Electronic Supporting Information

Catalytic double hydroarylation of alkynes to 9,9-disubstituted 9,10dihydroacridine derivatives by an electrophilic phenoxyphosphonium dication

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This PDF file includes:

1.	Mate	erials and Methods	4
2.	Catal	lyst Reactivity	5
	[(PhC	D)P(2-(N-Mepy))Ph ₂][B(C ₆ F ₅) ₄] ₂	5
3.	Pyrid	linium Phosphine Oxide Synthesis	9
	[OP(2	2-(N-Mepy))Ph ₂][B(C ₆ F ₅) ₄]	9
	[OP(2	2-(N-Mepy))Ph ₂][O ₃ SCF ₃]	10
4.	Catal	lyst Screening	12
5.	Cond	lition Screening	13
6.	Catal	lysis Scope	14
	(1)	2,7,9-trimethyl-9-(4-tolyl)-9,10-dihydoracridine	15
	(2)	2,7,9,10-tetramethyl-9-(4-tolyl)-9,10-dihydoracridine	16
	(3)	2,7,9,10-tetramethyl-9-phenyl-9,10-dihydoracridine	18
	(4)	2,7,9,10-tetramethyl-9-([1,1'-biphenyl]-4-yl)-9,10-dihydoracridine	20
	(5)	2,7,9,10-tetramethyl-9-(4-bromophenyl)-9,10-dihydoracridine	21
	(6)	2,7,9,10-tetramethyl-9-(2,4-difluorophenyl)-9,10-dihydoracridine	23
	(7)	2,7,9,10-tetramethyl-9-(3-thiophenyl)-9,10-dihydoracridine	25
	(8)	2,7,9,10-tetramethyl-9-(4-methoxyphenyl)-9,10-dihydoracridine	26
	(9)	2,7,9,10-tetramethyl-9-(4-trifluoromethylphenyl)-9,10-dihydoracridine	27
	(10)	2,7-dimethoxy-9,10-dimethyl-9-(4-tolyl)-9,10-dihydoracridine	29
	(11)	2,7-dibromo-9,10-dimethyl-9-(4-tolyl)-9,10-dihydoracridine	30
	(12)	9,10-dimethyl-9-(4-tolyl)-9,10-dihydoracridine	31
	(13)	2,7,9-trimethyl-9-(4-tolyl)-9H-xanthene	33

8. Computational Details						
7.	Num	Numbering Convention40				
	(17)	7-methoxy-9-methyl-9-(4-tolyl)acridin-2(9H)-one	38			
	(16)	1,4-bis(2,7,9,10-tetramethyl-9,10-dihydroacridin-9-yl)benzene	37			
	(15)	2-(1-mesitylvinyl)-N,4-dimethyl-N-(4-tolyl)aniline	35			
	(14)	2,7,9-trimethyl-9,10-(di-4-tolyl)-9,10-dihydoracridine	34			

1. Materials and Methods

General Remarks

All manipulations were performed in a MB Unilab glove box produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N₂. All glassware was ovenor flame-dried and cooled under vacuum before use. Dry, oxygen-free solvents (dichloromethane and *n*-pentane) were prepared using an Innovative Technologies solvent purification system or deoxygenated and distilled over sodium benzophenone. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, TCI Chemicals, or Alfa Aesar, and were used without further purification unless indicated otherwise. Phosphonium salts $[FP(C_6F_5)_3][B(C_6F_5)_4]^1$ $[(PhO)P(C_6F_5)_3][B(C_6F_5)_4]^2$ $[(PhO)P(2-(N-Mepy))Ph_2][B(C_6F_5)_4]_2^3$ $[FPPh_3][B(C_6F_5)_4]^4$ and starting materials [FP(2-(*N*-Mepy))Ph₂][B(C₆F₅)₄]₂,⁵ Ph₂NMe,⁶ (4-Tol)₂NMe,⁶ (4-(MeO)C₆H₄)₂NMe,⁷ (4-BrC₆H₄)₂NMe,⁸ and (4-Tol)₂NSiEt₃⁹ were prepared according to literature procedures or modified literature procedures. NMR spectra were obtained on an Agilent DD2-700 MHz, an Agilent DD2-500 MHz, a Bruker AvanceIII-400 MHz, or a Varian Mercury-300 MHz spectrometer. ¹H, ¹³C, ³¹P, ¹⁹F, and ¹¹B NMR chemical shifts (δ /ppm) are referenced to Me₄Si, Me₄Si, H₃PO₄, CFCl₃, and BF₃•OEt₂, respectively. Assignments of individual resonances were performed using 2D NMR techniques (HMBC, HSQC, ¹H-¹H–COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI) or a JEOL AccuTOF (DART) mass spectrometer.

X-ray Diffraction Studies

Single crystals were coated with paratone oil, mounted on a cryoloop, and frozen under a stream of cold nitrogen. Data were collected on a Bruker Apex2 X-ray diffractometer at 150 (2) K for all crystals using graphite monochromated Mo-Kα radiation (0.71073 Å). Data were collected using Bruker APEX-2 software and processed using SAINT. An empirical absorption correction was applied using SADABS. All structures were solved and refined by direct methods within the SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

2. Catalyst Reactivity



[(PhO)P(2-(N-Mepy))Ph₂][B(C₆F₅)₄]₂



Friedel-Crafts Type Dimerization of 1,1-Diphenylethylene

In a 20 mL vial, a solution of $[(PhO)P(2-(N-Mepy))Ph_2][B(C_6F_5)_4]_2$ (0.004 mmol, 0.02 eq.) was prepared in 1 mL CH₂Cl₂. 1,1-diphenylethylene (0.2 mmol, 1.0 eq.) was added at ambient temperature and the reaction mixture was left to stir for 2.5 h. The solution was then dried *in vacuo* and re-dissolved in 0.6 mL CDCl₃ affording a pale green solution. Conversion was determined by ¹H NMR spectroscopy.



Figure 1. ¹H (CD₂Cl₂) NMR spectrum of dimerization catalysis, t = 2.5 h.

Hydrodefluorination of 1-Fluoropentane



In a 20 mL vial, a solution of $[(PhO)P(2-(N-Mepy))Ph_2][B(C_6F_5)_4]_2$ (0.002 mmol, 0.05 eq.) was prepared in 0.6 mL CH₂Cl₂. Triethylsilane (Et₃SiH, 0.04 mmol, 1.0 eq.) was added at ambient temperature, the reaction was briefly stirred, and then 1-fluoropentane was added (0.04 mmol, 1.0 eq.). The reaction mixture was transferred to an NMR tube and left at ambient temperature for 1 h, before being monitored by ¹⁹F NMR spectroscopy. Conversion was determined from the proportion of Si-F bonds formed relative to C-F bonds remaining.



Figure 2. ¹⁹F (CD₂Cl₂) NMR spectrum for the hydrodefluorination of 1-fluoropentane.

Hydrosilylation of α-Methylstyrene



In a 20 mL vial, a solution of $[(PhO)P(2-(N-Mepy))Ph_2][B(C_6F_5)_4]_2$ (0.001 mmol, 0.02 eq.) was prepared in 0.6 mL CH₂Cl₂. Triethylsilane (Et₃SiH, 0.05 mmol, 1.0 eq.) was added at ambient temperature, the reaction mixture was briefly stirred, and then α -methylstyrene (0.05 mmol, 1.0 eq.) was added. The mixture was transferred to an NMR tube and heated at 45 °C for 4 h. The solution was then dried *in vacuo* and re-dissolved in 0.6 mL CDCl₃ affording a colourless solution. Conversion was determined by ¹H NMR spectroscopy.



Figure 3. ¹H (CD₂Cl₂) NMR spectrum of hydrosilylation catalysis.

Dehydrocoupling of Phenol with Et₃SiH

PhOH
$$\begin{array}{c} \text{Et}_{3}\text{SiH} \\ \underline{2 \text{ mol}\% \text{ cat.}} \\ \text{CH}_{2}\text{Cl}_{2} \\ 48 \text{ h}, 50 ^{\circ}\text{C} \\ - \text{H}_{2} \end{array} \qquad PhOSiEt_{3} \qquad \textbf{>99\%}$$

In a 20 mL vial, a solution of $[(PhO)P(2-(N-Mepy))Ph_2][B(C_6F_5)_4]_2$ (0.001 mmol., 0.02 eq.) was prepared in 0.6 mL CH₂Cl₂. Triethylsilane (Et₃SiH, 0.05 mmol, 1.0 eq.) was added at ambient temperature, the reaction mixture was briefly stirred, and then added to a vial containing phenol (0.05 mmol, 1.0 eq.). The mixture was transferred to an NMR tube and heated at 50 °C for 48 h. The solution was then dried *in vacuo* and re-dissolved in 0.6 mL CDCl₃ affording a colourless solution. Conversion was determined by ¹H NMR spectroscopy.



Figure 4. ¹H (CD₂Cl₂) NMR spectrum of dehydrocoupling catalysis.

Deoxygenation of Benzophenone



In a 20 mL vial, a solution of $[(PhO)P(2-(N-Mepy))Ph_2][B(C_6F_5)_4]_2$ (0.0002 mmol, 0.01 eq.) was prepared in 0.6 mL CH₂Cl₂. Triethylsilane (Et₃SiH, 0.04 mmol, 2.0 eq.) was added at ambient temperature, the reaction was briefly stirred, and then the solution was added to a vial containing benzophenone (0.02 mmol, 1.0 eq.). The reaction mixture was left to stir at ambient temperature for 2 h. The solution was then dried *in vacuo* and re-dissolved in 0.6 mL CDCl₃ affording a colourless solution. Conversion was determined by ¹H NMR spectroscopy. Toluene (0.02 mmol, 1.0 eq.) was added as an internal standard.



Figure 5. ¹H (CD_2Cl_2) NMR spectrum for the deoxygenation of benzophenone.

3. Pyridinium Phosphine Oxide Synthesis



[OP(2-(N-Mepy))Ph₂][B(C₆F₅)₄]

A CH₂Cl₂ solution of [FP(2-(*N*-Mepy))Ph₂][B(C₆F₅)₄]₂ was exposed to air for 48h. The resulting solution was then dried *in vacuo* and the off-white solid was washed with *n*-pentane (3 x 5 mL) to afford an off-white solid. Partial characterization. ¹⁹F NMR (377 MHz, CD₂Cl₂): δ -133.0 (s(br), 8F; B(*o*-C₆F₅)₄), -163.5 (t, ³J_{FF} = 22 Hz, 4F; B(*p*-C₆F₅)₄), -167.3 ppm (m(br), 8F; B(*m*-C₆F₅)₄). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ 28.7 ppm (s).



Figure 7. ${}^{31}P{}^{1}H{}(CH_2CI_2)$ NMR spectrum of [OP(2-(*N*-Mepy))Ph₂][B(C₆F₅)₄].



[OP(2-(N-Mepy))Ph₂][O₃SCF₃]

A CH₂Cl₂ solution of $[F_2P(2-(N-Mepy))Ph_2][O_3SCF_3]$ was exposed to air for 48h. The resulting solution was then dried *in vacuo* and the off-white solid was washed with *n*-pentane (3 x 5 mL) to afford an off-white solid. **HRMS (ESI-TOF+):** m/z [M] 294.1045 (calc'd for C₁₈H₁₇NOP: 294.1042). ¹H NMR (400 MHz, CD₂Cl₂): δ 4.52, (s, 3H; NCH₃), 7.61 (m, 5H; phenyl-*o*-CH, pyridyl-*o*-

CH), 7.73 (m, 6H; phenyl-*m*,*p*-CH), 8.23 (m, 1H; pyridyl-*p*-CH), 8.48 (m, 1H; pyridyl-*m*-CH), 9.21 ppm (m, 1H; pyridyl-*m*-CH). ¹⁹F NMR (377 MHz, CD₂Cl₂): δ -78.4 ppm (s, 3F; O₃SCF₃). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ 28.7 ppm (s). ¹³C{¹H} NMR (125 MHz, CD₂Cl₂): δ 48.9 (d, ³J_{CP} = 3 Hz, 1C; NCH₃), 126.9 (d, ¹J_{CP} = 111 Hz, 1C; phenyl-*i*-C), 130.0 (d, ²J_{CP} = 13 Hz, 4C; phenyl-*o*-CH), 131.3 (d, ⁴J_{CP} = 2 Hz, 1C; pyridyl-*p*-CH), 132.1 (d, ³J_{CP} = 11 Hz, 4C; phenyl-*m*-CH), 133.9 (d, ²J_{CP} = 13 Hz, 1C; pyridyl-*o*-CH), 134.5 (d, ⁴J_{CP} = 3 Hz, 2C; phenyl-*p*-CH), 145.6 (d, ³J_{CP} = 8 Hz, 1C; pyridyl-*m*-CH), 149.3 (d, ¹J_{CP} = 89 Hz, 1C; pyridyl-*i*-C), 151.8 ppm (d, ³J_{CP} = 4 Hz, 1C; pyridyl-*m*-CH), resonance for the sulfur-bound carbon atom of O₃SCF₃ anion was not observed.



Figure 9. ${}^{31}P{}^{1}H{}(CDCl_{3})$ NMR spectrum of $[OP(2-(N-Mepy))Ph_2][O_3SCF_3]$.



Figure 11. ¹³C (CDCl₃) NMR spectrum of [OP(2-(*N*-Mepy))Ph₂][O₃SCF₃]. Asterisks denote solvent impurities.

4. Catalyst Screening



General Procedure

Catalyst screening reactions for the hydroarylation of diarylamines with alkynes were performed according to a common procedure. A sample procedure is outlined below.

In a 20 mL vial, a solution of acid catalyst (0.004 mmol, 0.05 eq.) was prepared in CH_2Cl_2 (3 mL). A solution of $(4\text{-Tol})_2NH$ (16.0 mg, 0.08 mmol, 1.0 eq.) in CH_2Cl_2 (3 mL) was added at ambient temperature. The mixture was briefly stirred and then a solution of (4-Tol)CCH (9.4 mg, 0.08 mmol, 1.0 eq.) in CH_2Cl_2 (3 mL) was added. The reaction mixture was stirred at ambient temperature for 16 h. The solution was then dried *in vacuo*. Acid catalyst was removed by dissolving the residue in a 2:1 mixture of $CH_2Cl_2:n$ -pentane and filtering over a silica plug. Conversion was determined by GCMS.

Table 1. Catalyst Screening for Hydroarylation

Catalyst	Conversion to 1
[(PhO)P(2-(<i>N</i> -Mepy))Ph ₂] [B(C ₆ F ₅) ₄] ₂	62
$[FPPh_3][B(C_6F_5)_4]$	32
[(PhO)P(C ₆ F ₅) ₃][B(C ₆ F ₅) ₄]	32
[OP(2-(<i>N</i> -Mepy))Ph ₂] [B(C ₆ F ₅) ₄]	0
FeCl ₃	52
AICI ₃	22
$B(C_6F_5)_3$	0
$Bi(OSO_2CF_3)_3$	0
InCl₃	0
ZnCl ₂	0
(CF ₃ SO ₂) ₂ NH	18

5. Condition Screening

General Procedure

Condition screening reactions for the hydroarylation of diarylamines with alkynes were performed according to a common procedure. A sample procedure is outlined below.

In a 20 mL vial, a solution of $[(PhO)P(2-(N-Mepy))Ph_2][B(C_6F_5)_4]_2$ (10.2 mg, 0.006 mmol, 0.05 eq.) was prepared in CH₂Cl₂ (3 mL). A solution of (4-Tol)₂NMe (25.3 mg, 0.12 mmol, 1.0 eq.), prepared in CH₂Cl₂ (3 mL), was added at ambient temperature. The mixture was briefly stirred and then a solution of (4-Tol)CCH (13.9 mg, 0.12 mmol, 1.0 eq.), prepared in CH₂Cl₂ (3 mL), was added. The reaction mixture was stirred at ambient temperature for 24 h. The solution was then dried *in vacuo* and re-dissolved in CDCl₃ (0.6 mL). Conversion was determined by ¹H NMR spectroscopy.

Table 2.Condition Screening for the Formation of **2** via Hydroarylation Using [(PhO)P(2-
(*N*-Mepy))Ph2][B(C6F5)4]2 as the Catalyst

Cat. (mol %)	Equiv. alkyne ^a	Т (°С)	Solvent	Yield⁵ (%)
0	1.0	25	CH_2CI_2	0
5	1.0	25	CH_2CI_2	44
5	1.0	25	$C_2H_4Cl_2$	67
5	1.0	50	CH_2CI_2	71
5	1.0	50	$C_2H_4Cl_2$	85
5	1.0	80	$C_2H_4Cl_2$	92
5	1.5	80	$C_2H_4Cl_2$	97
5	1.5	80	$C_2H_4Cl_2$	95°
1	1.5	80	$C_2H_4Cl_2$	69
0	1.5	80	$C_2H_4Cl_2$	0

^a reaction scale = 0.12 mmol diarylamine; ^b reaction volume = 9 mL; ^c reaction volume = 2 mL.

6. Catalysis Scope



General Procedure

Hydroarylations of diarylamines were performed following a common procedure. A sample procedure is provided below. Reactions with $(4-\text{Tol})_2$ NH, $(4-(OMe)C_6H_4)_2$ NH, and $(4-\text{BrC}_6H_4)_2$ NH were carried out at ambient temperature instead of 80 °C. Reaction with 1,4-(HCC)_2Ph performed with 1.3 eq. (4-Tol)_2NMe. Reaction with (4-Tol)_3N performed with 1.0 eq. (4-Tol)CCH.

In a Schlenk bomb, a solution of $[(PhO)P(2-(N-Mepy))Ph_2][B(C_6F_5)_4]_2$ (10.2 mg, 0.006 mmol, 0.05 eq.) was prepared in C₂H₄Cl₂ (0.66 mL). A solution of $(4-XPh)_2NMe$ (0.12 mmol, 1.0 eq.) in C₂H₄Cl₂ (0.66 mL) was added at ambient temperature. The mixture was briefly stirred and then a solution of (R)CCH (0.18 mmol, 1.5 eq.) in C₂H₄Cl₂ (0.66 mL) was added. The reaction mixture was sealed and heated at 80 °C for 24 h. The solution was then dried *in vacuo* and re-dissolved in CDCl₃ (0.6 mL). Conversions were determined by ¹H NMR spectroscopy. Products were isolated by silica

chromatography (0-5 % EtOAc in pentane). Single crystals suitable for X-ray diffraction were obtained by recrystallization from hot ethanol.

Table 3.Catalytic Synthesis of 9,9-Disubstituted 9,10-Dihydroacridine Derivatives Using $[(PhO)P(2-(N-Mepy))Ph_2][B(C_6F_5)_4]_2$ as the Catalyst

E	Х	R	Т (°С)	Prod.	Conv (%) (isolated)
NH	Me	4-Tol	25	1	52 (37)
NMe	Me	4-Tol	80	2	95 (76)
NMe	Me	Ph	80	3	95 (74)
NMe	Me	4-biphenyl	80	4	92 (68)
NMe	Me	$4-BrC_6H_4$	80	5	93 (65)
NMe	Me	2,4-F ₂ C ₆ H ₃	80	6	68 (35)
NMe	Me	3-thiophene-yl	80	7	86 (63)
NMe	Me	4-(MeO)C ₆ H ₄	80	8	65(26)
NMe	Me	$4-CF_3C_6H_4$	80	9	10
NMe	MeO	4-Tol	80	10	97 (66)
NMe	Br	4-Tol	80	11	23 (20)
NMe	Н	4-Tol	80	12	55 (35)
0	Me	4-Tol	80	13	21
N(4-Tol)	Me	4-Tol	80	14	65
NH	Br	4-Tol	25, 80	-	0
NSiEt ₃	Me	4-Tol	80	-	0
S	H. Me	4-Tol	80	-	0



(1) 2,7,9-trimethyl-9-(4-tolyl)-9,10-dihydoracridine

Obtained as a light yellow solid (13.9 mg, 37% isolated yield). **HRMS (DART-TOF+):** m/z [M+H] 314.19074 (calc'd for C₂₃H₂₄N: 319.19087). ¹**H NMR (500 MHz, C₆D₆):** δ = 1.86 (s, 3H; 9-CH₃), 1.99 (s, 6H; 2,7-CH₃), 2.09 (s, 1H; 9-(tolyl-*p*-CH₃)), 5.50 (s, 1H; NH), 6.31 (d, ³J_{HH} = 8 Hz, 2H; 4,5-CH), 6.78 (s, 2H; 1,8-CH), 6.83 (dd, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz, 2H; 3,6-CH), 6.99 (d, ³J_{HH} = 8 Hz, 2H; 9-(tolyl-*m*-CH)), 7.39 ppm (dt, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz; 9-(tolyl-*o*-CH)). ¹³C{¹H} NMR (125 MHz, C₆D₆): δ =

20.9 (2C; 2,7-*C*H₃), 21.0 (1C; 9-(tolyl-*p*-*C*H₃)), 31.6 (1C; 9-*C*H₃), 46.0 (1C; 9-*C*), 113.6 (2C; 4,5-*C*H), 127.7 (2C; 3,6-*C*H), 128.9 (2C; 9-(tolyl-*m*-*C*H)), 129.4 (2C; 2,7-*C*), 129.5 (2C; 9-(tolyl-*o*-*C*H)), 129.7 (2C; 1,8-*C*H), 129.9 (2C; 12,13-*C*), 135.5 (1C; 9-(tolyl-*p*-*C*)), 136.5 (2C; 11,14-*C*), 147.5 ppm (1C; 9-(tolyl-*i*-*C*)).



Figure 13. ${}^{13}C{}^{1}H{}(C_6D_6)$ NMR spectrum of **1**. Asterisks denote solvent impurities.



(2) 2,7,9,10-tetramethyl-9-(4-tolyl)-9,10-dihydoracridine

Obtained as a white solid (29.9 mg, 76% isolated yield). **HRMS (DART-TOF+):** m/z [M+H] 328.20756 (calc'd for C₂₄H₂₆N: 328.20652). ¹**H NMR (500 MHz, CDCl₃):** δ = 1.79 (s, 3H; 9-CH₃), 2.22 (s, 6H; 2,7-CH₃), 2.33 (s, 3H; 9-(tolyl-*p*-CH₃)), 3.35 (s, 3H; NCH₃), 6.75 (d, ⁴J_{HH} = 2 Hz, 2H; 1,8-CH), 6.87 (d, ³J_{HH} = 8 Hz, 2H; 4,5-CH), 7.00 (d, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz, 2H; 3,6-CH), 7.05 ppm (s, 4H; 9-(tolyl-*o*,*m*-CH)). ¹³**C NMR (125 MHz, CDCl₃):** δ = 20.9 (2C; 2,7-CH₃), 21.2 (1C; 9-(tolyl-*p*-CH₃)), 28.5 (1C; 9-CH₃), 33.6 (1C; NCH₃), 45.8 (1C; 9-C), 111.7 (2C; 4,5-CH), 127.4 (2C; 3,6-CH), 128.0 (2C; 1,8-CH), 128.5 (2C; 9-(tolyl-*o*-CH))), 128.6 (2C; 9-(tolyl-*o*-CH)), 129.0 (2C; 2,7-C), 132.4 (2C; 12,13-C), 135.4 (1C; 9-(tolyl-*p*-CH₃)), 140.0 (2C; 11,14-C), 145.9 ppm (1C; 9-(tolyl-*i*-C)).











(3) 2,7,9,10-tetramethyl-9-phenyl-9,10-dihydoracridine

Obtained as a white solid (27.8 mg, 74% isolated yield). HRMS (DART-TOF+): m/z [M+H] 314.19205 (calc'd for C₂₃H₂₄N: 314.19087). ¹H NMR (500 MHz, CDCl₃): δ = 1.81 (s, 3H; 9-CH₃), 2.22 (s, 6H; 2,7-CH₃), 3.35 (s, 3H; NCH₃), 6.74 (d, ⁴J_{HH} = 2 Hz, 2H; 1,8-CH), 6.82 (d, ³J_{HH} = 8 Hz, 2H; 4,5-CH), 7.00 (dd, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz, 2H; 3,6-CH), 7.23 ppm (m, 5H; 9-(phenyl-*o*,*m*,*p*-CH). ¹³C NMR (125 MHz, CDCl₃): δ = 20.9 (2C; 2,7-CH₃), 28.3 (1C; 9-CH₃), 33.4 (1C; NCH₃), 46.1 (1C; 9-C),

111.7 (2C; 4,5-*C*H), 126.0 (1C; 9-(phenyl-*p*-*C*H), 127.4 (1C; 9-(phenyl-*m*-*C*H), 127.7 (2C; 3,6-*C*H), 127.9 (2C; 1,8-*C*H), 128.6 (1C; 9-(phenyl-*o*-*C*H), 129.0 (2C; 2,7-*C*), 132.2 (2C; 12,13-*C*), 140.0 (2C; 11,14-*C*), 149.0 ppm (1C; 9-phenyl-*C*).



Figure 18. ¹³C (CDCl₃) NMR spectrum of **3**. Asterisks denote solvent impurities.



Figure 19. Molecular structure of 3.



(4) 2,7,9,10-tetramethyl-9-([1,1'-biphenyl]-4-yl)-9,10-dihydoracridine

Obtained as a white solid (31.8 mg, 68% isolated yield). **HRMS (DART-TOF+):** m/z [M+H] 390.22252 (calc'd for $C_{29}H_{28}N$: 390.22217). ¹**H NMR (500 MHz, CDCl₃):** δ = 1.86 (s, 3H; 9-*CH*₃), 2.24 (s, 6H; 2,7-*CH*₃), 3.36 (s, 3H; NC*H*₃), 6.82 (d, ⁴*J*_{HH} = 2 Hz, 2H; 1,8-*CH*), 6.83 (d, ³*J*_{HH} = 8 Hz, 2H; 4,5-*CH*), 7.03 (m, 2H; 3,6-*CH*), 7.22 (dt, ³*J*_{HH} = 8 Hz, ⁴*J*_{HH} = 2 Hz, 2H; 9-(biphenyl-2,6-*CH*)), 7.32 (tt, ³*J*_{HH} = 8 Hz, ⁴*J*_{HH} = 1 Hz, 1H; 9-(biphenyl-4'-*CH*)), 7.42 (t, ³*J*_{HH} = 8 Hz, ⁴*J*_{HH} = 2 Hz, 2H; 9-(biphenyl-3,5'-*CH*)), 7.49 (dt, ³*J*_{HH} = 8 Hz, ⁴*J*_{HH} = 2 Hz, 2H; 9-(biphenyl-3,5-*CH*)), 7.61 ppm (m, 2H; 9-(biphenyl-2',6'-*CH*)). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 20.9 (2C; 2,7-*C*H₃), 28.3 (1C; 9-*C*H₃), 33.5 (1C; N*C*H₃), 45.9 (1C; 9-*C*), 111.8 (2C; 4,5-*C*H), 126.4 (2C; 9-(biphenyl-3,5-*C*H)), 127.1 (2C; 9-(biphenyl-2',6'-*C*H)), 127.2 (1C; 9-(biphenyl-4'-*C*H)), 127.5 (2C; 3,6-*C*H), 127.9 (2C; 1,8-*C*H), 128.8 (2C; 9-(biphenyl-3',5'-*C*H)), 129.0 (2C; 9-(biphenyl-2,6-*C*H)), 129.2 (2C; 2,7-*C*), 132.1 (2C; 12,13-*C*), 138.6 (1C; 9-(biphenyl-1-*C*)), 140.1 (2C; 11,14-*C*), 141.0 (1C; 9-(biphenyl-1'-*C*)), 148.2 ppm (1C; 9-(biphenyl-4-*C*)).





Figure 22. Molecular structure of 4.



(5) 2,7,9,10-tetramethyl-9-(4-bromophenyl)-9,10-dihydoracridine

Obtained as a white solid (30.6 mg, 65% isolated yield). **HRMS (DART-TOF+):** m/z [M+H] 392.10177 (calc'd for C₂₃H₂₃BrN: 392.10139). ¹**H NMR (500 MHz, CDCl₃):** δ = 1.79 (s, 3H; 9-CH₃), 2.24 (s, 6H; 2,7-CH₃), 3.33 (s, 3H; NCH₃), 6.75 (d, ⁴J_{HH} = 2 Hz, 2H; 1,8-CH), 6.81 (d, ³J_{HH} = 8 Hz, 2H; 4,5-CH), 7.02 (m, 4H; 3,6-CH, 9-(phenyl-*o*-CH)), 7.35 ppm (dt, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz, 2H; 9-(phenyl-*m*-CH)). ¹³**C NMR (125 MHz, CDCl₃):** δ = 20.9 (2C; 2,7-CH₃), 28.1 (1C; 9-CH₃), 33.4 (1C; NCH₃), 45.8 (1C; 9-C), 111.9 (2C; 4,5-CH), 120.0 (1C; 9-(phenyl-*p*-CBr)), 127.6 (4C; 1,8-CH, 3,6-CH), 129.3 (2C; 2,7-C), 130.4 (2C; 9-(phenyl-*o*-CH)), 130.8 (2C; 9-(phenyl-*m*-CH)), 131.6 (2C; 12,13-C), 140.1 (2C; 11,14-C), 148.3 ppm (1C; 9-(phenyl-*i*-C)).



Figure 23. ¹H (CDCl₃) NMR spectrum of **5**. Asterisks denote solvent impurities.



Figure 25. Molecular structure of 5.



(6) 2,7,9,10-tetramethyl-9-(2,4-difluorophenyl)-9,10-dihydoracridine

Obtained as a white solid (14.7 mg, 35% isolated yield). HRMS (DART-TOF+): m/z [M+H] 350.17171 (calc'd for $C_{23}H_{22}F_2N$: 350.17203). ¹H NMR (500 MHz, CDCl₃): δ = 1.73 (s, 3H; 9-CH₃),

2.17 (s, 6H; 2,7-CH₃), 3.41 (s, 3H; NCH₃), 6.50 (d, ${}^{4}J_{HH} = 2$ Hz, 2H; 1,8-CH), 6.73 (m, 1H; 9-(phenyl-3-CH)), 6.81 (d, ${}^{3}J_{HH} = 8$ Hz, 2H; 5,4-CH), 6.96 (m, 1H; 9-(phenyl-5-CH)), 7.00 (m, 2H; 3,6-CH), 7.49 ppm (dt, ${}^{3}J_{HH} = 8$ Hz, ${}^{3}J_{HF} = 6$ Hz, 1H; 9-(phenyl-6-CH)). ${}^{19}F{}^{1}H{}$ NMR (375 MHz, CDCl₃): $\delta = -99.20$ (d, ${}^{3}J_{FF} = 8$ Hz, 1F; 9-(phenyl-2-F)), -112.69 ppm (d, ${}^{3}J_{FF} = 8$ Hz, 1F; 9-(phenyl-4-F)). ${}^{13}C$ NMR (125 MHz, CDCl₃): $\delta = 20.8$ (2C; 2,7-CH₃), 29.6 (1C; 9-CH₃), 33.5 (1C; NCH₃), 44.0 (1C; 9-C), 105.5 (1C; 9-(phenyl-3-CH)), 110.1 (1C; 9-(phenyl-5-CH)), 111.8 (2C; 4,5-CH), 126.6 (2C; 1,8-CH), 127.7 (2C; 3,6-CH), 129.1 (2C; 2,7-C), 129.6 (1C: 9-(phenyl-6-CH)), 131.0 (1C: 9-(phenyl-1-C)), 131.2 (2C; 12,13-C), 138.9 (2C; 11,14-C), 161.2 (1C; 9-(phenyl-4-CF)), 162.4 ppm (1C; 9-(phenyl-2-CH)).



Figure 26. ¹H (CDCl₃) NMR spectrum of **6**. Asterisks denote solvent impurities.



Figure 27. ¹⁹F (CDCl₃) NMR spectrum of **6**.



Figure 28. ¹³C (CDCl₃) NMR spectrum of 6.



(7) 2,7,9,10-tetramethyl-9-(3-thiophenyl)-9,10-dihydoracridine

Obtained as a white solid (24.1 mg, 63% isolated yield). HRMS (DART-TOF+): m/z [M+H] 320.14802 (calc'd for C₂₁H₂₂NS: 320.14729). ¹H NMR (500 MHz, CDCl₃): δ = 1.72 (s, 3H; 9-CH₃), 2.19 (s, 6H; 2,7-CH₃), 3.40 (s, 3H; NCH₃), 6.61 (d, ⁴J_{HH} = 2Hz, 2H; 1,8-CH), 6.74 (dd, ³J_{HH} = 5Hz, ⁴J_{HH} = 1Hz, 1H; 9-(thiophenyl-2-CH)), 6.82 (d, ³J_{HH} = 8Hz, 2H; 4,5-CH), 7.01 (m, 2H; 3,6-CH), 7.18 (dd, ³J_{HH} = 3Hz, ³J_{HH} = 1Hz, 1H; 9-(thiophenyl-4-CH)), 7.25 ppm (dd, ³J_{HH} = 5Hz, ³J_{HH} = 3Hz, 1H; 9-(thiophenyl-4-CH)), 7.25 ppm (dd, ³J_{HH} = 5Hz, ³J_{HH} = 3Hz, 1H; 9-(thiophenyl-5-CH)). ¹³C NMR (125 MHz, CDCl₃): δ = 20.8 (2C; 2,7-CH₃), 29.3 (1C; 9-CH₃), 33.4 (1C; NCH₃), 44.3 (1C; 9-C), 111.6 (2C; 4,5-CH), 121.7 (1C; 9-(thiophenyl-4-CH)), 125.2 (1C; 9-(thiophenyl-5-CH)), 127.6 (4C; 1,3,6,8-CH), 129.2 (2C; 2,7-C), 129.6 (1C; 9-(thiophenyl-2-CH)), 131.7 (2C; 12,13-C), 139.5 (2C; 11,14-C), 149.3 ppm (1C; 9-(thiophenyl-3-C)).







(8) 2,7,9,10-tetramethyl-9-(4-methoxyphenyl)-9,10-dihydoracridine

Obtained as a white solid (10.5 mg, 26% isolated yield). HRMS (DART-TOF+): m/z [M+H] 344.20418 (calc'd for C₂₄H₂₅NO: 344.20144). ¹H NMR (500 MHz, CDCl₃): δ = 1.76 (s, 3H; 9-CH₃), 2.21 (s, 6H; 2,7-CH₃), 3.36 (s, 3H; NCH₃), 3.81 (s, 3H; 9-(phenyl-*p*-OCH₃)), 6.71 (d, ⁴J_{HH} = 2Hz, 2H;

1,8-*CH*), 6.80 (m, 4H; 4,5-*CH*, 9-(phenyl-*m*-*CH*)), 7.00 (m, 2H; 3,6-*CH*), 7.09 ppm (m, 2H; 9-(phenyl*o*-*CH*)). ¹³**C NMR (125 MHz, CDCl₃):** δ = 21.0 (2C; 2,7-*C*H₃), 28.7 (1C; 9-*C*H₃), 33.6 (1C; N*C*H₃), 45.7 (1C; 9-*C*), 55.4 (1C; 9-(phenyl-*p*-O*C*H₃)), 111.7 (2C; 9-(phenyl-*m*-*C*H)), 113.2 (2C; 4,5-*C*H), 127.5 (2C; 3,6-*C*H)), 128.1 (2C; 1,8-*C*H)), 129.1 (2C; 2,7-*C*), 129.9 (2C; 9-(phenyl-*o*-*C*H)), 132.7 (2C; 12,13-*C*), 140.0 (2C; 11,14-*C*), 141.1 (1C; 9-(phenyl-*i*-*C*)), 157.8 ppm (1C; 9-(phenyl-*p*-*C*)).



Figure 32. ¹³C{¹H} (CDCl₃) NMR spectrum of **8**. Asterisks denote solvent impurities.



(9) 2,7,9,10-tetramethyl-9-(4-trifluoromethylphenyl)-9,10-dihydoracridine

Partial characterization (10% conversion). **MS (EI+):** [m/z, (%)] 366.10 ($[M-CH_3]^+$, 100), 367.20 (33.6). ¹H NMR (500 MHz, CDCl_3): δ = 1.91 (s, 3H; 9-CH₃), 2.30 (s, 6H; 2,7-CH₃), 3.36 (s, 3H; NCH₃), 7.25 (d, ³J_{HH} = 8 Hz, 2H; 9-(phenyl-CH), 7.48 ppm (d, ³J_{HH} = 8 Hz, 2H; 9-(phenyl-CH). ¹⁹F{¹H} NMR (282 MHz, CDCl_3): -62.47 ppm.



Figure 33. ¹H (CDCl₃) NMR spectrum of reaction mixture of **9**. Asterisks denote product peaks.



Figure 34. ${}^{19}F{}^{1}H{}(CDCl_{3})$ NMR spectrum of reaction mixture of **9**.



(10) 2,7-dimethoxy-9,10-dimethyl-9-(4-tolyl)-9,10-dihydoracridine

Obtained as a white solid (28.4 mg, 66% isolated yield). **HRMS (DART-TOF+):** m/z [M+H] m/z 360.19568 (calc'd for C₂₄H₂₆NO₂: 360.1965). ¹**H NMR (500 MHz, CDCl₃):** δ = 1.81 (s, 3H; 9-CH₃), 2.31 (s, 3H; 9-(tolyl-*p*-CH₃)), 3.33 (s, 3H; NCH₃), 3.71 (s, 6H; 2,7-OCH₃), 6.61 (d, ⁴J_{HH} = 3 Hz, 2H; 1,8-CH), 6.78 (dd, ³J_{HH} = 8 Hz, ⁴J_{HH} = 3 Hz, 2H; 3,6-CH), 6.81 (d, ³J_{HH} = 8 Hz, 2H; 4,5-CH), 7.04 ppm (s, 4H; 9-(tolyl-*o*,*m*-CH)). ¹³C{¹H} **NMR (500 MHz, CDCl₃):** δ = 21.1 (1C; 9-(tolyl-*p*-CH₃)), 27.7 (1C; 9-CH₃), 33.6 (1C; NCH₃), 46.4 (1C; 9-C), 55.8 (2C; 2,7-OCH₃), 111.3 (2C; 3,6-CH), 112.1 (2C; 4,5-CH), 114.2 (2C; 1,8-CH), 128.4 (2C; 9-(tolyl-*o*-CH)), 128.6 (2C; 9-(tolyl-*m*-CH)), 133.6 (2C; 12,13-C), 135.6 (1C; 9-(tolyl-*p*-C)), 137.0 (2C; 11,14-*C*), 144.9 (1C; 9-(tolyl-*i*-*C*)), 153.7 ppm (2C; 2,7-COCH₃).



Figure 36. ¹³C{¹H} (CDCl₃) NMR spectrum of **10**. Asterisks denote solvent impurities.



(11) 2,7-dibromo-9,10-dimethyl-9-(4-tolyl)-9,10-dihydoracridine

Obtained as a light yellow solid (11.0 mg, 20% isolated yield). **HRMS (DART-TOF+):** m/z [M+H] 455.99605 (calc'd for $C_{22}H_{20}Br_2N$: 455.99625). ¹**H NMR (500 MHz, CDCl₃):** δ = 1.77 (s, 3H; 9-CH₃), 2.34 (s, 3H; 9-(tolyl-*p*-CH₃)), 3.35 (s, 3H; NCH₃), 6.80 (d, ³J_{HH} = 8 Hz, 2H; 4,5-CH), 7.01 (d, ³J_{HH} = 8

Hz, ${}^{4}J_{HH} = 1$ Hz, 2H; 9-(tolyl-*o*-C*H*)), 7.03 (m, 2H; 1,8-CH), 7.08 (d, ${}^{3}J_{HH} = 8$ Hz, 2H; 9-(tolyl-*m*-C*H*)), 7.32 ppm (m, 2H; 3,6-CH). ${}^{13}C{}^{1}H{}$ NMR (125 MHz, CDCl₃): $\delta = 21.1$ (1C; 9-(tolyl-*p*-CH₃), 28.2 (1C; 9-CH₃), 33.8 (1C; NCH₃), 45.9 (1C; 9-C), 113.3 (2C; 2,7-CBr), 113.8 (2C; 4,5-CH), 128.3 (2C; 9-(tolyl-*o*-CH)), 128.9 (2C; 9-(tolyl-*m*-CH)), 129.9 (2C; 3,6-CH), 130.1 (2C; 1,8-CH), 134.4 (2C; 12,13-C), 136.3 (1C; 9-(tolyl-*p*-C)), 140.7 (2C; 11,14-C), 144.0 ppm (1C; 9-(tolyl-*i*-C)).



Figure 38. ¹³C{¹H} (CDCl₃) NMR spectrum of **11**. Asterisks denote solvent impurities.



(12) 9,10-dimethyl-9-(4-tolyl)-9,10-dihydoracridine

Obtained as a white yellow solid (12.6 mg, 35% isolated yield). HRMS (DART-TOF+): m/z [M+H] 455.99605 (calc'd for $C_{22}H_{20}Br_2N$: 455.99625). ¹H NMR (500 MHz, CDCl₃): $\delta = 1.82$ (s, 3H; 9-CH₃), 2.34 (s, 3H; 9-(tolyl-*p*-CH₃)), 3.42 (s, 3H; NCH₃), 6.89 (m, 2H; 1,8-CH), 6.96 (m, 4H; 2,3,6,7-CH), 7.08 (s, 4H; 9-(tolyl-*o*,*m*-CH)), 7.23 ppm (m, 2H; 4,5-CH). ¹³C{¹H} NMR (125 MHz, CDCl₃): $\delta = 21.1$ (1C; 9-(tolyl-*p*-CH₃)), 28.3 (1C; 9-CH₃), 33.5 (1C; NCH₃), 45.9 (1C; 9-C), 112.0 (2C; 2,7-CH), 120.3 (2C; 1,8-CH), 126.9 (2C; 4,5-CH), 127.4 (2C; 3,6-CH), 128.5 (2C; 9-(tolyl-*o*-CH)), 128.7 (2C; 9-(tolyl-*m*-CH)), 132.6 (2C; 12,13-C), 135.6 (1C; 9-(tolyl-*p*-C)), 141.9 (2C; 11,14-C), 145.8 ppm (1C; 9-(tolyl-*i*-C)).



Figure 39. ¹H (CDCl₃) NMR spectrum of **12**. Asterisks denote solvent impurities.



Figure 40. ¹³C{¹H} (CDCl₃) NMR spectrum of **12**. Asterisks denote solvent impurities.







(13) 2,7,9-trimethyl-9-(4-tolyl)-9H-xanthene

Partial characterization (21% conversion). **MS (EI+):** [m/z, (%)] 313.20 ($[M-H]^+$, 100), 314.30 (23.4), 315.20 (2.5). ¹H NMR (500 MHz, CDCl₃): $\delta = 1.92$ (s, 3H; 9-CH₃), 2.21 (s, 6H; 2,7-CH₃), 6.67 (m, 2H; 1,8-CH), 6.99 ppm (m, 4H).



Figure 42. ¹H (CDCl₃) NMR spectrum of **13**. Asterisks denote product peaks.



(14) 2,7,9-trimethyl-9,10-(di-4-tolyl)-9,10-dihydoracridine

Product was inseparable from a by-product, putatively with two alkyne additions. Partial characterization (65% conversion). **HRMS (DART-TOF+):** m/z [M+H] 404.23847 (calc'd for $C_{30}H_{30}N$: 404.23782). **By-product HRMS (DART-TOF+):** m/z [M+H] 520.30039 (calc'd for $C_{39}H_{38}N$: 520.30042). ¹**H NMR (500 MHz, CDCl_3):** $\delta = 1.91$ (s, 3H; 9-CH₃), 2.12 (s, 6H; 2,7-CH₃), 2.38 (s, 3H; 9-(tolyl-*p*-CH₃)), 2.49 (s, 3H; *N*-(tolyl-*p*-CH₃)), 6.19 (d, ³J_{HH} = 8 Hz, 2H; 4,5-CH), 6.60 (d, ⁴J_{HH} = 2 Hz, 2H; 1,8-CH), 6.72 (dd, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz, 2H; 3,6-CH),7.16 (m, 2H; 9-(tolyl-*o*-CH)), 7.21 (dt, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz, 2H; *N*-(tolyl-*o*-CH)), 7.32 (dt, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz, 2H; 9-(tolyl-*m*-CH)), 7.41 ppm (m, 2H; *N*-(tolyl-*m*-CH)). ¹³C{¹H} NMR (125 MHz, CDCl₃): $\delta = 20.7$ (2C; 2,7-CH₃), 21.2 (1C; 9-(tolyl-*p*-CH₃)), 21.5 (1C; *N*-(tolyl-*p*-CH₃)), 32.4 (1C; 9-CH₃), 45.3 (1C; 9-C), 113.8 (2C; 4,5-CH), 127.1 (2C; 3,6-CH), 128.6 (2C; 9-(tolyl-*o*-CH)), 129.0 (2C; 9-(tolyl-*m*-CH)), 129.3 (2C; 1,8-CH), 130.3

(2C; 12,13-*C*H), 131.2 (2C; *N*-(tolyl-*o*-*C*H)), 131.6 (2C; *N*-(tolyl-*m*-*C*H)), 135.3 (1C; 9-(tolyl-*p*-*C*)), 137.9 (1C; *N*-(tolyl-*p*-*C*)), 138.8 (2C; 11,14-*C*H), 139.0 (1C; *N*-(tolyl-*i*-*C*)), 147.5 ppm (1C; 9-(tolyl-*i*-*C*)).



Figure 43. ¹H (CDCl₃) NMR spectrum of partially isolated **14**. Asterisks denote solvent impurities and by-product.



Figure 44. ¹³C{¹H} (CDCl₃) NMR spectrum of partially isolated **14**. Asterisks denote solvent impurities and by-product.



(15) 2-(1-mesitylvinyl)-N,4-dimethyl-N-(4-tolyl)aniline

Obtained as a white solid (28.1 mg, 66% isolated yield). **HRMS (DART-TOF+):** m/z [M+H] m/z 356.23764 (calc'd for C₂₆H₃₀N: 356.23782). ¹**H NMR (500 MHz, CDCl₃):** δ = 2.02 (s, 6H; mesityl-o-CH₃), 2.25 (s, 3H; tolyl-*p*-CH₃), 2.29 (s, 3H; mesityl-*o*-CH₃), 2.32 (s, 3H; aniline-4-CH₃), 2.71 (s, 3H; NCH₃), 5.14 (d, ¹J_{HH} = 2 Hz, 1H; vinyl-C=CH₂), 5.96 (d, ¹J_{HH} = 2 Hz, 1H; C=CH₂), 6.38 (dt, ³J_{HH} = 8 Hz, ⁴J_{HH} = 2 Hz, 2H; tolyl-*o*-CH), 6.84 (s, 2H; mesityl-*m*-CH), 6.96 (d, ³J_{HH} = 8 Hz, tolyl-*m*-CH, aniline-6-CH), 7.08 (m, aniline-3-CH), 7.11 ppm (m, aniline-5-CH). ¹³C NMR (125 MHz, CDCl₃): δ = 20.4 (1C; tolyl-*p*-CH₃), 20.8 (2C; mesityl-*o*-CH₃), 21.1 (1C; mesityl-*p*-CH₃), 21.3 (1C; aniline-4-CH₃), 38.6 (1C; NCH₃), 113.2 (2C; tolyl-*o*-CH), 119.7 (1C; vinyl-C=CH₂), 125.6 (1C; tolyl-*p*-C), 128.3 (2C; mesityl-*m*-CH), 129.4 (2C; tolyl-*m*-CH), 129.9 (1C; aniline-6-CH), 130.1 (1C; aniline-5-CH), 131.4 (1C; aniline-3-CH), 135.8 (1C; mesityl-*p*-C), 136.2 (2C; mesityl-*o*-C), 136.5 (1C; aniline-4-C), 139.4 (1C; mesityl-*i*-C), 139.6 (1C; aniline-2-C), 144.2 (1C; aniline-1-C), 145.7 (1C; vinyl-C=CH₂), 148.1 ppm (1C; tolyl-*i*-C).



Figure 45. ¹H (CDCl₃) NMR spectrum of **15**. Asterisks denote solvent impurities.





Figure 47. Molecular structure of 15.



(16) 1,4-bis(2,7,9,10-tetramethyl-9,10-dihydroacridin-9-yl)benzene

Obtained as a white solid (16.9 mg, 52% isolated yield). HRMS (DART-TOF+): m/z [M+H] 549.32585 (calc'd for $C_{40}H_{40}N_2$: 549.32697). ¹H NMR (500 MHz, CDCl₃): δ = 1.78 (s, 6H; 9,9'-CH₃),

2.22 (s, 12H; 2,2',7,7'-CH₃), 3.37 (s, 6H; NCH₃), 6.70 (d, ${}^{4}J_{HH} = 2$ Hz, 4H; 1,1',8,8'-CH), 6.80 (d, ${}^{3}J_{HH} = 8$ Hz, 4H; 4,4',5,5'-CH), 7.01 (m, 4H; 3,3',6,6'-CH), 7.12 ppm (s, 4H; benzene-2,3,5,6-CH). ¹³C NMR (125 MHz, CDCl₃): $\delta = 20.8$ (4C; 2,2',7,7'-CH₃), 28.4 (2C; 9,9'-CH₃), 33.4 (2C; NCH₃), 46.0 (2C, 9-C), 111.6 (4C; 4,4',5,5'-CH), 127.3 (4C; 3,3',6,6'-CH), 128.3 (8C; 1,1',8,8'-CH, benzene-2,3,5,6-CH), 128.9 (4C; 2,2',7,7'-C), 132.7 (4C; 12,12',13,13'-C), 139.9 (4C; 11,11',14,14'-C), 146.3 ppm (2C; benzene-1,4-C).



Figure 48. ¹H (CDCl₃) NMR spectrum of **16**. Asterisks denote solvent impurities.



Figure 49. ¹³C{¹H} (CDCl₃) NMR spectrum of **16**. Asterisks denote solvent impurities.



(17) 7-methoxy-9-methyl-9-(4-tolyl)acridin-2(9H)-one

Obtained as a yellow solid (12.7 mg, 33% isolated yield). **HRMS (DART-TOF+):** m/z [M+H] 330.15001 (calc'd for $C_{22}H_{20}NO_2$: 330.14940). ¹**H NMR (500 MHz, CDCl₃):** δ = 1.74 (s, 3H; 9-CH₃), 2.33 (s, 3H; 9-(tolyl-*p*-CH₃)), 3.74 (s, 3H; 7-OCH₃), 6.09 (d, ⁴J_{HH} = 2 Hz, 1H; 1-CH), 6.44 (d, ⁴J_{HH} = 3 Hz, 1H; 8-CH), 6.57 (dd, ³J_{HH} = 10 Hz, ⁴J_{HH} = 2 Hz, 1H; 3-CH), 6.88 (dd, ³J_{HH} = 8 Hz, ⁴J_{HH} = 3 Hz, 1H; 6-CH), 7.10 (m, 4H; 9-(tolyl-*o*,*m*-CH)), 7.41 (d, ³J_{HH} = 10 Hz, 1H; 4-CH), 7.67 ppm (d, ³J_{HH} = 8 Hz, 1H; 5-CH). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 21.1 (1C; 9-(tolyl-*p*-CH₃)), 33.4 (1C; 9-CH₃), 47.0 (1C; 9-C), 55.7 (1C; 7-OCH₃), 112.9 (1C; 6-CH), 114.9 (1C; 8-CH), 128.2 (2C; 9-(tolyl-*o*-CH))), 129.5 (2C; 9-(tolyl-*m*-CH))), 130.2 (1C; 1-CH), 131.4 (1C; 3-CH), 133.6 (1C; 5-CH), 137.0 (1C; 11-C), 137.2 (1C; 9-(tolyl-*p*-C))), 141.0 (1C; 12-C), 141.5 (1C; 4-CH), 142.5 (1C; 9-(tolyl-*i*-C))), 149.2 (1C; 13-C), 150.1 (1C; 14-C), 161.9 (1C; 7-C), 187.1 ppm (1C; 2-C).





Figure 51. ¹³C{¹H} (CDCl₃) NMR spectrum of **17**. Asterisks denote solvent impurities.

7. Numbering Convention



8. Computational Details

Electronic structure calculations were performed using *Gaussian 09*. Geometry optimizations were carried out at the BP86/def2-TZVP level and each geometry was confirmed to be a minimum on its potential energy surface by confirming the Hessian to be positive definite with a frequency calculation. The Cartesian coordinates of the optimized structures are collected in Tables S4-S11. Orbital and internal energies needed to calculate global electrophilicity indices (GEIs) and fluoride ion affinities (FIAs) were obtained from MP2/def2-TZVPP calculations at the BP86/def2-TZVP geometries. FIA and GEI were calculated as previously described.²



Figure 52. Electronic structure of $[(PhO)P(2-(N-Mepy))Ph_2]^{2+}$. A) Mulliken charges ranging from -0.446 (red) to 0.877 (green), highlighting the concentration of positive charge on phosphorus. B) Canonical LUMO+2 contoured at an isovalue of 0.04, featuring significant contribution from the P–O σ^* orbital with a lobe oriented opposite this bond.

Center	Atomic	Atomic	Coord	dinates (Ang:	stroms)
Number	Number	Type	Х	Y	Z
1	6	0	2.007734	-0.301247	-0.621687
2	6	0	3.035015	0.578952	-0.289645
3	1	0	2.802970	1.442827	0.333015
4	6	0	4.341708	0.372302	-0.750456
5	1	0	5.137038	1.068060	-0.477989
6	6	0	4.599913	-0.726907	-1.563331
7	1	0	5.594310	-0.932311	-1.960681
8	6	0	3.557580	-1.593437	-1.869728
9	1	0	3.701290	-2.475519	-2.493360
10	6	0	1.266606	-2.397059	-1.796264
11	1	0	0.647893	-1.986222	-2.602094
12	1	0	0.644883	-2.639067	-0.927895
13	1	0	1.780358	-3.301428	-2.136380
14	6	0	0.262161	1.791632	0.498874
15	6	0	0.306981	2.798317	-0.493559
16	1	0	0.343745	2.536121	-1.552990
17	6	0	0.292349	4.137236	-0.110545
18	1	0	0.319044	4.918758	-0.871313
19	6	0	0.236519	4.478851	1.248600
20	1	0	0.220483	5.530159	1.541341
21	6	0	0.198079	3.483938	2.231442
22	1	0	0.150837	3.756503	3.286645
23	6	0	0.212812	2.136813	1.866216
24	1	0	0.178004	1.362969	2.634059
25	6	0	-0.111656	-1.018774	1.342617
26	6	0	-1.409653	-0.936830	1.898092
27	1	0	-2.139857	-0.221114	1.516458
28	6	0	-1.758856	-1.786703	2.947063
29	1	0	-2.760548	-1.728578	3.375207
30	6	0	-0.829149	-2.703734	3.452027
31	1	0	-1.108947	-3.360954	4.277074
32	6	0	0.460174	-2.777471	2.912095
33	1	0	1.185311	-3.483886	3.318494
34	6	0	0.824608	-1.940923	1.857473
35	1	0	1.840707	-1.994295	1.461454
36	7	0	2.297471	-1.395789	-1.405758
37	15	0	0.297405	0.082355	0.002073
38	8	0	-0.543777	-0.138945	-1.341158
39	6	0	-1.992950	-0.184338	-1.409683
40	6	0	-2.696348	1.001904	-1.588206
41	6	0	-2.605785	-1.433714	-1.389079
42	6	0	-4.085892	0.924556	-1.742484
43	1	0	-2.182396	1.961688	-1.628159
44	6	U	-3.995141	-1.489136	-1.546937
45	1	U	-2.023582	-2.346825	-1.263253
46	6	U	-4.732947	-0.314370	-1.720877
47	1	U	-4.657745	1.841252	-1.892601
48	1	0	-4.496076	-2.458187	-1.542076
49	Ţ	U	-5.814/30	-0.365602	-1.849600

Table S4. Cartesian coordinates (Å) of $[(PhO)P(2-(N-Mepy))Ph_2]^{2+}$.

Center	Atomic	Atomic	Coord	dinates (Ang	stroms)
Number	Number	Туре	Х	Y	Z
1	6	0	1.759434	-0.359554	-1.176841
2	6	0	2.715327	0.658578	-1.283120
3	1	0	2.572584	1.561729	-0.691753
4	6	0	3.821827	0.523670	-2.114483
5	1	0	4.551527	1.330931	-2.192405
6	6	0	3.993892	-0.664531	-2.831749
7	1	0	4.848827	-0.826179	-3.487144
8	6	0	3.055628	-1.664511	-2.683204
9	1	0	3.132840	-2.624136	-3.192022
10	6	0	1.007948	-2.643435	-1.842109
11	1	0	0.255738	-2.503749	-2.627003
12	1	0	0.515702	-2.686744	-0.866484
13	1	0	1.568716	-3.569690	-2.009066
14	6	0	-0.012055	1.752730	0.194192
15	6	0	-0.098147	2.630992	-0.899153
16	1	0	-0.016415	2.246566	-1.91/022
17	6	0	-0.2816/2	3.999336	-0.684072
18	1 C	0	-0.331//6	4.6/9296	-1.536252
19	6	0	-0.411696	4.492582	0.61/800
20	1	0	-0.369286	2 610046	1 709127
21	1	0	-0.334479	4 002600	2 725090
22	L C	0	-0.434300	4.002033	1 602142
23	1	0	-0.022710	1 586031	2 359160
25	6	0	-0 702263	-1 162818	1 003372
26	6	0	-2 069214	-0 909906	1 213170
27	1	Ő	-2.556087	-0.050180	0.753434
28	6	Ő	-2.812681	-1.748030	2.049441
29	1	õ	-3.867445	-1.529946	2.223866
30	6	0	-2.213412	-2.854688	2.655042
31	1	0	-2.801275	-3.510797	3.299132
32	6	0	-0.853216	-3.108508	2.451094
33	1	0	-0.373347	-3.957636	2.940675
34	6	0	-0.094019	-2.257267	1.646392
35	1	0	0.979481	-2.426370	1.552352
36	7	0	1.962484	-1.509607	-1.880542
37	8	0	-0.612899	-0.233703	-1.518604
38	6	0	-1.979686	-0.331283	-1.786239
39	6	0	-2.753156	0.815946	-2.001810
40	6	0	-2.555475	-1.600610	-1.929566
41	6	0	-4.100368	0.685150	-2.353383
42	1	0	-2.307014	1.803825	-1.897338
43	6	0	-3.901884	-1.719832	-2.284207
44	1	U	-1.957623	-2.493975	-1.747829
45	6	0	-4.680054	-0.578458	-2.496223
46	1	U	-4.696944	1.583319	-2.523305
4'/	1	U	-4.342190	-2.712576	-2.393336
48	15	0	-5./30106	-0.6/3041	-2.//6041
49	10	U	1 504092	-0.028096	-U.U43234
JU	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		1.304082	0.040100	T.T.20130

Table S5. Cartesian coordinates (Å) of [(PhO)P(F)(2-(N-Mepy))Ph₂]⁺.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X Y Z		
1	15	0	-0.094390	0.039541	0.337819
2	9	0	4.231469	-3.452236	-1.783685
3	9	0	-1.443971	2.521219	1.223903
4	9	0	-1.769131	4.862386	-0.069784
5	9	0	-0.831687	5.161679	-2.618850
6	9	0	0.426797	3.092068	-3.873317
7	9	0	0.764889	0.747279	-2.622639
8	9	0	-1.950975	-0.475854	-1.905300
9	9	0	-4.452419	-1.500708	-1.863581
10	9	0	-5.527867	-2.374774	0.493596
11	9	0	-4.087173	-2.222732	2.801666
12	9	0	-1.613142	-1.219484	2.803110
13	9	0	-0.192137	-3.015329	-0.277407
14	9	0	1.796392	-4.542375	-1.216700
15	9	0	4.670221	-0.783512	-1.406108
16	9	0	2.684663	0.794156	-0.483506
17	8	0	0.249404	0.391504	1.843283
18	6	0	3.255204	-2.682046	-1.329043
19	6	0	2.003247	-3.239470	-1.037819
20	6	0	0.978848	-2.424541	-0.553263
21	6	0	1.165516	-1.038150	-0.359286
22	6	0	1.530580	0.645754	2.431661
23	6	0	1.955158	1.964335	2.556000
24	1	0	1.346197	2.783089	2.173257
25	6	0	3.166699	2.206640	3.210922
26	1	0	3.516717	3.233393	3.325626
27	6	0	3.916849	1.144572	3.725327
28	1	0	4.858153	1.342372	4.239511
29	6	0	-0.267469	1.561261	-0.620120
30	6	0	-0.946547	2.644136	-0.016702
31	6	0	-1.134932	3.859166	-0.673624
32	6	0	-0.656789	4.013474	-1.981872
33	6	0	-0.006111	2.950239	-2.622202
34	6	0	0.173455	1.742469	-1.947825
35	6	0	-1.708069	-0.743664	0.448857
36	6	0	-2.476272	-0.864165	-0.728126
37	6	0	-3.759410	-1.402488	-0.730846
38	6	0	-4.309258	-1.855530	0.476778
39	6	0	-3.566743	-1.774169	1.661421
40	6	0	-2.277383	-1.234604	1.645745
41	6	0	3.479115	-1.311267	-1.134335
42	6	0	2.443703	-0.515070	-0.653633
43	6	0	2.244103	-0.431883	2.947709
44	1	0	1.852070	-1.446544	2.871361
45	6	0	3.454989	-0.168510	3.597752
46	1	0	4.027851	-0.996422	4.017925

Table S6. Cartesian coordinates (Å) of $[(PhO)P(C_6F_5)_3]^+$.

Center	Atomic	Atomic	Coord	dinates (Angs	stroms)
Number	Number	Type	Х	Y	Z
1	6	0	-0.446151	-2.147810	4.090124
2	6	0	-1.095803	-1.641516	2.955449
3	6	0	-1.432953	-0.292221	2.833685
4	6	0	-1.143736	0.588166	3.879848
5	6	0	0.155363	-5.049478	2.723508
6	6	0	0.781887	-4.620286	1.544266
7	6	0	0.904610	-5.449340	0.426692
8	6	0	0.408522	-6.753996	0.473778
9	6	0	-0.215635	-7.213285	1.635402
10	6	0	-0.345544	-6.359926	2.733480
11	9	0	-1.414229	-2.449840	1.927609
12	9	0	-2.038174	0.161305	1.725936
13	9	0	-1.468639	1.882196	3.777765
14	9	0	1.254196	-3.367102	1.420110
15	9	0	1.486940	-4.995874	-0.693641
16	9	0	0.527813	-7.557959	-0.588860
17	9	0	-0.681047	-8.469982	1.693565
18	9	0	-0.939538	-6.865987	3.829203
19	15	0	-0.037263	-3.954474	4.199293
20	6	0	-0.176739	-1.242043	5.122329
21	6	0	-0.519773	0.109516	5.033260
22	6	0	-0.026472	-4.738163	5.870634
23	9	0	-1.697505	-4.247533	4.109614
24	9	0	0.395382	-1.653060	6.270209
25	9	0	-0.254861	0.945477	6.047580
26	6	0	-0.932151	-4.355354	6.874294
27	6	0	0.845800	-5.794640	6.178693
28	6	0	-0.944661	-4.960099	8.133224
29	9	0	-1.814636	-3.363741	6.672988
30	6	0	0.836431	-6.427818	7.424079
31	9	0	1.704351	-6.278588	5.263161
32	6	0	-0.057717	-6.003140	8.409116
33	9	0	-1.802091	-4.545969	9.077173
34	9	0	1.673374	-7.446026	7.673946
35	9	0	-0.068234	-6.595365	9.607899
36	8	0	1.660013	-3./40838	4.11804/
37	6	0	2.530909	-2.822151	4.6/4665
38	6	0	3.205111	-3.123605	5.865509
39	6	0	2.828888	-1.642///	3.9//445
40	6	0	4.154844	-2.231137	6.36/69/
41	1	0	3.000310	-4.062630	6.3/9568
42	6	U	3.//9639	-0./56494	4.491286
43	Ţ	U	2.332438	-1.442611	3.02/680
44	6	0	4.441646	-1.042/6/	5.688630
45	1	U	4.6/9519	-2.4/263/	1.294234
46	1	0	4.UII/86	0.158185	3.942028
4 /	T	U	5.180/11	-0.35040/	0.083838

Table S7. Cartesian coordinates (Å) of $[(PhO)P(F)(C_6F_5)_3]^+$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
1	6	0	-0.094953	2.489641	-0.656690
2	6	0	0.515293	1.487129	-1.433171
3	6	0	1.611722	1.905108	-2.210128
4	6	0	2.069444	3.221994	-2.234028
5	6	0	1.436055	4.179230	-1.434702
6	6	0	0.349688	3.810999	-0.634289
7	5	0	0.006554	0.001806	-1.434001
8	9	0	2.248187	1.026002	-3.012134
9	9	0	3.103895	3.580476	-3.009614
10	9	0	-0.248120	4.728704	0.140651
11	9	0	-1.135786	2.185124	0.146397
12	6	0	-1.534094	-0.299791	-1.440231
13	6	0	-2.443158	0.451045	-2.209290
14	6	0	-3.812186	0.188026	-2.241266
15	6	0	-4.326049	-0.850980	-1.458539
16	6	0	-3.465811	-1.618242	-0.666235
17	6	0	-2.099458	-1.340984	-0.680003
18	9	0	-1.999981	1.452779	-2.997326
19	9	0	-1.318258	-2.101370	0.115191
20	9	0	-3.963347	-2.605858	0.093382
21	9	0	-4.637892	0.914306	-3.009819
22	6	0	1.037863	-1.181754	-1.430635
23	6	0	0.844706	-2.347137	-2.196280
24	6	0	1.752099	-3.405460	-2.214062
25	6	0	2.901219	-3.332630	-1.419856
26	6	0	3.133662	-2.200729	-0.631809
27	6	0	2.215542	-1.151582	-0.660104
28	9	0	-0.238813	-2.463587	-2.992212
29	9	0	1.537974	-4.487284	-2.978070
30	9	0	4.230462	-2.139114	0.138400
31	9	0	2.480872	-0.091899	0.131896
32	9	0	3.775507	-4.343456	-1.413798
33	9	0	-5.637113	-1.110209	-1.467543
34	9	0	1.868432	5.443945	-1.435570

Table S8. Cartesian coordinates (Å) of $B(C_6F_5)_3$.

Table S6. Cartesian coordinates (Å) of $[FB(C_6F_5)_3]^-$.

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Туре	Х	Y	Z	
1	6	0	0.125172	2.589072	-0.607718	
2	6	0	0.550241	1.713780	-1.617001	
3	6	0	1.450908	2.276476	-2.525841	
4	6	0	1.931976	3.586852	-2.438268	
5	6	0	1.495770	4.408471	-1.400931	
6	6	0	0.579141	3.904818	-0.478797	
7	9	0	1.907043	1.563351	-3.590586	
8	9	0	2.810983	4.071141	-3.348529	
9	9	0	0.133179	4.703928	0.520273	
10	9	0	-0.799139	2.198028	0.302263	
11	6	0	-1.558038	0.001975	-2.151554	
12	6	0	-2.280662	0.972430	-2.850875	
13	6	0	-3.631257	0.843013	-3.192817	
14	6	0	-4.319975	-0.314903	-2.838493	
15	6	0	-3.641069	-1.324700	-2.157038	
16	6	0	-2.291911	-1.150834	-1.837734	
17	9	0	-1.689441	2.125606	-3.264131	
18	9	0	-1.698016	-2.196815	-1.214112	
19	9	0	-4.298208	-2.462371	-1.826627	
20	9	0	-4.278929	1.825155	-3.864822	
21	6	0	1.057013	-0.867034	-2.453887	
22	6	0	0.808433	-1.487096	-3.681125	
23	6	0	1.690533	-2.382622	-4.295192	
24	6	0	2.901965	-2.684220	-3.676389	
25	6	0	3.210119	-2.076730	-2.459674	
26	6	0	2.297159	-1.188723	-1.884341	
27	9	0	-0.332302	-1.231653	-4.376376	
28	9	0	1.387206	-2.957752	-5.483889	
29	9	0	4.394720	-2.348474	-1.861092	
30	9	0	2.693558	-0.611718	-0.724043	
31	9	0	3.770117	-3.546936	-4.251617	
32	9	0	-5.625843	-0.461476	-3.157757	
33	9	0	1.947171	5.678906	-1.295800	
34	5	0	0.016489	0.133319	-1.617410	
35	9	0	0.025449	-0.313482	-0.257156	

Table S10.	Cartesian	coordinates	(Å)) of	CF ₂ O.
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Center	Atomic	Atomic	Coord	dinates (Ang:	stroms)
Number	Number	Type	X	Y	Z
1	6	0	0.392343	-0.881189	0.000024
2	8	0	1.574231	-0.881188	-0.000009
3	9	0	-0.396439	0.193561	-0.000006
4	9	0	-0.396439	-1.955938	0.000039

Table S11. Cartesian coordinates (Å) of CF_3O^- .

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			Х	Y	Z
1	6	0	-0.922255	-0.027060	-0.141732
2	9	0	-0.535423	0.520074	1.151943
3	9	0	-0.535528	-1.420909	0.031214
4	9	0	-2.365460	-0.126958	0.031190
5	8	0	-0.515657	0.548010	-1.137934

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