered, washed with cold acetonitrile, and dried in vacuo to afford pure **3g**. **3g** must be stored under nitrogen in a refrigerator.

III. Procedures and Experimental Data for the Described Ligands



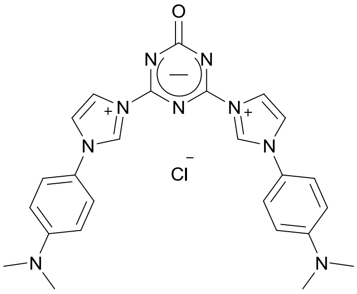
2-Oxo-4,6-bis(1-phenyl-1*H*-imidazol-3-ium-3-yl)-2*H*-1,3,5-triazin-5-ide chloride (3a)

Cyanuric chloride (0.184 g, 1.0 mmol) and 1-phenyl-*1H*-imidazole **2a** (0.317 g, 2.2 mmol) in acetonitrile were heated at 110 ℃ for 2.5 h. The pure **3a** was obtained as a white solid (0.296 g, 71% yield) after chromatography on silica gel (CH_2Cl_2/MeOH = 5/1, v/v). mp >250 ˚C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): *δ* 10.97 (s, 2H), 8.84 (s, 2H), 8.58 (s, 2H), 8.03 (d, *J* = 7.6 Hz, 4H), 7.72-7.64 (m, 6H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$): *δ* 165.4, 159.9, 135.2, 134.7, 130.5, 130.2, 122.8, 122.7, 119.7. HRMS-ESI $[M\text{-}Cl]^+$ calcd for $C_{21}H_{16}N_7O$, 382.1411; found, 382.1412. Elemental analysis calcd (%) for $C_{21}H_{16}ClN_7O \cdot 2.7CH_2Cl_2 \cdot 0.4CH_3CN$: C, 44.34; H, 3.43; N, 15.62. Found: C, 44.22; H, 3.45; N, 15.76.



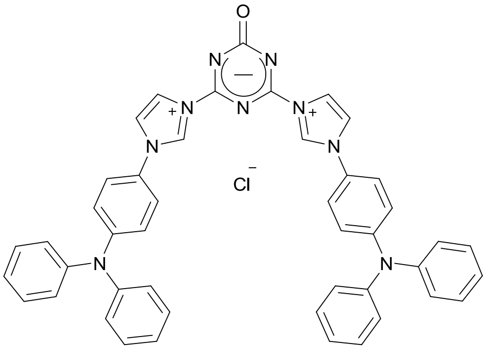
2-Oxo-4,6-bis(1-mesityl-1*H*-imidazol-3-ium-3-yl)-2*H*-1,3,5-triazin-5-ide chloride (3b)

Cyanuric chloride (0.184 g, 1.0 mmol) and 1-mesityl-*1H*-imidazole **2b** (0.409 g, 2.2 mmol) in acetonitrile were heated at 110 ℃ for 2.5 h. The pure **3b** was obtained as a white solid (0.341 g, 68% yield) after chromatography on silica gel (CH_2Cl_2/MeOH = 10/1, v/v). mp >250 ˚C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): *δ* 10.57 (s, 2H), 8.84 (s, 2H), 8.19 (s, 2H), 7.18 (s, 4H), 2.34 (s, 6 H), 2.10 (s, 12H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$): *δ* 165.3, 159.8, 140.6, 137.5, 134.2, 131.1, 129.3, 125.1, 119.7, 20.6, 17.0. HRMS-ESI $[M\text{-}Cl]^+$ calcd for $C_{27}H_{28}N_7O$, 466.2350; found, 466.2353. Elemental analysis calcd (%) for $C_{27}H_{28}ClN_7O \cdot 0.3CH_2Cl_2 \cdot 0.5H_2O$: C, 61.12; H, 5.56; N, 18.28. Found: C, 60.95; H, 5.75; N, 18.05.



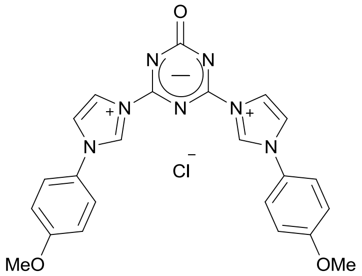
2-Oxo-4,6-bis{1-[4-(dimethylamino)phenyl]-1*H*-imidazol-3-ium-3-yl}-2*H*-1,3,5-triazin-5-ide chloride (3c)

Cyanuric chloride (0.184 g, 1.0 mmol) and 4-(1*H*-imidazol-1-yl)-*N*,*N*-dimethylaniline **2c** (0.412 g, 2.2 mmol) in acetonitrile were heated at 110 ℃ for 3 h. The pure **3c** was obtained as a greenish solid (0.322 g, 64% yield) after chromatography on silica gel (CH_2Cl_2/MeOH = 6/1, v/v). mp >250 ˚C. ^1H NMR (400 MHz, DMSO-d_6): δ 10.64 (s, 2H), 8.75 (s, 2H), 8.43 (s, 2H), 7.75 (d, J = 8.4 Hz, 4H), 6.88 (d, J = 8.8 Hz, 4H), 3.00 (s, 12H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.8, 160.0, 151.3, 133.9, 123.4, 123.3, 122.7, 119.5, 112.3, 40.1. HRMS-ESI $[M-Cl]^+$ calcd for $C_{25}H_{26}N_9O$, 468.2255; found, 468.2252. Elemental analysis calcd (%) for $C_{25}H_{26}ClN_9O$: C, 59.58; H, 5.20; N, 25.01. Found: C, 59.64; H, 5.11; N, 24.95.



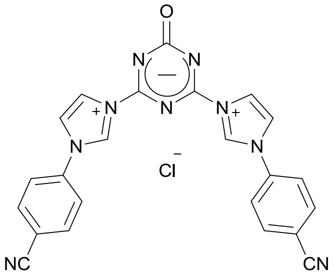
2-Oxo-4,6-bis{1-[4-(diphenylamino)phenyl]-1*H*-imidazol-3-ium-3-yl}-2*H*-1,3,5-triazin-5-ide chloride (3d)

Cyanuric chloride (0.184 g, 1.0 mmol) and 4-(1*H*-imidazol-1-yl)-*N*,*N*-diphenylaniline **2d** (0.684 g, 2.2 mmol) in acetonitrile were heated at 110 ℃ for 2.5 h. The pure **3d** was obtained as a yellow solid (0.466 g, 62% yield) after chromatography on silica gel (CH_2Cl_2/MeOH = 10/1, v/v). mp >250 ˚C. ^1H NMR (400 MHz, $CDCl_3$): δ 12.23 (s, 2H), 8.60 (s, 2H), 7.90 (d, J = 8.8 Hz, 4H), 7.64 (s, 2H), 7.32-7.28 (m, 8H), 7.17-7.11 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 160.3, 150.2, 146.6, 135.8, 129.9, 126.9, 125.9, 124.8, 122.8, 121.9, 120.6, 119.9. HRMS-ESI $[M-Cl]^+$ calcd for $C_{45}H_{34}N_9O$, 716.2881; found, 716.2881. Elemental analysis calcd (%) for $C_{45}H_{34}ClN_9O$ $0.5CH_2Cl_2$ $0.8CH_3CN$: C, 68.36; H, 4.56; N, 16.59. Found: C, 68.50; H, 4.72; N, 16.53.



2-Oxo-4,6-bis[1-(4-methoxyphenyl)-1*H*-imidazol-3-ium-3-yl]-2*H*-1,3,5-triazin-5-ide chloride (3e)

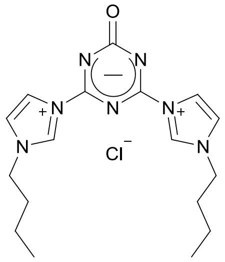
Cyanuric chloride (0.184 g, 1.0 mmol) and 1-(4-methoxyphenyl)-*1H*-imidazole **2e** (0.383 g, 2.2 mmol) in acetonitrile were heated at 110 ℃ for 2.5 h. The pure **3e** was obtained as a white solid (0.329 g, 69% yield) after chromatography on silica gel (CH_2Cl_2/MeOH = 10/1, v/v). mp >250 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.71 (s, 2 H), 8.79 (s, 2 H), 8.48 (s, 2 H), 7.90 (d, J = 8.4 Hz, 4 H), 7.22 (d, J = 8.8 Hz, 4H), 3.87 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.0, 160.5, 159.8, 134.8, 127.7, 124.3, 122.9, 119.5, 115.1, 55.9. HRMS-ESI $[M-Cl]^+$ calcd for $C_{23}H_{20}N_7O_3$, 442.1622; found, 442.1624. Elemental analysis calcd (%) for $C_{23}H_{20}ClN_7O_3$: C, 57.80; H, 4.22; N, 20.52. Found: C, 57.64; H, 4.29; N, 20.62.



2-Oxo-4,6-bis[1-(4-cyanophenyl)-1*H*-imidazol-3-ium-3-yl]-2*H*-1,3,5-triazin-5-ide chloride (3f)

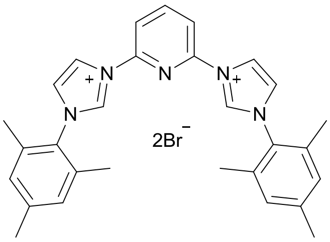
Cyanuric chloride (0.184 g, 1.0 mmol) and 4-(*1H*-imidazol-1-yl)-benzonitrile **2f** (0.372 g, 2.2 mmol) in acetonitrile were heated at 110 ˚C for 3.5 h. The pure **3f** was obtained as a brown solid (0.350 g, 75% yield) after a few washes with acetonitrile. mp >250 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.04 (s, 2H), 8.90 (s, 2H), 8.67 (s, 2H), 8.30-8.23 (m, 8H). ^{13}C NMR (100 MHz, DMSO-d_6): δ

163.2, 150.1, 138.7, 135.5, 134.5, 133.6, 123.2, 122.6, 120.3, 113.7. HRMS-ESI $[M-Cl]^+$ calcd for $C_{23}H_{14}N_9O$, 432.1316; found, 432.1317. Elemental analysis calcd (%) for $C_{23}H_{14}ClN_9O$ $0.9CH_3OH$ CH_2Cl_2: C, 51.42; H, 3.40; N, 21.67. Found: C, 51.13; H, 3.45; N, 21.55.



2-Oxo-4,6-bis[1-*n*-butyl-1*H*-imidazol-3-ium-3-yl]-2*H*-1,3,5-triazin-5-ide chloride (3g)

Cyanuric chloride (0.184 g, 1.0 mmol) and 1-butyl-1*H*-imidazole **2g** (0.273 g, 2.2 mmol) in acetonitrile were reacted at 0 ˚C for 20 min. The pure **3g** was obtained as a white solid (0.196 g, 52% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.39 (s, 2 H), 8.56 (s, 2 H), 8.05 (s, 2 H), 4.30 (t, J = 7.0 Hz, 4 H), 1.92-1.85 (m, 4 H), 1.34-1.28 (m, 4H), 0.93 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.7, 159.8, 136.5, 123.4, 119.0, 49.3, 31.0, 18.8, 13.3. HRMS-ESI $[M-Cl]^+$ calcd for $C_{17}H_{24}N_7O$, 342.2037; found, 342.2035. Elemental analysis calcd (%) for $C_{17}H_{24}ClN_7O$ $0.8CH_2Cl_2$: C, 47.95; H, 5.79; N, 21.99. Found: C: 48.21; H: 5.89; N: 21.76.



2,6-Bis(1-mesityl-1*H*-imidazol-3-ium-3-yl)pyridine dibromide[2] (3b′)

A sealed glass tube immersed in an oil bath containing a mixture of 2,6-dibromopyridine (0.50 g, 2.1 mmol) and 1-mesityl-*1H*-imidazole (1.08 g, 5.8 mmol) was heated at 150 ˚C for 3 days. After cooling to room temperature, the black residue was triturated with Et_2O and filtered. The resulting black solid was dissolved in a minimum amount of methanol and reprecipitated by adding Et_2O. The precipitate was collected by filtration and dried in vacuo to afford **3b′** as a brown solid (0.89 g, 70% yield). ^{1}H NMR (DMSO-d_6): δ 10.78 (s, 2H), 9.25 (s, 2H), 8.70 (t, J = 8.0 Hz, 1H), 8.48 (d, J = 8.0 Hz, 2H), 8.32 (s, 2H), 7.21 (s, 4H), 2.36 (s, 6H), 2.15 (s, 12H).

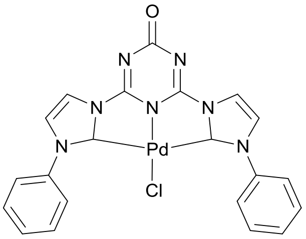
IV. Crystal Growth and X-ray Crystallographic Data of 3a (PF_6^-)·CH_3OH and 4·$(CH_3)_2CO$

Compound **3a** (PF_6^-) was easily obtained from **3a** through anion exchange with NH_4PF_6, and the single crystal was obtained by slow diffusion of MeOH/CH_2Cl_2 at ambient temperature for several days. The single crystal **4** was grown in acetone/EtOH/H_2O in the same way.

Table S1 Summary of Crystal Data for **3a**(PF_6^-)·CH_3OH and **4**·$(CH_3)_2CO$

	3a (PF_6^-)	**4**
Empirical formula	$C_{22}H_{20}F_6N_7O_2P$	$C_{13}H_{19}N_5O_3$
Formula weight	559.42	293.33
Temperature/K	100(2)	293.15
Crystal system	orthorhombic	triclinic
Space group	P n m a	P-1
a/Å	18.2455(3)	8.0418(5)
b/Å	15.6917(2)	9.8200(6)
c/Å	8.0286(10)	10.9614(8)
α/ °	90.000	89.012(5)
β/ °	90.000	77.986(6)
γ/ °	90.000	65.983(6)
Volume/Å^3	2298.61(6)	771.15(9)
Z	4	2
Calculated density (mg/mm^3)	1.617	1.263
m/mm^{-1}	0.207	0.093
F(000)	1144	312.0
Crystal size/mm^3	0.58 × 0.38 × 0.20	0.29 × 0.23 × 0.20
2Θ range for data collection	2.58 to 29.27^o	6.1 to 49.98^o
Index ranges	$-24 \leq h \leq 23, -19 \leq k \leq 21, -11 \leq l \leq 10$	$-9 \leq h \leq 9, -11 \leq k \leq 11, -12 \leq l \leq 13$
Reflections collected	18885	5798
Independent reflections	2998[R(int)= 0.0256]	2722[R(int) = 0.0185]
Data/restraints/parameters	2998 / 0 / 194	2722/0/193
Goodness-of-fit on F^2	1.170	1.068
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0312, wR2 = 0.0861	R_1 = 0.0644, wR_2 = 0.1793
Final R indexes [all data]	R1 = 0.0415, wR2 = 0.0882	R_1 = 0.0849, wR_2 = 0.1972
Largest diff. peak/hole (e Å^{-3})	0.255/-0.369	0.61/-0.31
CCDC No.	898254	898255

V. Synthesis and Characterization of the Pd(L_{3a})Cl Complex



2-Oxo-4,6-bis(1-phenyl-1*H*-imidazol-2-ylidene-3-yl)-2*H*-1,3,5-triazin-5-ide chloropalladium (Pd(L_{3a})Cl)

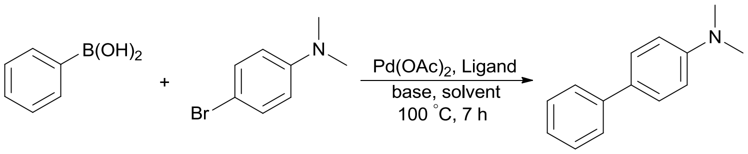
A mixture of the ligand **3a** (0.42 g, 1.0 mmol), ^{t}BuONa (0.24 g, 2.4 mmol), and $Pd(OAc)_2$ (0.27 g, 1.2 mmol) in dry THF (8 mL) were allowed to react in a flame-dried Schlenk test tube at room temperature under N_2 atmosphere for 5 h. After reaction, the volatiles were removed under reduced pressure. The residue was then dispersed in 50 mL CH_2Cl_2 and filtered. The organic phase was concentrated and passed through a silica gel column (CH_2Cl_2/MeOH = 10/1, v/v) to afford the complex as a white solid (0.24 g, 46% yield). mp >250 ˚C. ^{1}H NMR (400 MHz, DMSO): δ 8.51 (br, 2H), 7.46-7.42 (m, 6H), 7.36-7.30 (m, 6H). ^{13}C NMR (100 MHz, DMSO): δ 170.0, 161.4, 129.9, 129.4, 128.8, 126.3, 123.5, 122.6, 119.1. HRMS (ESI-TOF) (CH_3OH): m/z: 524.0211 $[Pd(L_{3a})Cl+H]^+$, 542.0385 $[Pd(L_{3a})Cl+H_2O+H]^+$, 556.0380 $[Pd(L_{3a})+CH_3OH+H]^+$, 560.0439 $[Pd(L_{3a})Cl+2H_2O+H]^+$. Elemental analysis calcd (%) for $C_{21}H_{16}ClN_7OPd$ 0.8CH_2Cl_2: C, 44.21; H, 3.00; N, 16.56. Found: C, 44.48; H, 3.22; N, 16.84.

VI. General Procedure for the Suzuki–Miyaura Coupling Reaction

A mixture of a bromoarene (1.0 mmol), an arylboronic acid (1.1 mmol), $Pd(OAc)_2$ (0.10 mL, 5.0×10^{-5} mmol), a ligand (0.10 mL, 5.0×10^{-5} mmol) and a base (0.424 g, 2.0 mmol) in a solvent (1 mL) were allowed to react in a sealed tube at 100 ˚C for 7 h. After reaction, the volatiles were removed under reduced pressure. The residue was then dispersed in 20 mL CH_2Cl_2 and filtered. The organic phase was concentrated and passed through a silica gel column to afford the desired coupling product.

VII. Optimization of the Suzuki–Miyaura Coupling Reaction

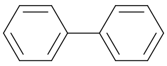
Table S2 Optimization of the Suzuki–Miyaura coupling reaction.[a]



Entry	Solvent	Base	Ligand	Yield[b] (%)
1	1,4-dioxane	K_3PO_4	**3a**	12
2	DMF	K_3PO_4	**3a**	18
3	H_2O	K_3PO_4	**3a**	39
4	MeOH	K_3PO_4	**3a**	64
5	MeOH/H_2O	K_3PO_4	**3a**	67
6	MeOH/H_2O	K_2CO_3	**3a**	56
7	MeOH/H_2O	NaOAc	**3a**	12
8	MeOH/H_2O	Et_3N	**3a**	25
9	MeOH/H_2O	K_3PO_4	**3b**	77
10	MeOH/H_2O	K_3PO_4	**3c**	94
11	MeOH/H_2O	K_3PO_4	**3d**	75
12	MeOH/H_2O	K_3PO_4	**3e**	83
13	MeOH/H_2O	K_3PO_4	**3f**	30
14	MeOH/H_2O	K_3PO_4	**3b′**	56
15	MeOH/H_2O	K_3PO_4	None	63

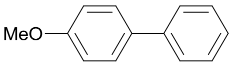
[a] Reaction conditions: 4-bromo-*N*,*N*-dimethylaniline (1.0 mmol), phenylboronic acid (1.1 mmol), $Pd(OAc)_2$ (0.005 mol%), ligand (0.005 mol%), base (2.0 mmol), solvent (1 mL) at 100 °C for 7 h. [b] Isolated yield.

VIII. Analytical Data of the Coupling Products



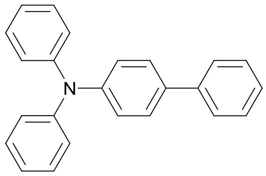
Biphenyl

White solid (0.151 g, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 7.2 Hz, 4H), 7.43 (t, J = 7.6 Hz, 4H), 7.33 (t, J = 7.2 Hz, 2H).



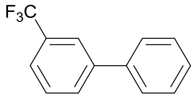
4-Methoxybiphenyl

White solid (0.173 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.53 (m, 4H), 7.45-7.41 (m, 2H), 7.33-7.29 (m, 1H), 6.98 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H).



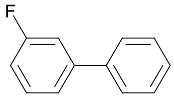
_N_,_N_-Diphenylbiphenyl-4-amine

White solid (0.308 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 7.6 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.32-7.24 (m, 5H), 7.12 (d, J = 8.0 Hz, 6H), 7.00 (t, J = 7.6 Hz, 2H).



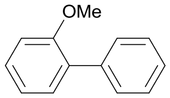
3-(Trifluoromethyl)biphenyl

Yellow oil (0.198 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.62-7.54 (m, 4H), 7.47 (t, J = 7.4 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H).



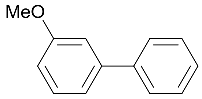
3-Fluorobiphenyl

Colorless oil (0.156 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.57 (m, 2H), 7.47-7.36 (m, 5H), 7.31-7.28 (m, 1H), 7.06-7.02 (m, 1H).



2-Methoxybiphenyl

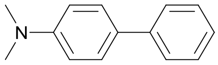
Colorless oil (0.164 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.35-7.32 (m, 3H), 7.06-6.99 (m, 2H), 3.89 (s, 3H).



3-Methoxybiphenyl

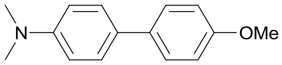
Yellow oil (0.178 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 7.6 Hz, 2H), 7.44 (t, J =

7.6 Hz, 2H), 7.40-7.36 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.16 (s, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 3.89 (s, 3H).



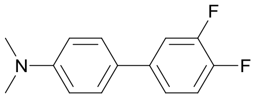
N,N-Dimethylbiphenyl-4-amine

White solid (0.185 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.30-7.27 (m, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.02 (s, 6H).



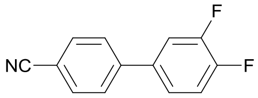
4'-Methoxy-N,N-dimethylbiphenyl-4-amine

Yellow solid (0.213 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.46 (m, 4H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 2H), 3.84 (s, 3H), 2.99 (s, 6H).



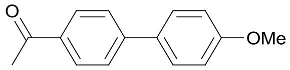
3',4'-Difluoro-N,N-dimethylbiphenyl-4-amine

White solid (0.214 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.35-7.30 (m, 1H), 7.25-7.23 (m, 1H), 7.19-7.13 (m, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 3.00 (s, 6H).



3',4'-Difluorobiphenyl-4-carbonitrile

White solid (0.206 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.42-7.37 (m, 1H), 7.30-7.24 (m, 2H).



1-(4'-Methoxybiphenyl-4-yl)ethanone

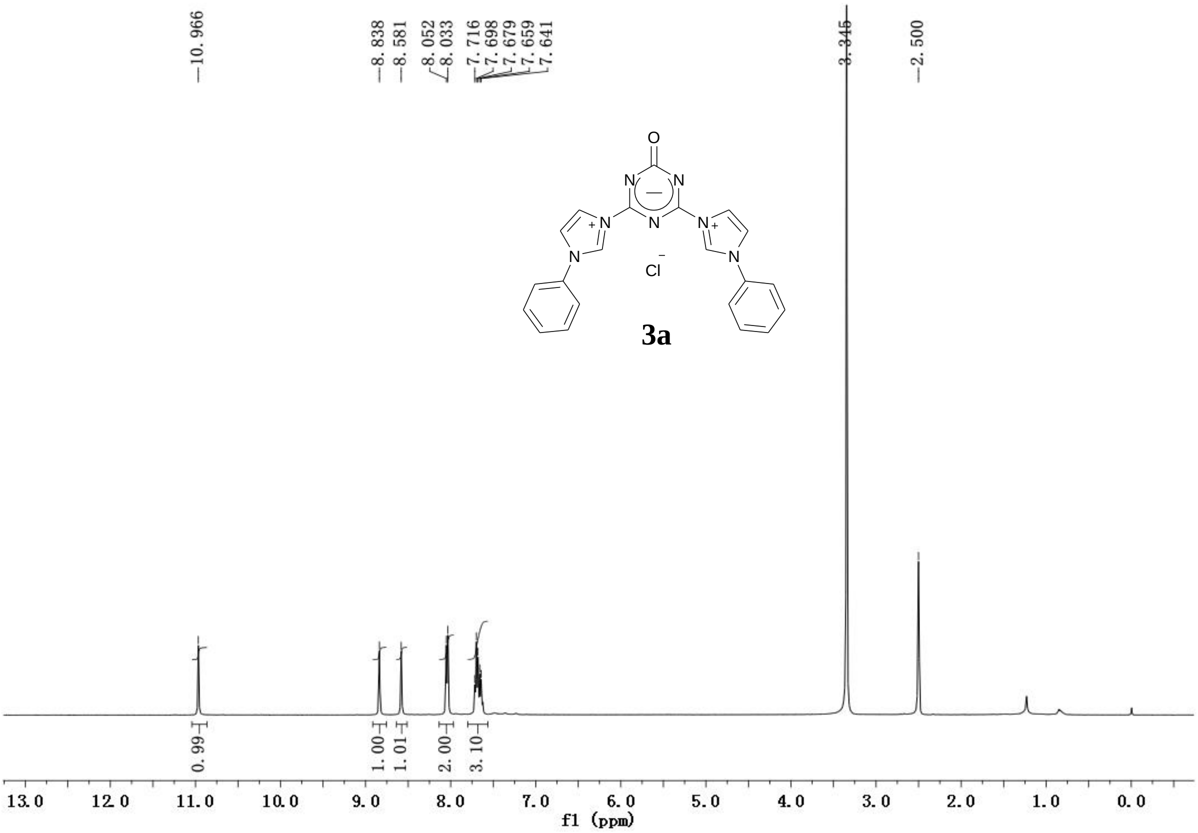
White solid (0.221 g, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 2.63 (s, 3H).

IX. References

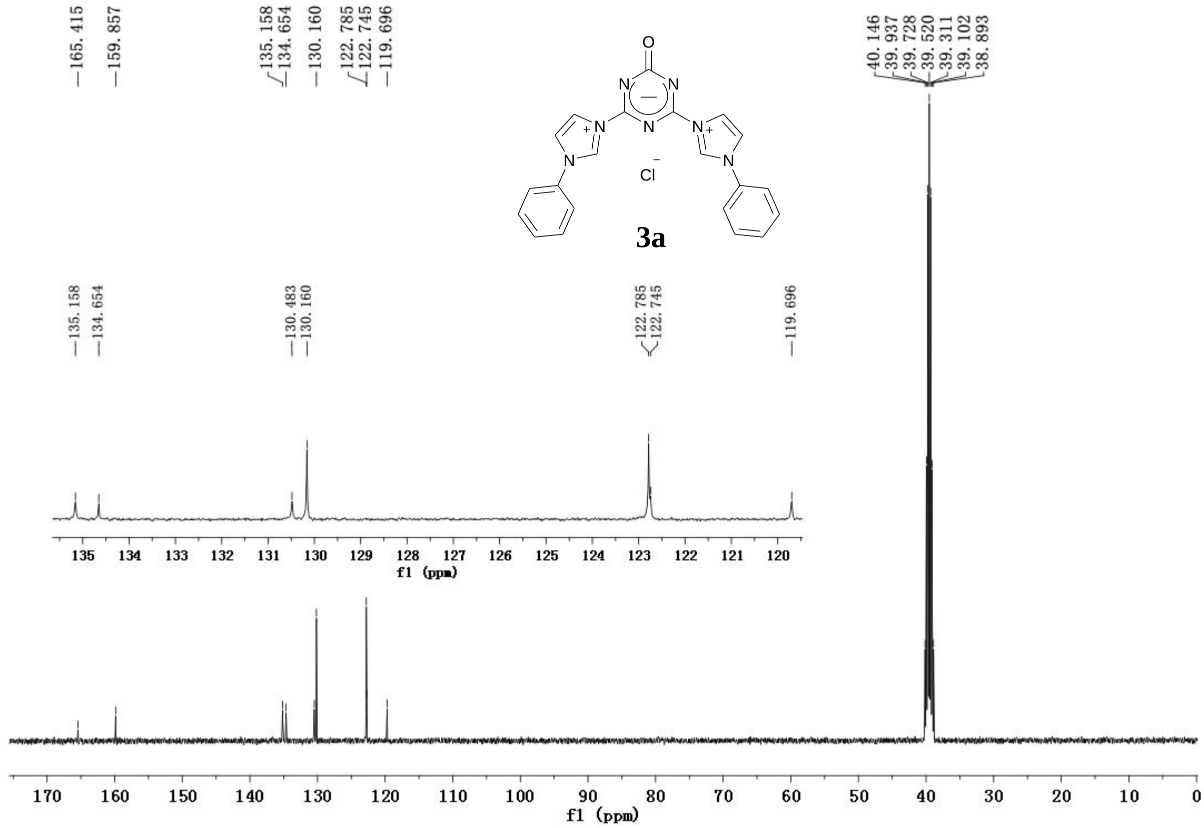
(1) (*a*) L. Zhu, P. Guo, G. Li, J. Lan, R. Xie and J. You, *J. Org. Chem.*, 2007, **72**, 8535; (*b*) A. J. Arduengo, F. P. Gentry, P. K. Taverkere, H. E. Simmons, **US** 6177575, 2001; (*c*) J.-Y. Cheng and Y.-H. Chu, *Tetrahedron Lett.*, 2006, **47**, 1575.

(2) D. Serra, P. Cao, J. Cabrera, R. Padilla, F. Rominger and M. Limbach, *Organometallics*, 2011, **30**, 1885.

X. Copies of ^{1}H NMR and ^{13}C NMR Spectra



3a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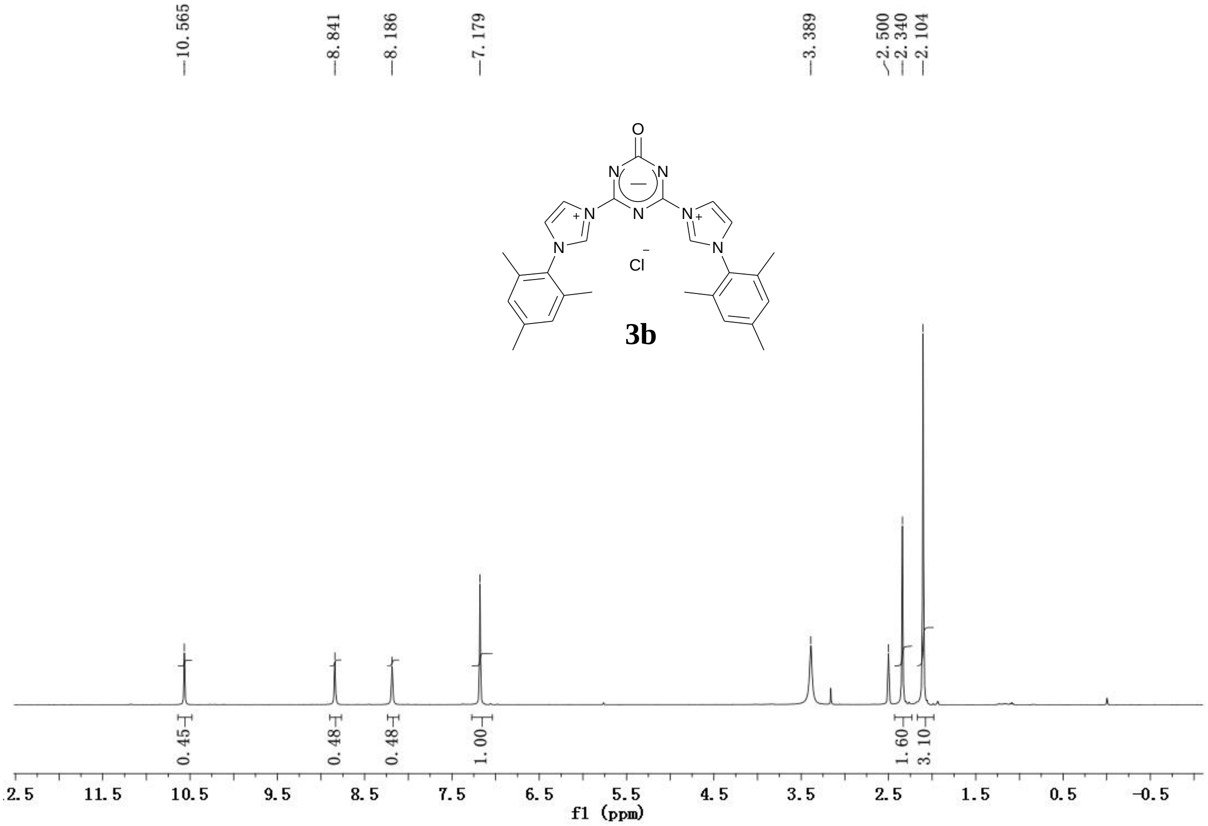
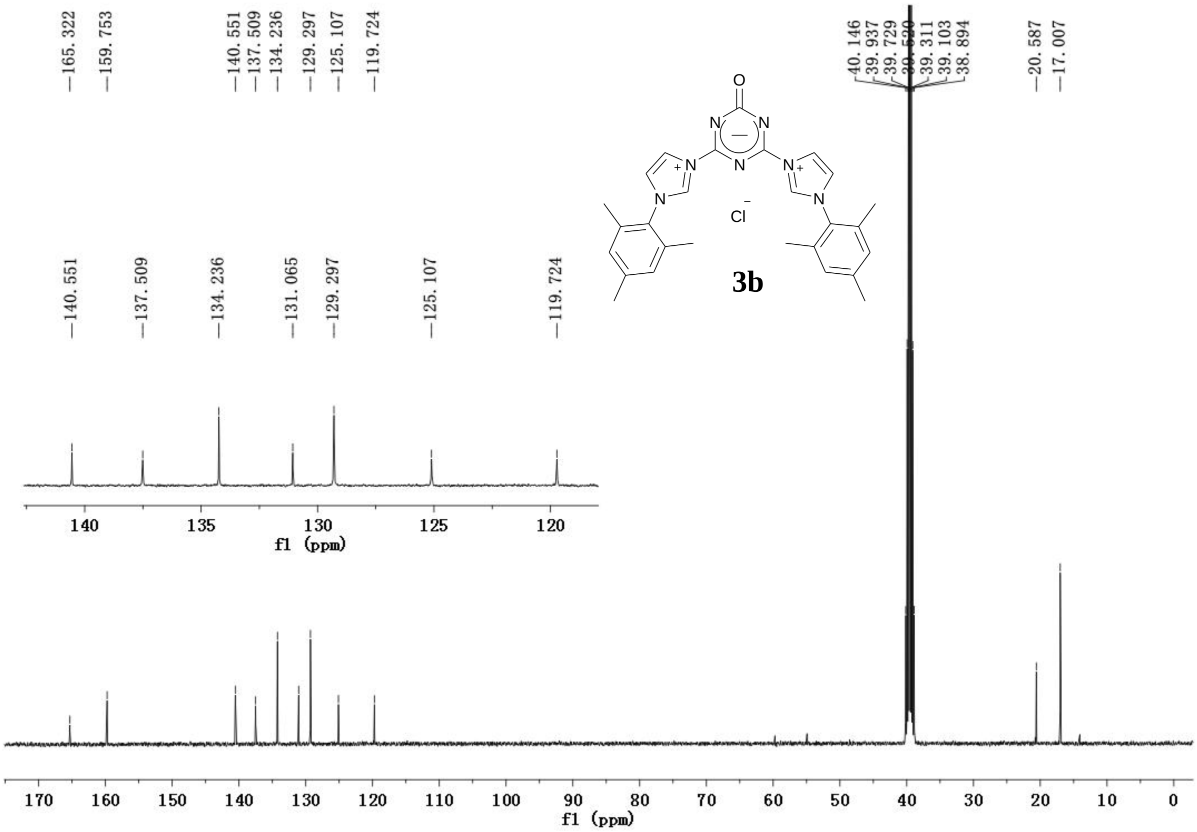
159. 857
135. 158
134. 654
130. 160
122. 785
122. 745
119. 696
40. 146
39. 937
39. 728
39. 520
39. 311
39. 102
38. 893
O
N
N
N
N
N
N
N
+
+
Cl
−
135. 158
134. 654
130. 483
130. 160
122. 785
122. 745
119. 696
135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


3b
10. 565
8. 841
8. 186
7. 179
3. 389
2. 500
2. 340
2. 104
O
N
N
N
N
N
N
N
+
+
Cl
−
0. 45
0. 48
0. 48
1. 00
1. 60
3. 10
2. 5
11. 5
10. 5
9. 5
8. 5
7. 5
6. 5
5. 5
4. 5
3. 5
2. 5
1. 5
0. 5
−0. 5
f1 (ppm)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159.753
140.551
137.509
134.236
129.297
125.107
119.724
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39.937
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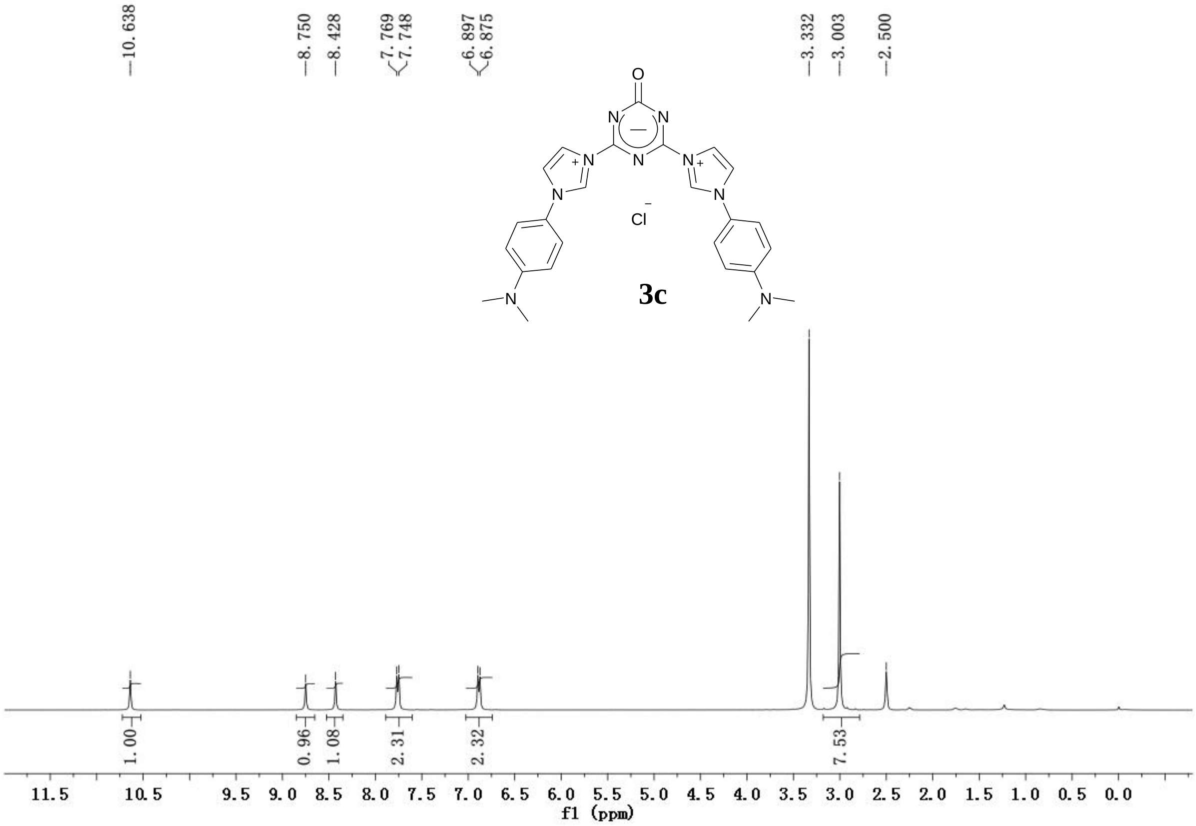
39.520
39.311
39.103
38.894
20.587
17.007
140.551
137.509
134.236
131.065
129.297
125.107
119.724
140
135
130
125
120
f1 (ppm)
O
N
N
N
N+
N+
N
N
Cl−
3b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.428
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7.748
6.897
6.875
3.332
3.003
2.500
O
N
N
N
N+
N+
N
N
Cl−
N
N
3c
1.00
0.96
1.08
2.31
2.32
7.53
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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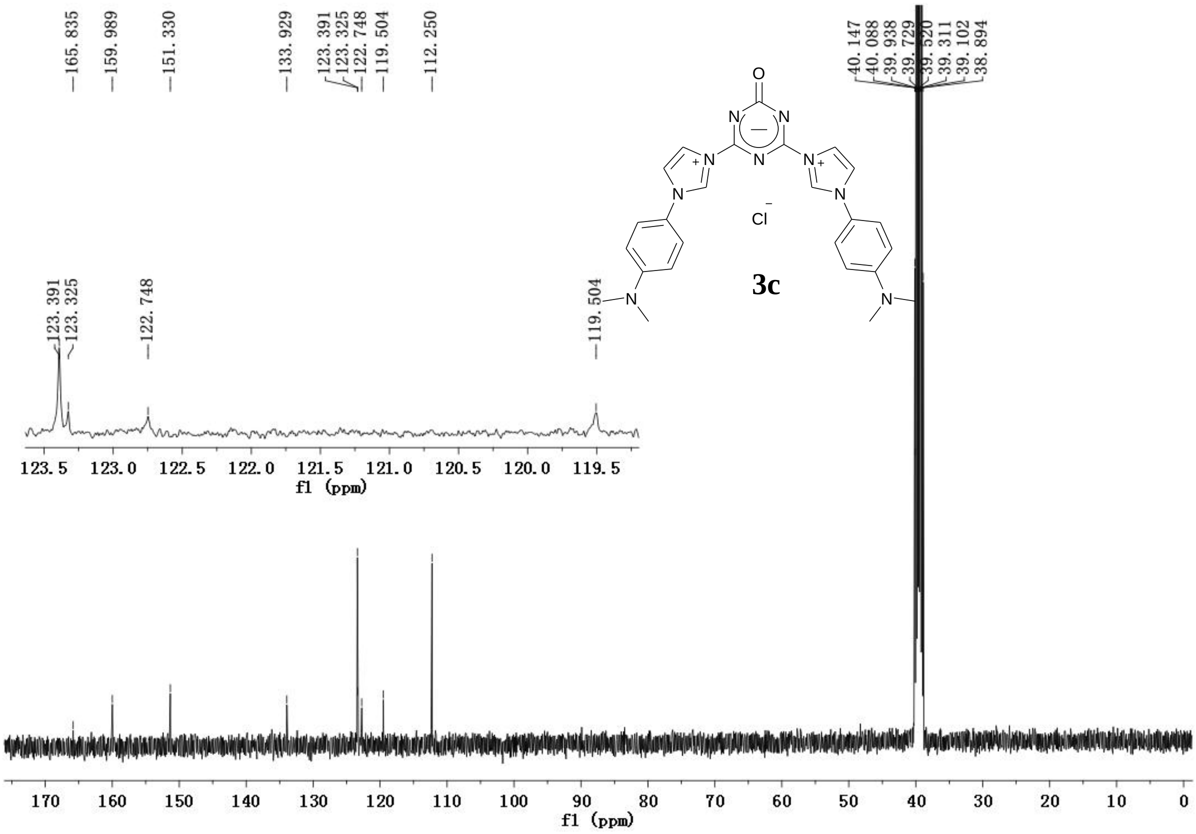
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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151.330
133.929
123.391
123.325
122.748
119.504
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40.147
40.088
39.938
39.729
39.520
39.311
39.102
38.894
O
N
N
N
N+
N+
N
N
Cl−
N
N
123.391
123.325
122.748
119.504
123.5
123.0
122.5
122.0
121.5
121.0
120.5
120.0
119.5
f1 (ppm)
170
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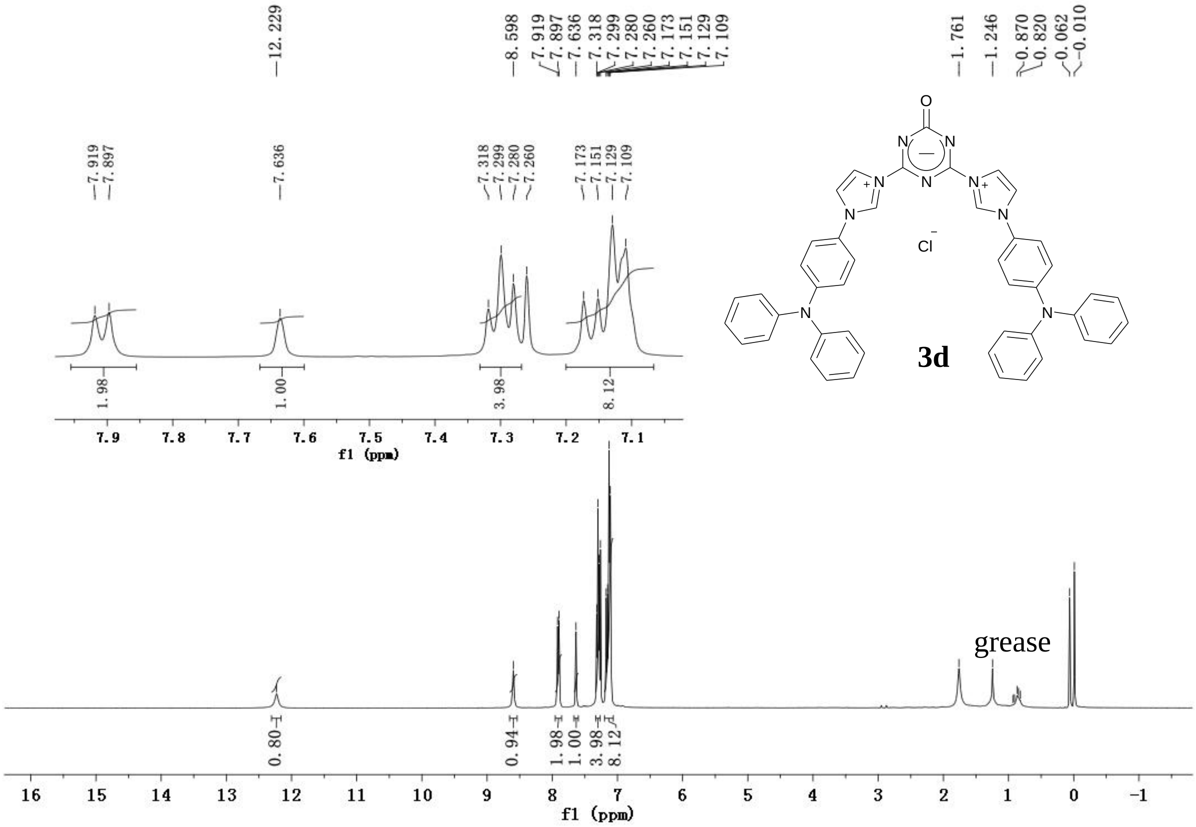
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3c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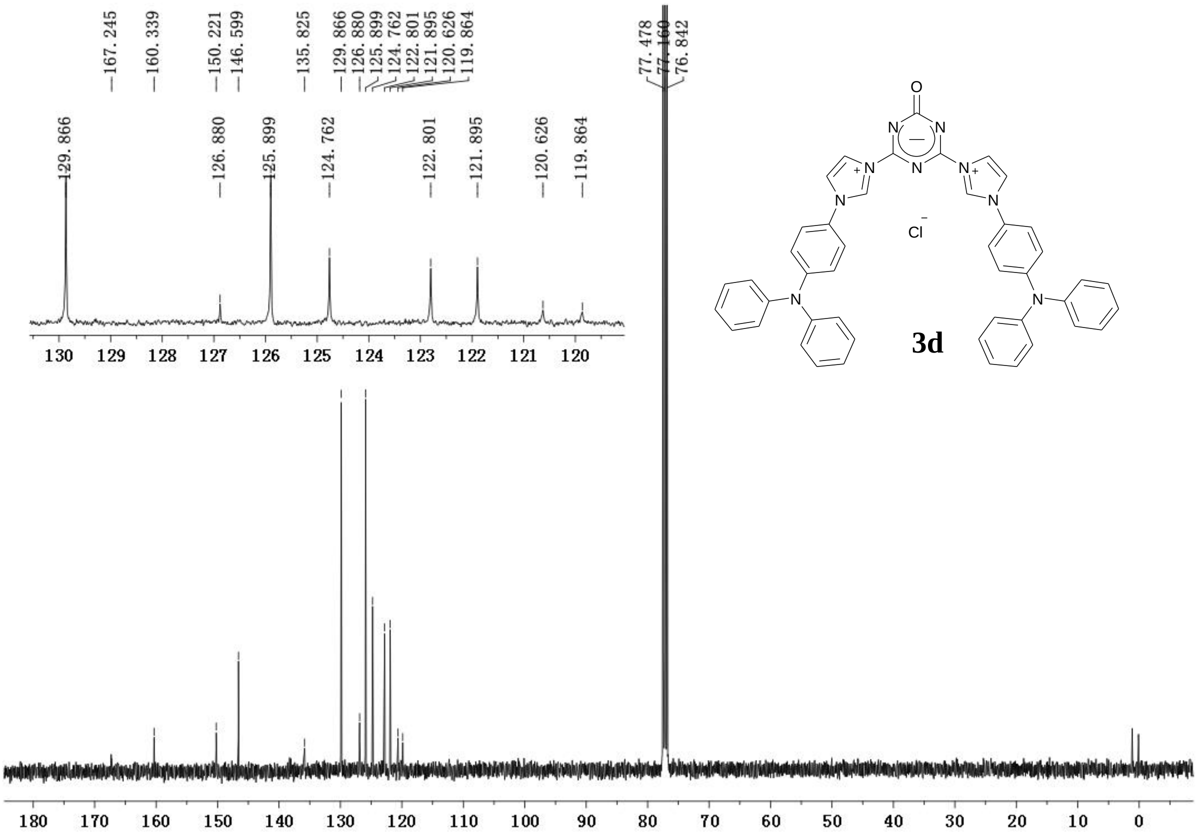
7.919
7.897
7.636
7.318
7.299
7.280
7.260
7.173
7.151
7.129
7.109
1.761
1.246
0.870
0.820
0.062
−0.010
7.919
7.897
7.636
7.318
7.299
7.280
7.260
7.173
7.151
7.129
7.109
1.98
1.00
3.98
8.12
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
O
N
N
N
N+
N+
N
N
Cl−
N
N
grease
0.80
0.94
1.98
1.00
3.98
8.12
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

3d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146.599
135.825
129.866
126.880
125.899
124.762
122.801
121.895
120.626
119.864
77.478
77.160
76.842
130 129 128 127 126 125 124 123 122 121 120
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
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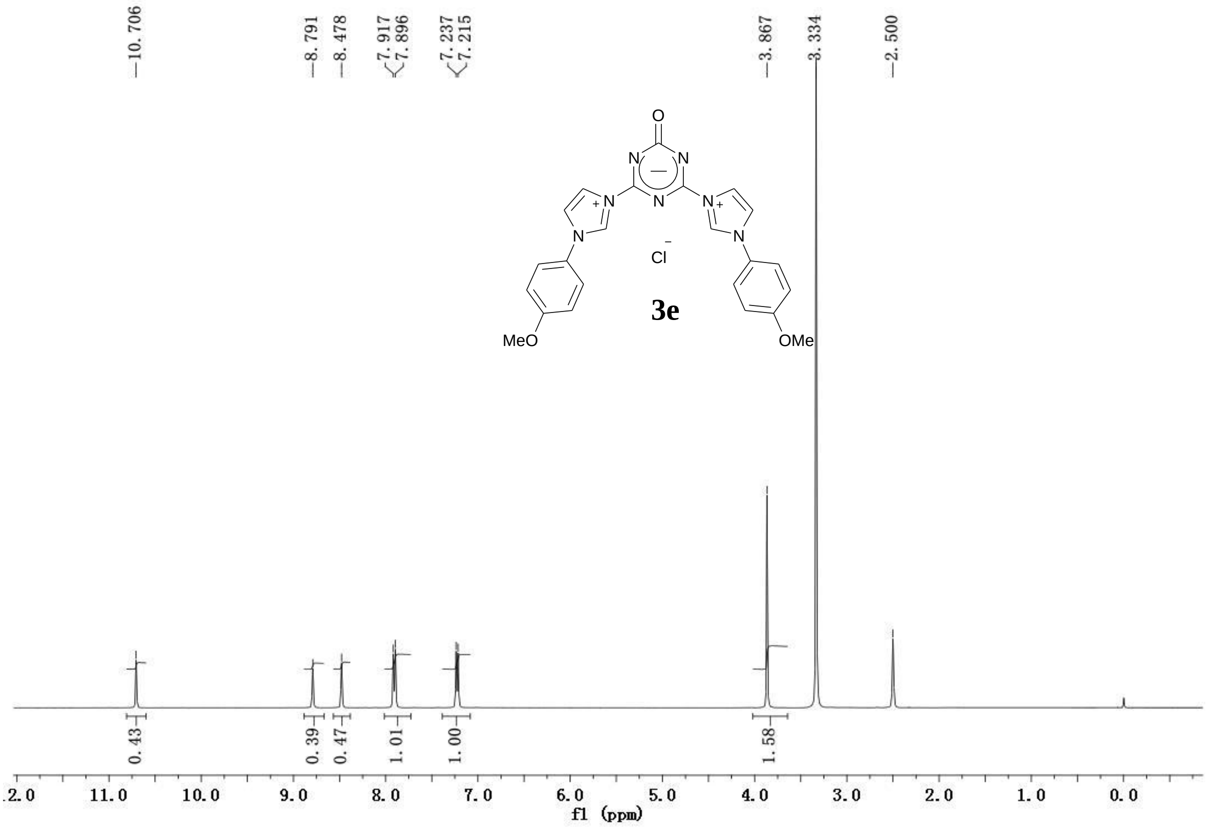
N
N
N
N
N
N
N
N
N
Cl
−
+

3d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8.478
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7.896
7.237
7.215
3.867
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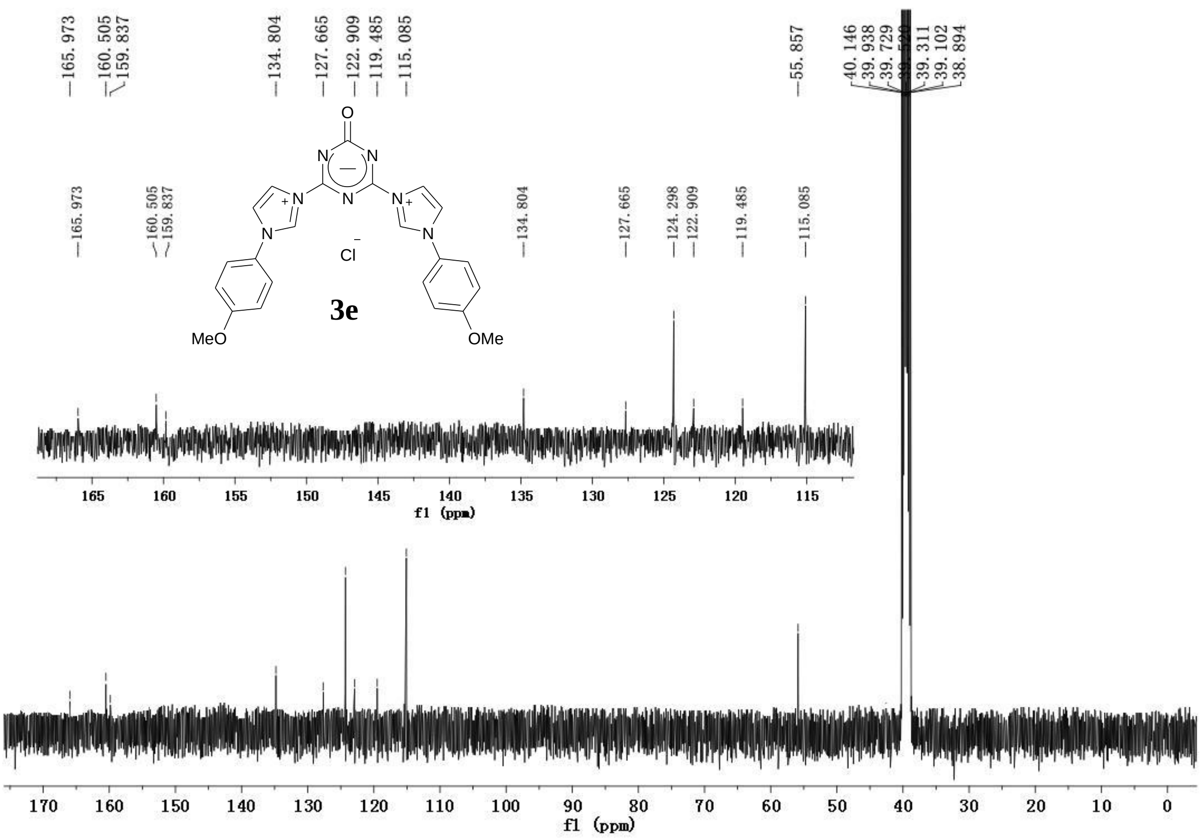
0.39
0.47
1.01
1.00
1.58
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)
O
N
N
N
N
N
N
N
Cl
−
+
MeO
OMe

3e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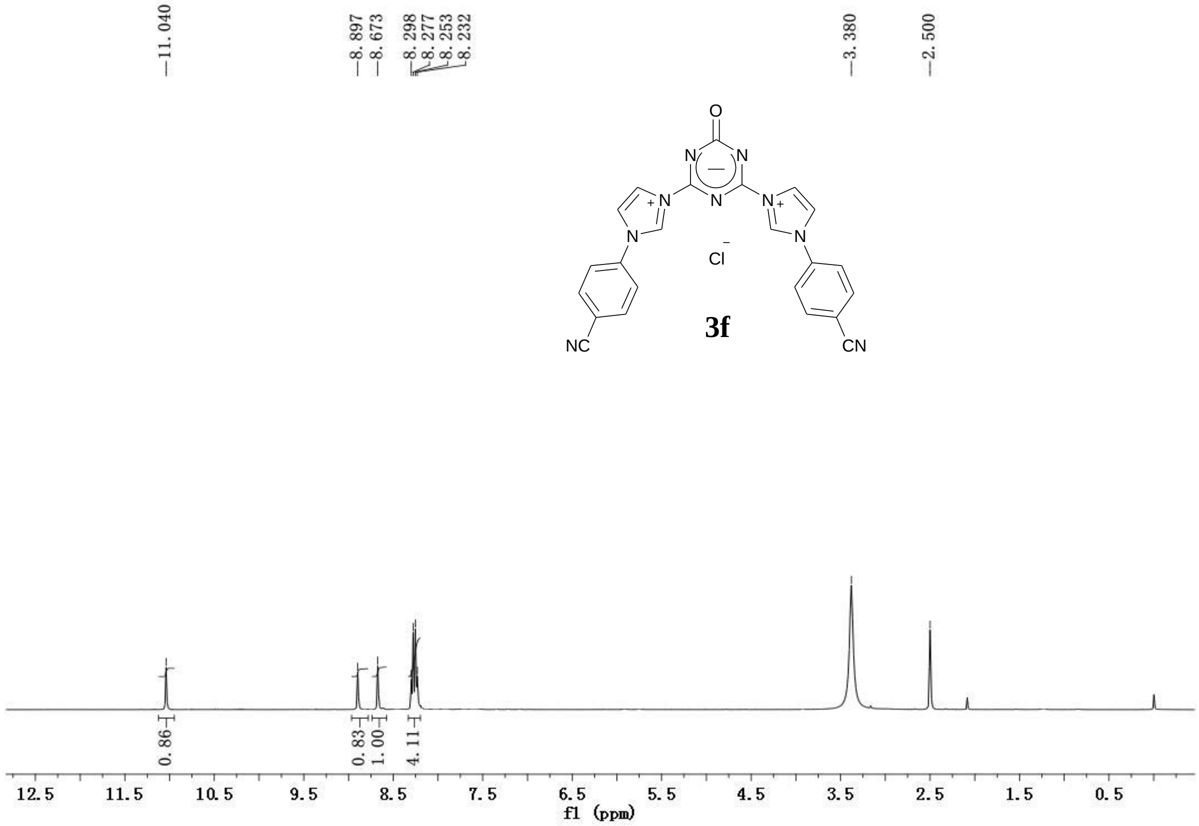
39.729
39.520
39.311
39.102
38.894
O
N
N
N
N
N
N
N
Cl
3e
MeO
OMe
165.973
160.505
159.837
134.804
127.665
124.298
122.909
119.485
115.085
165
160
155
150
145
140
135
130
125
120
115
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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N
N
N
Cl
3f
NC
CN
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0.83
1.00
4.11
12.5
11.5
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5.5
4.5
3.5
2.5
1.5
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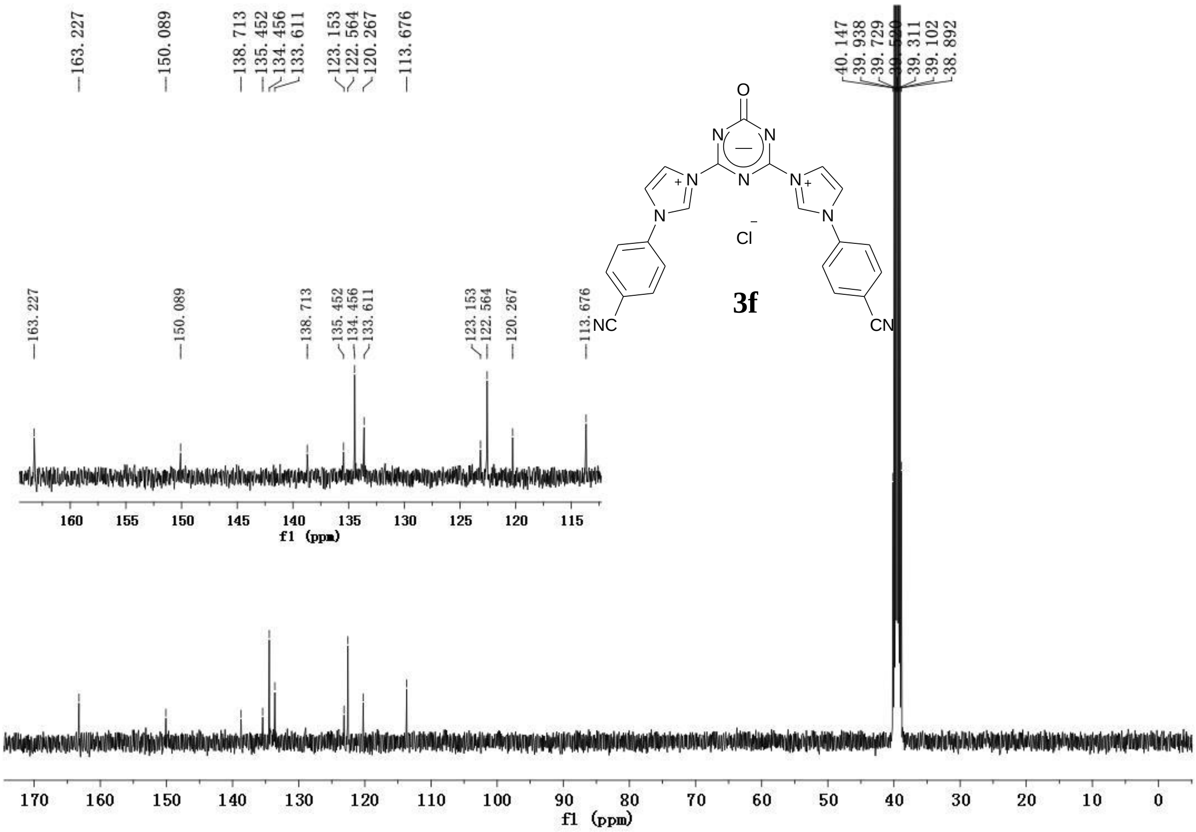
f1 (ppm)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113.676
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39.729
39.520
39.311
39.102
38.892
O
N
N
N
+N
N+
N
N
Cl⁻
NC
CN
160
155
150
145
140
135
130
125
120
115
f1 (ppm)
170
160
150
140
130
120
110
100
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70
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50
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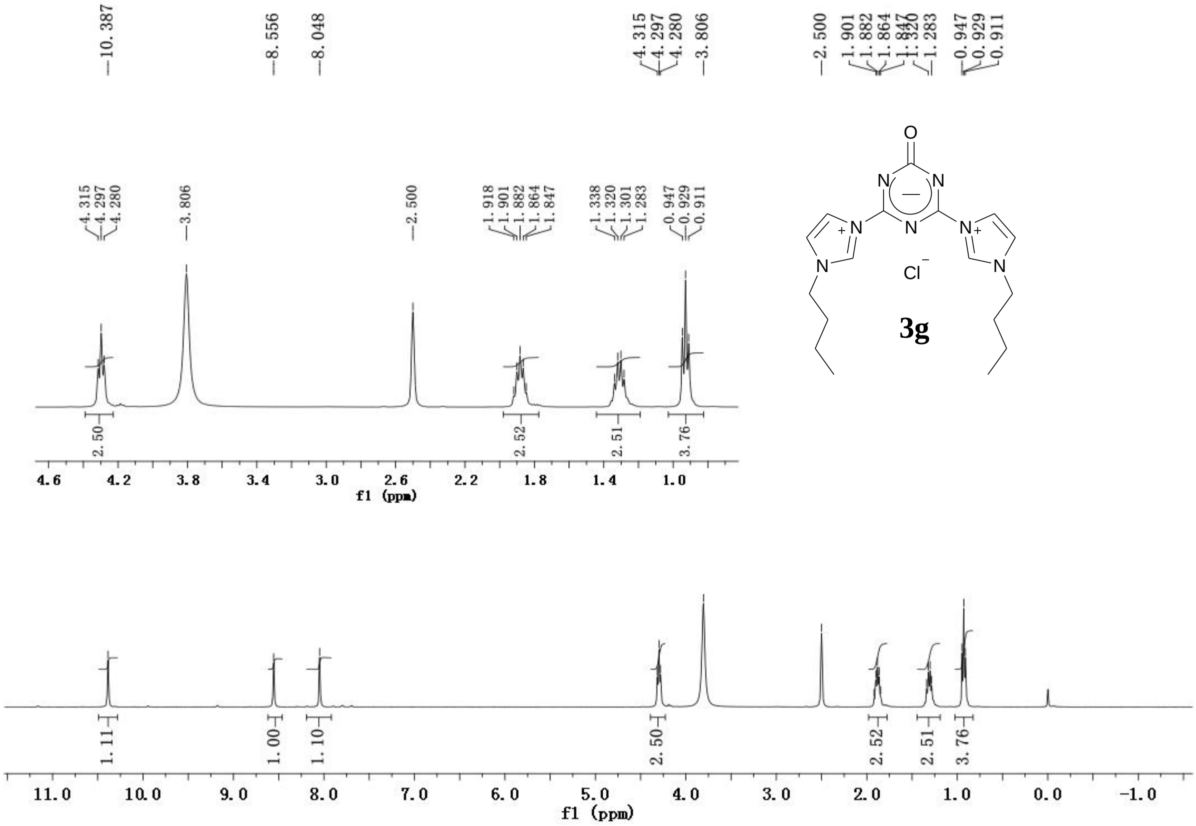
30
20
10
0
f1 (ppm)

3f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1.320
1.283
0.947
0.929
0.911
4.315
4.297
4.280
3.806
2.500
1.918
1.901
1.882
1.864
1.847
1.338
1.320
1.301
1.283
0.947
0.929
0.911
2.50
2.52
2.51
3.76
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
f1 (ppm)
O
N
N
N
+N
N+
N
N
Cl⁻
1.11
1.00
1.10
2.50
2.52
2.51
3.76
11.0
10.0
9.0
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7.0
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0.0
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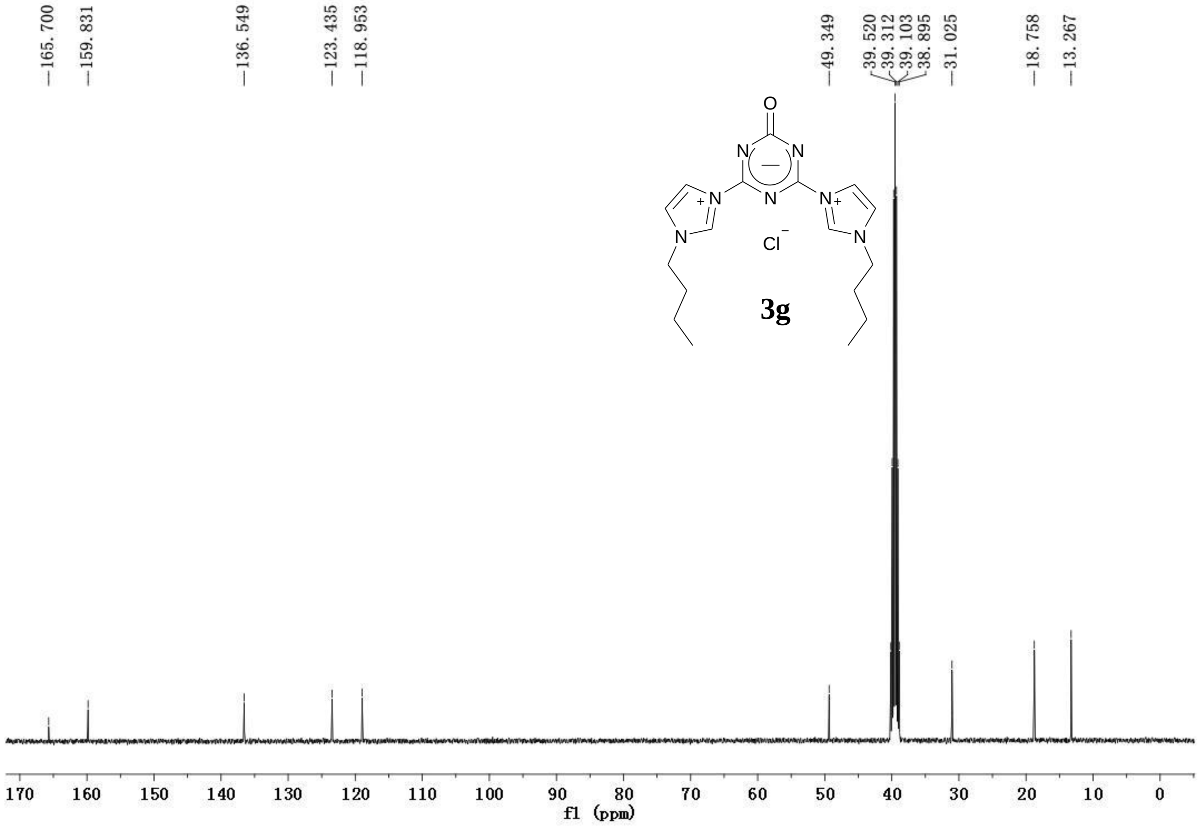
f1 (ppm)

3g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O
N
N
N
N
N
N
N
+
+
Cl⁻
170
160
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140
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100
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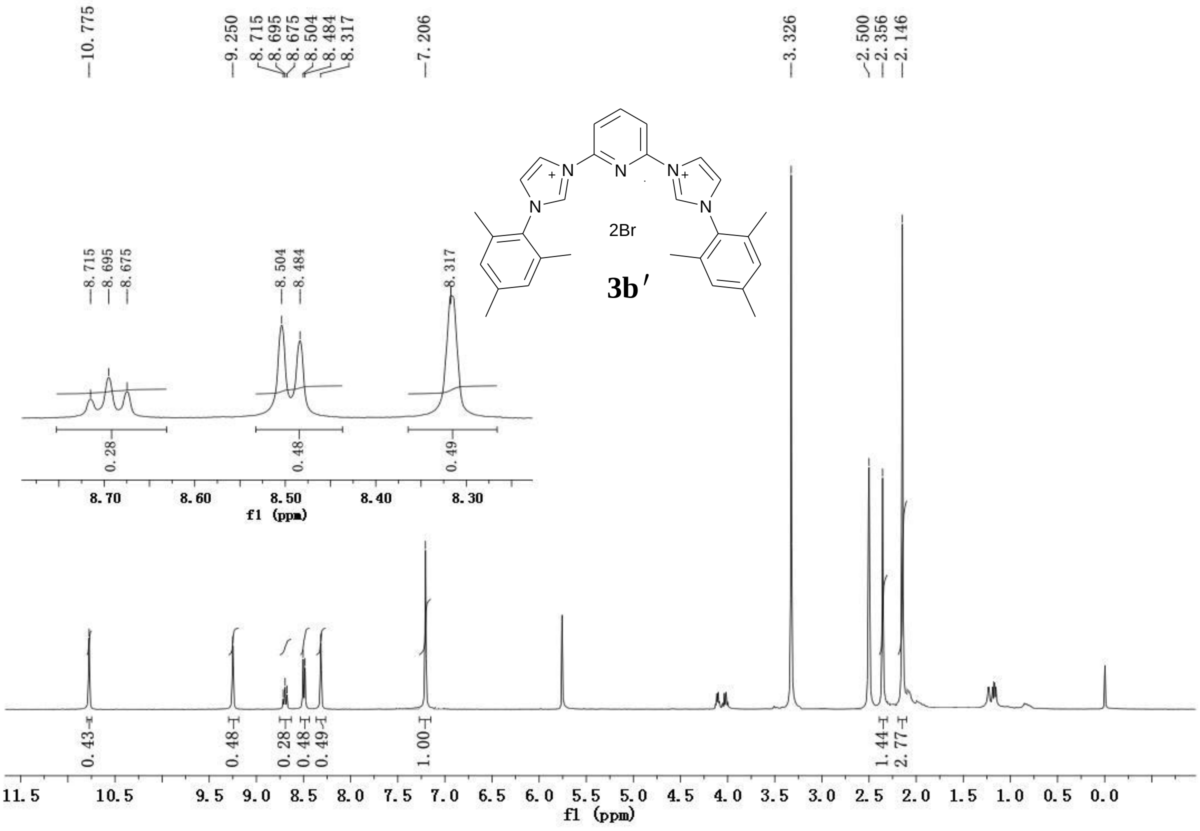
80
70
60
50
40
30
20
10
0
f1 (ppm)

3g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2.146
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N
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N
N
+
+
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8.504
8.484
8.317
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0.48
0.49
8.70
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8.40
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f1 (ppm)
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0.48
0.49
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9.5
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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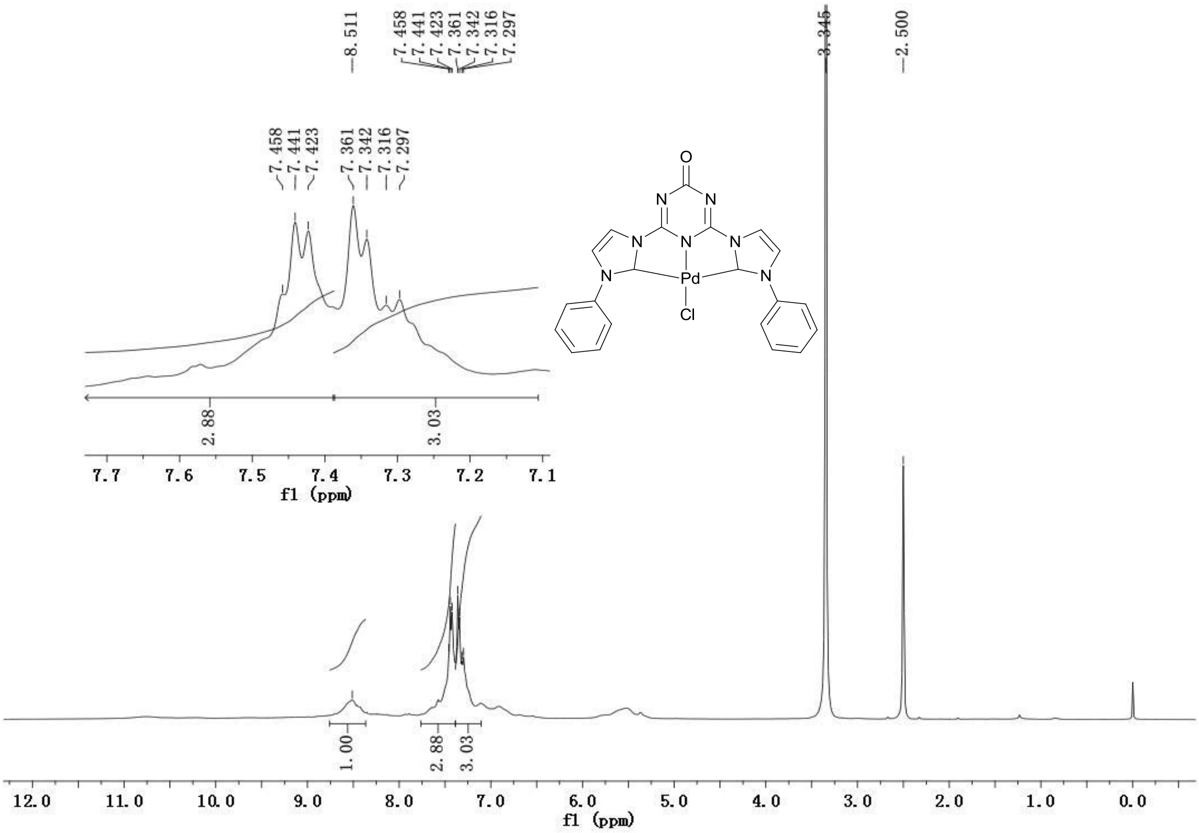
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3b′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7.297
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N
N
N
N
N
Pd
Cl
2.88
3.03
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
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12.0
11.0
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7.0
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5.0
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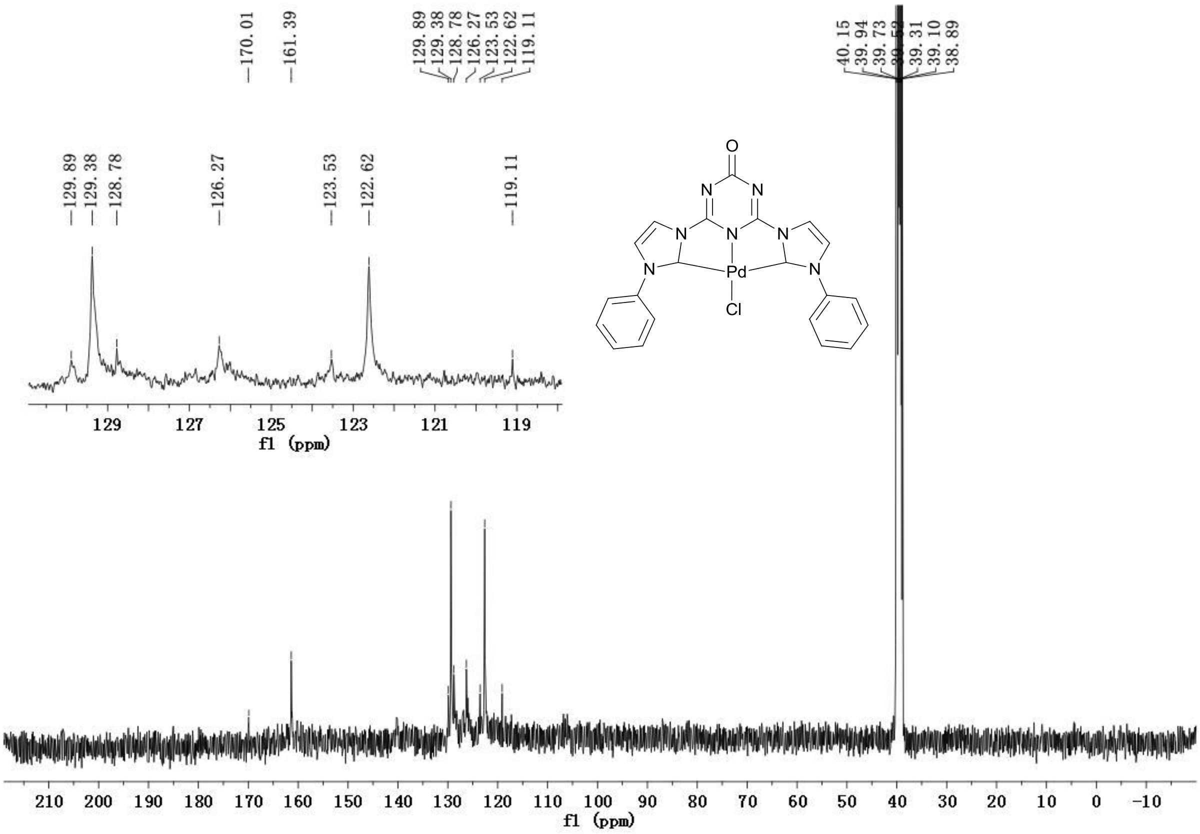
1.0
0.0
f1 (ppm)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Pd
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f1 (ppm)
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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)