Electronic Supplementary Material (ESI) for Chemical Communications

Synthesis of new cyclic aromatic carbene ligands bearing remote amino groups and their palladium complexes

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Contents

1. Experimental Section

General.

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. Column chromatography was carried out using Merck silica gel 60. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (376 MHz) and ^{31}P NMR (160 MHz) spectra were recorded using a JEOL EX-400 or AL-400 spectrometer. The ^{1}H NMR chemical shifts are reported (σ scale) from internal tetramethylsilane. The ^{13}C NMR chemical shifts are reported (σ scale) from internal tetramethylsilane. The ^{19}F NMR chemical shifts are reported (σ scale) from external $CFCl_3$. The ^{31}P NMR chemical shifts are reported (σ scale) from external 85% H_3PO_4. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from Na-Benzophenone. The elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra were measured with a Thermo Fisher Scientific model LTQ Orbitrap XL by using the ESI-TOF method in the positive ion mode with acetonitrile solution samples. Crystals suitable for X-ray structural determination were mounted on a Bruker SMART APEXII CCD diffractometer or a Rigaku SCXmini diffractometer and irradiated with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 173 K for data collection. The data were processed using the APEX program suite or the Rigaku SCXmini program. The structures were solved by a direct method using the SIR-2004 program.[S1] Refinement on F^2 was carried out by full-matrix least-squares using the SHELXL-97 program.[S2] All non-hydrogen atoms were refined using anisotropic thermal parameters except for disordered atoms. The hydrogen atoms were included in the refinement with isotropic thermal parameters. The crystallographic data are summarized in Table S1.

3,6-Diamino-9*H*-xanthen-9-one (**1**) was prepared by a literature method.[S3]

2. Synthesis

Synthesis of 3,6-bis(dimethylamino)-9*H*-xanthen-9-one (2)

3,6-Diamino-9*H*-xanthen-9-one (**1**) (645 mg, 2.85 mmol) and sodium hydride (60%, 729 mg, 18.2 mmol) were dissolved in dry THF (40 mL) under Ar and methyl iodide (1.42 mL, 22.8 mmol) was added dropwise. The reaction mixture was heated at reflux for 18 h. The reaction mixture was quenched by the addition of water and the solvent was concentrated. The remaining solution was extracted with CH_2Cl_2 (x3) and the combined organic layer was dried over Na_2SO_4. After the solvent was evaporated, chromatographic purification was achieved on neutral alumina (grade I) with AcOEt containing 1% NEt_3 as the eluent. The solution was evaporated in vacuo and the resulting solid was recrystallized from CH_2Cl_2/hexane to give **2** (376 mg, 1.33 mmol, 47%) as dark red crystals. M.p. 235-240 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.09 (12H, s), 6.47 (2H, d, ^5J = 2 Hz), 6.69 (2H, dd, ^3J = 9 Hz, ^5J = 2 Hz), 8.13 ppm (2H, d, ^3J = 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 40.14 (CH_3), 96.94 (CH), 108.89 (CH), 111.94 (C), 127.57 (CH), 154.23 (C), 158.10 (C), 175.14 ppm (C); HRMS (ESI): *m/z*: calcd for $C_{17}H_{18}N_2O_2$ $[M+H]^+$ 283.1441; found 283.1443; elemental analysis calcd (%) for $C_{17}H_{18}N_2O_2$: C 72.32, H 6.43, N 9.92; found: C 72.06, H 6.65, N 9.90.

Synthesis of 3

A solution of **2** (800 mg, 2.83 mmol) in dry THF (80 mL) was added to a solution of lithium aluminum hydride (215 mg, 5.66 mmol) in dry THF (27 mL) under Ar. After the reaction mixture was stirred for 3 h at ambient temperature, the mixture was quenched by the addition of AcOEt at 0 °C and then water. The solvent was concentrated and the remaining solution was extracted with CH_2Cl_2 (x3). The combined organic layer was washed with water and then dried over Na_2SO_4. Evaporation of the solvent gave a cationic product as a purple solid labile to air. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.93 (12H, s), 3.86 (2H, s), 6.42 (2H, d, ^5J = 3 Hz), 6.45 (2H, dd, ^3J = 8 Hz, ^5J = 3 Hz), 7.01 ppm (2H, d, ^3J = 8 Hz).

The resulting product and triphenylmethylium tetrafluoroborate (1.04 g, 3.15 mmol) were dissolved in dry CH_2Cl_2 (40 mL) and the reaction mixture was stirred for 5 h at ambient temperature. After the solvent was removed in vacuo, the crude product was washed with diethyl ether (x3). Recrystallization from CH_3CN / ether gave **3** (876 mg, 2.47 mmol, 87% for 2 steps) as a red-purple solid. M.p. > 300 °C; ^{1}H NMR (CD_3CN, 400 MHz): δ = 3.21 (12H, s), 6.63 (2H, d, ^5J = 2 Hz), 7.00 (2H, dd, ^3J = 9 Hz, ^5J = 2 Hz), 7.64 (2H, d, ^3J = 9 Hz), 8.34 ppm (1H, s); ^{13}C NMR (CD_3CN, 100 MHz) δ = 41.36 (CH_3), 97.03 (CH), 115.13 (C), 115.32 (CH), 133.94 (CH), 147.13 (CH), 158.81 (C), 158.88 ppm (C); ^{19}F NMR (CD_3CN, 376 MHz) δ = –150.21 (s, 1F), –150.26 ppm (s, 3F); HRMS (ESI, positive): *m/z*: calcd for $C_{17}H_{19}N_2O$ $[M]^+$ 267.1492; found 267.1491; elemental analysis calcd (%) for $C_{17}H_{19}BF_4N_2O$: C 57.65, H 5.41, N 7.91; found: C 57.22, H 5.30, N 7.84.

Synthesis of 4

To a solution of **3** (20 mg, 0.056 mmol) in dry THF (5 mL) was added 1.0 M KO*t*Bu in THF (0.060 mL, 0.060 mmol). The reaction mixture was stiired for 2 h at ambient temperature and then the solvent was removed in vacuo. After the resulting solid was dissolved with diethyl ether, the solution was filtered and the filtrate was evaporated to give **4** (17 mg, 0.048 mmol, 87%) as a gray solid. M.p. 138-142 °C; ^{1}H NMR (C_6D_6, 400 MHz): δ = 1.26 (9H, s), 2.50 (12H, s), 5.58 (1H, s), 6.47 (2H, dd, ^3J = 9 Hz, ^5J = 2 Hz), 6.68 (2H, d, ^5J = 2 Hz), 7.41 ppm (2H, d, ^3J = 9 Hz); ^{13}C NMR (C_6D_6, 100 MHz) δ = 29.84 ((CH_3), 40.11 (CH_3), 65.13 (CH), 73.73 (C), 100.63 (CH), 108.18 (CH), 114.51 (C), 129.82 (CH), 151.25 (C), 155.04 ppm (C); HRMS (ESI, positive): *m/z*: calcd for $C_{21}H_{29}N_2O_2$ $[M+H]^+$ 341.2224; found 341.2221.

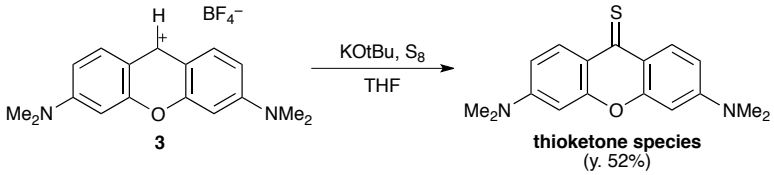
Synthesis of 5

To a solution of **3** (30 mg, 0.085 mmol) in dry THF (3 mL) was added 1.1 M NaHMDS in THF (0.086 mL, 0.094 mmol). The reaction mixture was stiired for 2 h at ambient temperature and then the solvent was removed in vacuo. After the resulting solid was dissolved with diethyl ether, the solution was filtered and the filtrate was evaporated to give **4** (24 mg, 0.055 mmol, 65%) as a yellow solid. M.p. 154-161 °C; ^{1}H NMR (C_6D_6, 400 MHz): δ = 0.08 (9H,br s), 0.39 (9H, br s), 2.52 (12H, s), 5.53 (1H, s), 6.46 (2H, d, ^{5}J = 2 Hz), 6.62 (2H, dd, ^{3}J = 9 Hz, ^{5}J = 2 Hz), 7.56 ppm (2H, d, ^{3}J = 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 2.91 (CH_3), 4.04 (CH_3), 40.07 (CH_3), 49.80 (CH), 99.86 (CH), 108.04 (CH), 115.42 (C), 129.67 (CH), 151.04 (C), 152.14 ppm (C); HRMS (ESI, positive): *m/z*: calcd for $C_{23}H_{38}N_3OSi_2$ $[M+H]^+$ 428.2548; found 428.2544.

Synthesis of 6

1.63 M *n*-Butyl lithium in hexane (0.19 mL, 0.31 mmol) was added to a solution of tetramethylpiperidine (0.052 mL, 0.31 mmol) in THF (5 mL) at –78 °C. The reaction mixture was stirred for 30 min at –78 °C and then added to a solution of **3** (100 mg, 0.282 mmol) in THF (10 mL) at –78 °C. The reaction mixture was stirred for 4 h at ambient temperature and then the solvent was removed in vacuo. After the resulting solid was dissolved with diethyl ether, the solution was filtered and the filtrate was evaporated. The crude product was recrystallized from erher/hexane to give **6** (14 mg, 0.027 mmol, 19%) as a purple solid. M.p. 142-144 °C (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.90 (24H, s), 4.00 (2H, s), 6.21 (4H, d, ^{5}J = 2 Hz), 6.34 (4H, dd, ^{3}J = 9 Hz, ^{5}J = 2 Hz), 6.53 ppm (4H, d, ^{3}J = 9 Hz); HRMS (ESI, positive): *m/z*: calcd for $C_{34}H_{39}N_2O_2$ $[M+H]^+$ 535.3068; found 535.3060.

Synthesis of 3,6-bis(dimethylamino)-9*H*-xanthene-9-thione



To a solution of **3** (101 mg, 0.285 mmol) and sulfur (91 mg, 2.8 mmol) in dry THF (20 mL) was added 1.0 M KO*t*Bu in THF (0.35 mL, 0.35 mmol). The reaction mixture was refluxed for 1.5 h and the solvent was evaporated. The residual solid was purified by silica gel column chromatography with CH_2Cl_2 as the eluent and the resulting product was recrystallized from CH_2Cl_2/hexane to give 3,6-bis(dimethylamino)-9*H*-xanthene-9-thione (44 mg, 0.15 mmol, 52%) as a dark green solid. M.p. 280-285 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.12 (12H, s), 6.41 (2H, d, ^{5}J = 2 Hz), 6.74 (2H, dd, ^{3}J = 9 Hz, ^{5}J = 2 Hz), 8.68 ppm (2H, d, ^{3}J = 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 40.20 (CH_3), 95.93 (CH), 110.46 (CH), 119.97 (C), 131.77 (CH), 153.01 (C), 154.56 (C), 196.19 ppm (C); HRMS (ESI, positive): *m/z*: calcd for $C_{17}H_{19}N_2OS$ $[M+H]^+$ 299.1213; found 299.1213.

Synthesis of 3,6-di(piperidin-1-yl)-9*H*-xanthen-9-one

Compound **1** (750 mg, 3.31 mmol) and sodium hydride (60%, 840 mg, 20.8 mmol) were dissolved in dry THF (50 mL) under Ar and 1,5-diiodopentane (1.23 mL, 8.30 mmol) was added dropwise. The reaction mixture was heated at reflux for 18 h. The reaction mixture was quenched by the addition of water and the solvent was concentrated. The remaining solution was extracted with CH_2Cl_2 (x3) and the combined organic layer was dried over Na_2SO_4. After the solvent was evaporated, the chromatographic purification was achieved on silica gel with AcOEt/hexane = 1:1 as the eluent. The solution was evaporated in vacuo and the resulting solid was recrystallized from CH_2Cl_2/hexane to give 3,6-di(piperidine-1-yl)-9*H*-xanthen-9-one (397 mg, 1.09 mmol, 33%.) as a red solid. M.p. 148-152 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.68 (12H, m), 3.39 (8H, m), 6.66 (2H, d, ^5J = 2 Hz), 6.86 (2H, dd, ^3J = 9 Hz, ^5J = 2 Hz), 8.10 ppm (2H, d, ^3J = 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 24.34 (CH_2), 25.30 (CH_2), 48.68 (CH_2), 99.55 (CH), 111.38 (CH), 113.00 (C), 127.51 (CH), 155.26 (C), 158.25 (C), 175.00 ppm (C); HRMS (ESI): *m/z*: calcd for $C_{23}H_{27}N_2O_2$ $[M+H]^+$ 363.2067; found 363.2062.

General procedure for the conversion of the xanthones into the chlorides (7 and 9)

Oxalyl chloride (1.2 eq.) was added to a solution of the xanthone in dry CCl_4 (7 mL/1 mmol). The reaction mixture was stirred for 16 h at 60 °C. After the reaction was completed, the solution was diluted with CH_3CN and evaporated. The crude product was recrystallized from CH_3CN/ether to give the chloride species. The chloride species and potassium hexafluorophosphate (5.0 eq.) were dissolved in CH_3CN and stirred at room temperature for 16 h. After the solvent was evaporated and replaced with CH_2Cl_2, the solution was filtered and the filtrate was evaporated. The crude product was recrystallized from CH_3CN/ether to give the corresponding hexafluorophosphate salts.

Data for **7**: Yield, 75% (2 steps, a brown solid); M.p. 250-254 °C (decomp.); ^{1}H NMR (CD_3CN, 400 MHz): δ = 3.27 (12H, s), 6.75 (2H, d, ^5J = 2 Hz), 7.16 (2H, dd, ^3J = 9 Hz, ^5J = 2 Hz), 8.03 ppm (2H, d, ^3J = 9 Hz); ^{13}C NMR (CD_3CN, 100 MHz): δ = 42.13 (CH_3), 97.42 (CH), 113.80 (C), 116.81 (CH), 130.70 (CH), 153.17 (C), 158.89 (C), 159.37 ppm (C); ^{19}F NMR (CD_3CN, 376 MHz): δ = –71.72 ppm (d, $J_{P–F}$ = 706 Hz); ^{31}P NMR (CD_3CN, 160 MHz): δ = –143.37 ppm (sept, $J_{P–F}$ = 706 Hz); HRMS (ESI, positive): *m/z*: calcd for $C_{17}H_{18}N_2OCl$ $[M]^+$ 301.1102; found 301.1108; elemental analysis calcd (%) for $C_{17}H_{18}ClF_6N_2OP$: C 45.70, H 4.06, N 6.27; found: C 45.85, H 3.74, N 6.21.

Data for **9**: Yield, 61% (2 steps, a green solid); M.p. 202-207 °C (decomp.);^{1}H NMR (CD_3CN, 400 MHz): δ = 1.72 (12H, m), 3.71 (8H, m), 6.83 (2H, d, ^5J = 2 Hz), 7.23 (2H, dd, ^3J = 9 Hz, ^5J = 2 Hz), 7.95 ppm (2H, d, ^3J = 9 Hz); ^{13}C NMR (CD_3CN, 100 MHz) δ = 24.72 (CH_2), 26.73 (CH_2), 49.86 (CH_2), 97.37 (CH), 113.43 (C), 116.46 (CH), 130.44 (CH), 151.40 (C), 157.79 (C), 159.01 ppm (C); ^{19}F NMR (CD_3CN, 376 MHz): δ = –71.71 ppm (d, $J_{P–F}$ = 708 Hz); ^{31}P NMR (CD_3CN, 160 MHz): δ = –143.36 ppm (sept, $J_{P–F}$ = 708 Hz); HRMS (ESI, positive): *m/z*: calcd for $C_{23}H_{26}N_2O_2Cl$ $[M]^+$ 381.1728; found 381.1722; elemental analysis calcd (%) for $C_{23}H_{26}ClF_6N_2OP$: C 52.43, H 4.97, N 5.32; found: C 52.15, H 5.04, N 5.23.

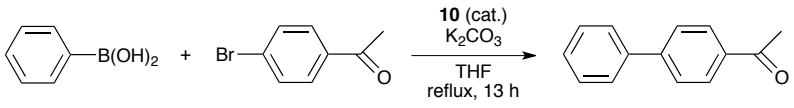
General procedure for the oxidative addition into the chloride species (7 and 9)

The chloride species and $Pd(PPh_3)_4$ (1.2 eq.) were dissolved in dry CH_2Cl_2 and the reaction mixture was refluxed under argon for 3 h. After the solvent was removed in vacuo, the resulting solid was washed with hexane (x3) to remove triphenylphosphines and then the crude product was recrystallized from CH_2Cl_2/hexane to give the palladium(II) complexes.

Data for **8**: Yield, 78% (a pale purple solid); M.p. 160-165 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.15 (12H, s), 6.10 (2H, d, ^5J = 2 Hz), 6.62 (2H, dd, ^3J = 9 Hz, ^5J = 2 Hz), 7.20-7.42 (18H, m), 7.46-7.62 (12H, m), 8.25 ppm (2H, d, ^3J = 9 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): δ = –73.98 ppm (d, $J_{P–F}$ = 717 Hz); ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 24.02 (s), –143.61 ppm (sept, $J_{P–F}$ = 717 Hz); HRMS (ESI, positive): *m/z*: calcd for $C_{53}H_{49}ClN_2OP_2Pd$ $[M]^+$ 931.1965; found 931.1971; elemental analysis calcd (%) for $C_{53}H_{48}ClF_6N_2OP_3Pd$: C 59.06, H 4.49, N 2.60; found: C 59.26, H 4.64, N 2.19.

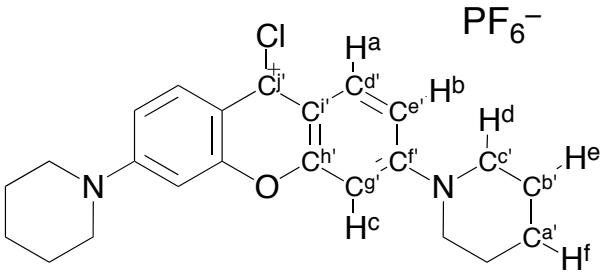
Data for **10**: Yield, 92% (a red-green solid); M.p. 198-200 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.69 (12H, m), 3.54 (8H, m), 6.22 (2H, d, ^5J = 2 Hz), 6.80 (2H, dd, ^3J = 9 Hz, ^5J = 2 Hz), 7.21-7.26 (12H, m), 7.30-7.36 (6H, m), 7.46-7.53 (12H, m), 8.18 ppm (2H, d, ^3J = 9 Hz); ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 24.50 (CH_2), 25.93 (CH_2), 48.90 (CH_2), 95.90 (CH), 113.38 (CH), 121.98 (C, t, J = 3 Hz), 128.50 (CH, t, J = 3 Hz), 129.36 (C, t, J = 24 Hz), 131.40 (CH), 134.52 (CH, t, J = 5 Hz), 137.39 (CH), 152.61 (C), 156.39 (C), 213.72 ppm (C, t, J = 6 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz): δ = –73.97 ppm (d, $J_{P–F}$ = 712 Hz); ^{31}P NMR ($CDCl_3$, 160 MHz): δ = 24.08 (s), –143.61 ppm (sept, $J_{P–F}$ = 712 Hz); HRMS (ESI, positive): *m/z*: calcd for $C_{59}H_{56}ClN_2OP_2Pd$ $[M]^+$ 1011.2586; found 1011.2584; elemental analysis calcd (%) for $C_{59}H_{56}ClF_6N_2OP_3Pd$+0.5$CH_2Cl_2$: C 59.54, H 4.79, N 2.33; found: C 59.76, H 4.65, N 2.06.

General procedure for the Suzuki-Miyaura coupling



A solution of phenylboronic acid (2.4 mmol, 1.2 equiv.), 4-bromoacetophenone (2.0 mmol, 1 equiv.), the Pd complex **10** (0.001 or 0.0003 mol%), and K_2CO_3 (3.0 mmol, 1.5 equiv.) in THF (2 mL) was refluxed for 13 h under argon. After cooling, the reaction mixture was diluted with water, and the aqueous phase was extracted with ethyl acetate (x3). The combined organic layer was washed with brine and dried over Na_2SO_4. After the solvent was evaporated, the residue was purified by silica gel column chromatography with CH_2Cl_2/hexane = 1:1 as the eluent to give 4-phenyl-acetophenone, the analytical and spectroscopic data of which were identical to those of an authentic sample.[S5]

3. 2D NMR spectra of compound 9



9

In order to assign the quaternary carbon atom at C9 position ($C^{j'}$ in above figure), we performed ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY and ^{1}H-^{13}C COLOC measurements as follows. Each of the protons was identified using ^{1}H-^{1}H COSY as shown in Figure S1. Then, the secondary and the tertiary carbon atoms were assigned with correlation spectroscopy between directly attached protons and carbons as shown in Figure S2. Finally, each of the quaternary carbons could be determined with correlation spectroscopy for long-range coupling (COLOC), through 2- and 3-bond correlations between proton and carbon nuclei. Judging from the correlation in Figure S3, the targeted peak of $C^{j'}$ could be determined to be the signal at 157.79 ppm since peak j' only had a correlation with proton H^{a}.

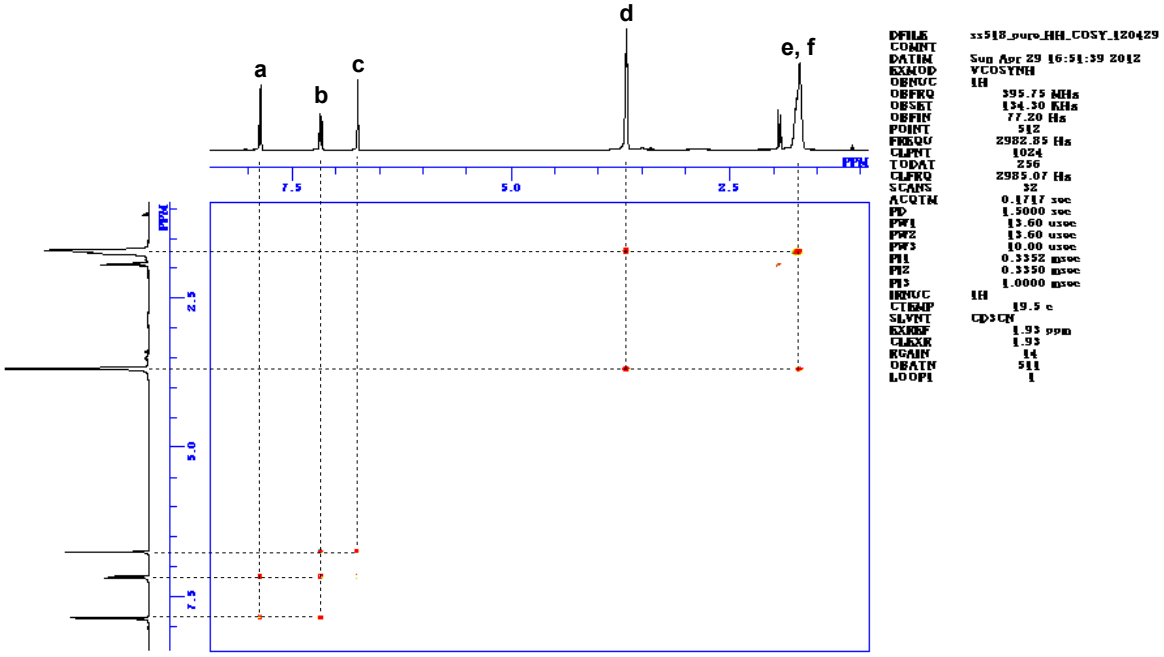


Figure S1. ^{1}H-^{1}H COSY spectrum of compound **9** in CD_3CN.

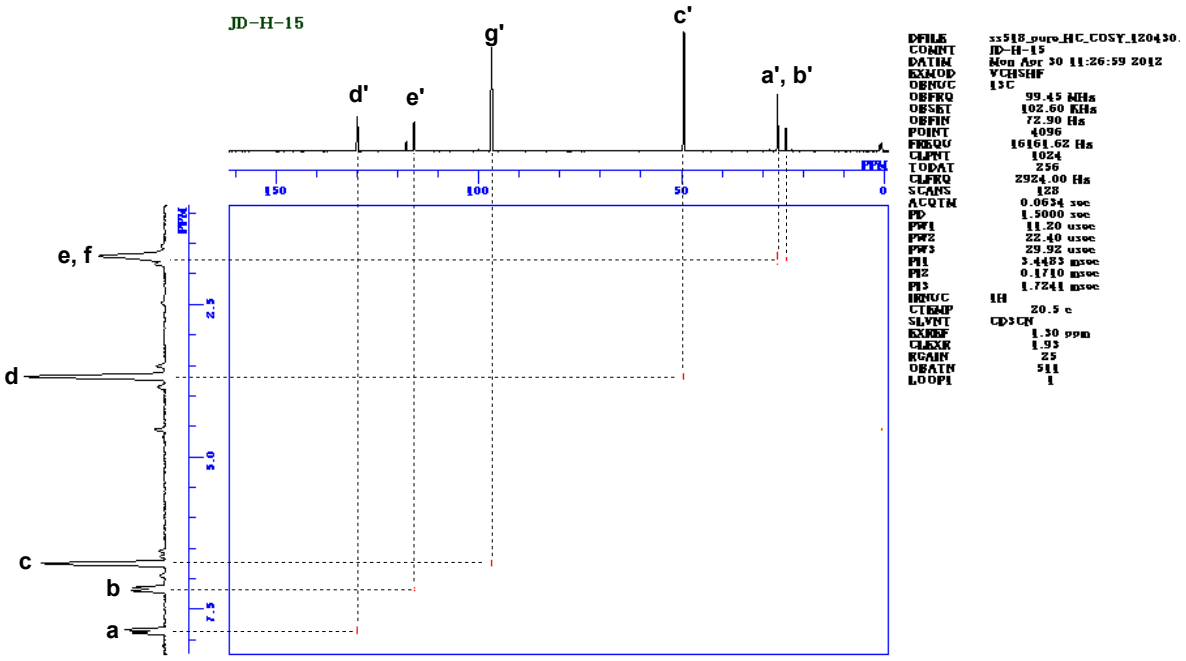


Figure S2. ^{1}H-^{13}C COSY spectrum of compound **9** in CD_3CN.

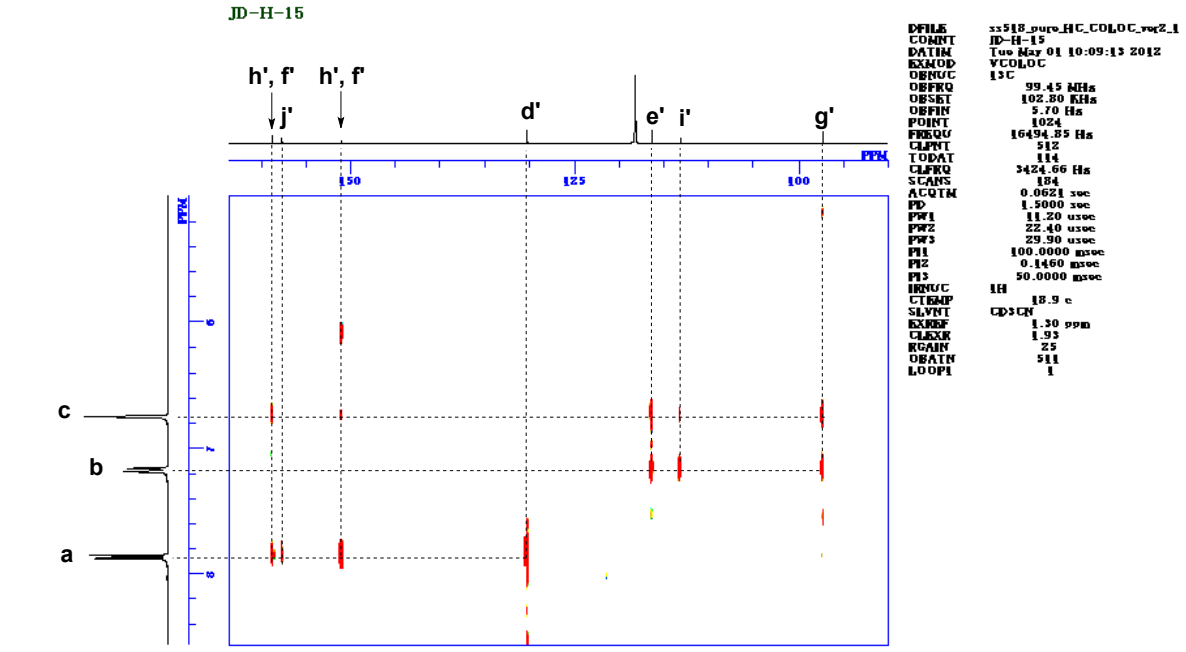
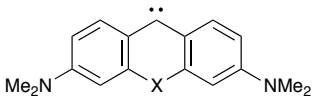


Figure S3. ^{1}H-^{13}C COLOC spectrum of compound **9** in CD_3CN.

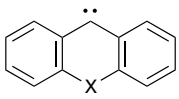
4. Computational Details

All computations were performed using the Gaussian 09 package of programs.[S4] The B3LYP hybrid functional was used with the 6-31G* basis set. All structures were optimized without any symmetry assumptions. Harmonic vibration frequency calculations at the same level were performed to verify that all the stationary points were local minima (with no imaginary frequency).

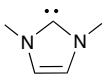
Table S1. DFT calculations of model compounds (Y = H, R = Me) of novel cyclic aromatic carbenes and reported carbenes.



1-X



2-X



NHC

Calculated compound [a]	Ground state ($\Delta E_{S\text{-}T}$) [b] (kcal/mol)	HOMO (eV) [c]	LUMO (eV) [c]
1-NMe	singlet (–14.4)	–3.67	–1.00
1-O	singlet (–13.7)	–3.98	–1.28
1-S	singlet (–8.0)	–3.86	–1.39
1-CH_2	singlet (–4.6)	–3.74	–1.37
1-SO	singlet (–3.0)	–4.21	–1.94
1-BMes	triplet (+9.6)	–3.94	–2.32
2-O	singlet (–6.5)	–4.76	–2.27
2-BMes	triplet (+12.8)	–5.04	–3.14
NHC	singlet (–77.6)	–5.34	+1.18

[a] Geometries optimized at the level of B3LYP/6-31G(d). [b] Energies include zero-point energy (ZPE) correction. [c] Energies of the HOMO and the LUMO in singlet states.

5. X-ray Crystallographic Details

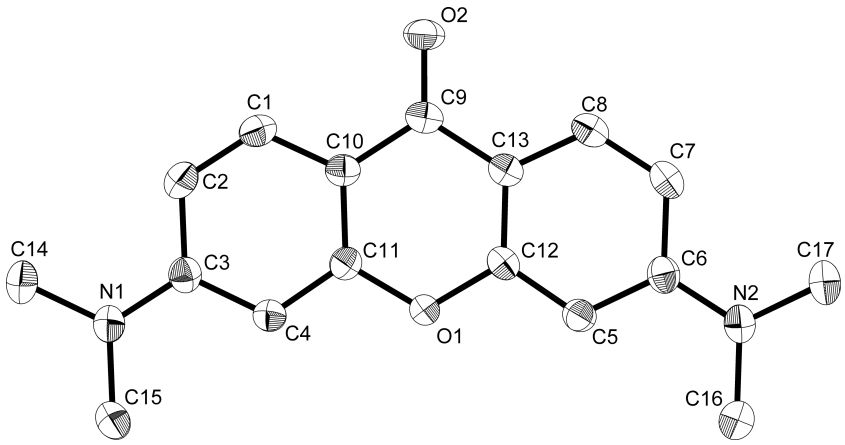


Figure S4. The ORTEP drawing of 3,6-bis(dimethylamino)-9*H*-xanthen-9-one (**2**) with the thermal ellipsoids shown at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C9–O2, 1.2362(14); C9–C10, 1.4533(16); C9–C13, 1.4508(17); C10–C1, 1.4033(17); C1–C2, 1.3646(18); C2–C3, 1.4176(17); C3–N1, 1.3615(15); C10–C9–C13, 114.36(10); C10–C9–O2, 122.74(11); C13–C9–O2, 122.90(11).

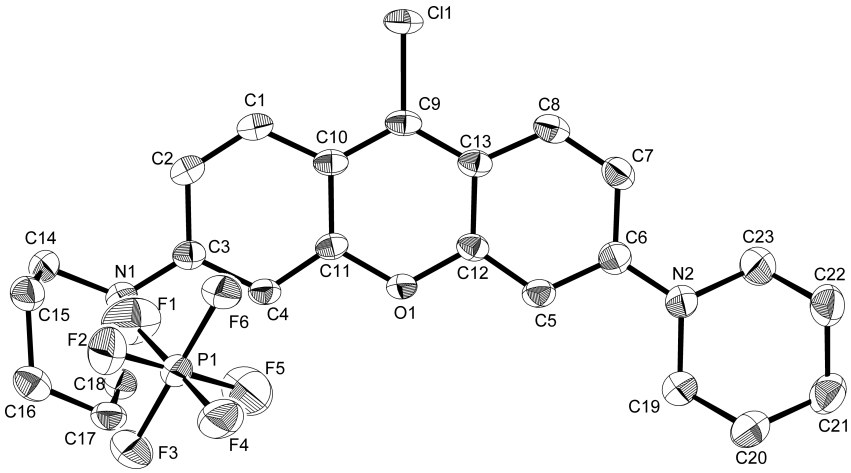


Figure S5. The ORTEP drawing of **9** with the thermal ellipsoids shown at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C9–Cl1, 1.7138(18); C9–C10, 1.397(3); C9–C13, 1.389(3); C10–C1, 1.413(3); C1–C2, 1.356(3); C2–C3, 1.434(3); C3–N1, 1.344(2); C10–C9–C13, 121.87(17); C10–C9–Cl1, 118.45(15); C13–C9–Cl1, 119.68(15).

Table S2. Crystallographic data for **2**, **9** and **10**.

	2	**9**[a]	**10**[b]
Formula	$C_{17}H_{18}N_2O_2$	$C_{25}H_{29}ClF_6N_3OP$	$C_{59}H_{56}F_6N_2OOP_3Pd$
Mol wt	282.33	567.93	1157.82
Crystal system	monoclinic	triclinic	triclinic
Space group	*P*21/n	*P*-1	*P*-1
Color	red	purple	red
Habit	block	block	plate
Cryst dimens, mm	0.88 x 0.60 x 0.44	0.81 x 0.43 x 0.34	0.12 x 0.07 x 0.05
a, Å	12.1248(10)	9.0244(10)	13.4314(18)
b, Å	8.8762(8)	11.0496(12)	23.977(3)
c, Å	13.9060(12)	14.0165(15)	28.786(4)
α, deg	90	103.630(3)	99.891(2)
β, deg	107.207(2)	91.184(3)	96.290(2)
γ, deg	90	109.380(3)	105.059(2)
V, Å^3	1429.6(2)	1273.9(2)	8702(2)
Z	4	2	6
D_{calc}, g cm^{-3}	1.321	1.481	1.326
Abs coeff, mm^{-1}	0.087	0.282	0.508
F(000)	600	588	3564
Temp, K	173(2)	173(2)	173(2)
Reflections	14303	13249	30765
Independent	3265	5818	30765
*R*int	0.0302	0.0282	0.0000
Parameters	194	335	1902
R_1 [$I > 2\sigma(I)$]	0.0411	0.0511	0.0595
wR_2 (all data)	0.1169	0.1503	0.1679
Goodness of fit	1.041	1.068	1.011
solv for crystallization	hexane/CH_2Cl_2	ether/CH_3CN	hexane/CH_2Cl_2

[a] These crystals contained solvent molecules in the crystal lattice (**9**: CH_3CN). [b] In these crystal structures, there are disordered solvent molecules, and their contribution to the scattering values have been removed by using the PLATON SQUEEZE program.[S6]

CCDC-880581 (**2**), 880580 (**9**), and 880579 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

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